

Palladium catalysed carbonylation of 2-iodoglycols for the synthesis of C-2 carboxylic acids and aldehydes taking formic acid as carbonyl Source

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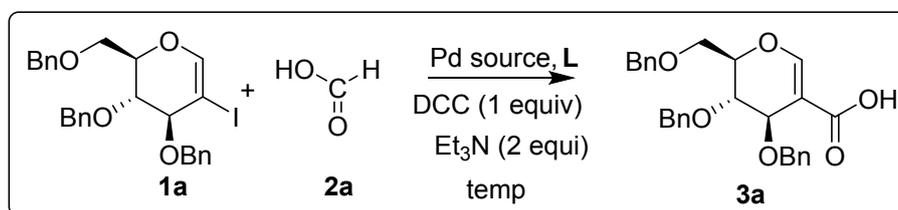
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1 General Consideration:

^1H and ^{13}C NMR spectra were recorded using 400, 101 and 126 MHz spectrometers with TMS as internal standard. Chemical shifts are expressed in parts per million (δ ppm). Silica gel coated aluminium plates were used for TLC. The products were purified by column chromatography on silica gel (60- 120 mesh) using petroleum ether–ethyl acetate as the eluent to obtain the pure products. Exact masses of all products were derived by using HRMS having QTOF analyzer. Reagents used were mostly purchased from Sigma Aldrich.

2. Optimization Tables:

Table 2.1. Effect of solvent on reaction for synthesis of 3a:



entry	Pd source (5 mol %)	ligand (mol %)	temp (°C)	time (h)	solvent	yield (%) ^b
1	Pd(OAc) ₂	L2 (10)	90	2	DMSO	27
2	Pd(OAc) ₂	L2 (10)	90	2	THF	53
3	Pd(OAc)₂	L2 (10)	90	2	DMF	82
4	Pd(OAc) ₂	L2 (10)	90	2	ACN	13
5	Pd(OAc) ₂	L2 (10)	90	2	MeOH	traces

In all cases reactions were carried out using 1a (1 equiv) and 2a (2 equiv) triethylamine (2 equiv) at 90 °C in a sealed tube.

Table 2.2. Optimization of equivalent of DCC used for the synthesis of 3a:

entry	Pd source	ligand (mol %)	temp (°C)	time (h)	DCC (equiv)	yield (%) ^b
1	Pd(OAc) ₂	L2 (10)	90	2	2.5	46
2	Pd(OAc) ₂	L2 (10)	90	2	2.0	53
3	Pd(OAc) ₂	L2 (10)	90	2	1.5	58
4	Pd(OAc) ₂	L2 (10)	90	2	0.4	64
5	Pd(OAc)₂	L2 (10)	90	2	1.0	82
6	Pd(OAc) ₂	L2 (10)	90	2	0.6	52
7	Pd(OAc) ₂	L2 (10)	90	2	1.1	78

In all cases reactions were carried out in DMF using 1a (1 equiv) and 2a (2 equiv) triethylamine (2 equiv) at 90 °C in a sealed tube.

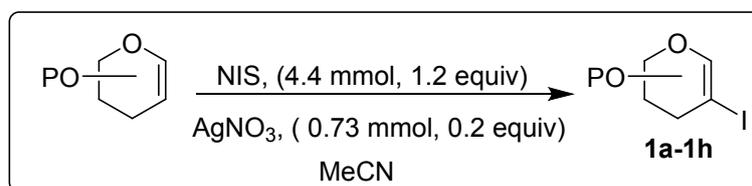
Table 2.3. Optimization of different bases for the synthesis of 3a:

entry	Pd source	ligand (mol %)	temp (°C)	time (h)	bases (2 equiv)	yield (%) ^b
1	Pd(OAc)₂	L2 (10)	90	2	Et₃N	82
2	Pd(OAc) ₂	L2 (10)	90	2	DBU	58
3	Pd(OAc) ₂	L2 (10)	90	2	K ₂ CO ₃	42
4	Pd(OAc) ₂	L2 (10)	90	2	Na ₂ CO ₃	45
5	Pd(OAc) ₂	L2 (10)	90	2	KO ^t Bu	32
6	Pd(OAc) ₂	L2 (10)	90	2	NaO ^t Bu	37

In all cases reactions were carried out in DMF using 1a (1 equiv) and 2a (2 equiv) DCC (1 equiv) at 90 °C in a sealed tube.

3 General procedures

3.1 General procedure for the Synthesis of 2-iodo glycals¹

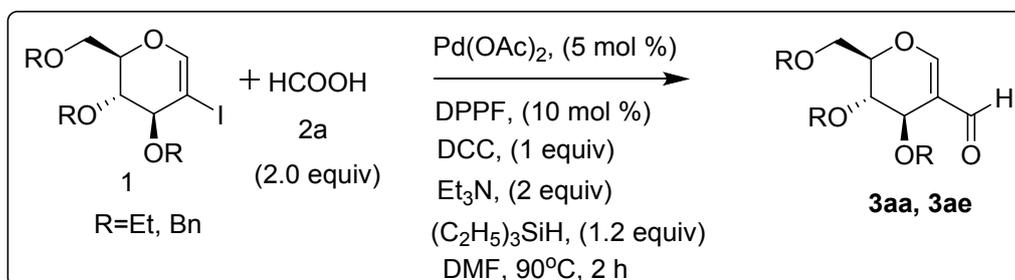


By taking tri-*O*-acetyl-D-glucal as an example, To a stirred solution of tri-*O*-acetyl-D-glucal (1g) in dry CH₃CN (10 mL) at 80 °C under N₂ atmosphere were added successively NIS (991 mg, 4.4 mmol) and AgNO₃ (124 mg, 0.73 mmol) and stirred for 4 h. On consumption of starting material (TLC monitoring), the reaction mixture was filtered through sintered funnel and the filtrate was evaporated to give a crude product which was purified by silica gel column chromatography (30% of EtOAc/hexane) to obtain **1a-1h**.

3.2 General Procedure for the synthesis of C-2 Sugar Carboxylic acids:

To a solution of 2-iodo glycals (1.0 equiv) in DMF in an oven dried screw capped sealed tube were added Pd(OAc)₂ (0.05 equiv), 1,1'-Bis(diphenylphosphino)ferrocene(DPPF) (0.10 equiv) N,N'-Dicyclohexylcarbodiimide(DCC) (1 equiv), formic Acid (2 equiv), and triethylamine (2 equiv). Closed sealed tube tightly with screw cork and the resulting mixtures was stirred at preheated oil bath at 90 °C for 2 h. Upon reaction completion, the resulting mixture was extracted with ethyl acetate and the combined organic extracts were washed with brine, dried over MgSO₄ and concentrated. The residue left was purified by column chromatography on silica gel (60-120 mesh) hexanes/ ethyl acetate as eluent to obtained **3** as desired product.

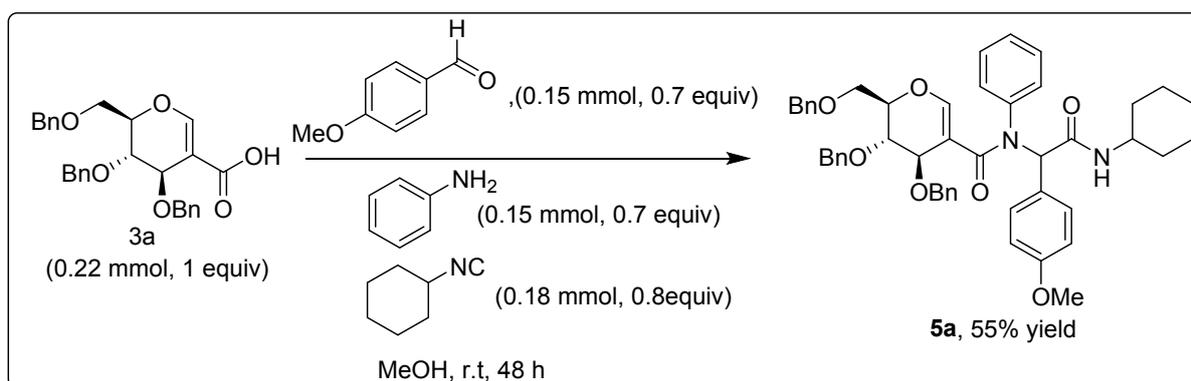
3.3 General Procedure for the Synthesis of 2-Formyl Glycals:



To a solution of 2-iodo glycals (1.0 equiv) in DMF in an oven dried screw capped sealed tube were added Pd(OAc)₂ (0.05 equiv), 1,1'-Bis(diphenylphosphino)ferrocene (DPPF) (0.10

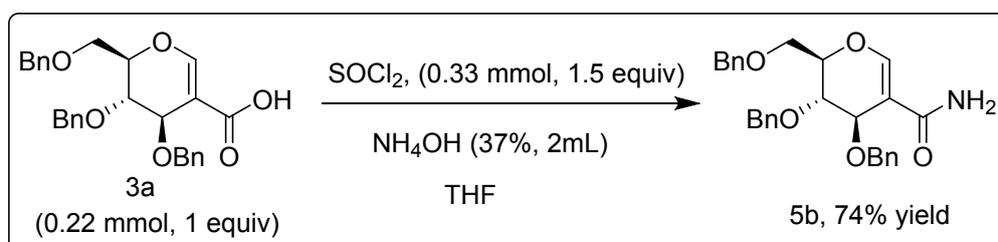
equiv) *N,N'*-Dicyclohexylcarbodiimide (DCC) (1 equiv), formic Acid (2 equiv), triethylamine (2 equiv) and triethylsilane. Closed sealed tube tightly with screw cork and the resulting mixtures was stirred at preheated oil bath at 90 °C for 2 h. Upon reaction completion, the resulting mixture was extracted with ethyl acetate and the combined organic extracts were washed with brine, dried over MgSO₄ and concentrated. The residue left was purified by column chromatography on silica gel (60-120 mesh) hexanes/ ethyl acetate as eluent to obtained **3aa-3ab** as desired products.

3.4 Procedure for synthesis of 5a



In an oven dried round bottom flask stirred mixture of anisaldehyde (0.15 mmol, 0.7 equiv) and aniline (0.15 mmol, 0.7 equiv) in methanol for 2 h at rt. Then, glycol based acid **3a** (0.22 mmol, 1 equiv) and cyclohexylisocyanide (0.18 mmol, 0.8 equiv) were added and resulting reaction mixture was stirred at rt for 48 h. After completion the reaction mixture was diluted with ethyl acetate and washed with brine. The organic layer was dried over sodium sulphate and evaporated in vacuo. The residue left was purified by column chromatography on silica gel (60-120 mesh) and pet ether/ ethyl acetate (82/18) as eluent to obtained desired product **5a** as colorless oil (93 mg, 55 %).

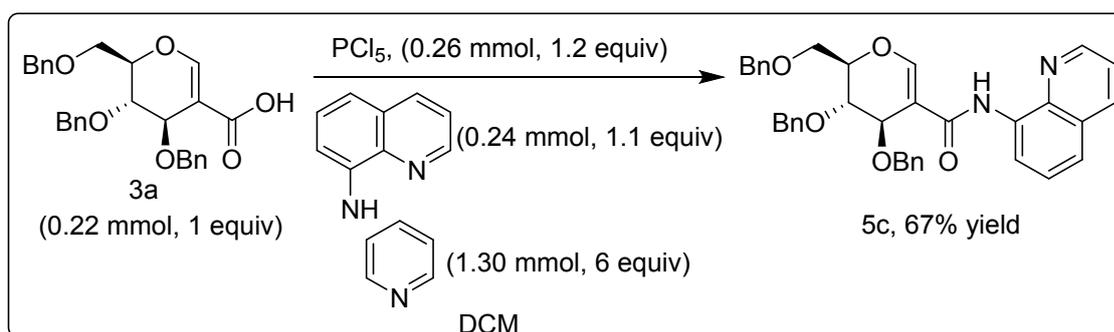
3.5 Procedure for Synthesis of 5b



To a solution of glycol based acid **3a** (0.22 mmol, 1 equiv) in 3 mL of anhydrous THF in an oven dried round bottom flask under N₂ atmosphere. Thionyl chloride (0.33 mmol, 1.5 equiv)

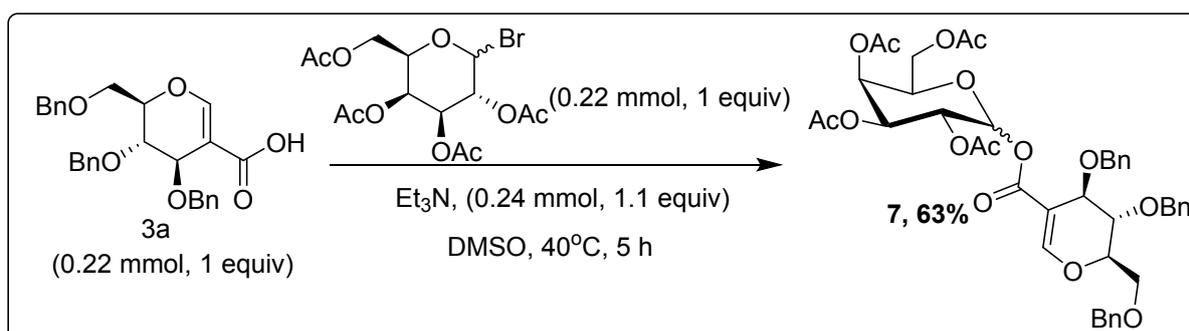
was also added and resulting reaction mixture was stirred at 50 °C in preheated oil bath under N₂ atmosphere for 1 h. then cooled the reaction mixture to 0 °C and add this reaction mixture to already prepared 37% ammonium hydroxide solution at 0 °C on continue stirring. After 5 minute the reaction mixture was diluted with chloroform and worked up with water. The organic layer was dried over sodium sulphate and evaporated in vacuo. The residue left was purified by column chromatography using silica gel (60-120 mesh) and pet ether/ ethyl acetate (65/35) as eluent to obtained **5b** as colorless semi solid product (74 mg, 74 %).

3.6 Procedure for Synthesis of 5c



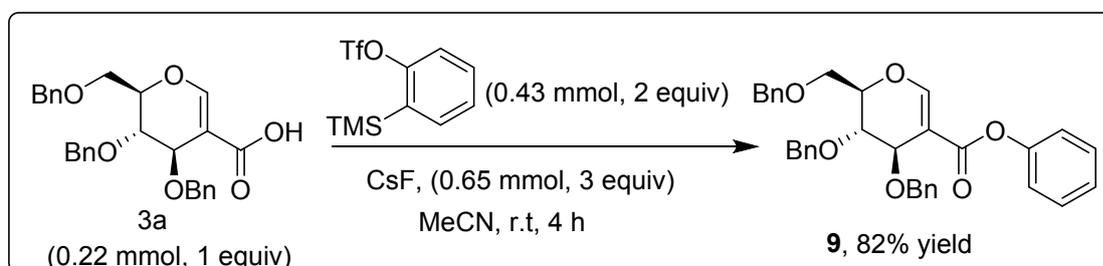
To a solution of glycal based acid **3a** (0.22 mmol, 1 equiv) in 3 mL of DCM in an oven dried round bottom flask. Phosphorous pentachloride (0.26 mmol, 1.2 equiv) was also added and resulting reaction mixture was allowed to stirr at 45 °C on reflux in preheated oil bath under N₂ atmosphere for 1 h. then cooled the reaction mixture to 0 °C and then added 8-aminoquinoline (0.24 mmol, 1.1 equiv), after 5 minutes pyridine (1.3 mmol, 6 equiv) was added, and resulting reaction mixture was stirred at rt for 2 h. After completion the reaction mixture was diluted with ethyl acetate and washed with brine. The organic layer was dried over sodium sulphate and evaporated in vacuo. The residue left was purified by column chromatography on silica gel (60-120 mesh) and pet ether/ ethyl acetate (90/10) as eluent to obtained desired product **5c** as colorless oil (86 mg, 67 %).

3.7 Procedure for synthesis of 7



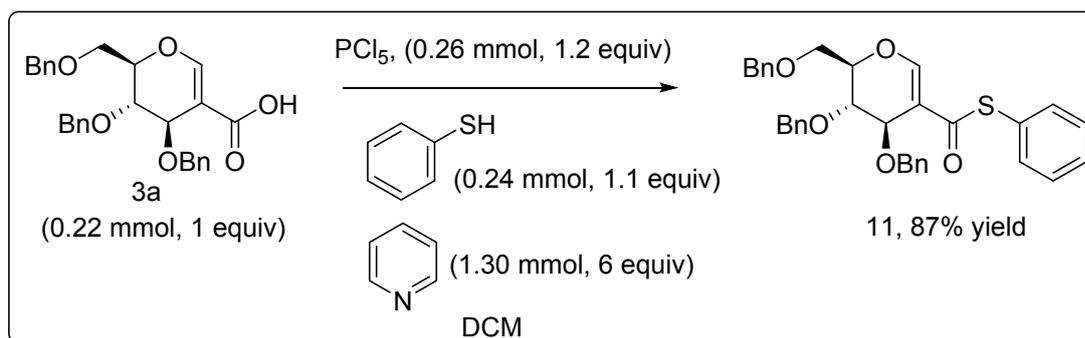
To a solution of glycal based acid **3a** (0.22 mmol, 1equiv) in 3 mL of anhydrous DMSO in an oven dried round bottom flask under N₂ atmosphere. 1,2,3,4,6-penta-*O*-acetyl-(α,β)-D-galactopyranosyl Bromide (0.22 mmol, 1 equiv) and triethylamine (0.24 mmol, 1.1 equiv) were also added and resulting reaction mixture was stirred at 40 °C in preheated oil bath under N₂ atmosphere until complete consumption of starting material (about 5 h) was observed by TLC analysis. After completion the reaction mixture was diluted with 25 mL of ethyl acetate and washed with 20 mL of brine. The organic layer was dried over sodium sulphate and evaporated in vacuo. The residue left was purified by column chromatography using silica gel (60-120 mesh) and pet ether/ ethyl acetate (85/15) as eluent to obtained **5e** as colourless gummy product (117 mg, 68 %).

3.8 Procedure for Synthesis of **9**



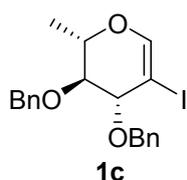
To a solution of glycal based acid **3a** (0.22 mmol, 1 equiv) in 1 mL of anhydrous MeCN in an oven dried round bottom flask under N₂ atmosphere. 2-(trimethylsilyl) phenyl trifluoromethanesulfonate (0.43 mmol, 2 equiv) and cesium fluoride (0.65 mmol, 3 equiv) were also added and resulting reaction mixture was stirred at rt under N₂ atmosphere until complete consumption of starting material (about 4 h) was observed by TLC analysis. After completion the reaction mixture was diluted with ethyl acetate and washed with brine. The organic layer was dried over sodium sulphate and evaporated in vacuo. The residue left was purified by column chromatography using silica gel (60-120 mesh) and pet ether/ ethyl acetate (93/7) as eluent to obtained **9** as colourless gummy product (95 mg, 82 %).

3.9 Procedure for Synthesis of 11



To a solution of glycal based acid **3a** (0.22 mmol, 1 equiv) in 3 mL of DCM in an oven dried round bottom flask. Phosphorous pentachloride (0.26 mmol, 1.2 equiv) was also added and resulting reaction mixture was allowed to stir at 45 °C on reflux in preheated oil bath under N_2 atmosphere for 1 h. then cooled the reaction mixture to 0 °C and then added Thiophenol (0.24 mmol, 1.1 equiv), after 5 minutes pyridine (1.3 mmol, 6 equiv) was added, and resulting reaction mixture was stirred at rt for 2 h. After completion the reaction mixture was diluted with ethyl acetate and washed with brine. The organic layer was dried over sodium sulphate and evaporated in vacuo. The residue left was purified by column chromatography on silica gel (60-120 mesh) and pet ether/ ethyl acetate (92/8) as eluent to obtained desired product **11** as colorless gummy (87 mg, 67 %).

Characterization of the products:



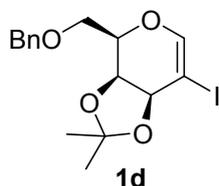
To a stirred solution of di-*O*-benzyl-L-rhamninal (0.5 g, 1.61 mmol) in dry CH₃CN (10 mL) at 80 °C under N₂ atmosphere were added successively NIS (435 mg, 1.93 mmol) and AgNO₃ (55 mg, 0.32 mmol) and stirred for 1.5 h. On consumption of starting material (TLC monitoring), the reaction mixture was filtered through sintered funnel and the filtrate was evaporated to give a crude product which was purified by silica gel column chromatography (3% of EtOAc/hexane) to obtain **1c** as amorphous solid (456 mg, 65%).

¹H NMR (400 MHz, CDCl₃) δ 7.49-7.45 (m, 2H), 7.43 – 7.35 (m, 8H), 6.74 (s, 1H), 4.80 (t, *J* = 10.6 Hz, 2H), 4.68 (t, *J* = 11.3 Hz, 2H), 4.25 – 4.20 (m, 1H), 4.17 (d, *J* = 5.2 Hz, 1H), 3.67 (dd, *J* = 7.2, 5.6 Hz, 1H), 1.41 (d, *J* = 6.6 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 148.9, 138.0, 137.8, 128.7, 128.5, 128.3, 128.1, 128.0, 128.0, 79.8, 79.1, 74.3, 73.7, 72.5, 71.3, 17.0.

HRMS calcd for C₂₀H₂₂IO₃ [M+H]⁺ 437.0614, found 437.0619;

[α]_D -29.7 (c 1, CHCl₃).



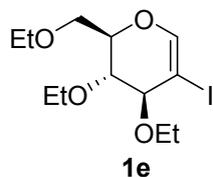
To a stirred solution of 4-((benzyloxy)methyl)-2,2-dimethyl-dihydro-4H-galactal (0.5 g, 1.81 mmol) in dry CH₃CN (10 mL) at 80 °C under N₂ atmosphere were added successively NIS (489 mg, 2.17 mmol) and AgNO₃ (62 mg, 0.36 mmol) and stirred for 20 minutes. On consumption of starting material (TLC monitoring), the reaction mixture was filtered through sintered funnel and the filtrate was evaporated to give a crude product which was purified by silica gel column chromatography (3% of EtOAc/hexane) to obtain **1d** as oil (436 mg, 60%).

¹H NMR (400 MHz, CDCl₃) δ 7.39-7.35 (m, 4H), 7.33 – 7.29 (m, 1H), 6.71 (s, 1H), 4.65 (d, *J* = 12.0 Hz, 2H), 4.61 – 4.55 (m, 1H), 4.38 (d, *J* = 5.8 Hz, 1H), 4.23 (t, *J* = 6.3 Hz, 1H), 3.83 – 3.79 (m, 1H), 3.75 – 3.71 (m, 1H), 1.48 (s, 3H), 1.39 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 148.4, 137.8, 128.5, 127.9, 127.8, 111.1, 74.8, 74.2, 74.1, 73.9, 73.65, 69.4, 27.8, 27.0.

HRMS calcd for C₁₆H₂₀IO₄ [M+H]⁺ 403.0406, found 403.0409;

[α]_D -38.6 (c 1, CHCl₃).



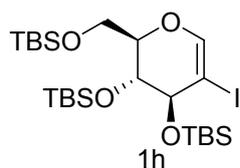
To a stirred solution of tri-*O*-ethyl-D-glucal (0.5 g, 2.17 mmol) in dry CH₃CN (10 mL) at 80 °C under N₂ atmosphere were added successively NIS (587 mg, 2.61 mmol) and AgNO₃ (74 mg, 0.43 mmol) and stirred for 1.5 h. On consumption of starting material (TLC monitoring), the reaction mixture was filtered through sintered funnel and the filtrate was evaporated to give a crude product which was purified by silica gel column chromatography (3% of EtOAc/hexane) to obtain **1e** as liquid (472 mg, 61%).

¹H NMR (400 MHz, CDCl₃) δ 6.59 (s, 1H), 4.04 (dd, *J* = 7.3, 3.9 Hz, 1H), 3.79 (d, *J* = 5.5 Hz, 1H), 3.73 – 3.66 (m, 3H), 3.64 – 3.58 (m, 4H), 3.50 – 3.43 (m, 2H), 1.23-1.19 (m, 4H), 1.18 – 1.14 (m, 5H).

¹³C NMR (126 MHz, CDCl₃) δ 148.2, 79.8, 77.2, 74.9, 71.7, 68.3, 67.1, 66.9, 66.0, 15.6, 15.1.

