Electronic Supplementary Material (ESI) for New Journal of Chemistry.

TFA-induced conversion of glycals to 2-deoxy-sugars and its utility in synthesizing 2-deoxy-glycosyl esters

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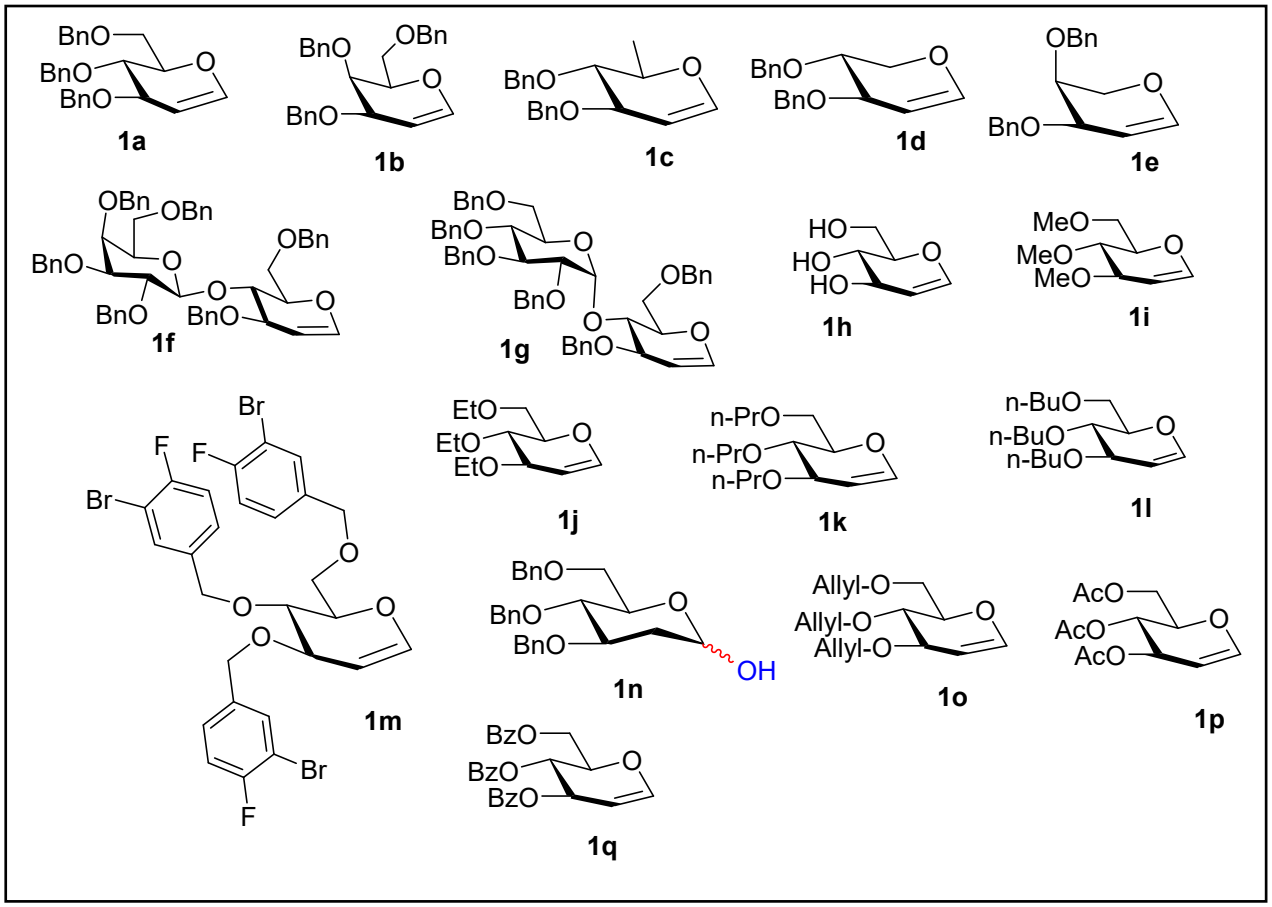
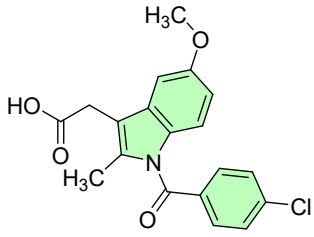
Table of Contents

General consideration

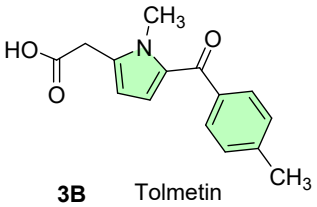
^{1}H and ^{13}C NMR spectra were recorded using 600 and 151 MHz respectively spectrometers with TMS as internal standards. Chemical shifts are expressed in parts per million (δ ppm). Silica gel-coated aluminum plates were used for TLC. The products were purified by column chromatography on silica gel (100-200 mesh) using petroleum ether–ethyl acetate as the eluent to obtain the pure products. All product's exact masses were derived using HRMS having a QTOF analyzer. Reagents used were mostly purchased from Sigma Aldrich, TCI, and SRL.

Starting materials used in the study

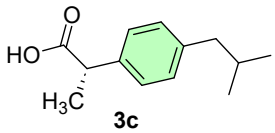




3A Indomethacine

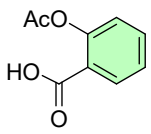


3B Tolmetin

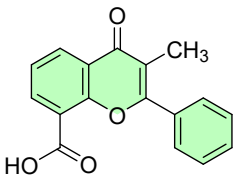


3c

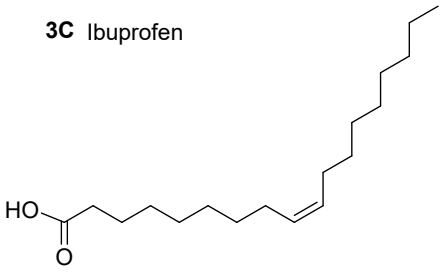
3C Ibuprofen



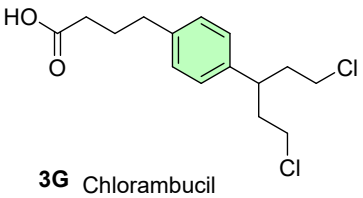
3D Acetylsalicylic acid



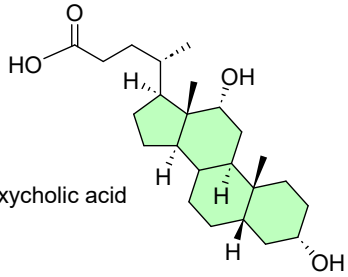
3E 3-Methyl flavone-8-carboxylic acid



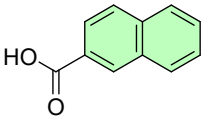
3F Oleic acid



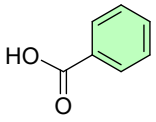
3G Chlorambucil



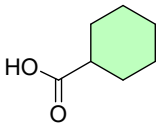
3H Deoxycholic acid



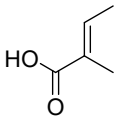
3I 2-nephthoic acid



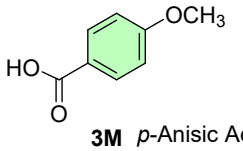
3J Benzoic acid



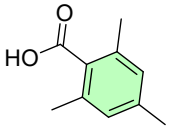
3K Cyclohexane carboxylic acid



3L Tiglic Acid

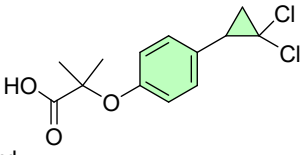


3M *p*-Anisic Acid



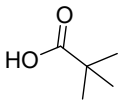
2, 4, 6-trimethyl benzoic acid

3N



Ciprofibrate

3O

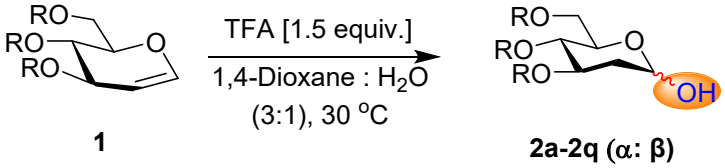


Pivalic acid

3P

Experimental procedures for all products

1a. General procedure for the products (2a-2q)

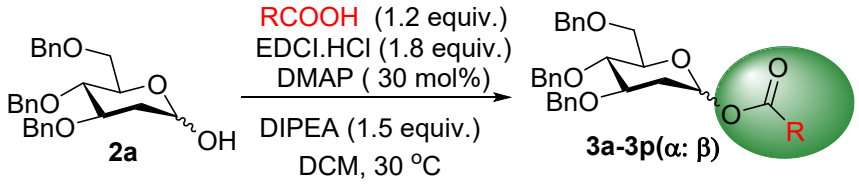


1

2a-2q (α: β)

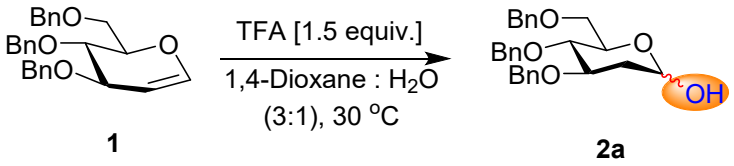
In an oven-dried round bottom flask protected as well as unprotected glycal **1** (here substrate **1a** is taken for calculations) (0.12 mmol, 1 equiv.), was dissolved in 2 mL of 1,4-Dioxane: water (3:1) at 30 ^{o}C, and TFA (Trifluoro acetic acid) (0.18 mmol, 1.5 equiv.) was added slowly at room temperature for 12 h. After the complete conversion of starting materials confirmed through TLC, the mixture was quenched with a saturated solution of sodium bicarbonate (10 mL), and the organic layer was extracted with DCM (Dichloromethane) (10 × 2 ml). The organic layer was dried over sodium sulfate and the residue left was purified by column chromatography over silica gel (100-200 mesh) using hexane/ethyl acetate as eluent.

1b. General procedure for the products (3a-3p)



In an oven-dried round bottom flask 2-deoxy glucose **2a** (0.11 mmol, 1.0 equiv.), were dissolved in DCM at room temperature, followed by acids (0.13 mmol,1.2 equiv.), DMAP (4-dimethylamino pyridine) (0.03 mmol, 30 mol%), EDCI.HCl [1-(3-Dimethylaminopropyl)-3-Ethyl Carbodiimide Hydrochloride] (0.20 mmol, 1.8 equiv.) and DIPEA (N, N-Diisopropylethylamine) (0.17 mmol, 1.5 equiv.) were added sequentially and the reaction mixture was stirred at room temperature for 12 h. After the complete conversion of the starting material as confirmed through TLC, the reaction mixture was quenched with 1N. HCl (10 mL), and the organic layer was extracted with DCM (10 × 2 ml). The organic layer was dried over sodium sulfate and the residue left was purified by column chromatography over silica gel (100-200 mesh) using hexane/ethyl acetate as eluent.

Reaction Development



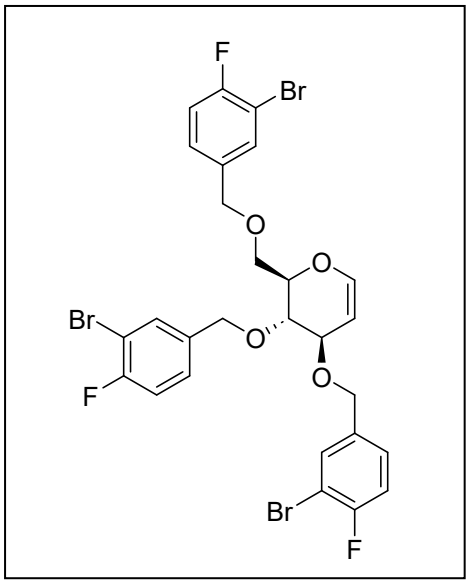
1 **2a**

Activator's optimization			
entry	**activator(equiv.)**	**solvent (3:1)**	**yield (%)**
1.	TFA (0.1)	1,4-Dioxane: H_2O	32
2.	TFA (0.2)	1,4-Dioxane: H_2O	45
3.	TFA (0.3)	1,4-Dioxane: H_2O	53
4.	TFA (0.5)	1,4-Dioxane: H_2O	55
5.	TFA (1.0)	1,4-Dioxane: H_2O	84
6.	TFA (1.2)	1,4-Dioxane: H_2O	≥90
7.	TFA (1.5)	1,4-Dioxane: H_2O	≥98
8.	TFA (2.5)	1,4-Dioxane: H_2O	78
9.	$BF_3 \cdot OEt_2$ (0.1)	DCM: H_2O	5
10.	$BF_3 \cdot OEt_2$ (0.2)	DCM: H_2O	10
11.	$BF_3 \cdot OEt_2$ (0.3)	DCM: H_2O	13
12.	$BF_3 \cdot OEt_2$ (0.5)	DCM: H_2O	15
13.	$BF_3 \cdot OEt_2$ (1.0)	DCM: H_2O	22
14.	$BF_3 \cdot OEt_2$ (1.2)	DCM: H_2O	25
15.	$BF_3 \cdot OEt_2$ (1.5)	DCM: H_2O	30
16.	$BF_3 \cdot OEt_2$ (1.5)	1,4-Dioxane: H_2O	70
Solvent's optimization			
entry	**activator (TFA 1.5 equiv.)**	**solvent**	**yield (%)**
17.	"	DCM: H_2O	30
18.	"	DCE: H_2O	45
19.	"	MeOH: H_2O	30
20.	"	EtOAc: H_2O	50
21.	"	DMSO: H_2O	15
22.	"	THF: H_2O	60
23.	"	$CHCl_3$: H_2O	14
24.	"	Isopropyl alcohol: H_2O	20
25.	"	DMF: H_2O	10

Temperature Optimization			
entry	**temperature** (°C)	**solvent** (1,4-Dioxane: H_2O)	**yield (%)**
26.	0	″	95
27.	30	″	≥98
28.	50	″	40-45 in 1h
(α: β ratio in different activators)			
S. N.	**activators (1.5 equiv.)**	**solvent** (1,4-Dioxane: H_2O)	**α: β**
29.	TMS·OTf	″	1.35:1
30.	$BF_3 \cdot OEt_2$	″	1.39:1
31.	$Sc(OTf)_3$	″	1.40:1
32.	$Bi(OTf)_3$	″	1.48:1
33.	$FeCl_3$	″	1.50:1

Characterization data

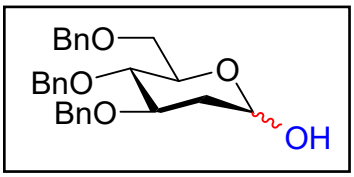
Tri-*O*-3-bromo-4-fluorobenzyl-D-Glucal (1m)



The title compound **1m** was prepared according to the general procedure of benzyl protection and purified by column chromatography giving a white solid (39 mg, 78% yield). R_f **(** Hexane: EtOAc =90:10): 0.45;**^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.43 (m, 2H), 7.36 (dd, *J* = 6.6, 1.9 Hz,

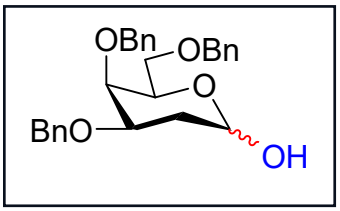
1H), 7.16 – 7.09 (m, 2H), 7.07 – 7.03 (m, 1H), 7.00 – 6.94 (m, 3H), 6.34 (dd, *J* = 6.1, 0.7 Hz, 1H), 4.78 (dd, *J* = 6.1, 2.5 Hz, 1H), 4.66 (d, *J* = 11.7 Hz, 1H), 4.55 – 4.43 (m, 3H), 4.39 (d, *J* = 12.8 Hz, 2H), 4.14 – 4.10 (m, 1H), 3.97 – 3.91 (m, 1H), 3.78 – 3.69 (m, 2H), 3.65 (dd, *J* = 10.8, 2.6 Hz, 1H).**^{13}C NMR (151 MHz, $CDCl_3$)** δ 159.3, 157.7, 145.0, 135.6, 135.4, 132.7, 132.6, 128.1, 128.0, 116.5, 116.3, 109.1, 109.1, 109.0, 99.5, 76.6, 76.2, 74.5, 72.3, 72.2, 68.9, 68.5.

2-Deoxy-3,4,6-tri-*O*-benzyl-D-glucopyranose (2a)



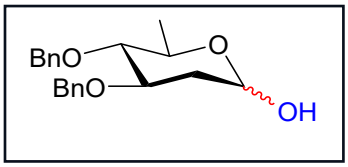
The title compound **2a** was prepared according to the general procedure **1a** and purified by column chromatography giving a white powder (51 mg, 98% yield). R_f (Hexane: EtOAc = 60:40): 0.45;**^{1}H NMR (600 MHz, $CDCl_3$) (α:β 2.5:1)** δ 7.26 (m, $13H_{benzyl}$), 7.12 (m, $2H_{benzyl}$), 5.27 (*bs*, 1H, H-1), 4.80 (d, *J* = 11.2 Hz, 1H, $OCH_{2benzyl}$), 4.55 (d, *J* = 11.8 Hz, 2H, $OCH_{2benzyl}$), 4.43 (dt, *J* = 16.5, 12.4 Hz, 3H, $OCH_{2benzyl}$), 3.99 – 3.93 (m, 2H, H-5 & H-3), 3.62 – 3.52 (m, 2H, $H\text{-}6_{ab}$), 3.38 (d, *J* = 9.4 Hz, 1H, H-4), 2.17 (dd, *J* = 12.8, 4.1 Hz, 1H, $H\text{-}2_a$), 1.61 (m, 1H, $H\text{-}2_b$).**^{13}C NMR (151 MHz, $CDCl_3$)** δ 138.7, 138.5, 138.0, 128.5, 128.4, 128.4, 128.4, 128.1, 128.0, 128.0, 128.0,127.0, 127.8, 127.8, 127.7, 127.7, 127.7, 127.6, 94.2(C-1)$_\beta$, 92.0 (C-1)$_\alpha$, 79.3(C-4)$_\beta$, 78.7(C-4)$_\alpha$, 77.9(C-5), 75.0$_\alpha$, 74.9$_\beta$, 74.0$_\beta$, 73.5$_\alpha$, 71.8$_\alpha$, 71.6$_\beta$, 70.6 (C-3), 69.4 (C-6)$_\alpha$, 69.3 (C-6)$_\beta$, 37.9 (C-2)$_\beta$, 35.6 (C-2)$_\alpha$. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{27}H_{30}O_5$ 457.1911 found 457.1973.

2-Deoxy-3,4,6-tri-*O*-benzyl-D-galactopyranose (2b)



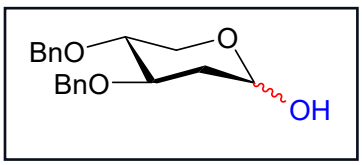
The title compound **2b** was prepared according to the general procedure 1a and purified by column chromatography giving a white powder solid (51 mg, 98% yield). R_f **(** Hexane: EtOAc =60:40): 0.45;**^{1}H NMR (600 MHz, $CDCl_3$) (α:β 3.5:1)** δ 7.26 (m, $13H_{benzyl}$), 7.12 (m, $2H_{benzyl}$), 5.27 (*bs*, 1H, H-1), 4.80 (d, *J* = 11.2 Hz, $1H_{benzyl}$), 4.55 (d, *J* = 11.8 Hz, $2H_{benzyl}$), 4.43 (dt, *J* = 16.5, 12.4 Hz, $3H_{benzyl}$), 3.99 – 3.93 (m, 2H, H-5 & H-3), 3.62 – 3.52 (m, 2H, $H\text{-}6_{ab}$), 3.38 (d, *J* = 9.4 Hz, 1H, H-4), 2.17 (dd, 4.1 Hz, 1H, $H\text{-}2_a$), 1.61 (m, 1H, $H\text{-}2_b$).**^{13}C NMR (151 MHz, $CDCl_3$)** δ 138.7, 138.5, 138.0, 128.5, 128.4, 128.4, 128.4, 128.1, 128.0, 128.0, 128.0,127.0, 127.8, 127.8, 127.7, 127.7, 127.7, 127.6, 94.2(C-1)$_\beta$, 92.0(C-1)$_\alpha$, 79.3(C-4)$_\beta$, 78.7(C-4)$_\alpha$, 77.9(C-5), 75.0$_\alpha$, 74.9$_\beta$, 74.0$_\beta$, 73.5$_\alpha$, 71.8$_\alpha$, 71.6$_\beta$, 70.6(C-3), 69.4(C-6)$_\alpha$, 69.3(C-6)$_\beta$, 37.9(C-2)$_\beta$, 35.6(C-2)$_\alpha$. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{27}H_{30}O_5$ 457.1985 found 457.1983.

2-Deoxy-3,4-di-*O*-benzyl-L-rhamnopyranose (2c)



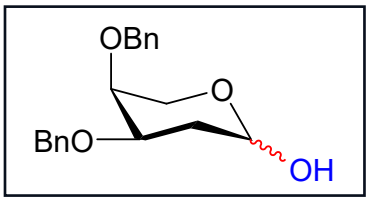
The title compound **2c** was prepared according to the general procedure **1a** and purified by column chromatography giving a white powder solid (42 mg, 80% yield). R_f **(** Hexane: EtOAc =70:30): 0.50;**^{1}H NMR (600 MHz, $CDCl_3$) (α:β 1.6:1)** δ 7.41 – 7.21 (m, $10H_{benzyl}$), 5.27 (s, 1H, H-1), 4.93 (dd, *J* = 11.0, 4.4 Hz, $1H_{benzyl}$), 4.74 – 4.52 (m, $3H_{benzyl}$), 3.99 (ddd, *J* = 15.4, 7.3, 4.5 Hz, 1H, H-4), 3.42 (s, 1H, H-5), 3.12 (t, *J* = 9.1 Hz, 1H, H-3), 2.43 – 2.23 (m, 1H, $H\text{-}2_b$), 1.74 – 1.46 (m, 1H, $H\text{-}2_a$), 1.34 – 1.20 (m, 3H, H-6).**^{13}C NMR (151 MHz, $CDCl_3$)** δ 138.6$_\beta$, 138.5$_\alpha$, 138.3$_\alpha$, 138.2$_\beta$, 128.5$_\beta$, 128.4$_\alpha$, 128.4, 128.3, 127.0, 127.0, 126.9$_\alpha$, 126.8$_\beta$, 126.7$_\beta$, 126.7$_\alpha$, 126.7, 126.6, 126.6, 93.8(C-1)$_\beta$, 91.9(C-1)$_\alpha$, 84.3(C-4)$_\alpha$, 83.4(C-4)$_\beta$, 79.0(C-5), 75.2$_\beta$, 75.1$_\alpha$, 71.8$_\alpha$, 71.5$_\beta$, 67.3(C-3)$_\alpha$, 65.8(C-3)$_\beta$, 38.3(C-2)$_\beta$, 35.8(C-2)$_\alpha$, 18.2(C-6)$_\beta$, 18.1(C-6)$_\alpha$.**HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{20}H_{24}O_4$ 351.1567 found 351.1564.

2-Deoxy-3,4-di-*O*-benzyl-D-xylopyranose (2d)



The title compound **2d** was prepared according to the general procedure **1a** and purified by column chromatography giving a white powder solid (42.5 mg, 95% yield). R_f **(** Hexane: EtOAc =60:40): 0.50;**^{1}H NMR (600 MHz, $CDCl_3$) (α:β 1:1)** δ 7.28 – 7.16 (m, 20$H_{benzyl\ ab}$), 5.22 (*bs*, 1H H-1$_a$), 5.01 (d, *J* = 9.9 Hz, 1H, H-1$_b$), 4.86 (d, *J* = 8.9 Hz, 1H_{benzyl}), 4.71 (d, *J* = 11.9 Hz, 1H_{benzyl}), 4.60 (d, *J* = 11.9 Hz, 2H_{benzyl}), 4.52 (dd, *J* = 9.5, 4.4 Hz, 3H_{benzyl}), 4.03 (dd, *J* = 11.4, 8.9 Hz, 1H_{benzyl}), 3.91 – 3.85 (m, 2H, H-5$_a$), 3.75 (dd, *J* = 12.0, 3.4 Hz, 2H, H-5$_b$), 3.61 – 3.43 (m, 4H, H-3$_{ab}$ & H-4$_{ab}$), 2.13 (dd, *J* = 9.8, 3.0 Hz, 1H, H-2$_a$), 2.00 (d, *J* = 2.4 Hz, 1H, H-2$_a$), 1.78 – 1.63 (m, 2H, H-2$_b$).**^{13}C NMR (151 MHz, $CDCl_3$)** δ 137.5$_β$, 137.5$_α$, 137.1$_β$, 136.8$_α$, 127.5, 127.4, 127.3, 126.9, 126.8, 126.7, 126.7, 126.5, 126.5, 126.5, 91.6(C-1)$_α$, 91.3(C-1)$_β$, 73.0$_α$, 72.9$_β$, 71.9$_α$, 71.6$_β$, 70.3(C-4)$_β$, 70.2(C-4)$_α$, 69.6(C-5)$_α$, 69.4(C-5)$_β$, 60.3(C-3)$_α$, 57.5(C-3)$_β$, 33.4(C-2)$_α$, 32.0(C-2)$_β$. **HRMS (ESI)** m/z: [M+Na] $^+$ calcd for $C_{19}H_{22}O_4$ 337.1402 found 337.1409.

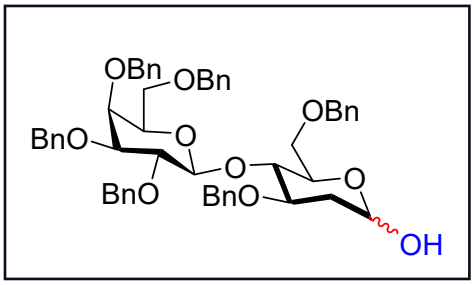
2-Deoxy-3,4-di-*O*-benzyl-D-arabinopyranose (**2e**)



The title compound **2e** was prepared according to the general procedure **1a** and purified by column chromatography giving a white powder solid (51.5 mg, 98% yield). R_f **(** Hexane: EtOAc =60:40): 0.47;**^{1}H NMR (600 MHz, $CDCl_3$) (α:β 1:1)** δ 7.28 – 7.16 (m, 20$H_{benzyl\ ab}$), 5.22 (bs, 1H, H-1$_a$), 5.01 (d, *J* = 9.9 Hz, 1H, H-1$_b$), 4.86 (d, *J* = 8.9 Hz, 1H_{benzyl}), 4.71 (d, *J* = 11.9 Hz, 1H_{benzyl}), 4.60 (d, *J* = 11.9 Hz, 2H_{benzyl}), 4.52 (dd, *J* = 19.5, 14.4 Hz, 3H_{benzyl}), 4.03 (dd, *J* = 11.4, 8.9 Hz, 1H_{benzyl}), 3.91 – 3.85 (m, 2H, H-5$_a$), 3.75 (dd, *J* = 12.0, 3.4 Hz, 2H, H-5$_b$), 3.61 – 3.43 (m, 4H, H-3$_{ab}$ & H-4$_{ab}$), 2.13 (dd, *J* = 9.8, 3.0 Hz, 1H, H-2$_a$), 2.00 (d, *J* = 2.4 Hz, 1H, H-2$_a$), 1.78 – 1.63 (m, 2H, H-2$_b$).**^{13}C NMR (151 MHz, $CDCl_3$)** δ 137.5$_β$, 137.5$_α$, 137.1$_β$, 136.8$_α$, 127.5, 127.4, 127.3, 126.9, 126.8, 126.7, 126.7, 126.5, 126.5, 126.5, 91.6(C-1)$_α$, 91.3(C-1)$_β$, 73.0$_α$, 72.9$_β$, 71.9$_α$, 71.6$_β$, 70.3(C-4)$_β$, 70.2(C-4)$_α$, 69.6(C-5)$_α$, 69.4(C-5)$_β$, 60.3(C-3)$_α$, 57.5(C-3)$_β$,

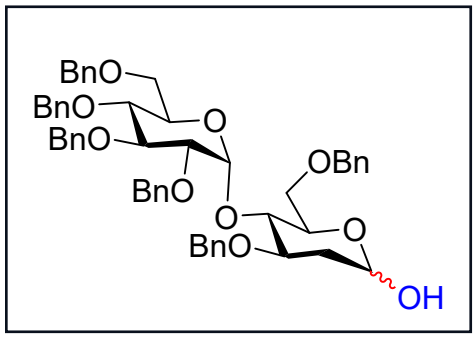
33.4(C-2)$_{\alpha}$, 32.0(C-2)$_{\beta}$. **HRMS (ESI)** m/z: [M+Na] $^{+}$ calcd for $C_{19}H_{22}O_4$ 337.1410 found 337.1409.

2-Deoxy-3,6-di-*O*-benzyl-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-β-D-galactopyranose(2f)



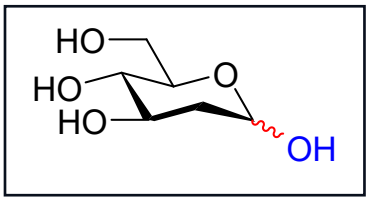
The title compound **2f** was prepared according to the general procedure **1a** and purified by column chromatography giving a white powder solid (39 mg, 78% yield). R_f **(** Hexane: EtOAc =70:30): 0.45;**^{1}H NMR (600 MHz, CDCl$_3$) (a:β 1.3:1)** δ 7.24 – 7.11 (m, 28H$_{benzyl}$), 7.10 – 7.06 (m, 1H$_{benzyl}$), 7.05 – 7.01 (m, 1H$_{benzyl}$), 5.74 (d, *J* = 3.6 Hz, 1H, H-1$_{glu}$), 5.68 (d, *J* = 3.7 Hz, 1H, H-1$_{gal}$), 5.31 (s, 1H, H-2$_{gal}$), 4.84 (d, *J* = 10.8 Hz, 2H$_{benzyl}$), 4.70 (dd, *J* = 18.7, 10.9 Hz, 1H$_{benzyl}$), 4.55 – 4.41 (m, 6H$_{benzyl}$), 4.35 (s, 1H$_{benzyl}$), 4.23 (d, *J* = 12.2 Hz, 1H$_{benzyl}$), 4.10 (d, *J* = 4.4 Hz, 1H$_{benzyl}$), 3.89 – 3.84 (m, 1H, H-3$_{glu}$), 3.79 (t, *J* = 9.3 Hz, 1H, H-5$_{glu}$), 3.63 (m, *J* = 13.8, 7.8, 3.9 Hz, 4H H-6$_{ab}$ & H-3 & H-5$_{gal}$), 3.47 – 3.41 (m, 1H, H-4$_{gal}$), 3.33 (d, *J* = 10.5 Hz, 2H, H-6$_{abglu}$), 2.99 (s, 1H, H-4$_{glu}$), 2.27 – 2.20 (m, 1H, H-2$_a$), 1.61 (d, *J* = 9.4 Hz, 1H, H-2$_b$). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 137.9$_{\alpha}$, 137.8$_{\beta}$, 137.5, 137.4$_{\beta}$, 137.4$_{\alpha}$, 137.0, 137.0, 136.9$_{\alpha}$, 136.9, 127.5, 127.4, 127.4, 127.3, 127.3, 127.2, 127.2, 127.2, 127.0, 126.9, 126.9, 126.8, 126.8, 126.7, 126.7, 126.6, 126.6, 126.5, 126.5, 126.4, 126.4, 126.1, 126.0, 95.4(C-1)$_{gal}$, 90.7(C-1)$_{glu}$, 80.7(C-4)$_{glu}$, 78.5(C-4)$_{gal}$, 76.6(C-5)$_{glu\beta}$, 76.5(C-5)$_{glu\alpha}$, 74.5(C-5)$_{gal}$, 73.9, 73.3, 72.5, 72.3, 72.0, 71.4, 69.9(C-2)$_{gal}$, 69.1(C-3)$_{gal}$, 69.0(C-3)$_{glu}$, 68.6(C-6)$_{gal}$, 67.1(C-6)$_{glu}$, 35.8(C-2)$_{glu\beta}$, 33.6(C-2)$_{glu\alpha}$. **HRMS (ESI)** m/z: [M+Na] $^{+}$ calcd for $C_{54}H_{58}O_{10}$ 889.3922 found 889.3829.

2-Deoxy-3,6-di-*O*-benzyl-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranose (2g)



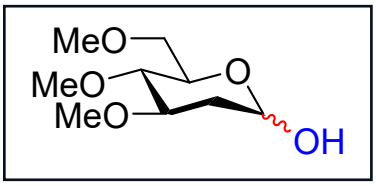
The title compound **2g** was prepared according to the general procedure 1a and purified by column chromatography giving a white powder solid (38.5 mg, 77% yield). R_f **(** Hexane: EtOAc =70:30): 0.45;**^{1}H NMR (600 MHz, $CDCl_3$) (a:β 1.3:1)** δ 7.24 – 7.11 (m, 28H_{benzyl}), 7.10 – 7.06 (m, 1H_{benzyl}), 7.05 – 7.01 (m, 1H_{benzyl}), 5.74 (d, *J* = 3.6 Hz, 1H), 5.68 (d, *J* = 3.7 Hz, 1H), 5.31 (s, 1H), 4.84 (d, *J* = 10.8 Hz, 2H), 4.70 (dd, *J* = 18.7, 10.9 Hz, 1H), 4.55 – 4.41 (m, 6H), 4.35 (s, 1H), 4.23 (d, *J* = 12.2 Hz, 1H), 4.10 (d, *J* = 4.4 Hz, 1H), 3.89 – 3.84 (m, 1H), 3.79 (t, *J* = 9.3 Hz, 1H), 3.63 (ddd, *J* = 13.8, 7.8, 3.9 Hz, 4H), 3.56 (d, *J* = 9.1 Hz, 1H), 3.47 – 3.41 (m, 2H), 2.99 (s, 1H), 2.27 – 2.20 (m, 1H), 1.61 (d, *J* = 9.4 Hz, 1H).**^{13}C NMR (151 MHz, $CDCl_3$)** δ 137.9$_\alpha$, 137.8$_\beta$, 137.5, 137.4$_\beta$, 137.4$_\alpha$, 137.0, 137.0, 136.9$_\alpha$, 136.9, 127.5, 127.4, 127.4, 127.3, 127.3, 127.2, 127.2, 127.2, 127.0, 126.9, 126.9, 126.8, 126.8, 126.7, 126.7, 126.6, 126.6, 126.5, 126.5, 126.4, 126.4, 126.1, 126.0, 95.4, 90.7(C-1), 80.7, 78.5, 76.6$_\beta$, 76.5$_\alpha$, 74.5, 73.9, 73.3, 72.5, 72.3, 72.0, 71.4, 69.9, 69.1, 69.0, 68.6, 67.1, 35.8(C-2)$_\beta$, 33.6(C-2)$_\alpha$. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{54}H_{58}O_{10}$ 889.3922 found 889.3829.

2-Deoxy-D-glucopyranose (**2h**)



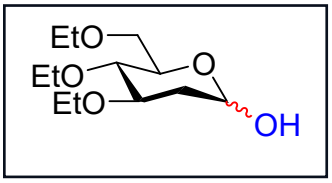
The title compound **2h** was prepared according to the general procedure 1a and purified by column chromatography giving a yellow gummy solid (42.5 mg, 85% yield). R_f **(** DCM: MeOH =60:40): 0.50;**^{1}H NMR (600 MHz, MeOD) (α:β 1:1)**δ 5.28 (d, *J* = 3.0 Hz, 1H, H-1), 3.93 – 3.84 (m, 2H, H-5$_{ab}$), 3.80 (dd, *J* = 11.1, 2.1 Hz, 1H, H-3$_a$), 3.75 – 3.68 (m, 2H, H-4$_{ab}$), 3.62 – 3.54 (m, 1H, H-3$_b$), 3.33 (d, *J* = 5.9 Hz, 1H, H-6$_a$), 3.27 (d, *J* = 9.2 Hz, 2H, H-6$_b$), 3.18 (d, *J* = 8.9 Hz, 1H, H-6$_a$), 2.14 (dd, *J* = 7.4, 1.9 Hz, 1H, H-2$_b$), 2.04 (dd, *J* = 7.7, 0.9 Hz, 1H, H-2$_a$), 1.60 (dd, *J* = 6.3, 5.5 Hz, 1H, H-2$_b$), 1.48 (d, *J* = 9.8 Hz, 1H, H-2$_a$).**^{13}C NMR (151 MHz, MeOD)** δ 93.8(C-1)$_\beta$, 91.4(C-1)$_\alpha$, 76.6(C-4), 72.2(C-5)$_\beta$, 71.6(C-5)$_\alpha$, 71.1(C-3)$_\alpha$, 68.2(C-3)$_\beta$, 61.6(C-6)$_\alpha$, 61.4(C-6)$_\beta$, 40.4(C-2)$_\alpha$, 38.1(C-2)$_\beta$. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_6H_{12}O_5$ 187.0577 found 187.0581.

2-Deoxy-3,4,6-tri-*O*-methyl-D-glucopyranose (2i)



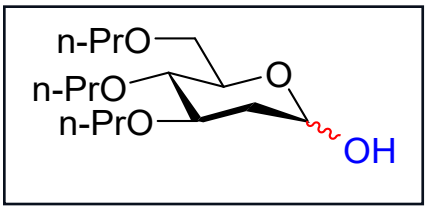
The title compound **2i** was prepared according to the general procedure **1a** and purified by column chromatography giving a white powder solid (48.5 mg, 89% yield). R_f **(** Hexane: EtOAc =60:40): 0.52;**^{1}H NMR (600 MHz, $CDCl_3$) (α:β 2.8:1)** δ 5.32 (s, 1H, H-1), 3.89 (m, 1H, H-5), 3.65 – 3.55 (m, 1H, H-6_a), 3.52 (d, J = 2.8 Hz, 1H, H-6_a), 3.47 (d, J = 6.2 Hz, 3H), 3.40 (m, 3H), 3.33 (m, 3H), 3.05 – 2.97 (m, 2H, H-4 & H-3), 2.18 (dd, J = 13.0, 4.8 Hz, 1H, H-2_a), 1.47 (td, J = 13.1, 3.3 Hz, 1H, H-2_b).**^{13}C NMR (151 MHz, $CDCl_3$)** δ 93.1(C-1)$_\alpha$, 91.1(C-1)$_\beta$, 79.8(C-4)$_\beta$, 79.4(C-4)$_\alpha$, 78.5(C-5)$_\beta$, 77.1(C-5)$_\alpha$, 70.9(C-3)$_\alpha$, 70.8(C-3)$_\beta$, 69.5(C-6), 59.5$_\beta$, 59.4$_\alpha$, 58.2$_\beta$, 58.1$_\alpha$, 56.2$_\alpha$, 56.0$_\beta$, 36.3(C-2)$_\beta$, 33.9(C-2)$_\alpha$. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_9H_{18}O_5$ 229.1046 found 229.1043.

2-Deoxy-3,4,6-tri-*O*-ethyl-D-glucopyranose (2j)



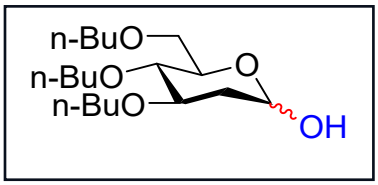
The title compound **2j** was prepared according to the general procedure **1a** and purified by column chromatography giving a white powder solid (52 mg, 97% yield). R_f **(** Hexane: EtOAc =60:40): 0.50;**^{1}H NMR (600 MHz, $CDCl_3$) (α:β 3:1)** δ 5.32 (s, 1H, H-1), 3.83(m, 2H, H-5 & H-3), 3.73 (m, 1H, H-6_a), 3.55 (dd, J = 8.0, 5.8 Hz, 6H), 3.36 – 3.24 (m, 1H, H-6_b), 3.12 (d, J = 9.4 Hz, 1H, H-4), 2.22 (m, 1H, H-2_a), 1.50 (d, J = 2.2 Hz, 1H, H-2_b), 1.20 (m, 9H).**^{13}C NMR (151 MHz, $CDCl_3$)** δ 94.2(C-1)$_\beta$, 92.1(C-1)$_\alpha$, 79.3(C-4)$_\beta$, 78.9(C-4)$_\alpha$, 76.6(C-5), 70.7(C-3)$_\alpha$, 70.5(C-3)$_\beta$, 69.9(C-6)$_\alpha$, 69.7(C-6)$_\beta$, 68.2$_\beta$, 68.1$_\alpha$, 66.9$_\beta$, 66.8$_\alpha$, 65.3$_\alpha$, 65.1$_\beta$, 38.2(C-2)$_\beta$, 35.8(C-2)$_\alpha$, 15.8$_\alpha$, 15.7$_\beta$, 15.5$_\beta$, 15.5$_\alpha$, 15.0$_\alpha$, 15.0$_\beta$.**HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{12}H_{24}O_5$ 271.1516 found 271.1499.

