Supporting Information

Excited-State Palladium-Catalyzed Radical Migratory Mizoroki-Heck Reaction Enables C2-Alkenylation 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 chromatography was performed on SiliaFlash® Silica Gel 40-63μm 60Å 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.

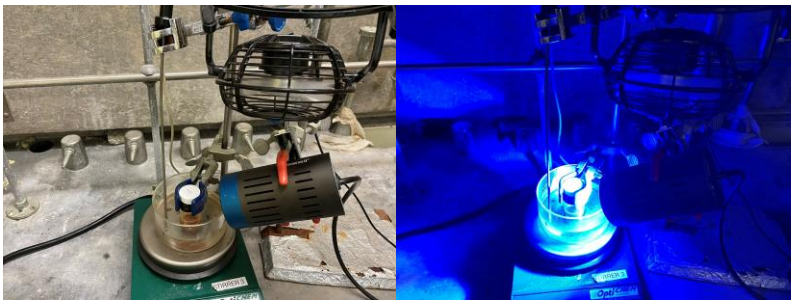
All air and moisture-sensitive manipulations were performed using oven-dried glassware, including standard Schlenk and glovebox techniques under an atmosphere of nitrogen. All reaction vials were capped using green caps with F-217 PTFE liners. Isopropyl acetate was distilled from calcium chloride $CaCl_2$. Diethyl ether and THF were distilled from deep purple sodium benzophenone ketyl. Acetonitrile were 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. Chemical shifts were referenced to the residual proton solvent peaks (^{1}H: $CDCl_3$, δ 7.26; CD_3CN, δ 1.94), solvent ^{13}C 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 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 high vacuum (0.01–0.05 Torr).

Photoredox reaction setup

Reaction set up: A 20 mL capped vial was placed in oil bath at 90°C. The blue LED lamp (Kessil KSH150B LED Grow Light, 34W) was placed nearly perpendicular to the vial. The distance between blue LED lamps and the vial was 5.00 cm.

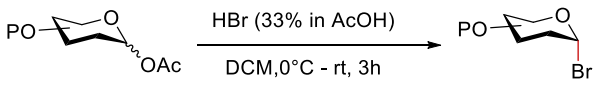


Reaction set up

Experimental Data

Preparation of Substrates:

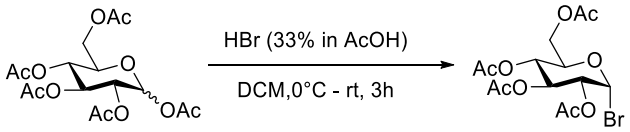
General Procedure A (for synthesizing 1-bromosugar):



1a-1n

The C-1 acetyl protected sugar (1.00 equiv) was dissolved in dry CH_2Cl_2 (0.500 M) and cooled to 0 °C. HBr (33% in AcOH, 2.00 M) was added and the reaction mixture was slowly warmed to room temp and stirred for 3 h. The reaction mixture was then poured into an ice/water mixture. The aqueous phase was extracted with CH_2Cl_2 (3 times) and the combined organic layers were washed sequentially with satd. $NaHCO_3$, brine, dried over $MgSO_4$ and filtered to remove $MgSO_4$. The filtrate was concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel to afford the desired compound.

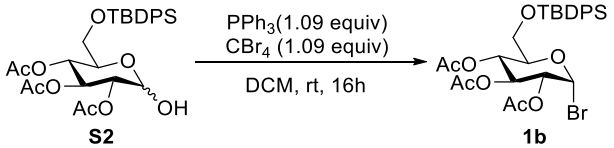
(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-bromotetrahydro-2H-pyran-3,4,5-triyl triacetate (1a)



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% yield) as 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. These spectroscopic data correspond to previously reported data.[3]

(2R,3R,4S,5R,6R)-2-bromo-6-(((tert-butyldiphenylsilyl)oxy)methyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (1b)

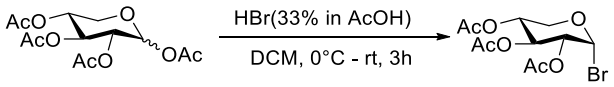


S2 **1b**

To a solution of **S2** (571 mg, 1.05 mmol, 1.00 equiv) in dry CH_2Cl_2 (2.00 mL) was added triphenylphosphine (303 mg, 1.15 mmol, 1.09 equiv) and tetrabromomethane (383 mg, 1.15 mmol, 1.09 equiv). The reaction mixture was stirred at rt under nitrogen atmosphere for 16 h. Saturated $NaHCO_3$ was

added until the pH of the solution became neutral. The organic layer was collected, and the aqueous phase was extracted with DCM twice (2×20 ml). The combined organic layers were washed with brine, dried with anhydrous $MgSO_4$, and filtered. The filtrate was concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel, eluting with Hexanes: EtOAc [8:1 (v/v)] to afford the title compound **1b** (171 mg, 0.28 mmol, 27% yield) as 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. These spectroscopic data correspond to previously reported data.[4]

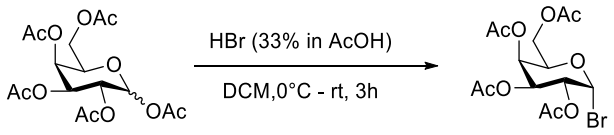
(2R,3R,4S,5R)-2-bromotetrahydro-2H-pyran-3,4,5-triyl triacetate (1c)



S3 **1c**

The reaction was performed according to the **General Procedure A** using **S3** (2.20 g, 6.90 mmol, 1.00 equiv) as the substrate. After work up, the reaction mixture was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [3:1 (v/v)] to afford the title compound **1c** (1.30 g, 3.85 mmol, 57% yield) as white solid. $\mathbf{R}_f$ = 0.50 [Hexanes: EtOAc 2:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ) 6.57 (d, *J* = 4.2 Hz, 1H), 5.55 (t, *J* = 9.8 Hz, 1H), 5.03 (td, *J* = 9.8, 6.3 Hz, 1H), 4.76 (dd, *J* = 9.8, 4.2 Hz, 1H), 4.04 (dd, *J* = 11.2, 6.3 Hz, 1H), 3.87 (t, *J* = 11.2 Hz, 1H), 2.09 (s, 3H), 2.05 (s, 3H), 2.05 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 169.98, 169.98, 169.89, 87.70, 70.98, 69.61, 68.20, 62.64, 20.81, 20.80, 20.77. These spectroscopic data correspond to previously reported data.[5]

(2R,3S,4S,5R,6R)-2-(acetoxymethyl)-6-bromotetrahydro-2H-pyran-3,4,5-triyl triacetate (1d)

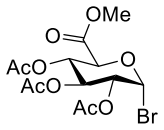


S4 **1d**

The reaction was performed according to the **General Procedure A** using **S4** (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 **1d** (1.73 g, 4.21 mmol, 82% yield) as 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. These spectroscopic data correspond to previously reported data.[3]

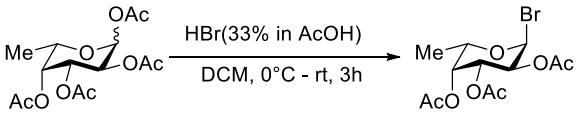
(2R,3R,4S,5S,6S)-2-bromo-6-(methoxycarbonyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (1e)



1e

The title compound was prepared according to the literature procedure.[6] **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 6.63 (d, *J* = 4.0 Hz, 1H), 5.60 (t, *J* = 9.7 Hz, 1H), 5.23 (t, *J* = 9.9 Hz, 1H), 4.84 (dd, *J* = 10.0, 4.1 Hz, 1H), 4.57 (d, *J* = 10.3 Hz, 1H), 3.75 (s, 3H), 2.09 (s, 3H), 2.04 (s, 3H), 2.04 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 169.78, 169.75, 169.57, 166.78, 85.48, 72.15, 70.43, 69.40, 68.60, 53.25, 20.72, 20.57. The spectroscopic data corresponds to previously reported data.[6]

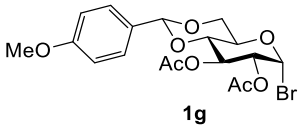
(2S,3S,4R,5R,6S)-2-bromo-6-methyltetrahydro-2H-pyran-3,4,5-triyl triacetate (1f)



S5 **1f**

The reaction was performed according to the **General Procedure A** using **S5** (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 **1f** (1.66 g, 4.70 mmol, 78% yield) as 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. These spectroscopic data correspond to previously reported data.[7]

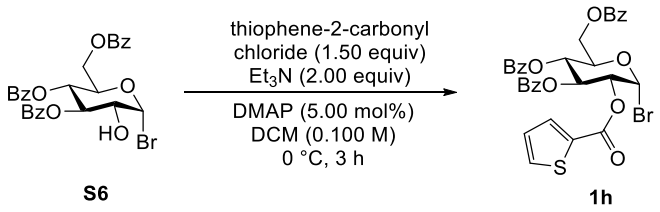
(2R,4aR,6R,7R,8S,8aR)-6-bromo-2-(4-methoxyphenyl)hexahydropyrano[3,2-d][1,3]dioxine-7,8-diyl diacetate (1g)



1g

The title compound was prepared according to the literature procedure.[8] **^{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. These spectroscopic data correspond to previously reported data.[8]

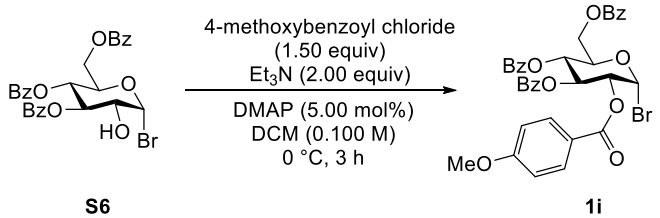
(2R,3R,4S,5R,6R)-2-((benzoyloxy)methyl)-6-bromo-5-((thiophene-2-carbonyl)oxy)tetrahydro-2H-pyran-3,4-diyl dibenzoate (1h)



S6 **1h**

To a solution of **S6** (278 mg, 0.500 mmol, 1.00 equiv) in dry DCM (5.00 mL) was added Et_3N (101 mg, 1.00 mmol, 2.00 equiv), thiophene-2-carbonyl chloride (110 mg, 0.75 mmol, 1.50 equiv) and DMAP (3.05 mg, 0.025 mmol, 0.0500 equiv) 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 $MgSO_4$ 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 **1h** (219 mg, 0.33 mmol, 66% yield) as 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.

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

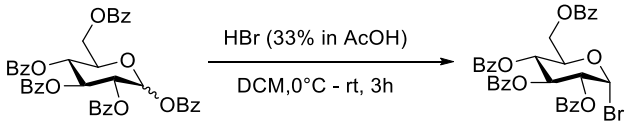


S6 **1i**

The reaction was performed according to the same procedure as synthesizing **1h** using 4-methoxybenzoyl chloride (128 mg, 0.75 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 the title compound **1i** (189 mg, 0.28 mmol, 55% yield) as 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.

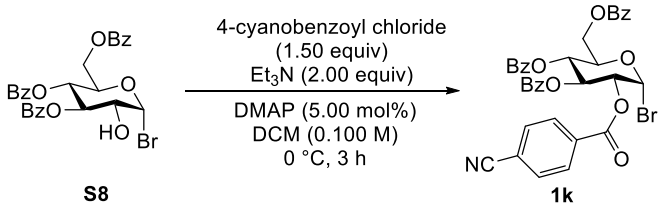
(2R,3R,4S,5R,6R)-2-((benzoyloxy)methyl)-6-bromotetrahydro-2H-pyran-3,4,5-triyl tribenzoate (1j)



S7 **1j**

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 **1j** (1.51 g, 2.29 mmol, 80% yield) as 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. These spectroscopic data correspond to previously reported data.[9]

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

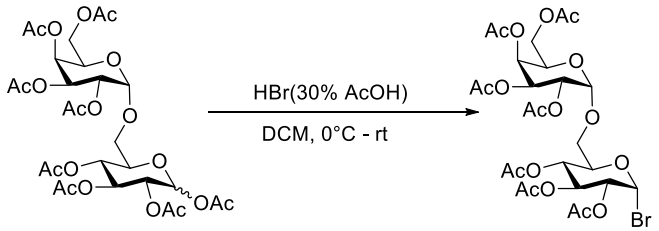


S8 **1k**

The reaction was performed according to the same procedure as synthesizing **1h** using 4-cyanobenzoyl chloride (124 mg, 0.75 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 the title compound (256 mg, 0.38 mmol, 75% yield) as 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.

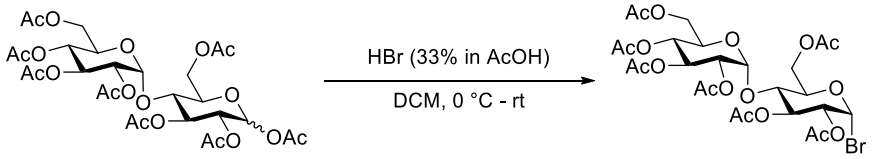
(2R,3S,4S,5S,6S)-2-(acetoxymethyl)-6-(((2R,3R,4S,5R,6R)-3,4,5-triacetoxy-6-bromotetrahydro-2H-pyran-2-yl)methoxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (1l)



S9 **1l**

The reaction was performed according to the **General Procedure A** using **S9** (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, 0.46 mmol, 25% yield) as 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. These spectroscopic data correspond to previously reported data.[9]

2,3,6,2',3',4',6'-Hepta-O-acetyl-α-D-maltose bromide (1m)

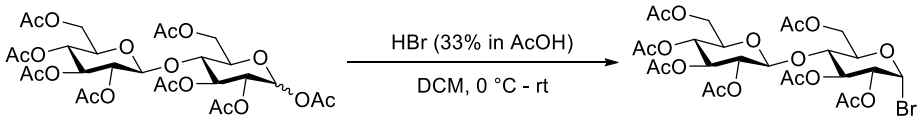


S10 **1m**

The reaction was performed according to the **General Procedure A** using **S10** (750 mg, 1.10 mmol, 1.00 equiv) as the substrate. After work up, the reaction mixture was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [2.5:1 (v/v)] to afford the title compound (420 mg, 0.600 mmol, 55% yield) as a white solid. $\mathbf{R}_f$ = 0.50 [Hexanes: EtOAc 3:1 (v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 6.45 (d, *J* = 4.0 Hz, 1H), 5.55 (t, *J* = 9.4 Hz, 1H), 5.36 (d, *J* = 4.0 Hz, 1H), 5.31 (t, *J* = 10.0 Hz, 1H), 5.01 (t, *J* = 9.9 Hz, 1H), 4.81 (dd, *J* = 10.5, 4.0 Hz, 1H), 4.66 (dd, *J* = 9.9, 4.0 Hz, 1H), 4.46 (dd, *J* = 13.7, 3.4

Hz, 1H), 4.28 – 4.13 (m, 3H), 4.03 – 3.96 (m, 2H), 3.92 – 3.84 (m, 1H), 2.09 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H), 1.97 (s, 3H), 1.95 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 171.07, 170.66, 170.45, 170.25, 169.83, 169.50, 169.41, 95.79, 86.14, 72.57, 72.34, 71.60, 71.01, 70.02, 69.24, 68.65, 67.92, 61.86, 61.35, 60.35, 21.03, 20.86, 20.76, 20.67, 20.63, 20.59. The spectroscopic data corresponds to previously reported data.[10]

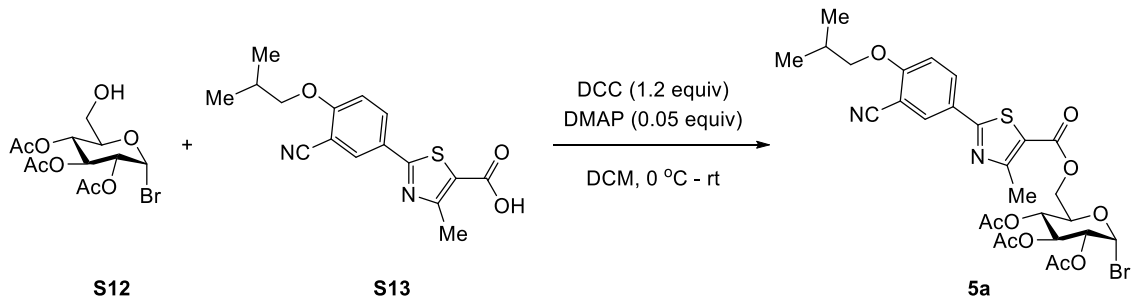
2,3,6,2',3',4',6'-Hepta-O-acetyl-α-D-cellobiose bromide (1n)



S11 **1n**

The reaction was performed according to the **General Procedure A** using **S11** (3.49 g, 5.14 mmol, 1.00 equiv) as the substrate. After work up, the reaction mixture was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [2.5:1 (v/v)] to afford the title compound (2.00 g, 2.86 mmol, 56% yield) as a white solid. $\mathbf{R}_f$ = 0.50 [Hexanes: EtOAc 3:1 (v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 6.53 (d, *J* = 4.0 Hz, 1H), 5.53 (t, *J* = 9.7 Hz, 1H), 5.15 (t, *J* = 9.3 Hz, 1H), 5.08 (t, *J* = 9.7 Hz, 1H), 4.98 – 4.87 (m, 1H), 4.77 (dd, *J* = 10.0, 4.1 Hz, 1H), 4.54 (t, *J* = 8.6 Hz, 2H), 4.37 (dd, *J* = 12.5, 4.4 Hz, 1H), 4.23 – 4.14 (m, 2H), 4.05 (dd, *J* = 12.5, 2.0 Hz, 1H), 3.84 (t, *J* = 9.7 Hz, 1H), 3.67 (ddd, *J* = 9.9, 4.2, 2.2 Hz, 1H), 2.14 (s, 3H), 2.09 (s, 6H), 2.04 (s, 6H), 2.01 (s, 3H), 1.99 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 170.64, 170.40, 170.24, 170.13, 169.43, 169.12, 100.72, 86.55, 75.38, 73.16, 73.09, 72.20, 71.75, 70.92, 69.57, 67.90, 61.74, 61.07, 20.97, 20.83, 20.74, 20.69. The spectroscopic data corresponds to previously reported data.[10]

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

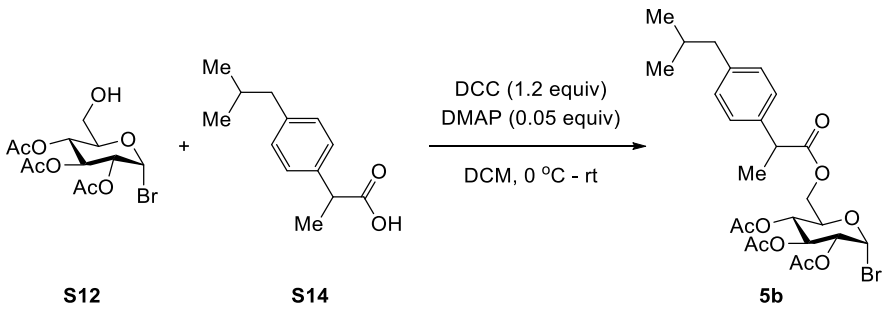


S12 **S13** **5a**

A suspension of febuxostat **S13** (190 mg, 0.60 mmol, 1.20 equiv) and DMAP (3.00 mg, 0.025 mmol, 0.05 equiv) in DCM (3.00 mL) was added a solution of DCC (124 mg, 0.60 mmol, 1.20 equiv) in DCM (1.00 mL) at 0 ºC. After stirring for 10 min at 0 ºC, **S12** (185 mg, 0.50 mmol, 1.00 equiv) was added. The reaction mixture stirred at rt overnight, quenched with saturated $NaHCO_3$ solution (6.00 mL), extracted with DCM (3×20 ml). The organic layer was collected, washed with brine, dried with anhydrous $MgSO_4$, and filtered.

The filtrate was concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel, eluting with Hexanes: EtOAc [2:1 (v/v)] to afford the title compound (214 mg, 0.32 mmol, 64% yield) as white solid. $\mathbf{R_f}$ = 0.30 [Hexanes: EtOAc 2:1 (v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 8.20 (d, *J* = 2.2 Hz, 1H), 8.11 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.00 (d, *J* = 8.9 Hz, 1H), 6.63 (d, *J* = 4.0 Hz, 1H), 5.59 (t, *J* = 9.7 Hz, 1H), 5.20 (t, *J* = 9.8 Hz, 1H), 4.85 (dd, *J* = 10.0, 4.1 Hz, 1H), 4.44 (d, *J* = 4.0 Hz, 2H), 4.40 (dd, *J* = 10.3, 2.7 Hz, 1H), 3.90 (d, *J* = 6.5 Hz, 2H), 2.75 (s, 3H), 2.26 – 2.13 (m, 1H), 2.10 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H), 1.08 (d, *J* = 6.7 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 169.96, 169.94, 169.54, 168.01, 162.71, 162.32, 161.45, 132.83, 132.33, 126.00, 120.80, 115.48, 112.71, 103.13, 86.57, 75.81, 72.23, 70.75, 70.23, 67.46, 61.72, 28.28, 20.77, 20.75, 20.70, 19.17, 17.71. **HRMS** (ESI-TOF) *m/z* calcd for $C_{28}H_{32}BrN_2O_{10}S$ $[(M + H)^+]$, 667.0956, found, 667.0966.

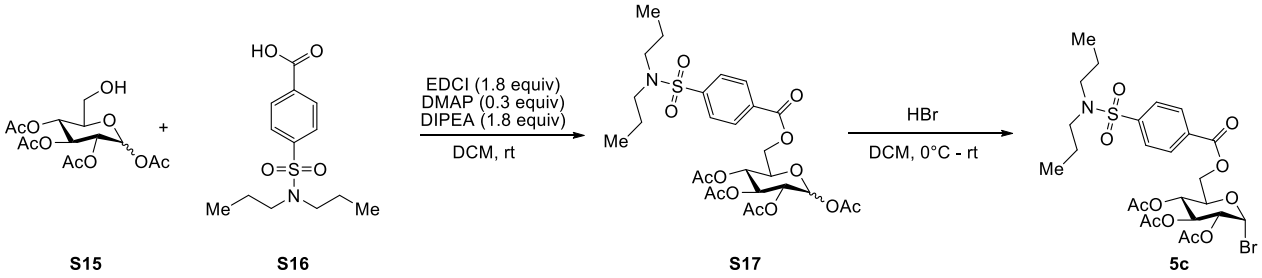
(2R,3R,4S,5R,6R)-2-bromo-6-(((2-(4-isopropylphenyl)propanoyl)oxy)methyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate(5b)



S12 **S14** **5b**

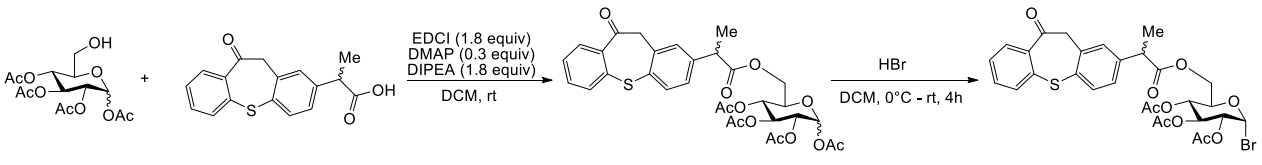
The reaction was performed according to the same procedure as synthesizing **5a**. Ibuprofen **S14** (115 mg, 0.60 mmol, 1.50 equiv). After work up, the reaction mixture was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [3:1 (v/v)] to afford the title compound (196 mg, 0.36 mmol, 72% yield) as white solid. $\mathbf{R_f}$ = 0.60 [Hexanes: EtOAc 2:1 (v/v)].**^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 7.20 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 6.52 (d, *J* = 4.0 Hz, 1H), 5.50 (td, *J* = 9.7, 2.2 Hz, 1H), 5.06 – 4.99 (m, 1H), 4.67 (dd, *J* = 10.0, 4.1 Hz, 1H), 4.23 (ddd, *J* = 11.9, 10.7, 5.6 Hz, 3H), 3.73 (q, *J* = 7.1 Hz, 1H), 2.43 (d, *J* = 7.2 Hz, 2H), 2.08 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 1.49 (d, *J* = 7.2 Hz, 3H), 1.86 (dt, *J* = 13.5, 6.8 Hz, 1H), 0.89 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 174.29, 169.95, 169.82, 169.50, 140.78, 137.37, 129.49, 127.37, 86.63, 72.43, 70.68, 70.26, 67.26, 60.98, 45.10, 30.25, 30.23, 22.50, 20.73, 20.71, 20.65, 18.43. **HRMS** (ESI-TOF) *m/z* calcd for $C_{25}H_{34}BrO_9$ $[(M + H)^+]$, 557.1381, found, 557.1388.

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



To a solution of compound **S15** (294 mg, 0.80 mmol, 1.00 equiv) in dry CH_2Cl_2 (4.00 mL, 0.20 M) were added Probenecid **S16** (274 mg, 0.96 mmol, 1.20 equiv), DMAP (29.3 mg, 0.24 mmol, 0.30 equiv), EDCI (186 mg, 0.42 mmol, 1.50 equiv) and DIPEA (0.25 ml, 1.44 mmol, 1.80 equiv). After stirring at rt for overnight, the reaction mixture was diluted with CH_2Cl_2 and washed with saturated $NaHCO_3$ and brine successively. The organic phase was dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by silica gel column chromatograph Hexanes: EtOAc [3:1 (v/v)] to give **S17** (209 mg, 0.34 mml, 46.4% yield) as colorless oil. **5c** was synthesized according to the **General Procedure A** using **S17** (209 mg, 0.34 mml, 46% yield) as the substrate. After work up, the reaction mixture was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [4:1 (v/v)] to afford the title compound (90.0 mg, 0.14 mmol, 40%) as 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.

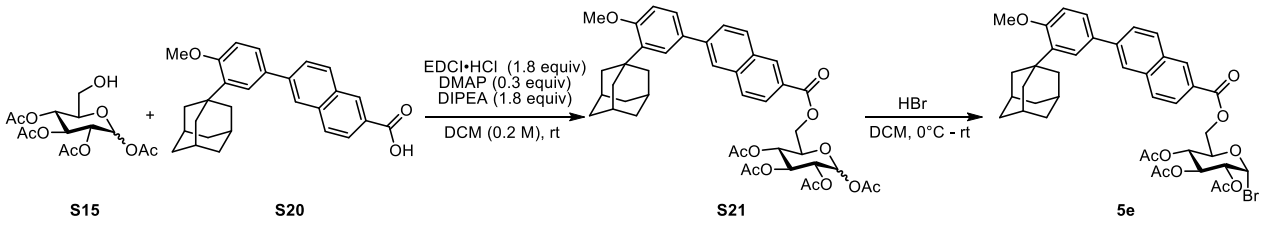
(2R,3R,4S,5R,6R)-2-bromo-6-(((2-(10-oxo-10,11-dihydrodibenzo[b,f]thiepin-2-yl)propanoyl)oxy) methyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate(5d)



To a solution of compound **S15** (452 mg, 1.30 mmol, 1.00 equiv) in dry CH_2Cl_2 (6.5 mL, 0.20 M) were added Zaltoprofen **S18** (237 mg, 1.43 mmol, 1.10 equiv), DMAP (47.6 mg, 0.39 mmol, 0.30 equiv), EDCI (448 mg, 2.34 mmol, 1.80 equiv) and DIPEA (0.48 ml, 2.34 mmol, 1.80 equiv). After stirring at rt for overnight, the reaction mixture was diluted with CH_2Cl_2 and washed with saturated $NaHCO_3$ and brine successively. The organic phase was dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified

by silica gel column chromatograph Hexanes: EtOAc [2:1 (v/v)] to give **S19** (700 mg, 1.11 mml, 86% yield) as colorless oil. **5d** was synthesized according to the **General Procedure A** using **S19** (440 mg, 0.70 mml, 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, 0.45 mmol, 64% yield) as 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.

(2R,3R,4S,5R,6R)-2-(((6-(3-((3r,5r,7r)-adamantan-1-yl)-4-methoxyphenyl)-2-naphthoyl)oxy)methyl)-6-bromotetrahydro-2H-pyran-3,4,5-triyl triacetate (5e)

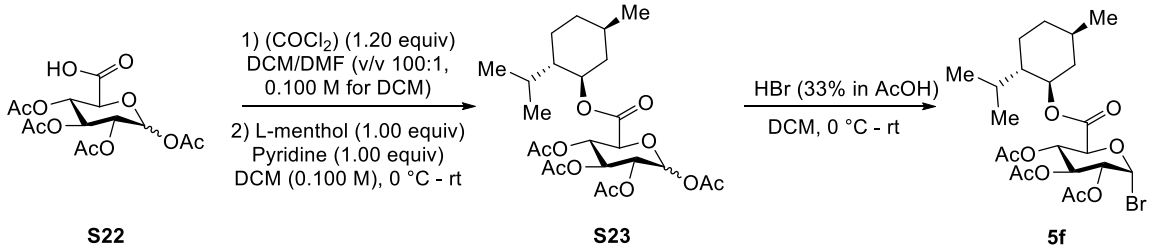


To a solution of compound **S15** (522 mg, 1.50 mmol, 1.00 equiv) in dry DCM (7.50 mL, 0.20 M) were added Adapalene **S20** (743 mg, 1.80 mmol, 1.20 equiv), DMAP (55.0 mg, 0.450 mmol, 0.300 equiv), EDCI·HCl (518 mg, 2.70 mmol, 1.80 equiv) and DIPEA (0.470 mL, 2.70 mmol, 1.80 equiv). After stirring at 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 $MgSO_4$ and concentrated *in vacuo*. The residue was purified by silica gel column chromatograph Hexanes: EtOAc [4:1 (v/v)] to give **S21** (790 mg, 1.06 mmol, 71% yield) as white solid.

5e was synthesized according to the **General Procedure A** using **S21** (790 mg, 1.06 mmol, 1.00 equiv) as the substrate. After work up, the reaction mixture was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [6:1 (v/v)] to afford the title compound (340 mg, 0.445 mmol, 42% yield) as a white foam. $\mathbf{R}_f$ = 0.42 [Hexanes: EtOAc 2:1 (v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 8.62 (s,

1H), 8.07-8.02 (m, 3H), 7.94 (d, *J* = 9.0 Hz, 1H), 7.81 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.61 (d, *J* = 3.0 Hz, 1H), 7.55 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.00 (d, *J* = 8.5 Hz, 1H), 6.68 (d, *J* = 4.5 Hz, 1H), 5.63 (t, *J* = 9.5 Hz, 1H), 5.33 (t, *J* = 10 Hz, 1H), 4.89 (dd, *J* = 10, 4.0 Hz, 1H), 4.60-4.48 (m, 3H), 3.91 (s, 3H), 2.19 (s, 6H), 2.12-2.08 (m, 9H), 2.05 (s, 3H), 1.81 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 170.05, 169.97, 169.58, 166.38, 159.11, 141.75, 139.17, 136.31, 132.66, 131.40, 131.36, 130.02, 128.54, 126.68, 126.24, 126.13, 125.91, 125.69, 124.87, 112.26, 86.78, 72.48, 70.84, 70.42, 67.75, 61.84, 55.32, 40.75, 37.36, 37.28, 29.26, 20.82, 20.80, 20.76. **HRMS** (ESI-TOF) *m/z* calcd for $C_{40}H_{43}BrO_{10}$ [(M + H)$^+$], 763.2112, found, 763.2105.

(2R,3R,4S,5S,6S)-2-bromo-6-((((1S,2R,5S)-2-isopropyl-5-methylcyclohexyl)oxy)carbonyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (5f)

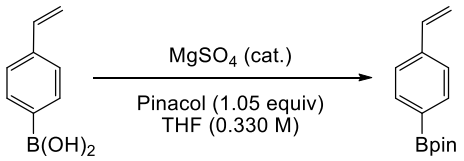


To a solution of **S22** (681 mg, 1.88 mmol, 1.00 equiv) in DCM (18.8 ml, 0.100 M) was added DMF (0.190 ml) and the solution was cooled to 0 °C. To that solution, oxalyl chloride (0.193 ml, 2.26 mmol, 1.20 equiv) was added dropwise. The reaction was allowed to run at room temperature for 3-4 h. Then the excess oxalyl chloride was removed under reduced pressure. In another round bottom flask, L-menthol (294 mg, 1.88 mmol, 1.00 equiv) was dissolved in DCM (16.0 ml) and to it pyridine (0.150 ml, 1.88 mmol, 1.00 equiv) was added. It was cooled to 0 °C and the solution of the formed acid chloride in DCM (2.80 ml) was added dropwise to it. The reaction was allowed to run overnight after which it was quenched with satd. $NaHCO_3$. The organic layers were collected and washed with brine. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography Hexanes: EtOAc [4:1 (v/v)] to give **S23** (470 mg, 0.94 mmol, 50% yield) as a colorless solid.

5f was synthesized according to the **General Procedure A** using **S23** (440 mg, 0.700 mmol, 1.00 equiv) as the substrate. After work up, the reaction mixture was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [4:1 (v/v)] to afford the title compound (55.0 mg, 0.106 mmol, 15 % yield) as a white foam. $\mathbf{R}_f$ = 0.42 [Hexanes: EtOAc 4:1 (v/v)]. **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ºC, δ): 6.64 (d, *J* = 4.0 Hz, 1H), 5.57 (t, *J* = 9.7 Hz, 1H), 5.29 (dd, *J* = 10.3, 9.5 Hz, 1H), 4.87 (dd, *J* = 10.0, 4.0 Hz, 1H), 4.77 (td, *J* = 10.9, 4.4 Hz, 1H), 4.58 (d, *J* = 10.4 Hz, 1H), 2.10 (s, 3H), 2.06 – 2.03 (m, 6H), 1.98 – 1.92 (m, 1H), 1.81 (dtd, *J* = 13.9, 7.0, 2.7 Hz, 1H), 1.69 (dd, *J* = 14.2, 2.5 Hz, 2H), 1.53 – 1.34 (m, 2H), 1.10 – 0.98 (m, 1H), 0.96 – 0.80 (m, 8H), 0.74 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, 25 ºC, δ): 169.95, 169.84, 169.18, 165.96, 85.75, 76.73, 72.52, 70.40, 70.03, 68.59, 47.03, 40.55, 34.18, 31.50, 26.17, 23.35, 22.07, 20.90, 20.76, 20.70, 16.22. **HRMS** (ESI-TOF) *m/z* calcd for $C_{22}H_{34}BrO_9$ [(M + H)$^+$], 521.1381, found, 521.1382.

Alkene Substrates Synthesis:

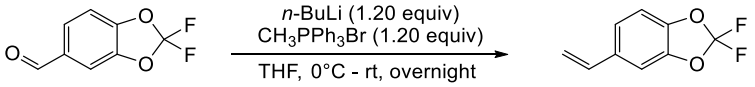
4,4,5,5-tetramethyl-2-(4-vinylphenyl)-1,3,2-dioxaborolane (2h)



S24 **2h**

Pinacol (1.20 g, 10.2 mmol) was added in one portion to a suspension of 4-vinylphenylboronic acid **S24** (1.48 g, 10.0 mmol) and $MgSO_4$ (cat.) in THF (30.0 mL). The resulting mixture was stirred for 2h at ambient temperature before filtration and concentration under vacuum. The crude product was then purified by column chromatography on silica gel, eluting with Hexanes: EtOAc [50 : 1 (v/v)], the title compound was obtained as a colorless oil (1.51 g, 6.60 mmol, 97%). $\mathbf{R_f}$ = 0.63 [Hexanes: EtOAc 20:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 7.75-7.80 (m, 2H), 7.39-7.44 (m, 2H), 6.73 (dd, *J* = 11.2, 17.5 Hz, 1H), 5.82 (d, *J* = 17.5 Hz, 1H), 5.30 (d, *J* = 11.2 Hz, 1H), 1.35 (s, 12H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 140.33, 137.00, 135.14, 135.14, 135.14, 125.65, 125.65, 115.00, 83.90, 83.90, 24.99, 24.99, 24.99, 24.99. **HRMS** (ESI-TOF) *m/z* calcd for $C_{14}H_{20}BO_2$ [$(M + H)^+$], 231.1551, found, 231.1555.

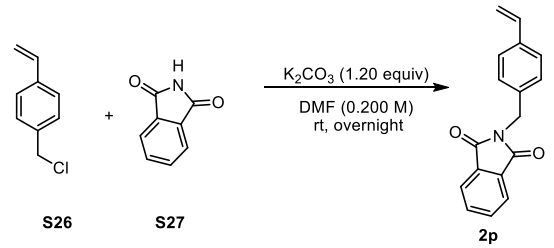
2,2-difluoro-5-vinylbenzo[d][1,3]dioxole (2l)



S25 **2l**

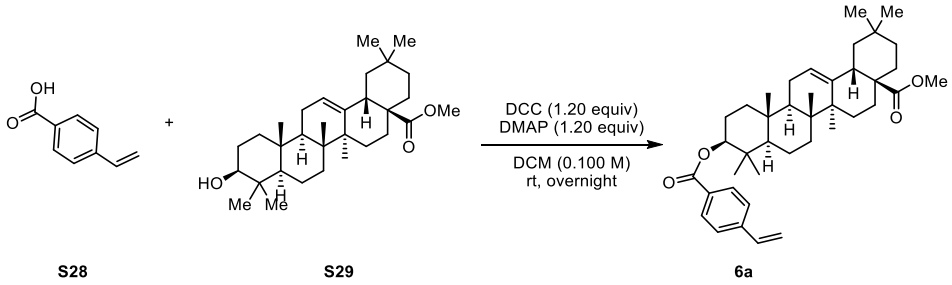
CH_3PPh_3Br (4.29 g, 12.0 mmol) was added to a 100 mL flamed dried round bottom flask charged with a stirring bar. The flask was evacuated and filled with nitrogen. Anhydrous tetrahydrofuran (40.0 mL) was added, and then *n*-BuLi (2.50 M, 4.80 mL, 12.0 mmol) was added dropwise to the solution at 0 °C. The mixture was stirred at 0 °C for 15 min, then the THF solution of **S25** (10.0 mmol, 1.00 equiv) was added at 0 °C. The reaction mixture was stirred at room temperature for overnight. The resulting solution was quenched with aqueous solution of NH_4Cl and the mixture was extracted with ethyl acetate (3×40 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc [100 : 1 (v/v)], to afford the title compound as colorless oil (1.47 g, 7.70 mmol, 77% yield). $\mathbf{R_f}$ = 0.83 [Hexanes: EtOAc 20:1 (v/v)]. **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ºC, δ): 7.15 (d, *J* = 1.6 Hz, 1H), 7.07 (dd, *J* = 1.6, 8.0 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 6.66 (dd, *J* = 10.8, 17.6 Hz, 1H), 5.66 (dd, J = 0.4, 17.6 Hz, 1H), 5.25 (dd, *J* = 0.4, 10.8 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, 25 ºC, δ): 144.38, 143.43, 135.73, 134.33, 131.79 (t, $J^1_{C\text{-}F}$ = 254.0 Hz), 122.47, 114.31, 109.41, 106.64. **^{19}F NMR** (376 MHz, $CDCl_3$, 25 ºC, δ): -50.23. These spectroscopic data correspond to previously reported data.[11]

2-(4-vinylbenzyl)isoindoline-1,3-dione (2p)



Phthalimide **S27** (2.94 g, 20.0 mmol, 1.00 equiv), K_2CO_3 (3.32g, 24.0 mmol, 1.20 equiv) and DMF (100 ml, 0.200 M) were added to a 200 mL round flask, after that, injecting **S26** (1.41 ml, 20.0 mmol, 1.00 equiv). After the reaction mixture was stirred at room temperature for overnight, the suspension was diluted with Et_2O and then washed with water, saturated $NaHCO_3$, and brine. The combined organic phases were dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc (20 : 1 (v/v)), to afford the title compound as white solid (3.94 g, 15.0 mmol, 75% yield). $\mathbf{R_f}$ = 0.14 [Hexanes: EtOAc 20:1 (v/v)]. **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ºC, δ): 7.80-7.86 (m, 2H), 7.66-7.72 (m, 2H), 7.32-7.41 (m, 4H), 6.67 (dd, *J* = 10.8, 17.6 Hz, 1H), 5.71 (dd, *J* = 0.8, 17.6 Hz, 1H), 5.22 (dd, *J* = 0.8, 10.8 Hz, 1H), 4.83 (s, 2H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 168.14, 168.14, 137.31, 136.42, 135.96, 134.11, 134.11, 132.22, 128.98, 128.98, 126.60, 126.60, 123.46, 123.46, 114.27, 114.27, 41.44. **HRMS** (ESI-TOF) *m/z* calcd for $C_{17}H_{14}NO_2$ [$(M + H)^+$], 264.1019, found, 264.1020.

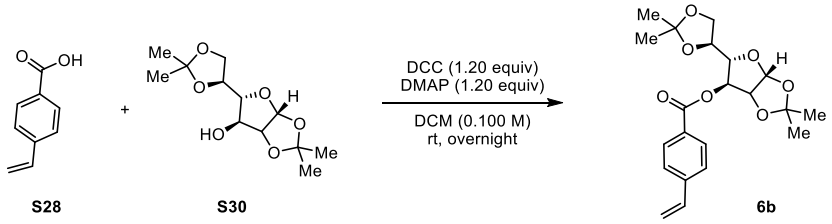
Methyl (4aS,6aS,6bR,8aR,10S,12aR,12bR,14bS)-2,2,6a,6b,9,9,12a-heptamethyl-10-((4-vinylbenzoyl)oxy)-1,3,4,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14b-octadecahydropicene-4a(2H)-carboxylate (6a)



Under nitrogen atmosphere, a 50 mL flame-dried round bottom flask was charged with **S28** (325 mg, 2.20 mmol, 1.00 equiv), *N,N'*-dicyclohexylcarbodiimide (DCC) (545 mg, 2.64 mmol, 1.20 equiv), DMAP (322 mg, 2.64 mmol, 1.20 equiv), **S29** (1.03 g, 2.20 mmol, 1.00 equiv), and DCM (22.0 mL). After the reaction mixture was stirred at room temperature for overnight, it was concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel, eluting with Hexanes:EtOAc [50 : 1 (v/v)], to afford the title compound as a white solid (1.09 g, 1.86 mmol, 83% yield). $\mathbf{R_f}$ = 0.46 [Hexanes: EtOAc 20:1 (v/v)]. **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ºC, δ): 7.99 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 6.75 (dd, *J* = 10.8, 17.6 Hz, 1H), 5.85 (d, *J* = 17.6 Hz, 1H), 5.37 (d, *J* = 10.8 Hz, 1H), 5.29 (t, *J* = 3.6 Hz, 1H), 4.73 (dd, *J* = 5.6, 10.4 Hz, 1H), 3.63 (s, 3H), 2.87 (dd, *J* = 4.4, 14.0 Hz, 1H), 0.95-2.05 (m, 22H), 1.15 (s, 3H), 1.01 (s,

3H), 0.98 (s, 3H), 0.93 (s, 3H), 0.93 (s, 3H), 0.90 (s, 3H), 0.74 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 178.43, 166.17, 143.94, 141.87, 136.19, 130.21, 129.96, 126.19, 122.40, 116.46, 81.63, 55.48, 51.66, 47.68, 46.84, 45.97, 41.77, 41.41, 39.42, 38.23, 38.21, 37.10, 35.04, 33.98, 33.24, 32.72, 32.50, 30.82, 28.33, 27.81, 26.05, 25.57, 23.77, 23.72, 23.55, 23.19, 18.36, 17.11, 16.97, 15.50. **HRMS** (ESI-TOF) *m/z* calcd for $C_{40}H_{57}O_4$ [$(M + H)^+$], 601.4251, found, 601.4245.

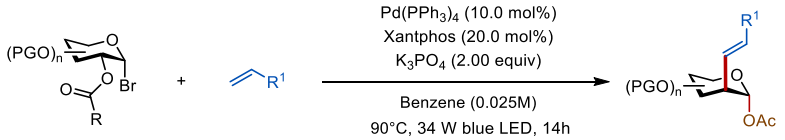
(3aR,5S,6S)-5-((S)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl 4-vinylbenzoate (6b)



S28 **S30** **6b**

Under nitrogen atmosphere, a 200 mL flame-dried round bottom flask was charged with **S28** (740 mg, 5.00 mmol, 1.00 equiv), *N*,*N'*-dicyclohexylcarbodiimide (DCC) (1.24 g, 6.00 mmol, 1.20 equiv), DMAP (733 mg, 6.00 mmol, 1.20 equiv), **S30** (1.30 g, 5.00 mmol, 1.00 equiv), and DCM (50.0 mL). After the reaction mixture was stirred at room temperature for overnight, it was concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel, eluting with Hexanes: EtOAc (20 : 1 (v/v)), to afford the title compound as a white solid (1.65 g, 4.25 mmol, 85 % yield). $\mathbf{R}_f$ = 0.11 [Hexanes: EtOAc 20:1 (v/v)]. **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ºC, δ): 7.98 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 6.75 (dd, *J* = 10.8, 17.6 Hz, 1H), 5.95 (d, *J* = 3.6 Hz, 1H), 5.87 (dd, *J* = 0.4, 17.6 Hz, 1H), 5.49 (d, *J* = 2.4 Hz, 1H), 5.40 (dd, *J* = 0.4, 10.8 Hz, 1H), 4.63 (d, *J* = 3.6 Hz, 1H), 4.30-4.40 (m, 2H), 4.04-4.14 (m, 2H), 1.55 (s, 3H), 1.41 (s, 3H), 1.32 (s, 3H), 1.26 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, 25 ºC, δ): 165.09, 142.64, 135.99, 130.17, 130.17, 128.72, 126.39, 126.39, 117.08, 112.50, 109.52, 105.28, 83.53, 80.12, 76.73, 72.73, 67.39, 26.96, 26.88, 26.35, 25.34. **HRMS** (ESI-TOF) *m/z* calcd for $C_{21}H_{26}O_7Na$ [$(M + H)^+$], 413.1571, found, 413.1570.

General Procedure B (for migratory alkenylation reaction):

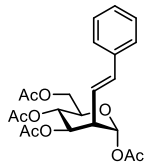


1a-1n, 5a-5f **2a-2u, 6a-6b** **3a-3u, 4b-4n, 7a-7h**

In a glovebox, to an oven-dried 20 mL screw cap vial was added $Pd(PPh_3)_4$ (23.1 mg, 0.0200 mmol, 10 mol%), Xantphos (23.1 mg, 0.0400 mmol, 20 mol%), bromosugar (0.200 mmol, 1.00 equiv), alkene substrate (0.300 mmol, 1.50 equiv), K_3PO_4 (84.9 mg, 0.400 mmol, 2.00 equiv), benzene (8.00 mL, 0.025 M) and a stir bar. Next, the vial was capped, taken out of the glovebox, and sealed with a black tape. The reaction mixture was heated to 90 °C and stirred for 5 min, then it was irradiated with 34W Blue LEDs for 14h. After that, the reaction mixture was concentrated *in vacuo*. The residue was purified by flash

chromatography on silica gel or use preparative TLC to separate the desired compound. If the diastereomers could not be separated by the flash column chromatography, they were purified by HPLC [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.

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



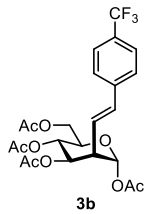
3a

According to the **General Procedure B**, the title compound was obtained as a white foam (65.0 mg, 0.150 mmol, 75% yield, axial: equatorial = 4.3:1). $\mathbf{R}_f$ = 0.20 Hexanes: EtOAc [3:1 (v/v)].

Data for axial product (**3a-*ax***): t_R = 7.83 min, 10% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min (Lux® 5µm i-cellouse 5). **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 7.31-7.40 (m, 4H), 7.26-7.30 (m, 1H), 6.55 (d, *J* = 16.0 Hz, 1H), 6.16 (dd, *J* = 9.0, 16.0 Hz, 1H), 6.17 (d, *J* = 1.5 Hz, 1H, H-1), 5.30-5.37 (m, 2H), 4.25 (dd, *J* = 5.0, 12.5 Hz, 1H), 4.15 (dd, *J* = 2.0, 12.5 Hz, 1H), 4.09-4.13 (m, 1H), 3.22 (dd, *J* = 5.0, 9.0 Hz, 1H, H-2), 2.18 (s, 3H), 2.11 (s, 3H), 2.06 (s, 3H), 2.01 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 170.84, 170.46, 169.72, 168.97, 136.50, 135.93, 128.79, 128.79, 128.23, 126.65, 126.65, 122.26, 94.27, 70.90, 70.84, 66.15, 62.47, 46.16, 21.22, 21.02, 20.90, 20.86. **HRMS** (ESI-TOF) *m/z* calcd for $C_{22}H_{26}O_9Na$ [$(M + Na)^+$], 457.1469, found, 457.1473.

Data for equatorial product (**3a-*eq***): t_R = 9.30 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): 7.24-7.33 (m, 5H), 6.54 (d, *J* = 16.1 Hz, 1H), 6.17(d, *J* = 3.5 Hz, 1H), 5.80 (dd, *J* = 9.1, 16.1 Hz, 1H), 5.45 (dd, *J* = 9.8, 11.2 Hz, 1H), 5.15 (t, *J* = 9.8 Hz, 1H), 4.33 (dd, *J* = 4.2, 12.6 Hz, 1H), 4.10 (ddd, *J* = 2.1, 4.2, 10.5 Hz, 1H), 4.07 (dd, *J* = 2.1, 12.6 Hz, 1H), 2.88-2.92 (m, 1H), 2.18 (s, 3H), 2.10 (s, 3H), 2.05 (s, 3H), 1.94 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.88, 170.57, 169.84, 169.04, 136.40, 135.96, 128.78, 128.78, 128.24, 126.63, 126.63, 122.56, 92.87, 70.75, 70.09, 68.66, 62.05, 49.01, 21.08, 20.89, 20.89, 20.84. **HRMS** (ESI-TOF) *m/z* calcd for $C_{22}H_{26}O_9Na$ [$(M + Na)^+$], 457.1469, found, 457.1473.

(2R,3S,4R,5S,6R)-6-(acetoxymethyl)-3-((E)-4-(trifluoromethyl)styryl)tetrahydro-2H-pyran-2,4,5-triyl triacetate (3b)



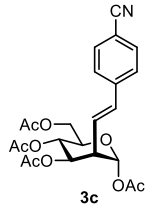
3b

According to the **General Procedure B**, the title compound was obtained as a white foam (69.2 mg, 0.138 mmol, 69% yield, axial: equatorial = 4.3:1). $\mathbf{R}_f$ = 0.20 Hexanes: EtOAc [3:1 (v/v)].

Data for axial product (**3b-*ax***): t_R = 16.8 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): 7.62 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 6.62 (d, *J* = 16.0 Hz, 1H), 6.29 (dd, *J* = 9.0, 16.0 Hz, 1H), 6.20 (d, *J* = 1.5 Hz, 1H, H-1), 5.28-5.40 (m, 2H), 4.26 (dd, *J* = 5.0, 12.5 Hz, 1H), 4.10-4.17 (m, 2H), 3.22-3.26 (m, 1H, H-2), 2.21 (s, 3H), 2.12 (s, 3H), 2.09 (s, 3H), 2.04 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 170.78, 170.35, 169.74, 168.93, 139.82, 134.63, 130.09 (q, $J^2_{C\text{-}F}$ = 32.12 Hz), 126.84, 126.84, 125.79 (q, $J^3_{C\text{-}F}$ = 3.75 Hz), 125.79 (q, $J^3_{C\text{-}F}$ = 3.75 Hz), 125.15, 124.23 (q, $J^1_{C\text{-}F}$ = 271.63 Hz), 93.99, 70.87, 70.75, 66.07, 62.41, 46.20, 21.21, 20.99, 20.89, 20.85. **^{19}F NMR** (376 MHz, CDCl3, 25 ºC) δ -62.59 (s, 3F). **HRMS** (ESI-TOF) *m/z* calcd for $C_{23}H_{25}F_3O_9Na$ [(M + Na)$^+$], 525.1343, found, 525.1344.

Data for equatorial product (**3b-*eq***): t_R = 6.8 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): 7.56 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 6.56 (d, *J* = 16.1 Hz, 1H), 6.18 (d, *J* = 3.5 Hz, 1H), 5.90 (dd, *J* = 9.1, 16.1 Hz, 1H), 5.46 (dd, *J* = 9.8, 11.2 Hz, 1H), 5.16 (t, *J* = 9.8 Hz, 1H), 4.34 (dd, *J* = 4.2, 12.6 Hz, 1H), 4.11 (ddd, *J* = 2.1, 3.5, 9.8 Hz, 1H), 4.07 (dd, *J* = 2.1, 11.9 Hz, 1H), 2.93 (ddd, *J* = 3.5, 9.8, 11.9 Hz, 1H), 2.18 (s, 3H), 2.10 (s, 3H), 2.06 (s, 3H), 1.94 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.84, 170.53, 169.80, 168.96, 139.72, 134.52, 130.10 (q, $J^2_{C\text{-}F}$ = 31.85 Hz), 126.81, 126.81, 125.78 (q, $J^3_{C\text{-}F}$ = 3.75 Hz), 125.78 (q, $J^3_{C\text{-}F}$ = 3.75 Hz), 125.46, 124.18 (q, $J^1_{C\text{-}F}$ = 269.67 Hz), 92.61, 70.64, 70.14, 68.50, 61.98, 49.07, 21.08, 20.98, 20.86, 20.83. **^{19}F NMR** (376 MHz, CDCl3, 25 ºC) δ -62.63 (s, 3F). **HRMS** (ESI-TOF) *m/z* calcd for $C_{23}H_{25}F_3O_9Na$ [(M + Na)$^+$], 525.1343, found, 525.1335.

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



3c

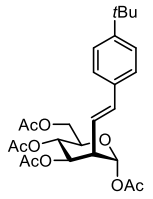
According to the **General Procedure B**, the title compound was obtained as a white foam (51.4 mg, 0.112 mmol, 56% yield, axial: equatorial = 5.6:1). $\mathbf{R}_f$ = 0.11 Hexanes: EtOAc [3:1 (v/v)].

Data for axial product (**3c-*ax***): t_R = 27.5 min, 10% (v/v) isopropanol in hexane at the flow rate of 0.8 ml/min. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 7.63 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 6.58 (d, *J* = 16.0 Hz, 1H), 6.30 (dd, *J* = 9.0, 16.0 Hz, 1H), 6.17 (d, *J* = 1.0 Hz, 1H, H-1), 5.38 (dd, *J* = 5.5, 10.0 Hz, 1H), 5.29 (t, *J* = 10.0 Hz, 1H), 4.26 (dd, *J* = 5.0, 12.5 Hz, 1H), 4.10-4.19 (m, 2H), 3.21-3.35 (m, 1H), 2.18 (s, 3H), 2.09 (s, 3H), 2.07 (s, 3H), 2.01 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 170.72, 170.28, 169.75, 168.89, 140.73, 134.32, 132.66, 132.66, 127.16, 127.16, 126.52, 118.89, 111.61, 93.83, 70.87, 70.67, 66.04,

62.39, 46.22, 21.19, 20.97, 20.88, 20.84. **HRMS** (ESI-TOF) *m/z* calcd for $C_{23}H_{26}NO_9$ [$(M + H)^+$], 460.1602, found, 460.1592.

Data for equatorial product (**3c-*eq***): t_R = 23.08 min, 10% (v/v) isopropanol in hexane at the flow rate of 0.8 ml/min. **^{1}H NMR** (700 MHz, C8l$_3$, 25 ºC, δ): 7.60 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 6.54 (d, *J* = 16.1 Hz, 1H), 6.18 (d, *J* = 3.5 Hz, 1H, H-1), 5.94 (dd, *J* = 9.1, 14.7 Hz, 1H), 5.45 (dd, *J* = 9.8, 10.5 Hz, 1H), 5.16 (t, *J* = 9.8 Hz, 1H), 4.33 (dd, *J* = 4.2, 12.6 Hz, 1H), 4.11 (ddd, *J* = 2.1, 4.2, 10.5 Hz, 1H), 4.07 (dd, *J* = 2.1, 12.6 Hz, 1H), 2.93 (ddd, *J* = 3.5, 9.8, 12.1 Hz, 1H), 2.18 (s, 3H), 2.10 (s, 3H), 2.06 (s, 3H), 1.94 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.82, 170.53, 169.79, 168.94, 140.65, 134.18, 132.66, 132.66, 127.14, 127.14, 126.82, 118.86, 111.63, 92.50, 70.60, 70.17, 68.43, 61.95, 49.11, 21.09, 20.88, 20.86, 20.82. **HRMS** (ESI-TOF) *m/z* calcd for $C_{23}H_{25}NO_9Na$ [$(M + Na)^+$], 482.1422, found, 482.1421.

(2R,3S,4R,5S,6R)-6-(acetoxymethyl)-3-((E)-4-(tert-butyl)styryl)tetrahydro-2H-pyran-2,4,5-triyl triacetate (3d)



3d

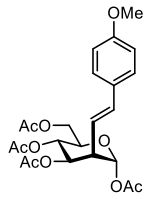
According to the **General Procedure B**, the title compound was obtained as a white foam (68.4 mg, 0.140 mmol, 70% yield, axial: equatorial = 4.3:1). **R_f** = 0.28 Hexanes: EtOAc [3:1 (v/v)].

Data for axial product (**3d-*ax***): t_R = 9.9 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): 7.30-7.38 (m, 4H), 6.53 (d, *J* = 16.0 Hz, 1H), 6.15 (d, *J* = 1.5 Hz, 1H, H-1), 6.12 (dd, *J* = 9.5, 16.0 Hz, 1H), 5.29-5.36 (m, 2H), 4.24 (dd, *J* = 4.5, 12.0, Hz, 1H), 4.15 (dd, *J* = 2.5, 12.0 Hz, 1H), 4.08-4.12 (m, 1H), 3.20 (dd, *J* = 4.5, 9.5Hz, 1H, H-2), 2.17 (s, 3H), 2.11 (s, 3H), 2.06 (s, 3H), 2.00 (s, 3H), 1.32 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 170.86, 170.48, 169.67, 168.98, 151.42, 135.67, 133.78, 126.39, 126.39, 125.71, 125.71, 121.45, 94.34, 70.95, 70.82, 66.14, 62.48, 46.18, 34.78, 31.41, 31.41, 31.41, 21.23, 21.02, 20.92, 20.86. **HRMS** (ESI-TOF) *m/z* calcd for $C_{26}H_{34}O_9Na$ [$(M + Na)^+$], 513.2095, found, 513.2083.

Data for equatorial product (**3d-*eq***): t_R = 4.9 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): 7.32-7.34 (m, 2H), 7.23-7.25 (m, 2H), 6.51 (d, *J* = 16.1 Hz, 1H), 6.15 (d, *J* = 3.5 Hz, 1H), 5.76 (dd, *J* = 9.1, 16.1 Hz, 1H), 5.45 (dd, *J* = 9.8, 11.2 Hz, 1H), 5.14 (t, *J* = 9.8 Hz, 1H), 4.33 (dd, *J* = 4.2, 12.6 Hz, 1H), 4.09 (ddd, *J* = 2.1, 4.2, 9.8 Hz, 1H), 4.06 (dd, *J* = 2.1, 12.6 Hz, 1H), 2.86-2.91 (m, 1H), 2.17 (s, 3H), 2.10 (s, 3H), 2.05 (s, 3H), 1.94 (s, 3H), 1.30 (s, 9H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.89, 170.58, 169.86, 169.03, 151.42, 135.69, 133.67, 126.38, 126.38, 125.69, 125.69, 121.76, 92.96, 70.80, 70.06, 68.71, 62.06, 48.97, 34.75, 31.39, 31.39, 31.39, 21.07, 20.91,

20.89, 20.84. **HRMS** (ESI-TOF) *m/z* calcd for $C_{26}H_{34}O_9Na$ [(M + Na)$^+$], 513.2095, found, 513.2096.

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



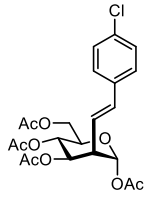
3e

According to the **General Procedure B**, the title compound was obtained as a white foam (71.0 mg, 0.154 mmol, 77% yield, axial: equatorial = 4.5:1). $\mathbf{R_f}$ = 0.17 Hexanes: EtOAc [3:1 (v/v)].

Data for axial product (**3e-*ax***): t_R = 16.2 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): 7.30-7.33 (m, 2H), 6.85-6.88 (m, 2H), 6.48 (d, *J* = 15.4 Hz, 1H), 6.15 (d, *J* = 1.4 Hz, 1H, H-1), 6.01 (dd, *J* = 9.1, 15.4 Hz, 1H), 5.30-5.35 (m, 2H), 4.24 (dd, *J* = 4.9, 12.6 Hz, 1H), 4.15 (dd, *J* = 2.1, 12.6 Hz, 1H), 4.10 (ddd, *J* = 2.1, 4.9, 9.8 Hz, 1H), 3.82 (s, 3H), 3.16-3.20 (m, 1H), 2.17 (s, 3H), 2.11 (s, 3H), 2.06 (s, 3H), 2.00 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.86, 170.48, 169.74, 169.00, 159.69, 135.30, 129.29, 127.86, 127.86, 119.84, 114.16, 114.16, 94.42, 70.96, 70.81, 66.18, 62.50, 55.48, 46.18, 21.23, 21.03, 20.92, 20.88. **HRMS** (ESI-TOF) *m/z* calcd for $C_{23}H_{28}O_{10}Na$ [(M + Na)$^+$], 487.1575, found, 487.1575.

Data for equatorial product (**3e-*eq***): t_R = 11.7 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): 7.22-7.24 (m, 2H), 6.82-6.85 (m, 2H), 6.47 (d, *J* = 15.4 Hz, 1H), 6.15 (d, *J* = 3.5 Hz, 1H), 5.64 (dd, *J* = 9.1, 15.4 Hz, 1H), 5.43 (dd, *J* = 9.8, 11.2 Hz, 1H), 5.14 (t, *J* = 9.8 Hz, 1H), 4.33 (dd, *J* = 3.5, 12.6 Hz, 1H), 4.07-4.11 (m, 1H), 4.06 (dd, *J* = 2.1, 11.9 Hz, 1H), 3.80 (s, 3H), 2.87 (ddd, *J* = 3.5, 9.1, 12.0 Hz, 1H), 2.17 (s, 3H), 2.10 (s, 3H), 2.05 (s, 3H), 1.94 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.89, 170.59, 169.85, 169.07, 159.71, 135.34, 129.20, 127.85, 127.85, 120.20, 114.16, 114.16, 93.00, 70.83, 70.08, 68.70, 62.07, 55.47, 49.04, 21.09, 20.90, 20.90, 20.85. **HRMS** (ESI-TOF) *m/z* calcd for $C_{23}H_{28}O_{10}Na$ [(M + Na)$^+$], 487.1575, found, 487.1576.

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



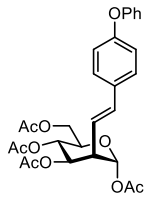
3f

According to the **General Procedure B**, the title compound was obtained as a white foam (74.0 mg, 0.158 mmol, 79% yield, axial: equatorial = 4.5:1). $\mathbf{R_f}$ = 0.22 Hexanes: EtOAc [3:1 (v/v)].

Data for axial product (**3f-*ax***): t_R = 25.0 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): 7.33 (s, 4H), 6.53 (dd, *J* = 0.5, 16.0 Hz, 1H), 6.15 (d, *J* = 1.5 Hz, 1H, H-1), 6.14 (dd, *J* = 9.0, 16.0 Hz, 1H), 5.28-5.38 (m, 2H), 4.28 (dd, *J* = 5.0, 12.0 Hz, 1H), 4.09-4.17 (m, 2H), 3.23 (dd, *J* = 5.0, 9.0 Hz, 1H, H-2), 2.20 (s, 3H), 2.12 (s, 3H), 2.09 (s, 3H), 2.03 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 170.80, 170.39, 169.75, 168.95, 134.93, 134.71, 133.96, 128.98, 128.98, 127.87, 127.87, 122.98, 94.14, 70.85, 70.82, 66.12, 62.45, 46.17, 21.21, 21.00, 20.90, 20.86. **HRMS** (ESI-TOF) *m/z* calcd for $C_{22}H_{25}ClO_9Na$ [(M + Na)$^+$], 491.1079, found, 491.1079.

Data for equatorial product (**3f-*eq***): t_R = 22.8 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): 7.19-7.31 (m, 4H), 6.51 (d, *J* = 16.0 Hz, 1H), 6.19 (d, *J* = 3.5 Hz, 1H, H-1), 5.80 (dd, *J* = 9.0, 16.0 Hz, 1H), 5.46 (dd, J = 9.0, 11.0 Hz, 1H), 5.17 (t, *J* = 10.0 Hz, 1H), 4.35 (dd, *J* = 4.0, 12.5 Hz, 1H), 4.04-4.13 (m, 2H), 2.85-2.92 (m, 1H, H-2), 2.20 (s, 3H), 2.12 (s, 4H), 2.07 (s, 3H), 1.96 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 170.85, 170.55, 169.82, 169.00, 134.84, 134.67, 134.00, 128.98, 128.98, 127.84, 127.84, 123.32, 92.74, 70.70, 70.13, 68.59, 62.03, 49.05, 21.08, 20.87, 20.89, 20.83. **HRMS** (ESI-TOF) *m/z* calcd for $C_{22}H_{25}ClO_9Na$ [(M + Na)$^+$], 491.1079, found, 491.1078.

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



3g

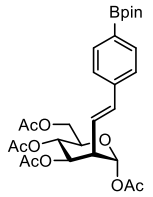
According to the **General Procedure B**, the title compound was obtained as a white foam (84.1 mg, 0.160 mmol, 80% yield, axial: equatorial = 4.3:1). **R_f** = 0.22 Hexanes: EtOAc [3:1 (v/v)].

Data for axial product (**3g-*ax***): t_R = 11.3 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): 7.31-7.38 (m, 4H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.5 Hz, 2H), 6.52 (d, *J* = 16.0 Hz, 1H), 6.16 (d, *J* = 1.5 Hz, 1H, H-1), 6.07 (dd, *J* = 9.0, 16.0 Hz, 1H), 5.29-5.38 (m, 2H), 4.25 (dd, *J* = 4.5, 12.5 Hz, 1H), 4.07-4.18 (m, 2H), 3.20 (dd, *J* = 4.5, 9.0 Hz, 1H, H-2), 2.18 (s, 3H), 2.10 (s, 3H), 2.06 (s, 3H), 2.01 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 170.82, 170.43, 169.73, 168.97, 157.40, 157.12, 135.08, 131.67, 129.94, 129.94, 128.03, 128.03, 123.61, 121.22, 119.15, 119.15, 119.03, 119.03, 94.30, 70.92, 70.84, 66.15, 62.47, 46.16, 21.22, 21.03, 20.90, 20.86. **HRMS** (ESI-TOF) *m/z* calcd for $C_{28}H_{30}O_{10}Na$ [(M + Na)$^+$], 549.1731, found, 549.1729.

Data for equatorial product (**3g-*eq***): t_R = 7.41 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): 7.36 (dd, *J* = 7.0, 8.4 Hz, 2H), 7.24-7.28 (m, 2H), 7.12 (dd, *J* = 7.0, 7.7 Hz, 2H), 7.00 (d, *J* = 7.7 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 6.52 (d, *J* = 16.1 Hz, 1H), 6.19 (d, *J* = 3.5 Hz, 1H, H-1), 5.73 (dd, *J* = 9.1, 16.1 Hz, 1H), 5.46 (dd, *J* = 9.8, 11.0 Hz, 1H), 5.17 (t, *J* = 9.8 Hz,

1H), 4.33 (d, *J* = 4.2, 12.6 Hz, 1H), 4.08-4.11 (m, 1H), 4.06 (dd, J = 2.1, 12.6 Hz, 1H), 2.91 (ddd, *J* = 3.5, 9.1, 11.9 Hz, 1H), 2.20 (s, 3H), 2.12 (s, 3H), 2.08 (s, 3H), 1.98 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.88, 170.58, 169.06, 157.44, 135.10, 129.94, 129.94, 128.01, 128.01, 123.66, 121.51, 119.19, 119.19, 118.93, 118.93, 92.91, 77.34, 77.16, 76.97, 70.79, 70.09, 68.65, 62.05, 49.02, 21.09, 20.91, 20.89, 20.84. **HRMS** (ESI-TOF) *m/z* calcd for $C_{28}H_{30}O_{10}Na$ [(M + Na)$^+$], 549.1731, found, 549.1732.

(2R,3S,4R,5S,6R)-6-(acetoxymethyl)-3-((E)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)styryl)tetrahydro-2H-pyran-2,4,5-triyl triacetate (3h)



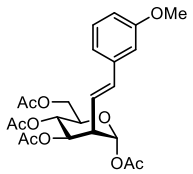
3h

According to the **General Procedure B**, the title compound was obtained as a white foam (73.5 mg, 0.132 mmol, 66% yield, axial: equatorial = 4.1:1). $\mathbf{R}_f$ = 0.22 Hexanes: EtOAc [3:1 (v/v)].

Data for axial product (**3h-*ax***): t_R = 15.1 min, 6% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 7.78 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 6.56 (d, *J* = 16.0 Hz, 1H), 6.23 (dd, *J* = 9.5, 16.0 Hz, 1H), 6.17 (d, *J* = 1.0 Hz, 1H, H-1), 5.30-5.38 (m, 2H), 4.25 (dd, *J* = 4.5, 12.5 Hz, 1H), 4.15 (dd, *J* = 2.5, 12.5 Hz, 1H), 4.08-4.13 (m, 1H), 3.22 (dd, *J* = 4.5, 9.0 Hz, 1H), 2.18 (s, 3H), 2.10 (s, 3H), 2.06 (s, 3H), 2.00 (s, 3H), 1.35 (s, 12H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 170.84, 170.45, 169.72, 168.93, 139.07, 135.96, 135.27, 135.27, 135.27, 125.94, 125.94, 123.31, 94.20, 83.99, 70.84, 66.14, 62.42, 46.22, 29.85, 29.85, 25.01, 25.01, 25.01, 25.01, 21.21, 21.01, 20.88, 20.86. **HRMS** (ESI-TOF) *m/z* calcd for $C_{28}H_{37}BO_{11}Na$ [(M + Na)$^+$], 583.2321, found, 583.2321.

Data for equatorial product (**3h-*eq***): t_R = 8.5 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): 7.74 (d, *J* = 7.7 Hz, 2H), 7.29 (d, *J* = 7.7 Hz, 3H), 6.54 (d, *J* = 16.1 Hz, 1H), 6.16 (d, *J* = 2.8 Hz, 1H, H-1), 5.86 (dd, *J* = 9.1, 16.1 Hz, 1H), 5.45 (dd, *J* = 9.8, 11.2 Hz, 1H), 5.15 (t, *J* = 9.8 Hz, 1H), 4.33 (dd, *J* = 4.2, 12.6 Hz, 1H), 4.03-4.11 (m, 2H), 2.89-2.93 (m, 1H), 2.18 (s, 3H), 2.10 (s, 3H), 2.05 (s, 3H), 1.93 (s, 3H), 1.34 (s,12H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.85, 170.50, 169.81, 169.02, 138.92, 135.96, 135.21, 135.21, 128.77, 125.88, 125.88, 123.49, 92.76, 83.95, 83.95, 70.65, 70.06, 68.62, 62.01, 49.03, 24.96, 24.96, 24.96, 24.96, 21.06, 20.87, 20.81, 20.81. **HRMS** (ESI-TOF) *m/z* calcd for $C_{28}H_{37}BO_{11}Na$ [(M + Na)$^+$], 583.2321, found, 583.2329.

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



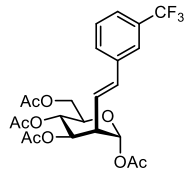
3i

According to the **General Procedure B**, the title compound was obtained as a white foam (66.5 mg, 0.144 mmol, 72% yield, axial: equatorial = 4.1:1). $\mathbf{R}_f$ = 0.18 Hexanes: EtOAc [3:1 (v/v)].

Data for axial product (**3i-*ax***): t_R = 9.6 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): 7.23-7.28 (m, 1H), 6.95-7.00 (m, 1H), 6.90-6.91 (m, 1H), 6.83 (ddd, *J* = 0.7, 2.1, 7.7 Hz, 1H), 6.52 (d, *J* = 15.4 Hz, 1H), 6.16 (dd, *J* = 9.1, 15.4 Hz, 1H), 6.16 (s, 1H, H-1), 5.29-5.36 (m, 2H), 4.25 (dd, *J* = 4.9, 12.6 Hz, 1H), 4.15 (dd, *J* = 2.1, 12.6 Hz, 1H), 4.11 (ddd, *J* = 2.8, 4.9, 9.8 Hz, 1H), 3.83 (s, 3H), 3.21 (ddt, *J* = 0.7, 4.9, 9.1 Hz, 1H, H-2), 2.18 (s, 3H), 2.11 (s, 3H), 2.06 (s, 3H), 2.01 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.84, 170.46, 169.71, 168.97, 159.97, 137.90, 135.84, 129.77, 122.56, 119.27, 113.75, 112.10, 94.21, 70.86, 70.81, 66.14, 62.47, 55.43, 46.14, 21.22, 21.02, 20.90, 20.86. **HRMS** (ESI-TOF) *m/z* calcd for $C_{23}H_{28}O_{10}Na$ [$(M + Na)^+$], 487.1575, found, 487.1575.

Data for equatorial product (**3i-*eq***): t_R = 7.6 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): 7.22 (t, *J* = 7.7 Hz, 1H), 6.87-6.91 (m, 1H), 6.78-6.84 (m, 2H), 6.50 (d, *J* = 15.4 Hz, 1H), 6.16 (d, *J* = 3.5 Hz, 1H), 5.79 (dd, *J* = 9.1, 16.1Hz, 1H), 5.44 (dd, *J* = 9.8, 10.5 Hz, 1H), 5.15 (t, *J* = 9.8 Hz, 1H), 4.33 (dd, *J* = 4.2, 12.6 Hz, 1H), 4.09 (ddd, *J* = 2.1, 3.5, 9.8 Hz, 1H), 4.06 (dd, *J* = 2.1, 12.6 Hz, 1H), 3.81 (s, 3H), 2.89 (ddd, *J* = 3.5, 9.8, 11.9 Hz, 1H), 2.18 (s, 3H), 2.10 (s, 3H), 2.05 (s, 3H), 1.94 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.87, 170.54, 169.84, 169.02, 159.93, 137.84, 135.84, 129.78, 122.90, 119.20, 113.51, 112.32, 92.83, 70.71, 70.08, 68.67, 62.04, 55.41, 48.96, 21.08, 20.89, 20.89, 20.79. **HRMS** (ESI-TOF) *m/z* calcd for $C_{23}H_{28}O_{10}Na$ [$(M + Na)^+$], 487.1575, found, 487.1572.

(2R,3S,4R,5S,6R)-6-(acetoxymethyl)-3-((E)-3-(trifluoromethyl)styryl)tetrahydro-2H-pyran-2,4,5-triyl triacetate (3j)



3j

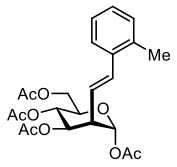
According to the **General Procedure B**, the title compound was obtained as a white foam (78.0 mg, 0.150 mmol, 75% yield, axial: equatorial = 4.7:1). $\mathbf{R}_f$ = 0.18 Hexanes: EtOAc [3:1 (v/v)].

Data for axial product (**3j-*ax***): t_R = 6.60 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): 7.62 (s, 1H), 7.54 (t, *J* = 8.0 Hz, 2H), 7.44-7.49 (m, 1H), 6.60 (d, *J* = 15.5 Hz, 1H), 6.25 (dd, *J* = 9.5, 15.5 Hz, 1H), 6.17 (d, *J* = 1.5 Hz, 1H, H-1), 5.30-5.40 (m, 2H), 4.26 (dd, *J* = 4.5, 12.5 Hz, 1H), 4.16 (dd, *J* = 2.5, 12.5 Hz, 1H), 4.12 (ddd, *J* = 2.0, 4.0, 9.5 Hz, 1H), 3.23 (dd, *J* = 5.5, 9.5 Hz, 1H, H-2), 2.19 (s, 3H), 2.11 (s, 3H), 2.07 (s, 3H), 2.02 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.81, 170.39, 169.74, 168.92, 137.14, 134.57, 131.28 (q, J^2_{C-F} = 30.45 Hz), 129.82, 129.30, 124.82 (q, J^3_{C-F} = 3.79 Hz), 124.41, 124.14 (q, J^1_{C-F} = 271.25 Hz), 123.26 (q, J^3_{C-F} = 3.79 Hz), 94.01, 70.88, 70.71, 66.02, 62.34, 46.15, 21.22, 21.02, 20.86, 20.83. **^{19}F NMR** (376 MHz, CDCl3, 25 ºC) δ -62.80 (s, 3F). **HRMS** (ESI-TOF) *m/z* calcd for $C_{23}H_{25}F_3O_9Na$ [(M + Na)$^+$], 525.1343, found, 525.1343.

Data for equatorial product (**3j-*eq***): t_R = 21.2 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): 7.40-7.52 (m, 4H), 6.56 (d, *J* = 16.1 Hz, 1H), 6.18 (d, *J* = 3.5 Hz, 1H, H-1), 5.88 (dd, *J* = 9.1, 16.1 Hz, 1H), 5.46 (dd, *J* = 9.8, 11.2 Hz, 1H), 5.16 (t, *J* = 9.8 Hz, 1H), 4.34 (dd, *J* = 3.5, 12.6 Hz, 1H), 4.11 (ddd, *J* = 2.1, 4..2, 10.5 Hz, 1H), 4.07 (dd, *J* = 2.1, 12.6 Hz, 1H), 2.93 (ddd, *J* = 3.5, 9.1, 11.9 Hz, 1H), 2.19 (s, 3H), 2.10 (s, 3H), 2.06 (s, 3H), 1.95 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.86, 170.53, 169.82, 169.01, 137.05, 134.55, 131.25 (q, J^2_{C-F} = 33.25 Hz), 129.63 (q, J^1_{C-F} = 260.75 Hz), 129.30, 128.80, 124.85 (q, J^3_{C-F} = 3.50 Hz), 124.69, 123.39 (q, J^3_{C-F} = 3.50 Hz), 92.66, 70.63, 70.11, 68.56, 61.99, 49.01, 21.10, 20.89, 20.86, 20.83. **^{19}F NMR** (376 MHz, CDCl3, 25 ºC) δ -62.79 (s, 3F). **HRMS** (ESI-TOF) *m/z* calcd for $C_{23}H_{25}F_3O_9Na$ [(M + Na)$^+$], 525.1343, found, 525.1344.

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



3k

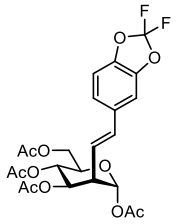
According to the **General Procedure B**, the title compound was obtained as a white foam (71.4 mg, 0.160 mmol, 80% yield, axial: equatorial = 3.6:1). $\mathbf{R}_f$ = 0.24 Hexanes: EtOAc [3:1 (v/v)].

Data for axial product (**3k-*ax***): t_R = 5.7 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): 7.440-7.44 (m, 1H), 7.13-7.22 (m, 3H), 6.76 (d, *J* = 16.0 Hz, 1H), 6.19 (d, *J* = 1.5 Hz, 1H), 6.02 (dd, *J* = 9.5, 16.0 Hz, 1H), 5.30-5.39 (m, 2H), 4.25 (dd, *J* = 4.5, 12.0 Hz, 1H), 4.09-4.16 (m, 2H), 3.24 (dd, *J* = 4.5, 9.5Hz, 1H, H-2), 2.33 (s, 2H), 2.18 (s, 2H), 2.09 (s, 2H), 2.06 (s, 2H), 2.02 (s, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 170.86, 170.40, 169.69, 168.99, 135.97, 135.51, 134.11, 130.42, 128.12, 126.36, 126.22, 123.98, 94.26, 70.93, 70.86, 66.11, 62.45, 46.36, 21.22, 21.03, 20.89, 20.86, 19.95. **HRMS** (ESI-TOF) *m/z* calcd for $C_{23}H_{28}O_9Na$ [(M + Na)$^+$], 471.1626, found, 471.1621.

Data for equatorial product (**3k-*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): 7.22-7.30 (m, 1H), 7.09-7.19 (m, 3H), 6.74 (d, *J* = 16.1 Hz, 1H), 6.20 (d, *J* = 2.8 Hz, 1H, H-1), 5.67 (dd, *J* = 9.1, 15.4 Hz, 1H), 5.47 (t, *J* = 10.5 Hz, 1H), 5.16 (t, *J* = 9.8 Hz, 1H), 4.33 (dd, *J* = 3.5, 11.9 Hz, 1H), 4.11 (d, *J* = 9.1 Hz, 1H), 4.07 (d, *J* = 11.9 Hz, 1H), 2.94 (t, *J*

= 9.8 Hz, 1H, H-2), 2.29 (s, 3H), 2.17 (s, 3H), 2.10 (s, 3H), 2.05 (s, 3H), 1.97 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.88, 170.54, 169.87, 169.07, 135.76, 135.50, 134.00, 130.37, 128.15, 126.38, 126.17, 124.05, 92.87, 70.71, 70.12, 68.68, 62.05, 49.18, 21.09, 20.92, 20.90, 20.85, 19.85. **HRMS** (ESI-TOF) *m/z* calcd for $C_{23}H_{28}O_9Na$ [$(M + Na)^+$], 471.1626, found, 471.1622.

(2R,3S,4R,5S,6R)-6-(acetoxymethyl)-3-((E)-2-(2,2-difluorobenzo[d][1,3]dioxol-5-yl)vinyl)tetrahydro-2H-pyran-2,4,5-triyl triacetate (3l)



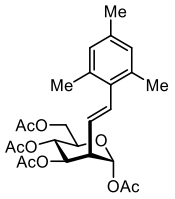
3l

According to the **General Procedure B**, the title compound was obtained as a yellow oil (81.6 mg, 0.159 mmol, 80% yield, axial: equatorial = 5.2:1). $\mathbf{R}_f$ = 0.15 Hexanes: EtOAc [3:1 (v/v)].

Data for axial product (**3l-*ax***): 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): 7.13 (d, *J* = 1.4 Hz, 1H), 7.05 (dd, *J* = 1.4, 8.4 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 1H), 6.51 (d, *J* = 16.1 Hz, 1H), 6.15 (d, *J* = 1.4 Hz, 1H, H-1), 6.08 (dd, *J* = 9.1, 16.1 Hz, 1H), 5.35 (dd, *J* = 5.6, 9.8 Hz, 1H), 5.30 (t, *J* = 9.8 Hz, 1H), 4.26 (dd, *J* = 4.2, 12.6 Hz, 1H), 4.14 (dd, *J* = 2.1, 12.6 Hz, 1H), 4.11 (ddd, *J* = 2.1, 4.2, 9.8 Hz, 1H), 3.18-3.21 (m, 1H), 2.18 (s, 3H), 2.11 (s, 3H), 2.07 (s, 3H), 2.01 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.80, 170.36, 169.74, 168.96, 144.41, 143.62, 134.59, 132.96, 131.77 (t, $J^1_{C\text{-}F}$ = 252 Hz), 122.74, 122.74, 109.59, 107.03, 94.08, 70.84, 70.79, 66.05, 62.42, 46.07, 21.21, 21.00, 20.91, 20.86. **^{19}F NMR** (376 MHz, CDCl3, 25 ºC) δ -50.18 (s, 2F). **HRMS** (ESI-TOF) *m/z* calcd for $C_{23}H_{24}F_2O_{11}Na$ [$(M + Na)^+$], 537.1179, found, 537.1180.

Data for equatorial product (**3l-*eq***): t_R = 7.6 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): 7.04 (d, *J* = 1.4 Hz, 1H), 6.94-7.00 (m, 2H), 6.47 (d, *J* = 15.4 Hz, 1H), 6.16 (d, *J* = 3.5 Hz, 1H, H-1), 5.71 (dd, *J* = 9.1, 15.4 Hz, 1H), 5.43 (dd, *J* = 9.8, 11.2 Hz, 1H), 5.15 (t, *J* = 9.8 Hz, 1H), 4.33 (dd, *J* = 4.2, 11.9 Hz, 1H), 4.10 (ddd, *J* = 2.1, 4.2, 10.5 Hz, 1H), 4.06 (dd, *J* = 2.1, 11.9 Hz, 1H), 2.85-2.91 (m, 1H), 2.19 (s, 3H), 2.10 (s, 3H), 2.05 (s, 3H), 1.94 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.86, 170.54, 169.81, 169.01, 144.38, 143.64, 134.49, 132.85, 131.75 (t, $J^1_{C\text{-}F}$ = 252 Hz), 123.14, 122.76, 109.57, 106.96, 92.69, 70.69, 70.13, 68.50, 62.00, 48.99, 21.10, 20.89, 20.87, 20.83. **^{19}F NMR** (376 MHz, CDCl3, 25 ºC) δ -50.18 (s, 2F). **HRMS** (ESI-TOF) m/z calcd for $C_{23}H_{24}F_2O_{11}Na$ [$(M + Na)^+$], 537.1179, found, 537.1175.

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



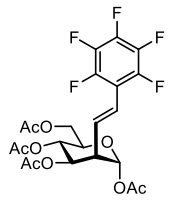
3m

According to the **General Procedure B**, the title compound was obtained as a white foam (52.4 mg, 0.108 mmol, 55% yield, axial: equatorial = 3.5:1). $\mathbf{R}_f$ = 0.24 Hexanes: EtOAc [3:1 (v/v)].

Data for axial product (**3m-*ax***): t_R = 4.4 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): 6.88 (s, 2H), 6.51 (d, *J* = 16.0 Hz, 1H), 6.20 (s, 1H, H-1), 5.70 (dd, *J* = 9.0, 16.0 Hz, 1H), 5.39 (dd, *J* = 5.0, 10.0 Hz, 1H), 5.33 (t, *J* = 10.0 Hz, 1H), 4.22 (dd, *J* = 4.5, 12.5 Hz, 1H), 4.07-4.14 (m, 2H), 3.22 (dd, *J* = 5.0, 9.0 Hz, 1H, H-2), 2.28 (s, 9H), 2.19 (s, 3H), 2.05 (s, 6H), 2.03 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 170.86, 170.35, 169.63, 169.04, 136.81, 135.93, 135.93, 133.80, 133.64, 128.72, 128.72, 127.63, 94.35, 70.88, 70.85, 65.96, 62.29, 46.56, 21.24, 21.08, 21.05, 21.00, 21.00, 20.87, 20.82. **HRMS** (ESI-TOF) *m/z* calcd for $C_{25}H_{32}O_9Na$ [$(M + Na)^+$], 499.1939, found, 499.1937.

Data for equatorial product (**3m-*eq***): t_R = 3.1 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): 6.84 (s, 1H), 6.51 (d, *J* = 16.1 Hz, 1H), 6.24 (d, *J* = 3.7 Hz, 1H), 5.47 (dd, *J* = 9.4, 11.2 Hz, 1H), 5.31 (dd, *J* = 9.1, 16.1 Hz, 1H), 5.15 (dd, *J* = 9.8 Hz, 1H), 4.34 (dd, *J* = 4.2, 12.6 Hz, 1H), 4.08-4.12 (m, 1H), 4.07 (dd, *J* = 2.1, 11.9 Hz, 1H), 2.98 (ddd, *J* = 3.5, 9.1, 11.9 Hz, 1H), 2.25 (s, 3H), 2.16 (s, 6H), 2.13 (s, 3H), 2.10 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.88, 170.40, 169.93, 169.02, 136.87, 135.74, 135.74, 134.13, 133.28, 128.71, 128.71, 127.77, 93.14, 70.79, 70.08, 68.95, 62.02, 48.93, 21.05, 21.01, 20.96, 20.89, 20.83, 20.78 , 20.78. **HRMS** (ESI-TOF) *m/z* calcd for $C_{25}H_{32}O_9Na$ [$(M + Na)^+$], 499.1939, found, 499.1936.

(2R,3S,4R,5S,6R)-6-(acetoxymethyl)-3-((E)-2-(perfluorophenyl)vinyl)tetrahydro-2H-pyran-2,4,5-triyl triacetate (3n)



3n

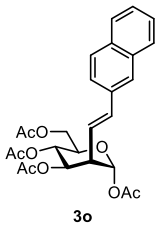
According to the **General Procedure B**, the title compound was obtained as a white foam (61.5 mg, 0.117 mmol, 60% yield, axial: equatorial = 4.8:1). $\mathbf{R}_f$ = 0.21 Hexanes: EtOAc [3:1 (v/v)].

Data for axial product (**3n-*ax***): t_R = 10.3 min, 3% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min.

^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC, δ): 6.53 (dd, *J* = 9.1, 16.8 Hz, 1H), 6.45 (d, *J* = 16.8 Hz, 1H), 6.18 (d, *J* = 1.4 Hz, 1H, H-1), 5.39 (dd, *J* = 5.6, 10.5 Hz, 1H), 5.30 (t, *J* = 10.5 Hz, 1H), 4.23 (dd, *J* = 4.2, 12.6 Hz, 1H), 4.16 (dd, *J* = 2.1, 12.6 Hz, 1H), 4.09-4.13 (m, 1H), 3.21 (dd, *J* = 5.6, 9.1 Hz, 1H), 2.19 (s, 3H), 2.11 (s, 3H), 2.06 (s, 3H), 2.03 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ):13C NMR (176 MHz, CDCl3) δ 170.86, 170.32, 169.65, 168.88, 144.87 (m), 144.87 (m), 140.42 (m), 137.91 (m), 137.91 (m), 132.29 (m), 120.23, 111.31 (m), 93.44, 70.88, 70.46, 65.74, 62.04, 47.12, 21.18, 20.92, 20.83, 20.75. **^{19}F NMR** (376 MHz, CDCl3, 25 ºC) δ (-142.86)-(-142.74) (m), -155.08 (t, $J_{C\text{-}F}$ = 22.0 Hz), (-162.55)-(-162.38) (m). **HRMS** (ESI-TOF) *m/z* calcd for $C_{22}H_{21}F_5O_9Na$ [(M + Na)$^+$], 547.0998, found, 547.0996.

Data for equatorial product (**3n-*eq***): t_R = 11.3 min, 3% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 6.43 (d, *J* = 16.1 Hz, 1H), 6.21 (d, *J* = 3.5 Hz, 1H, H-1), 6.13 (dd, *J* = 9.1, 16.1 Hz, 1H), 5.45 (t, *J* = 10.5 Hz, 1H), 5.15 (t, *J* = 9.8 Hz, 1H), 4.33 (dd, *J* = 3.5, 12.6 Hz, 1H), 4.05-4.13 (m, 2H), 2.94 (dt, *J* = 3.5, 9.1 Hz, 1H), 2.18 (s, 3H), 2.10 (s, 3H), 2.05 (s, 3H), 1.98 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.70, 170.26, 169.67, 168.82, 132.51 (m)0, 119.87, 92.16, 70.31, 70.04, 68.32, 61.77, 49.65, 20.80, 20.74, 20.67, 20.65. **^{19}F NMR** (376 MHz, CDCl3, 25 ºC) δ (-162.94)-(-142.82) (m), -154.96 (t, $J_{C\text{-}F}$ = 22.0 Hz), (-162.42)-(-162.25) (m). **HRMS** (ESI-TOF) *m/z* calcd for $C_{22}H_{21}F_5O_9Na$ [(M + Na)$^+$], 547.0998, found, 547.0993.

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



3o

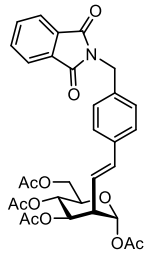
According to the **General Procedure B**, the title compound was obtained as a white foam (46.0 mg, 0.095 mmol, 48% yield, axial: equatorial = 4.2:1). **R_f** = 0.15 Hexanes: EtOAc [3:1 (v/v)].

Data for axial product (**3o-*ax***): t_R = 25.5 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): 7.80-7.83 (m, 3H), 7.73 (s, 1H), 7.60 (dd, *J* = 1.4, 8.4 Hz, 1H), 7.44-7.50 (m, 2H), 6.71 (d, *J* = 15.4 Hz, 1H), 6.29 (dd, *J* = 9.1, 15.4 Hz, 1H), 6.21 (d, *J* = 1.4 Hz, 1H, H-1), 5.34-5.41 (m, 2H), 4.27 (dd, *J* = 4.2, 12.6 Hz, 1H), 4.18 (dd, J = 2.1, 12.6 Hz, 1H), 4.12-4.15 (m, 1H), 3.28 (dd, *J* = 4.9, 9.8 Hz, 1H, H-2), 2.19 (s, 3H), 2.13 (s, 3H), 2.07 (s, 3H), 2.02 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.86, 170.49, 169.77, 168.99, 136.04, 133.88, 133.62, 133.33, 128.47, 128.17, 127.86, 126.81, 126.57, 126.30, 123.57, 122.51, 94.30, 70.93, 70.86, 66.21, 62.51, 46.32, 21.25, 21.05, 20.93, 20.89. **HRMS** (ESI-TOF) *m/z* calcd for $C_{26}H_{28}O_9Na$ [(M + Na)$^+$], 507.1626, found, 507.1621.

Data for equatorial product (**3o-*eq***): t_R = 14.9 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): 7.74-7.83 (m, 3H), 7.67 (s, 1H), 7.42-7.51 (m, 3H), 6.70 (d, *J* = 16.1 Hz, 1H), 6.21 (s, 1H, H-1), 5.92 (dd, *J* = 9.1, 16.1 Hz, 1H), 5.49 (t, *J* = 9.8 Hz, 1H), 5.18 (t, *J*

= 9.8 Hz, 1H), 4.32-4.38 (m, 1H), 4.05-4.16 (m, 2H), 2.96 (t, *J* = 10.5 Hz, 1H), 2.20 (s, 3H), 2.11 (s, 3H), 2.06 (s, 3H), 1.94 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.89, 170.60, 169.86, 169.07, 136.05, 133.77, 133.56, 133.30, 128.48, 128.17, 127.83, 126.71, 126.58, 126.33, 123.55, 122.78, 92.88, 70.78, 70.12, 68.69, 62.06, 49.14, 21.12, 20.90, 20.89, 20.85. **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-((E)-4-((1,3-dioxoisoindolin-2-yl)methyl)styryl)tetrahydro-2H-pyran-2,4,5-triyl triacetate (3p)



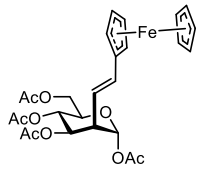
3p

According to the **General Procedure B**, the title compound was obtained as a white foam (90.2 mg, 0.152 mmol, 77% yield, axial: equatorial = 4.1:1). $\mathbf{R}_f$ = 0.06 Hexanes: EtOAc [3:1 (v/v)].

Data for axial product (**3p-*ax***): t_R = 32.3 min, 30% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 7.83-7.86 (m, 2H), 7.69-7.22 (m, 2H), 7.40-7.42 (m, 2H), 7.31-7.34 (m, 2H), 6.51 (d, *J* = 15.4 Hz, 1H), 6.09-6.15 (m, 2H), 5.33 (dd, *J* = 5.6, 10.5 Hz, 1H), 5.28 (t, *J* = 10.5 Hz, 1H), 4.84 (s, 2H), 4.23 (dd, *J* = 4.2, 12.6 Hz, 1H), 4.13 (dd, *J* = 2.1, 12.6 Hz, 1H), 4.09 (ddd, J = 2.1, 4.2, 9.8 Hz, 1H), 3.16-3.20 (m, 1H), 2.16 (s, 3H), 2.10 (s, 3H), 2.04 (s, 3H), 1.98 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.86, 170.43, 169.65, 168.95, 168.17, 168.17, 136.34, 136.12, 135.38, 135.38, 134.17, 134.17, 132.24, 129.17, 129.17, 126.93, 126.93, 123.53, 123.53, 122.62, 94.16, 70.85, 70.79, 66.04, 62.37, 46.14, 41.46, 21.21, 20.99, 20.92, 20.84. **HRMS** (ESI-TOF) *m/z* calcd for $C_{31}H_{31}NO_{11}Na$ [$(M + Na)^+$], 616.1789, found, 616.1789.

Data for equatorial product (**3p-*eq***): t_R = 18.8 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): 7.81 (d, *J* = 9.1 Hz, 2H), 7.73 (s, 1H), 7.60 (dd, *J* = 1.4, 8.4 Hz, 1H), 7.44-7.50 (m, 2H), 6.71 (d, *J* = 15.4 Hz, 1H), 6.29 (dd, *J* = 9.1, 15.4 Hz, 1H), 6.21 (d, *J* = 1.4 Hz, 1H, H-1), 5.34-5.40 (m, 2H), 4.27 (dd, *J* = 4.2, 12.6 Hz, 1H), 4.18 (dd, *J* = 2.8, 12.6 Hz, 1H), 4.12-4.15 (m, 1H), 3.28 (dd, *J* = 4.9, 9.8 Hz, 1H), 2.19 (s, 3H), 2.13 (s, 3H), 2.07 (s, 3H), 2.02 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.86, 170.49, 169.77, 168.99, 136.04, 136.04, 133.88, 133.62, 133.32, 128.47, 128.17, 128.17, 127.86, 127.86, 126.81, 126.57, 126.30, 123.57, 123.57, 122.51, 122.51, 94.30, 70.93, 70.86, 66.21, 62.51, 46.32, 21.25, 21.05, 20.93, 20.89. **HRMS** (ESI-TOF) *m/z* calcd for $C_{31}H_{31}NO_{11}Na$ [$(M + Na)^+$], 616.1789, found, 616.1787.

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



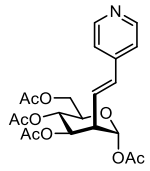
3q

According to the **General Procedure B**, the title compound was obtained as a yellow foam. (91.1 mg, 0.168 mmol, 84% yield, axial: equatorial = 5.2:1). $\mathbf{R_f}$ = 0.22 Hexanes: EtOAc [3:1 (v/v)].

Data for axial product (**3q-*ax***): t_R = 11.2 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): 6.29 (d, *J* = 15.4 Hz, 1H), 6.11 (d, *J* = 1.4 Hz, 1H, H-1), 5.75 (dd, *J* = 9.8, 15.4 Hz, 1H), 5.28-5.35 (m, 2H), 4.32-4.36 (m, 2H), 4.25 (dd, *J* = 4.9, 12.6 Hz, 1H), 4.22-4.24 (m, 2H), 4.15 (dd, *J* = 2.1, 12.6 Hz, 1H), 4.10-4.13 (m, 5H), 4.09 (ddd, *J* = 2.1, 4.2, 9.1 Hz, 1H), 3.08 (ddq, *J* = 1.4, 5.6, 9.8 Hz, 1H, H-2), 2.18 (s, 3H), 2.13 (s, 3H), 2.06 (s, 3H), 2.06 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.84, 170.40, 169.71, 169.05, 133.71, 118.94, 94.32, 82.14, 70.87, 70.79, 69.39, 69.39, 69.39, 69.39, 69.39, 69.11, 69.08, 67.15, 66.89, 66.13, 62.50, 46.07, 21.24, 21.12, 20.96, 20.86. **HRMS** (ESI-TOF) *m/z* calcd for $C_{26}H_{31}FeO_9$ [$(M + H)^+$], 543.1312, found, 543.1274.

Data for equatorial product (**3q-*eq***): t_R = 8.5 min, 10% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ºC, δ): 1H NMR (400 MHz, Chloroform-d) δ 6.27 (d, *J* = 16.0 Hz, 1H), 6.11 (d, *J* = 3.6 Hz, 1H, H-1), 5.33-5.45 (m, 2H), 5.11 (t, *J* = 10.0 Hz, 1H4.18-4.35 (m, 5H), 4.02-4.10 (m, 7H), 2.80 (ddd, *J* = 3.6, 9.2, 12.0 Hz, 1H), 2.17 (s, 3H), 2.09 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 13C NMR (176 MHz, CDCl3) δ 170.87, 170.52, 169.88, 169.01, 133.74, 119.52, 93.07, 70.88, 70.01, 69.42, 69.19, 68.85, 67.47, 66.76, 62.05, 48.69, 21.04. **HRMS** (ESI-TOF) *m/z* calcd for $C_{26}H_{31}FeO_9$ [$(M + H)^+$], 543.1312, found, 543.1290.

(2R,3S,4R,5S,6R)-6-(acetoxymethyl)-3-((E)-2-(pyridin-4-yl)vinyl)tetrahydro-2H-pyran-2,4,5-triyl triacetate (3r)



3r

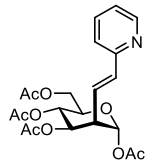
According to the **General Procedure B**, the title compound was obtained as a white foam (66.9 mg, 0.155 mmol, 78% yield, axial: equatorial = 4.3:1). $\mathbf{R_f}$ = 0.11 Hexanes: EtOAc [1:1 (v/v)].

Data for axial product (**3r-*ax***): t_R = 7.6 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): 8.50-8.69 (m, 2H), 7.20-7.35 (m, 2H), 6.53 (d, *J* = 16.1 Hz, 1H),

6.41 (dd, *J* = 9.1, 16.1 Hz, 1H), 6.17 (d, *J* = 1.1 Hz, 1H, H-1), 5.38 (dd, *J* = 5.6, 9.8 Hz, 1H), 5.30 (t, *J* = 9.8 Hz, 1H), 4.26 (dd, *J* = 4.2, 11.9 Hz, 1H), 4.11- 4.16 (m, 2H), 3.25 (dd, J = 6.3, 8.4 Hz, 1H), 2.19 (s, 3H), 2.10 (s, 3H), 2.07 (s, 3H), 2.02 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.76, 170.31, 169.73, 168.90, 150.33, 143.67, 133.70, 133.70, 127.54, 127.54, 121.15, 93.73, 70.87, 70.61, 65.99, 62.34, 46.12, 21.19, 20.98, 20.89, 20.84. **HRMS** (ESI-TOF) *m/z* calcd for $C_{21}H_{26}NO_9$ [$(M + Na)^+$], 436.1602, found, 436.1598.

Data for equatorial product (**3r-*eq***): t_R = 15.4 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): 8.49-8.61 (m, 2H), 7.14-7.20 (m, 2H), 6.48 (d, *J* = 16.1 Hz, 1H), 6.18 (d, *J* = 3.5 Hz, 1H, H-1), 6.04 (dd, *J* = 9.1, 15.4 Hz, 1H), 5.46 (dd, *J* = 9.1, 10.5 Hz, 1H), 5.16 (t, *J* = 9.8 Hz, 1H), 4.34 (dd, *J* = 4.2, 12.6 Hz, 1H), 4.11 (ddd, *J* = 2.1, 3.5, 9.8 Hz, 1H), 4.07 (dd, *J* = 2.1, 12.6 Hz, 1H), 2.94 (ddd, *J* = 3.5, 9.1, 11.8 Hz, 1H), 2.19 (s, 3H), 2.10 (s, 3H), 2.06 (s, 3H), 1.95 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.84, 170.52, 169.80, 168.93, 150.31, 143.60 133.58, 133.58, 127.82, 127.82, 121.13, 92.44, 70.53, 70.15, 68.43, 61.95, 49.02, 21.08, 20.88, 20.84, 20.81. **HRMS** (ESI-TOF) *m/z* calcd for $C_{21}H_{26}NO_9$ [$(M + Na)^+$], 436.1602, found, 436.1595.

(2R,3S,4R,5S,6R)-6-(acetoxymethyl)-3-((E)-2-(pyridin-2-yl)vinyl)tetrahydro-2H-pyran-2,4,5-triyl triacetate (3s)



3s

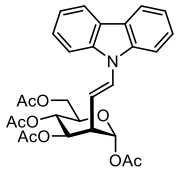
According to the **General Procedure B**, the title compound was obtained as a white foam (39.0 mg, 0.090 mmol, 45% yield, axial: equatorial = 4.6:1). **R_f** = 0.22 Hexanes: EtOAc [1:1 (v/v)].

Data for axial product (**3s-*ax***): t_R = 10.6 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): 8.57 (dd, *J* = 4.0 Hz, 1H), 7.65 (dt, *J* = 2.0, 6.0 Hz, 1H), 7.29 (d, *J* = 6.0 Hz, 1H), 7.17 (ddd, *J* = 0.5, 4.5, 7.5 Hz, 1H), 6.63-6.75 (m, 2H), 6.21 (d, *J* = 1.0 Hz, 1H, H-1), 5.40 (dd, *J* = 5.5, 10.0 Hz, 1H), 5.34 (t, *J* = 10.0 Hz, 1H), 4.24 (dd, *J* = 5.0, 12.0 Hz, 1H), 4.17 (dd, *J* = 2.5, 12.0 Hz, 1H), 4.11 (ddd, *J* = 2.5, 4.5, 9.5 Hz, 1H), 3.25 (ddd, *J* = 1.5, 5.5, 8.5 Hz, 1H), 2.18 (s, 3H), 2.11 (s, 3H), 2.06 (s, 3H), 2.02 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 170.88, 170.46, 169.70, 168.92, 154.65, 149.78, 136.68, 135.63, 126.91, 122.77, 121.92, 93.97, 70.97, 70.72, 66.33, 62.52, 45.84, 21.22, 21.04, 20.90, 20.86. **HRMS** (ESI-TOF) *m/z* calcd for $C_{21}H_{26}NO_9$ [$(M + Na)^+$], 436.1602, found, 436.1597.

Data for equatorial product (**3s-*eq***): t_R = 6.10 min, 20% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ºC, δ): 8.50-8.58 (m, 1H), 7.62 (dt, *J* = 2.0, 7.6 Hz, 1H), 7.22-7.26 (m, 1H), 7.15 (ddd, *J* = 0.8, 5.2, 7.6 Hz, 1H), 6.62 (d, *J* = 15.6 Hz, 1H), 6.31 (dd, *J* = 8.8, 15.6 Hz, 1H), 6.19 (d, *J* = 3.6 Hz, 1H, H-1), 5.48 (dd, *J* = 9.6, 10.8 Hz, 1H), 5.16 (t, *J* = 9.6 Hz, 1H), 4.33 (dd, *J* = 4.0, 12.0 Hz, 1H), 4.03-4.14 (m, 2H), 2.93-3.01 (m, 1H), 2.18 (s, 3H), 2.10 (s, 3H), 2.05 (s, 3H), 1.95 (s, 3H).

^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC, δ): 170.85, 170.48, 169.83, 169.03, 154.57, 149.71, 136.68, 135.86, 126.82, 122.75, 121.62, 92.60, 70.61, 69.98, 68.72, 61.98, 48.59, 21.10, 20.86, 20.86, 20.80. **HRMS** (ESI-TOF) *m/z* calcd for $C_{21}H_{26}NO_9$ [$(M + Na)^+$], 436.1602, found, 436.1596.

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



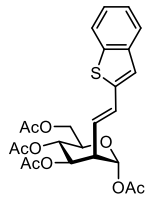
3t

According to the **General Procedure B**, the title compound was obtained as a white solid (67.0 mg, 0.128 mmol, 64% yield, axial: equatorial = 3.0:1). $\mathbf{R_f}$ = 0.14 Hexanes: EtOAc [3:1 (v/v)].

Data for axial product (**3t-*ax***): t_R = 15.1 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): 8.09 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.49 (dt, *J* = 1.5, 7.5 Hz, 2H), 7.31 (dt, *J* = 1.0, 8.0 Hz, 2H), 7.17 (d, *J* = 14.0 Hz, 1H), 6.30 (d, *J* = 1.5 Hz, 1H, H-1), 6.11 (dd, *J* = 10.0, 14.5 Hz, 1H), 5.42-5.48 (m, 2H), 4.30 (dd, *J* = 4.5, 12.5 Hz, 1H), 4.15-4.20 (m, 2H), 3.37 (dd, J = 2.5, 10.0 Hz, 1H, H-2), 2.23 (s, 3H), 2.08 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 170.85, 170.47, 169.65, 169.00, 139.48, 139.48, 128.19, 126.54, 126.54, 124.16, 124.16, 121.00, 121.00, 120.55, 120.55, 112.87, 110.29, 110.29, 94.47, 70.91, 70.82, 65.80, 62.18, 44.70, 21.24, 21.12, 20.87, 20.85. **HRMS** (ESI-TOF) *m/z* calcd for $C_{28}H_{29}NO_9Na$ [$(M + Na)^+$], 546.1735, found, 546.1729.

Data for equatorial product (**3t-*eq***): t_R = 17.9 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): 8.06 (d, *J* = 8.0 Hz, 2H), 7.45-7.53 (m, 4H), 7.30 (dt, *J* = 1.5, 7.0 Hz, 2H), 7.18 (d, *J* = 14.0 Hz, 1H), 6.30 (d, *J* = 3.5 Hz, 1H, H-1), 5.72 (dd, *J* = 9.5, 14.5 Hz, 1H), 5.56 (dd, *J* = 9.5, 11.0 Hz, 1H), 5.23 (t, *J* = 9.5 Hz, 1H), 4.37 (dd, *J* = 4.5, 12.5 Hz, 1H), 4.16 (ddd, *J* = 2.0, 3.5, 10.0 Hz, 1H), 4.11 (dd, *J* = 2.0, 12.5 Hz, 1H), 3.03 (ddd, *J* = 3.5, 9.5, 11.0 Hz, 1H, H-2), 2.20 (s, 3H), 2.12 (s, 3H), 2.08 (s, 3H), 1.98 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 170.86, 170.70, 169.85, 169.08, 139.35, 139.35, 128.30, 126.58, 126.58, 124.14, 124.14, 121.05, 121.05, 120.52, 120.52, 112.20, 110.21, 110.21, 93.11, 70.82, 70.22, 68.69, 62.04, 47.36, 21.07, 20.94, 20.90, 20.84. **HRMS** (ESI-TOF) *m/z* calcd for $C_{28}H_{29}NO_9Na$ [$(M + Na)^+$], 546.1735, found, 546.1730.

(2R,3S,4R,5S,6R)-6-(acetoxymethyl)-3-((E)-2-(benzo[b]thiophen-2-yl)vinyl)tetrahydro-2H-pyran-2,4,5-triyl triacetate (3u)

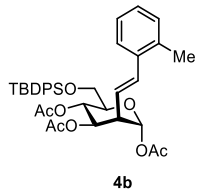


3u

According to the **General Procedure B**, the title compound was obtained as a white foam (76.1 mg, 0.156 mmol, 78% yield, axial: equatorial = 3.7:1). $\mathbf{R_f}$ = 0.14 Hexanes: EtOAc [3:1 (v/v)].

Data for axial product (**3u-*ax***): t_R = 13.80 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): 7.74-7.79 (m, 1H), 7.66-7.72 (m, 1H), 7.28 -7.34 (m, 2H), 7.16 (s, 1H), 6.79 (d, *J* = 15.5 Hz, 1H), 6.19 (d, *J* = 1.0 Hz, 1H, H-1), 6.08 (dd, *J* = 9.0, 15.5 Hz, 1H), 5.29-5.40 (m, 2H), 4.24 (dd, *J* = 4.5, 12.5 Hz, 1H), 4.18 (dd, *J* = 2.5, 12.5 Hz, 1H), 4.11 (ddd, *J* = 2.5, 4.0, 9.5 Hz, 1H), 3.22 (dd, *J* = 5.0, 9.0 Hz, 1H, H-2), 2.18 (s, 3H), 2.14 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 170.88, 170.48, 169.66, 168.94, 141.44, 139.97, 139.10, 129.59, 125.15, 124.71, 124.38, 123.78, 123.65, 122.42, 93.93, 70.90, 70.73, 66.06, 62.31, 46.03, 21.21, 21.04, 20.93, 20.86. **HRMS** (ESI-TOF) *m/z* calcd for $C_{24}H_{26}O_9SNa$ [$(M + Na)^+$], 513.1190, found, 513.1187.
Data for equatorial product (**3u-*eq***): t_R = 9.87 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): δ 7.71-7.74 (m, 1H), 7.66-7.69 (m, 1H), 7.28-7.32 (m, 2H), 7.13 (s, 1H), 6.74 (d, *J* = 16.1 Hz, 1H), 6.19 (d, *J* = 3.5 Hz, 1H, H-1), 5.73 (dd, *J* = 9.1, 16.1 Hz, 1H), 5.45 (dd, *J* = 9.8, 11.2 Hz, 1H), 5.15 (t, *J* = 9.8 Hz, 1H), 4.34 (dd, *J* = 3.5, 11.9 Hz, 1H), 4.09-4.11 (m, 1H), 4.07 (dd, *J* = 2.8, 12.6 Hz, 1H), 2.92 (ddd, *J* = 4.2, 9.1, 11.9 Hz, 1H), 2.20 (s, 3H), 2.10 (s, 3H), 2.05 (s, 3H), 1.96 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25 ºC, δ): 170.87, 170.47, 169.86, 169.05, 141.19, 139.94, 139.11, 129.49, 125.17, 124.72, 124.55, 123.77, 123.56, 122.37, 92.57, 70.62, 70.11, 68.62, 62.01, 48.85, 21.06, 20.89, 20.85, 20.84. **HRMS** (ESI-TOF) *m/z* calcd for $C_{24}H_{26}O_9SNa$ [$(M + Na)^+$], 513.1190, found, 513.1188.

(2R,3S,4R,5S,6R)-6-((2,2-dimethyl-1,1-diphenylpropoxy)methyl)-3-((E)-2-methylstyryl)tetrahydro-2H-pyran-2,4,5-triyl triacetate (4b)



4b

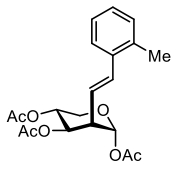
According to the **General Procedure B**, the title compound was obtained as a white foam (97.7 mg, 0.152 mmol, 76% yield, axial: equatorial = 4.7:1). $\mathbf{R_f}$ = 0.55 Hexanes: EtOAc [3:1 (v/v)].

Data for axial product (**4b-*ax***): t_R = 3.2 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): 7.70 (d, *J* = 6.3 Hz, 1H), 7.65 (d, *J* = 6.3 Hz, 1H), 7.33-7.46 (m, 7H), 7.11-7.20 (m, 3H), 6.74 (d, *J* = 15.4 Hz, 1H), 6.22 (d, *J* = 1.4 Hz, 1H, H-1), 6.12 (dd, *J* = 9.8, 15.4 Hz, 1H), 5.57 (t, *J* = 9.8 Hz, 1H), 5.35 (dd, *J* = 5.6, 9.8 Hz, 1H), 3.93 (dt, *J* = 2.8, 9.8 Hz, 1H), 3.76 (dd, *J* = 1.4, 11.9 Hz, 1H), 3.70 (dd, *J* = 3.5, 11.9 Hz, 1H), 3.20 (dd, *J* = 5.6, 9.8 Hz, 1H), 2.32 (s, 3H), 2.15 (s, 3H), 2.01 (s, 3H), 1.94 (s, 3H), 1.06 (s, 9H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.66, 169.42, 169.12, 135.87, 135.87, 135.87, 135.86, 135.86, 135.41, 133.66, 133.26, 133.16, 130.33, 129.84, 129.80, 127.96, 127.83, 127.83, 127.80, 127.80, 126.31, 126.21, 124.36, 94.51, 73.47, 71.42, 66.00, 62.25, 46.81, 26.85, 26.85, 26.85, 21.27, 21.12, 20.83, 19.93, 19.36. **HRMS** (ESI-TOF) *m/z* calcd for $C_{37}H_{44}O_8SiNa$ [(M + Na)$^+$], 667.2698, found, 667.2697.

Data for equatorial product (**4b-*eq***): t_R = 3.1 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): 7.63-7.69 (m, 4H), 7.36-7.45 (m, 6H), 7.27-7.29 (m, 1H), 7.11-7.18 (m, 3H), 6.75 (d, *J* = 15.4 Hz, 1H), 6.25 (d, *J* = 3.5 Hz, 1H), 5.68 (dd, *J* = 9.1, 154 Hz, 1H), 5.44 (dd, *J* = 9.8, 11.2 Hz, 1H), 5.27 (t, *J* = 9.8 Hz, 1H), 3.92-3.97 (m, 1H), 3.70-3.76 (m, 2H), 2.91 (ddd, *J* = 3.5, 9.8, 10.8 Hz, 1H), 2.31 (s, 3H), 2.12 (s, 3H), 1.96 (s, 3H), 1.93 (s, 3H), 1.06 (s, 9H).**^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.75, 169.68, 169.13, 135.94, 135.86, 135.86, 135.84, 135.84, 135.50, 133.71, 133.30, 133.28, 130.34, 129.86, 129.82, 128.03, 127.82, 127.82, 127.82, 127.82, 126.35, 126.17, 124.53, 92.93, 72.85, 71.26, 68.97, 62.52, 49.18, 26.88, 26.88, 26.88, 21.11, 20.99, 20.83, 19.89, 19.38. **HRMS** (ESI-TOF) *m/z* calcd for $C_{37}H_{44}O_8SiNa$ [(M + Na)$^+$], 667.2698, found, 667.2691.

(2R,3S,4R,5R)-3-((E)-2-methylstyryl)tetrahydro-2H-pyran-2,4,5-triyl triacetate (4c)



4c

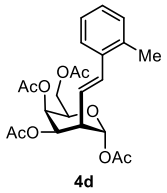
According to the **General Procedure B**, the title compound was obtained as a colorless oil (49.5 mg, 0.132 mmol, 66% yield, axial: equatorial = 3.7:1). $\mathbf{R_f}$ = 0.36 Hexanes: EtOAc [3:1 (v/v)].

Data for axial product (**4c-*ax***): t_R = 6.18 min, 3% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 7.35-7.39 (m, 1H), 7.16-7.20 (m, 2H), 7.13-7.15 (m, 1H), 6.75 (d, *J* = 15.4 Hz, 1H), 6.05 (d, *J* = 5.6 Hz, 1H, H-1), 5.93 (dd, *J* = 9.1, 15.4 Hz, 1H), 5.31 (dd, *J* = 4.9, 7.0 Hz, 1H), 5.00-5.04 (m, 1H), 4.05 (dd, *J* = 4.2, 12.6 Hz, 1H), 3.87 (dd, *J* = 6.3, 12.6 Hz, 1H), 3.12-3.17 (m, 1H), 2.32 (s, 3H), 2.14 (s, 3H), 2.11 (s, 3H), 2.08 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.06, 169.99, 169.42, 135.95, 135.45, 133.62, 130.39, 128.05, 126.36, 126.07, 124.13, 93.42, 70.64, 66.67, 63.01, 45.31, 21.15, 21.08, 21.05, 19.92. **HRMS** (ESI-TOF) *m/z* calcd for $C_{20}H_{24}O_7Na$ [(M + Na)$^+$], 399.1414, found, 399.1411.

Data for equatorial product (**4c-*eq***): t_R = 11.22 min, 20% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min (using Lux® 5µm i-Cellulose-5 column). **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 7.27-7.30 (m, 1H), 7.11-7.21 (m, 3H), 6.73 (d, *J* = 16.1 Hz, 1H), 6.11 (d, *J* = 3.5 Hz, 1H), 5.71 (dd, *J* = 9.1, 16.1 Hz, 1H), 5.46

(dd, *J* = 9.8, 11.2 Hz, 1H), 5.02-5.08 (m, 1H), 3.96 (dd, *J* = 5.6, 10.5 Hz, 1H), 3.71 (t, *J* = 10.5 Hz, 1H), 2.85 (dddd, *J* = 0.8, 3.5, 9.8, 11.2 Hz, 1H), 2.30 (s, 3H), 2.16 (s, 3H), 2.06 (s, 3H), 1.98 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.52, 170.20, 169.41, 135.85, 135.48, 133.74, 130.35, 128.09, 126.38, 126.20, 124.47, 93.13, 70.20, 69.41, 61.16, 49.24, 21.08, 21.00, 20.96, 19.87. **HRMS** (ESI-TOF) *m/z* calcd for $C_{20}H_{24}O_7Na$ [$(M + Na)^+$], 399.1414, found, 399.1410.

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



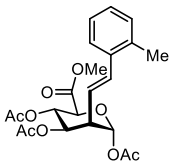
4d

According to the **General Procedure B**, the title compound was obtained as a white foam (49.0 mg, 0.110 mmol, 55% yield, axial: equatorial = 2.3:1). $\mathbf{R_f}$ = 0.27 Hexanes: EtOAc [3:1 (v/v)].

Data for axial product (**4d-*ax***): t_R = 7.67 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): 7.43-7.47 (m, 1H), 7.11 -7.20 (m, 3H), 6.65 (d, *J* = 16.1 Hz, 1H), 6.32 (dd, *J* = 9.8, 16.1 Hz, 1H), 6.23 (s, 1H, H-1), 5.40-5.43 (m, 1H), 5.38 (dd, *J* = 3.5, 5.6 Hz, 1H), 4.36-4.40 (m, 1H), 4.20 (dd, *J* = 7.0, 11.2 Hz, 1H), 4.12-4.17 (m, 1H), 2.95 (dd, *J* = 6.3, 9.8 Hz, 1H), 2.33 (s, 3H), 2.17 (s, 3H), 2.05 (s, 3H), 2.05 (s, 3H), 2.00 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.67, 170.22, 170.10, 169.03, 136.09, 135.37, 132.06, 130.52, 127.77, 126.30, 125.99, 125.47, 95.05, 68.97, 67.32, 66.35, 61.88, 44.78, 21.25, 20.97, 20.92, 20.86, 19.94. **HRMS** (ESI-TOF) *m/z* calcd for $C_{23}H_{28}O_9Na$ [$(M + Na)^+$], 471.1626, found, 471.1620.

Data for equatorial product (**4d-*eq***): t_R = 7.98 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): 7.28 (dd, *J* = 3.1, 7.7 Hz, 1H), 7.11-7.19 (m, 3H), 6.75 (d, *J* = 15.4 Hz, 1H), 6.25 (d, *J* = 3.5 Hz, 1H, H-1), 5.67 (dd, *J* = 8.4, 15.4 Hz, 1H), 5.42-5.45 (m, 1H), 5.38 (dd, *J* = 2.8, 11.9 Hz, 1H), 4.29-4.33 (m, 1H), 4.14 (dd, *J* = 7.0, 11.2 Hz, 1H), 4.09 (dd, *J* = 6.3, 11.2 Hz, 1H), 3.15 (ddd, *J* = 3.5, 8.4, 12.1 Hz, 1H), 2.31 (s, 3H), 2.19 (s, 3H), 2.14 (s, 3H), 2.05 (s, 3H), 1.96 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.64, 170.44, 170.39, 169.22, 135.94, 135.46, 133.74, 130.40, 128.04, 126.34, 126.04, 124.82, 93.57, 68.87, 68.29, 66.25, 61.78, 43.13, 21.09, 20.94, 20.86, 20.86, 19.92. **HRMS** (ESI-TOF) *m/z* calcd for $C_{23}H_{28}O_9Na$ [$(M + Na)^+$], 471.1626, found, 471.1622.

(2R,3S,4R,5S,6S)-6-(methoxycarbonyl)-3-((E)-2-methylstyryl)tetrahydro-2H-pyran-2,4,5-triyl triacetate (4e)



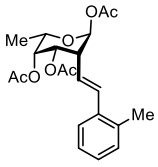
4e

According to the **General Procedure B**, the title compound was obtained as a white solid (27.5 mg, 0.064 mmol, 32% yield, axial: equatorial = 3.6:1). $\mathbf{R_f}$ = 0.30 Hexanes: EtOAc [3:1 (v/v)].

Data for axial product (**4e-*ax***): t_R = 7.90 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): 7.38-7.42 (m, 1H), 7.16-7.20 (m, 2H), 7.13-7.16 (m, 1H), 6.78 (d, *J* = 16.1 Hz, 1H), 6.34 (d, *J* = 3.5 Hz, 1H, H-1), .98 (dd, *J* = 9.1, 16.1 Hz, 1H), 5.39 (t, *J* = 7.7 Hz, 1H), 5.34 (dd, *J* = 4.2, 8.4 Hz, 1H), 4.51 (d, *J* = 7.7 Hz, 1H), 3.79 (s, 3H), 3.19 (dt, *J* = 4.2, 9.1 Hz, 1H), 2.32 (s, 3H), 2.16 (s, 3H), 2.11 (s, 3H), 2.03 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 169.94, 169.72, 168.84, 168.14, 135.79, 135.50, 134.15, 130.38, 128.15, 126.36, 126.20, 123.56, 92.69, 72.45, 70.34, 66.90, 52.98, 45.15, 21.13, 20.95, 20.89, 19.89. **HRMS** (ESI-TOF) *m/z* calcd for $C_{22}H_{26}O_9Na$ [(M + Na)$^+$], 457.1469, found, 457.1465.

Data for equatorial product (**4e-*eq***): t_R = 8.60 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): 7.10-7.20 (m, 4H), 6.74 (d, *J* = 15.5 Hz, 1H), 6.27 (d, *J* = 3.*4* Hz, 1H, H-1), 5.66 (dd, *J* = 9.5, 15.5 Hz, 1H), 5.51 (dd, *J* = 9.5, 11.0 Hz, 1H), 5.24 (q, *J* = 10.5 Hz, 1H), 4.40 (d, *J* = 10.0 Hz, 1H), 3.76 (s, 3H), 2.96 (ddd, *J* = 3.5, 10.0, 11.5 Hz, 1H), 2.30 (s, 3H), 2.17 (s, 3H), 2.06 (s, 3H), 1.98 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.39, 169.86, 168.79, 167.94, 135.66, 135.54, 134.24, 130.37, 128.21, 126.38, 126.19, 123.66, 92.57, 73.17, 71.03, 69.81, 53.57, 48.86, 21.01, 20.90, 20.74, 19.85. . **HRMS** (ESI-TOF) *m/z* calcd for $C_{22}H_{26}O_9Na$ [(M + Na)$^+$], 457.1469, found, 457.1465.

(2S,3S,4S,5R,6S)-6-methyl-3-((E)-2-methylstyryl)tetrahydro-2H-pyran-2,4,5-triyl triacetate (4f)



4f

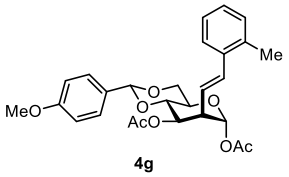
According to the **General Procedure B**, the title compound was obtained as a white foam (56.0 mg, 0.144 mmol, 72% yield, axial: equatorial = 2.4:1). $\mathbf{R_f}$ = 0.39 Hexanes: EtOAc [3:1 (v/v)].

Data for axial product (**4f-*ax***): t_R = 6.30 min, 3% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 7.47 (d, *J* = 6.3 Hz, 1H), 7.12-7.22 (m, 3H), 6.63 (d, *J* = 15.4 Hz, 1H), 6.34 (d, *J* = 9.8, 15.4 Hz, 1H), 6.19 (s, 1H, H-1), 5.35-5.39 (m, 1H), 5.24-5.27 (m, 1H), 4.23-4.31 (m, 1H), 2.90-2.97 (m, 1H), 2.33 (s, 3H), 2.15 (s, 3H), 2.08 (s, 3H), 2.00 (s, 3H), 1.21 (d, *J* = 5.6 Hz, 3H). **^{13}C**

NMR (175 MHz, $CDCl_3$, 25 ºC, δ): 170.51, 170.30, 169.28, 136.23, 135.35, 131.76, 130.49, 127.64, 126.57, 126.24, 125.50, 95.36, 69.47, 67.91, 67.41, 44.51, 21.31, 21.02, 20.96, 19.94, 16.43. **HRMS** (ESI-TOF) *m/z* calcd for $C_{21}H_{26}O_7Na$ [$(M + Na)^+$], 413.1571, found, 413.1565.

Data for equatorial product (**4f-*eq***): t_R = 5.05 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): δ 7.28 (dd, *J* = 2.1, 7.0 Hz, 1H), 7.10-7.18 (m, 3H), 6.74 (d, *J* = 16.1 Hz, 1H), 6.22 (d, *J* = 3.5 Hz, 1H, H-1), 5.68 (dd, *J* = 9.1, 16.1 Hz, 1H), 5.39 (dd, *J* = 2.8, 11.9 Hz, 1H), 5.27 (dd, *J* = 1.4, 2.8 Hz, 1H), 4.18-4.25 (m, 1H), 3.12 (ddd, *J* = 3.5, 8.4, 12.1 Hz, 1H), 2.31 (s, 3H), 2.22 (s, 3H), 2.13 (s, 3H), 1.96 (s, 3H), 1.18 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.79, 170.50, 169.46, 136.07, 135.43, 133.46, 130.37, 127.94, 126.32, 126.06, 125.32, 93.84, 69.54, 68.81, 67.33, 42.94, 21.14, 20.95, 20.92, 19.92, 16.55. **HRMS** (ESI-TOF) *m/z* calcd for $C_{21}H_{26}O_7Na$ [$(M + Na)^+$], 413.1571, found, 413.1567.

(2R,4aR,6R,7S,8R,8aS)-2-(4-methoxyphenyl)-7-((E)-2-methylstyryl)hexahydropyrano[3,2-d][1,3]dioxine-6,8-diyl diacetate (4g)



4g

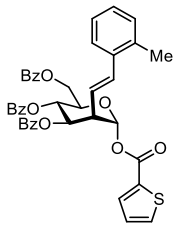
According to the **General Procedure B**, the title compound was obtained as a white solid (62.6 mg, 0.130 mmol, 65% yield, axial: equatorial = 10:1). **R_f** = 0.55 Hexanes: EtOAc [3:1 (v/v)].

Data for axial product (**4g-*ax***): t_R = 5.37 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): 7.45 (dd, *J* = 3.5, 4.9 Hz, 1H), 7.38-7.42 (m, 2H), 7.18-7.22 (m, 2H), 7.15-7.18 (m, 1H), 6.87-6.91 (m, 2H), 6.75 (d, *J* = 15.4 Hz, 1H), 6.16 (d, *J* = 1.4 Hz, 1H), 6.07 (dd, *J* = 9.8, 15.4 Hz, 1H), 5.54 (s, 1H), 5.39 (dd, *J* = 5.6, 10.5 Hz, 1H), 4.31 (dd, *J* = 4.2, 10.5 Hz, 1H), 4.08 (dt, *J* = 4.2, 9.8 Hz, 1H), 4.00 (t, *J* = 10.5 Hz, 1H), 3.78-3.83 (m, 1H), 3.80 (s, 3H), 3.33-3.38 (m, 1H), 2.34 (s, 3H), 2.20 (s, 3H), 2.04 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.42, 169.31, 160.34, 135.95, 135.52, 133.87, 130.46, 129.62, 128.10, 127.66, 127.66, 126.33, 126.03, 124.59, 113.80, 113.80, 102.14, 94.71, 76.56, 70.08, 68.86, 66.18, 55.45, 46.57, 21.28, 21.20, 19.95. **HRMS** (ESI-TOF) *m/z* calcd for $C_{27}H_{31}O_8$ [$(M + H)^+$], 483.2013, found, 483.2006.

Data for equatorial product (**4g-*eq***): t_R = 12.00 min, 7% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 7.36-7.41 (m, 2H), 7.28-7.33 (m, 1H), 7.11-7.20 (m, 3H), 6.86-6.91 (m, 2H), 6.73 (d, *J* = 16.1 Hz, 1H), 6.14 (d, *J* = 4.2 Hz, 1H, H-1), 5.75 (dd, *J* = 9.1, 15.4 Hz, 1H), 5.57 (t, *J* = 9.8 Hz, 1H), 5.52 (s, 1H), 4.29 (dd, *J* = 4.9, 10.5 Hz, 1H), 4.02 (dt, *J* = 3.5, 10.5 Hz, 1H), 3.81 (s, 3H), 3.72-3.80 (m, 2H), 2.89 (dt, *J* = 3.5, 10.5 Hz, 1H), 2.31 (s, 3H), 2.17 (s, 3H), 1.99 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.39, 169.48, 160.29, 135.90, 135.44, 133.61, 130.32, 129.68, 128.07, 127.65, 127.65, 126.42, 126.33, 124.80, 113.74, 113.74, 101.84, 93.42, 79.81, 69.50, 68.90, 65.43, 55.45, 50.10, 21.14, 21.12, 19.88. **HRMS** (ESI-TOF) *m/z* calcd for $C_{27}H_{31}O_8$ [$(M + H)^+$], 483.2013, found,

483.2008.

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

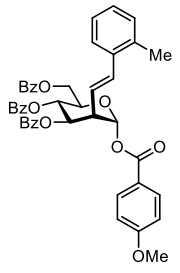


4h

According to the **General Procedure B** (0.1 mmol of bromosugar was used), the title compound was obtained as a white foam (49.1 mg, 0.07 mmol, 70% yield, axial: equatorial = 4.0:1). $\mathbf{R_f}$ = 0.48 Hexanes: EtOAc [3:1 (v/v)].

Data for axial product (**4h-*ax***): t_R = 6.72 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): 8.03 (dd, *J* = 1.4, 8.4 Hz, 2H), 8.01 (dd, *J* = 0.7, 3.5 Hz, 1H), 7.97 (dd, *J* = 1.4, 8.4 Hz, 2H), 7.95 (dd, 1.4, 8.4 Hz, 2H), 7.70 (dd, *J* = 1.4, 4.9 Hz, 1H), 7.50-7.55 (m, 2H), 7.47-7.50 (m, 1H), 7.42 (dd, *J* = 0.7, 7.7 Hz, 1H), 7.32-7.40 (m, 6H), 7.21 (dd, *J* = 4.2, 4.9 Hz, 1H), 7.14-7.20 (m, 2H), 7.07-7.11 (m, 1H), 6.82 (d, *J* = 15.4 Hz, 1H), 6.53 (d, *J* = 1.4 Hz, 1H, H-1), 6.27 (dd, *J* = 9.1, 15.4 Hz, 1H), 6.07 (t, *J* = 9.8 Hz, 1H), 5.94 (dd, *J* = 5.6, 9.8 Hz, 1H), 4.66 (dd, *J* = 2.1, 11.9 Hz, 1H), 4.55 (dt, *J* = 2.8, 9.8 Hz, 1H), 4.45 (dd, *J* = 3.5, 11.9 Hz, 1H), 3.63-3.70 (m, 1H), 2.07 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 166.25, 165.97, 165.49, 160.09, 135.86, 135.73, 134.79, 134.51, 133.85, 133.61, 133.52, 133.21, 132.75, 130.41, 129.98, 129.98, 129.90, 129.90, 129.84, 129.84, 129.80, 129.31, 129.10, 128.62, 128.62, 128.59, 128.59, 128.57, 128.57, 128.37, 128.08, 126.36, 126.05, 123.53, 94.94, 71.83, 71.53, 66.52, 62.73, 46.65, 19.62. **HRMS** (ESI-TOF) *m/z* calcd for $C_{41}H_{34}O_9SNa$ $[(M + Na)^+]$, 725.1816, found, 725.1814.

(2R,3S,4R,5S,6R)-2-((benzoyloxy)methyl)-6-((4-methoxybenzoyl)oxy)-5-((E)-2-methylstyryl)tetrahydro-2H-pyran-3,4-diyl dibenzoate (4i)

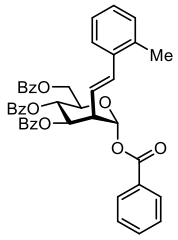


4i

According to the **General Procedure B** (0.1 mmol of bromosugar was used), the title compound was obtained as a white foam (34.1 mg, 0.047 mmol, 47% yield, axial: equatorial = 3.6:1). $\mathbf{R_f}$ = 0.45 Hexanes: EtOAc [3:1 (v/v)].

Data for axial product (**4i-*ax***): t_R = 10.9 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): 8.14-8.19 (m, 2H), 8.03 (dd, *J* = 1.4, 8.4 Hz, 2H), 7.94-7.98 (m, 4H), 7.47-7.55 (m, 3H), 7.43 (dd, *J* = 1.4, 7.0 Hz, 1H), 7.37 (dd, *J* = 7.7, 8.4 Hz, 2H), 7.31-7.35 (m, 4H), 7.15-7.21 (m, 2H), 7.07-7.10 (m, 1H), 7.01-7.05 (m, 2H), 6.83 (d, *J* = 16.1 Hz, 1H), 6.55 (d, *J* = 1.4 Hz, 1H), 6.30 (dd, *J* = 9.1, 16.1 Hz, 1H), 6.08 (t, *J* = 10.5 Hz, 1H), 5.97 (dd, *J* = 5.6, 10.5 Hz, 1H), 4.64 (dd, *J* = 2.8, 12.6 Hz, 1H), 4.54 (dt, *J* = 2.8, 9.8 Hz, 1H), 4.44 (dd, *J* = 3.5, 11.9 Hz, 1H), 3.92 (s, 3H), 3.62-3.68 (m, 1H), 2.08 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 166.26, 166.04, 165.50, 164.30, 164.21, 135.93, 135.72, 134.37, 133.59, 133.52, 133.19, 132.33, 132.33, 130.40, 129.97, 129.97, 129.90, 129.90, 129.83, 129.83, 129.34, 129.13, 128.62, 128.62, 128.57, 128.57, 128.55, 128.55, 128.55, 128.03, 126.35, 126.07, 123.79, 121.68, 114.17, 114.17, 94.56, 71.97, 71.38, 66.63, 62.79, 55.72, 46.73, 19.63. **HRMS** (ESI-TOF) *m/z* calcd for $C_{44}H_{38}O_{10}Na$ [$(M + Na)^+$], 749.2357, found, 749.2352.

(2R,3S,4R,5S,6R)-6-((benzoyloxy)methyl)-3-((E)-2-methylstyryl)tetrahydro-2H-pyran-2,4,5-triyl tribenzoate (4j)



4j

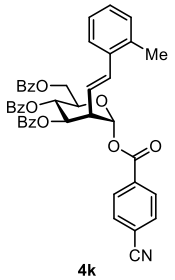
According to the **General Procedure B**, the title compound was obtained as a white solid (83.4 mg, 0.120 mmol, 60% yield, axial: equatorial = 5.0:1). **R_f** = 0.40 Hexanes: EtOAc [3:1 (v/v)].

Data for axial product (**4j-*ax***): t_R = 8.59 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): 8.19-8.22 (m, 2H), 8.01-8.04 (m, 2H), 7.93-7.99 (m, 4H), 7.65-7.70 (m, 1H), 7.56 (t, *J* = 7.0 Hz, 2H), 7.46-7.54 (m, 3H), 7.42-7.45 (m, 1H), 7.35-7.39 (m, 2H), 7.30-7.35 (m, 4H), 7.14-7.22 (m, 2H), 7.07-7.12 (m, 1H), 6.84 (d, *J* = 16.1 Hz, 1H), 6.58 (d, *J* = 1.4 Hz, 1H), 6.30 (dd, *J* = 9.1, 16.1 Hz, 1H), 6.09 (t, *J* = 9.8 Hz, 1H), 5.97 (dd, *J* = 4.9, 9.8 Hz, 1H), 4.65 (dd, *J* = 2.8, 12.6 Hz, 1H), 4.56 (dt, *J* = 2.8, 9.8 Hz, 1H), 4.45 (dd, *J* = 3.5, 12.6 Hz, 1H), 3.68 (dd, *J* = 4.9, 9.1 Hz, 1H), 2.08 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 166.25, 166.03, 165.49, 164.62, 135.89, 135.73, 134.47, 133.98, 133.61, 133.54, 133.20, 130.41, 130.19, 130.19, 129.97, 129.97, 129.90, 129.90, 129.83, 129.83, 129.81, 129.41, 129.30, 129.10, 128.91, 128.91, 128.63, 128.63, 128.58, 128.58, 128.56, 128.56, 128.07, 126.36, 126.06, 123.64, 94.89, 71.92, 71.49, 66.57, 62.76, 46.68, 19.63. **HRMS** (ESI-TOF) *m/z* calcd for $C_{43}H_{36}O_9Na$ [$(M + Na)^+$], 719.2252, found, 719.2244.