HRMS calcd for C₁₂H₂₂IO₄ [M+H]⁺ 357.0563, found 357.0565.

[α]_D +48.9 (c 1, CHCl₃).



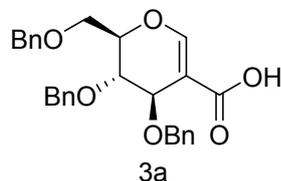
To a stirred solution of tri-*O*-tertbutyldimethylsilyl-D-glucal (0.5 g, 1.02 mmol) in dry CH₃CN (10 mL) at 80 °C under N₂ atmosphere were added successively NIS (276 mg, 1.23 mmol) and AgNO₃ (35 mg, 0.20 mmol) and stirred for 1.5 h. On consumption of starting material (TLC monitoring), the reaction mixture was filtered through sintered funnel and the filtrate was evaporated to give a crude product which was purified by silica gel column chromatography (3% of EtOAc/hexane) to obtain **1h** as liquid (424 mg, 67%).

¹H NMR (400 MHz, CDCl₃) δ 6.64 (s, 1H), 4.17 (dd, *J* = 6.6, 5.7 Hz, 1H), 3.98 (s, 1H), 3.95 – 3.89 (m, 1H), 3.85 (d, *J* = 1.6 Hz, 1H), 3.77 (dd, *J* = 11.4, 4.9 Hz, 1H), 0.93 (s, 9H), 0.90 (d, *J* = 2.0 Hz, 18H), 0.24 (s, 3H), 0.14 (s, 3H), 0.10 (s, 6H), 0.05 (d, *J* = 5.1 Hz, 6H).

^{13}C NMR (126 MHz, CDCl_3) δ 146.0, 79.5, 73.2, 70.5, 70.2, 61.2, 26.0, 25.8, 25.7, 18.4, 18.0, 18.0, -4.1, -4.3, -4.6, -4.7, -5.2, -5.3.

HRMS calcd for $\text{C}_{24}\text{H}_{52}\text{IO}_4\text{Si}_3$ $[\text{M}+\text{H}]^+$ 615.2218, found 615.2229.

$[\alpha]_{\text{D}} +24.0$ (c 1, CHCl_3).



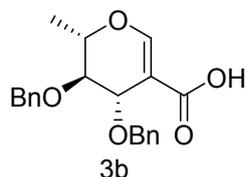
To a solution of **1a** (0.18 mmol, 1.0 equiv) in DMF in an oven dried screw capped sealed tube were added $\text{Pd}(\text{OAc})_2$ (0.009 mmol, 0.05 equiv), (DPPF) (0.018 mmol, 0.10 equiv), (DCC) (0.18 mmol, 1 equiv), formic Acid (0.36 mmol, 2 equiv), and triethylamine (0.36 mmol, 2 equiv). Closed sealed tube tightly with screw cork and the resulting mixtures was stirred at preheated oil bath at 90 °C for 1.5 h. Upon reaction completion, the resulting mixture was extracted with ethyl acetate and the combined organic extracts were washed with brine, dried over MgSO_4 and concentrated. The residue left was purified by column chromatography on silica gel (60-120 mesh) hexanes/ ethyl acetate (85/15) as eluent to obtained **3a** as colourless gummy product (68 mg, 80%).

^1H NMR (400 MHz, CDCl_3) δ 7.76 (s, 1H), 7.33 – 7.27 (m, 6H), 7.26-7.23 (m, 9H), 4.64 (d, $J = 11.1$ Hz, 2H), 4.54-4.52 (m, 3H), 4.44 (d, $J = 17.1$ Hz, 2H), 4.32 (s, 1H), 3.82 – 3.73 (m, 2H), 3.64 – 3.59 (m, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ 172.9, 157.5, 138.2, 137.8, 137.4, 128.6, 128.4, 128.4, 128.0, 127.8, 127.8, 127.7, 104.7, 77.4, 73.4, 72.3, 71.5, 71.3, 68.3, 67.7.

HRMS (ESI) calculated $\text{C}_{28}\text{H}_{27}\text{O}_6$ $[\text{M}-\text{H}]^-$: 459.1808, Found: 459.1827;

$[\alpha]_{\text{D}} +43.2$ (c 1, CHCl_3).



To a solution of **1b** (0.23 mmol, 1.0 equiv) in DMF in an oven dried screw capped sealed tube were added $\text{Pd}(\text{OAc})_2$ (0.001 mmol, 0.05 equiv), (DPPF) (0.002 mmol, 0.10 equiv), (DCC) (0.23 mmol, 1 equiv), formic Acid (0.46 mmol, 2 equiv), and triethylamine (0.46 mmol, 2 equiv). Closed sealed tube tightly with screw cork and the resulting mixtures was stirred at preheated oil bath at 90 °C for 1.5 h. Upon reaction completion, the resulting

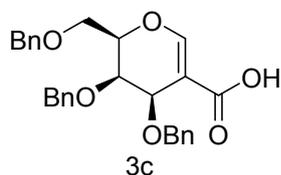
mixture was extracted with ethyl acetate and the combined organic extracts were washed with brine, dried over MgSO_4 and concentrated. The residue left was purified by column chromatography on silica gel (60-120 mesh) hexanes/ ethyl acetate (85/15) as eluent to obtained **3b** as colourless gummy product (69 mg, 85%).

^1H NMR (400 MHz, CDCl_3) δ 7.73 (s, 1H), 7.36 – 7.28 (m, 7H), 7.27-7.23 (m, 3H), 4.72 (d, $J = 11.5$ Hz, 1H), 4.60 – 4.52 (m, 3H), 4.45 (d, $J = 12.1$ Hz, 1H), 4.36 (s, 1H), 3.59 (s, 1H), 1.38 (d, $J = 7.1$ Hz, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 173.4, 157.5, 138.5, 137.6, 128.6, 128.4, 128.0, 127.9, 127.7, 127.7, 104.2, 74.8, 74.8, 72.5, 71.6, 68.5, 16.6.

HRMS (ESI) calculated $\text{C}_{21}\text{H}_{21}\text{O}_5$ $[\text{M}-\text{H}]^-$: 353.1389, Found: 353.1408;

$[\alpha]_{\text{D}} -32.5$ (c 1, CHCl_3).



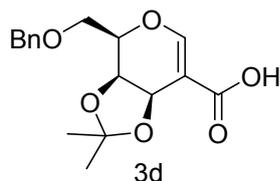
To a solution of **1c** (0.18 mmol, 1.0 equiv) in DMF in an oven dried screw capped sealed tube were added $\text{Pd}(\text{OAc})_2$ (0.009 mmol, 0.05 equiv), (DPPF) (0.018 mmol, 0.10 equiv), (DCC) (0.18 mmol, 1 equiv), formic Acid (0.36 mmol, 2 equiv), and triethylamine (0.36 mmol, 2 equiv). Closed sealed tube tightly with screw cork and the resulting mixtures was stirred at preheated oil bath at 90 °C for 1.5 h. Upon reaction completion, the resulting mixture was extracted with ethyl acetate and the combined organic extracts were washed with brine, dried over MgSO_4 and concentrated. The residue left was purified by column chromatography on silica gel (60-120 mesh) hexanes/ ethyl acetate (85/15) as eluent to obtained **3c** as colourless gummy product (65 mg, 76%).

^1H NMR (400 MHz, CDCl_3) δ 7.62 (s, 1H), 7.32-7.28 (m, 7H), 7.28-7.24 (m, 8H), 4.80 – 4.71 (m, 2H), 4.65 (dd, $J = 17.6, 8.3$ Hz, 2H), 4.58 (d, $J = 7.0$ Hz, 1H), 4.55 – 4.51 (m, 2H), 4.45 (d, $J = 11.9$ Hz, 1H), 4.00 – 3.95 (m, 2H), 3.89 – 3.85 (m, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ 172.3, 157.5, 138.9, 138.0, 137.5, 128.6, 128.4, 128.2, 128.0, 127.9, 127.7, 127.6, 127.4, 106.2, 77.2, 74.1, 73.8, 73.5, 71.7, 68.3, 67.3.

HRMS (ESI) calculated $\text{C}_{28}\text{H}_{27}\text{O}_6$ $[\text{M}-\text{H}]^-$: 459.1808, Found: 459.1825;

$[\alpha]_{\text{D}} -25.7$ (c 1, CHCl_3).



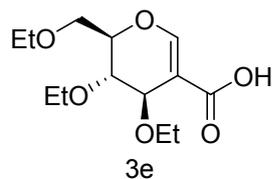
To a solution of **1d** (0.25 mmol, 1.0 equiv) in DMF in an oven dried screw capped sealed tube were added Pd(OAc)₂ (0.012 mmol, 0.05 equiv), (DPPF) (0.025 mmol, 0.10 equiv), (DCC) (0.25 mmol, 1 equiv), formic Acid (0.49 mmol, 2 equiv), and triethylamine (0.49 mmol, 2 equiv). Closed sealed tube tightly with screw cork and the resulting mixtures was stirred at preheated oil bath at 90 °C for 1.5 h. Upon reaction completion, the resulting mixture was extracted with ethyl acetate and the combined organic extracts were washed with brine, dried over MgSO₄ and concentrated. The residue left was purified by column chromatography on silica gel (60-120 mesh) hexanes/ ethyl acetate (82/18) as eluent to obtained **3d** as colourless gummy product (60 mg, 75 %).

¹H NMR (400 MHz, CDCl₃) δ 7.61 (s, 1H), 7.34 – 7.23 (m, 5H), 4.94 (d, *J* = 6.3 Hz, 1H), 4.65 – 4.52 (m, 2H), 4.38 (d, *J* = 6.2 Hz, 1H), 4.16 – 4.09 (m, 1H), 3.88 – 3.82 (m, 1H), 3.79 – 3.74 (m, 1H), 1.36 (s, 3H), 1.33 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 171.7, 157.6, 137.6, 128.5, 127.9, 127.8, 111.0, 107.9, 75.8, 73.7, 72.0, 69.2, 67.6, 27.8, 26.5.

HRMS (ESI) calculated C₁₇H₁₉O₆ [M-H]⁻ : 319.1182, Found: 319.1196;

[α]_D -29.0 (c 1, CHCl₃).



To a solution of **1e** (0.28 mmol, 1.0 equiv) in DMF in an oven dried screw capped sealed tube were added Pd(OAc)₂ (0.014 mmol, 0.05 equiv), (DPPF) (0.028 mmol, 0.10 equiv), (DCC) (0.28 mmol, 1 equiv), formic Acid (0.56 mmol, 2 equiv), and triethylamine (0.56 mmol, 2 equiv). Closed sealed tube tightly with screw cork and the resulting mixtures was stirred at preheated oil bath at 90 °C for 2 h. Upon reaction completion, the resulting mixture was extracted with ethyl acetate and the combined organic extracts were washed with brine, dried over MgSO₄ and concentrated. The residue left was purified by column chromatography on

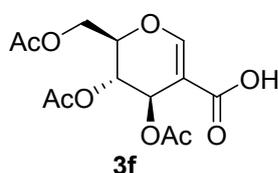
silica gel (60-120 mesh) hexanes/ ethyl acetate (90/10) as eluent to obtained **3e** as colorless gummy product (59 mg, 76 %).

¹H NMR (400 MHz, CDCl₃) δ 7.66 (s, 1H), 4.56 – 4.48 (m, 1H), 4.09 (d, *J* = 2.2 Hz, 1H), 3.71 – 3.66 (m, 2H), 3.65 – 3.60 (m, 2H), 3.59 – 3.53 (m, 3H), 3.51 – 3.43 (m, 2H), 1.19 – 1.15 (m, 4H), 1.15 – 1.12 (m, 5H).

¹³C NMR (126 MHz, CDCl₃) δ 172.7, 157.2, 104.7, 77.6, 72.0, 68.6, 67.8, 66.8, 65.4, 65.1, 15.5, 15.4, 15.1.

HRMS (ESI) calculated C₁₃H₂₁O₆ [M-H]⁻ : 273.1338, Found: 273.1351;

[α]_D +58.0 (c 1, CHCl₃).



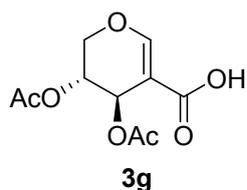
To a solution of **1f** (0.25 mmol, 1.0 equiv) in DMF in an oven dried screw capped sealed tube were added Pd(OAc)₂ (0.012 mmol, 0.05 equiv), (DPPF) (0.025 mmol, 0.10 equiv), (DCC) (0.25 mmol, 1 equiv), formic Acid (0.5 mmol, 2 equiv), and triethylamine (0.5 mmol, 2 equiv). Closed sealed tube tightly with screw cork and the resulting mixtures was stirred at preheated oil bath at 90 °C for 2.5 h. Upon reaction completion, the resulting mixture was extracted with ethyl acetate and the combined organic extracts were washed with brine, dried over MgSO₄ and concentrated. The residue left was purified by column chromatography on silica gel (60-120 mesh) hexanes/ ethyl acetate (68/32) as eluent to obtained **3f** as colourless gummy product (58 mg, 73 %).

¹H NMR (400 MHz, CDCl₃) δ 7.81 (s, 1H), 5.66 (dd, *J* = 2.8, 1.6 Hz, 1H), 5.19 (t, *J* = 3.0 Hz, 1H), 4.66 – 4.56 (m, 1H), 4.46 (dd, *J* = 12.1, 7.9 Hz, 1H), 4.19 (dd, *J* = 12.1, 4.4 Hz, 1H), 2.12 (s, 3H), 2.10 (s, 3H), 2.07 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 170.4, 170.3, 169.5, 169.3, 158.0, 103.3, 74.9, 65.9, 62.1, 60.9, 20.7, 20.7, 20.6.

HRMS (ESI) calculated C₁₃H₁₅O₉ [M-H]⁻ : 315.0716, Found: 315.0728;

[α]_D +46.8 (c 1, CHCl₃).



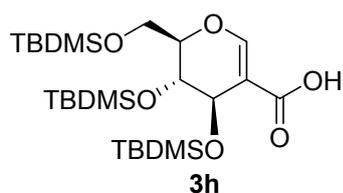
To a solution of **1g** (0.31 mmol, 1.0 equiv) in DMF in an oven dried screw capped sealed tube were added Pd(OAc)₂ (0.015 mmol, 0.05 equiv), (DPPF) (0.031 mmol, 0.10 equiv), (DCC) (0.31 mmol, 1 equiv), formic Acid (0.62 mmol, 2 equiv), and triethylamine (0.62 mmol, 2 equiv). Closed sealed tube tightly with screw cork and the resulting mixtures was stirred at preheated oil bath at 90 °C for 2.5 h. Upon reaction completion, the resulting mixture was extracted with ethyl acetate and the combined organic extracts were washed with brine, dried over MgSO₄ and concentrated. The residue left was purified by column chromatography on silica gel (60-120 mesh) hexanes/ ethyl acetate (70/30) as eluent to obtained **3g** as colourless gummy product (56 mg, 75 %).

¹H NMR (400 MHz, CDCl₃) δ 7.91 (s, 1H), 5.61 (t, J = 2.0 Hz, 1H), 5.02 (d, J = 1.9 Hz, 1H), 4.51 – 4.43 (m, 1H), 4.06 (d, J = 12.6 Hz, 1H), 2.11 (s, 3H), 2.10 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 171.2, 169.5, 169.2, 160.3, 102.9, 65.3, 64.6, 61.0, 20.9, 20.8.

HRMS (ESI) calculated C₁₀H₁₁O₇ [M-H]⁻: 243.0505, Found: 243.0516;

[α]_D +63.9 (c 1, CHCl₃).



To a solution of **1h** (0.16 mmol, 1.0 equiv) in DMF in an oven dried screw capped sealed tube were added Pd(OAc)₂ (0.008 mmol, 0.05 equiv), (DPPF) (0.016 mmol, 0.10 equiv), (DCC) (0.16 mmol, 1 equiv), formic Acid (0.32 mmol, 2 equiv), and triethylamine (0.32 mmol, 2 equiv). Closed sealed tube tightly with screw cork and the resulting mixtures was stirred at preheated oil bath at 90 °C for 2 h. Upon reaction completion, the resulting mixture was extracted with ethyl acetate and the combined organic extracts were washed with brine, dried over MgSO₄ and concentrated. The residue left was purified by column

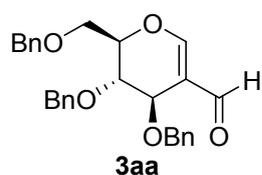
chromatography on silica gel (60-120 mesh) hexanes/ ethyl acetate (90/10) as eluent to obtained **3f** as colourless gummy product (66 mg, 76 %).

¹H NMR (400 MHz, CDCl₃) δ 7.74 (s, 1H), 4.27-4.24 (m, 2H), 3.90 – 3.83 (m, 2H), 3.72 (dd, *J* = 12.7, 4.5 Hz, 1H), 0.85-0.77 (m, 27H), 0.18 – -0.01 (m, 18H).

¹³C NMR (101 MHz, CDCl₃) δ 172.7, 158.1, 105.0, 80.8, 69.8, 63.6, 62.2, 25.7, 25.6, 18.0, 17.9, -4.6, -4.8, -4.8, -4.9.

HRMS (ESI) calculated C₂₅H₅₁O₆Si₃ [M-H]⁻ : 531.2993, Found: 531.3003;

[α]_D +24.0 (c 1, CHCl₃).



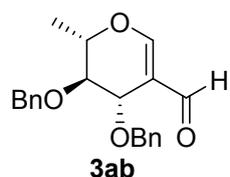
To a solution of **1a** (0.18 mmol, 1.0 equiv) in DMF in an oven dried screw capped sealed tube were added Pd(OAc)₂ (0.009 mmol, 0.05 equiv), (DPPF) (0.018 mmol, 0.10 equiv), (DCC) (0.18 mmol, 1 equiv), formic Acid (0.36 mmol, 2 equiv), triethylamine (0.36 mmol, 2 equiv) and TMSH (0.22 mmol, 1.2 equiv). Closed sealed tube tightly with screw cork and the resulting mixtures was stirred at preheated oil bath at 90 °C for 2 h. Upon reaction completion, the resulting mixture was extracted with ethyl acetate and the combined organic extracts were washed with brine, dried over MgSO₄ and concentrated. The residue left was purified by column chromatography on silica gel (60-120 mesh) hexanes/ ethyl acetate (92/8) as eluent to obtained **3aa** as colourless gummy product (59 mg, 72%).

¹H NMR (400 MHz, CDCl₃) δ 9.44 (s, 1H), 7.43 (s, 1H), 7.40 – 7.37 (m, 2H), 7.36 – 7.34 (m, 3H), 7.34 – 7.31 (m, 5H), 7.30 – 7.26 (m, 5H), 4.80 – 4.68 (m, 2H), 4.64 – 4.50 (m, 5H), 4.46 (t, *J* = 2.2 Hz, 1H), 3.88 (t, *J* = 2.2 Hz, 1H), 3.86 – 3.81 (m, 1H), 3.70 – 3.66 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 190.5, 164.4, 138.1, 137.6, 137.2, 128.8, 128.6, 128.5, 128.4, 128.1, 127.9, 127.9, 127.8, 127.7, 117.7, 79.4, 73.4, 72.5, 71.7, 71.3, 68.4, 65.2.

HRMS (ESI) calculated C₂₈H₂₈O₅ [M+H]⁺ : 445.2015, Found: 445.2029;

[α]_D +47.9 (c 1, CHCl₃).



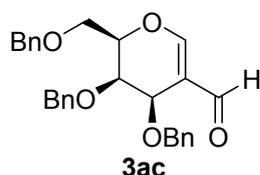
To a solution of **1b** (0.23 mmol, 1.0 equiv) in DMF in an oven dried screw capped sealed tube were added Pd(OAc)₂ (0.011 mmol, 0.05 equiv), (DPPF) (0.023 mmol, 0.10 equiv), (DCC) (0.23 mmol, 1 equiv), formic Acid (0.46 mmol, 2 equiv), triethylamine (0.46 mmol, 2 equiv) and TMSH (0.27 mmol, 1.2 equiv). Closed sealed tube tightly with screw cork and the resulting mixtures was stirred at preheated oil bath at 90 °C for 2 h. Upon reaction completion, the resulting mixture was extracted with ethyl acetate and the combined organic extracts were washed with brine, dried over MgSO₄ and concentrated. The residue left was purified by column chromatography on silica gel (60-120 mesh) hexanes/ ethyl acetate (92/8) as eluent to obtained **3ab** as colourless gummy product (61 mg, 78%).

¹H NMR (400 MHz, CDCl₃) δ 9.36 (s, 1H), 7.34 – 7.27 (m, 7H), 7.23-7.19 (m, 3H), 4.72 (d, *J* = 11.5 Hz, 1H), 4.60 (dd, *J* = 9.3, 4.3 Hz, 2H), 4.52 (d, *J* = 12.0 Hz, 1H), 4.41 (d, *J* = 12.1 Hz, 2H), 3.61 (s, 1H), 1.41 (d, *J* = 7.1 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 190.6, 164.6, 138.5, 137.5, 128.6, 128.4, 128.0, 127.9, 127.7, 127.7, 117.5, 76.9, 74.8, 72.7, 71.7, 66.2, 16.9.

HRMS (ESI) calculated C₂₁H₂₃O₄ [M+H]⁺ : 339.1596, Found: 339.1591;

[α]_D -36.0 (c 1, CHCl₃).



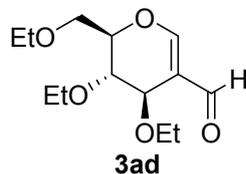
To a solution of **1c** (0.18 mmol, 1.0 equiv) in DMF in an oven dried screw capped sealed tube were added Pd(OAc)₂ (0.009 mmol, 0.05 equiv), (DPPF) (0.018 mmol, 0.10 equiv), (DCC) (0.18 mmol, 1 equiv), formic Acid (0.36 mmol, 2 equiv), triethylamine (0.36 mmol, 2 equiv) and TMSH (0.22 mmol, 1.2 equiv). Closed sealed tube tightly with screw cork and the resulting mixtures was stirred at preheated oil bath at 90 °C for 2 h. Upon reaction completion, the resulting mixture was extracted with ethyl acetate and the combined organic extracts were washed with brine, dried over MgSO₄ and concentrated. The residue left was purified by column chromatography on silica gel (60-120 mesh) hexanes/ ethyl acetate (92/8) as eluent to obtained **3ac** as colourless gummy product (65 mg, 79%).

¹H NMR (400 MHz, CDCl₃) δ 9.32 (s, 1H), 7.38-7.31 (m, 9H), 7.30-7.27 (m, 5H), 7.22 (s, 1H), 4.76 (s, 2H), 4.73 – 4.66 (m, 2H), 4.61 (d, *J* = 2.3 Hz, 1H), 4.57-4.53 (m, 4H), 4.03 – 3.98 (m, 2H), 3.84 – 3.80 (m, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ 189.5, 164.5, 138.8, 138.1, 137.5, 128.6, 128.5, 128.3, 128.1, 128.0, 127.8, 127.8, 127.7, 127.5, 119.3, 78.8, 73.8, 73.5, 73.2, 71.6, 68.5, 64.8.

HRMS (ESI) calculated $\text{C}_{28}\text{H}_{29}\text{O}_5$ $[\text{M}+\text{H}]^+$: 445.2015, Found: 445.2026;

$[\alpha]_{\text{D}} -29.4$ (c 1, CHCl_3).



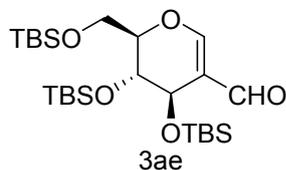
To a solution of **1e** (0.28 mmol, 1.0 equiv) in DMF in an oven dried screw capped sealed tube were added $\text{Pd}(\text{OAc})_2$ (0.014 mmol, 0.05 equiv), (DPPF) (0.028 mmol, 0.10 equiv), (DCC) (0.28 mmol, 1 equiv), formic Acid (0.56 mmol, 2 equiv), triethylamine (0.56 mmol, 2 equiv) and TMSH (0.337 mmol, 1.2 equiv). Closed sealed tube tightly with screw cork and the resulting mixtures was stirred at preheated oil bath at 90 °C for 2 h. Upon reaction completion, the resulting mixture was extracted with ethyl acetate and the combined organic extracts were washed with brine, dried over MgSO_4 and concentrated. The residue left was purified by column chromatography on silica gel (60-120 mesh) hexanes/ ethyl acetate (91/9) as eluent to obtained **3ad** as colourless gummy product (50 mg, 69%).

