Supporting information

Synthesis of photolabile protecting group (PPG) protected uronic acid building blocks: Applications in carbohydrate synthesis with the assistance of continuous flow photoreactor

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# These authors contributed equally to this work

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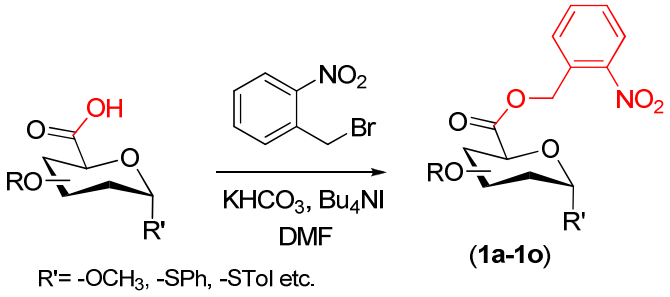
1. General Information

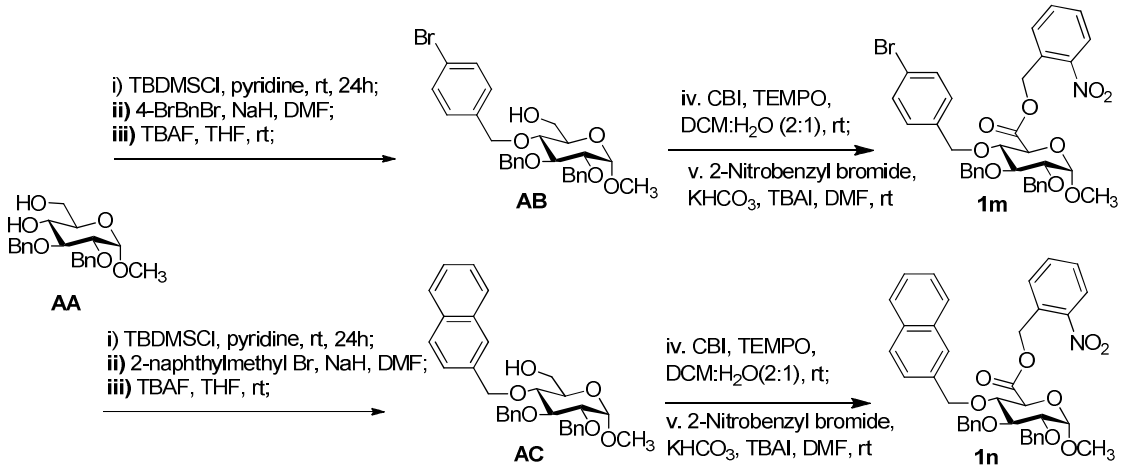
Starting materials were prepared using literature procedures or modified procedures. Solvents and chemicals were purchased from commercial sources and used without further purification. Thin layer chromatography was performed using pre-coated plates contained from E. Merck (TLC silica gel 60 F254). TLC plates were visualized by exposure to ultraviolet light (UV), and then further analyzed by charring in stain solution (5% H_2SO_4 in MeOH). The column chromatography was performed on silica gel (100-200 mesh) using a mixture of ethyl acetate/hexane and methanol/ethyl acetate as an eluent. The Continuous Flow Photoreactor was constructed with the help of M/s Lelesil innovative systems, Mumbai, India. The NMR spectra were recorded on BrukerAvance 500 MHz NMR spectrometer and Mass spectra were measured on Water's Quattro Micro V 4.1. All given ^{13}C spectra are proton decoupled. The ^{1}H NMR and ^{13}C NMRs of the monosaccharide primary alcohol and corresponding uronic acids were compared with literature reports.

2 (a)- General procedure for synthesis of uronic acid esters with 2-nitrobenzyl bromide: (1a-1o)



To a stirred solution of appropriate uronicacid (0.5 equiv.) in dry DMF, $KHCO_3$(4.0 equiv.), Bu_4NI (0.2 equiv.) and 2-nitrobenzyl bromide (3 equiv.) were added under argon atmosphere. The resulting mixture was stirred for 16 h at room temperature. After completion, the reaction mixture was filtered on celite. The filtrate was washed with water (2×50 mL) and dried over anhydrous sodium sulfate. The solvent was concentrated under reduced pressure to provide crude product which was purified by column chromatography on silica gel of 100-200 mesh size. Ethyl acetate/hexane was used as an eluent.

(b)- Preparation of uronic acid esters 1m and 1n:



1m preparation: The compound **AA** (3.0 g, 8.0 mmol) was stirred in dry pyridine (20 mL) in the presence of *tert*-butyldimethylsilyl chloride (1.81 g, 12.0 mmol) for overnight at room temperature. After completion, the reaction mixture was evaporated till dryness and dissolved in ethyl acetate. The resulting solution was washed with 0.1N HCl solution and brine solution. The crude was subjected for the column chromatography on silica (30% EtOAc: Hexane) to afford the primary TBDMS protected compound as a colorless syrup (3.13 g, 80% yield).

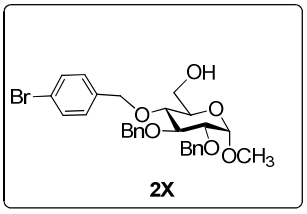
The TBDMS protected compound (1.0 g, 2.0 mmol) was dissolved in DMF (20 ml) at 0^{o}C to which NaH (98 mg, 2 equiv.) followed by 4-bromobenzylbromide (562 mg, 1.1 eq.) was added. The reaction was stirred until TLC starting material got consumed. The reaction was quenched using water (5 mL) and diluted with ethyl acetate (20 mL). The ethyl acetate layer was washed with cold water and evaporated in vacuo. The crude product was further dried under high vacuum and dissolved in THF (20 ml) to which TBAF (3.0 equiv.) was added and stirred until starting material disappeared. The solvent was evaporated and the residue was dissolved in ethyl acetate and washed with brine. The organic layer was evaporated in vacuo and purified using column chromatography (20% EtOAc: Hexane) to afford the pure compound **AB** (723 mg, 70%) as yellowish oil.

To a vigorously stirred solution of **AB** (700 mg, 1.3 mmol) in DCM and H_2O was added TEMPO (0.3 eq) and 1-chloro-1, 2-benziodoxol-3(1H)-one (CBI) (909 mg, 2.5 eq). Stirring was allowed until TLC indicated complete conversion of the starting material to a lower running spot (~ 45 min). The reaction mixture was quenched by the addition of 10 ml $Na_2S_2O_3$ solution (10% in H_2O). The mixture was then extracted twice with EtOAc (10 ml)

and the combined organic layers were dried (Na_2SO_4), filtered and concentrated. The crude compound was purified by column chromatography using EtOAc/petroleum ether which afforded the pure glucuronic acid (560 mg, 78%). Further the glucuronic acid (279 mg, 0.5 mmol) was converted into corresponding 2-nitrobenzyl ester **1m** by using the general procedure (**2a**) mentioned above. The reaction provided **1m** as pale yellow viscous liquid (325 mg, 94%).

1n preparation: The same procedure was adopted as above described for the preparation of **1m**. In the place of 4-bromobenzylbromide, 2-napthylmethylbromide (497mg, 1.1 eq.) was used. The compound **AC** was obtained as yellowish oil (736 mg, 75%). Corresponding glucuronic acid was obtained as pale yellow viscous compound (532 mg, 74%). The ester **1n** was obtained as pale yellow viscous liquid (309 mg, 93%).

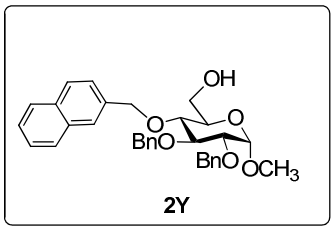
((2R,3R,4S,5R,6R)-4,5-bis(benzyloxy)-3-((4-bromobenzyl)oxy)-6-methoxytetrahydro-2H-pyran-2-yl)methanol (AB):



2X

Yellowish oil (667 mg, 60%); R_f value =0.4 in 20% EtOAc/ Hexane.IR: ν_{max}(neat) 3320, 1099, 652 cm^{-1}.$[\alpha]_D^{24}$= +45.0 [c 0.1, $CHCl_3$];^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 8.6, 1.9 Hz, 2H), 7.35–7.26 (m, 10H), 7.11 (d, *J* = 8.4 Hz, 2H), 4.98 (d, *J* = 11.0 Hz, 1H), 4.83–4.73 (m, 3H), 4.64 (d, *J* = 12.1 Hz, 1H), 4.57 (dd, *J* = 7.4, 3.9 Hz, 2H), 3.98 (t, *J* = 9.3 Hz, 1H), 3.76 (dd, *J* = 11.7, 2.4 Hz, 1H), 3.69–3.62 (m, 2H), 3.52–3.47 (m, 2H), 3.35 (s, 3H), 1.95 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.8, 138.1, 137.3, 131.6, 129.5, 128.6, 128.5, 128.2, 128.0, 127.9, 127.7, 121.7, 98.2, 81.9, 80.1, 77.6, 75.8, 74.2, 73.4, 70.8, 61.8, 55.3. HRMS: Calc. for $C_{28}H_{36}BrO_6[M+H]^+$: 543.1382, Obser. 543.1383

((2R,3R,4S,5R,6R)-4,5-bis(benzyloxy)-6-methoxy-3-(naphthalen-2-ylmethoxy)tetrahydro-2H-pyran-2-yl)methanol (AC):



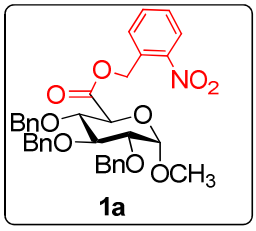
2Y

Yellowish oil (685 mg, 65 %); $R_f$value =0.4 in 20% EtOAc/ Hexane.IR: ν_{max}(neat) 3233, 1052, 631 cm^{-1}.$[\alpha]_D^{24}$= +25.0 [c 0.1, $CHCl_3$];^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79–7.74 (m, 3H), 7.69 (s, 1H), 7.45–7.41 (m, 2H), 7.39 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.36–7.24 (m,

10H), 5.01 (dd, *J* = 11.1, 6.6 Hz, 2H), 4.85 (d, *J* = 11.0 Hz, 1H), 4.79 (dd, *J* = 11.7, 7.1 Hz, 2H), 4.65 (d, *J* = 12.1 Hz, 1H), 4.57 (d, *J* = 3.6 Hz, 1H), 4.04 (t, *J* = 9.3 Hz, 1H), 3.78 (dd, *J* = 11.5, 2.3 Hz, 1H), 3.72–3.66 (m, 2H), 3.58 (t, *J* = 9.3 Hz, 1H), 3.51 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.35 (s, 3H), 1.89 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.9, 138.2, 135.7, 133.4, 133.1, 128.6, 128.5, 128.3, 128.2, 128.1, 127.8, 127.7, 126.8, 126.26, 126.0, 126.0, 98.3, 82.1, 80.1, 77.6, 75.8, 75.2, 73.5, 70.9, 62.0, 55.3. HRMS: Calc. for $C_{32}H_{34}O_6$ $[M+H]^+$: 515.2434, Obser. 515.2436

3. Analytical data of 2-nitrobenzyl protected uronic acid esters:

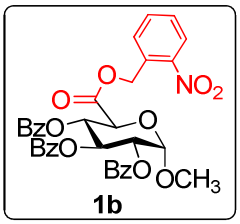
α-D-Glucopyranosiduronic acid, methyl-2,3,4-tris-*O*-(phenylmethyl)-2-nitrophenylmethyl ester(1a)



1a

Pale yellow viscous liquid (289 mg, 94%), $R_f$value =0.7 in 30% EtOAc/ Hexane. IR: ν_{max}(neat) 1742, 1425, 1120, 1090 cm^{-1}. $[\alpha]_D^{24}$= -21.7 [c 0.1, $CHCl_3$];^{1}H NMR (500 MHz, $CDCl_3$) *δ* 8.12 (dd, *J* = 5.9, 3.6 Hz, 1H), 7.53 (dd, *J* = 5.7, 3.5 Hz, 1H), 7.47–7.43 (m, 2H), 7.41–7.32 (m, 11H), 7.27 (dd, *J* = 4.8, 1.7 Hz, 2H), 7.21–7.19 (m, 2H), 5.60–5.53 (m, 2H), 5.02 (d, *J* = 10.9 Hz, 1H), 4.90–4.84 (m, 3H), 4.69 (t, *J* = 7.7 Hz, 2H), 4.60 (d, *J* = 11.0 Hz, 1H), 4.34 (d, *J* = 10.0 Hz, 1H), 4.07 (t, *J* = 9.3 Hz, 1H), 3.84 (t, *J* = 9.5 Hz, 1H), 3.64 (dd, *J* = 9.6, 3.5 Hz, 1H), 3.47 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) *δ* 169.1, 147.1, 138.4, 137.9, 133.9, 131.5, 128.7, 128.6, 128.5, 128.4, 128.4, 128.3, 128.2, 128.1, 128.0, 127.7, 127.7, 125.0, 98.8, 81.5, 79.4, 79.3, 75.9, 75.0, 73.6, 70.3, 63.7, 55.7. HRMS: Calc. for $C_{35}H_{36}NO_9$[M+H]$^+$:614.2390, Obser.614.2397.

α-D-Glucopyranosiduronic acid, methyl-2,3,4-tri-O-benzoyl-2-nitrophenylmethyl ester(1b)

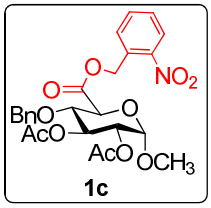


1b

Pale yellow viscous liquid (304 mg, 91%); $R_f$value =0.4 in 30% EtOAc/ Hexane.IR: ν_{max}(neat) 1750, 1719, 1420, 1099 cm^{-1}.$[\alpha]_D^{24}$= +93.0 [c 0.1, $CHCl_3$];^{1}H NMR (500 MHz, $CDCl_3$) *δ* 8.16–8.10 (m, 2H), 8.00 (dd, *J* = 17.6, 9.4 Hz, 3H), 7.77 (d, *J* = 7.7 Hz, 1H), 7.70 (dd, *J*= 11.9, 5.7 Hz, 2H), 7.62–7.33 (m, 11H), 5.86 (t, *J* = 9.6 Hz, 1H), 5.73 (d, *J* = 6.8 Hz, 1H), 5.51–5.41 (m, 1H), 5.26 (tdd, *J* = 42.0, 9.9, 3.6 Hz, 2H), 5.00 (s, 1H), 4.60 (d, *J* = 10.1 Hz, 1H), 4.49 (d, *J* = 9.8 Hz, 1H), 4.22 (td, *J* = 9.5, 2.7 Hz, 1H), 3.52 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) *δ* 169.0, 167.5, 166.8, 165.9, 147.4, 136.8, 134.1, 134.0, 133.6, 133.5, 133.4, 133.4, 131.3, 129.9, 129.9, 129.8, 129.4, 129.2, 129.0,

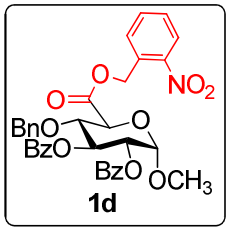
129.0, 128.9, 128.9, 128.4, 128.4, 128.4, 127.9, 125.2, 125.0, 97.5, 72.6, 71.0, 70.6, 64.1, 62.5, 56.0. HRMS: Calc. for $C_{35}H_{30}NO_{12}[M+H]^+$: 656.1768, Obser. 656.1772.

α-D-Glucopyranosiduronic acid, methyl 2, 3-di-O-acetyl-4-O-benzyl-2-nitrophenylmethyl ester (1c)



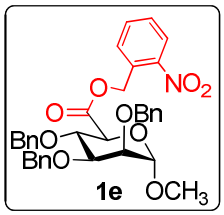
Pale yellow viscous liquid (240 mg, 93%); $R_f$value = 0.36 in 30% EtOAc/ Hexane. IR: ν_{max}(neat) 1745, 1735, 1410, 1215, 1090 cm^{-1}.$[\alpha]_D^{23}$= +44.5 [c 0.1, $CHCl_3$];^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15–8.13 (m, 1H), 7.54–7.48 (m, 3H), 7.29–7.27 (m, 4H), 7.20–7.18 (m, 2H), 5.65–5.56 (m, 3H), 5.00 (d, *J* = 3.5 Hz, 1H), 4.90 (dd, *J* = 10.2, 3.6 Hz, 1H), 4.59 (s, 2H), 4.40 (d, *J* = 9.9 Hz, 1H), 3.96 (t, *J* = 9.6 Hz, 1H), 3.48 (s, 3H), 2.09 (s, 3H), 1.98 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.3, 169.7, 168.4, 147.2, 137.3, 133.9, 131.4, 128.8, 128.5, 128.4, 127.9, 127.8, 125.1, 97.4, 77.6, 74.7, 71.3, 70.9, 69.9, 63.9, 55.7, 20.8, 20.7. HRMS: Calc. for $C_{25}H_{28}NO_{11}$ $[M+H]^+$: 518.1662, Obser. 518.1668

α-D-Glucopyranosiduronic acid, methyl 2, 3-di-O-benzoyl-4-O-benzyl-2-nitrophenylmethyl ester (1d)



Yellow viscous liquid (312 mg, 95%); R_f value = 0.42 in 30% EtOAc/ Hexane. IR: ν_{max}(neat) 1736, 1716, 1290, 1088, 1375 $cm^{-1}$$[\alpha]_D^{24}$= +62.9 [c 0.1, $CHCl_3$];^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 8.0, 1.2 Hz, 1H), 8.01–7.98 (m, 4H), 7.60–7.48 (m, 5H), 7.40 (ddd, *J* = 12.9, 7.5, 5.3 Hz, 4H), 7.16–7.08 (m, 5H), 6.11 (t, *J* = 9.7 Hz, 1H), 5.65 (q, *J* = 15.2 Hz, 2H), 5.26–5.21 (m, 2H), 4.63–4.58 (m, 2H), 4.55 (d, *J* = 9.9 Hz, 1H), 4.21 (t, *J* = 9.5 Hz, 1H), 3.50 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.4, 165.8, 165.4, 147.0, 136.9, 133.9, 133.3, 133.2, 131.4, 129.8, 129.6, 129.3, 128.8, 128.7, 128.4, 128.3, 128.2, 127.9, 127.8, 125.0, 97.5, 77.4, 74.7, 71.8, 71.7, 70.0, 63.8, 55.8. HRMS: Calc. for $C_{35}H_{32}NO_{11}$ $[M+H]^+$: 642.1975, Obser. 642.1970

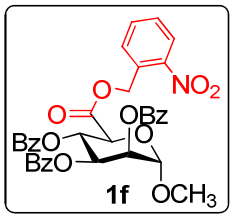
α-D-Mannopyranosiduronic acid, methyl-2, 3, 4-tris-*O*-(phenylmethyl)-2-nitrophenylmethyl ester (1e)



Pale yellow viscous liquid (261 mg, 85%); R_f value = 0.5 in 20% EtOAc/ Hexane. IR: ν_{max}(neat) 1752, 1445, 1135, 1075 cm^{-1}. $[\alpha]_D^{24}$= +4.7 [c 0.1, $CHCl_3$];^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11–8.13 (m, 1H), 7.55-7.53 (m, 1H), 7.45–7.22 (m, 18H), 5.54 (q, *J* = 15.3 Hz, 2H), 4.94 (d, *J* = 2.9 Hz, 1H), 4.85-4.73 (m, 3H), 4.66-4.60 (m, 3H), 4.36–4.27 (m, 2H), 3.93 (dd, *J* = 8.1, 3.0 Hz, 1H), 3.80 (t, *J* = 3.1 Hz, 1H), 3.46 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.8, 147.1, 138.2, 138.0, 138.0, 133.8, 131.9, 128.5, 128.5, 128.3, 128.3, 127.8, 127.7, 127.6, 127.6, 125.0,

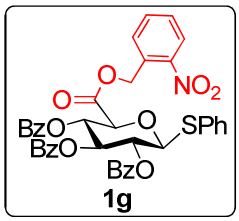
99.7, 78.7, 75.6, 74.5, 74.3, 72.9, 72.3, 72.0, 63.5, 55.6. HRMS: Calc. for $C_{35}H_{36}NO_9$ $[M+H]^+$: 614.2390, Obser. 614.2386

α-D-Mannopyranosiduronic acid, methyl 2, 3, 4-tri-O-benzoyl-2-nitrophenylmethyl ester (1f)



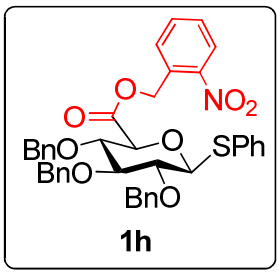
Pale yellow solid (291 mg, 89%); M.P:133-135 □; R_f value = 0.6 in 30% EtOAc/ Hexane. IR: ν_{max}(neat) 1755, 1729, 1414, 1040 cm^{-1}. $[\alpha]_D^{25}$= -60.2 [c 0.1, $CHCl_3$];^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14–8.08 (m, 4H), 7.99–7.97 (m, 2H), 7.87 (d, J = 8.1 Hz, 2H), 7.63–7.58 (m, 2H), 7.54–7.51 (m, 1H), 7.46–7.37 (m, 7H), 7.30–7.27 (m, 2H), 6.14 (t, J = 10.1 Hz, 1H), 5.95 (dd, J = 10.1, 3.3 Hz, 1H), 5.74 (dd, J = 3.1, 1.7 Hz, 1H), 5.03 (s, 1H), 4.75 (dd, J = 12.1, 2.4 Hz, 1H), 4.54 (dd, J = 12.1, 4.4 Hz, 1H), 4.47–4.39 (m, 1H), 3.57 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.2, 165.5, 165.4, 133.4, 133.4, 133.1, 133.0, 129.8, 129.8, 129.8, 129.7, 129.7, 129.3, 129.1, 129.0, 128.6, 128.47, 128.3, 98.7, 70.4, 70.0, 68.7, 66.9, 62.9, 55.6. HRMS: Calc. for $C_{35}H_{30}NO_{12}$ $[M+H]^+$: 656.1768, Obser. 656.1770

β-D-Glucopyranosiduronic acid, phenyl 2, 3, 4-tri-*O*-benzoyl-1-thio-2-nitrophenylmethyl ester (1g)



Yellow viscous liquid (338 mg, 92%); R_f value = 0.48 in 30% EtOAc/ Hexane.IR: ν_{max}(neat) 1748, 1718, 1422, 1140 cm^{-1} .$[\alpha]_D^{24}$= +18.7 [c 0.1, $CHCl_3$];^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (dd, J = 8.0, 1.5 Hz, 1H), 8.00–7.98(m, 2H), 7.86–7.82 (m, 4H), 7.58–7.28 (m, 17H), 5.94 (t, J = 9.4 Hz, 1H), 5.73 (t, J = 9.7 Hz, 1H), 5.65–5.51 (m, 3H), 5.11 (d, J = 9.9 Hz, 1H), 4.51 (d, J = 9.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.9, 165.6, 165.0, 164.9, 147.2, 133.8, 133.7, 133.4, 133.4, 133.3, 131.0, 130.9, 129.9, 129.8, 129.8, 129.0, 128.8, 128.7, 128.6, 128.5, 128.4, 128.4, 128.3, 125.0, 86.4, 77.2, 76.6, 73.5, 70.0, 69.9, 64.3. HRMS: Calc. for $C_{40}H_{32}NO_{11}S$ $[M+H]^+$: 734.1696, Obser. 734.1699

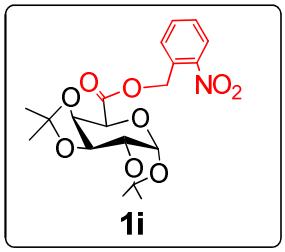
β-D-Glucopyranosiduronic acid, phenyl-2, 3, 4-tris-*O*-(phenylmethyl)-1-thio-2-nitrophenylmethyl ester (1h)



Pale yellow viscous liquid (311 mg, 90%); R_f value = 0.6 in 30% EtOAc/ Hexane. IR: ν_{max}(neat) 1743, 1520, 1145, 1130 cm^{-1}. $[\alpha]_D^{24}$= -2.9 [c 0.1, $CHCl_3$];^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18–8.10 (m, 1H), 7.56–7.20 (m, 22H), 5.53 (d, J = 5.3 Hz, 2H), 5.28 (d, J = 3.1 Hz, 1H), 4.94 (d, J = 10.8 Hz, 1H), 4.87–4.80 (m, 3H), 4.71 (d, J = 11.8 Hz, 1H), 4.61 (t, J = 10.4 Hz, 2H), 4.04 (t, J = 9.0 Hz, 1H), 3.84 (t, J = 9.2 Hz, 1H), 3.65 (dd, J = 9.1, 3.3

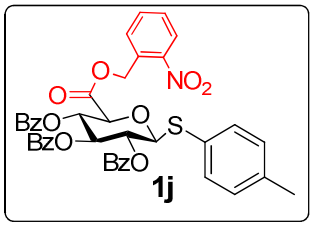
Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.1, 147.0, 138.2, 137.7, 137.5, 133.9, 131.6, 128.6, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.1, 127.9, 127.9, 127.8, 127.7, 125.0, 97.8, 91.7, 80.7, 79.2, 78.9, 75.7, 74.9, 73.5, 70.6, 63.6. HRMS: Calc. for $C_{40}H_{38}NO_8S$ $[M+H]^+$: 692.2318, Obser. 692.2315

α-D-galactopyranosiduronic acid- 1, 2, 3, 4-Di-*O*-isopropylidene-2-nitrophenylmethyl ester (1i)



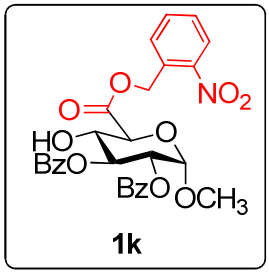
Pale yellow viscous liquid (180 mg, 88%); R_f value = 0.5 in 30% EtOAc/ Hexane. IR: ν_{max}(neat) 1747, 1465, 1235 cm^{-1}. $[\alpha]_D^{24}$= -62.4 [c 0.1, $CHCl_3$];^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, J = 8.2 Hz, 1H), 7.75 (d, J = 7.8 Hz, 1H), 7.64 (t, J = 7.6 Hz, 1H), 7.49 (t, J = 7.8 Hz, 1H), 5.75–5.67 (m, 11H), 5.31 (s, 1H), 4.68 (ddd, J = 28.6, 7.7, 2.3 Hz, 2H), 4.56 (d, J = 2.0 Hz, 1H), 4.41 (dd, J = 4.9, 2.6 Hz, 1H), 1.55 (s, 3H), 1.46 (s, 3H), 1.36 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 167.8, 147.2, 133.6, 132.0, 129.0, 128.6, 124.9, 110.0, 109.1, 96.5, 72.1, 70.7, 70.2, 68.6, 63.5, 25.9, 25.8, 24.7, 24.6. HRMS: Calc. for $C_{19}H_{24}NO_9$ $[M+H]^+$: 410.1451, Obser. 410.1448

β-D-Glucopyranosiduronic acid, 4-Methylphenyl-2, 3, 4-*tri*-*O*-benzoyl-1-thio-2-nitrophenyl-methyl ester (1j)



Pale yellow viscous liquid (347 mg, 93%); R_f value = 0.5 in 30% EtOAc/ Hexane.IR:ν_{max}(neat) 1738, 1720, 1255, 1445 $cm^{-1}$$[\alpha]_D^{24}$= +10.7 [c 0.1, $CHCl_3$];^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (dd, J = 8.0, 1.4 Hz, 1H), 7.99–7.97 (m, 2H), 7.84–7.80 (m, 4H), 7.52 (dd, J = 10.5, 4.2 Hz, 2H), 7.46–7.38 (m, 8H), 7.32–7.25 (m, 5H), 7.13 (d, J = 7.9 Hz, 2H), 5.93 (t, J = 9.4 Hz, 1H), 5.69 (t, J = 9.7 Hz, 1H), 5.58 (dd, J = 38.5, 14.8 Hz, 2H), 5.48 (t, J = 9.6 Hz, 1H), 5.04 (d, J = 9.9 Hz, 1H), 4.48 (d, J = 9.8 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.9, 165.6, 165.0, 164.9, 147.2, 139.1, 134.4, 133.7, 133.4, 133.4, 133.3, 131.0, 129.8, 129.8, 129.8, 129.8, 129.1, 129.0, 128.8, 128.6, 128.5, 128.4, 128.4, 128.3, 126.8, 125.0, 86.5, 76.6, 73.5, 70.0, 69.9, 64.2, 21.2. HRMS: Calc. for $C_{41}H_{34}NO_{11}S$ $[M+H]^+$: 748.1853, Obser. 748.1855

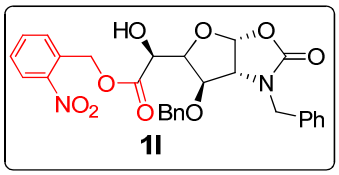
α-D-Glucopyranosiduronic acid, methyl-2-nitrophenylmethyl ester-2, 3-dibenzoate (1k)



1k

Pale yellow viscous liquid (177 mg, 83%); R_f value = 0.5 in 40% EtOAc/ Hexane. IR: ν_{max}(neat) 3250, 1756, 1718, 1360, 1180, 1080 cm^{-1} $[\alpha]_D^{23}$= +134.5 [c 0.1, $CHCl_3$]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.2 Hz, 1H), 8.00–7.95 (m, 4H), 7.73–7.68 (m, 1H), 7.50 (dd, *J* = 4.5, 2.9 Hz, 3H), 7.36 (t, *J* = 7.5 Hz, 5H), 5.89–5.85 (m, 1H), 5.71 (q, *J* = 15.0 Hz, 2H), 5.25 (s, 2H), 4.49 (d, *J* = 9.9 Hz, 1H), 4.22 (t, *J* = 9.6 Hz, 1H), 3.49 (s, 3H), 3.47 (d, *J* = 0.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.9, 165.7, 162.5, 147.1, 133.9, 133.3, 133.2, 131.3, 129.7, 129.7, 129.5, 129.1, 128.8, 128.8, 128.7, 128.3, 128.2, 125.0, 97.4, 72.4, 71.0, 70.6, 70.5, 63.9, 55.8. HRMS: Calc. for $C_{28}H_{26}NO_{11}$ $[M+H]^+$: 552.1506, Obser. 552.1501

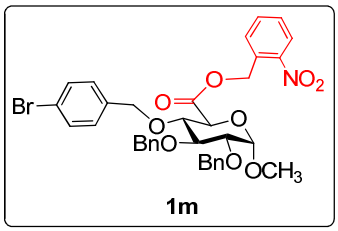
(2S)-2-nitrobenzyl-2-((3aR, 6R, 6aR)-1-benzyl-6-(benzyloxy)-2-oxohexahydrofuro[3, 2-d]oxazol-5-yl)-2-hydroxyacetate (1l)



1l

Pale yellow viscous liquid (214 mg, 80%); R_f value = 0.6 in 50% EtOAc/ Hexane. IR: ν_{max}(neat) 3355, 1762, 1751, 1290, 1120, 1075 cm^{-1}. $[\alpha]_D^{24}$= -48.6 [c 0.1, $CHCl_3$]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10–8.09(m, 1H), 7.52–7.45 (m, 3H), 7.41–7.38 (m, 3H), 7.29–7.27 (m, 4H), 7.24–7.22 (m, 2H), 7.12–7.10 (m, 2H), 6.22 (d, *J* = 5.5 Hz, 1H), 5.61 (dd, *J* = 80.6, 14.8 Hz, 2H), 4.85 (d, *J* = 3.6 Hz, 1H), 4.69 (d, *J* = 15.1 Hz, 1H), 4.32 (s, 2H), 4.20–4.17 (m, 2H), 4.10 (d, *J* = 5.6 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.0, 156.3, 147.3, 136.2, 134.9, 133.8, 131.1, 129.2, 129.1, 129.0, 128.6, 128.6, 128.3, 128.2, 127.6, 125.0, 101.0, 80.0, 79.9, 77.2, 72.4, 63.8, 63.7, 47.6. HRMS: Calc. for $C_{28}H_{27}N_2O_9$ $[M+H]^+$: 535.1717, Obser. 535.1723

(2S,3S,4S,5R,6R)-2-nitrobenzyl-4,5-bis(benzyloxy)-3-(4-bromobenzyloxy)-6-methoxytetra-hydro-2H-pyran-2-carboxylate (1m)

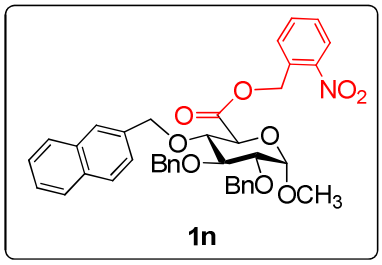


1m

Pale yellow viscous liquid (325 mg, 94%); R_f value = 0.52 in 20% EtOAc/ Hexane. IR: ν_{max}(neat)1730, 1520, 1250, 1070, 565 cm^{-1} $[\alpha]_D^{24}$= -7.8 [c 0.1, $CHCl_3$]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17–8.06 (m, 1H), 7.50–7.46 (m, 3H), 7.38–7.28 (m, 12H), 7.02 (d, *J* = 8.1 Hz, 2H), 5.57 (q, *J* = 15.0 Hz, 2H), 4.99 (d, *J* = 10.9 Hz, 1H), 4.83–4.76 (m, 3H), 4.69–4.66 (m, 2H), 4.50 (d, *J* = 11.3 Hz, 1H), 4.29 (d, *J* = 10.0 Hz, 1H), 4.02 (t, *J* = 9.3 Hz, 1H), 3.77 (t, *J* = 9.5 Hz, 1H), 3.61 (dd, *J* = 9.6, 3.5 Hz, 1H), 3.46 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.0,

147.3, 138.4, 137.8, 136.9, 133.7, 131.3, 131.3, 129.2, 128.8, 128.7, 128.5, 128.4, 128.1, 128.1, 127.9, 127.7, 125.1, 121.5, 98.8, 81.3, 79.4, 79.3, 75.8, 74.1, 73.6, 70.1, 63.7, 55.7. HRMS: Calc. for $C_{35}H_{34}BrNO_9[M+H]^+$: 691.1417, Obser.691.1415

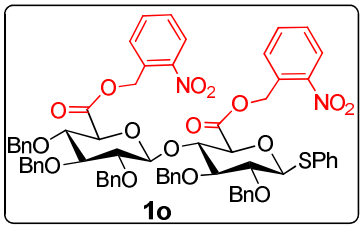
(2S,3S,4S,5R,6R)-2-nitrobenzyl-4,5-bis(benzyloxy)-6-methoxy-3-(naphthalen-2-ylmethoxy)-tetrahydro-2H-pyran-2-carboxylate (1n)



1n

Pale yellow viscous liquid (309 mg, 93%); R_f value = 0.5 in 20% EtOAc/ Hexane. IR: ν_{max}(neat) 1735, 1515, 1268, 1077 cm^{-1}. $[\alpha]_D^{25}$= -8.9 [c 0.1, $CHCl_3$];^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, J = 7.9 Hz, 1H), 7.79–7.78 (m, 1H), 7.73–7.68 (m, 2H), 7.61 (s, 1H), 7.47–7.25 (m, 17H), 5.50 (dd, J = 45.3, 15.2 Hz, 2H), 5.03 (dd, J = 11.0, 5.5 Hz, 2H), 4.87 (dd, J = 14.7, 11.6 Hz, 2H), 4.71 (dd, J = 21.0, 8.6 Hz, 3H), 4.36 (d, J = 9.9 Hz, 1H), 4.10 (t, J = 9.2 Hz, 1H), 3.88 (t, J = 9.5 Hz, 1H), 3.66 (dd, J = 9.6, 3.4 Hz, 1H), 3.47 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 169.0, 147.0, 138.4, 137.9, 135.3, 133.7, 133.1, 132.9, 131.4, 128.5, 128.4, 128.1, 128.1, 128.0, 128.0, 127.8, 127.7, 127.6, 126.4, 126.0, 125.9, 125.7, 124.9, 98.8, 81.5, 79.4, 79.3, 75.9, 75.1, 73.6, 70.3, 63.7, 55.7. HRMS: Calc. for $C_{39}H_{37}NO_9$ $[M+H]^+$: 663.2468, Obser. 663.2471

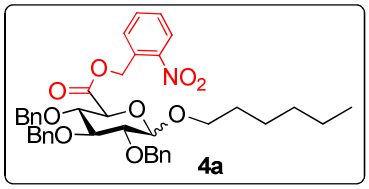
β-D-Glucopyranosiduronic acid, phenyl-4-*O*-[6-methyl-2, 3, 4-*tris*-*O*-(phenylmethyl)-β-D-mannopyranuronosyl]-2, 3-*bis*-*O*-(phenylmethyl)-1-thio-2-nitrophenylmethyl ester (1o)



1o

Pale yellow viscous liquid (532 mg, 92%); R_f value = 0.5 in 30% EtOAc/ Hexane. IR: ν_{max}(neat) 1755, 1745, 1395, 1285, 1076 cm^{-1}. $[\alpha]_D^{24}$= +8.8 [c 0.1, $CHCl_3$];^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12-7.20 (m, 38H), 5.88 (s, 1H), 5.57 (dd, J = 42.3, 15.3 Hz, 2H), 4.96–4.47 (m, 15H), 4.06 (t, J = 9.3 Hz, 1H), 3.91-3.83 (m, 3H), 3.64–3.61 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.7, 168.9, 147.1, 138.5, 138.0, 138.0, 137.1, 137.0, 134.1, 131.7, 128.8, 128.7, 128.7, 128.7, 128.6, 128.5, 128.2, 128.2, 128.0, 128.0, 128.0, 127.9, 127.9, 127.8, 127.8, 125.2, 102.5, 98.9, 81.2, 79.3, 77.4, 75.9, 75.3, 75.3, 74.1, 73.5, 73.0, 73.0, 72.3, 72.2, 71.1, 63.9. HRMS: Calc. for $C_{67}H_{63}N_2O_{16}S$ $[M+H]^+$: 1183.3898, Obser. 1183.3900

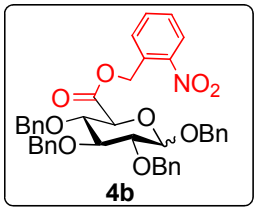
β-D-Glucopyranosiduronicacid,hexyl, 2, 3, 4-*tri-O*-benzyl-2-nitrophenylmethyl ester (4a)



