Supplementary Information (SI) for ChemComm.

Supporting information

Practical Synthesis of C-aryl Glycosides via Redox-Neutral Borono-Catellani Reaction

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Table of Contents

1. General information

All reactions dealing with moisture-sensitive compound were performed by standard Schlenk techniques in oven-dried reaction vessels under Air atmosphere. Unless otherwise noted, all solvents were dried by JC Meyer Solvent Drying System. Most reagents were purchased from commercial sources and used without further purification, unless otherwise stated. Reactions were monitored by thin layer chromatography (TLC) carried out on 0.2 mm commercial silica gel plates, using UV light as the visualizing agent. All NMR spectra were recorded on a Bruker spectrometer at 400 MHz (^{1}H NMR), 101 MHz (^{13}C NMR), 376 MHz (^{19}F NMR) and were calibrated using residual (un)deuterated solvent as an internal reference ($CDCl_3$ @ 7.26 ppm ^{1}H NMR, 77.16 ppm ^{13}C NMR; CD_3OD @ 3.31 ppm ^{1}H NMR, 49.00 ppm ^{13}C NMR). The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, ddd = doublet of doublet of doublets, m = multiplet. High resolution mass spectra (HRMS) were recorded on DIONEX UltiMate 3000 & Bruker Compact TOF mass spectrometer.

2. Representatives of C-aryl glycosides

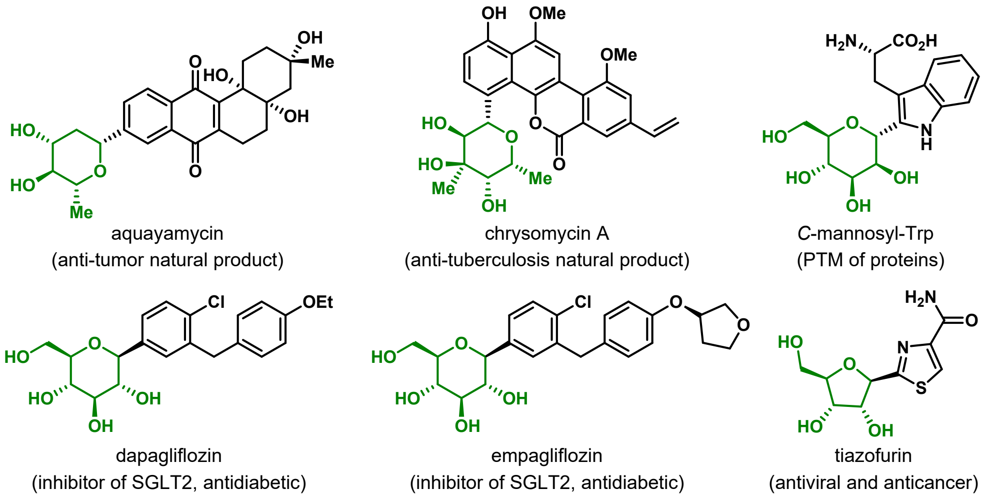


Figure S1. Representatives of C-aryl glycoside natural products and medicines.

3. Preparation of glycosyl chlorides

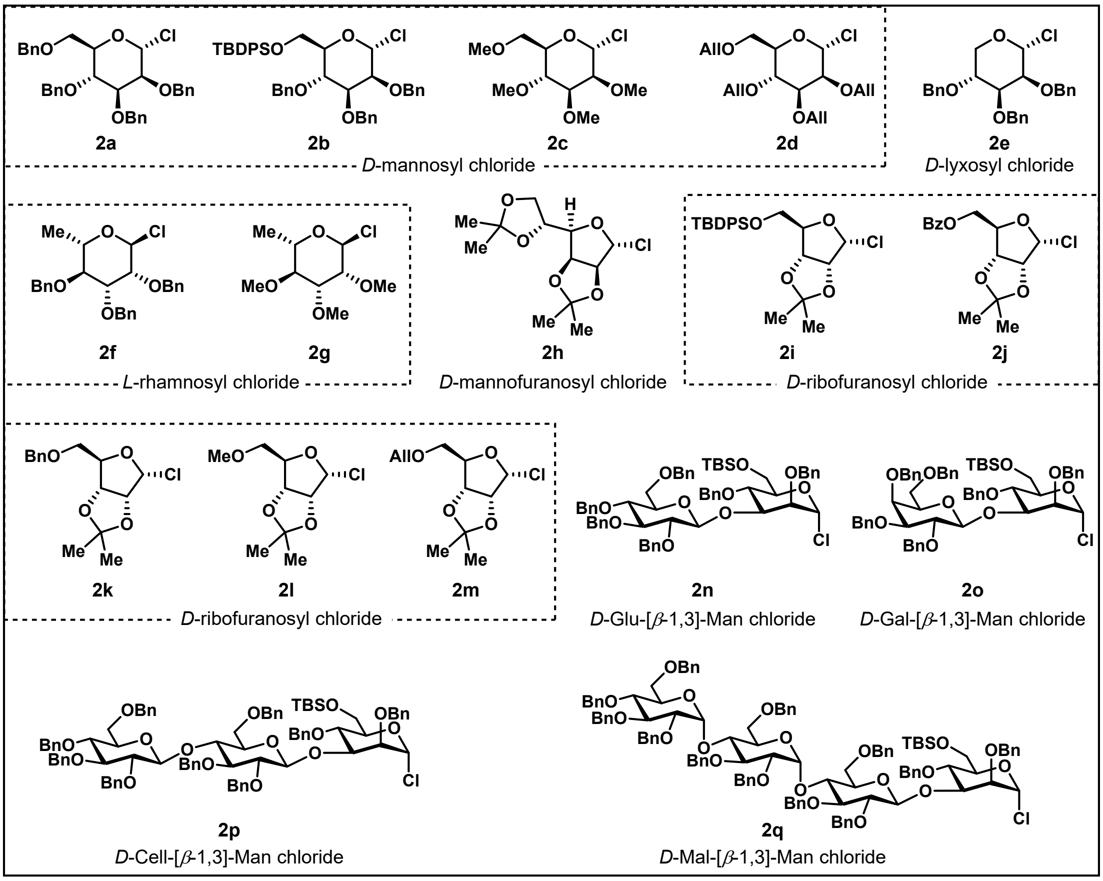
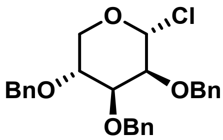


Figure S2. The glycosyl chlorides prepared in this study.

Glycosyl chlorides **2a**, **2b**, **2f**, **2h**, **2i** were prepared following the method described by Chen G. et al[1].

Glycosyl chlorides **2c**, **2d**, **2g**, **2k**, **2l**, **2m** were prepared following the method described by Liang Y.-M. et al[2].

Glycosyl chlorides **2e** and **2j** were prepared from the corresponding hemiacetal following a procedure described by Chen G. et al[1].

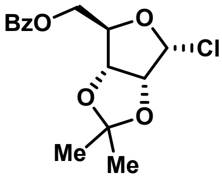


2e

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 15H), 5.95 (d, *J* = 1.9 Hz, 1H), 4.83 (d, *J* = 11.5 Hz, 1H), 4.75 (dd, *J* = 12.0, 5.1 Hz, 2H), 4.65 (d, *J* = 12.2 Hz, 3H), 4.10 (dd, *J* = 9.4, 3.0 Hz, 1H), 4.08 – 4.00 (m, 1H), 3.91 (dd, *J* = 11.4, 5.0 Hz, 1H), 3.86 (t, *J* = 2.4 Hz, 1H), 3.73 (dd, *J* = 11.4, 9.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.47, 138.40, 137.69, 128.66, 128.57, 128.17, 128.15, 127.94, 127.90, 92.12, 78.44, 77.80, 74.19, 73.92, 73.56, 73.08, 63.69.

HRMS (ESI-TOF): calc'd for $C_{26}H_{31}ClNO_4^+$ [M+NH_4^+] 456.1936, found 456.1932.



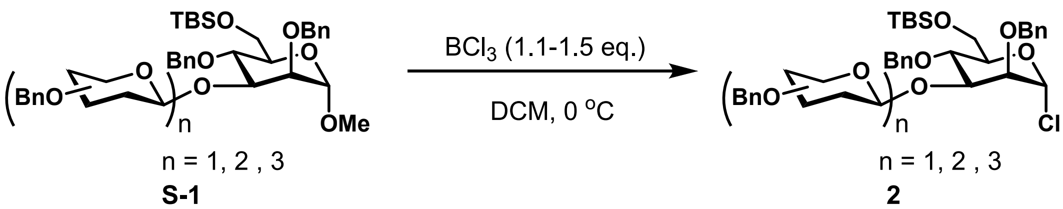
2j

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.03 (m, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.49 – 7.42 (m, 2H), 6.19 (s, 1H), 5.08 (d, *J* = 5.7 Hz, 1H), 4.95 (dd, *J* = 5.9, 1.5 Hz, 1H), 4.69 – 4.58 (m, 2H), 4.53 (dd, *J* = 11.3, 6.2 Hz, 1H), 1.50 (s, 3H), 1.35 (s, 3H).

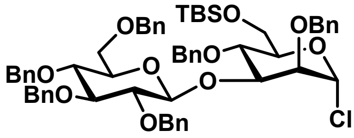
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.21, 133.46, 129.97, 129.66, 128.60, 113.89, 98.27, 89.68, 87.62, 81.70, 64.04, 26.71, 25.48.

HRMS (ESI-TOF): calc'd for $C_{15}H_{21}ClNO_5^+$ [M+NH_4^+] 330.1103, found 330.1098.

General procedure for the synthesis of **2n**–**2q**[1,3].



To a 0 °C cooled solution of **S-1** (0.8 mmol) in DCM, was slowly added boron trichloride (1.1–1.5 eq., 1M in DCM). After the complete consumption of starting material monitored by TLC analysis, the reaction mixture was diluted with DCM (20 mL) and washed with saturated $NaHCO_3$ (aq.), water and brine. The resulting residue was purified by silica gel flash chromatography to give corresponding compound.

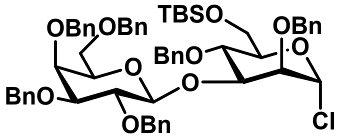


2n

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.12 (m, 30H), 6.02 (d, *J* = 2.2 Hz, 1H), 4.96 – 4.83 (m, 3H), 4.81 – 4.73 (m, 2H), 4.69 (d, *J* = 11.5 Hz, 1H), 4.60 – 4.47 (m, 6H), 4.47 – 4.40 (m, 2H), 4.09 (t, *J* = 9.1 Hz, 1H), 3.96 – 3.85 (m, 2H), 3.82 – 3.73 (m, 2H), 3.68 – 3.55 (m, 4H), 3.47 – 3.41 (m, 1H), 3.41 – 3.34 (m, 1H), 0.85 (s, 9H), 0.01 (s, 3H), 0.01 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.96, 138.67, 138.62, 138.46, 138.33, 137.79, 128.55, 128.50, 128.43, 128.38, 128.36, 128.07, 127.99, 127.97, 127.89, 127.85, 127.82, 127.80, 127.73, 127.61, 127.58, 127.51, 100.67, 92.05, 85.02, 82.49, 78.13, 75.84, 75.67, 75.45, 75.38, 75.11, 74.80, 74.70, 73.58, 73.49, 72.79, 68.96, 61.98, 26.04, 18.46, -5.02, -5.16.

HRMS (ESI-TOF): calc'd for $C_{60}H_{75}ClNO_{10}Si^{+}$ [$M+NH_4^{+}$] 1032.4843, found 1032.4841.

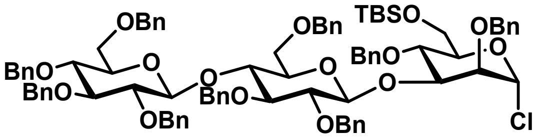


2o

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 14H), 7.26 – 7.12 (m, 16H), 6.03 (d, *J* = 2.0 Hz, 1H), 4.99 (dd, *J* = 10.9, 2.8 Hz, 2H), 4.93 – 4.80 (m, 2H), 4.78 – 4.69 (m, 2H), 4.67 – 4.49 (m, 6H), 4.40 (d, *J* = 11.7 Hz, 1H), 4.31 (d, *J* = 11.6 Hz, 1H), 4.14 (t, *J* = 9.4 Hz, 1H), 3.97 (dt, *J* = 8.0, 4.0 Hz, 2H), 3.94 – 3.86 (m, 2H), 3.83 (d, *J* = 2.6 Hz, 1H), 3.82 – 3.77 (m, 1H), 3.64 (t, *J* = 8.3 Hz, 1H), 3.60 – 3.52 (m, 2H), 3.45 (dd, *J* = 8.8, 5.0 Hz, 1H), 0.91 (s, 9H), 0.07 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.11, 138.98, 138.87, 138.51, 138.10, 138.06, 128.54, 128.49, 128.40, 128.33, 128.30, 128.24, 128.08, 127.97, 127.88, 127.70, 127.67, 127.61, 127.52, 127.44, 127.30, 101.65, 92.19, 82.75, 79.57, 78.81, 76.19, 75.78, 74.98, 74.85, 73.75, 73.68, 73.58, 73.08, 72.94, 72.85, 68.52, 61.89, 26.04, 18.44, -5.02, -5.17.

HRMS (ESI-TOF): calc'd for $C_{60}H_{75}ClNO_{10}Si^{+}$ [$M+NH_4^{+}$] 1032.4843, found 1032.4845.

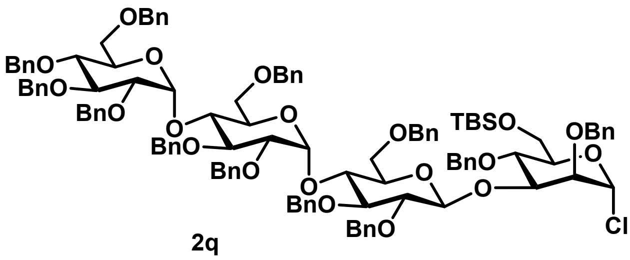


2p

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 6.8, 2.9 Hz, 2H), 7.29 – 7.12 (m, 43H), 6.03 (d, *J* = 2.1 Hz, 1H), 5.09 (d, *J* = 11.3 Hz, 1H), 4.94 (d, *J* = 11.1 Hz, 1H), 4.85 (dd, *J* = 11.3, 3.2 Hz, 2H), 4.82 – 4.69 (m, 6H), 4.62 – 4.46 (m, 8H), 4.41 – 4.34 (m, 3H), 4.09 (dt, *J* = 15.7, 9.3 Hz, 2H), 3.95 – 3.88 (m, 2H), 3.84 – 3.73 (m, 3H), 3.69 – 3.57 (m, 4H), 3.56 – 3.49 (m, 2H), 3.43 (dd, *J* = 9.0, 7.6 Hz, 1H), 3.37 (t, *J* = 8.4 Hz, 1H), 3.32 – 3.24 (m, 2H), 0.88 (s, 9H), 0.04 (s, 3H), 0.03 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.36, 138.95, 138.74, 138.63, 138.58, 138.42, 137.86, 128.50, 128.46, 128.37, 128.35, 128.23, 128.14, 127.96, 127.94, 127.91, 127.79, 127.74, 127.72, 127.66, 127.63, 127.57, 127.54, 127.47, 127.36, 127.27, 102.59, 100.75, 92.07, 85.03, 83.28, 82.94, 81.81, 78.17, 76.61, 75.79, 75.72, 75.64, 75.18, 75.09, 74.97, 74.86, 74.76, 73.42, 73.28, 72.84, 69.06, 68.05, 61.96, 26.03, 18.45, -5.02, -5.16.

HRMS (ESI-TOF): calc'd for $C_{87}H_{103}ClNO_{15}Si^+$ [$M+NH_4^+$] 1464.6780, found 1464.6772.



2q

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 8H), 7.26 – 7.05 (m, 51H), 6.09 (d, *J* = 2.2 Hz, 1H), 5.64 (d, *J* = 3.6 Hz, 1H), 5.54 (d, *J* = 3.6 Hz, 1H), 4.97 – 4.81 (m, 6H), 4.81 – 4.73 (m, 3H), 4.68 – 4.61 (m, 3H), 4.61 – 4.56 (m, 3H), 4.55 – 4.47 (m, 4H), 4.45 (s, 3H), 4.43 – 4.38 (m, 3H), 4.28 (d, *J* = 12.1 Hz, 1H), 4.16 – 4.07 (m, 2H), 4.07 – 3.98 (m, 3H), 3.97 – 3.89 (m, 3H), 3.88 – 3.77 (m, 4H), 3.76 – 3.70 (m, 3H), 3.70 – 3.63 (m, 1H), 3.58 – 3.46 (m, 6H), 3.39 (dd, *J* = 10.7, 1.9 Hz, 1H), 0.91 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.02, 138.91, 138.88, 138.64, 138.53, 138.46, 138.30, 138.08, 137.98, 137.71, 128.52, 128.44, 128.42, 128.37, 128.35, 128.31, 128.27, 128.16, 127.98, 127.95, 127.92, 127.90, 127.87, 127.78, 127.73, 127.68, 127.66, 127.59, 127.57, 127.51, 127.50, 127.44, 127.24, 127.10, 126.89, 126.71, 100.10, 97.10, 96.73, 91.99, 84.85, 82.21, 82.17, 81.74, 79.67, 79.53, 77.98, 77.77, 75.67, 75.61, 75.33, 75.10, 74.96, 74.82, 74.52, 74.21, 74.08, 73.61, 73.54, 73.39, 73.37, 73.11, 73.09, 72.79, 71.10, 70.99, 69.05, 68.96, 68.32, 62.00, 26.03, 18.45, -5.02, -5.16.

HRMS (ESI-TOF): calc'd for $C_{114}H_{131}ClNO_{20}Si^+$ $[M+NH_4^+]$ 1896.8717, found 1896.8721.

4. Preparation of arylboronic ester 1r

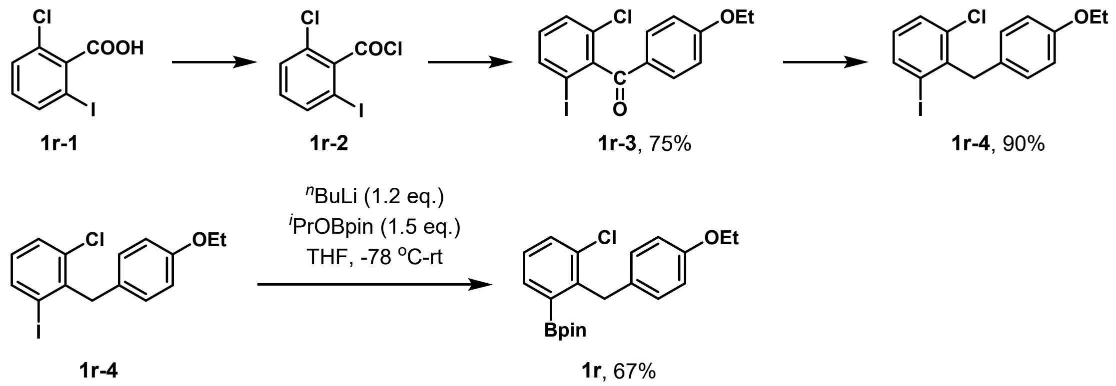
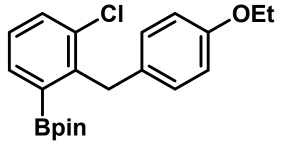


Figure S3. The synthesis of arylboronic ester **1r**.

Compound **1r-4** was synthesized according to the literature[4].

To a solution of **1r-4** (372 mg, 1.0 mmol, 1.0 equiv.) in anhydrous THF (10 mL) was added ^{n}BuLi (2.5 M, 0.48 mL, 1.2 mmol, 1.2 equiv.) slowly under Ar atmosphere at -78 °C. After stirring at -78 °C for 1 h, ^{i}PrOBpin (279 mg, 1.5 mmol, 1.5 equiv.) was added slowly under Ar atmosphere at -78 °C. The mixture was warmed to rt, stirred at rt for 5 h. The reaction mixture was quenched with saturated NH_4Cl solution (10 mL), extracted with EtOAc (3×15 mL). The combined organic layers were then washed with brine (10 mL), dried over Na_2SO_4, filtered and concentrated under vacuum to give a residue, which was purified by column chromatography (petroleum ether:DCM = 15:1 to 8:1) to afford **1r** (249 mg, 67%) as a white solid.

2-(3-Chloro-2-(4-ethoxybenzyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1r)



1r

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, J = 7.4 Hz, 1H), 7.46 (d, J = 7.9 Hz, 1H), 7.19 (t, J = 7.7 Hz, 1H), 7.05 (d, J = 8.6 Hz, 2H), 6.77 (d, J = 8.7 Hz, 2H), 4.48 (s, 2H), 3.99 (q, J = 7.0 Hz, 2H), 1.39 (t, J = 7.0 Hz, 3H), 1.28 (s, 12H).

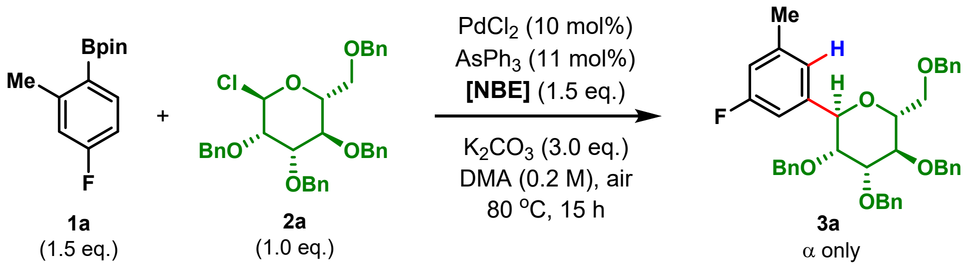
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.02, 144.54, 135.62, 134.68, 132.94, 132.44, 129.73, 127.10, 114.14, 84.03, 63.47, 36.58, 24.89, 15.05.

HRMS (ESI-TOF): calc'd for $C_{21}H_{27}BClO_3^+$ [M+H$^+$] 373.1736, found 373.1739.

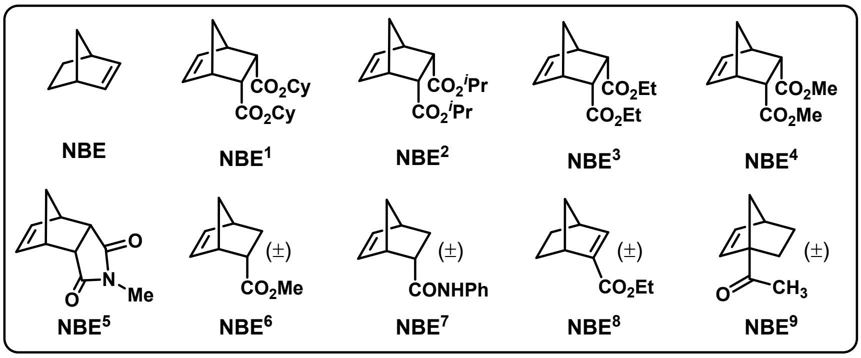
5. Optimization of reaction conditions

4.1. Optimization of reaction conditions of *ortho*-C–H glycosylation/*ipso*-protonation of arylboronic esters

Table S1. Screening of the [NBE] mediator[a]

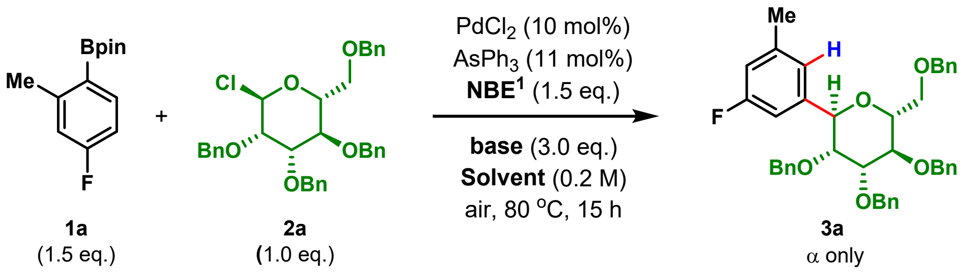


Entry	[NBE]	Yield[%][b]
1	**NBE**	17
2	**NBE[1]**	**36**
3	**NBE[2]**	25
4	**NBE[3]**	16
5	**NBE[4]**	15
6	**NBE[5]**	24
7	**NBE[6]**	1
8	**NBE[7]**	5
9	**NBE[8]**	0
10	**NBE[9]**	5



[a]All reactions were performed on a 0.1 mmol scale. [b]Yield determined by ^{19}F NMR analysis of the crude products using 2-fluoropyridine as an internal standard.

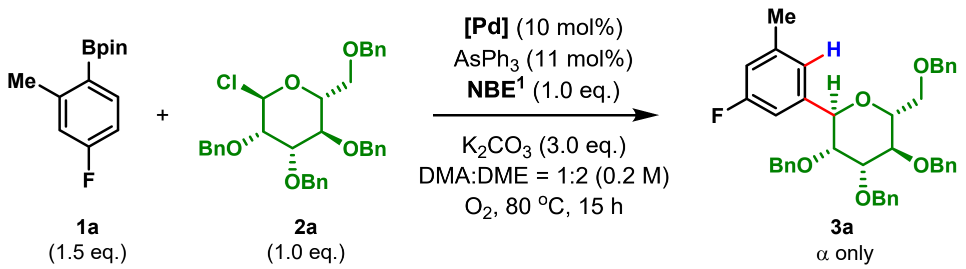
Table S2. Screening of the solvent and base[a]



Entry	Solvent	Base	Yield[%][b]
1	DMA	K_2CO_3	36
2	DMF	K_2CO_3	16
3	NMP	K_2CO_3	31
4	DMSO	K_2CO_3	trace
5	DME	K_2CO_3	27
6	1,4-dioxane	K_2CO_3	33
7	PhMe	K_2CO_3	21
8	mesitylene	K_2CO_3	23
9[c]	DMA	K_2CO_3	31
10[d]	DMA	K_2CO_3	40
11[d]	DMA: DME = 1:2	K_2CO_3	56
11[d]	DMA: DME = 1:2	$KHCO_3$	27
12[d]	DMA: DME = 1:2	K_3PO_4	31
13[d]	DMA: DME = 1:2	Cs_2CO_3	trace
14 [d,e]	**DMA: DME = 1:2**	**K_2CO_3**	**61 (58)[f]**
15 [d,e]	DMA: mesitylene = 1:1	K_2CO_3	55
16 [d,e]	DMA: mesitylene = 1:2	K_2CO_3	67
17 [d,e]	**DMA: mesitylene = 1:3**	**K_2CO_3**	**68 (64)[f]**
18 [d,e,g]	**DMA: mesitylene = 1:3**	**K_2CO_3**	**65**

[a]All reactions were performed on a 0.1 mmol scale. [b]Yield determined by ^{19}F NMR analysis of the crude products using 2-fluoropyridine as an internal standard. [c]The reaction was carried out under argon atomsphere. [d] The reaction was carried out under O_2 atomsphere. [e]**1a** (2.0 eq.) and K_2CO_3 (4.0 eq.) were applied. [f]Isolated yield. [g]**NBE**[1] (1.0 eq.) was applied.

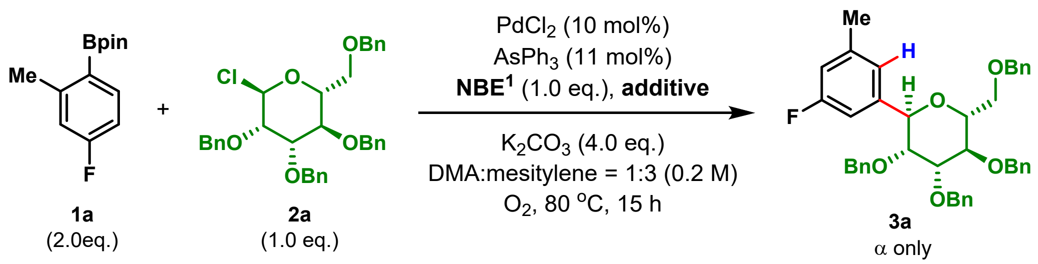
Table S3. Screening of the [Pd] catalyst[a]



Entry	[Pd]	Yield[%][b]
1	**$PdCl_2$**	**56**
2	$Pd(OAc)_2$	52
3	$Pd(TFA)_2$	45
4	$Pd[P(o\text{-Tol})_3]_2Cl_2$	38
5	$Pd(MeCN)_2Cl_2$	55
6	$Pd(PhCN)_2Cl_2$	50
7	$Pd(dppf)Cl_2$	46
8	$Pd(PPh_3)_2Cl_2$	47
9	$Pd_2(dba)_3{\cdot}CHCl_3$	43
10	$Pd(PPh_3)_4$	43

[a]All reactions were performed on a 0.1 mmol scale. [b]Yield determined by ^{19}F NMR analysis of the crude products using 2-fluoropyridine as an internal standard.

Table S4. Screening of the additive[a]



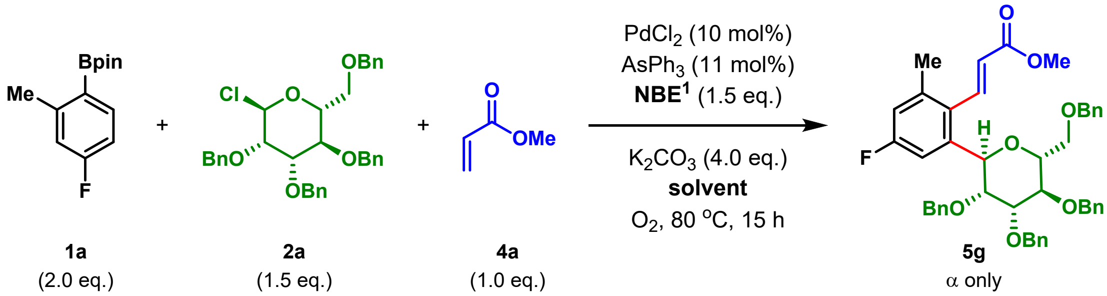
Entry	Additive	Yield[%][b]
1	-	65
2	Pyridine (7 mol%)	68
3	DMAP (7 mol%)	78
4	**DMAP (10 mol%)**	**82 (79)**[c]
5	DMAP (15 mol%)	75
6	DBU (10 mol%)	69
7	DBU (6 mol%)	79
8	DBN (7 mol%)	84
9	DABCO (5 mol%)	24
10	DIPEA (5 mol%)	60
11	Et_3N (5 mol%)	60
12	TMSOTf (10 mol%)	60

[a]All reactions were performed on a 0.1 mmol scale. [b]Yield determined by ^{19}F NMR analysis of the crude products using 2-fluoropyridine as an internal standard. [c]Isolated yield. DMAP: *N*,*N*-4-dimethylaminopyridine; DBU: 1,8-diazabicyclo[5.4.0]undec-7-ene; DBN: 1,5-diazabicyclo[4.3.0]non-5-ene; DABCO: 1,4-diazabicyclo[2.2.2]octane; DIPEA: *N*,*N*-

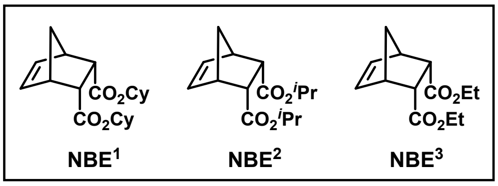
diisopropylethylamine.

4.2. Optimization of reaction conditions of *ortho*-C–H glycosylation/*ipso* -olefination of arylboronic esters

Table S5. Screening of the solvent and others[a]



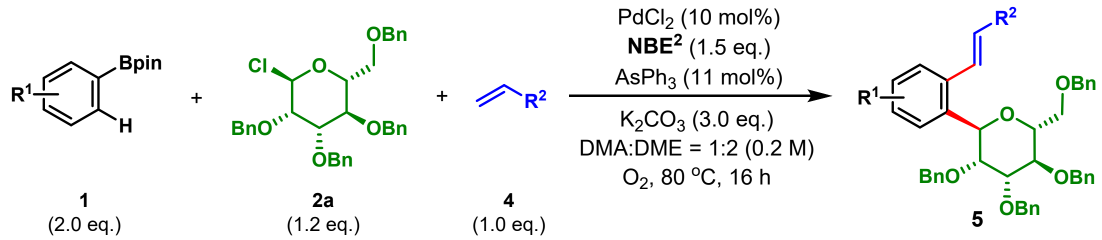
Entry	Solvent	Yield[%][b]
1[c]	DMA:mesitylene = 1:3	65
2	DMA:mesitylene = 1:3	72
3	DMA	40
4	mesitylene	21
5	DME	22
6	DMA:DME = 1:1	66
7	DMA:DME = 1:2	77
8	DMA:DME = 1:3	74
9[d]	DMA:DME = 1:2	72
10[e]	DMA:DME = 1:2	81
11[e,f]	**DMA:DME = 1:2**	**80 (76)[g]**

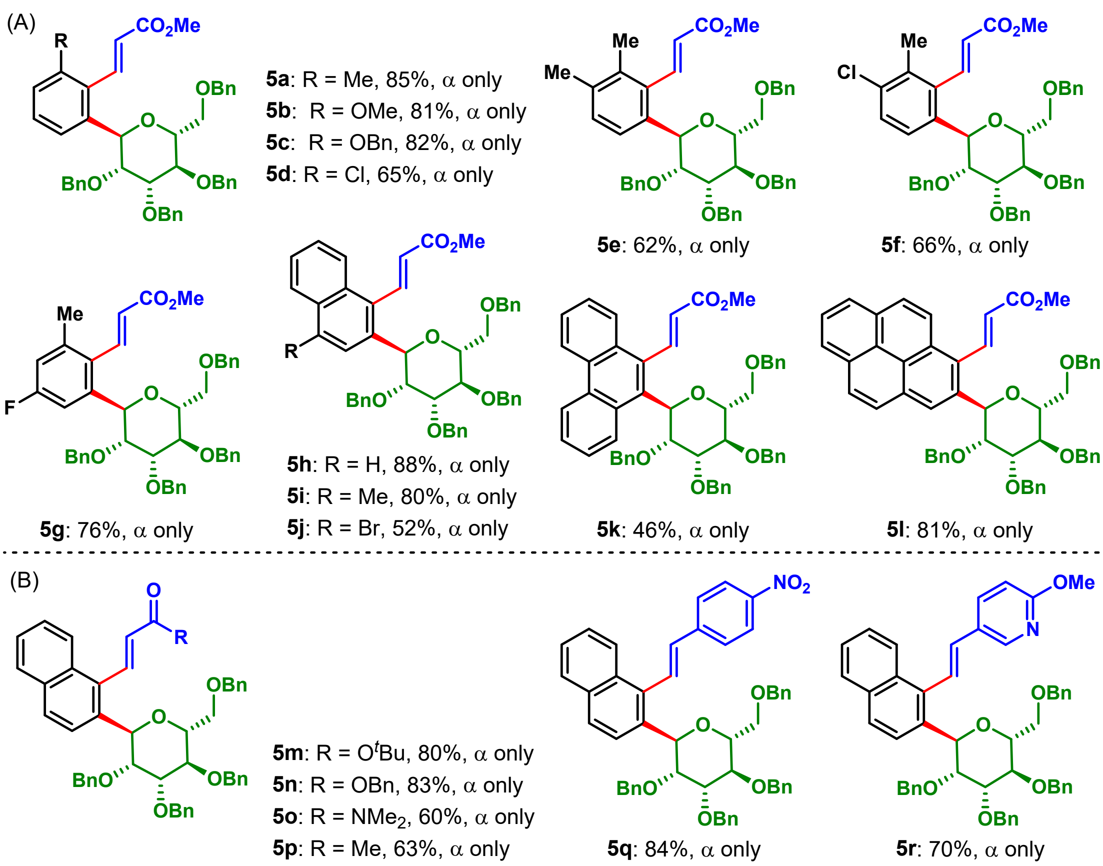


[a]All reactions were performed on a 0.1 mmol scale. [b]Yield determined by ^{19}F NMR analysis of the crude products using 2-fluoropyridine as an internal standard. [c]DMAP (10 mol%) was added. [d]**NBE[3]** was used instead of **NBE[1]**. [e]**NBE[2]** was used instead of **NBE[1]**. [f]**2a** (1.2 eq.) and K_2CO_3 (3.0 eq.) were applied. [g]Isolated yield in parenthesis.

6. Reaction Scope of three-component Borono-Catellani reaction

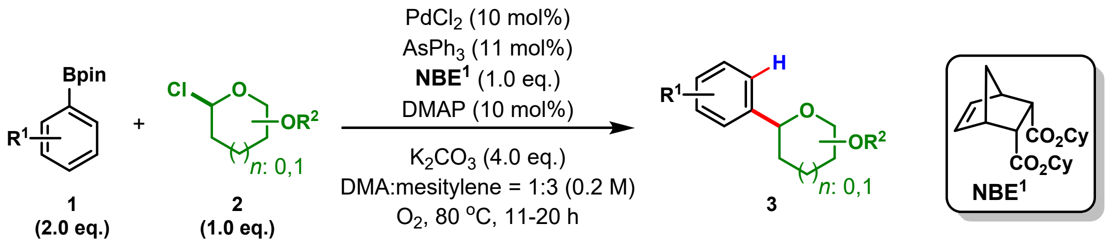
Table S6. Reaction scope with respect to arylboronic ester and the olefin terminating reagent[a]





[a]All reactions were performed on a 0.1 mmol scale, and isolated yields were reported.

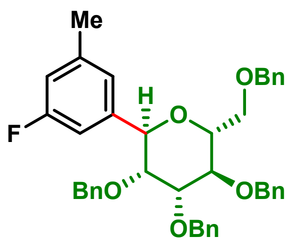
7. General procedure for redox-neutral synthesis of C-aryl glycosides 3



To a 10 mL oven-dried Schlenk tube equipped with a magnetic stir bar was charged with aryl boron compound **1** (0.2 mmol, 2.0 equiv), glycosyl chloride **2** (0.1 mmol, 1.0 equiv), $PdCl_2$ (1.8 mg, 0.01 mmol, 0.1 equiv), $AsPh_3$ (3.4 mg, 0.011 mmol, 0.11 equiv), DMAP (1.2 mg, 0.01 mmol, 0.1 equiv), **NBE¹** (34.7 mg, 0.1 mmol, 1.0 equiv), K_2CO_3 (55.3 mg, 0.4 mmol, 4.0 equiv) and DMA:mesitylene = 1:3 (0.5 mL) under O_2. The reaction was stirred at 80 °C for 11-20 h until the completion of the reaction (monitored by TLC). Then the mixture was filtered through a thin pad of celite eluting with ethyl acetate (15 mL), and the filtrate was sequentially washed with water, brine, dried over Na_2SO_4. After concentrated in vacuo, the residue was purified by column chromatography on silica gel to give the desired product.

8. Characterization data for C-aryl glycosides 3

(2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-Tris(benzyloxy)-2-((benzyloxy)methyl)-6-(3-fluoro-5-methylphenyl)tetrahydro-2*H*-pyran (3a)



3a

Physical state: colorless oil;

Yield: 79%;

$\mathbf{R_f}$ = 0.4 (silica gel, PE:EtOAc = 10:1);

[α]25 D: -61.3 (c = 0.23, $CHCl_3$);

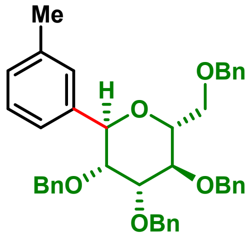
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 16H), 7.24 – 7.18 (m, 4H), 6.87 (s, 1H), 6.82 – 6.72 (m, 2H), 4.92 (d, J = 5.7 Hz, 1H), 4.67 – 4.58 (m, 4H), 4.57 – 4.50 (m, 2H), 4.49 – 4.41 (m, 2H), 3.95 (dd, J = 5.7, 3.0 Hz, 1H), 3.93 – 3.88 (m, 2H), 3.84 (dd, J = 10.3, 5.6 Hz, 1H), 3.77 (dd, J = 10.3, 3.6 Hz, 1H), 3.70 (dd, J = 6.3, 2.9 Hz, 1H), 2.27 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.06 (d, J = 245.1 Hz), 141.05 (d, J = 7.5 Hz), 140.40 (d, J = 7.9 Hz), 138.50, 138.34, 138.29, 138.14, 128.56, 128.53, 128.45, 128.44, 128.14, 128.12, 127.99, 127.94, 127.85, 127.81, 127.79, 127.64, 123.25 (d, J = 2.5 Hz), 115.14 (d, J = 20.8 Hz), 110.98 (d, J = 22.5 Hz), 76.49, 75.19, 74.48, 73.52, 73.34, 73.15, 73.13, 72.82, 72.14, 68.93, 21.52 (d, J = 1.9 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -114.1.

HRMS (ESI-TOF): calc'd for $C_{41}H_{41}FNaO_5^+$ [M+Na$^+$] 655.2830, found 655.2828.

(2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-Tris(benzyloxy)-2-((benzyloxy)methyl)-6-(mtolyl)tetrahydro-2*H*-pyran (3b)



3b

Physical state: colorless oil;

Yield: 79%;

R_f = 0.4 (silica gel, PE:EtOAc = 10:1);

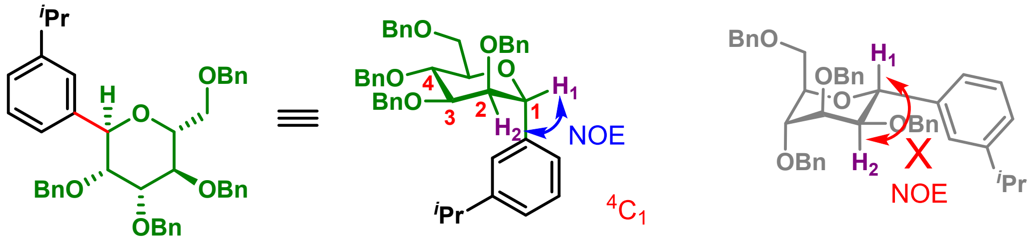
[α]25 D: -17.4 (c = 0.19, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.23 (m, 18H), 7.19 (dd, J = 7.5, 2.1 Hz, 2H), 7.14 (d, J = 7.6 Hz, 1H), 7.10 (s, 1H), 7.02 (dd, J = 15.8, 7.7 Hz, 2H), 5.01 (d, J = 5.0 Hz, 1H), 4.72 – 4.58 (m, 4H), 4.58 – 4.48 (m, 4H), 4.08 (dd, J = 5.1, 2.9 Hz, 1H), 3.95 (t, J = 6.5 Hz, 1H), 3.90 – 3.86 (m, 1H), 3.86 – 3.75 (m, 2H), 3.71 (dd, J = 7.0, 2.9 Hz, 1H), 2.28 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ138.60, 138.50, 138.41, 138.38, 138.17, 128.52, 128.50, 128.45, 128.44, 128.42, 128.35, 128.13, 128.02, 127.86, 127.80, 127.71, 127.60, 127.49, 123.82, 76.28, 75.43, 74.19, 73.81, 73.79, 73.34, 72.69, 72.08, 69.23, 21.63.

HRMS (ESI-TOF): calc'd for $C_{41}H_{46}NO_5^+$ [M+NH_4^+] 637.2924, found 637.2931.

(2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-Tris(benzyloxy)-2-((benzyloxy)methyl)-6-(3-isopropylph-enyl)tetrahydro-2*H*-pyran (3c)



(**Note**: Compound **3c** adopts a $^4C_1$ conformation based on 2D-NMR analysis.)

Physical state: colorless oil;

Yield: 50%;

R_f = 0.4 (silica gel, PE:EtOAc = 10:1);

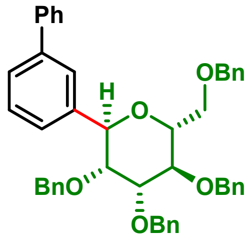
[α]25 D: -28.1 (c = 0.32, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.22 (m, 19H), 7.22 – 7.15 (m, 3H), 7.10 (d, J = 7.6 Hz, 1H), 6.98 (d, J = 7.5 Hz, 1H), 5.06 (d, J = 4.7 Hz, 1H), 4.71 (d, J = 11.2 Hz, 1H), 4.67 – 4.57 (m, 4H), 4.56 – 4.50 (m, 3H), 4.15 (dd, J = 4.8, 2.9 Hz, 1H), 3.99 – 3.92 (m, 1H), 3.90 – 3.78 (m, 3H), 3.71 (dd, J = 7.1, 2.9 Hz, 1H), 2.83 (hept, J = 6.8 Hz, 1H), 1.21 (d, J = 2.5 Hz, 3H), 1.19 (d, J = 2.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.25, 138.58, 138.49, 138.39, 138.35, 138.28, 128.56, 128.52, 128.50, 128.42, 128.10, 128.08, 127.84, 127.81, 127.71, 127.59, 125.62, 125.19, 123.91, 77.77, 76.09, 75.48, 74.09, 73.98, 73.95, 73.37, 72.60, 72.04, 69.30, 34.29, 24.24, 24.04.

HRMS (ESI-TOF): calc'd for $C_{43}H_{50}NO_5^+$ [M+NH_4^+] 660.3684, found 660.3690.

(2*R*,3*R*,4*R*,5*R*,6*R*)-2-([1,1'-Biphenyl]-3-yl)-3,4,5-tris(benzyloxy)-6-((benzyloxy)-methyl)tetrahydro-2*H*-pyran (3d)



3d

Physical state: colorless oil;

Yield: 44%;

R_f = 0.4 (silica gel, PE:EtOAc = 10:1);

[α]25 D: +37.1 (c = 0.35, $CHCl_3$);

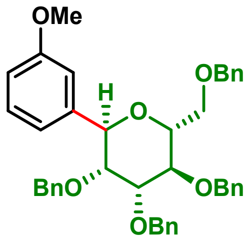
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.55 – 7.45 (m, 4H), 7.43 – 7.26 (m, 21H), 7.23 – 7.15 (m, 3H), 5.09 (d, J = 5.2 Hz, 1H), 4.69 (d, J = 11.3 Hz, 1H), 4.66 – 4.57 (m, 4H), 4.56 – 4.50 (m, 3H), 4.12 (dd, J = 5.3, 2.9 Hz, 1H), 3.99 – 3.92 (m, 2H), 3.89 –

3.79 (m, 2H), 3.75 (dd, *J* = 6.5, 2.9 Hz, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 141.55, 141.20, 139.14, 138.55, 138.40, 138.35, 138.27, 128.98, 128.83, 128.53, 128.47, 128.45, 128.15, 128.13, 128.02, 127.88, 127.84, 127.82, 127.76, 127.62, 127.39, 127.38, 126.47, 125.86, 125.50, 77.30, 76.41, 75.44, 74.33, 73.77, 73.75, 73.44, 72.74, 72.15, 69.28.

HRMS (ESI-TOF): calc'd for $C_{46}H_{48}NO_5^+$ [M+NH$_4^+$] 694.3527, found 694.3520.

(2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-Tris(benzyloxy)-2-((benzyloxy)methyl)-6-(3-methoxyphenyl)tetrahydro-2*H*-pyran (3e)



3e

Physical state: colorless oil;

Yield: 79%;

R$_f$ = 0.3 (silica gel, PE:EtOAc = 10:1);

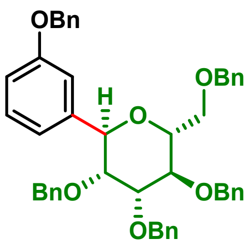
[α]25 D: +37.3 (c = 0.11, CHCl$_3$);

^{1}H NMR (400 MHz, CDCl$_3$) 7.36 – 7.26 (m, 18H), 7.21 – 7.14 (m, 3H), 6.94 (s, 1H), 6.78 (dd, *J* = 8.2, 2.6 Hz, 1H), 6.71 (d, *J* = 7.6 Hz, 1H), 5.03 (d, *J* = 4.7 Hz, 1H), 4.71 (d, *J* = 11.2 Hz, 1H), 4.64 – 4.50 (m, 7H), 4.10 (dd, *J* = 4.8, 2.9 Hz, 1H), 3.94 (t, *J* = 6.9 Hz, 1H), 3.90 – 3.85 (m, 1H), 3.85 – 3.76 (m, 2H), 3.73 – 3.67 (m, 4H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 160.00, 140.05, 138.52, 138.44, 138.39, 138.33, 129.57, 128.53, 128.50, 128.45, 128.44, 128.14, 128.00, 127.91, 127.85, 127.79, 127.75, 127.64, 118.69, 113.60, 112.16, 77.87, 76.11, 75.41, 74.24, 73.95, 73.92, 73.47, 72.68, 72.11, 69.41, 55.31.

HRMS (ESI-TOF): calc'd for $C_{41}H_{42}NaO_6^+$ [M+Na$^+$] 653.2874, found 653.2882.

(2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-Tris(benzyloxy)-2-((benzyloxy)methyl)-6-(3-(benzyloxy)-phenyl)tetrahydro-2*H*-pyran (3f)



3f

Physical state: colorless oil;

Yield: 76%;

$\mathbf{R_f}$ = 0.2 (silica gel, PE:EtOAc = 10:1);

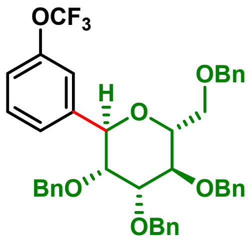
[α]25 D: +35.8 (c = 0.45, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.23 (m, 23H), 7.21 – 7.15 (m, 3H), 7.02 (s, 1H), 6.86 (dd, *J* = 8.2, 2.5 Hz, 1H), 6.74 (d, *J* = 7.6 Hz, 1H), 5.04 (d, *J* = 4.7 Hz, 1H), 4.98 (s, 2H), 4.71 (d, *J* = 11.2 Hz, 1H), 4.65 – 4.58 (m, 3H), 4.58 – 4.50 (m, 4H), 4.09 (dd, *J* = 4.8, 2.9 Hz, 1H), 3.95 (t, *J* = 6.9 Hz, 1H), 3.90 – 3.85 (m, 1H), 3.85 – 3.80 (m, 1H), 3.80 – 3.73 (m, 1H), 3.70 (dd, *J* = 7.1, 2.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.20, 140.08, 138.50, 138.42, 138.38, 138.33, 137.11, 129.60, 128.65, 128.51, 128.48, 128.43, 128.12, 128.01, 127.99, 127.84, 127.78, 127.73, 127.65, 127.61, 119.02, 114.40, 113.07, 77.82, 76.13, 75.38, 74.22, 73.94, 73.88, 73.45, 72.67, 72.10, 70.02, 69.33.

HRMS (ESI-TOF): calc'd for $C_{47}H_{50}NO_6^+$ [M+NH_4^+]724.3633, found 724.3631.

(2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-Tris(benzyloxy)-2-((benzyloxy)methyl)-6-(3-(trifluorometh-oxy)phenyl)tetrahydro-2*H*-pyran (3g)



3g

Physical state: colorless oil;

Yield: 45%;

$\mathbf{R_f}$ = 0.3 (silica gel, PE:EtOAc = 10:1);

[α]25 D: +29.4 (c = 0.12, $CHCl_3$);

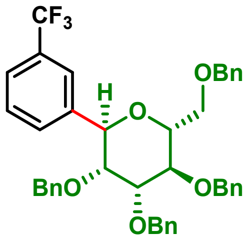
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.25 (m, 18H), 7.22 – 7.16 (m, 5H), 7.11 (d, *J* = 8.3 Hz, 1H), 4.94 (d, *J* = 6.2 Hz, 1H), 4.64 – 4.57 (m, 4H), 4.57 – 4.49 (m, 2H), 4.39 (s, 2H), 3.97 – 3.91 (m, 2H), 3.91 – 3.87 (m, 1H), 3.87 – 3.80 (m, 1H), 3.75 (dd, *J* = 10.2, 4.3 Hz, 1H), 3.70 (dd, *J* = 6.1, 2.9 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 149.51, 141.55, 138.41, 138.25, 138.18, 137.97, 129.78, 128.58, 128.57, 128.48, 128.46, 128.17, 128.10, 128.01, 127.98, 127.91, 127.85, 127.83, 127.70, 125.33, 120.60 (q, *J* = 257.2 Hz), 120.09, 119.75, 76.54, 76.36, 75.08, 74.61, 73.35, 72.91, 72.77, 72.13, 68.71.

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.6.

HRMS (ESI-TOF): calc'd for $C_{41}H_{43}F_3NO_6^+$ [M+NH_4^+] 702.3037, found 702.3031.

(2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-Tris(benzyloxy)-2-((benzyloxy)methyl)-6-(3-(trifluoro-methyl)phenyl)tetrahydro-2*H*-pyran (3h)



3h

Physical state: colorless oil;

Yield: 34%;

R_f = 0.4 (silica gel, PE:EtOAc = 10:1);

[α]25 D: +32.5 (c = 0.4, $CHCl_3$);

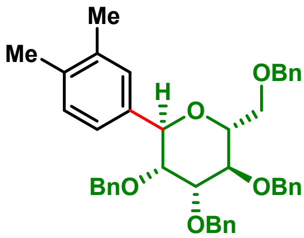
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.36 – 7.17 (m, 18H), 7.13 – 7.08 (m, 2H), 4.94 (d, *J* = 7.0 Hz, 1H), 4.64 – 4.50 (m, 6H), 4.37 – 4.25 (m, 2H), 4.04 (dt, *J* = 6.8, 4.6 Hz, 1H), 3.94 – 3.83 (m, 3H), 3.79 – 3.71 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.43, 138.38, 138.20, 138.14, 137.82, 130.66 (q, *J* = 32.3 Hz), 130.5, 128.79, 128.57, 128.48, 128.43, 128.12, 128.06, 127.96, 127.92, 127.83, 127.80, 127.71, 125.31 (q, *J* = 272.2 Hz), 124.53 (q, *J* = 3.7 Hz), 124.22 (q, *J* = 3.8 Hz), 76.81, 75.60, 74.95, 74.75, 73.28, 72.94, 72.92, 72.44, 72.04, 68.47.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.4.

HRMS (ESI-TOF): calc'd for $C_{41}H_{39}F_3NaO_5^+$ [M+Na$^+$] 691.2642, found 691.2648.

(2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-Tris(benzyloxy)-2-((benzyloxy)methyl)-6-(3,4-dimethyl-phenyl)tetrahydro-2*H*-pyran (3i)



3i

Physical state: colorless oil;

Yield: 90%;

R_f = 0.4 (silica gel, PE:EtOAc = 10:1);

[α]25 D: +33.1 (c = 0.35, $CHCl_3$);

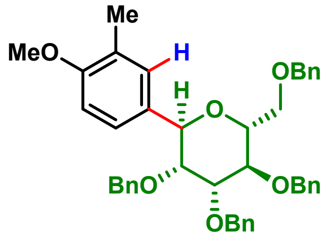
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.24 (m, 18H), 7.20 – 7.16 (m, 2H), 7.06 – 6.99 (m, 2H), 6.91 (d, *J* = 7.1 Hz, 1H), 5.01 (d, *J* = 4.6 Hz, 1H), 4.71 (d, *J* = 11.2 Hz, 1H), 4.67 – 4.59 (m, 3H), 4.58 – 4.49 (m, 4H), 4.10 (dd, *J* = 4.7, 2.9 Hz, 1H), 3.95 (t, *J* = 6.7

Hz, 1H), 3.87 – 3.77 (m, 3H), 3.70 (dd, J = 7.3, 2.9 Hz, 1H), 2.21 (s, 3H), 2.18 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.62, 138.54, 138.47, 138.44, 136.73, 135.84, 135.66, 129.77, 128.51, 128.46, 128.42, 128.41, 128.14, 128.13, 127.98, 127.96, 127.83, 127.80, 127.73, 127.68, 127.57, 124.07, 77.83, 76.09, 75.52, 74.00, 73.94, 73.81, 73.33, 72.63, 72.05, 69.35, 19.96, 19.51.

HRMS (ESI-TOF): calc'd for $C_{42}H_{48}NO_5^+$ [M+NH_4^+] 646.3527, found 646.3525.

(2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-Tris(benzyloxy)-2-((benzyloxy)methyl)-6-(4-methoxy-3-methylphenyl)tetrahydro-2*H*-pyran (3j)



3j

Physical state: colorless oil;

Yield: 69%;

R$_f$ = 0.3 (silica gel, PE:EtOAc = 10:1);

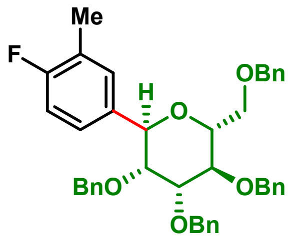
[α]25 D: +30.5 (c = 0.43, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.24 (m, 18H), 7.22 – 7.18 (m, 2H), 7.07 – 6.98 (m, 2H), 6.71 (d, J = 8.4 Hz, 1H), 4.98 (d, J = 5.0 Hz, 1H), 4.73 – 4.60 (m, 4H), 4.59 – 4.49 (m, 4H), 4.07 (dd, J = 5.1, 2.9 Hz, 1H), 3.95 (t, J = 6.5 Hz, 1H), 3.88 (dd, J = 10.9, 5.3 Hz, 1H), 3.85 – 3.76 (m, 5H), 3.74 (dd, J = 6.9, 2.9 Hz, 1H), 2.16 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.22, 138.62, 138.53, 138.44, 130.01, 129.15, 128.49, 128.46, 128.41, 128.37, 128.11, 127.96, 127.81, 127.77, 127.74, 127.65, 127.56, 126.68, 125.29, 109.85, 77.48, 76.19, 75.46, 74.03, 73.72, 73.44, 73.30, 72.64, 72.02, 69.24, 55.49, 16.40.

HRMS (ESI-TOF): calc'd for $C_{42}H_{48}NO_6^+$ [M+NH_4^+] 662.3476, found 662.3471.

(2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-Tris(benzyloxy)-2-((benzyloxy)methyl)-6-(4-fluoro-3-methyl-phenyl)tetrahydro-2*H*-pyran (3k)



3k

Physical state: colorless oil;

Yield: 74%;

R$_f$ = 0.3 (silica gel, PE:EtOAc = 10:1);

[α]25 D: +26.1 (c = 0.28, $CHCl_3$);

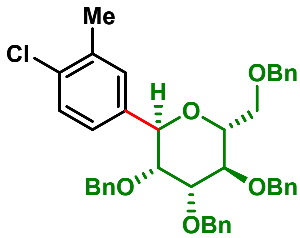
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 16H), 7.23 – 7.17 (m, 4H), 7.12 (dd, *J* = 7.5, 2.3 Hz, 1H), 7.04 – 6.98 (m, 1H), 6.90 (t, *J* = 8.9 Hz, 1H), 4.91 (d, *J* = 6.0 Hz, 1H), 4.67 – 4.58 (m, 4H), 4.57 – 4.52 (m, 2H), 4.46 – 4.38 (m, 2H), 3.99 – 3.92 (m, 2H), 3.90 (t, *J* = 5.7 Hz, 1H), 3.88 – 3.83 (m, 1H), 3.78 (dd, *J* = 10.2, 4.5 Hz, 1H), 3.74 (dd, *J* = 6.1, 2.9 Hz, 1H), 2.21 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.84 (d, *J* = 244.5 Hz), 138.52, 138.39, 138.30, 138.19, 134.27 (d, *J* = 3.4 Hz), 130.15 (d, *J* = 5.1 Hz), 128.54, 128.46, 128.41, 128.14, 128.11, 127.98, 127.90, 127.85, 127.78, 127.75, 127.65, 125.93 (d, *J* = 8.1 Hz), 124.76 (d, *J* = 17.3 Hz), 114.85 (d, *J* = 22.3 Hz), 76.58, 76.50, 75.24, 74.41, 73.35, 73.32, 72.86, 72.81, 72.06, 68.91, 14.70 (d, *J* = 3.5 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -119.4.

HRMS (ESI-TOF): calc'd for $C_{41}H_{45}FNO_5^+$ [M+NH_4^+] 650.3276, found 650.3273.

(2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-Tris(benzyloxy)-2-((benzyloxy)methyl)-6-(4-chloro-3-methyl-phenyl)tetrahydro-2*H*-pyran (3l)



3l

Physical state: colorless oil;

Yield: 60%;

R$_f$ = 0.4 (silica gel, PE:EtOAc = 10:1);

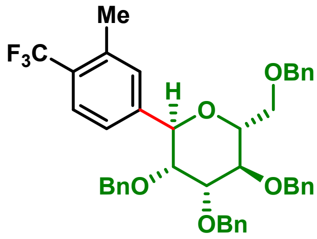
[α]25 D: +29 (c = 0.4, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.23 (m, 16H), 7.23 – 7.12 (m, 6H), 6.98 (dd, *J* = 8.3, 2.2 Hz, 1H), 4.90 (d, *J* = 6.0 Hz, 1H), 4.67 – 4.56 (m, 4H), 4.56 – 4.50 (m, 2H), 4.47 – 4.37 (m, 2H), 4.01 – 3.91 (m, 2H), 3.89 (t, *J* = 5.8 Hz, 1H), 3.87 – 3.81 (m, 1H), 3.77 (dd, *J* = 10.2, 4.3 Hz, 1H), 3.71 (dd, *J* = 6.1, 2.9 Hz, 1H), 2.30 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.49, 138.35, 138.27, 138.11, 137.42, 136.02, 133.54, 129.59, 128.98, 128.54, 128.54, 128.46, 128.42, 128.14, 128.12, 127.96, 127.92, 127.86, 127.78, 127.66, 125.75, 76.53, 76.47, 75.20, 74.49, 73.35, 73.32, 72.84, 72.08, 68.88, 20.20.

HRMS (ESI-TOF): calc'd for $C_{41}H_{45}ClNO_5^+$ [M+NH_4^+] 666.2981, found 666.2979.

(2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-Tris(benzyloxy)-2-((benzyloxy)methyl)-6-(3-methyl-4-(trifluoromethyl)phenyl)tetrahydro-2*H*-pyran (3m)



3m

Physical state: colorless oil;

Yield: 40%;

$\mathbf{R_f}$ = 0.4 (silica gel, PE:EtOAc = 10:1);

[α]25 D: +28.4 (c = 0.31, $CHCl_3$);

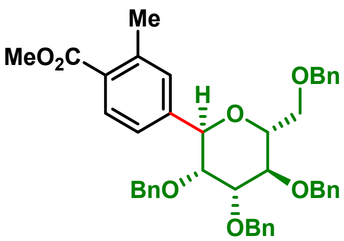
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.1 Hz, 1H), 7.34 – 7.24 (m, 16H), 7.23 – 7.19 (m, 3H), 7.17 – 7.11 (m, 3H), 4.93 (d, *J* = 6.3 Hz, 1H), 4.65 – 4.57 (m, 4H), 4.56 – 4.51 (m, 2H), 4.46 – 4.34 (m, 2H), 4.00 – 3.95 (m, 1H), 3.93 (dd, *J* = 6.3, 2.9 Hz, 1H), 3.91 – 3.82 (m, 2H), 3.77 (dd, *J* = 10.2, 4.5 Hz, 1H), 3.71 (dd, *J* = 6.0, 2.9 Hz, 1H), 2.40 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.84, 138.45, 138.29, 138.21, 137.94, 136.79, 130.49, 128.58, 128.49, 128.44, 128.16, 128.13, 127.98, 127.92, 127.86, 127.80, 127.71, 127.19 (q, *J* = 228.2 Hz), 125.86 (q, *J* = 5.6 Hz), 124.36, 76.56, 76.09, 75.11, 74.70, 73.35, 73.27, 72.91, 72.74, 72.02, 68.78, 19.46.

^{19}F NMR (376 MHz, $CDCl_3$) δ -61.5.

HRMS (ESI-TOF): calc’d for $C_{42}H_{45}F_3NO_5^+$ [$M+NH_4^+$] 700.3244, found 700.3243.

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



3n

Physical state: colorless oil;

Yield: 56%;

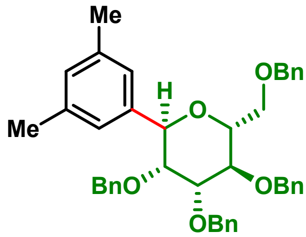
$\mathbf{R_f}$ = 0.3 (silica gel, PE:EtOAc = 7:1);

[α]25 D: +28.9 (c = 0.36, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.1 Hz, 1H), 7.37 – 7.25 (m, 16H), 7.24 – 7.18 (m, 5H), 7.14 (d, *J* = 8.2 Hz, 1H), 4.97 (d, *J* = 6.0 Hz, 1H), 4.68 – 4.52 (m, 6H),

4.47 – 4.39 (m, 2H), 4.02 – 3.94 (m, 2H), 3.94 – 3.83 (m, 5H), 3.79 (dd, *J* = 10.3, 4.3 Hz, 1H), 3.71 (dd, *J* = 6.2, 2.9 Hz, 1H), 2.55 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.95, 143.04, 140.48, 138.47, 138.32, 138.25, 138.06, 130.83, 130.24, 128.73, 128.54, 128.52, 128.45, 128.42, 128.12, 127.95, 127.93, 127.85, 127.79, 127.78, 127.65, 124.27, 76.56, 75.14, 74.62, 73.35, 73.31, 73.04, 72.86, 72.13, 68.86, 51.91, 21.96.
HRMS (ESI-TOF): calc'd for $C_{43}H_{48}NO_7^+$ [M+NH_4^+] 690.3425, found 690.3424.

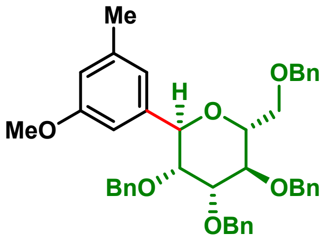
(2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-Tris(benzyloxy)-2-((benzyloxy)methyl)-6-(3,5-dimethyl-phenyl)tetrahydro-2*H*-pyran (3o)



3o

Physical state: colorless oil;
Yield: 60%;
R_f = 0.4 (silica gel, PE:EtOAc = 10:1);
[α]25 D: +3.9 (c = 1.00, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 18H), 7.20 (dd, *J* = 7.2, 1.9 Hz, 2H), 6.92 – 6.84 (m, 3H), 4.99 (d, *J* = 5.0 Hz, 1H), 4.72 – 4.61 (m, 4H), 4.59 – 4.50 (m, 4H), 4.09 (dd, *J* = 5.2, 3.0 Hz, 1H), 3.97 – 3.87 (m, 2H), 3.87 – 3.79 (m, 2H), 3.73 (dd, *J* = 6.9, 2.9 Hz, 1H), 2.24 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.63, 138.56, 138.44, 138.42, 138.34, 138.02, 129.22, 128.52, 128.50, 128.42, 128.41, 128.14, 128.08, 128.01, 127.85, 127.77, 127.70, 127.58, 124.56, 76.32, 75.46, 74.15, 73.79, 73.31, 72.61, 72.09, 69.27, 21.50.
HRMS (ESI-TOF): calc'd for $C_{42}H_{48}NO_5^+$ [M+NH_4^+] 646.3527, found 646.3524.

(2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-Tris(benzyloxy)-2-((benzyloxy)methyl)-6-(3-methoxy-5-methylphenyl)tetrahydro-2*H*-pyran (3p)



3p

Physical state: colorless oil;

Yield: 83%;

$\mathbf{R_f}$ = 0.3 (silica gel, PE:EtOAc = 10:1);

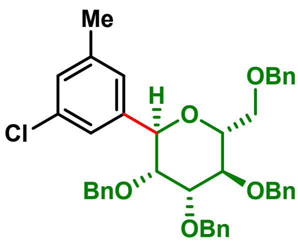
[α]25 D: +25.6 (c = 0.25, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 18H), 7.19 (dd, J = 7.3, 2.1 Hz, 2H), 6.73 (s, 1H), 6.60 (s, 2H), 5.00 (d, J = 4.8 Hz, 1H), 4.71 (d, J = 11.3 Hz, 1H), 4.64 – 4.59 (m, 3H), 4.58 – 4.51 (m, 4H), 4.10 (dd, J = 4.8, 2.9 Hz, 1H), 3.96 – 3.85 (m, 2H), 3.84 – 3.75 (m, 2H), 3.72 (dd, J = 6.9, 2.9 Hz, 1H), 3.69 (s, 3H), 2.25 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.98, 139.82, 139.58, 138.56, 138.50, 138.42, 138.37, 128.53, 128.50, 128.43, 128.14, 128.05, 127.99, 127.87, 127.85, 127.78, 127.73, 127.62, 119.63, 114.31, 109.26, 77.79, 76.18, 75.43, 74.21, 73.91, 73.90, 73.42, 72.59, 72.12, 69.40, 55.30, 21.75.

HRMS (ESI-TOF): calc'd for $C_{42}H_{48}NO_6^+$ [M+NH_4^+] 662.3476, found 662.3473.

(2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-Tris(benzyloxy)-2-((benzyloxy)methyl)-6-(3-chloro-5-methylphenyl)tetrahydro-2*H*-pyran (3q)



3q

Physical state: colorless oil;

Yield: 70%;

$\mathbf{R_f}$ = 0.4 (silica gel, PE:EtOAc = 10:1);

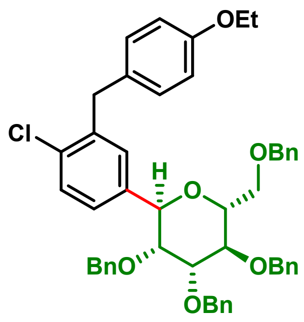
[α]25 D: -55.0 (c = 0.39, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.25 (m, 16H), 7.24 – 7.18 (m, 4H), 7.13 (s, 1H), 7.07 (s, 1H), 7.00 (s, 1H), 4.89 (d, J = 6.1 Hz, 1H), 4.67 – 4.51 (m, 6H), 4.47 – 4.36 (m, 2H), 4.01 – 3.95 (m, 1H), 3.93 (dd, J = 6.2, 2.8 Hz, 1H), 3.91 – 3.83 (m, 2H), 3.77 (dd, J = 10.2, 4.4 Hz, 1H), 3.73 (dd, J = 6.1, 2.9 Hz, 1H), 2.27 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.79, 139.86, 138.46, 138.31, 138.24, 138.05, 134.15, 128.58, 128.54, 128.46, 128.44, 128.14, 128.10, 127.98, 127.96, 127.87, 127.81, 127.79, 127.66, 125.99, 124.27, 76.84, 76.61, 76.42, 75.11, 74.56, 73.30, 72.88, 72.83, 72.17, 68.79, 21.35.

HRMS (ESI-TOF): calc'd for $C_{41}H_{45}ClNO_5^+$ [M+NH_4^+] 666.2981, found 666.2978.

(2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-2-((benzyloxy)methyl)-6-(4-chloro-3-(4-ethoxybenzyl)phenyl)tetrahydro-2*H*-pyran (3r)



3r

Physical state: colorless oil;

Yield: 41%; run with $AsPh_3$ (50 mol%), and HCO_2K (1.0 eq.) as an additive.

R_f = 0.4 (silica gel, PE:EtOAc = 8:1);

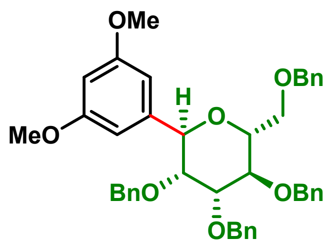
[α]25 D: 30.1 (c = 0.50, MeOH);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 17H), 7.21 – 7.15 (m, 4H), 7.13 (d, *J* = 2.1 Hz, 1H), 7.06 – 7.00 (m, 3H), 6.78 – 6.73 (m, 2H), 4.91 (d, *J* = 5.6 Hz, 1H), 4.60 (dd, *J* = 11.8, 9.7 Hz, 2H), 4.54 – 4.45 (m, 4H), 4.41 (s, 2H), 4.00 – 3.92 (m, 4H), 3.91 – 3.86 (m, 2H), 3.88 – 3.75 (m, 3H), 3.70 (dd, *J* = 9.5, 3.2 Hz, 1H), 3.63 (dd, *J* = 6.4, 2.9 Hz, 1H), 1.36 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.52, 139.20, 138.47, 138.33, 138.27, 138.13, 137.55, 133.38, 131.46, 130.00, 129.67, 129.64, 128.56, 128.50, 128.47, 128.16, 128.12, 128.04, 127.93, 127.89, 127.84, 127.80, 127.70, 126.08, 114.53, 77.04, 76.01, 75.12, 74.35, 73.59, 73.35, 72.99, 72.72, 72.07, 68.85, 63.43, 38.48, 15.03.

HRMS (ESI-TOF): calc'd for $C_{49}H_{49}ClNaO_6^+$ [M+Na$^+$] 791.3110, found 791.3107.

(2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-Tris(benzyloxy)-2-((benzyloxy)methyl)-6-(3,5-dimethoxyphenyl)tetrahydro-2*H*-pyran (3s)



3s

Physical state: colorless oil;

Yield: 53%;

R_f = 0.4 (silica gel, PE:EtOAc = 10:1);

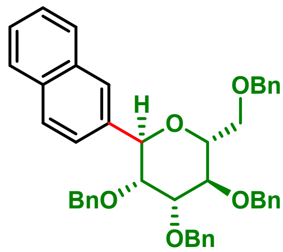
[α]25 D: +29.4 (c = 0.34, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.25 (m, 18H), 7.19 (dd, *J* = 7.3, 2.2 Hz, 2H), 6.49 (d, *J* = 2.3 Hz, 2H), 6.34 (t, *J* = 2.3 Hz, 1H), 5.01 (d, *J* = 4.5 Hz, 1H), 4.73 (d, *J* = 11.3 Hz, 1H), 4.64 – 4.54 (m, 6H), 4.52 (d, *J* = 11.3 Hz, 1H), 4.11 (dd, *J* = 4.7, 3.0 Hz, 1H), 3.94 – 3.88 (m, 2H), 3.85 – 3.79 (m, 2H), 3.72 (dd, *J* = 7.0, 3.0 Hz, 1H), 3.69 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.07, 140.85, 138.49, 138.41, 138.38, 138.29, 128.53, 128.48, 128.45, 128.42, 128.15, 127.98, 127.96, 127.94, 127.82, 127.77, 127.65, 104.62, 99.73, 78.16, 75.95, 75.35, 74.29, 74.08, 73.95, 73.51, 72.56, 72.15, 69.56, 55.43.

HRMS (ESI-TOF): calc'd for $C_{42}H_{48}NO_7^+$ [M+NH_4^+] 678.3425, found 678.3431.