Data for equatorial product (**4j-*eq***): t_R = 10.2 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): 8.18-8.22 (m, 2H), 7.98-8.03 (m, 2H), 7.92-7.95 (m, 2H), 7.88-7.92 (m, 2H), 7.65-7.69 (m, 1H), 7.52-7.58 (m, 3H), 7.44-7.52 (m, 2H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.30-7.37 (m, 4H), 7.20 (dd, J = 7.6, 1.6 Hz, 1H), 7.01-7.08 (m, 2H), 6.99 (d, *J* = 7.0 Hz, 1H), 6.79 (d, *J* = 15.4

Hz, 1H), 6.57 (d, *J* = 3.5 Hz, 1H, H-1), 6.11 (dd, *J* = 9.8, 10.5 Hz, 1H), 5.90 (dd, *J* = 9.1, 16.1 Hz, 1H), 5.80 (t, *J* = 9.8 Hz, 1H), 4.59 (dd, *J* = 2.8, 11.9 Hz, 1H), 4.55 (dt, *J* = 2.8, 9.8 Hz, 1H), 4.46 (dd, *J* = 4.2, 11.9 Hz, 1H), 3.32 (ddd, *J* = 3.5, 9.8, 11.9 Hz, 1H), 2.06 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 166.25, 166.21, 165.56, 164.67, 135.81, 135.49, 134.33, 134.03, 133.54, 133.34, 133.17, 130.14, 130.14, 130.10, 129.96, 129.96, 129.90, 129.90, 129.83, 129.77, 129.77, 129.42, 129.26, 129.08, 128.97, 128.97, 128.54, 128.54, 128.49, 128.49, 128.47, 128.47, 127.92, 126.34, 126.19, 124.09, 93.73, 71.44, 70.82, 69.80, 62.99, 50.14, 19.56. **HRMS** (ESI-TOF) *m/z* calcd for $C_{43}H_{36}O_9Na$ [$(M + Na)^+$], 719.2252, found, 719.2250.

(2R,3S,4R,5S,6R)-2-((benzoyloxy)methyl)-6-((4-cyanobenzoyl)oxy)-5-((E)-2-methylstyryl)tetrahydro-2H-pyran-3,4-diyl dibenzoate (4k)

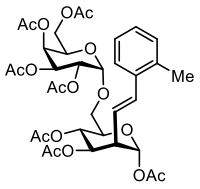


4k

According to the **General Procedure B** (0.1 mmol of bromosugar was used), the title compound was obtained as a white solid (41.0 mg, 0.057 mmol, 57% yield, axial: equatorial = 3.0:1). $\mathbf{R_f}$ = 0.56 Hexanes: EtOAc [3:1 (v/v)].

Data for axial product (**4k-*ax***): t_R = 12.5 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): 8.27-8.30 (m, 2H), 8.01-8.04 (m, 2H), 7.93-7.98 (m, 4H), 7.84-7.87 (m, 2H), 7.48-7.55 (m, 3H), 7.31-7.42 (m, 7H), 7.14-7.22 (m, 2H), 7.08-7.11 (m, 1H), 6.83 (d, *J* = 16.1 Hz, 1H), 6.58 (d, *J* = 1.4 Hz, 1H, H-1), 6.27 (dd, J = 9.1, 16.1 Hz, 1H), 6.08 (t, *J* = 10.5 Hz, 1H), 5.92 (dd, *J* = 4.9, 9.8 Hz, 1H), 4.68 (dd, *J* = 2.8, 11.9 Hz, 1H), 4.53 (dt, *J* = 2.8, 9.8 Hz, 1H), 4.45 (dd, *J* = 4.2, 12.6 Hz, 1H), 3.68 (dd, *J* = 5.6, 9.8 Hz, 1H), 2.07 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 166.20, 166.07, 165.45, 163.13, 135.73, 135.69, 134.75, 133.72, 133.67, 133.30, 133.22, 132.72, 132.72, 130.64, 130.64, 130.45, 129.95, 129.95, 129.90, 129.90, 129.81, 129.81, 129.69, 129.13, 128.97, 128.67, 128.67, 128.62, 128.62, 128.59, 128.59, 128.20, 126.38, 126.03, 123.12, 117.96, 117.37, 95.77, 71.80, 71.68, 66.43, 62.64, 46.56, 19.60. **HRMS** (ESI-TOF) *m/z* calcd for $C_{44}H_{35}NO_9Na$ [$(M + Na)^+$], 744.2204, found, 744.2196.

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



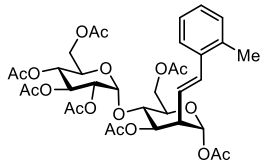
4l

According to the **General Procedure B** (0.1 mmol of bromosugar was used), the title compound was obtained as a white solid (40.4 mg, 0.055 mmol, 55% yield, axial: equatorial = 3.2:1). $\mathbf{R}_f$ = 0.46 Hexanes: EtOAc [1:1 (v/v)].

Data for axial product (**4l-*ax***): t_R = 7.74 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): 7.44 (d, *J* = 7.7 Hz, 1H), 7.10-7.18 (m, 3H), 6.73 (d, *J* = 15.4 Hz, 1H), 6.10 (d, *J* = 1.4 Hz, 1H, H-1), 6.02 (dd, *J* = 9.8,15.4 Hz, 1H), 5.48 (d, *J* = 2.8 Hz, 1H), 5.41 (dd, *J* = 3.5, 10.5 Hz, 1H), 5.33-5.37 (m, 2H), 5.13 (d, *J* = 3.5 Hz, 1H), 5.11 (dd, *J* = 3.5, 10.5 Hz, 1H), 4.30 (t, *J* = 6.3 Hz, 1H), 4.12 (dd, *J* = 6.3, 11.2 Hz, 1H), 4.02-4.08 (m, 2H), 3.77 (dd, *J* = 4.9, 11.2 Hz, 1H), 3.57 (dd, *J* = 2.8, 10.5 Hz, 1H), 3.19-3.26 (m, 1H), 2.31 (s, 3H), 2.20 (s, 3H), 2.14 (s, 3H), 2.07 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H), 2.00 (s, 3H), 1.93 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.71, 170.56, 173.46, 170.37, 169.84, 169.70, 169.14, 135.77, 135.47, 134.07, 130.36, 128.07, 126.28, 126.28, 123.95, 96.01, 94.24, 71.23, 71.01, 68.41, 68.29, 67.57, 66.80, 66.60, 66.47, 61.86, 46.50, 21.20, 21.06, 20.90, 20.84, 20.84, 20.82, 20.66, 19.92. **HRMS** (ESI-TOF) *m/z* calcd $C_{35}H_{44}O_{17}Na$ [(M + Na)$^+$], 759.2471, found, 759.2455.

Data for equatorial product (**4l-*eq***): t_R = 6.37 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): 7.28 (dd, *J* = 1.4, 7.7 Hz, 1H), 7.09-7.20 (m, 3H), 6.74 (d, *J* = 16.1 Hz, 1H), 6.13 (d, *J* = 3.5 Hz, 1H, H-1), 5.68 (dd, *J* = 9.1, 16.1 Hz, 1H), 5.43-4.48 (m, 2H), 5.37 (dd, *J* = 3.5, 10.5 Hz, 1H), 5.13-5.20 (m, 2H), 5.10 (dd, *J* = 3.5, 11.2 Hz, 1H), 4.24-4.29 (m, 1H), 4.12 (dd, *J* = 6.3, 11.2 Hz, 1H), 4.02-4.08 (m, 2H), 3.75 (dd, *J* = 4.2, 11.2 Hz, 1H), 3.60 (dd, *J* = 2.1, 11.2 Hz, 1H), 2.88 (ddd, *J* = 3.5, 9.8, 11.9 Hz, 1H), 2.30 (s, 3H), 2.18 (s, 3H), 2.14 (s, 3H), 2.12 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 2.00 (s, 3H), 1.96 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.72, 170.59, 170.56, 170.38, 170.03, 169.82, 169.18, 135.79, 135.50, 133.88, 130.37, 128.13, 126.38, 126.18, 124.19, 95.96, 92.72, 70.84, 70.71, 69.27, 68.37, 68.33, 67.52, 66.41, 66.28, 61.70, 49.14, 21.04, 20.98, 20.92, 20.90, 20.88, 20.84, 20.83, 19.87. **HRMS** (ESI-TOF) *m/z* calcd $C_{35}H_{44}O_{17}Na$ [(M + Na)$^+$], 759.2471, found, 759.2466.

(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(((2R,3S,4R,5S,6R)-4,6-diacetoxy-2-(acetoxymethyl)-5-((E)-2-methylstyryl)tetrahydro-2H-pyran-3-yl)oxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (4m)

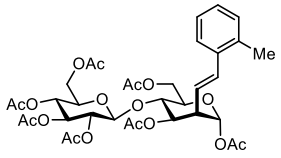


4m

According to the **General Procedure B** (0.1 mmol of bromosugar was used), the title compound was obtained as a white foam (50.0 mg, 0.068 mmol, 68% yield, axial: equatorial = 10.0: 1). $\mathbf{R}_f$ = 0.54 Hexanes: EtOAc [1:1 (v/v)].

Data for axial product (**4m-*ax***): t_R = 10.2 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): 7.37 (dd, *J* = 2.8, 6.3 Hz, 1H), 7.13-7.21 (m, 3H), 6.69 (d, *J* = 16.1 Hz, 1H), 6.12 (d, *J* = 2.8 Hz, 1H, H-1), 5.90 (dd, *J* = 9.1, 15.4 Hz, 1H), 5.54 (d, *J* = 4.2 Hz, 1H), 5.42 (dd, *J* = 9.8, 10.5 Hz, 1H), 5.19 (dd, *J* = 4.9, 7.7 Hz, 1H), 5.08 (t, *J* = 9.8 Hz, 1H), 4.90 (dd, *J* = 4.2, 10.5 Hz, 1H), 4.40 (dd, *J* = 2.1, 12.6 Hz, 1H), 4.25 (dt, *J* = 3.5, 12.6 Hz, 2H), 4.05-4.14 (m, 3H), 3.97-4.02 (m, 1H), 3.19-3.24 (m, 1H), 2.31 (s, 3H), 2.21 (s, 3H), 2.13 (s, 3H), 2.09 (s, 3H), 2.04 (s, 2H), 2.03 (s, 3H), 2.03 (s, 3H), 2.02 (s, 2H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.76, 170.72, 170.31, 170.31, 170.27, 169.61, 169.29, 135.67, 135.44, 133.88, 130.51, 128.22, 126.38, 125.99, 124.18, 95.96, 93.73, 74.47, 71.26, 70.69, 70.26, 69.66, 68.62, 68.12, 63.37, 61.55, 45.51, 21.31, 21.23, 20.94, 20.82, 20.81, 20.75, 20.69, 19.93. **HRMS** (ESI-TOF) *m/z* calcd for $C_{35}H_{44}O_{17}Na$ [$(M + Na)^+$], 759.2471, found, 759.2462.

(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-(((2R,3S,5S,6R)-4,6-diacetoxy-2-(acetoxymethyl)-5-((E)-2-methylstyryl)tetrahydro-2H-pyran-3-yl)oxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (4n)



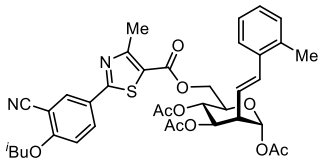
4n

According to the **General Procedure B**, the title compound was obtained as a white foam (91.2 mg, 0.124 mmol, 62% yield, axial: equatorial = 5.7:1). $\mathbf{R}_f$ = 0.30 Hexanes: EtOAc [2:1 (v/v)].

Data for axial product (**4n-*ax***): t_R = 28.9 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): 7.36-7.41 (m, 1H), 7.13-7.22 (m, 3H), 6.75 (d, *J* = 15.5 Hz, 1H), 6.14 (d, *J* = 3.0 Hz, 1H, H-1), 5.92 (dd, *J* = 9.0, 16.0 Hz, 1H), 5.40 (dd, *J* = 5.0, 7.5 Hz, 1H), 5.17 (t, *J* = 9.5 Hz, 1H), 5.07 (t, *J* = 9.5 Hz, 1H), 4.97 (dd, *J* = 8.5, 9.0 Hz, 1H), 4.61 (d, *J* = 7.5 Hz, 1H), 4.37 (dd, *J* = 2.0, 12.0 Hz, 1H), 4.30 (dd, *J* = 4.5, 12.5 Hz, 1H), 4.14 (dd, *J* = 5.0, 12.0 Hz, 1H), 4.04 (dd, *J* = 2.0, 12.5 Hz, 1H), 4.00 (ddd, *J* = 2.0, 4.5, 9.5 Hz, 1H), 3.84 (dd, *J* = 7.5, 9.5 Hz, 1H), 3.70 (ddd, *J* = 2.0, 4.5, 10.0 Hz, 1H), 3.17 (dt, *J* = 4.0, 8.5 Hz, 1H), 2.32 (s, 3H), 2.15 (s, 3H), 2.10 (s, 3H), 2.05 (s, 6H), 2.01 (s, 3H), 1.99 (s, 3H), 1.96 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.69, 170.62, 170.37, 170.05,

169.52, 169.46, 169.43, 135.97, 135.52, 133.56, 130.51, 128.12, 126.33, 125.88, 124.53, 101.39, 93.69, 73.03, 72.03, 71.69, 71.59, 71.09, 68.09, 62.67, 61.94, 31.09, 21.27, 21.00, 20.97, 20.72, 20.72, 20.72, 20.72, 20.64, 19.92. **HRMS** (ESI-TOF) *m/z* calcd for $C_{35}H_{44}O_{17}Na$ [(M + Na)$^+$], 759.2471, found, 759.2464.

(2R,3S,4R,5S,6R)-6-(((2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carbonyl)oxy)methyl)-3-((E)-2-methylstyryl)tetrahydro-2H-pyran-2,4,5-triyl triacetate (7a)



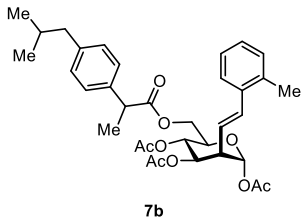
7a

According to the **General Procedure B** (0.1 mmol of bromosugar was used), the title compound was obtained as a white solid (43.0 mg, 0.061 mmol, 61% yield, axial: equatorial = 4.1:1). $\mathbf{R}_f$ = 0.18 Hexanes: EtOAc [3:1 (v/v)].

Data for axial product (**7a-*ax***): t_R = 9.80 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): 8.07 (d, *J* = 2.1 Hz, 1H), 7.93 (dd, *J* = 2.1, 9.1 Hz, 1H), 7.35-7.45 (m, 1H), 7.07-7.14 (m, 2H), 6.99-7.04 (m, 1H), 6.94 (d, *J* = 9.1 Hz, 1H), 6.78 (d, *J* = 16.1 Hz, 1H), 6.23 (d, *J* = 1.4 Hz, 1H), 6.08 (dd, *J* = 9.1, 16.1 Hz, 1H), 5.50 (t, *J* = 9.8 Hz, 1H), 5.42 (dd, *J* = 5.6, 9.8 Hz, 1H), 4.49 (dd, *J* = 2.1, 12.6 Hz, 1H), 4.34 (dd, *J* = 3.5, 11.9 Hz, 1H), 4.19 (dt, *J* = 2.8, 9.8 Hz, 1H), 3.91 (d, *J* = 6.3 Hz, 2H), 3.23-3.28 (m, 1H), 2.77 (s, 3H), 2.30 (s, 3H), 2.20 (s, 3H), 2.18-2.25 (m, 1H) 2.08 (s, 3H), 2.05 (s, 3H), 1.11 (d, *J* = 7.0 Hz, 6H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.45, 169.71, 168.98, 167.81, 162.64, 162.07, 161.67, 135.85, 135.55, 133.99, 132.95, 132.27, 130.48, 128.10, 126.32, 126.02, 125.91, 123.78, 121.14, 115.50, 112.63, 103.09, 94.13, 75.81, 70.86, 70.82, 65.91, 62.62, 46.26, 28.31, 21.23, 21.08, 20.87, 19.92, 19.22, 19.22, 17.69. **HRMS** (ESI-TOF) *m/z* calcd for $C_{37}H_{41}N_2O_{10}S$ [(M + H)$^+$], 705.2476, found, 705.2465.

Data for equatorial product (**7a-*eq***): t_R = 13.4 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): 8.20 (d, *J* = 2.1 Hz, 1H), 8.12 (dd, *J* = 2.1, 8.4 Hz, 1H), 7.27-7.39 (m, 1H), 7.11-7.20 (m, 3H), 7.02 (d, *J* = 9.1 Hz, 1H), 6.77 (d, *J* = 16.1 Hz, 1H), 6.22 (d, *J* = 3.5 Hz, 1H, H-1), 5.69 (dd, *J* = 9.1, 16.1 Hz, 1H), 5.50 (dd, *J* = 9.1, 11.2 Hz, 1H), 5.20 (t, *J* = 9.8 Hz, 1H), 4.38-4.46 (m, 2H), 4.21 (ddd, *J* = 2.1, 3.5, 10.5 Hz, 1H), 3.91 (d, *J* = 7.0 Hz, 2H), 2.95 (ddd, *J* = 3.5, 9.1, 11.9 Hz, 1H), 2.77 (s, 3H), 2.30 (s, 3H), 2.18-2.24 (m, 1H), 2.18 (s, 3H), 2.08 (s, 3H), 1.98 (s, 3H), 1.10 (d, *J* = 7.0 Hz, 6H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.54, 169.81, 169.04, 167.90, 162.71, 162.02, 161.69, 135.74, 135.53, 134.09, 132.82, 132.39, 130.39, 128.18, 126.39, 126.18, 126.11, 123.97, 121.27, 115.58, 112.74, 103.12, 92.85, 75.85, 70.73, 70.11, 68.88, 62.74, 49.24, 28.31, 21.09, 20.94, 20.88, 19.89, 19.21, 19.21, 17.73. **HRMS** (ESI-TOF) *m/z* calcd for $C_{37}H_{41}N_2O_{10}S$ [(M + H)$^+$], 705.2476, found, 705.2467.

(2R,3S,4R,5S,6R)-6-(((2-(4-isobutylphenyl)propanoyl)oxy)methyl)-3-((E)-2-methylstyryl)tetrahydro-2H-pyran-2,4,5-triyl triacetate (7b)

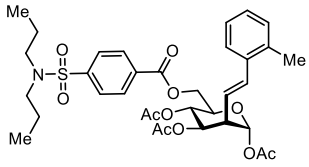


7b

According to the **General Procedure B** (0.1 mmol of bromosugar was used), the title compound was obtained as a white solid (39.2 mg, 0.066 mmol, 66% yield, axial: equatorial = 4.4:1). $\mathbf{R}_f$ = 0.38 Hexanes: EtOAc [3:1 (v/v)].

Data for axial product (**7b-*ax***): t_R = 5.40 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): 7.40-7.44 (m, 1H), 7.13-7.22 (m, 5H), 7.03-7.06 (m, 2H), 6.72-6.76 (m, 1H), 6.12-6.17 (m, 1H), 6.00 (dd, *J* = 9.1, 15.4 Hz, 1H), 5.25-5.35 (m, 2H), 4.22-4.29 (m, 1H), 4.04-4.17 (m, 2H), 3.70-3.75 (m, 1H), 3.20-3.24 (m, 1H), 2.38-2.42 (m, 2H), 2.33 (s, 3H), 2.12-2.16 (m, 3H), 2.04 (s, 3H), 2.00-2.04 (m, 6H), 1.76-1.85 (m, 1H), 1.47-1.53 (m, 3H), 0.86-0.89 (m, 6H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 174.57, 174.42, 170.41, 169.67, 169.56, 168.98, 168.97, 140.71, 137.50, 137.30, 135.98, 135.93, 135.51, 135.48, 134.12, 134.09, 130.42, 130.40, 129.46, 128.14, 127.39, 127.36, 126.36, 126.24, 126.22, 124.01, 123.99, 94.17, 94.10, 70.96, 70.90, 70.86, 66.25, 66.04, 62.81, 62.59, 46.46, 46.41, 45.31, 45.16, 45.14, 45.07, 30.29, 30.28, 22.53, 22.53, 21.19, 21.16, 21.03, 20.85, 20.83, 19.96, 19.94, 18.73, 18.53. **HRMS** (ESI-TOF) *m/z* calcd for $C_{34}H_{42}O_9Na$ [$(M + Na)^+$], 617.2721, found, 617.2717.

(2R,3S,4R,5S,6R)-6-(((4-(N,N-dipropylsulfamoyl)benzoyl)oxy)methyl)-3-((E)-2-methylstyryl)tetrahydro-2H-pyran-2,4,5-triyl triacetate (7c)



7c

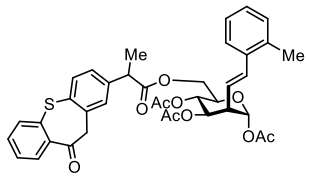
According to the **General Procedure B** (0.113 mmol of bromosugar was used), the title compound was obtained as a white solid (60.1 mg, 0.090 mmol, 79% yield, axial: equatorial = 4.0:1). $\mathbf{R}_f$ = 0.18 Hexanes: EtOAc [3:1 (v/v)].

Data for axial product (**7c-*ax***): t_R = 10.7 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): 8.12 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.40 (dd, *J* = 0.7, 8.4 Hz, 1H), 7.19-7.25 (m, 2H), 7.16 (d, *J* = 7.0 Hz, 1H), 6.81 (d, *J* = 16.1 Hz, 1H), 6.25 (d, *J* = 1.4 Hz, 1H, H-1), 6.08 (dd, *J* = 9.1, 16.1 Hz, 1H), 5.52 (t, *J* = 9.8 Hz, 1H), 5.44 (dd, *J* = 5.6, 9.8 Hz, 1H), 4.51 (dd, *J* = 2.1, 12.6 Hz, 1H), 4.38 (dd, *J* = 3.5, 12.6 Hz, 1H), 4.22 (dt, *J* = 2.8, 10.5 Hz, 1H), 3.25-3.29 (m, 1H), 3.03-

3.08 (m, 4H), 2.30 (s, 3H), 2.20 (s, 3H), 2.07 (s, 3H), 2.05 (s, 3H), 1.55 (h, *J* = 7.7 Hz, 4H), 0.87 (t, *J* = 7.7 Hz, 6H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.38, 169.77, 169.02, 164.96, 144.52, 135.77, 135.55, 133.91, 133.04, 130.58, 130.39, 130.39, 128.36, 127.24, 127.24, 126.49, 125.88, 123.74, 94.06, 70.83, 70.75, 65.96, 63.09, 50.22, 50.22, 45.97, 22.21, 22.21, 21.22, 21.04, 20.85, 19.92, 11.31, 11.31. **HRMS** (ESI-TOF) *m/z* calcd for $C_{34}H_{44}NO_{11}S$ [$(M + H)^+$], 674.2630, found, 674.2621.

Data for equatorial product (**7c-*eq***): t_R = 8.27 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): 8.17 (d, *J* = 8.4 Hz, 2H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.28 (dd, *J* = 1.4, 7.7 Hz, 1H), 7.09-7.21 (m, 3H), 6.76 (d, *J* = 15.4 Hz, 1H), 6.21 (d, *J* = 3.5 Hz, 1H, H-1), 5.69 (dd, *J* = 9.1, 15.4 Hz, 1H), 5.51 (dd, *J* = 9.1, 11.2 Hz, 1H), 5.26 (t, *J* = 9.8 Hz, 1H), 4.51 (dd, *J* = 2.1, 11.9 Hz, 1H), 4.45 (dd, *J* = 4.2, 12.6 Hz, 1H), 4.24 (ddd, *J* = 2.8, 3.5, 10.5 Hz, 1H), 3.07-3.18 (m, 4H), 2.93-2.98 (m, 1H), 2.30 (s, 3H), 2.18 (s, 3H), 2.07 (s, 3H), 1.97 (s, 3H), 1.52-1.60 (m, 4H), 0.88 (t, *J* = 7.0 Hz, 6H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.50, 169.88, 169.07, 165.03, 144.59, 135.69, 135.51, 134.11, 133.11, 130.55, 130.55, 130.40, 128.21, 127.24, 127.24, 126.40, 126.16, 123.90, 92.90, 70.70, 70.08, 68.85, 63.04, 50.20, 50.20, 49.27, 22.18, 22.18, 21.09, 20.92, 20.87, 19.86, 11.32, 11.32. **HRMS** (ESI-TOF) *m/z* calcd for $C_{34}H_{44}NO_{11}S$ [$(M + H)^+$], 674.2630, found, 674.2620.

(2R,3S,4R,5S,6R)-3-((E)-2-methylstyryl)-6-(((2-(10-oxo-10,11-dihydrodibenzo[b,f]thiepin-2-yl)propanoyl)oxy)methyl)tetrahydro-2H-pyran-2,4,5-triyl triacetate (7d)



7d

According to the **General Procedure B** (0.08 mmol of bromosugar was used), the title compound was obtained as a white solid (30.7 mg, 0.045 mmol, 56% yield, axial: equatorial = 4.6:1). **R_f** = 0.24 Hexanes: EtOAc [3:1 (v/v)].

Data for axial product (**7d-*ax***)

isomer **1 (7d-*ax*-iso-1)**: t_R = 11.0 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): 8.19 (dd, *J* = 1.4, 8.4 Hz, 1H), 7.59 (dd, *J* = 1.4, 8.4 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.39-7.43 (m, 2H), 7.37 (d, *J* = 1.4 Hz, 1H), 7.29-7.33 (m, 1H), 7.19-7.21 (m, 2H), 7.15-7.18 (m, 1H), 7.13 (dd, *J* = 2.1, 7.7 Hz, 1H), 6.74 (d, *J* = 15.4 Hz, 1H), 6.15 (d, *J* = 1.4 Hz, 1H), 5.99 (dd, *J* = 9.1, 15.4 Hz, 1H), 5.29-5.35 (m, 2H), 4.35 (s, 2H), 4.27 (dd, *J* = 4.9, 12.6 Hz, 1H), 4.10 (dd, *J* = 2.1, 12.6 Hz, 1H), 4.06 (ddd, *J* = 2.1, 4.9, 9.1 Hz, 1H), 3.74 (q, *J* = 7.0 Hz, 1H), 3.22 (dd, *J* = 5.6, 9.8 Hz, 1H), 2.32 (s, 3H), 2.12 (s, 3H), 2.05 (s, 3H), 2.02 (s, 3H), 1.49 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 191.47, 173.70, 170.38, 169.71, 168.95, 142.46, 140.30, 138.08, 136.31, 135.94, 135.50, 134.12, 133.45, 132.63, 131.68, 131.60, 131.01, 130.44, 128.73, 128.17, 126.99, 126.75, 126.39, 126.17, 123.91, 94.08, 70.91, 70.81, 65.95, 62.80, 51.19, 46.33, 45.18, 21.14, 21.03, 20.84, 19.96, 18.71. **HRMS** (ESI-

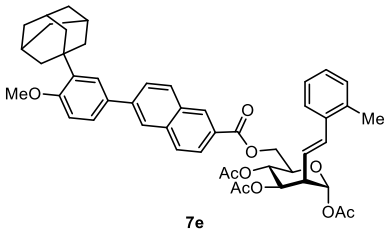
TOF) *m/z* calcd for $C_{38}H_{38}O_{10}SNa$ [(M + Na)$^+$], 709.2078, found, 709.2066.

Isomer **2 (7d-*ax*-iso-2)**: t_R = 12.1 min, 10% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. Isomer **1**. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 8.19 (dd, *J* = 1.4, 8.4 Hz, 1H), 7.58 (dd, *J* = 1.4, 7.7 Hz, 1H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.35-7.44 (m, 3H), 7.28-7.31 (m, 1H), 7.08-7.21 (m, 4H), 6.75 (d, *J* = 16.1 Hz, 1H), 6.17 (d, *J* = 1.4 Hz, 1H), 5.99 (dd, *J* = 9.1, 16.1 Hz, 1H), 5.33 (dd, *J* = 5.6, 9.8 Hz, 1H), 5.25 (t, *J* = 9.8 Hz, 1H), 4.35 (s, 2H), 4.22 (dd, *J* = 2.1, 11.9 Hz, 1H), 4.16 (dd, *J* = 4.9, 11.9 Hz, 1H), 4.09 (ddd, *J* = 2.1, 4.9, 9.8 Hz, 1H), 3.75 (q, *J* = 7.0 Hz, 1H), 3.19-3.27 (m, 1H), 2.32 (s, 3H), 2.14 (s, 3H), 2.01 (s, 3H), 2.01 (s, 3H), 1.50 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 191.50, 173.62, 170.39, 169.57, 168.96, 142.22, 140.35, 138.04, 136.34, 135.93, 135.49, 134.15, 133.45, 132.61, 131.66, 131.60, 131.02, 130.44, 128.83, 128.17, 126.97, 126.63, 126.39, 126.17, 123.93, 94.12, 70.89, 70.78, 66.16, 63.04, 51.19, 46.35, 45.25, 21.18, 21.04, 20.80, 19.95, 18.44. **HRMS** (ESI-TOF) *m/z* calcd for $C_{38}H_{38}O_{10}SNa$ [(M + Na)$^+$], 709.2078, found, 709.2070.

Data for equatorial product (**7d-*eq***)

isomer **1 (7d-*eq*-iso-1)**: t_R = 11.5 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): 8.20 (dd, *J* = 1.4, 8.4 Hz, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.59 (dd, *J* = 0.7, 7.7 Hz, 1H), 7.44 (d, *J* = 1.4 Hz, 1H), 7.42 (dt, *J* = 2.1, 7.7 Hz, 1H), 7.25-7.32 (m, 2H), 7.10-7.19 (m, 4H), 6.77 (d, *J* = 16.1 Hz, 1H), 6.14 (d, *J* = 3.5 Hz, 1H, H-1), 5.64 (dd, *J* = 9.1, 15.4 Hz, 1H), 5.41 (dd, *J* = 9.8, 11.2 Hz, 1H), 4.99 (t, *J* = 9.8 Hz, 1H), 4.35-4.44 (m, 2H), 4.15-4.21 (m, 2H), 4.06 (ddd, *J* = 2.1, 3.5, 9.8 Hz, 1H), 3.7-3.80 (m, 1H), 2.80 (ddd, *J* = 3.5, 9.1, 11.9 Hz, 1H), 2.31 (s, 3H), 2.12 (s, 3H), 1.99 (s, 3H), 1.96 (s, 3H), 1.52 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 191.53, 173.59, 170.55, 169.60, 169.03, 142.30, 140.31, 138.04, 136.35, 135.82, 135.52, 134.01, 133.39, 132.64, 131.68, 131.56, 130.99, 130.36, 128.98, 128.13, 126.99, 126.88, 126.37, 126.18, 124.06, 92.77, 70.67, 70.04, 68.75, 62.51, 51.21, 49.06, 45.25, 21.03, 20.94, 20.76, 19.90, 18.21. **HRMS** (ESI-TOF) *m/z* calcd for $C_{38}H_{38}O_{10}SNa$ [(M + Na)$^+$], 709.2078, found, 709.2075.

(2R,3S,4R,5S,6R)-6-(((6-(3-(adamantan-1-yl)-4-methoxyphenyl)-2-naphthoyl)oxy)methyl)-3-((E)-2-methylstyryl)tetrahydro-2H-pyran-2,4,5-triyl triacetate (7e)



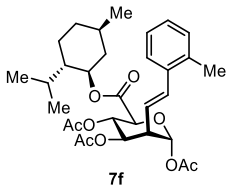
7e

According to the **General Procedure B** (0.1 mmol of bromosugar was used), the title compound was obtained as a white solid (51.2 mg, 0.064 mmol, 64% yield, axial: equatorial = 4.0:1). $\mathbf{R}_f$ = 0.26 Hexanes: EtOAc [3:1 (v/v)].

Data for axial product (**7e-*ax***): t_R = 10.8 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): 8.60-8.63 (m, 1H), 8.06 (dd, *J* = 1.4, 8.4 Hz, 1H), 7.99 (d, *J* = 1.4 Hz, 1H), 7.88 (d, *J* = 9.1 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.75 (dd, *J* = 1.4, 8.4 Hz, 1H), 7.60 (d, *J* = 2.1 Hz, 1H), 7.55 (dd, *J* = 2.1, 8.4 Hz, 1H), 7.36 (d, *J* = 7.7 Hz, 1H), 7.16 (t, *J* = 7.7 Hz, 1H), 7.11 (d, J = 7.7 Hz, 1H), 6.98-7.05 (m, 2H), 6.79 (d, *J* = 15.4 Hz, 1H), 6.26 (d, *J* = 1.4 Hz, 1H, H-1), 6.11 (dd, *J* = 9.1, 15.4 Hz, 1H), 5.58 (t, *J* = 9.8 Hz, 1H), 5.45 (dd, *J* = 5.6, 9.8 Hz, 1H), 4.62 (dd, *J* = 2.1, 11.9 Hz, 1H), 4.43 (dd, *J* = 3.5, 11.9 Hz, 1H), 4.28 (dt, *J* = 3.5, 9.8 Hz, 1H), 3.92 (s, 3H), 3.25-3.30 (m, 1H), 2.29 (s, 3H), 2.20 (s, 3H), 2.18-2.22 (m, 6H), 2.09-2.13 (m, 3H), 2.08 (s, 3H), 2.04 (s, 3H), 1.78-1.85 (m, 6H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.47, 169.69, 169.06, 166.47, 159.07, 141.65, 139.15, 136.20, 135.79, 135.53, 133.91, 132.76, 131.36, 131.24, 130.44, 130.06, 128.51, 128.05, 126.62, 126.56, 126.41, 126.16, 125.98, 125.91, 125.64, 124.86, 123.81, 112.24, 94.26, 71.11, 70.96, 66.25, 62.72, 55.32, 46.31, 40.73, 40.73, 40.73, 37.35, 37.26, 37.26, 37.26, 29.24, 29.24, 29.24, 21.25, 21.07, 20.89, 19.92. **HRMS** (ESI-TOF) *m/z* calcd for $C_{49}H_{52}O_{10}Na$ [$(M + Na)^+$], 823.3453, found, 823.3448.

(2R,3S,4R,5S,6S)-6-((((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl)oxy)carbonyl)-3-((E)-2-methylstyryl)tetrahydro-2H-pyran-2,4,5-triyl triacetate (7f)



7f

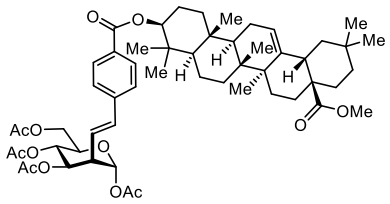
According to the **General Procedure B** (0.1 mmol of bromosugar was used), the title compound was obtained as a white foam (25.1 mg, 0.045 mmol, 45% yield, axial: equatorial = 3.5:1). $\mathbf{R_f}$ = 0.53 Hexanes: EtOAc [3:1 (v/v)].

Data for axial product (**7f-*ax***): t_R = 6.60 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): 7.38-7.41 (m, 1H), 7.12-7.19 (m, 3H), 6.76 (d, *J* = 15.4 Hz, 1H), 6.35 (d, *J* = 3.5 Hz, 1H), 5.98 (dd, *J* = 9.8, 15.4 Hz, 1H), 5.42 (t, *J* = 7.7 Hz, 1H), 5.34 (dd, *J* = 4.9, 8.4 Hz, 1H), 4.76 (dt, *J* = 4.2, 11.2 Hz, 1H), 4.49 (d, *J* = 8.4 Hz, 1H), 3.13-3.20 (m, 1H), 2.32 (s, 3H), 2.17 (s, 3H), 2.09 (s, 3H), 2.03 (s, 3H), 1.99-2.05 (m, 1H), 1.87-1.90 (m, 1H), 1.65-1.72 (m, 2H), 1.41-1.52 (m, 2H), 1.02-1.11 (m, 1H), 0.97 (q, *J* = 11.2 Hz, 1H), 0.90 (dd, *J* = 3.5, 7.0 Hz, 6H), 0.77 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.11, 169.30, 168.78, 167.36, 135.86, 135.50, 133.96, 130.37, 128.10, 126.37, 126.18, 123.72, 92.89, 76.53, 72.66, 70.63, 66.87, 46.93, 45.38, 40.63, 34.20, 31.49, 26.28, 23.44, 22.11, 21.19, 21.05, 20.97, 20.91, 19.93, 16.41. **HRMS** (ESI-TOF) *m/z* calcd for $C_{31}H_{42}O_9Na$ [$(M + Na)^+$], 581.2721, found, 581.2714.

Data for equatorial product (**7f-*eq***): t_R = 5.10 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): 7.25-7.27 (m, 1H), 7.10-7.19 (m, 3H), 6.74 (d, *J* = 15.4 Hz, 1H), 6.29 (d, *J* = 2.8 Hz, 1H), 5.64 (dd, *J* = 8.4, 15.4 Hz, 1H), 5.47 (dd, *J* = 9.1, 11.2 Hz, 1H), 5.28 (t, *J* = 9.8 Hz, 1H), 4.77 (dt, *J* = 4.9, 11.2 Hz, 1H), 4.42 (d, *J* = 10.5 Hz, 1H), 2.98 (ddd, *J* = 3.5, 9.1, 11.9 Hz, 1H), 2.29 (s, 3H), 2.18 (s, 3H), 2.04 (s, 3H), 1.97 (s, 3H), 1.93-1.99 (m, 1H), 1.82-1.88 (m, 1H), 1.66-1.72 (m,

2H), 1.44-1.51 (m, 1H), 1.36-1.45 (m, 1H), 1.00-1.09 (m, 1H), 0.96 (q, *J* = 11.9 Hz, 1H), 0.90 (dd, *J* = 2.8, 7.0 Hz, 6H), 0.82-0.89 (m, 1H), 0.75 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.50, 169.38, 168.76, 167.09, 135.73, 135.53, 134.16, 130.37, 128.17, 126.37, 126.17, 123.74, 92.57, 76.35, 71.45, 70.40, 69.78, 48.71, 46.97, 40.59, 34.23, 31.50, 26.11, 23.35, 22.10, 21.07, 20.94, 20.90, 20.83, 19.85, 16.23. **HRMS** (ESI-TOF) *m/z* calcd for $C_{31}H_{42}O_9Na$ [(M + Na)$^+$], 581.2721, found, 581.2719.

(2R,3S,4R,6R)-6-(acetoxymethyl)-3-((E)-4-((((3S,4aR,6aR,6bS,8aS,12aS,14aR,14bR)-8a-(methoxycarbonyl)-4,4,6a,6b,11,11,14b-heptamethyl 1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,14,14a,14b-icosahydropicen-3-yl)oxy)carbonyl)styryl)tetrahydro-2H-pyran-2,4,5-triyl triacetate (7g)



7g

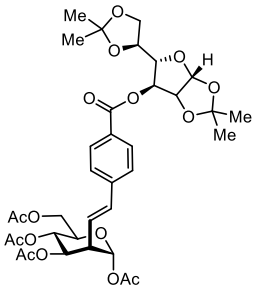
According to the **General Procedure B** (0.1 mmol of bromosugar was used), the title compound was obtained as a white solid (59.6 mg, 0.640 mmol, 64% yield, axial: equatorial = 5.4:1). $\mathbf{R}_f$ = 0.22 Hexanes: EtOAc [3:1 (v/v)].

Data for axial product (**7g-*ax***): t_R = 22.5 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): 8.00 (d, *J* = 7.7 Hz, 2H), 7.43 (d, *J* = 7.7 Hz, 2H), 6.60 (d, *J* = 16.1 Hz, 1H), 6.28 (dd, *J* = 9.1, 16.1 Hz, 1H), 6.18 (s, *J* = 1.4 Hz, 1H, H-1), 5.37 (dd, *J* = 5.6, 10.5 Hz, 1H), 5.32 (d, *J* = 10.5 Hz, 1H), 5.29 (t, *J* = 4.2 Hz, 1H), 4.74 (dd, *J* = 5.6, 11.2 Hz, 1H), 4.25 (dd, *J* = 4.2, 12.6 Hz, 1H), 4.15 (dd, *J* = 2.1, 12.6 Hz, 1H), 4.12 (ddd, *J* = 2.1, 4.2, 9.8 Hz, 1H), 3.63 (s, 3H), 3.24 (dd, *J* = 5.6, 9.1 Hz, 1H), 2.87 (dd, *J* = 4.2, 14.0 Hz, 1H), 2.18 (s, 3H), 2.10 (s, 3H), 2.06 (s, 3H), 2.00 (s, 3H), 1.85-2.01 (m, 3H), 1.37-1.80 (m, 13H), 1.27-1.37 (m, 2H), 1.15 (s, 3H), 1.03-1.22 (m, 4H), 1.01 (s, 3H), 0.98 (s, 3H), 0.94 (s, 3H), 0.93 (s, 3H), 0.90 (s, 3H), 0.74 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 178.47, 170.80, 170.38, 169.70, 168.93, 166.06, 143.96, 140.58, 135.09, 130.50, 130.09, 130.09, 126.50, 126.50, 124.90, 122.42, 94.00, 81.76, 70.83, 70.77, 66.05, 62.38, 55.49, 51.68, 47.70, 46.87, 46.22, 45.98, 41.79, 41.43, 39.44, 38.24, 38.24, 37.12, 33.99, 33.25, 32.74, 32.52, 30.84, 28.35, 27.83, 26.07, 23.78, 23.73, 23.57, 23.21, 21.21, 21.00, 20.91, 20.85, 18.38, 17.12, 16.99, 15.52. **HRMS** (ESI-TOF) *m/z* calcd for $C_{54}H_{74}O_{13}Na$ [(M + Na)$^+$], 953.5022, found, 953.5013.

Data for equatorial product (**7g-*eq***): t_R = 10.3 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): 7.97 (d, *J* = 8.4 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 2H), 6.57 (d, *J* = 15.4 Hz, 1H), 6.18 (d, *J* = 3.5 Hz, 1H, H-1), 5.91 (dd, *J* = 9.8, 15.4 Hz, 1H), 5.46 (dd, *J* = 9.8, 10.5 Hz, 1H), 5.29 (t, *J* = 3.5 Hz, 1H), 5.16 (t, *J* = 9.8 Hz, 1H), 4.72 (dd, *J* = 4.9, 11.2 Hz, 1H), 4.33 (dd, *J* = 4.2, 12.6 Hz, 1H), 4.10 (ddd, *J* = 2.1, 4.2, 10.5 Hz, 1H), 4.07 (dd, *J* = 2.1, 11.9 Hz, 1H), 3.63 (s, 3H), 2.92 (ddd, *J* = 3.5, 9.8, 11.2 Hz, 1H), 2.87 (dd, *J* = 4.2, 14.0 Hz, 1H), 2.18 (s, 3H), 2.10 (s, 3H), 2.05 (s, 3H), 1.93 (s,

3H), 1.85-2.03 (s, 3H), 1.26-1.85 (m, 15H), 1.15 (s, 3H), 1.03-1.22 (m, 4H), 1.00 (s, 3H), 0.98 (s, 3H), 0.93 (s, 3H), 0.92 (s, 3H), 0.90 (s, 3H), 0.74 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 13C NMR (176 MHz, CDCl3) δ 178.48, 170.86, 170.52, 169.82, 168.99, 166.02, 143.97, 140.50, 135.06, 130.54, 130.09, 130.09, 126.49, 126.49, 125.19, 122.42, 92.65, 81.77, 70.65, 70.14, 68.54, 62.01, 55.50, 51.69, 49.11, 47.70, 46.88, 46.00, 41.80, 41.44, 39.45, 38.24, 38.24, 37.12, 34.00, 33.26, 32.74, 32.53, 30.85, 28.34, 27.84, 26.08, 23.79, 23.73, 23.7, 23.21, 21.08, 20.89, 20.84, 20.83, 18.39, 17.12, 17.00, 15.52. **HRMS** (ESI-TOF) *m/z* calcd for $C_{54}H_{74}O_{13}Na$ [$(M + Na)^+$], 953.5022, found, 953.5016.

(2R,4R,6R)-6-(acetoxymethyl)-3-((E)-4-((((3aR,5S,6S)-5-((S)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl)oxy)carbonyl)styryl)tetrahydro-2H-pyran-2,4,5-triyl triacetate (7h)



7h

According to the **General Procedure B** (0.1 mmol of bromosugar was used), the title compound was obtained as a white foam (58.3 mg, 0.081 mmol, 81% yield, axial: equatorial = 5.0:1). $\mathbf{R}_f$ = 0.08 Hexanes: EtOAc [3:1 (v/v)].

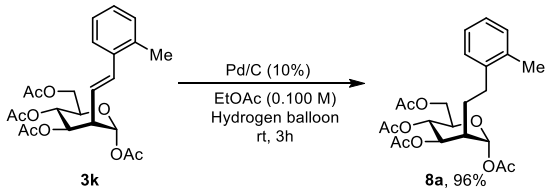
Data for axial product (**7h-*ax***): t_R = 18.4 min, 20% (v/v) isopropanol in hexane at the flow rate of 1.0 ml/min. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 7.99 (d, *J* = 8.4 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 2H), 6.61 (d, *J* = 15.4 Hz, 1H), 6.30 (dd, *J* = 9.1, 15.4 Hz, 1H), 6.18 (d, *J* = 1.4 Hz, 1H, H-1), 5.96 (d, *J* = 3.5 Hz, 1H), 5.50 (d, *J* = 2.8 Hz, 1H), 5.38 (dd, *J* = 5.6, 9.8 Hz, 1H), 5.31 (t, *J* = 9.8 Hz, 1H), 4.64 (d, *J* = 4.2 Hz, 1H), 4.34-4.38 (m, 1H), 4.33 (dd, *J* = 2.8, 8.4 Hz, 1H), 4.26 (dd, *J* = 4.2, 11.9 Hz, 1H), 4.10-4.17 (m, 3H), 4.09 (dd, *J* = 4.9, 9.1 Hz, 1H), 3.22-3.26 (m, 1H), 2.19 (s, 3H), 2.10 (s, 3H), 2.07 (s, 3H), 2.01 (s, 3H), 1.56 (s, 3H), 1.42 (s, 3H), 1.33 (s, 3H), 1.27 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.79, 170.35, 169.76, 168.94, 164.99, 141.33, 134.85, 130.29, 130.29, 128.97, 126.69, 126.69, 125.56, 112.53, 109.56, 105.30, 93.93, 83.52, 80.13, 76.79, 72.71, 70.86, 70.74, 67.42, 66.04, 62.37, 46.20, 26.98, 26.88, 26.36, 25.35, 21.21, 21.00, 20.91, 20.85. **HRMS** (ESI-TOF) *m/z* calcd for $C_{35}H_{44}O_{16}Na$ [$(M + Na)^+$], 743.2522, found, 743.2511.

Data for equatorial product (**7h-*eq***): t_R = 9.50 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): 7.96 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 6.57 (d, *J* = 16.1 Hz, 1H), 6.18 (d, *J* = 3.5 Hz, 1H, H-1), 5.89-5.95 (m, 2H), 5.48 (d, *J* = 2.8 Hz, 1H), 5.46 (dd, *J* = 9.1, 10.5 Hz, 1H), 5.16 (t, *J* = 9.8 Hz, 1H), 4.62 (d, *J* = 3.5 Hz, 1H), 4.29-4.38 (m, 3H), 4.04-4.14 (m, 4H),

2.93 (ddd, *J* = 3.5, 9.8, 12.0 Hz, 1H), 2.19 (s, 3H), 2.10 (s, 3H), 2.05 (s, 3H), 1.94 (s, 3H), 1.56 (s, 3H), 1.41 (s, 3H), 1.32 (s, 3H), 1.27 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.84, 170.52, 169.80, 169.00, 164.96, 141.25, 134.78, 130.29, 130.29, 129.02, 126.65, 126.65, 125.89, 112.54, 109.57, 105.27, 92.60, 83.51, 80.10, 76.81, 72.71, 70.64, 70.15, 68.50, 67.41, 61.98, 49.10, 26.99, 26.89, 26.36, 25.37, 21.09, 20.89, 20.86, 20.83. **HRMS** (ESI-TOF) *m/z* calcd for $C_{35}H_{44}O_{16}Na$ [(M + Na)$^+$], 743.2522, found, 743.2518.

Post-Functionalization

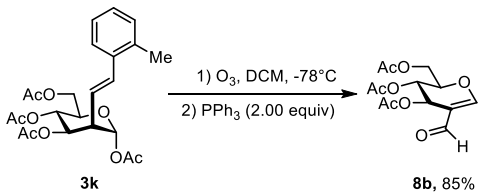
(2R,3S,4R,5S,6R)-6-(acetoxymethyl)-3-(2-methylphenethyl)tetrahydro-2H-pyran-2,4,5-triyl triacetate (8a)



3k **8a**, 96%

To a solution of **3k** (8.96 mg, 0.0200 mmol, 1.00 equiv) in EtOAc (0.200 ml, 0.100 M) was added Palladium on carbon (8.96 mg, 10 wt. % loading). After gas exchanged using hydrogen balloon for 10 min, the reaction mixture was stirred under hydrogen atmosphere at room temperature for 3h. Upon completion, the reaction was filtered through a pad of celite. The mixture was concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel, eluting with Hexanes: EtOAc [3:1 (v/v)] to afford the desired compound **8a** as a white foam (8.60 mg, 96% yield). Data for **8a**: $\mathbf{R_f}$ = 0.10 Hexanes: EtOAc [3:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 7.10-7.17 (m, 4H), 6.21 (d, *J* = 1.4 Hz, 1H), 5.37 (dd, *J* = 4.9, 9.8 Hz, 1H), 5.17 (t, *J* = 9.8 Hz, 1H), 4.18 (dd, *J* = 4.2, 12.6 Hz, 1H), 4.11 (dd, *J* = 2.1, 12.6 Hz, 1H), 4.02 (ddd, *J* = 2.1, 4.2, 9.8 Hz, 1H), 2.78 (ddd, *J* = 5.6, 10.5, 14.0 Hz, 1H), 2.57 (ddd, *J* = 7.0, 10.5, 14.0 Hz, 1H), 2.30 (s, 3H), 2.25-2.30 (m, 1H), 2.16 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H), 2.00 (s, 3H), 1.93-2.00 (m, 1H), 1.72-1.79 (m, 1H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.86, 170.15, 169.78, 169.26, 139.31, 135.88, 130.56, 128.94, 126.57, 126.30, 93.31, 70.64, 70.58, 66.11, 62.38, 41.93, 31.43, 25.71, 21.26, 20.98, 20.88, 20.84, 19.34. **HRMS** (ESI-TOF) *m/z* calcd for $C_{23}H_{30}O_9Na$ [(M + Na)$^+$], 473.1782, found, 473.1780.

(2R,3S,4R,5S,6R)-6-(((6-(3-(adamantan-1-yl)-4-methoxyphenyl)-2-naphthoyl)oxy)methyl)-3-((E)-2-methylstyryl)tetrahydro-2H-pyran-2,4,5-triyl triacetate (8b)

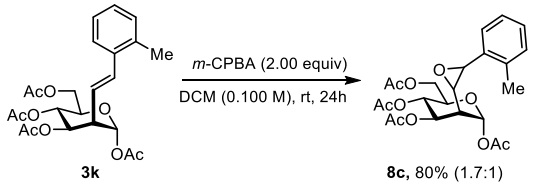


3k **8b**, 85%

Ozone was passed through a stirred solution of **3k** (8.96 mg, 0.0200 mmol, 1.00 equiv) in DCM (0.100 ml, 0.200 M) at -78 °C for 45 min. Oxygen was then bubbled through reaction mixture for 20 min and followed

by nitrogen gas. After PPh_3 (2.0 equiv) was added, the mixture was warmed slowly to room temperature and stirred overnight. Then the mixture was concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel, eluting with Hexanes: EtOAc [3:1 (v/v)] to afford the desired compound **8b** as white foam (5.10 mg, 85% yield). $\mathbf{R}_f$ = 0.10 Hexanes: EtOAc [3:1 (v/v)]. Data for **8b**: **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 9.37 (s, 1H), 7.46 (s, 1H), 5.70 (dd, *J* = 1.4, 2.8 Hz, 1H), 5.20 (t, *J* = 3.5 Hz, 1H), 4.62-4.67 (m, 1H), 4.49 (dd, *J* = 7.7, 11.9 Hz, 1H), 4.17 (dd, *J* = 4.2, 11.9 Hz, 1H), 2.11 (s, 3H), 2.08 (s, 2H), 2.06 (s, 2H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 188.23, 170.46, 169.58, 169.34, 163.80, 115.90, 76.44, 65.75, 60.94, 60.73, 20.89, 20.81, 20.81. **HRMS** (ESI-TOF) *m/z* calcd for $C_{13}H_{16}O_8Na$ [$(M + Na)^+$], 323.0737, found, 323.0736.

(2R,3S,4R,5S,6R)-6-(acetoxymethyl)-3-(3-(o-tolyl)oxiran-2-yl)tetrahydro-2H-pyran-2,4,5-triyl triacetate (8c)

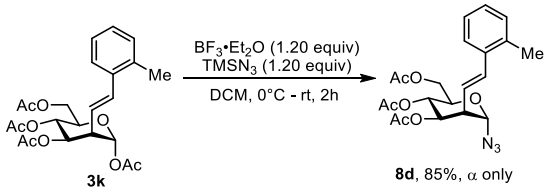


A solution of compound **3k** (8.96 mg, 0.0200 mmol, 1.00 equiv) in DCM (0.100 ml, 0.200 M) was cooled to 0 °C and *m*-CPBA (6.90 mg, 2.00 equiv) was added in one portion. After the reaction mixture was stirred at 0 °C for 15 min, it was warm to rt and stirred for overnight. The reaction was then quenched with a 1:1 mixture of saturated $Na_2S_2O_{3(aq)}$ and $NaHCO_{3(aq)}$ (1 mL), extracted with DCM (2 x 5 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by flash column chromatography (Hexanes: EtOAc [3:1 (v/v)]) to give **8c-*iso*-1** and **8c-*iso*-2** as colorless oil (7.40 mg (1.7:1), 80% yield) $\mathbf{R}_f$ = 0.30, 0.29 Hexanes: EtOAc [3:1 (v/v)].

Data for **8c-*iso*-1**: **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ºC, δ): 7.14-7.24 (m, 4H), 6.27 (d, *J* = 1.2 Hz, 1H), 5.40-5.44 (m, 2H), 4.23 (dd, *J* = 5.2, 12.8 Hz, 1H), 4.06-4.13 (m, 2H), 3.94 (d, *J* = 2.0 Hz, 1H), 3.09 (dd, *J* = 2.0, 7.2 Hz, 1H), 2.46-2.52 (m, 1H), 2.45 (s, 3H), 2.17 (s, 3H), 2.13 (s, 3H), 2.08 (s, 3H), 1.99 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.80, 170.60, 169.69, 168.91, 136.38, 134.57, 130.17, 128.21, 126.36, 124.58, 92.28, 70.77, 70.28, 65.94, 62.21, 58.25, 54.67, 44.81, 21.17, 21.06, 20.84, 20.79, 19.23. **HRMS** (ESI-TOF) *m/z* calcd for $C_{23}H_{28}O_{10}Na$ [$(M + Na)^+$], 487.1575, found, 487.1576.

Data for **8c-*iso*-2** : **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ºC, δ): 7.15-7.27 (m, 4H), 6.42 (d, *J* = 1.6 Hz, 1H, H-1), 5.55 (dd, *J* = 5.6, 10.0 Hz, 1H), 5.32 (t, *J* = 10.0 Hz, 1H), 4.24 (dd, *J* = 4.0, 12.0 Hz, 1H), 4.07-4.17 (m, 2H), 3.86 (d, *J* = 2.0 Hz, 1H), 3.16 (dd, *J* = 2.0, 8.8 Hz, 1H), 2.44 (s, 3H), 2.25 (ddd, *J* = 1.5, 5.2, 8.4 Hz, 1H), 2.17 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.04 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 13C NMR (176 MHz, CDCl3) δ 170.85, 170.21, 169.77, 168.67, 136.54, 134.57, 130.18, 128.40, 126.44, 125.13, 92.33, 70.52, 69.89, 66.42, 62.27, 57.68, 57.62, 46.15, 21.14, 21.09, 20.85, 20.81, 19.12. **HRMS** (ESI-TOF) *m/z* calcd for $C_{23}H_{28}O_{10}Na$ [$(M + Na)^+$], 487.1575, found, 487.1571.

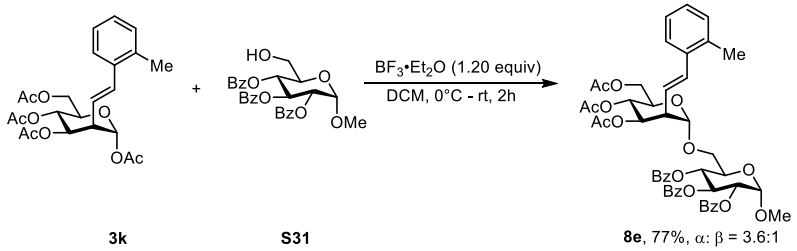
(2R,3S,4R,5S,6S)-2-(acetoxymethyl)-6-azido-5-((E)-2-methylstyryl)tetrahydro-2H-pyran-3,4-diyl diacetate (8d)



3k (8.96 mg, 0.0200 mmol, 1.00 equiv) was dissolved under argon atmosphere in DCM (0.200 mL) and cooled to 0 °C. $TMSN_3$ (3.20 µL, 0.0240 mmol, 1.20 equiv) and $BF_3{\cdot}OEt_2$ (3.10 µL, 0.0240 mmol, 1.20 equiv) were added to the reaction mixture. The reaction mixture was stirred for 2 h and slowly reached room temperature during this time. After complete consumption of the starting material (monitored by TLC), the reaction mixture was diluted with DCM. The organic phase was washed with cold saturated $NaHCO_3$ solution (3x1 ml) and water (3x1 ml). The organic phase was dried over $MgSO_4$, concentrated, and purified by flash column chromatography (Hexanes: EtOAc [5:1 (v/v)]) to give **8d** as colorless oil (7.30 mg, 85% yield). $\mathbf{R}_f$ = 0.54 Hexanes: EtOAc [3:1 (v/v)].

Data for **8d**: **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ºC, δ): 7.39-7.44 (m, 1H), 7.13-7.23 (m, 3H), 6.72 (d, *J* = 15.6 Hz, 1H), 6.02 (dd, *J* = 9.2, 15.6 Hz, 1H), 5.45 (d, *J* = 1.6 Hz, 1H), 5.23-5.26 (m, 2H), 4.28 (dd, *J* = 5.6, 12.4 Hz, 1H), 4.16-4.24 (m, 2H), 3.11-3.17 (m, 1H), 2.32 (s, 3H), 2.11 (s, 3H), 2.06 (s, 3H), 2.00 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.83, 170.20, 169.80, 135.80, 135.50, 133.88, 130.46, 128.19, 126.38, 126.13, 124.41, 90.53, 70.87, 70.73, 66.11, 62.46, 46.75, 20.99, 20.89, 20.87, 19.94. **HRMS** (ESI-TOF) *m/z* calcd for $C_{21}H_{25}N_3O_7Na$ [$(M + Na)^+$], 454.1585, found, 454.1583.

(2R,3R,4S,5R,6S)-2-((((2S,3S,4R,5S,6R)-4,5-diacetoxy-6-(acetoxymethyl)-3-((E)-2-methylstyryl)tetrahydro-2H-pyran-2-yl)oxy)methyl)-6-methoxytetrahydro-2H-pyran-3,4,5-triyl tribenzoate (8e-α)& (2R,3R,4S,5R,6S)-2-((((2R,3S,4R,5S,6R)-4,5-diacetoxy-6-(acetoxymethyl)-3-((E)-2-methylstyryl)tetrahydro-2H-pyran-2-yl)oxy)methyl)-6-methoxytetrahydro-2H-pyran-3,4,5-triyl tribenzoate(8e-β)



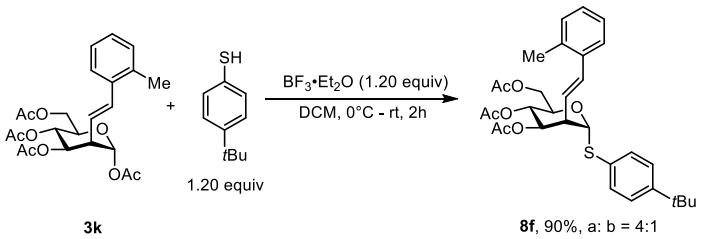
According to the procedure of synthesizing **8d**, **3k** (8.07 mg, 0.0180 mmol, 1.00 equiv) and **S31** (10.9 mg, 1.20 equiv) was used to obtain the title compound **8e-α** and **8e-β** as colorless oil (**8e-α**, 9.70 mg; **8e-β**, 2.70 mg, total 77% yield).

Data for **α isomer (8e-α)**: $\mathbf{R}_f$ = 0.23 Hexanes: EtOAc [3:1 (v/v)]. (purify using HPLC: Lux® 5µm i-Amylose 1 column, t_R = 10.00 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): 8.10-8.13 (m, 2H), 7.93-7.97 (m, 2H), 7.87-7.91 (m, 2H), 7.59-7.63 (m, 1H), 7.47-7.52 (m, 3H), 7.34-7.38 (m, 2H), 7.18-7.22 (m, 1H), 7.15 (t, *J* = 7.7 Hz, 2H), 7.08-7.12 (m, 1H), 7.01-7.06 (m, 2H), 6.95-6.98 (m, 1H), 6.11 (dd, *J* = 9.8, 10.5 Hz, 1H), 6.01 (d, *J* = 16.1 Hz, 1H), 5.62 (dd, *J* = 9.1, 16.1 Hz, 1H), 5.29 (dd, *J* = 5.6, 9.8 Hz, 1H), 5.18 (d, *J* = 1.4 Hz, 1H, H-1), 5.08-5.17 (m, 3H), 4.75 (dd, *J* = 2.1, 11.9 Hz, 1H), 4.61 (dd, *J* = 4.9, 11.9 Hz, 1H), 4.27 (ddd, *J* = 2.1, 4.9, 9.8 Hz, 1H), 4.21 (dd, *J* = 4.2, 11.9 Hz, 1H), 4.17 (t, *J* = 9.1 Hz, 1H), 4.12 (ddd, *J* = 2.1, 4.2, 9.8 Hz, 1H), 4.01 (dd, *J* = 2.1, 12.6 Hz, 1H), 3.46 (s, 3H), 2.90-2.94 (m, 1H), 2.03 (s, 3H), 2.00 (s, 3H), 2.00 (s, 3H), 1.91 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.74, 169.91, 169.75, 166.38, 166.10, 165.39, 135.92, 135.15, 133.52, 133.50, 133.38, 133.32, 130.09, 130.09, 130.01, 129.90, 129.90, 129.78, 129.72, 129.72, 129.08, 128.94, 128.74, 128.74, 128.55, 128.55, 128.49, 128.49, 127.67, 126.17, 125.93, 124.23, 102.36, 96.94, 76.11, 73.03, 72.11, 70.49, 70.04, 68.31, 66.44, 63.58, 62.54, 55.65, 47.95, 20.91, 20.85, 20.81, 19.74. **HRMS** (ESI-TOF) *m/z* calcd for $C_{49}H_{50}O_{16}Na$ [$(M + Na)^+$], 917.2991, found, 917.2990.

Data for **β isomer (8e-β)**: $\mathbf{R}_f$ = 0.23 Hexanes: EtOAc [3:1 (v/v)]. (purify using HPLC: Lux® 5µm i-Amylose 1 column, t_R = 13.18 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): 8.07-8.11 (m, 2H), 8.02-8.05 (m, 2H), 7.96-7.99 (m, 2H), 7.59-7.63 (m, 1H), 7.52-7.57 (m, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.21-7.29 (m, 3H), 7.10 (t, *J* = 7.7 Hz, 1H), 7.01-7.06 (m, 2H), 6.97 (d, *J* = 7.7 Hz, 1H), 5.97 (d, *J* = 16.1 Hz, 1H), 5.59-5.68 (m, 2H), 5.34 (dd, *J* = 4.2, 9.8 Hz, 1H), 5.00-5.14 (m, 4H), 4.61 (t, *J* = 9.8 Hz, 1H), 4.56 (dd, *J* = 2.8, 12.6 Hz, 1H), 4.40 (dd, *J* = 4.9, 12.6 Hz, 1H), 4.23-4.28 (m, 1H), 3.88 (d, *J* = 9.8 Hz, 1H), 3.79 (dd, *J* = 2.1, 11.9 Hz, 1H), 3.65 (dd, *J* = 3.5, 12.6 Hz, 1H), 3.45 (s, 3H), 2.91 (dd, *J* = 5.6, 9.8 Hz, 1H), 2.01 (s, 3H), 1.99 (s, 3H), 1.85 (s, 3H), 1.74 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.77, 169.81, 169.57, 166.38, 165.79, 164.98, 136.12, 135.13, 133.76, 133.73, 133.26, 133.04, 130.03, 129.98, 129.98, 129.93, 129.93, 129.87, 129.87, 129.79, 129.68, 128.70, 128.70, 128.65, 128.65, 128.64, 128.55, 128.55, 127.62, 126.20, 125.91, 124.76, 101.72, 97.26, 75.21, 72.38, 71.86, 70.63, 68.65, 67.64, 65.91, 63.10, 61.99, 55.71, 47.80, 20.90, 20.82, 20.64, 19.74. **HRMS** (ESI-TOF) *m/z* calcd for $C_{49}H_{50}O_{16}Na$ [$(M + Na)^+$], 917.2991, found, 917.2990.

(2R,3S,4R,5S,6R)-2-(acetoxymethyl)-6-((4-(tert-butyl)phenyl)thio)-5-((E)-2-methylstyryl)tetrahydro-2H-pyran-3,4-diyl diacetate (8f-α)& (2R,3S,4R,5S,6S)-2-(acetoxymethyl)-6-((4-(tert-butyl)phenyl)thio)-5-((E)-2-methylstyryl)tetrahydro-2H-pyran-3,4-diyl diacetate (8f-β)



3k **8f**, 90%, a: b = 4:1

According to the procedure of synthesizing **8d**, **3k** (8.96 mg, 0.0200 mmol, 1.00 equiv) and 4-*tert*-butylthiophenol (4.06 mg, 1.20 equiv) was used to obtain the title compound **8f-α** and **8f-β** as colorless oil (**8f-α**, 7.95 mg; **8f-β**, 2.00 mg, total 90% yield).

Data for **α isomer (8f-α)**: $\mathbf{R}_f$ = 0.56 Hexanes: EtOAc [3:1 (v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 7.37-7.46 (m, 3H), 7.31-7.36 (m, 2H), 7.11-7.20 (m, 3H), 6.69 (d, *J* = 15.5 Hz, 1H), 6.15 (dd, *J* = 9.5, 15.5 Hz, 1H), 5.54 (s, 1H, H-1), 5.34 (dd, *J* = 5.5, 9.5 Hz, 1H), 5.26 (t, *J* = 10.0Hz, 1H), 4.64 (ddd, *J* = 2.0, 5.5, 10.1 Hz, 1H), 4.28 (dd, *J* = 5.5, 12.0 Hz, 1H), 4.14 (dd, *J* = 2.5, 12.0 Hz, 1H), 3.96-3.45 (m, 1H), 2.32 (s, 3H), 2.08 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H), 1.30 (s, 9H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.79, 170.22, 169.91, 151.24, 136.01, 135.46, 132.89, 132.01, 132.01, 130.39, 130.19, 127.98, 126.33, 126.30, 126.30, 126.29, 126.16, 88.06, 71.75, 69.38, 67.01, 62.84, 48.17, 34.72, 31.36, 31.36, 31.36, 21.03, 20.92, 20.90, 19.97. **HRMS** (ESI-TOF) *m/z* calcd for $C_{31}H_{39}O_7S$ [$(M + H)^+$], 555.2411, found, 555.2407.

Data for **β isomer (8f-β)**: $\mathbf{R}_f$ = 0.46 Hexanes: EtOAc [3:1 (v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ºC, δ): 7.50-7.54 (m, 1H), 7.41-7.46 (m, 2H), 7.29-7.34 (m, 2H), 7.13-7.22 (m, 3H), 6.73 (d, *J* = 15.5 Hz, 1H), 6.17 (dd, *J* = 10.0, 15.5 Hz, 1H), 5.26 (t, *J* = 10.0 Hz, 1H), 4.97-5.03 (m, 1H), 4.98 (d, *J* = 2.0 Hz, 1H, H-1), 4.26 (dd, *J* = 6.0, 12.5 Hz, 1H), 4.19 (dd, *J* = 2.0, 12.5 Hz, 1H), 3.71 (ddd, *J* = 2.0, 5.5, 9.9 Hz, 1H), 3.42-3.48 (m, 1H), 2.36 (s, 3H), 2.10 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H), 1.31 (s, 9H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.86, 170.44, 169.82, 151.09, 136.16, 135.42, 135.11, 131.65, 131.65, 130.28, 127.99, 126.65, 126.33, 126.10, 126.10, 122.75, 87.69, 76.59, 74.60, 66.38, 63.10, 49.14, 34.71, 31.38, 31.38, 31.38, 20.99, 20.95, 20.90, 20.85, 20.00. **HRMS** (ESI-TOF) *m/z* calcd for $C_{31}H_{39}O_7S$ [$(M + H)^+$], 555.2411, found, 555.2409.

(2R,3S,4R,5S,6S)-2-(acetoxymethyl)-6-(furan-2-yl)-5-((E)-styryl)tetrahydro-2H-pyran-3,4-diyl diacetate (8g-α)& (2R,3S,4R,5S,6R)-2-(acetoxymethyl)-6-(furan-2-yl)-5-((E)-styryl)tetrahydro-2H-pyran-3,4-diyl diacetate (8g-β)

3k **8g**, 56%, α: β = 4:1

According to the procedure of synthesizing **8d**, **3k** (8.96 mg, 0.0200 mmol, 1.00 equiv) and Furan (40.7 μL, 20.0 equiv) was used to obtain the title compound **8g-α** and **8g-β** as colorless oil (**8g-α**, 4.04 mg; **8g-β**, 1.00 mg, total 56% yield).

Data for **α isomer (8g-α)**: $\mathbf{R}_f$ = 0.41 Hexanes: EtOAc [3:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 7.46-7.48 (m, 1H), 7.37-7.41(m, 1H), 7.11-7.20 (m, 3H), 6.70 (d, *J* = 15.4 Hz, 1H), 6.55 (d, *J* = 2.8 Hz, 1H), 6.38-6.42 (m, 1H), 6.15 (dd, *J* = 9.1, 15.4 Hz, 1H), 5.36 (dd, *J* = 4.9, 9.4 Hz, 1H), 5.21 (t, *J* = 7.7 Hz, 1H), 5.10 (d, *J* = 3.5 Hz, 1H), 4.37 (dd, *J* = 5.6, 11.9 Hz, 1H), 4.14 (dd, *J* = 2.8, 11.9 Hz, 1H), 3.82-3.88 (m, 1H), 3.56-3.62 (m, 1H), 2.29 (s, 3H), 2.10 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H). **^{13}C NMR** (175 MHz,

$CDCl_3$, 25 ºC, δ): 170.97, 170.42, 169.80, 151.29, 143.20, 136.24, 135.41, 132.56, 130.33, 127.87, 126.54, 126.32, 126.18, 110.60, 110.03, 72.16, 72.01, 71.94, 66.70, 62.37, 43.57, 21.09, 20.97, 20.97, 19.93. **HRMS** (ESI-TOF) *m/z* calcd for $C_{25}H_{28}O_8Na$ [$(M + Na)^+$], 479.1676, found, 479.1673.

Data for **β isomer (8g-β)**: $\mathbf{R_f}$ = 0.38 Hexanes: EtOAc [3:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 7.32-7.37 (m, 2H), 7.15-7.19 (m, 2H), 7.09-7.13 (m, 1H), 6.51 (d, *J* = 15.4 Hz, 1H), 6.30 (d, *J* = 2.8 Hz, 1H), 6.27 (dd, *J* = 2.1, 3.5 Hz, 1H), 6.12 (dd, *J* = 9.8, 15.4 Hz, 1H), 5.31 (t, *J* = 9.8 Hz, 1H), 5.14 (dd, *J* = 4.9, 9.8 Hz, 1H), 4.84-4.86 (m, 1H), 4.29 (dd, *J* = 4.9, 11.9 Hz, 1H), 4.22 (dd, *J* = 2.1, 11.9 Hz, 1H), 3.84 (ddd, *J* = 2.8, 4.9, 9.8 Hz, 1H), 3.46 (ddd, *J* = 2.1, 4.9, 9.8 Hz, 1H), 2.23 (s, 3H), 2.10 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.99, 170.56, 169.82, 151.25, 142.15, 136.63, 135.23, 133.92, 130.22, 127.74, 126.35, 126.30, 124.26, 110.34, 108.04, 75.13, 74.92, 66.42, 62.98, 47.06, 21.07, 20.99, 20.92, 19.86. **HRMS** (ESI-TOF) *m/z* calcd for $C_{25}H_{28}O_8Na$ [$(M + Na)^+$], 479.1676, found, 479.1674.

Mechanistic Studies

Radical Trapping Experiments

The procedure is based on General Procedure B: In a glovebox, to an oven-dried 4 mL screw cap vial was added $Pd(PPh_3)_4$ (2.31 mg, 0.00200 mmol, 10.00 mol%), Xantphos (2.31 mg, 0.00400 mmol, 20.00 mol%), 1-bromosugar **1a** (0.0200 mmol, 1.00 equiv), styrene (3.12 mg, 0.0300 mmol, 1.50 equiv), TEMPO (3.12 mg, 0.0200 mmol, 1.00 equiv) *or* butylated hydroxytoluene (BHT, 4.41 mg, 0.0200 mmol, 1.00 equiv), K_3PO_4 (8.49 mg, 0.0400 mmol, 2.00 equiv), benzene (8.00 mL, 0.0250 M), and a stir bar. Next, the vial was capped, taken out of the glovebox, and sealed with a black tape. After the reaction mixture was heated to 90 °C and stirred for 5 min, it was irradiated with 34W Blue LEDs for 14h. The yield was determined based on crude ^{1}H-NMR spectrum using dibromomethane as an internal standard.

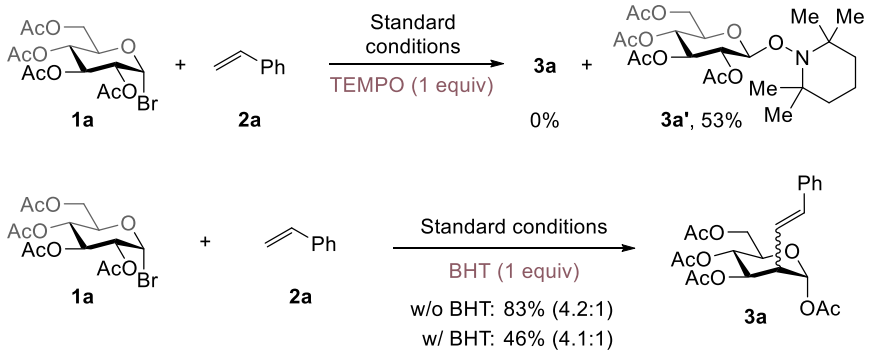
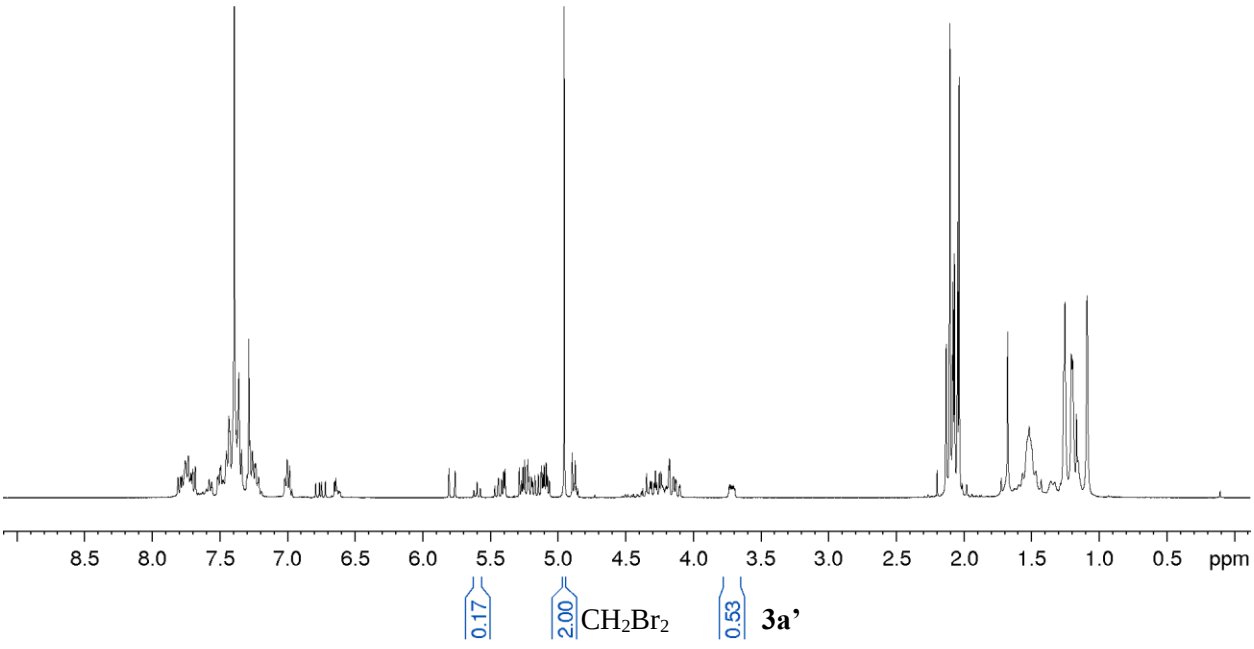


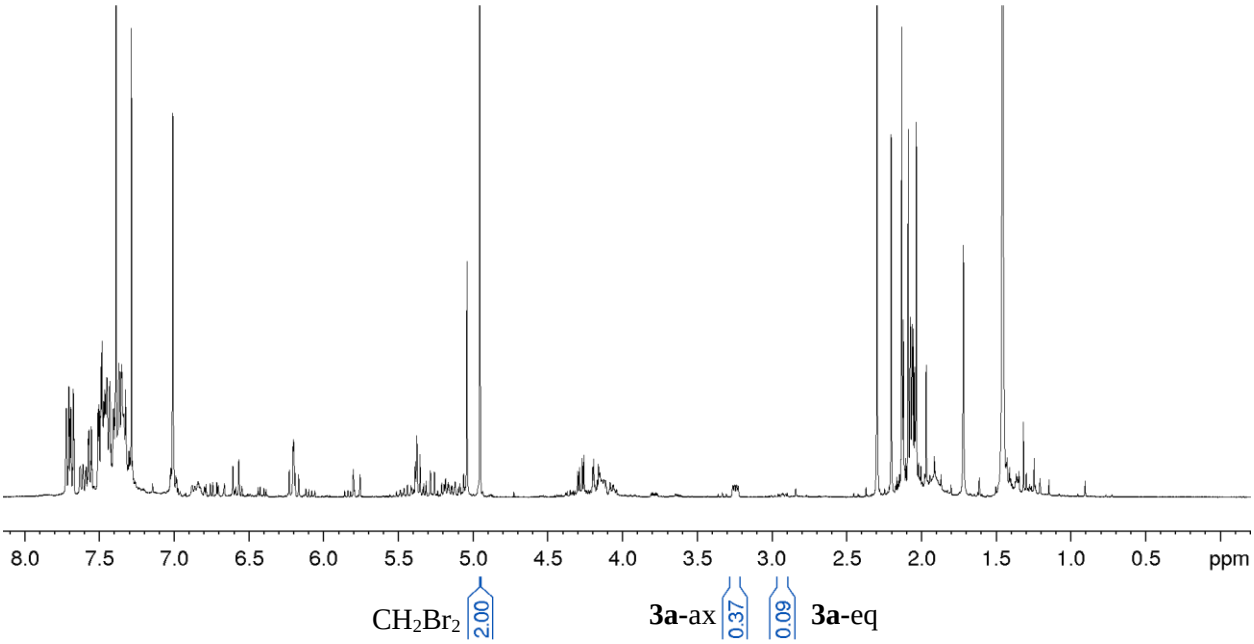
Figure S1. Radical trapping experiments with TEMPO or BHT

The crude NMR of reaction mixture with the TEMPO additive:



Characterization data for TEMPO adduct **3a'**: **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC, δ): 5.21 (t, *J* = 9.8 Hz, 1H), 5.06 (q, *J* = 9.1 Hz, 2H), 4.85 (d, *J* = 9.1 Hz, 1H), 4.23 (dd, *J* = 4.9, 11.9 Hz, 1H), 4.13 (dd, *J* = 2.8, 11.9 Hz, 1H), 3.66-3.70 (m, 1H), 2.07 (s, 3H), 2.07 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H), 1.23-1.60 (m, 6H), 1.23 (s, 3H), 1.17 (s, 3H), 1.05 (s, 6H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC, δ): 170.88, 170.53, 169.65, 169.33, 103.43, 73.46, 71.55, 70.95, 68.96, 62.29, 61.32, 59.76, 40.61, 40.39, 34.37, 32.65, 20.98, 20.91, 20.79, 20.79, 20.64, 19.99, 17.12. **HRMS** (ESI-TOF) *m/z* calcd for $C_{23}H_{38}NO_{10}$ [$(M + H)^+$], 488.2490, found, 488.2487.

The crude NMR of reaction mixture with the BHT additive:



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

Stern–Volmer Luminescence Quenching Experiments

Emission intensities were recorded using a Perkin Elmer LS50B Luminescence spectrometer. All quenching data was recorded in the dark using a 1.00 cm screw-top quartz cuvette at 23 °C in the presence of $Pd(PPh_3)_4$ (0.600 µM) and varying concentration of quencher in degassed benzene. Excitation of the sample was performed at 375 nm and emission was detected at 580 nm. After the acquisition, the data were plotted according to the Stern-Volmer equation shown below.

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

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

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

Results and Conclusion: The results indicate that while the 1-bormosugar and styrene can both quench the excited state of $Pd(PPh_3)_4$, 1-bromosugar is more effective and likely to be the quencher in the reaction.

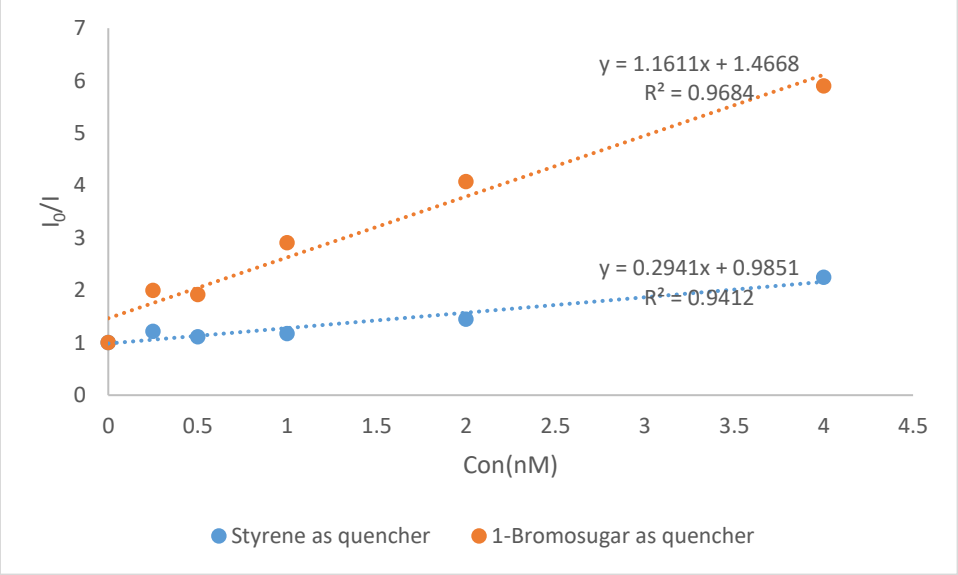


Figure S2. Stern-Volmer plot for the emission quenching of $Pd(PPh_3)_4$ by various concentrations of 1-bromosugar and styrene. (*benzene* as solvent)

Quantum Yield Experiment

Quantum yield experiments suggest that an extended radical chain propagation is unlikely under our reaction conditions. The following quantum yield measurements are adapted from the procedure developed by Yoon et al.[12]

Determination of the Light Intensity at 450 nm:

The fraction of light absorbed (*f*) by ferrioxalate solution was calculated as shown in **Figure S3**, where the absorbance of the ferrioxalate solution at 450 nm was measured to be 1.85441 (A), based on eqation ($f = 1-10^{-A}$), indicating $f = 0.98602$).

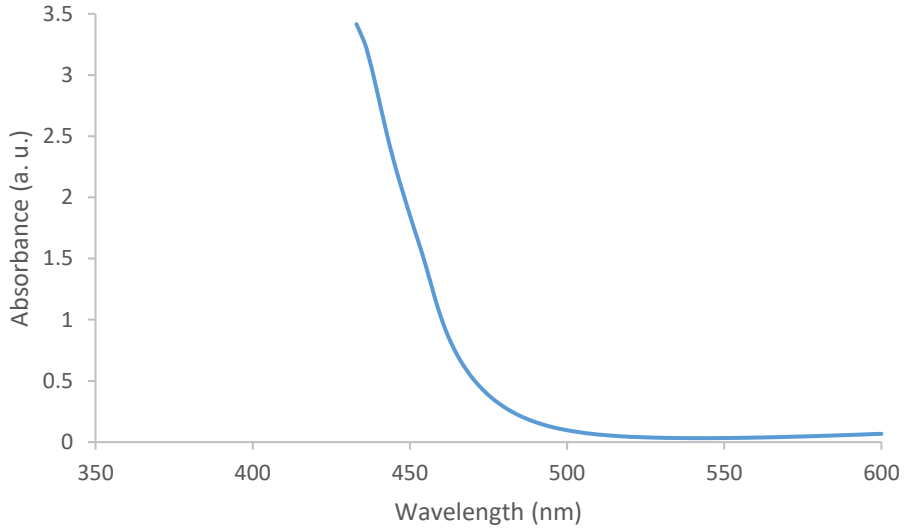


Figure S3. Absorbance of the ferrioxalate solution at 450 nm (A = 1.85441).

The photon flux of the 30 W Blue LEDs (λ_{max} = 450 nm) was determined by standard ferrioxalate actinometry.[13] A 0.150 M solution of ferrioxalate was prepared by dissolving 2.21 g of potassium ferrioxalate hydrate ($K_3[Fe(C_2O_4)_3] \bullet 3H_2O$) in 30.0 mL of 0.05 M H_2SO_4 (aq). Next, a buffered solution of phenanthroline was prepared by dissolving 50.0 mg of phenanthroline and 11.25 g of sodium acetate in 50.0 mL of 0.500 M H_2SO_4. Both solutions were stored in an amber vial in the dark. To determine the photon flux of the 30 W Blue LEDs, 2.00 mL of the ferrioxalate solution was placed in a cuvette and irradiated for 5.00 seconds at λ = 450 nm. After irradiation, 0.500 mL of the phenanthroline solution was added to the cuvette. The solution was then rested for 1 h in the dark to allow the ferrous ions to completely coordinate to the phenanthroline. A non-irradiated sample was also prepared and developed in the dark as well *(note: after developing the non/irradiated samples they were diluted with a dilution factor of 4 to prevent deviation from the Beer-Lambert law at high concentrations A = >2. Thus, to obtain the actual mol of Fe^{2+} they were multiplied by four. The values of the optical difference are the average of three trials*).

1 Ferrioxalate Actinometry

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

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

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

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

2 Determination of photon flux of 30W Blue Led

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

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

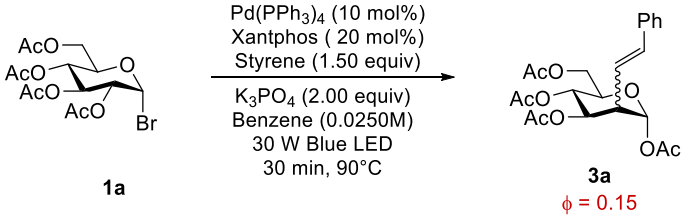
$$= 8.836 \times 10^{-8} \text{ einstein } s^{-1}$$

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

Figure S4. Determination of the light intensity (photon flux) at 450 nm via ferrioxalate actinometry (ε = 11,100 L $mol^{-1}cm^{-1}$).[13a]

Afterward, the absorbance of both solutions was measured at 510 nm and with mol of Fe^{2+} known, next, the photon flux determined to be 8.84×10^{-8} einstein s^{-1}. We can obtain the quantum yield of our reaction provided if it is irradiated using the same geometry (*note: although Φ = 1.01 at 436 nm was used for the calculation of the photon flux it known that the ferrioxalate system varied little with the wavelength as the Φ remained between 0.9 and 1.1 at wavelength between 400–480 nm*).[13a]

Determination of Quantum Yield of migration reduction reaction:



To determine the photon flux, in a glovebox, the cuvette was charged with **1a** (20.5 mg, 0.050 mmol, 1.00 equiv), $Pd(PPh_3)_4$ (5.78 mg, 10 mol%), xantphos (5.79 mg, 20 mol%), K_3PO_4 (21.2 mg, 0.100 mmol) and benzene (2.00 mL, 0.0250 M). To this suspension was added styrene (25.8 mg, 0.100 mmol, 1.50 equiv). Afterward the cuvette was capped with a PTFE stopper and taken out of the glovebox. The cuvette was heated up in the oil bath and the reaction mixture was irradiated (λ_{max} = 450 nm) for 1800 s (30 min) with the same 30 W Blue LEDs at 90 °C. To determine the yield of the product, the solvent is removed under vacuum, an internal standard, dibromomethane (CH_2Br_2) (8.70 mg, 0.0500 mmol, 1.00 equiv) was added

to the cuvette, followed by 500 μL $CDCl_3$. The reaction was repeated three times with yield to be: 10%, 12%, 10.5%. The quantum yield was determined using the equation shown below.

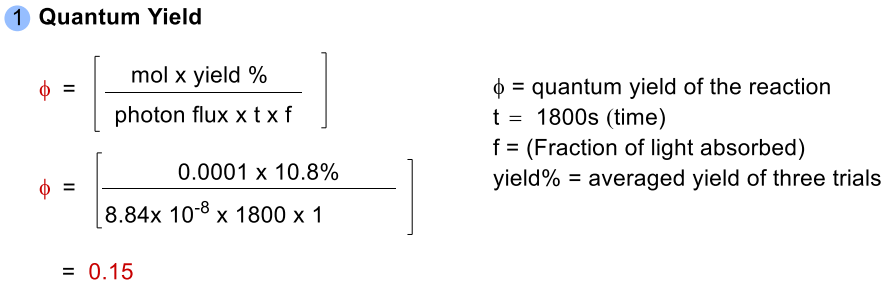


Figure S5. Quantum yield determination of migration reduction reaction.

Results and Conclusion: Quantum yield of the C2 alkenylation reaction was 0.15, suggesting that an extended radical chain propagation is unlikely under our reaction conditions.

Light On-Off Experiment

The procedure is based on General Procedure B: In a glovebox, to an oven-dried 4 mL screw cap vial was added $Pd(PPh_3)_4$ (2.31 mg, 0.00200 mmol, 10.00 mol%), xantphos (2.31 mg, 0.0400 mmol, 20.00 mol%), bromosugar (0.0500 mmol, 1.00 equiv), Styrene (3.12 mg, 0.0300 mmol, 1.50 equiv), K_3PO_4 (8.49 mg, 0.0400 mmol, 2.00 equiv) and benzene (8.00 mL, 0.0250 M). A magnetic stir bar was then added. Six parallel reaction mixtures in six vials were prepared and next, the vials were capped, taken out of the glovebox, and sealed with a black tape. The vials were heated to 90 °C at the same time and stir for 5 min, then they were irradiated with 34W Blue LEDs. After 30min, the light is turned off and one vial is removed from oil bath. After another 30min in dark, another vial is removed. Then the light is turned on for another 30mins. Repeat the same procedure until the last vial is removed from the oil bath. The yields were determined based on crude ^{1}H-NMR spectrum with dibromomethane as an internal standard.

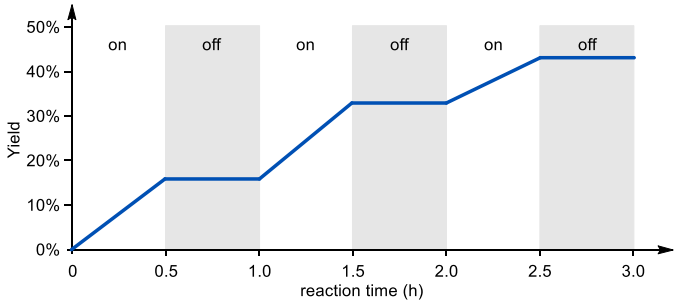


Figure S6. Light on-off experiment

Results and Conclusion: The result indicated that an extended radical chain propagation is unlikely under our reaction conditions.

Studies of Stereochemical Outcome Using 2-Iodo Sugar

The procedure is based on **General Procedure B** with **9a**-eq or **9a**-ax (0.0500 mmol, 1.00 equiv), styrene (3.12 mg, 0.0300 mmol, 1.50 equiv) as substrates. The yields were determined based on crude ^{1}H-NMR spectrum with dibromomethane as an internal standard.

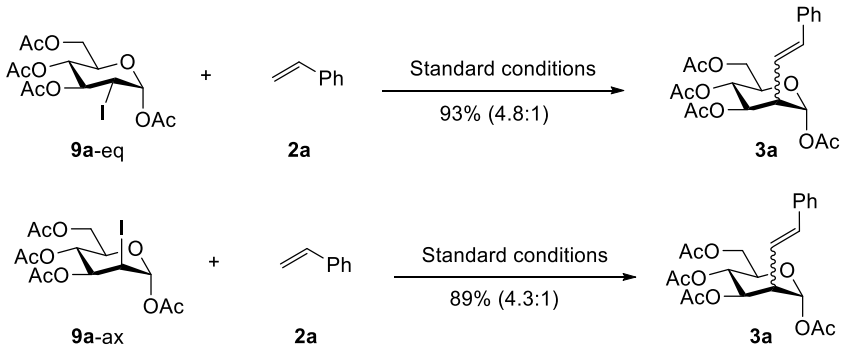
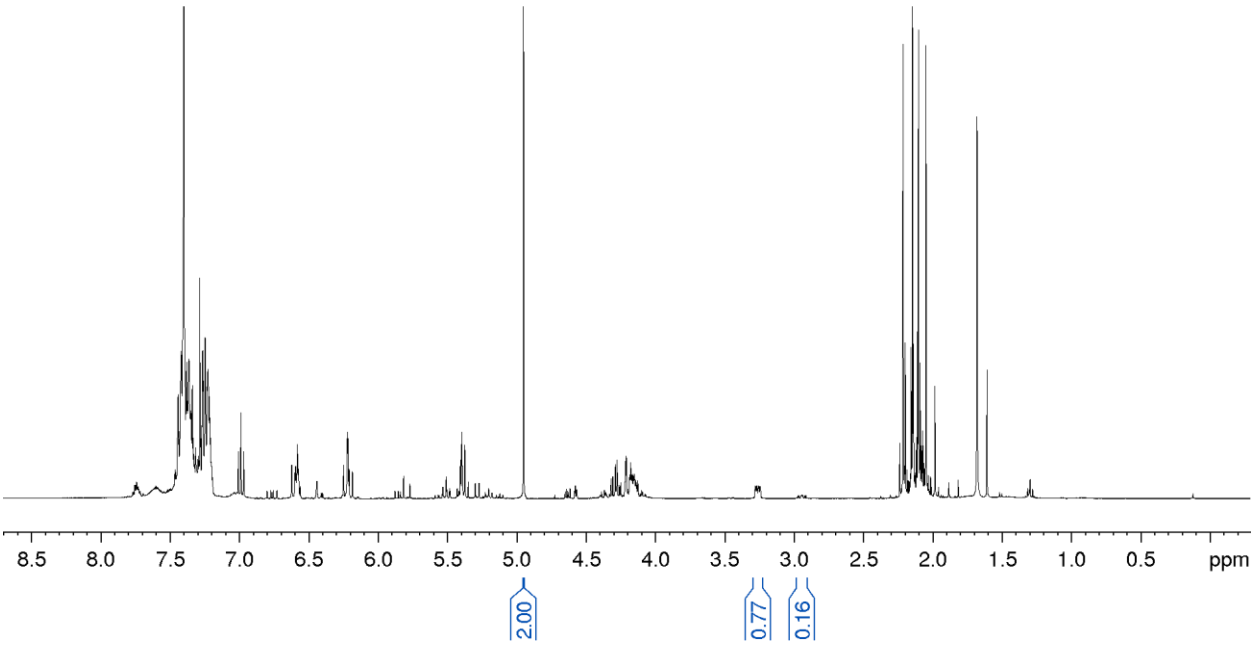
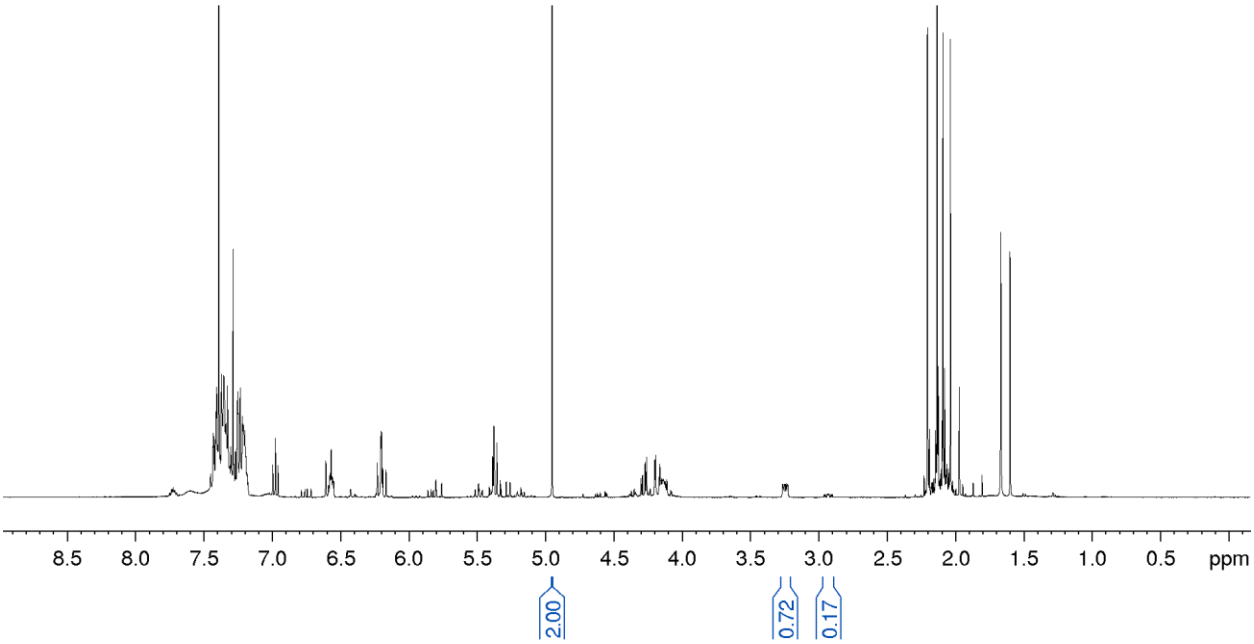


Figure S7. Alkenylation reaction with different 2-iodosugars as substrates

Crude NMR spectrum of the reaction using **9a**-eq as the starting material:



Crude NMR spectrum of the reaction using **9a**-ax as starting material:



Results and Conclusion: The results indicate that the reaction involves the formation of C2 radical species.

Kinetic Isotope Effect Measurements

The substrates **2e**-d_1 and **2e**-d_2 were prepared according to the literature procedure.[14]

For the top reaction, the procedure is based on **General Procedure B** with **1a** (0.02 mol, 1.00 equiv), **2e**-d_2 (0.0150 mol, 0.750 equiv) and **2e** (0.0150 mol, 0.750 equiv). For the bottom reaction, the procedure is based on **General Procedure B** with **1a** (0.02 mol, 1.00 equiv), **2e**-d_1 (0.0300 mol, 1.00 equiv). The yield was determined based on crude ^{1}H-NMR spectrum with dibromomethane as internal standard.

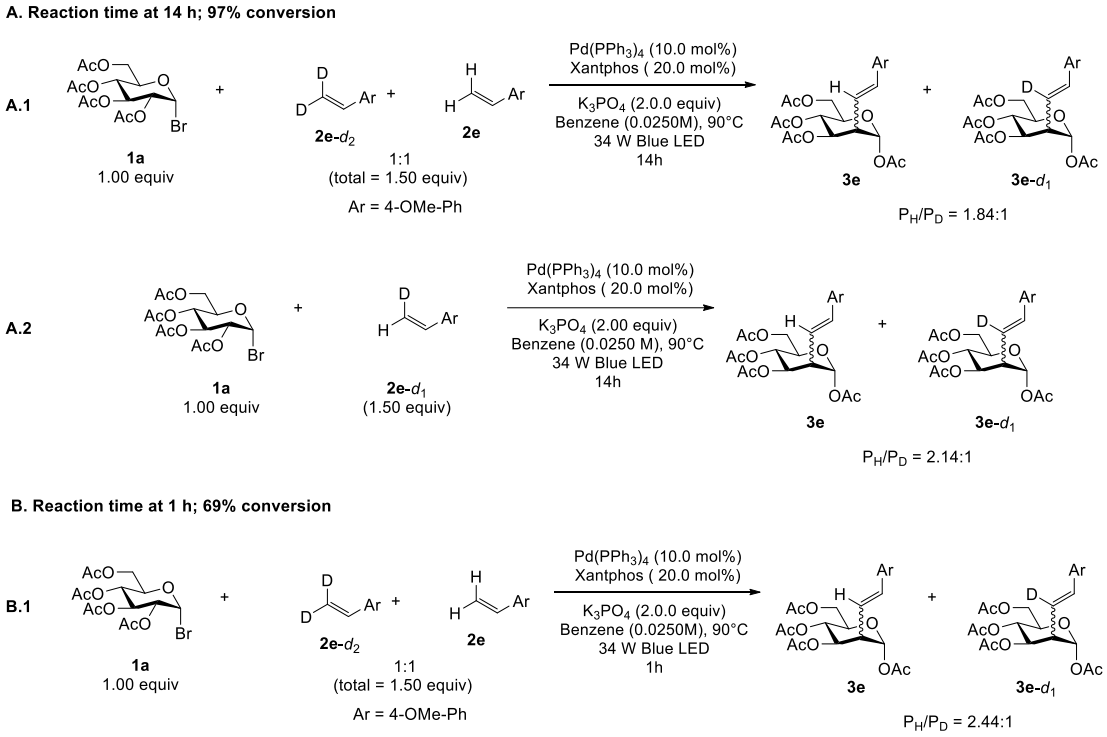
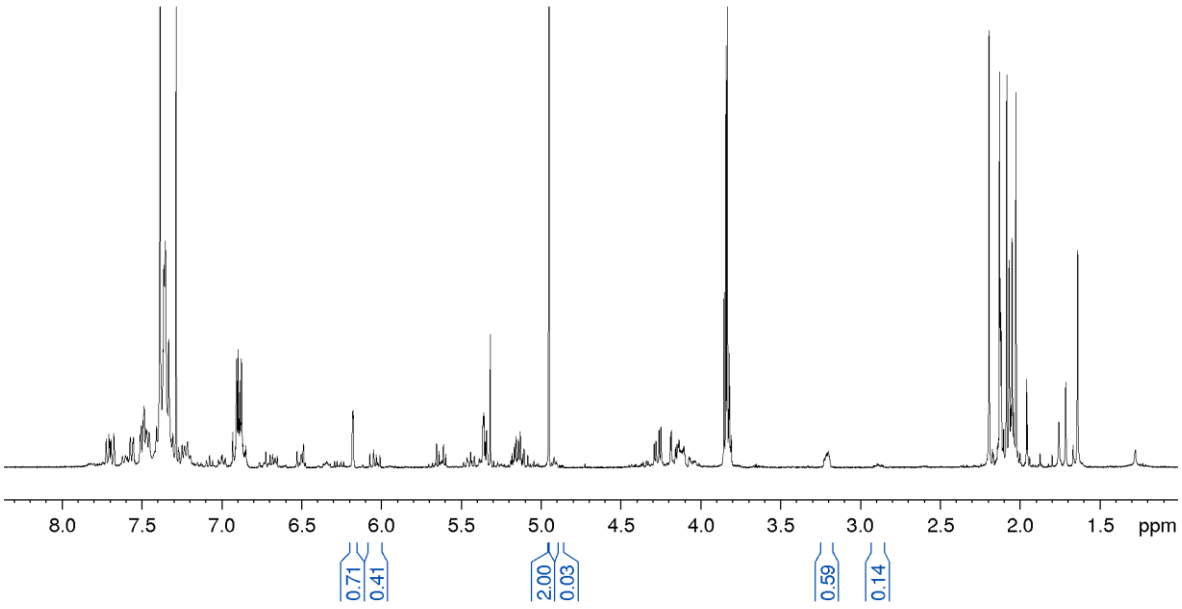


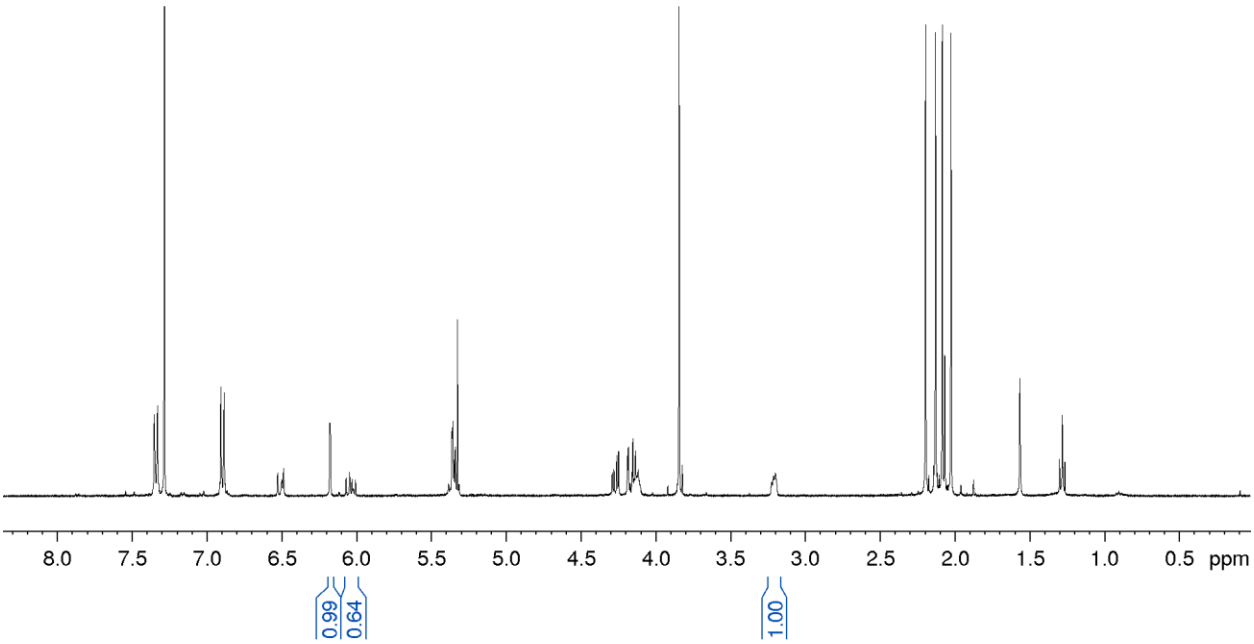
Figure S8. Kinetic isotope effect measurements

Crude spectrum of reaction A.1: (H-ax+D-ax = 59%, H-eq+D-eq =14%) (97% conversion)

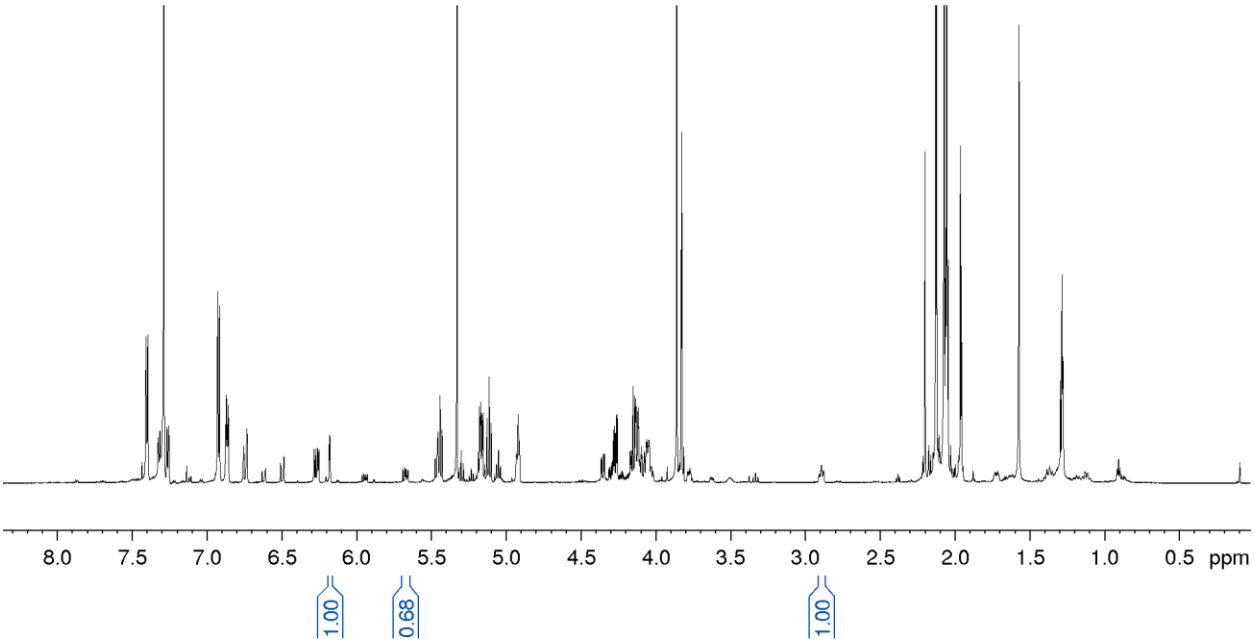


After prep TLC separation:

Spectrum for axial product: (H-ax:D-ax=64%:36%)



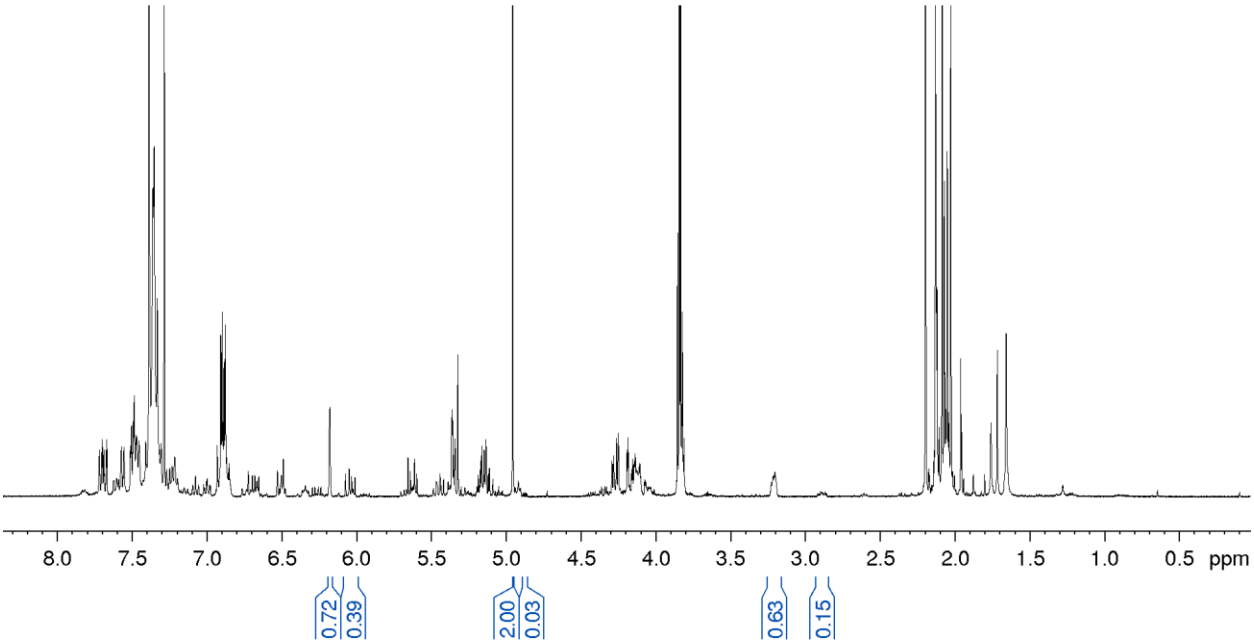
Spectrum for equatorial product: (H-eq:D-eq=68%:32%)



KIE Calculations:

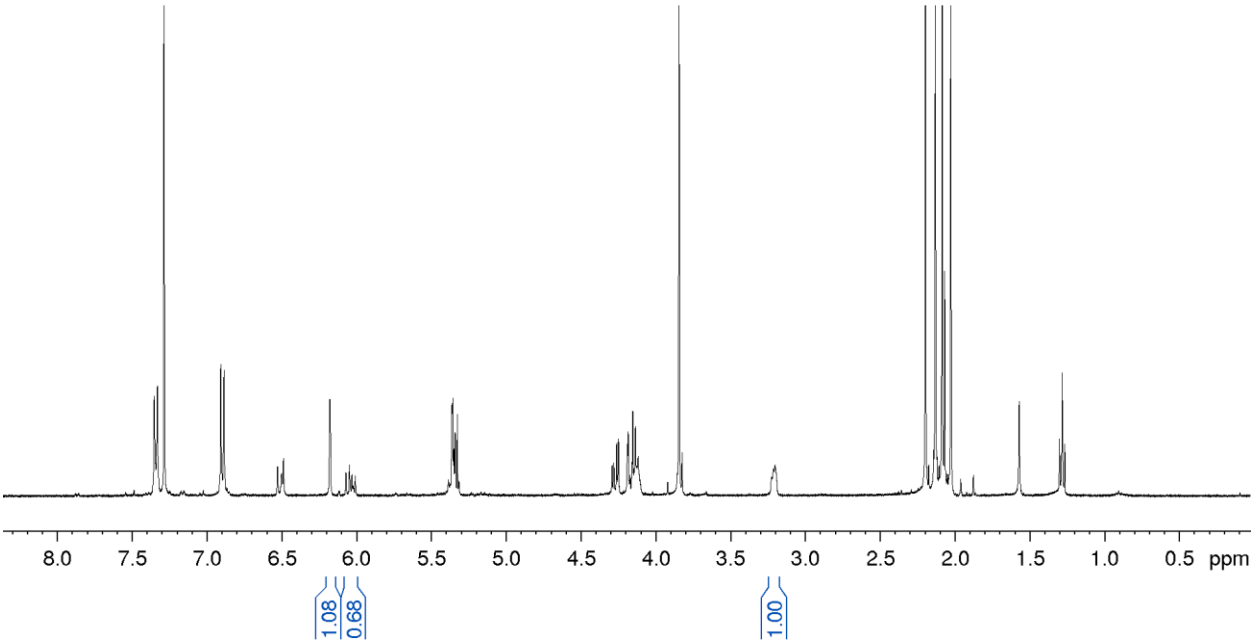
H-product: axial = 59% x 0.64 = 37.8%; equatorial: 14% x 0.68 = 9.5%; Total H-product = 47.3%
D-product: axial = 59% x 0.36 = 21.2%; equatorial: 14% x 0.32 = 4.5%; Total D-product = 25.7%
KIE = 47.3/25.7 = 1.84

Crude spectrum of reaction A.2: (H-ax+D-ax = 63%, H-eq+D-eq =15%) (97% conversion)

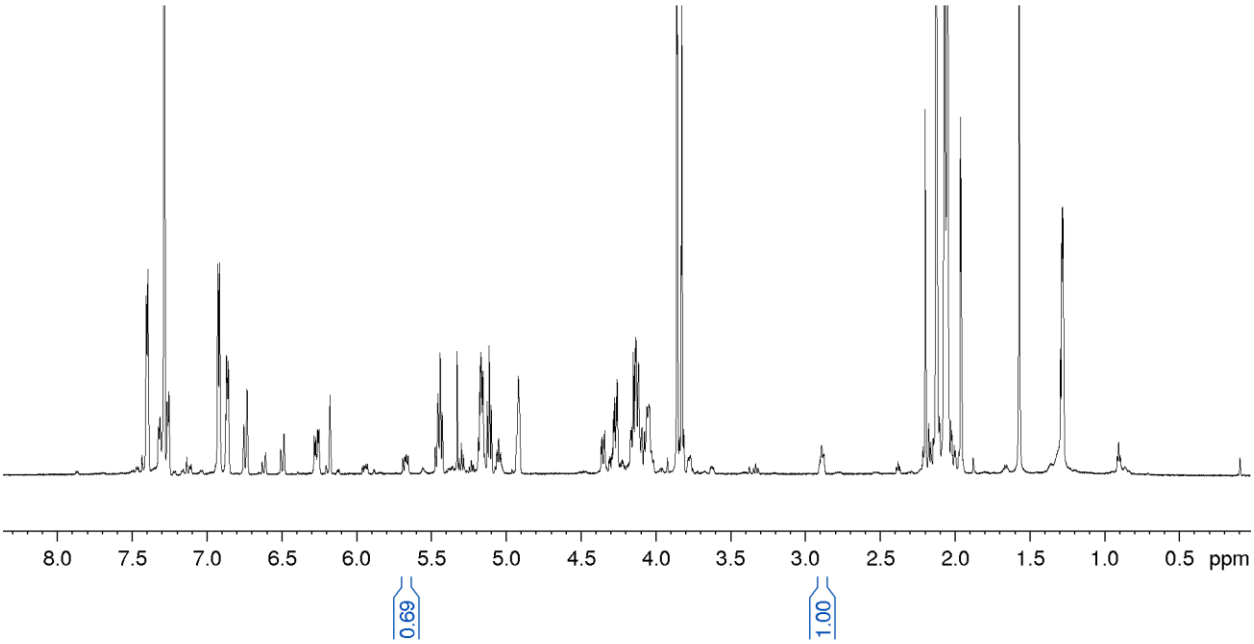


After prep TLC separation:

Spectrum for axial product: (H-ax:D-ax=68%:32%)

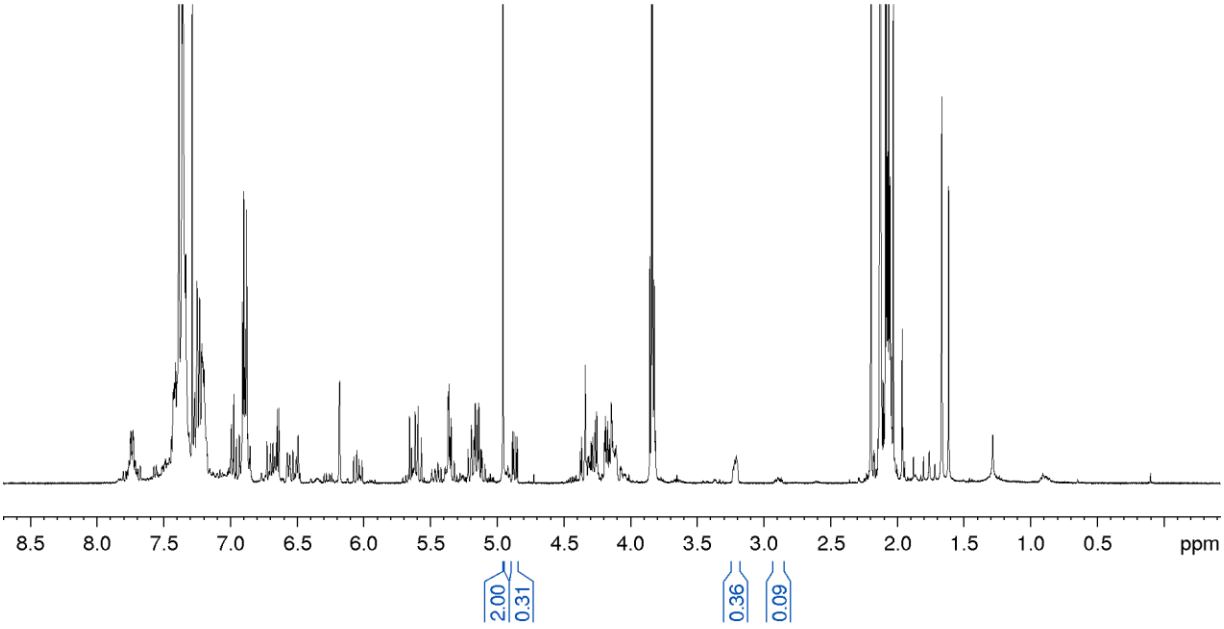


Spectrum for equatorial product: (H-eq:D-eq=69%:31%)



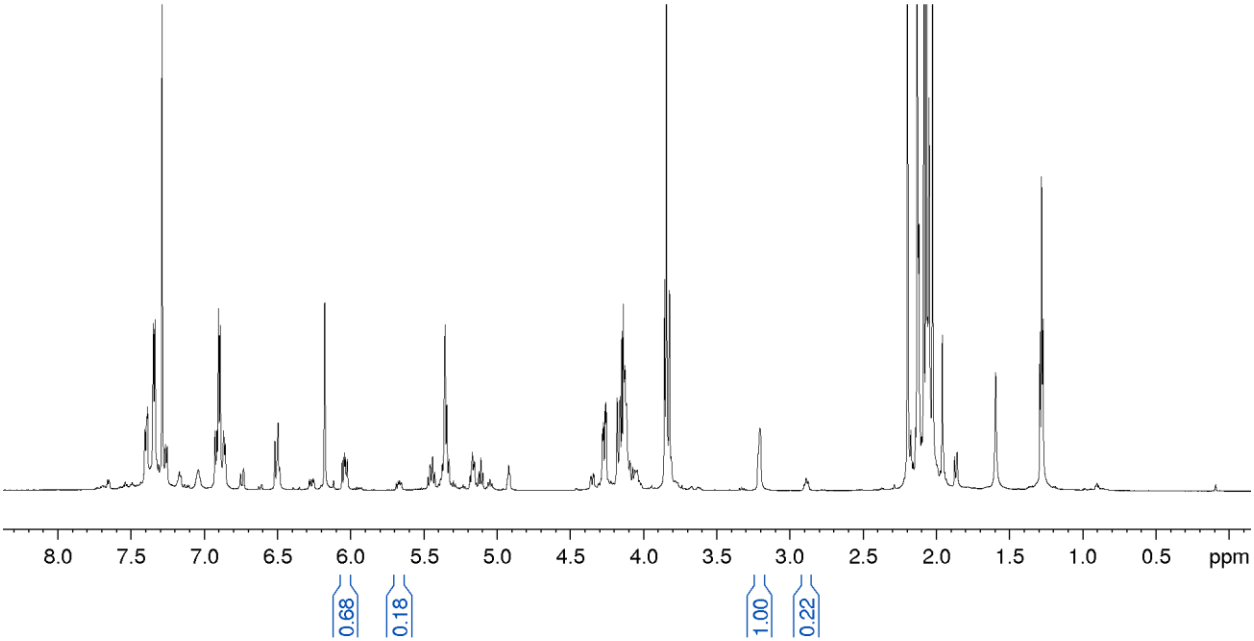
KIE Calculations:
H-product: axial = 63% x 0.68 = 42.8%; equatorial: 15% x 0.69 = 10.4%; Total H-product = 53.2%
D-product: axial = 63% x 0.32 = 20.2%; equatorial: 15% x 0.31 = 4.7%; Total D-product = 24.9%
KIE = 53.2/24.9 = 2.14

Crude NMR spectrum of reaction B.1: (H-ax+D-ax = 36%, H-eq+D-eq =9%) (69% conversion)



After Pre TLC separation:

Spectrum for axial product: (H-ax:D-ax = 68%:32%; H-eq:D-eq = 82%:18%)



H-product: axial = 36% x 0.68 = 24.5%; equatorial: 9% x 0.82 = 7.4%; Total H-product = 31.9%
D-product: axial = 36% x 0.32 = 11.5%; equatorial: 9% x 0.18 = 1.6%; Total D-product = 13.1%
KIE = 31.9/13.1 = 2.44

Results and Conclusion: These results showed primary kinetic isotope effect.

DFT Calculations

Computational Details

All density functional theory (DFT) calculations were carried out using Gaussian 16.[15] Geometries of intermediates and transition states were optimized using the dispersion-corrected B3LYP-D3 functional,[16] using Grimme's DFT-D3 dispersion correction,[17] with a mixed basis set of SDD for Pd 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. The M06 functional[18] with a mixed basis set of SDD for Pd and 6-311+G(d,p) for other atoms was used in single-point energy calculations. Solvation energy corrections were calculated in benzene solvent with the SMD continuum solvation model[19] based on the gas-phase optimized geometries. Thermal corrections to the Gibbs free energies and enthalpies were calculated using GoodVibes[20] with Truhlar's quasi-harmonic oscillator approximation[21] at 363.15 K. Conformational sampling of carbohydrate structures and transition states was carried out using the iterative metadynamic sampling and genetic crossover (iMTD-GC) method implemented in the CREST program[22] with the GFN2-xTB method.[23] Default settings in CREST were used in the conformational sampling and the forming/breaking bonds in the transition state structures were constrained to the corresponding distances obtained from the DFT-optimized TS structures in the CREST conformational sampling. Low-energy conformers from CREST/xTB were then re-optimized using DFT at the M06/SDD-6-311+G(d,p)/SMD//B3LYP-D3/SDD-6-31G(d) level of theory. Only the lowest energy conformer from the DFT calculations were reported in this manuscript. DFT calculations were performed using a simplified model of the glucosyl radical (**II)**, where OMe groups were used in place of the OAc groups at the C3, 4, and 6 positions of the pyranose ring. Images of 3D molecular structures were generated using CYLview 2.0.[24]

Reaction Energy Profile of the C2-Selective Alkenylation at 90 °C

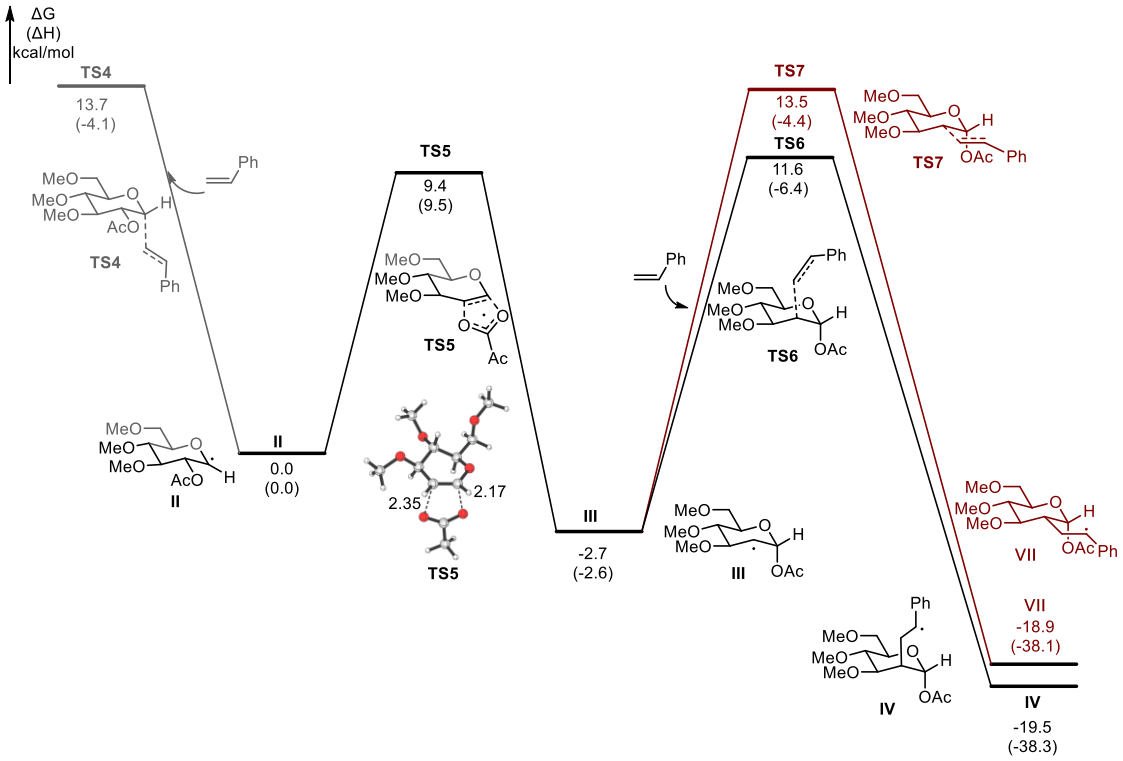


Figure S9. Reaction energy profile of C2-selective alkenylation at 90 °C. The disfavored C1-selective pathway (via **TS4**) is shown in grey. Gibbs free energies and enthalpies are with respect to **II** and styrene (**2a**).

Optimized Geometry of C2 Radical Addition Transition States

The DFT-computed energy profiles indicate that the radical alkene addition (**TS6** and **TS7**, Figure S9) is exergonic and irreversible. Therefore, axial/equatorial selectivity is determined in the radical addition step. The computed styrene addition transition state leading to the C2-axial product (**TS6**) is 1.9 kcal/mol more stable than the styrene addition transition state leading to the C2-equatorial product (**TS7**). This energy difference qualitatively agrees with the preference for the axial isomer observed experimentally. Here, the equatorial radical addition transition state **TS7** is destabilized due to steric repulsions with the C1-OAc group. This is evidenced by a short H···O distance (2.75 Å) between the styrene terminal CH_2 group and the C1-O atoms in **TS7**. A twist boat conformer of the equatorial radical addition transition state was also considered (**TS8**), which is even less stable.

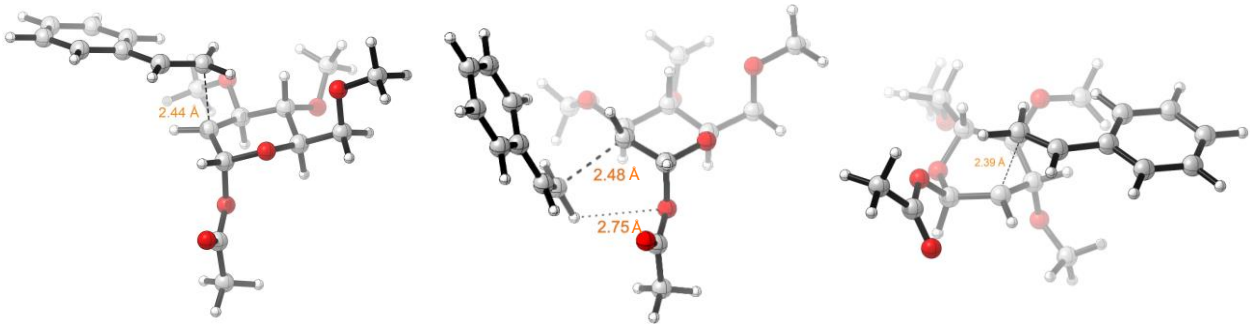


Figure S10. Optimized geometry of the axial radical addition transition state **TS6** and low-energy conformers of the equatorial radical addition transition states **TS7**. All energies are with respect to the anomeric glycosyl radical **II** and styrene **2a**.

Optimized Geometry of C1 Radical Addition Transition States

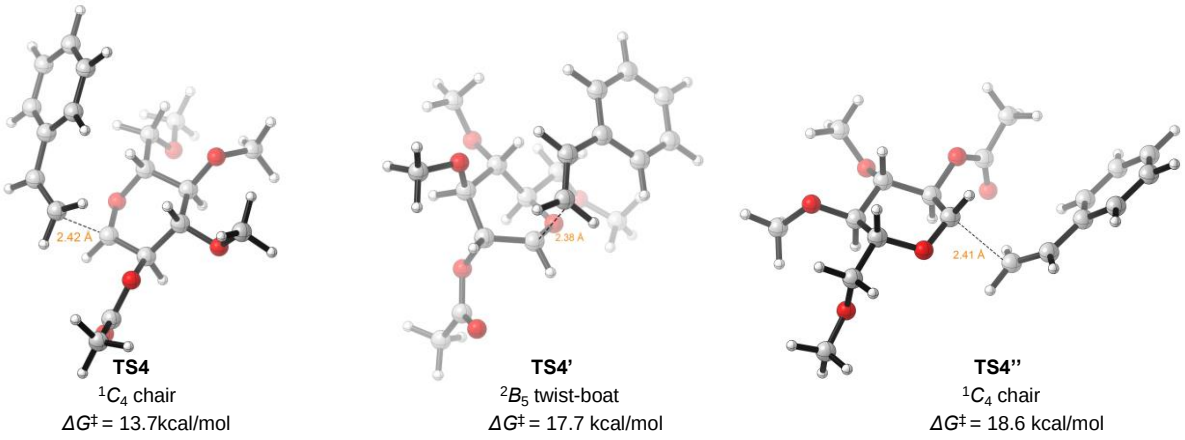


Figure S11. Optimized geometry of the α-radical addition transition state **TS4** and β-radical addition transition states **TS4'** and **TS4''**. All energies are with respect to the anomeric glycosyl radical **II** and styrene **2a**.

Optimize Geometry of Alkene Formation Transitions States

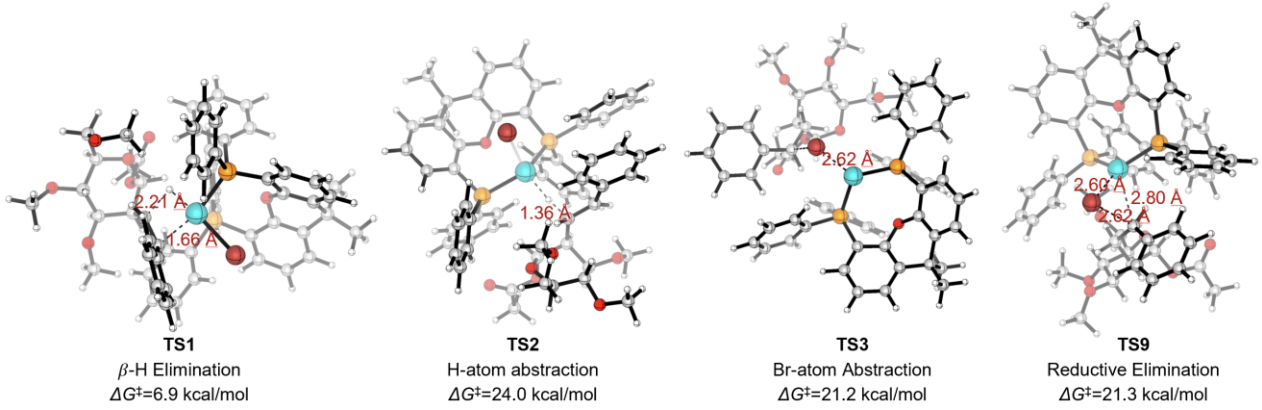


Figure S12. Possible transition states for the alkene formation step. All energies are with respect to **IV** and (Xantphos)Pd^{I}Br.