2-Deoxy-3,4,6-tri-*O*-propyl-D-glucopyranose (2k)



The title compound **2k** was prepared according to the general procedure **1a** and purified by column chromatography giving a white powder solid (51.5 mg, 97% yield). R_f **(** Hexane: EtOAc =60:40): 0.48;**^{1}H NMR (600 MHz, $CDCl_3$) (α:β 2.6:1)** δ 5.29 (d, *J* = 2.0 Hz, 1H, H-1), 3.90 – 3.77 (m, 1H, H-5), 3.73 (dd, *J* = 6.6, 2.4 Hz, 2H, H-6_{ab}), 3.55 (t, *J* = 3.6 Hz, 2H), 3.50 – 3.48 (m, 1H, H-3), 3.45 – 3.38 (m, 2H), 3.38 – 3.26 (m, 2H), 3.10 (t, *J* = 9.4 Hz, 1H, H-4), 2.12 (d, *J* = 8.1 Hz, 1H, H-2_a), 1.52 (d, *J* = 6.7 Hz, 7H, H-2_b & (CH2 n-OPr)$_3$), 0.87 – 0.77 (m, 9H).**^{13}C NMR (151 MHz, $CDCl_3$)** δ 93.2(C-1)$_\beta$, 91.0(C-1)$_\alpha$, 78.6(C-4)$_\beta$, 77.9(C-4)$_\alpha$, 77.0(C-5), 74.0$_\beta$, 73.6$_\alpha$, 72.3$_\beta$, 72.3$_\alpha$, 70.6$_\alpha$, 70.3$_\beta$, 69.7(C-3)$_\alpha$, 69.7(C-3)$_\beta$, 69.1(C-6)$_\alpha$, 69.1(C-6)$_\beta$, 37.0(C-2)$_\beta$, 34.7(C-2)$_\alpha$, 22.5$_\alpha$, 22.5$_\beta$, 22.4$_\alpha$, 22.3$_\beta$, 21.7$_\beta$, 21.6$_\alpha$, 9.7, 9.6, 9.5$_\alpha$, 9.5$_\beta$. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{15}H_{30}O_5$ 313.1985 found 313.1979.

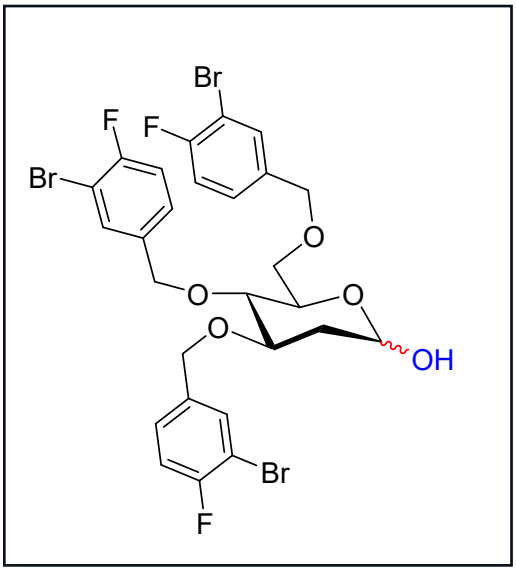
2-Deoxy-3,4,6-tri-*O*-butyl-D-glucopyranose (2l)



The title compound **2l** was prepared according to the general procedure **1a** and purified by column chromatography giving a white sticky solid (42.5 mg, 95% yield). R_f **(** Hexane: EtOAc =60:40): 0.50;**^{1}H NMR (600 MHz, $CDCl_3$) (α:β 2.9:1)** δ 5.27 (s, 1H, H-1), 4.21 (m, 1H, H-5), 3.84 (dd, *J* = 6.2, 3.7 Hz, 1H, H-6_a), 3.76 (ddd, *J* = 8.9, 7.8, 4.2 Hz, 1H, H-6_b), 3.70 – 3.65 (m, 1H, H-3), 3.57 – 3.49 (m, 3H), 3.43 (ddd, *J* = 13.9, 7.2, 4.6 Hz, 2H), 3.34 (t, *J* = 8.1 Hz, 1H), 3.09 (s, 1H, H-4), 2.16 – 2.02 (m, 1H, H-2_a), 1.57 – 1.44 (m, 7H, H-2_b & (CH2 n-OBu)$_3$), 1.31 (d, *J* = 2.1 Hz, 6H), 0.89 – 0.75 (m, 9H).**^{13}C NMR (151 MHz, $CDCl_3$)** δ 93.2(C-1)$_\beta$, 90.9(C-1)$_\alpha$, 78.7(C-4)$_\beta$, 77.9(C-4)$_\alpha$, 77.0(C-5), 71.7(C-3)$_\beta$, 71.6(C-3)$_\alpha$, 70.4(C-6)$_\beta$, 70.3(C-6)$_\alpha$, 69.8$_\beta$, 69.6$_\alpha$,

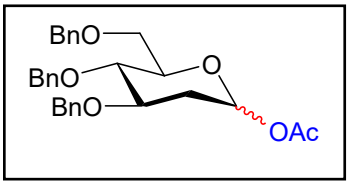
69.1$_{\alpha}$, 69.1$_{\beta}$, 68.6$_{\alpha}$, 68.3$_{\beta}$, 37.0(C-2)$_{\beta}$, 34.8(C-2)$_{\alpha}$, 31.5$_{\alpha}$, 31.5$_{\beta}$, 31.3$_{\alpha}$, 31.2$_{\beta}$, 30.6$_{\beta}$, 30.6$_{\alpha}$, 18.4, 18.3, 18.3$_{\alpha}$, 18.3$_{\beta}$, 13.0, 12.9$_{\alpha}$, 12.9$_{\alpha}$, 12.9$_{\beta}$, 12.8$_{\beta}$. **HRMS (ESI)** m/z: [M+Na] $^{+}$ calcd for $C_{18}H_{36}O_5$ 355.2455 found 355.2460.

2-Deoxy-3,4,6-tri-*O*-3-bromo-4-fluro-benzyl-D-glucopyranose (2m)



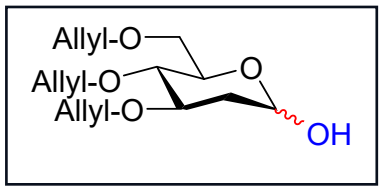
The title compound **2m** was prepared according to the general procedure **1a** and purified by column chromatography giving a white powder solid (42 mg, 85% yield). R_f **(** Hexane: EtOAc =50:50): 0.47;**^{1}H NMR (600 MHz, CDCl$_3$) (α:β 3.3:1)** δ 7.52 – 7.39 (m, 2H$_{benzyl}$), 7.33 (dd, *J* = 6.4, 1.8 Hz, 1H$_{benzyl}$), 7.26 – 7.08 (m, 2H$_{benzyl}$), 7.02 – 6.93 (m, 4H$_{benzyl}$), 5.33 (s, 1H, H-1), 4.71 (d, *J* = 11.5 Hz, 1H), 4.52 (d, *J* = 11.8 Hz, 1H), 4.46 (s, 1H), 4.43 – 4.39 (m, 2H), 4.35 (d, *J* = 12.1 Hz, 1H), 3.96 – 3.88 (m, 1H, H-5), 3.64 – 3.59 (m, 1H, H-3), 3.53 (d, *J* = 1.8 Hz, 1H, H-6$_a$), 3.37 (dd, *J* = 16.0, 6.5 Hz, 1H, H-6$_b$), 3.06 (d, 1H, H-4), 2.21 (dd, *J* = 12.7, 4.6 Hz, 1H, H-2$_a$), 1.58 (td, *J* = 12.9, 3.0 Hz, 1H, H-2$_b$).**^{13}C NMR (151 MHz, CDCl$_3$)** δ 158.4$_{\alpha}$, 158.3$_{\alpha}$, 158.3$_{\beta}$, 156.7$_{\alpha}$, 156.6$_{\beta}$, 156.6$_{\beta}$, 134.9, 134.8, 134.8$_{\alpha}$, 134.6$_{\beta}$, 134.5$_{\alpha}$, 134.5$_{\beta}$, 134.3$_{\alpha}$, 134.3$_{\beta}$, 131.9, 131.5$_{\alpha}$, 131.4$_{\beta}$, 127.4$_{\alpha}$, 127.3$_{\beta}$, 127.0$_{\alpha}$, 126.9$_{\beta}$, 126.9$_{\alpha}$, 126.8$_{\beta}$, 115.4$_{\alpha}$, 115.3$_{\beta}$, 115.3$_{\alpha}$, 115.2$_{\beta}$, 108.1, 108.0$_{\beta}$, 108.0$_{\alpha}$, 107.9$_{\alpha}$, 107.8$_{\beta}$, 93.1(C-1)$_{\beta}$, 91.0(C-1)$_{\alpha}$, 78.3(C-4)$_{\beta}$, 77.4(C-4)$_{\alpha}$, 76.6(C-5), 73.6$_{\beta}$, 72.3$_{\alpha}$, 71.1$_{\beta}$, 71.1$_{\alpha}$, 69.5, 69.0(C-3)$_{\alpha}$, 68.8(C-3)$_{\beta}$, 68.4(C-6)$_{\alpha}$, 68.3(C-6)$_{\beta}$, 36.7(C-2)$_{\beta}$, 34.3(C-2)$_{\alpha}$. **HRMS (ESI)** m/z: [M+Na] $^{+}$ calcd for $C_{27}H_{24}Br_3F_3O_5$ 744.9818 found 744.9056.

1-*O*-Acetyl-2-deoxy-3,4,6-tri-*O*-benzyl-D-glucopyranose (2n)



The title compound **2n** was prepared according to the general procedure **1a** and purified by column chromatography giving a yellow gummy solid (49 mg, 90% yield). R_f **(** Hexane: EtOAc = 70:30): 0.50;**^{1}H NMR (600 MHz, $CDCl_3$)(α:β 1.5:1)** δ 7.23 (ddd, *J* = 13.6, 8.4, 6.2 Hz, 13H_{benzyl}), 7.11 (dd, *J* = 12.6, 6.1 Hz, 2H_{benzyl}), 6.18 (d, *J* = 1.8 Hz, 1H, H-1), 4.82 (m, 1H_{benzyl}), 4.59 (d, *J* = 7.4 Hz, 1H_{benzyl}), 4.55 (dd, *J* = 8.2, 4.0 Hz, 2H_{benzyl}), 4.47 – 4.43 (m, 2H_{benzyl}), 3.90 – 3.85 (m, 1H, H-5), 3.77 (d, *J* = 9.9 Hz, 1H, H-3), 3.65 (d, *J* = 9.6 Hz, 2H, H-6_{ab}), 3.60 (d, *J* = 1.6 Hz, 1H, H-4), 2.21 (dd, *J* = 13.5, 4.9 Hz, 1H, H-2_b), 1.97 (s, 3H), 1.81 – 1.72 (m, 1H, H-2_a).**^{13}C NMR (151 MHz, $CDCl_3$)** δ 169.4$_\alpha$, 169.3$_\beta$, 138.4, 138.3$_\alpha$, 138.1$_\beta$, 138.0, 128.5, 128.5, 128.4, 128.4, 128.1, 128.0, 128.0, 128.0, 127.0, 127.9, 127.8, 127.7, 127.7, 127.7, 127.6, 92.2(C-1), 79.0(C-4), 77.6(C-5), 75.8(C-3), 75.2$_\alpha$, 75.0$_\beta$, 73.6$_\alpha$, 73.4$_\beta$, 71.9$_\beta$, 71.7$_\alpha$, 68.6(C-6)$_\beta$, 68.5(C-6)$_\alpha$, 35.4(C-2)$_\beta$, 34.3(C-2)$_\alpha$, 21.1$_\beta$, 21.1$_\alpha$. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{29}H_{32}O_6$ 499.2199 found 499.2101.

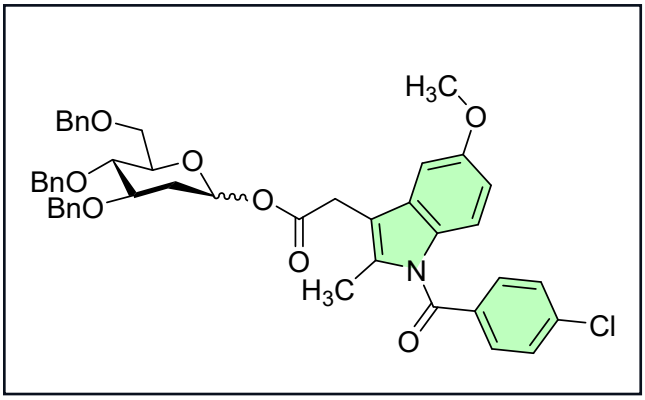
2-Deoxy-3,4,6-tri-*O*-allyl-D-glucopyranose (2o)



The title compound **2o** was prepared according to the general procedure **1a** and purified by column chromatography giving a yellow gummy solid (41.5 mg, 88% yield). R_f **(** Hexane: EtOAc =70:30): 0.45;**^{1}H NMR (600 MHz, $CDCl_3$) (α:β 3:1)** δ 5.84 (ddd, *J* = 19.4, 9.7, 4.5 Hz, 3H_{allyl}), 5.28 (s, 1H, H-1), 5.21 (dd, *J* = 17.3, 6.2 Hz, 3H_{allyl}), 5.12 – 5.06 (m, 3H_{allyl}), 4.28 (dd, *J* = 12.4, 5.7 Hz, 1H, H-3), 4.02 – 3.93 (m, 6H_{allyl}), 3.79 – 3.75 (m, 1H, H-5), 3.57 (dd, *J* = 8.2, 6.1 Hz, 2H, H-6_{ab}), 3.21 (t, *J* = 9.5 Hz, 1H, H-4), 2.16 – 2.08 (m, 1H, H-2_b), 1.52 (td, *J* = 12.9, 3.2

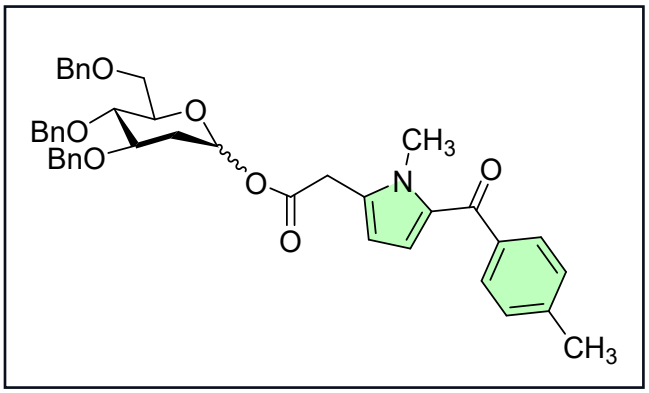
Hz, 1H, H-2_a).**^{13}C NMR (151 MHz, $CDCl_3$)** δ 135.1_α, 135.1_β, 134.9, 134.6, 117.4_α, 117.4_β, 116.8_α, 116.7_β, 116.6_β, 116.5_α, 94.1(C-1)$_\beta$, 91.9(C-1)$_\alpha$, 78.9(C-4)$_\beta$, 78.6(C-4)$_\alpha$, 76.5(C-5), 73.7, 72.4, 70.8, 70.5(C-3)$_\beta$, 70.5(C-3)$_\alpha$, 69.3(C-6)$_\alpha$, 69.3(C-6)$_\beta$, 38.0(C-2)$_\beta$, 35.7(C-2)$_\alpha$. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{15}H_{24}O_5$ 307.1516 found 307.1507.

1-*O*-Indomethacyl-2-Deoxy-3,4,6-tri-*O*-benzyl-D-glucopyranose (3a)



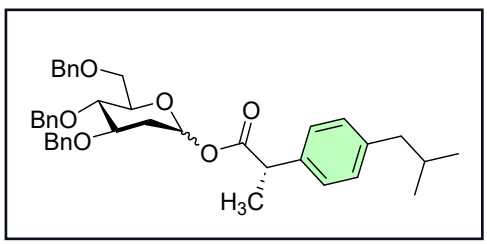
The title compound **3a** was prepared according to the general procedure **1b** and purified by column chromatography giving a light yellowish gummy solid (66.5 mg, 77% yield). R_f **(** Hexane: EtOAc =70:30): 0.42;**^{1}H NMR (500 MHz,$CDCl_3$) (α:β 1.3:1)** δ 6.79 (d, *J* = 8.8 Hz, 1H), 6.71 (d, *J* = 8.8 Hz, 1H), 6.59 (d, *J* = 8.2 Hz, 1H), 6.49 – 6.38 (m, 13H_{benzyl}), 6.34 (m, 1H_{benzyl}), 6.31 (m, 1H_{benzyl}), 6.13 (*bs*, 1H,H-1), 6.05 (s, 1H), 5.98 (d, *J* = 9.2 Hz, 1H), 5.85 – 5.79 (m, 1H), 5.41 (s, 1H), 4.86 (d, *J* = 9.4 Hz, 1H_{benzyl}), 4.07 – 3.97 (m, 1H_{benzyl}), 3.78 – 3.70 (m, 2H_{benzyl}), 3.62 (dd, *J* = 21.0, 7.9 Hz, 2H_{benzyl}), 2.97 (s, 3H), 2.90 (s, 2H, H-3 & H-5), 2.87(s, 1H, H-4), 2.82 (s, 2H, H-6_{ab}), 2.79 (s, 1H), 2.68 (d, *J* = 11.0 Hz, 1H), 1.53 (s, 3H), 1.38 – 1.33 (m, 1H, H-2_b), 0.93 (d, *J* = 10.6 Hz, 1H, H-2_a).**^{13}C NMR (126 MHz, $CDCl_3$)** δ 168.4_α, 168.2_β, 167.5, 155.4_β, 155.4_α, 138.5_α, 138.4_β, 137.7_α, 137.5_β, 137.4_α, 137.3_β, 135.4_α, 135.2_β, 133.1_α, 133.0_β, 130.4, 130.3, 130.1, 129.8, 129.7, 128.4, 128.4, 127.7, 127.7, 127.6, 127.6, 127.2, 127.0, 127.0, 126.8, 114.3_β, 114.2_α, 111.6_β, 111.2_α, 111.1_α, 110.9_β, 100.6_β, 100.5_α, 92.0(C-1)$_\beta$, 92.0(C-1)$_\alpha$, 78.0(C-4), 75.1(C-5), 74.2_β, 74.2_α, 72.9, 72.7_α, 72.7_β, 71.1(C-3)$_\beta$, 71.0(C-3)$_\alpha$, 67.8(C-6)$_\alpha$, 67.6(C-6)$_\beta$, 55.0_α, 54.9_β, 34.6(C-2)$_\alpha$, 33.5(C-2)$_\beta$, 30.0_β, 29.6_α, 12.7_α, 12.5_β .**HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{51}H_{44}O_8$ 774.2828 found 774.2871.

1-*O*-Tolmetyl-2-deoxy-3,4,6-tri-*O*-benzyl-D-glucopyranose (3b)



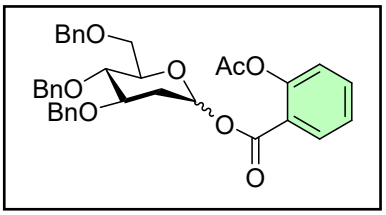
The title compound **3b** was prepared according to the general procedure **1b** and purified by column chromatography giving a light yellowish gummy solid (53.5 mg, 73% yield). R_f **(** Hexane: EtOAc =70:30): 0.50;**^{1}H NMR (600 MHz, $CDCl_3$) (a:β 1.3:1)**δ 7.61 (dd, *J* = 20.1, 7.9 Hz, 2H), 7.28 – 7.13 (m, 15H_{benzyl}), 7.10 (d, *J* = 7.3 Hz, 3H), 6.63 – 6.53 (m, 1H), 6.00 (d, *J* = 3.9 Hz, 1H, H-1), 4.81 (d, *J* = 10.5 Hz, 1H, H-5), 4.72 – 4.58 (m, 3H), 4.52 (d, *J* = 12.6 Hz, 2H), 4.45 – 4.37 (m, 1H, H-3), 3.94 – 3.79 (m, 3H, H-6_{ab} & H-4), 3.63 (dt, *J* = 15.1, 12.4 Hz, 6H_{benzyl}), 2.41 – 2.27 (m, 3H), 2.25 – 2.11 (m, 1H, H-2_b), 1.89 – 1.73 (m, 1H, H-2_a).**^{13}C NMR (151 MHz, $CDCl_3$)** δ 186.0, 167.8$_\beta$, 167.7$_\alpha$, 142.0$_\alpha$, 141.8$_\beta$, 138.6, 138.2$_\alpha$, 138.2$_\beta$, 138.1, 138.0$_\beta$, 137.9$_\alpha$, 137.5, 137.3$_\beta$, 137.2$_\alpha$, 136.7, 133.9$_\alpha$, 133.7$_\beta$, 131.5$_\beta$, 131.5$_\alpha$, 129.5, 128.7, 128.7, 128.5, 128.5, 128.4, 128.3, 128.0, 128.0, 127.8, 127.8, 127.7, 127.7, 127.6, 127.6, 122.5$_\beta$, 122.3$_\alpha$, 109.7$_\beta$, 109.4$_\alpha$, 108.8, 93.1(C-1)$_\alpha$, 92.2(C-1)$_\beta$, 78.7(C-4)$_\beta$, 78.6(C-4)$_\alpha$, 75.1(C-5)$_\alpha$, 74.9(C-5)$_\beta$, 73.7$_\beta$, 73.5$_\alpha$, 72.0, 71.8$_\beta$, 71.8$_\alpha$, 70.8(C-3)$_\alpha$, 69.3(C-3)$_\beta$, 68.5(C-6)$_\beta$, 68.4(C-6)$_\alpha$, 36.7(C-2)$_\alpha$, 35.5(C-2)$_\beta$, 34.3$_\beta$, 33.1$_\alpha$, 24.7$_\alpha$, 23.4$_\beta$, 21.5$_\alpha$, 20.5$_\beta$. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{42}H_{43}NO_7$674.3112 found 674.3122.

1-*O*-Ibuprofenyl-2-deoxy-3,4,6-tri-*O*-benzyl-D-glucopyranose (3c)



The title compound **3c** was prepared according to the general procedure **1b** and purified by column chromatography giving a light-yellow sticky solid (50.5 mg, 78% yield). R_f **(** Hexane: EtOAc =90:10): 0.48;**^{1}H NMR (600 MHz, $CDCl_3$) (a:β 3.2:1)** δ 7.21 (m, $13H_{benzyl}$), 7.12 (dd, *J* = 13.1, 7.6 Hz, 4H), 6.99 (d, *J* = 7.9 Hz, $2H_{benzyl}$), 5.63 – 5.57 (m, 1H, H-1), 4.78 (d, *J* = 10.8 Hz, $1H_{benzyl}$), 4.59 (d, *J* = 11.6 Hz, $1H_{benzyl}$), 4.51 (d, *J* = 11.6 Hz, $1H_{benzyl}$), 4.50 – 4.41 (m, $2H_{benzyl}$), 4.39 (d, *J* = 12.1 Hz, $1H_{benzyl}$), 3.68 – 3.57 (m, 3H, $H\text{-}6_{ab}$ & H-5), 3.52 (t, *J* = 8.9 Hz, 1H, H-3), 3.42 (dd, *J* = 9.3, 2.8 Hz, 1H, H-4), 2.34 (d, *J* = 7.2 Hz, 3H), 2.31 – 2.23 (m, 1H), 1.78 – 1.71 (m, 1H, $H\text{-}2_b$), 1.68 (d, *J* = 11.3 Hz, 1H, $H\text{-}2_a$), 1.43 (d, *J* = 7.3 Hz, 3H), 0.81 (t, *J* = 6.4 Hz, 6H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 172.1_α, 171.8_β, 139.8_α, 139.7_β, 139.6, 137.3_β, 137.2_α, 137.1, 137.0_α, 136.4_β, 136.1_β, 135.9_α, 128.4, 128.3, 127.4, 127.4, 127.3, 127.3, 127.0, 127.0, 127.0, 126.7, 126.6, 126.6, 126.5, 126.3, 126.2, 126.1, 91.7(C-1)$_\beta$, 91.5(C-1)$_\alpha$, 77.7(C-4), 75.0(C-5), 74.0_β, 73.9_α, 72.6_β, 72.6_β, 72.5_α,72.5_α, 70.7(C-3)$_\beta$, 70.6(C-3)$_\alpha$, 67.5(C-6)$_\alpha$, 67.4(C-6)$_\beta$, 44.0, 44.0, 34.0(C-2), 29.1, 21.4, 17.6. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{40}H_{46}O_6$ 645.3187 found 645.3201.

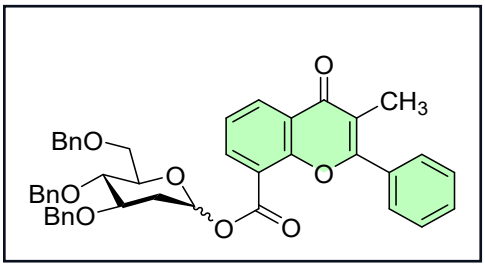
1-*O*-Aspirenyl-2-deoxy-3,4,6-tri-*O*-benzyl-D-glucopyranose (3d)



The title compound **3d** was prepared according to the general procedure **1b** and purified by column chromatography giving a yellow gummy solid (44mg, 89% yield). R_f **(** Hexane: EtOAc =80:20): 0.55;**^{1}H NMR (600 MHz, $CDCl_3$)(α:β 3:2)** δ 7.32 – 7.19 (m, $17H_{benzyl\ \&\ Ar}$), 7.15 – 7.04 (m, $2H_{benzyl}$), 5.60 (d, *J* = 9.9 Hz, 1H, H-1), 4.81 (dd, *J* = 14.7, 10.8 Hz, $1H_{benzyl}$), 4.63 – 4.53 (m, $4H_{benzyl}$), 4.52 – 4.40 (m, $3H_{benzyl}$ & H-3 &H-5), 3.65 (dd, *J* = 12.2, 6.9 Hz, 2H, $H\text{-}6_{ab}$), 3.55 (s, 1H, H-4), 2.25 (s, 1H, $H\text{-}2_b$), 2.01 (s, 3H), 1.67 (d, *J* = 11.1 Hz, 1H, $H\text{-}2_a$). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 169.4, 169.3, 138.4, 138.3, 138.2, 138.0, 128.5,128.5, 128.5, 128.4, 128.4, 128.4, 128.4,128.4, 128.3, 128.0,128.0, 128.0, 128.0, 127.9, 127.8, 127.7, 127.7, 127.7, 127.7,127.8, 92.2(C-1), 79.0(C-4), 75.8(C-5), 75.2(C-3)$_\beta$, 75.0(C-3)$_\alpha$, 73.6_β, 73.5_α, 73.5, 71.9_α, 71.7_β, 68.6(C-

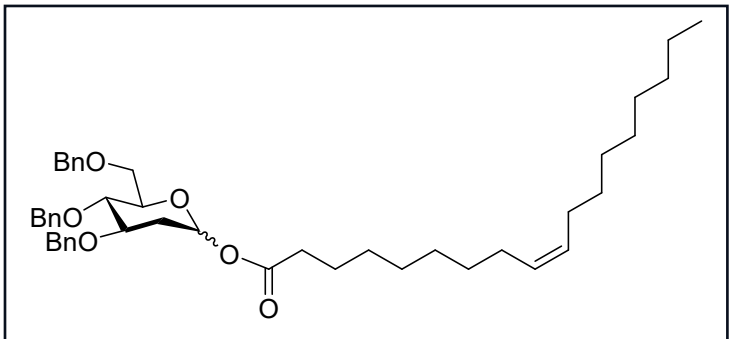
6)$_\alpha$, 68.5(C-6)$_\beta$, 35.4(C-2)$_\alpha$, 34.3(C-2)$_\beta$, 21.2$_\alpha$, 21.2$_\beta$. **HRMS (ESI)** m/z: [M+Na] $^+$ calcd for $C_{36}H_{36}O_8$ 619.2302 found 619.2347.

2-Deoxy-3,4,6-tri-*O*-benzyl-D-glucopyranose (3-methyl-4-oxo-2-phenyl-4H-chromene-8-carboxylate) (3e)



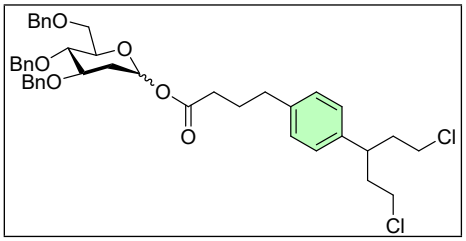
The title compound **3e** was prepared according to the general procedure **1b** and purified by column chromatography giving a light-brownish liquid (62 mg, 70% yield). R_f **(** Hexane: EtOAc =80:20): 0.50;**^{1}H NMR (600 MHz, $CDCl_3$) (α:β 1.25:1)** δ 8.45 – 8.36 (m, 1H), 8.26 (d, *J* = 7.4 Hz, 1H), 7.74 (d, *J* = 7.7 Hz, 1H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.44 (s, 1H), 7.39 (d, *J* = 7.0 Hz, 2H), 7.26 – 7.19 (m, 15H$_{benzyl}$), 7.13 (d, *J* = 7.1 Hz, 1H), 5.90 (d, *J* = 9.6 Hz, 1H, H-1), 4.81 (dd, *J* = 23.2, 10.6 Hz, 1H$_{benzyl}$), 4.52 (t, *J* = 10.3 Hz, 3H$_{benzyl}$), 4.44 (dd, *J* = 22.1, 11.3 Hz, 2H$_{benzyl}$), 3.79 – 3.74 (m, 1H, H-5), 3.73 – 3.67 (m, 2H, H-6$_{ab}$), 3.65 – 3.61 (m, 1H, H-3), 3.54 (d, *J* = 9.2 Hz, 1H, H-4), 2.39 – 2.28 (m, 1H, H-2$_a$), 2.18 (s, 3H), 1.85 (s, 1H, H-2$_b$). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 178.3$_\alpha$, 178.2$_\beta$, 162.5$_\alpha$, 162.3$_\beta$, 161.2$_\beta$, 161.1$_\alpha$, 154.7$_\alpha$, 154.7$_\beta$, 138.2$_\alpha$, 138.2$_\beta$, 138.2$_\beta$, 138.1$_\alpha$, 138.0$_\alpha$, 138.0$_\beta$, 136.8$_\alpha$, 136.0$_\beta$, 132.9$_\beta$, 131.5$_\alpha$, 131.2$_\beta$, 130.6$_\alpha$, 129.5, 129.5, 129.3, 129.3, 128.6, 128.5, 128.5, 128.4,128.4, 128.4, 128.4, 128.1, 128.0, 128.0, 128.0, 127.8, 127.8, 127.7, 127.7, 124.0,124.0, 123.4$_\beta$, 123.3$_\alpha$, 120.2$_\beta$, 119.7$_\alpha$, 117.9$_\beta$, 117.7$_\alpha$, 93.4(C-1)$_\alpha$, 92.9(C-1)$_\beta$, 78.7(C-4), 76.0(C-5), 75.3(C-3)$_\beta$, 75.0(C-3)$_\alpha$, 73.9, 73.6$_\beta$, 73.5$_\alpha$, 71.8$_\beta$, 71.7$_\alpha$, 68.6(C-6)$_\alpha$, 68.3(C-6)$_\beta$, 36.7(C-2)$_\beta$, 35.3(C-2)$_\alpha$, 11.8$_\alpha$, 11.8$_\beta$. **HRMS (ESI)** m/z: [M+Na]$^+$ calcd for $C_{44}H_{40}O_8$ 719.2615 found 719.2656.

1-*O*-Oleic acid-2-deoxy-3,4,6-tri-*O*-benzyl-D-glucopyranose (3f)



The title compound **3f** was prepared according to the general procedure **1b** and purified by column chromatography giving a yellow gummy solid (64mg, 80% yield). R_f (Hexane: EtOAc =80:20): 0.45;**^{1}H NMR (600 MHz, $CDCl_3$) (α:β 3:2)** δ 7.32 – 7.19 (m, $13H_{benzyl}$), 7.17 – 7.01 (m, $2H_{benzyl}$), 6.19 (s, 1H, H-1), 5.61 (d, *J* = 8.9 Hz, 1H), 5.27 (dd, *J* = 8.5, 4.9 Hz, $5H_{benzyl}$ & 1CH), 4.81 (d, *J* = 2.3 Hz, $2H_{benzyl}$), 4.57 (dd, *J* = 18.7, 8.2 Hz, 3H, H-6_{ab} & H-4), 4.47 – 4.43 (m, 2H, H-3 & H-5), 3.89 – 3.85 (m, 1H), 3.64 (d, *J* = 10.0 Hz, 2H), 3.59 – 3.54 (m, 1H), 2.26 (t, *J* = 7.3 Hz, 2H), 2.19 (d, *J* = 7.6 Hz, 1H, H-2_b), 1.95 – 1.91 (m, 4H), 1.76 (s, 1H, H-2_a), 1.55 (d, *J* = 7.3 Hz, 2H), 1.19 (s, 16H), 0.80 (s, 3H).**^{13}C NMR (151 MHz, $CDCl_3$)** δ 171.1, 137.3, 137.2, 137.1, 137.0, 137.0, 129.0, 128.7, 128.7, 127.4, 127.4, 127.4, 127.3, 127.3, 127.0, 127.0, 126.9, 126.7, 126.7, 126.6, 126.6, 91.1(C-1)$_\beta$, 91.0(C-1)$_\alpha$, 78.0(C-4), 76.6(C-5), 74.8(C-3), 74.2$_\alpha$, 74.0$_\beta$, 72.5$_\alpha$, 72.5$_\beta$, 70.8$_\alpha$, 70.7$_\beta$, 67.5(C-6)$_\beta$, 67.4(C-6)$_\alpha$, 34.3(C-2), 33.4$_\alpha$, 33.3$_\beta$, 33.2, 30.9, 28.7, 28.7, 28.7, 28.5, 28.3, 28.1, 28.0, 26.2$_\alpha$, 26.1$_\beta$, 23.8$_\beta$, 23.7$_\alpha$, 23.6, 21.7, 13.1. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{45}H_{62}O_6$ 721.4439 found 721.4471.

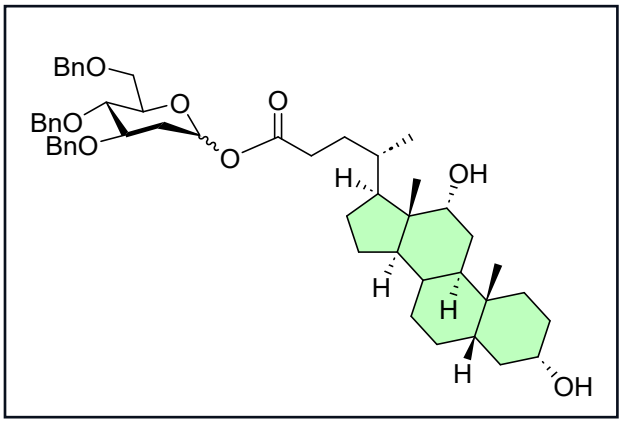
1-*O*-Chlorambucil-2-deoxy-3,4,6-tri-*O*-benzyl-D-glucopyranose (3g)



The title compound **3g** was prepared according to the general procedure **1b** and purified by column chromatography giving a light-yellow liquid (74.5 mg, 90% yield). R_f (Hexane: EtOAc =90:10): 0.50;**^{1}H NMR (600 MHz, $CDCl_3$) (a:β 5:3)**δ 7.27 – 7.17 (m, $14H_{benzyl}$), 7.10 (s, $1H_{benzyl}$), 6.96 (d, *J* = 8.4 Hz, 2H), 6.58 – 6.47 (m, 2H), 6.10 (d, *J* = 10.2 Hz, 1H, H-1), 4.81 (t, *J* = 11.2 Hz, $1H_{benzyl}$), 4.64 – 4.51 (m, $3H_{benzyl}$), 4.44 (dd, *J* = 26.3, 19.1 Hz, $3H_{benzyl}$ & H-5), 3.69 – 3.58 (m, 4H, $2CH_2$), 3.54 (dd, *J* = 18.9, 12.9 Hz, 4H, H-3 & $1CH_2$ & 1CH), 2.46 (t, *J* = 7.5 Hz, 3H, H-4 & H-6_{ab}), 2.35 – 2.18 (m, 5H, H-2_b & $2CH_2$), 1.89 – 1.76 (m, 5H, H-2_a & $2CH_2$).**^{13}C NMR (151 MHz, $CDCl_3$)** δ 172.5$_\beta$, 171.9$_\alpha$, 144.4$_\beta$, 144.4$_\alpha$, 138.4$_\alpha$, 138.3$_\beta$, 138.2$_\beta$, 138.1$_\alpha$,

138.1$_{\beta}$, 138.0$_{\alpha}$, 137.8$_{\beta}$, 137.8$_{\alpha}$, 131.9, 130.5$_{\beta}$, 130.5$_{\alpha}$, 129.8$_{\alpha}$, 129.7$_{\beta}$, 128.9, 128.5, 128.5, 128.4, 128.4, 128.1, 128.0, 128.0, 127.9$_{\alpha}$, 127.9$_{\beta}$, 127.8, 127.8, 127.7, 127.7, 126.8, 124.7, 112.2$_{\beta}$, 112.2$_{\alpha}$, 92.1(C-1)$_{\alpha}$, 92.1(C-1)$_{\beta}$, 88.7$_{\alpha}$, 88.7$_{\beta}$, 79.0(C-4), 75.2(C-5)$_{\alpha}$, 75.0(C-5)$_{\beta}$, 73.5$_{\beta}$, 73.5$_{\alpha}$, 71.8$_{\alpha}$, 71.6$_{\beta}$, 69.8(C-3)$_{\alpha}$, 69.4(C-3)$_{\beta}$, 68.5(C-6)$_{\alpha}$, 68.5(C-6)$_{\beta}$, 53.6, 40.6, 35.4(C-2)$_{\alpha}$, 34.4(C-2)$_{\beta}$, 33.9$_{\beta}$, 33.9$_{\alpha}$, 33.9$_{\beta}$, 33.8$_{\alpha}$, 33.7$_{\alpha}$, 33.5$_{\beta}$, 29.7, 26.7$_{\alpha}$, 26.6$_{\beta}$, 26.5$_{\alpha}$, 26.5$_{\beta}$.**HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{42}H_{48}Cl_2O_6$ 720.2901 found 720.2890.

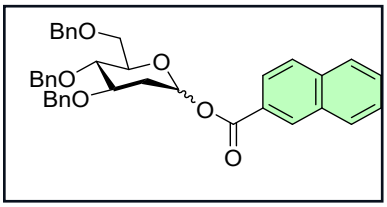
4-((3S,5S,9R,10R,12R,13S,14R,17S)-3,12-dihydroxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)2-deoxy-3,4,6-tri-*O*-benzyl-D-glucopyronose (pentanoate) (3h)



The title compound **3h** was prepared according to the general procedure **1b** and purified by column chromatography giving a light-yellow gummy solid (85 mg, 90% yield). R_f **(** Hexane: EtOAc =40:60): 0.45;**^{1}H NMR (600 MHz, $CDCl_3$) (a:β 1.2:1)** δ 7.22 (m, *J* = 19.9, 14.0, 5.2 Hz, 14H$_{benzyl}$), 7.11 (d, *J* = 12.4 Hz, 1H$_{benzyl}$), 6.21 (d, *J* = 11.6 Hz, 1H, H-1), 4.81 (dd, *J* = 14.5, 11.0 Hz, 1H, H-4), 4.64 – 4.53 (m, 2H$_{benzyl}$), 4.49 – 4.41 (m, 2H$_{benzyl}$), 3.89 (m, 2H$_{benzyl}$), 3.65 (d, *J* = 9.2 Hz, 2H, H-6$_{ab}$), 3.57 (d, *J* = 22.6 Hz, 2H, H-5 & H-3), 2.29 – 2.16 (m, 3H, H-2$_a$ & 1CH_2), 1.74 (dd, *J* = 18.2, 8.1 Hz, 8H), 1.60 (s, 3H, H-2$_b$ & 1CH_2), 1.43 (s, 5H), 1.32 (d, *J* = 8.5 Hz, 6H), 1.18 (s, 4H), 0.91 – 0.86 (m, 6H), 0.83 (s, 3H), 0.61 – 0.58 (m, 3H).**^{13}C NMR (151 MHz, $CDCl_3$)** δ 172.1$_{\alpha}$, 171.4$_{\beta}$, 137.3$_{\alpha}$, 137.3$_{\beta}$, 137.1$_{\alpha}$, 137.1$_{\beta}$, 137.0$_{\beta}$, 136.7$_{\alpha}$, 130.9, 127.5, 127.4,127.4, 127.4, 127.0, 127.0, 126.9, 126.9, 126.9, 126.8, 126.7, 126.7, 126.6, 123.7, 91.1(C-1)$_{\alpha}$, 91.0(C-1)$_{\beta}$, 87.7, 77.9(C-4), 74.8(C-5), 74.1$_{\beta}$, 74.0$_{\alpha}$, 72.5$_{\beta}$, 72.4$_{\alpha}$, 72.2$_{\beta}$, 72.1$_{\alpha}$, 70.8(C-3)$_{\beta}$, 70.8(C-3)$_{\alpha}$, 70.6(C-6)$_{\alpha}$, 70.5(C-6)$_{\beta}$, 67.4$_{\alpha}$, 67.4$_{\beta}$, 47.2, 46.3$_{\alpha}$, 46.2$_{\beta}$, 45.5, 41.1, 35.4(C-2), 35.0,

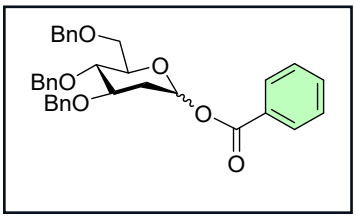
34.3$_\beta$, 34.2$_\alpha$, 34.1$_\beta$, 34.1$_\alpha$, 33.3$_\beta$, 33.1$_\alpha$, 32.6, 30.8$_\beta$, 30.5$_\alpha$, 30.4$_\beta$, 30.2$_\alpha$, 29.7$_\alpha$, 29.7$_\beta$, 29.5$_\beta$, 29.4$_\alpha$, 28.7, 27.6, 26.5$_\alpha$, 26.4$_\beta$, 26.1, 25.1, 22.6$_\beta$, 22.1$_\alpha$, 16.3$_\beta$, 16.3$_\alpha$, 11.7.**HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{51}H_{68}O_8$ 829.5225 found 829.5413.