4a

Pale yellow solid (304 mg, 89%); M.P: 96-97 □; R_f value = 0.7 in 30% EtOAc/ Hexane. β:α isomer (>20:1); IR: ν_{max}(neat) 1751, 1517, 1305, 1125 cm^{-1}. $[\alpha]_D^{24}$= -9.6 [c 0.1, $CHCl_3$];^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15–8.13 (m, 1H), 7.58–7.56 (m, 1H), 7.49–7.45 (m, 2H), 7.39–7.30 (m, 10H), 7.29–7.25 (m, 3H), 7.19 (dd, *J* = 6.8, 2.8 Hz, 2H), 5.63 (d, *J* = 15.3 Hz, 1H), 5.53 (d, *J* = 15.2 Hz, 1H), 4.97 (dd, *J* = 10.8, 9.6 Hz, 2H), 4.85 (dd, *J* = 16.8, 11.0 Hz, 2H), 4.76 (d, *J* = 10.9 Hz, 1H), 4.61 (d, *J* = 11.0 Hz, 1H), 4.53 (d, *J* = 7.7 Hz, 1H), 4.04–3.96 (m, 2H), 3.92 (t, *J* = 9.4 Hz, 1H), 3.73 (t, *J* = 9.1 Hz, 1H), 3.61-3.53 (m, 2H), 1.71–1.66 (m, 3H), 1.45–1.29 (m, 7H), 0.92 (dd, *J* = 9.5, 4.6 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.9, 147.1, 138.3, 138.2, 137.8, 133.8, 131.7, 128.6, 128.5, 128.4, 128.3, 128.1, 127.9, 127.8, 127.8, 127.7, 127.7, 125.0, 104.0, 83.9, 81.7, 78.9, 75.7, 74.9, 74.8, 74.5, 70.5, 63.6, 31.6, 29.6, 25.8, 22.5, 14.0. HRMS: Calc. for $C_{40}H_{46}NO_9$ $[M+H]^+$: 684.3173, Obser. 684.3168

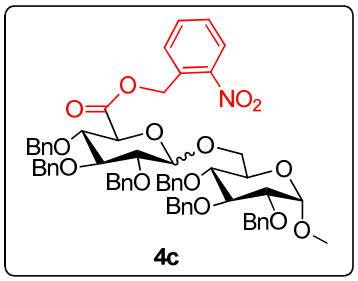
β-D-Glucopyranosiduronic acid-1, 2, 3, 4-*tetra-O*-benzyl-2-nitrophenylmethyl ester (4b)



4b

Pale yellow powder. (293 mg, 85%); M.P: 124-126 □; R_f value = 0.72 in 30% EtOAc/ Hexane. β:α isomer (>20:1); IR: ν_{max}(neat) 1775, 1480, 1310, 1095 cm^{-1}. $[\alpha]_D^{24}$= -22.9 [c 0.1, $CHCl_3$];^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15–8.13(m, 1H), 7.59–7.57 (m, 1H), 7.48–7.45 (m, 2H), 7.41–7.26 (m, 19H), 7.21–7.18 (m, 2H), 5.59 (dd, *J* = 49.7, 15.2 Hz, 2H), 5.02–4.93 (m, 3H), 4.84 (dd, *J* = 21.8, 11.0 Hz, 2H), 4.73 (dd, *J* = 22.2, 11.3 Hz, 2H), 4.64 (dd, *J* = 13.2, 9.3 Hz, 2H), 4.05 (d, *J* = 9.7 Hz, 1H), 3.96–3.93 (m, 1H), 3.74 (t, *J* = 9.0 Hz, 1H), 3.63 (dd, *J* = 9.0, 7.6 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.9, 147.2, 138.2, 138.1, 137.8, 137.0, 133.8, 131.6, 128.7, 128.6, 128.5, 128.4, 128.4, 128.4, 128.3, 128.1, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 127.7, 125.0, 102.8, 83.9, 81.8, 78.9, 75.7, 74.9, 74.6, 71.4, 63.7. HRMS: Calc. for $C_{41}H_{40}NO_9$ $[M+H]^+$: 690.2703, Obser. 690.2702

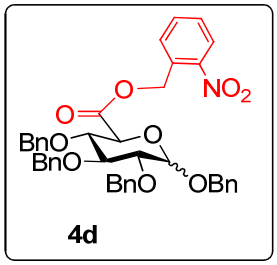
α-D-Glucopyranoside,methyl-6-*O*-[6-methyl-2,3,4-*tris*-*O*-(phenylmethyl)-D-glucopyranurono-syl]-2, 3, 4-*tris*-*O*-(phenylmethyl)-2-nitrophenylmethyl ester (4c)



4c

Yellow solid (408 mg, 78%); M.P: 103-105 □; R_f value = 0.5 in 30% EtOAc/ Hexane. β:α isomer (3:2); IR: ν_{max}(neat) 1762, 1487, 1254, 1082 cm^{-1}. $[\alpha]_D^{24}$= +12.1 [c 0.1, $CHCl_3$];^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12–8.09 (m, 1H), 7.45–7.39 (m, 2H), 7.38–7.24 (m, 29H), 7.18 (ddd, *J* = 7.7, 6.7, 1.7 Hz, 3H), 5.62–5.43(m, 2H), 5.03–4.92 (m, 3H), 4.88–4.52 (m, 10H), 4.44 (t, *J* = 8.8 Hz, 1H), 4.17 (dd, *J* = 10.8, 1.7 Hz, 1H), 4.04–3.97 (m, 2H), 3.91–3.78 (m, 3H), 3.71–3.46 (m, 4H), 3.37 (d, *J* = 29.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.2, 167.7, 147.1, 138.8, 138.4, 138.3, 138.3, 138.2, 138.1, 138.1, 138.0, 137.8, 133.8, 133.7, 131.6, 131.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.2, 128.1, 128.0, 128.0, 127.9, 127.9, 127.9, 127.8, 127.7, 127.7, 127.7, 127.6, 127.6, 127.6, 127.5, 127.5, 125.0, 124.9, 104.1, 98.0, 98.0, 97.8, 84.0, 82.1, 81.9, 81.5, 81.0, 80.1, 79.8, 79.5, 79.3, 78.8, 77.9, 77.7, 77.2, 75.7, 75.7, 75.6, 75.0, 74.9, 74.9, 74.8, 74.6, 73.3, 72.7, 70.4, 70.3, 69.8, 68.9, 66.7, 63.6, 63.5, 55.2. HRMS: Calc. for $C_{62}H_{64}NO_{14}$ $[M+H]^+$: 1046.4327, Obser. 1046.4329

D-Glucopyranosiduronic acid-1, 2, 3, 4-*tetra*-*O*-benzyl-2-nitrophenylmethyl ester (4d)



4d

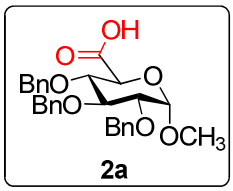
White solid. (165 mg, 52%); M.P: 123-125 □;R_f value = 0.5 in 20% EtOAc/ Hexane. β:α isomer (3:1); IR: ν_{max}(neat) 1775, 1480, 1310, 1095 cm^{-1}. $[\alpha]_D^{24}$= -9.9 [c 0.1, $CHCl_3$];^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15–8.14 (m, 1H), 7.60–7.20 (m, 24H), 5.66–5.53 (m, 2H), 5.03–4.95 (m, 3H), 4.89–4.71 (m, 4H), 4.65 (dd, *J* = 12.6, 9.4 Hz, 2H), 4.07 (d, *J* = 9.7 Hz, 1H), 3.97 (t, *J* = 9.3 Hz, 1H), 3.75 (t, *J* = 9.0 Hz, 1H), 3.65–3.62 (m, 1H).^{13}C NMR (125 MHz, $CDCl_3$) δ 169.1, 168.0, 147.2, 138.5, 138.3, 138.1, 137.9, 137.8, 137.0, 136.7, 133.8, 131.6, 128.7, 128.7, 128.6, 128.6, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 128.0, 128.0, 127.9, 127.8, 127.8, 127.8, 127.7, 125.1, 102.8, 96.1, 83.9, 81.8, 81.5, 79.4, 79.4, 78.9, 75.9, 75.7, 75.1, 74.9, 74.6, 73.2, 71.4, 70.6, 69.6, 63.7. Calc. for $C_{41}H_{40}NO_9$ $[M+H]^+$: 690.2703, Obser. 690.2705

4. Experimental procedure for deprotection of photolabile 2-nitrobenzyl protecting group by using a continuous flow photoreactor:

Approximately 0.005M solution of photolabile protected uronic acid building blocks were prepared in methanol and added to the reactor B. The solution was circulated with the help of peristaltic pump to the flexi coil with a flow rate 50 RPM which required approx. 3 minutes for completing one cycle. Total six cycles were repeated after which the solvent was evaporated and purified through column chromatography.

5. Analytical data for various deprotected uronic acids:

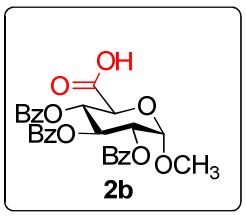
Methyl-2, 3, 4-tri-*O*-benzyl-α-D-glucopyranosiduronic acid (2a)[1]



2a

Colourless oily syrup (110mg, 92%); $R_f$value =0.6 in 50% EtOAc/ Hexane. IR:ν_{max}(neat) 3482, 1712, 1120 cm^{-1}. $[\alpha]_D^{24}$= +4.4 [c 0.1, $CHCl_3$]; ^{1}H NMR (500 MHz, DMSO-D_6) δ 7.40–7.22 (m, 16H), 4.91 (d, J = 3.4 Hz, 1H), 4.84 (d, J = 11.3 Hz, 1H), 4.75–4.66 (m, 4H), 4.58 (d, J = 11.0 Hz, 1H), 3.93 (d, J = 9.9 Hz, 1H), 3.79 (t, J = 9.3 Hz, 1H), 3.66–3.62 (m, 1H), 3.56 (dd, J = 9.6, 3.4 Hz, 1H), 3.34 (s, 3H).^{13}C NMR (125 MHz, DMSO-D_6) δ 170.9, 139.0, 138.8, 138.6, 128.7, 128.6, 128.6, 128.1, 128.1, 128.0, 127.9, 127.9, 127.8, 127.8, 98.0, 80.8, 79.6, 75.0, 74.5, 72.0, 70.4, 55.3.HRMS: Calc. for $C_{28}H_{31}O_7[M+H]^+$: 479.2070, Obser.479.2075.

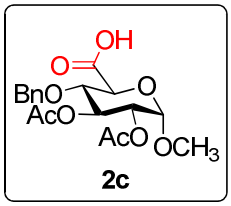
Methyl-2, 3, 4-tri-*O*-benzoyl-α-D-glucopyranosiduronic acid (2b)



2b

Colourless Oily syrup (116 mg, 89%);$R_f$value =0.5 in 60% EtOAc/ Hexane. IR: ν_{max}(neat) 3545, 1718, 1710 cm^{-1}. $[\alpha]_D^{24}$= +62.2 [c 0.1, $CHCl_3$];^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00–7.89 (m, 6H), 7.53 (q, J = 7.6 Hz, 2H), 7.46 (t, J = 7.4 Hz, 1H), 7.41-7.36 (m, 4H), 7.32 (t, J = 7.8 Hz, 2H), 6.20 (t, J = 9.8 Hz, 1H), 5.75 (t, J = 9.8 Hz, 1H), 5.37 (d, J = 3.6 Hz, 1H), 5.33 (dd, J = 10.1, 3.6 Hz, 1H), 4.66 (d, J = 10.1 Hz, 1H), 3.54 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 171.1, 165.7, 165.6, 165.4, 133.4, 133.4, 133.2, 129.9, 129.9, 129.7, 129.0, 128.8, 128.4, 128.4, 128.3, 97.4, 77.2, 71.4, 69.8, 68.0, 56.3.HRMS: Calc. for $C_{28}H_{25}O_{10}[M+H]^+$: 521.1448, Obser. 521.1446

Methyl-2, 3-di-*O*-acetyl-4-benzyl-α-D-glucopyranosiduronic acid (2c)

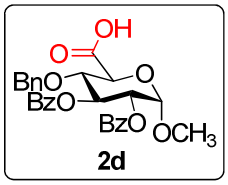


2c

Colourless oily syrup (87mg, 91 %); $R_f$value =0.5 in 50% EtOAc/Hexane. IR: ν_{max}(neat) 3353, 1735, 1719, 1082 cm^{-1}. $[\alpha]_D^{24}$= +53.6 [c 0.1, $CHCl_3$];^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.29 (m, 7H), 7.26–7.25 (m, 2H), 5.59–5.55 (m, 1H), 4.99 (d, J = 3.5 Hz, 1H), 4.88 (dd, J = 10.2, 3.6 Hz, 1H), 4.65 (dd, J

= 54.8, 11.1 Hz, 3H), 4.33 (d, *J* = 9.9 Hz, 1H), 3.89 (t, *J* = 9.5 Hz, 1H), 3.46 (s, 3H), 2.09 (s, 3H), 1.97 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 172.2, 170.3, 169.7, 137.2, 128.4, 128.0, 128.0, 97.3, 77.5, 74.7, 71.3, 70.8, 69.4, 55.8, 20.7, 20.7. HRMS: Calc. for $C_{18}H_{23}O_9[M+H]^+$: 383.1342, Obser. 383.1343

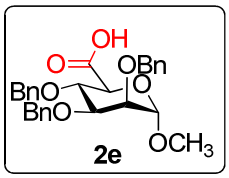
Methyl-2, 3-di-*O*-benzoyl-4-benzyl-α-D-glucopyranosiduronic acid (2d)



2d

Colourless oily liquid (119 mg, 94%);$R_f$value =0.6 in 50% EtOAc/ Hexane. IR: ν_{max}(neat) 3260, 1715, 1708, 1124 cm^{-1}. $[\alpha]_D^{24}$= +108.1 [c 0.1, $CHCl_3$];^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10–8.08 (m, 4H), 7.62 (dd, *J* = 15.5, 7.5 Hz, 2H), 7.49 (dt, *J* = 15.8, 7.9 Hz, 4H), 7.26 (s, 5H), 6.20 (t, *J* = 9.6 Hz, 1H), 5.35 (dt, *J* = 10.0, 3.6 Hz, 2H), 4.77 (dd, *J* = 38.0, 10.9 Hz, 2H), 4.61 (d, *J* = 9.9 Hz, 1H), 4.28 (t, *J*= 9.5 Hz, 1H), 3.58 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 173.6, 166.0, 165.6, 136.9, 133.5, 133.3, 129.9, 129.7, 129.4, 128.8, 128.4, 128.3, 128.2, 128.0, 97.5, 77.4, 77.3, 77.1, 76.9, 74.8, 71.9, 71.7, 69.8, 55.9.HRMS:Calc. for $C_{28}H_{27}O_9[M+H]^+$: 507.1650, Obser.507.1648

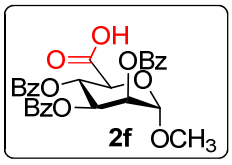
Methyl-2, 3, 4-tri-*O*-benzyl-α-D-mannopyranosiduronic acid (2e)[1]



2e

Colourless oily syrup (105 mg, 88 %); $R_f$value =0.5 in50% EtOAc/PE; IR:ν_{max} (neat) 3386, 1725, 1135 cm^{-1}.$[\alpha]_D^{23}$=+15.0 (c, 1.2 in CHCl3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39–7.28 (m, 15H), 4.96 (s, 1H), 4.76 (dt, *J* = 24.4, 11.2 Hz, 4H), 4.64 (d, *J* = 3.9 Hz, 2H), 4.31–4.21 (m, 2H), 3.93–3.91 (m, 1H), 3.80–3.79 (m, 1H), 3.46 (d, *J* = 1.3 Hz, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 174.1, 138.1, 138.0, 137.7, 128.4, 128.1, 127.9, 127.8, 127.7, 127.7, 127.6, 99.6, 78.5, 75.6, 74.5, 72.9, 72.4, 71.3, 55.7.HRMS: Calc. for $C_{28}H_{30}O_7Na$ $[M+Na]^+$: 501.1890, Obser.501.1893.

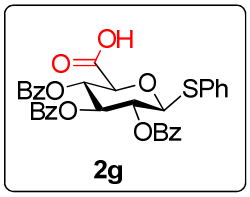
Methyl-2, 3, 4-tri-*O*-benzoyl-α-D-mannopyranosiduronic acid (2f)



Colorless oily syrup (121 mg, 93 %); R_f value =0.4 in 50% EtOAc/PE; IR: ν_{max}(neat) 3558, 1712, 1708 cm^{-1}. $[\alpha]_D^{24}$= -61.4 [c 0.1, $CHCl_3$];^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.98–7.97 (m, 2H), 7.87 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.62 (t, *J*= 7.4 Hz, 1H), 7.54–7.45 (m, 4H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.31 (t, *J* = 7.8 Hz, 2H), 6.05 (t, *J* = 9.5 Hz, 1H), 5.92 (dd, *J* = 9.6, 3.4 Hz, 1H), 5.69 (dd, *J* = 3.2, 2.5 Hz, 1H), 5.16 (d, *J* = 2.2 Hz, 1H), 4.69 (d, *J* = 9.4 Hz, 1H), 3.59 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.4, 165.5, 165.4, 165.3, 133.6, 133.4, 133.3, 129.9, 129.8, 129.7, 129.1, 129.0, 128.9, 128.6,

128.4, 128.3, 98.8, 69.8, 69.4, 69.3, 67.4, 56.2. HRMS: Calc. for $C_{28}H_{25}O_{10}$ $[M+H]^{+\beta}$: 521.1448, Obser. 521.1455

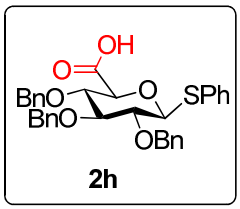
Phenyl-2, 3, 4-tri-*O*-benzoyl-1-thio-β-D-glucopyranosyduronic acid (2g)



2g

Colorless oily syrup (133 mg, 89%); R_f value = 0.53 in 50% EtOAc/PE; IR: ν_{max}(neat) 3440, 1712, 1705 cm^{-1}. $[\alpha]_D^{24}$= +23.3 [c 0.1, $CHCl_3$];^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99–7.97 (m, 2H), 7.92–7.91 (m, 2H), 7.84–7.83 (m, 2H), 7.56–7.28 (m, 14H), 5.92 (t, *J* = 9.3 Hz, 1H), 5.73 (t, *J* = 9.6 Hz, 1H), 5.54 (t, *J* = 9.6 Hz, 1H), 5.11 (d, *J* = 9.9 Hz, 1H), 4.39 (d, *J* = 9.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ170.4, 165.6, 165.1, 164.9, 133.3, 133.3, 133.2, 131.7, 129.9, 129.8, 129.8, 129.2, 129.0, 129.0, 128.8, 128.4, 128.4, 128.3, 128.2, 86.5, 73.8, 70.3, 69.9, 66.2. HRMS: Calc. for $C_{33}H_{27}O_9S$ $[M+H]^+$: 599.1376, Obser. 599.1377

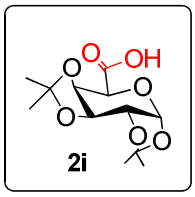
Phenyl-2, 3, 4-tri-*O*-benzyl-1-thio-β-D-glucopyranosyduronic acid (2h)



2h

Colorless oily syrup (132 mg, 95%); R_f value = 0.56 in 50% EtOAc/PE; IR:ν_{max} (neat) 3280, 1730, 1095 cm^{-1}. $[\alpha]_D^{24}$= -7.5 [c 0.1, $CHCl_3$];^{1}H NMR (500 MHz, $CDCl_3$) δ7.60–7.58 (m, 2H), 7.42–7.26 (m, 19H), 4.93 (d, *J* = 10.3 Hz, 1H), 4.88 (t, *J*= 7.8 Hz, 2H), 4.81–4.75 (m, 3H), 4.70 (d, *J* = 10.8 Hz, 1H), 4.01 (d, *J* = 9.3 Hz, 1H), 3.87 (t, *J* = 9.0 Hz, 1H), 3.77 (t, *J* = 8.6 Hz, 1H), 3.58 (dd, *J* = 9.6, 8.4 Hz, 1H).. ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.3, 138.0, 137.7, 137.3, 133.0, 132.3, 129.1, 128.5, 128.4, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 88.1, 85.3, 80.2, 78.7, 77.5, 75.7, 75.4, 75.0. HRMS: Calc. for $C_{33}H_{33}O_6S$ $[M+H]^+$: 557.1998, Obser.557.2001

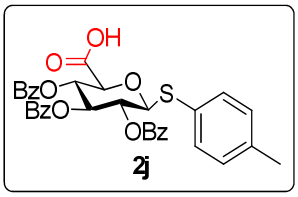
1, 2, 3, 4-Di-*O*-isopropylidene-α-D-galactopyranosiduronic acid (2i)



2i

Colorless viscous liquid (62 mg, 90%); R_f value = 0.6 in 50% EtOAc/ Hexane.IR:ν_{max} (neat) 3315, 1715 cm^{-1}.^{1}H NMR (500 MHz, DMSO-d_6) δ 5.53 (d, *J* = 5.0 Hz, 1H), 4.65 (dd, *J* = 7.7, 2.5 Hz, 1H), 4.51 (dd, *J* = 7.7, 2.3 Hz, 1H), 4.40 (dd, *J* = 5.0, 2.5 Hz, 1H), 4.18 (d, *J* = 2.2 Hz, 1H), 1.43 (s, 3H), 1.32 (s, 3H), 1.28 (d, *J* = 3.3 Hz, 6H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 169.3, 109.1, 108.5, 96.2, 71.9, 70.5, 69.9, 67.7, 26.2, 26.1, 25.1, 24.8. HRMS: Calc. for$C_{12}H_{19}O_7$ $[M+H]^+$: 275.1131, Obser. 275.1129

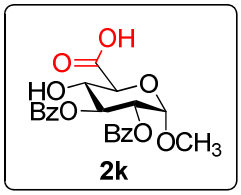
Tolyl-2, 3, 4-tri-*O*-benzoyl-1-thio-β-D-glucopyranosyduronic acid (2j)



2j

White solid (147 mg, 96%); M.P: 195-197 □;R_f value = 0.5 in 50% EtOAc/ Hexane. IR:ν_{max} (neat) 3356, 1727, 1702 cm^{-1}[α]$_D^{24}$= +12.6 [c 0.1, $CHCl_3$];^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00–7.98 (m, 2H), 7.92 (dd, J = 8.4, 1.2 Hz, 2H), 7.85–7.83 (m, 2H), 7.57–7.53 (m, 1H), 7.52–7.48 (m, 1H), 7.47–7.45 (m, 3H), 7.43–7.40 (m, 2H), 7.35 (dd, J = 10.8, 4.9 Hz, 2H), 7.31–7.28 (m, 2H), 7.16 (d, J = 7.9 Hz, 2H), 5.93 (t, J = 9.3 Hz, 1H), 5.70 (t, J = 9.6 Hz, 1H), 5.51–5.47 (m, 1H), 5.05 (d, J = 9.9 Hz, 1H), 4.42 (d, J = 9.7 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.1, 165.7, 165.2, 164.9, 139.1, 134.3, 133.4, 133.4, 133.3, 129.9, 129.9, 129.8, 129.8, 129.1, 128.7, 128.6, 128.4, 128.4, 128.3, 127.0, 86.5, 75.9, 73.5, 70.0, 69.7, 21.2. HRMS: Calc. for$C_{34}H_{29}O_9S$ $[M+H]^+$: 613.1532, Obser. 613.1536

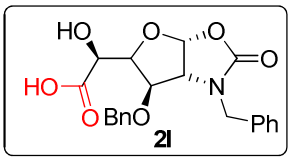
Methyl-2, 3-di-*O*-benzoyl-α-D-glucopyranosiduronic acid (2k)



2k

Colorless oil (94 mg, 90%);R_f value = 0.55 in 50% EtOAc/PE; [α]$_D^{24}$= +4.4 [c 0.1, $CHCl_3$]; IR:ν_{max} (neat) 3520, 3286, 1725, 1718, 1135 cm^{-1}[α]$_D^{24}$= +151.7 [c 0.1, $CHCl_3$];^{1}H NMR (500 MHz, MeOD-d_4) δ 8.00–7.98 (m, 2H), 7.91 (dd, J = 6.0, 4.7 Hz, 2H), 7.54 (t, J = 7.4 Hz, 2H), 7.42-7.37 (m, 4H), 5.83–5.78 (m, 1H), 5.20 (dd, J = 8.8, 2.7 Hz, 2H), 4.28 (d, J = 10.0 Hz, 1H), 4.09 (t, J = 9.7 Hz, 1H), 3.49 (s, 3H).^{13}C NMR (125 MHz, MeOD-d_4) δ 170.9, 166.1, 165.6, 133.2, 132.9, 129.6, 129.3, 129.2, 128.9, 128.1, 128.1, 97.5, 72.5, 71.7, 71.1, 69.8, 54.7. HRMS: Calc. for $C_{21}H_{21}O_9$ $[M+H]^+$: 417.1186, Obser.416.1190

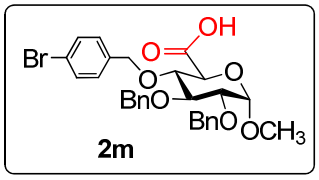
2-(1-benzyl-6-(benzyloxy)-2-oxohexahydrofuro[3, 2-d]oxazol-5-yl)-2-hydroxyacetic acid (2l)



2l

Colorless oily syrup (54 mg, 79%); R_f value = 0.43 in 60% EtOAc/PE; IR:ν_{max} (neat) 3306, 3120, 1711, 1302, 1135, 1070 cm^{-1}. [α]$_D^{24}$= -49.4 [c 0.1, $CHCl_3$];^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37–7.27 (m, 8H), 7.17 (t, J = 7.4 Hz, 3H), 6.14 (d, J = 5.0 Hz, 1H), 4.73 (s, 1H), 4.65 (d, J = 15.1 Hz, 1H), 4.40–4.31 (m, 2H), 4.17 (d, J = 3.3 Hz, 1H), 4.10 (s, 1H), 4.06–4.04 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ169.3, 156.8, 136.3, 134.7, 129.2, 128.6, 128.6, 128.3, 128.2, 127.8, 101.2, 79.5, 77.4, 77.1, 76.9, 72.6, 64.2, 47.5.HRMS: Calc. for $C_{21}H_{22}NO_7$ $[M+H]^+$: 400.1396, Obser. 400.1395

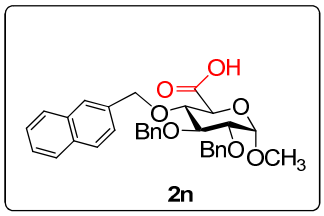
(2S,3S,4S,5R,6R)-4,5-bis(benzyloxy)-3-(4-bromobenzyloxy)-6-methoxytetrahydro-2H-pyran-2-carboxylic acid (2m)



2m

Colorless viscous liquid (124 mg, 89%); R_f value = 0.20 in 50% EtOAc/PE. IR:ν_{max} (neat) 3263, 1727, 1077, 585 cm^{-1};$[\alpha]_D^{24}$= -1.9 [c 0.1, $CHCl_3$];^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.28 (m, 12H), 7.09 (d, J = 8.3 Hz, 2H), 4.99 (d, J = 11.0 Hz, 1H), 4.83–4.74 (m, 3H), 4.66 (t, J = 7.3 Hz, 2H), 4.58 (d, J = 11.1 Hz, 1H), 4.24 (d, J = 10.0 Hz, 1H), 4.02 (t, J = 9.3 Hz, 1H), 3.70 (t, J = 9.5 Hz, 1H), 3.60–3.58 (m, 1H), 3.44 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 173.9, 138.3, 137.7, 136.6, 131.4, 129.5, 128.5, 128.4, 128.2, 128.1, 127.9, 127.8, 121.7, 98.6, 81.3, 79.2, 79.1, 75.9, 74.3, 73.6, 69.6, 55.8. HRMS: Calc. for $C_{28}H_{29}BrO_7$ $[M+H]^+$: 556.1097 , Obser. 556.1094

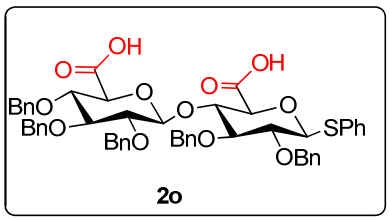
(2S,3S,4S,5R,6R)-4,5-bis(benzyloxy)-6-methoxy-3-(naphthalen-2-ylmethoxy)tetrahydro-2H-pyran-2-carboxylic acid (2n)



2n

Colorless viscous liquid (115 mg, 87%); $R_f$value = 0.20 in 50% EtOAc/PE; IR:ν_{max} (neat) 3215, 1712, 1120 cm^{-1}. $[\alpha]_D^{25}$= -6.2 [c 0.1, $CHCl_3$];^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79–7.74 (m, 3H), 7.66 (s, 1H), 7.47–7.44 (m, 2H), 7.39–7.32 (m, 11H), 4.99 (dd, J = 26.3, 10.9 Hz, 2H), 4.86–4.78 (m, 3H), 4.67 (t, J = 7.9 Hz, 2H), 4.29 (d, J = 10.1 Hz, 1H), 4.07 (t, J = 9.3 Hz, 1H), 3.78 (t, J = 9.5 Hz, 1H), 3.62 (dd, J = 9.6, 3.4 Hz, 1H), 3.44 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 173.3, 138.4, 137.8, 134.9, 133.2, 133.0, 128.5, 128.4, 128.2, 128.1, 128.1, 127.9, 127.9, 127.7, 127.6, 126.8, 126.0, 125.9, 125.8, 98.6, 81.4, 79.2, 79.2, 75.9, 75.3, 73.6, 69.6, 55.8. HRMS: Calc. for $C_{32}H_{32}O_7$ $[M+H]^+$: 528.2148, Obser. 528.2150

***β*-D-Glucopyranosiduronic acid, phenyl-2, 3-di-*O*-(benzyl)-1-thio-4-*O*-[2, 3, 4-tri-*O*-(benzyl)-*β*-D-glucopyranosiduronic acid] (2o)**

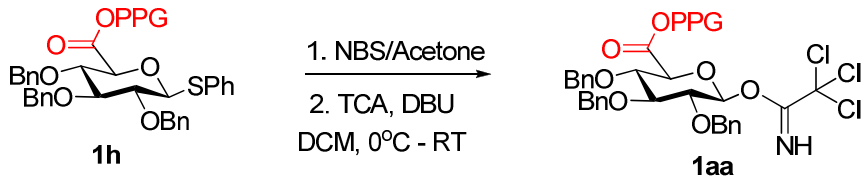


2o

Colorless viscous liquid (207 mg, 91%); R_f value = 0.40 in 60% EtOAc/PE; IR:ν_{max} (neat) 3540, 3325, 1722, 1710, 1130 cm^{-1}. $[\alpha]_D^{24}$= +21.0 [c 0.1, $CHCl_3$];^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.26 (m, 31H), 5.88 (s, 1H), 4.97–4.72 (m, 8H), 4.64–4.57 (m, 4H), 4.49 (t, J = 11.6 Hz, 2H), 4.06 (t, J = 9.3 Hz, 1H), 3.90 (d, J = 16.9 Hz, 2H), 3.80 (t, J = 9.5 Hz, 1H), 3.62 (dd, J = 10.0, 3.8 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.8, 169.6,

138.4, 137.9, 137.6, 137.0, 136.9, 128.6, 128.6, 128.4, 128.4, 128.2, 128.1, 128.1, 128.0, 127.9, 127.9, 127.7, 127.7, 102.3, 98.4, 81.0, 79.1, 79.0, 77.3, 75.7, 75.2, 75.0, 73.8, 73.4, 72.7, 72.7, 72.2, 72.0, 70.5. HRMS: Calc. for $C_{53}H_{53}O_{12}S$ $[M+H]^+$: 913.3258, Obser. 913.3262

6. Procedure for synthesis of D-Glucopyranuronic acid, 2,3,4-tris-*O*-(phenylmethyl)-,2-nitrophenylmethyl ester, 1-(2,2,2-trichloroethanimidate) (1aa):



To a stirred solution of thioglycosides,**1h** (4g, 5.78 mmol) in 40 ml acetone-water (9:1; v/v) was added N-bromosuccinamide (3.09 g, 17.35 mmol) and stirred for 1hour at room temperature. After thatthe reaction was quenched with $NaHCO_3$ and evaporated to dryness. The residue was dissolved in ethyl acetate (150mL) and successively washed with sat.aq.$NaHCO_3$, water and brine. Organic layer was separated, dried using anhydrous sodium sulphate, evaporated in vacuo. The resulting residue was purified using silica gel column chromatography (2:1 hexane/ EtOAc) to give the corresponding hemiacetal2.43 g (70%) as viscous oil. The hemiacetalwas dissolved in dry CH_2Cl_2 (20mL) and cooled to 0^oC under argon atmosphere. DBU (0.2 ml,1.33mmol) andtrichloroacetonitrile (3.34 ml, 33.35 mmol)were added slowly and allowed to stir for 2h. After complete consumption of starting material, the reaction mixture was concentrated in vacuo and purified by silica gel column chromatography (30% EtOAc/ Hexane) with 1% added Et_3N to afford 2.23g (90%) as colourless foam; α:β isomer (15.31:1); R_f value =0.6 in 20% EtOAc/ Hexane. ^1H NMR (500 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.13 (dd, J = 7.7, 1.7 Hz, 1H), 7.54-7.46 (m, 3H), 7.37–7.33 (m, 10H), 7.30-7.28 (m, 3H), 7.23 (dd, J = 6.6, 3.0 Hz, 2H), 6.61 (d, J = 3.5 Hz, 1H), 5.56 (q, J = 15.3 Hz, 2H), 5.03 (d, J = 10.9 Hz, 1H), 4.91 (t, J = 11.2 Hz, 2H), 4.78 (dd, J = 25.2, 11.7 Hz, 2H), 4.61 (dd, J = 29.5, 10.5 Hz, 2H), 4.16 (t, J = 9.3 Hz, 1H), 3.97–3.87 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.1, 161.0, 147.1, 138.2, 137.6, 137.6, 133.9, 131.4, 128.7, 128.5, 128.5, 128.4, 128.4, 128.1, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 125.0, 94.0, 91.0, 80.8, 78.8, 78.5, 75.8, 75.3, 73.1, 72.7, 63.8.

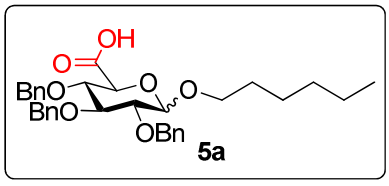
7. General procedure for Glycosylation:

7.a. Glycosylation through Glycosyl Imidate donor: Donor **1aa**(0.5 mmol, 1equiv.) and acceptor (non- sugar 3 equiv. and sugar 1.2equiv.) were dissolved in freshly dried CH_2Cl_2 (8ml)and added to a flame dried round bottomed flask containing activated 4Å molecular sieves (300mg) under argon atmosphere. The reaction mixture was then cooled to 0^oC to which the activator $B(C_6F_5)_3$ (10mol%) was added. The reaction was stirred further for 1.5 h allowing temperature to reach room temperature slowly.Quenching was done by the addition of Et_3N and filtered through Celite. The mixture was concentrated in vacuo and the resulting residue was purified by silica gel column chromatography to afford the desired glycosylated product (78-89%).

7.b.Glycosylation through thioglycoside donor: Typical NIS/TfOH-promoted glycosylation procedure: A mixture of glycosyl donor (**1h**)(0.5 mmol, 1equiv.), glycosyl acceptor (3 equiv.), and freshly activated molecular sieves (4□, 300 mg) in CH_2Cl_2(8.0 mL) was stirred under argon for 1 h. The solution was cooled to – 78 °C and NIS (1.1equiv.) and TfOH (10mol %) were added. The reaction was slowly allowed to reach 0 °C. Upon completion, the reaction was quenched by adding Et_3N. The solid was filtered off and the filtrate was washed with 1 M HCl, sat. $NaHCO_3$ solution, 10% $Na_2S_2O_3$and brine. The organic layer was separated, dried with anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel to afford the corresponding glycoside with 52% yield.