^1H NMR (400 MHz, CDCl_3) δ 9.28 (s, 1H), 7.27 (s, 1H), 4.62 – 4.50 (m, 1H), 4.13 (s, 1H), 3.69 – 3.63 (m, 2H), 3.60 – 3.56 (m, 2H), 3.57-3.51 (m, 3H), 3.46 – 3.42 (m, 2H), 1.19-1.13 (m, 4H), 1.13 – 1.08 (m, 5H).

^{13}C NMR (126 MHz, CDCl_3) δ 190.4, 164.3, 117.8, 79.6, 72.0, 68.8, 66.7, 65.5, 65.4, 15.5, 15.4, 15.1.

HRMS (ESI) calculated $\text{C}_{13}\text{H}_{22}\text{O}_5$ $[\text{M}+\text{H}]^+$: 259.1545, Found: 259.1556;

$[\alpha]_{\text{D}} +41.0$ (c 1, CHCl_3).



To a solution of **1h** (0.16 mmol, 1.0 equiv) in DMF in an oven dried screw capped sealed tube were added $\text{Pd}(\text{OAc})_2$ (0.008 mmol, 0.05 equiv), (DPPF) (0.016 mmol, 0.10 equiv), (DCC) (0.16 mmol, 1 equiv), formic Acid (0.32 mmol, 2 equiv), triethylamine (0.32 mmol, 2 equiv) and TMSH (0.192 mmol, 1.2 equiv). Closed sealed tube tightly with screw cork and the resulting mixtures was stirred at preheated oil bath at 90 °C for 2 h. Upon reaction completion, the resulting mixture was extracted with ethyl acetate and the combined organic

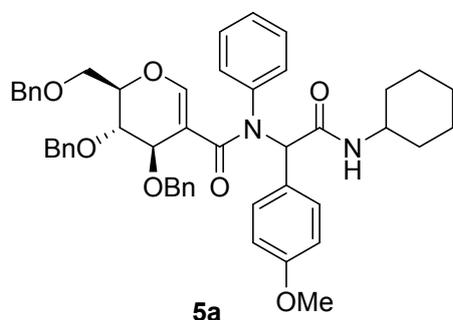
extracts were washed with brine, dried over MgSO₄ and concentrated. The residue left was purified by column chromatography on silica gel (60-120 mesh) hexanes/ ethyl acetate (91/9) as eluent to obtained **3ae** as colourless gummy product (59 mg, 70%).

¹H NMR (400 MHz, CDCl₃) δ 9.30 (s, 1H), 7.42 (s, 1H), 4.37 (d, *J* = 1.7 Hz, 2H), 3.95 – 3.89 (m, 2H), 3.83 (dd, *J* = 12.8, 4.5 Hz, 1H), 0.87 (s, 16H), 0.84 (s, 11H), 0.30-0.22 (m, 4H), 0.20-0.16 (m, 5H), 0.13-0.06 (m, 9H).

¹³C NMR (126 MHz, CDCl₃) δ 190.0, 165.3, 118.1, 82.3, 69.9, 62.3, 61.2, 25.7, 25.5, -4.7, -4.9, -5.1.

HRMS (ESI) calculated C₂₅H₅₃O₅Si₃ [M+H]⁺: 517.3201, Found: 517.3208;

[α]_D +26.3 (c 1, CHCl₃).



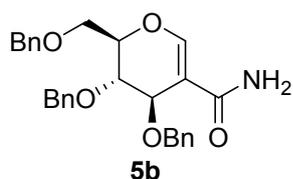
Synthesized according to general procedure 3.4

¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.32 (m, 5H), 7.32 – 7.30 (m, 5H), 7.25 – 7.21 (m, 6H), 7.18 – 7.11 (m, 5H), 6.73 (d, *J* = 8.7 Hz, 2H), 6.60 (s, 1H), 6.29 (d, *J* = 8.0 Hz, 1H), 6.15 (s, 1H), 4.71 (d, *J* = 11.5 Hz, 1H), 4.64 – 4.56 (m, 2H), 4.48 – 4.36 (m, 3H), 4.33 – 4.24 (m, 2H), 3.90 – 3.84 (m, 1H), 3.76 (s, 3H), 3.73 (t, *J* = 4.1 Hz, 1H), 3.50-4.46 (m, 2H), 2.00 – 1.88 (m, 2H), 1.74 – 1.63 (m, 8H).

¹³C NMR (126 MHz, CDCl₃) δ 169.6, 169.2, 159.1, 151.2, 142.7, 138.5, 137.8, 137.6, 130.7, 129.4, 128.9, 128.8, 128.5, 128.4, 128.3, 127.9, 127.8, 127.7, 127.6, 127.5, 127.0, 127.0, 113.7, 110.0, 76.7, 73.5, 72.5, 72.5, 72.1, 71.6, 68.0, 66.8, 55.2, 48.6, 32.9, 32.9, 25.5, 24.8, 24.8.

HRMS (ESI) calculated C₄₉H₅₃N₂O₇ [M+H]⁺: 781.3853, Found: 781.3867;

[α]_D +138.0 (c 1, CHCl₃).



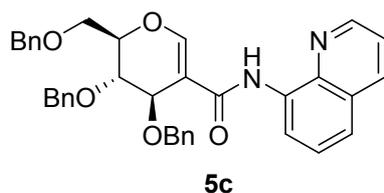
Synthesized according to general procedure 3.5

¹H NMR (400 MHz, CDCl₃) δ 7.61 (s, 1H), 7.41 – 7.37 (m, 3H), 7.36-7.34 (m, 5H), 7.33-7.31 (m, 4H), 7.30-7.28 (m, 1H), 7.27 – 7.23 (m, 2H), 5.59 (s, 2H), 4.70 (s, 2H), 4.61 – 4.54 (m, 2H), 4.52 – 4.47 (m, 2H), 4.38 (d, *J* = 3.3 Hz, 1H), 4.10 (t, *J* = 4.1 Hz, 1H), 3.85 – 3.81 (m, 1H), 3.76 – 3.72 (m, 1H), 3.45 (s, 1H).

¹³C NMR (126 MHz,) δ 168.8, 154.2, 137.6, 137.4, 137.1, 128.7, 128.6, 128.5, 128.2, 128.1, 128.1, 128.0, 127.9, 127.8, 106.9, 76.6, 73.5, 72.2, 71.3, 70.3, 69.8, 67.5.

HRMS (ESI) calculated C₂₈H₃₀NO₅ [M+H]⁺: 460.2124, Found: 460.2139;

[α]_D +89.6 (c 1, CHCl₃).



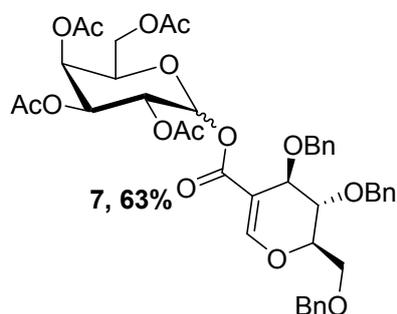
Synthesized according to general procedure 3.6

¹H NMR (400 MHz, CDCl₃) δ 10.57 (s, 1H), 8.86 (d, *J* = 7.5 Hz, 1H), 8.41 (d, *J* = 3.2 Hz, 1H), 8.15 (d, *J* = 7.3 Hz, 1H), 7.81 (s, 1H), 7.59-7.50 (m, 3H), 7.41 – 7.37 (m, 5H), 7.36-7.34 (m, 2H), 7.33-7.31 (m, 3H), 7.29 – 7.27 (m, 4H), 7.26-7.24 (m, 1H), 5.11 (d, *J* = 11.2 Hz, 1H), 4.72 – 4.67 (m, 3H), 4.58 (s, 1H), 4.53-4.50 (m, 1H), 4.46 – 4.41 (m, 2H), 4.10 (s, 1H), 3.87 – 3.80 (m, 1H), 3.71 – 3.66 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 165.5, 153.4, 149.4, 147.9, 138.7, 137.9, 137.7, 137.4, 136.3, 135.1, 128.6, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.6, 127.5, 127.5, 121.5, 121.1, 116.8, 108.2, 76.2, 73.4, 71.8, 70.9, 70.5, 70.5, 67.5.

HRMS (ESI) calculated C₃₇H₃₄N₂O₅ [M+H]⁺: 587.2546, Found: 587.2555;

[α]_D +76.9 (c 1, CHCl₃).



Synthesized according to general procedure 3.7

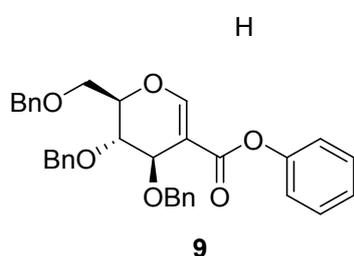
¹H NMR (400 MHz, CDCl₃) δ 7.81 (s, 1H), 7.76 (s, 1H), 7.40-7.36 (m, 4H), 7.35 – 7.33 (m, 5H), 7.32-7.30 (m, 5H), 7.30-7.29 (m, 6H), 7.29 – 7.27 (m, 6H), 7.27-7.25 (m, 2H), 5.82 (d, *J* = 8.4 Hz, 1H), 5.74 (d, *J* = 8.3 Hz, 1H), 5.49 – 5.35 (m, 3H), 5.16 – 5.11 (m, 1H), 4.72 – 4.64

(m, 3H), 4.61 – 4.42 (m, 9H), 4.40 – 4.36 (m, 2H), 4.22 – 4.08 (m, 6H), 3.87 – 3.75 (m, 3H), 3.66-3.62 (m, 2H), 2.21 (s, 2H), 2.20 (s, 3H), 2.15 (s, 2H), 2.08 (d, J = 1.9 Hz, 6H), 2.05 (s, 2H), 2.03 (s, 3H), 1.96 (s, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 172.3, 170.3, 170.2, 170.1, 170.0, 169.9, 169.5, 169.4, 169.0, 165.2, 157.2, 157.3, 138.2, 138.2, 137.8, 137.8, 137.5, 137.4, 128.6, 128.4, 128.3, 128.1, 128.0, 127.8, 127.7, 127.7, 104.7, 104.1, 92.2, 92.1, 77.3, 73.4, 73.4, 72.3, 72.2, 71.7, 71.6, 71.5, 71.4, 71.3, 71.3, 70.9, 70.9, 68.3, 68.2, 67.9, 67.8, 67.8, 67.6, 66.9, 66.9, 61.1, 61.0, 60.4, 22.7, 21.0, 20.8, 20.6, 20.6, 20.5.

HRMS (ESI) calculated C₄₂H₄₇O₁₅ [M+H]⁺: 791.2915, Found: 791.2929;

[α]_D +123.7 (c 1, CHCl₃).



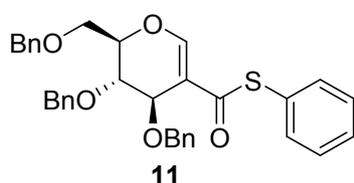
Synthesized according to general procedure 3.8

¹H NMR (400 MHz, CDCl₃) δ 7.95 (s, 1H), 7.46 – 7.40 (m, 4H), 7.39 – 7.37 (m, 3H), 7.35-7.34 (m, 3H), 7.33 – 7.30 (m, 6H), 7.30 – 7.24 (m, 2H), 7.20-7.16 (m, 2H), 4.76-4.72 (m, 2H), 4.67 – 4.58 (m, 4H), 4.54-4.52 (m, 1H), 4.48 (t, J = 2.1 Hz, 1H), 3.93 (t, J = 2.0 Hz, 1H), 3.90 – 3.85 (m, 1H), 3.77 – 3.73 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 165.8, 156.9, 150.8, 138.1, 137.8, 137.4, 129.4, 128.6, 128.5, 128.4, 128.1, 128.1, 127.9, 127.8, 127.8, 127.7, 125.6, 121.9, 105.0, 77.3, 73.4, 72.7, 71.6, 71.4, 68.2, 68.0.

HRMS (ESI) calculated C₃₄H₃₂O₆ [M+H]⁺: 537.2277, Found: 537.2282;

[α]_D +74.0 (c 1, CHCl₃).



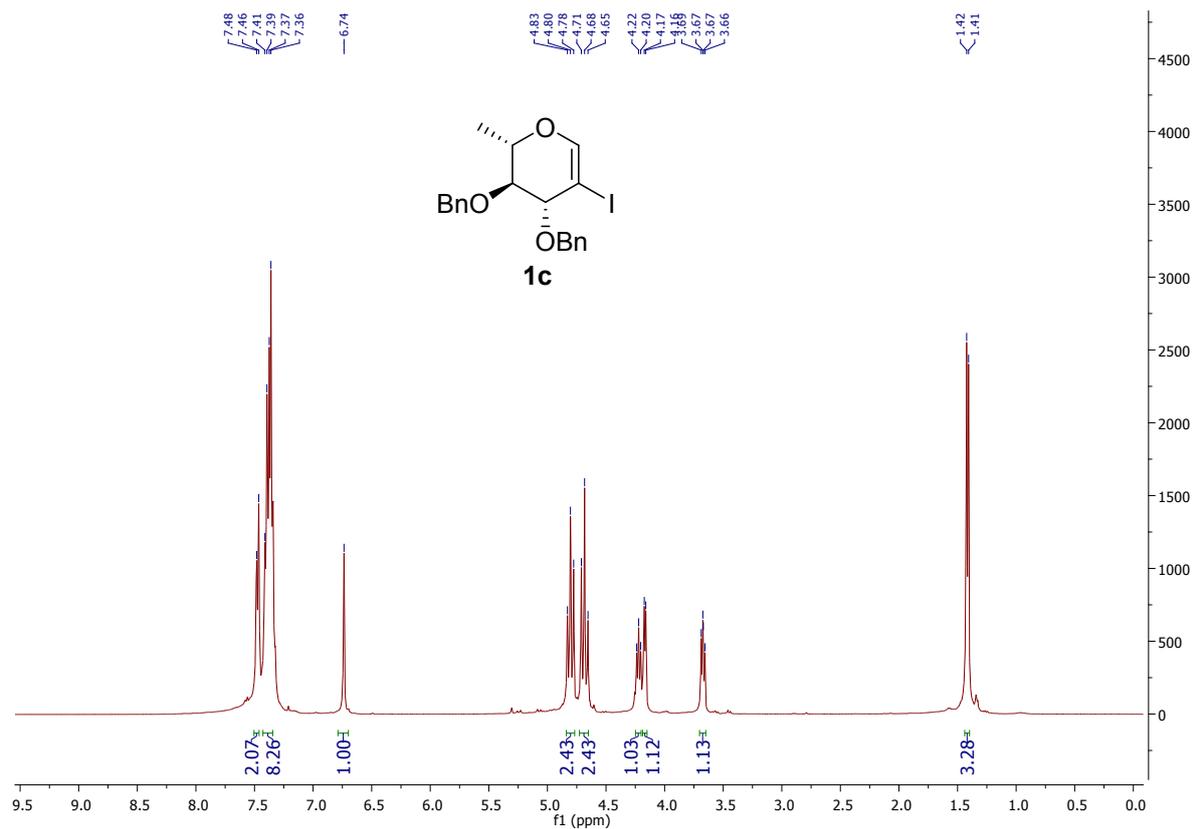
¹H NMR (400 MHz, CDCl₃) δ 7.94 (s, 1H), 7.62 – 7.56 (m, 1H), 7.54 – 7.51 (m, 2H), 7.48 – 7.45 (m, 3H), 7.43 – 7.39 (m, 3H), 7.38 – 7.35 (m, 3H), 7.34-7.32 (m, 2H), 7.31-7.29 (m, 3H), 7.28 – 7.25 (m, 3H), 4.76 – 4.67 (m, 2H), 4.62 – 4.55 (m, 3H), 4.54 – 4.48 (m, 3H), 3.90 – 3.82 (m, 2H), 3.71 – 3.66 (m, 1H).

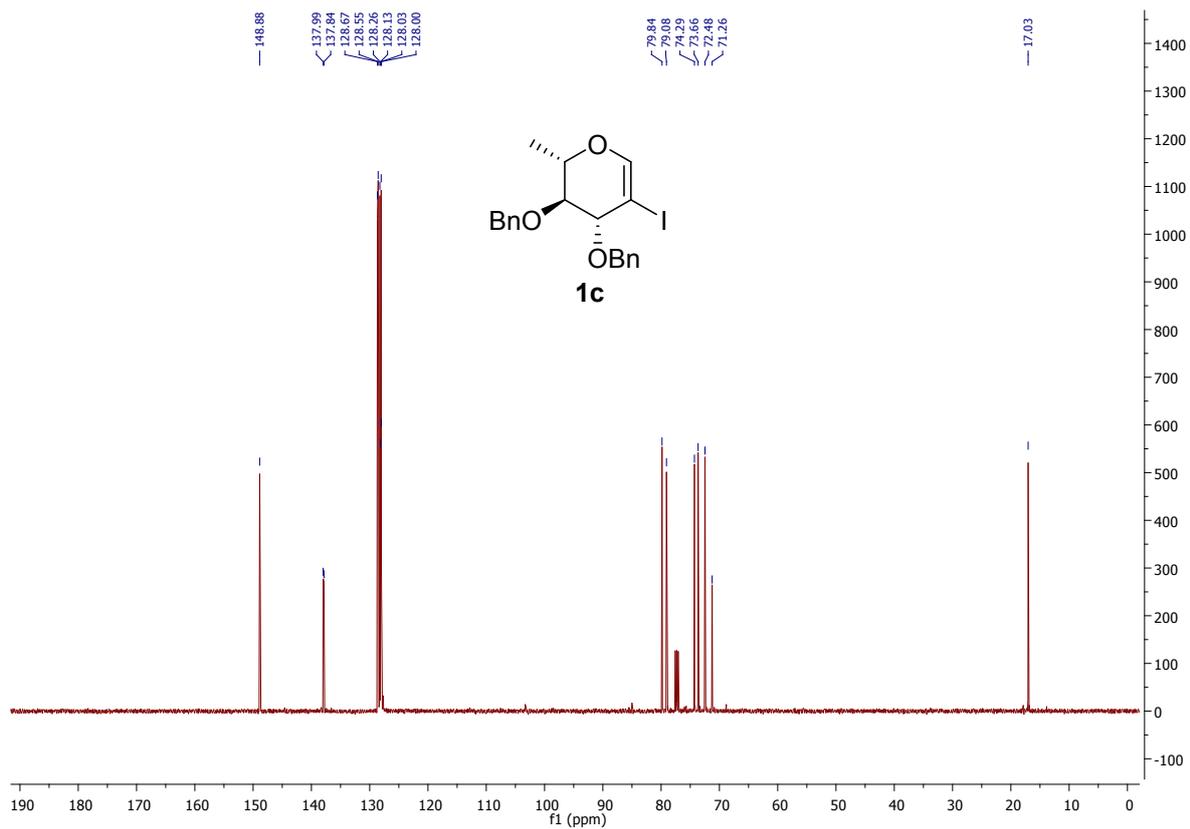
^{13}C NMR (126 MHz, CDCl_3) δ 188.1, 155.4, 138.0, 137.7, 137.3, 135.4, 129.4, 129.2, 128.6, 128.49, 128.4, 128.1, 128.1, 127.9, 127.9, 127.8, 127.8, 127.3, 77.8, 73.4, 72.64, 71.6, 71.3, 68.1, 67.8.

HRMS (ESI) calculated $\text{C}_{34}\text{H}_{32}\text{O}_5\text{S}$ $[\text{M}+\text{H}]^+$: 553.2049, Found: 553.2062;

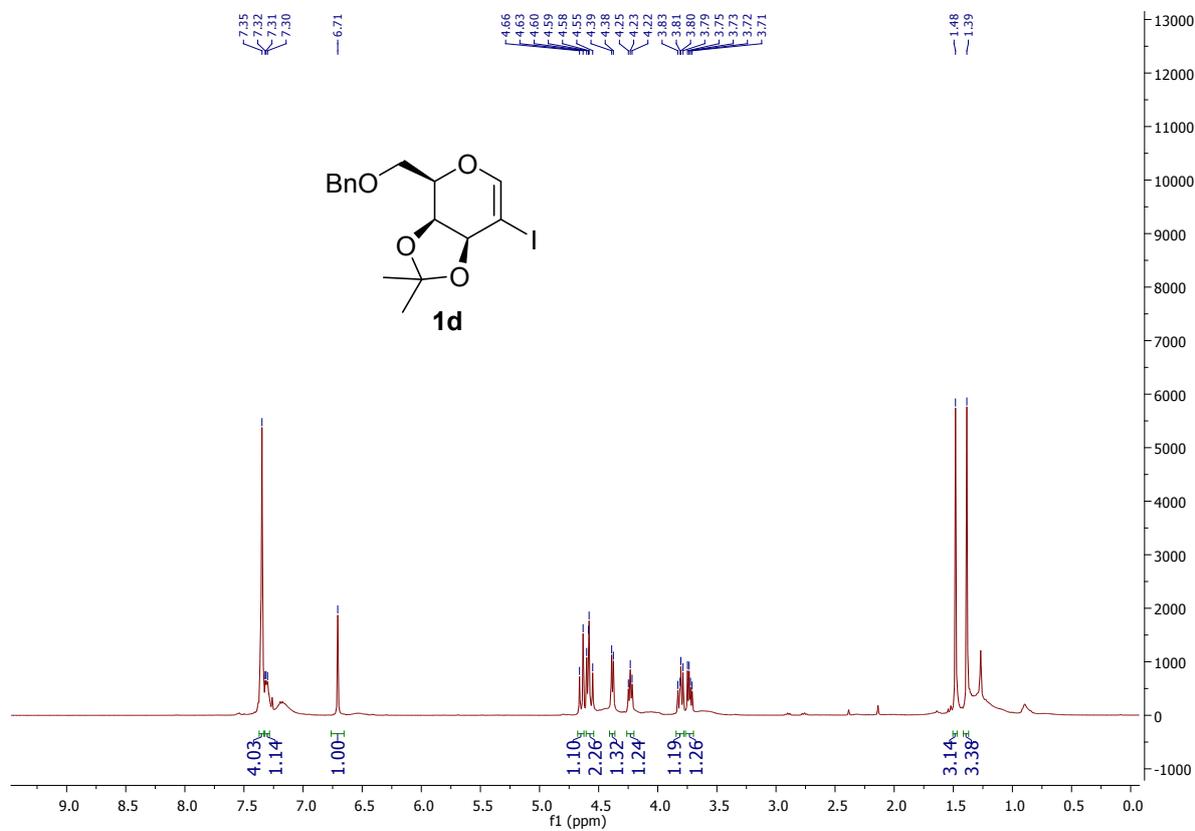
$[\alpha]_{\text{D}} +57.3$ (c 1, CHCl_3).

