Supporting Information

Highly Stereoselective Synthesis of α-Glycosylated Carboxylic Acids by Phenanthroline Catalysis

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1. General Information

Methods and Reagents

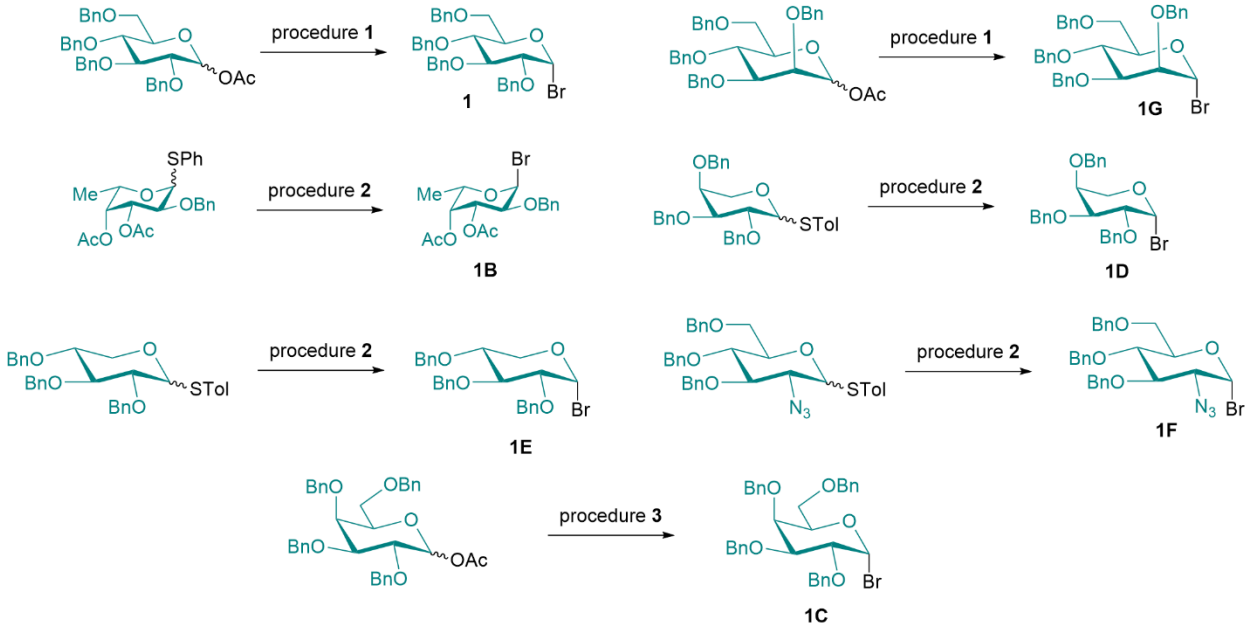
All reactions were performed in oven-dried Schlenk flasks fitted with glass stoppers under positive argon/nitrogen pressure. Organic solutions were concentrated by rotary evaporation below 40 °C at 25 torr. Analytical thin-layer chromatography (TLC) was routinely used to monitor the progress of the reactions and performed using pre-coated glass plates with silica gel 60 F_{254} from Sigma Aldrich. Visualization was accomplished by using UV light, potassium permanganate, or 5% sulfuric acid in methanol. Flash chromatography was performed on silica gel flash chromatography columns or a Biotage Isolera One system using normal phase pre-column cartridges and Sfär Silica HC D 10 g column. The α:β ratio was determined by crude NMR. Dry solvents were obtained from a SG Waters solvent system utilizing activated alumina columns under an argon pressure or purchased from Sigma-Aldrich in seal bottles. All other reagents were used as received from Sigma Aldrich, Alfa Aesar, Acros Organics, TCI, Amreed, and AA Blocks, unless otherwise noted.

Instrumentation

All proton (^{1}H) nuclear magnetic resonance spectra were recorded on a 400 MHz, 500 MHz or 600 MHz spectrometer. All carbon (^{13}C) nuclear magnetic resonance spectra were recorded on a 101 MHz or 126 MHz NMR spectrometer. All proton decoupled fluorine (^{19}F) nuclear magnetic resonance spectra were recorded on a 471 MHz NMR spectrometer. Chemical shifts are expressed in parts per million (δ scale) and are referenced to residual $CHCl_3$ (^{1}H: δ 7.26 ppm, ^{13}C: δ 77.16 ppm), CD_2Cl_2 (^{1}H: δ 5.32 ppm, ^{13}C: δ 53.84 ppm), C_6D_6 (^{1}H: δ 7.16 ppm) in the NMR solvent. Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and bs = broad singlet), integration, and coupling constant in hertz (Hz). High-resolution mass spectrometry utilizing electrospray ionization (TOF ESI+) was performed to confirm the identity of the synthesized compounds at Wayne State University. UV-visible absorption measurements were performed utilizing a Thermo Scientific Genesys 50 UV−Vis spectrophotometer.

2. Experimental Procedures

2.1 General Procedure for Preparation of Glycosyl Bromide Donors



General Procedure 1: A 25 mL round bottle flask was charged with glycosyl acetate (0.2 mmol, 1 equiv) and dichloromethane (DCM) (2 mL, 0.1 M). The solution was cooled to 0 °C in an ice bath, and 33% HBr/acetic acid (105 µL, 0.6 mmol, 3 equiv) was added to the flask. The resulting solution was stirred at 0 °C for 1 h under an argon balloon. The reaction was monitored by TLC. Upon completion, the reaction mixture was diluted with ethyl acetate, washed with water, saturated aqueous $NaHCO_3$ (2x), brine, and dried over Na_2SO_4. The organic layer was concentrated in *vacuo*, and the crude glycosyl bromide donor was used for the next step without further purification.[1]

General Procedure 2: A 10 mL oven-dried Schlenk flask was charged with thioglycoside (0.2 mmol, 1 equiv) and dried dichloromethane (DCM) (2 mL, 0.1 M). The solution was cooled to 0 °C in an ice bath, and Br_2 (20 µL, 0.4 mmol, 2 equiv) was added. The resulting solution was stirred in an ice bath and monitored by TLC. Upon completion (~30 min), the reaction mixture was quenched with cyclohexene and then concentrated in *vacuo* to give glycosyl bromide as pale yellow syrup. The crude glycosyl bromide donor was used without further purification.[2]

General Procedure 3: A 25 mL round bottle flask was charged with glycosyl acetate (0.3 mmol, 1 equiv), a stir bar, and evacuated, filled with argon (3x), and then cooled to -40 °C. After adding dry CH_2Cl_2 (3 mL, 0.1 M) via a syringe, TMSBr (118 µL, 0.9 mmol, 3 equiv) was added dropwise.

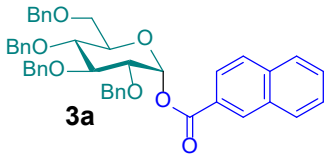
The reaction mixture was then slowly warmed to room temperature. After stirring at room temperature for 2 h, the resulting mixture was poured into an ice/water mixture. The organic phase was collected, and the aqueous phase was extracted with CH_2Cl_2 (2x). The combined organic layers were washed with saturated aqueous $NaHCO_3$, brine, and dried over Na_2SO_4. The organic layer was concentrated in *vacuo*, and the crude glycosyl bromide donor was used for the next step without further purification.[3]

2.2 Phenanthroline-Catalyzed Glycosylation for Glycosyl Ester Synthesis

General Procedure A:
A 10 mL oven-dried Schlenk flask was charged with glycosyl bromide (0.2 mmol, 2 equiv) and kept under high vacuum for 1 h. The reaction flask was then backfilled with argon (3x). Carboxylic acid (0.1 mmol, 1 equiv), 2,9-dibutyl-1,10-phenanthroline **C6** (5.8 mg, 0.02 mmol, 10 mol% with respect to glycosyl bromide), DTBMP (41.1 mg, 0.2 mmol, 2 equiv), a mixture of MTBE/DCE solvent (5:1, 0.2 mL, 0.5 M) were then added to the reaction flask. The resulting mixture was stirred at 50 °C for 18 h. Upon completion, the reaction mixture was diluted with dichloromethane, washed with water, saturated aqueous $NaHCO_3$ (2x), dried over Na_2SO_4, concentrated *in vacuo*. The crude product was purified by silica gel flash chromatography (100 mL of dichloromethane and then 2% - 30% ethyl acetate/hexanes) to give the desired product.

General Procedure B:
A 10 mL oven-dried Schlenk flask was charged with glycosyl bromide (0.3 mmol, 3 equiv) and kept under high vacuum for 1 h. The flask was then backfilled with argon (3x). Carboxylic acid (0.1 mmol, 1 equiv), 2,9-dibutyl-1,10-phenanthroline **C6** (5.8 mg, 0.02 mmol, 7 mol% with respect to glycosyl bromide), DTBMP (41.1 mg, 0.2 mmol, 2 equiv), a mixture of MTBE/DCE solvent (5:1, 0.2 mL, 0.5 M) were added to the reaction flask. The resulting mixture was stirred at 50 °C for 18 h. Upon completion, the reaction mixture was diluted with dichloromethane, washed with water, saturated aqueous $NaHCO_3$ (2x), dried over Na_2SO_4, concentrated *in vacuo*. The crude product was purified by silica gel flash chromatography (100 mL of dichloromethane and then 2% - 30% ethyl acetate/hexanes) to give the desired product.

3. Spectral Characterization of Products



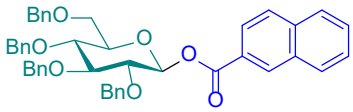
3a

(2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl 2-naphthoate (3a): This compound was prepared according to the General Procedure A. After purification by silica gel column chromatography, compound **3a** was isolated as a white semi-solid (56 mg, 81%, α:β 19:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (d, *J* = 1.7 Hz, 1H), 8.10 (dd, *J* = 8.6, 1.7 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.91 (dd, *J* = 8.6, 2.5 Hz, 2H), 7.67–7.54 (m, 2H), 7.44–7.23 (m, 18H), 7.19 (dd, *J* = 7.2, 2.4 Hz, 2H), 6.70 (d, *J* = 3.5 Hz, 1H), 5.04 (d, *J* = 10.9 Hz, 1H), 4.91 (d, *J* = 10.7 Hz, 2H), 4.80 (d, *J* = 11.6 Hz, 1H), 4.71 (d, *J* = 11.6 Hz, 1H), 4.65 (d, *J* = 12.1 Hz, 1H), 4.58 (d, *J* = 10.5 Hz, 1H), 4.51 (d, *J* = 12.1 Hz, 1H), 4.16 (t, *J* = 9.3 Hz, 1H), 4.11–4.03 (m, 1H), 3.91–3.78 (m, 3H), 3.70 (dd, *J* = 10.9, 2.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.3, 138.8, 138.1, 138.0, 137.8, 135.9, 132.6, 131.7, 129.6, 128.6, 128.6, 128.6, 128.5, 128.5, 128.5, 128.5, 128.3, 128.2, 128.1, 128.1, 128.0, 127.9, 127.9, 127.8, 127.1, 126.9, 125.6, 91.0, 82.0, 79.3, 77.2, 75.8, 75.7, 73.8, 73.3, 73.3, 68.3.

HRMS (TOF ESI+) *m/z* calcd for $C_{45}H_{46}O_7N$ $[(M+ NH_4)^+]$ 712.3269, found 712.3258.

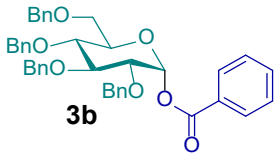


3a" β

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.62 (d, *J* = 1.6 Hz, 1H), 8.06 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.5 Hz, 2H), 7.61–7.51 (m, 2H), 7.36–7.09 (m, 20H), 5.96 (d, *J* = 7.3 Hz, 1H), 4.93 (d, *J* = 11.0 Hz, 1H), 4.89–4.78 (m, 4H), 4.59 (dd, *J* = 20.4, 11.4 Hz, 2H), 4.47 (d, *J* = 12.1 Hz, 1H), 3.88–3.80 (m, 3H), 3.80–3.74 (m, 2H), 3.68 (dt, *J* = 9.1, 2.9 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 165.2, 138.6, 138.2, 138.0, 137.9, 135.9, 132.5, 132.0, 129.6, 128.7, 128.6, 128.5, 128.5, 128.5, 128.4, 128.2, 128.1, 128.0, 128.0, 127.9, 127.9, 127.9, 127.8, 127.8, 126.9, 126.7, 125.5, 94.9, 85.1, 81.0, 77.5, 77.4, 75.8, 75.8, 75.1, 73.7, 68.3.

HRMS (TOF ESI+) *m/z* calcd for $C_{45}H_{42}O_7Na$ $[(M+ Na)^+]$ 717.2823, found 717.2818.



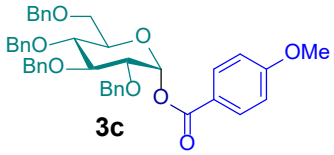
3b

(2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl benzoate (3b): This compound was prepared according to the General Procedure A. After purification by silica gel column chromatography, compound **3b** was isolated as a viscous oil (48 mg, 74%, α:β 16:1). The spectral data match with literature.[4]

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.12–8.05 (m, 2H), 7.63–7.56 (m, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.38–7.22 (m, 18H), 7.16 (dd, *J* = 7.5, 2.0 Hz, 2H), 6.61 (d, *J* = 3.5 Hz, 1H), 4.99 (d, *J* = 10.9 Hz, 1H), 4.87 (dd, *J* = 10.7, 6.7 Hz, 2H), 4.76 (d, *J* = 11.7 Hz, 1H), 4.67 (d, *J* = 11.6 Hz, 1H), 4.61 (d, *J* = 12.1 Hz, 1H), 4.54 (d, *J* = 10.5 Hz, 1H), 4.48 (d, *J* = 12.2 Hz, 1H), 4.07 (t, *J* = 9.4 Hz, 1H), 4.01–3.95 (m, 1H), 3.86–3.75 (m, 3H), 3.66 (dd, *J* = 10.9, 2.0 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 165.1, 138.8, 138.2, 138.0, 137.8, 133.6, 130.1, 129.9, 128.6, 128.6, 128.6, 128.5, 128.3, 128.2, 128.1, 128.1, 128.0, 128.0, 127.9, 127.8, 90.8, 82.0, 79.2, 77.4, 75.9, 75.6, 73.7, 73.3, 73.2, 68.3.

HRMS (TOF ESI+) *m/z* calcd for $C_{41}H_{44}O_7N$ $[(M+ NH_4)^+]$ 662.3112, found 662.3102.



3c

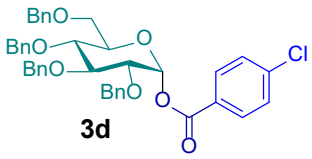
(2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl 4-methoxybenzoate (3c): This compound was prepared according to the General Procedure A. After purification by silica gel column chromatography, compound **3c** was isolated as a white semi-solid (56 mg, 83%, α:β >20:1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.8 Hz, 2H), 7.41–7.22 (m, 18H), 7.20–7.12 (m, 2H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.59 (d, *J* = 3.5 Hz, 1H), 5.00 (d, *J* = 10.9 Hz, 1H), 4.87 (dd, *J* = 10.7, 7.5 Hz, 2H), 4.76 (d, *J* = 11.6 Hz, 1H), 4.66 (d, *J* = 11.6 Hz, 1H), 4.62 (d, *J* = 12.1 Hz, 1H), 4.54 (d, *J* = 10.5 Hz, 1H), 4.48 (d, *J* = 12.1 Hz, 1H), 4.06 (t, *J* = 9.4 Hz, 1H), 3.97 (d, *J* = 10.0 Hz, 1H), 3.87 (s, 3H), 3.85–3.75 (m, 3H), 3.66 (dd, *J* = 11.0, 2.0 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 164.8, 163.9, 138.8, 138.2, 138.0, 137.9, 132.2, 128.6, 128.6,

128.5, 128.3, 128.2, 128.1, 128.1, 128.0, 128.0, 127.9, 127.8, 122.2, 113.9, 90.5, 82.0, 79.2, 77.4, 75.8, 75.6, 73.7, 73.2, 73.1, 68.3, 55.6.

HRMS (TOF ESI+) *m/z* calcd for $C_{42}H_{46}O_8N$ $[(M+ NH_4)^+]$ 692.3218, found 692.3212.



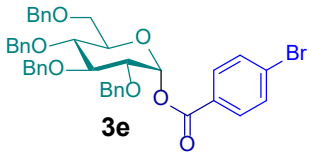
3d

(2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl 4-chlorobenzoate (3d): This compound was prepared according to the General Procedure A. The reaction was run for 40 h. After purification by silica gel column chromatography, compound **3d** was isolated as a white semi-solid (60 mg, 88%, α:β 13:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.39–7.23 (m, 18H), 7.16 (dd, *J* = 7.2, 2.3 Hz, 2H), 6.58 (d, *J* = 3.5 Hz, 1H), 4.98 (d, *J* = 10.9 Hz, 1H), 4.87 (dd, *J* = 10.7, 5.4 Hz, 2H), 4.75 (d, *J* = 11.6 Hz, 1H), 4.67 (d, *J* = 11.6 Hz, 1H), 4.61 (d, *J* = 12.1 Hz, 1H), 4.54 (d, *J* = 10.5 Hz, 1H), 4.49 (d, *J* = 12.2 Hz, 1H), 4.03 (t, *J* = 9.3 Hz, 1H), 3.95 (dt, *J* = 9.8, 1.9 Hz, 1H), 3.86–3.74 (m, 3H), 3.66 (dd, *J* = 10.9, 2.0 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 164.3, 140.1, 138.7, 138.1, 137.9, 137.7, 131.5, 129.0, 128.6, 128.6, 128.6, 128.3, 128.3, 128.2, 128.1, 128.1, 128.1, 127.9, 127.8, 91.1, 81.9, 79.1, 77.1, 75.8, 75.6, 73.8, 73.4, 73.3, 68.2.

HRMS (TOF ESI+) *m/z* calcd for $C_{41}H_{39}O_7ClNa$ $[(M+ Na)^+]$ 701.2277, found 701.2273.



3e

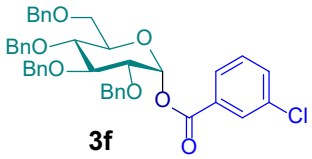
(2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl 4-bromobenzoate (3e): This compound was prepared according to the General Procedure A. After purification by silica gel column chromatography, compound **3e** was isolated as a viscous oil (54 mg, 75%, α:β 11:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.97–7.89 (m, 2H), 7.64–7.56 (m, 2H), 7.38–7.23 (m, 18H), 7.19–7.13 (m, 2H), 6.59 (d, *J* = 3.5 Hz, 1H), 4.99 (d, *J* = 10.9 Hz, 1H), 4.87 (dd, *J* = 10.7, 5.8 Hz, 2H), 4.75 (d, *J* = 11.6 Hz, 1H), 4.67 (d, *J* = 11.6 Hz, 1H), 4.62 (d, *J* = 12.1 Hz, 1H), 4.55 (d, *J* = 10.5

Hz, 1H), 4.49 (d, *J* = 12.2 Hz, 1H), 4.04 (t, *J* = 9.3 Hz, 1H), 3.96 (ddd, *J* = 10.0, 3.3, 2.0 Hz, 1H), 3.87–3.74 (m, 3H), 3.66 (dd, *J* = 11.0, 2.0 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 164.4, 138.7, 138.1, 137.9, 137.7, 132.0, 131.6, 128.8, 128.8, 128.6, 128.6, 128.6, 128.5, 128.5, 128.3, 128.2, 128.1, 128.1, 128.1, 127.9, 127.8, 91.2, 81.9, 79.1, 77.1, 75.8, 75.6, 73.7, 73.4, 73.3, 68.2.

HRMS (TOF ESI+) *m/z* calcd for $C_{41}H_{39}O_7BrNa$ [(M+ Na)$^+$] 745.1771, found 745.1780.



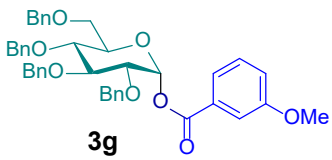
3f

(2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl 3-chlorobenzoate (3f): This compound was prepared according to the General Procedure A. After purification by silica gel column chromatography, compound **3f** was isolated as a viscous oil (40 mg, 59%, α:β 11:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01 (t, *J* = 1.9 Hz, 1H), 7.93 (dt, *J* = 7.6, 1.4 Hz, 1H), 7.58–7.52 (m, 1H), 7.39 (t, *J* = 7.9 Hz, 1H), 7.36–7.21 (m, 17H), 7.18–7.10 (m, 3H), 6.57 (d, *J* = 3.6 Hz, 1H), 4.97 (d, *J* = 10.9 Hz, 1H), 4.89–4.83 (m, 2H), 4.73 (d, *J* = 11.7 Hz, 1H), 4.66 (d, *J* = 11.6 Hz, 1H), 4.59 (d, *J* = 12.1 Hz, 1H), 4.53 (d, *J* = 10.5 Hz, 1H), 4.47 (d, *J* = 12.1 Hz, 1H), 4.02 (t, *J* = 9.4 Hz, 1H), 3.94 (dt, *J* = 10.3, 2.7 Hz, 1H), 3.84–3.71 (m, 3H), 3.64 (dd, *J* = 10.7, 2.1 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 164.0, 138.7, 138.1, 137.9, 137.7, 134.8, 133.6, 131.6, 130.0, 130.0, 128.6, 128.6, 128.6, 128.5, 128.5, 128.3, 128.2, 128.2, 128.1, 128.1, 128.0, 127.9, 127.8, 91.4, 81.8, 79.1, 77.1, 75.8, 75.6, 73.8, 73.4, 73.4, 68.2.

HRMS (TOF ESI+) *m/z* calcd for $C_{41}H_{39}O_7ClNa$ [(M+ Na)$^+$] 701.2277, found 701.2263.



3g

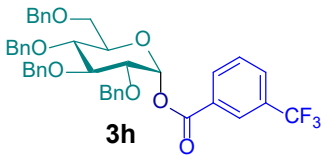
(2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl 3-methoxybenzoate (3g): This compound was prepared according to the General Procedure A. After purification by silica gel column chromatography, compound **3g** was isolated as a viscous oil (53

mg, 79%, α:β 12:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.0 Hz, 1H), 7.62–7.58 (m, 1H), 7.39–7.23 (m, 19H), 7.14 (m, 3H), 6.59 (d, *J* = 3.5 Hz, 1H), 4.98 (d, *J* = 10.9 Hz, 1H), 4.87 (dd, *J* = 10.7, 7.3 Hz, 2H), 4.75 (d, *J* = 11.6 Hz, 1H), 4.67 (d, *J* = 11.6 Hz, 1H), 4.61 (d, *J* = 12.1 Hz, 1H), 4.54 (d, *J* = 10.6 Hz, 1H), 4.48 (d, *J* = 12.1 Hz, 1H), 4.05 (t, *J* = 9.3 Hz, 1H), 3.97 (dt, *J* = 10.2, 2.6 Hz, 1H), 3.85 (s, 3H), 3.84–3.75 (m, 3H), 3.65 (dd, *J* = 10.9, 2.0 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 165.0, 159.8, 138.8, 138.2, 138.0, 137.8, 131.2, 129.7, 128.6, 128.6, 128.5, 128.2, 128.2, 128.1, 128.1, 128.0, 128.0, 127.9, 127.8, 122.5, 119.8, 114.9, 91.0, 82.0, 79.1, 77.1, 75.8, 75.5, 73.7, 73.3, 73.2, 68.2, 55.6.

HRMS (TOF ESI+) *m/z* calcd for $C_{42}H_{42}O_8Na$ [(M+ Na)$^+$] 697.2772, found 697.2763.



3h

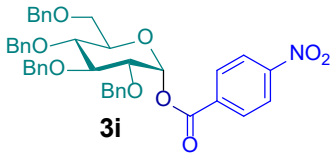
(2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl 3-(trifluoromethyl)benzoate (3h): This compound was prepared according to the General Procedure A. After purification by silica gel column chromatography, compound **3h** was isolated as a white semi-solid (39 mg, 55%, α:β 9:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.33 (s, 1H), 8.23 (d, *J* = 7.9 Hz, 1H), 7.90–7.82 (m, 1H), 7.61 (t, *J* = 7.8 Hz, 1H), 7.42–7.22 (m, 17H), 7.17 (dd, *J* = 7.3, 2.3 Hz, 3H), 6.61 (d, *J* = 3.5 Hz, 1H), 4.99 (d, *J* = 10.9 Hz, 1H), 4.88 (dd, *J* = 10.7, 3.4 Hz, 2H), 4.75 (d, *J* = 11.6 Hz, 1H), 4.69 (d, *J* = 11.6 Hz, 1H), 4.62 (d, *J* = 12.1 Hz, 1H), 4.55 (d, *J* = 10.5 Hz, 1H), 4.50 (d, *J* = 12.1 Hz, 1H), 4.04 (t, *J* = 9.4 Hz, 1H), 4.01–3.93 (m, 1H), 3.88–3.74 (m, 3H), 3.67 (dd, *J* = 10.9, 2.0 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 163.9, 138.7, 138.1, 137.9, 137.7, 133.2, 133.2, 131.44 (q, $^2J_{C\text{-}F}$ = 33.1 Hz), 130.8, 130.65 (q, $^3J_{C\text{-}F}$ = 3.6 Hz), 129.3, 128.6, 128.6, 128.6, 128.3, 128.2, 128.1, 128.1, 127.9, 127.8, 127.05 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 123.73 (q, $^1J_{C\text{-}F}$ = 272.5 Hz), 91.6, 81.8, 79.1, 77.0, 75.8, 75.6, 73.8, 73.5, 73.4, 68.2.

^{19}F NMR (471 MHz, $CDCl_3$): δ -62.7.

HRMS (TOF ESI+) *m/z* calcd for $C_{42}H_{43}O_7NF_3$ [(M+ NH_4)$^+$] 730.2986, found 730.2976.



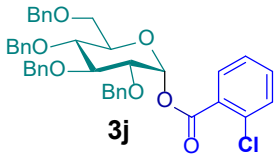
3i

(2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl 4-nitrobenzoate (3i): This compound was prepared according to the General Procedure A. After purification by silica gel column chromatography, compound **3i** was isolated as a white semi-solid (23 mg, 33%, α:β 5:1). The spectral data match with literature.[4]

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.29 (d, *J* = 8.7 Hz, 2H), 8.20 (d, *J* = 8.8 Hz, 2H), 7.41–7.21 (m, 17H), 7.21–7.09 (m, 3H), 6.59 (d, *J* = 3.5 Hz, 1H), 4.97 (d, *J* = 10.8 Hz, 1H), 4.86 (dd, *J* = 10.7, 2.7 Hz, 2H), 4.77–4.65 (m, 2H), 4.60 (d, *J* = 12.2 Hz, 1H), 4.51 (dd, *J* = 24.8, 11.4 Hz, 2H), 4.01 (t, *J* = 9.3 Hz, 1H), 3.95 (d, *J* = 10.0 Hz, 1H), 3.89–3.70 (m, 3H), 3.65 (dd, *J* = 10.9, 2.0 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 163.3, 150.9, 138.6, 138.0, 137.8, 137.6, 135.3, 131.2, 128.7, 128.6, 128.6, 128.3, 128.2, 128.2, 128.1, 128.1, 128.0, 128.0, 127.9, 123.8, 92.0, 81.8, 79.0, 77.0, 75.9, 75.7, 73.8, 73.6, 73.5, 68.2.

HRMS (TOF ESI+) *m/z* calcd for $C_{41}H_{43}O_9N_2$ $[(M+NH_4)^+]$ 707.2963, found 707.2960.



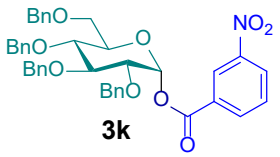
3j

(2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl 2-chlorobenzoate (3j): This compound was prepared according to the General Procedure A. After purification by silica gel column chromatography, compound **3j** was isolated as a viscous oil (34 mg, 50%, α:β 7:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.87 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.50–7.41 (m, 2H), 7.36–7.27 (m, 19H), 7.15 (dd, *J* = 7.3, 2.3 Hz, 2H), 6.64 (d, *J* = 3.5 Hz, 1H), 4.96 (d, *J* = 10.9 Hz, 1H), 4.89–4.74 (m, 3H), 4.68 (d, *J* = 11.5 Hz, 1H), 4.62 (d, *J* = 12.2 Hz, 1H), 4.51 (dd, *J* = 20.3, 11.4 Hz, 2H), 4.06–3.95 (m, 2H), 3.84–3.74 (m, 3H), 3.68 (dd, *J* = 10.9, 2.0 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 164.1, 138.8, 138.2, 138.0, 137.8, 134.3, 133.1, 132.1, 131.4, 129.6, 128.6, 128.6, 128.6, 128.5, 128.2, 128.2, 128.1, 128.1, 128.0, 128.0, 127.9, 127.8, 126.8, 91.4, 81.8, 79.2, 77.1, 75.8, 75.5, 73.7, 73.6, 73.3, 68.2.

HRMS (TOF ESI+) *m/z* calcd for $C_{41}H_{39}O_{10}ClNa$ [$(M+Na)^+$] 701.2277, found 701.2270.



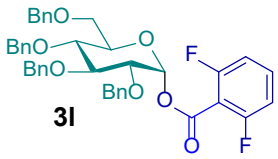
3k

(2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl 3-nitrobenzoate (3k): This compound was prepared according to the General Procedure A. After purification by silica gel column chromatography, compound was **3k** isolated as a viscous oil (22 mg, 32%, α:β 4:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.88 (t, *J* = 2.0 Hz, $1H_\alpha$), 8.80 (t, *J* = 2.0 Hz, $1H_\beta$), 8.44 (m, $1H_\alpha$ + $1H_\beta$), 8.36 (dt, *J* = 7.8, 1.5 Hz, $1H_\alpha$), 8.29 (dd, *J* = 7.8, 1.5 Hz, $1H_\beta$), 7.67 (t, *J* = 8.0 Hz, $1H_\alpha$), 7.63 (t, *J* = 8.0 Hz, $1H_\beta$), 7.30 (m, $17H_\alpha$ + $17H_\beta$), 7.22–7.10 (m, $3H_\alpha$ + $3H_\beta$), 6.62 (d, *J* = 3.6 Hz, $1H_\alpha$), 5.91 (d, *J* = 7.5 Hz, $1H_\beta$), 4.99 (d, *J* = 10.9 Hz, $1H_\alpha$), 4.93 (d, *J* = 11.0 Hz, $1H_\beta$), 4.93–4.80 (m, $2H_\alpha$ + $2H_\beta$), 4.78–4.67 (m, $2H_\alpha$ + $2H_\beta$), 4.64–4.45 (m, $3H_\alpha$ + $3H_\beta$), 4.04 (t, *J* = 9.3 Hz, $1H_\alpha$), 3.97 (dt, *J* = 10.0, 2.0 Hz, 1 H_α), 3.87–3.73 (m, $3H_\alpha$ + $5H_\beta$), 3.70–3.64 (m, $1H_\alpha$ + $1H_\beta$).

^{13}C NMR (126 MHz, $CDCl_3$): δ 163.2, 163.0, 148.5, 148.4, 138.6, 138.4, 138.1, 138.0, 137.9, 137.9, 137.6, 135.7, 135.6, 131.7, 131.2, 129.9, 129.8, 128.6, 128.6, 128.6, 128.5, 128.5, 128.2, 128.2, 128.2, 128.1, 128.1, 128.1, 128.0, 128.0, 127.9, 127.9, 127.9, 127.9, 125.1, 125.1, 95.2, 92.1, 85.1, 81.8, 80.9, 79.0, 77.3, 77.0, 75.9, 75.8, 75.6, 75.2, 75.2, 73.8, 73.7, 73.6, 73.6, 68.2.

HRMS (TOF ESI+) *m/z* calcd for $C_{41}H_{39}O_9NNa$ [$(M+Na)^+$] 712.2517, found 712.2508.



3l

(2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl 2,6-difluorobenzoate (3l): This compound was prepared according to the General Procedure A. After purification by silica gel column chromatography, compound **3l** was isolated as a viscous oil (32 mg, 47%, α:β 3:1).

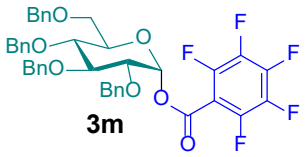
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50–7.40 (m, $1H_\alpha$ + $1H_\beta$), 7.38–7.20 (m, $18H_\alpha$ + $18H_\beta$), 7.18–7.12 (m, $2H_\alpha$ + $2H_\beta$), 7.00–6.93 (m, $2H_\alpha$ + $2H_\beta$), 6.63 (d, *J* = 3.4 Hz, $1H_\alpha$), 5.9 (d, *J* = 7.8 Hz,

1H β), 4.99–4.72 (m, 4H α + 4H β), 4.72–4.56 (m, 2H α + 3H β), 4.56– 4.45(m, 2H α + 1H β), 4.05–3.95 (m, 2H α + 1H β), 3.83–3.75 (m, 3H α + 3H β), 3.75–3.63 (m, 1H α + 2H β).

^{13}C NMR (126 MHz, $CDCl_3$): δ 162.3, 162.3, 162.3, 162.2, 160.3, 160.2, 160.2, 160.2, 160.1, 160.0, 138.8, 138.6, 138.3, 138.2, 138.2, 138.1, 138.0, 137.8, 133.6, 133.5, 133.4, 133.4, 128.6, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.3, 128.1, 128.1, 128.1, 128.0, 127.9, 127.9, 127.9, 127.9, 127.8, 127.8, 127.7, 112.5, 112.5, 112.4, 112.4, 112.3, 112.3, 112.3, 110.7, 110.5, 110.4, 95.2, 91.6, 85.0, 81.8, 81.0, 79.1, 77.4, 77.2, 77.0, 76.9, 76.1, 75.9, 75.4, 75.2, 73.7, 73.6, 73.5, 73.4, 68.2, 68.2.

^{19}F NMR (471 MHz, $CDCl_3$): δ -108.46 (β), -108.83 (α).

HRMS (TOF ESI+) *m/z* calcd for $C_{41}H_{38}O_7F_2Na$ [$(M+Na)^+$] 703.2478, found 703.2464.



3m

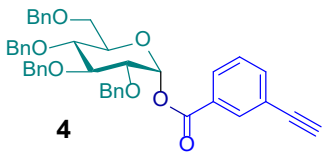
(2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl 2,3,4,5,6-pentafluorobenzoate (3m): This compound was prepared according to the General Procedure A. After purification by silica gel column chromatography, compound **3m** was isolated as a viscous oil (43 mg, 59%, α:β 2:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37–7.23 (m, 18Hα + 18Hβ), 7.17 (m, 2Hα + 2Hβ), 6.63 (d, *J* = 3.5 Hz, 1Hα), 5.88 (d, *J* = 7.8 Hz, 1Hβ), 4.94 (d, *J* = 10.9 Hz, 1Hα), 4.92–4.76 (m, 2Hα + 5Hβ), 4.76–4.66 (m, 2Hα), 4.65–4.57 (m, 1Hα + 2Hβ), 4.56–4.46 (m, 2Hα + 1Hβ), 3.98–3.91 (m, 2Hα), 3.85–3.64 (m, 4Hα + 6Hβ).

^{13}C NMR (126 MHz, $CDCl_3$): δ 157.7, 157.6, 147.1–146.8 (m), 145.0–144.7 (m), 142.8–142.6 (m), 139.1–138.8 (m), 138.6, 138.4, 138.1, 138.1, 138.0, 138.0, 137.8, 137.5, 137.1–136.7 (m), 128.7, 128.6, 128.6, 128.6, 128.5, 128.5, 128.5, 128.3, 128.2, 128.1, 128.1, 128.0, 128.0, 128.0, 128.0, 127.9, 127.9, 127.9, 127.8, 107.8–107.3 (m), 95.6, 92.8, 84.9, 81.7, 80.9, 78.9, 77.2, 76.8, 76.1, 75.9, 75.8, 75.4, 75.2, 75.2, 73.9, 73.7, 73.7, 73.7, 68.2, 68.1.

^{19}F NMR (471 MHz, $CDCl_3$): δ -136.43, -136.52 (m, β), -136.90, -136.99 (m, α), -146.94, -147.23 (m, β), -147.39, -147.64 (m, α), -159.90, -160.18 (m, α, β).

HRMS (TOF ESI+) *m/z* calcd for $C_{41}H_{35}O_7F_5Na$ [$(M+ Na)^+$] 757.2195, found 757.2192.



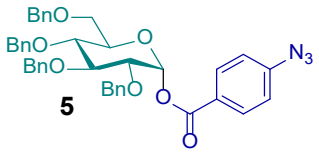
4

(2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl 3-ethynylbenzoate (4): This compound was prepared according to the General Procedure A. After purification by silica gel column chromatography, compound **4** was isolated as a viscous oil (39 mg, 58%, α:β 15:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.19–8.15 (m, 1H), 8.05 (dt, *J* = 7.9, 1.5 Hz, 1H), 7.70 (dt, *J* = 7.8, 1.5 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.40–7.24 (m, 18H), 7.17 (dd, *J* = 7.3, 2.3 Hz, 2H), 6.61 (d, *J* = 3.5 Hz, 1H), 5.00 (d, *J* = 10.9 Hz, 1H), 4.88 (dd, *J* = 10.8, 2.2 Hz, 2H), 4.74 (s, 1H), 4.68 (d, *J* = 11.6 Hz, 1H), 4.62 (d, *J* = 12.1 Hz, 1H), 4.56 (d, *J* = 10.5 Hz, 1H), 4.49 (d, *J* = 12.2 Hz, 1H), 4.06 (t, *J* = 9.4 Hz, 1H), 3.98 (dt, *J* = 10.1, 2.5 Hz, 1H), 3.87–3.75 (m, 3H), 3.67 (dd, *J* = 10.9, 2.0 Hz, 1H), 3.16 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 164.3, 138.7, 138.1, 137.9, 137.7, 136.9, 133.6, 130.3, 130.2, 128.8, 128.6, 128.6, 128.6, 128.3, 128.2, 128.1, 128.1, 128.0, 127.9, 127.8, 122.9, 91.2, 82.6, 81.9, 79.1, 78.7, 77.1, 75.8, 75.6, 73.8, 73.4, 73.3, 68.2.

HRMS (TOF ESI+) *m/z* calcd for $C_{43}H_{44}O_7N$ $[(M+ NH_4)^+]$ 686.3112, found 686.3104.



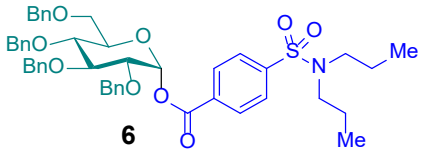
5

(2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl 4-azidobenzoate (5): This compound was prepared according to the General Procedure A. After purification by silica gel column chromatography, compound **5** was isolated as a white semi-solid (42 mg, 61%, α:β 18:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08–8.03 (m, 2H), 7.38–7.23 (m, 18H), 7.15 (dd, *J* = 7.3, 2.2 Hz, 2H), 7.11–7.05 (m, 2H), 6.58 (d, *J* = 3.5 Hz, 1H), 4.99 (d, *J* = 10.9 Hz, 1H), 4.87 (dd, *J* = 10.6, 6.4 Hz, 2H), 4.75 (d, *J* = 11.6 Hz, 1H), 4.67 (d, *J* = 11.6 Hz, 1H), 4.61 (d, *J* = 12.1 Hz, 1H), 4.54 (d, *J* = 10.4 Hz, 1H), 4.48 (d, *J* = 12.1 Hz, 1H), 4.04 (t, *J* = 9.4 Hz, 1H), 3.95 (ddd, *J* = 10.3, 3.3, 2.0 Hz, 1H), 3.85 – 3.75 (m, 3H), 3.66 (dd, *J* = 11.0, 2.0 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 164.3, 145.5, 138.7, 138.1, 137.9, 137.8, 132.0, 128.6, 128.6, 128.6, 128.3, 128.2, 128.1, 128.1, 127.9, 127.8, 126.4, 119.1, 90.9, 82.0, 79.1, 75.9, 75.6, 73.8, 73.3, 73.3, 68.2.

HRMS (TOF ESI+) *m/z* calcd for $C_{41}H_{39}O_7N_3Na$ [(M+ Na)$^+$] 708.2680, found 708.2667.



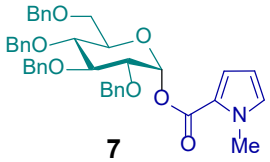
6

(2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl 4-(N,N-dipropylsulfamoyl)benzoate (6): This compound was prepared according to the General Procedure B. After purification by silica gel column chromatography, compound **6** was isolated as a viscous oil (72 mg, 89%, α:β 18:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.17 (d, *J* = 8.4 Hz, 2H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.38–7.26 (m, 18H), 7.18–7.12 (m, 2H), 6.60 (d, *J* = 3.4 Hz, 1H), 4.99 (d, *J* = 10.9 Hz, 1H), 4.92–4.83 (m, 2H), 4.79–4.66 (m, 2H), 4.61 (d, *J* = 12.1 Hz, 1H), 4.52 (dd, *J* = 24.5, 11.3 Hz, 2H), 4.04 (t, *J* = 9.3 Hz, 1H), 3.96 (dt, *J* = 10.1, 2.4 Hz, 1H), 3.87–3.74 (m, 3H), 3.67 (dd, *J* = 11.0, 2.1 Hz, 1H), 3.16–3.05 (m, 4H), 1.56 (h, *J* = 7.5 Hz, 4H), 0.88 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 163.8, 144.8, 138.6, 138.0, 137.9, 137.6, 133.2, 130.7, 128.7, 128.6, 128.6, 128.3, 128.2, 128.1, 128.1, 128.0, 128.0, 127.9, 127.3, 91.6, 81.9, 79.1, 77.0, 75.9, 75.6, 73.8, 73.5, 73.5, 68.2, 50.2, 22.1, 11.3.

HRMS (TOF ESI+) *m/z* calcd for $C_{47}H_{53}O_9SN_2$ [(M+NH_4)$^+$] 825.3779, found 825.3783.



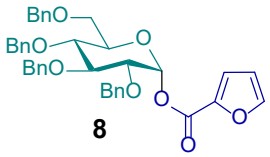
7

(2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl 1-methyl-1H-pyrrole-2-carboxylate (7): This compound was prepared according to the General Procedure A. After purification by silica gel column chromatography, compound **7** was isolated as a viscous oil (49 mg, 76%, α:β 21:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38–7.26 (m, 18H), 7.16 (dd, *J* = 7.3, 2.1 Hz, 2H), 7.04 (dd, *J* = 4.0, 1.7 Hz, 1H), 6.82 (t, *J* = 2.1 Hz, 1H), 6.52 (d, *J* = 3.6 Hz, 1H), 6.13 (dd, *J* = 4.0, 2.4 Hz, 1H), 4.98 (d, *J* = 10.9 Hz, 1H), 4.86 (t, *J* = 10.8 Hz, 2H), 4.76 (d, *J* = 11.7 Hz, 1H), 4.67 (d, *J* = 11.7 Hz, 1H), 4.61 (d, *J* = 12.1 Hz, 1H), 4.54 (d, *J* = 10.6 Hz, 1H), 4.47 (d, *J* = 12.1 Hz, 1H), 4.03 (t, *J* = 9.3 Hz, 1H), 3.99–3.88 (m, 4H), 3.84–3.74 (m, 3H), 3.65 (dd, *J* = 10.9, 2.1 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 159.5, 138.8, 138.3, 138.0, 138.0, 130.4, 128.5, 128.5, 128.5, 128.5, 128.2, 128.1, 128.1, 127.9, 127.9, 127.8, 127.8, 121.9, 119.2, 108.2, 89.6, 82.0, 79.1, 77.4, 75.8, 75.5, 73.7, 73.0, 72.9, 68.3, 37.0.

HRMS (TOF ESI+) *m/z* calcd for $C_{40}H_{41}O_7NNa$ [(M+ Na)$^+$] 670.2775, found 670.2773.



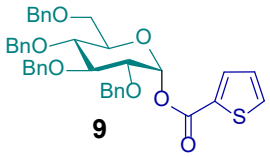
8

(2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl furan-2-carboxylate (8): This compound was prepared according to the General Procedure A. After purification by silica gel column chromatography, compound **8** was isolated as a viscous oil (49 mg, 77%, α:β 20:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62–7.59 (m, 1H), 7.38–7.23 (m, 19H), 7.16 (dd, *J* = 7.3, 2.1 Hz, 2H), 6.55 (d, *J* = 3.5 Hz, 1H), 6.53 (dd, *J* = 3.5, 1.7 Hz, 1H), 4.98 (d, *J* = 10.9 Hz, 1H), 4.86 (dd, *J* = 10.7, 7.0 Hz, 2H), 4.76 (d, *J* = 11.6 Hz, 1H), 4.67 (d, *J* = 11.6 Hz, 1H), 4.61 (d, *J* = 12.1 Hz, 1H), 4.53 (d, *J* = 10.5 Hz, 1H), 4.48 (d, *J* = 12.1 Hz, 1H), 4.04 (t, *J* = 9.4 Hz, 1H), 4.01–3.94 (m, 1H), 3.84–3.74 (m, 3H), 3.66 (dd, *J* = 10.8, 2.0 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 157.1, 147.0, 144.2, 138.8, 138.2, 138.0, 137.7, 128.6, 128.5, 128.3, 128.3, 128.1, 128.1, 128.0, 128.0, 127.9, 127.8, 119.2, 112.1, 90.8, 81.9, 79.0, 77.1, 75.9, 75.6, 73.7, 73.4, 73.3, 68.2.

HRMS (TOF ESI+) *m/z* calcd for $C_{39}H_{38}O_8Na$ [(M+ Na)$^+$] 657.2459, found 657.2457.



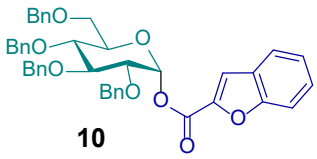
9

((2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl thiophene-2-carboxylate (9): This compound was prepared according to the General Procedure A. After purification by silica gel column chromatography, compound **9** was isolated as a viscous oil (43 mg, 66%, α:β 17:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.87 (dd, *J* = 3.8, 1.2 Hz, 1H), 7.61 (dd, *J* = 5.1, 1.4 Hz, 1H), 7.40–7.22 (m, 18H), 7.17 (dd, *J* = 7.3, 2.2 Hz, 2H), 7.13 (dd, *J* = 5.0, 3.7 Hz, 1H), 6.54 (d, *J* = 3.4 Hz, 1H), 4.98 (d, *J* = 10.9 Hz, 1H), 4.86 (dd, *J* = 10.7, 8.5 Hz, 2H), 4.76 (d, *J* = 11.6 Hz, 1H), 4.67 (d, *J* = 11.6 Hz, 1H), 4.61 (d, *J* = 12.1 Hz, 1H), 4.54 (d, *J* = 10.6 Hz, 1H), 4.48 (d, *J* = 12.0 Hz, 1H), 4.03 (t, *J* = 9.4 Hz, 1H), 3.97 (ddd, *J* = 10.1, 3.3, 2.0 Hz, 1H), 3.84–3.75 (m, 3H), 3.66 (dd, *J* = 10.9, 2.0 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 160.6, 138.8, 138.2, 138.0, 137.8, 134.3, 133.3, 133.3, 128.6, 128.6, 128.5, 128.5, 128.2, 128.2, 128.1, 128.1, 128.0, 128.0, 128.0, 127.9, 127.8, 91.1, 81.9, 79.1, 77.1, 75.9, 75.5, 73.7, 73.3, 73.2, 68.2.

HRMS (TOF ESI+) *m/z* calcd for $C_{39}H_{38}O_7SNa$ [(M+ Na)$^+$] 673.2230, found 673.2228.



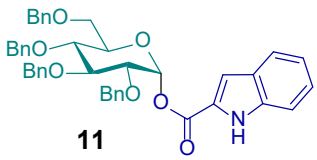
10

(2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl benzofuran-2-carboxylate (10): This compound was prepared according to the General Procedure A. After purification by silica gel column chromatography, compound **10** was isolated as a viscous oil (54 mg, 79%, α:β 15:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.64–7.59 (m, 2H), 7.48 (ddd, *J* = 8.3, 7.1, 1.3 Hz, 1H), 7.42–7.22 (m, 19H), 7.22–7.13 (m, 2H), 6.62 (d, *J* = 3.4 Hz, 1H), 5.01 (d, *J* = 10.9 Hz, 1H), 4.93–4.85 (m, 2H), 4.78 (d, *J* = 11.6 Hz, 1H), 4.70 (d, *J* = 11.6 Hz, 1H), 4.63 (d, *J* = 12.1 Hz, 1H), 4.56 (d, *J* = 10.4 Hz, 1H), 4.50 (d, *J* = 12.1 Hz, 1H), 4.14–4.01 (m, 2H), 3.88–3.76 (m, 3H), 3.69 (dd, *J* = 10.9, 2.0 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 158.1, 156.1, 145.0, 138.8, 138.1, 137.9, 137.7, 128.6, 128.6, 128.6, 128.3, 128.3, 128.1, 128.1, 128.1, 128.0, 127.9, 127.8, 127.0, 124.0, 123.0, 115.2, 112.7, 91.3, 81.8, 79.1, 77.1, 75.9, 75.7, 73.7, 73.5, 73.4, 68.2.

HRMS (TOF ESI+) *m/z* calcd for $C_{43}H_{40}O_8Na$ [(M+ Na)$^+$] 707.2615, found 707.2612.



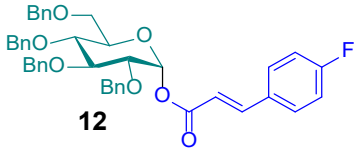
11

(2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl 1H-indole-2-carboxylate (11): This compound was prepared according to the General Procedure A. After purification by silica gel column chromatography, compound **11** was isolated as a white semi-solid (42 mg, 61%, α:β 9:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.90 (s, 1H), 7.74–7.67 (m, 1H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.38–7.23 (m, 20H), 7.17 (dd, *J* = 7.0, 2.2 Hz, 3H), 6.59 (d, *J* = 3.4 Hz, 1H), 5.00 (d, *J* = 10.9 Hz, 1H), 4.88 (d, *J* = 10.8 Hz, 2H), 4.76 (d, *J* = 11.6 Hz, 1H), 4.69 (d, *J* = 11.6 Hz, 1H), 4.61 (d, *J* = 12.1 Hz, 1H), 4.55 (d, *J* = 10.5 Hz, 1H), 4.48 (d, *J* = 12.1 Hz, 1H), 4.09 (t, *J* = 9.4 Hz, 1H), 4.01 (dt, *J* = 9.9, 2.6 Hz, 1H), 3.90–3.72 (m, 3H), 3.66 (dd, *J* = 10.9, 2.0 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 160.4, 138.7, 138.1, 137.9, 137.8, 137.3, 128.6, 128.6, 128.6, 128.5, 128.2, 128.2, 128.1, 128.1, 128.0, 128.0, 127.9, 127.8, 127.5, 126.6, 126.0, 122.9, 121.1, 112.1, 110.2, 90.9, 81.9, 79.1, 77.4, 77.1, 75.8, 75.6, 73.7, 73.3, 68.2.

HRMS (TOF ESI+) *m/z* calcd for $C_{43}H_{41}O_7NNa$ $[(M+Na)^+]$ 706.2775, found 706.2767.



12

(2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl (E)-3-(4-fluorophenyl)acrylate (12): This compound was prepared according to the General Procedure A. After purification by silica gel column chromatography, compound **12** was isolated as a viscous oil (50 mg, 73%, α:β 20:1).

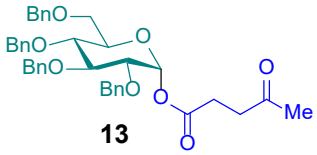
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (d, *J* = 16.0 Hz, 1H), 7.58–7.48 (m, 2H), 7.38–7.27 (m, 18H), 7.16 (dd, *J* = 7.3, 2.2 Hz, 2H), 7.13–7.06 (m, 2H), 6.49 (d, *J* = 3.5 Hz, 1H), 6.41 (d, *J* = 15.9 Hz, 1H), 5.00 (d, *J* = 10.9 Hz, 1H), 4.86 (dd, *J* = 10.7, 5.4 Hz, 2H), 4.75 (d, *J* = 11.6 Hz, 1H), 4.68 (d, *J* = 11.6 Hz, 1H), 4.62 (d, *J* = 12.1 Hz, 1H), 4.56–4.45 (m, 2H), 4.03 (t, *J* = 9.3 Hz, 1H), 3.94 (ddd, *J* = 10.1, 3.3, 2.1 Hz, 1H), 3.84–3.73 (m, 3H), 3.67 (dd, *J* = 10.9, 2.0 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 165.3, 164.2 (d, $^1J_{CF}$ = 251.8 Hz), 144.9, 138.8, 138.2, 138.0,

137.7, 130.6 (d, $^{4}J_{CF}$ = 3.3 Hz), 130.3 (d, $^{3}J_{CF}$ = 8.5 Hz), 128.6, 128.6, 128.6, 128.5, 128.3, 128.2, 128.1, 128.1, 128.0, 127.9, 127.8, 117.4, 117.4, 116.3 (d, $^{2}J_{CF}$ = 22.0 Hz), 90.4, 82.0, 79.1, 77.4, 75.8, 75.5, 73.7, 73.3, 73.1, 68.3.

^{19}F NMR (471 MHz, $CDCl_3$): δ -109.1.

HRMS (TOF ESI+) *m/z* calcd for $C_{43}H_{41}O_7FNa$ [$(M+Na)^+$] 711.2729, found 711.2727.



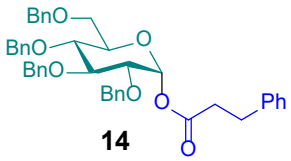
13

(2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl 4-oxopentanoate (13): This compound was prepared according to the General Procedure A. After purification by silica gel column chromatography, compound **13** was isolated as a viscous oil (48 mg, 75%, α:β 10:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39–7.26 (m, 18H), 7.15 (dd, *J* = 7.3, 2.2 Hz, 2H), 6.33 (d, *J* = 3.4 Hz, 1H), 4.96 (d, *J* = 10.9 Hz, 1H), 4.83 (dd, *J* = 10.8, 9.0 Hz, 2H), 4.72–4.58 (m, 3H), 4.49 (dd, *J* = 21.4, 11.4 Hz, 2H), 3.94 (t, *J* = 9.3 Hz, 1H), 3.91–3.85 (m, 1H), 3.81–3.72 (m, 2H), 3.67 (ddd, *J* = 16.1, 10.2, 2.8 Hz, 2H), 2.83–2.63 (m, 4H), 2.17 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 206.2, 171.5, 138.8, 138.2, 138.0, 137.8, 128.6, 128.5, 128.5, 128.5, 128.2, 128.1, 128.1, 128.1, 128.0, 127.9, 127.9, 127.8, 90.5, 81.8, 79.0, 77.0, 75.8, 75.4, 73.7, 73.2, 73.0, 68.2, 38.0, 29.9, 28.2.

HRMS (TOF ESI+) *m/z* calcd for $C_{39}H_{42}O_8Na$ [$(M+ Na)^+$] 661.2772, found 661.2760.



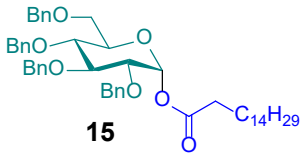
14

(2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl 3-phenylpropanoate (14): This compound was prepared according to the General Procedure B. After purification by silica gel column chromatography, compound **14** was isolated as a viscous oil (60 mg, 89%, α:β 13:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42–7.24 (m, 20H), 7.24–7.10 (m, 5H), 6.40 (d, *J* = 3.5 Hz, 1H), 4.95 (d, *J* = 10.9 Hz, 1H), 4.83 (dd, *J* = 14.9, 10.8 Hz, 2H), 4.73–4.57 (m, 3H), 4.50 (dd, *J* = 16.5, 11.4 Hz, 2H), 3.95–3.86 (m, 1H), 3.80–3.66 (m, 4H), 3.60 (dd, *J* = 11.0, 1.7 Hz, 1H), 2.99 (t, *J* = 7.7 Hz, 2H), 2.81–2.66 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 171.5, 140.3, 138.8, 138.2, 138.0, 137.8, 128.6, 128.6, 128.5, 128.5, 128.4, 128.2, 128.1, 128.1, 128.0, 127.9, 127.9, 127.8, 126.4, 90.2, 81.8, 79.0, 77.0, 75.8, 75.4, 73.7, 73.3, 73.0, 68.2, 35.9, 30.9.

HRMS (TOF ESI+) *m/z* calcd for $C_{43}H_{44}O_7Na$ [(M+ Na)$^+$] 695.2979, found 695.2972.



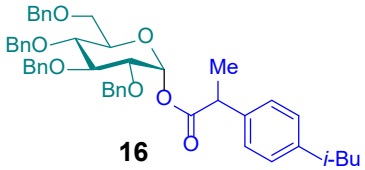
15

(2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl palmitate (15): This compound was prepared according to the General Procedure A. After purification by silica gel column chromatography, compound **15** was isolated as a viscous oil (53 mg, 69%, α:β 20:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39–7.27 (m, 18H), 7.21–7.12 (m, 2H), 6.42 (d, *J* = 3.5 Hz, 1H), 4.98 (d, *J* = 10.9 Hz, 1H), 4.85 (dd, *J* = 15.5, 10.8 Hz, 2H), 4.72 (d, *J* = 11.4 Hz, 1H), 4.68–4.59 (m, 2H), 4.52 (dd, *J* = 15.6, 11.3 Hz, 2H), 3.95 (t, *J* = 9.3 Hz, 1H), 3.89 (dt, *J* = 10.0, 2.7 Hz, 1H), 3.79–3.73 (m, 2H), 3.71 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.66 (dd, *J* = 10.9, 2.1 Hz, 1H), 2.39 (td, *J* = 7.5, 3.9 Hz, 2H), 1.66 (p, *J* = 7.4 Hz, 2H), 1.44–1.16 (m, 24H), 0.90 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 172.4, 138.8, 138.2, 138.0, 137.8, 128.5, 128.5, 128.5, 128.2, 128.1, 128.1, 128.0, 127.9, 127.9, 127.8, 89.9, 81.9, 79.1, 77.1, 75.8, 75.4, 73.7, 73.2, 73.0, 68.3, 34.5, 32.1, 29.8, 29.8, 29.8, 29.8, 29.6, 29.5, 29.4, 29.2, 25.1, 22.8, 14.3.

HRMS (TOF ESI+) *m/z* calcd for $C_{50}H_{66}O_7Na$ [(M+ Na)$^+$] 801.4701, found 801.4694.



16

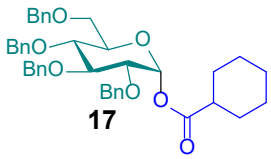
(2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl 2-

(4-isobutylphenyl)propanoate (16): This compound was prepared according to the General Procedure A. After purification by silica gel column chromatography, compound **16** was isolated as a gummy liquid (44 mg, 60%, α:β 20:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38–7.26 (m, 33H), 7.24–7.16 (m, 7H), 7.16–7.08 (m, 4H), 7.02 (dd, *J* = 17.9, 8.1 Hz, 4H), 6.40 (d, *J* = 3.2 Hz, 1H), 6.34 (d, *J* = 3.5 Hz, 1H), 4.93 (d, *J* = 11.0 Hz, 1H), 4.84–4.75 (m, 4H), 4.73–4.62 (m, 4H), 4.60 (d, *J* = 5.5 Hz, 1H), 4.58–4.54 (m, 1H), 4.52 (d, *J* = 1.5 Hz, 1H), 4.51–4.43 (m, 3H), 4.37 (d, *J* = 12.0 Hz, 1H), 3.86–3.74 (m, 4H), 3.73–3.58 (m, 7H), 3.53 (dd, *J* = 10.9, 3.0 Hz, 1H), 3.35 (dd, *J* = 10.9, 2.0 Hz, 1H), 3.30 (dt, *J* = 10.0, 2.5 Hz, 1H), 2.39 (dd, *J* = 7.2, 2.0 Hz, 4H), 1.77 (dtp, *J* = 13.6, 6.8, 3.4 Hz, 2H), 1.51 (dd, *J* = 8.7, 7.1 Hz, 6H), 0.91–0.80 (m, 12H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 173.3, 173.1, 140.7, 140.5, 138.8, 138.8, 138.4, 138.3, 138.0, 138.0, 137.9, 137.8, 137.7, 137.4, 129.5, 129.3, 128.6, 128.5, 128.5, 128.5, 128.5, 128.4, 128.2, 128.1, 128.1, 128.1, 128.1, 128.0, 128.0, 128.0, 128.0, 127.9, 127.9, 127.8, 127.8, 127.8, 127.7, 127.6, 127.4, 90.3, 90.2, 81.9, 81.5, 79.4, 79.0, 76.9, 75.8, 75.7, 75.3, 75.2, 73.7, 73.6, 73.3, 73.2, 73.0, 72.6, 68.3, 67.9, 45.4, 45.3, 45.1, 45.1, 30.3, 30.3, 22.5, 22.5, 18.3, 18.2.

HRMS (TOF ESI+) *m/z* calcd for $C_{47}H_{52}O_7Na$ [(M+ Na)$^+$] 751.3605, found 751.3601.



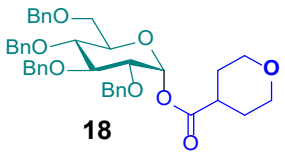
17

(2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl cyclohexanecarboxylate (17): This compound was prepared according to the General Procedure A. After purification by silica gel column chromatography, compound **17** was isolated as a viscous oil (60 mg, 92%, α:β 20:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40–7.22 (m, 18H), 7.15 (dd, *J* = 7.3, 2.2 Hz, 2H), 6.40 (d, *J* = 3.4 Hz, 1H), 4.96 (d, *J* = 10.9 Hz, 1H), 4.84 (dd, *J* = 13.5, 10.7 Hz, 2H), 4.69 (d, *J* = 11.4 Hz, 1H), 4.65–4.57 (m, 2H), 4.50 (dd, *J* = 15.7, 11.3 Hz, 2H), 3.92 (t, *J* = 9.3 Hz, 1H), 3.86 (ddd, *J* = 10.1, 3.2, 2.0 Hz, 1H), 3.79–3.67 (m, 3H), 3.65 (dd, *J* = 10.9, 2.0 Hz, 1H), 2.38 (tt, *J* = 11.1, 3.6 Hz, 1H), 1.98–1.86 (m, 2H), 1.74 (dq, *J* = 11.0, 3.5 Hz, 2H), 1.63 (dd, *J* = 11.1, 4.7 Hz, 1H), 1.46 (qd, *J* = 11.7, 4.6 Hz, 2H), 1.26 (dddd, *J* = 26.1, 18.0, 11.5, 3.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 174.5, 138.8, 138.2, 138.0, 137.9, 128.6, 128.5, 128.5, 128.2, 128.2, 128.1, 128.1, 128.0, 127.9, 127.8, 89.7, 81.8, 79.2, 77.1, 75.8, 75.5, 73.7, 73.1, 73.0, 68.3, 43.3, 29.1, 29.0, 25.9, 25.5, 25.4.

HRMS (TOF ESI+) *m/z* calcd for $C_{41}H_{46}O_7Na$ [(M+ Na)$^+$] 673.3136, found 673.3131.



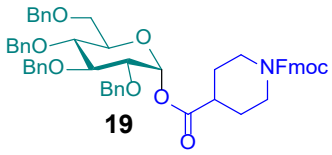
18

(2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl tetrahydro-2H-pyran-4-carboxylate (18): This compound was prepared according to the General Procedure A. After purification by silica gel column chromatography, compound **18** was isolated as a viscous oil (53 mg, 81%, α:β 20:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36–7.27 (m, 18H), 7.18–7.12 (m, 2H), 6.42 (d, *J* = 3.4 Hz, 1H), 4.95 (d, *J* = 10.9 Hz, 1H), 4.84 (dd, *J* = 14.6, 10.7 Hz, 2H), 4.68 (d, *J* = 11.3 Hz, 1H), 4.66–4.58 (m, 2H), 4.50 (dd, *J* = 13.4, 11.3 Hz, 2H), 3.94 (dq, *J* = 11.4, 3.6 Hz, 2H), 3.89 (t, *J* = 9.3 Hz, 1H), 3.85 (ddd, *J* = 10.1, 3.4, 2.0 Hz, 1H), 3.78–3.68 (m, 3H), 3.65 (dd, *J* = 10.9, 2.0 Hz, 1H), 3.42 (tdd, *J* = 11.1, 5.7, 3.1 Hz, 2H), 2.67–2.57 (m, 1H), 1.90–1.74 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 172.9, 138.7, 138.1, 137.9, 137.8, 128.6, 128.6, 128.6, 128.5, 128.2, 128.2, 128.1, 128.1, 128.0, 127.9, 127.8, 90.2, 81.7, 79.2, 77.0, 75.8, 75.5, 73.7, 73.3, 73.2, 68.3, 67.1, 67.1, 40.3, 28.7, 28.7.

HRMS (TOF ESI+) *m/z* calcd for $C_{40}H_{44}O_8Na$ [(M+ Na)$^+$] 675.2928, found 675.2925.



19

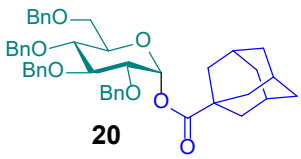
1-((9*H*-fluoren-9-yl)methyl)4-((2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy) methyl)tetrahydro-2*H*-pyran-2-yl) piperidine-1,4-dicarboxylate (19): This compound was prepared according to the General Procedure A. After purification by silica gel column chromatography, compound **19** was isolated as a viscous oil (65 mg, 74%, α:β 20:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 (d, *J* = 7.5 Hz, 2H), 7.57 (d, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.5

Hz, 2H), 7.37–7.22 (m, 20H), 7.16 (dd, *J* = 7.3, 2.3 Hz, 2H), 6.43 (d, *J* = 3.5 Hz, 1H), 4.96 (d, *J* = 10.9 Hz, 1H), 4.85 (t, *J* = 10.3 Hz, 2H), 4.74–4.56 (m, 3H), 4.51 (dd, *J* = 12.7, 11.4 Hz, 2H), 4.43 (d, *J* = 6.9 Hz, 2H), 4.25 (t, *J* = 6.8 Hz, 1H), 4.10–3.81 (m, 4H), 3.73 (ddd, *J* = 19.3, 9.8, 3.4 Hz, 3H), 3.66 (dd, *J* = 10.9, 2.0 Hz, 1H), 2.97 (d, *J* = 11.8 Hz, 2H), 2.56 (tt, *J* = 10.4, 4.0 Hz, 1H), 1.88 (s, 2H), 1.65 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 172.7, 155.2, 144.2, 144.2, 141.5, 138.6, 138.1, 137.9, 137.7, 128.6, 128.6, 128.6, 128.5, 128.2, 128.2, 128.1, 128.1, 128.1, 128.0, 127.9, 127.8, 127.8, 127.2, 125.1, 120.1, 90.3, 81.7, 79.1, 77.0, 75.8, 75.5, 73.7, 73.3, 73.3, 68.2, 67.4, 47.5, 43.2, 43.1, 41.0, 27.9, 27.8.

HRMS (TOF ESI+) *m/z* calcd for $C_{55}H_{55}O_9NNa$ [(M+ Na)$^+$] 896.3769, found 896.3767.



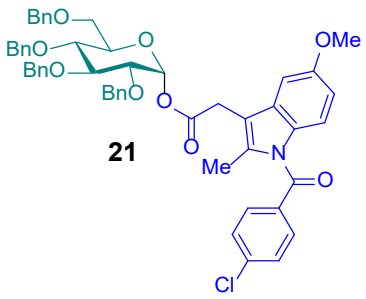
20

(2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl (3*R*,5*R*,7*R*)-adamantane-1-carboxylate (20): This compound was prepared according to the General Procedure A. After purification by silica gel column chromatography, compound **20** was isolated as a viscous oil (61 mg, 87%, α:β 17:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37–7.26 (m, 18H), 7.17 (dd, *J* = 7.2, 2.2 Hz, 2H), 6.41 (d, *J* = 3.5 Hz, 1H), 4.97 (d, *J* = 10.9 Hz, 1H), 4.85 (dd, *J* = 12.5, 10.7 Hz, 2H), 4.68 (d, *J* = 11.4 Hz, 1H), 4.64–4.57 (m, 2H), 4.54 (d, *J* = 10.6 Hz, 1H), 4.50 (d, *J* = 12.1 Hz, 1H), 3.91 (t, *J* = 9.3 Hz, 1H), 3.86 (dt, *J* = 10.1, 2.8 Hz, 1H), 3.81–3.73 (m, 2H), 3.71 (dd, *J* = 9.5, 3.6 Hz, 1H), 3.66 (dd, *J* = 10.9, 2.0 Hz, 1H), 2.02 (p, *J* = 3.0 Hz, 3H), 1.92 (dd, *J* = 3.4, 1.7 Hz, 6H), 1.79–1.65 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 175.9, 138.8, 138.2, 138.0, 138.0, 128.6, 128.5, 128.5, 128.3, 128.1, 128.1, 128.1, 128.0, 127.9, 127.9, 127.7, 89.6, 81.7, 79.4, 77.1, 75.7, 75.6, 73.7, 73.1, 72.9, 68.3, 41.3, 38.9, 36.6, 28.0.

HRMS (TOF ESI+) *m/z* calcd for $C_{45}H_{50}O_7Na$ [(M+ Na)$^+$] 725.3449, found 725.3443.



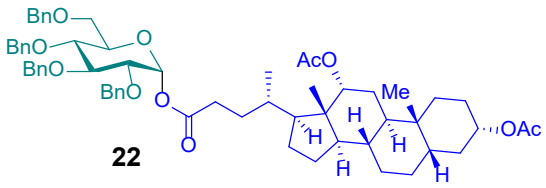
21

(2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (21): This compound was prepared according to the General Procedure A. After purification by silica gel column chromatography, compound **21** was isolated as a viscous oil (67 mg, 76%, α:β 19:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55–7.51 (m, 2H), 7.37–7.19 (m, 20H), 7.14 (dd, *J* = 6.7, 2.9 Hz, 2H), 7.01 (d, *J* = 2.5 Hz, 1H), 6.87 (d, *J* = 9.0 Hz, 1H), 6.68 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.41 (d, *J* = 2.5 Hz, 1H), 4.80 (d, *J* = 10.9 Hz, 1H), 4.71 (d, *J* = 11.0 Hz, 1H), 4.66 (d, *J* = 11.3 Hz, 1H), 4.62–4.54 (m, 3H), 4.47 (dd, *J* = 11.5, 9.1 Hz, 2H), 3.78 (s, 2H), 3.71 (s, 3H), 3.68–3.59 (m, 5H), 3.58–3.50 (m, 1H), 2.37 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 169.2, 168.3, 156.3, 139.2, 138.7, 138.3, 137.9, 137.7, 136.1, 133.9, 131.1, 130.9, 130.7, 129.1, 128.5, 128.5, 128.5, 128.1, 128.0, 128.0, 128.0, 127.9, 127.8, 127.7, 115.2, 112.5, 112.0, 101.3, 90.8, 81.8, 79.2, 76.8, 75.7, 75.1, 73.6, 73.3, 73.3, 68.2, 55.6, 30.6, 13.4.

HRMS (TOF ESI+) *m/z* calcd for $C_{53}H_{50}O_9NClNa$ [(M+ Na)$^+$] 902.3066, found 902.3045.



22

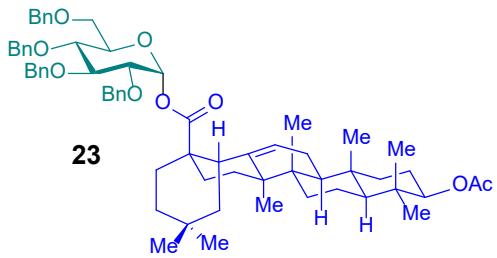
(3*S*,5*S*,8*S*,9*R*,10*R*,12*R*,13*S*,14*R*,17*S*)-10,13-dimethyl-17-((*S*)-5-oxo-5-(((2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)oxy)pentan-2-yl)hexadecahydro-1*H*-cyclopenta[a]phenanthrene-3,12-diyl diacetate (22):

This compound was prepared according to the General Procedure A. After purification by silica gel column chromatography, compound **22** was isolated as a viscous oil (63 mg, 63%, α:β 17:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44–7.21 (m, 18H), 7.15 (dd, *J* = 6.9, 2.6 Hz, 2H), 6.39 (d, *J* = 3.6 Hz, 1H), 5.08 (d, *J* = 2.6 Hz, 1H), 4.96 (d, *J* = 10.9 Hz, 1H), 4.84 (t, *J* = 10.9 Hz, 2H), 4.70 (d, *J* = 12.0 Hz, 2H), 4.66–4.58 (m, 2H), 4.50 (dd, *J* = 11.5, 10.0 Hz, 2H), 3.93 (t, *J* = 9.3 Hz, 1H), 3.87 (ddd, *J* = 10.2, 3.3, 2.0 Hz, 1H), 3.79 – 3.72 (m, 2H), 3.70 (dd, *J* = 9.6, 3.5 Hz, 1H), 3.65 (dd, *J* = 10.8, 2.0 Hz, 1H), 2.41 (ddd, *J* = 15.2, 9.9, 5.1 Hz, 1H), 2.29 (ddd, *J* = 15.7, 9.5, 6.7 Hz, 1H), 2.11 (s, 3H), 2.04 (s, 3H), 1.93–1.77 (m, 4H), 1.76–1.52 (m, 8H), 1.53–1.18 (m, 9H), 1.18–0.96 (m, 3H), 0.91 (s, 3H), 0.82 (d, *J* = 6.5 Hz, 3H), 0.70 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 172.7, 170.7, 170.6, 138.8, 138.1, 138.0, 137.8, 128.6, 128.5, 128.5, 128.2, 128.2, 128.1, 128.0, 128.0, 127.9, 127.8, 90.0, 81.8, 79.0, 77.1, 76.0, 75.8, 75.4, 74.3, 73.7, 73.2, 73.0, 68.2, 49.5, 47.9, 45.1, 42.0, 35.8, 34.9, 34.7, 34.5, 34.2, 32.4, 31.5, 30.9, 27.5, 27.0, 26.8, 26.0, 25.8, 23.5, 23.2, 21.6, 21.5, 17.6, 12.6.