8. Analytical data for various deprotected uronic acids:

***n*-Hexyl-2, 3, 4-tri-*O*-benzyl-D-glucopyranosiduronic acid (5a)**

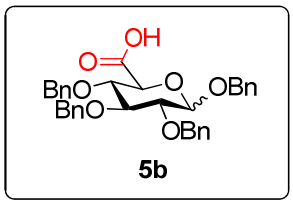


5a

White foam (123 mg, 90%);$R_f$value =0.5 in 50% EtOAc/ Hexane. IR:ν_{max} (neat) 3105, 1716, 1132 cm^{-1}; β:α isomer (>20:1);$[\alpha]_D^{24}$= -6.4 [c 0.1, $CHCl_3$];^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.25 (m, 16H), 4.94 (dd, J = 17.6, 11.0 Hz, 2H), 4.81 (d, J = 10.2 Hz, 2H), 4.75 (d, J = 11.0 Hz, 1H), 4.67 (d, J = 10.7 Hz, 1H), 4.54 (d, J = 7.6 Hz, 1H), 4.01–3.96 (m, 2H), 3.85 (t, J = 9.1 Hz, 1H), 3.72 (t, J = 8.8 Hz, 1H), 3.59–3.52 (m, 2H), 1.70–1.64(m, 2H), 1.43–1.30 (m, 8H), 0.92–0.89 (m, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 172.9, 138.2, 138.1, 137.4, 128.4, 128.4, 128.1, 128.1, 127.9, 127.8, 127.7, 127.7, 103.7, 83.5,

81.5, 78.8, 75.6, 75.0, 74.7, 74.0, 70.5, 31.6, 29.6, 25.7, 22.5, 14.0.HRMS: Calc. for $C_{33}H_{41}O_7[M+H]^+$:549.2852, Obser. 549.2849

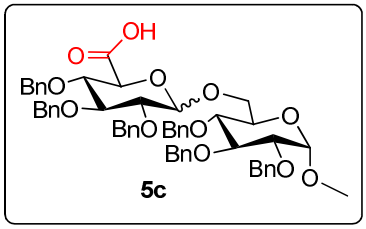
(Phenylmethyl)-2,3,4-tri-*O*-benzyl-D-glucopyranosiduronic acid (5b)



5b

Viscous liquid. (130 mg, 94%); R_f value =0.6 in 50% EtOAc/ Hexane. IR:ν_{max} (neat) 3215, 1705, 1145 cm^{-1}. β:α isomer (>20:1);$[\alpha]_D^{24}$= -19.6 [c 0.1, $CHCl_3$];^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-7.24 (m, 21H), 4.98 (d, J = 12.1 Hz, 1H), 4.90 (dd, J = 15.9, 10.9 Hz, 2H), 4.79 (t, J = 10.4 Hz, 2H), 4.68 (ddd, J = 18.2, 16.6, 9.2 Hz, 4H), 4.00 (d, J = 9.3 Hz, 1H), 3.88–3.84 (m, 1H), 3.70 (t, J = 8.7 Hz, 1H), 3.59 (t, J = 7.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.7, 138.2, 138.0, 137.4, 136.9, 128.5, 128.4, 128.4, 128.3, 128.1, 128.0, 128.0, 127.9, 127.8, 127.7, 127.7, 102.5, 83.5, 81.6, 78.7, 75.6, 75.0, 74.8, 74.0, 71.5. HRMS: Calc. for $C_{34}H_{35}O_7[M+H]^+$:555.2383, Obser. 555.2387

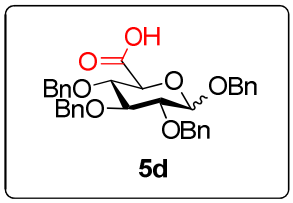
(2S,4S,5S,6R)-3,4,5-*tris*(benzyloxy)-6-(((2R,4S,5S,6S)-3,4,5-*tris*(benzyloxy)-6-methoxytetra-hydro-2H-pyran-2-yl)methoxy)tetrahydro-2H-pyran-2-carboxylic acid (5c)



5c

White solid (198 mg, 87%); M.P: 93-95 ^oC; $R_f$value =0.5 in 60% EtOAc/ Hexane. IR:ν_{max} (neat) 3345, 1701, 1065 cm^{-1}. β:α isomer (3:2); $[\alpha]_D^{24}$= +34.5 [c 0.1, $CHCl_3$];^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.19 (m, 31H), 5.01–4.50 (m, 14H), 4.10–3.44 (m, 10H), 3.36 (d, J = 20.3 Hz, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ172.0, 170.4, 138.8, 138.7, 138.3, 138.2, 138.2, 138.1, 138.1, 138.0, 138.0, 137.5, 137.5, 128.4, 128.4, 128.3, 128.3, 128.3, 128.1, 128.1, 128.0, 128.0, 127.9, 127.9, 127.8, 127.8, 127.8, 127.7, 127.7, 127.6, 127.5, 103.5, 98.1, 98.0, 97.5, 96.1, 83.1, 82.0, 81.9, 81.2, 80.9, 80.1, 79.9, 79.3, 79.0, 78.7, 77.8, 77.7, 75.7, 75.7, 75.6, 75.3, 75.1, 75.0, 74.9, 74.8, 74.6, 73.9, 73.3, 72.6, 70.3, 69.9, 69.4, 69.0, 66.7, 55.3, 55.2.HRMS: Calc. for $C_{55}H_{59}O_{12}[M+H]^+$:911.4007, Obser. 911.4012

(Phenylmethyl)-2, 3, 4-tri-*O*-benzyl-D-glucopyranosiduronic acid (5d)

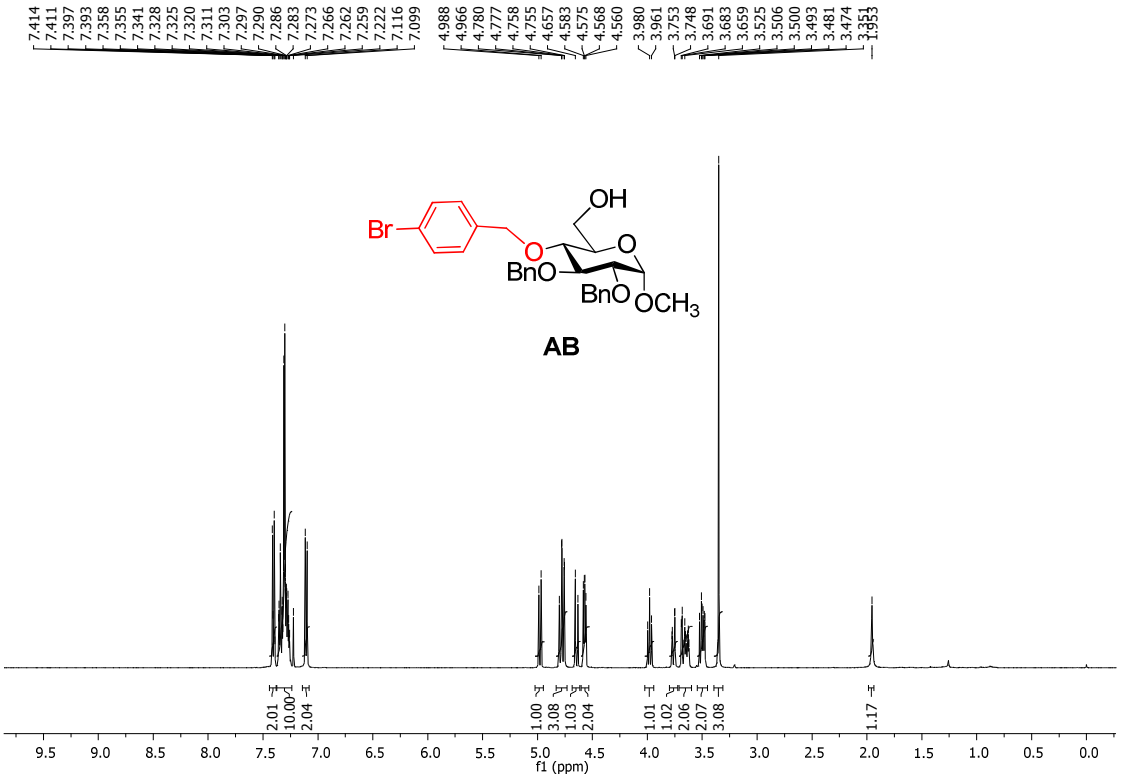


5d

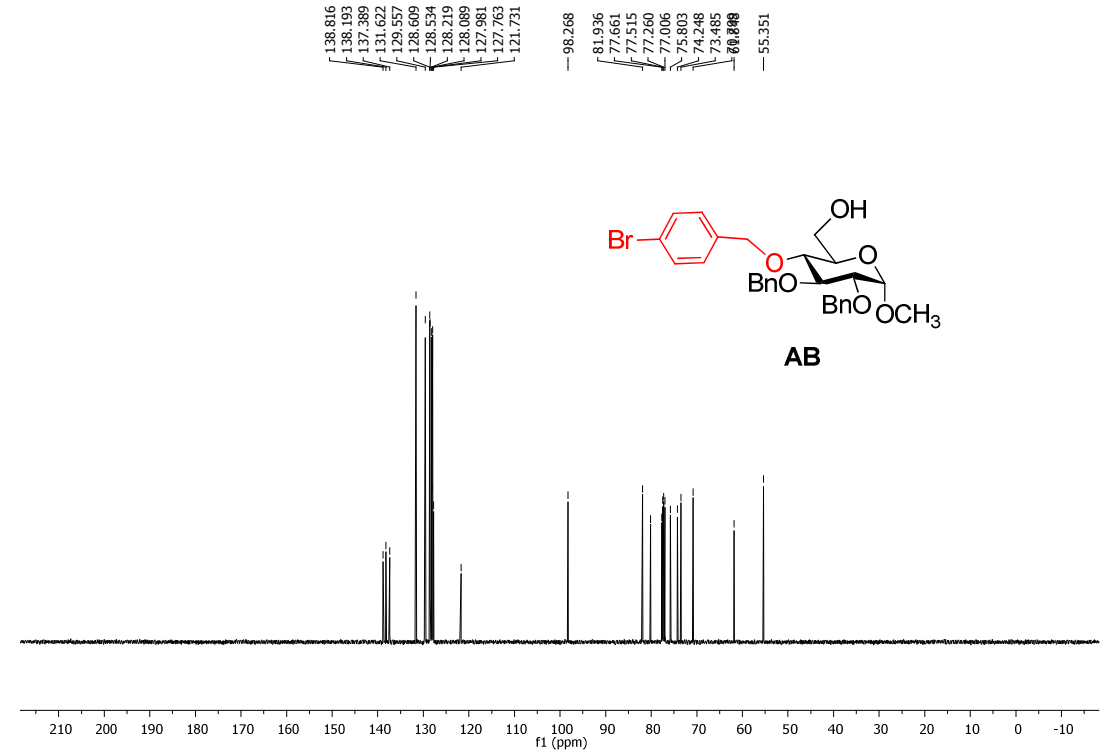
Viscous liquid. (116 mg, 84%); R_f value = 0.6 in 50% EtOAc/ Hexane. IR:ν_{max} (neat) 3217, 1708, 1085 cm^{-1}.β:α isomer (~3:1);$[\alpha]_D^{24}$= +8.8 [c 0.1, $CHCl_3$];^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43–7.26 (m, 20H), 5.00 (dd, J = 17.1, 11.4 Hz, 1H), 4.93–4.85 (m, 2H), 4.83–4.66 (m, 5H), 4.03 (d, J = 9.1 Hz, 1H), 3.87 (t, J = 8.9 Hz, 1H), 3.71 (t, J = 8.6 Hz, 1H), 3.61–3.58 (m, 1H).^{13}C NMR (125 MHz, $CDCl_3$) δ 174.0, 173.0, 138.5, 138.2, 138.0, 137.8, 137.5, 136.96, 136.5, 128.5, 128.5, 128.5, 128.4, 128.4, 128.4, 128.2, 128.1, 128.1, 128.0, 128.0, 128.0, 127.9, 127.9, 127.8, 127.7, 127.7, 102.6, 95.9, 83.6, 81.6, 81.4, 79.3, 79.1, 78.7, 75.9, 75.6, 75.3, 75.0, 74.8, 74.0, 73.2, 71.5, 69.9, 69.7. HRMS: Calc. for $C_{34}H_{35}O_7$ $[M+H]^+$:555.2383, Obser. 555.2381

References:

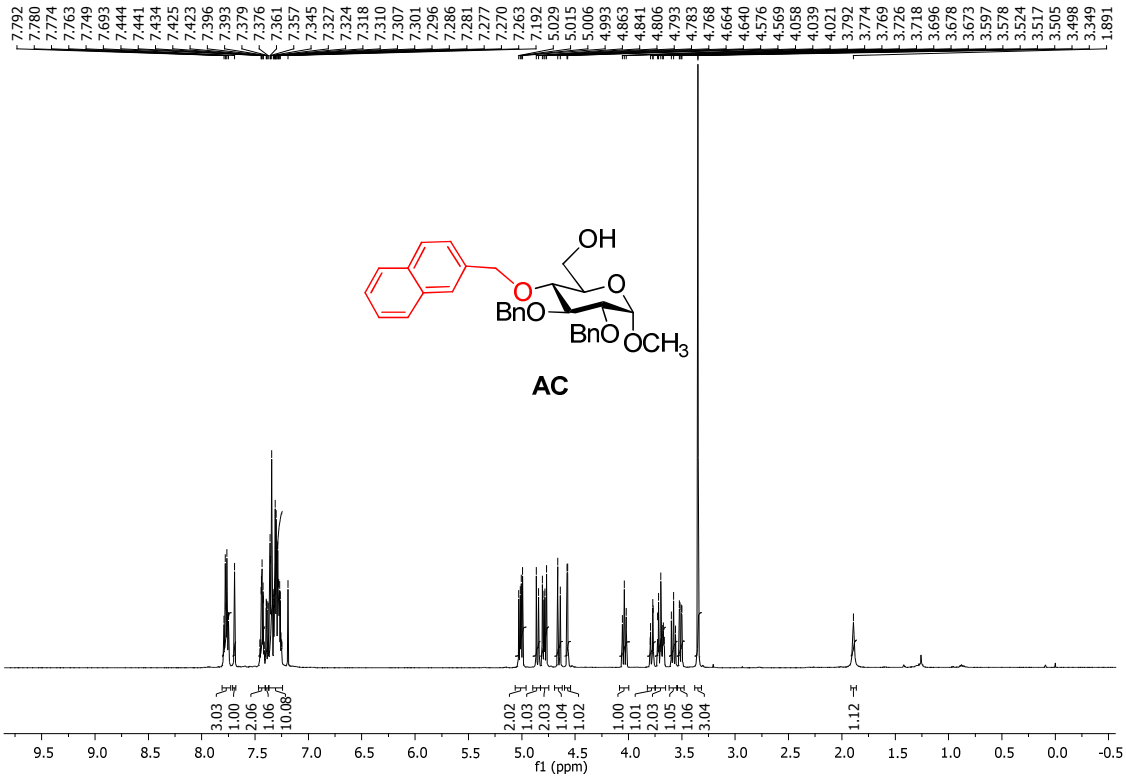
1. D. J. Chambers, G. R. Evans and A. J. Fairbanks, *Tetrahedron* 2005, 61, 7184–7192.



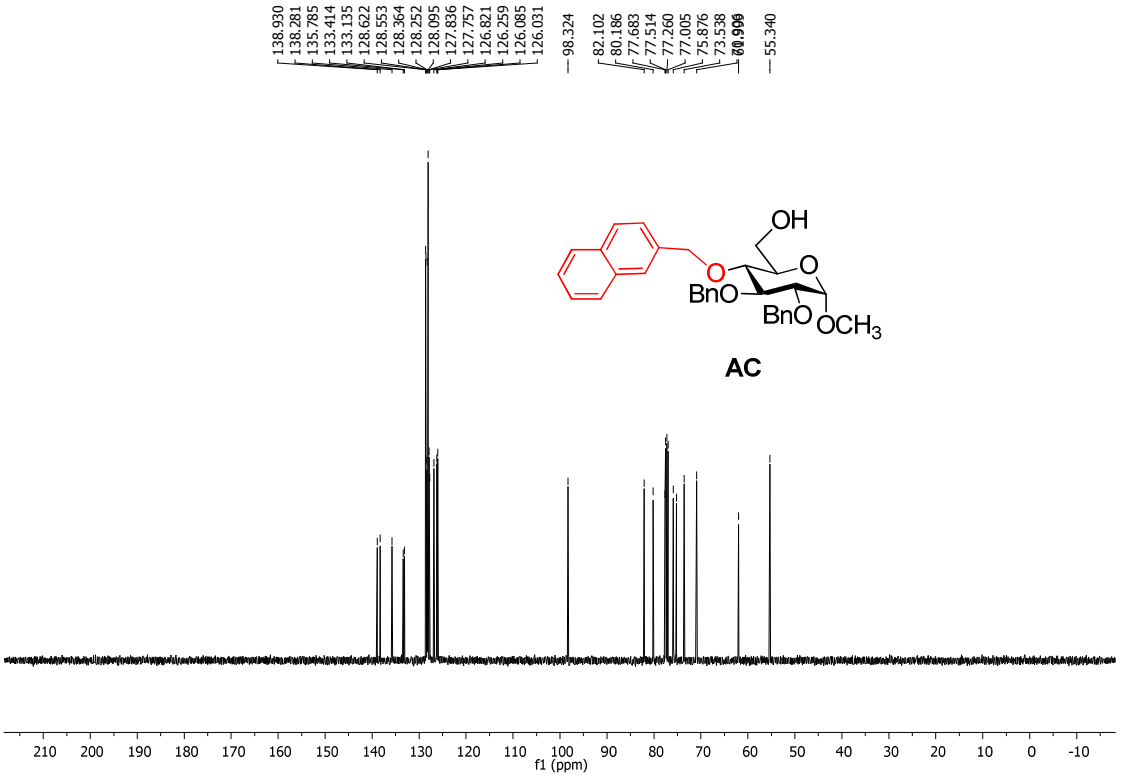
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of compound AB



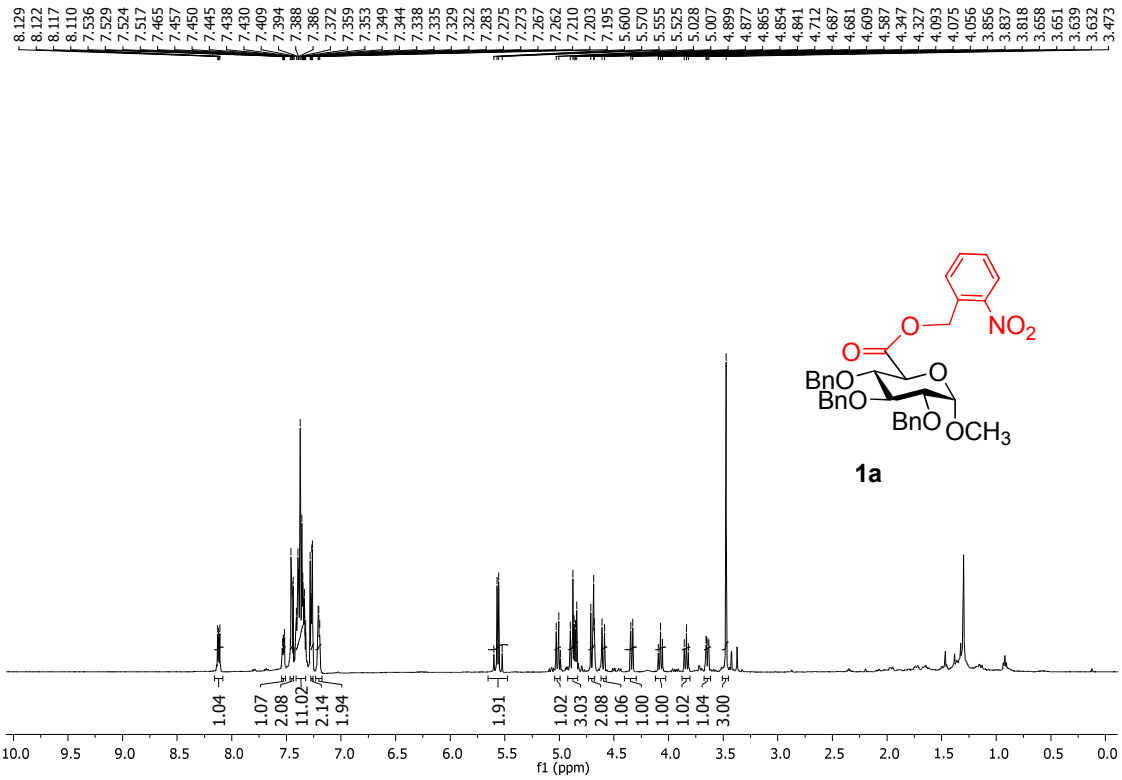
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound AB



^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of compound AC

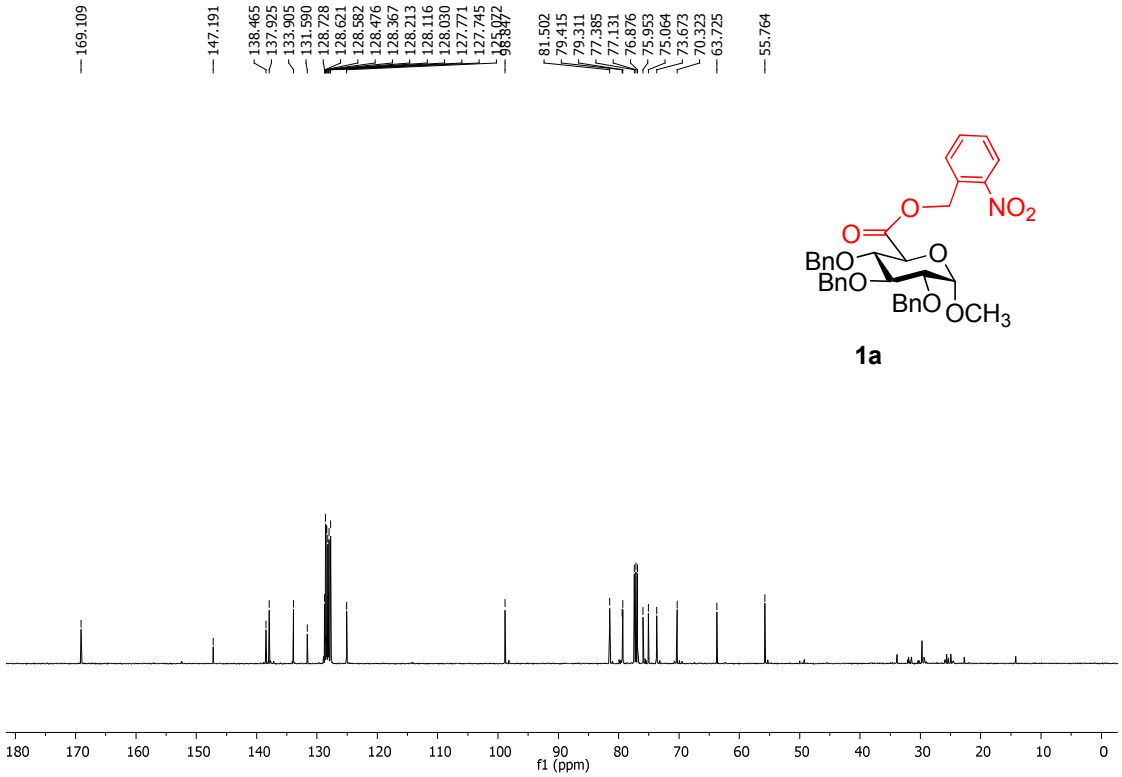


^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound AC



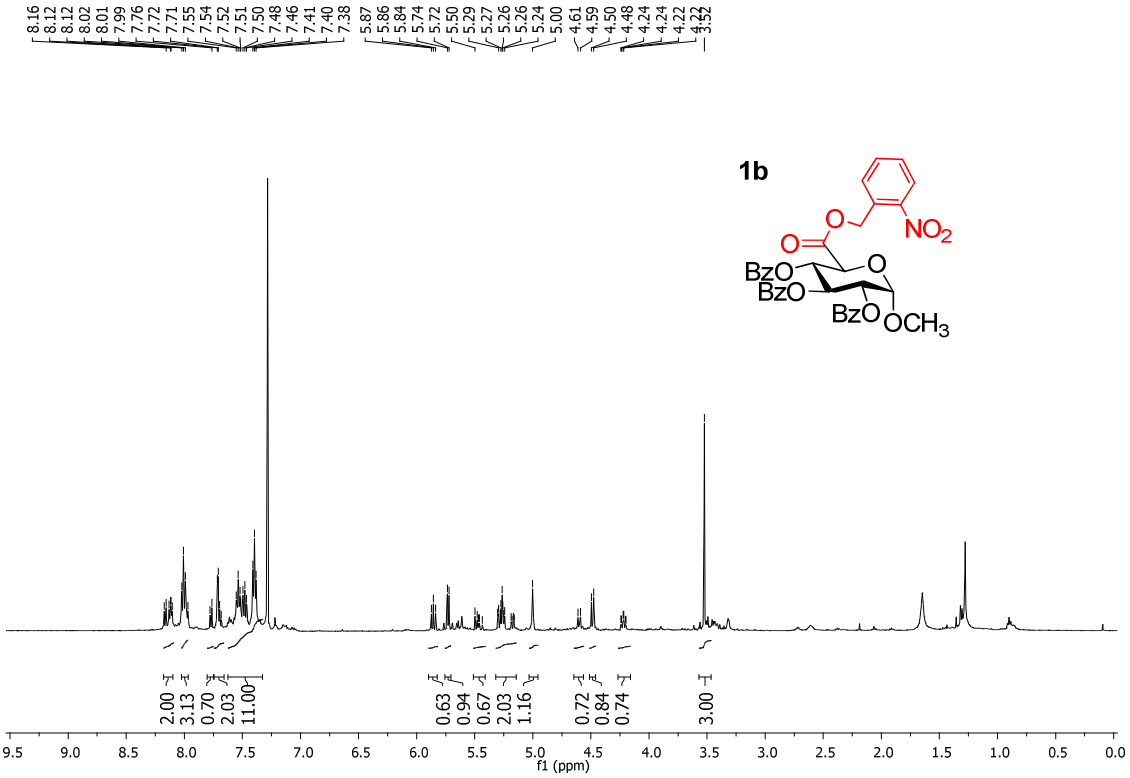
1a

^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of compound 1a

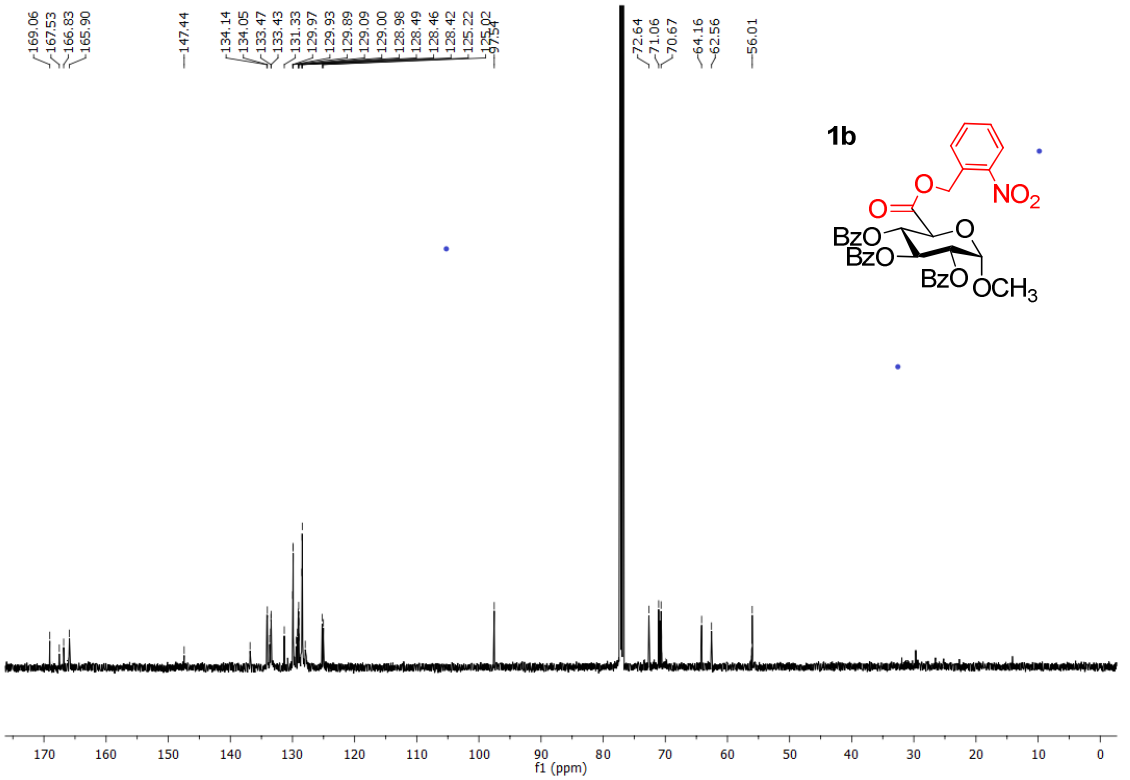


1a

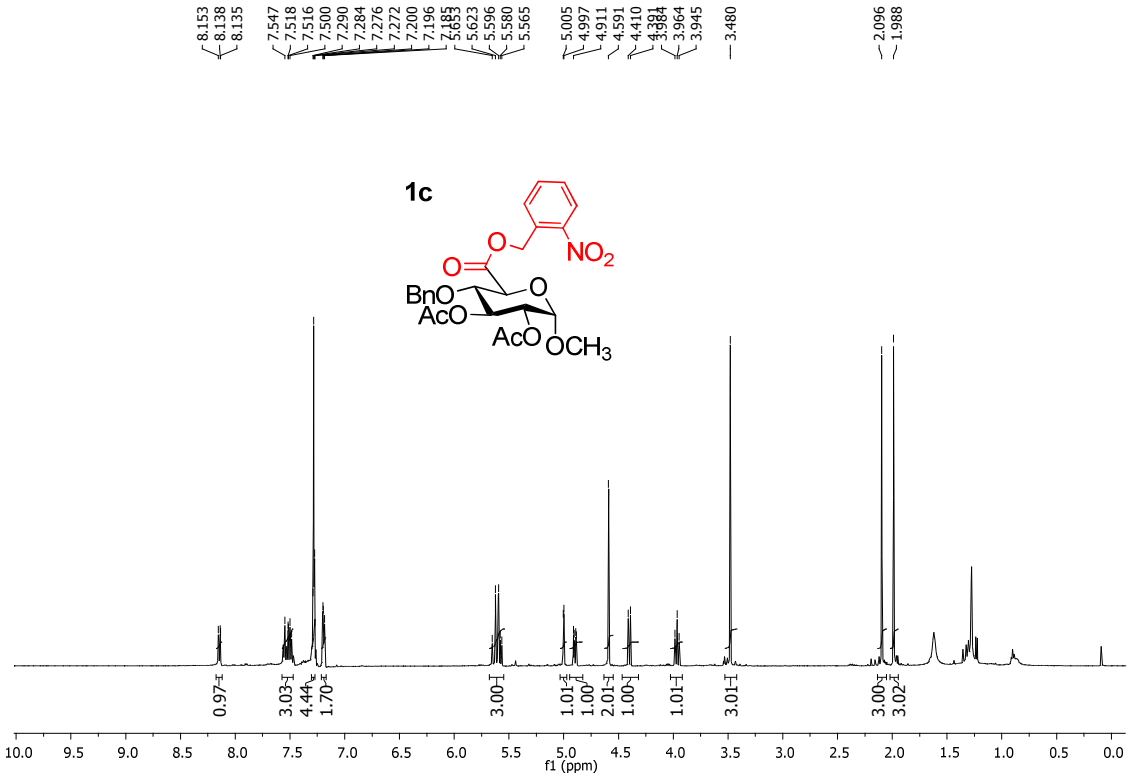
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound 1a



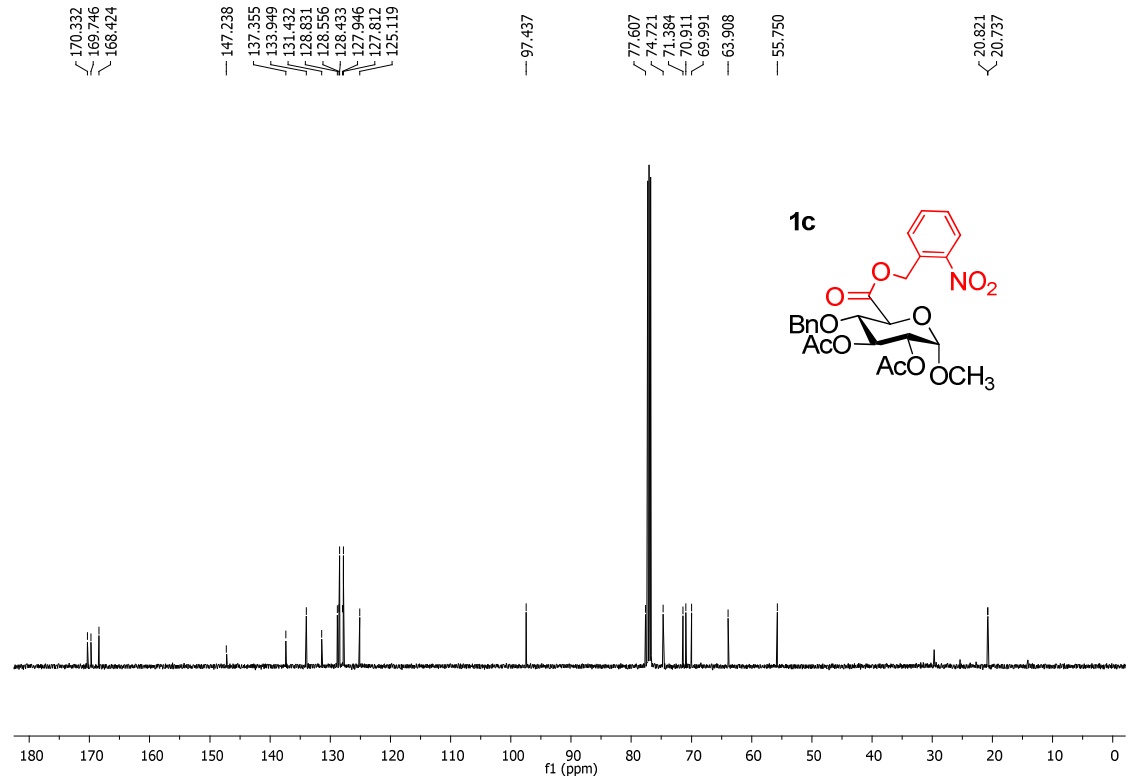
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of compound 1b



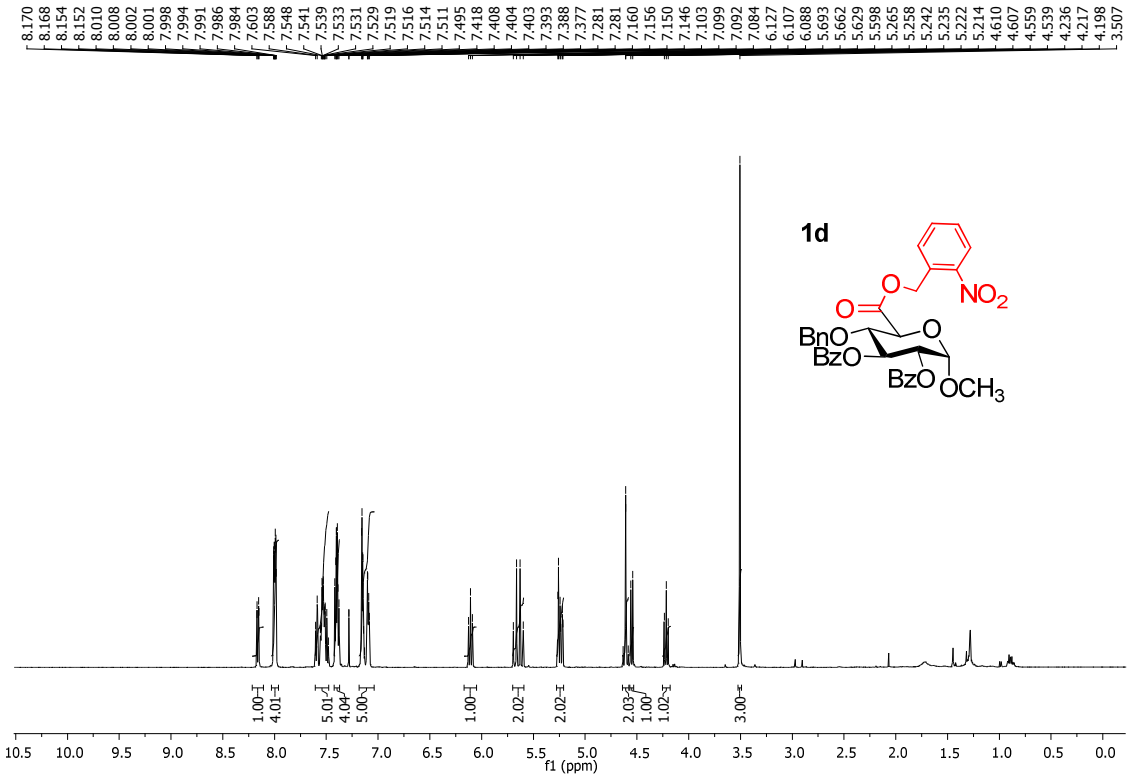
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound 1b



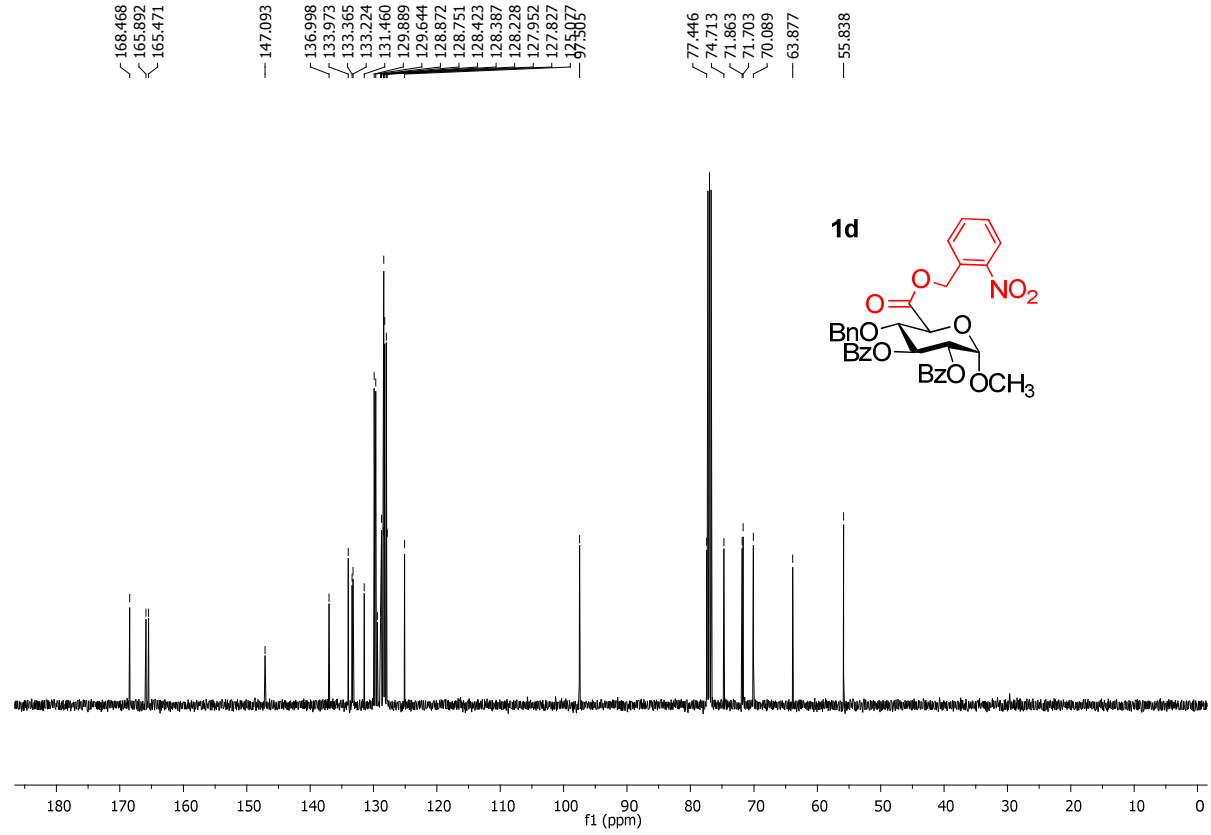
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of compound 1c