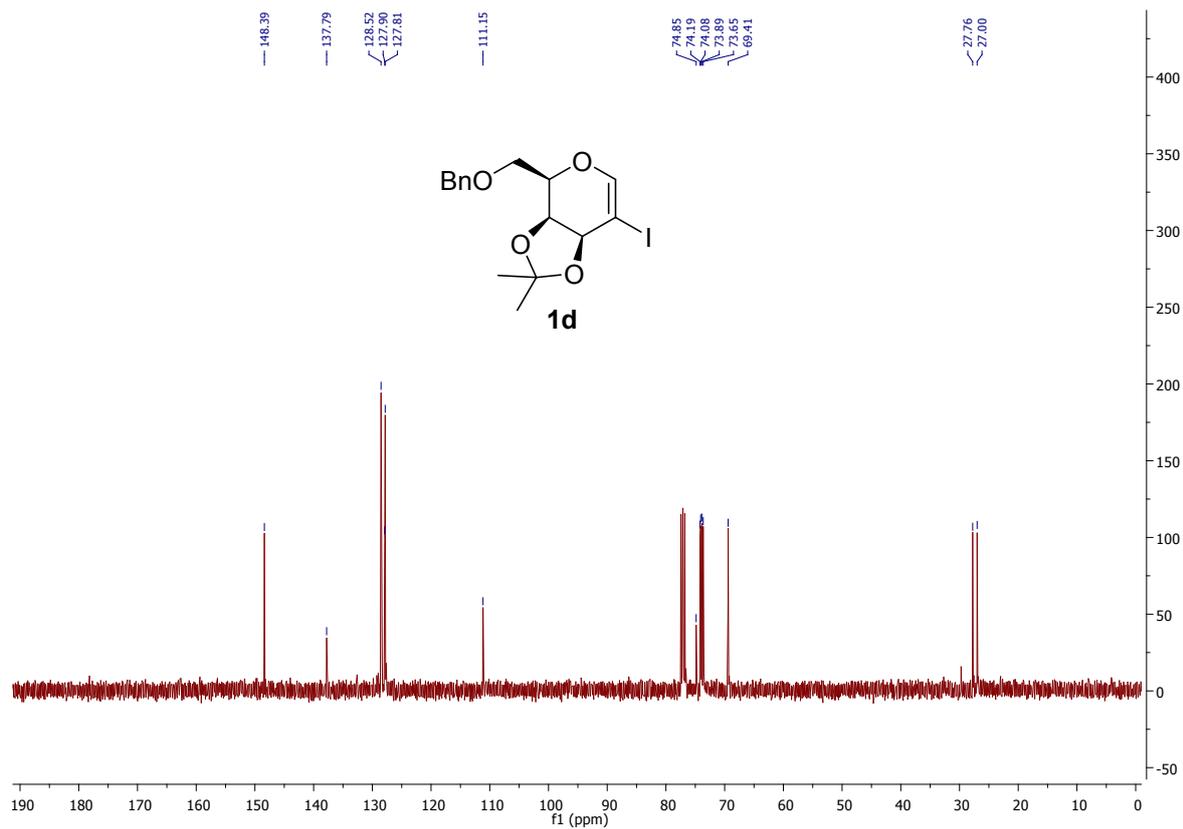
^1H NMR (400 MHz) and ^{13}C NMR (126 MHz) of compound **1c**



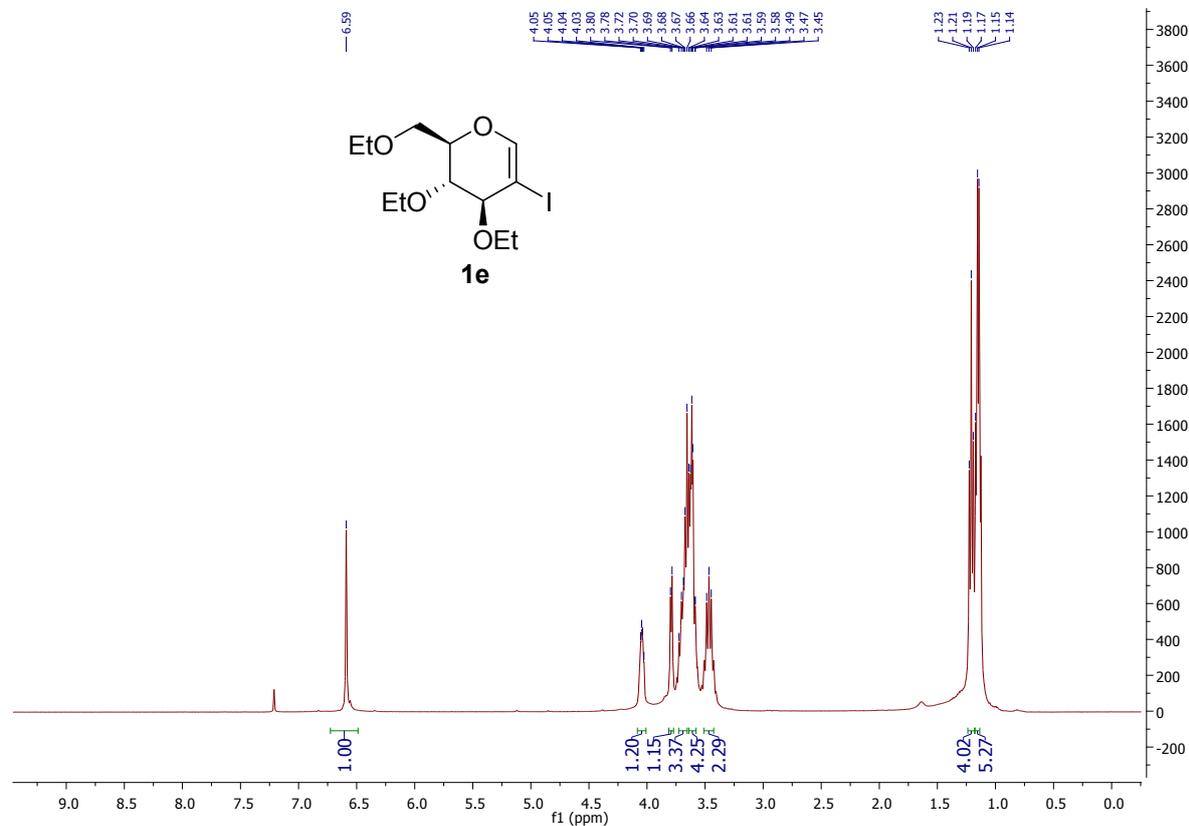


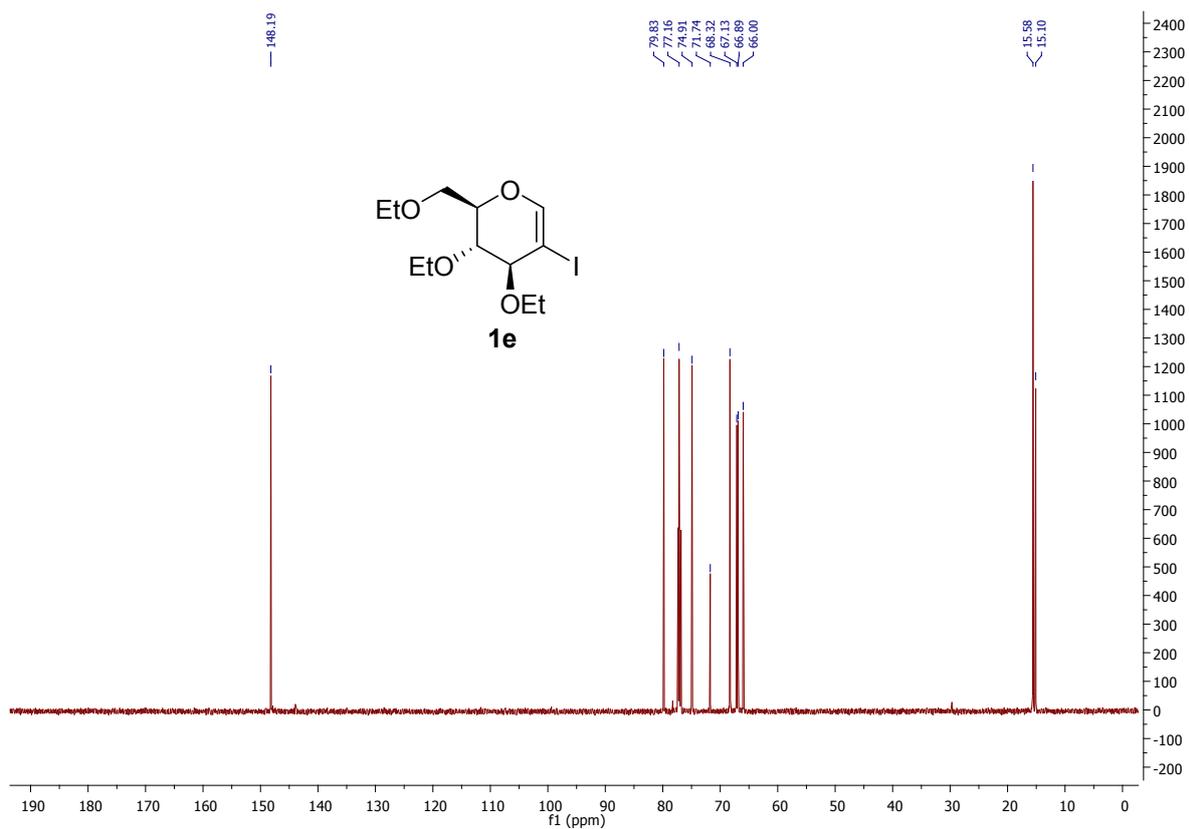
¹H NMR (400 MHz) and ¹³C NMR (126 MHz) of compound 1d



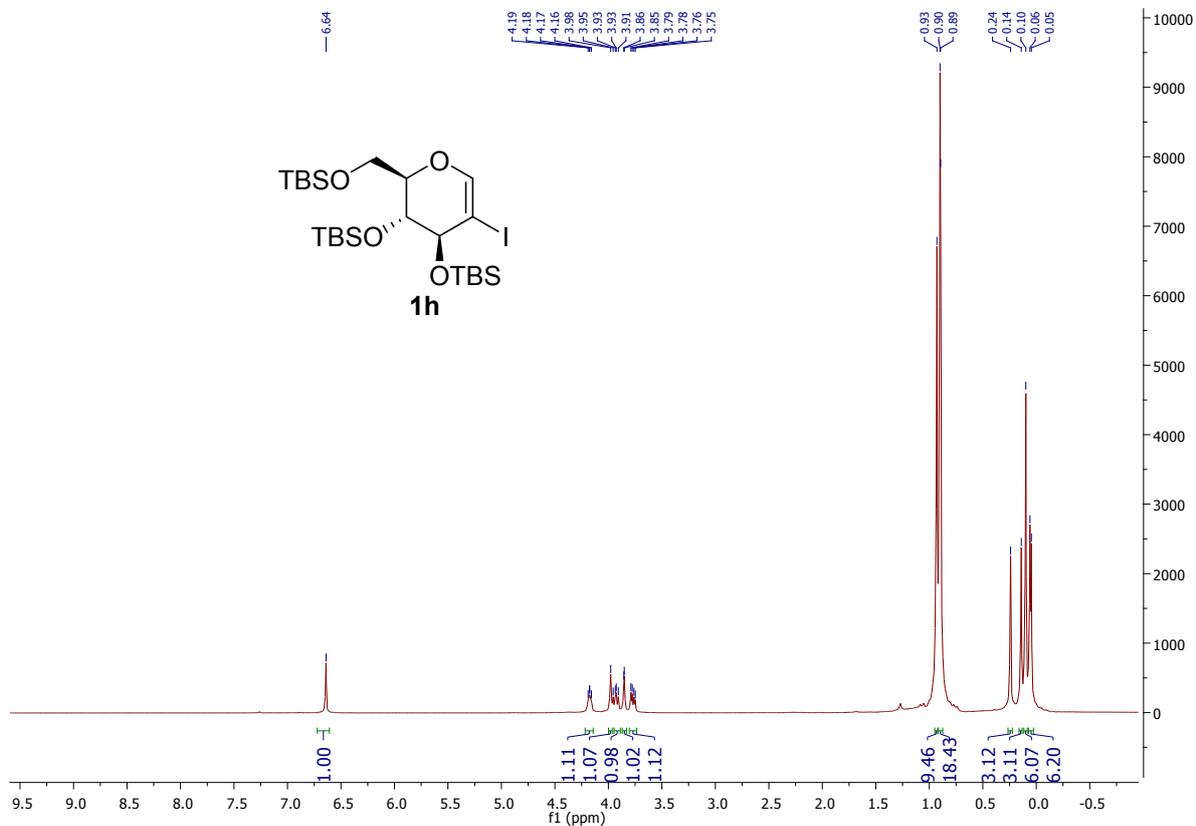


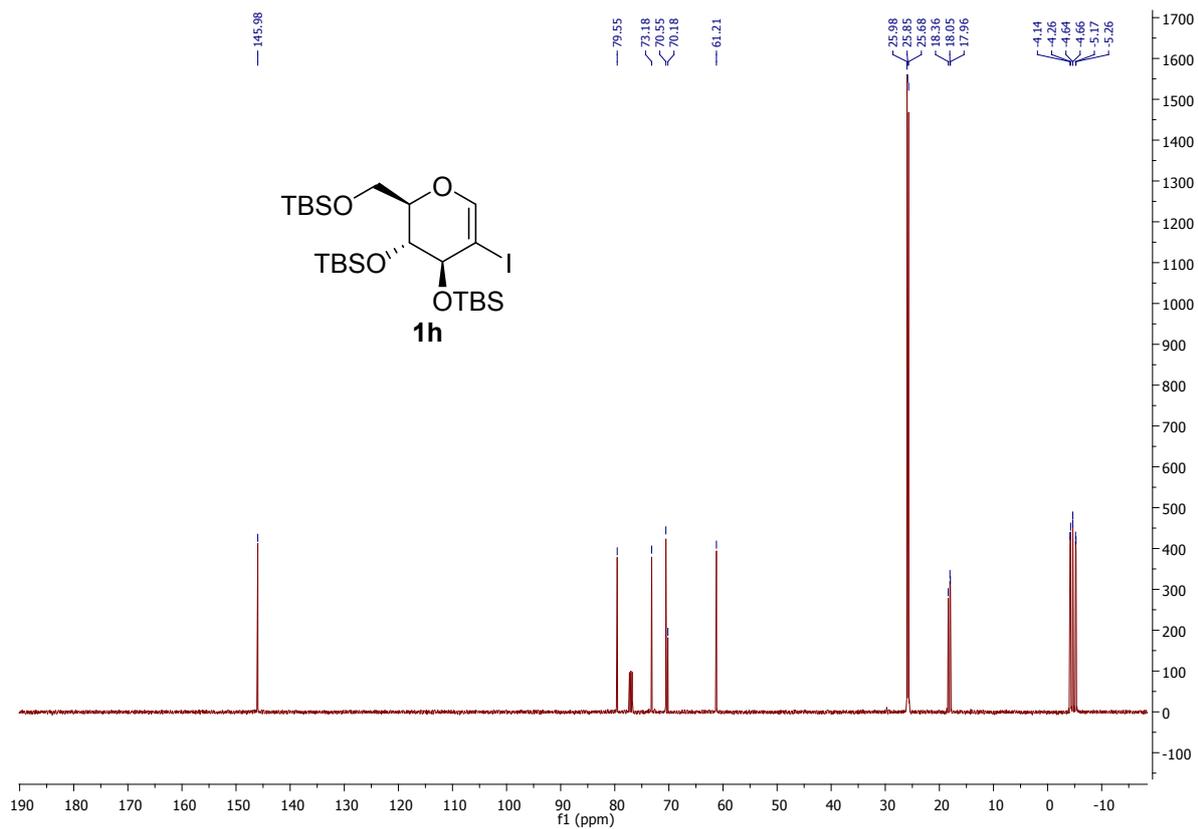
¹H NMR (400 MHz) and ¹³C NMR (126 MHz) of compound 1e



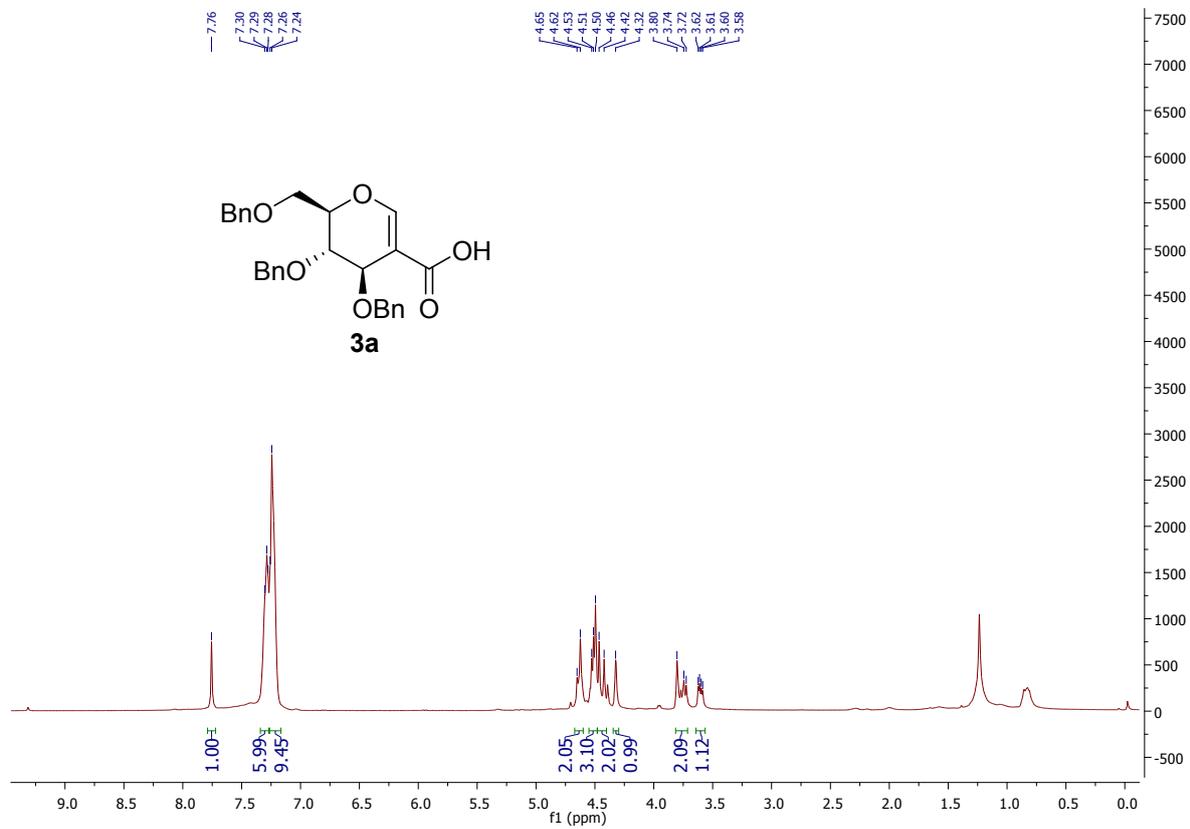


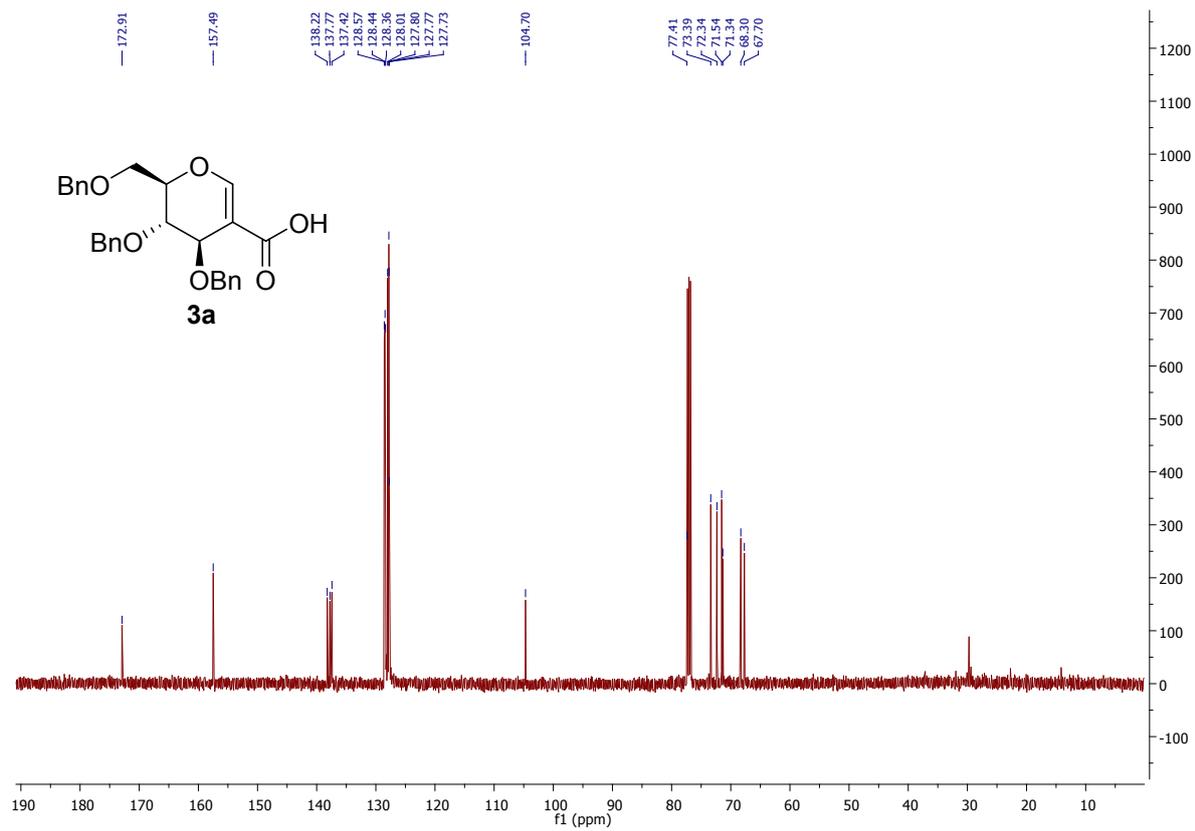
¹H NMR (400 MHz) and ¹³C NMR (126 MHz) of compound 1h



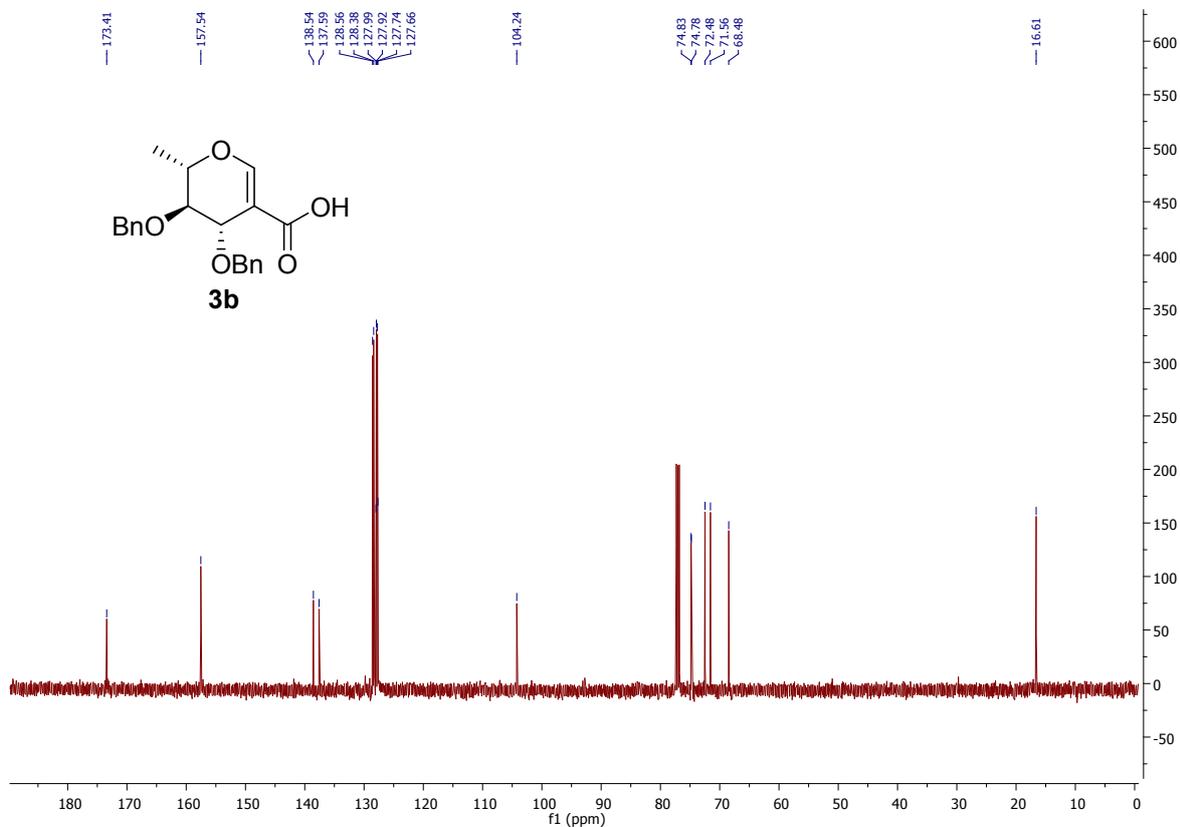
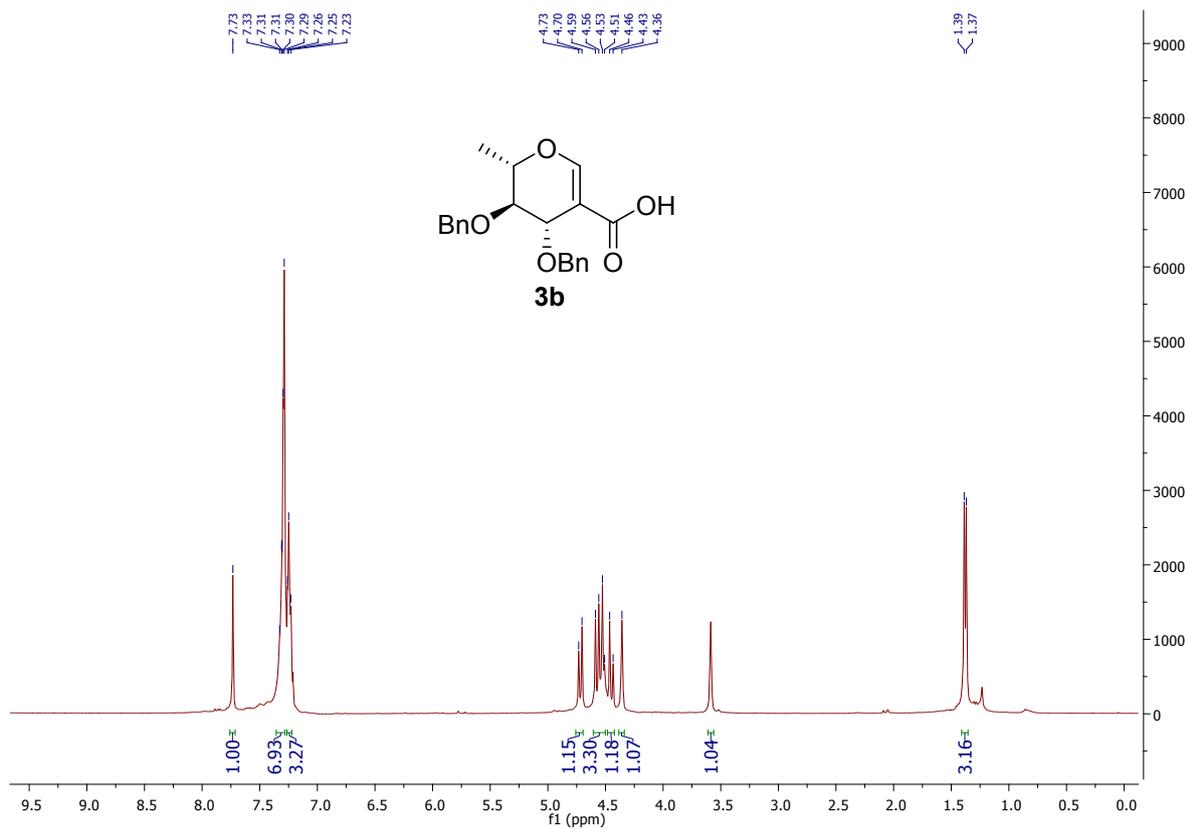