Outersphere Single Electron Transfer (OSET) Pathway

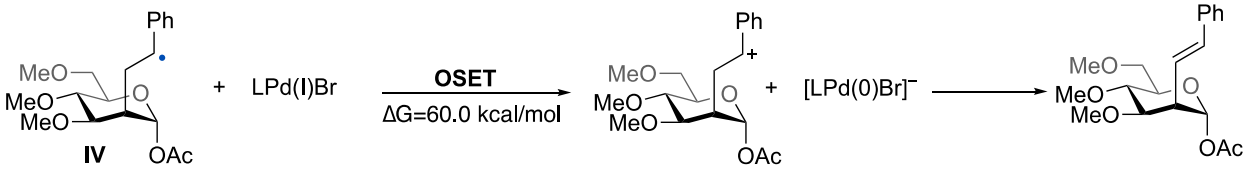
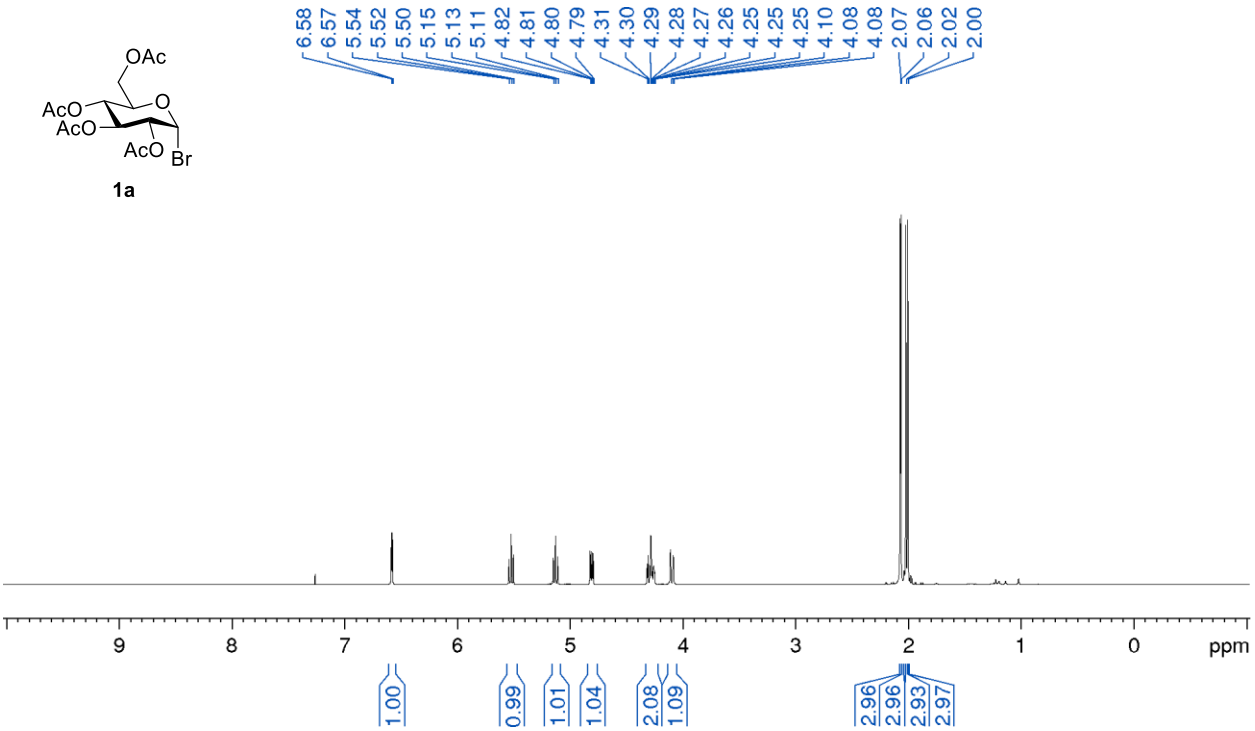


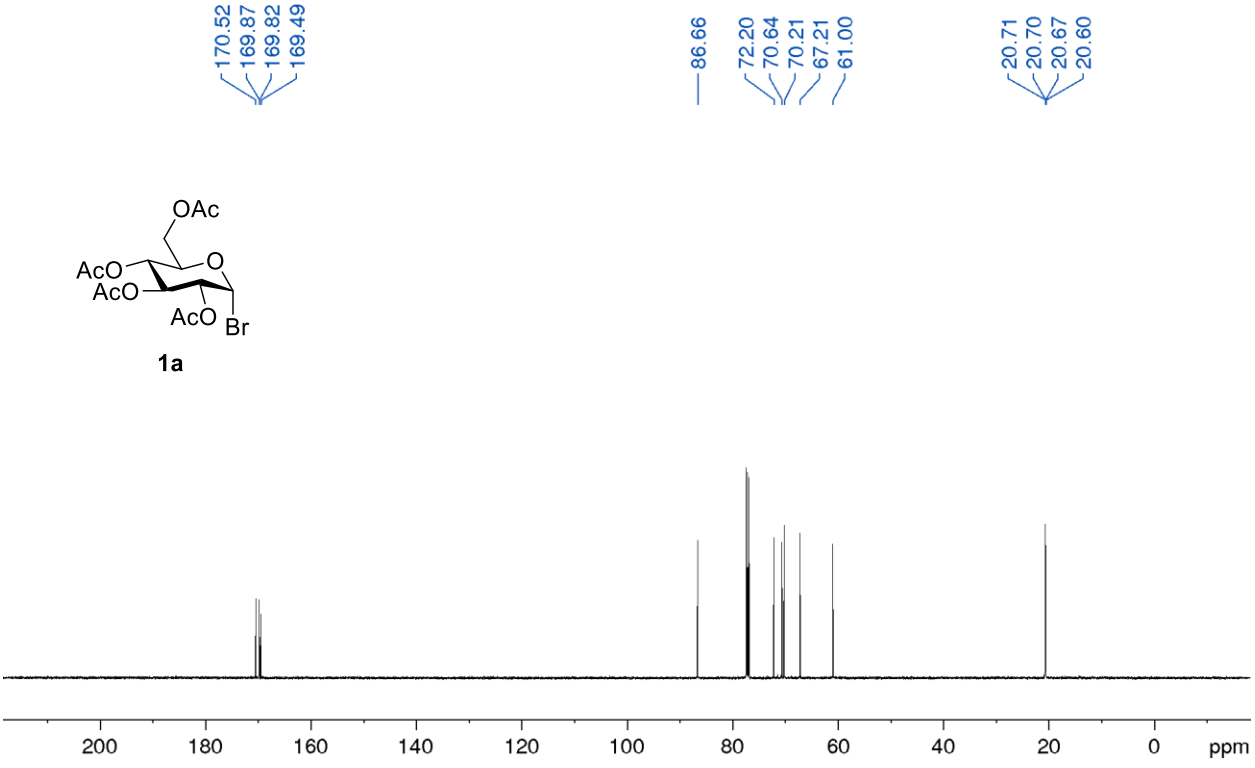
Figure S13. Reaction energy of the outersphere single electron transfer pathway. L = Xantphos.

Spectroscopic Data

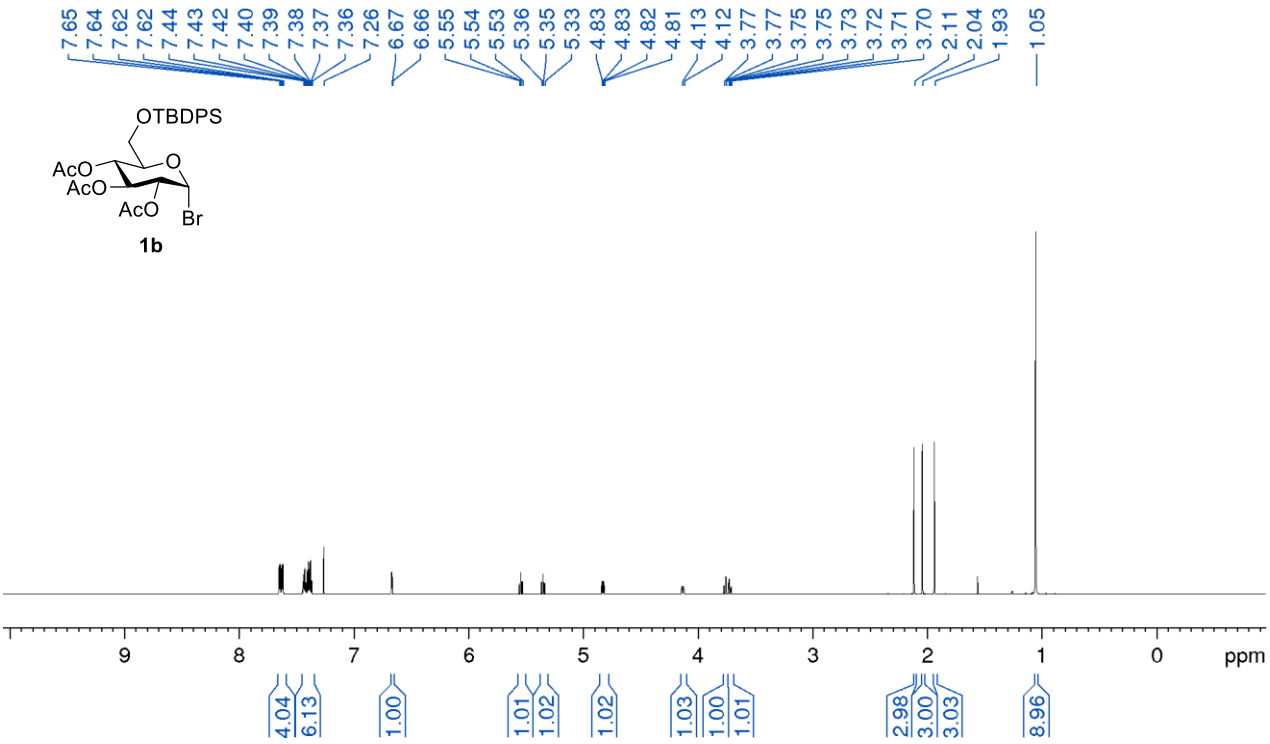
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (1a)



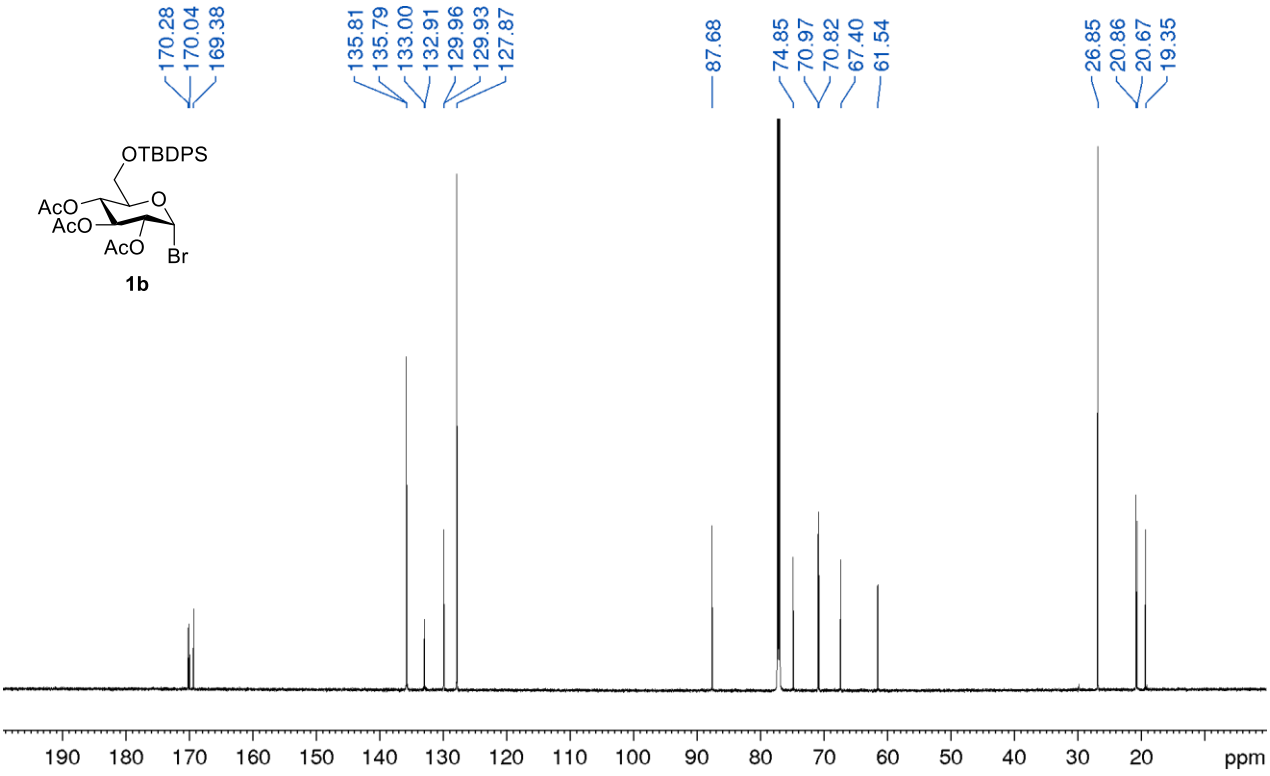
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (1a)



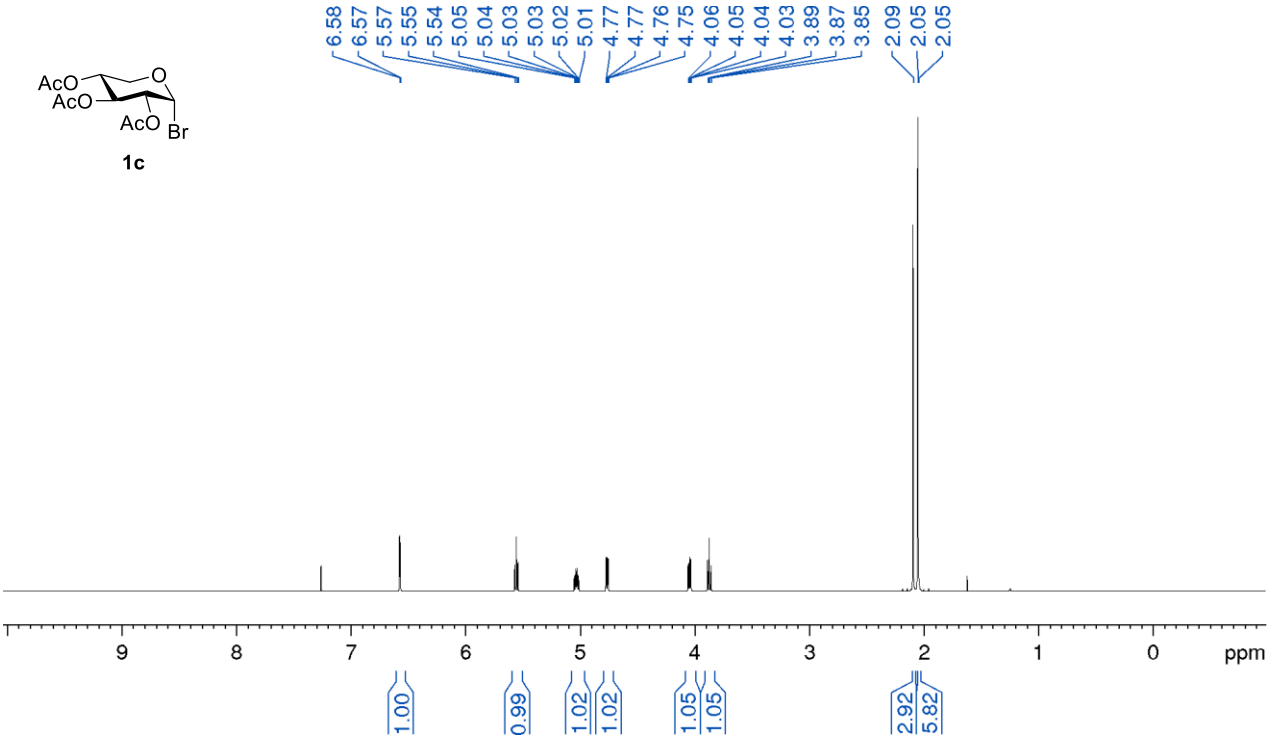
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (1b)



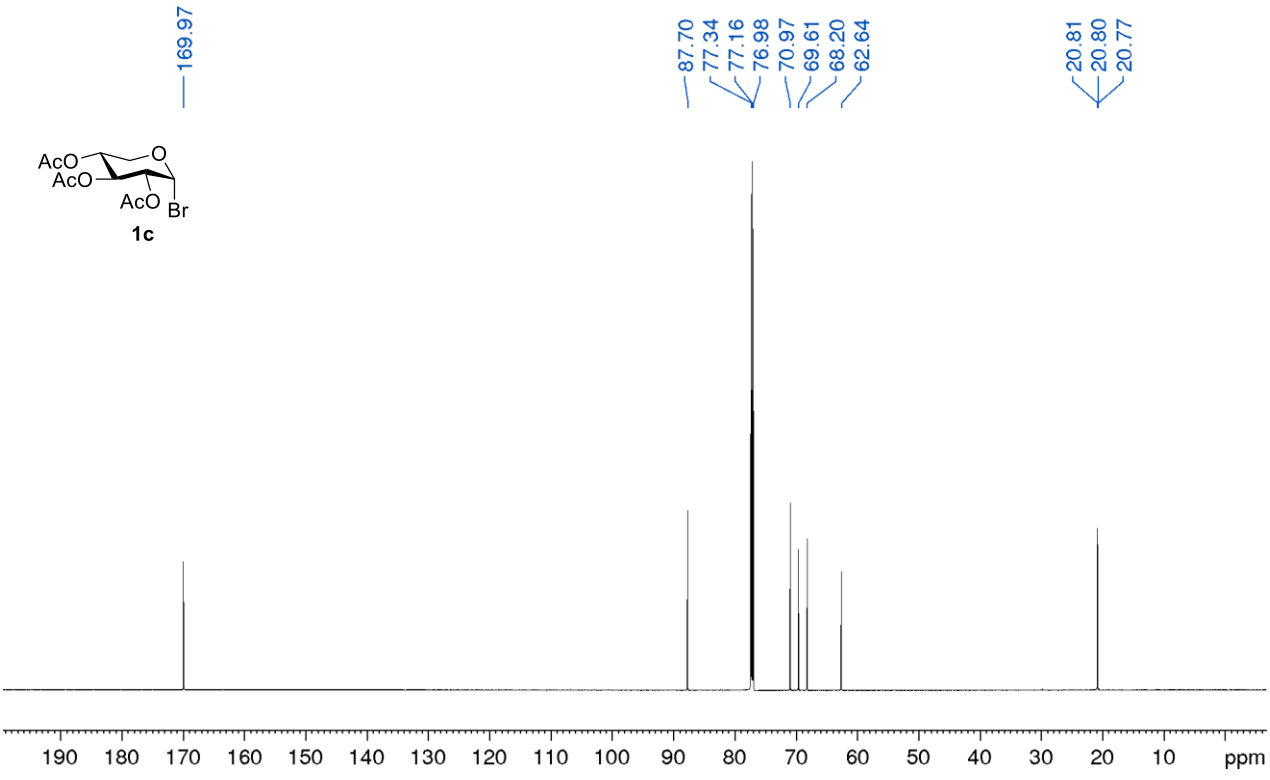
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (1b)



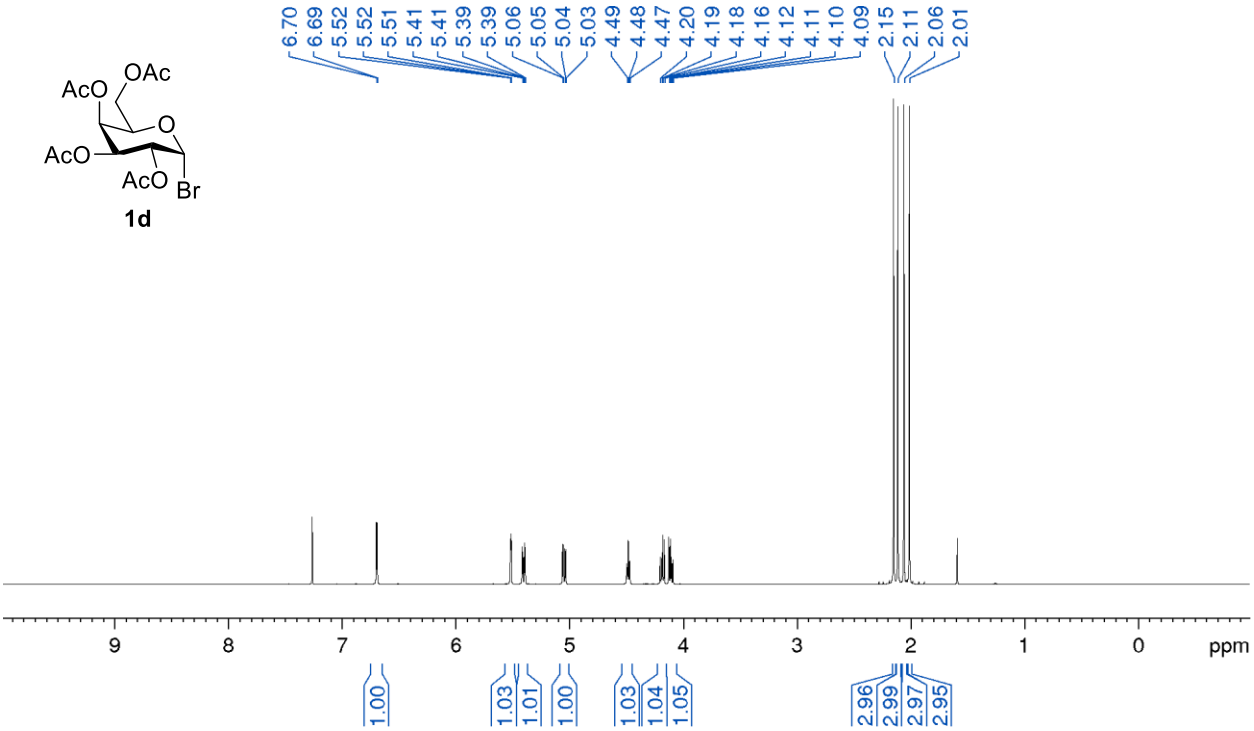
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (1c)



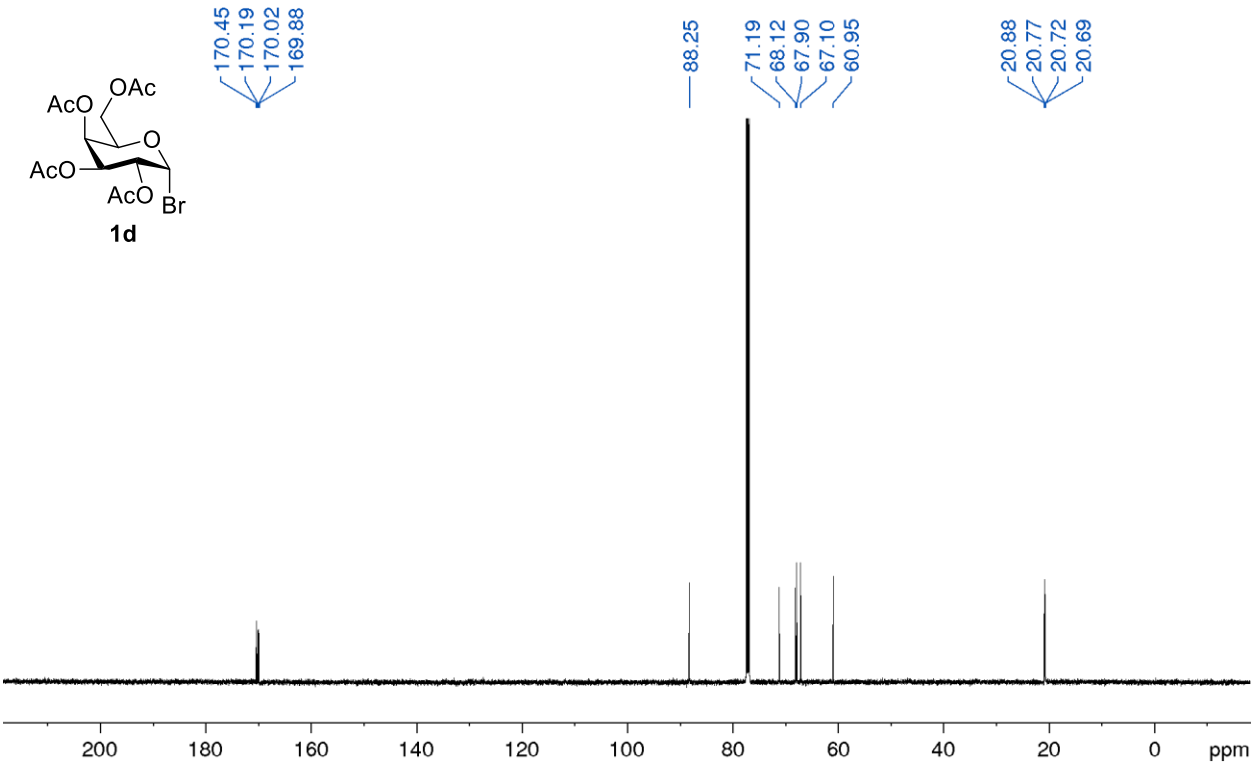
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (1c)



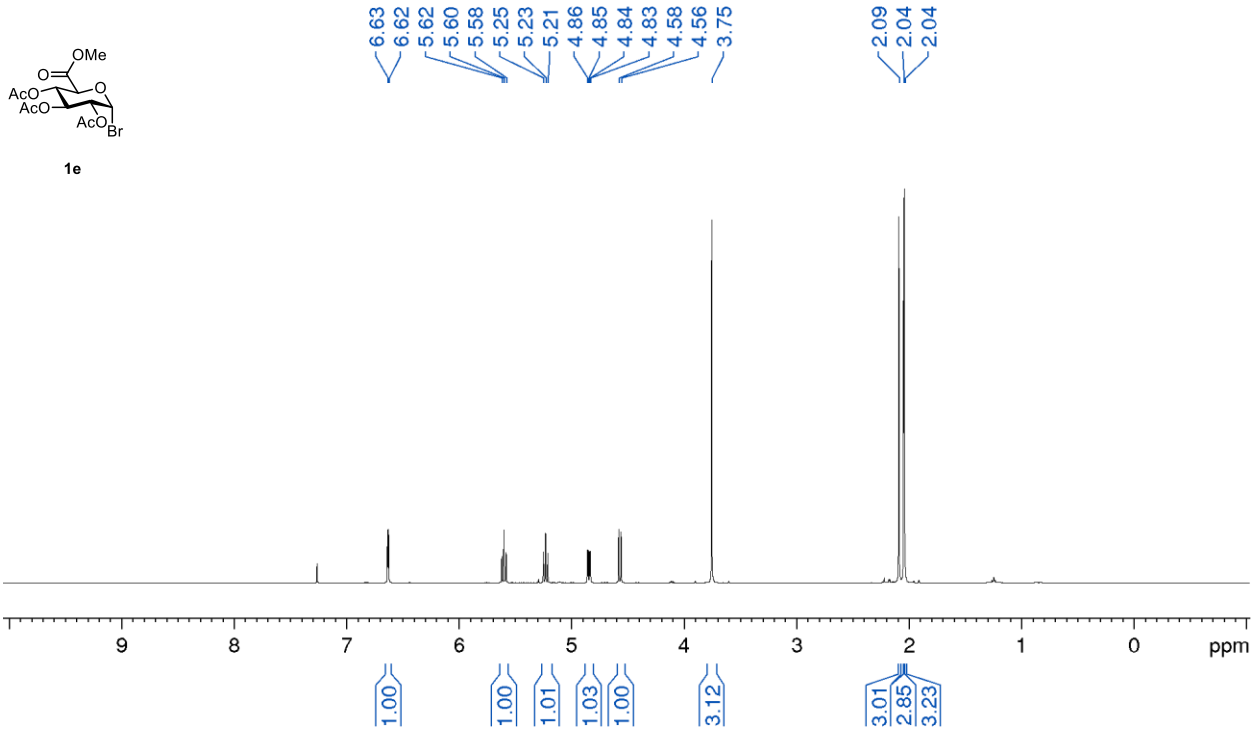
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (1d)



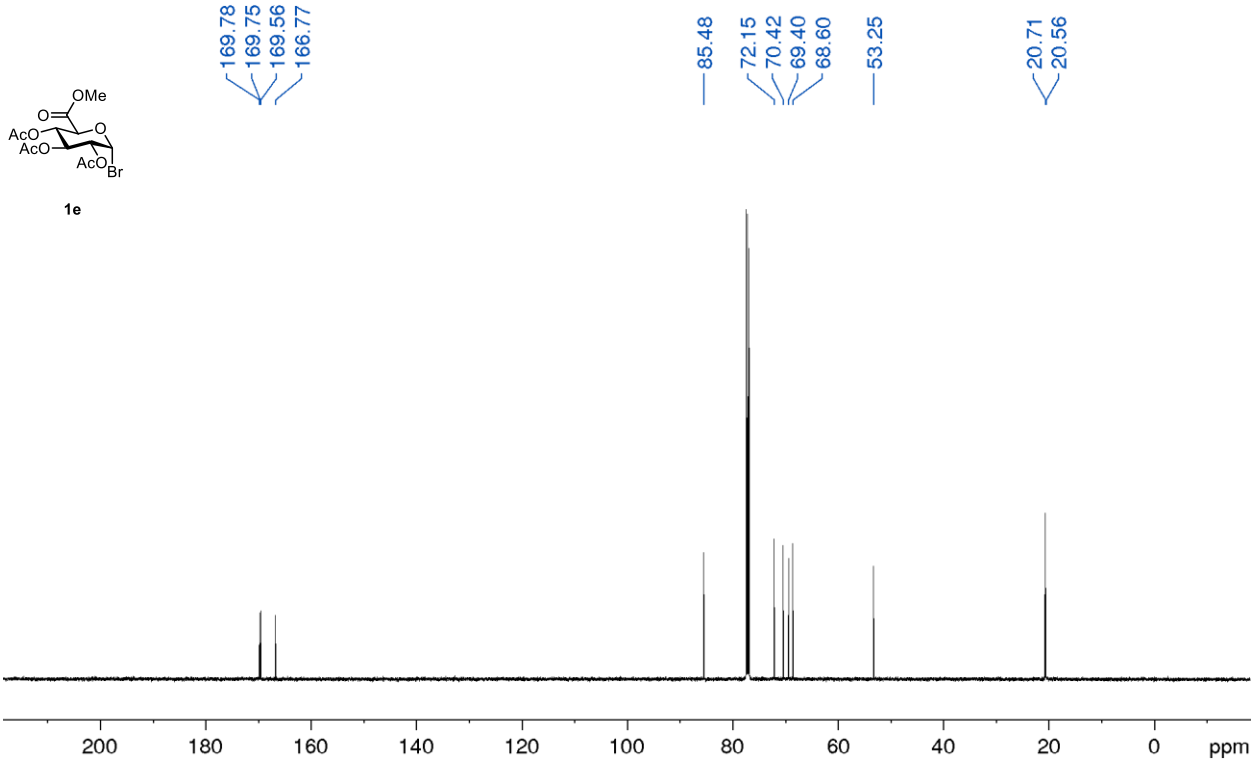
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (1d)



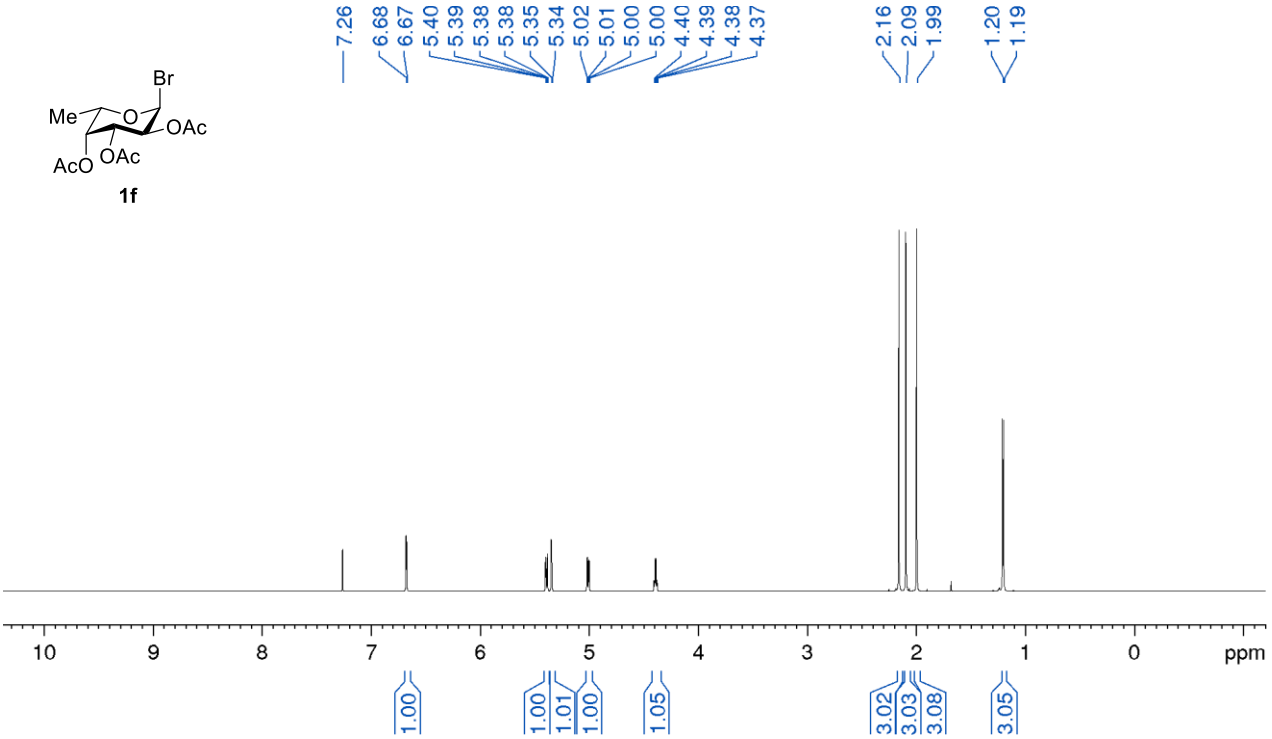
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (1e)



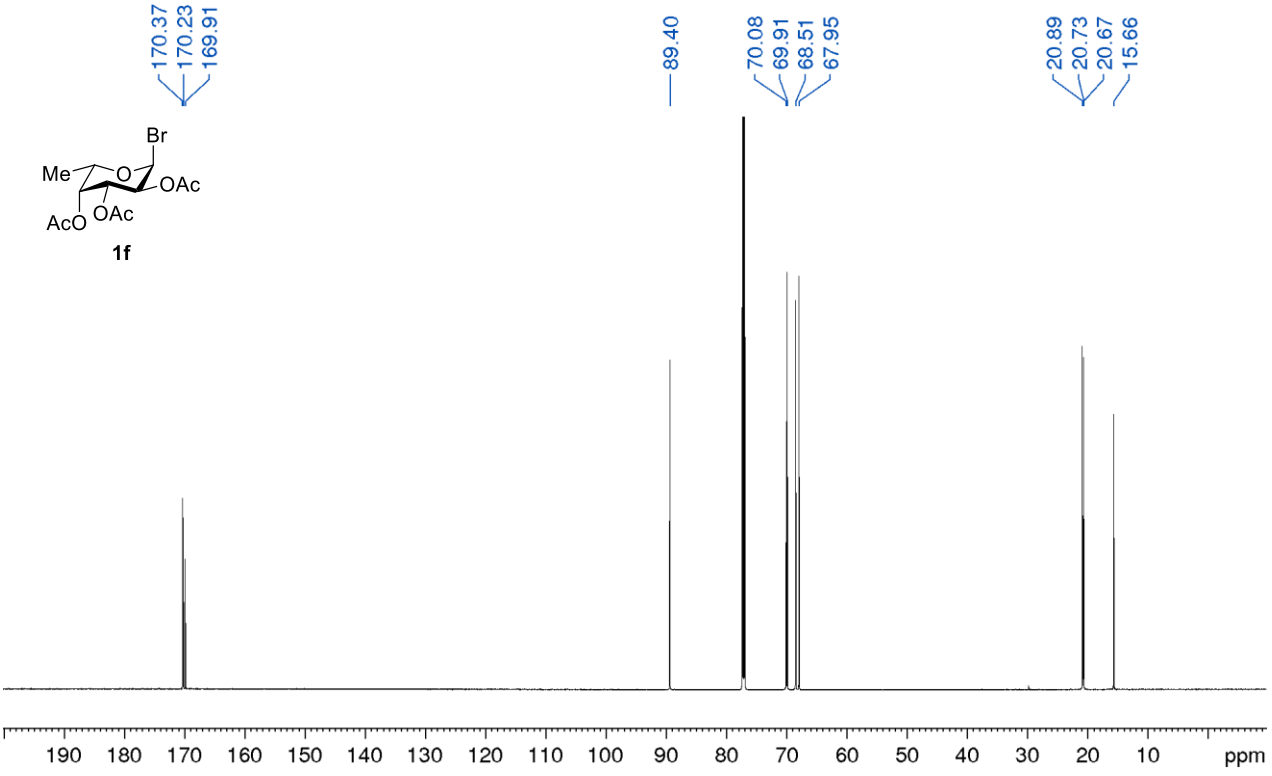
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (1e)



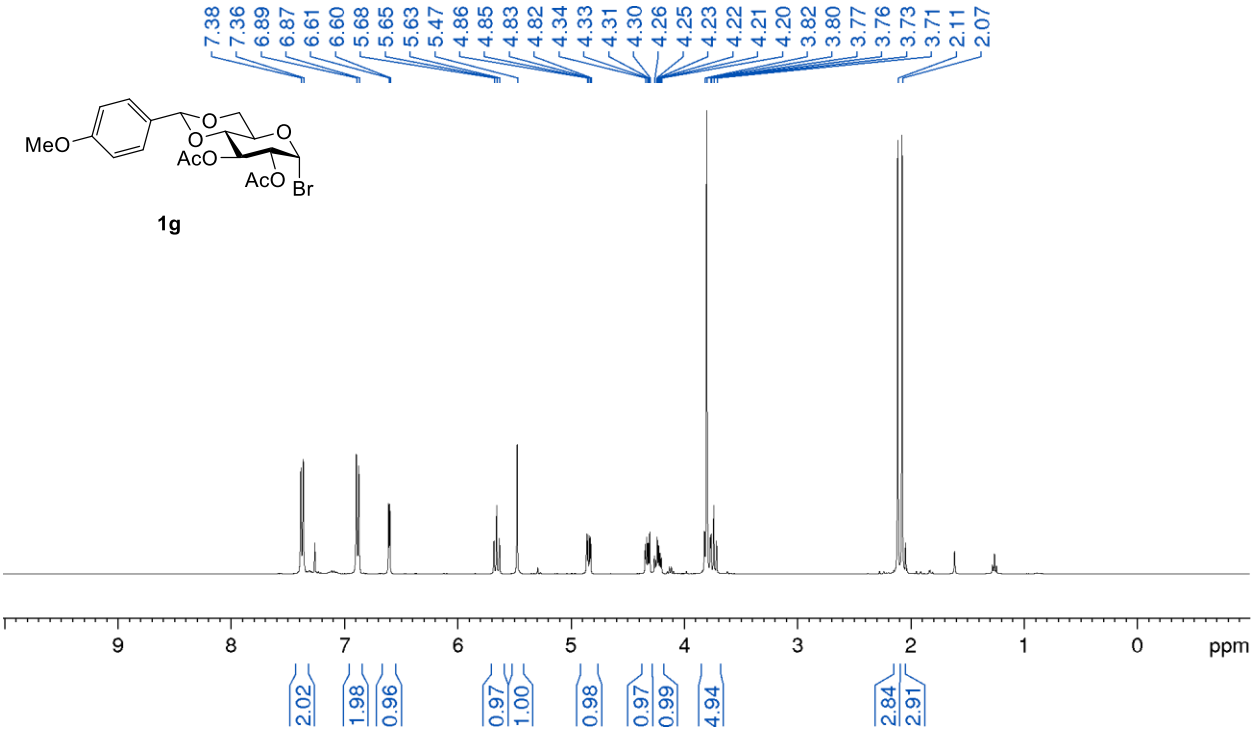
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (1f)



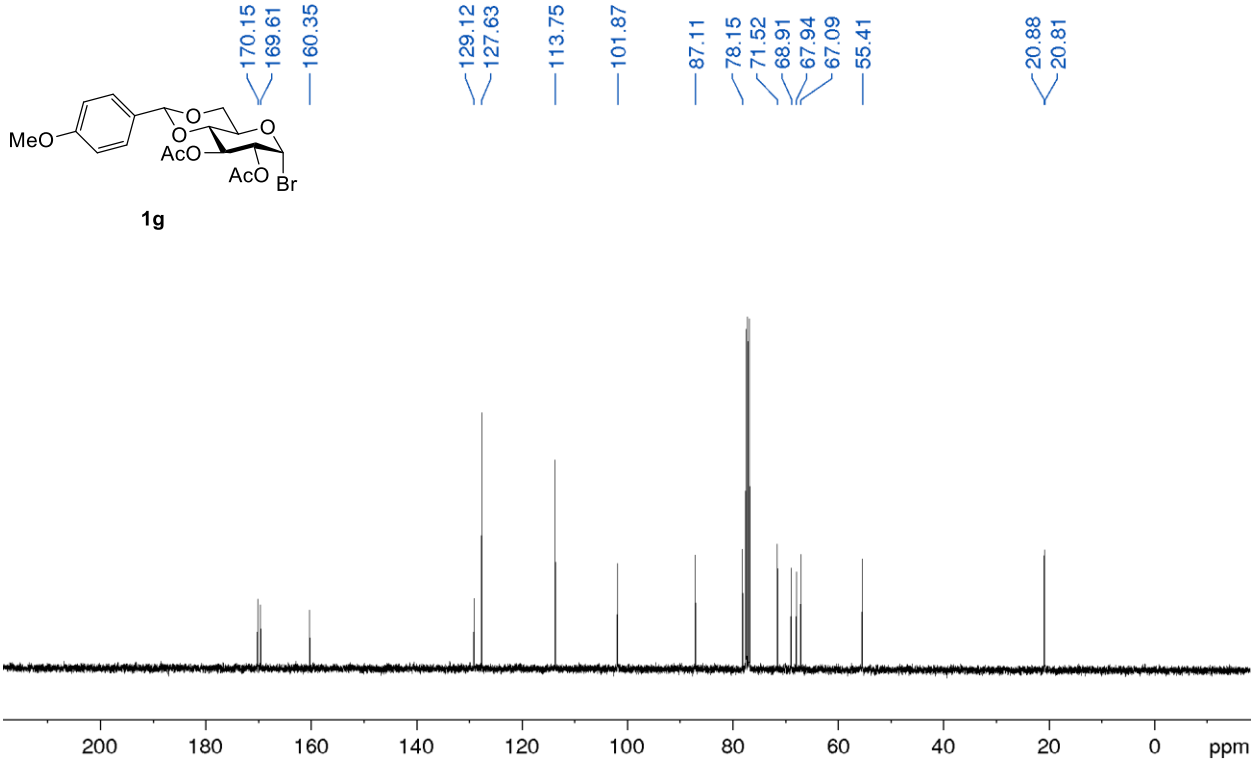
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (1f)



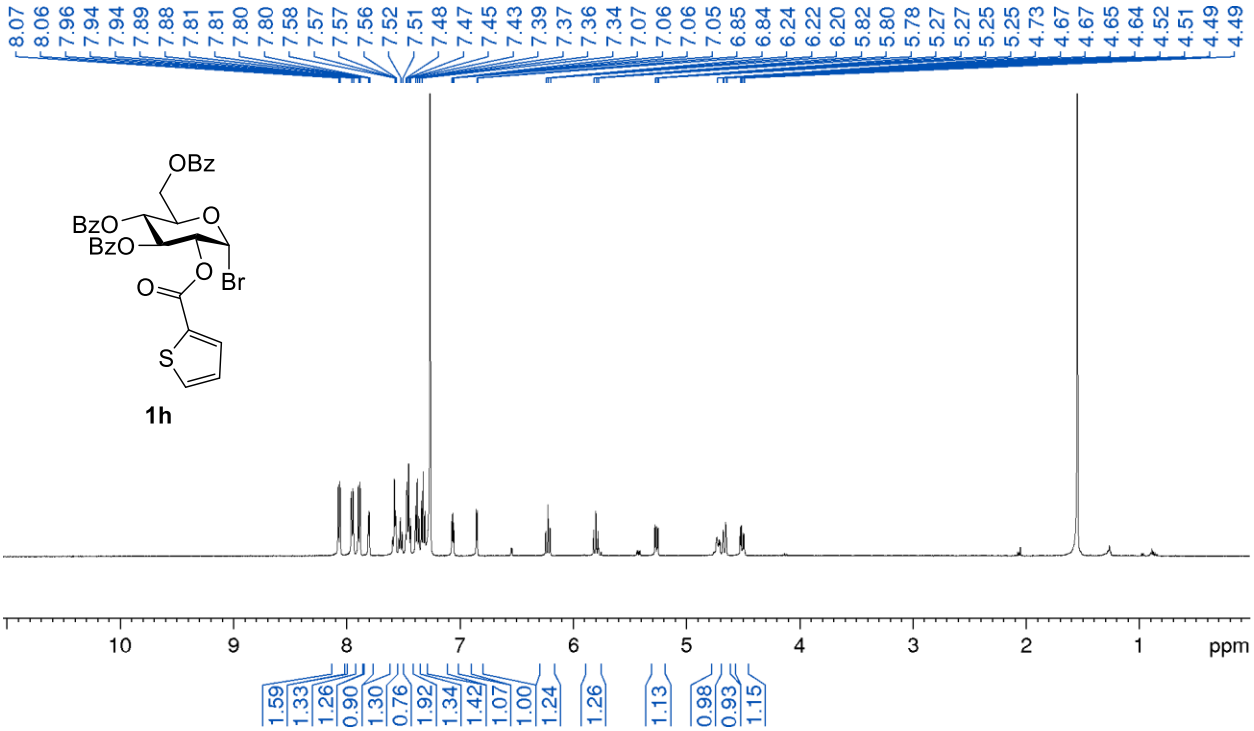
^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) of (1g)



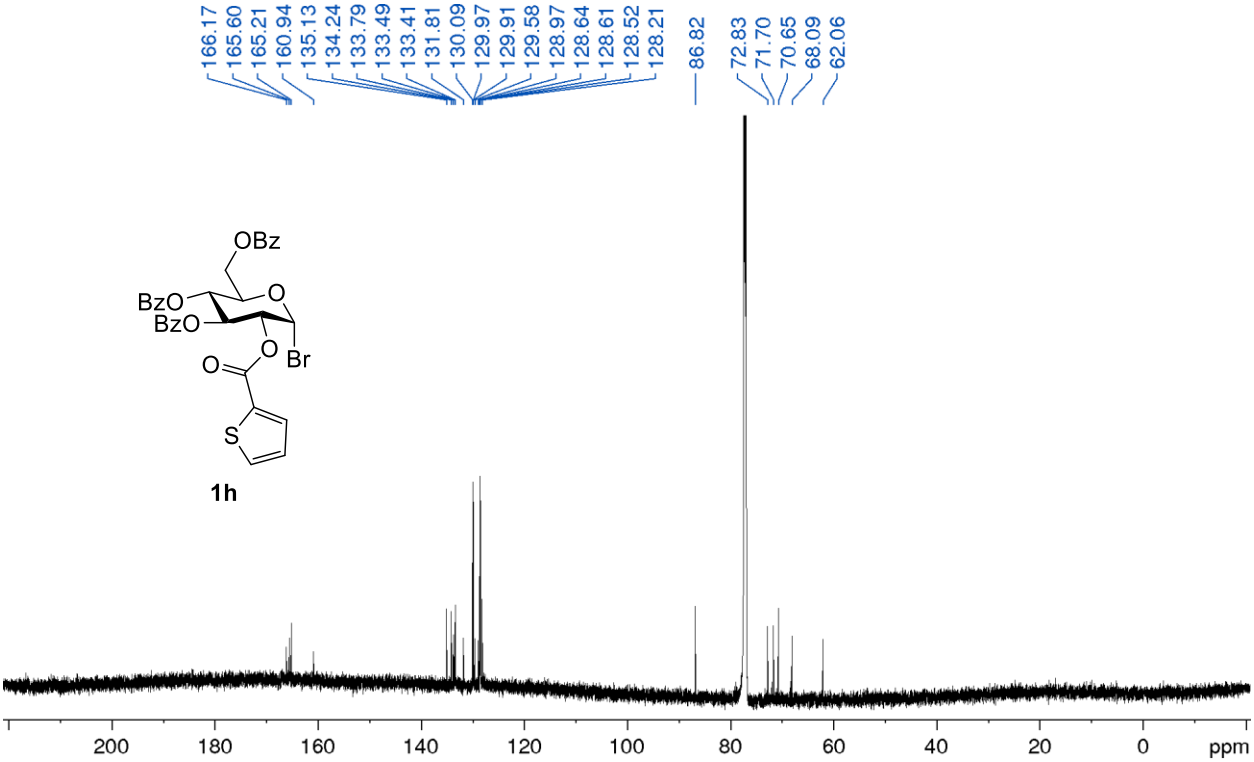
^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) of (1g)



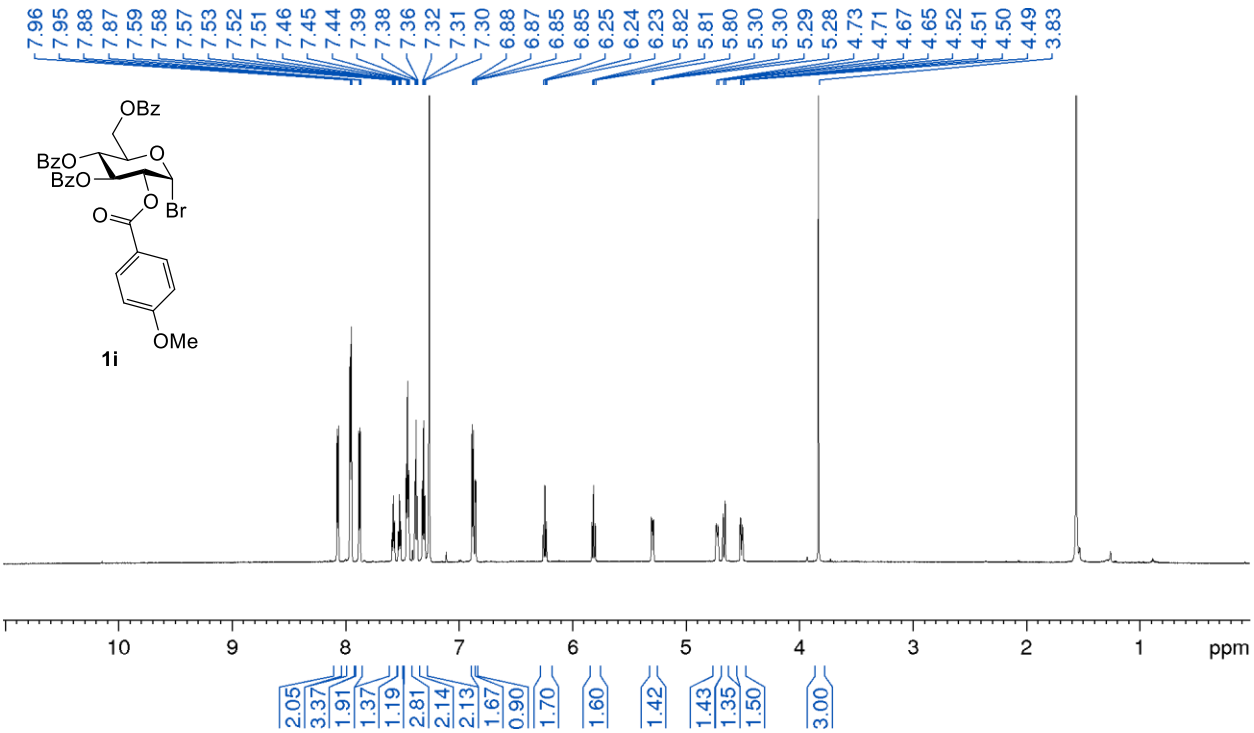
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (1h)



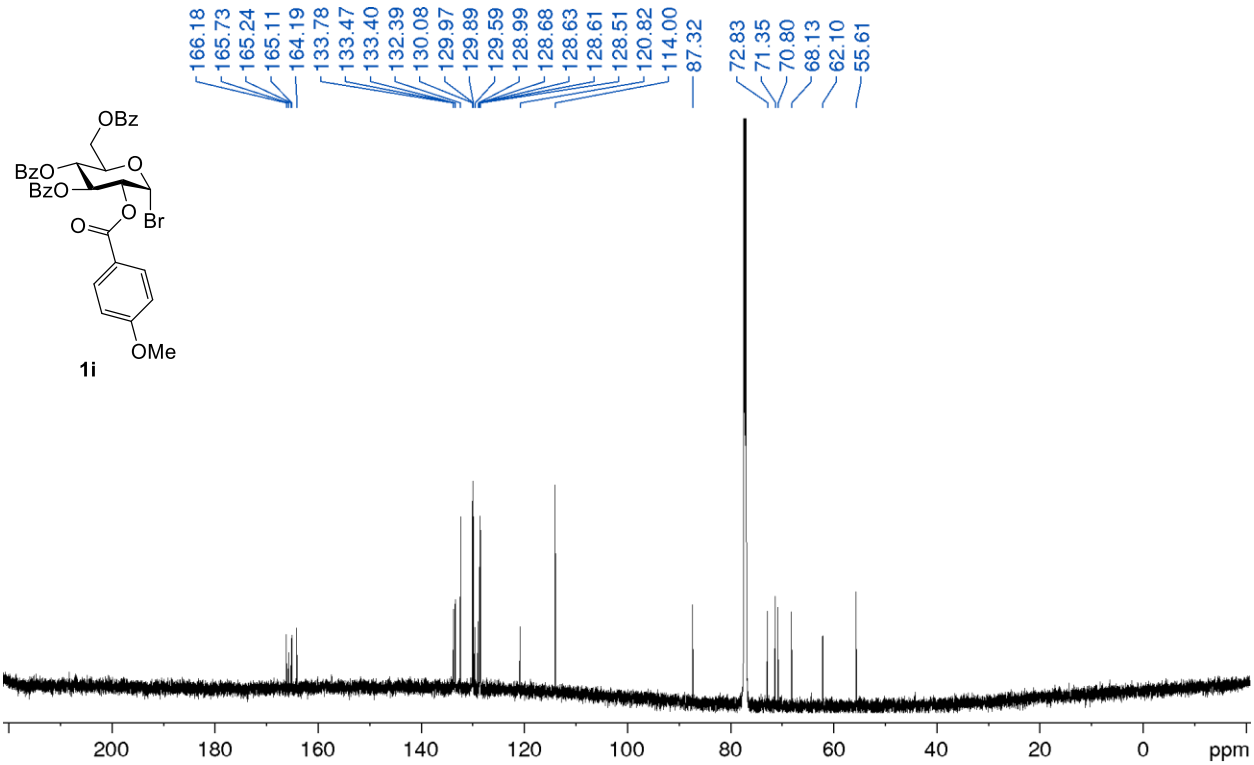
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (1h)



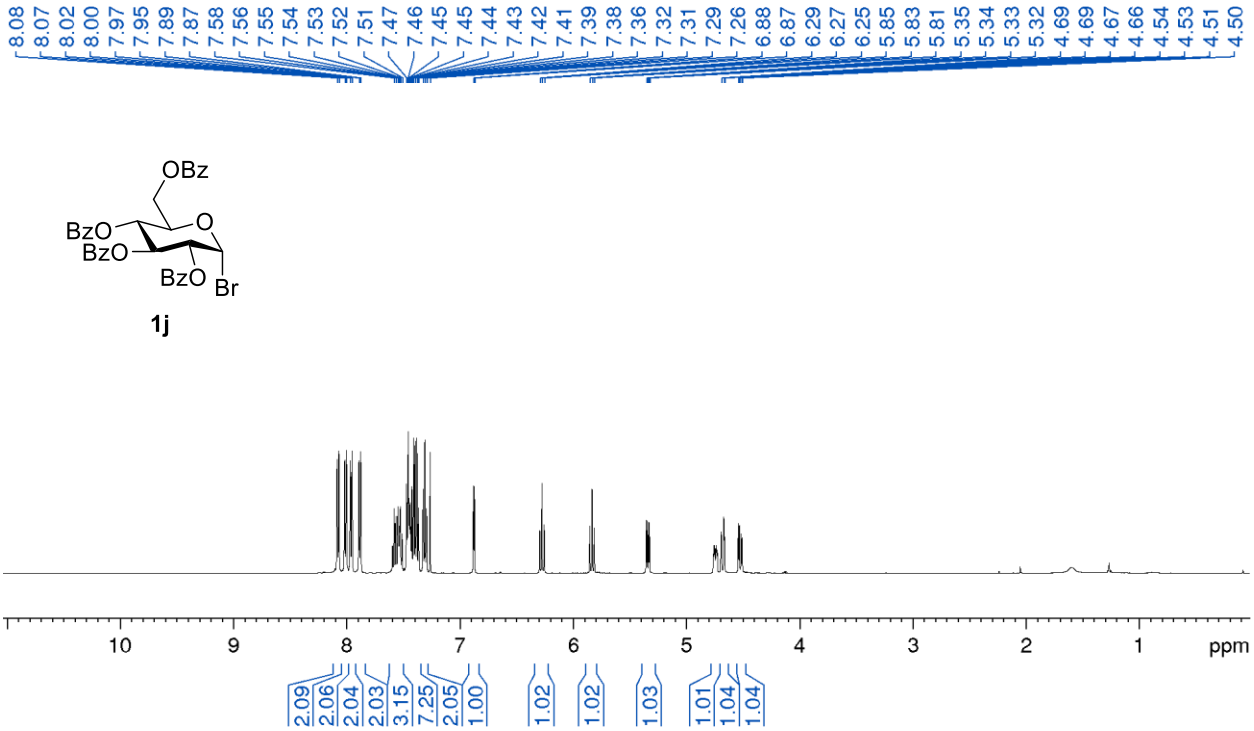
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (1i)



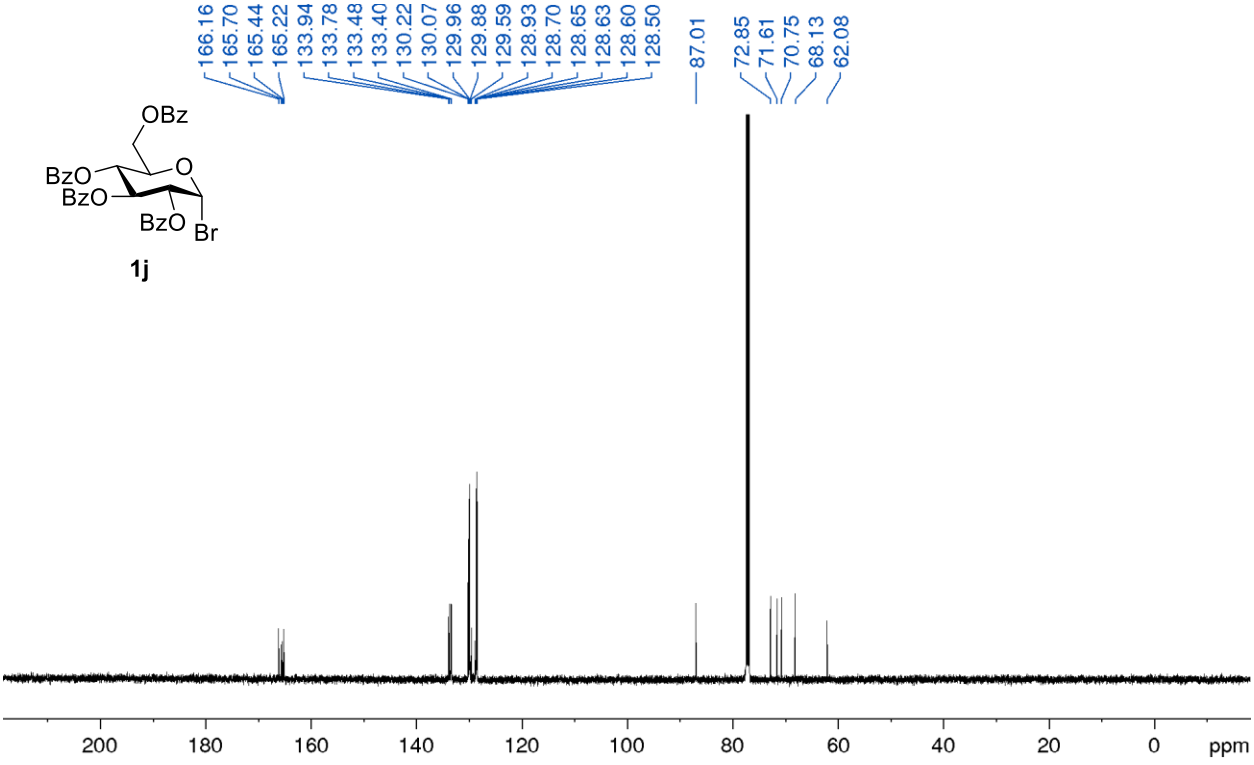
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (1i)



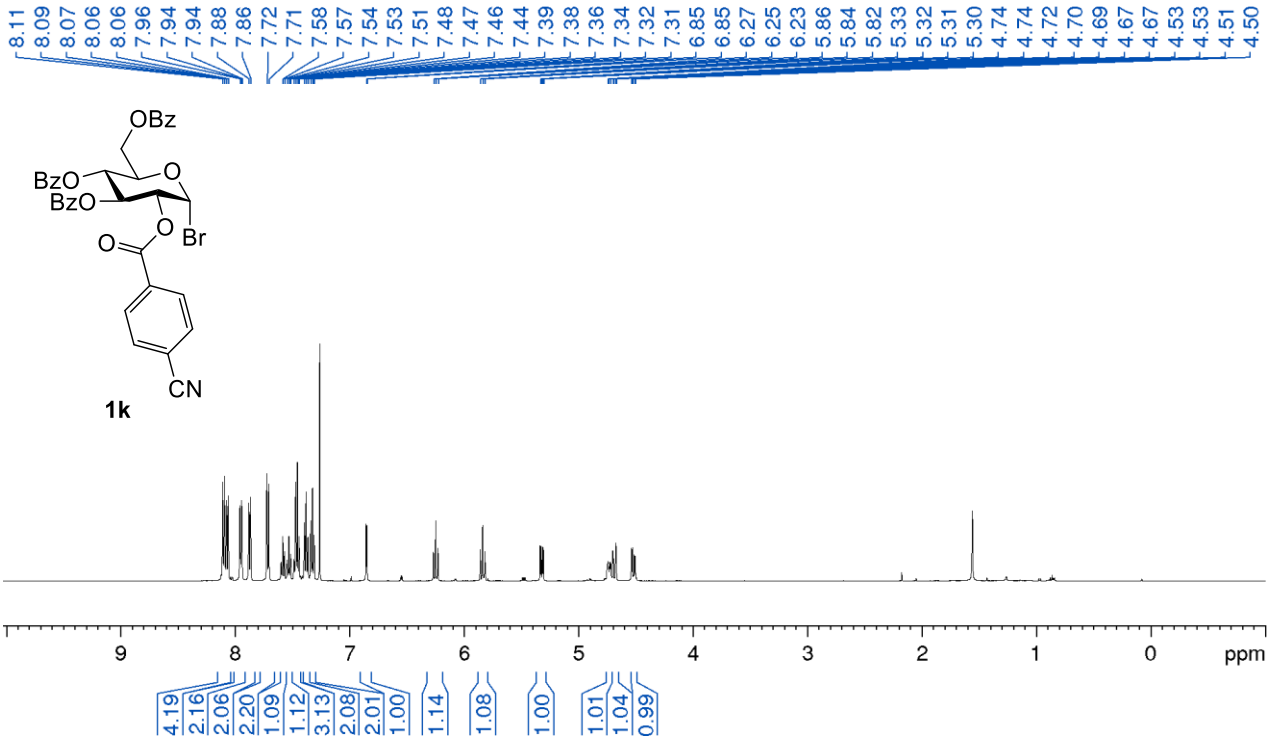
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (1j)



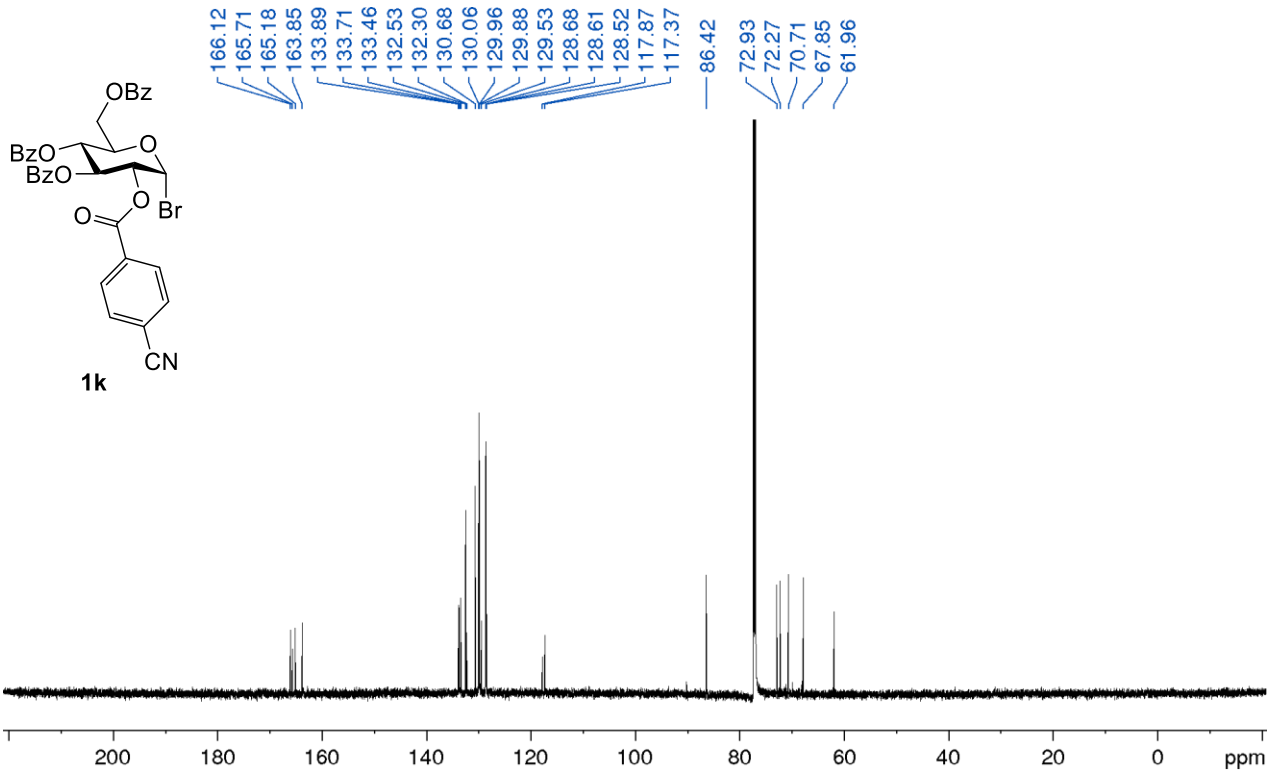
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (1j)



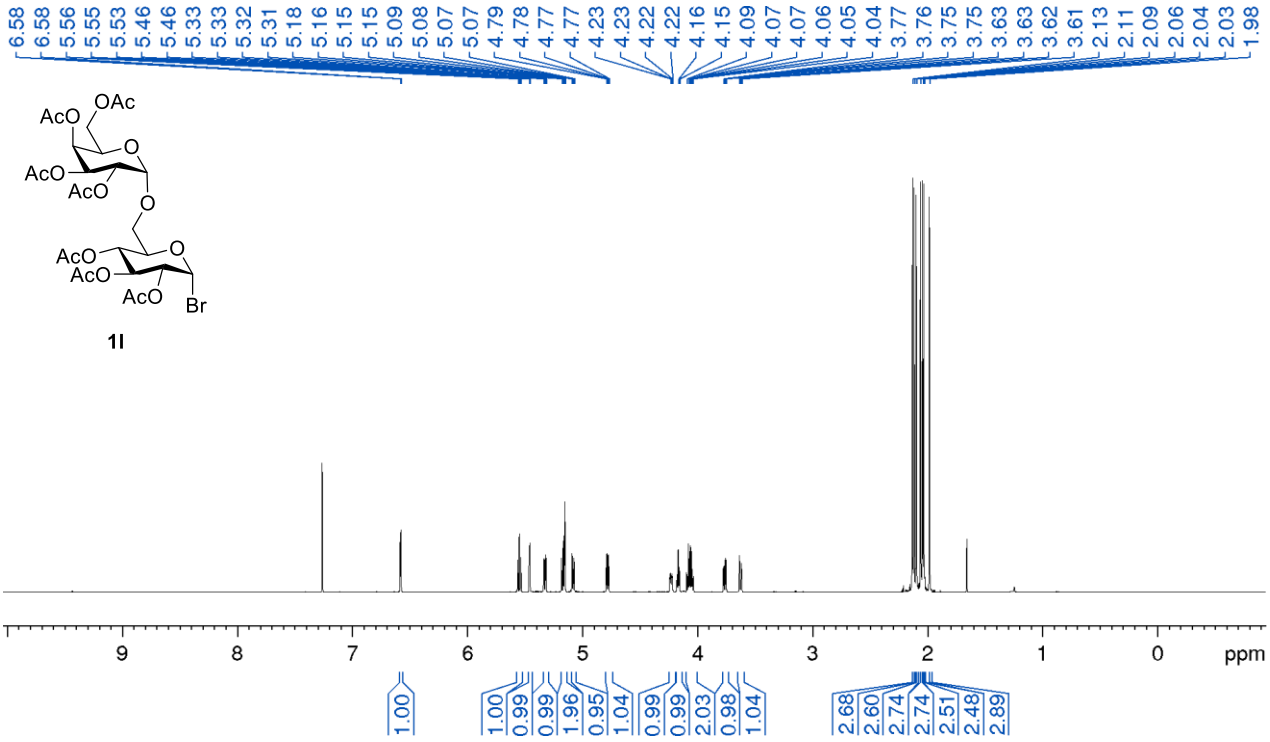
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (1k)



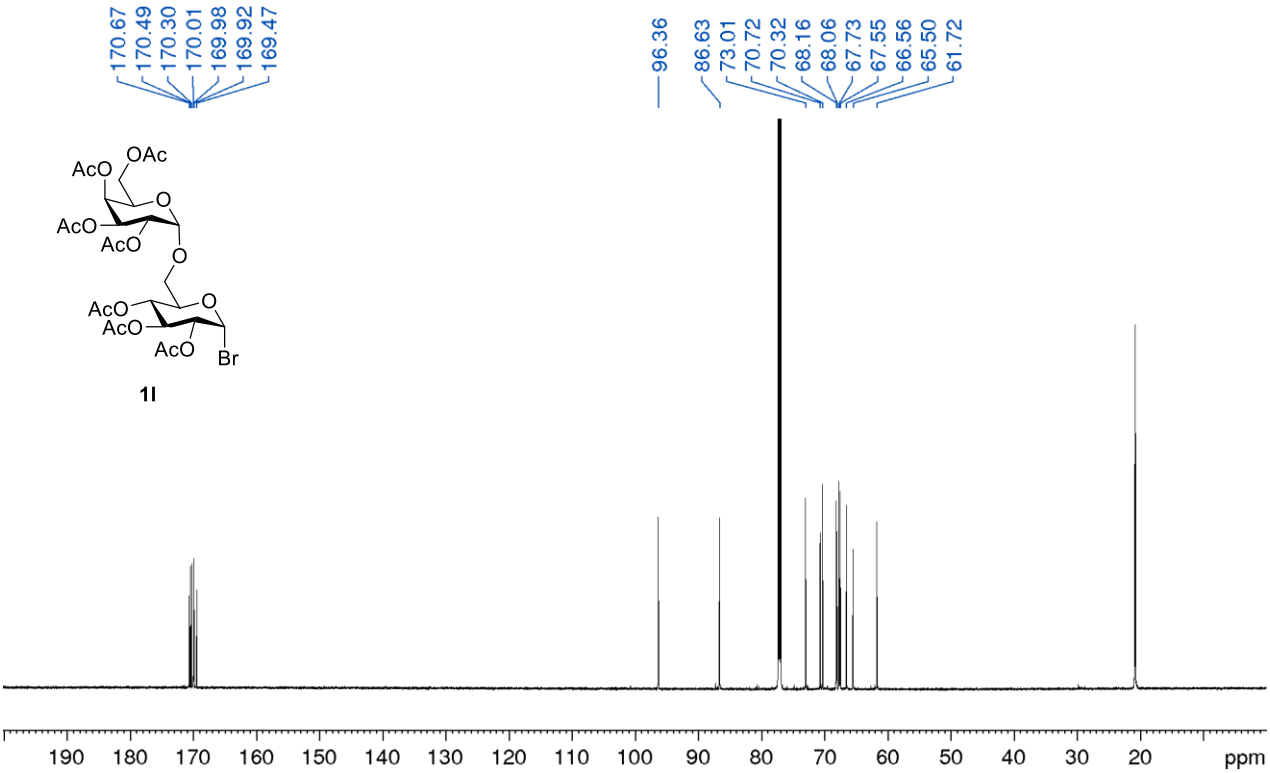
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (1k)



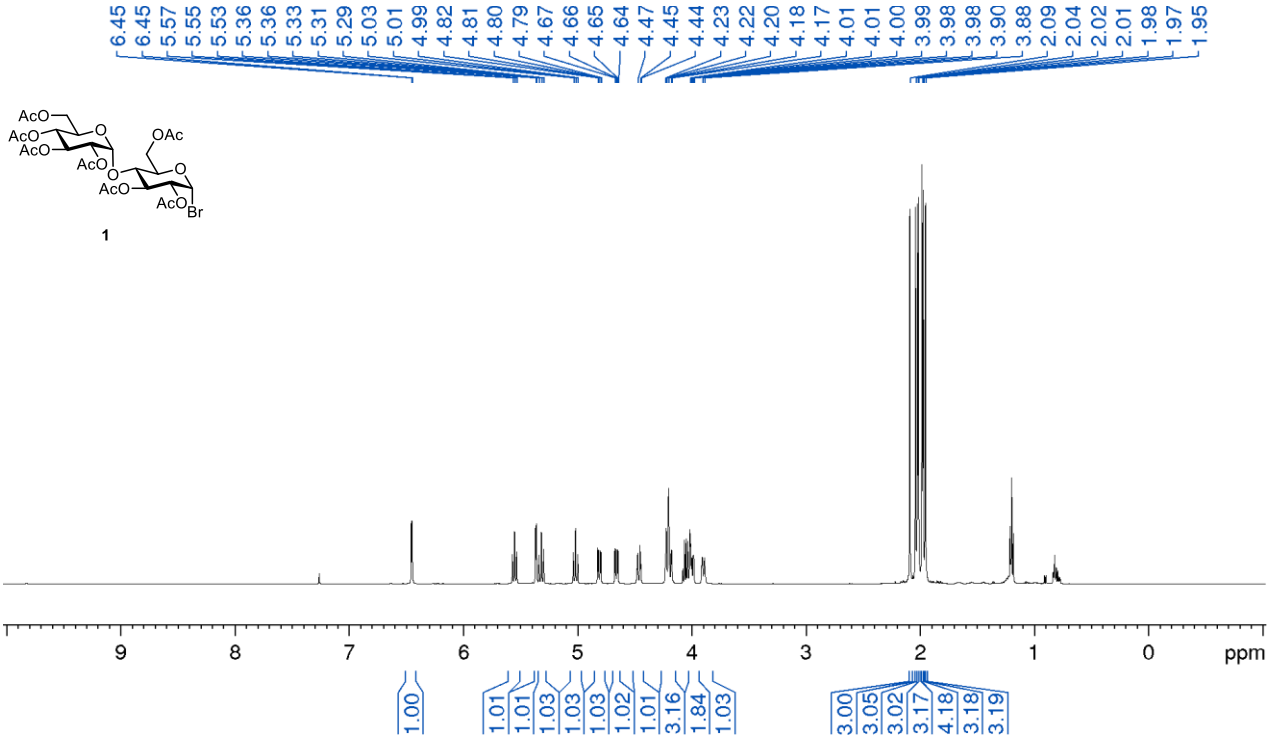
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (1l)



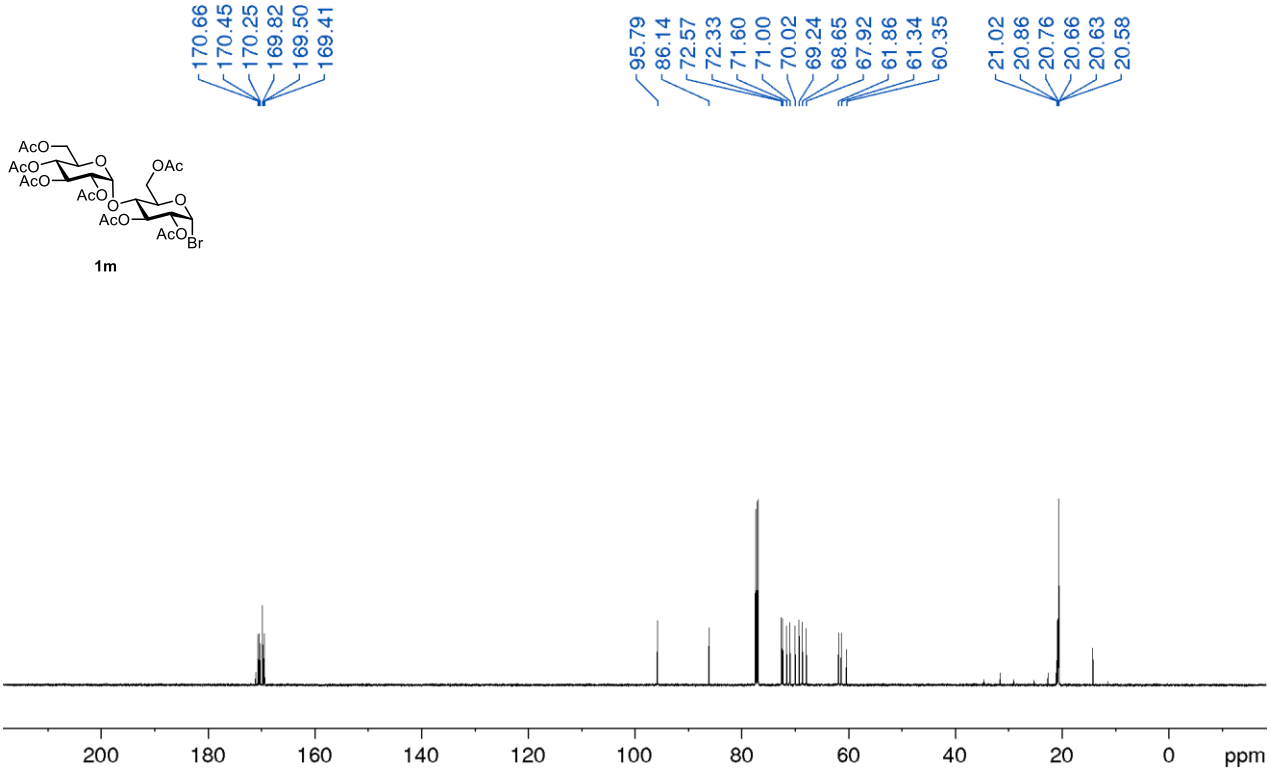
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (1l)



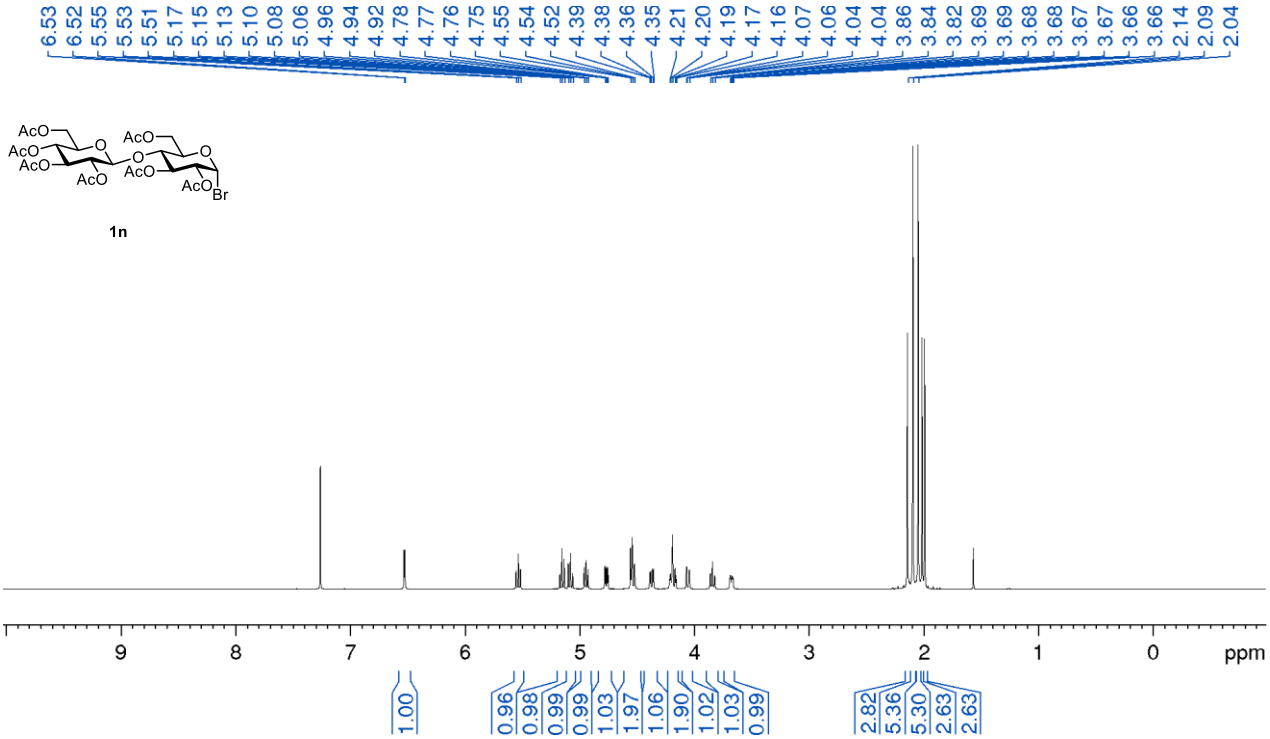
^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC) of (1m)



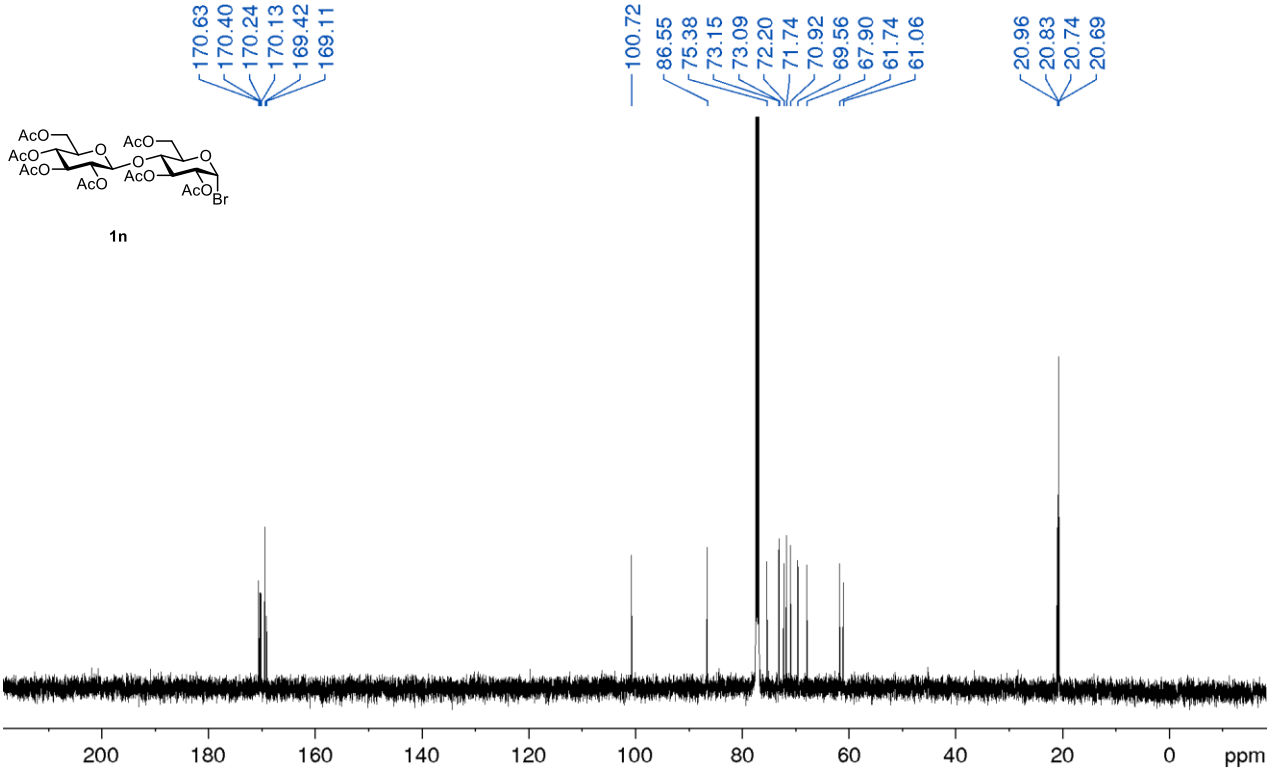
^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC) of (1m)



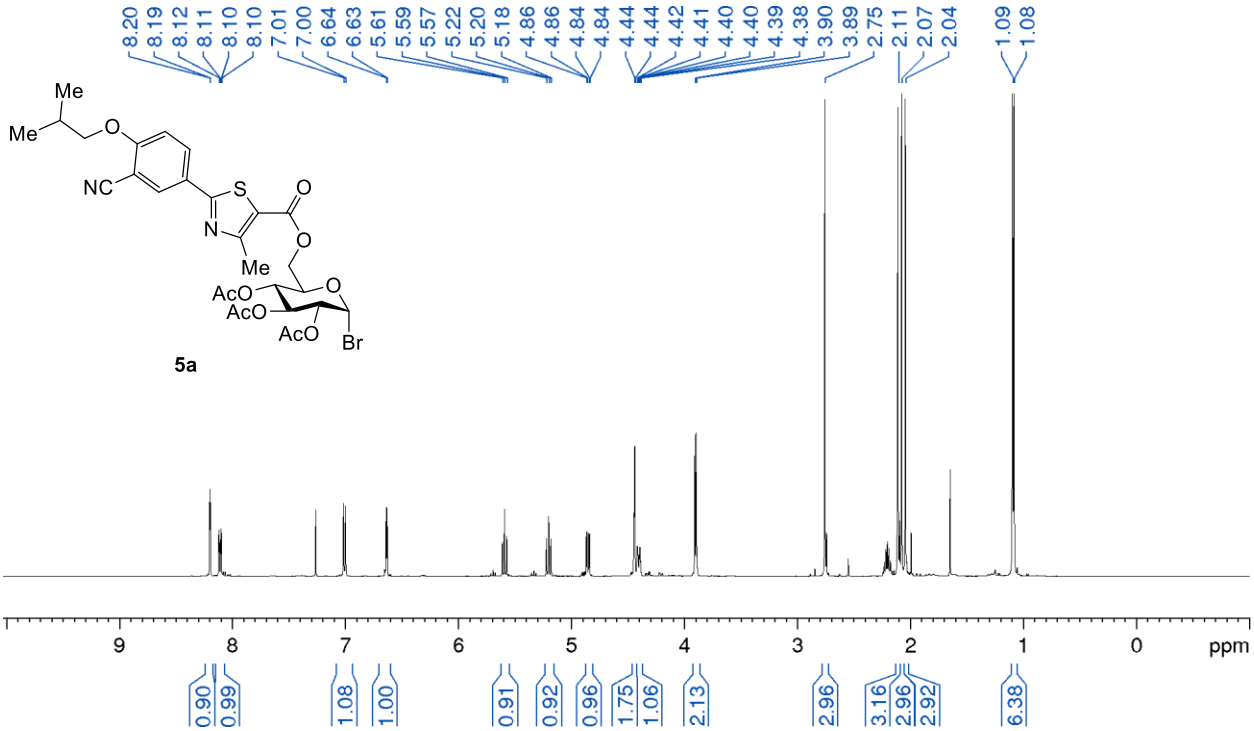
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (1n)



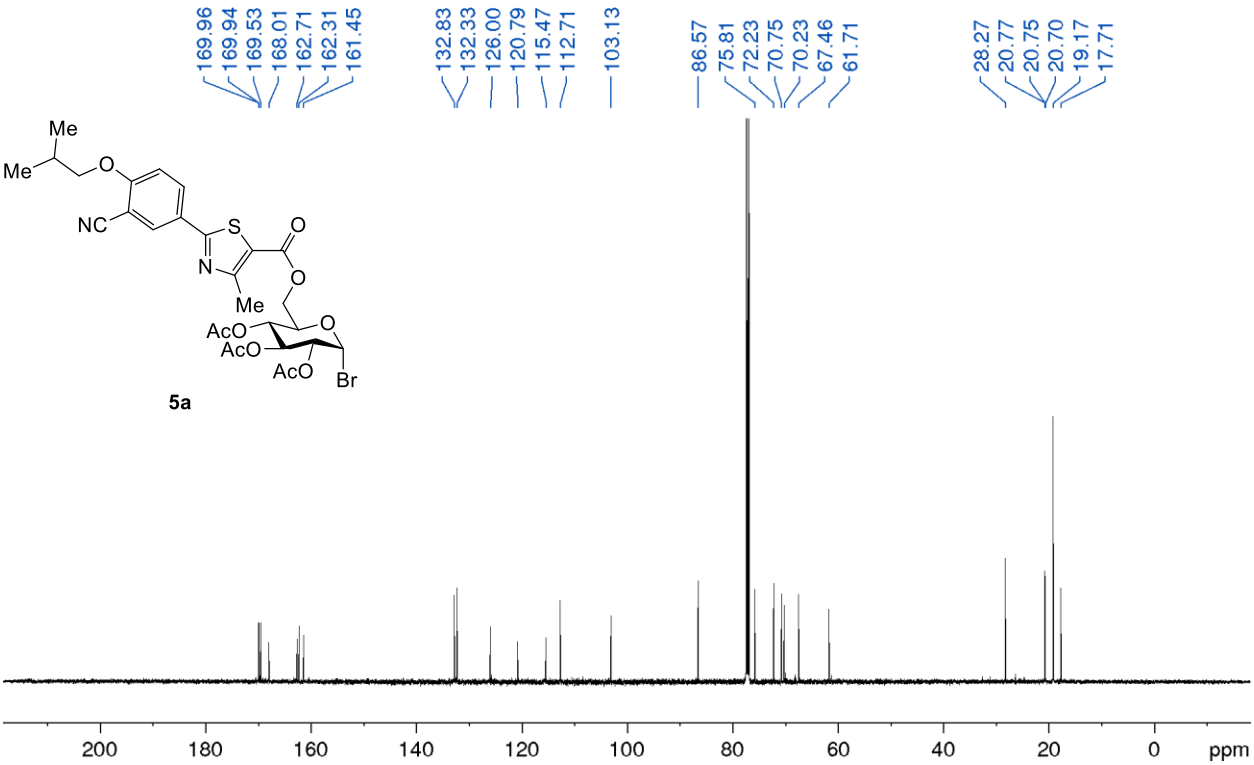
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (1n)



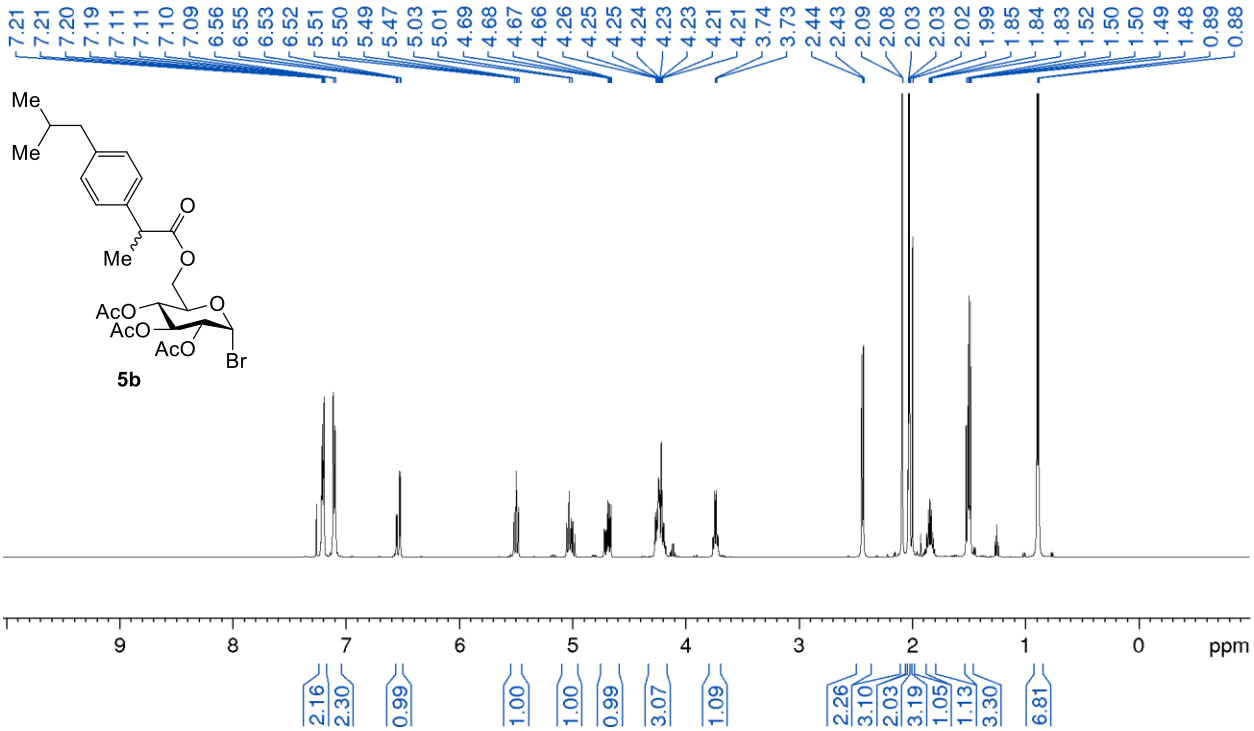
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (5a)



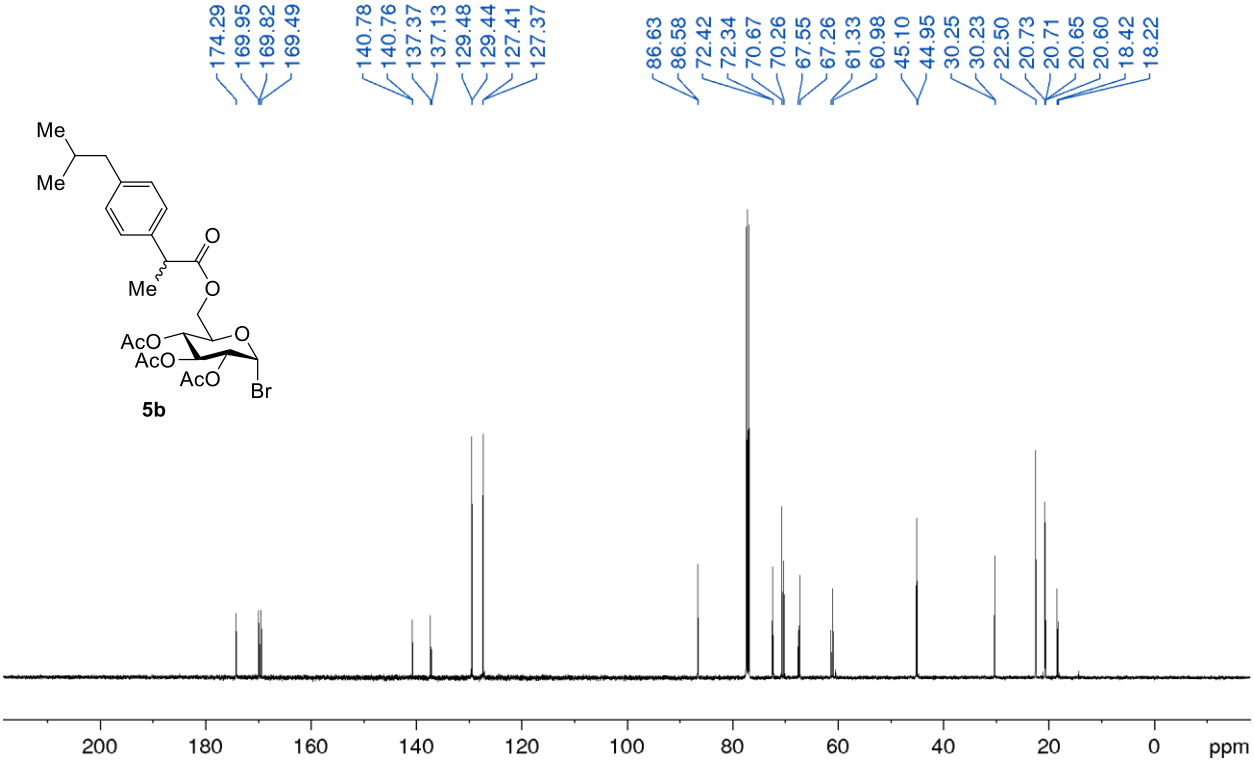
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (5a)



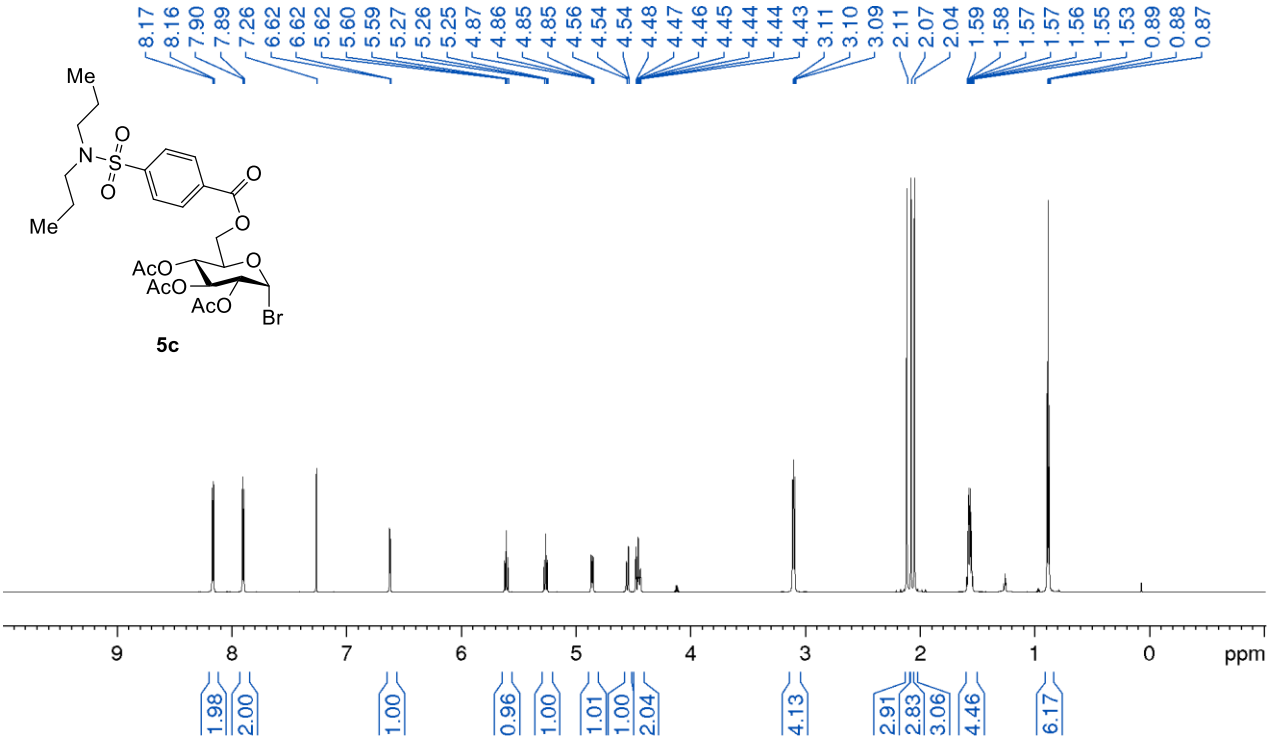
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (5b)



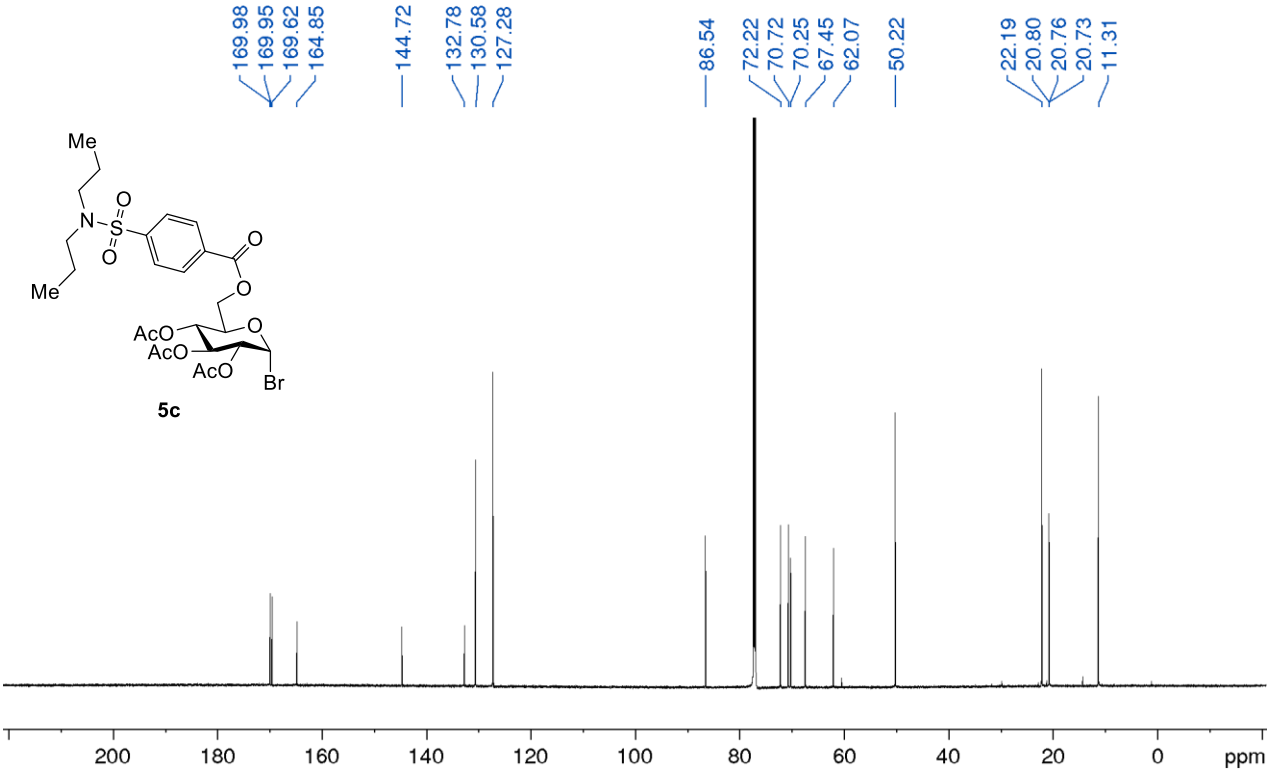
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (5b)



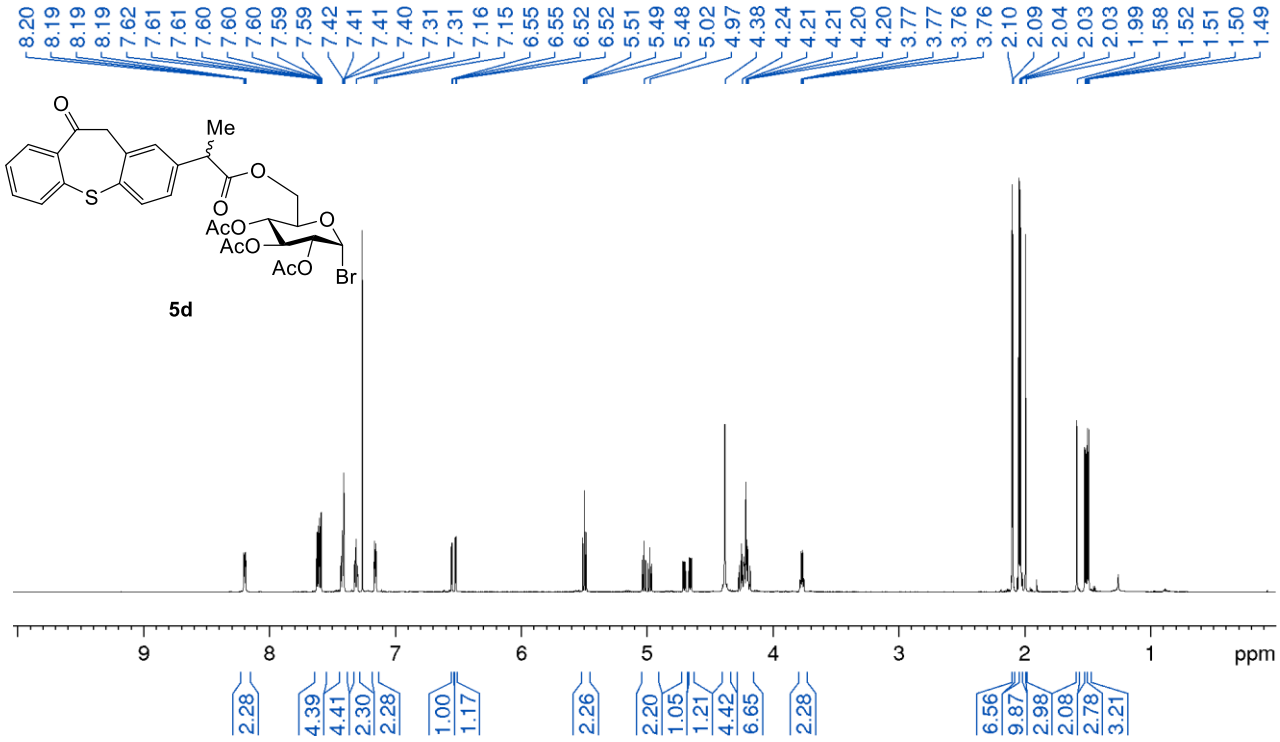
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (5c)



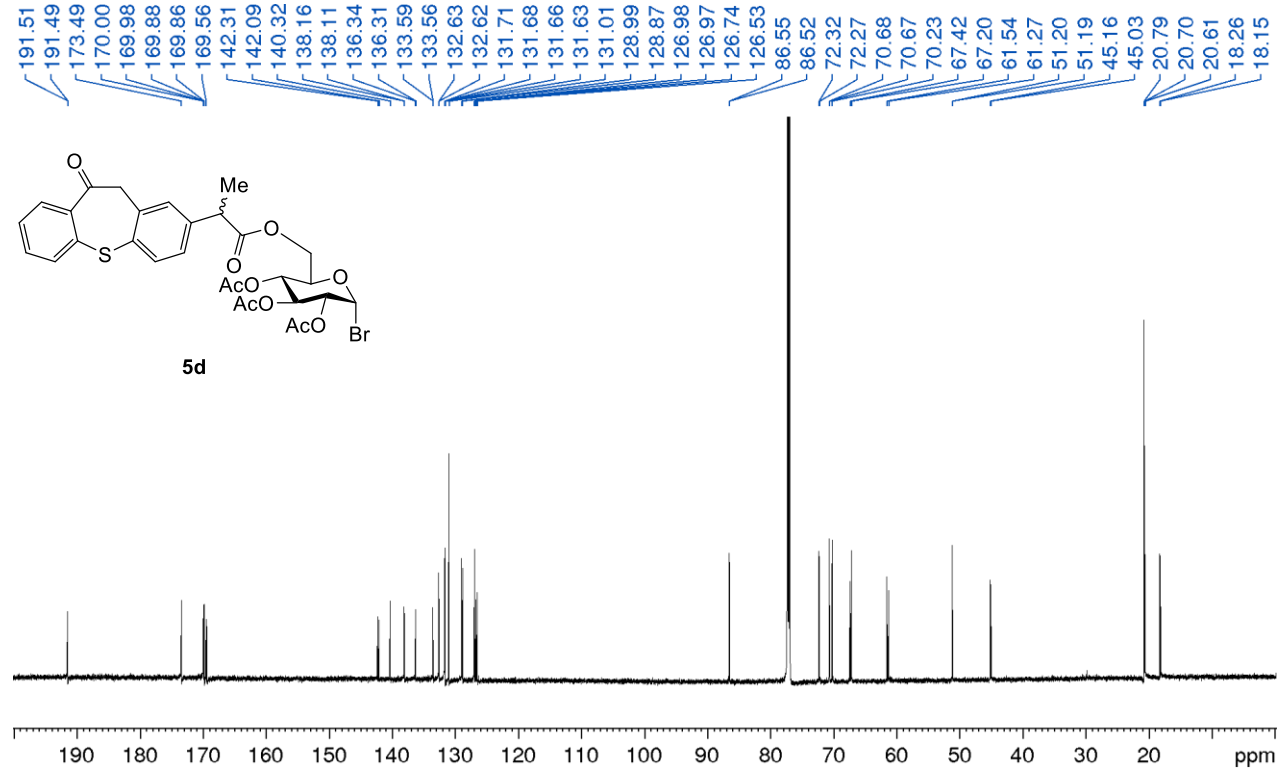
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (5c)



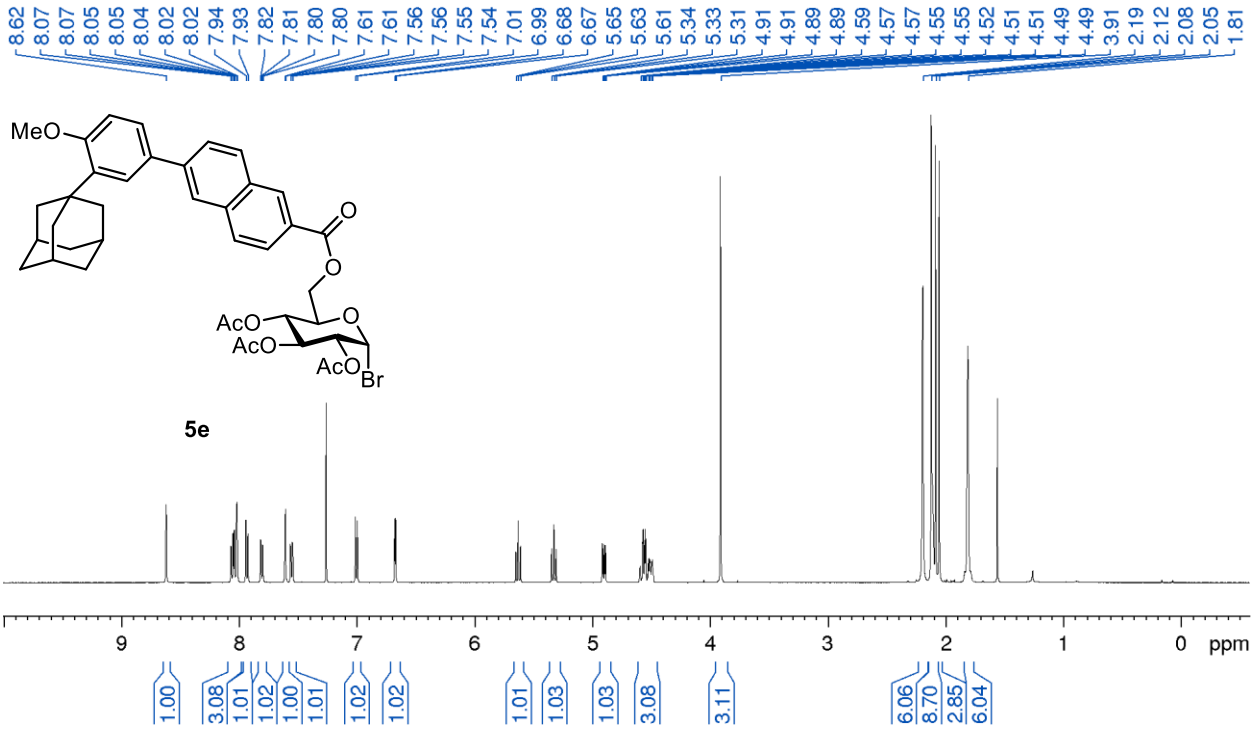
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (5d)



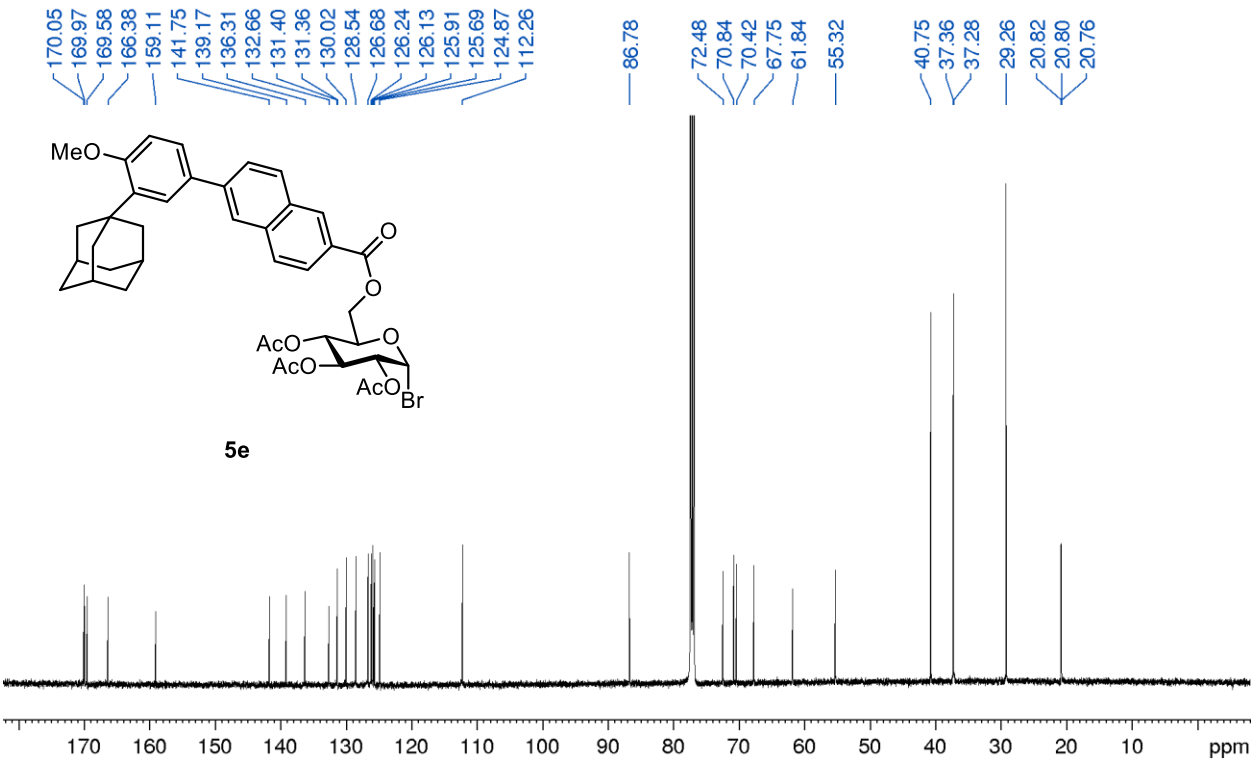
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (5d)



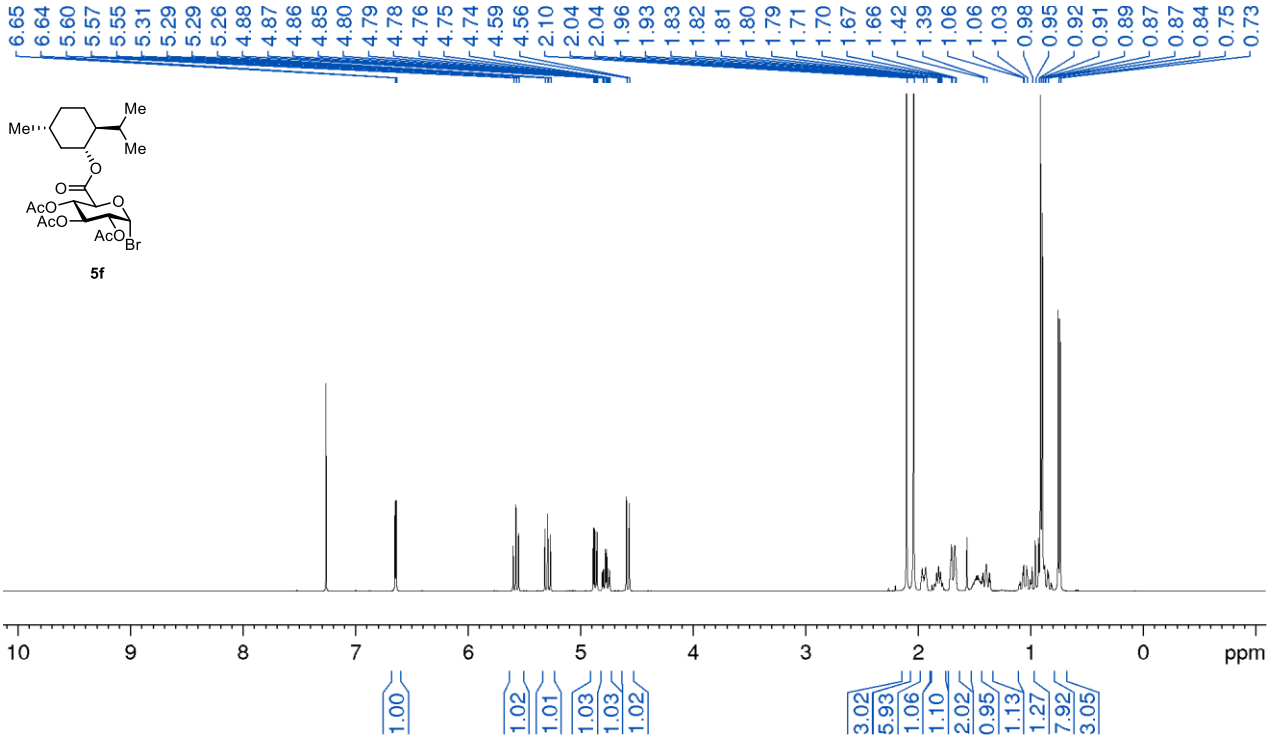
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (5e)



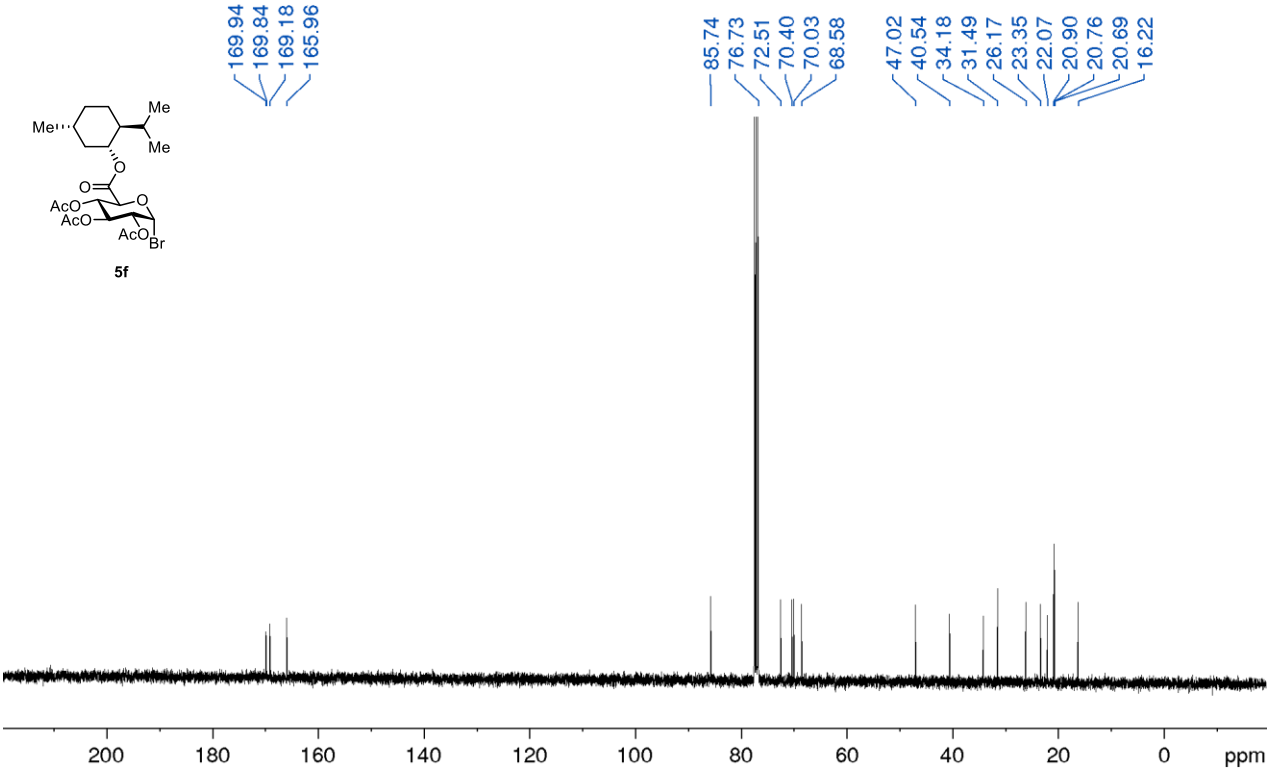
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (5e)



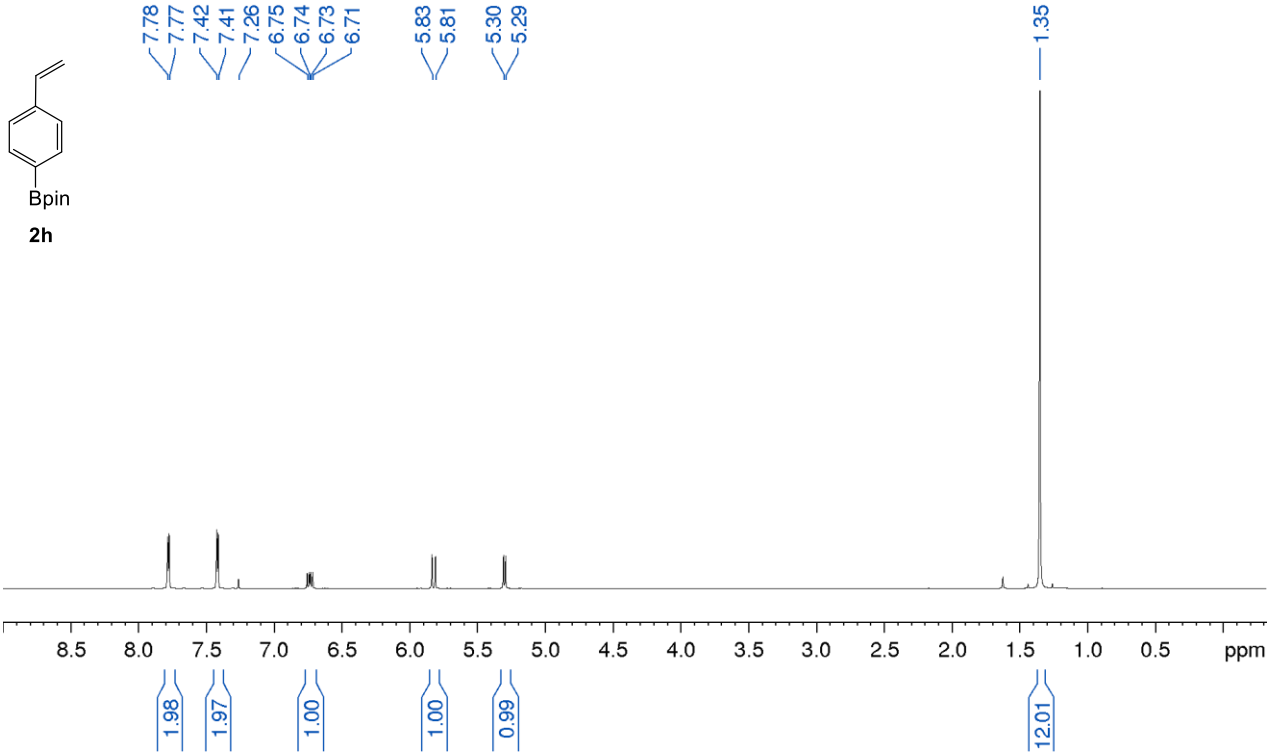
^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) of (5f)



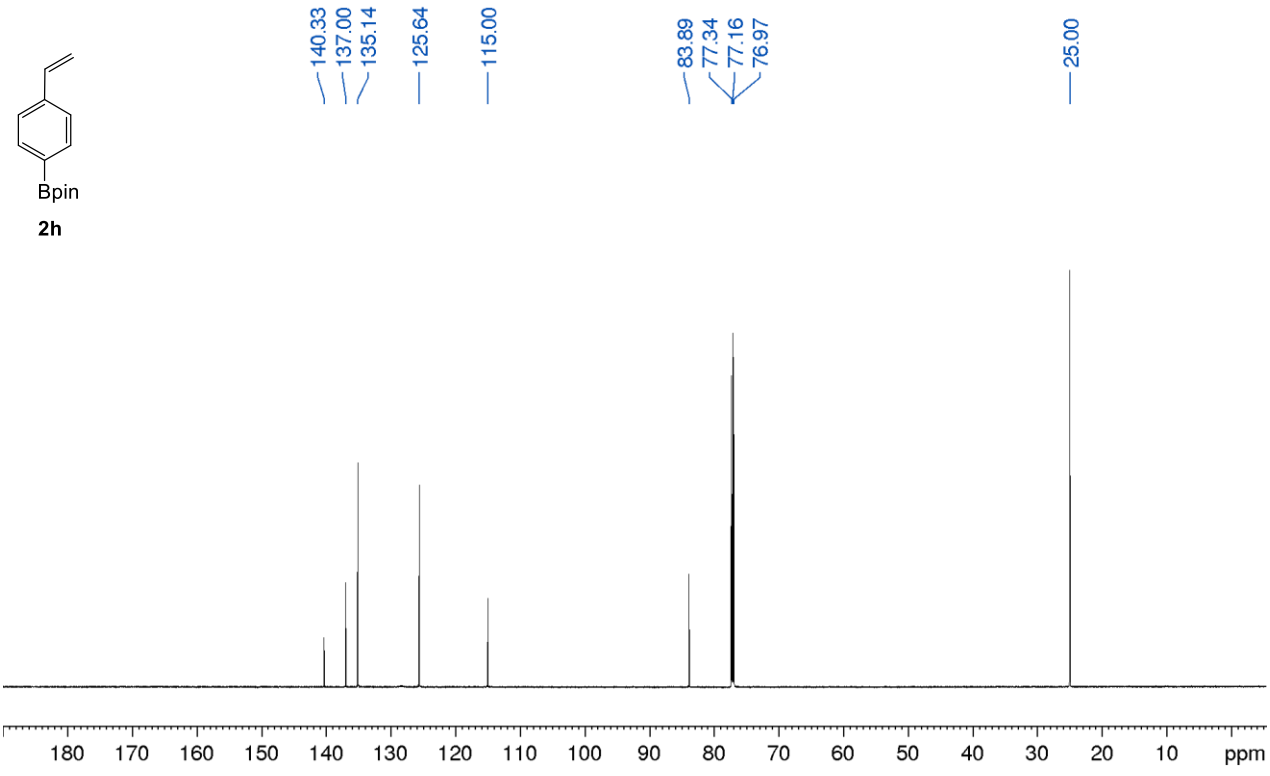
^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) of (5f)



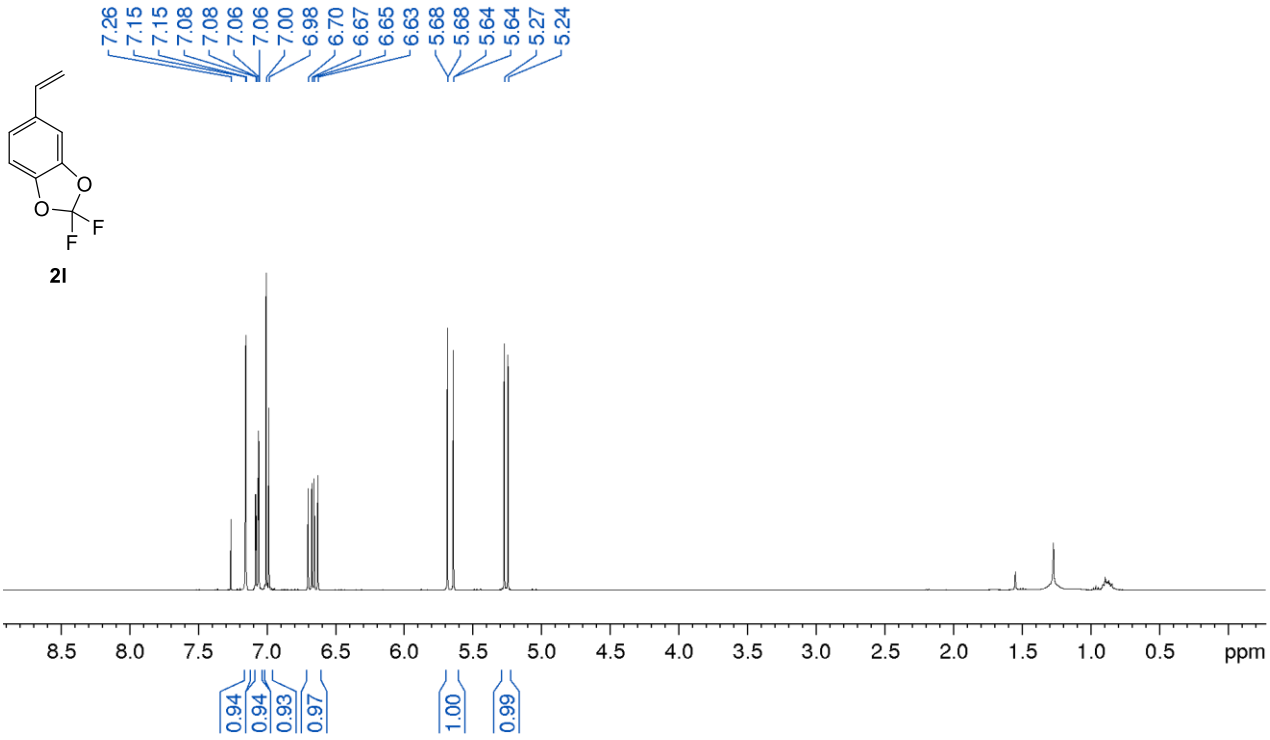
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (2h)



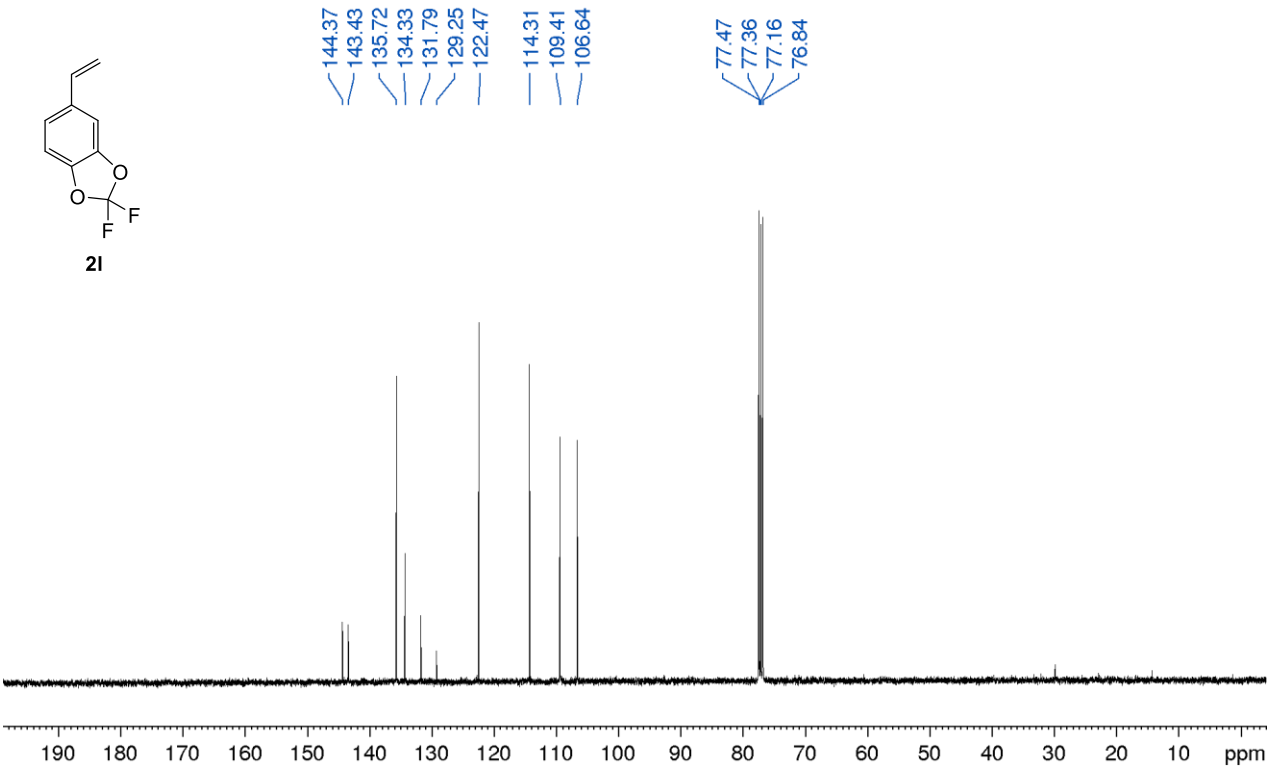
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (2h)



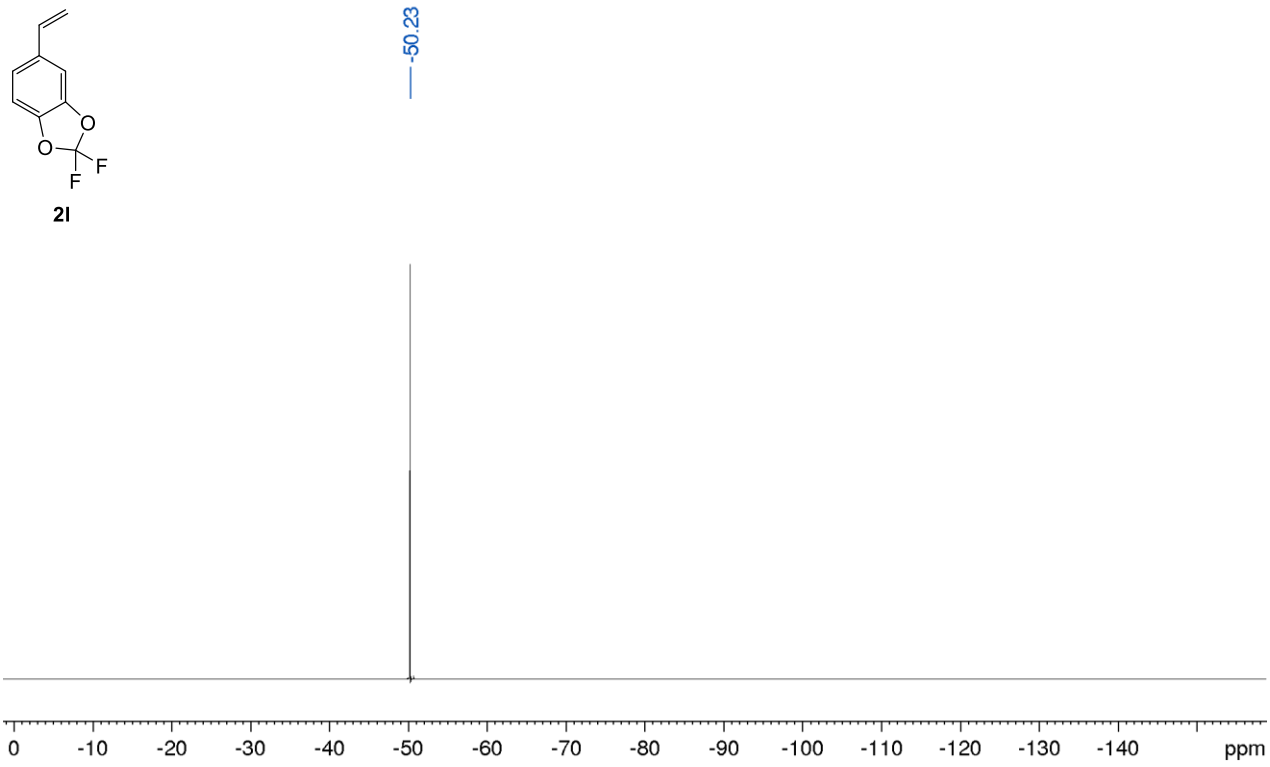
^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) of (2l)



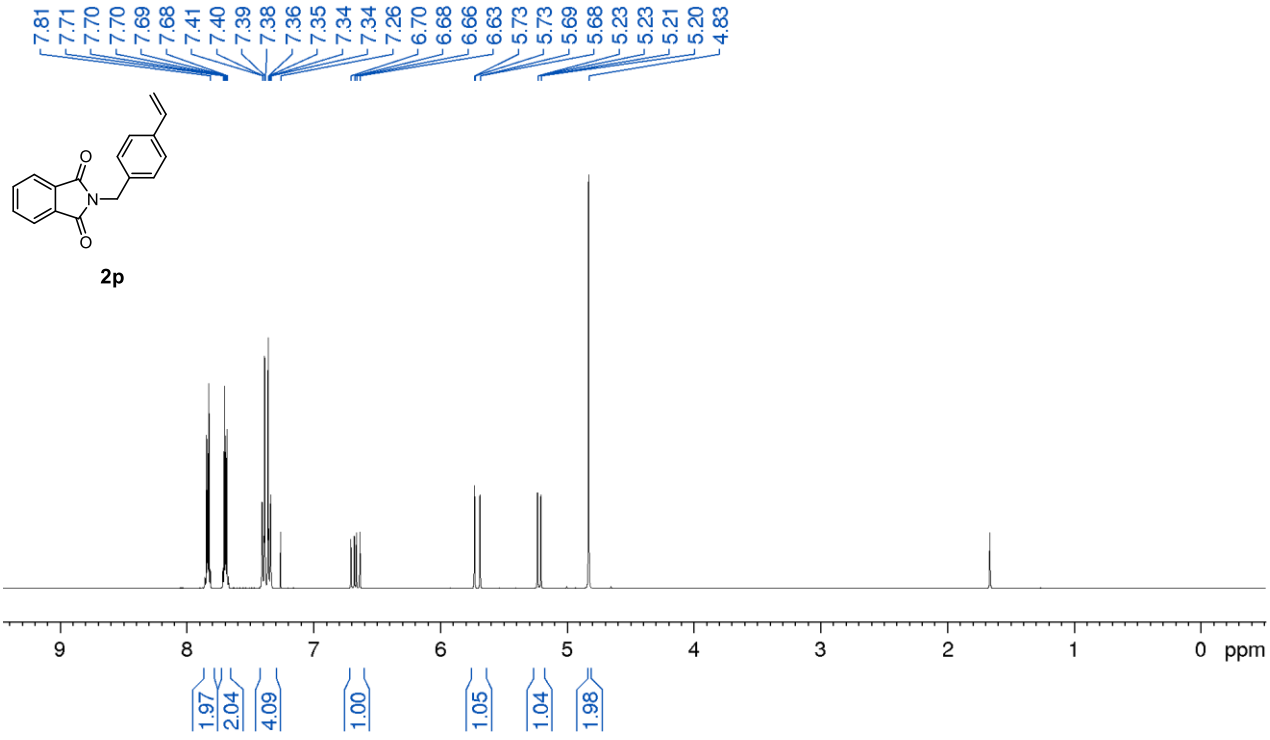
^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) of (2l)