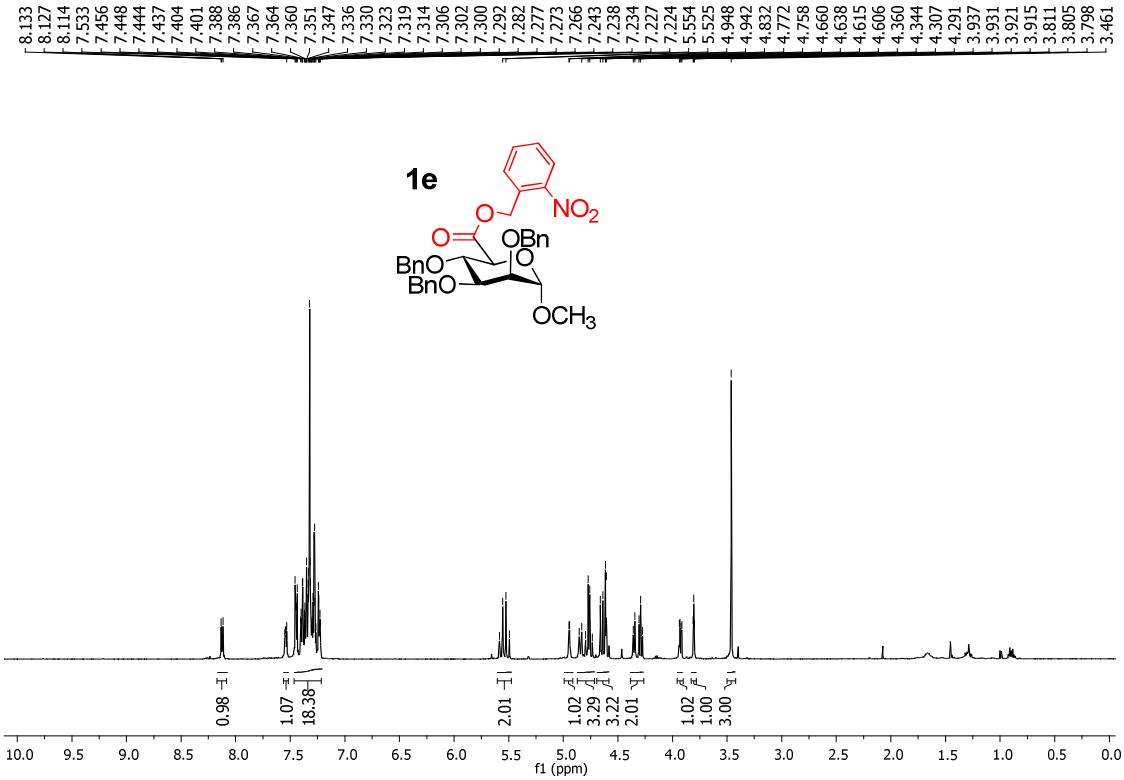
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound 1c



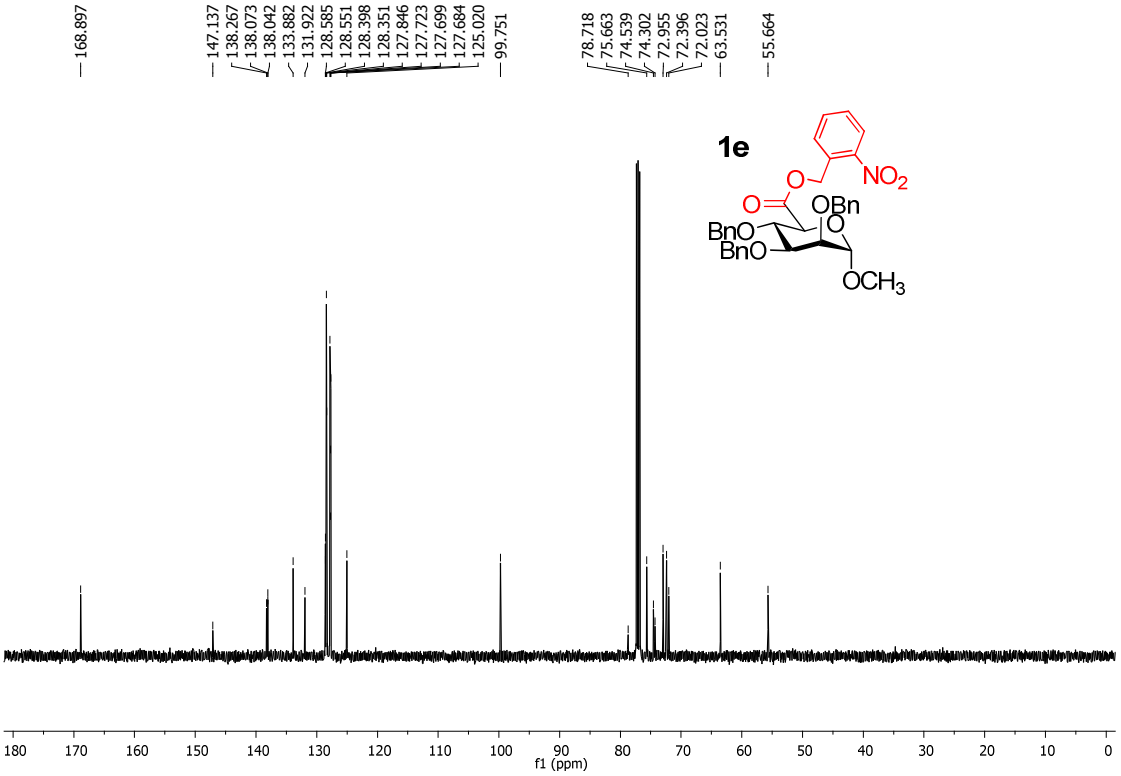
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of compound 1d



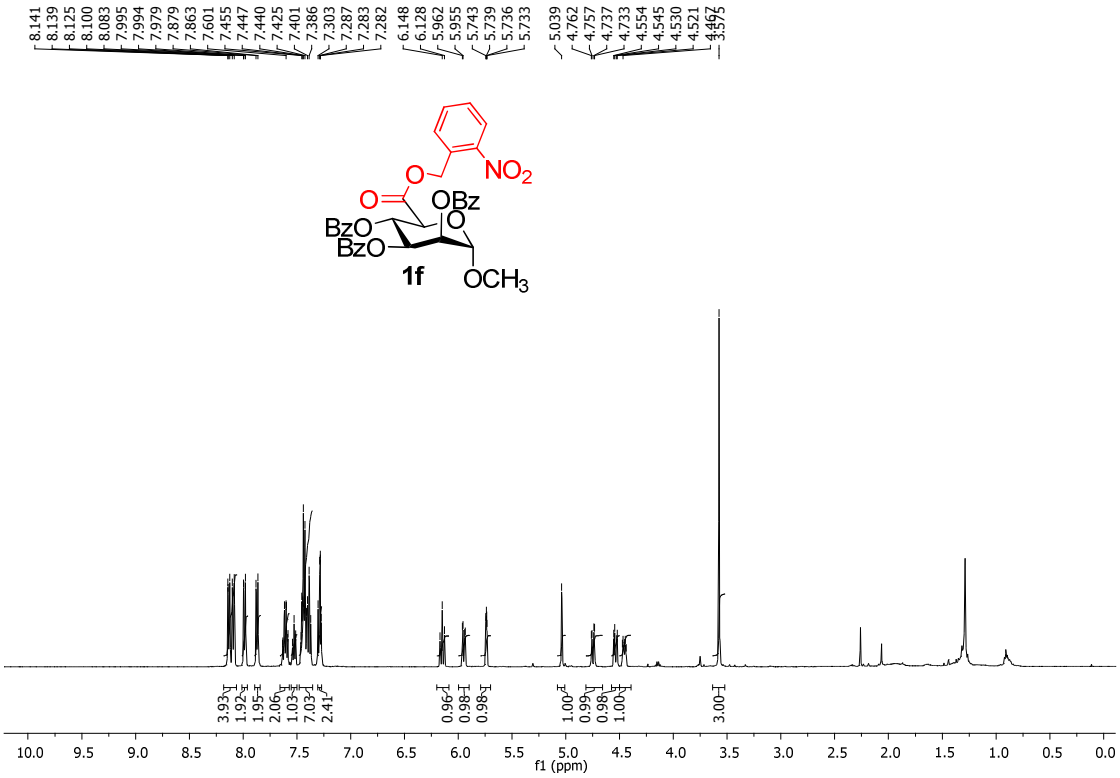
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound 1d



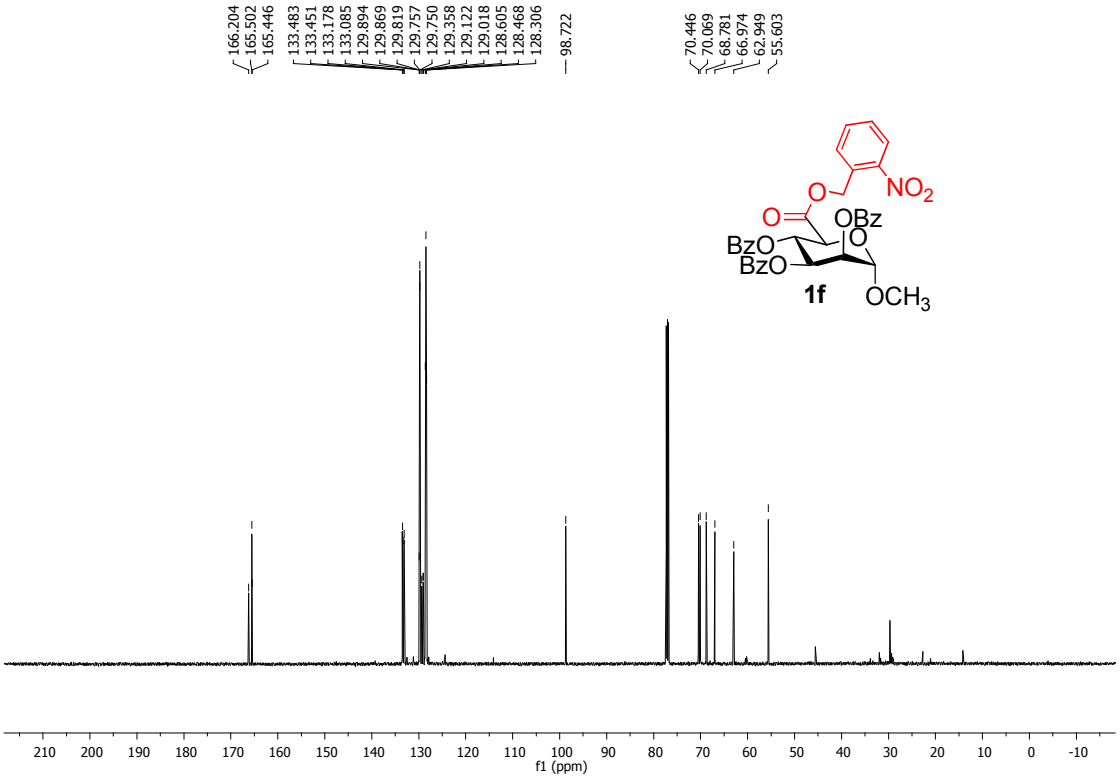
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of compound 1e



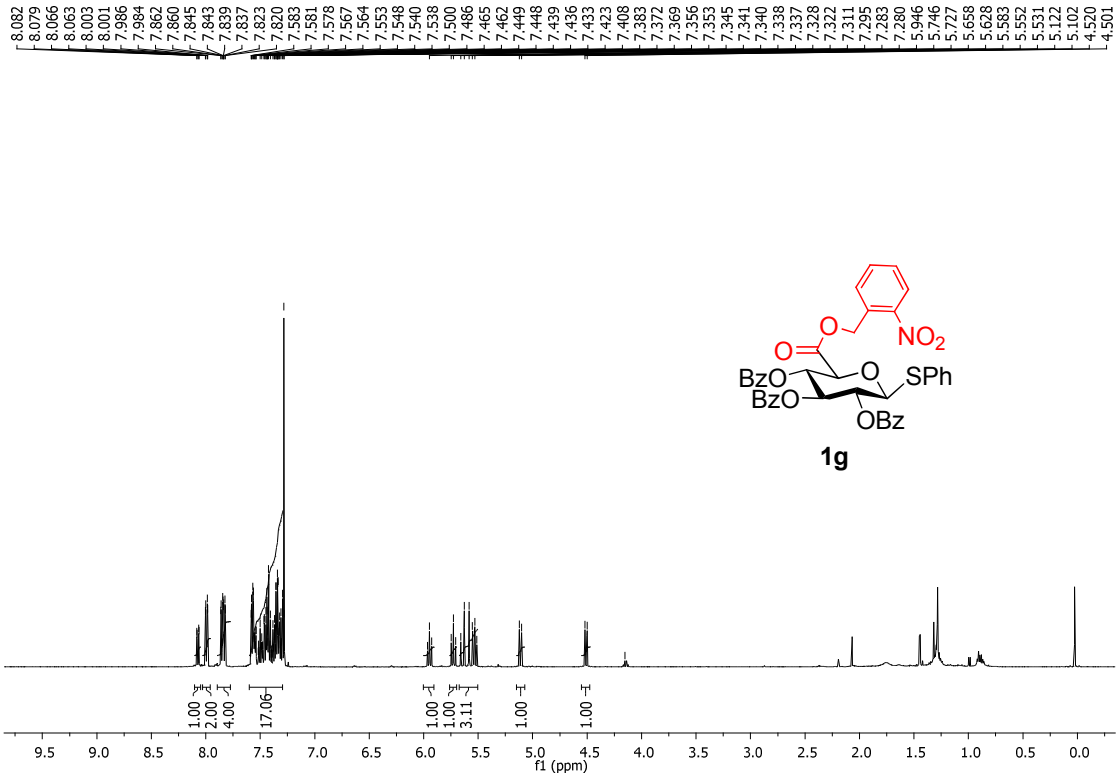
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound 1e



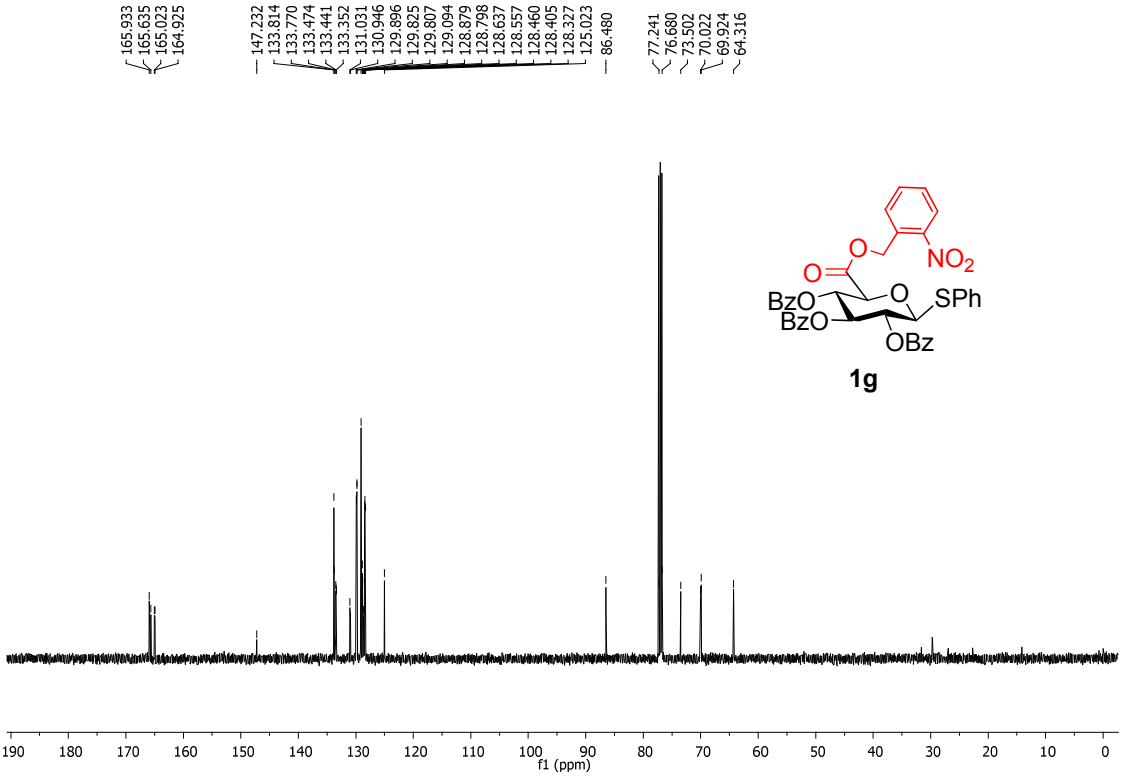
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of compound 1f



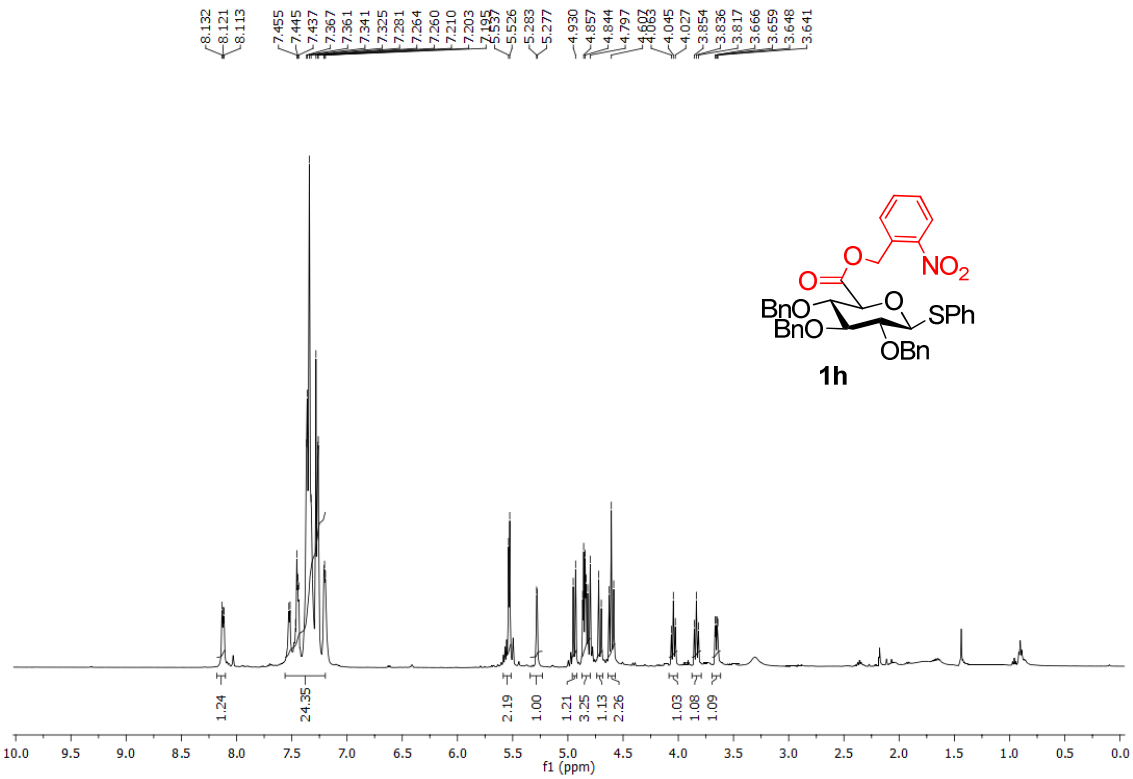
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound 1f



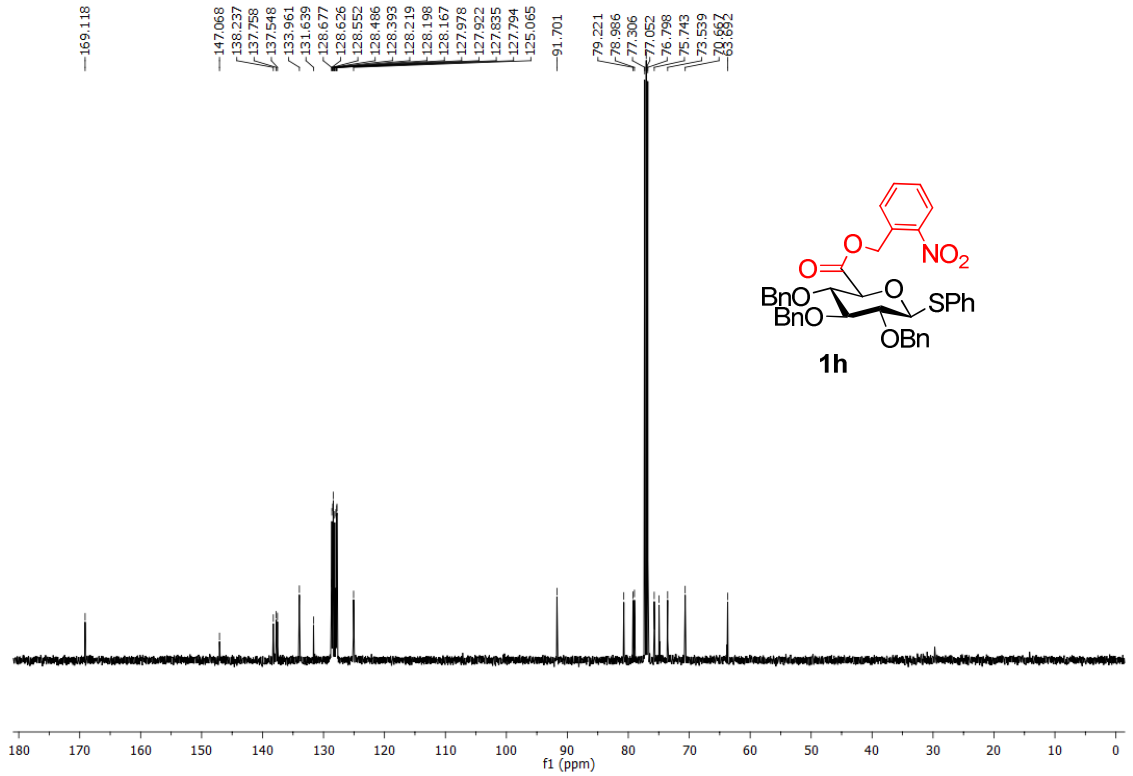
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of compound 1g



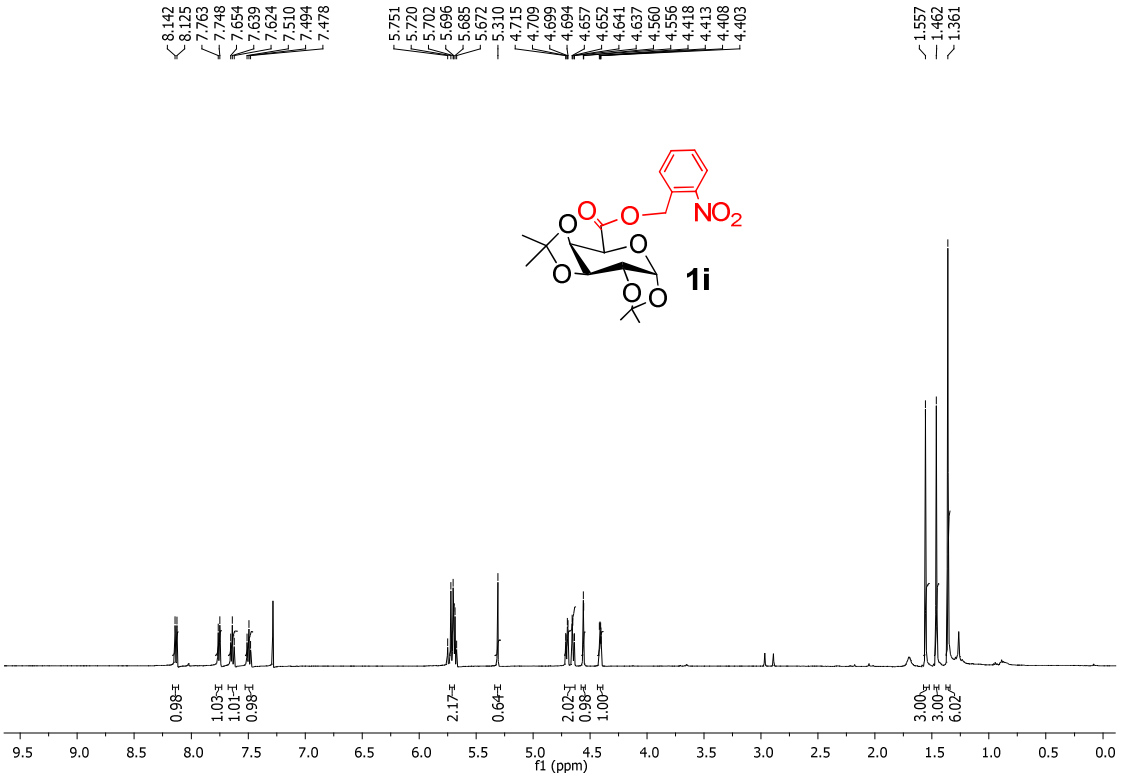
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound 1g



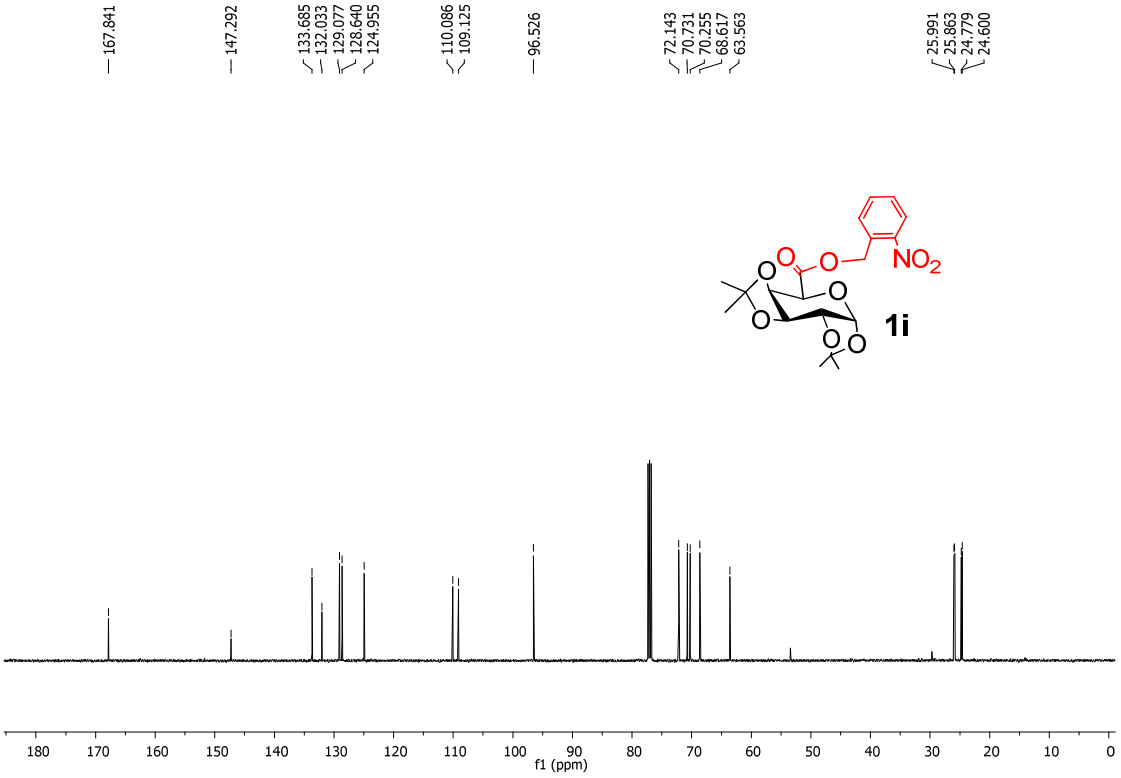
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of compound 1h



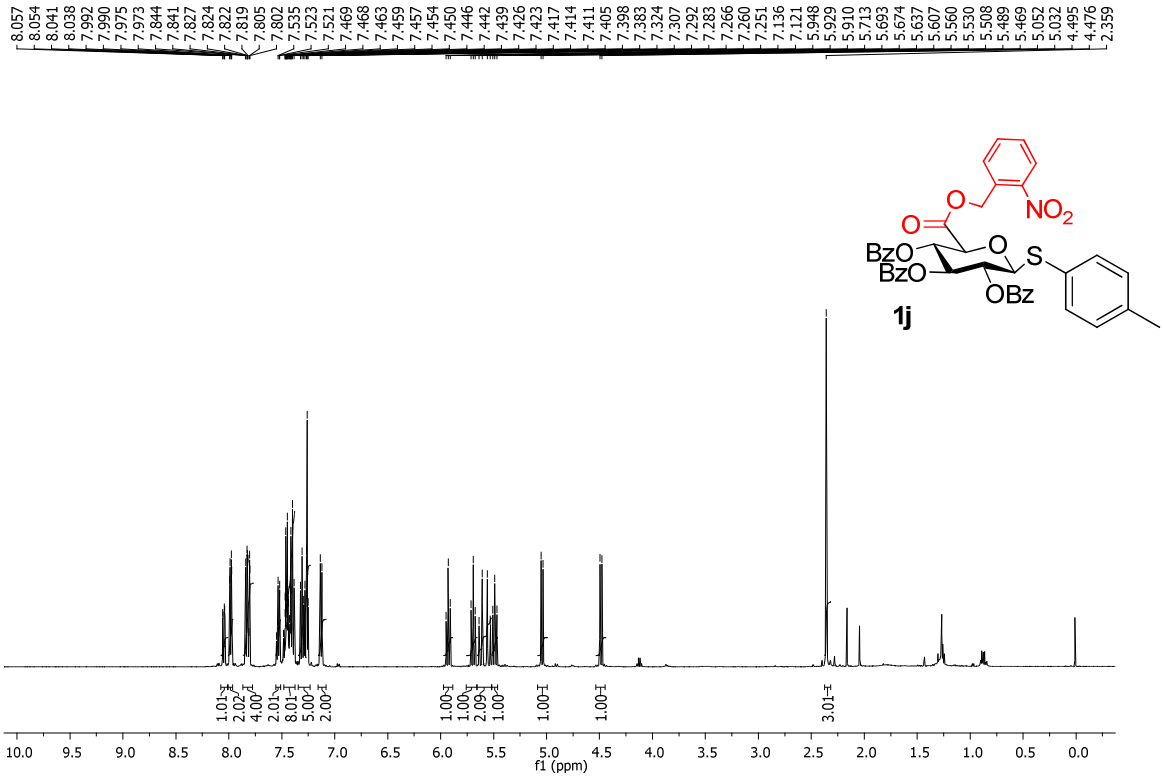
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound 1h



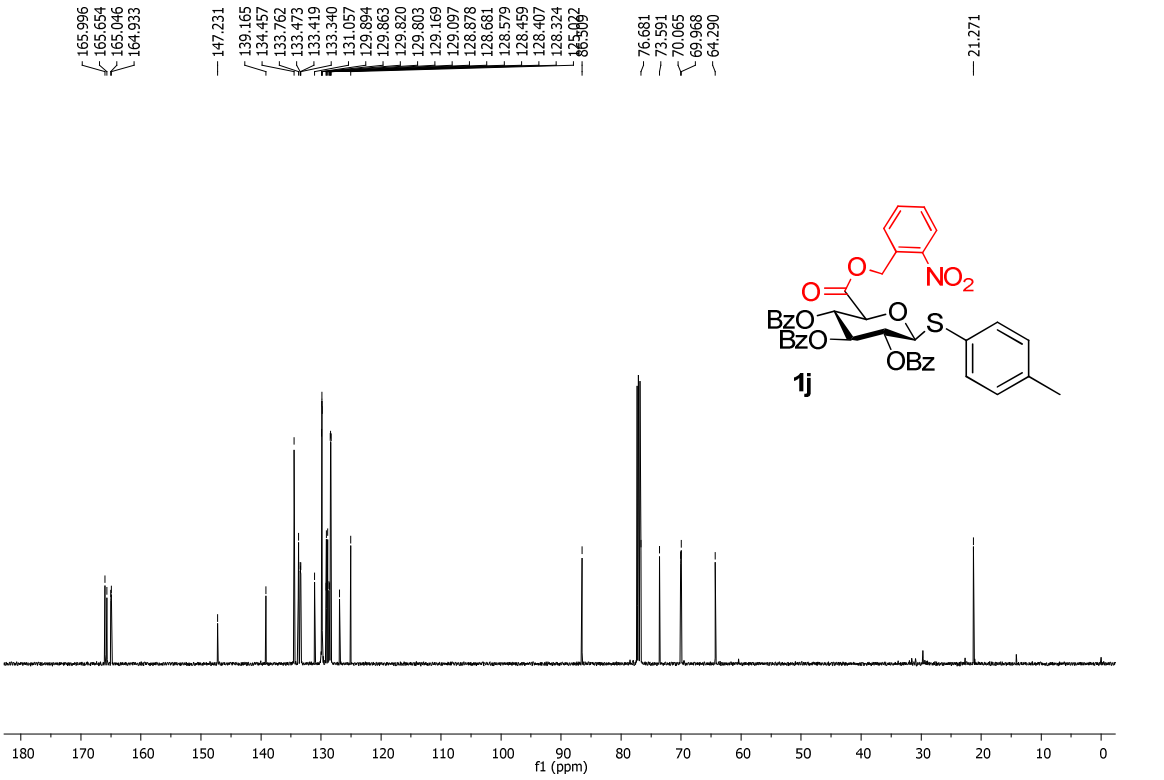
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of compound 1i



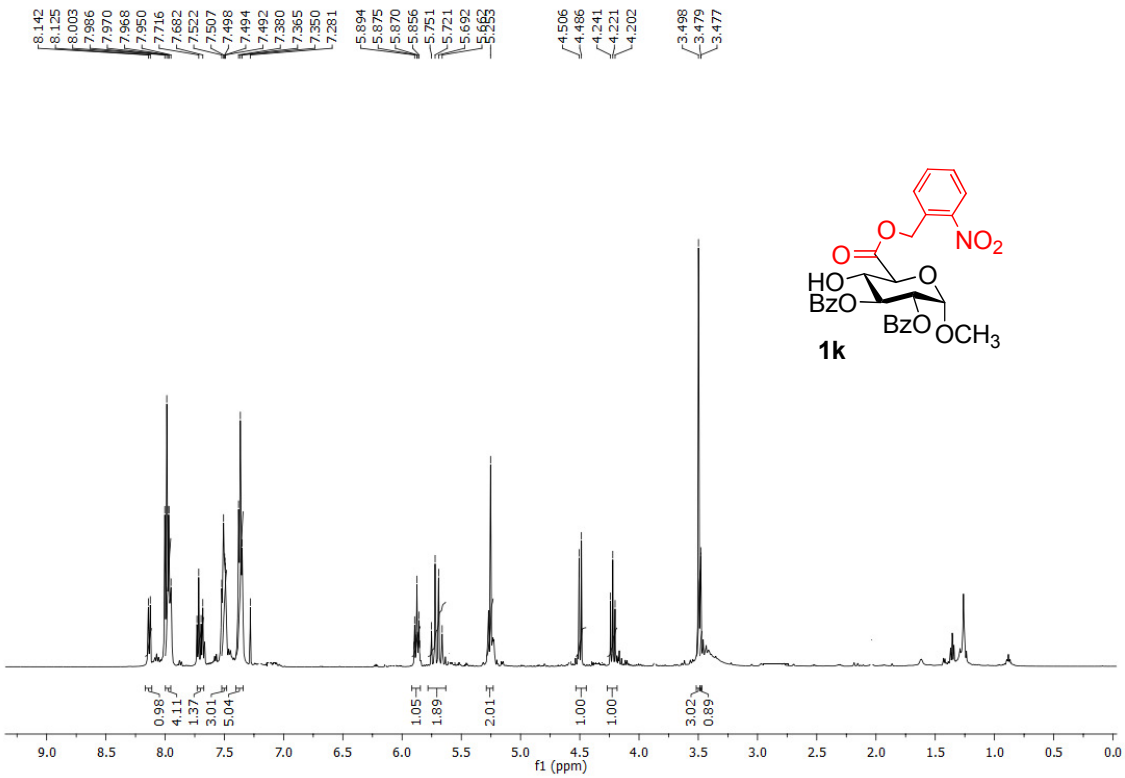
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound 1i



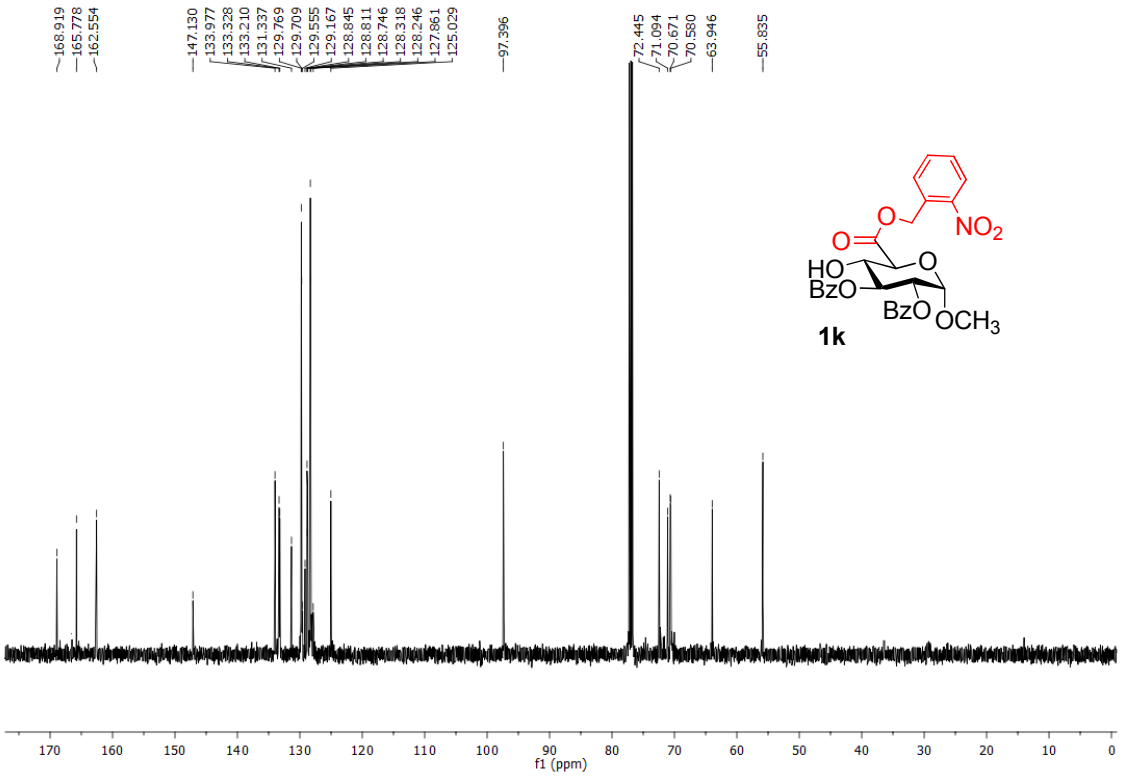
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of compound 1j