¹H NMR (400 MHz) and ¹³C NMR (101 MHz) of compound 3a

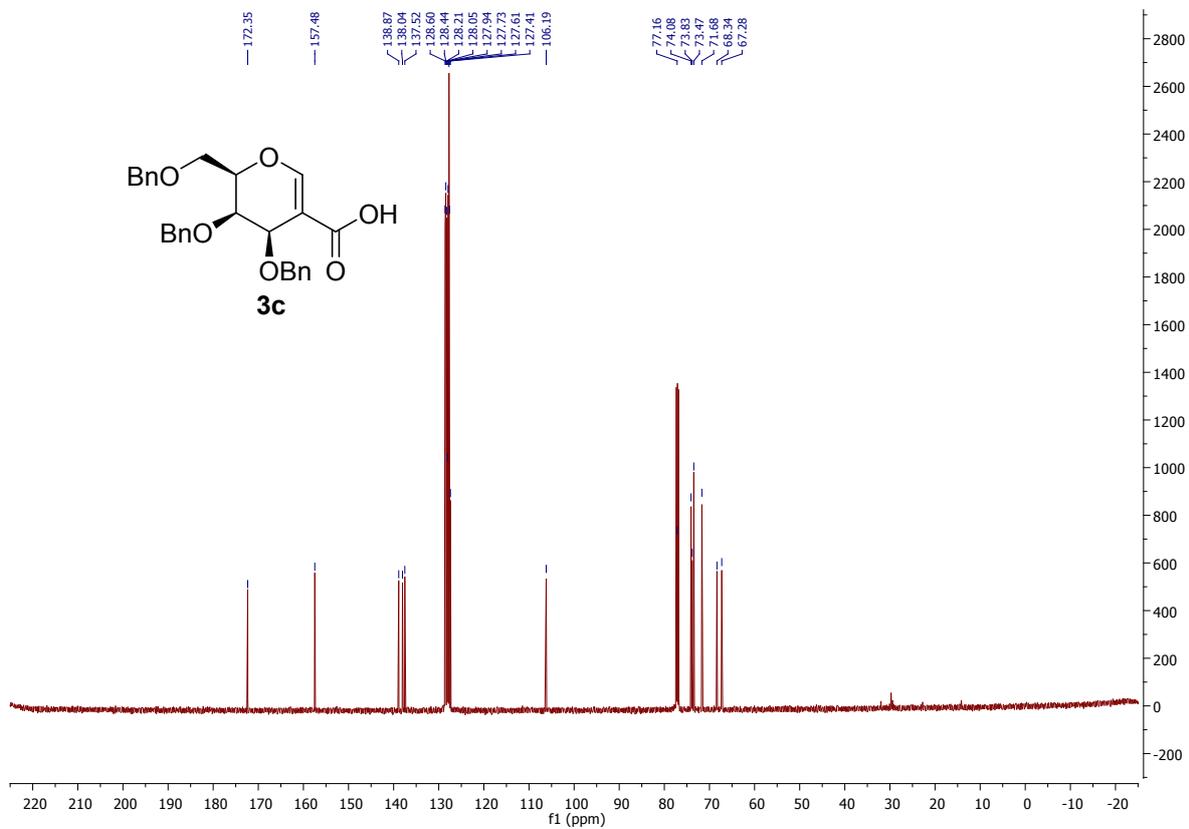
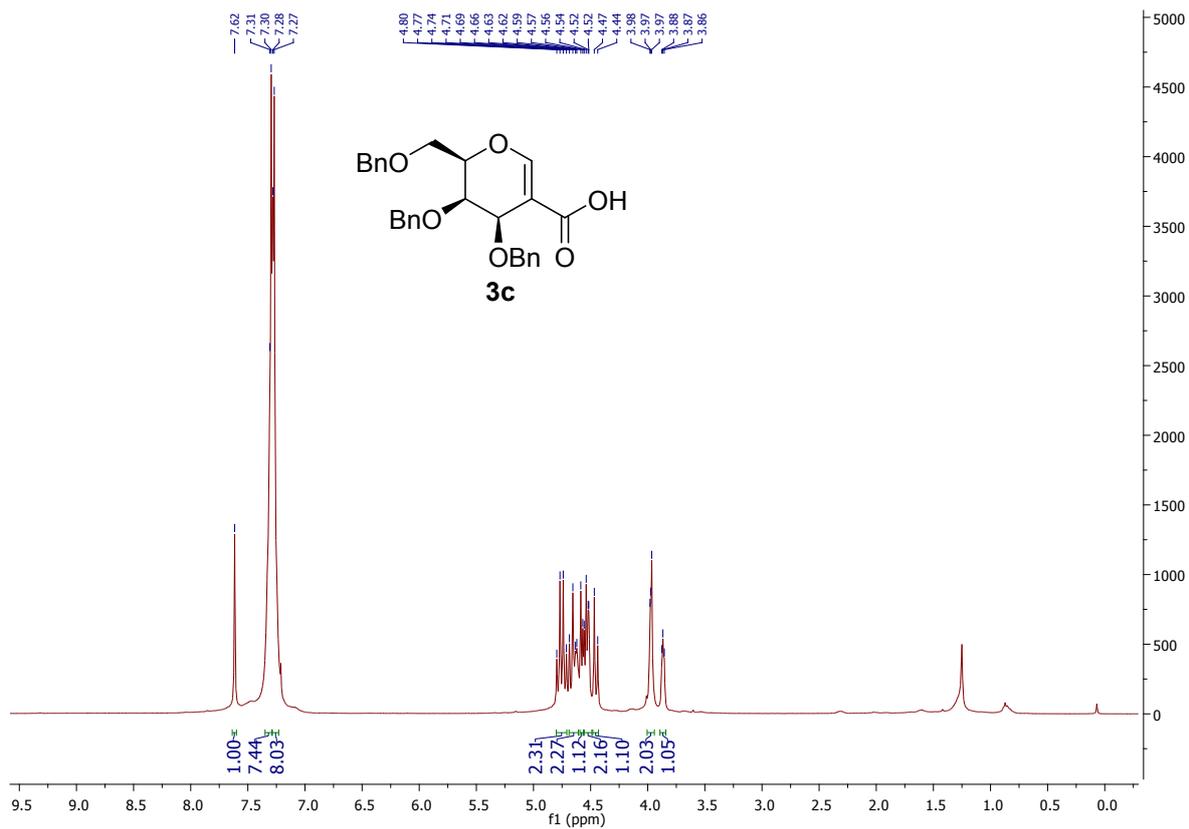




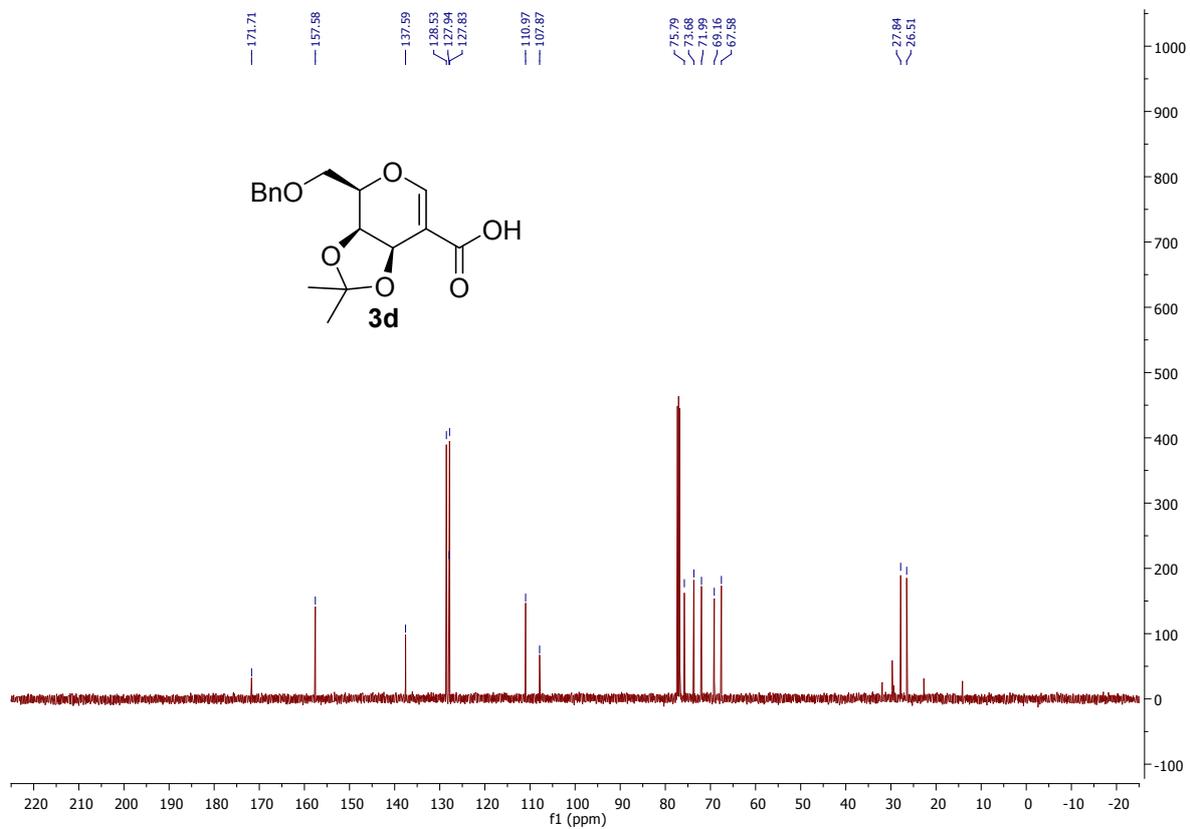
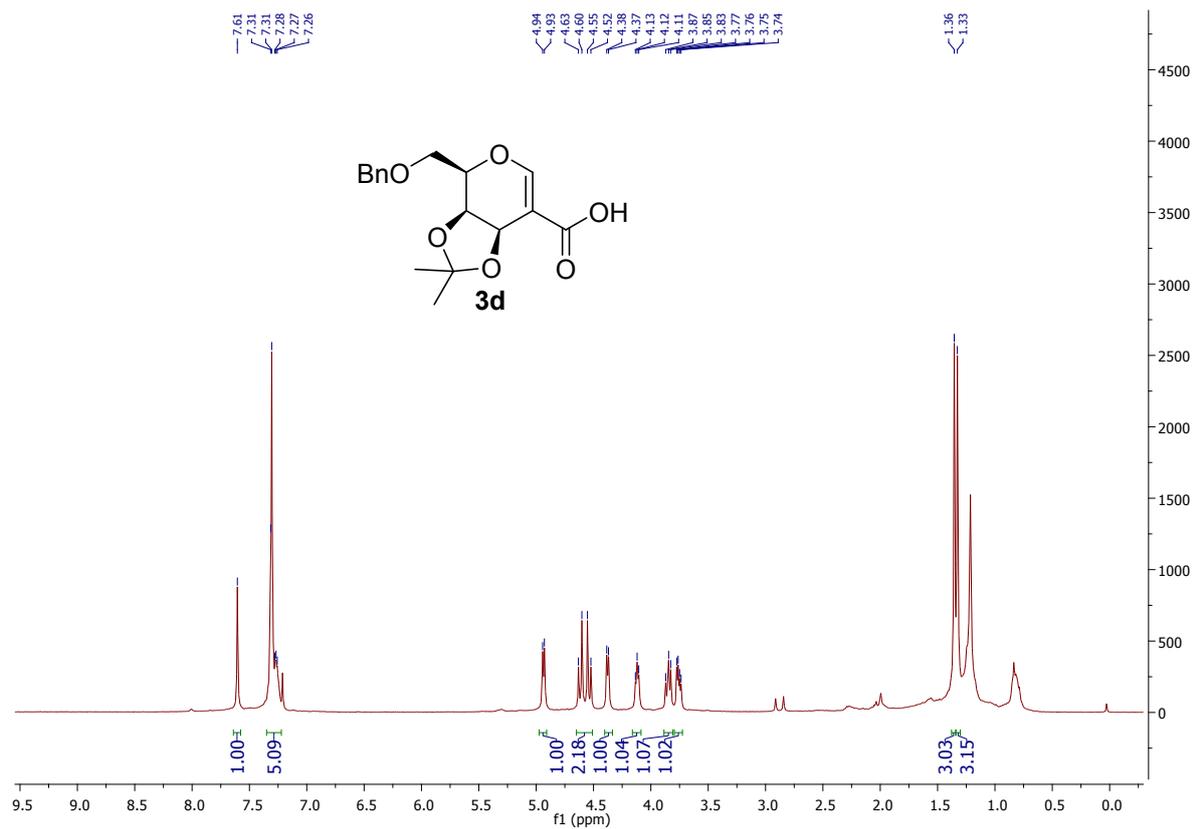
¹H NMR (400 MHz) and ¹³C NMR (126 MHz) of compound 3b



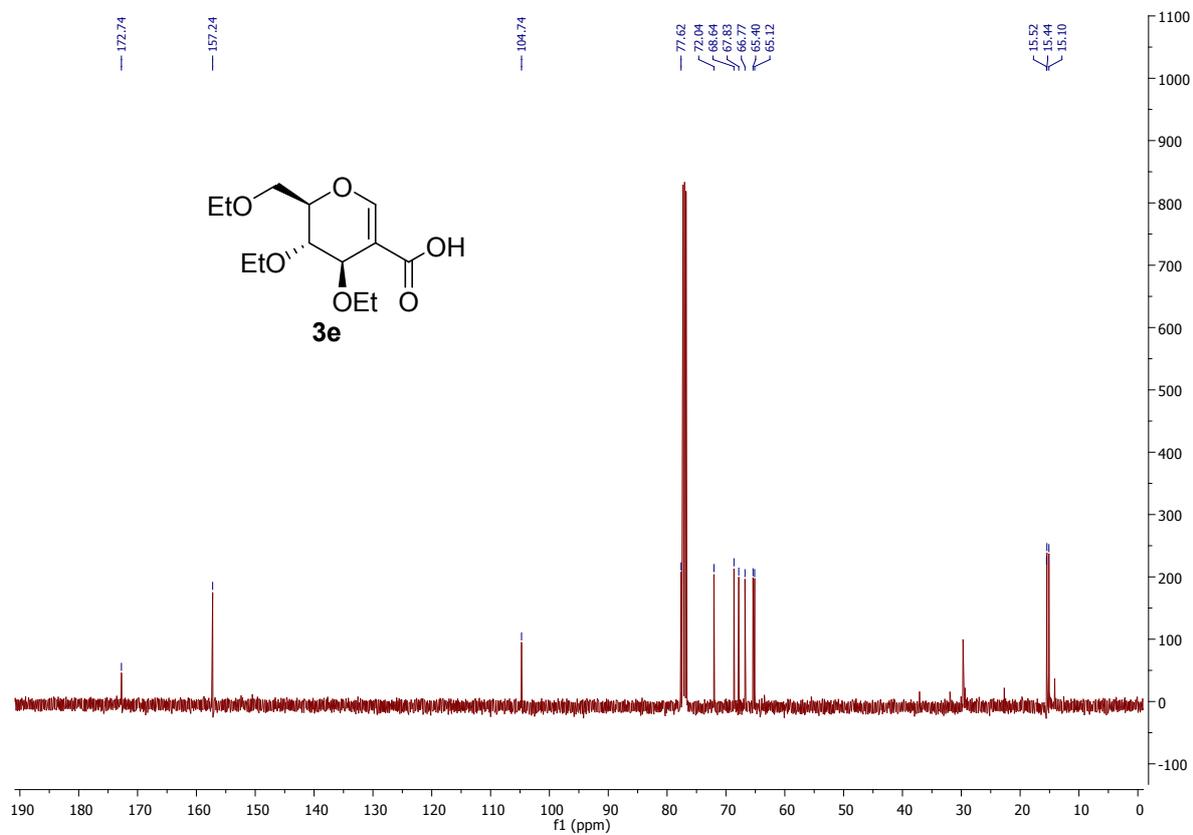
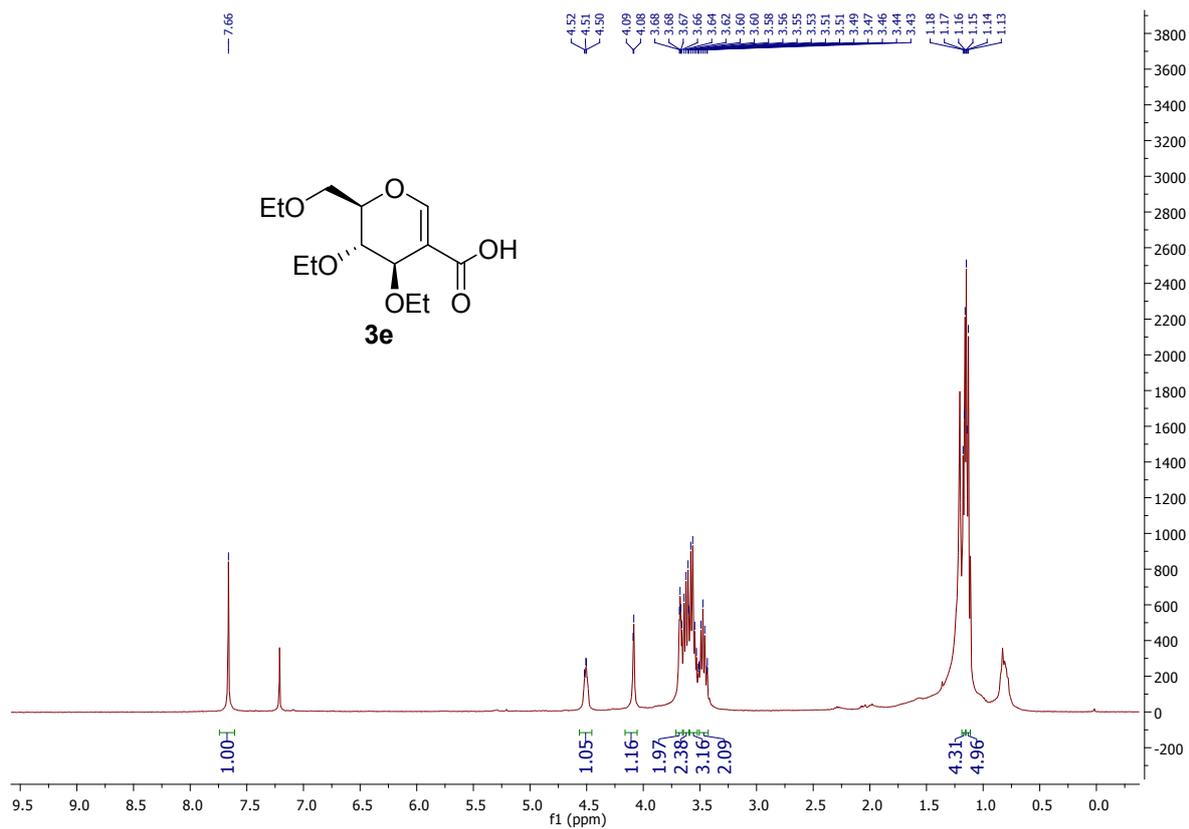
¹H NMR (400 MHz) and ¹³C NMR (126 MHz) of compound 3c