1-*O*-Nephthanyl-2-deoxy-3,4,6-tri-*O*-benzyl-D-glucopyranose (3i)



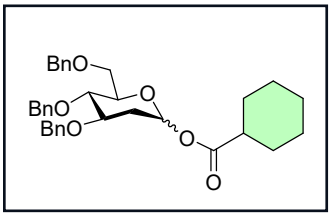
The title compound **3i** was prepared according to the general procedure 1b and purified by column chromatography giving a light-yellow sticky solid (54 mg, 80% yield). R_f **(** Hexane: EtOAc =60:40): 0.48;**^{1}H NMR (600 MHz, $CDCl_3$) (α:β 3:2)** δ 8.56 (d, *J* = 32.4 Hz, 1H), 8.00 (dd, *J* = 10.7, 9.6 Hz, 1H), 7.87 (d, *J* = 8.8 Hz, 1H), 7.83 – 7.78 (m, 2H), 7.54 – 7.48 (m, 1H), 7.47 (d, *J* = 6.8 Hz, 1H), 7.29 – 7.18 (m, 15H$_{benzyl}$), 6.56 (s, 1H, H-1), 4.85 (dd, *J* = 19.3, 10.6 Hz, 1H$_{benzyl}$), 4.66 (s, 1H$_{benzyl}$), 4.61 – 4.53 (m, 3H$_{benzyl}$), 4.44 (d, *J* = 12.1 Hz, 1H$_{benzyl}$), 3.79 – 3.57 (m, 5H, H-6$_{ab}$ & H-5 & H-4 & H-3), 2.52 – 2.33 (m, 1H, H-2$_b$), 1.92 (d, *J* = 11.2 Hz, 1H, H-2$_a$).**^{13}C NMR (151 MHz, $CDCl_3$)** δ 164.6$_\beta$, 163.9$_\alpha$, 137.3$_\alpha$, 137.2$_\beta$, 137.1$_\alpha$, 137.0$_\beta$, 137.0$_\beta$, 136.7$_\alpha$, 134.7$_\alpha$, 134.6$_\beta$, 131.4$_\beta$, 131.4$_\alpha$, 131.3$_\beta$, 130.8$_\alpha$, 130.4$_\alpha$, 130.3$_\beta$, 128.4$_\beta$, 128.4$_\alpha$, 127.5, 127.4, 127.4, 127.3, 127.2, 127.2, 127.0, 127.0, 127.0, 126.9, 126.8, 126.8, 126.8, 126.8, 126.8, 126.7, 126.6, 126.1$_\beta$, 126.0$_\alpha$, 125.8$_\beta$, 125.7$_\alpha$, 125.7$_\alpha$, 125.6$_\beta$, 124.4$_\beta$, 124.3$_\alpha$, 124.2$_\beta$, 123.7$_\alpha$, 91.9(C-1)$_\beta$, 91.8(C-1)$_\alpha$, 88.4(C-4), 77.9$_\alpha$, 76.7$_\beta$, 74.9$_\beta$, 73.9$_\alpha$, 72.8$_\beta$, 72.5$_\alpha$, 71.1(C-5)$_\alpha$, 70.8(C-5)$_\beta$, 70.7(C-3)$_\alpha$, 68.8(C-3)$_\beta$, 67.6(C-6)$_{\boldsymbol{\beta}}$, 67.4(C-6)$_\alpha$, 34.4(C-2)$_{\boldsymbol{\alpha}}$, 33.6(C-2)$_\beta$.**HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{38}H_{36}O_6$ 611.2402 found 611.2436.

1-*O*-Benzoyl-2-deoxy-3,4,6-tri-*O*-benzyl-D-glucopyronose (3j)



The title compound **3j** was prepared according to the general procedure **1b** and purified by column chromatography giving a light-yellow gummy solid (52.5 mg, 85% yield). R_f **(** Hexane: EtOAc =70:30): 0.50;**^{1}H NMR (600 MHz, $CDCl_3$) (α:β 6.6:1)** δ 8.02 – 7.97 (m, 1H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 6.3 Hz, 2H), 7.27 – 7.18 (m, 14H_{benzyl}), 7.13 (d, *J* = 5.2 Hz, 1H_{benzyl}), 6.52 – 6.39 (m, 1H, H-1), 4.84 (dd, *J* = 16.8, 10.7 Hz, 1H_{benzyl}), 4.65 – 4.61 (m, 1H_{benzyl}), 4.58 – 4.54 (m, 2H_{benzyl}), 4.50 (dd, *J* = 10.7, 5.6 Hz, 1H_{benzyl}), 4.43 (d, *J* = 12.3 Hz, 1H_{benzyl}), 4.00 (dd, *J* = 7.6, 3.2 Hz, 1H, H-5), 3.74 – 3.69 (m, 2H, H-4 & H-3), 3.69 – 3.58 (m, 2H, H-6_{ab}), 2.54 – 2.26 (m, 1H, H-2_b), 1.86 (d, *J* = 11.1 Hz, 1H, H-2_a).**^{13}C NMR (151 MHz, $CDCl_3$)** δ 164.8$_\beta$, 164.7$_\alpha$, 138.3$_\alpha$, 138.3$_\beta$, 138.2$_\beta$, 138.1$_\alpha$, 138.0$_\beta$, 137.7$_\alpha$, 133.5$_\beta$, 133.4$_\alpha$, 133.3, 132.3, 130.1$_\alpha$, 129.9$_\beta$, 129.8$_\alpha$, 129.8$_\beta$, 128.5, 128.5, 128.5, 128.4, 128.4, 128.2, 128.0, 128.0, 128.0, 127.8, 127.8, 127.8, 127.7, 127.7, 127.7, 124.6, 92.8(C-1)$_\beta$, 92.7(C-1)$_\alpha$, 89.4(C-4)$_\alpha$, 88.9(C-4)$_\beta$, 78.9(C-5)$_\beta$, 77.7(C-5)$_\alpha$, 75.9(C-3)$_\alpha$, 75.4(C-3)$_\beta$, 74.9, 73.5$_\beta$, 73.5$_\alpha$, 72.0$_\beta$, 71.7$_\alpha$, 68.6(C-6)$_\beta$, 68.4(C-6)$_\alpha$, 35.3(C-2)$_\beta$, 34.6(C-2)$_\alpha$. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{34}H_{34}O_6$ 561.2248 found 561.2264.

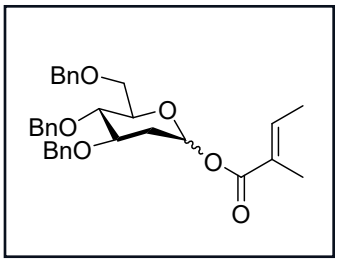
1-*O*-Cyclohexyl-2-deoxy-3,4,6-tri-*O*-benzyl-D-glucopyranose (3k)



The title compound **3k** was prepared according to the general procedure **1b** and purified by column chromatography giving a brownish-yellow gummy solid (61 mg, 90% yield). R_f **(** Hexane: EtOAc =95:05): 0.42;**^{1}H NMR (600 MHz, $CDCl_3$) (α:β 1.5:1)** δ 7.28 – 7.17 (m, 13H_{benzyl}), 7.12 (d, *J* = 8.3 Hz, 2H_{benzyl}), 6.17 (s, 1H, H-1), 4.81 (dd, *J* = 15.6, 10.8 Hz, 1H_{benzyl}), 4.60 (d, *J* = 11.2 Hz, 2H_{benzyl}), 4.58 – 4.50 (m, 1H_{benzyl}), 4.45 (ddd, *J* = 17.0, 11.4, 3.9 Hz, 2H_{benzyl}), 3.87 – 3.80 (m, 1H, H-5), 3.75 (d, *J* = 9.7 Hz, 1H, H-3), 3.70 (dd, *J* = 10.8, 3.4 Hz, 1H, H-6_a), 3.64 (td, *J* = 9.2, 3.7 Hz, 1H H-6_b), 3.58 (d, *J* = 12.2 Hz, 1H, H-4), 2.30 – 2.22 (m, 2H), 2.17 (dd, *J* = 12.1, 5.8 Hz, 1H, H-2_b), 1.85 (d, *J* = 13.0 Hz, 3H), 1.78 – 1.74 (m, 1H, H-2_a), 1.68 (dd, *J* = 9.5, 3.6 Hz, 3H), 1.57 (d, *J* = 10.8 Hz, 1H), 1.38 (d, *J* = 10.8 Hz, 1H), 1.22 – 1.13 (m,

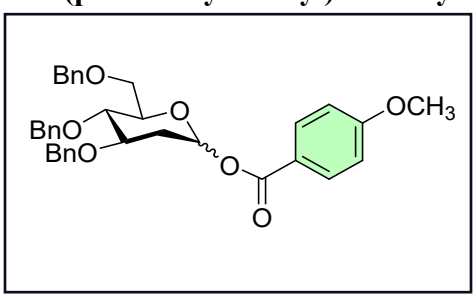
1H).**^{13}C NMR (151 MHz, $CDCl_3$)** δ 173.32$_\beta$, 173.12$_\alpha$, 137.2$_\alpha$, 137.2$_\beta$, 137.1$_\beta$, 137.1$_\alpha$, 137.0, 127.4, 127.4, 127.4, 127.3, 127.3, 127.2, 127.2, 126.9,126.9, 126.8, 126.8, 126.7, 126.7, 126.7, 126.6, 91.1(C-1)$_\beta$, 90.8(C-1)$_\alpha$, 77.9(C-4), 76.7(C-5)$_\alpha$, 76.3(C-5)$_\beta$, 75.7$_\alpha$, 74.8$_\beta$, 74.2$_\alpha$, 73.9$_\beta$, 72.5$_\alpha$, 72.5$_\beta$, 70.8(C-3)$_\alpha$, 70.6(C-3)$_\beta$, 67.6(C-6)$_\beta$, 67.4(C-6)$_\alpha$, 42.2$_\beta$, 41.9$_\alpha$, 34.2(C-2)$_\beta$, 33.3(C-2)$_\alpha$, 27.9$_\beta$, 27.8$_\alpha$, 27.8$_\beta$, 27.8$_\alpha$, 24.7$_\alpha$, 24.6$_\beta$, 24.4$_\beta$, 24.3$_\alpha$, 24.2.**HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{34}H_{40}O_6$ 567.2717 found 567.2724.

1-*O*-Tiglicyl-2-deoxy-3,4,6-tri-*O*-benzyl-D-glucopyranose (3l)



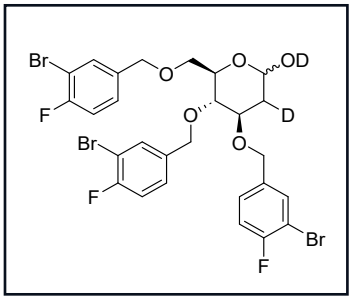
The title compound **3l** was prepared according to the general procedure 1b and purified by column chromatography giving a light-yellow liquid (50.5 mg, 85% yield). R_f **(** Hexane: EtOAc =80:20): 0.50;**^{1}H NMR (600 MHz, $CDCl_3$) (α:β 1.17:1)** δ 7.23 (m, *J* = 13.3, 10.6, 4.6 Hz, 13H_{benzyl}), 7.11 (t, *J* = 8.1 Hz, 2H_{benzyl}), 6.25 (s, 1H, H-1), 4.82 (dd, *J* = 14.4, 10.9 Hz, 1H_{benzyl}), 4.63 – 4.57 (m, 2H_{benzyl}), 4.54 (d, *J* = 6.3 Hz, 1H_{benzyl}), 4.48 (s, 1H_{benzyl}), 4.42 (d, *J* = 12.1 Hz, 1H_{benzyl}), 3.77 (d, *J* = 9.8 Hz, 1H), 3.73 – 3.69 (m, 1H, H-5), 3.67 (d, *J* = 5.2 Hz, 2H, H-4 & H-3), 3.58 (d, *J* = 9.8 Hz, 1H, H-6$_a$), 2.31 (dd, *J* = 12.2, 4.6 Hz, 1H, H-6$_b$), 2.23 (dd, *J* = 13.5, 4.6 Hz, 1H, H-2$_b$), 1.83 – 1.77 (m, 1H, H-2$_a$), 1.76 (d, 3H), 1.71 (s, 3H).**^{13}C NMR (151 MHz, $CDCl_3$)** δ 165.0$_\alpha$, 165.0$_\beta$, 138.2, 137.4$_\alpha$, 137.3$_\alpha$, 137.2$_\beta$, 137.2$_\beta$, 137.0$_\alpha$, 137.0$_\beta$, 127.4, 127.4, 127.3, 127.3, 127.3, 127.1, 127.0, 126.9, 126.8, 126.7, 126.7, 126.7, 126.6, 126.6, 91.3(C-1)$_\alpha$, 91.1(C-1)$_\beta$, 78.0(C-4), 76.7(C-5)$_\alpha$, 76.3(C-5)$_\beta$, 74.7$_\beta$, 74.3$_\alpha$, 73.9$_\alpha$, 72.5$_\beta$, 72.5$_\alpha$, 72.4$_\beta$, 70.8, 70.6(C-3), 67.6(C-6)$_\beta$, 67.4(C-6)$_\alpha$, 34.3(C-2)$_\alpha$, 33.5(C-2)$_\beta$, 13.5$_\alpha$, 13.4$_\beta$, 10.9$_\beta$ 10.9$_\alpha$.**HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{32}H_{36}O_6$ 539.2404 found 539.2402.

1-*O*-(p-methoxybenzoyl)-2-deoxy-3,4,6-tri-*O*-benzyl-D-glucopyranose (3m)



The title compound **3m** was prepared according to the general procedure **1b** and purified by column chromatography giving a light-brownish liquid (45.5 mg, 70% yield). R_f **(** Hexane: EtOAc =60:40): 0.50; **^{1}H NMR (600 MHz, $CDCl_3$) (a:β 2.5:1)** δ 7.98 (dd, *J* = 37.1, 8.8 Hz, 2H), 7.28 – 7.12 (m, $15H_{benzyl}$), 6.82 (d, *J* = 8.7 Hz, 2H), 5.84 (dd, *J* = 9.8, 1.8 Hz, 1H, H-1), 4.87 – 4.81 (m, $1H_{benzyl}$), 4.64 – 4.61 (m, $1H_{benzyl}$), 4.54 (dd, *J* = 11.9, 4.1 Hz, $2H_{benzyl}$), 4.49 (s, $1H_{benzyl}$), 4.42 (d, *J* = 12.2 Hz, $1H_{benzyl}$), 3.76 (s, 3H, H-6_{ab} & H-4), 3.72 – 3.68 (m, 3H), 3.62 (t, *J* = 9.0 Hz, 1H, H-5), 3.55 – 3.50 (m, 1H, H-3), 2.43 – 2.35 (m, 1H, H-2_b), 1.84 (d, *J* = 10.6 Hz, 1H, H-2_a).**^{13}C NMR (151 MHz, $CDCl_3$)** δ 164.5$_a$, 164.4$_\beta$, 163.8$_a$, 163.8$_\beta$, 138.4$_a$, 138.3$_\beta$, 138.3$_\beta$, 138.2$_a$, 138.1$_a$, 138.1$_\beta$, 132.9$_\beta$, 132.2$_a$, 132.0$_\beta$, 131.9$_a$, 128.5, 128.5, 128.5, 128.4, 128.4, 128.2, 128.0, 128.0, 127.8, 127.8, 127.8, 127.7, 127.7, 122.1$_\beta$, 121.8$_a$, 114.2, 113.8$_\beta$, 113.7$_a$, 92.5(C-1)$_a$, 92.5(C-1)$_\beta$, 79.0(C-4), 77.7(C-5), 75.9(C-3), 75.4$_\beta$, 75.0$_a$, 73.6$_\beta$, 73.5$_a$, 72.0$_\beta$, 71.7$_a$, 68.6(C-6)$_a$, 68.5(C-6)$_\beta$, 55.5$_\beta$, 55.5$_a$, 35.4(C-2)$_a$, 34.6(C-2)$_\beta$.**HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{35}H_{36}O_7$ 591.2353 found 591.2356.

2-Deoxy-3,4,6-tri-*O*-3-bromo-4-fluro-benzyl-D-glucopyranose (4a)



The title compound **4a** was prepared according to the general procedure 1a and purified by column chromatography giving a white powder solid (43.5 mg, 87% yield). R_f **(** Hexane: EtOAc =50:50): 0.48;**^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.55 – 7.48 (m, $2H_{benzyl}$), 7.39 (d, *J* = 6.6 Hz, $1H_{benzyl}$), 7.22 – 7.14 (m, $2H_{benzyl}$), 7.09 – 7.00 (m, $4H_{benzyl}$), 5.40 (s, 1H, H-1), 4.77 (d, *J* = 11.5 Hz, 1H, H-3), 4.63 – 4.40 (m, $6H_{benzyl}$), 4.04 – 3.89 (m, 1H, H-5), 3.75 – 3.63 (m, 1H, H-6_b), 3.60 (d, *J* = 9.1 Hz, 1H, H-6_a), 3.45 (dd, *J* = 16.0, 6.6 Hz, 1H, H-4), 1.64 (d, *J* = 11.7 Hz, 1H, H-2).**HRMS (ESI)** m/z: $[M+NH_4]^+$ calcd for $C_{27}H_{22}D_2Br_3F_3O_5$ 741.7252 found 741.9482.