(2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-Tris(benzyloxy)-2-((benzyloxy)methyl)-6-(naphtha-alen-2-yl)tetrahydro-2*H*-pyran (3t)



3t

Physical state: colorless oil;

Yield: 83%;

R_f = 0.3 (silica gel, PE:EtOAc = 10:1);

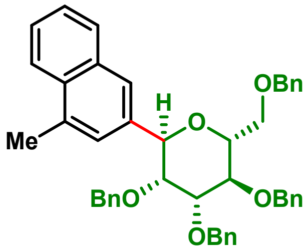
[α]25 D: +24.6 (c = 0.46, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.77 (m, 2H), 7.78 (d, *J* = 8.6 Hz, 2H), 7.74 – 7.66 (m, 1H), 7.66 (s, 1H), 7.50 – 7.42 (m, 3H), 7.38 – 7.25 (m, 16H), 7.27 – 7.16 (m, 10H), 5.17 (d, *J* = 5.4 Hz, 1H), 4.73 – 4.61 (m, 4H), 4.61 – 4.46 (m, 4H), 4.18 (dd, *J* = 5.4, 2.9 Hz, 1H), 4.01 – 3.91 (m, 2H), 3.94 – 3.84 (m, 1H), 3.82 (dd, *J* = 10.1, 3.1 Hz, 1H), 3.78 (dd, *J* = 6.8, 3.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.59, 138.51, 138.39, 138.27, 136.23, 133.32, 132.96, 128.59, 128.51, 128.47, 128.42, 128.25, 128.18, 128.15, 127.96, 127.92, 127.84, 127.79, 127.74, 127.68, 127.64, 126.13, 126.07, 125.95, 124.89, 76.51, 75.44, 74.50, 73.79, 73.60, 73.35, 72.85, 72.19, 69.11.

HRMS (ESI-TOF): calc'd for $C_{44}H_{46}NO_5^+$ [M+NH_4^+] 673.2924, found 673.2927.

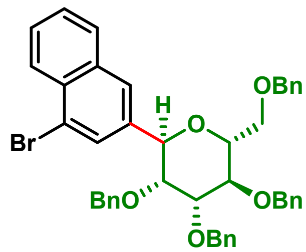
(2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-Tris(benzyloxy)-2-((benzyloxy)methyl)-6-(4-methylnaphthal-en-2-yl)tetrahydro-2*H*-pyran (3u)



3u

Physical state: colorless oil;
Yield: 80%;
$\mathbf{R_f}$ = 0.3 (silica gel, PE:EtOAc = 10:1);
[α]25 D: +24.5 (c = 0.42, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.0 Hz, 1H), 7.70 (d, J = 7.6 Hz, 1H), 7.53 – 7.42 (m, 3H), 7.36 – 7.18 (m, 21H), 5.14 (d, J = 5.3 Hz, 1H), 4.73 – 4.60 (m, 4H), 4.60 – 4.46 (m, 4H), 4.18 (dd, J = 5.4, 2.9 Hz, 1H), 4.01 – 3.92 (m, 2H), 3.91 – 3.76 (m, 3H), 2.63 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.60, 138.52, 138.41, 138.27, 135.74, 134.71, 133.44, 132.17, 128.77, 128.56, 128.48, 128.44, 128.38, 128.17, 128.13, 127.92, 127.89, 127.78, 127.76, 127.71, 127.60, 125.92, 125.80, 125.47, 124.34, 123.99, 77.21, 76.40, 75.45, 74.46, 73.79, 73.59, 73.31, 72.78, 72.16, 69.18, 19.55.
HRMS (ESI-TOF): calc'd for $C_{45}H_{48}NO_5^+$ [M+NH_4^+] 682.3527, found 682.3521.

(2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-Tris(benzyloxy)-2-((benzyloxy)methyl)-6-(4-bromonaphthal-en-2-yl)tetrahydro-2*H*-pyran (3v)

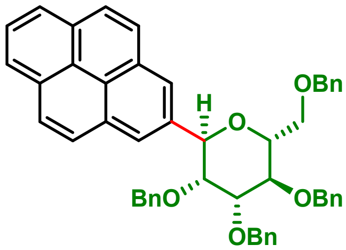


3v

Physical state: pink oil;
Yield: 60%;
$\mathbf{R_f}$ = 0.4 (silica gel, PE:EtOAc = 10:1);
[α]25 D: +31.2 (c = 0.25, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 8.3 Hz, 1H), 7.86 (d, J = 1.6 Hz, 1H), 7.77 – 7.64 (m, 2H), 7.62 – 7.56 (m, 1H), 7.55 – 7.49 (m, 1H), 7.36 – 7.19 (m, 18H), 7.17 – 7.12 (m, 2H), 5.06 (d, J = 6.5 Hz, 1H), 4.69 – 4.52 (m, 6H), 4.45 – 4.32 (m, 2H), 4.11 – 3.99 (m, 2H), 3.95 – 3.87 (m, 2H), 3.84 – 3.75 (m, 2H).

^{13}**C NMR** (101 MHz, $CDCl_3$) δ 138.47, 138.34, 138.24, 137.89, 137.44, 134.32, 131.57, 129.09, 128.61, 128.59, 128.56, 128.49, 128.41, 128.20, 128.15, 127.99, 127.94, 127.88, 127.83, 127.68, 127.44, 127.01, 126.92, 126.06, 123.08, 76.73, 75.16, 74.82, 73.31, 73.12, 72.95, 72.70, 72.21, 68.71.
HRMS (ESI-TOF): calc'd for $C_{44}H_{45}BrNO_5^+$ [M+NH_4^+] 746.2476, found 746.2485.

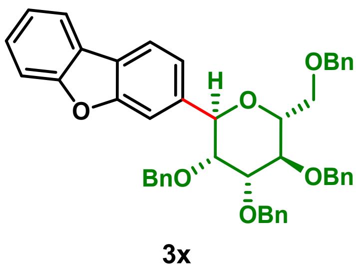
(2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-Tris(benzyloxy)-2-((benzyloxy)methyl)-6-(pyren-2-yl)tetrahydro-2*H*-pyran (3w)



3w

Physical state: colorless oil;
Yield: 48%;
$\mathbf{R_f}$ = 0.4 (silica gel, PE:EtOAc = 12:1);
[α]25 D: +27.9 (c = 0.19, $CHCl_3$);
^{1}**H NMR** (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.6 Hz, 2H), 8.12 (s, 2H), 8.06 (d, *J* = 9.0 Hz, 2H), 8.02 – 7.94 (m, 3H), 7.39 – 7.27 (m, 12H), 7.26 – 7.10 (m, 8H), 5.42 (d, *J* = 6.0 Hz, 1H), 4.73 – 4.63 (m, 4H), 4.60 (dd, *J* = 11.9, 8.2 Hz, 2H), 4.40 (q, *J* = 12.1 Hz, 2H), 4.28 (dd, *J* = 6.0, 3.0 Hz, 1H), 4.16 (q, *J* = 5.4 Hz, 1H), 4.03 – 3.94 (m, 2H), 3.90 (dd, *J* = 10.2, 4.4 Hz, 1H), 3.86 (dd, *J* = 6.2, 2.9 Hz, 1H).
^{13}**C NMR** (101 MHz, $CDCl_3$) δ 138.58, 138.48, 138.33, 138.10, 136.66, 131.24, 128.60, 128.52, 128.49, 128.35, 128.19, 127.95, 127.83, 127.73, 127.66, 127.65, 127.61, 125.99, 125.09, 124.61, 124.24, 123.53, 77.16, 76.74, 75.41, 74.80, 73.88, 73.35, 72.94, 72.25, 69.05.
HRMS (ESI-TOF): calc'd for $C_{50}H_{48}NO_5^+$ [M+NH_4^+] 742.3527, found 742.3525.

3-((2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-Tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)dibenzo[*b*,*d*]furan (3x)



3x

Physical state: colorless oil;

Yield: 30%;

R$_f$ = 0.3 (silica gel, PE:EtOAc = 10:1);

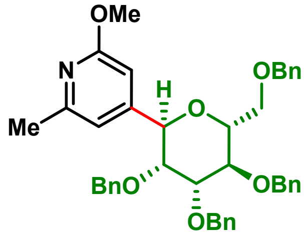
[α]25 D: +50.8 (c = 0.13, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.6 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.60 – 7.53 (m, 2H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.40 – 7.18 (m, 22H), 5.14 (d, *J* = 5.8 Hz, 1H), 4.69 – 4.60 (m, 4H), 4.60 – 4.52 (m, 2H), 4.44 (s, 2H), 4.09 (dd, *J* = 5.9, 2.8 Hz, 1H), 4.02 (q, *J* = 5.4 Hz, 1H), 3.95 (t, *J* = 6.0 Hz, 1H), 3.90 (dd, *J* = 10.4, 6.1 Hz, 1H), 3.82 (dd, *J* = 10.2, 4.2 Hz, 1H), 3.77 (dd, *J* = 6.4, 2.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.65, 156.60, 138.65, 138.53, 138.39, 138.34, 138.19, 128.58, 128.52, 128.49, 128.42, 128.20, 128.13, 127.95, 127.86, 127.81, 127.74, 127.67, 127.23, 124.14, 123.73, 122.83, 121.67, 120.79, 120.51, 111.84, 110.35, 77.00, 76.79, 75.25, 74.58, 73.74, 73.43, 73.38, 72.93, 72.21, 68.95.

HRMS (ESI-TOF): calc'd for $C_{46}H_{46}NO_6^+$ [M+NH_4^+] 708.3320, found 708.3310.

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



3y

Physical state: colorless oil;

Yield: 43%;

R$_f$ = 0.3 (silica gel, PE:EtOAc = 10:1);

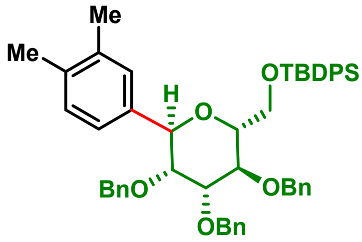
[α]25 D: +38.5 (c = 0.2, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.25 (m, 18H), 7.21 – 7.16 (m, 2H), 6.62 (s, 1H), 6.46 (s, 1H), 4.89 (d, *J* = 5.2 Hz, 1H), 4.70 – 4.58 (m, 4H), 4.57 – 4.48 (m, 4H), 3.96 (dd, *J* = 5.2, 2.9 Hz, 1H), 3.93 – 3.87 (m, 2H), 3.87 (s, 3H), 3.84 – 3.79 (m, 1H), 3.75 (dd, *J* = 10.2, 3.4 Hz, 1H), 3.63 (dd, *J* = 6.5, 2.9 Hz, 1H), 2.38 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.27, 156.64, 150.86, 138.45, 138.27, 138.01, 128.57, 128.53, 128.50, 128.46, 128.16, 128.12, 127.97, 127.88, 127.84, 127.67, 114.03, 104.97, 76.09, 75.10, 74.64, 73.77, 73.40, 72.97, 72.80, 72.19, 69.06, 53.62, 24.35.

HRMS (ESI-TOF): calc'd for $C_{41}H_{44}NO_6^+$ [M+H^+] 646.3163, found 646.3164.

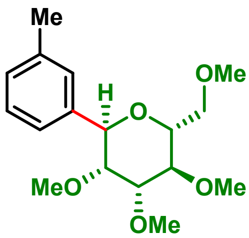
***tert*-Butyldiphenyl(((2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-(3,4-dimethylphenyl)-tetrahydro-2*H*-pyran-2-yl)methoxy)silane (3A)**



3A

Physical state: colorless oil;
Yield: 80%;
$\mathbf{R_f}$ = 0.5 (silica gel, PE:EtOAc = 20:1);
[α]25 D: +40.0 (c = 0.15, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.64 (m, 4H), 7.45 – 7.37 (m, 2H), 7.36 – 7.23 (m, 17H), 7.17 (dd, *J* = 6.7, 2.9 Hz, 2H), 7.06 (s, 1H), 7.01 (d, *J* = 7.8 Hz, 1H), 6.96 (dd, *J* = 7.8, 1.8 Hz, 1H), 4.97 (d, *J* = 5.0 Hz, 1H), 4.72 – 4.59 (m, 3H), 4.57 – 4.46 (m, 3H), 4.13 – 4.05 (m, 2H), 4.03 (t, *J* = 6.7 Hz, 1H), 3.92 (dd, *J* = 10.4, 6.0 Hz, 1H), 3.82 (q, *J* = 5.9 Hz, 1H), 3.75 (dd, *J* = 7.0, 2.9 Hz, 1H), 2.22 (s, 3H), 2.18 (s, 3H), 1.07 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.59, 138.55, 138.51, 136.62, 136.11, 135.89, 135.78, 133.81, 133.68, 129.69, 129.65, 128.51, 128.47, 128.37, 128.17, 128.04, 128.02, 127.96, 127.81, 127.79, 127.73, 127.70, 127.61, 124.27, 76.51, 75.63, 75.03, 73.73, 73.53, 72.61, 72.08, 63.42, 26.99, 19.95, 19.54, 19.42.
HRMS (ESI-TOF): calc'd for $C_{51}H_{60}NO_5Si^+$ [M+NH_4^+] 794.4235, found 794.4234.

(2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-Trimethoxy-2-(methoxymethyl)-6-(m-tolyl)tetrahydro-2*H*-pyran (3B)



3B

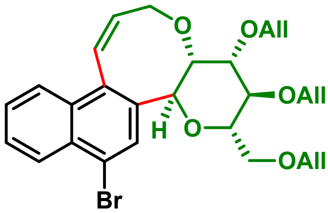
Physical state: colorless oil;
Yield: 67%;
$\mathbf{R_f}$ = 0.3 (silica gel, PE:EtOAc = 5:1);
[α]25 D: +30.5 (c = 0.40, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.18 (m, 3H), 7.08 (d, *J* = 6.3 Hz, 1H), 4.99 (d, *J* = 5.0 Hz, 1H), 3.94 (dd, *J* = 5.0, 3.0 Hz, 1H), 3.77 (td, *J* = 6.0, 4.3 Hz, 1H), 3.72 – 3.64 (m, 2H), 3.57 (t, *J* = 6.7 Hz, 1H), 3.53 (s, 3H), 3.52 – 3.49 (m, 1H), 3.48 (s, 3H),

3.42 (s, 3H), 3.36 (s, 3H), 2.35 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.36, 138.25, 128.51, 128.40, 127.36, 123.75, 79.63, 78.31, 76.71, 73.33, 73.06, 71.61, 59.50, 59.27, 58.21, 58.18, 21.64.

HRMS (ESI-TOF): calc'd for $C_{17}H_{30}NO_5^+$ [M+NH_4^+] 328.2118, found 328.2120.

(4a*S*,5*S*,6*S*,7*S*,8a*S*,*Z*)-10-Bromo-5,6-bis(((*E*)-prop-1-en-1-yl)oxy)-7-((((*E*)-prop-1-en-1-yl)oxy)methyl)-3,4a,5,6,7,8a-hexahydronaphtho[2,1-*d*]pyrano[3,2-*b*]oxocine (3C)



3C

Yield: 31%;

R_f = 0.3 (silica gel, PE:EtOAc = 20:1);

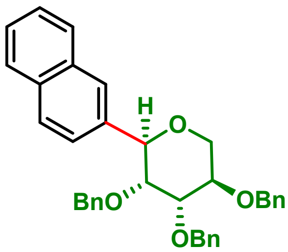
[α]25 D: +56.8 (c = 0.22, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.5 Hz, 2H), 8.13 (d, *J* = 8.6 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 1H), 6.11 – 5.76 (m, 4H), 5.43 – 5.10 (m, 8H), 4.66 (d, *J* = 11.7 Hz, 1H), 4.36 – 3.70 (m, 12H), 3.60 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.27, 134.91, 134.48, 132.44, 131.84, 127.48, 126.94, 126.69, 126.23, 122.82, 117.70, 117.29, 117.12, 74.61, 72.57, 72.08, 70.79.

HRMS (ESI-TOF): calc'd for $C_{28}H_{25}BrNO_5^+$ [M+NH_4^+] 544.1693, found 544.1691.

(2*R*,3*R*,4*S*,5*R*)-3,4,5-Tris(benzyloxy)-2-(naphthalen-2-yl)tetrahydro-2*H*-pyran (3D)



3D

Physical state: white solid;

Melting point: 89–91 °C;

Yield: 74%;

R_f = 0.4 (silica gel, PE:EtOAc = 10:1);

$[\alpha]^{25}_D$: -17.5 (c = 0.10, $CHCl_3$);

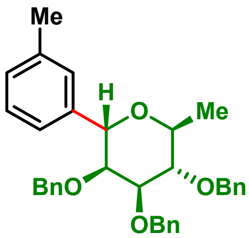
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.91 (m, 1H), 7.90 – 7.76 (m, 3H), 7.62 (dt, *J* =

8.5, 2.2 Hz, 1H), 7.51 – 7.44 (m, 2H), 7.38 – 7.25 (m, 10H), 7.20 – 7.07 (m, 3H), 6.95 – 6.84 (m, 2H), 4.87 (dd, J = 9.6, 2.9 Hz, 1H), 4.83 (dd, J = 12.3, 3.0 Hz, 1H), 4.67 – 4.59 (m, 2H), 4.48 (dd, J = 12.3, 3.0 Hz, 1H), 4.09 – 3.92 (m, 5H), 3.87 (dt, J = 9.6, 2.9 Hz, 1H), 3.61 (t, J = 3.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.72, 138.34, 138.08, 137.69, 133.37, 128.60, 128.52, 128.27, 128.20, 128.03, 127.95, 127.90, 127.83, 127.79, 127.76, 127.71, 127.57, 126.88, 125.92, 125.84, 125.68, 78.38, 77.54, 75.42, 73.80, 73.29, 72.33, 71.06, 65.23.

HRMS (ESI-TOF): calc'd for $C_{36}H_{38}NO_4^+$ [M+NH$_4^+$] 548.2795, found 548.2789.

(2*S*,3*S*,4*R*,5*S*,6*S*)-3,4,5-Tris(benzyloxy)-2-methyl-6-(*m*-tolyl)tetrahydro-2*H*-pyran (3E)



3E

Physical state: colorless oil;

Yield: 72%;

R$_f$ = 0.5 (silica gel, PE:EtOAc = 10:1);

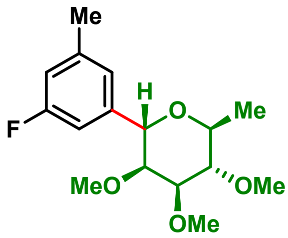
[α]25 D: -40.6 (c = 0.34, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.22 (m, 15H), 7.14 (t, J = 7.6 Hz, 1H), 7.02 (d, J = 7.7 Hz, 2H), 6.94 (d, J = 7.7 Hz, 1H), 5.01 (d, J = 4.2 Hz, 1H), 4.78 (d, J = 11.2 Hz, 1H), 4.68 – 4.55 (m, 5H), 4.13 (d, J = 2.6 Hz, 1H), 3.73 – 3.61 (m, 3H), 2.28 (s, 3H), 1.40 (d, J = 5.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.61, 138.58, 138.44, 138.43, 138.21, 128.52, 128.52, 128.46, 128.23, 128.19, 128.15, 128.00, 127.85, 127.79, 127.76, 127.14, 123.55, 80.46, 78.09, 76.18, 74.39, 73.90, 72.69, 72.22, 70.62, 21.66, 17.96.

HRMS (ESI-TOF): calc'd for $C_{34}H_{40}NO_4^+$ [M+NH$_4^+$] 526.2952, found 526.2945.

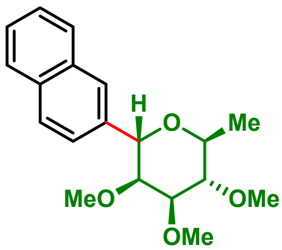
(2*S*,3*S*,4*R*,5*S*,6*S*)-2-(3-Fluoro-5-methylphenyl)-3,4,5-trimethoxy-6-methyltetrahydro-2*H*-pyran (3F)



3F

Physical state: colorless oil;
Yield: 56%;
R_f = 0.3 (silica gel, PE:EtOAc = 5:1);
[α]25 D: -12.5 (c = 0.12, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (s, 1H), 6.92 (d, *J* = 9.9 Hz, 1H), 6.79 (d, *J* = 9.5 Hz, 1H), 4.93 (d, *J* = 5.1 Hz, 1H), 3.86 (dd, *J* = 5.2, 3.1 Hz, 1H), 3.71 (p, *J* = 6.5 Hz, 1H), 3.52 (s, 3H), 3.49 (s, 3H), 3.46 (dd, *J* = 6.8, 3.1 Hz, 1H), 3.37 (s, 3H), 3.31 (t, *J* = 6.5 Hz, 1H), 2.34 (s, 3H), 1.38 (d, *J* = 6.6 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.19 (d, *J* = 245.0 Hz), 141.22 (d, *J* = 7.4 Hz), 140.64 (d, *J* = 8.0 Hz), 122.94 (d, *J* = 2.5 Hz), 115.19 (d, *J* = 21.1 Hz), 110.82 (d, *J* = 22.4 Hz), 81.19, 79.55, 78.58, 72.20 (d, *J* = 2.0 Hz), 70.48, 59.67, 58.31, 58.26, 21.60 (d, *J* = 2.0 Hz), 17.48.
^{19}F NMR (376 MHz, $CDCl_3$) δ -114.0.
HRMS (ESI-TOF): calc'd for $C_{18}H_{27}FNO_4^+$ [$M+NH_4^+$] 316.1919, found 316.1918.

(2*S*,3*S*,4*R*,5*S*,6*S*)-3,4,5-Trimethoxy-2-methyl-6-(naphthalen-2-yl)tetrahydro-2*H*-pyran (3G)

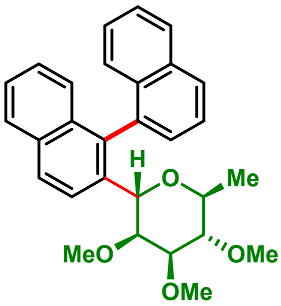


3G

Physical state: colorless oil;
Yield: 58%;
R_f = 0.3 (silica gel, PE:EtOAc = 5:1);
[α]25 D: -32.7(c = 0.30, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.77 (m, 4H), 7.57 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.52 – 7.44 (m, 2H), 5.18 (d, *J* = 4.8 Hz, 1H), 4.09 (dd, *J* = 4.9, 3.1 Hz, 1H), 3.75 (p, *J* = 6.4 Hz, 1H), 3.56 (s, 4H), 3.55 – 3.52 (m, 1H), 3.51 (s, 3H), 3.40 (s, 3H), 3.36 (t, *J* = 6.7 Hz, 1H), 1.43 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.38, 133.38, 132.92, 128.41, 128.10, 127.72, 126.27, 126.13, 125.60, 124.67, 81.47, 79.88, 78.65, 72.83, 70.49, 59.76, 58.42, 58.27, 17.60.
HRMS (ESI-TOF): calc'd for $C_{19}H_{28}NO_4^+$ [M+NH_4^+] 334.2013, found 334.2011.

(2*S*,3*S*,4*R*,5*S*,6*S*)-2-([1,1'-Binaphthalen]-2-yl)-3,4,5-trimethoxy-6-methyltetrahydro-2*H*-pyran (3G')



3G'

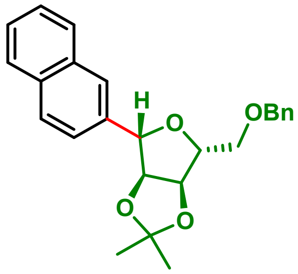
Physical state: colorless oil;
Yield: 16.6% (major diastereoisomer);
R_f = 0.3 (major diastereoisomer, silica gel, PE:EtOAc = 5:1);
[α]25 D: +65.6 (c = 0.34, $CHCl_3$) (major diastereoisomer);
^{1}H NMR (400 MHz, $CDCl_3$) (major diastereoisomer) δ 8.02 – 7.87 (m, 4H), 7.83 (d, *J* = 8.8 Hz, 1H), 7.59 (dd, *J* = 8.2, 7.0 Hz, 1H), 7.49 – 7.39 (m, 3H), 7.29 – 7.26 (m, 2H), 7.24 – 7.18 (m, 1H), 7.10 (d, *J* = 8.6 Hz, 1H), 4.96 (d, *J* = 6.0 Hz, 1H), 4.09 – 3.96 (m, 1H), 3.60 (dd, *J* = 6.0, 2.9 Hz, 1H), 3.49 (dd, *J* = 6.2, 2.9 Hz, 1H), 3.43 (s, 3H), 3.16 (dd, *J* = 6.2, 4.8 Hz, 1H), 2.95 (s, 3H), 2.79 (s, 3H), 1.16 (d, *J* = 6.7 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) (major diastereoisomer) δ 137.48, 136.40, 135.58, 133.69, 133.45, 133.43, 132.96, 128.28, 128.25, 128.11, 127.88, 127.23, 127.18, 126.16, 126.12, 126.04, 125.94, 125.65, 124.72, 81.11, 78.61, 78.26, 71.76, 70.74, 59.10, 57.70, 57.27, 17.37.

Yield: 3.4% (minor diastereoisomer);
R_f = 0.4 (minor diastereoisomer, silica gel, PE:EtOAc = 5:1);
[α]25 D: +62.8 (c = 0.10, $CHCl_3$) (minor diastereoisomer);
^{1}H NMR (400 MHz, $CDCl_3$) (minor diastereoisomer) δ 8.00 (d, *J* = 8.6 Hz, 1H), 7.98 – 7.87 (m, 3H), 7.84 (d, *J* = 8.7 Hz, 1H), 7.62 (dd, *J* = 8.3, 7.0 Hz, 1H), 7.49 (dd, *J* = 7.0, 1.3 Hz, 1H), 7.47 – 7.39 (m, 2H), 7.25 – 7.22 (m, 3H), 4.68 (d, *J* = 8.5 Hz, 1H), 3.93 – 3.86 (m, 1H), 3.75 (dd, *J* = 8.5, 3.1 Hz, 1H), 3.68 (t, *J* = 3.8 Hz, 1H), 3.38 (s, 3H), 3.28 (s, 3H), 3.15 (dd, *J* = 4.5, 2.4 Hz, 1H), 3.02 (s, 3H), 0.54 (d, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) (minor diastereoisomer) δ 137.79, 136.18, 135.75, 133.61, 133.41, 133.22, 133.11, 133.08, 129.17, 128.34, 127.98, 127.93, 127.81,

127.20, 126.82, 126.10, 126.03, 125.92, 125.88, 125.52, 124.49, 79.73, 78.96, 77.73, 70.93, 68.02, 58.26, 58.12, 57.95, 15.49.

HRMS (ESI-TOF): calc'd for $C_{29}H_{34}NO_4^+$ [M+NH$_4^+$] 460.2482, found 460.2476.

(3a*R*,4*R*,6*S*,6a*S*)-4-((Benzyloxy)methyl)-2,2-dimethyl-6-(naphthalen-2-yl)tetrahydro-furo[3,4-*d*][1,3]dioxole (3H)



3H

Physical state: colorless oil;

Yield: 28%; standard conditions.

Yield: 32%; run with HCO_2Na (1.0 eq.) as an additive.

R$_f$ = 0.3 (silica gel, PE:EtOAc = 10:1);

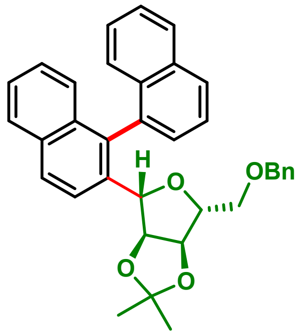
[α]25 D: -47.1 (c = 0.17, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.85 – 7.76 (m, 3H), 7.51 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.49 – 7.43 (m, 2H), 7.39 – 7.27 (m, 5H), 5.08 (d, *J* = 5.0 Hz, 1H), 4.75 (dd, *J* = 6.8, 4.2 Hz, 1H), 4.67 – 4.60 (m, 3H), 4.34 (q, *J* = 4.3 Hz, 1H), 3.81 – 3.72 (m, 2H), 1.66 (s, 3H), 1.37 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.18, 137.47, 133.36, 133.19, 128.55, 128.41, 128.16, 127.86, 127.83, 127.80, 126.24, 125.99, 124.73, 123.94, 114.97, 87.13, 86.25, 83.59, 82.36, 73.76, 70.47, 27.76, 25.73.

HRMS (ESI-TOF): calc'd for $C_{25}H_{30}NO_4^+$ [M+NH$_4^+$] 408.2169, found 408.2168.

(3a*S*,4*S*,6*R*,6a*R*)-4-([1,1'-Binaphthalen]-2-yl)-6-((benzyloxy)methyl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxole (3H')



3H'

Physical state: colorless oil;

Yield: 31.4% (major diastereoisomer);

$\mathbf{R_f}$ = 0.4 (major diastereoisomer, silica gel, PE:EtOAc = 10:1);

[α]25 D: -63.8 (c = 0.13, $CHCl_3$) (major diastereoisomer);

^{1}H NMR (400 MHz, $CDCl_3$) (major diastereoisomer) δ 8.00 – 7.90 (m, 3H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.81 (d, *J* = 8.7 Hz, 1H), 7.56 (dd, *J* = 8.2, 7.0 Hz, 1H), 7.50 – 7.35 (m, 7H), 7.33 (dt, *J* = 7.1, 3.0 Hz, 1H), 7.26 – 7.19 (m, 3H), 7.13 (dd, *J* = 8.5, 1.1 Hz, 1H), 4.71 – 4.55 (m, 5H), 3.99 (q, *J* = 3.6 Hz, 1H), 3.73 (dd, *J* = 10.4, 3.6 Hz, 1H), 3.67 (dd, *J* = 10.4, 4.0 Hz, 1H), 1.24 (s, 3H), 1.13 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) (major diastereoisomer) δ 138.27, 136.39, 136.21, 135.28, 133.49, 133.18, 133.11, 132.84, 130.56, 128.72, 128.58, 128.18, 128.03, 127.95, 127.88, 127.85, 127.29, 126.58, 126.42, 126.19, 125.95, 125.27, 124.17, 114.26, 87.43, 83.01, 82.53, 82.43, 73.76, 70.51, 27.60, 25.97.

Yield: 13.6% (minor diastereoisomer);

$\mathbf{R_f}$ = 0.3 (minor diastereoisomer, silica gel, PE:EtOAc = 10:1);

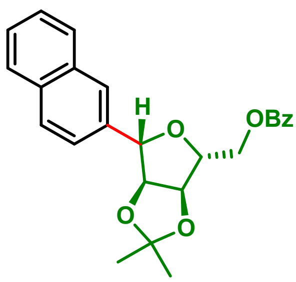
[α]25 D: -54.2 (c = 0.21, $CHCl_3$) (minor diastereoisomer);

^{1}H NMR (400 MHz, $CDCl_3$) (minor diastereoisomer) δ 7.97 – 7.86 (m, 4H), 7.77 (d, *J* = 8.6 Hz, 1H), 7.59 (dd, *J* = 8.3, 6.9 Hz, 1H), 7.47 – 7.40 (m, 3H), 7.40 – 7.27 (m, 5H), 7.26 – 7.17 (m, 3H), 7.14 (dd, *J* = 8.5, 1.1 Hz, 1H), 4.67 – 4.58 (m, 3H), 4.55 – 4.47 (m, 2H), 4.06 – 4.00 (m, 1H), 3.68 (dd, *J* = 10.4, 3.6 Hz, 1H), 3.59 (dd, *J* = 10.4, 4.3 Hz, 1H), 0.95 (s, 3H), 0.55 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) (minor diastereoisomer) δ 138.28, 137.11, 136.26, 135.68, 134.07, 133.69, 133.22, 133.14, 128.57, 128.10, 127.94, 127.88, 127.85, 127.83, 127.59, 127.47, 127.31, 126.22, 126.00, 125.88, 125.83, 125.55, 124.23, 113.69, 86.51, 82.84, 82.63, 82.21, 73.73, 70.54, 26.64, 25.74.

HRMS (ESI-TOF): calc'd for $C_{35}H_{36}NO_4^+$ [M+NH_4^+] 534.2639, found 534.2634.

((3a*R*,4*R*,6*S*,6a*S*)-2,2-Dimethyl-6-(naphthalen-2-yl)tetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)methyl benzoate (3l)



3l

Physical state: colorless oil;

Yield: 30%;

$\mathbf{R_f}$ = 0.4 (silica gel, PE:EtOAc = 10:1);

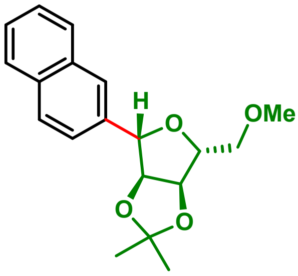
[α]25 D: -84.7 (c = 0.17, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.93 (m, 2H), 7.87 (s, 1H), 7.84 – 7.77 (m, 2H), 7.77 – 7.71 (m, 1H), 7.57 – 7.42 (m, 4H), 7.41 – 7.33 (m, 2H), 5.17 (d, *J* = 4.8 Hz, 1H), 4.81 (dd, *J* = 6.7, 4.1 Hz, 1H), 4.74 – 4.66 (m, 2H), 4.59 (dd, *J* = 11.9, 4.4 Hz, 1H), 4.52 (q, *J* = 4.0 Hz, 1H), 1.69 (s, 3H), 1.39 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.48, 137.20, 133.35, 133.28, 133.17, 129.86, 129.80, 128.53, 128.13, 127.79, 126.33, 126.07, 124.46, 123.64, 115.15, 87.30, 86.28, 82.33, 82.15, 64.72, 27.76, 25.75.

HRMS (ESI-TOF): calc'd for $C_{25}H_{28}NO_5^+$ [M+NH_4^+] 422.1962, found 422.1956.

(3a*R*,4*R*,6*S*,6a*S*)-4-(Methoxymethyl)-2,2-dimethyl-6-(naphthalen-2-yl)tetrahydro-furo[3,4-*d*][1,3]dioxole (3J)



3J

Physical state: colorless oil;

Yield: 30%; run with HCOONa (1.0 eq.) as an additive.

R_f = 0.3 (silica gel, PE:EtOAc = 10:1);

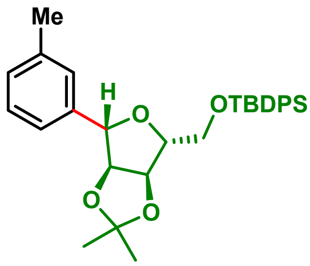
[α]25 D: 27.7 (c = 0.13, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.74 (m, 4H), 7.57 – 7.41 (m, 3H), 5.06 (d, *J* = 4.9 Hz, 1H), 4.70 (dd, *J* = 6.9, 4.3 Hz, 1H), 4.63 (t, *J* = 6.0 Hz, 1H), 4.28 (q, *J* = 4.7 Hz, 1H), 3.68 (d, *J* = 4.8 Hz, 2H), 3.46 (s, 3H), 1.66 (s, 3H), 1.37 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.27, 133.35, 133.20, 128.45, 128.17, 127.81, 126.26, 126.02, 124.76, 123.91, 115.19, 87.05, 86.22, 83.39, 82.35, 73.07, 59.71, 27.70, 25.69.

HRMS (ESI-TOF): calc'd for $C_{19}H_{23}O_4^+$ [M+H^+] 315.1591, found315.1588.

***tert*-Butyl(((3a*R*,4*R*,6*S*,6a*S*)-2,2-dimethyl-6-(*m*-tolyl)tetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)methoxy)diphenylsilane (3K)**



3K

Physical state: colorless oil;

Yield: 38%;

R_f = 0.4 (silica gel, PE:EtOAc = 20:1);

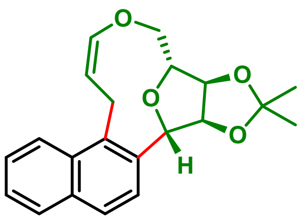
[α]25 D: +8.0 (c = 0.10, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.65 (m, 4H), 7.47 – 7.32 (m, 6H), 7.26 (d, *J* = 2.3 Hz, 2H), 7.26 – 7.17 (m, 3H), 7.12 – 7.04 (m, 1H), 4.86 (d, *J* = 5.4 Hz, 1H), 4.81 (dd, *J* = 6.7, 3.9 Hz, 1H), 4.53 (dd, *J* = 6.7, 5.4 Hz, 1H), 4.19 (q, *J* = 3.7 Hz, 1H), 3.95 (dd, *J* = 11.3, 3.5 Hz, 1H), 3.88 (dd, *J* = 11.3, 3.8 Hz, 1H), 2.31 (s, 3H), 1.62 (s, 3H), 1.36 (s, 3H), 1.07 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.07, 138.19, 135.81, 133.43, 133.37, 129.89, 129.84, 128.58, 128.43, 127.88, 127.84, 126.49, 123.08, 114.65, 87.23, 85.91, 84.44, 81.75, 64.09, 27.81, 26.97, 25.76, 21.54, 19.43.

HRMS (ESI-TOF): calc'd for $C_{31}H_{42}NO_4Si^+$ [M+NH_4^+] 520.2878, found 520.2875.

(6*R*,6a*R*,9a*S*,10*S*,*Z*)-8,8-Dimethyl-1,5,6,6a,9a,10-hexahydro-6,10-epoxy[1,3]-dioxolo[4,5-*d*]naphtho[2,1-*g*][1]oxacycloundecine (3L)



3L

Physical state: colorless oil;

Yield: 32%;

R_f = 0.3 (silica gel, PE:EtOAc = 10:1);

[α]25 D: +65.0 (c = 0.14, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.5 Hz, 1H), 7.83 (d, *J* = 7.5 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.58 – 7.51 (m, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 1H), 6.19 (dd, *J* = 5.4, 2.0 Hz, 1H), 5.57 (dd, *J* = 7.4, 4.9 Hz, 1H), 5.22 (dd, *J* = 7.4, 4.0 Hz, 1H), 5.19 – 5.12 (m, 2H), 4.29 (dd, *J* = 4.9, 2.0 Hz, 1H), 4.16 (d, *J* = 12.8 Hz, 1H), 4.06 (dd, *J* = 14.2, 11.4 Hz, 1H), 3.83 (dd, *J* = 12.8, 2.2 Hz, 1H), 3.65 (dt, *J* = 14.2, 2.8

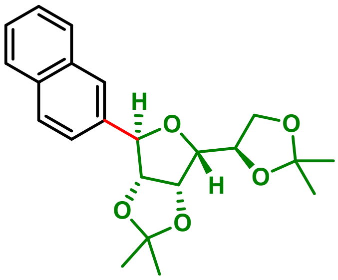
Hz, 1H), 1.65 (s, 3H), 1.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.43, 135.21, 134.93, 134.08, 133.17, 128.85, 127.02, 126.52, 125.91, 123.83, 116.22, 115.35, 92.13, 87.55, 87.18, 82.32, 69.17, 27.36, 25.57, 25.33.

HRMS (ESI-TOF): calc'd for $C_{21}H_{23}O_4^+$ [M+H$^+$] 339.1591, found 339.1585.

Note: The configuration of Compound **3J** was determined by 2D-HSQC and 2D-NOESY spectrum analysis.

(3a*S*,4*R*,6*R*,6a*R*)-4-((*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyl-6-(naphthalen-2-yl)tetrahydrofuro[3,4-*d*][1,3]dioxole (3M)



3M

Physical state: colorless oil;

Yield: 65%;

R$_f$ = 0.3 (silica gel, PE:EtOAc = 10:1);

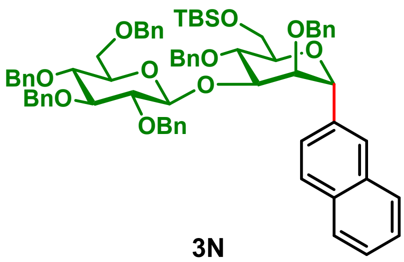
[α]25 D: +23.8 (c = 0.39, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.81 (m, 3H), 7.76 (s, 1H), 7.54 – 7.46 (m, 2H), 7.45 (dd, *J* = 8.5, 1.8 Hz, 1H), 5.35 (s, 1H), 5.09 (dd, *J* = 6.1, 1.2 Hz, 1H), 4.80 (dd, *J* = 6.0, 3.8 Hz, 1H), 4.57 – 4.51 (m, 1H), 4.30 – 4.21 (m, 2H), 3.98 (dd, *J* = 7.5, 3.7 Hz, 1H), 1.61 (s, 3H), 1.45 (s, 3H), 1.41 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.00, 133.28, 132.83, 128.76, 128.14, 127.80, 126.55, 126.27, 124.22, 123.72, 113.13, 109.41, 87.48, 85.37, 81.72, 81.32, 73.70, 67.24, 27.05, 26.42, 25.36, 25.00.

HRMS (ESI-TOF): calc'd for $C_{22}H_{26}O_5^+$ [M+NH$_4^+$] 393.1672, found 393.1672.

(((2*R*,3*R*,4*R*,5*R*,6*R*)-3,5-Bis(benzyloxy)-6-(naphthalen-2-yl)-4-(((2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)oxy)-tetrahydro-2*H*-pyran-2-yl)methoxy)(*tert*-butyl)dimethylsilane (3N)



3N

Physical state: colorless oil;

Yield: 55%;

R$_f$ = 0.5 (silica gel, PE:EtOAc = 6:1);

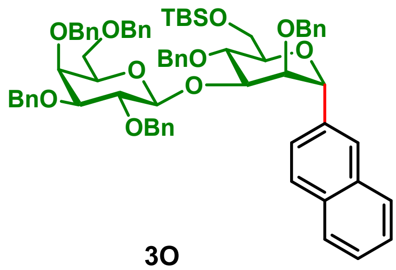
[α]25 D: +27.9 (c = 0.34, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.77 (m, 2H), 7.75 (d, *J* = 8.6 Hz, 1H), 7.73 – 7.68 (m, 1H), 7.53 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.48 – 7.42 (m, 2H), 7.42 – 7.38 (m, 2H), 7.32 – 7.22 (m, 21H), 7.21 – 7.17 (m, 2H), 7.17 – 7.13 (m, 1H), 7.12 – 7.07 (m, 2H), 7.03 – 6.94 (m, 2H), 5.25 (d, *J* = 10.7 Hz, 1H), 5.01 (d, *J* = 8.5 Hz, 1H), 4.95 (d, *J* = 10.9 Hz, 1H), 4.86 – 4.73 (m, 3H), 4.62 – 4.51 (m, 4H), 4.50 – 4.41 (m, 2H), 4.23 – 4.12 (m, 3H), 4.10 – 4.03 (m, 2H), 4.03 – 3.97 (m, 2H), 3.93 (q, *J* = 7.9 Hz, 1H), 3.69 – 3.55 (m, 4H), 3.53 – 3.46 (m, 1H), 3.45 – 3.38 (m, 1H), 0.87 (s, 9H), 0.04 (s, 3H), 0.01 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.78, 138.75, 138.74, 138.26, 138.21, 138.16, 137.43, 133.33, 133.20, 128.56, 128.52, 128.49, 128.46, 128.43, 128.24, 128.20, 128.15, 128.10, 127.96, 127.93, 127.79, 127.76, 127.74, 127.71, 127.68, 127.54, 126.50, 125.90, 125.80, 125.50, 104.38, 84.77, 82.75, 77.99, 77.60, 76.92, 76.87, 75.95, 75.93, 75.16, 74.89, 74.81, 73.56, 72.42, 72.24, 72.11, 69.35, 62.20, 26.14, 18.51, -4.93, -4.99.

HRMS (ESI-TOF): calc'd for $C_{70}H_{82}NO_{10}Si^+$ [M+NH_4^+] 1124.5703, found 1124.5707.

(((2*R*,3*R*,4*R*,5*R*,6*R*)-3,5-Bis(benzyloxy)-6-(naphthalen-2-yl)-4-(((2*S*,3*R*,4*S*,5*S*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)oxy)-tetrahydro-2*H*-pyran-2-yl)methoxy)(*tert*-butyl)dimethylsilane (3O)



3O

Physical state: colorless oil;

Yield: 60%;

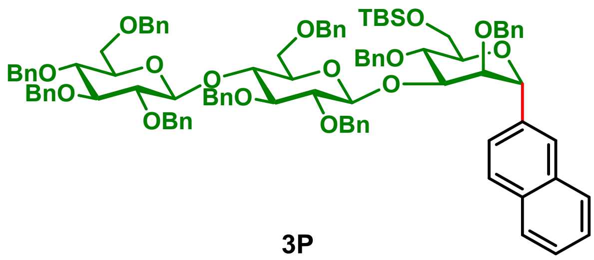
R$_f$ = 0.5 (silica gel, PE:EtOAc = 6:1);

[α]25 D: +19.7 (c = 0.29, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.63 (m, 4H), 7.51 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.48 – 7.38 (m, 4H), 7.37 – 7.18 (m, 23H), 7.13 (t, *J* = 7.2 Hz, 1H), 7.07 (t, *J* = 7.3 Hz, 2H), 6.99 (d, *J* = 7.2 Hz, 2H), 5.19 (d, *J* = 10.8 Hz, 1H), 5.04 (d, *J* = 8.1 Hz, 1H), 4.96 (d, *J* = 11.4 Hz, 1H), 4.84 – 4.70 (m, 3H), 4.63 – 4.50 (m, 4H), 4.43 – 4.33 (m, 2H), 4.25 – 4.12 (m, 3H), 4.07 – 3.92 (m, 5H), 3.89 (d, *J* = 2.9 Hz, 1H), 3.84 (dd, *J* = 9.7, 7.6 Hz,

1H), 3.60 – 3.44 (m, 3H), 3.40 (dd, J = 8.3, 5.0 Hz, 1H), 0.82 (s, 9H), -0.02 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 139.09, 138.98, 138.72, 138.30, 137.97, 137.37, 133.33, 133.16, 128.59, 128.48, 128.41, 128.34, 128.31, 128.27, 128.18, 128.00, 127.98, 127.86, 127.81, 127.78, 127.74, 127.70, 127.67, 127.63, 127.59, 127.51, 127.42, 126.46, 125.88, 125.78, 125.47, 104.58, 82.29, 79.83, 77.36, 77.02, 76.52, 75.88, 75.11, 74.86, 74.00, 73.65, 73.35, 73.30, 72.62, 72.23, 71.95, 68.79, 62.24, 26.11, 18.43, -5.06, -5.12.
HRMS (ESI-TOF): calc'd for $C_{70}H_{82}NO_{10}Si^+$ [M+NH_4^+] 1124.5703, found 1124.5711.

(((2*R*,3*R*,4*R*,5*R*,6*R*)-3,5-Bis(benzyloxy)-4-(((2*S*,3*R*,4*S*,5*R*,6*R*)-3,4-bis(benzyloxy)-6-((benzyloxy)methyl)-5-(((2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)-methyl)tetrahydro-2*H*-pyran-2-yl)oxy)tetrahydro-2*H*-pyran-2-yl)oxy)-6-(naphthalen-2-yl)tetrahydro-2*H*-pyran-2-yl)methoxy)(*tert*-butyl)dimethylsilane (3P)



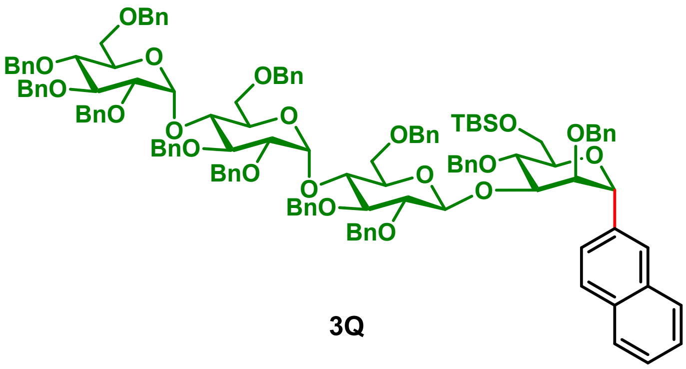
3P

Physical state: colorless oil;
Yield: 78%;
R_f = 0.5 (silica gel, PE:EtOAc = 6:1);
[α]25 D: +33.2 (c = 0.25, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.79 (m, 1H), 7.79 – 7.71 (m, 2H), 7.72 – 7.66 (m, 1H), 7.53 (d, J = 8.5 Hz, 1H), 7.48 – 7.41 (m, 2H), 7.40 – 7.34 (m, 4H), 7.32 – 7.26 (m, 12H), 7.26 – 7.15 (m, 23H), 7.14 – 7.05 (m, 4H), 7.00 (d, J = 7.4 Hz, 2H), 5.17 (d, J = 10.7 Hz, 1H), 5.08 (d, J = 11.3 Hz, 1H), 5.03 (d, J = 8.2 Hz, 1H), 4.89 (d, J = 10.9 Hz, 1H), 4.85 – 4.72 (m, 6H), 4.61 – 4.49 (m, 5H), 4.46 – 4.38 (m, 3H), 4.32 (d, J = 12.0 Hz, 1H), 4.24 – 4.12 (m, 3H), 4.10 – 3.97 (m, 4H), 3.94 (t, J = 3.6 Hz, 1H), 3.89 (q, J = 7.9 Hz, 1H), 3.78 (dd, J = 11.1, 4.1 Hz, 1H), 3.73 – 3.64 (m, 2H), 3.63 – 3.53 (m, 3H), 3.52 – 3.43 (m, 2H), 3.40 (t, J = 8.5 Hz, 1H), 3.35 – 3.30 (m, 1H), 3.26 (dd, J = 10.3, 3.8 Hz, 1H), 0.84 (s, 9H), 0.01 (s, 3H), -0.01 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 139.45, 138.83, 138.71, 138.66, 138.57, 138.38, 138.22, 138.18, 137.34, 133.31, 133.17, 128.51, 128.50, 128.47, 128.47, 128.44, 128.38, 128.34, 128.22, 128.17, 128.15, 128.08, 127.97, 127.93, 127.90, 127.80, 127.71, 127.70, 127.66, 127.57, 127.49, 127.25, 126.45, 125.90, 125.80, 125.46, 104.14, 102.62, 85.09, 82.95, 82.89, 82.13, 78.13, 77.52, 76.90, 76.74, 75.79, 75.28,

75.18, 75.01, 74.90, 73.42, 73.32, 72.39, 72.17, 72.07, 69.02, 68.33, 62.21, 26.10, 18.47, -4.94, -5.01.

HRMS (ESI-TOF): calc'd for $C_{97}H_{106}NaO_{15}Si^+$ [M+Na$^+$] 1561.7193, found 1561.7190.

(((2*R*,3*R*,4*R*,5*R*,6*R*)-3,5-Bis(benzyloxy)-4-(((2*S*,3*R*,4*S*,5*R*,6*R*)-3,4-bis(benzyloxy)-6-((benzyloxy)methyl)-5-(((2*R*,3*R*,4*S*,5*R*,6*R*)-3,4-bis(benzyloxy)-6-((benzyloxy)methyl)-5-(((2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)oxy)tetrahydro-2*H*-pyran-2-yl)oxy)tetrahydro-2*H*-pyran-2-yl)oxy)-6-(naphthalen-2-yl)tetrahydro-2*H*-pyran-2-yl)methoxy)(*tert*-butyl)dimethylsilane (3Q)



3Q

Physical state: colorless oil;

Yield: 77%;

R$_f$ = 0.4 (silica gel, PE:EtOAc = 6:1);

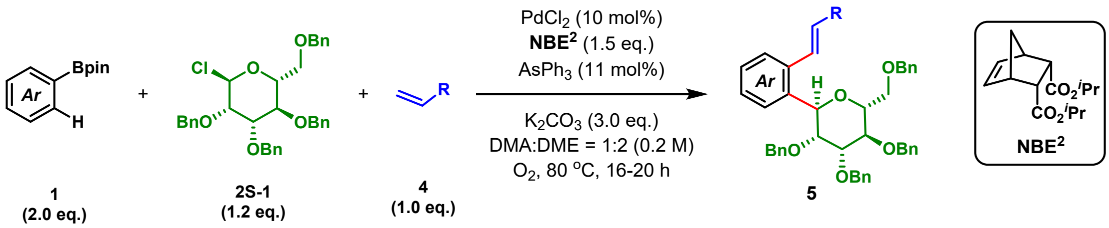
[α]25 D: +73.3 (c = 0.12, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.79 (m, 1H), 7.78 (s, 1H), 7.75 (d, *J* = 8.6 Hz, 1H), 7.72 (dd, *J* = 6.8, 2.9 Hz, 1H), 7.53 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.47 – 7.41 (m, 2H), 7.34 – 7.28 (m, 3H), 7.26 – 7.06 (m, 55H), 7.01 – 6.97 (m, 2H), 5.67 (d, *J* = 3.5 Hz, 1H), 5.62 (d, *J* = 3.6 Hz, 1H), 5.24 (d, *J* = 10.6 Hz, 1H), 4.99 (t, *J* = 9.6 Hz, 2H), 4.92 (d, *J* = 11.7 Hz, 1H), 4.87 – 4.80 (m, 2H), 4.80 – 4.73 (m, 3H), 4.67 (d, *J* = 10.6 Hz, 1H), 4.62 (d, *J* = 7.6 Hz, 1H), 4.58 – 4.49 (m, 4H), 4.49 – 4.43 (m, 4H), 4.43 – 4.33 (m, 5H), 4.28 (d, *J* = 12.1 Hz, 1H), 4.19 – 4.12 (m, 3H), 4.11 – 4.04 (m, 4H), 4.04 – 3.98 (m, 2H), 3.97 – 3.88 (m, 4H), 3.84 – 3.78 (m, 2H), 3.77 – 3.72 (m, 2H), 3.68 (d, *J* = 9.2 Hz, 1H), 3.66 – 3.56 (m, 2H), 3.56 – 3.44 (m, 6H), 3.40 (d, *J* = 8.9 Hz, 1H), 0.86 (s, 9H), 0.04 (s, 3H), 0.01 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.97, 138.92, 138.88, 138.72, 138.60, 138.53, 138.46, 138.29, 138.21, 138.12, 138.05, 137.85, 137.37, 133.31, 133.20, 128.48, 128.45, 128.43, 128.41, 128.36, 128.29, 128.27, 128.19, 128.15, 127.99, 127.95, 127.80, 127.77, 127.74, 127.70, 127.66, 127.62, 127.59, 127.50, 127.29, 127.13, 126.90, 126.68, 126.52, 125.90, 125.80, 125.48, 104.21, 97.04, 96.46, 84.75, 82.53, 82.20, 81.76, 79.72, 79.50, 77.77, 77.66, 77.41, 76.97, 75.86, 75.59, 75.12, 74.61, 74.17, 74.11, 73.62, 73.48, 73.38, 73.20, 73.15, 73.09, 72.94, 72.34, 72.22, 72.17, 71.11, 70.99, 69.18, 69.02, 68.31, 62.16, 26.15, 18.52, -4.90, -5.00.

HRMS (ESI-TOF): calc'd for $C_{124}H_{134}NaO_{20}Si^+$ [M+Na$^+$] 1993.9130, found 1993.9126.

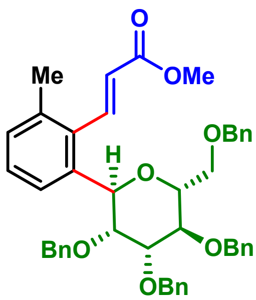
9. General procedure for the synthesis of C-aryl glycosides 5



To a 10 mL oven-dried Schlenk tube equipped with a magnetic stir bar was charged with aryl boron compound **1** (0.2 mmol, 2.0 equiv), glycosyl chloride **2S-1** (67.1 mg, 0.12 mmol, 1.2 equiv), olefin **4** (0.1 mmol, 1.0 equiv), $PdCl_2$ (1.8 mg, 0.01 mmol, 0.1 equiv), $AsPh_3$ (3.4 mg, 0.011 mmol, 0.11 equiv), **NBE^2** (40.0 mg, 0.15 mmol, 1.5 equiv), K_2CO_3 (41.5 mg, 0.3 mmol, 3.0 equiv) and DMA:DME = 1:2 (0.5 mL) under O_2. The reaction was stirred at 80 °C for 16-20 h until the completion of the reaction (monitored by TLC). Then the mixture was filtered through a thin pad of celite eluting with ethyl acetate (15 mL), and the filtrate was sequentially washed with water, brine, dried over Na_2SO_4. After concentrated in vacuo, the residue was purified by column chromatography on silica gel to give the desired product.

10. Characterization data for C-aryl glycosides 5

Methyl (*E*)-3-(2-methyl-6-((2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)phenyl)acrylate (5a)



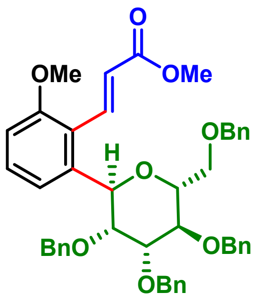
5a

Physical state: colorless oil;

Yield: 85%;

R$_f$ = 0.3 (silica gel, PE:EtOAc = 6:1);
[α]25 D: -12.5 (c = 0.12, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 16.3 Hz, 1H), 7.41 (d, *J* = 8.3 Hz, 1H), 7.37 – 7.20 (m, 19H), 7.17 (d, *J* = 7.4 Hz, 1H), 7.03 – 6.94 (m, 2H), 6.24 (d, *J* = 16.3 Hz, 1H), 5.29 (d, *J* = 8.8 Hz, 1H), 4.72 (d, *J* = 12.2 Hz, 1H), 4.62 – 4.54 (m, 2H), 4.53 – 4.41 (m, 3H), 4.23 – 4.10 (m, 3H), 4.01 – 3.96 (m, 1H), 3.94 (t, *J* = 3.5 Hz, 1H), 3.88 – 3.78 (m, 3H), 3.69 (s, 3H), 2.32 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.11, 143.59, 138.71, 138.54, 138.30, 138.24, 137.88, 136.19, 135.39, 129.74, 128.53, 128.50, 128.40, 128.35, 128.25, 127.85, 127.82, 127.76, 127.69, 127.66, 127.57, 127.52, 125.36, 124.93, 78.24, 75.39, 75.32, 75.21, 73.31, 73.14, 71.97, 71.95, 68.59, 68.54, 51.61, 21.09.
HRMS (ESI-TOF): calc'd for $C_{45}H_{46}NaO_7^+$ [M+Na$^+$]721.3136, found 721.3126.

Methyl (*E*)-3-(2-methoxy-6-((2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)phenyl)acrylate (5b)

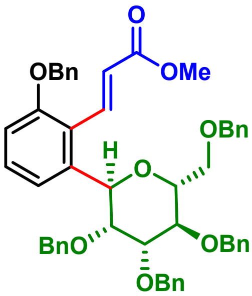


5b

Physical state: colorless oil;
Yield: 81%;
R$_f$ = 0.3 (silica gel, PE:EtOAc = 5:1);
[α]25 D: -44.4 (c = 0.48, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 16.3 Hz, 1H), 7.33 – 7.18 (m, 20H), 7.04 – 6.98 (m, 2H), 6.86 (d, *J* = 8.1 Hz, 1H), 6.66 (d, *J* = 16.2 Hz, 1H), 5.37 (d, *J* = 8.7 Hz, 1H), 4.72 (d, *J* = 12.3 Hz, 1H), 4.59 – 4.53 (m, 2H), 4.50 – 4.42 (m, 3H), 4.20 – 4.11 (m, 3H), 3.98 – 3.93 (m, 1H), 3.91 (t, *J* = 3.4 Hz, 1H), 3.89 – 3.86 (m, 1H), 3.85 (s, 3H), 3.84 – 3.78 (m, 2H), 3.65 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.94, 158.17, 140.36, 139.34, 138.69, 138.55, 138.30, 138.26, 129.92, 128.53, 128.41, 128.40, 128.23, 127.86, 127.82, 127.73, 127.69, 127.58, 127.56, 127.47, 124.30, 123.89, 120.17, 110.16, 78.19, 75.48, 75.39, 75.21, 73.29, 73.20, 71.94, 68.44, 68.28, 55.80, 51.52.
HRMS (ESI-TOF): calc'd for $C_{45}H_{46}NaO_8^+$ [M+Na$^+$] 737.3085, found 737.3083.

Methyl (*E*)-3-(2-(benzyloxy)-6-((2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-

((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)phenyl)acrylate (5c)



5c

Physical state: colorless oil;

Yield: 82%;

$\mathbf{R_f}$ = 0.3 (silica gel, PE:EtOAc = 5:1);

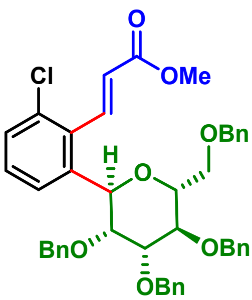
[α]25 D: -43.5 (c = 0.54, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 16.3 Hz, 1H), 7.40 – 7.22 (m, 21H), 7.20 – 7.16 (m, 4H), 7.03 – 6.96 (m, 2H), 6.87 (dd, *J* = 7.9, 1.5 Hz, 1H), 6.68 (d, *J* = 16.2 Hz, 1H), 5.38 (d, *J* = 8.7 Hz, 1H), 5.15 (s, 2H), 4.72 (d, *J* = 12.3 Hz, 1H), 4.60 – 4.53 (m, 2H), 4.51 – 4.42 (m, 3H), 4.21 – 4.11 (m, 3H), 3.95 (dd, *J* = 8.7, 2.6 Hz, 1H), 3.92 (t, *J* = 3.4 Hz, 1H), 3.89 – 3.78 (m, 3H), 3.66 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.86, 157.02, 140.44, 139.37, 138.68, 138.54, 138.29, 138.24, 136.96, 129.80, 128.71, 128.53, 128.41, 128.23, 127.94, 127.86, 127.82, 127.74, 127.70, 127.59, 127.56, 127.47, 127.08, 124.93, 124.18, 120.52, 112.10, 78.19, 75.47, 75.32, 75.20, 73.29, 73.19, 71.94, 71.91, 70.63, 68.43, 68.29, 51.51.

HRMS (ESI-TOF): calc'd for $C_{51}H_{54}NO_8^+$ [M+NH_4^+] 808.3844, found 808.3843.

Methyl (*E*)-3-(2-chloro-6-((2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)-methyl)tetrahydro-2*H*-pyran-2-yl)phenyl)acrylate (5d)



5d

Physical state: colorless oil;

Yield: 65%;

$\mathbf{R_f}$ = 0.4 (silica gel, PE:EtOAc = 5:1);

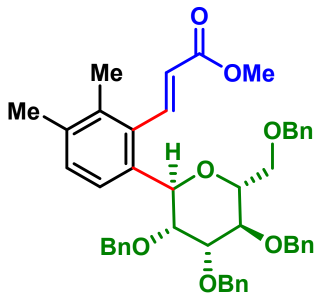
[α]25 D: -113.3 (c = 0.10, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 16.2 Hz, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.39 – 7.20 (m, 20H), 6.99 – 6.88 (m, 2H), 6.46 (d, *J* = 16.3 Hz, 1H), 5.28 (d, *J* = 9.1 Hz, 1H), 4.69 (d, *J* = 12.2 Hz, 1H), 4.61 – 4.52 (m, 2H), 4.51 – 4.40 (m, 3H), 4.25 – 4.15 (m, 2H), 4.08 (d, *J* = 12.0 Hz, 1H), 3.95 – 3.89 (m, 2H), 3.87 – 3.82 (m, 1H), 3.81 – 3.78 (m, 1H), 3.78 – 3.72 (m, 1H), 3.69 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.83, 140.87, 140.49, 138.53, 138.41, 138.17, 137.82, 134.40, 133.56, 129.43, 129.03, 128.59, 128.44, 128.35, 127.92, 127.85, 127.82, 127.71, 127.66, 126.49, 126.40, 78.28, 75.64, 75.06, 74.68, 73.30, 73.22, 71.83, 71.82, 68.24, 67.99, 51.74.

HRMS (ESI-TOF): calc'd for $C_{44}H_{43}ClNaO_7^+$ [M+Na$^+$] 741.2590, found 741.2590.

Methyl (*E*)-3-(2,3-dimethyl-6-((2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)-methyl)tetrahydro-2*H*-pyran-2-yl)phenyl)acrylate (5e)



5e

Physical state: colorless oil;

Yield: 62%;

R$_f$ = 0.4 (silica gel, PE:EtOAc = 5:1);

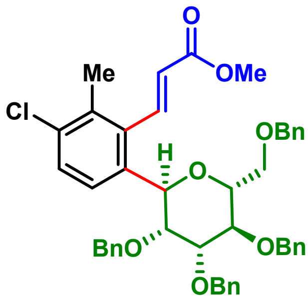
[α]25 D: -35.6 (c = 0.52, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 16.3 Hz, 1H), 7.35 – 7.27 (m, 9H), 7.26 – 7.19 (m, 10H), 7.10 (d, *J* = 7.9 Hz, 1H), 7.05 – 6.98 (m, 2H), 6.14 (d, *J* = 16.3 Hz, 1H), 5.22 (d, *J* = 8.5 Hz, 1H), 4.69 (d, *J* = 12.2 Hz, 1H), 4.59 – 4.53 (m, 2H), 4.51 – 4.41 (m, 3H), 4.26 – 4.15 (m, 2H), 4.10 (td, *J* = 6.6, 2.3 Hz, 1H), 3.97 (dd, *J* = 8.5, 2.7 Hz, 1H), 3.94 – 3.90 (m, 1H), 3.83 (dd, *J* = 4.5, 2.3 Hz, 1H), 3.81 (d, *J* = 6.6 Hz, 2H), 3.68 (s, 3H), 2.30 (s, 3H), 2.20 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.10, 144.81, 138.75, 138.59, 138.38, 136.46, 135.69, 135.12, 134.35, 129.90, 128.53, 128.41, 128.40, 128.24, 127.87, 127.81, 127.71, 127.69, 127.57, 127.55, 127.50, 124.89, 124.85, 77.97, 75.65, 75.28, 75.20, 73.34, 73.08, 72.07, 72.00, 69.05, 68.70, 51.62, 20.62, 17.08.

HRMS (ESI-TOF): calc'd for $C_{46}H_{52}NO_7^+$ [M+NH$_4^+$] 730.3738, found 730.3744.

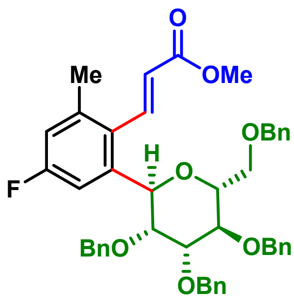
Methyl (*E*)-3-(3-chloro-2-methyl-6-((2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)phenyl)acrylate (5f)



5f

Physical state: colorless oil;
Yield: 66%;
$\mathbf{R_f}$ = 0.4 (silica gel, PE:EtOAc = 7:1);
[α]25 D: -28.7 (c = 0.54, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 16.3 Hz, 1H), 7.35 – 7.19 (m, 20H), 6.95 (dd, *J* = 7.2, 2.3 Hz, 2H), 6.16 (d, *J* = 16.3 Hz, 1H), 5.18 (d, *J* = 8.7 Hz, 1H), 4.68 (d, *J* = 12.2 Hz, 1H), 4.61 – 4.52 (m, 2H), 4.51 – 4.39 (m, 3H), 4.22 (d, *J* = 12.0 Hz, 1H), 4.17 (t, *J* = 6.7 Hz, 1H), 4.09 (d, *J* = 12.1 Hz, 1H), 3.93 – 3.87 (m, 2H), 3.85 – 3.78 (m, 2H), 3.75 (dd, *J* = 10.0, 6.7 Hz, 1H), 3.68 (s, 3H), 2.33 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.73, 143.24, 138.58, 138.45, 138.20, 137.95, 137.39, 136.56, 134.33, 133.58, 129.05, 128.56, 128.43, 128.42, 128.29, 127.88, 127.84, 127.81, 127.69, 127.63, 127.61, 126.26, 125.91, 78.07, 75.44, 75.10, 74.82, 73.31, 73.16, 71.88, 71.82, 68.37, 68.24, 51.72, 17.88.
HRMS (ESI-TOF): calc'd for $C_{45}H_{49}ClNaO_7^+$ [M+Na$^+$] 750.3192, found 750.3192.

Methyl (*E*)-3-(4-fluoro-2-methyl-6-((2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)phenyl)acrylate (5g)



5g

Physical state: colorless oil;
Yield: 76%;
$\mathbf{R_f}$ = 0.4 (silica gel, PE:EtOAc = 7:1);
[α]25 D: -54.4 (c = 0.54, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 16.2 Hz, 1H), 7.37 – 7.20 (m, 18H), 7.15 (dd, *J* = 9.9, 2.7 Hz, 1H), 7.00 – 6.92 (m, 2H), 6.88 (dd, *J* = 9.0, 2.7 Hz, 1H), 6.25 (d, *J*

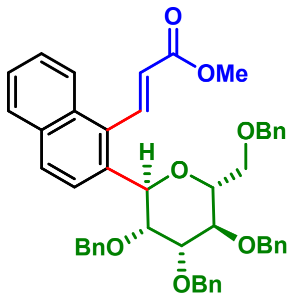
= 16.3 Hz, 1H), 5.27 (d, J = 9.2 Hz, 1H), 4.71 (d, J = 12.2 Hz, 1H), 4.61 – 4.52 (m, 2H), 4.51 – 4.40 (m, 3H), 4.25 – 4.17 (m, 2H), 4.08 (d, J = 12.0 Hz, 1H), 3.93 (t, J = 3.3 Hz, 1H), 3.90 – 3.82 (m, 2H), 3.80 (dd, J = 4.0, 1.5 Hz, 1H), 3.75 (dd, J = 10.0, 6.8 Hz, 1H), 3.67 (s, 3H), 2.31 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.05, 162.54 (d, J = 247.4 Hz), 142.53, 140.85 (d, J = 7.8 Hz), 138.86 (d, J = 8.0 Hz), 138.58, 138.43, 138.17, 137.92, 131.25 (d, J = 2.9 Hz), 128.58, 128.42, 128.29, 127.90, 127.83, 127.75, 127.70, 127.65, 127.61, 125.24, 116.65 (d, J = 21.4 Hz), 112.20 (d, J = 21.9 Hz), 78.36, 75.52, 75.08, 74.82, 73.28, 73.21, 71.85, 71.82, 68.27, 67.87, 51.64, 21.18.

^{19}F NMR (376 MHz, $CDCl_3$) δ -113.6.

HRMS (ESI-TOF): calc'd for $C_{45}H_{45}FNaO_7^+$ [M+Na$^+$] 739.3042, found 739.3032.

Methyl (*E*)-3-(2-((2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)naphthalen-1-yl)acrylate (5h)



5h

Physical state: colorless oil;

Yield: 88%;

R$_f$ = 0.3 (silica gel, PE:EtOAc = 5:1);

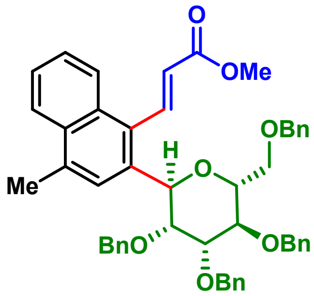
[α]25 D: -35.7 (c = 0.53, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 16.2 Hz, 1H), 8.03 – 7.97 (m, 1H), 7.87 – 7.80 (m, 2H), 7.72 (d, J = 8.6 Hz, 1H), 7.51 (dt, J = 6.4, 3.4 Hz, 2H), 7.36 – 7.23 (m, 15H), 7.15 – 7.11 (m, 1H), 7.08 – 7.02 (m, 2H), 6.88 – 6.80 (m, 2H), 6.45 (d, J = 16.2 Hz, 1H), 5.48 (d, J = 9.4 Hz, 1H), 4.75 (d, J = 12.2 Hz, 1H), 4.58 (dd, J = 15.8, 12.1 Hz, 2H), 4.52 – 4.41 (m, 3H), 4.26 (t, J = 6.9 Hz, 1H), 4.12 – 4.00 (m, 3H), 3.96 (t, J = 3.2 Hz, 1H), 3.89 (dd, J = 9.9, 6.9 Hz, 1H), 3.85 – 3.79 (m, 2H), 3.72 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.98, 142.43, 138.73, 138.50, 138.27, 138.01, 135.26, 133.06, 132.81, 131.34, 129.00, 128.57, 128.42, 128.37, 128.18, 127.87, 127.84, 127.73, 127.70, 127.61, 127.59, 127.58, 127.49, 126.72, 126.54, 126.22, 125.50, 124.88, 77.87, 75.52, 75.27, 75.09, 73.32, 73.30, 71.94, 71.76, 68.47, 68.38, 51.74.

HRMS (ESI-TOF): calc'd for $C_{48}H_{46}NaO_7^+$ [M+Na$^+$] 757.3136, found 757.3130.

Methyl (*E*)-3-(4-methyl-2-((2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)naphthalen-1-yl)acrylate (5i)



5i

Physical state: colorless oil;

Yield: 80%;

R_f = 0.4 (silica gel, PE:EtOAc = 6:1);

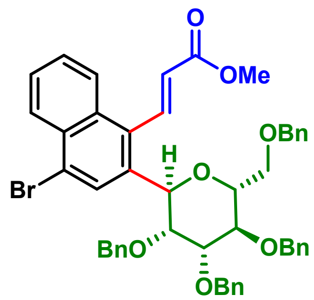
[α]25 D: -63.5 (c = 0.20, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 16.1 Hz, 1H), 8.08 – 7.97 (m, 2H), 7.60 – 7.50 (m, 3H), 7.39 – 7.23 (m, 15H), 7.16 – 7.11 (m, 1H), 7.05 (t, *J* = 7.5 Hz, 2H), 6.84 (d, *J* = 7.1 Hz, 2H), 6.48 (d, *J* = 16.2 Hz, 1H), 5.49 (d, *J* = 9.4 Hz, 1H), 4.77 (d, *J* = 12.2 Hz, 1H), 4.65 – 4.55 (m, 2H), 4.53 – 4.47 (m, 2H), 4.43 (d, *J* = 12.1 Hz, 1H), 4.28 (t, *J* = 6.9 Hz, 1H), 4.14 (d, *J* = 12.1 Hz, 1H), 4.08 – 4.01 (m, 2H), 3.99 (t, *J* = 3.2 Hz, 1H), 3.92 – 3.82 (m, 3H), 3.73 (s, 3H), 2.68 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.11, 142.59, 138.75, 138.52, 138.28, 137.97, 135.47, 134.77, 132.35, 131.52, 131.17, 128.58, 128.41, 128.10, 127.90, 127.88, 127.80, 127.68, 127.58, 127.56, 127.46, 126.42, 126.18, 126.08, 126.04, 125.40, 124.47, 77.53, 75.56, 75.24, 75.00, 73.32, 73.29, 71.74, 68.48, 68.24, 51.70, 19.82.

HRMS (ESI-TOF): calc'd for $C_{49}H_{48}NaO_7^+$ [M+Na$^+$] 771.3292, found 771.3287.