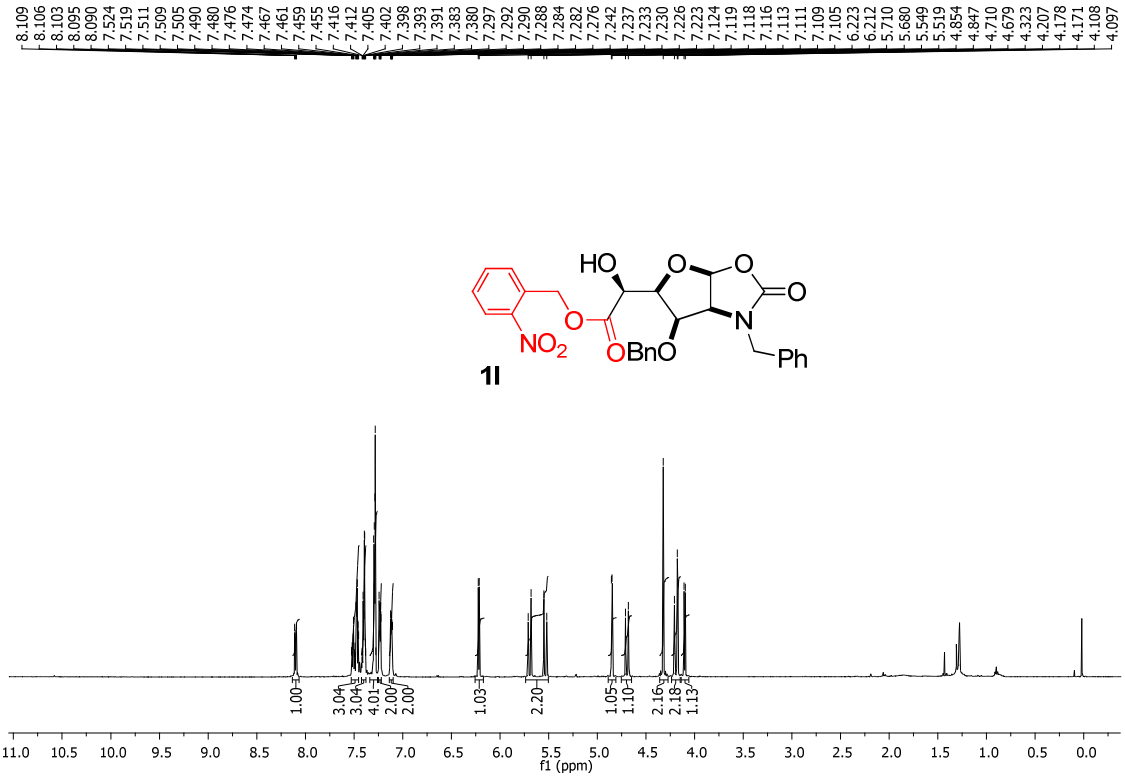
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound 1j



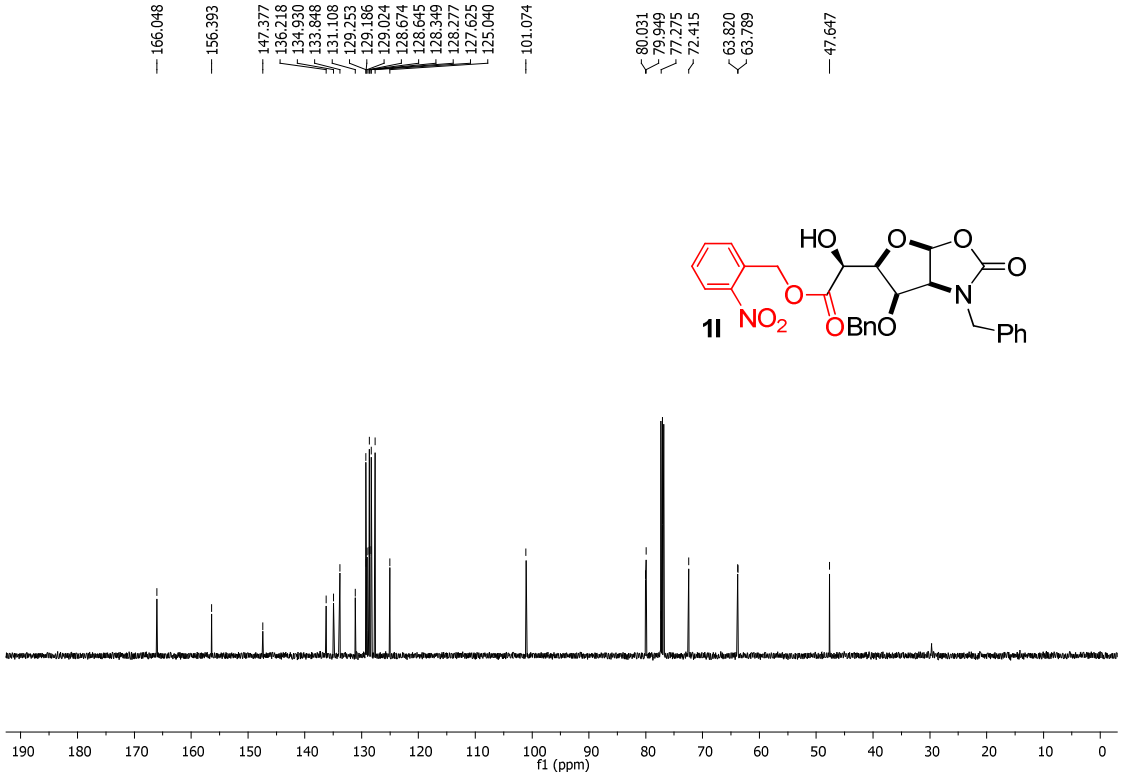
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of compound 1k



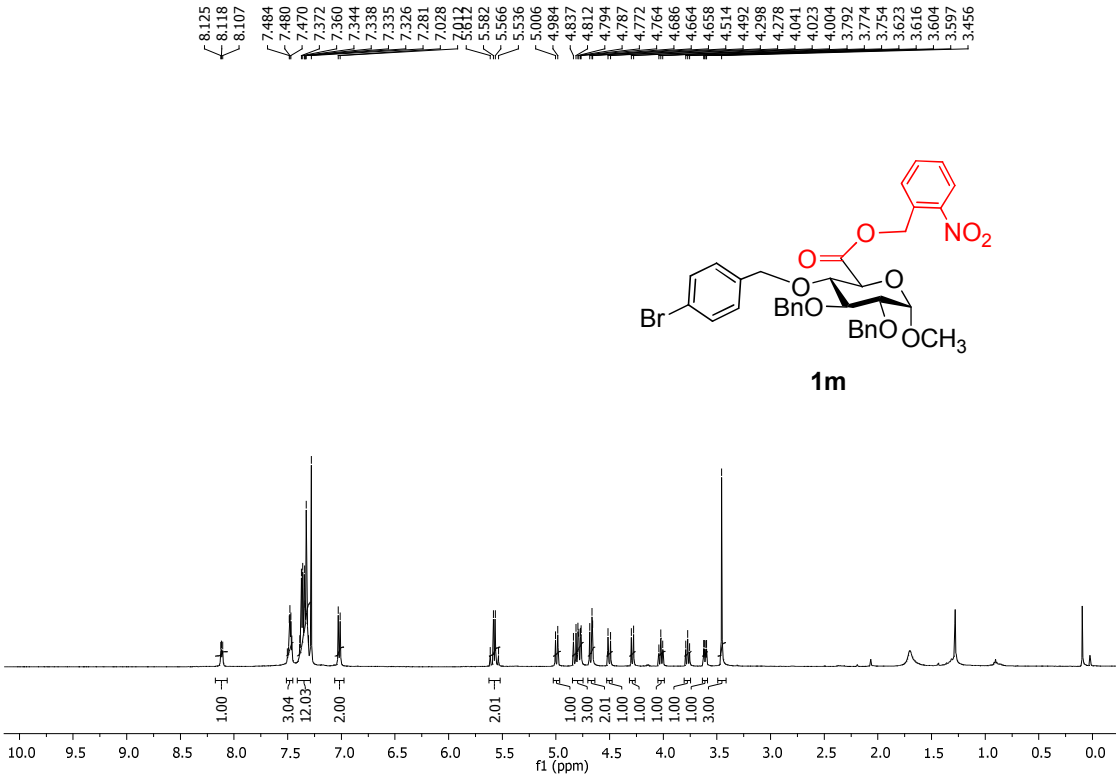
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound 1k



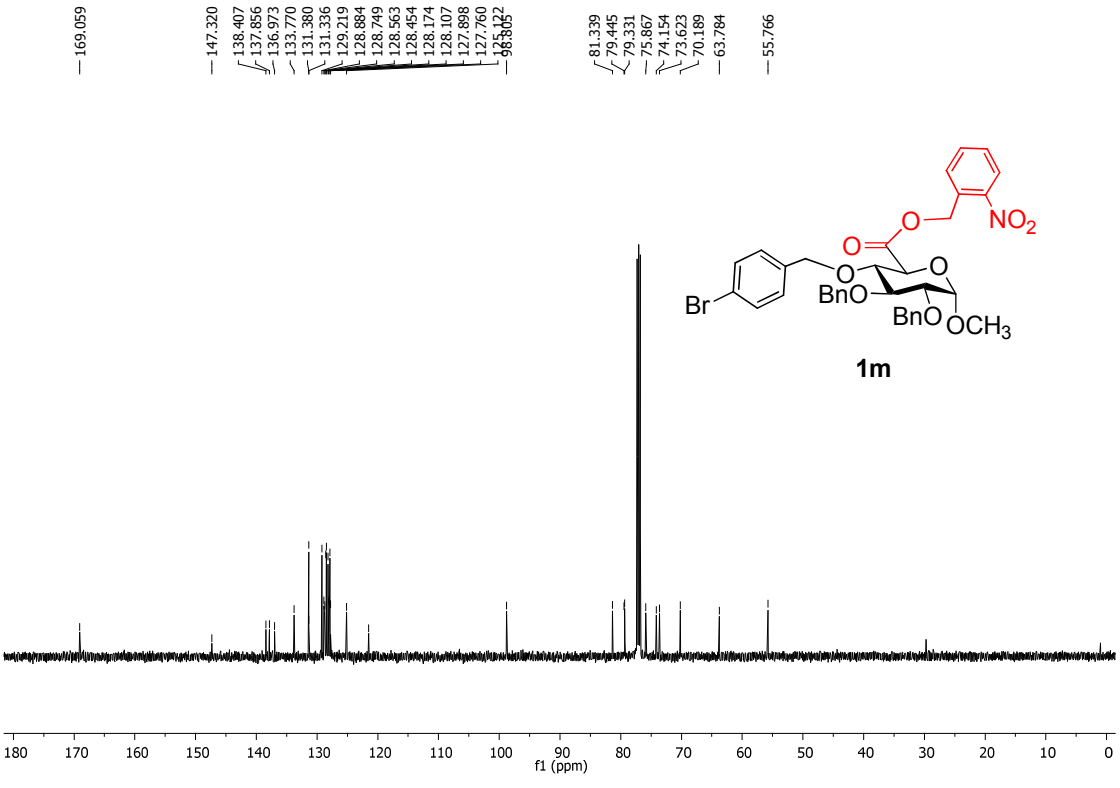
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of compound 1l



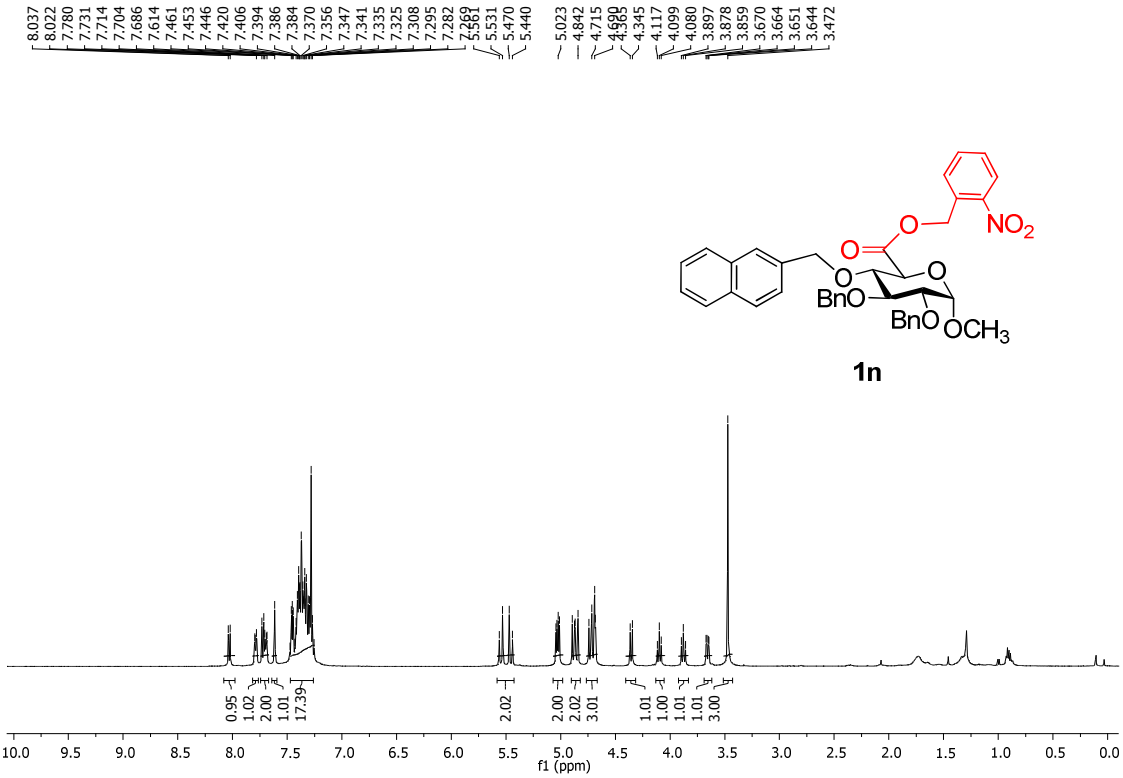
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound 1l



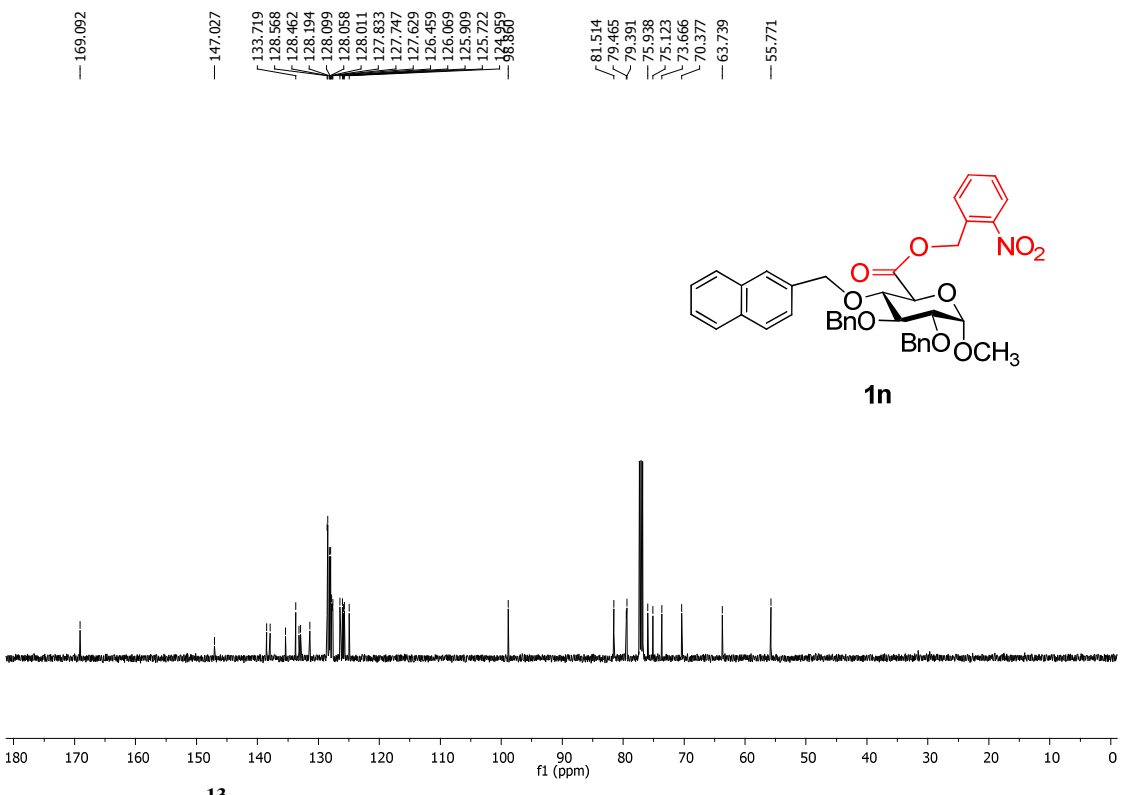
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of compound 1m



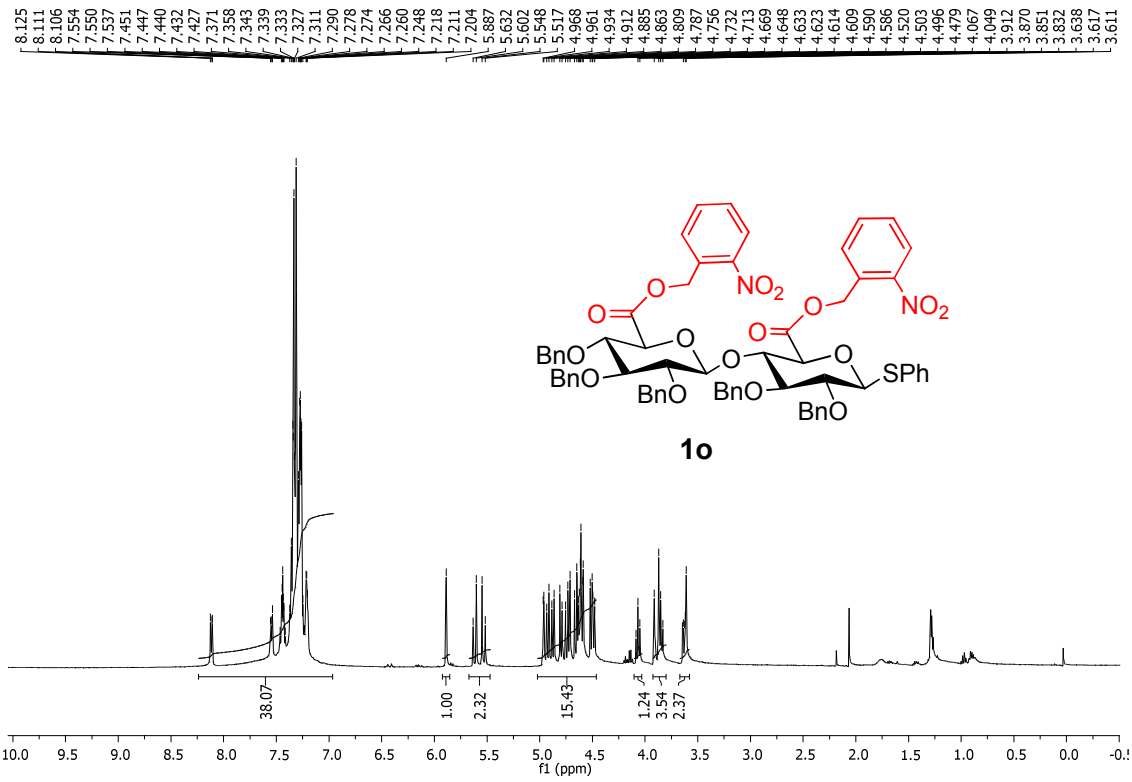
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound 1m



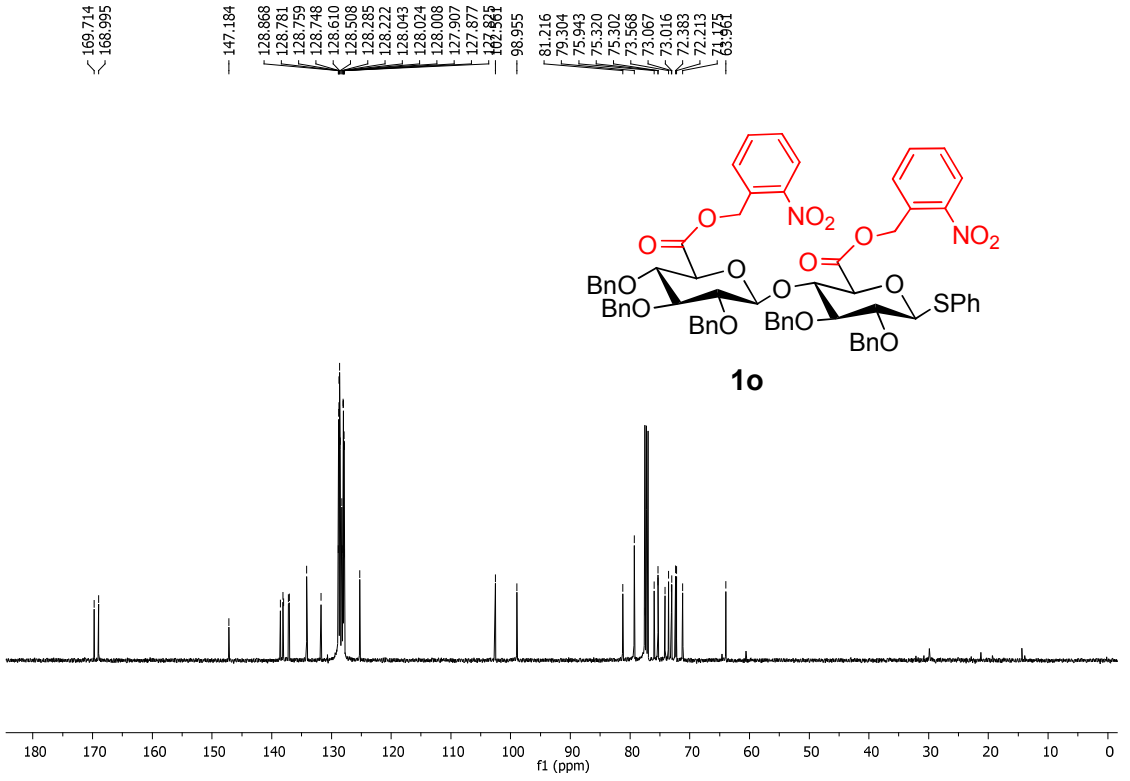
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of compound 1n



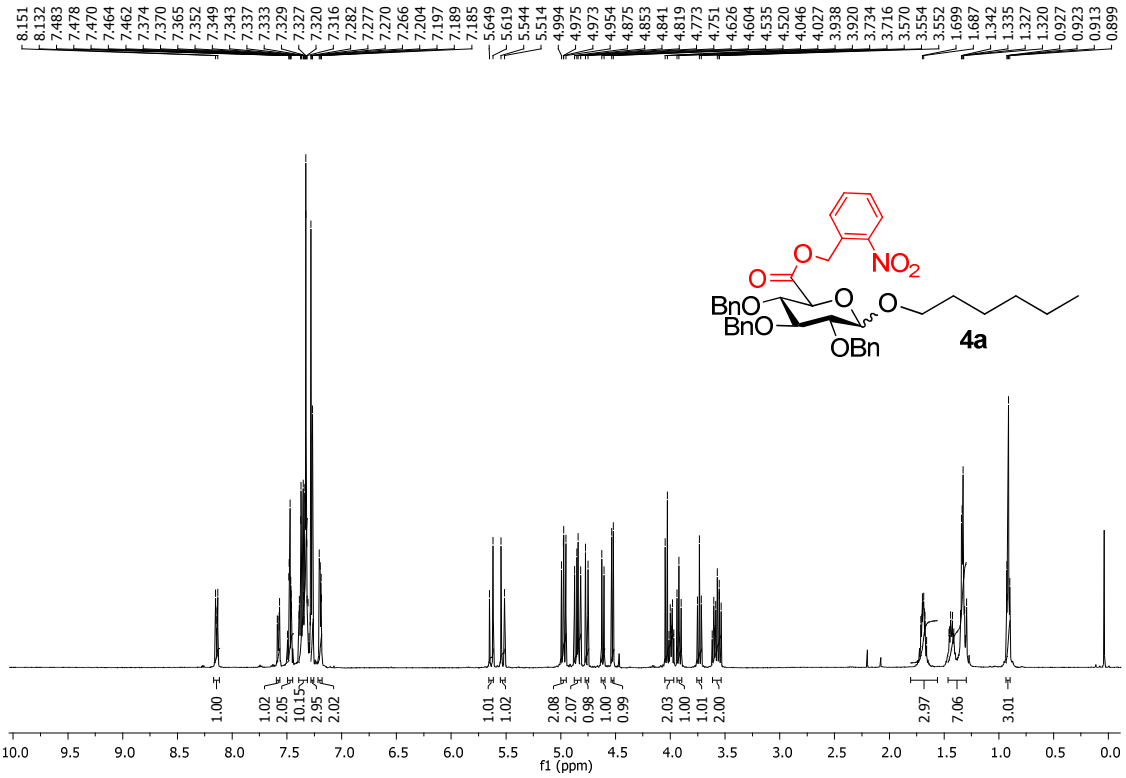
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound 1n



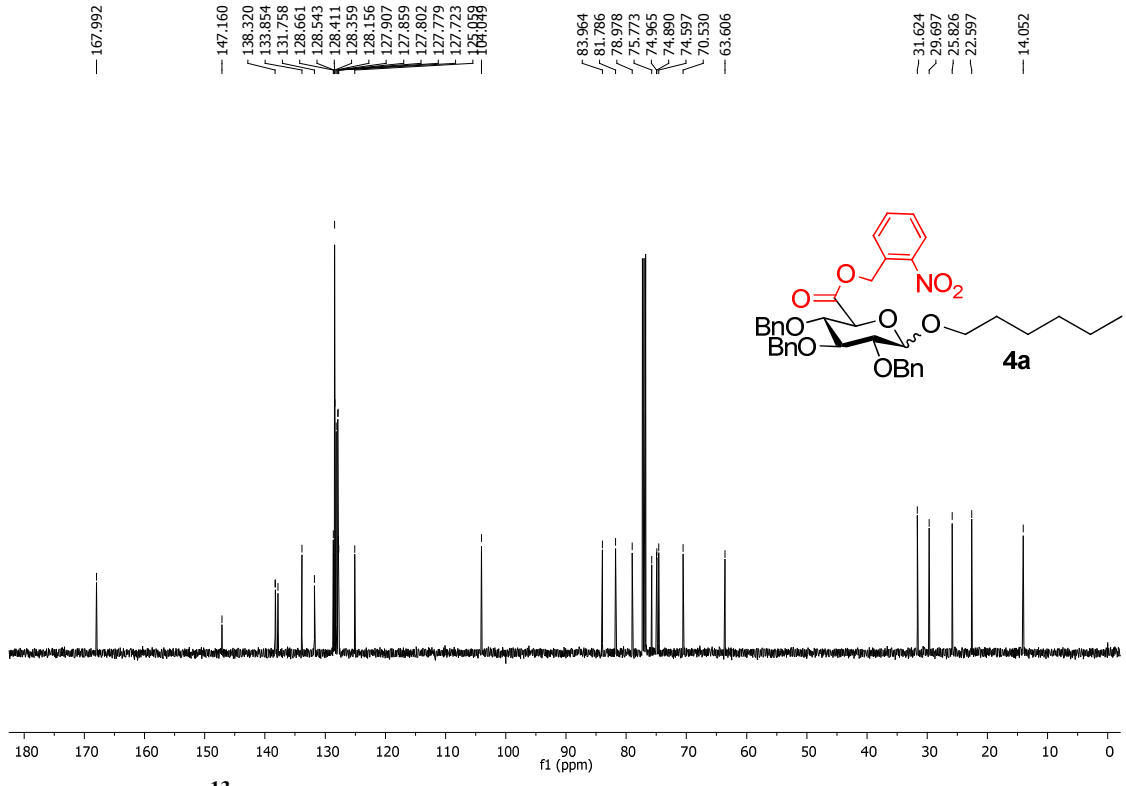
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of compound 1o



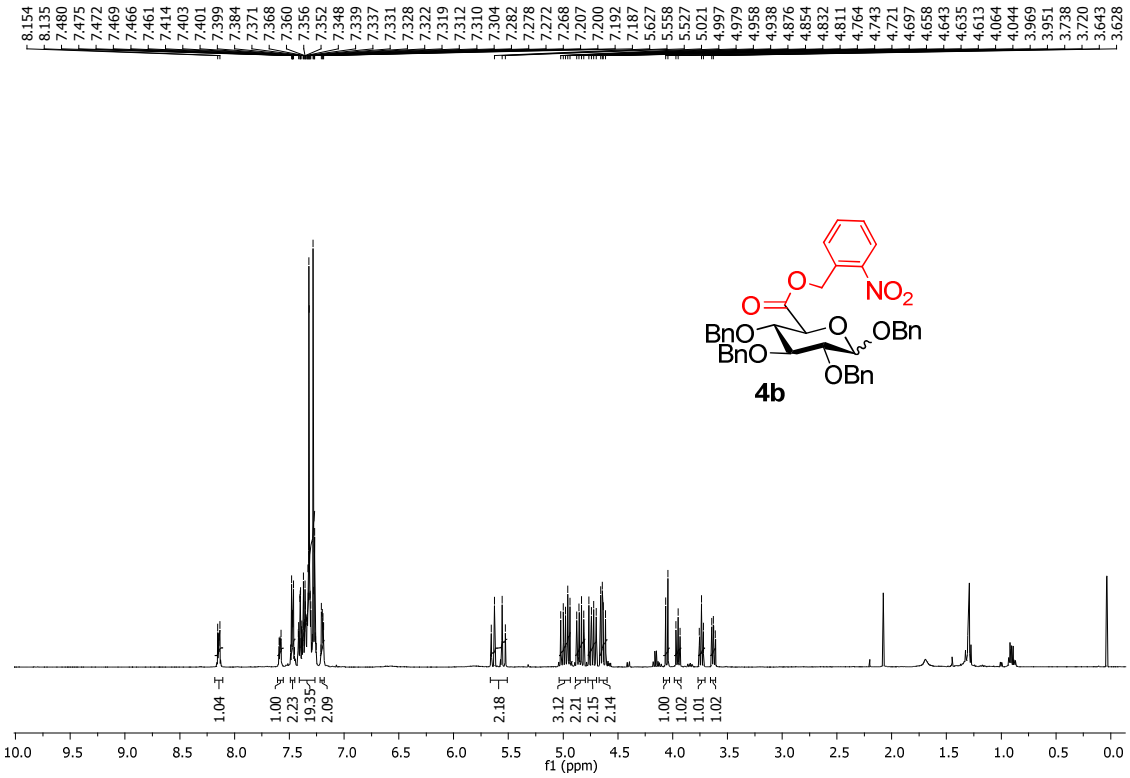
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound 1o



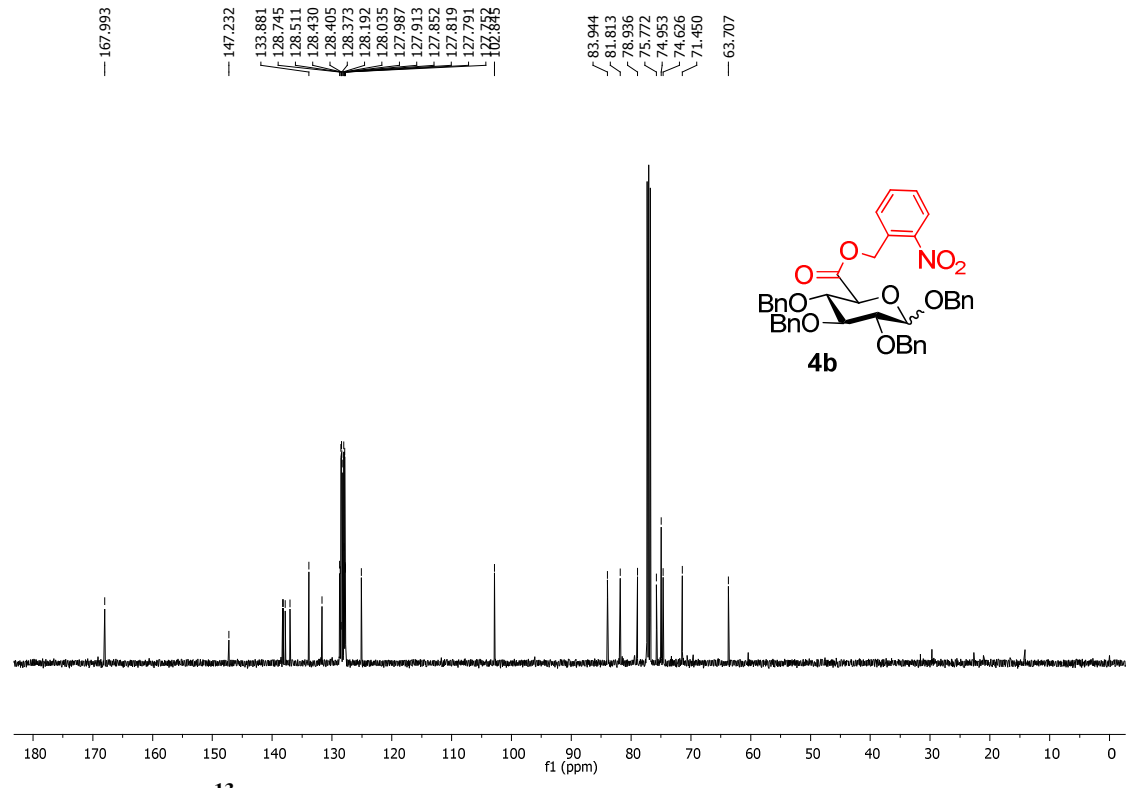
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of compound 4a



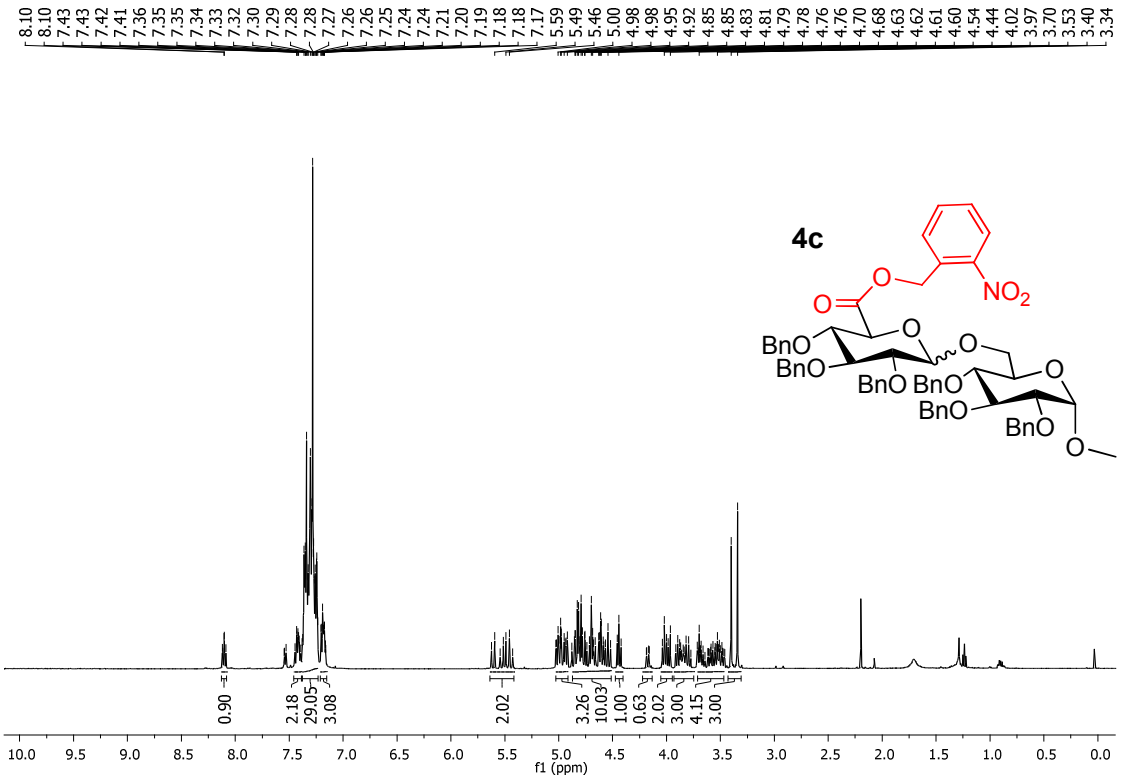
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound 4a



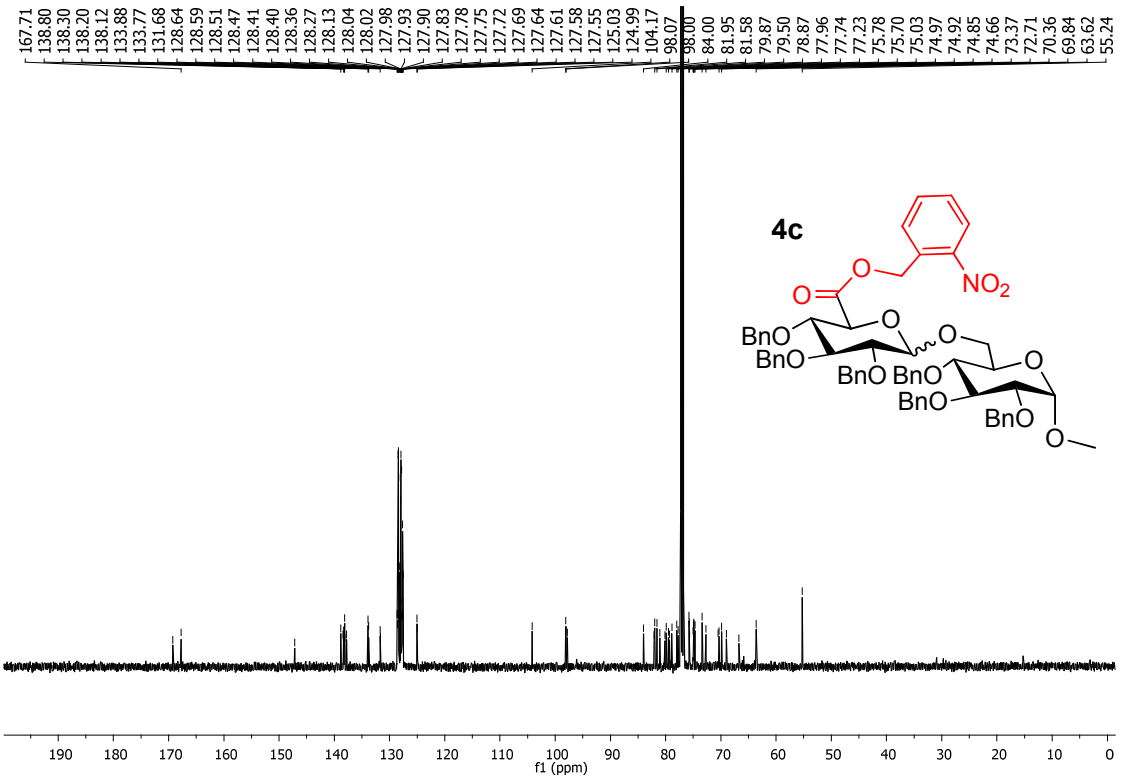
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of compound 4b