NMR Spectra

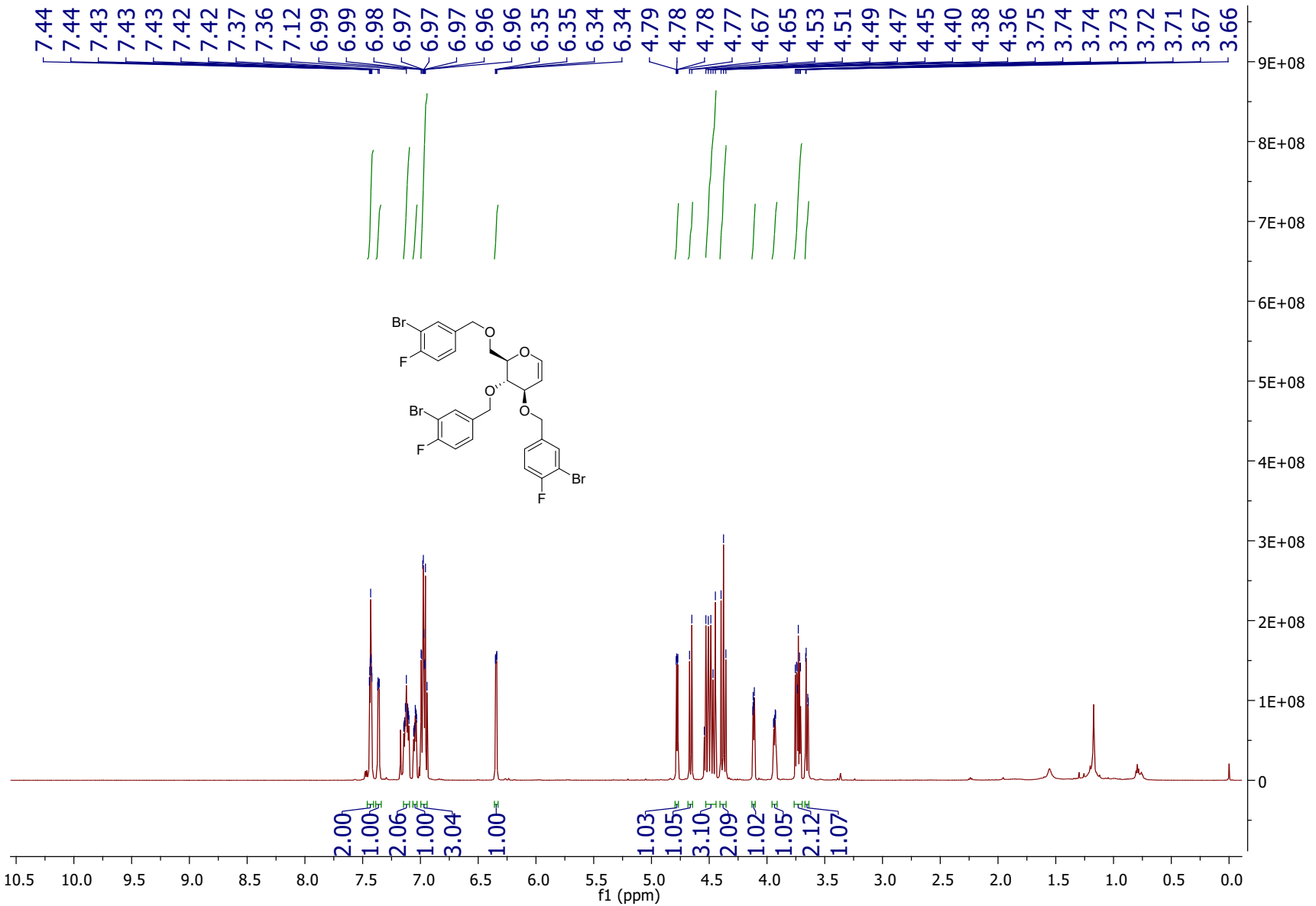


Fig- ^{1}H NMR (600 MHz, $CDCl_3$) of compound **1m**

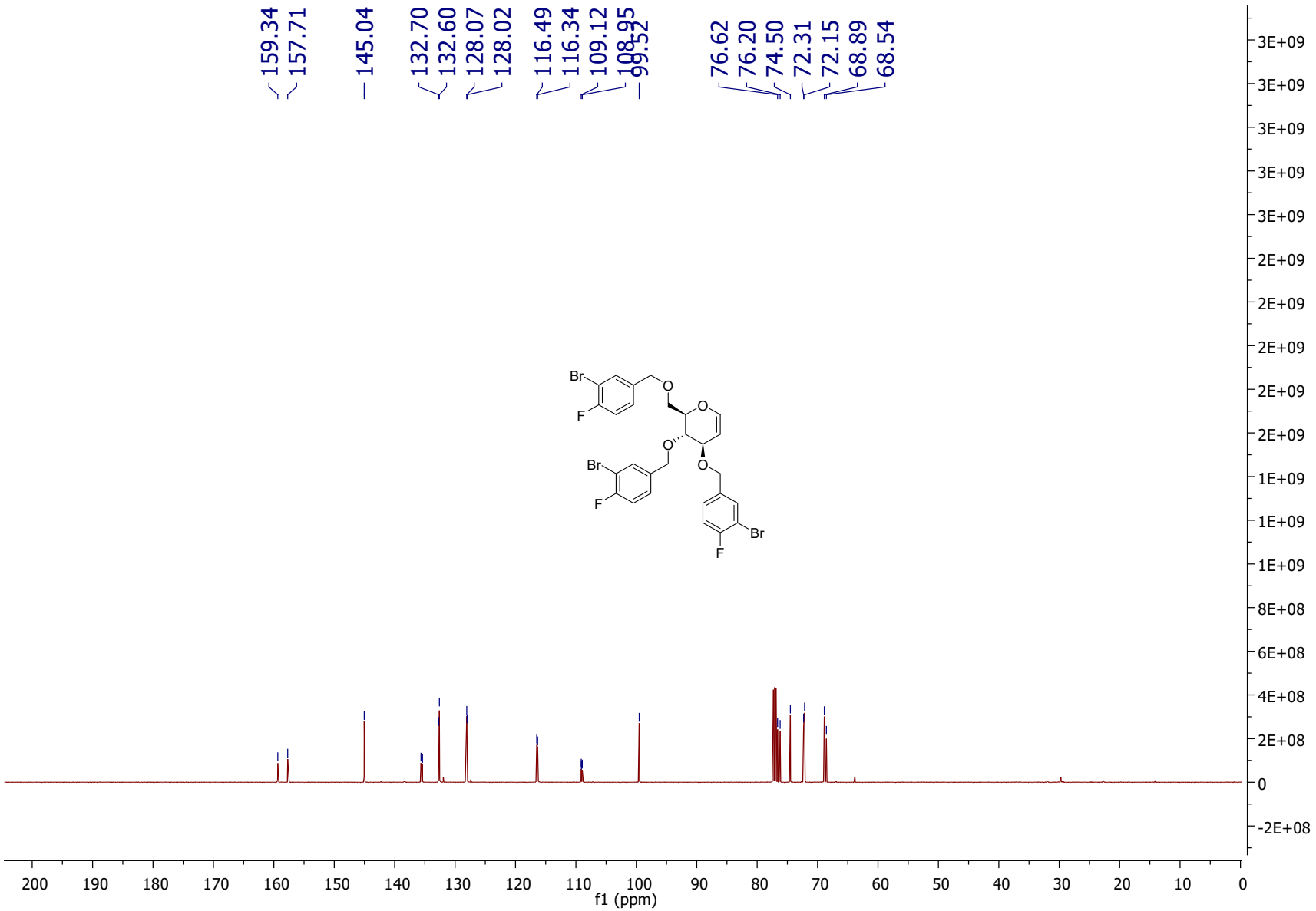


Fig-^{13}C NMR (151 MHz, $CDCl_3$) of compound **1m**

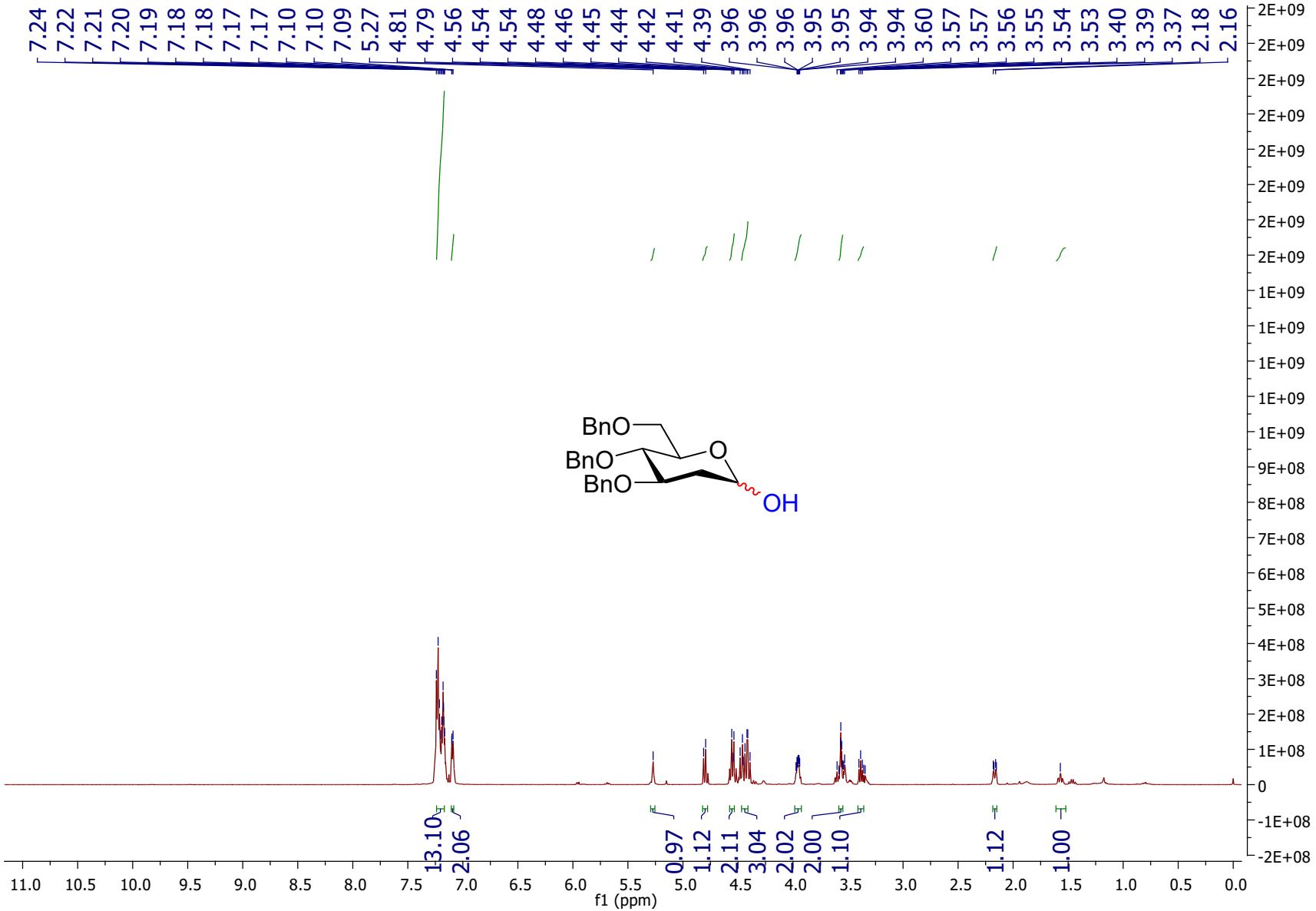


Fig- ^{1}H NMR (600 MHz, $CDCl_3$) of compound **2a**

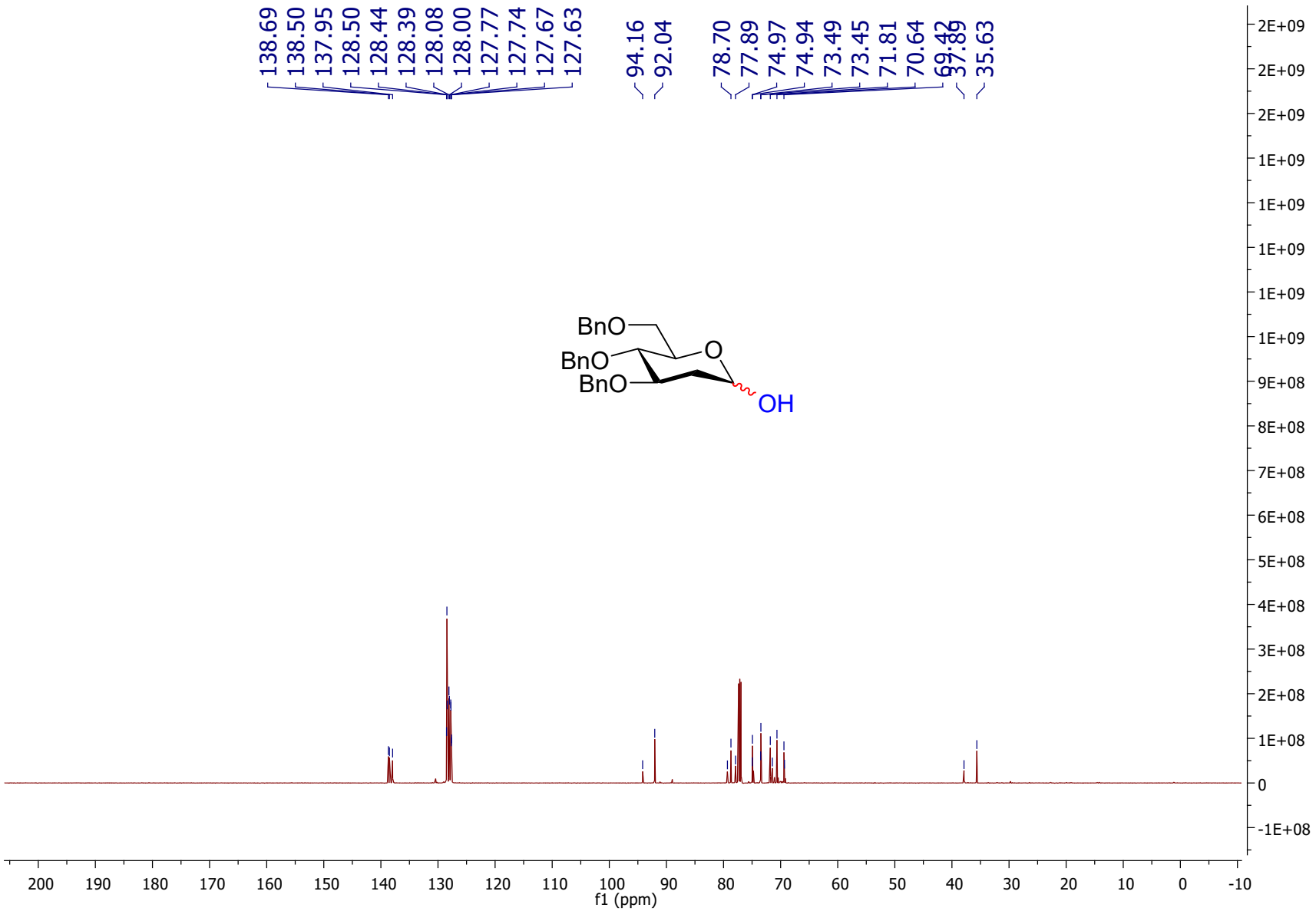


Fig-^{13}C NMR (151 MHz, $CDCl_3$) of compound **2a**

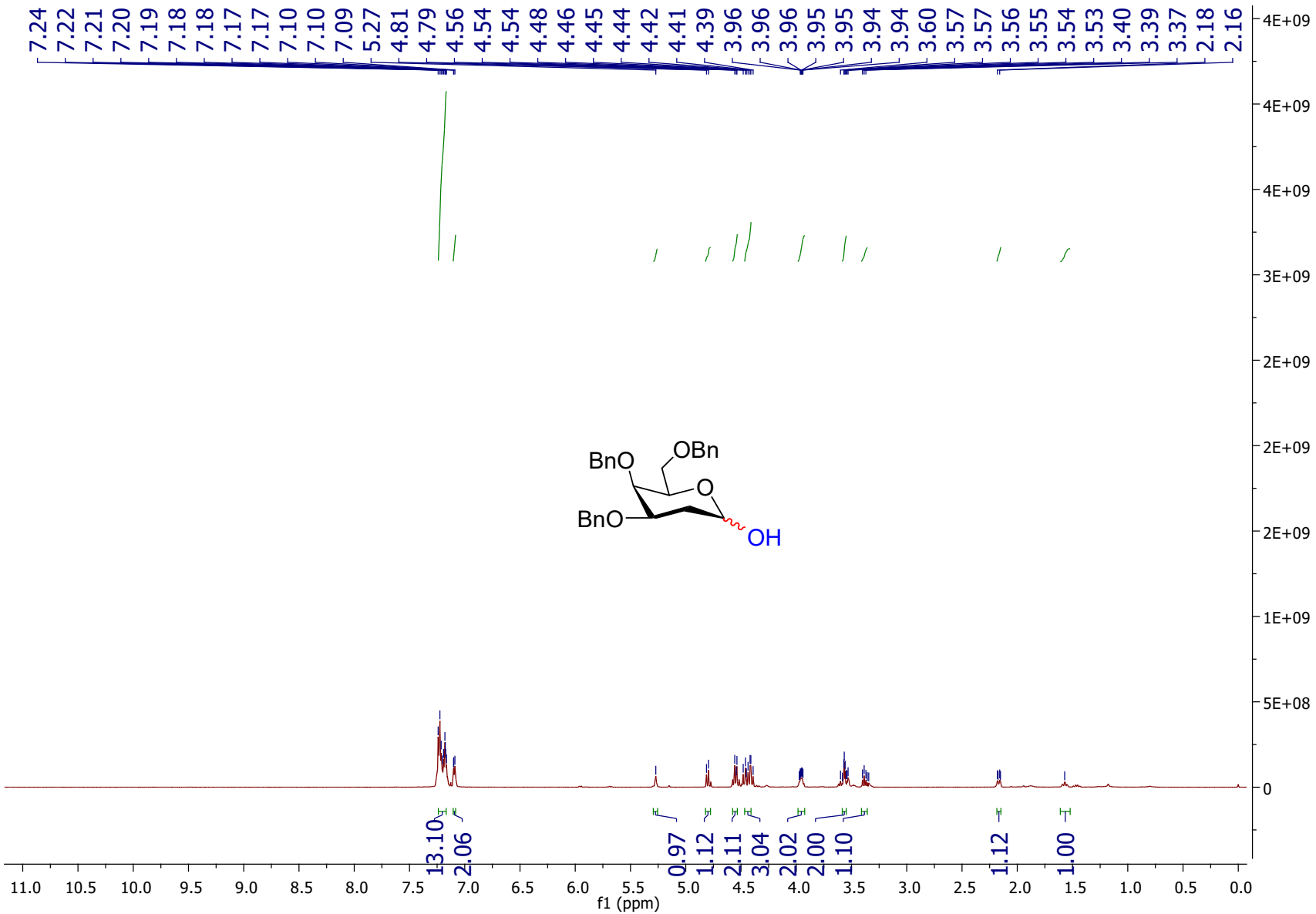


Fig- ^{1}H NMR (600 MHz, $CDCl_3$) of compound **2b**

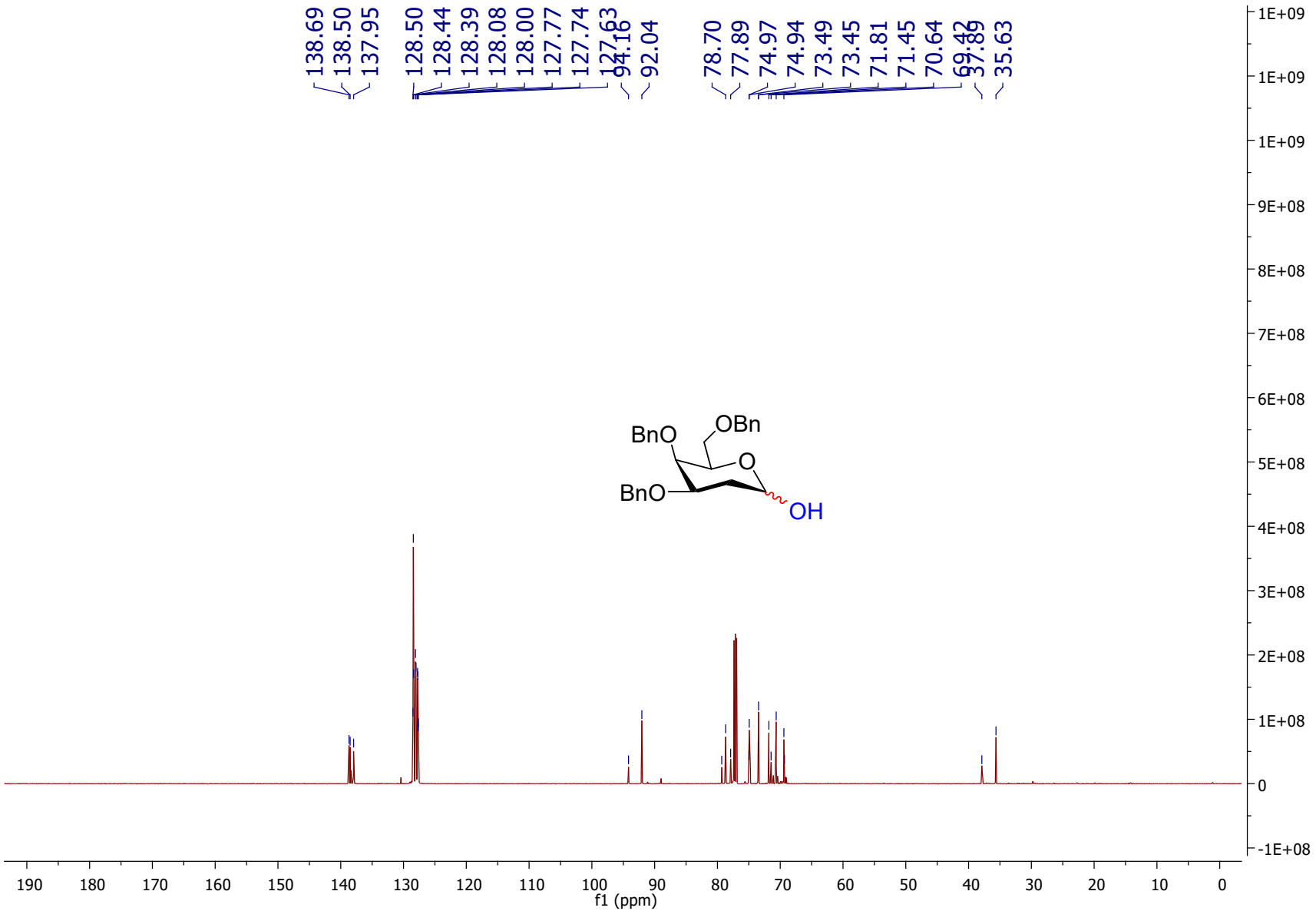


Fig-^{13}C NMR (151 MHz, $CDCl_3$) of compound **2b**

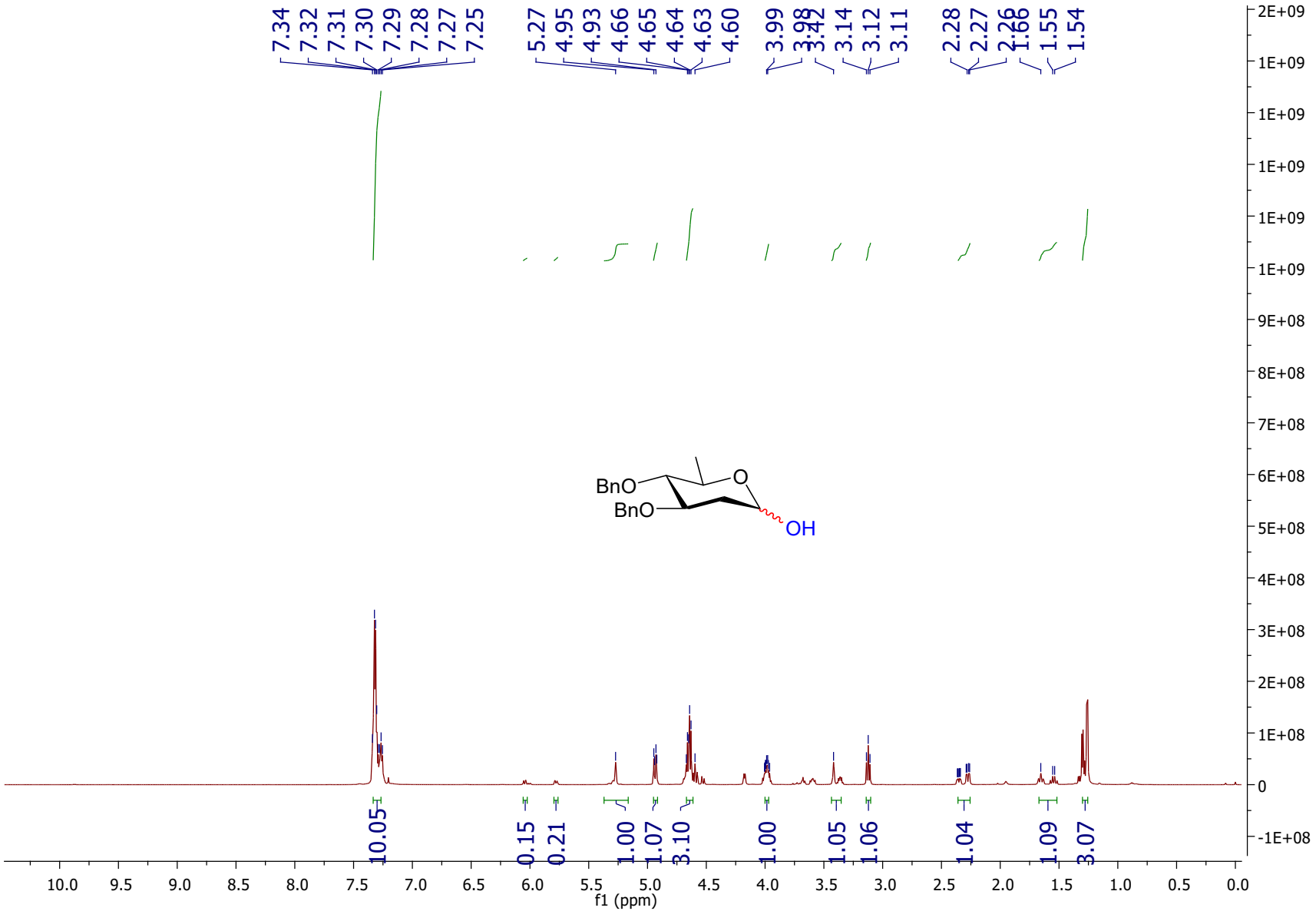


Fig- ^{1}H NMR (600 MHz, $CDCl_3$) of compound **2c**

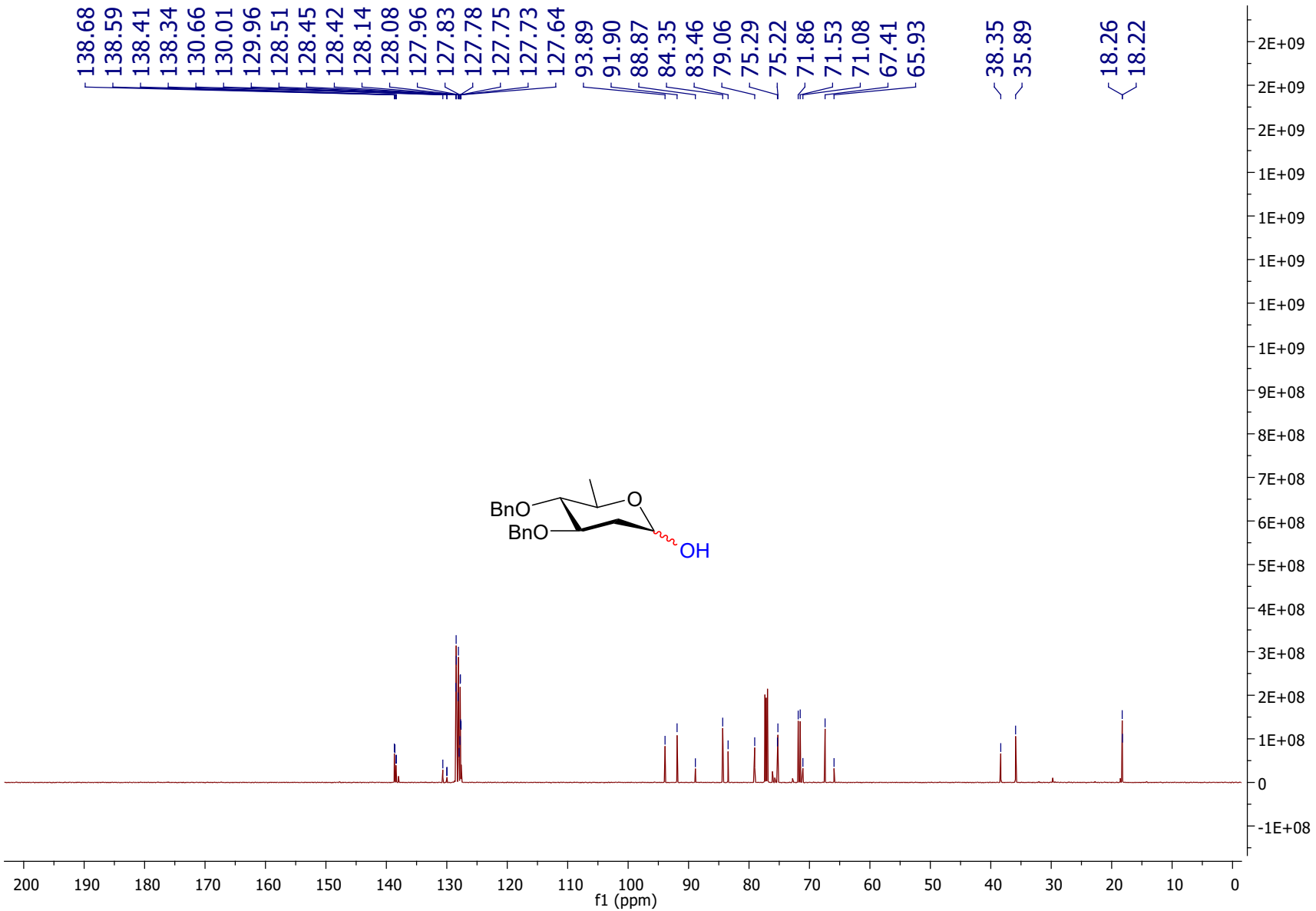


Fig-^{13}C NMR (151 MHz, $CDCl_3$) of compound **2c**

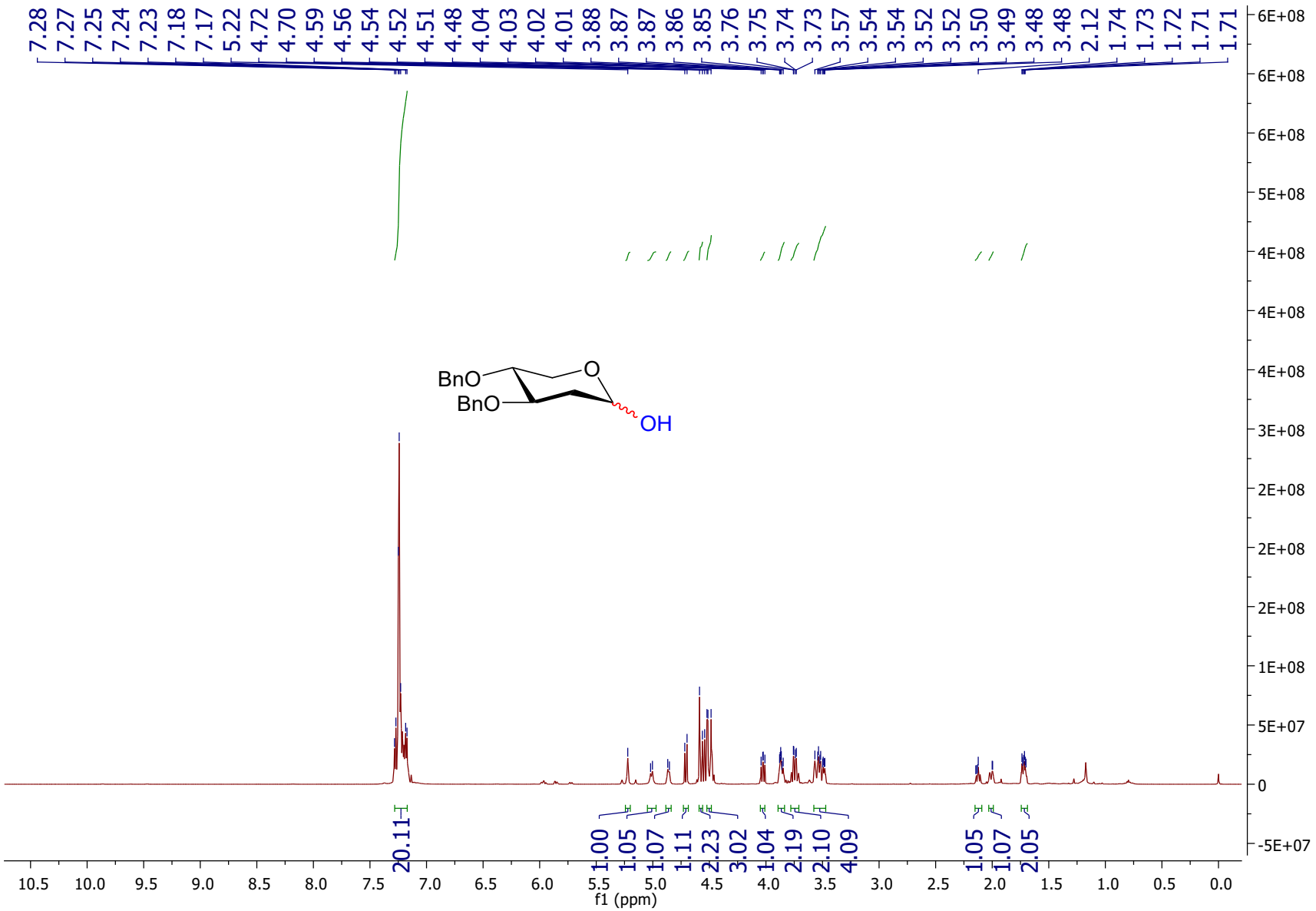


Fig- ^{1}H NMR (600 MHz, $CDCl_3$) of compound **2d**

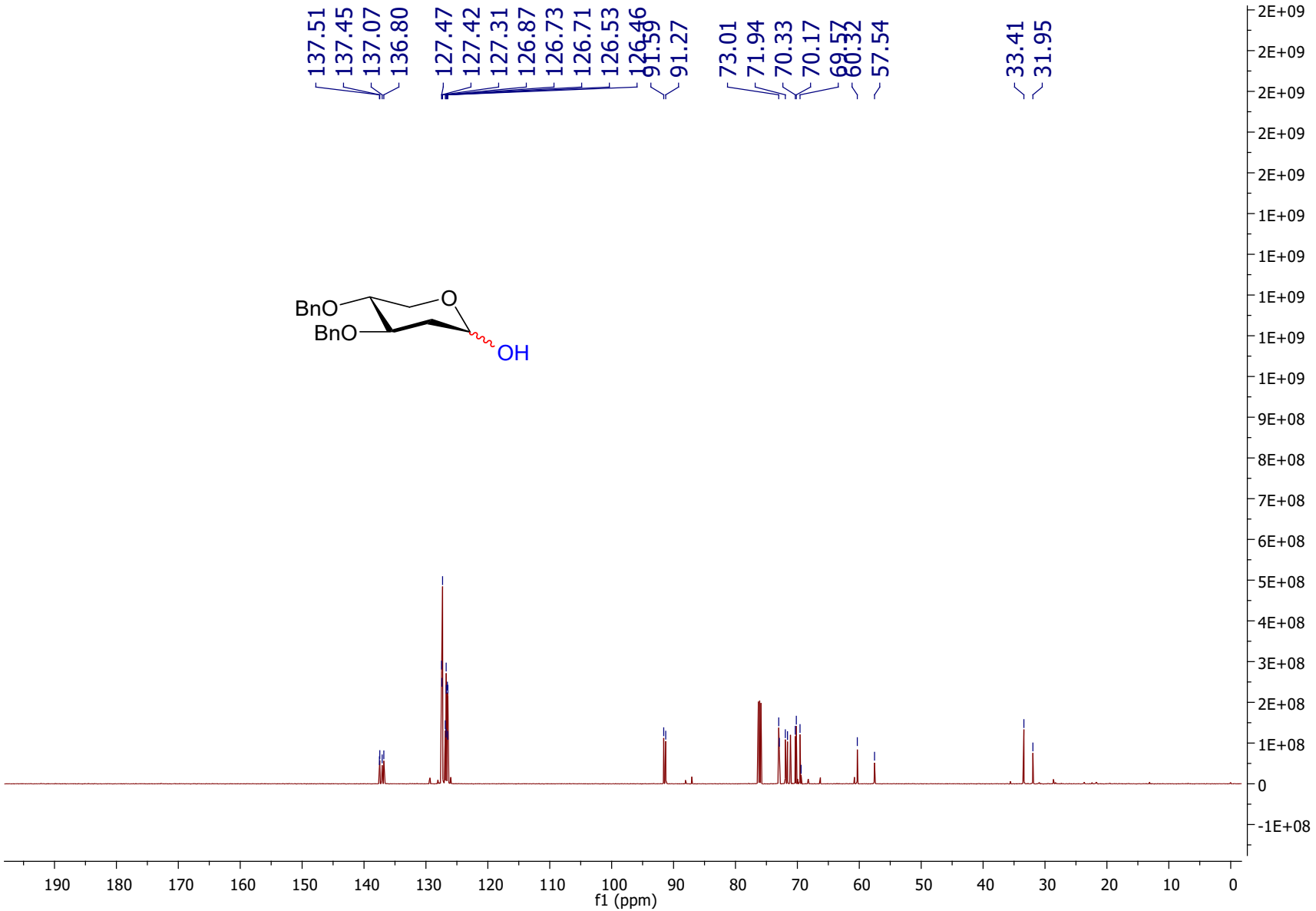


Fig-^{13}C NMR (151 MHz, $CDCl_3$) of compound **2d**

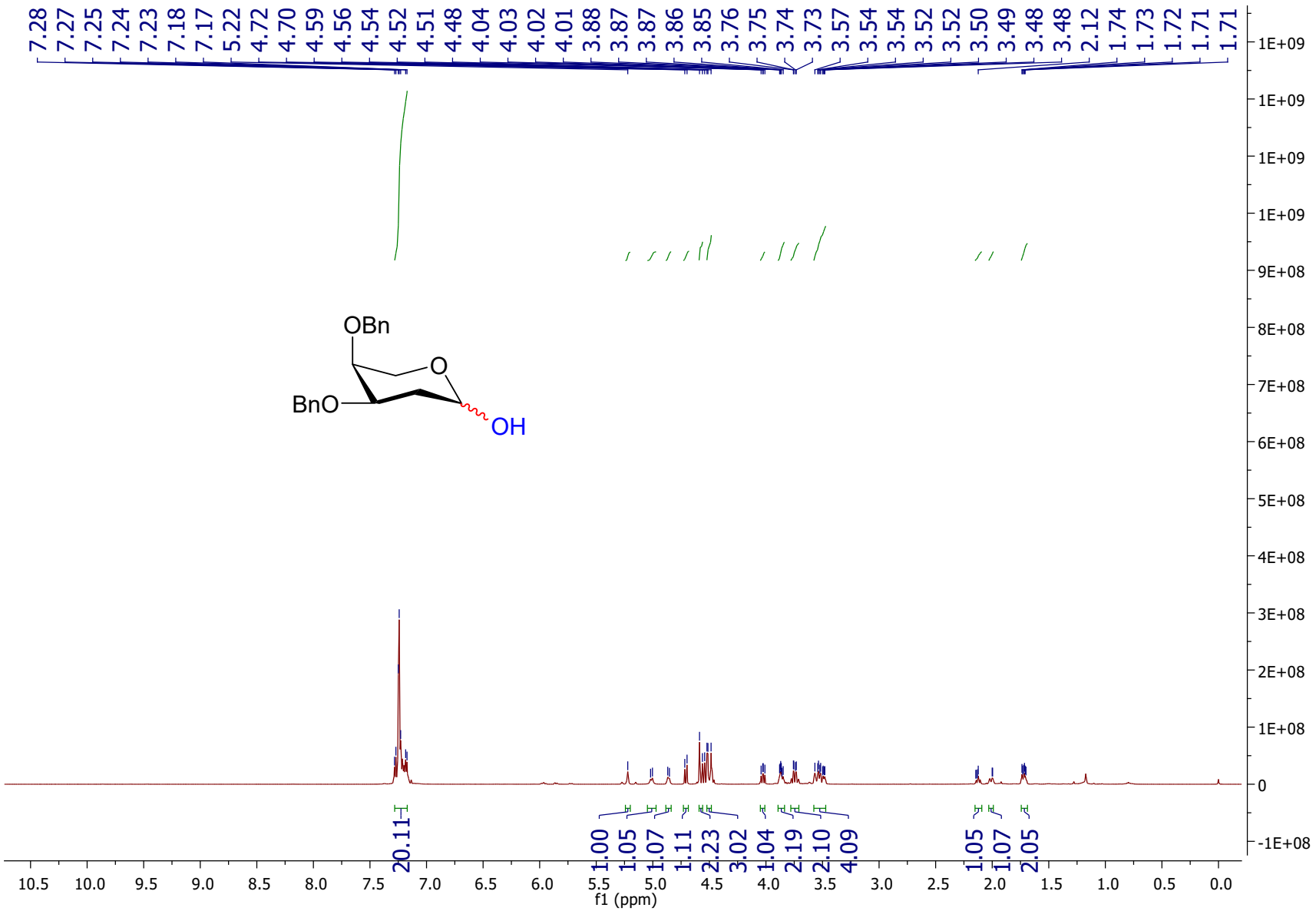


Fig- ^{1}H NMR (600 MHz, $CDCl_3$) of compound **2e**

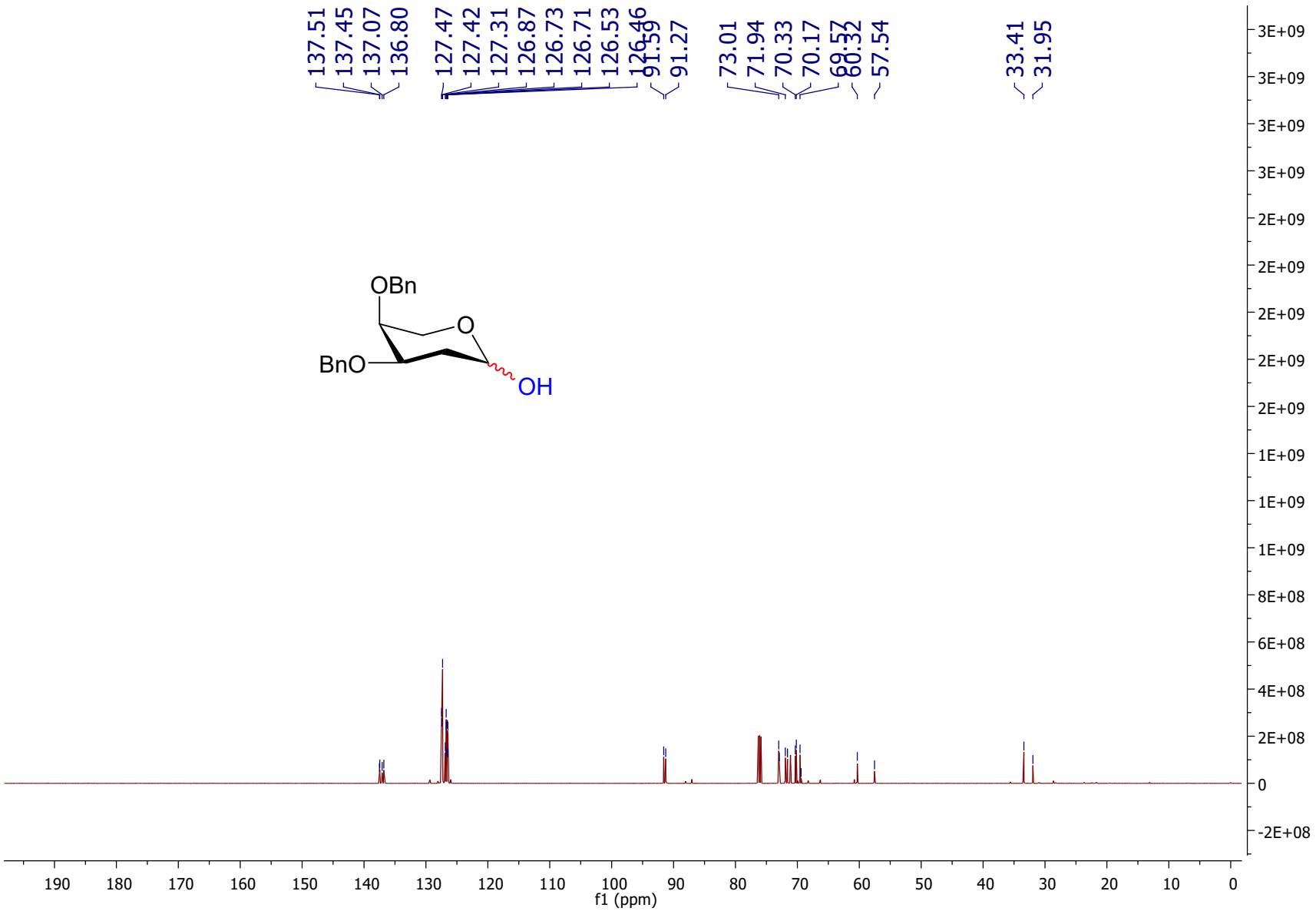