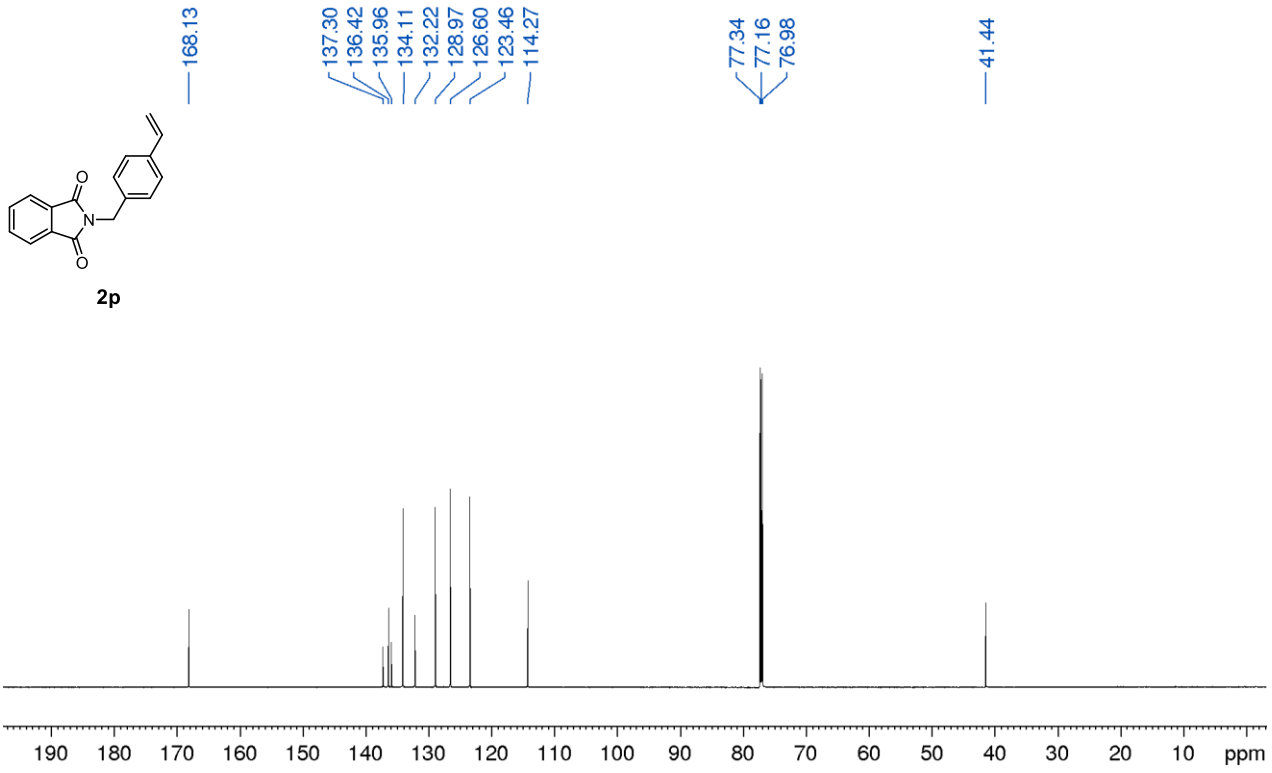
^{19}F NMR (376 MHz, $CDCl_3$, 25 °C) of (2l)



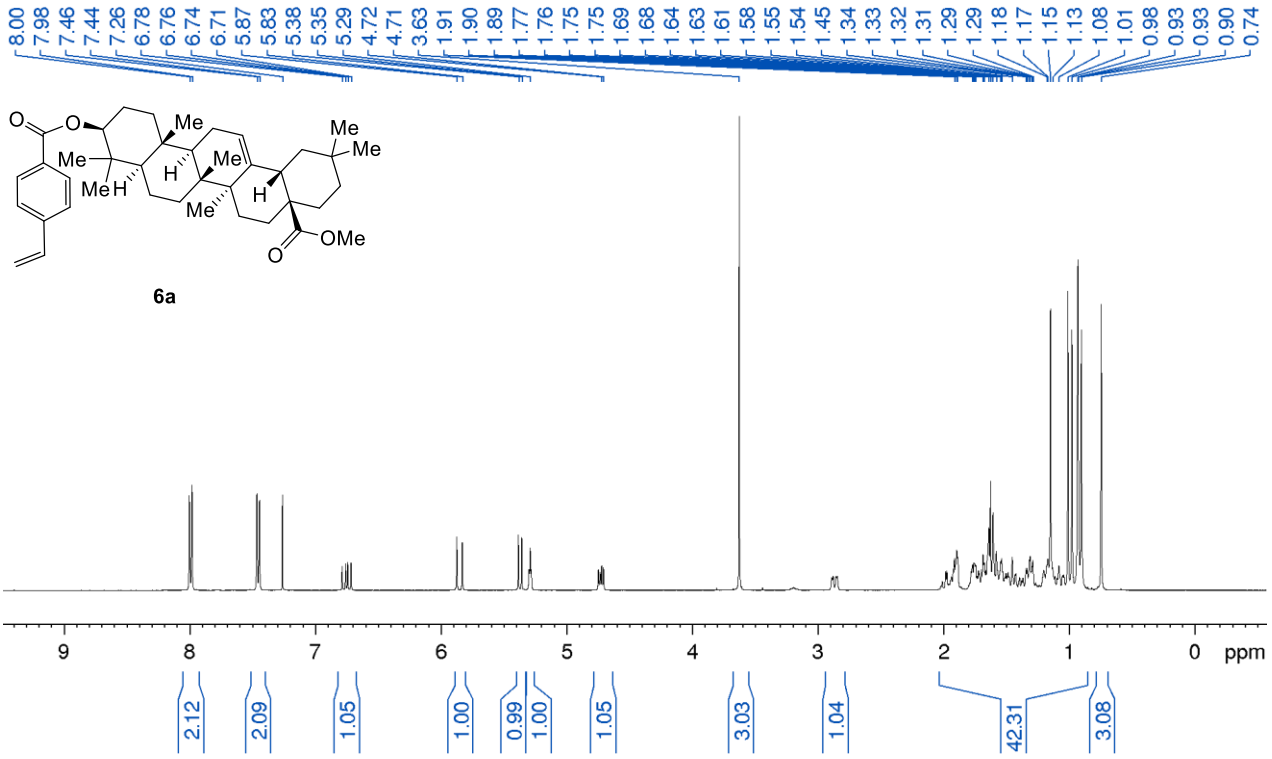
^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) of (2p)



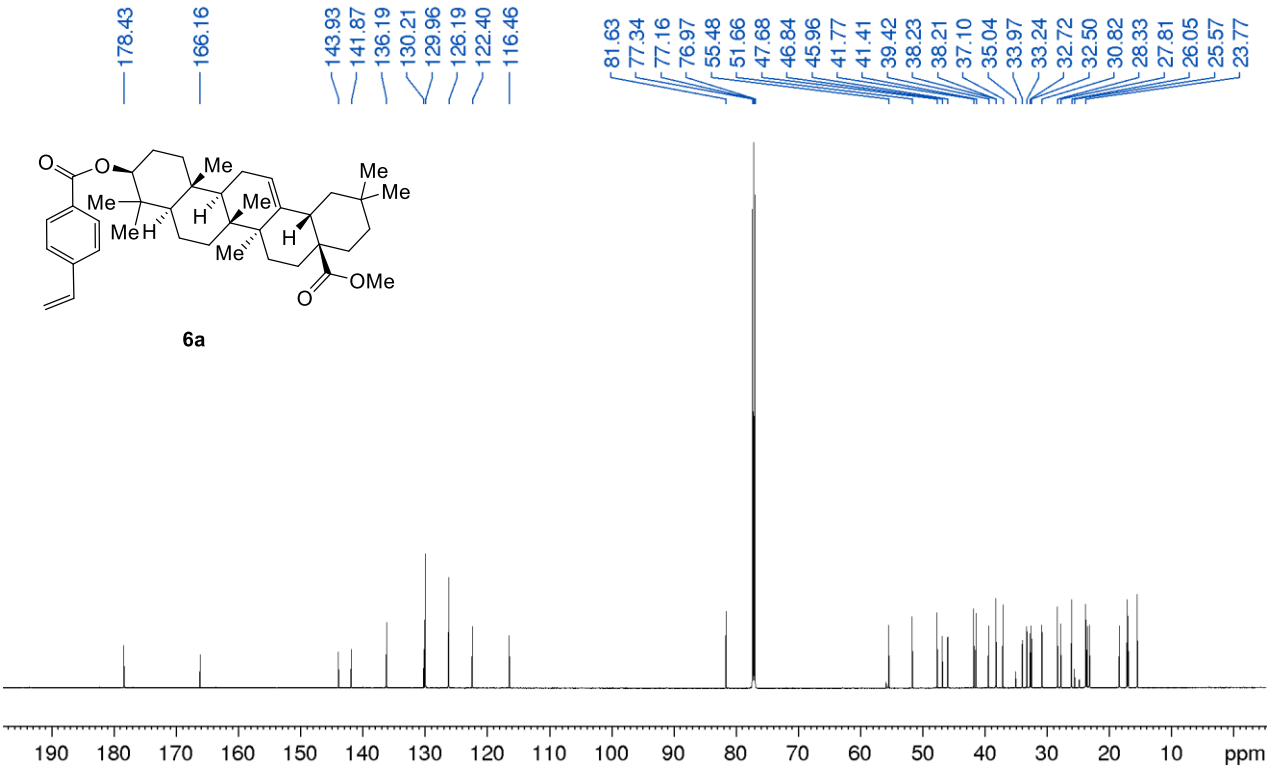
^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC) of (2p)



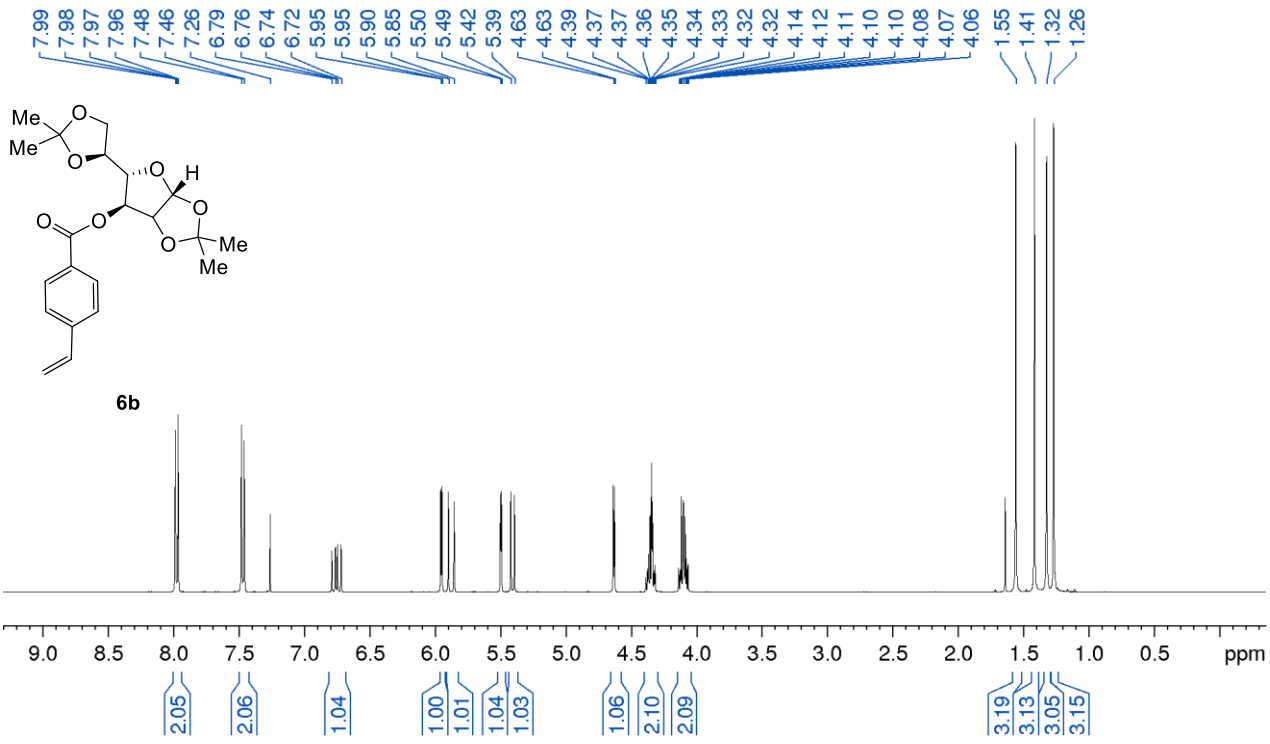
^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC) of (6a)



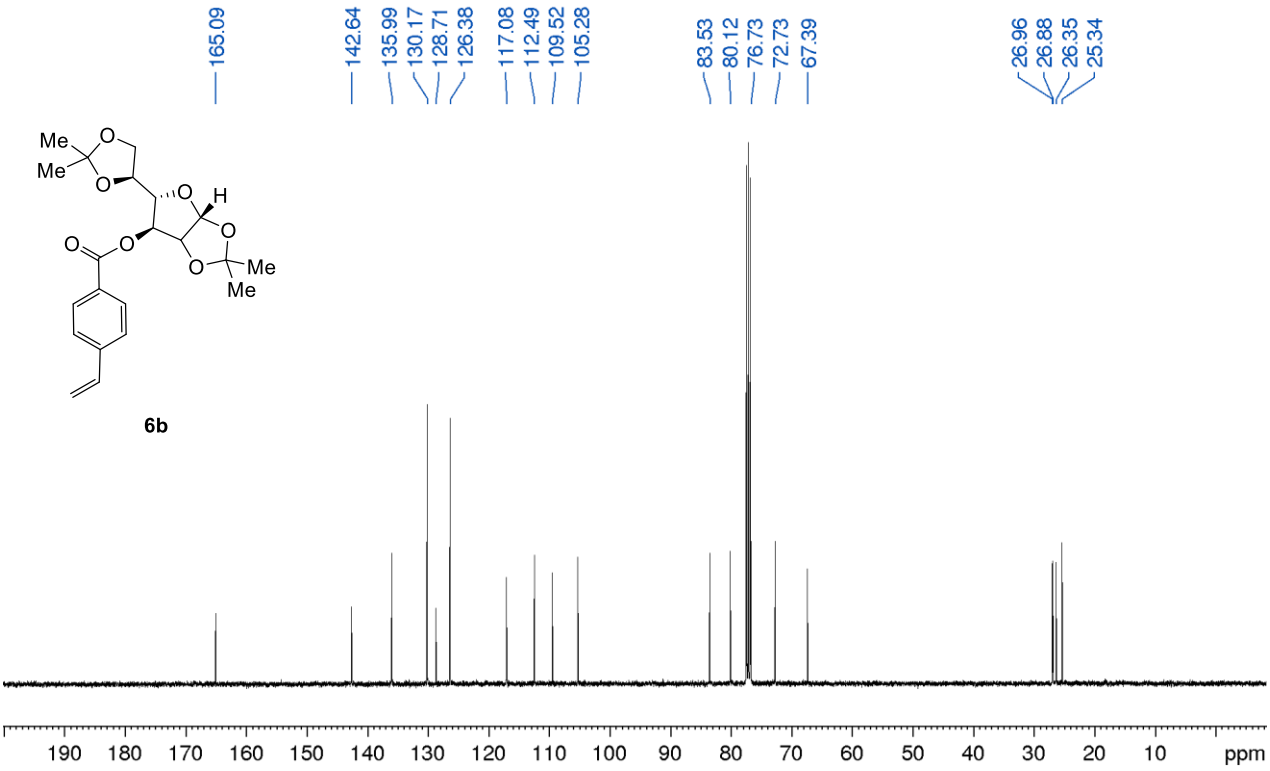
^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC) of (6a)



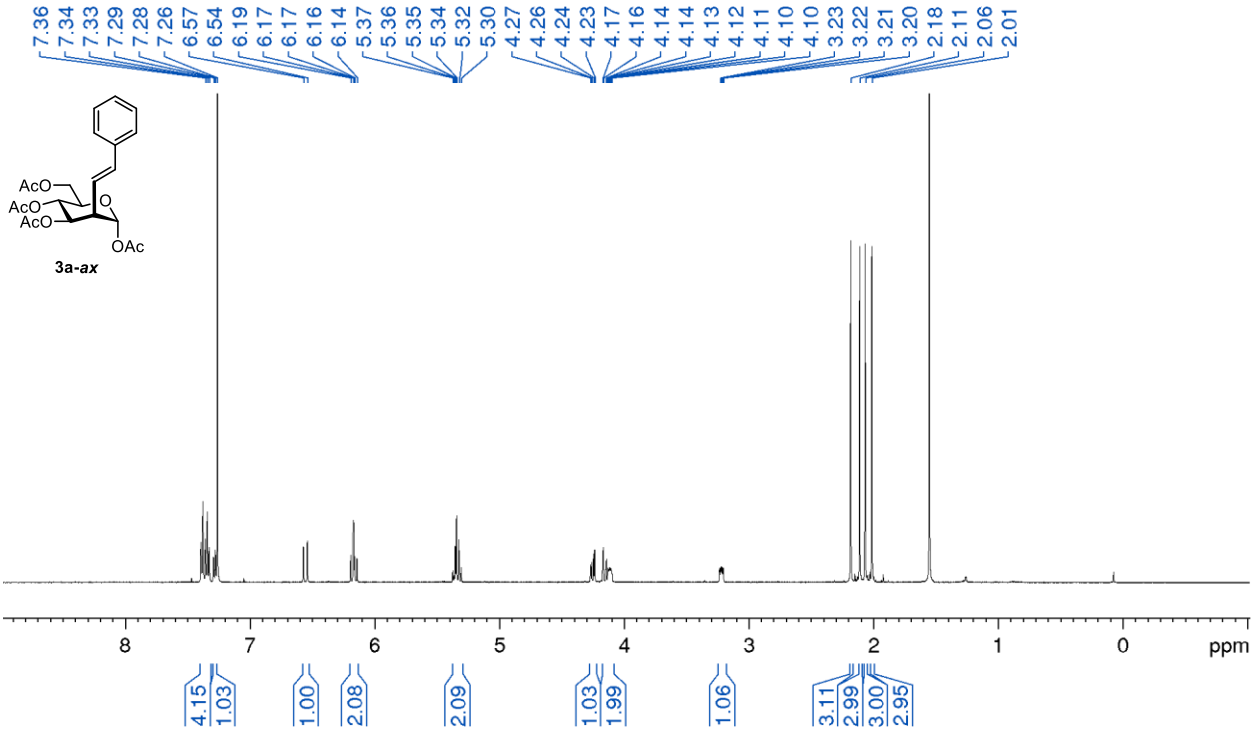
^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC) of (6b)



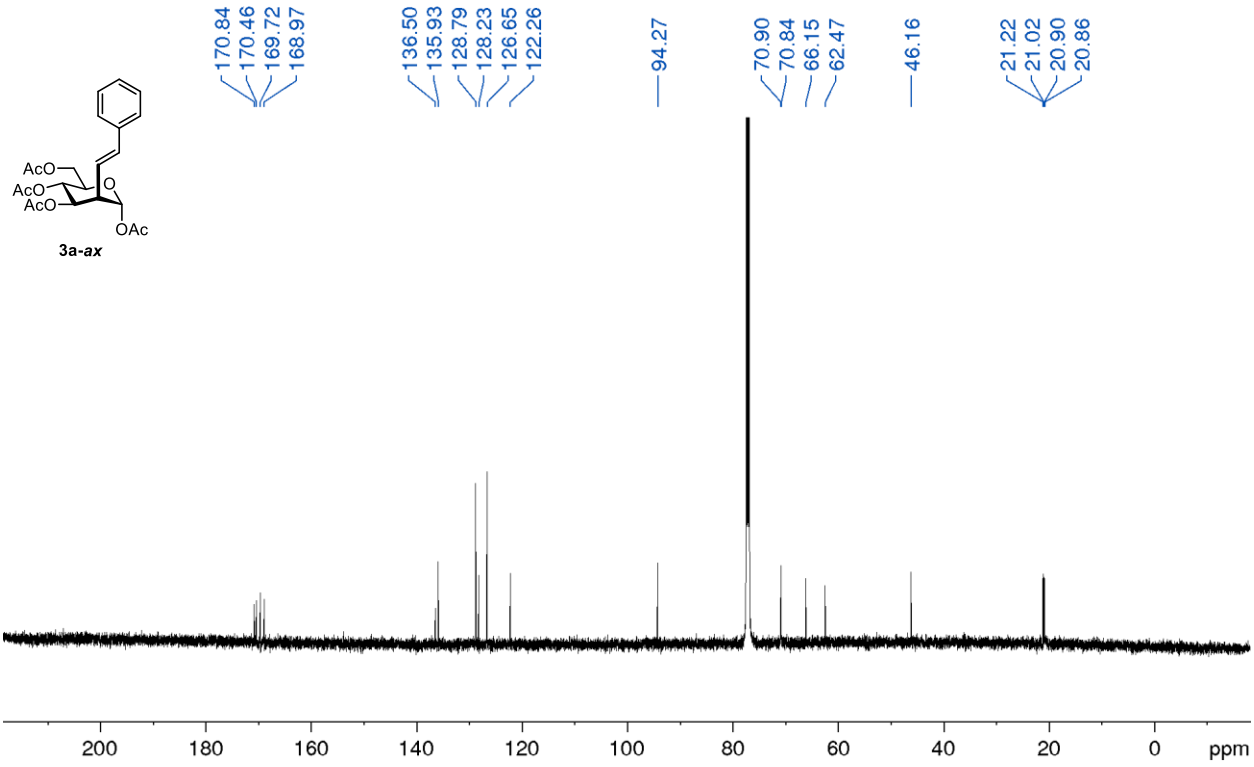
^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC) of (6b)



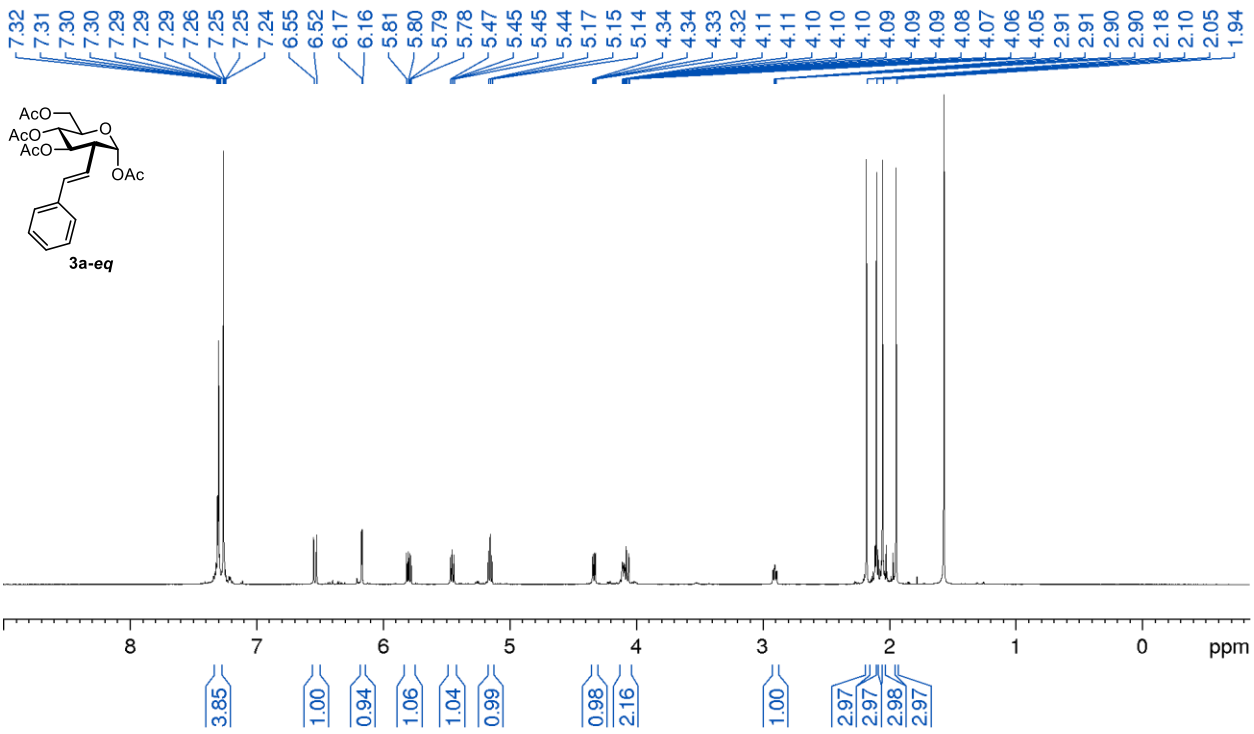
^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC) of (3a-*ax*)



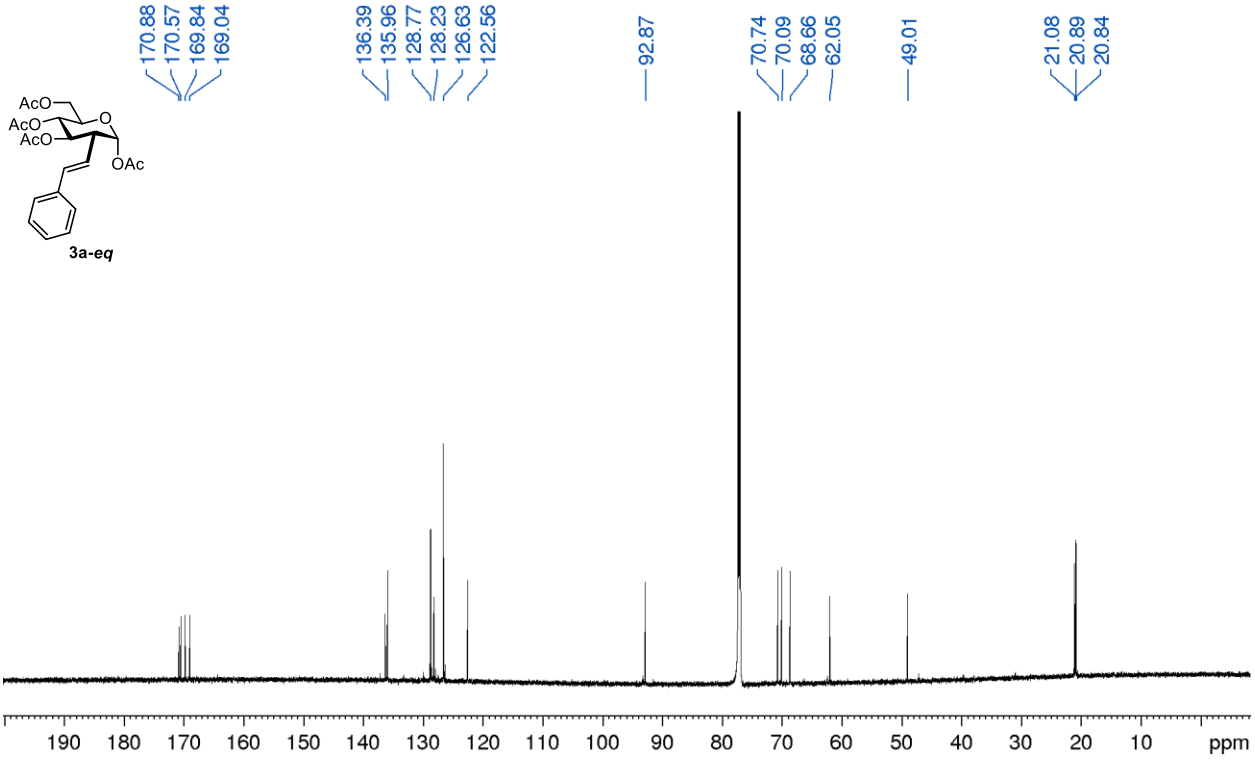
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (3a-*ax*)



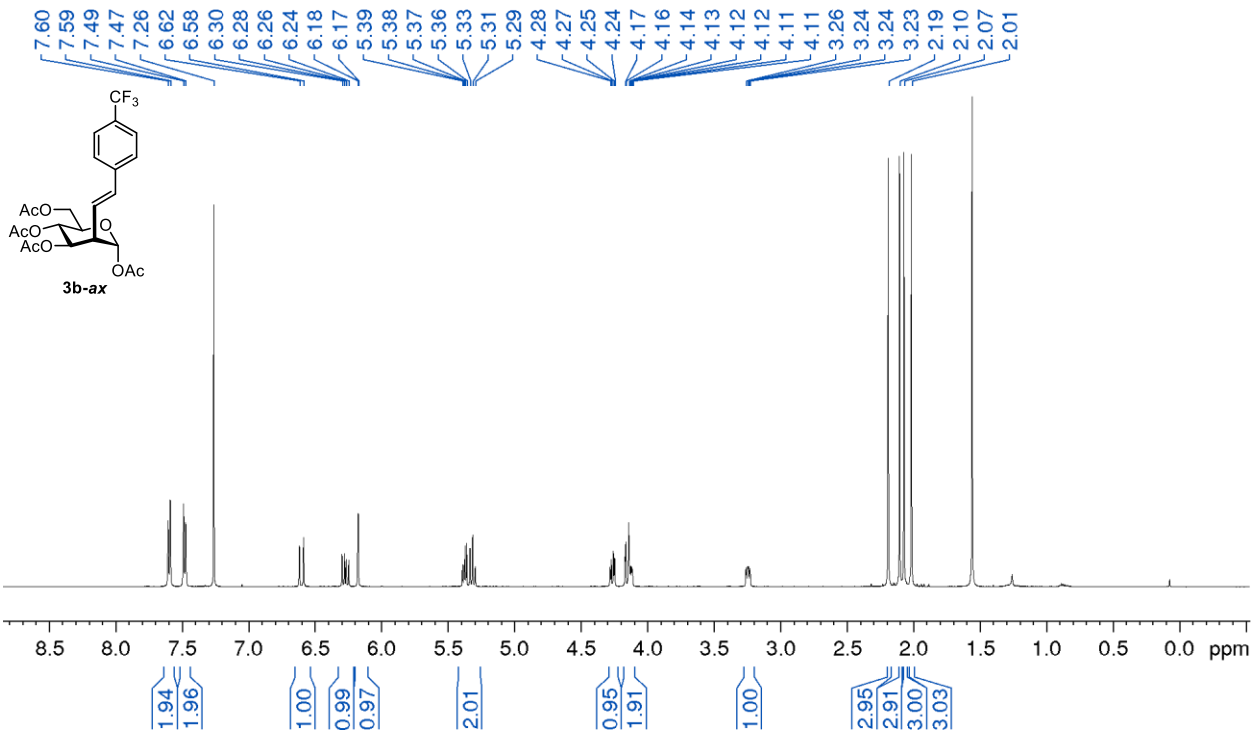
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (3a-*eq*)



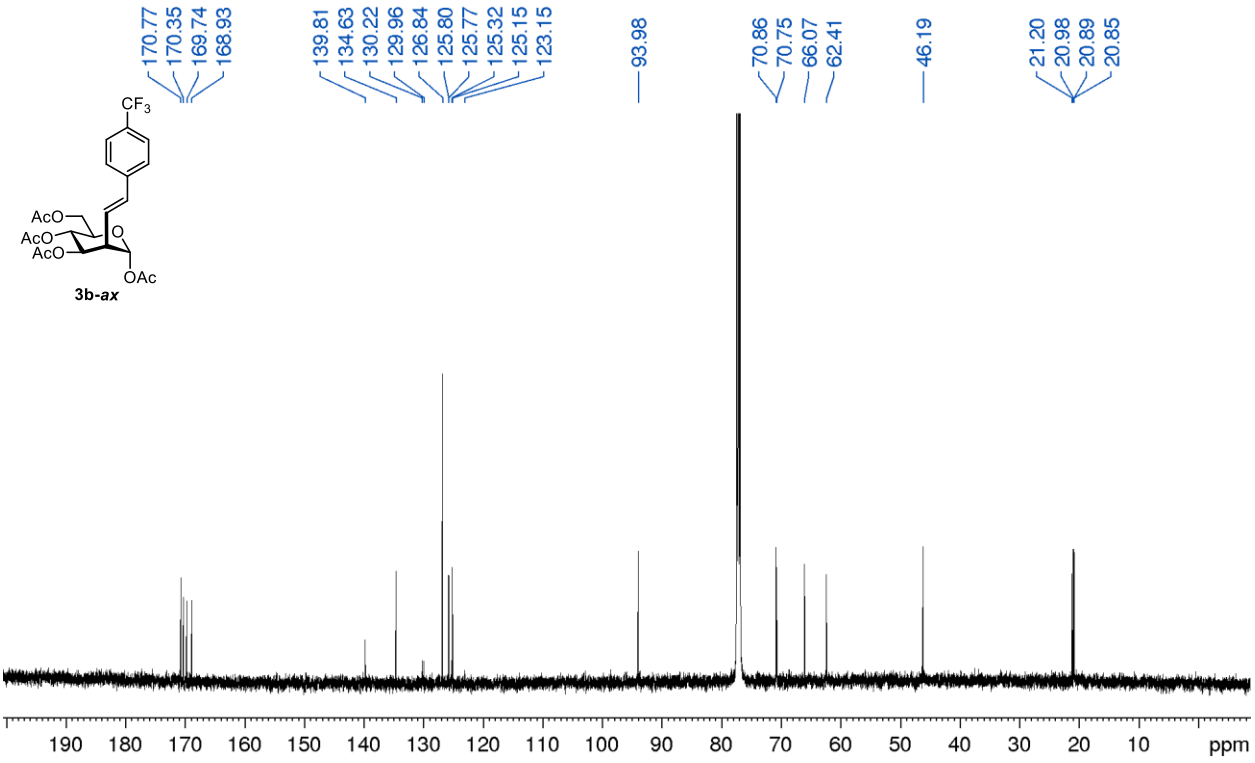
^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC) of (3a-*eq*)



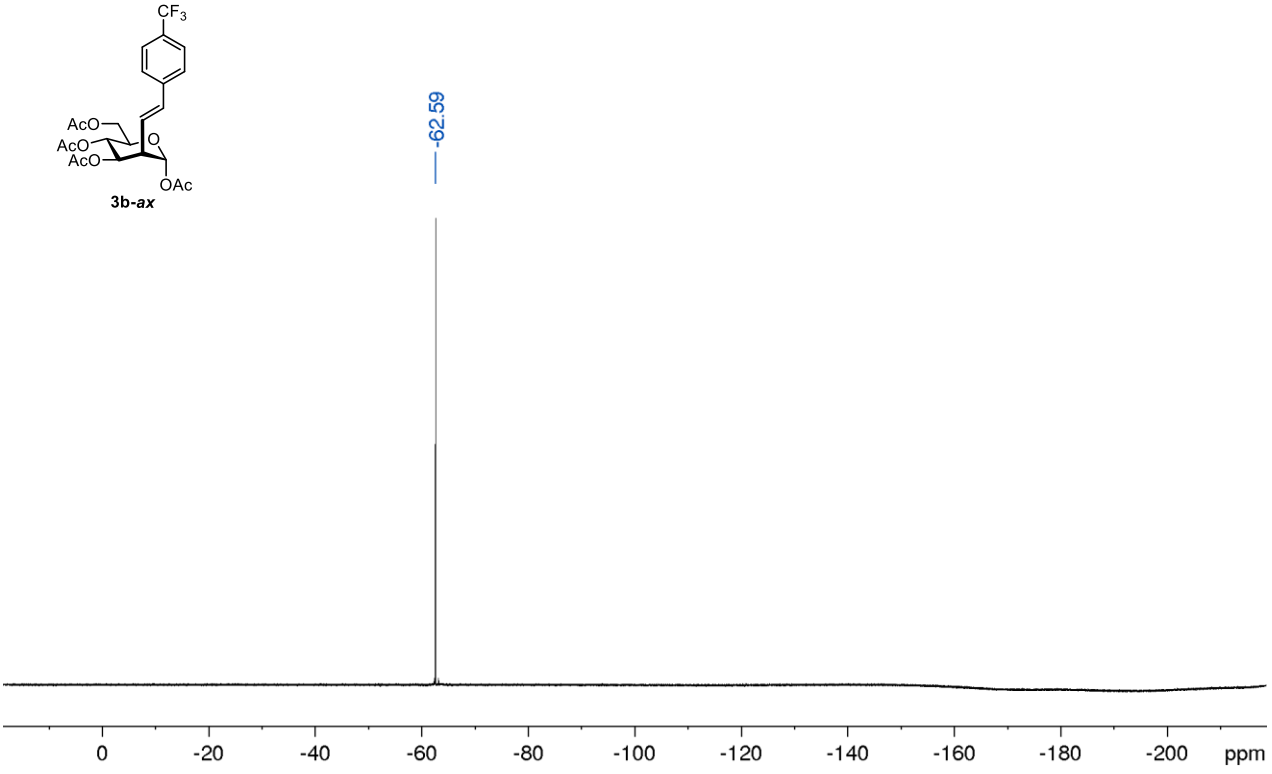
^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC) of (3b-*ax*)



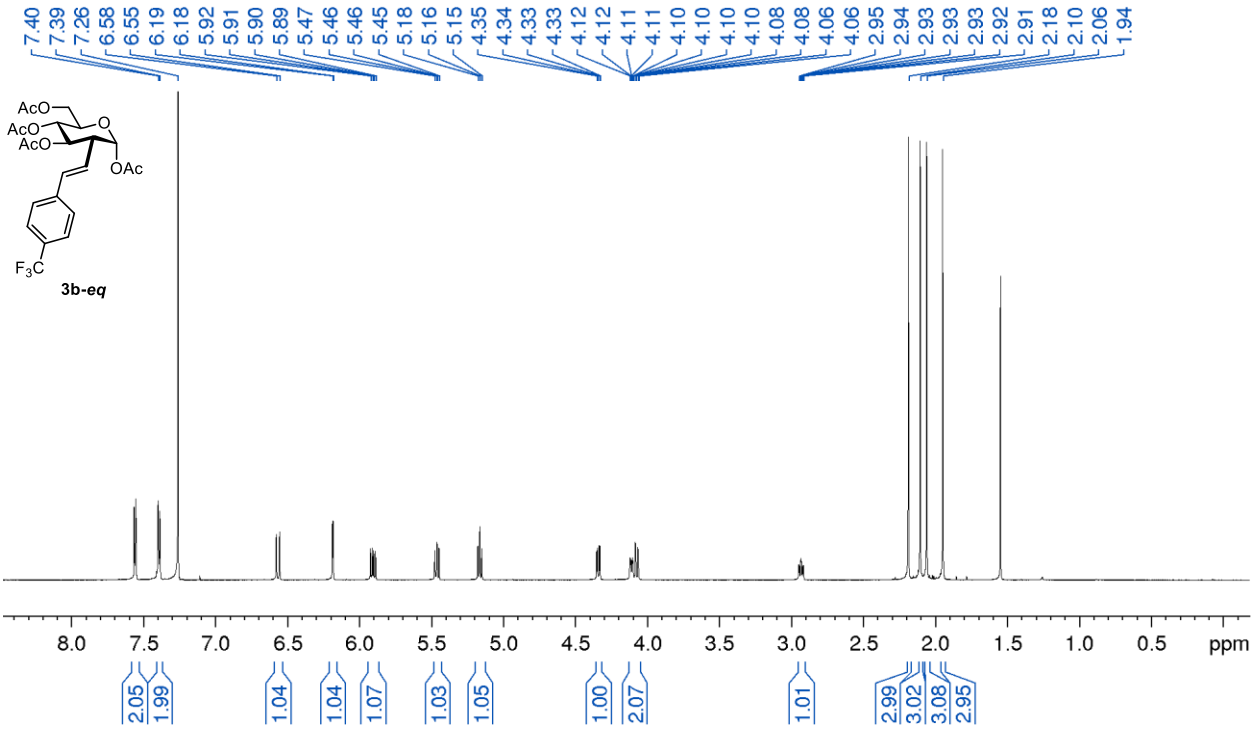
^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC) of (3b-*ax*)



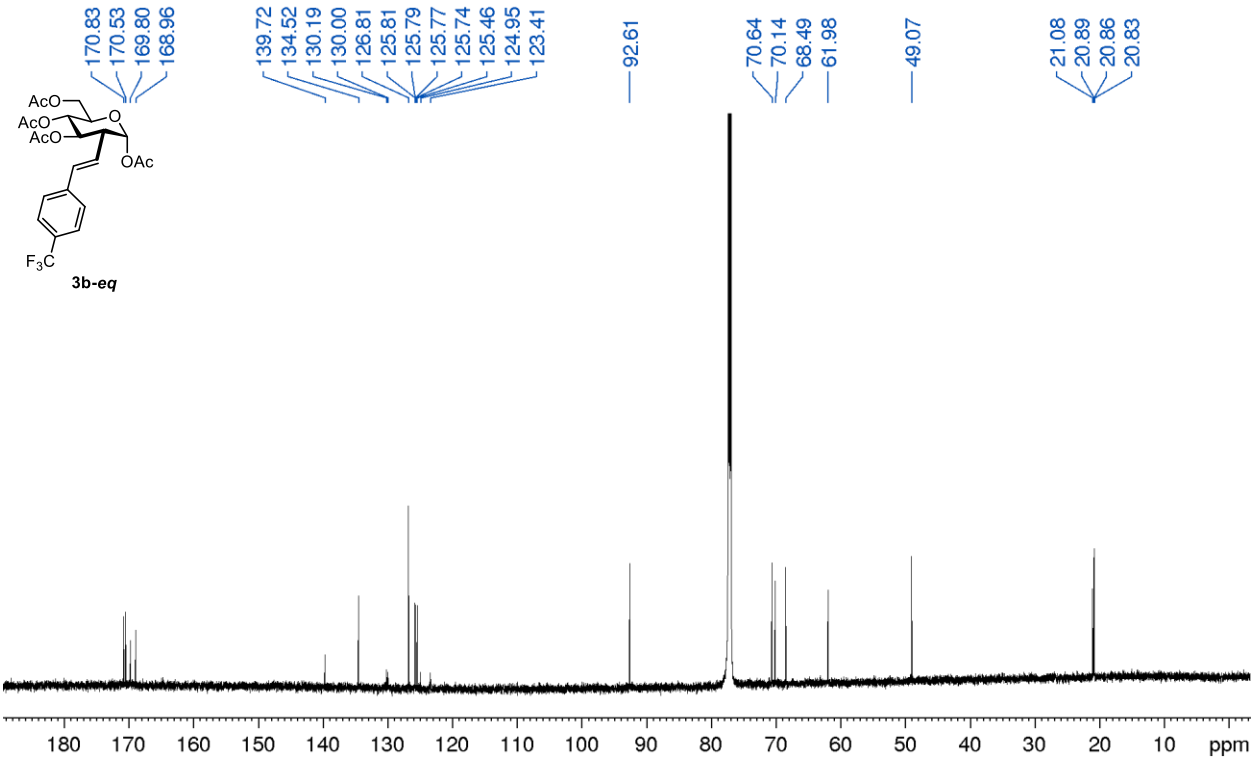
^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC) of (3b-*ax*)



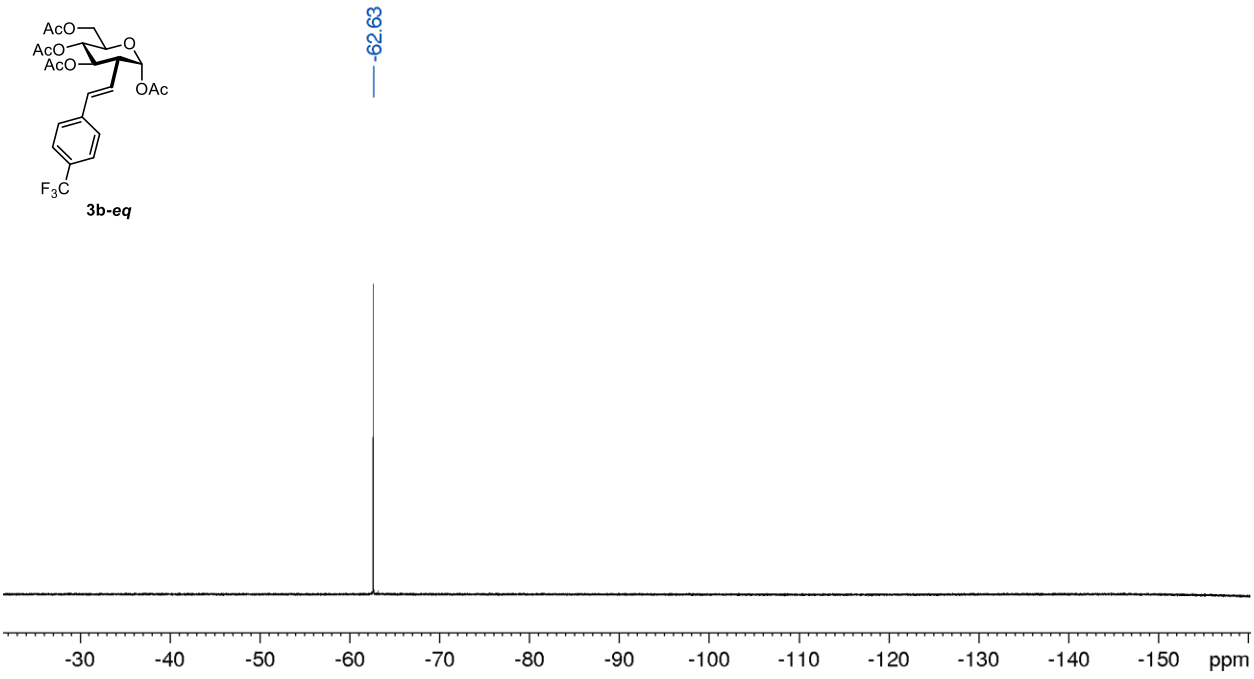
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3b-*eq*)



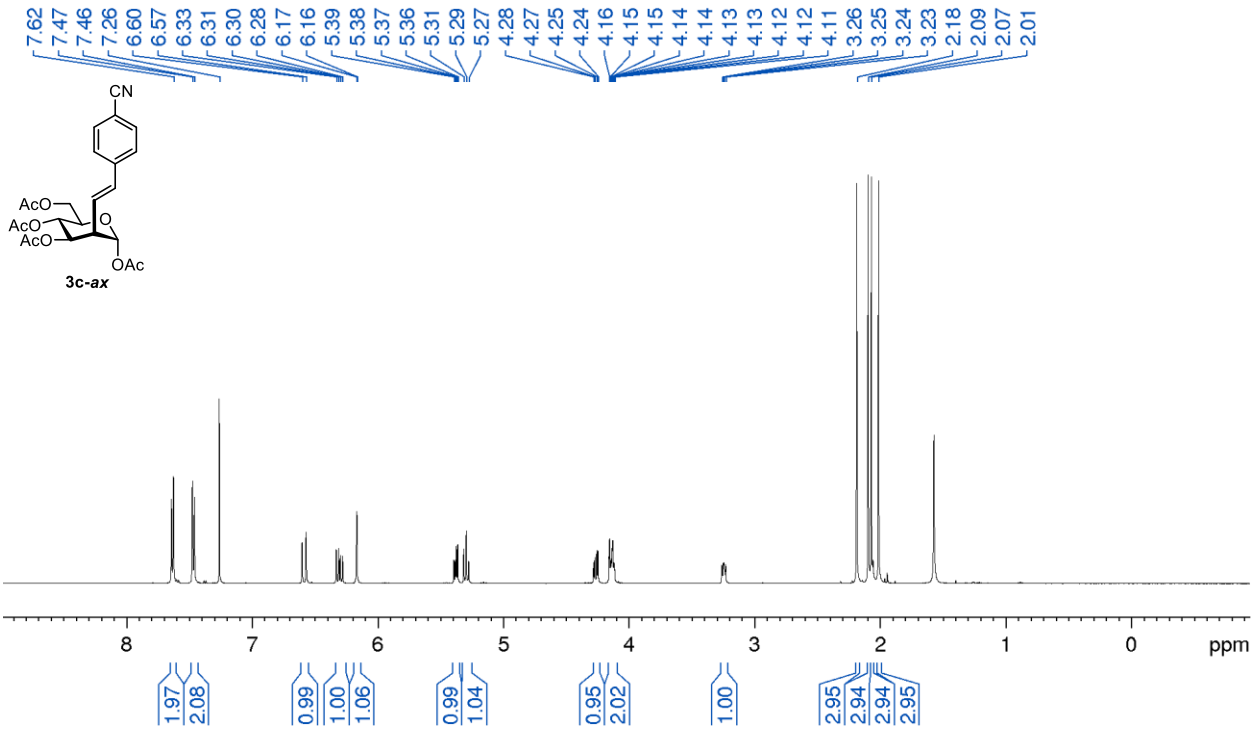
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3b-*eq*)



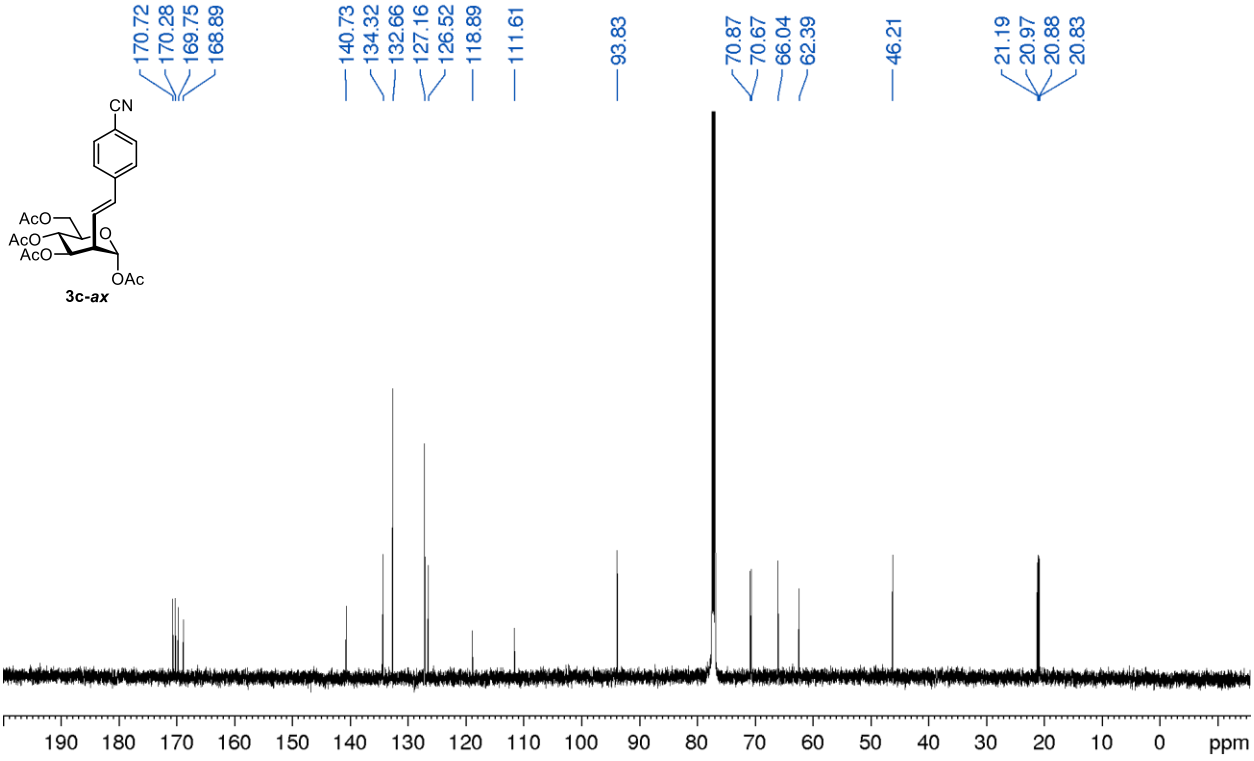
^{19}F NMR (376 MHz, $CDCl_3$, 25 °C) of (3b-*eq*)



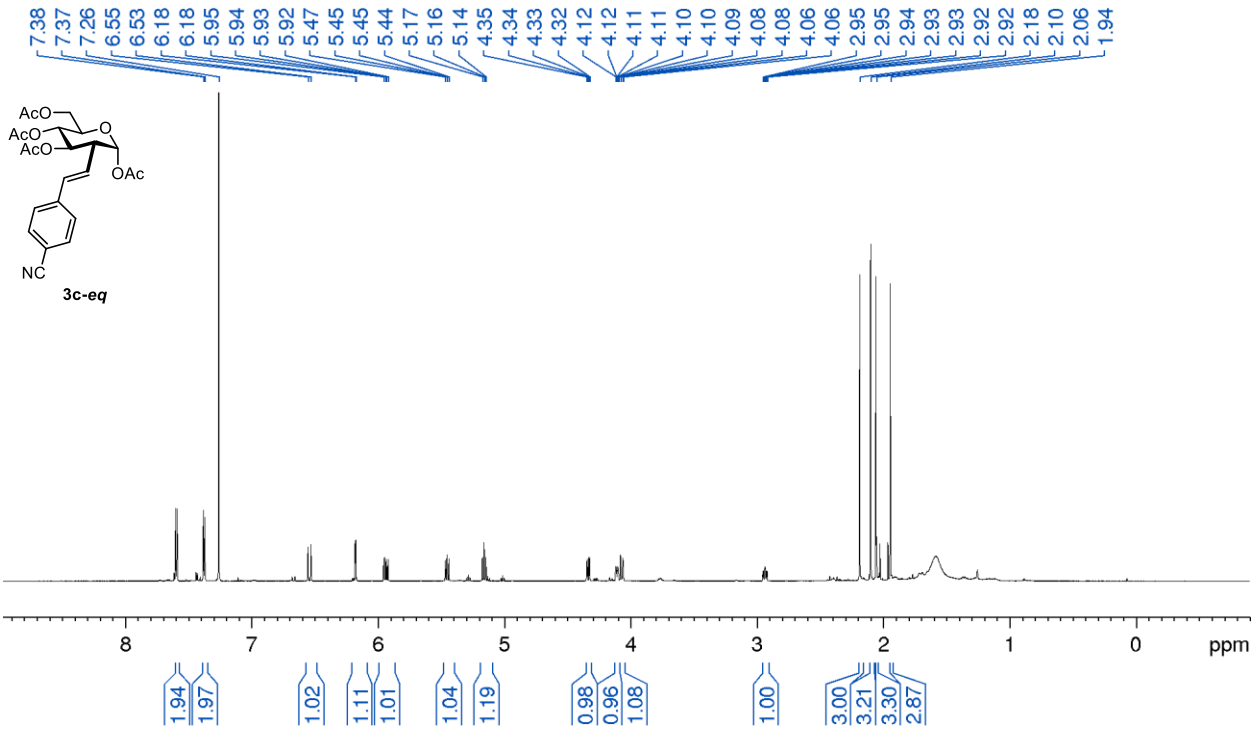
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (3c-*ax*)



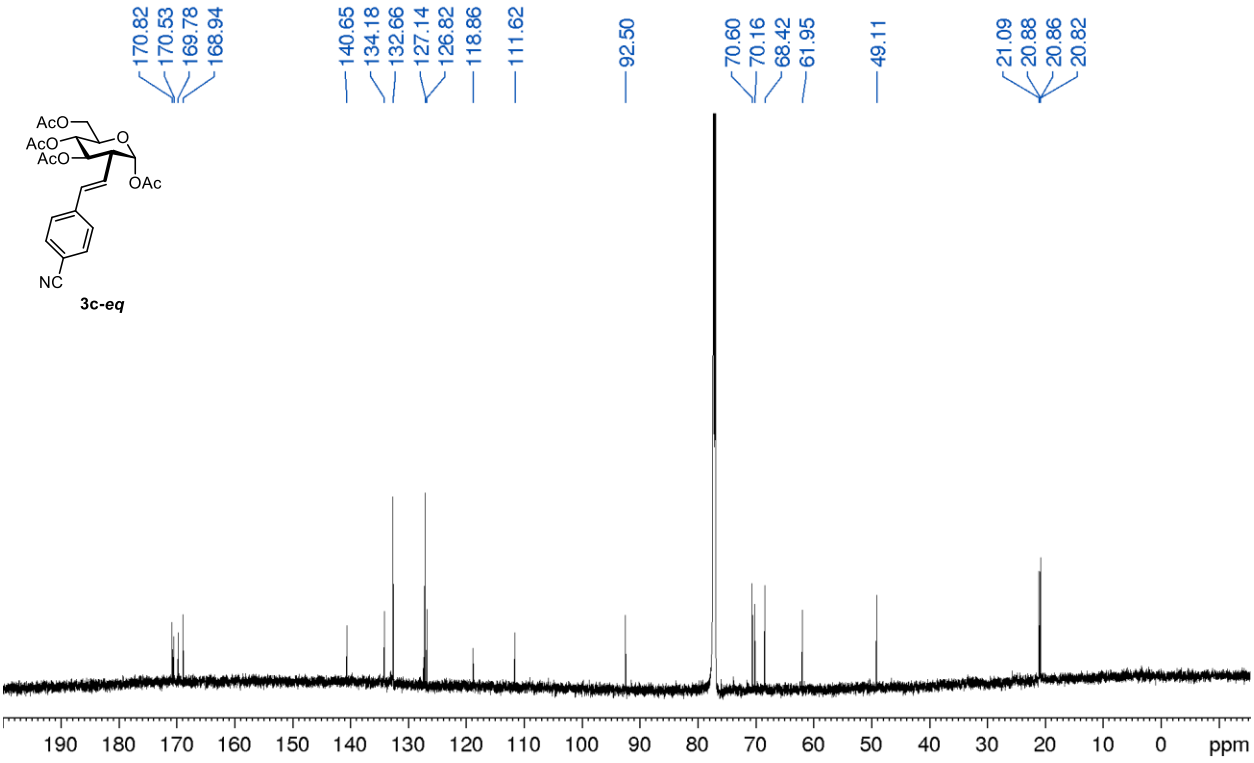
^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC) of (3c-*ax*)



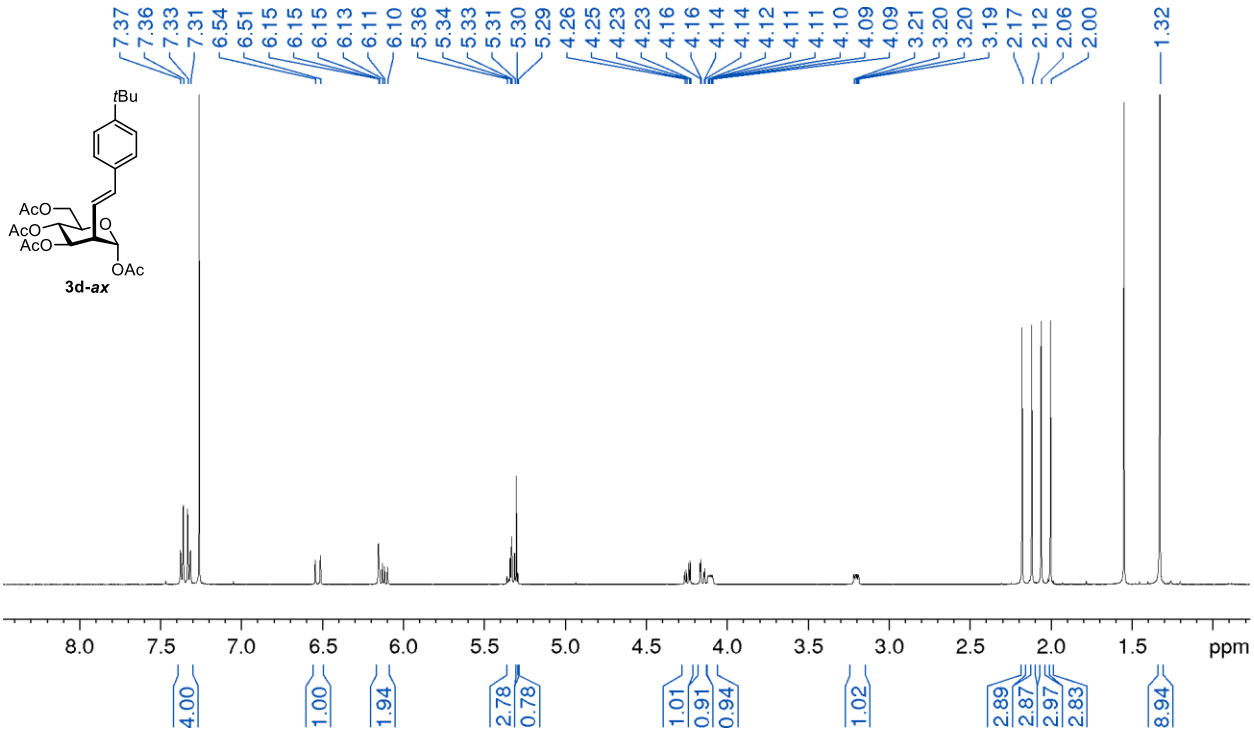
^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC) of (3c-*eq*)



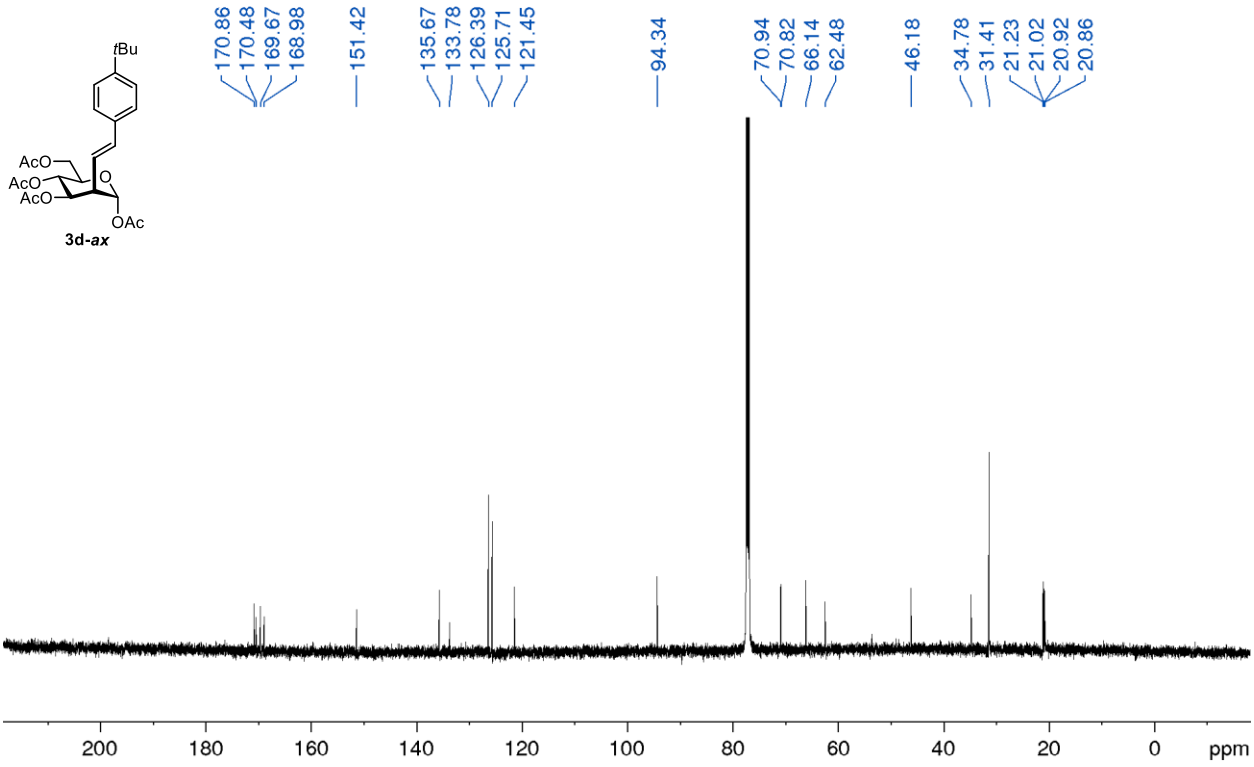
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3c-*eq*)



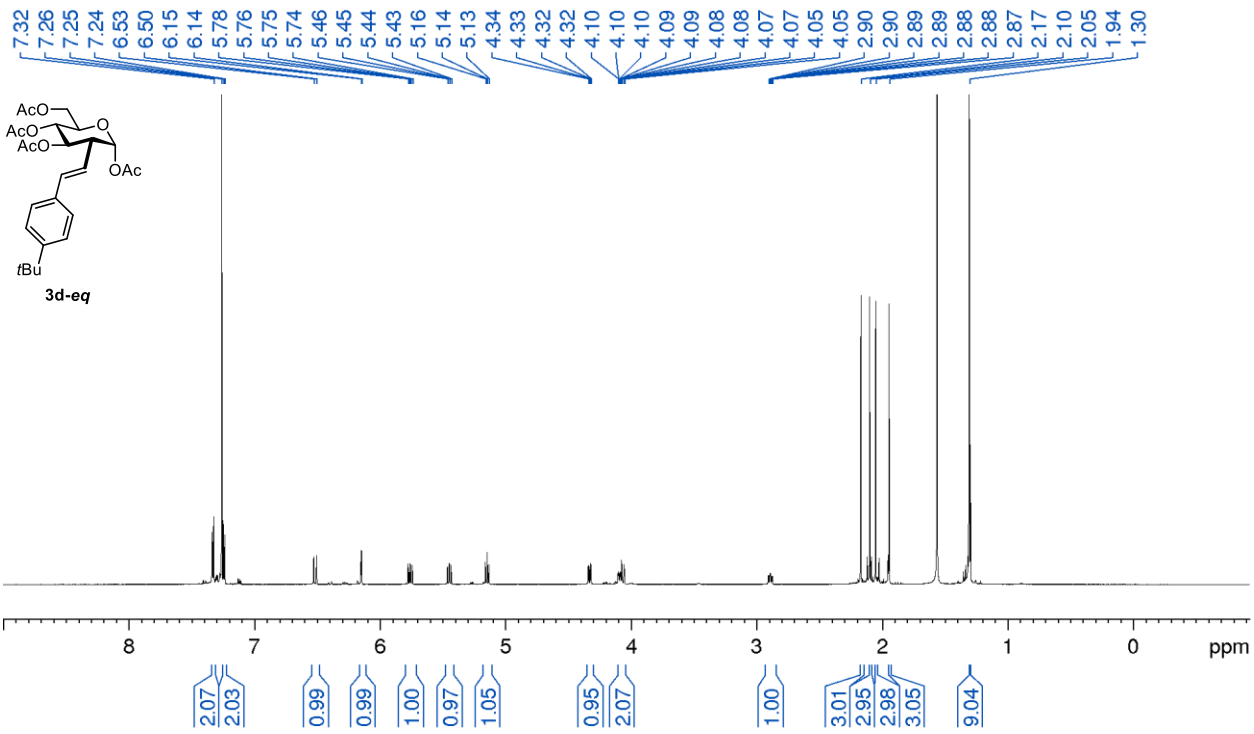
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (3d-*ax*)



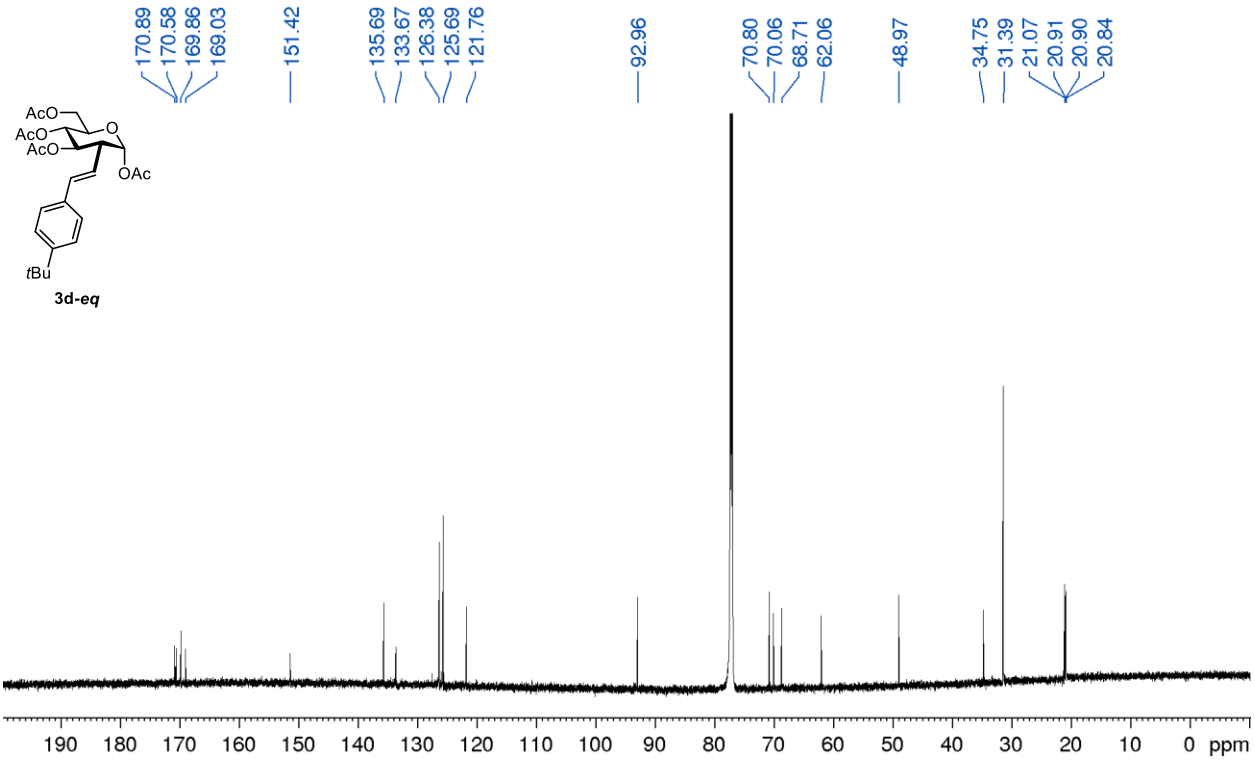
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (3d-*ax*)



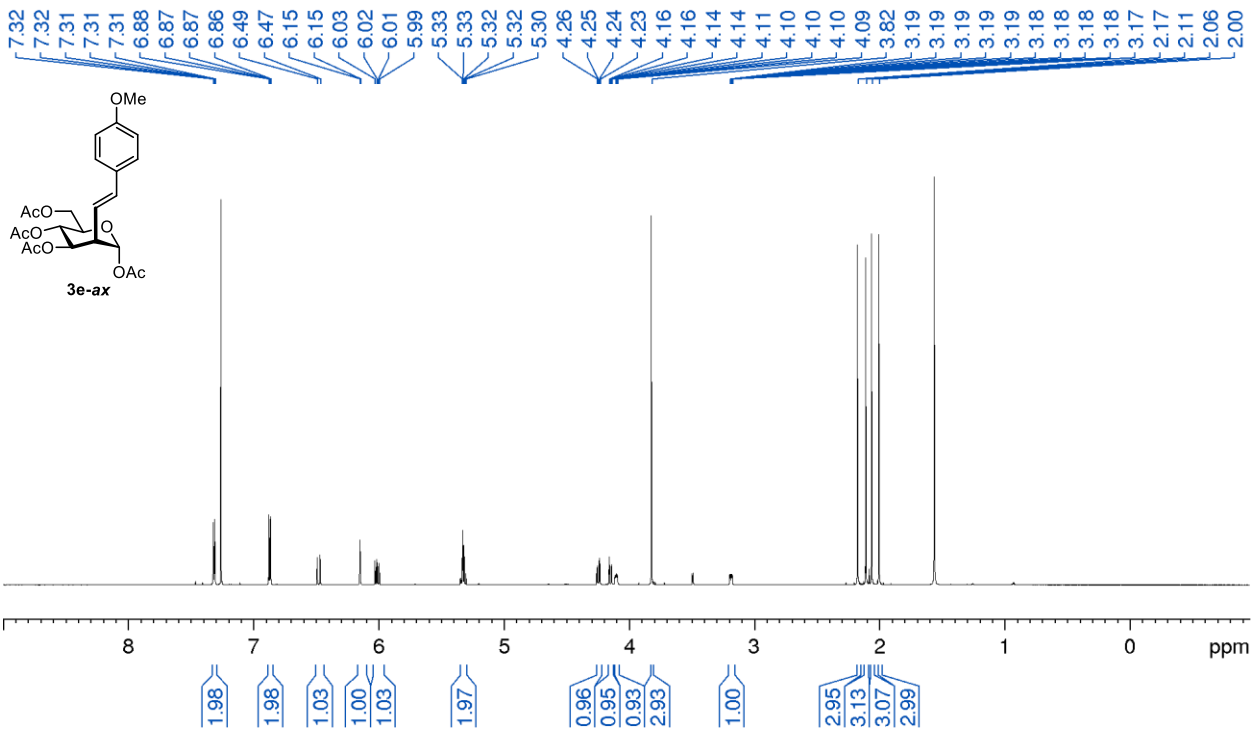
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3d-*eq*)



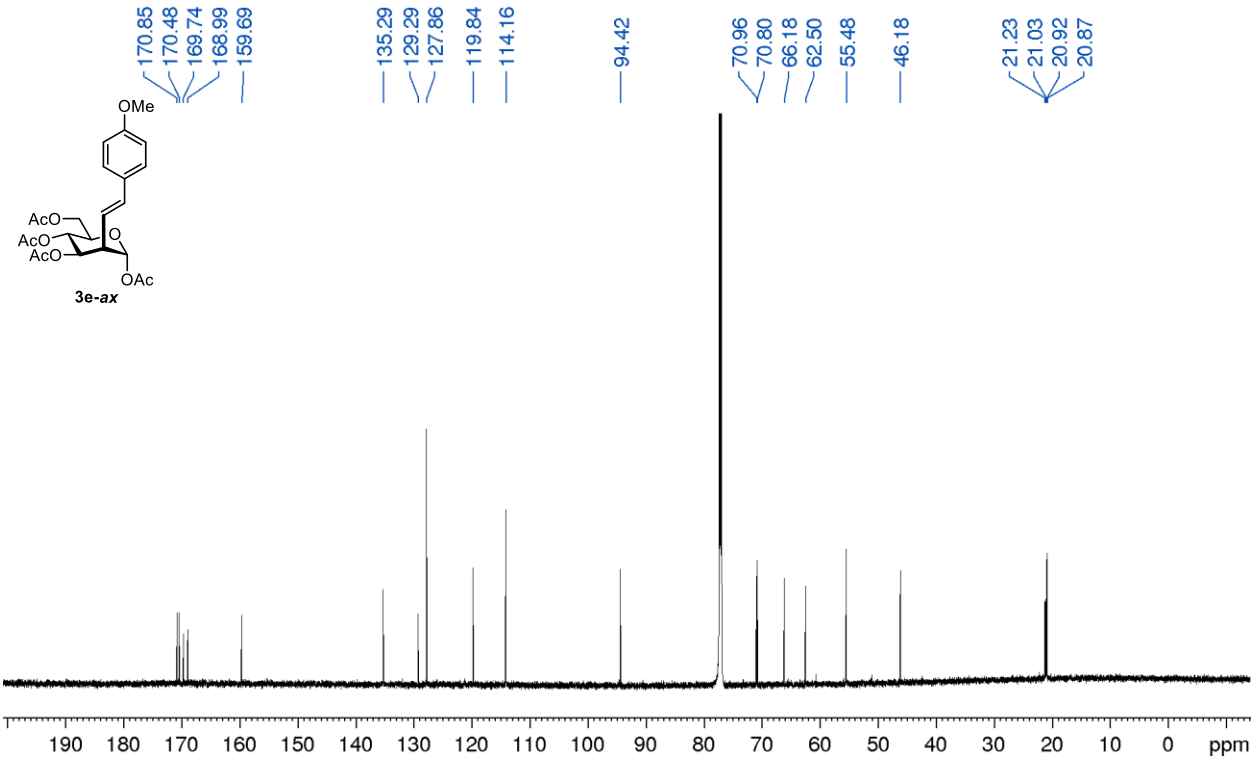
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3d-*eq*)



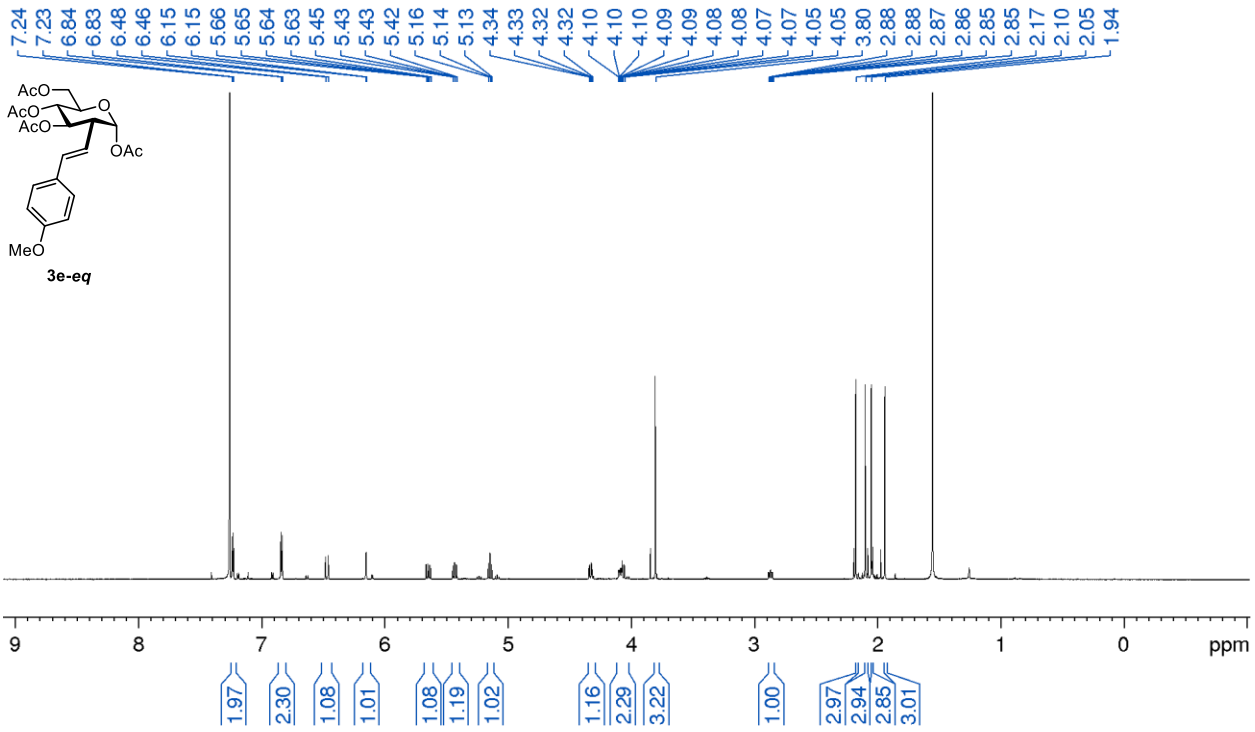
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3e-*ax*)



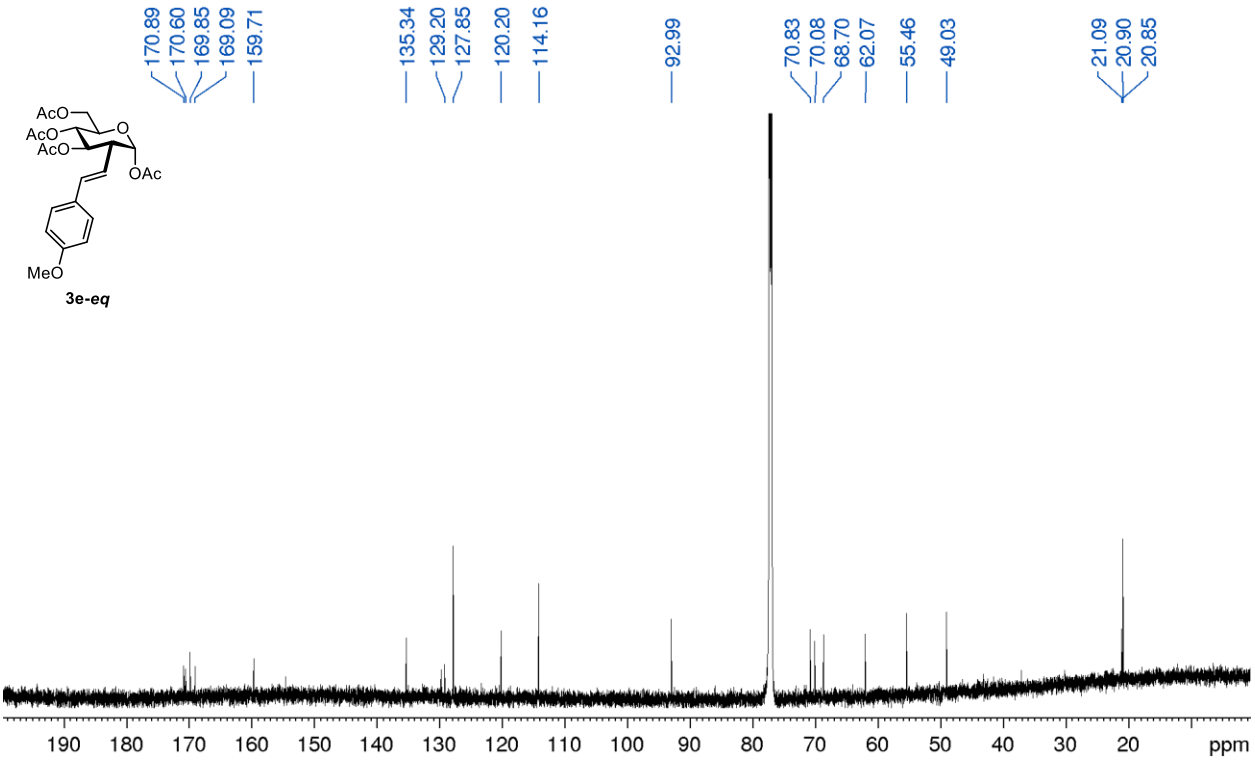
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3e-*ax*)



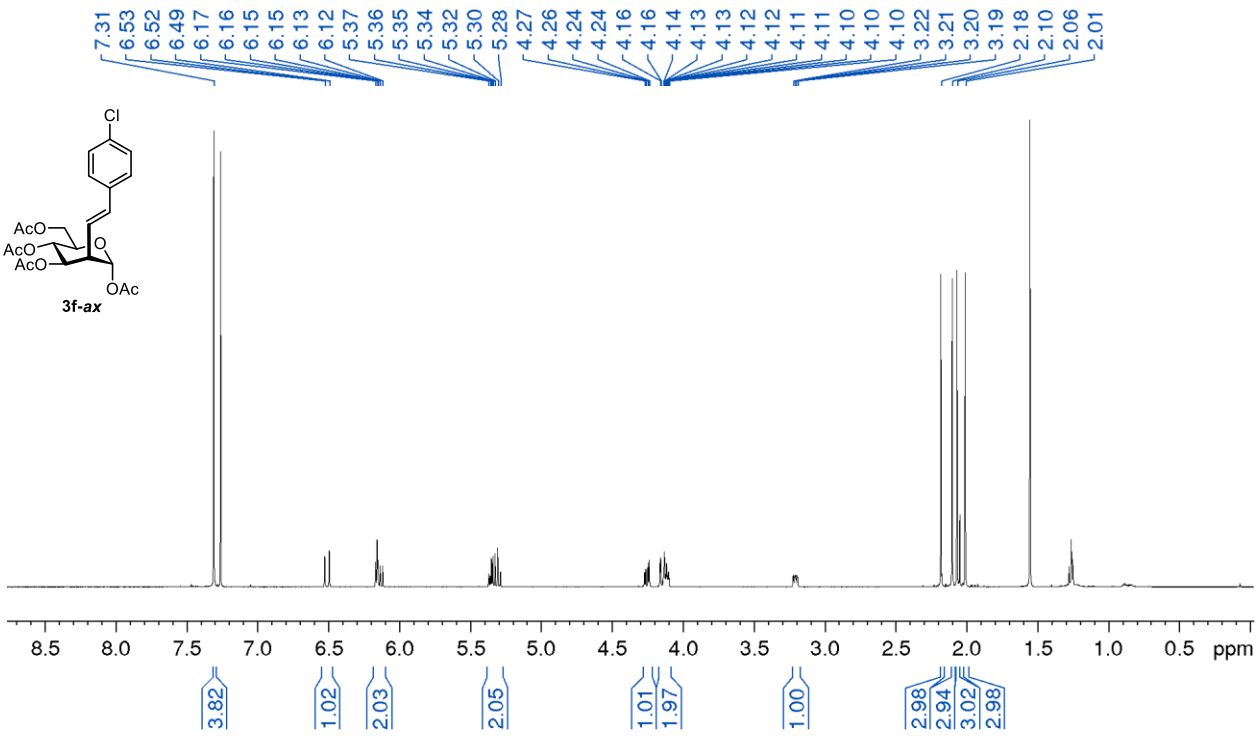
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3e-*eq*)



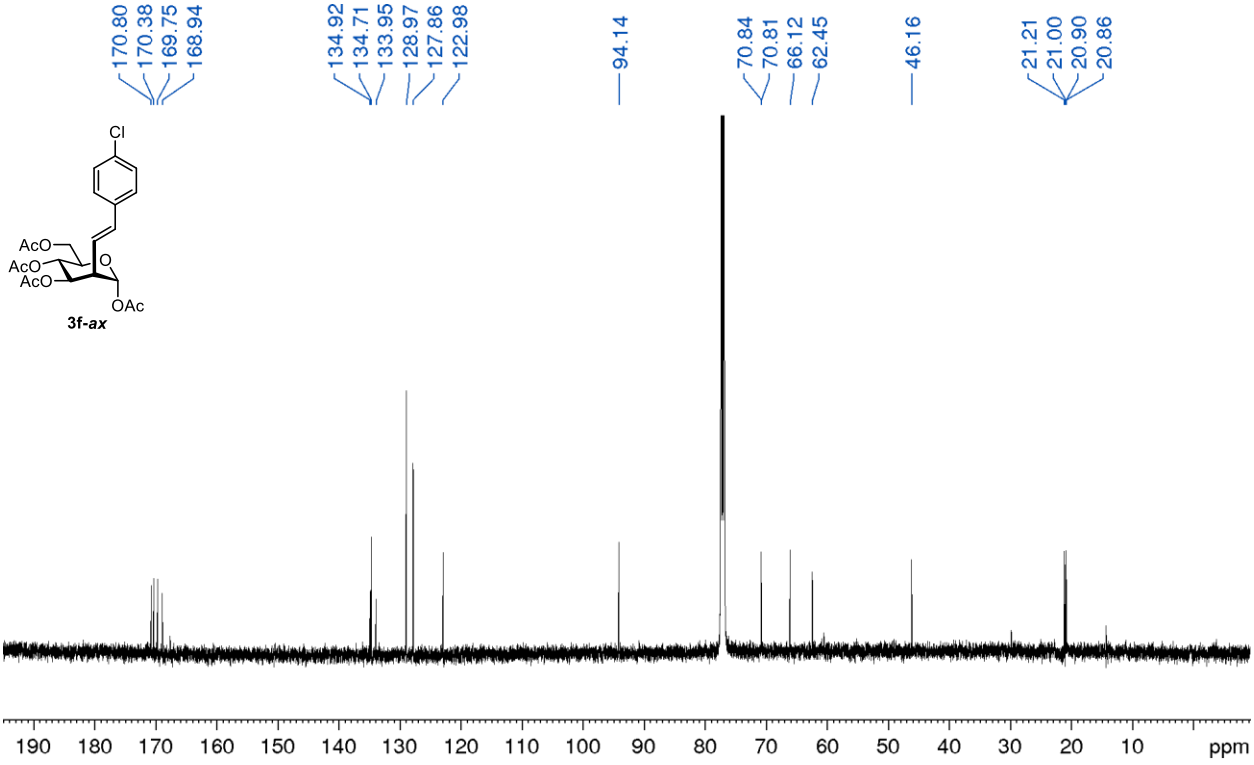
^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC) of (3e-*eq*)



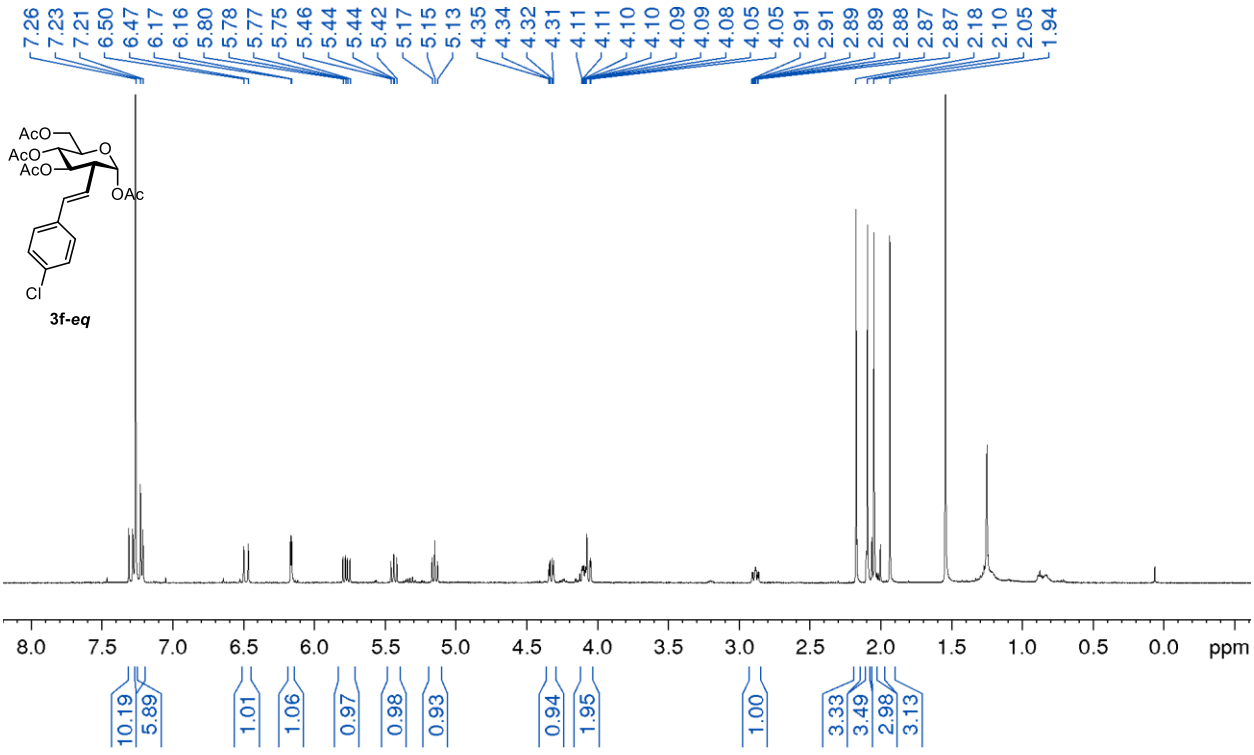
^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC) of (3f-*ax*)



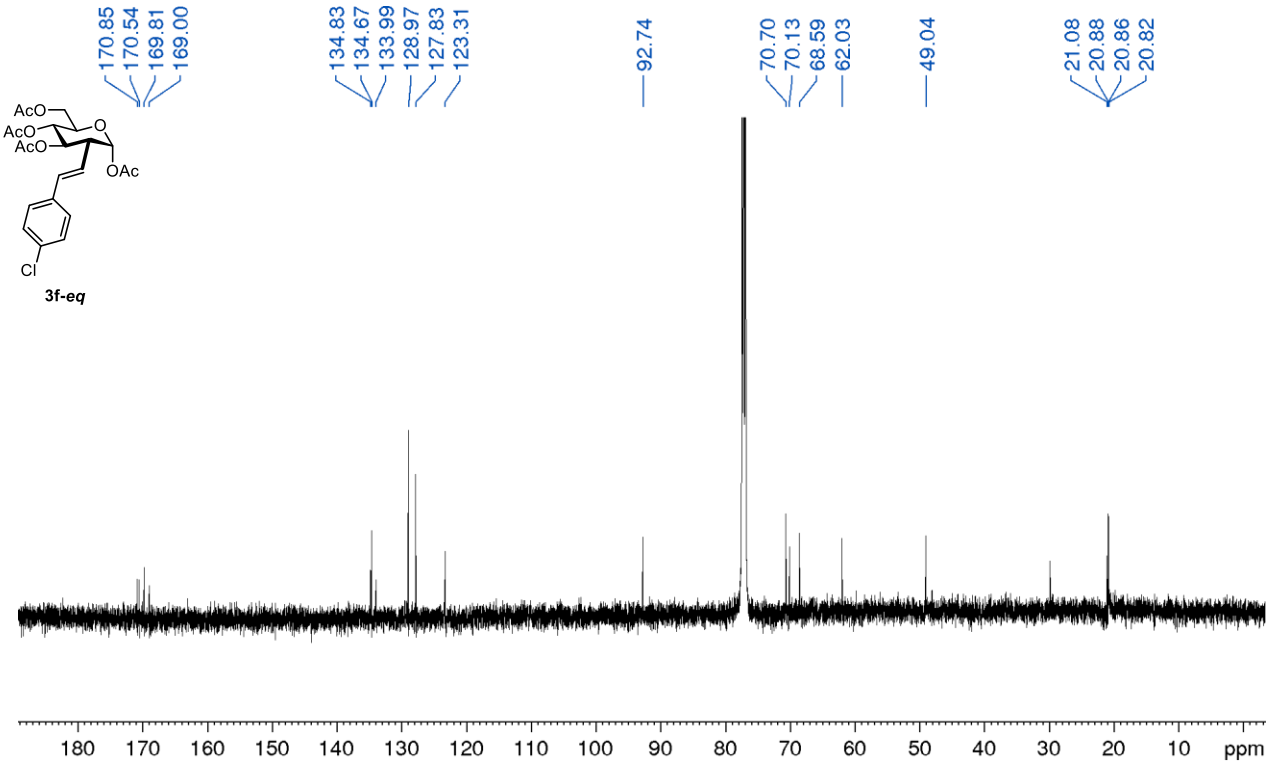
^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC) of (3f-*ax*)



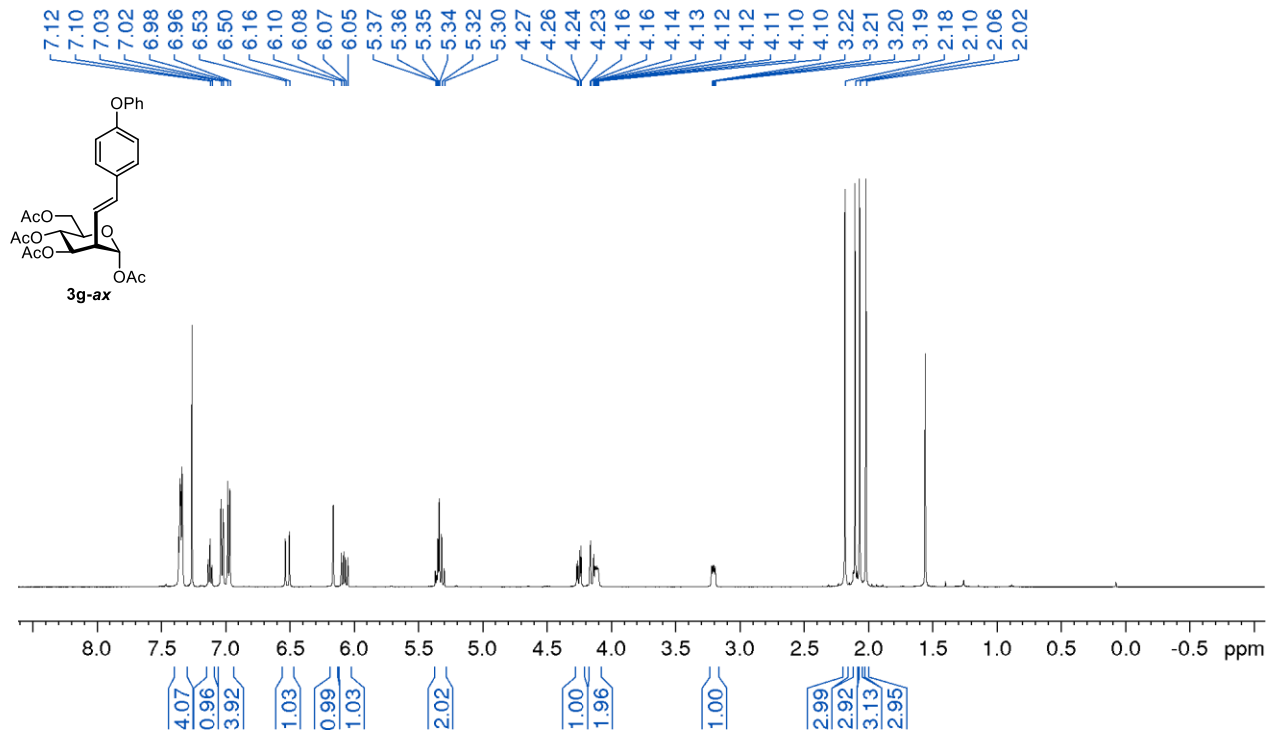
^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC) of (3f-*eq*)



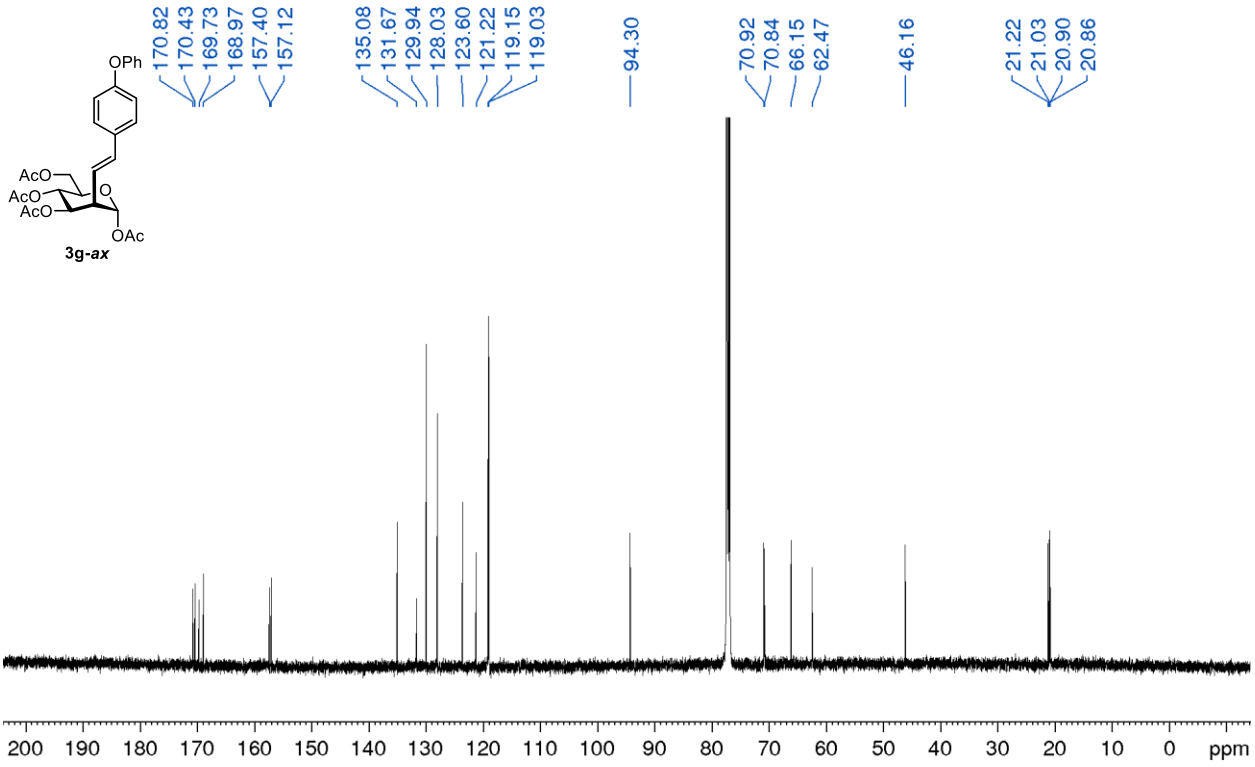
^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC) of (3f-*eq*)



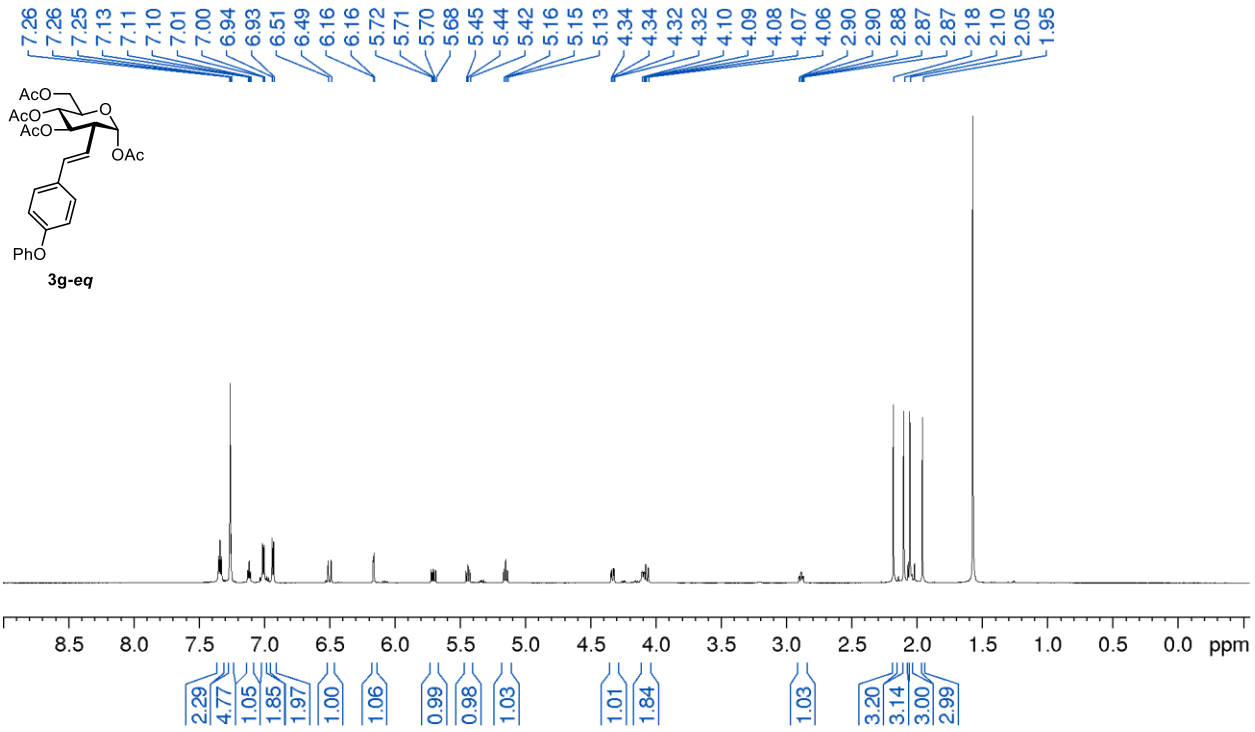
^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC) of (3g-*ax*)



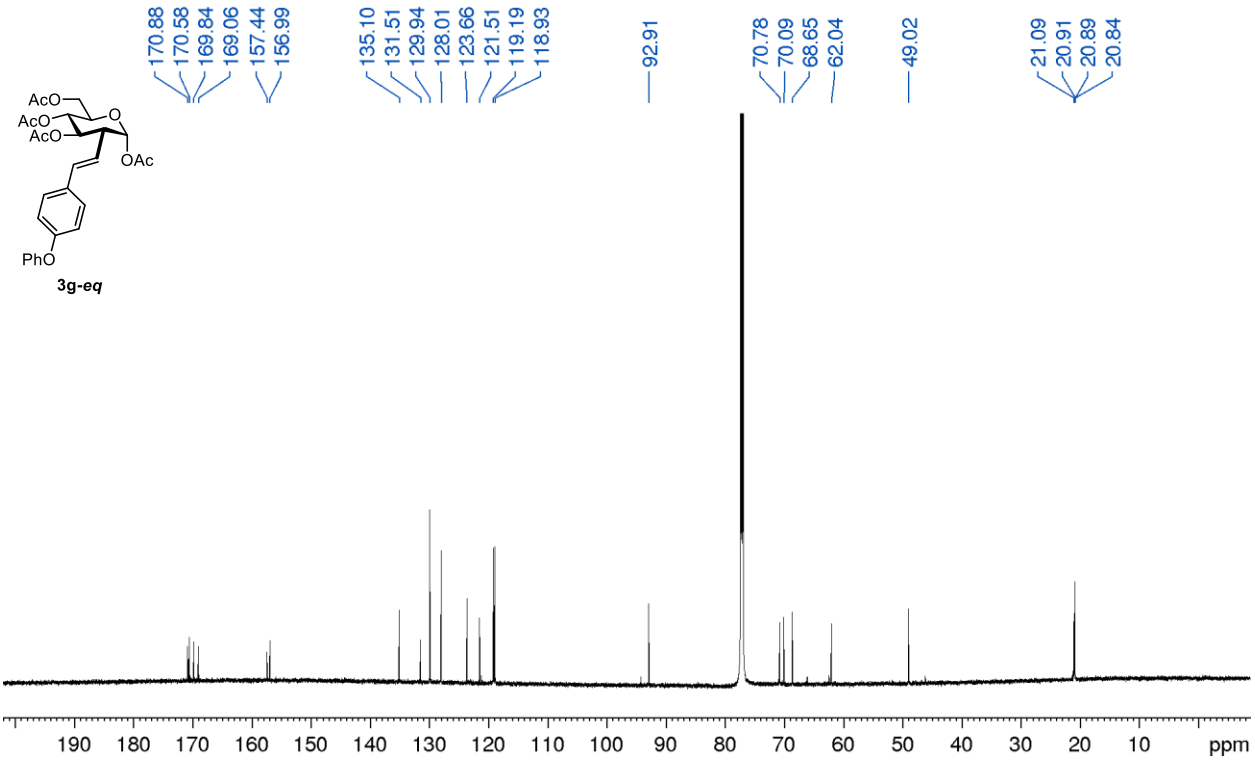
^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC) of (3g-*ax*)



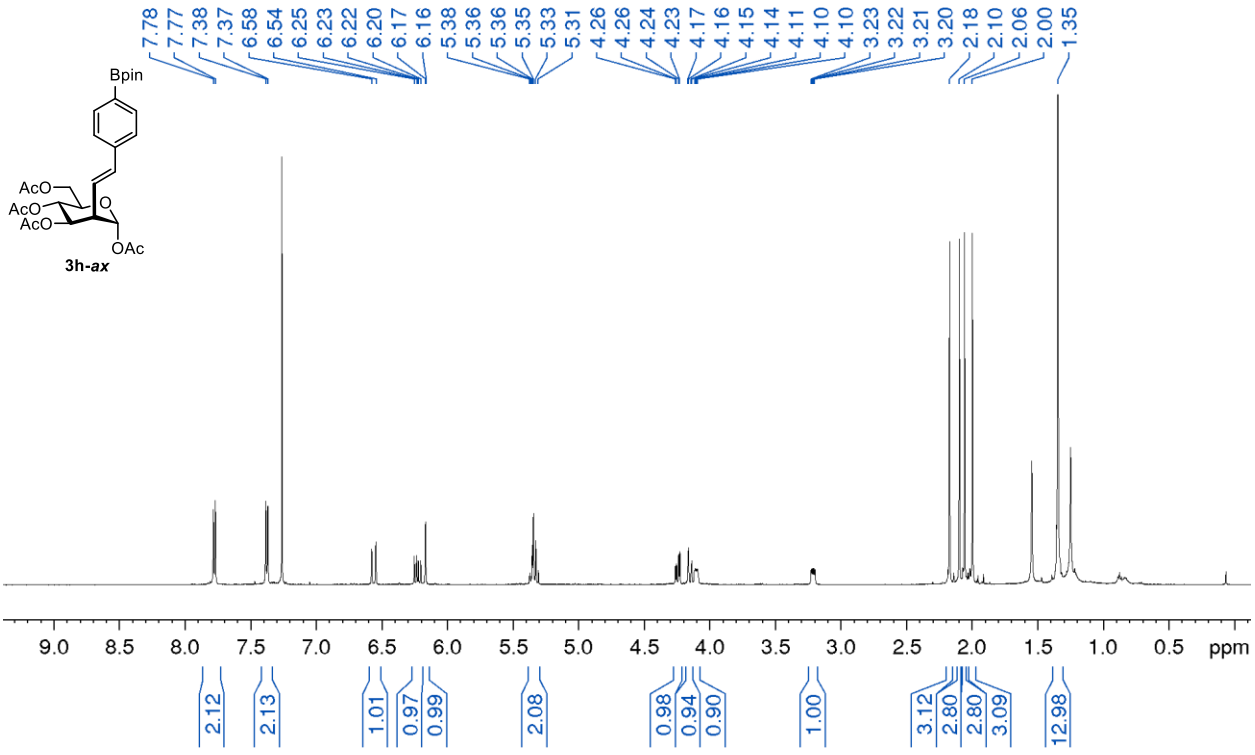
^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC) of (3g-*eq*)



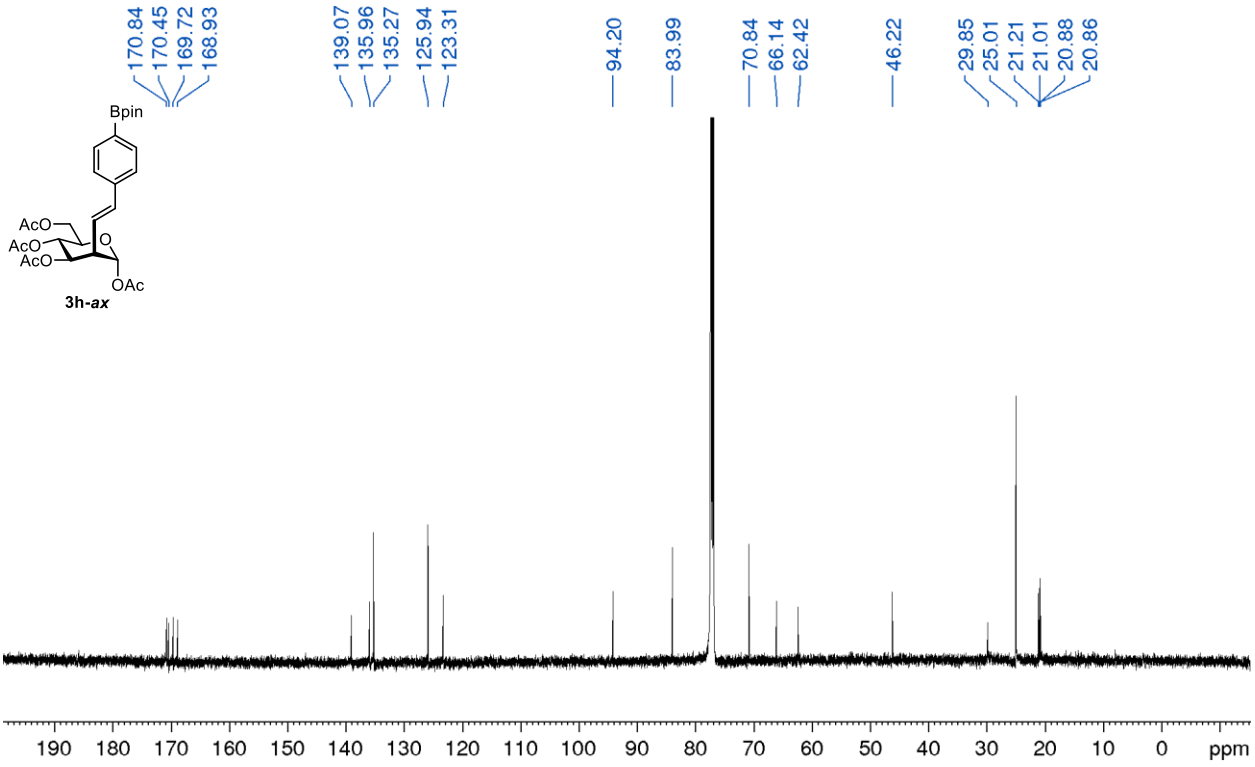
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3g-*eq*)



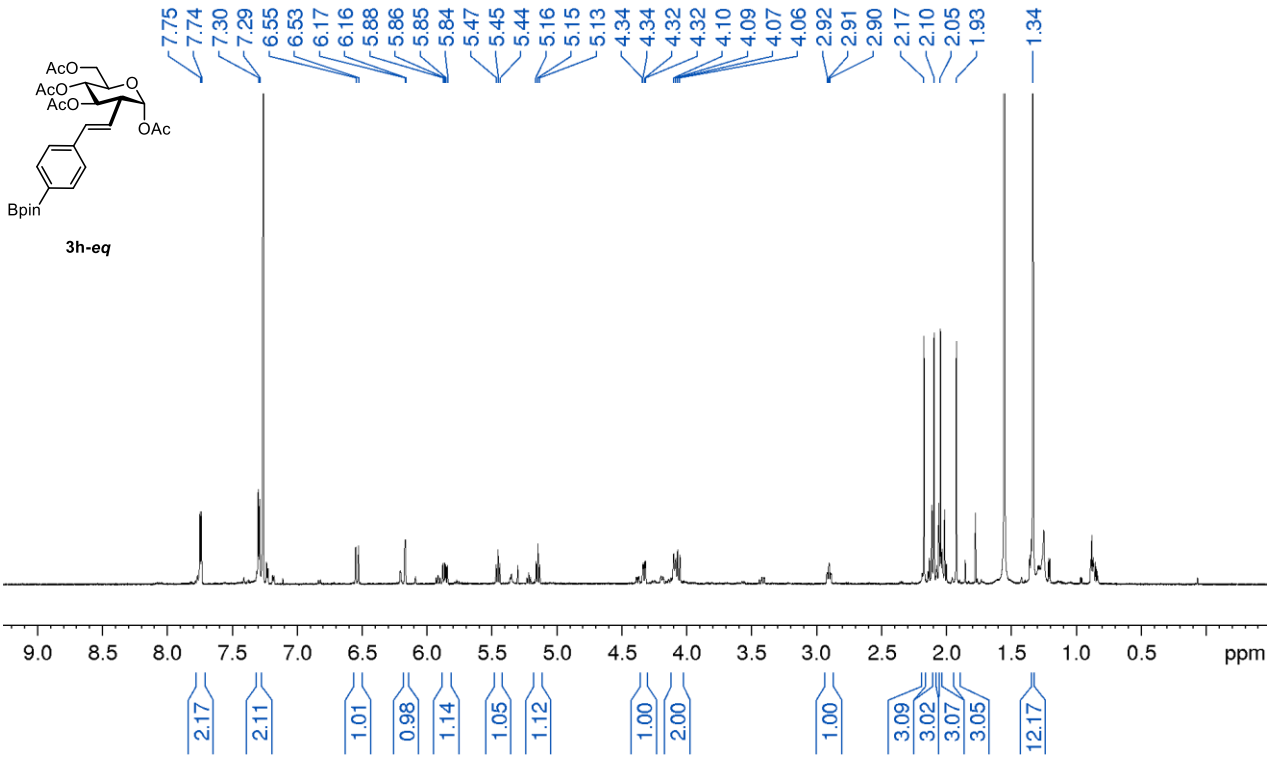
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (3h-*ax*)



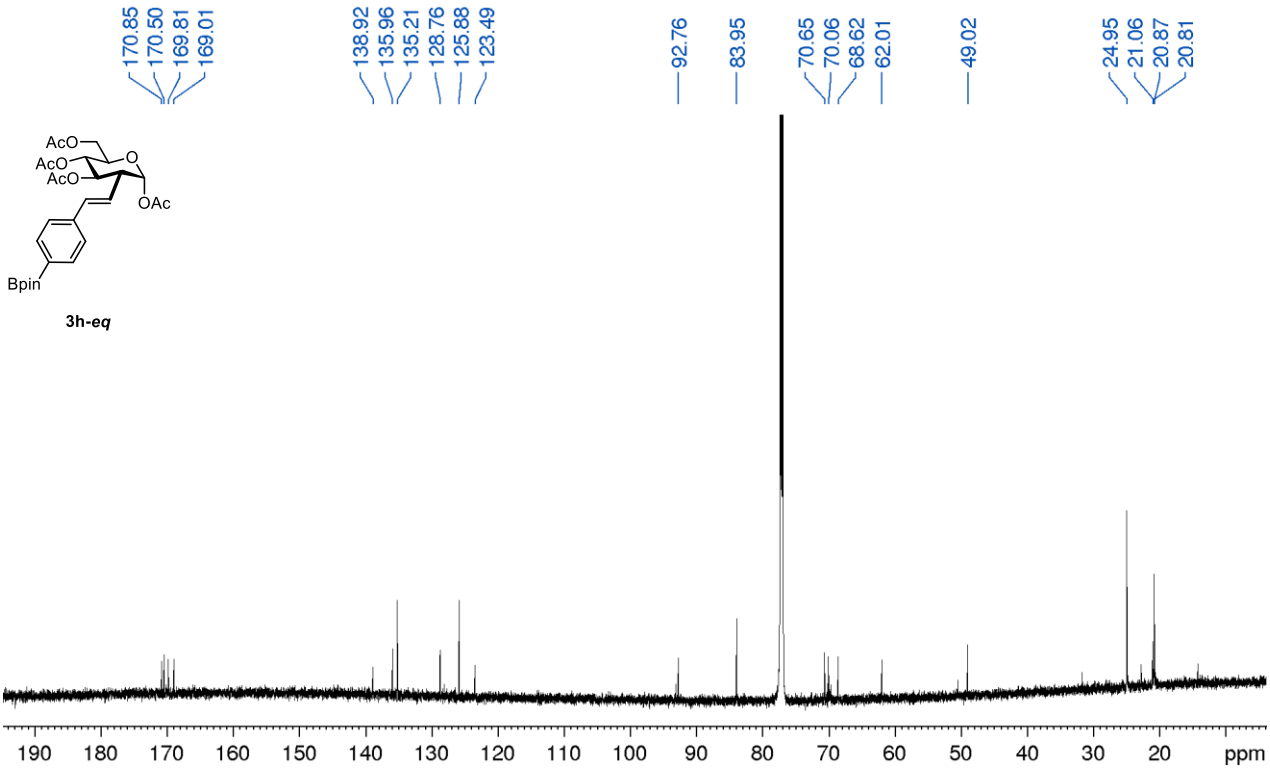
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (3h-*ax*)



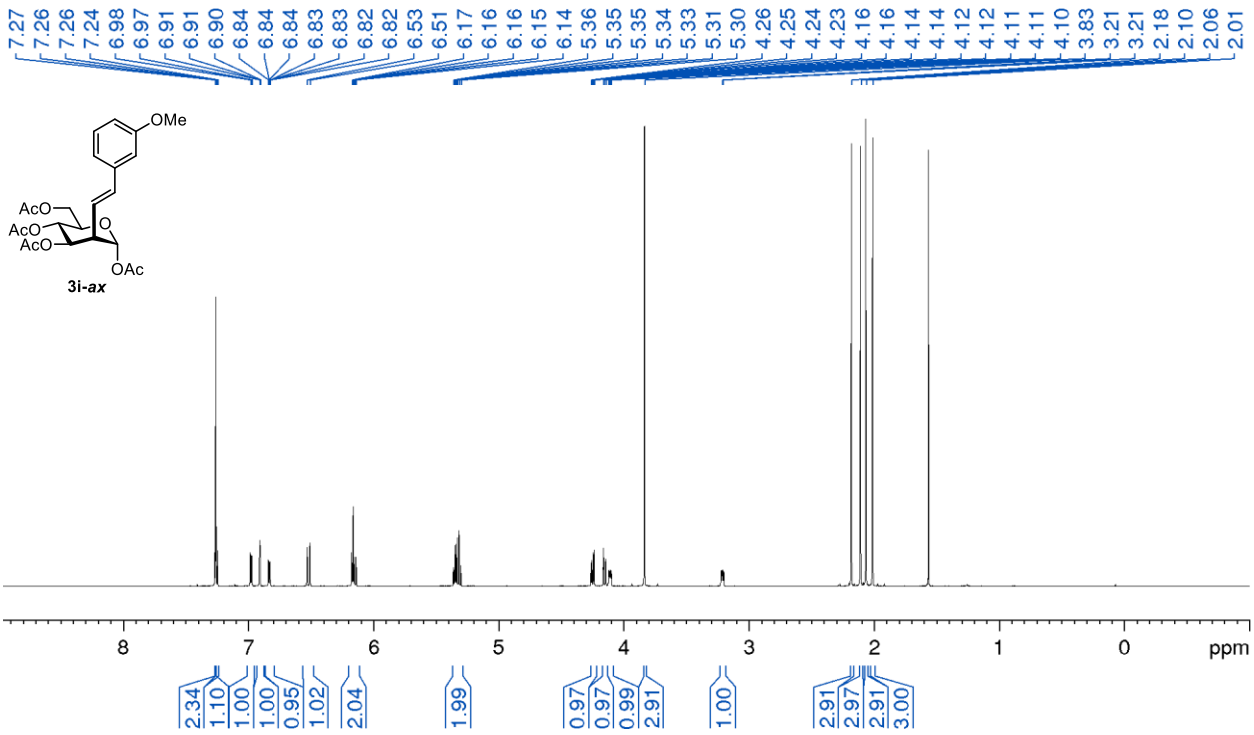
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3h-*eq*)



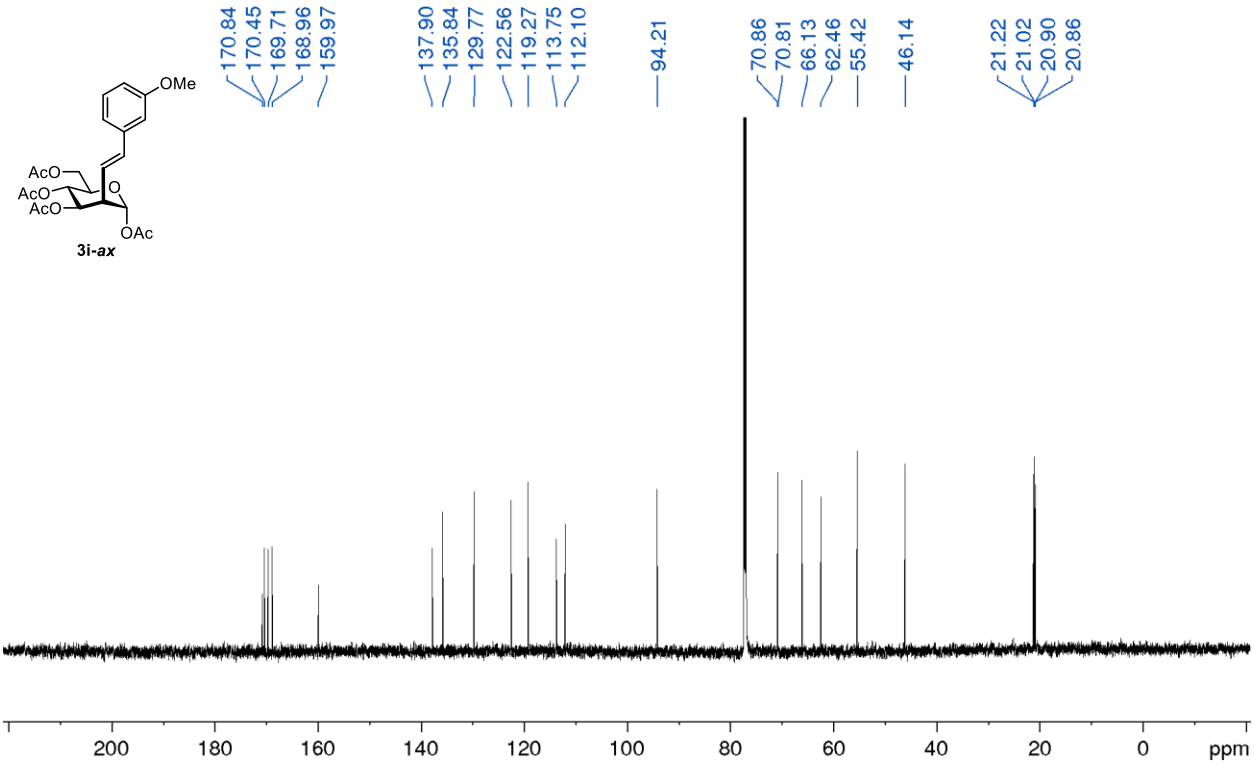
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3h-*eq*)



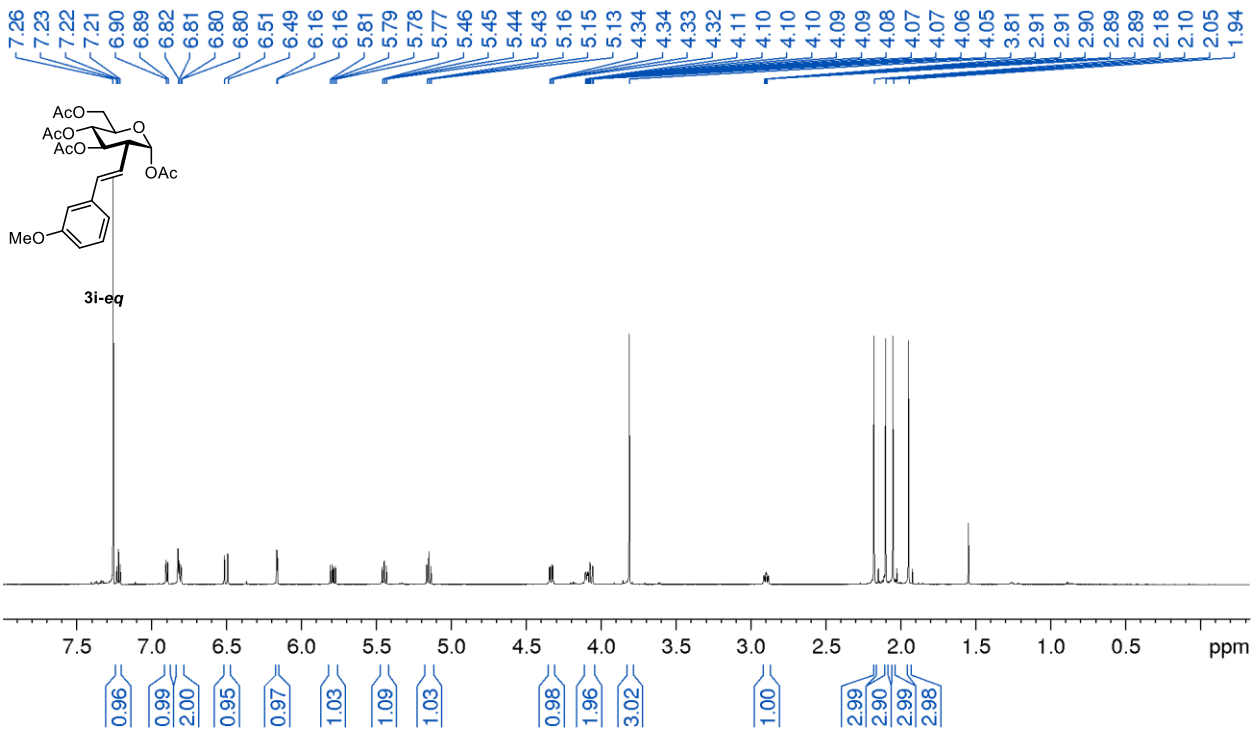
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (3i-*ax*)



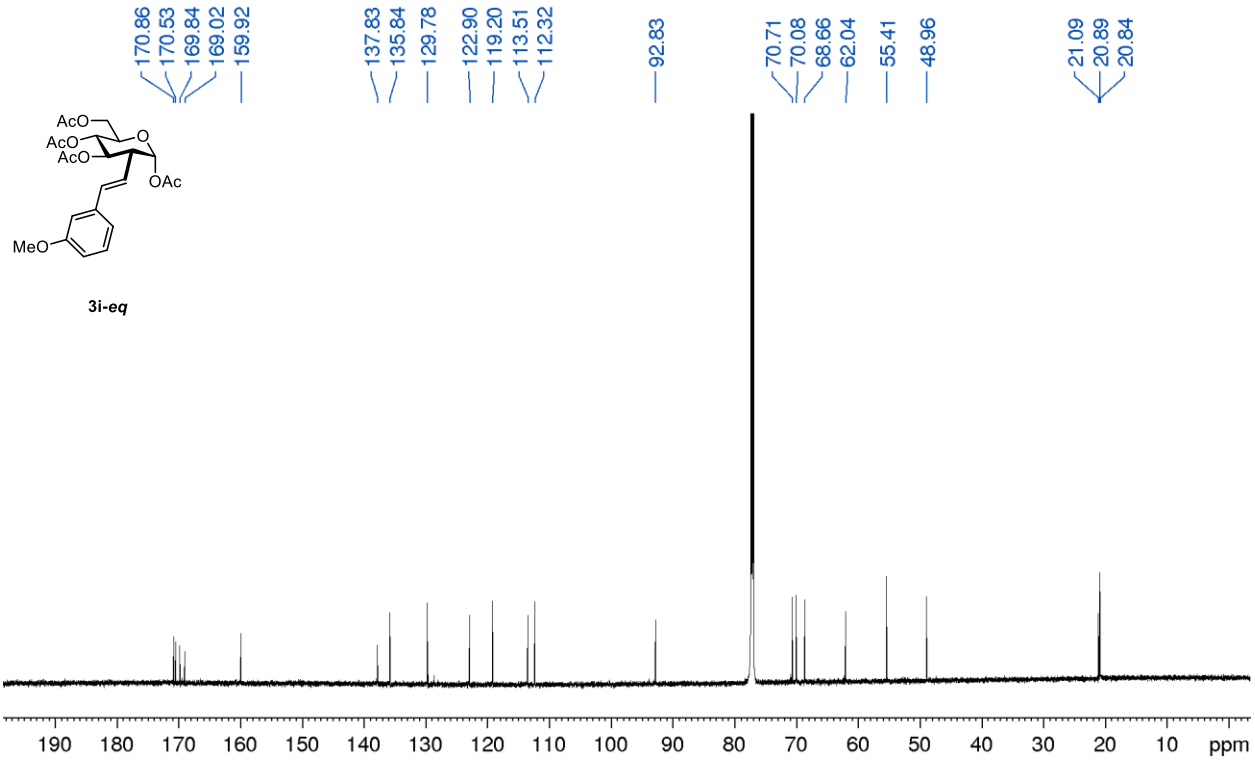
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (3i-*ax*)



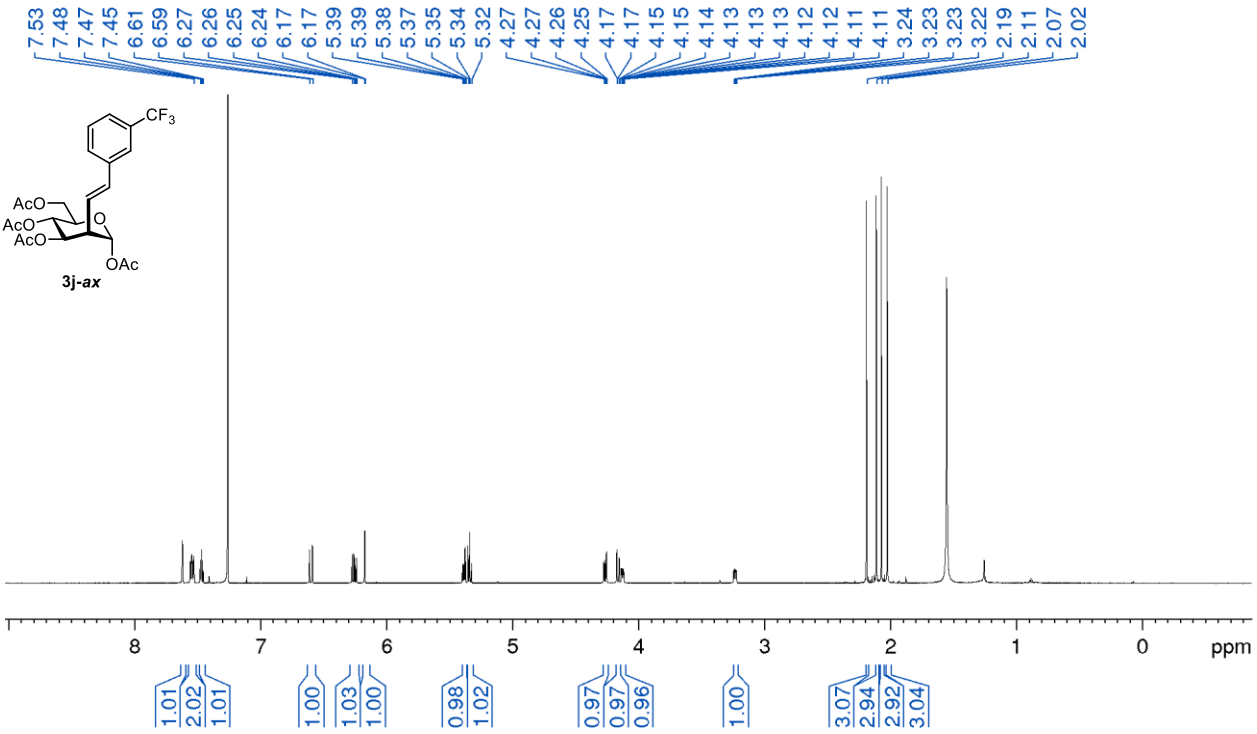
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3i-*eq*)



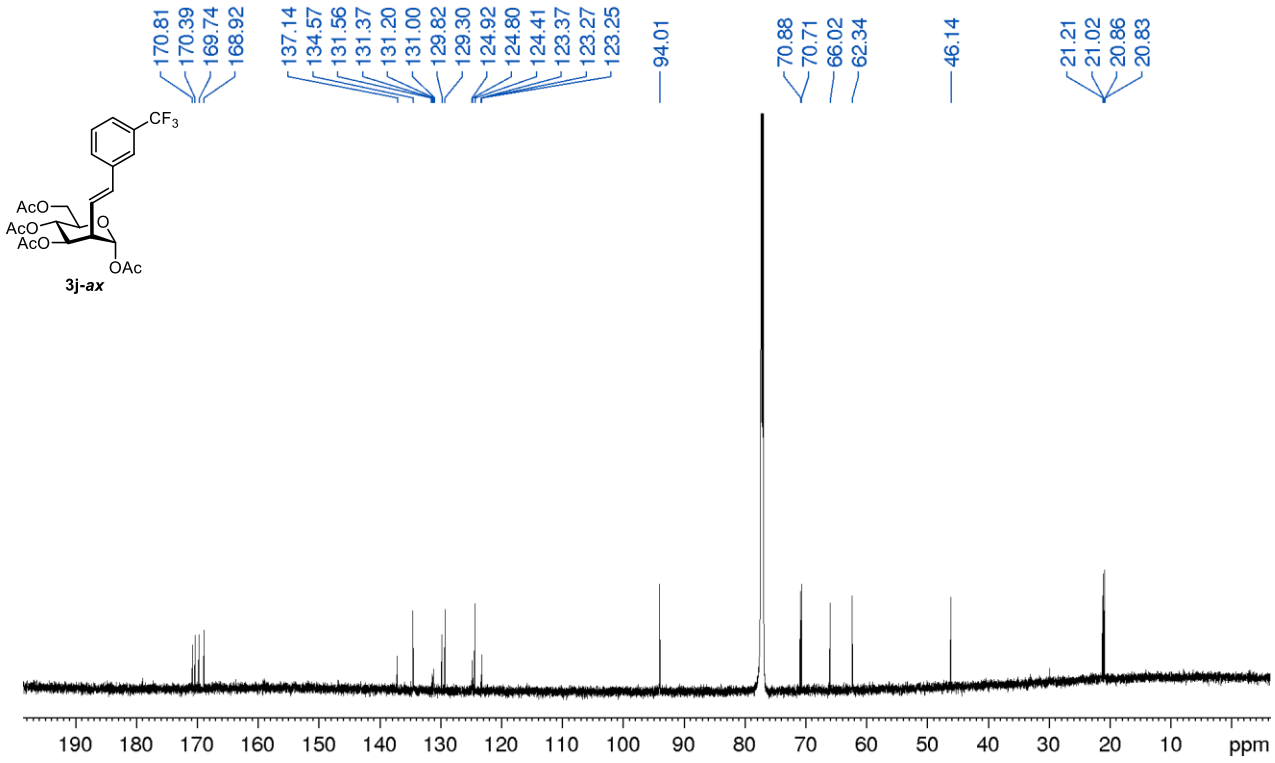
^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC) of (3i-*eq*)



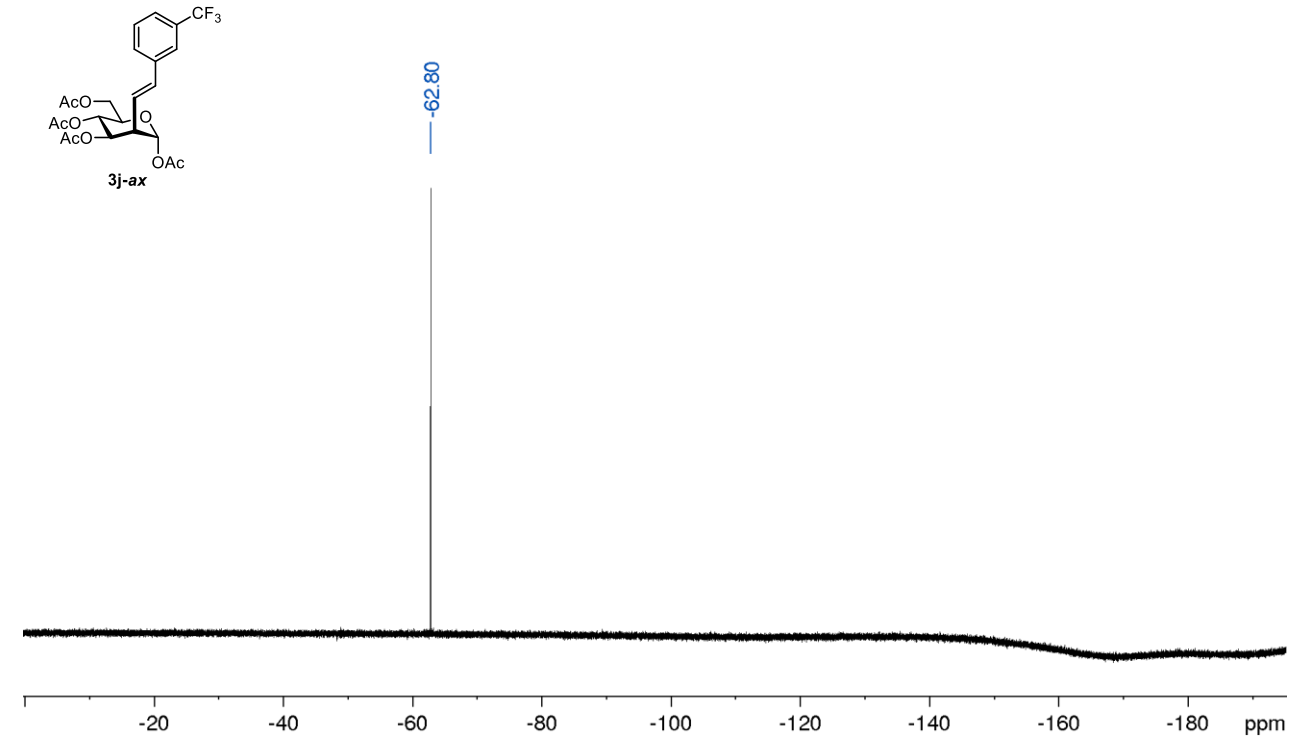
^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC) of (3j-*ax*)