HRMS (TOF ESI+) *m/z* calcd for $C_{62}H_{78}O_{11}Na$ $[(M+Na)^+]$ 1021.5436, found 1021.5436.



23

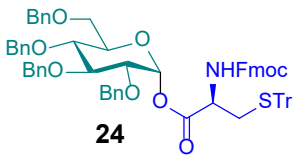
(2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl (4a*R*,6a*R*,6b*S*,8a*S*,10*R*,12a*S*,12b*S*,14b*R*)-10-acetoxy-2,2,6a,6b,9,9,12a-heptamethyl-1,3,4,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14b-octadecahydropicene-4a(2*H*)-carboxylate (23): This compound was prepared according to the General Procedure B. After purification by silica gel column chromatography, compound **23** was isolated as a white semi-solid (89 mg, 87%, α:β 20:1).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.38–7.26 (m, 18H), 7.21 (dd, *J* = 7.6, 2.1 Hz, 2H), 6.36 (d, *J* = 3.5 Hz, 1H), 5.36–5.29 (m, 1H), 4.94 (d, *J* = 11.0 Hz, 1H), 4.83 (dd, *J* = 22.5, 10.9 Hz, 2H), 4.67 (d, *J* = 11.4 Hz, 1H), 4.58 (dd, *J* = 11.2, 6.2 Hz, 2H), 4.52 (d, *J* = 6.6 Hz, 2H), 4.50–4.43 (m, 1H), 3.91–3.79 (m, 2H), 3.77–3.58 (m, 4H), 2.88 (dd, *J* = 13.8, 4.4 Hz, 1H), 2.01 (s, 4H), 1.89 (dq, *J* = 7.3, 3.7 Hz, 2H), 1.71–1.56 (m, 9H), 1.50–1.41 (m, 2H), 1.40–1.24 (m, 3H), 1.23–1.12 (m, 6H), 1.12–0.99 (m, 2H), 0.91 (d, *J* = 7.2 Hz, 9H), 0.86 (s, 6H), 0.74 (s, 3H).

^{13}C NMR (126 MHz, CD_2Cl_2): δ 176.2, 171.1, 144.0, 139.4, 138.9, 138.7, 138.5, 128.7, 128.7,

128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.1, 128.0, 127.9, 122.9, 89.6, 82.1, 81.1, 79.6, 77.6, 75.8, 75.6, 73.7, 73.7, 73.0, 68.9, 55.7, 48.0, 47.6, 46.2, 42.2, 41.7, 39.7, 38.6, 38.0, 37.3, 34.2, 33.2, 33.1, 32.8, 31.0, 28.2, 28.1, 25.8, 23.9, 23.9, 23.8, 23.6, 21.4, 18.6, 17.4, 16.9, 15.6.

HRMS (TOF ESI+) *m/z* calcd for $C_{66}H_{84}O_9Na$ [$(M+Na)^+$] 1043.6008, found 1043.5999.



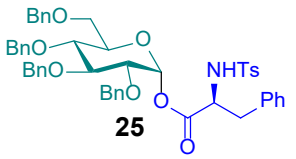
24

(2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl N-(2-(9*H*-fluoren-9-yl)acetyl)-S-trityl-L-cysteinate (24): This compound was prepared according to the General Procedure A. After purification by silica gel column chromatography, compound **24** was isolated as a viscous oil (63 mg, 57%, α:β 9:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73 (t, *J* = 6.7 Hz, 2H), 7.55 (dd, *J* = 11.6, 7.5 Hz, 2H), 7.40–7.30 (m, 9H), 7.30–7.20 (m, 16H), 7.17 (dd, *J* = 8.5, 6.8 Hz, 7H), 7.15–7.07 (m, 7H), 6.29 (d, *J* = 3.5 Hz, 1H), 5.12 (d, *J* = 8.6 Hz, 1H), 4.79 (d, *J* = 11.0 Hz, 1H), 4.73 (d, *J* = 10.8 Hz, 1H), 4.64–4.51 (m, 4H), 4.48 (d, *J* = 10.9 Hz, 1H), 4.40 (d, *J* = 12.1 Hz, 1H), 4.37–4.28 (m, 2H), 4.27–4.13 (m, 2H), 3.81–3.65 (m, 4H), 3.65–3.53 (m, 2H), 2.65 (dd, *J* = 5.6, 3.3 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): 169.5, 155.8, 144.4, 144.1, 143.8, 141.4, 141.4, 138.7, 138.4, 137.9, 137.8, 129.7, 128.5, 128.5, 128.5, 128.2, 128.1, 128.1, 128.0, 128.0, 127.9, 127.8, 127.8, 127.8, 127.2, 127.1, 125.3, 125.3, 120.1, 91.8, 81.9, 79.0, 76.7, 75.9, 75.2, 73.7, 73.4, 73.3, 68.0, 67.4, 67.3, 53.3, 47.3, 34.5.

HRMS (TOF ESI+) *m/z* calcd for $C_{71}H_{65}O_9NSNa$ [$(M+Na)^+$] 1130.4272, found 1130.4265.



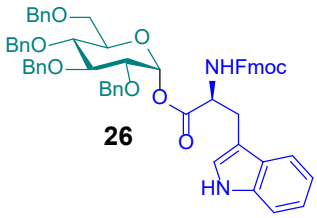
25

(2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl tosyl-L-phenylalaninate (25): This compound was prepared according to the General Procedure A. After purification by silica gel column chromatography, compound **25** was isolated as a white semi-solid (65 mg, 77%, α:β 8:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63–7.58 (m, 2H), 7.37–7.23 (m, 18H), 7.20–7.14 (m, 5H), 7.13–7.05 (m, 4H), 6.21 (d, *J* = 3.4 Hz, 1H), 4.98 (d, *J* = 9.1 Hz, 1H), 4.93 (d, *J* = 11.0 Hz, 1H), 4.84 (dd, *J* = 10.9, 8.1 Hz, 2H), 4.66 (d, *J* = 3.4 Hz, 2H), 4.60 (d, *J* = 12.1 Hz, 1H), 4.50 (dd, *J* = 21.4, 11.4 Hz, 2H), 4.27 (dt, *J* = 9.0, 5.7 Hz, 1H), 3.86 (t, *J* = 9.2 Hz, 1H), 3.82–3.61 (m, 4H), 3.55 (dd, *J* = 10.8, 1.9 Hz, 1H), 3.09 (dd, *J* = 14.0, 5.6 Hz, 1H), 2.96 (dd, *J* = 14.0, 5.9 Hz, 1H), 2.34 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): 169.8, 143.6, 138.5, 138.1, 137.8, 137.6, 136.9, 134.8, 129.8, 129.8, 128.6, 128.6, 128.6, 128.6, 128.6, 128.2, 128.1, 128.1, 128.1, 128.0, 128.0, 128.0, 127.9, 127.3, 127.2, 92.1, 81.5, 78.7, 76.8, 75.8, 75.4, 73.7, 73.6, 73.3, 68.0, 56.4, 39.2, 21.6.

HRMS (TOF ESI+) *m/z* calcd for $C_{50}H_{51}O_9NSNa$ [$(M+Na)^+$] 864.3177, found 864.3170.



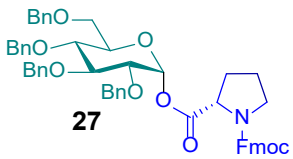
26

(2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl (((9*H*-fluoren-9-yl)methoxy)carbonyl)-L-tryptophanate (26): This compound was prepared according to the General Procedure A. After purification by silica gel column chromatography, compound **26** was isolated as a viscous oil (58 mg, 61%, α:β 8:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78–7.71 (m, 2H), 7.55 (t, *J* = 7.6 Hz, 2H), 7.52–7.46 (m, 1H), 7.44–7.20 (m, 23H), 7.20–7.13 (m, 4H), 7.09 (td, *J* = 7.9, 1.3 Hz, 1H), 6.98 (d, *J* = 2.6 Hz, 1H), 6.50 (d, *J* = 3.4 Hz, 1H), 5.30 (d, *J* = 8.8 Hz, 1H), 4.94 (d, *J* = 11.1 Hz, 1H), 4.85 (d, *J* = 10.6 Hz, 3H), 4.73 (d, *J* = 3.8 Hz, 2H), 4.62 (d, *J* = 12.1 Hz, 1H), 4.55 (d, *J* = 10.6 Hz, 1H), 4.49 (d, *J* = 12.0 Hz, 1H), 4.38 (dd, *J* = 10.5, 7.6 Hz, 1H), 4.30 (dd, *J* = 10.6, 7.1 Hz, 1H), 4.18 (t, *J* = 7.3 Hz, 1H), 3.95 (t, *J* = 9.3 Hz, 1H), 3.92 – 3.59 (m, 5H), 3.38 (dd, *J* = 14.9, 5.4 Hz, 1H), 3.28 (dd, *J* = 14.9, 4.6 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 170.6, 155.9, 144.1, 143.9, 141.4, 138.6, 138.1, 137.9, 136.0, 128.7, 128.6, 128.6, 128.6, 128.5, 128.1, 128.1, 128.1, 128.0, 128.0, 127.9, 127.9, 127.8, 127.2, 125.4, 124.2, 122.1, 120.1, 119.9, 118.6, 111.3, 109.1, 91.5, 81.6, 79.5, 77.4, 75.8, 75.4, 74.0, 73.7, 73.4, 68.1, 67.3, 55.3, 47.3, 27.6.

HRMS (TOF ESI+) *m/z* calcd for $C_{60}H_{56}O_9N_2Na$ [$(M+ Na)^+$] 971.3878, found 971.3874.



27

1-((9*H*-fluoren-9-yl)methyl)2-((2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6(benzyloxy)methyl) tetrahydro-2*H*-pyran-2-yl) (*S*)-pyrrolidine-1,2-dicarboxylate (27): This compound was prepared according to the General Procedure A using **BPhen** as a catalyst. After purification by silica gel column chromatography, compound **27** was isolated as a viscous oil (57 mg, 66%, α:β 20:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (ddd, *J* = 13.0, 6.4, 2.2 Hz, 5H), 7.66–7.61 (m, 1H), 7.61–7.55 (m, 2H), 7.54–7.49 (m, 1H), 7.44–7.19 (m, 42H), 7.14 (ddd, *J* = 9.3, 7.0, 2.4 Hz, 5H), 6.52 (d, *J* = 3.4 Hz, 1H), 6.47 (d, *J* = 3.4 Hz, 1H), 4.94 (dd, *J* = 16.4, 11.0 Hz, 2H), 4.88–4.78 (m, 4H), 4.73–4.57 (m, 5H), 4.57–4.39 (m, 7H), 4.39–4.15 (m, 6H), 3.98–3.86 (m, 3H), 3.86–3.76 (m, 3H), 3.75–3.68 (m, 3H), 3.68–3.61 (m, 3H), 3.62–3.56 (m, 1H), 3.49 (tt, *J* = 9.8, 7.6 Hz, 2H), 3.33 (dd, *J* = 10.9, 2.0 Hz, 1H), 2.28–2.01 (m, 4H), 1.94–1.62 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 171.1, 171.0, 155.0, 154.6, 144.5, 144.4, 144.0, 143.9, 141.5, 141.4, 141.4, 141.3, 138.7, 138.6, 138.3, 138.2, 138.0, 137.9, 137.8, 137.6, 128.5, 128.5, 128.5, 128.5, 128.3, 128.2, 128.1, 128.1, 128.1, 128.0, 127.9, 127.9, 127.9, 127.8, 127.8, 127.8, 127.7, 127.3, 127.2, 127.2, 125.4, 125.3, 125.3, 120.1, 120.1, 120.0, 120.0, 91.2, 91.1, 81.7, 81.5, 79.4, 79.4, 77.4, 75.8, 75.7, 75.4, 73.7, 73.6, 73.5, 73.5, 73.3, 73.2, 68.1, 68.0, 67.8, 67.6, 67.2, 59.2, 58.9, 47.4, 47.1, 46.6, 31.1, 29.9, 24.1, 23.2.

HRMS (TOF ESI+) *m/z* calcd for $C_{54}H_{53}O_9NNa$ $[(M+Na)^+]$ 882.3613, found 882.3609.

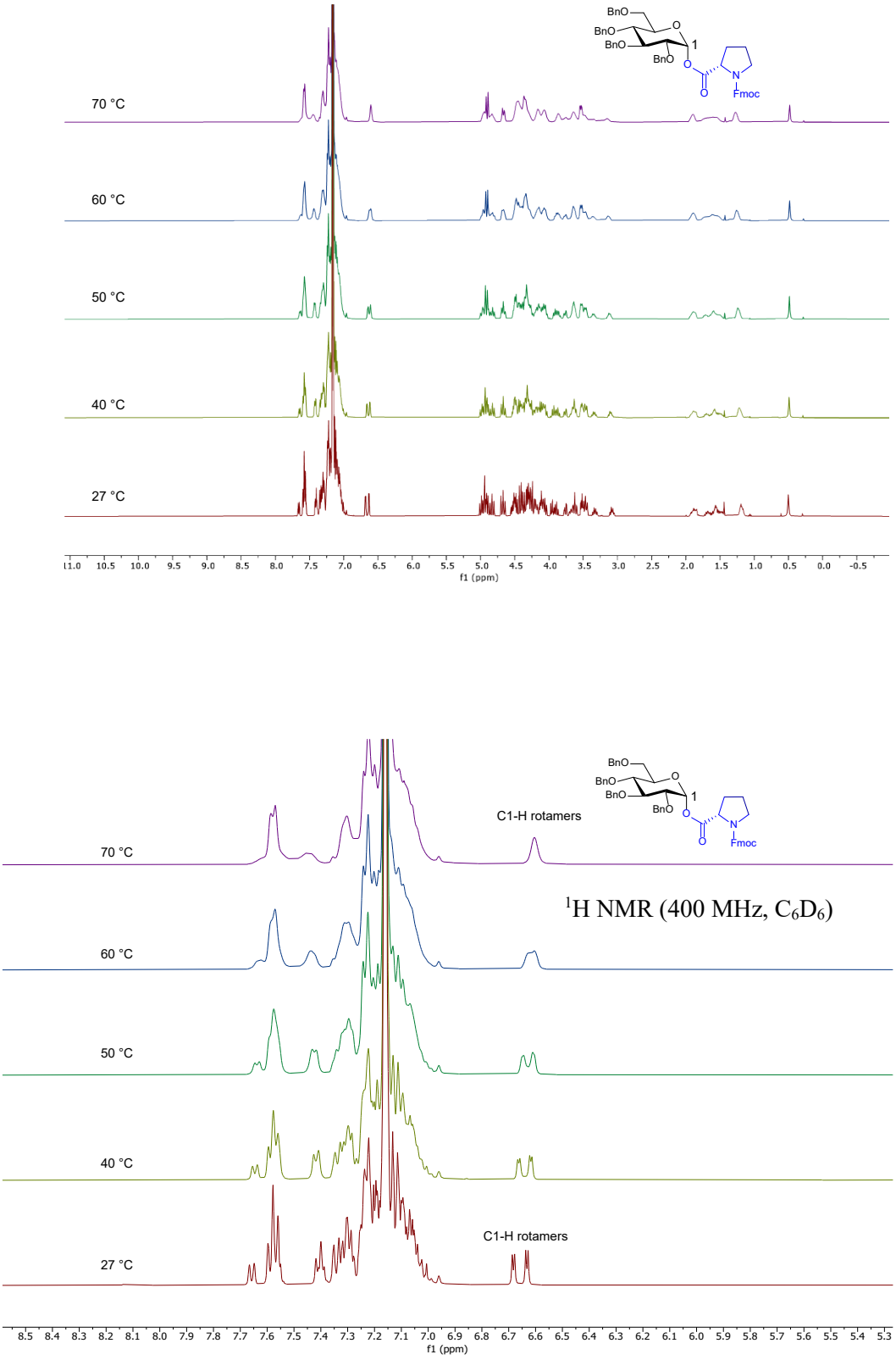
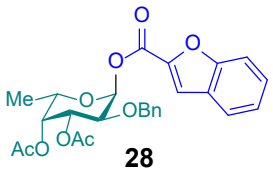


Figure S1. VT NMR experiment for determination of existence of rotamers.



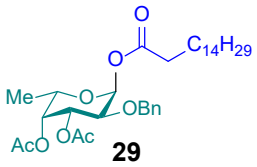
28

6-((benzofuran-2-carbonyl)oxy)-5-(benzyloxy)-2-methyltetrahydro-2*H*-pyran-3,4-diyl diacetate (28): This compound was prepared according to the General Procedure B. After purification by silica gel column chromatography, compound **28** was isolated as a viscous oil (30 mg, 62%, α:β 16:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70 (d, *J* = 7.9 Hz, 1H), 7.66–7.60 (m, 2H), 7.51–7.45 (m, 1H), 7.35–7.27 (m, 6H), 6.61 (d, *J* = 3.6 Hz, 1H), 5.48–5.39 (m, 2H), 4.71 (d, *J* = 12.1 Hz, 1H), 4.64 (d, *J* = 12.1 Hz, 1H), 4.39 (q, *J* = 6.7 Hz, 1H), 4.04 (dd, *J* = 10.4, 3.6 Hz, 1H), 2.16 (s, 3H), 2.02 (s, 3H), 1.16 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 170.6, 170.3, 144.7, 137.7, 128.6, 128.2, 128.1, 127.9, 127.0, 124.1, 123.1, 115.3, 112.7, 91.6, 73.3, 72.4, 71.1, 70.2, 67.6, 21.0, 20.8, 16.1.

HRMS (TOF ESI+) *m/z* calcd for $C_{26}H_{26}O_9Na$ $[(M+Na)^+]$ 505.1469, found 505.1466.



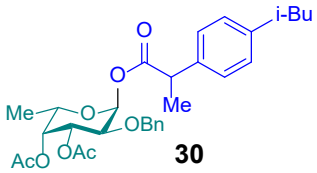
29

(2*S*,3*R*,4*R*,5*S*,6*S*)-5-(benzyloxy)-2-methyl-6-(palmitoyloxy)tetrahydro-2*H*-pyran-3,4-diyl diacetate (29): This compound was prepared according to the General Procedure B. After purification by silica gel column chromatography, compound **29** was isolated as a viscous oil (40 mg, 69%, α:β 20:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38–7.24 (m, 5H), 6.41 (d, *J* = 3.7 Hz, 1H), 5.31 (dd, *J* = 3.3, 1.3 Hz, 1H), 5.27 (dd, *J* = 10.5, 3.3 Hz, 1H), 4.65 (d, *J* = 11.9 Hz, 1H), 4.56 (d, *J* = 11.8 Hz, 1H), 4.26–4.18 (m, 1H), 3.93 (dd, *J* = 10.5, 3.7 Hz, 1H), 2.44–2.34 (m, 2H), 2.13 (s, 3H), 2.00 (s, 3H), 1.64 (q, *J* = 7.4 Hz, 2H), 1.37–1.19 (m, 24H), 1.12 (d, *J* = 6.5 Hz, 3H), 0.88 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 172.4, 170.6, 170.3, 137.8, 128.5, 128.0, 127.8, 90.1, 77.4, 73.1, 72.5, 71.2, 70.1, 67.1, 34.5, 32.1, 29.8, 29.8, 29.8, 29.7, 29.6, 29.5, 29.4, 29.2, 25.0, 22.8, 20.9, 20.8, 16.1, 14.3.

HRMS (TOF ESI+) *m/z* calcd for $C_{33}H_{52}O_8Na$ $[(M+Na)^+]$ 599.3554, found 599.3550.



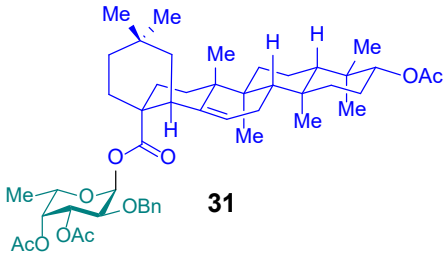
30

5-(benzyloxy)-6-((2-(4-isobutylphenyl)propanoyl)oxy)-2-methyltetrahydro-2*H*-pyran-3,4-diyl diacetate(30): This compound was prepared according to the General Procedure B. After purification by silica gel column chromatography, compound **30** was isolated as a viscous oil (34 mg, 65%, α:β 17:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38–7.24 (m, 8H), 7.24–7.18 (m, 4H), 7.17–7.12 (m, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 7.06–7.00 (m, 2H), 6.33 (d, *J* = 3.6 Hz, 1H), 6.31 (d, *J* = 3.7 Hz, 1H), 5.24 (dd, *J* = 3.4, 1.3 Hz, 1H), 5.21–5.09 (m, 3H), 4.67–4.56 (m, 2H), 4.56–4.43 (m, 2H), 4.04–3.94 (m, 1H), 3.88 (ddd, *J* = 10.5, 9.1, 3.7 Hz, 2H), 3.79 (qd, *J* = 7.2, 1.8 Hz, 2H), 3.54–3.45 (m, 1H), 2.43 (dd, *J* = 9.8, 7.2 Hz, 4H), 2.11 (s, 3H), 2.09 (s, 3H), 1.99 (s, 3H), 1.97 (s, 3H), 1.81 (ddp, *J* = 13.6, 8.8, 6.7 Hz, 2H), 1.56 (d, *J* = 7.2 Hz, 3H), 1.49 (d, *J* = 7.1 Hz, 3H), 1.05 (d, *J* = 6.5 Hz, 3H), 0.91–0.83 (m, 15H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 173.3, 173.3, 170.6, 170.5, 170.2, 170.1, 140.9, 140.8, 137.8, 137.8, 137.7, 136.9, 129.6, 129.4, 128.6, 128.4, 128.1, 127.9, 127.8, 127.7, 127.4, 127.4, 90.5, 90.3, 73.1, 72.8, 72.6, 72.4, 71.1, 70.0, 67.1, 66.7, 45.4, 45.3, 45.1, 45.1, 30.3, 30.3, 22.5, 22.5, 22.5, 20.9, 20.9, 20.8, 20.7, 18.1, 17.9, 16.1, 15.8.

HRMS (TOF ESI+) *m/z* calcd for $C_{30}H_{38}O_8Na$ $[(M+Na)^+]$ 549.2459, found 549.2455.



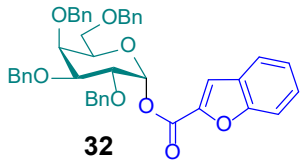
31

(2*S*,3*R*,4*R*,5*S*,6*S*)-6-(((4a*R*,6a*R*,6b*S*,8a*S*,10*R*,12a*S*,12b*S*,14b*R*)-10-acetoxy-2,2,6a,6b,9,9,12a-heptamethyl-1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14b-icosahydropicene-4a-carbonyl)oxy)-5-(benzyloxy)-2-methyltetrahydro-2*H*-pyran-3,4-diyl diacetate(31): This compound was prepared according to the General Procedure B. After purification by silica gel column chromatography, compound **31** was isolated as a viscous oil (58 mg, 69%, α:β 20:1).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.39–7.20 (m, 5H), 6.30 (d, *J* = 3.8 Hz, 1H), 5.39–5.21 (m, 3H), 4.68–4.53 (m, 2H), 4.47–4.40 (m, 1H), 4.20 (qd, *J* = 6.4, 1.1 Hz, 1H), 3.95 (dd, *J* = 9.9, 3.7 Hz, 1H), 2.96–2.85 (m, 1H), 2.12 (s, 3H), 2.00 (s, 3H), 1.96 (s, 3H), 1.91–1.75 (m, 3H), 1.75–1.50 (m, 8H), 1.50–1.37 (m, 3H), 1.37–1.25 (m, 2H), 1.22–1.10 (m, 6H), 1.10–1.00 (m, 5H), 0.97–0.88 (m, 9H), 0.85 (d, *J* = 4.5 Hz, 7H), 0.68 (s, 3H).

^{13}C NMR (126 MHz, CD_2Cl_2): δ 176.3, 171.1, 170.8, 170.4, 144.6, 138.4, 128.6, 128.0, 127.8, 122.8, 90.1, 81.1, 73.4, 73.2, 71.4, 70.7, 67.4, 55.6, 47.9, 47.9, 46.2, 42.2, 41.9, 39.7, 38.5, 38.0, 37.3, 34.1, 33.1, 33.0, 32.9, 31.0, 28.2, 27.9, 25.9, 23.9, 23.6, 23.4, 21.4, 21.0, 20.8, 18.6, 17.3, 16.8, 16.2, 15.5.

HRMS (TOF ESI+) *m/z* calcd for $C_{49}H_{70}O_{10}Na$ [$(M+Na)^+$] 841.4861, found 841.4841.



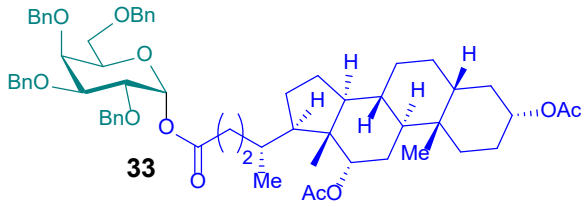
32

(2*R*,3*R*,4*S*,5*S*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl benzofuran-2-carboxylate (32): This compound was prepared according to the General Procedure B. After purification by silica gel column chromatography, compound **32** was isolated as a viscous oil (41 mg, 60%, α:β 9:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69 (dt, *J* = 7.8, 0.9 Hz, 1H), 7.64–7.57 (m, 1H), 7.54–7.44 (m, 2H), 7.43–7.22 (m, 21H), 6.62 (d, *J* = 3.6 Hz, 1H), 4.99 (d, *J* = 11.3 Hz, 1H), 4.86 (d, *J* = 11.8 Hz, 1H), 4.84–4.71 (m, 3H), 4.68–4.57 (m, 1H), 4.50–4.38 (m, 2H), 4.27 (dd, *J* = 10.1, 3.6 Hz, 1H), 4.20 (td, *J* = 5.6, 2.6 Hz, 1H), 4.15–4.11 (m, 1H), 4.06 (dd, *J* = 10.1, 2.8 Hz, 1H), 3.63 (dd, *J* = 9.3, 7.6 Hz, 1H), 3.55 (dd, *J* = 9.3, 5.4 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 158.2, 156.1, 145.2, 138.7, 138.6, 138.1, 137.9, 128.6, 128.5, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 128.0, 127.8, 127.8, 127.7, 127.7, 127.1, 124.0, 123.0, 114.8, 112.6, 92.3, 78.6, 75.6, 75.1, 74.7, 73.9, 73.6, 73.2, 72.4, 68.4.

HRMS (TOF ESI+) *m/z* calcd for $C_{43}H_{40}O_8Na$ [$(M+Na)^+$] 707.2615, found 707.2609.



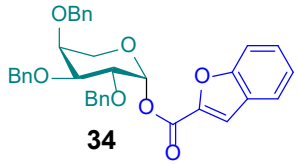
33

(3*R*,5*R*,8*R*,9*S*,10*S*,12*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-5-oxo-5-(((2*R*,3*R*,4*S*,5*S*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)oxy)pentan-2-yl)hexadecahydro-1*H*-cyclopenta[a]phenanthrene-3,12-diyl diacetate (33): This compound was prepared according to the General Procedure B. After purification by silica gel column chromatography, compound **33** was isolated as a viscous oil (72 mg, 72%, α:β 8:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43–7.27 (m, 20H), 6.40 (d, *J* = 3.8 Hz, 1H), 5.08 (d, *J* = 3.1 Hz, 1H), 4.96 (d, *J* = 11.4 Hz, 1H), 4.82 (d, *J* = 11.8 Hz, 1H), 4.77–4.66 (m, 4H), 4.58 (d, *J* = 11.4 Hz, 1H), 4.51–4.37 (m, 2H), 4.17 (dd, *J* = 10.1, 3.7 Hz, 1H), 4.06–3.99 (m, 2H), 3.87 (dd, *J* = 10.1, 2.8 Hz, 1H), 3.58 (dd, *J* = 9.2, 7.6 Hz, 1H), 3.52 (dd, *J* = 9.1, 5.4 Hz, 1H), 2.39 (ddd, *J* = 15.3, 10.0, 5.1 Hz, 1H), 2.26 (ddd, *J* = 15.6, 9.7, 6.6 Hz, 1H), 2.10 (s, 3H), 2.04 (s, 3H), 1.90–1.75 (m, 4H), 1.75–1.53 (m, 8H), 1.52–1.34 (m, 5H), 1.33–1.18 (m, 4H), 1.18–0.97 (m, 3H), 0.91 (s, 3H), 0.80 (d, *J* = 6.5 Hz, 3H), 0.69 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 172.7, 170.7, 170.6, 138.7, 138.6, 138.2, 137.9, 128.6, 128.5, 128.4, 128.4, 128.3, 128.1, 128.0, 128.0, 127.8, 127.8, 127.7, 127.5, 90.8, 78.7, 76.1, 75.6, 75.0, 74.7, 74.3, 73.7, 73.4, 73.1, 72.0, 68.6, 49.6, 47.9, 45.1, 42.0, 35.8, 34.9, 34.7, 34.5, 34.2, 32.4, 31.6, 31.0, 27.5, 27.0, 26.8, 26.0, 25.8, 23.6, 23.2, 21.6, 21.5, 17.6, 12.6.

HRMS (TOF ESI+) *m/z* calcd for $C_{62}H_{78}O_{11}Na$ $[(M+Na)^+]$ 1021.5436, found 1021.5435.



34

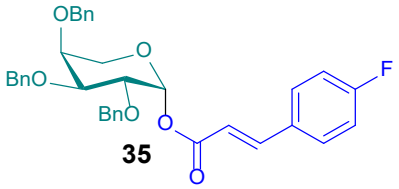
3,4,5-tris(benzyloxy)tetrahydro-2*H*-pyran-2-yl benzofuran-2-carboxylate (34): This compound was prepared according to the General Procedure A. After purification by silica gel column chromatography, compound **34** was isolated as a viscous oil (44 mg, 78%, α:β 8:1)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 7.8 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.49 (s, 1H), 7.48–7.42 (m, 1H), 7.42–7.22 (m, 16H), 6.58 (d, *J* = 3.4 Hz, 1H), 4.88–4.64 (m, 6H), 4.25

(dd, J = 9.7, 3.4 Hz, 1H), 4.02 (dd, J = 9.7, 2.9 Hz, 1H), 3.95–3.87 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.2, 156.1, 145.2, 138.6, 138.2, 138.2, 128.6, 128.5, 128.5, 128.1, 128.0, 127.9, 127.9, 127.8, 127.8, 127.0, 124.0, 123.0, 114.8, 112.6, 92.8, 76.9, 75.5, 73.7, 73.6, 72.8, 72.0, 63.1.

HRMS (TOF ESI+) *m/z* calcd for $C_{35}H_{32}O_7Na$ [$(M+Na)^+$] 587.2040, found 587.2037.



35

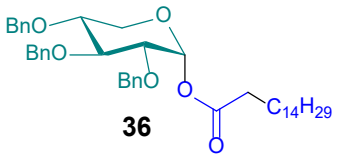
(2*R*,3*R*,4*S*,5*S*)-3,4,5-tris(benzyloxy)tetrahydro-2*H*-pyran-2-yl (E)-3-(4-fluorophenyl) Acrylate (35): This compound was prepared according to the General Procedure A. After purification by silica gel column chromatography, compound **35** was isolated as a viscous oil (38 mg, 67%, α:β 9:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68 (d, J = 16.0 Hz, 1H), 7.56–7.47 (m, 2H), 7.41–7.26 (m, 15H), 7.15–7.04 (m, 2H), 6.45 (d, J = 3.5 Hz, 1H), 6.40 (d, J = 15.9 Hz, 1H), 4.80–4.67 (m, 6H), 4.21 (dd, J = 9.6, 3.5 Hz, 1H), 3.94 (dd, J = 9.6, 3.0 Hz, 1H), 3.87 (dt, J = 6.4, 3.2 Hz, 2H), 3.78 (dd, J = 13.1, 2.0 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 165.5, 164.2 (d, $^{1}J_{CF}$ = 251.7 Hz), 144.7, 138.7, 138.3, 138.2, 130.7 (d, $^{4}J_{CF}$ = 3.4 Hz), 130.3 (d, $^{3}J_{CF}$ = 8.6 Hz), 128.6, 128.5, 128.5, 128.1, 128.1, 127.9, 127.7, 127.7, 117.6, 117.6, 116.2 (d,$^{2}J_{CF}$ = 21.9 Hz). 91.7, 77.1, 75.5, 73.7, 73.6, 72.8, 72.0, 62.6.

^{19}F NMR (471 MHz, $CDCl_3$): δ -109.2.

HRMS (TOF ESI+) *m/z* calcd for $C_{35}H_{37}O_6NF$ [$(M+ NH_4)^+$] 586.2599, found 586.2601.



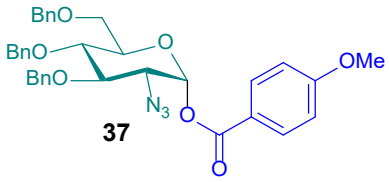
36

(2*R*,3*R*,4*S*,5*R*)-3,4,5-tris(benzyloxy)tetrahydro-2*H*-pyran-2-yl pentadecanoate (36): This compound was prepared according to the General Procedure A. After purification by silica gel column chromatography, compound **36** was isolated as a viscous oil (45 mg, 68%, α:β 6:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40–7.27 (m, 15H), 6.24 (d, *J* = 3.6 Hz, 1H), 4.93–4.83 (m, 2H), 4.79–4.72 (m, 1H), 4.68–4.61 (m, 3H), 3.85 (t, *J* = 8.8 Hz, 1H), 3.74 (dd, *J* = 5.2, 2.4 Hz, 1H), 3.65–3.55 (m, 3H), 2.40 (td, *J* = 7.4, 3.2 Hz, 2H), 1.73–1.59 (m, 2H), 1.25 (d, *J* = 3.9 Hz, 24H), 0.88 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 172.6, 138.9, 138.2, 137.9, 128.6, 128.6, 128.5, 128.2, 128.1, 128.1, 128.0, 128.0, 127.8, 89.9, 81.3, 78.8, 77.5, 77.4, 75.9, 73.9, 73.4, 62.3, 34.5, 32.1, 29.9, 29.8, 29.8, 29.8, 29.6, 29.5, 29.5, 29.2, 25.1, 22.8, 14.3.

HRMS (TOF ESI+) *m/z* calcd for $C_{42}H_{58}O_6Na$ [(M+ Na)$^+$] 681.4126, found 681.4116



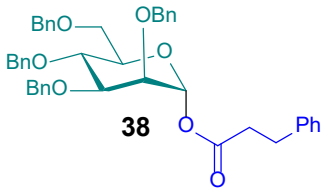
37

(2*R*,3*R*,4*R*,5*S*,6*R*)-3-azido-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl 4-methoxybenzoate (37): This compound was prepared according to the General Procedure B. After purification by silica gel column chromatography, compound **37** was isolated as a viscous oil (20 mg, 33%, α:β 15:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.9 Hz, 2H), 7.43–7.27 (m, 13H), 7.18 (dd, *J* = 7.4, 2.1 Hz, 2H), 6.99–6.91 (m, 2H), 6.48 (d, *J* = 3.6 Hz, 1H), 4.96 (d, *J* = 4.5 Hz, 2H), 4.85 (d, *J* = 10.6 Hz, 1H), 4.61 (dd, *J* = 15.5, 11.3 Hz, 2H), 4.49 (d, *J* = 12.0 Hz, 1H), 4.11–4.03 (m, 1H), 3.92 (d, *J* = 7.9 Hz, 2H), 3.88 (s, 3H), 3.80 (dd, *J* = 11.1, 2.5 Hz, 1H), 3.72 (dd, *J* = 10.1, 3.6 Hz, 1H), 3.66 (dd, *J* = 11.1, 1.5 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 164.3, 164.2, 137.9, 137.9, 132.2, 128.7, 128.7, 128.6, 128.2, 128.2, 128.1, 128.1, 127.9, 121.6, 114.0, 91.2, 80.8, 77.8, 75.7, 75.5, 73.8, 73.5, 68.0, 63.3, 55.7.

HRMS (TOF ESI+) *m/z* calcd for $C_{35}H_{35}O_7N_3Na$ [(M+Na)$^+$] 632.2367, found 632.2359.



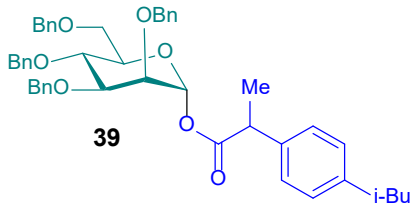
38

(2*R*,3*S*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl 3-phenylpropanoate (38): This compound was prepared according to the General Procedure B using catalyst **C7** in dichloroethane. After purification by silica gel column chromatography, compound **38** was isolated as a viscous oil (43 mg, 64%, α:β 20:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 (dd, *J* = 7.6, 2.1 Hz, 2H), 7.39–7.27 (m, 18H), 7.19 (ddd, *J* = 13.7, 7.5, 1.8 Hz, 5H), 6.26 (d, *J* = 2.0 Hz, 1H), 4.90 (d, *J* = 10.7 Hz, 1H), 4.83–4.72 (m, 2H), 4.69 (d, *J* = 12.1 Hz, 1H), 4.60–4.50 (m, 4H), 4.09 (t, *J* = 9.2 Hz, 1H), 3.82–3.74 (m, 3H), 3.74–3.64 (m, 2H), 2.92 (t, *J* = 7.6 Hz, 2H), 2.63 (qt, *J* = 15.9, 7.6 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 171.0, 140.1, 138.4, 138.4, 138.3, 138.0, 128.7, 128.5, 128.5, 128.4, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 126.5, 92.0, 79.2, 75.4, 74.6, 74.3, 73.6, 73.5, 72.5, 72.2, 69.0, 36.0, 30.9.

HRMS (TOF ESI+) *m/z* calcd for $C_{43}H_{44}O_7Na$ [(M+ Na)$^+$] 695.2979, found 695.2966



39

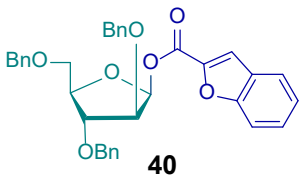
(2*R*,3*S*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl 2-(4-isobutylphenyl)propanoate (39): This compound was prepared according to the General Procedure B using catalyst **C7** in dichloroethane. After purification by silica gel column chromatography, compound **39** was isolated as a viscous oil (37 mg, 51%, α:β >20:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41–7.18 (m, 35H), 7.18–7.08 (m, 9H), 7.04 (dd, *J* = 8.2, 6.4 Hz, 4H), 6.23 (d, *J* = 2.1 Hz, 1H), 6.20 (d, *J* = 1.6 Hz, 1H), 4.83 (dd, *J* = 10.8, 9.0 Hz, 2H), 4.77–4.59 (m, 6H), 4.57–4.46 (m, 5H), 4.43 (d, *J* = 12.0 Hz, 1H), 4.26 (s, 2H), 4.01 (dt, *J* = 23.7, 9.5 Hz, 2H), 3.81–3.58 (m, 8H), 3.58–3.47 (m, 3H), 3.35 (ddd, *J* = 10.0, 4.3, 1.8 Hz, 1H), 2.38 (dd, *J* = 7.2, 5.6 Hz, 4H), 1.77 (dpd, *J* = 13.6, 6.7, 3.7 Hz, 2H), 1.45 (d, *J* = 7.1 Hz, 6H), 0.87–0.80 (m, 12H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 172.8, 172.8, 140.9, 140.9, 138.6, 138.5, 138.4, 138.4, 138.4, 138.3, 138.1, 138.0, 137.5, 137.2, 129.6, 129.6, 128.5, 128.5, 128.5, 128.5, 128.5, 128.4, 128.4, 128.2, 128.1, 128.1, 128.0, 128.0, 128.0, 127.9, 127.9, 127.8, 127.8, 127.8, 127.7, 127.7, 127.6,

127.3, 127.2, 92.4, 91.9, 79.6, 79.4, 75.3, 75.2, 74.8, 74.3, 74.2, 74.2, 73.9, 73.6, 73.5, 73.4, 72.6, 72.6, 72.3, 72.1, 69.1, 68.7, 45.4, 45.3, 45.1, 45.1, 30.3, 30.3, 29.8, 22.5, 22.5, 18.0, 18.0.

HRMS (TOF ESI+) *m/z* calcd for $C_{47}H_{52}O_7Na$ [$(M+Na)^+$] 751.3605, found 751.3588



40

***(2S,3S,4S,5R)-3,4-bis(benzyloxy)-5-((benzyloxy)methyl)tetrahydrofuran-2-yl benzofuran-2-carboxylate* (40):** This compound was prepared according to the General Procedure A. After purification by silica gel column chromatography, compound **40** was isolated as a viscous oil (45 mg, 80%, α:β 1:3).

For β-isomer **40:**

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.62 (dt, *J* = 7.8, 1.1 Hz, 1H), 7.58 (dd, *J* = 8.4, 1.0 Hz, 1H), 7.46 (ddd, *J* = 8.4, 7.1, 1.3 Hz, 1H), 7.39–7.23 (m, 16H), 7.23–7.17 (m, 1H), 6.56 (d, *J* = 3.6 Hz, 1H), 4.75–4.70 (m, 1H), 4.69–4.58 (m, 3H), 4.56 (d, *J* = 2.4 Hz, 2H), 4.35–4.29 (m, 2H), 4.30–4.23 (m, 1H), 3.67 (dd, *J* = 5.2, 1.9 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 158.4, 156.1, 145.1, 138.1, 138.1, 137.4, 128.6, 128.6, 128.5, 128.2, 128.2, 127.9, 127.9, 127.9, 127.8, 127.8, 127.0, 123.9, 123.1, 114.7, 112.6, 95.6, 84.1, 81.8, 73.5, 73.4, 72.8, 71.1.

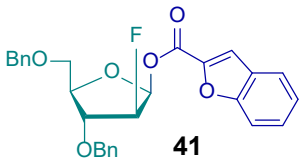
HRMS (TOF ESI+) *m/z* calcd for $C_{35}H_{32}O_7Na$ [$(M+ Na)^+$] 587.2040, found 587.2040.

For α-isomer **40:**

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (d, *J* = 7.7 Hz, 1H), 7.60 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.51 (d, *J* = 1.0 Hz, 1H), 7.46 (ddd, *J* = 8.5, 7.2, 1.3 Hz, 1H), 7.41–7.23 (m, 16H), 6.52 (s, 1H), 4.72 (d, *J* = 11.9 Hz, 1H), 4.62–4.57 (m, 3H), 4.52 (d, *J* = 16.0 Hz, 3H), 4.27 (d, *J* = 2.1 Hz, 1H), 4.06 (dd, *J* = 5.3, 2.1 Hz, 1H), 3.67 (dd, *J* = 5.1, 2.2 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 158.5, 156.1, 145.1, 138.1, 137.8, 137.3, 128.7, 128.6, 128.5, 128.2, 128.1, 128.0, 127.9, 127.9, 127.8, 127.0, 124.0, 123.1, 115.0, 112.6, 101.5, 87.0, 84.0, 83.8, 77.4, 77.2, 76.9, 73.6, 72.4, 72.3, 69.8.

HRMS (TOF ESI+) *m/z* calcd for $C_{35}H_{32}O_7Na$ [$(M+ Na)^+$] 587.2040, found 587.2036.



41

***(2S,3S,4S,5R*)-4-(benzyloxy)-5-((benzyloxy)methyl)-3-fluorotetrahydrofuran-2-yl benzofuran-2-carboxylate (41):** This compound was prepared according to General Procedure B. After purification by silica gel column chromatography, compound **41** was isolated as a viscous oil (30 mg, 63%, α:β 1:4).

For β-isomer **41:**

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.62 (dt, *J* = 7.8, 0.9 Hz, 1H), 7.57 (dd, *J* = 8.4, 1.0 Hz, 1H), 7.46 (ddd, *J* = 8.4, 7.1, 1.3 Hz, 1H), 7.39 – 7.29 (m, 7H), 7.28–7.22 (m, 4H), 7.21–7.17 (m, 1H), 6.59 (d, *J* = 4.4 Hz, 1H), 5.28 (ddd, $J_{C\text{-}F}$ = 52.4, 6.4, 4.5 Hz, 1H), 4.78 (dd, *J* = 11.7, 1.1 Hz, 1H), 4.67 (d, *J* = 11.8 Hz, 1H), 4.60 – 4.53 (m, 2H), 4.53 – 4.45 (m, 1H), 4.33 – 4.26 (m, 1H), 3.71 – 3.64 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 158.0, 156.2, 144.7, 137.9, 137.4, 128.7, 128.5, 128.2, 128.1, 128.0, 128.0, 127.8, 127.8, 127.0, 124.0, 123.1, 115.1, 112.6, 94.94 (d, $^{1}J_{C\text{-}F}$ = 201.4 Hz), 94.43 (d, $^{2}J_{C\text{-}F}$ =18.3 Hz), 81.53 (d, $^{3}J_{C\text{-}F}$ = 9.4 Hz), 80.38 (d, $^{2}J_{C\text{-}F}$ = 20.8 Hz), 76.9, 73.6, 72.6, 70.4.

^{19}F NMR (471 MHz, $CDCl_3$) δ = -203.02.

HRMS (TOF ESI+) *m/z* calcd for $C_{28}H_{25}O_6FNa$ [(M+ Na)$^{+}$] 499.1527, found 499.1522.

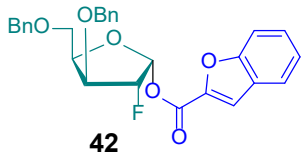
For α-isomer **41:**

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.59 (dq, *J* = 8.4, 0.9 Hz, 1H), 7.53 (d, *J* = 1.0 Hz, 1H), 7.47 (ddd, *J* = 8.5, 7.2, 1.3 Hz, 1H), 7.38–7.28 (m, 11H), 6.59 (d, *J* = 11.0 Hz, 1H), 5.25 (dd, $J_{C\text{-}F}$ = 50.3, 1.6 Hz, 1H), 4.71 (d, *J* = 11.8 Hz, 1H), 4.66 – 4.54 (m, 3H), 4.51 (q, *J* = 5.0 Hz, 1H), 4.27–4.17 (m, 1H), 3.67 (t, *J* = 4.3 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 58.0, 156.2, 144.8, 138.2, 137.4, 128.7, 128.5, 128.2, 128.1, 127.82, 127.8, 127.7, 127.0, 124.0, 123.1, 115.2, 112.6, 99.6 (d, $^{2}J_{C\text{-}F}$ = 73.4 Hz), 99.05 (d, $^{1}J_{C\text{-}F}$ = 296.6 Hz), 84.11 (d, $^{3}J_{C\text{-}F}$ = 3.1 Hz), 82.62 (d, $^{2}J_{C\text{-}F}$ = 25.8 Hz),73.6, 73.0, 68.7.

^{19}F NMR (471 MHz, $CDCl_3$) δ = -188.40

HRMS (TOF ESI+) *m/z* calcd for $C_{28}H_{25}O_6FNa$ [(M+ Na)$^{+}$] 499.1527, found 499.1523.



42

(*2R,3R,4S,5R*)-4-(benzyloxy)-5-((benzyloxy)methyl)-3-fluorotetrahydrofuran-2-yl benzofuran-2-carboxylate (42): This compound was prepared according to General Procedure B. After purification by silica gel column chromatography, compound **42** was isolated as a viscous oil (35 mg, 74%, α:β 4:1).

For α-isomer **42:**

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.69 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.47 (ddd, *J* = 8.5, 7.0, 1.3 Hz, 1H), 7.40–7.27 (m, 11H), 6.64 (dd, *J* = 4.4, 2.5 Hz, 1H), 5.34 (dt, $J_{C\text{-}F}$ = 52.3, 4.5 Hz, 1H), 4.78 (d, *J* = 11.9 Hz, 1H), 4.68–4.55 (m, 4H), 4.50 (ddd, *J* = 15.7, 6.6, 4.7 Hz, 1H), 3.82–3.66 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 158.2, 156.2, 144.8, 138.1, 137.4, 128.7, 128.6, 128.2, 128.1, 127.88, 127.9, 127.8, 127.0, 124.0, 123.1,115.2, 112.7, 94.78 (d, $^{2}J_{C\text{-}F}$ = 17.1 Hz), 94.00 (d, $^{1}J_{C\text{-}F}$ = 199.3 Hz), 79.81 (d, $^{2}J_{C\text{-}F}$ = 22.7 Hz), 78.96 (d, $^{3}J_{C\text{-}F}$ = 6.8 Hz), 73.8, 72.8, 68.2.

^{19}F NMR (471 MHz, $CDCl_3$) δ = -201.75.

HRMS (TOF ESI+) *m/z* calcd for $C_{28}H_{25}O_6FNa$ [(M+ Na)$^{+}$] 499.1527, found 499.1525.

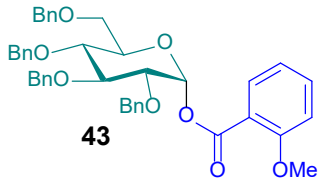
For β-isomer **42:**

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64–7.54 (m, 2H), 7.47 (ddd, *J* = 8.4, 7.1, 1.3 Hz, 1H), 7.40–7.24 (m, 11H), 7.20 (t, *J* = 7.1 Hz, 1H), 6.53 (d, *J* = 12.4 Hz, 1H), 5.27 (dd, $J_{C\text{-}F}$ = 49.8, 1.7 Hz, 1H), 4.76–4.64 (m, 3H), 4.61–4.53 (m, 2H), 4.34 (ddd, *J* = 14.9, 5.7, 1.7 Hz, 1H), 3.87 (dd, *J* = 10.3, 5.4 Hz, 1H), 3.78 (dd, *J* = 10.3, 6.3 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 158.0, 156.2, 144.8, 138.2, 137.4, 128.7, 128.5, 128.2, 128.1, 127.82, 127.8, 127.7, 127.0, 124.0, 123.1, 115.2, 112.6, 99.57 (d, $^{2}J_{C\text{-}F}$ = 37.0 Hz), 96.69 (d, $^{1}J_{C\text{-}F}$ = 184.5 Hz), 82.8, 80.16 (d, $^{2}J_{C\text{-}F}$= 25.4 Hz), 73.6, 73.0, 68.7.

^{19}F NMR (471 MHz, $CDCl_3$) δ = -193.85;

HRMS (TOF ESI+) *m/z* calcd for $C_{28}H_{25}O_6FNa$ [(M+ Na)$^{+}$] 499.1527, found 499.1522.



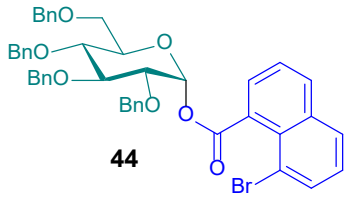
43

(2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl 2-methoxybenzoate (43): This compound was prepared according to the General Procedure A. After purification by silica gel column chromatography, compound **43** was isolated as a viscous oil (50 mg, 74%, α:β >20:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.48 (ddd, *J* = 8.3, 7.4, 1.8 Hz, 1H), 7.36–7.21 (m, 18H), 7.18–7.13 (m, 2H), 7.00–6.94 (m, 2H), 6.61 (d, *J* = 3.4 Hz, 1H), 4.97 (d, *J* = 10.9 Hz, 1H), 4.92–4.74 (m, 3H), 4.66 (d, *J* = 11.6 Hz, 1H), 4.61 (d, *J* = 12.2 Hz, 1H), 4.53 (d, *J* = 10.8 Hz, 1H), 4.47 (d, *J* = 12.2 Hz, 1H), 4.10–3.99 (m, 2H), 3.87 (s, 3H), 3.83–3.72 (m, 3H), 3.66 (dd, *J* = 10.9, 2.0 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 164.5, 159.8, 138.8, 138.4, 138.0, 137.9, 134.2, 132.4, 128.5, 128.5, 128.5, 128.2, 128.1, 128.0, 127.9, 127.8, 127.8, 127.7, 120.3, 119.5, 112.2, 90.4, 82.0, 79.2, 77.2, 75.8, 75.3, 73.7, 73.2, 73.0, 68.3, 56.0.

HRMS (TOF ESI+) *m/z* calcd for $C_{42}H_{42}O_8Na$ $[(M+Na)^+]$ 697.2772, found 697.2758.



44

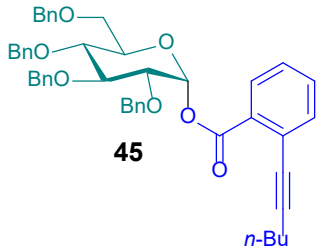
(2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl 8-bromo-1-naphthoate (44): This compound was prepared according to the General Procedure B. After purification by silica gel column chromatography, compound **44** was isolated as a viscous oil (56 mg, 72%, α:β 15:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.95 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.90–7.83 (m, 2H), 7.62 (dd, *J* = 7.1, 1.3 Hz, 1H), 7.52–7.45 (m, 1H), 7.45–7.40 (m, 2H), 7.41–7.23 (m, 17H), 7.17–7.09 (m, 2H), 6.81 (d, *J* = 3.5 Hz, 1H), 4.98 (d, *J* = 11.0 Hz, 1H), 4.91–4.75 (m, 4H), 4.69 (d, *J* = 12.1 Hz, 1H),

4.53 (dd, J = 11.4, 3.8 Hz, 2H), 4.08 (dt, J = 10.1, 2.7 Hz, 1H), 3.99 (t, J = 9.3 Hz, 1H), 3.91–3.79 (m, 3H), 3.75 (dd, J = 10.8, 2.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 168.7, 138.8, 138.2, 138.1, 138.0, 135.6, 133.3, 132.0, 131.5, 128.8, 128.7, 128.6, 128.5, 128.5, 128.4, 128.2, 128.1, 128.0, 128.0, 127.9, 127.8, 127.7, 127.0, 125.4, 119.8, 91.1, 81.8, 79.4, 75.7, 75.3, 73.7, 73.4, 73.2, 68.4.

HRMS (TOF ESI+) *m/z* calcd for $C_{45}H_{41}O_7BrNa$ [(M+Na)$^+$] 795.1928, found 795.1877.



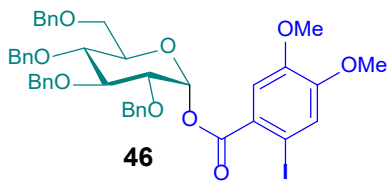
45

(2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl 2-(hex-1-yn-1-yl)benzoate (45): This compound was prepared according to the General Procedure A. After purification by silica gel column chromatography, compound **45** was isolated as a viscous oil (20 mg, 33%, α:β 20:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.96 (dd, J = 8.0, 1.4 Hz, 1H), 7.54 (dd, J = 7.8, 1.3 Hz, 1H), 7.49 – 7.41 (m, 1H), 7.37–7.22 (m, 19H), 7.17–7.11 (m, 2H), 6.67 (d, J = 3.6 Hz, 1H), 4.96 (d, J = 10.9 Hz, 1H), 4.91–4.74 (m, 3H), 4.70–4.58 (m, 2H), 4.52 (dd, J = 26.3, 11.4 Hz, 2H), 4.11–4.02 (m, 2H), 3.85–3.76 (m, 3H), 3.68 (dd, J = 10.9, 2.0 Hz, 1H), 2.45 (t, J = 7.1 Hz, 2H), 1.55 (m, 2H), 1.47–1.35 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 164.7, 138.8, 138.3, 138.0, 137.9, 135.1, 132.1, 131.0, 128.5, 128.5, 128.5, 128.3, 128.1, 128.1, 128.1, 128.0, 127.9, 127.9, 127.7, 127.3, 125.3, 97.0, 91.0, 81.9, 79.9, 79.2, 75.8, 75.5, 73.7, 73.4, 73.1, 68.3, 30.9, 22.2, 19.8, 13.8.

HRMS (TOF ESI+) *m/z* calcd for $C_{47}H_{48}O_7Na$ [(M+ Na)$^+$] 747.3292, found 747.3282.



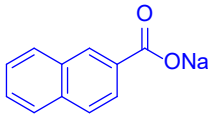
46

(2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl 2-iodo-4,5-dimethoxybenzoate (43): This compound was prepared according to the General Procedure A. After purification by silica gel column chromatography, compound **46** was isolated as a viscous oil (62 mg, 75%, α:β >20:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44 (s, 1H), 7.38 (s, 1H), 7.34–7.24 (m, 18H), 7.15 (dd, *J* = 7.4, 2.1 Hz, 2H), 6.62 (d, *J* = 3.6 Hz, 1H), 4.95 (d, *J* = 10.9 Hz, 1H), 4.86 (d, *J* = 10.8 Hz, 1H), 4.82 (d, *J* = 11.0 Hz, 1H), 4.77 (d, *J* = 11.3 Hz, 1H), 4.68 (d, *J* = 11.3 Hz, 1H), 4.61 (d, *J* = 12.1 Hz, 1H), 4.54 (d, *J* = 10.8 Hz, 1H), 4.49 (d, *J* = 12.1 Hz, 1H), 4.07 (t, *J* = 9.4 Hz, 1H), 4.01 (dt, *J* = 10.4, 2.5 Hz, 1H), 3.91 (s, 3H), 3.84–3.74 (m, 6H), 3.69 (dd, *J* = 10.9, 2.0 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 164.4, 152.3, 148.8, 138.7, 138.3, 138.0, 137.8, 128.5, 128.5, 128.5, 128.2, 128.1, 128.1, 128.0, 128.0, 127.9, 127.9, 127.8, 126.3, 123.9, 114.7, 91.6, 84.8, 81.9, 79.2, 77.0, 75.7, 75.3, 73.7, 73.6, 73.2, 68.2, 56.4, 56.1.

HRMS (TOF ESI+) *m/z* calcd for $C_{43}H_{43}O_9INa$ [(M+ Na)$^+$] 853.1844, found 853.1829.



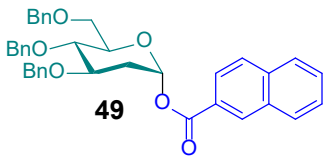
47

Sodium 2-naphthoate (**47**): A 25 mL oven-dried round bottom flask was charged with 2-naphthoic acid (172 mg, 1 mmol, 1 equiv), $NaHCO_3$ (252 mg, 3 mmol, 3 equiv), and methanol (5 mL, 0.2 M). The reaction mixture was stirred at rt for 24 h. After completion, solvent was removed by rotary evaporator, and washed with ethyl acetate to remove unreacted 2-naphthoic acid. The compound **44** was dried under vacuum to obtain a white semi-solid (170 mg, 88%).

^{1}H NMR (500 MHz, CD_3OD): δ 8.42 (dd, *J* = 1.7, 0.8 Hz, 1H), 8.00 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.91–7.85 (m, 1H), 7.84–7.80 (m, 1H), 7.78 (dd, *J* = 8.5, 0.8 Hz, 1H), 7.48–7.42 (m, 2H).

^{13}C NMR (126 MHz, CD_3OD): δ175.5, 136.6, 135.9, 134.4, 130.3, 129.9, 128.5, 128.1, 127.8, 127.6, 126.9

HRMS (TOF ESI-) *m/z* calcd for $C_{11}H_7O_2$ [(M)$^-$] 171.0452, found 171.0451.



49

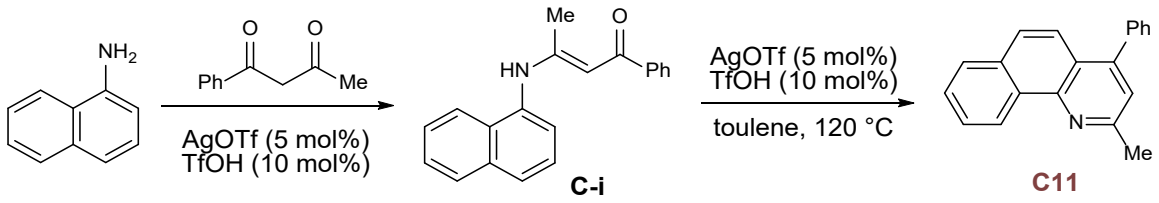
(2*R*,4*R*,5*S*,6*R*)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl 2 naphthoate (49): This compound was prepared according to the General Procedure A using glycosyl chloride. After purification by silica gel column chromatography, the title compound was isolated as a gummy liquid (7 mg, 12%, α:β 10:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.54 (d, *J* = 1.9 Hz, 1H), 8.00 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.96 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.93–7.78 (m, 2H), 7.59 (dddd, *J* = 23.5, 8.2, 6.9, 1.4 Hz, 2H), 7.41–7.37 (m, 2H), 7.37–7.27 (m, 11H), 7.22 (dd, *J* = 7.6, 1.9 Hz, 2H), 6.59 (d, *J* = 1.7 Hz, 1H), 4.95 (d, *J* = 10.5 Hz, 1H), 4.78–4.69 (m, 2H), 4.63 (dd, *J* = 27.3, 11.3 Hz, 2H), 4.53 (d, *J* = 12.2 Hz, 1H), 4.16 (ddd, *J* = 11.4, 8.9, 4.9 Hz, 1H), 4.03 (ddd, *J* = 10.0, 3.3, 1.9 Hz, 1H), 3.88–3.80 (m, 2H), 3.71 (dd, *J* = 10.9, 2.0 Hz, 1H), 2.48 (ddd, *J* = 13.8, 4.9, 1.7 Hz, 1H), 2.00 (ddd, *J* = 13.7, 11.5, 3.5 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 165.0, 138.4, 138.3, 138.2, 135.9, 132.6, 131.5, 129.6, 128.6, 128.6, 128.5, 128.5, 128.4, 128.1, 128.0, 128.0, 127.9, 127.8, 127.1, 126.9, 125.4, 93.1, 77.9, 77.0, 75.6, 74.0, 73.8, 72.1, 68.6, 34.8.

HRMS (TOF ESI+) *m/z* calcd for $C_{38}H_{36}O_6Na$ $[(M+Na)^+]$ 611.2404, found 611.2395.

3.2 Synthesis of Catalyst C11



A 25 mL round bottle flask was charged with 1-naphthylamine (143 mg, 1.0 mmol, 1 equiv), 1,3-diketone (243 mg, 1.5 mmol, 1.5 equiv), AgOTf (13 mg, 0.05 mmol, 5 mol%), TfOH (8.8μL, 0.1 mmol, 10 mol%),) and toluene (5 mL, 0.2 M) were added. The mixture was stirred at 60 °C for 12 h. Upon completion, the reaction mixture was cooled down to room temperature, diluted with DCM (10 mL), and washed with water (10 mL). The aqueous layer was extracted with DCM (2 x 10 mL). The combined organic phase was dried over Na_2SO_4. After evaporation of the solvents,

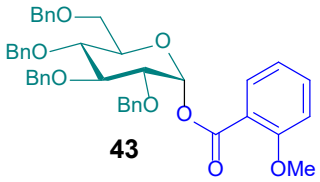
the residue was purified by silica gel flash chromatography (2% -10% ethyl acetate/hexanes) to afford **C-i**.

To a solution of **C-i** in toluene (5 mL, 0.2 M), AgOTf (13 mg, 0.05 mmol, 5 mol%), TfOH (8.8 µL, 0.1 mmol, 10 mol%) and toluene (5 mL) were added to the reaction flask. The mixture was stirred at 120 °C for 12 h. Upon completion, the reaction mixture was cooled down to room temperature, diluted with DCM (10 mL), and washed with water (10 mL). The aqueous layer was extracted with DCM (5 x 10 mL). The combined organic phase was dried over Na_2SO_4. After evaporation of the solvents, the residue was purified by silica gel flash chromatography (50% dichloromethane/hexanes) to afford **C-11** as a viscous oil (137 mg, 51%).[5,6] The spectral data match with literature.[7]

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.46–9.38 (m, 1H), 7.90–7.83 (m, 1H), 7.80–7.65 (m, 4H), 7.60–7.46 (m, 5H), 7.35 (s, 1H), 2.87 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 157.2, 148.5, 146.6, 138.8, 133.6, 131.7, 129.8, 128.6, 128.3, 128.1, 127.7, 126.9, 126.6, 125.0, 123.1, 122.8, 122.5, 25.6.

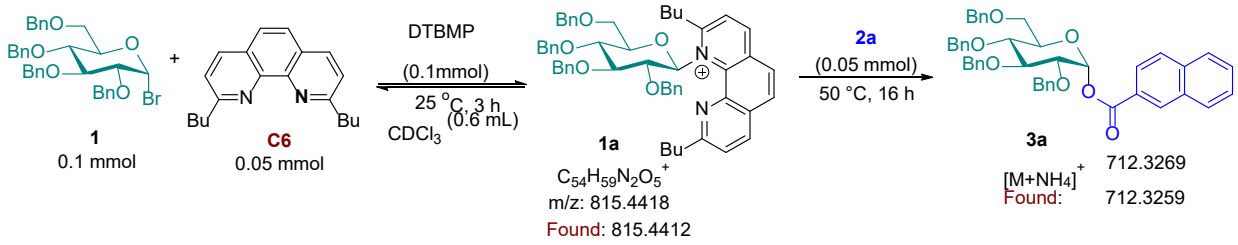
3.3 Gram Scale Glycosylation Reaction:



43

A 25 mL oven-dried Schlenk flask was charged with glucosyl bromide (1.05 g, 6 mmol, 2 equiv) and kept under high vacuum for 1 h. The reaction flask was backfilled with argon (3x), and 2-methoxy benzoic acid (456 mg, 3 mmol, 1 equiv), 2,9-dibutyl phenanthroline (175 mg, 0.06 mmol, 10 mol% with respect to glycosyl bromide), DTBMP (1230 mg, 6 mmol, 2 equiv), and a mixture of MTBE/DCE solvent (5:1, 4 mL, 0.8 M) was added to the flask. The reaction mixture was stirred at 50 °C for 18 h. Upon completion, the reaction mixture was diluted with dichloromethane, washed with water, saturated with aqueous $NaHCO_3$ (2 times), dried over Na_2SO_4, and concentrated *in vacuo*. The crude product was purified by silica gel flash chromatography (10% -30% ethyl acetate/hexanes) to give **43** as a viscous oil (1.05 g, 52%, α:β >20:1).

4. Detection of Phenanthrolinium Intermediate by HRMS



A 10 mL reaction vial was charged with glycosyl bromide **1** (60 mg, 0.1 mmol, 2 equiv), **C6** (14.6 mg, 0.05 mmol, 1.0 equiv), and $CDCl_3$ (0.8 mL, 0.06 M). The reaction mixture was stirred at rt for 3 h. The formation of the glycosyl phenanthrolinium ion intermediate **1a** was confirmed by HMRS using electrospray ionization (TOF ESI+) with an m/z ratio of 815.4412 (see below). Naphthoic acid (0.05 mmol. 8.6 mg, 1 equiv) was subsequently added to the reaction mixture and stirred at 50 ºC for 16 h. Formation of product **3a** was confirmed using electrospray ionization (TOF ESI+) with an m/z ratio of 712.3259.

Sample Preparation: The reaction mixture (50 µL) of glycosyl bromide **1** and catalyst **C6** was diluted with 1 mL of dry acetonitrile (ACN), and HRMS was taken to confirm the intermediate and product.

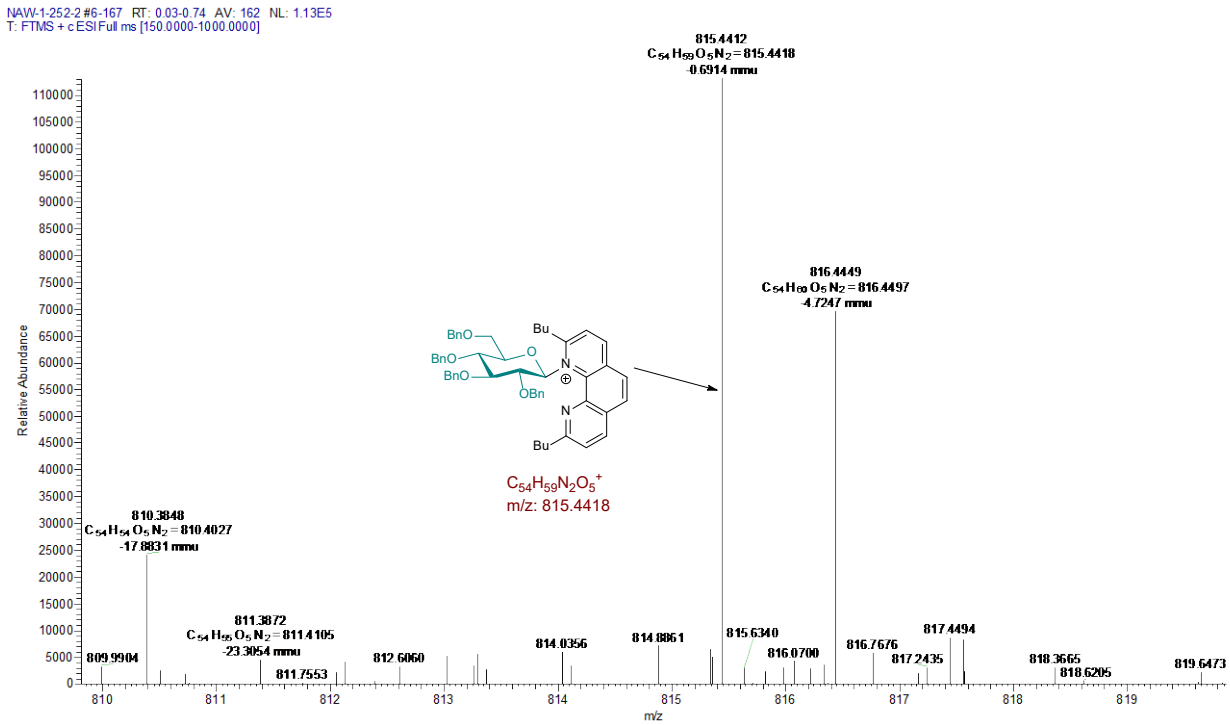
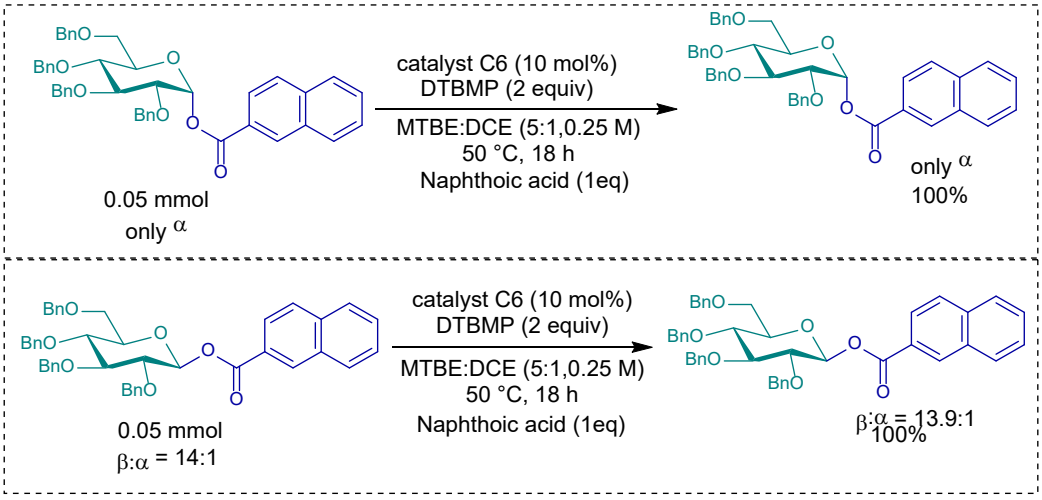


Figure S2. Detection of phenanthrolinium intermediate by HRMS

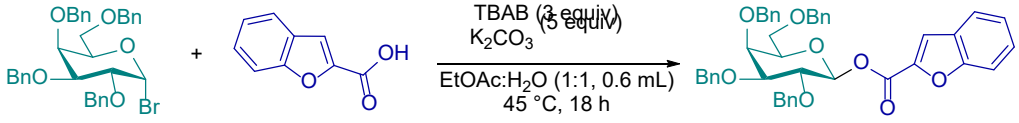
Experiment for Isomerization of α- and β-Isomers of Glycosyl Ester 3a

A 10 mL oven-dried Schlenk flask was charged with β-isomer of glycosyl ester product **3a** (0.05 mmol, 1 equiv) and kept under high vacuum for 1 h. The flask was backfilled with argon (3x), naphthoic acid (8.5 mg, 0.05 mmol, 1 equiv), 2,9-dibutyl-1,10-phenanthroline (3.9 mg, 0.01 mmol, 20 mol%), DTBMP (20.5 mg, 0.1 mmol, 2 equiv), a mixture of MTBE/DCE solvent (5:1, 0.2 mL, 0.25 M) were added to the flask. The reaction mixture was stirred at 50 °C for 18 h. The reaction mixture was diluted with dichloromethane, washed with water, saturated aqueous $NaHCO_3$ (2x), dried over Na_2SO_4, and concentrated *in vacuo*. The crude NMR was taken to calculate the yield and α:β ratio using 1,3-dinitrobenzene as an internal standard, and change in yield and selectivity were not observed. No conversion of the β-isomer to the corresponding α-isomer **3a** was observed. A similar result was observed for α-glycosyl ester **3a**.