Fig-^{13}C NMR (151 MHz, $CDCl_3$) of compound **2e**

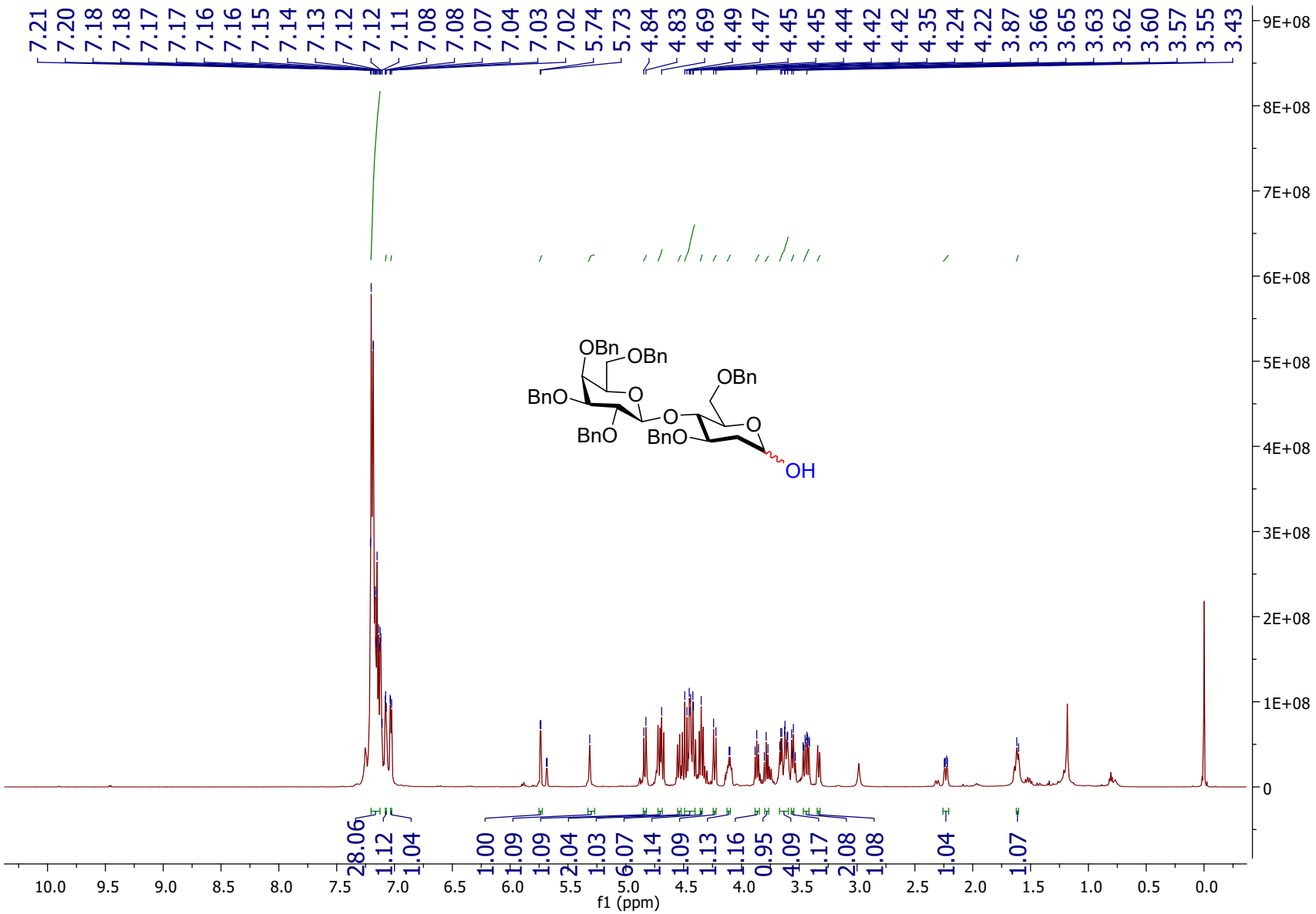


Fig- ^{1}H NMR (600 MHz, $CDCl_3$) of compound **2f**

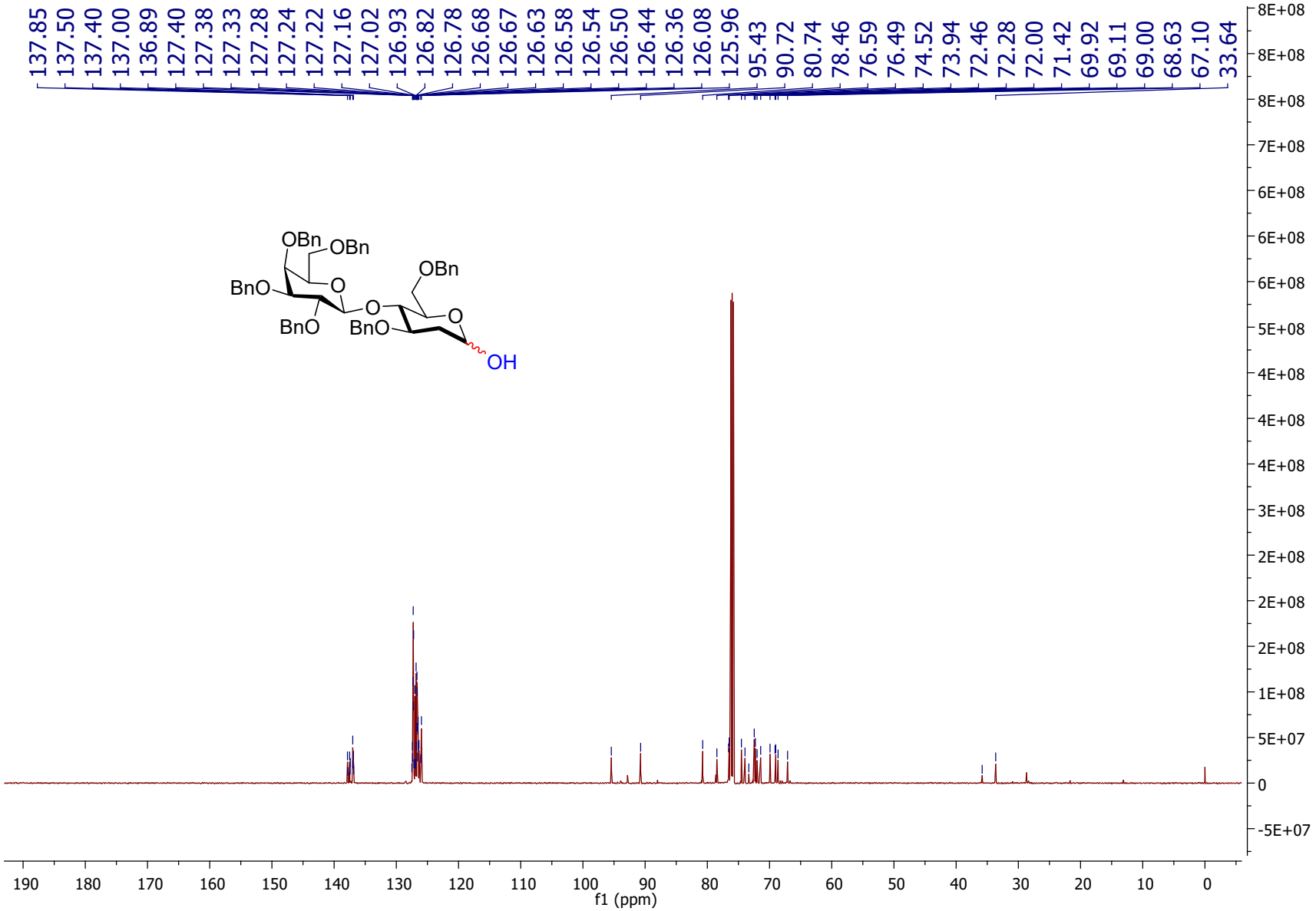


Fig-^{13}C NMR (151 MHz, $CDCl_3$) of compound **2f**

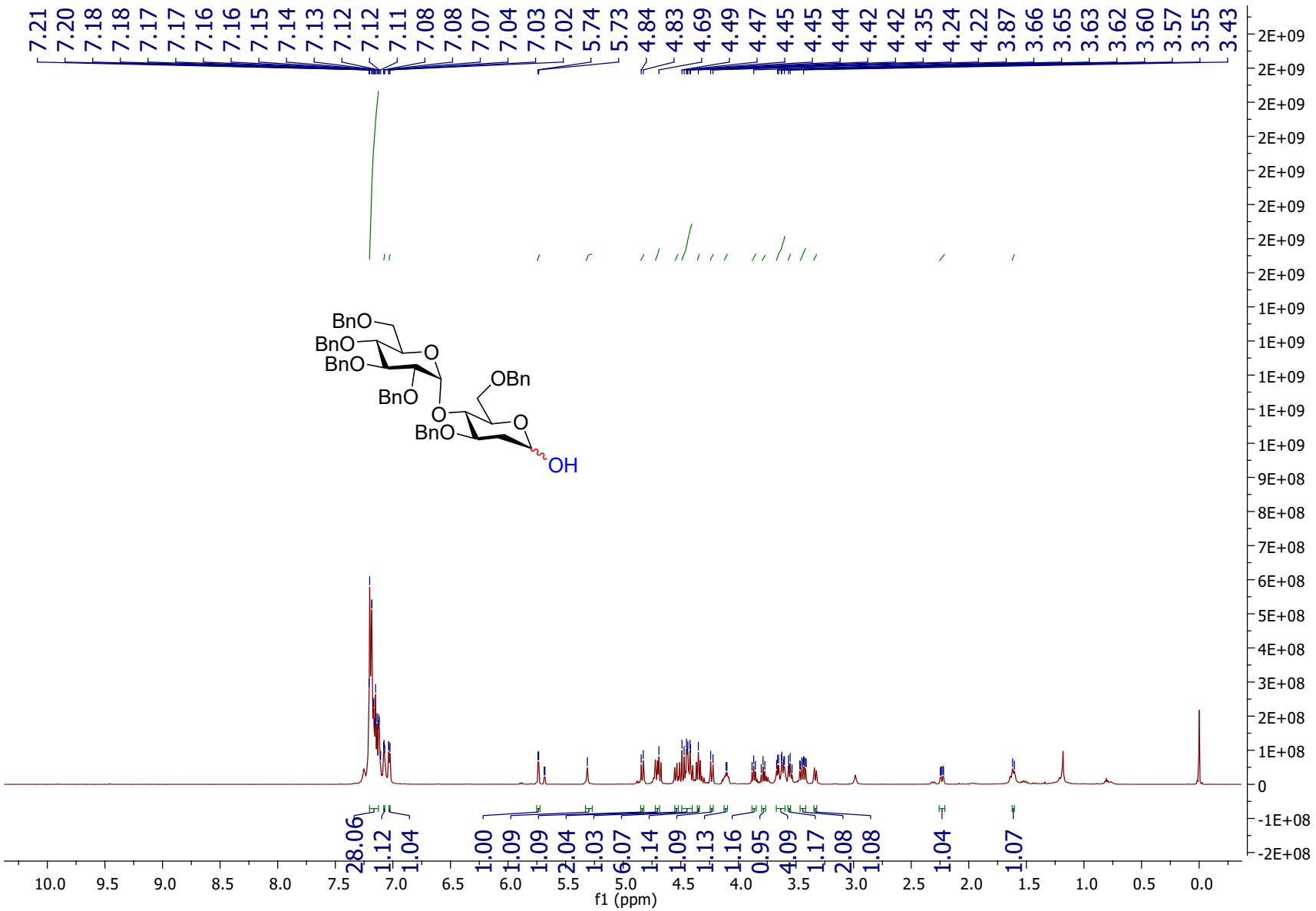


Fig- ^{1}H NMR (600 MHz, $CDCl_3$) of compound **2g**

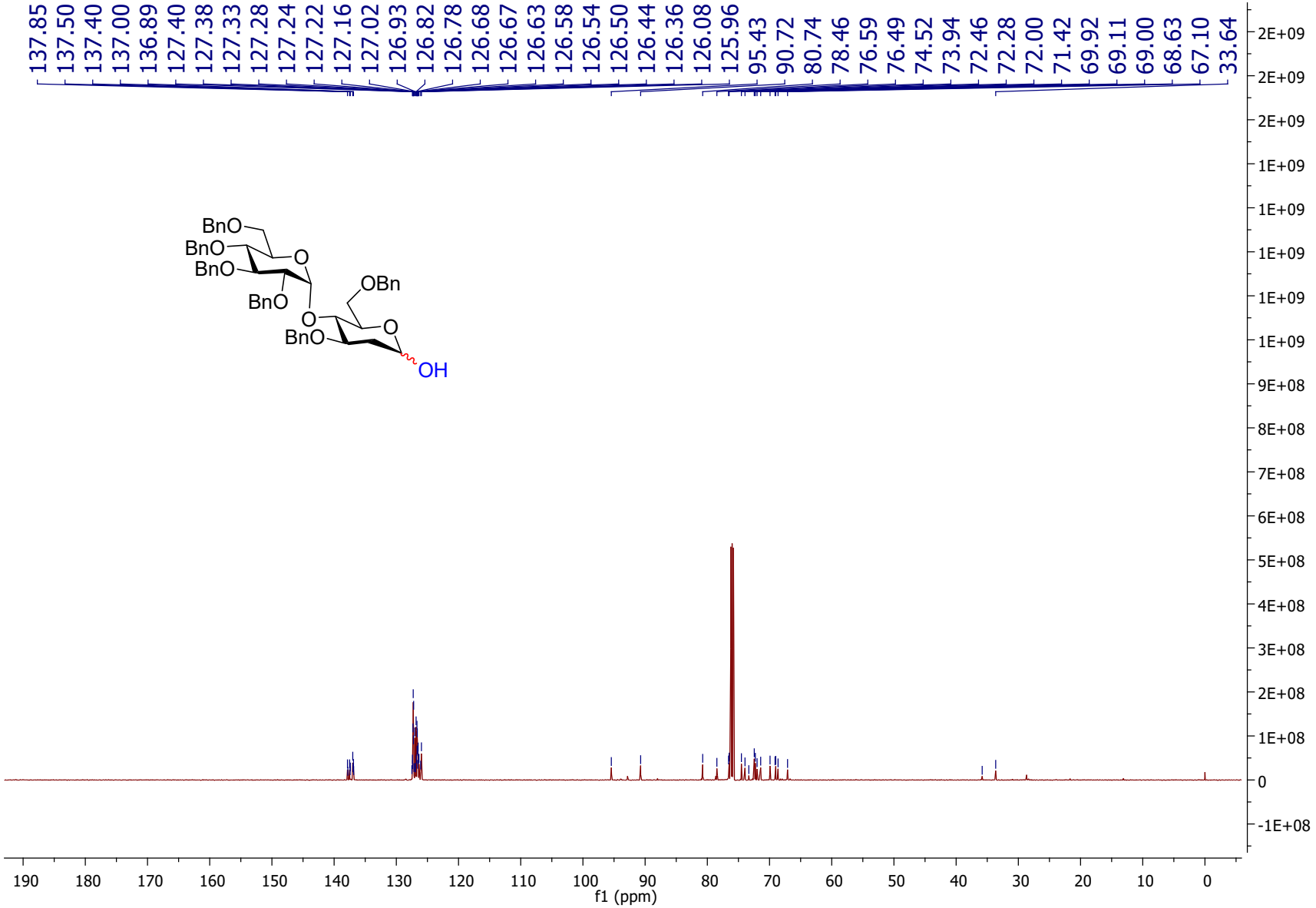


Fig-^{13}C NMR (151 MHz, $CDCl_3$) of compound **2g**

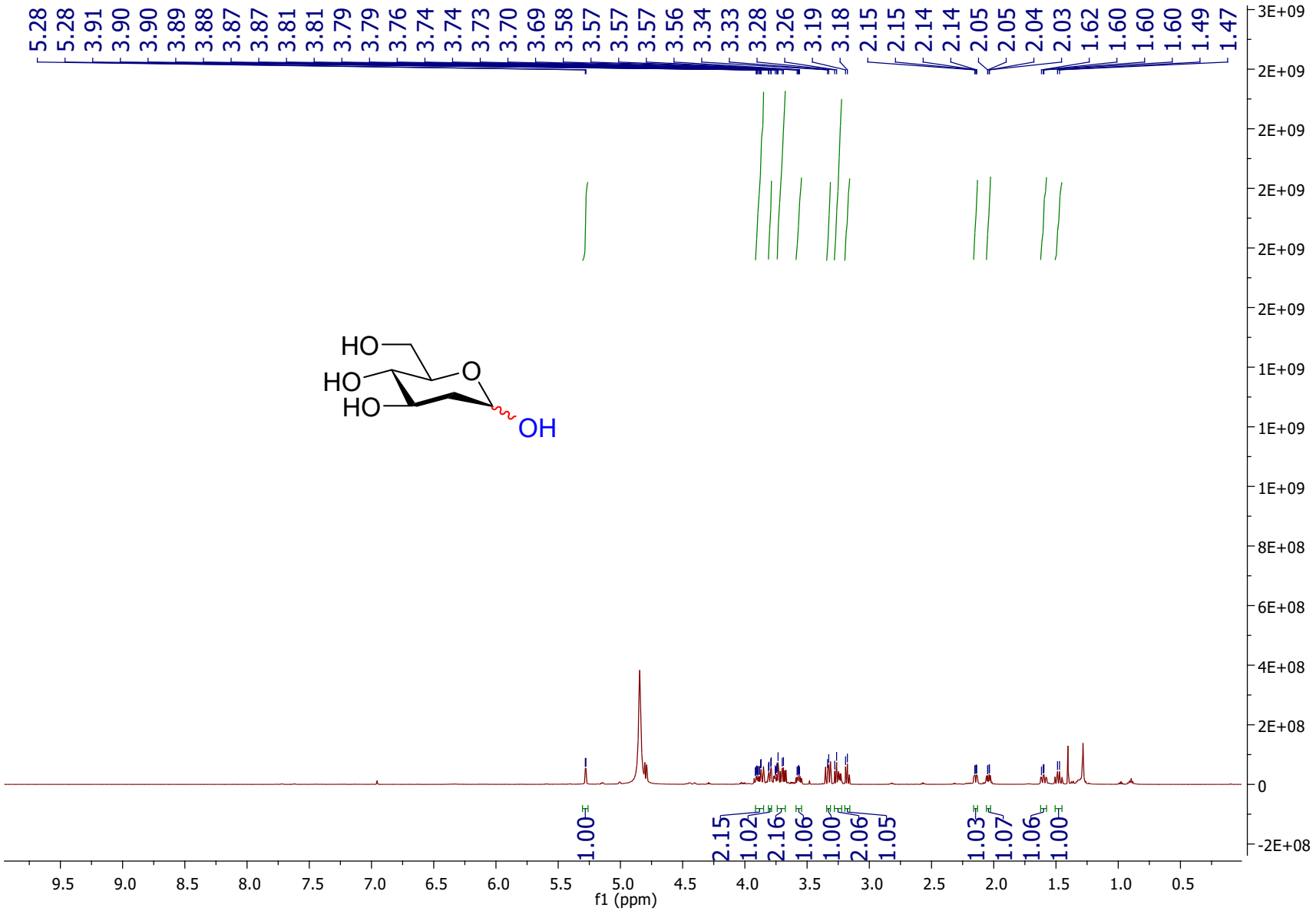


Fig-^{1}H NMR (600 MHz, MeOD) of compound **2h**

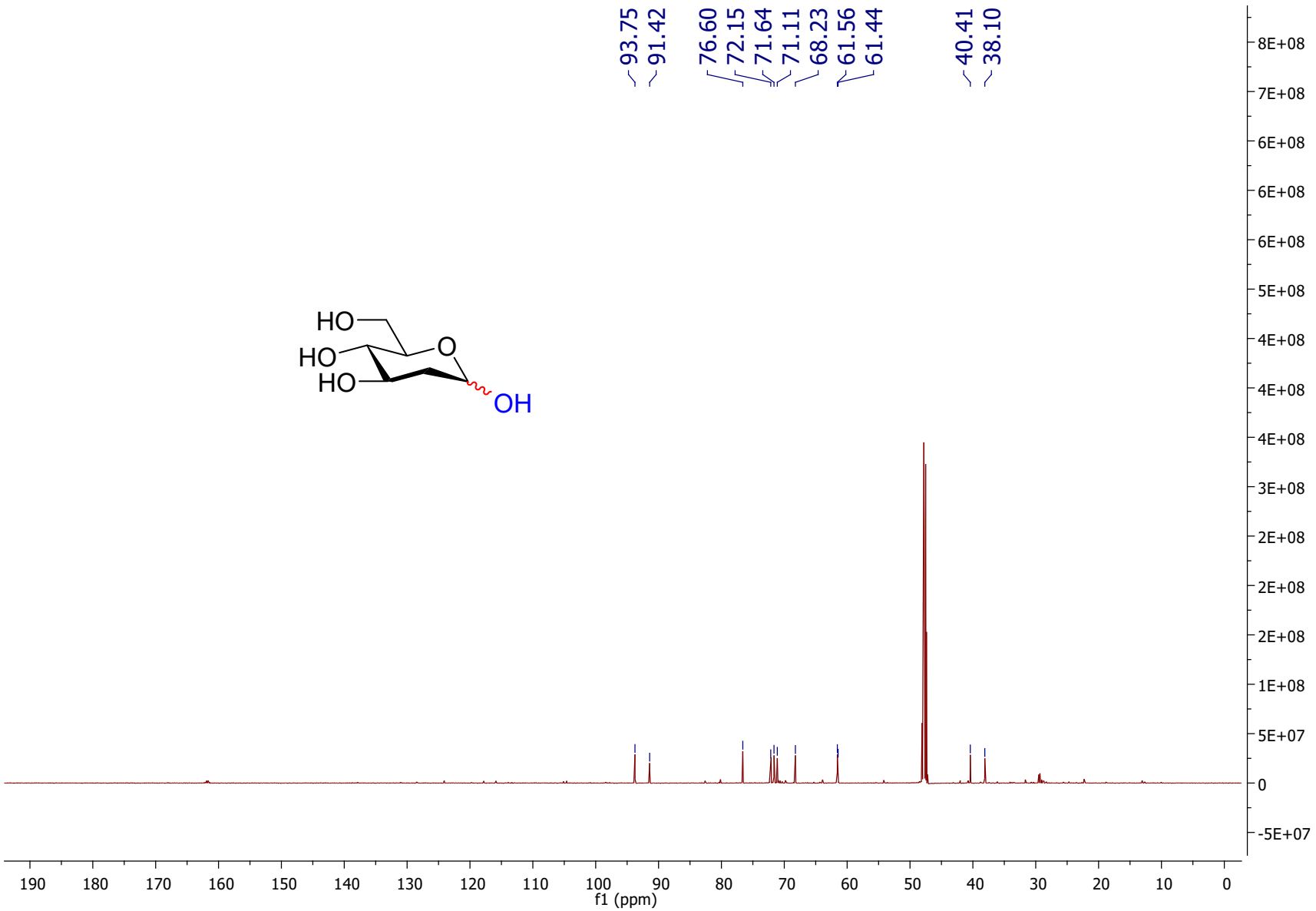


Fig-^{13}C NMR (151 MHz, MeOD) of compound **2h**

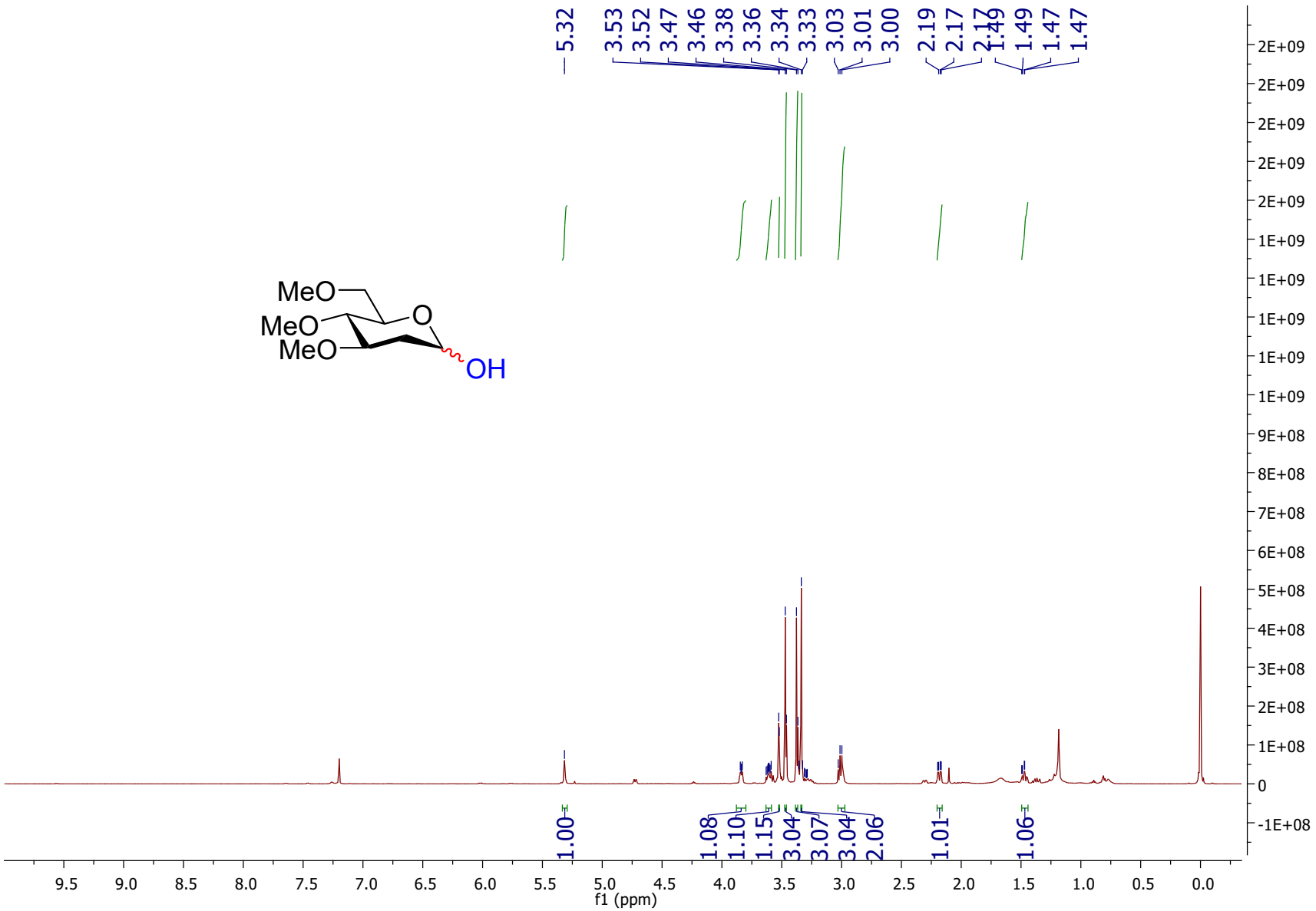


Fig- ^{1}H NMR (600 MHz, $CDCl_3$) of compound **2i**

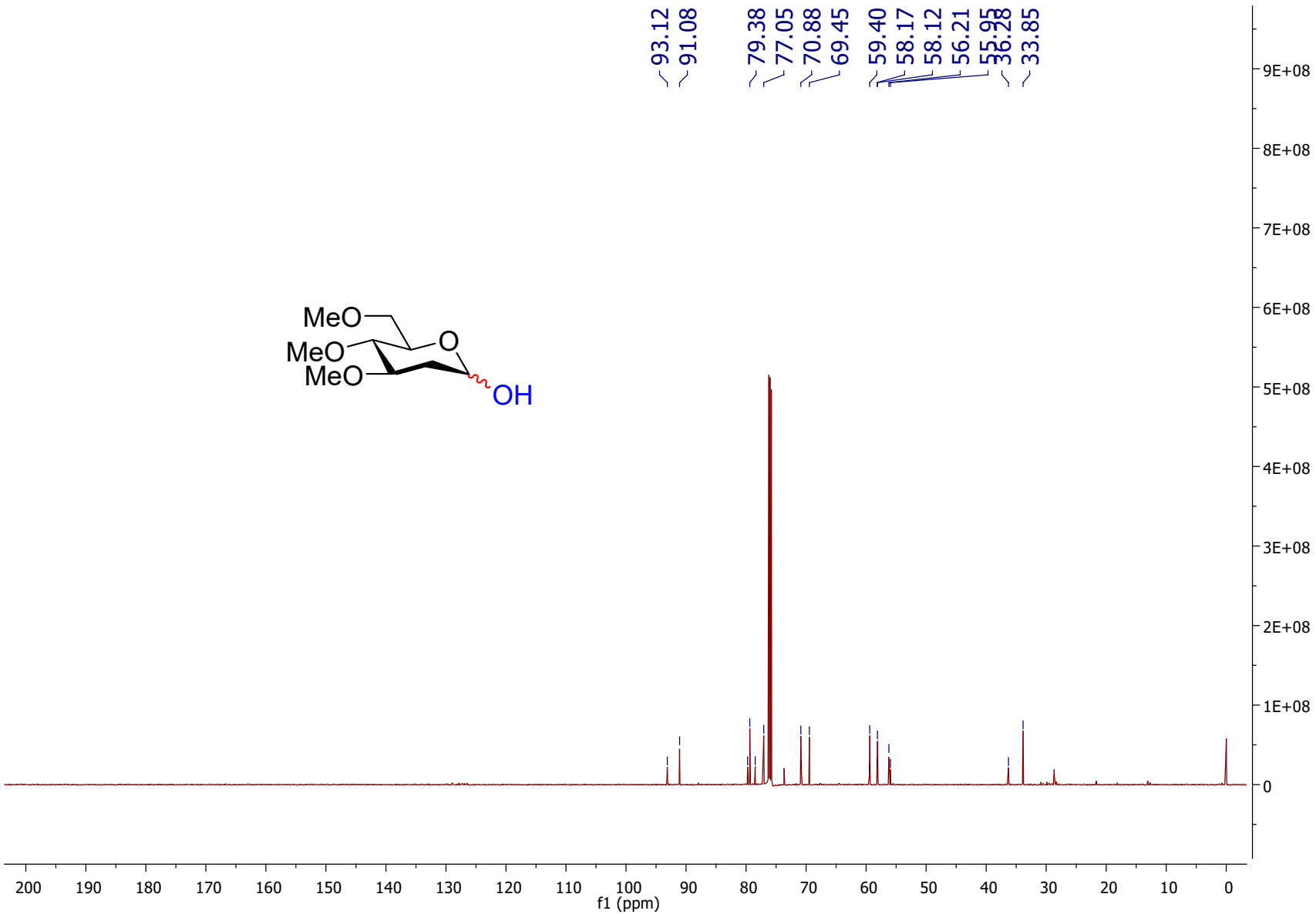


Fig-^{13}C NMR (151 MHz, $CDCl_3$) of compound **2i**

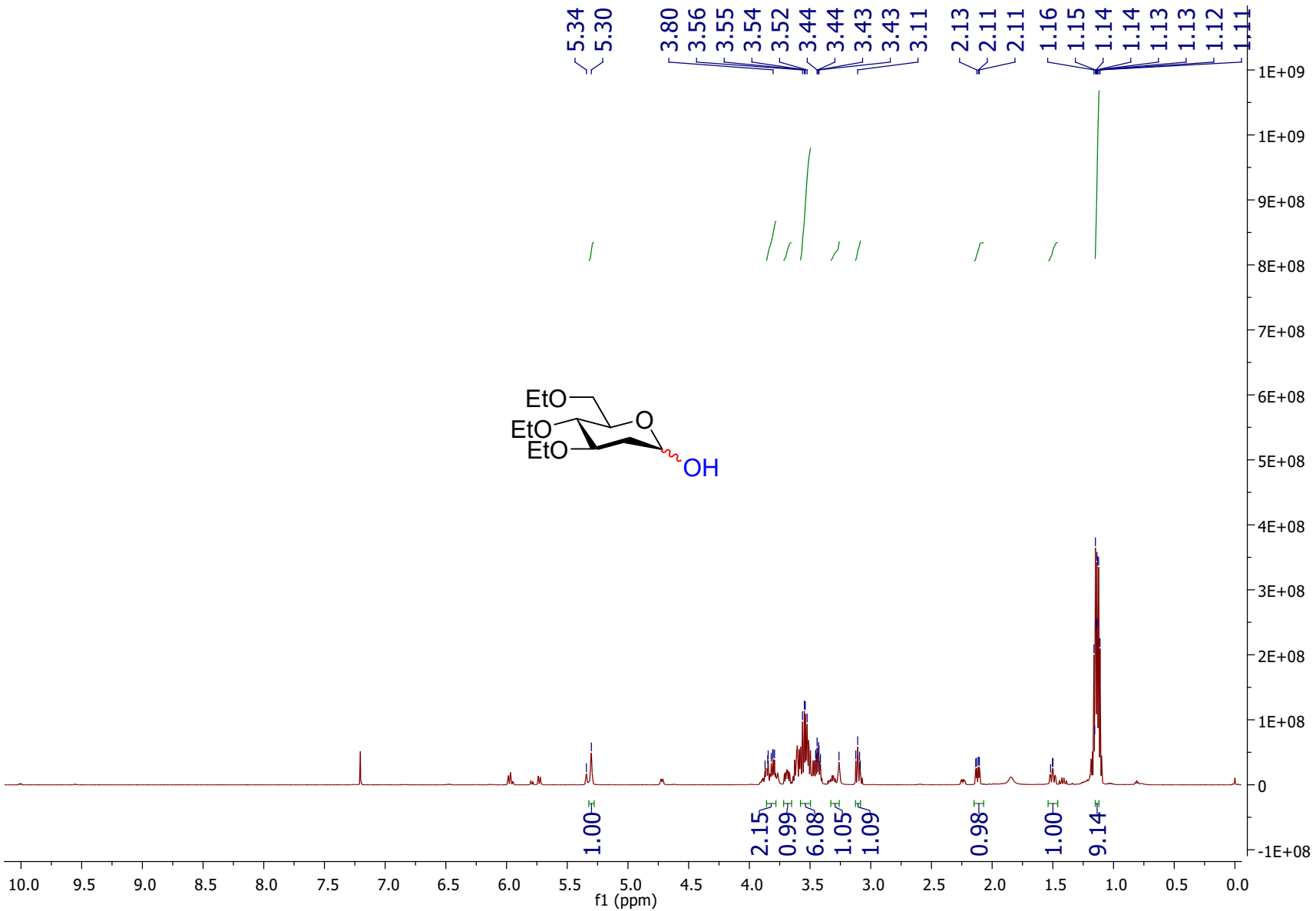


Fig- ^{1}H NMR (600 MHz, $CDCl_3$) of compound **2j**

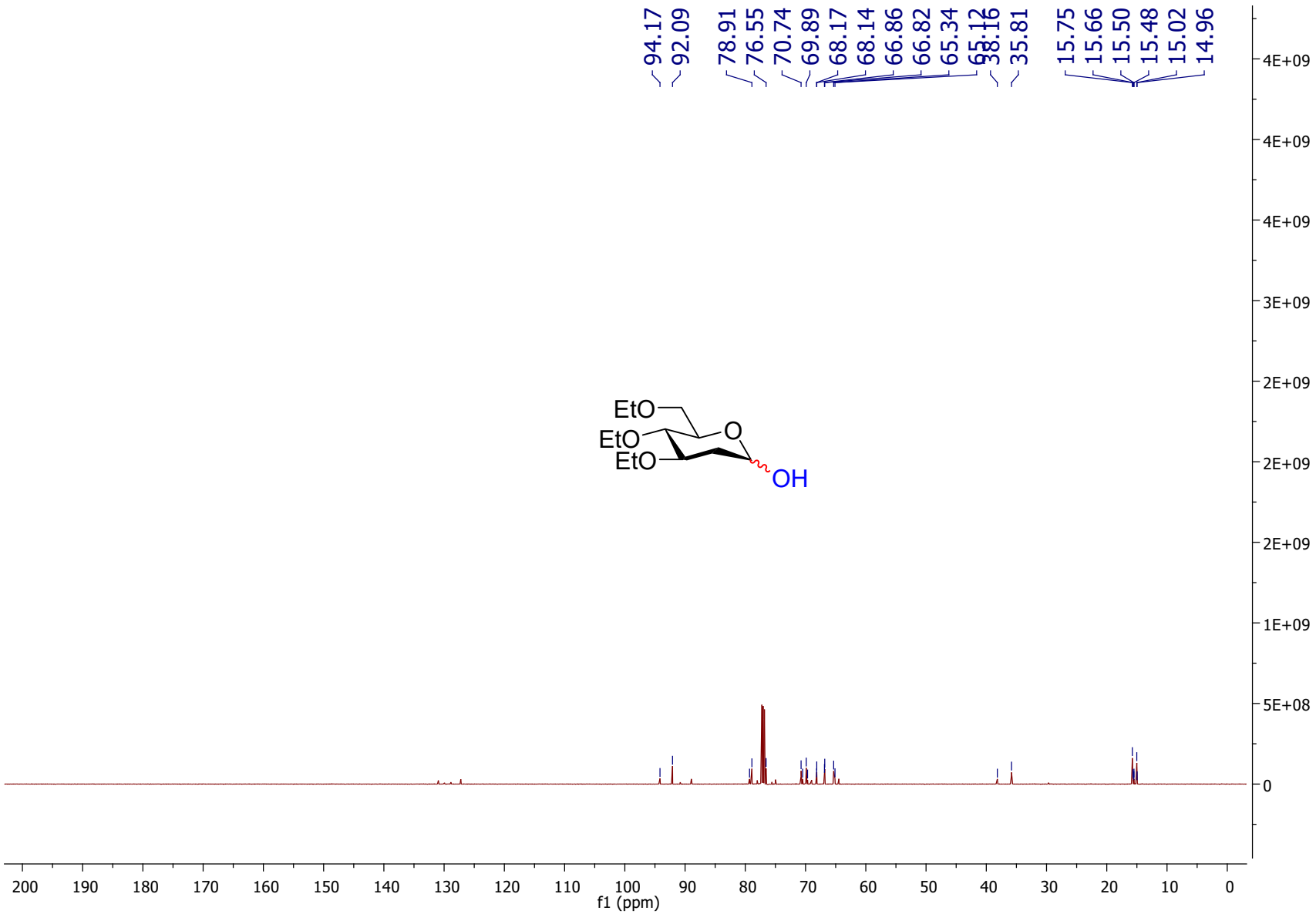


Fig-^{13}C NMR (151 MHz, $CDCl_3$) of compound **2j**

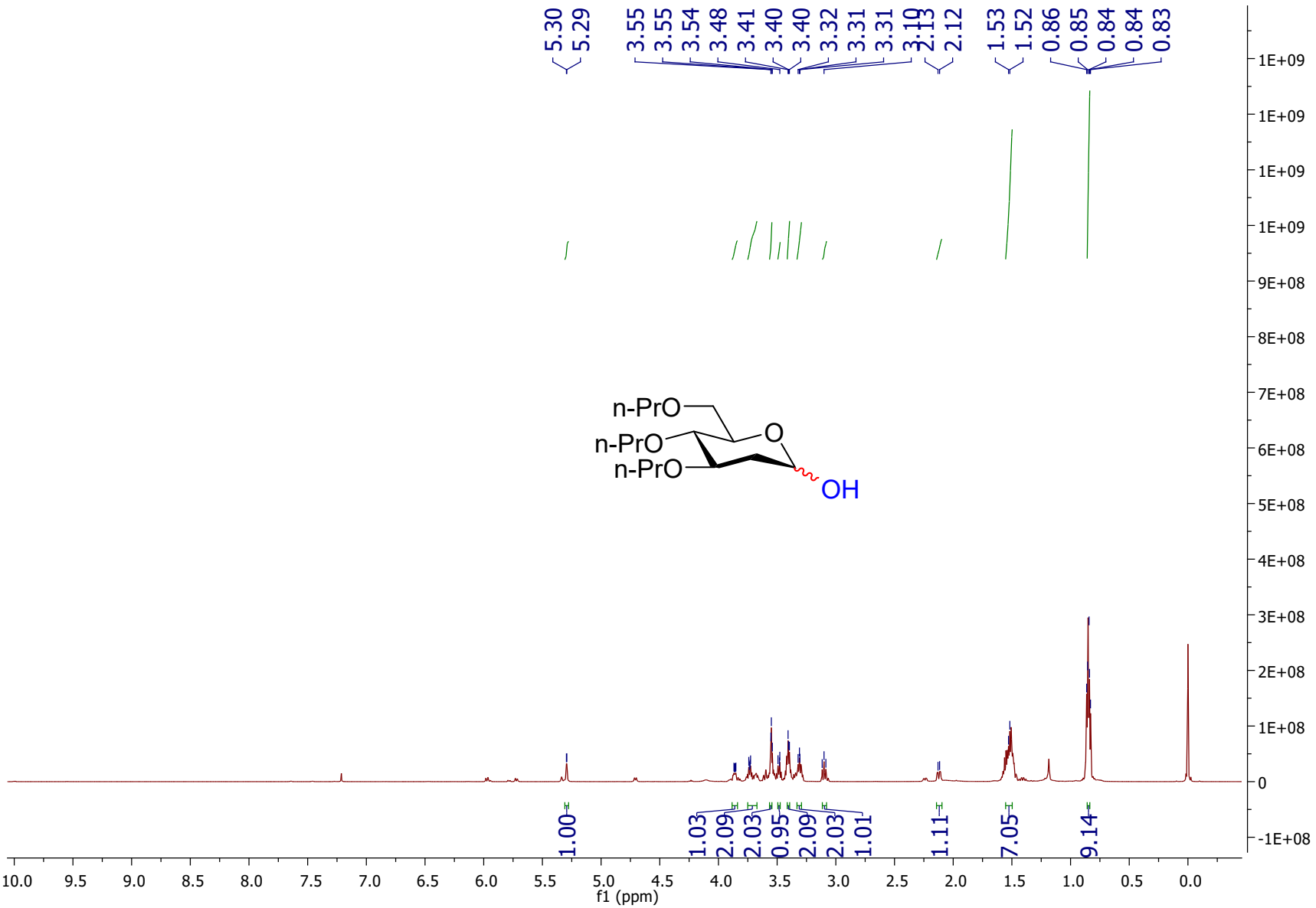


Fig- ^{1}H NMR (600 MHz, $CDCl_3$) of compound **2k**

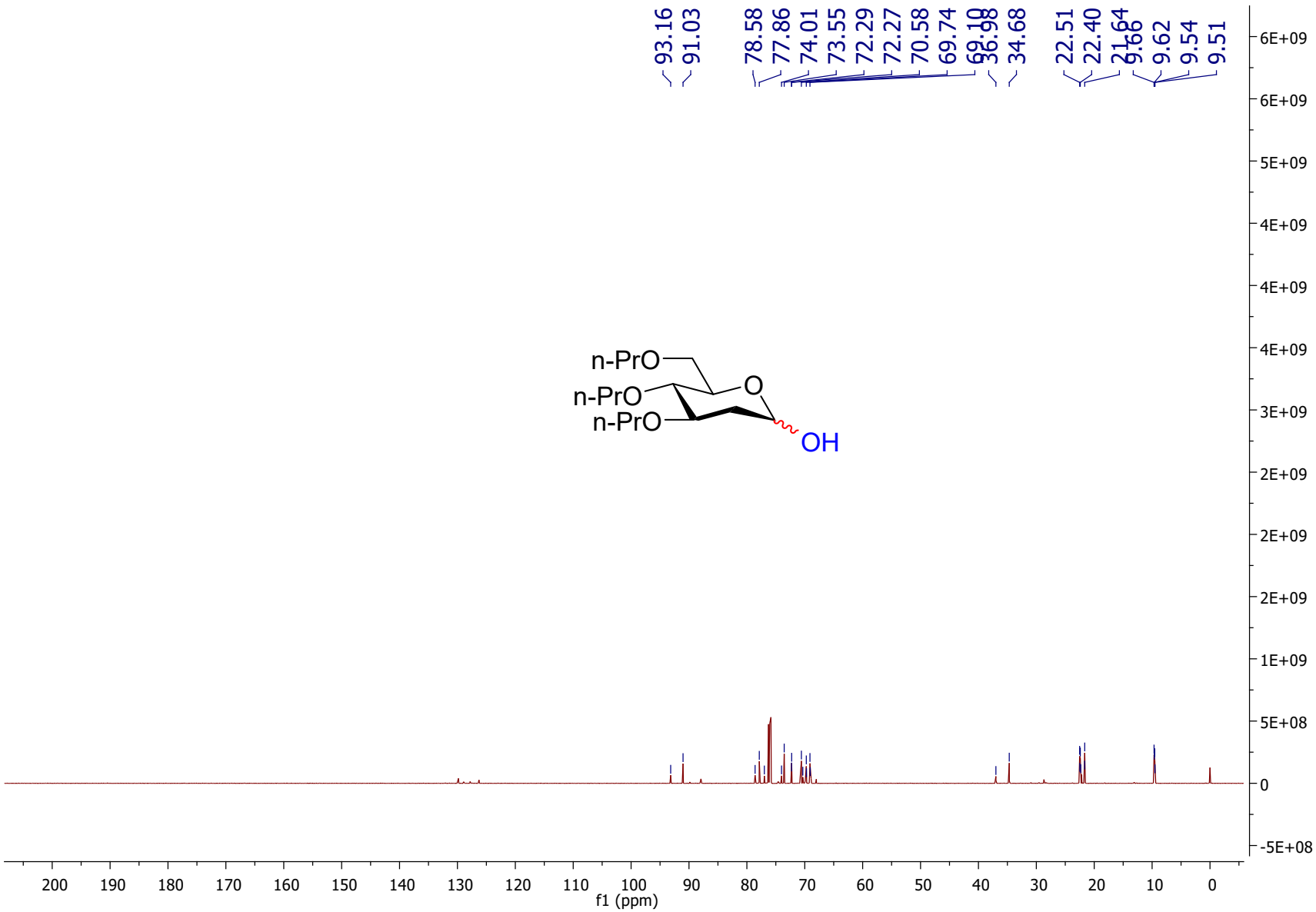