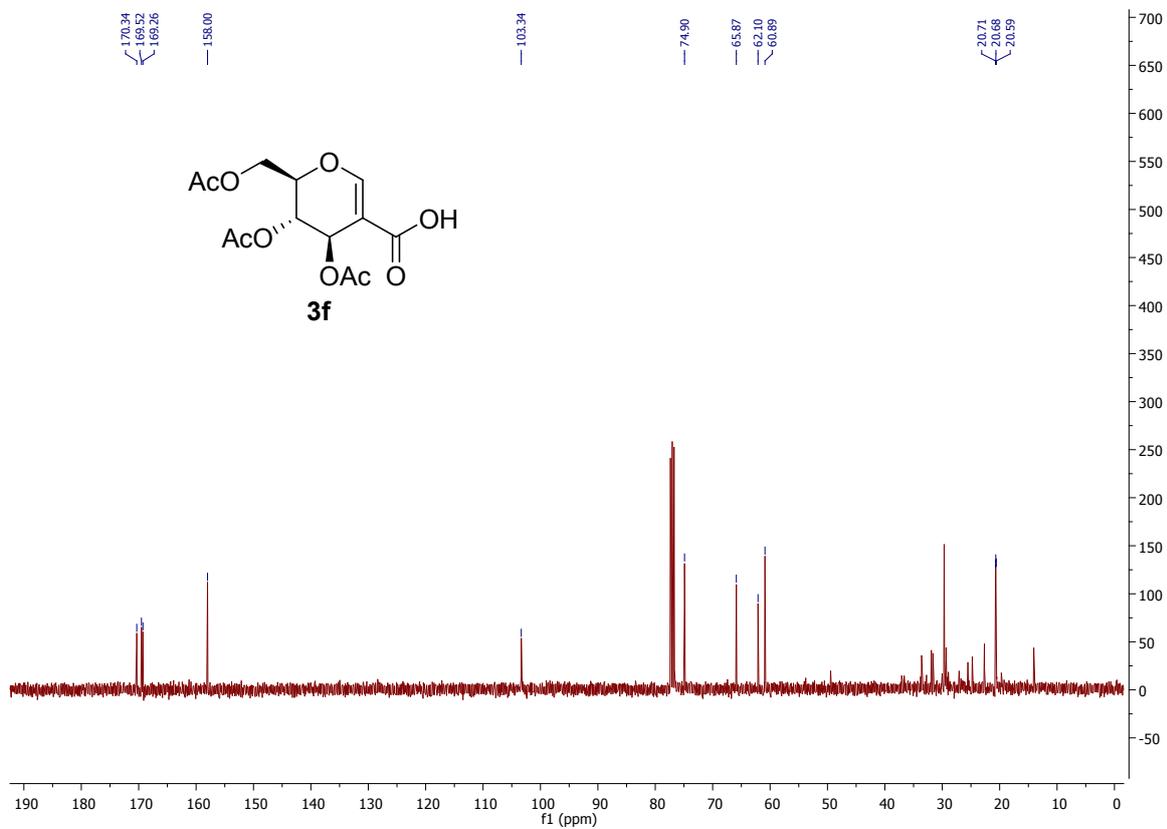
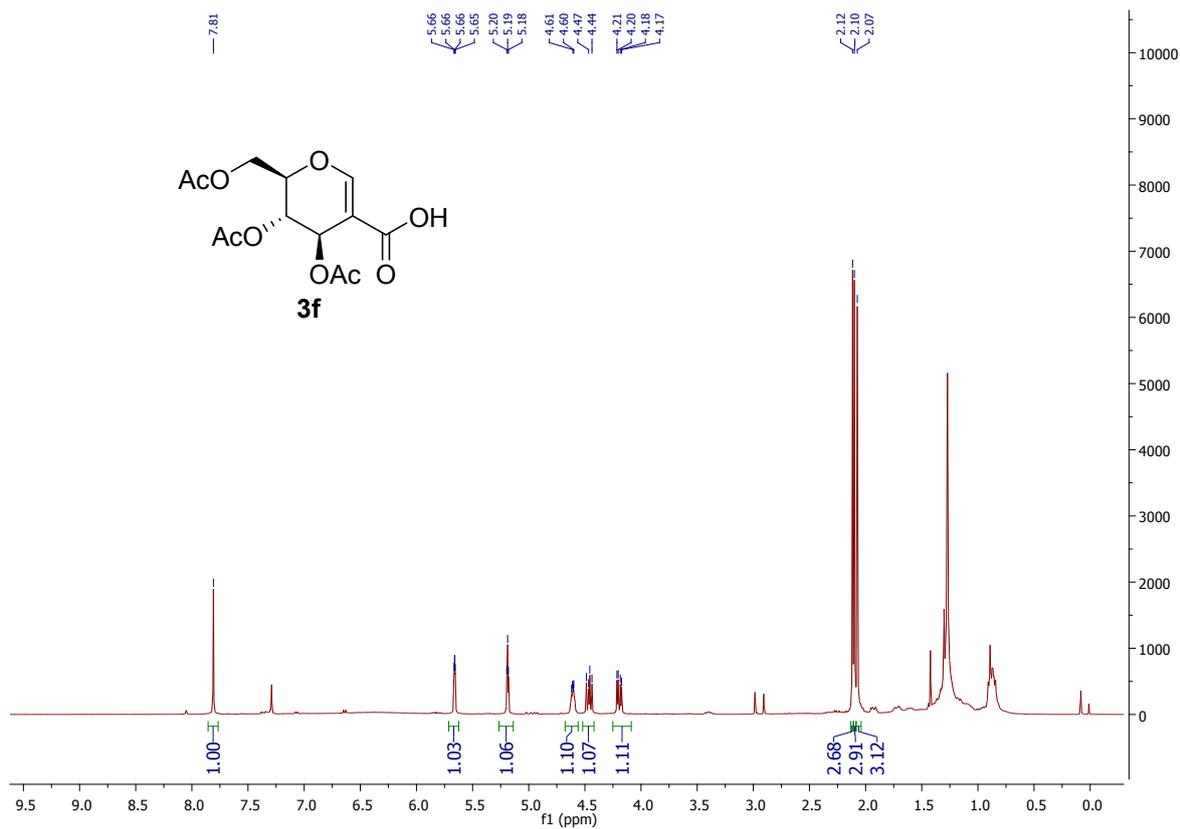
¹H NMR (400 MHz) and ¹³C NMR (126 MHz) of compound 3d



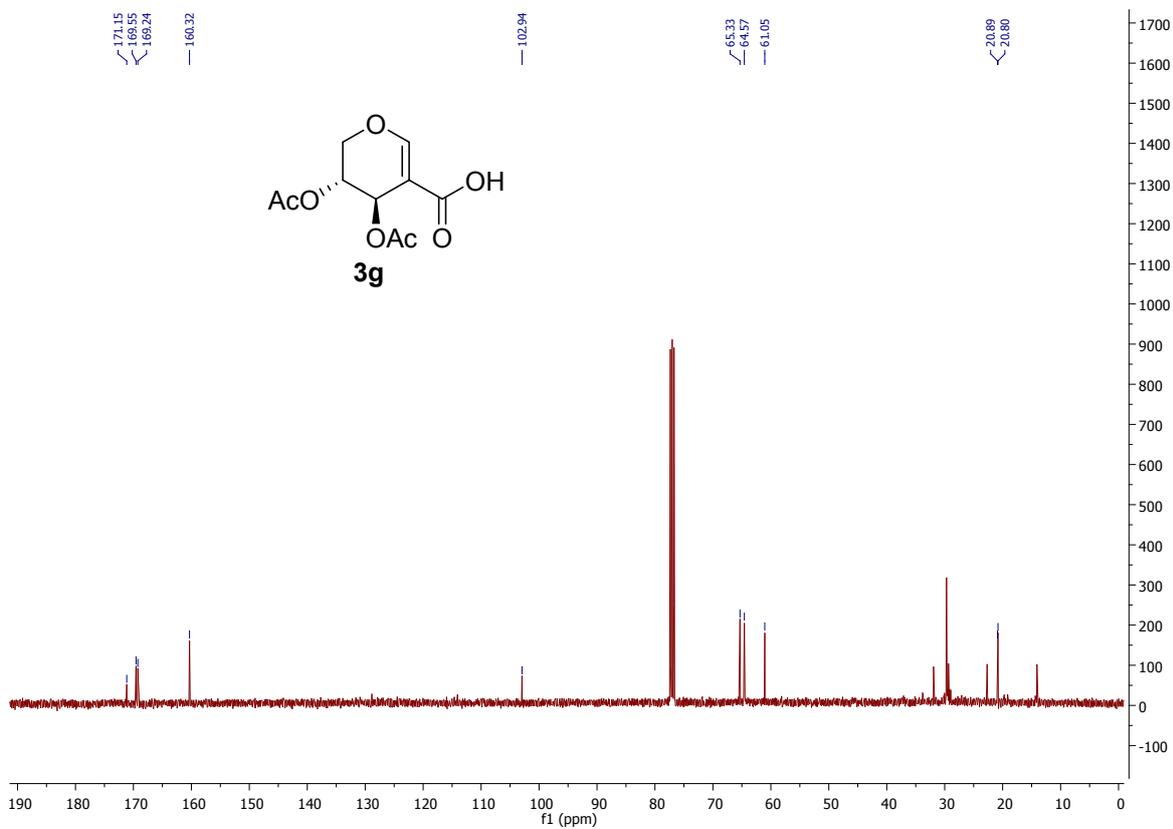
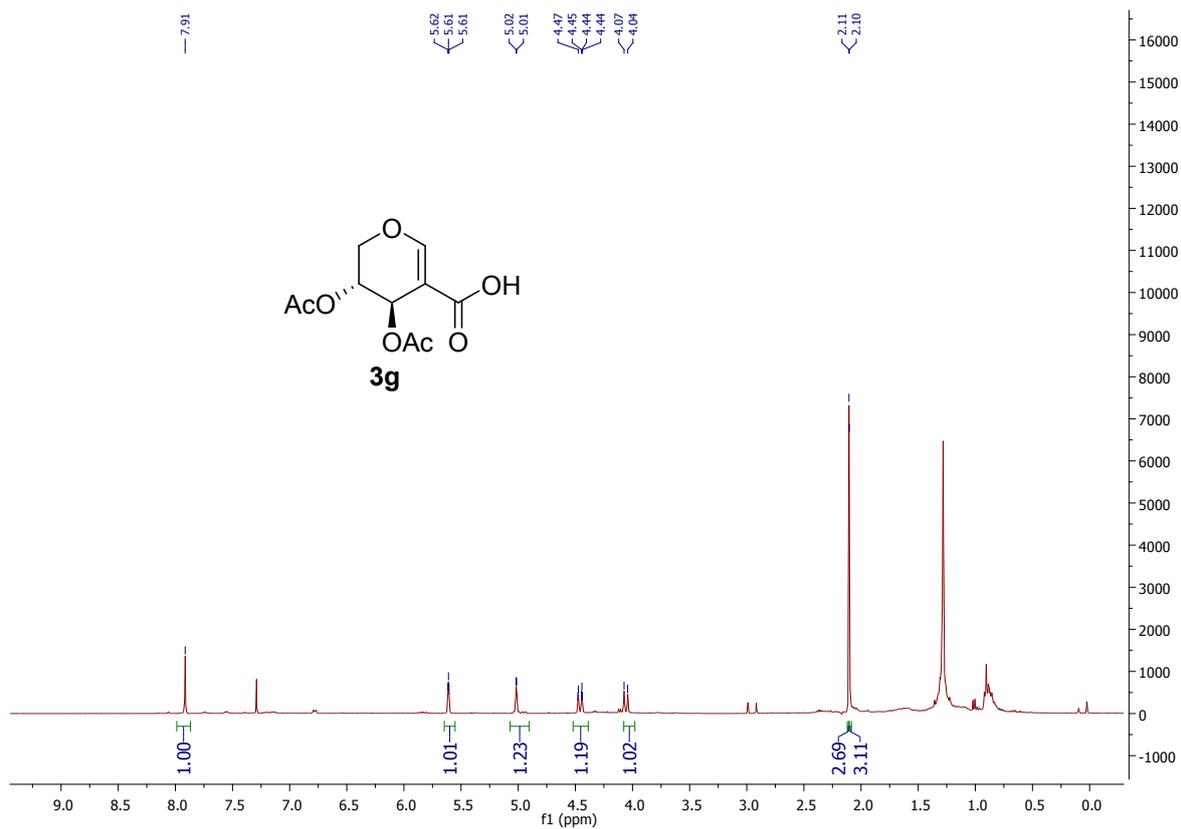
¹H NMR (400 MHz) and ¹³C NMR (126 MHz) of compound 3e



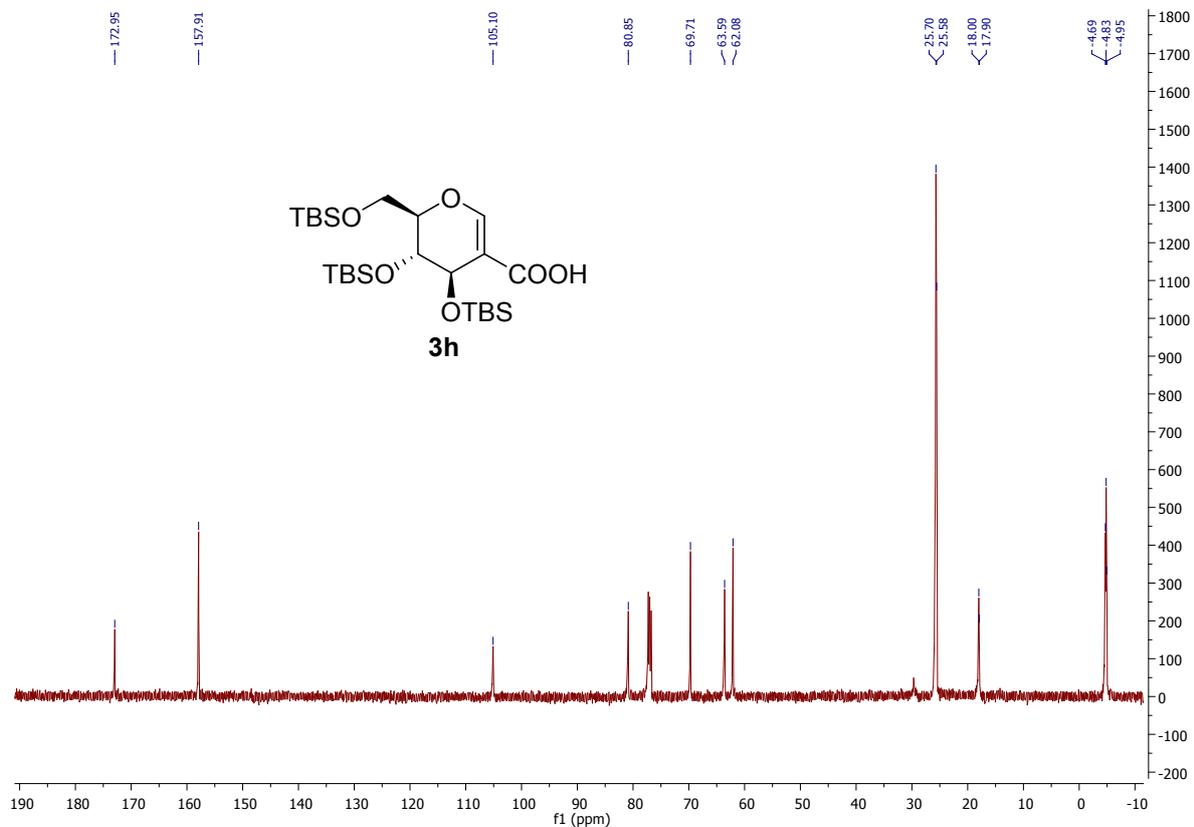
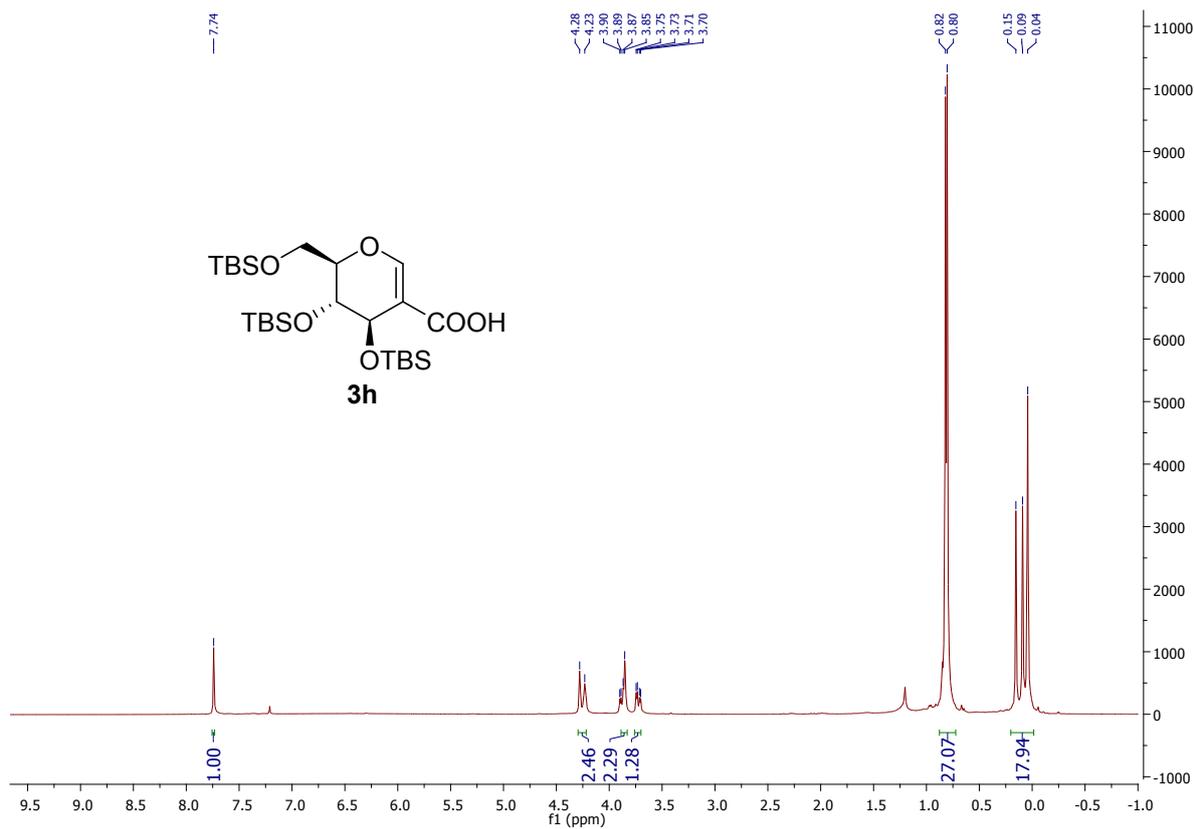
¹H NMR (400 MHz) and ¹³C NMR (101 MHz) of compound **3f**



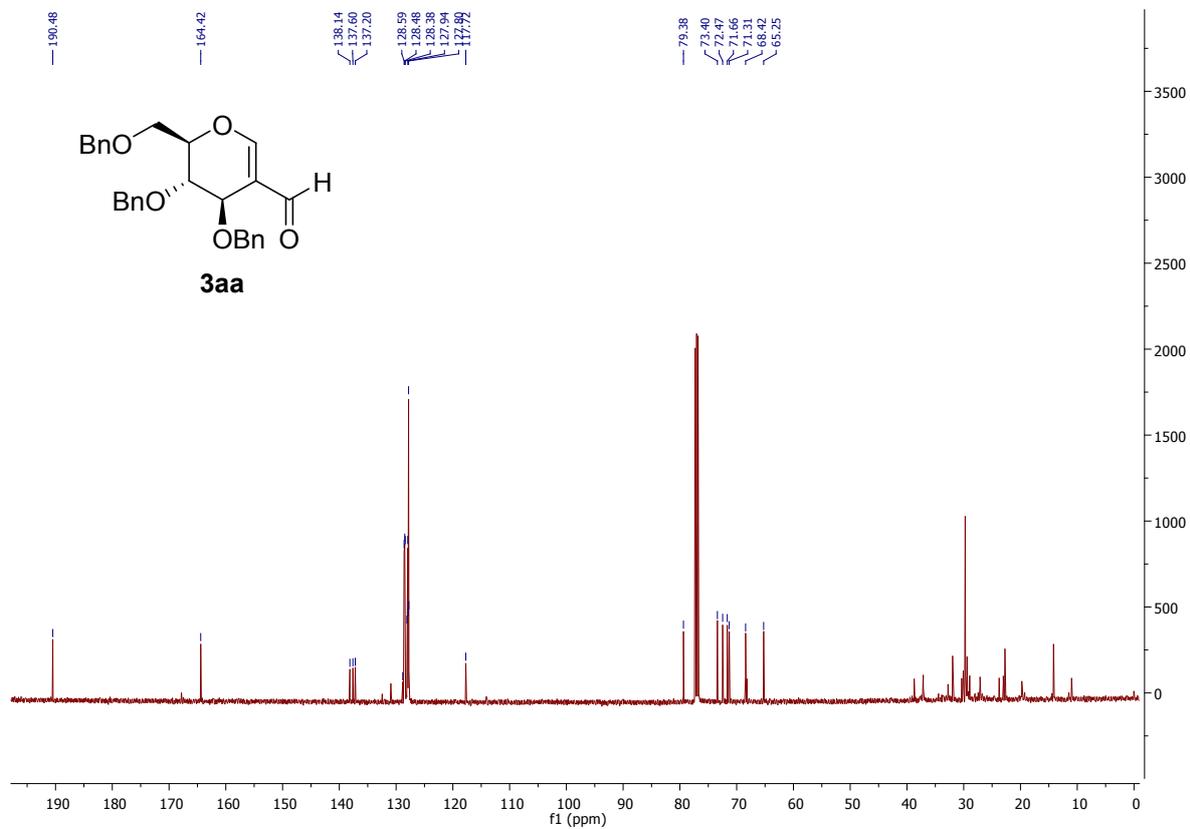
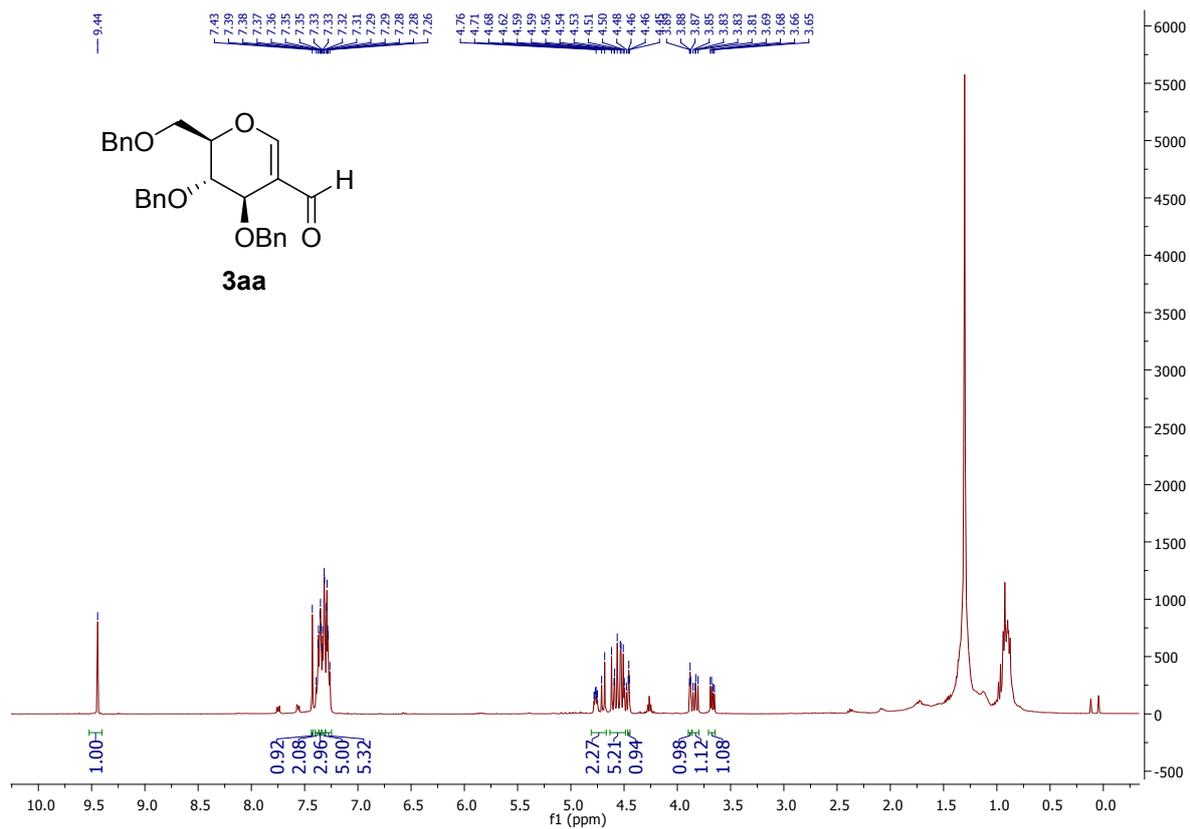
¹H NMR (400 MHz) and ¹³C NMR (101 MHz) of compound 3g