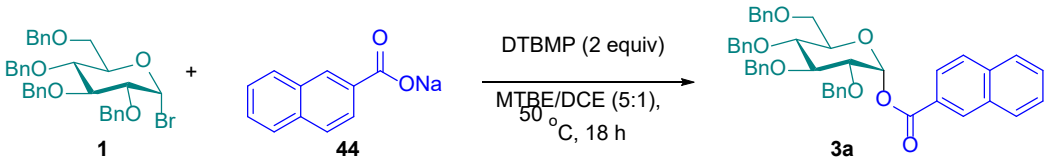


6. Effect of Carboxylic Acid's pKa on Stereoselectivity of Glycosyl Ester

Control Experiments:



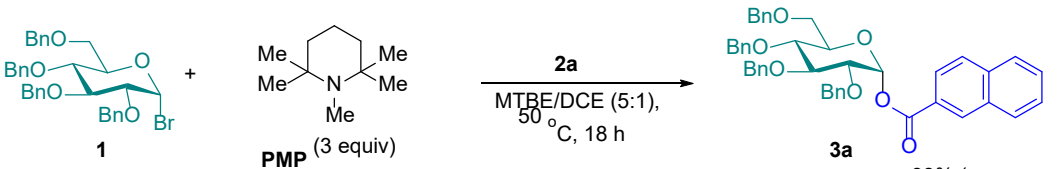
32
69% (α:β = 1:2)



1 **44** **3a**

10 mol% **C6** 30% (α:β = 1:1)

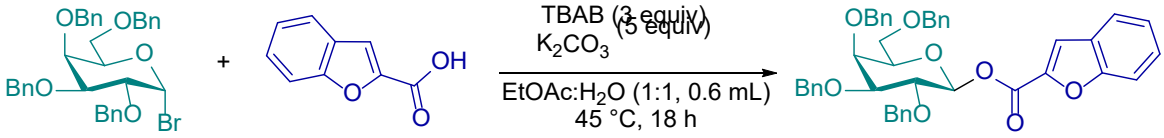
without **C6** 9% (α:β = 1:2)



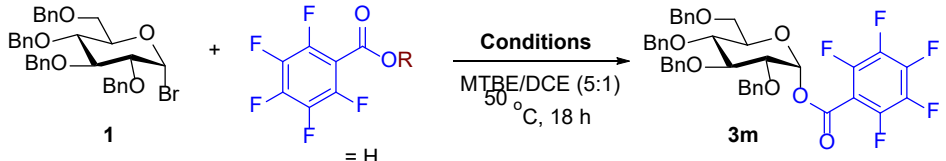
1 **3a**

10 mol% **C6** 93% (α:β = 1:3)

without **C6** 88% (α:β = 1:3)



32
69% (α:β = 1:2)



1 **3m**

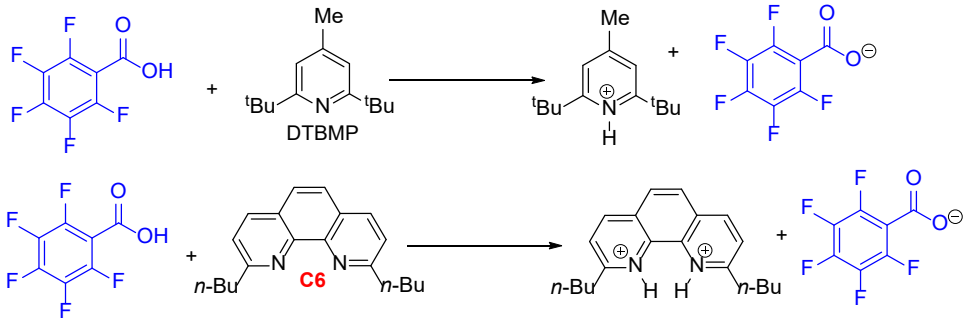
2m: **R** = H
2mm: **R** = Na

Conditions:	**Results**
2m, 10 mol% **C6**, DTBMP (2 equiv)	59% (α:β = 2:1)
2m, Without **C6,** DTBMP (2 equiv)	72% (α:β = 1.3:1)
2m, Without **C6** and DTBMP	0%
2mm, 10 mol% **C6**, DTBMP (2 equiv),	82% (α:β = 1:2)
2mm, Without **C6** and DTBMP)	22% β only

7. NMR Titration Experiment for Acidity of Carboxylic and Acid Hydrogen Bonding

7.1. NNR Titration Experiment for the Effect of Acidity of Carboxylic Acid.

The ^{1}H NMR was recorded in $CDCl_3$ (0.7 mL) for 2-naphthoic acid (8.6 mg, 0.05 mmol,), pentafluorobenzoic acid (10.6 mg, 0.05 mmol), DTBMP (10.3 mg, 0.05 mmol), catalyst **6** (7.3 mg, 0.025 mmol), mixture of pentafluorobenzoic acid (10.6 mg, 0.05 mmol) and DTBMP (10.3 mg, 0.05 mmol), mixture of naphthoic acid (8.6 mg, 0.05 mmol) and DTBMP (10.3 mg, 0.05 mmol), mixture of pentafluorobenzoic acid (10.6 mg, 0.05 mmol) and catalyst **6** (7.3 mg, 0.025 mmol), mixture of naphthoic acid (8.6 mg, 0.05 mmol) and catalyst **6** (7.3 mg, 0.025 mmol). The NMR data suggested the protonation of DTBMP and catalyst **6** by pentafluorobenzoic acid but no protonation by naphthoic acid.



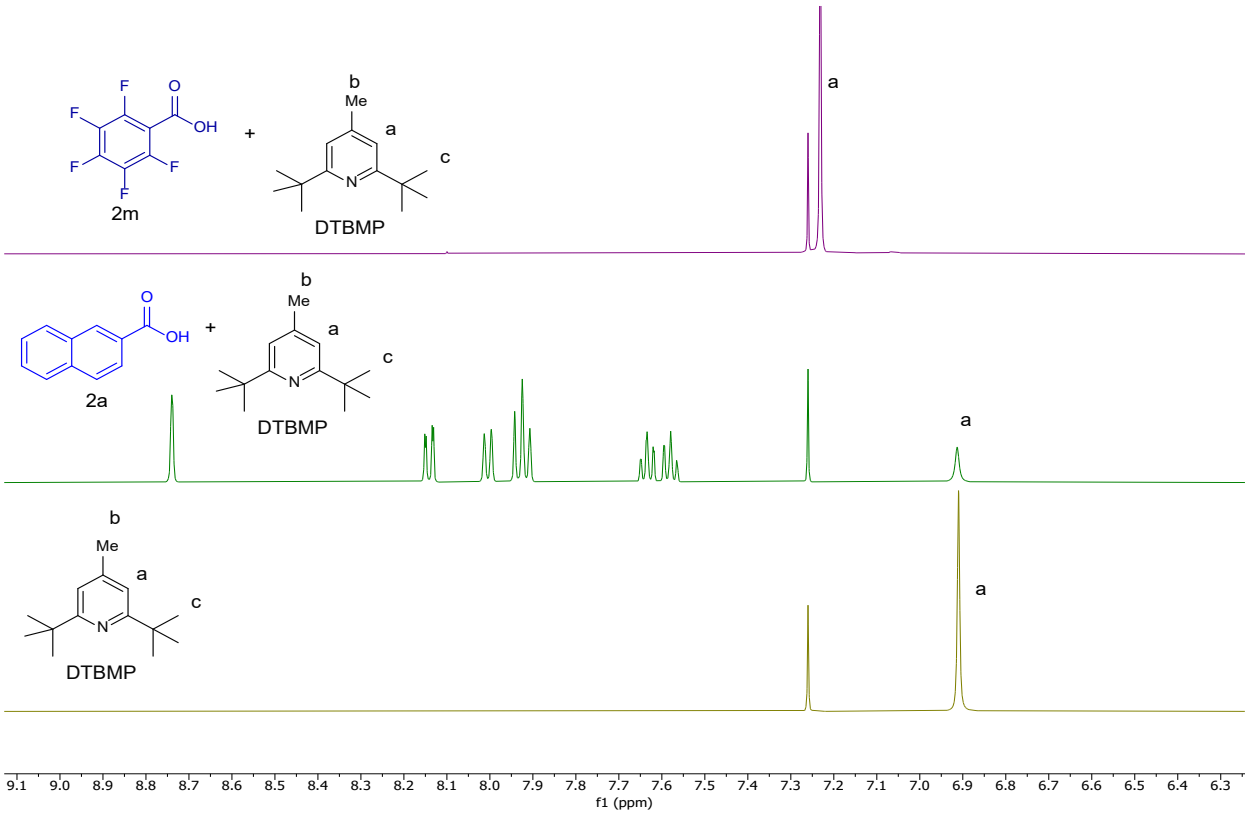


Figure S3. NMR experiment for effect of acidity on DTBMP

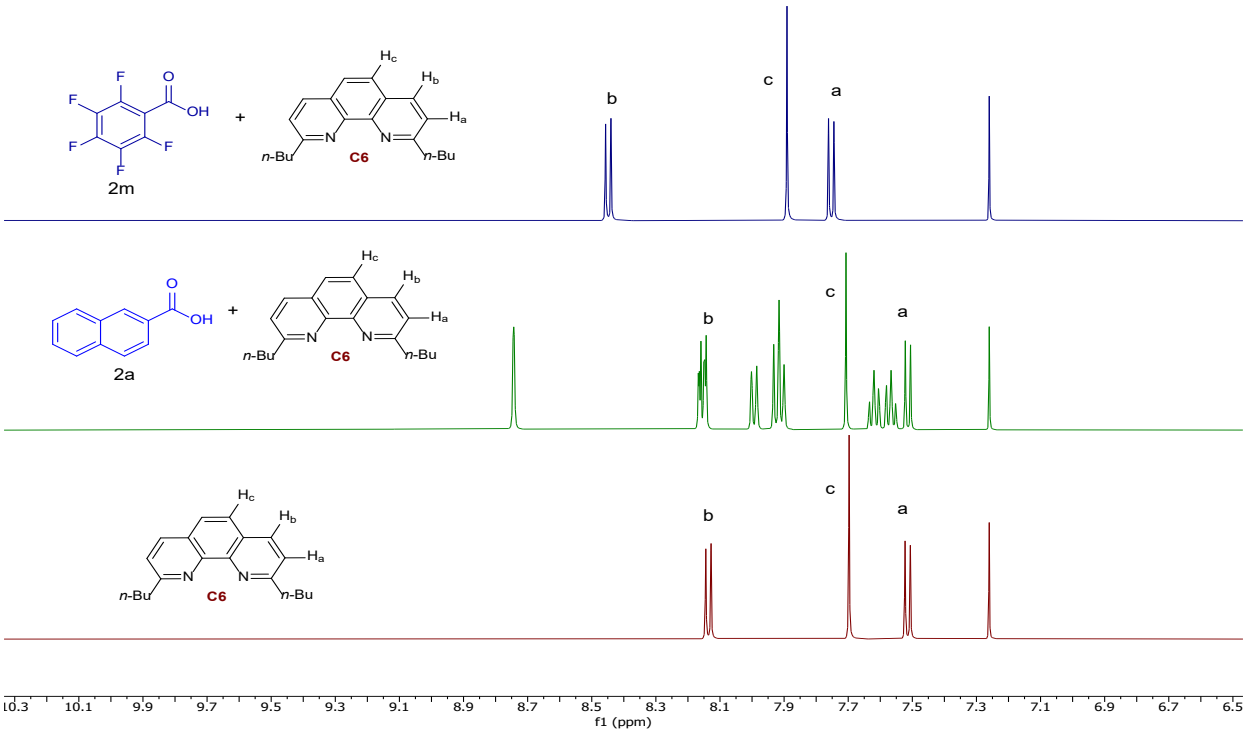


Figure S4. NMR experiment for effect of acidity on catalyst **C6**

7.2 NMR Titration Experiment for Hydrogen Bonding

^{13}C NMR titrations were carried out using a Bruker 500 MHz spectrometer. The stock solutions of benzoic acid **2b** (0.02 M) in $CDCl_3$ and the mixture of benzoic acid **2b** (0.02 M) and methyl benzylated glucoside **47** (0.1 M) in $CDCl_3$ were prepared separately. The NMR samples were prepared by adding increasing amount of mixture stock solutions to the host benzoic acid solution (0.7 mL) to avoid dilution of the host during the course of the experiment. The NMR spectra were stacked together to see the observed changes in chemical shift due to hydrogen bonding.

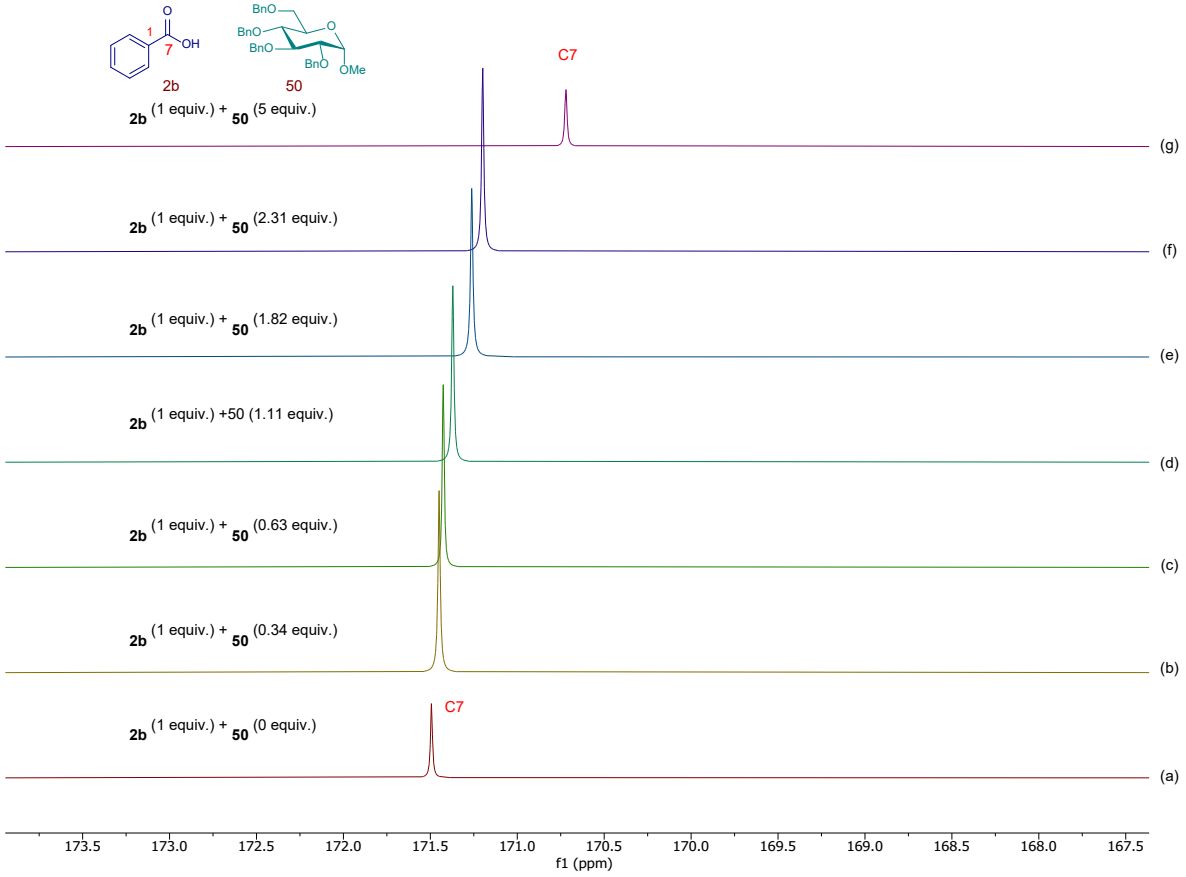


Figure S5. NMR experiment for H-bonding

8. Manual UV-vis Titration for Hydrogen Bonding Constant

Titrations were carried out using a thermoscientific Genesys 50 UV−vis spectrophotometer. A 10 mL dichloromethane sample of the host benzoic acid **2b** was prepared at a known concentration (0.1 mM). 1 mL of this solution was removed and added to a 4 mL quartz cuvette, and the UV−vis spectrum was recorded. The guest glucoside **S** (0.05 mmol) was then dissolved in the host solution (5 mL) to avoid dilution of the host during the titration. Aliquots of guest solution were added successively to the cuvette containing the host solution. The cuvette was shaken, and the UV−vis absorption spectrum was recorded after each addition. The observed changes in UV−vis absorption were fit to a 1:1 binding isotherm using GraphPad to obtain average association constants, K_A= 263 M^{-1} for benzoic acid at different wavelength of 228 nm, 230, 232 nm. The UV-vis titration for pentafluorobenzoic acid **2m** was done similar way and its association constant, K_A= 378 M^{-1}, was determined at different wavelength of 226 nm, 228 nm, 230 nm.

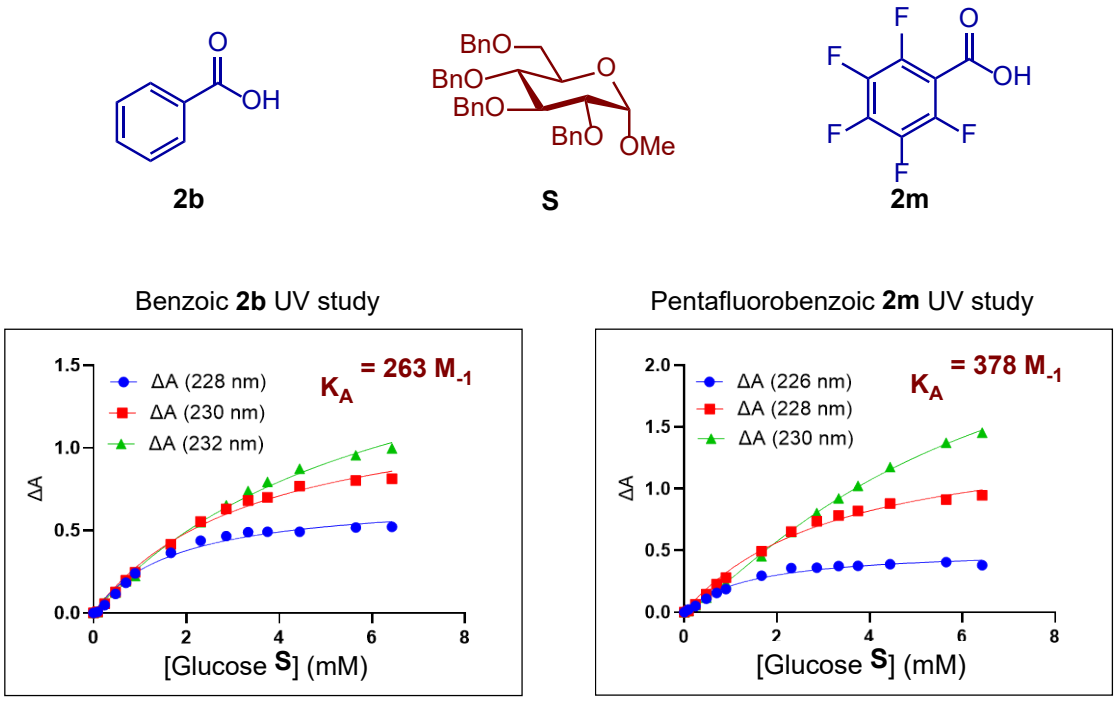


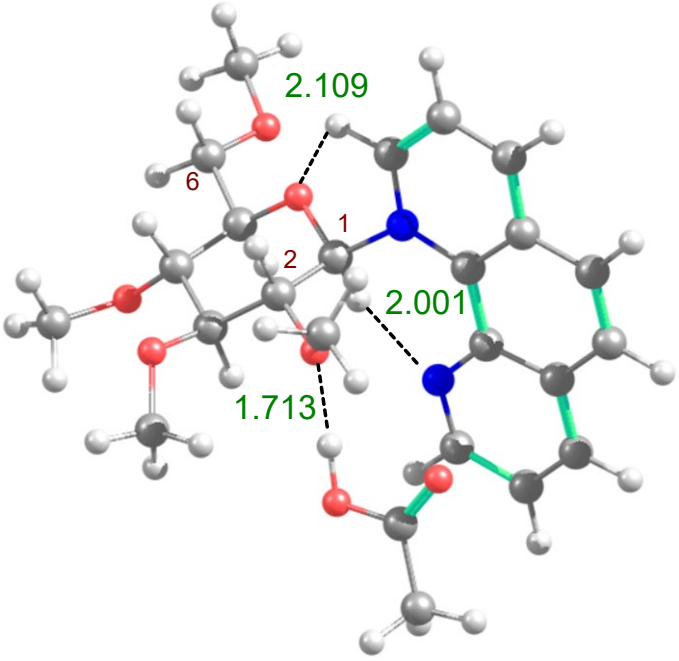
Figure S6. Binding isotherm for UV-vis titration.

9. Computational Studies

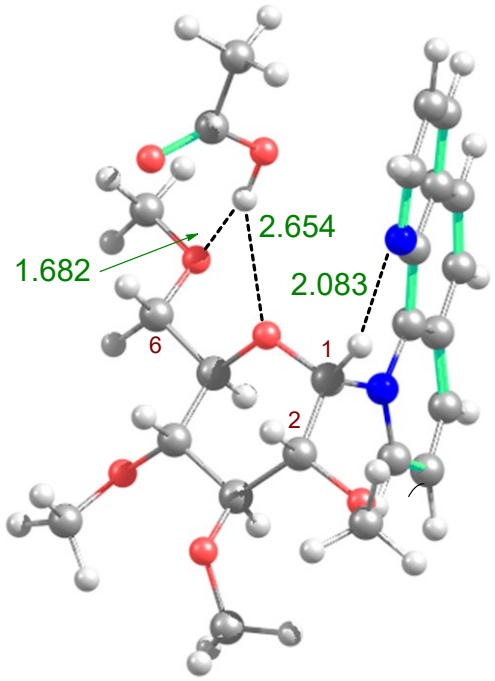
All calculations were carried out using density functional theory (DFT) as implemented in Gaussian 16 program[8] using the hybrid exchange-correlation functional M06-2X.[9,10] Ahlrich's def2-SVP basis set[11] was utilized for geometry optimizations and vibrational mode calculations. Accurate energies were obtained by performing single-point calculations on the def2-SVP optimized structures utilizing the def2-TZVPP basis set.[12] Solvation effects in diethyl ether were incorporated using the implicit SMD solvation model[3] and included during structure optimization. All the optimized structures were confirmed as minima by harmonic vibrational frequency calculations and the converged wave functions were tested for the SCF stability. The zero-point energy, thermal corrections, and entropic contributions were included in the calculation of the free energies. The standard states of 1 M concentration were considered for all the reactants and products to calculate the reactions' free energies. The OPT=TS keyword that requests optimization to a transition state rather than a local minimum was utilized using the Berny algorithm. All the transition state structures had only one imaginary frequency.

9.1 Optimized Structures of Intermediates and Transition states.

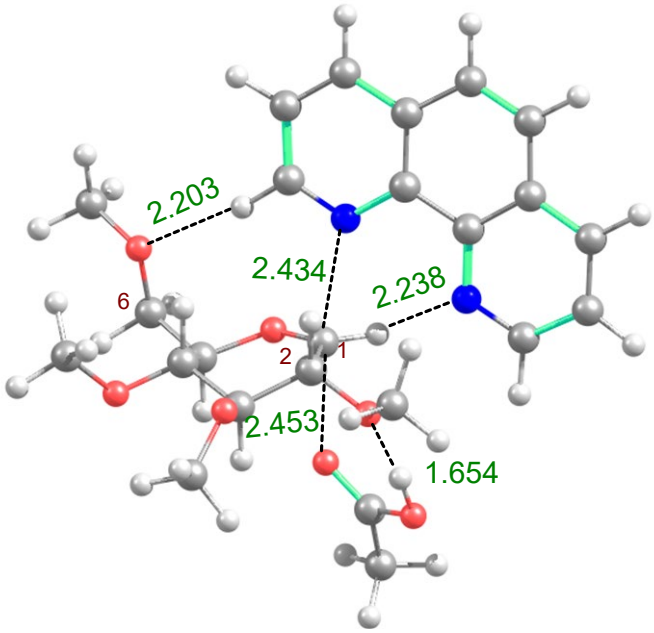
Intermediate 1 (-COOH)



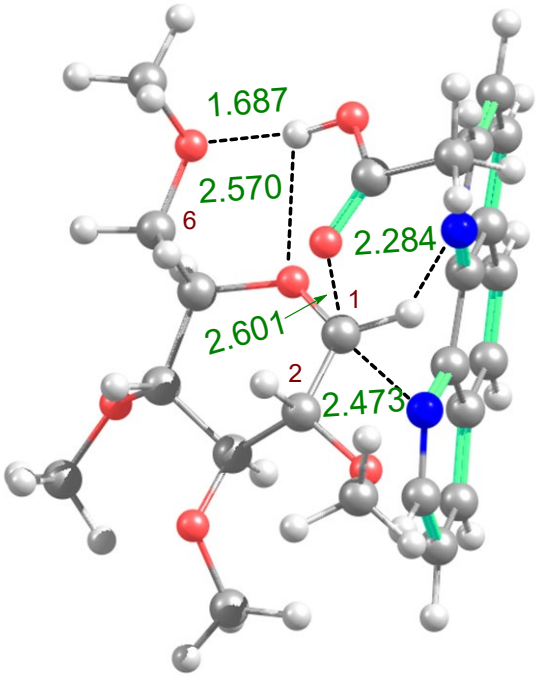
Intermediate 1'(-COOH)



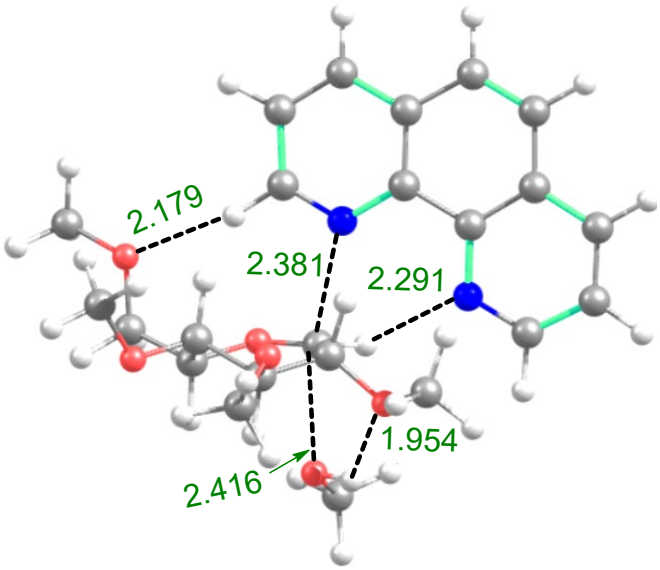
TS for alpha product (COOH)



TS for beta product (-COOH)



TS for alpha product (-OH)



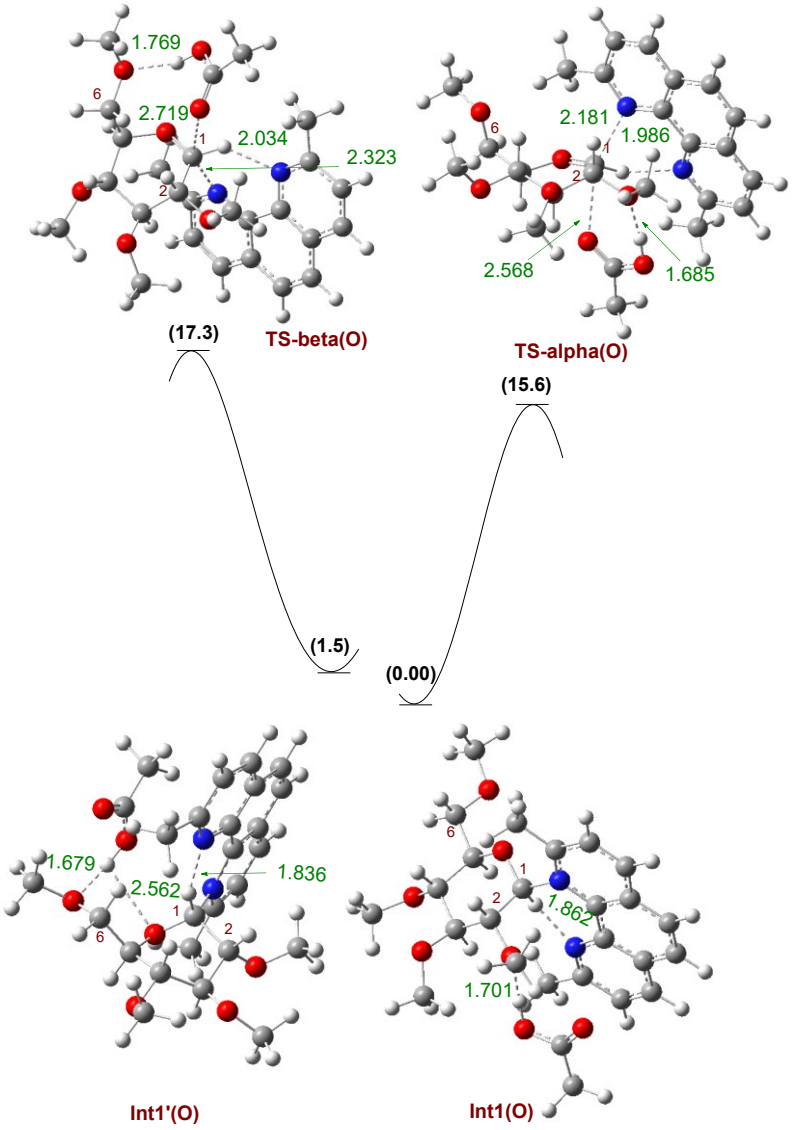


Figure S7. Kinetic barriers for the α- and β-glycosyl ester products from glucosyl bromide with a 2,9-dimethyl-1,10-phenanthroline catalyst. The free energy changes (ΔG at 50°C) are in kcal/mol and are computed with the Gaussian 16 program and at M06-2X/def2-SVP level of theory using diethyl ether with SMD implicit solvation. Hydrogen bonding interactions are reported in Å.

9.2 XYZ Coordinates of DFT-Calculated Structures.

Intermediate 1 (-COOH)

Gibbs free energy: -984332.51 kcal/mol

O	-1.223777000	1.003710000	0.141084000
C	-1.675822000	-0.986023000	1.350185000
C	-2.087947000	-1.715260000	0.073598000
H	-1.218704000	-2.291580000	-0.304954000
C	-2.498760000	-0.714037000	-1.014936000
H	-3.484393000	-0.295357000	-0.719248000
C	-1.488508000	0.435707000	-1.138081000
H	-0.546738000	0.036216000	-1.559001000
O	-3.174633000	-2.559432000	0.331476000
C	-2.866491000	-3.906270000	0.603260000
H	-2.196958000	-4.328414000	-0.170142000
H	-2.390884000	-4.036066000	1.591162000
H	-3.816021000	-4.462765000	0.592050000
O	-2.572184000	-1.304508000	-2.276912000
C	-3.680813000	-2.136595000	-2.530592000
H	-3.541336000	-3.152664000	-2.122985000
H	-4.607450000	-1.709352000	-2.104922000
H	-3.786091000	-2.204137000	-3.624486000
C	-1.995342000	1.537478000	-2.038879000
H	-2.867402000	2.026756000	-1.554658000
H	-2.342021000	1.076818000	-2.984142000
O	-0.966987000	2.451218000	-2.263772000
C	-1.352779000	3.504801000	-3.099631000
H	-1.678372000	3.138080000	-4.093652000
H	-2.182082000	4.092941000	-2.657531000
H	-0.482437000	4.164985000	-3.232501000
C	-0.636448000	0.080635000	0.992967000
H	-2.566288000	-0.463417000	1.747489000
O	-1.178795000	-1.881122000	2.310536000
C	-1.793174000	-1.823162000	3.587160000
H	-2.855976000	-2.115620000	3.519857000
H	-1.243381000	-2.520840000	4.234149000
H	-1.719394000	-0.804804000	4.012929000
H	0.258963000	-0.365813000	0.552662000
C	0.819357000	0.356397000	3.051078000
C	-1.022945000	1.799202000	2.595779000
C	1.774745000	-0.698138000	2.705447000
C	0.980820000	1.025278000	4.295213000
C	-0.877855000	2.487108000	3.793035000
H	-1.802419000	2.051912000	1.877709000
C	2.808420000	-0.993352000	3.634594000
C	2.025063000	0.658166000	5.208436000

C	0.120147000	2.083880000	4.650270000
H	-1.555634000	3.308633000	4.025301000
C	3.754246000	-1.983439000	3.284775000
C	2.909167000	-0.315870000	4.890877000
C	2.595010000	-2.261154000	1.220046000
H	2.084792000	1.197904000	6.155621000
H	0.269601000	2.580323000	5.612529000
C	3.660626000	-2.619943000	2.070673000
H	4.551817000	-2.223237000	3.992632000
H	3.714378000	-0.595866000	5.573682000
H	2.475865000	-2.754418000	0.249436000
H	4.378307000	-3.382986000	1.763974000
N	-0.222989000	0.783255000	2.244438000
N	1.697650000	-1.353795000	1.532281000
H	-0.220610000	-3.273758000	2.029845000
O	0.265688000	-4.137978000	1.970216000
C	0.995877000	-4.292479000	3.072934000
O	0.972620000	-3.501191000	3.985762000
C	1.818684000	-5.550081000	3.047560000
H	2.407105000	-5.598553000	2.117565000
H	2.479067000	-5.582565000	3.924143000
H	1.144497000	-6.423257000	3.057171000

Intermediate 1’ (-COOH)

Gibbs free energy: -984329.48 kcal/mol

O	-0.931930000	0.662622000	0.309589000
C	-1.780197000	-1.255554000	1.481288000
C	-2.369380000	-1.828188000	0.187132000
H	-1.685692000	-2.559429000	-0.284673000
C	-2.582647000	-0.709802000	-0.830136000
H	-3.391969000	-0.045192000	-0.462971000
C	-1.290952000	0.102990000	-0.953054000
H	-0.481768000	-0.566603000	-1.307762000
N	0.970671000	1.781626000	2.220222000
C	2.924200000	-0.488239000	0.054584000
C	2.972854000	-1.851286000	-0.307704000
C	1.954501000	-2.698942000	0.061729000
C	0.832121000	-2.148274000	0.676404000
N	0.736341000	-0.847784000	0.970308000
H	1.972515000	-3.767414000	-0.153685000
C	1.812697000	0.006132000	0.780818000
C	3.005213000	2.157721000	0.982905000
C	4.019385000	0.372786000	-0.290439000
C	4.044384000	1.660235000	0.131549000

H	4.829401000	-0.048168000	-0.889279000
H	4.874921000	2.323069000	-0.122445000
H	-0.021785000	-2.770581000	0.933634000
C	1.887077000	1.355404000	1.330875000
C	1.094651000	2.968280000	2.764761000
C	3.102754000	3.443159000	1.564671000
C	2.149994000	3.855781000	2.463023000
H	0.327901000	3.256330000	3.492626000
H	2.199243000	4.835006000	2.943240000
O	-3.592758000	-2.444694000	0.491645000
C	-3.551957000	-3.850247000	0.553508000
H	-3.292484000	-4.287527000	-0.430284000
H	-2.824334000	-4.207789000	1.304995000
H	-4.558059000	-4.193790000	0.837429000
O	-2.881601000	-1.200497000	-2.102732000
C	-4.200905000	-1.652345000	-2.310970000
H	-4.358825000	-2.673338000	-1.923420000
H	-4.933477000	-0.976185000	-1.833064000
H	-4.371941000	-1.653457000	-3.398528000
C	-1.423521000	1.234662000	-1.942042000
H	-2.168494000	1.970589000	-1.587439000
H	-1.751276000	0.811736000	-2.906787000
O	-0.162007000	1.849383000	-2.083573000
C	-0.116728000	2.768827000	-3.156714000
H	-0.295580000	2.249532000	-4.115802000
H	-0.872187000	3.564423000	-3.025010000
H	0.889770000	3.212948000	-3.168873000
H	3.952676000	4.078760000	1.302541000
H	3.841529000	-2.219099000	-0.860082000
O	-1.727897000	4.147363000	-0.606888000
C	-0.676713000	4.389445000	-0.062853000
O	0.394985000	3.614221000	-0.181785000
H	0.172790000	2.828191000	-0.757141000
C	-0.442024000	5.579341000	0.828659000
H	0.568828000	5.987158000	0.678355000
H	-1.203962000	6.345182000	0.628648000
H	-0.530379000	5.259463000	1.881334000
C	-0.628624000	-0.255596000	1.298294000
H	-2.578633000	-0.615974000	1.900674000
O	-1.442132000	-2.258914000	2.397571000
C	-2.316018000	-2.380489000	3.502286000
H	-3.353722000	-2.561567000	3.171807000
H	-1.966670000	-3.236865000	4.097179000
H	-2.286865000	-1.470816000	4.130005000
H	-0.489919000	0.295372000	2.227900000

TS for alpha product (-COOH)

Gibbs free energy: -984315.59 kcal/mol

O	1.274062000	-0.027791000	-1.406566000
C	0.410288000	0.907400000	0.684479000
C	1.846015000	1.188378000	1.117746000
H	2.158199000	2.164836000	0.703576000
C	2.745972000	0.093763000	0.556191000
H	2.392894000	-0.885121000	0.932043000
C	2.665955000	0.097352000	-0.966264000
H	2.978421000	1.076053000	-1.361519000
H	-0.637572000	0.593740000	-1.283048000
N	-0.833943000	-1.661754000	-0.385238000
C	-4.447582000	-1.098382000	0.211222000
C	-5.339844000	-0.003717000	0.260423000
C	-4.864394000	1.269881000	0.033170000
C	-3.491814000	1.431974000	-0.246126000
N	-2.640970000	0.428548000	-0.298559000
H	-5.524383000	2.139013000	0.061545000
C	-3.088186000	-0.820509000	-0.072513000
C	-2.603416000	-3.240744000	0.081218000
C	-4.878724000	-2.452660000	0.430478000
C	-3.993672000	-3.480499000	0.363749000
H	-5.934770000	-2.634347000	0.645327000
H	-4.317993000	-4.511994000	0.522664000
H	-3.081943000	2.432538000	-0.429612000
C	-2.136094000	-1.920601000	-0.128119000
C	0.019361000	-2.661821000	-0.469442000
C	-1.666072000	-4.294817000	-0.001464000
C	-0.348999000	-4.009468000	-0.283843000
H	1.064009000	-2.410492000	-0.695513000
H	0.404507000	-4.795274000	-0.363610000
O	1.877829000	1.200857000	2.515357000
C	2.713752000	2.188760000	3.079463000
H	3.750855000	2.100052000	2.713162000
H	2.334609000	3.203061000	2.851541000
H	2.699235000	2.039061000	4.169044000
O	4.079407000	0.313623000	0.905600000
C	4.608484000	-0.615210000	1.828337000
H	4.039317000	-0.607079000	2.775452000
H	4.600791000	-1.637163000	1.406014000
H	5.647324000	-0.314748000	2.029053000
C	3.479487000	-0.988500000	-1.624035000

H	4.544412000	-0.699414000	-1.538462000
H	3.224048000	-1.036988000	-2.701230000
O	3.238762000	-2.206823000	-0.984021000
C	3.971390000	-3.273857000	-1.534322000
H	3.708513000	-3.434826000	-2.597154000
H	5.059597000	-3.087011000	-1.460801000
H	3.723231000	-4.178415000	-0.959854000
H	-2.002695000	-5.323336000	0.155403000
H	-6.396605000	-0.183217000	0.476942000
O	1.048206000	2.648309000	-1.572987000
C	0.489982000	3.730812000	-1.612485000
O	-0.432013000	4.072704000	-0.735134000
H	-0.511991000	3.328042000	-0.075499000
C	0.779651000	4.791131000	-2.629710000
H	-0.155451000	5.083341000	-3.133806000
H	1.173059000	5.684102000	-2.116515000
H	1.510129000	4.422865000	-3.360894000
C	0.306721000	0.456986000	-0.754438000
H	0.056506000	0.038321000	1.271471000
O	-0.441582000	1.996609000	0.903726000
C	-1.161507000	1.968576000	2.130330000
H	-0.467133000	2.001243000	2.984464000
H	-1.807852000	2.858120000	2.140534000
H	-1.786444000	1.061170000	2.185513000

TS for alpha product (-OH)

Gibbs free energy: -913173.85 kcal/mol

O	1.269799000	0.021251000	-1.428608000
C	0.527032000	0.994935000	0.716185000
C	1.948696000	0.810696000	1.249366000
H	2.538812000	1.712285000	0.997303000
C	2.598117000	-0.393118000	0.576451000
H	1.994117000	-1.296013000	0.786340000
C	2.631335000	-0.163982000	-0.929994000
H	3.138045000	0.786701000	-1.159192000
H	-0.489769000	0.992835000	-1.290662000
N	-1.048785000	-1.239459000	-0.479758000
C	-4.415341000	-0.119060000	0.592536000
C	-5.100381000	1.102768000	0.777210000
C	-4.453139000	2.289549000	0.508689000
C	-3.119517000	2.237038000	0.052912000
N	-2.459526000	1.112284000	-0.126424000
H	-4.951076000	3.252337000	0.637943000
C	-3.075697000	-0.054372000	0.137396000
C	-2.991113000	-2.525025000	0.164262000
C	-5.036068000	-1.392382000	0.837266000
C	-4.353928000	-2.547091000	0.624011000

H	-6.070725000	-1.408117000	1.188519000
H	-4.825033000	-3.518012000	0.795919000
H	-2.576985000	3.163527000	-0.169412000
C	-2.336231000	-1.291040000	-0.065872000
C	-0.397301000	-2.361199000	-0.707391000
C	-2.267149000	-3.714243000	-0.075774000
C	-0.967413000	-3.636668000	-0.522420000
H	0.641438000	-2.276181000	-1.049035000
H	-0.375897000	-4.530612000	-0.728209000
O	1.873012000	0.633064000	2.636041000
C	2.887691000	1.278523000	3.373615000
H	3.893308000	0.952452000	3.057045000
H	2.817262000	2.378037000	3.266823000
H	2.735838000	1.014356000	4.430684000
O	3.913519000	-0.557426000	1.013875000
C	4.125567000	-1.691740000	1.826966000
H	3.502367000	-1.652521000	2.738728000
H	3.901385000	-2.620635000	1.270589000
H	5.187169000	-1.689678000	2.114764000
C	3.288473000	-1.275376000	-1.708969000
H	4.378400000	-1.199941000	-1.533006000
H	3.105573000	-1.122130000	-2.791380000
O	2.796299000	-2.509187000	-1.276500000
C	3.391352000	-3.603038000	-1.929366000
H	3.212972000	-3.564223000	-3.020837000
H	4.482461000	-3.628400000	-1.746816000
H	2.937946000	-4.519089000	-1.522700000
H	-2.753075000	-4.679274000	0.092607000
H	-6.135680000	1.088550000	1.128690000
O	1.500388000	2.734768000	-1.212837000
C	0.390381000	0.638222000	-0.753160000
H	-0.119133000	0.272680000	1.248606000
H	1.047667000	3.215781000	-0.497366000
C	1.101295000	3.229745000	-2.474476000
H	0.000802000	3.268673000	-2.574236000
H	1.511049000	4.238590000	-2.658849000
H	1.500137000	2.547782000	-3.241057000
O	0.040101000	2.294026000	0.899783000
C	-0.559586000	2.533779000	2.159328000
H	-1.038806000	3.521840000	2.102279000
H	-1.326555000	1.768689000	2.377121000
H	0.189854000	2.537076000	2.968549000

TS for beta product (-COOH)

Gibbs free energy: -984309.69 kcal/mol

O	-0.499287000	0.685566000	-0.514836000
C	-1.780155000	-0.675989000	0.956682000
C	-1.927667000	-1.696318000	-0.185324000
H	-0.991593000	-2.270532000	-0.303044000

C	-2.185793000	-0.950851000	-1.497351000
H	-3.272696000	-0.722709000	-1.500791000
C	-1.411256000	0.375873000	-1.618054000
H	-0.738910000	0.314906000	-2.482313000
H	0.013866000	0.669507000	1.407468000
N	2.037464000	1.303092000	0.556195000
C	3.319297000	-2.116217000	-0.020547000
C	2.969643000	-3.443248000	0.310607000
C	1.786687000	-3.685964000	0.970950000
C	0.936433000	-2.596122000	1.235974000
N	1.220869000	-1.349426000	0.904452000
H	1.491426000	-4.692834000	1.271905000
C	2.418463000	-1.078907000	0.332461000
C	4.057327000	0.555524000	-0.546789000
C	4.558337000	-1.815030000	-0.684989000
C	4.905461000	-0.531265000	-0.953764000
H	5.211566000	-2.645757000	-0.962391000
H	5.845170000	-0.295432000	-1.459696000
H	-0.025284000	-2.757253000	1.732303000
C	2.823058000	0.304578000	0.103790000
C	2.417576000	2.549693000	0.364340000
C	4.434483000	1.902159000	-0.747525000
C	3.612554000	2.908101000	-0.293353000
H	1.748015000	3.330866000	0.739185000
H	3.869795000	3.960951000	-0.423970000
O	-3.007674000	-2.541309000	0.071874000
C	-2.682512000	-3.774476000	0.675094000
H	-1.915718000	-4.314641000	0.086828000
H	-2.318240000	-3.646487000	1.709602000
H	-3.603965000	-4.374971000	0.692056000
O	-1.850038000	-1.692604000	-2.628652000
C	-2.647826000	-2.830309000	-2.869022000
H	-2.400188000	-3.661653000	-2.185197000
H	-3.723330000	-2.594167000	-2.767134000
H	-2.442766000	-3.147980000	-3.901974000
C	-2.357694000	1.551163000	-1.759118000
H	-3.067834000	1.586122000	-0.910788000
H	-2.933745000	1.384365000	-2.688889000
O	-1.622373000	2.742061000	-1.838886000
C	-2.425456000	3.864773000	-2.162115000
H	-2.890581000	3.730454000	-3.154413000
H	-3.216904000	4.013819000	-1.404366000
H	-1.766486000	4.744265000	-2.186478000
H	5.378719000	2.123172000	-1.252975000
H	3.652466000	-4.256808000	0.051147000
O	-2.083223000	2.302564000	1.354535000

C	-1.300121000	3.226231000	1.466821000
O	-0.625706000	3.708439000	0.437004000
H	-0.884721000	3.224566000	-0.399801000
C	-0.963659000	3.896576000	2.764564000
H	-0.926825000	4.988649000	2.635566000
H	-1.698556000	3.618288000	3.530973000
H	0.039088000	3.560142000	3.082007000
C	-0.652838000	0.245360000	0.655954000
H	-2.680542000	-0.024992000	0.923533000
O	-1.625933000	-1.252280000	2.207110000
C	-2.761965000	-1.150925000	3.047544000
H	-3.645968000	-1.617087000	2.577703000
H	-2.519175000	-1.683424000	3.977913000
H	-2.980848000	-0.093493000	3.280221000

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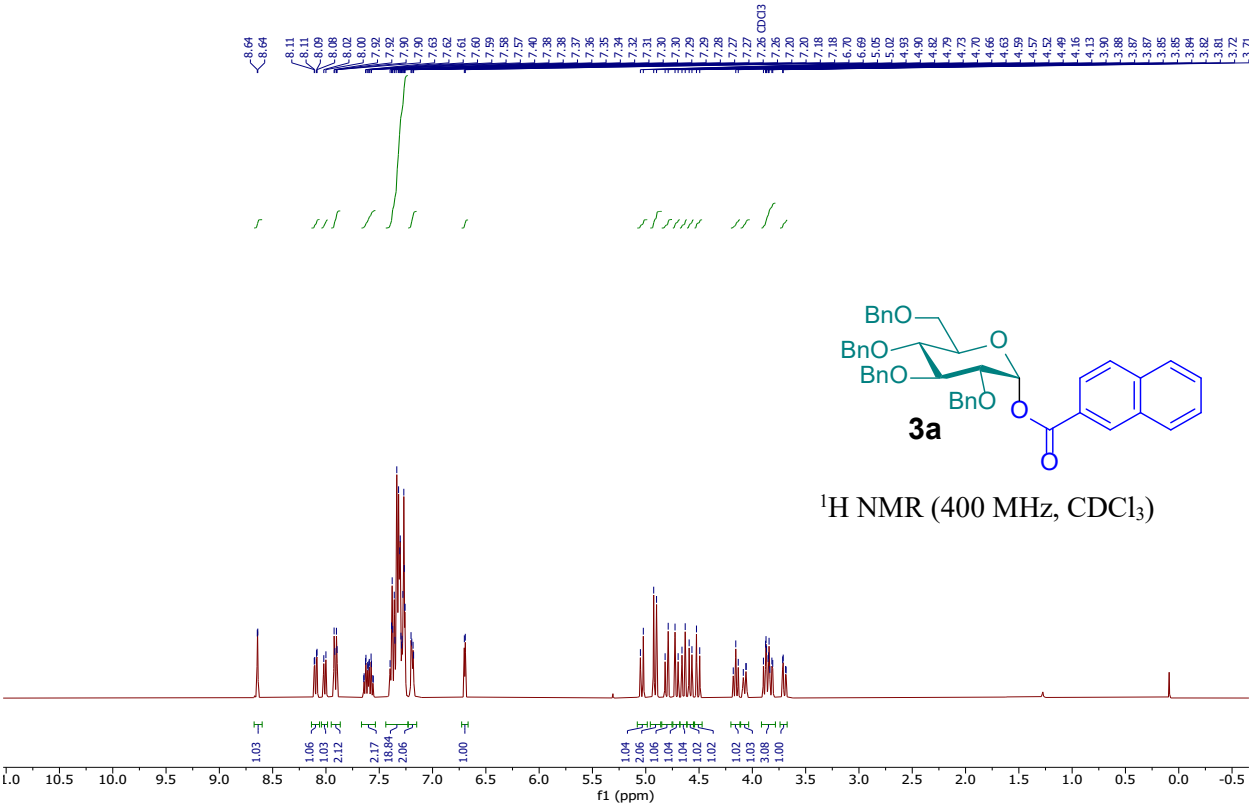
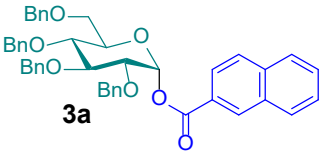
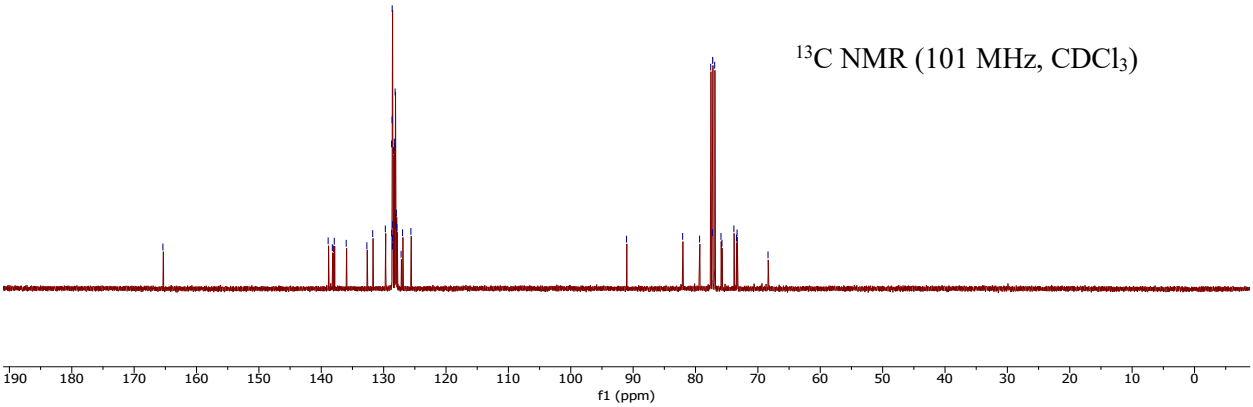
10. NMR Spectral Data

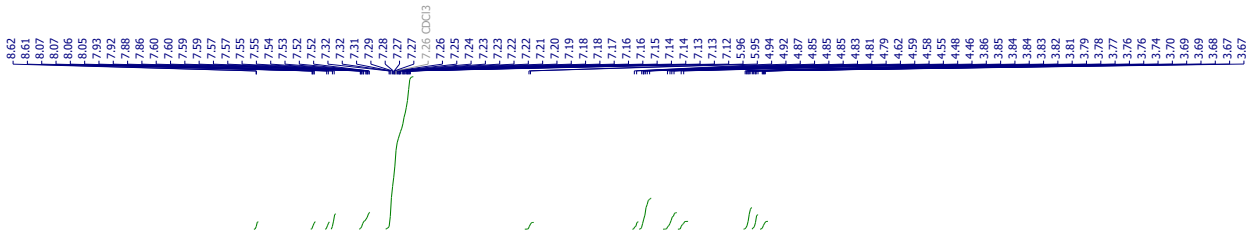


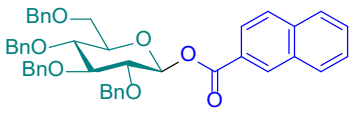
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

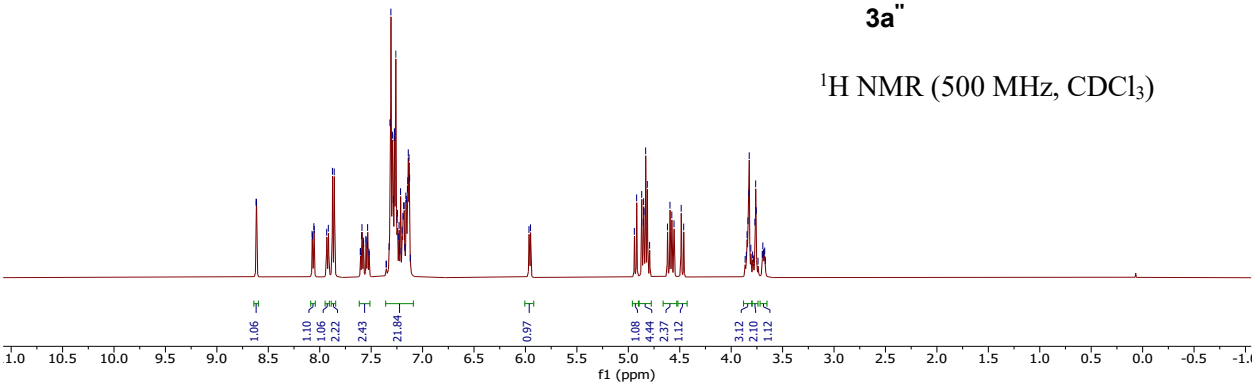


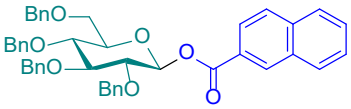




3a"

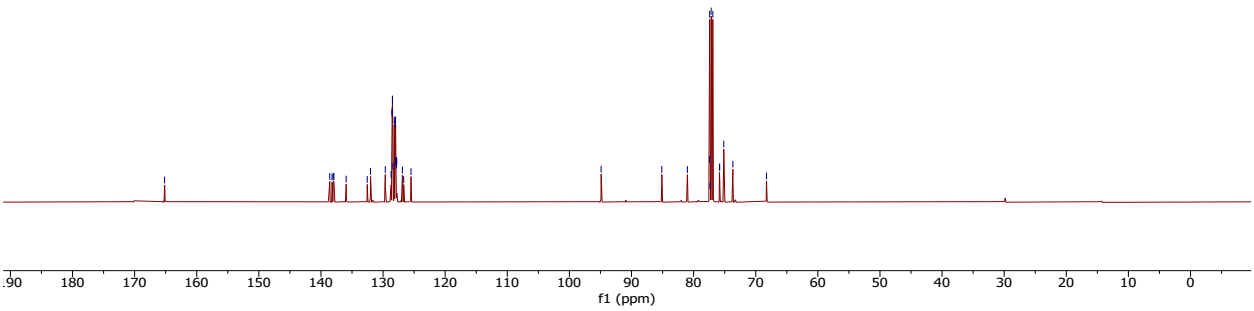
^{1}H NMR (500 MHz, $CDCl_3$)

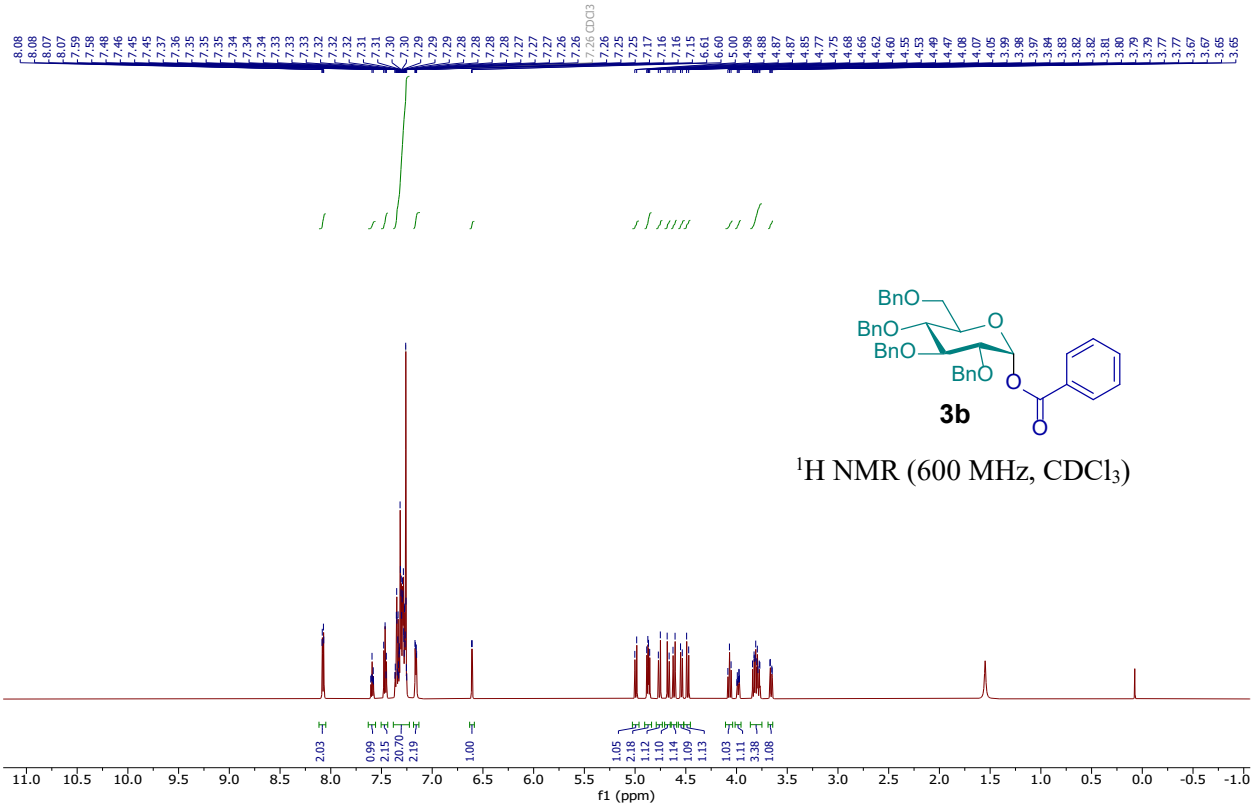




3a"

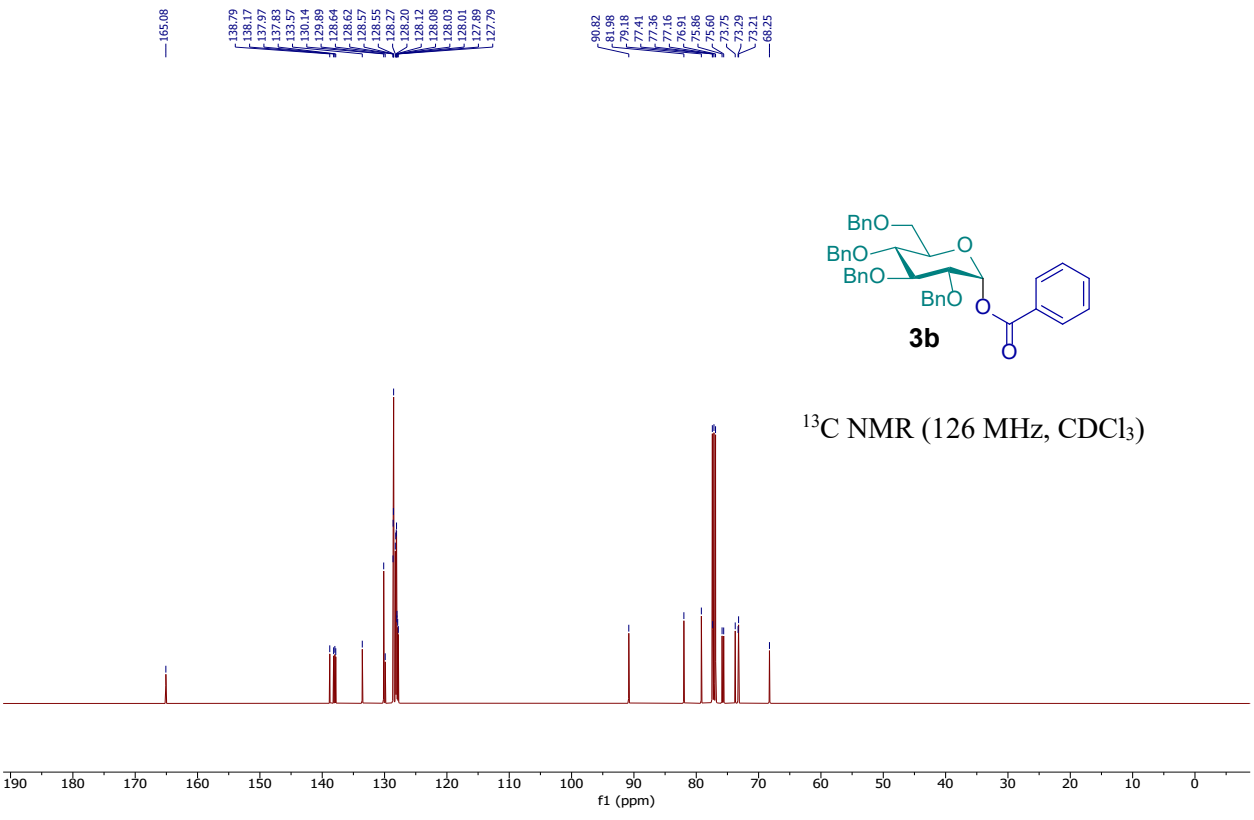
^{13}C NMR (126 MHz, $CDCl_3$)





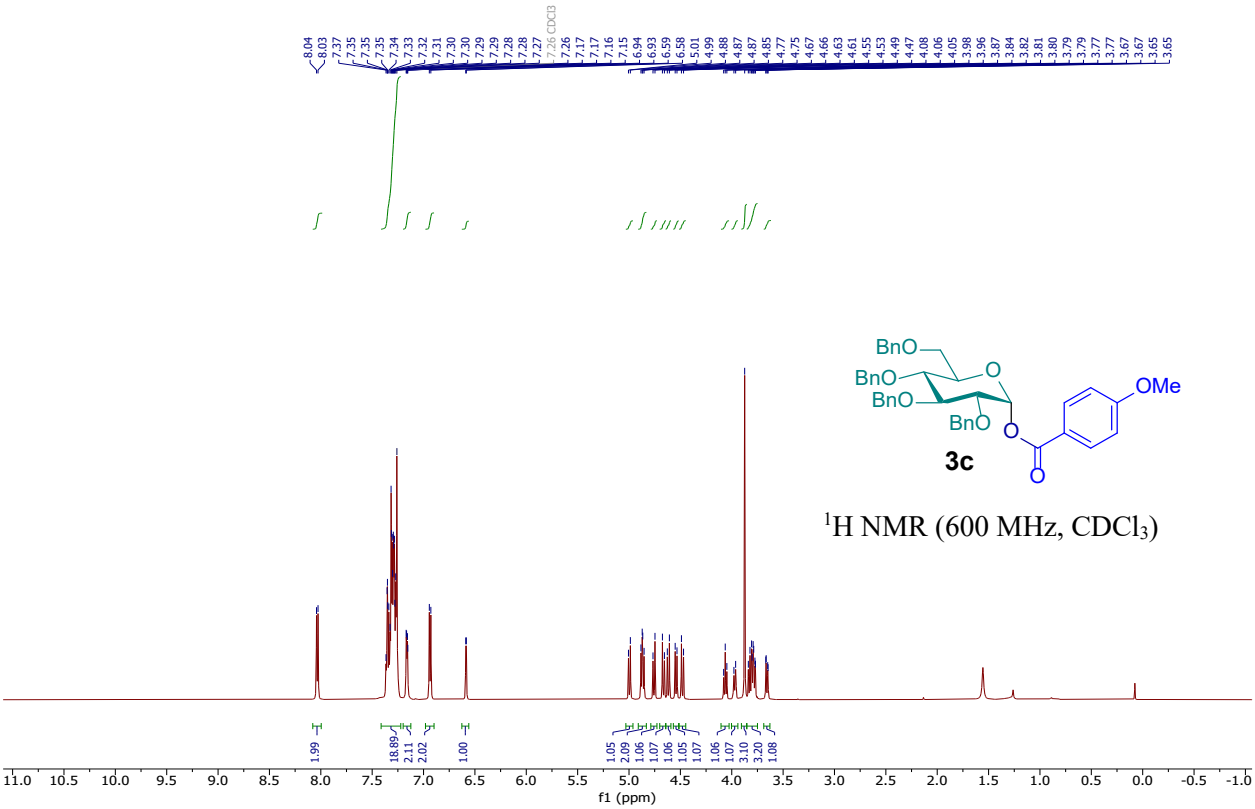
3b

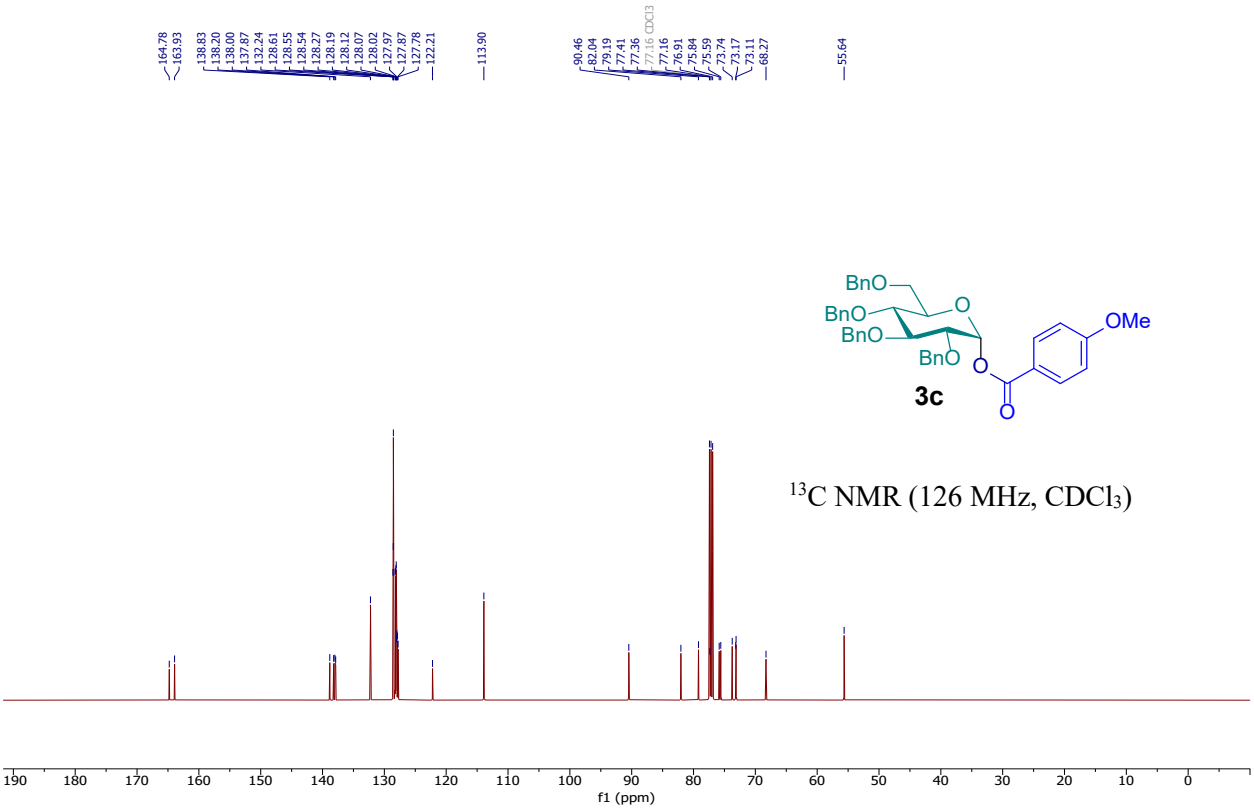
^{1}H NMR (600 MHz, $CDCl_3$)

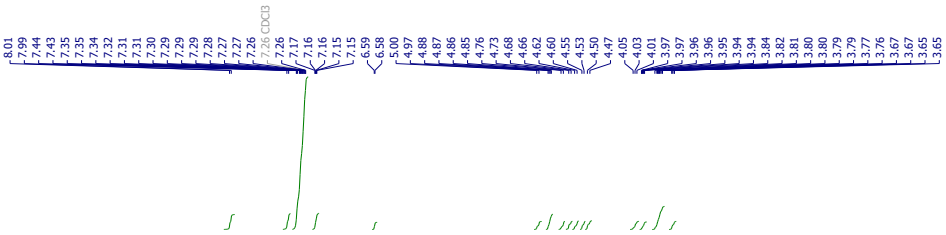


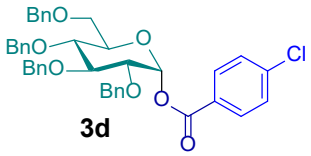
3b

^{13}C NMR (126 MHz, $CDCl_3$)


BnO
BnO
BnO
BnO
O
OMe
O
O
3c
1H NMR (600 MHz, CDCl3)
f1 (ppm)

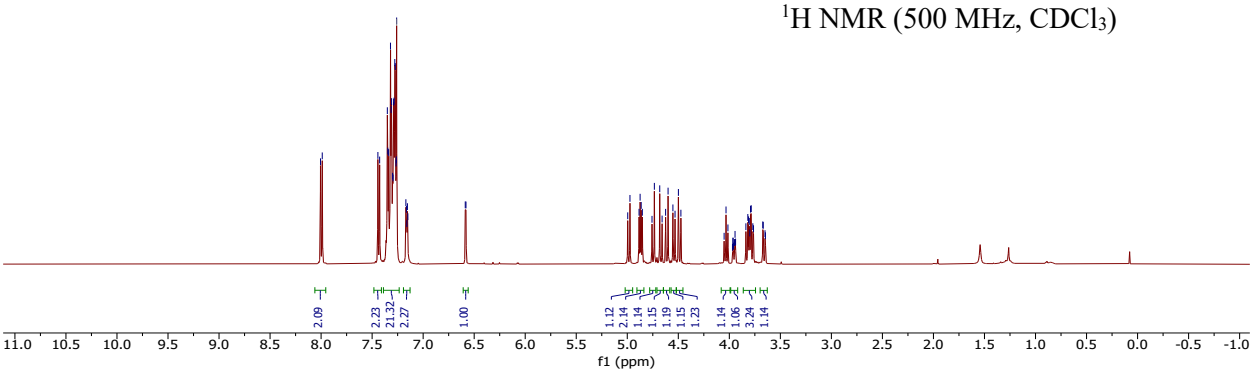

BnO
BnO
BnO
BnO
O
OMe
O
O
3c
13C NMR (126 MHz, CDCl3)
f1 (ppm)