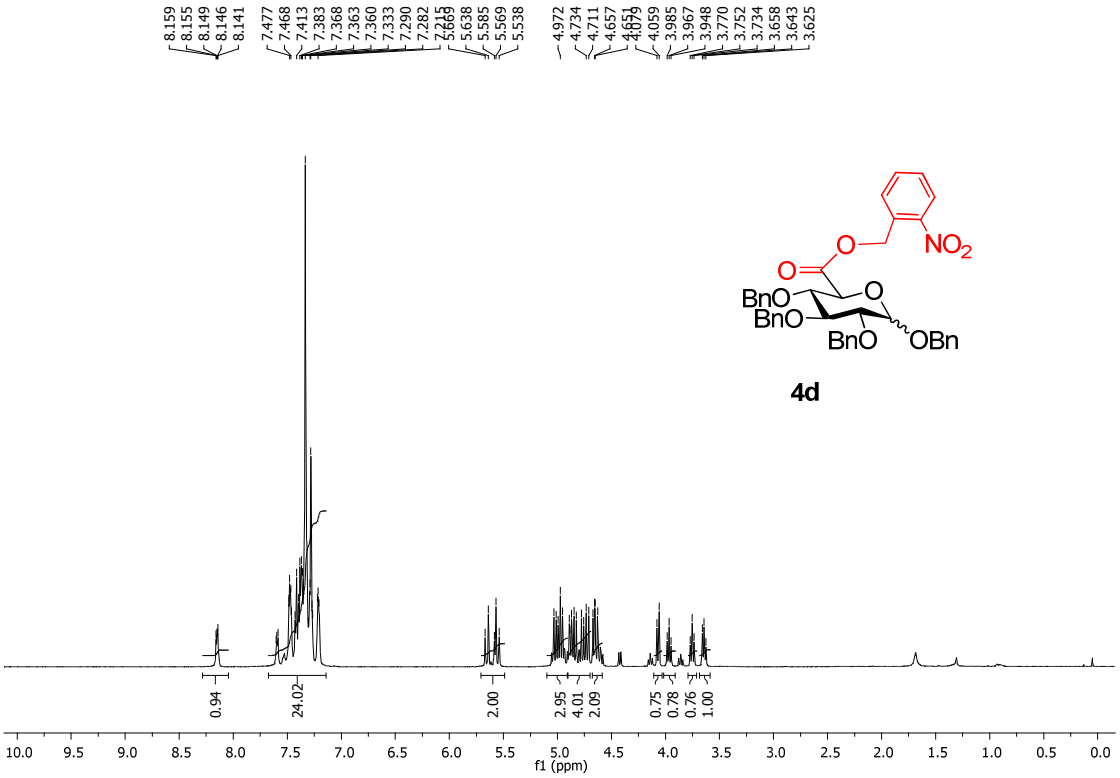
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound 4b



^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of compound 4c

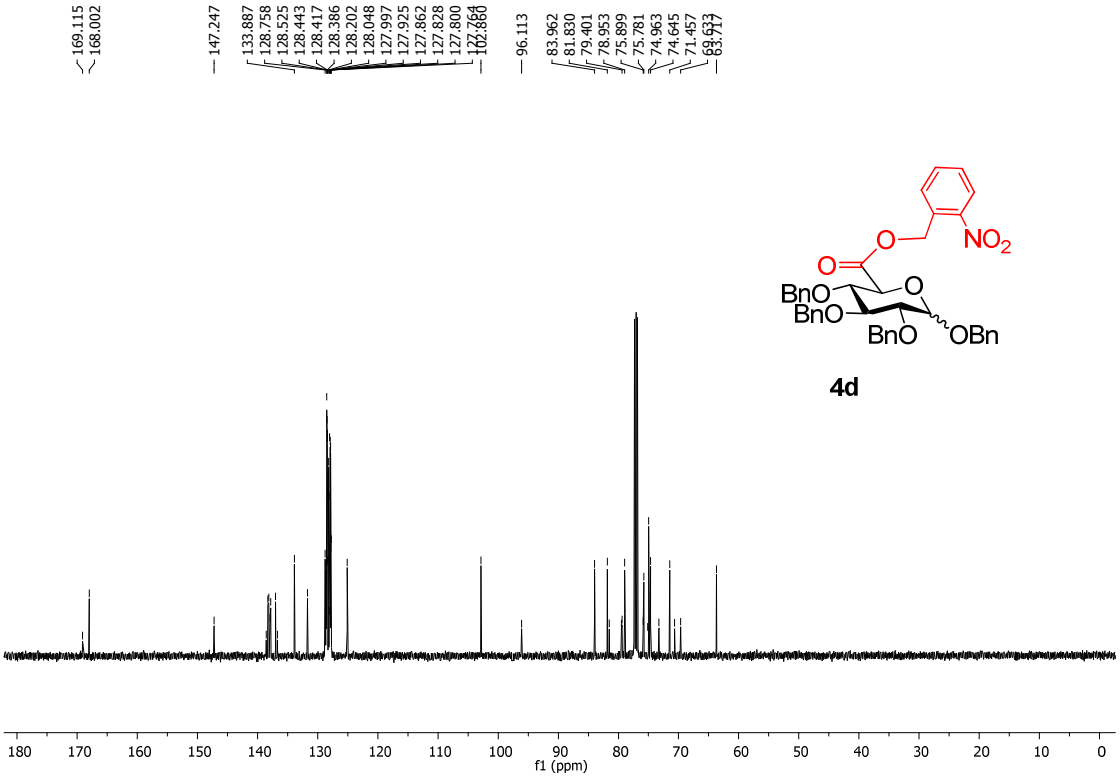


^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound 4c



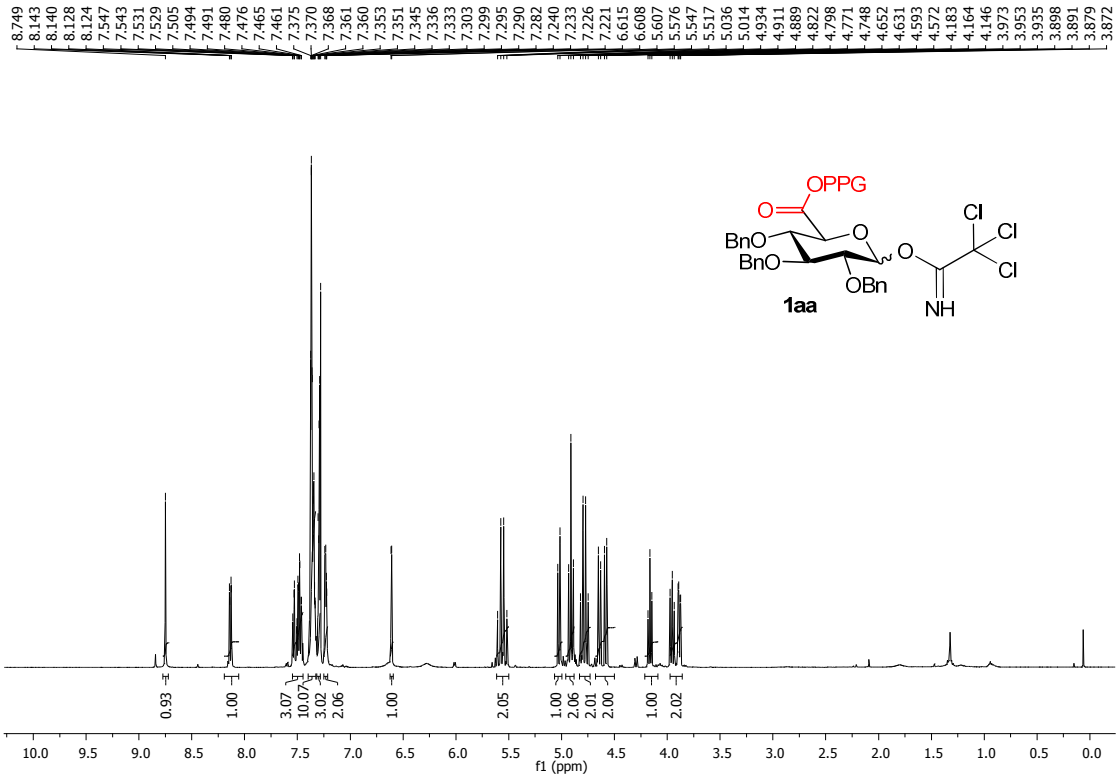
4d

^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of compound 4d

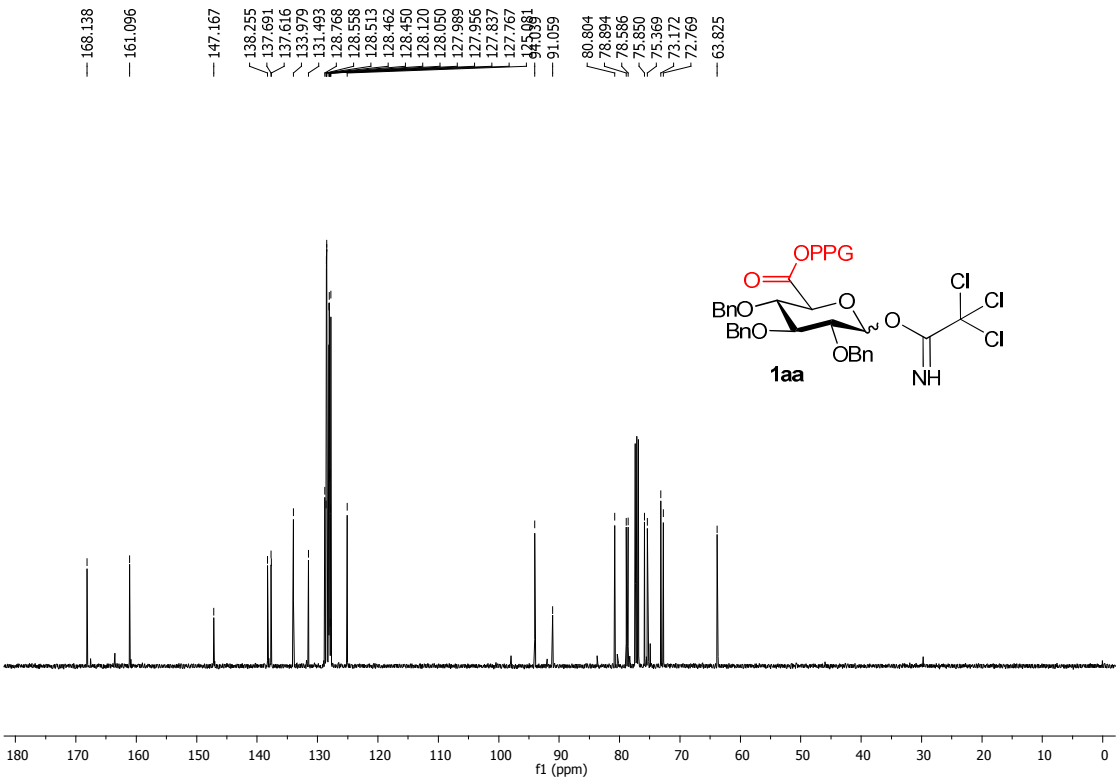


4d

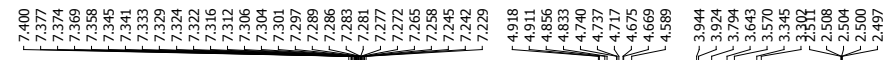
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound 4d

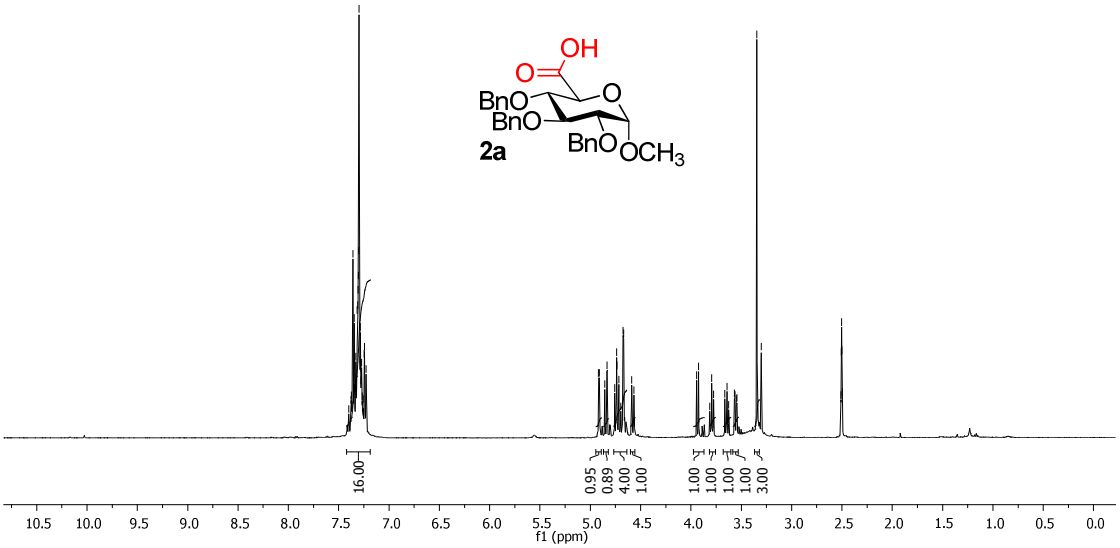


^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of compound 1aa

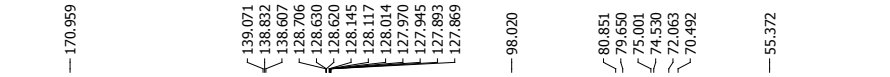


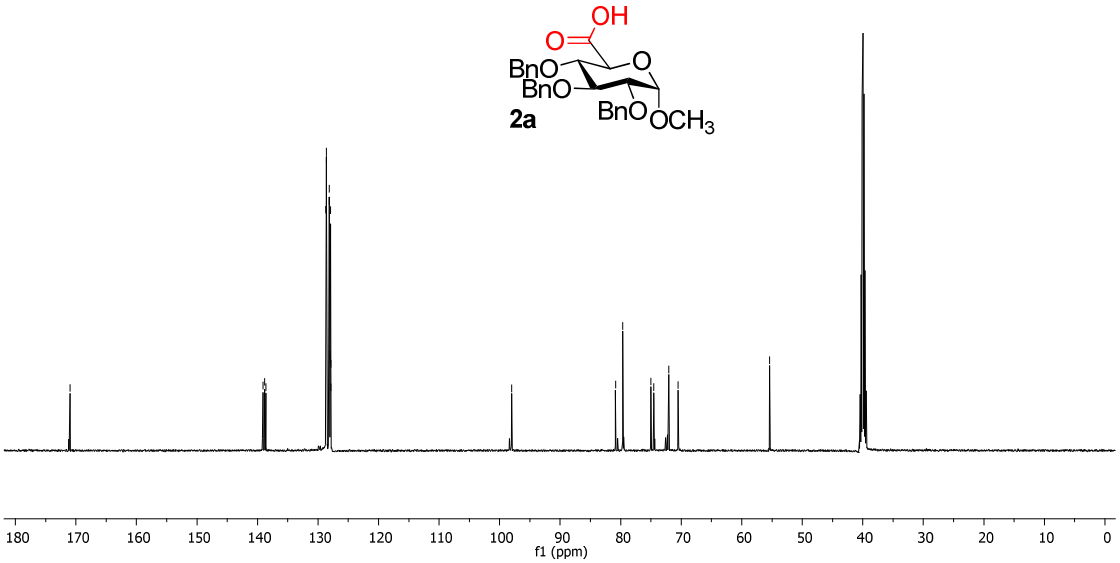
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound 1aa



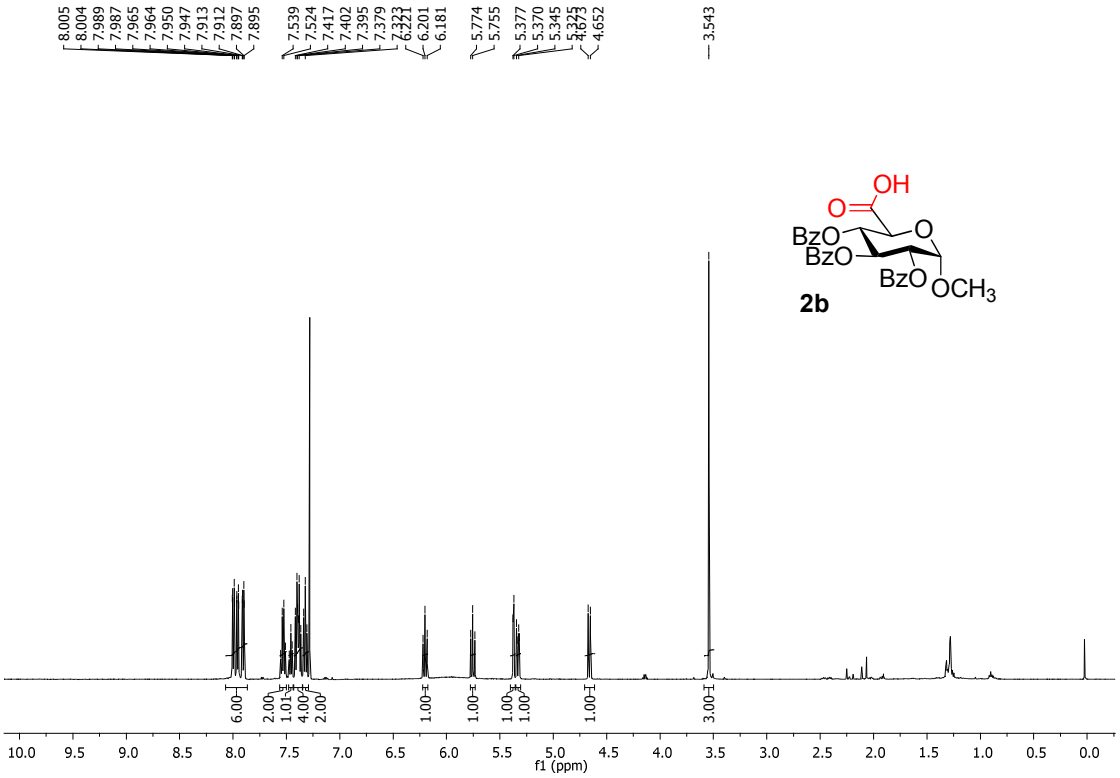


^{1}H-NMR (500 MHz, DMSO-d$_6$) spectrum of compound 2a

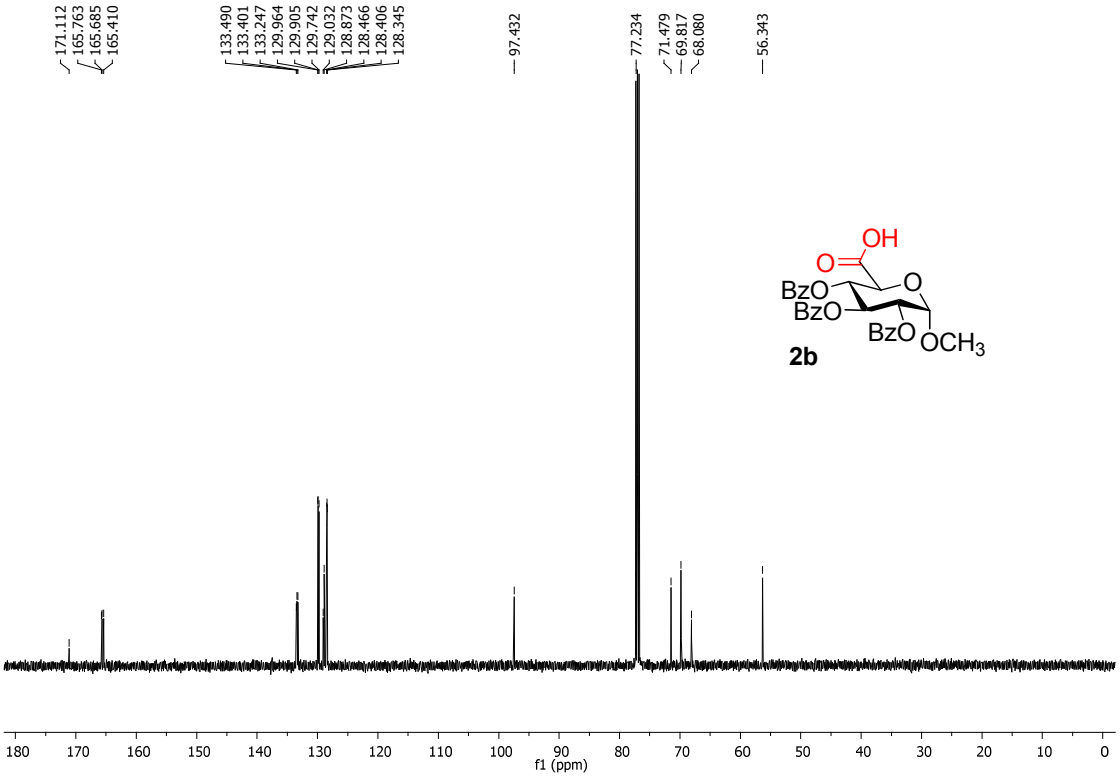




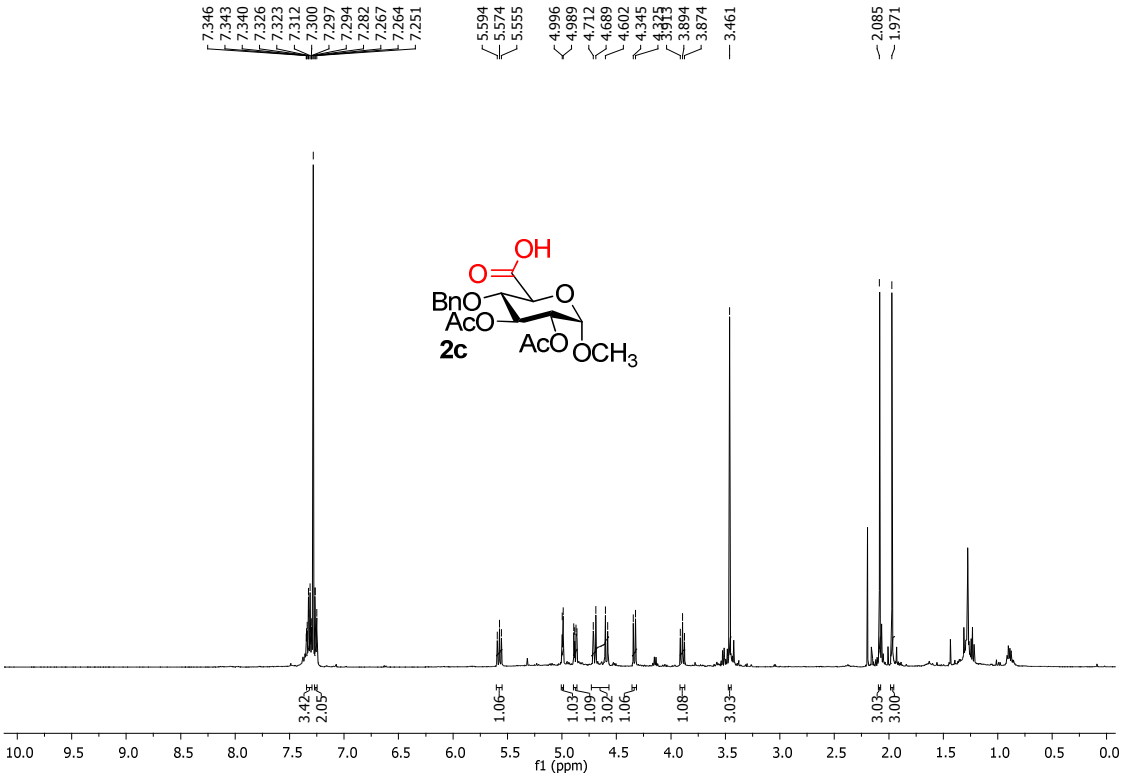
^{13}C-NMR (125 MHz, DMSO-d$_6$) spectrum of compound 2a



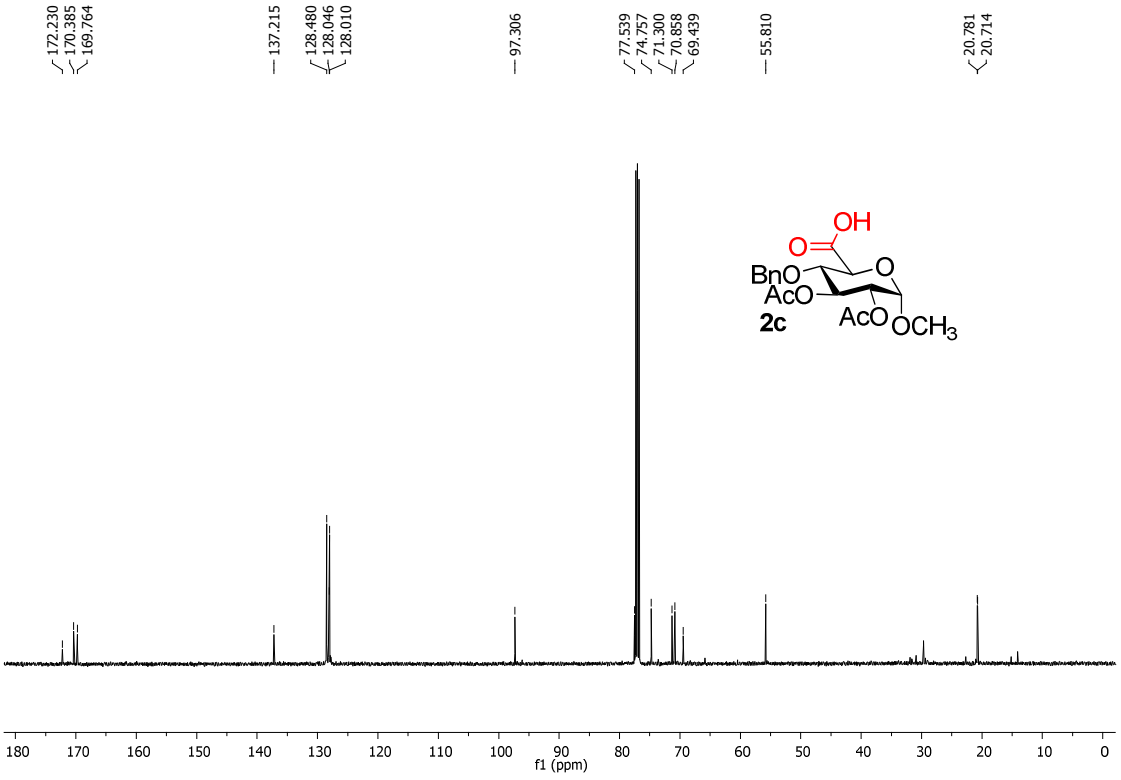
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of compound 2b



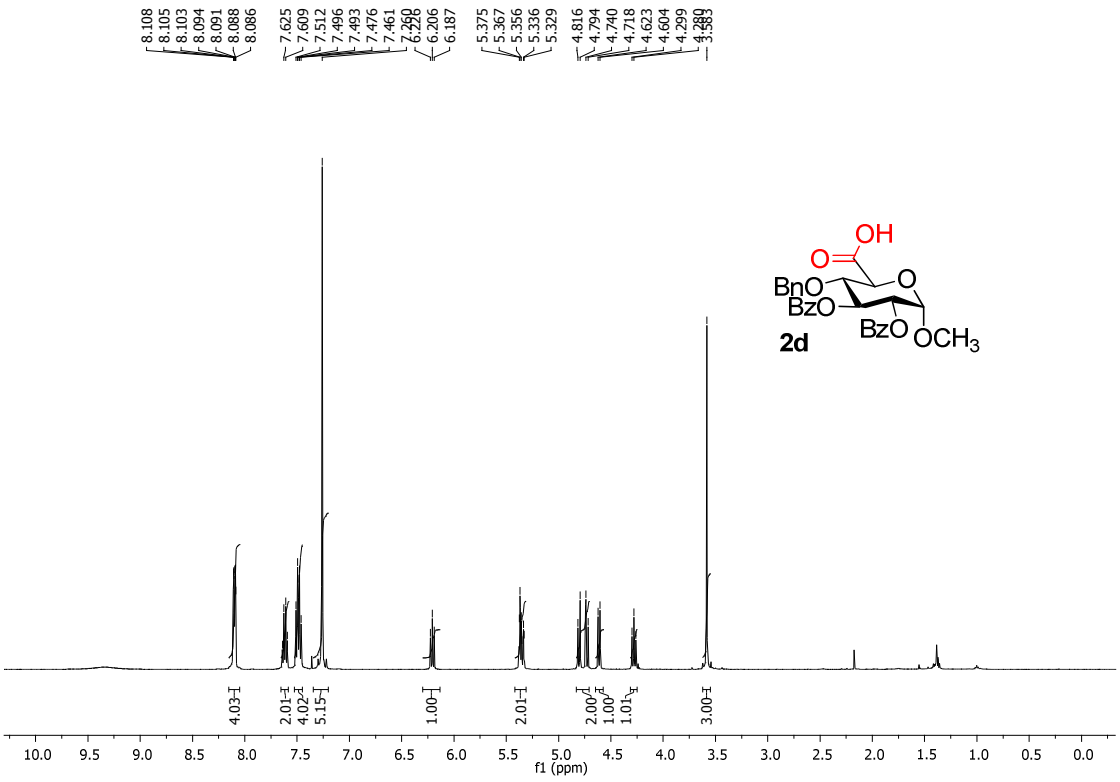
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound 2b



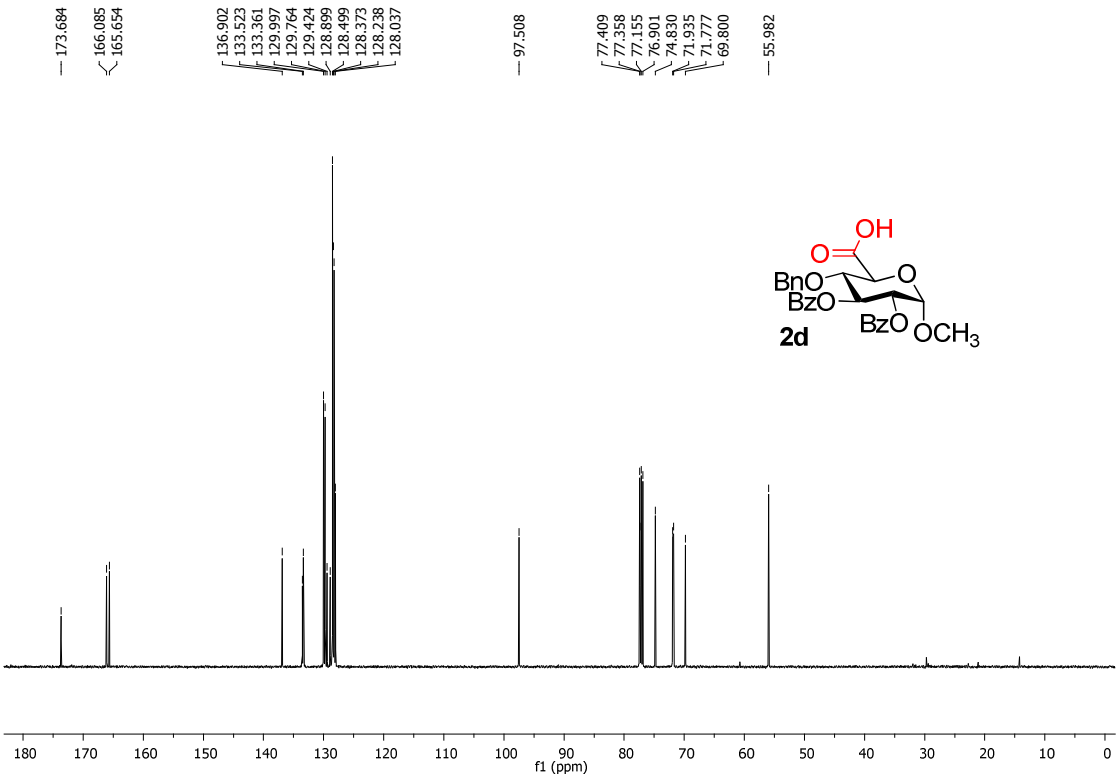
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of compound 2c



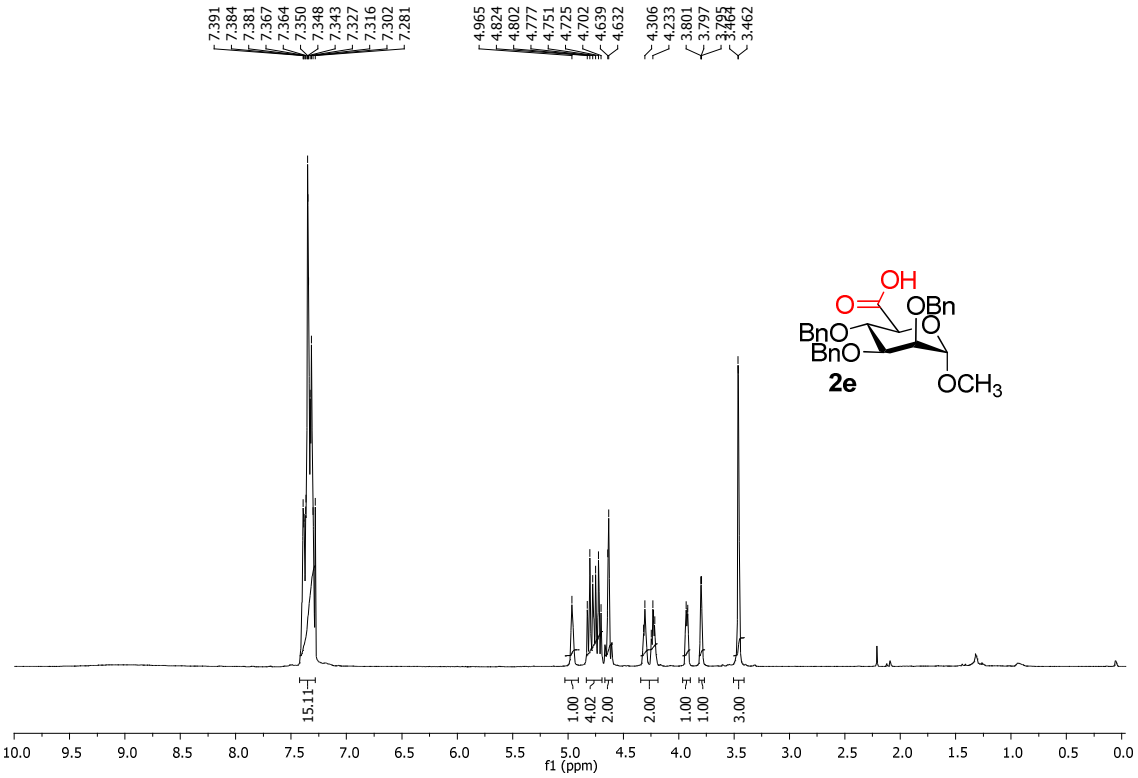
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound 2c



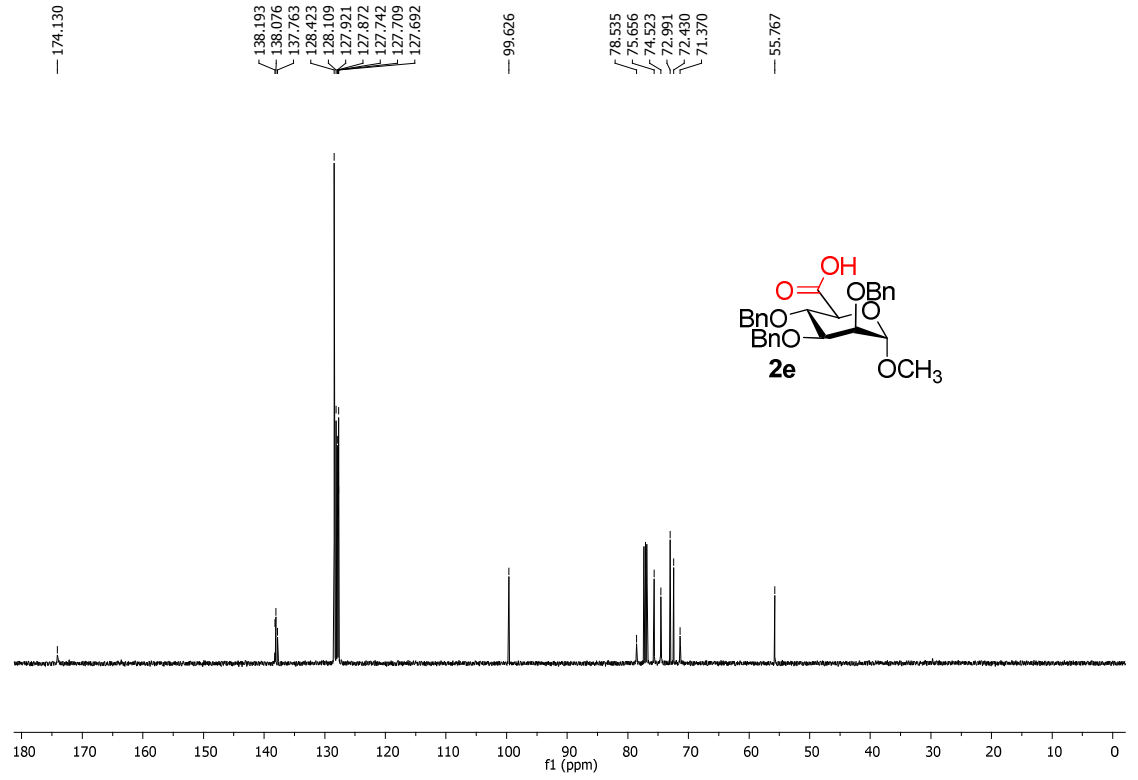
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of compound 2d