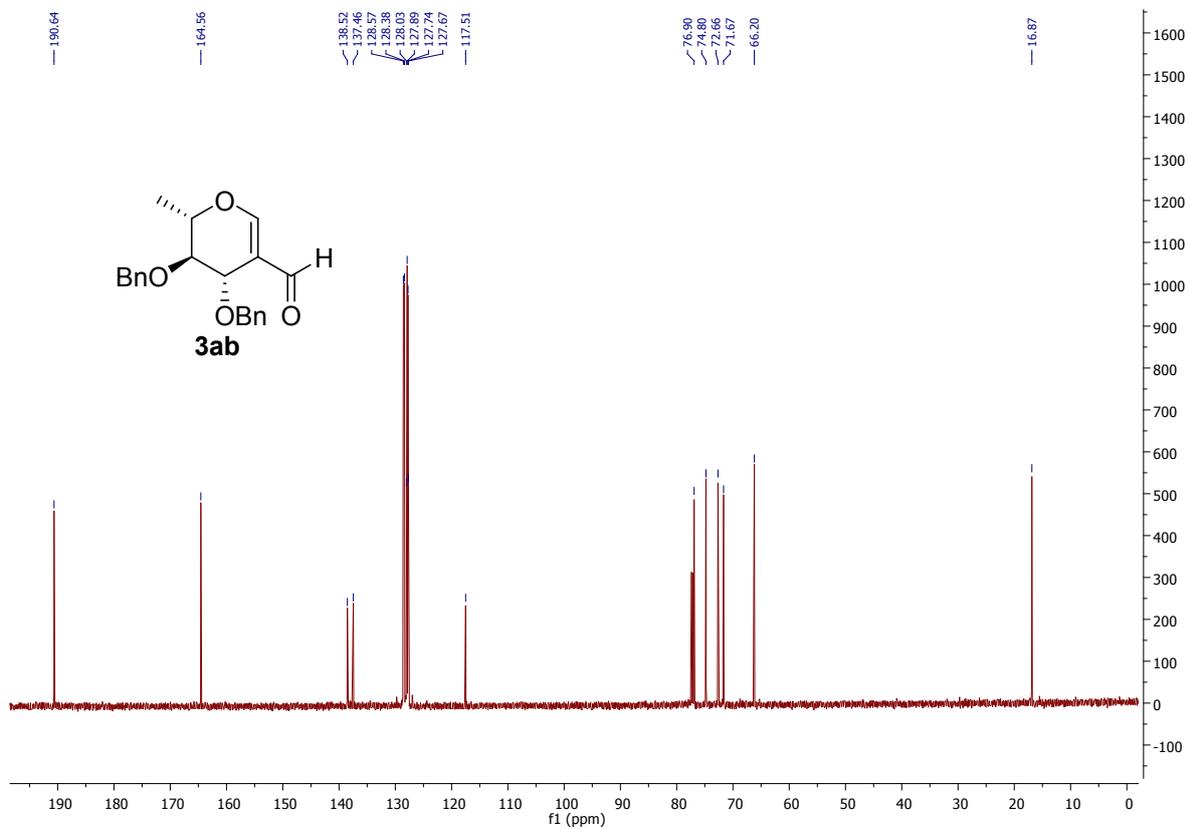
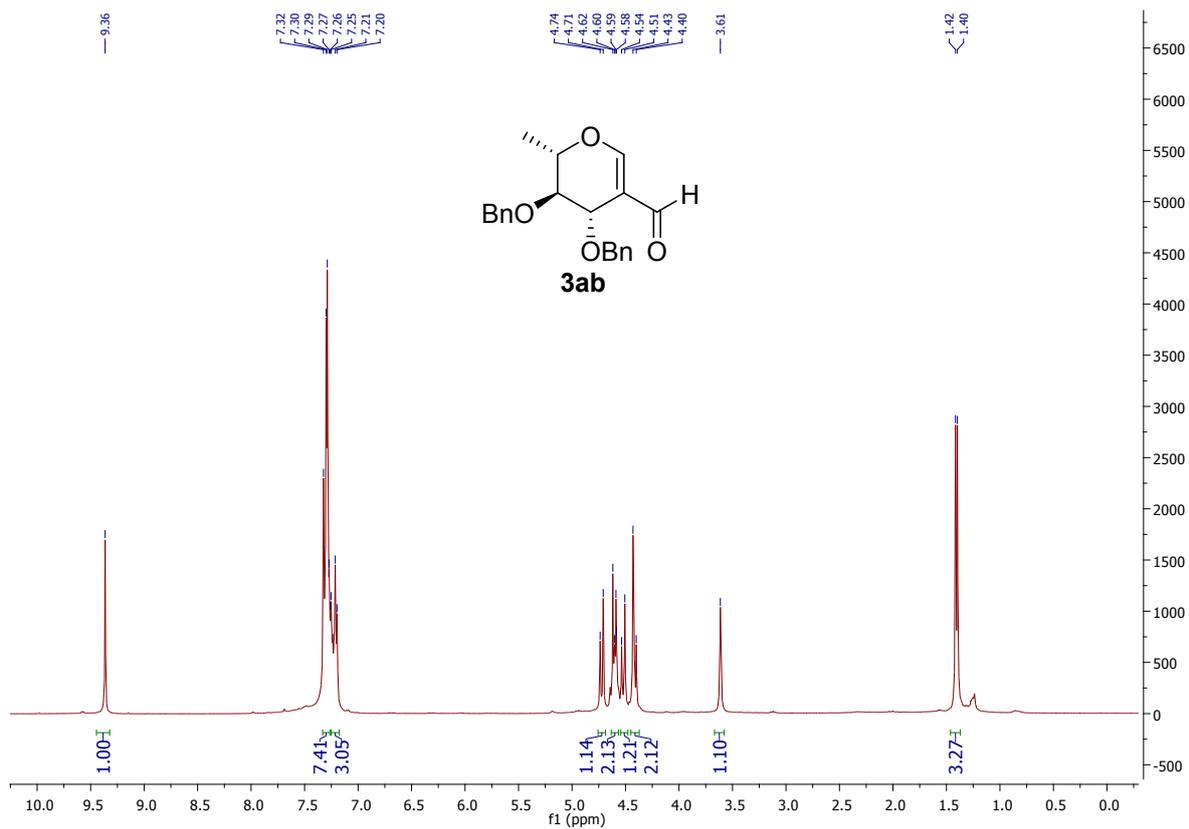
¹H NMR (400 MHz) and ¹³C NMR (101 MHz) of compound 3h



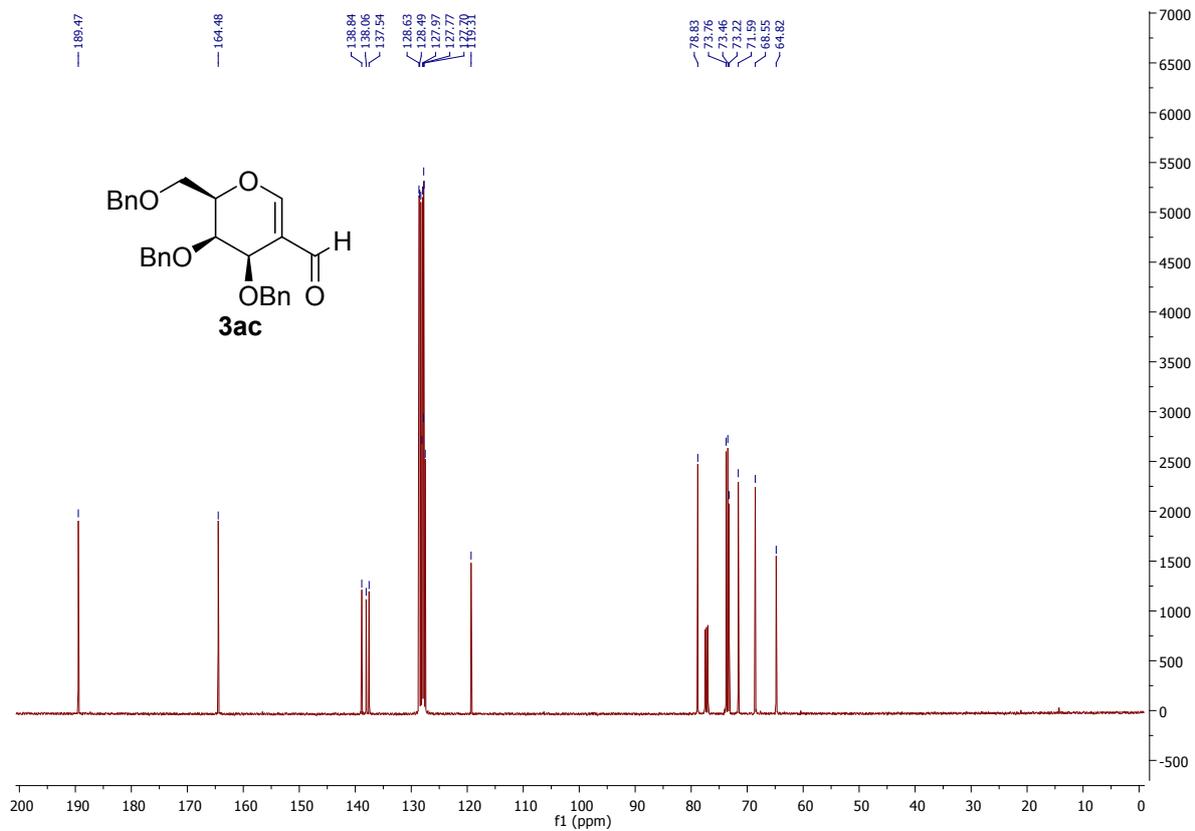
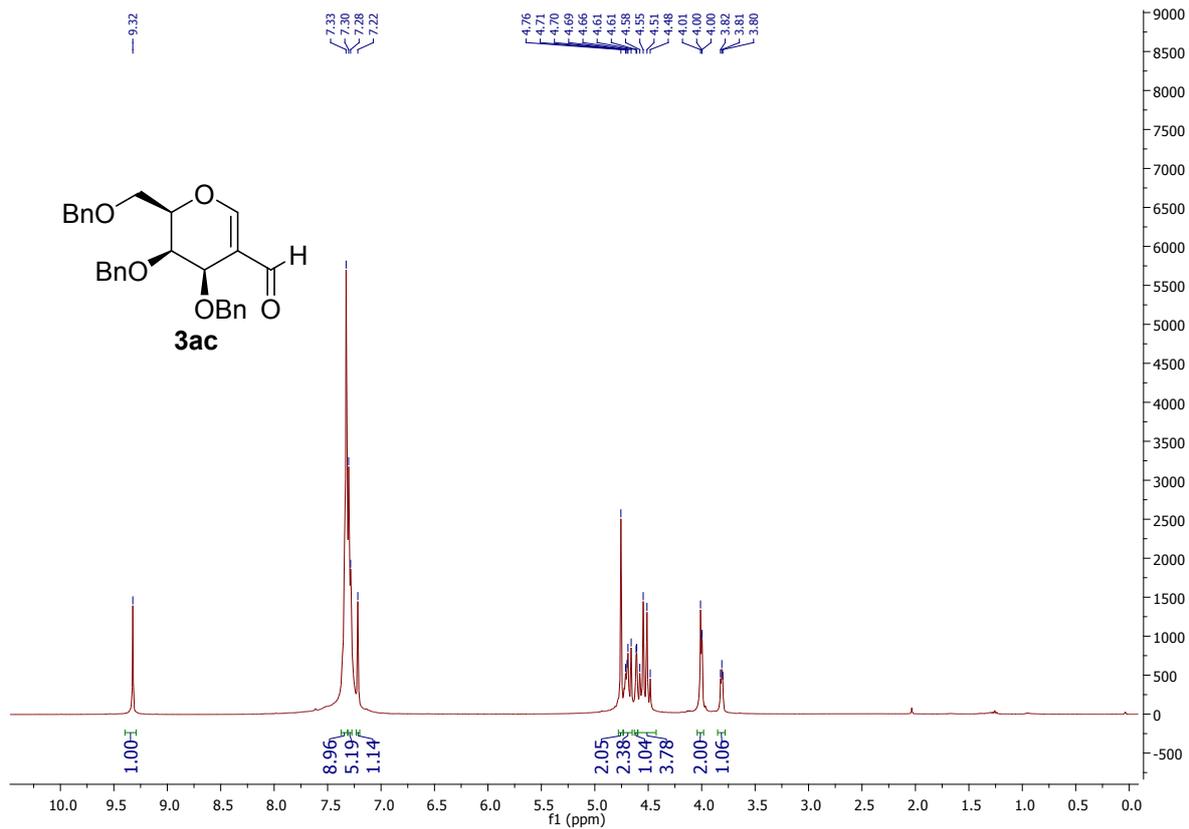
¹H NMR (400 MHz) and ¹³C NMR (126 MHz) of compound 3aa



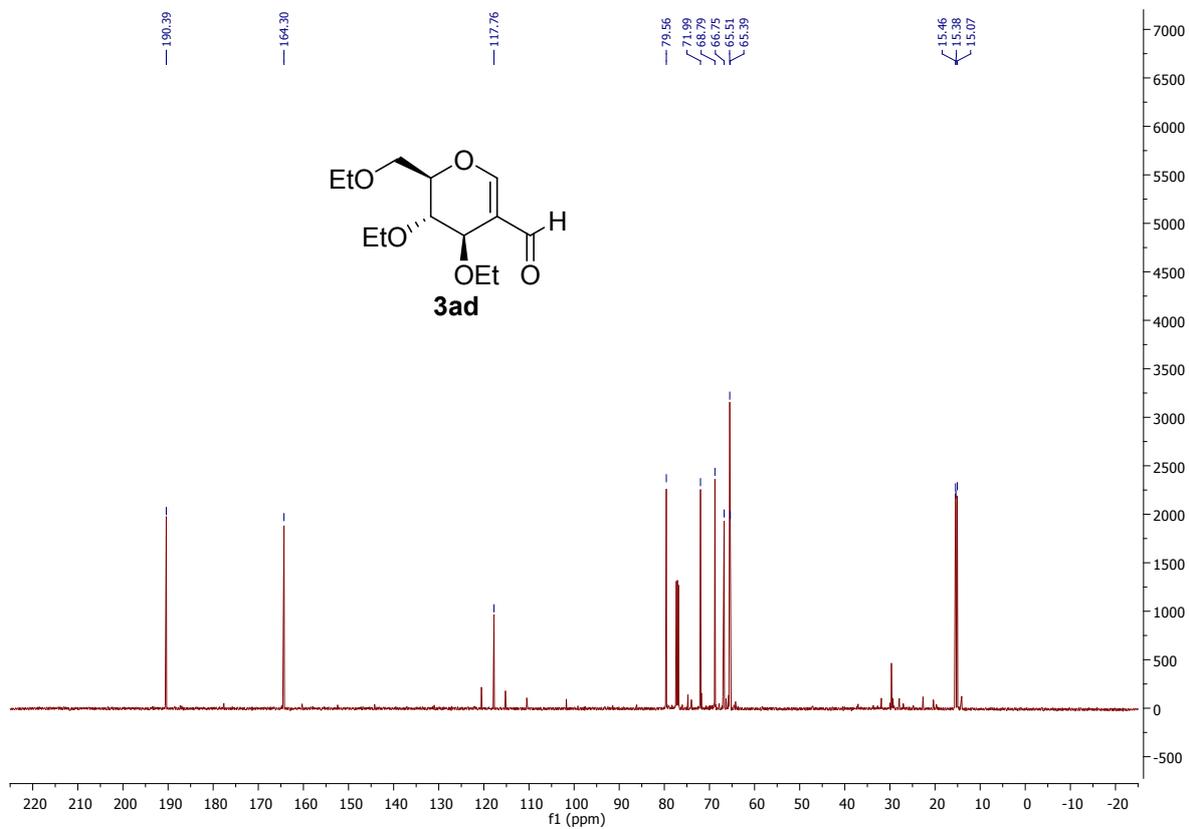
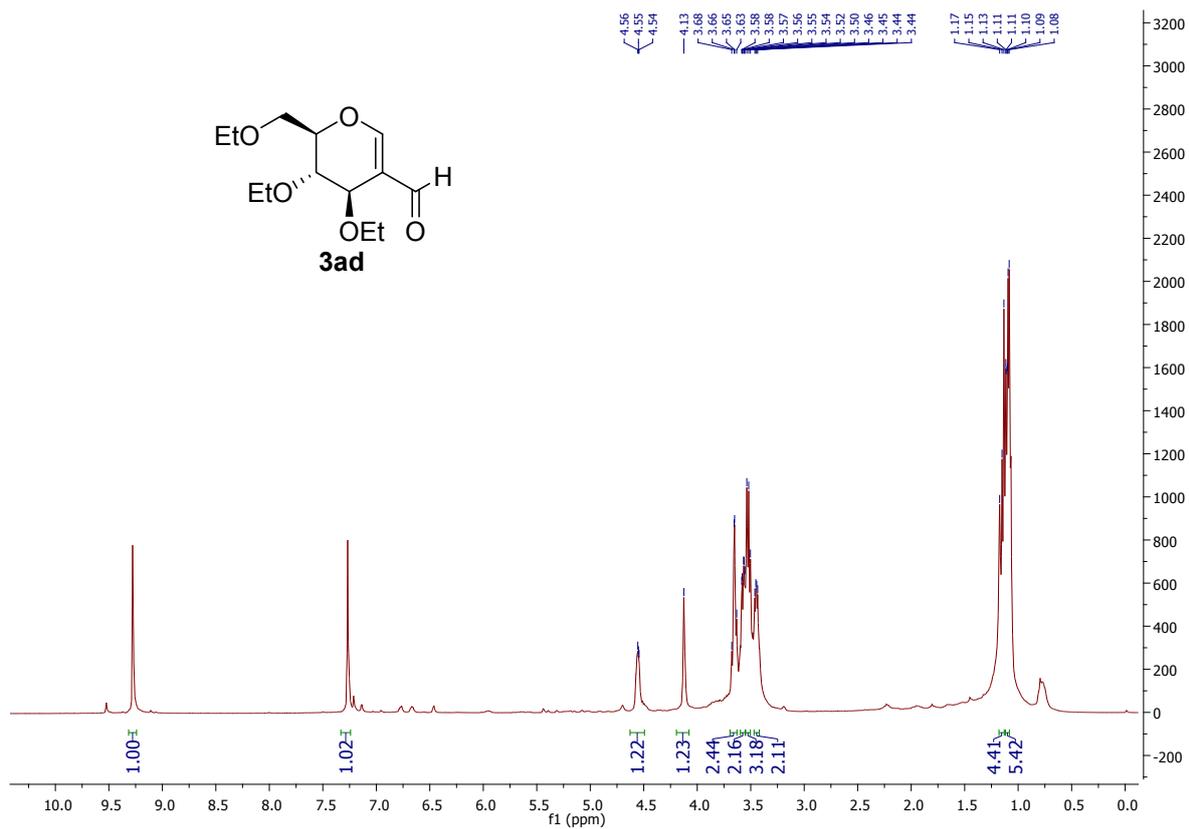
¹H NMR (400 MHz) and ¹³C NMR (126 MHz) of compound 3ab



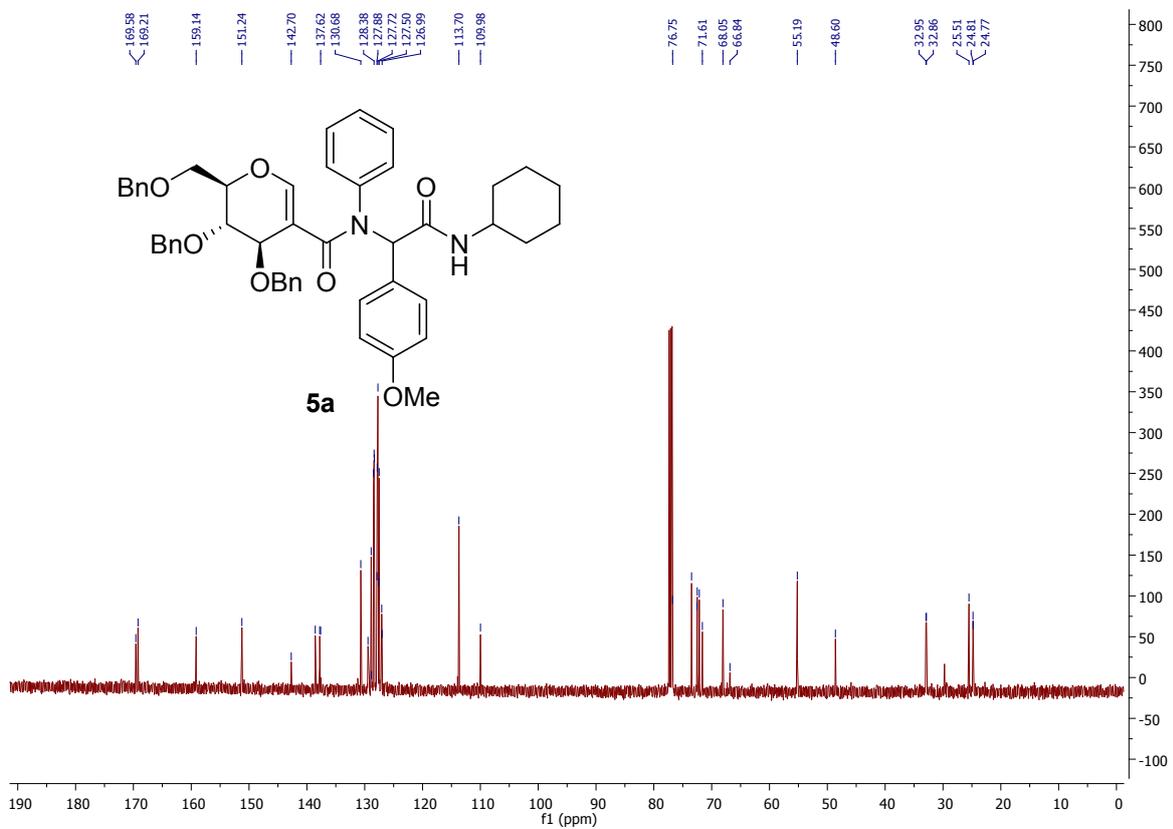
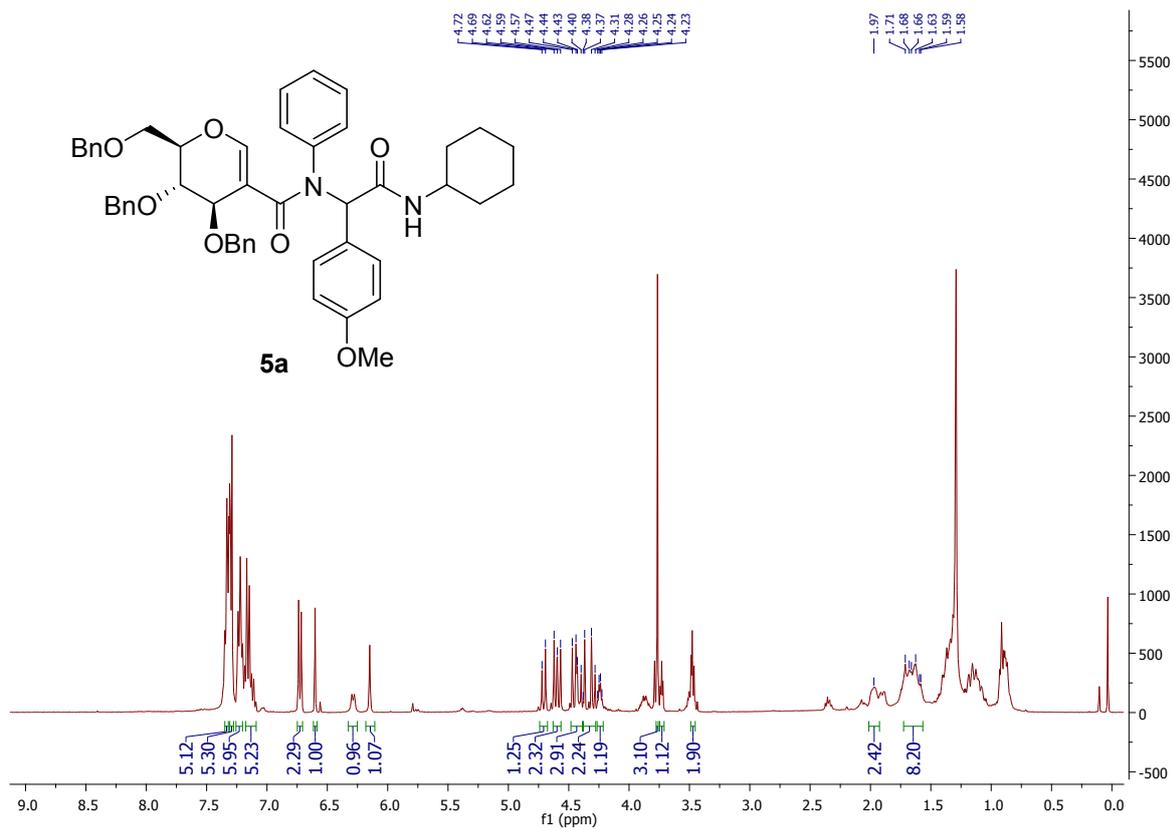
^1H NMR (400 MHz) and ^{13}C NMR (126 MHz) of compound **3ac**