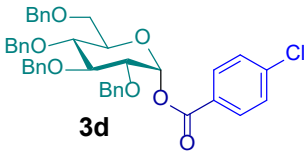




3d

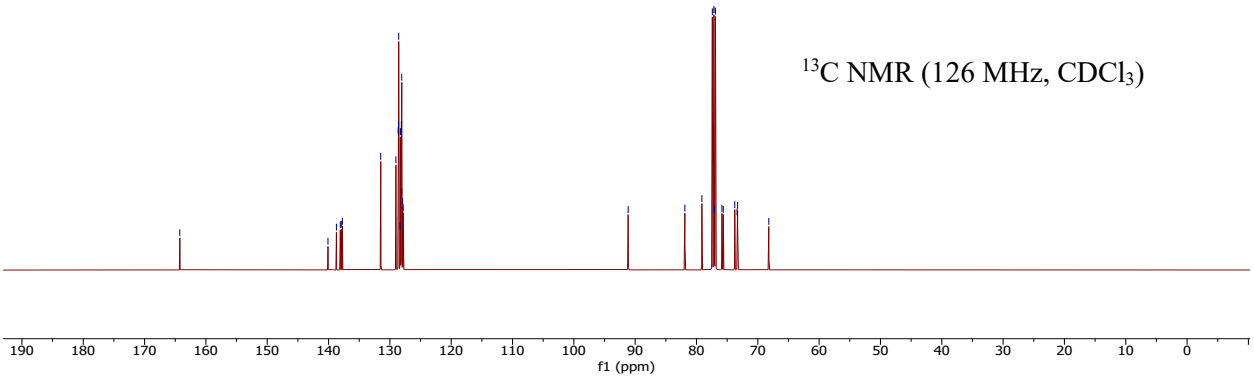
^{1}H NMR (500 MHz, $CDCl_3$)

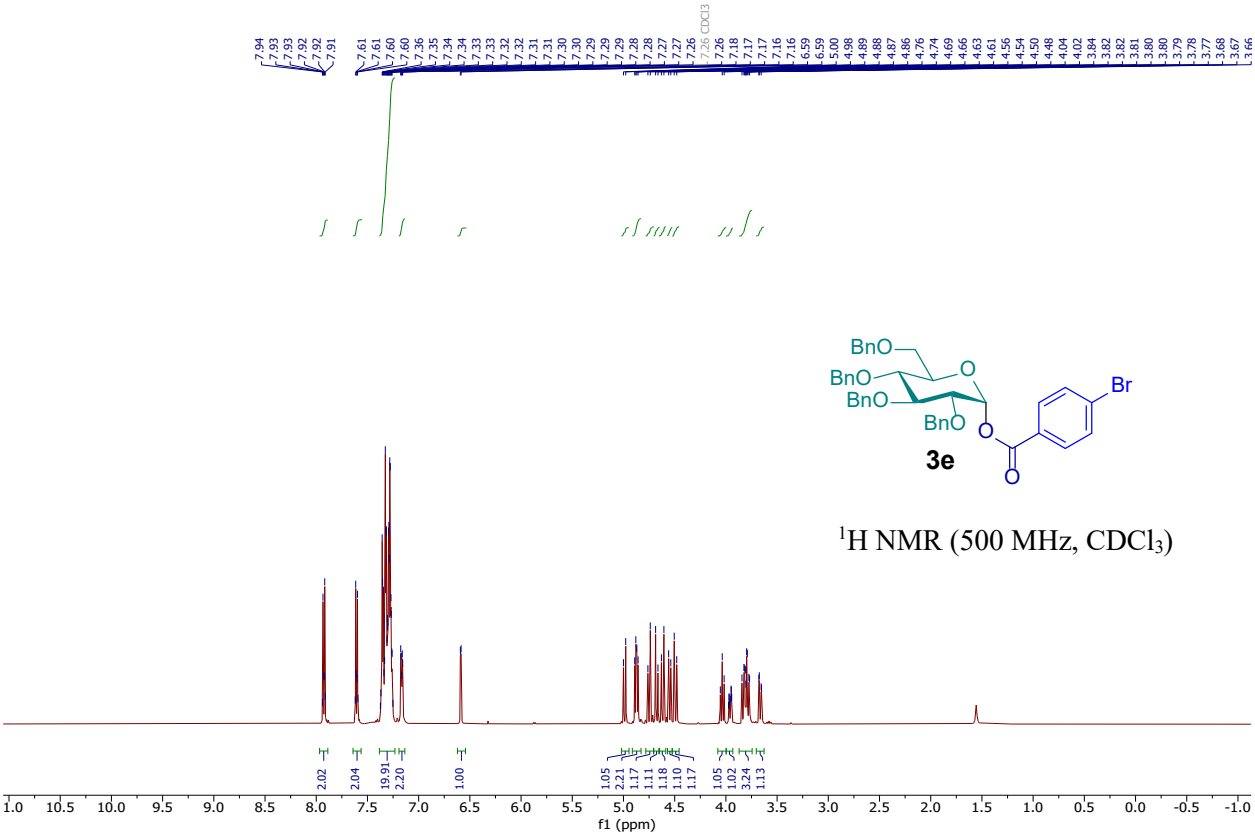




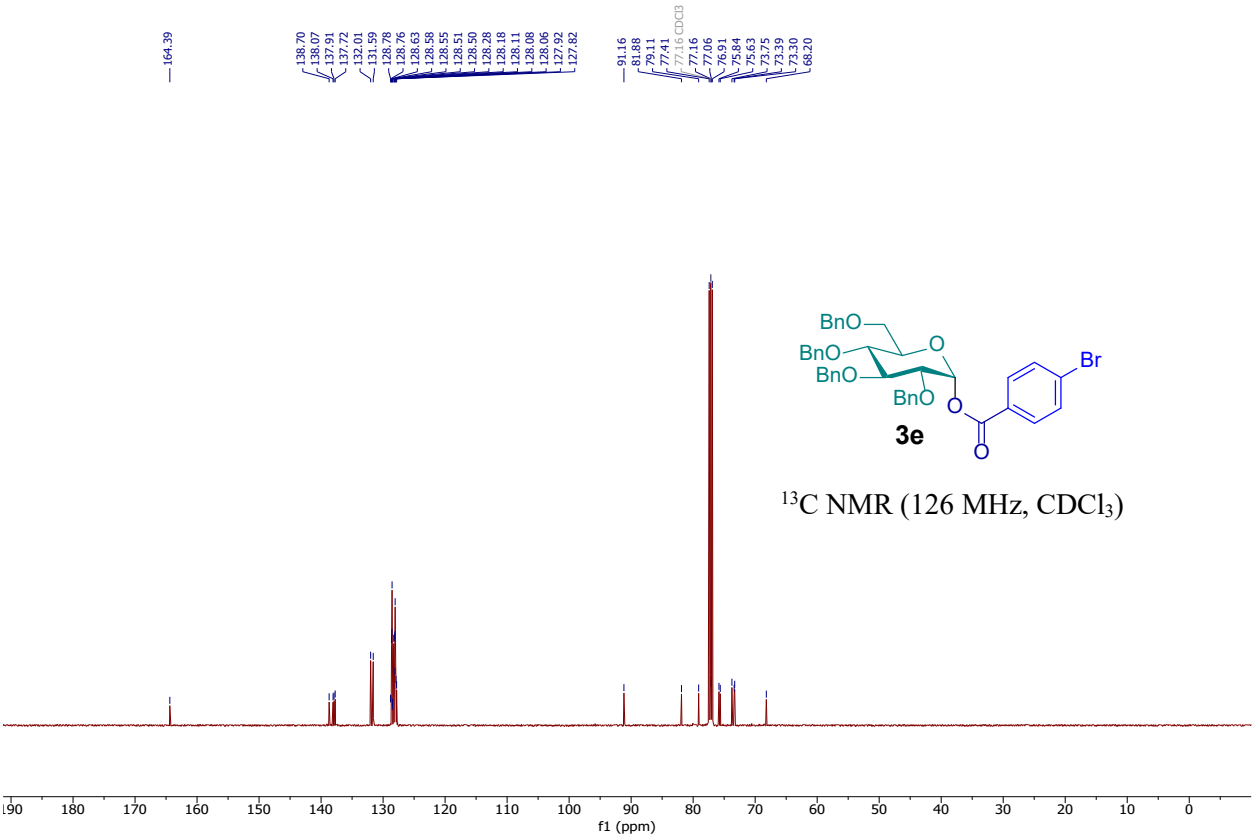
3d

^{13}C NMR (126 MHz, $CDCl_3$)

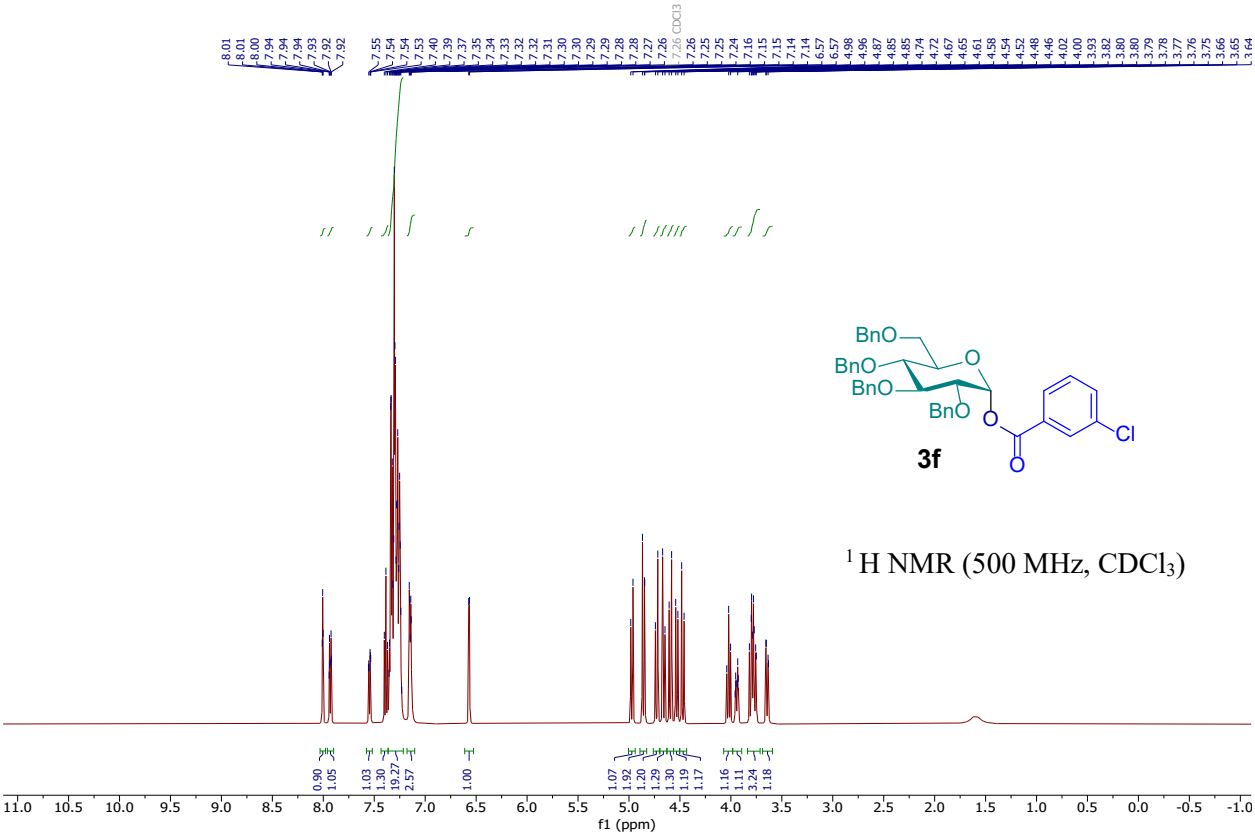




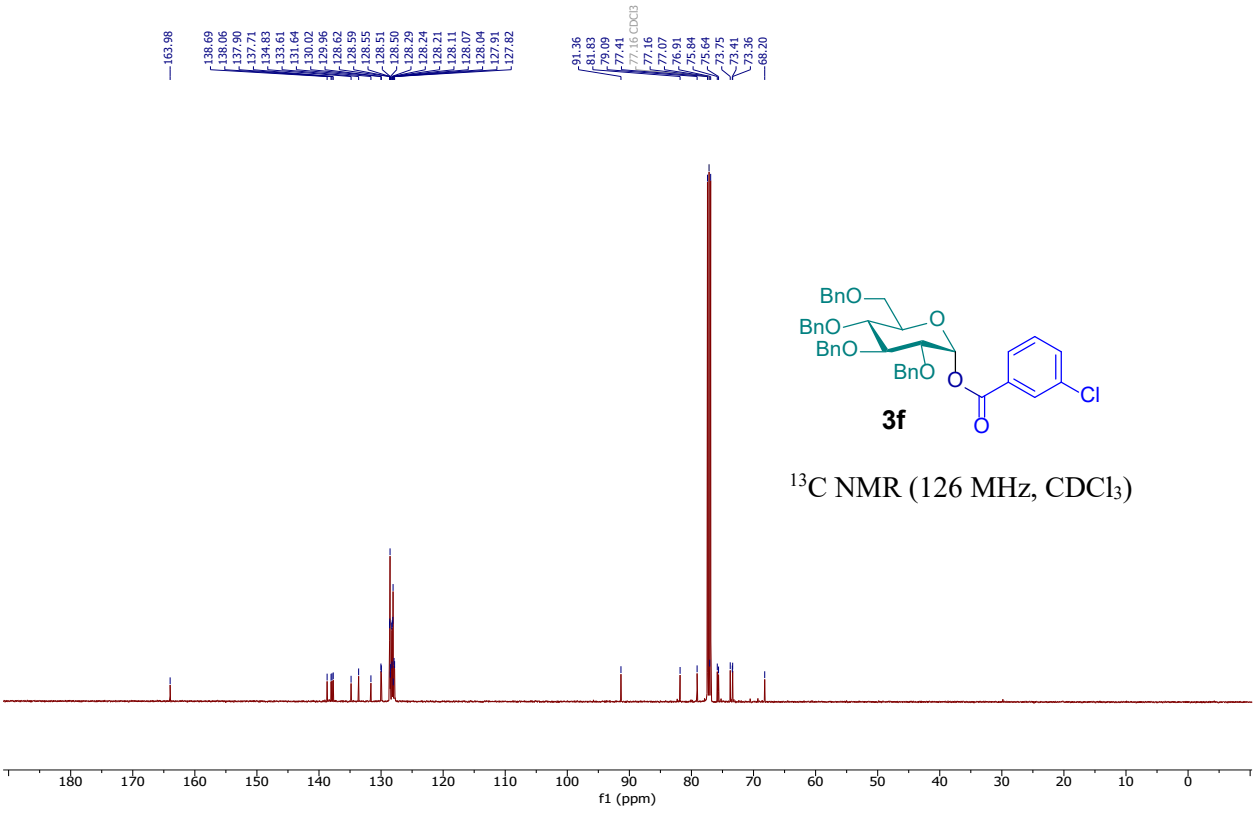
^{1}H NMR (500 MHz, $CDCl_3$)



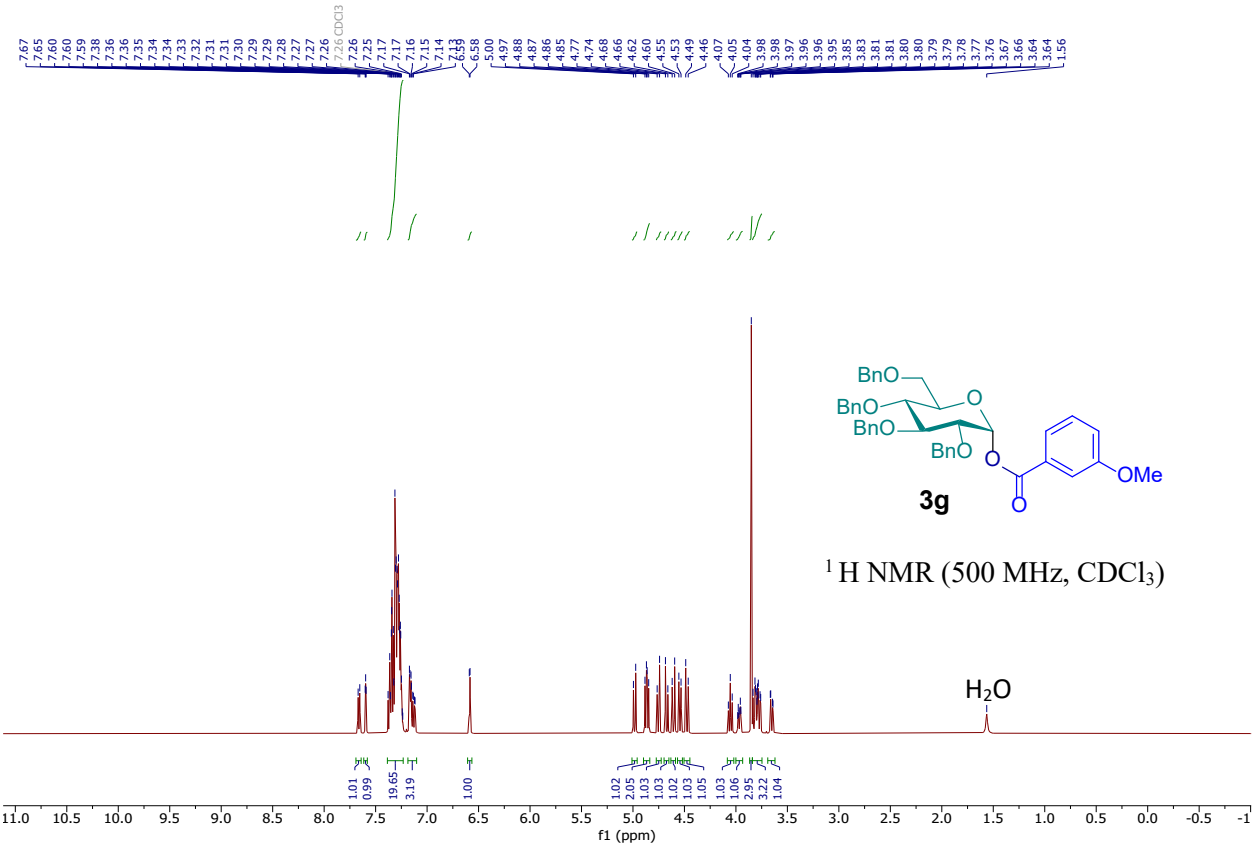
^{13}C NMR (126 MHz, $CDCl_3$)

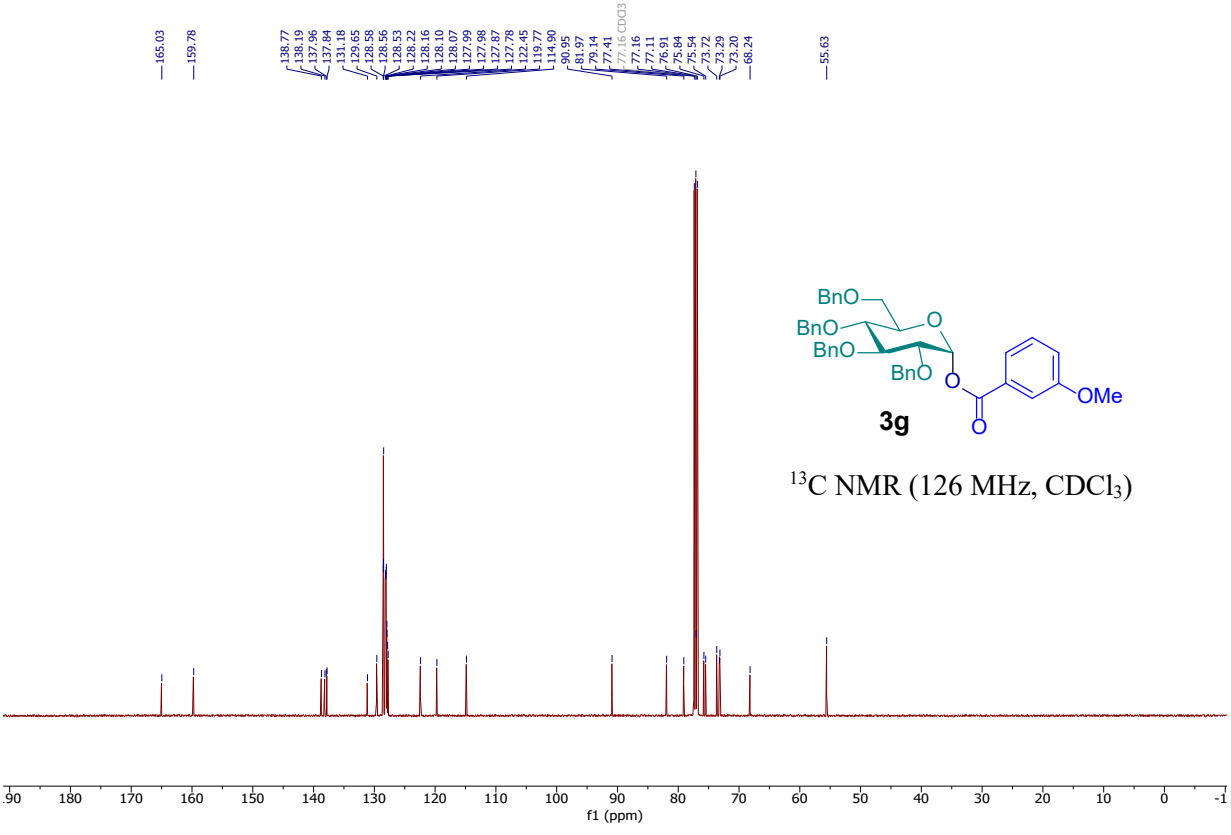


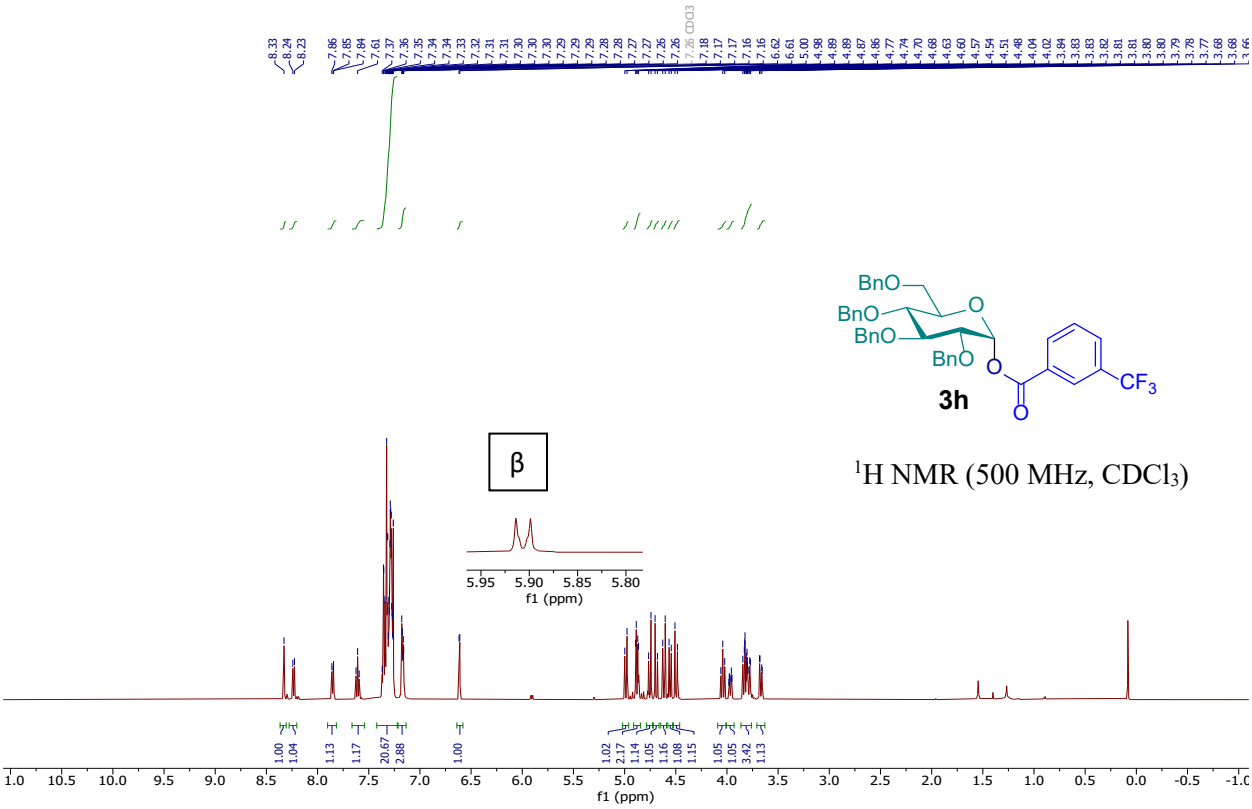
^{1}H NMR (500 MHz, $CDCl_3$)



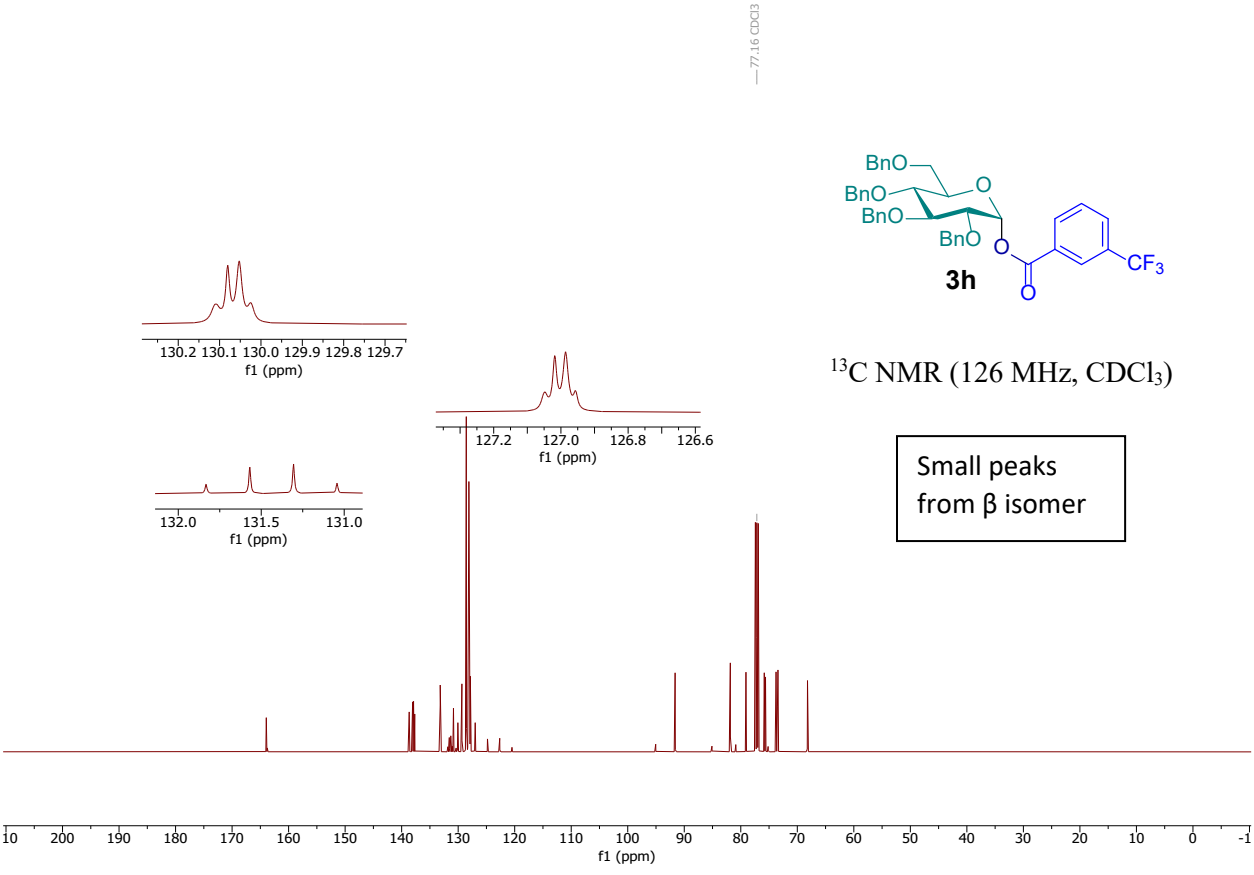
^{13}C NMR (126 MHz, $CDCl_3$)


BnO
BnO
BnO
BnO
O
O
OMe
O
3g
^{1}H NMR (500 MHz, $CDCl_3$)
H_2O
f1 (ppm)


BnO
BnO
BnO
BnO
O
O
OMe
O
3g
^{13}C NMR (126 MHz, $CDCl_3$)
f1 (ppm)

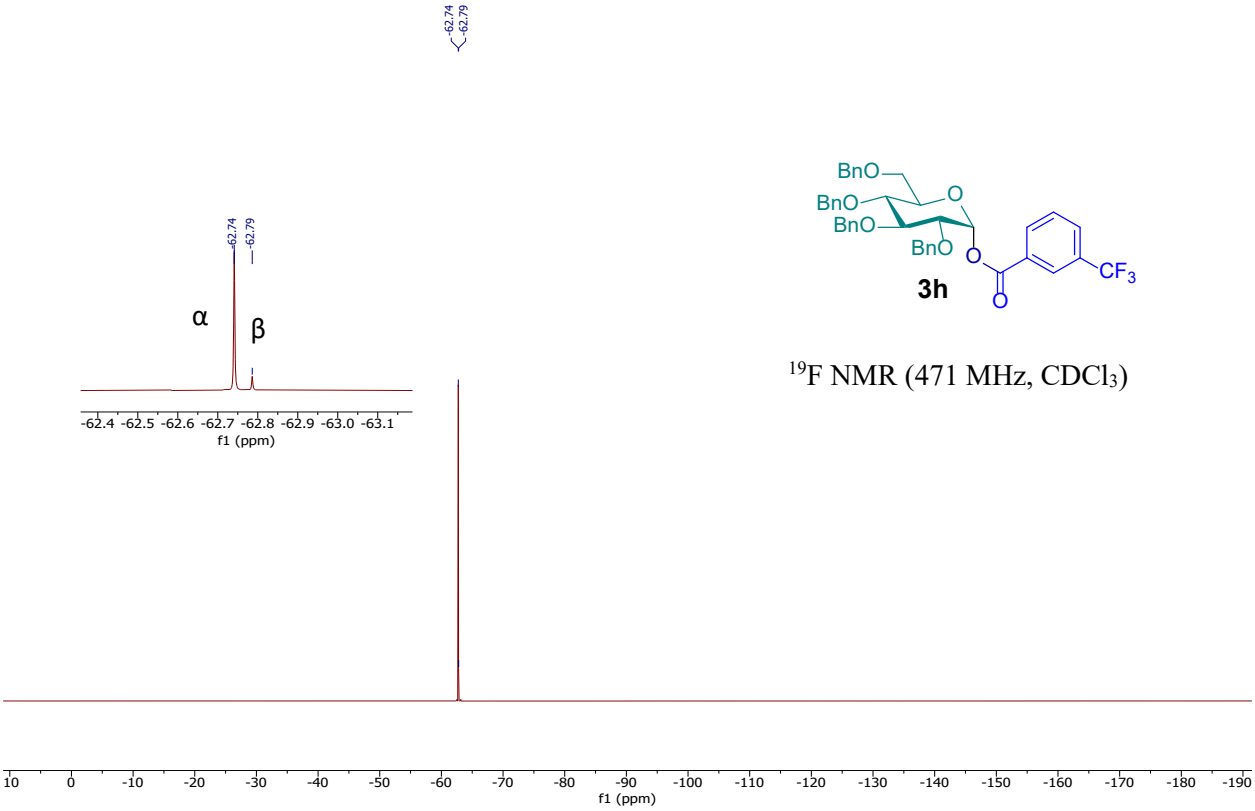


^{1}H NMR (500 MHz, $CDCl_3$)

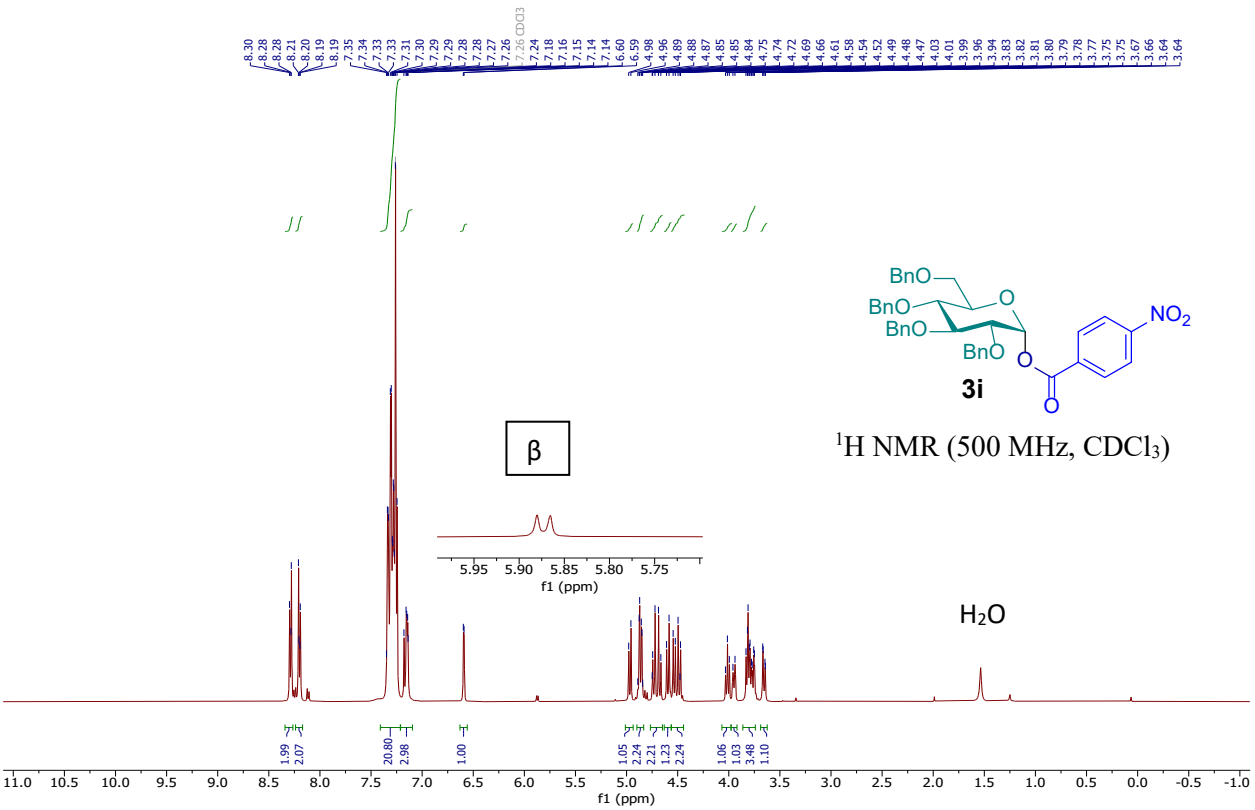


^{13}C NMR (126 MHz, $CDCl_3$)

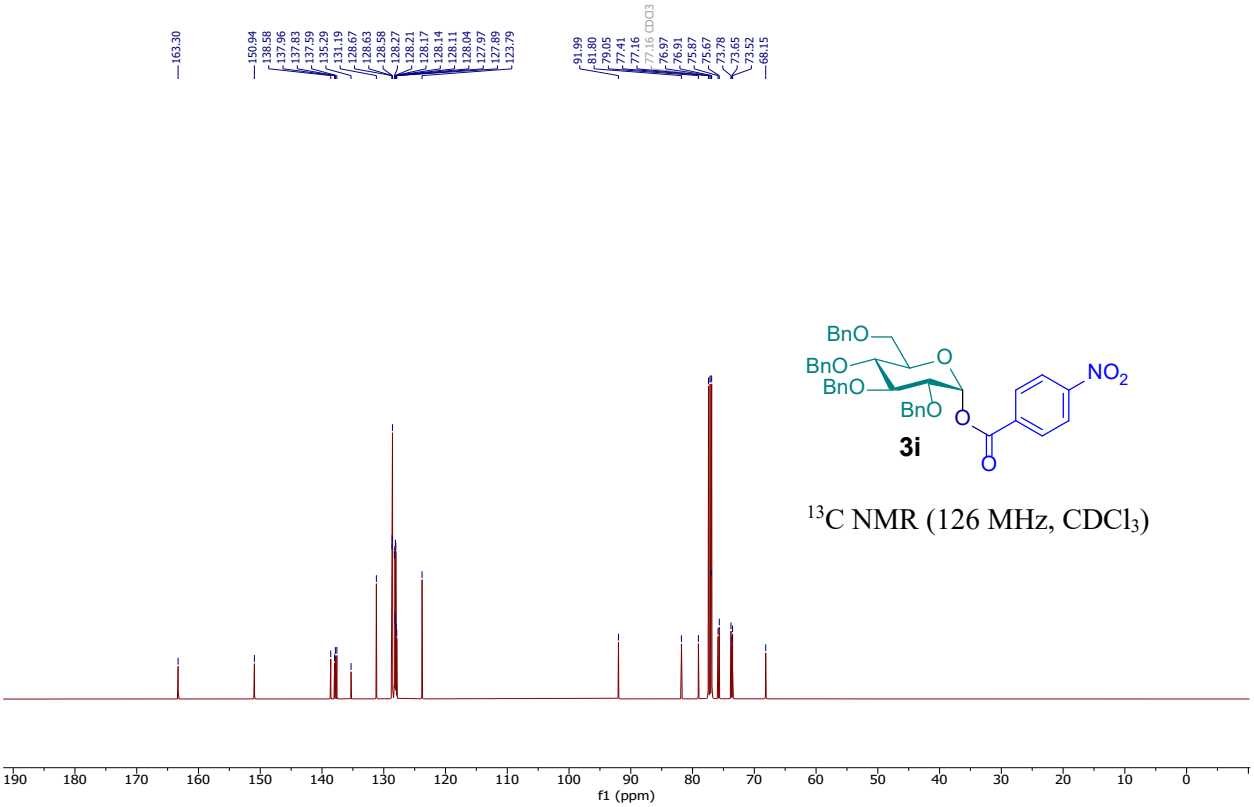
Small peaks from β isomer

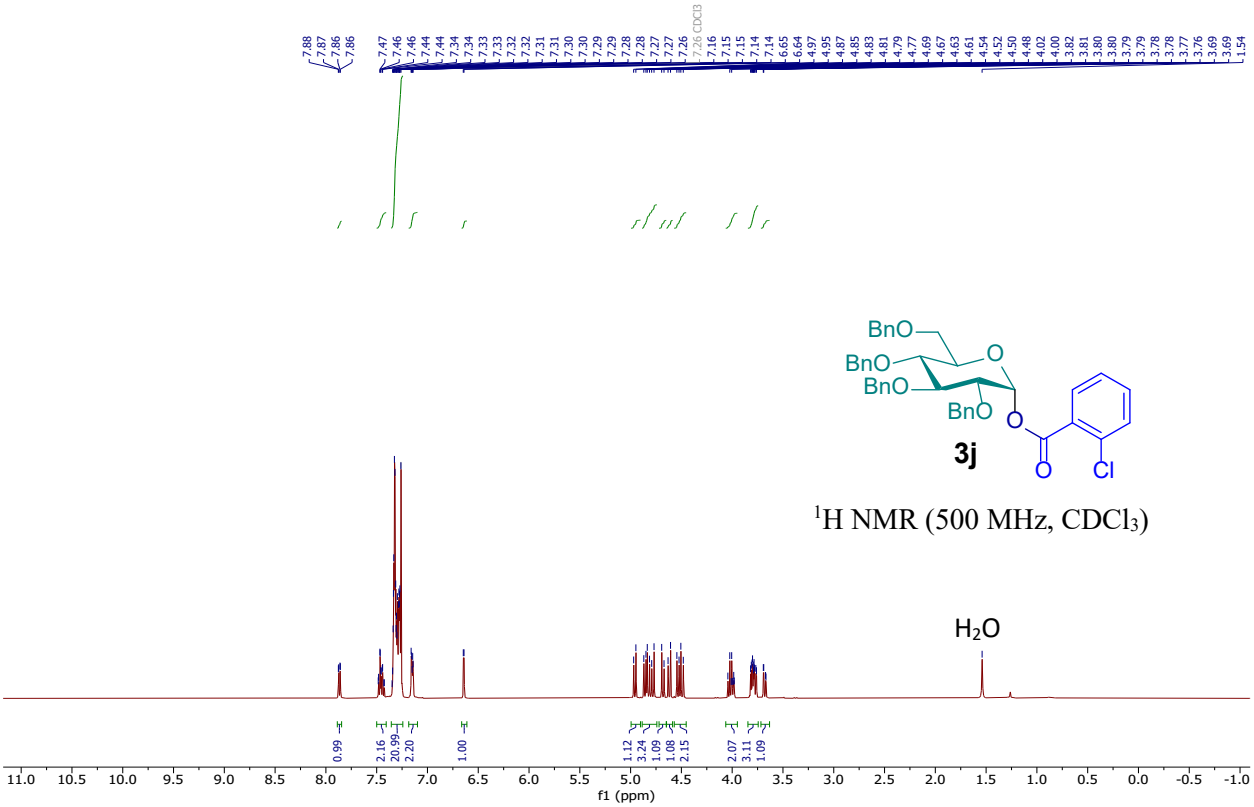


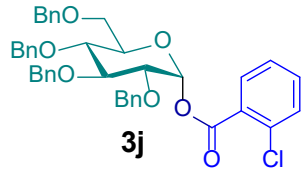
^{19}F NMR (471 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)

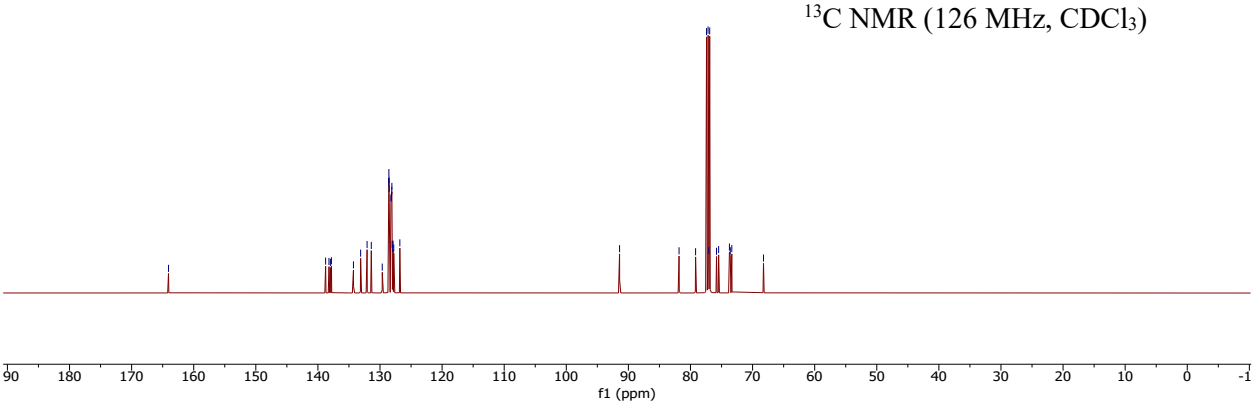

163.30
150.94
138.58
137.96
137.83
137.59
135.29
131.19
128.67
128.63
128.58
128.27
128.21
128.17
128.14
128.11
128.04
127.97
127.89
123.79
91.99
81.80
79.05
77.41
77.16
CDCl3
76.97
76.91
75.87
75.67
73.78
73.65
73.52
68.15
BnO
BnO
BnO
BnO
O
O
O
NO2
3i
13C NMR (126 MHz, CDCl3)
f1 (ppm)

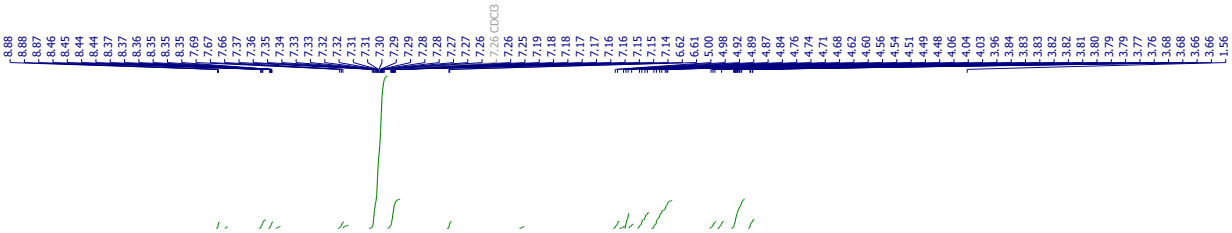

7.88
7.87
7.86
7.86
7.47
7.46
7.46
7.44
7.44
7.34
7.34
7.33
7.33
7.32
7.32
7.31
7.31
7.30
7.30
7.29
7.29
7.28
7.28
7.27
7.27
7.26
CDCl3
7.16
7.15
7.15
7.14
7.14
6.65
6.64
4.97
4.95
4.87
4.85
4.83
4.81
4.79
4.77
4.69
4.67
4.63
4.61
4.54
4.52
4.50
4.48
4.02
4.00
3.82
3.81
3.80
3.80
3.79
3.79
3.78
3.78
3.77
3.76
3.69
3.69
1.54
BnO
BnO
BnO
BnO
O
O
O
Cl
3j
1H NMR (500 MHz, CDCl3)
H2O
0.99
2.16
20.99
2.20
1.00
1.12
3.24
1.09
1.08
2.15
2.07
3.11
1.09
f1 (ppm)

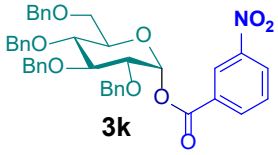


3j

^{13}C NMR (126 MHz, $CDCl_3$)

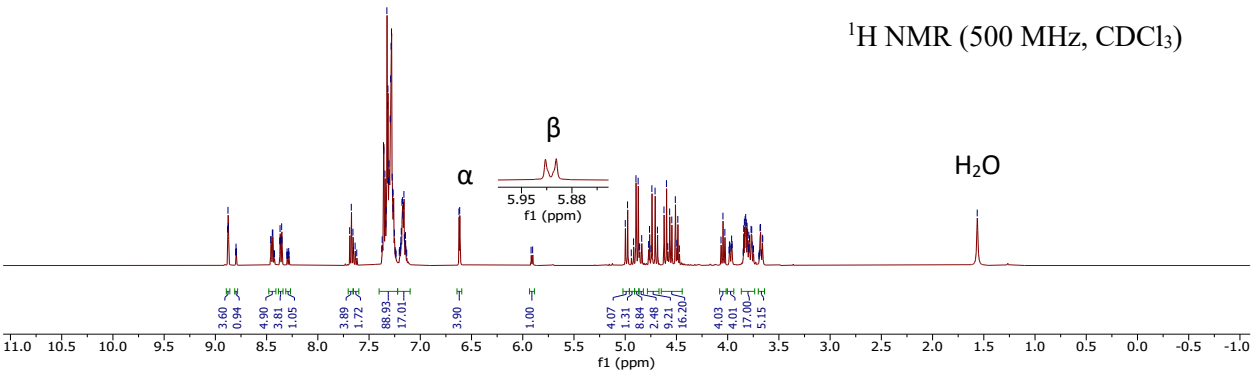


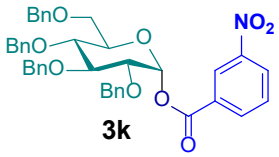




3k

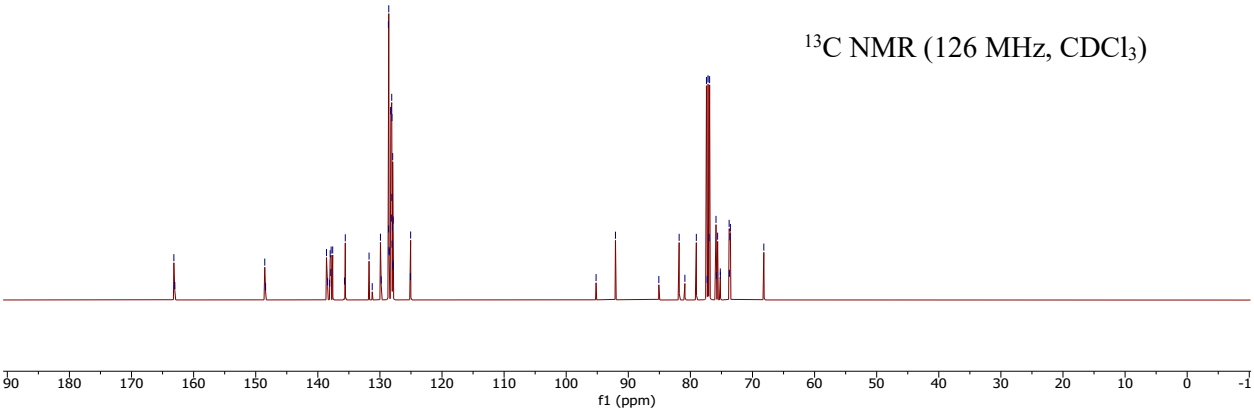
^{1}H NMR (500 MHz, $CDCl_3$)

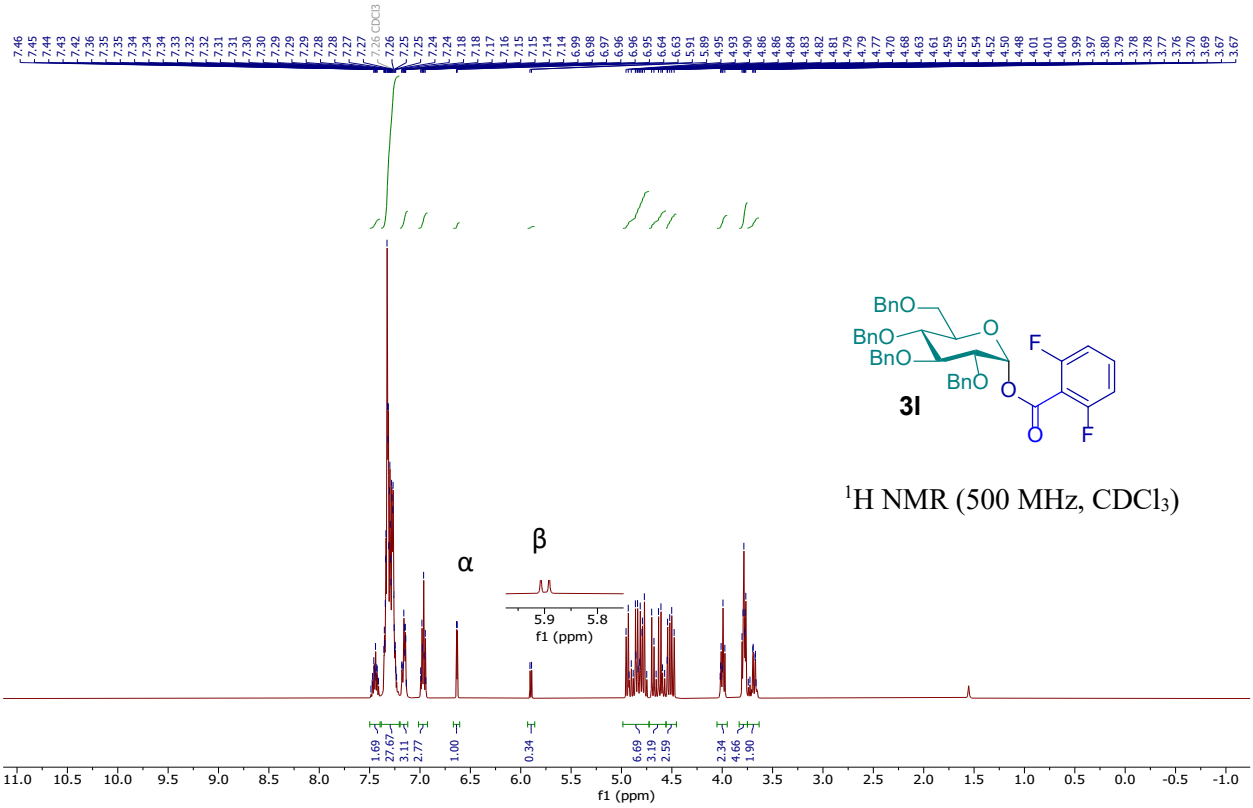




3k

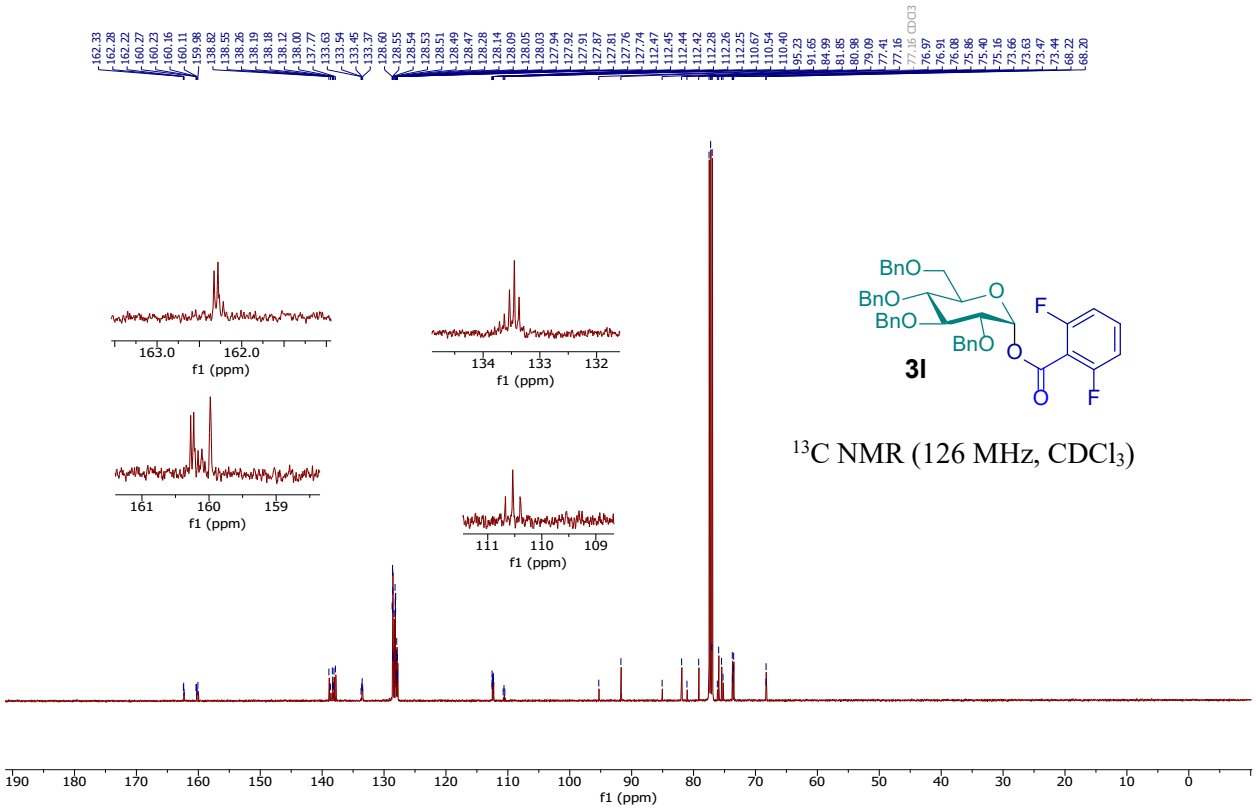
^{13}C NMR (126 MHz, $CDCl_3$)



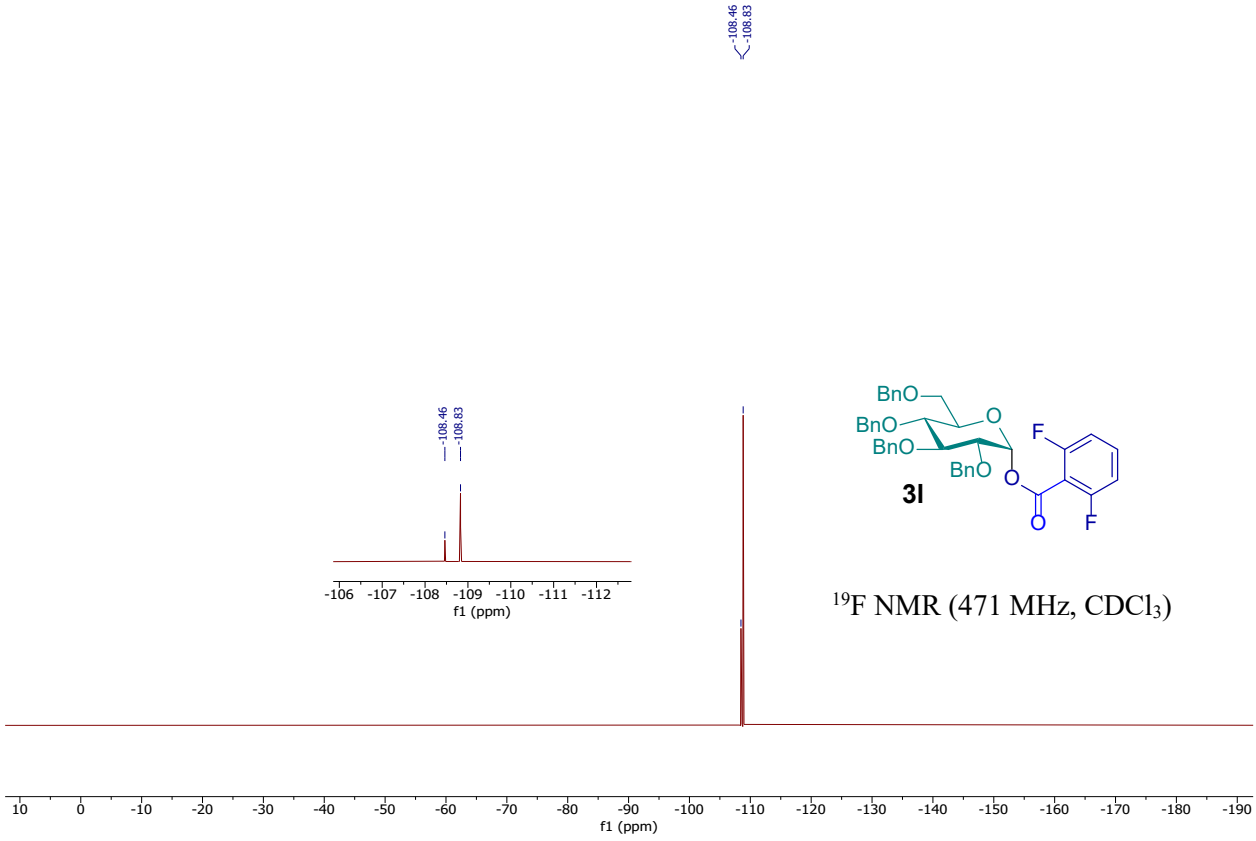


3l

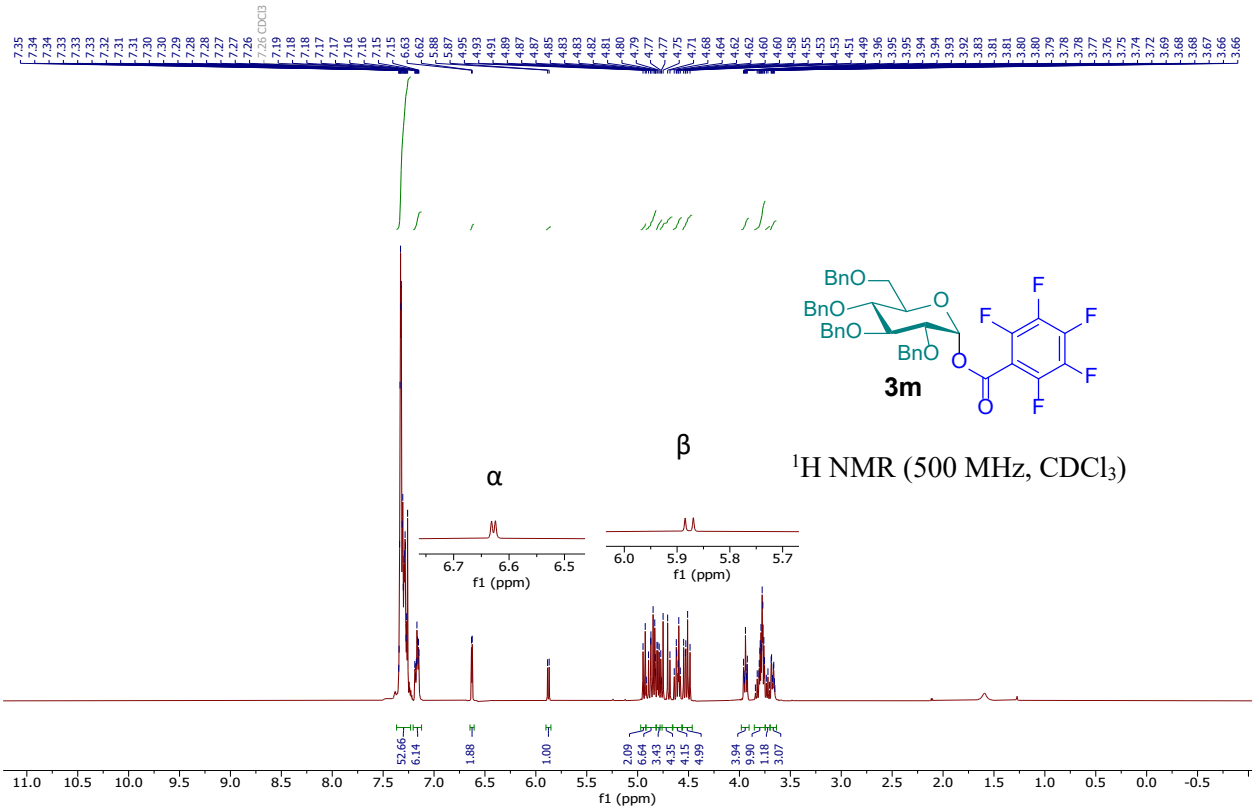
^{1}H NMR (500 MHz, $CDCl_3$)



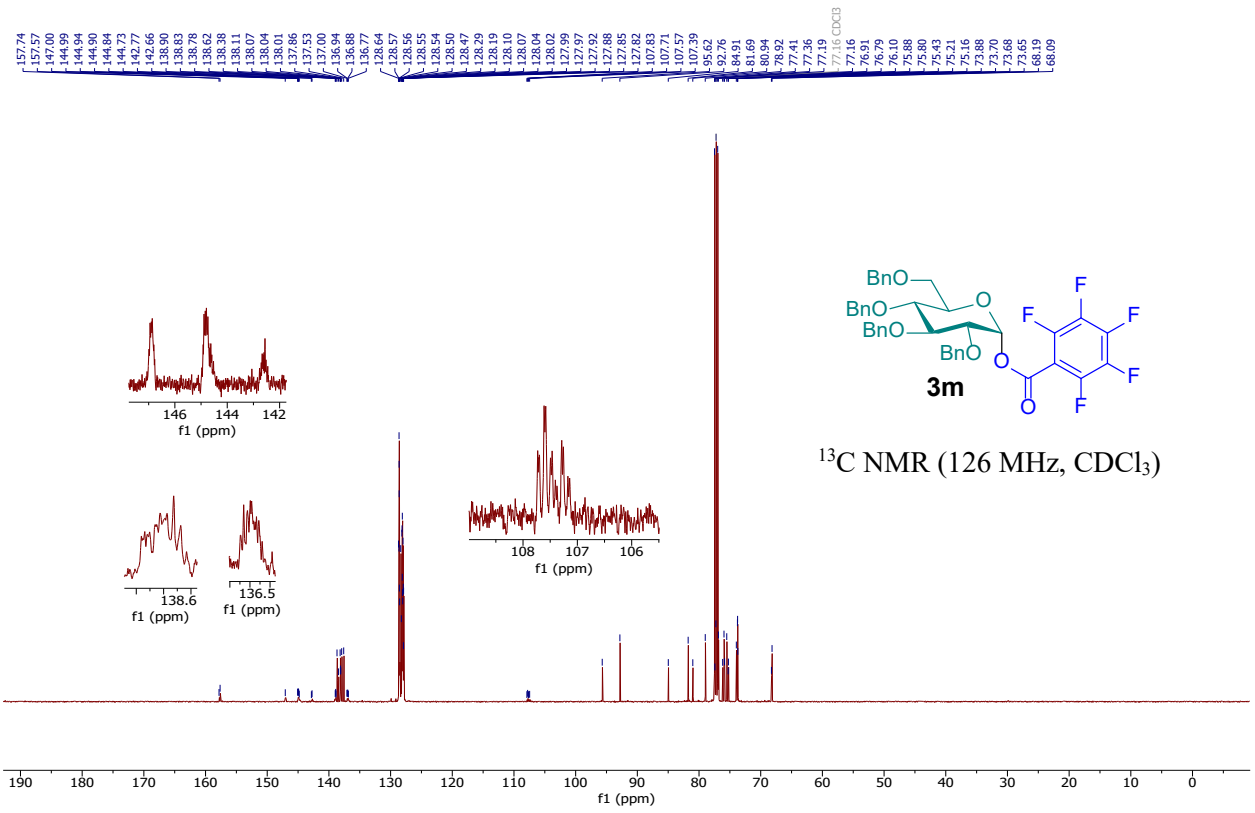
^{13}C NMR (126 MHz, $CDCl_3$)



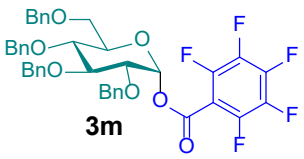
^{19}F NMR (471 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)

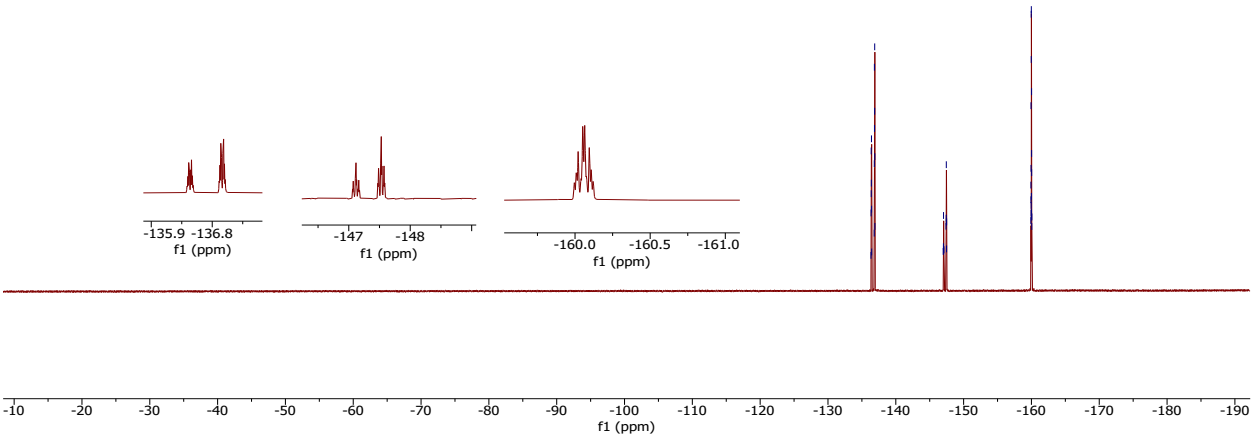


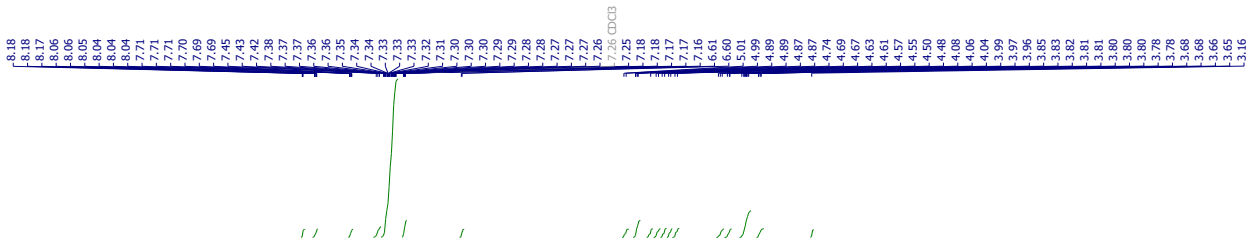
^{13}C NMR (126 MHz, $CDCl_3$)

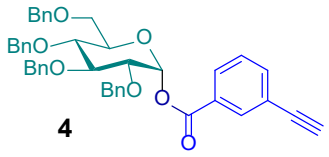


3m

^{19}F NMR (471 MHz, $CDCl_3$)