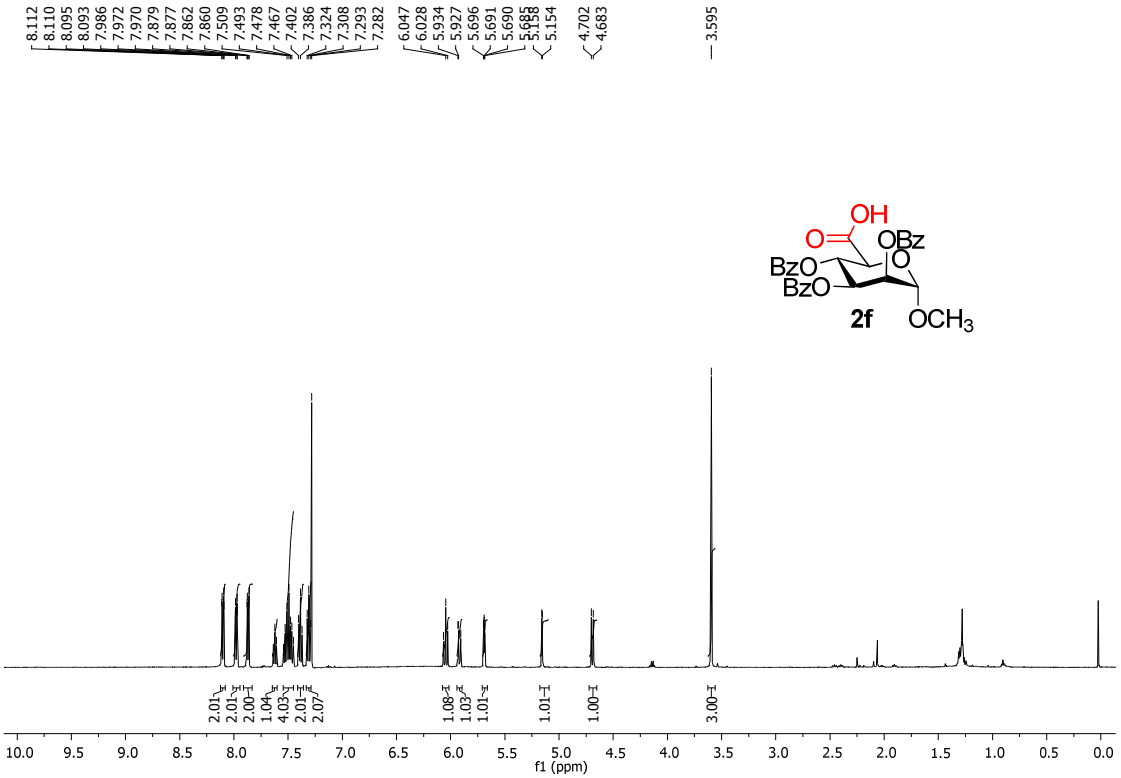
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound 2d



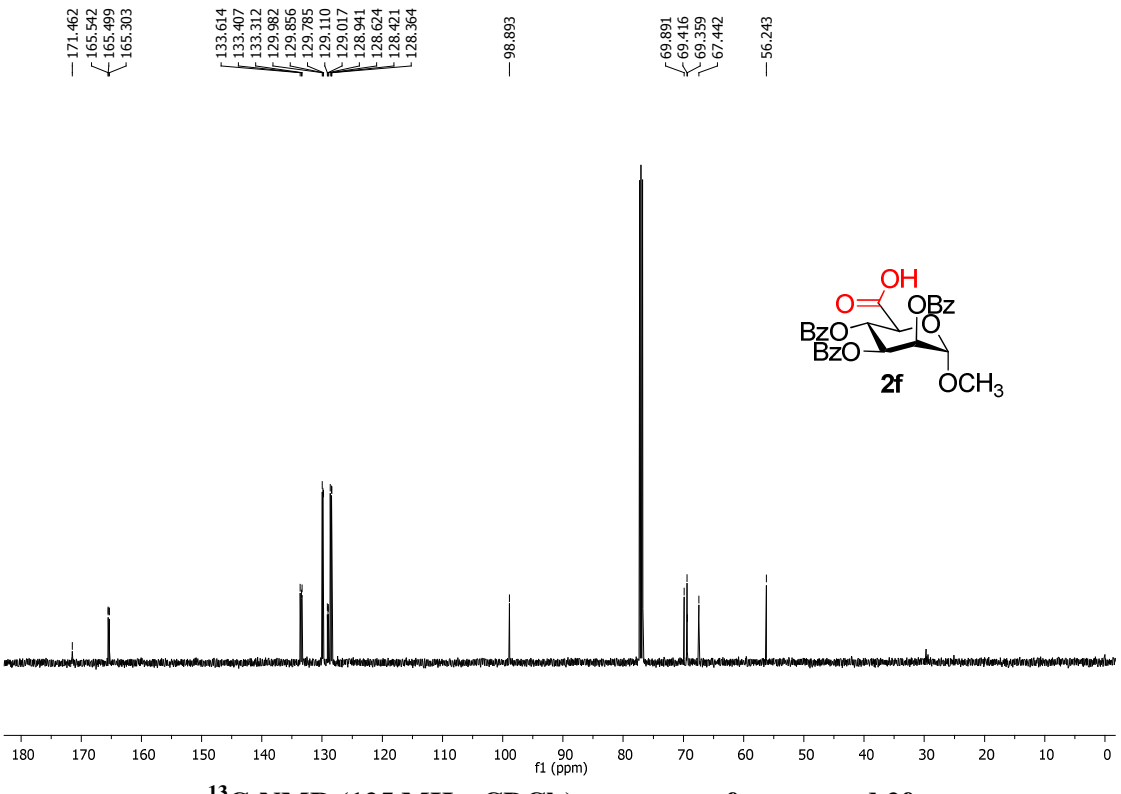
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of compound 2e



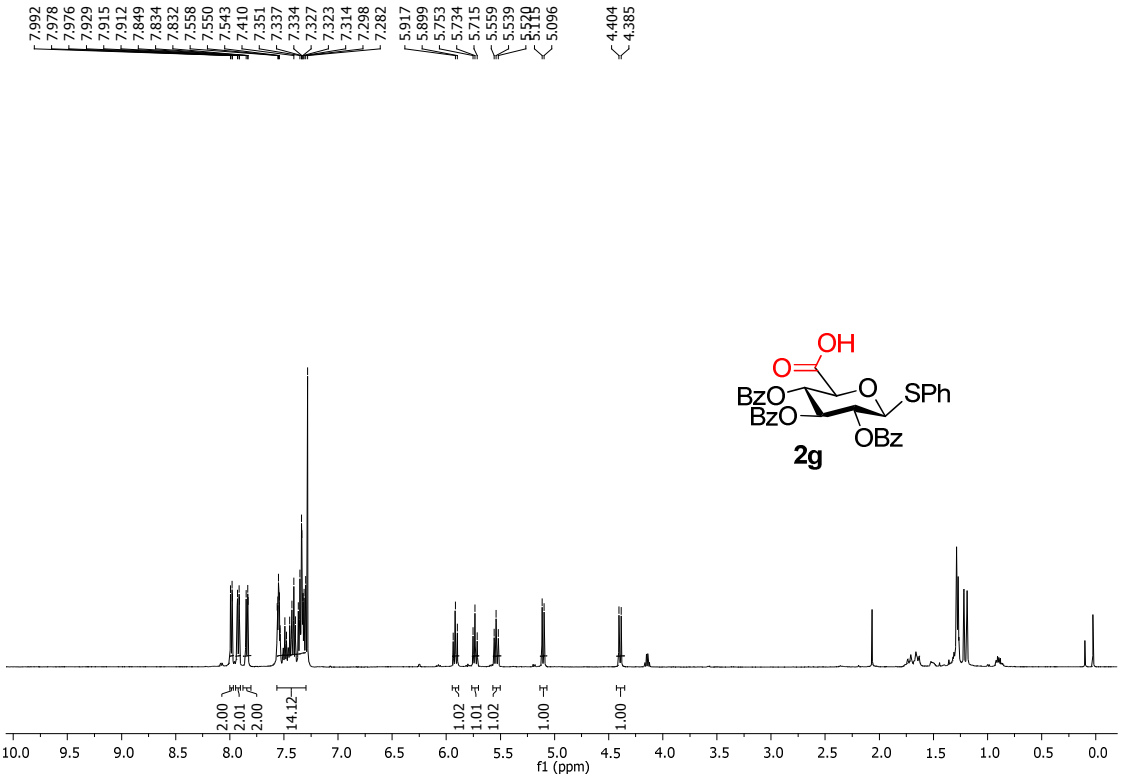
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound 2e



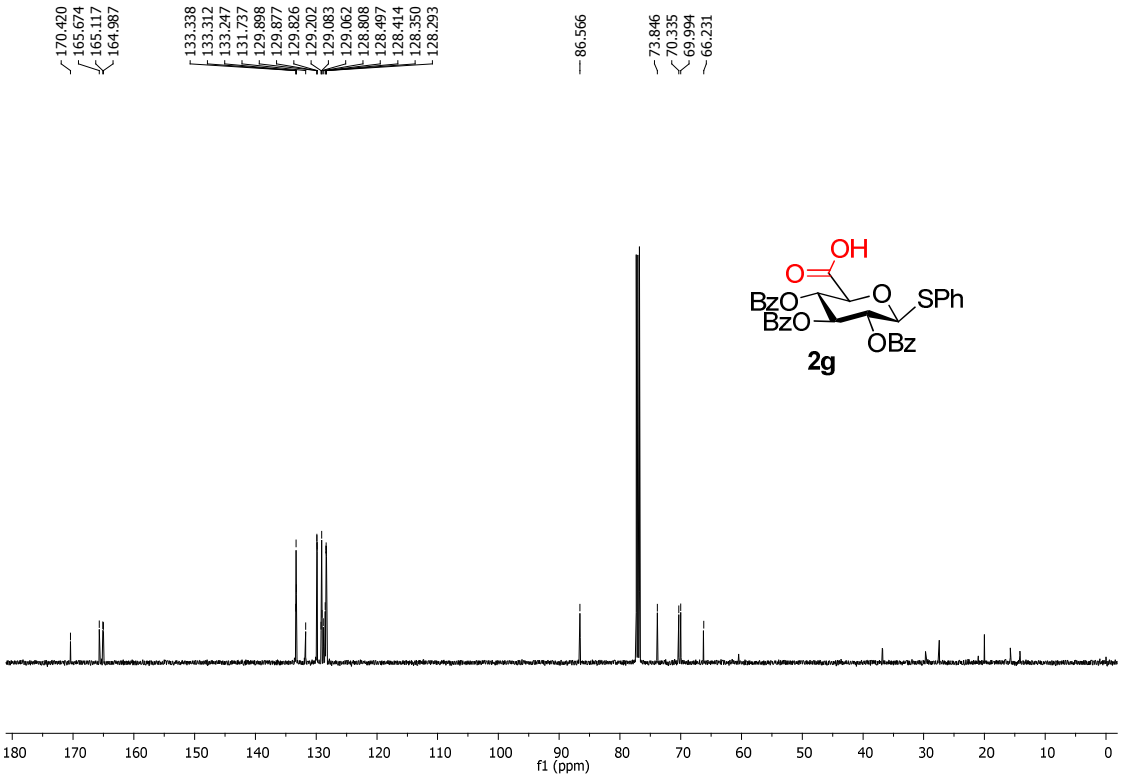
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of compound 2f



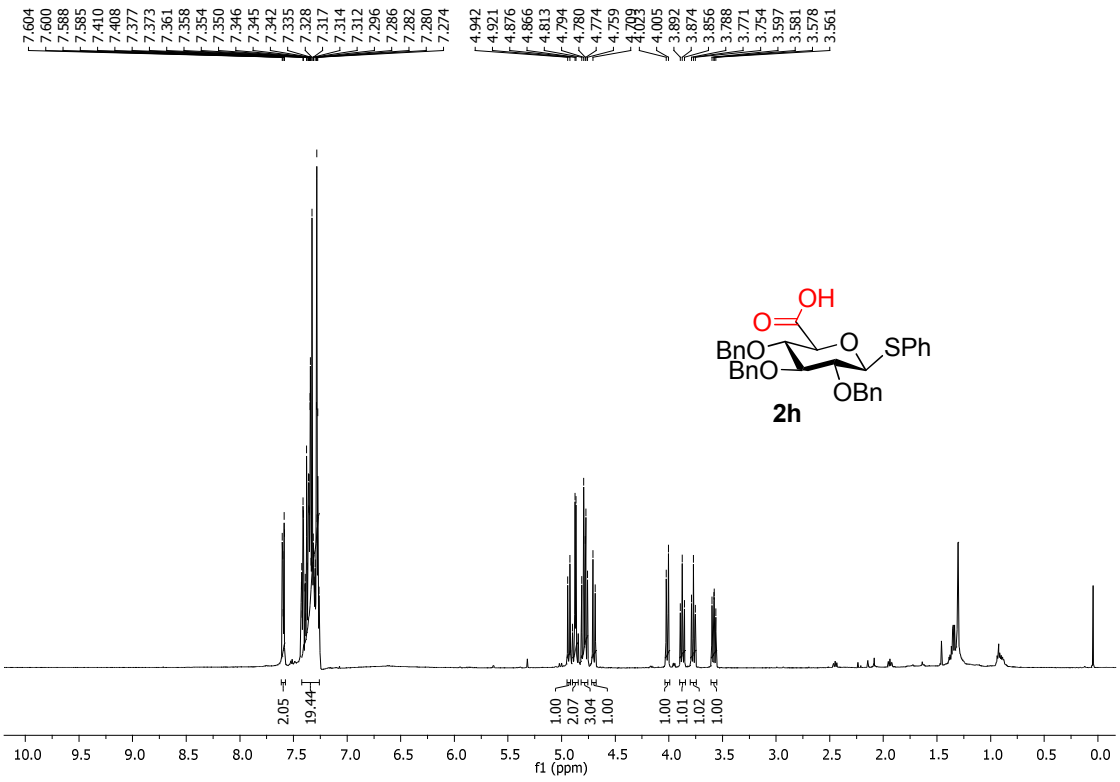
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound 2f



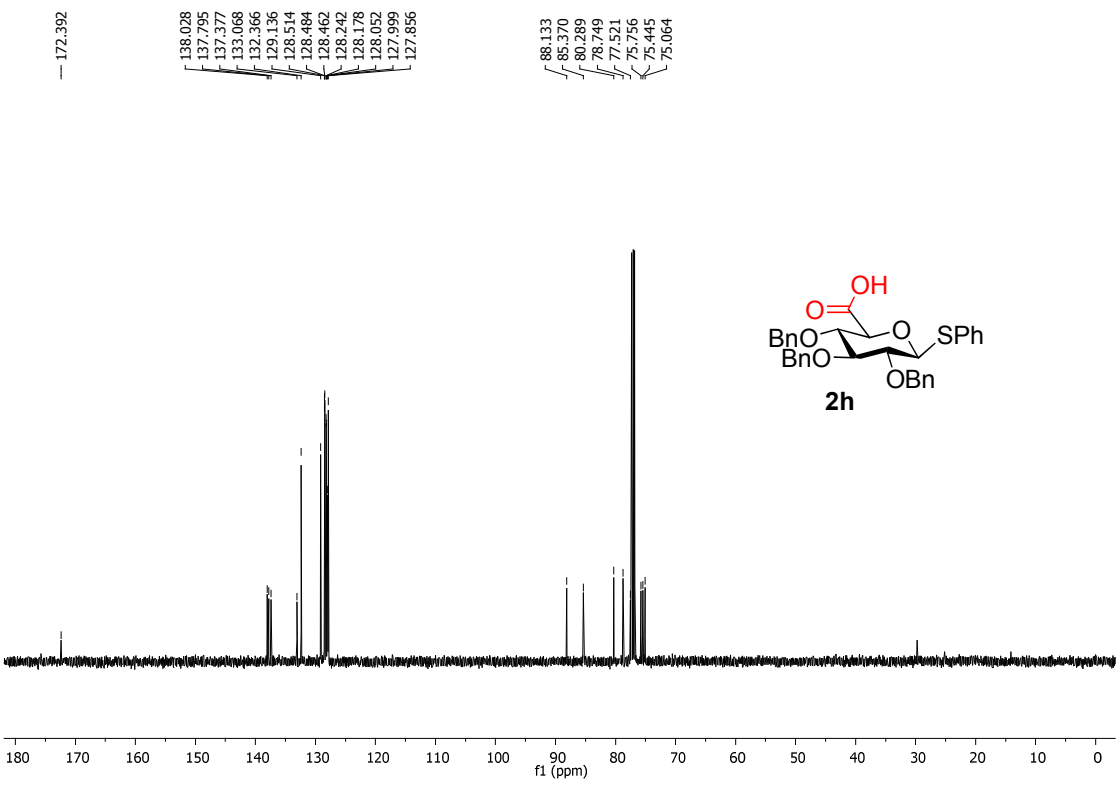
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of compound 2g



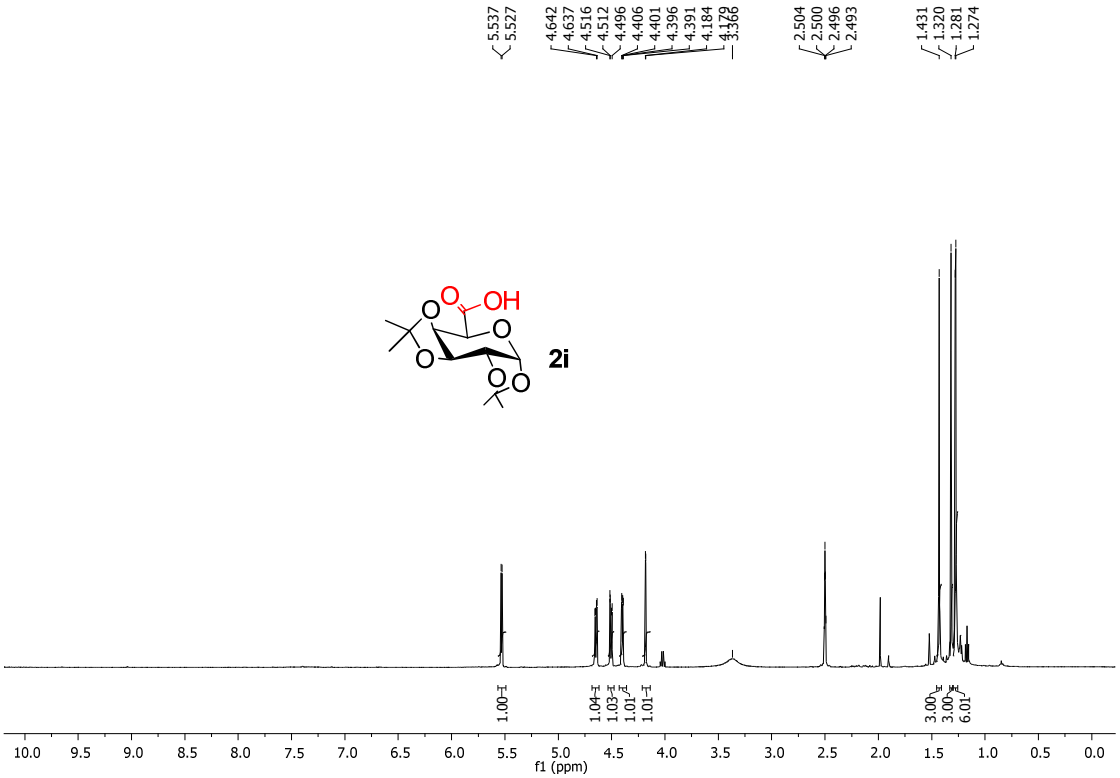
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound 2g



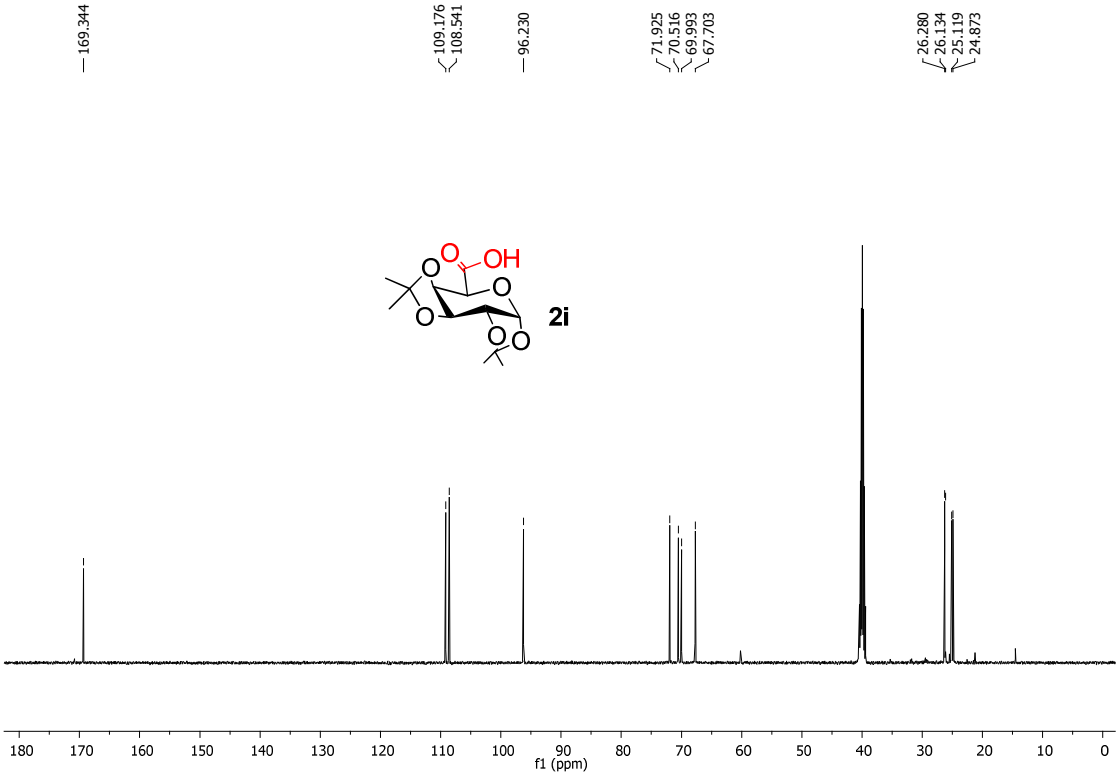
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of compound 2h



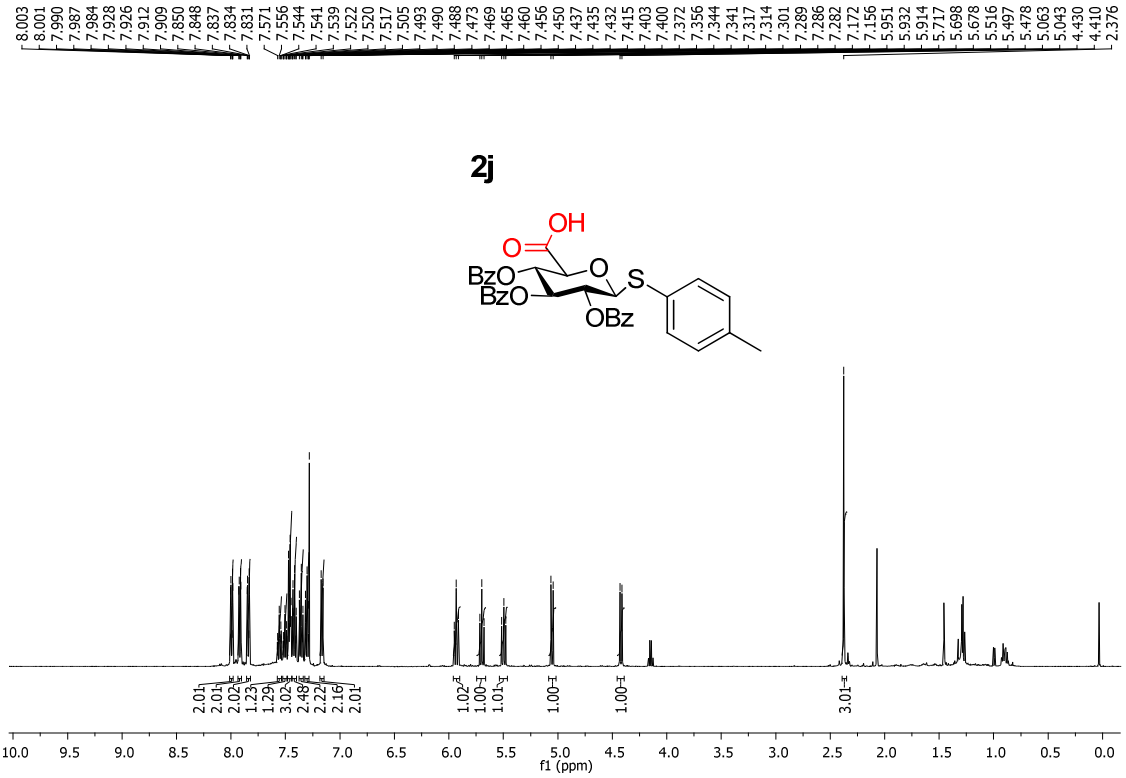
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound 2h



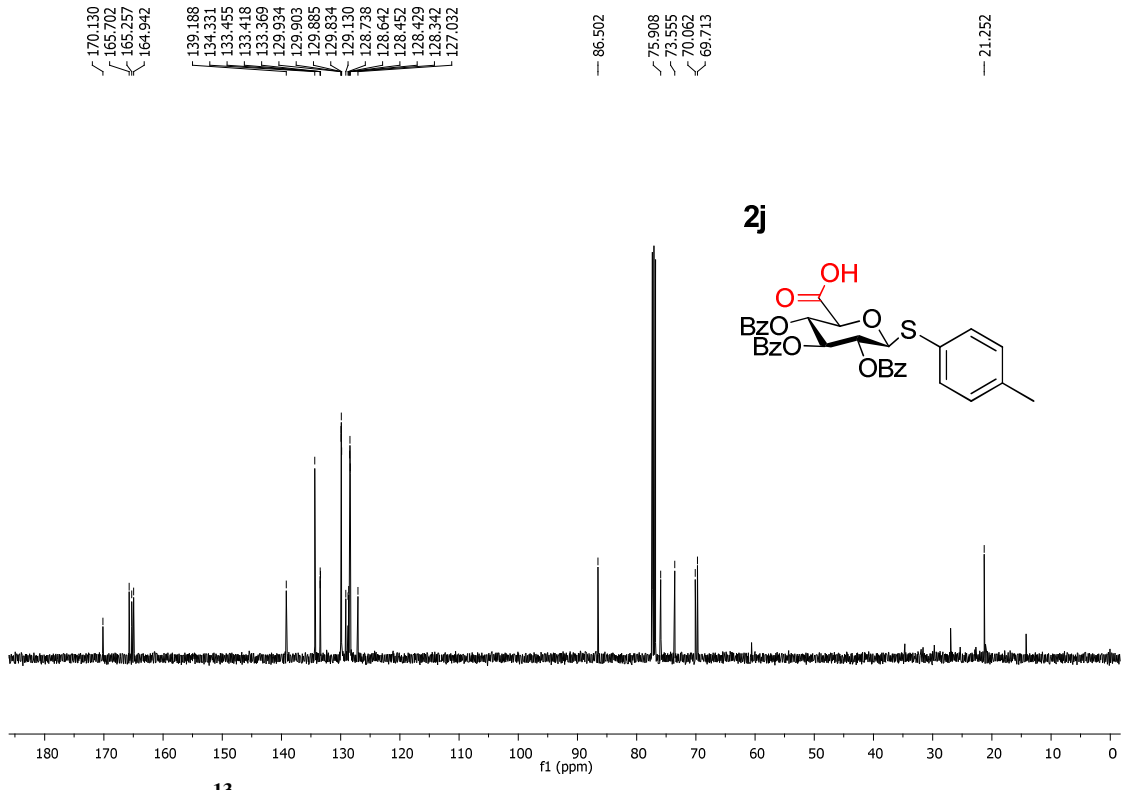
^{1}H-NMR (500 MHz, DMSO-d$_6$) spectrum of compound 2i



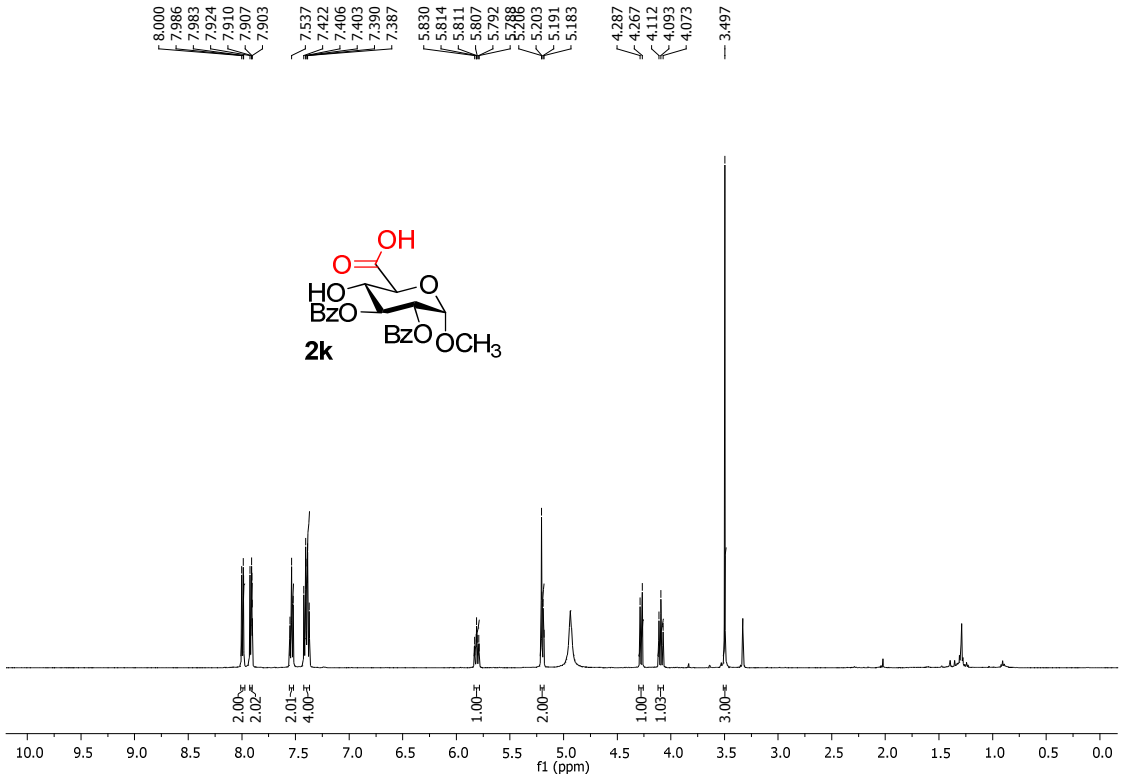
^{13}C-NMR (125 MHz, DMSO-d$_6$) spectrum of compound 2i



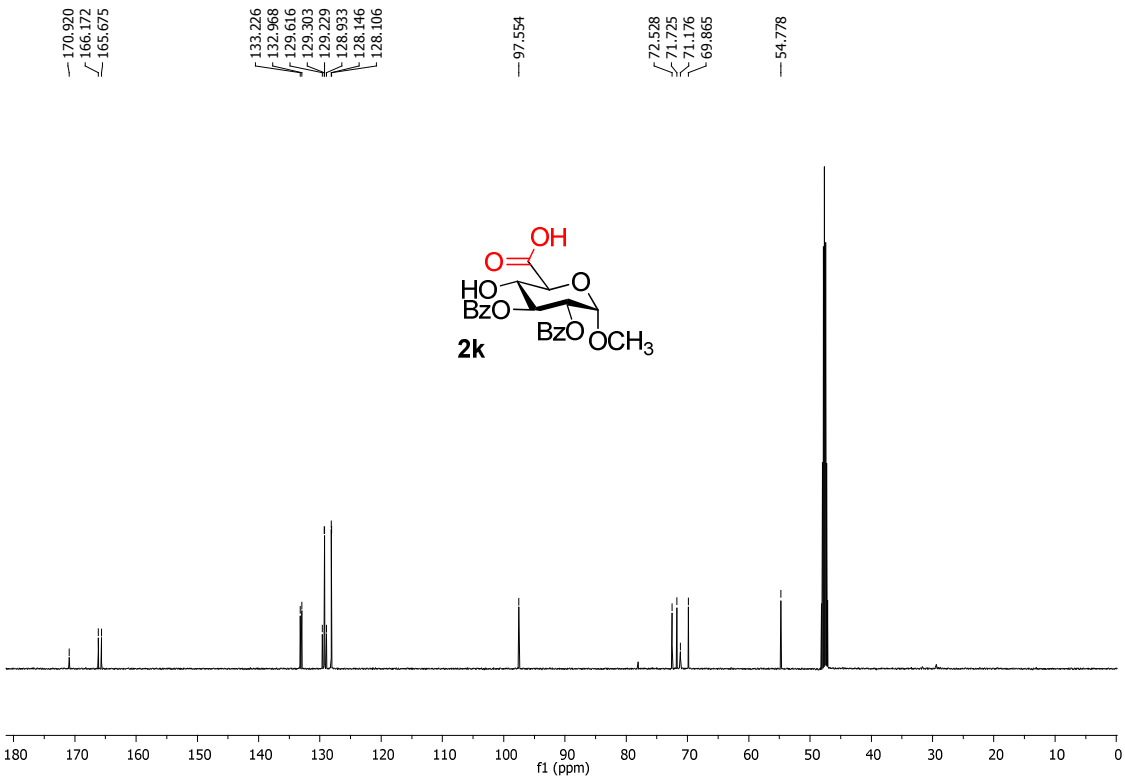
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of compound 2j



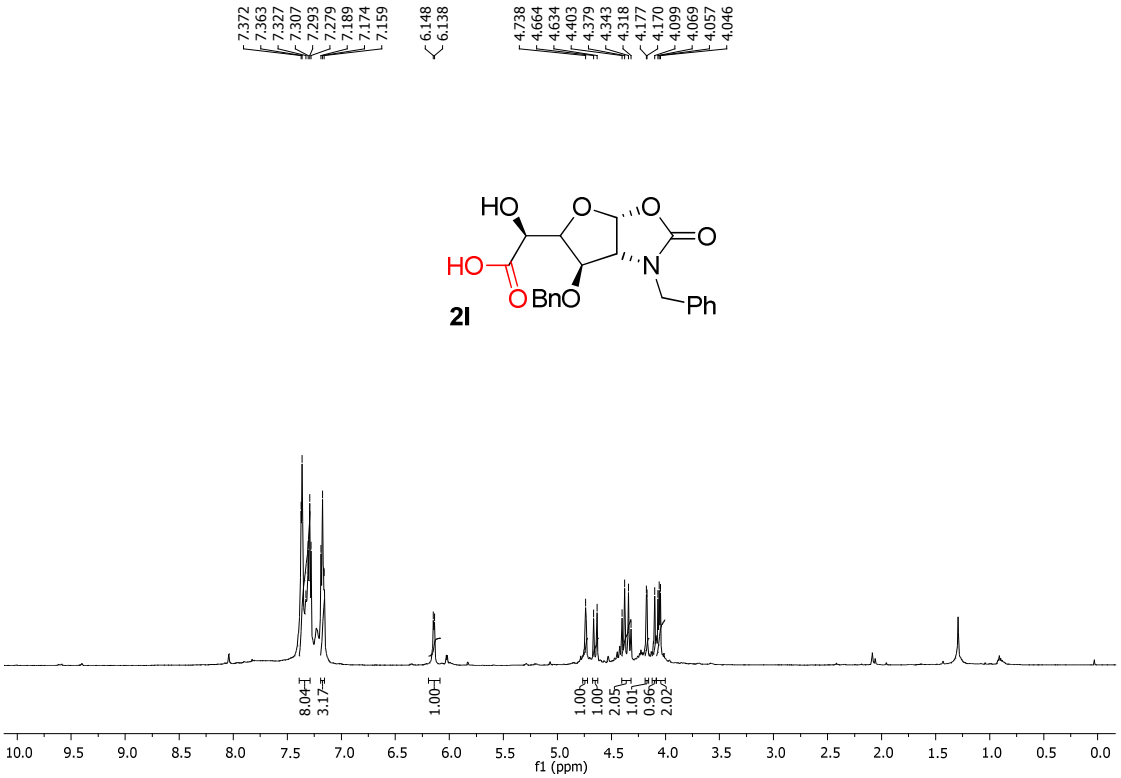
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound 2j



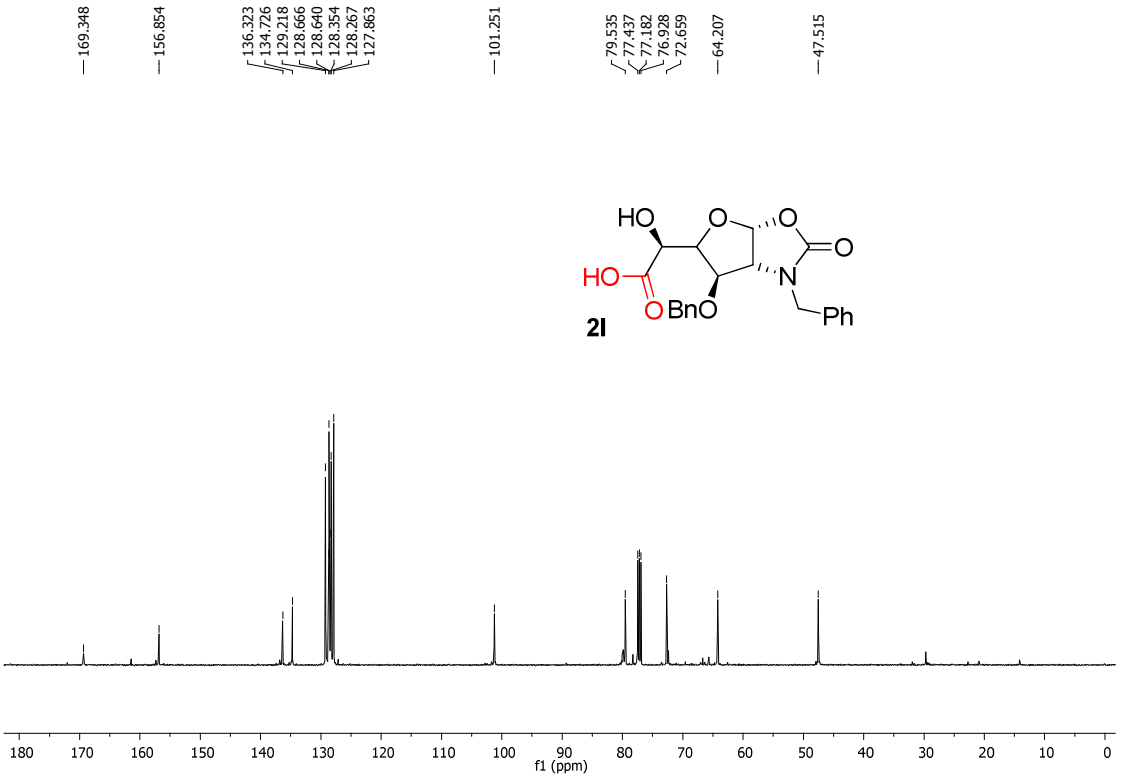
^{1}H-NMR (500 MHz, Methanol-d$_4$) spectrum of compound 2k