Fig-^{13}C NMR (151 MHz, $CDCl_3$) of compound **2k**

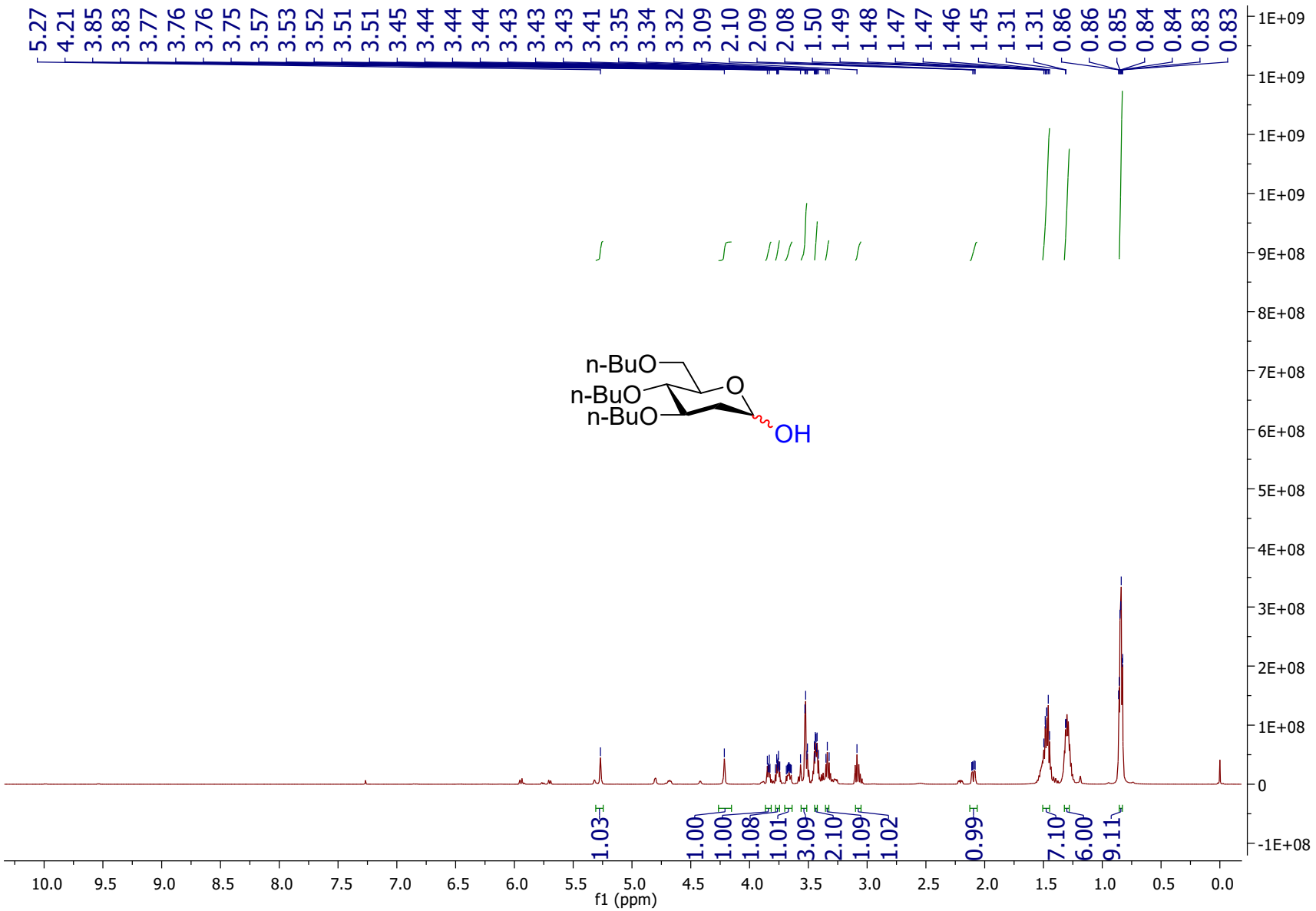


Fig- ^{1}H NMR (600 MHz, $CDCl_3$) of compound**2l**

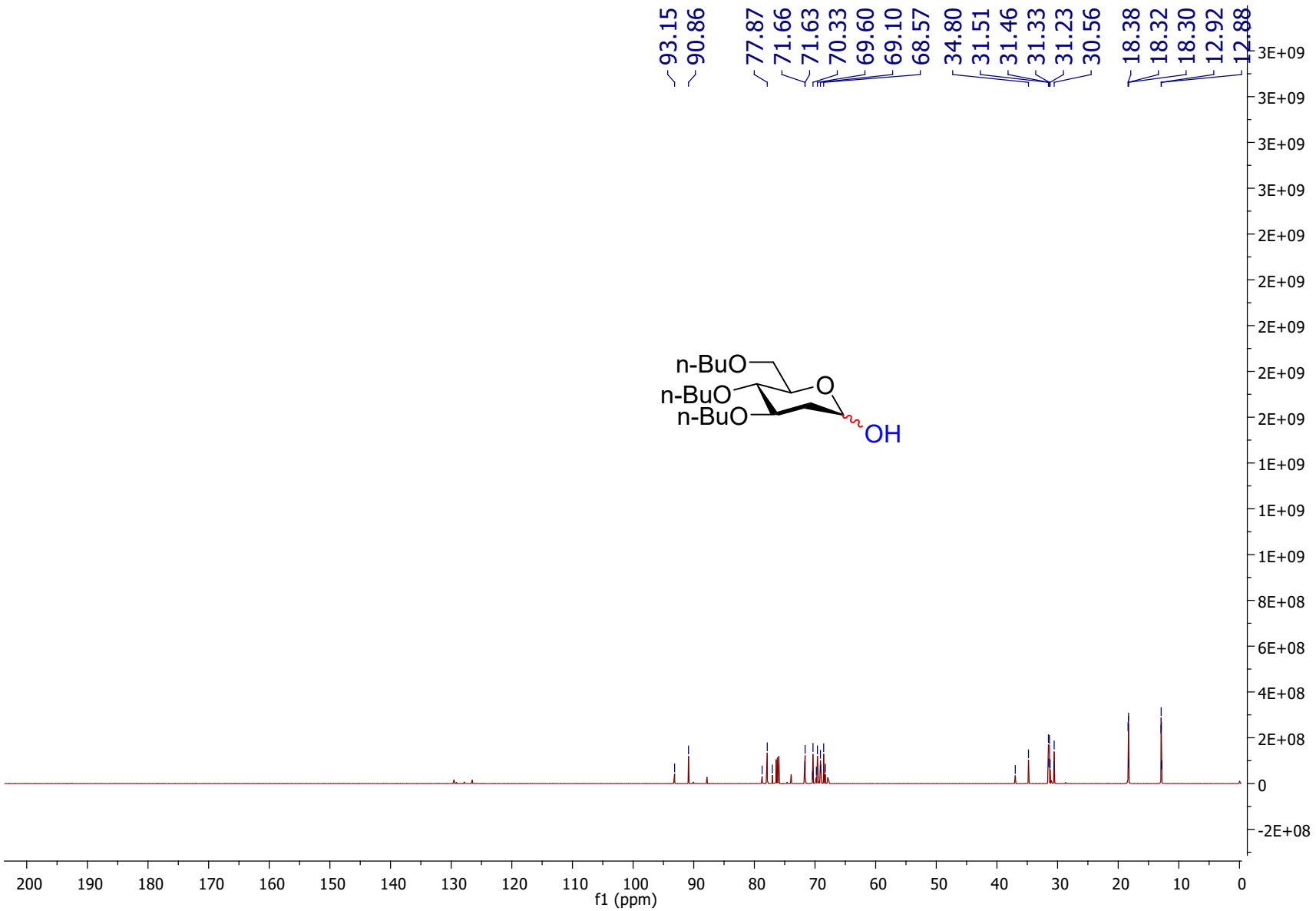


Fig-^{13}C NMR (151 MHz, $CDCl_3$) of compound **2l**

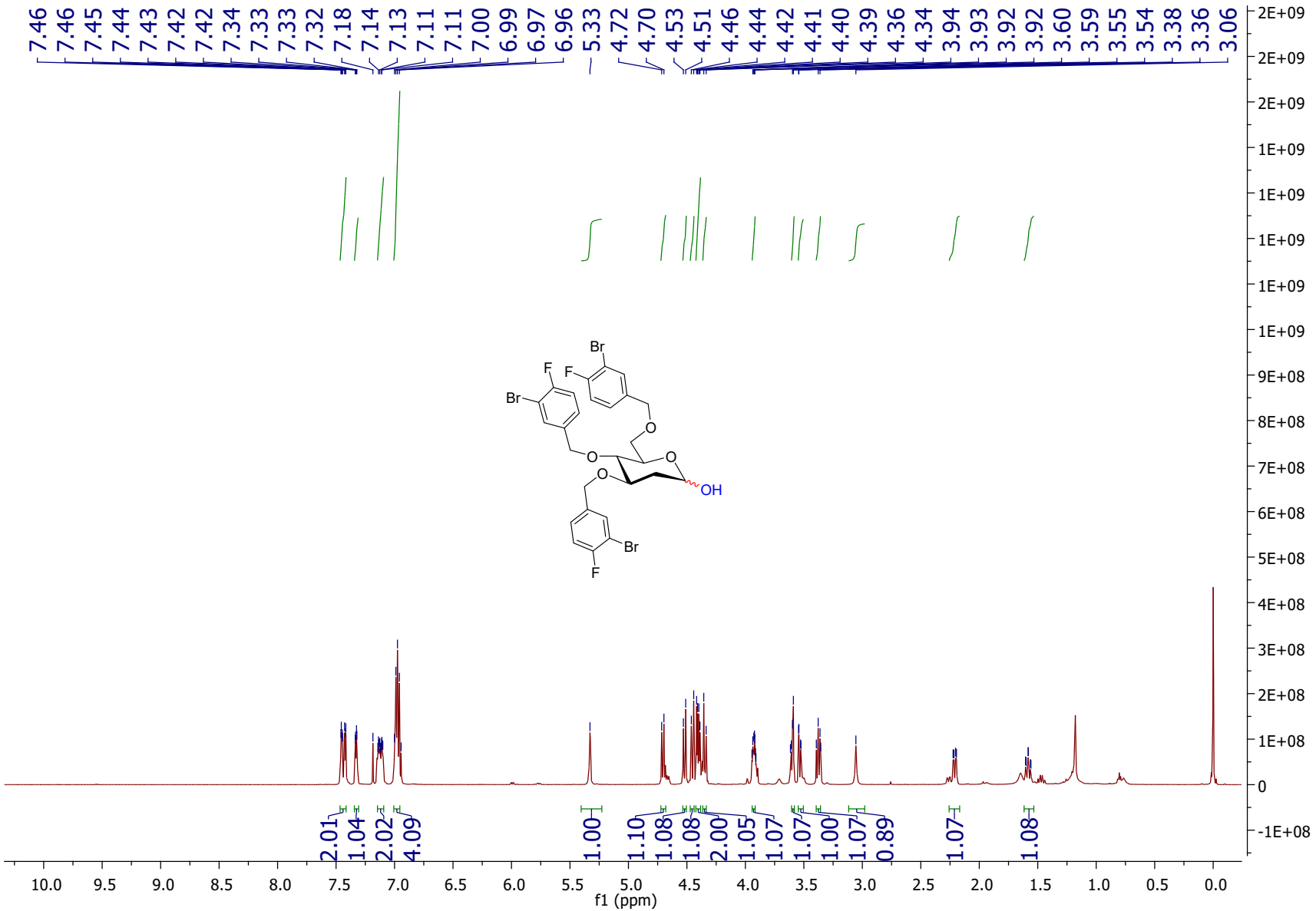


Fig- ^{1}H NMR (600 MHz, $CDCl_3$) of compound **2m**

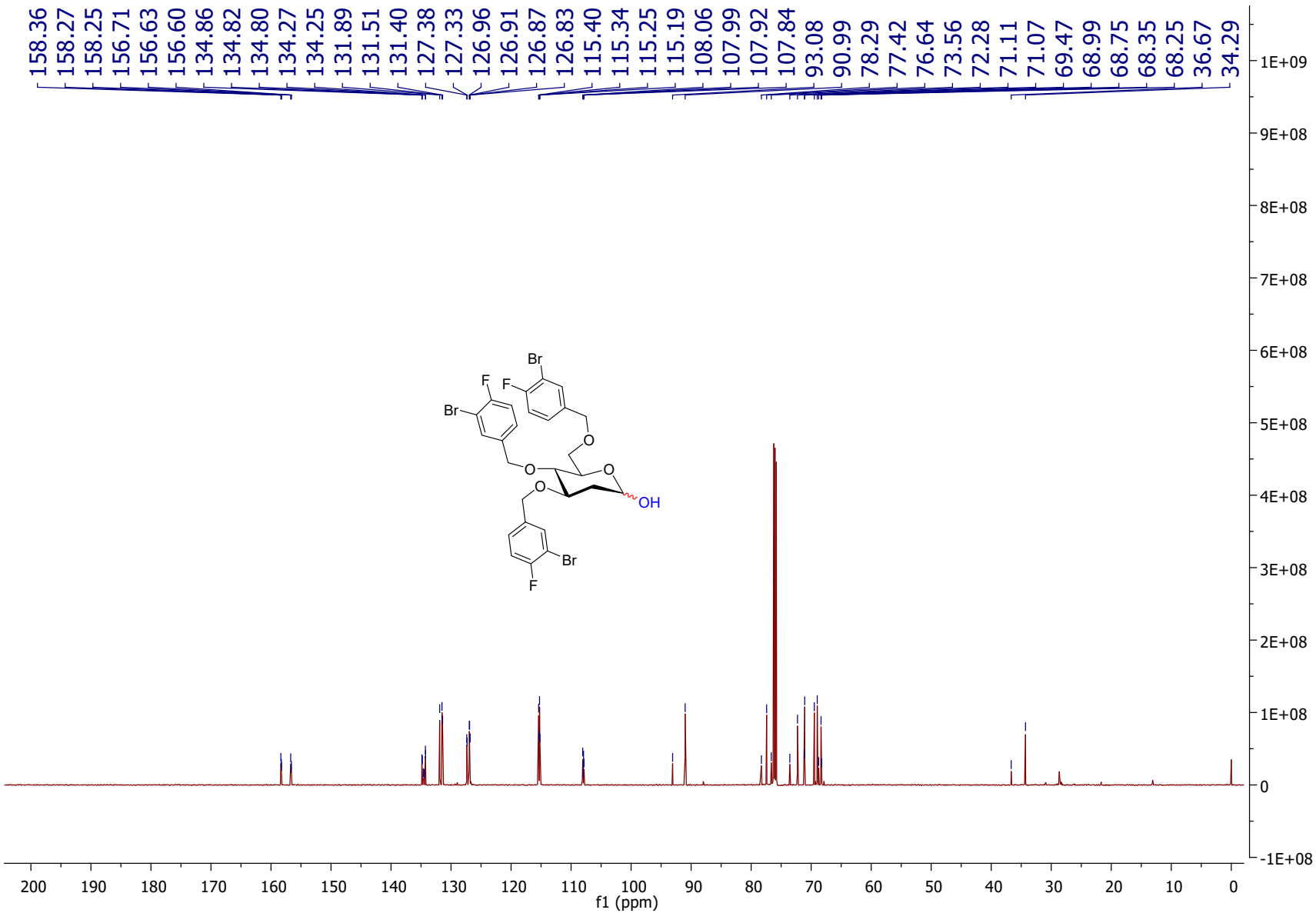


Fig-^{13}C NMR (151 MHz, $CDCl_3$) of compound **2m**

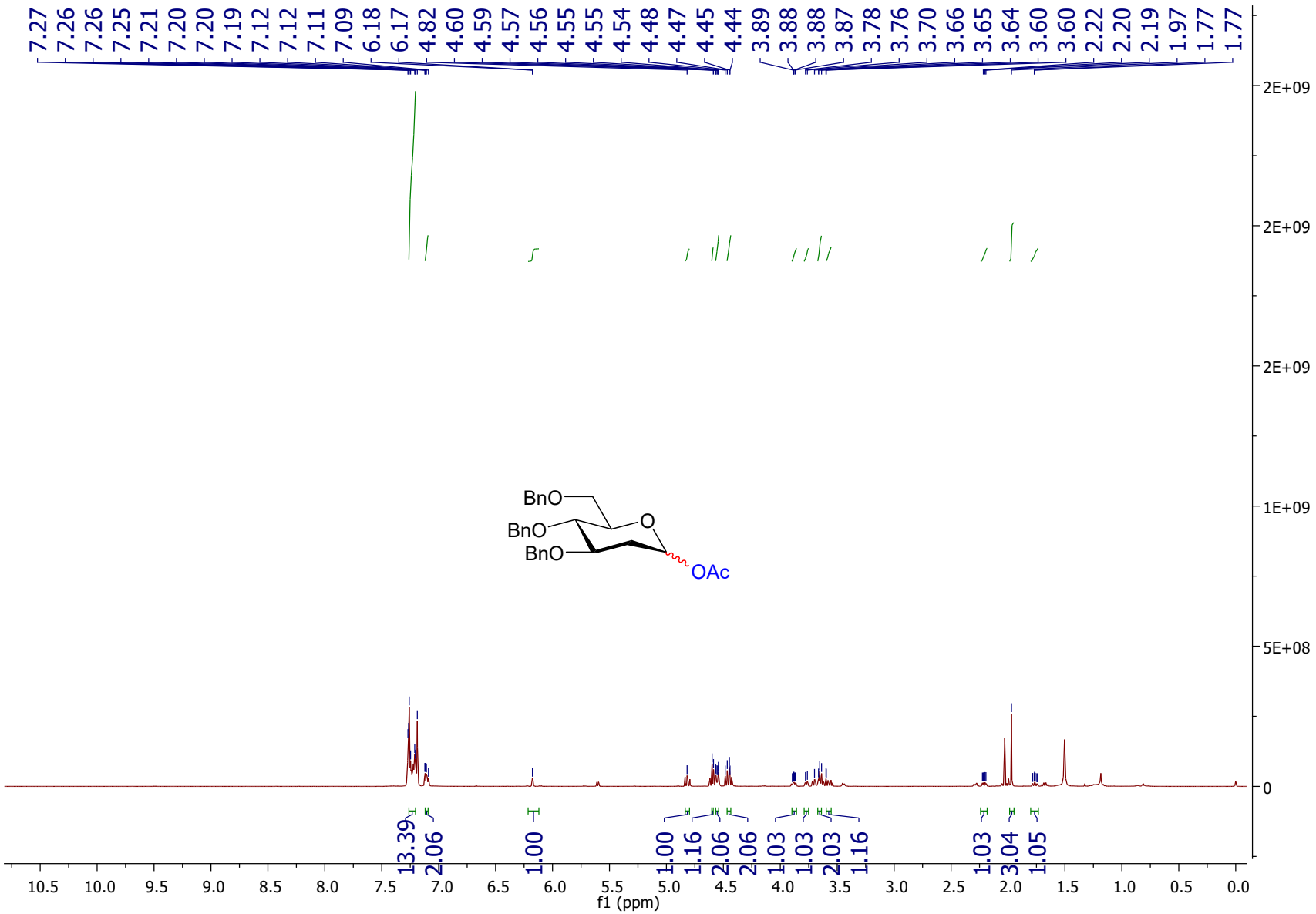


Fig- ^{1}H NMR (600 MHz, $CDCl_3$) of compound **2n**

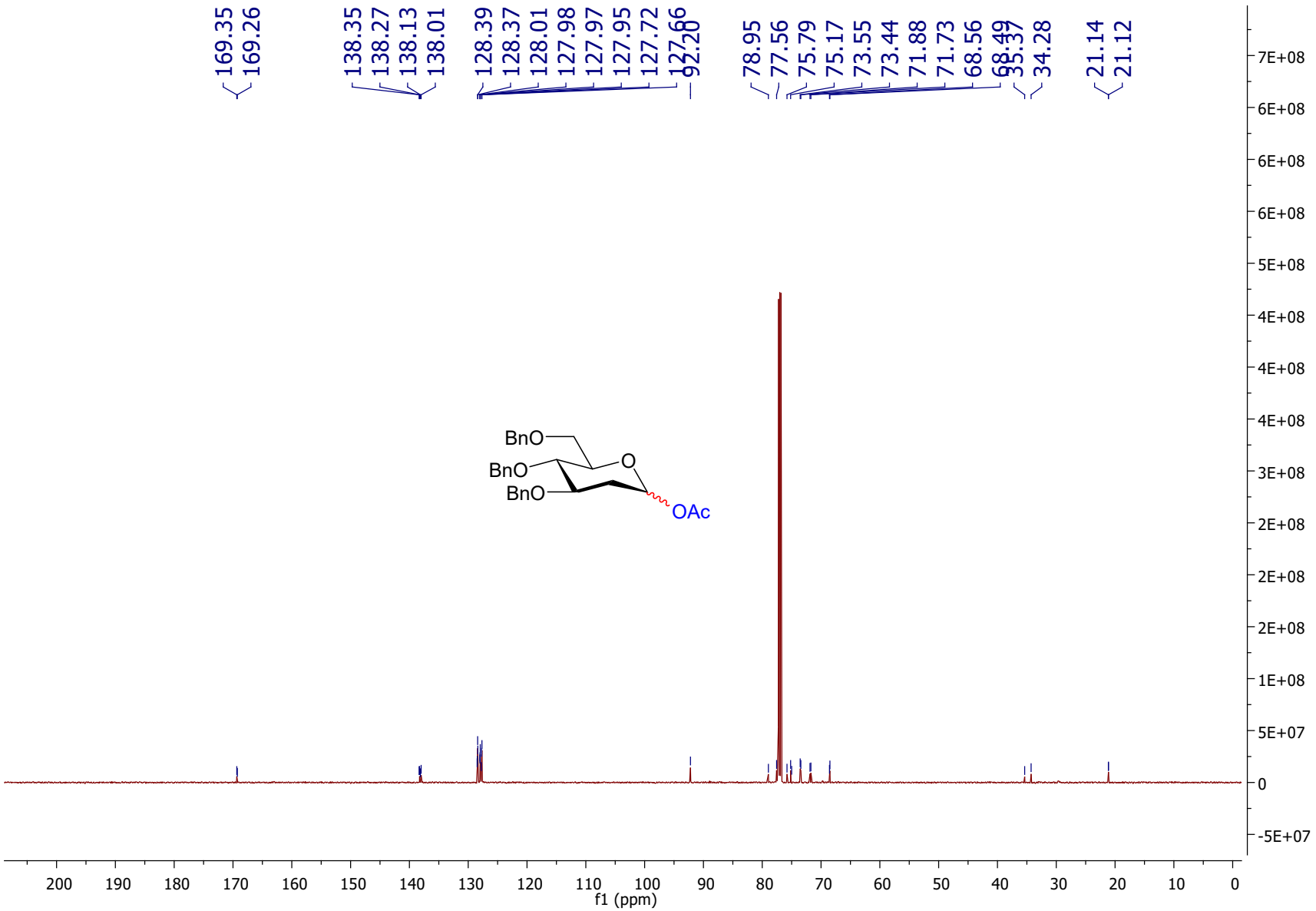


Fig-^{13}C NMR (151 MHz, $CDCl_3$) of compound **2n**

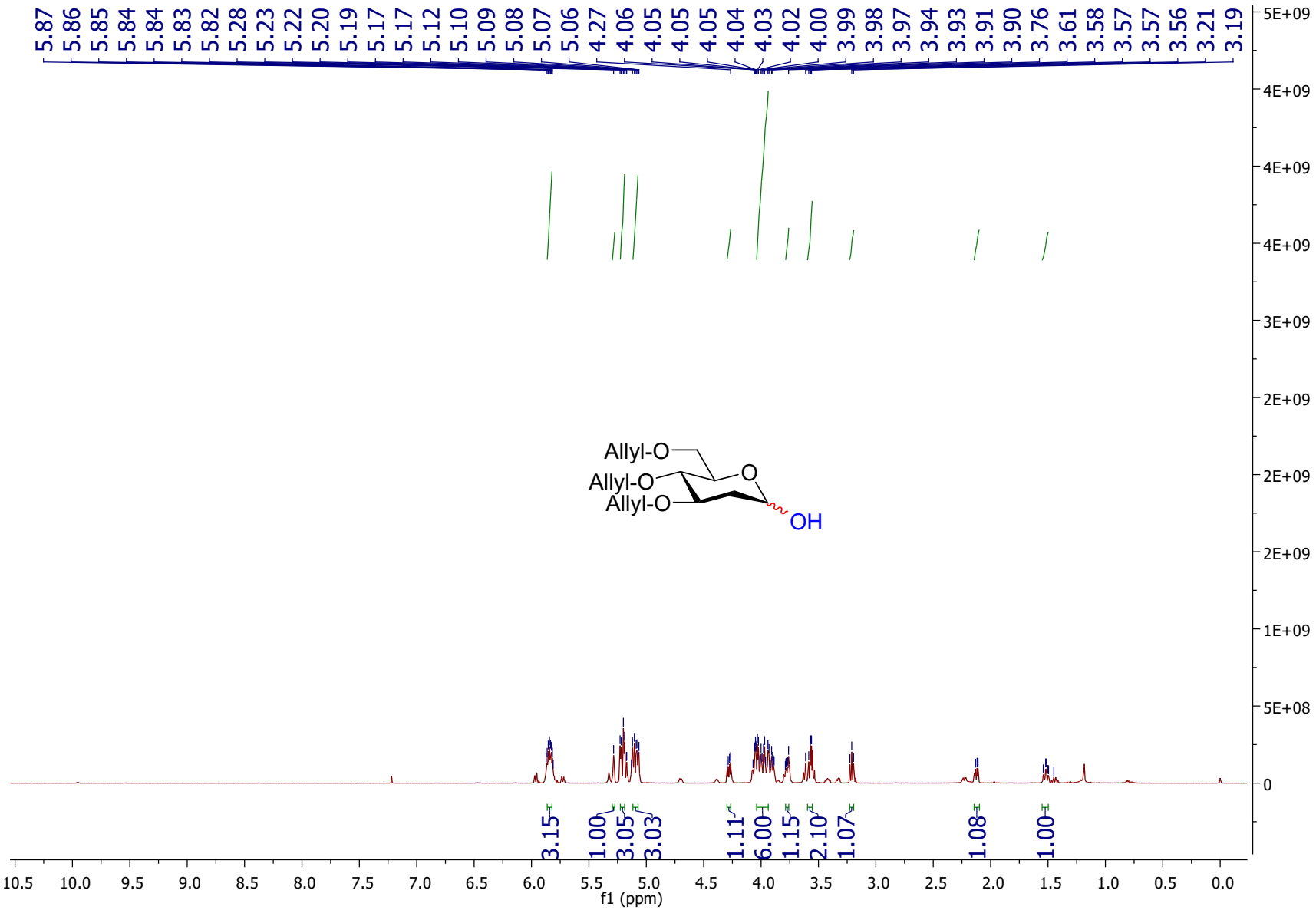


Fig- ^{1}H NMR (600 MHz, $CDCl_3$) of compound **2o**

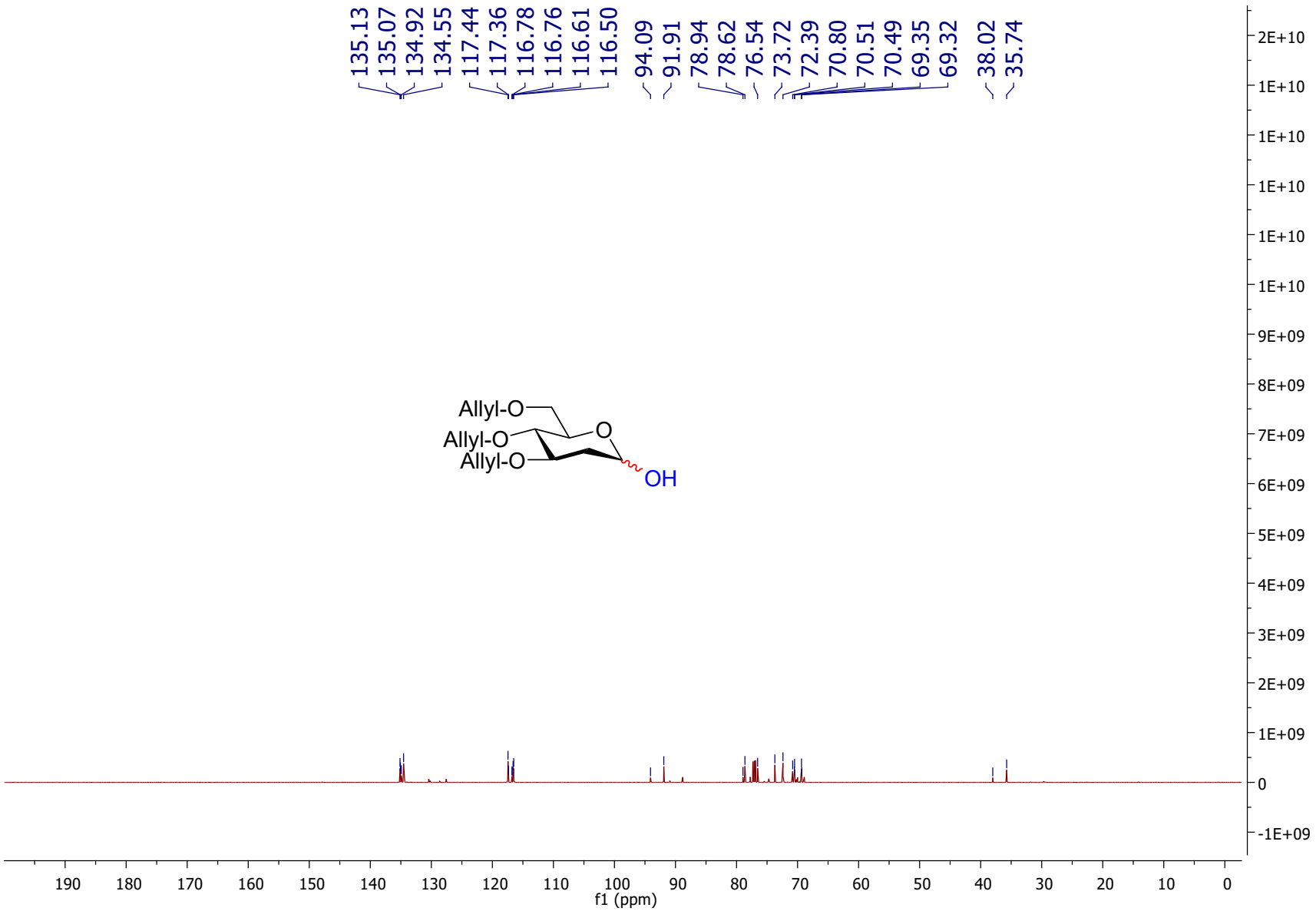


Fig-^{13}C NMR (151 MHz, $CDCl_3$) of compound **2o**

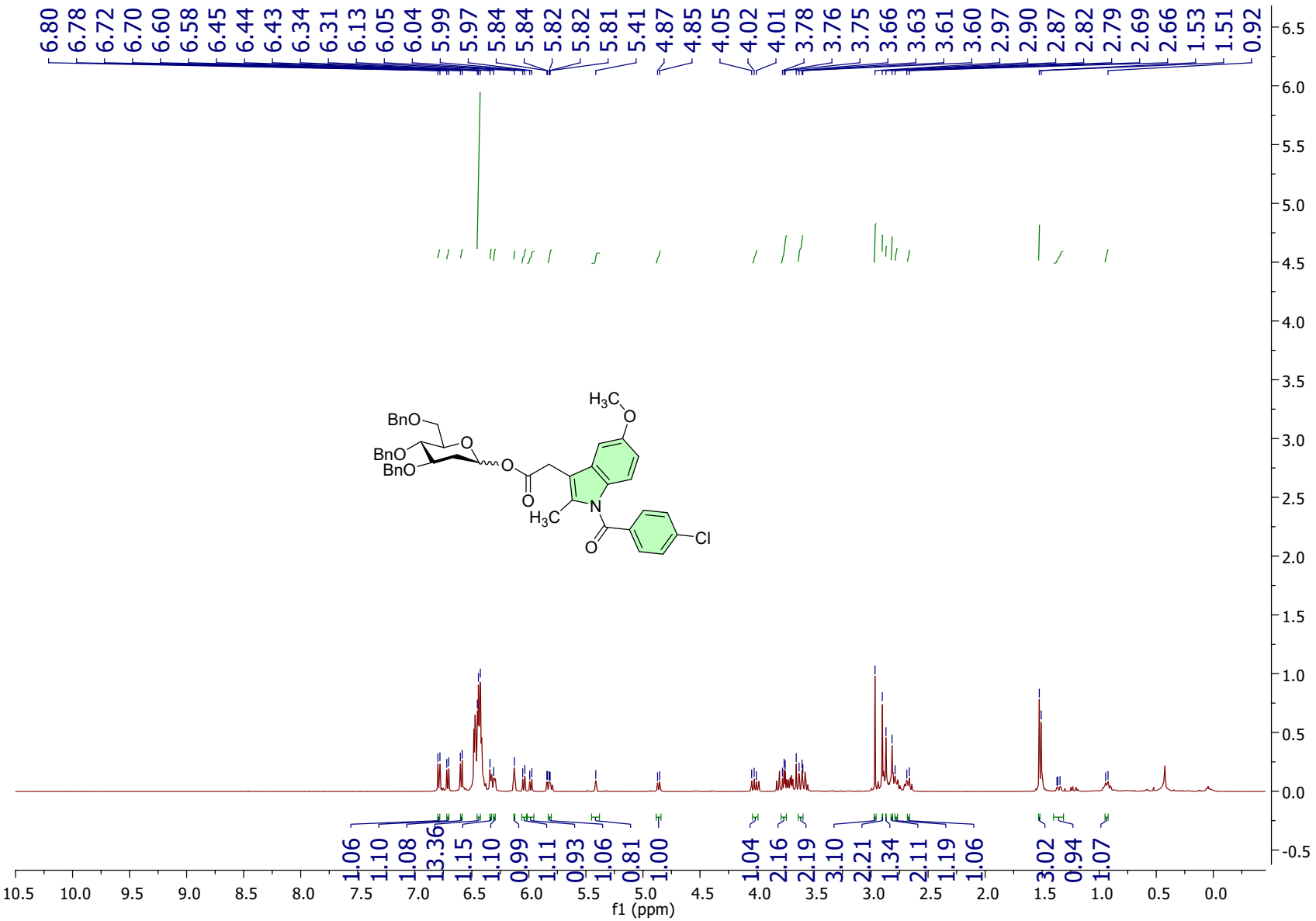


Fig- ^{1}H NMR (600 MHz, $CDCl_3$) of compound **3a**

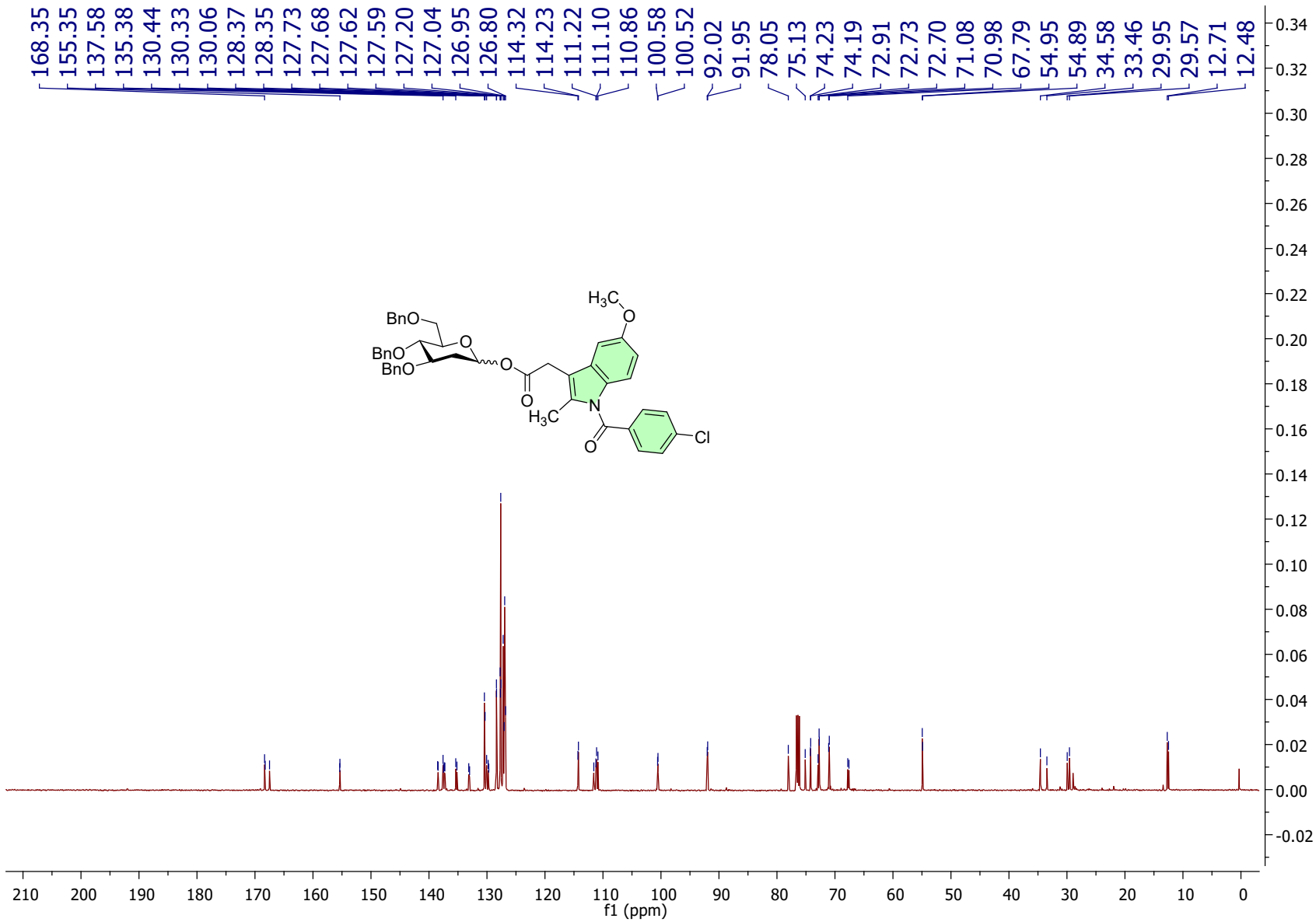


Fig-^{13}C NMR (151 MHz, $CDCl_3$) of compound **3a**

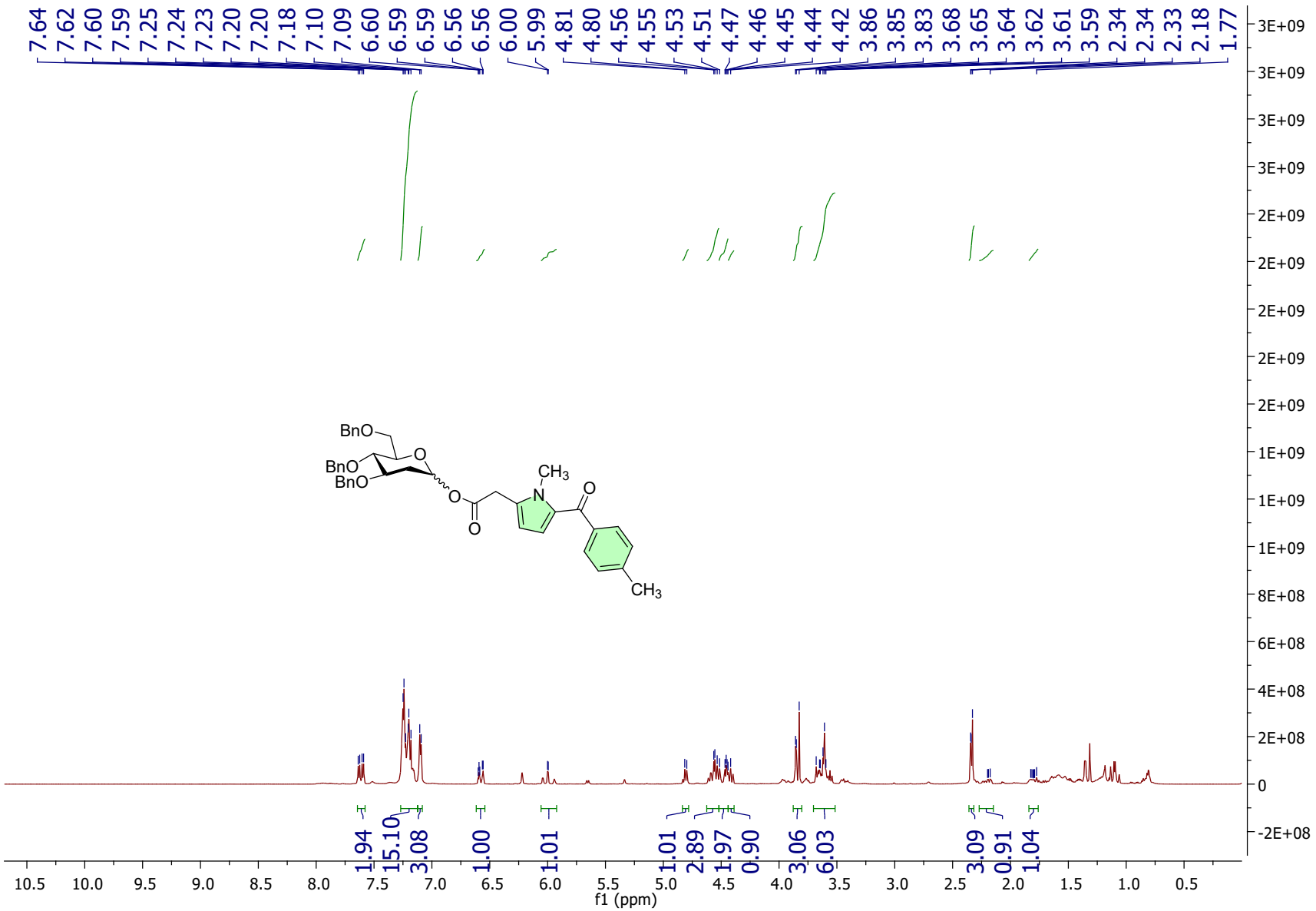


Fig- ^{1}H NMR (600 MHz, $CDCl_3$) of compound**3b**

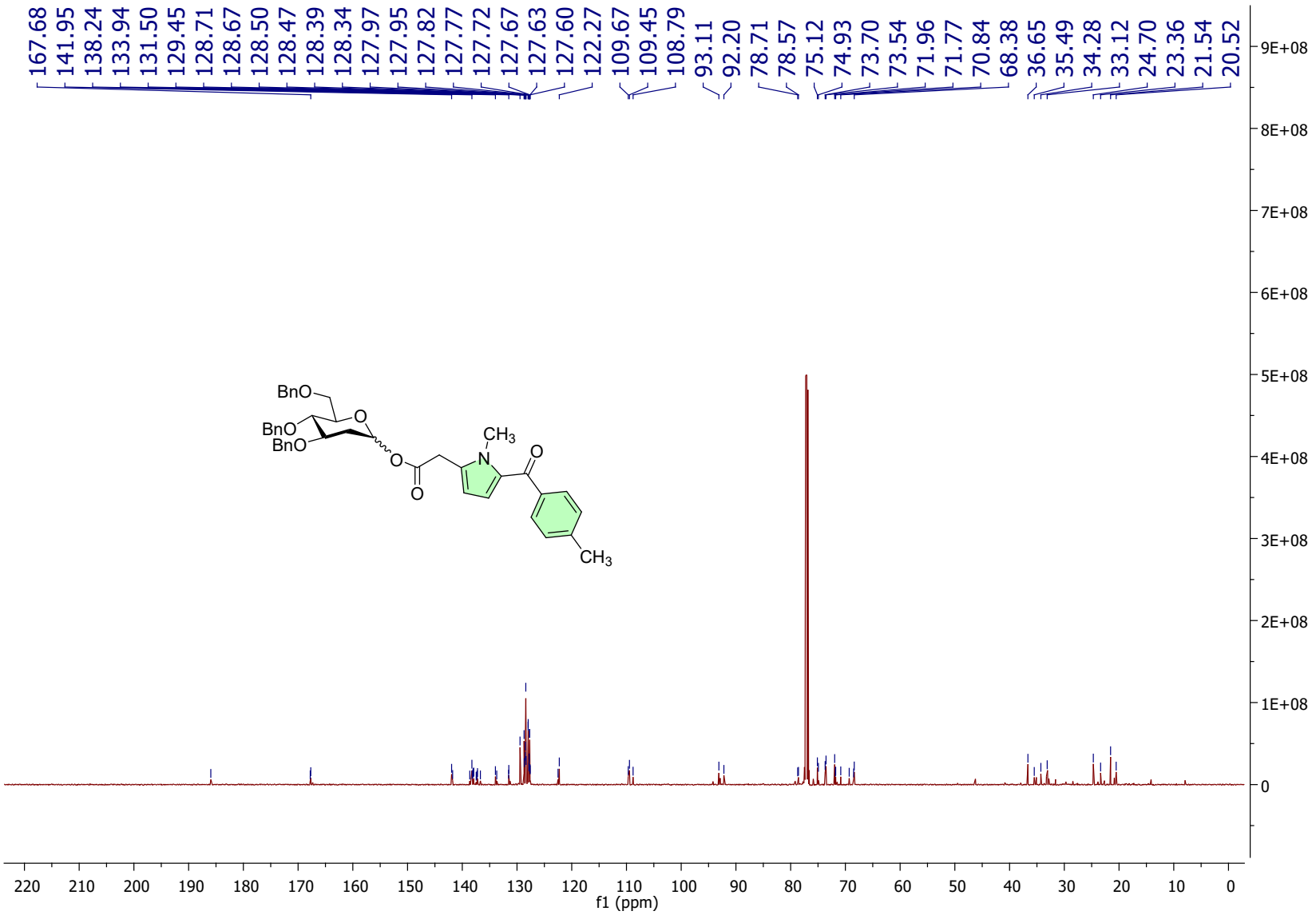