Methyl (*E*)-3-(4-bromo-2-((2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)naphthalen-1-yl)acrylate (5j)



5j

Physical state: colorless oil;

Yield: 52%;

R_f = 0.4 (silica gel, PE:EtOAc = 5:1);

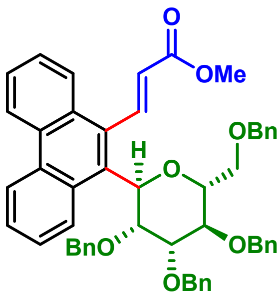
[α]25 D: 31.9 (c = 0.31, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, J = 8.9 Hz, 1H), 8.20 (d, J = 16.2 Hz, 1H), 8.03 – 7.94 (m, 2H), 7.62 (t, J = 7.8 Hz, 1H), 7.56 (t, J = 7.6 Hz, 1H), 7.39 – 7.21 (m, 15H), 7.12 (t, J = 7.4 Hz, 1H), 7.02 (t, J = 7.5 Hz, 2H), 6.81 (d, J = 7.1 Hz, 2H), 6.46 (d, J = 16.2 Hz, 1H), 5.41 (d, J = 9.7 Hz, 1H), 4.73 (d, J = 12.2 Hz, 1H), 4.64 – 4.53 (m, 2H), 4.51 – 4.40 (m, 3H), 4.28 (t, J = 6.9 Hz, 1H), 4.16 (d, J = 12.1 Hz, 1H), 4.01 (d, J = 12.1 Hz, 1H), 3.98 – 3.93 (m, 2H), 3.88 (dd, J = 9.9, 7.2 Hz, 1H), 3.81 (d, J = 3.4 Hz, 1H), 3.76 (dd, J = 10.0, 6.8 Hz, 1H), 3.72 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.79, 141.65, 138.60, 138.40, 138.15, 137.57, 136.00, 132.74, 132.42, 131.56, 128.96, 128.63, 128.44, 128.19, 127.96, 127.87, 127.79, 127.70, 127.66, 127.64, 127.57, 127.55, 127.30, 127.24, 125.92, 124.12, 75.60, 75.06, 74.55, 73.32, 73.30, 71.71, 71.68, 68.23, 67.80, 51.81.

HRMS (ESI-TOF): calc'd for $C_{48}H_{45}BrNaO_7^+$ [M+NH_4^+] 835.2241, found 835.2234.

Methyl (*E*)-3-(10-((2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)-tetrahydro-2*H*-pyran-2-yl)phenanthren-9-yl)acrylate (5k)



5k

Physical state: colorless oil;

Yield: 46%;

R_f = 0.4 (silica gel, PE:EtOAc = 5:1);

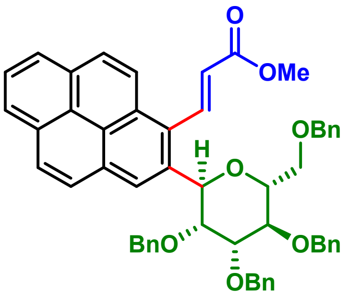
[α]25 D: -58.5 (c = 0.26, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (d, J = 8.5 Hz, 1H), 8.71 (dd, J = 8.4, 3.3 Hz, 2H), 8.32 (d, J = 16.3 Hz, 1H), 7.96 (d, J = 8.1 Hz, 1H), 7.67 (t, J = 7.5 Hz, 1H), 7.60 (dt, J = 11.5, 7.5 Hz, 2H), 7.44 – 7.26 (m, 14H), 7.26 – 7.23 (m, 2H), 7.01 (t, J = 7.4 Hz, 1H), 6.89 (t, J = 7.5 Hz, 2H), 6.56 (d, J = 7.4 Hz, 2H), 6.36 (d, J = 16.1 Hz, 1H), 5.95 (d, J = 10.3 Hz, 1H), 4.86 (d, J = 12.1 Hz, 1H), 4.72 – 4.64 (m, 2H), 4.58 (dd, J = 12.0, 8.2 Hz, 2H), 4.50 – 4.39 (m, 3H), 4.05 – 3.97 (m, 2H), 3.89 – 3.83 (m, 2H), 3.79 (s, 2H), 3.72 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.73, 144.66, 138.88, 138.52, 138.37, 137.85, 133.91, 130.93, 130.52, 130.44, 130.40, 130.03, 128.57, 128.44, 128.41, 128.29, 127.94, 127.83, 127.80, 127.71, 127.60, 127.53, 127.50, 127.37, 127.09, 126.76, 126.75, 126.71, 126.61, 122.90, 122.86, 75.65, 75.22, 75.11, 74.75, 73.76, 73.50, 71.93, 71.43, 70.30, 68.26, 51.76.

HRMS (ESI-TOF): calc'd for $C_{52}H_{48}NaO_7^+$ [M+Na$^+$] 807.3292, found 807.3287.

Methyl (*E*)-3-(2-((2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)-tetrahydro-2*H*-pyran-2-yl)pyren-1-yl)acrylate (5l)



5l

Physical state: pale yellow oil;

Yield: 81%;

$\mathbf{R_f}$ = 0.4 (silica gel, PE:EtOAc = 5:1);

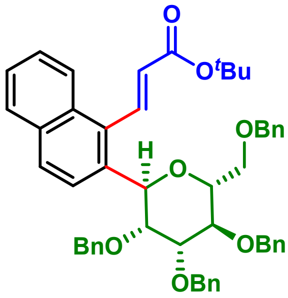
[α]25 D: -21.7 (c = 0.54, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 16.3 Hz, 1H), 8.38 (s, 1H), 8.32 (d, *J* = 9.3 Hz, 1H), 8.23 – 8.17 (m, 2H), 8.13 – 8.06 (m, 2H), 8.05 – 7.98 (m, 2H), 7.41 – 7.23 (m, 15H), 7.05 – 6.98 (m, 1H), 6.92 (t, *J* = 7.5 Hz, 2H), 6.78 – 6.69 (m, 2H), 6.50 (d, *J* = 16.3 Hz, 1H), 5.70 (d, *J* = 9.1 Hz, 1H), 4.80 (d, *J* = 12.2 Hz, 1H), 4.70 – 4.60 (m, 2H), 4.57 – 4.46 (m, 3H), 4.35 (t, *J* = 6.8 Hz, 1H), 4.23 – 4.15 (m, 1H), 4.10 (d, *J* = 12.1 Hz, 1H), 4.05 (t, *J* = 3.3 Hz, 1H), 4.01 – 3.94 (m, 2H), 3.94 – 3.86 (m, 2H), 3.77 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.99, 143.28, 138.71, 138.49, 138.26, 137.75, 135.73, 131.51, 131.36, 130.93, 130.75, 128.88, 128.61, 128.47, 128.43, 128.05, 128.02, 128.01, 127.94, 127.81, 127.76, 127.71, 127.69, 127.65, 127.60, 127.44, 126.91, 126.29, 125.56, 125.35, 124.86, 124.63, 124.41, 124.06, 78.54, 75.86, 75.36, 75.01, 73.34, 73.28, 71.99, 71.79, 69.12, 68.44, 51.78.

HRMS (ESI-TOF): calc'd for $C_{54}H_{48}NaO_7^+$ [M+Na$^+$] 831.3292, found 831.3282.

***tert*-Butyl (*E*)-3-(2-((2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)naphthalen-1-yl)acrylate (5m)**



5m

Physical state: colorless oil;

Yield: 80%;

$\mathbf{R_f}$ = 0.4 (silica gel, PE:EtOAc = 5:1);

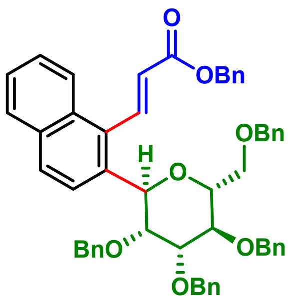
[α]25 D: +75.6 (c = 0.70, $CHCl_3$);

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 16.1 Hz, 1H), 8.06 – 8.02 (m, 1H), 7.87 – 7.80 (m, 2H), 7.72 (d, *J* = 8.7 Hz, 1H), 7.54 – 7.50 (m, 2H), 7.37 – 7.23 (m, 17H), 7.17 – 7.12 (m, 1H), 7.10 – 7.05 (m, 2H), 6.89 – 6.84 (m, 2H), 6.36 (d, *J* = 16.2 Hz, 1H), 5.51 (d, *J* = 9.3 Hz, 1H), 4.74 (d, *J* = 12.5 Hz, 1H), 4.60 (d, *J* = 5.5 Hz, 1H), 4.58 – 4.53 (m, 2H), 4.45 (dd, *J* = 12.0, 8.1 Hz, 2H), 4.28 (t, *J* = 6.8 Hz, 1H), 4.10 (d, *J* = 12.0 Hz, 1H), 4.07 – 4.00 (m, 2H), 3.97 – 3.94 (m, 1H), 3.93 – 3.86 (m, 2H), 3.84 (dd, *J* = 3.9, 1.5 Hz, 1H), 1.50 (s, 9H).

^{13}**C NMR** (101 MHz, $CDCl_3$) δ 165.85, 141.04, 138.70, 138.51, 138.29, 138.12, 135.15, 133.18, 133.10, 131.40, 128.90, 128.78, 128.56, 128.47, 128.43, 128.32, 128.16, 127.86, 127.79, 127.74, 127.66, 127.64, 127.62, 127.42, 126.43, 126.15, 125.68, 124.82, 80.48, 77.86, 75.53, 75.25, 74.74, 73.42, 73.18, 71.91, 71.75, 68.58, 68.39, 28.36.

HRMS (ESI-TOF): calc'd for $C_{51}H_{52}NaO_7^+$ [M+Na$^+$] 799.3605, found 799.3015.

Benzyl (*E*)-3-(2-((2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)naphthalen-1-yl)acrylate (5n)



5n

Physical state: colorless oil;

Yield: 83%;

$\mathbf{R_f}$ = 0.3 (silica gel, PE:EtOAc = 5:1);

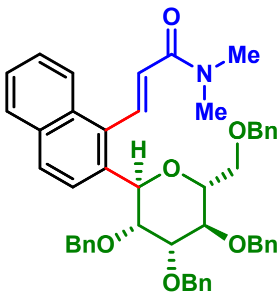
[α]25 D: -53.1 (c = 0.60, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 16.2 Hz, 1H), 8.00 (dt, *J* = 7.0, 3.5 Hz, 1H), 7.88 – 7.79 (m, 2H), 7.72 (d, *J* = 8.7 Hz, 1H), 7.51 (dt, *J* = 6.3, 3.4 Hz, 2H), 7.36 – 7.18 (m, 20H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 2H), 6.82 (d, *J* = 7.0 Hz, 2H), 6.50 (d, *J* = 16.2 Hz, 1H), 5.50 (d, *J* = 9.4 Hz, 1H), 5.25 (d, *J* = 12.5 Hz, 1H), 5.13 (d, *J* = 12.5 Hz, 1H), 4.68 (d, *J* = 12.4 Hz, 1H), 4.61 – 4.50 (m, 2H), 4.48 – 4.41 (m, 2H), 4.38 (d, *J* = 12.0 Hz, 1H), 4.26 (t, *J* = 6.9 Hz, 1H), 4.08 (d, *J* = 12.0 Hz, 1H), 4.05 – 3.96 (m, 2H), 3.94 (t, *J* = 3.2 Hz, 1H), 3.89 (dd, *J* = 10.0, 6.9 Hz, 1H), 3.85 – 3.78 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.35, 142.78, 138.69, 138.51, 138.27, 138.01, 136.26, 135.33, 133.06, 132.80, 131.32, 129.04, 128.63, 128.57, 128.43, 128.41, 128.37, 128.22, 128.20, 128.17, 127.87, 127.86, 127.70, 127.69, 127.62, 127.58, 127.46, 126.79, 126.57, 126.23, 125.52, 124.89, 77.88, 75.56, 75.22, 74.74, 73.29, 73.16, 71.92, 71.74, 68.48, 68.36, 66.33.

HRMS (ESI-TOF): calc'd for $C_{54}H_{50}NaO_7^+$ [M+Na$^+$] 833.3449, found 833.3456.

(*E*)-*N*,*N*-Dimethyl-3-(2-((2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)-tetrahydro-2*H*-pyran-2-yl)naphthalen-1-yl)acrylamide (5o)



5o

Physical state: colorless oil;

Yield: 60%;

R_f = 0.4 (silica gel, PE:EtOAc = 1:1);

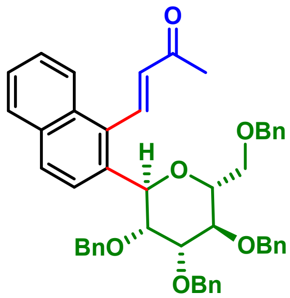
[α]25 D: -54.1 (c = 0.50, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 15.5 Hz, 1H), 8.10 – 8.04 (m, 1H), 7.89 – 7.81 (m, 3H), 7.56 – 7.50 (m, 2H), 7.40 – 7.26 (m, 10H), 7.25 – 7.20 (m, 4H), 7.16 – 7.11 (m, 1H), 7.08 – 7.01 (m, 2H), 6.92 (d, *J* = 15.5 Hz, 1H), 6.82 – 6.73 (m, 2H), 5.51 (d, *J* = 9.7 Hz, 1H), 4.68 (d, *J* = 12.2 Hz, 1H), 4.57 (s, 2H), 4.53 – 4.46 (m, 2H), 4.42 (d, *J* = 12.0 Hz, 1H), 4.31 (t, *J* = 7.2 Hz, 1H), 4.16 (d, *J* = 11.0 Hz, 1H), 4.12 (dd, *J* = 9.7, 2.9 Hz, 1H), 4.04 (t, *J* = 2.9 Hz, 1H), 3.97 – 3.90 (m, 3H), 3.82 (dd, *J* = 9.6, 6.6 Hz, 1H), 2.88 (s, 3H), 2.49 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.29, 138.45, 138.35, 138.32, 138.26, 137.75, 134.95, 133.99, 132.92, 131.81, 128.64, 128.61, 128.51, 128.43, 128.24, 128.22, 127.93, 127.74, 127.68, 127.66, 127.60, 127.45, 127.34, 126.41, 126.23, 125.78, 124.91, 78.16, 75.51, 74.85, 74.08, 73.30, 72.75, 72.66, 71.72, 68.47, 67.91, 36.71, 35.69.

HRMS (ESI-TOF): calc'd for $C_{49}H_{49}NaO_6^+$ [M+Na$^+$] 770.3452, found 770.3462.

(*E*)-4-(2-((2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-Tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)naphthalen-1-yl)but-3-en-2-one (5p)



5p

Physical state: colorless oil;

Yield: 63%;

R$_f$ = 0.2 (silica gel, PE:EtOAc = 5:1);

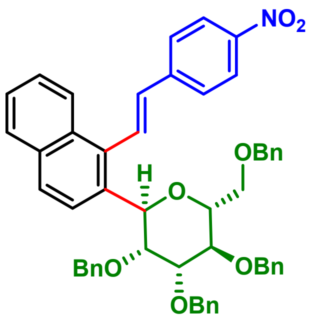
[α]25 D: -57.0 (c = 0.50, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 16.6 Hz, 1H), 8.01 – 7.94 (m, 1H), 7.90 – 7.80 (m, 2H), 7.70 (d, *J* = 8.6 Hz, 1H), 7.54 – 7.46 (m, 2H), 7.38 – 7.21 (m, 15H), 7.17 – 7.11 (m, 1H), 7.11 – 7.02 (m, 2H), 6.83 (d, *J* = 6.9 Hz, 2H), 6.51 (d, *J* = 16.6 Hz, 1H), 5.37 (d, *J* = 9.4 Hz, 1H), 4.65 (d, *J* = 12.0 Hz, 1H), 4.62 – 4.55 (m, 2H), 4.52 – 4.43 (m, 3H), 4.28 (t, *J* = 6.9 Hz, 1H), 4.13 (d, *J* = 11.8 Hz, 1H), 4.03 (dd, *J* = 9.4, 2.7 Hz, 1H), 4.01 – 3.93 (m, 2H), 3.91 – 3.78 (m, 3H), 2.16 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.58, 141.41, 138.40, 138.38, 138.14, 137.97, 135.60, 135.24, 133.23, 132.90, 131.16, 128.99, 128.61, 128.53, 128.46, 128.42, 128.22, 127.96, 127.91, 127.82, 127.80, 127.68, 127.61, 126.59, 126.23, 125.55, 125.07, 77.57, 75.41, 75.00, 74.92, 73.27, 73.23, 72.02, 71.91, 68.97, 68.22, 27.46.

HRMS (ESI-TOF): calc'd for $C_{48}H_{46}NaO_6^+$ [M+Na$^+$] 741.3187, found 741.3196.

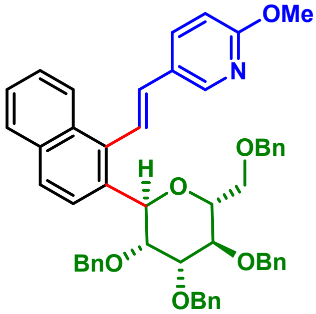
(2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-Tris(benzyloxy)-2-((benzyloxy)methyl)-6-(1-((*E*)-4-nitrostyryl)naphthalene-2-yl)tetrahydro-2*H*-pyran (5q)



5q

Physical state: yellow oil;
Yield: 84%;
R$_f$ = 0.3 (silica gel, PE:EtOAc = 5:1);
[α]25 D: -104.7 (c = 0.40, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.04 (m, 1H), 8.04 – 7.98 (m, 2H), 7.91 – 7.87 (m, 1H), 7.85 (d, *J* = 8.6 Hz, 1H), 7.76 (d, *J* = 5.0 Hz, 1H), 7.73 (d, *J* = 12.9 Hz, 1H), 7.54 – 7.48 (m, 2H), 7.43 – 7.39 (m, 2H), 7.38 – 7.27 (m, 5H), 7.26 – 7.21 (m, 4H), 7.20 – 7.11 (m, 7H), 7.07 (t, *J* = 7.5 Hz, 2H), 6.92 – 6.82 (m, 3H), 5.52 (d, *J* = 9.5 Hz, 1H), 4.64 (dd, *J* = 15.0, 12.0 Hz, 2H), 4.51 (dd, *J* = 18.6, 12.0 Hz, 2H), 4.40 (s, 2H), 4.31 (t, *J* = 6.8 Hz, 1H), 4.19 (d, *J* = 11.7 Hz, 1H), 4.12 (dd, *J* = 9.5, 2.7 Hz, 1H), 4.03 (d, *J* = 11.7 Hz, 1H), 4.00 (t, *J* = 3.3 Hz, 1H), 3.88 (dd, *J* = 10.1, 7.2 Hz, 1H), 3.82 (dd, *J* = 3.9, 1.4 Hz, 1H), 3.73 (dd, *J* = 10.1, 6.4 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.87, 143.99, 138.38, 138.36, 138.16, 138.11, 135.06, 134.62, 134.53, 133.35, 131.83, 130.38, 128.62, 128.43, 128.41, 128.31, 128.24, 127.96, 127.87, 127.84, 127.71, 127.64, 127.53, 127.33, 127.01, 126.32, 126.10, 125.77, 125.20, 124.12, 77.78, 75.50, 75.40, 75.19, 73.35, 73.19, 72.17, 71.89, 68.77, 68.21.
HRMS (ESI-TOF): calc'd for $C_{52}H_{47}NaNO_7^+$ [M+Na$^+$] 820.3245, found 820.3248.

2-Methoxy-5-((*E*)-2-(2-((2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)-tetrahydro-2*H*-pyran-2-yl)naphthalen-1-yl)vinyl)pyridine (5r)



5r

Physical state: colorless oil;

Yield: 70%;

$\mathbf{R_f}$ = 0.4 (silica gel, PE:EtOAc = 5:1);

[α]25 D: -80.7 (c = 0.40, $CHCl_3$);

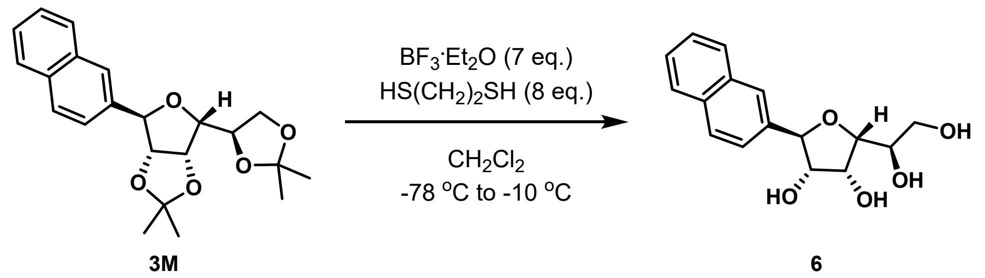
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 2.4 Hz, 1H), 8.13 – 8.07 (m, 1H), 7.89 – 7.83 (m, 1H), 7.81 (d, *J* = 8.6 Hz, 1H), 7.75 – 7.68 (m, 2H), 7.52 – 7.43 (m, 3H), 7.38 – 7.30 (m, 3H), 7.29 – 7.20 (m, 7H), 7.19 – 7.12 (m, 6H), 7.10 – 7.05 (m, 2H), 6.90 – 6.83 (m, 2H), 6.75 (d, *J* = 16.6 Hz, 1H), 6.64 (d, *J* = 8.6 Hz, 1H), 5.57 (d, *J* = 9.4 Hz, 1H), 4.67 (d, *J* = 12.1 Hz, 1H), 4.60 (d, *J* = 12.2 Hz, 1H), 4.52 (d, *J* = 12.1 Hz, 1H), 4.47 (d, *J* = 12.2 Hz, 1H), 4.39 (q, *J* = 12.1 Hz, 2H), 4.28 (t, *J* = 6.8 Hz, 1H), 4.16 (d, *J* = 11.8 Hz, 1H), 4.11 (dd, *J* = 9.4, 2.7 Hz, 1H), 4.03 (d, *J* = 11.7 Hz, 1H), 3.97 (d, *J* = 3.3 Hz, 1H), 3.96 (s, 3H), 3.86 (dd, *J* = 10.0, 7.0 Hz, 1H), 3.81 (dd, *J* = 4.0, 1.4 Hz, 1H), 3.76 (dd, *J* = 10.0, 6.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.73, 145.91, 138.49, 138.43, 138.28, 138.22, 135.63, 134.71, 133.38, 132.82, 132.17, 128.56, 128.38, 128.28, 128.20, 127.86, 127.85, 127.81, 127.66, 127.64, 127.56, 127.52, 127.49, 126.97, 126.11, 126.02, 125.89, 125.14, 124.63, 111.08, 77.82, 75.40, 75.31, 75.21, 73.24, 73.20, 72.20, 71.79, 68.89, 68.37, 53.66.

HRMS (ESI-TOF): calc'd for $C_{52}H_{49}NaNO_6^+$ [M+Na$^+$] 806.3452, found 806.3459.

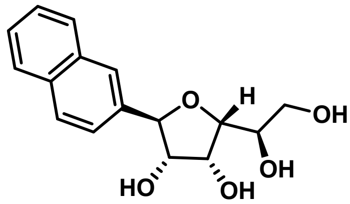
11. Synthetic applications

Synthesis of 6.



1,2-ethanedithiol (35 µL, 0.4 mmol, 8.0 equiv) and boron trifluoride diethyl etherate (43 µL, 0.35 mmol, 7.0 equiv) were added sequentially to a stirred solution of compound **3M** (19 mg, 0.05 mmol, 1.0 equiv) in CH_2Cl_2 at -78 °C. After the mixture was stirred at –10 °C for 16 h, the volatiles were then removed by rotary evaporation, the resulting residue was directly purified by preparative TLC (CH_2Cl_2/MeOH = 8:1) to give the desired product **6** (11.7 mg, 81%) as a white solid.

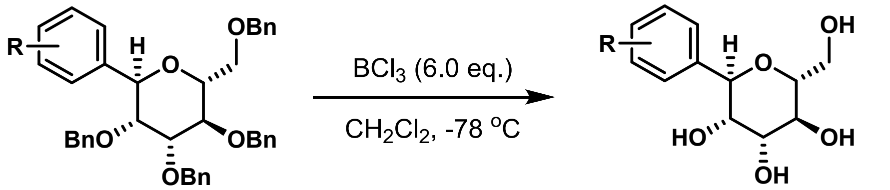
(2*R*,3*R*,4*S*,5*R*)-2-((*R*)-1,2-dihydroxyethyl)-5-(naphthalen-2-yl)tetrahydrofuran-3,4-diol (6)



6

Physical state: white solid;
Yield: 81%;
$\mathbf{R_f}$ = 0.4 (silica gel, CH_2Cl_2:MeOH = 8:1);
Melting point: 101–103 ^{o}C;
[α]25 D: 29.5 (c = 0.32, MeOH);
^{1}H NMR (400 MHz, CD_3OD) δ 7.87 – 7.78 (m, 4H), 7.55 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.49 – 7.40 (m, 2H), 4.93 (d, *J* = 8.6 Hz, 1H), 4.34 (t, *J* = 3.7 Hz, 1H), 4.23 (dd, *J* = 8.3, 3.2 Hz, 1H), 4.11 (dd, *J* = 8.6, 4.1 Hz, 1H), 4.05 (ddd, *J* = 8.5, 5.9, 3.2 Hz, 1H), 3.86 (dd, *J* = 11.5, 3.3 Hz, 1H), 3.71 (dd, *J* = 11.5, 5.9 Hz, 1H).
^{13}C NMR (101 MHz, CD_3OD) δ 140.38, 134.76, 134.60, 129.07, 128.88, 128.67, 127.07, 126.74, 125.89, 125.03, 83.99, 81.81, 81.01, 73.81, 71.81, 64.92.
HRMS (ESI-TOF): calc'd for $C_{16}H_{18}NaO_5^+$ [M+Na$^+$] 313.1046, found 313.1048.

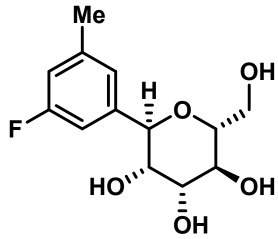
General procedure for the synthesis of 7–9.



3a or **3q** or **3r** **7** or **8** or **9**

BCl_3 (0.3 mmol, 6.0 eq.) was added slowly to a stirred solution of compound **3a** or **3q** or **3r** (0.05 mmol, 1.0 eq.) in CH_2Cl_2 (1 mL) at -78 ^{o}C. The reaction was stirred for 0.5-1.0 h until the completion of the reaction (monitored by TLC). Then the residue was directly purified by preparative TLC (CH_2Cl_2/MeOH = 7:1) to give the desired product **7** or **8** or **9** as a white solid.

(2*R*,3*S*,4*R*,5*S*,6*R*)-2-(3-fluoro-5-methylphenyl)-6-(hydroxymethyl)tetrahydro-2*H*-pyran-3,4,5-triol (7)



7

Physical state: white solid;

Yield: 85%;

$\mathbf{R_f}$ = 0.4 (silica gel, CH_2Cl_2:MeOH = 6:1);

Melting point: 163–165 °C;

[α]25 D: 121.5 (c = 0.70, MeOH);

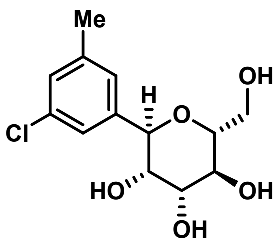
^{1}H NMR (400 MHz, CD_3OD) δ 7.11 (s, 1H), 7.03 (d, *J* = 10.1 Hz, 1H), 6.84 (d, *J* = 9.5 Hz, 1H), 4.92 (d, *J* = 3.5 Hz, 1H), 4.38 (t, *J* = 3.2 Hz, 1H), 3.90 – 3.78 (m, 2H), 3.75 (t, *J* = 7.8 Hz, 1H), 3.59 (dd, *J* = 8.0, 2.9 Hz, 1H), 3.48 (dt, *J* = 9.0, 4.5 Hz, 1H), 2.35 (s, 3H).

^{13}C NMR (101 MHz, CD_3OD) δ 164.48 (d, *J* = 243.8 Hz), 142.04 (dd, *J* = 7.7, 3.1 Hz), 124.04 (d, *J* = 2.6 Hz), 115.66 (d, *J* = 21.4 Hz), 111.62 (d, *J* = 22.9 Hz) 77.80, 77.75, 72.62, 71.61, 69.50, 62.65, 21.42.

^{19}F NMR (376 MHz, CD_3OD) δ -115.1.

HRMS (ESI-TOF): calc'd for $C_{13}H_{17}FNaO_5^+$ [M+Na$^+$] 295.0952, found 295.0951.

(2*R*,3*S*,4*R*,5*S*,6*R*)-2-(3-chloro-5-methylphenyl)-6-(hydroxymethyl)tetrahydro-2*H*-pyran-3,4,5-triol (8)



8

Physical state: white solid;

Yield: 82%;

$\mathbf{R_f}$ = 0.4 (silica gel, CH_2Cl_2:MeOH = 6:1);

Melting point: 194–196 °C;

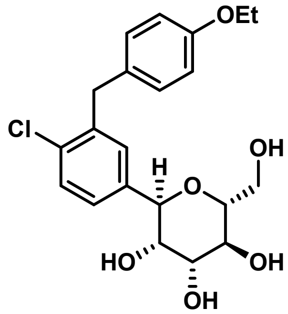
[α]25 D: 54.6 (c = 0.51, MeOH);

^{1}H NMR (400 MHz, CD_3OD) δ 7.30 (s, 1H), 7.24 (s, 1H), 7.12 (s, 1H), 4.88 (d, *J* = 4.4 Hz, 1H), 4.31 (dd, *J* = 4.4, 3.1 Hz, 1H), 3.87 (dd, *J* = 11.9, 6.7 Hz, 1H), 3.81 (dd, *J* = 11.9, 3.2 Hz, 1H), 3.75 (t, *J* = 7.4 Hz, 1H), 3.60 (dd, *J* = 7.6, 3.1 Hz, 1H), 3.50 (td, *J* = 7.0, 3.2 Hz, 1H), 2.35 (s, 3H).

^{13}**C NMR** (101 MHz, CD_3OD) δ 142.03, 141.54, 135.33, 129.05, 126.99, 125.06, 78.29, 77.32, 72.67, 71.53, 69.81, 62.66, 21.29.

HRMS (ESI-TOF): calc'd for $C_{13}H_{17}ClNaO_5^+$ [M+Na$^+$] 311.0657, found 311.0653.

(2*R*,3*S*,4*R*,5*S*,6*R*)-2-(4-chloro-3-(4-ethoxybenzyl)phenyl)-6-(hydroxymethyl)-tetrahydro-2*H*-pyran-3,4,5-triol (9)



9

Physical state: white solid;

Yield: 88%;

$\mathbf{R_f}$ = 0.4 (silica gel, CH_2Cl_2:MeOH = 5:1);

Melting point: 162–164 °C;

[α]25 D: 24.0 (c = 0.34, MeOH);

^{1}**H NMR** (400 MHz, CD_3OD) δ 7.38 – 7.33 (m, 2H), 7.29 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.08 (d, *J* = 8.7 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 4.88 (d, *J* = 3.2 Hz, 1H), 4.31 (t, *J* = 3.6 Hz, 1H), 4.01 (d, *J* = 3.3 Hz, 2H), 3.97 (q, *J* = 7.0 Hz, 2H), 3.82 (dd, *J* = 11.9, 6.4 Hz, 1H), 3.77 – 3.70 (m, 2H), 3.54 (dd, *J* = 7.9, 3.1 Hz, 1H), 3.41 (ddd, *J* = 7.7, 6.4, 2.9 Hz, 1H), 1.34 (t, *J* = 7.0 Hz, 3H).

^{13}**C NMR** (101 MHz, CD_3OD) δ 158.87, 140.69, 138.64, 134.07, 132.77, 130.87, 130.69, 130.56, 127.11, 115.48, 77.85, 77.59, 72.66, 71.62, 69.59, 64.41, 62.55, 39.25, 15.21.

HRMS (ESI-TOF): calc'd for $C_{21}H_{25}ClNaO_6^+$ [M+Na$^+$] 431.1232, found 431.1231.

12. Proposed stereochemical model

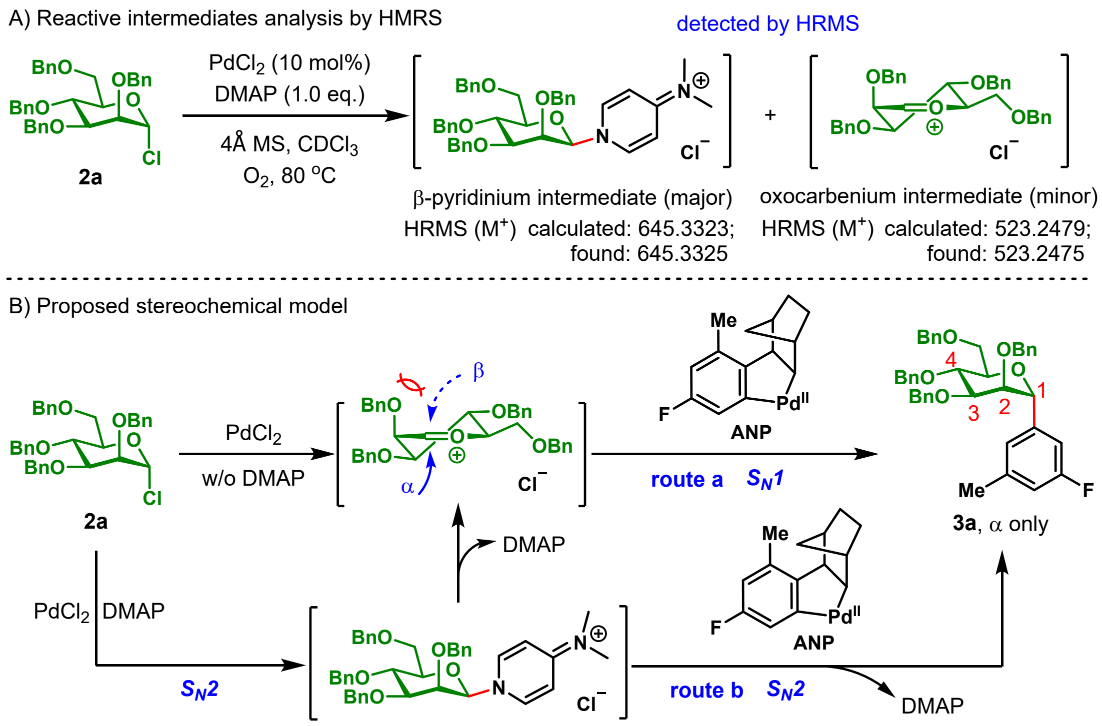
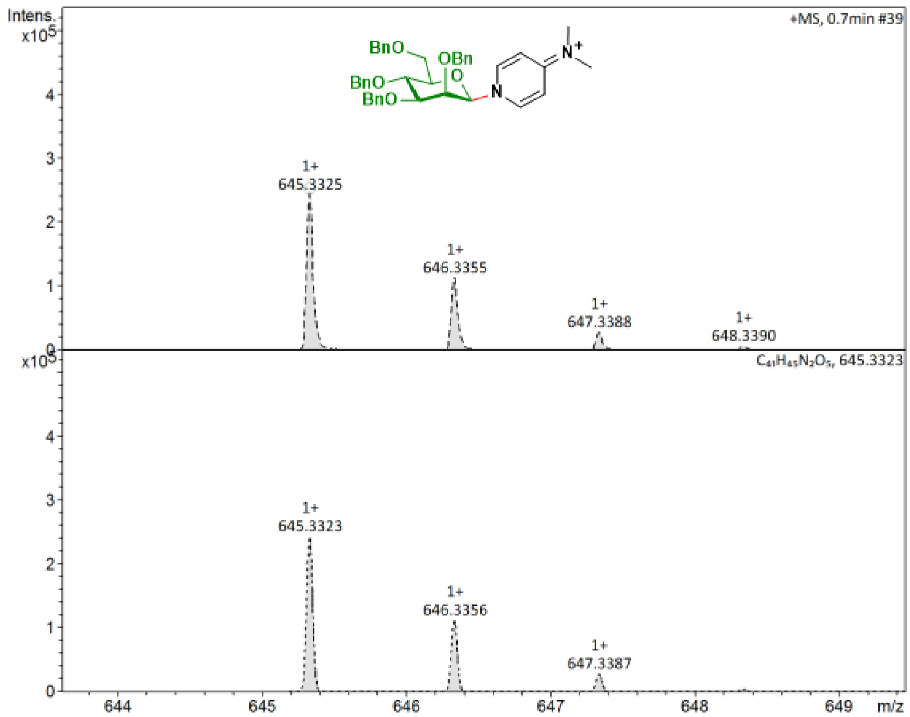


Figure S4. Reactive intermediates analysis and the proposed stereochemical model.

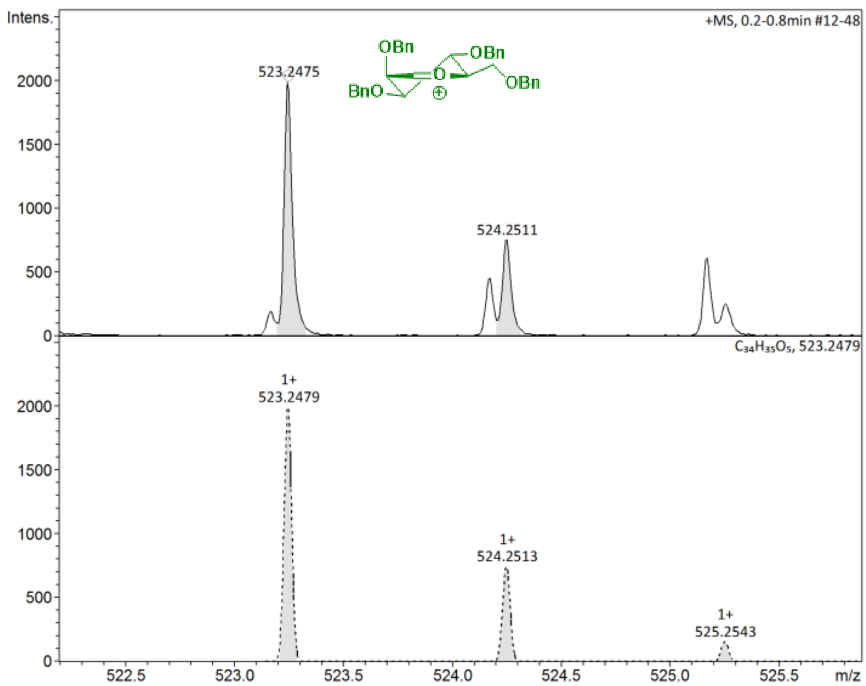
To a 10 mL oven-dried Schlenk tube equipped with a magnetic stir bar was charged with *α*-mannosyl chloride **2a** (55.9 mg, 0.1 mmol, 1.0 equiv), $PdCl_2$ (1.8 mg, 0.01 mmol, 0.1 equiv), DMAP (12.2 mg, 0.1 mmol, 1.0 equiv), 4 Å MS (80 mg) and $CDCl_3$ (2.0mL) under O_2. The reaction was stirred at 80 °C for 24 h. The formation of *β*-pyridiniumtype salt intermediate and oxocarbenium-ion intermediate in this reaction were demonstrated by using HRMS. MS analysis of the reaction mixture showed a $[M]^+$ peak at m/z 645.3325 with a molecular formula of $C_{41}H_{45}N_2O_5$ which corresponded to *β*-pyridinium-type salt intermediate. Additionally, it exhibited a $[M]^+$ peak at m/z 523.2475 with a molecular formula of $C_{34}H_{35}O_5$, corresponding to the oxocarbenium-ion intermediate.

+MS, 0.7min #39



Meas. m/z	#	Ion Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule	Adduct
645.332501	1	C41H45N2O5	100.00	645.332299	-0.2	-0.3	3.4	20.5	even	ok	M

+MS, 0.2-0.8min #12-48



Meas. m/z	#	Ion Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule	Adduct
523.247547	1	C34H35O5	100.00	523.247901	0.4	0.7	39.5	17.5	even	ok	M

Figure S5. HRMS spectra of β-pyridinium-type salt intermediate and oxocarbenium-ion intermediate from **2a**.

13. References

1. Wang, Q.; An, S.; Deng, Z.; Zhu, W.; Huang, Z.; He, G.; Chen, G. Palladium-catalysed C–H glycosylation for synthesis of C-aryl glycosides. *Nat. Catal.* **2019**, *2*, 793−800.

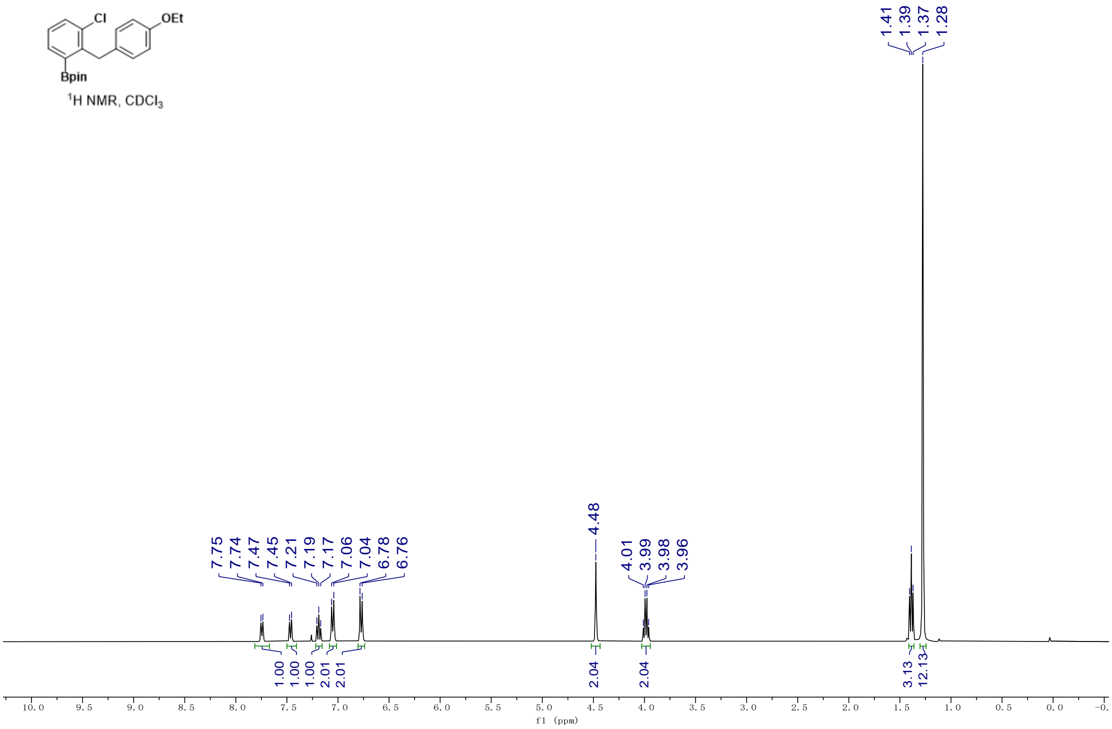
2. An, Y.; Zhang, B.-S.; Ding, Y.-N.; Zhang, Z.; Gou, X.-Y.; Li, X.-S.; Wang, X.; Li, Y.; Liang, Y.-M. Palladium-catalyzed C–H glycosylation and retro Diels–Alder tandem reaction *via* structurally modified norbornadienes (smNBDs). *Chem. Sci.*, **2021**, *12*, 13144-13150.

3. Gouliaras C.; Lee D.; Chan L.; Taylor M. S. Regioselective activation of glycosyl acceptors by a diarylborinic acid-derived catalyst. *J. Am. Chem. Soc.* **2011**, *133*, 13926-13929.

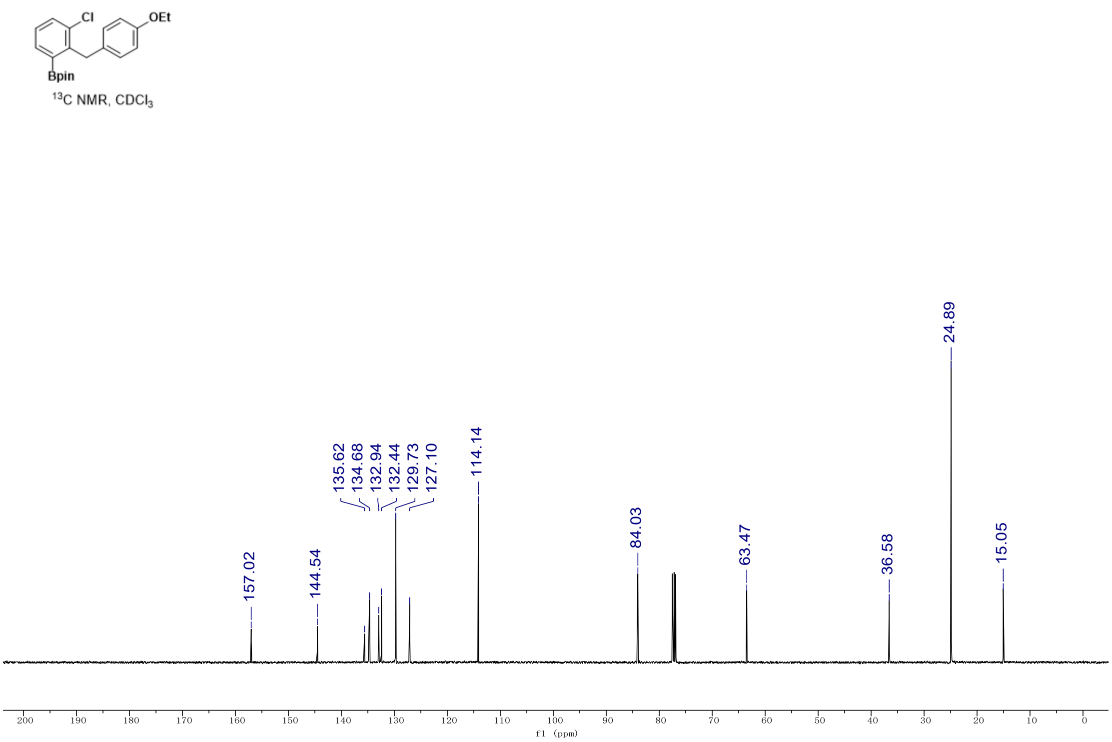
4. Feng, G.-J.; Guo Y.-F.; Tang Y.; Li M.; Jia Y.; Li Z.; Wang S.; Liu H.; Wu, Y.; Dong H. Design, synthesis, and biological evaluation of thioglucoside analogues of Gliflozin as potent new Gliflozin grugs. *J. Med. Chem.* **2023**, *66*, 12536−12543.

14. Copies of NMR spectra

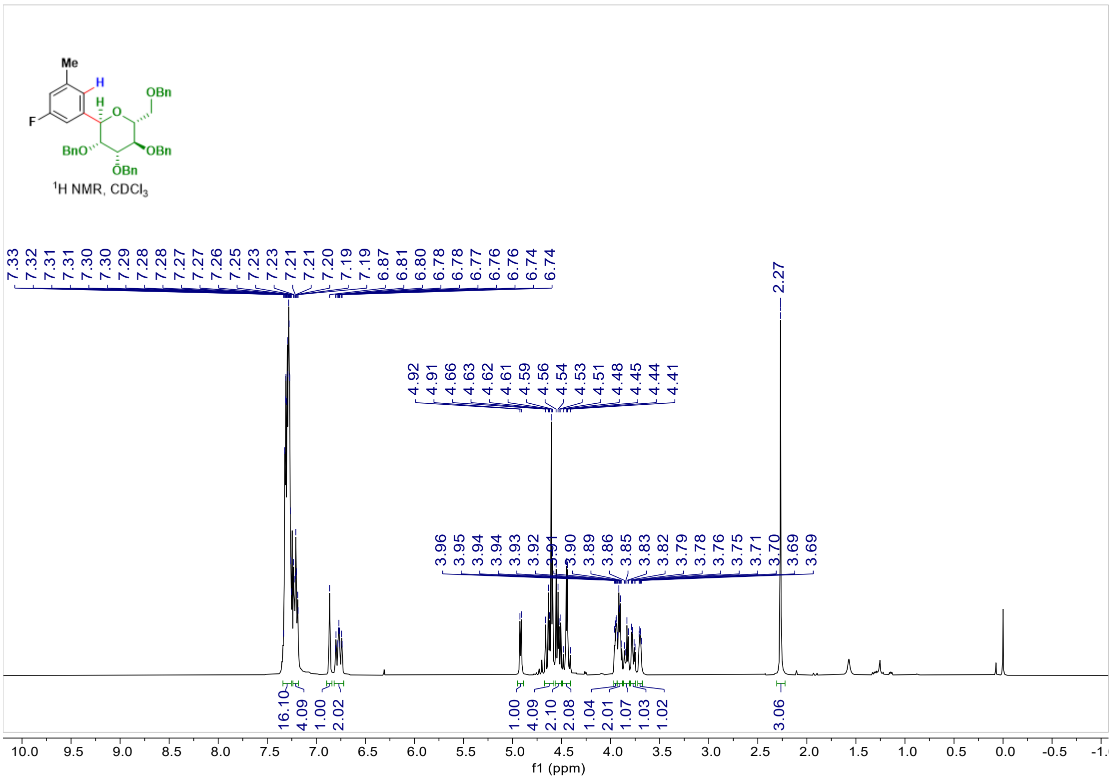
[1]H NMR spectrum of **1r**



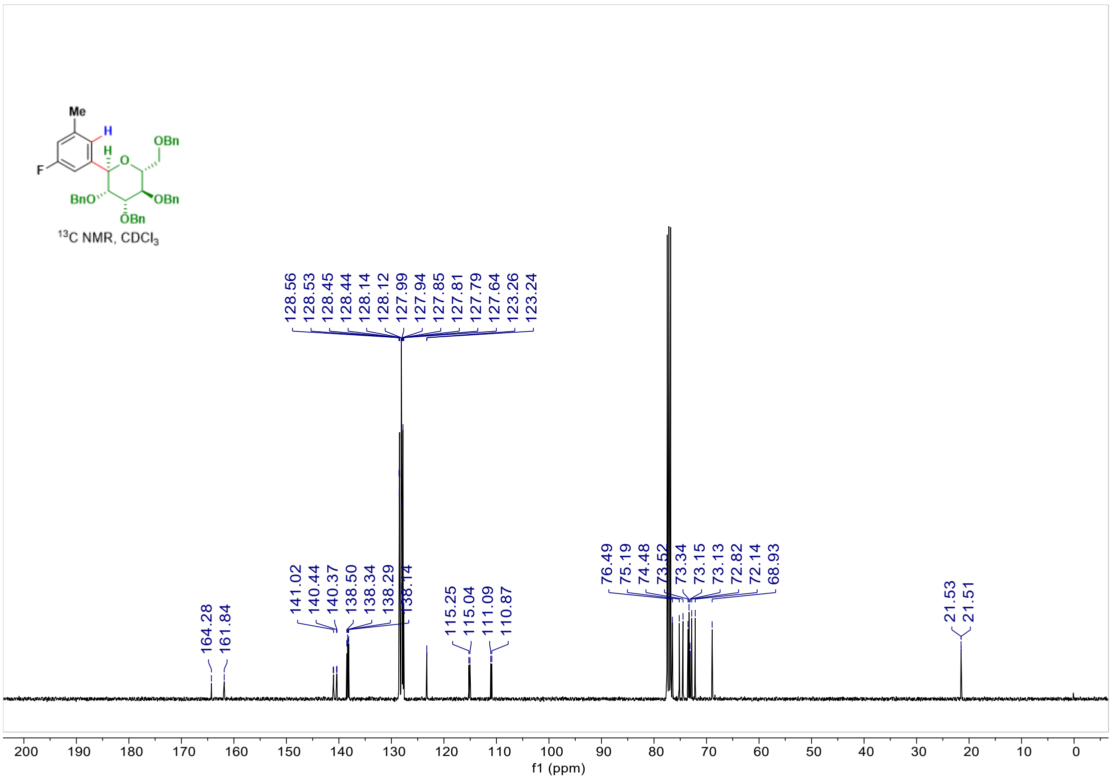
[13]C NMR spectrum of **1r**



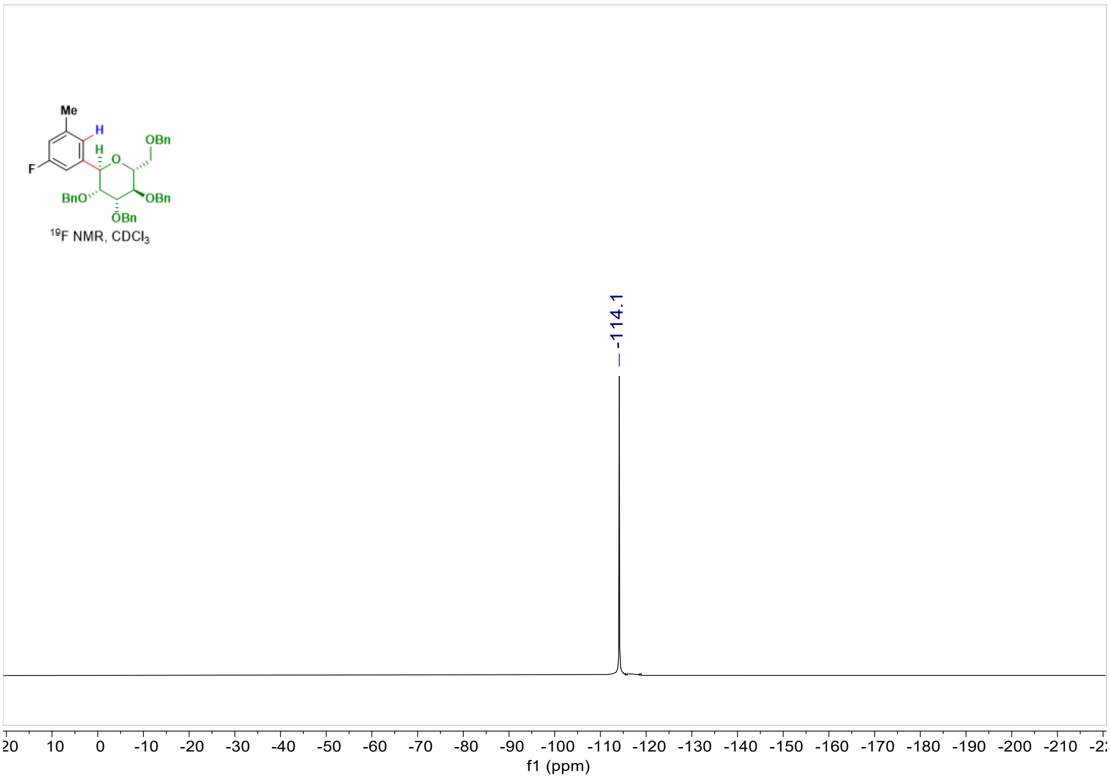
^{1}H NMR spectrum of **3a**



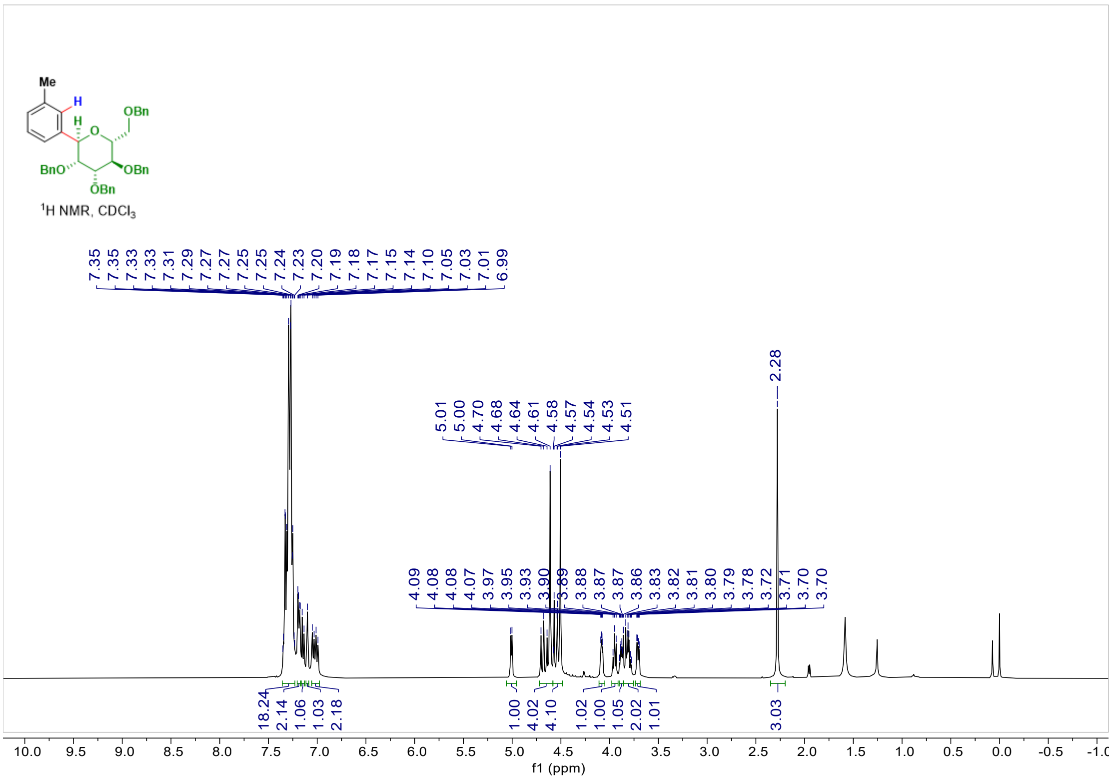
^{13}C NMR spectrum of **3a**



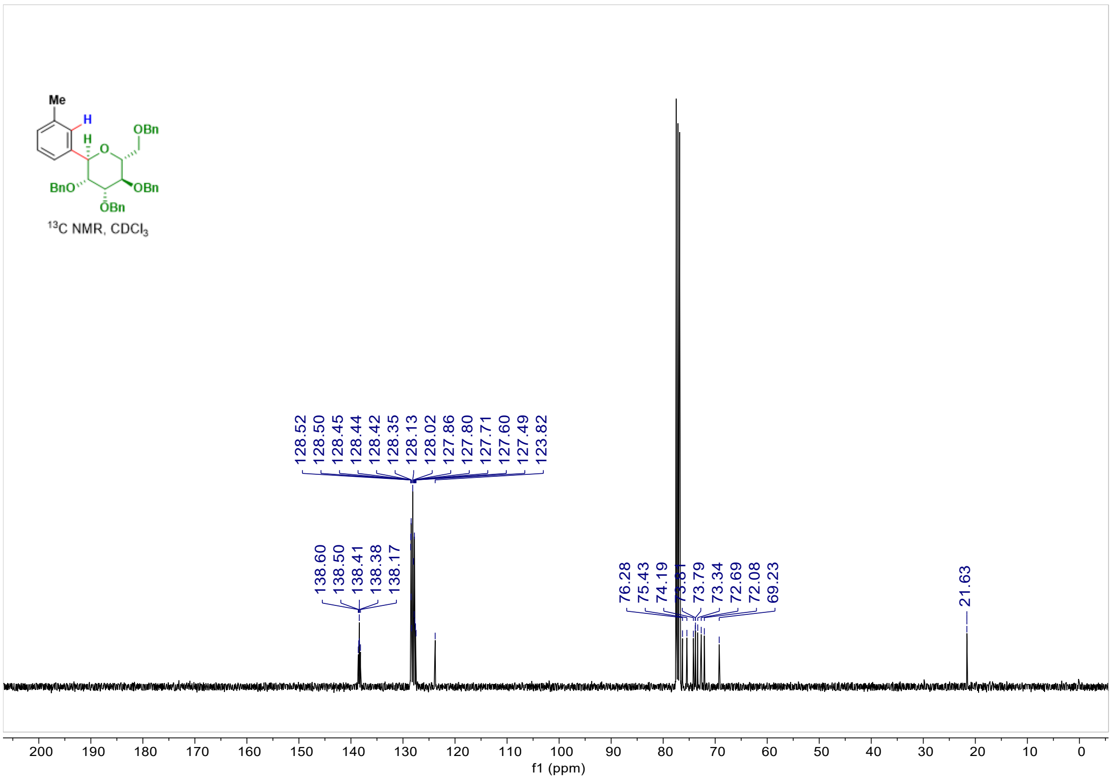
^{19}F NMR spectrum of **3a**



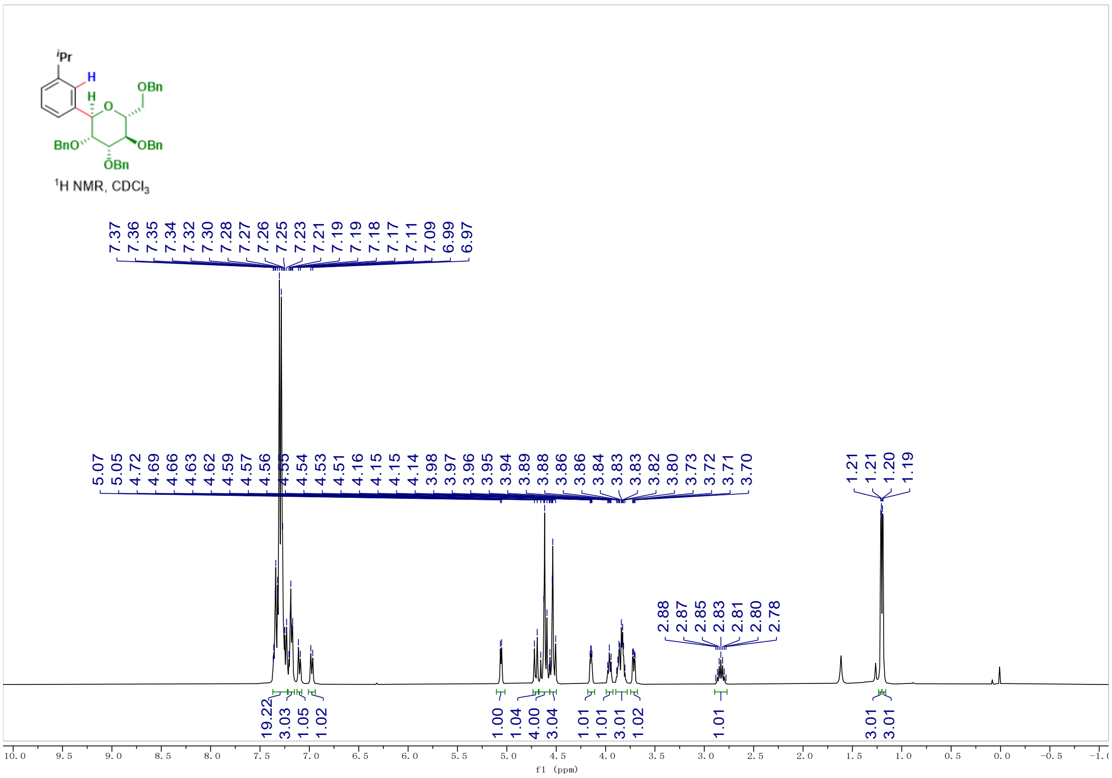
^{1}H NMR spectrum of **3b**



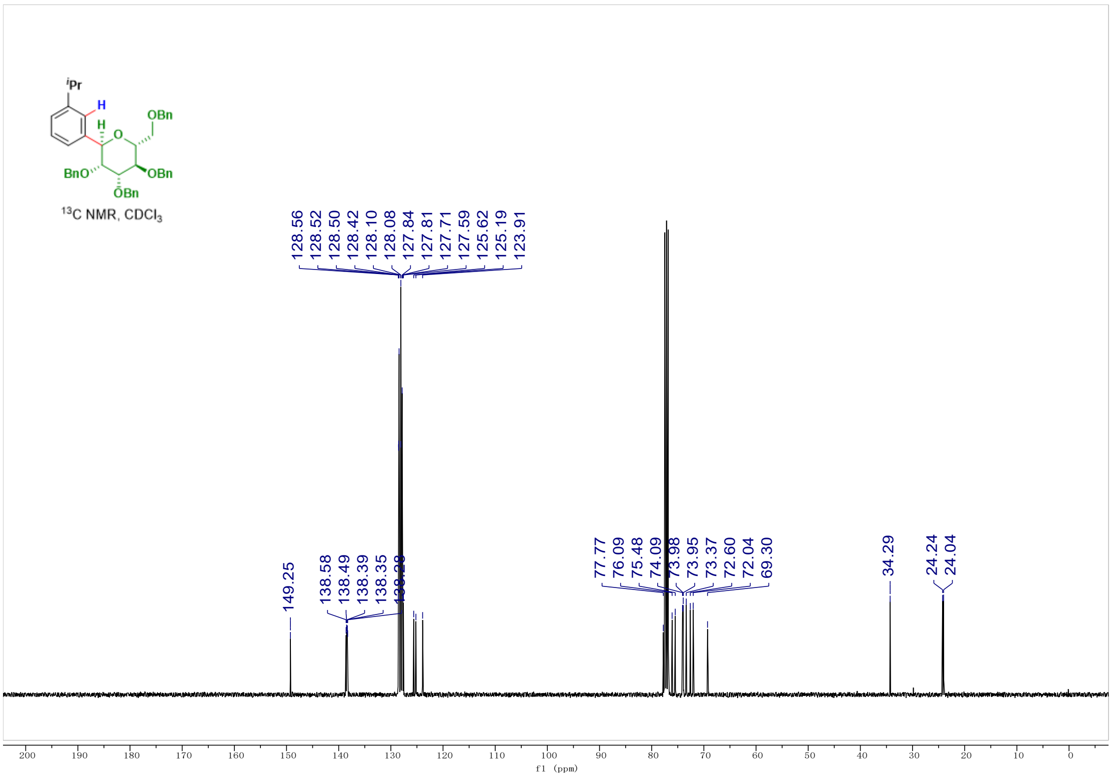
^{13}C NMR spectrum of **3b**



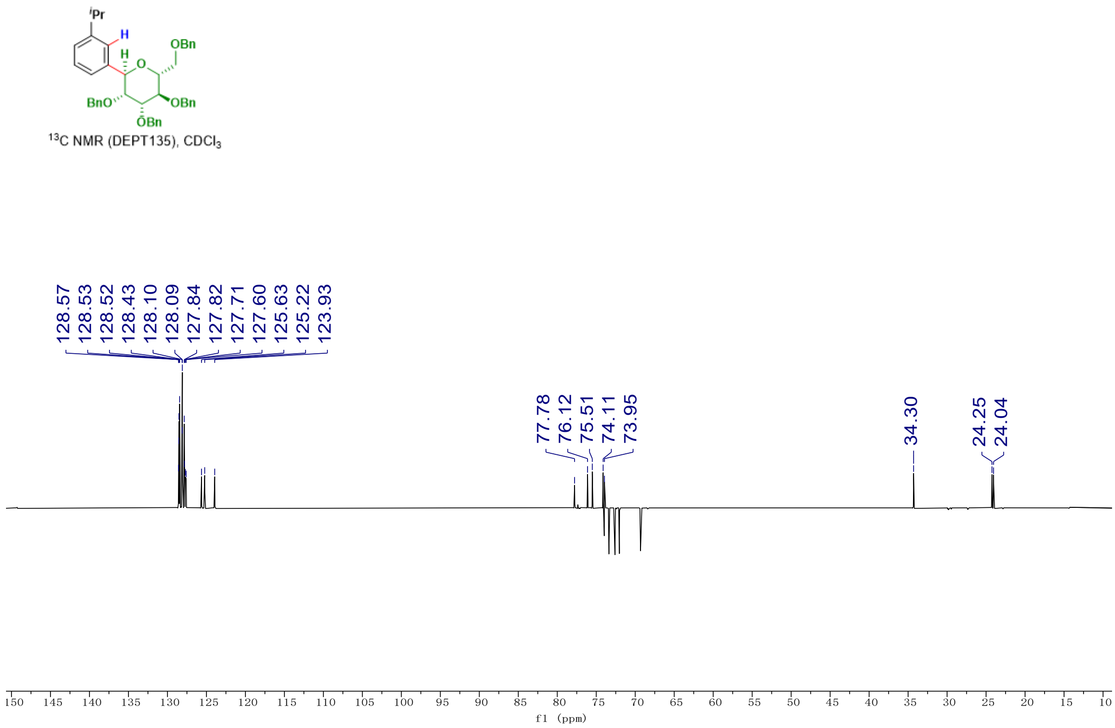
^{1}H NMR spectrum of **3c**



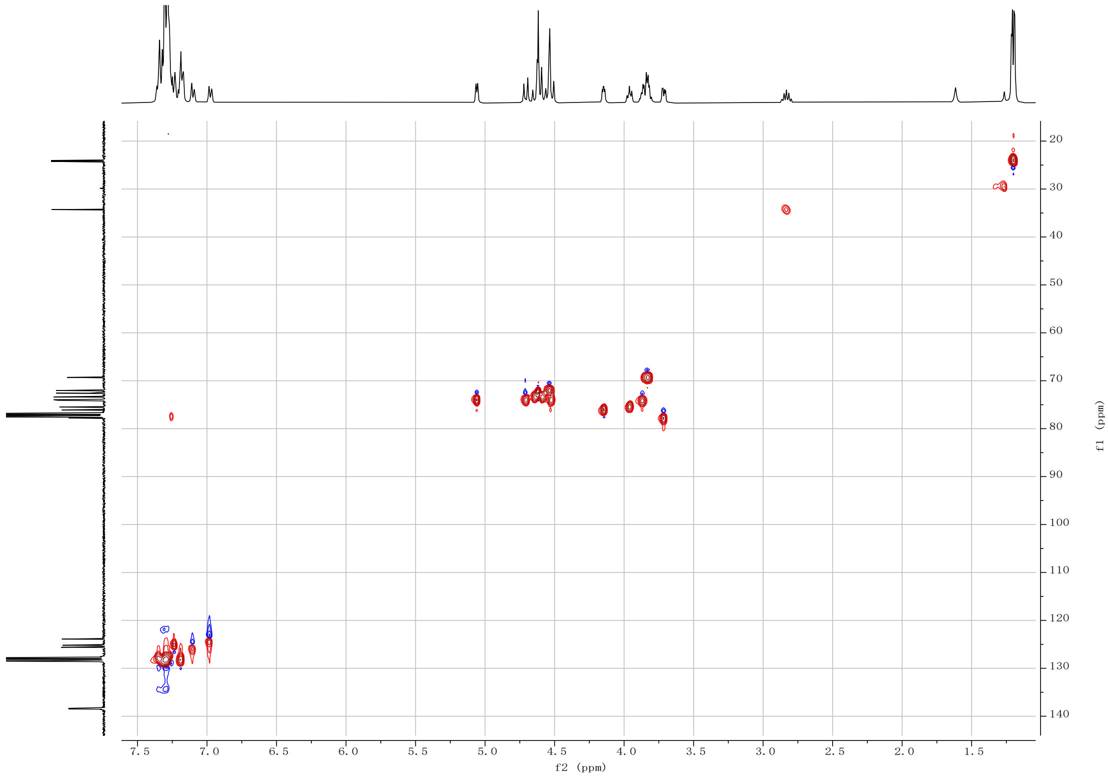
^{13}C NMR spectrum of **3c**



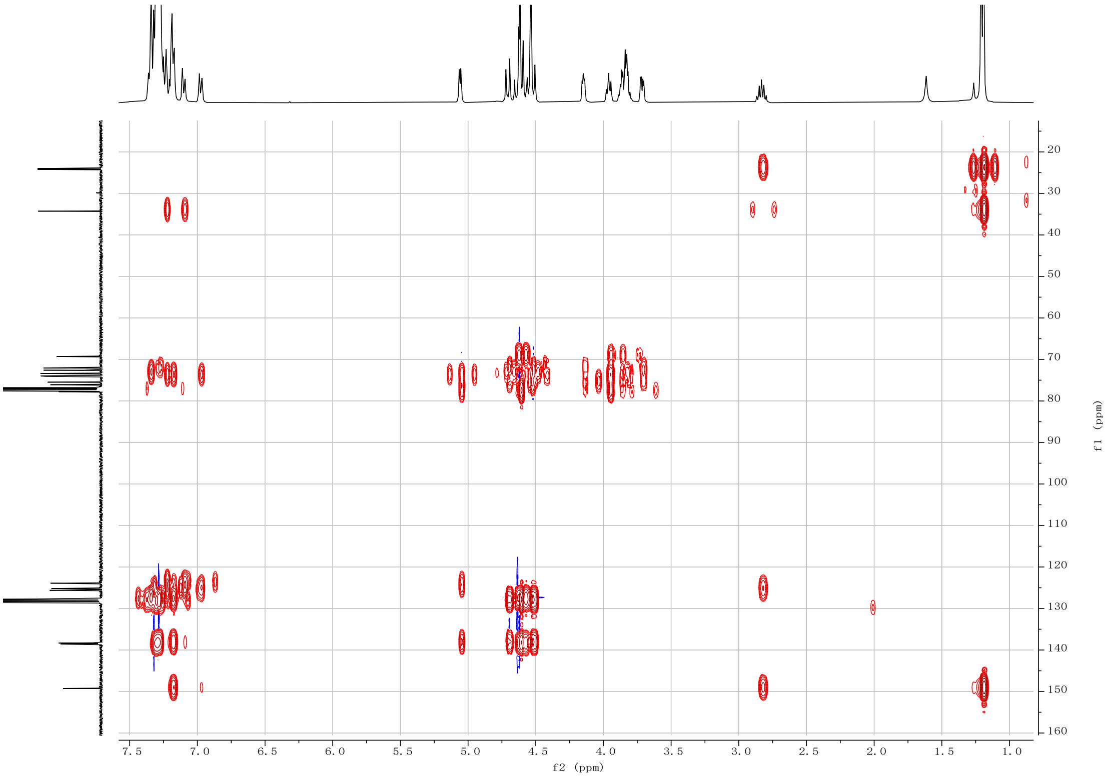
^{13}C NMR (DEPT135) spectrum of **3c**



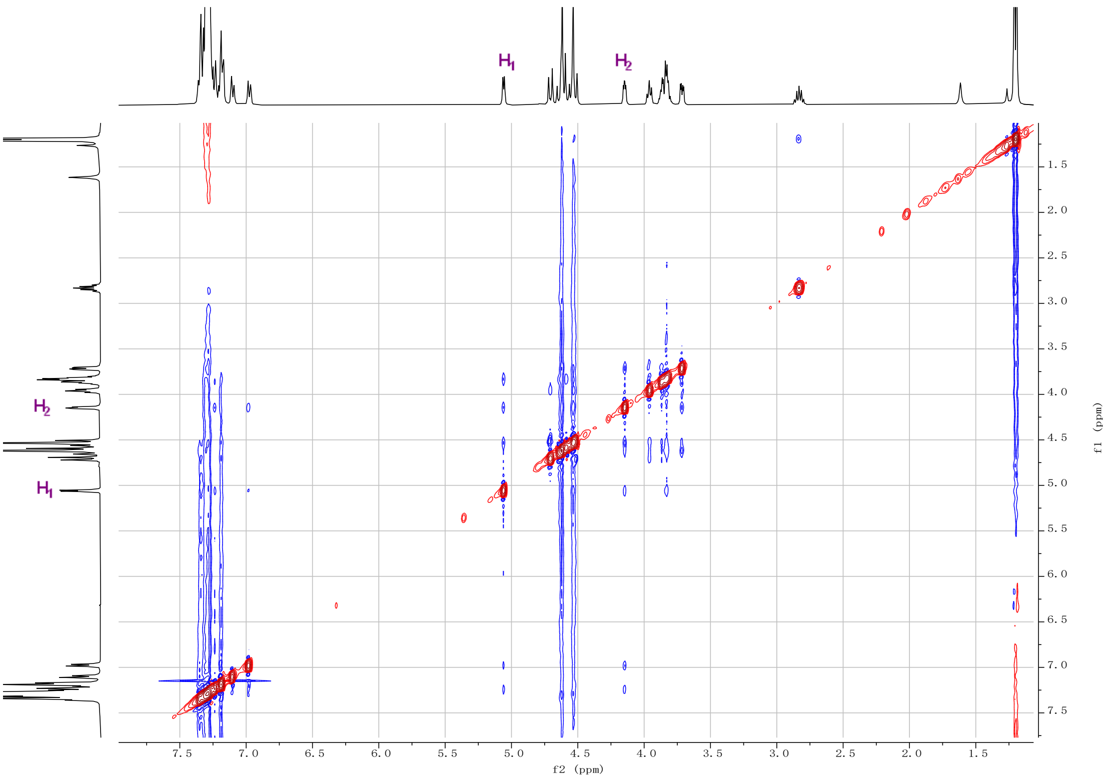
^{1}H-^{13}C HSQC NMR spectrum of **3c**