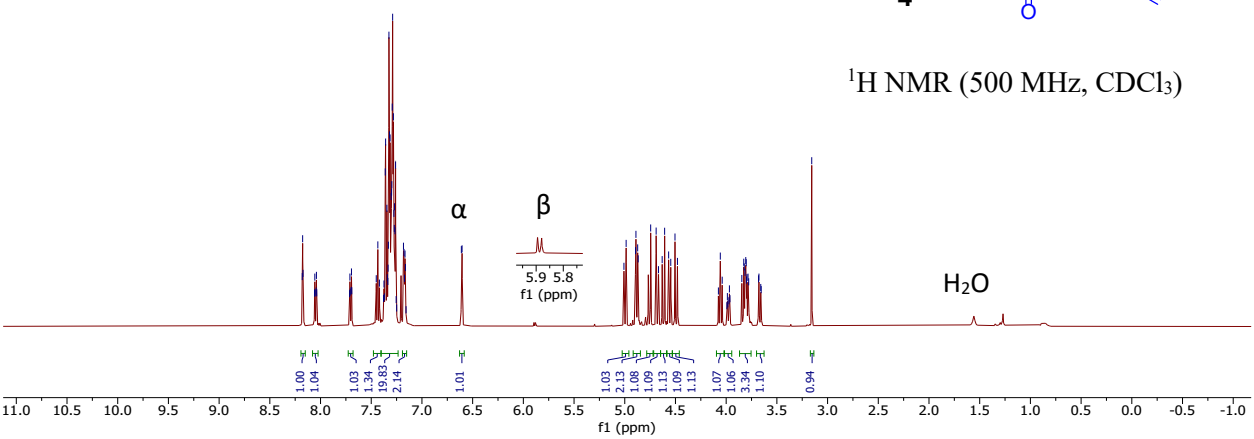


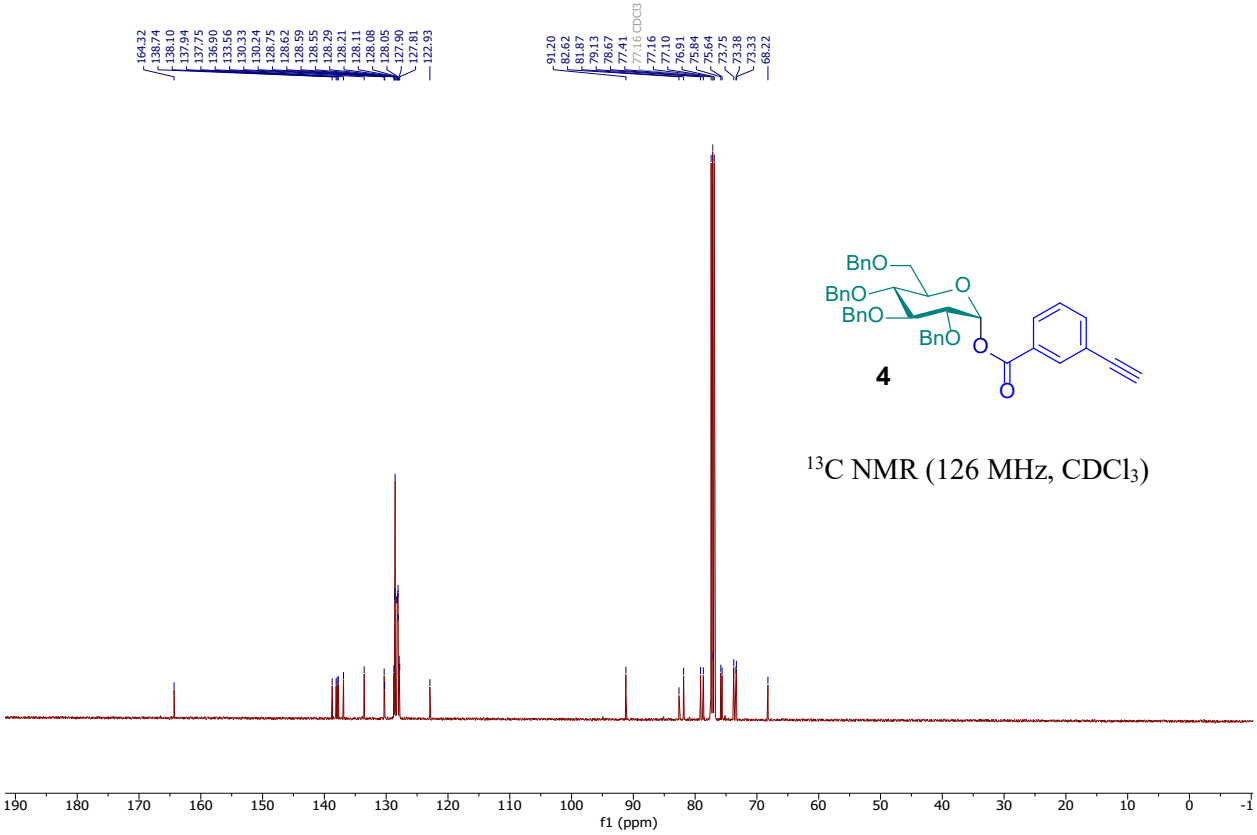


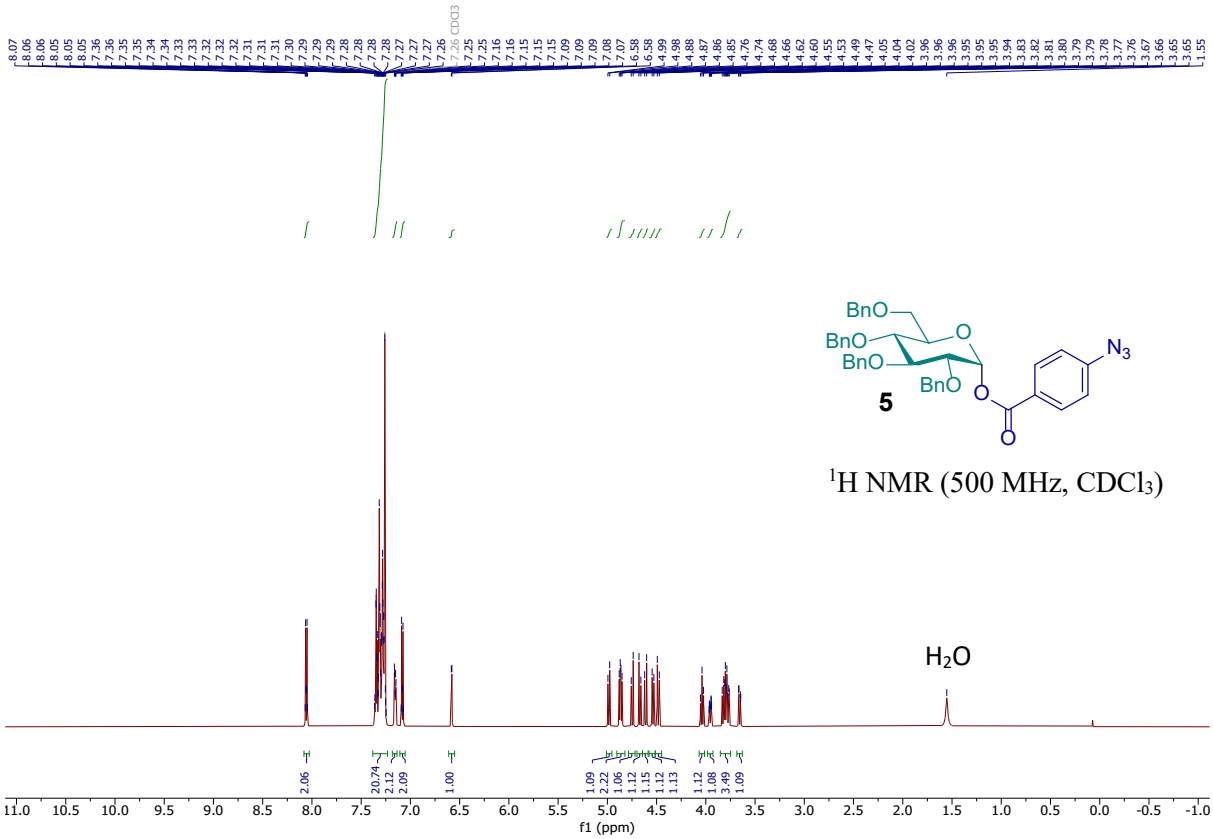


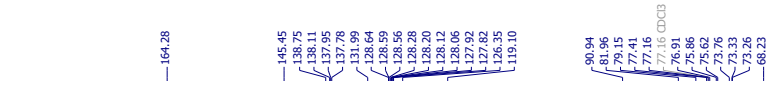
4

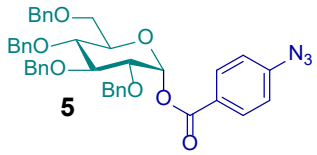
^{1}H NMR (500 MHz, $CDCl_3$)




164.32
138.74
138.10
137.94
137.75
136.90
133.56
130.33
130.24
128.75
128.62
128.59
128.55
128.29
128.21
128.11
128.08
128.05
127.90
127.81
122.93
91.20
82.62
81.87
79.13
78.67
77.41
77.16 CDCl3
77.16
77.10
76.91
75.84
75.64
73.75
73.38
73.33
68.22
BnO
BnO
BnO
BnO
O
O
O
4
13C NMR (126 MHz, CDCl3)
f1 (ppm)

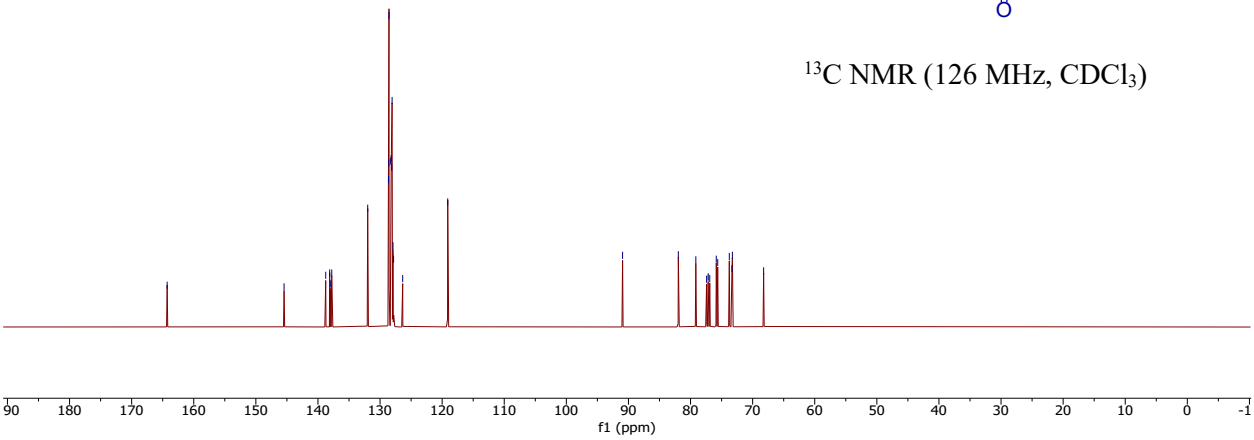

7.26 CDCl3
BnO
BnO
BnO
BnO
O
O
O
N3
5
1H NMR (500 MHz, CDCl3)
H2O
2.06
20.74
2.12
2.09
1.00
1.09
2.22
1.06
1.12
1.15
1.12
1.13
1.12
1.08
3.49
1.09
f1 (ppm)

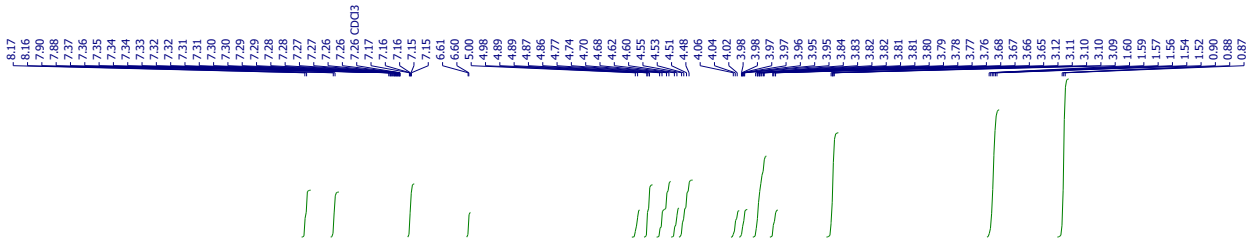


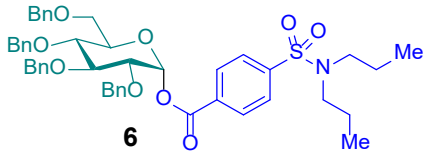


5

^{13}C NMR (126 MHz, $CDCl_3$)

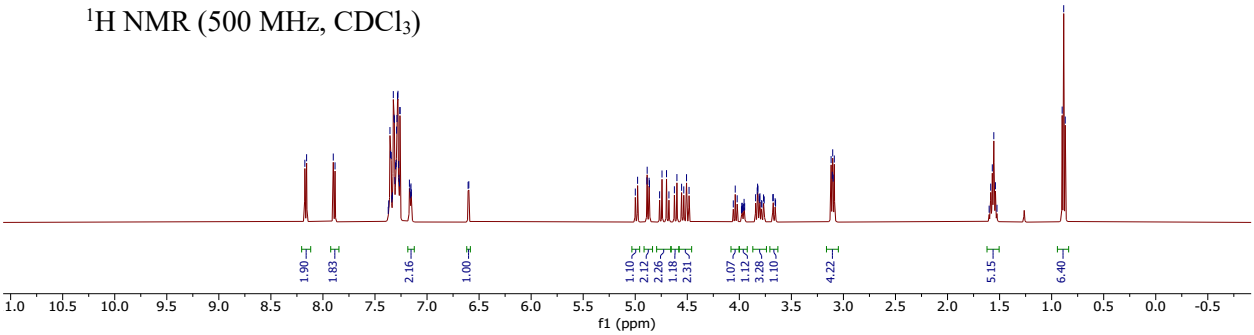


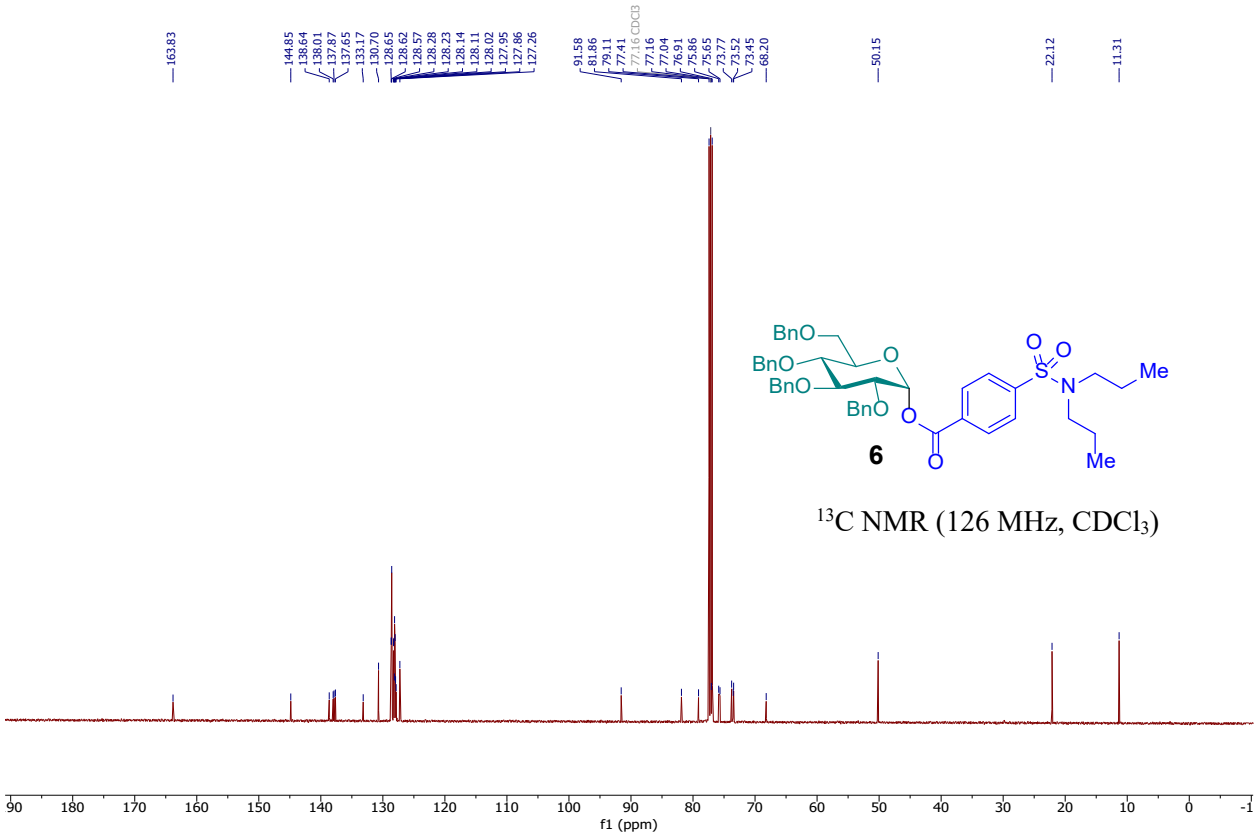




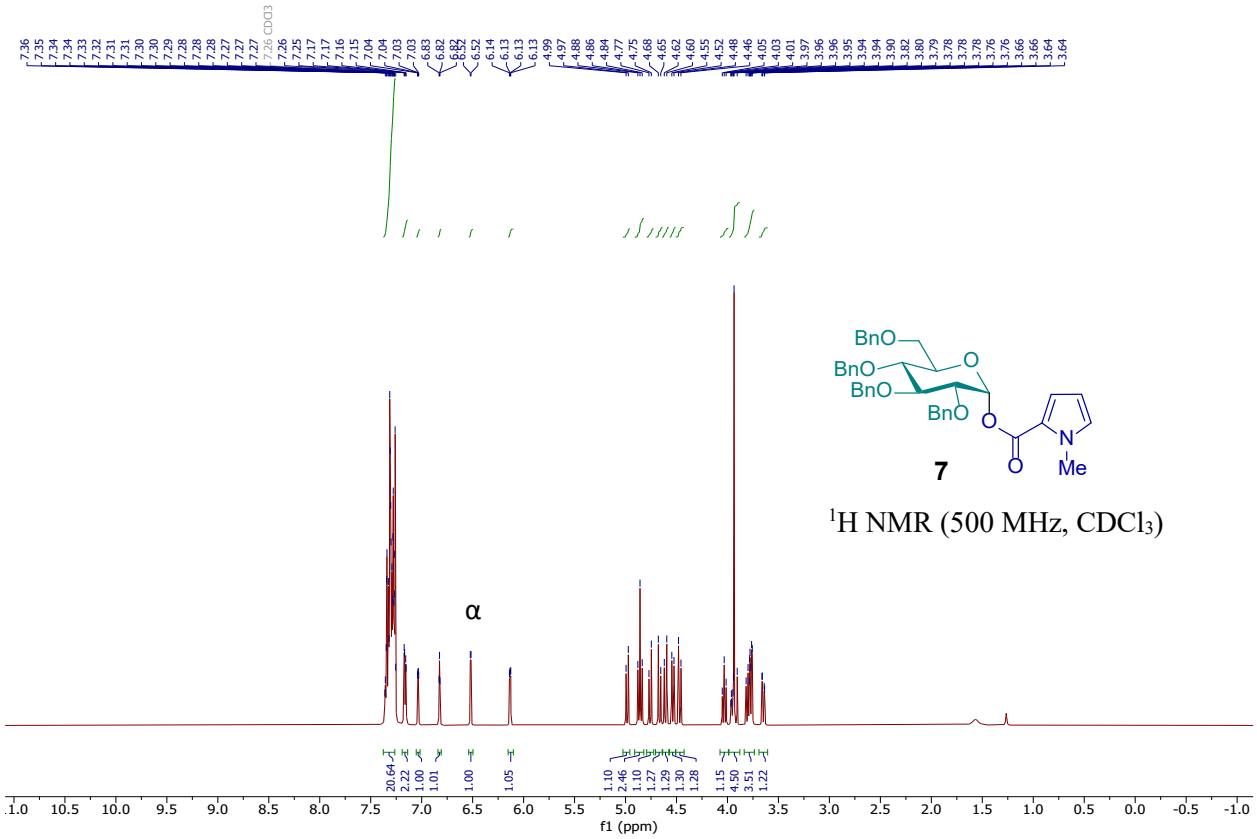
6

^{1}H NMR (500 MHz, $CDCl_3$)

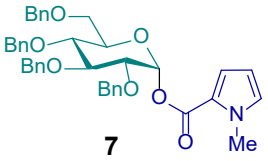




^{13}C NMR (126 MHz, $CDCl_3$)

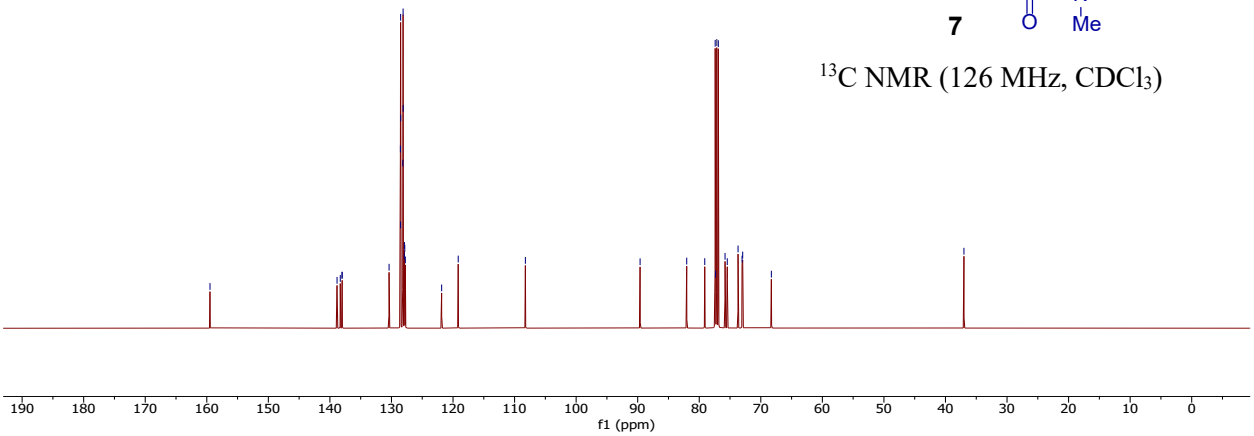


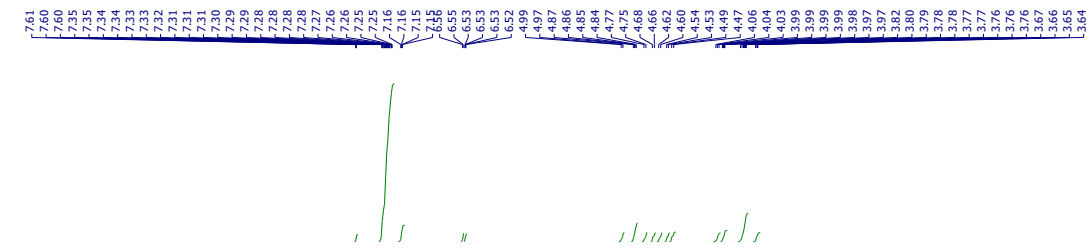
^{1}H NMR (500 MHz, $CDCl_3$)

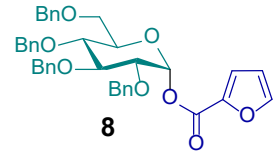


7

^{13}C NMR (126 MHz, $CDCl_3$)

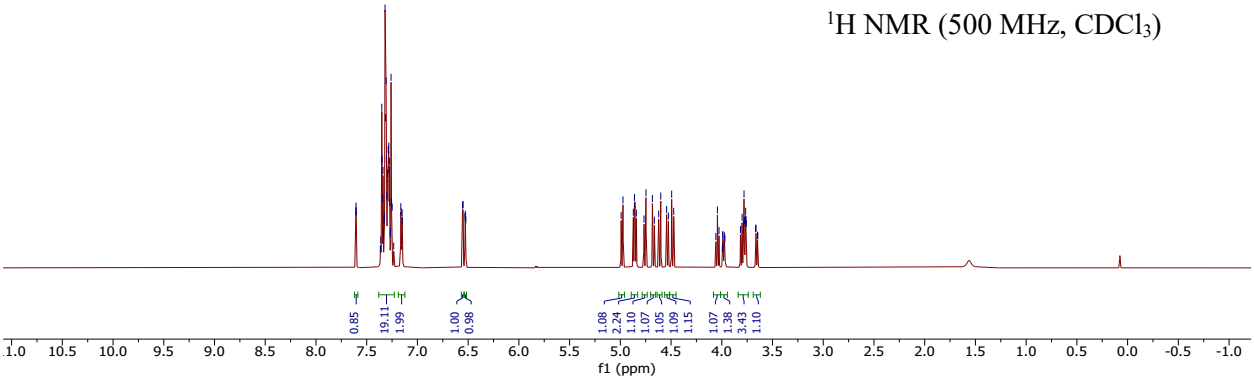


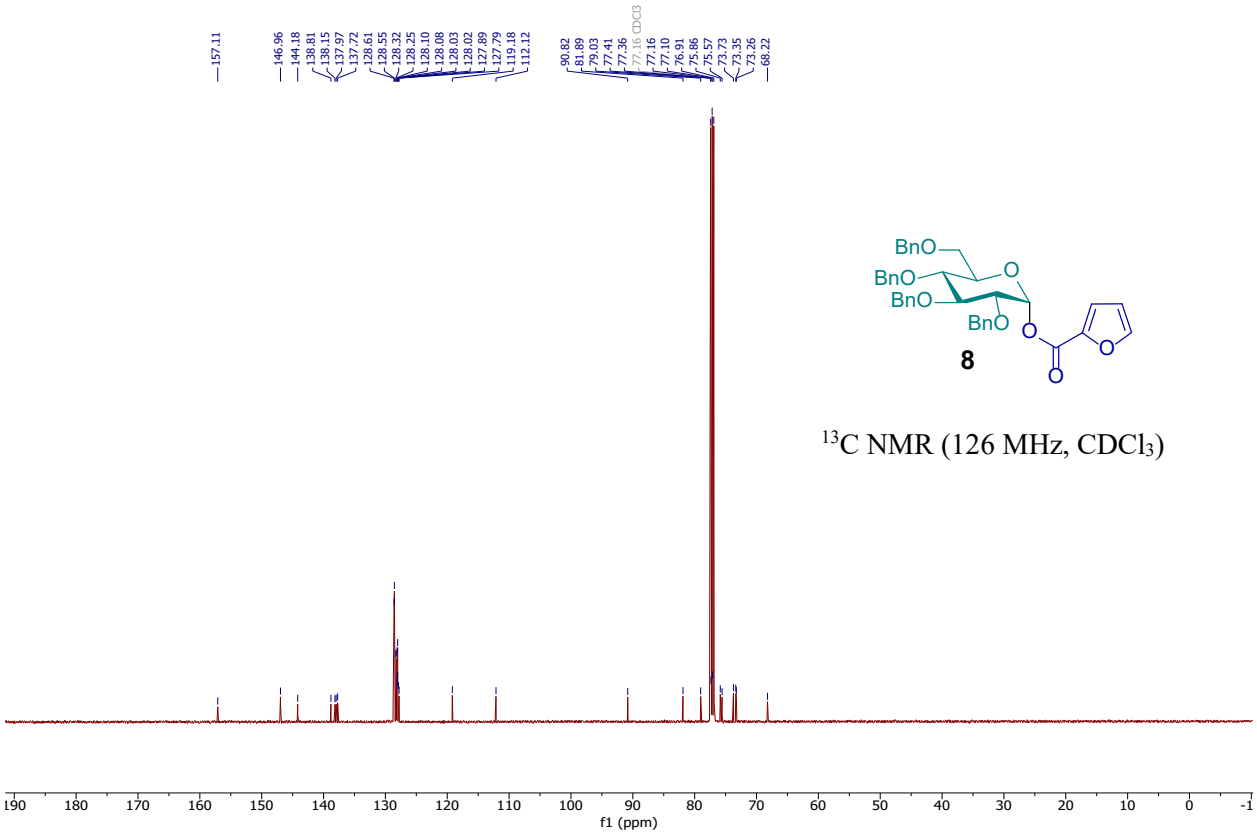




8

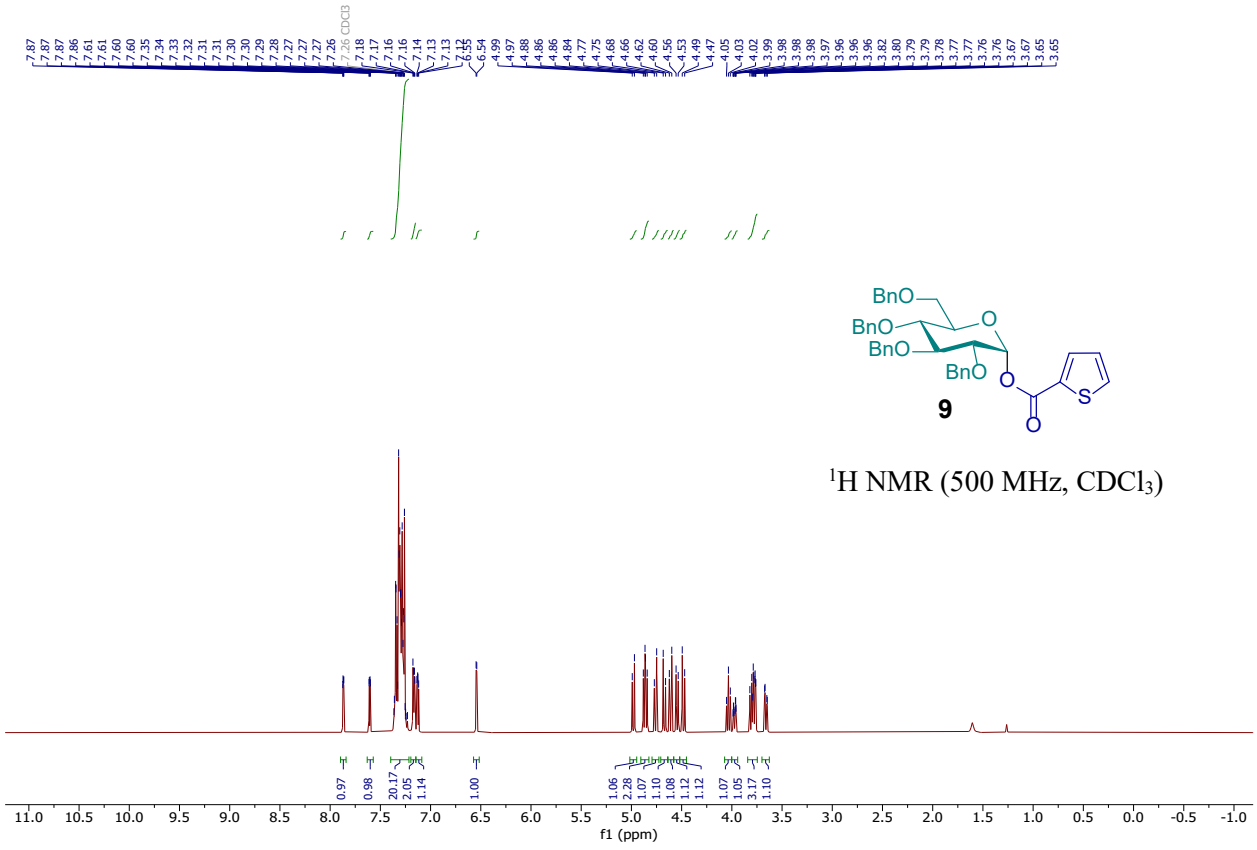
^{1}H NMR (500 MHz, $CDCl_3$)





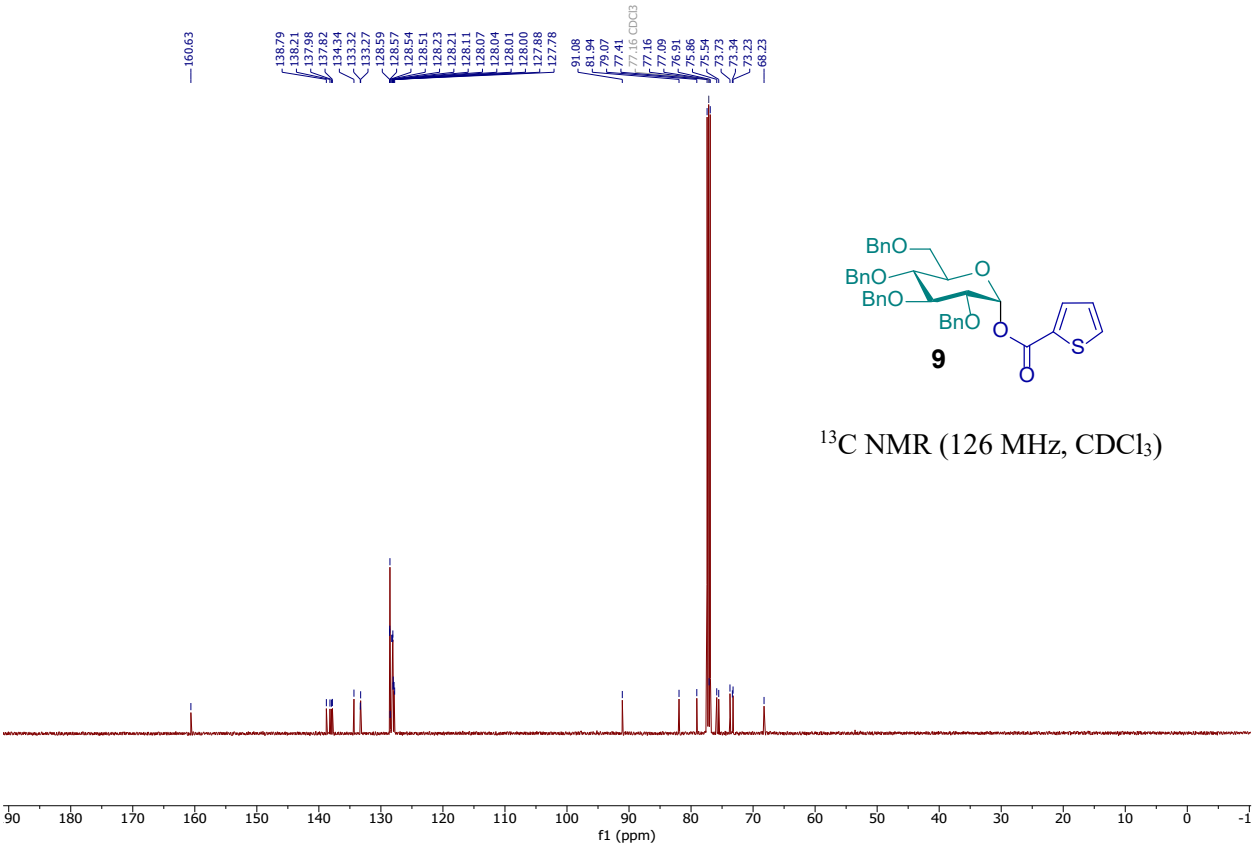
8

^{13}C NMR (126 MHz, $CDCl_3$)



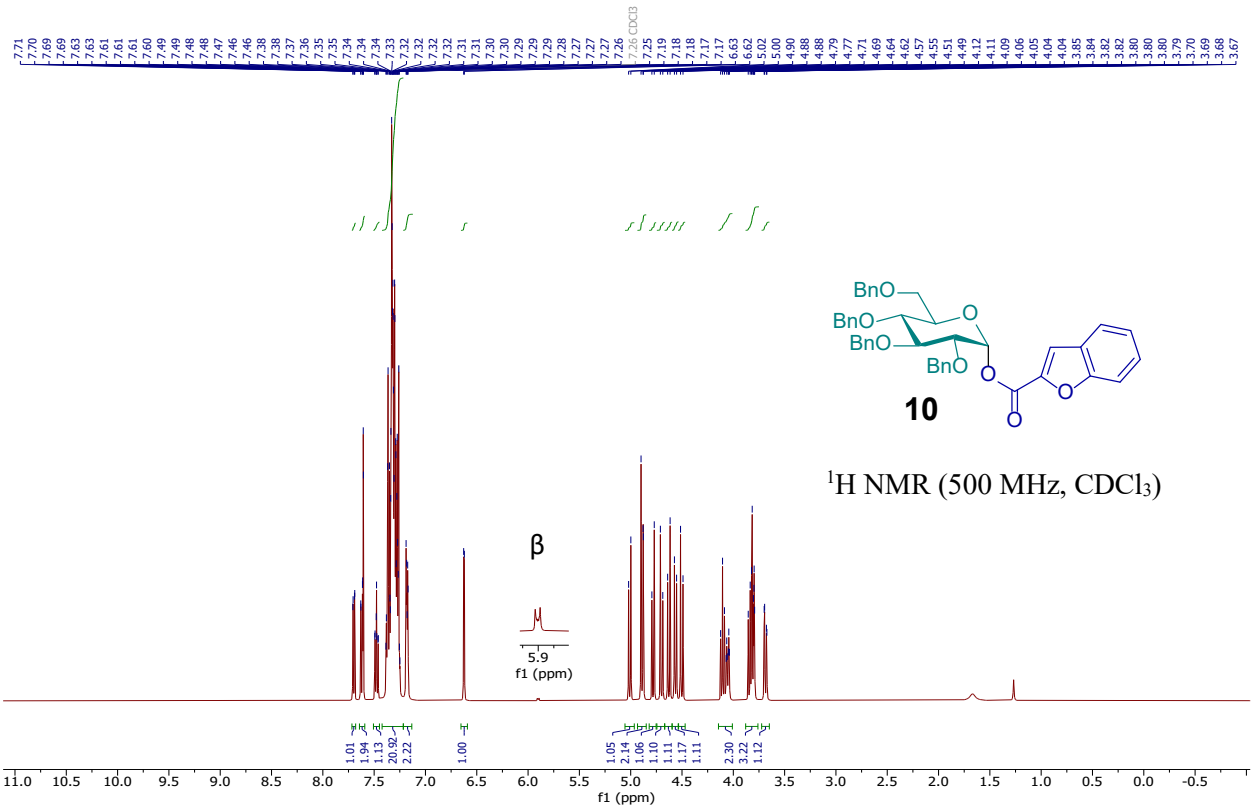
9

^{1}H NMR (500 MHz, $CDCl_3$)



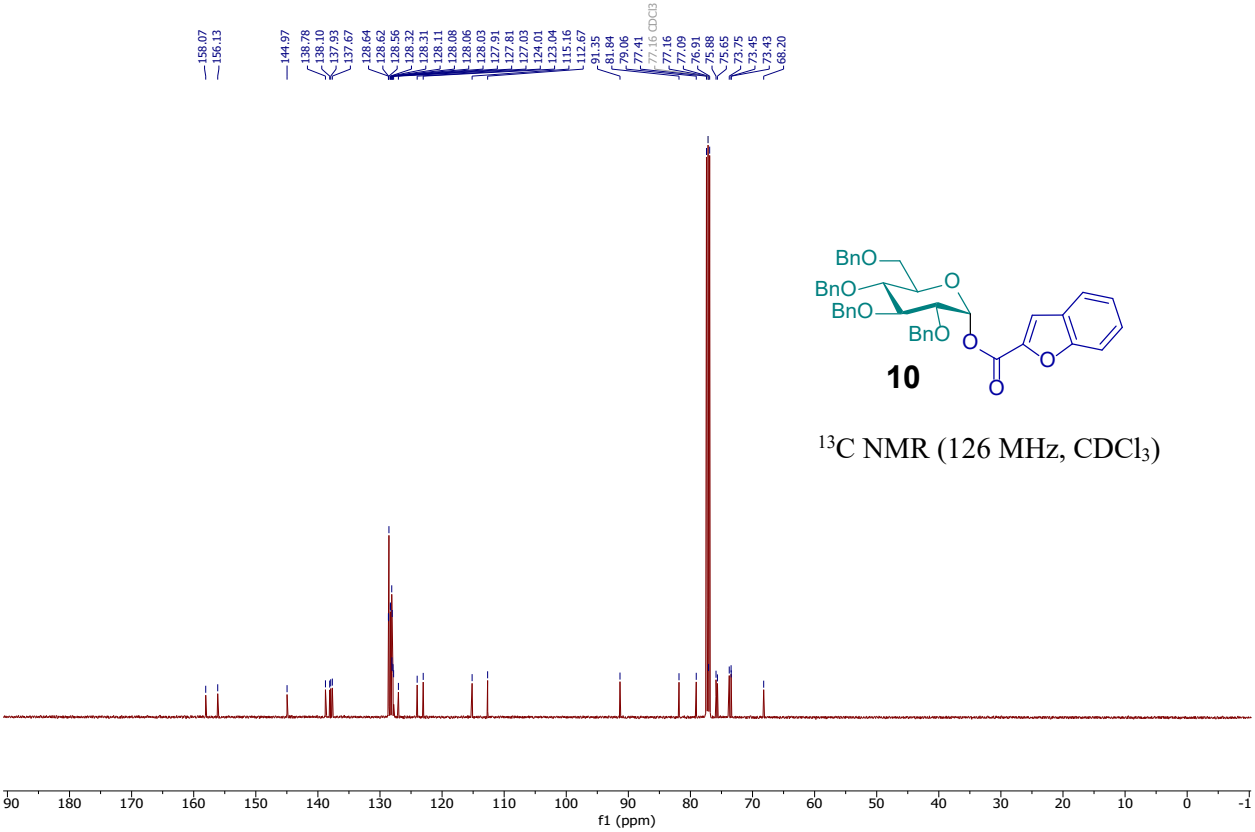
9

^{13}C NMR (126 MHz, $CDCl_3$)

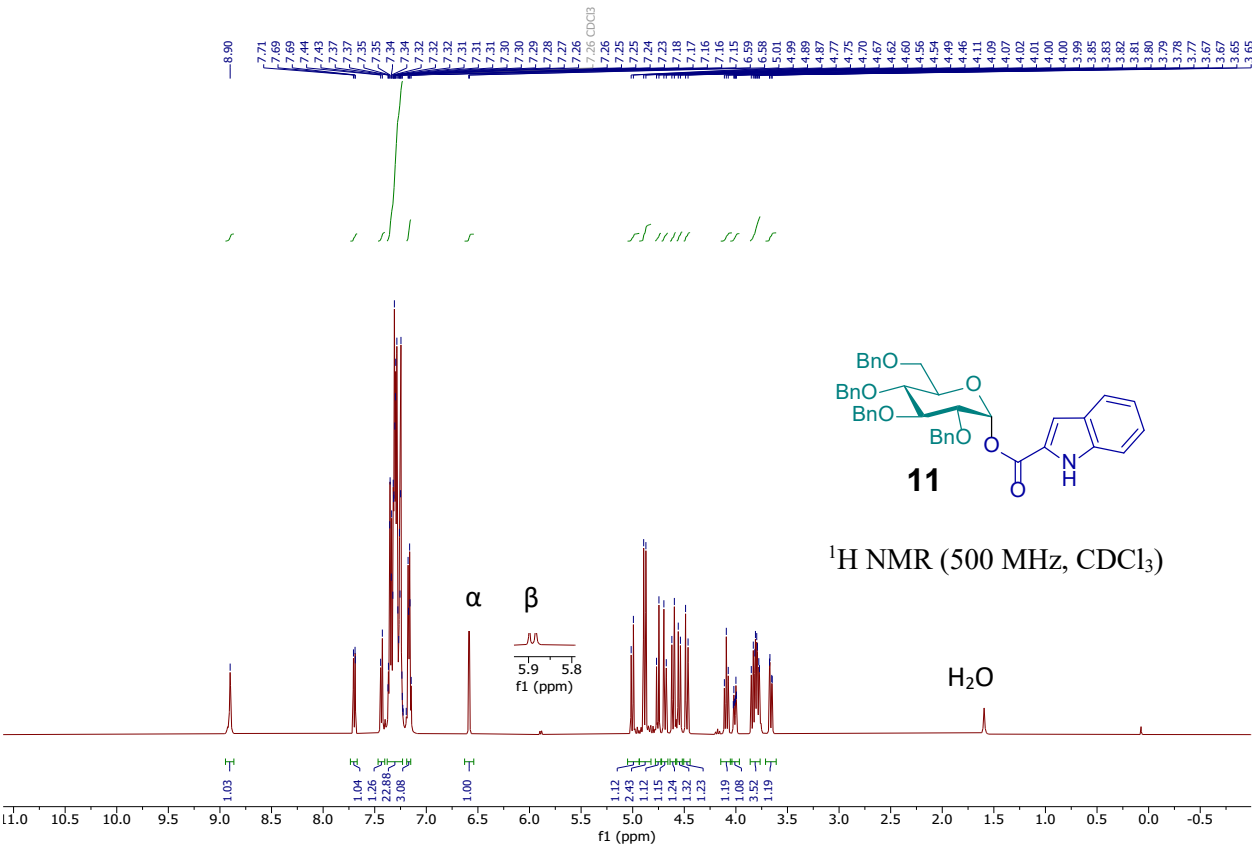


10

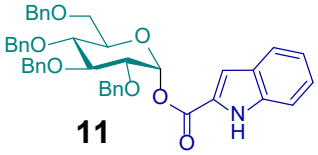
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

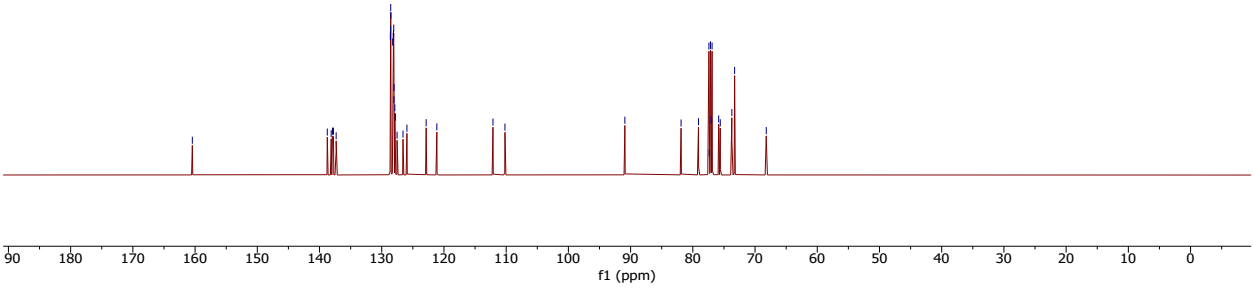


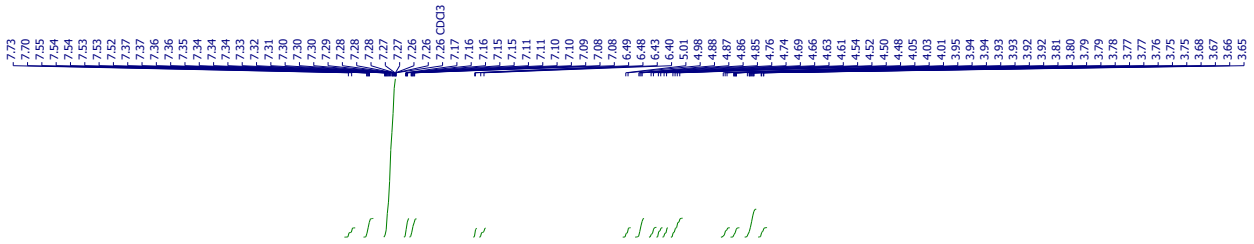
^{1}H NMR (500 MHz, $CDCl_3$)

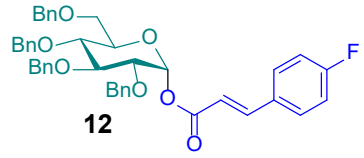


11

^{13}C NMR (126 MHz, $CDCl_3$)

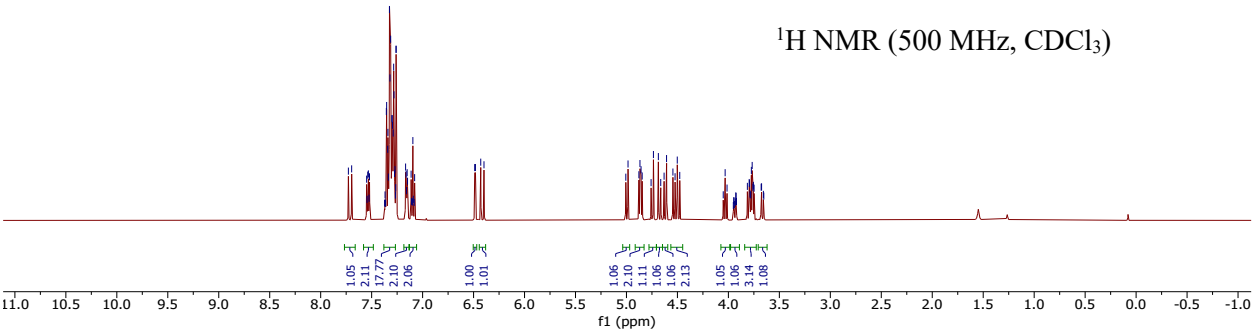


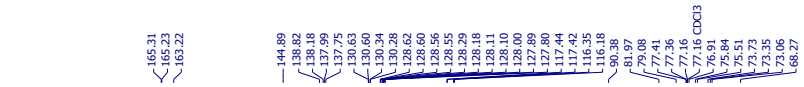


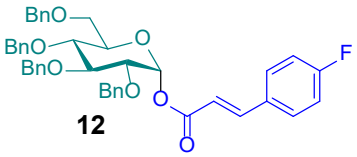


12

^{1}H NMR (500 MHz, $CDCl_3$)

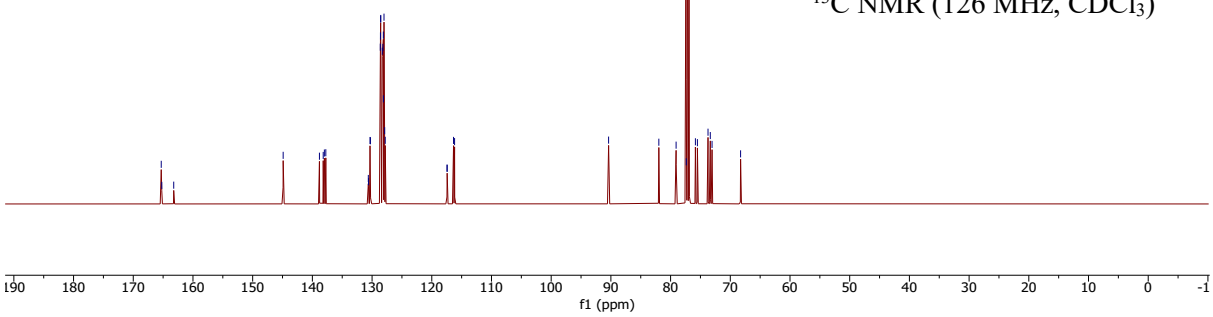


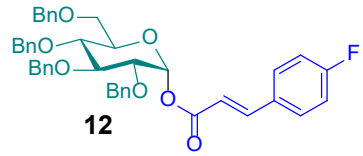




12

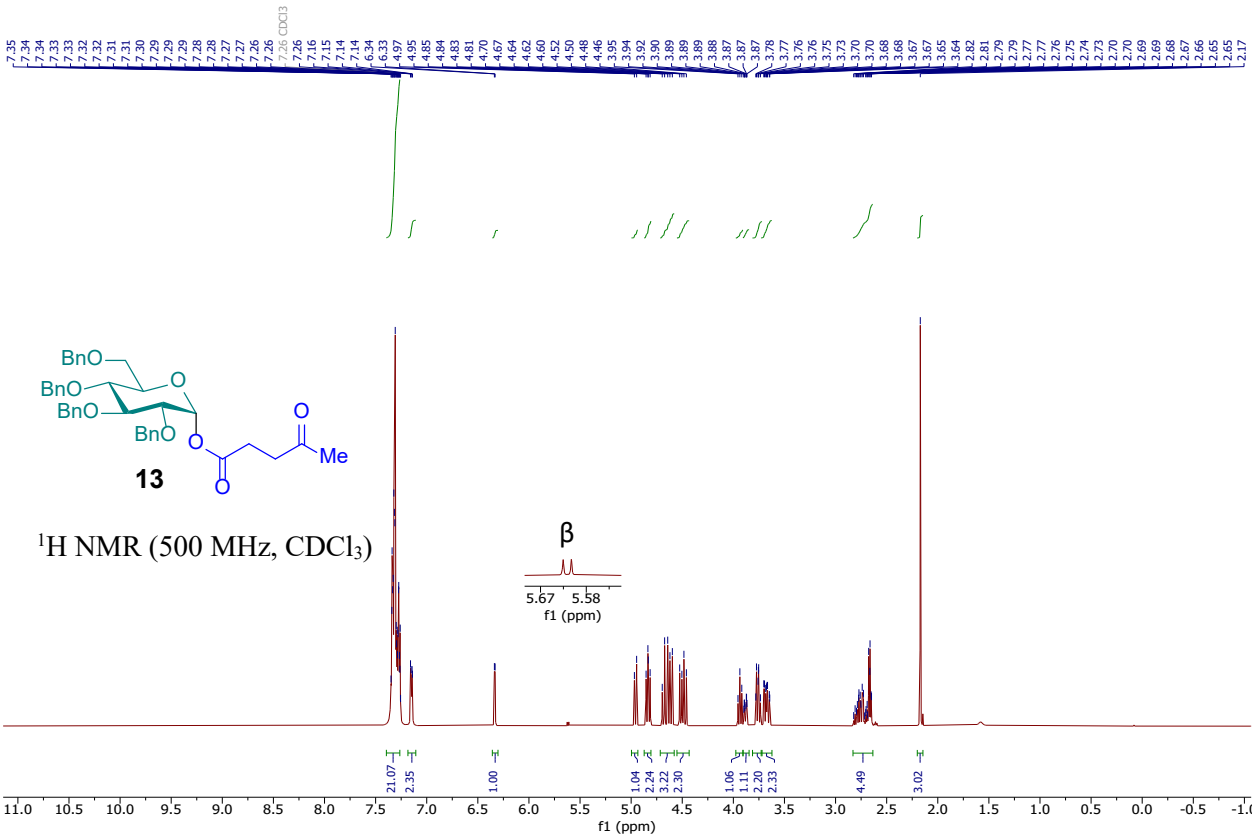
^{13}C NMR (126 MHz, $CDCl_3$)



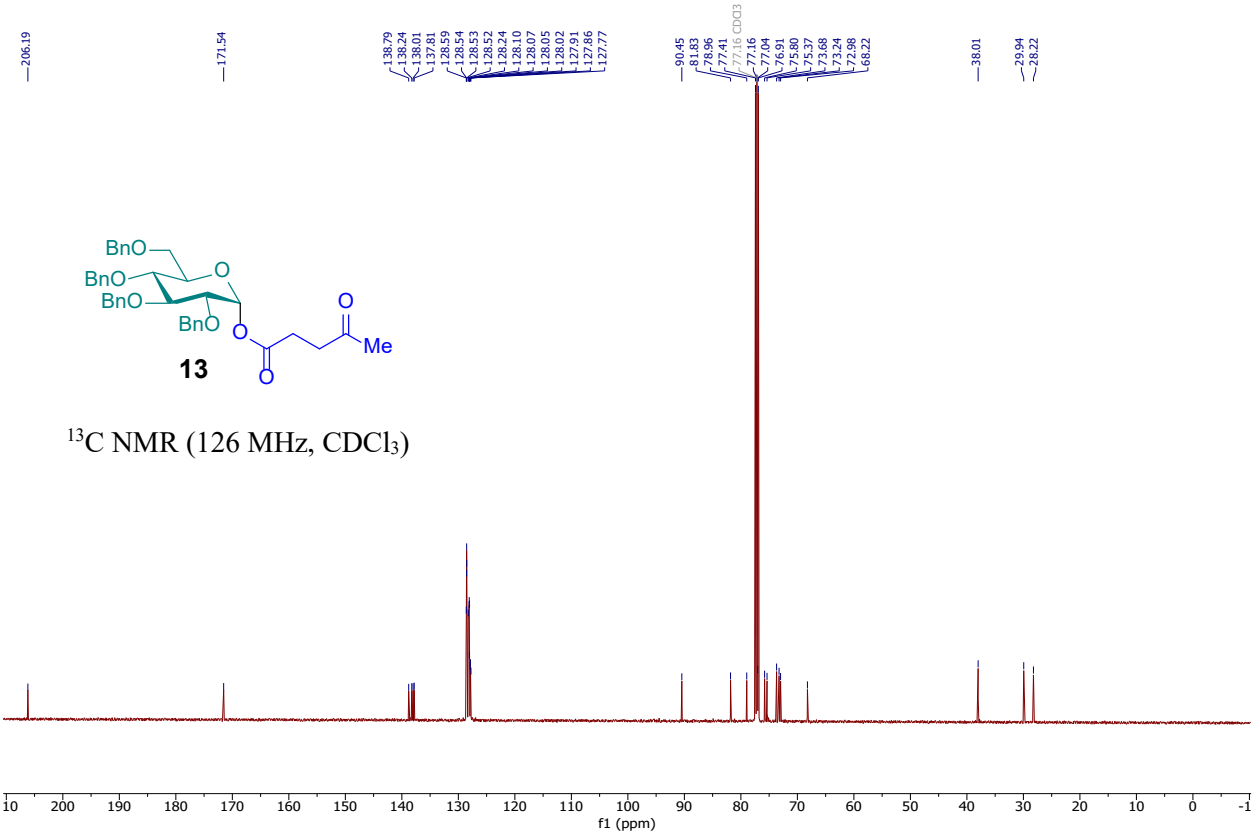


12

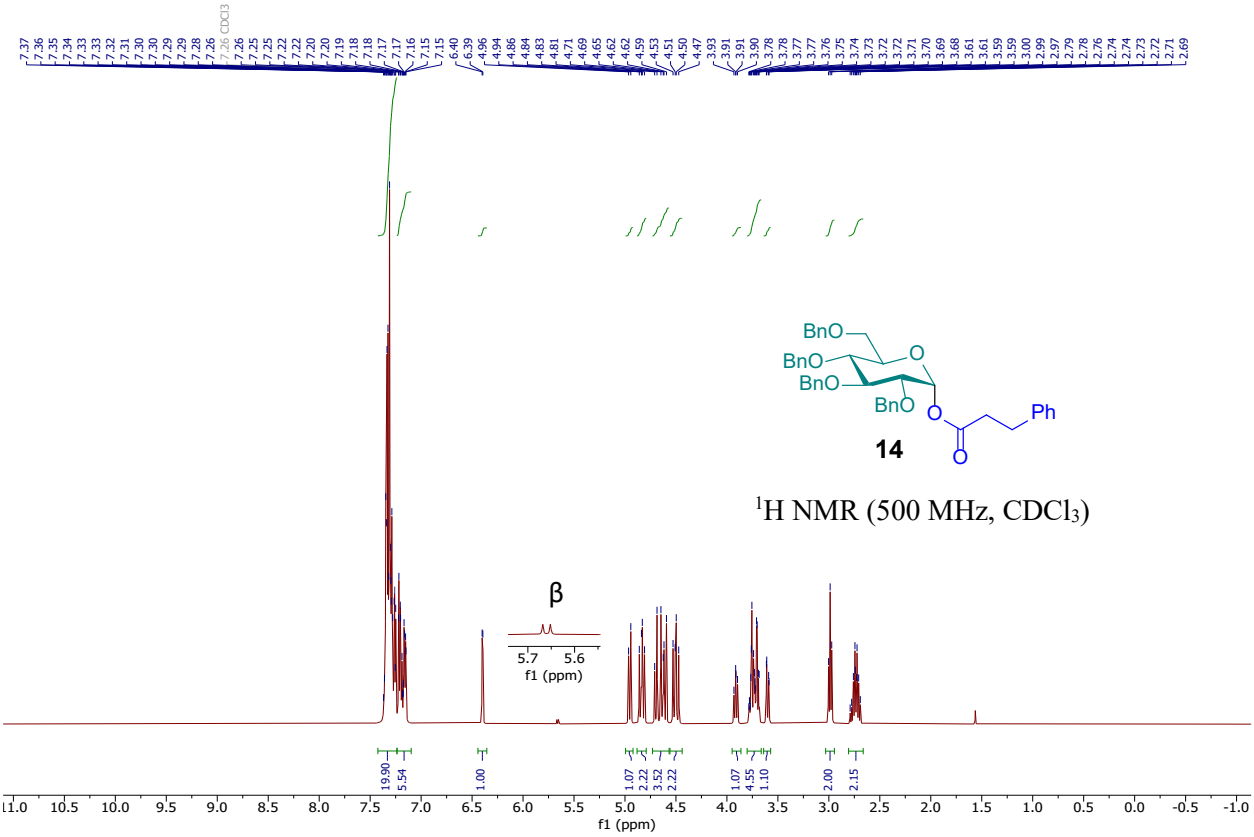
^{19}F NMR (471 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)

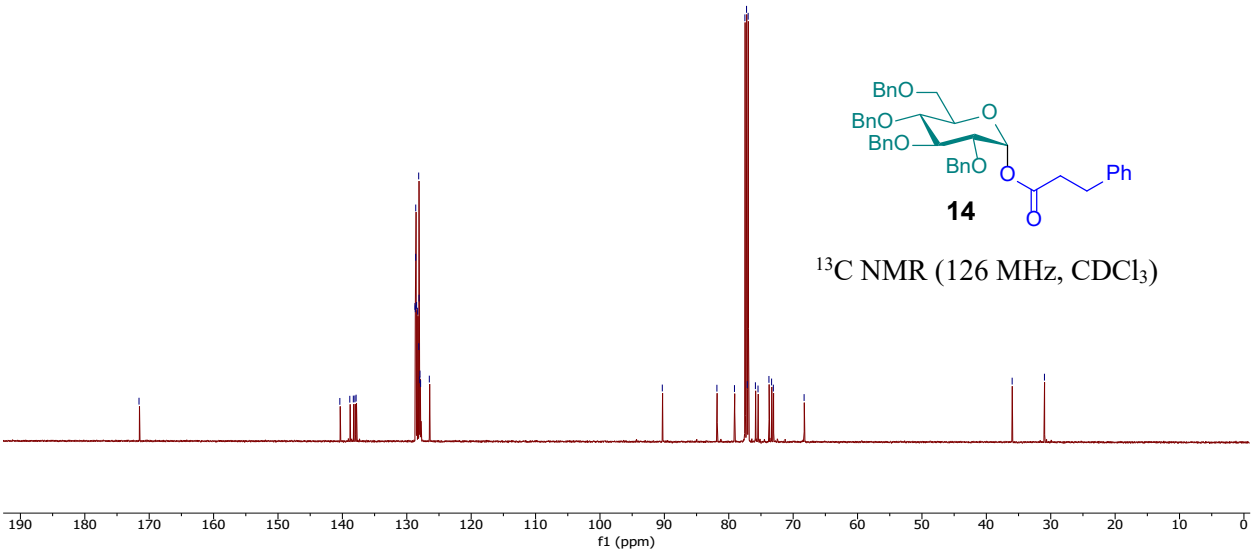


^{13}C NMR (126 MHz, $CDCl_3$)



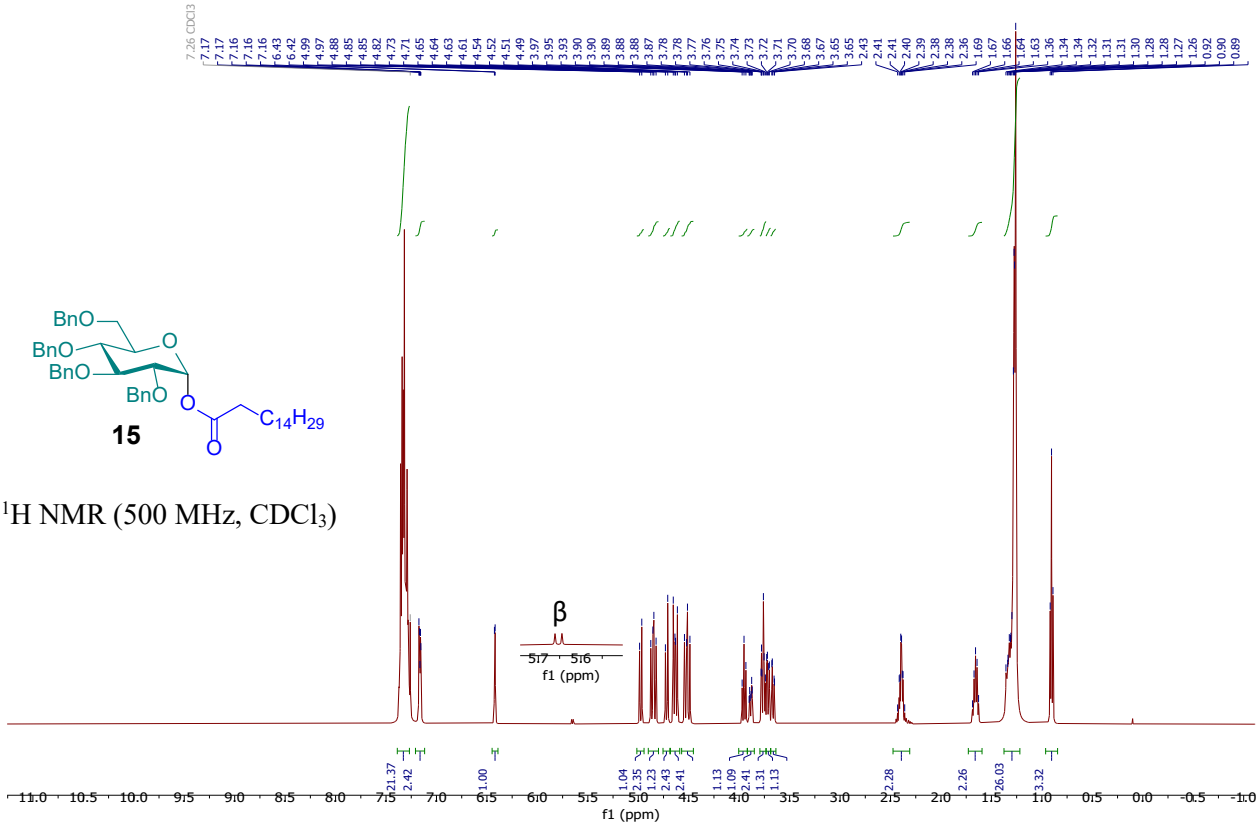
14

^{1}H NMR (500 MHz, $CDCl_3$)

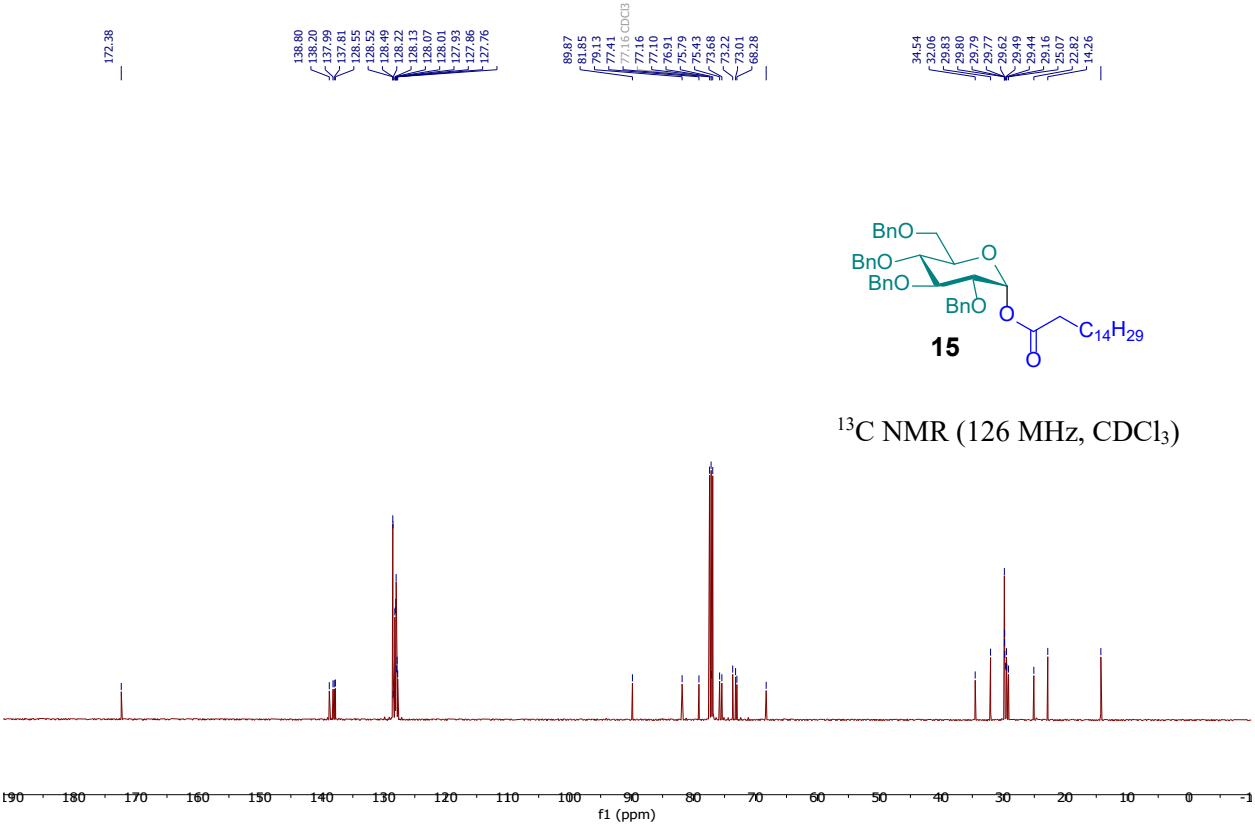


14

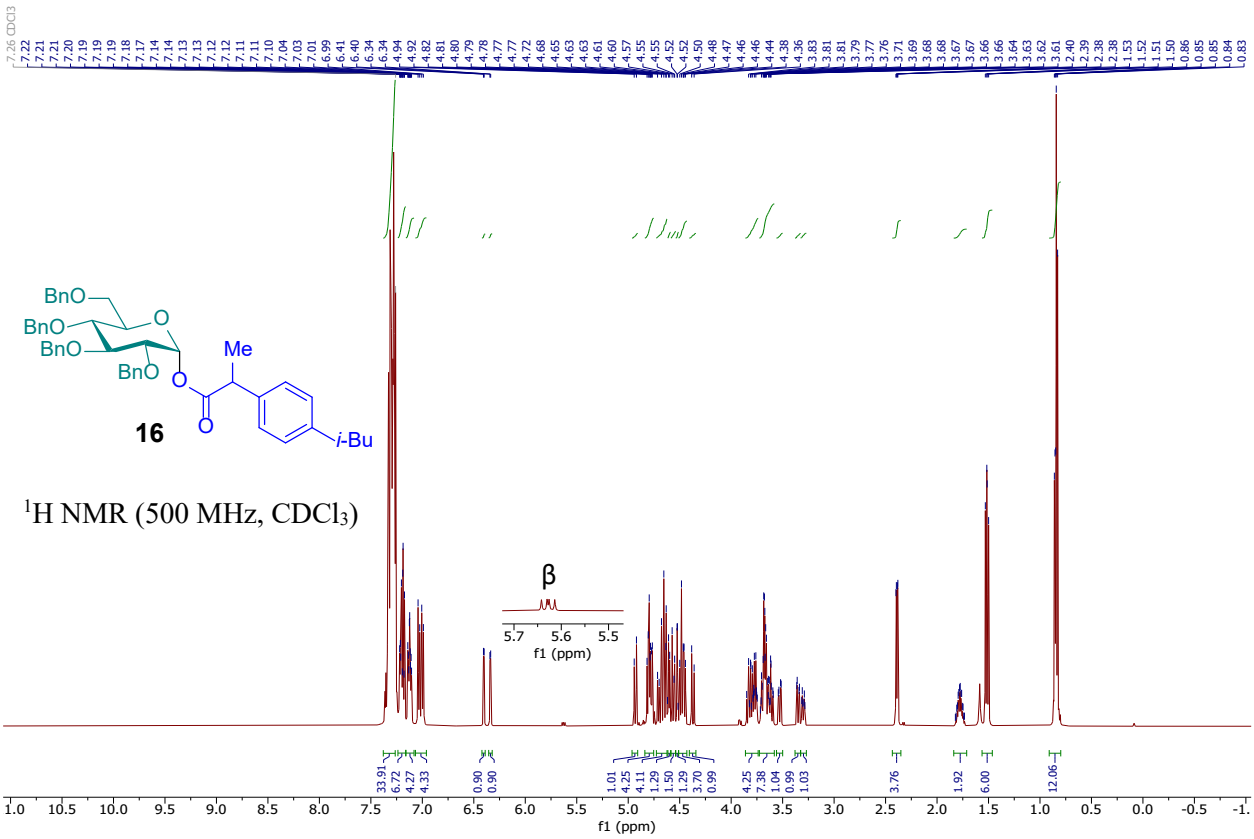
^{13}C NMR (126 MHz, $CDCl_3$)



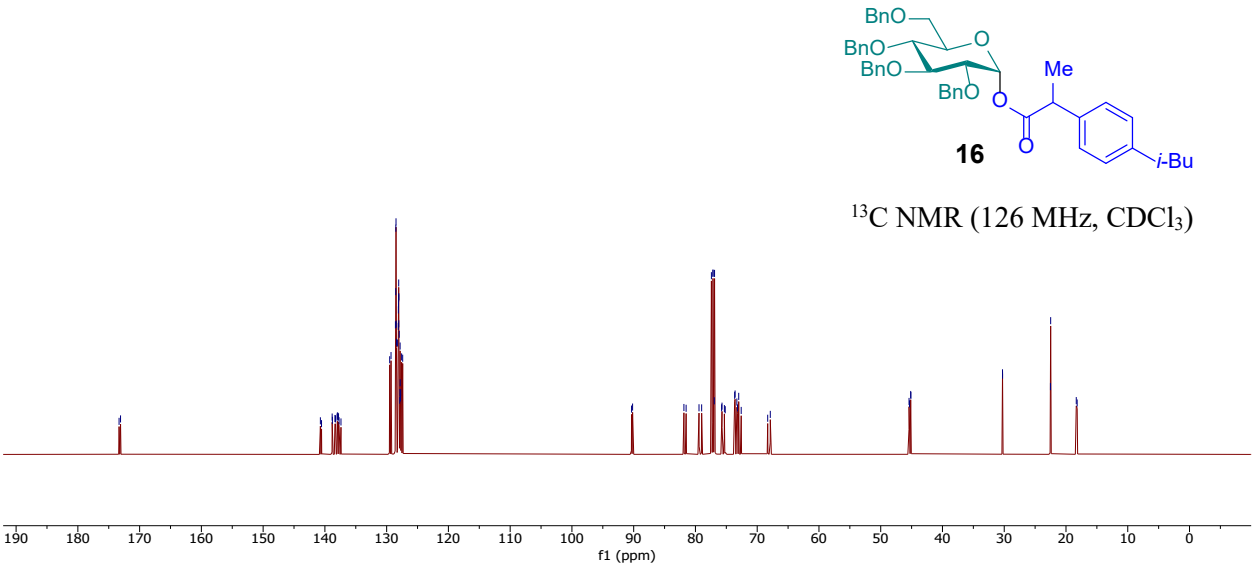
^{1}H NMR (500 MHz, $CDCl_3$)