Fig-^{13}C NMR (151 MHz, $CDCl_3$) of compound**3b**

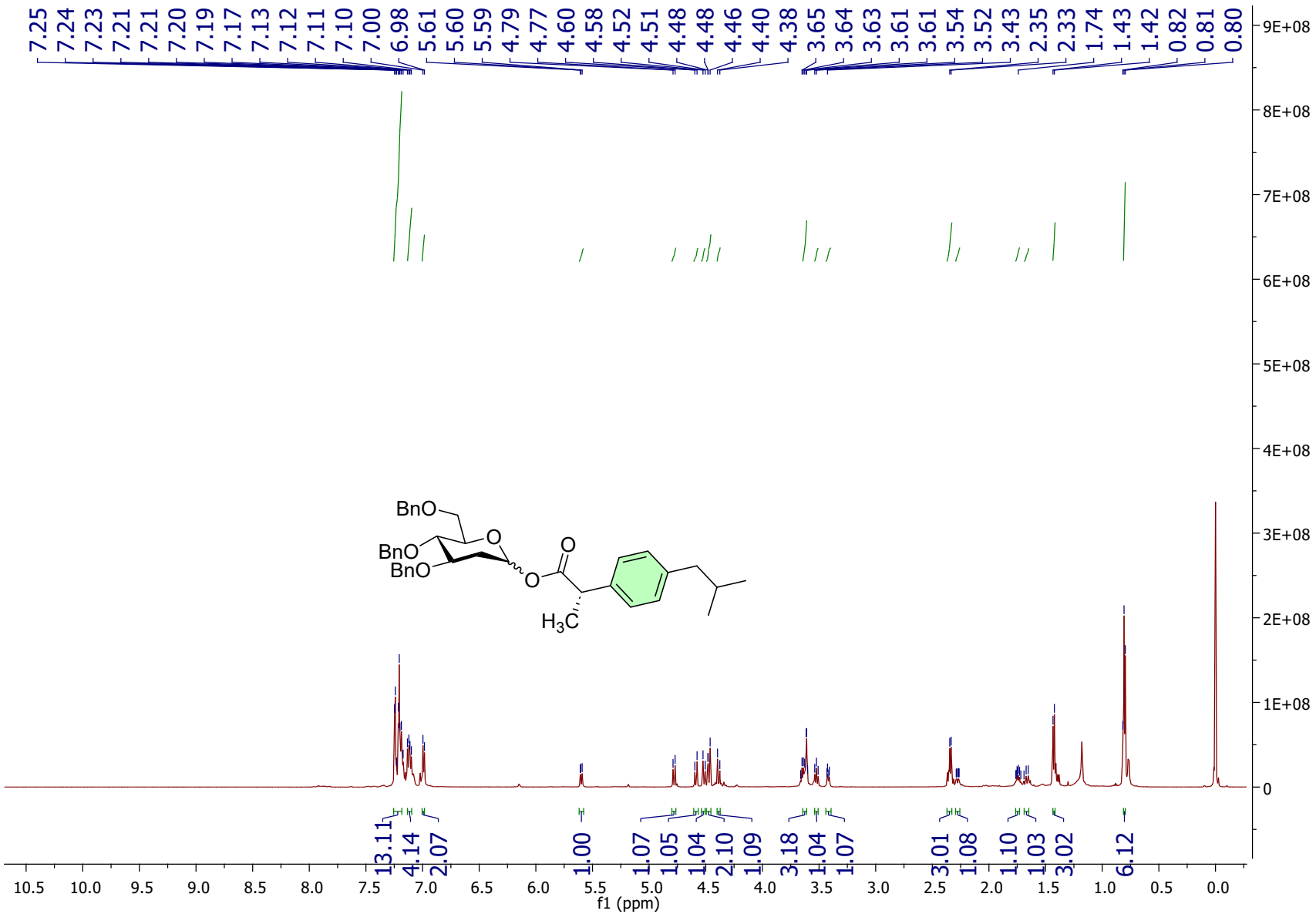


Fig- ^{1}H NMR (600 MHz, $CDCl_3$) of compound **3c**

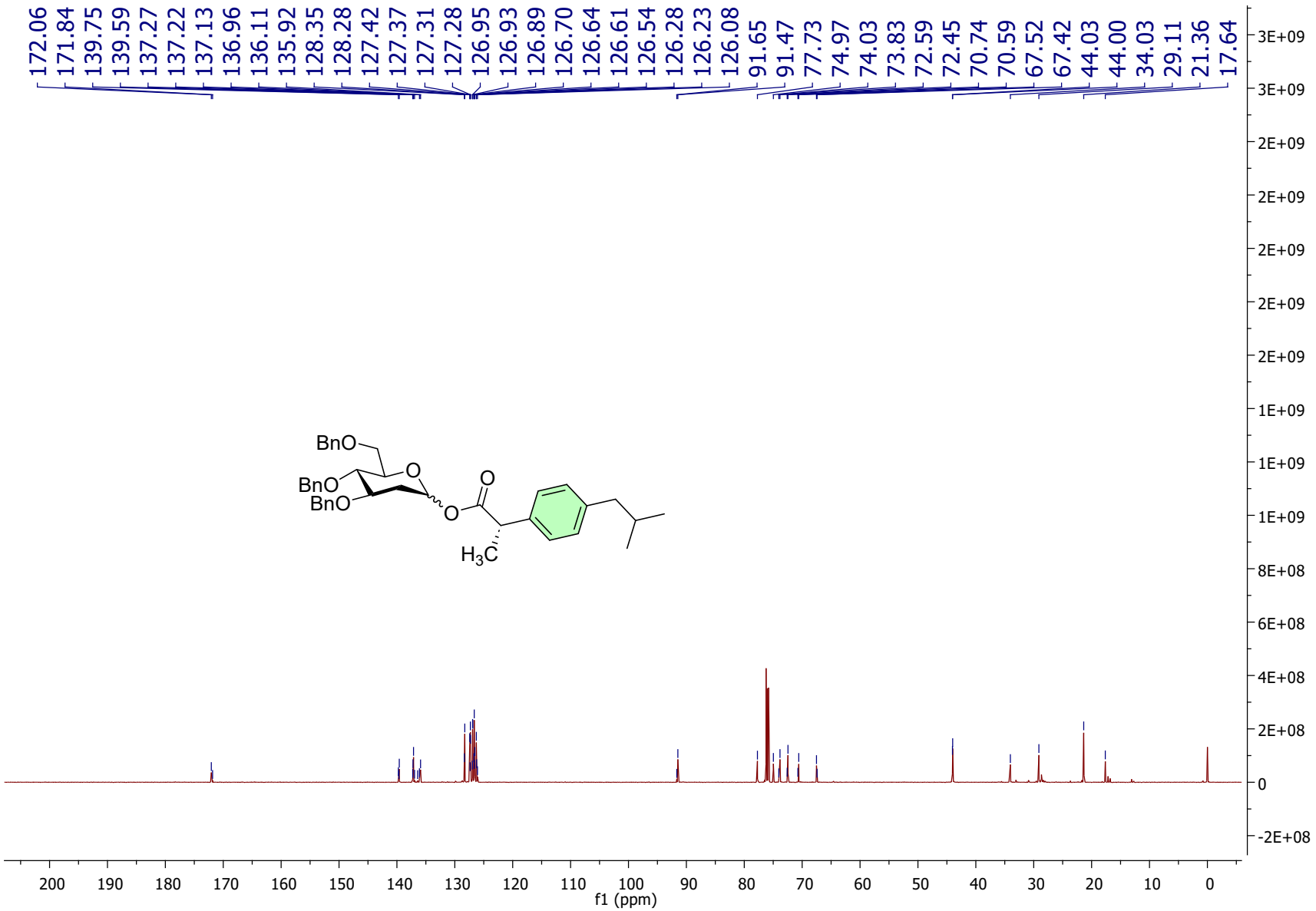


Fig-^{13}C NMR (151 MHz, $CDCl_3$) of compound **3c**

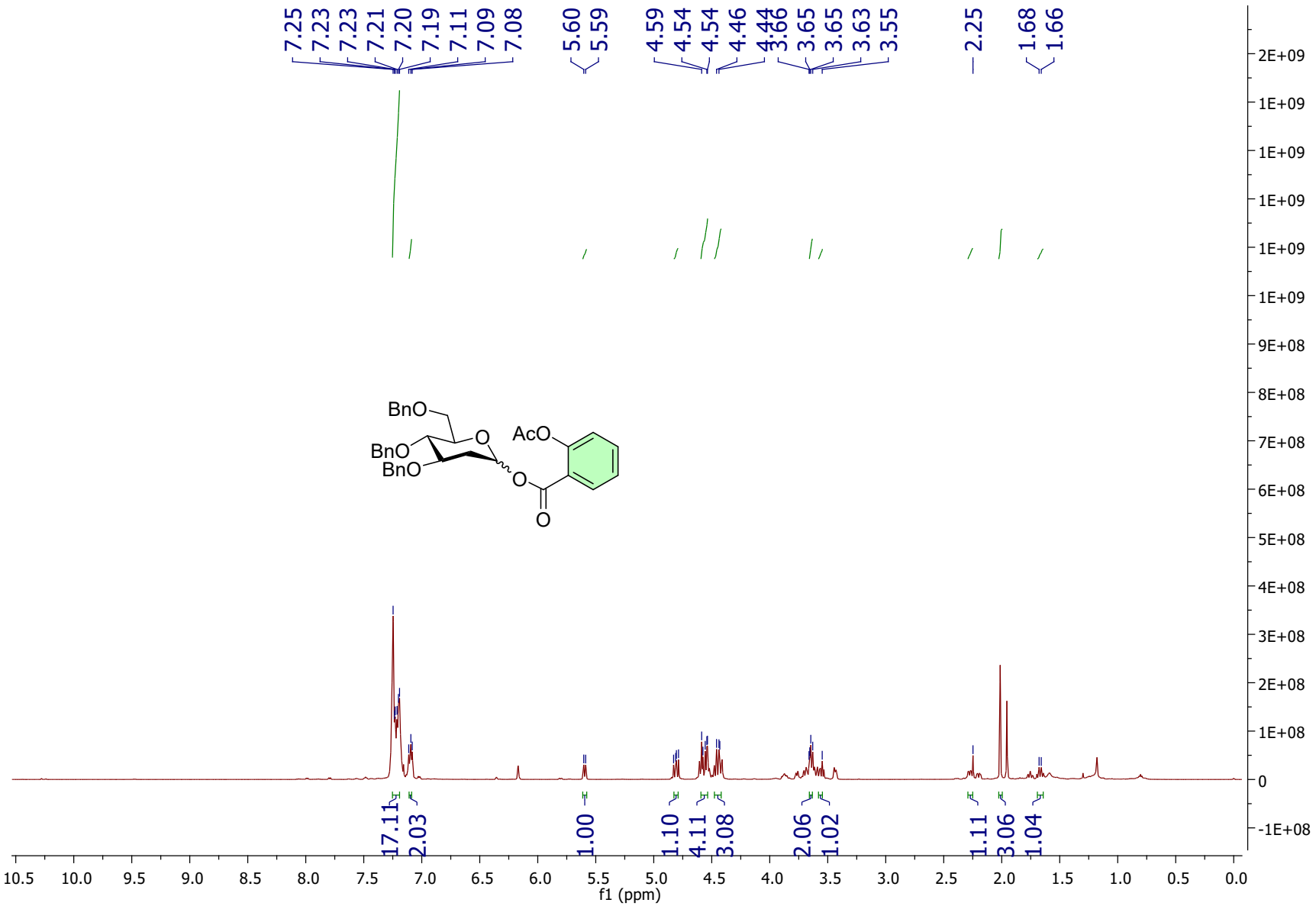


Fig- ^{1}H NMR (600 MHz, $CDCl_3$) of compound **3d**

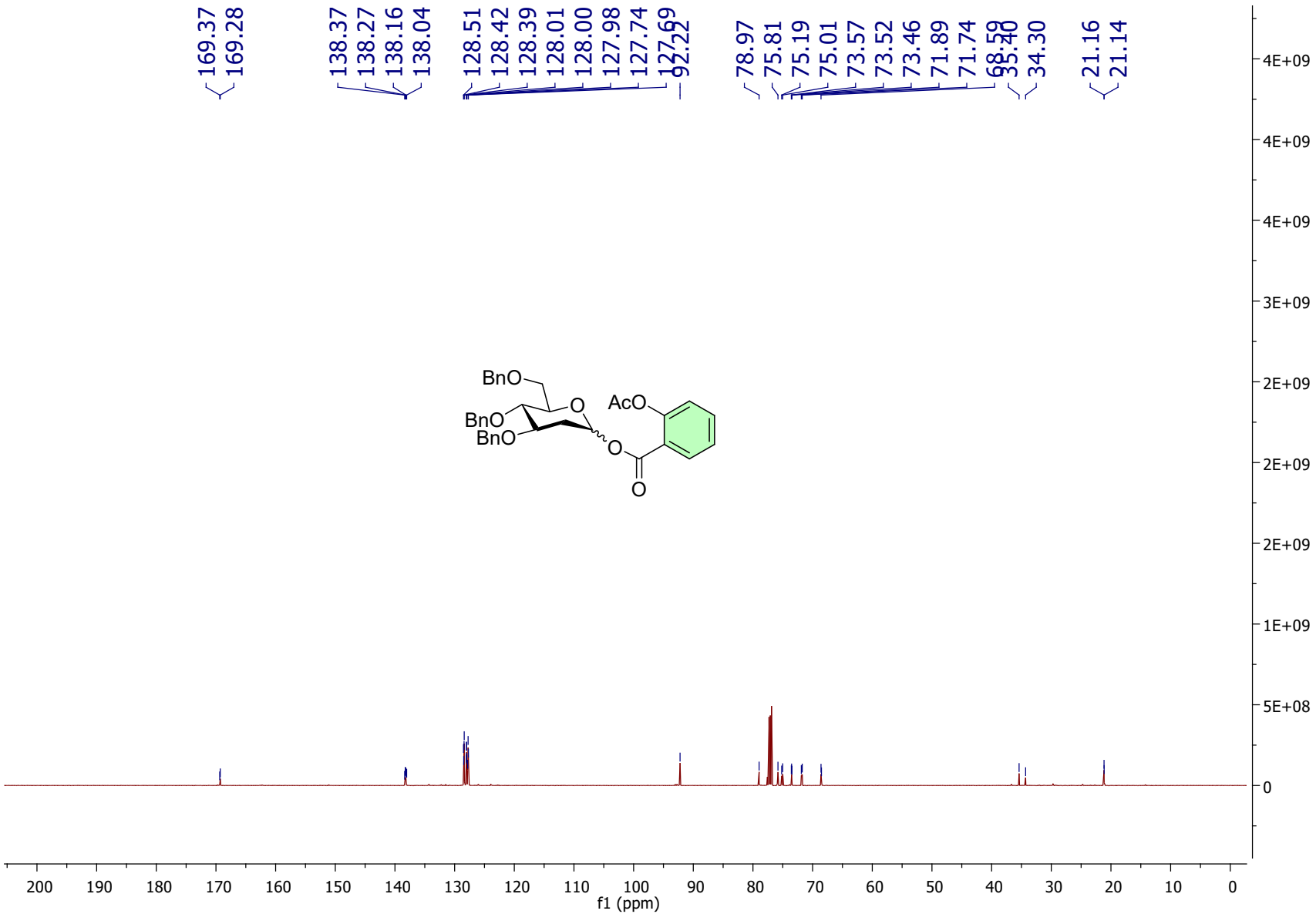


Fig-^{13}C NMR (151 MHz, $CDCl_3$) of compound **3d**

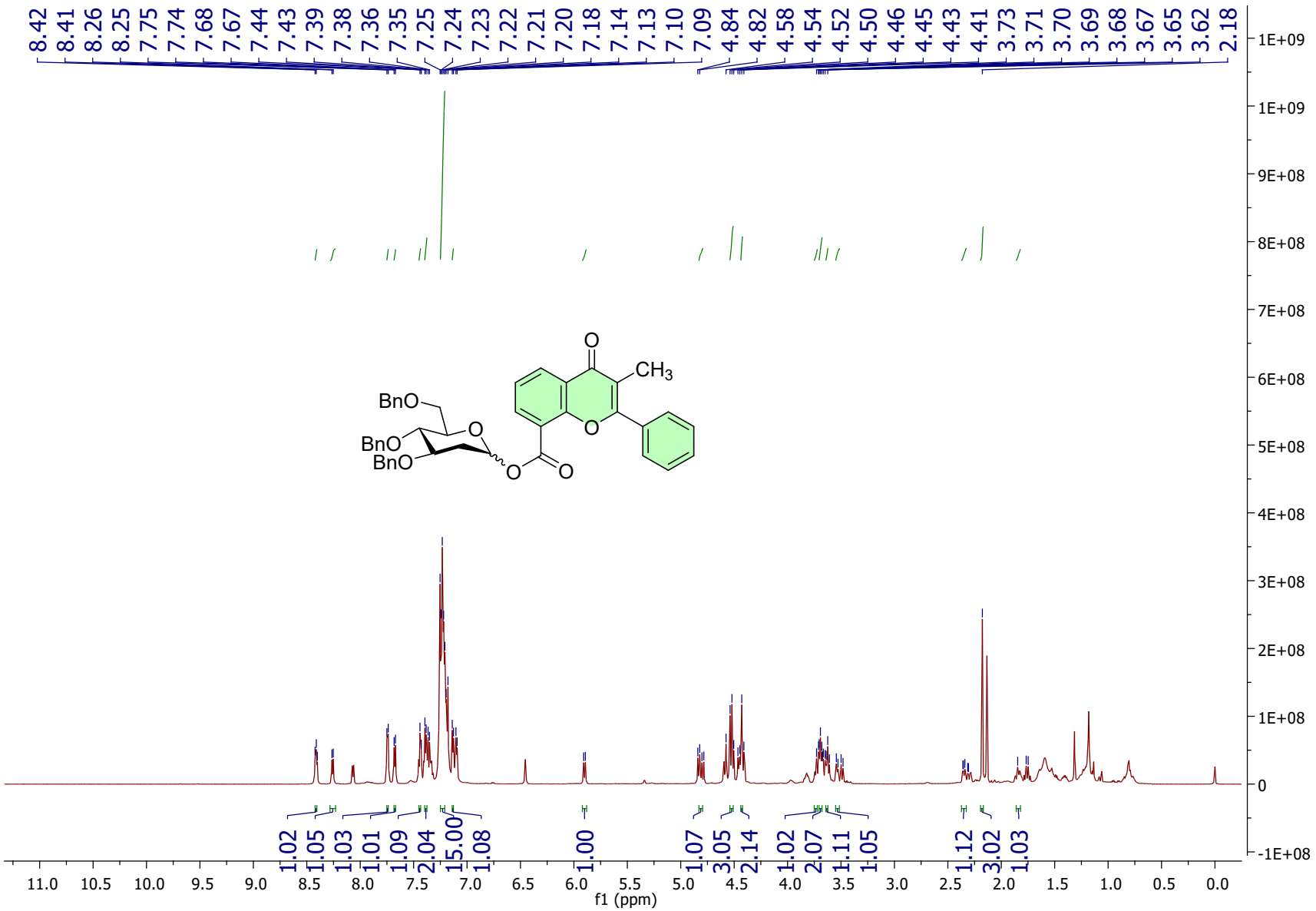


Fig- ^{1}H NMR (600 MHz, $CDCl_3$) of compound **3e**

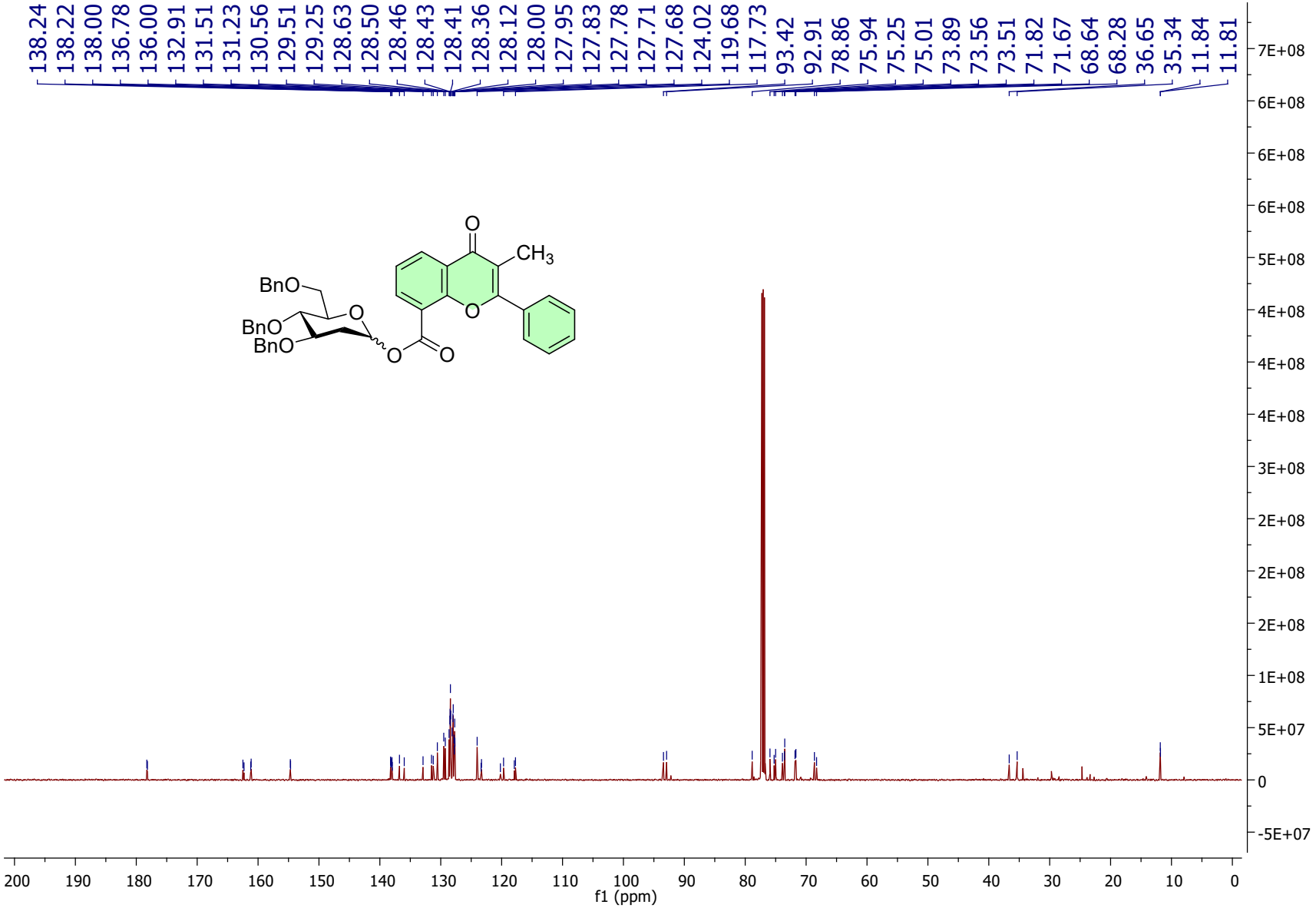


Fig-^{13}C NMR (151 MHz, $CDCl_3$) of compound **3e**

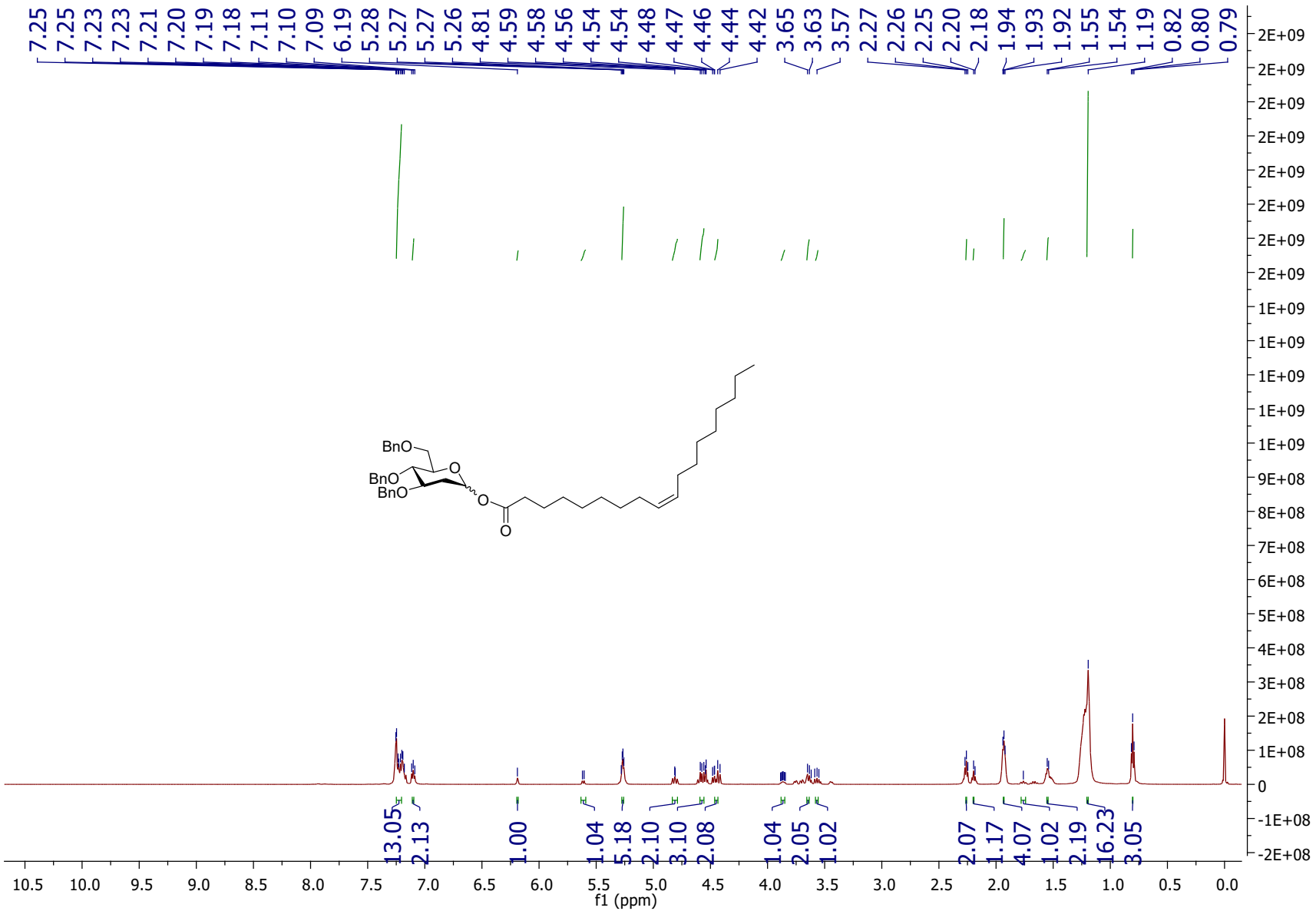


Fig- ^{1}H NMR (600 MHz, $CDCl_3$) of compound **3f**

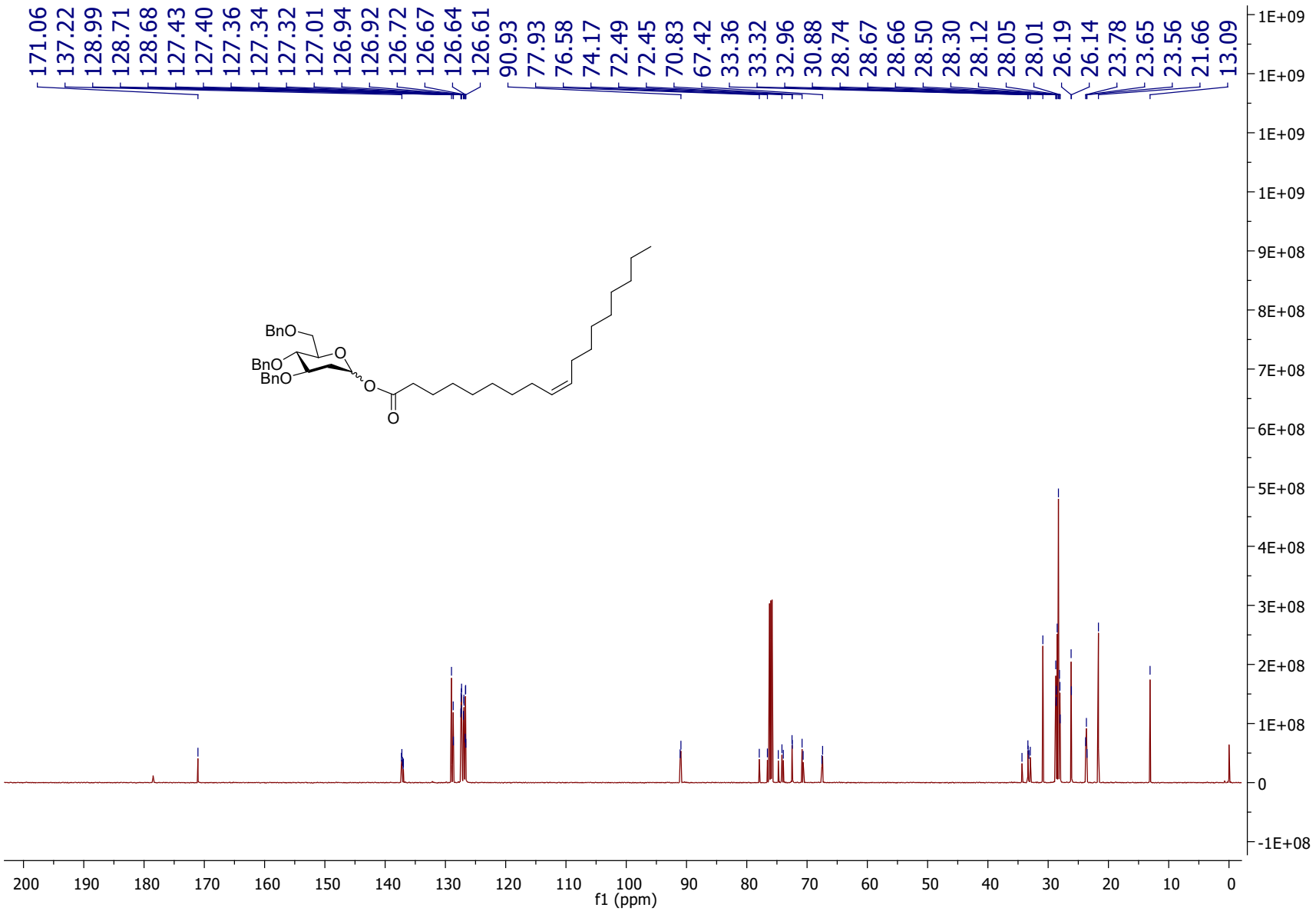


Fig-^{13}C NMR (151 MHz, $CDCl_3$) of compound **3f**

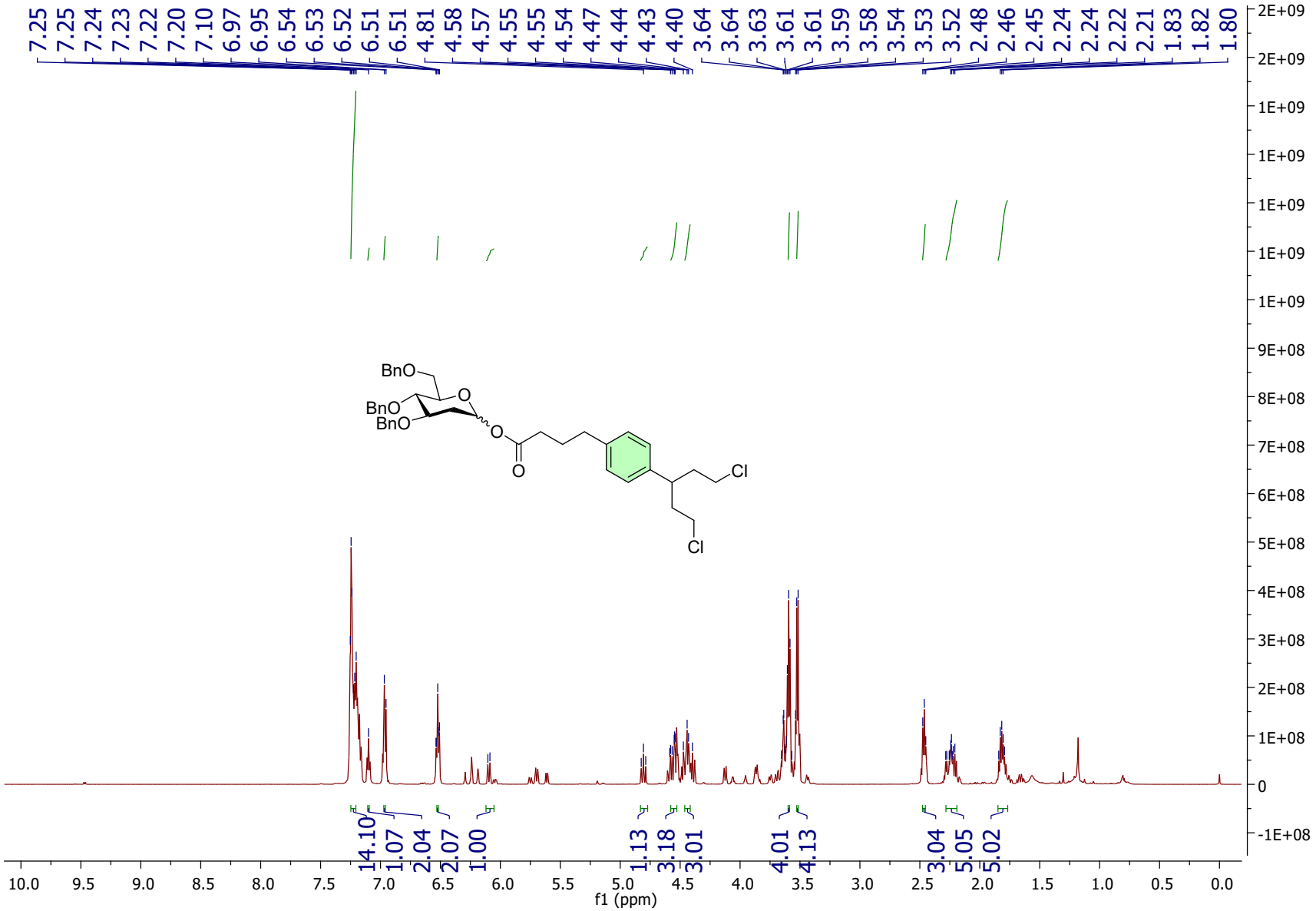


Fig- ^{1}H NMR (600 MHz, $CDCl_3$) of compound **3g**

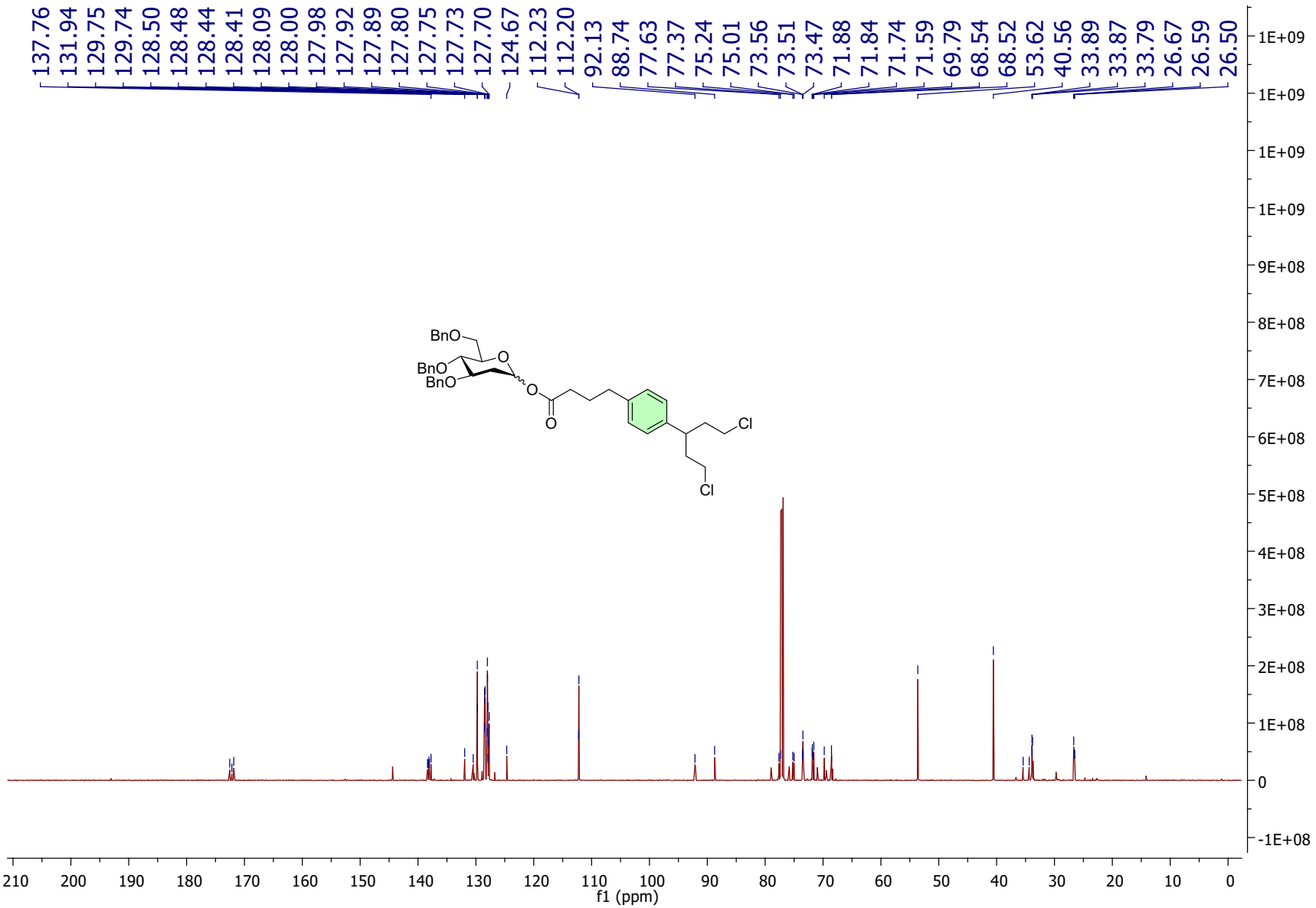


Fig-^{13}C NMR (151 MHz, $CDCl_3$) of compound **3g**

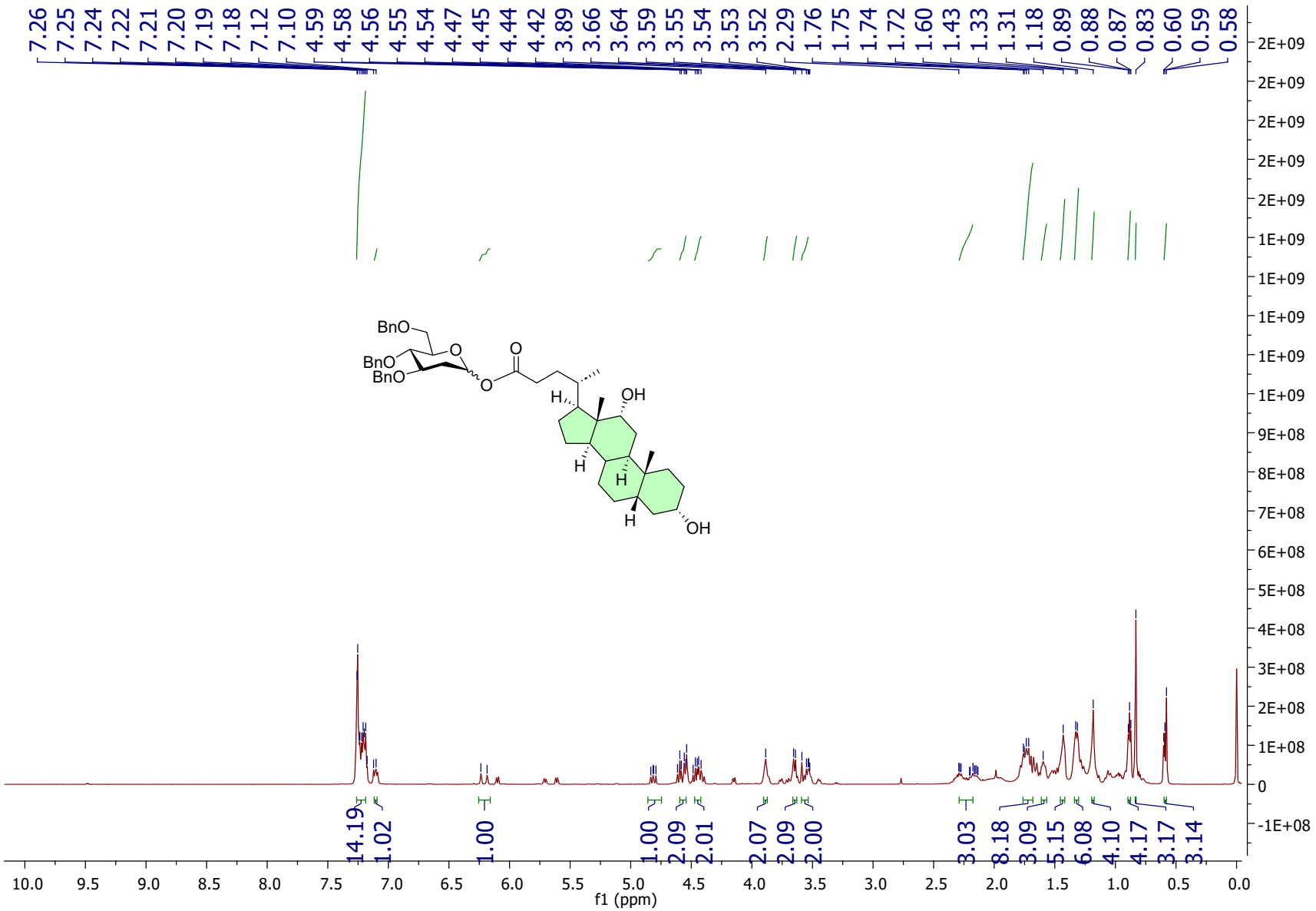


Fig- ^{1}H NMR (600 MHz, $CDCl_3$) of compound **3h**