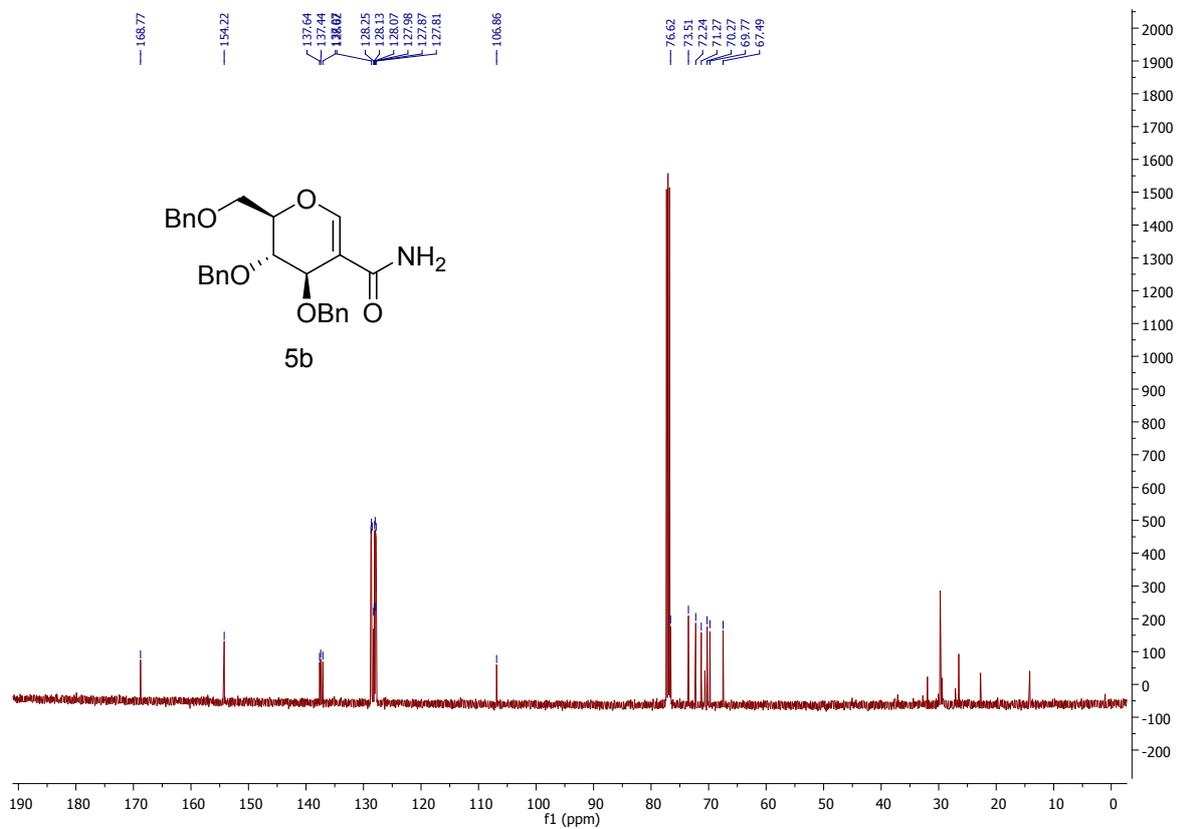
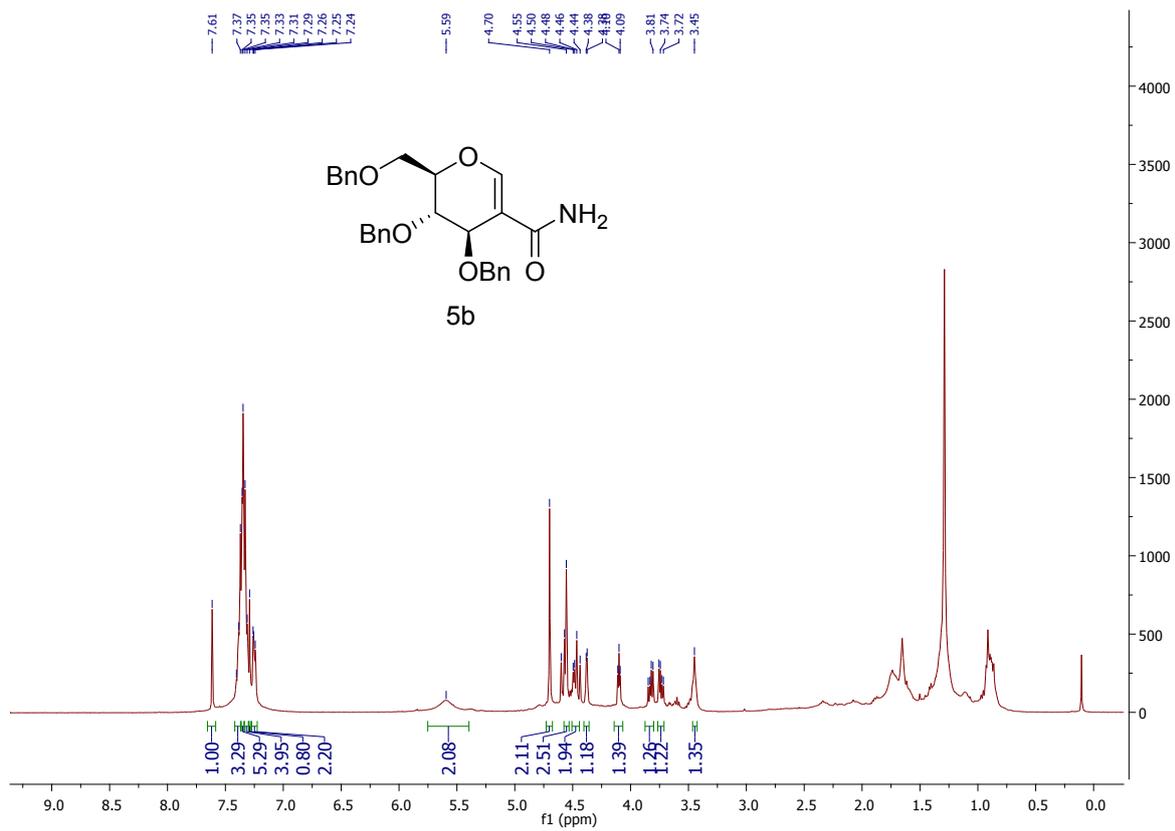
¹H NMR (400 MHz) and ¹³C NMR (126 MHz) of compound 3ad



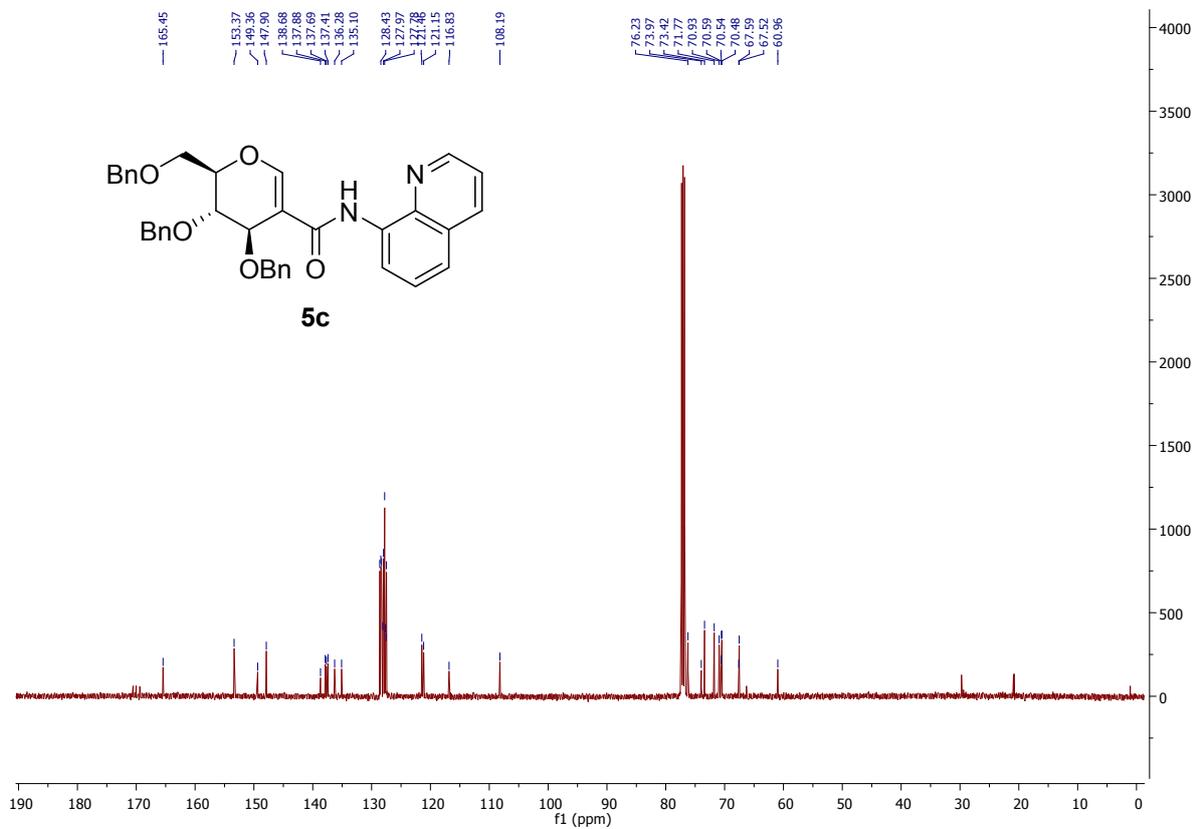
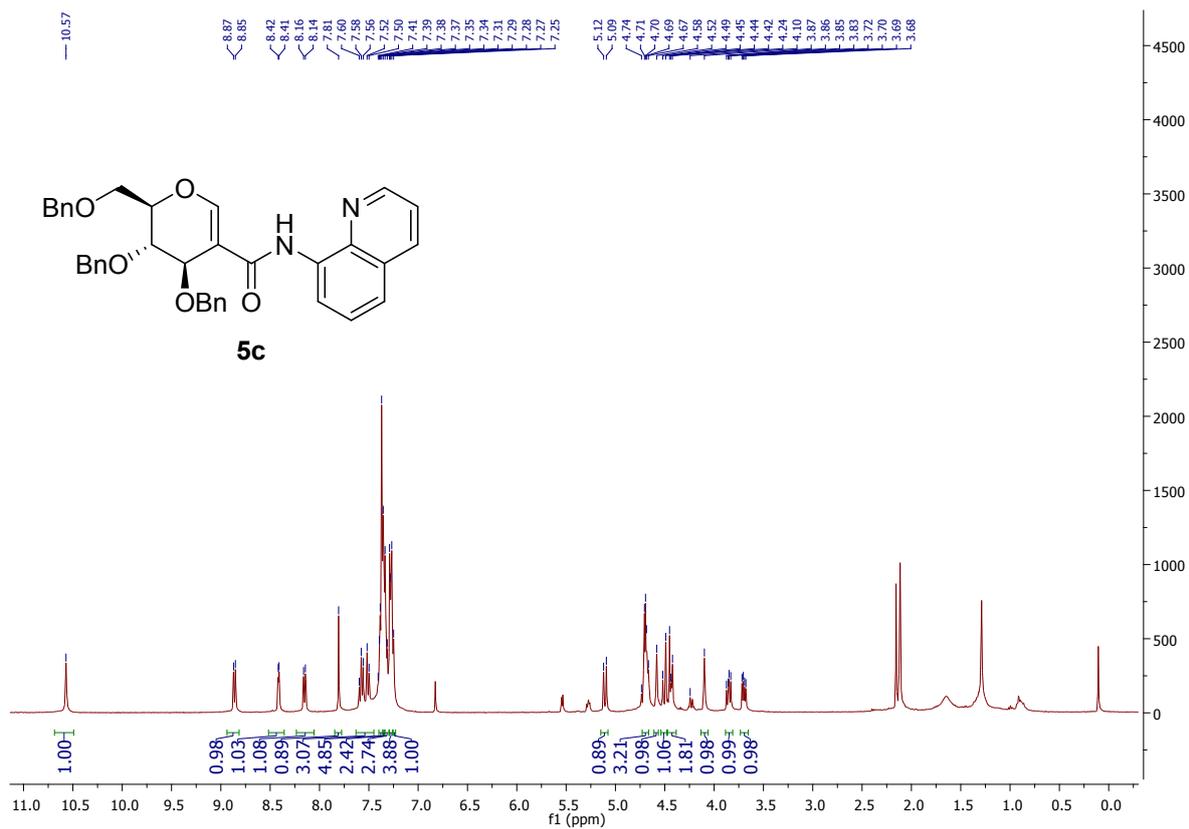
¹H NMR (400 MHz) and ¹³C NMR (126 MHz) of compound 3ae



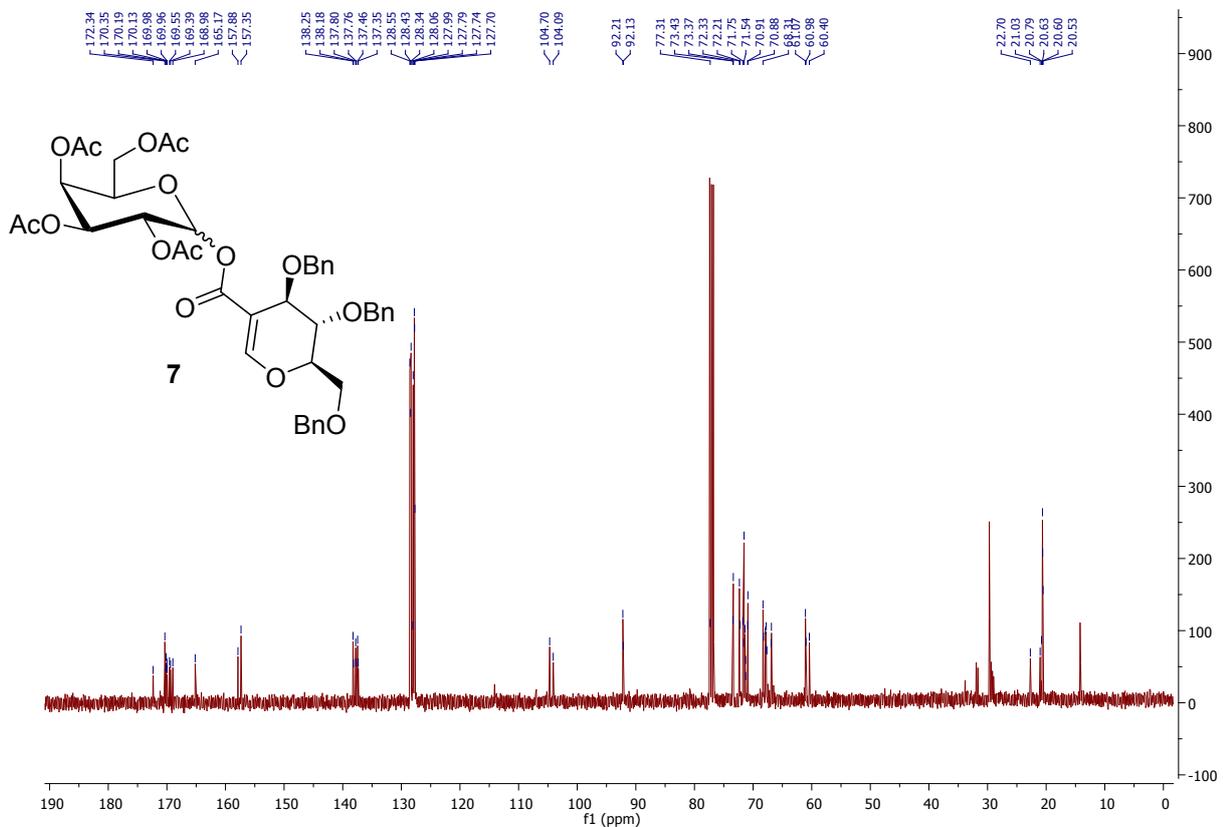
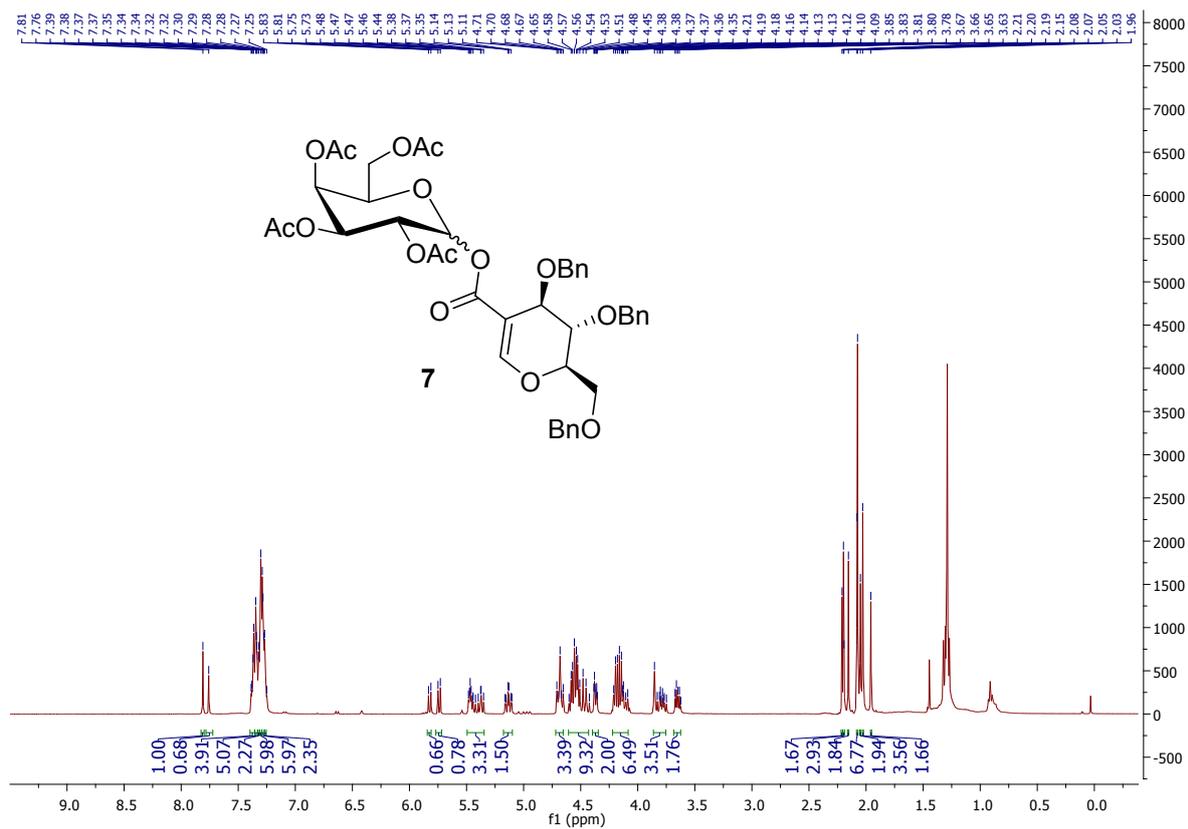
¹H NMR (400 MHz) and ¹³C NMR (126 MHz) of compound 5b



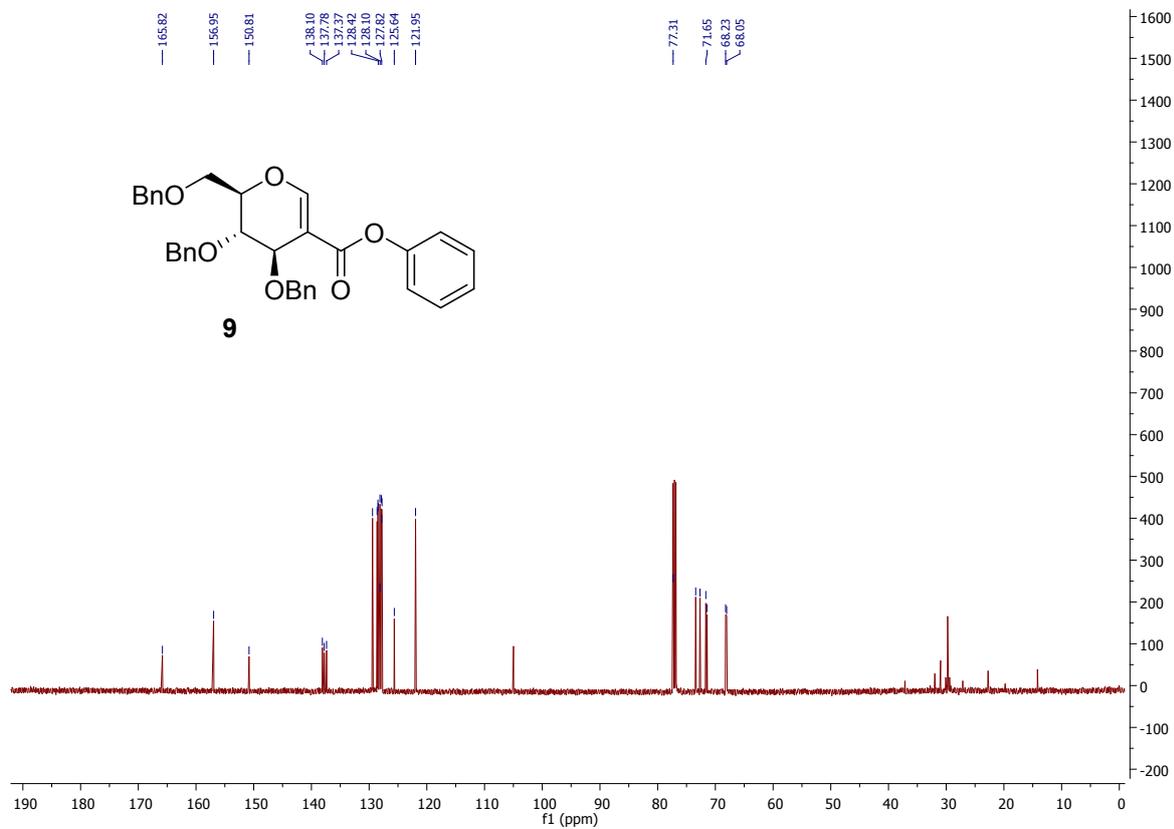
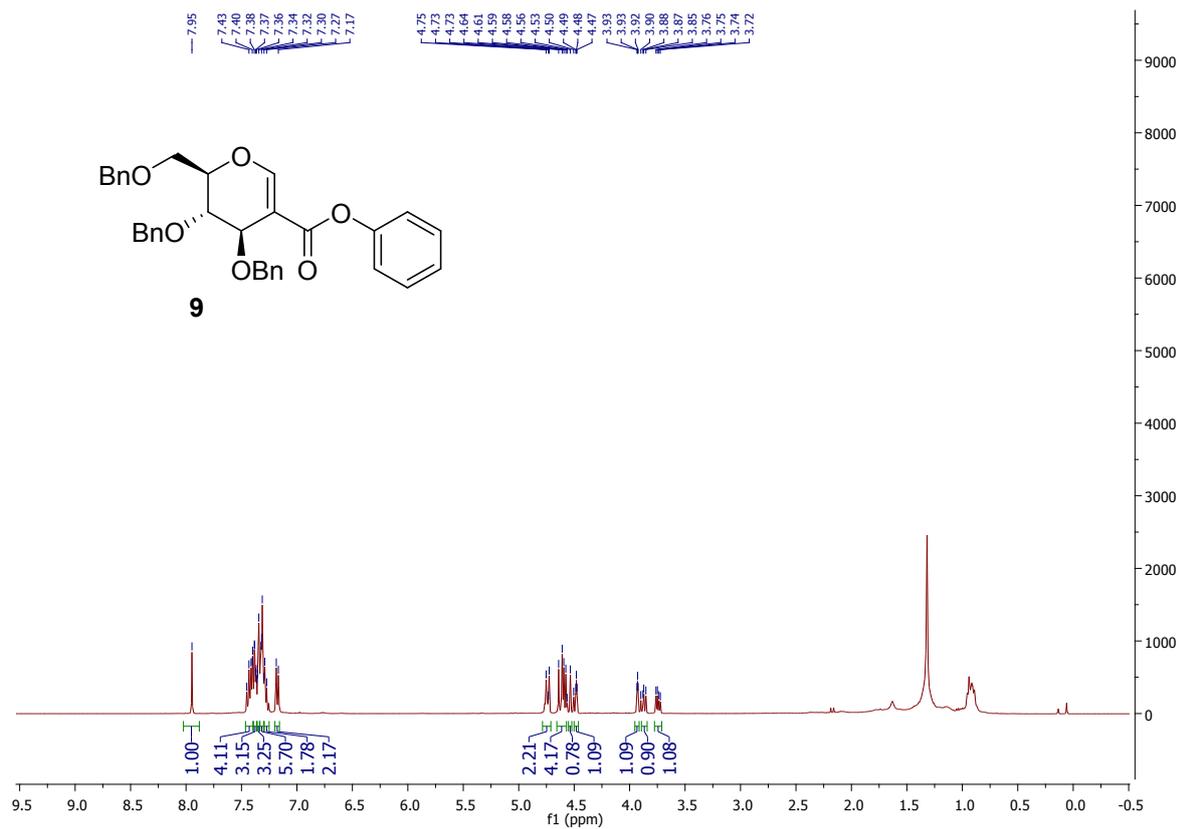
¹H NMR (400 MHz) and ¹³C NMR (126 MHz) of compound 5c



¹H NMR (400 MHz) and ¹³C NMR (101 MHz) of compound 7



¹H NMR (400 MHz) and ¹³C NMR (126 MHz) of compound 9



¹H NMR (400 MHz) and ¹³C NMR (126 MHz) of compound 11