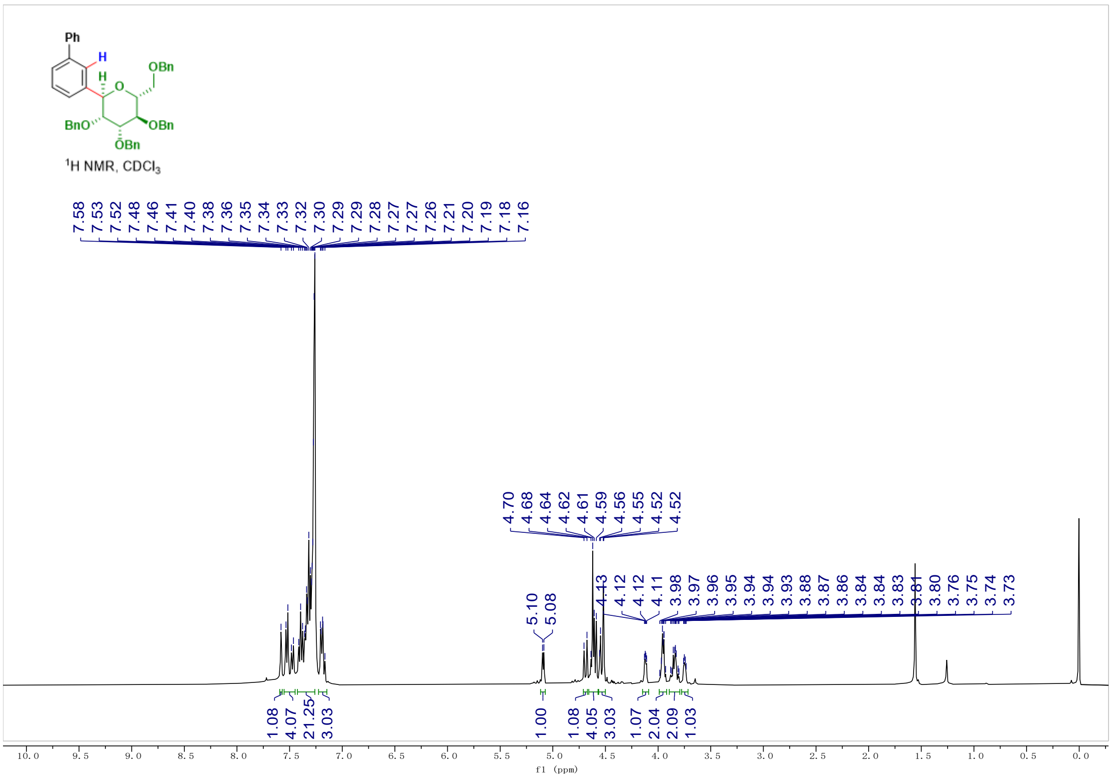
^{1}H-^{13}C HMBC NMR spectrum of **3c**



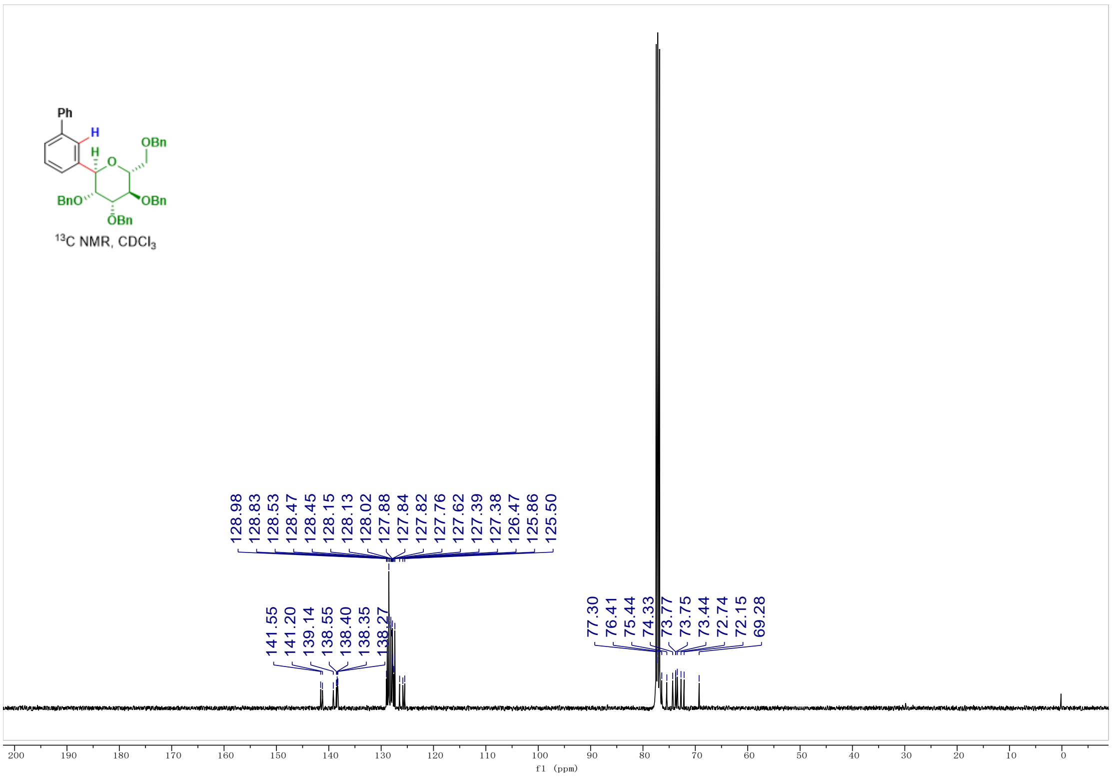
^{1}H-^{1}H NOESY NMR spectrum of **3c**