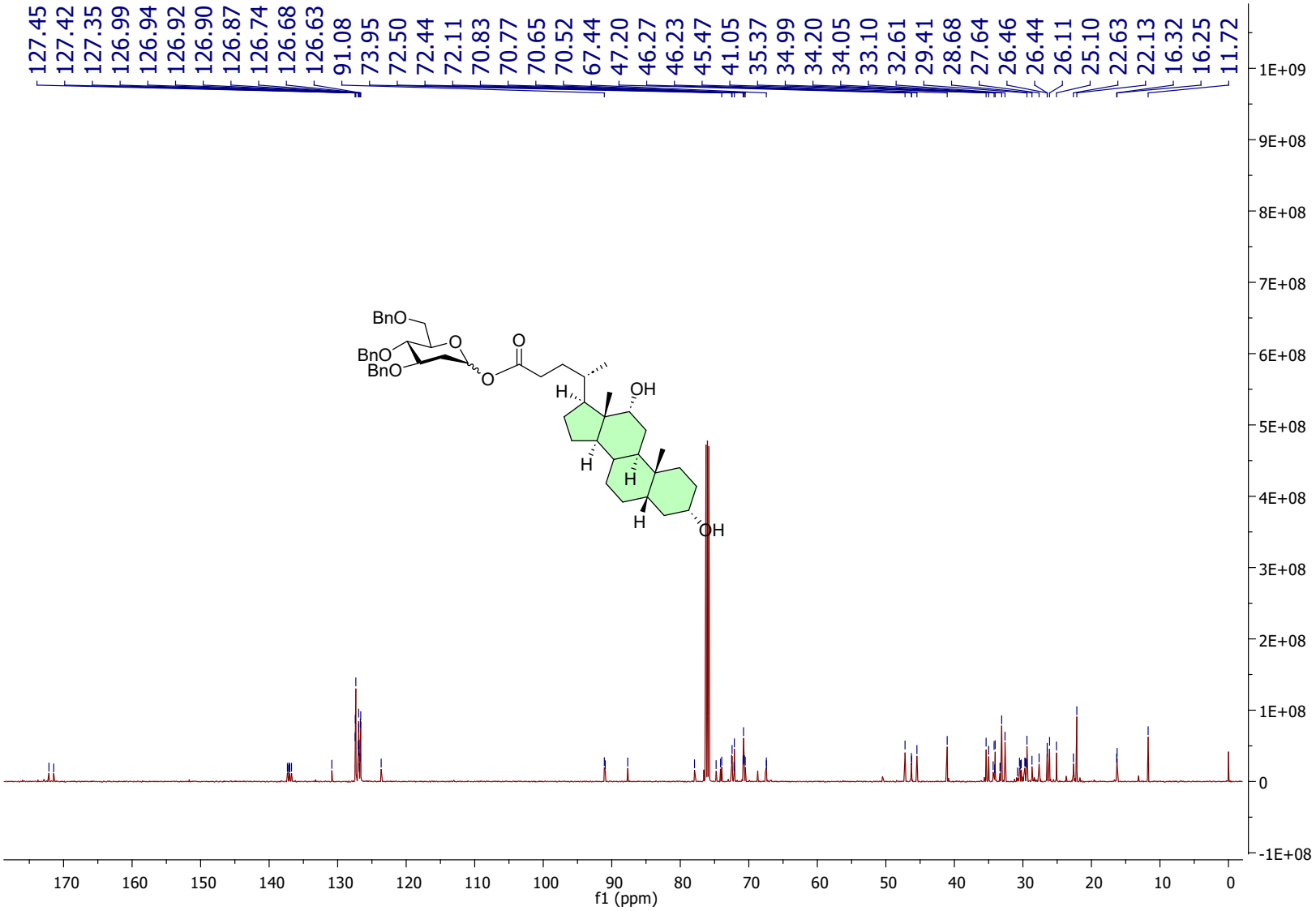


Fig-^{13}C NMR (151 MHz, $CDCl_3$) of compound **3h**

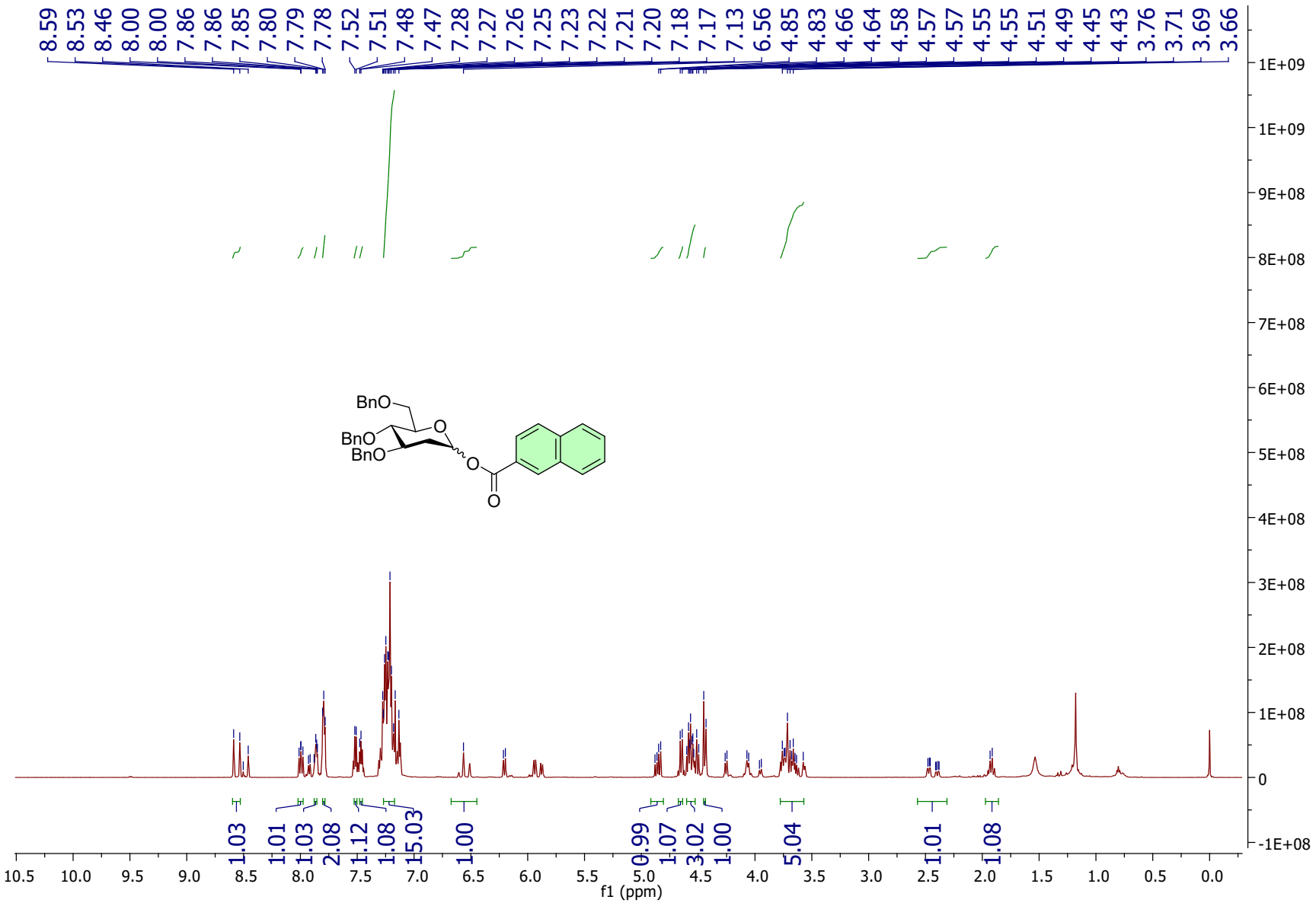


Fig- ^{1}H NMR (600 MHz, $CDCl_3$) of compound **3i**

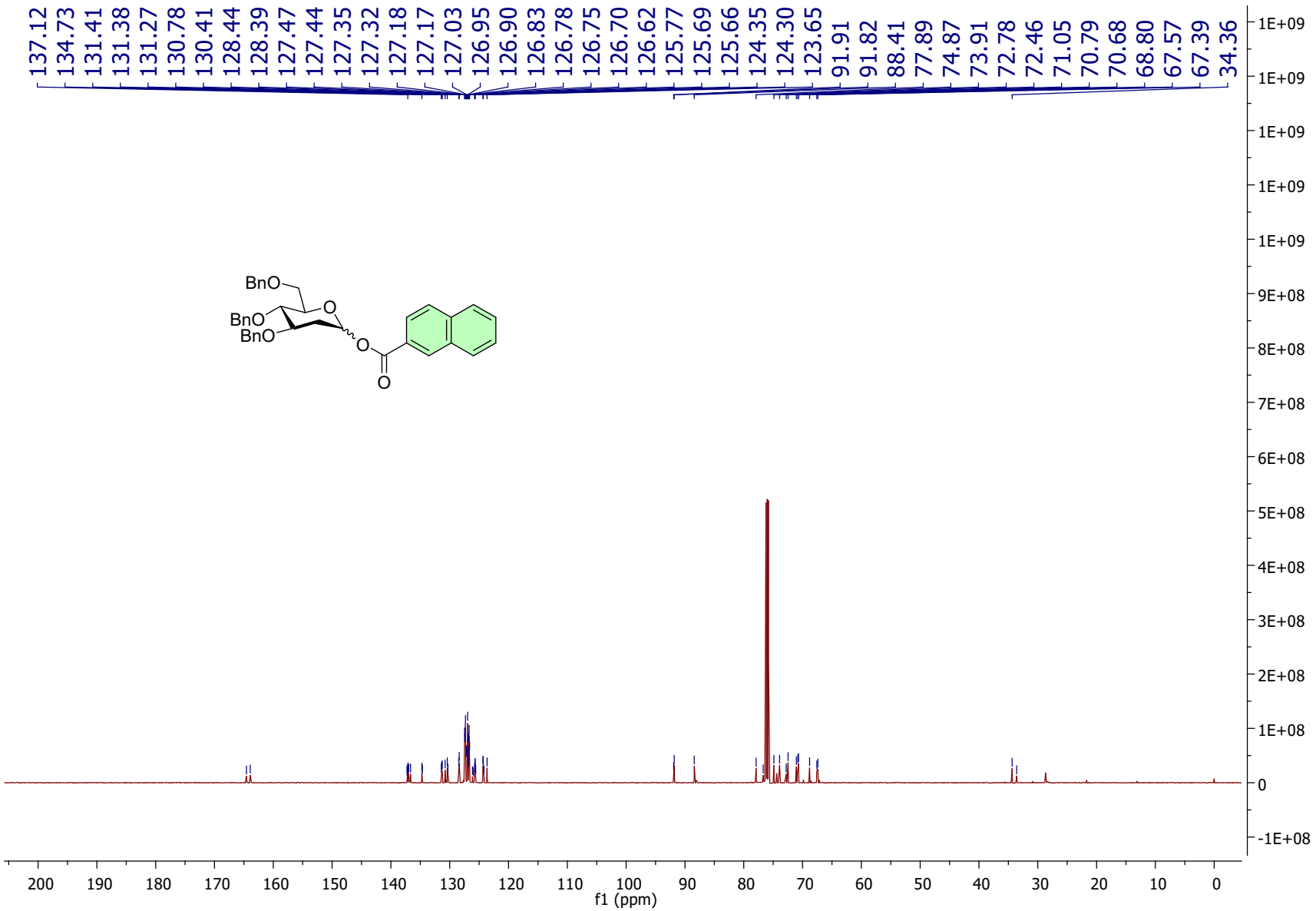


Fig-^{13}C NMR (151 MHz, $CDCl_3$) of compound **3i**

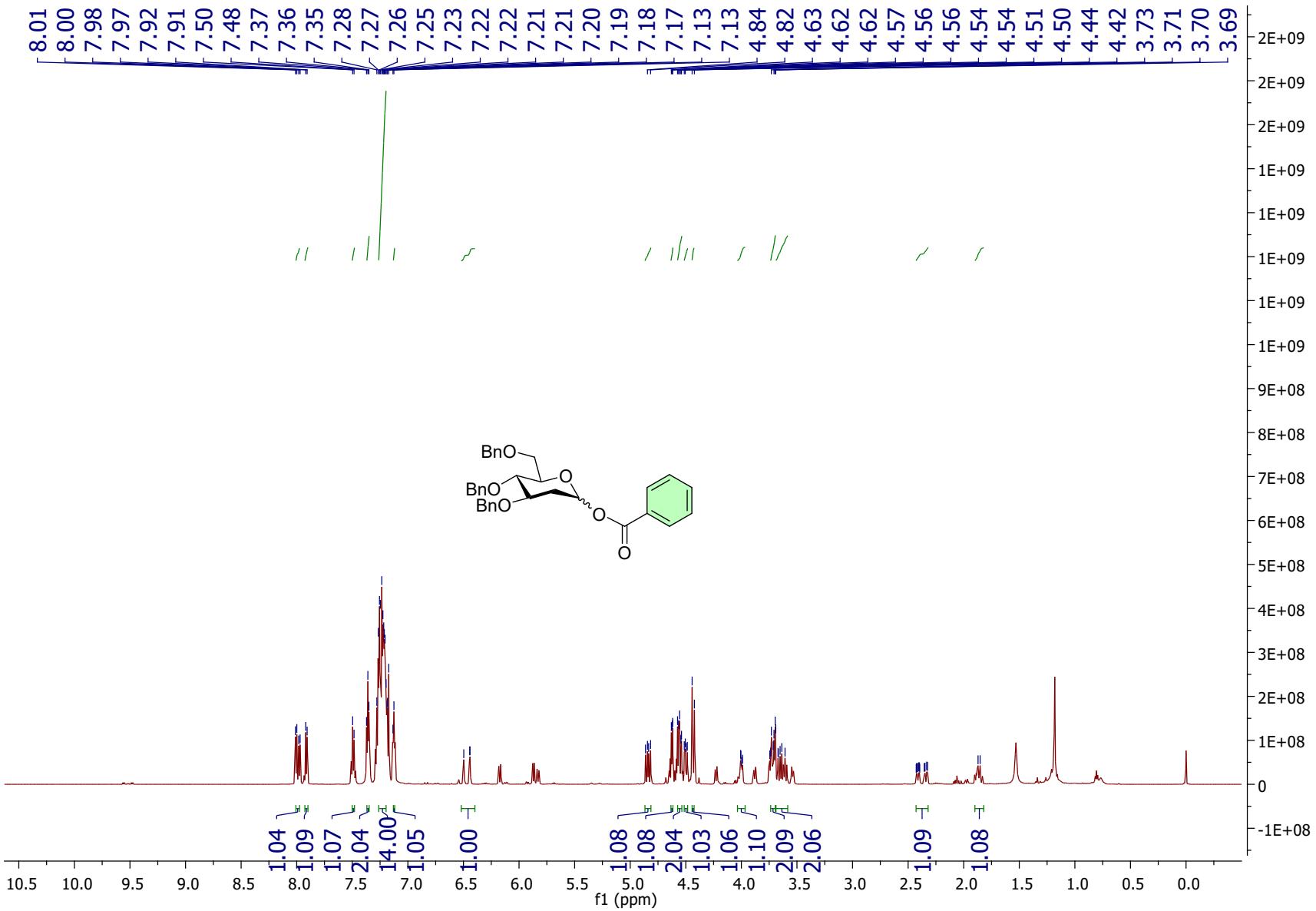


Fig- ^{1}H NMR (600 MHz, $CDCl_3$) of compound **3j**

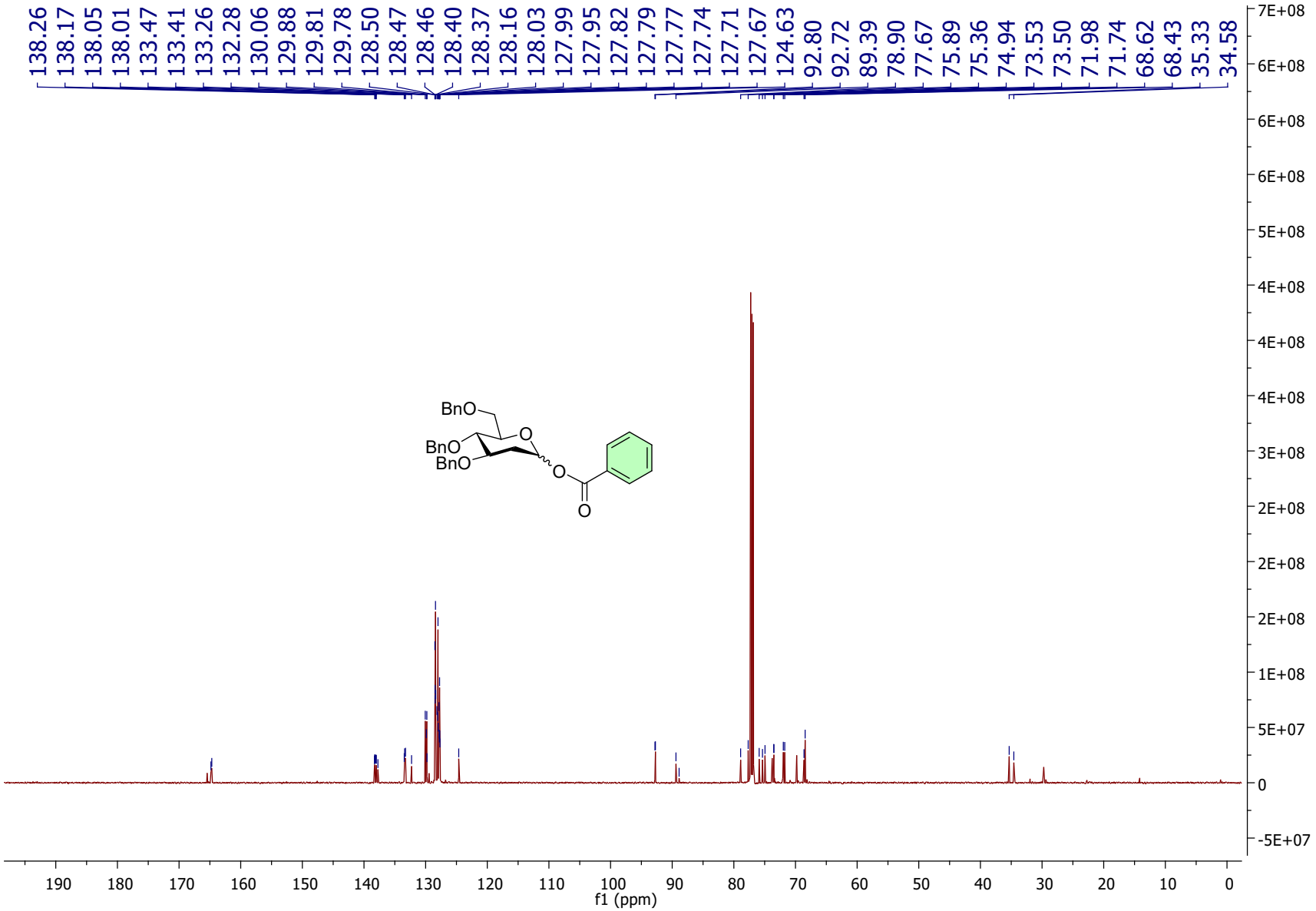


Fig-^{13}C NMR (151 MHz, $CDCl_3$) of compound **3j**

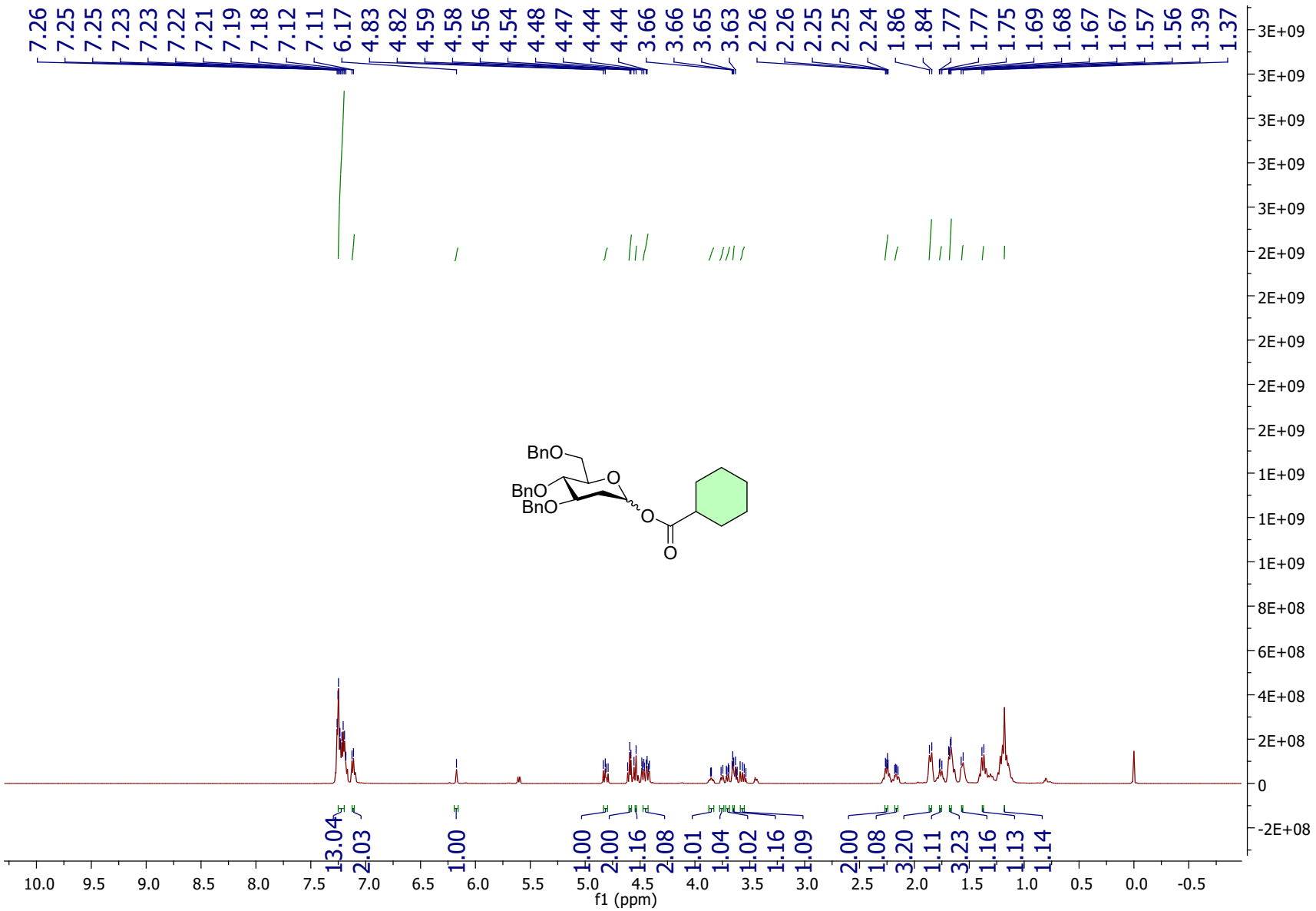


Fig- ^{1}H NMR (600 MHz, $CDCl_3$) of compound **3k**

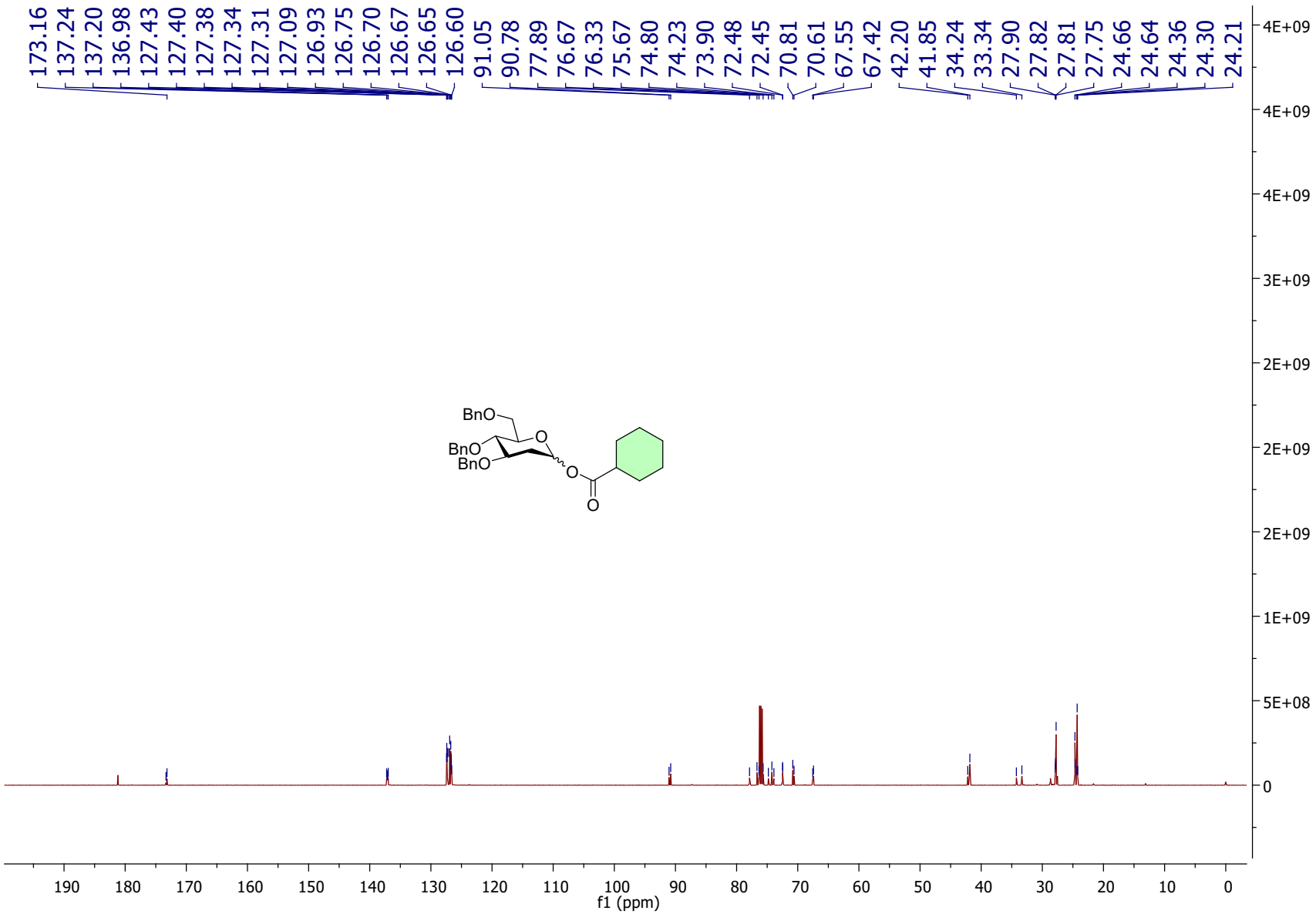


Fig-^{13}C NMR (151 MHz, $CDCl_3$) of compound **3k**

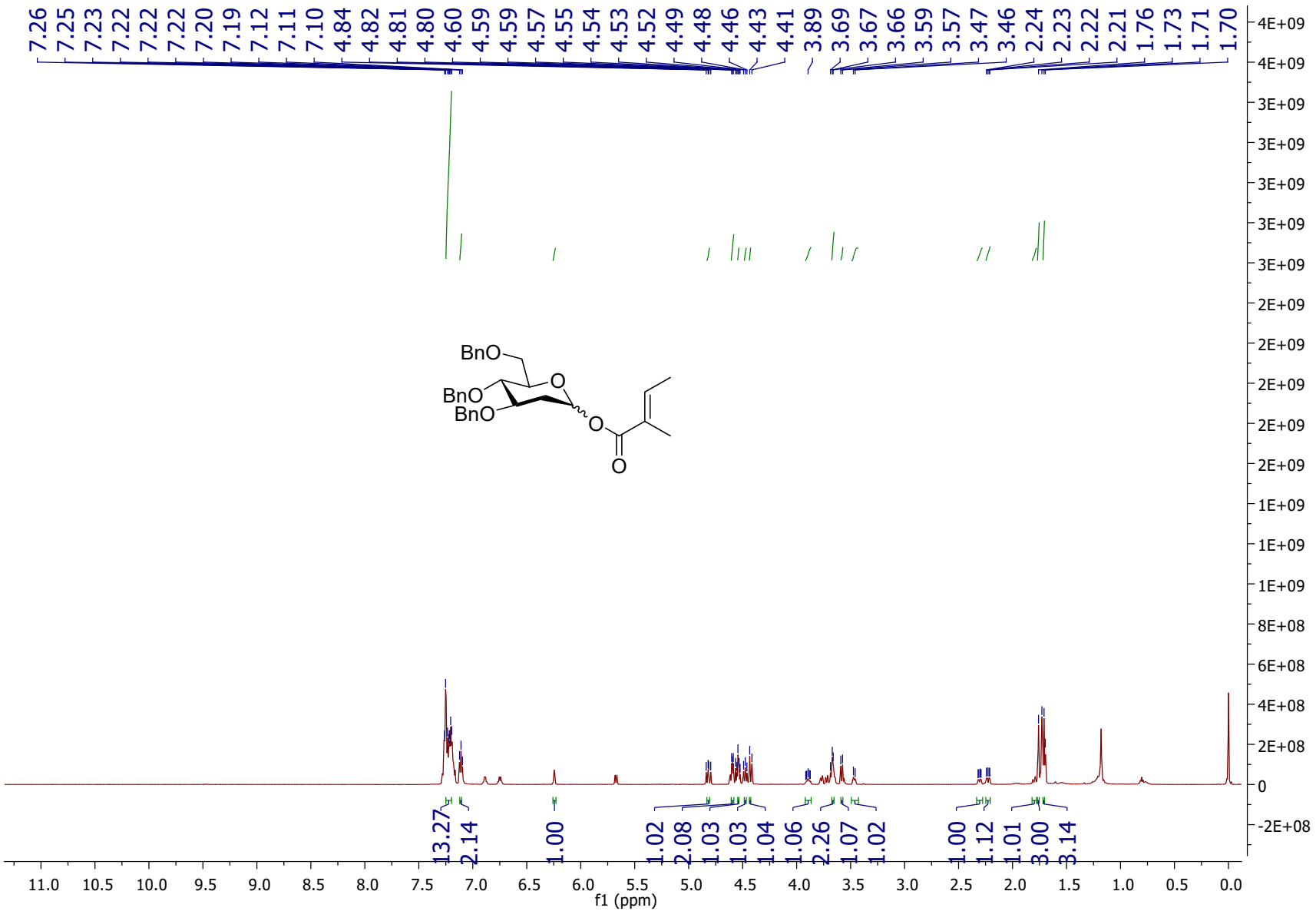


Fig- ^{1}H NMR (600 MHz, $CDCl_3$) of compound **3l**

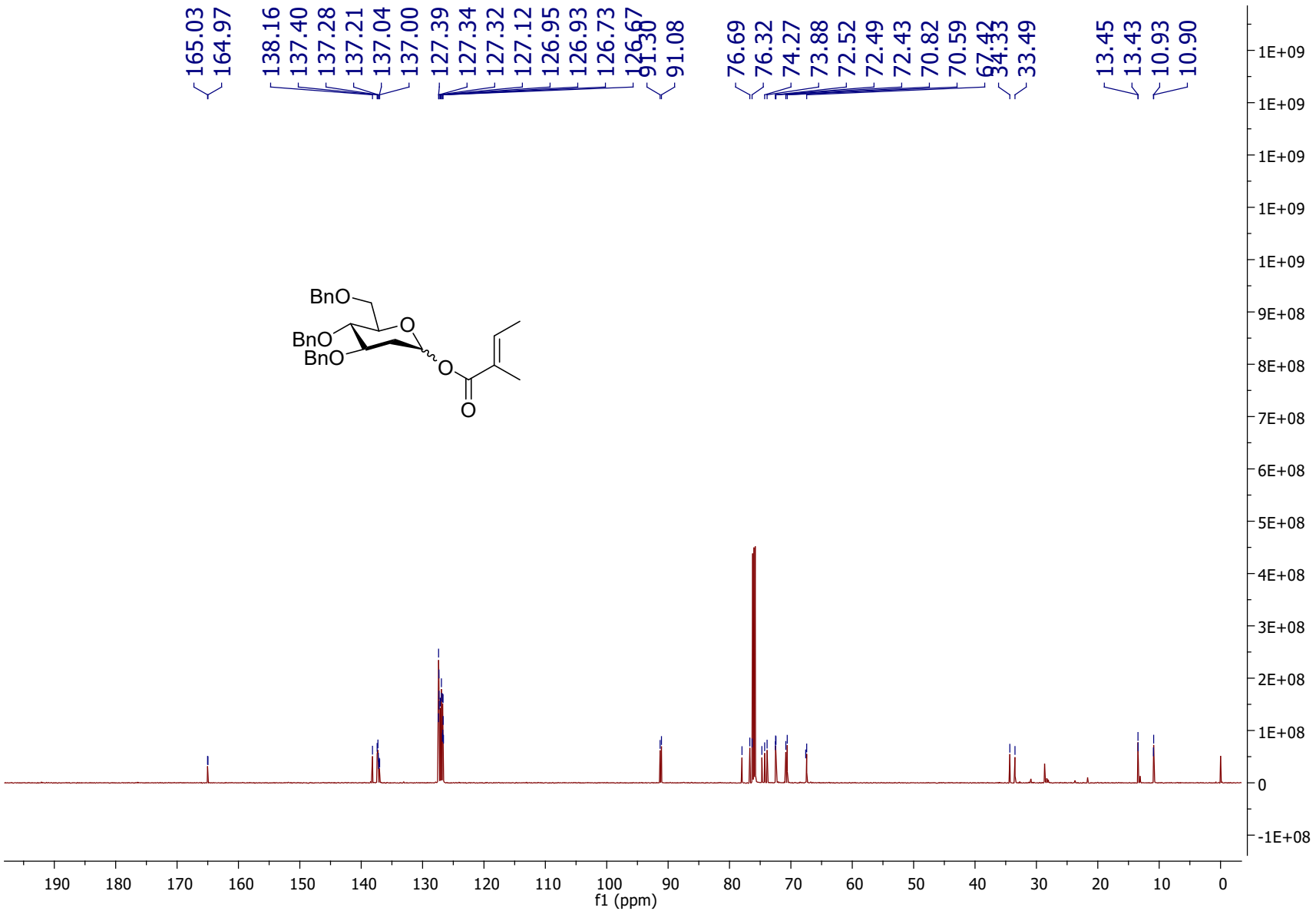


Fig-^{13}C NMR (151 MHz, $CDCl_3$) of compound **3l**

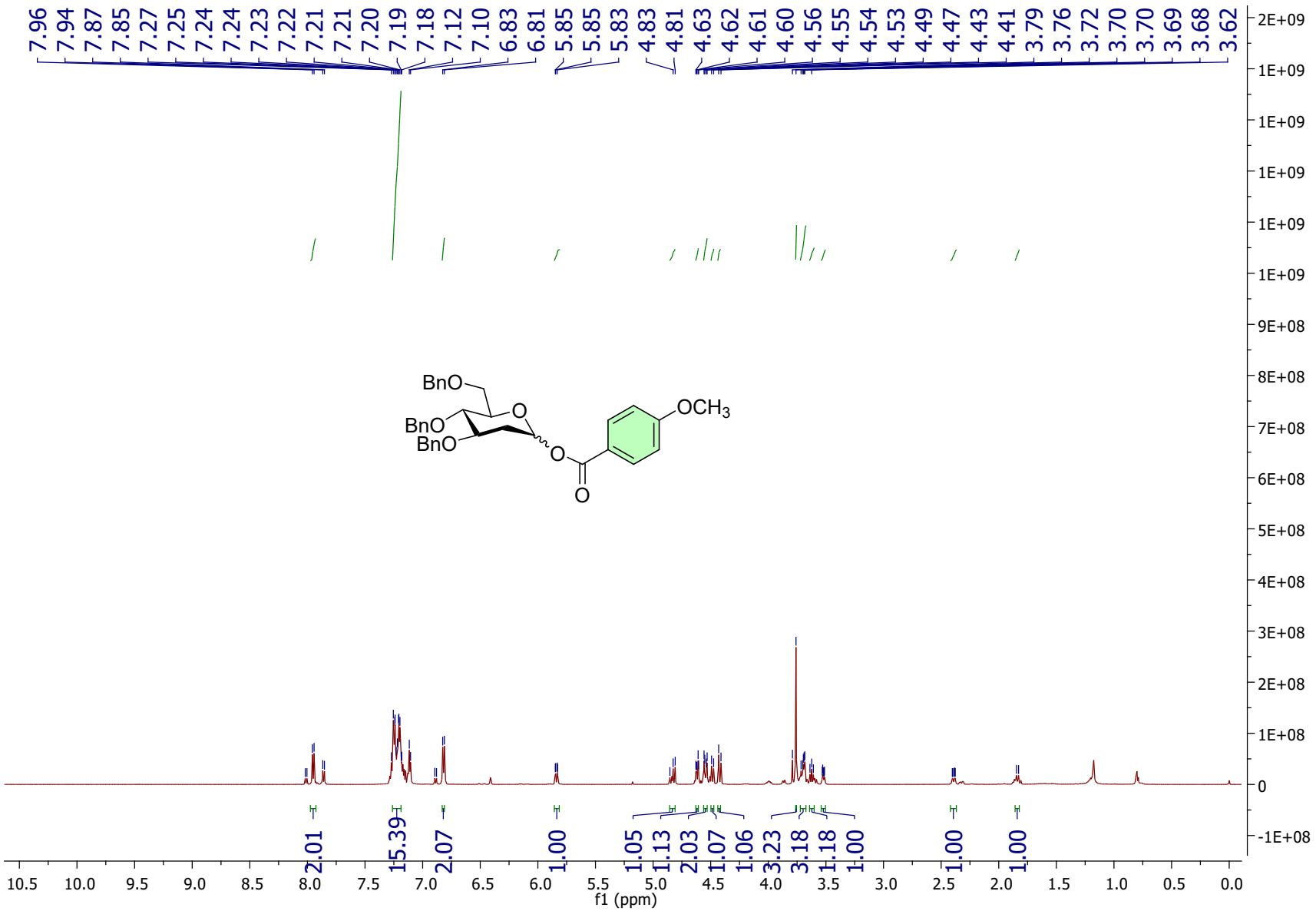


Fig- ^{1}H NMR (600 MHz, $CDCl_3$) of compound **3m**

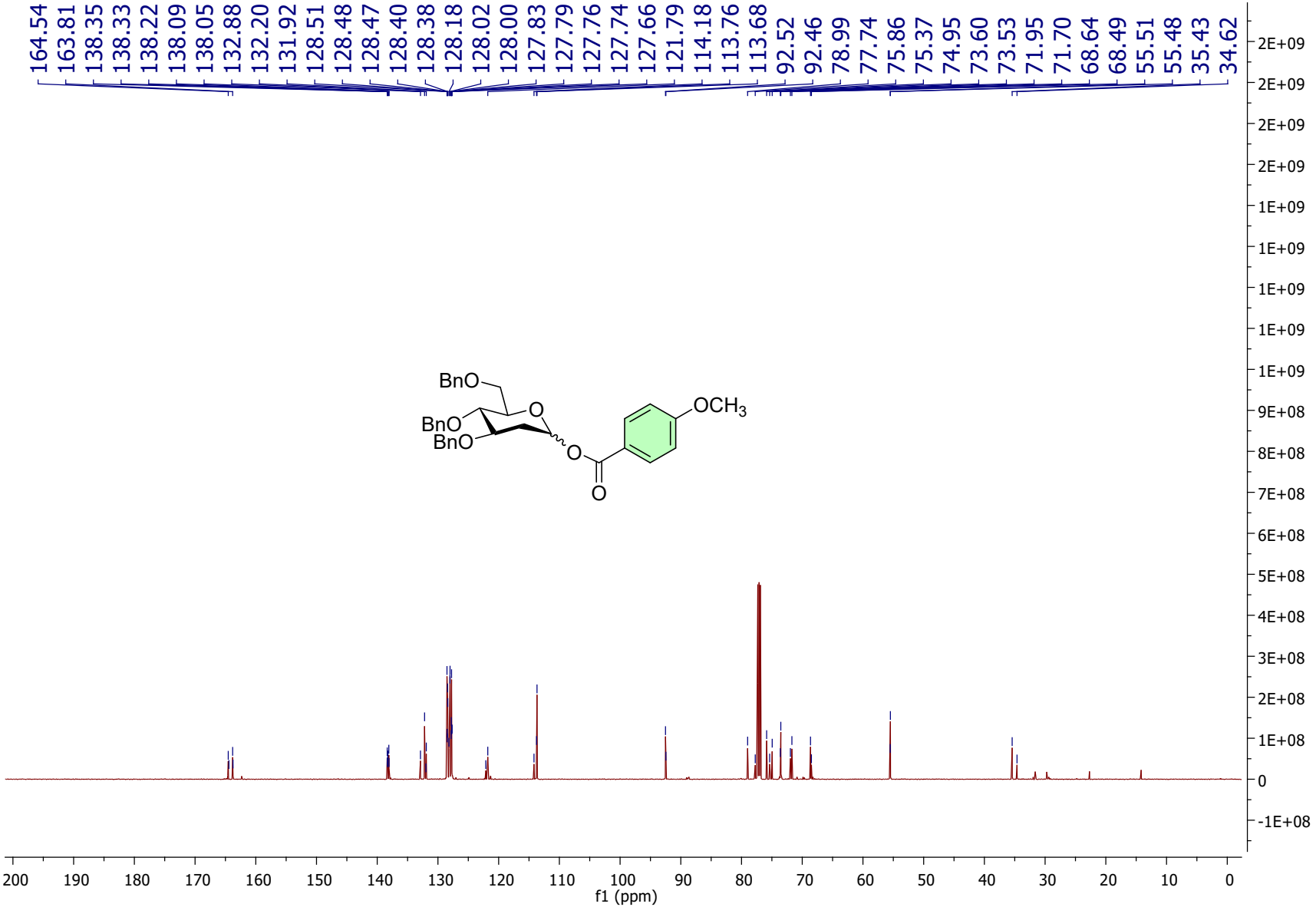


Fig-^{13}C NMR (151 MHz, $CDCl_3$) of compound **3m**

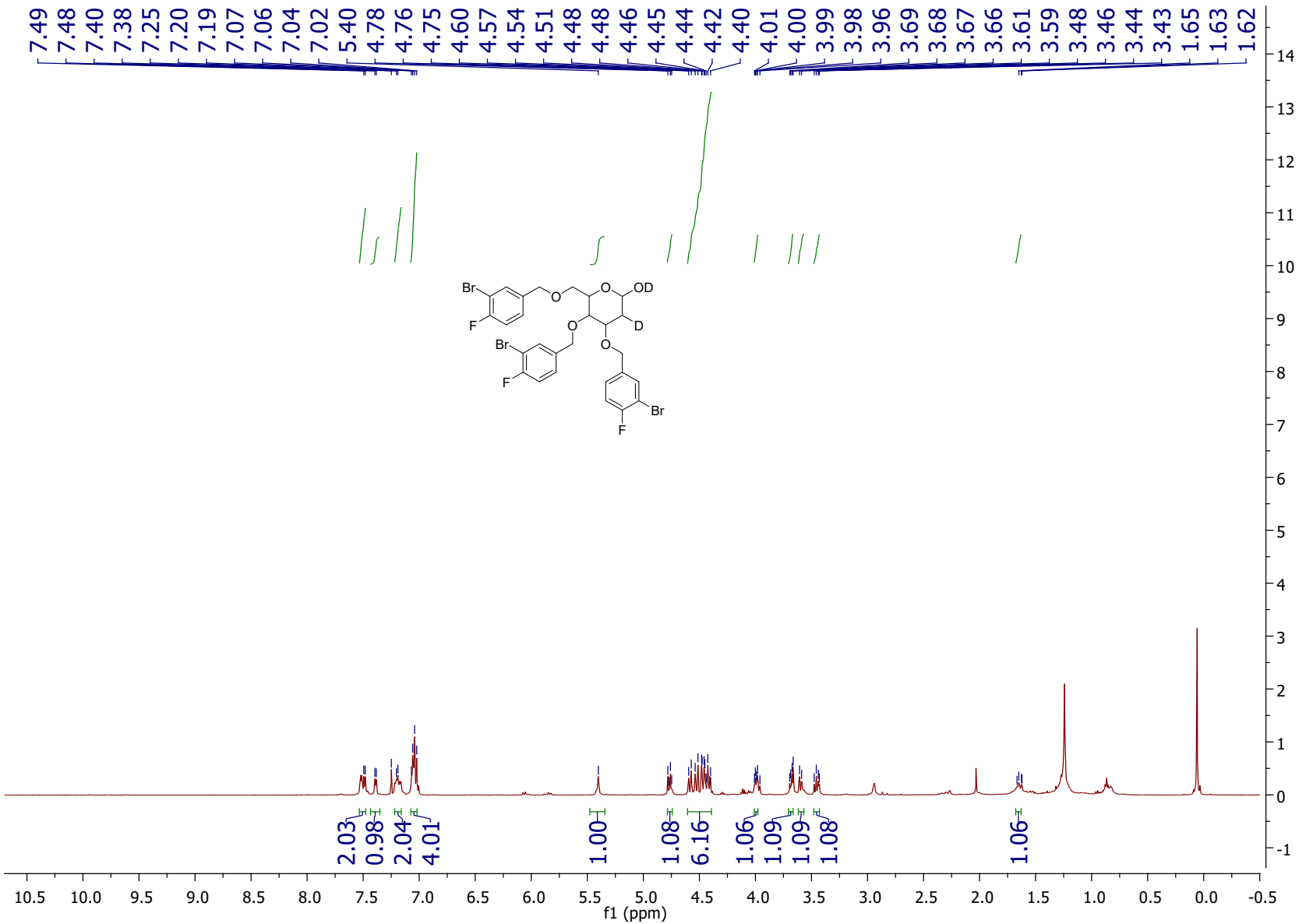


Fig- ^{1}H NMR (600 MHz, $CDCl_3$) of compound **4a**