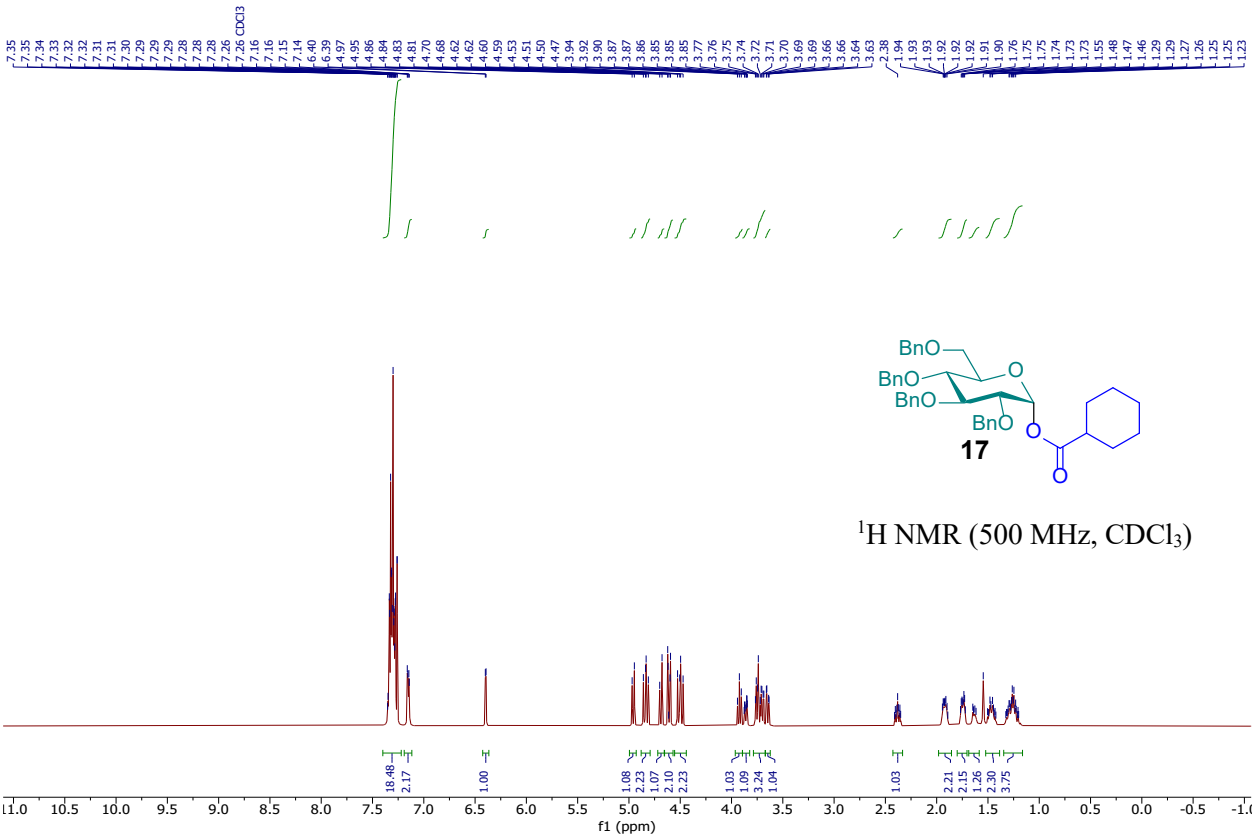
^{13}C NMR (126 MHz, $CDCl_3$)



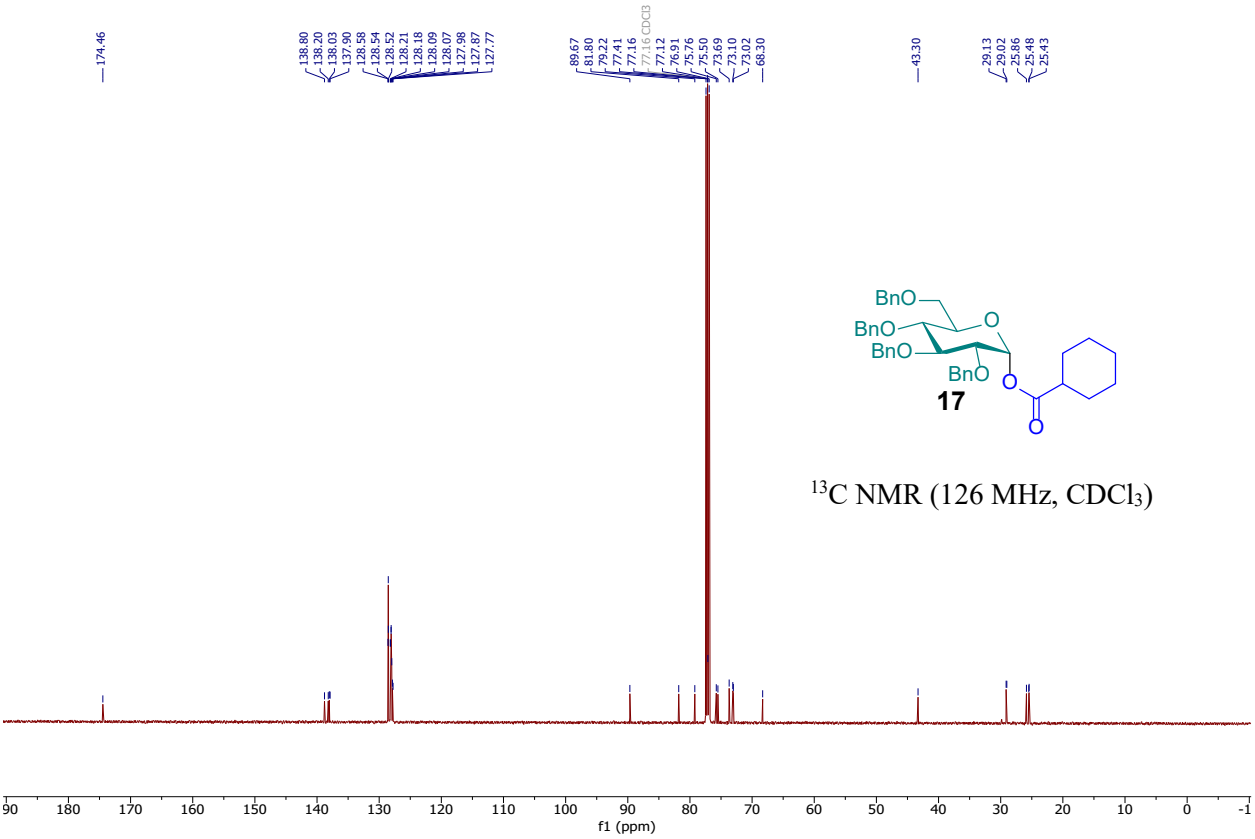
^{1}H NMR (500 MHz, $CDCl_3$)



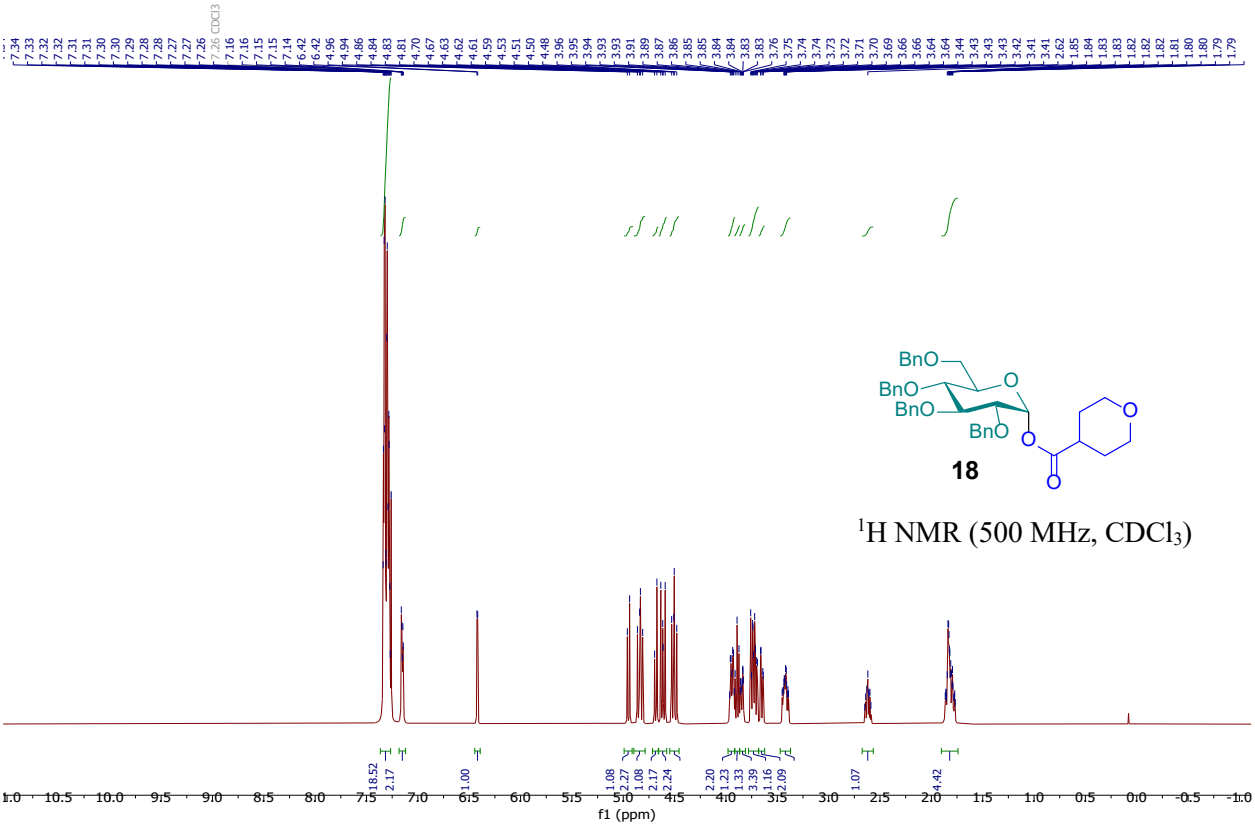
^{13}C NMR (126 MHz, $CDCl_3$)



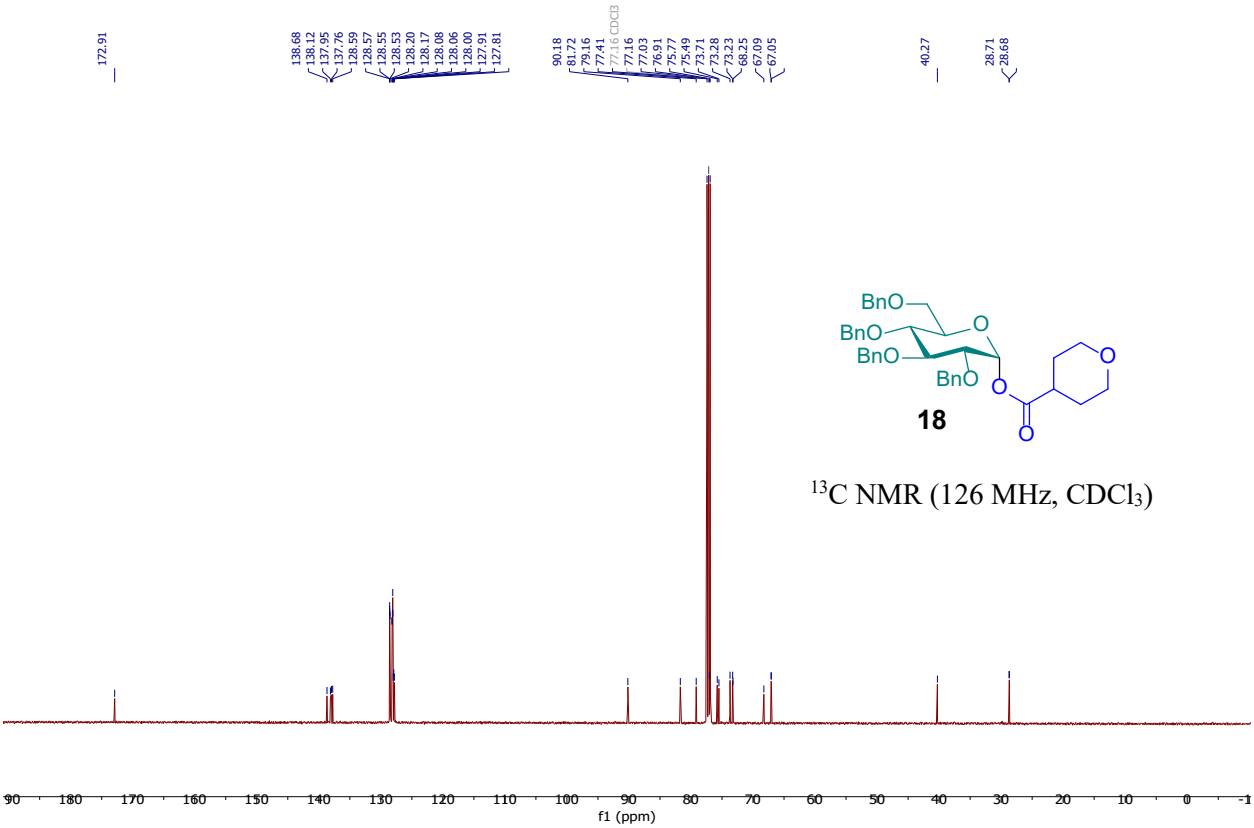
^{1}H NMR (500 MHz, $CDCl_3$)



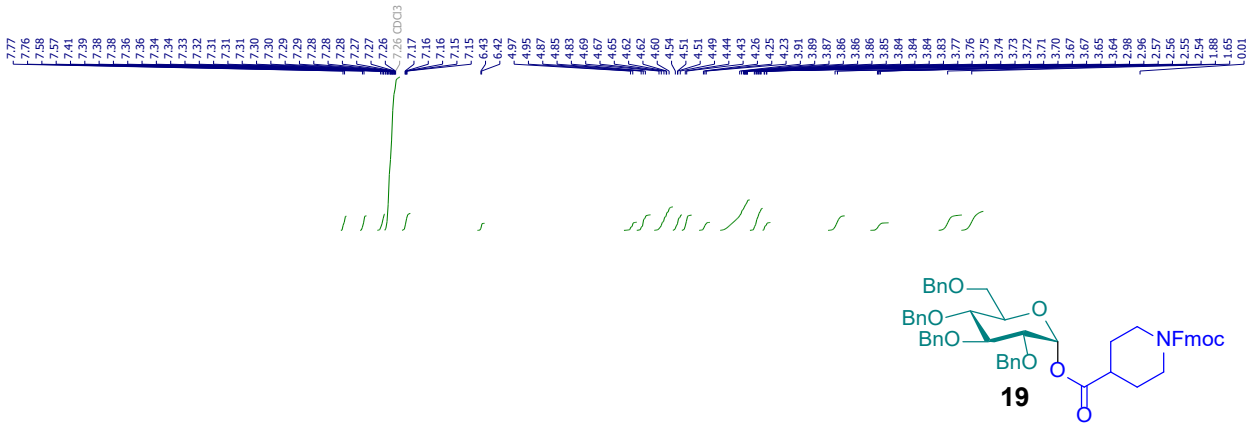
^{13}C NMR (126 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)

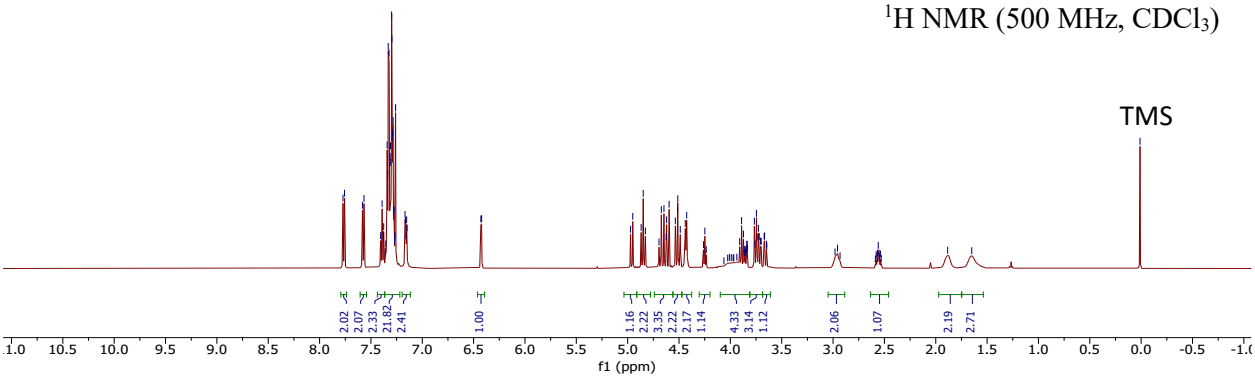


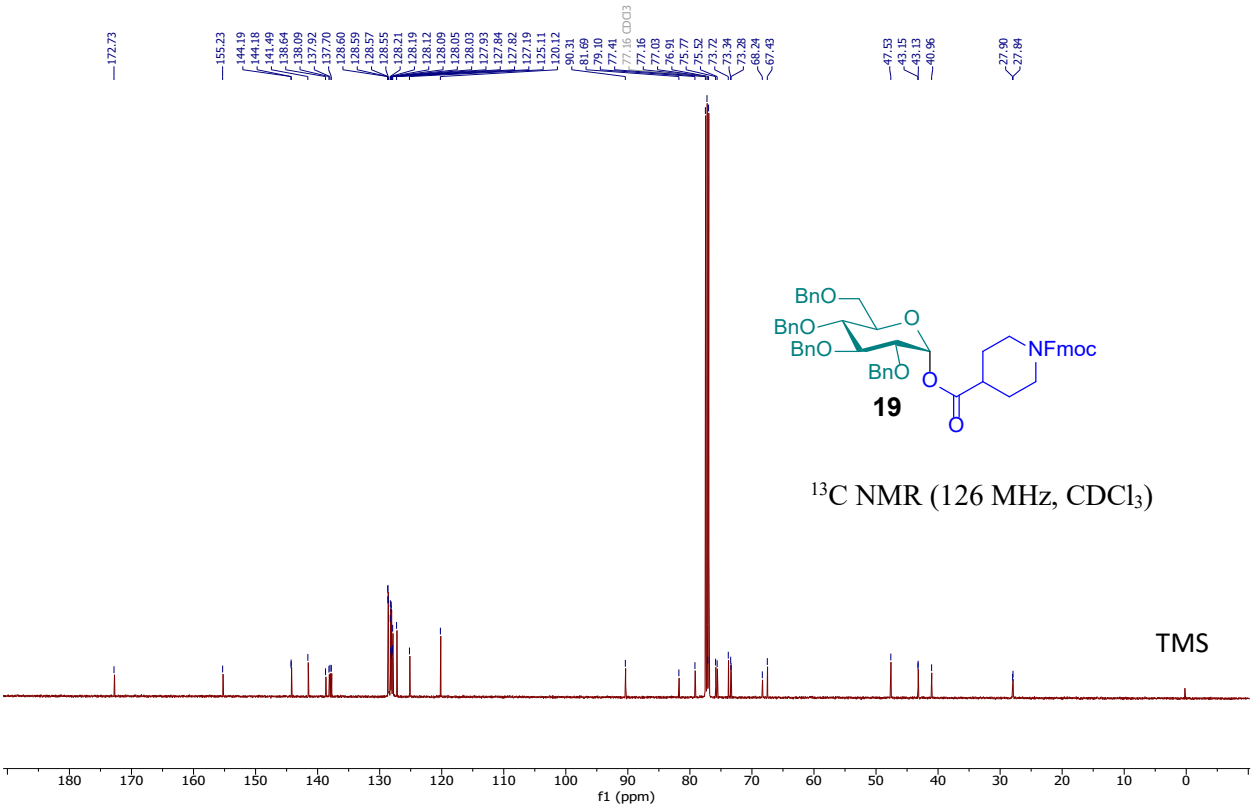
^{13}C NMR (126 MHz, $CDCl_3$)



19

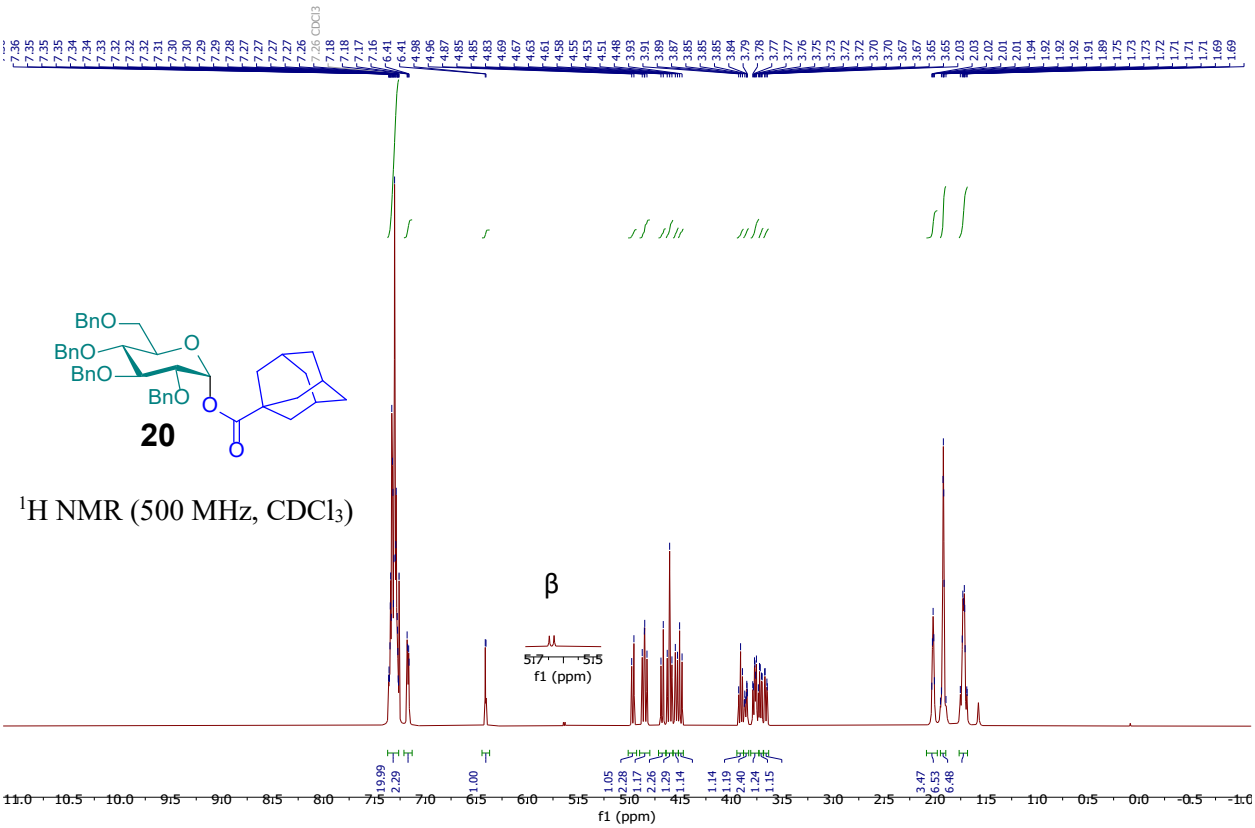
^{1}H NMR (500 MHz, $CDCl_3$)





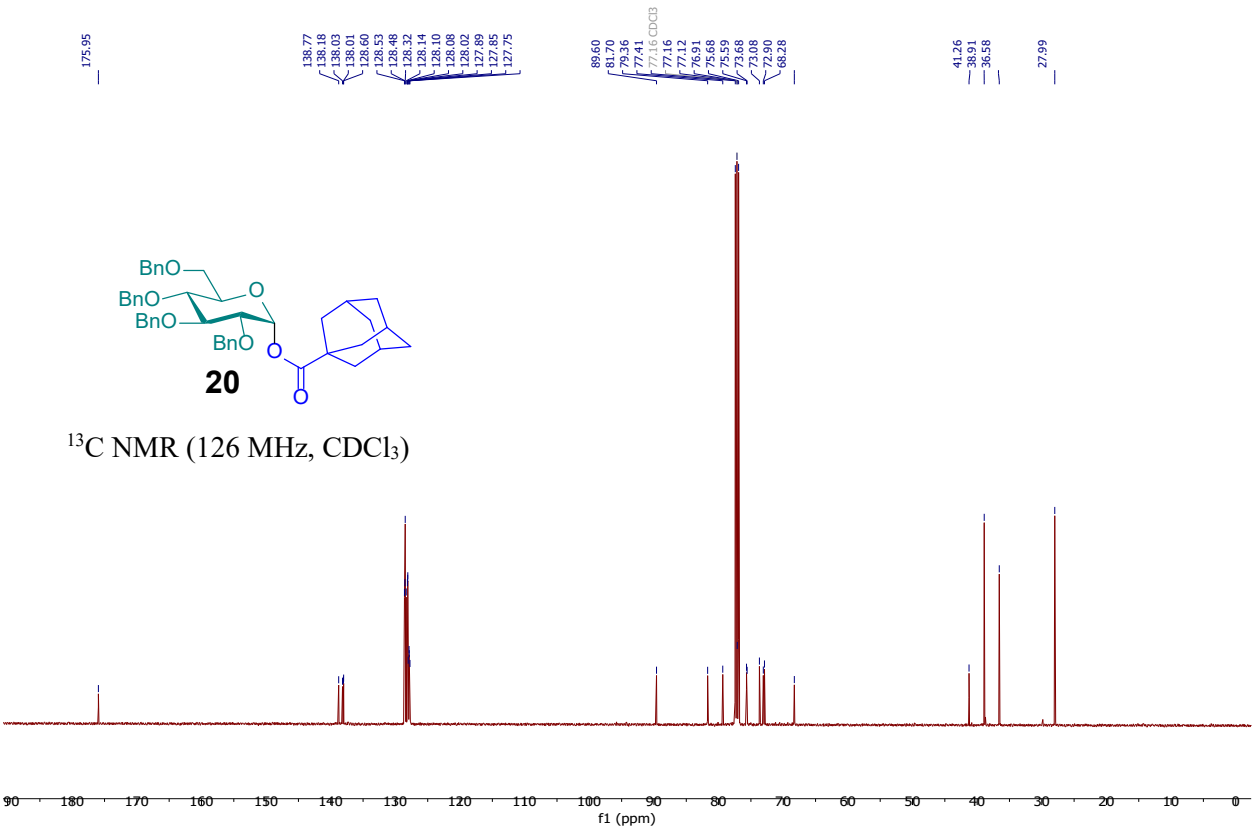
19

^{13}C NMR (126 MHz, $CDCl_3$)



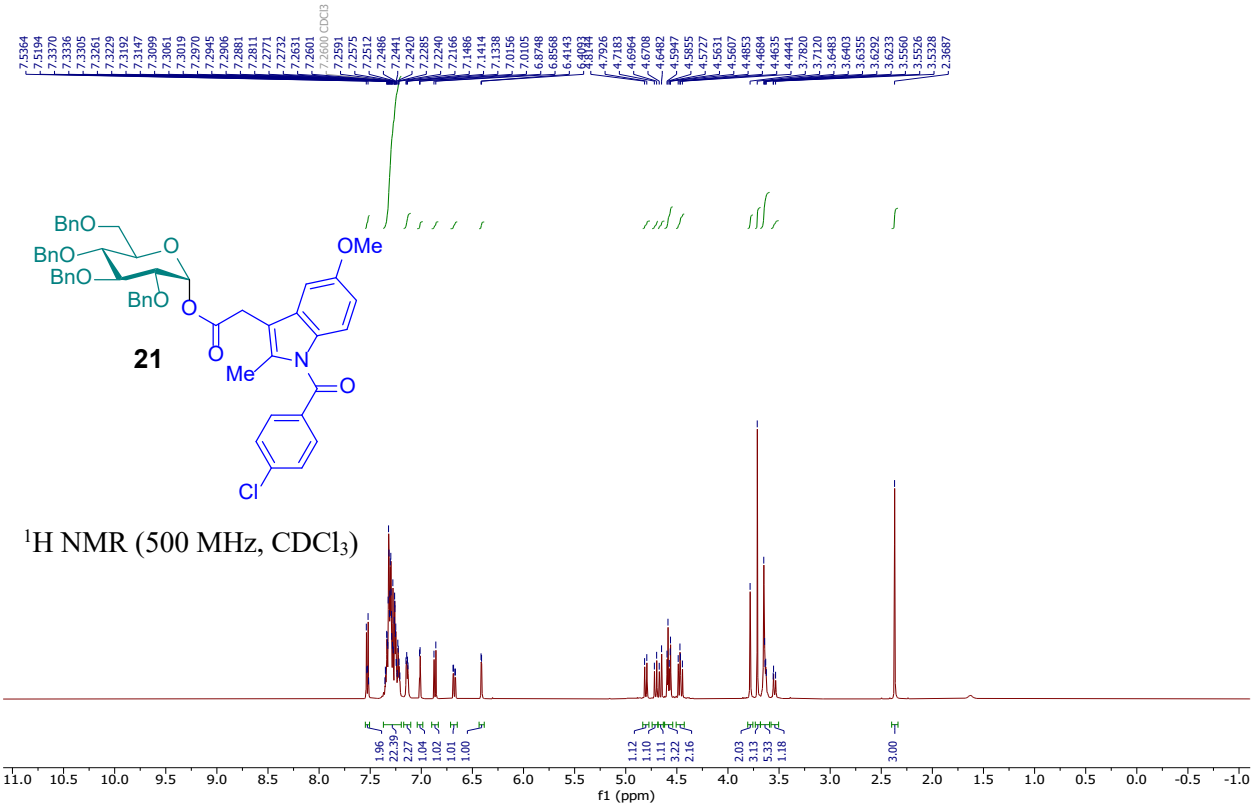
20

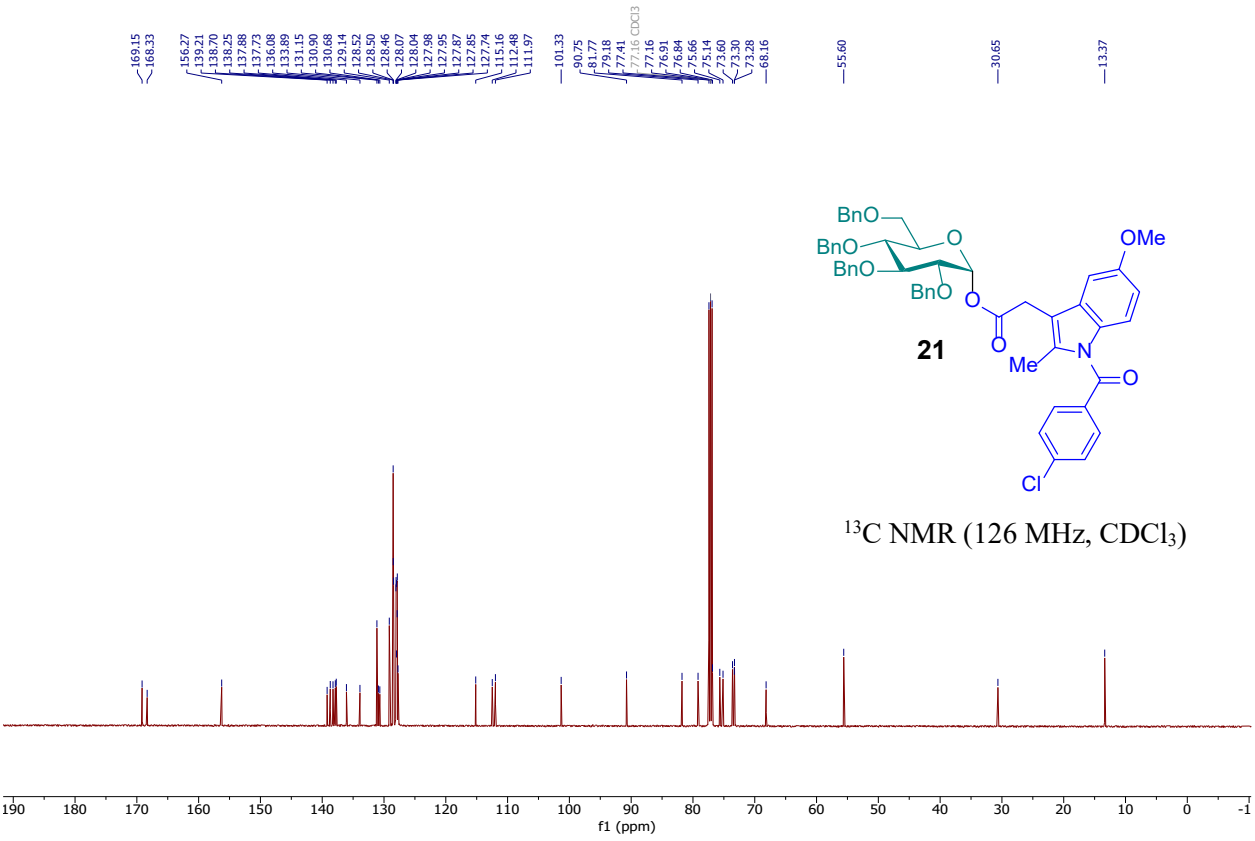
^{1}H NMR (500 MHz, $CDCl_3$)

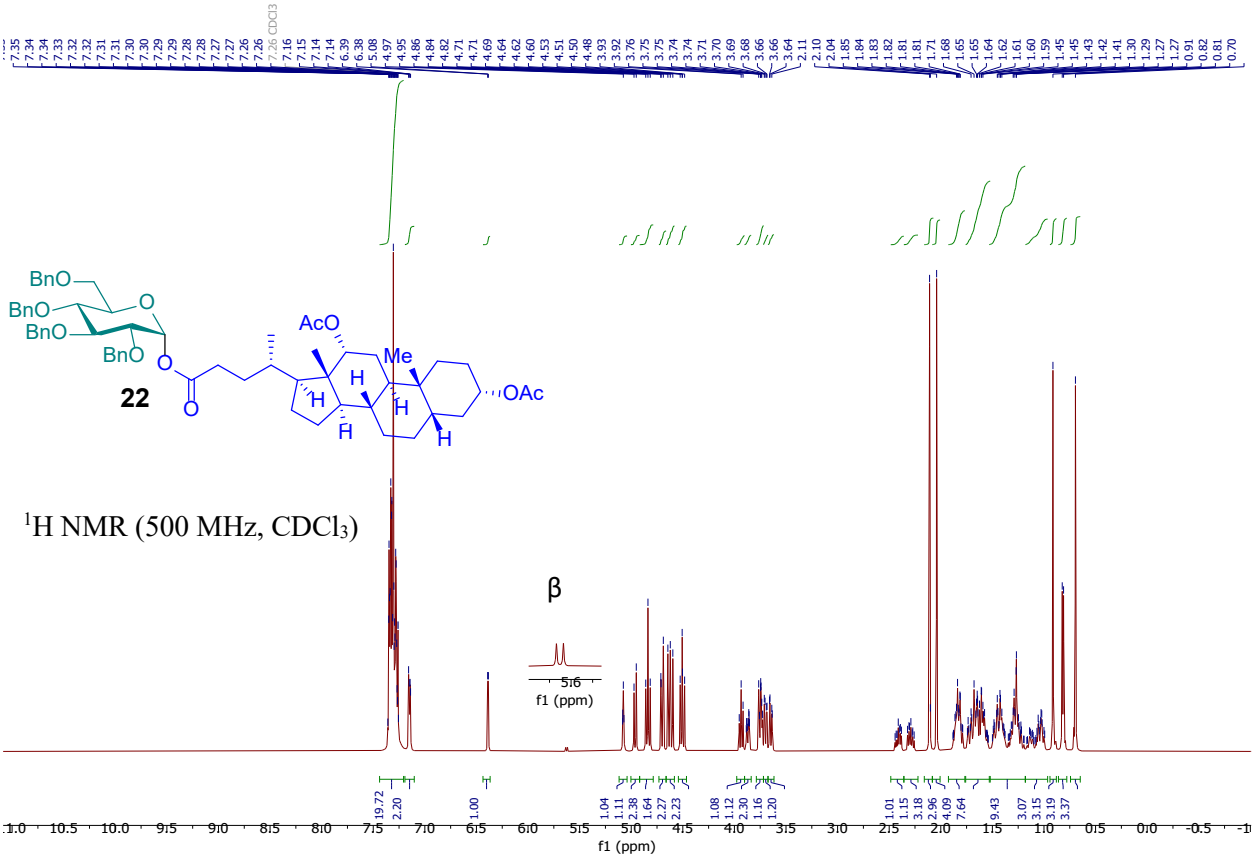


20

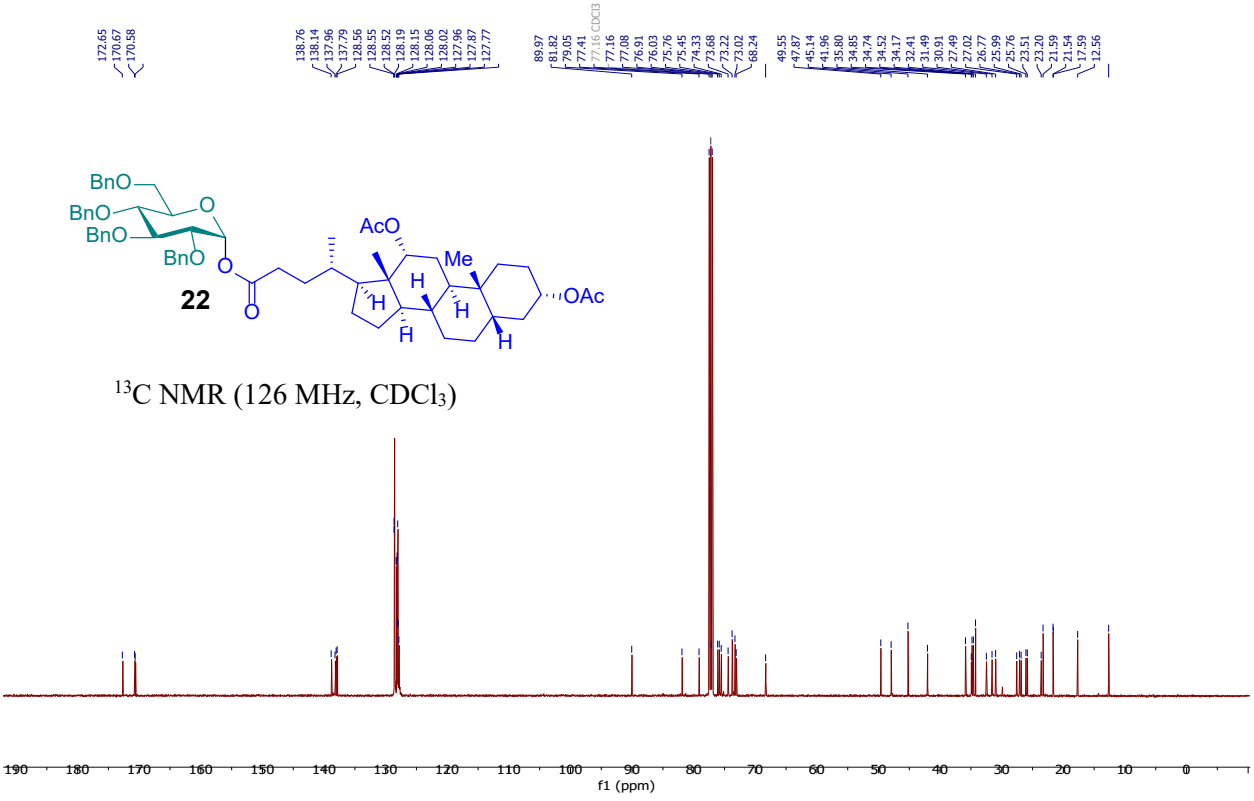
^{13}C NMR (126 MHz, $CDCl_3$)


BnO
BnO
BnO
BnO
O
O
OMe
O
N
Me
O
Cl
21
^{1}H NMR (500 MHz, $CDCl_3$)
f1 (ppm)

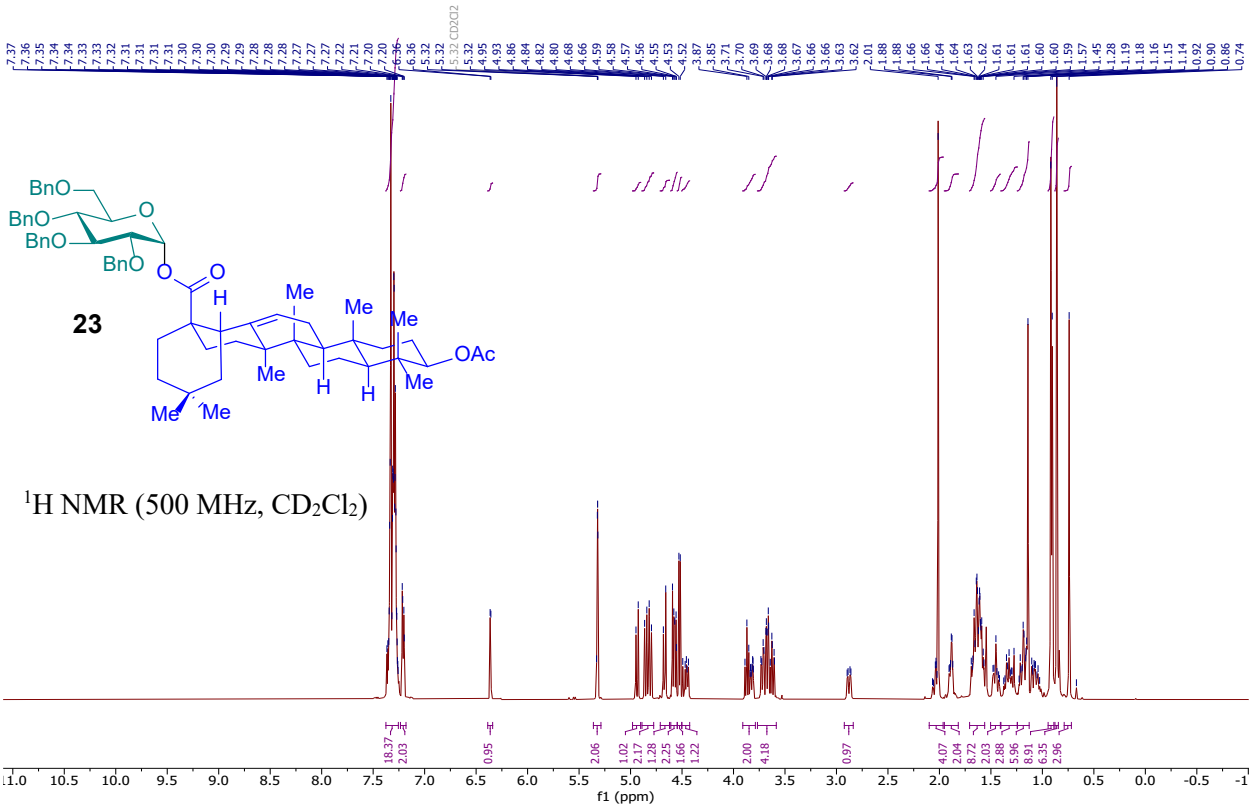

BnO
BnO
BnO
BnO
O
O
OMe
O
N
Me
O
Cl
21
^{13}C NMR (126 MHz, $CDCl_3$)
f1 (ppm)



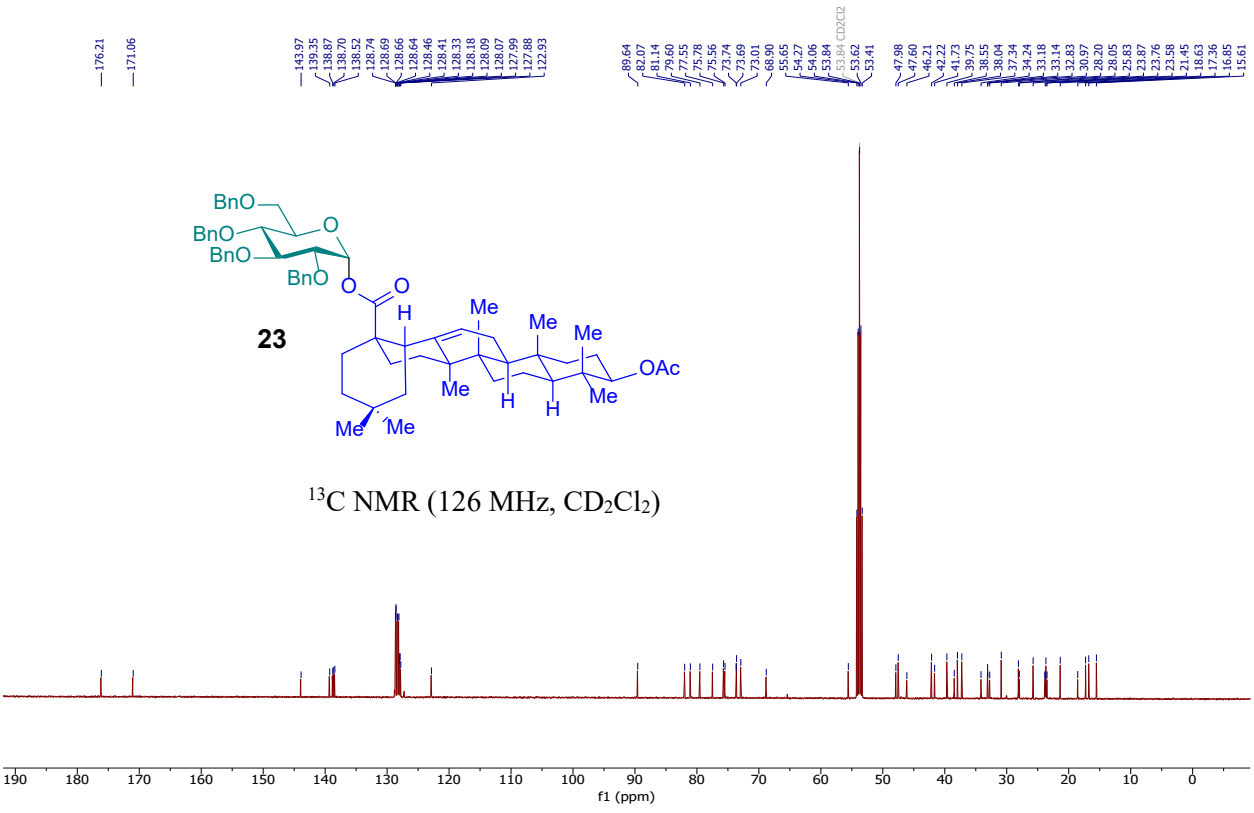
^{1}H NMR (500 MHz, $CDCl_3$)



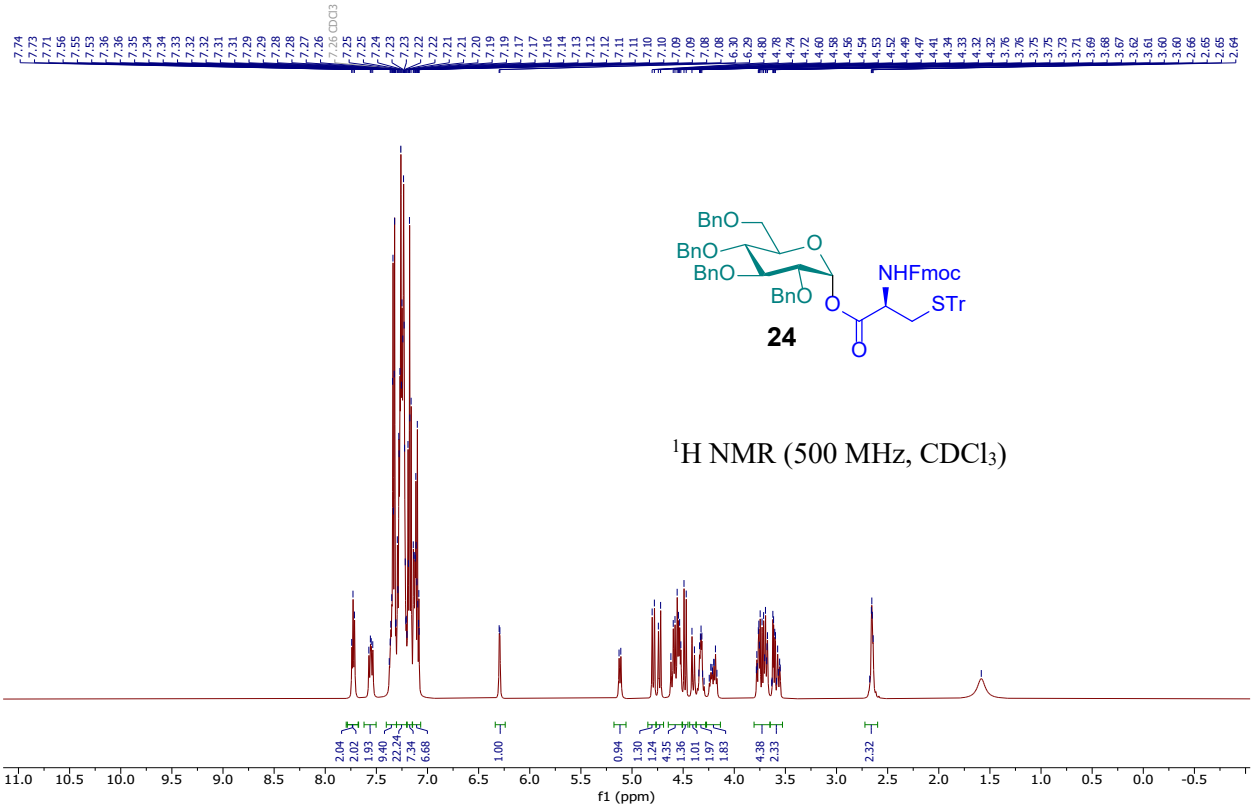
^{13}C NMR (126 MHz, $CDCl_3$)



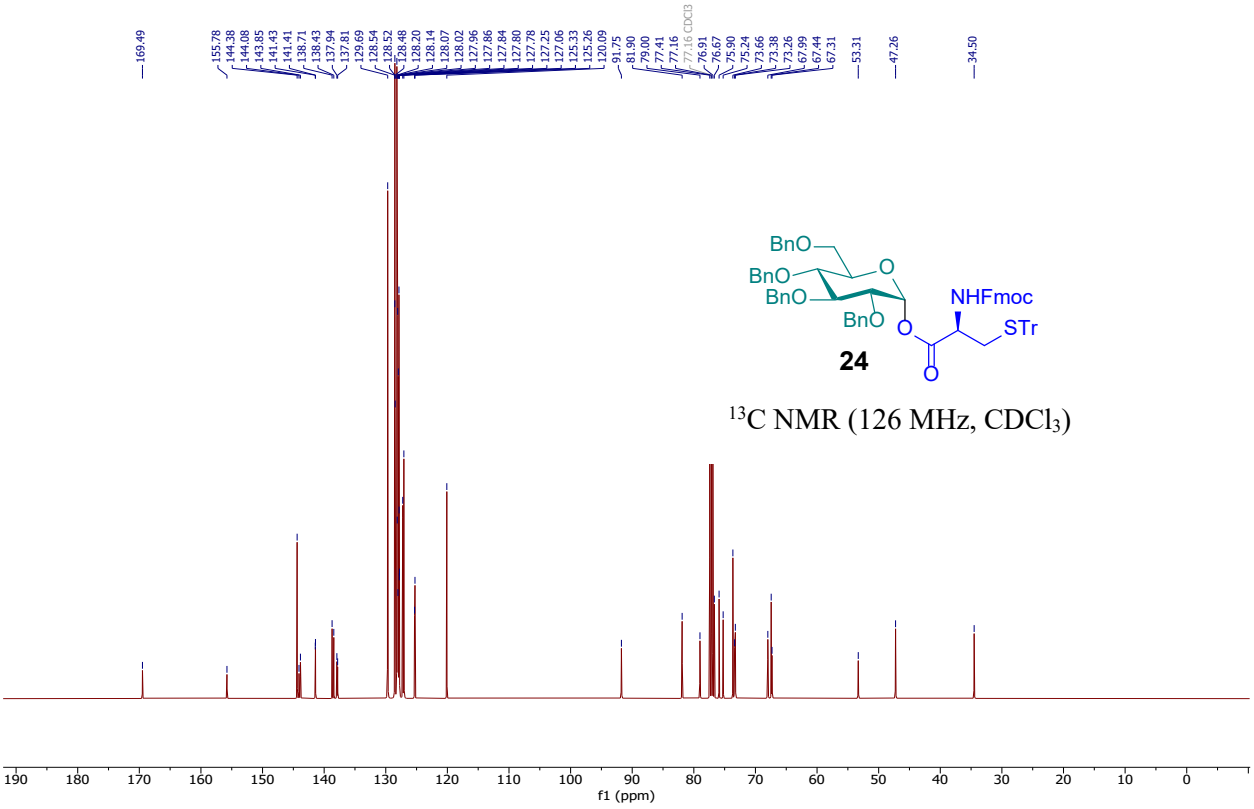
^{1}H NMR (500 MHz, CD_2Cl_2)



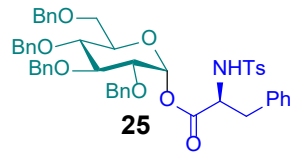
^{13}C NMR (126 MHz, CD_2Cl_2)



^{1}H NMR (500 MHz, $CDCl_3$)

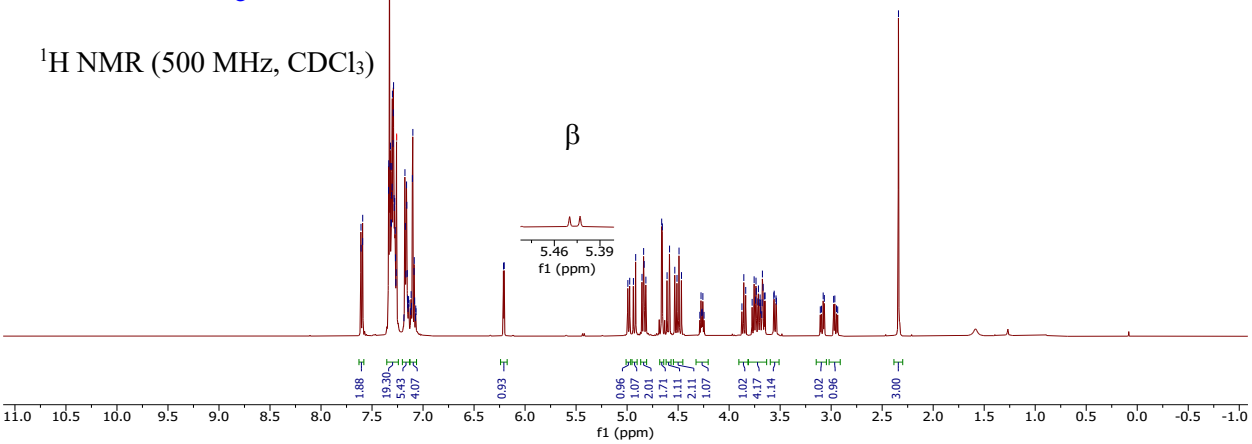


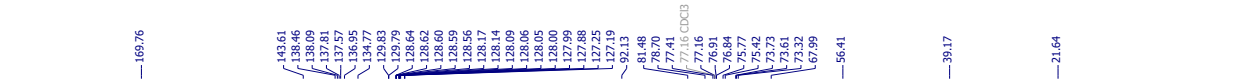
^{13}C NMR (126 MHz, $CDCl_3$)

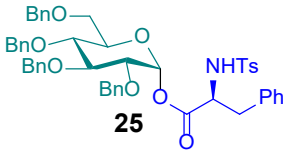


25

^{1}H NMR (500 MHz, $CDCl_3$)

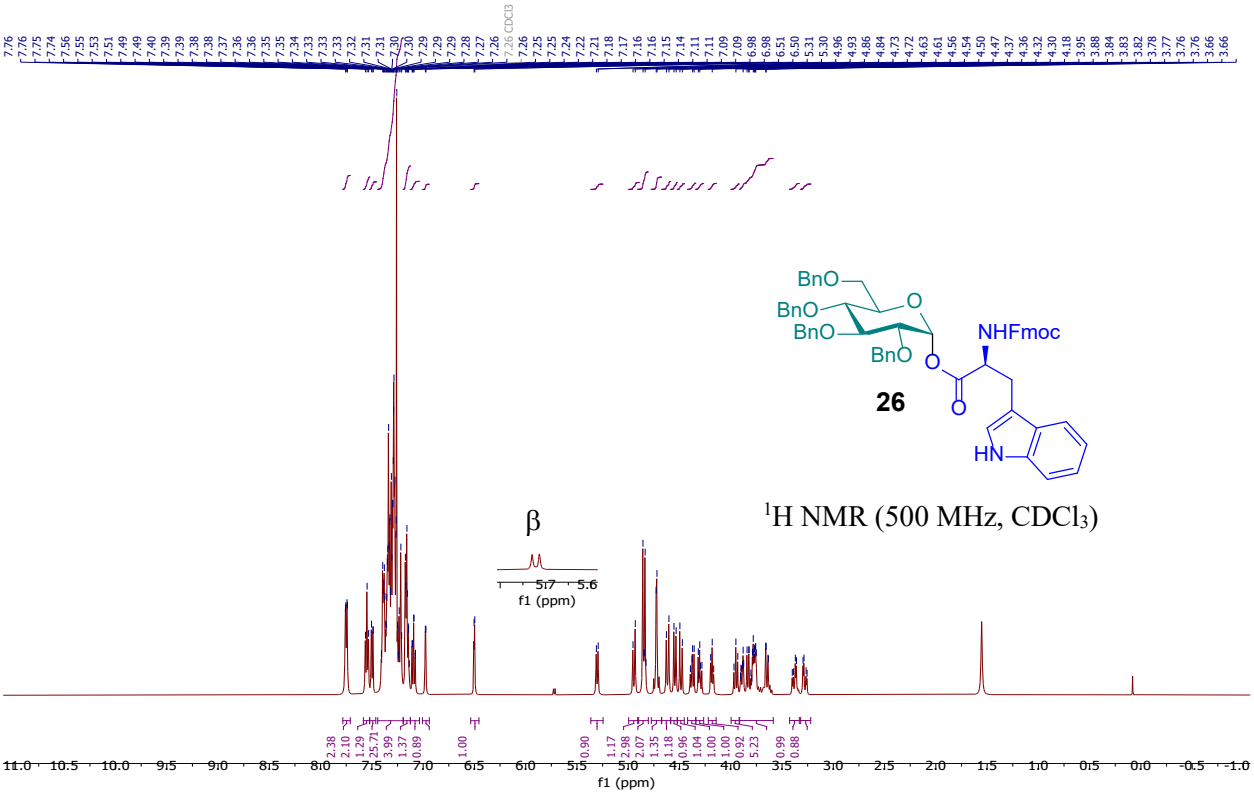




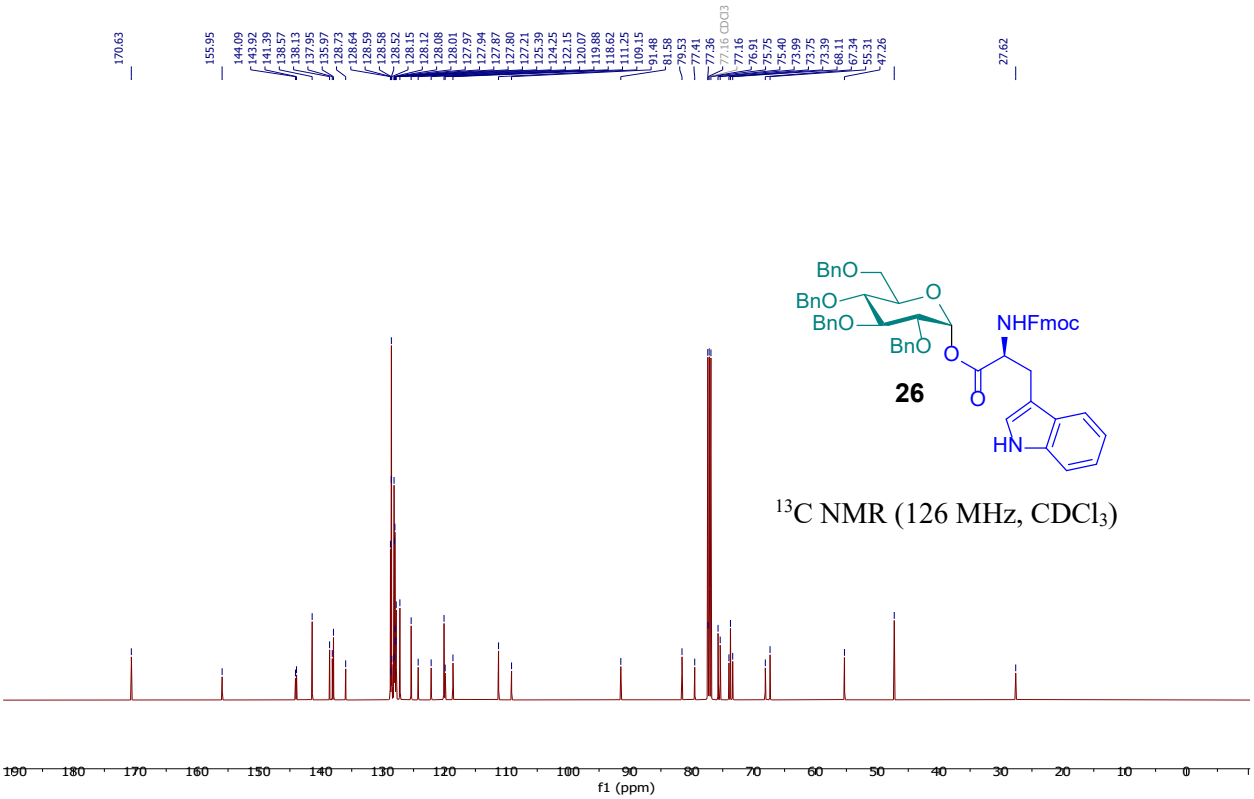


25

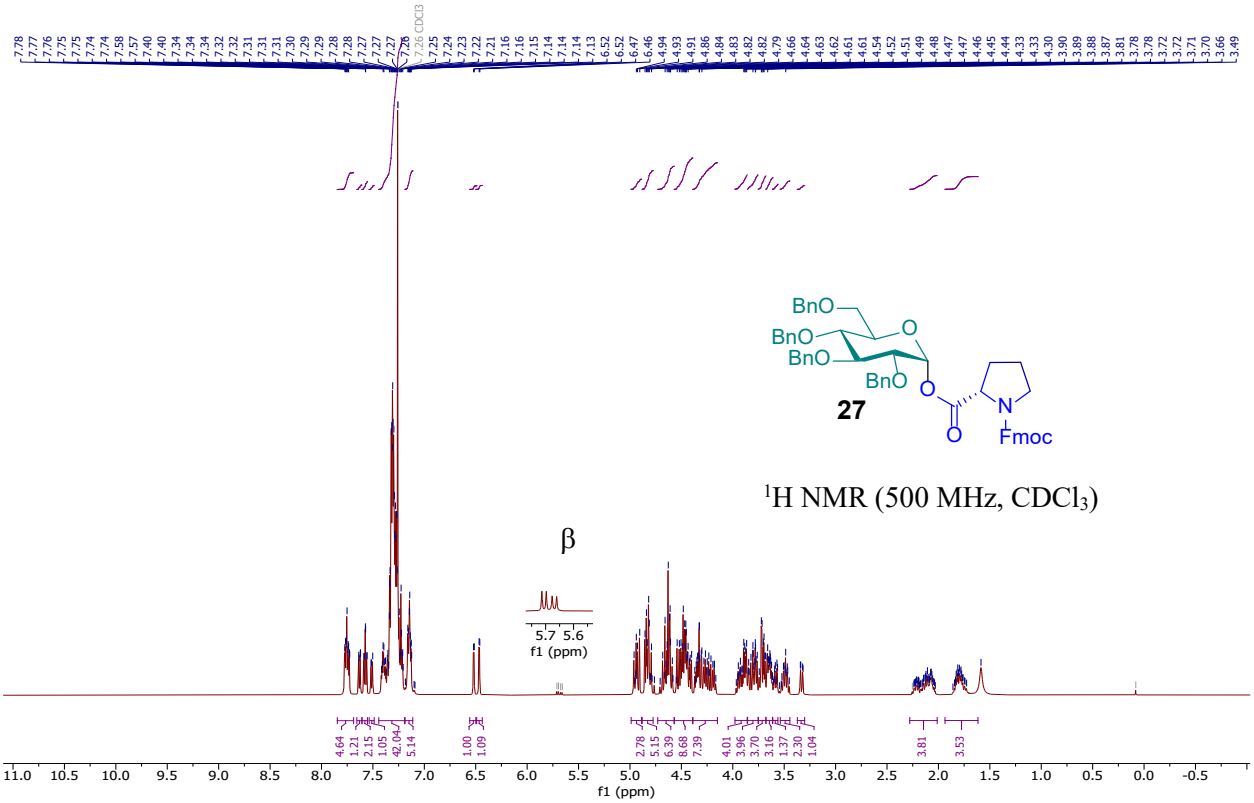
^{13}C NMR (126 MHz, $CDCl_3$)



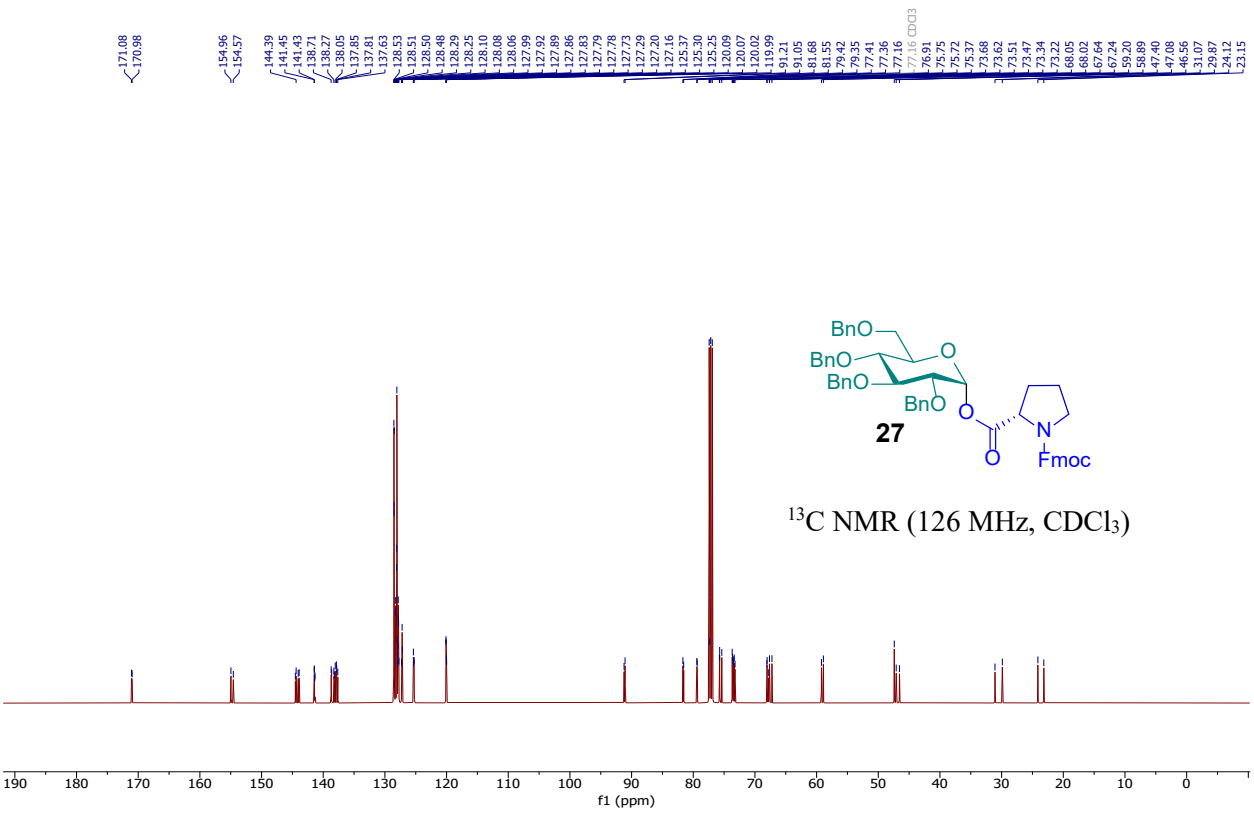
^{1}H NMR (500 MHz, $CDCl_3$)



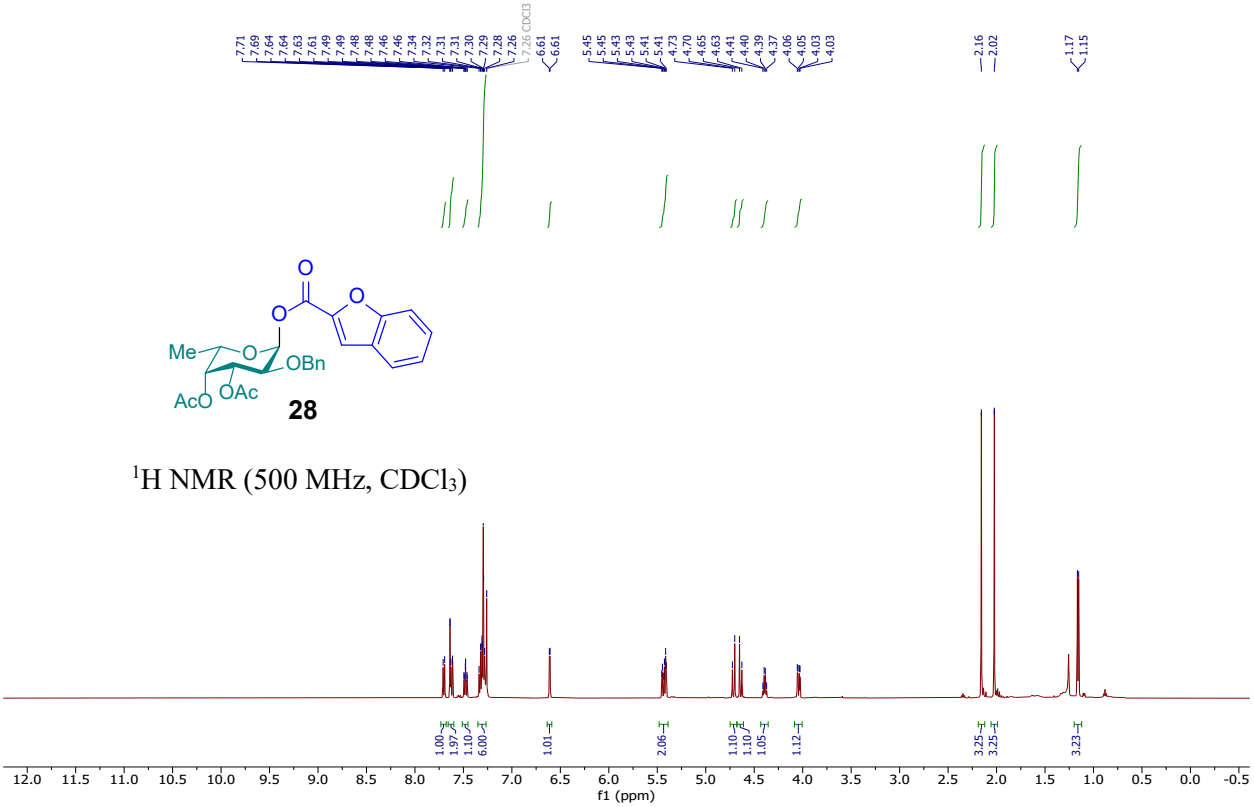
^{13}C NMR (126 MHz, $CDCl_3$)



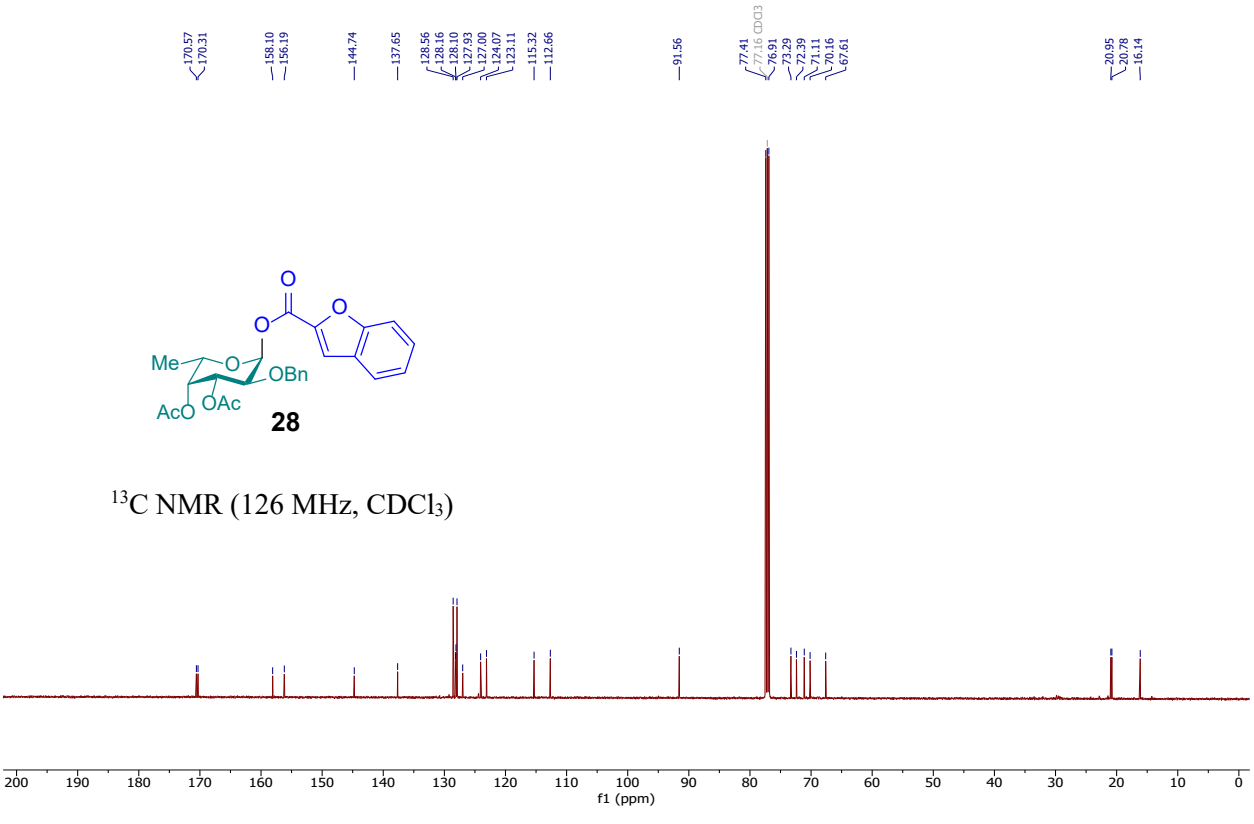
^{1}H NMR (500 MHz, $CDCl_3$)