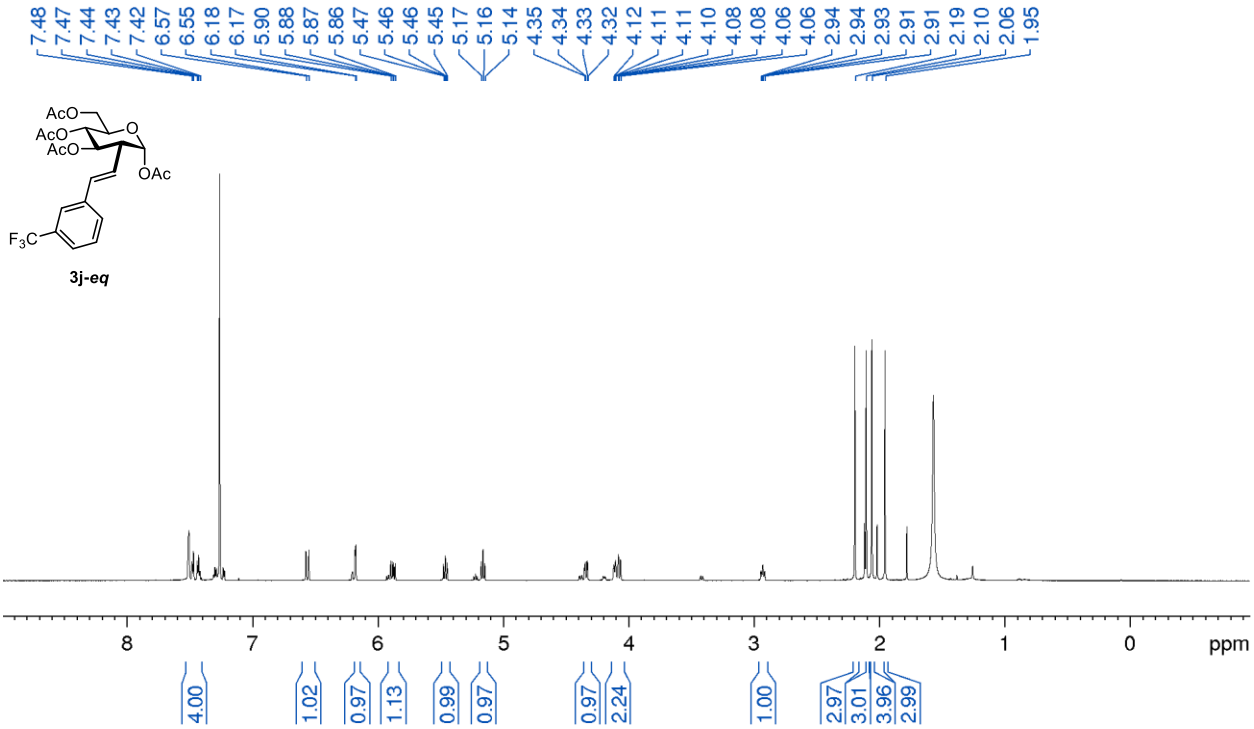
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3j-*ax*)



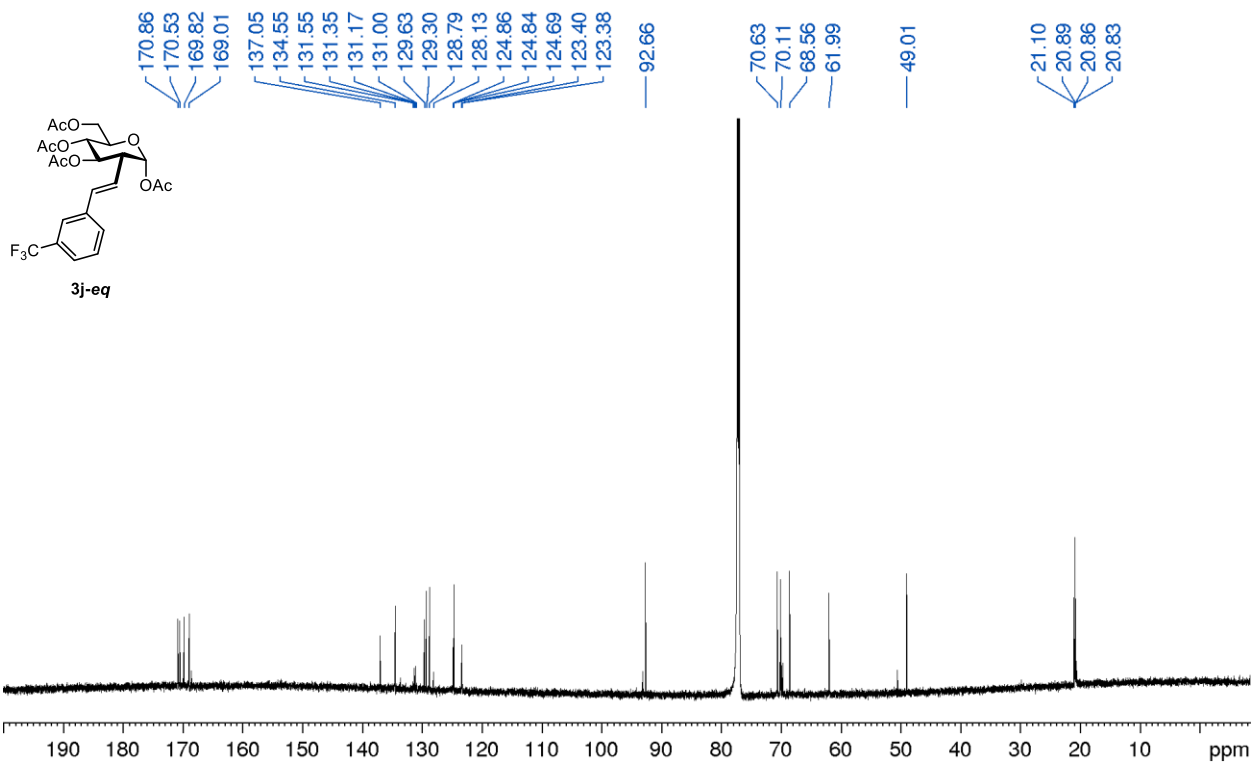
^{19}F NMR (376 MHz, $CDCl_3$, 25 °C) of (3j-*ax*)



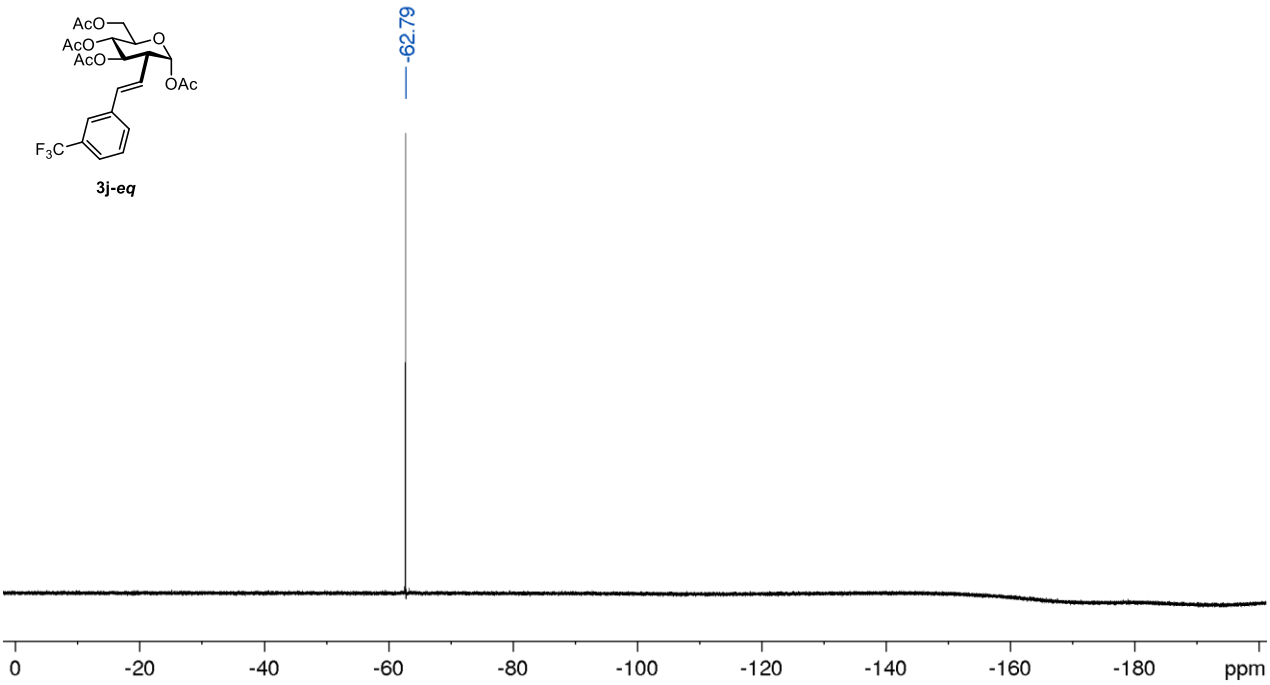
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3j-*eq*)



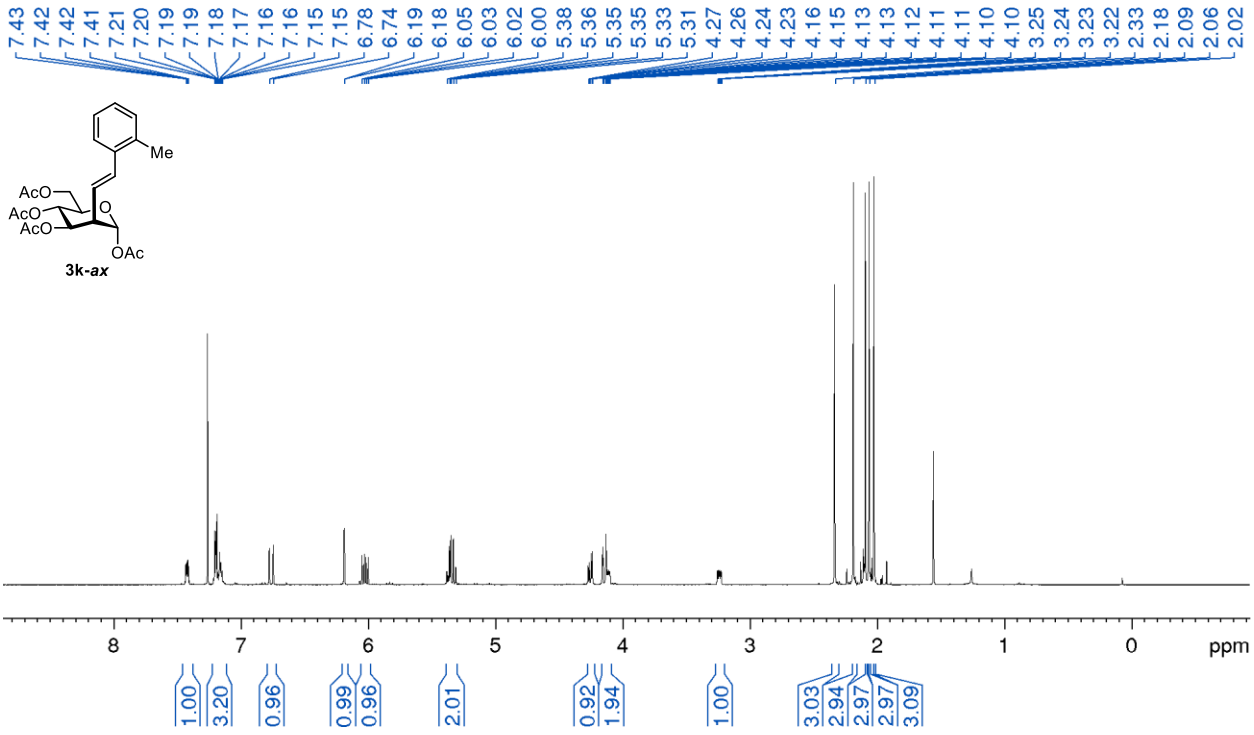
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3j-*eq*)



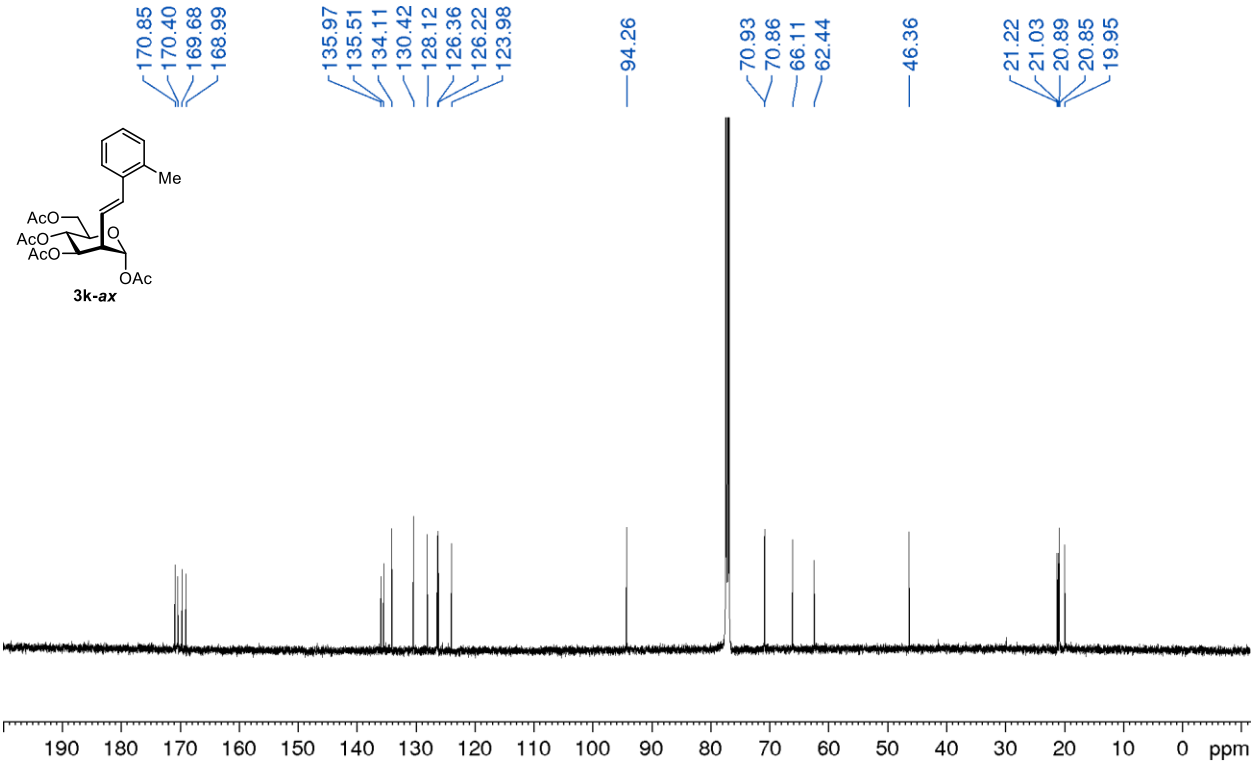
^{19}F NMR (376 MHz, $CDCl_3$, 25 °C) of (3j-*eq*)



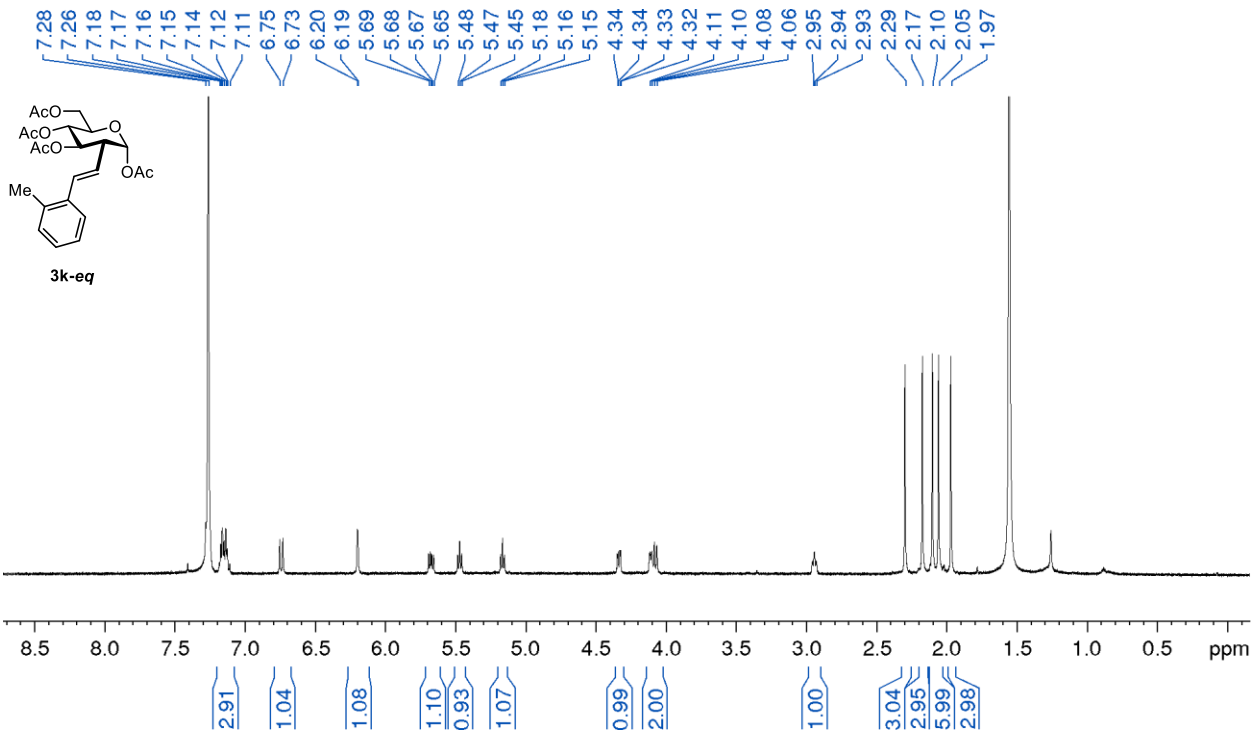
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (3k-*ax*)



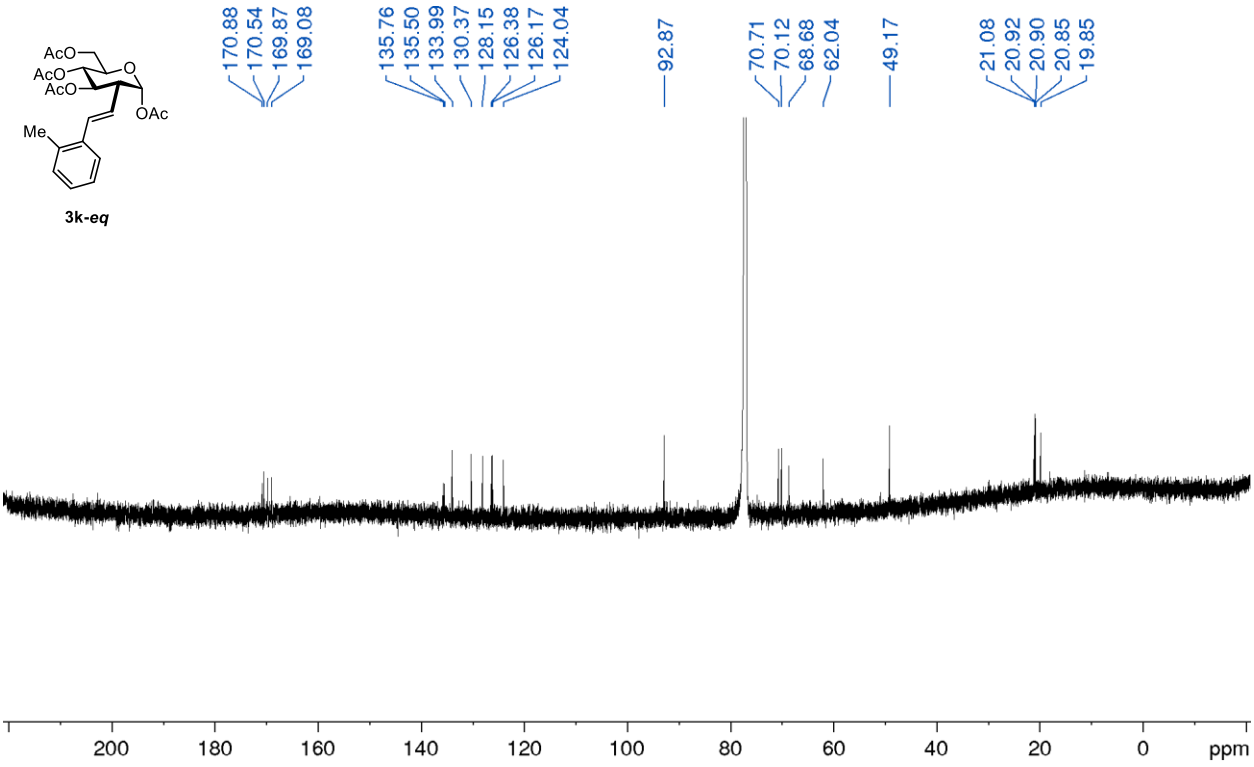
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (3k-*ax*)



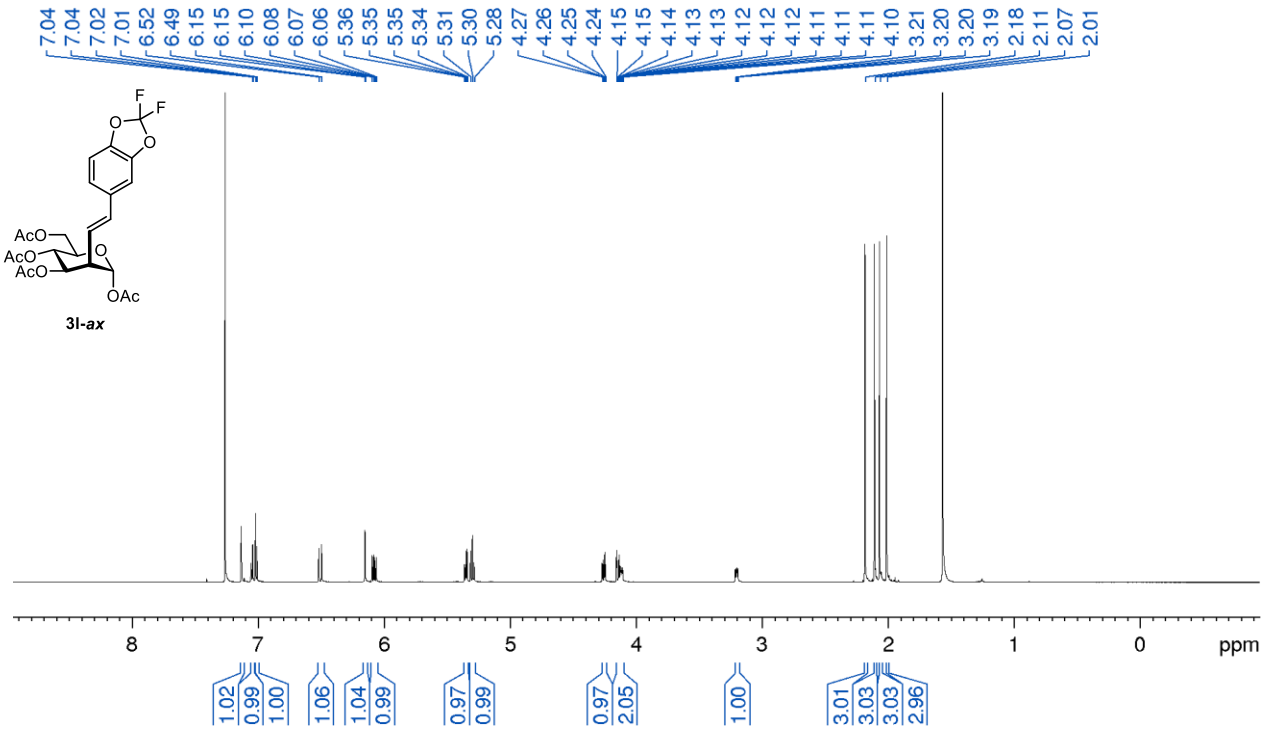
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3k-*eq*)



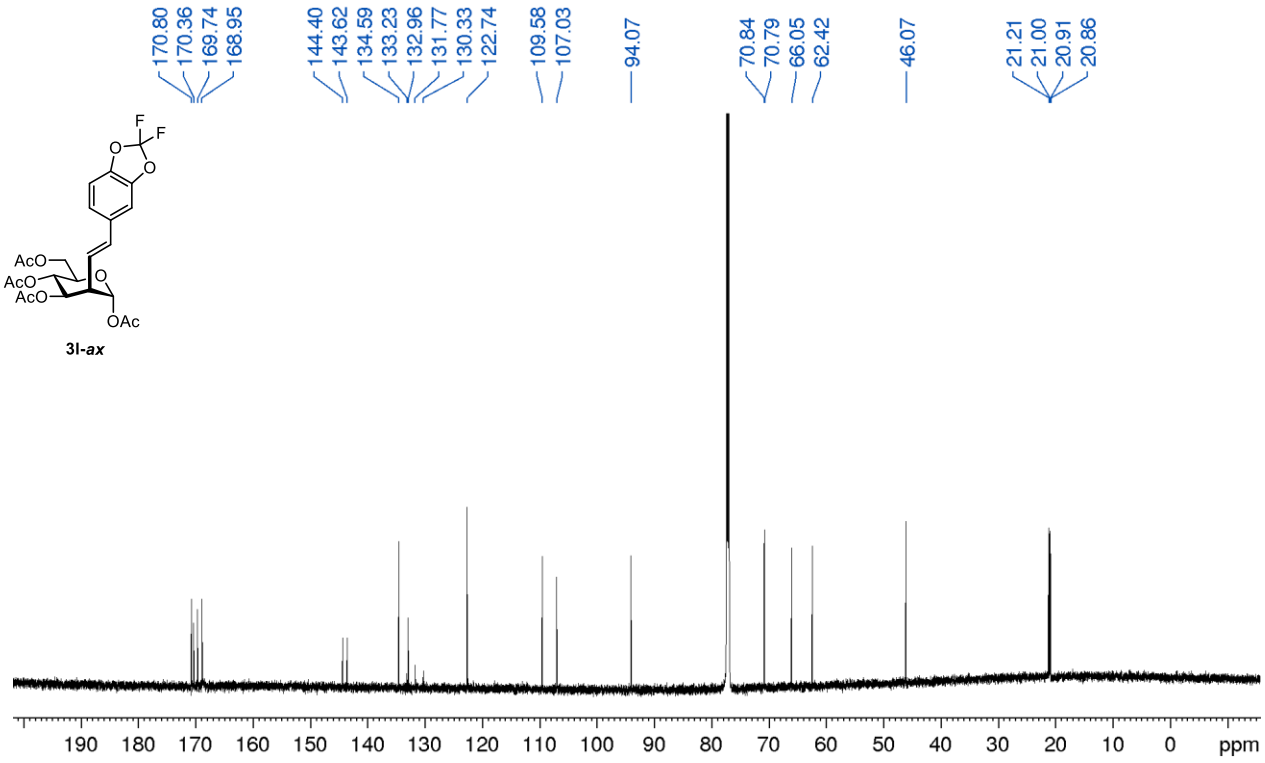
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3k-*eq*)



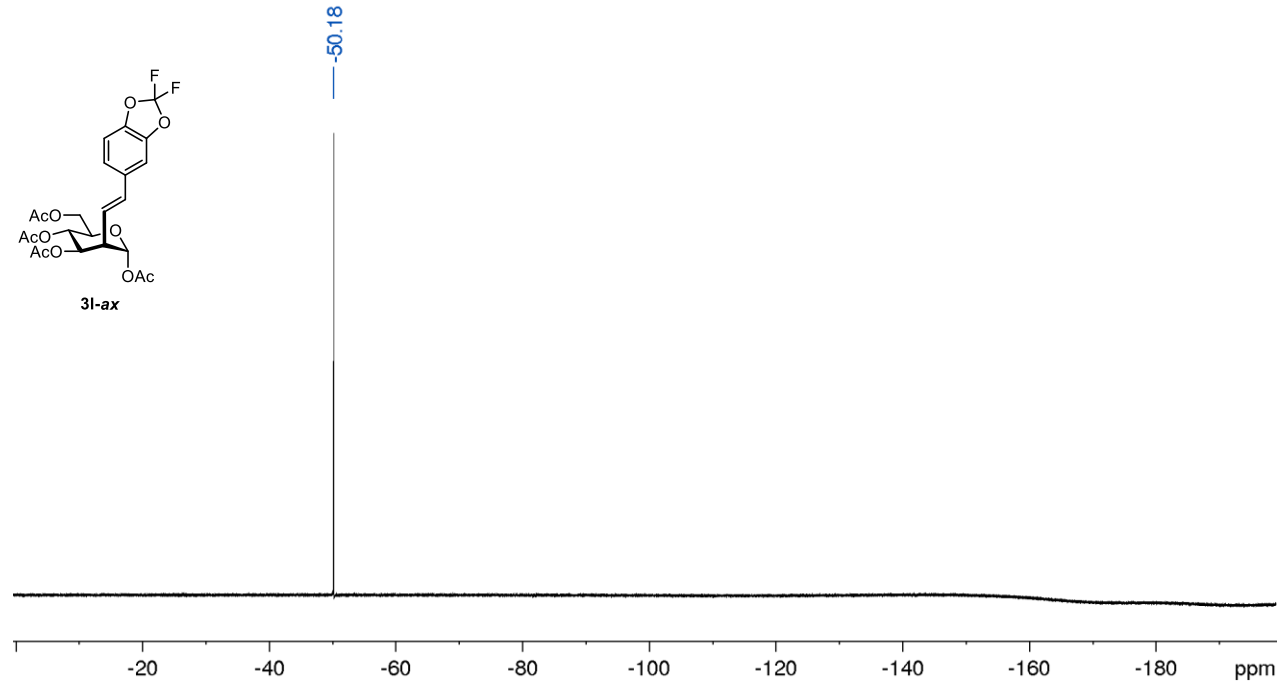
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3l-*ax*)



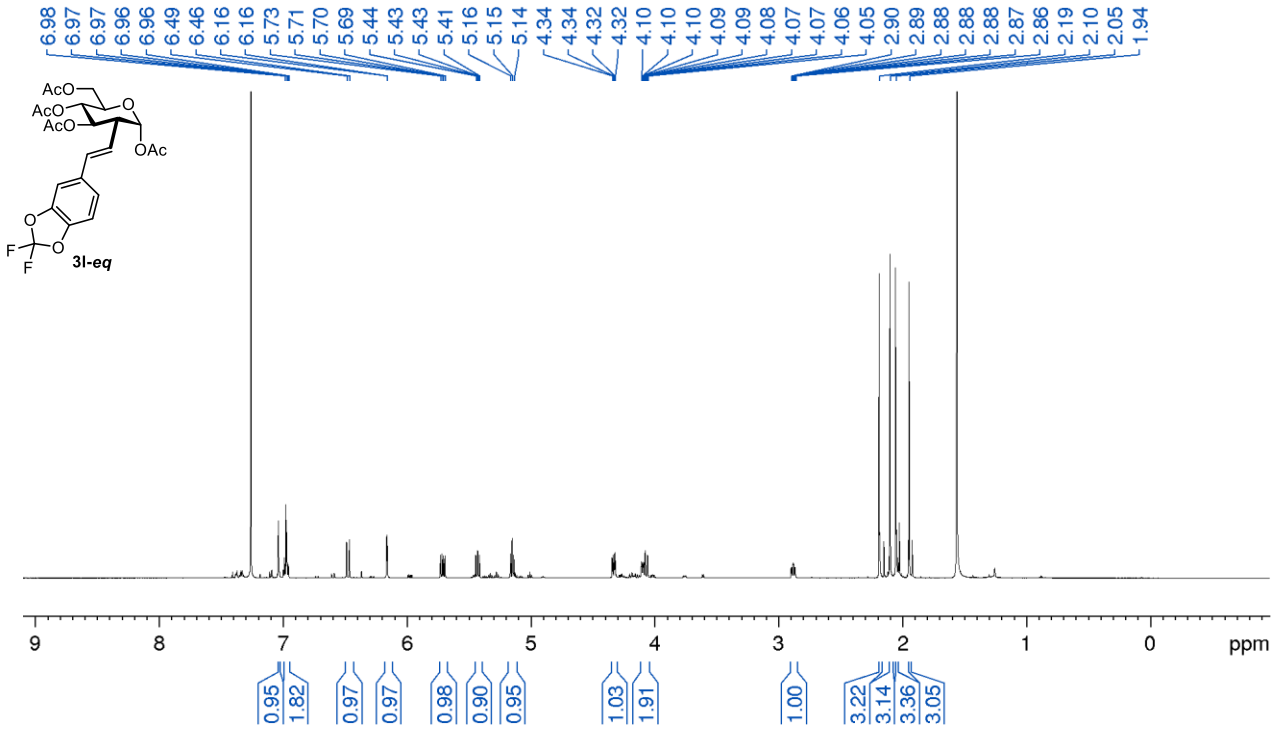
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3l-*ax*)



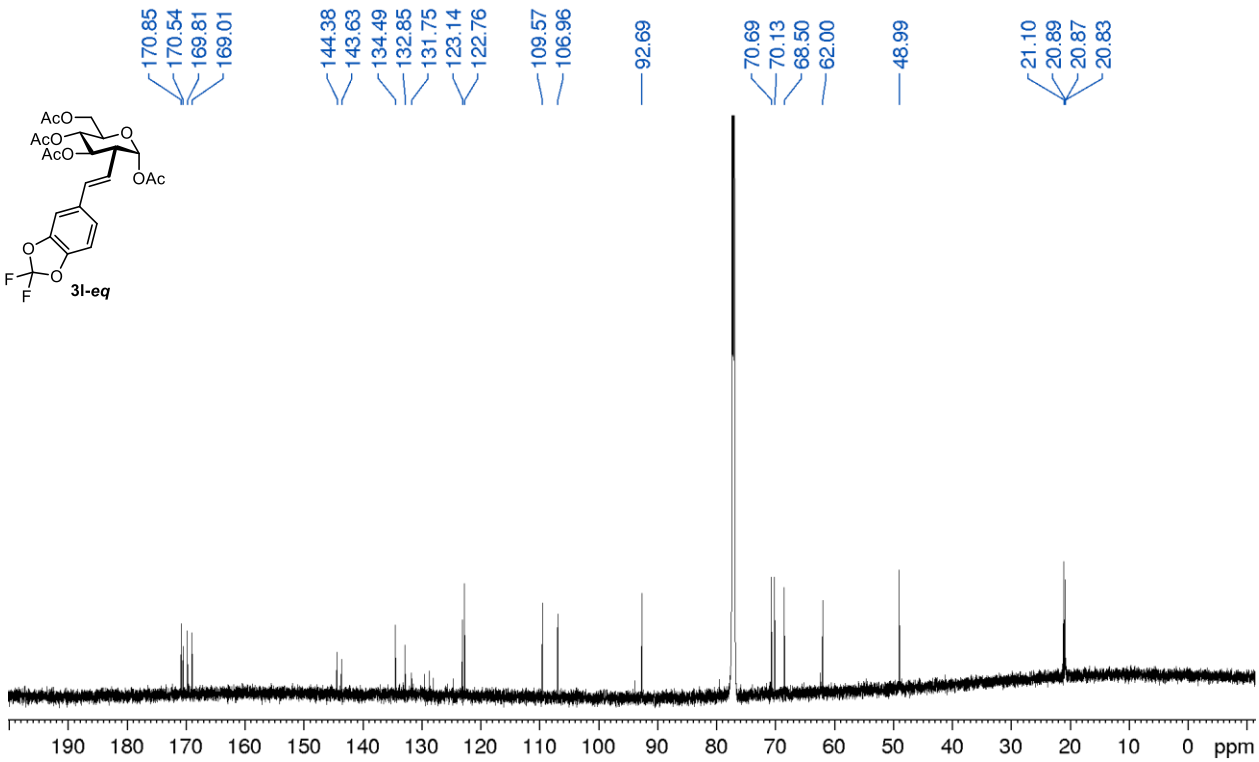
^{19}F NMR (376 MHz, $CDCl_3$, 25 °C) of (3l-*ax*)



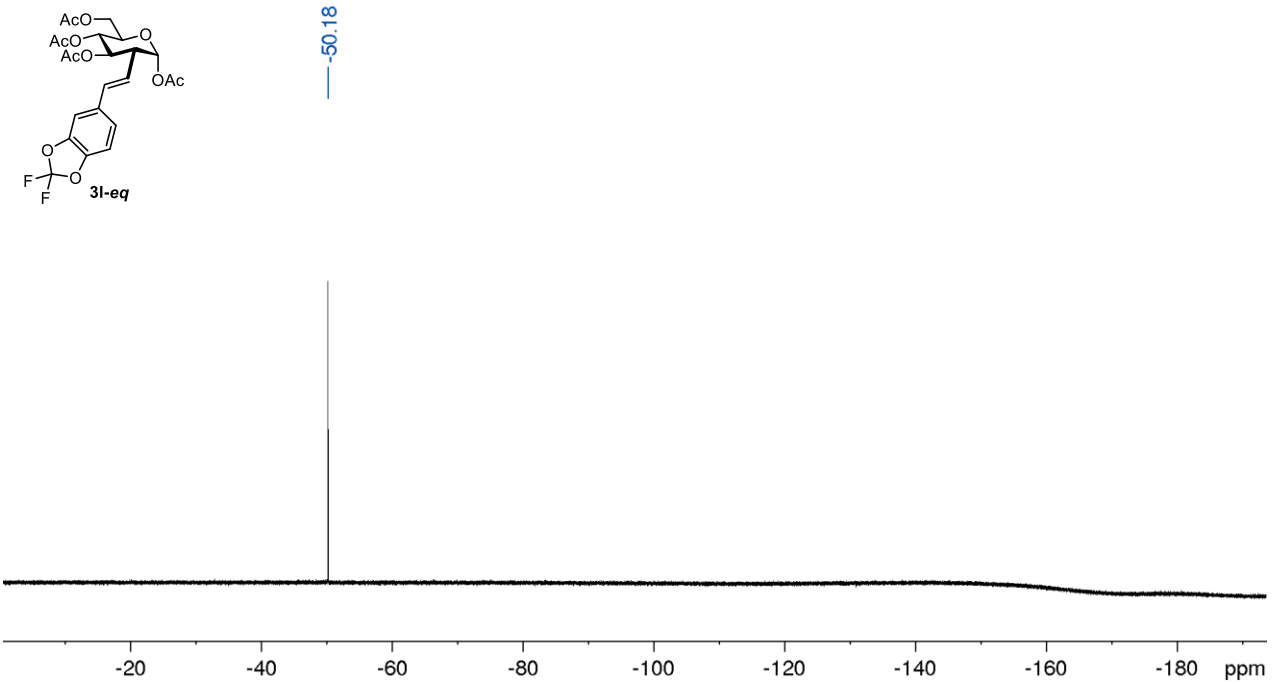
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3l-*eq*)



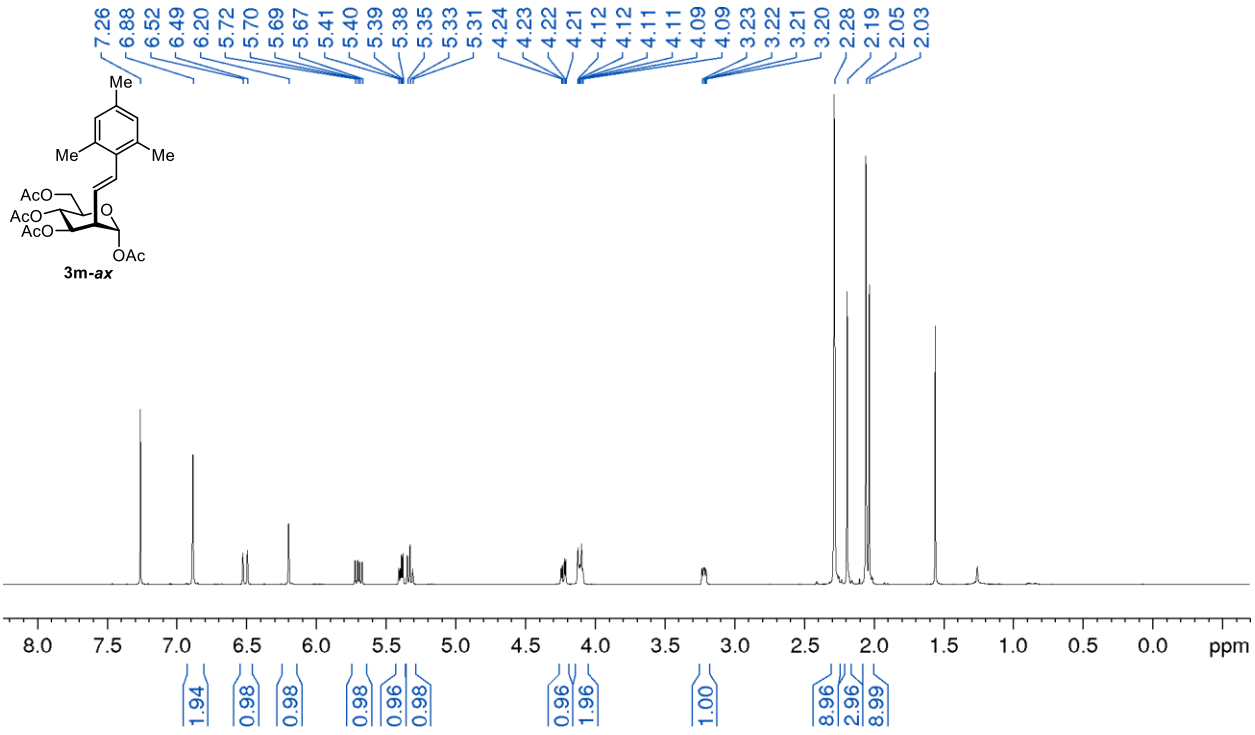
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3l-*eq*)



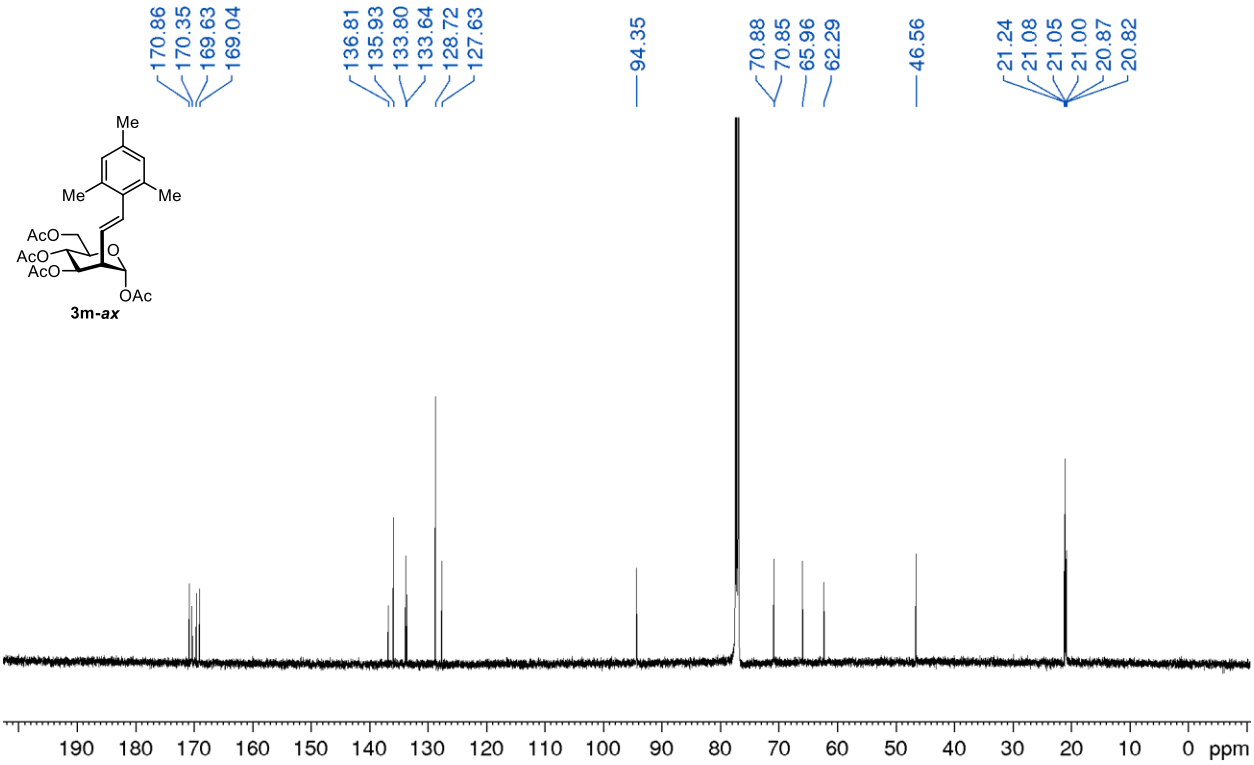
^{19}F NMR (376 MHz, $CDCl_3$, 25 °C) of (3l-*eq*)



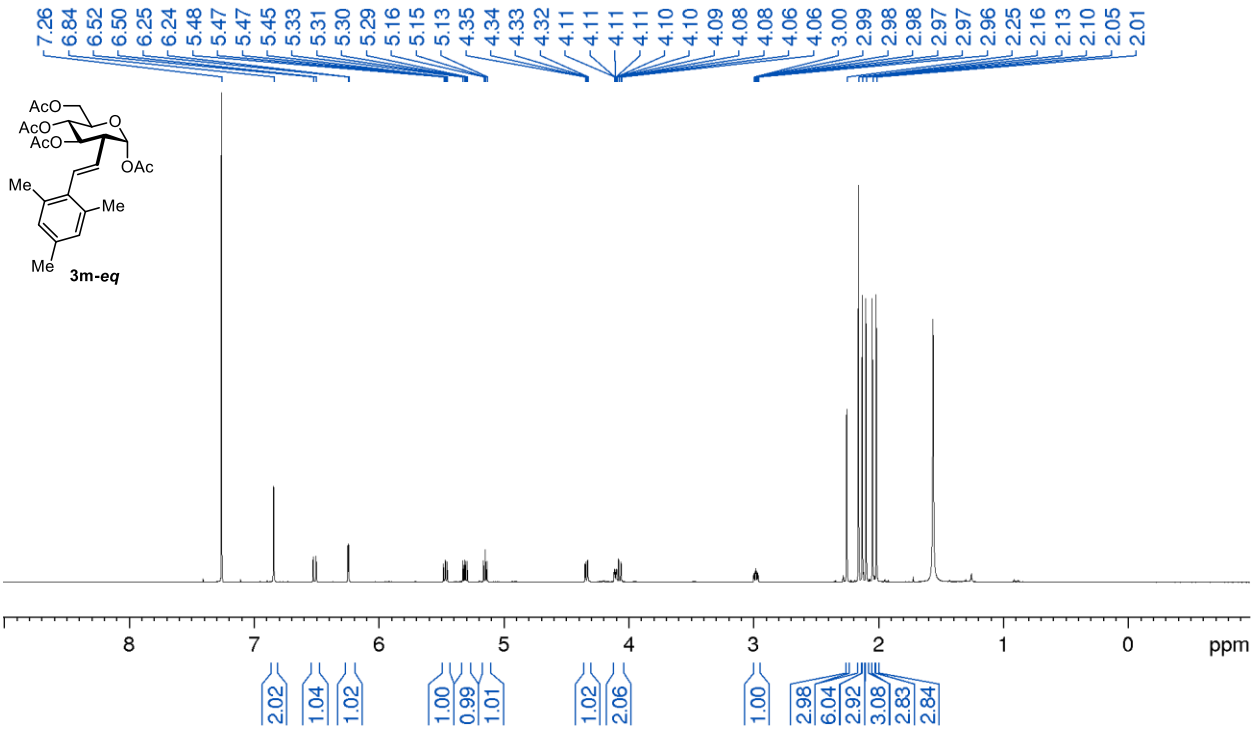
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (3m-*ax*)



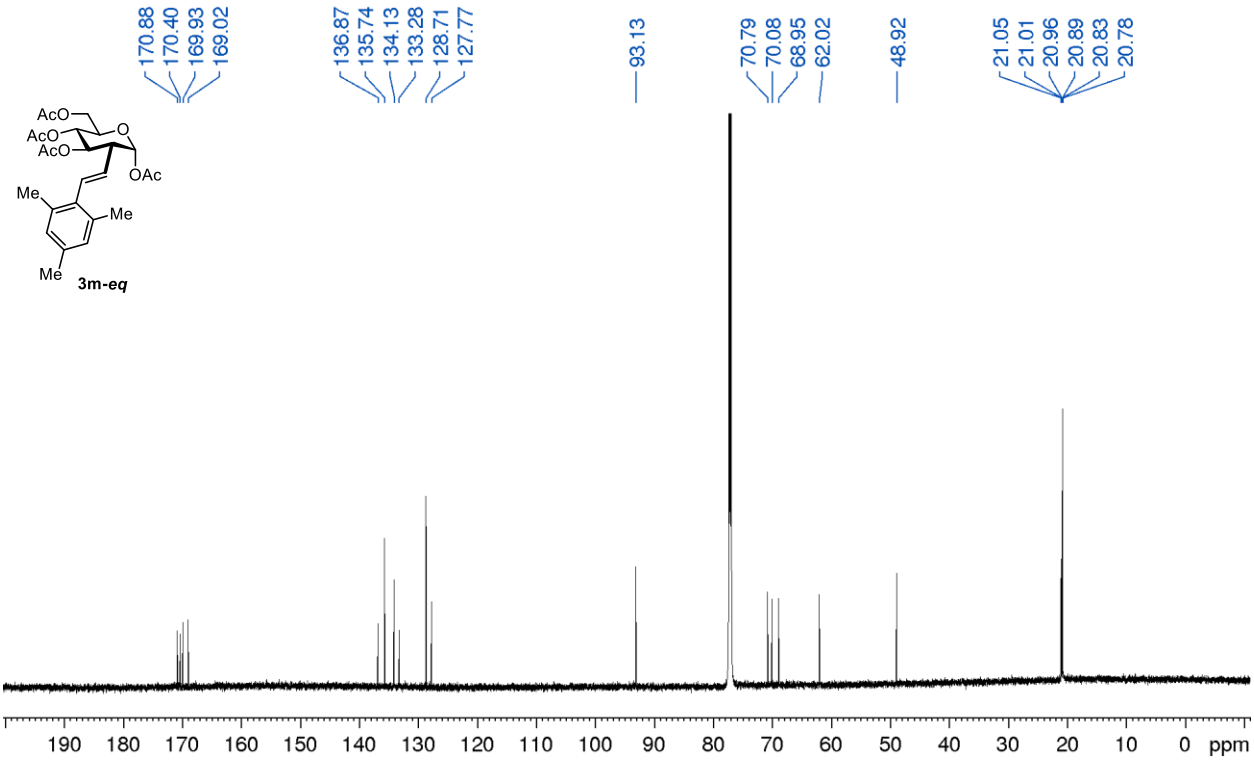
^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC) of (3m-*ax*)



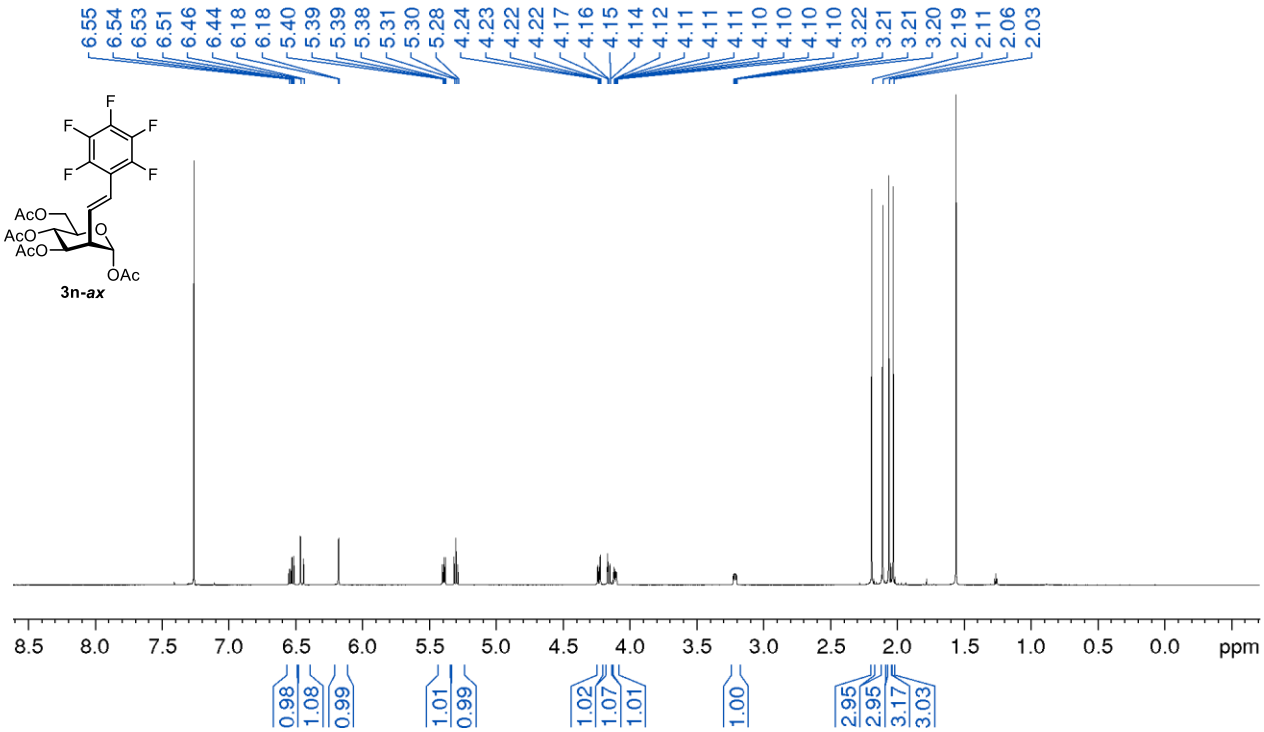
^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC) of (3m-*eq*)



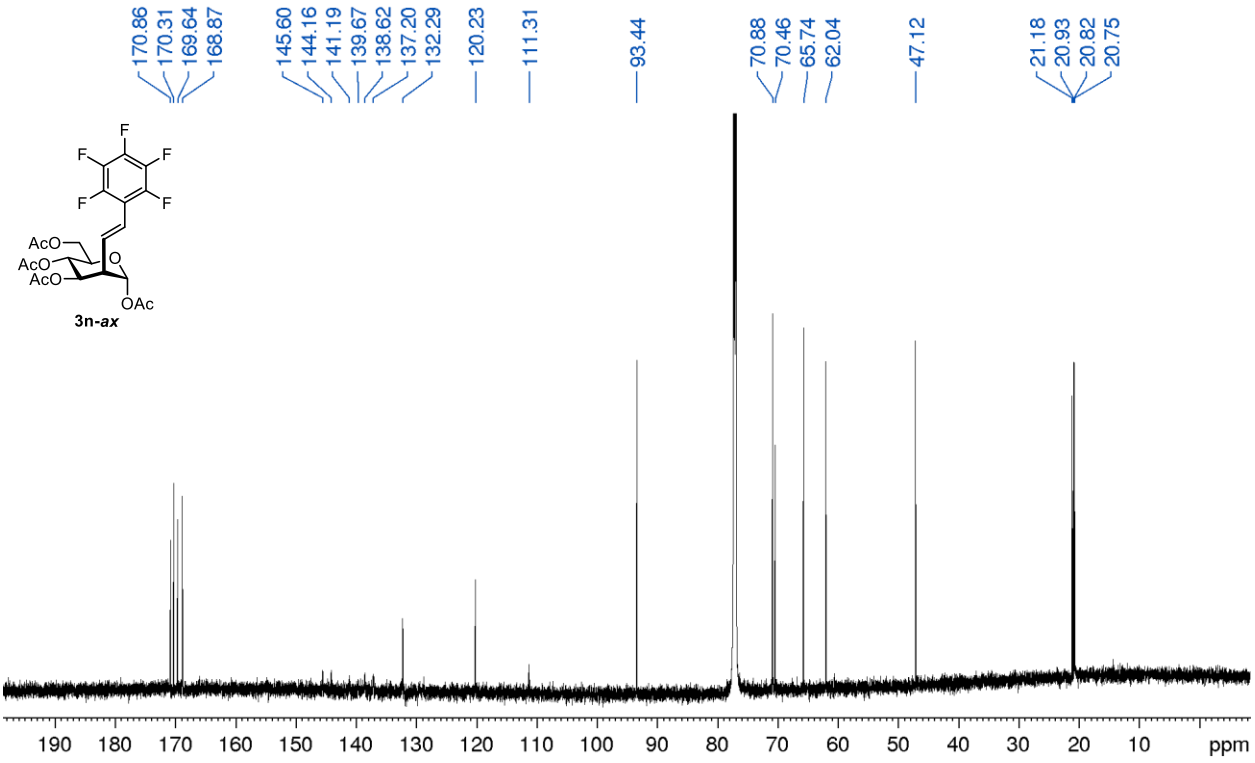
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3m-*eq*)



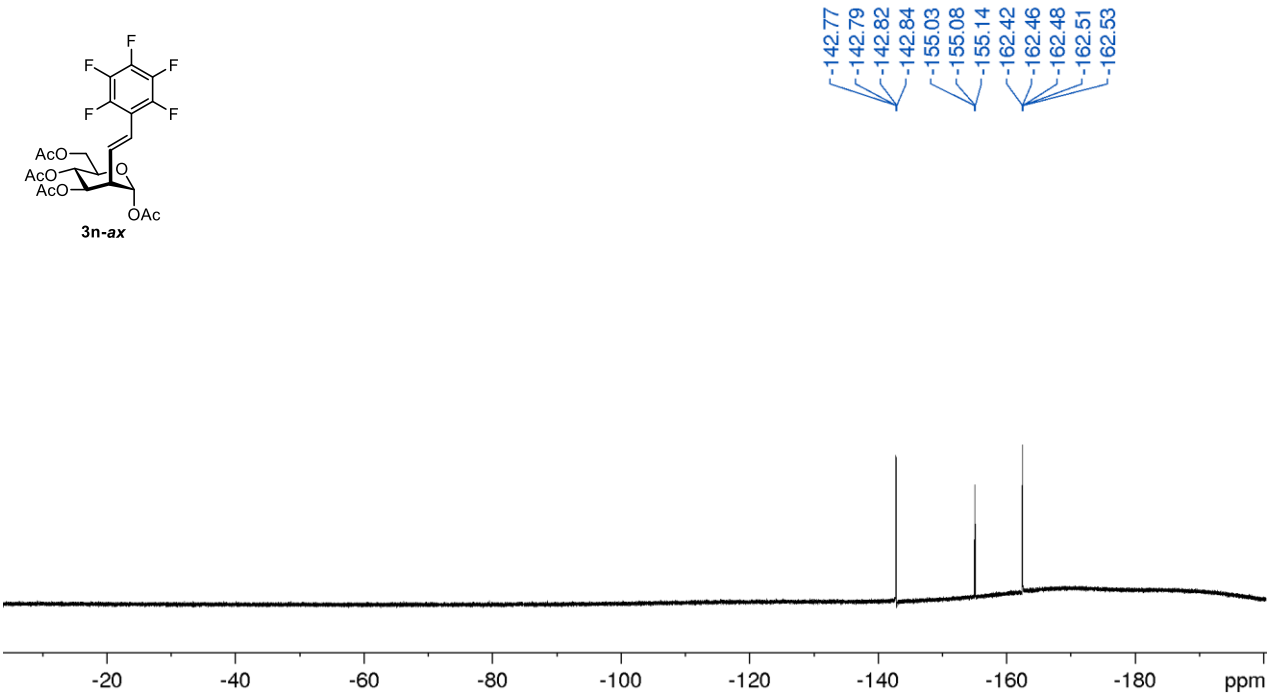
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3n-*ax*)



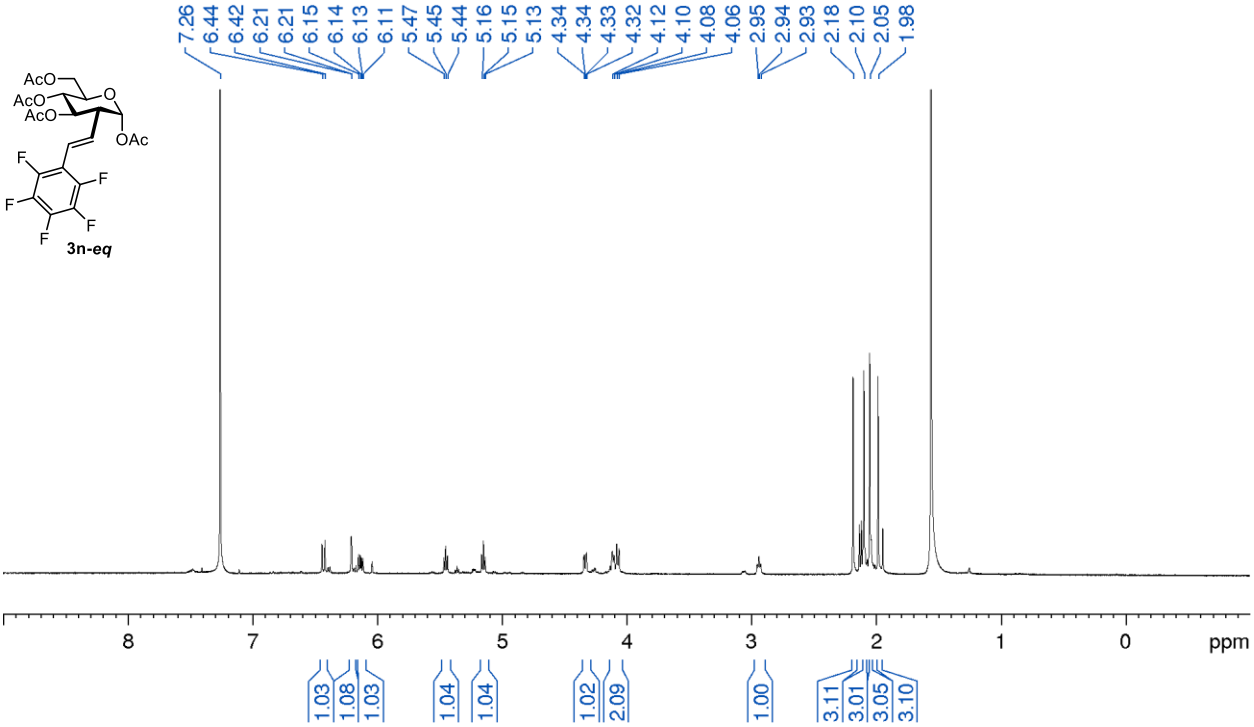
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3n-*ax*)



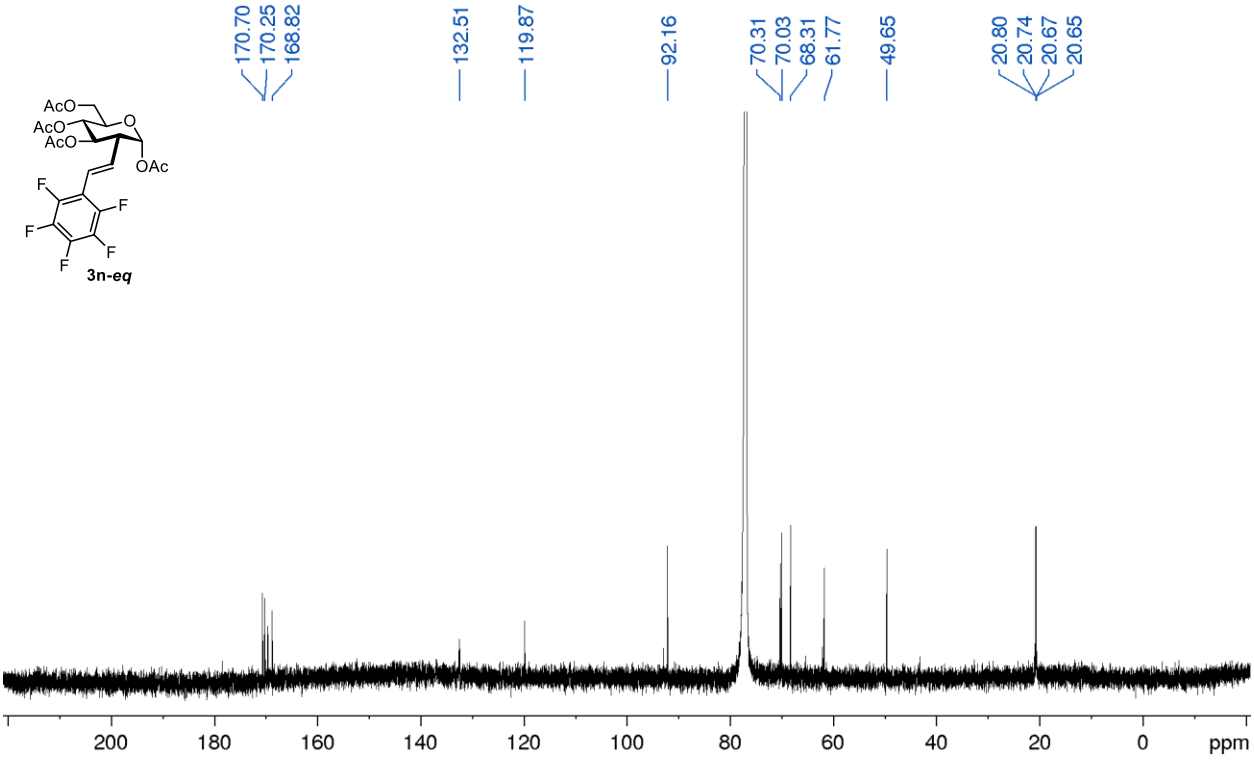
^{19}F NMR (376 MHz, $CDCl_3$, 25 °C) of (3n-*ax*)



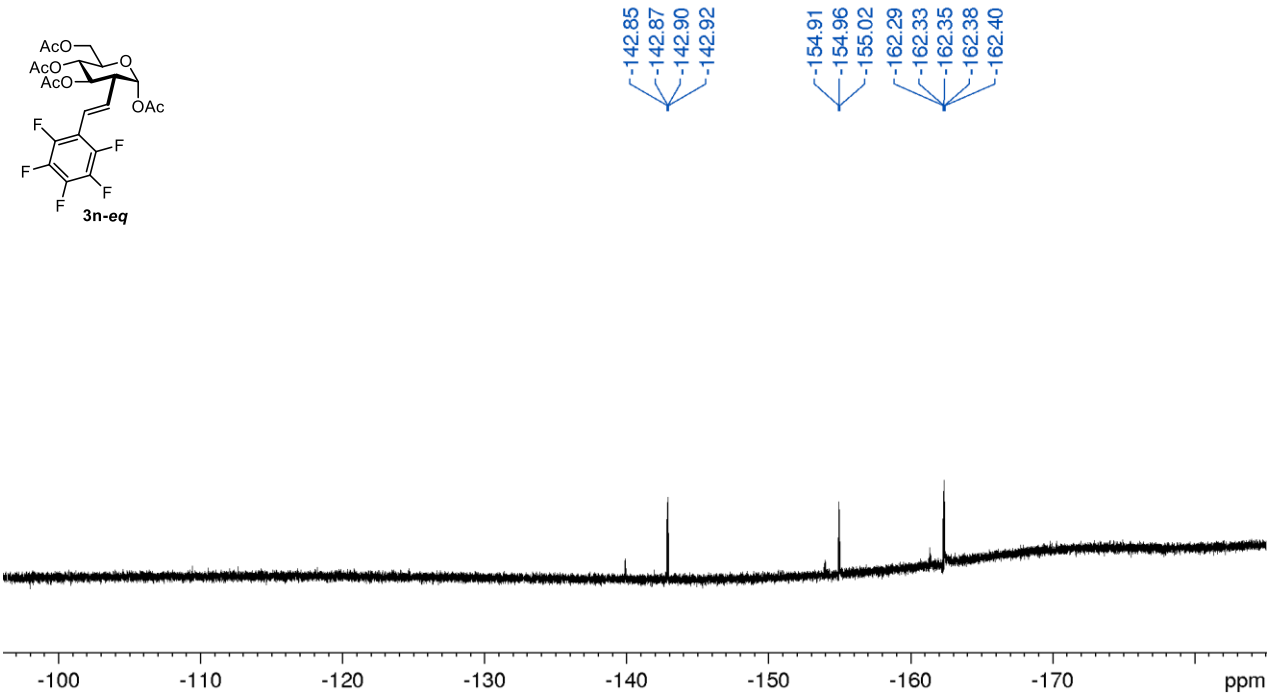
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3n-*eq*)



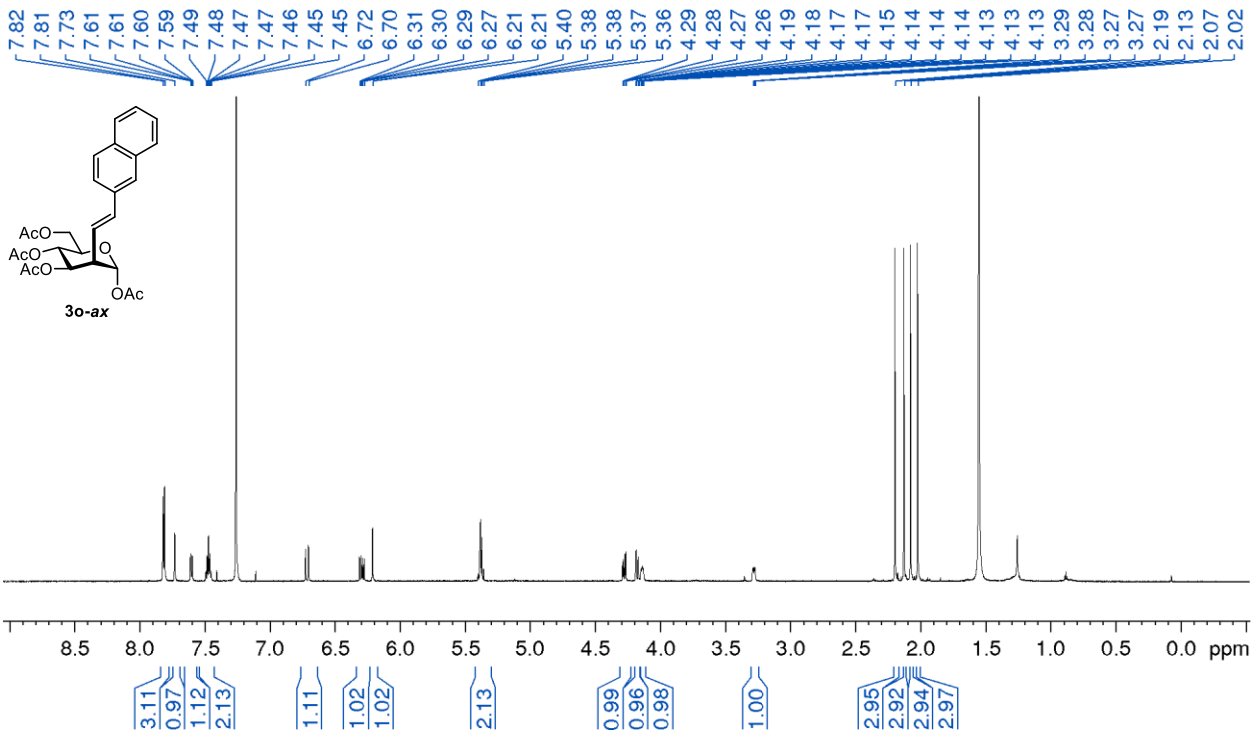
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3n-*eq*)



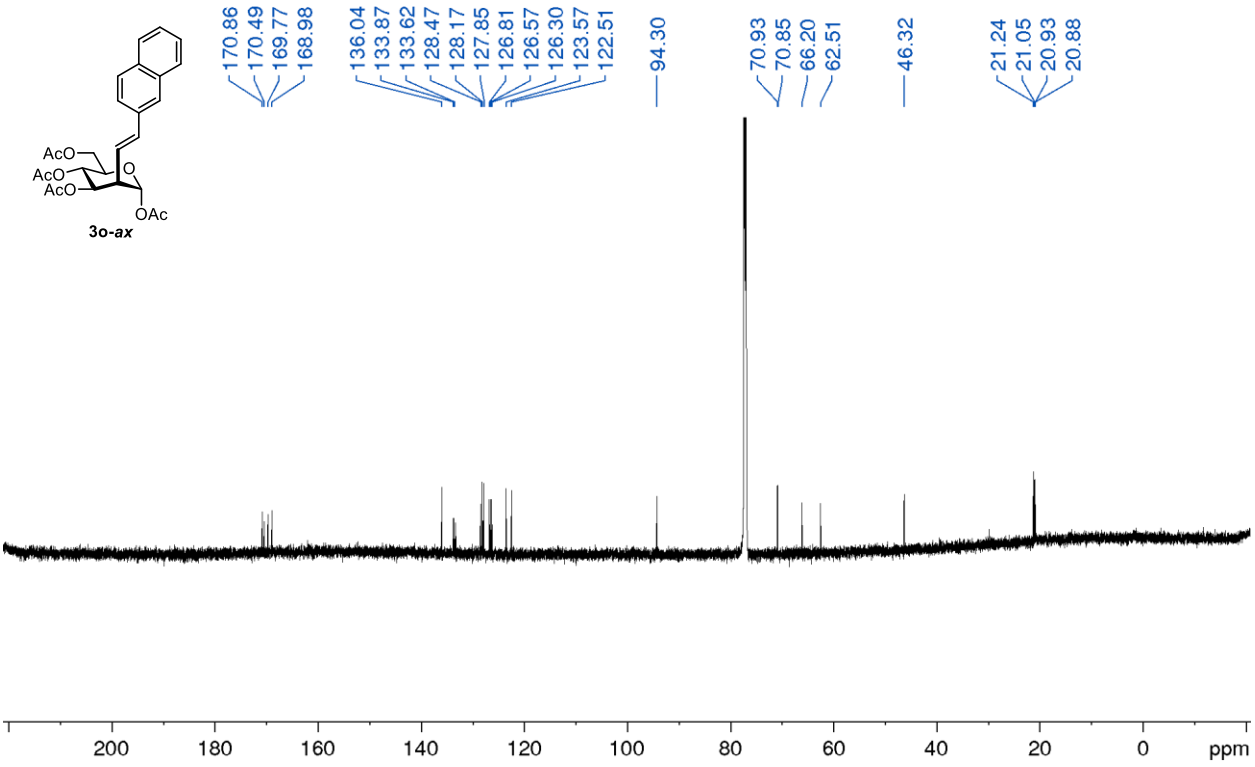
^{19}F NMR (376 MHz, $CDCl_3$, 25 °C) of (3n-*eq*)



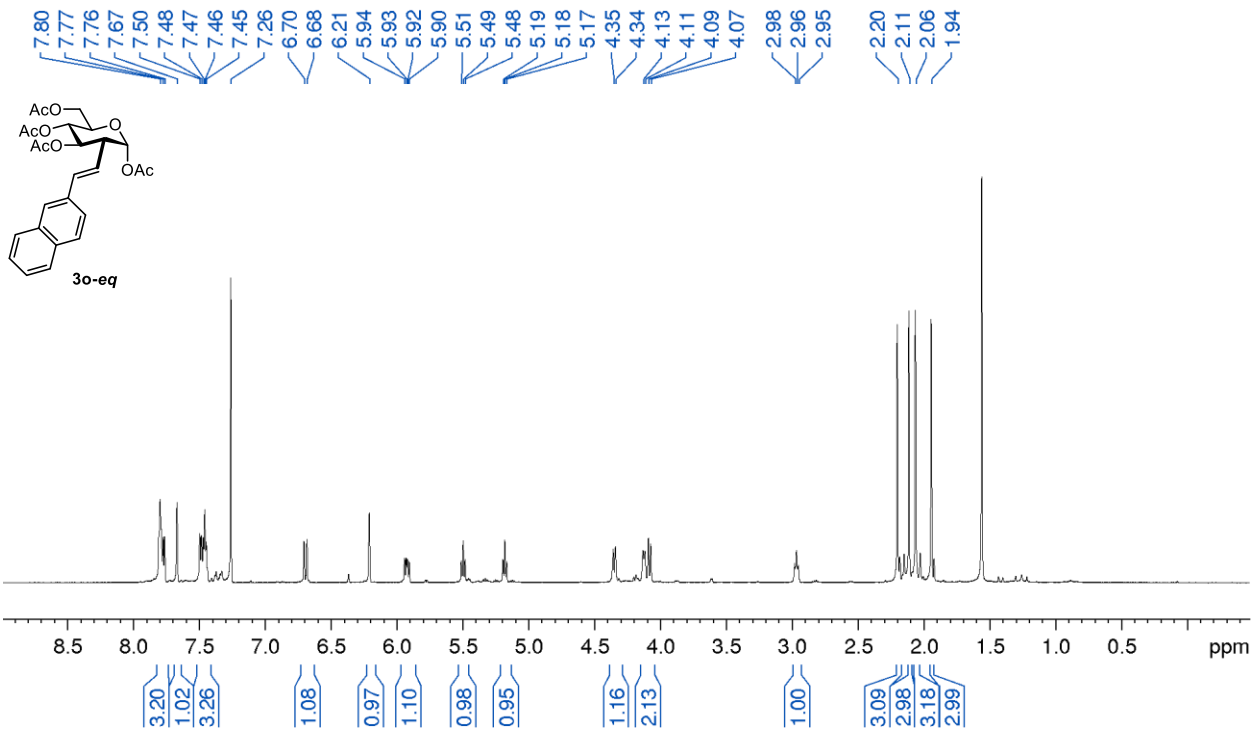
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3o-*ax*)



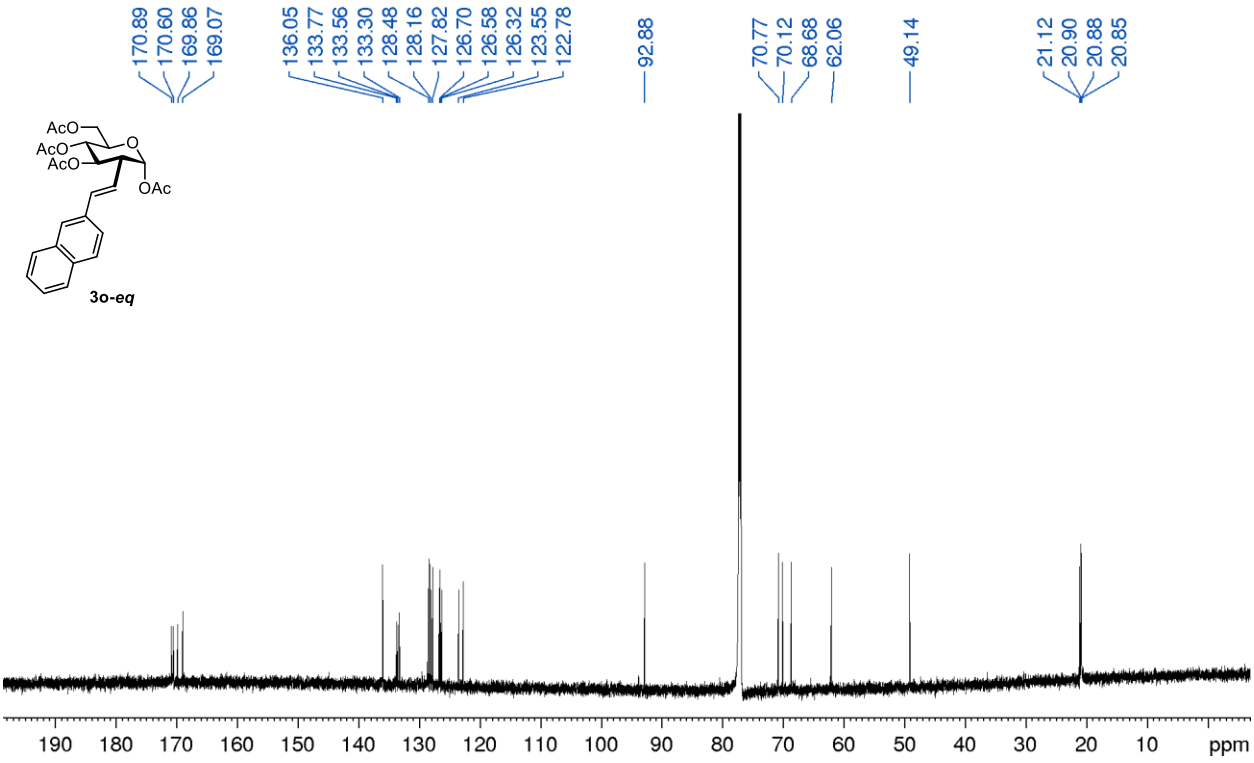
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3o-*ax*)



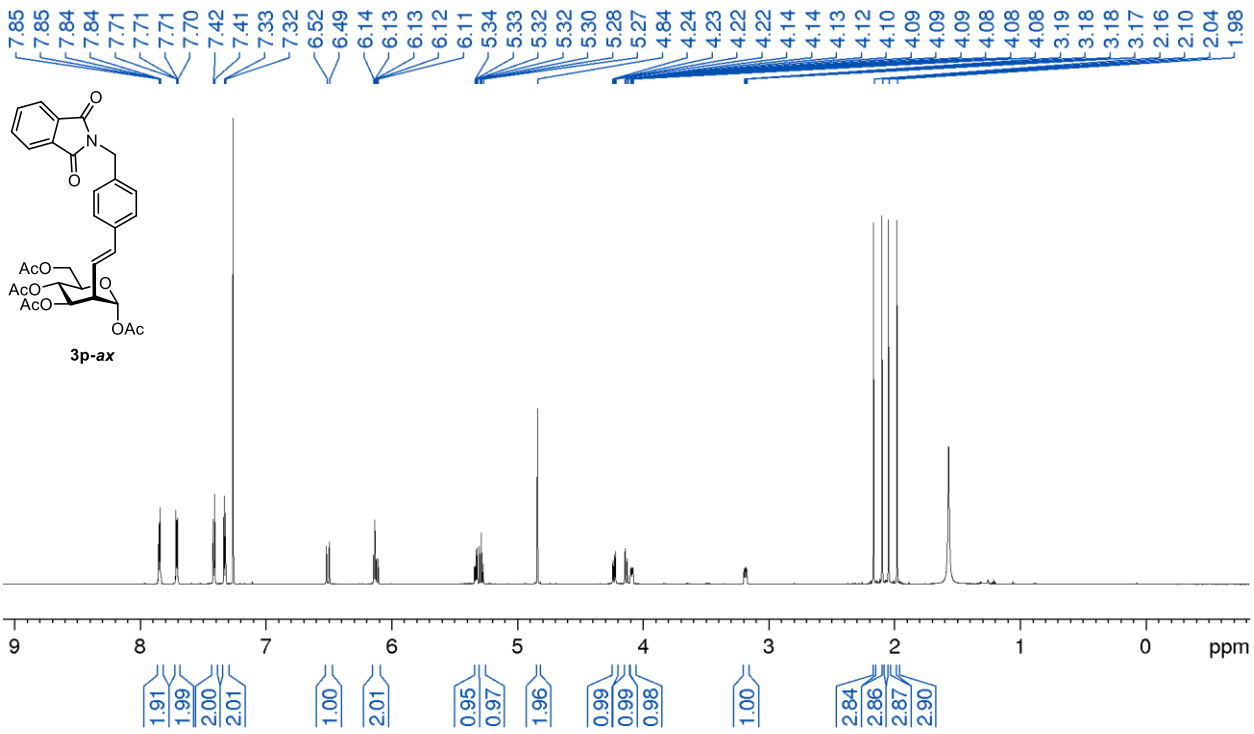
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3o-*eq*)



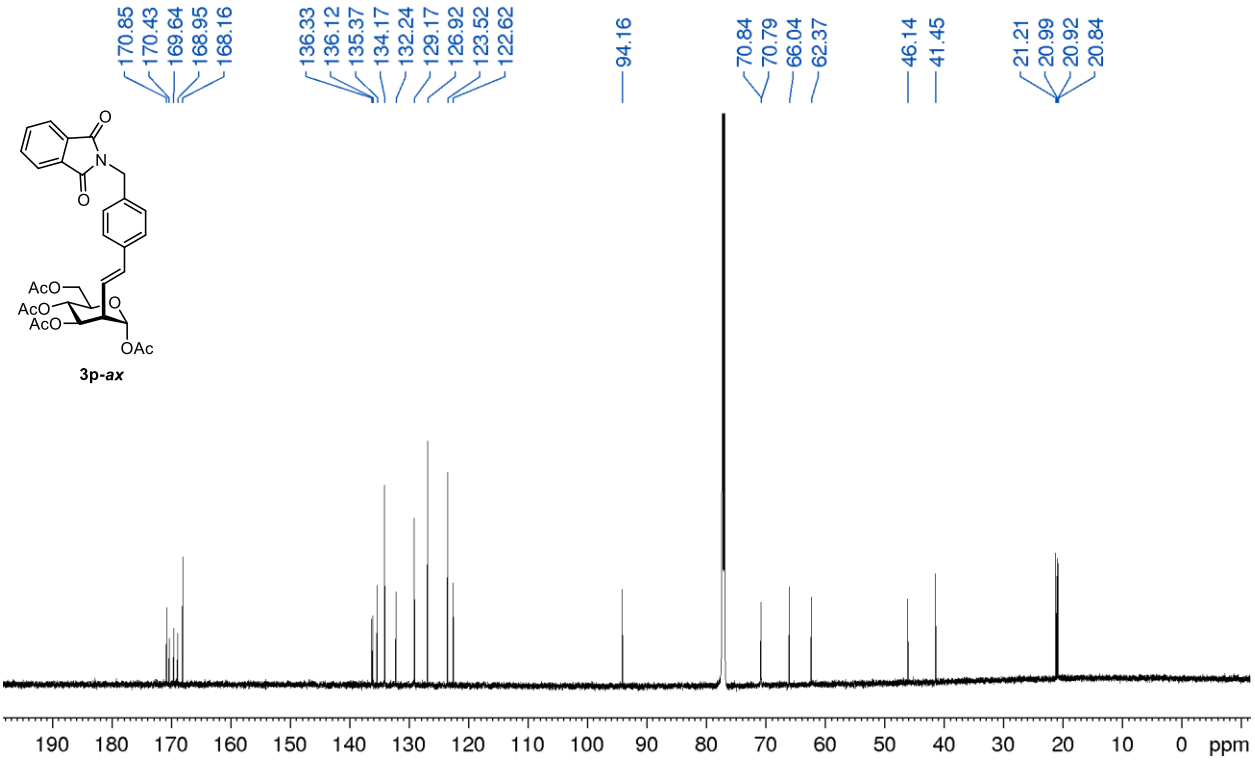
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3o-*eq*)



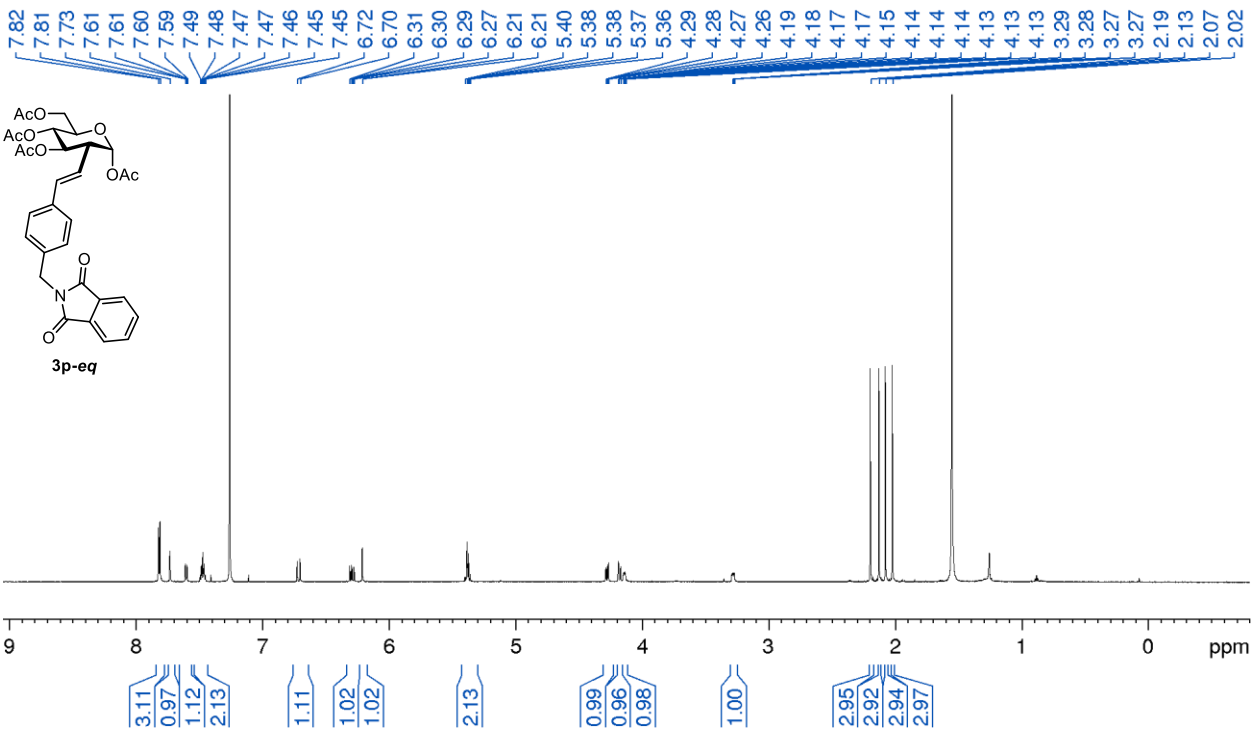
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3p-*ax*)



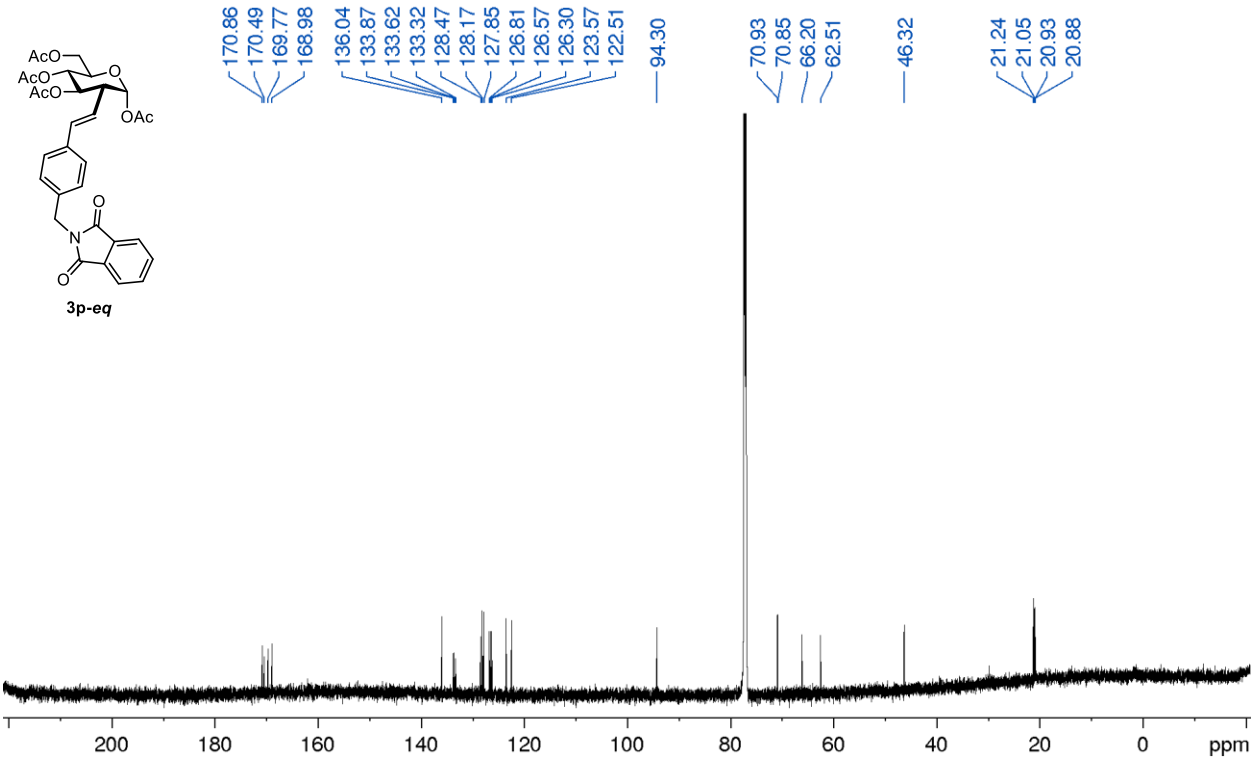
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3p-*ax*)



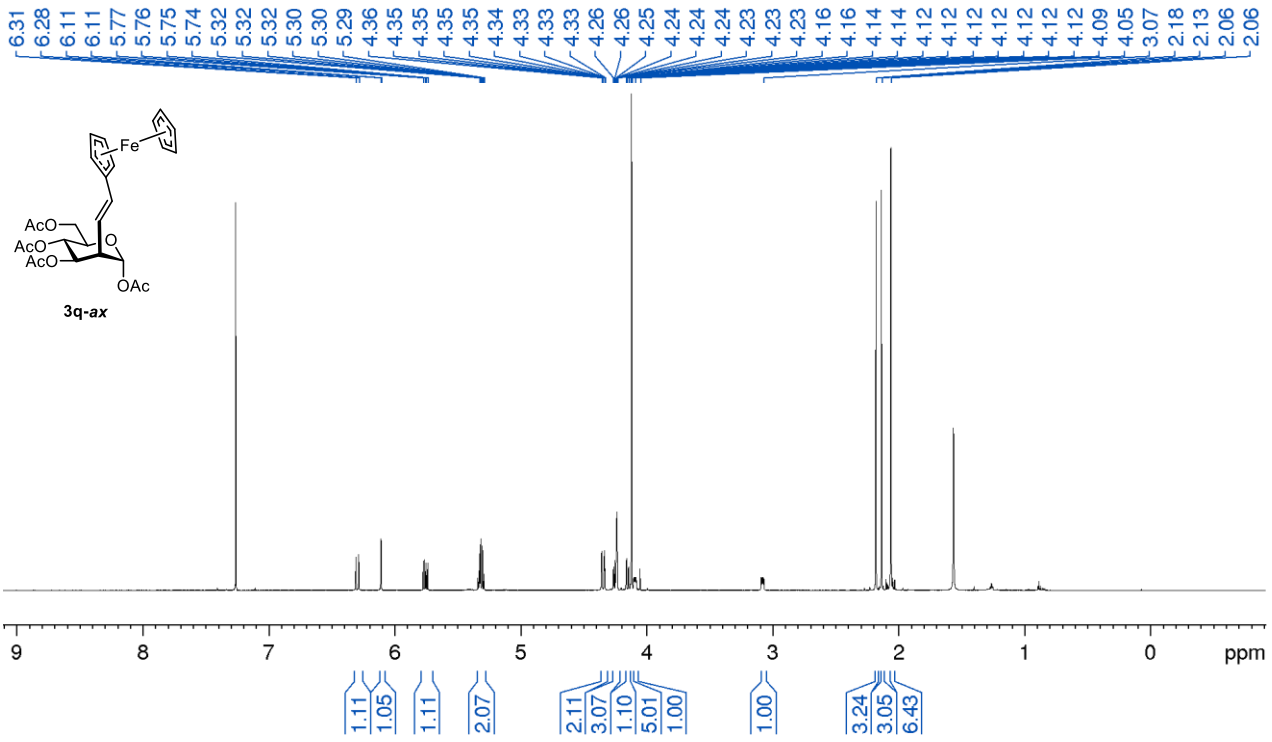
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3p-*eq*)



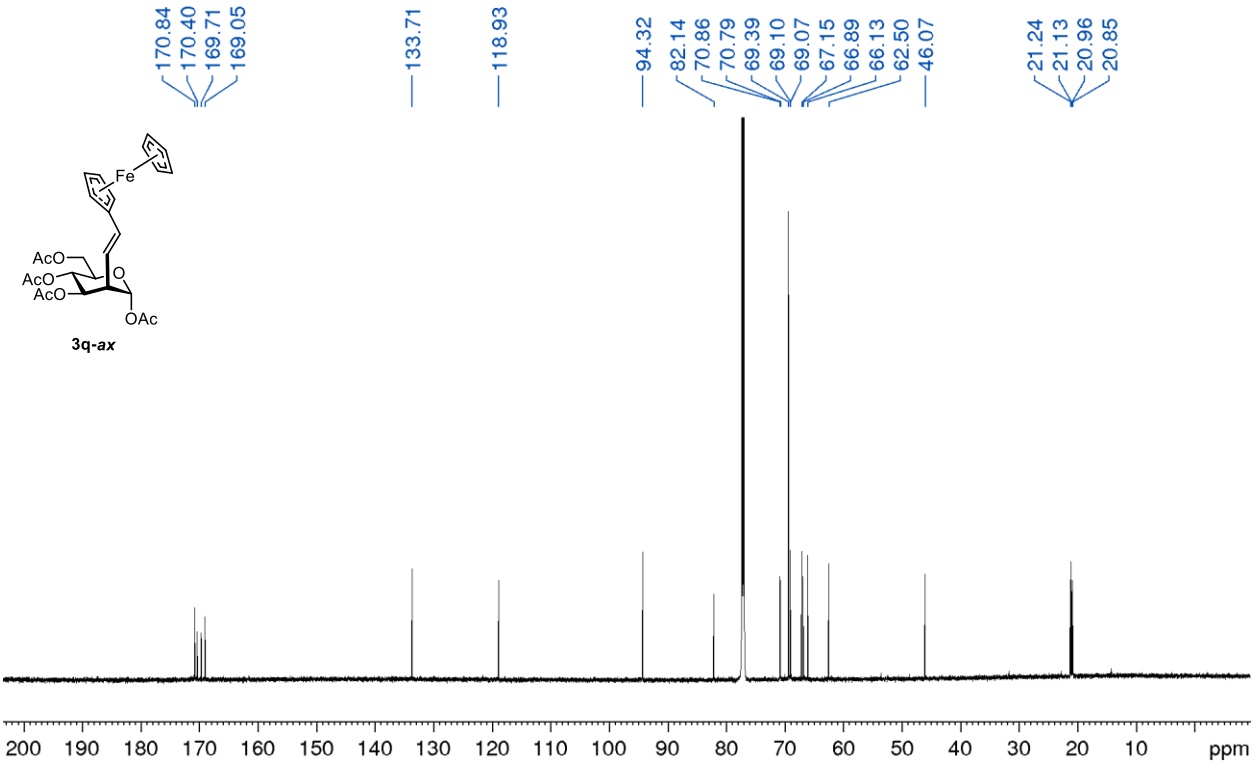
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3p-*eq*)



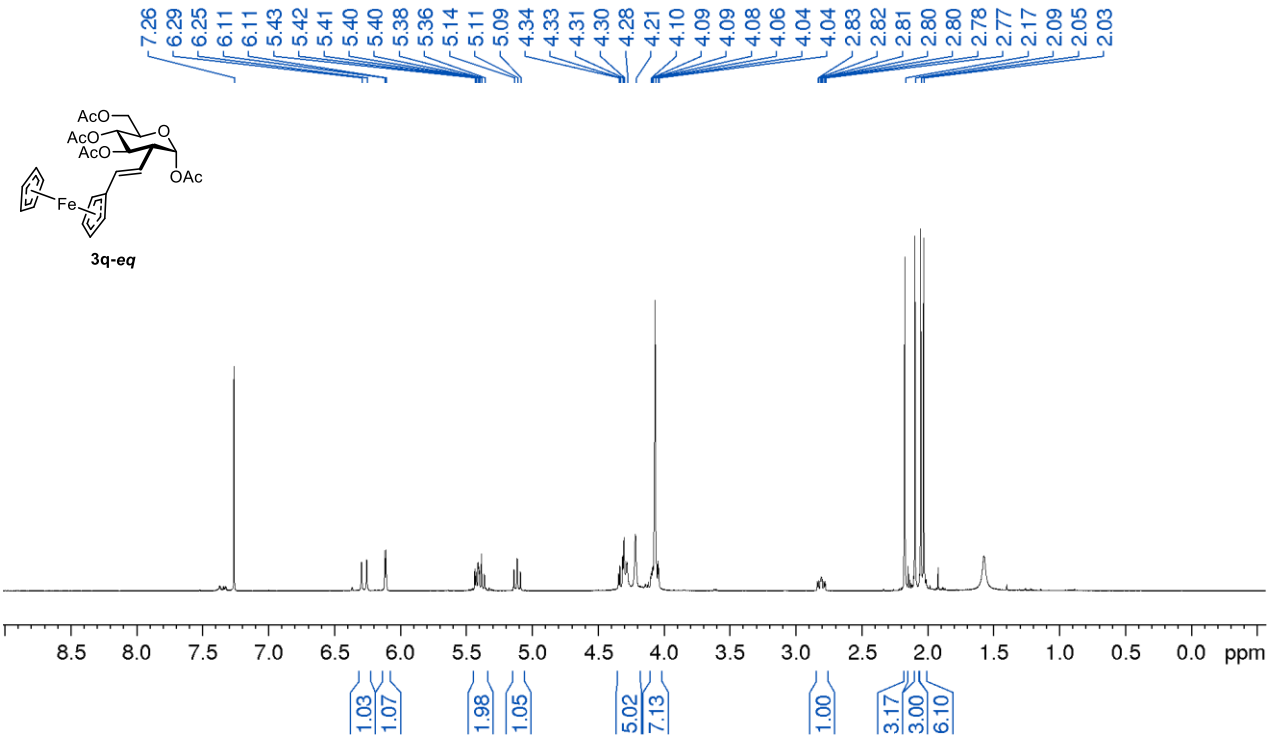
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3q-*ax*)



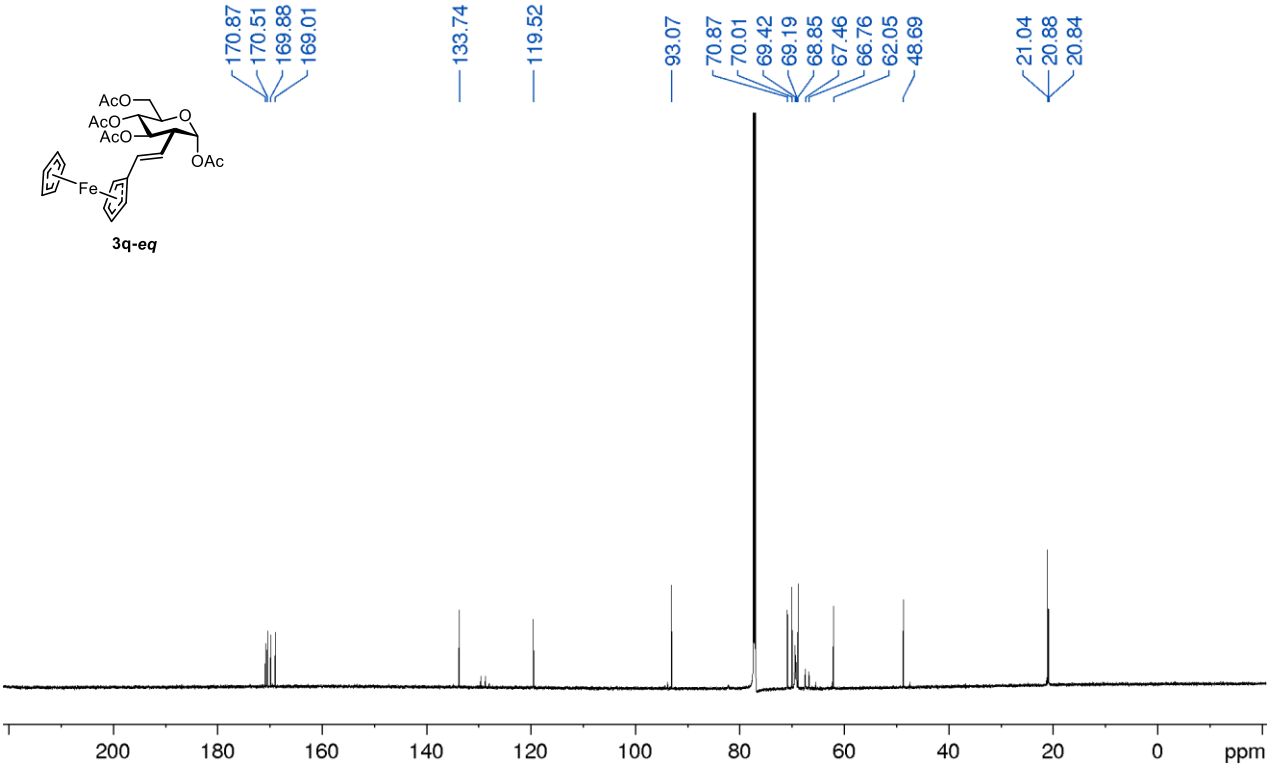
^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC) of (3q-*ax*)



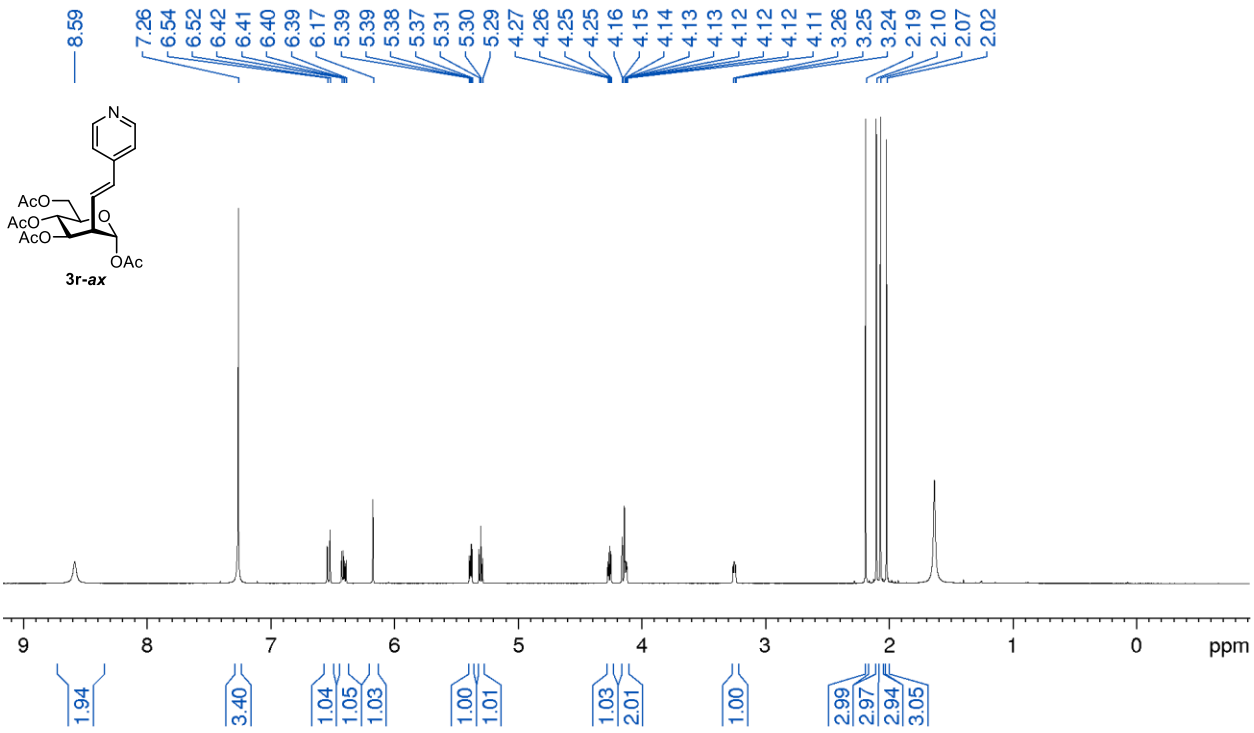
^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC) of (3q-*eq*)



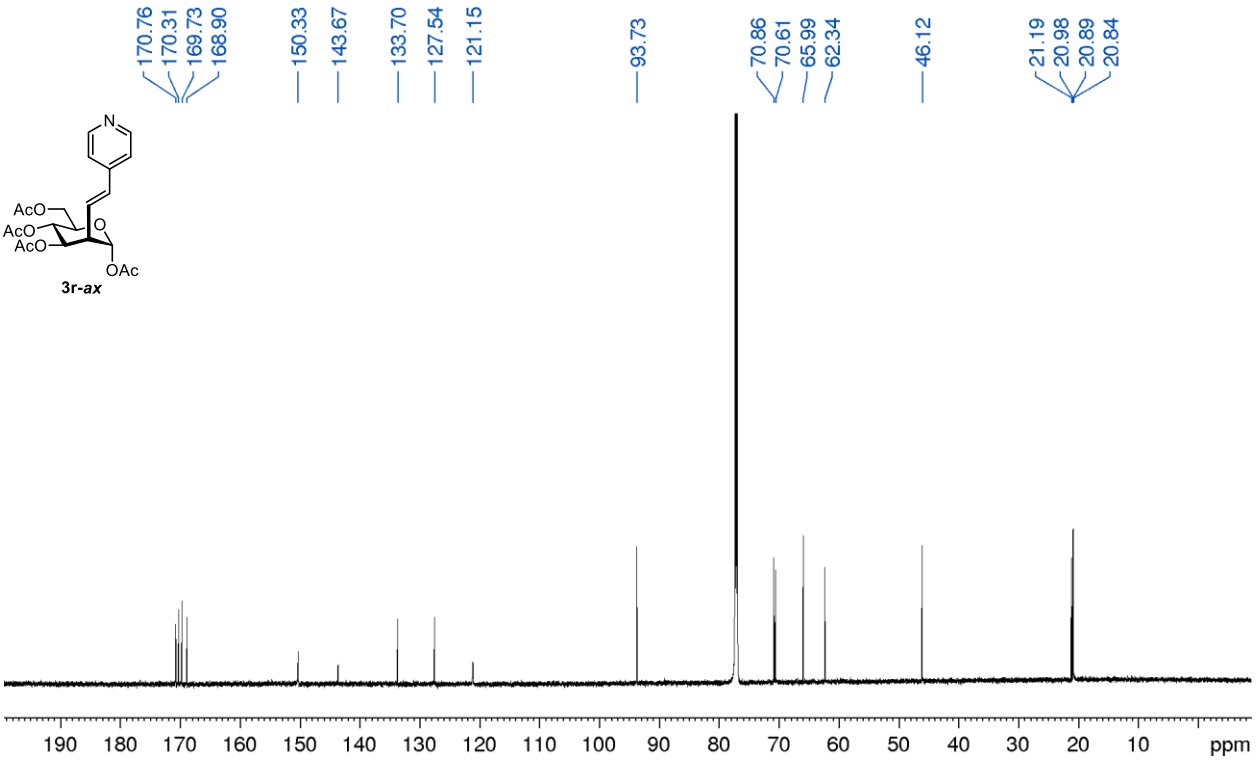
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3q-*eq*)



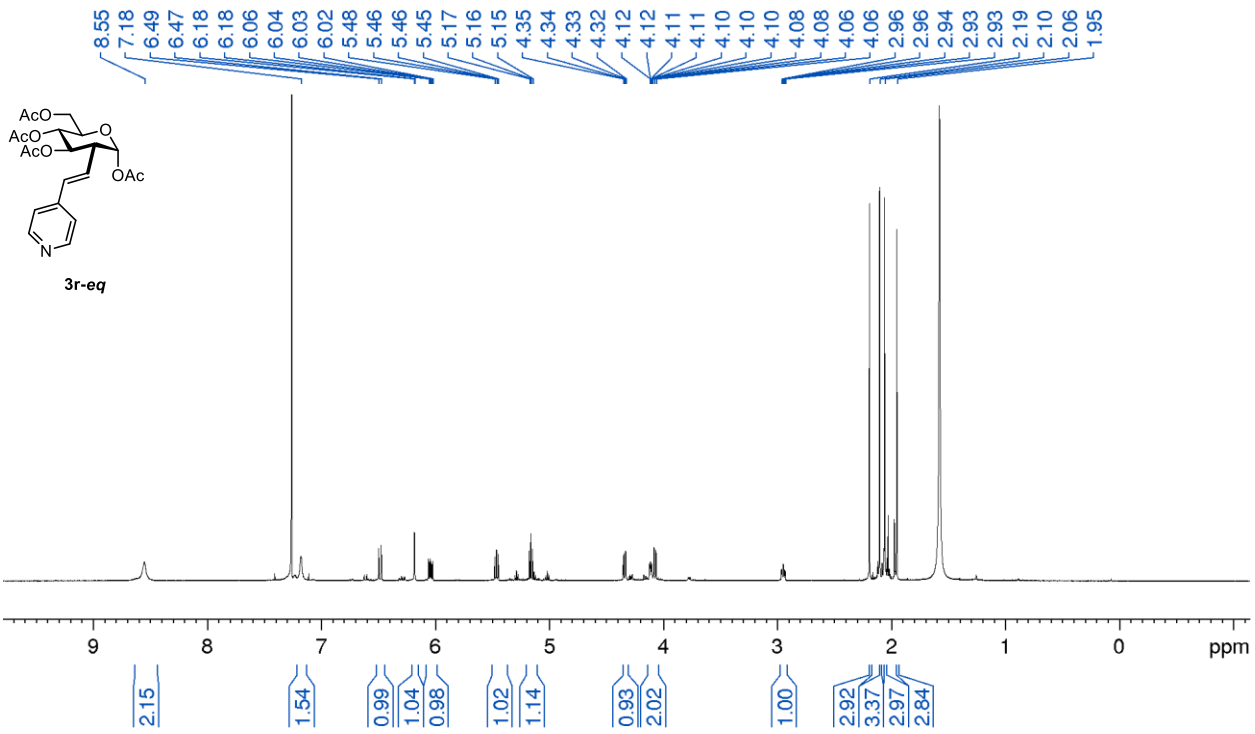
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3r-*ax*)



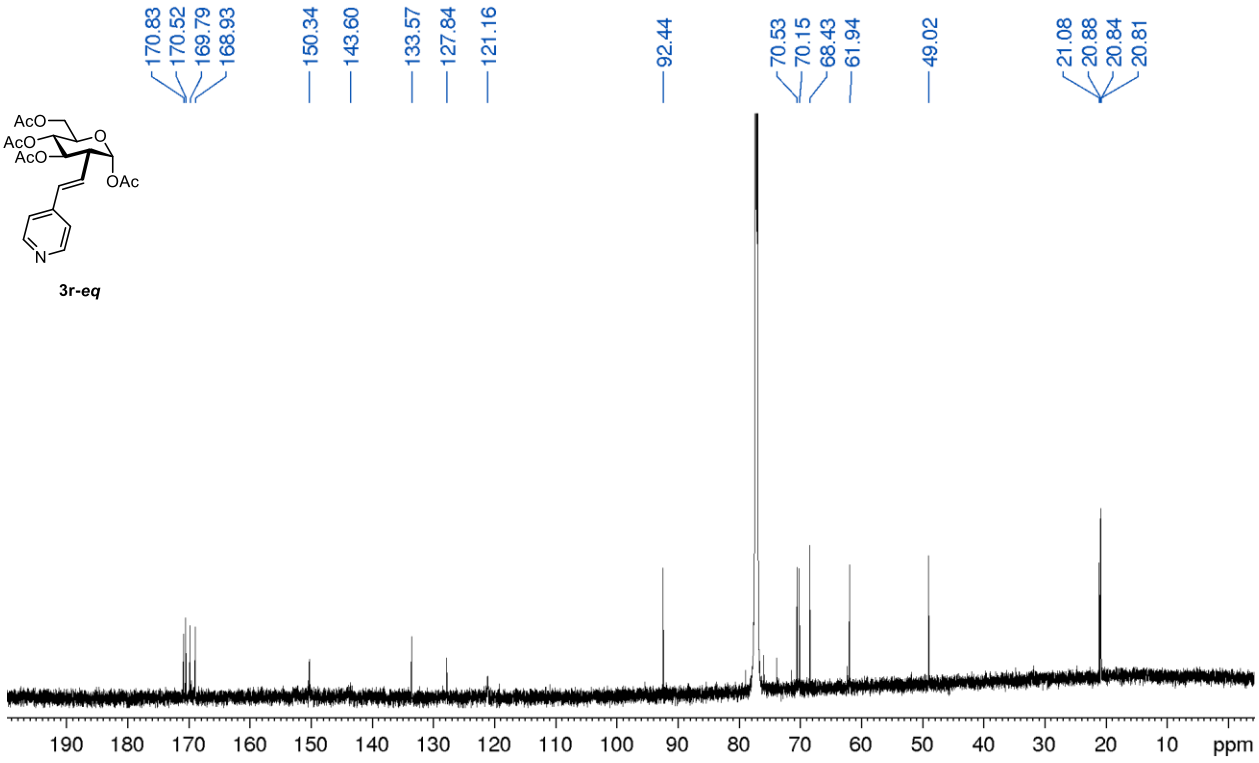
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3r-*ax*)



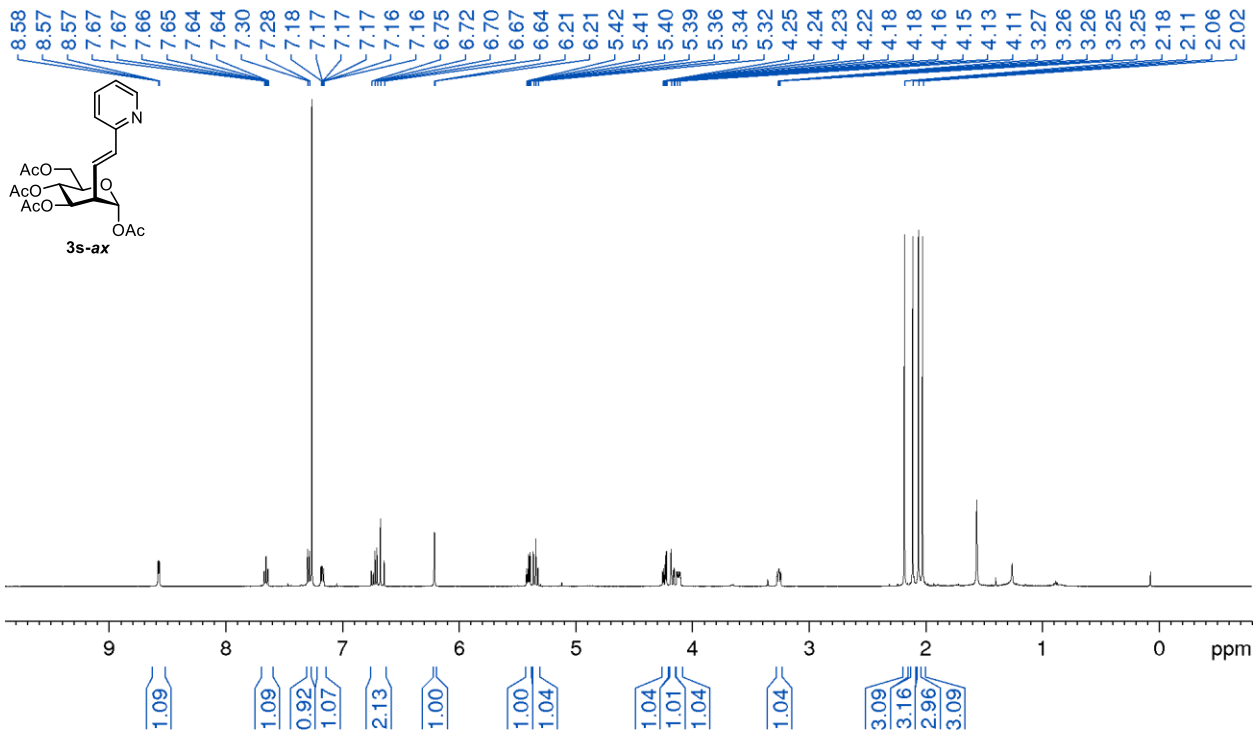
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3r-*eq*)



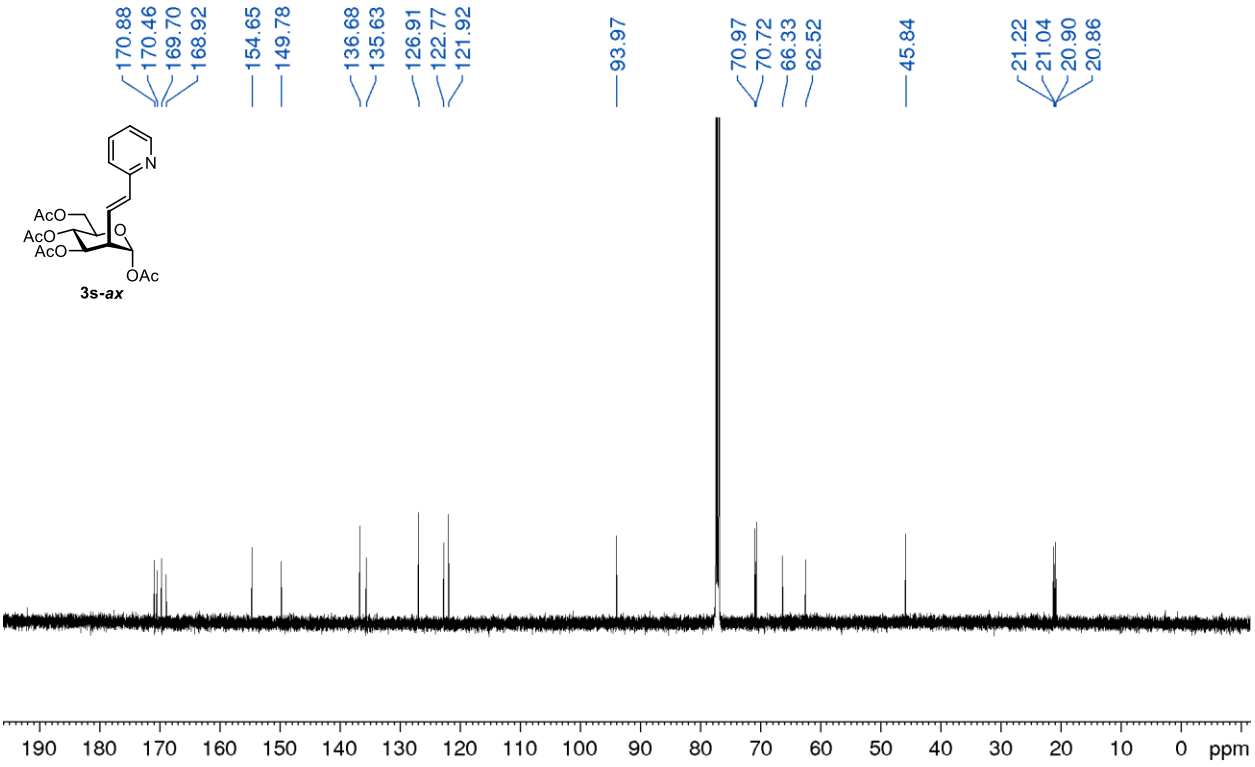
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3r-*eq*)



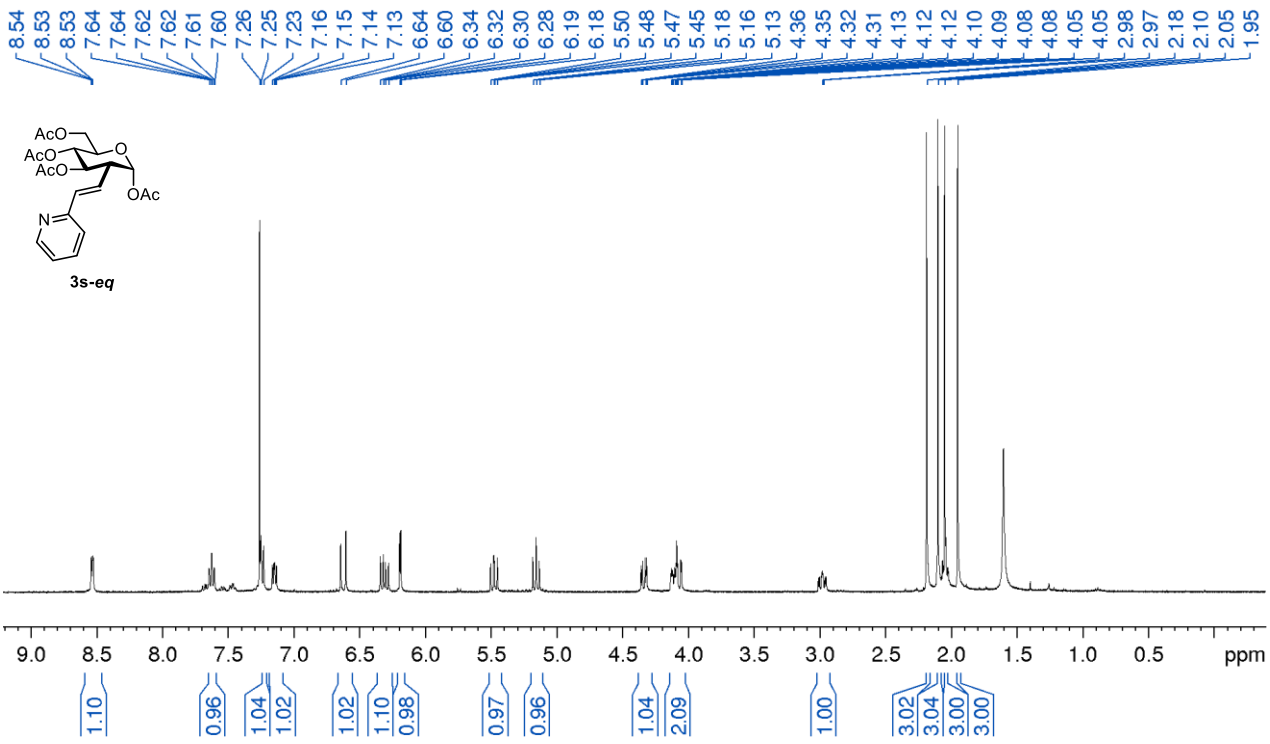
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (3s-*ax*)



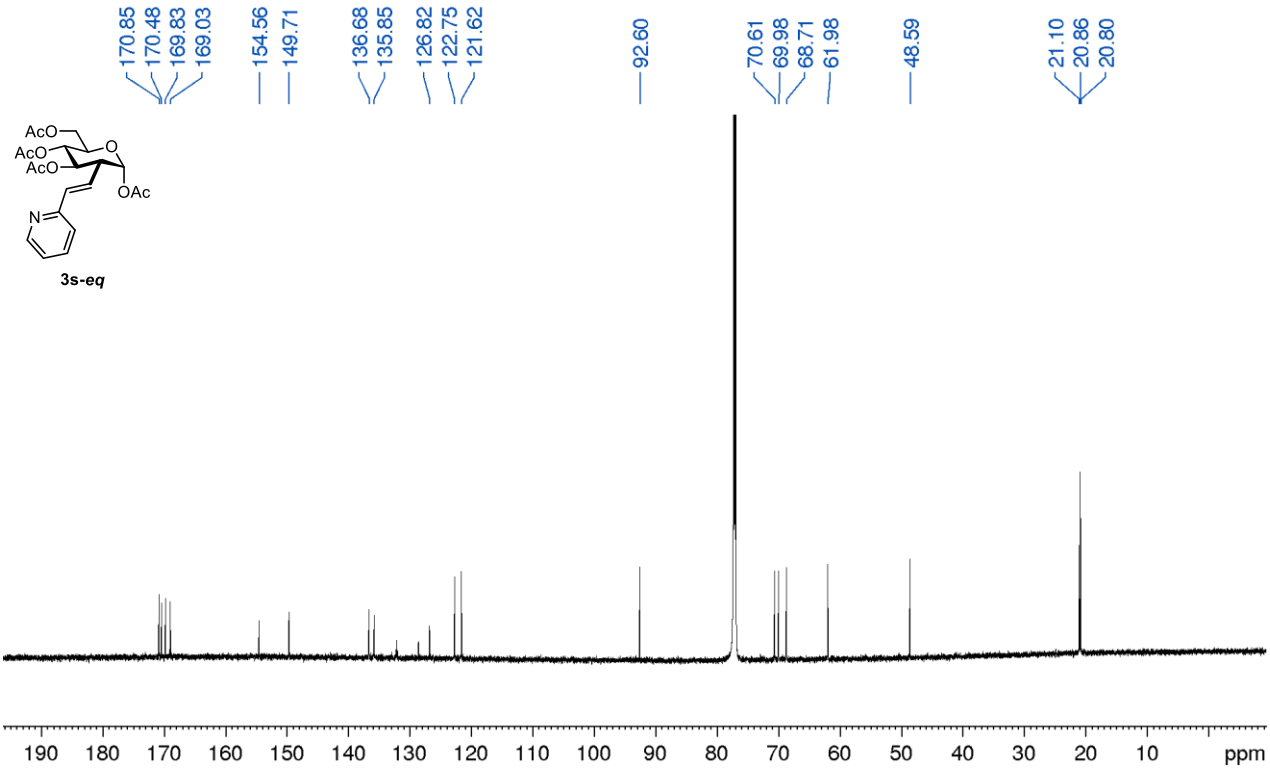
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (3s-*ax*)



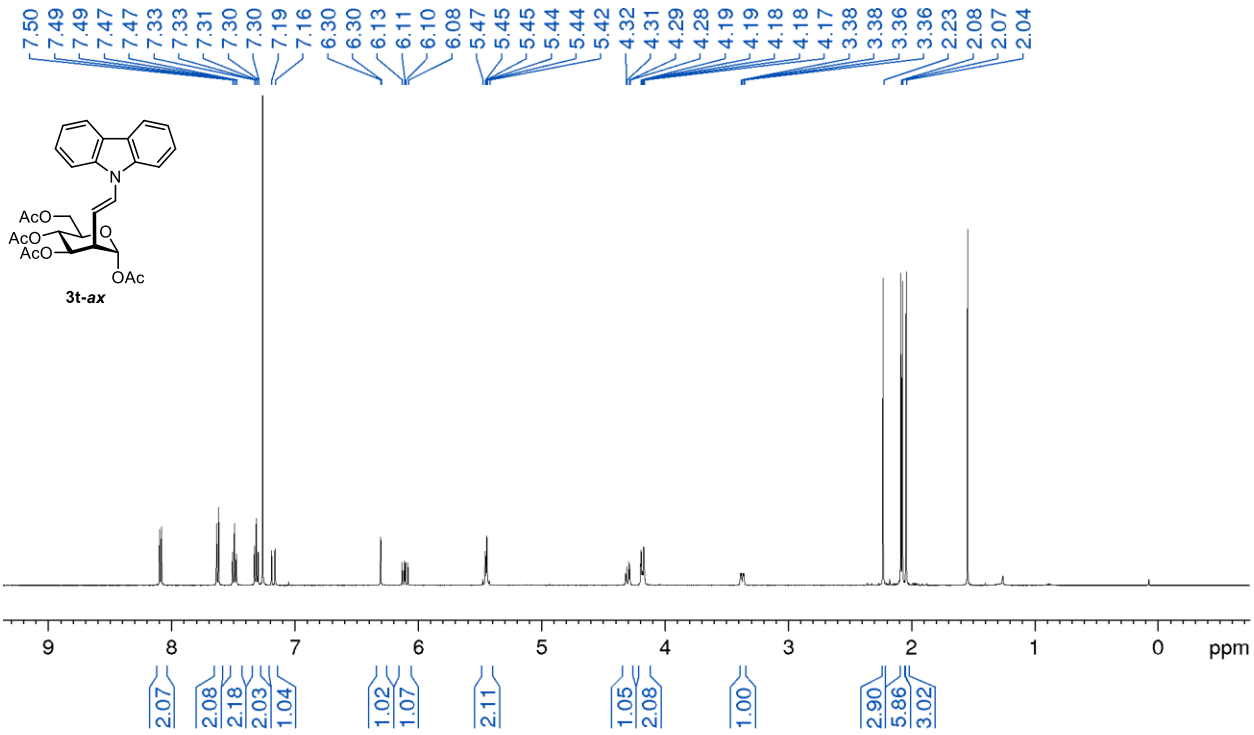
^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) of (3s-*eq*)



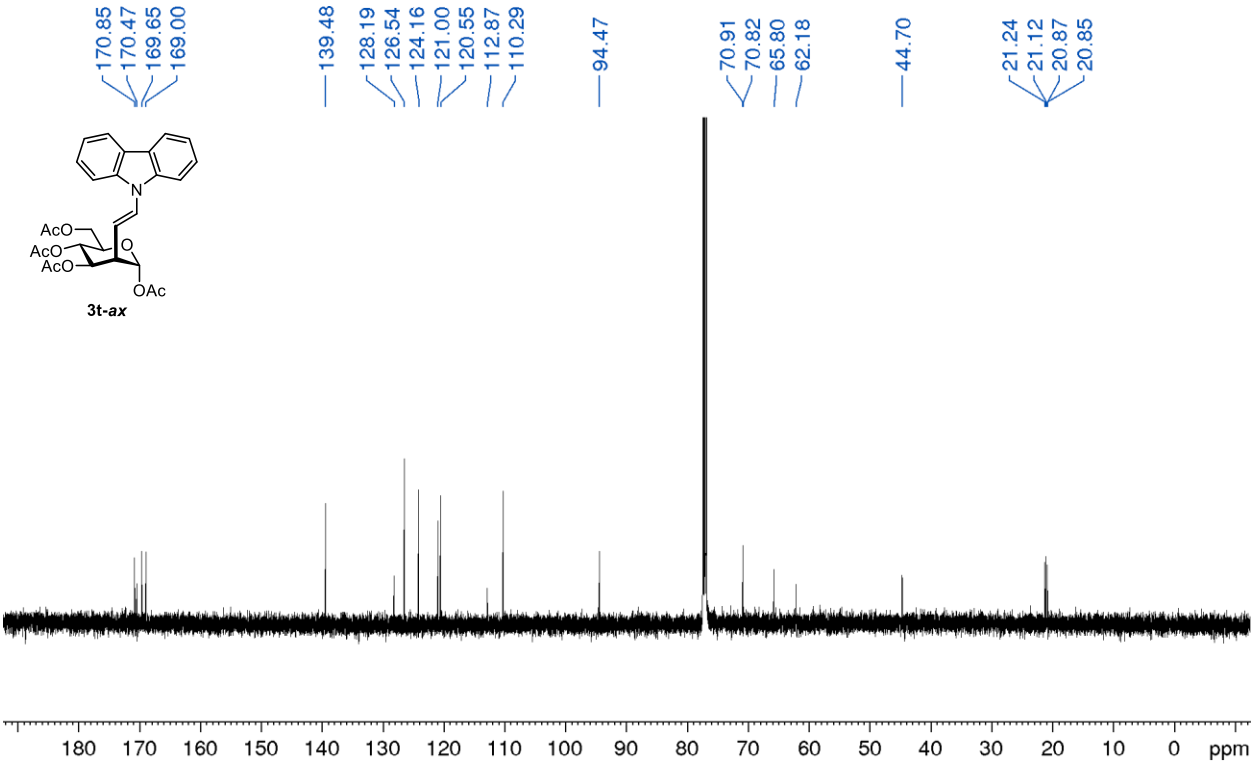
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3s-*eq*)



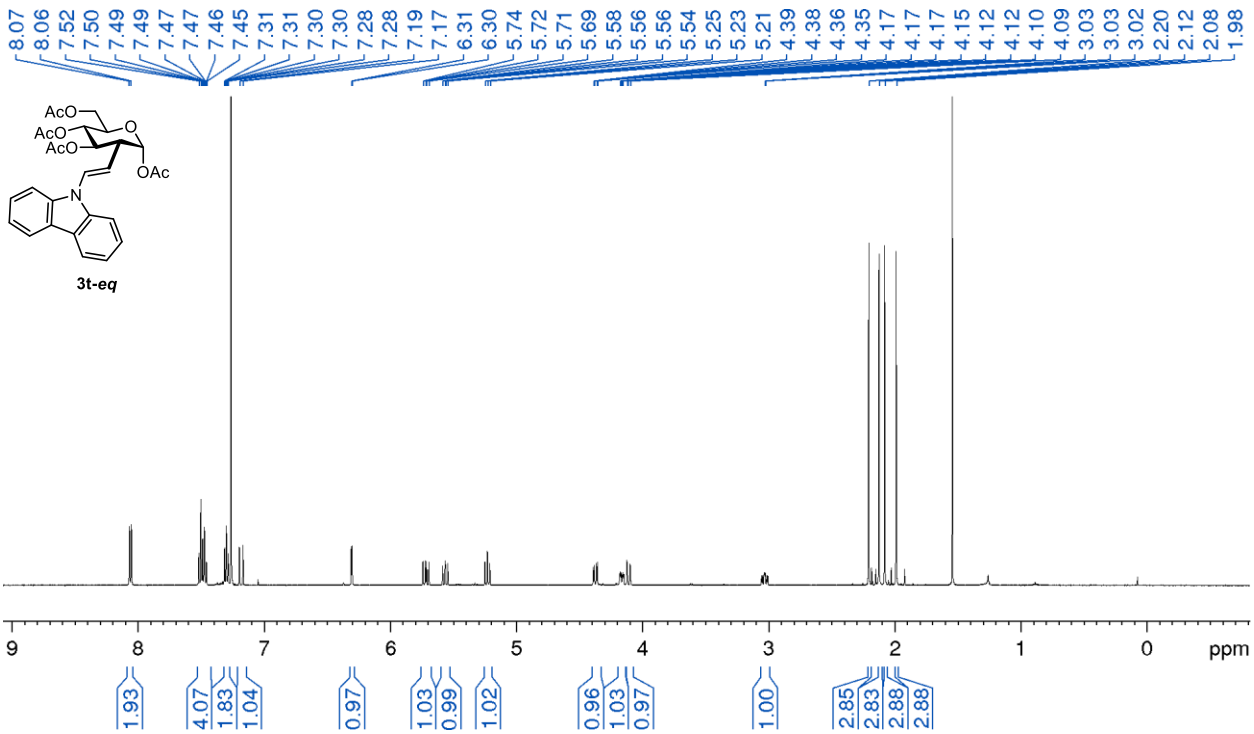
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3t-*ax*)