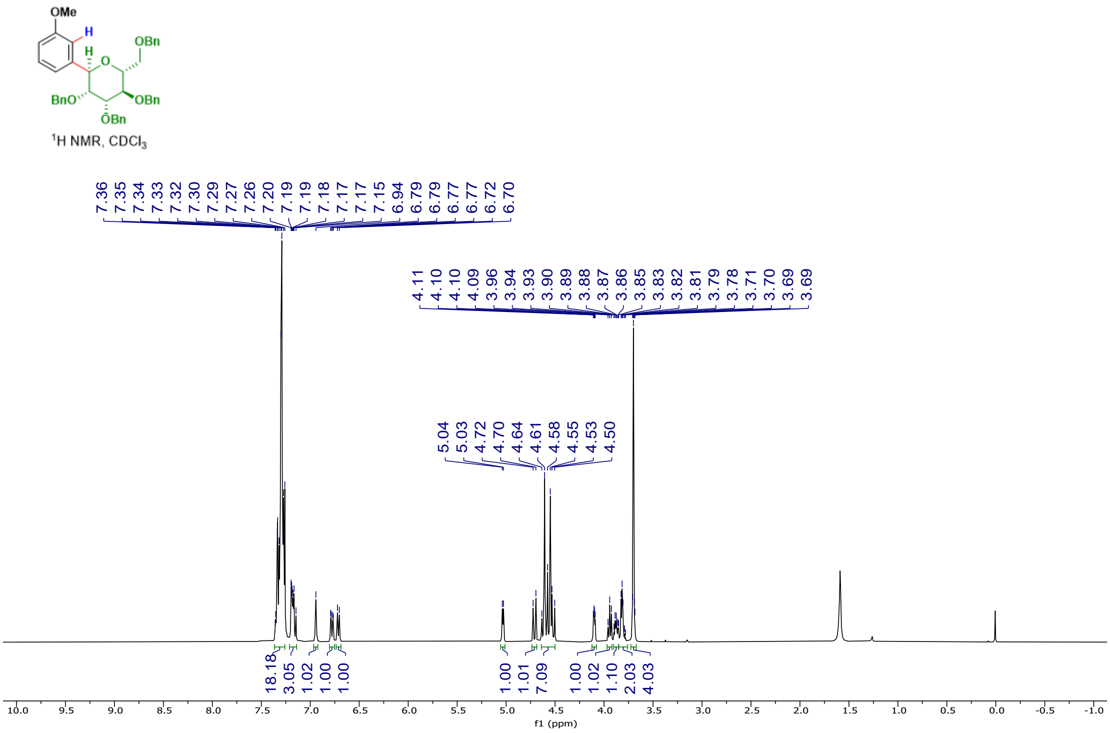
^{1}H NMR spectrum of **3d**



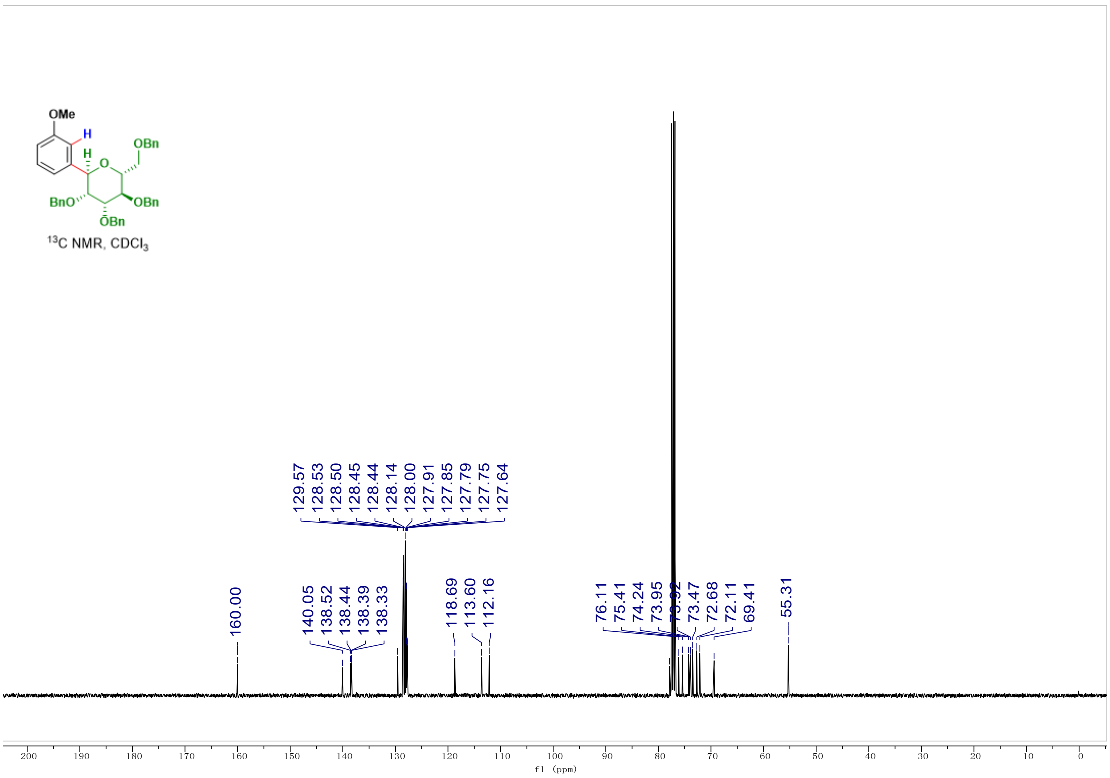
^{13}C NMR spectrum of **3d**



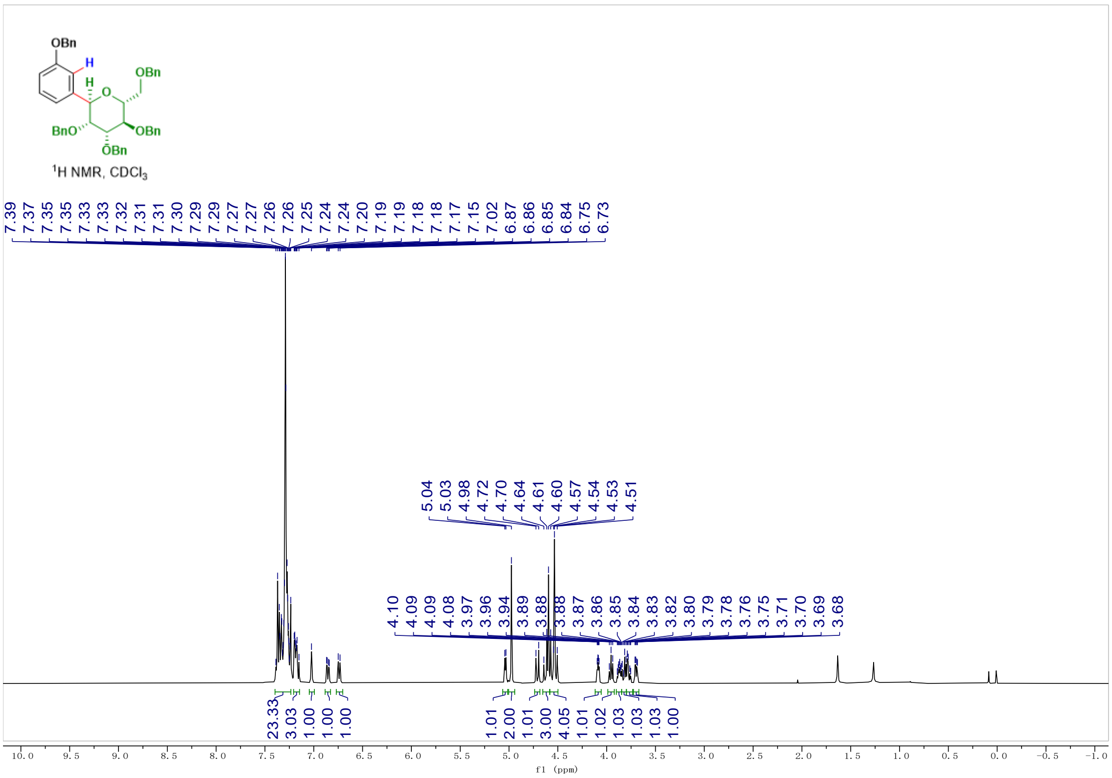
[1]H NMR spectrum of **3e**



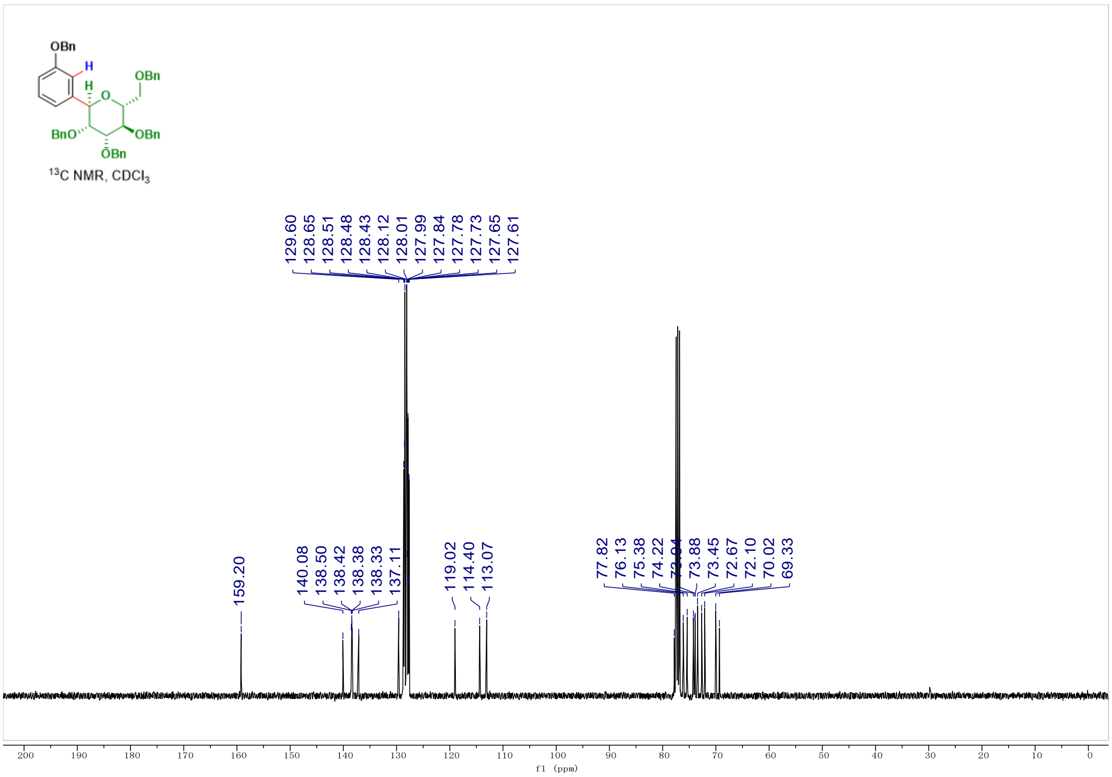
[13]C NMR spectrum of **3e**



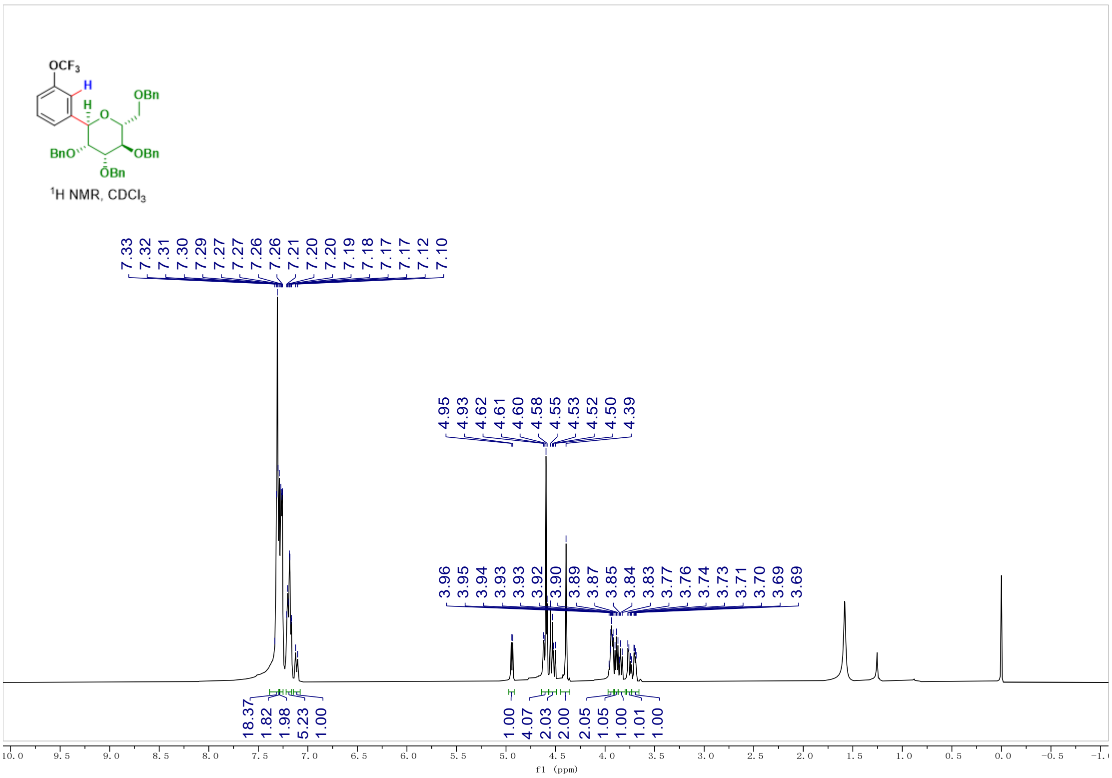
^{1}H NMR spectrum of **3f**



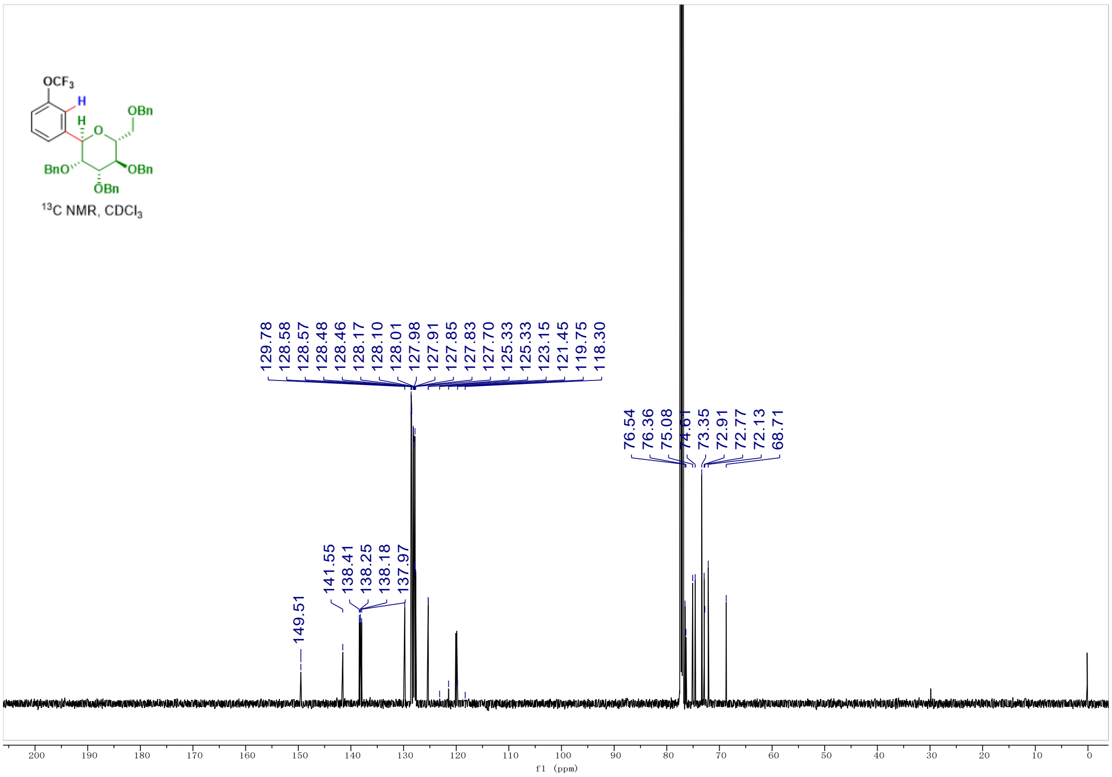
^{13}C NMR spectrum of **3f**



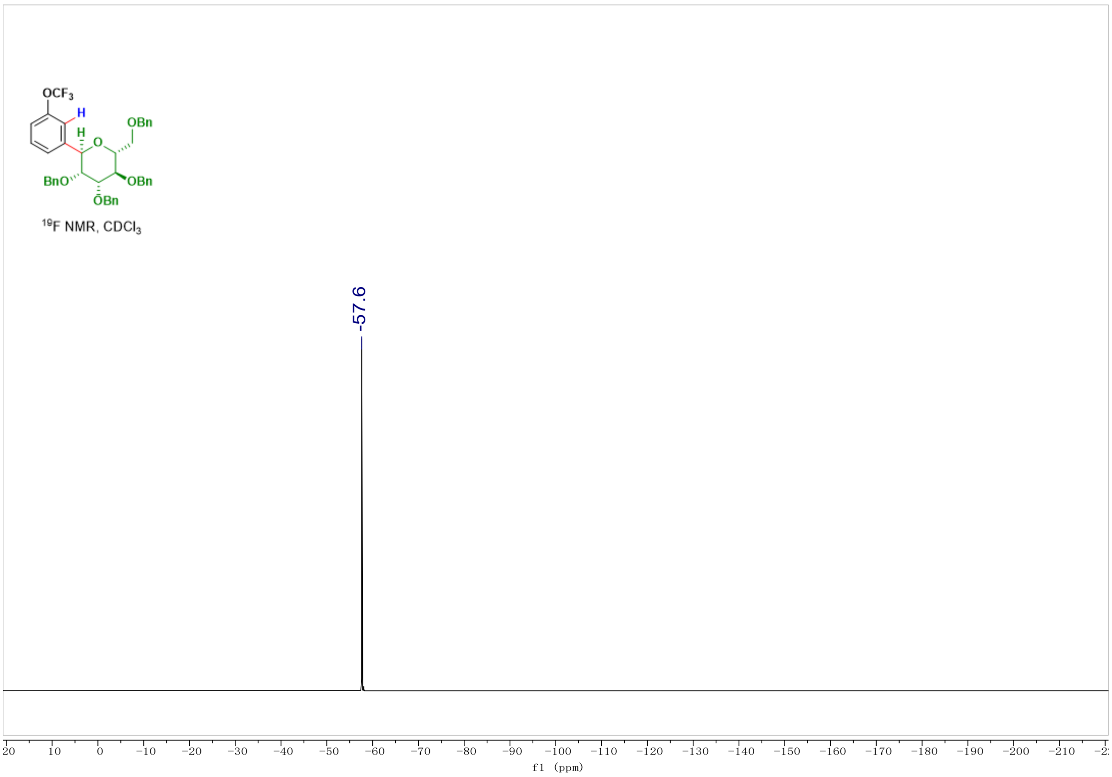
[1]H NMR spectrum of **3g**



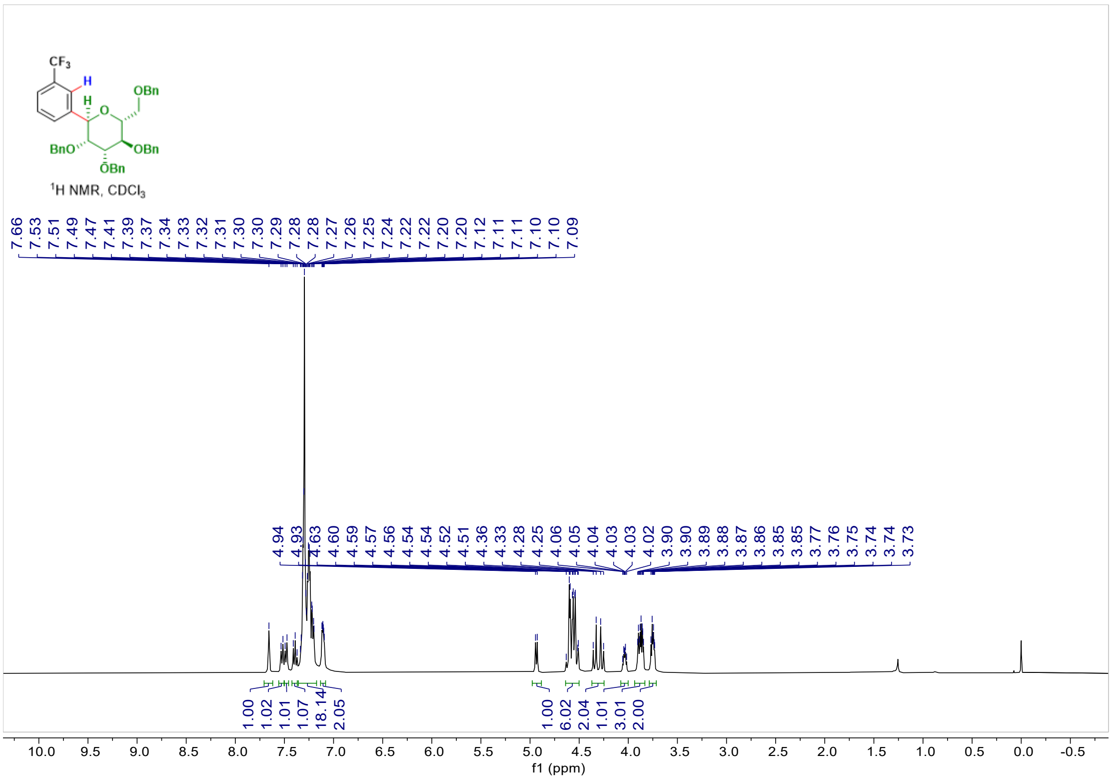
[13]C NMR spectrum of **3g**



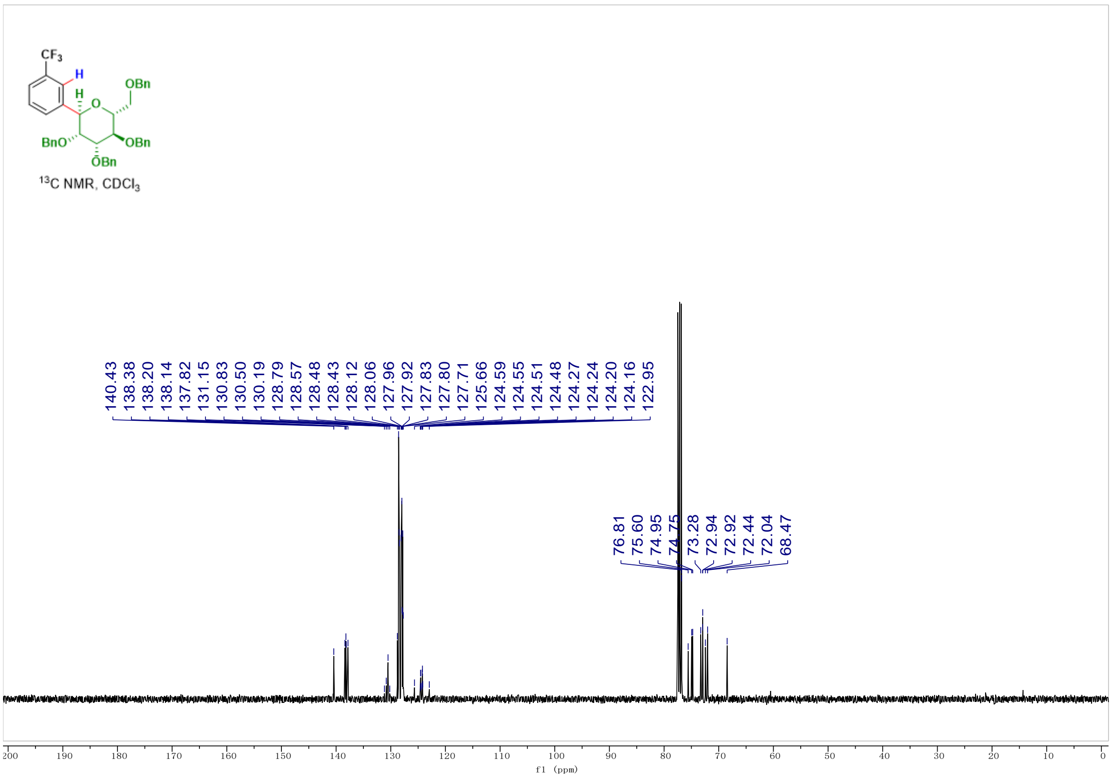
^{19}F NMR spectrum of **3g**



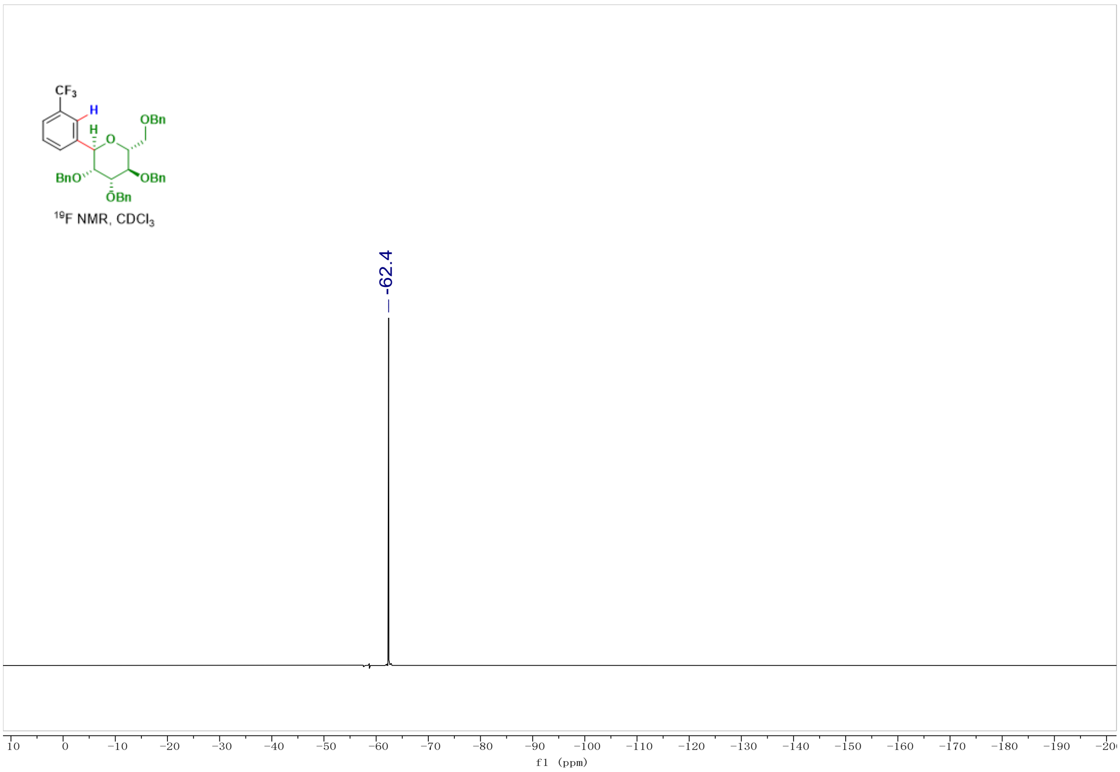
^{1}H NMR spectrum of **3h**



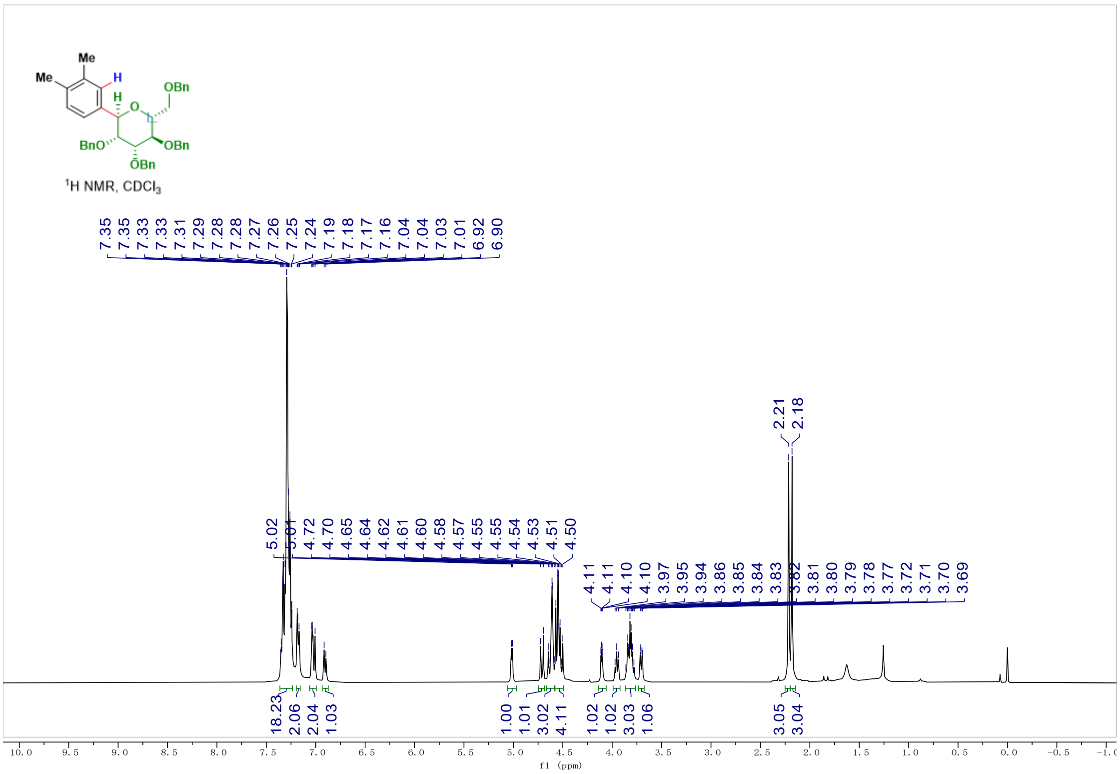
^{13}C NMR spectrum of **3h**



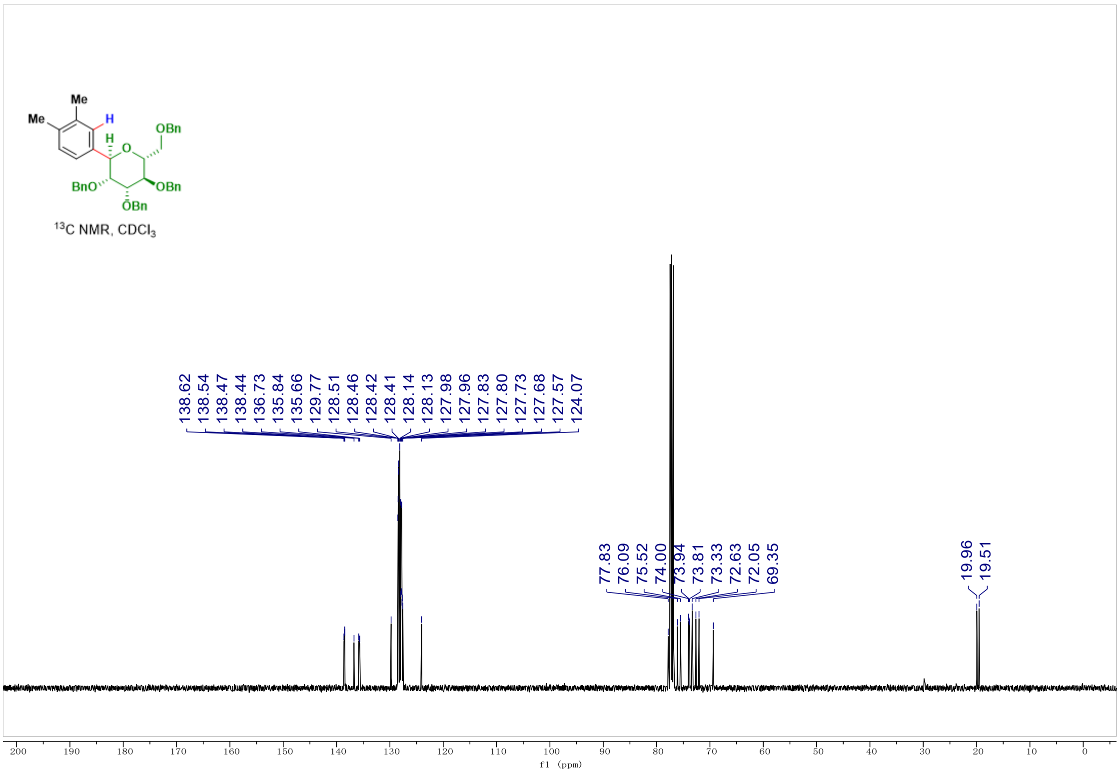
^{19}F NMR spectrum of **3h**



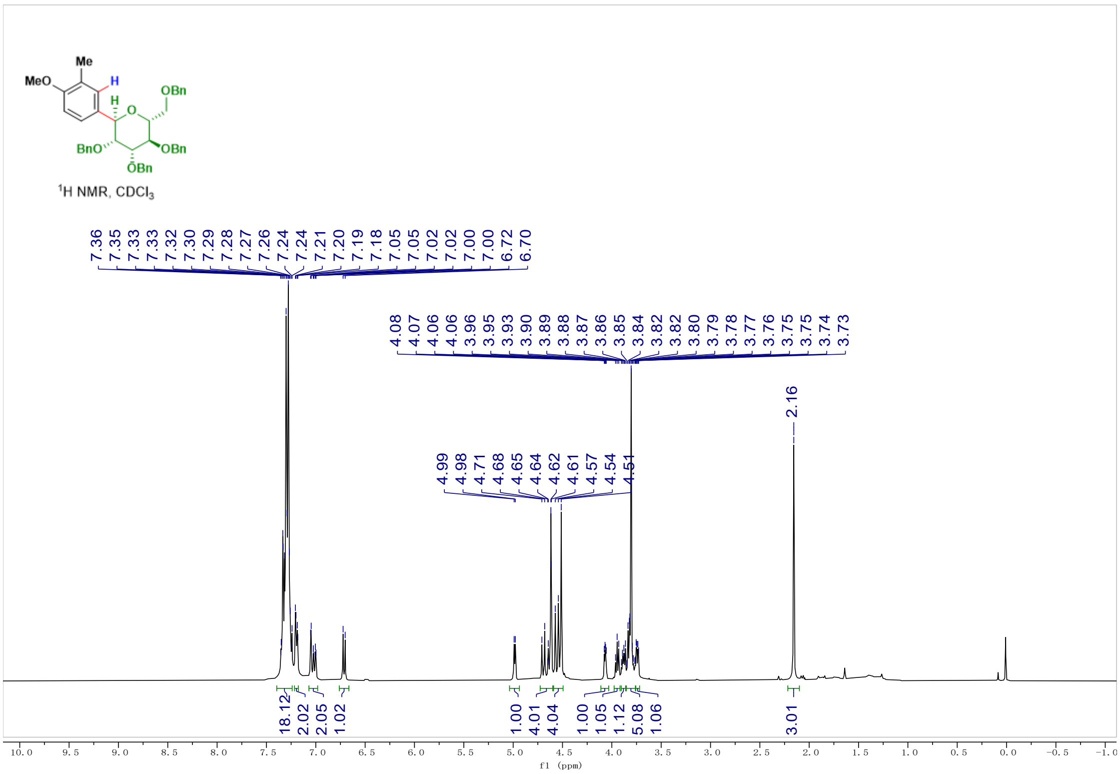
[1]H NMR spectrum of **3i**



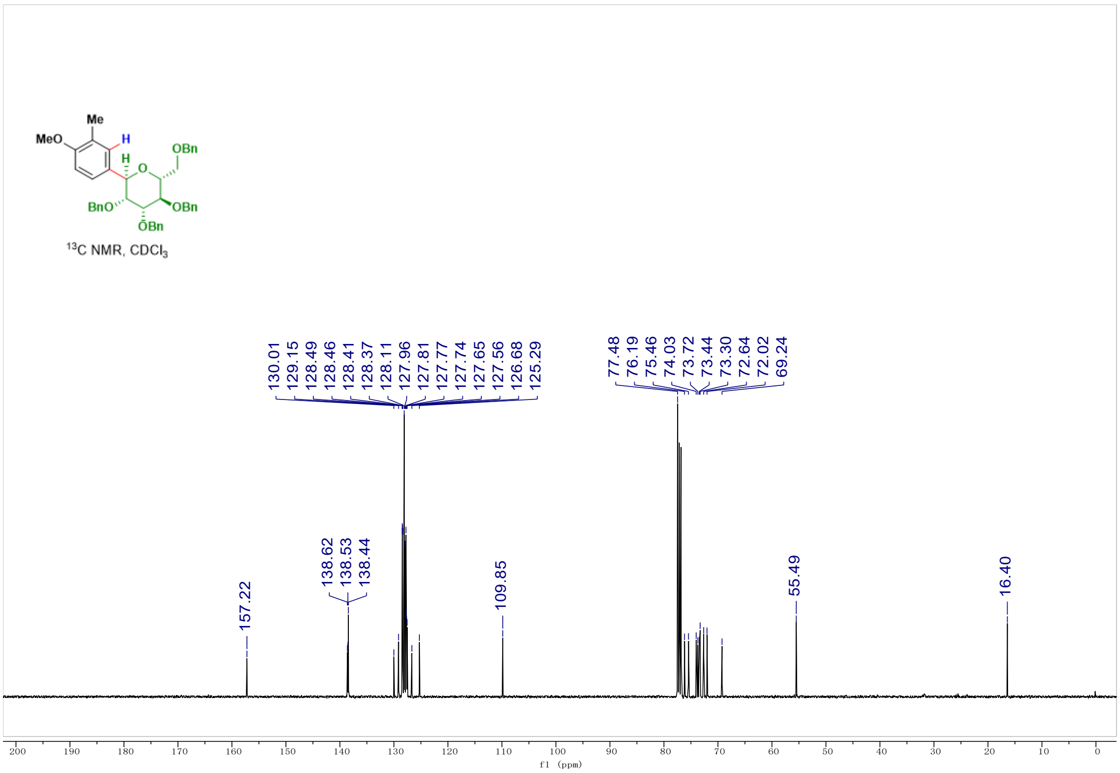
[13]C NMR spectrum of **3i**



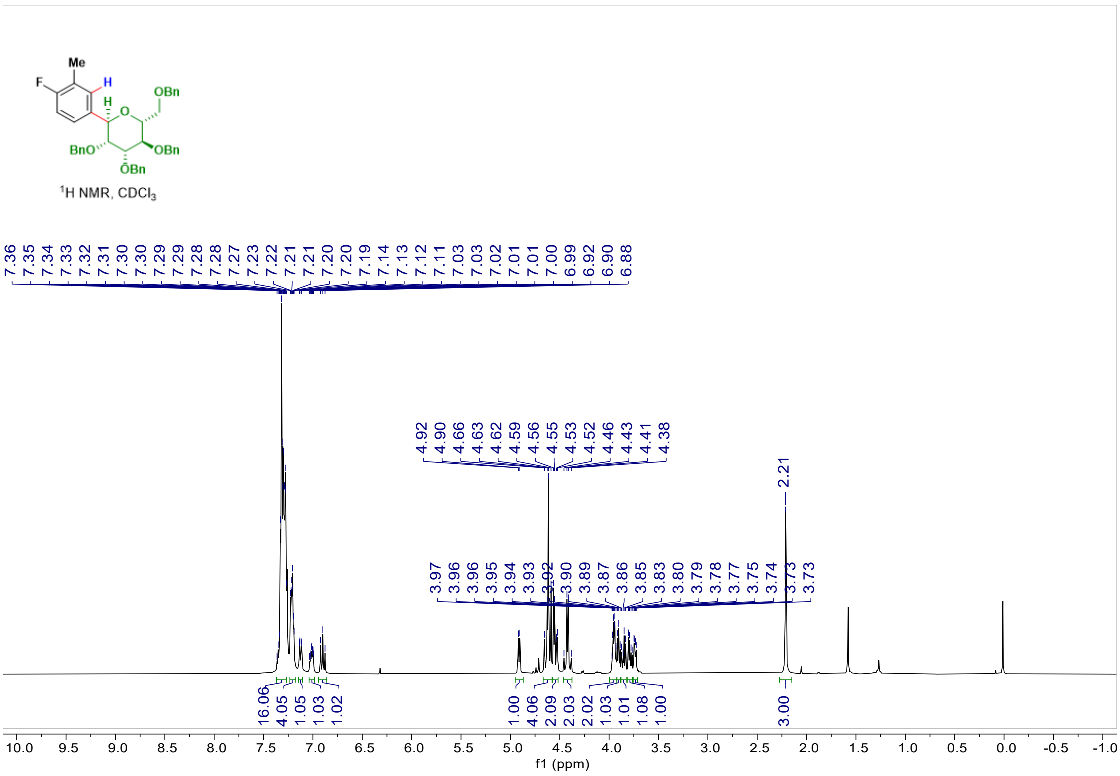
^{1}H NMR spectrum of **3j**



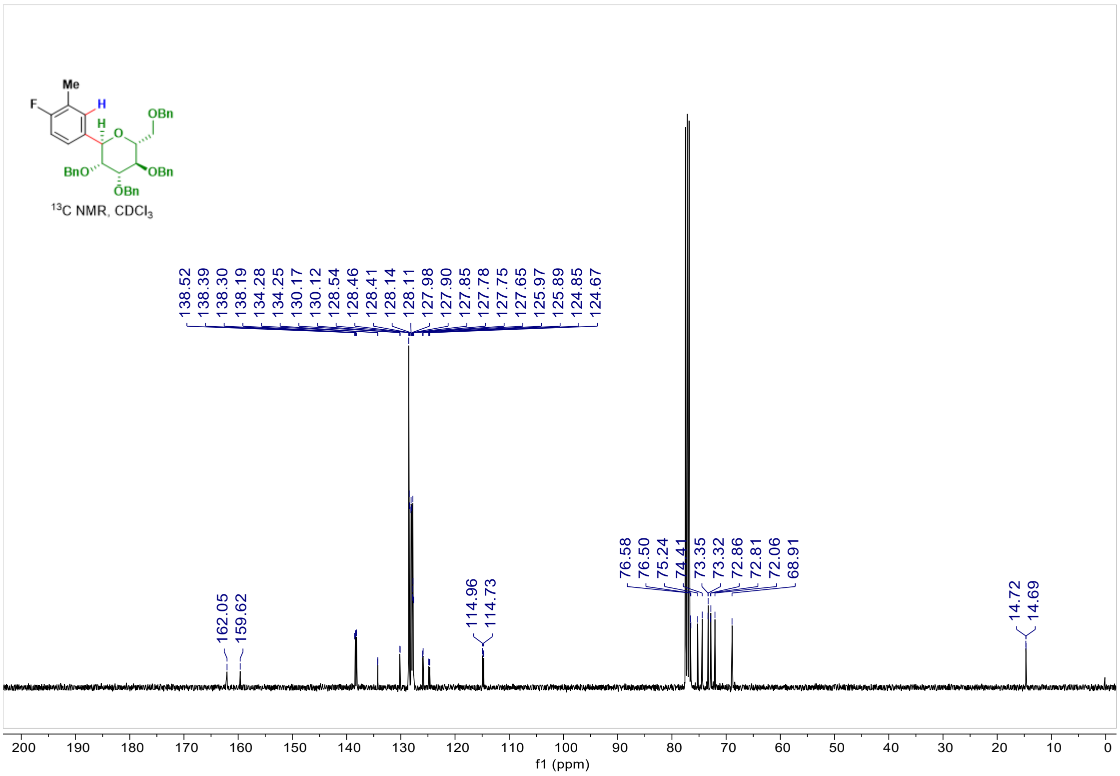
^{13}C NMR spectrum of **3j**



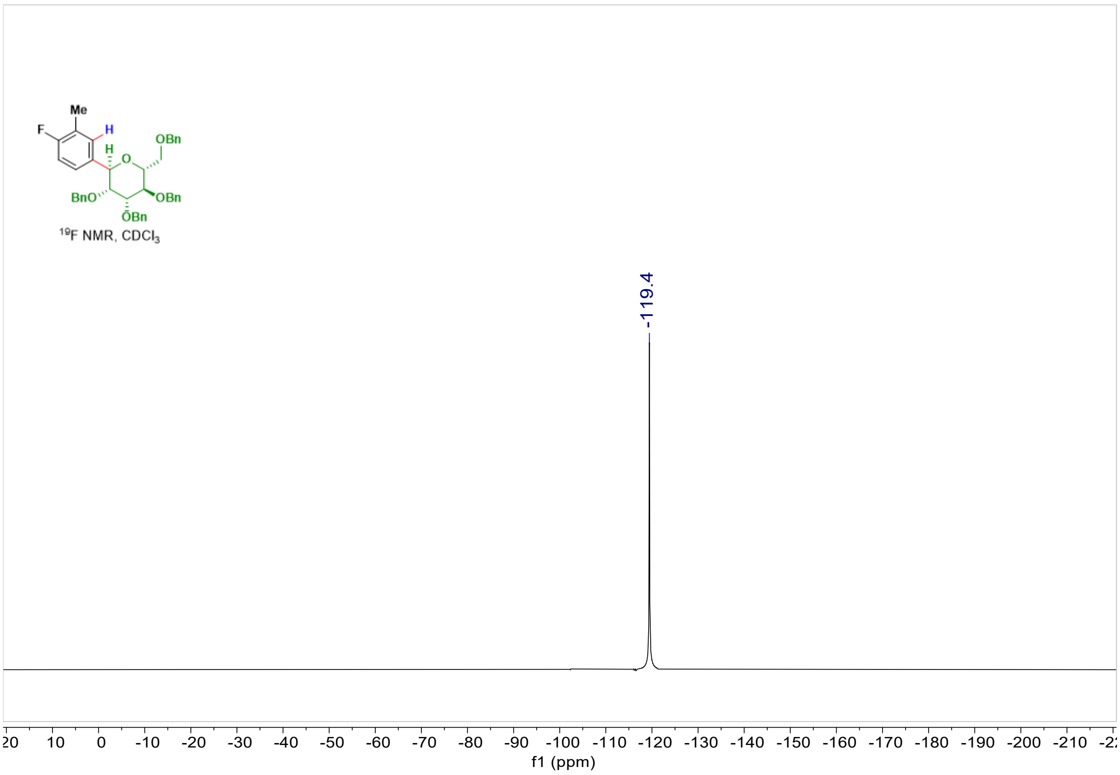
^{1}H NMR spectrum of **3k**



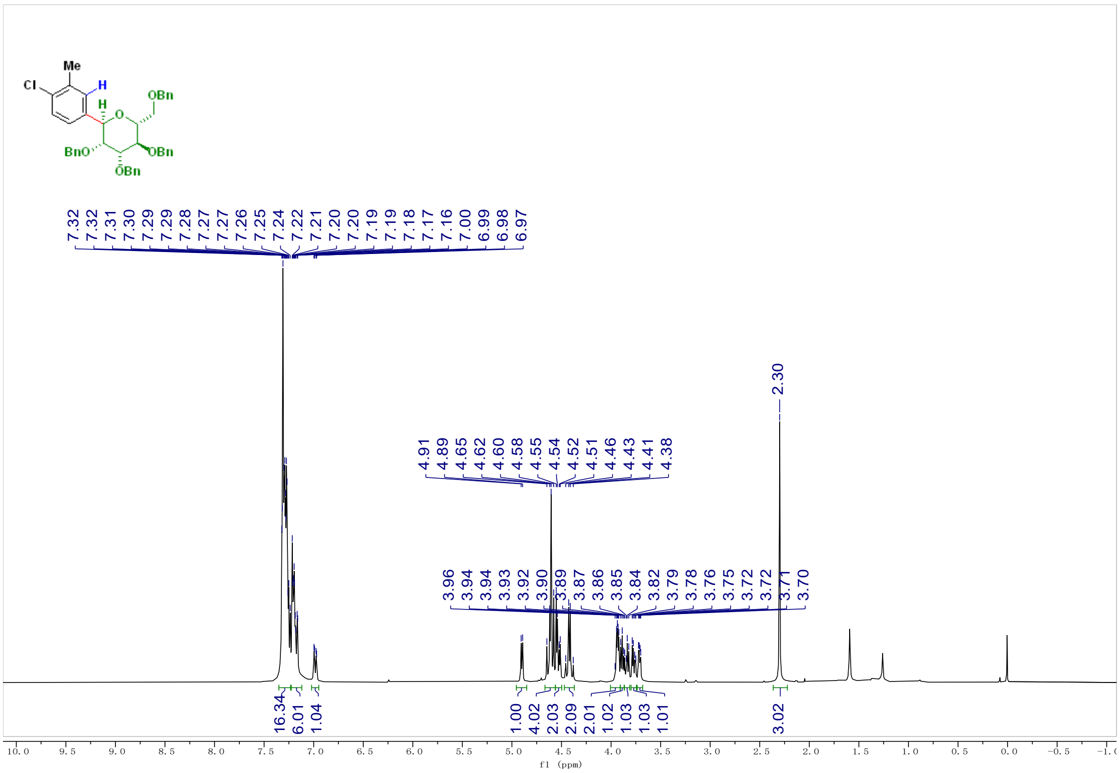
^{13}C NMR spectrum of **3k**



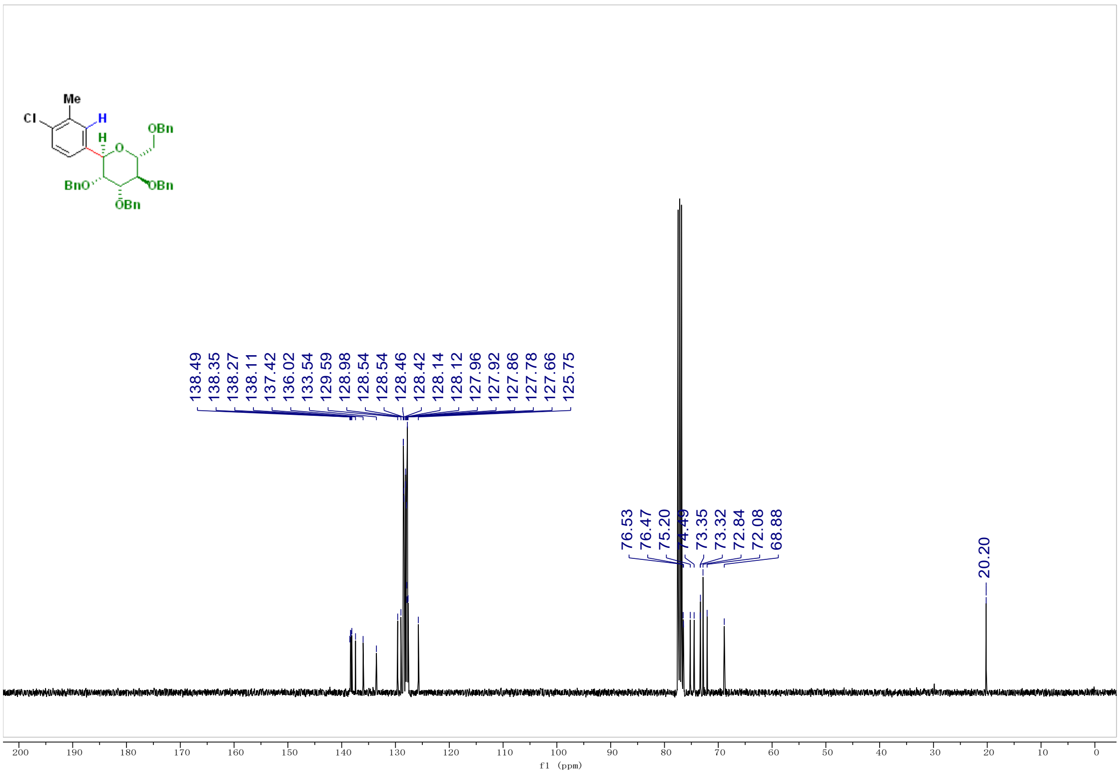
[19]F NMR spectrum of **3k**



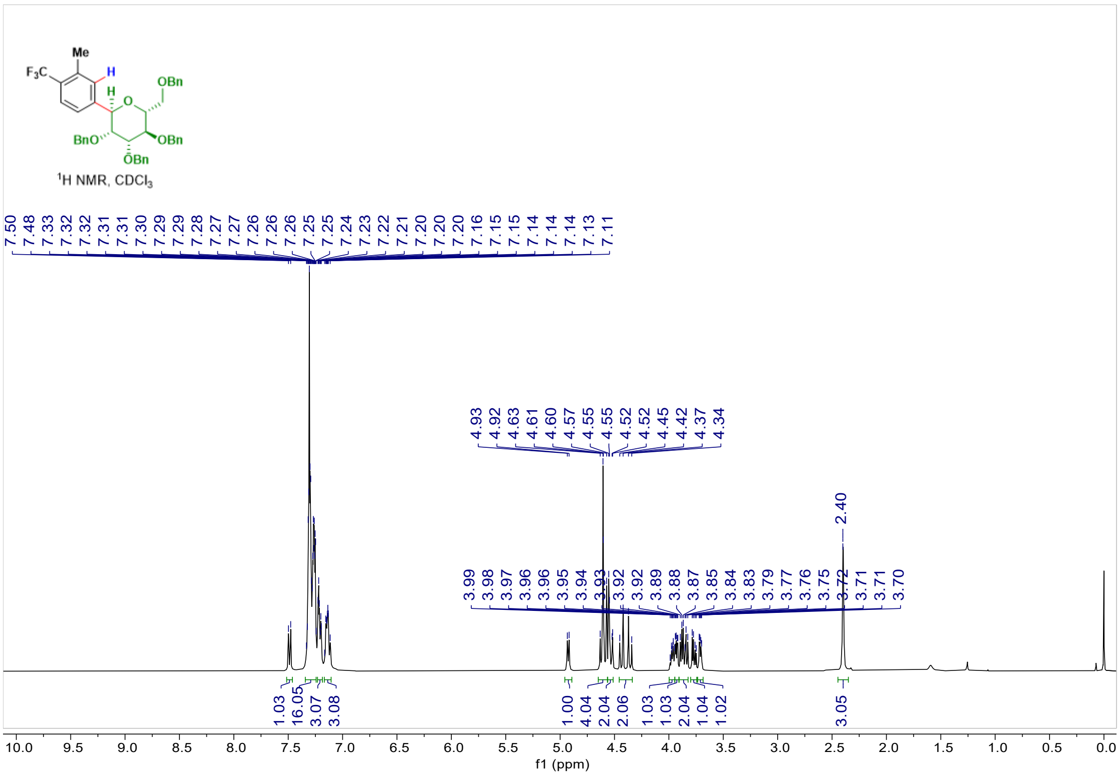
[1]H NMR spectrum of **3l**



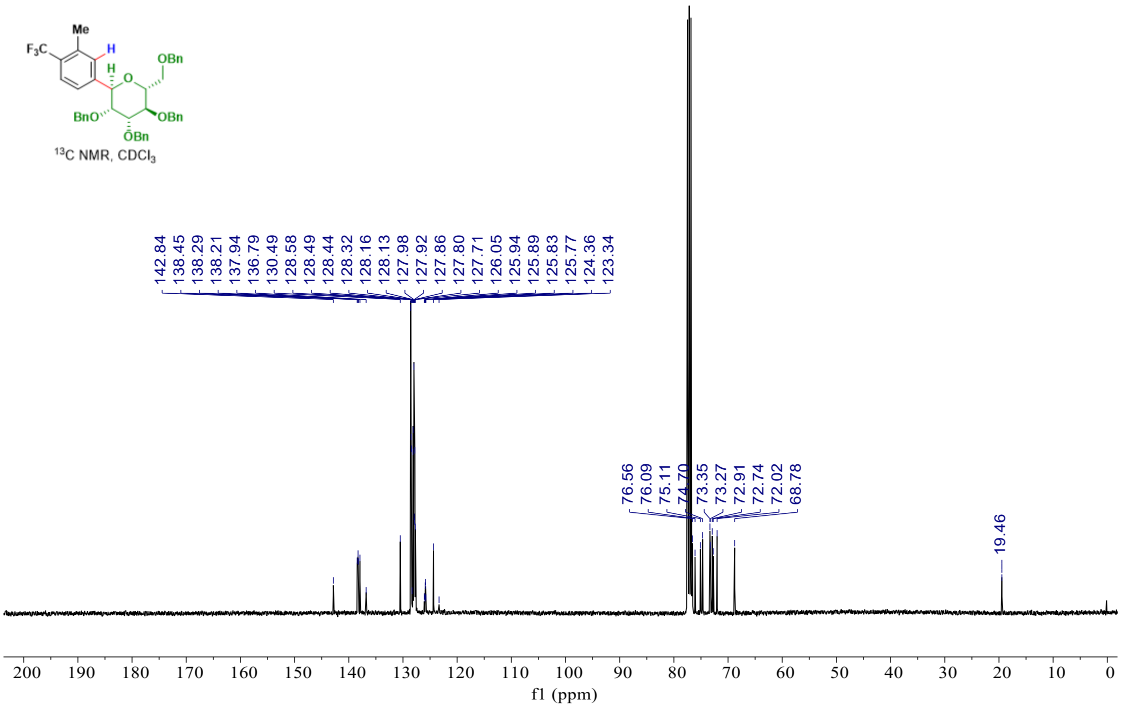
^{13}C NMR spectrum of **3l**



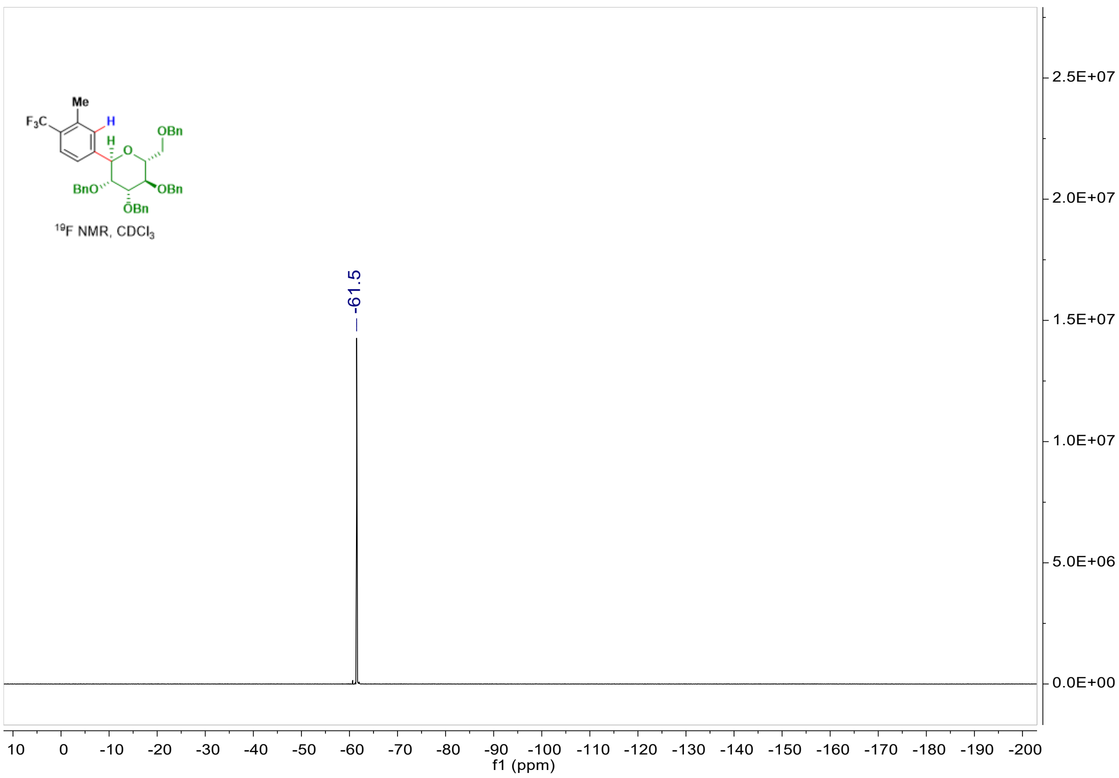
^{1}H NMR spectrum of **3m**



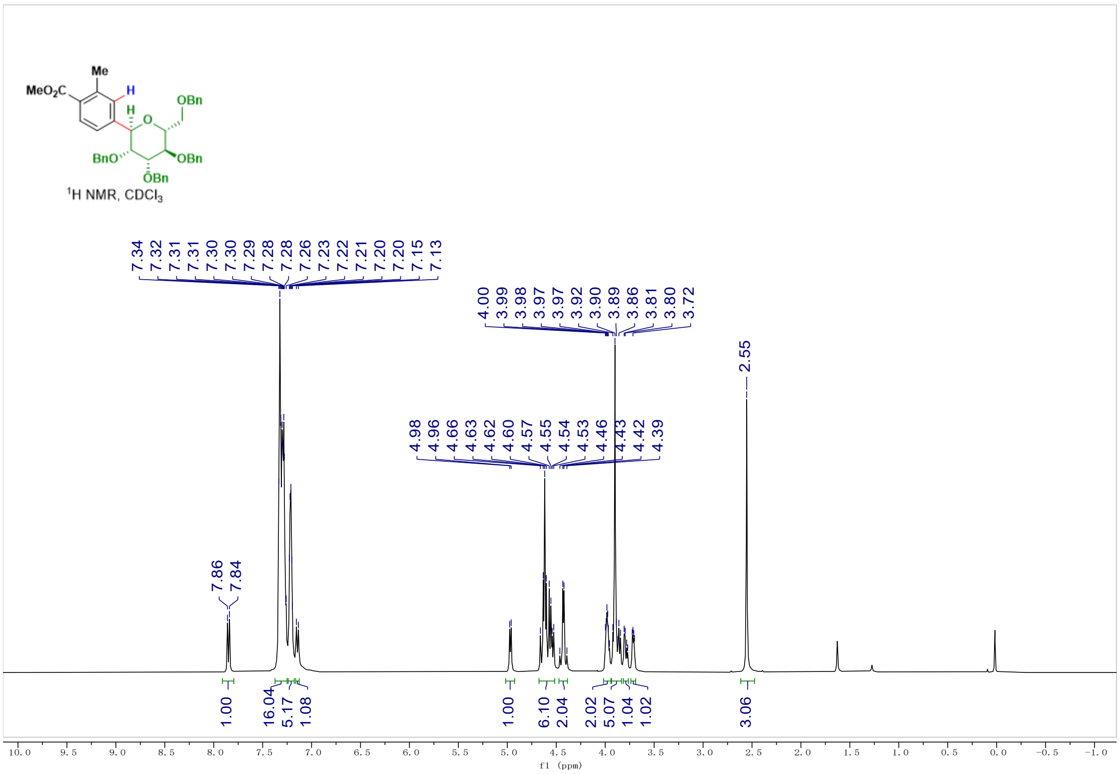
[13]C NMR spectrum of **3m**



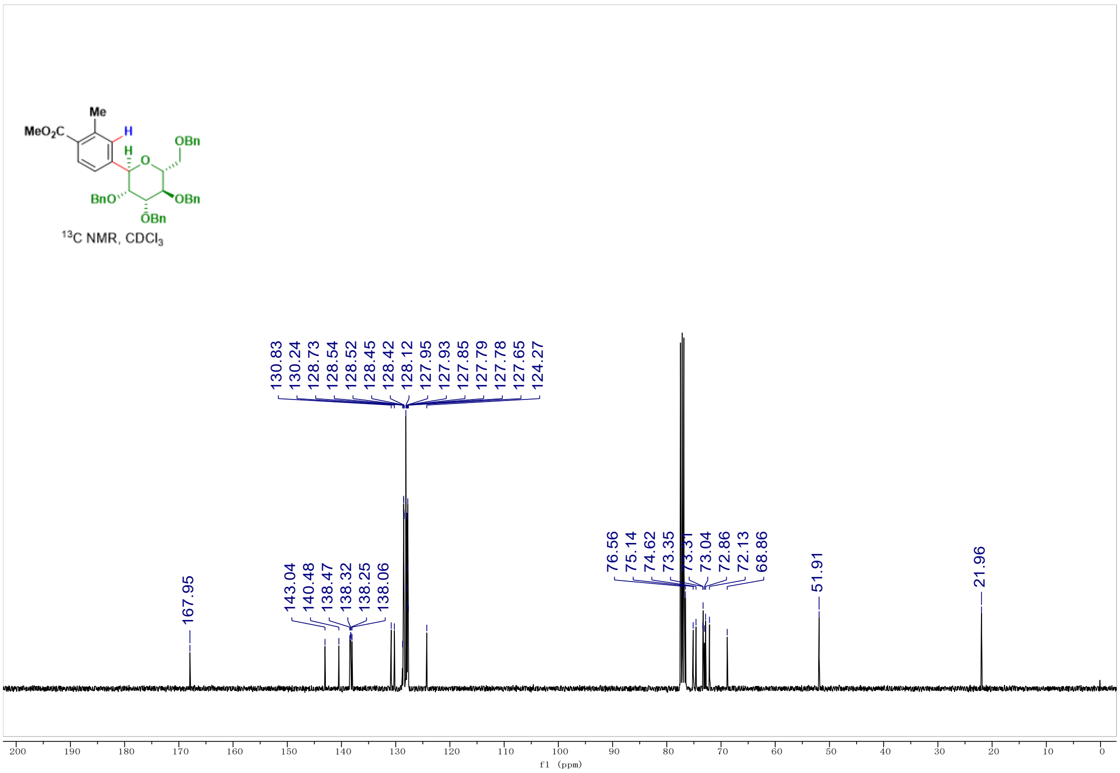
[19]F NMR spectrum of **3m**



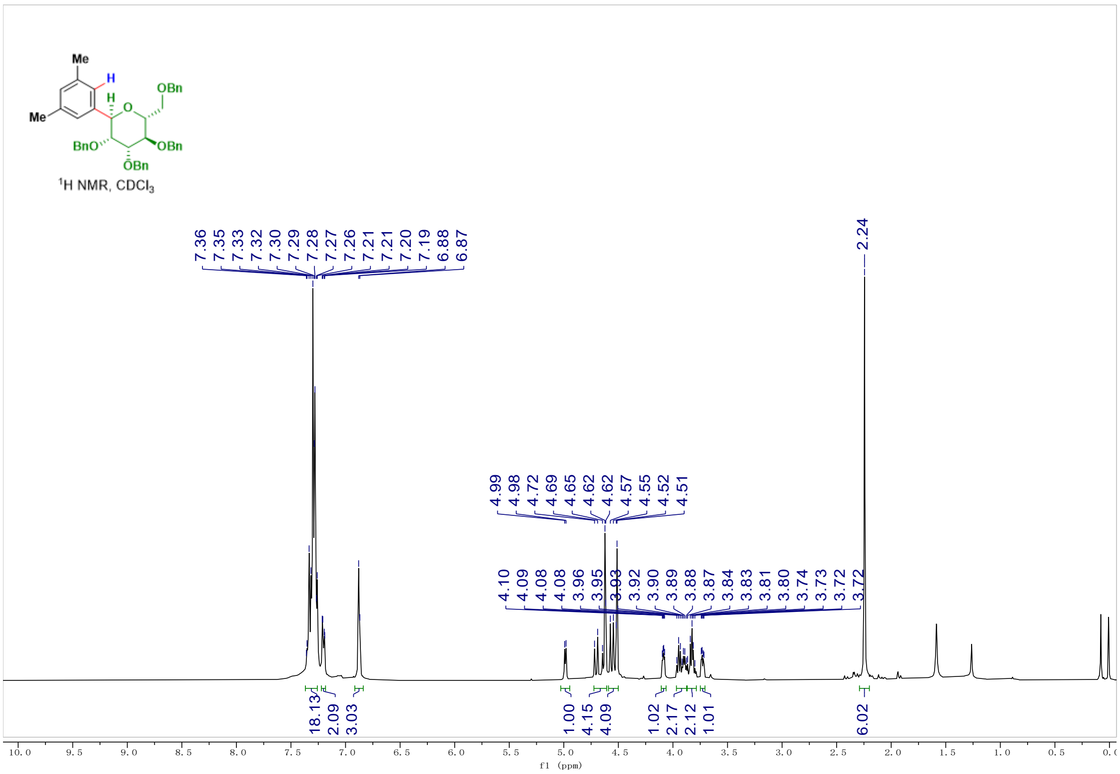
[1]H NMR spectrum of **3n**



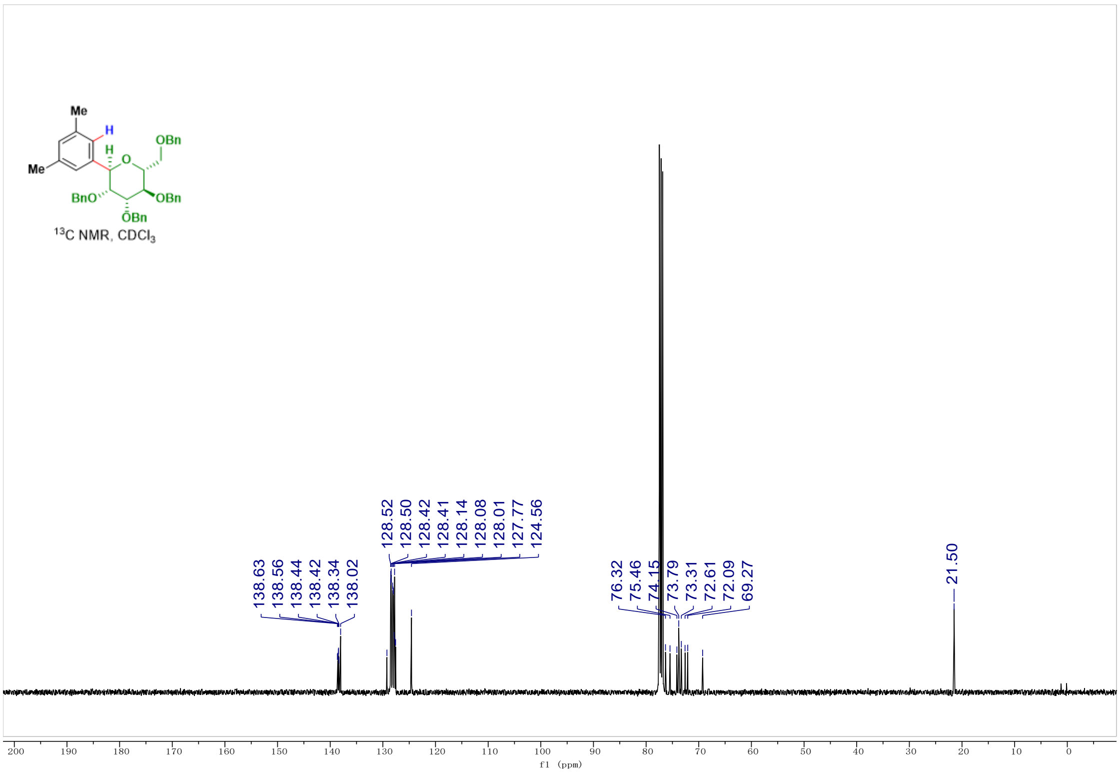
[13]C NMR spectrum of **3n**



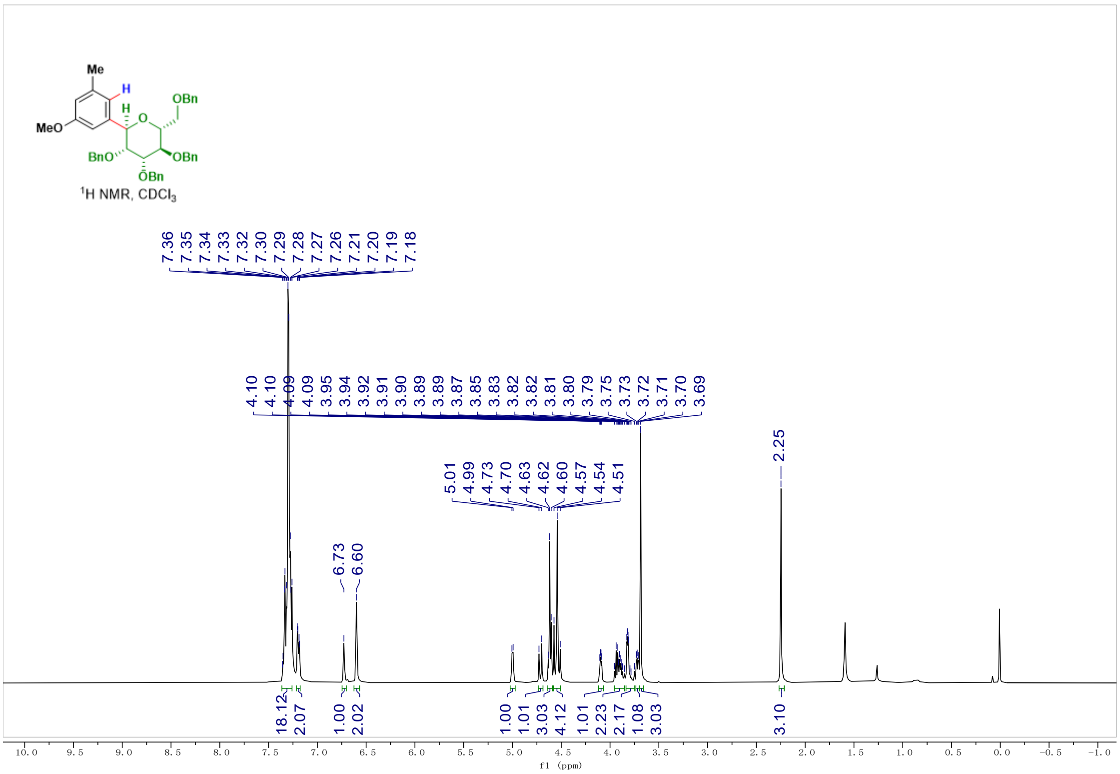
[1]H NMR spectrum of **3o**



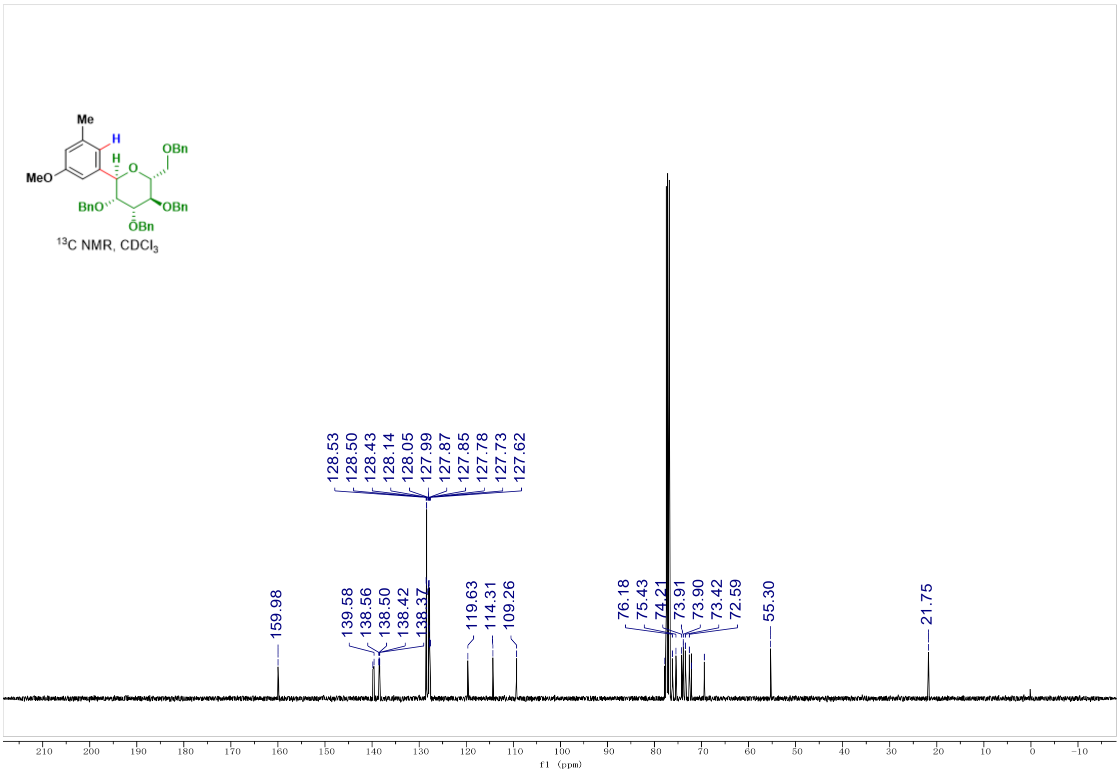
[13]C NMR spectrum of **3o**



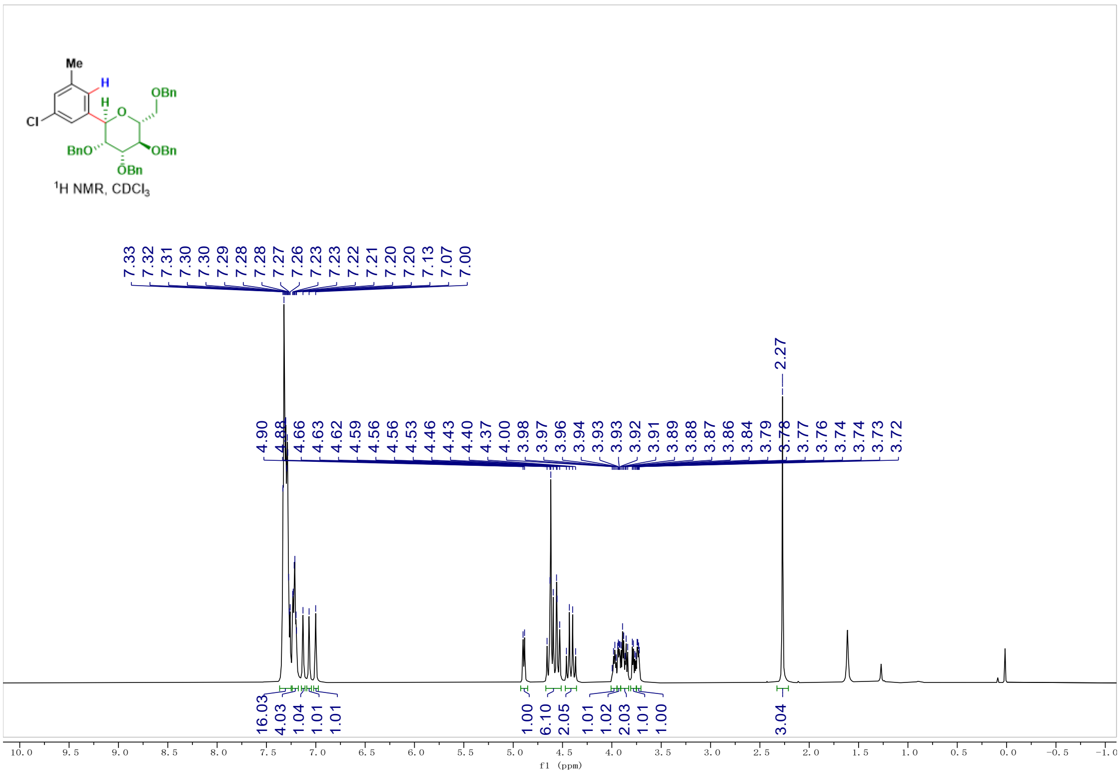
^{1}H NMR spectrum of **3p**



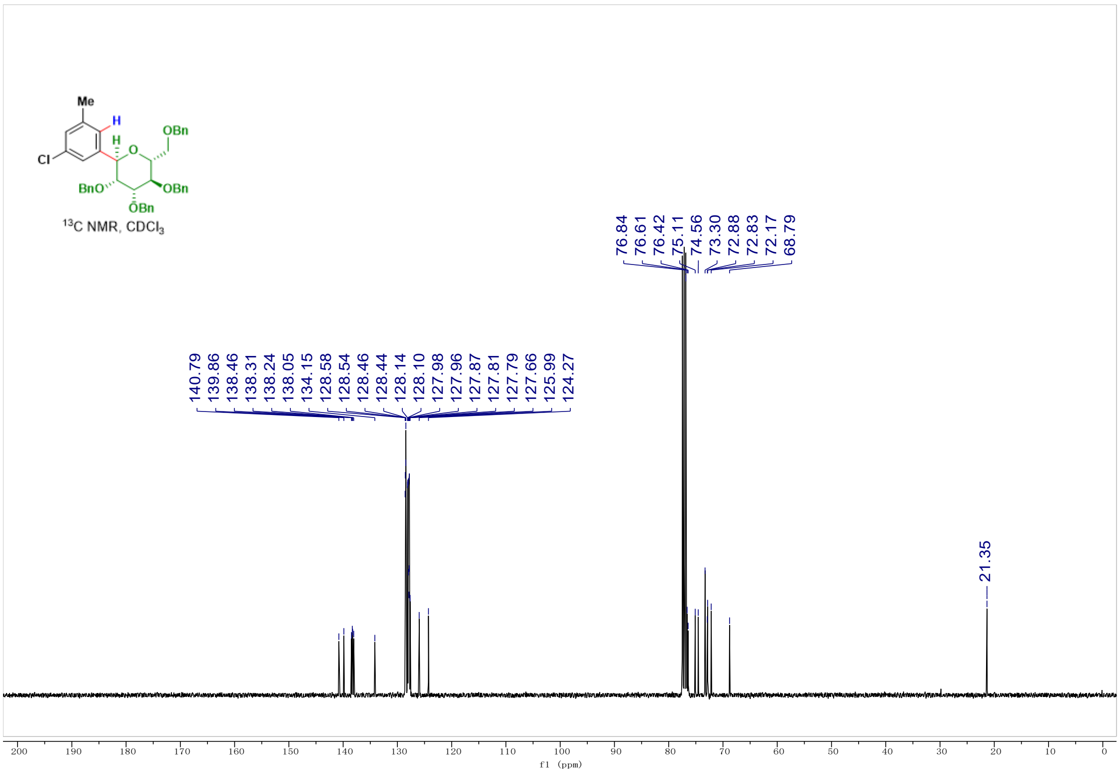
^{13}C NMR spectrum of **3p**



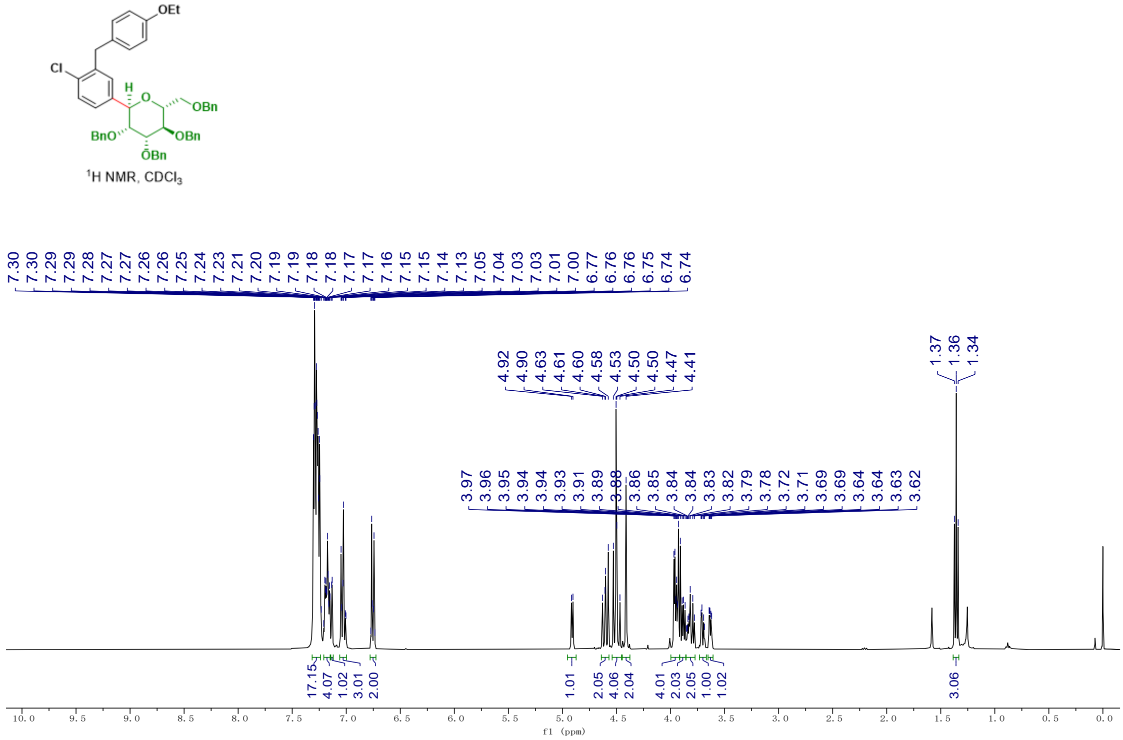
[1]H NMR spectrum of **3q**



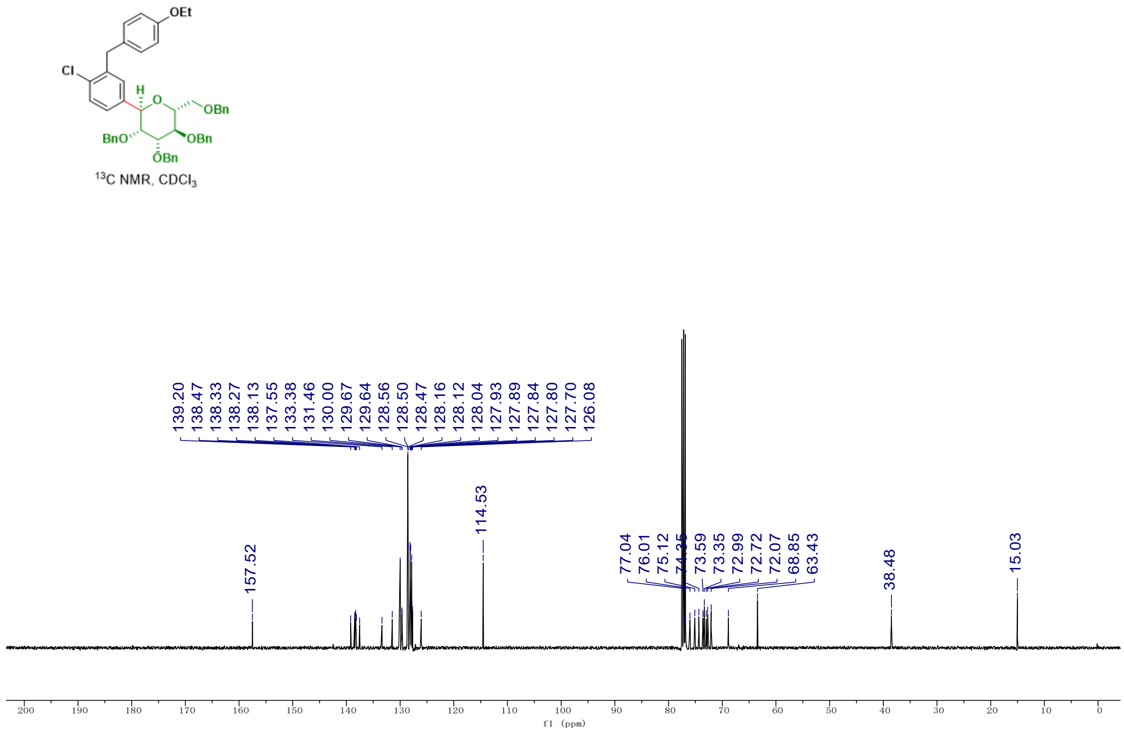
[13]C NMR spectrum of **3q**



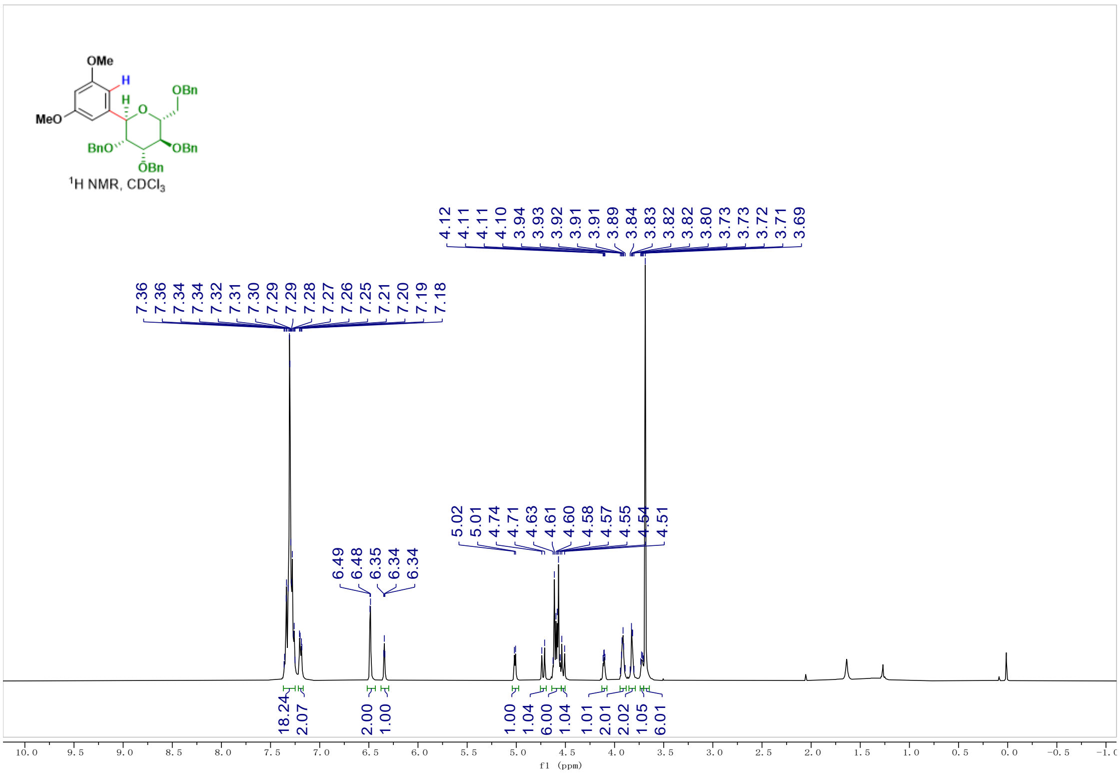
[1]H NMR spectrum of **3r**



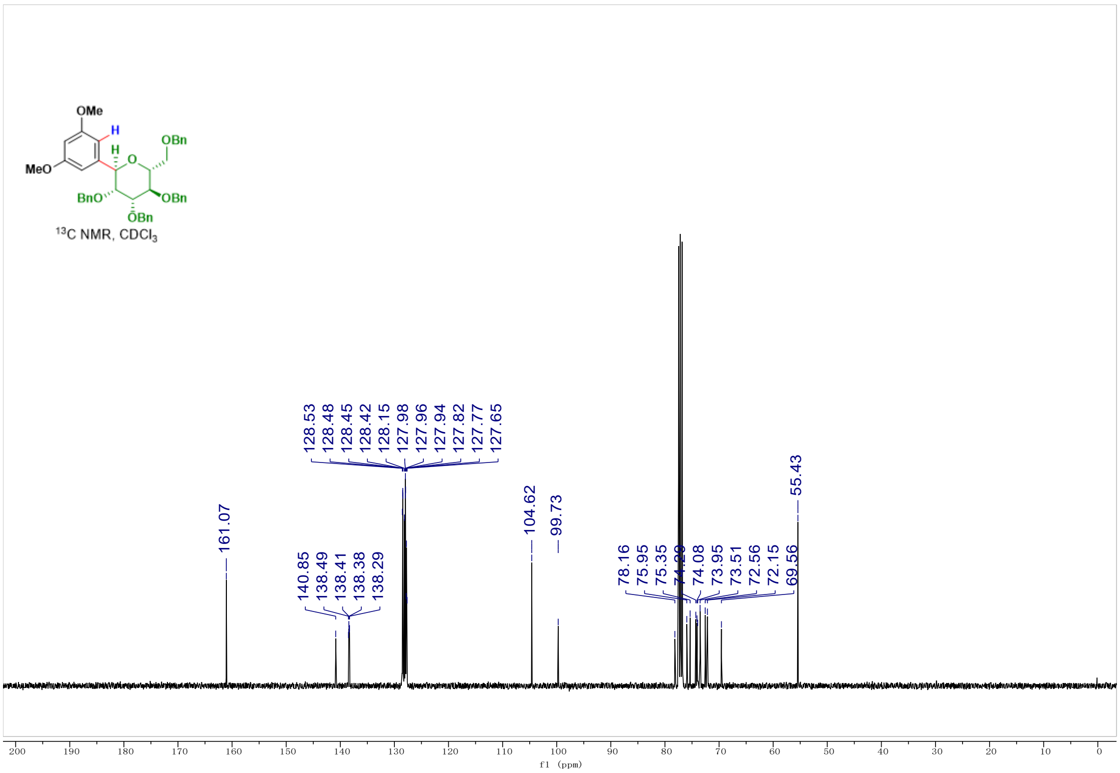
[13]C NMR spectrum of **3r**



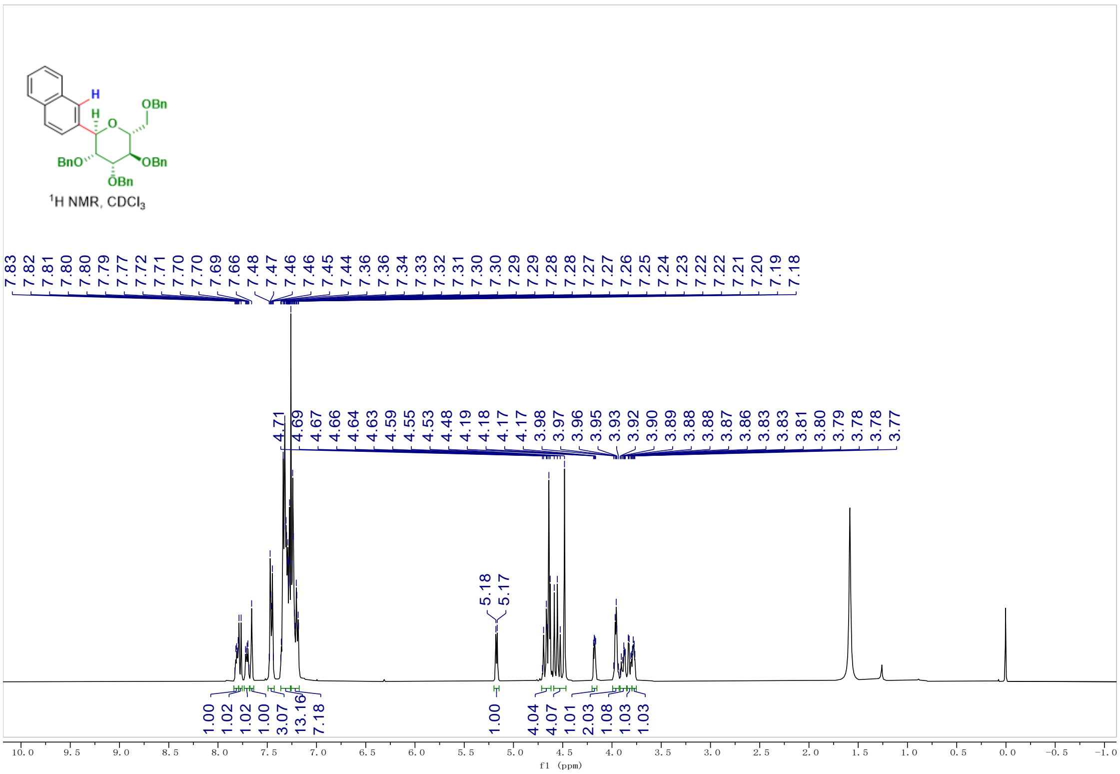
^{1}H NMR spectrum of **3s**



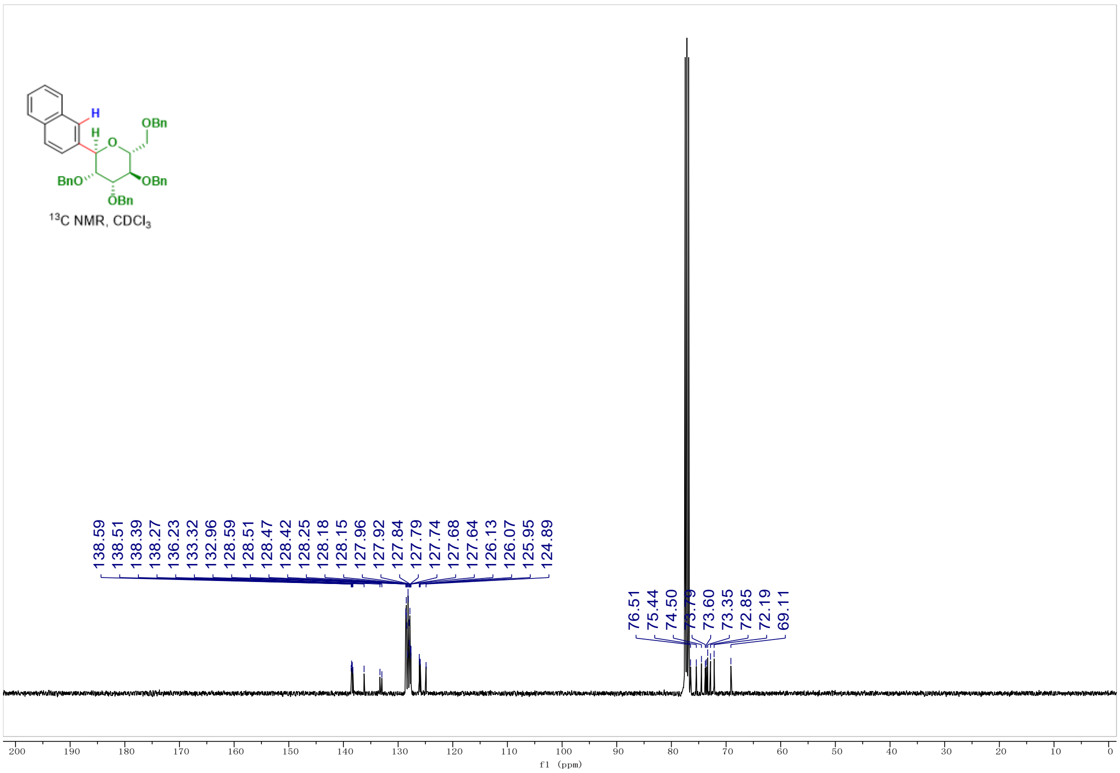
^{13}C NMR spectrum of **3s**



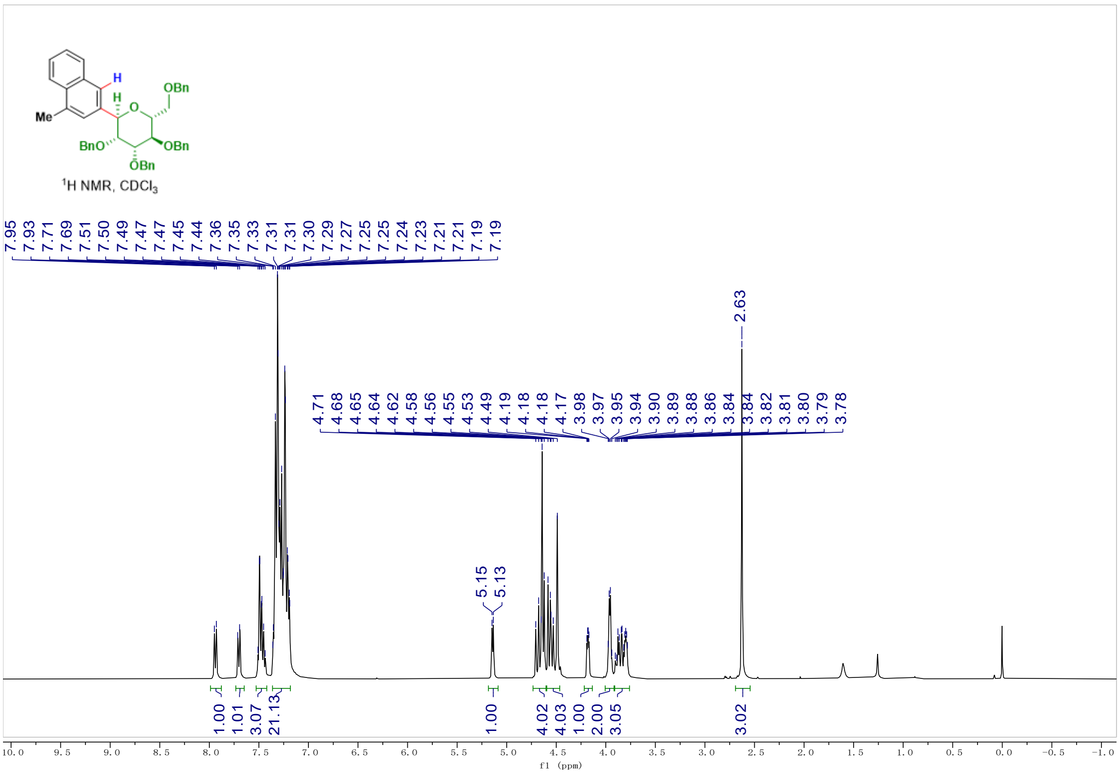
^{1}H NMR spectrum of **3t**



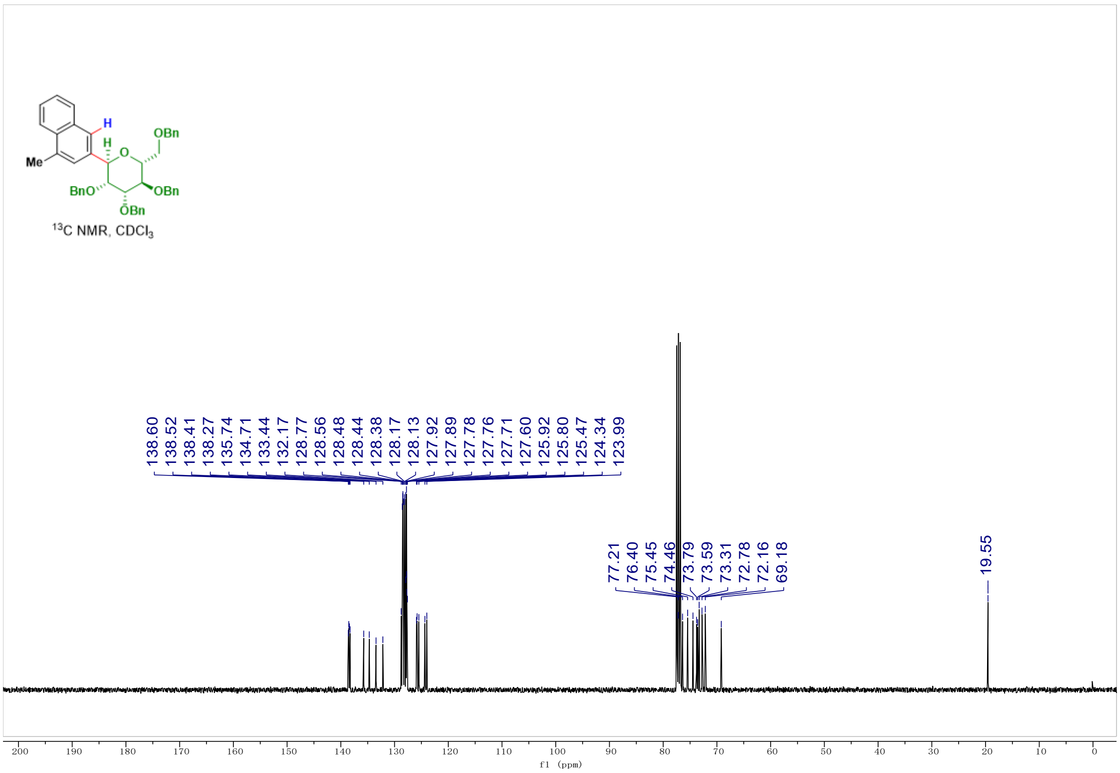
^{13}C NMR spectrum of **3t**



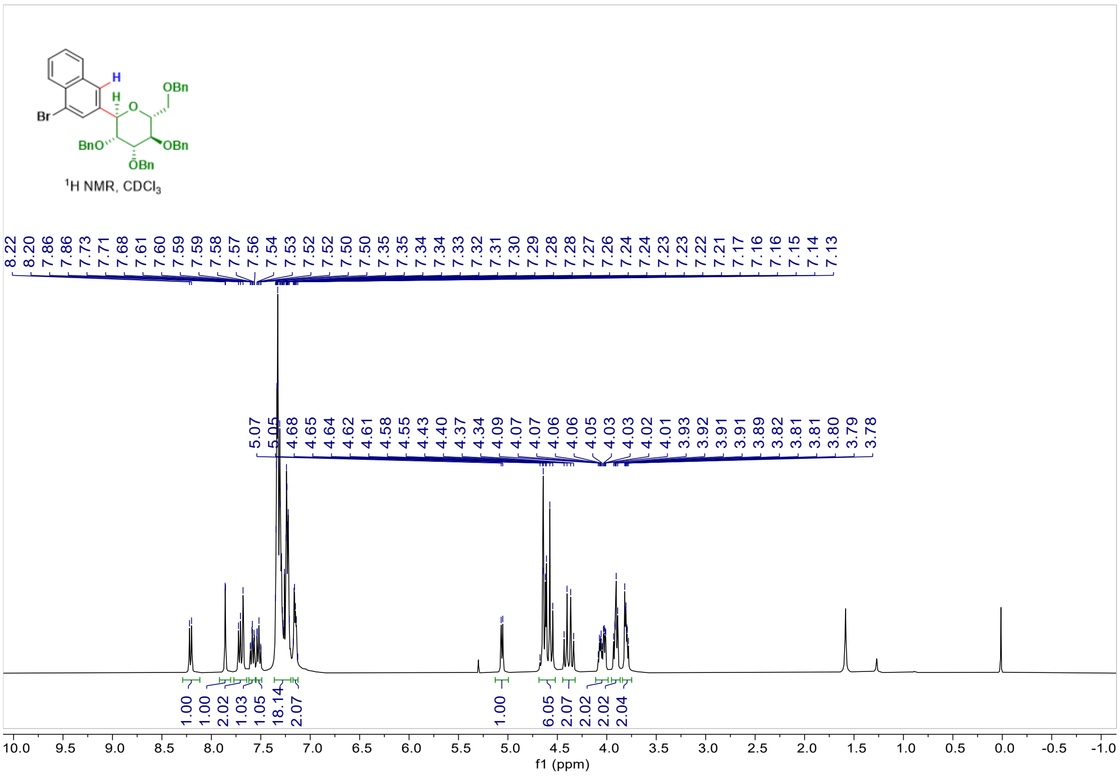
[1]H NMR spectrum of **3u**



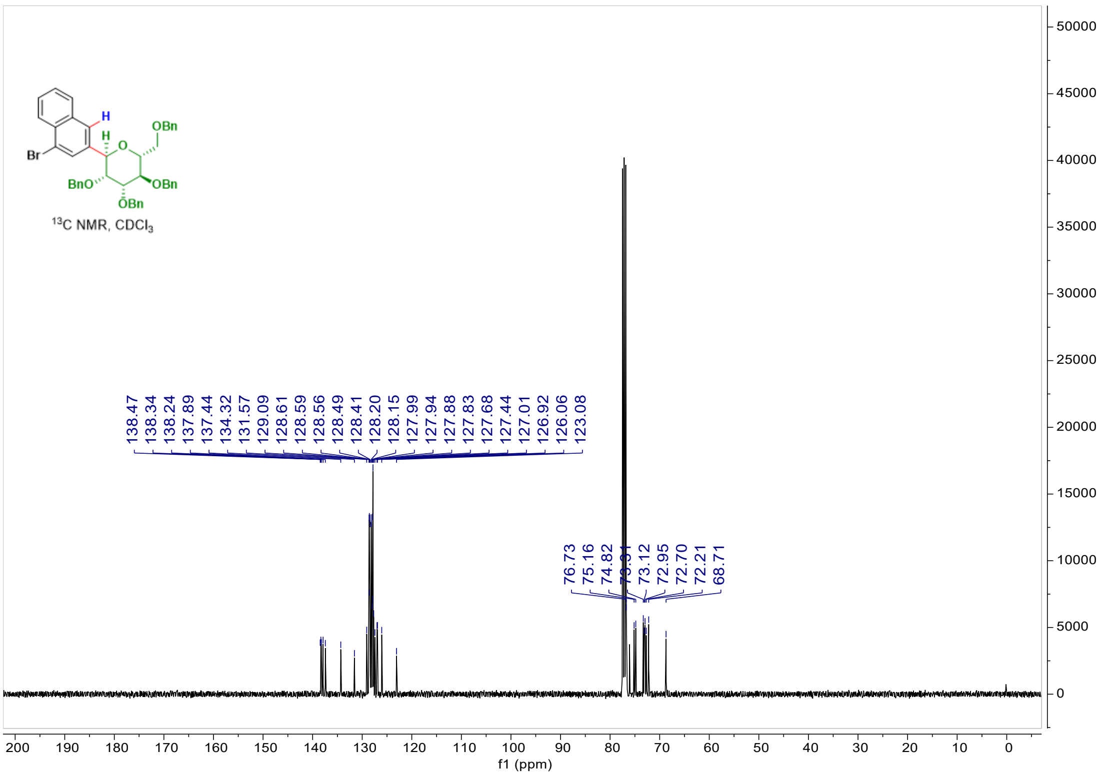
[13]C NMR spectrum of **3u**



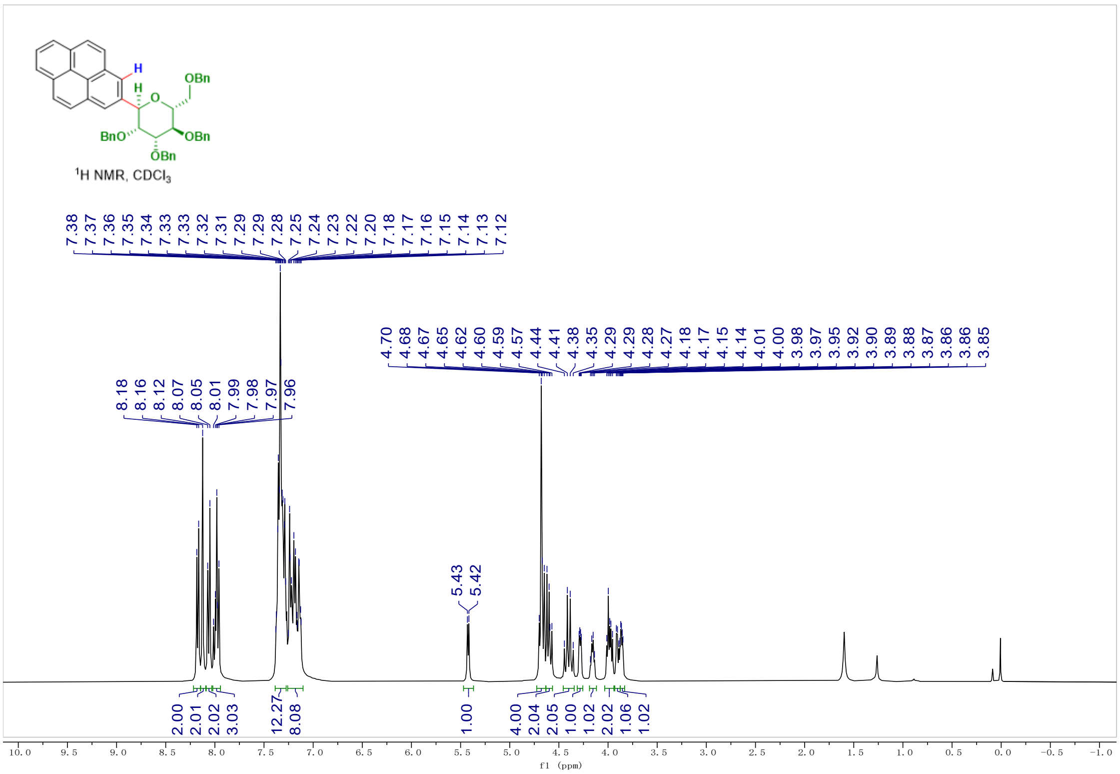
^{1}H NMR spectrum of **3v**



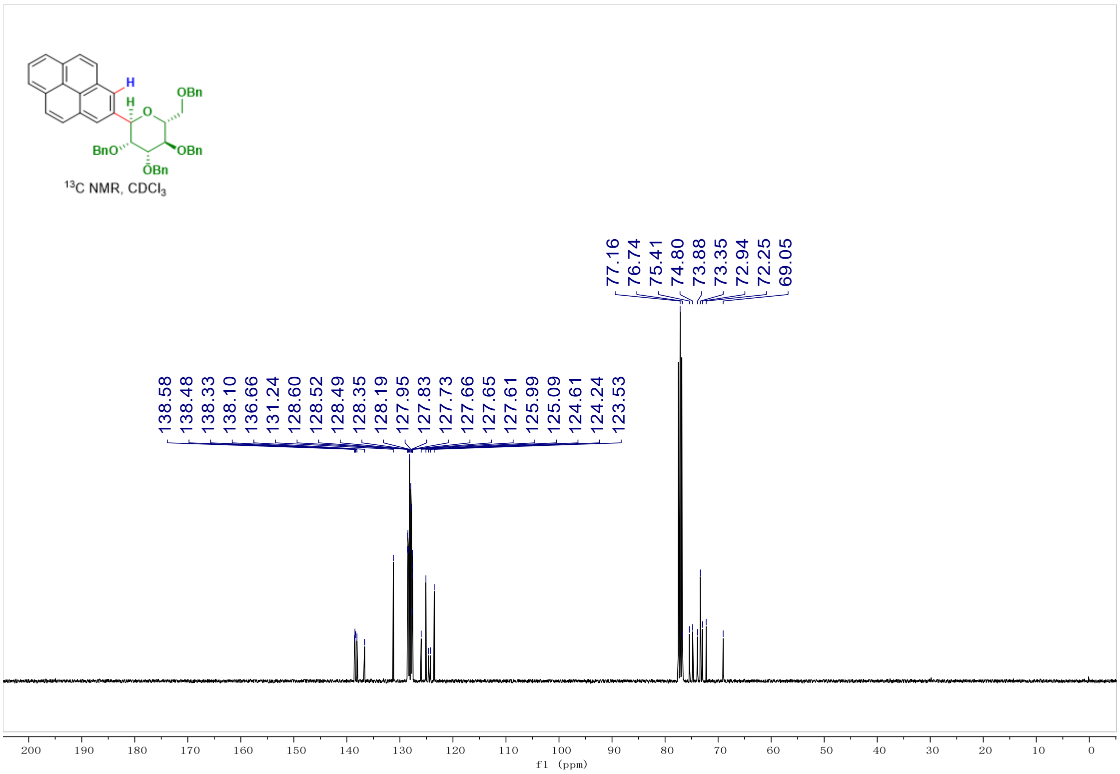