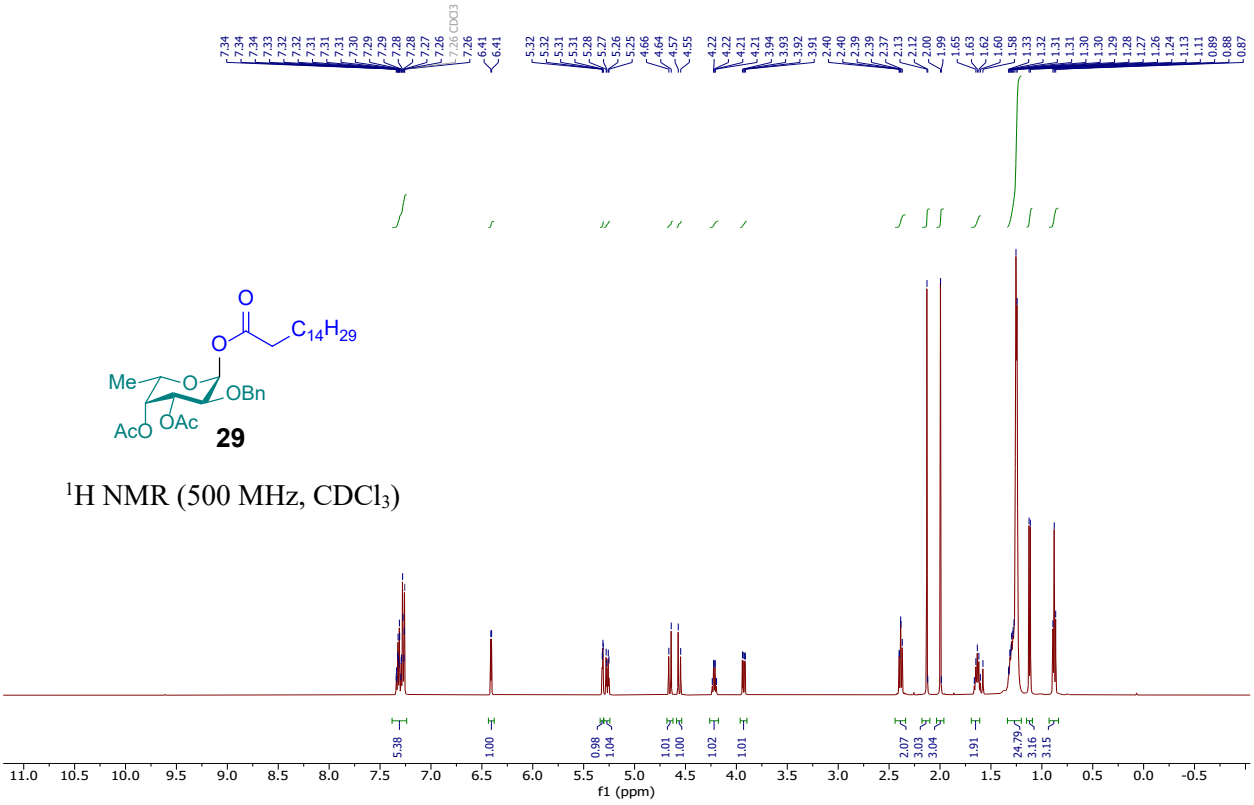
^{13}C NMR (126 MHz, $CDCl_3$)



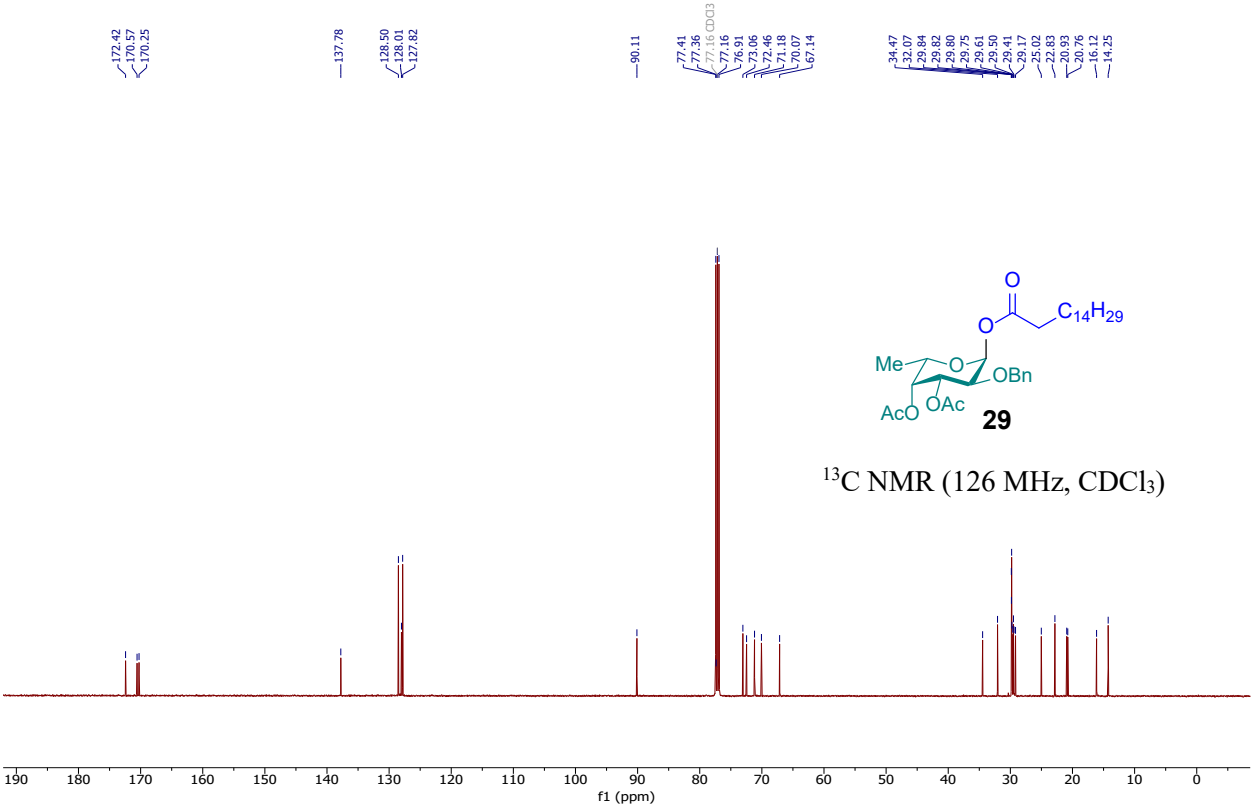
^{1}H NMR (500 MHz, $CDCl_3$)



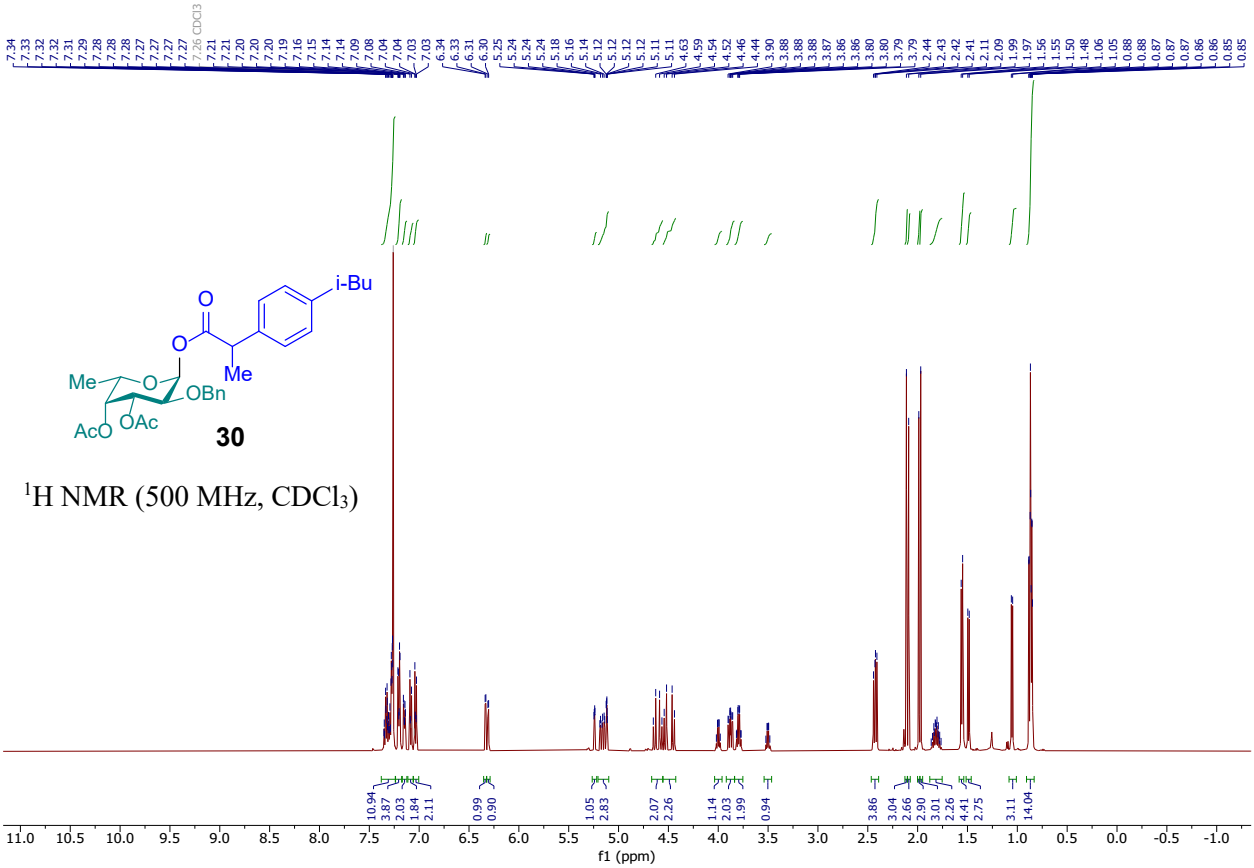
^{13}C NMR (126 MHz, $CDCl_3$)



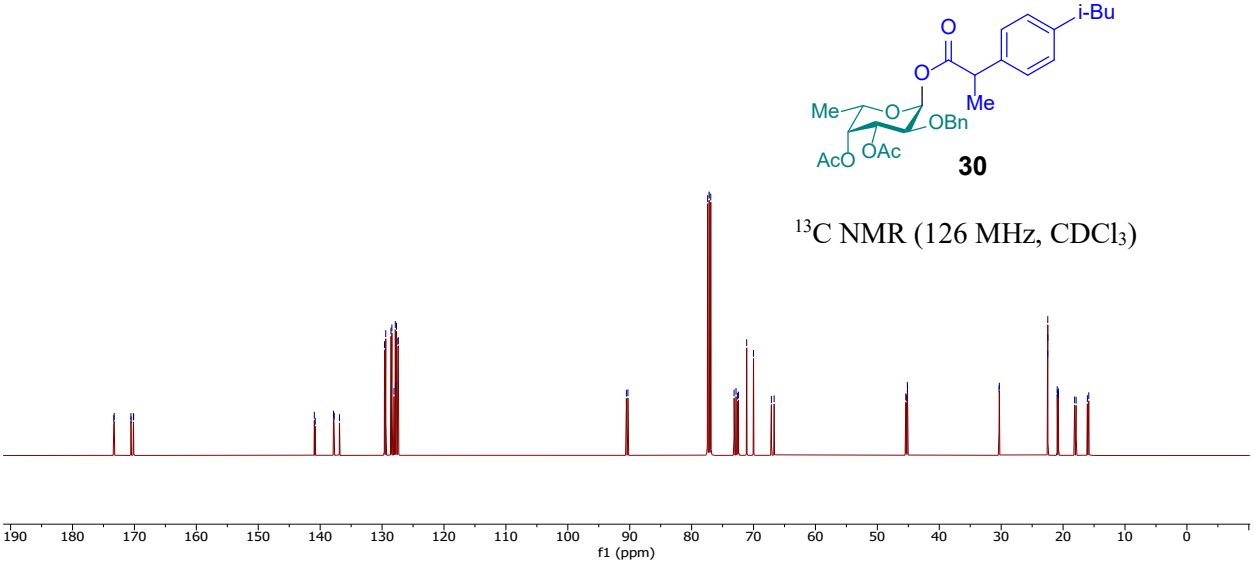
^{1}H NMR (500 MHz, $CDCl_3$)



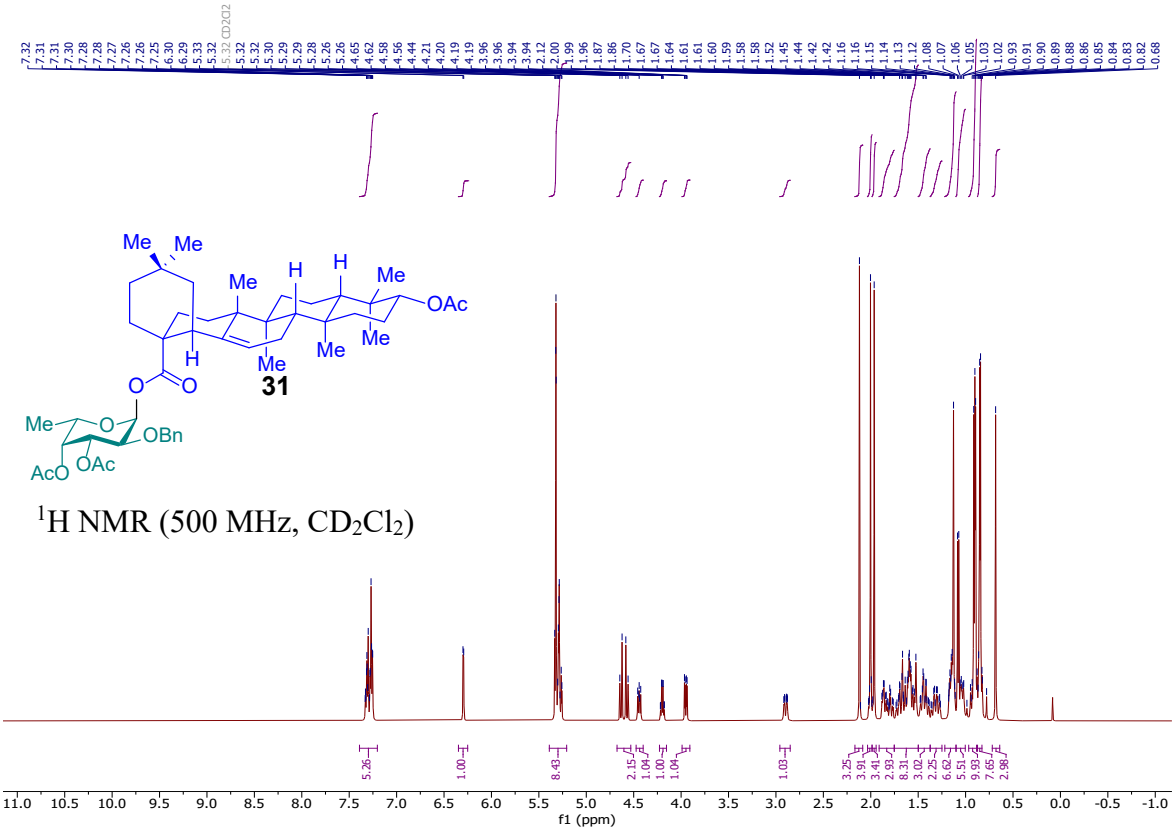
^{13}C NMR (126 MHz, $CDCl_3$)



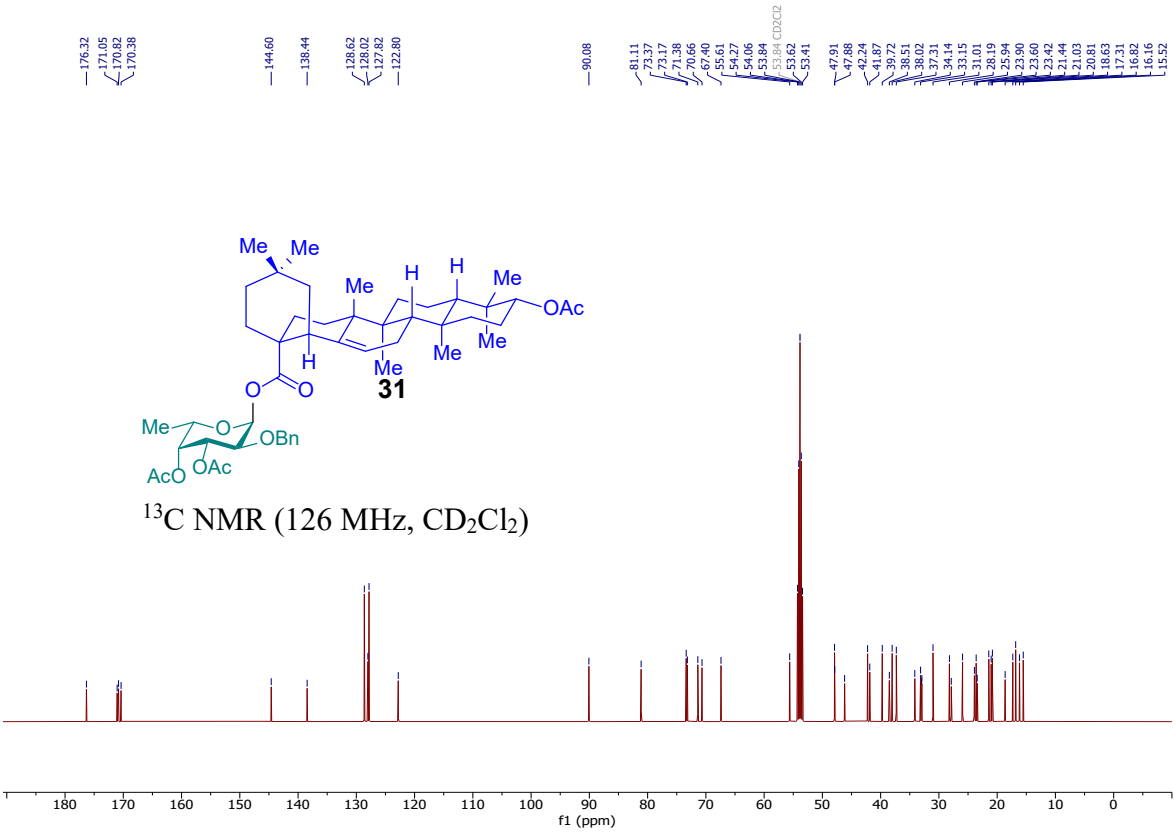
^{1}H NMR (500 MHz, $CDCl_3$)



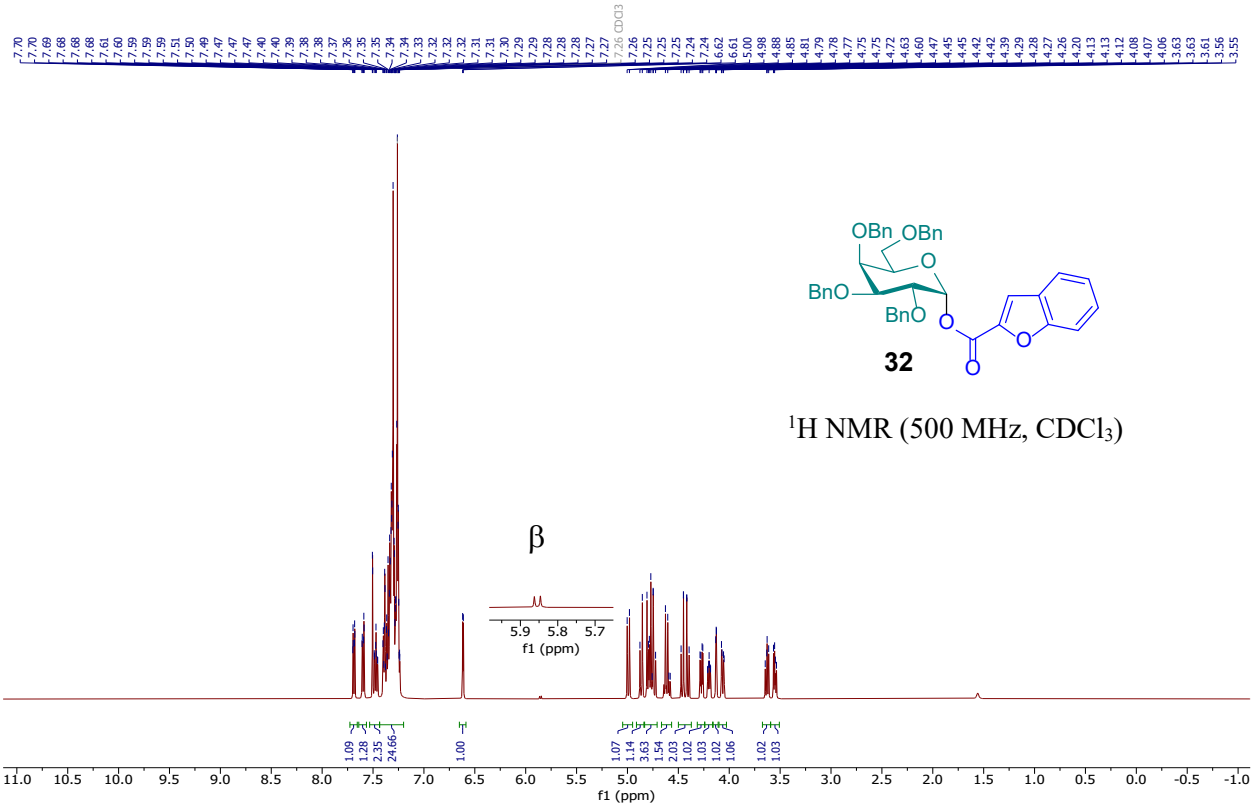
^{13}C NMR (126 MHz, $CDCl_3$)



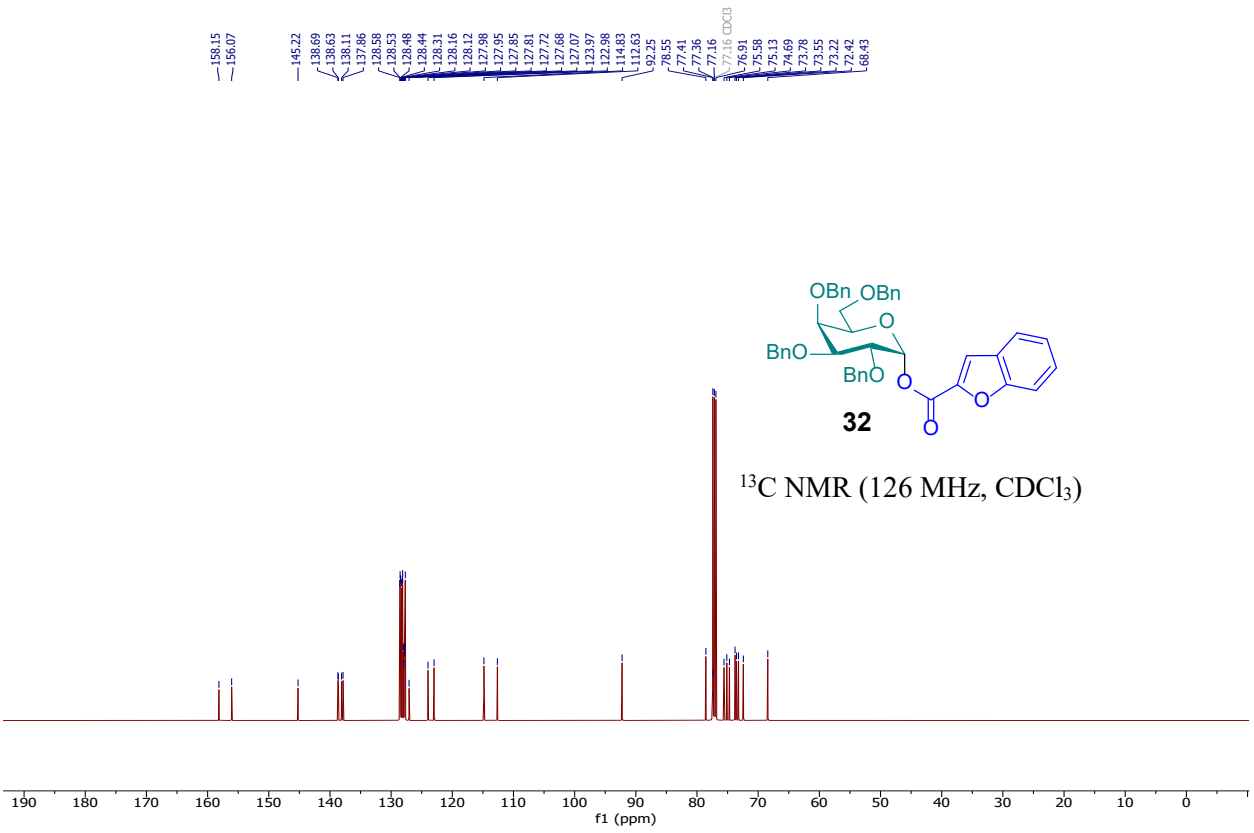
^{1}H NMR (500 MHz, CD_2Cl_2)



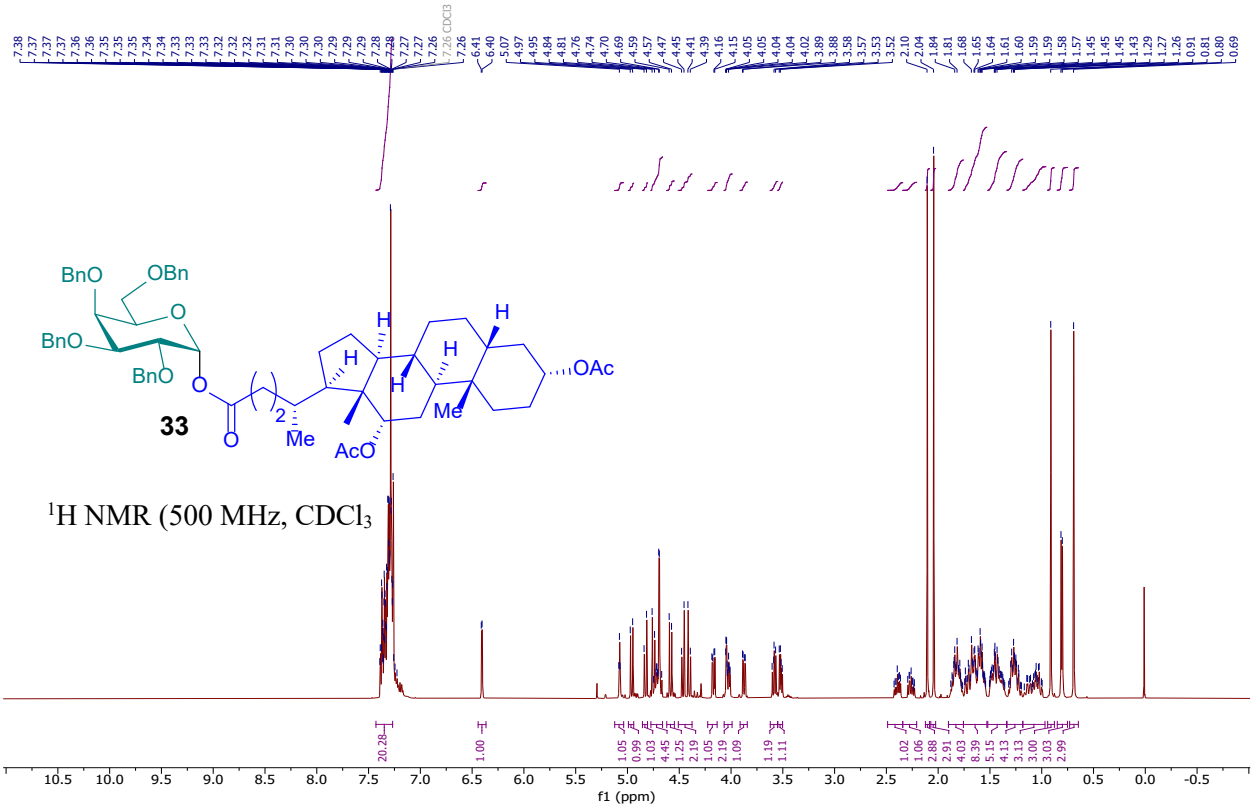
^{13}C NMR (126 MHz, CD_2Cl_2)



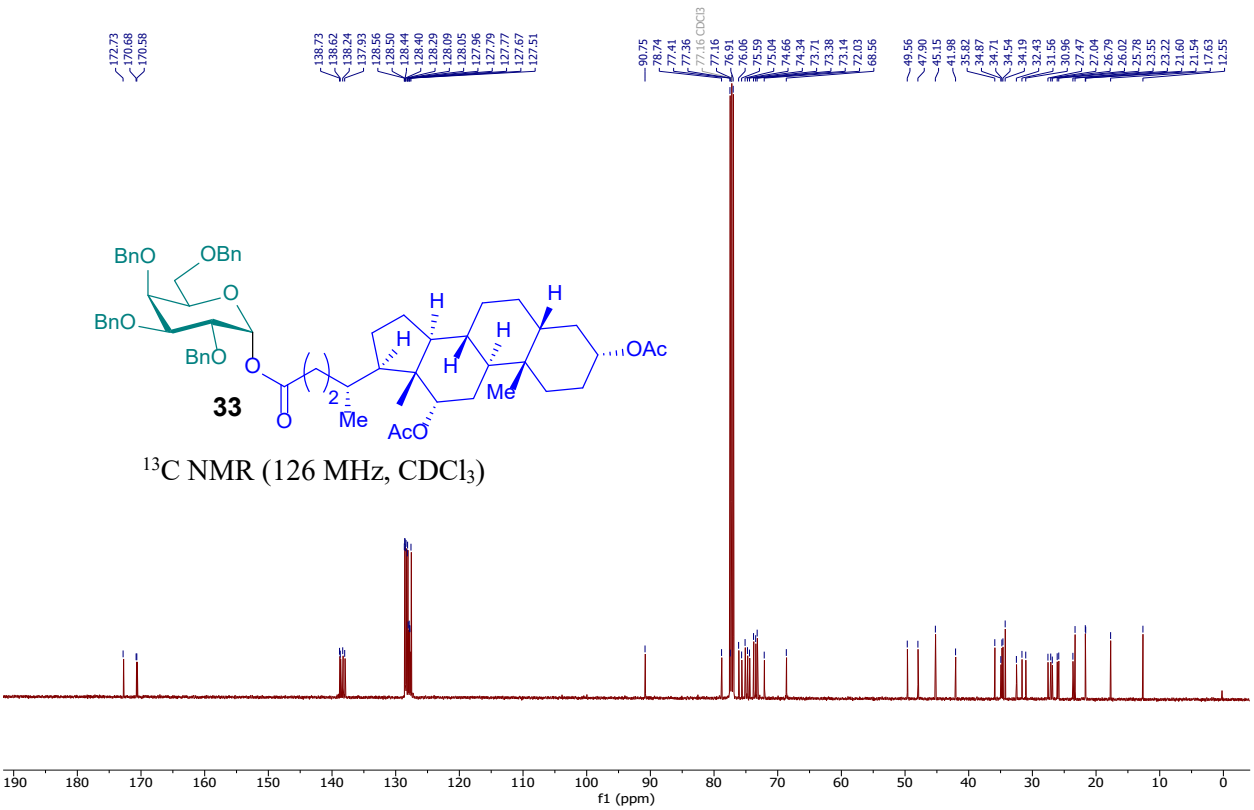
^{1}H NMR (500 MHz, $CDCl_3$)



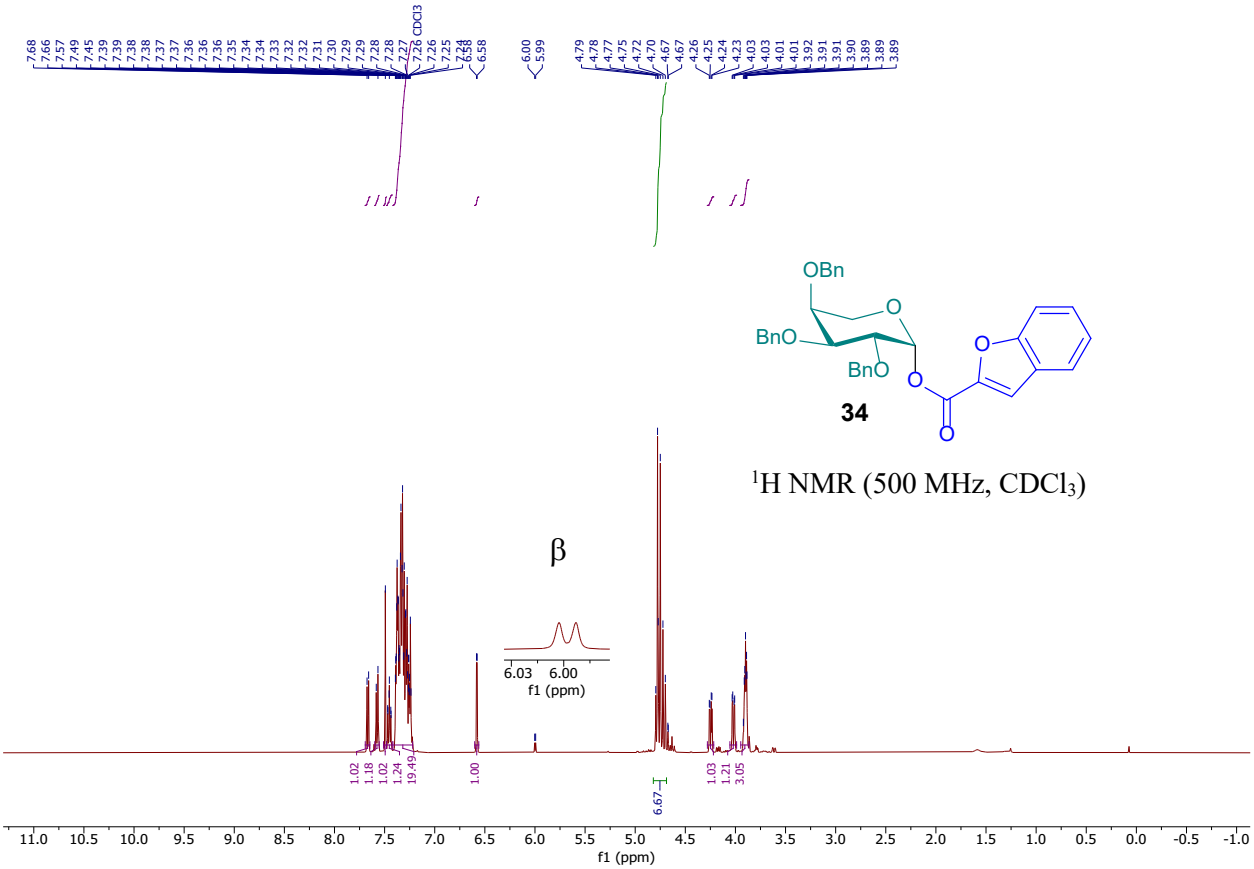
^{13}C NMR (126 MHz, $CDCl_3$)



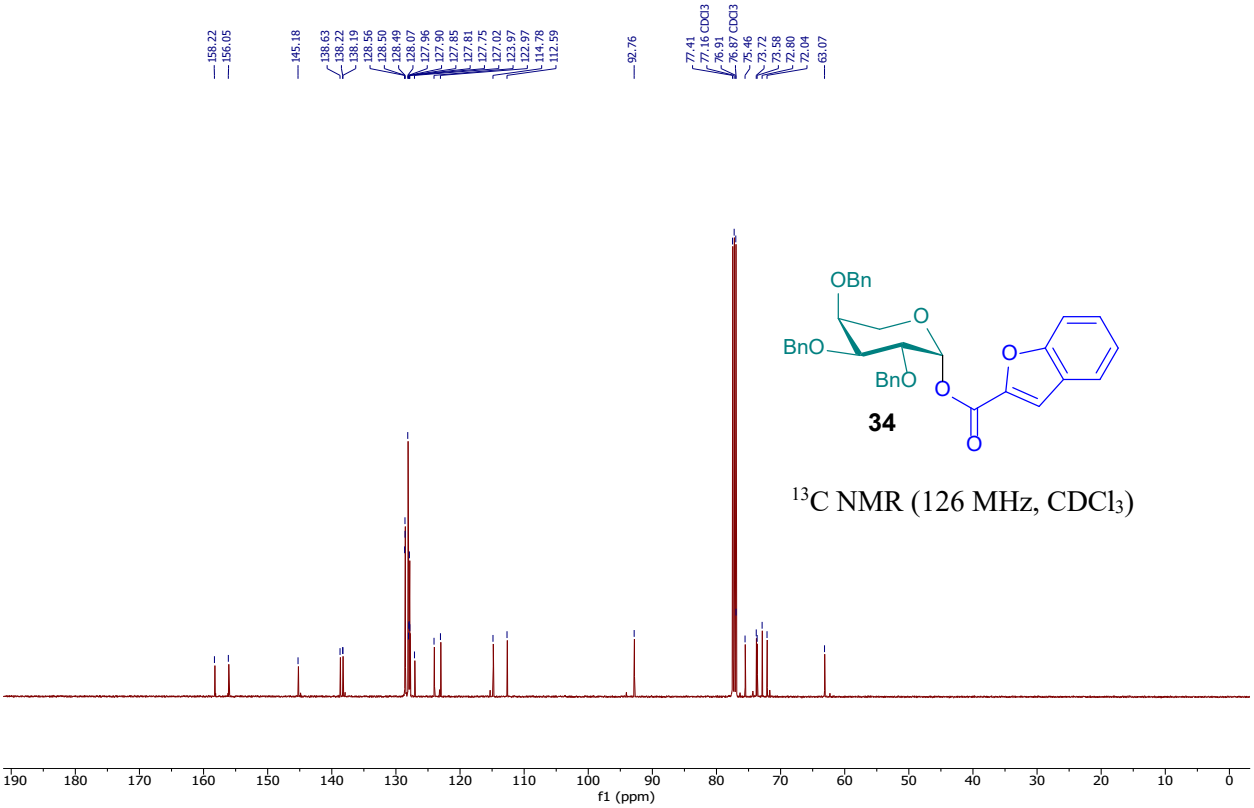
^{1}H NMR (500 MHz, $CDCl_3$)



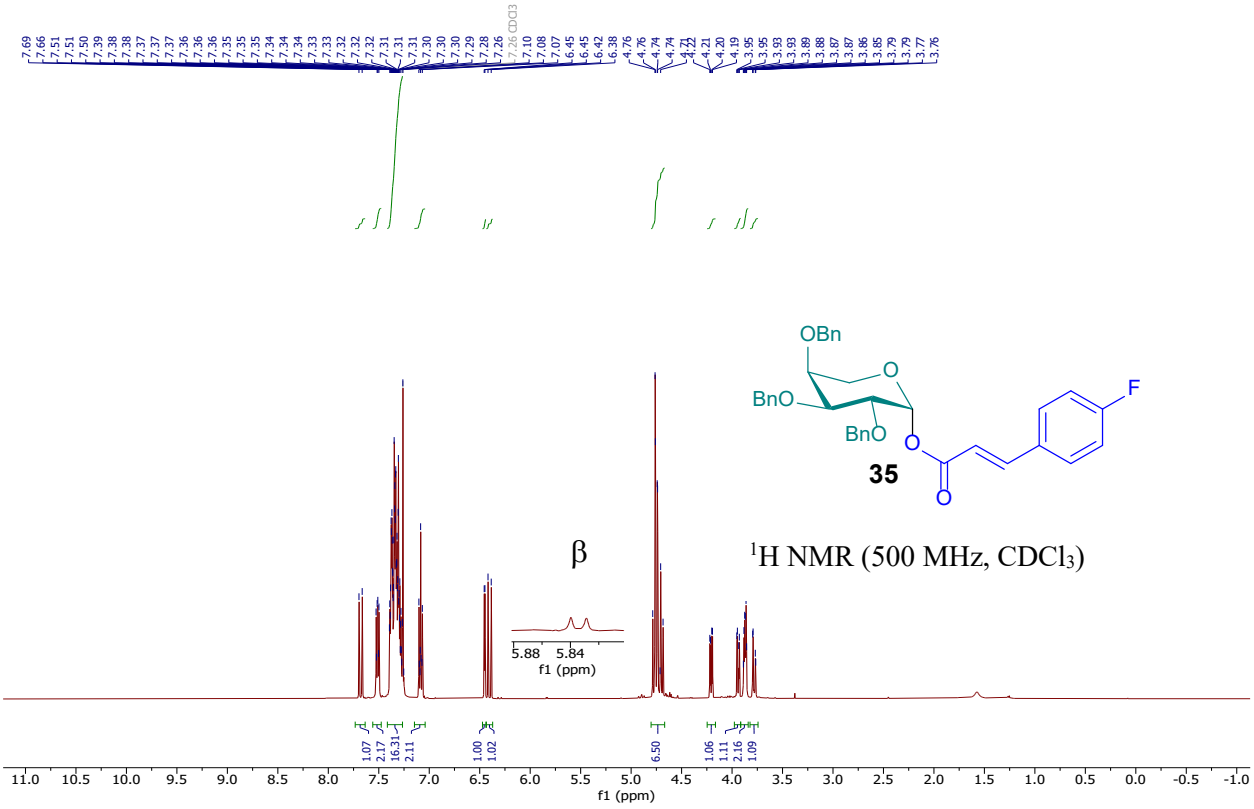
^{13}C NMR (126 MHz, $CDCl_3$)



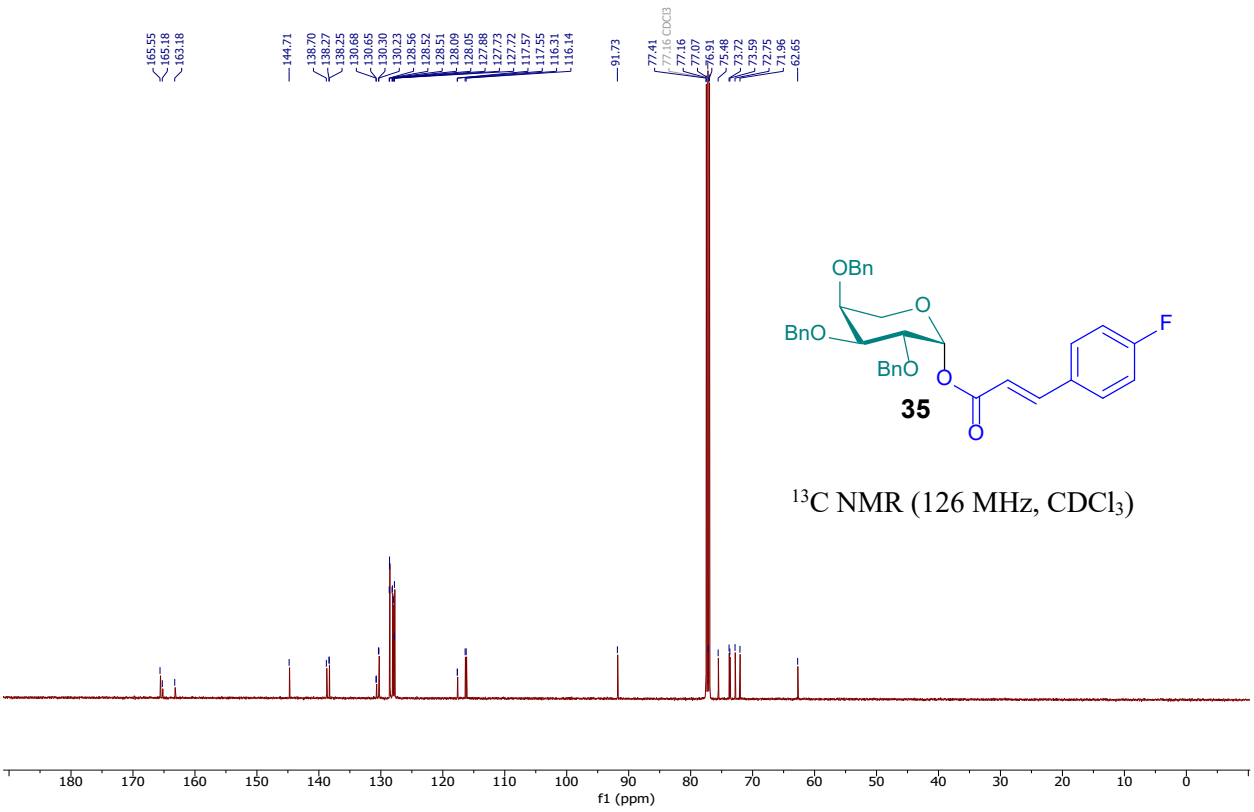
^{1}H NMR (500 MHz, $CDCl_3$)



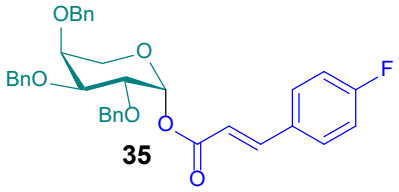
^{13}C NMR (126 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)

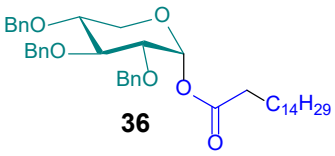


^{13}C NMR (126 MHz, $CDCl_3$)



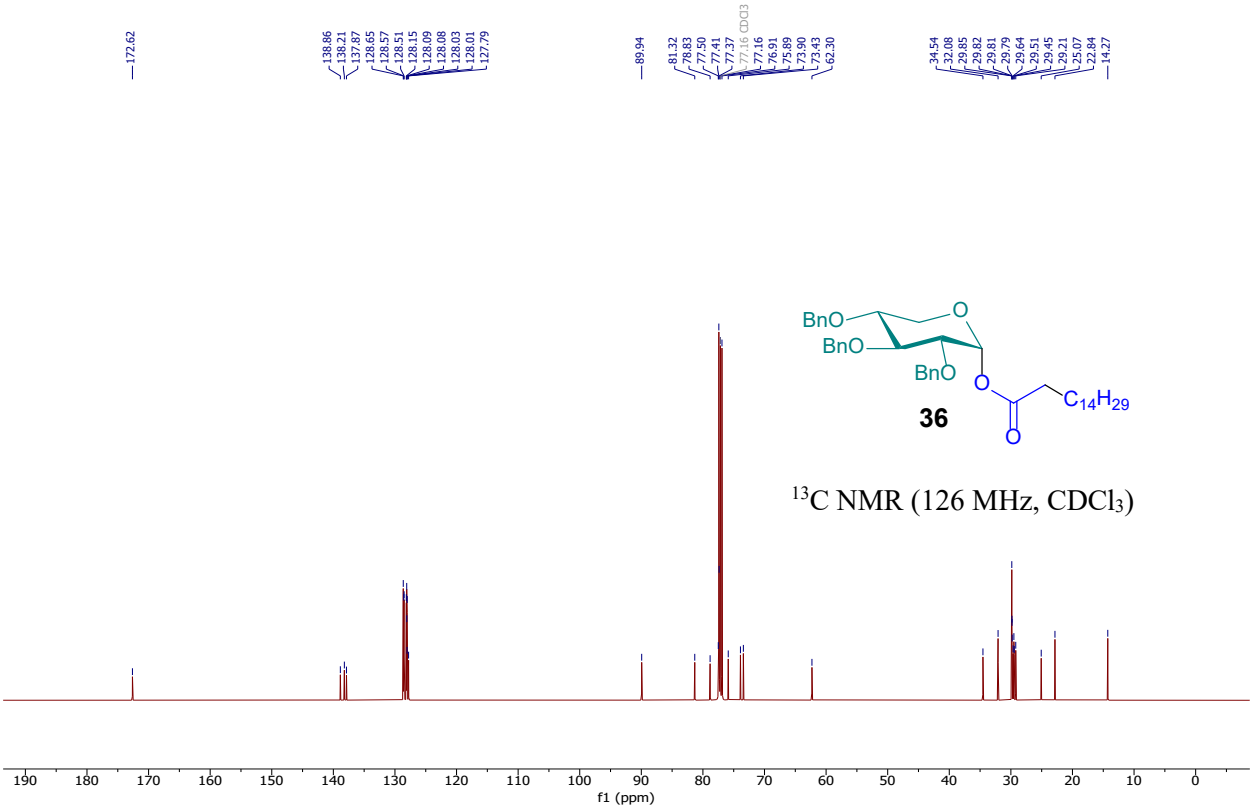
35

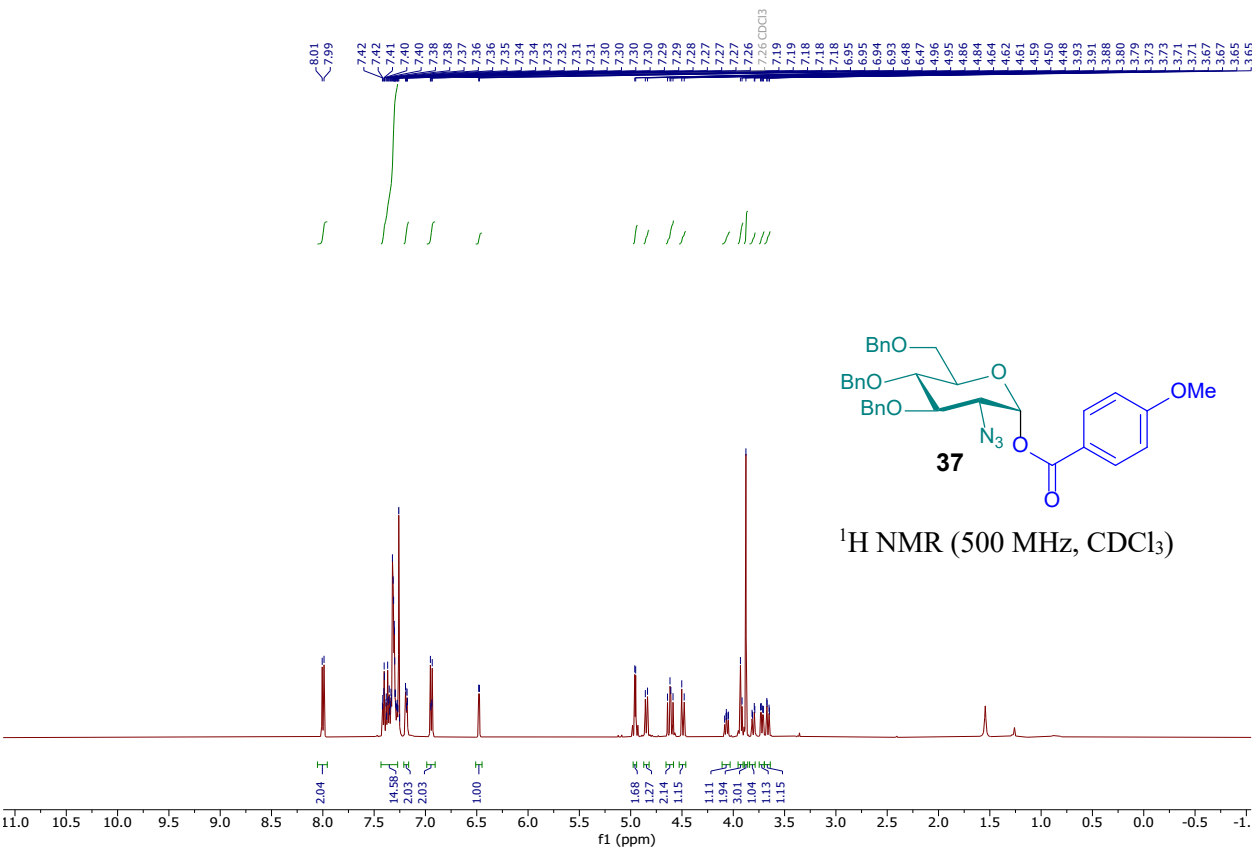
^{19}F NMR (471 MHz, $CDCl_3$)

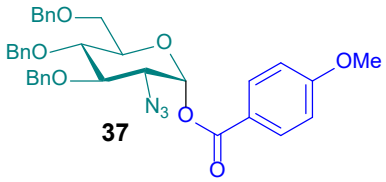


36

^{1}H NMR (500 MHz, $CDCl_3$)

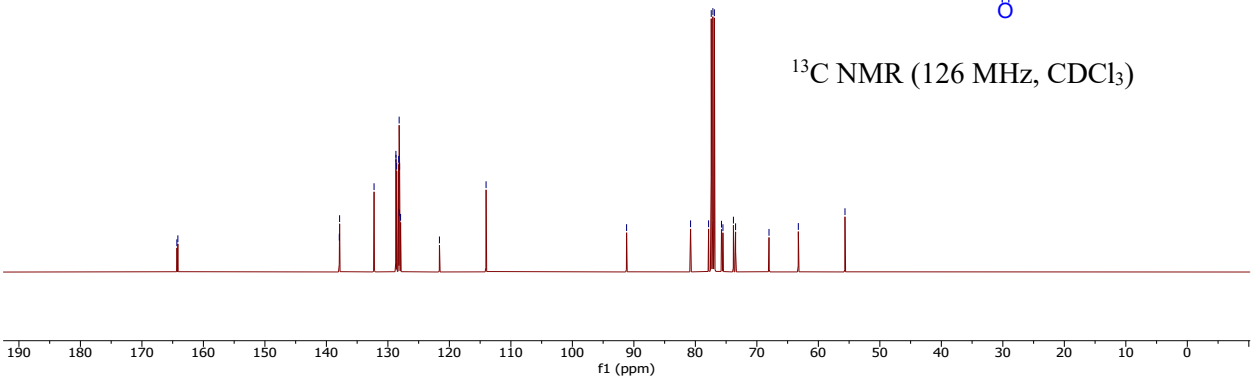

BnO
BnO
BnO
O
O
C14H29
O
36
13C NMR (126 MHz, CDCl3)
f1 (ppm)

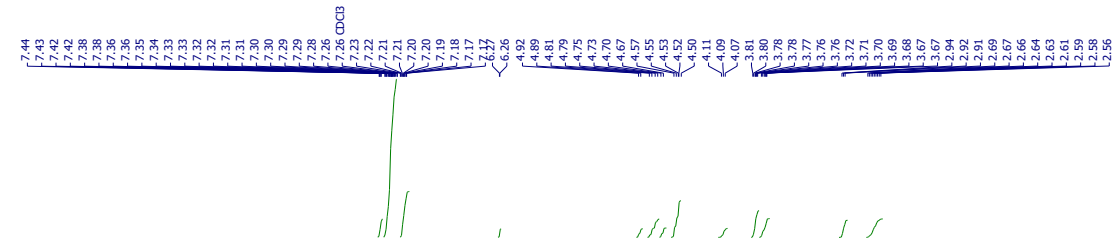

BnO
BnO
BnO
O
N3
O
OMe
O
37
1H NMR (500 MHz, CDCl3)
f1 (ppm)

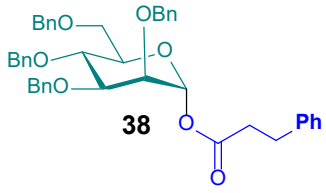


37

^{13}C NMR (126 MHz, $CDCl_3$)

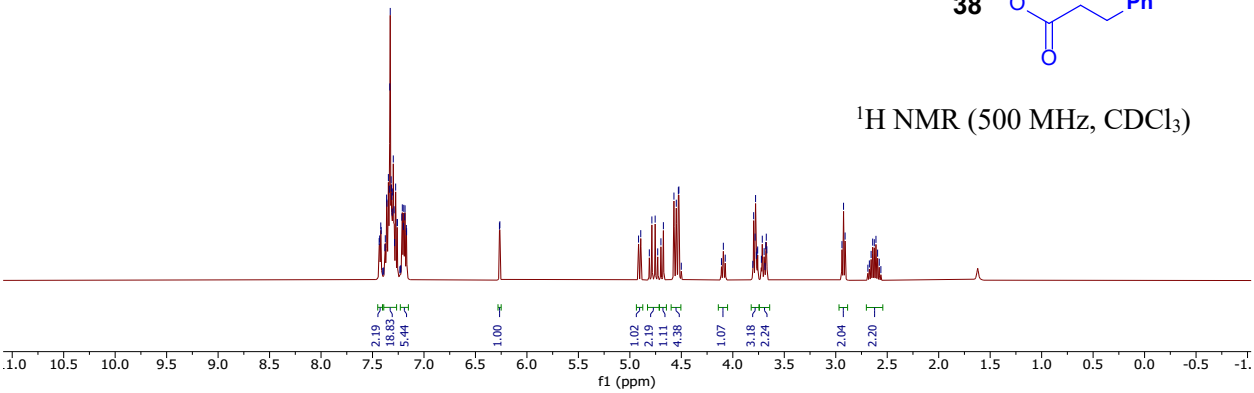


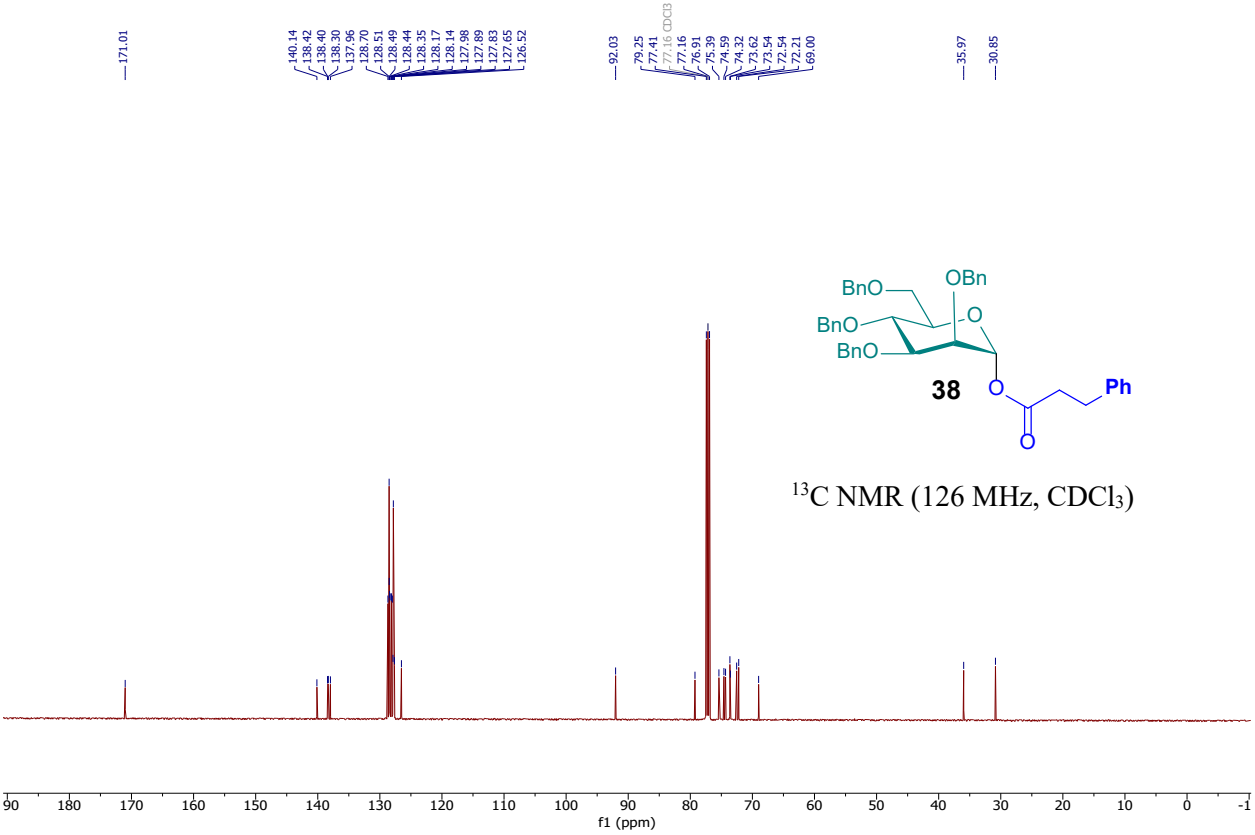


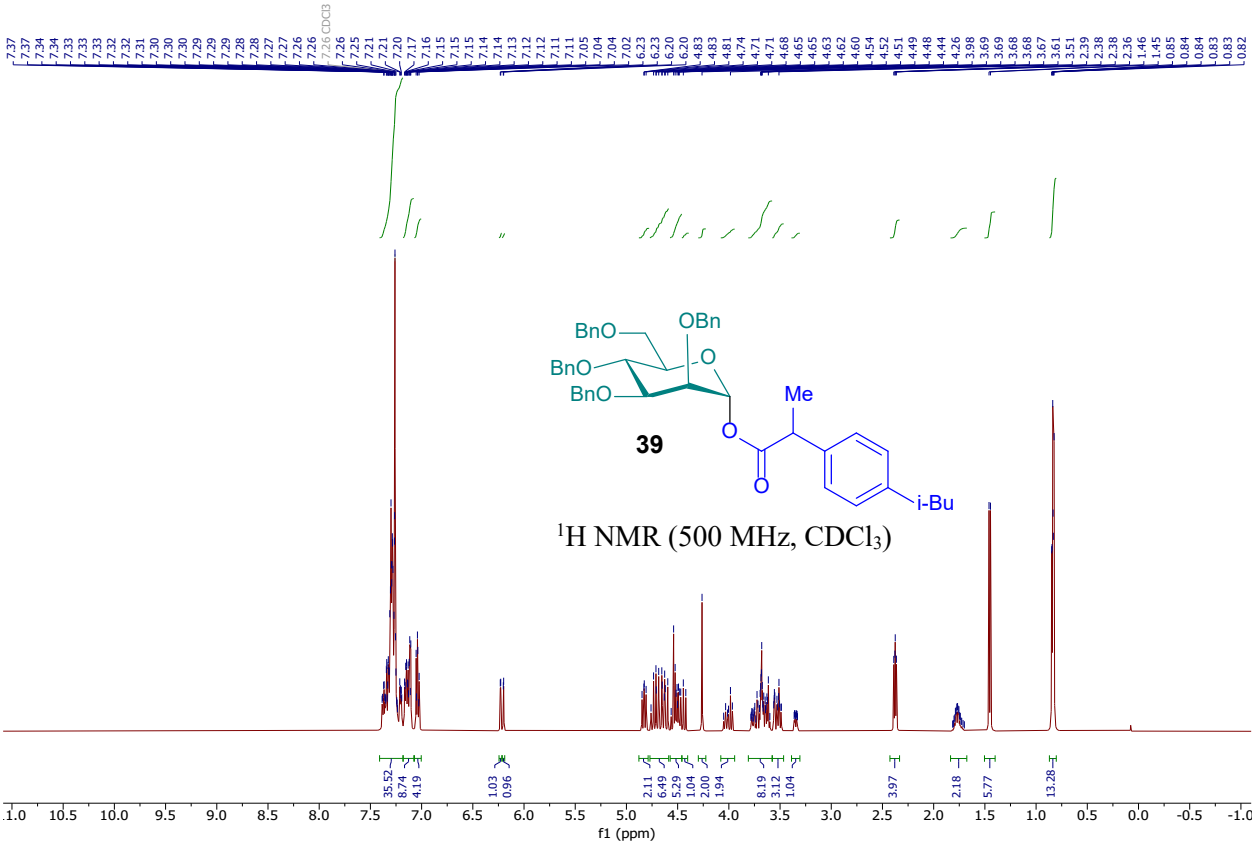


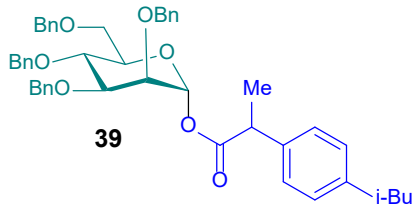
38

^{1}H NMR (500 MHz, $CDCl_3$)



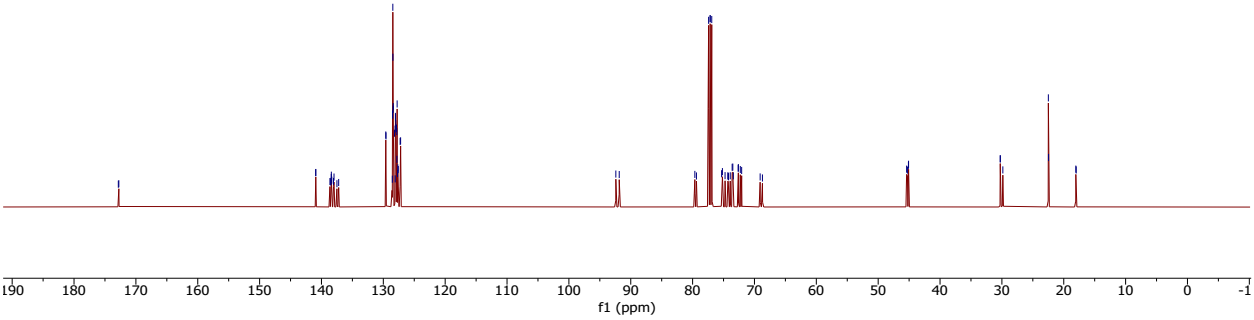

BnO
BnO
BnO
OBn
O
O
Ph
O
38
^{13}C NMR (126 MHz, $CDCl_3$)
f1 (ppm)

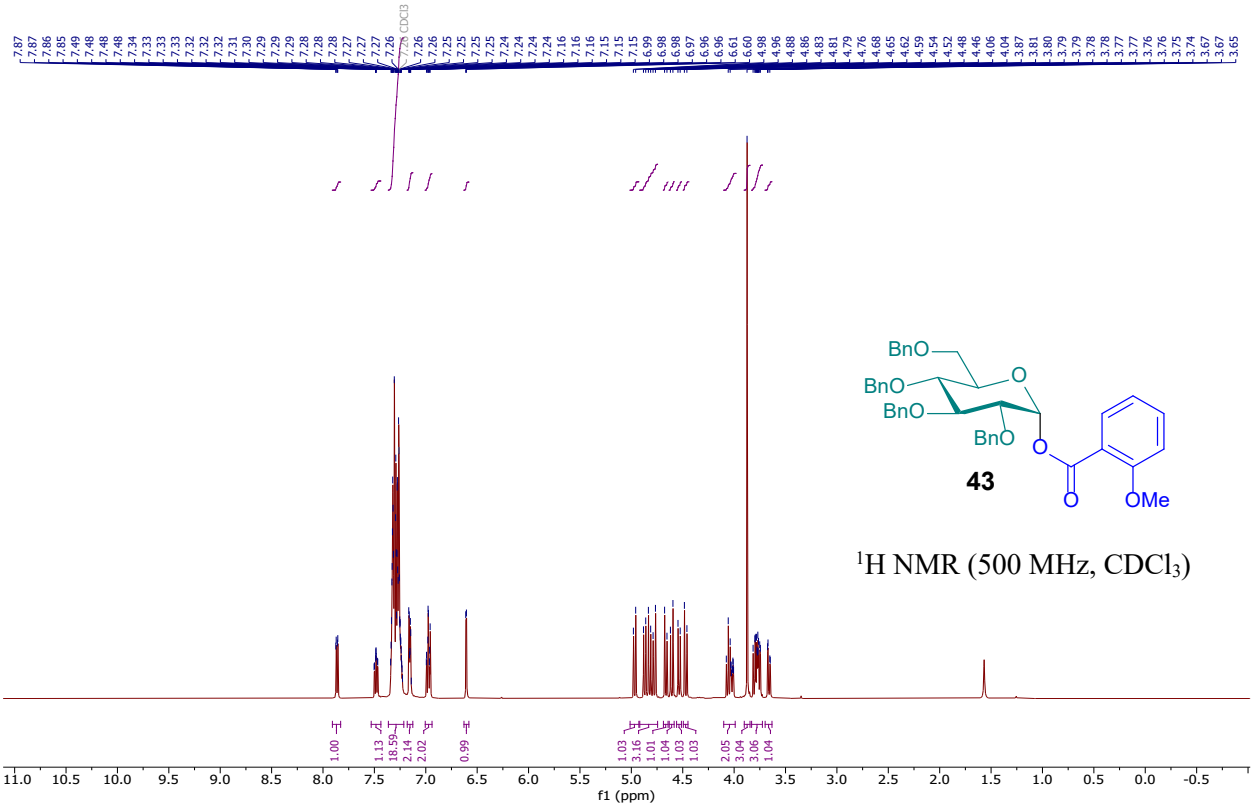

BnO
BnO
BnO
OBn
O
Me
O
O
i-Bu
39
^{1}H NMR (500 MHz, $CDCl_3$)
f1 (ppm)



39

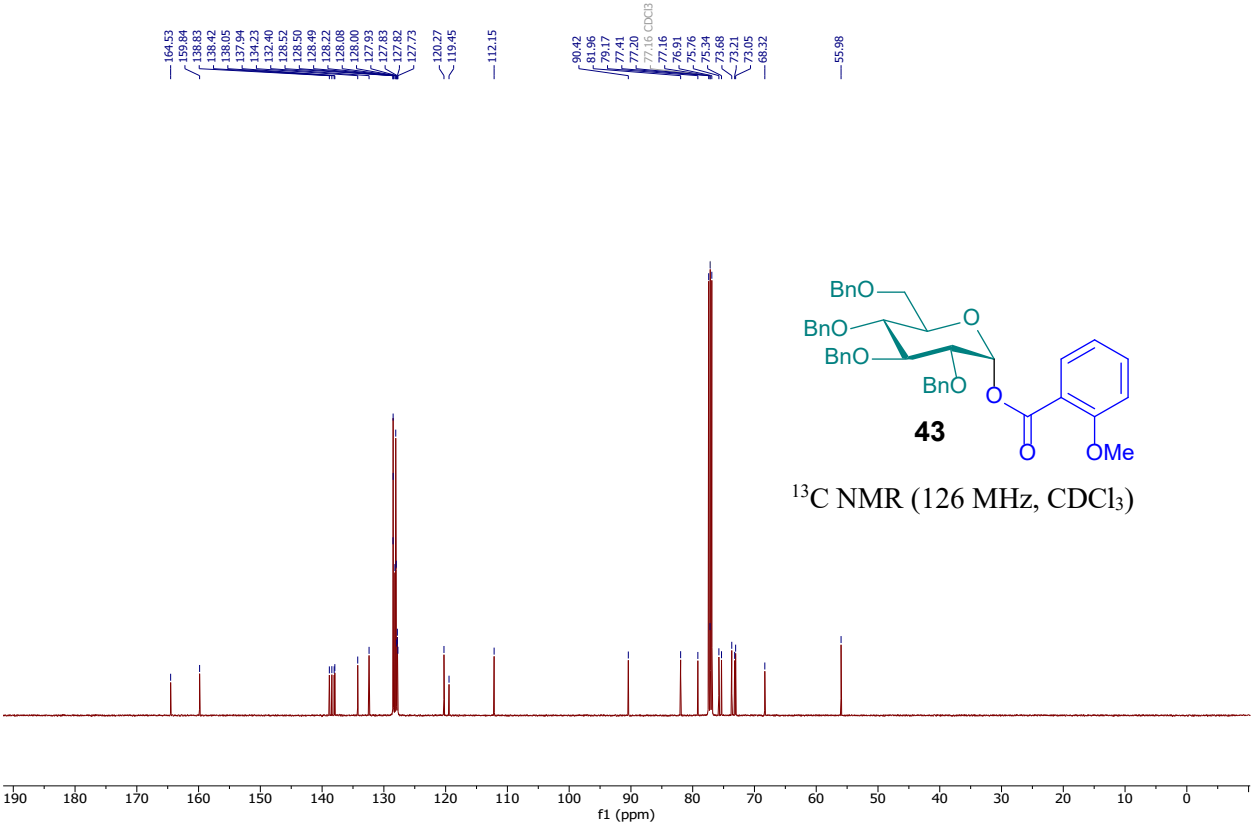
^{13}C NMR (126 MHz, $CDCl_3$)