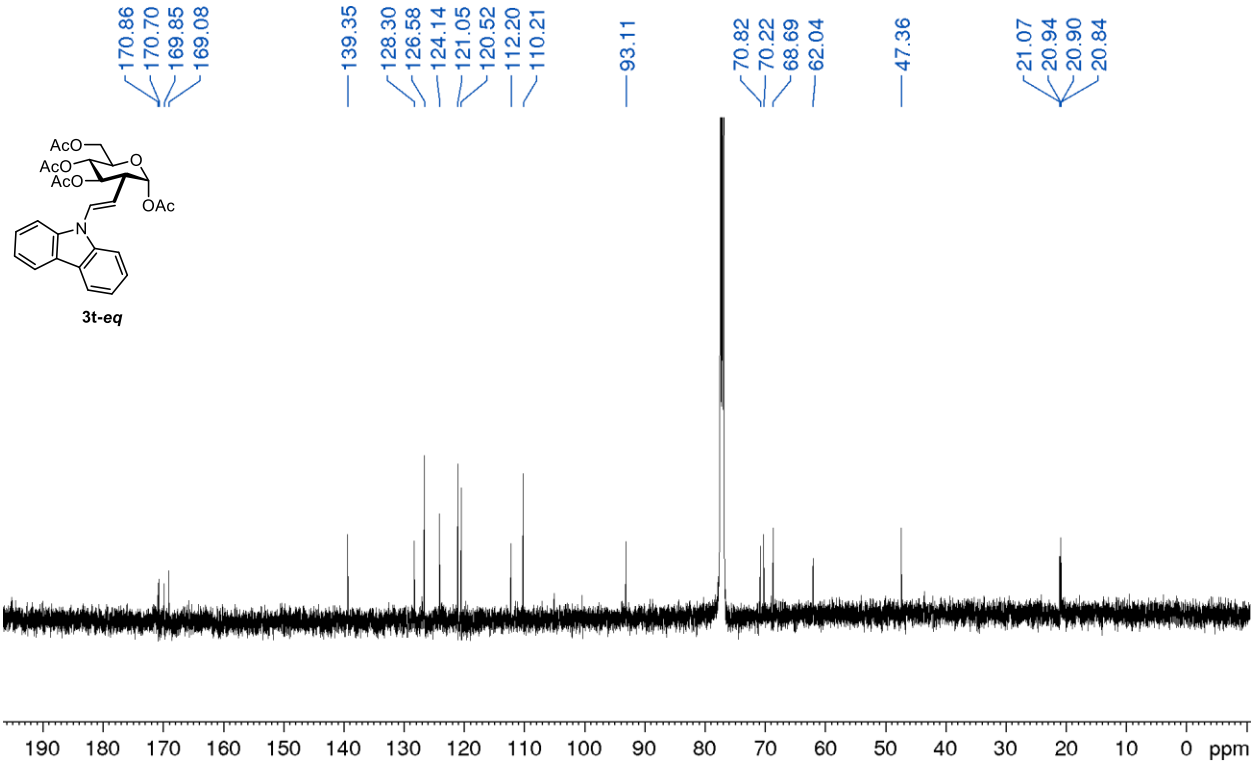
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3t-*ax*)



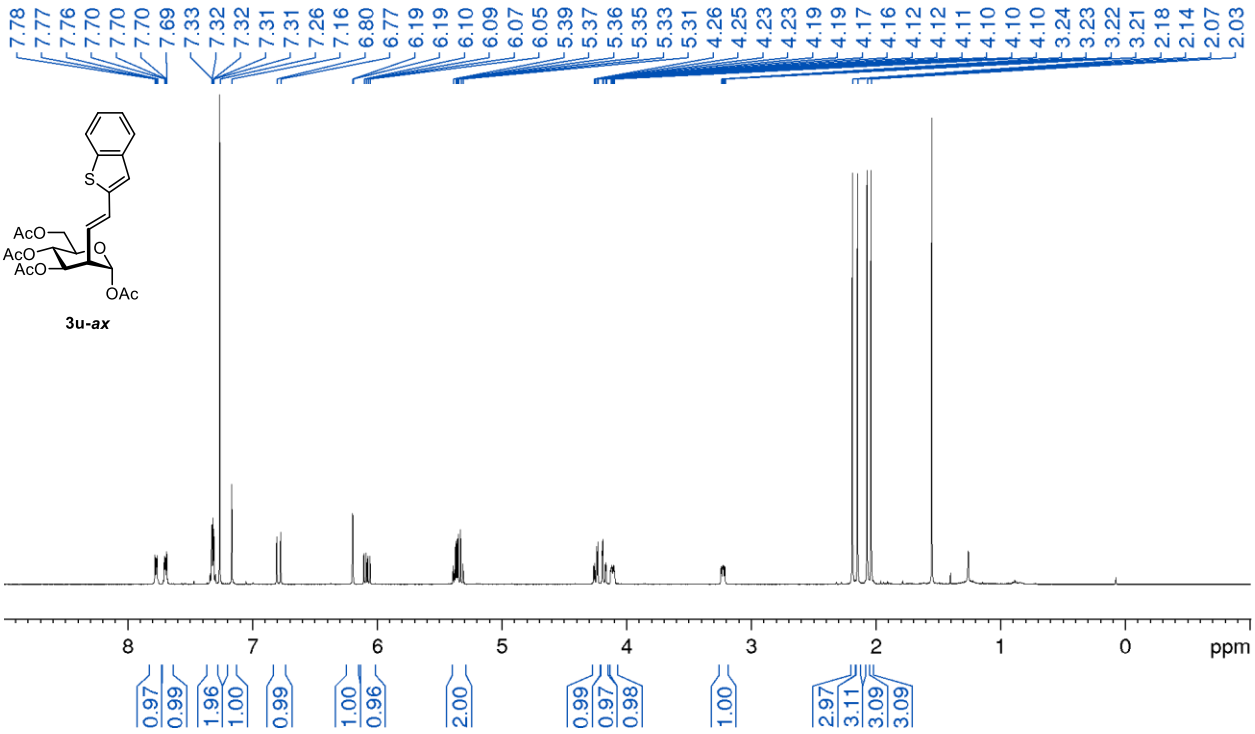
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3t-*eq*)



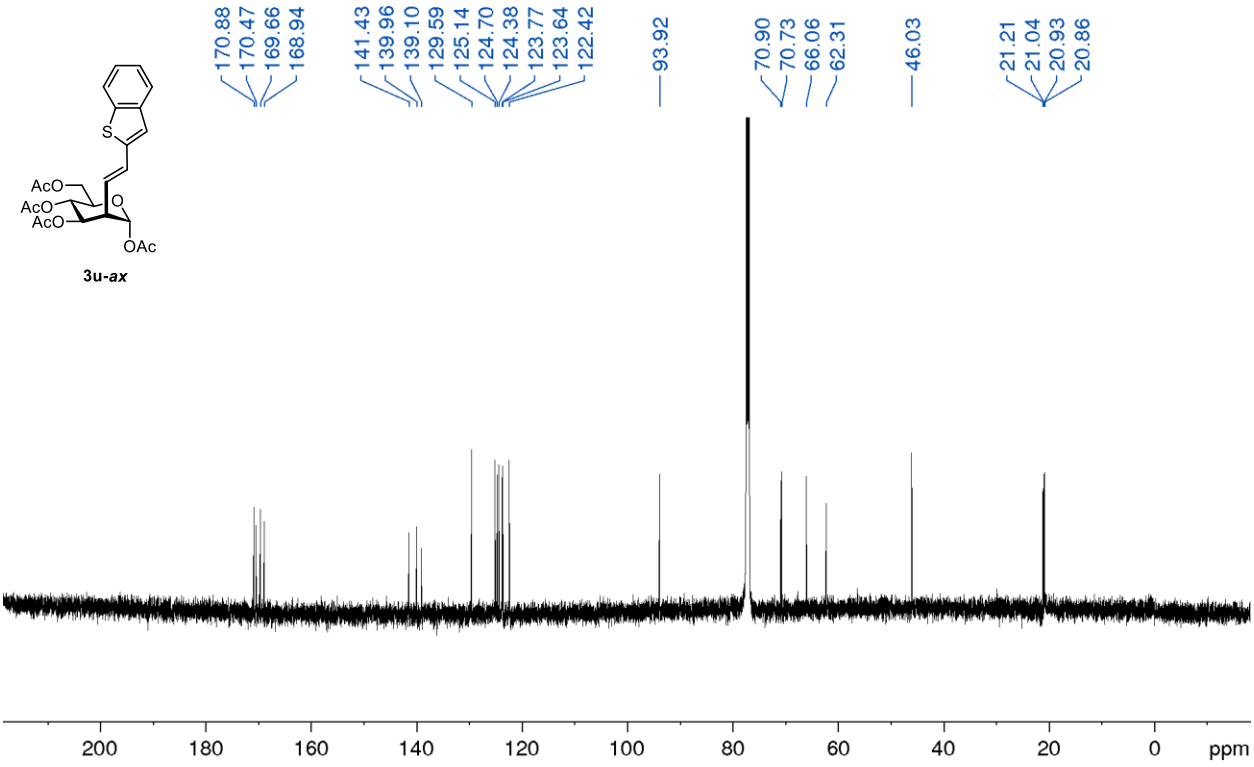
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3t-*eq*)



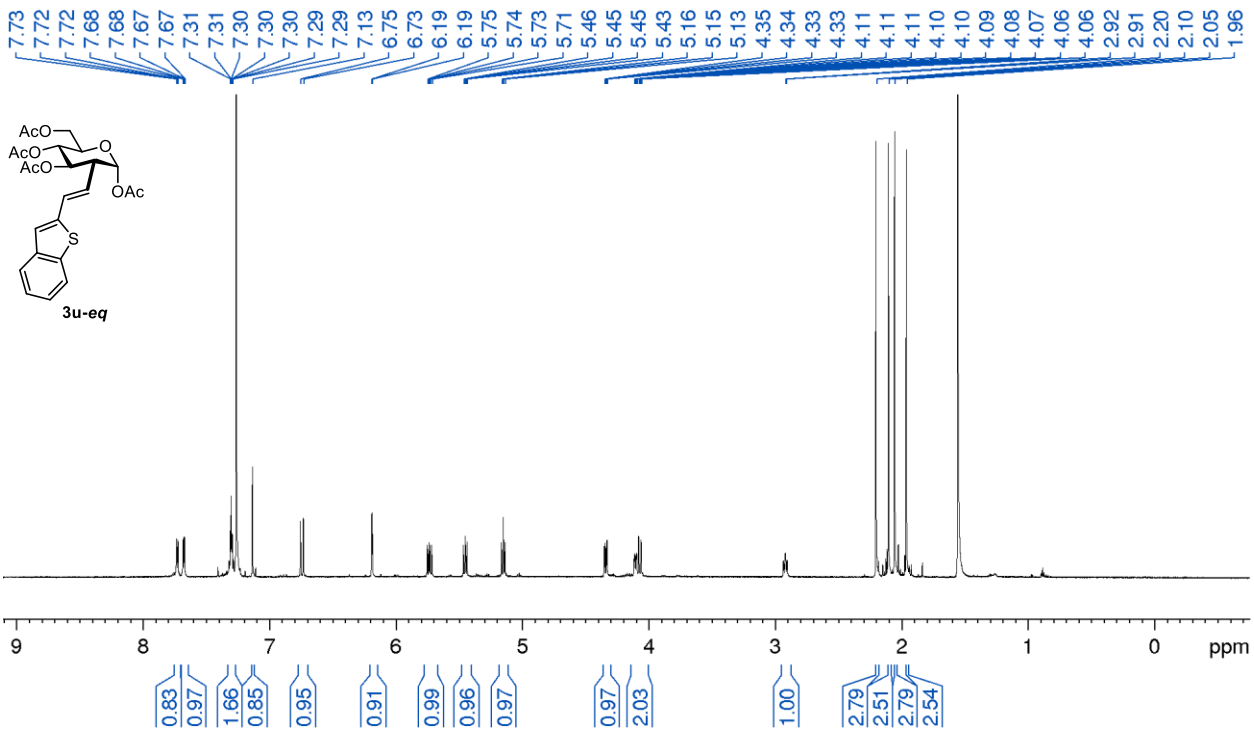
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (3u-*ax*)



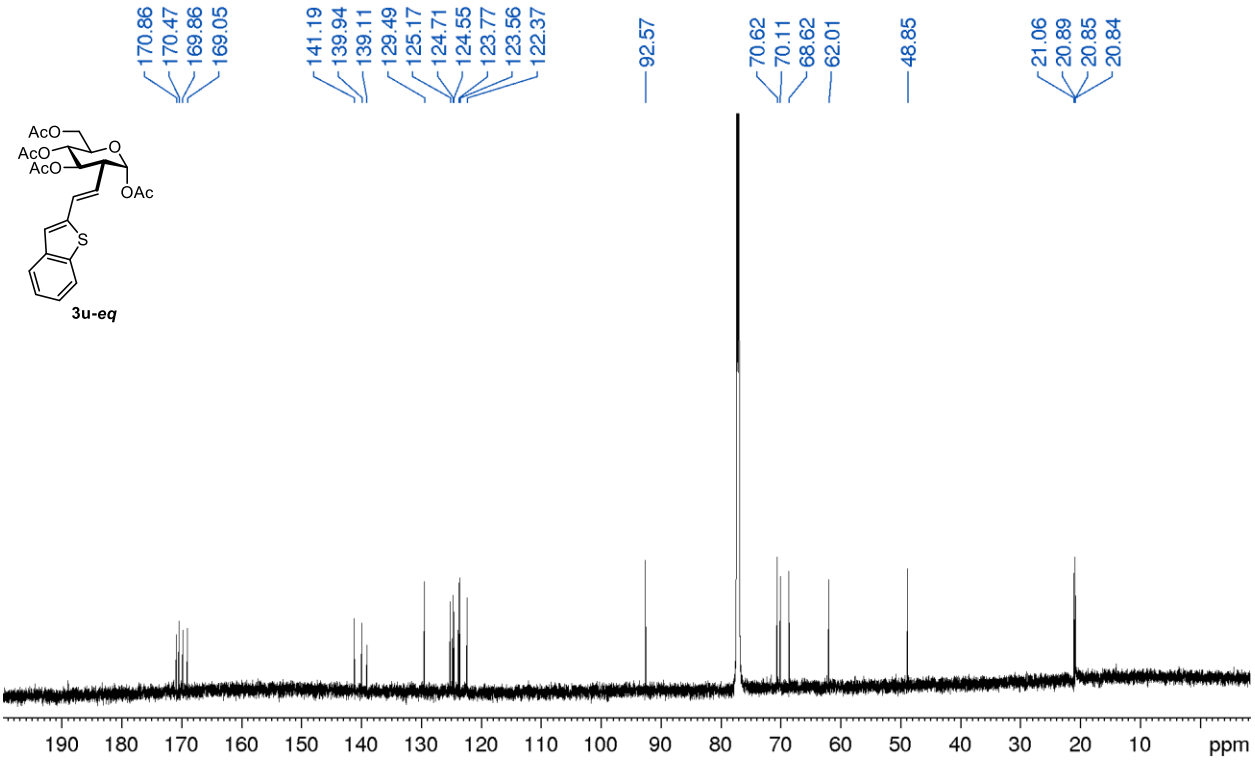
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (3u-*ax*)



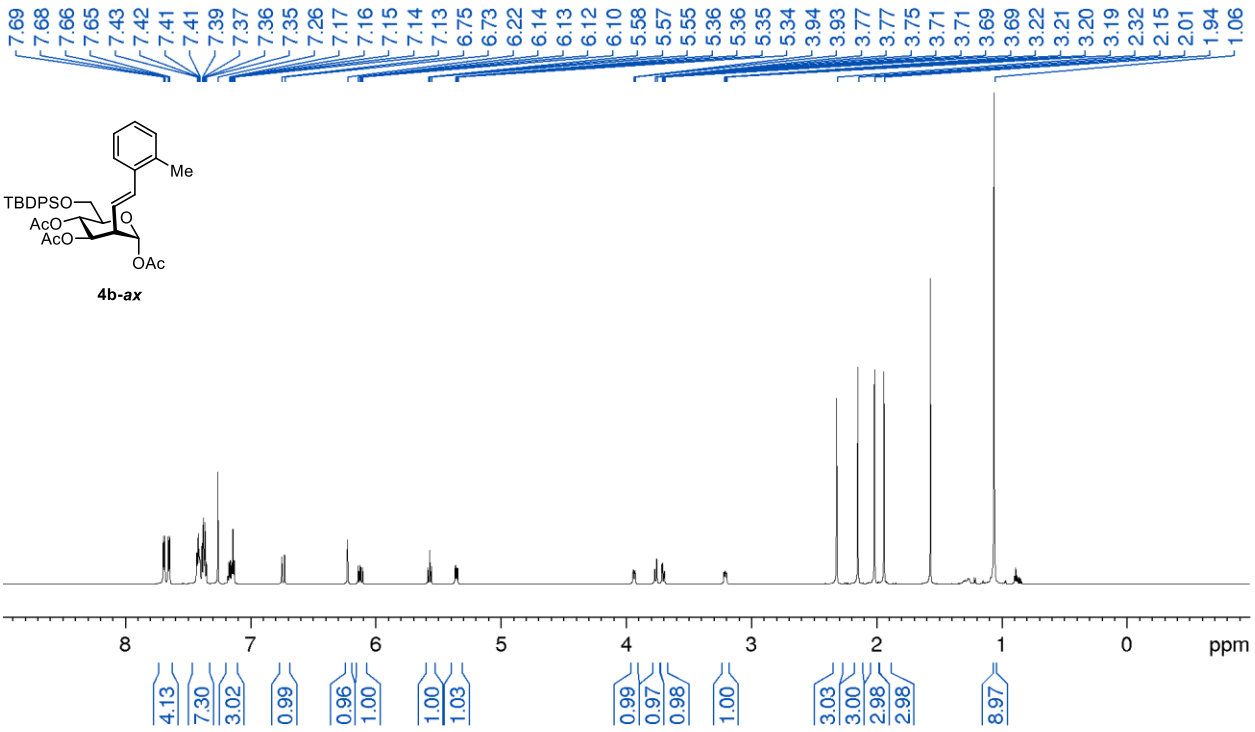
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (3u-*eq*)



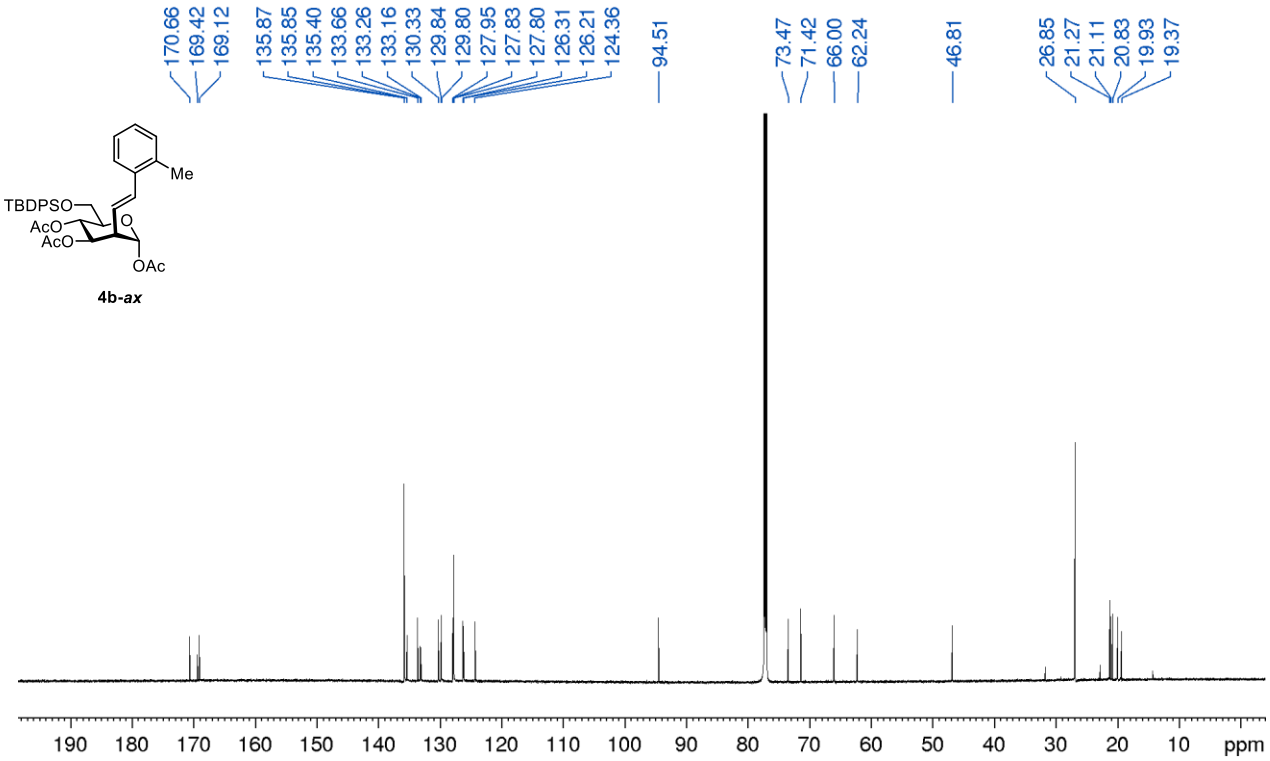
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) of (3u-*eq*)



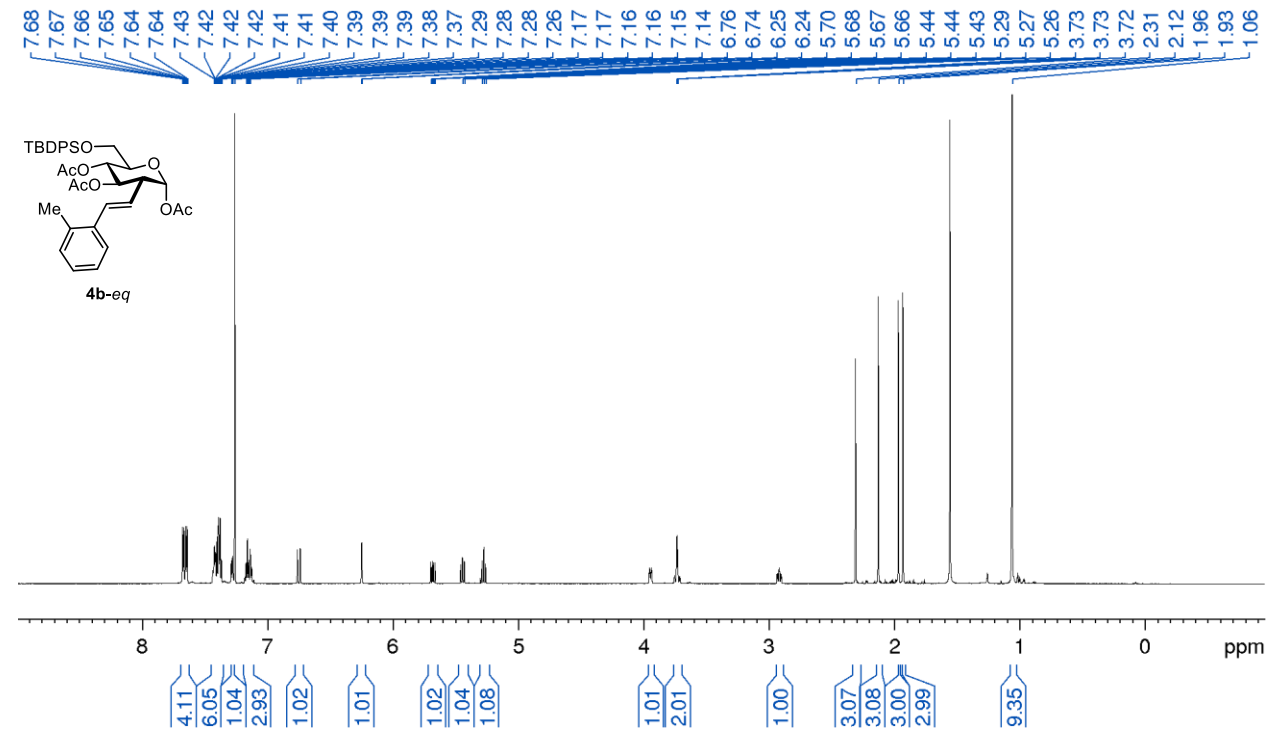
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (4b-*ax*)



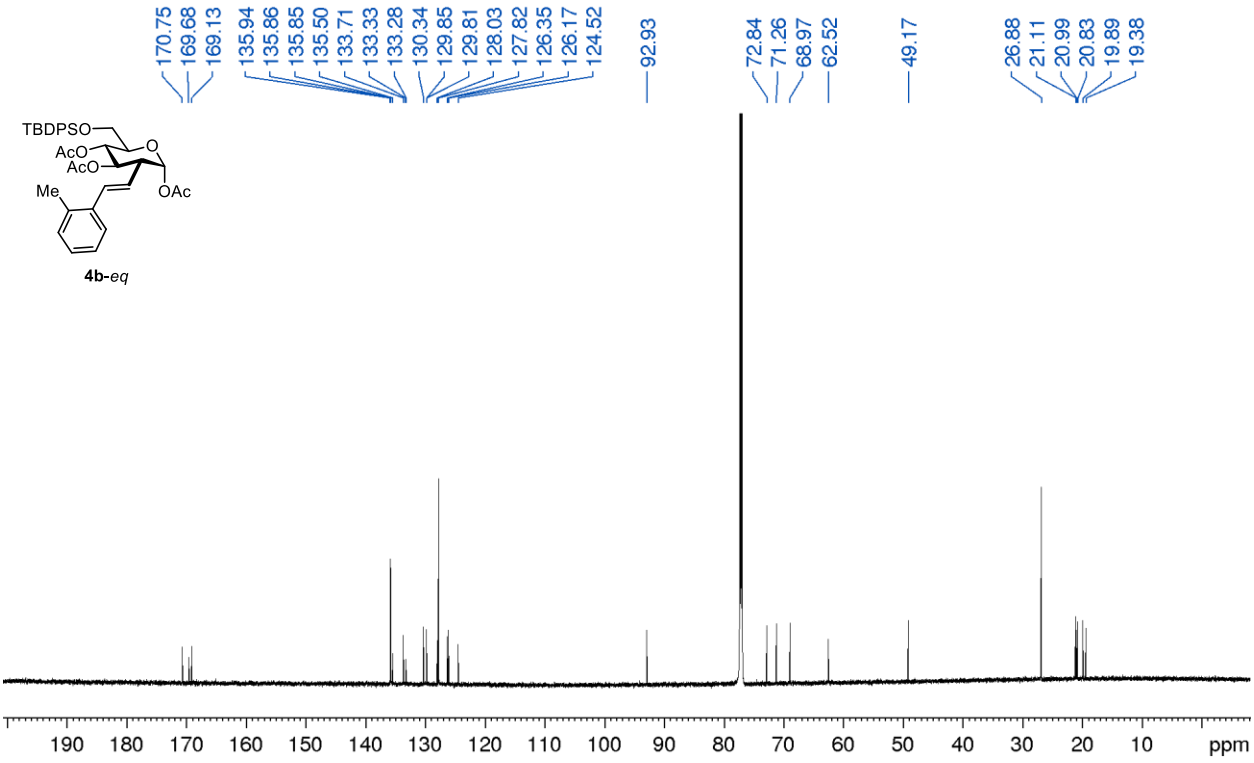
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (4b-*ax*)



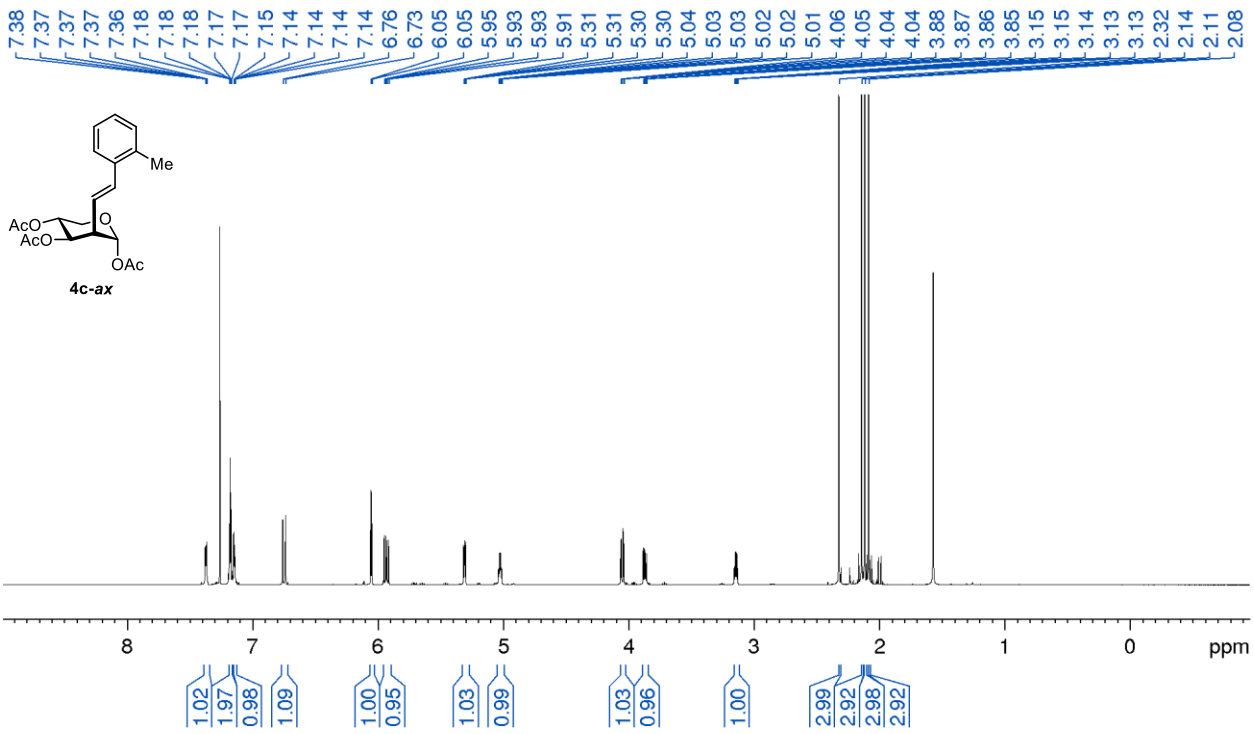
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (4b-*eq*)



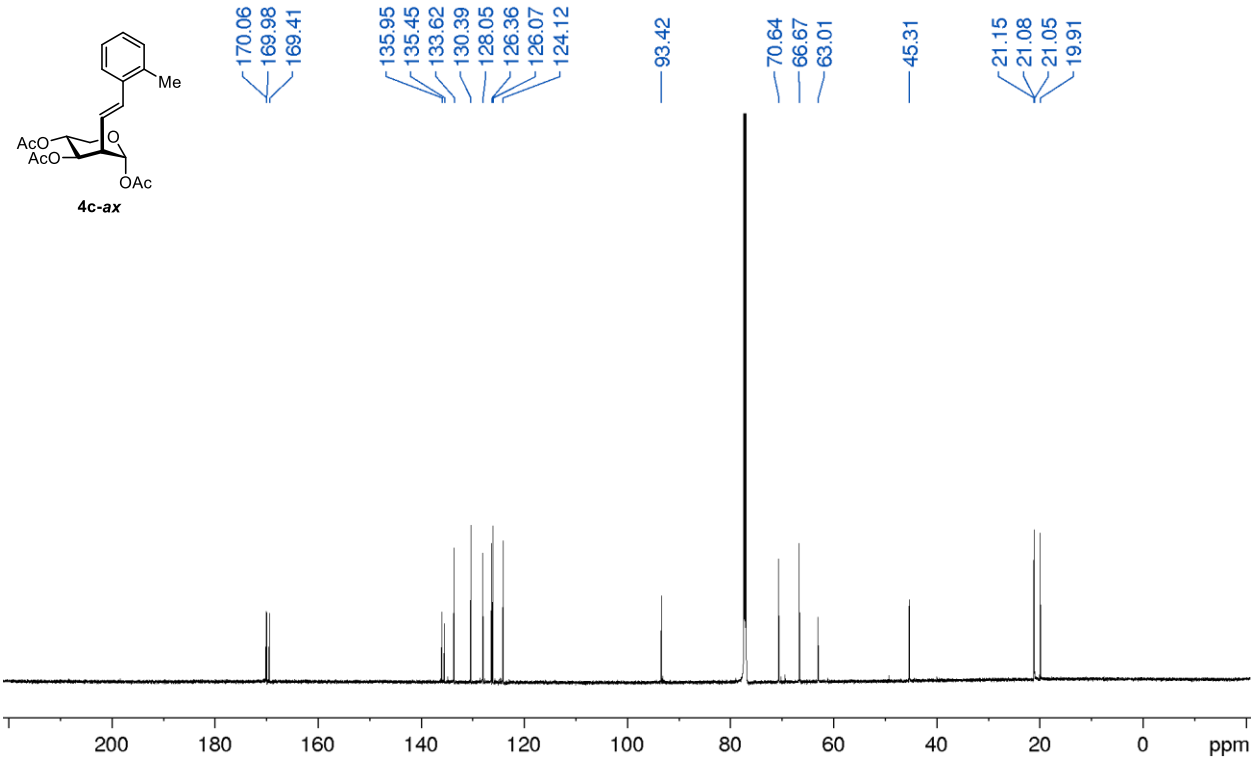
^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC) of (4b-*eq*)



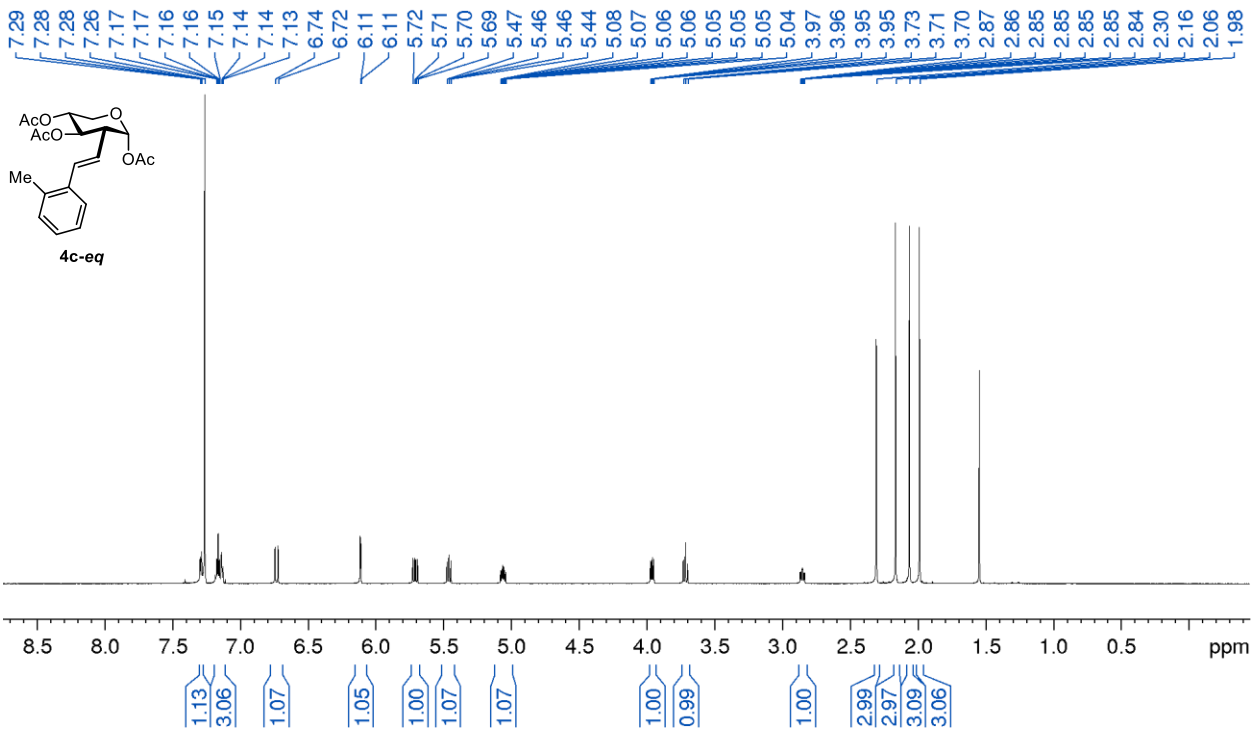
^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC) of (4c-*ax*)



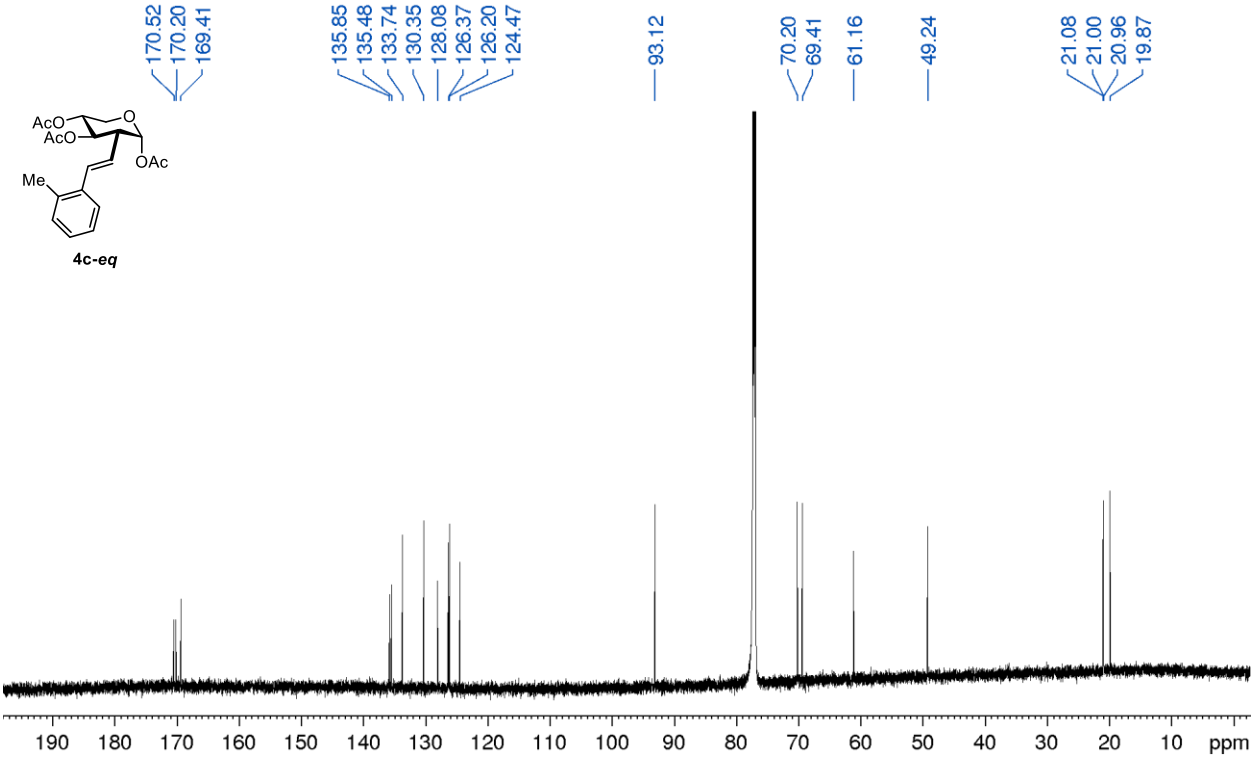
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (4c-*ax*)



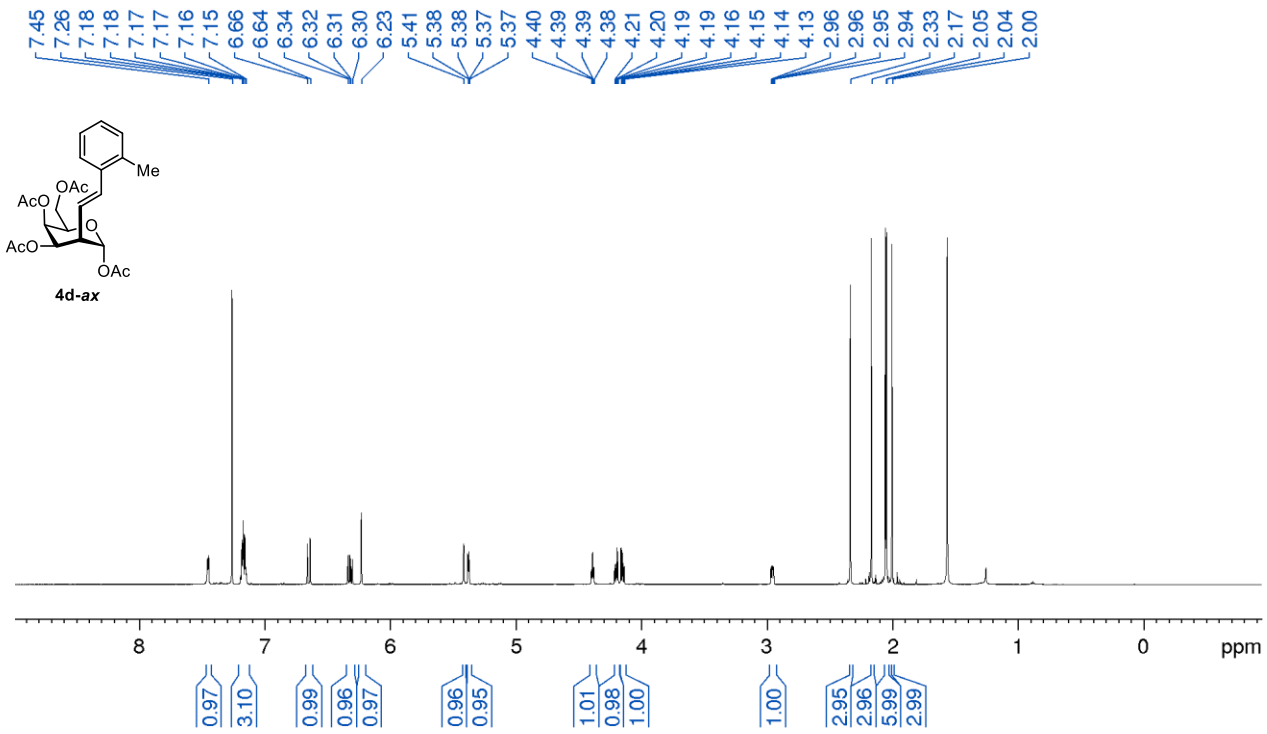
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (4c-*eq*)



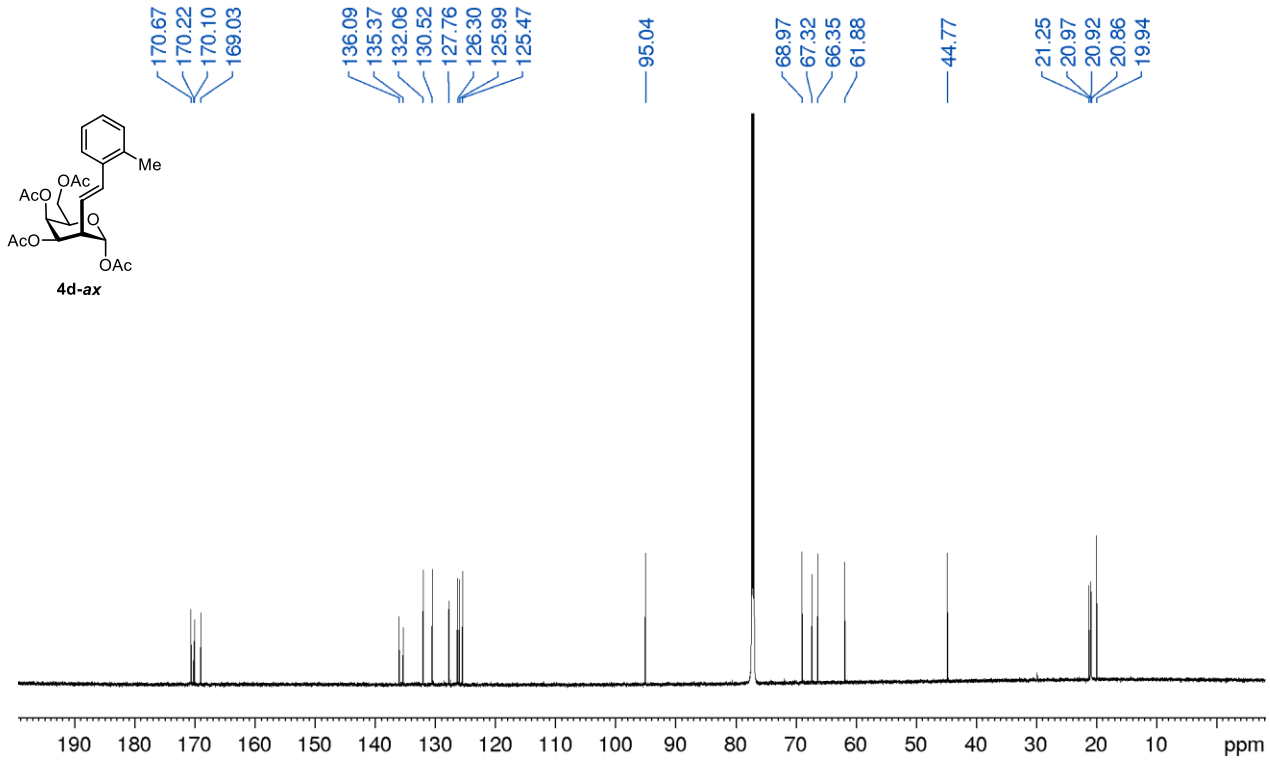
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (4c-*eq*)



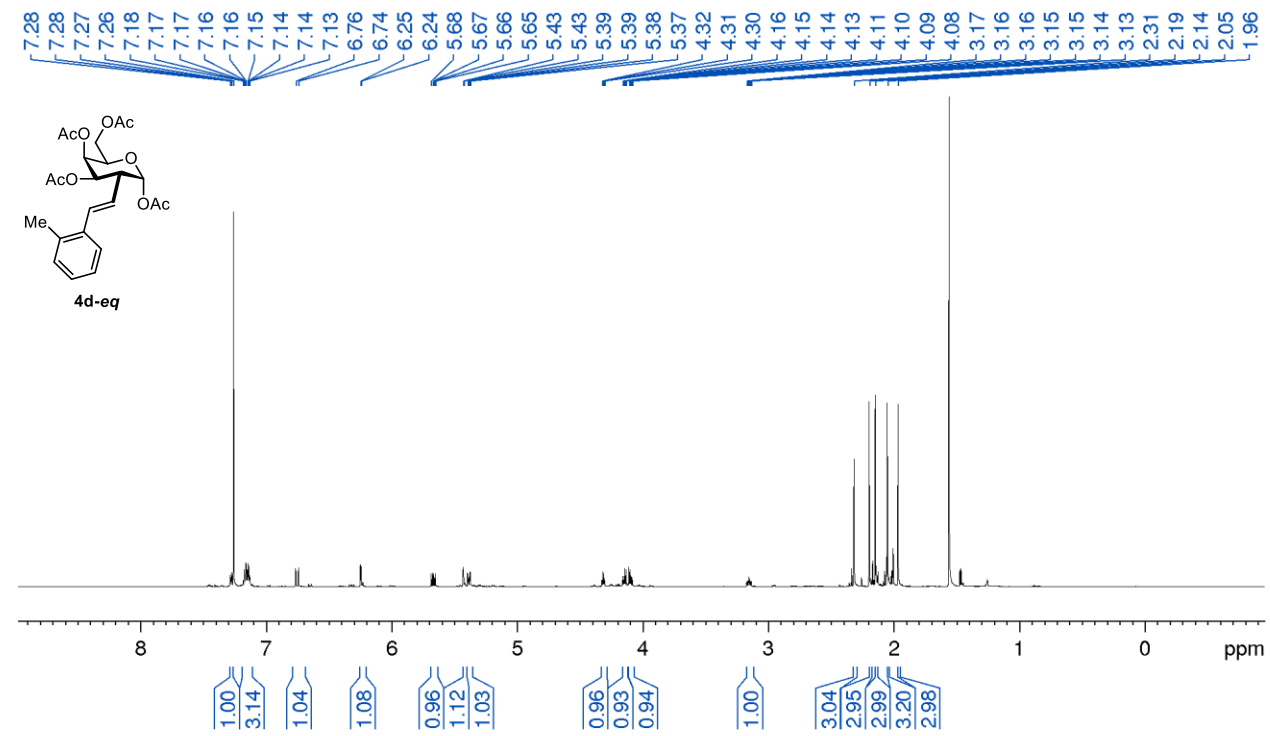
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (4d-*ax*)



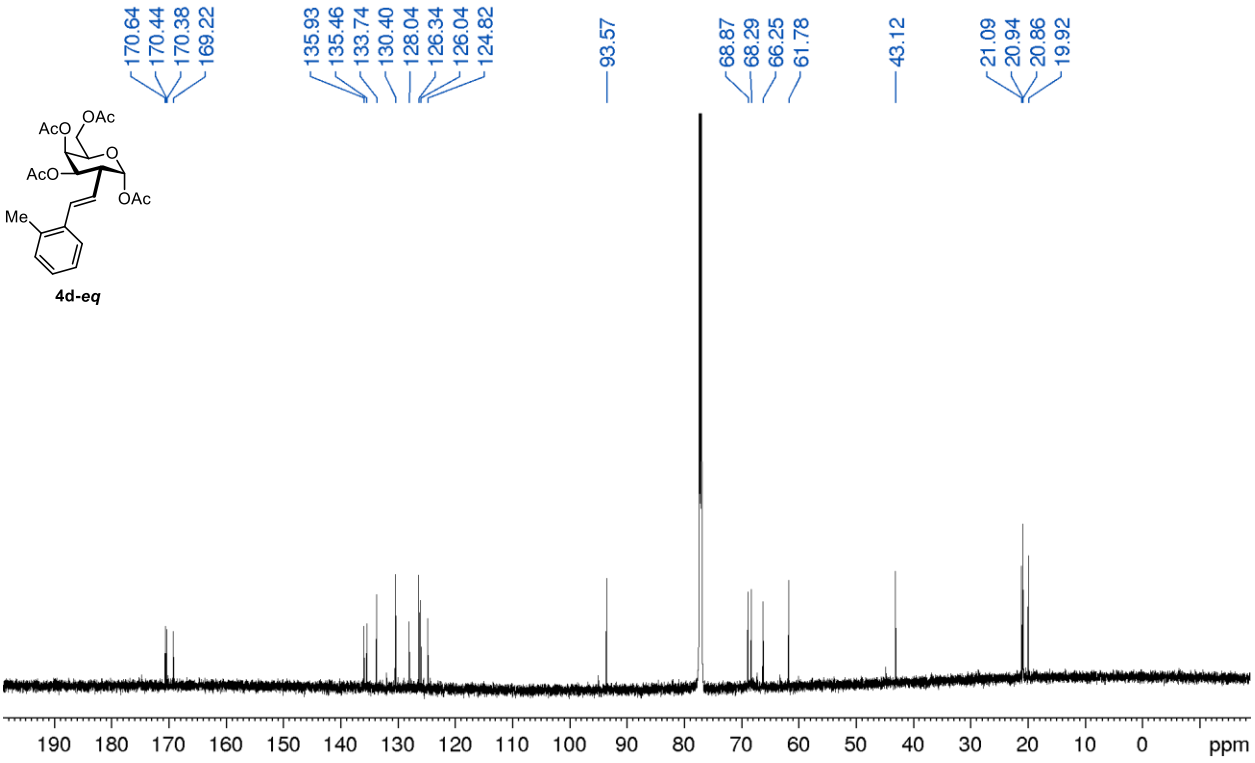
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (4d-*ax*)



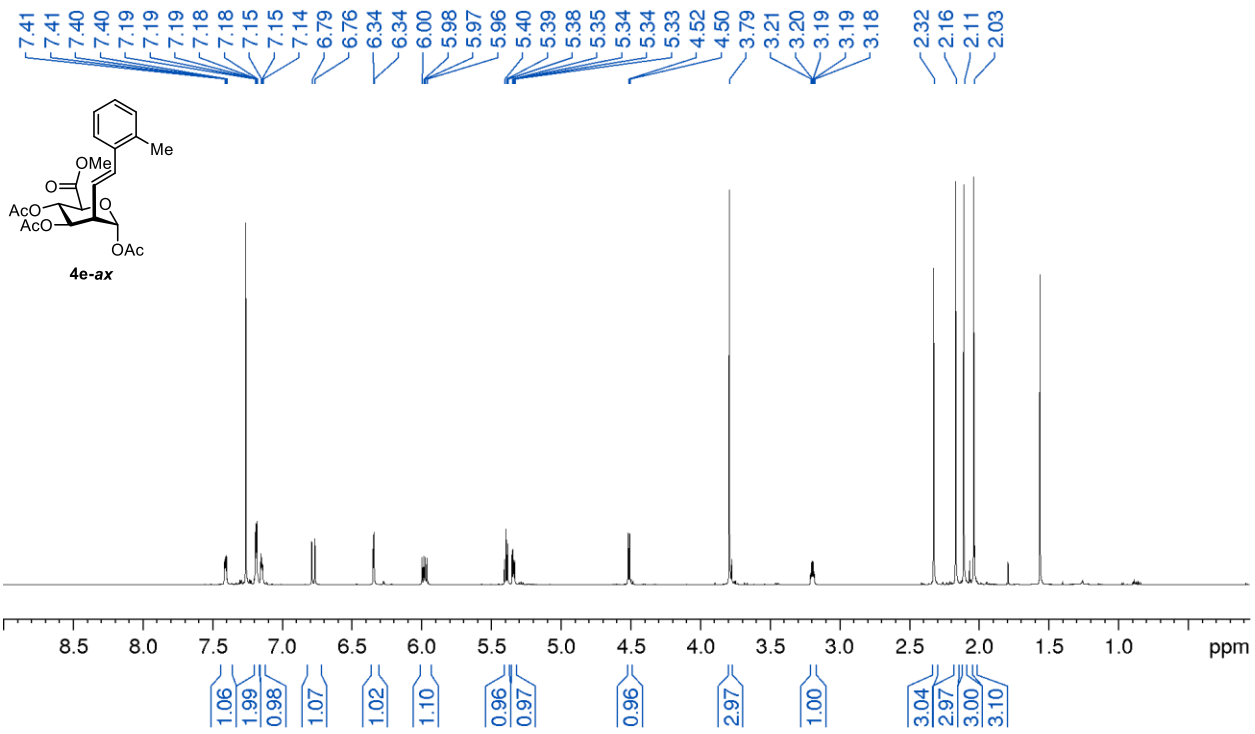
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (4d-*eq*)



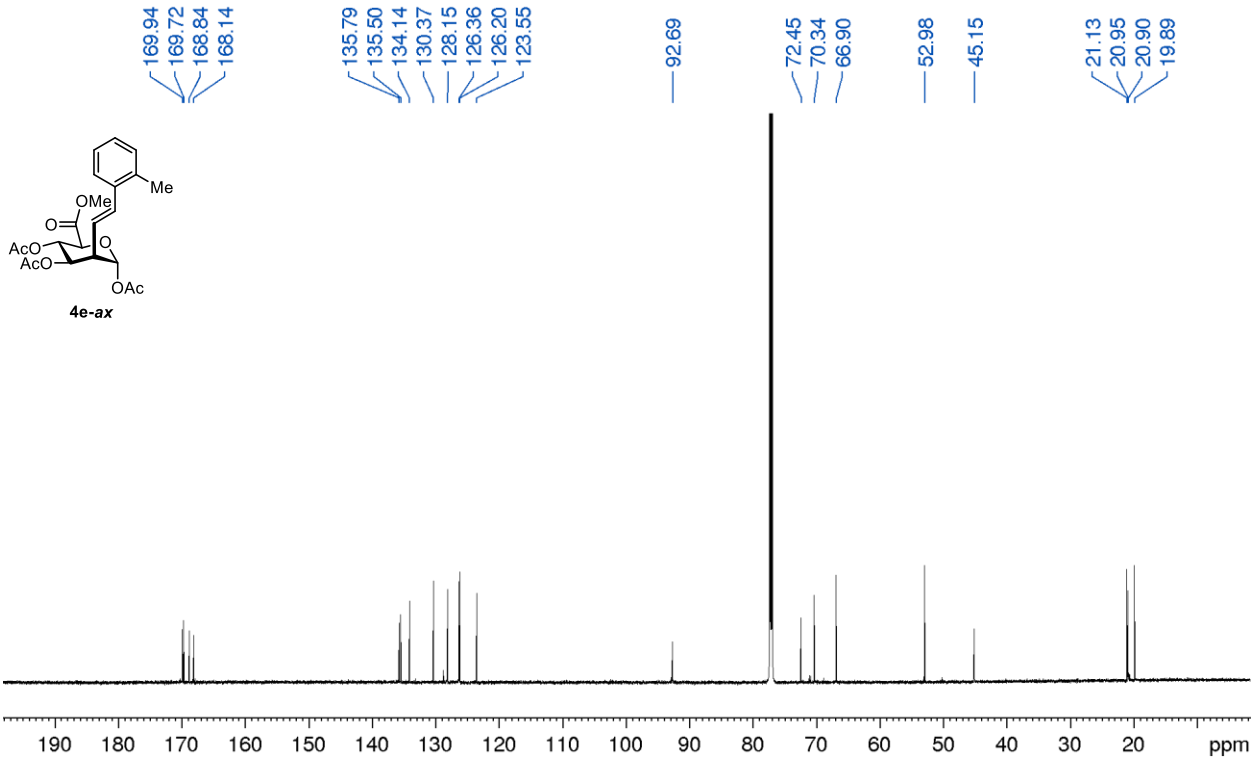
^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC) of (4d-*eq*)



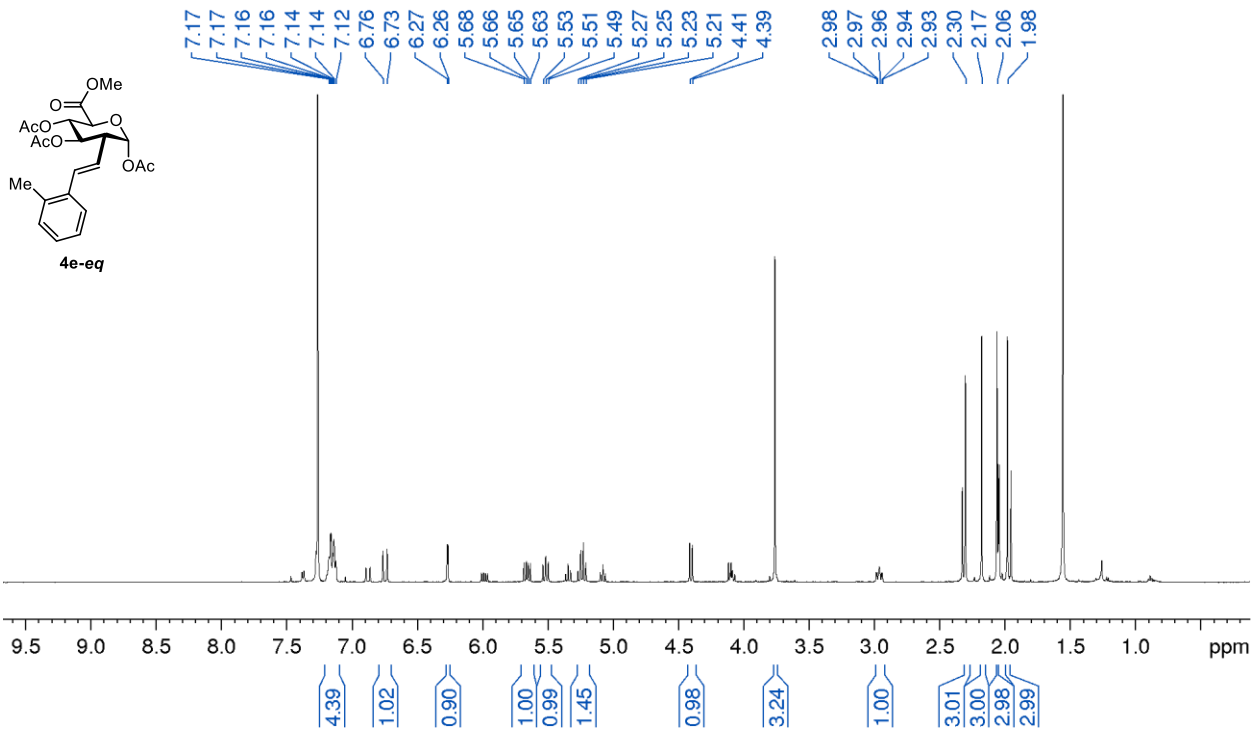
^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC) of (4e-*ax*)



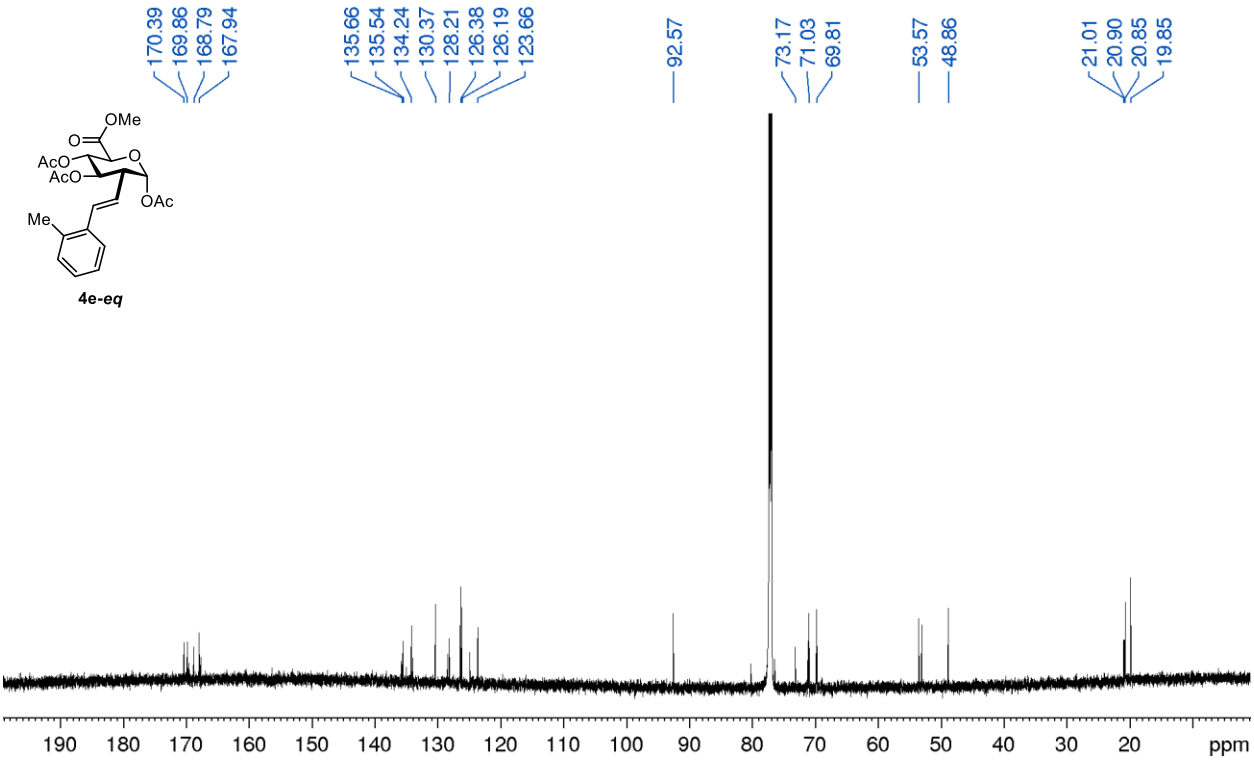
^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC) of (4e -*ax*)



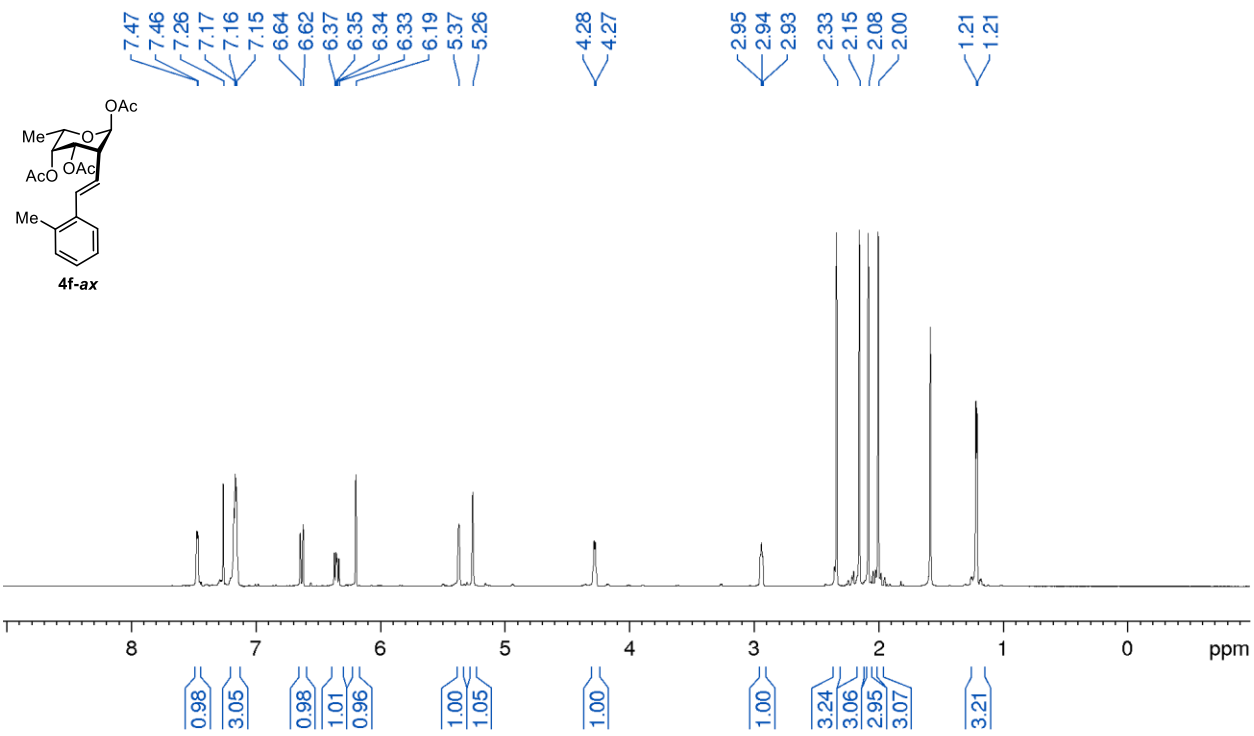
^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC) of (4e -*eq*)



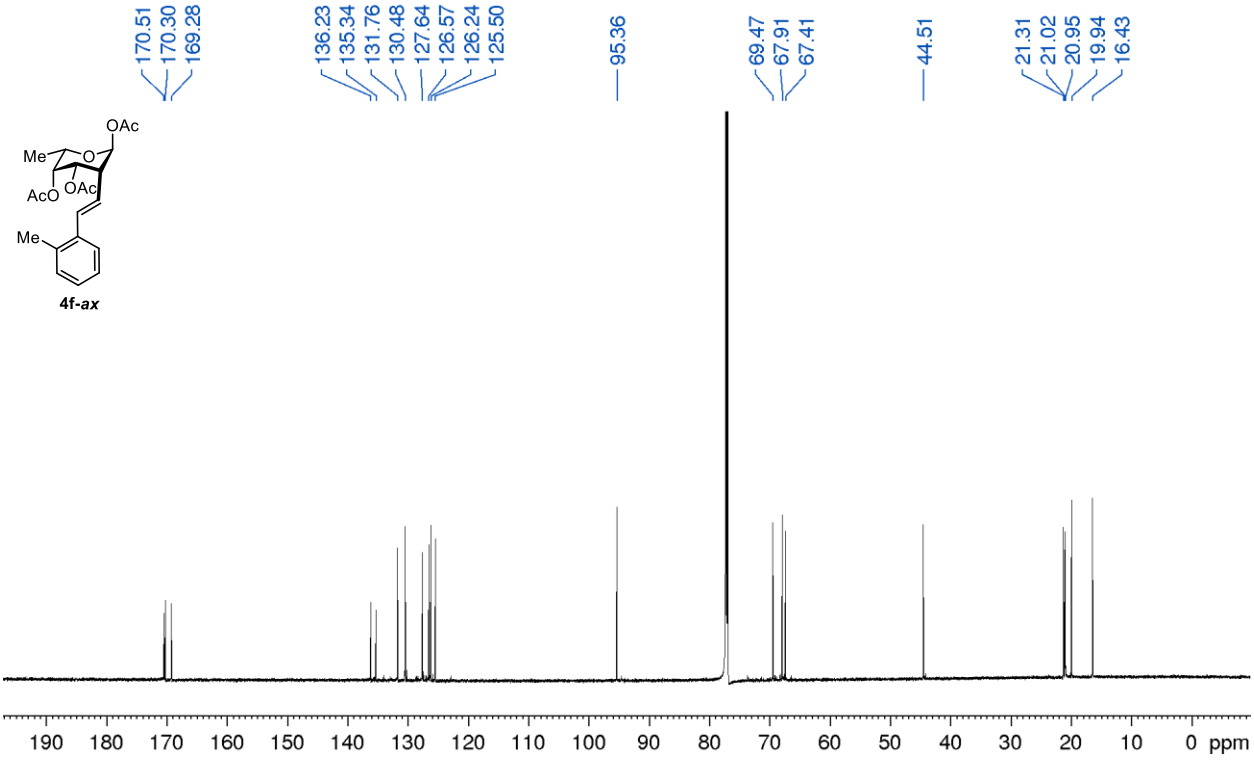
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (4e-*eq*)



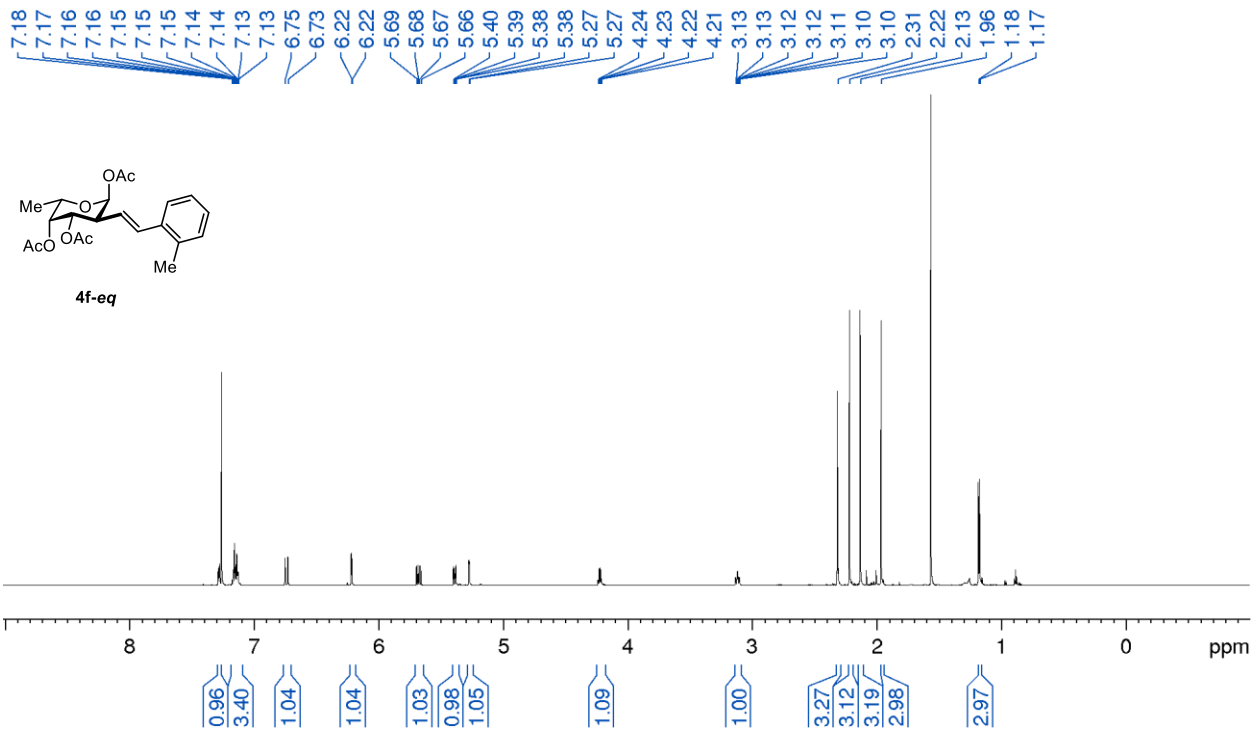
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (4f-*ax*)



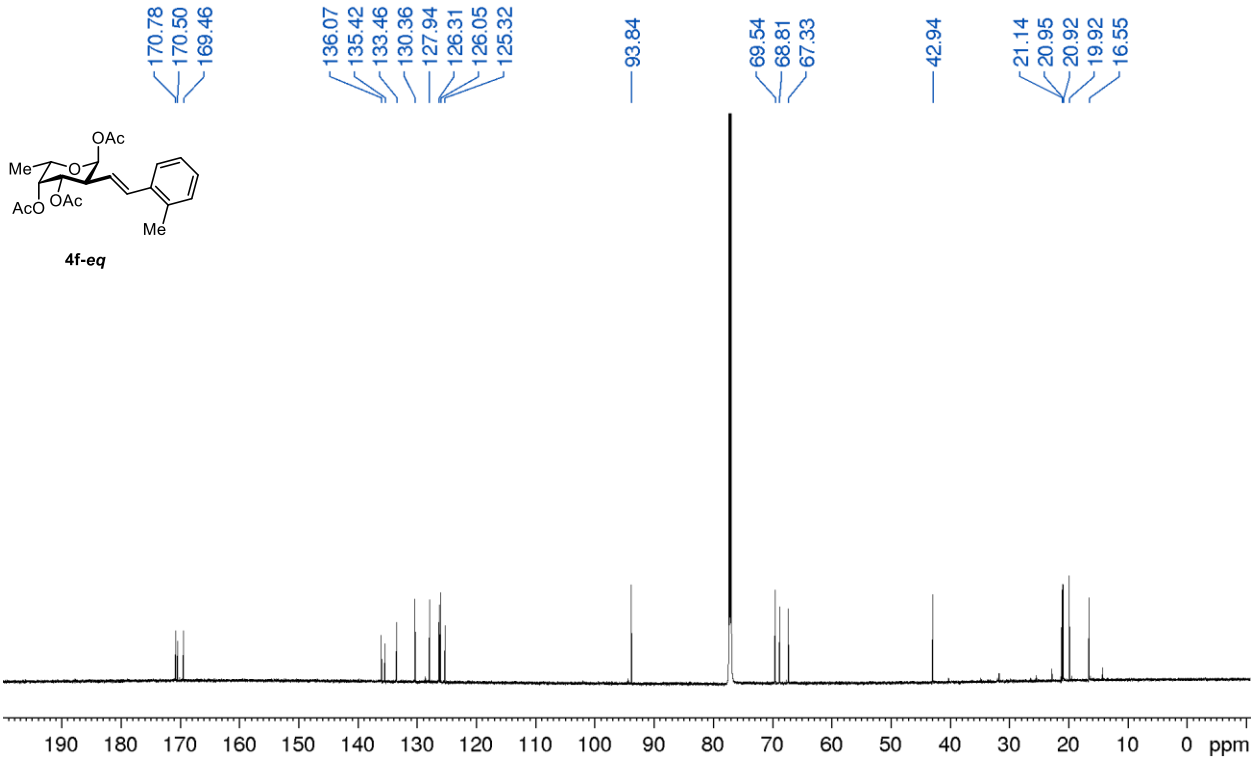
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (4f-*ax*)



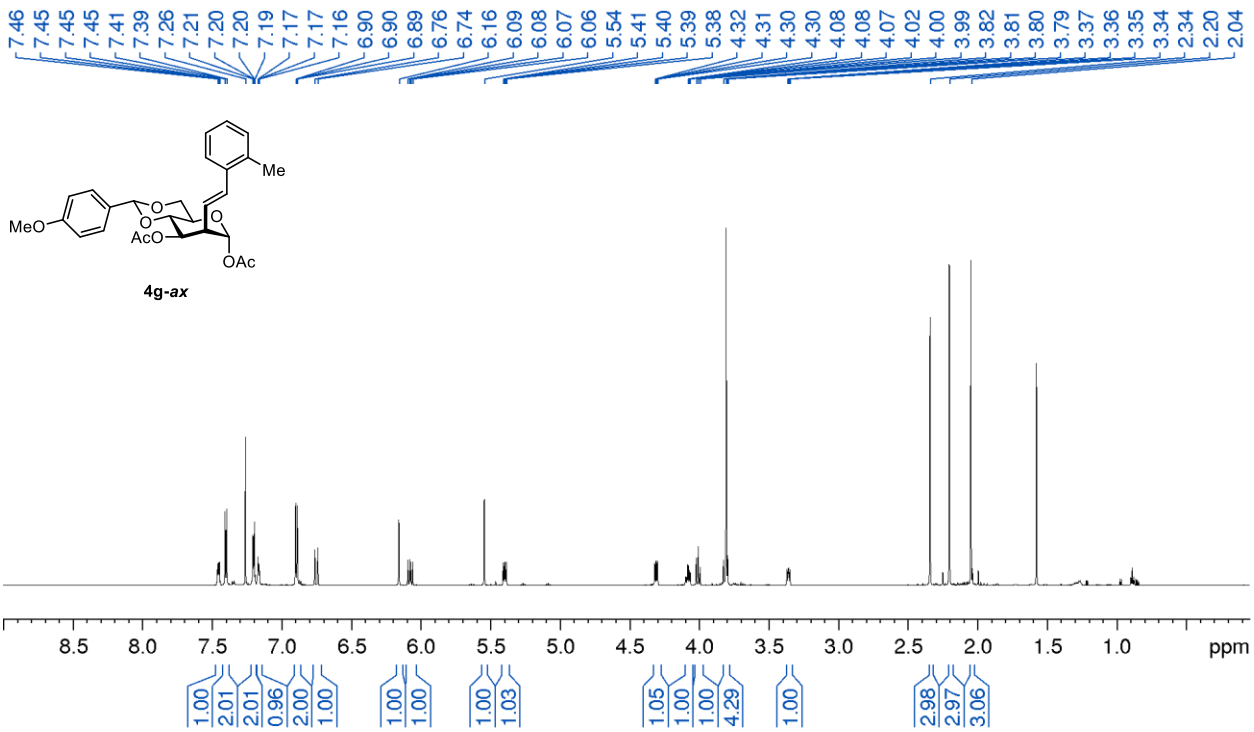
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (4f-*eq*)



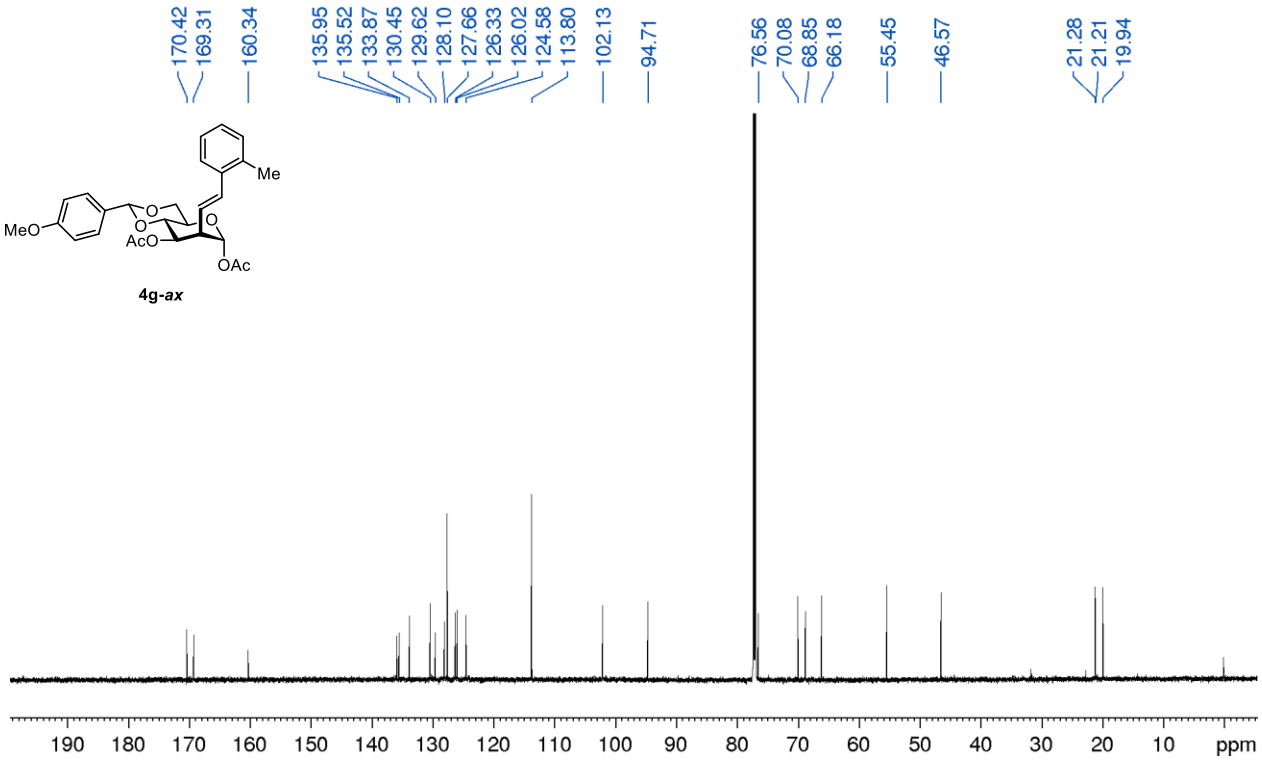
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (4f-*eq*)



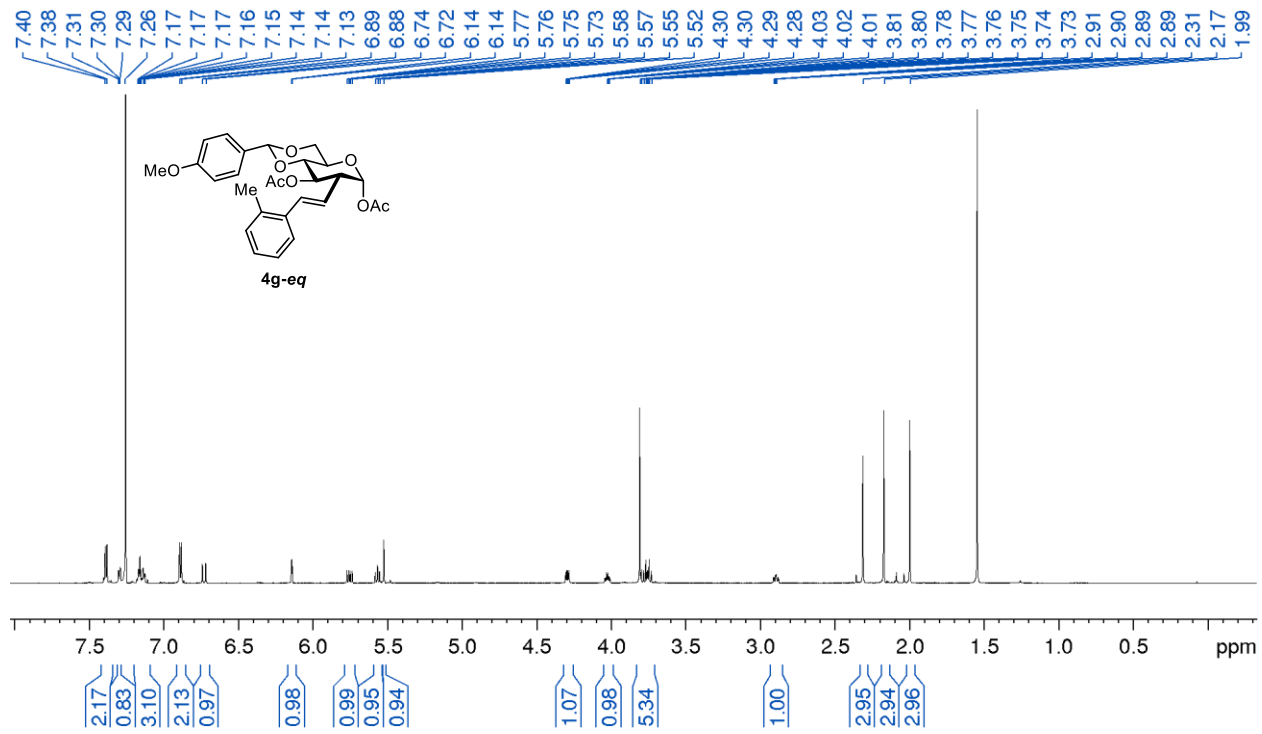
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (4g-*ax*)



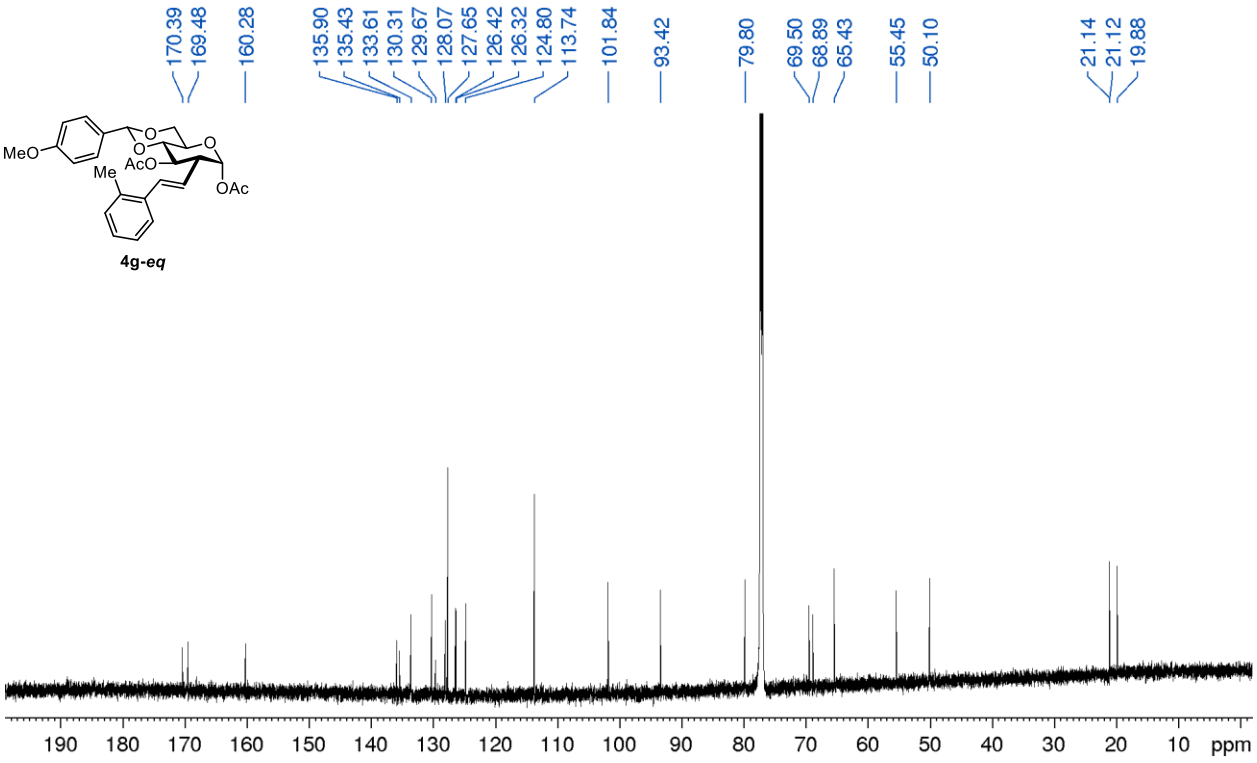
^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC) of (4g-*ax*)



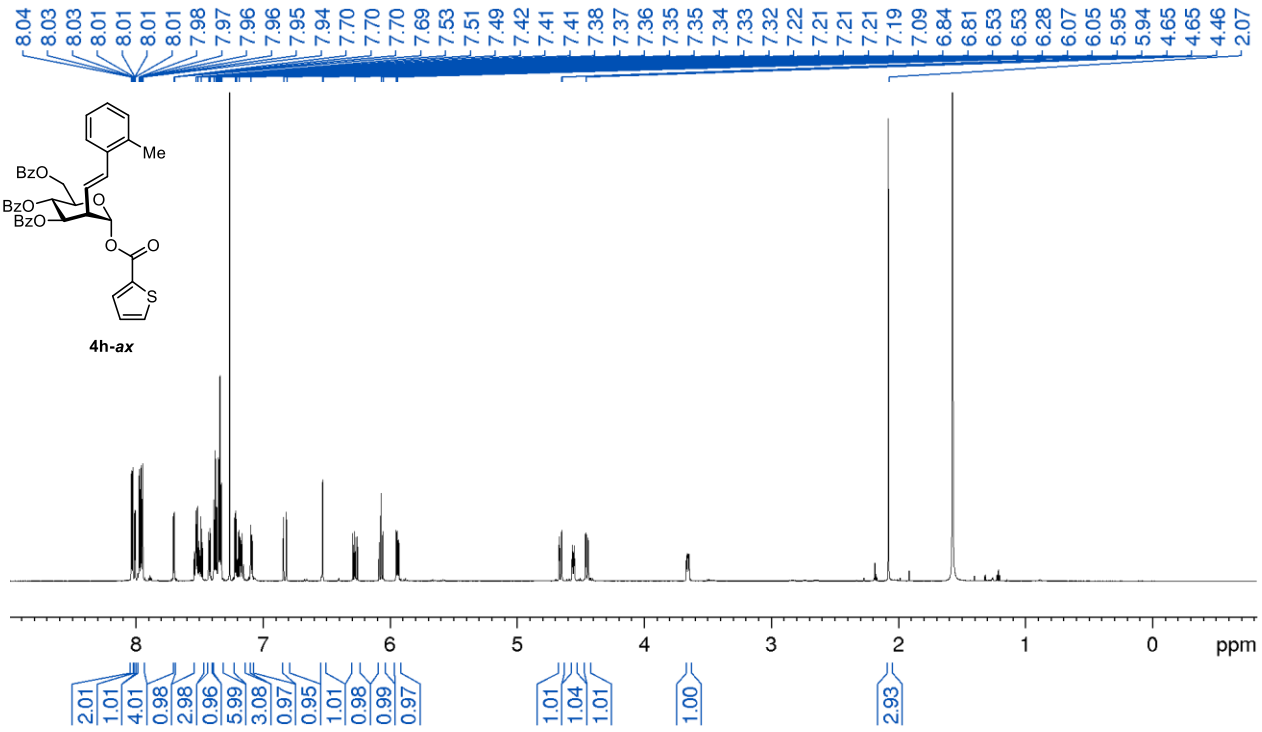
^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC) of (4g-*eq*)



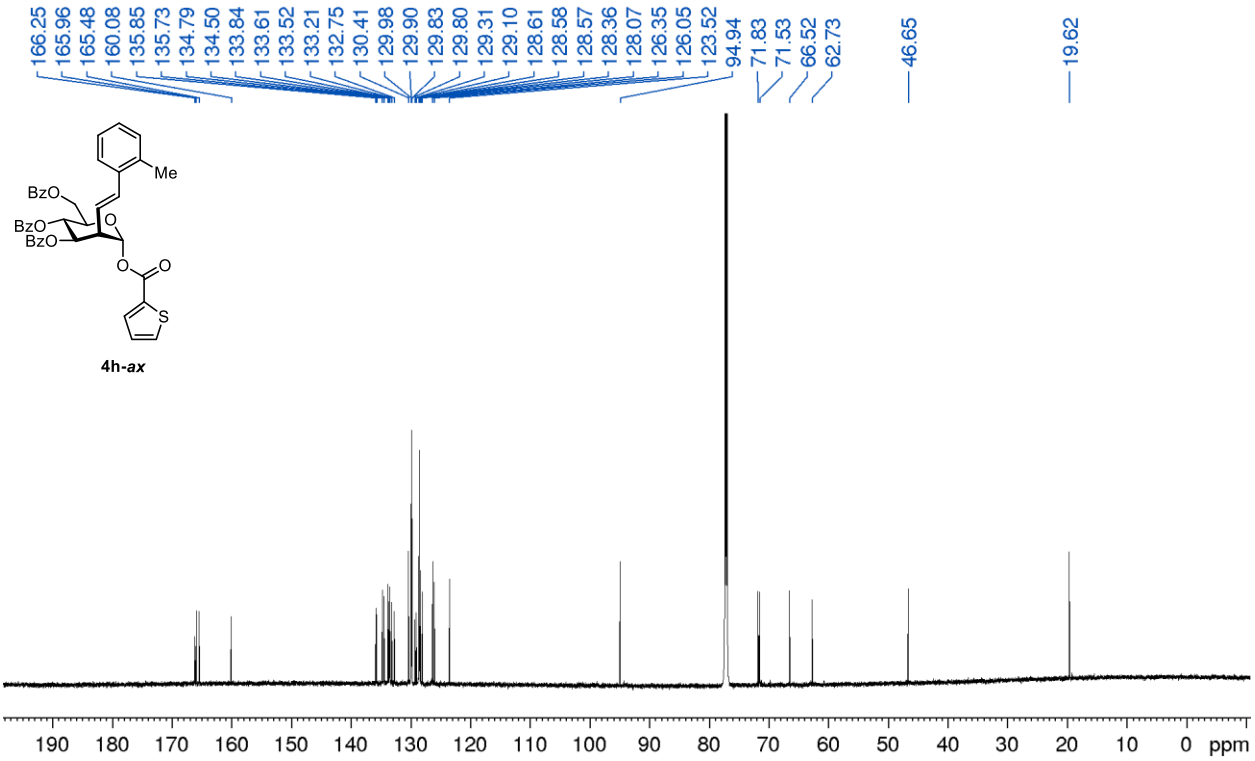
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (4g-*eq*)



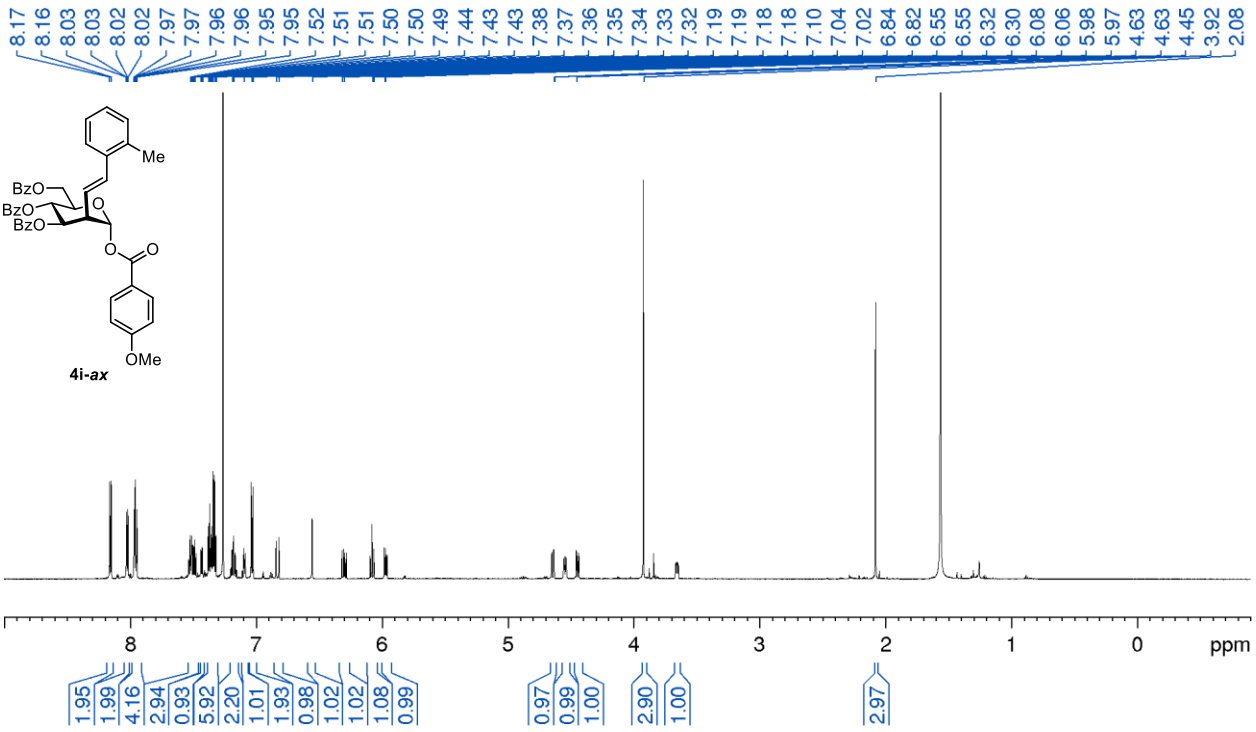
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (4h-*ax*)



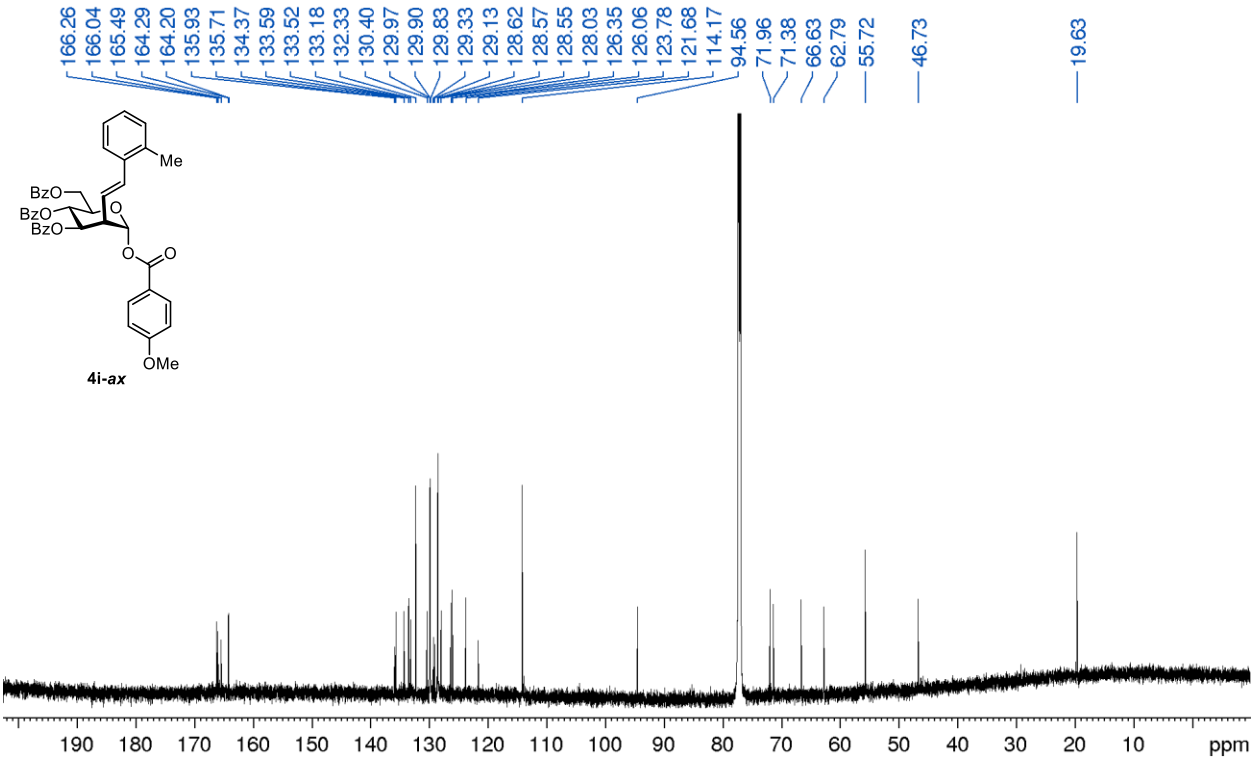
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (4h-*ax*)



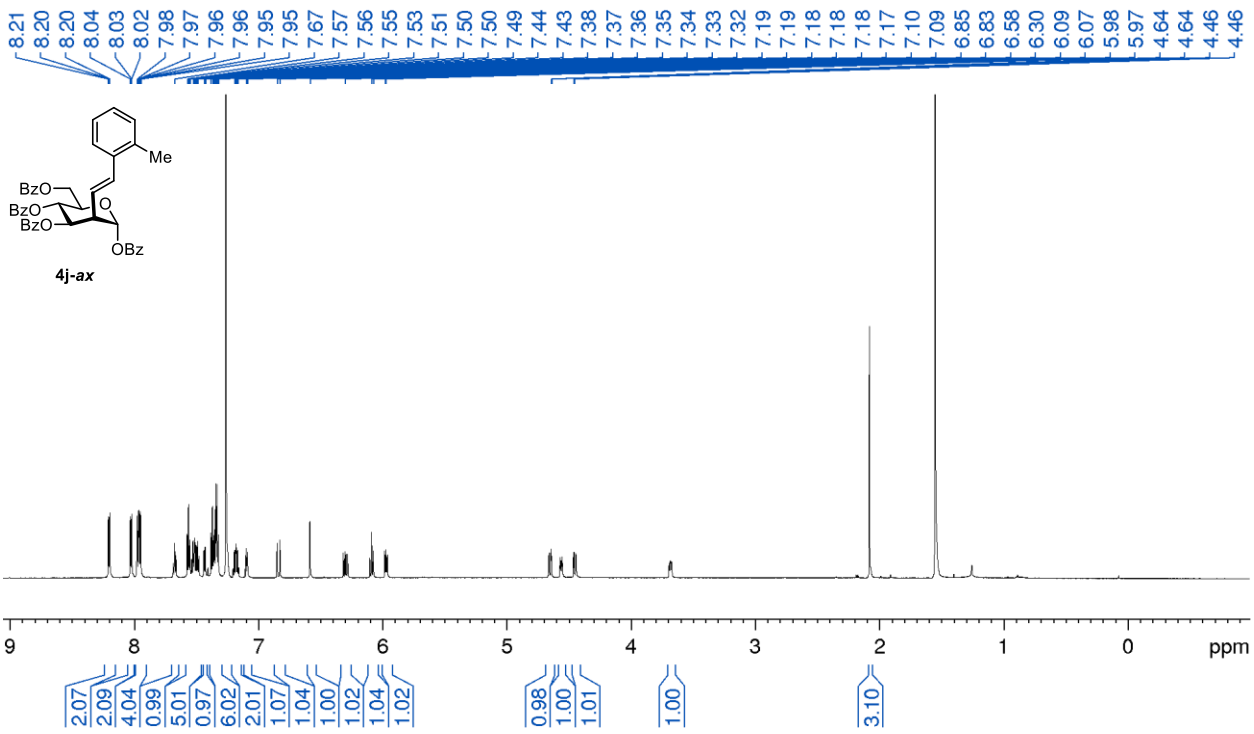
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (4i-*ax*)



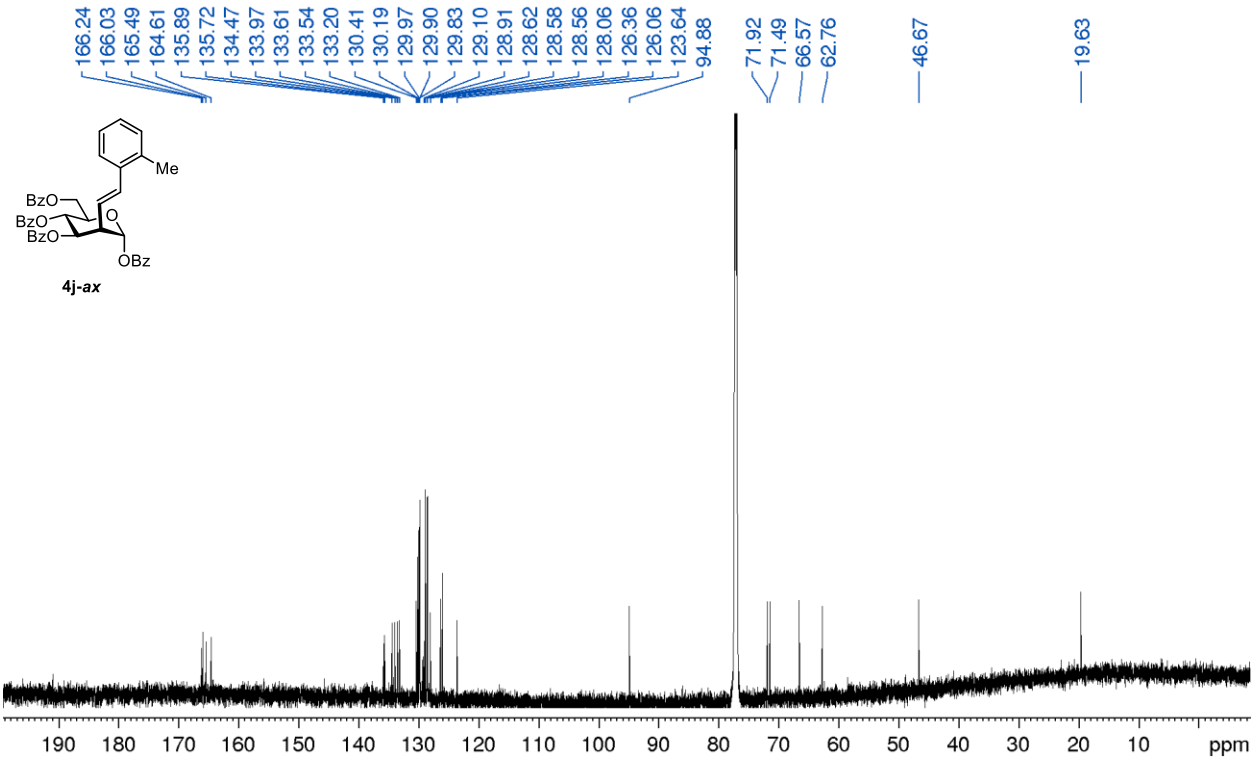
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (4i-*ax*)



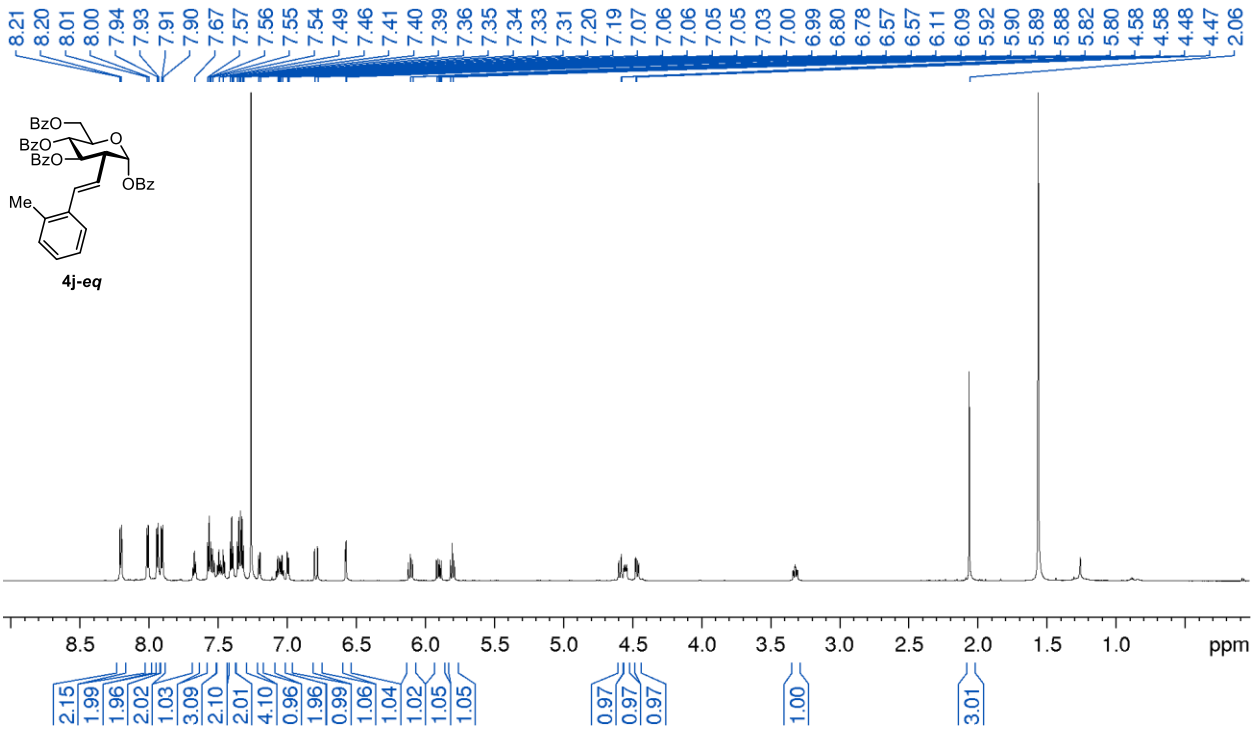
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (4j-*ax*)



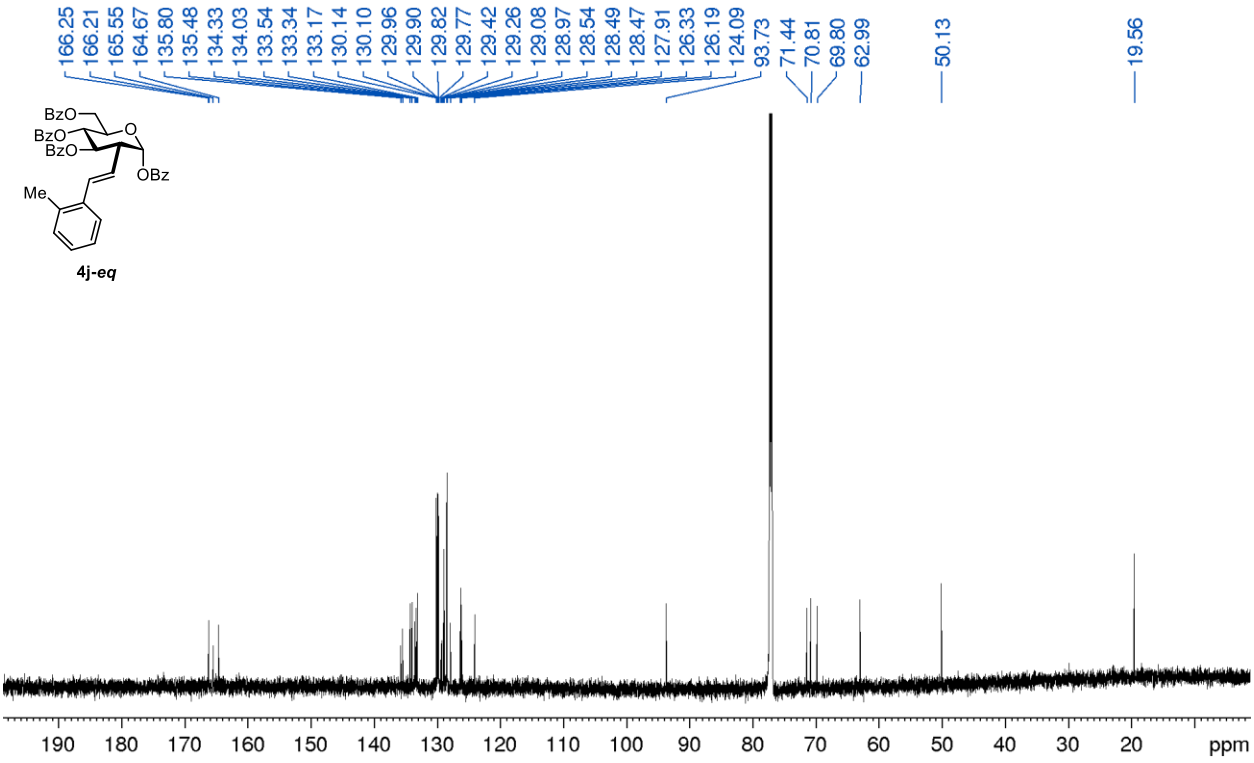
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (4j-*ax*)



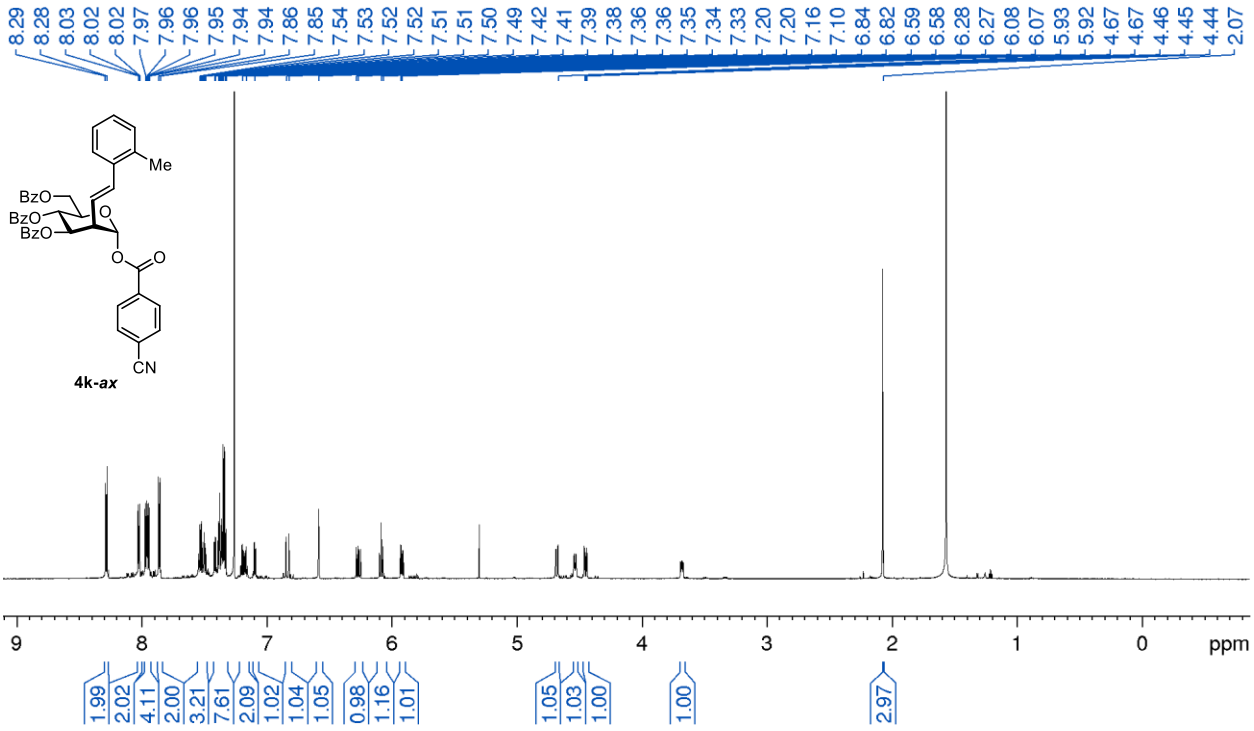
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (4j-*eq*)



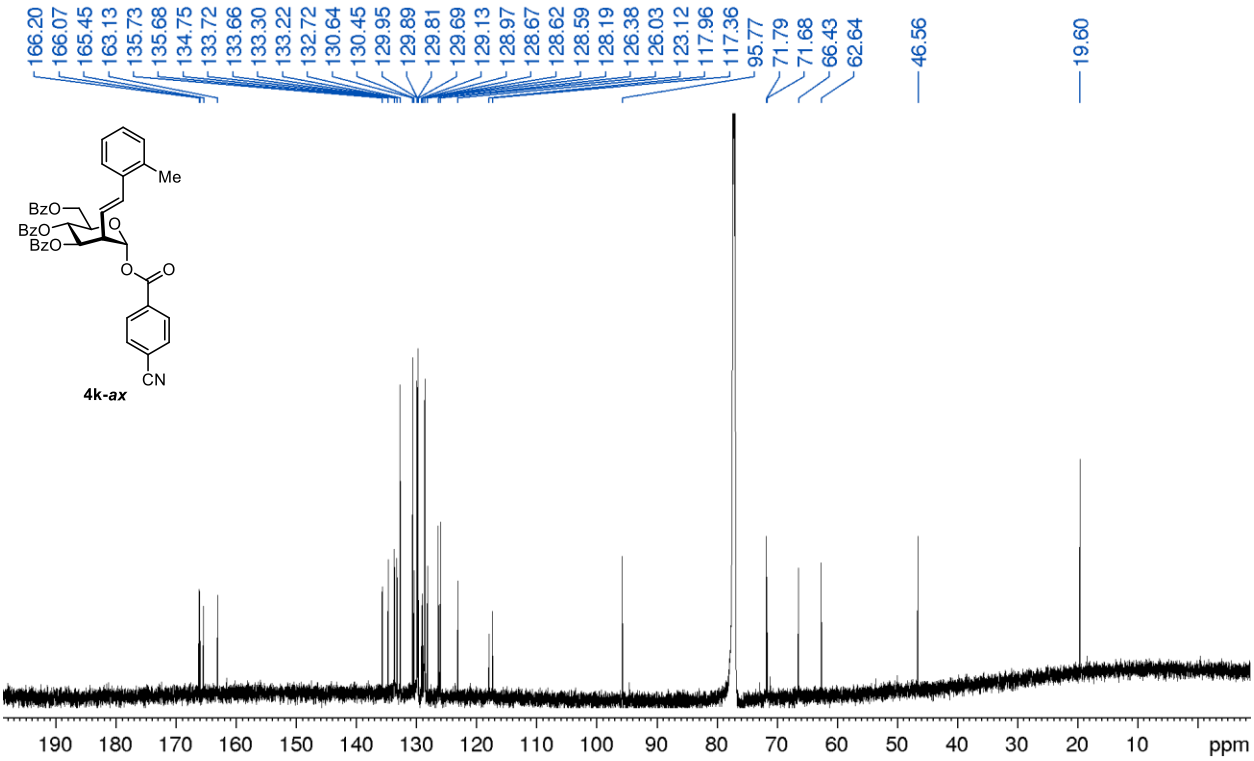
^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC) of (4j-*eq*)



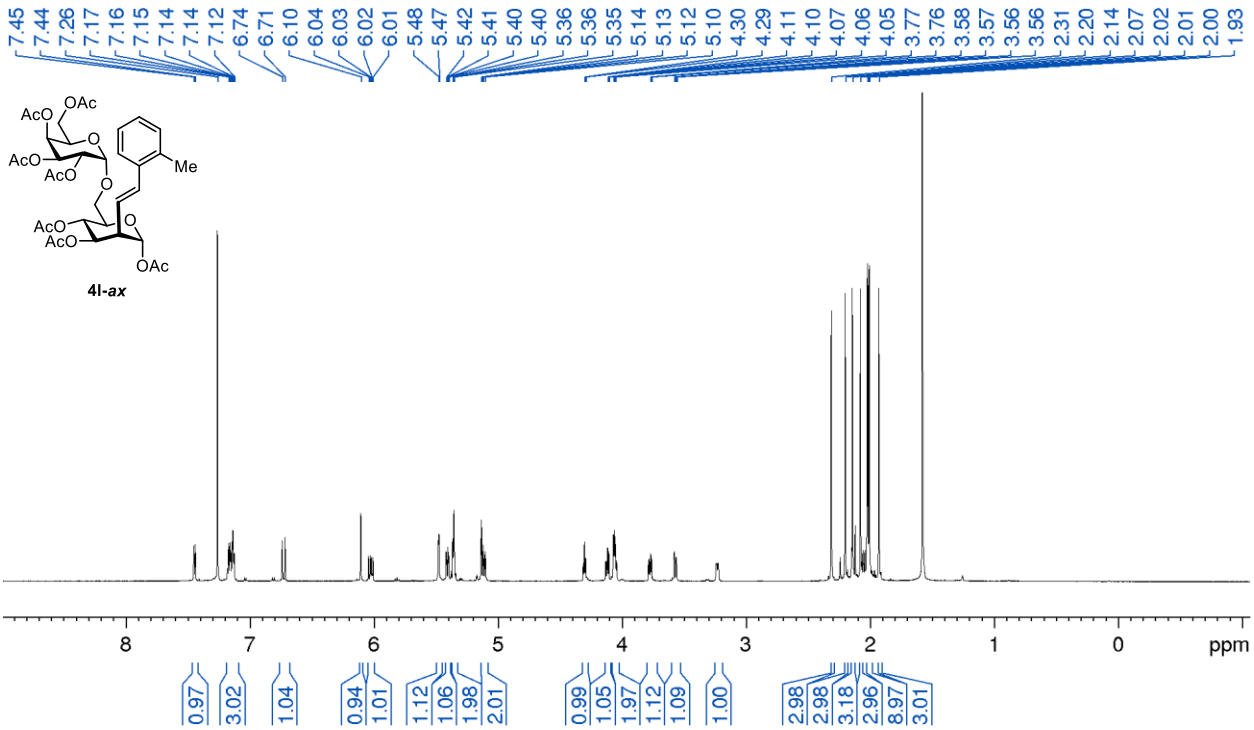
^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC) of (4k-*ax*)



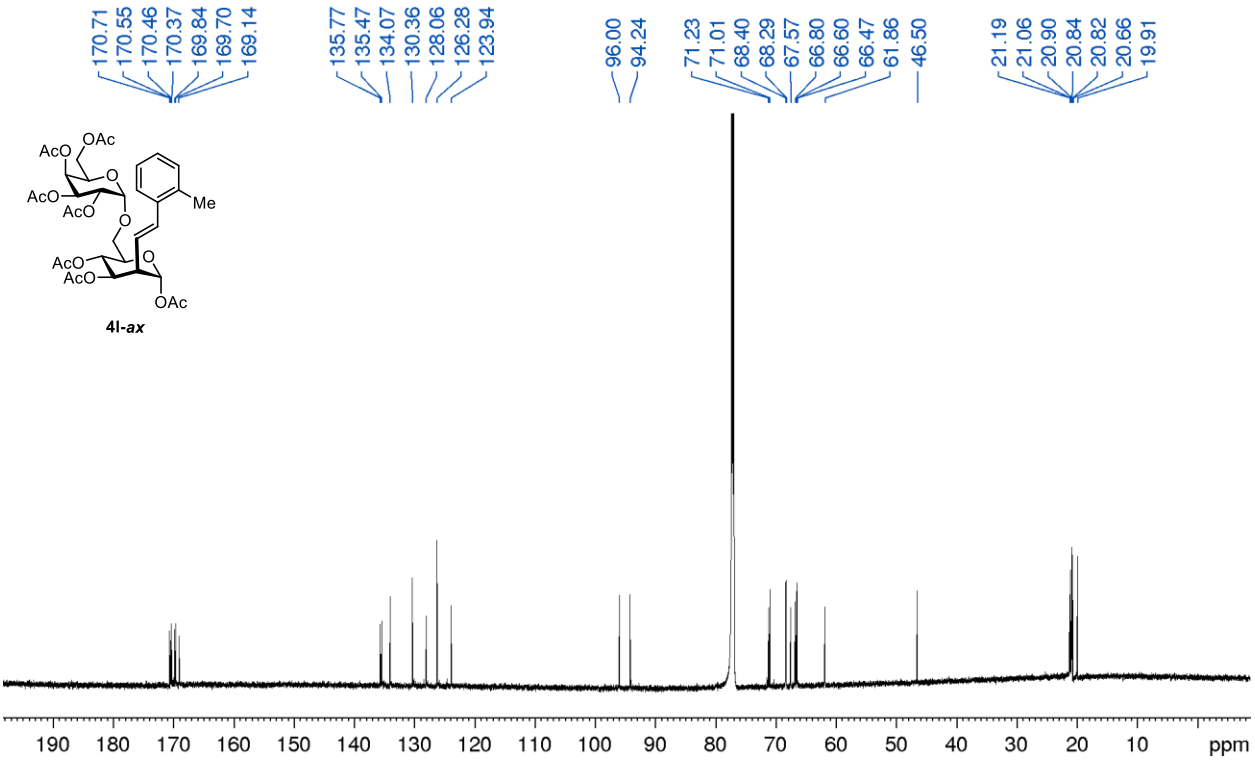
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (4k-*ax*)



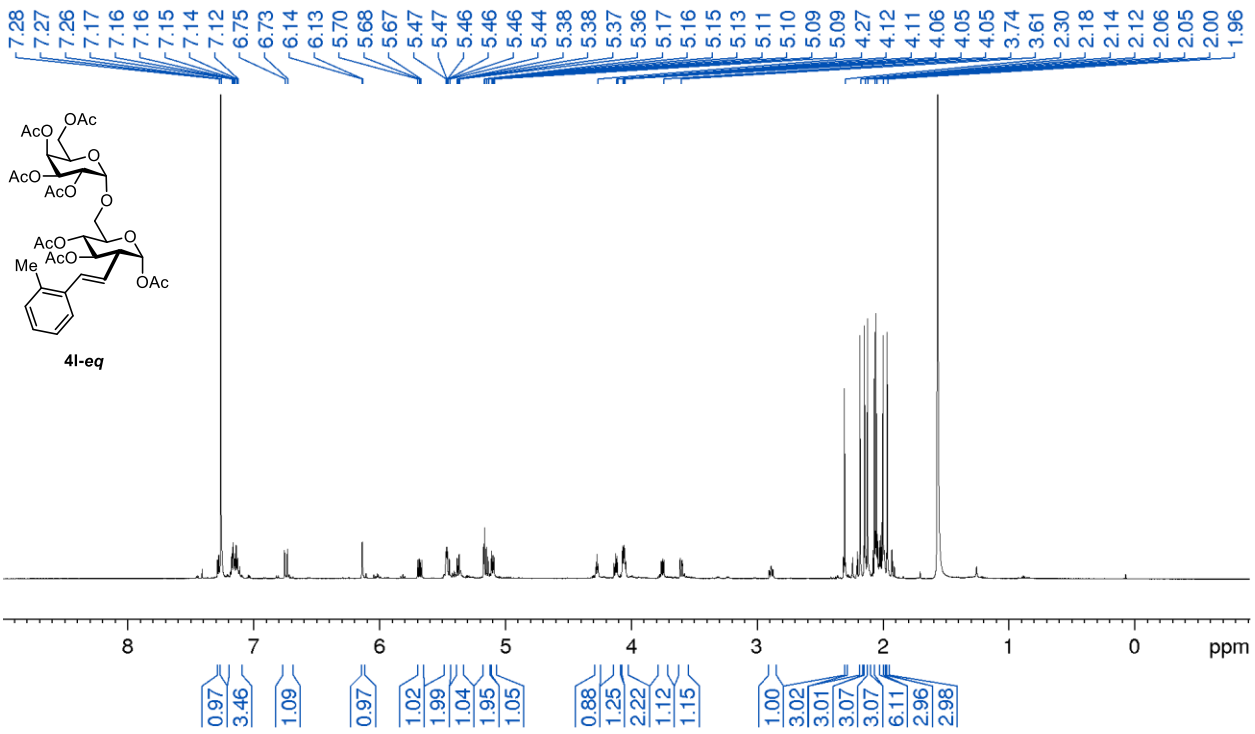
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (4l-*ax*)



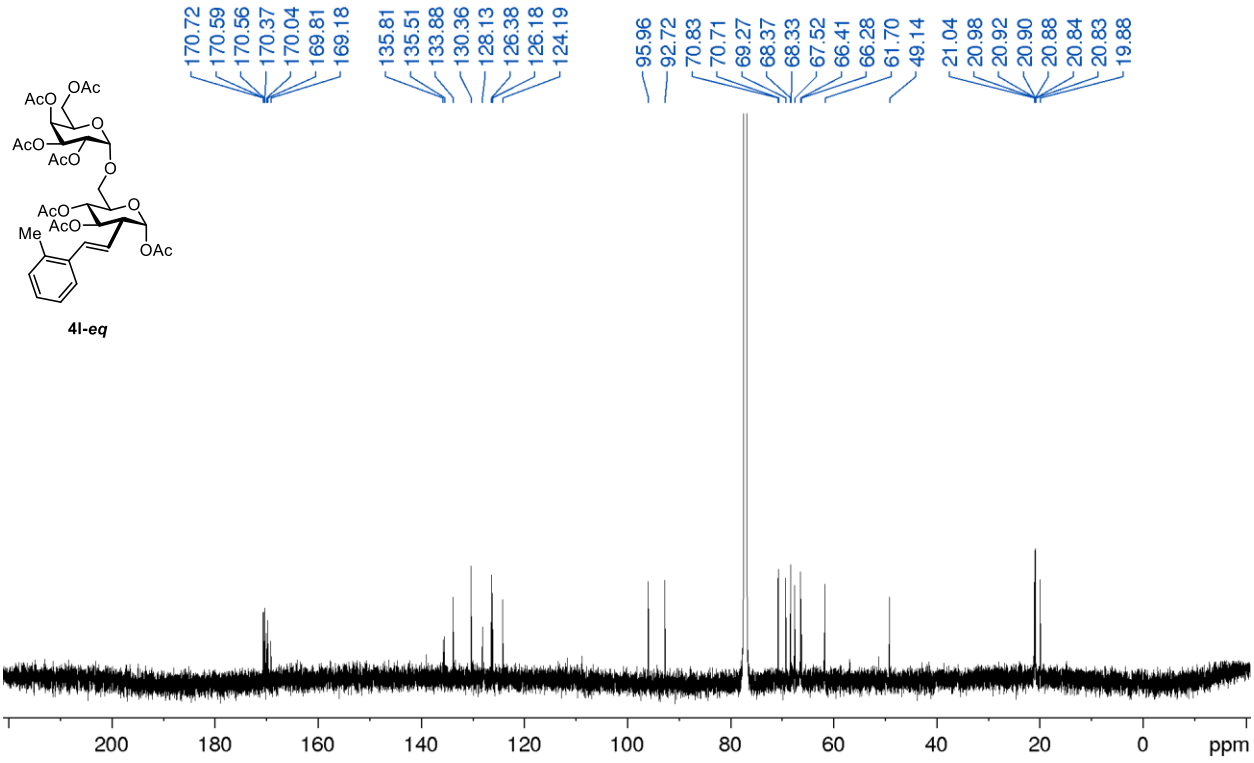
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (4l-*ax*)



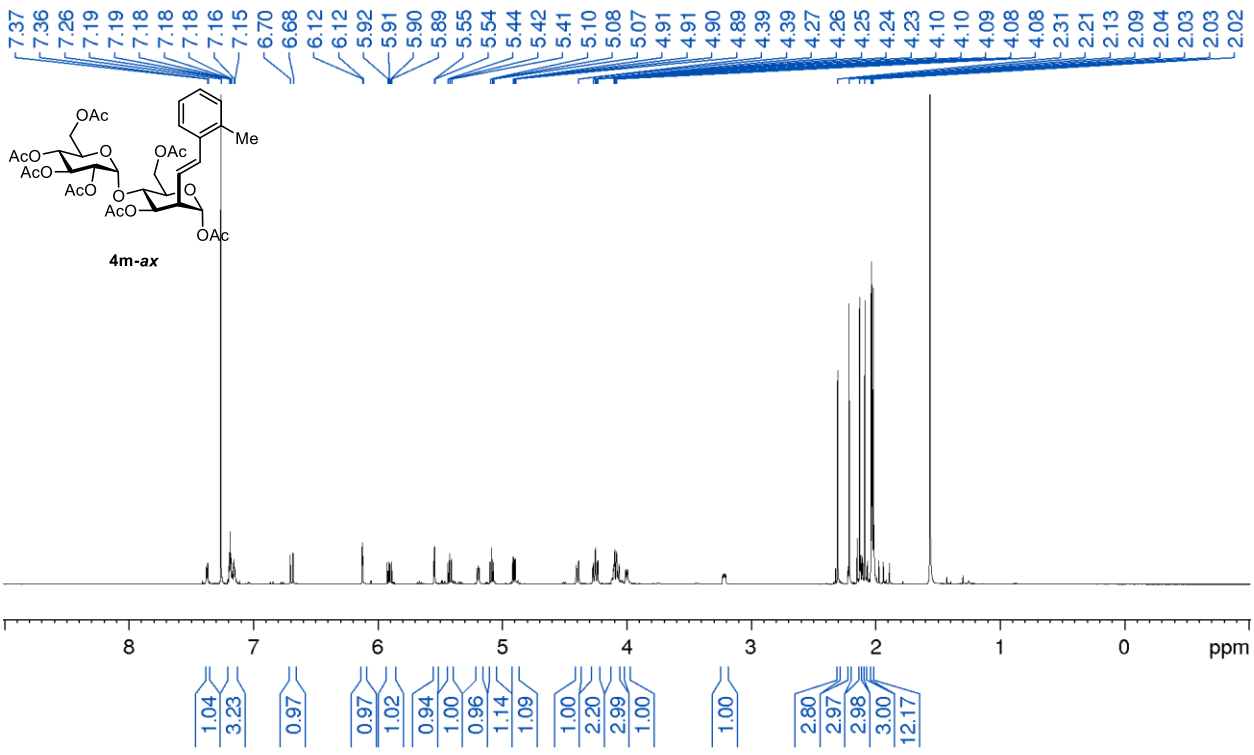
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (4l-*eq*)



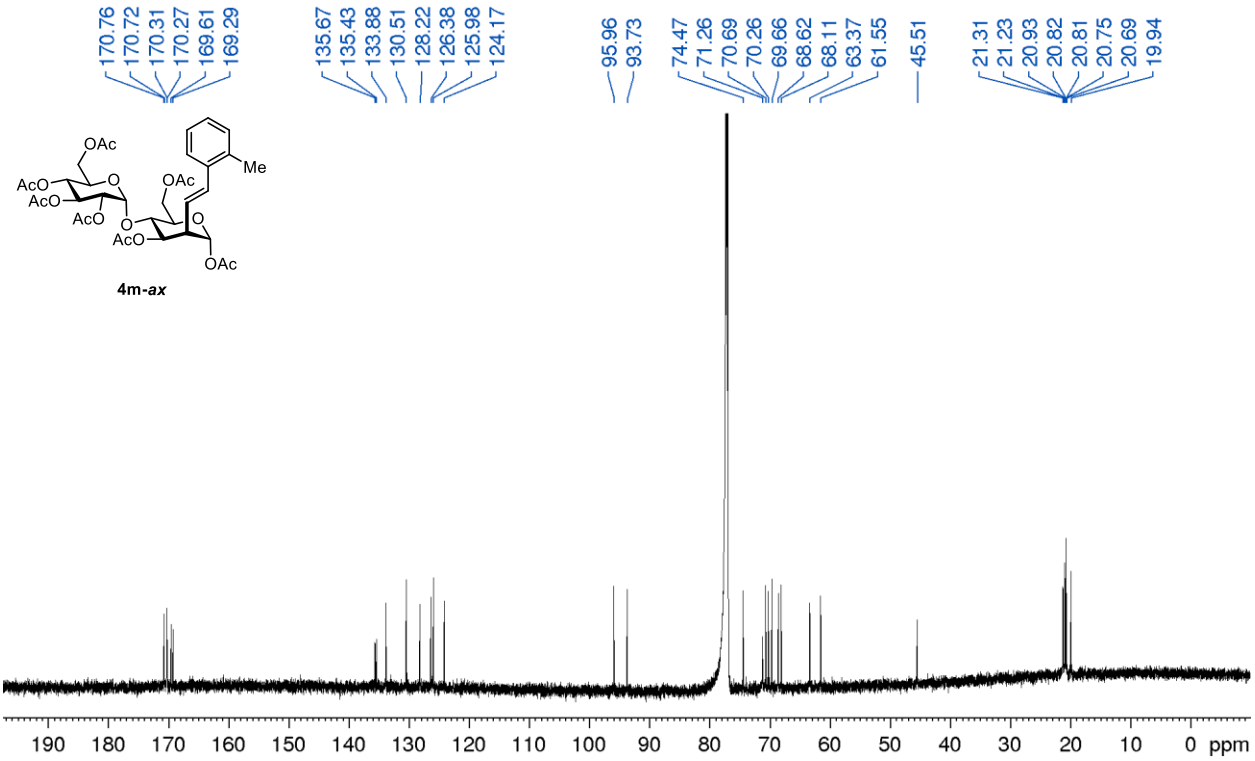
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (4l-*eq*)



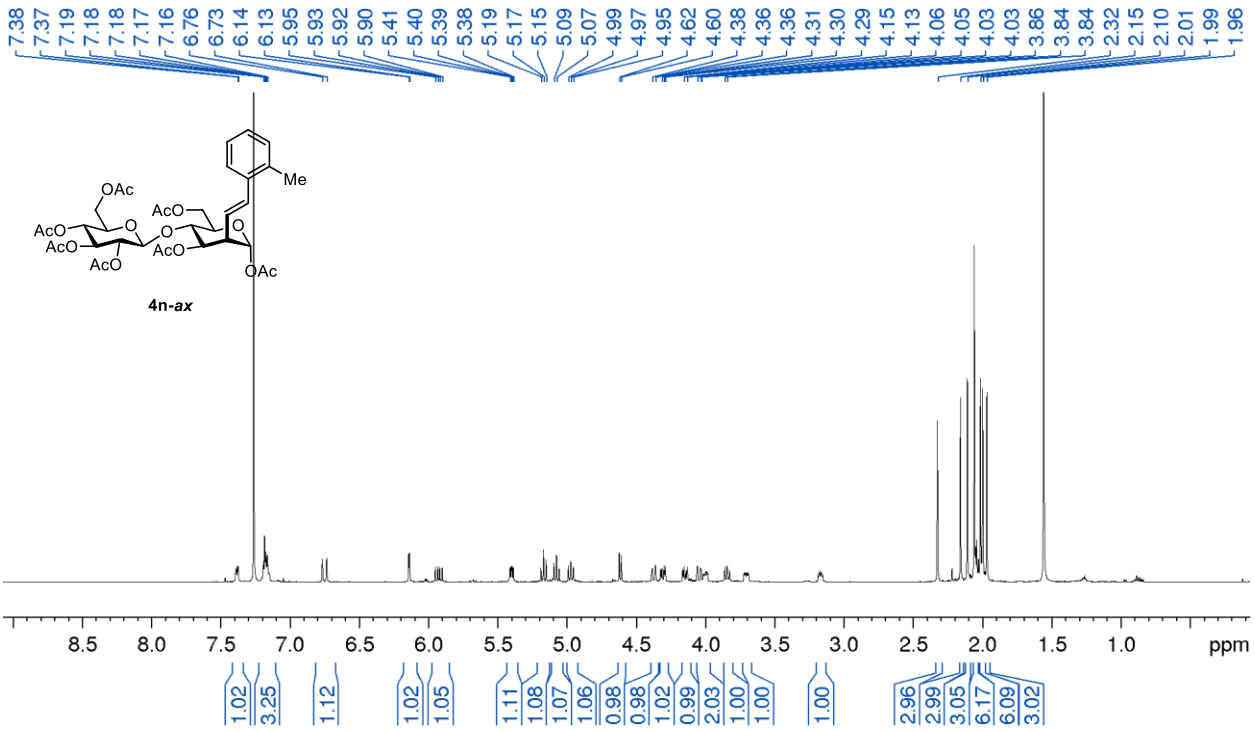
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (4m-*ax*)