^{13}C NMR spectrum of **3v**



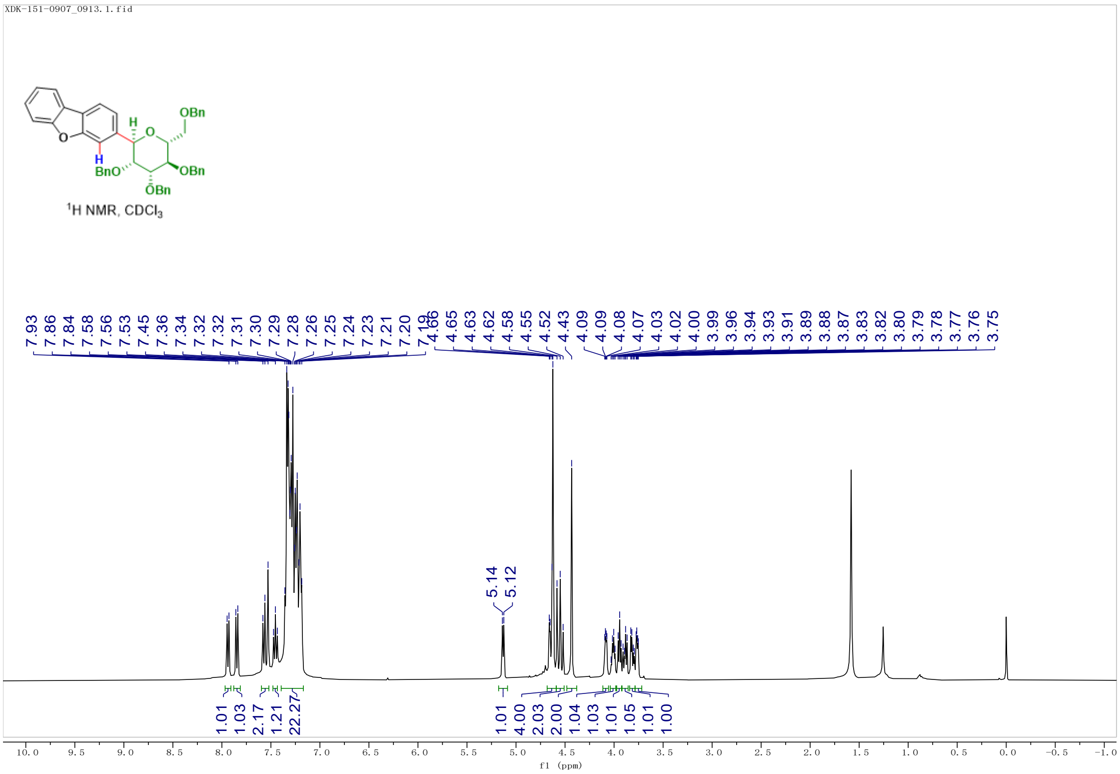
^{1}H NMR spectrum of **3w**



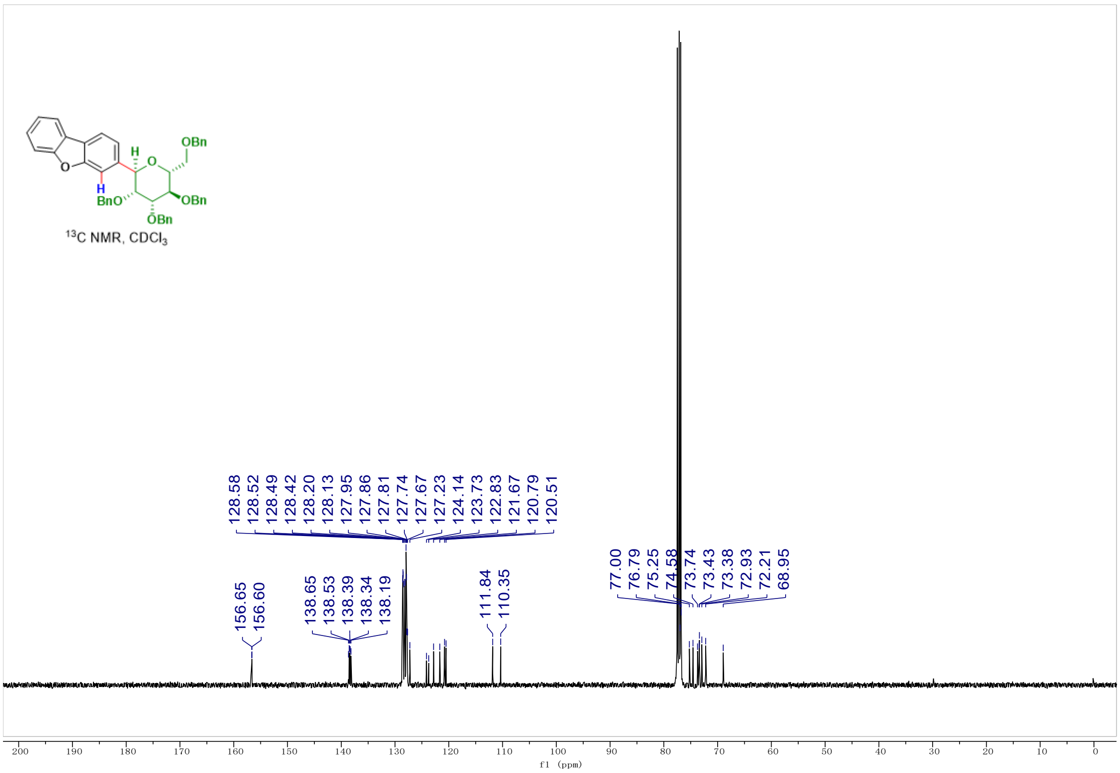
^{13}C NMR spectrum of **3w**



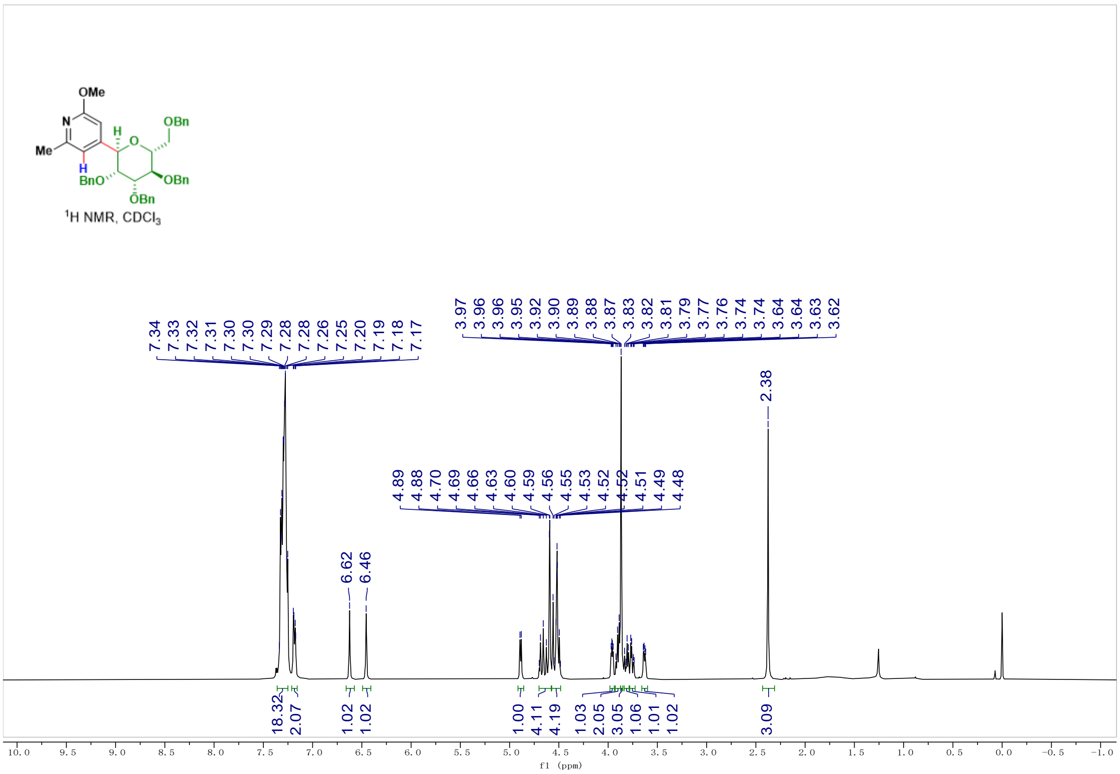
^{1}H NMR spectrum of **3x**



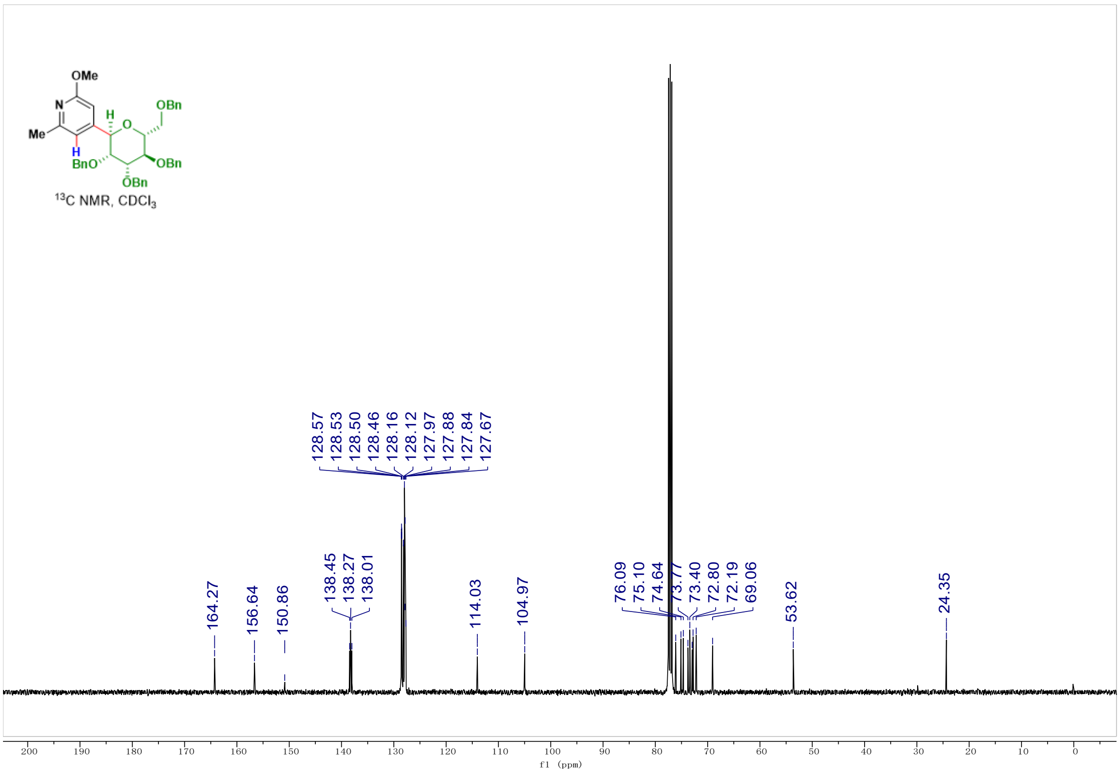
^{13}C NMR spectrum of **3x**



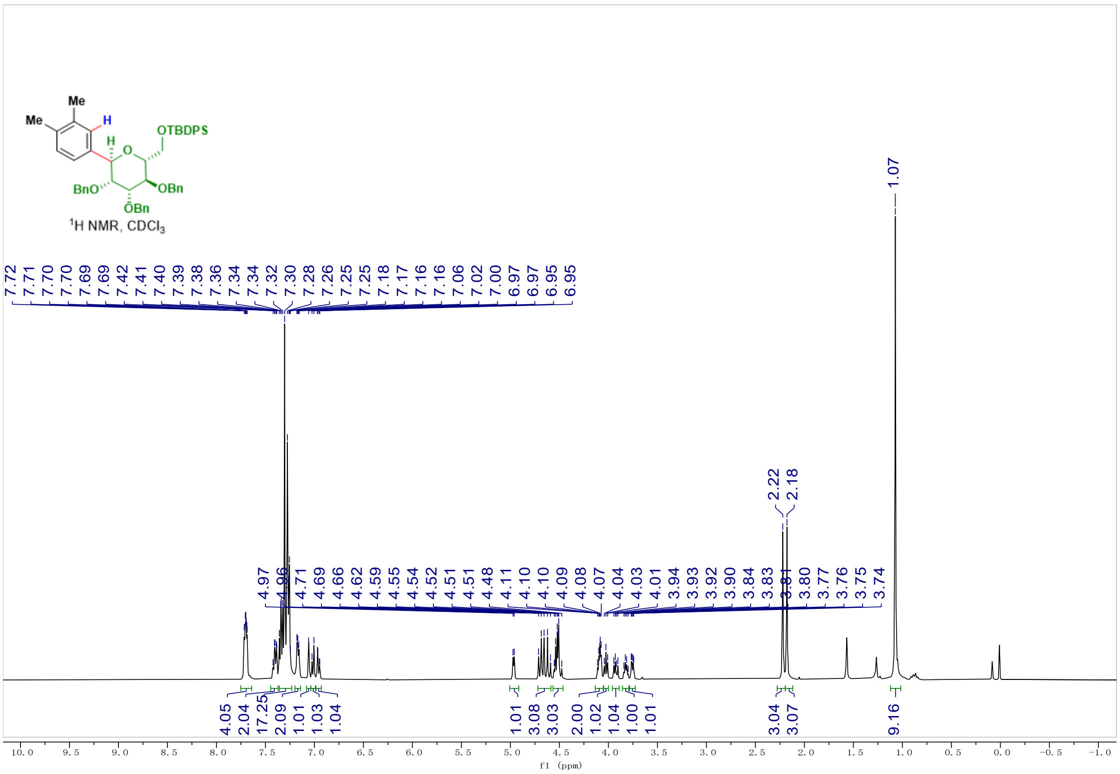
^1H NMR spectrum of **3y**



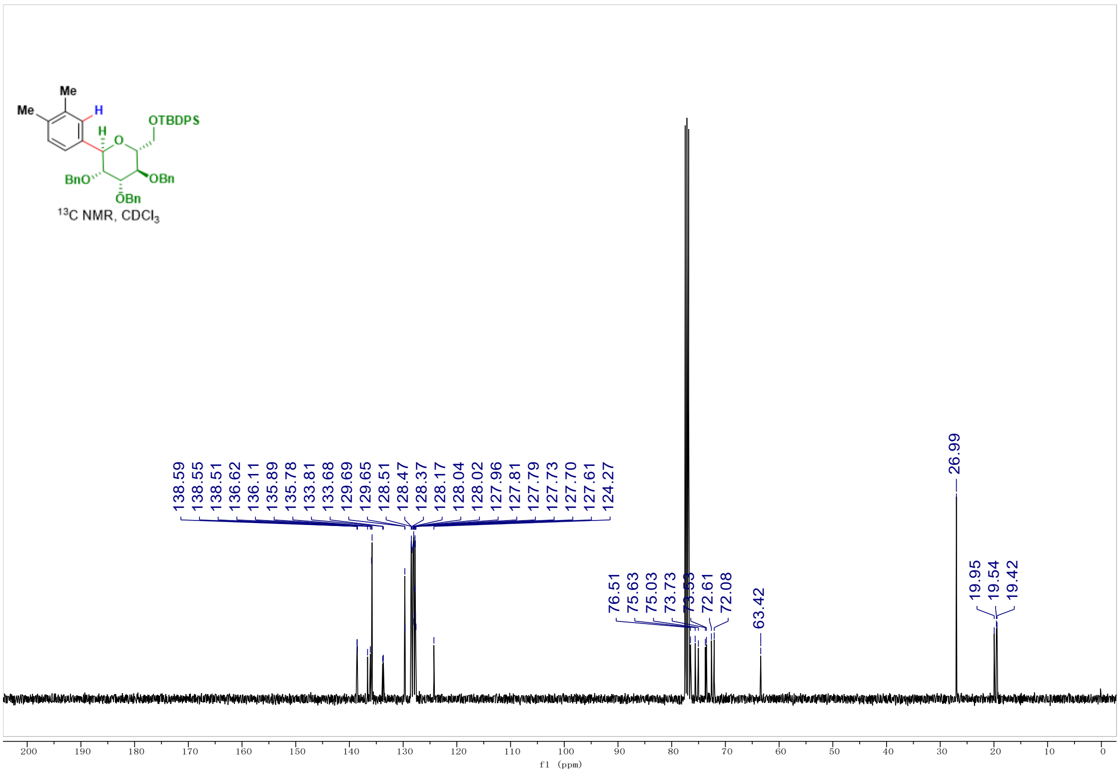
^{13}C NMR spectrum of **3y**



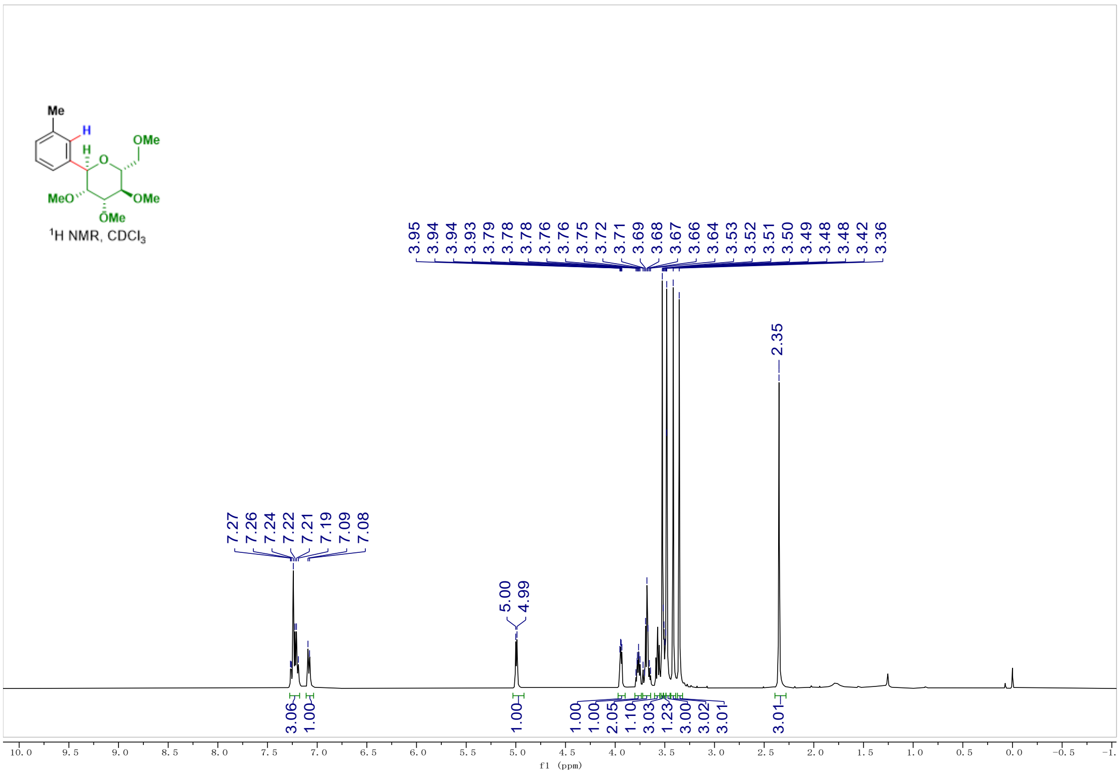
^{1}H NMR spectrum of **3A**



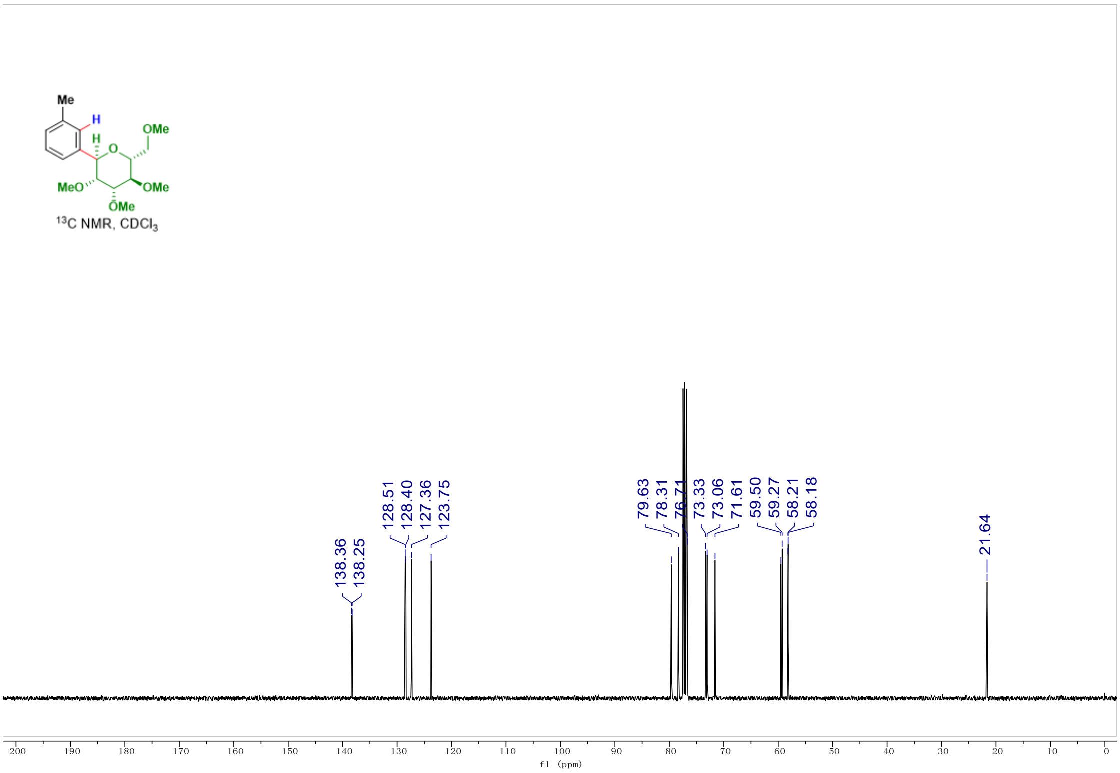
^{13}C NMR spectrum of **3A**



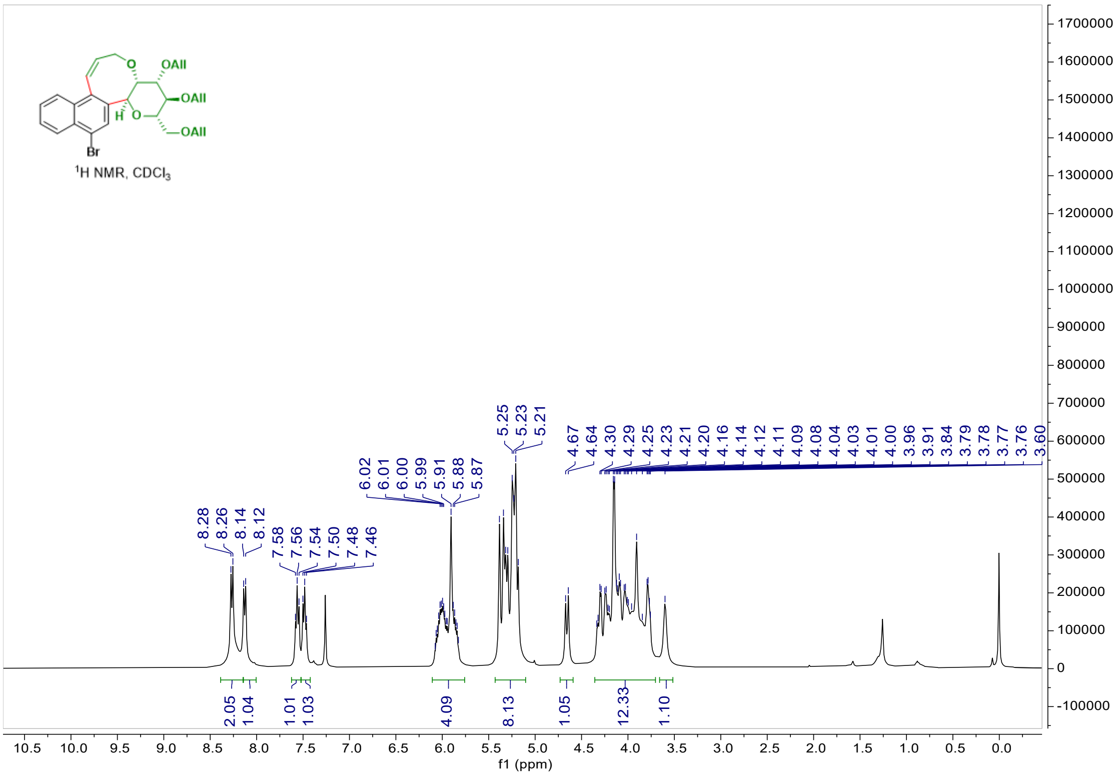
[1]H NMR spectrum of **3B**



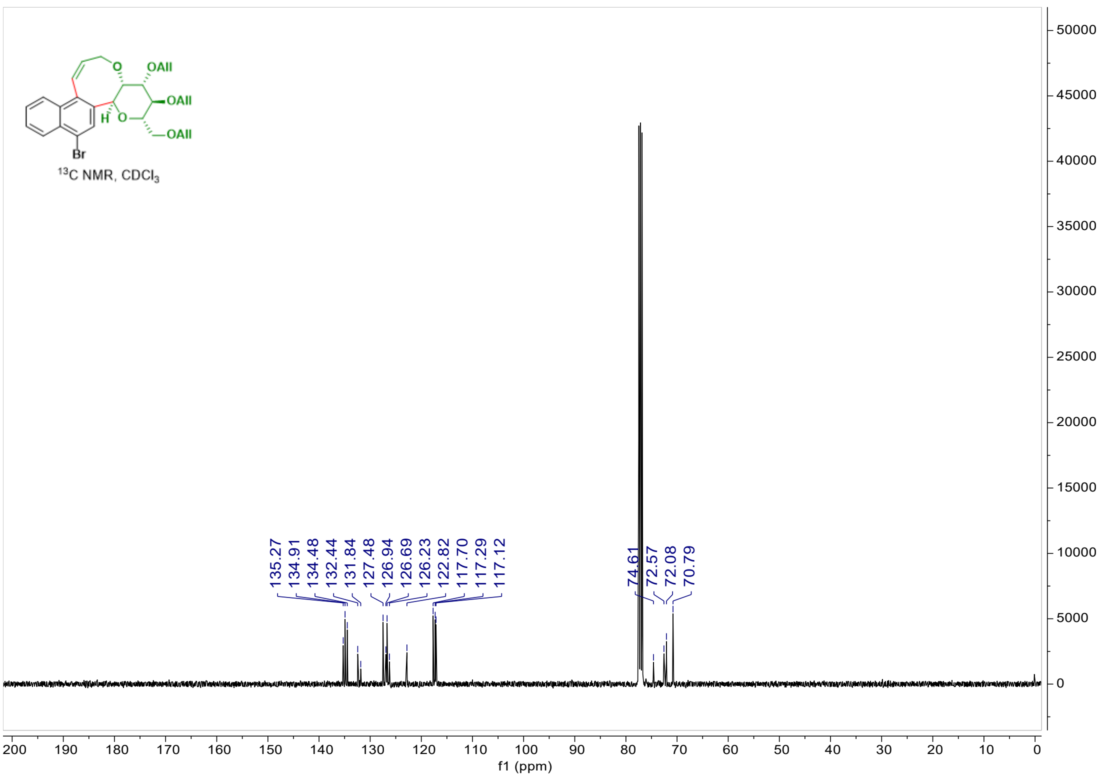
[13]C NMR spectrum of **3B**



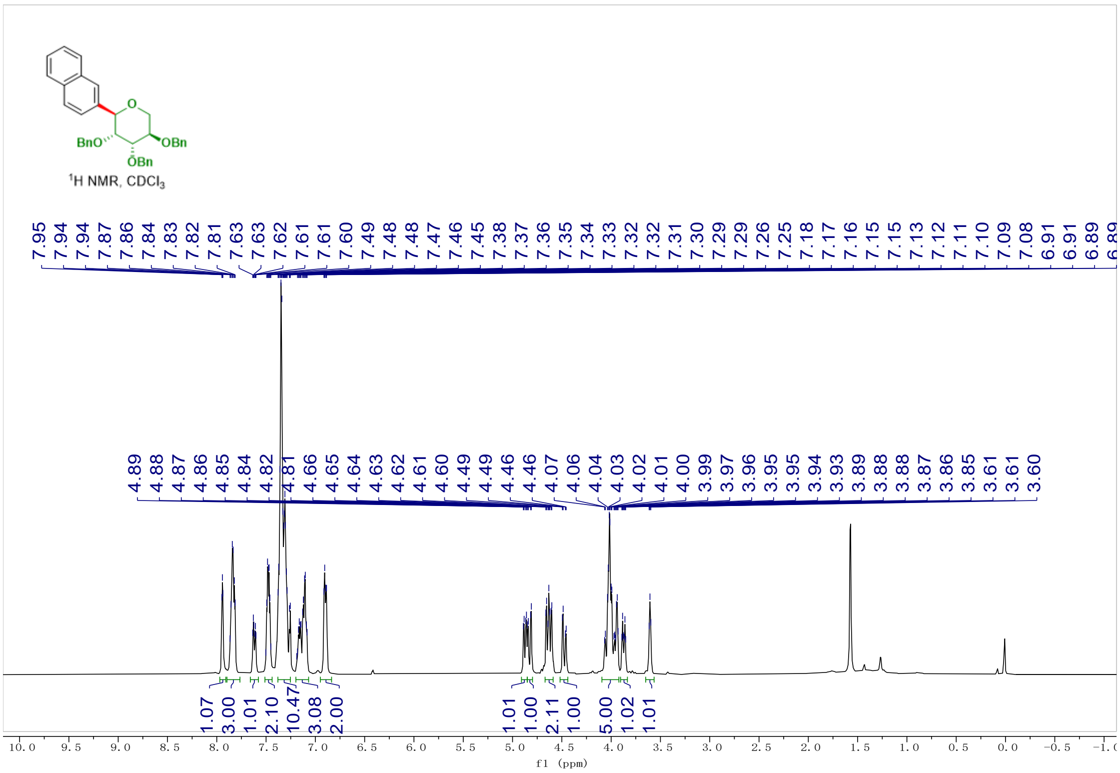
[1]H NMR spectrum of **3C**



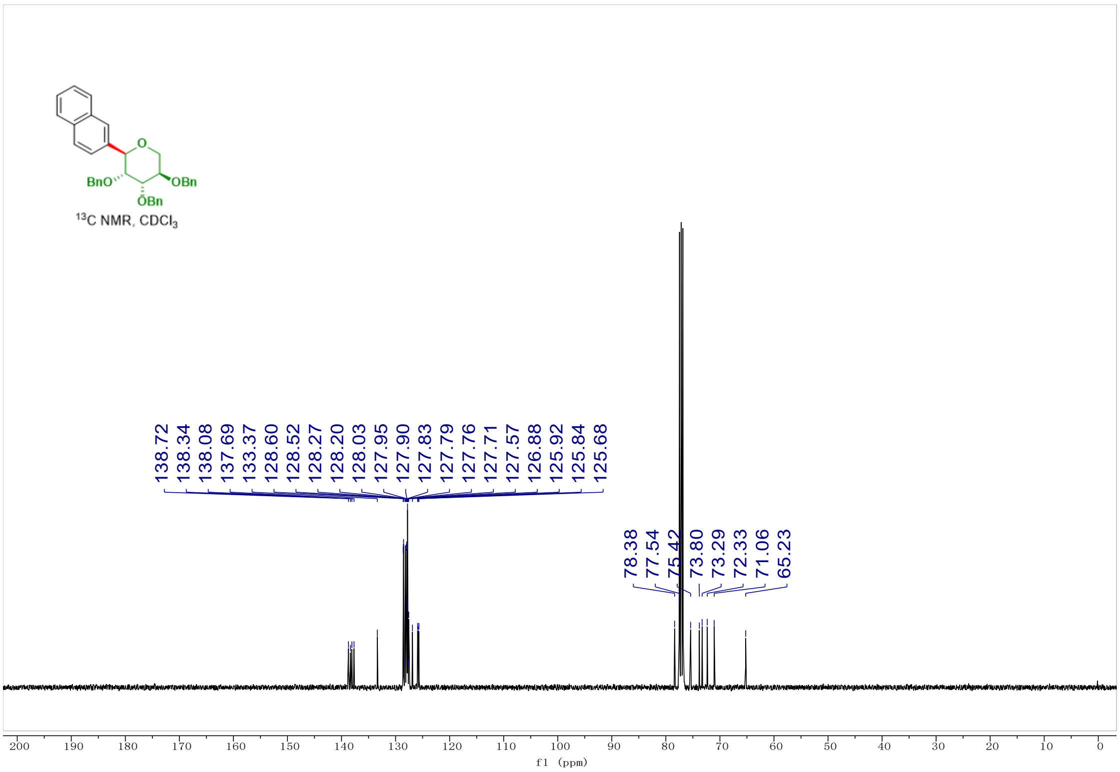
[13]C NMR spectrum of **3C**



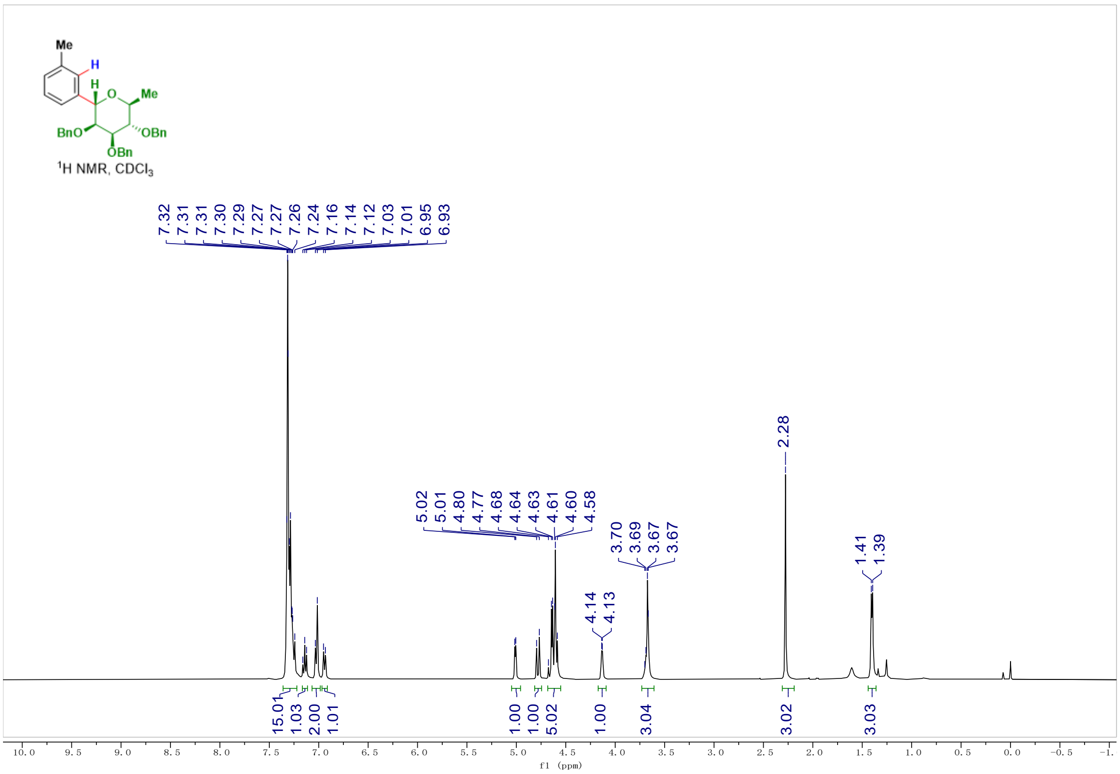
^{1}H NMR spectrum of **3D**



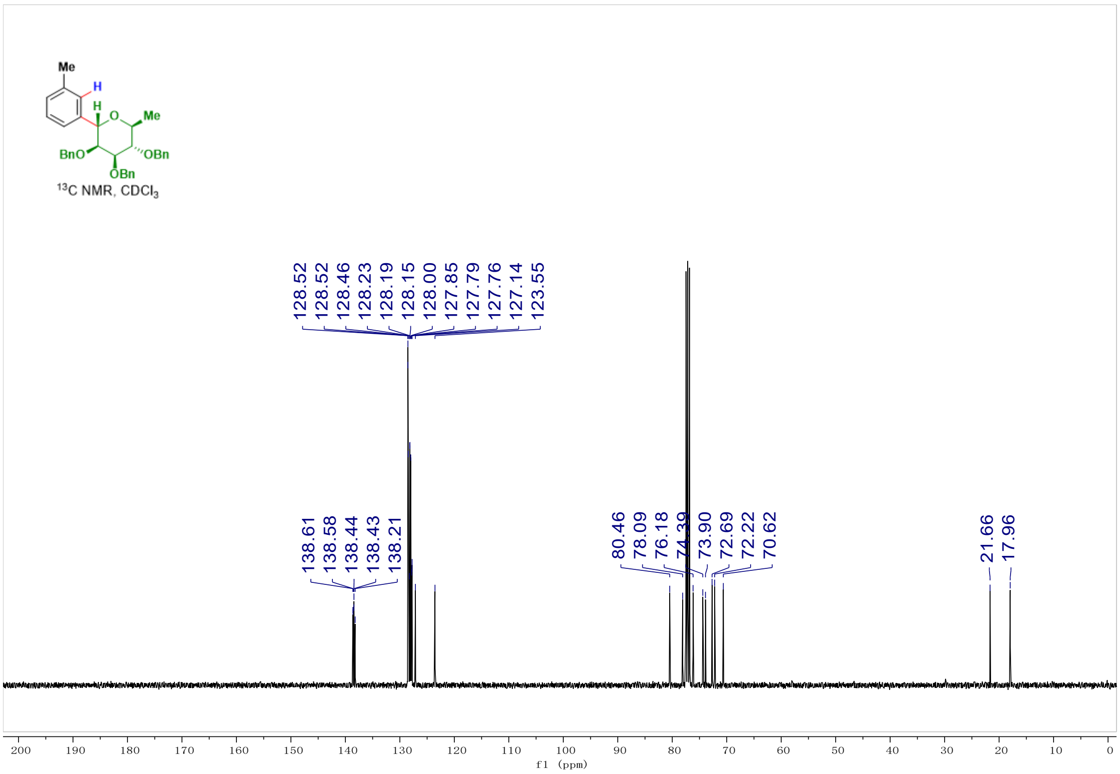
^{13}C NMR spectrum of **3D**



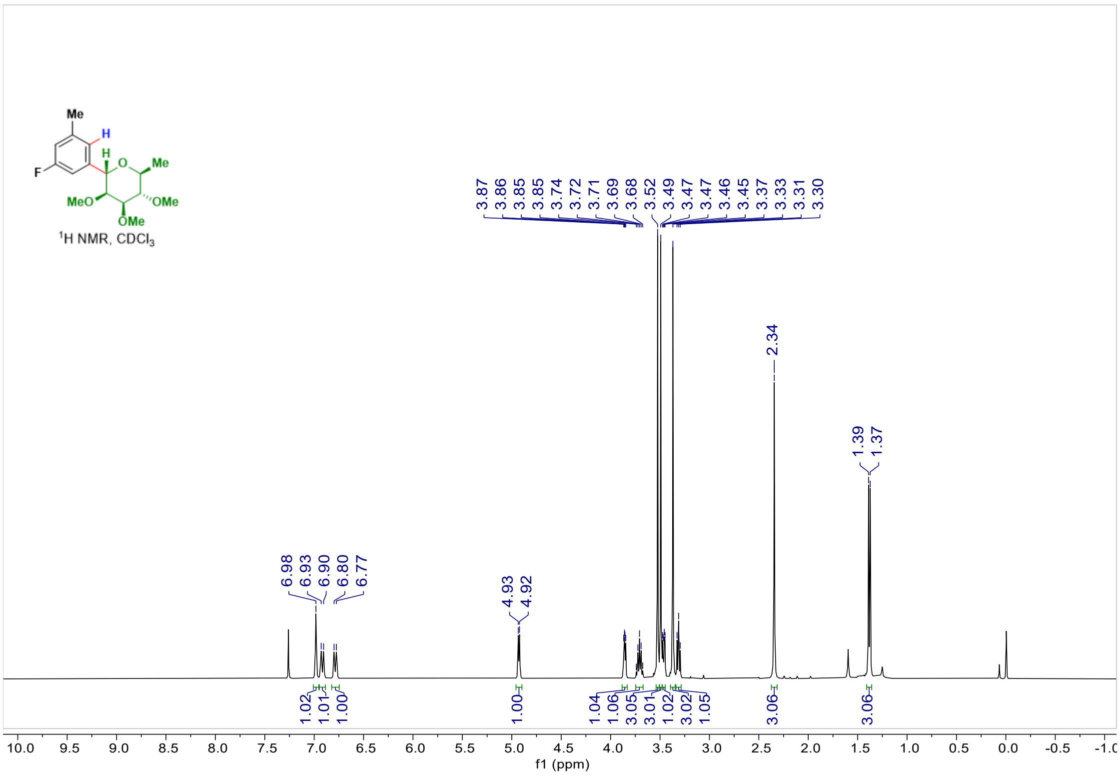
^{1}H NMR spectrum of **3E**



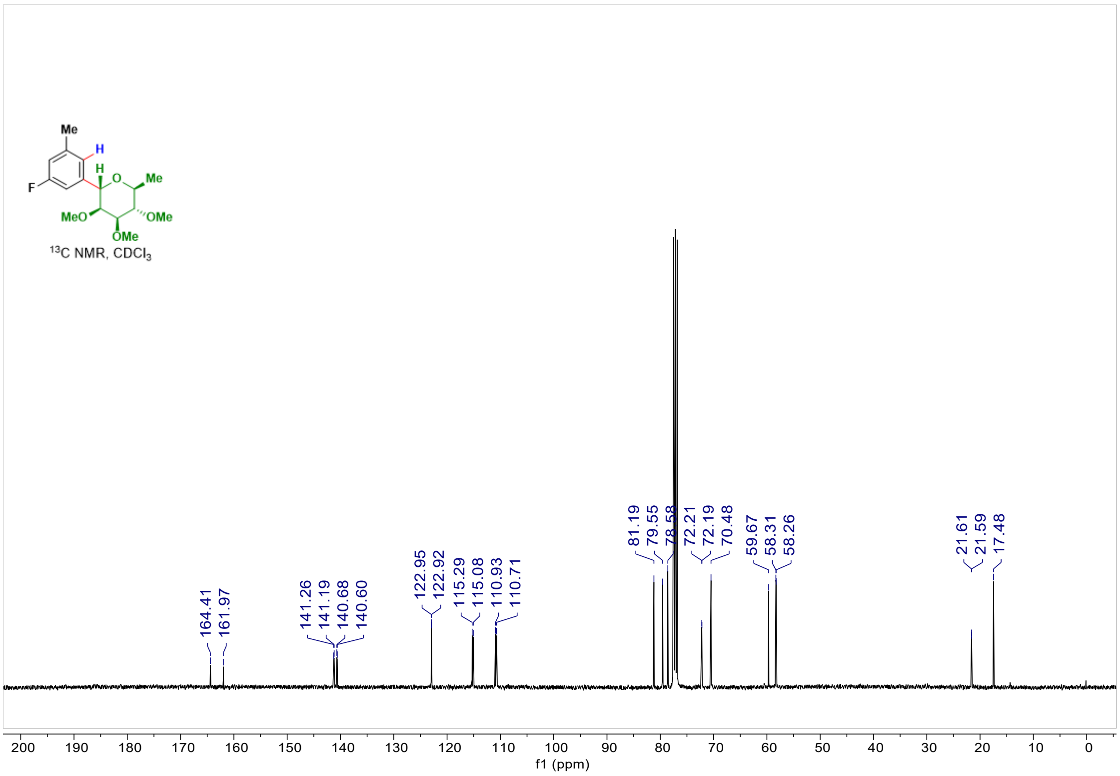
^{13}C NMR spectrum of **3E**



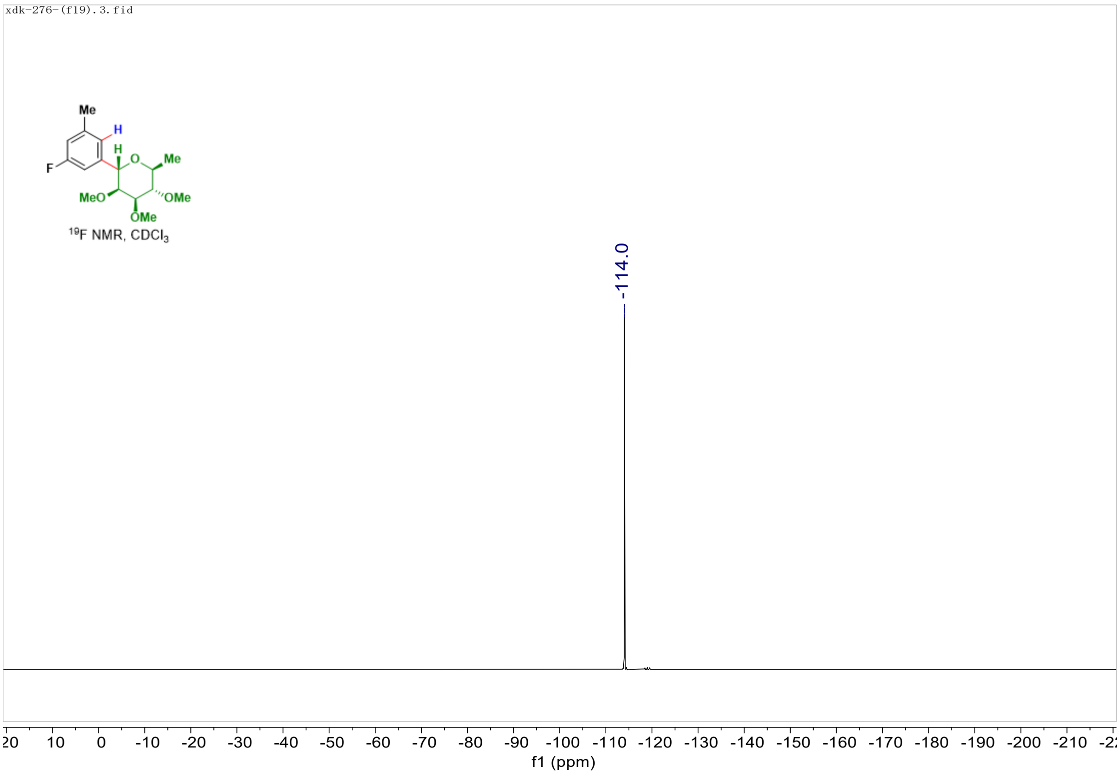
[1]H NMR spectrum of **3F**



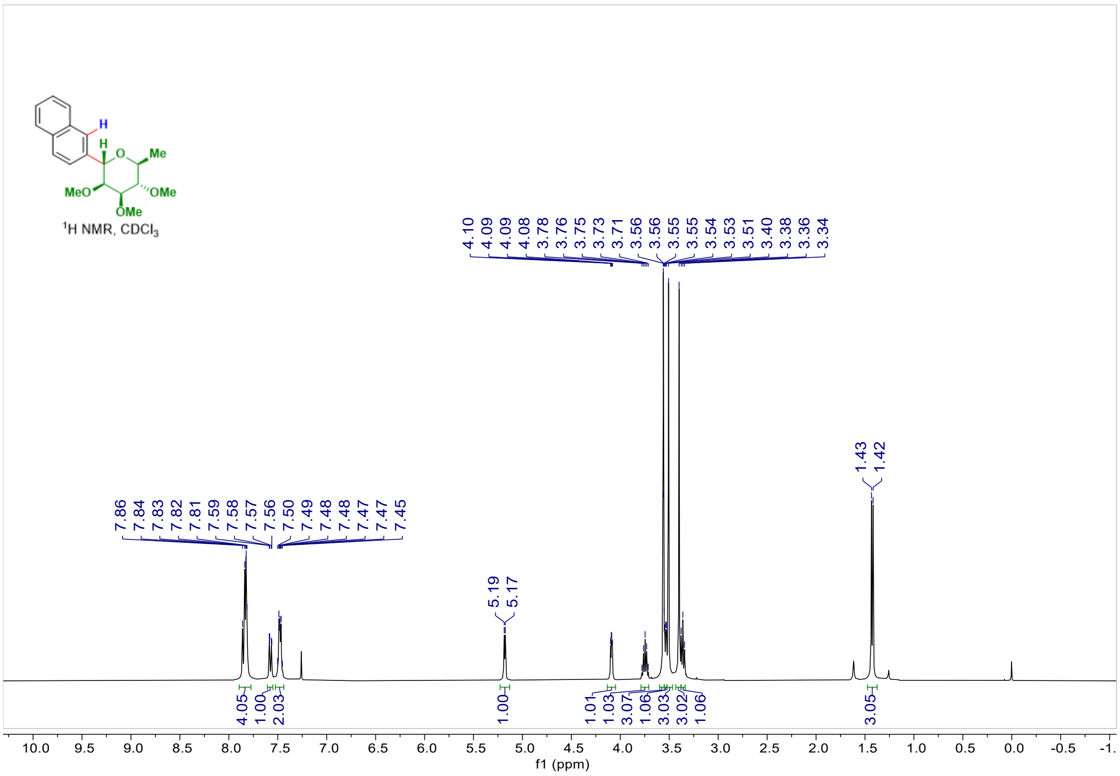
[13]C NMR spectrum of **3F**



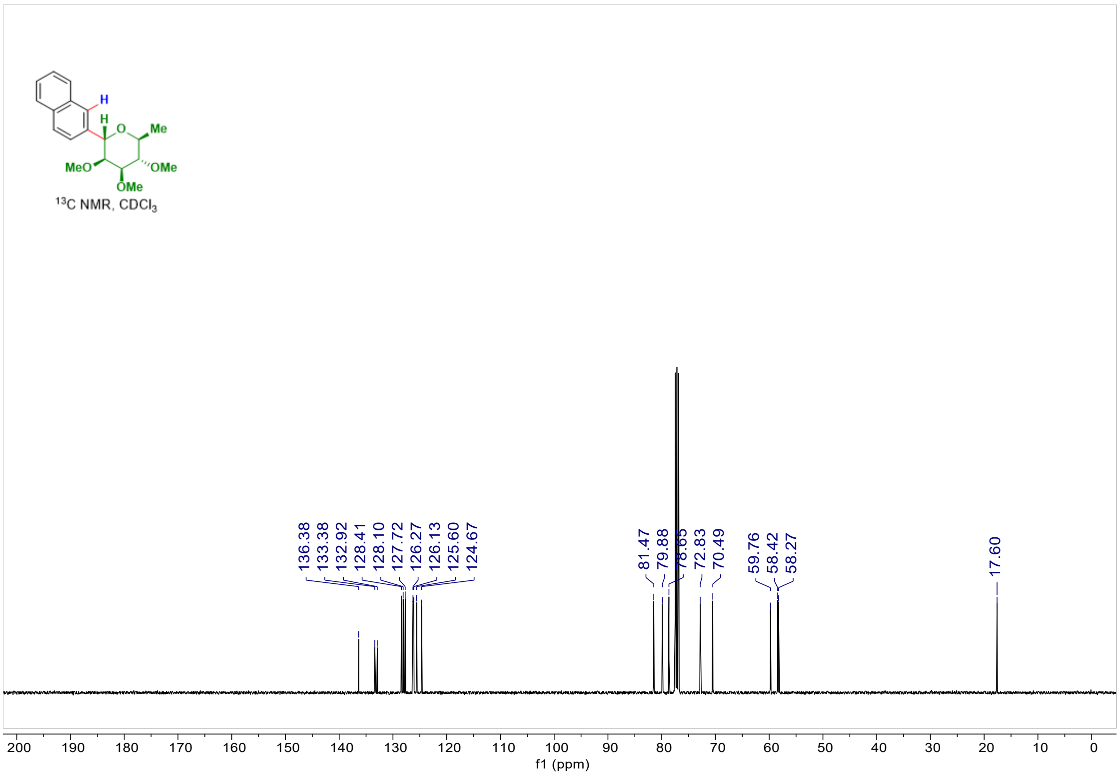
^{19}F NMR spectrum of **3F**



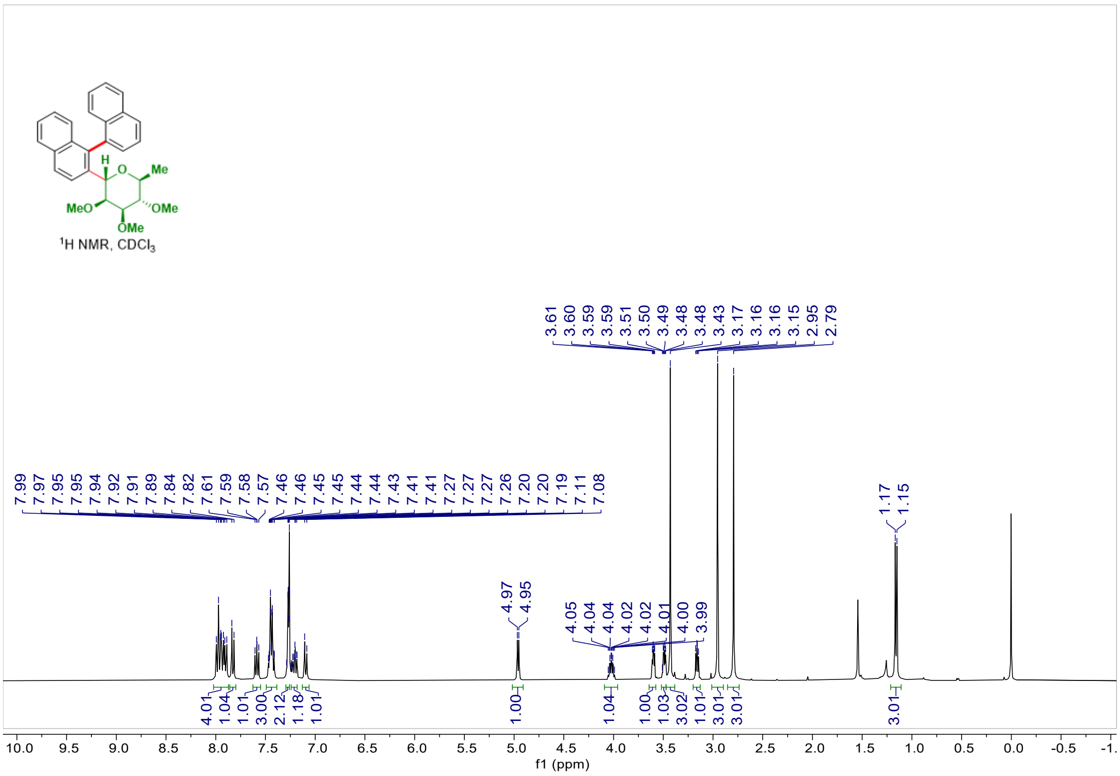
^{1}H NMR spectrum of **3G**



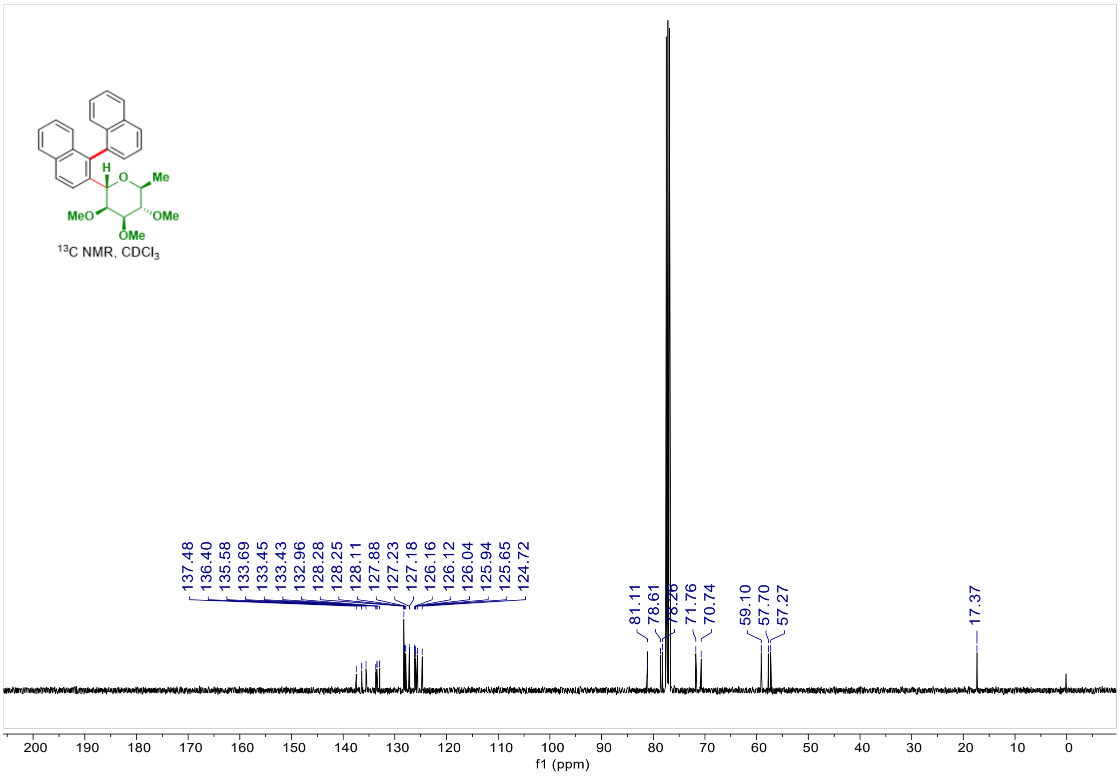
^{13}C NMR spectrum of **3G**



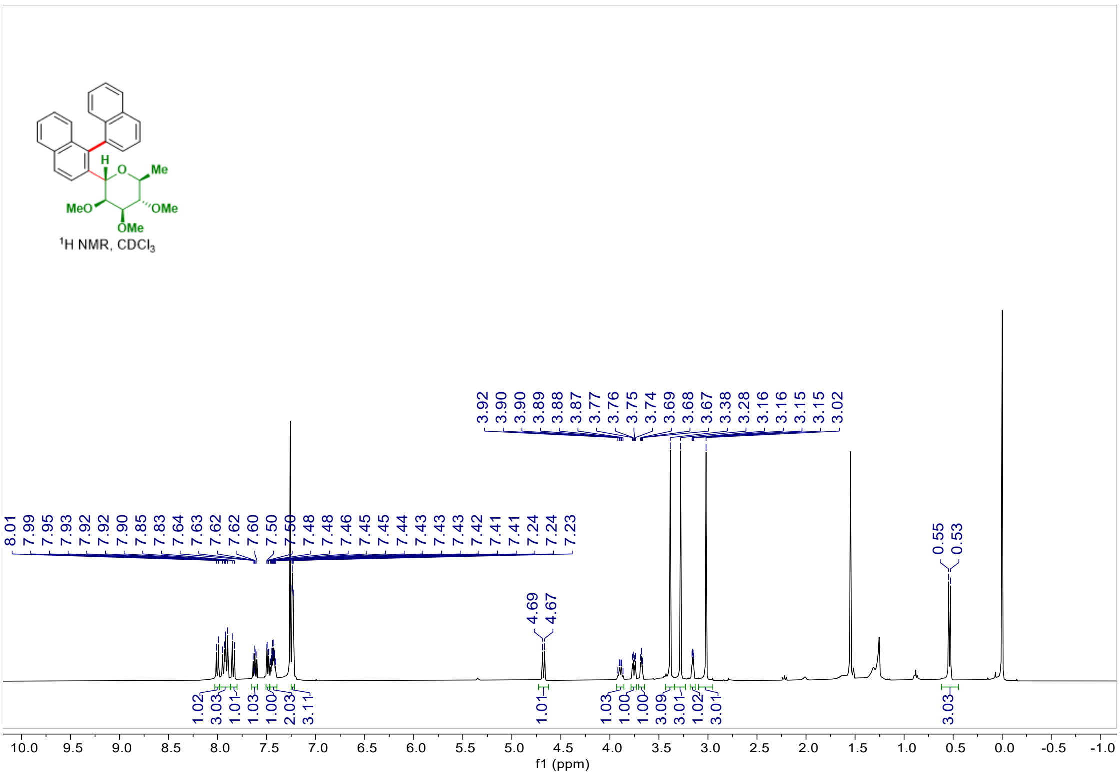
[1]H NMR spectrum of **3G′** (major)



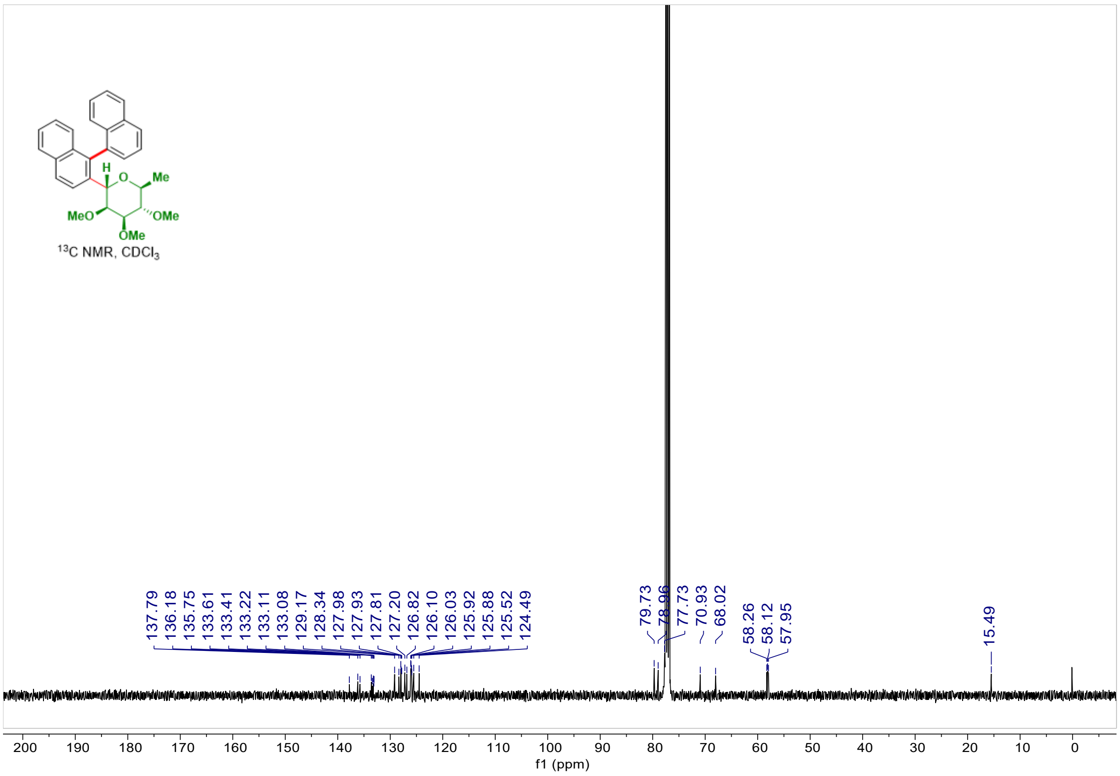
[13]C NMR spectrum of **3G′** (major)



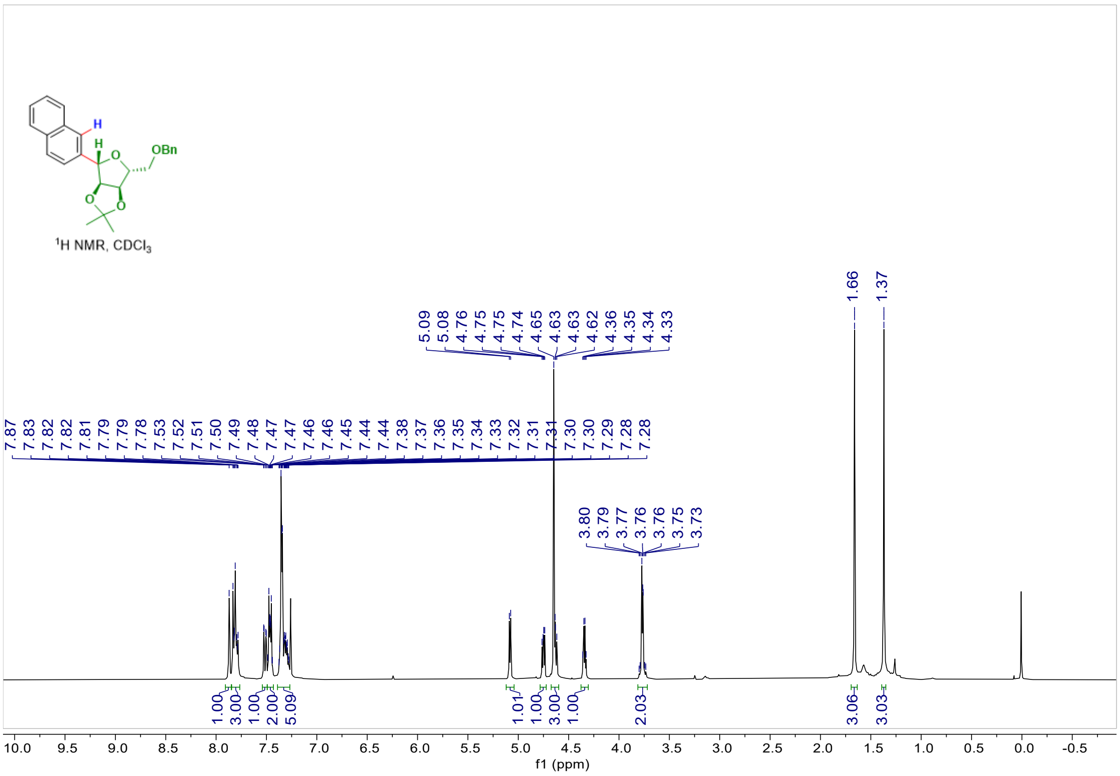
^{1}H NMR spectrum of **3G′** (minor)



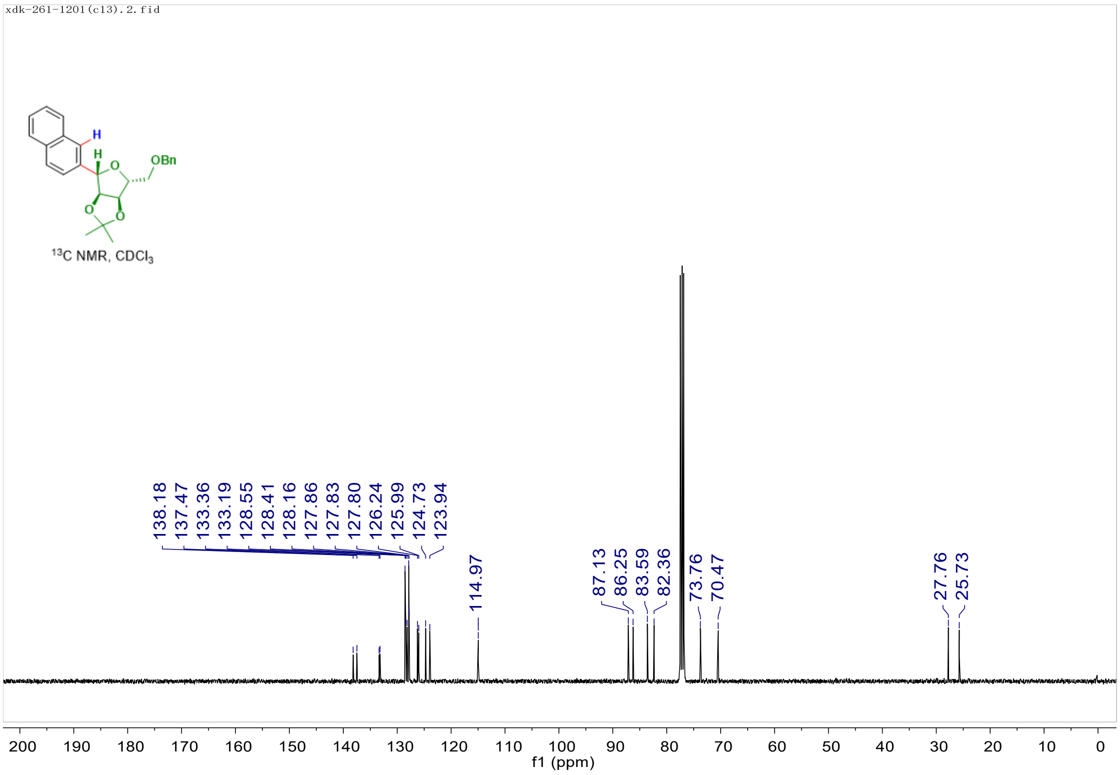
^{13}C NMR spectrum of **3G′** (minor)



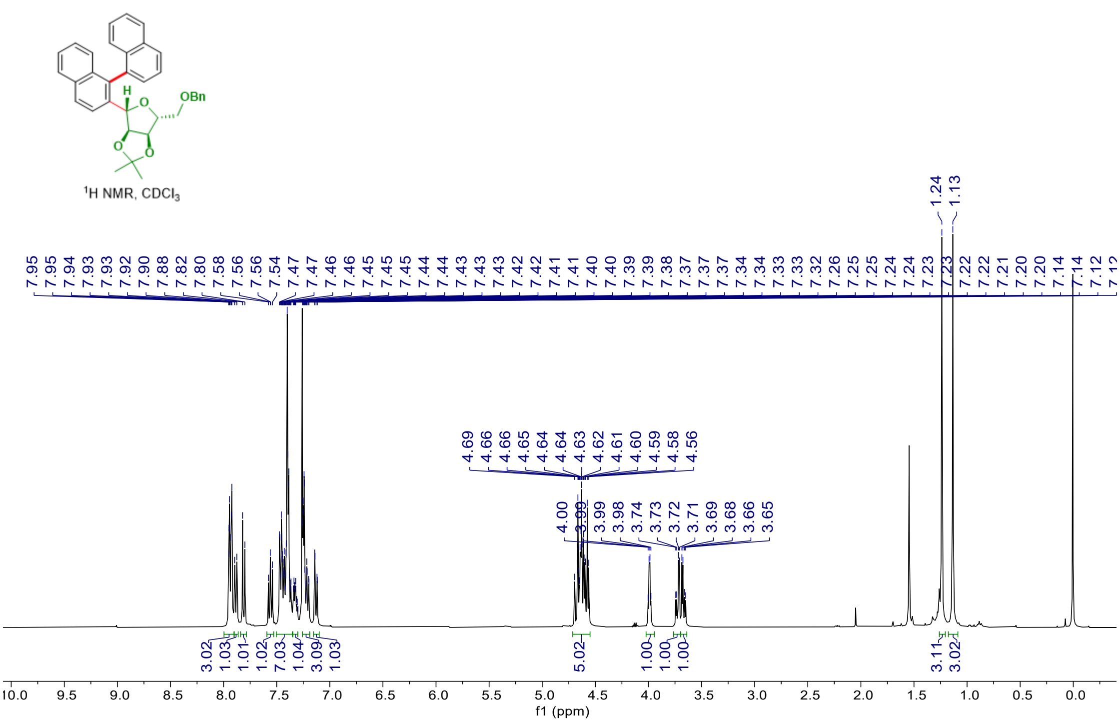
^1H NMR spectrum of **3H**



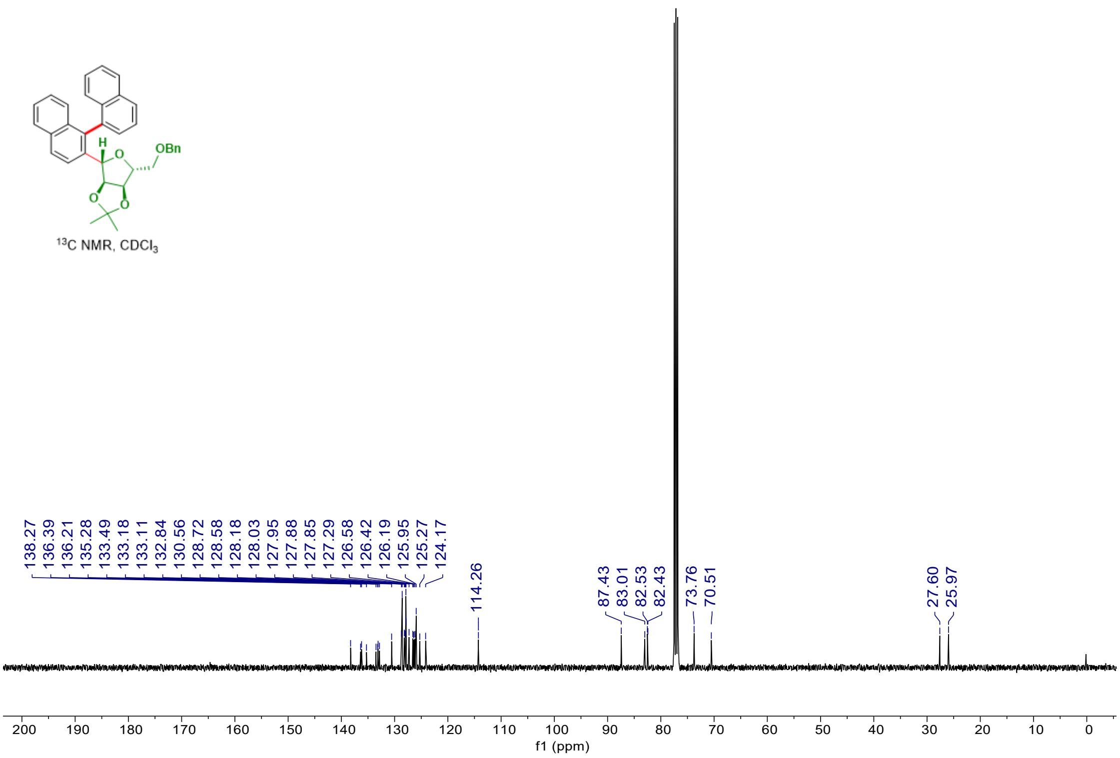
^{13}C NMR spectrum of **3H**



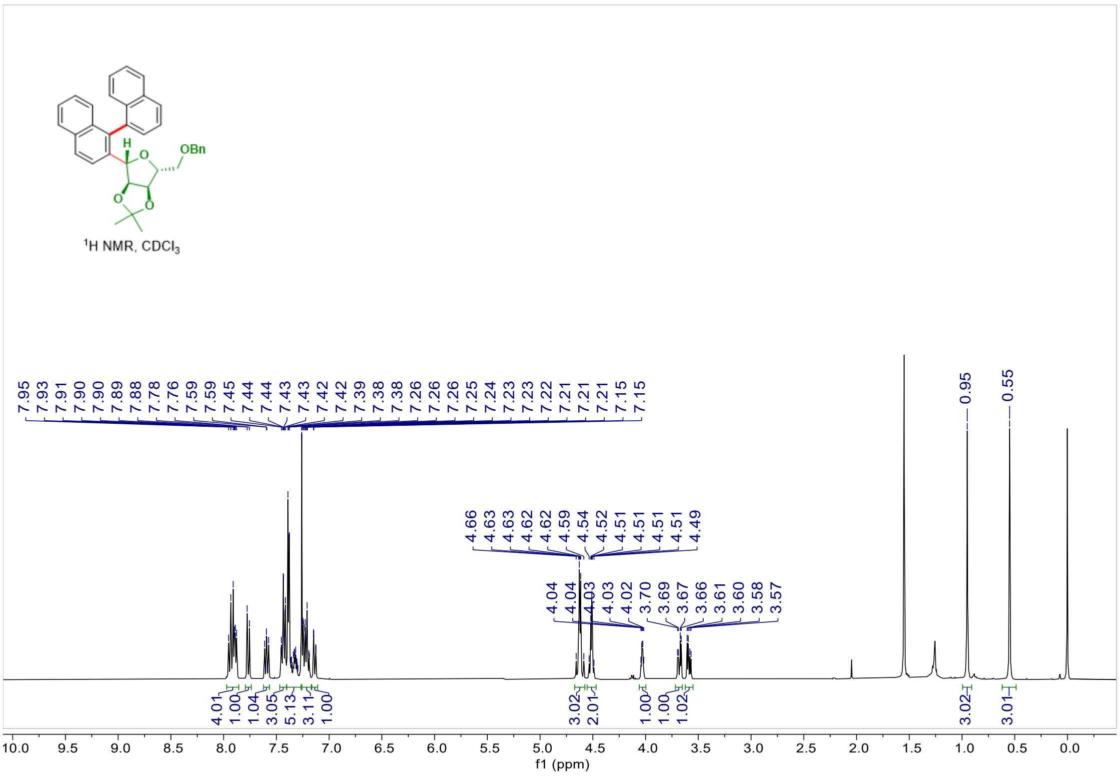
^{1}H NMR spectrum of **3H′** (major)



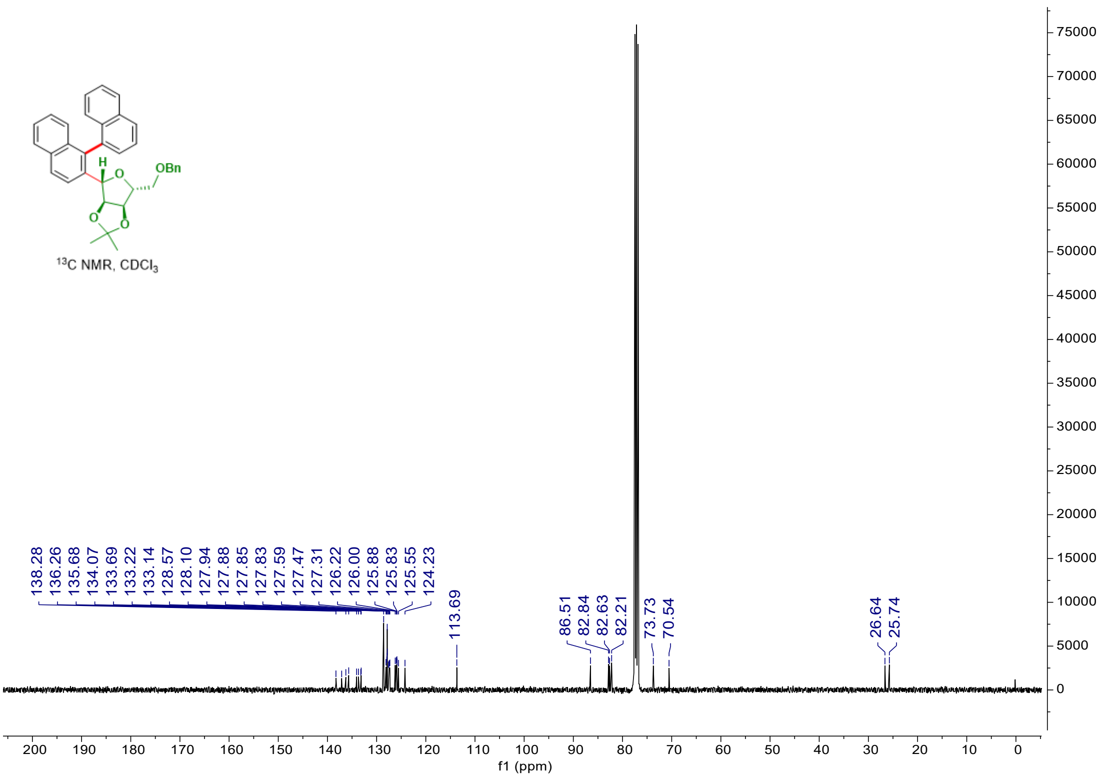
^{13}C NMR spectrum of **3H′** (major)



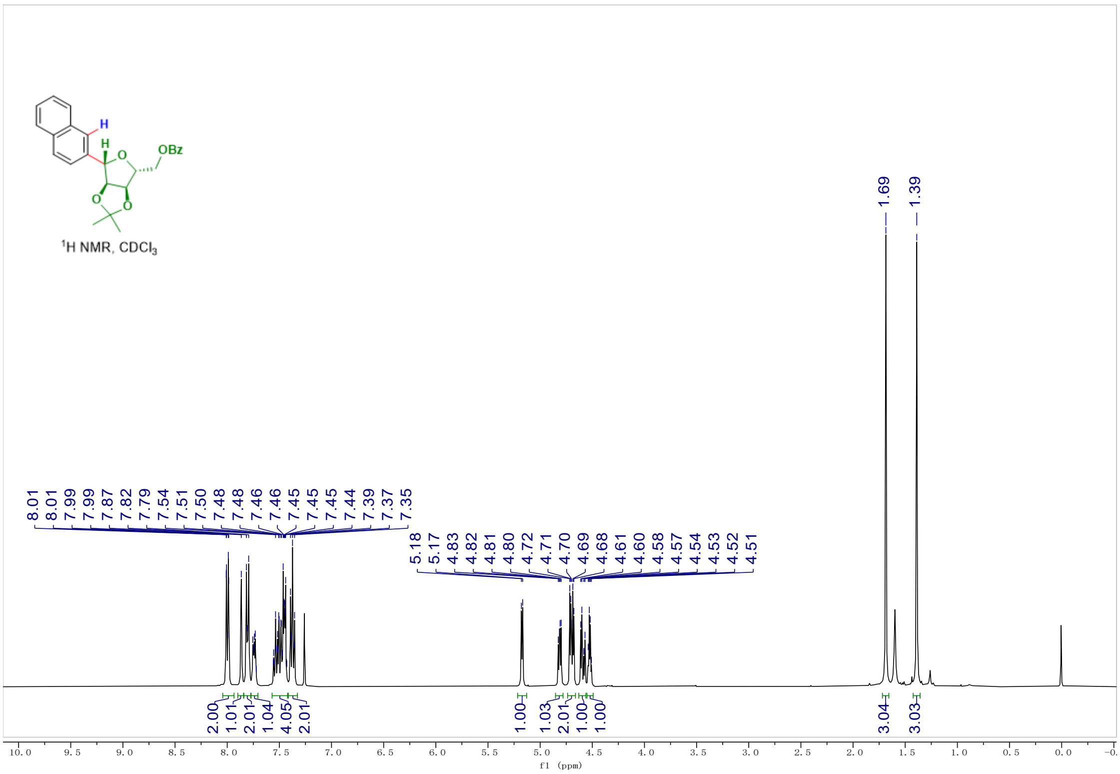
^{1}H NMR spectrum of **3H′** (minor)



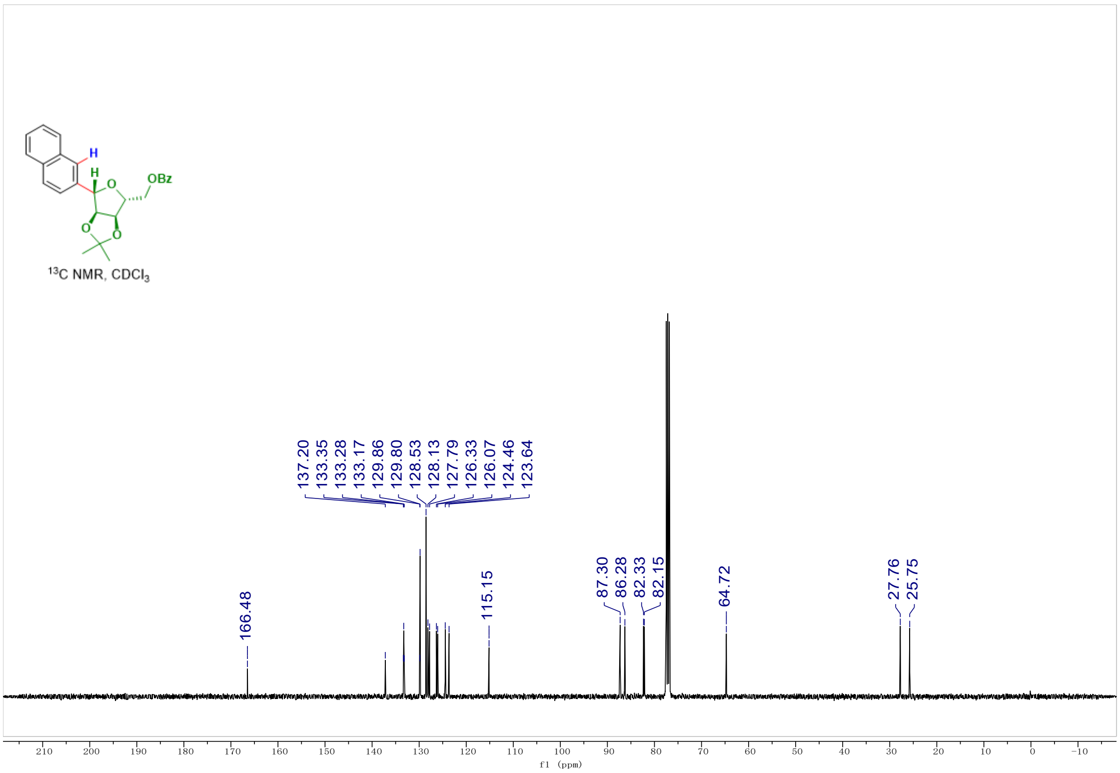
^{13}C NMR spectrum of **3H′** (minor)



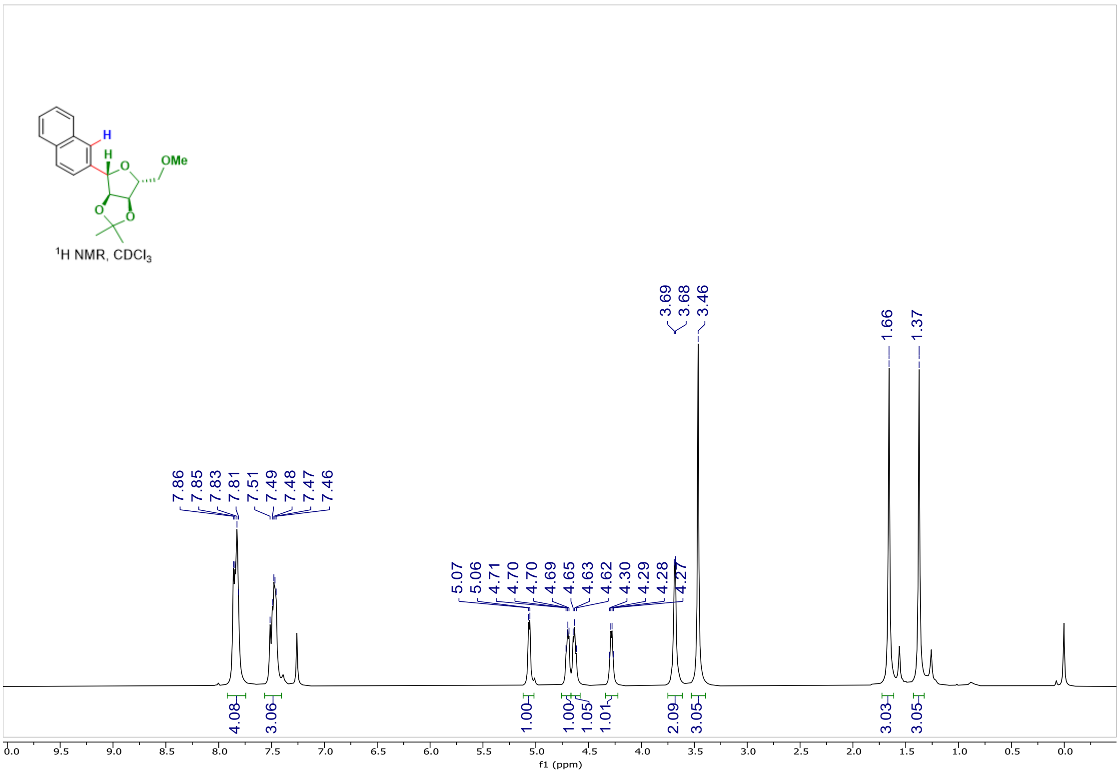
^{1}H NMR spectrum of **3l**



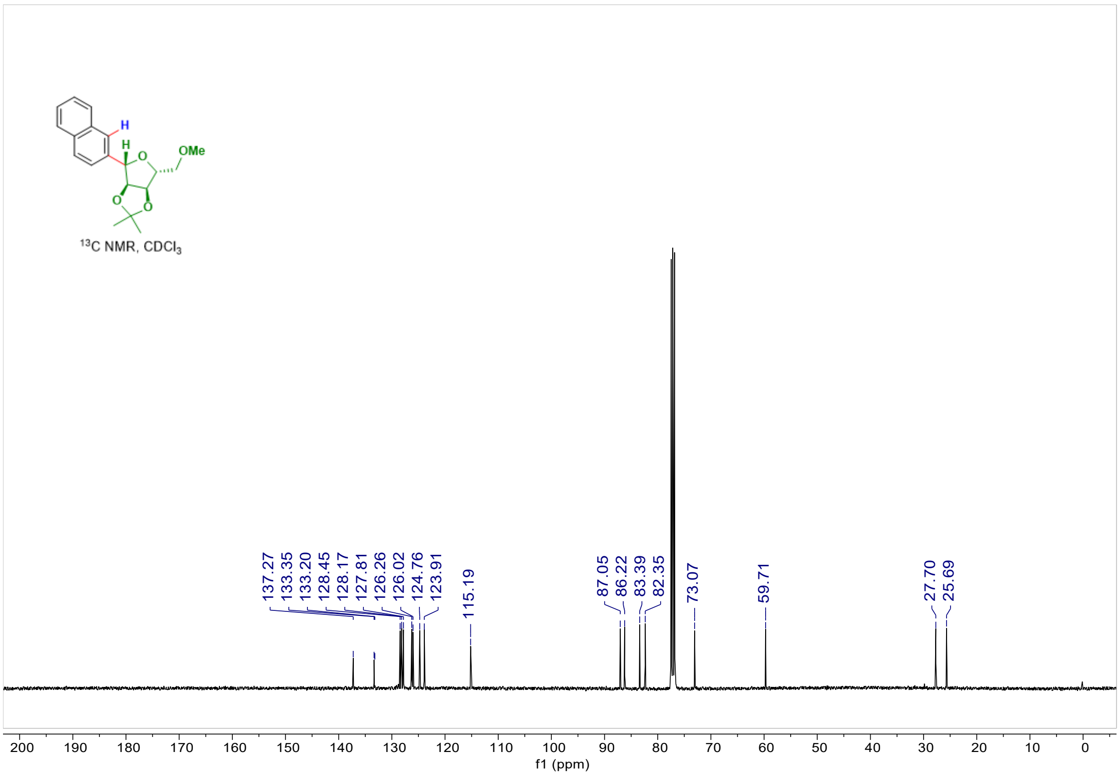
^{13}C NMR spectrum of **3l**



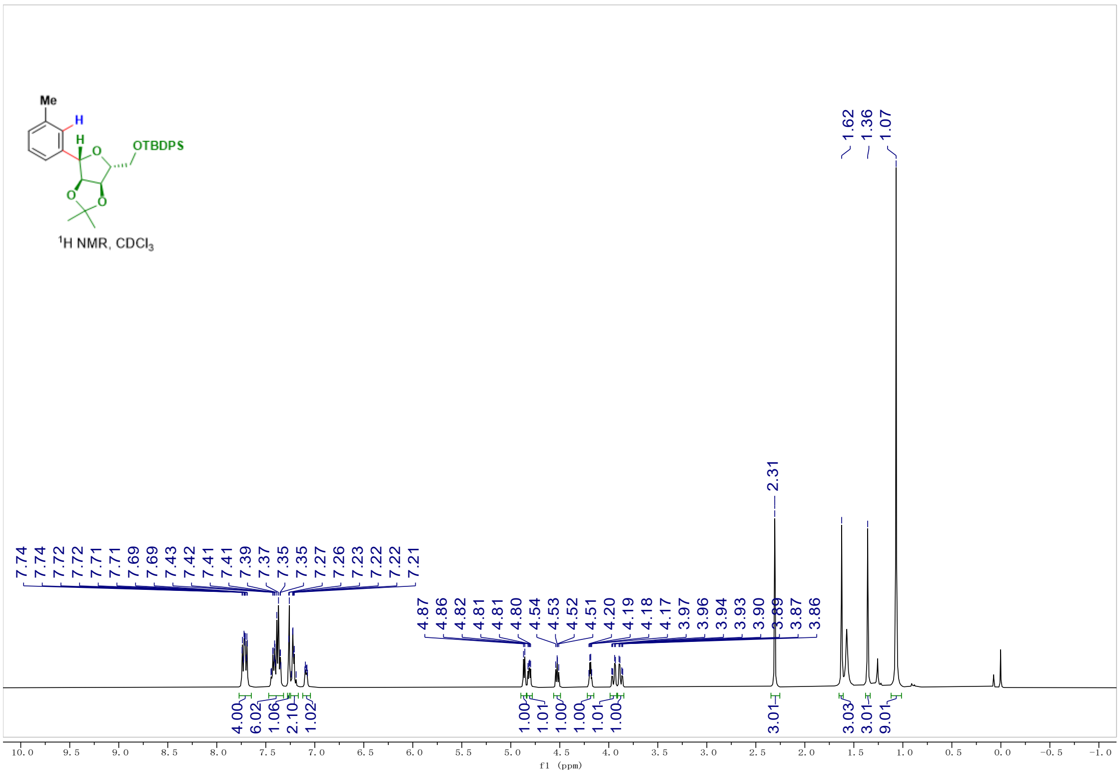
^{1}H NMR spectrum of **3J**



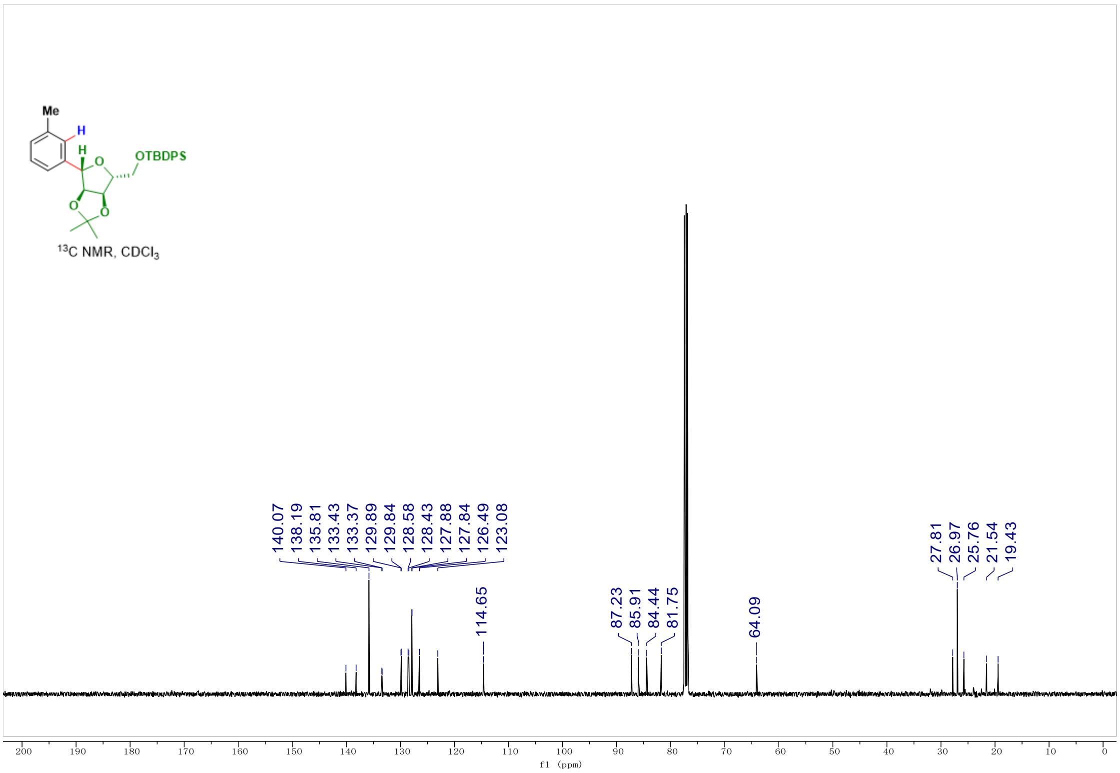
^{13}C NMR spectrum of **3J**



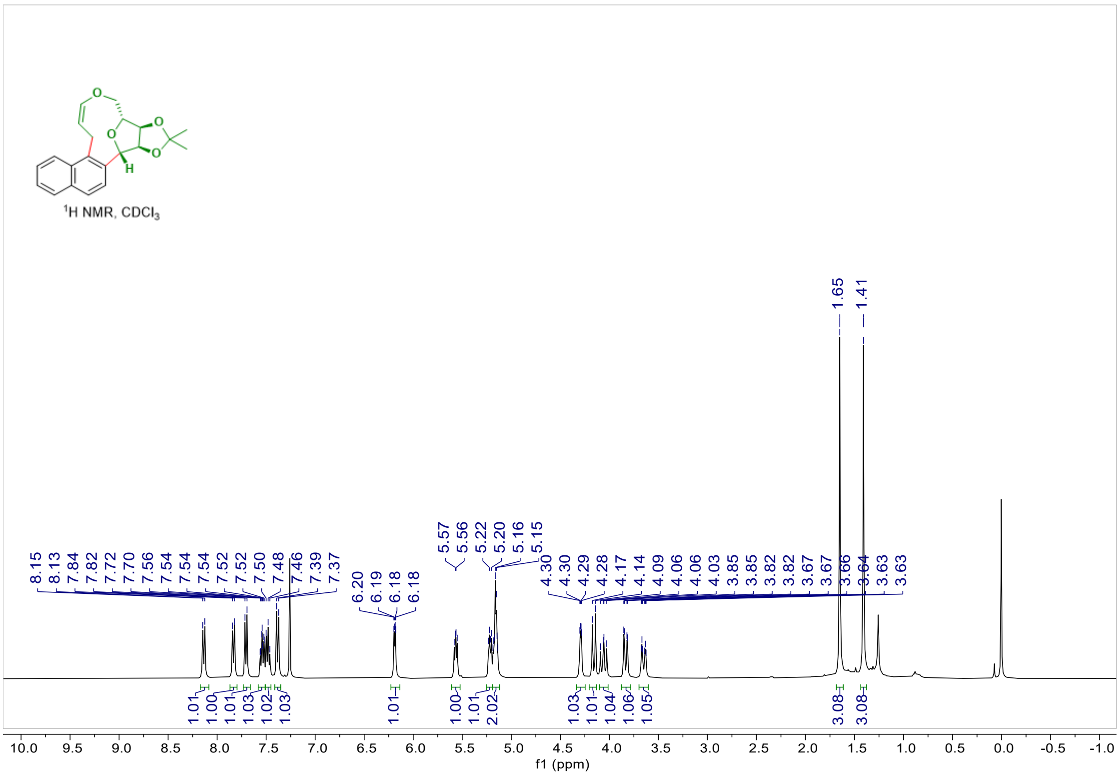
^{1}H NMR spectrum of **3K**



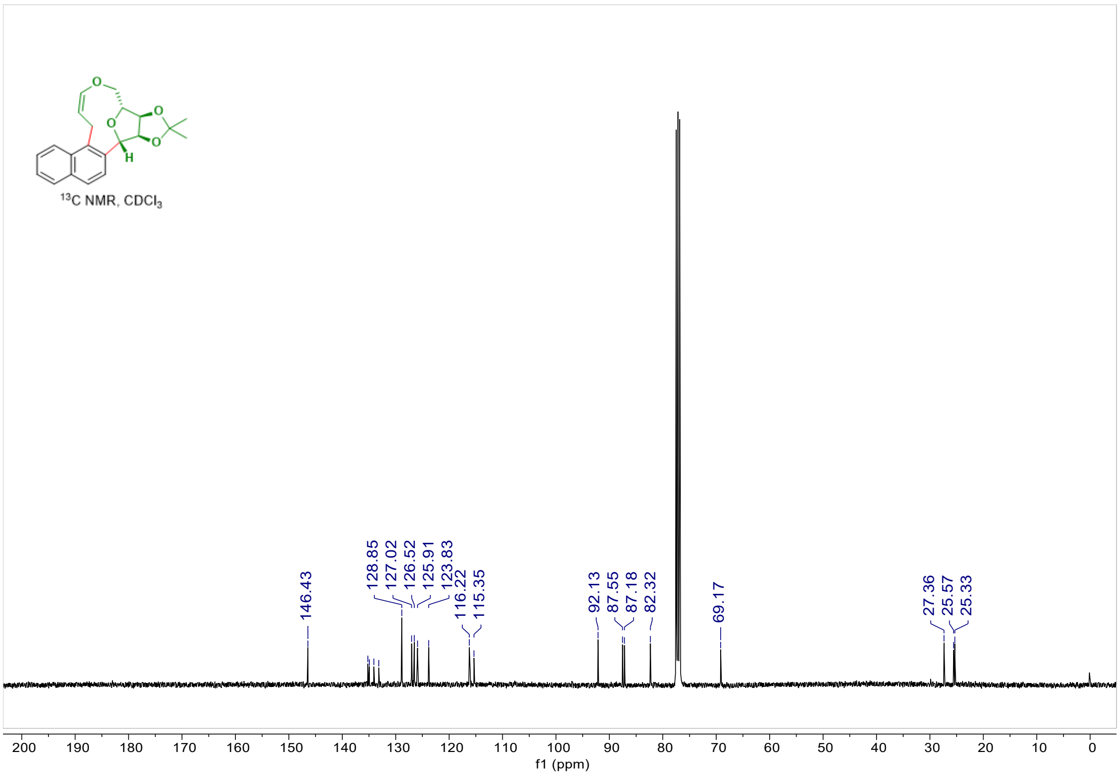
^{13}C NMR spectrum of **3K**



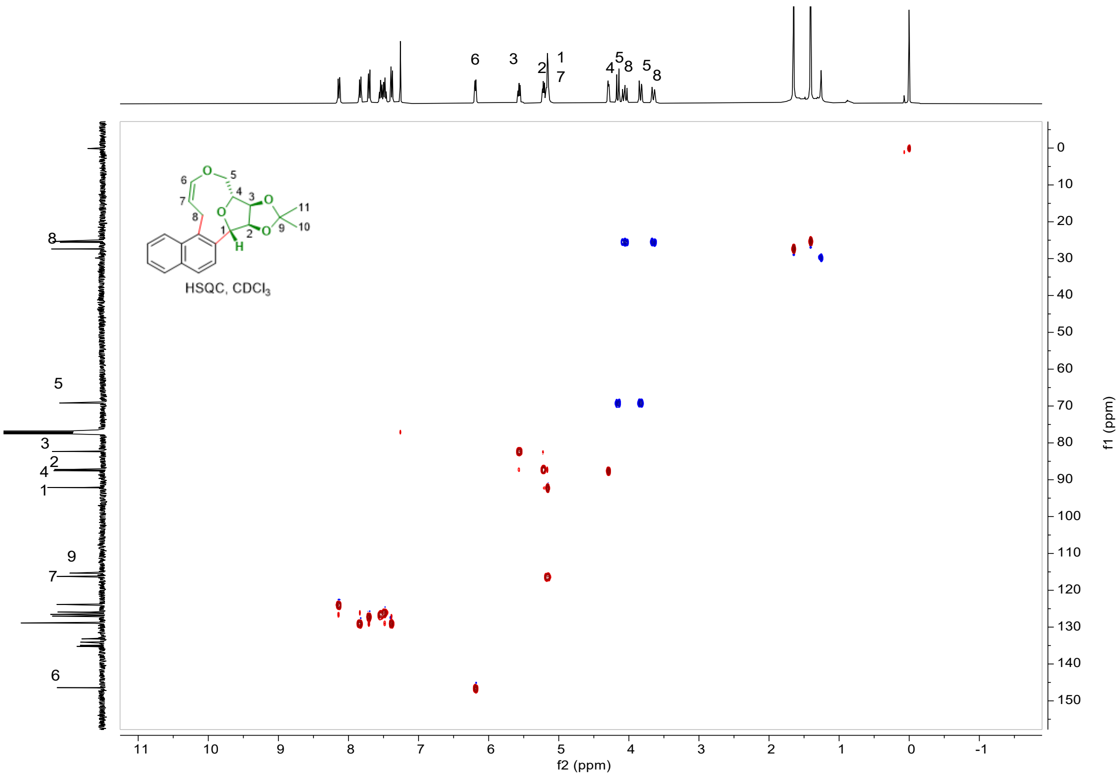
^{1}H NMR spectrum of **3L**



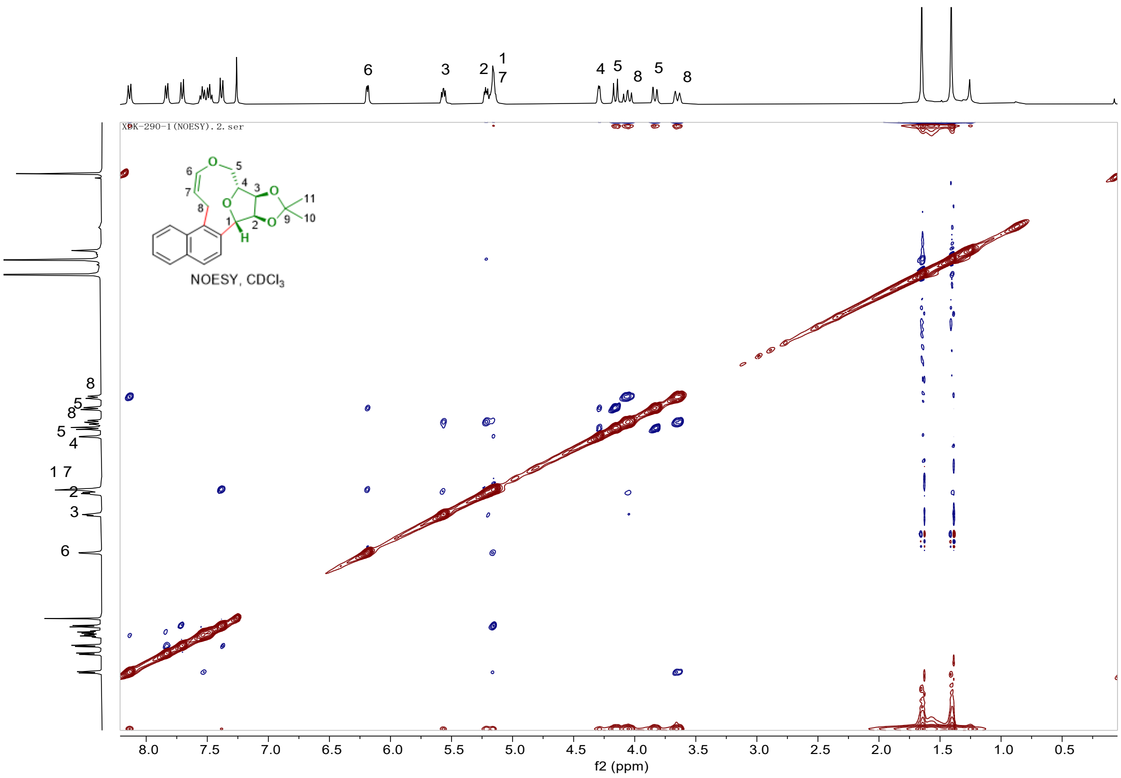
^{13}C NMR spectrum of **3L**



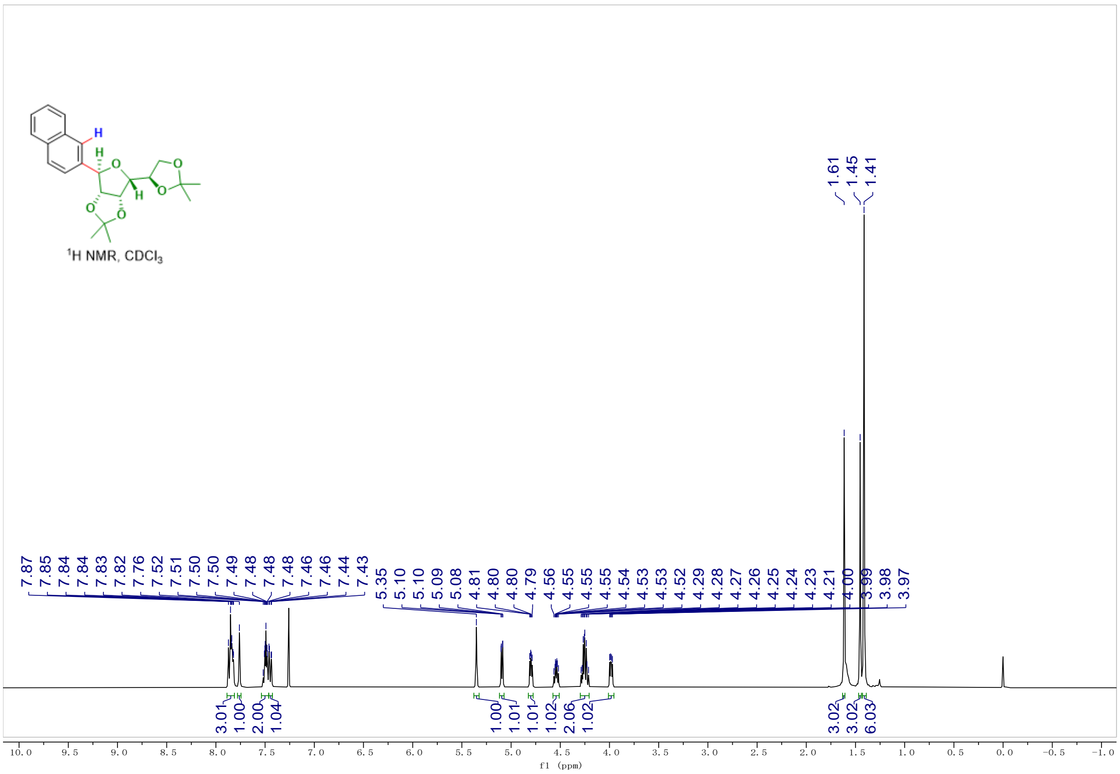
^{1}H-^{13}C HSQC NMR spectrum of **3L**