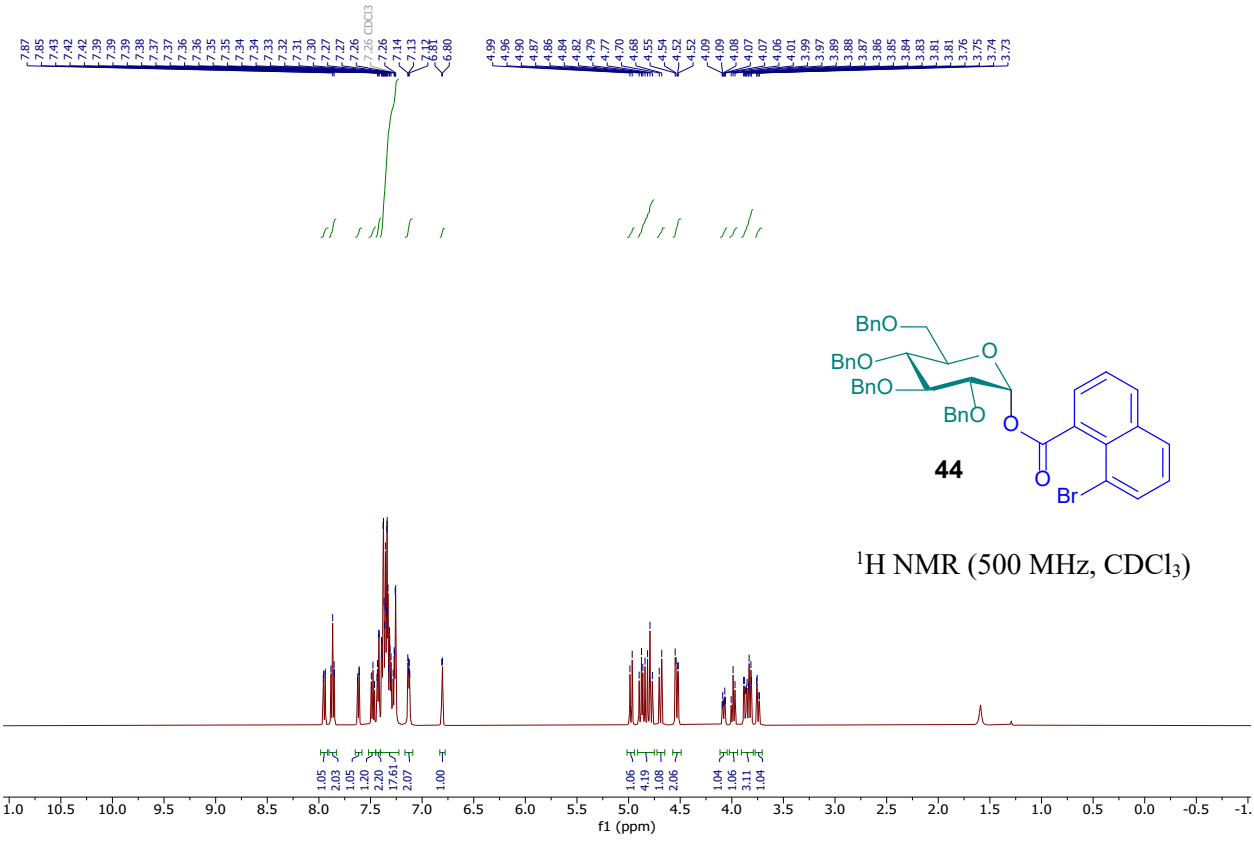


43

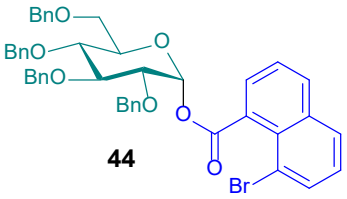
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

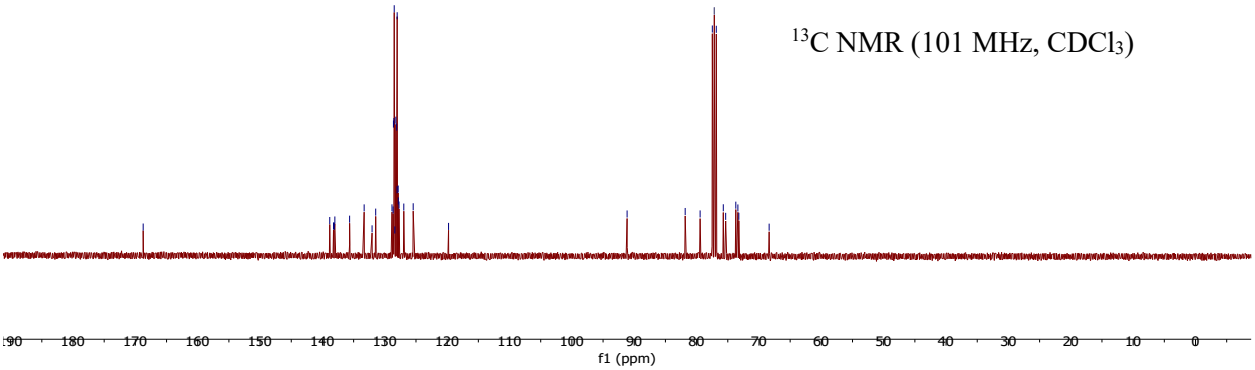


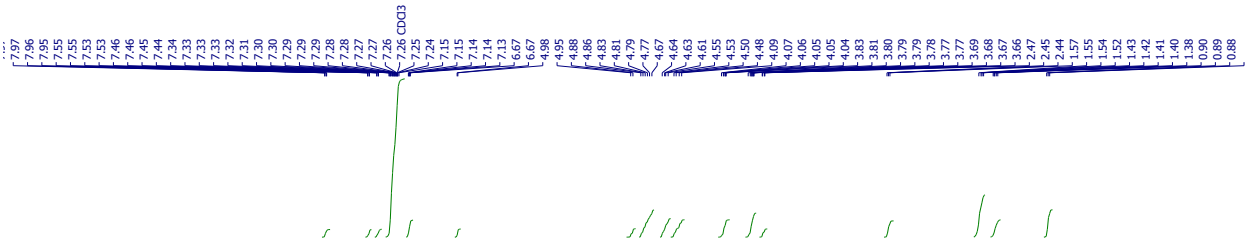
^{1}H NMR (500 MHz, $CDCl_3$)

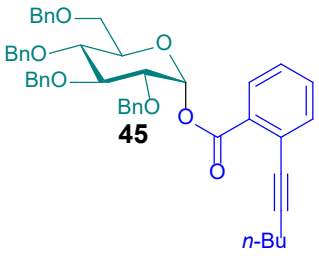


44

^{13}C NMR (101 MHz, $CDCl_3$)

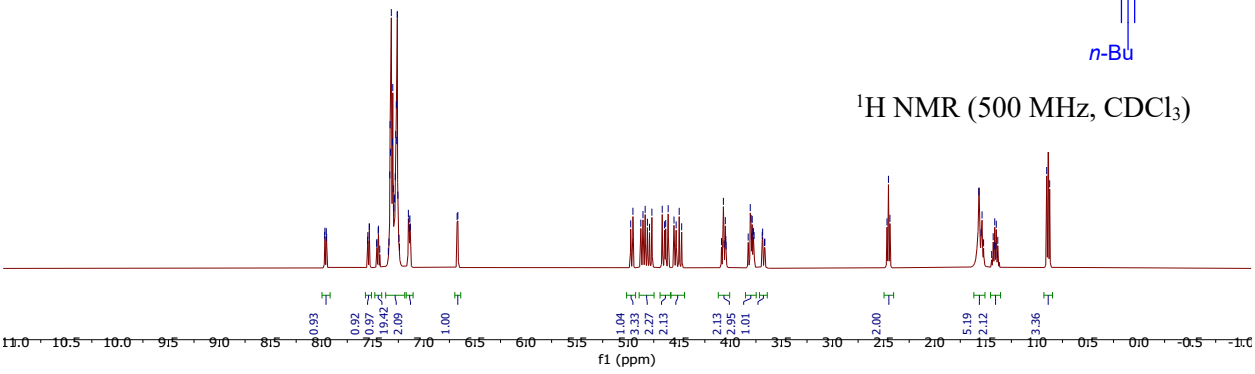


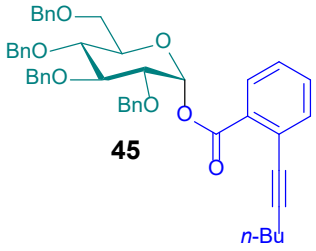




45

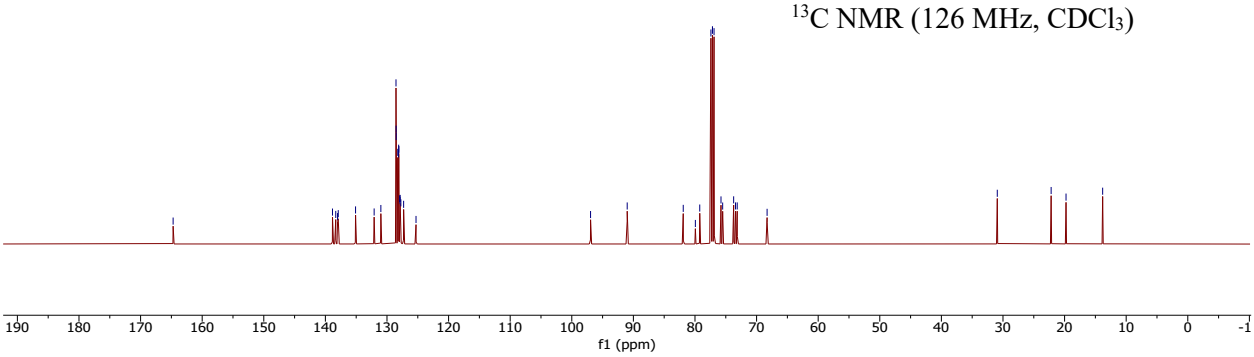
^{1}H NMR (500 MHz, $CDCl_3$)

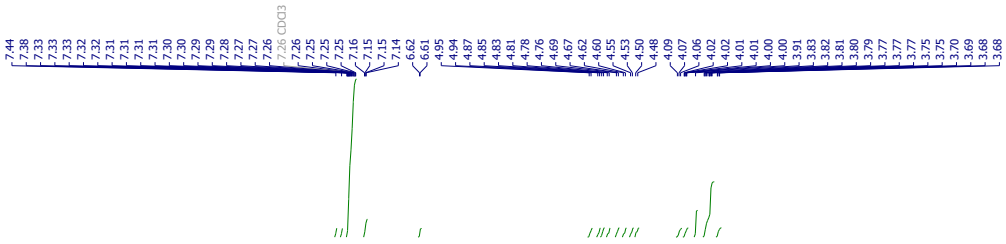


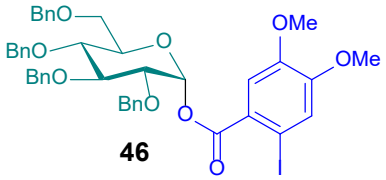


45

^{13}C NMR (126 MHz, $CDCl_3$)

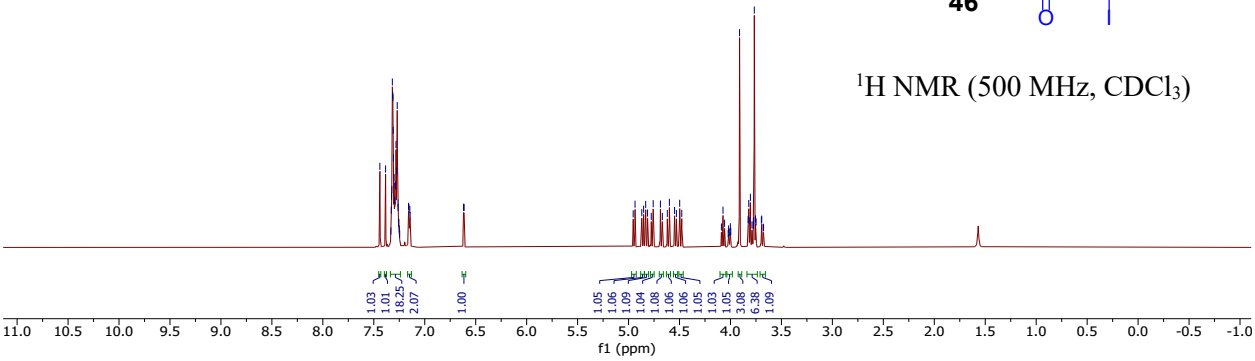


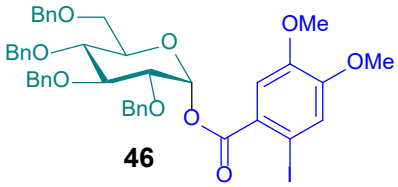




46

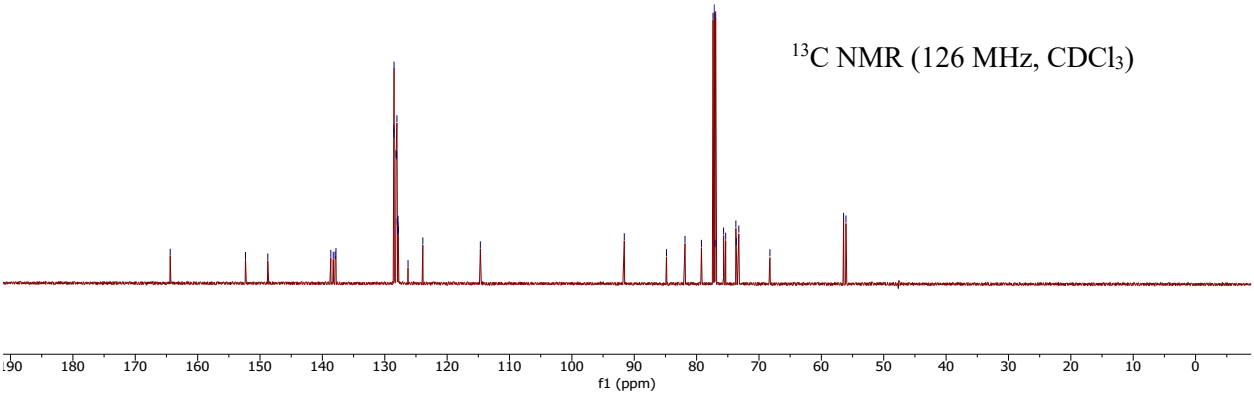
^{1}H NMR (500 MHz, $CDCl_3$)

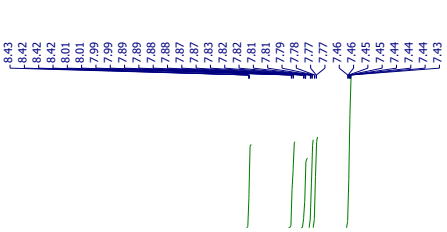


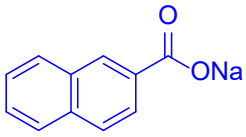


46

^{13}C NMR (126 MHz, $CDCl_3$)

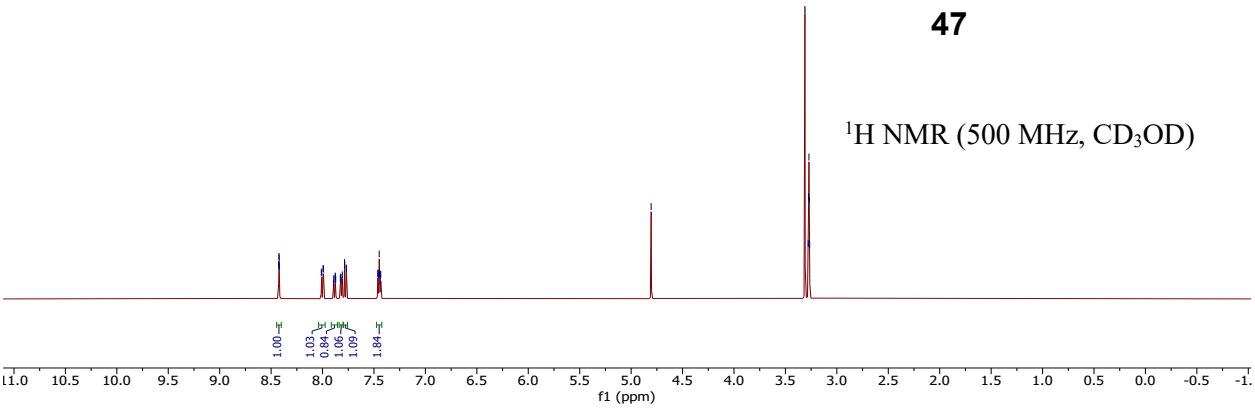


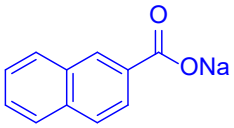




47

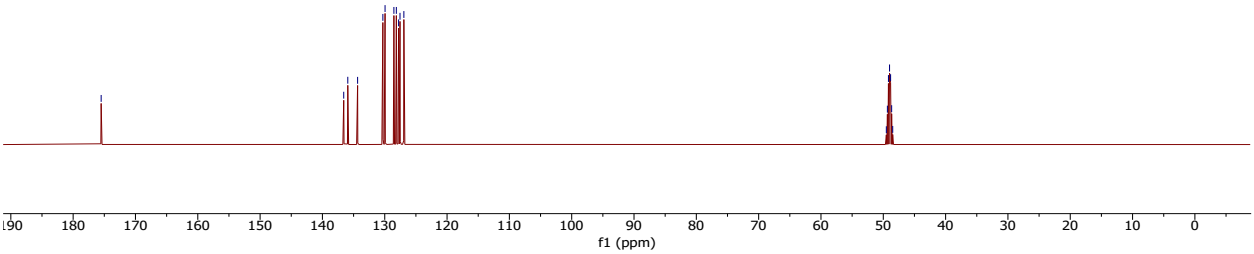
^{1}H NMR (500 MHz, CD_3OD)

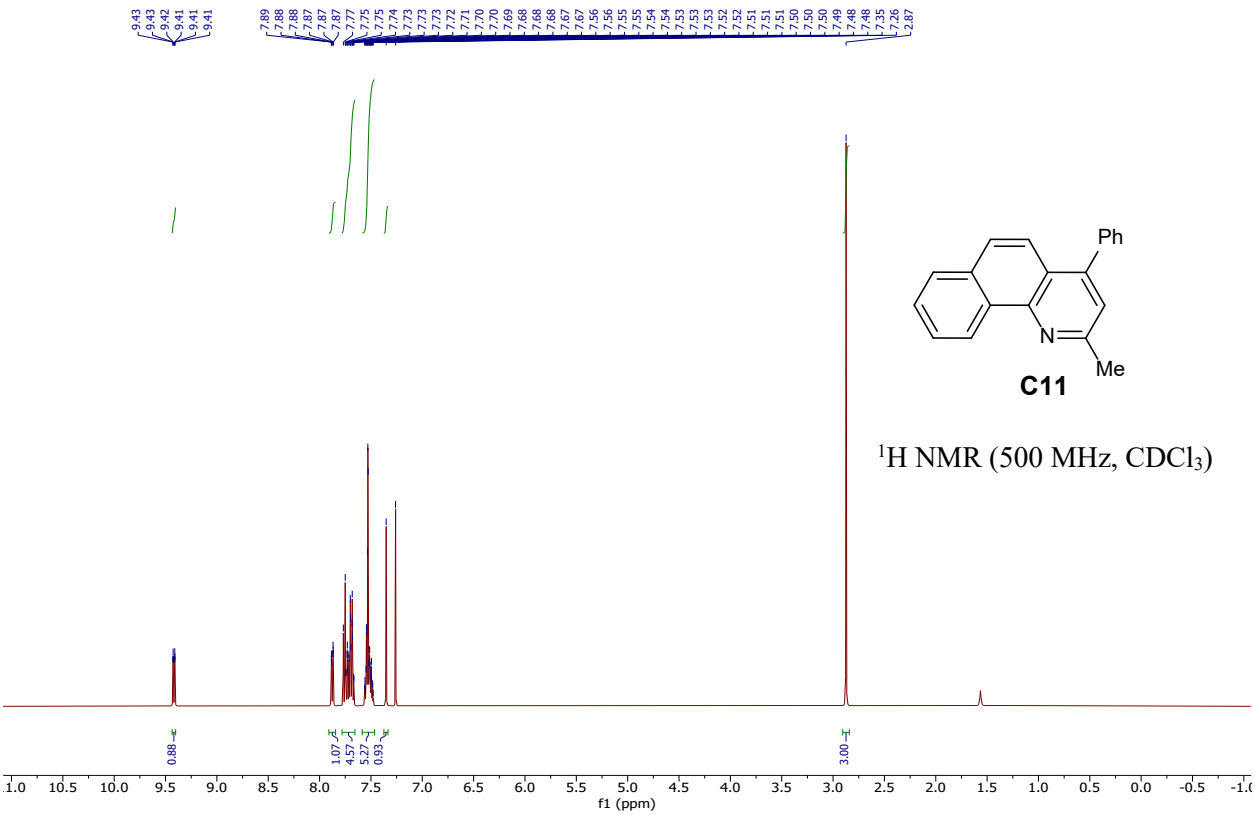




47

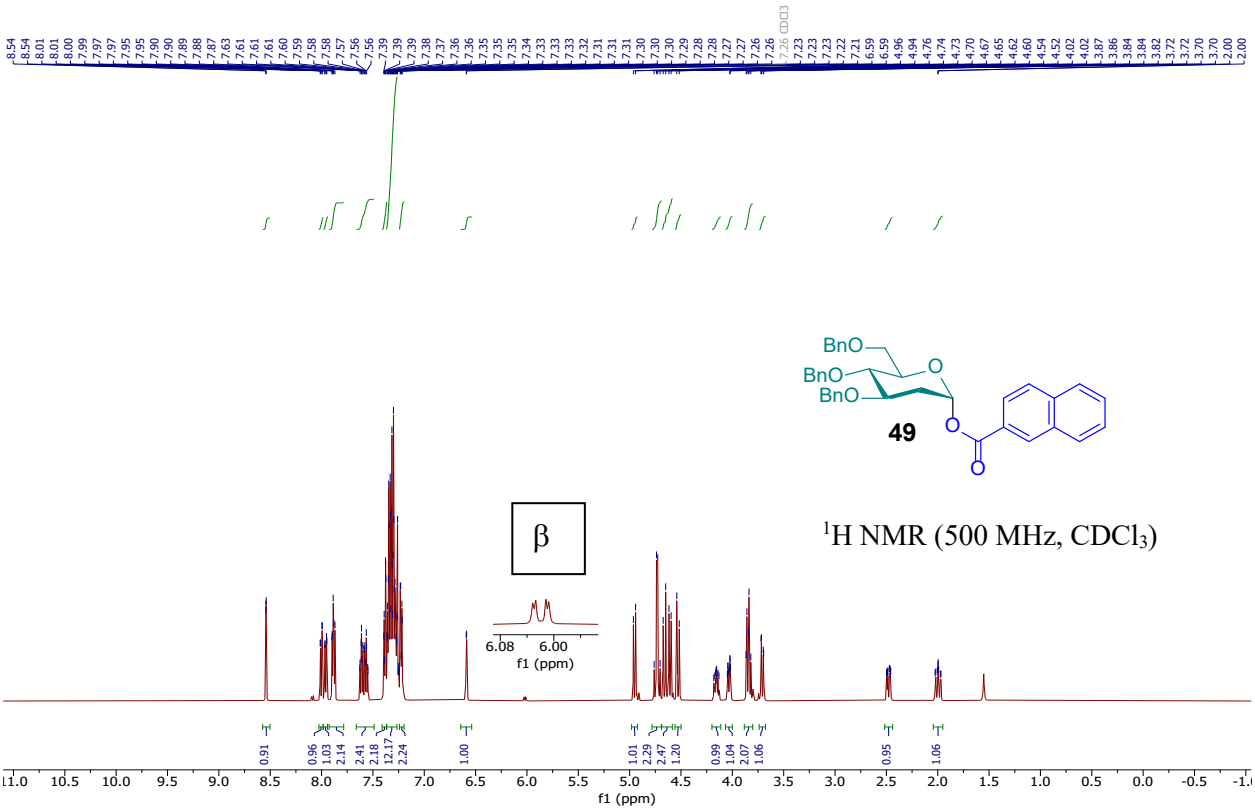
^{13}C NMR (126 MHz, CD_3OD)



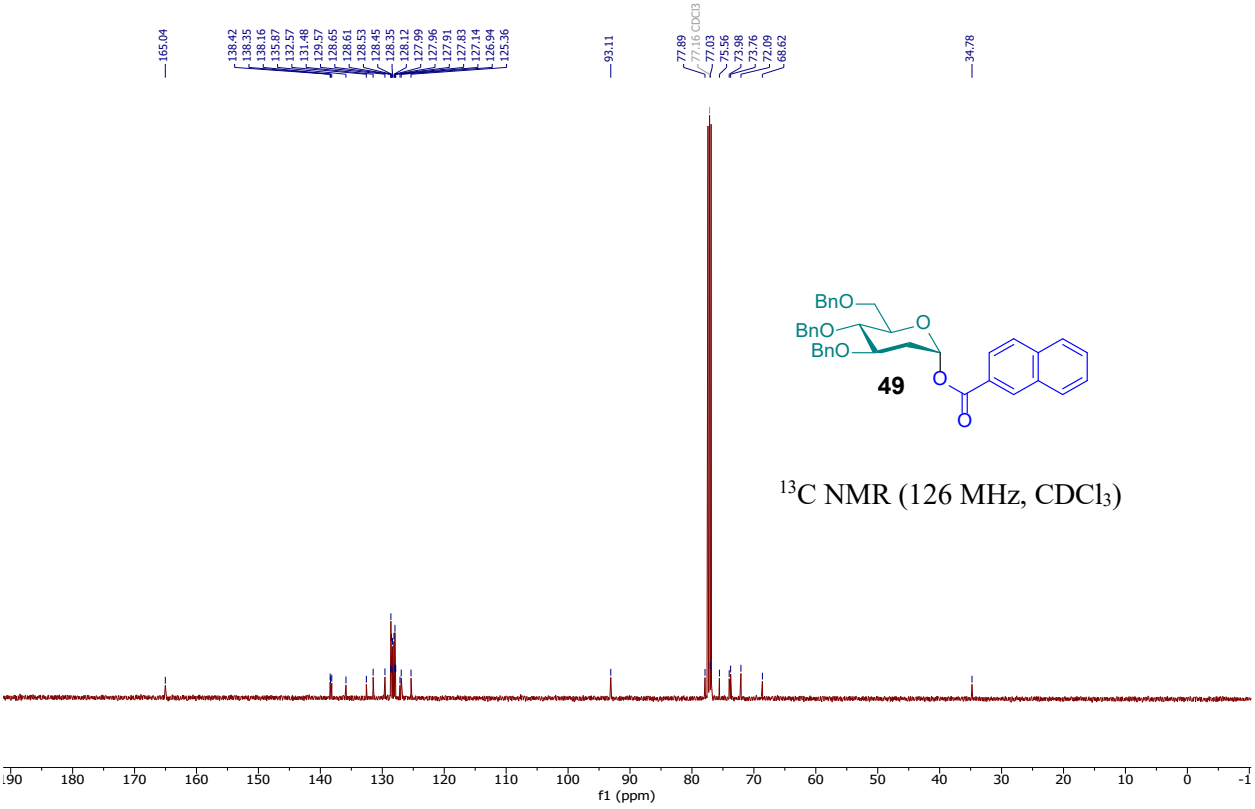


C11

^{1}H NMR (500 MHz, $CDCl_3$)

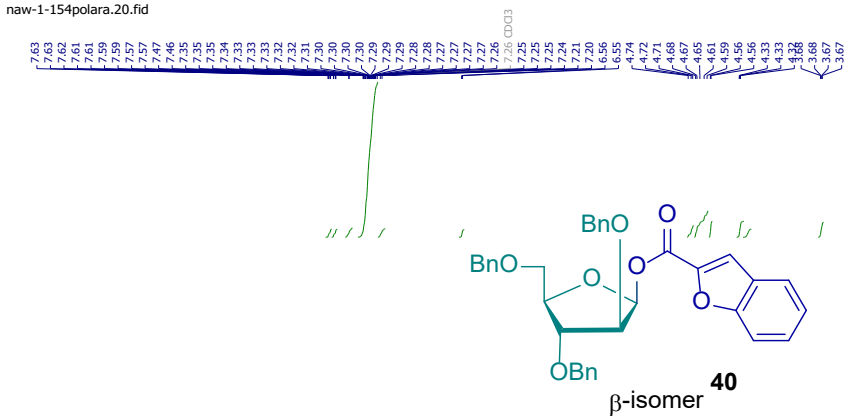


^{1}H NMR (500 MHz, $CDCl_3$)



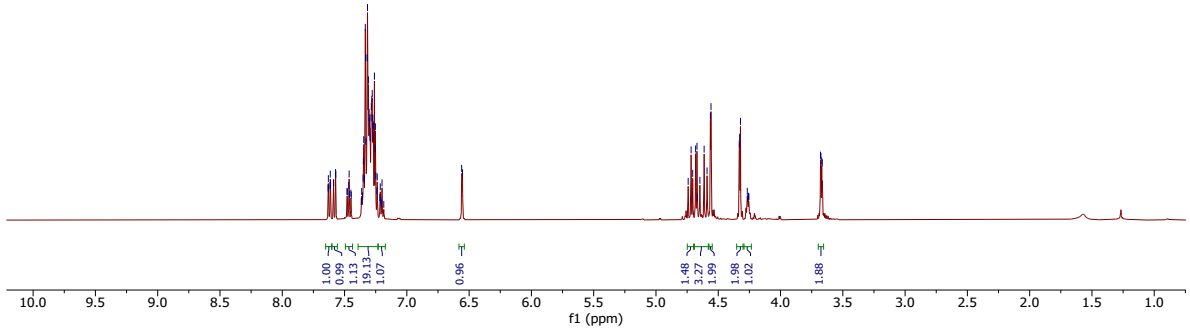
^{13}C NMR (126 MHz, $CDCl_3$)

naw-1-154polara.20.fid

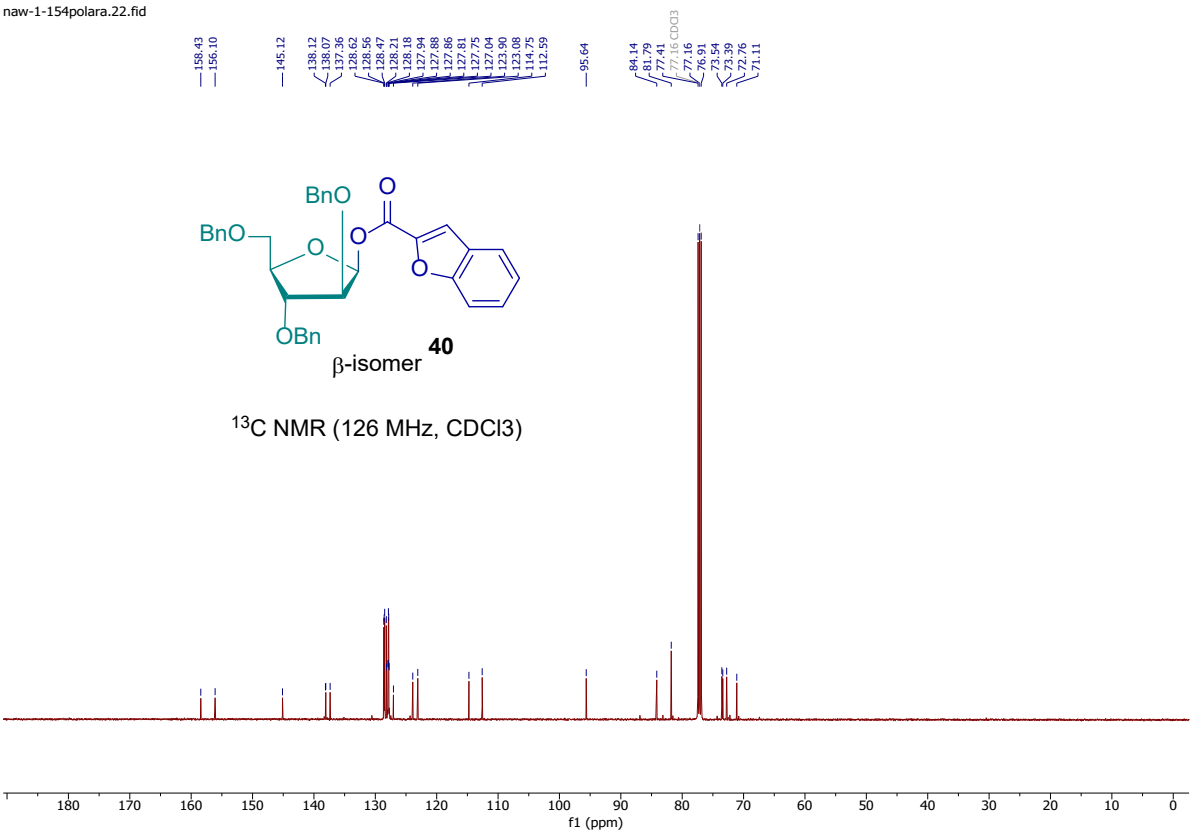


β-isomer **40**

^{1}H NMR (600 MHz, CDCl3)

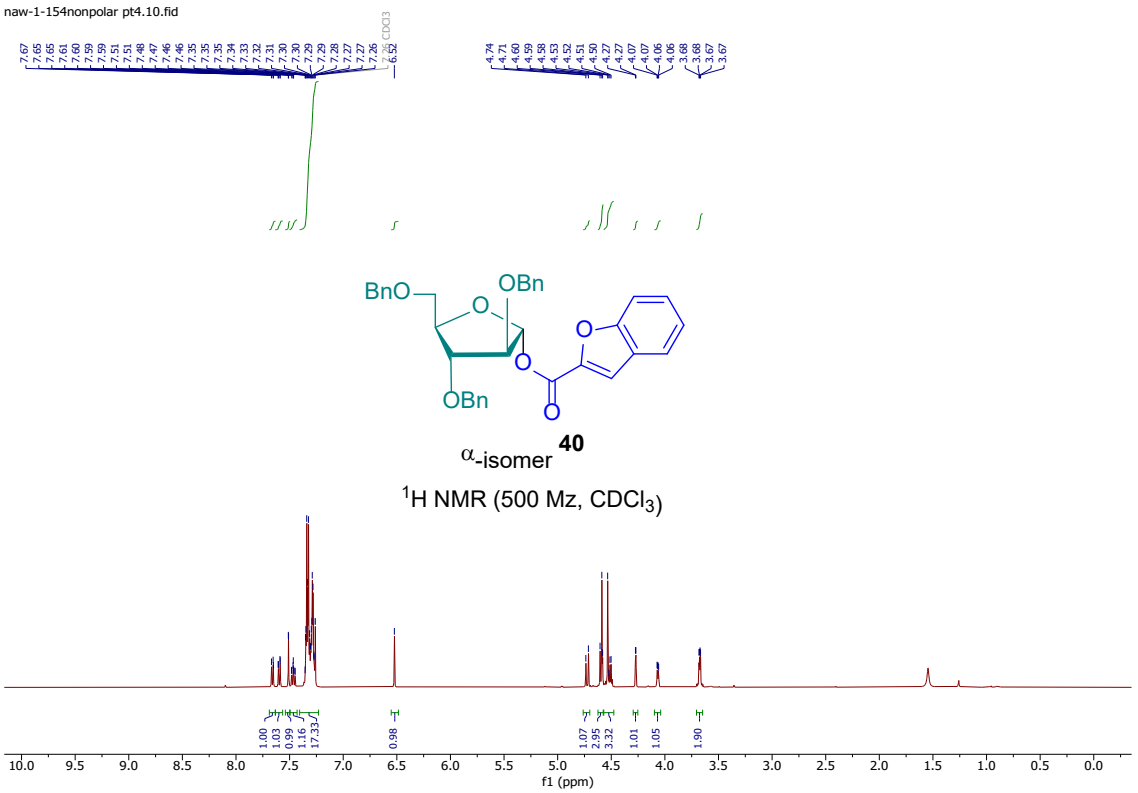


naw-1-154polara.22.fid



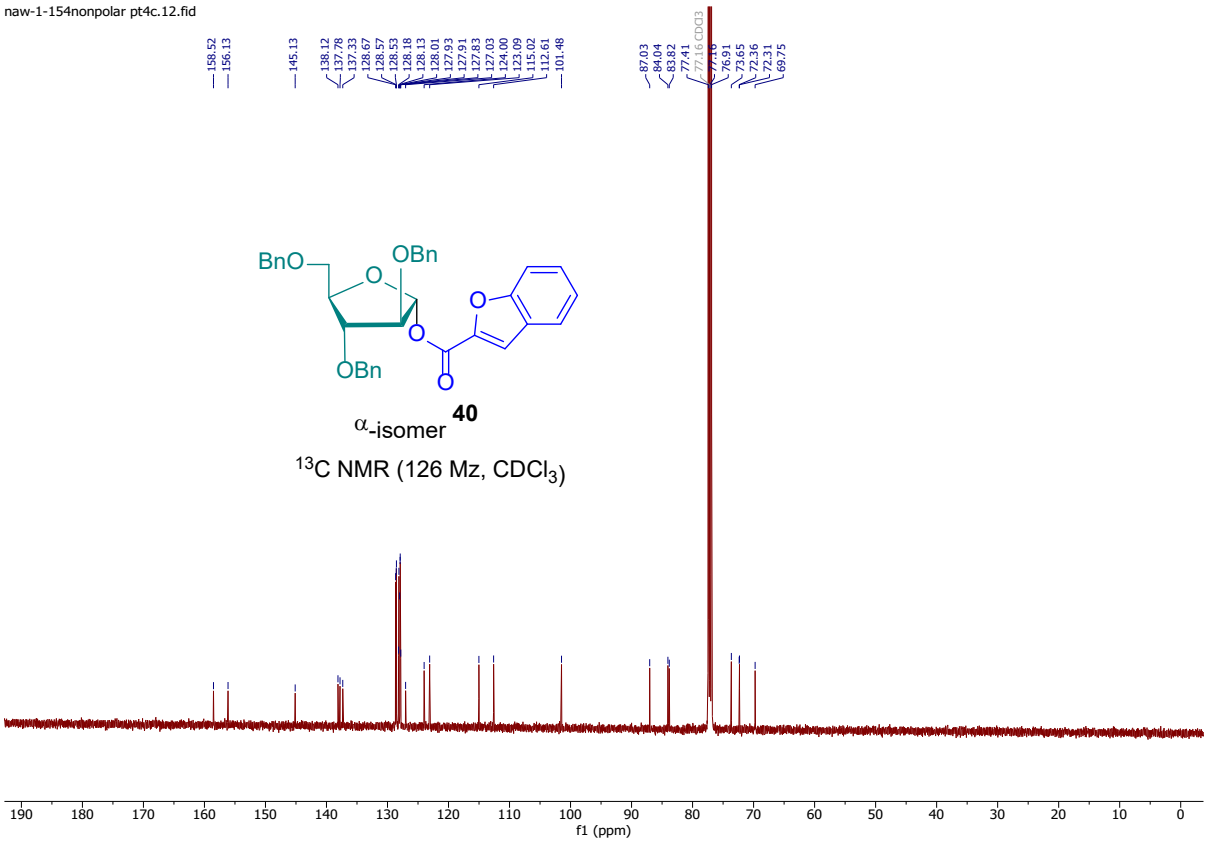
β-isomer **40**

^{13}C NMR (126 MHz, CDCl3)



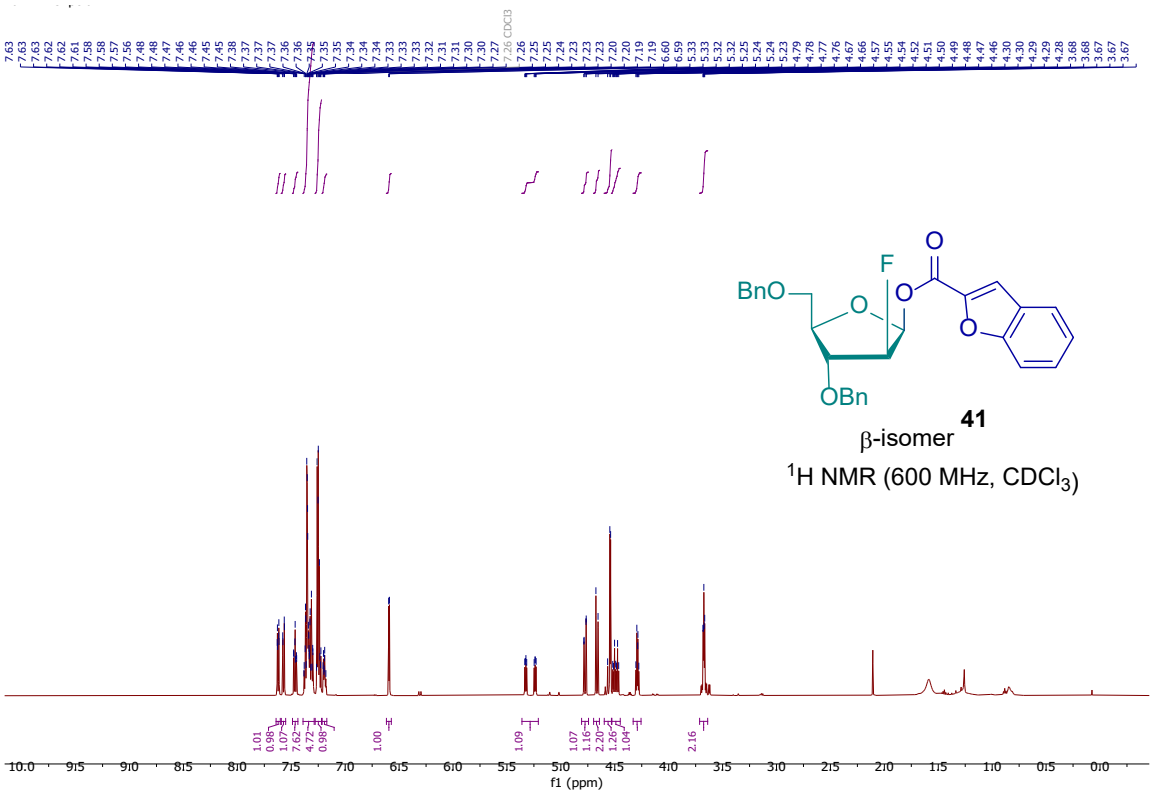
α-isomer **40**

^{1}H NMR (500 Mz, $CDCl_3$)



α-isomer **40**

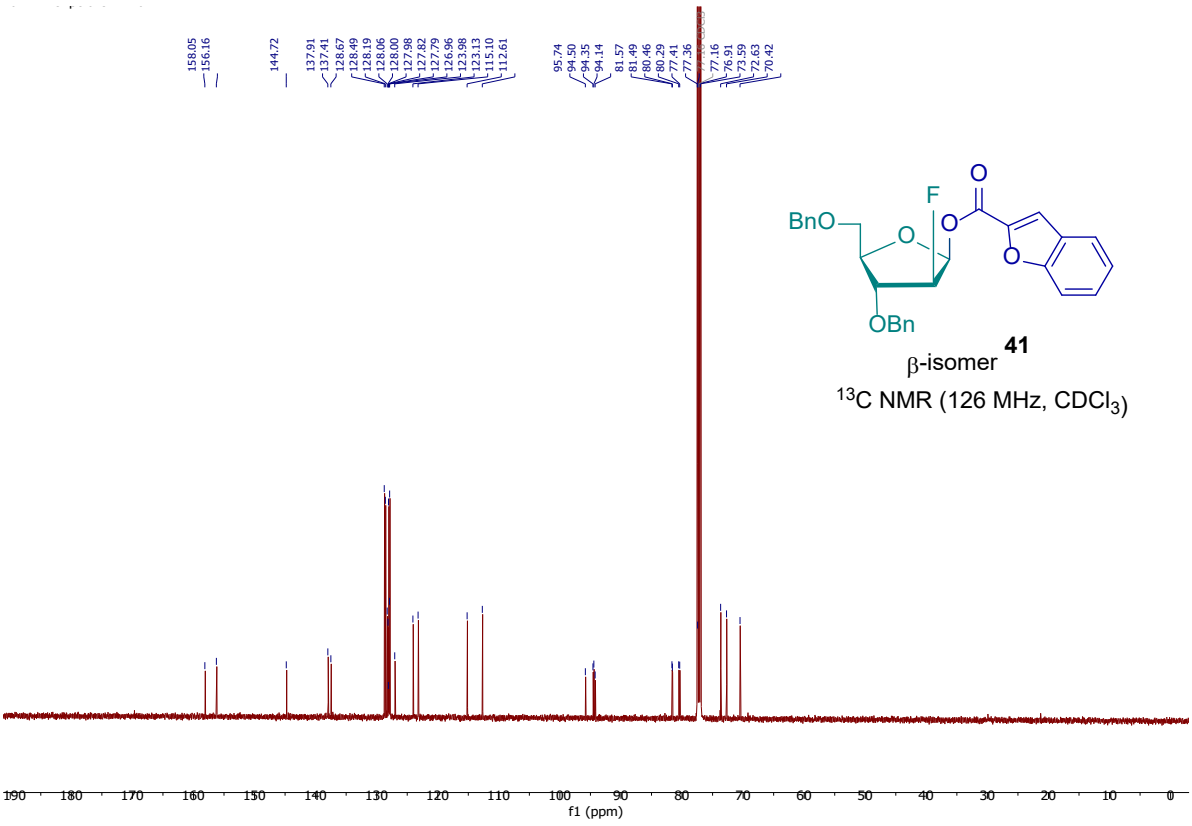
^{13}C NMR (126 Mz, $CDCl_3$)



41

β-isomer

^{1}H NMR (600 MHz, $CDCl_3$)

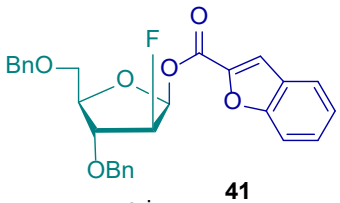


41

β-isomer

^{13}C NMR (126 MHz, $CDCl_3$)

naw-1-182polarF.20.fid

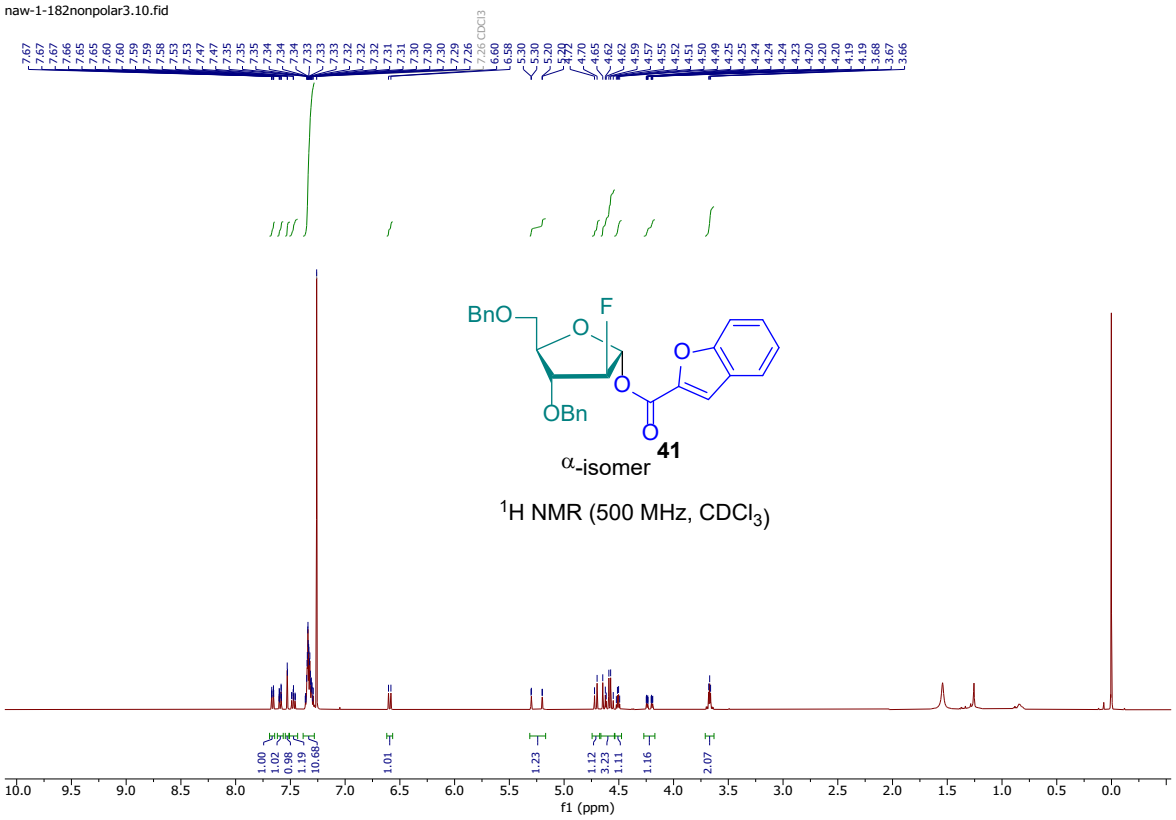


41

β-isomer

^{19}F NMR (471 MHz, $CDCl_3$)

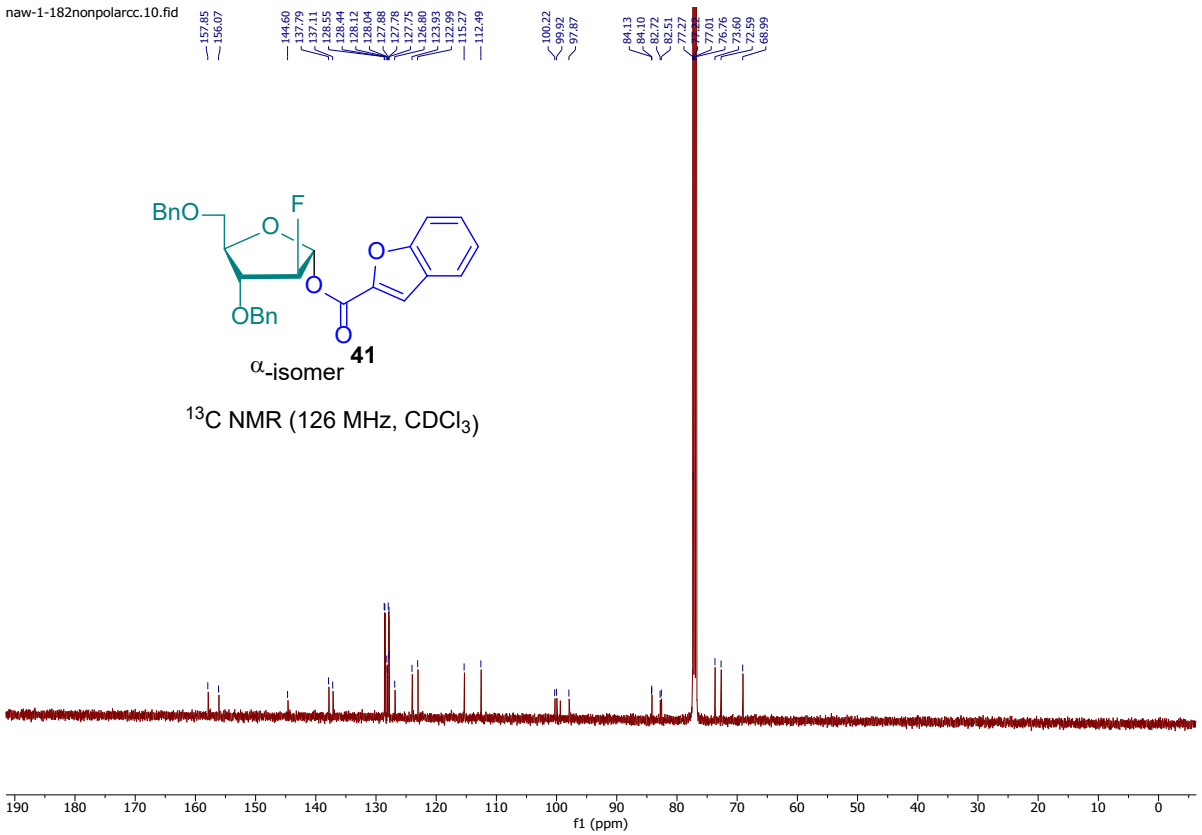
naw-1-182nonpolar3.10.fid



41

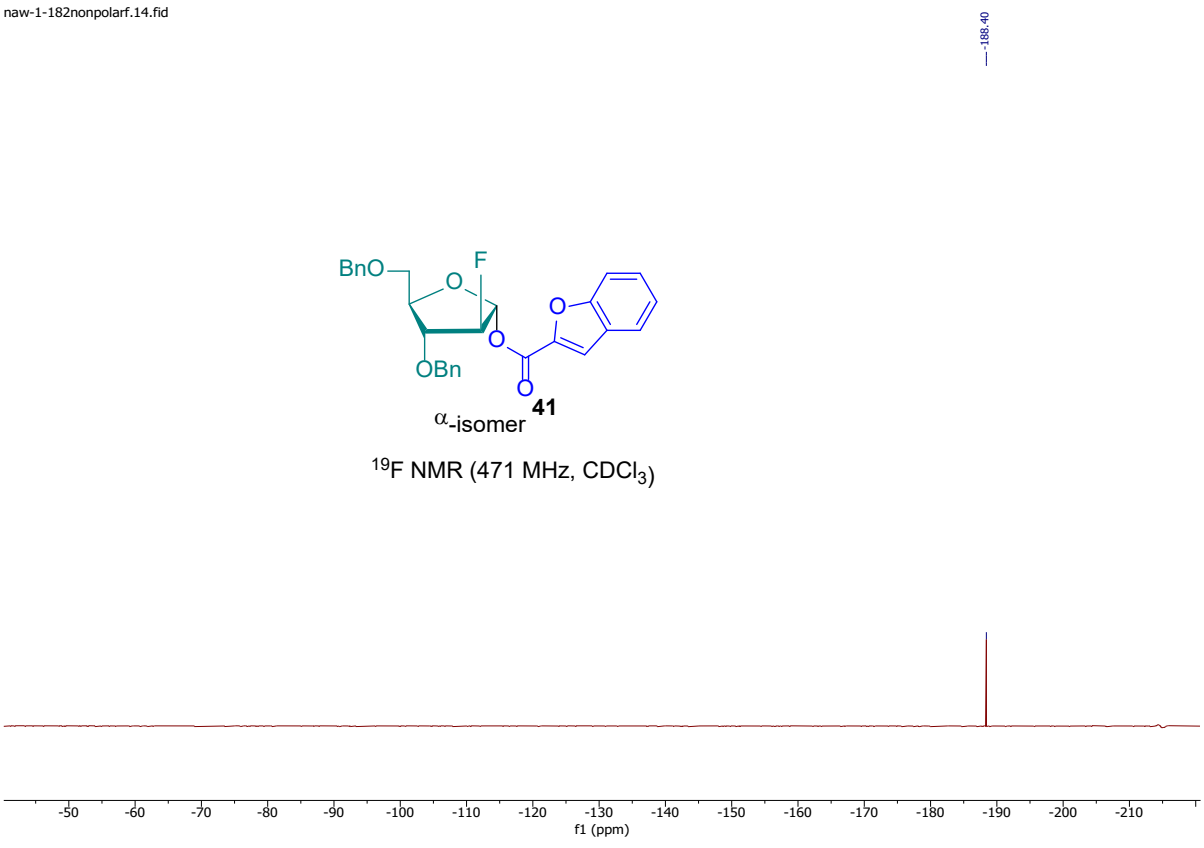
α-isomer

^{1}H NMR (500 MHz, $CDCl_3$)



α-isomer **41**

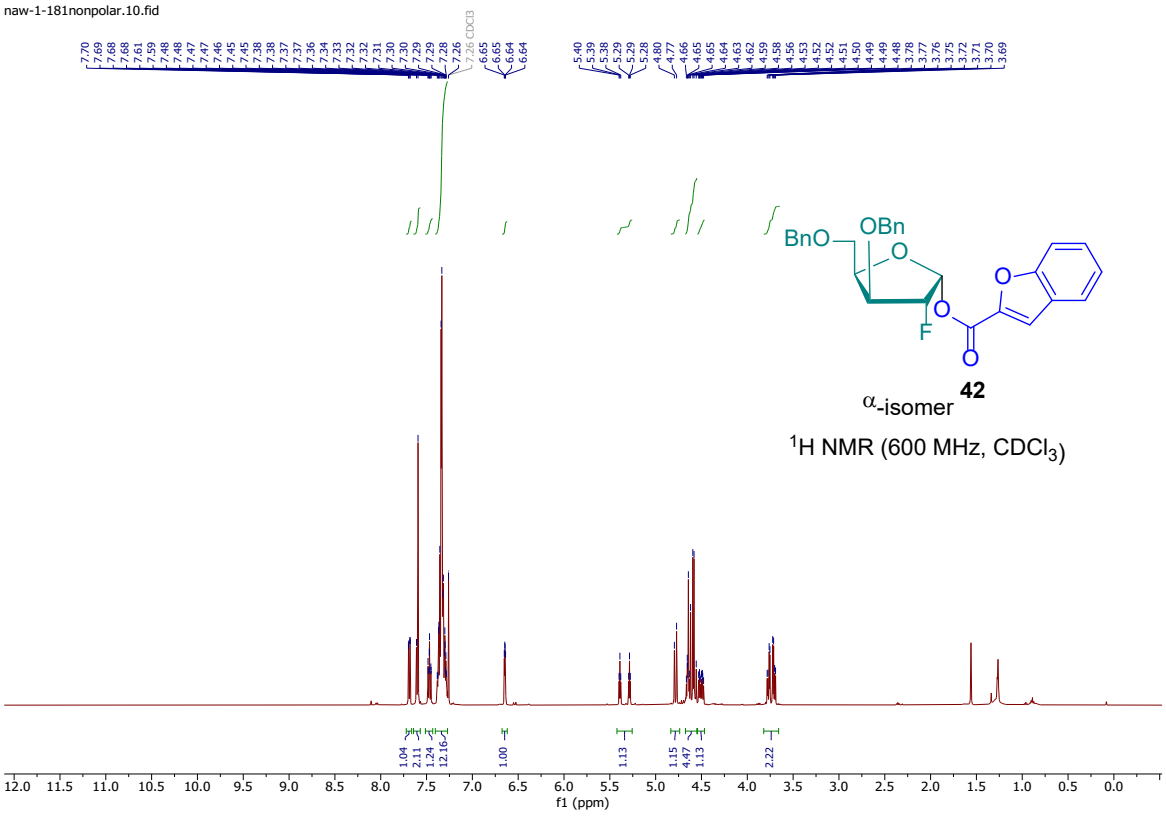
^{13}C NMR (126 MHz, $CDCl_3$)



α-isomer **41**

^{19}F NMR (471 MHz, $CDCl_3$)

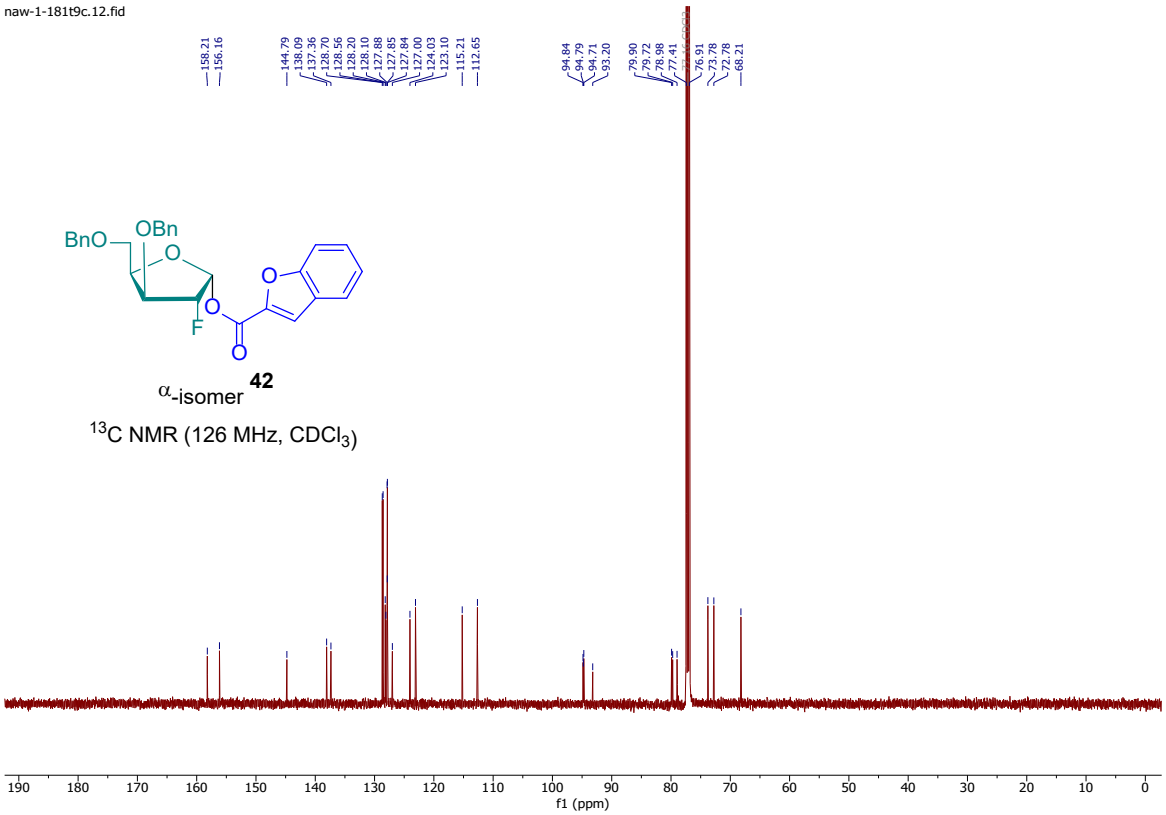
naw-1-181nonpolar.10.fid



α-isomer **42**

^{1}H NMR (600 MHz, $CDCl_3$)

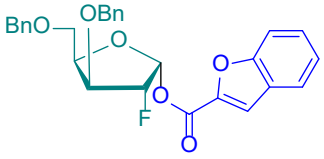
naw-1-181t9c.12.fid



α-isomer **42**

^{13}C NMR (126 MHz, $CDCl_3$)

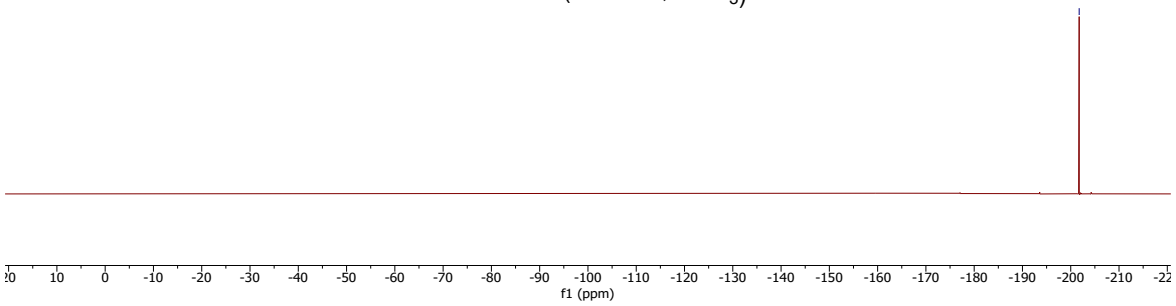
naw-1-181t9F.10.fid



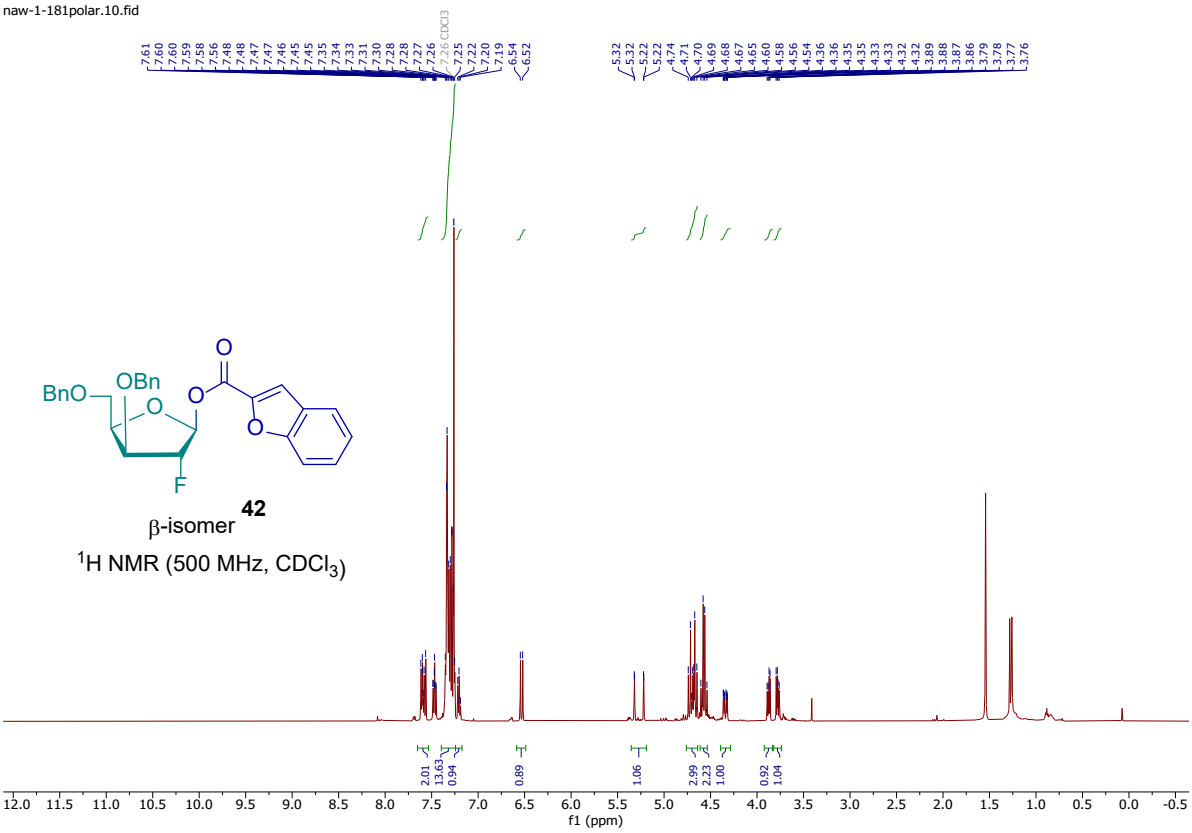
42

α-isomer

^{19}F NMR (471 MHz, $CDCl_3$)



naw-1-181polar.10.fid

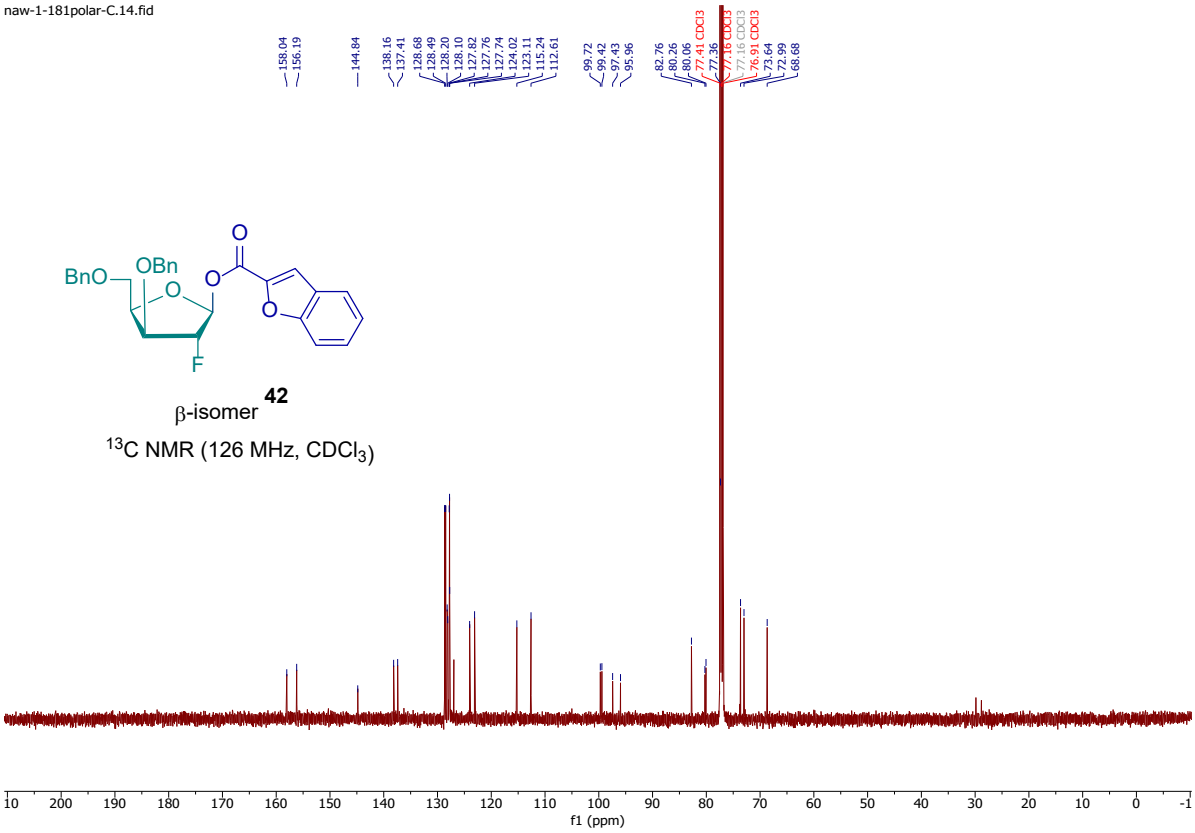


42

β-isomer

^{1}H NMR (500 MHz, $CDCl_3$)

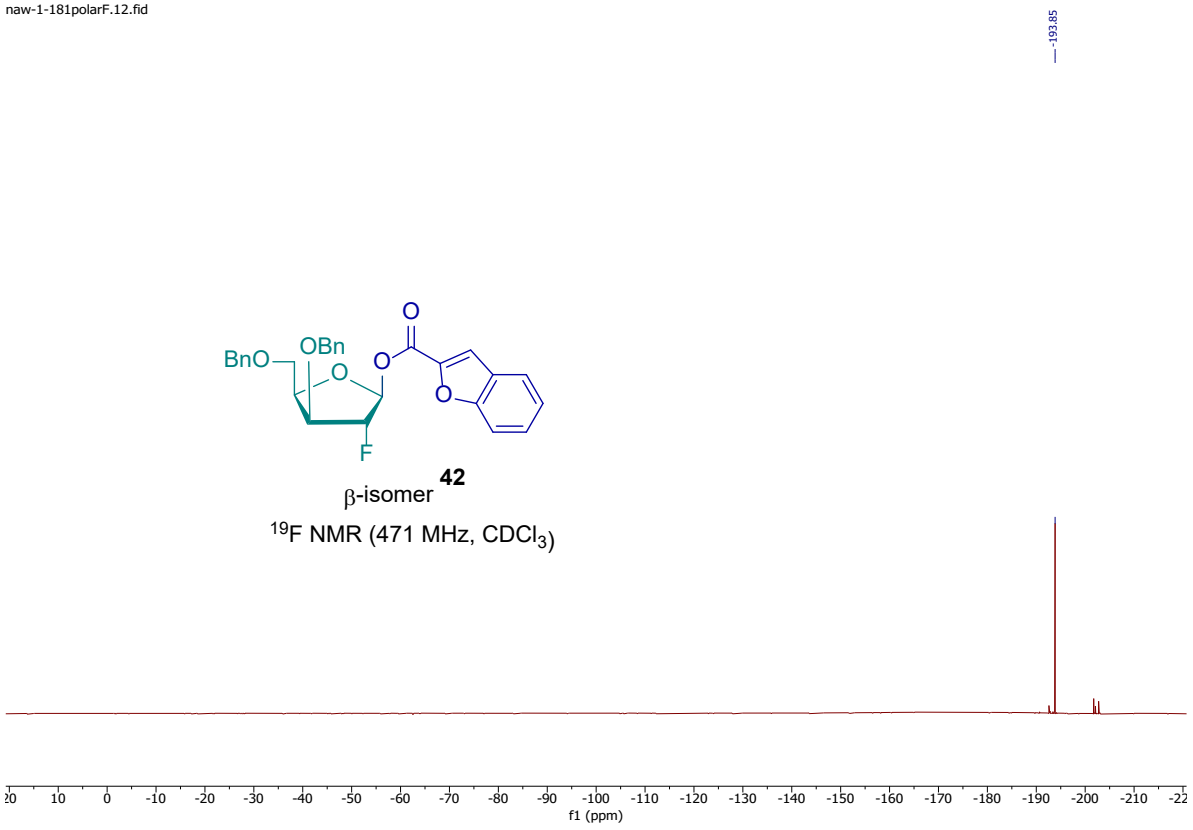
naw-1-181polar-C.14.fid



β-isomer **42**

^{13}C NMR (126 MHz, $CDCl_3$)

naw-1-181polarF.12.fid



β-isomer **42**

^{19}F NMR (471 MHz, $CDCl_3$)

11. Reference

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