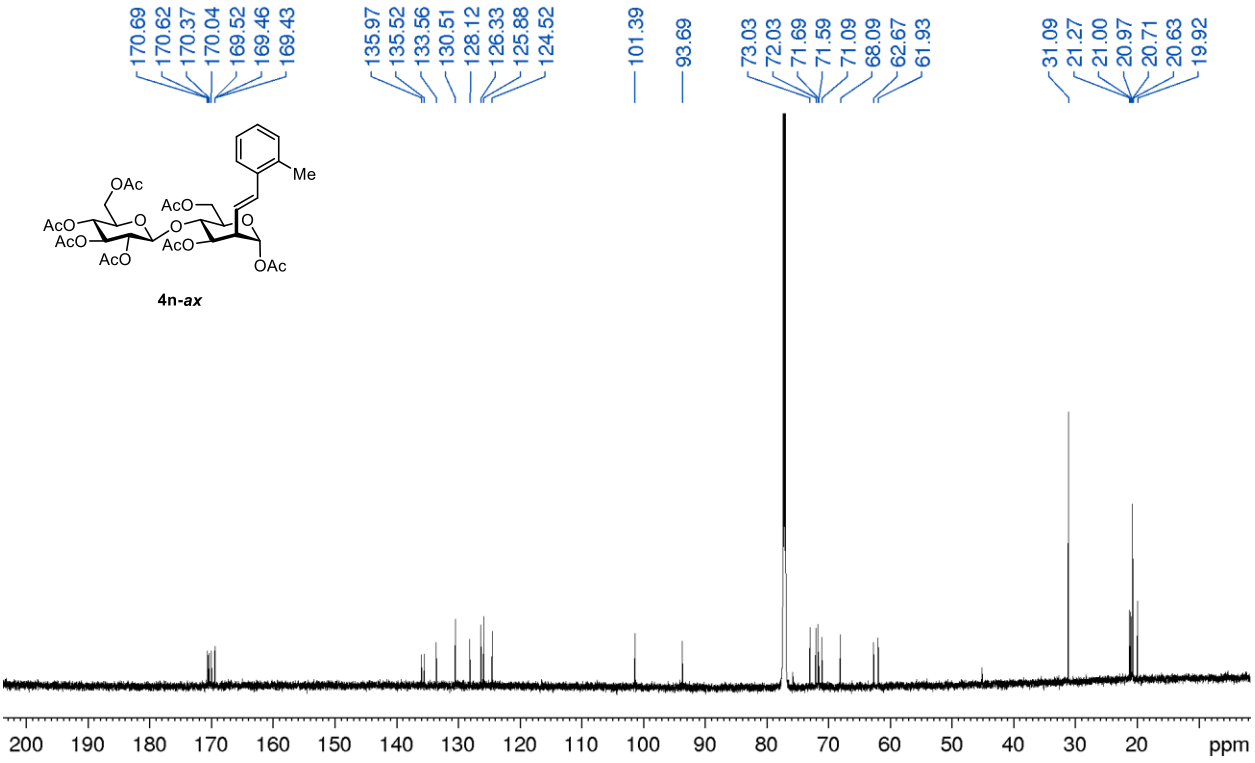
^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC) of (4m-*ax*)



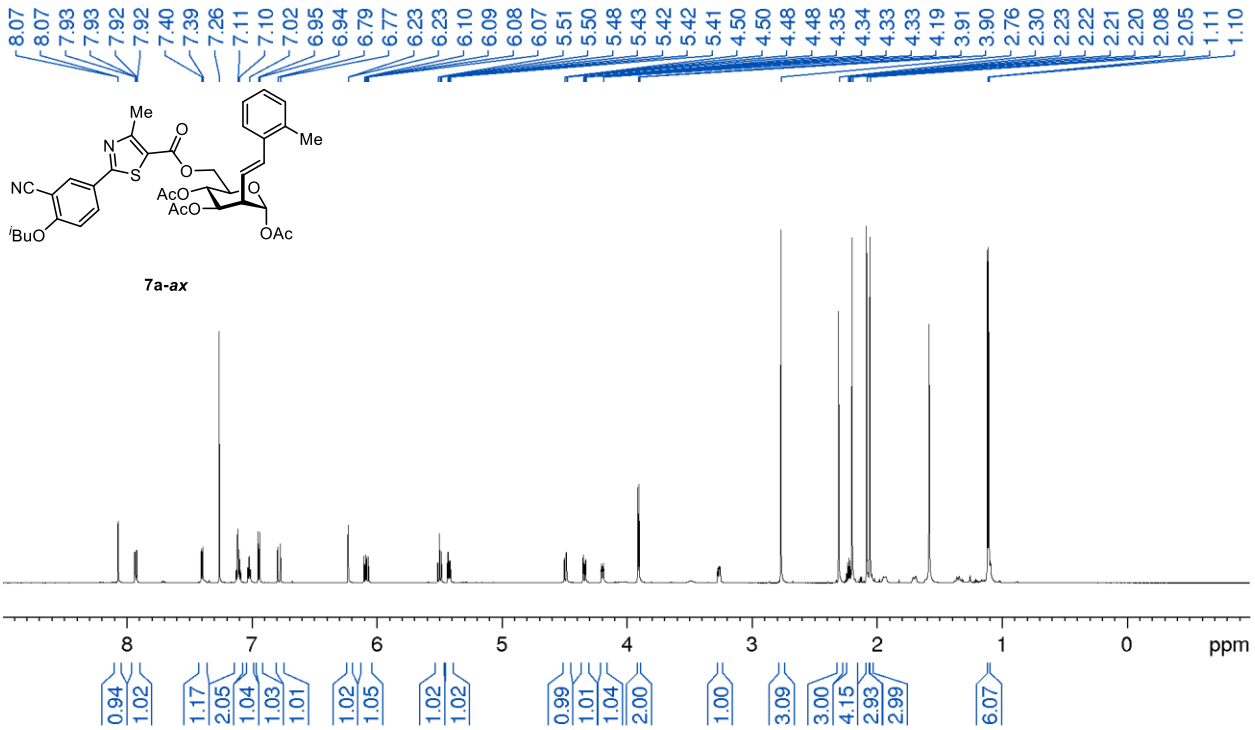
^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC) of (4n-*ax*)



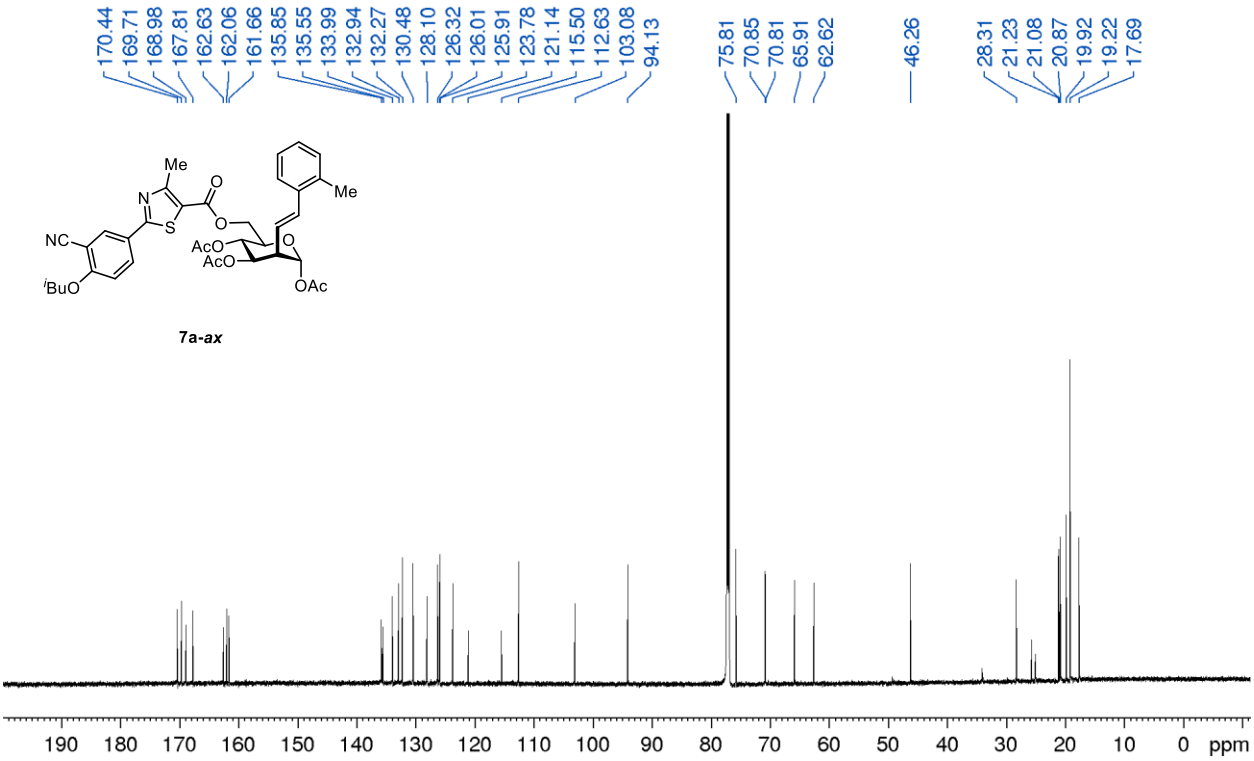
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (4n-*ax*)



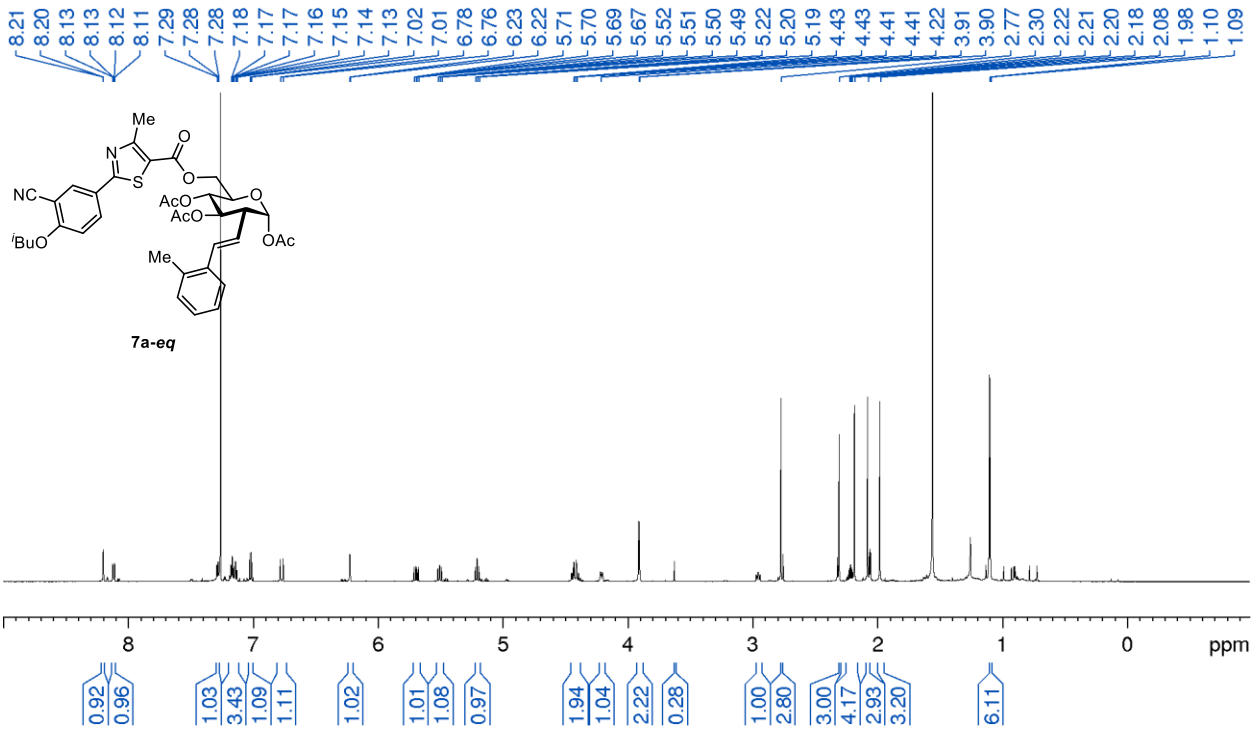
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (7a-*ax*)



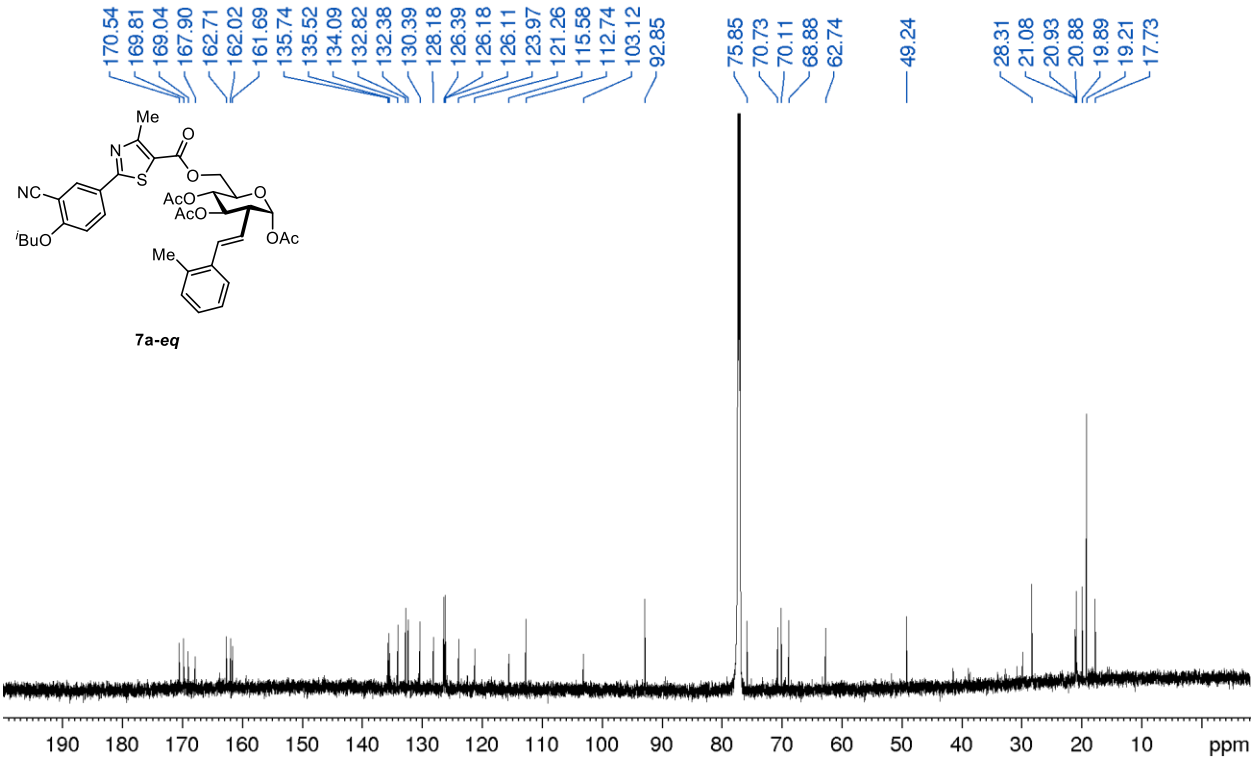
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (7a-*ax*)



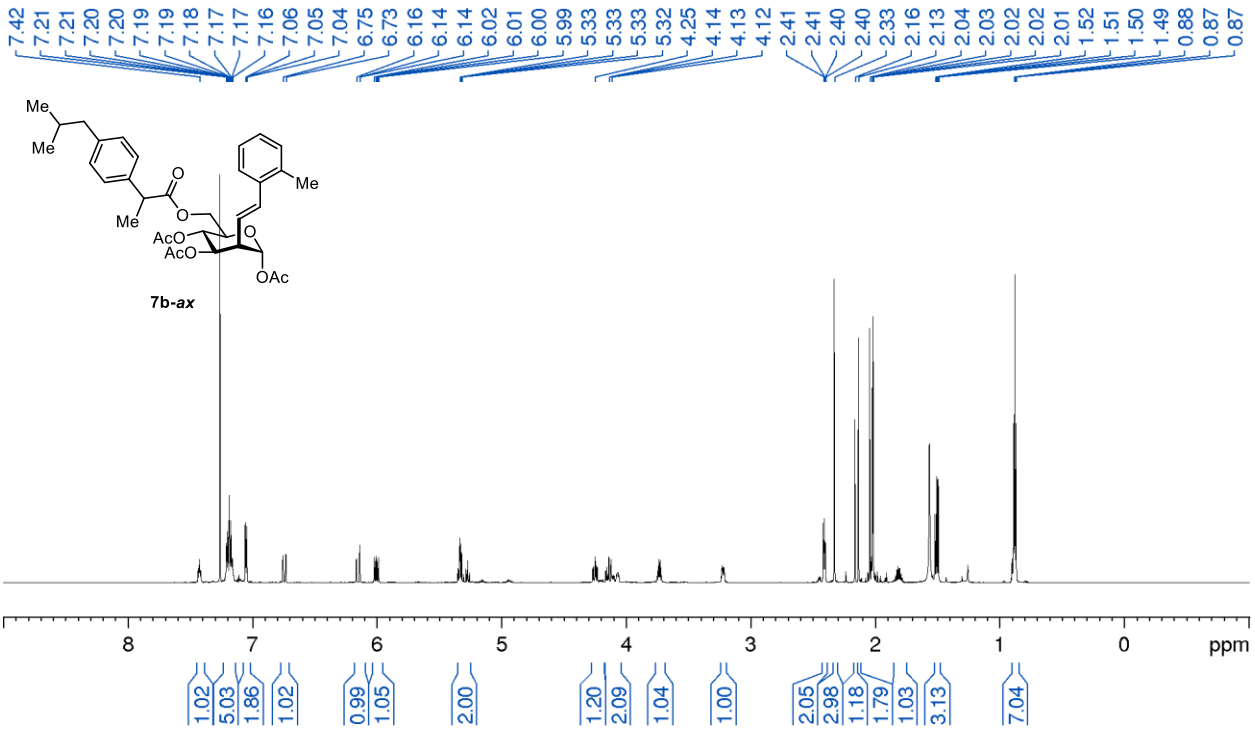
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (7a-*eq*)



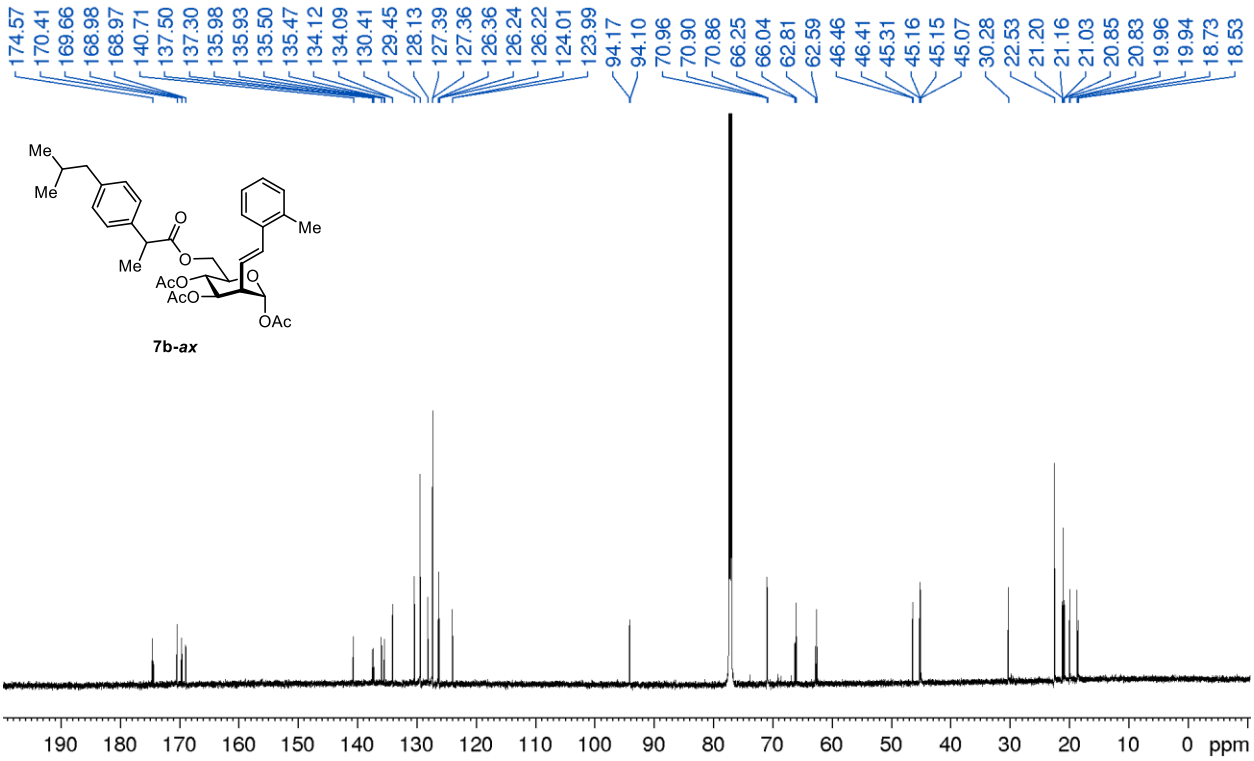
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (7a-*eq*)



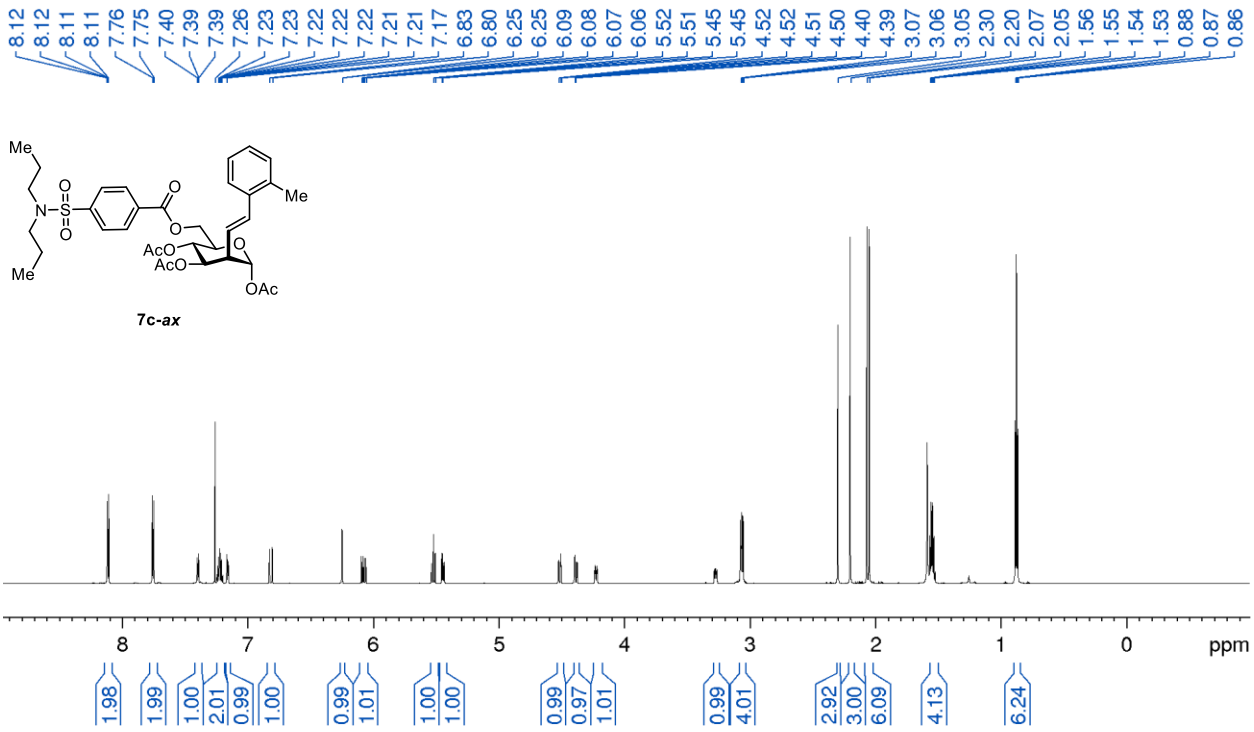
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (7b-*ax*)



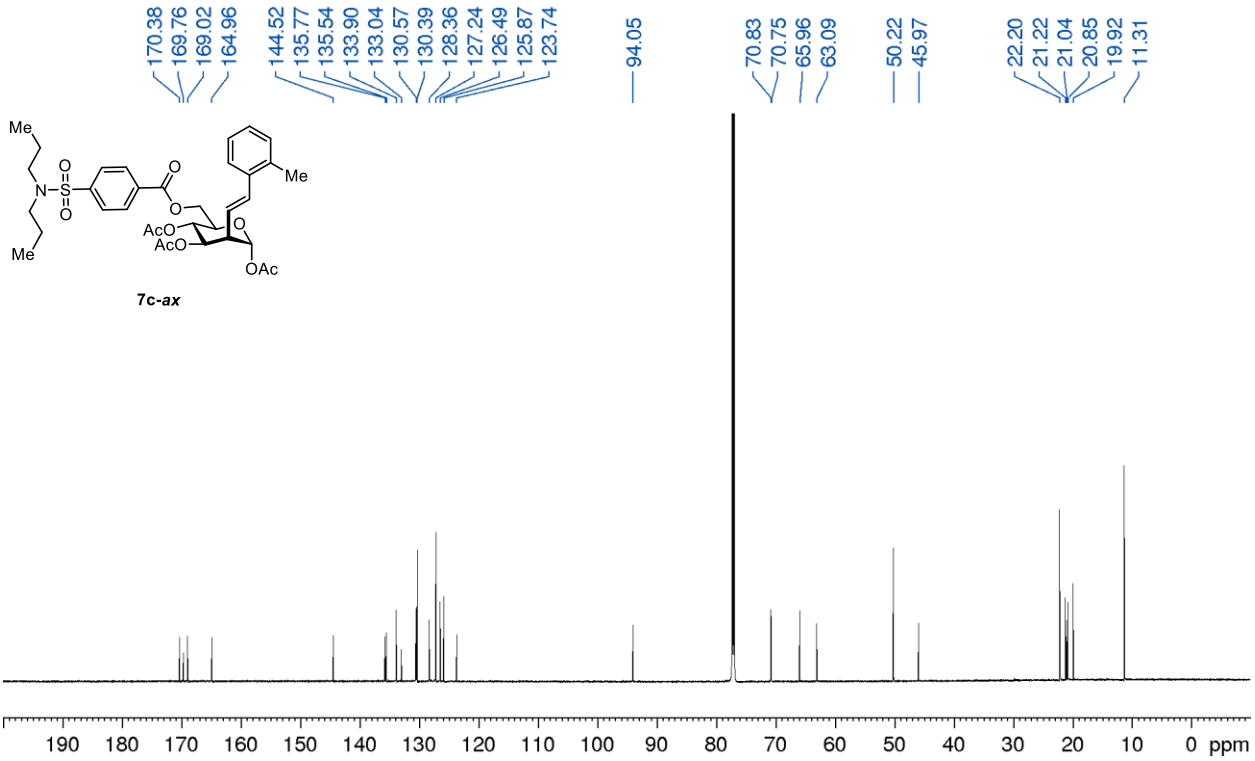
^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC) of (7b-*ax*)



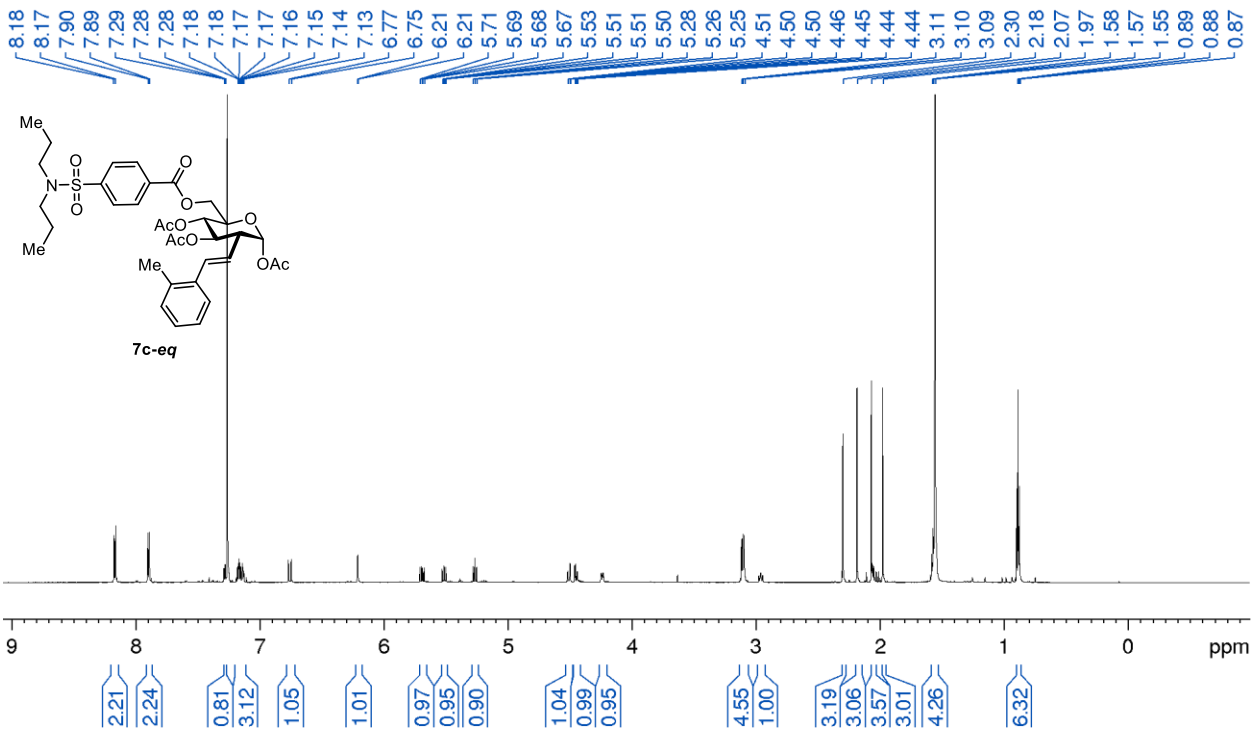
^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC) of (7c-*ax*)



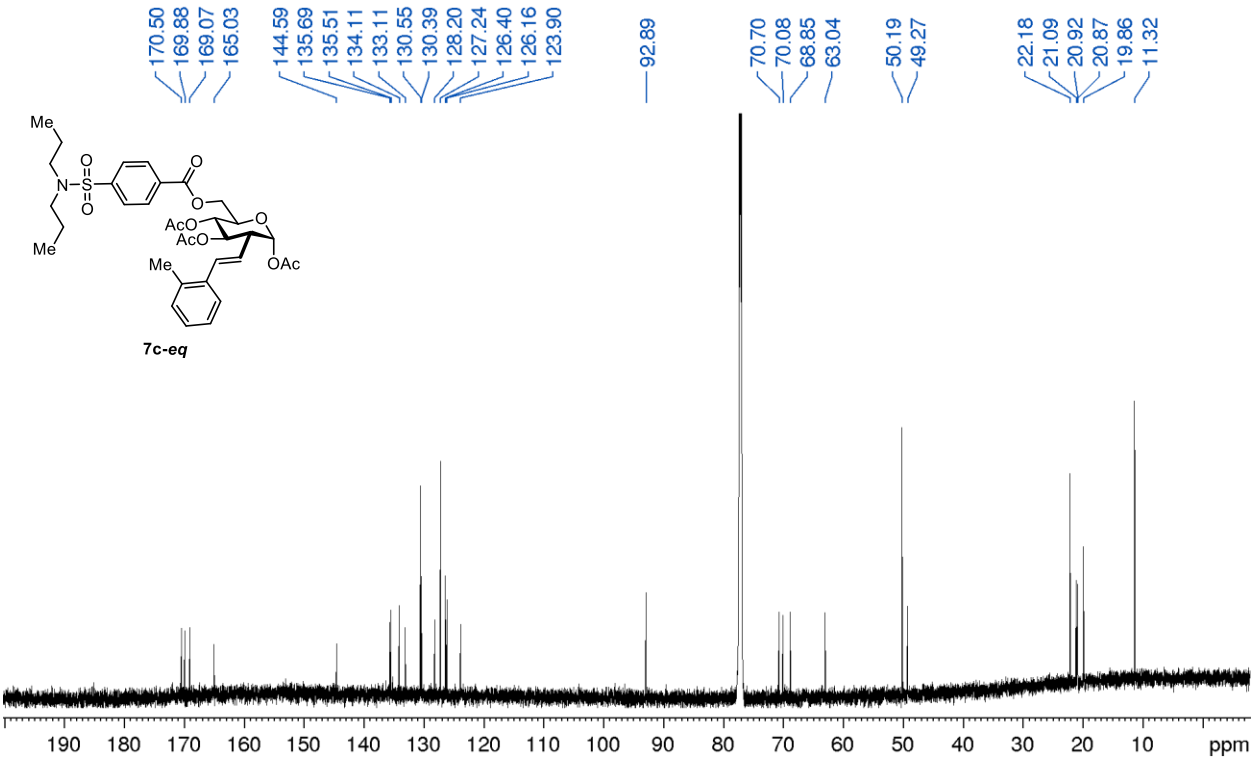
^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC) of (7c-*ax*)



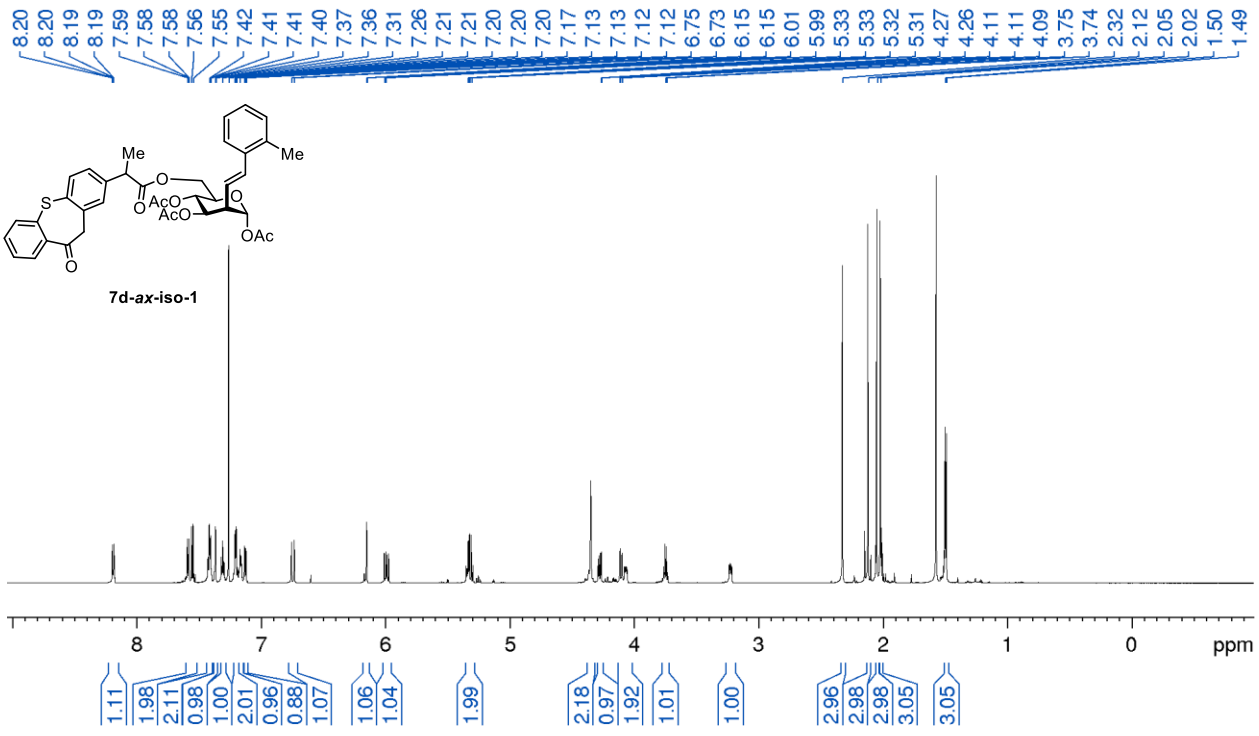
^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC) of (7c-*eq*)



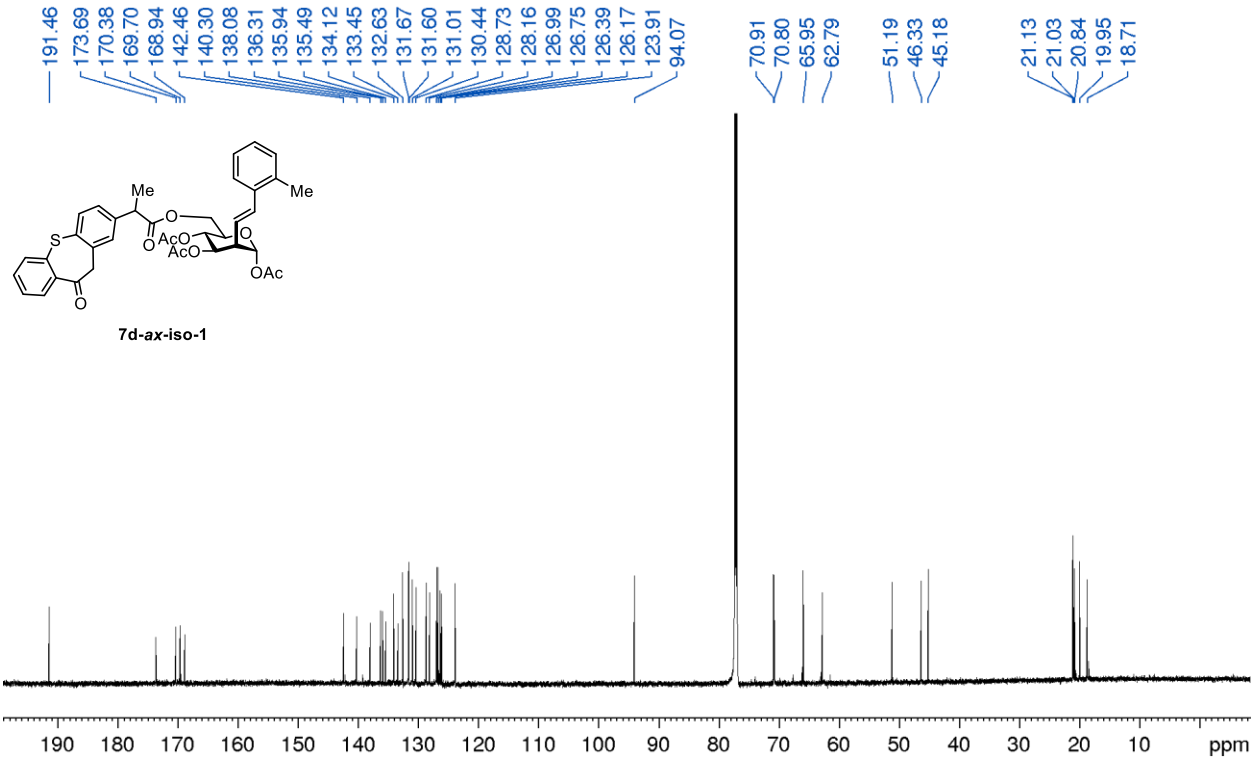
^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC) of (7c-*eq*)



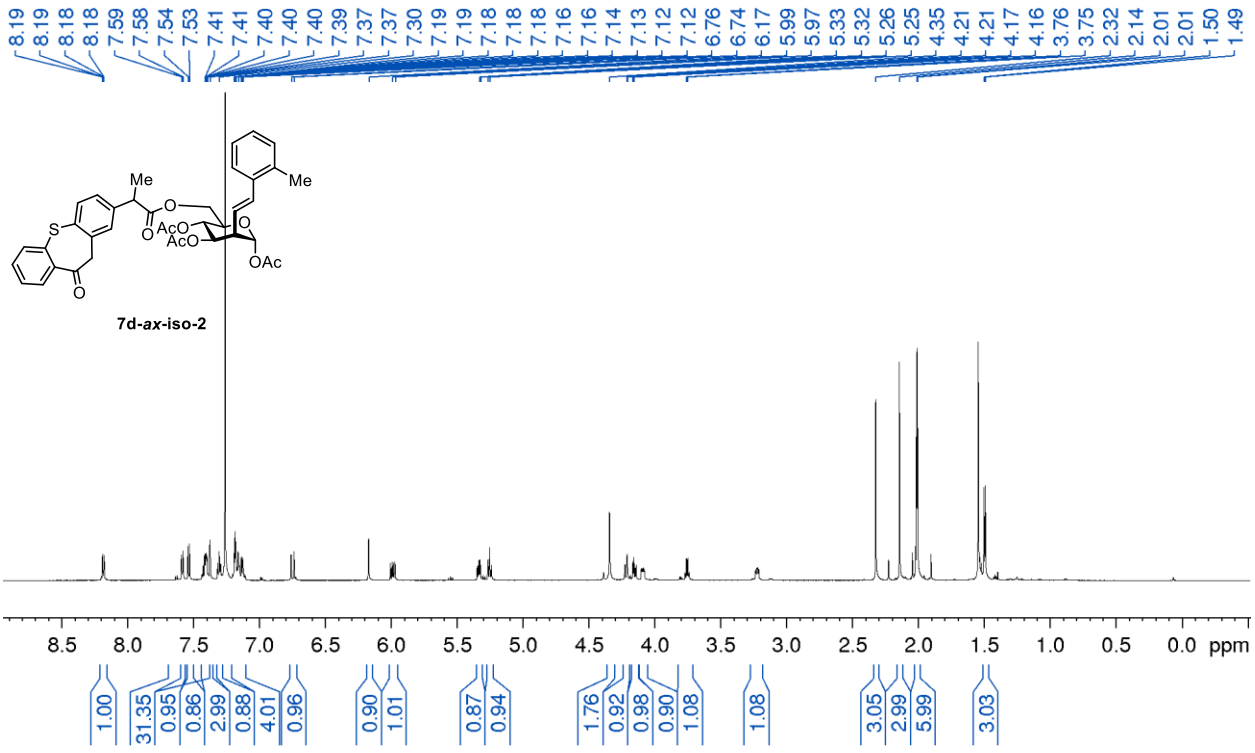
^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC) of (7d-*ax*-iso-1)



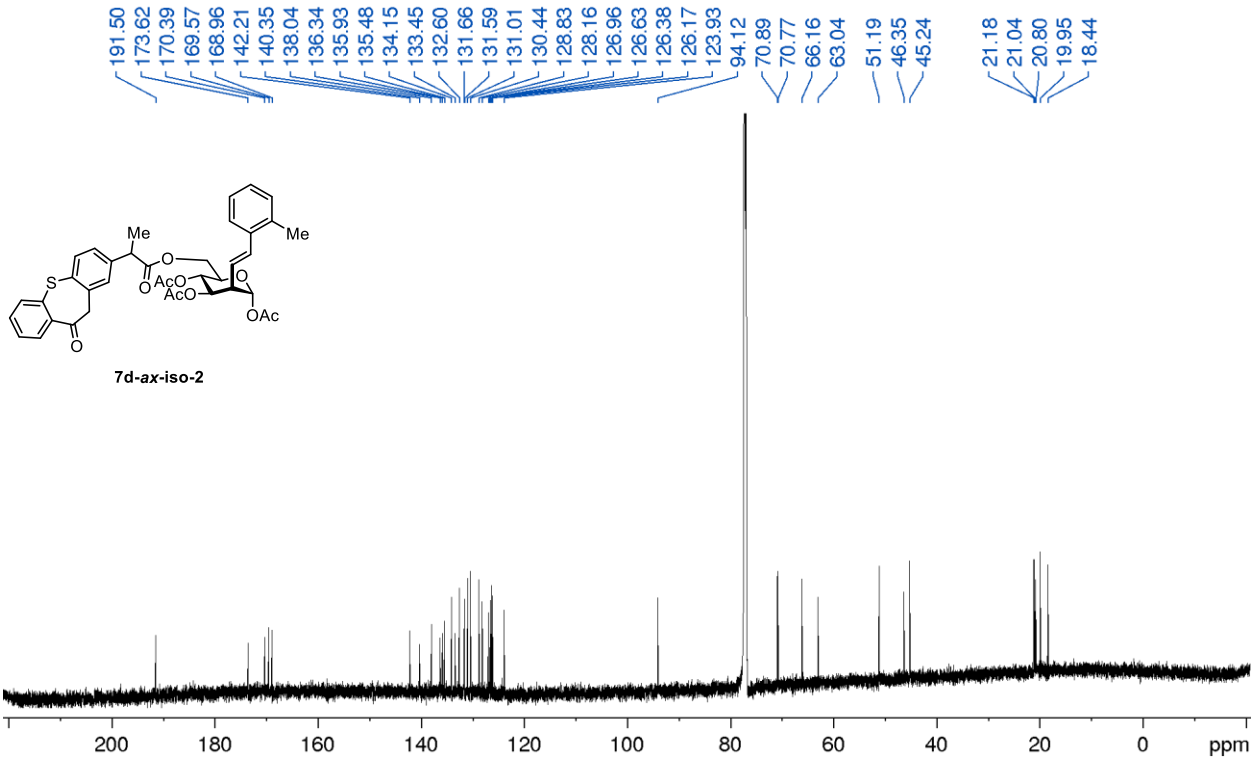
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (7d-*ax*-iso-1)



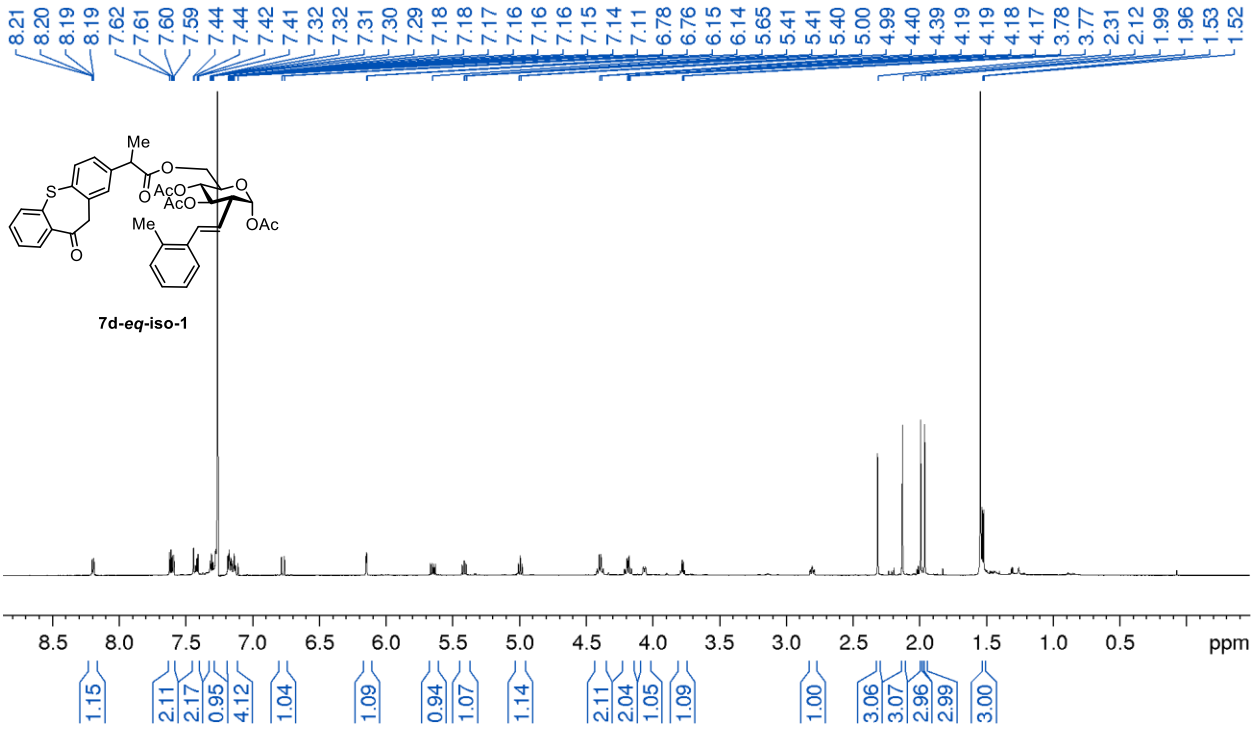
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (7d-*ax*-iso-2)



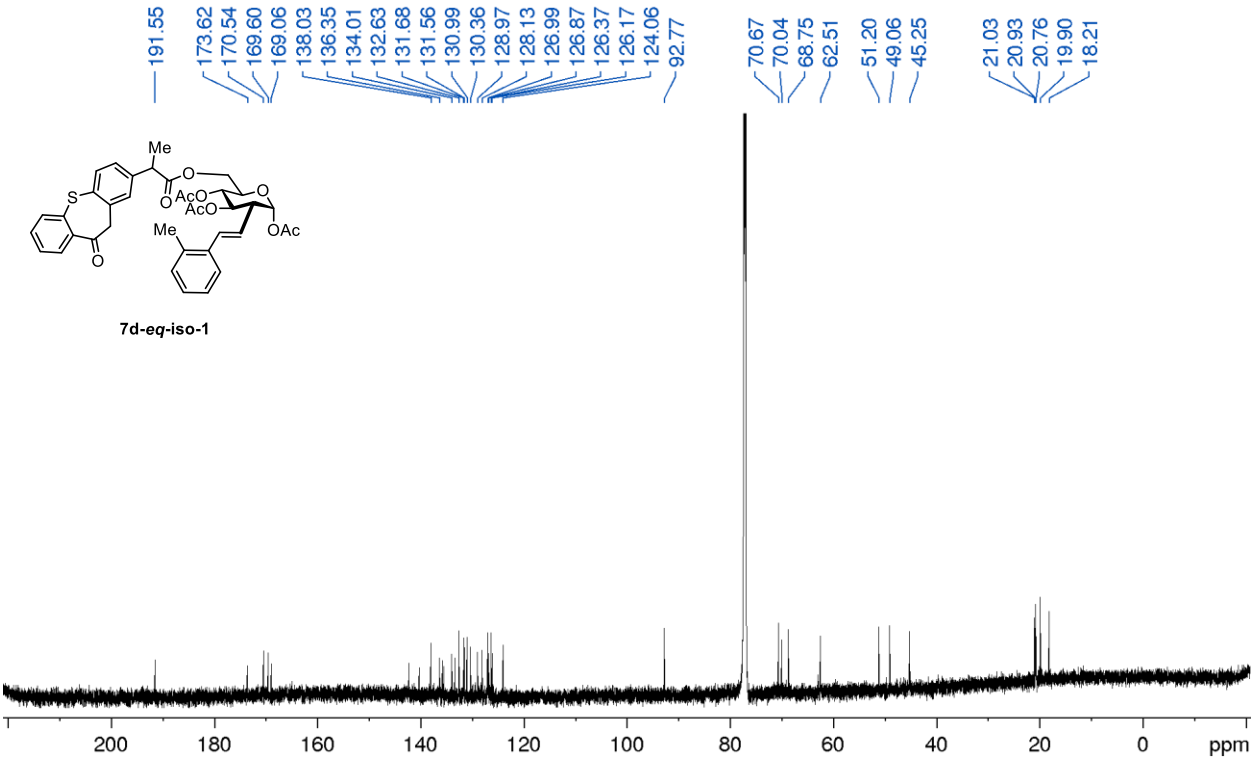
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (7d-*ax*-iso-2)



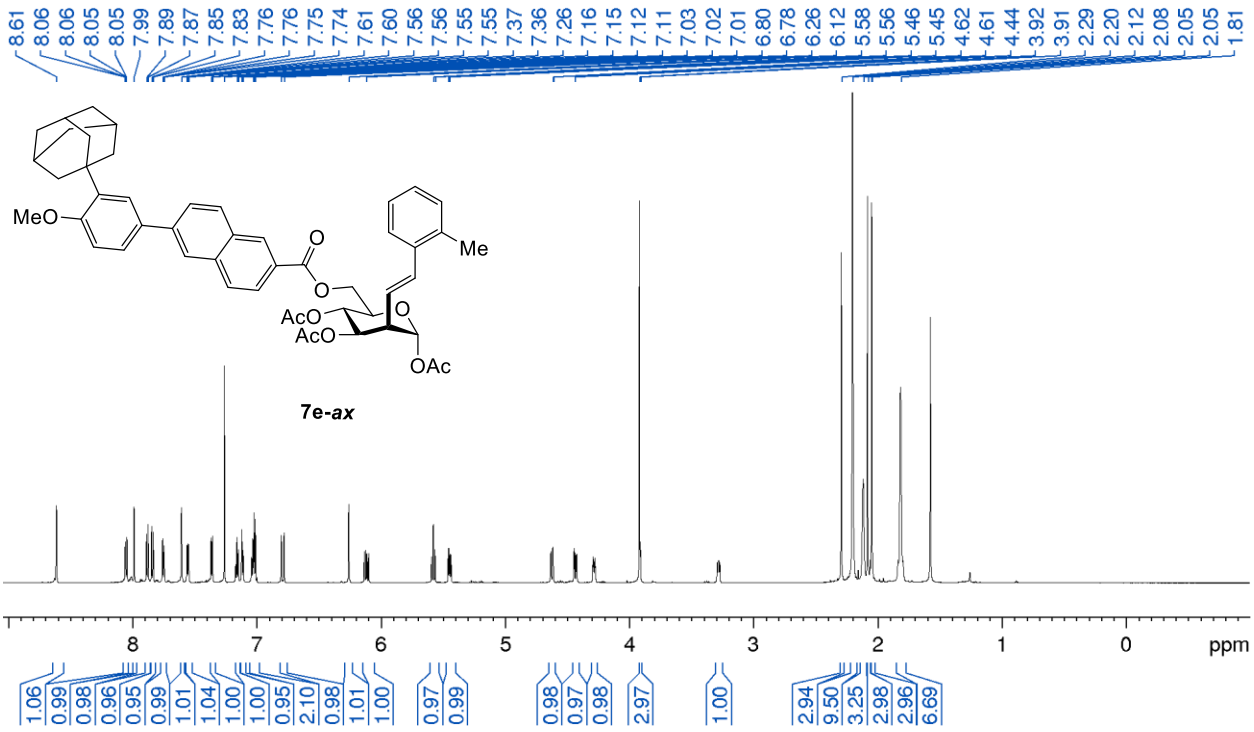
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (7d-*eq*-iso-1)



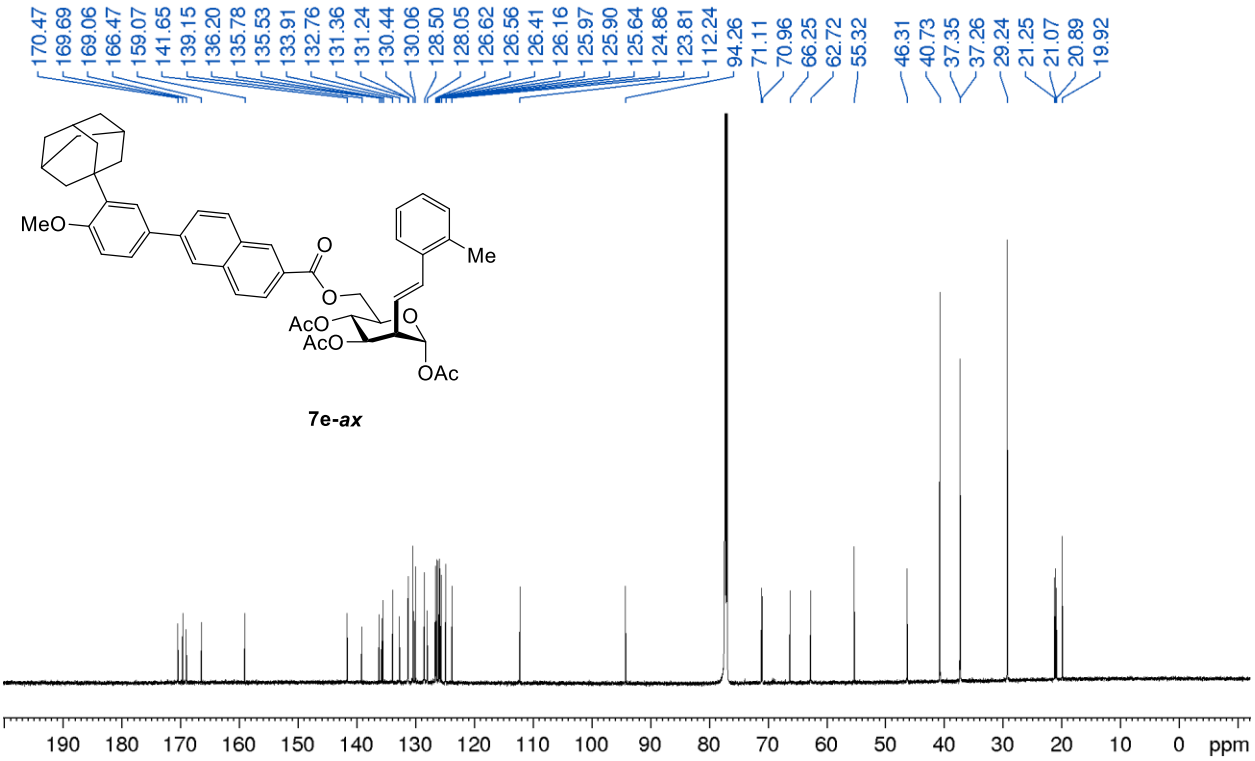
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (7d-*eq*-iso-1)



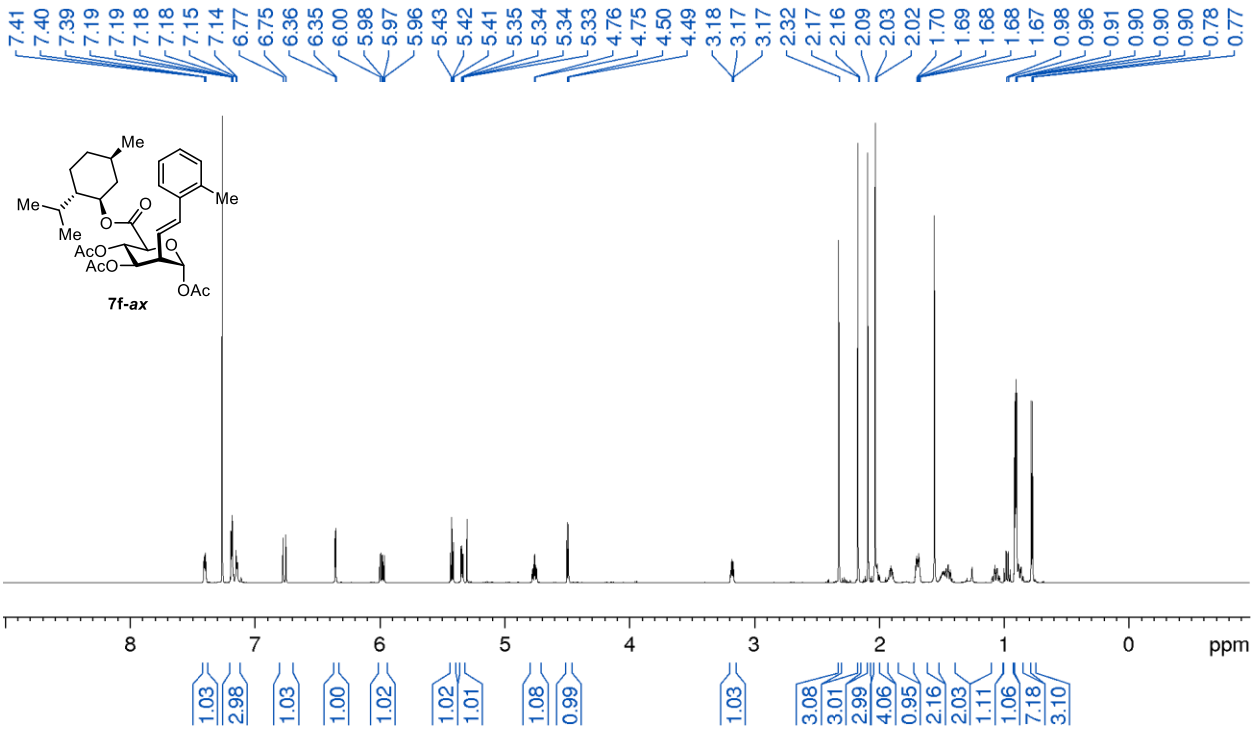
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (7e-*ax*)



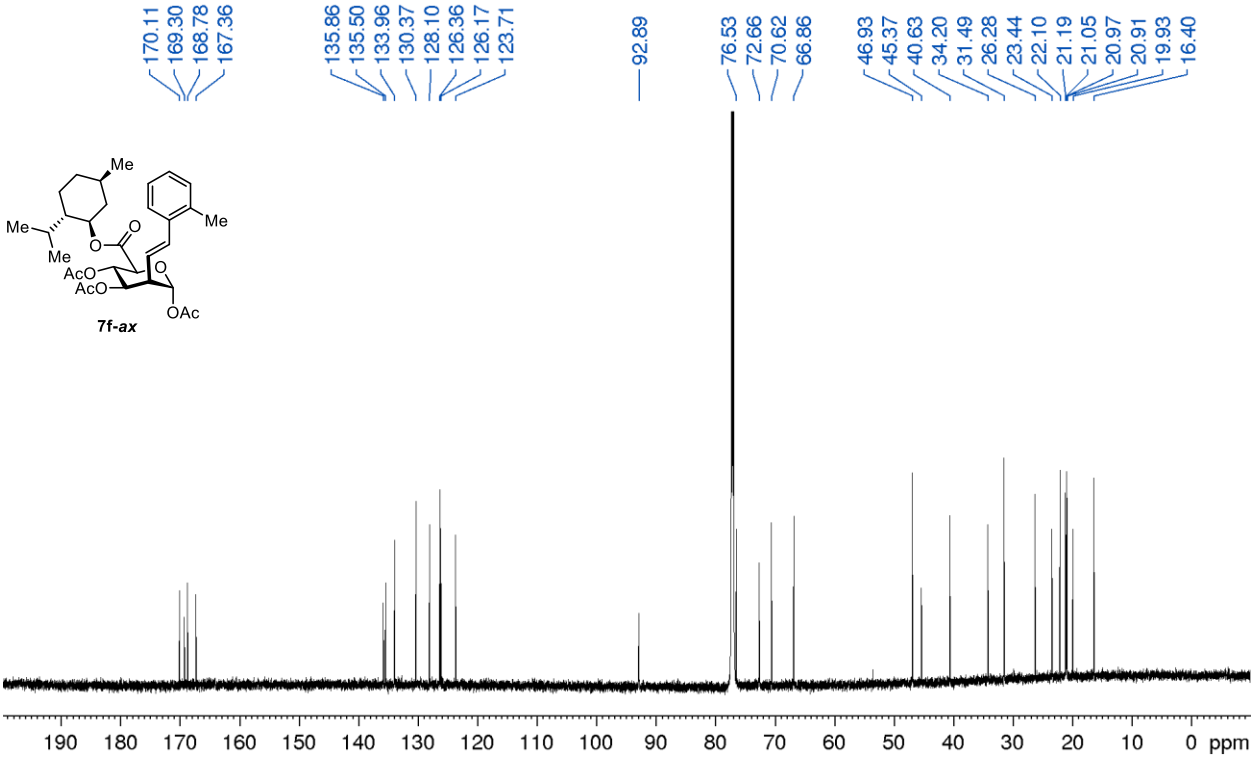
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (7e-*ax*)



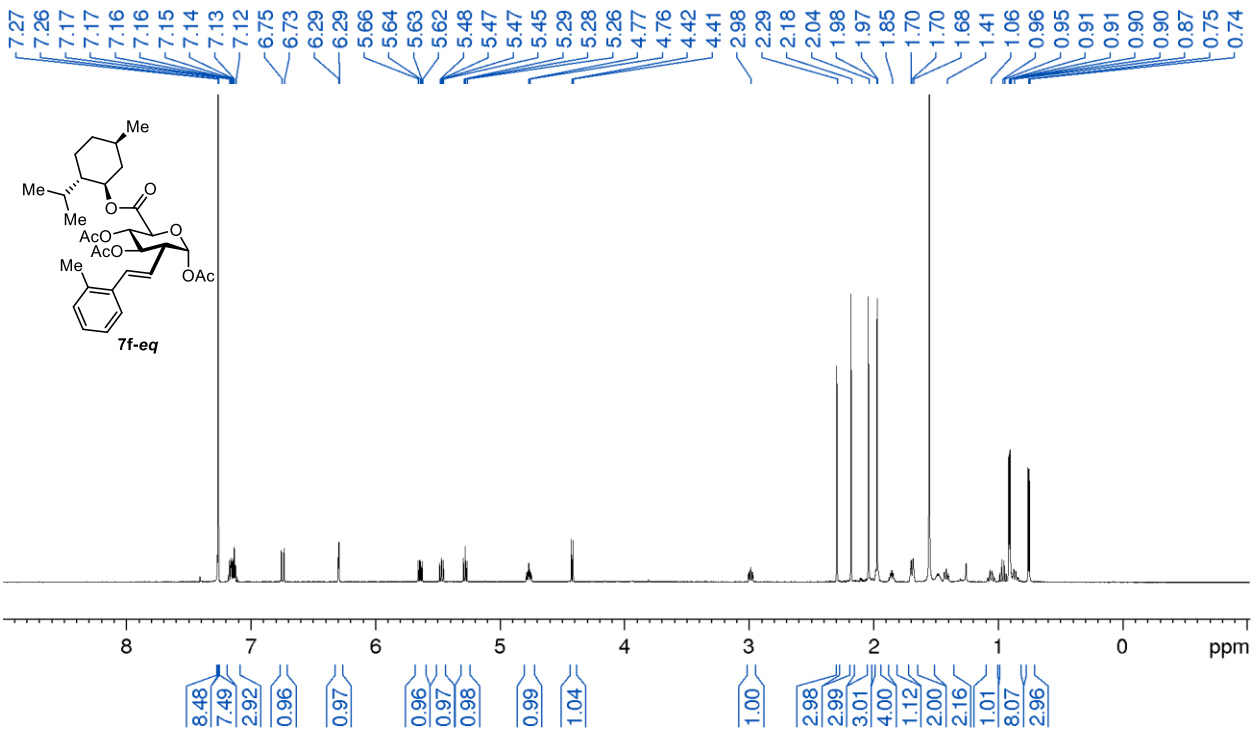
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (7f-*ax*)



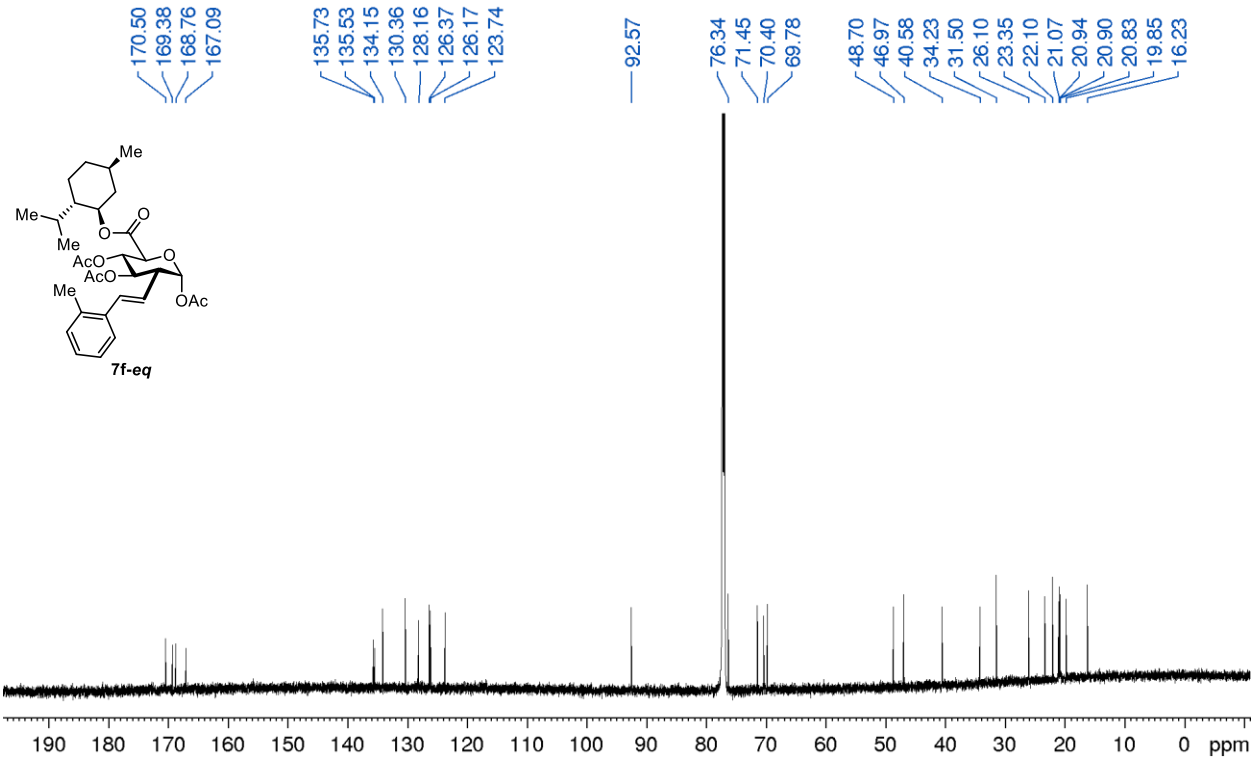
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (7f-*ax*)



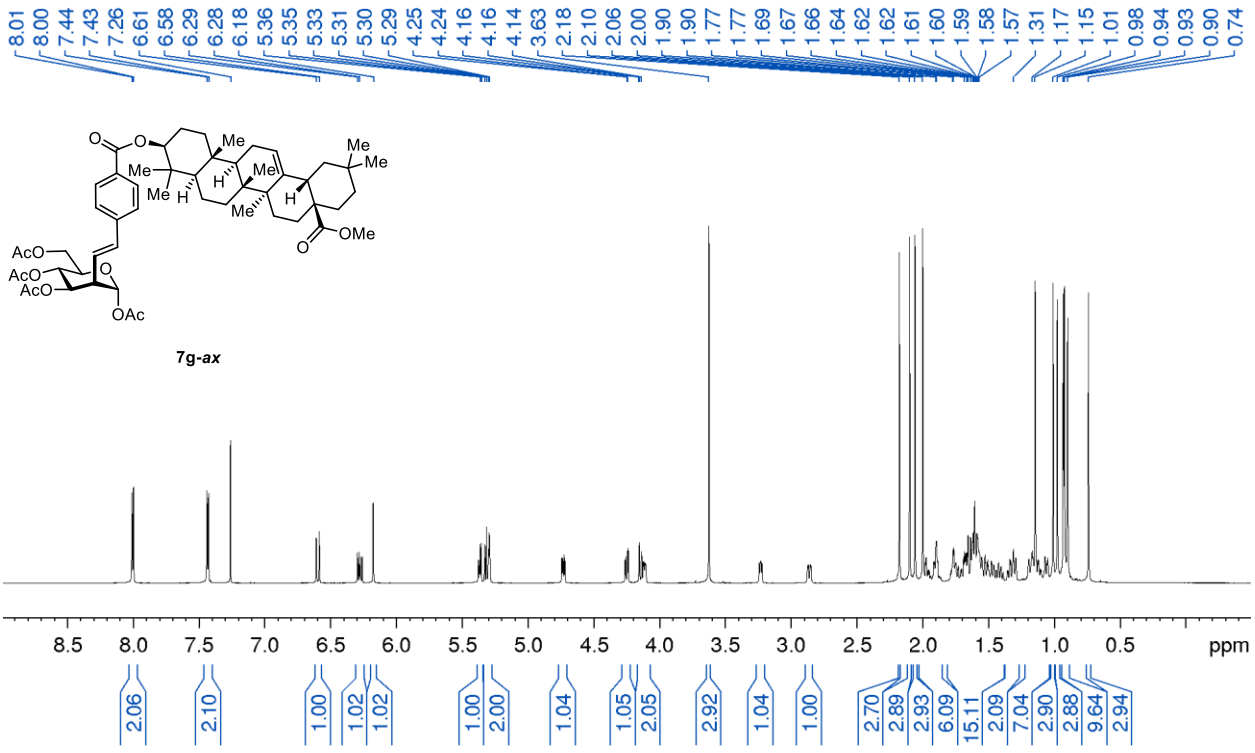
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (7f-*eq*)



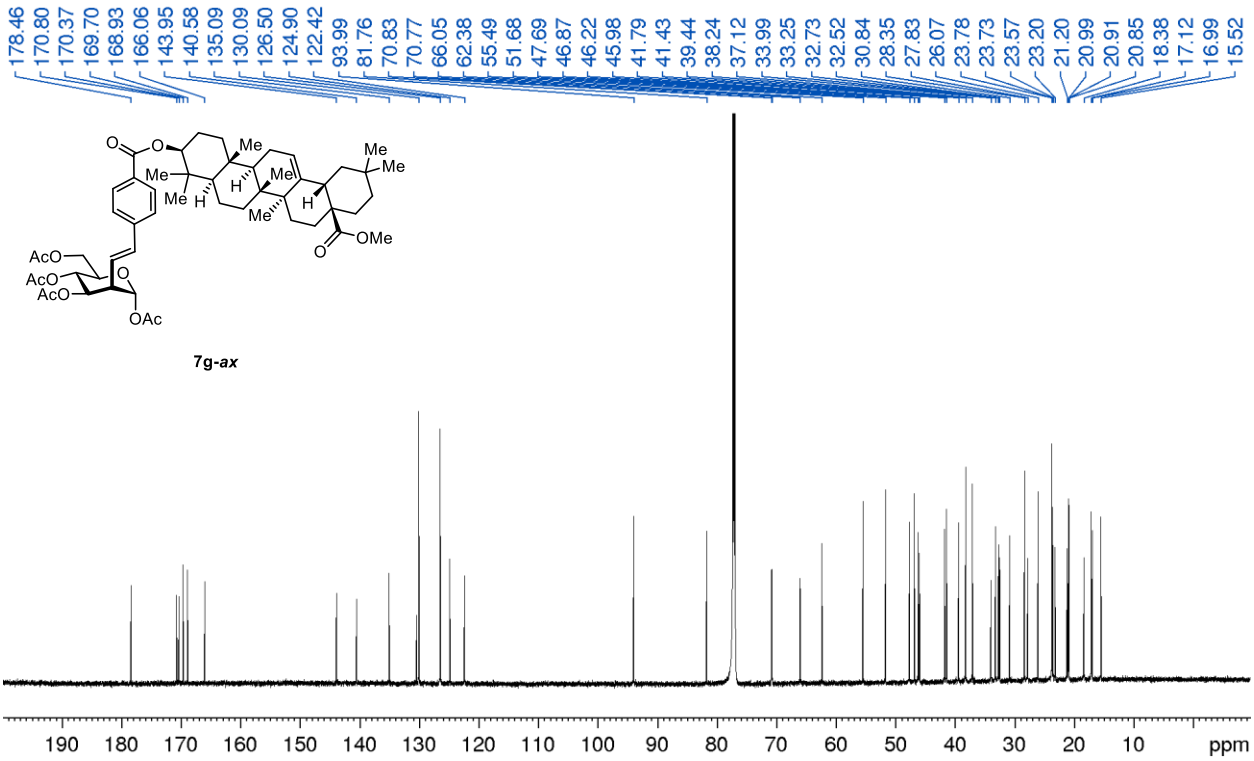
^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC) of (7f-*eq*)



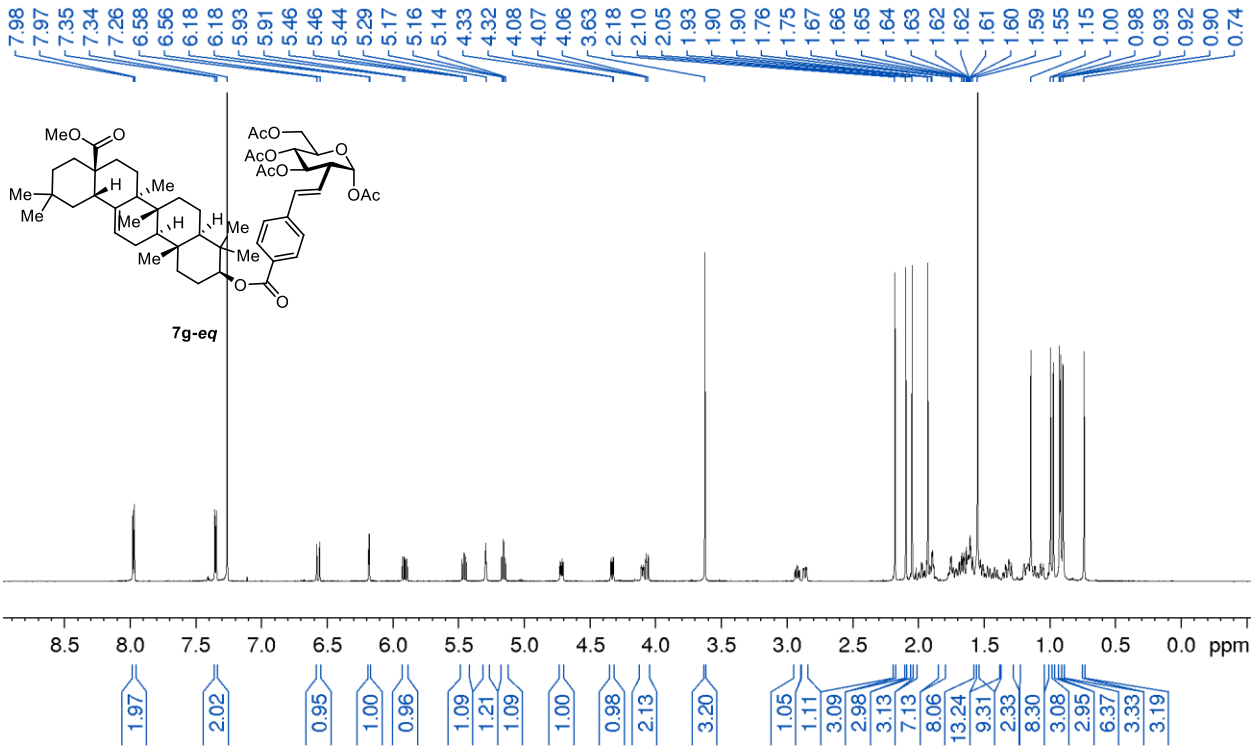
^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC) of (7g-*ax*)



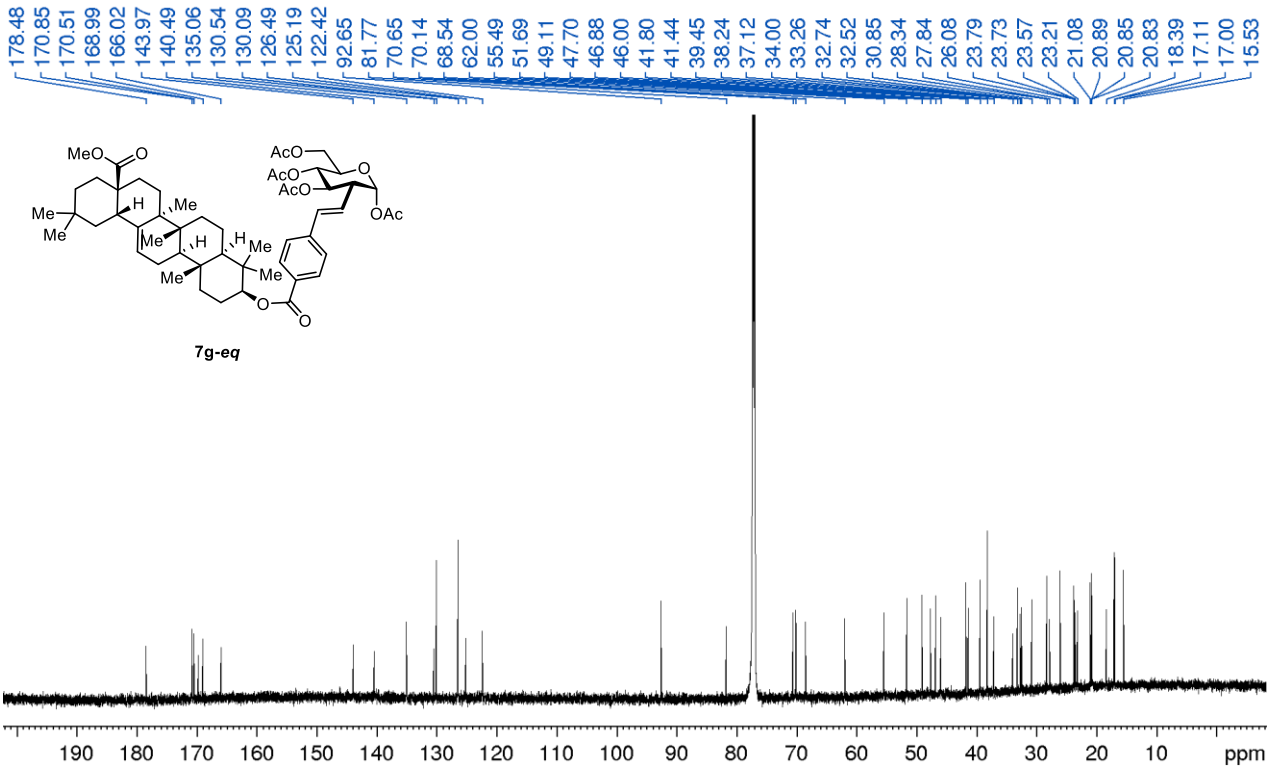
^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC) of (7g-*ax*)



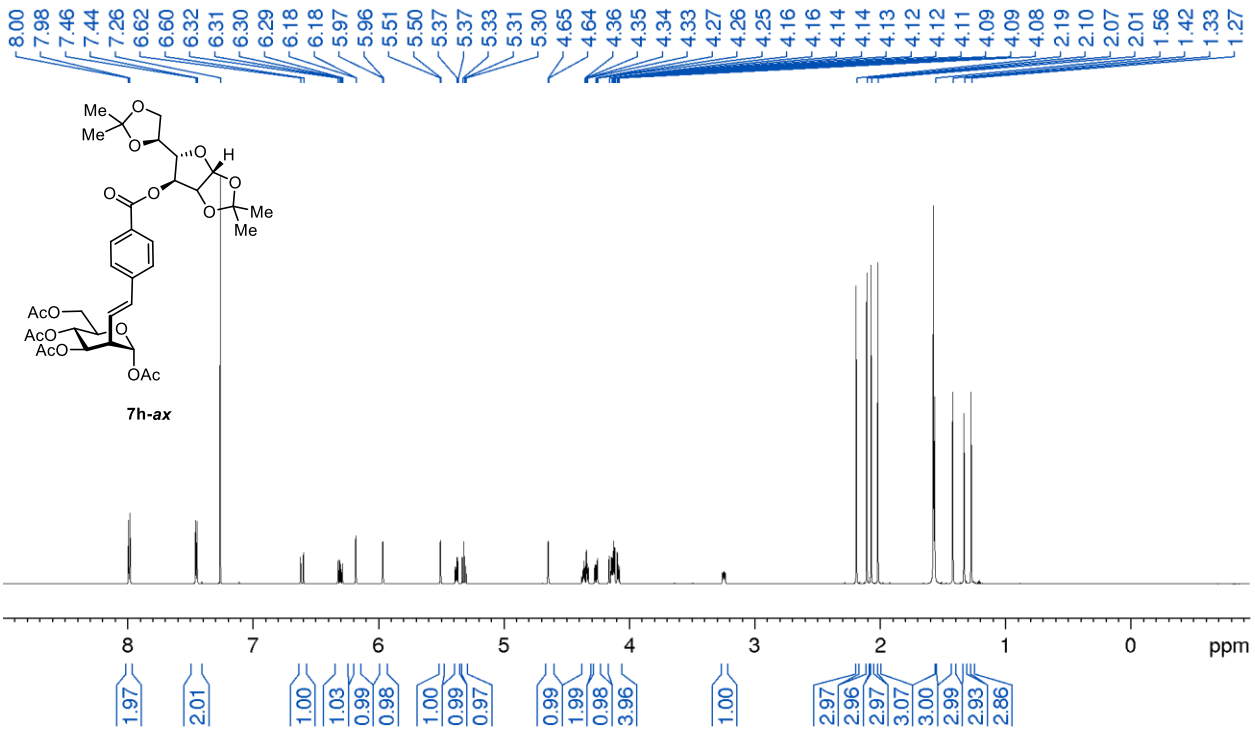
^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC) of (7g-*eq*)



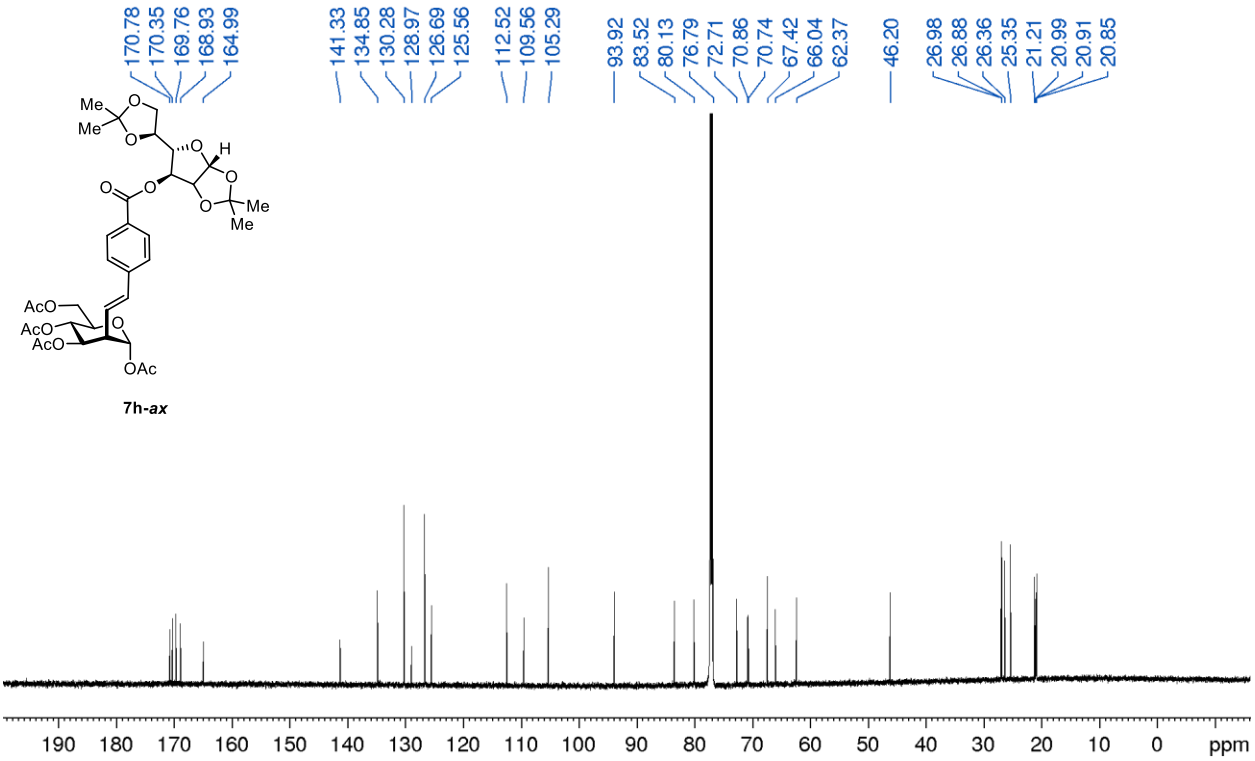
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (7g-*eq*)



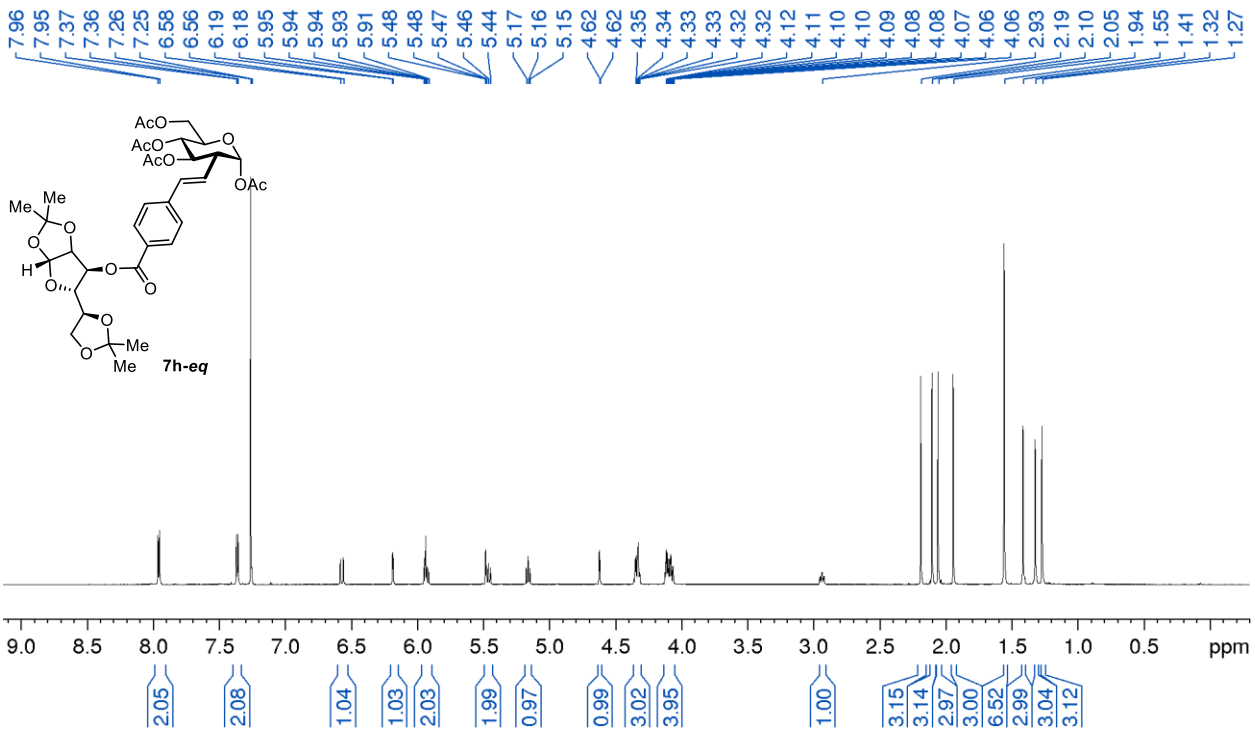
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (7h-*ax*)



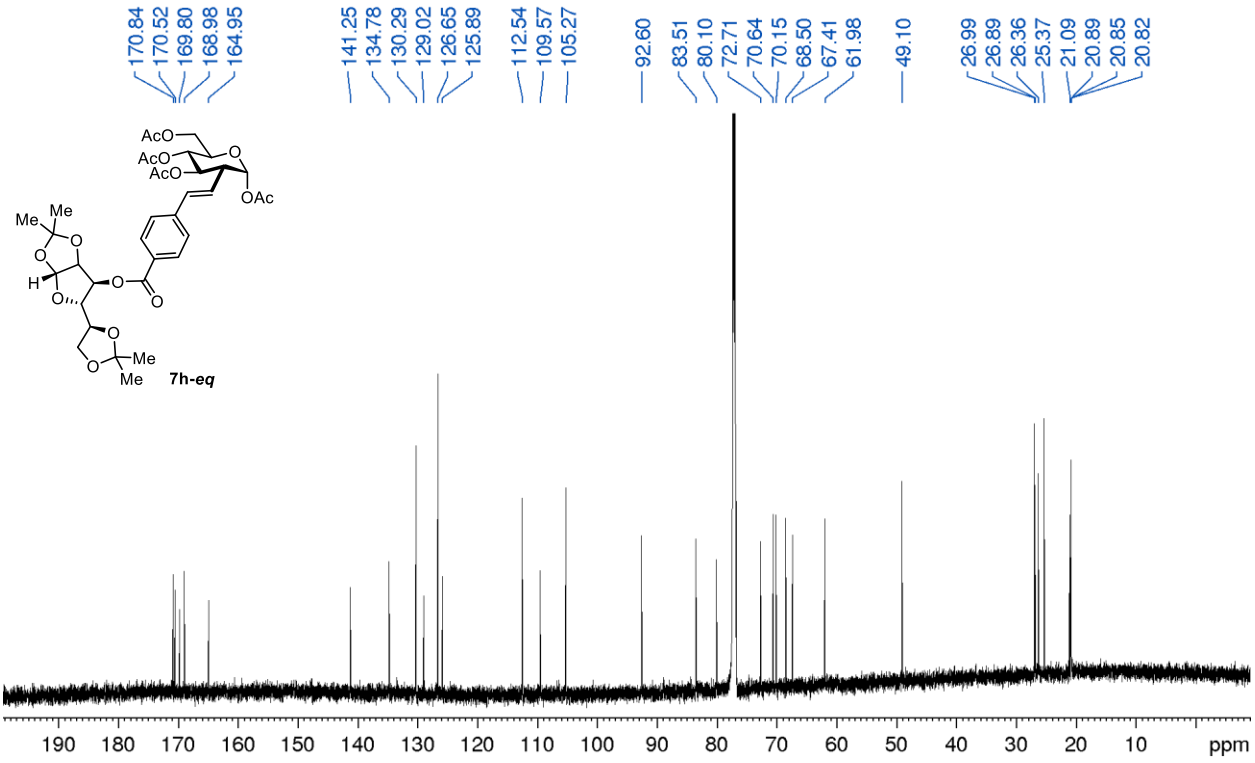
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (7h-*ax*)



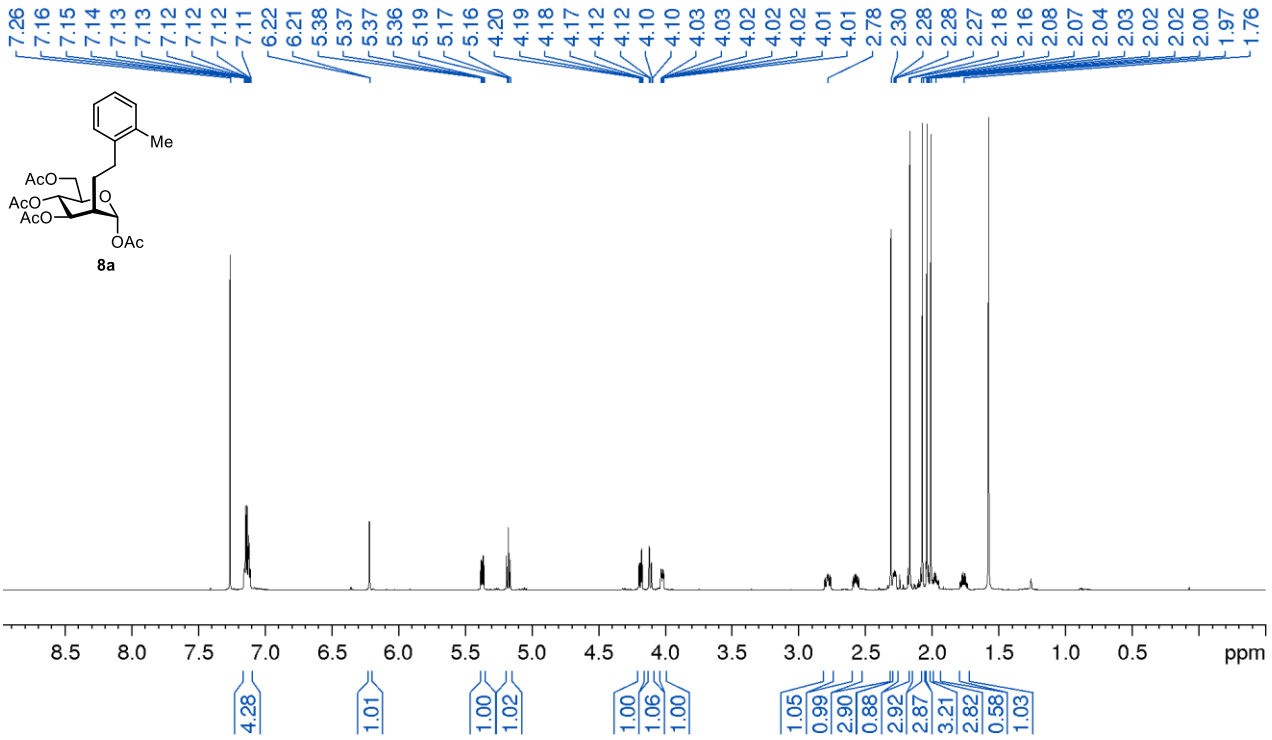
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (7h-*eq*)



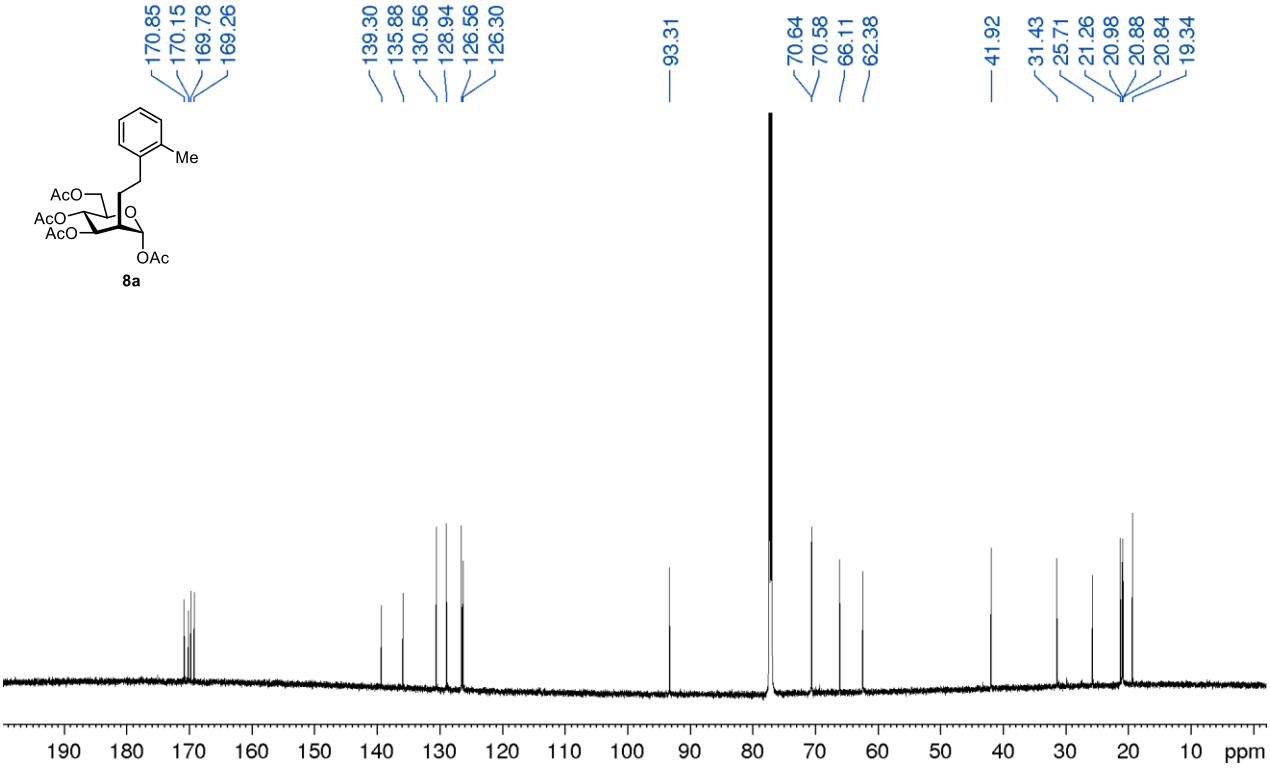
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (7h-*eq*)



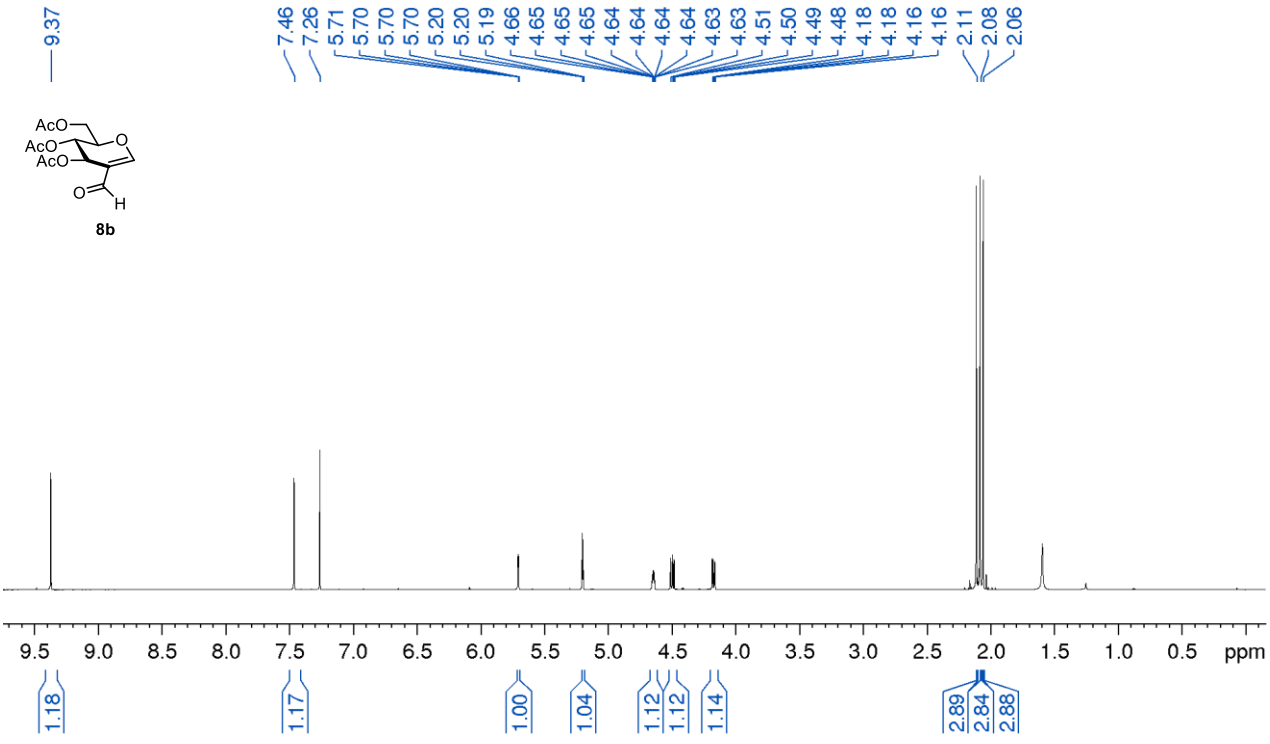
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (8a)



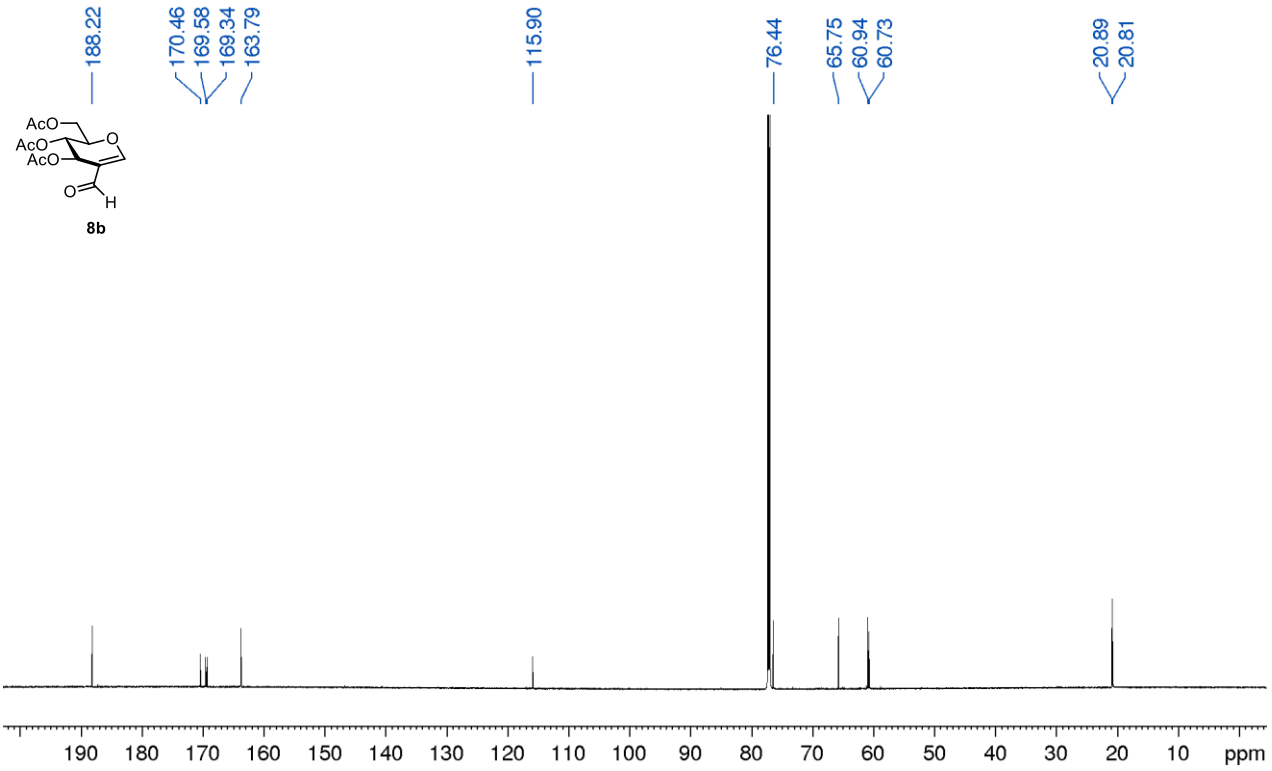
^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC) of (8a)



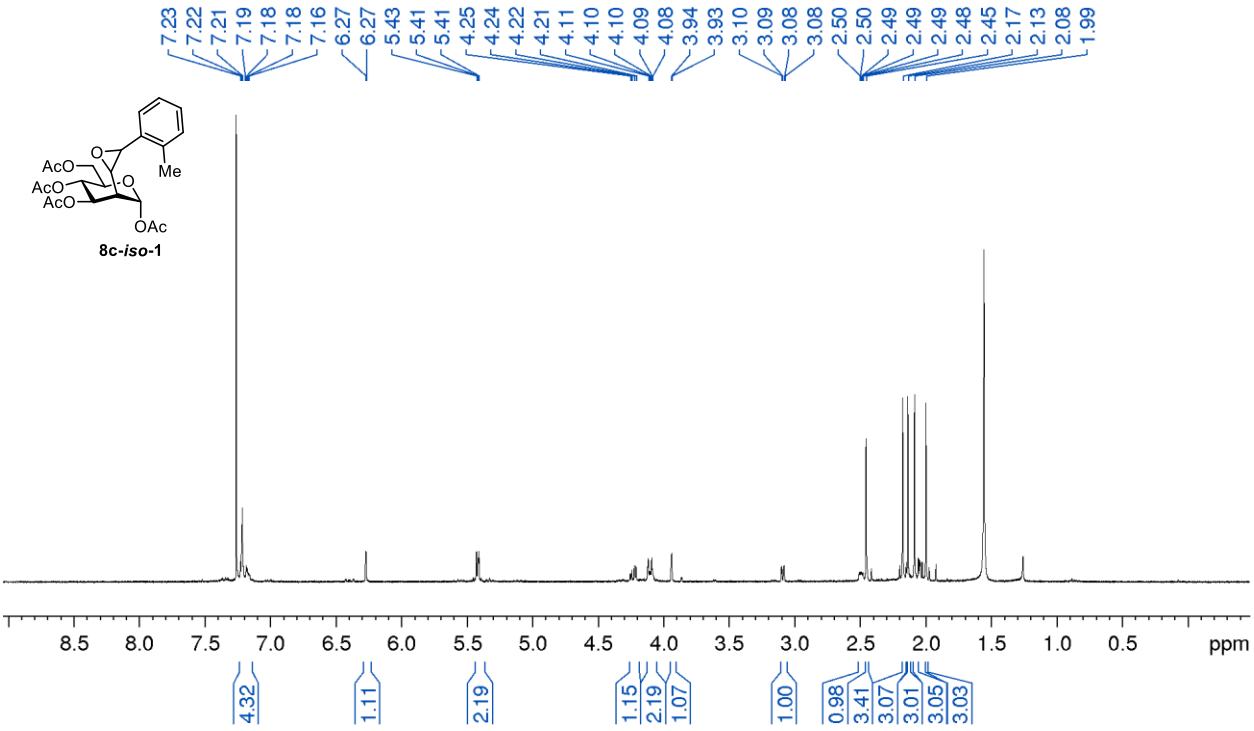
^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC) of (8b)



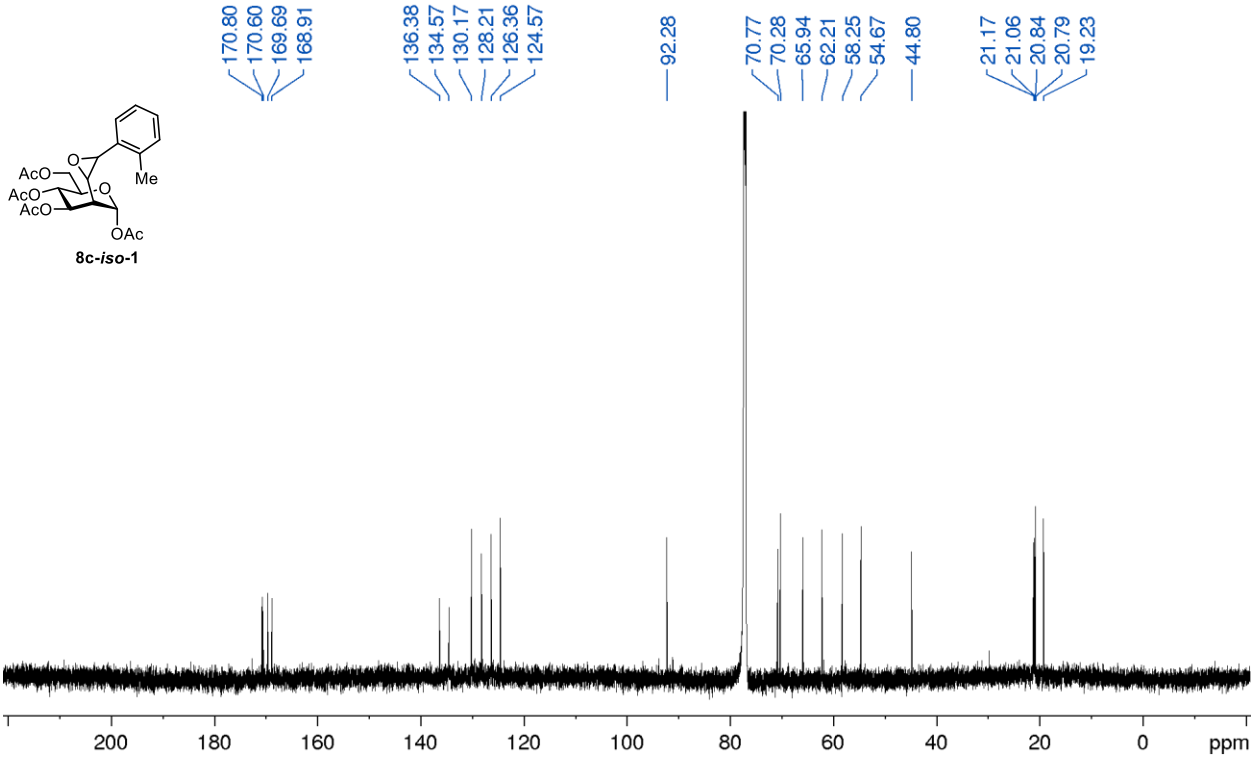
^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC) of (8b)



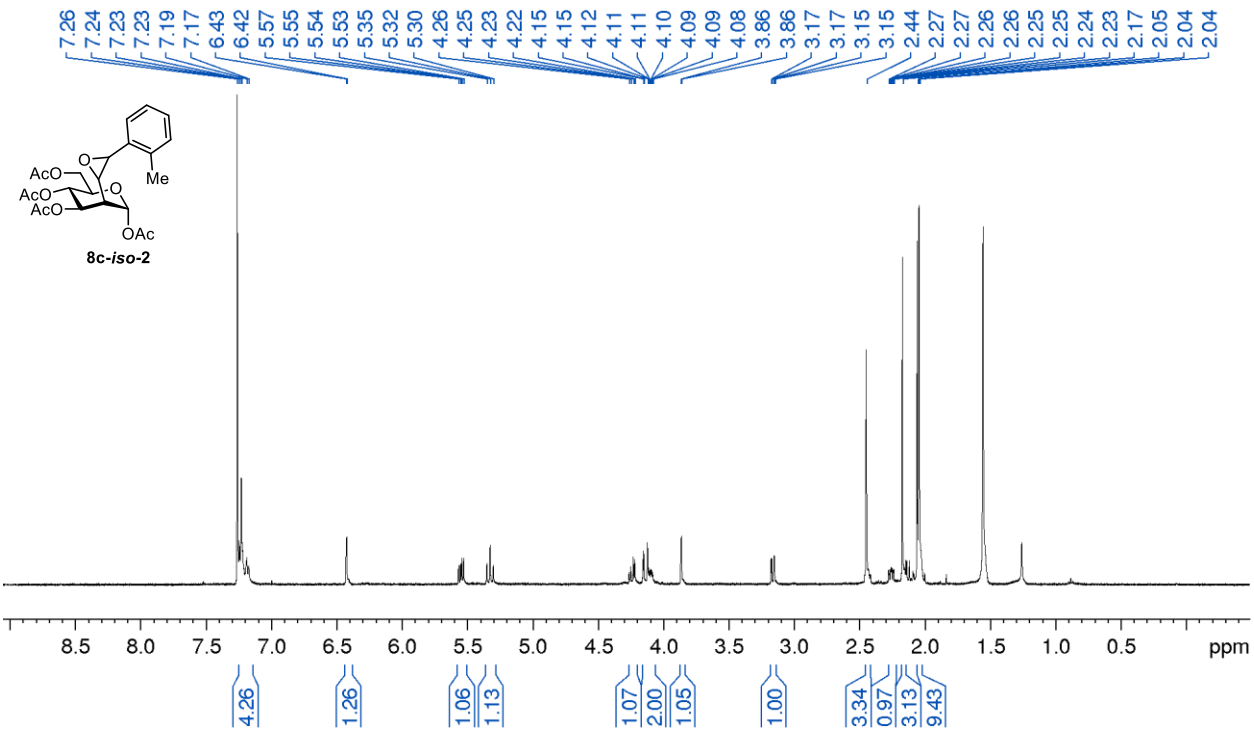
^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC) of (8c-*iso*-1)



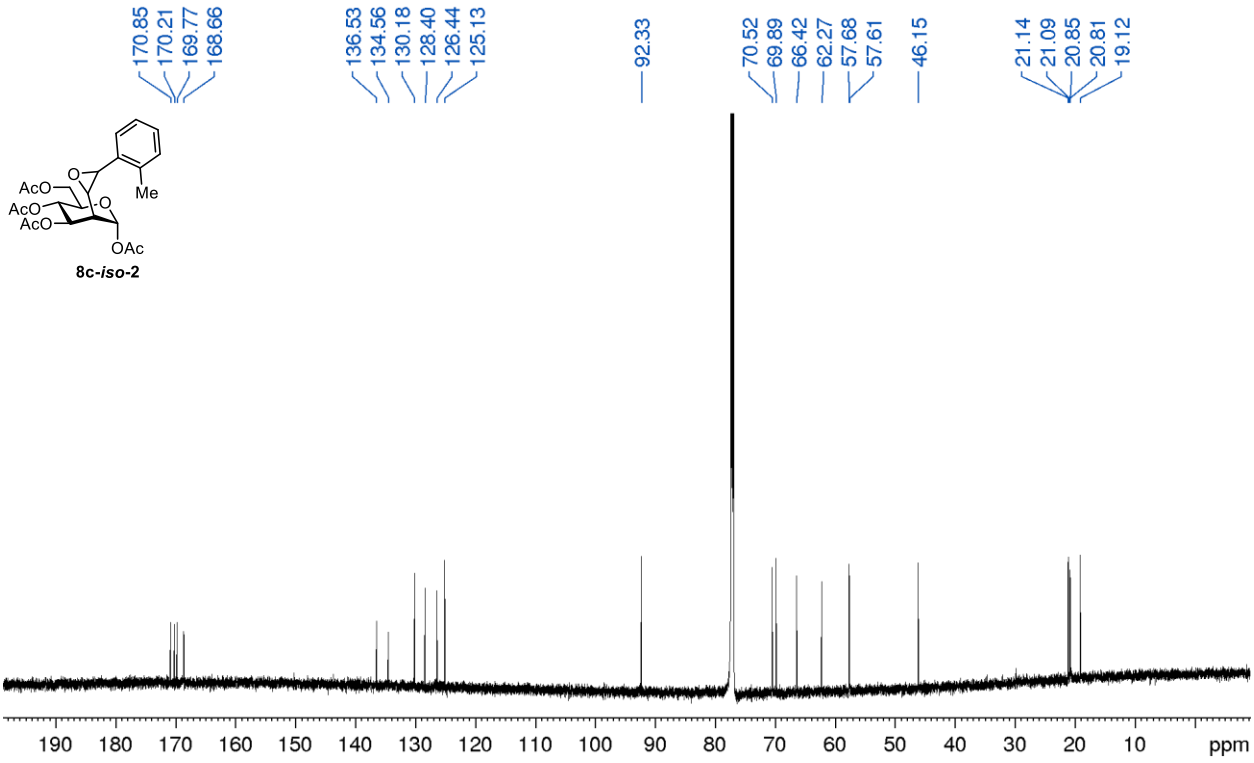
^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC) of (8c-*iso*-1)



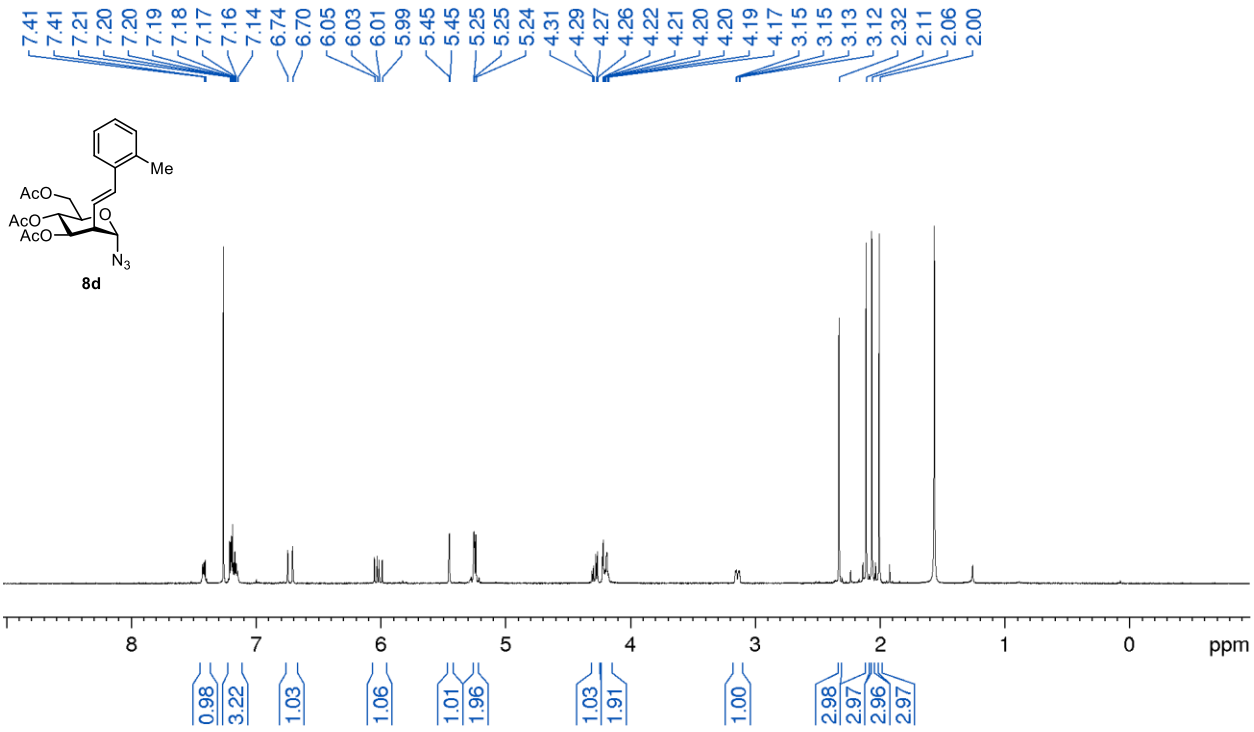
^{1}H NMR (700 MHz, $CDCl_3$, 25 ºC) of (8c-*iso*-2)



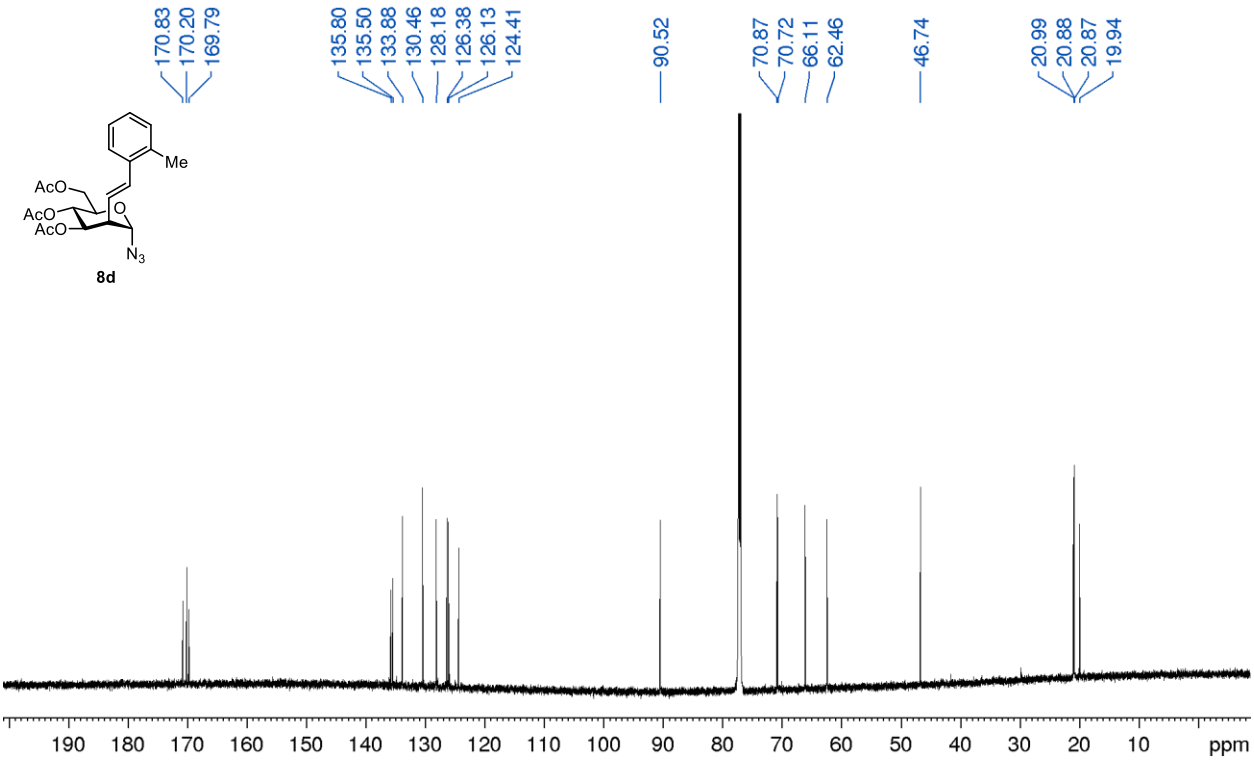
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (8c-*iso*-2)



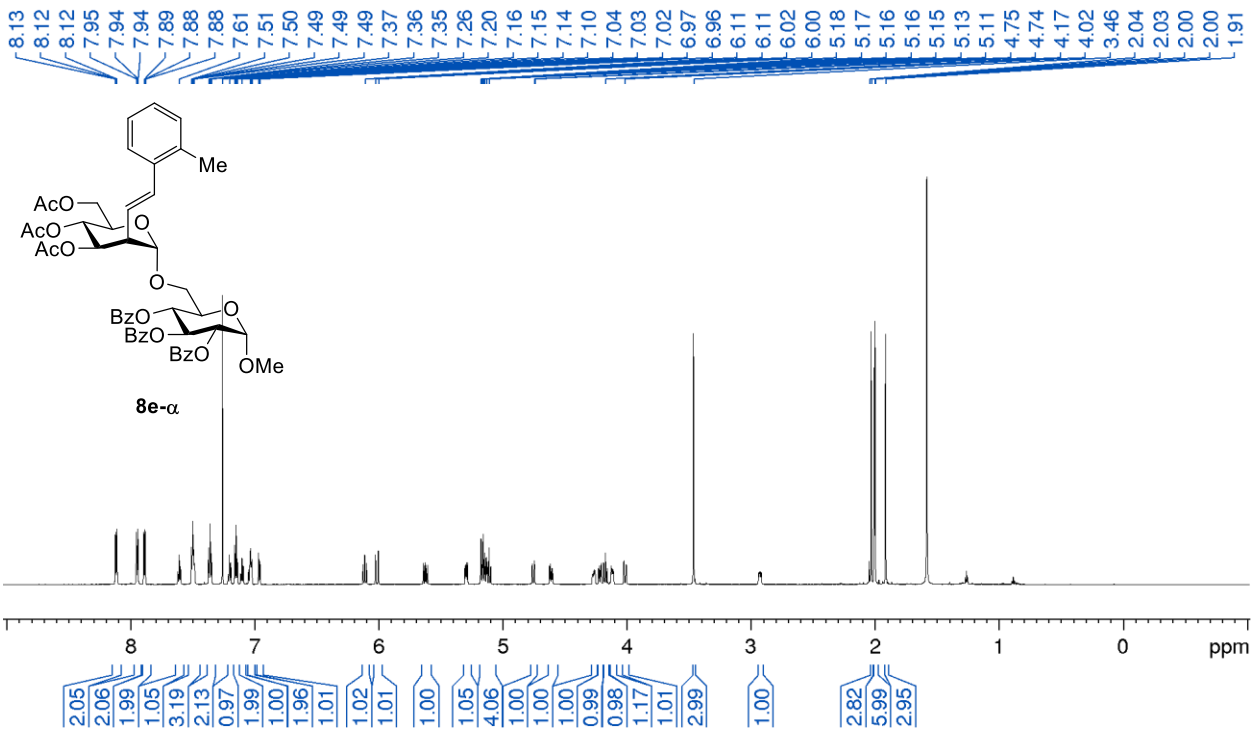
^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) of (8d)



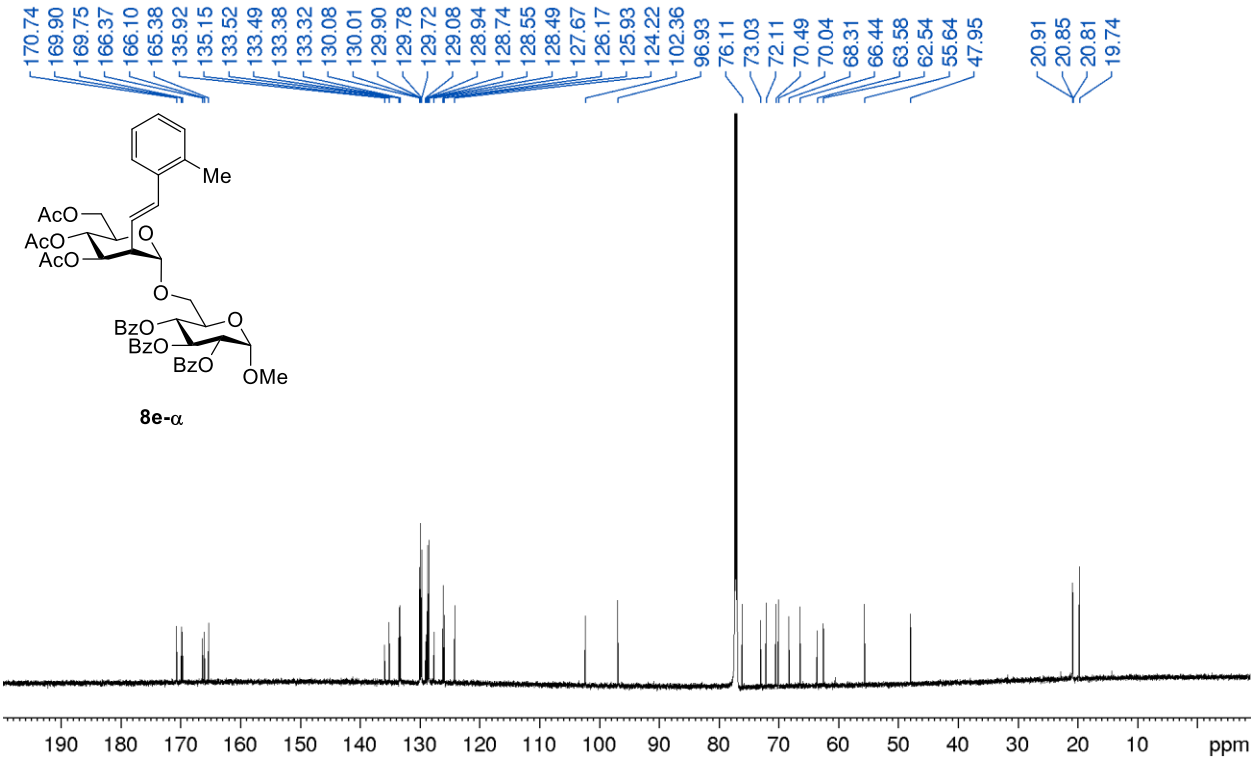
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (8d)



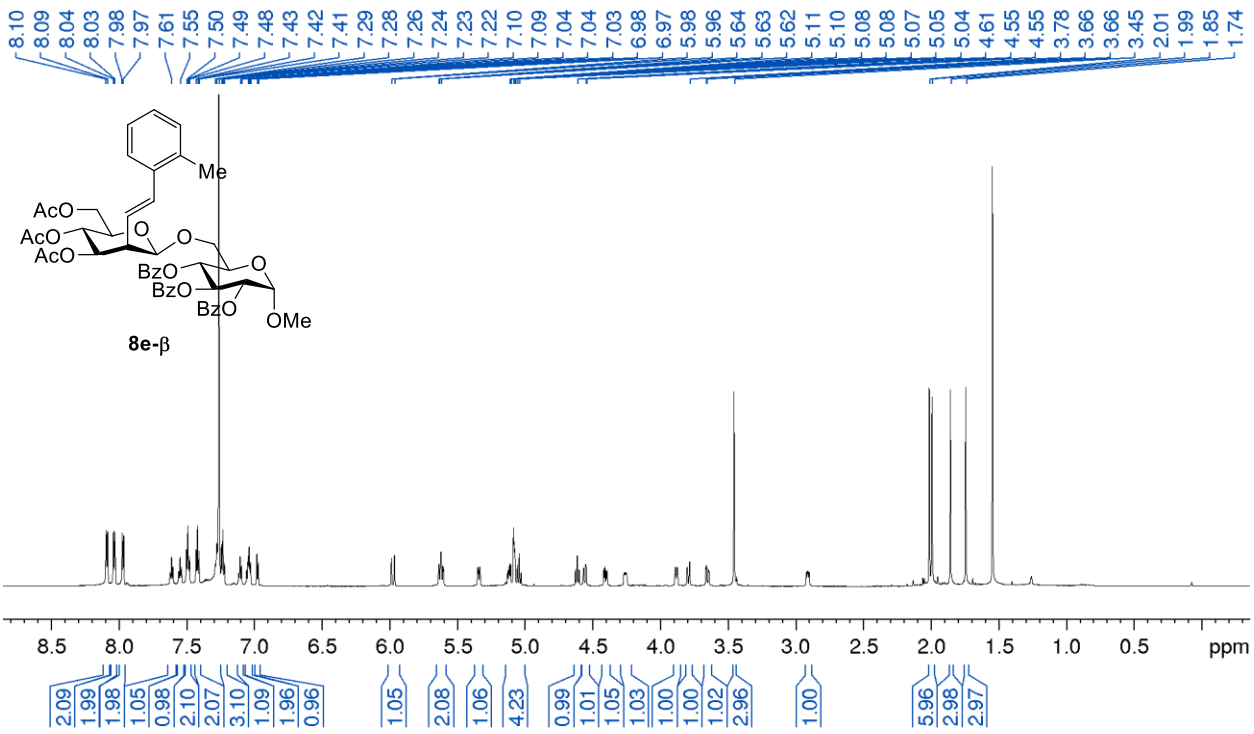
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (8e-α)



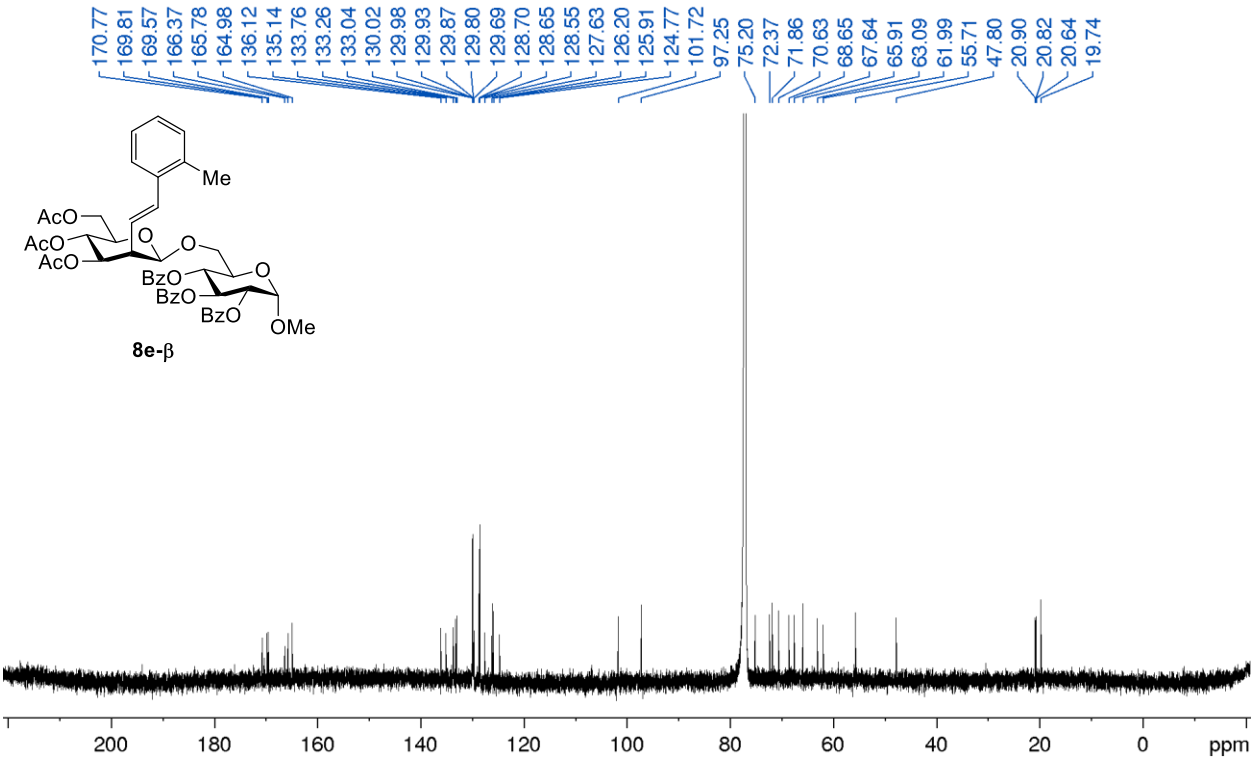
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (8e-α)



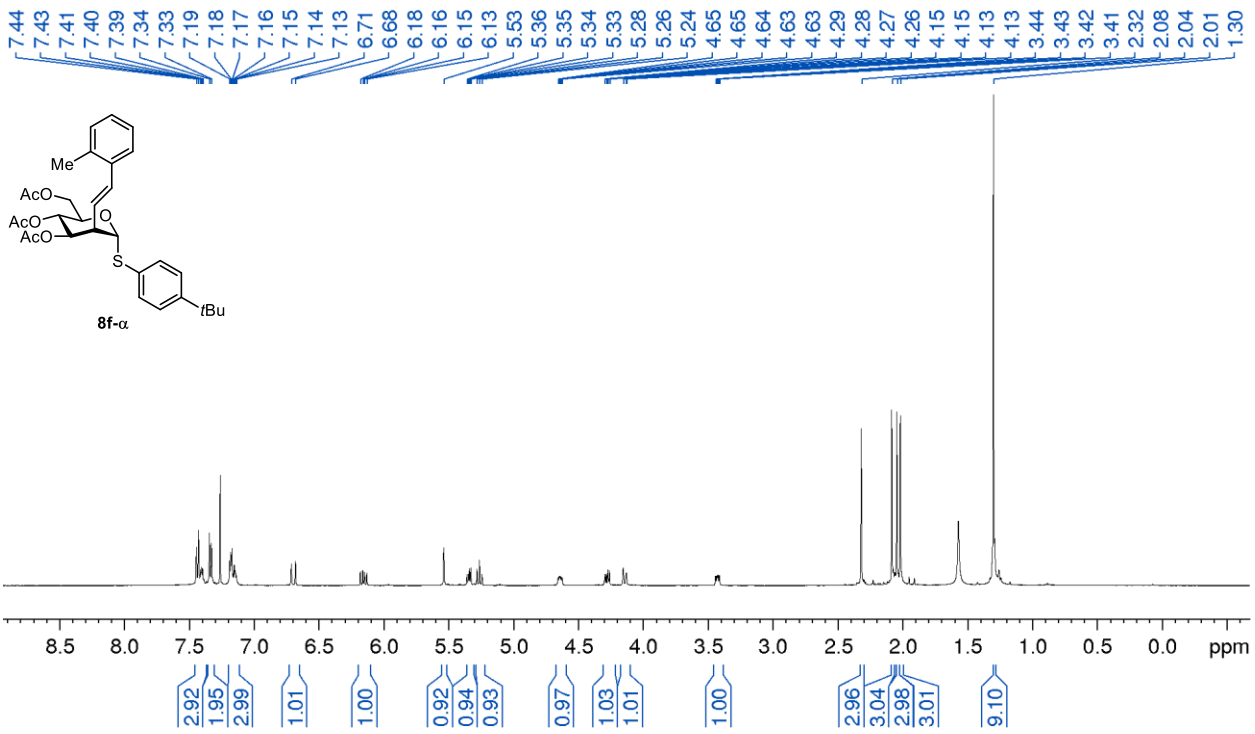
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (8e-β)