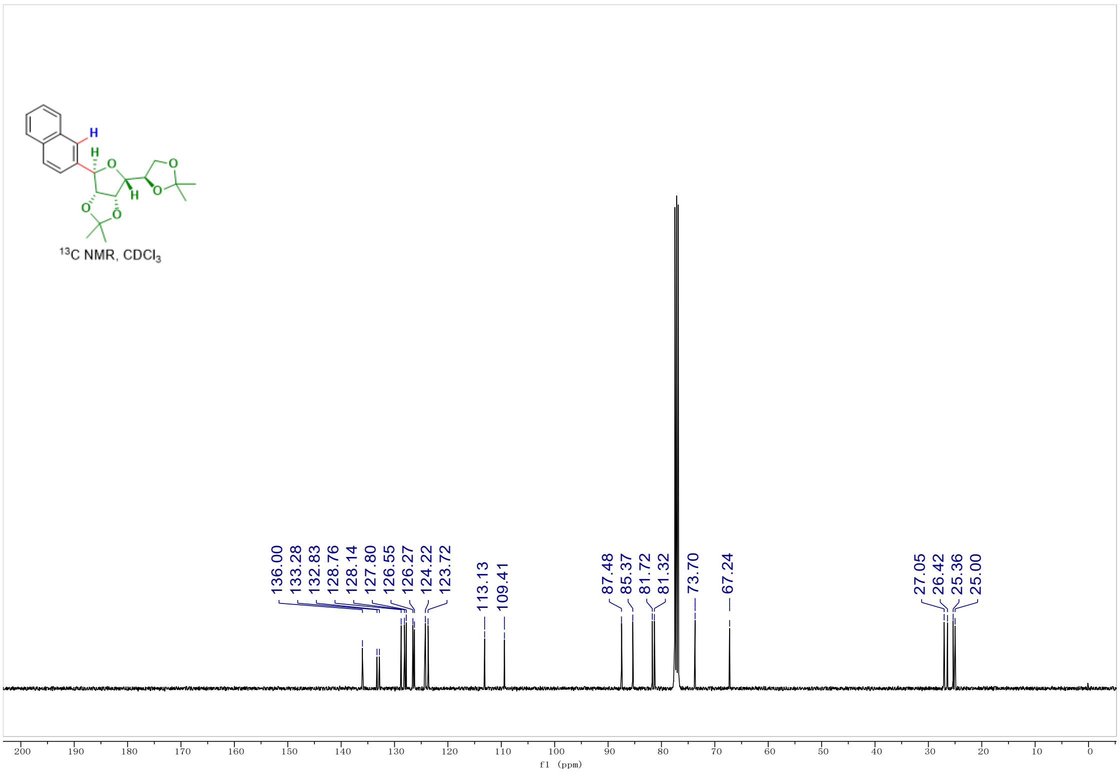
^{1}H-^{1}H NOESY NMR spectrum of **3L**