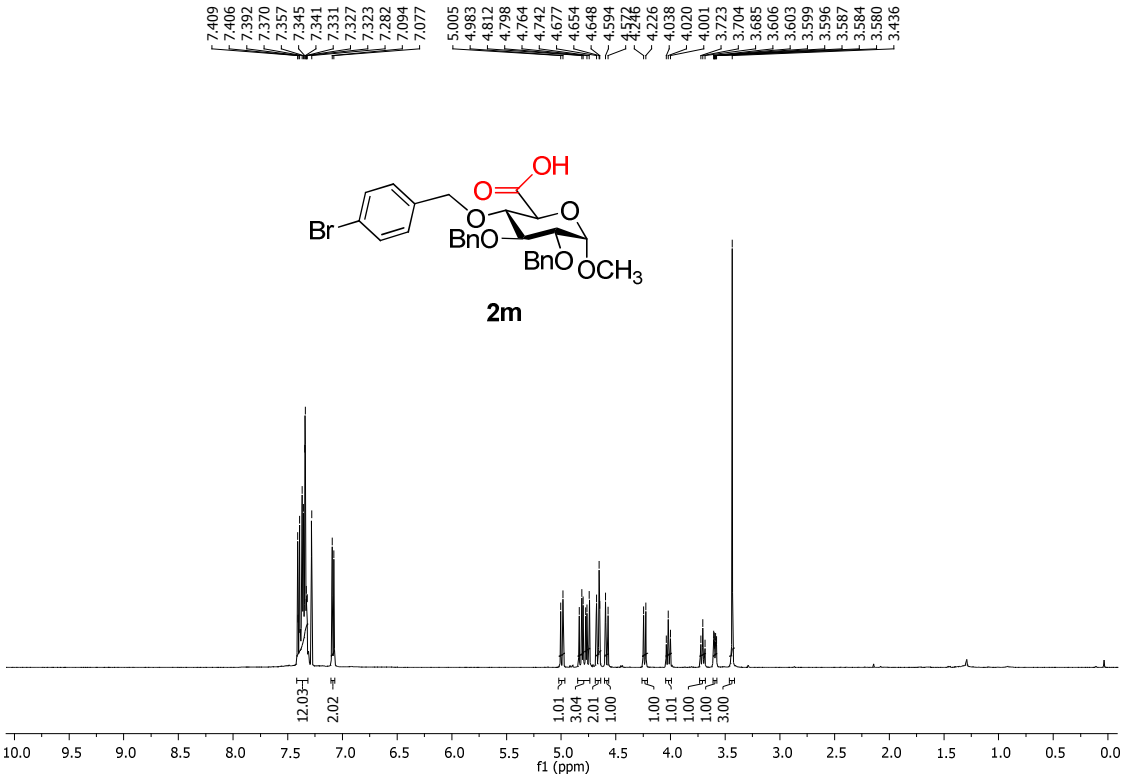
^{13}C-NMR (125 MHz, Methanol-d$_4$) spectrum of compound 2k



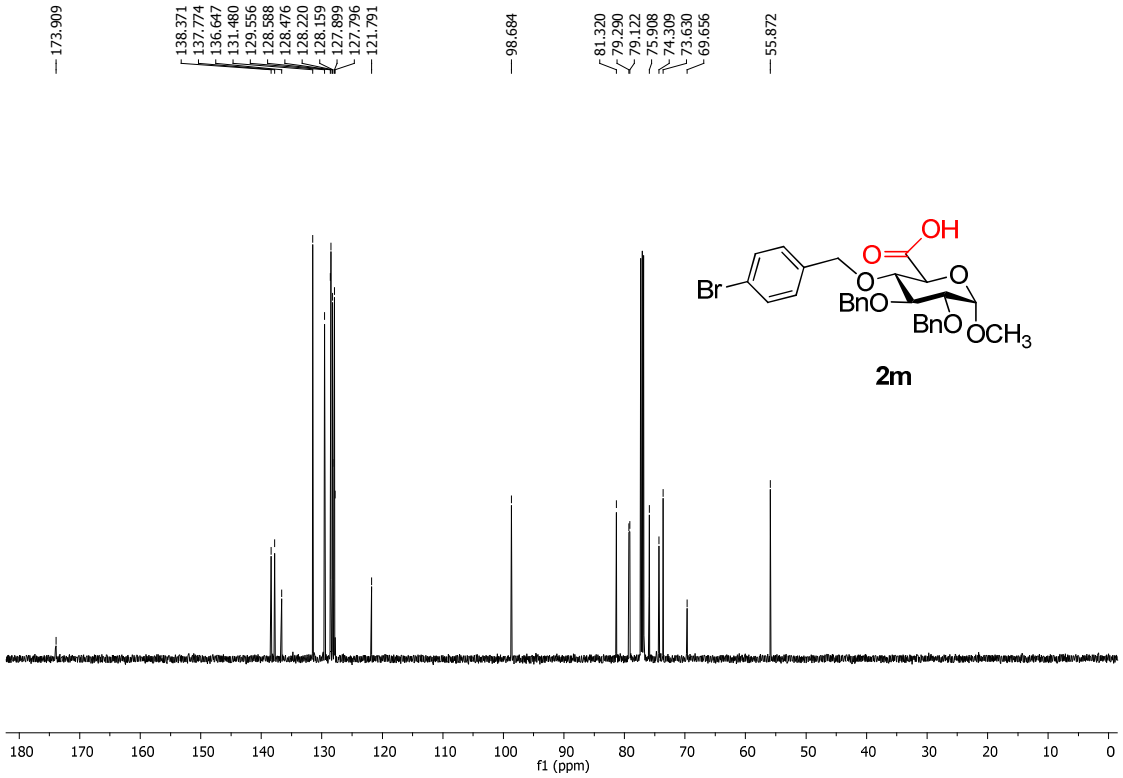
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of compound 2l



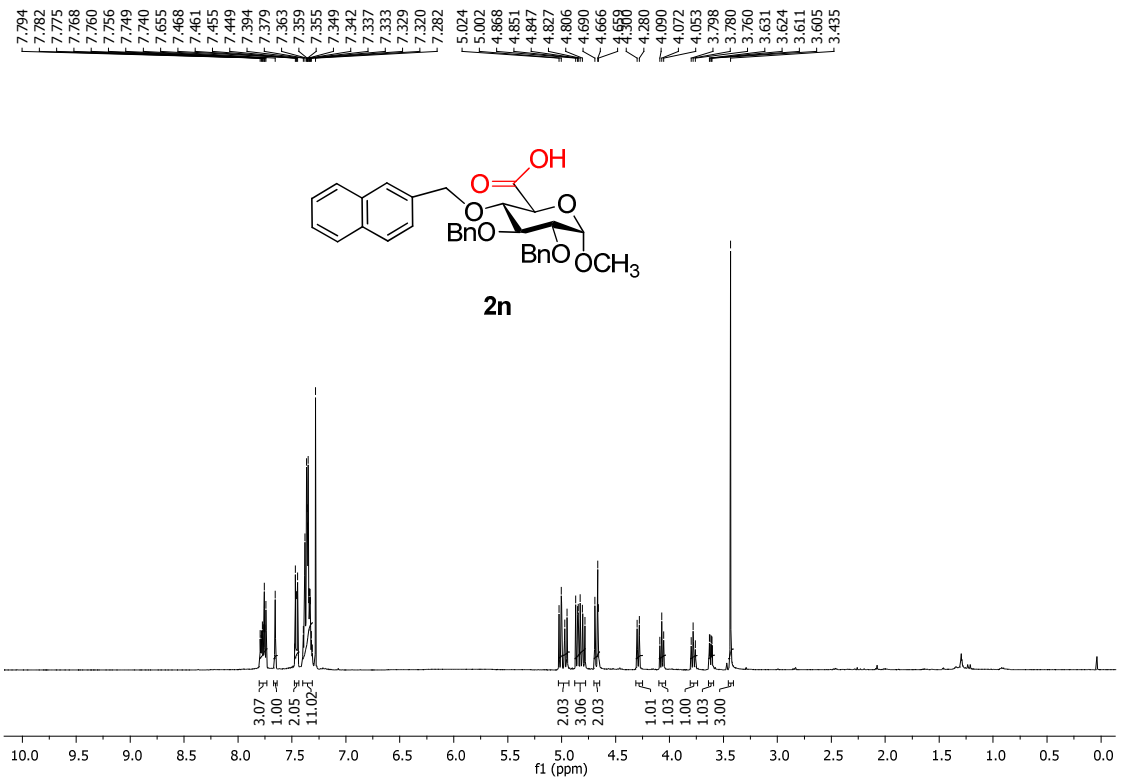
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound 2l



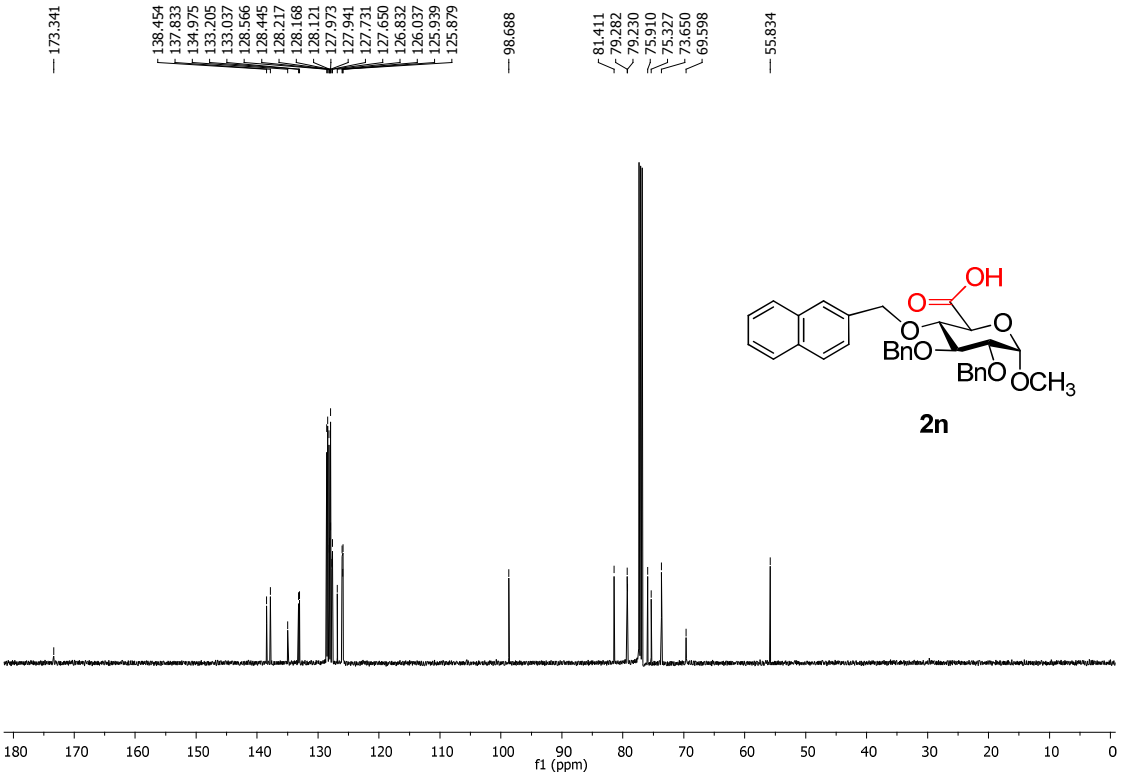
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of compound 2m



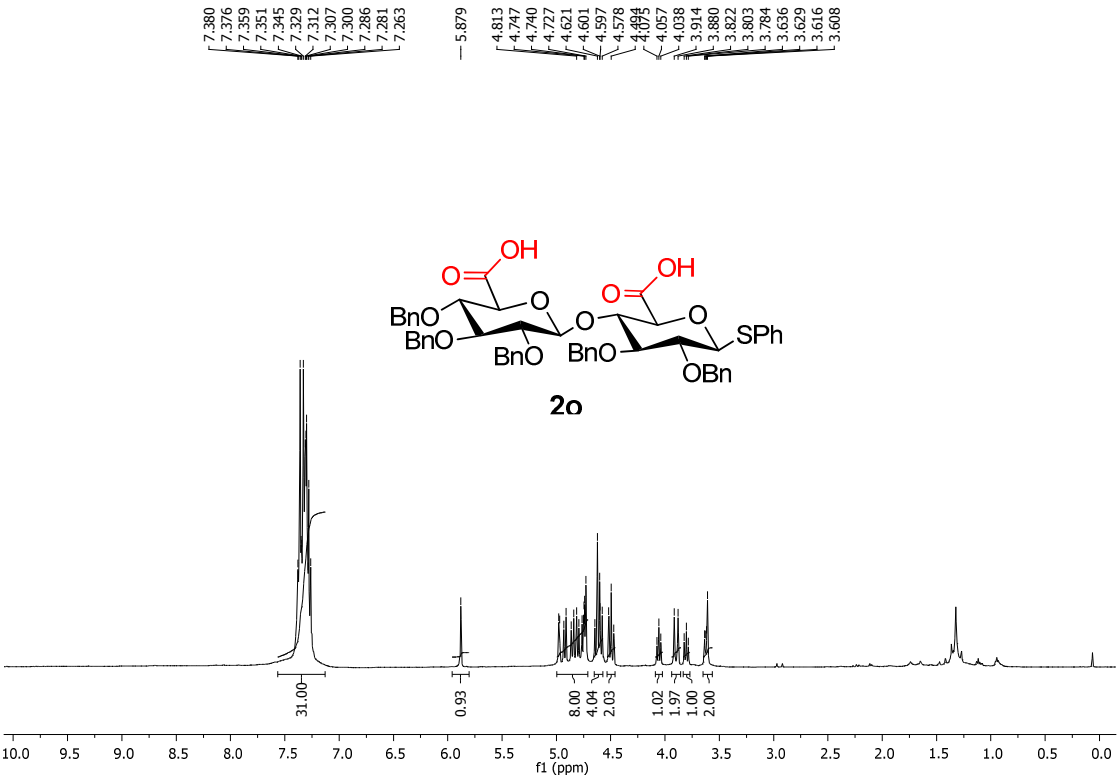
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound 2m



^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of compound 2n

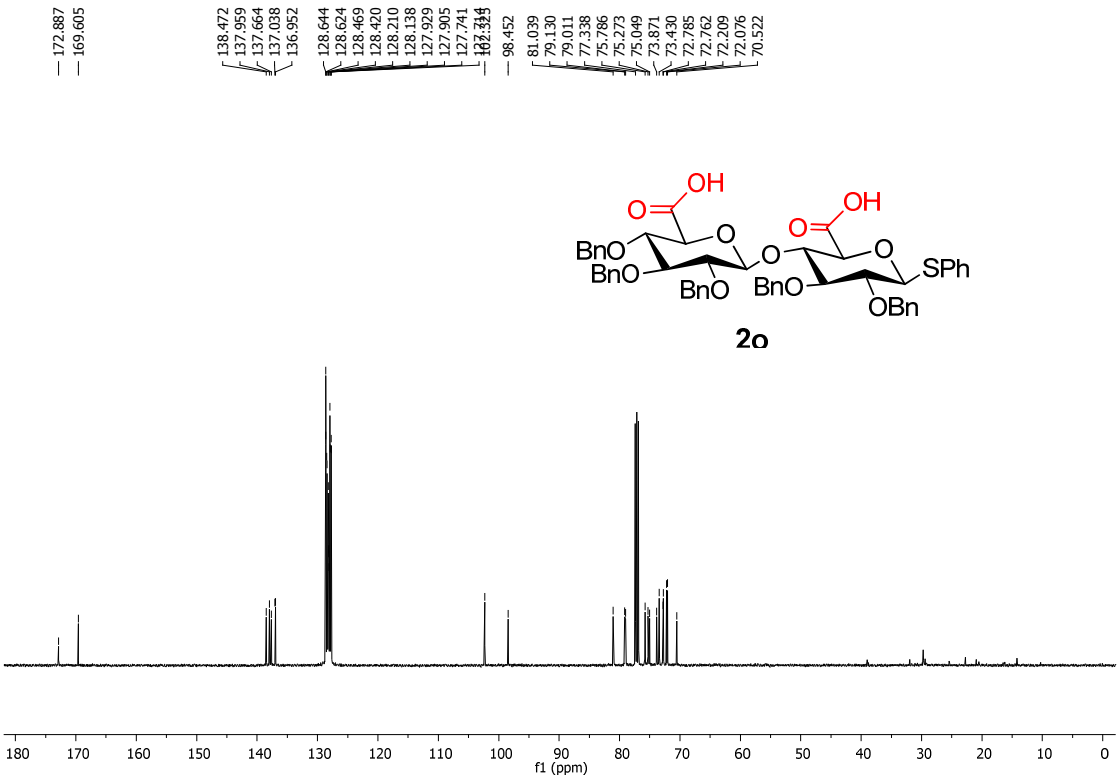


^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound 2n



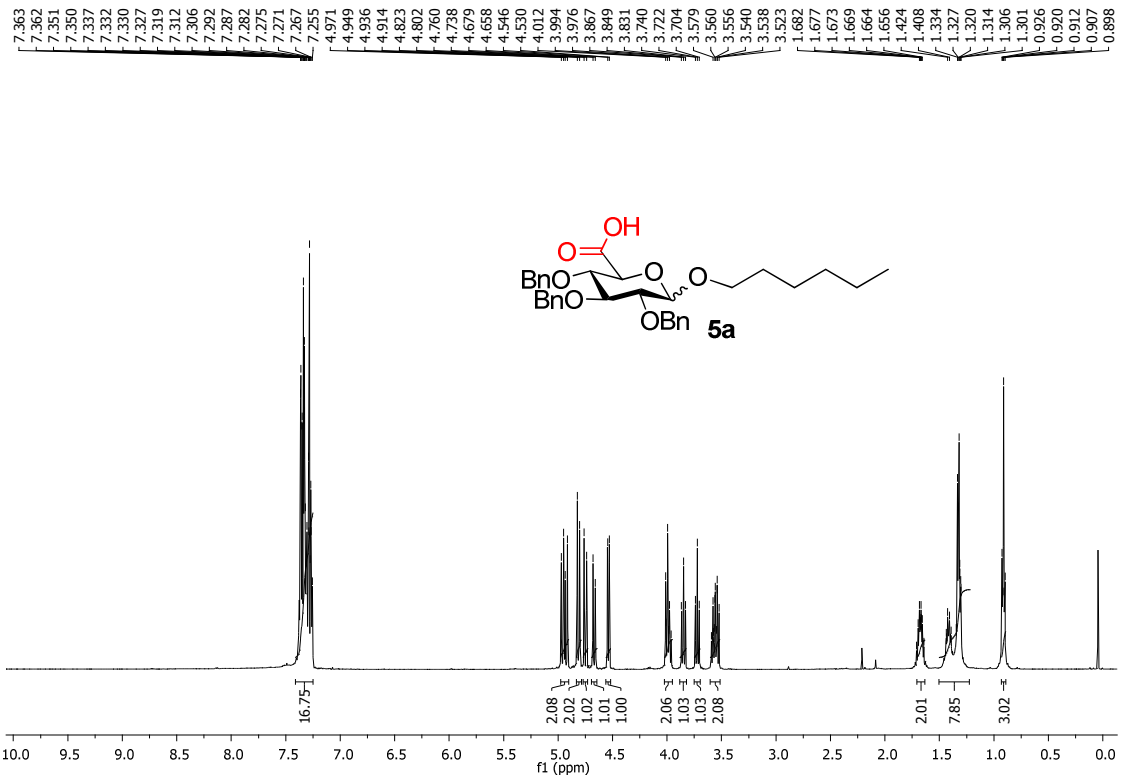
2o

^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of compound 2o

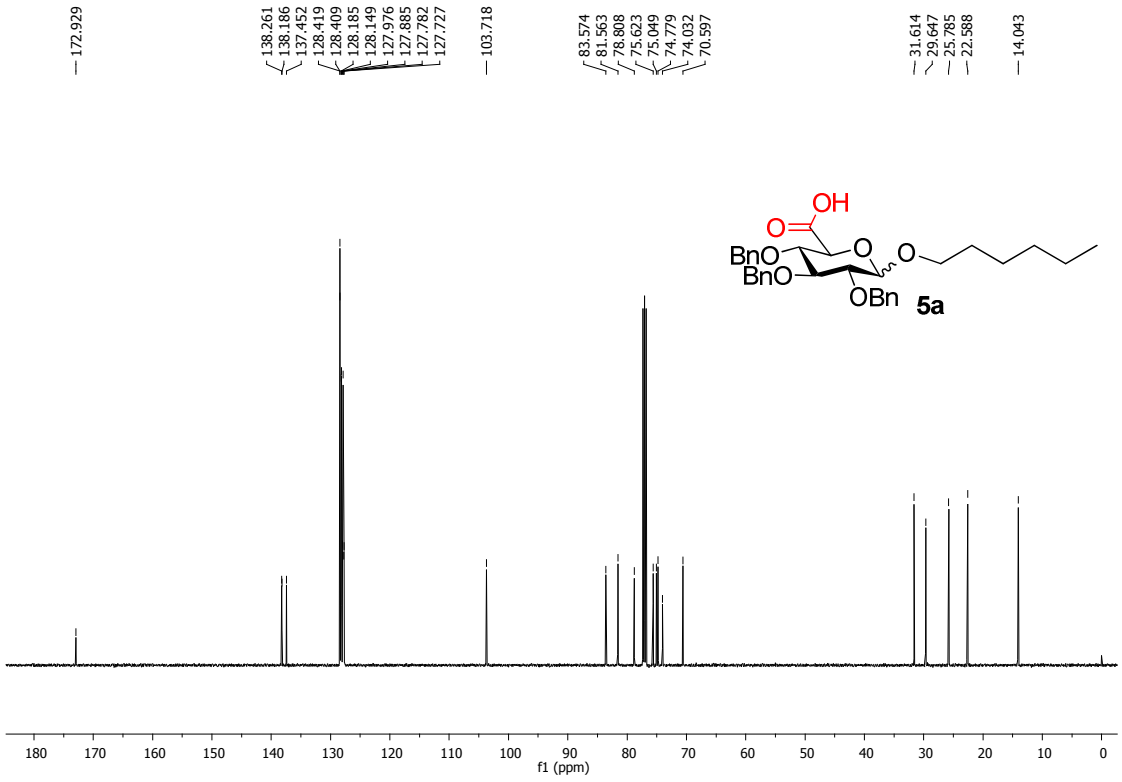


2o

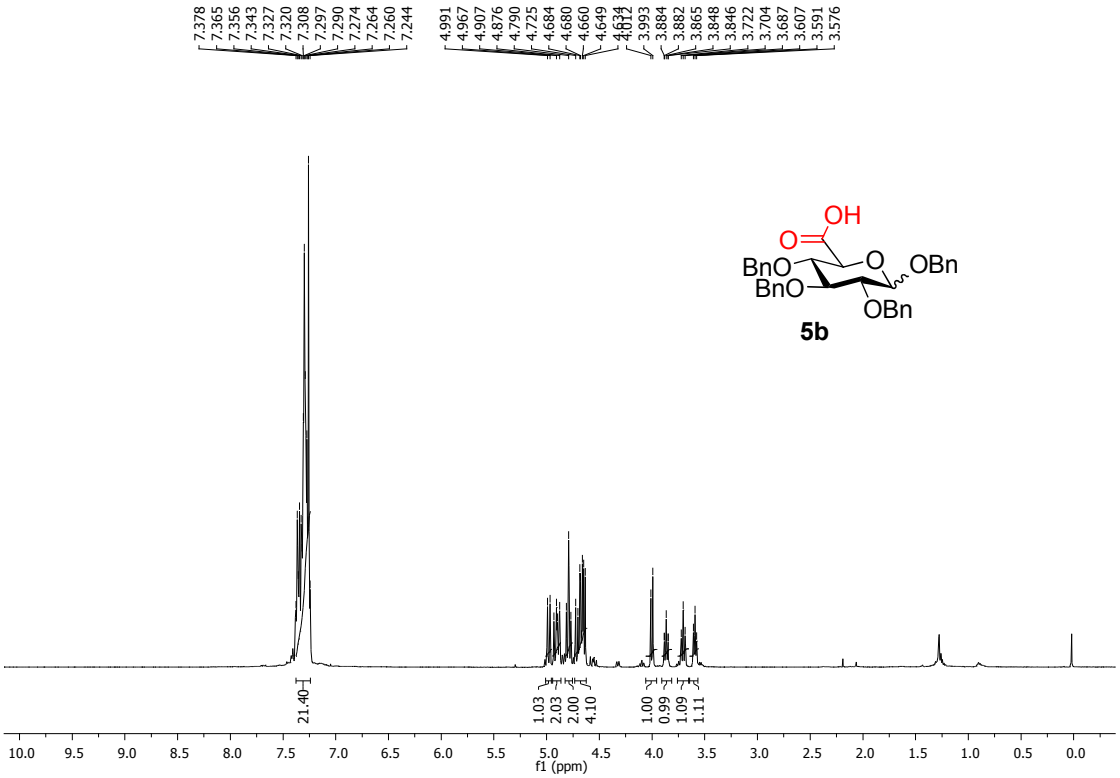
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound 2o



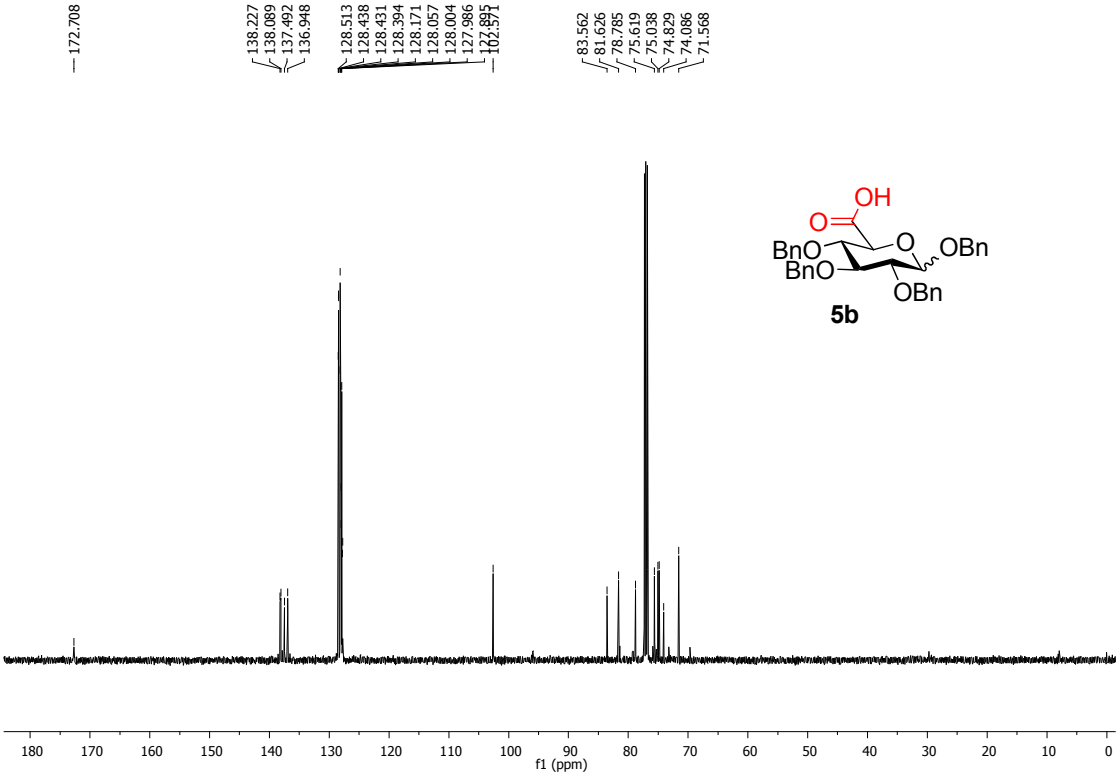
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of compound 5a



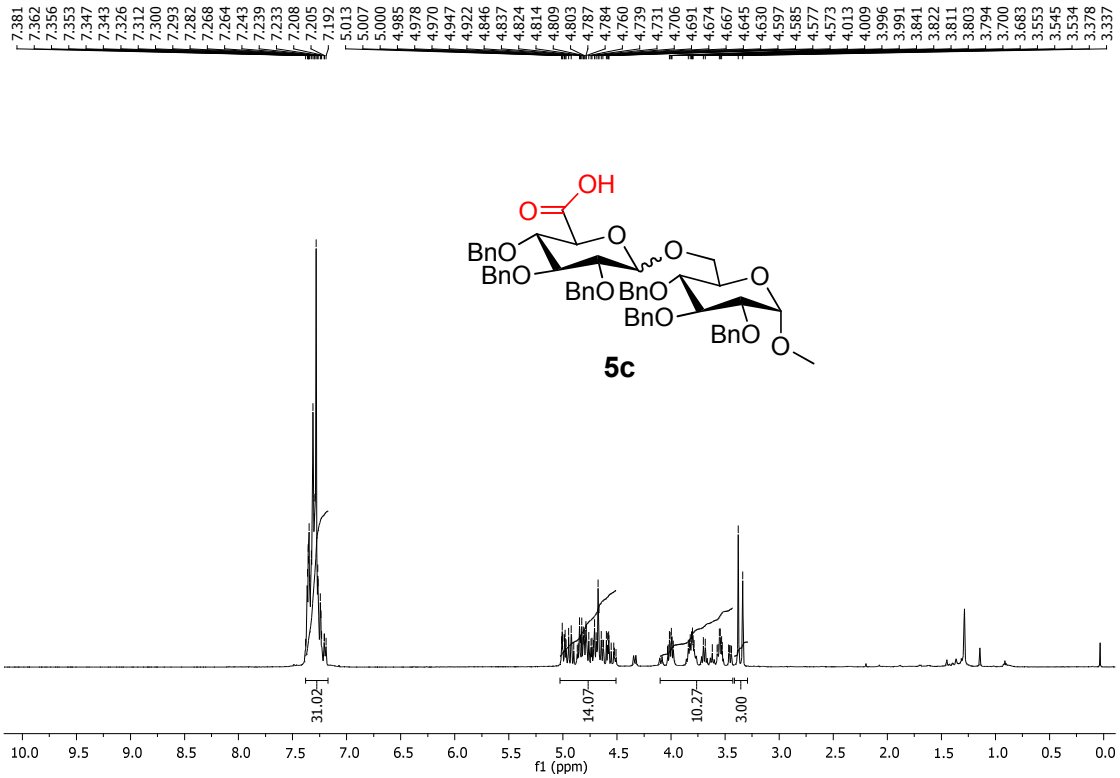
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound 5a



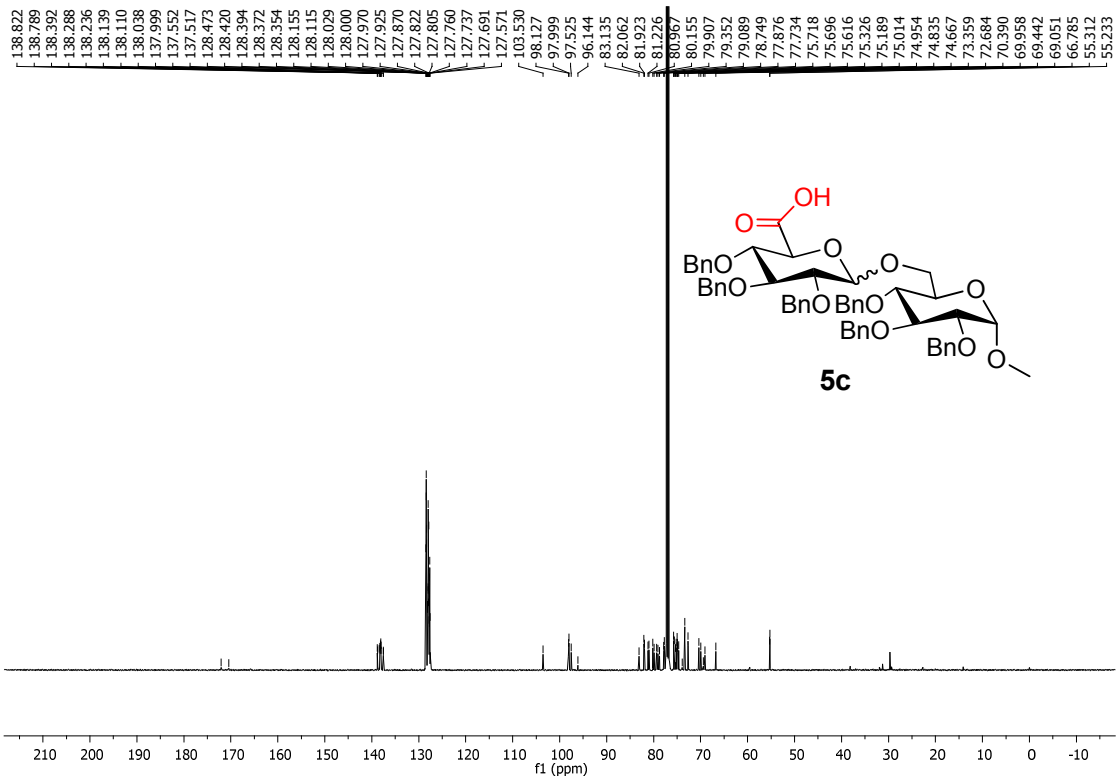
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of compound 5b



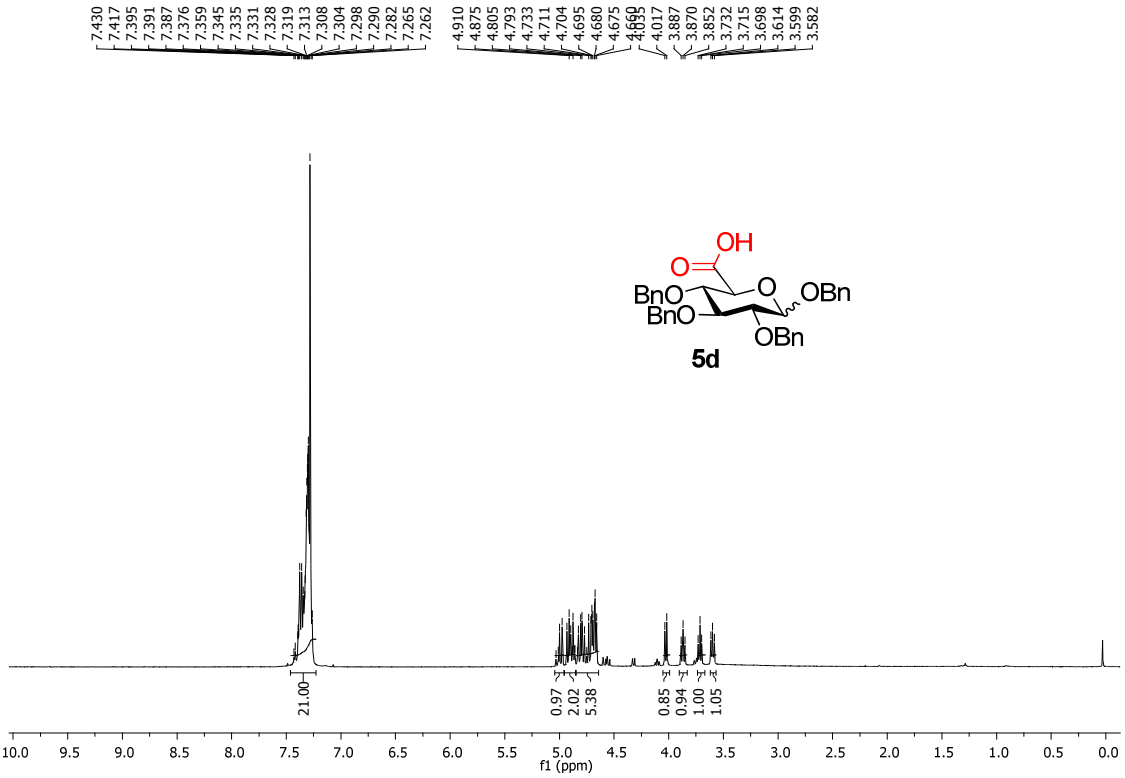
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound 5b



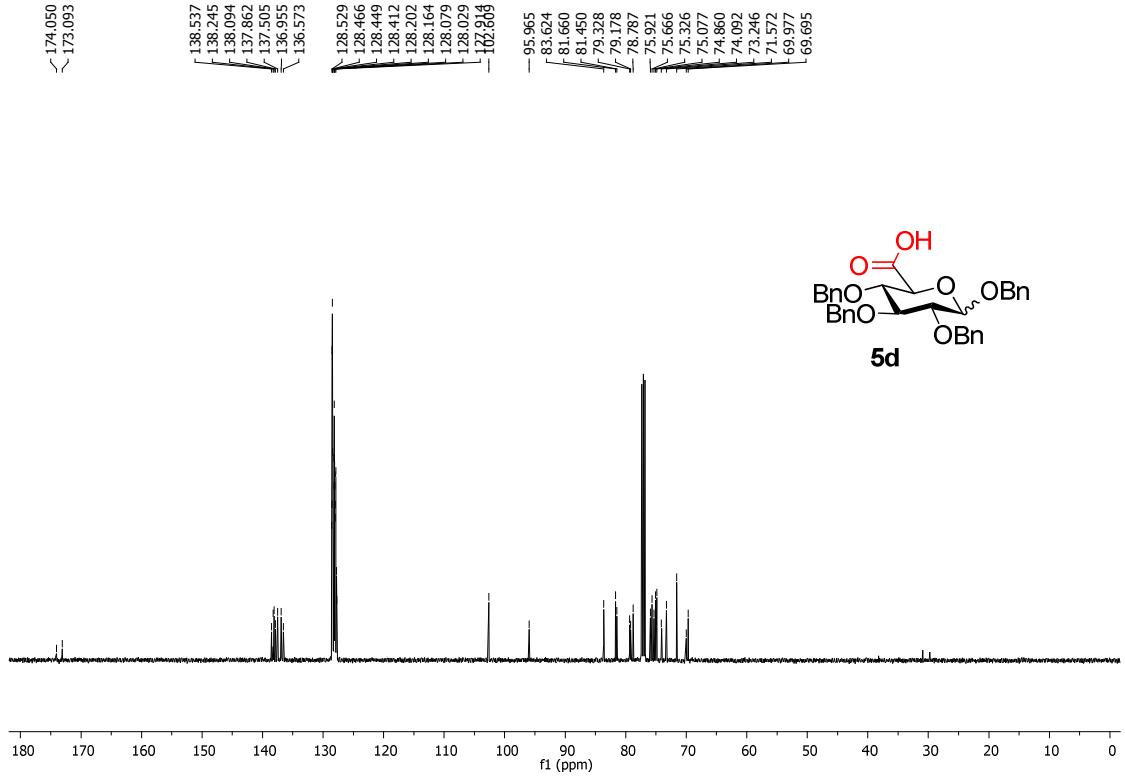
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of compound 5c



^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound 5c



^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of compound 5d



^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound 5d