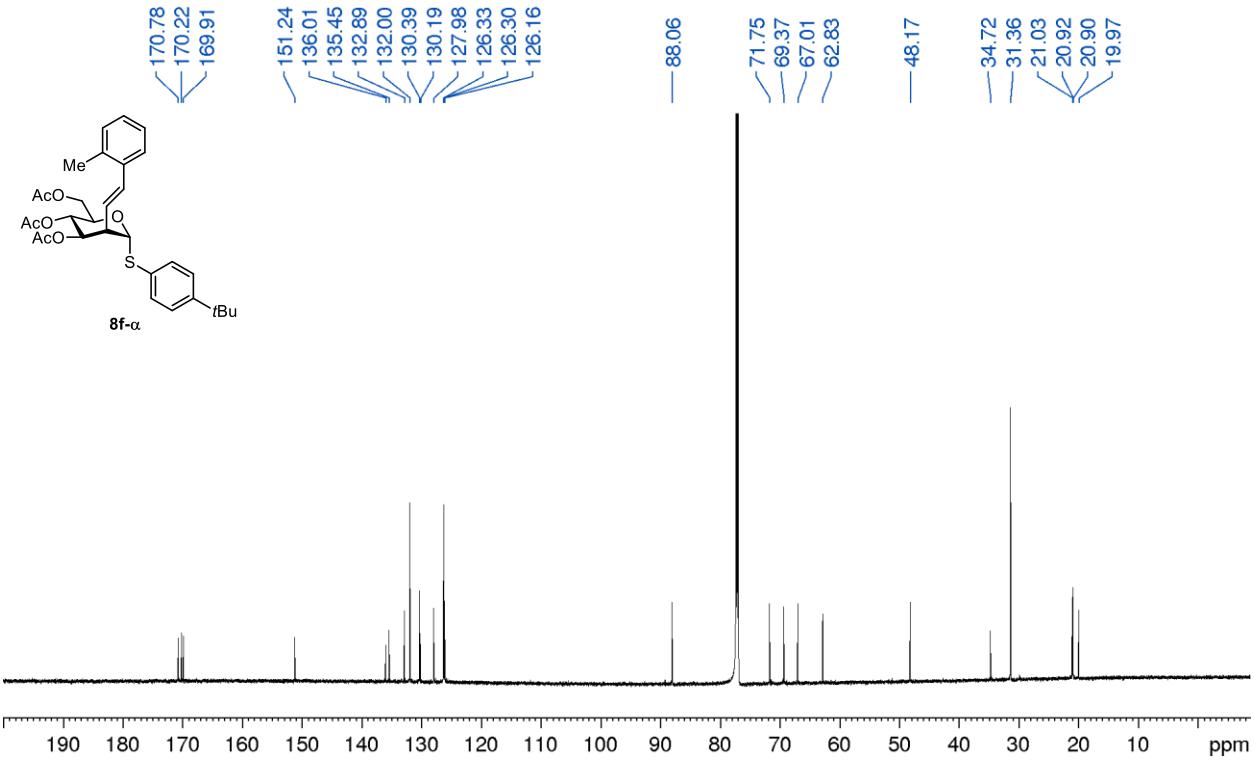
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (8e-β)



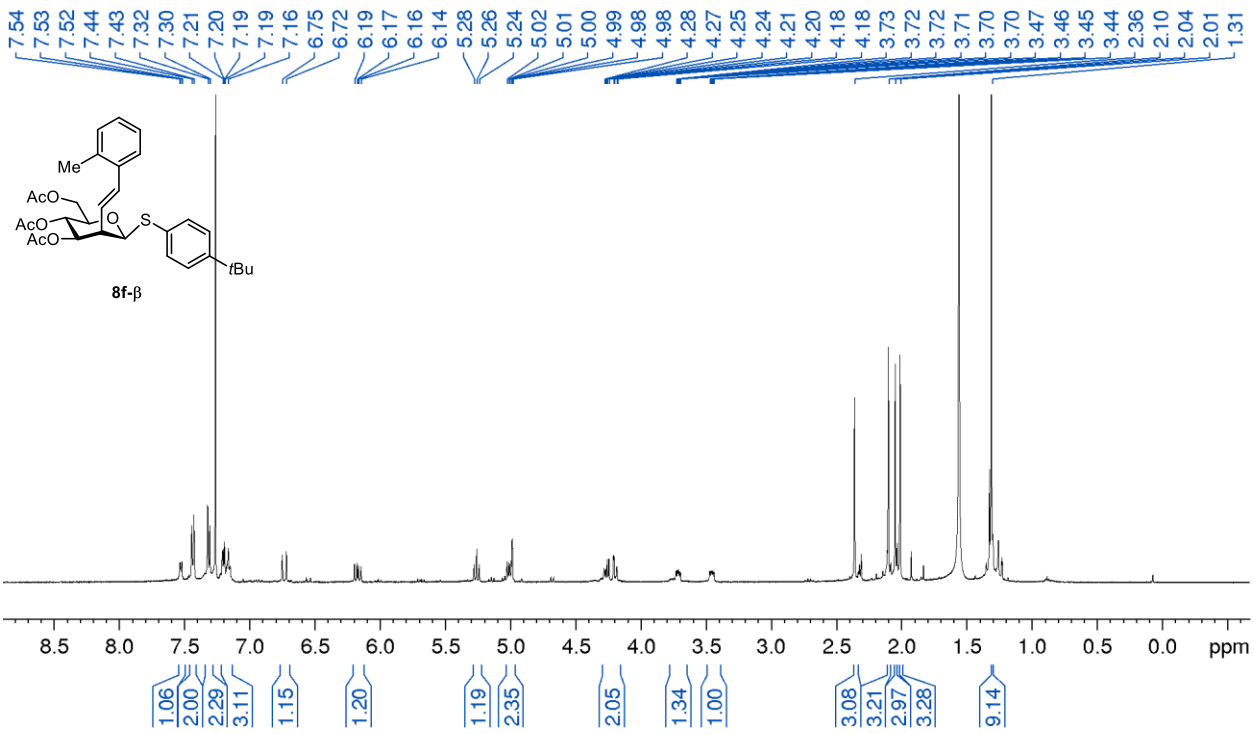
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (8f-α)



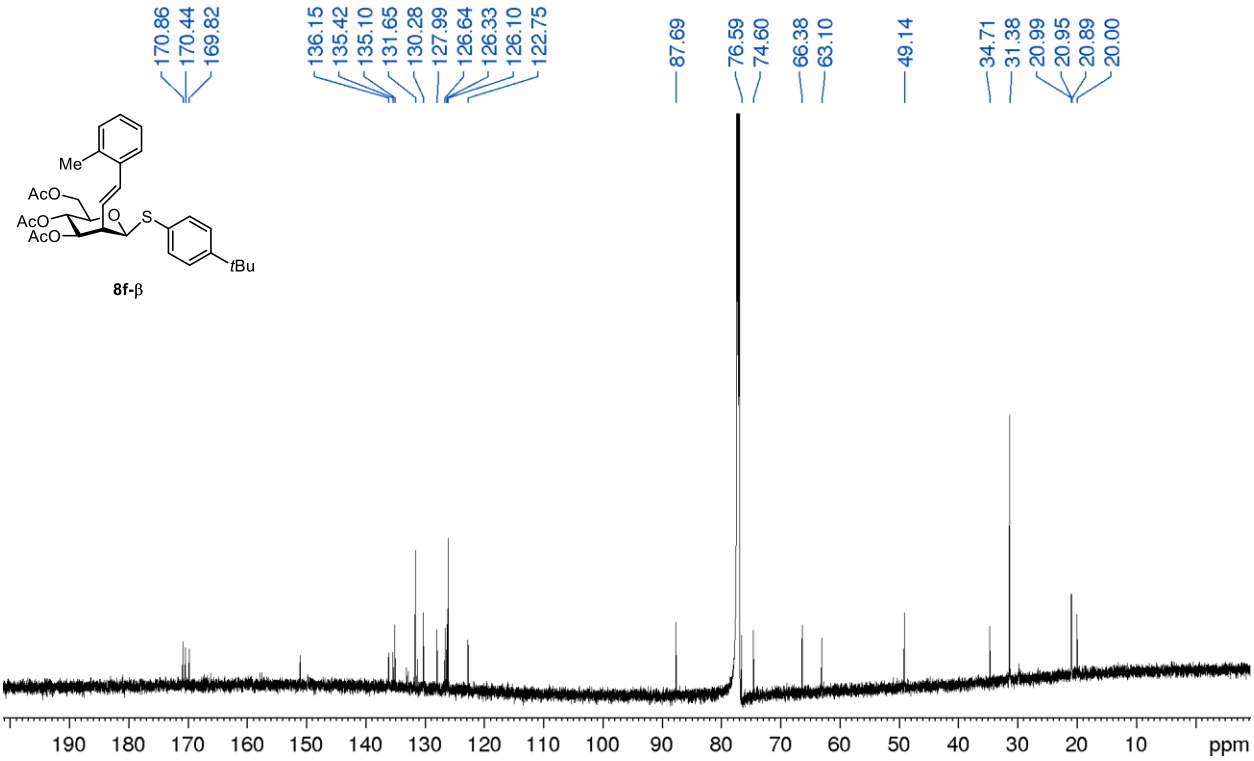
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (8f-α)



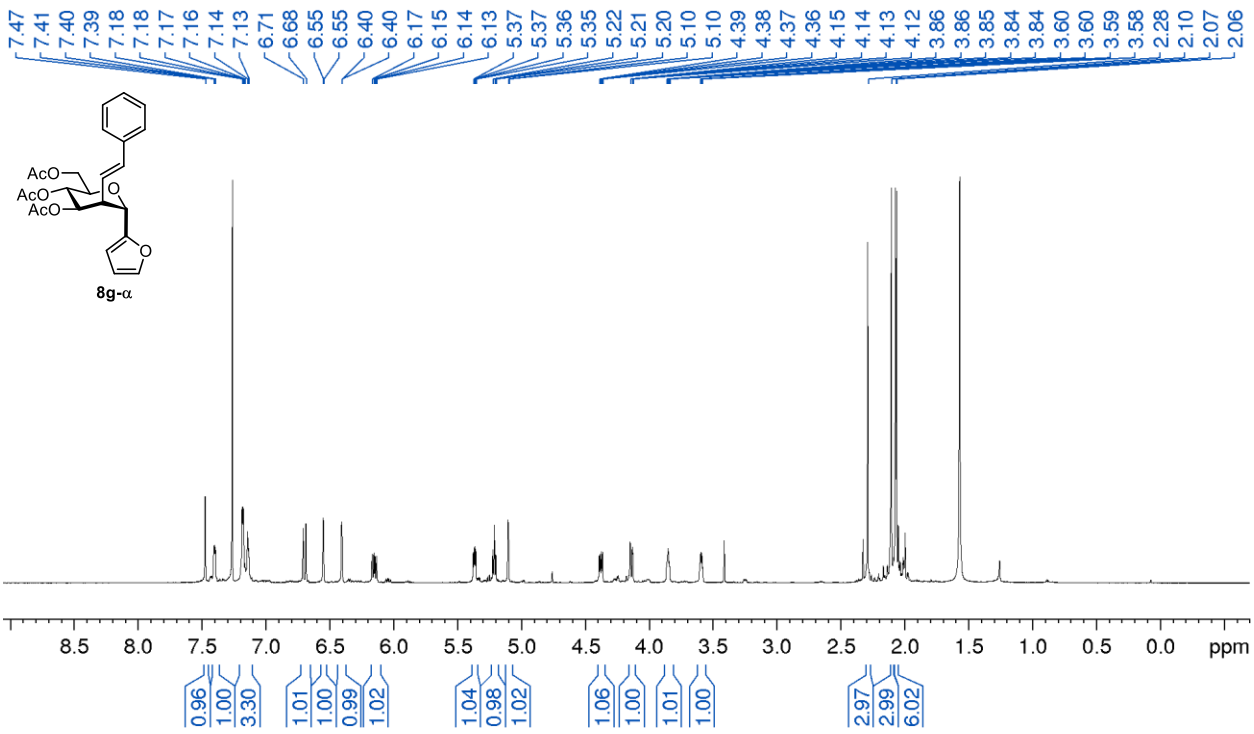
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of (8f-β)



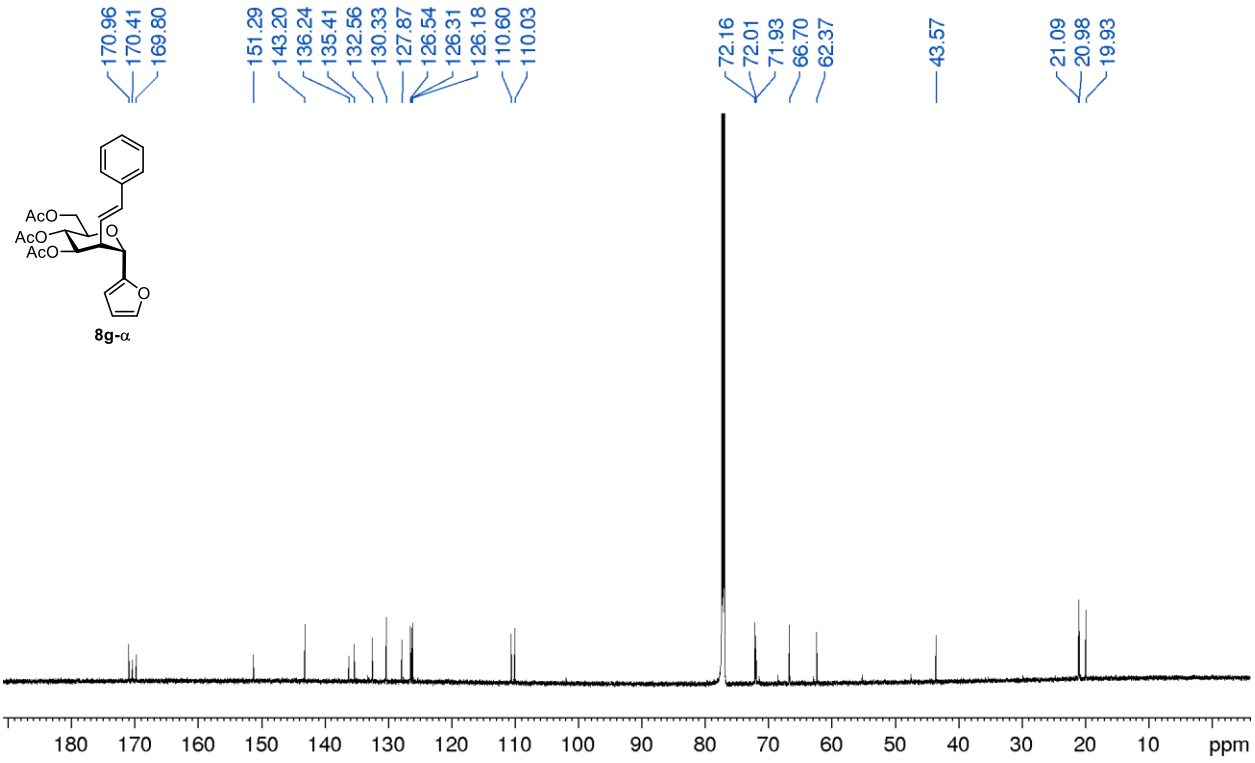
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (8f-β)



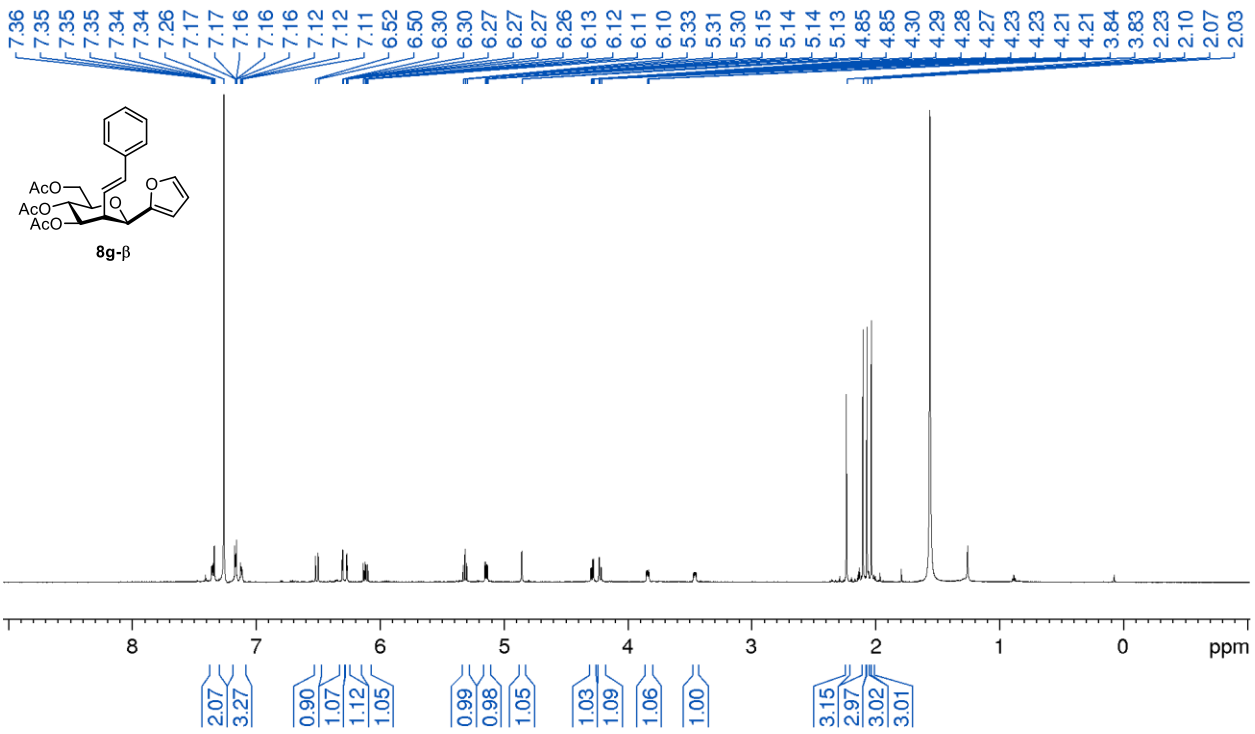
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (8g-α)



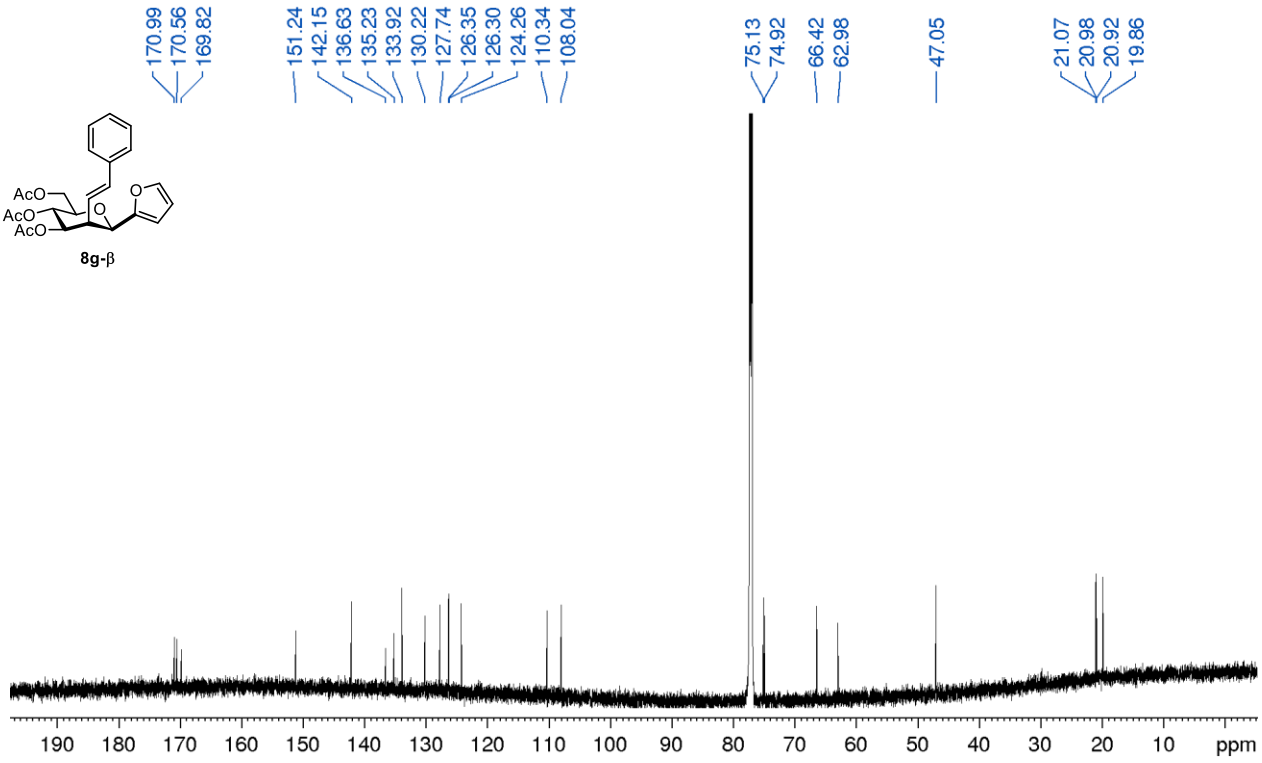
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (8g-α)



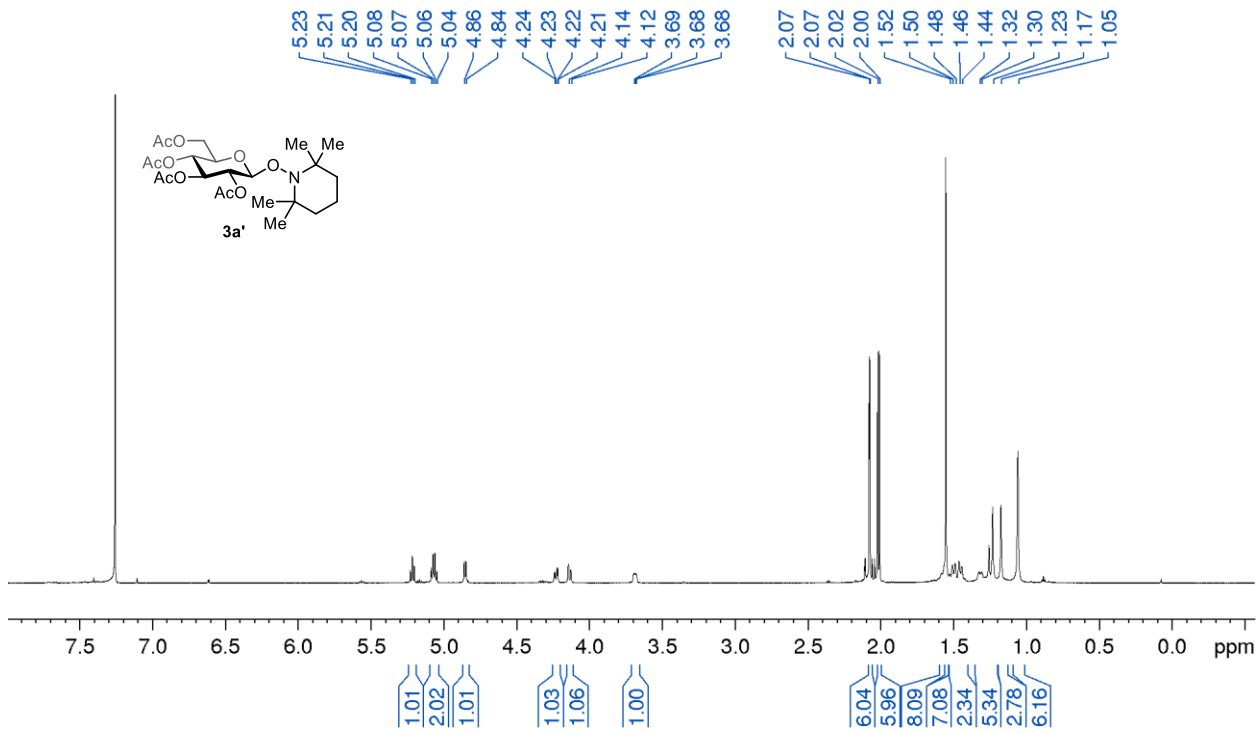
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (8g-β)



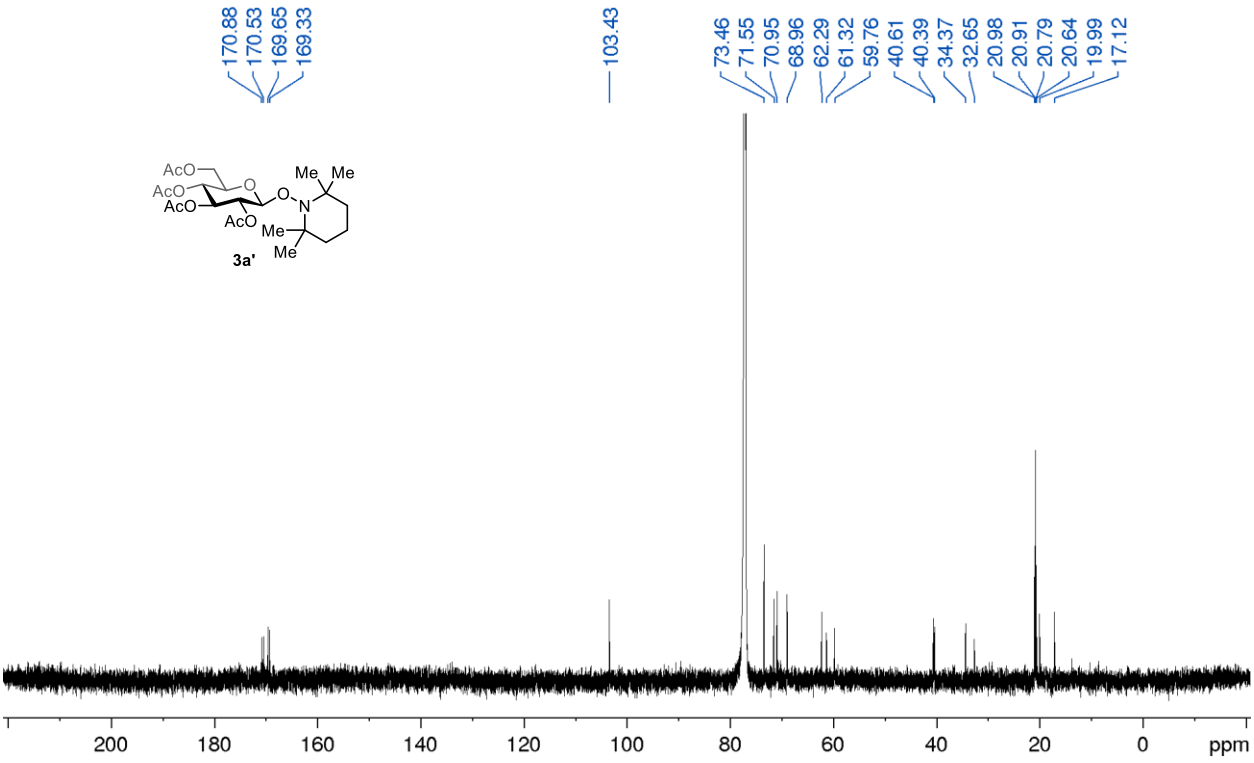
^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC) of (8g-β)



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



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



Cartesian Coordinates (Å) and Energies of the Optimized Structures

2a

B3LYP-D3 SCF energy:	-309.657298 a.u.
B3LYP-D3 enthalpy:	-309.515812 a.u.
B3LYP-D3 free energy:	-309.555289 a.u.
M06 SCF energy in solution:	-309.477372 a.u.
M06 enthalpy in solution:	-309.332672 a.u.
M06 free energy in solution:	-309.383170 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-1.361304000000	1.329996000000	-0.000002000000
C	0.009781000000	1.091916000000	-0.000004000000
C	0.515512000000	-0.221399000000	-0.000010000000
C	-0.407042000000	-1.281933000000	0.000001000000
C	-1.781284000000	-1.045760000000	0.000014000000
C	-2.265167000000	0.262783000000	0.000001000000
H	-1.728684000000	2.353006000000	-0.000015000000
H	0.694691000000	1.934824000000	-0.000017000000
H	-0.037458000000	-2.305120000000	0.000003000000
H	-2.472923000000	-1.884137000000	0.000017000000
H	-3.335165000000	0.452175000000	0.000003000000
C	1.954995000000	-0.530320000000	-0.000018000000
H	2.188389000000	-1.595494000000	-0.000042000000
C	2.976301000000	0.335621000000	0.000017000000
H	2.836229000000	1.413284000000	0.000056000000
H	4.004161000000	-0.013969000000	0.000011000000

3

B3LYP-D3 SCF energy:	-1191.026542 a.u.
B3LYP-D3 enthalpy:	-1190.568248 a.u.
B3LYP-D3 free energy:	-1190.654630 a.u.
M06 SCF energy in solution:	-1190.535655 a.u.
M06 enthalpy in solution:	-1190.066565 a.u.
M06 free energy in solution:	-1190.174911 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-1.279229000000	0.020511000000	1.586796000000
C	-0.842967000000	-1.225441000000	0.764842000000
C	-1.485126000000	-1.144155000000	-0.623220000000
O	-1.195837000000	0.035743000000	-1.306734000000
C	-1.476597000000	1.259399000000	-0.614132000000
C	-0.889909000000	2.374285000000	-1.464560000000
H	-1.216986000000	3.340258000000	-1.050804000000
O	0.523993000000	2.272087000000	-1.447097000000
C	1.158574000000	3.279899000000	-2.205155000000
H	2.236263000000	3.118336000000	-2.114209000000
H	0.877139000000	3.229130000000	-3.269441000000

H	0.915040000000	4.287512000000	-1.830008000000
H	-1.273157000000	2.282310000000	-2.493067000000
C	-0.924748000000	1.294498000000	0.824318000000
H	0.165176000000	1.389469000000	0.788881000000
O	-1.514780000000	2.441539000000	1.424492000000
C	-0.650697000000	3.154113000000	2.298990000000
H	-1.219428000000	4.014080000000	2.665025000000
H	0.242634000000	3.517228000000	1.767296000000
H	-0.334897000000	2.533891000000	3.144957000000
H	-2.565087000000	1.403108000000	-0.555955000000
H	-1.154819000000	-1.951095000000	-1.277219000000
O	-2.916461000000	-1.260498000000	-0.414554000000
C	-3.653561000000	-1.780960000000	-1.438010000000
O	-3.182652000000	-2.233418000000	-2.453880000000
C	-5.124254000000	-1.711182000000	-1.102547000000
H	-5.701972000000	-2.188184000000	-1.894856000000
H	-5.316381000000	-2.204026000000	-0.144180000000
H	-5.428641000000	-0.664212000000	-0.997995000000
H	-1.264283000000	-2.117324000000	1.244750000000
O	-0.634207000000	0.090434000000	2.851278000000
C	-1.122506000000	-0.827951000000	3.809421000000
H	-0.622869000000	-0.595234000000	4.753501000000
H	-2.211115000000	-0.731206000000	3.946615000000
H	-0.897197000000	-1.872308000000	3.543666000000
H	-2.370608000000	-0.005743000000	1.727110000000
C	1.476613000000	-0.892424000000	-0.227527000000
C	0.663546000000	-1.365250000000	0.730019000000
H	1.088776000000	-1.837972000000	1.613187000000
C	2.944928000000	-0.964962000000	-0.239227000000
C	3.686345000000	-1.862007000000	0.550354000000
C	3.648275000000	-0.086662000000	-1.082929000000
C	5.078322000000	-1.865067000000	0.510563000000
H	3.167308000000	-2.573488000000	1.186675000000
C	5.041552000000	-0.088206000000	-1.122681000000
H	3.083794000000	0.609050000000	-1.699691000000
C	5.763657000000	-0.977010000000	-0.324035000000
H	5.632469000000	-2.569294000000	1.126010000000
H	5.564209000000	0.603188000000	-1.778868000000
H	6.849887000000	-0.984710000000	-0.356156000000
H	1.040979000000	-0.348423000000	-1.060938000000

II

B3LYP-D3 SCF energy:	-881.886481 a.u.
B3LYP-D3 enthalpy:	-881.563622 a.u.
B3LYP-D3 free energy:	-881.634300 a.u.
M06 SCF energy in solution:	-881.578555 a.u.
M06 enthalpy in solution:	-881.247829 a.u.
M06 free energy in solution:	-881.336912 a.u.

Cartesian coordinates

ATOM	X	Y	Z

O	0.604318000000	-1.824143000000	-0.511287000000
O	3.206002000000	-1.113901000000	0.585324000000
O	1.771723000000	1.654591000000	-0.549131000000
O	-0.859628000000	1.930340000000	0.609574000000
O	-2.648291000000	-0.144268000000	-0.331386000000
O	-3.457604000000	-1.646794000000	1.160714000000
C	-0.748457000000	-1.642742000000	-0.441003000000
H	-1.272998000000	-2.572485000000	-0.248494000000
C	-1.298453000000	-0.375364000000	0.150631000000
H	-1.343252000000	-0.432243000000	1.247935000000
C	-0.482427000000	0.854600000000	-0.235684000000
H	-0.688600000000	1.095922000000	-1.288608000000
C	1.006657000000	0.548127000000	-0.085187000000
H	1.218541000000	0.337658000000	0.969122000000
C	1.383843000000	-0.687720000000	-0.913706000000
H	1.178486000000	-0.474679000000	-1.974164000000
C	-3.639934000000	-0.827458000000	0.287107000000
C	-4.984563000000	-0.418171000000	-0.266930000000
H	-5.154218000000	0.646879000000	-0.076957000000
H	-5.768221000000	-1.010346000000	0.206634000000
H	-5.004080000000	-0.564830000000	-1.351571000000
C	2.850255000000	-1.059833000000	-0.783622000000
H	3.012462000000	-2.034941000000	-1.269930000000
H	3.450573000000	-0.303186000000	-1.312447000000
C	4.538383000000	-1.539909000000	0.786208000000
H	4.716420000000	-1.540053000000	1.864679000000
H	4.702471000000	-2.556980000000	0.395848000000
H	5.261376000000	-0.862124000000	0.302914000000
C	2.593373000000	2.245268000000	0.450460000000
H	3.151534000000	3.049216000000	-0.037616000000
H	1.986922000000	2.668326000000	1.263236000000
H	3.295793000000	1.512319000000	0.869391000000
C	-0.984593000000	3.178816000000	-0.053994000000
H	-1.788286000000	3.152394000000	-0.806095000000
H	-1.243622000000	3.914733000000	0.712577000000
H	-0.047971000000	3.474147000000	-0.542583000000

III

B3LYP-D3 SCF energy:	-881.888056 a.u.
B3LYP-D3 enthalpy:	-881.566074 a.u.
B3LYP-D3 free energy:	-881.636778 a.u.
M06 SCF energy in solution:	-881.581808 a.u.
M06 enthalpy in solution:	-881.251907 a.u.
M06 free energy in solution:	-881.341213 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	0.475730000000	-1.696916000000	-0.208249000000
C	-0.702829000000	-1.459105000000	-1.088205000000
C	-1.500344000000	-0.216340000000	-0.920865000000
O	-0.715966000000	0.913927000000	-0.669961000000

C	0.252548000000	0.743948000000	0.373538000000
C	0.929718000000	2.085375000000	0.593198000000
H	1.520864000000	2.034525000000	1.521426000000
O	1.759986000000	2.388337000000	-0.512609000000
C	2.333320000000	3.676852000000	-0.426340000000
H	2.956341000000	3.811597000000	-1.314371000000
H	1.562198000000	4.463381000000	-0.406928000000
H	2.962209000000	3.785612000000	0.473036000000
H	0.150855000000	2.854072000000	0.718762000000
C	1.239303000000	-0.377575000000	0.003043000000
H	1.729763000000	-0.114174000000	-0.939847000000
O	2.186048000000	-0.535496000000	1.053982000000
C	3.515262000000	-0.175826000000	0.697903000000
H	4.120262000000	-0.275789000000	1.603551000000
H	3.566174000000	0.857150000000	0.331613000000
H	3.914936000000	-0.847174000000	-0.076223000000
H	-0.256999000000	0.471624000000	1.309843000000
H	-2.113408000000	0.025192000000	-1.789151000000
O	-2.404250000000	-0.434555000000	0.219193000000
C	-3.613834000000	0.189860000000	0.177905000000
O	-4.021865000000	0.831316000000	-0.762348000000
C	-4.365220000000	-0.048490000000	1.467223000000
H	-5.356869000000	0.400276000000	1.399691000000
H	-4.447490000000	-1.122558000000	1.661600000000
H	-3.812429000000	0.393545000000	2.303090000000
H	-1.061966000000	-2.260263000000	-1.723642000000
O	1.301278000000	-2.692572000000	-0.798266000000
C	1.963783000000	-3.536800000000	0.131985000000
H	2.555053000000	-4.243321000000	-0.457405000000
H	2.623548000000	-2.973616000000	0.801741000000
H	1.243766000000	-4.103220000000	0.744283000000
H	0.136720000000	-2.034413000000	0.792185000000

IV

B3LYP-D3 SCF energy:	-1191.608795 a.u.
B3LYP-D3 enthalpy:	-1191.139790 a.u.
B3LYP-D3 free energy:	-1191.227365 a.u.
M06 SCF energy in solution:	-1191.118629 a.u.
M06 enthalpy in solution:	-1190.638521 a.u.
M06 free energy in solution:	-1190.748098 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-0.629974000000	-0.731003000000	-1.170521000000
C	0.319542000000	0.066887000000	-0.253243000000
C	-0.398600000000	1.327070000000	0.228784000000
O	-1.598048000000	1.036052000000	0.883853000000
C	-2.546465000000	0.276041000000	0.121436000000
C	-3.725722000000	-0.006193000000	1.036367000000
H	-4.548842000000	-0.415940000000	0.430687000000
O	-3.329106000000	-0.928184000000	2.034957000000

C	-4.366197000000	-1.227794000000	2.944160000000
H	-3.967017000000	-1.949065000000	3.662401000000
H	-4.703495000000	-0.330878000000	3.488761000000
H	-5.239086000000	-1.672512000000	2.437513000000
H	-4.059927000000	0.940767000000	1.489469000000
C	-1.946962000000	-1.020671000000	-0.456089000000
H	-1.771311000000	-1.727390000000	0.362486000000
O	-2.921291000000	-1.531661000000	-1.357800000000
C	-3.042726000000	-2.946822000000	-1.343455000000
H	-3.819158000000	-3.200789000000	-2.071144000000
H	-3.352077000000	-3.309280000000	-0.350745000000
H	-2.101846000000	-3.433301000000	-1.624977000000
H	-2.905444000000	0.881831000000	-0.722963000000
H	0.197165000000	1.897758000000	0.941878000000
O	-0.641634000000	2.150432000000	-0.938076000000
C	-0.724769000000	3.498226000000	-0.743291000000
O	-0.527119000000	4.046279000000	0.314647000000
C	-1.084881000000	4.185631000000	-2.038653000000
H	-1.102034000000	5.265189000000	-1.886124000000
H	-0.359565000000	3.925211000000	-2.816195000000
H	-2.066955000000	3.840747000000	-2.379464000000
H	1.196177000000	0.378741000000	-0.831311000000
O	-0.058386000000	-1.973717000000	-1.575724000000
C	0.767159000000	-1.879210000000	-2.723599000000
H	1.133161000000	-2.887927000000	-2.933618000000
H	0.202468000000	-1.513626000000	-3.594848000000
H	1.631683000000	-1.217731000000	-2.564355000000
H	-0.862122000000	-0.128147000000	-2.060433000000
C	2.027942000000	-0.192223000000	1.607395000000
C	0.796287000000	-0.762472000000	0.975079000000
H	0.968980000000	-1.788576000000	0.631642000000
H	-0.016571000000	-0.801617000000	1.707282000000
C	3.334471000000	-0.337770000000	1.080878000000
C	3.613593000000	-1.131134000000	-0.071590000000
C	4.438044000000	0.323351000000	1.695854000000
C	4.904576000000	-1.242886000000	-0.568282000000
H	2.804363000000	-1.664226000000	-0.559953000000
C	5.723245000000	0.204306000000	1.190885000000
H	4.254519000000	0.934293000000	2.576734000000
C	5.970072000000	-0.577687000000	0.052887000000
H	5.088945000000	-1.855790000000	-1.447289000000
H	6.544167000000	0.721910000000	1.680693000000
H	6.978145000000	-0.668904000000	-0.341440000000
H	1.908542000000	0.431755000000	2.490439000000

IV^{+}

B3LYP-D3 SCF energy:	-1191.386689 a.u.
B3LYP-D3 enthalpy:	-1190.915292 a.u.
B3LYP-D3 free energy:	-1191.000707 a.u.
M06 SCF energy in solution:	-1190.920331 a.u.
M06 enthalpy in solution:	-1190.437888 a.u.

M06 free energy in solution: -1190.545944 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	0.622528000000	-0.486492000000	1.052085000000
C	-0.254458000000	0.264484000000	0.038814000000
C	0.457102000000	1.518077000000	-0.493277000000
O	1.727398000000	1.247483000000	-0.962249000000
C	2.618130000000	0.607136000000	-0.020580000000
C	3.948784000000	0.423122000000	-0.727807000000
H	4.710806000000	0.150153000000	0.018884000000
O	3.812770000000	-0.585898000000	-1.709661000000
C	4.988889000000	-0.758776000000	-2.485359000000
H	4.785717000000	-1.560662000000	-3.198860000000
H	5.244909000000	0.158499000000	-3.036323000000
H	5.848259000000	-1.043250000000	-1.858665000000
H	4.241819000000	1.381925000000	-1.182320000000
C	2.021747000000	-0.723456000000	0.481766000000
H	1.950485000000	-1.419774000000	-0.361640000000
O	2.864543000000	-1.242982000000	1.497614000000
C	3.577041000000	-2.423728000000	1.128254000000
H	4.253849000000	-2.648855000000	1.955395000000
H	4.153460000000	-2.272245000000	0.208014000000
H	2.890159000000	-3.269701000000	0.982463000000
H	2.769500000000	1.271377000000	0.839703000000
H	-0.097880000000	1.959161000000	-1.325403000000
O	0.536924000000	2.503451000000	0.563872000000
C	-0.602673000000	3.217447000000	0.786792000000
O	-1.647074000000	2.972987000000	0.217508000000
C	-0.371979000000	4.308251000000	1.796075000000
H	-1.320901000000	4.786457000000	2.039353000000
H	0.091946000000	3.898698000000	2.698626000000
H	0.319989000000	5.049032000000	1.381102000000
H	-1.176596000000	0.568772000000	0.535332000000
O	-0.051294000000	-1.697060000000	1.378495000000
C	0.170775000000	-2.178973000000	2.708576000000
H	-0.381663000000	-3.117838000000	2.790557000000
H	1.232860000000	-2.351372000000	2.895659000000
H	-0.215203000000	-1.465406000000	3.450540000000
H	0.712499000000	0.147249000000	1.947005000000
C	-1.940566000000	-0.322154000000	-1.695611000000
C	-0.611310000000	-0.677538000000	-1.184224000000
H	-0.599181000000	-1.703630000000	-0.804809000000
H	0.156902000000	-0.562827000000	-1.952525000000
C	-3.163059000000	-0.661938000000	-1.113068000000
C	-3.240203000000	-1.427261000000	0.097260000000
C	-4.370065000000	-0.213725000000	-1.738596000000
C	-4.474885000000	-1.726659000000	0.635357000000
H	-2.327042000000	-1.741056000000	0.596633000000
C	-5.598122000000	-0.528767000000	-1.189824000000
H	-4.307816000000	0.373553000000	-2.650455000000

C	-5.647518000000	-1.284117000000	-0.006981000000
H	-4.547458000000	-2.299658000000	1.553825000000
H	-6.515885000000	-0.194897000000	-1.661929000000
H	-6.613546000000	-1.528852000000	0.426163000000
H	-1.987073000000	0.301711000000	-2.588871000000

V

B3LYP-D3 SCF energy:	-6154.532662 a.u.
B3LYP-D3 enthalpy:	-6153.418440 a.u.
B3LYP-D3 free energy:	-6153.593743 a.u.
M06 SCF energy in solution:	-6155.742011 a.u.
M06 enthalpy in solution:	-6154.598729 a.u.
M06 free energy in solution:	-6154.819241 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	5.111516000000	-0.941113000000	-1.081271000000
C	4.165440000000	-0.851284000000	0.124708000000
C	5.408724000000	1.585192000000	-0.808995000000
C	5.138993000000	0.412187000000	-1.786005000000
H	6.124217000000	-1.181941000000	-0.730670000000
H	6.496391000000	1.656588000000	-0.675128000000
H	4.166645000000	0.561051000000	-2.261493000000
O	4.784795000000	1.470304000000	0.481298000000
O	6.169003000000	0.459609000000	-2.776219000000
O	4.658665000000	-1.961169000000	-1.972172000000
C	4.875971000000	2.887744000000	-1.395098000000
H	5.396713000000	3.085570000000	-2.346224000000
H	5.079295000000	3.722275000000	-0.705672000000
O	3.487480000000	2.722292000000	-1.597444000000
C	2.868236000000	3.712569000000	-2.389811000000
H	1.845382000000	3.366150000000	-2.554930000000
H	2.863273000000	4.693641000000	-1.886147000000
H	3.373743000000	3.824560000000	-3.363287000000
C	5.675924000000	0.520185000000	-4.105687000000
H	5.064218000000	-0.358246000000	-4.352512000000
H	6.548319000000	0.550392000000	-4.765386000000
H	5.069689000000	1.423425000000	-4.273906000000
C	5.701941000000	-2.722991000000	-2.554097000000
H	6.259181000000	-3.292678000000	-1.792358000000
H	5.230956000000	-3.429067000000	-3.244711000000
H	6.410792000000	-2.092778000000	-3.105277000000
C	4.718923000000	0.218500000000	1.067967000000
C	2.728289000000	-0.490716000000	-0.324006000000
H	2.708521000000	0.504459000000	-0.763409000000
H	2.454613000000	-1.173681000000	-1.126794000000
C	1.716740000000	-0.581530000000	0.792207000000
C	1.544022000000	0.510639000000	1.748094000000
C	1.201218000000	0.246041000000	3.105006000000
C	1.592366000000	1.868028000000	1.322129000000
C	0.920128000000	1.276827000000	3.985597000000

H	1.199265000000	-0.785500000000	3.444925000000
C	1.289598000000	2.897593000000	2.222946000000
H	1.928433000000	2.111661000000	0.320277000000
C	0.950667000000	2.610524000000	3.540109000000
H	0.673985000000	1.054066000000	5.020605000000
H	1.309888000000	3.925719000000	1.877224000000
H	0.714640000000	3.417727000000	4.228091000000
H	4.163406000000	-1.811613000000	0.651755000000
C	-2.108019000000	-3.801600000000	-1.717879000000
C	-2.268785000000	-2.584021000000	-1.038151000000
C	-3.257685000000	-1.716516000000	-1.511228000000
C	-4.046591000000	-1.972834000000	-2.638636000000
C	-3.829243000000	-3.179698000000	-3.307349000000
C	-2.878375000000	-4.091094000000	-2.842478000000
C	-4.559745000000	0.444088000000	-2.683446000000
C	-3.757205000000	0.562638000000	-1.548906000000
C	-3.210485000000	1.764718000000	-1.100259000000
C	-3.515442000000	2.924309000000	-1.821800000000
C	-4.313248000000	2.845395000000	-2.964360000000
C	-4.824026000000	1.618554000000	-3.395527000000
H	-1.364697000000	-4.514275000000	-1.380676000000
H	-4.408098000000	-3.422355000000	-4.192005000000
H	-2.733017000000	-5.032221000000	-3.364945000000
H	-3.110150000000	3.879531000000	-1.506564000000
H	-4.535360000000	3.747140000000	-3.527791000000
H	-5.435527000000	1.584881000000	-4.290949000000
C	-5.125462000000	-0.944025000000	-3.000442000000
O	-3.456879000000	-0.556491000000	-0.797163000000
P	-2.091394000000	1.652535000000	0.348825000000
P	-1.194478000000	-2.057999000000	0.371677000000
C	-1.513340000000	3.390110000000	0.545909000000
C	-1.884132000000	4.192521000000	1.632260000000
C	-0.610905000000	3.894166000000	-0.407830000000
C	-1.358833000000	5.481082000000	1.766897000000
H	-2.575720000000	3.813952000000	2.377948000000
C	-0.101151000000	5.184402000000	-0.275116000000
H	-0.299680000000	3.259426000000	-1.234107000000
C	-0.469342000000	5.980954000000	0.814872000000
H	-1.648432000000	6.092675000000	2.617600000000
H	0.595904000000	5.562439000000	-1.018312000000
H	-0.062881000000	6.983487000000	0.921124000000
C	-3.245070000000	1.405812000000	1.758927000000
C	-2.714706000000	0.898683000000	2.954066000000
C	-4.613103000000	1.705413000000	1.687985000000
C	-3.537472000000	0.706126000000	4.063302000000
H	-1.659664000000	0.646392000000	3.008167000000
C	-5.437000000000	1.497298000000	2.795382000000
H	-5.034261000000	2.097850000000	0.766978000000
C	-4.900376000000	0.999842000000	3.985125000000
H	-3.116896000000	0.301287000000	4.978693000000
H	-6.497728000000	1.725400000000	2.728486000000

H	-5.543454000000	0.835424000000	4.845855000000
C	0.096763000000	-3.372811000000	0.320119000000
C	0.282049000000	-4.360137000000	1.294997000000
C	1.002801000000	-3.293168000000	-0.753438000000
C	1.373972000000	-5.230990000000	1.213396000000
H	-0.414863000000	-4.452656000000	2.121383000000
C	2.094393000000	-4.154248000000	-0.827429000000
H	0.862490000000	-2.528582000000	-1.513200000000
C	2.285978000000	-5.123394000000	0.163085000000
H	1.511745000000	-5.989089000000	1.979994000000
H	2.811662000000	-4.035438000000	-1.633659000000
H	3.144422000000	-5.788171000000	0.116841000000
C	-2.203380000000	-2.414328000000	1.868474000000
C	-1.574807000000	-2.344051000000	3.124095000000
C	-3.582480000000	-2.657286000000	1.817636000000
C	-2.298873000000	-2.550474000000	4.295879000000
H	-0.512947000000	-2.127534000000	3.180383000000
C	-4.312309000000	-2.833928000000	2.995062000000
H	-4.091614000000	-2.708124000000	0.861246000000
C	-3.674320000000	-2.791144000000	4.234840000000
H	-1.792176000000	-2.508773000000	5.256691000000
H	-5.383111000000	-3.010360000000	2.939280000000
H	-4.244682000000	-2.935904000000	5.148334000000
Pd	-0.232675000000	0.116765000000	0.278969000000
Br	0.259316000000	0.832013000000	-2.294798000000
O	6.072212000000	-0.142543000000	1.501080000000
C	6.166981000000	-0.995889000000	2.542859000000
C	7.615437000000	-1.239208000000	2.902011000000
O	5.213472000000	-1.494456000000	3.104599000000
H	8.148826000000	-1.653722000000	2.039979000000
H	8.100299000000	-0.292275000000	3.160994000000
H	7.670975000000	-1.931069000000	3.743292000000
H	4.108211000000	0.326672000000	1.963137000000
H	1.695603000000	-1.566147000000	1.260489000000
C	-6.350178000000	-1.186845000000	-2.072899000000
H	-7.133449000000	-0.448182000000	-2.278412000000
H	-6.759615000000	-2.189990000000	-2.239054000000
H	-6.065547000000	-1.100117000000	-1.019413000000
C	-5.572660000000	-1.065304000000	-4.464518000000
H	-6.002090000000	-2.052918000000	-4.659001000000
H	-6.354492000000	-0.333751000000	-4.690510000000
H	-4.736430000000	-0.905852000000	-5.152926000000

VI

B3LYP-D3 SCF energy:	-3763.372711 a.u.
B3LYP-D3 enthalpy:	-3762.898155 a.u.
B3LYP-D3 free energy:	-3762.988090 a.u.
M06 SCF energy in solution:	-3765.191157 a.u.
M06 enthalpy in solution:	-3764.705105 a.u.
M06 free energy in solution:	-3764.817901 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	1.093367000000	0.784195000000	1.233918000000
C	0.162397000000	0.572611000000	0.018419000000
C	0.908963000000	0.937204000000	-1.268067000000
O	2.120786000000	0.280544000000	-1.407959000000
C	3.044582000000	0.435345000000	-0.317307000000
C	4.260371000000	-0.415350000000	-0.641467000000
H	5.058262000000	-0.168798000000	0.075634000000
O	3.907633000000	-1.782577000000	-0.553474000000
C	4.984141000000	-2.645297000000	-0.852491000000
H	4.614795000000	-3.668941000000	-0.748170000000
H	5.349205000000	-2.500573000000	-1.882391000000
H	5.831115000000	-2.497307000000	-0.161886000000
H	4.610622000000	-0.165580000000	-1.656001000000
C	2.417129000000	0.051151000000	1.033323000000
H	2.239918000000	-1.030554000000	1.045895000000
O	3.369632000000	0.419655000000	2.021093000000
C	3.458102000000	-0.483458000000	3.114801000000
H	4.231774000000	-0.090155000000	3.780698000000
H	3.755435000000	-1.487865000000	2.775870000000
H	2.507669000000	-0.552495000000	3.655439000000
H	3.364471000000	1.484964000000	-0.260640000000
H	0.321789000000	0.691286000000	-2.154757000000
O	1.170029000000	2.375941000000	-1.294300000000
C	0.165205000000	3.164678000000	-1.734050000000
O	-0.924839000000	2.747549000000	-2.070308000000
C	0.585677000000	4.614186000000	-1.744191000000
H	-0.240583000000	5.230573000000	-2.099589000000
H	0.878106000000	4.923496000000	-0.735294000000
H	1.458561000000	4.744778000000	-2.391888000000
H	-0.682686000000	1.260384000000	0.107045000000
O	0.518902000000	0.316006000000	2.445611000000
C	-0.551784000000	1.111356000000	2.932632000000
H	-0.814799000000	0.711827000000	3.915413000000
H	-0.247831000000	2.164107000000	3.043773000000
H	-1.438610000000	1.061779000000	2.287200000000
H	1.317667000000	1.859182000000	1.326548000000
C	-0.366132000000	-0.875293000000	-0.076302000000
H	-0.473597000000	-1.288183000000	0.930321000000
H	0.356106000000	-1.497911000000	-0.613357000000
C	-2.830238000000	-0.268505000000	0.004975000000
C	-3.310485000000	-0.833066000000	1.195286000000
C	-3.309796000000	0.983749000000	-0.398478000000
C	-4.249858000000	-0.155892000000	1.968916000000
H	-2.955960000000	-1.814600000000	1.496380000000
C	-4.247266000000	1.665337000000	0.382547000000
H	-2.923492000000	1.442072000000	-1.304547000000
C	-4.719753000000	1.098494000000	1.566039000000
H	-4.618342000000	-0.606971000000	2.886431000000
H	-4.606275000000	2.639157000000	0.060581000000

H	-5.452583000000	1.626055000000	2.170758000000
C	-1.725669000000	-0.923462000000	-0.785051000000
Br	-2.162513000000	-2.849993000000	-1.162670000000
H	-1.663626000000	-0.484813000000	-1.782033000000

VII

B3LYP-D3 SCF energy:	-1191.607511 a.u.
B3LYP-D3 enthalpy:	-1191.138600 a.u.
B3LYP-D3 free energy:	-1191.225205 a.u.
M06 SCF energy in solution:	-1191.118302 a.u.
M06 enthalpy in solution:	-1190.638281 a.u.
M06 free energy in solution:	-1190.747229 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-1.382905000000	1.346037000000	0.591966000000
C	-0.234903000000	1.043873000000	-0.389116000000
C	0.045102000000	-0.461384000000	-0.431153000000
O	-1.104154000000	-1.206306000000	-0.700512000000
C	-2.169723000000	-1.025151000000	0.237828000000
C	-3.309355000000	-1.935577000000	-0.186444000000
H	-4.058200000000	-1.955643000000	0.620019000000
O	-3.878969000000	-1.449263000000	-1.387509000000
C	-4.946682000000	-2.249928000000	-1.845535000000
H	-5.322320000000	-1.792409000000	-2.764961000000
H	-4.619823000000	-3.278972000000	-2.067354000000
H	-5.766701000000	-2.299752000000	-1.109502000000
H	-2.913949000000	-2.954474000000	-0.326041000000
C	-2.600156000000	0.448616000000	0.322148000000
H	-3.073057000000	0.712319000000	-0.632652000000
O	-3.542059000000	0.509820000000	1.384414000000
C	-4.521112000000	1.529504000000	1.267617000000
H	-5.237848000000	1.367654000000	2.078068000000
H	-5.054485000000	1.462202000000	0.306184000000
H	-4.080963000000	2.528190000000	1.367895000000
H	-1.840018000000	-1.341781000000	1.237827000000
H	0.758365000000	-0.720416000000	-1.213549000000
O	0.615506000000	-0.832114000000	0.846505000000
C	1.380541000000	-1.965765000000	0.864367000000
O	1.623242000000	-2.632591000000	-0.111405000000
C	1.901191000000	-2.229263000000	2.256226000000
H	2.164820000000	-3.284020000000	2.348884000000
H	2.805043000000	-1.628485000000	2.405131000000
H	1.169247000000	-1.943908000000	3.015878000000
H	-0.564515000000	1.285313000000	-1.408367000000
O	-1.714387000000	2.737624000000	0.651498000000
C	-2.101995000000	3.361890000000	-0.561788000000
H	-2.402742000000	4.378312000000	-0.294398000000
H	-1.277609000000	3.424058000000	-1.286530000000
H	-2.953017000000	2.862818000000	-1.045113000000
H	-1.043376000000	1.122489000000	1.609339000000

C	2.170645000000	1.593867000000	-0.973111000000
C	1.025496000000	1.877216000000	-0.054593000000
H	1.289109000000	1.691047000000	0.989731000000
H	0.744177000000	2.936917000000	-0.113965000000
C	3.382755000000	0.945838000000	-0.639179000000
C	3.721381000000	0.546801000000	0.688592000000
C	4.339383000000	0.662186000000	-1.660101000000
C	4.921615000000	-0.092706000000	0.961355000000
H	3.028373000000	0.744668000000	1.499044000000
C	5.533461000000	0.019624000000	-1.376083000000
H	4.111321000000	0.954502000000	-2.682511000000
C	5.838049000000	-0.366605000000	-0.063039000000
H	5.153679000000	-0.381308000000	1.983949000000
H	6.236611000000	-0.187656000000	-2.178609000000
H	6.774028000000	-0.871144000000	0.158174000000
H	2.023695000000	1.857671000000	-2.020238000000

LPd(I)Br

B3LYP-D3 SCF energy:	-4962.880777 a.u.
B3LYP-D3 enthalpy:	-4962.239963 a.u.
B3LYP-D3 free energy:	-4962.356307 a.u.
M06 SCF energy in solution:	-4964.580791 a.u.
M06 enthalpy in solution:	-4963.922257 a.u.
M06 free energy in solution:	-4964.069362 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-3.323416000000	1.777532000000	-1.292650000000
C	-2.139371000000	1.391704000000	-0.646186000000
C	-1.045988000000	2.257843000000	-0.749216000000
C	-1.055117000000	3.450200000000	-1.478883000000
C	-2.249339000000	3.792289000000	-2.119555000000
C	-3.373655000000	2.968541000000	-2.017116000000
C	1.406161000000	3.294086000000	-1.537028000000
C	1.280206000000	2.118588000000	-0.795113000000
C	2.265559000000	1.130467000000	-0.716941000000
C	3.461286000000	1.355345000000	-1.412204000000
C	3.623704000000	2.520720000000	-2.163646000000
C	2.606446000000	3.477162000000	-2.232025000000
H	-4.196460000000	1.136116000000	-1.249471000000
H	-2.310847000000	4.703373000000	-2.705068000000
H	-4.294502000000	3.252226000000	-2.518458000000
H	4.251898000000	0.613207000000	-1.378467000000
H	4.549970000000	2.683614000000	-2.707010000000
H	2.756443000000	4.368392000000	-2.832034000000
C	0.234431000000	4.283223000000	-1.480394000000
O	0.111394000000	1.876962000000	-0.098294000000
P	1.832948000000	-0.416301000000	0.180372000000
P	-1.879730000000	-0.253352000000	0.153965000000
C	3.391402000000	-1.393822000000	0.078689000000
C	4.488783000000	-1.110303000000	0.909556000000

C	3.495800000000	-2.416046000000	-0.876596000000
C	5.672920000000	-1.835474000000	0.780814000000
H	4.416514000000	-0.326134000000	1.657481000000
C	4.685699000000	-3.136979000000	-1.001882000000
H	2.647299000000	-2.660988000000	-1.509282000000
C	5.773633000000	-2.849378000000	-0.176411000000
H	6.515533000000	-1.610947000000	1.429630000000
H	4.753463000000	-3.930010000000	-1.741425000000
H	6.696145000000	-3.416008000000	-0.272590000000
C	1.781265000000	0.097361000000	1.943229000000
C	1.270188000000	-0.824680000000	2.868834000000
C	2.251621000000	1.336700000000	2.398510000000
C	1.251145000000	-0.520271000000	4.228226000000
H	0.876113000000	-1.775148000000	2.518604000000
C	2.219972000000	1.643676000000	3.760393000000
H	2.646558000000	2.061078000000	1.692493000000
C	1.725233000000	0.714779000000	4.676915000000
H	0.843515000000	-1.237547000000	4.933899000000
H	2.585579000000	2.608147000000	4.103433000000
H	1.699194000000	0.955095000000	5.736411000000
C	-3.491064000000	-1.102348000000	-0.138928000000
C	-4.643872000000	-0.762981000000	0.591434000000
C	-3.575918000000	-2.083241000000	-1.138194000000
C	-5.858505000000	-1.392378000000	0.322783000000
H	-4.588837000000	-0.009516000000	1.371754000000
C	-4.795892000000	-2.710795000000	-1.403202000000
H	-2.690306000000	-2.371735000000	-1.698461000000
C	-5.936230000000	-2.367893000000	-0.676145000000
H	-6.743140000000	-1.123500000000	0.894089000000
H	-4.846571000000	-3.473958000000	-2.174730000000
H	-6.882856000000	-2.860834000000	-0.881421000000
C	-1.934257000000	0.068774000000	1.965018000000
C	-2.207272000000	-1.018394000000	2.813371000000
C	-1.673981000000	1.323706000000	2.529917000000
C	-2.247411000000	-0.844509000000	4.195124000000
H	-2.407065000000	-1.998580000000	2.388323000000
C	-1.701076000000	1.490674000000	3.915712000000
H	-1.451726000000	2.173973000000	1.895435000000
C	-1.994873000000	0.412538000000	4.750757000000
H	-2.473395000000	-1.691464000000	4.837652000000
H	-1.491157000000	2.468266000000	4.340829000000
H	-2.019892000000	0.548091000000	5.828645000000
Pd	-0.065763000000	-1.476930000000	-0.704420000000
Br	0.022048000000	-3.366464000000	-2.315105000000
C	0.270830000000	5.290234000000	-2.638410000000
H	-0.560031000000	5.998267000000	-2.561271000000
H	1.191791000000	5.880534000000	-2.606926000000
H	0.211985000000	4.788682000000	-3.609971000000
C	0.317843000000	5.056004000000	-0.133592000000
H	1.245901000000	5.637142000000	-0.088033000000
H	-0.531417000000	5.741833000000	-0.036855000000

H 0.302922000000 4.366530000000 0.716224000000

[LPd(0)Br]$^{-1}$

B3LYP-D3 SCF energy:	-4962.937662 a.u.
B3LYP-D3 enthalpy:	-4962.299272 a.u.
B3LYP-D3 free energy:	-4962.414909 a.u.
M06 SCF energy in solution:	-4964.685544 a.u.
M06 enthalpy in solution:	-4964.029360 a.u.
M06 free energy in solution:	-4964.175882 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-3.242904000000	1.846880000000	-1.394192000000
C	-2.094665000000	1.410237000000	-0.712352000000
C	-0.966238000000	2.243982000000	-0.796778000000
C	-0.933244000000	3.443027000000	-1.519546000000
C	-2.096078000000	3.829624000000	-2.191662000000
C	-3.242977000000	3.035853000000	-2.123265000000
C	1.521307000000	3.227576000000	-1.555410000000
C	1.364281000000	2.046831000000	-0.823914000000
C	2.334467000000	1.033966000000	-0.753704000000
C	3.524944000000	1.254339000000	-1.463108000000
C	3.710687000000	2.419244000000	-2.210003000000
C	2.717791000000	3.400228000000	-2.259792000000
H	-4.139292000000	1.237174000000	-1.371058000000
H	-2.113880000000	4.747210000000	-2.770998000000
H	-4.144239000000	3.344551000000	-2.647582000000
H	4.303704000000	0.499004000000	-1.441199000000
H	4.638215000000	2.563797000000	-2.758912000000
H	2.881240000000	4.297284000000	-2.848529000000
C	0.375133000000	4.242977000000	-1.478882000000
O	0.181427000000	1.846721000000	-0.135664000000
P	1.888398000000	-0.534902000000	0.130476000000
P	-1.930372000000	-0.264460000000	0.087282000000
C	3.490358000000	-1.476326000000	0.018188000000
C	4.656562000000	-1.172387000000	0.739062000000
C	3.493038000000	-2.578644000000	-0.852037000000
C	5.808733000000	-1.944836000000	0.582613000000
H	4.660784000000	-0.331816000000	1.428143000000
C	4.650605000000	-3.345320000000	-1.012445000000
H	2.576748000000	-2.841576000000	-1.380458000000
C	5.808814000000	-3.031016000000	-0.298261000000
H	6.705786000000	-1.701166000000	1.148663000000
H	4.638769000000	-4.197398000000	-1.687955000000
H	6.706426000000	-3.634314000000	-0.418189000000
C	1.939595000000	0.059599000000	1.890946000000
C	1.250995000000	-0.704210000000	2.845802000000
C	2.591486000000	1.229051000000	2.310861000000
C	1.233013000000	-0.322619000000	4.186577000000
H	0.699574000000	-1.581594000000	2.518564000000
C	2.563036000000	1.619729000000	3.652028000000

H	3.116241000000	1.843487000000	1.584099000000
C	1.887477000000	0.842279000000	4.594387000000
H	0.673979000000	-0.914934000000	4.905090000000
H	3.067587000000	2.533958000000	3.958622000000
H	1.856447000000	1.150320000000	5.637202000000
C	-3.641990000000	-0.954781000000	-0.164007000000
C	-4.789470000000	-0.499023000000	0.507383000000
C	-3.760036000000	-2.016521000000	-1.073889000000
C	-6.033300000000	-1.082559000000	0.264276000000
H	-4.703676000000	0.313435000000	1.224699000000
C	-5.008714000000	-2.596228000000	-1.319333000000
H	-2.865267000000	-2.401193000000	-1.562798000000
C	-6.144997000000	-2.131889000000	-0.654356000000
H	-6.914631000000	-0.721608000000	0.790912000000
H	-5.085873000000	-3.421417000000	-2.023266000000
H	-7.114242000000	-2.589595000000	-0.841810000000
C	-2.030145000000	0.149211000000	1.894110000000
C	-2.315275000000	-0.904397000000	2.782956000000
C	-1.752360000000	1.413318000000	2.433750000000
C	-2.346073000000	-0.694240000000	4.159667000000
H	-2.518380000000	-1.895541000000	2.384477000000
C	-1.766207000000	1.619923000000	3.815128000000
H	-1.521682000000	2.245059000000	1.777240000000
C	-2.069966000000	0.572425000000	4.684746000000
H	-2.578310000000	-1.522913000000	4.825388000000
H	-1.535849000000	2.606738000000	4.210439000000
H	-2.080403000000	0.736027000000	5.759891000000
Pd	-0.091198000000	-1.426554000000	-0.563651000000
Br	-0.237144000000	-3.547267000000	-2.076651000000
C	0.461588000000	4.972898000000	-0.108484000000
H	1.403302000000	5.530373000000	-0.034673000000
H	-0.373801000000	5.675096000000	0.001384000000
H	0.421957000000	4.256227000000	0.716915000000
C	0.450589000000	5.288512000000	-2.600163000000
H	-0.365081000000	6.013341000000	-2.508669000000
H	1.386872000000	5.852918000000	-2.538419000000
H	0.391190000000	4.821278000000	-3.588901000000

LPd(0)

B3LYP-D3 SCF energy:	-2391.415774 a.u.
B3LYP-D3 enthalpy:	-2390.778772 a.u.
B3LYP-D3 free energy:	-2390.889101 a.u.
M06 SCF energy in solution:	-2390.515212 a.u.
M06 enthalpy in solution:	-2389.861065 a.u.
M06 free energy in solution:	-2390.001281 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-3.499459000000	1.711883000000	-0.910352000000
C	-2.305954000000	1.110297000000	-0.486547000000
C	-1.276889000000	1.962271000000	-0.052985000000

C	-1.395547000000	3.355625000000	-0.019778000000
C	-2.594933000000	3.916105000000	-0.470300000000
C	-3.637618000000	3.100374000000	-0.912139000000
C	1.064903000000	3.459363000000	0.094215000000
C	1.067221000000	2.059458000000	0.041626000000
C	2.195383000000	1.302569000000	-0.321092000000
C	3.365433000000	2.013643000000	-0.630961000000
C	3.388607000000	3.406952000000	-0.597851000000
C	2.246246000000	4.125347000000	-0.242461000000
H	-4.320448000000	1.089039000000	-1.249446000000
H	-2.725300000000	4.992918000000	-0.471346000000
H	-4.566500000000	3.548898000000	-1.253320000000
H	4.260276000000	1.472778000000	-0.917577000000
H	4.303040000000	3.936305000000	-0.850679000000
H	2.283949000000	5.209138000000	-0.223306000000
C	-0.221431000000	4.140049000000	0.574654000000
O	-0.093178000000	1.381965000000	0.368087000000
P	2.064733000000	-0.541116000000	-0.497426000000
P	-2.005334000000	-0.718483000000	-0.512354000000
C	3.752505000000	-0.993447000000	-1.101562000000
C	4.876392000000	-1.089563000000	-0.264911000000
C	3.901346000000	-1.248832000000	-2.472333000000
C	6.122157000000	-1.430737000000	-0.792742000000
H	4.773476000000	-0.900096000000	0.799774000000
C	5.149795000000	-1.581259000000	-3.002044000000
H	3.028260000000	-1.192213000000	-3.118847000000
C	6.261524000000	-1.674640000000	-2.162226000000
H	6.984863000000	-1.505856000000	-0.135641000000
H	5.251492000000	-1.776867000000	-4.066302000000
H	7.232401000000	-1.942328000000	-2.570955000000
C	2.120264000000	-1.149442000000	1.248689000000
C	2.273538000000	-2.532378000000	1.449663000000
C	1.957504000000	-0.319550000000	2.364650000000
C	2.285231000000	-3.067123000000	2.735947000000
H	2.387529000000	-3.189796000000	0.591039000000
C	1.949952000000	-0.859738000000	3.653345000000
H	1.836515000000	0.750638000000	2.235617000000
C	2.119515000000	-2.230589000000	3.844419000000
H	2.415570000000	-4.137597000000	2.873724000000
H	1.812844000000	-0.203015000000	4.508423000000
H	2.116822000000	-2.647414000000	4.848128000000
C	-3.638756000000	-1.360560000000	-1.095061000000
C	-4.744198000000	-1.580518000000	-0.258996000000
C	-3.759808000000	-1.633648000000	-2.466521000000
C	-5.944927000000	-2.058409000000	-0.787308000000
H	-4.666412000000	-1.382595000000	0.805751000000
C	-4.964233000000	-2.098663000000	-2.996314000000
H	-2.898854000000	-1.483823000000	-3.114689000000
C	-6.059140000000	-2.314191000000	-2.156069000000
H	-6.792537000000	-2.230345000000	-0.128693000000
H	-5.043909000000	-2.303221000000	-4.060809000000

H	-6.995014000000	-2.686610000000	-2.564433000000
C	-2.014111000000	-1.098701000000	1.298797000000
C	-1.318763000000	-2.230833000000	1.748061000000
C	-2.666201000000	-0.285517000000	2.238786000000
C	-1.287811000000	-2.551719000000	3.104983000000
H	-0.774003000000	-2.841140000000	1.033409000000
C	-2.629168000000	-0.604140000000	3.597676000000
H	-3.196761000000	0.603613000000	1.910051000000
C	-1.941396000000	-1.738802000000	4.033064000000
H	-0.727063000000	-3.419757000000	3.437415000000
H	-3.134794000000	0.037087000000	4.315418000000
H	-1.905682000000	-1.981936000000	5.091909000000
Pd	0.061579000000	-1.160159000000	-1.397875000000
C	-0.266680000000	5.628436000000	0.200803000000
H	-1.185678000000	6.091476000000	0.572991000000
H	0.566007000000	6.168406000000	0.661889000000
H	-0.218228000000	5.774023000000	-0.883519000000
C	-0.289961000000	4.009777000000	2.123493000000
H	0.562172000000	4.522493000000	2.584426000000
H	-1.216376000000	4.458805000000	2.499688000000
H	-0.269052000000	2.959666000000	2.430241000000

LPd(II)HBr

B3LYP-D3 SCF energy:	-4963.473285 a.u.
B3LYP-D3 enthalpy:	-4962.824303 a.u.
B3LYP-D3 free energy:	-4962.937482 a.u.
M06 SCF energy in solution:	-4965.172525 a.u.
M06 enthalpy in solution:	-4964.505621 a.u.
M06 free energy in solution:	-4964.650993 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-3.293834000000	1.873286000000	-0.485300000000
C	-2.109268000000	1.299286000000	-0.009810000000
C	-1.048517000000	2.162811000000	0.281676000000
C	-1.105064000000	3.549792000000	0.144073000000
C	-2.303966000000	4.087778000000	-0.336005000000
C	-3.383765000000	3.257130000000	-0.647223000000
C	1.363645000000	3.539969000000	0.131943000000
C	1.290562000000	2.148128000000	0.237956000000
C	2.324039000000	1.280508000000	-0.139106000000
C	3.512268000000	1.861756000000	-0.603862000000
C	3.627099000000	3.248866000000	-0.699418000000
C	2.560266000000	4.079574000000	-0.348954000000
H	-4.130743000000	1.237676000000	-0.752586000000
H	-2.402193000000	5.159133000000	-0.474935000000
H	-4.302779000000	3.693213000000	-1.027772000000
H	4.335934000000	1.231681000000	-0.919806000000
H	4.550417000000	3.686076000000	-1.068208000000
H	2.667124000000	5.153554000000	-0.456855000000
C	0.134279000000	4.344974000000	0.576249000000

O	0.129321000000	1.571690000000	0.713695000000
P	1.958952000000	-0.530677000000	-0.229627000000
P	-1.751116000000	-0.501584000000	0.098344000000
C	3.533567000000	-1.265364000000	-0.849773000000
C	4.683244000000	-1.237830000000	-0.038107000000
C	3.609772000000	-1.862119000000	-2.114265000000
C	5.883511000000	-1.779472000000	-0.492769000000
H	4.635892000000	-0.793495000000	0.951949000000
C	4.813445000000	-2.411450000000	-2.565128000000
H	2.726687000000	-1.899256000000	-2.743748000000
C	5.950642000000	-2.368990000000	-1.759255000000
H	6.764684000000	-1.746541000000	0.142305000000
H	4.855489000000	-2.874531000000	-3.547053000000
H	6.885542000000	-2.796869000000	-2.111225000000
C	1.988315000000	-1.135195000000	1.510810000000
C	2.146744000000	-2.516525000000	1.713226000000
C	1.888439000000	-0.289906000000	2.622181000000
C	2.234139000000	-3.036471000000	3.002470000000
H	2.225931000000	-3.183292000000	0.858393000000
C	1.965734000000	-0.816150000000	3.913123000000
H	1.755306000000	0.777158000000	2.488885000000
C	2.147973000000	-2.185136000000	4.106969000000
H	2.369608000000	-4.105365000000	3.144489000000
H	1.879525000000	-0.151030000000	4.767583000000
H	2.212284000000	-2.589228000000	5.113587000000
C	-3.361734000000	-1.341792000000	-0.182151000000
C	-4.473806000000	-1.051410000000	0.626865000000
C	-3.463866000000	-2.342159000000	-1.157478000000
C	-5.675248000000	-1.733491000000	0.444834000000
H	-4.393576000000	-0.298335000000	1.406241000000
C	-4.667262000000	-3.031020000000	-1.329780000000
H	-2.613981000000	-2.562770000000	-1.792980000000
C	-5.773063000000	-2.725485000000	-0.536093000000
H	-6.531122000000	-1.498182000000	1.072012000000
H	-4.737939000000	-3.801720000000	-2.092391000000
H	-6.709050000000	-3.260067000000	-0.676076000000
C	-1.566119000000	-0.790579000000	1.912043000000
C	-1.223782000000	-2.087163000000	2.323181000000
C	-1.824398000000	0.184509000000	2.884390000000
C	-1.164082000000	-2.407547000000	3.677485000000
H	-1.004113000000	-2.848624000000	1.579243000000
C	-1.753312000000	-0.135520000000	4.242092000000
H	-2.092532000000	1.193283000000	2.586804000000
C	-1.430582000000	-1.432427000000	4.641698000000
H	-0.893296000000	-3.414747000000	3.980201000000
H	-1.958458000000	0.630207000000	4.986008000000
H	-1.378938000000	-1.681992000000	5.698178000000
Br	-1.491823000000	-0.554070000000	-3.445802000000
Pd	0.076041000000	-0.755909000000	-1.515262000000
H	1.136859000000	-0.700468000000	-2.656114000000
C	0.139661000000	4.425160000000	2.129191000000

H	1.035380000000	4.950710000000	2.479530000000
H	-0.745685000000	4.965821000000	2.482559000000
H	0.130697000000	3.424967000000	2.573672000000
C	0.137482000000	5.768239000000	0.001340000000
H	-0.741341000000	6.323034000000	0.343958000000
H	1.014966000000	6.323776000000	0.346584000000
H	0.138304000000	5.759494000000	-1.093518000000

TS1

B3LYP-D3 SCF energy:	-6154.512184 a.u.
B3LYP-D3 enthalpy:	-6153.403906 a.u.
B3LYP-D3 free energy:	-6153.577604 a.u.
M06 SCF energy in solution:	-6155.721220 a.u.
M06 enthalpy in solution:	-6154.583871 a.u.
M06 free energy in solution:	-6154.803467 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	2.324314000000	-0.532040000000	0.836619000000
H	1.303809000000	-0.825215000000	-0.435957000000
H	2.964593000000	-1.286316000000	0.389430000000
C	1.699532000000	-0.875557000000	2.055239000000
C	1.800439000000	-2.203714000000	2.687878000000
C	2.283775000000	-3.339887000000	2.011409000000
C	1.374211000000	-2.351564000000	4.018102000000
C	2.336470000000	-4.577716000000	2.646927000000
H	2.600263000000	-3.263855000000	0.975055000000
C	1.432585000000	-3.589163000000	4.654952000000
H	0.973396000000	-1.487934000000	4.540489000000
C	1.911950000000	-4.709455000000	3.972725000000
H	2.711454000000	-5.442918000000	2.105601000000
H	1.092305000000	-3.681189000000	5.682893000000
H	1.953085000000	-5.676273000000	4.467017000000
C	-3.236121000000	2.739883000000	2.225178000000
C	-2.743229000000	1.921182000000	1.199859000000
C	-3.637808000000	1.021859000000	0.605213000000
C	-4.982234000000	0.916648000000	0.985043000000
C	-5.423789000000	1.733639000000	2.028866000000
C	-4.559673000000	2.639221000000	2.646141000000
C	-5.067233000000	-1.229677000000	-0.245732000000
C	-3.721389000000	-1.023451000000	-0.560800000000
C	-2.896344000000	-2.037093000000	-1.066550000000
C	-3.446358000000	-3.311408000000	-1.247207000000
C	-4.778252000000	-3.551907000000	-0.913868000000
C	-5.577197000000	-2.520421000000	-0.417616000000
H	-2.568058000000	3.438002000000	2.719103000000
H	-6.453693000000	1.675110000000	2.363412000000
H	-4.922764000000	3.270137000000	3.452606000000
H	-2.826727000000	-4.116358000000	-1.628218000000
H	-5.197416000000	-4.545356000000	-1.043961000000
H	-6.612489000000	-2.728766000000	-0.170537000000

C	-5.891777000000	-0.010822000000	0.172894000000
O	-3.151481000000	0.221523000000	-0.412773000000
P	-1.125197000000	-1.666261000000	-1.316928000000
P	-0.993126000000	1.971508000000	0.601859000000
C	-0.394343000000	-3.249245000000	-1.911551000000
C	-0.299745000000	-3.577026000000	-3.271385000000
C	0.128550000000	-4.134188000000	-0.952815000000
C	0.323802000000	-4.762925000000	-3.667006000000
H	-0.697927000000	-2.900536000000	-4.021546000000
C	0.742422000000	-5.321157000000	-1.351492000000
H	0.068604000000	-3.882715000000	0.103181000000
C	0.847800000000	-5.634671000000	-2.709781000000
H	0.401974000000	-5.002840000000	-4.724080000000
H	1.147473000000	-5.992917000000	-0.599384000000
H	1.337597000000	-6.553581000000	-3.020914000000
C	-1.056781000000	-0.568894000000	-2.789740000000
C	0.203643000000	-0.144107000000	-3.240095000000
C	-2.205301000000	-0.122260000000	-3.457726000000
C	0.315963000000	0.707503000000	-4.337937000000
H	1.106322000000	-0.461425000000	-2.730007000000
C	-2.091587000000	0.739779000000	-4.550804000000
H	-3.187810000000	-0.442326000000	-3.128092000000
C	-0.834260000000	1.154926000000	-4.993560000000
H	1.296827000000	1.055201000000	-4.639876000000
H	-2.990074000000	1.088218000000	-5.053162000000
H	-0.749843000000	1.831436000000	-5.839930000000
C	-0.106313000000	2.604299000000	2.091863000000
C	0.870574000000	3.611824000000	2.016247000000
C	-0.271184000000	1.920104000000	3.312479000000
C	1.643294000000	3.943617000000	3.132253000000
H	1.041203000000	4.133655000000	1.080093000000
C	0.501329000000	2.256533000000	4.424531000000
H	-0.991851000000	1.109466000000	3.380034000000
C	1.458238000000	3.273081000000	4.342521000000
H	2.390679000000	4.729022000000	3.051760000000
H	0.354445000000	1.718784000000	5.357874000000
H	2.057587000000	3.533915000000	5.210796000000
C	-1.059655000000	3.446690000000	-0.519390000000
C	-0.855579000000	3.210849000000	-1.885359000000
C	-1.328747000000	4.759092000000	-0.091111000000
C	-0.903348000000	4.260786000000	-2.806958000000
H	-0.648245000000	2.206349000000	-2.235699000000
C	-1.372927000000	5.807791000000	-1.008370000000
H	-1.496488000000	4.959106000000	0.963277000000
C	-1.158600000000	5.559949000000	-2.370403000000
H	-0.720497000000	4.052467000000	-3.856477000000
H	-1.578207000000	6.818610000000	-0.664634000000
H	-1.190260000000	6.380161000000	-3.083089000000
Pd	0.074568000000	-1.002500000000	0.556284000000
Br	-1.689739000000	-1.442722000000	2.315163000000
C	2.760289000000	0.897984000000	0.557394000000

C	4.292557000000	1.018706000000	0.781429000000
C	2.450762000000	1.340015000000	-0.875170000000
H	2.235381000000	1.574257000000	1.233699000000
C	5.070846000000	0.252311000000	-0.293923000000
O	4.698764000000	0.494237000000	2.036223000000
H	4.571455000000	2.080084000000	0.709625000000
O	3.116099000000	0.546402000000	-1.807605000000
H	1.391017000000	1.254541000000	-1.113690000000
O	2.810336000000	2.740953000000	-0.940247000000
C	4.546753000000	0.524846000000	-1.716612000000
H	4.989783000000	-0.822708000000	-0.091402000000
O	6.437538000000	0.639343000000	-0.323473000000
C	4.348919000000	1.299234000000	3.150602000000
C	2.463228000000	3.434636000000	-2.061430000000
C	5.028309000000	-0.542013000000	-2.700269000000
H	4.940652000000	1.500210000000	-2.036254000000
C	7.299993000000	-0.163184000000	0.472553000000
H	4.816098000000	0.840414000000	4.025630000000
H	4.726131000000	2.327515000000	3.035556000000
H	3.265153000000	1.345058000000	3.311716000000
O	2.063262000000	2.921891000000	-3.079718000000
C	2.596579000000	4.918413000000	-1.827579000000
H	6.118300000000	-0.469366000000	-2.761685000000
O	4.744588000000	-1.872497000000	-2.303192000000
H	4.598350000000	-0.327633000000	-3.690920000000
H	8.311286000000	0.224976000000	0.320313000000
H	7.270201000000	-1.216143000000	0.152329000000
H	7.036872000000	-0.106391000000	1.534113000000
H	3.408895000000	5.145747000000	-1.133292000000
H	2.745381000000	5.426552000000	-2.781790000000
H	1.653617000000	5.272644000000	-1.392568000000
C	3.430251000000	-2.341675000000	-2.576102000000
H	3.459931000000	-3.432912000000	-2.507781000000
H	2.691966000000	-1.964687000000	-1.860213000000
H	3.101601000000	-2.057274000000	-3.587077000000
H	1.400639000000	-0.062620000000	2.712645000000
C	-6.308038000000	0.746162000000	-1.121135000000
H	-6.931195000000	0.103470000000	-1.754081000000
H	-6.875113000000	1.648984000000	-0.866852000000
H	-5.426766000000	1.047486000000	-1.696701000000
C	-7.158226000000	-0.408159000000	0.946817000000
H	-7.750058000000	0.475680000000	1.202574000000
H	-7.802463000000	-1.046242000000	0.334400000000
H	-6.911694000000	-0.943124000000	1.869636000000

TS2

B3LYP-D3 SCF energy:	-6154.491513 a.u.
B3LYP-D3 enthalpy:	-6153.384566 a.u.
B3LYP-D3 free energy:	-6153.559930 a.u.
M06 SCF energy in solution:	-6155.691230 a.u.
M06 enthalpy in solution:	-6154.555179 a.u.

M06 free energy in solution: -6154.776243 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-2.270286000000	0.879976000000	0.218524000000
H	-0.967435000000	0.504159000000	0.349038000000
H	-2.430643000000	0.425666000000	-0.759859000000
C	-2.332911000000	2.285226000000	0.224415000000
C	4.289828000000	2.690593000000	0.863308000000
C	3.398822000000	1.610807000000	0.773945000000
C	3.945001000000	0.335193000000	0.545018000000
C	5.321683000000	0.116654000000	0.400842000000
C	6.169648000000	1.224191000000	0.472653000000
C	5.660251000000	2.501424000000	0.707986000000
C	4.767140000000	-2.075391000000	-0.600305000000
C	3.419030000000	-1.764254000000	-0.398368000000
C	2.374407000000	-2.449995000000	-1.039231000000
C	2.719677000000	-3.483456000000	-1.918195000000
C	4.056685000000	-3.794121000000	-2.160744000000
C	5.071108000000	-3.094748000000	-1.507529000000
H	3.902244000000	3.689719000000	1.029599000000
H	7.239630000000	1.095435000000	0.352132000000
H	6.333718000000	3.351611000000	0.766701000000
H	1.938141000000	-4.030765000000	-2.434226000000
H	4.308841000000	-4.587530000000	-2.858604000000
H	6.105204000000	-3.356165000000	-1.703295000000
C	5.797833000000	-1.331773000000	0.253662000000
O	3.088874000000	-0.748192000000	0.485291000000
P	0.623915000000	-1.988404000000	-0.667792000000
P	1.572372000000	1.879129000000	0.838603000000
C	-0.372173000000	-2.854910000000	-1.937786000000
C	-1.449110000000	-3.697014000000	-1.628420000000
C	-0.126608000000	-2.503886000000	-3.280098000000
C	-2.242926000000	-4.215361000000	-2.655655000000
H	-1.697447000000	-3.929145000000	-0.599812000000
C	-0.917603000000	-3.035315000000	-4.296690000000
H	0.671492000000	-1.803337000000	-3.516038000000
C	-1.975207000000	-3.898765000000	-3.988020000000
H	-3.074436000000	-4.868868000000	-2.404253000000
H	-0.712610000000	-2.768181000000	-5.330173000000
H	-2.591432000000	-4.311941000000	-4.782761000000
C	0.417672000000	-2.906901000000	0.922635000000
C	0.282060000000	-2.176944000000	2.111548000000
C	0.481125000000	-4.306990000000	0.985647000000
C	0.177113000000	-2.833989000000	3.339318000000
H	0.259179000000	-1.092094000000	2.073059000000
C	0.370356000000	-4.962837000000	2.210202000000
H	0.603425000000	-4.884698000000	0.074086000000
C	0.213627000000	-4.228460000000	3.389249000000
H	0.075101000000	-2.247431000000	4.248350000000
H	0.401707000000	-6.048415000000	2.244523000000

H	0.127763000000	-4.743749000000	4.342682000000
C	1.393805000000	3.685445000000	0.577753000000
C	1.349387000000	4.634124000000	1.610312000000
C	1.313405000000	4.110195000000	-0.759138000000
C	1.217536000000	5.991532000000	1.309024000000
H	1.418348000000	4.315965000000	2.646414000000
C	1.201095000000	5.468001000000	-1.052528000000
H	1.338441000000	3.374509000000	-1.559301000000
C	1.146385000000	6.409595000000	-0.021621000000
H	1.177996000000	6.721057000000	2.114031000000
H	1.129126000000	5.785035000000	-2.088214000000
H	1.044301000000	7.466538000000	-0.254136000000
C	1.121069000000	1.581865000000	2.595951000000
C	-0.113377000000	2.053732000000	3.080925000000
C	1.887091000000	0.738344000000	3.414819000000
C	-0.566429000000	1.687097000000	4.347344000000
H	-0.714687000000	2.713172000000	2.463982000000
C	1.428286000000	0.369529000000	4.681265000000
H	2.838023000000	0.355732000000	3.058964000000
C	0.199918000000	0.837476000000	5.151649000000
H	-1.515451000000	2.072118000000	4.712133000000
H	2.035139000000	-0.286757000000	5.299461000000
H	-0.154007000000	0.552082000000	6.138605000000
Pd	0.533852000000	0.331558000000	-0.556152000000
Br	1.963270000000	0.762569000000	-2.715360000000
C	-2.972667000000	0.095656000000	1.333167000000
C	-4.488412000000	0.421978000000	1.414500000000
C	-2.865155000000	-1.400563000000	1.032779000000
H	-2.497737000000	0.288805000000	2.300692000000
C	-5.139066000000	0.141013000000	0.062979000000
O	-4.763506000000	1.775809000000	1.750208000000
H	-4.946176000000	-0.235113000000	2.166885000000
O	-3.454869000000	-1.738744000000	-0.173819000000
H	-1.835587000000	-1.732247000000	0.950669000000
O	-3.458916000000	-2.085632000000	2.170014000000
C	-4.770417000000	-1.260398000000	-0.485841000000
H	-4.802583000000	0.909121000000	-0.641612000000
O	-6.558993000000	0.137033000000	0.140731000000
C	-4.591781000000	2.081436000000	3.120008000000
C	-3.240543000000	-3.421858000000	2.277787000000
C	-4.833569000000	-1.278310000000	-2.008326000000
H	-5.509392000000	-1.964132000000	-0.079873000000
C	-7.170946000000	1.383300000000	-0.158356000000
H	-4.907870000000	3.119296000000	3.255297000000
H	-5.207733000000	1.431287000000	3.760497000000
H	-3.542825000000	1.988308000000	3.440292000000
O	-2.680808000000	-4.097384000000	1.446188000000
C	-3.769015000000	-3.934457000000	3.596503000000
H	-5.869844000000	-1.092851000000	-2.334478000000
O	-3.963330000000	-0.270088000000	-2.490463000000
H	-4.517248000000	-2.268965000000	-2.365673000000

H	-8.251395000000	1.216509000000	-0.116191000000
H	-6.903178000000	1.727606000000	-1.169647000000
H	-6.888148000000	2.157148000000	0.563641000000
H	-3.100194000000	-3.597764000000	4.396698000000
H	-4.765146000000	-3.531901000000	3.801214000000
H	-3.790362000000	-5.024851000000	3.580747000000
C	-3.725414000000	-0.333961000000	-3.883255000000
H	-3.062553000000	0.500803000000	-4.125541000000
H	-3.233583000000	-1.276355000000	-4.162303000000
H	-4.659944000000	-0.229619000000	-4.458911000000
C	5.804037000000	-1.980245000000	1.668069000000
H	6.108894000000	-3.030882000000	1.601384000000
H	6.503649000000	-1.450558000000	2.325163000000
H	4.808133000000	-1.941842000000	2.120424000000
C	7.213124000000	-1.419974000000	-0.336718000000
H	7.260561000000	-0.972555000000	-1.334879000000
H	7.935225000000	-0.911141000000	0.309013000000
H	7.537948000000	-2.462458000000	-0.405865000000
C	-2.088348000000	3.133316000000	-0.910289000000
C	-1.633479000000	2.638258000000	-2.158003000000
C	-2.302421000000	4.526565000000	-0.789706000000
C	-1.409970000000	3.499732000000	-3.223907000000
H	-1.414410000000	1.582722000000	-2.280272000000
C	-2.099017000000	5.381028000000	-1.866879000000
H	-2.634386000000	4.927219000000	0.165252000000
C	-1.651896000000	4.873067000000	-3.091004000000
H	-1.025971000000	3.098853000000	-4.157627000000
H	-2.273690000000	6.447273000000	-1.750012000000
H	-1.478659000000	5.541720000000	-3.929972000000
H	-2.545763000000	2.789138000000	1.162066000000

TS3

B3LYP-D3 SCF energy:	-6154.496156 a.u.
B3LYP-D3 enthalpy:	-6153.383166 a.u.
B3LYP-D3 free energy:	-6153.555615 a.u.
M06 SCF energy in solution:	-6155.703990 a.u.
M06 enthalpy in solution:	-6154.562085 a.u.
M06 free energy in solution:	-6154.780640 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-5.169620000000	-1.120351000000	0.151320000000
C	-4.140323000000	0.005512000000	0.342689000000
C	-3.715980000000	-2.579308000000	1.595159000000
C	-4.474431000000	-2.475000000000	0.260151000000
H	-5.927212000000	-1.049910000000	0.946488000000
H	-4.450536000000	-2.589212000000	2.412263000000
H	-3.758171000000	-2.567743000000	-0.561660000000
O	-2.821842000000	-1.467333000000	1.779018000000
O	-5.429967000000	-3.531741000000	0.213131000000
O	-5.787780000000	-0.954874000000	-1.120398000000

C	-2.877874000000	-3.842441000000	1.686228000000
H	-3.553107000000	-4.708600000000	1.776933000000
H	-2.253112000000	-3.795257000000	2.590590000000
O	-2.079028000000	-3.949506000000	0.526666000000
C	-1.145138000000	-5.011405000000	0.595511000000
H	-0.649212000000	-5.058053000000	-0.372714000000
H	-0.393758000000	-4.829061000000	1.377649000000
H	-1.645445000000	-5.973780000000	0.795330000000
C	-5.182414000000	-4.478372000000	-0.818074000000
H	-5.290238000000	-4.020975000000	-1.812372000000
H	-5.928609000000	-5.270218000000	-0.705422000000
H	-4.174988000000	-4.907461000000	-0.734047000000
C	-7.160703000000	-1.312311000000	-1.162619000000
H	-7.761095000000	-0.671829000000	-0.496643000000
H	-7.492324000000	-1.155507000000	-2.192939000000
H	-7.315479000000	-2.359169000000	-0.879373000000
C	-3.388929000000	-0.204919000000	1.659255000000
C	-3.120831000000	0.074524000000	-0.829922000000
H	-2.287389000000	-0.606450000000	-0.641024000000
H	-3.609991000000	-0.273381000000	-1.742572000000
C	-2.590495000000	1.463388000000	-1.032338000000
H	-4.680020000000	0.954457000000	0.408370000000
C	3.706767000000	3.717925000000	0.344257000000
C	3.252727000000	2.388992000000	0.382830000000
C	4.234044000000	1.390081000000	0.420912000000
C	5.610752000000	1.646891000000	0.389135000000
C	6.016119000000	2.981845000000	0.330710000000
C	5.069574000000	4.008422000000	0.319185000000
C	5.910921000000	-0.670489000000	-0.382201000000
C	4.525768000000	-0.818763000000	-0.279022000000
C	3.793326000000	-1.821878000000	-0.925266000000
C	4.513003000000	-2.704941000000	-1.744261000000
C	5.895180000000	-2.573234000000	-1.886889000000
C	6.591194000000	-1.569270000000	-1.209576000000
H	2.990841000000	4.530738000000	0.312873000000
H	7.071573000000	3.229840000000	0.296925000000
H	5.397087000000	5.043653000000	0.282533000000
H	3.990930000000	-3.487371000000	-2.283362000000
H	6.435512000000	-3.261449000000	-2.530904000000
H	7.666127000000	-1.490605000000	-1.332400000000
C	6.551810000000	0.437945000000	0.459331000000
O	3.806524000000	0.077273000000	0.490036000000
P	1.958686000000	-1.762436000000	-0.741091000000
P	1.456578000000	1.921008000000	0.247745000000
C	1.419993000000	-3.329939000000	-1.564283000000
C	1.925411000000	-4.587251000000	-1.191462000000
C	0.458511000000	-3.254150000000	-2.580354000000
C	1.502102000000	-5.742824000000	-1.846911000000
H	2.650271000000	-4.658627000000	-0.384931000000
C	0.019319000000	-4.415932000000	-3.223206000000
H	0.053326000000	-2.283912000000	-2.859708000000

C	0.545840000000	-5.657918000000	-2.865430000000
H	1.906203000000	-6.709430000000	-1.556796000000
H	-0.731068000000	-4.345603000000	-4.006115000000
H	0.209530000000	-6.559437000000	-3.371091000000
C	1.700142000000	-2.184142000000	1.040556000000
C	0.424678000000	-1.944749000000	1.576429000000
C	2.699968000000	-2.709764000000	1.870643000000
C	0.156802000000	-2.222556000000	2.916022000000
H	-0.364478000000	-1.536073000000	0.953967000000
C	2.429201000000	-2.989563000000	3.212409000000
H	3.695301000000	-2.892202000000	1.475063000000
C	1.158449000000	-2.745627000000	3.737566000000
H	-0.829111000000	-1.998181000000	3.308537000000
H	3.214560000000	-3.393306000000	3.846941000000
H	0.953393000000	-2.950540000000	4.785365000000
C	0.732623000000	3.574088000000	-0.166966000000
C	0.370315000000	4.548905000000	0.777391000000
C	0.628535000000	3.883572000000	-1.533941000000
C	-0.086327000000	5.802032000000	0.361748000000
H	0.450507000000	4.334199000000	1.838236000000
C	0.190996000000	5.142554000000	-1.946533000000
H	0.870877000000	3.127026000000	-2.274310000000
C	-0.168823000000	6.104855000000	-1.000140000000
H	-0.370692000000	6.543232000000	1.104078000000
H	0.109584000000	5.360850000000	-3.007511000000
H	-0.521010000000	7.081795000000	-1.320836000000
C	0.962426000000	1.627181000000	2.001098000000
C	-0.362000000000	1.862579000000	2.410333000000
C	1.855343000000	1.055556000000	2.920916000000
C	-0.771477000000	1.562479000000	3.710008000000
H	-1.081003000000	2.307347000000	1.728119000000
C	1.438212000000	0.739785000000	4.213750000000
H	2.875861000000	0.837825000000	2.630090000000
C	0.127072000000	0.996390000000	4.616456000000
H	-1.792163000000	1.786010000000	4.002374000000
H	2.142944000000	0.284277000000	4.903861000000
H	-0.193090000000	0.755100000000	5.626685000000
Pd	0.893053000000	0.227472000000	-1.292169000000
Br	-0.943043000000	0.757789000000	-2.945675000000
O	-4.309380000000	-0.028318000000	2.780426000000
C	-4.480198000000	1.232810000000	3.231828000000
C	-5.437459000000	1.259156000000	4.399864000000
O	-3.925172000000	2.203814000000	2.758412000000
H	-6.391292000000	0.803808000000	4.114680000000
H	-5.027983000000	0.669390000000	5.226978000000
H	-5.593641000000	2.290168000000	4.718890000000
H	-2.572306000000	0.505238000000	1.772214000000
C	6.615771000000	-0.048791000000	1.935162000000
H	7.257333000000	-0.934073000000	2.013464000000
H	7.024988000000	0.740063000000	2.576573000000
H	5.620565000000	-0.312859000000	2.305560000000

C	7.971946000000	0.778470000000	-0.013338000000
H	8.415787000000	1.551982000000	0.620973000000
H	8.621764000000	-0.099304000000	0.057965000000
H	7.977882000000	1.132423000000	-1.049613000000
C	-3.423449000000	2.546815000000	-1.471720000000
C	-4.681173000000	2.336999000000	-2.092551000000
C	-2.993989000000	3.879543000000	-1.260634000000
C	-5.455599000000	3.419140000000	-2.494319000000
H	-5.051066000000	1.326374000000	-2.234557000000
C	-3.774562000000	4.953470000000	-1.664339000000
H	-2.043515000000	4.053131000000	-0.770124000000
C	-5.008047000000	4.730340000000	-2.288957000000
H	-6.417720000000	3.243918000000	-2.968920000000
H	-3.422183000000	5.966695000000	-1.490881000000
H	-5.619203000000	5.570677000000	-2.607447000000
H	-1.710281000000	1.741741000000	-0.463641000000

TS4

B3LYP-D3 SCF energy:	-1191.554034 a.u.
B3LYP-D3 enthalpy:	-1191.088457 a.u.
B3LYP-D3 free energy:	-1191.178125 a.u.
M06 SCF energy in solution:	-1191.060768 a.u.
M06 enthalpy in solution:	-1190.583985 a.u.
M06 free energy in solution:	-1190.695270 a.u.

Cartesian coordinates

ATOM	X	Y	Z
O	-0.158749000000	0.049171000000	1.478978000000
O	-1.816648000000	-2.311306000000	1.785888000000
O	-0.277798000000	-2.477847000000	-1.180356000000
O	2.564805000000	-1.985660000000	-0.918740000000
O	3.051254000000	0.750311000000	-0.138080000000
O	3.988084000000	1.258629000000	1.861222000000
C	1.041603000000	0.645652000000	1.243771000000
H	1.368512000000	1.216557000000	2.105401000000
C	2.106548000000	-0.138627000000	0.514841000000
H	2.672859000000	-0.757415000000	1.225010000000
C	1.555189000000	-1.049149000000	-0.579046000000
H	1.291978000000	-0.430984000000	-1.450278000000
C	0.286712000000	-1.751528000000	-0.094518000000
H	0.539110000000	-2.417360000000	0.738860000000
C	-0.720051000000	-0.700033000000	0.387707000000
H	-0.931186000000	-0.014765000000	-0.441221000000
C	3.954184000000	1.371482000000	0.655277000000
C	4.889123000000	2.217928000000	-0.175885000000
H	5.405304000000	1.592449000000	-0.911207000000
H	5.613616000000	2.707001000000	0.475898000000
H	4.316394000000	2.969441000000	-0.729658000000
C	-2.044213000000	-1.272665000000	0.848497000000
H	-2.639317000000	-0.459719000000	1.291442000000
H	-2.585041000000	-1.651049000000	-0.032655000000

C	-3.015740000000	-2.816446000000	2.335835000000
H	-2.740677000000	-3.609135000000	3.036740000000
H	-3.573663000000	-2.036181000000	2.877896000000
H	-3.676502000000	-3.237215000000	1.559629000000
C	-0.523007000000	-3.849600000000	-0.895854000000
H	-1.011303000000	-4.269821000000	-1.779651000000
H	0.416732000000	-4.390477000000	-0.713110000000
H	-1.177566000000	-3.964733000000	-0.022591000000
C	2.667932000000	-2.259791000000	-2.307749000000
H	2.954371000000	-1.358140000000	-2.871649000000
H	3.456446000000	-3.009505000000	-2.419284000000
H	1.728465000000	-2.651902000000	-2.714682000000
C	-3.198179000000	1.413840000000	-2.129675000000
C	-2.008506000000	1.925409000000	-1.619422000000
C	-1.945213000000	2.462319000000	-0.314890000000
C	-3.139602000000	2.497048000000	0.434419000000
C	-4.330608000000	1.987318000000	-0.077602000000
C	-4.366537000000	1.434783000000	-1.360976000000
H	-3.216936000000	1.001719000000	-3.135398000000
H	-1.115150000000	1.917008000000	-2.237871000000
H	-3.117848000000	2.911774000000	1.439603000000
H	-5.233415000000	2.018528000000	0.527200000000
H	-5.294206000000	1.035940000000	-1.761929000000
C	-0.704776000000	2.938286000000	0.285065000000
H	-0.820725000000	3.523203000000	1.196827000000
C	0.558779000000	2.601949000000	-0.099622000000
H	0.762724000000	2.066637000000	-1.021698000000
H	1.417619000000	3.082711000000	0.356034000000

TS4'

B3LYP-D3 SCF energy:	-1191.554025 a.u.
B3LYP-D3 enthalpy:	-1191.088355 a.u.
B3LYP-D3 free energy:	-1191.176145 a.u.
M06 SCF energy in solution:	-1191.055642 a.u.
M06 enthalpy in solution:	-1190.578760 a.u.
M06 free energy in solution:	-1190.688900 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	1.537083000000	1.249345000000	0.467794000000
C	2.070591000000	0.253339000000	-0.582603000000
C	1.014984000000	-0.623357000000	-1.150329000000
C	0.126139000000	-0.778832000000	1.082932000000
C	0.255162000000	0.749042000000	1.159662000000
H	2.586671000000	0.771530000000	-1.392407000000
H	2.307932000000	1.355713000000	1.244527000000
H	0.978590000000	-1.248536000000	1.590508000000
H	-0.605555000000	1.187259000000	0.639940000000
O	0.126890000000	-1.206252000000	-0.297114000000
O	0.235037000000	1.102584000000	2.533919000000
O	1.246268000000	2.517068000000	-0.112678000000

C	-1.171536000000	-1.272219000000	1.718985000000
H	-2.021679000000	-0.924567000000	1.112838000000
H	-1.240399000000	-0.820739000000	2.711810000000
O	-1.209477000000	-2.673428000000	1.914944000000
C	-1.607020000000	-3.430418000000	0.781167000000
H	-1.766839000000	-4.454197000000	1.133222000000
H	-2.545260000000	-3.046261000000	0.353361000000
H	-0.844890000000	-3.430961000000	-0.007395000000
C	-0.065751000000	2.468650000000	2.772284000000
H	-1.026953000000	2.751118000000	2.315927000000
H	0.710336000000	3.138737000000	2.378691000000
H	-0.132006000000	2.589084000000	3.856735000000
C	2.384319000000	3.338609000000	-0.308786000000
H	2.026085000000	4.273858000000	-0.746039000000
H	2.890688000000	3.555641000000	0.644849000000
H	3.116137000000	2.887389000000	-0.995183000000
O	3.081102000000	-0.554039000000	0.144209000000
C	3.977360000000	-1.216890000000	-0.624029000000
O	4.011032000000	-1.149246000000	-1.834243000000
C	4.904067000000	-2.044615000000	0.234949000000
H	5.364966000000	-1.421633000000	1.007654000000
H	4.328955000000	-2.825455000000	0.744371000000
H	5.671303000000	-2.500205000000	-0.391986000000
H	1.288775000000	-1.282028000000	-1.967800000000
C	-1.228936000000	1.373573000000	-1.820648000000
C	-0.267061000000	0.777933000000	-2.584881000000
H	-0.464928000000	-0.133239000000	-3.139421000000
H	0.590539000000	1.354090000000	-2.917155000000
C	-2.460336000000	0.759686000000	-1.347186000000
C	-2.871266000000	-0.540220000000	-1.715651000000
C	-3.273632000000	1.465341000000	-0.433704000000
C	-4.034524000000	-1.098049000000	-1.196901000000
H	-2.262659000000	-1.123174000000	-2.399184000000
C	-4.433941000000	0.902211000000	0.092013000000
H	-2.976417000000	2.467895000000	-0.132590000000
C	-4.823247000000	-0.384854000000	-0.286311000000
H	-4.327414000000	-2.100925000000	-1.497506000000
H	-5.035119000000	1.467812000000	0.799288000000
H	-5.726497000000	-0.828879000000	0.122436000000
H	-1.005916000000	2.357529000000	-1.414330000000

TS4''

B3LYP-D3 SCF energy:	-1191.548729 a.u.
B3LYP-D3 enthalpy:	-1191.083498 a.u.
B3LYP-D3 free energy:	-1191.171851 a.u.
M06 SCF energy in solution:	-1191.053026 a.u.
M06 enthalpy in solution:	-1190.576581 a.u.
M06 free energy in solution:	-1190.687468 a.u.

Cartesian coordinates

ATOM	X	Y	Z

O	1.190660000000	-1.505359000000	-0.358206000000
O	3.815873000000	-2.196244000000	0.693774000000
O	4.031131000000	0.772430000000	-0.863844000000
O	2.018221000000	2.518518000000	0.291998000000
O	-0.653457000000	1.639023000000	-0.313845000000
O	-1.520029000000	1.718498000000	1.785403000000
C	0.144070000000	-0.616932000000	-0.451705000000
H	-0.477353000000	-0.691785000000	-1.344938000000
C	0.406758000000	0.756437000000	0.100841000000
H	0.461394000000	0.741654000000	1.194538000000
C	1.724451000000	1.334592000000	-0.431582000000
H	1.607601000000	1.552007000000	-1.503934000000
C	2.835491000000	0.299487000000	-0.251076000000
H	2.982772000000	0.134722000000	0.821955000000
C	2.444346000000	-1.037558000000	-0.896855000000
H	2.337238000000	-0.884481000000	-1.983007000000
C	-1.539371000000	2.056682000000	0.620630000000
C	-2.581083000000	2.951746000000	-0.001795000000
H	-2.145678000000	3.590160000000	-0.774140000000
H	-3.052585000000	3.552118000000	0.777866000000
H	-3.344009000000	2.316304000000	-0.466226000000
C	3.481379000000	-2.125053000000	-0.679520000000
H	3.067035000000	-3.083010000000	-1.032104000000
H	4.370345000000	-1.886924000000	-1.285025000000
C	4.713839000000	-3.248335000000	0.982688000000
H	4.914556000000	-3.213577000000	2.056617000000
H	4.283198000000	-4.230518000000	0.730210000000
H	5.664738000000	-3.136025000000	0.435904000000
C	5.124013000000	0.905142000000	0.036547000000
H	5.984088000000	1.224369000000	-0.558870000000
H	4.915717000000	1.662782000000	0.804941000000
H	5.352214000000	-0.049875000000	0.528659000000
C	2.534574000000	3.576810000000	-0.500732000000
H	1.800226000000	3.909076000000	-1.251041000000
H	2.740242000000	4.406140000000	0.181933000000
H	3.459721000000	3.285118000000	-1.012650000000
C	-2.439243000000	-2.152530000000	0.366919000000
C	-1.383321000000	-1.675593000000	1.082210000000
H	-1.445034000000	-0.756975000000	1.657515000000
H	-0.532168000000	-2.315598000000	1.288717000000
H	-2.326514000000	-3.119336000000	-0.123840000000
C	-3.699365000000	-1.464909000000	0.098839000000
C	-4.084092000000	-0.275891000000	0.756089000000
C	-4.585826000000	-2.000229000000	-0.857889000000
C	-5.289750000000	0.349685000000	0.450747000000
H	-3.439372000000	0.158658000000	1.512393000000
C	-5.791937000000	-1.372710000000	-1.161579000000
H	-4.313946000000	-2.919752000000	-1.371914000000
C	-6.150649000000	-0.190138000000	-0.511191000000
H	-5.564633000000	1.261752000000	0.975140000000
H	-6.453024000000	-1.807349000000	-1.907119000000

H -7.091669000000 0.301182000000 -0.743331000000

TS5

B3LYP-D3 SCF energy:	-881.870877 a.u.
B3LYP-D3 enthalpy:	-881.550156 a.u.
B3LYP-D3 free energy:	-881.621782 a.u.
M06 SCF energy in solution:	-881.561155 a.u.
M06 enthalpy in solution:	-881.232643 a.u.
M06 free energy in solution:	-881.321971 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	2.324314000000	-0.532040000000	0.836619000000
H	1.303809000000	-0.825215000000	-0.435957000000
H	2.964593000000	-1.286316000000	0.389430000000
C	1.699532000000	-0.875557000000	2.055239000000
C	1.800439000000	-2.203714000000	2.687878000000
C	2.283775000000	-3.339887000000	2.011409000000
C	1.374211000000	-2.351564000000	4.018102000000
C	2.336470000000	-4.577716000000	2.646927000000
H	2.600263000000	-3.263855000000	0.975055000000
C	1.432585000000	-3.589163000000	4.654952000000
H	0.973396000000	-1.487934000000	4.540489000000
C	1.911950000000	-4.709455000000	3.972725000000
H	2.711454000000	-5.442918000000	2.105601000000
H	1.092305000000	-3.681189000000	5.682893000000
H	1.953085000000	-5.676273000000	4.467017000000
C	-3.236121000000	2.739883000000	2.225178000000
C	-2.743229000000	1.921182000000	1.199859000000
C	-3.637808000000	1.021859000000	0.605213000000
C	-4.982234000000	0.916648000000	0.985043000000
C	-5.423789000000	1.733639000000	2.028866000000
C	-4.559673000000	2.639221000000	2.646141000000
C	-5.067233000000	-1.229677000000	-0.245732000000
C	-3.721389000000	-1.023451000000	-0.560800000000
C	-2.896344000000	-2.037093000000	-1.066550000000
C	-3.446358000000	-3.311408000000	-1.247207000000
C	-4.778252000000	-3.551907000000	-0.913868000000
C	-5.577197000000	-2.520421000000	-0.417616000000
H	-2.568058000000	3.438002000000	2.719103000000
H	-6.453693000000	1.675110000000	2.363412000000
H	-4.922764000000	3.270137000000	3.452606000000
H	-2.826727000000	-4.116358000000	-1.628218000000
H	-5.197416000000	-4.545356000000	-1.043961000000
H	-6.612489000000	-2.728766000000	-0.170537000000
C	-5.891777000000	-0.010822000000	0.172894000000
O	-3.151481000000	0.221523000000	-0.412773000000
P	-1.125197000000	-1.666261000000	-1.316928000000
P	-0.993126000000	1.971508000000	0.601859000000
C	-0.394343000000	-3.249245000000	-1.911551000000
C	-0.299745000000	-3.577026000000	-3.271385000000

C	0.128550000000	-4.134188000000	-0.952815000000
C	0.323802000000	-4.762925000000	-3.667006000000
H	-0.697927000000	-2.900536000000	-4.021546000000
C	0.742422000000	-5.321157000000	-1.351492000000
H	0.068604000000	-3.882715000000	0.103181000000
C	0.847800000000	-5.634671000000	-2.709781000000
H	0.401974000000	-5.002840000000	-4.724080000000
H	1.147473000000	-5.992917000000	-0.599384000000
H	1.337597000000	-6.553581000000	-3.020914000000
C	-1.056781000000	-0.568894000000	-2.789740000000
C	0.203643000000	-0.144107000000	-3.240095000000
C	-2.205301000000	-0.122260000000	-3.457726000000
C	0.315963000000	0.707503000000	-4.337937000000
H	1.106322000000	-0.461425000000	-2.730007000000
C	-2.091587000000	0.739779000000	-4.550804000000
H	-3.187810000000	-0.442326000000	-3.128092000000
C	-0.834260000000	1.154926000000	-4.993560000000
H	1.296827000000	1.055201000000	-4.639876000000
H	-2.990074000000	1.088218000000	-5.053162000000
H	-0.749843000000	1.831436000000	-5.839930000000
C	-0.106313000000	2.604299000000	2.091863000000
C	0.870574000000	3.611824000000	2.016247000000
C	-0.271184000000	1.920104000000	3.312479000000
C	1.643294000000	3.943617000000	3.132253000000
H	1.041203000000	4.133655000000	1.080093000000
C	0.501329000000	2.256533000000	4.424531000000
H	-0.991851000000	1.109466000000	3.380034000000
C	1.458238000000	3.273081000000	4.342521000000
H	2.390679000000	4.729022000000	3.051760000000
H	0.354445000000	1.718784000000	5.357874000000
H	2.057587000000	3.533915000000	5.210796000000
C	-1.059655000000	3.446690000000	-0.519390000000
C	-0.855579000000	3.210849000000	-1.885359000000
C	-1.328747000000	4.759092000000	-0.091111000000
C	-0.903348000000	4.260786000000	-2.806958000000
H	-0.648245000000	2.206349000000	-2.235699000000
C	-1.372927000000	5.807791000000	-1.008370000000
H	-1.496488000000	4.959106000000	0.963277000000
C	-1.158600000000	5.559949000000	-2.370403000000
H	-0.720497000000	4.052467000000	-3.856477000000
H	-1.578207000000	6.818610000000	-0.664634000000
H	-1.190260000000	6.380161000000	-3.083089000000
Pd	0.074568000000	-1.002500000000	0.556284000000
Br	-1.689739000000	-1.442722000000	2.315163000000
C	2.760289000000	0.897984000000	0.557394000000
C	4.292557000000	1.018706000000	0.781429000000
C	2.450762000000	1.340015000000	-0.875170000000
H	2.235381000000	1.574257000000	1.233699000000
C	5.070846000000	0.252311000000	-0.293923000000
O	4.698764000000	0.494237000000	2.036223000000
H	4.571455000000	2.080084000000	0.709625000000

O	3.116099000000	0.546402000000	-1.807605000000
H	1.391017000000	1.254541000000	-1.113690000000
O	2.810336000000	2.740953000000	-0.940247000000
C	4.546753000000	0.524846000000	-1.716612000000
H	4.989783000000	-0.822708000000	-0.091402000000
O	6.437538000000	0.639343000000	-0.323473000000
C	4.348919000000	1.299234000000	3.150602000000
C	2.463228000000	3.434636000000	-2.061430000000
C	5.028309000000	-0.542013000000	-2.700269000000
H	4.940652000000	1.500210000000	-2.036254000000
C	7.299993000000	-0.163184000000	0.472553000000
H	4.816098000000	0.840414000000	4.025630000000
H	4.726131000000	2.327515000000	3.035556000000
H	3.265153000000	1.345058000000	3.311716000000
O	2.063262000000	2.921891000000	-3.079718000000
C	2.596579000000	4.918413000000	-1.827579000000
H	6.118300000000	-0.469366000000	-2.761685000000
O	4.744588000000	-1.872497000000	-2.303192000000
H	4.598350000000	-0.327633000000	-3.690920000000
H	8.311286000000	0.224976000000	0.320313000000
H	7.270201000000	-1.216143000000	0.152329000000
H	7.036872000000	-0.106391000000	1.534113000000
H	3.408895000000	5.145747000000	-1.133292000000
H	2.745381000000	5.426552000000	-2.781790000000
H	1.653617000000	5.272644000000	-1.392568000000
C	3.430251000000	-2.341675000000	-2.576102000000
H	3.459931000000	-3.432912000000	-2.507781000000
H	2.691966000000	-1.964687000000	-1.860213000000
H	3.101601000000	-2.057274000000	-3.587077000000
H	1.400639000000	-0.062620000000	2.712645000000
C	-6.308038000000	0.746162000000	-1.121135000000
H	-6.931195000000	0.103470000000	-1.754081000000
H	-6.875113000000	1.648984000000	-0.866852000000
H	-5.426766000000	1.047486000000	-1.696701000000
C	-7.158226000000	-0.408159000000	0.946817000000
H	-7.750058000000	0.475680000000	1.202574000000
H	-7.802463000000	-1.046242000000	0.334400000000
H	-6.911694000000	-0.943124000000	1.869636000000

TS6

B3LYP-D3 SCF energy:	-1191.557238 a.u.
B3LYP-D3 enthalpy:	-1191.091870 a.u.
B3LYP-D3 free energy:	-1191.181100 a.u.
M06 SCF energy in solution:	-1191.064177 a.u.
M06 enthalpy in solution:	-1190.587613 a.u.
M06 free energy in solution:	-1190.698585 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-0.465812000000	-0.565987000000	-1.323270000000
C	0.160218000000	0.513592000000	-0.495153000000

C	-0.762433000000	1.452868000000	0.198384000000
O	-1.818031000000	0.804694000000	0.846017000000
C	-2.552964000000	-0.118712000000	0.032827000000
C	-3.630671000000	-0.726059000000	0.915386000000
H	-4.328560000000	-1.292392000000	0.280145000000
O	-3.022138000000	-1.573636000000	1.872671000000
C	-3.954768000000	-2.156384000000	2.757627000000
H	-3.392167000000	-2.794817000000	3.444092000000
H	-4.495232000000	-1.393440000000	3.341134000000
H	-4.696939000000	-2.772009000000	2.222513000000
H	-4.184597000000	0.087694000000	1.409991000000
C	-1.643892000000	-1.200601000000	-0.577705000000
H	-1.255702000000	-1.825199000000	0.233162000000
O	-2.457829000000	-1.962332000000	-1.457355000000
C	-2.186610000000	-3.357059000000	-1.437135000000
H	-2.875942000000	-3.819824000000	-2.149366000000
H	-2.366957000000	-3.780980000000	-0.437386000000
H	-1.153149000000	-3.568518000000	-1.735489000000
H	-3.044784000000	0.423857000000	-0.787437000000
H	-0.265339000000	2.058685000000	0.955185000000
O	-1.306962000000	2.359642000000	-0.822878000000
C	-1.606941000000	3.627996000000	-0.429044000000
O	-1.381270000000	4.074967000000	0.671576000000
C	-2.246763000000	4.387745000000	-1.568096000000
H	-2.427421000000	5.419011000000	-1.262834000000
H	-1.597647000000	4.361654000000	-2.449141000000
H	-3.192604000000	3.909829000000	-1.844849000000
H	1.130976000000	0.897999000000	-0.789369000000
O	0.456506000000	-1.607589000000	-1.660284000000
C	1.277225000000	-1.308545000000	-2.777253000000
H	1.893378000000	-2.192973000000	-2.960941000000
H	0.672466000000	-1.099490000000	-3.672910000000
H	1.941646000000	-0.452823000000	-2.589424000000
H	-0.876620000000	-0.140174000000	-2.259596000000
C	2.131463000000	0.031044000000	1.793308000000
C	1.003710000000	-0.659096000000	1.473468000000
H	1.032661000000	-1.514847000000	0.807906000000
H	0.083332000000	-0.518456000000	2.030359000000
C	3.423305000000	-0.090689000000	1.124029000000
C	3.610442000000	-0.899670000000	-0.017980000000
C	4.528867000000	0.639560000000	1.602595000000
C	4.852174000000	-0.976256000000	-0.640837000000
H	2.772191000000	-1.458025000000	-0.422070000000
C	5.772003000000	0.559019000000	0.979001000000
H	4.404006000000	1.274580000000	2.476970000000
C	5.941169000000	-0.250143000000	-0.146809000000
H	4.972637000000	-1.603943000000	-1.520476000000
H	6.609696000000	1.130442000000	1.370403000000
H	6.908938000000	-0.312169000000	-0.637016000000
H	2.071199000000	0.794634000000	2.568429000000

TS7

B3LYP-D3 SCF energy:	-1191.554503 a.u.
B3LYP-D3 enthalpy:	-1191.089089 a.u.
B3LYP-D3 free energy:	-1191.178061 a.u.
M06 SCF energy in solution:	-1191.061139 a.u.
M06 enthalpy in solution:	-1190.584507 a.u.
M06 free energy in solution:	-1190.695555 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	0.738151000000	-0.584285000000	1.010649000000
C	-0.106049000000	0.114508000000	-0.005068000000
C	0.508785000000	1.305724000000	-0.657928000000
O	1.794544000000	1.030128000000	-1.160132000000
C	2.692397000000	0.445379000000	-0.205447000000
C	4.027486000000	0.237806000000	-0.900030000000
H	4.789387000000	0.011588000000	-0.137306000000
O	3.923361000000	-0.823790000000	-1.831351000000
C	5.104700000000	-1.004953000000	-2.584583000000
H	4.928544000000	-1.844194000000	-3.262574000000
H	5.348812000000	-0.109763000000	-3.178689000000
H	5.968882000000	-1.239259000000	-1.940736000000
H	4.310130000000	1.174598000000	-1.405756000000
C	2.115274000000	-0.862074000000	0.374225000000
H	1.973493000000	-1.578091000000	-0.442133000000
O	3.022593000000	-1.366575000000	1.349350000000
C	3.602040000000	-2.619234000000	1.006629000000
H	4.319536000000	-2.860416000000	1.796153000000
H	4.120426000000	-2.567799000000	0.040480000000
H	2.840322000000	-3.411100000000	0.959802000000
H	2.855219000000	1.149635000000	0.623297000000
H	-0.081652000000	1.680681000000	-1.492088000000
O	0.661126000000	2.384841000000	0.320557000000
C	-0.182174000000	3.440296000000	0.235441000000
O	-1.085147000000	3.537573000000	-0.566771000000
C	0.156134000000	4.465312000000	1.293384000000
H	-0.520589000000	5.315847000000	1.205694000000
H	0.065178000000	4.016865000000	2.288541000000
H	1.193585000000	4.794922000000	1.177560000000
H	-0.725888000000	-0.517313000000	-0.632450000000
O	0.088005000000	-1.790239000000	1.400899000000
C	0.329803000000	-2.180730000000	2.746071000000
H	-0.202533000000	-3.124045000000	2.896463000000
H	1.397668000000	-2.322554000000	2.943487000000
H	-0.064685000000	-1.434991000000	3.454519000000
H	0.904097000000	0.062255000000	1.888937000000
C	-3.793473000000	-0.167620000000	-0.131827000000
C	-4.932273000000	0.115297000000	-0.910478000000
C	-5.672124000000	-0.905097000000	-1.503522000000
C	-5.283400000000	-2.236931000000	-1.342158000000
C	-4.144927000000	-2.534670000000	-0.586529000000

C	-3.405663000000	-1.517589000000	0.010945000000
H	-5.236917000000	1.151088000000	-1.042603000000
H	-6.550508000000	-0.661084000000	-2.095526000000
H	-5.855655000000	-3.034891000000	-1.807739000000
H	-3.826211000000	-3.567456000000	-0.469668000000
H	-2.507594000000	-1.768271000000	0.568914000000
C	-3.044179000000	0.932870000000	0.471586000000
H	-3.268659000000	1.930267000000	0.097552000000
C	-2.048005000000	0.798401000000	1.380027000000
H	-1.549458000000	1.670078000000	1.788619000000
H	-1.835797000000	-0.146537000000	1.868509000000

TS8

B3LYP-D3 SCF energy:	-1191.550971 a.u.
B3LYP-D3 enthalpy:	-1191.085368 a.u.
B3LYP-D3 free energy:	-1191.173100 a.u.
M06 SCF energy in solution:	-1191.057882 a.u.
M06 enthalpy in solution:	-1190.581114 a.u.
M06 free energy in solution:	-1190.691200 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-0.044167000000	-0.510383000000	1.008022000000
C	-0.321831000000	0.941338000000	0.749126000000
C	-1.765459000000	1.337344000000	0.644850000000
O	-2.615354000000	0.288317000000	0.331976000000
C	-2.049633000000	-0.662748000000	-0.575975000000
C	-3.163721000000	-1.562697000000	-1.080165000000
H	-2.755957000000	-2.193503000000	-1.887361000000
O	-3.653954000000	-2.357744000000	-0.020191000000
C	-4.696590000000	-3.219535000000	-0.421496000000
H	-4.998801000000	-3.791352000000	0.459916000000
H	-5.567493000000	-2.659205000000	-0.799400000000
H	-4.369578000000	-3.919900000000	-1.208597000000
H	-3.964528000000	-0.933621000000	-1.501746000000
C	-0.933904000000	-1.436032000000	0.140260000000
H	-1.396701000000	-2.167743000000	0.812122000000
O	-0.192740000000	-2.098165000000	-0.884303000000
C	0.500544000000	-3.247198000000	-0.423559000000
H	1.006202000000	-3.681002000000	-1.290901000000
H	-0.195278000000	-3.986582000000	-0.000774000000
H	1.254602000000	-2.996814000000	0.336644000000
H	-1.632730000000	-0.142971000000	-1.448521000000
H	-2.128692000000	1.776972000000	1.579754000000
O	-1.963025000000	2.366140000000	-0.397312000000
C	-1.591901000000	3.621716000000	-0.075620000000
O	-1.072904000000	3.928496000000	0.978483000000
C	-1.896464000000	4.578251000000	-1.206340000000
H	-1.654346000000	5.595519000000	-0.896652000000
H	-1.304184000000	4.310500000000	-2.088525000000
H	-2.951603000000	4.507660000000	-1.487807000000

H	0.309263000000	1.681133000000	1.226093000000
O	-0.303711000000	-0.873012000000	2.378811000000
C	0.651009000000	-0.370972000000	3.295455000000
H	0.412669000000	-0.809583000000	4.268301000000
H	1.676197000000	-0.661099000000	3.011852000000
H	0.615077000000	0.724589000000	3.386192000000
H	1.010444000000	-0.721143000000	0.782586000000
C	2.122834000000	1.480354000000	-0.951905000000
C	0.840707000000	1.194322000000	-1.326862000000
H	0.156395000000	1.989384000000	-1.594628000000
H	0.556742000000	0.196431000000	-1.642179000000
C	3.188438000000	0.518171000000	-0.700887000000
C	3.061843000000	-0.859523000000	-0.989074000000
C	4.403849000000	0.963234000000	-0.141476000000
C	4.098929000000	-1.743901000000	-0.712703000000
H	2.141394000000	-1.234338000000	-1.423655000000
C	5.442103000000	0.075687000000	0.131222000000
H	4.524794000000	2.020198000000	0.085264000000
C	5.295115000000	-1.284492000000	-0.150188000000
H	3.976770000000	-2.799753000000	-0.941149000000
H	6.367175000000	0.445502000000	0.565731000000
H	6.103166000000	-1.979052000000	0.062271000000
H	2.372281000000	2.519895000000	-0.740637000000

TS9

B3LYP-D3 SCF energy:	-6154.490635 a.u.
B3LYP-D3 enthalpy:	-6153.378407 a.u.
B3LYP-D3 free energy:	-6153.552065 a.u
M06 SCF energy in solution:	-6155.702391 a.u.
M06 enthalpy in solution:	-6154.561213 a.u.
M06 free energy in solution:	-6154.780507 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-1.820486000000	1.591434000000	-1.124098000000
C	4.715848000000	2.627558000000	0.316920000000
C	3.816677000000	1.549775000000	0.350952000000
C	4.357816000000	0.263806000000	0.204139000000
C	5.717775000000	0.017788000000	-0.023405000000
C	6.572806000000	1.121471000000	-0.076761000000
C	6.077027000000	2.414545000000	0.105553000000
C	5.048629000000	-2.184317000000	-0.912263000000
C	3.730176000000	-1.841286000000	-0.603956000000
C	2.607941000000	-2.492412000000	-1.135611000000
C	2.845822000000	-3.525464000000	-2.052742000000
C	4.150847000000	-3.872583000000	-2.407509000000
C	5.243520000000	-3.213042000000	-1.840191000000
H	4.343253000000	3.639369000000	0.433791000000
H	7.633184000000	0.979538000000	-0.256270000000
H	6.756177000000	3.261955000000	0.073772000000

H	2.007620000000	-4.052817000000	-2.495953000000
H	4.318030000000	-4.669373000000	-3.127017000000
H	6.248395000000	-3.508703000000	-2.122417000000
C	6.154288000000	-1.446882000000	-0.148026000000
O	3.490862000000	-0.805780000000	0.281000000000
P	0.948361000000	-1.847656000000	-0.651594000000
P	1.979186000000	1.766316000000	0.426775000000
C	-0.201361000000	-3.108113000000	-1.371642000000
C	-0.216607000000	-4.452376000000	-0.967390000000
C	-1.121619000000	-2.679205000000	-2.338618000000
C	-1.143074000000	-5.345047000000	-1.505759000000
H	0.497659000000	-4.796194000000	-0.224010000000
C	-2.055024000000	-3.572120000000	-2.873468000000
H	-1.099108000000	-1.647797000000	-2.677281000000
C	-2.069986000000	-4.903658000000	-2.455716000000
H	-1.146639000000	-6.383078000000	-1.182077000000
H	-2.769649000000	-3.221139000000	-3.613291000000
H	-2.797338000000	-5.597983000000	-2.869011000000
C	0.904611000000	-2.270763000000	1.150573000000
C	-0.031154000000	-1.594784000000	1.944859000000
C	1.772105000000	-3.189534000000	1.760321000000
C	-0.097323000000	-1.824788000000	3.317590000000
H	-0.709450000000	-0.881016000000	1.493722000000
C	1.712131000000	-3.414511000000	3.137640000000
H	2.511144000000	-3.717606000000	1.164167000000
C	0.780229000000	-2.728816000000	3.920587000000
H	-0.818225000000	-1.272569000000	3.911666000000
H	2.399397000000	-4.120028000000	3.598468000000
H	0.744408000000	-2.891868000000	4.994938000000
C	1.826015000000	3.596454000000	0.198526000000
C	1.754019000000	4.525433000000	1.247577000000
C	1.737484000000	4.057686000000	-1.126752000000
C	1.591952000000	5.886843000000	0.975387000000
H	1.816947000000	4.186152000000	2.276944000000
C	1.598414000000	5.418515000000	-1.396439000000
H	1.741054000000	3.337273000000	-1.941779000000
C	1.520495000000	6.336886000000	-0.345232000000
H	1.528805000000	6.595654000000	1.797263000000
H	1.522891000000	5.757650000000	-2.425884000000
H	1.396105000000	7.396413000000	-0.554115000000
C	1.572178000000	1.537699000000	2.209548000000
C	0.267075000000	1.846250000000	2.632528000000
C	2.472828000000	1.004094000000	3.139824000000
C	-0.122228000000	1.654009000000	3.956292000000
H	-0.452683000000	2.254296000000	1.926573000000
C	2.078691000000	0.792831000000	4.463225000000
H	3.483112000000	0.751215000000	2.833961000000
C	0.787937000000	1.124012000000	4.876216000000
H	-1.135356000000	1.905486000000	4.251874000000
H	2.786579000000	0.369716000000	5.171330000000
H	0.486929000000	0.961355000000	5.908036000000

Pd	0.750098000000	0.473127000000	-1.052704000000
Br	-0.455575000000	1.010167000000	-3.281246000000
H	-1.117644000000	1.554192000000	-0.293023000000
C	6.234265000000	-2.053590000000	1.282257000000
H	6.511924000000	-3.112632000000	1.228076000000
H	6.986227000000	-1.522660000000	1.877474000000
H	5.270490000000	-1.977038000000	1.795017000000
C	7.523928000000	-1.588792000000	-0.826620000000
H	8.299188000000	-1.080769000000	-0.244681000000
H	7.815698000000	-2.641780000000	-0.888122000000
H	7.517417000000	-1.169974000000	-1.838433000000
C	-2.218213000000	2.929214000000	-1.506947000000
C	-1.625090000000	4.037304000000	-0.867287000000
C	-3.227171000000	3.161502000000	-2.468790000000
C	-2.034963000000	5.333287000000	-1.165169000000
H	-0.837154000000	3.874249000000	-0.140208000000
C	-3.635813000000	4.456677000000	-2.760237000000
H	-3.676036000000	2.319380000000	-2.985365000000
C	-3.040656000000	5.546966000000	-2.111377000000
H	-1.558356000000	6.171212000000	-0.665834000000
H	-4.412746000000	4.623949000000	-3.501164000000
H	-3.358986000000	6.558608000000	-2.348796000000
C	-2.750416000000	0.413571000000	-1.209953000000
C	-3.970122000000	0.591449000000	-0.265672000000
H	-2.195575000000	-0.486540000000	-0.941334000000
H	-3.134317000000	0.271979000000	-2.220287000000
C	-4.988066000000	-0.552813000000	-0.445644000000
C	-3.534714000000	0.679083000000	1.200028000000
H	-4.466077000000	1.533512000000	-0.521978000000
C	-4.455185000000	-1.850767000000	0.166881000000
H	-5.911806000000	-0.281433000000	0.088209000000
O	-5.256907000000	-0.699023000000	-1.833483000000
O	-3.102552000000	-0.539306000000	1.727392000000
O	-4.675339000000	1.172236000000	1.949598000000
H	-2.709139000000	1.372671000000	1.348945000000
C	-4.066147000000	-1.604914000000	1.633016000000
H	-3.570876000000	-2.180536000000	-0.387067000000
O	-5.468384000000	-2.852477000000	0.135410000000
C	-6.596077000000	-1.049360000000	-2.146288000000
C	-4.416978000000	1.952039000000	3.032430000000
H	-4.969987000000	-1.312697000000	2.186319000000
C	-3.495074000000	-2.832382000000	2.319754000000
C	-5.080115000000	-4.033575000000	-0.557170000000
H	-7.301598000000	-0.272886000000	-1.808905000000
H	-6.651813000000	-1.124628000000	-3.236057000000
H	-6.883395000000	-2.004611000000	-1.694038000000
C	-5.700348000000	2.292497000000	3.750314000000
O	-3.311929000000	2.323248000000	3.358686000000
H	-4.324971000000	-3.529157000000	2.519689000000
H	-3.060054000000	-2.525589000000	3.284082000000
O	-2.522917000000	-3.448216000000	1.502707000000

H	-4.918581000000	-3.832876000000	-1.625611000000
H	-5.901306000000	-4.747587000000	-0.443790000000
H	-4.157818000000	-4.455223000000	-0.139546000000
H	-5.487303000000	2.967724000000	4.579621000000
H	-6.406966000000	2.757099000000	3.055258000000
H	-6.166725000000	1.375272000000	4.125854000000
C	-1.939148000000	-4.575124000000	2.129597000000
H	-1.223742000000	-4.994276000000	1.423102000000
H	-1.408583000000	-4.290039000000	3.048140000000
H	-2.700117000000	-5.335783000000	2.372052000000

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