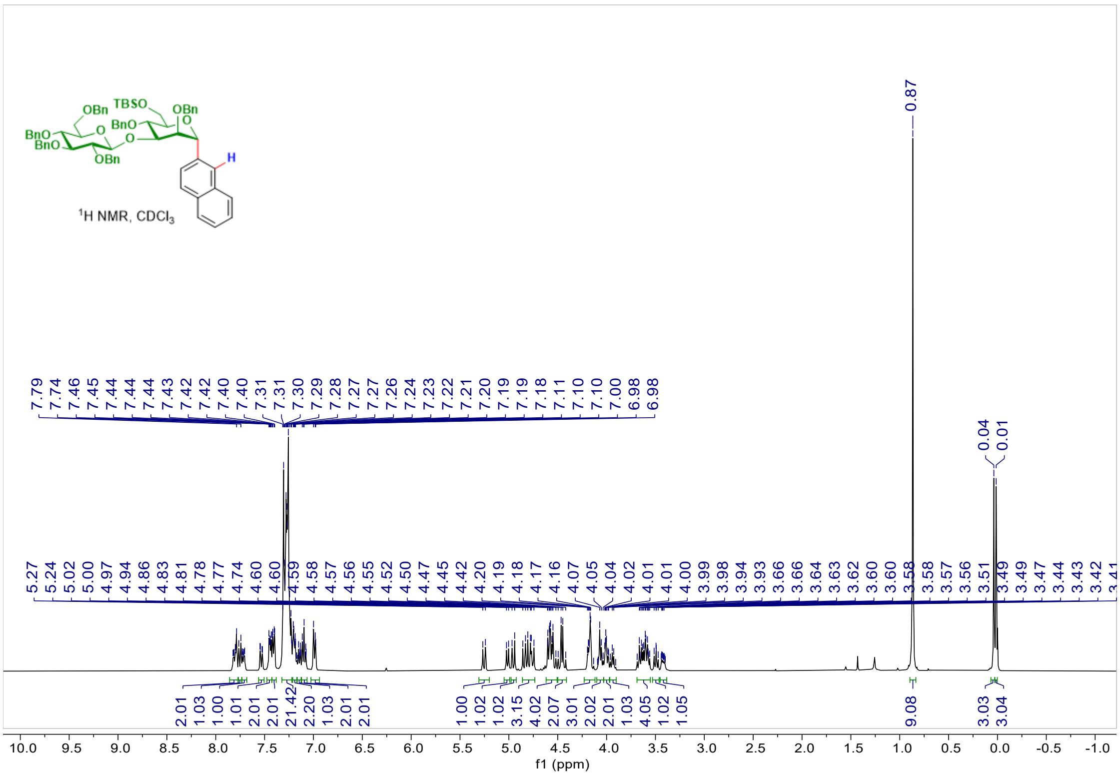
[1]H NMR spectrum of **3M**



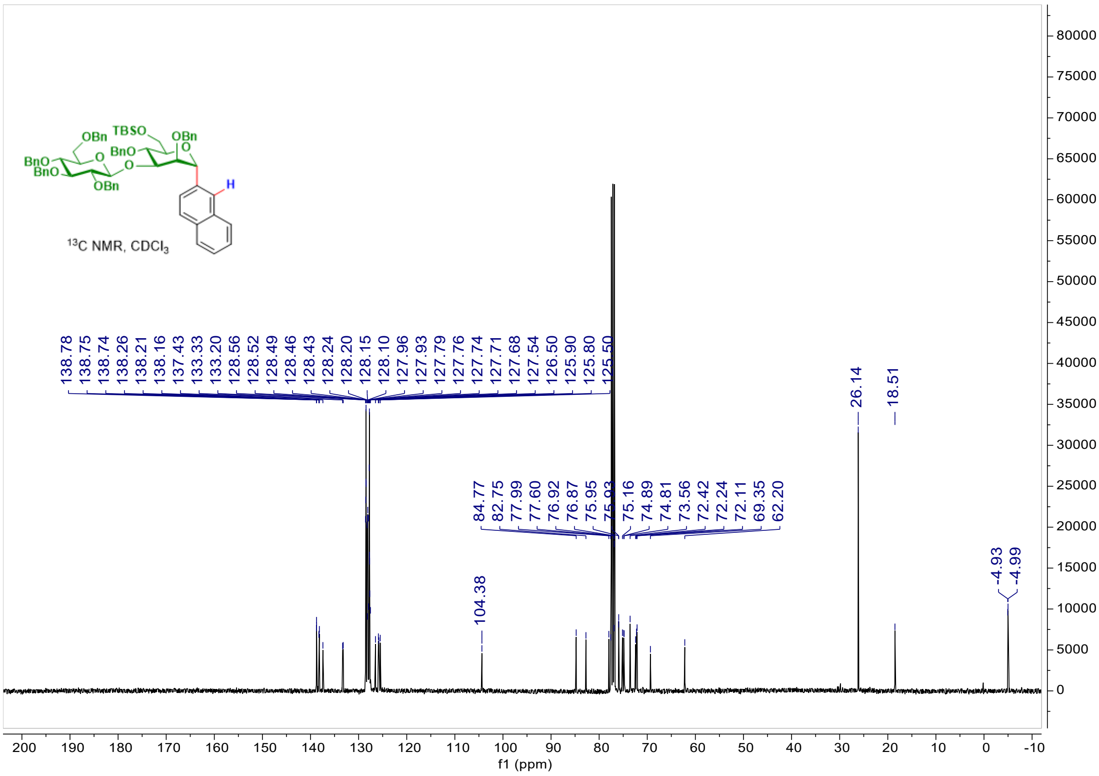
[13]C NMR spectrum of **3M**



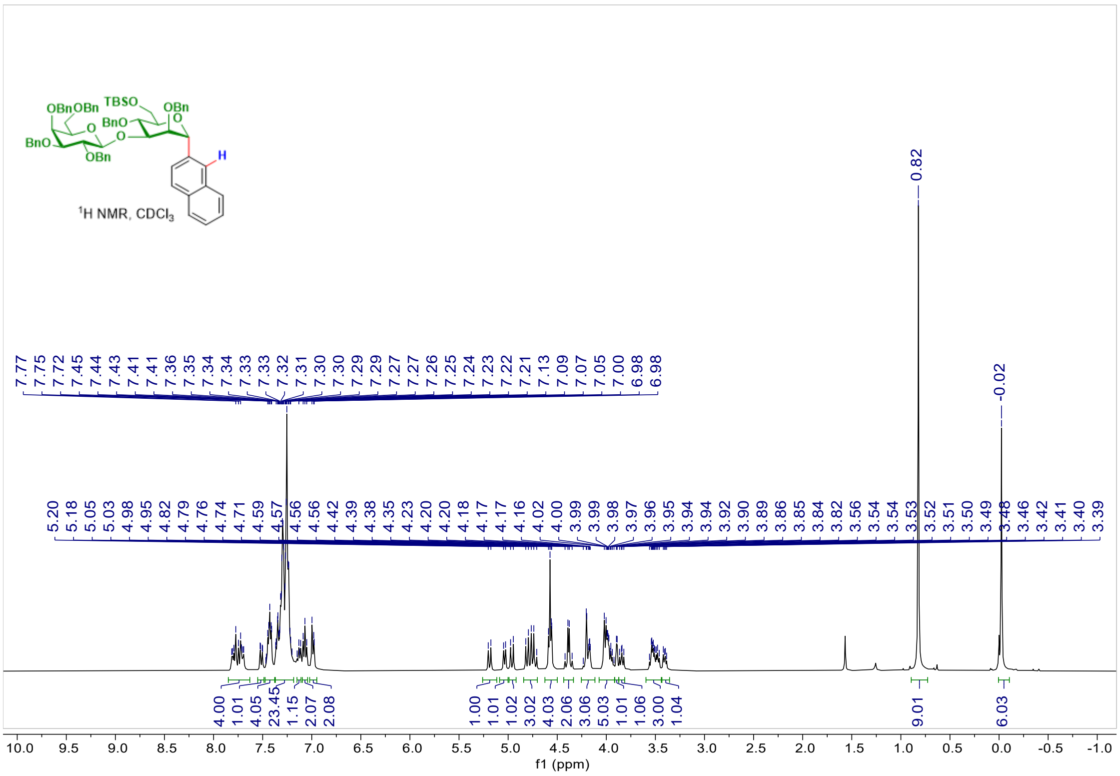
^{1}H NMR spectrum of **3N**



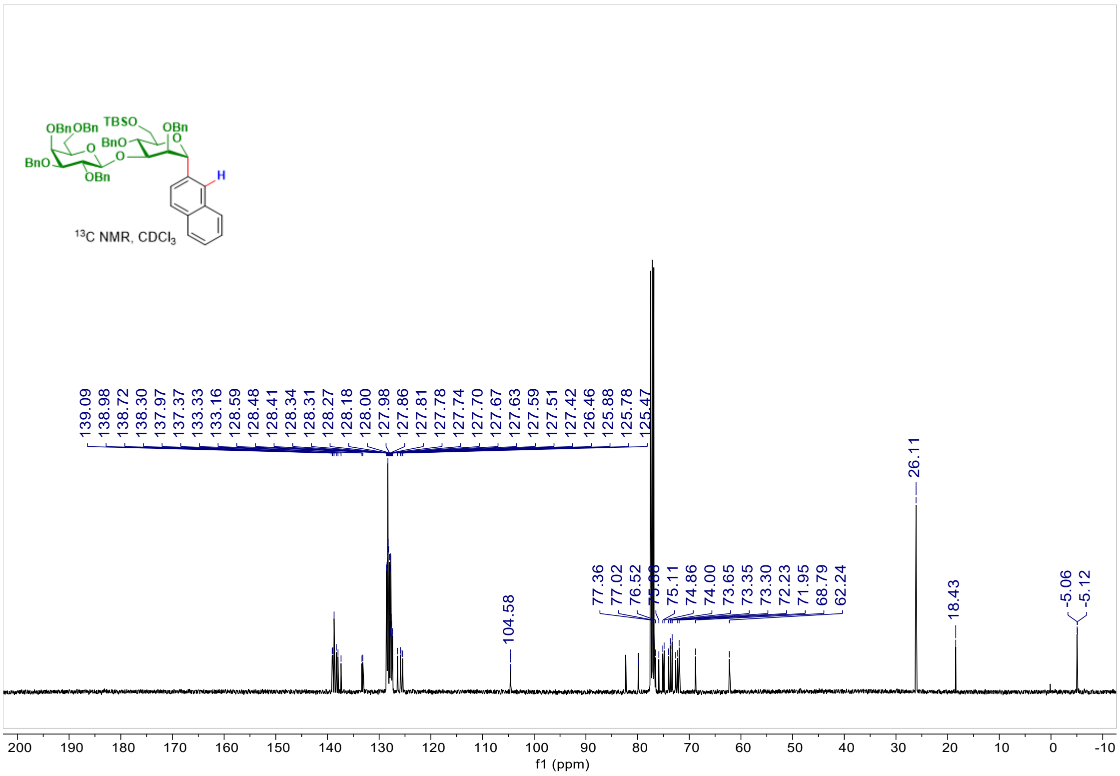
^{13}C NMR spectrum of **3N**



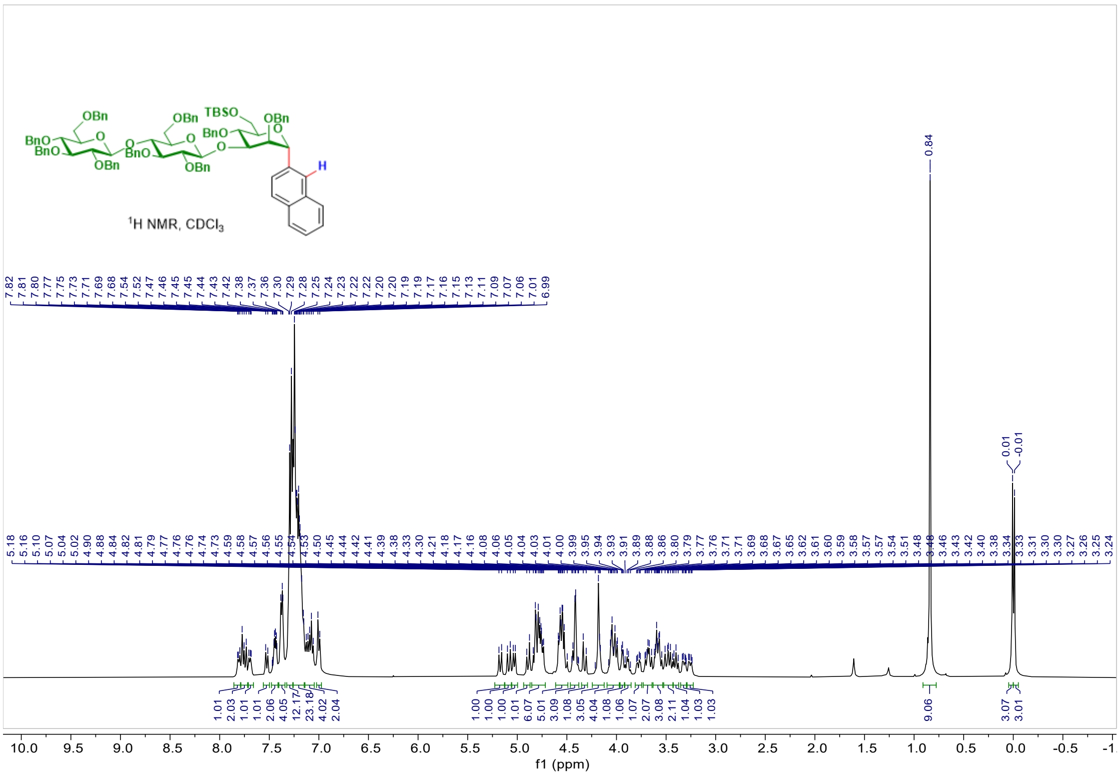
^{1}H NMR spectrum of **3O**



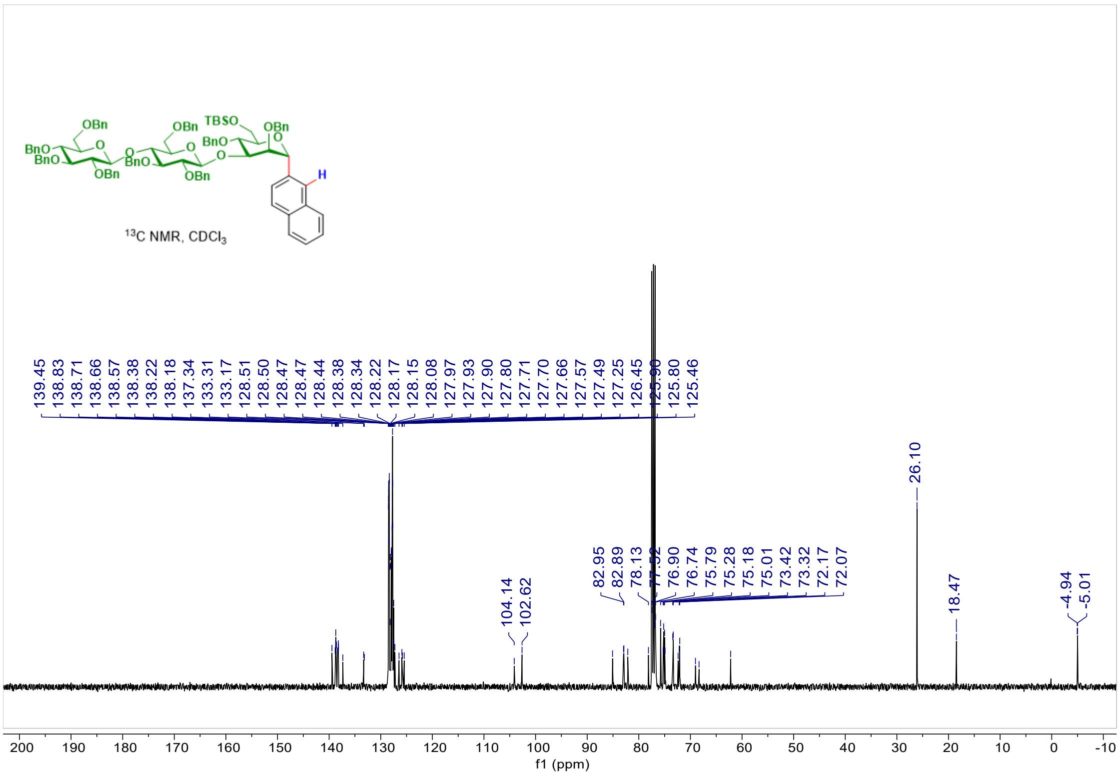
^{13}C NMR spectrum of **3O**



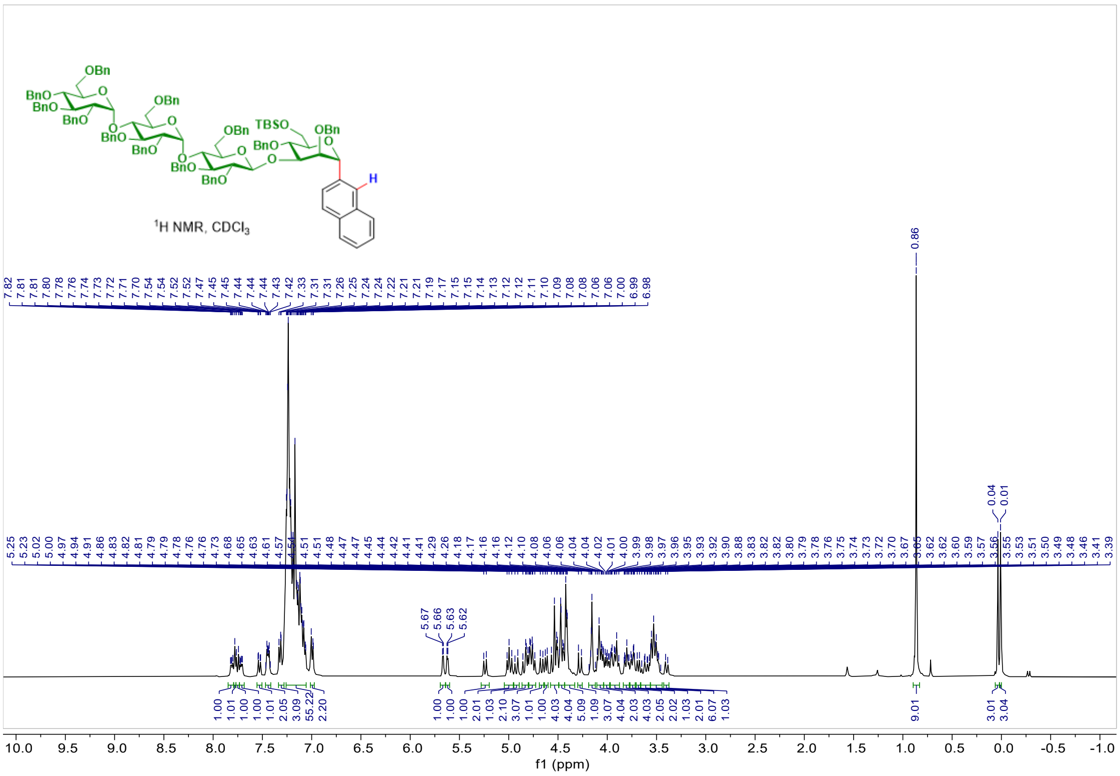
[1]H NMR spectrum of **3P**



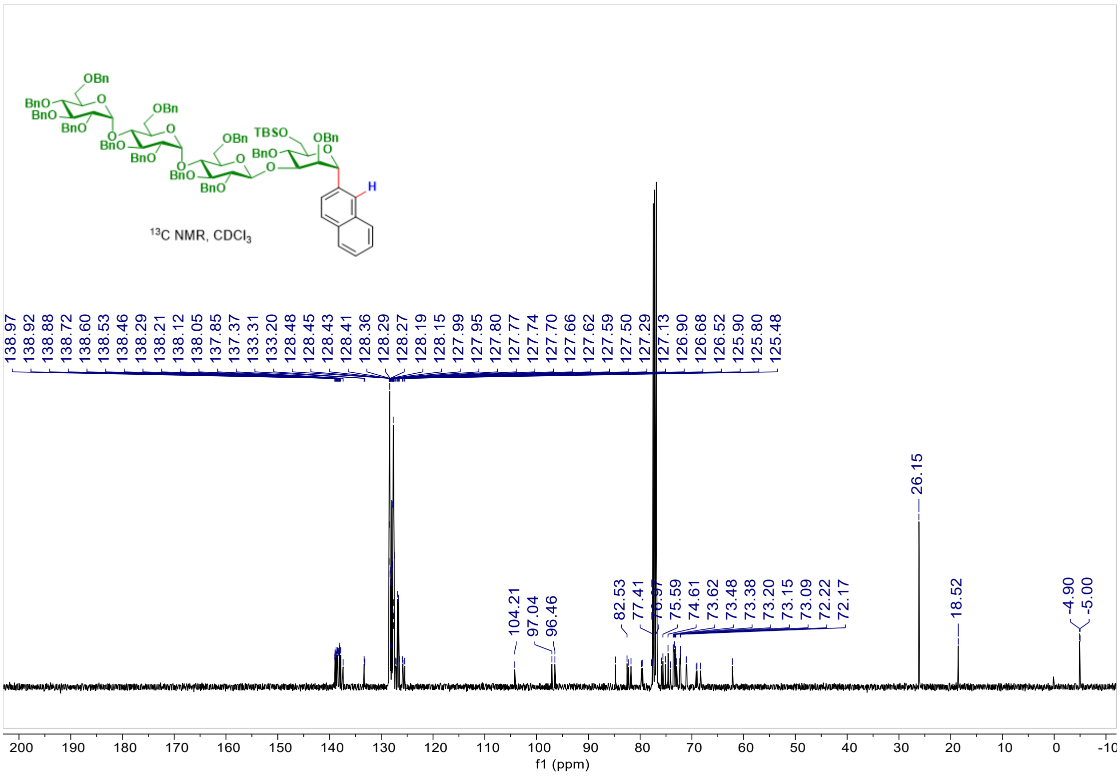
[13]C NMR spectrum of **3P**



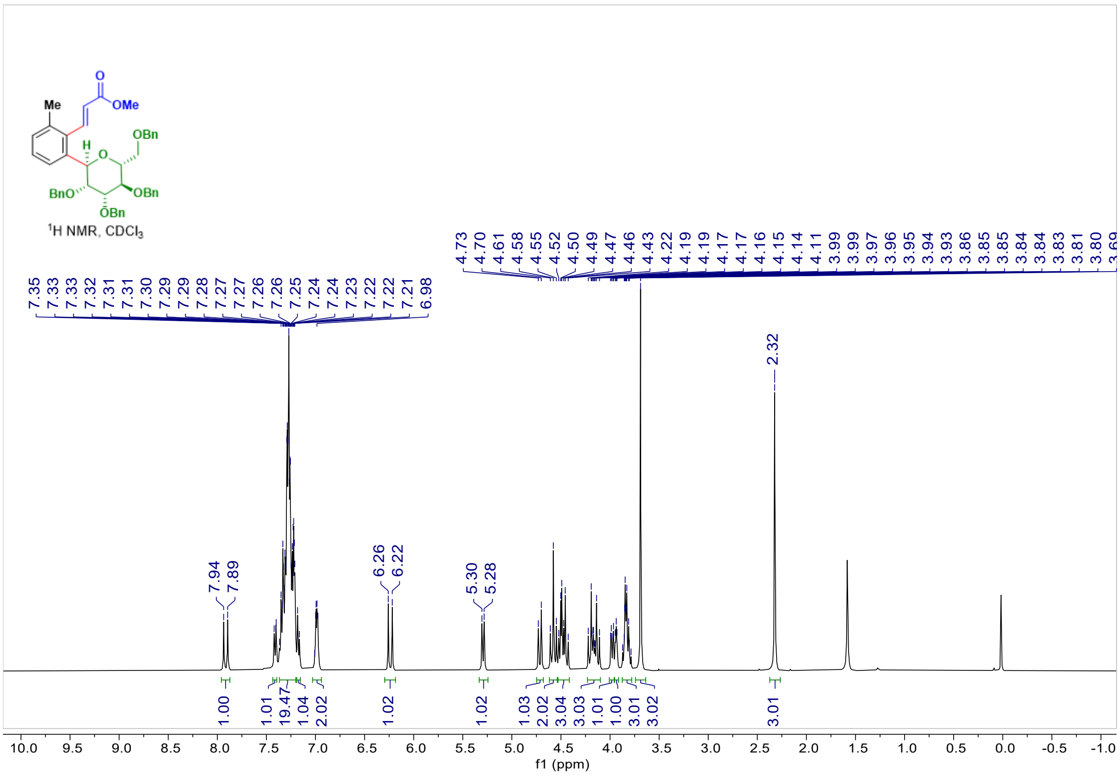
^{1}H NMR spectrum of **3Q**



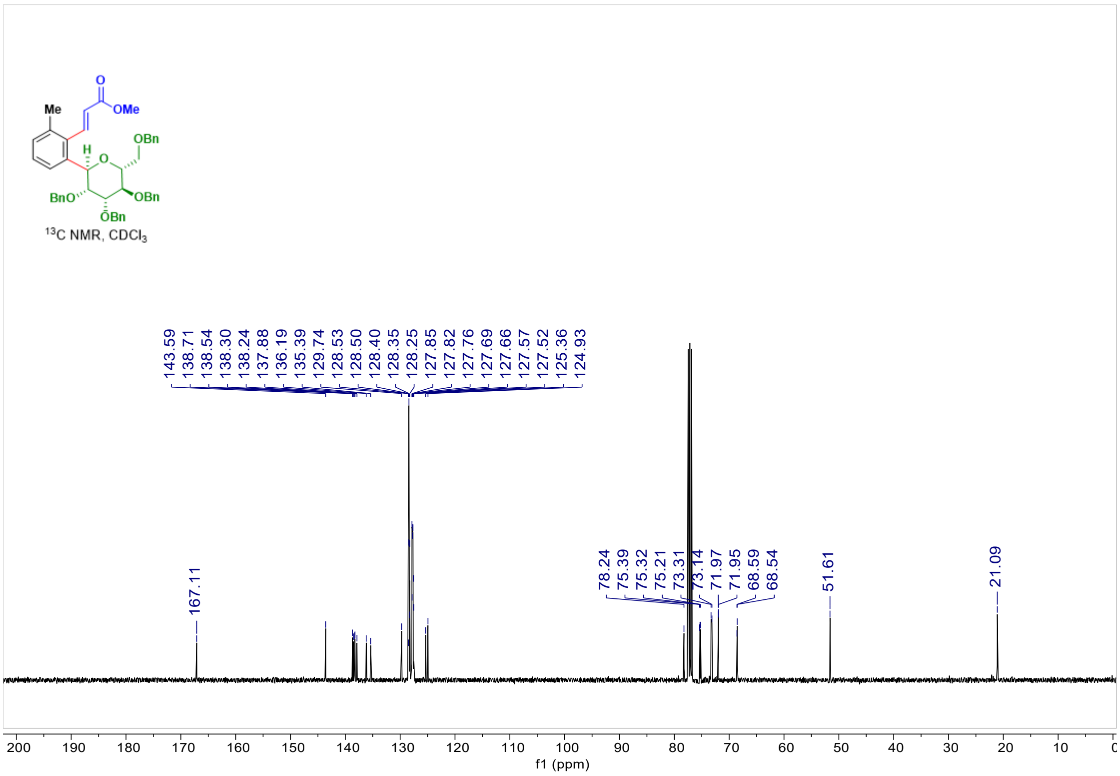
^{13}C NMR spectrum of **3Q**



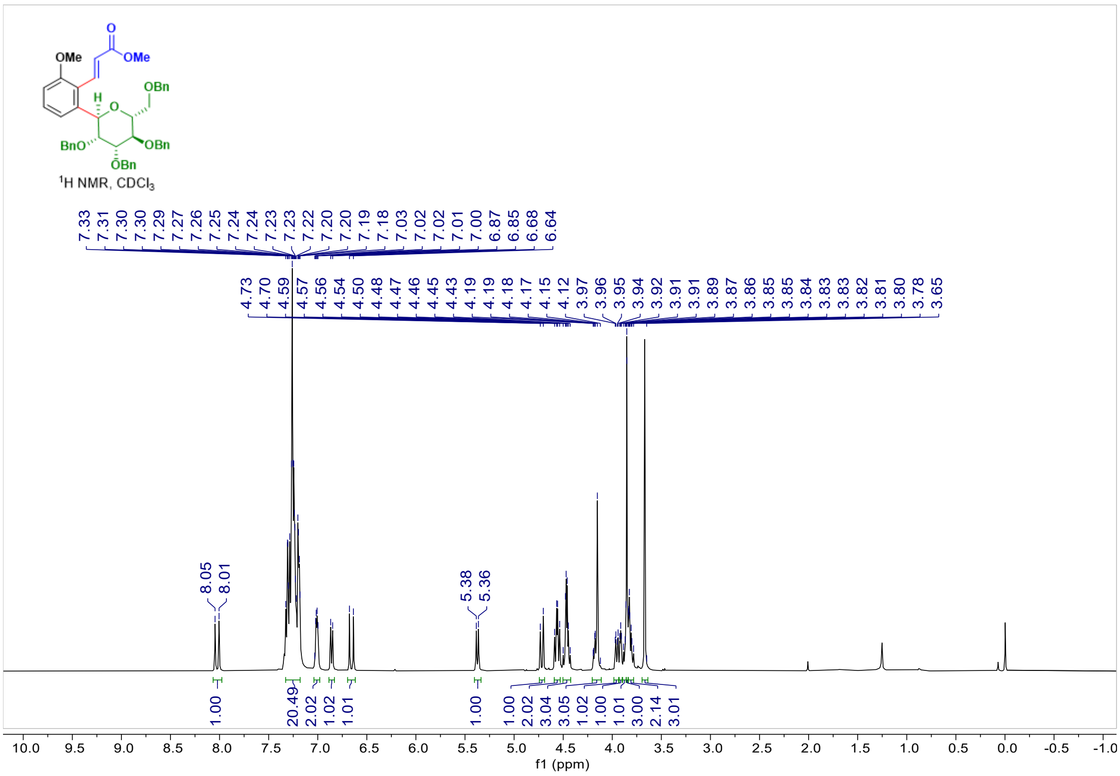
^{1}H NMR spectrum of **5a**



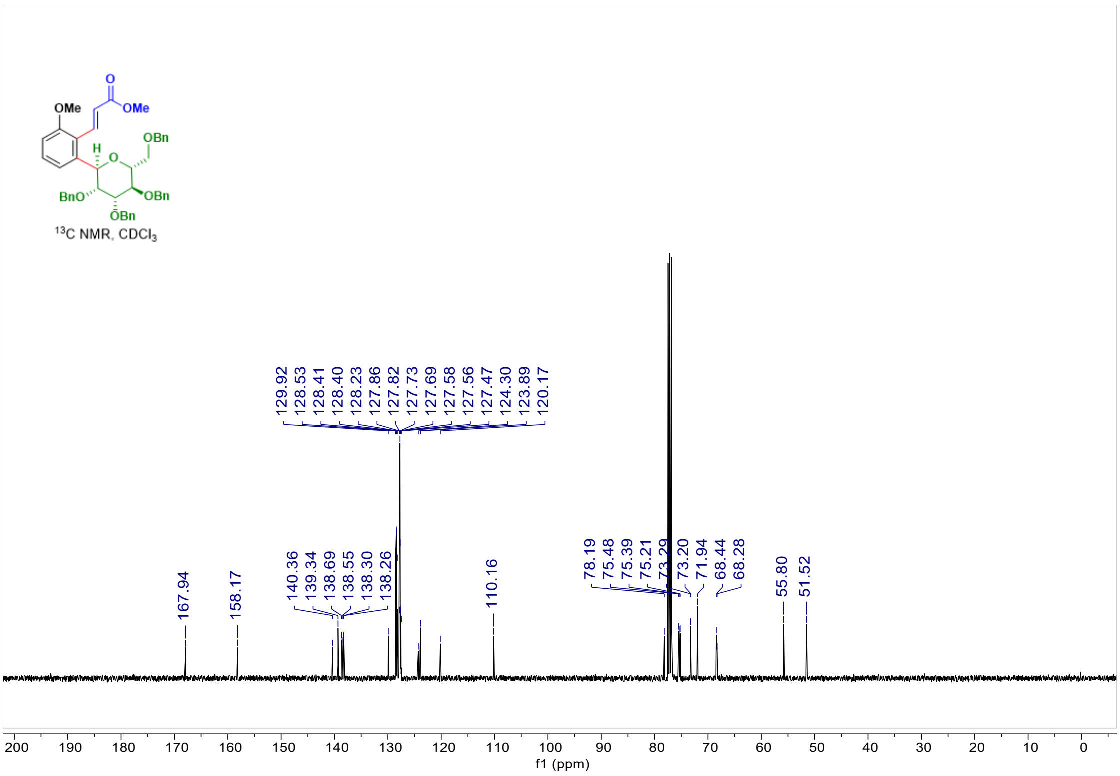
^{13}C NMR spectrum of **5a**



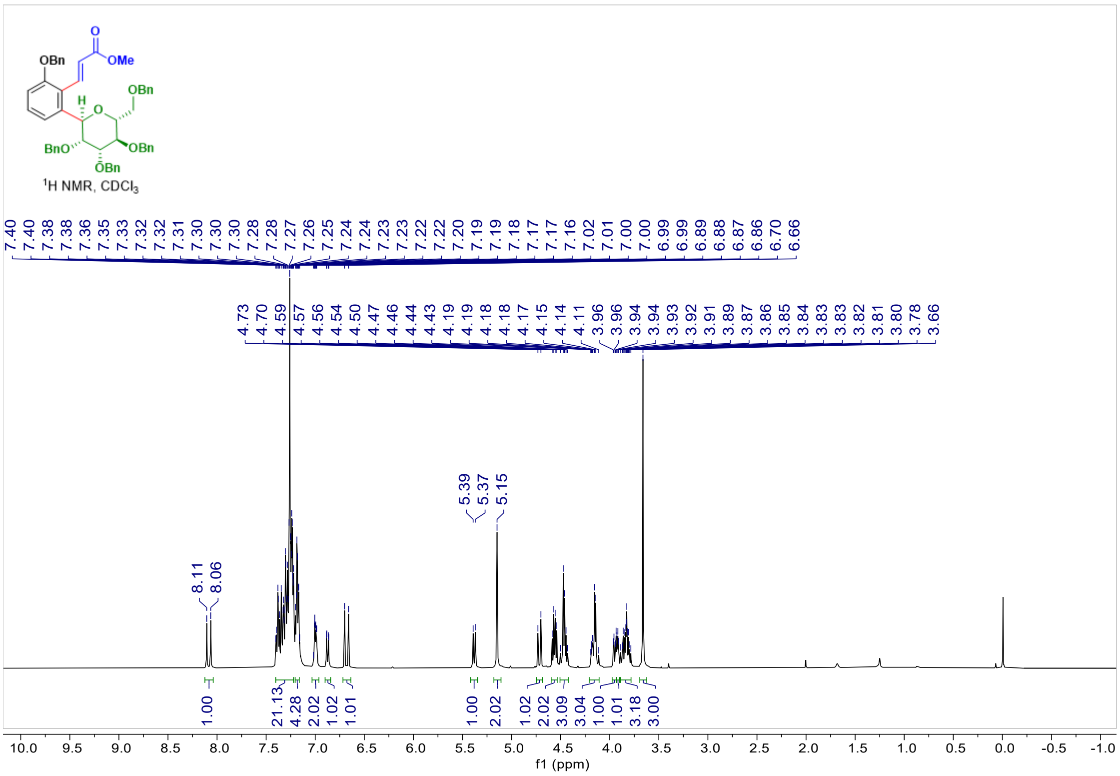
^{1}H NMR spectrum of **5b**



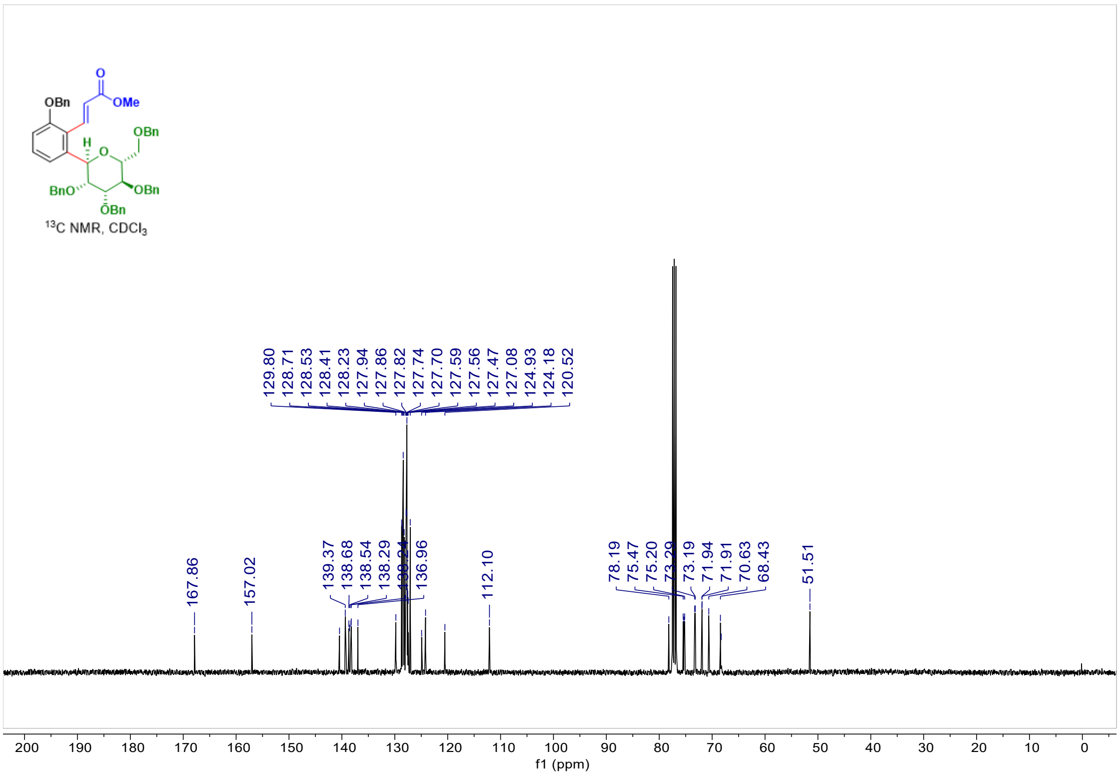
^{13}C NMR spectrum of **5b**



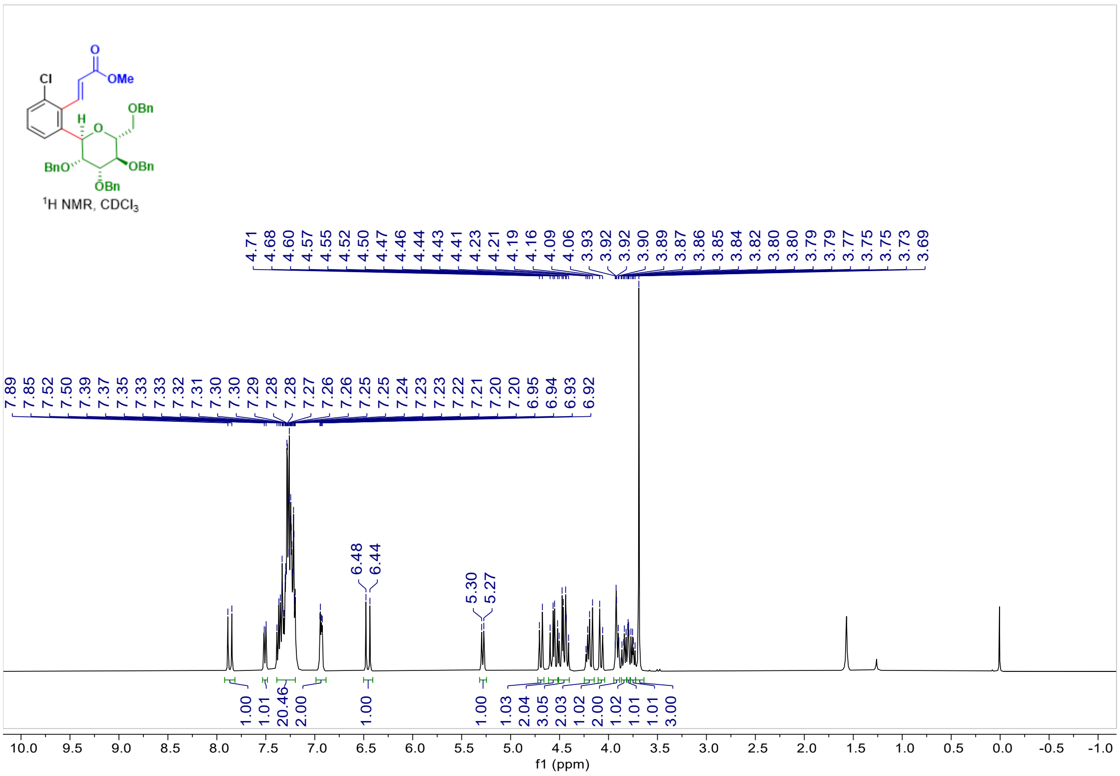
^{1}H NMR spectrum of **5c**



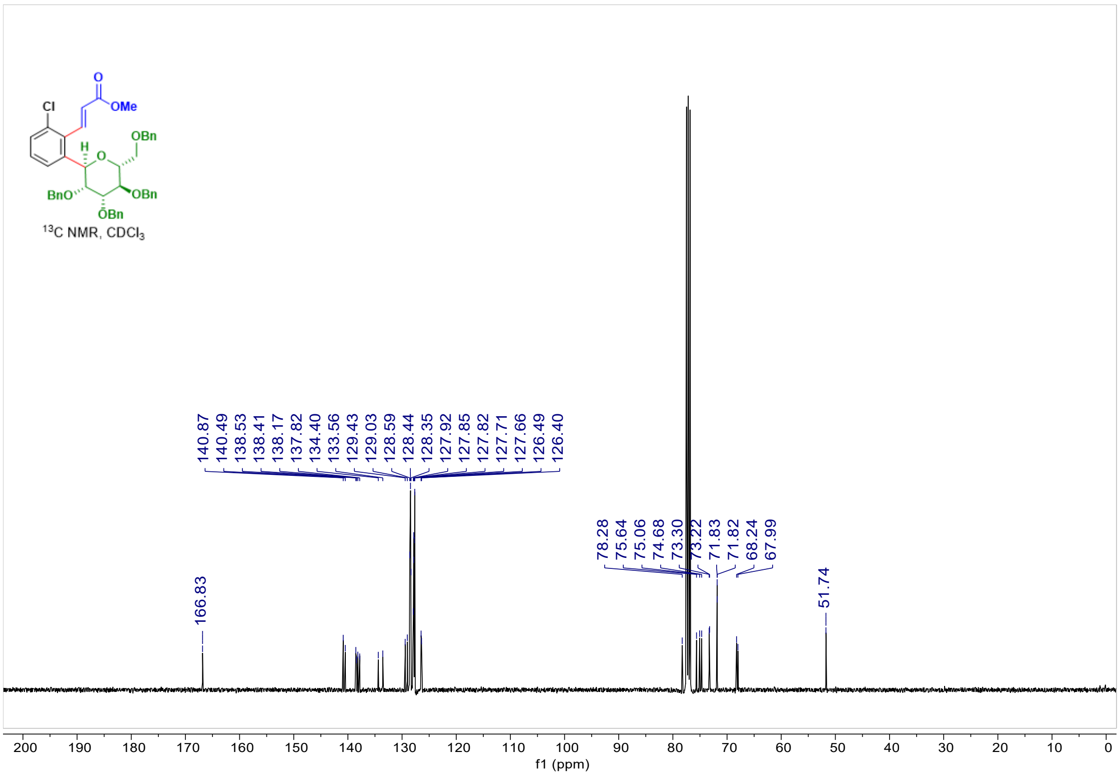
^{13}C NMR spectrum of **5c**



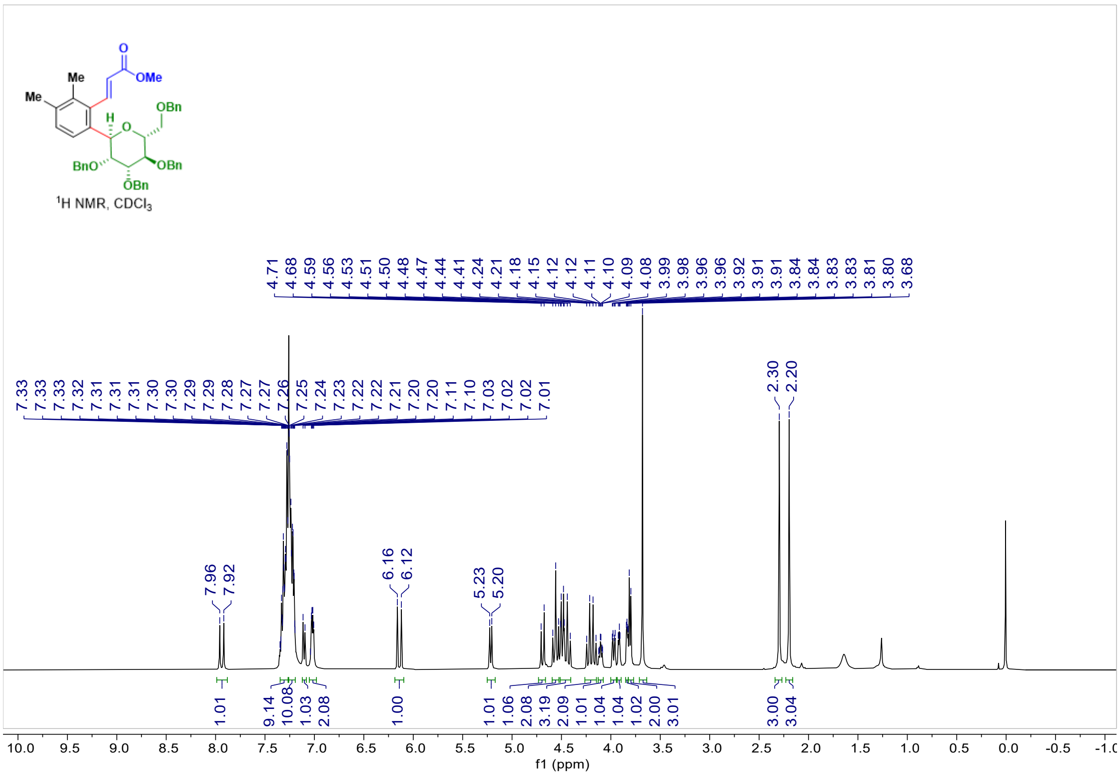
[1]H NMR spectrum of **5d**



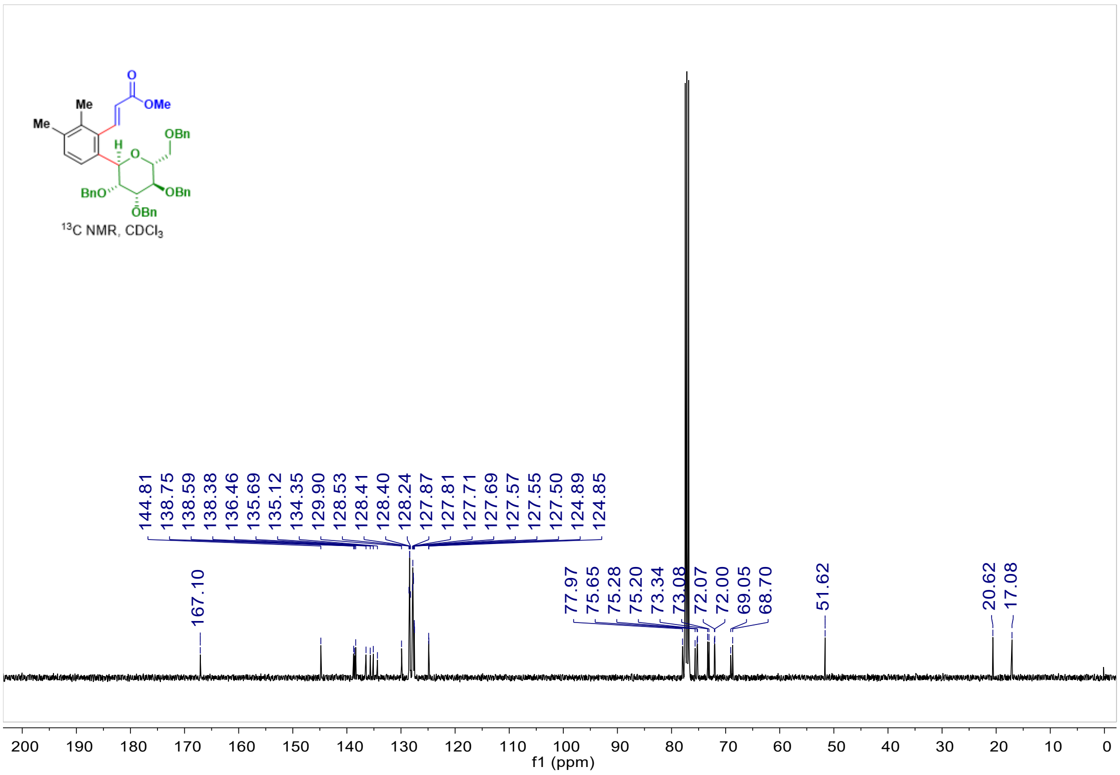
[13]C NMR spectrum of **5d**



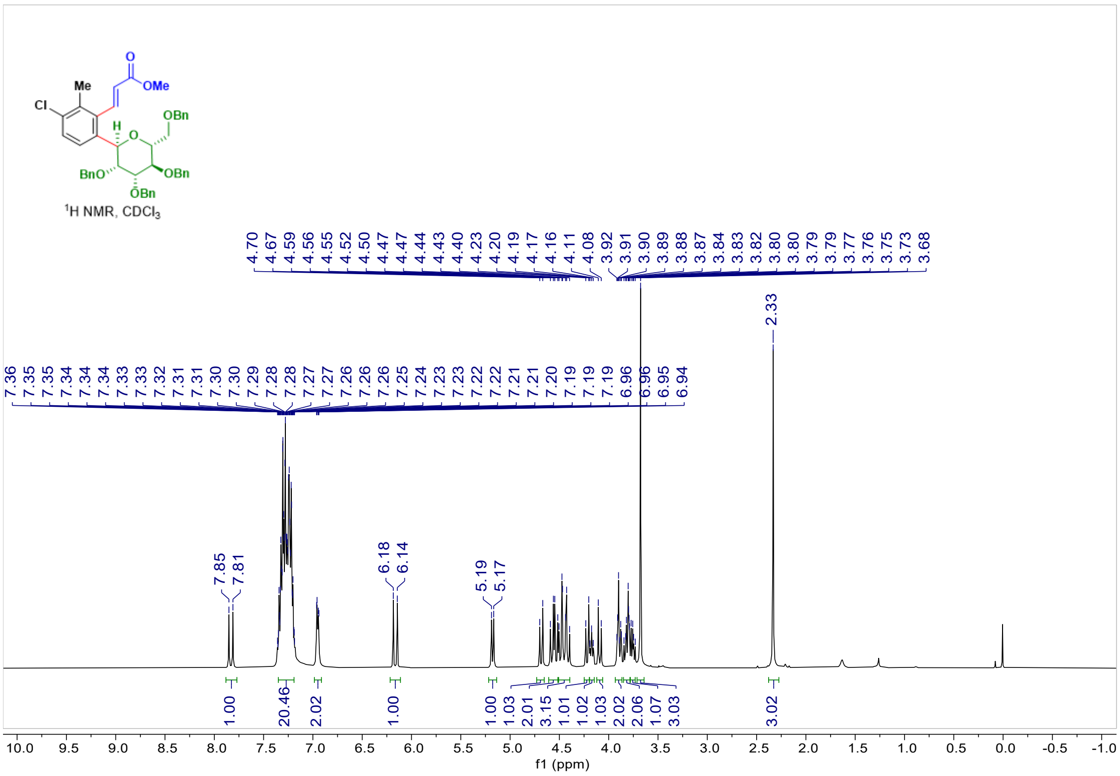
[1]H NMR spectrum of **5e**



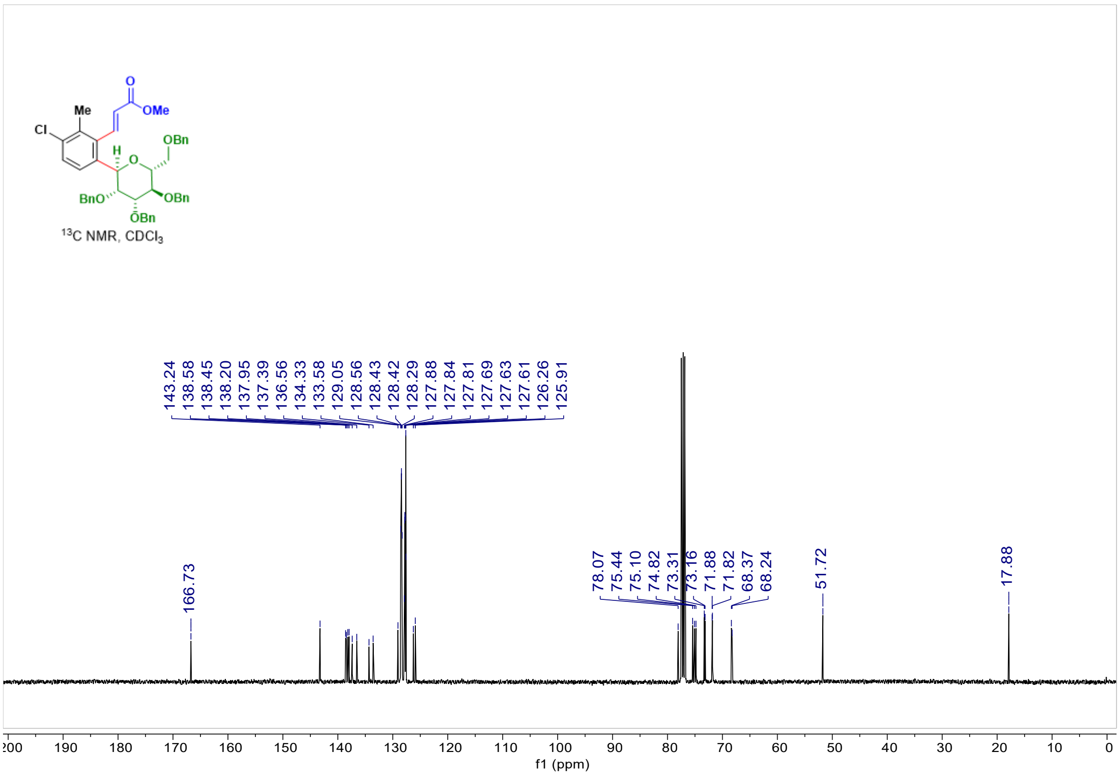
[13]C NMR spectrum of **5e**



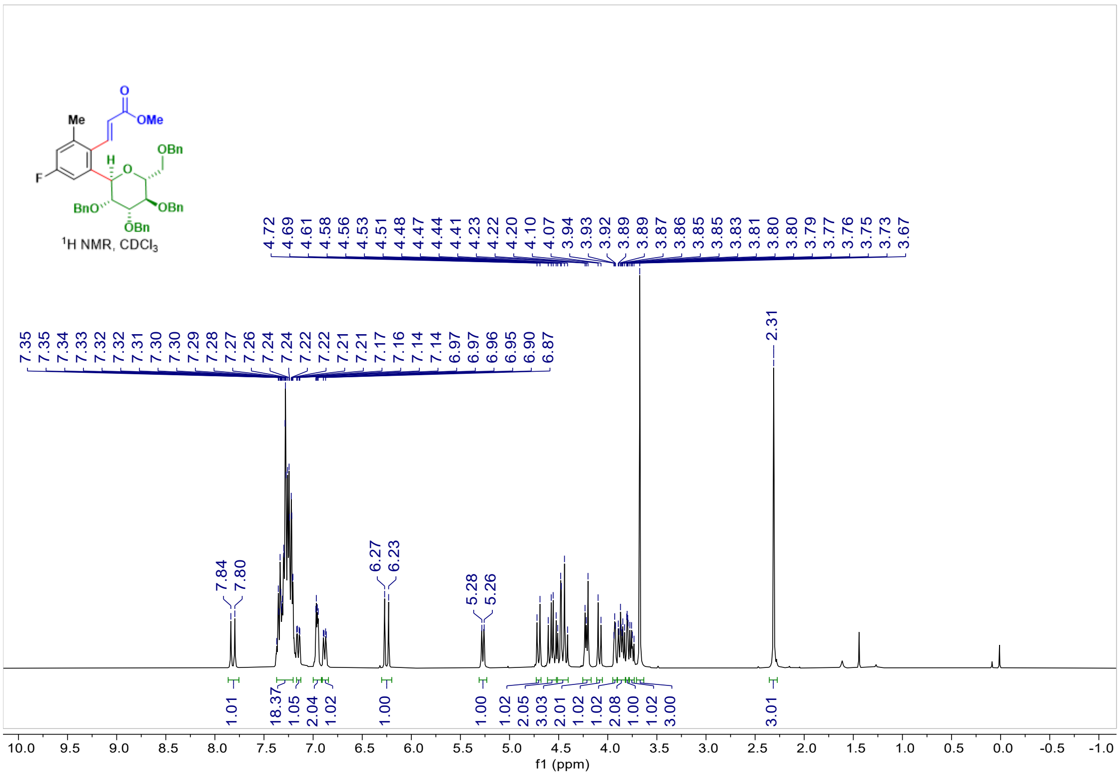
^{1}H NMR spectrum of **5f**



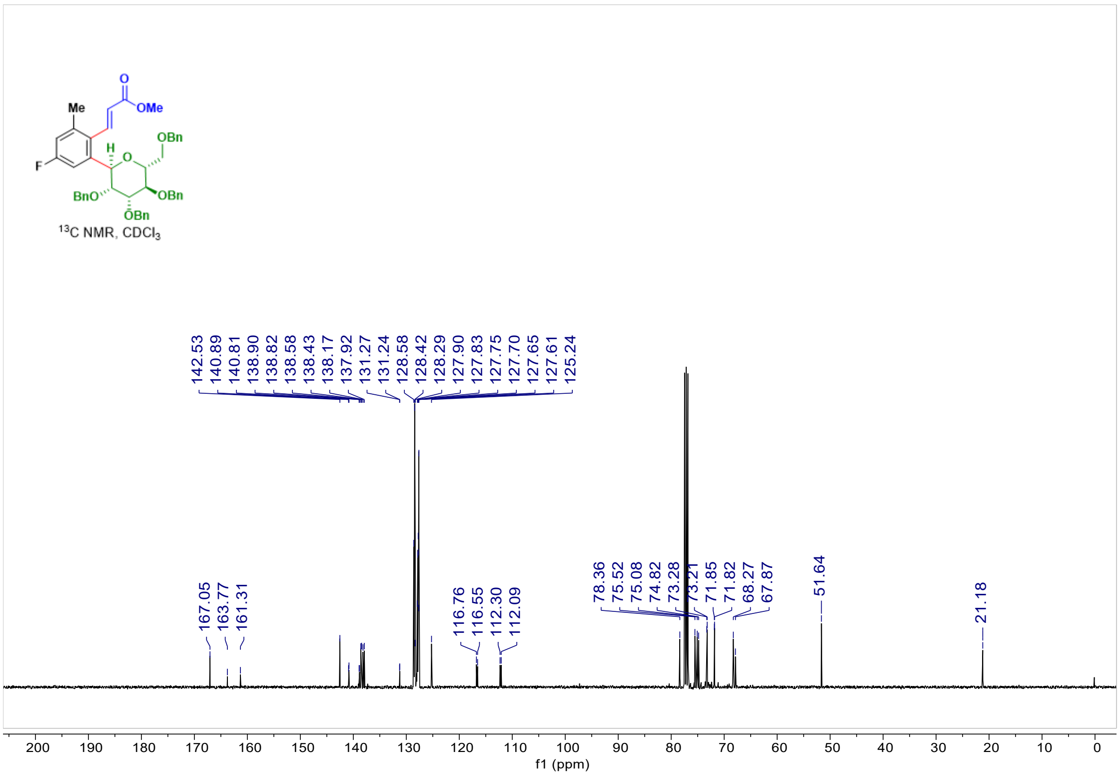
^{13}C NMR spectrum of **5f**



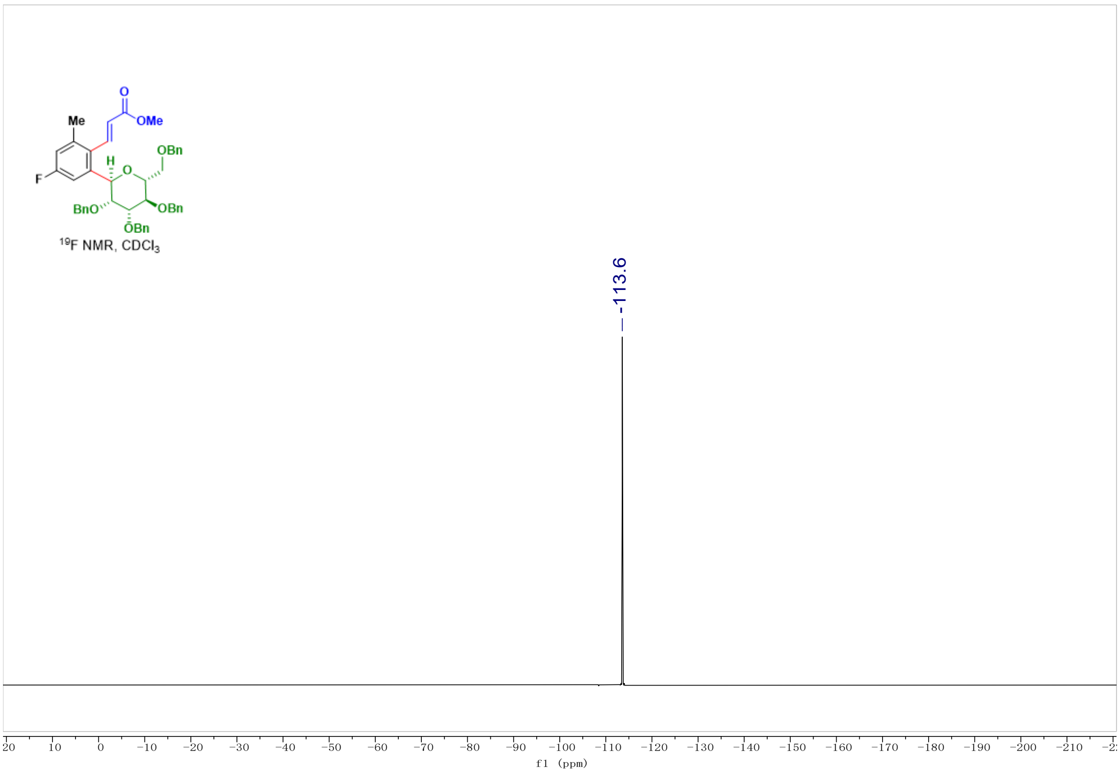
^{1}H NMR spectrum of **5g**



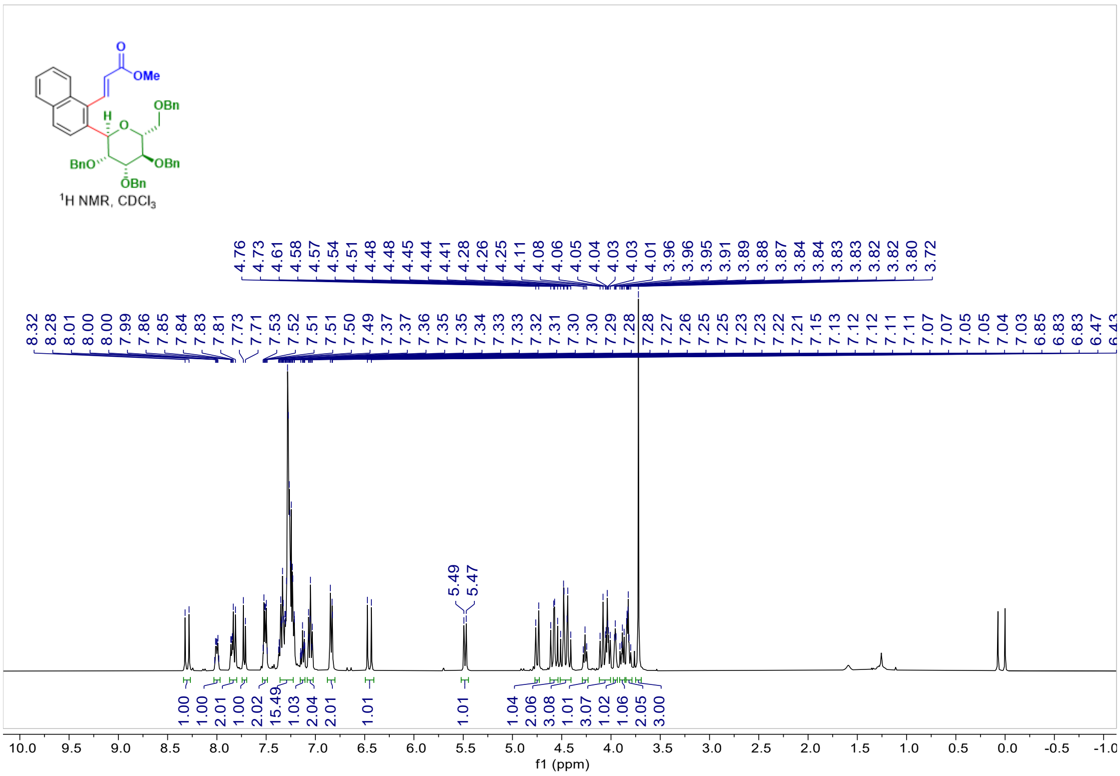
^{13}C NMR spectrum of **5g**



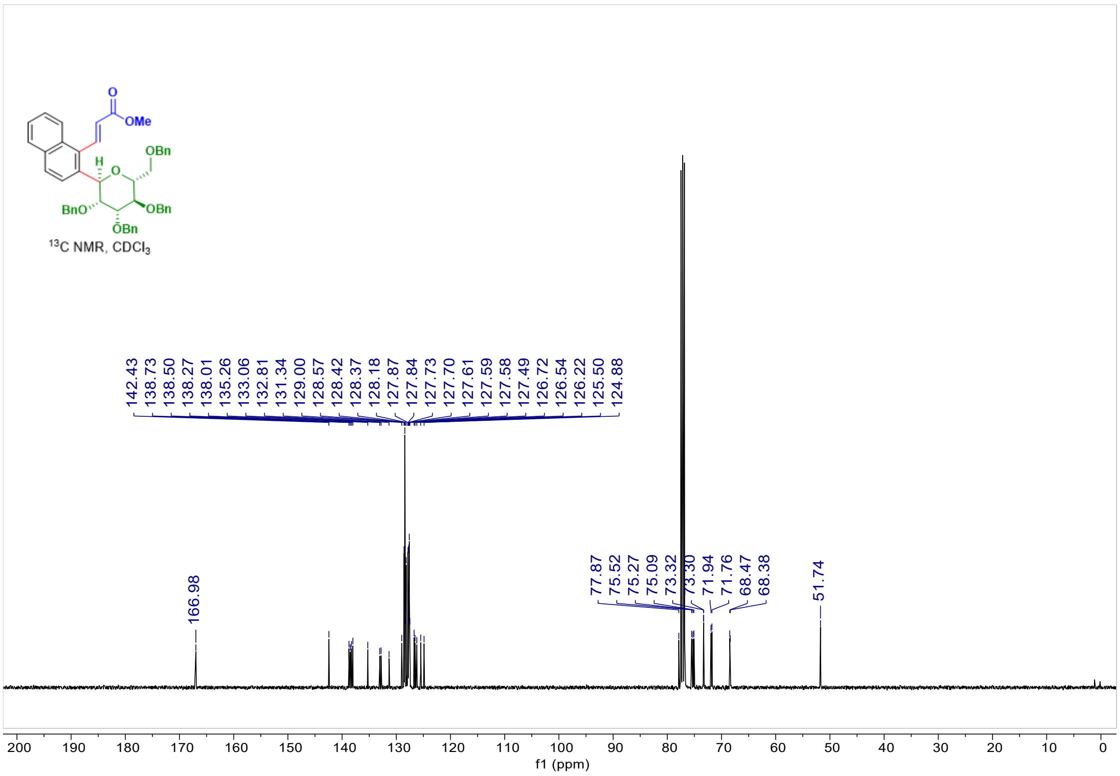
^{19}F NMR spectrum of **5g**



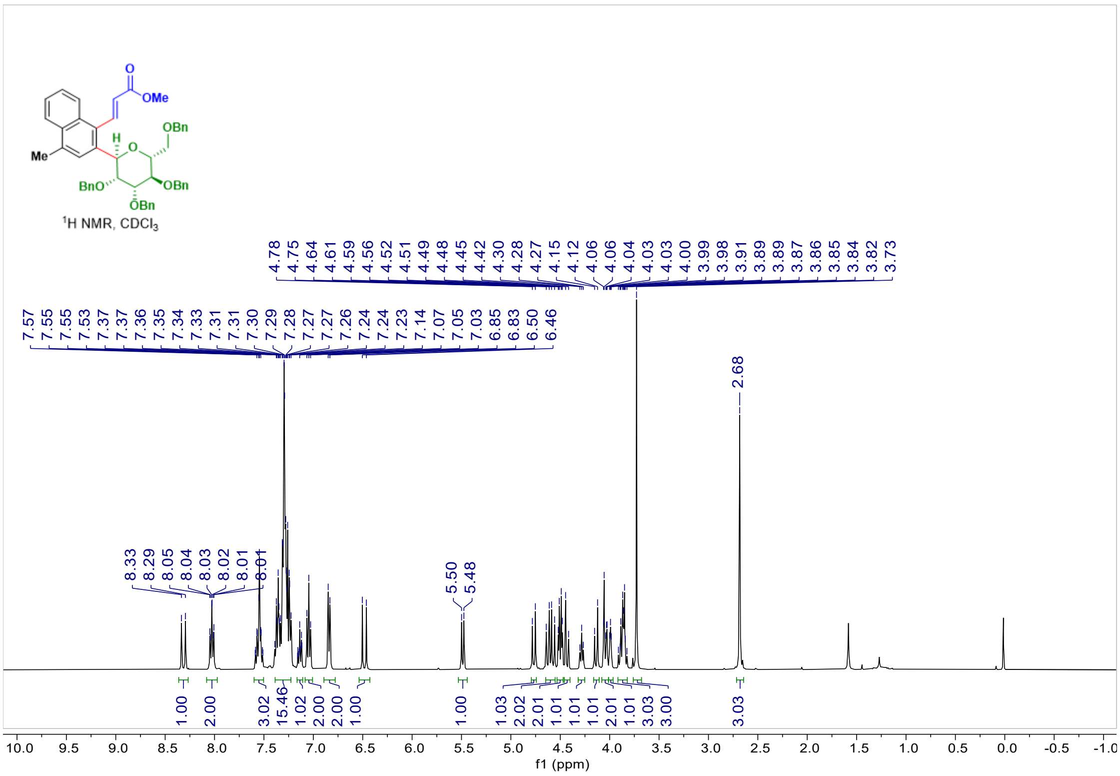
^1H NMR spectrum of **5h**



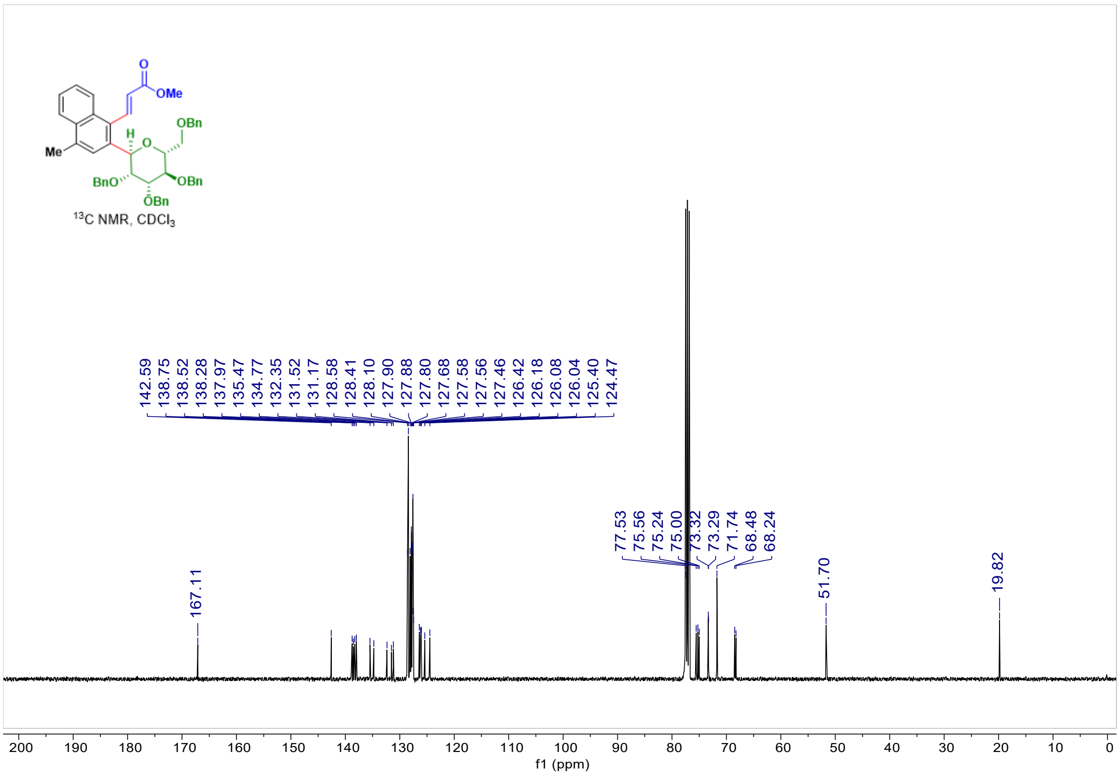
^{13}C NMR spectrum of **5h**



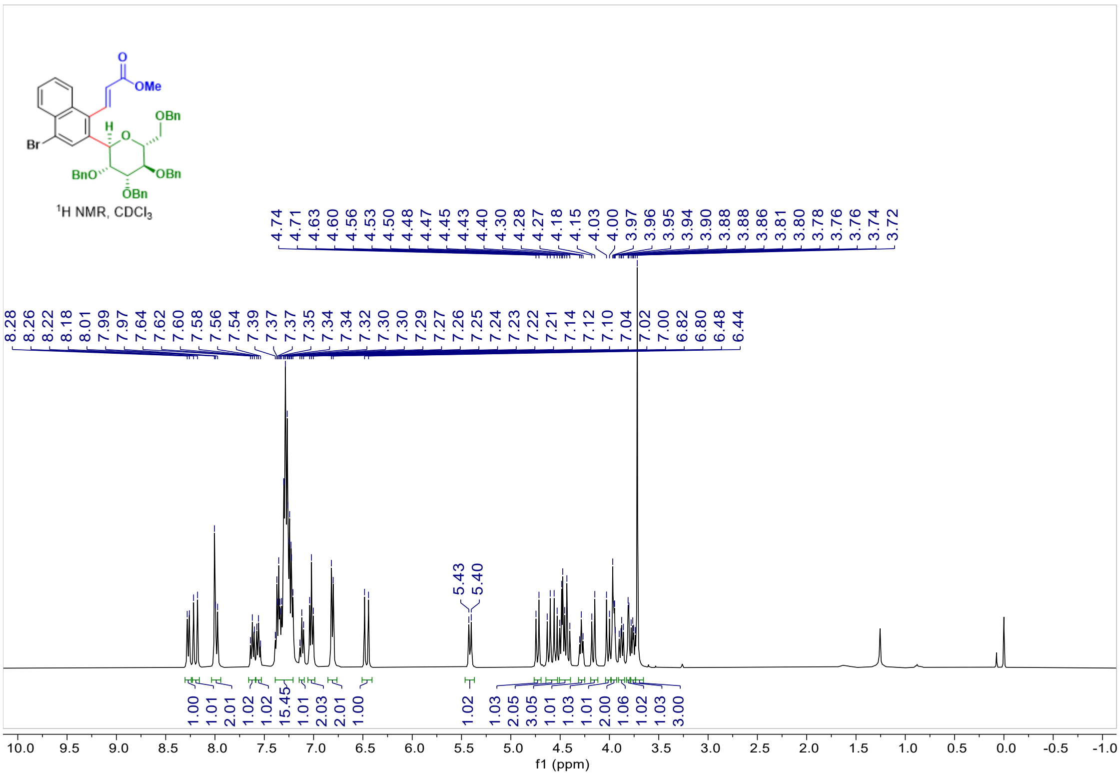
^{1}H NMR spectrum of **5i**



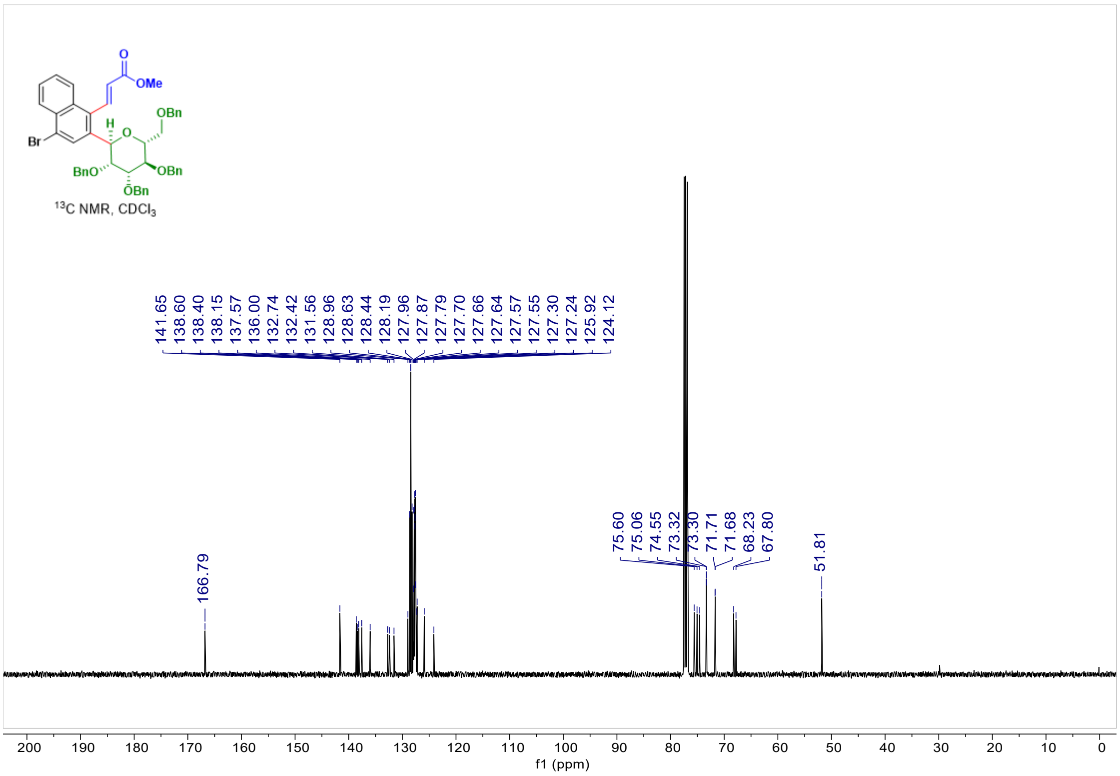
^{13}C NMR spectrum of **5i**



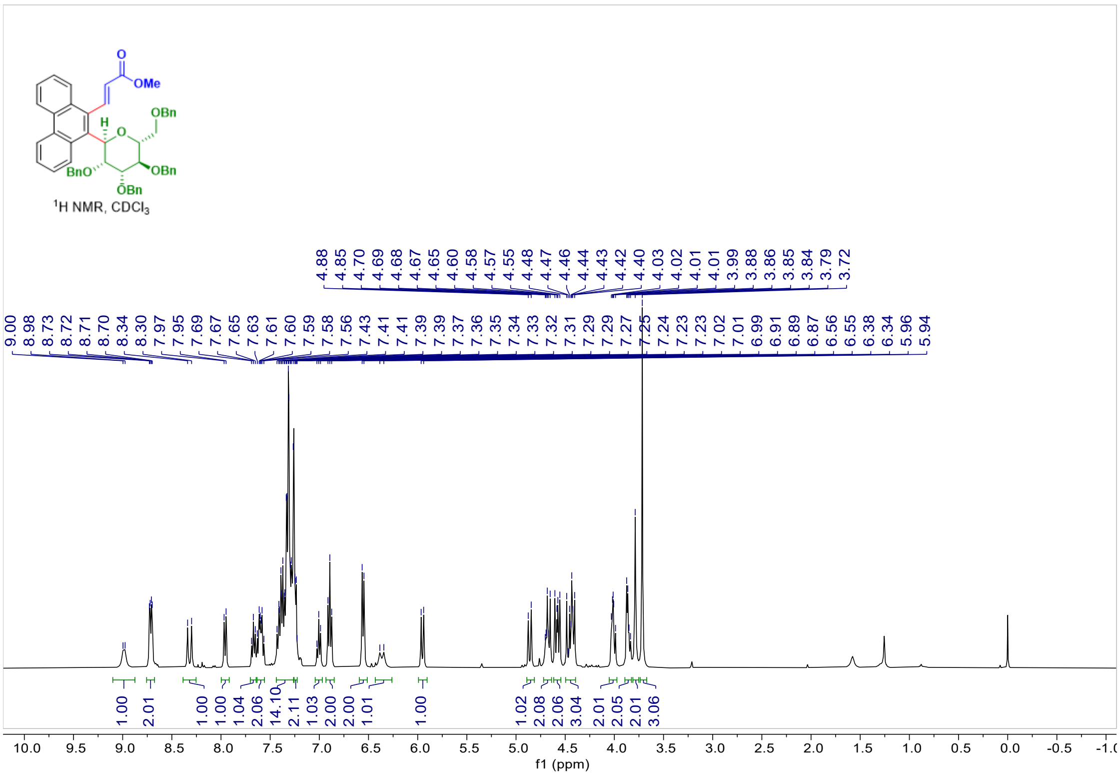
^{1}H NMR spectrum of **5j**



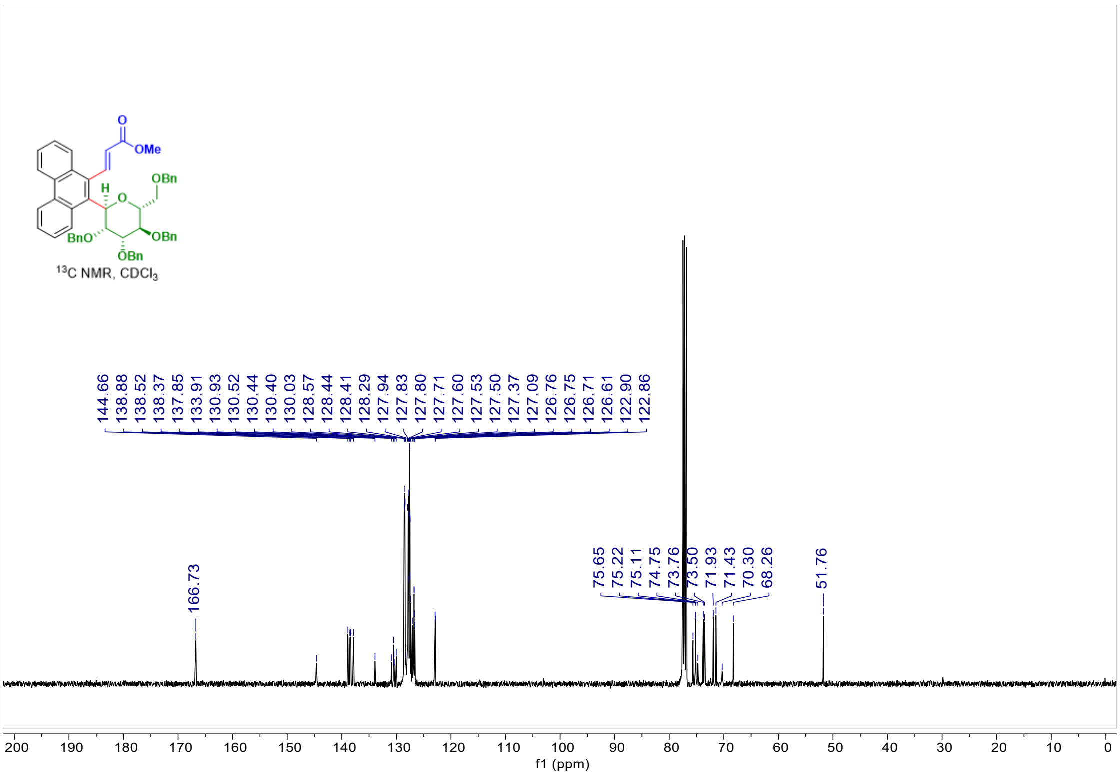
^{13}C NMR spectrum of **5j**



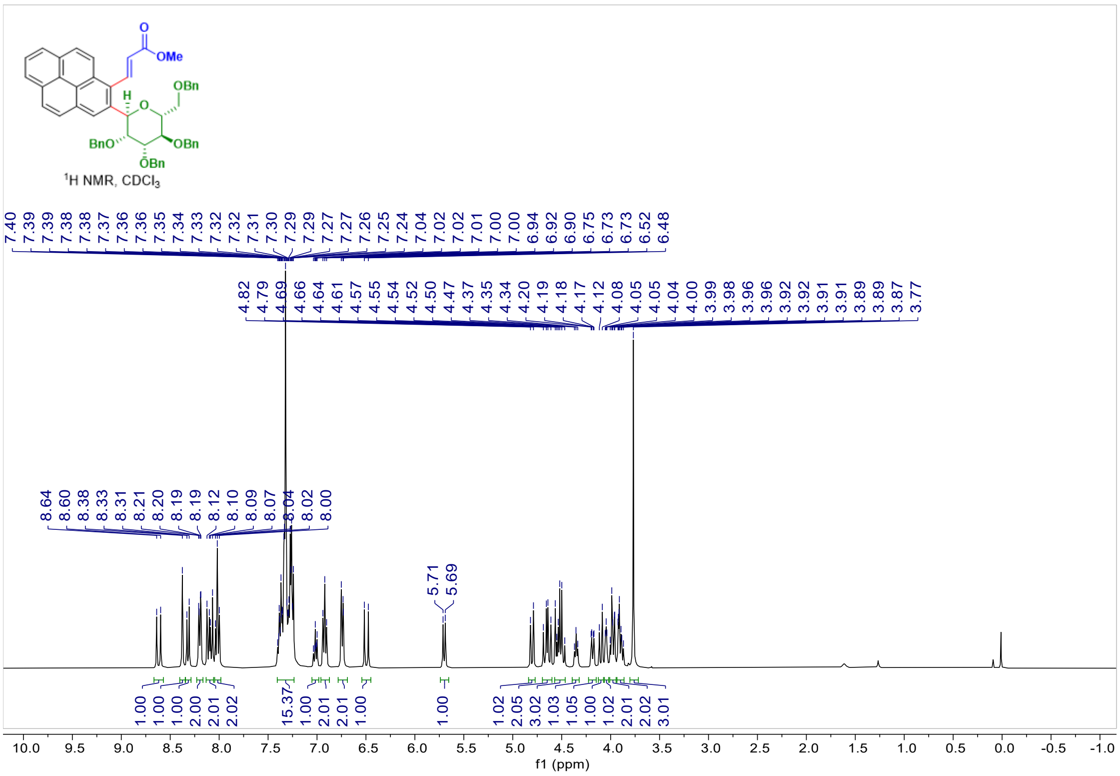
[1]H NMR spectrum of **5k**



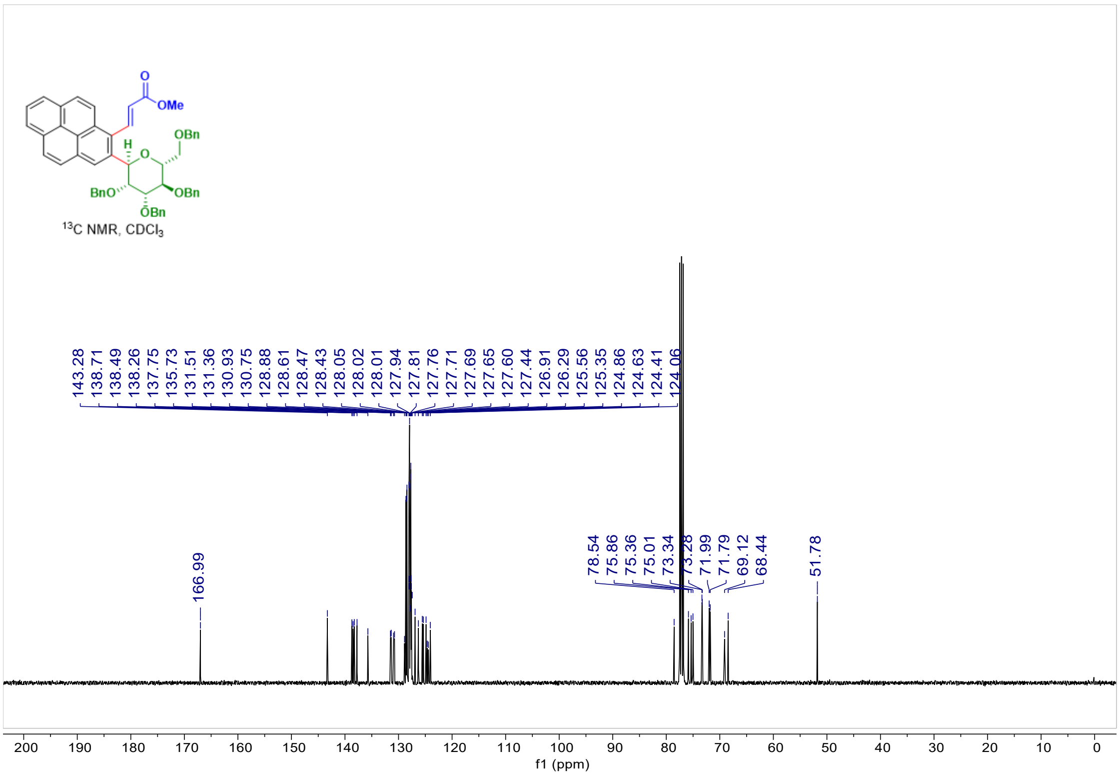
[13]C NMR spectrum of **5k**



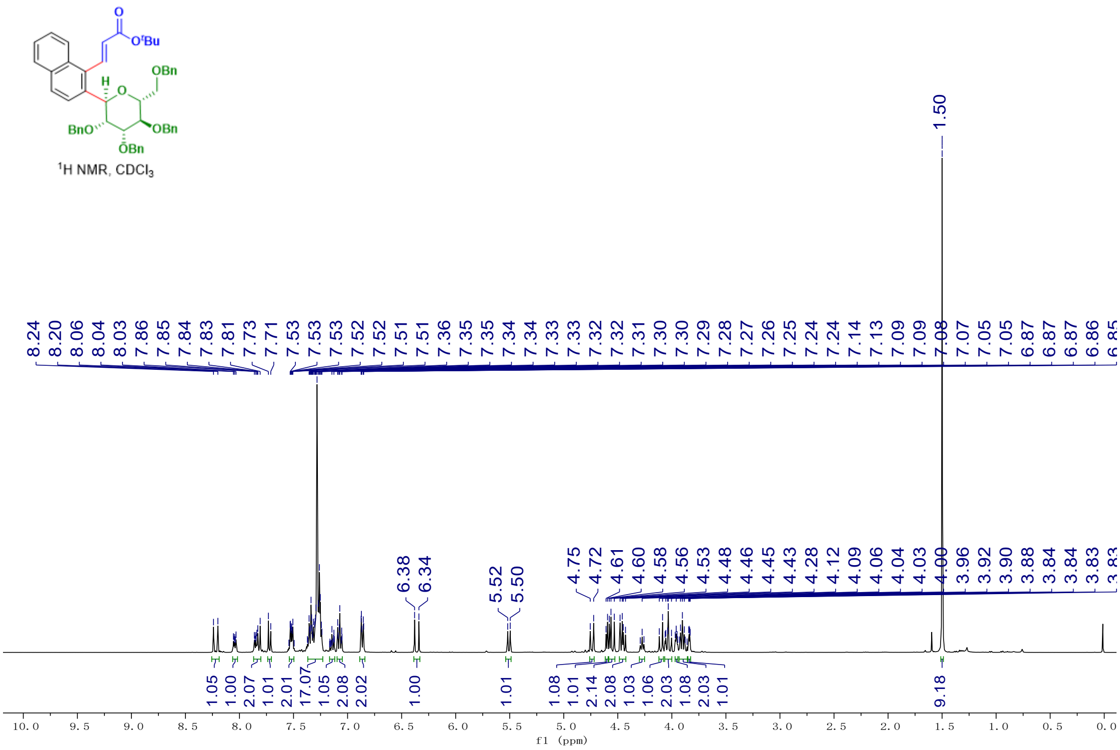
^{1}H NMR spectrum of **5l**



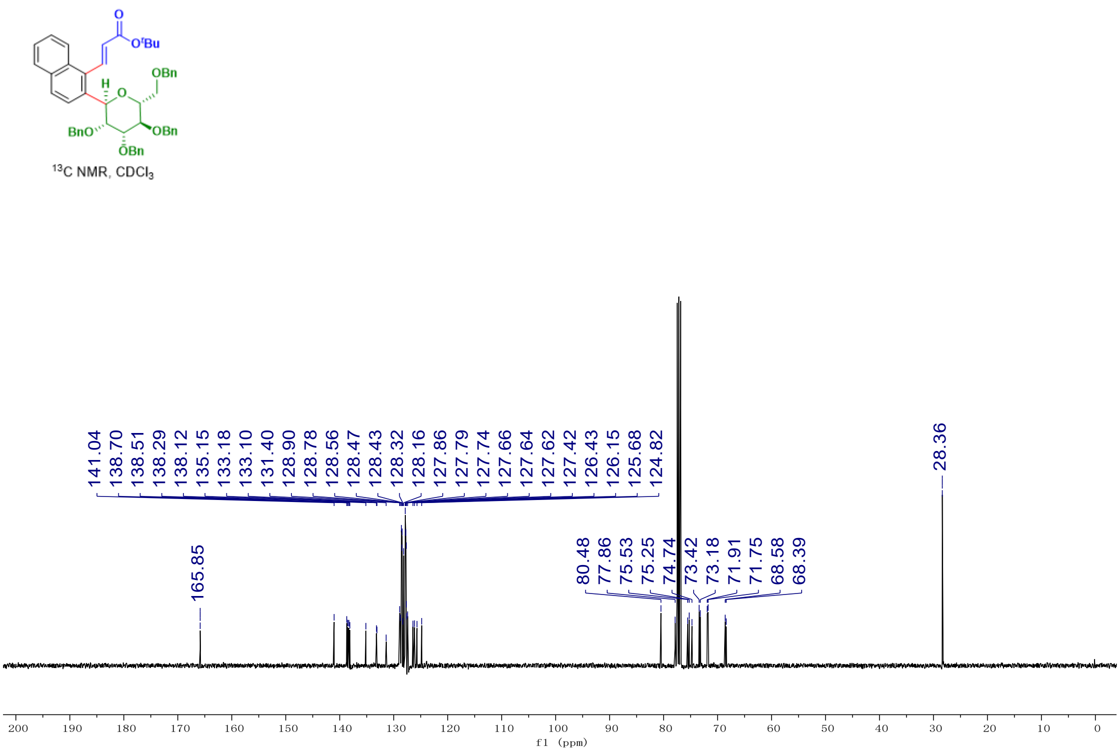
^{13}C NMR spectrum of **5l**



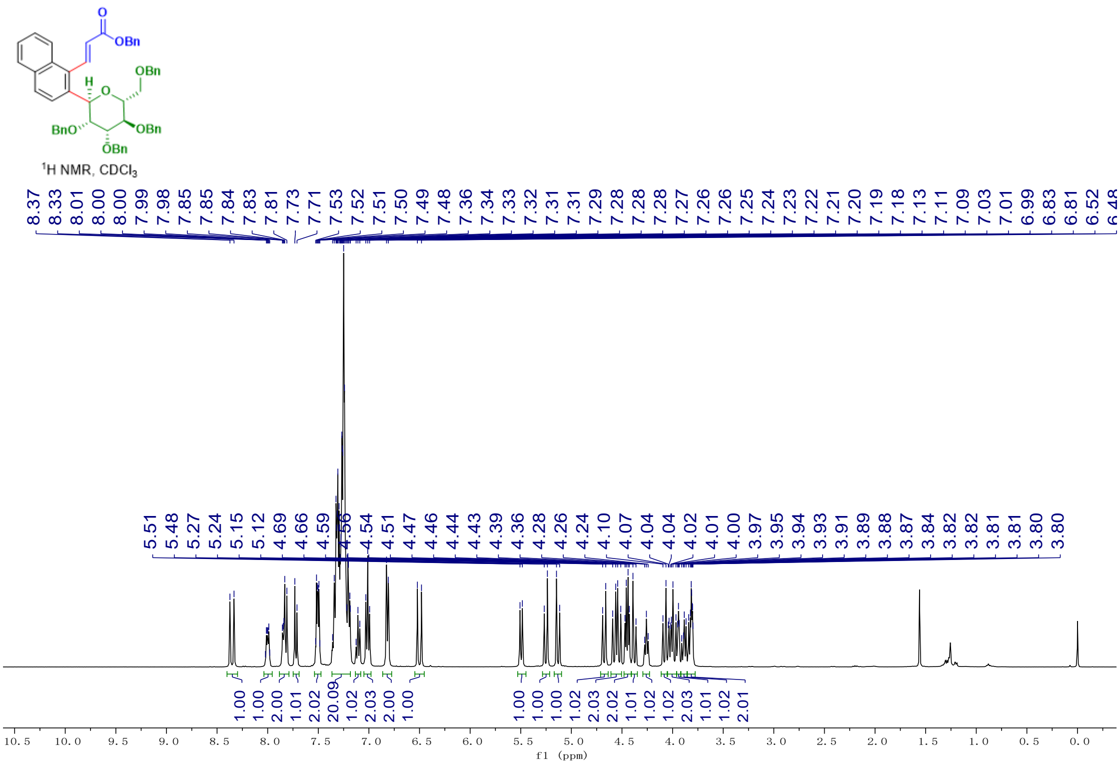
[1]H NMR spectrum of **5m**



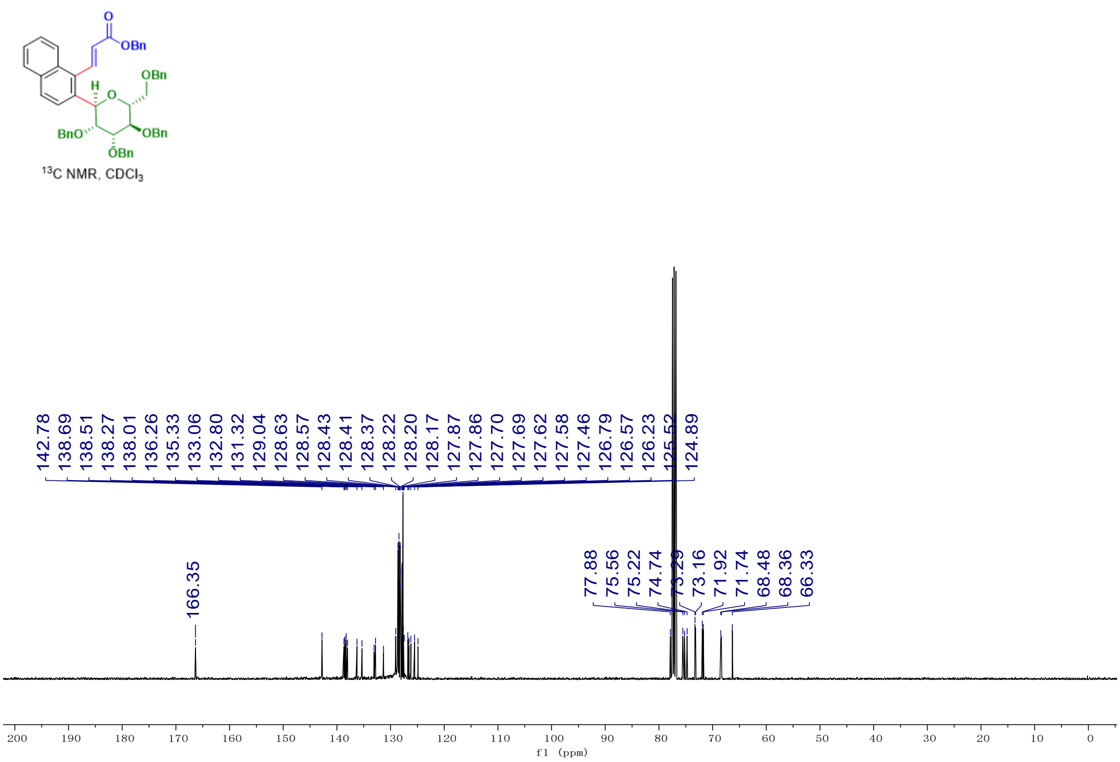
[13]C NMR spectrum of **5m**



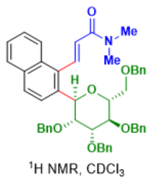
^{1}H NMR spectrum of **5n**

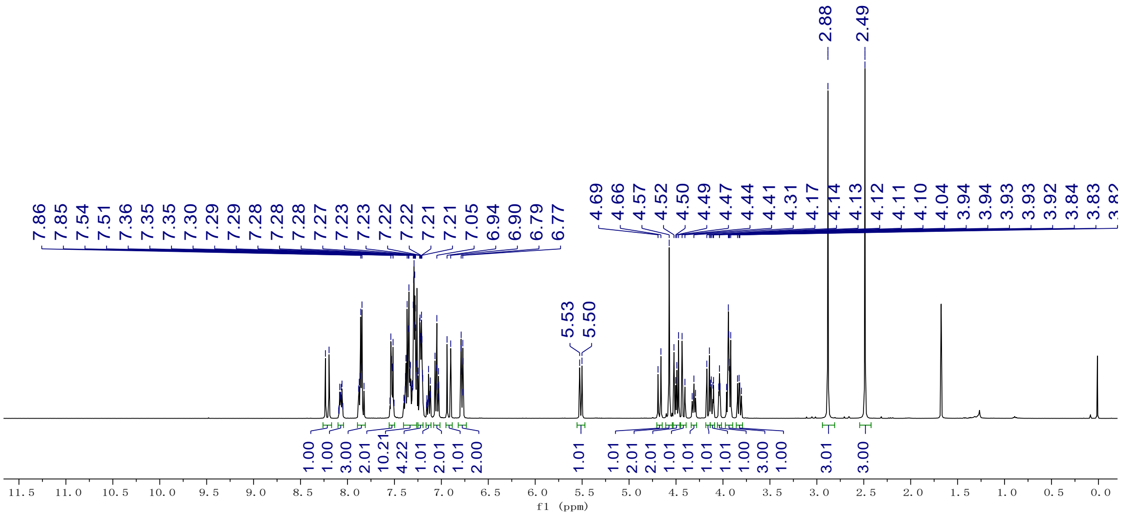


^{13}C NMR spectrum of **5n**

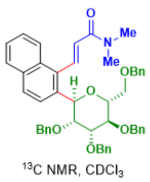


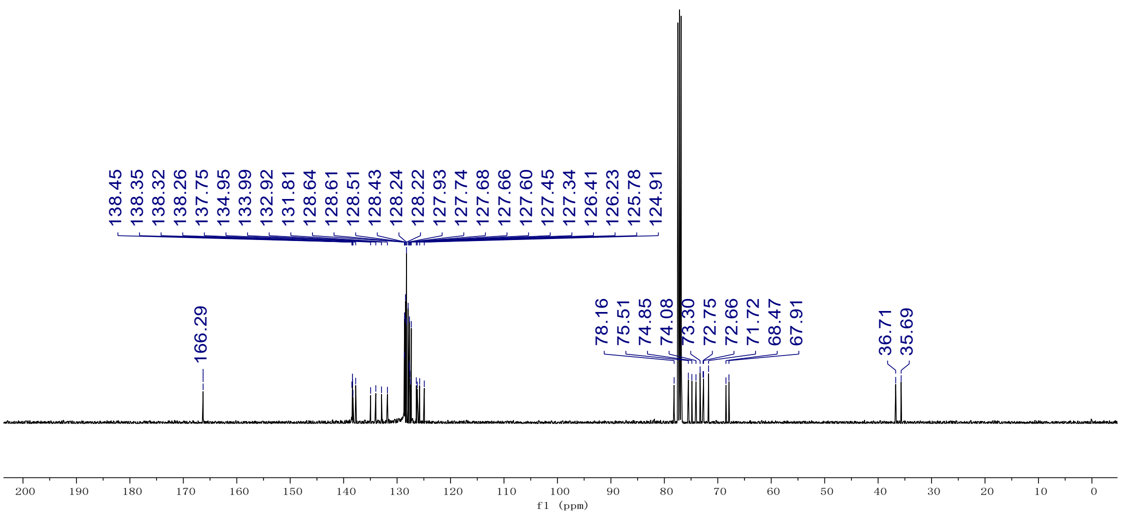
[1]H NMR spectrum of **5o**



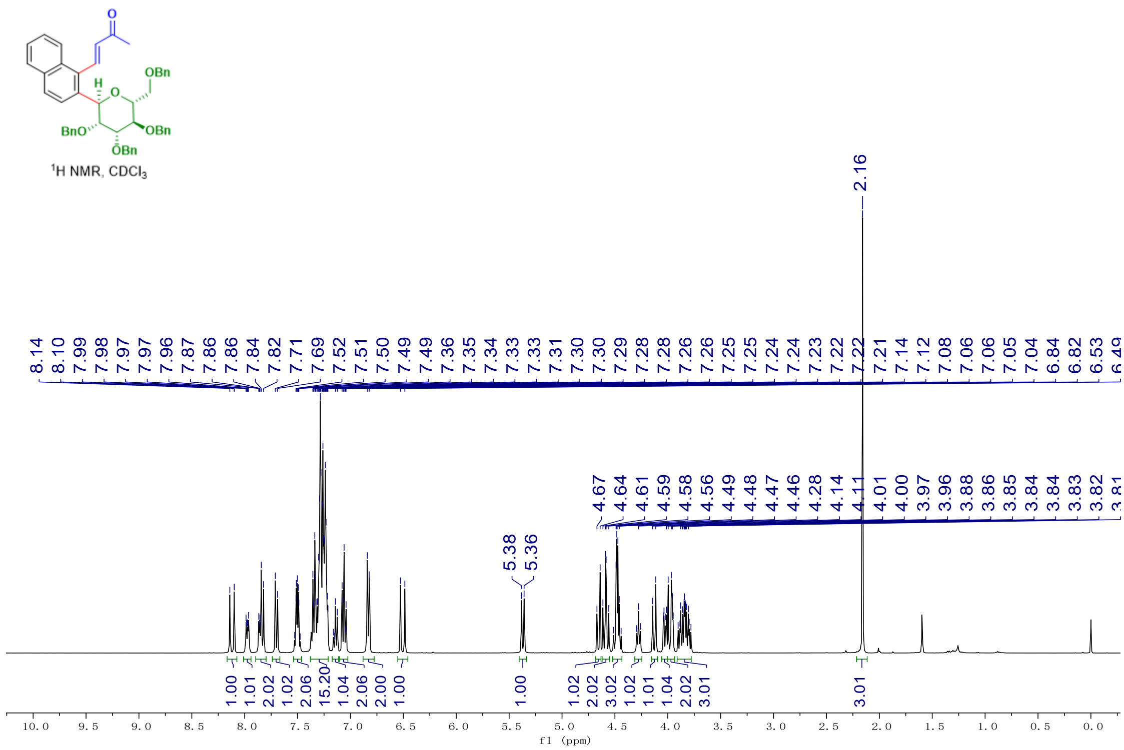


[13]C NMR spectrum of **5o**

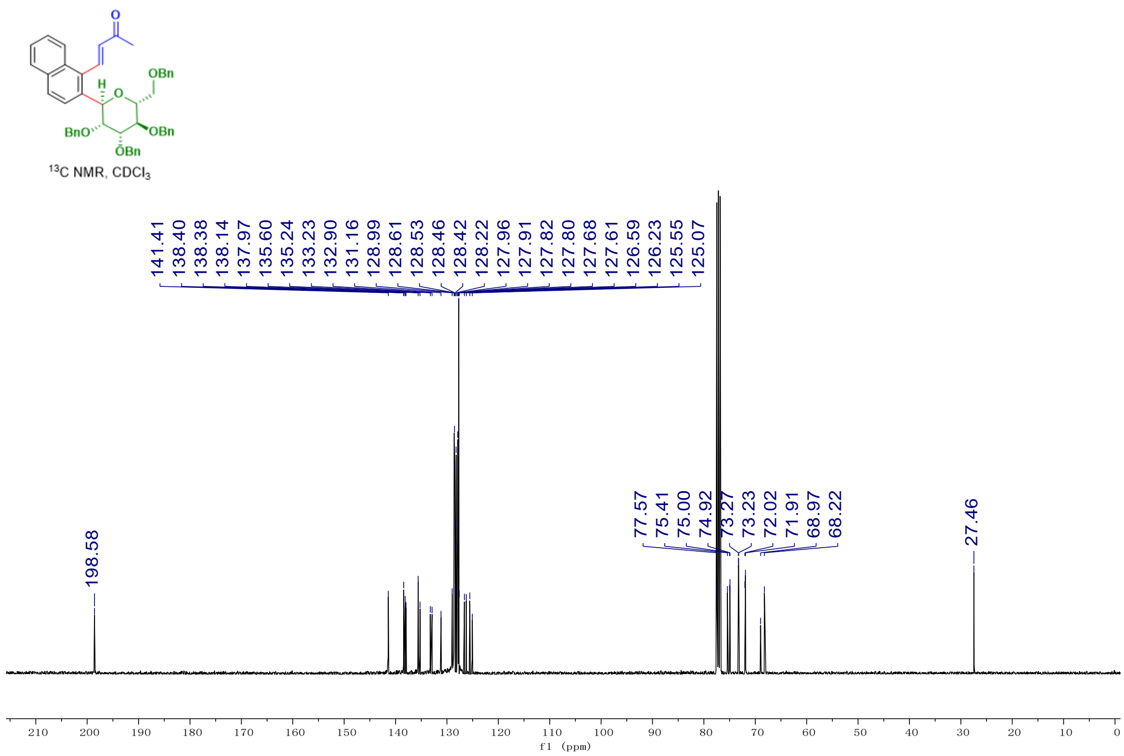




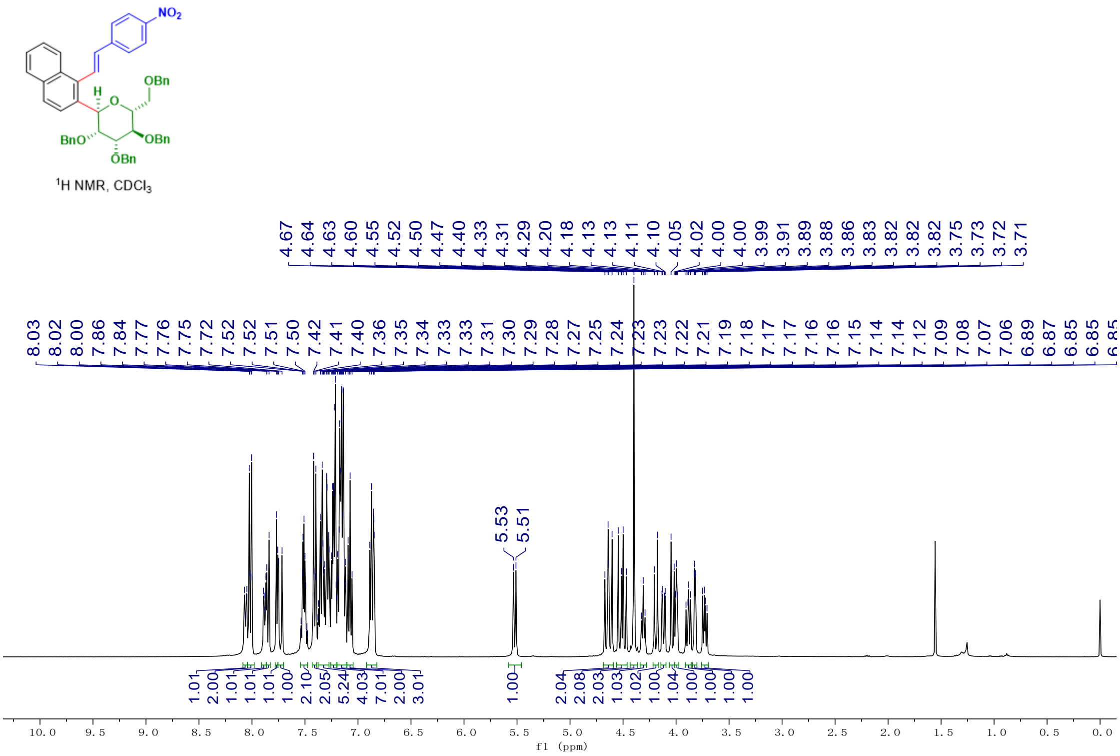
^{1}H NMR spectrum of **5p**



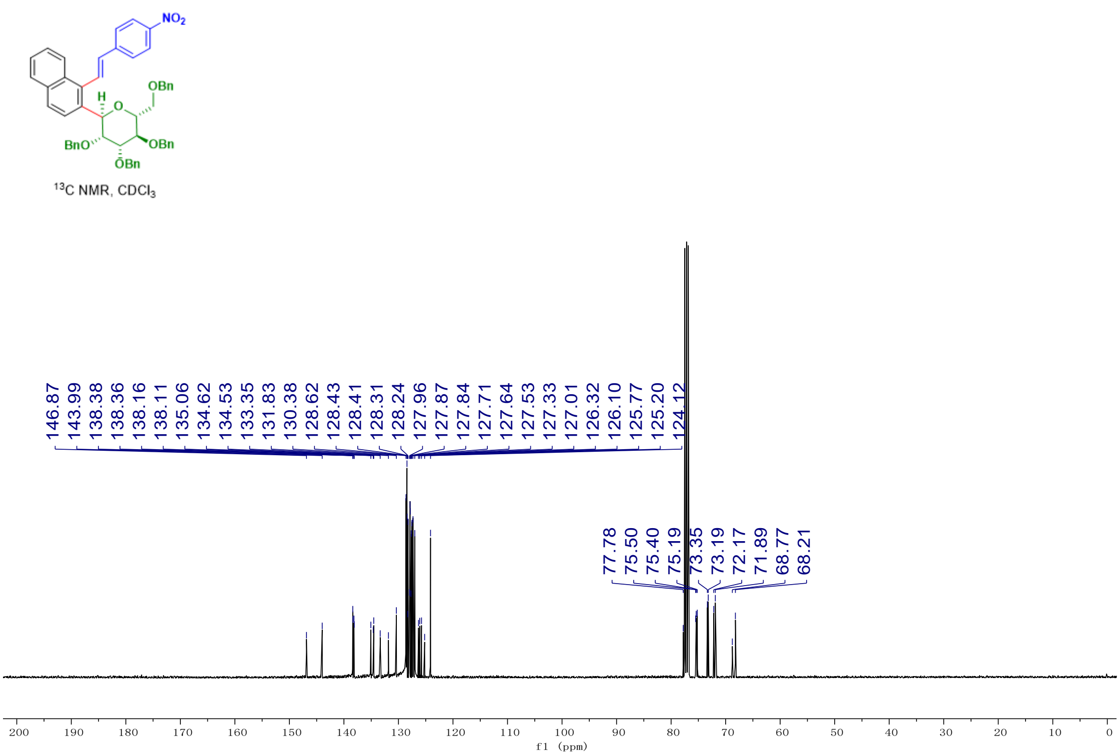
^{13}C NMR spectrum of **5p**



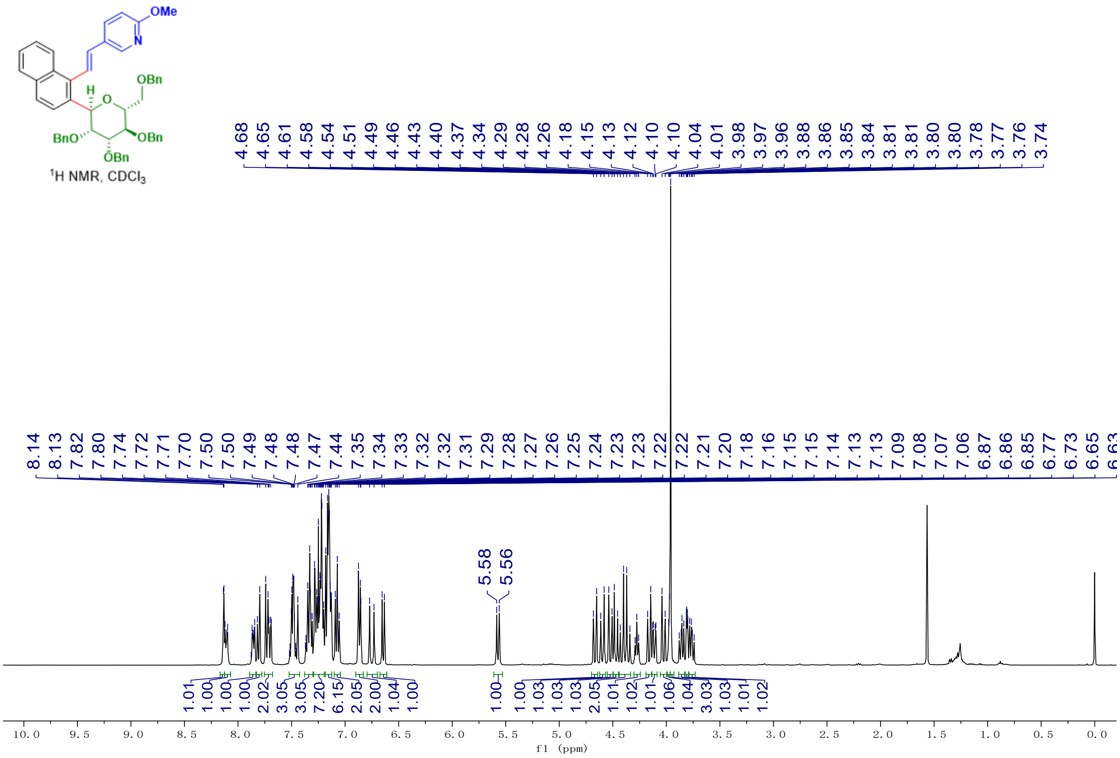
^{1}H NMR spectrum of **5q**



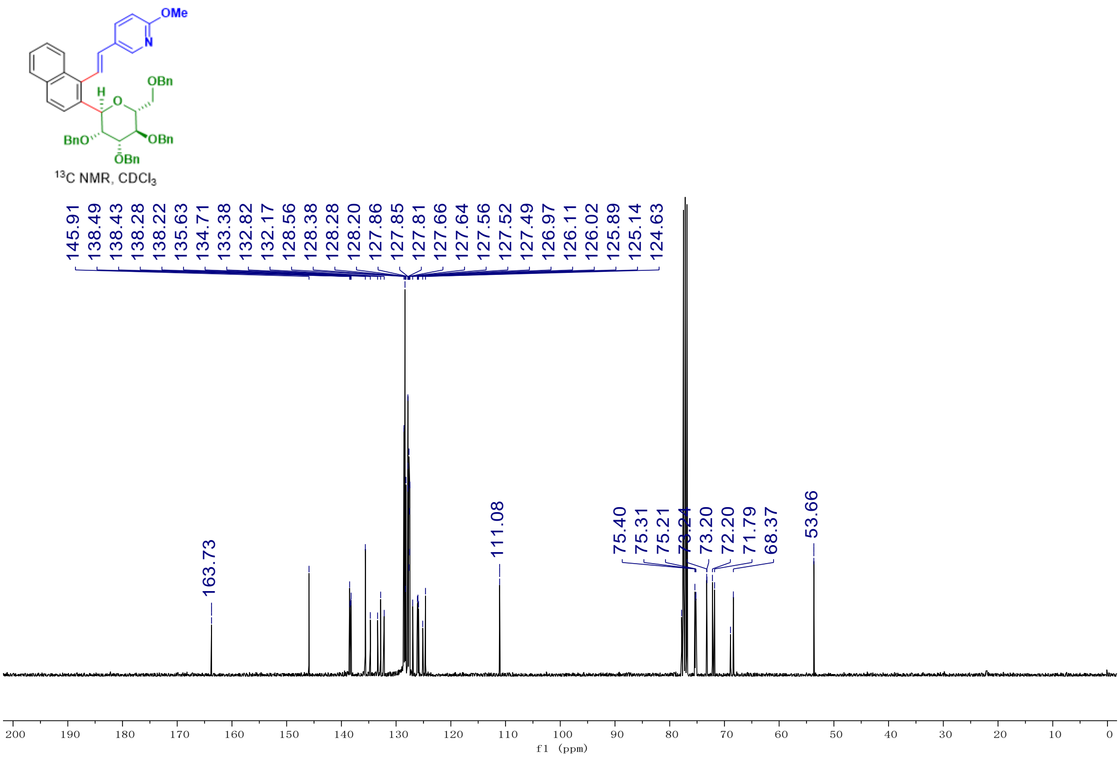
^{13}C NMR spectrum of **5q**



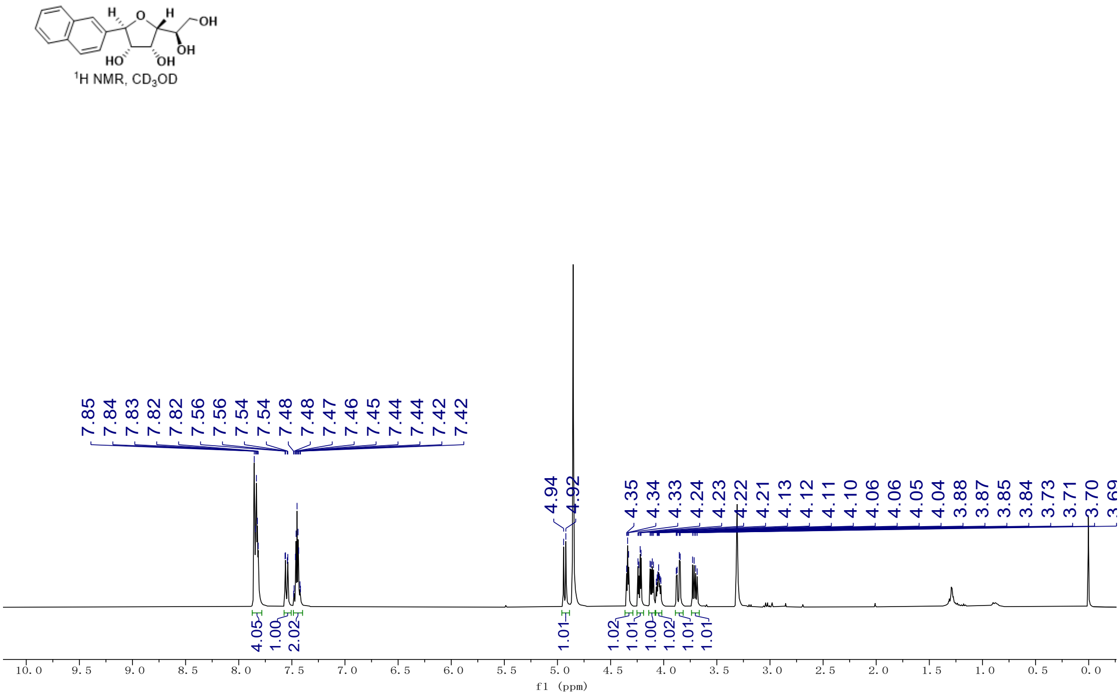
^{1}H NMR spectrum of **5r**



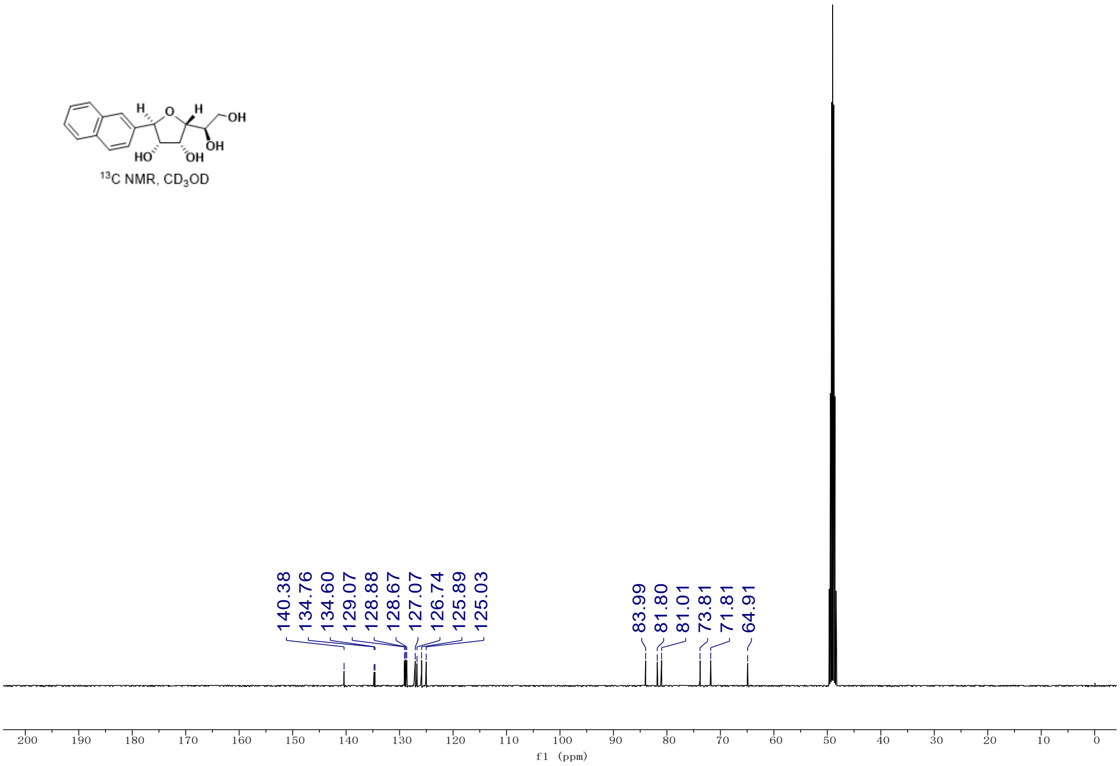
^{13}C NMR spectrum of **5r**



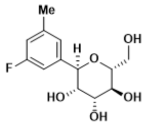
^{1}H NMR spectrum of **6**



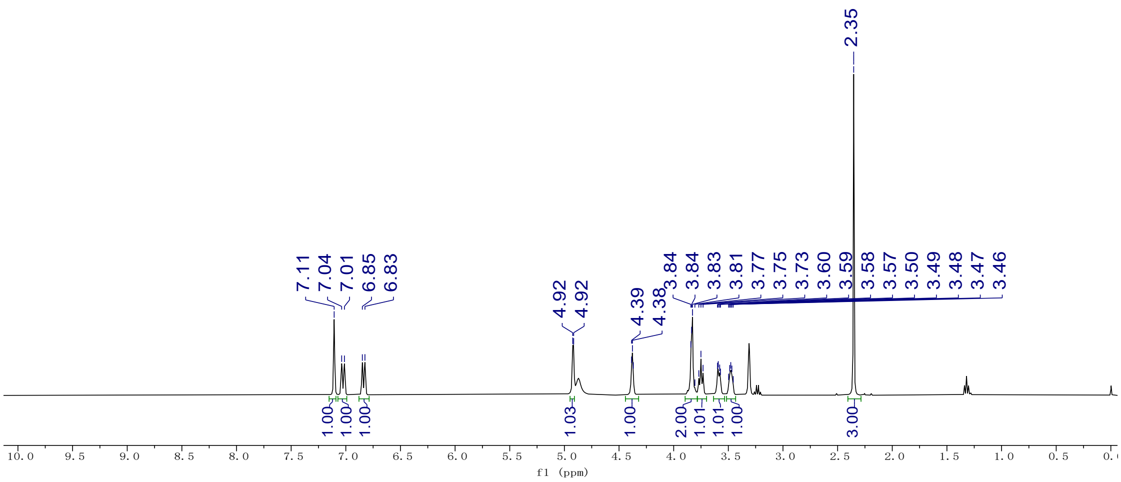
^{13}C NMR spectrum of **6**



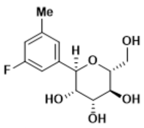
^{1}H NMR spectrum of **7**



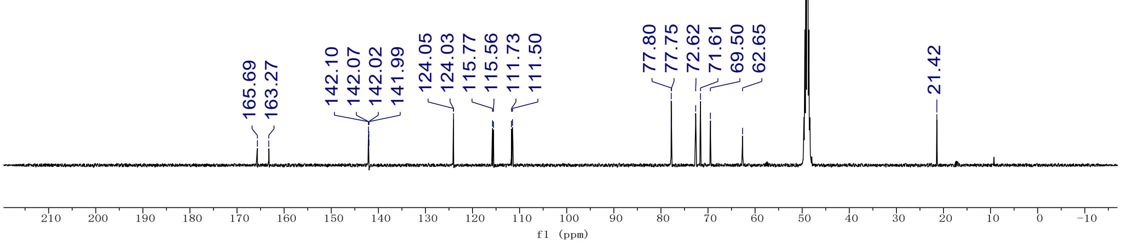
^{1}H NMR, CD_3OD



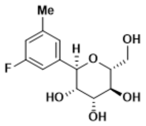
^{13}C NMR spectrum of **7**



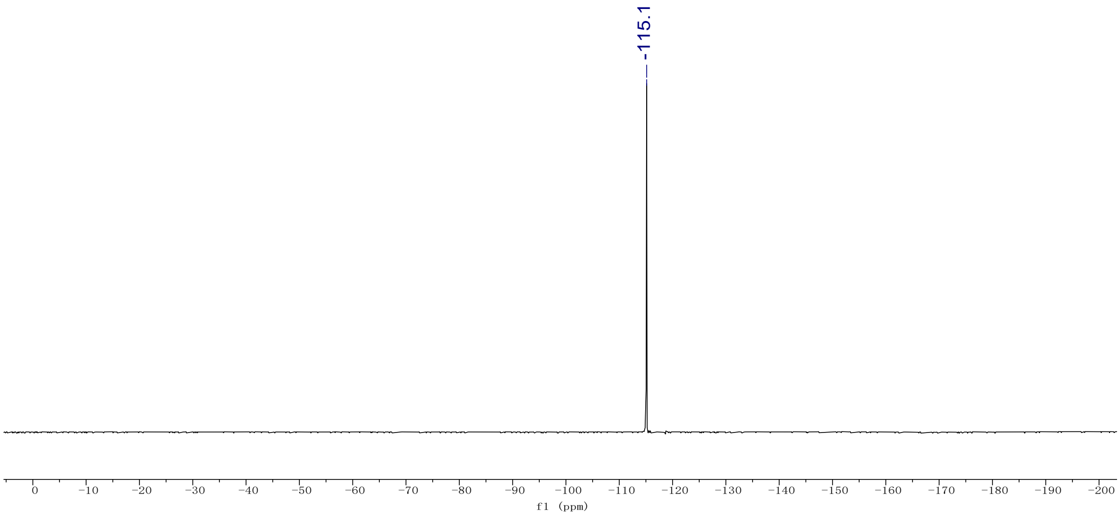
^{13}C NMR, CD_3OD



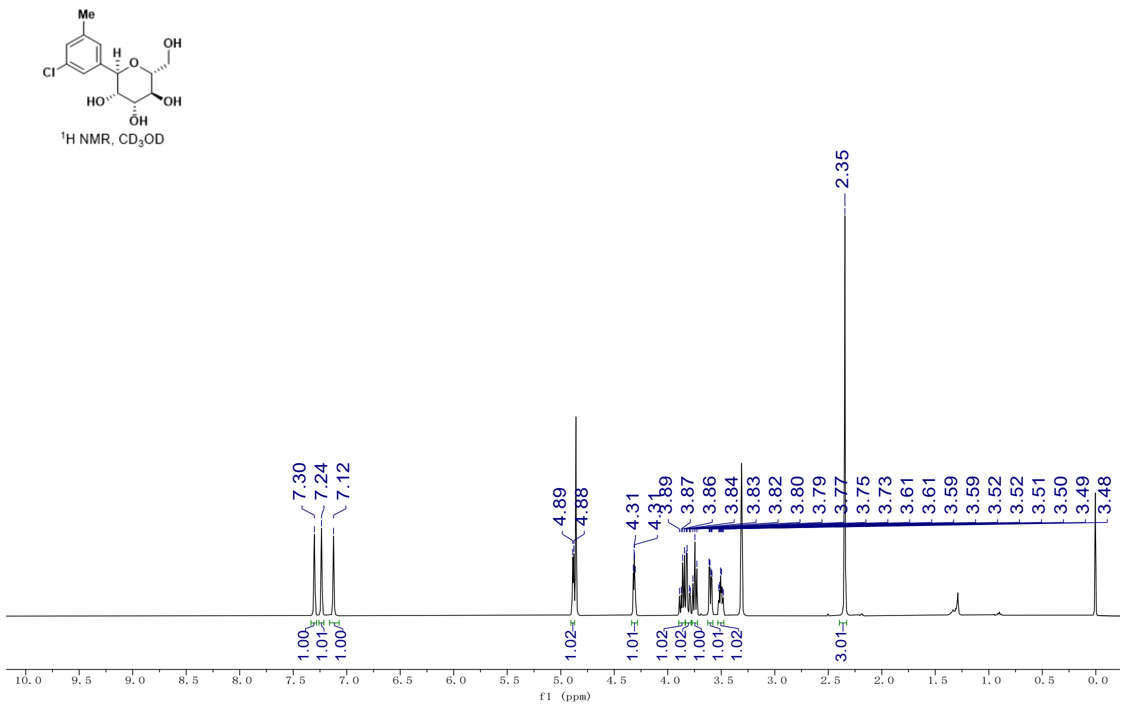
^{19}F NMR spectrum of **7**



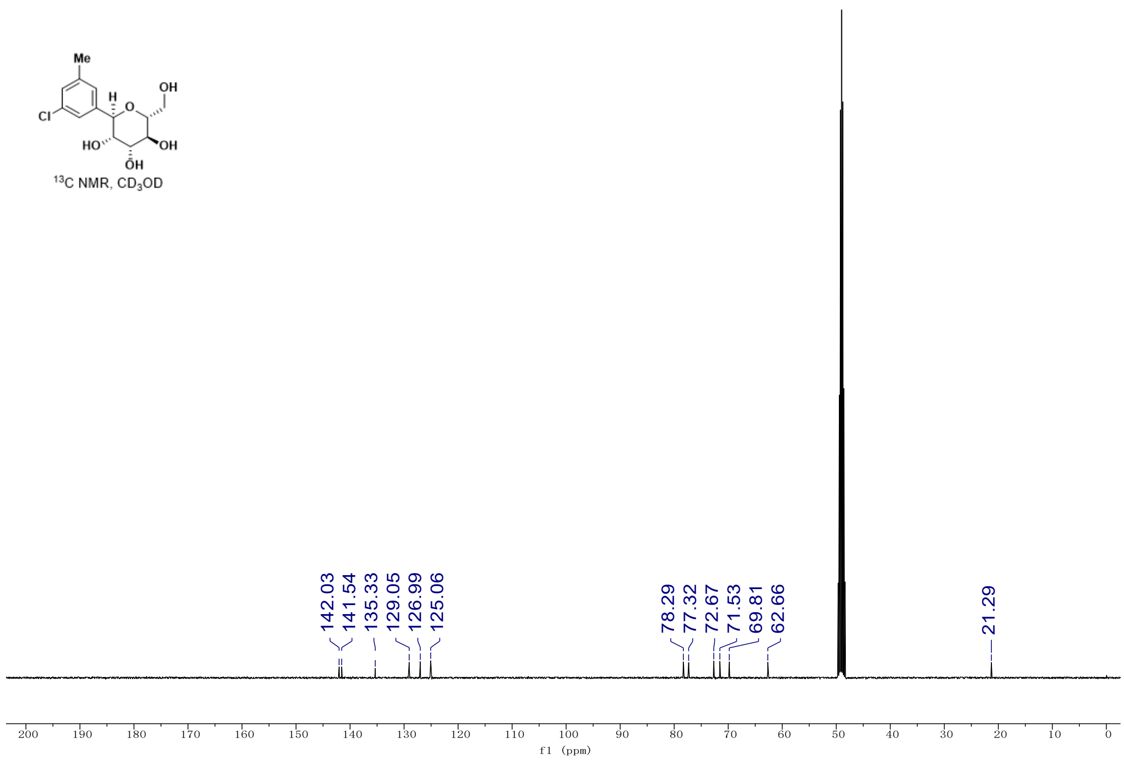
^{19}FNMR, CD_3OD



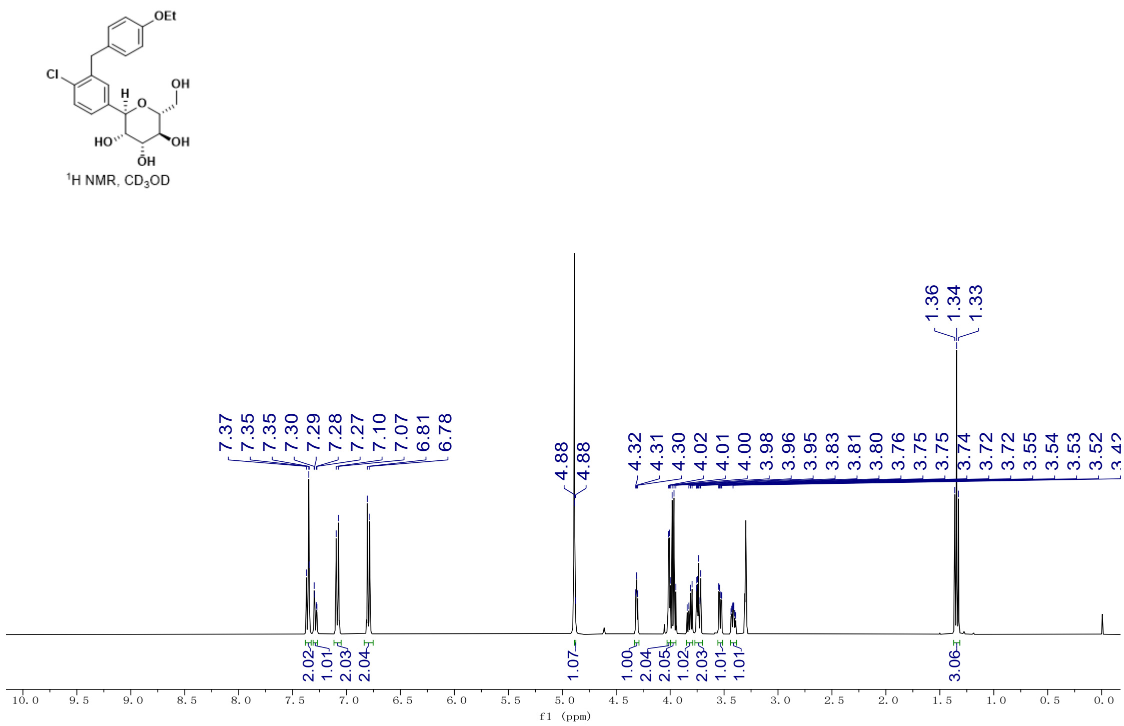
^{1}H NMR spectrum of **8**



^{13}C NMR spectrum of **8**



^{1}H NMR spectrum of **9**



^{13}C NMR spectrum of **9**