Supporting Information

Electrochemical Synthesis of Glycosyl Fluorides Using Sulfur(VI) Hexafluoride as the Fluorinating Agent

Sungjin Kim, Pavel Nagorny*

Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109, United States.

*nagorny@umich.edu

Table of contents

I. General Information

Methods and Reagents:

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All reactions were carried out in flame- or oven-dried glassware with magnetic stirring. Reactions were cooled using external cooling baths: ice water (0 °C). Deionized water was used in the preparation of all aqueous solutions and for all aqueous extractions. Solvents used for extraction and chromatography were ACS or HPLC grade. Purification of reaction mixtures was performed by flash column chromatography (FCC) using SiliCycle SilicaFlash P60 (230-400 mesh). Diastereomeric ratios were determined by ^{1}H NMR or ^{19}F NMR analysis.

Instrumentation:

^{1}H NMR spectra were recorded on Varian vnmrs 700 (700 MHz), Varian vnmrs 600 (600 MHz), or Varian vnmrs 500 (500 MHz) spectrometers and chemical shifts (δ) are reported in parts per million (ppm) with solvent resonance as the internal standard ($CDCl_3$ at δ 7.26, CD_3CN at δ 1.94). Data are reported as (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constant(s) in Hz; integration). Proton-decoupled ^{13}C NMR spectra were recorded on Varian vnmrs 700 (700 MHz), Varian vnmrs 600 (600 MHz), or Varian vnmrs 500 (500 MHz) spectrometers and chemical shifts (δ) are reported in ppm with solvent resonance as the internal standard ($CDCl_3$ at δ 77.0, CD_3CN at δ 118.7). ^{19}F NMR spectra were recorded on Varian vnmrs 600 (600 MHz), Varian vnmrs 500 (500 MHz), or Varian vnmrs 400 (400 MHz) spectrometers and chemical shifts (δ) are reported in parts per million (ppm) and are referenced to $CFCl_3$ (δ 0.0). High resolution mass spectra (HRMS) were recorded on Micromass AutoSpec Ultima or VG (Micromass) 70-250-S Magnetic sector mass spectrometers in the University of Michigan mass spectrometry laboratory. Infrared (IR) spectra were recorded as thin films on NaCl plates on a Perkin Elmer Spectrum BX FT-IR spectrometer. Absorption peaks were reported in wavenumbers (cm^{-1}).

Information of the DC power supply equipment:

a. Tekpower TP3005P
   - Output Voltage: 0-30 V
   - Output Current: 0-5 A
   - Setup Resolution: 10 mV / 1 mA
   - Setup Accuracy: ≤ 0.5 % + 20 mV / ≤ 0.5 % + 10 mA

Assignment of Stereochemistry:

Stereochemistry of glycosyl fluoride products (except mannose and rhamnose) are characterized by:

1. One-bond C-F coupling of anomeric carbon in H-coupled ^{13}C NMR; α-glycosyl fluoride, $^{1}J_{C\text{-}F}$ = 224 - 228 Hz and β-glycosyl fluoride, $^{1}J_{C\text{-}F}$ = 213 - 219 Hz.

2. Three-bond H-H coupling between anomeric hydrogen and C2-hydrogen in ^{1}H NMR; α-glycosyl fluoride, $^{3}J_{H\text{-}H}$ = < 3 Hz, and β-glycosyl fluoride, $^{3}J_{H\text{-}H}$ = 5.6 – 7.8 Hz.

For D-mannosyl fluorides and L-rhamnosyl fluorides:

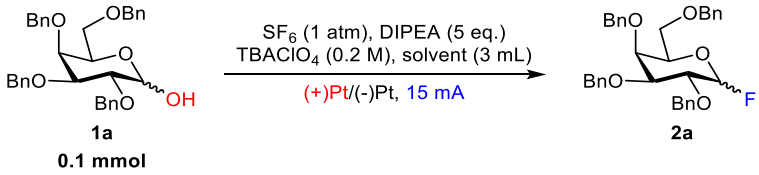
1. One-bond C-F coupling of anomeric carbon in H-coupled ^{13}C NMR; α-anomers, $^{1}J_{C\text{-}F}$ = 221 - 224 Hz and β-anomers, $^{1}J_{C\text{-}F}$ = 213-218 Hz

When previously reported NMR spectra were available, the stereochemistry of the product was confirmed again by comparing with them.

II. Optimization

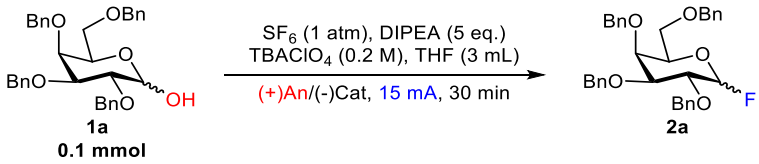
a. Reaction Condition Optimization

Table S1. Solvent Screening



Entry	Solvent	Reaction Time	^{19}F NMR %Yield	Comments
1	MeCN	2 h 30 min	28%	3 eq. of DIPEA instead of 5 eq.
2	DCE	1h	32%	-
3	DCM	20 min	16%	Cathode was coated with brown chunks
4	DMF	1h	0%	-
5	**THF**	**45 min**	**35%**	**^{1}H NMR shows 67% consumption of starting material ^{19}F NMR shows fluorinated side products**

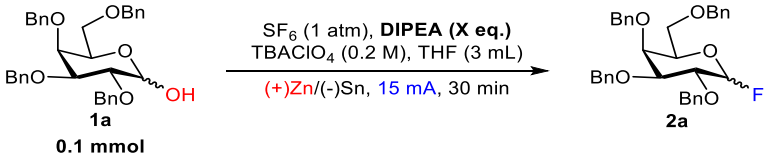
Table S2. Electrode Screening



Entry	(+)An/(-)Cat	Comment	Current Density	Isolated Yield	BRSM[a]
1	**(+)Zn/(-)Pt**	**Worked up ~1h after the reaction was stopped**	**56 mA/cm^2**	**94% (51 mg) α : β = 1 : 1.3**	**95%**
2	(+)Zn/(-)Pt	Worked up right after the reaction was stopped	56 mA/cm^2	90% (48.9 mg)	-
3	(+)Zn/(-)Pt	reaction time = 20min	56 mA/cm^2	80% (43.5 mg)	93.2%
4	**(+)Zn/(-)Sn**	**soldering wire (98% Sn / 2% Ag and Cu)**	**13 mA/cm^2**	**84% (45.6 mg) α : β = 1 : 1.5**	**-**
5	(+)Zn/(-)C	-	3.3 mA/cm^2	22% (11.7 mg) α : β = 1 : 1.3	-
6	(+)Mg/(-)Sn	Mg plate (from Amazon) + soldering wire	13 mA/cm^2	66% (36 mg) α : β = 1 : 1.2	-

[a]Yield based on the recovered starting material.

Table S3. DIPEA Loading and Reaction Time Screening



Entry	DIPEA (X eq.)	Deviation	Isolated Yield
1	5	-	84% (43.5 mg, α : β = 1 : 1.5)
2	3	-	77% (42 mg, α : β = 1 : 1.4)
3	3	New Zn electrode	77.6% (42.1 mg, α : β = 1 : 1.4)
4	3	0.6 mm soldering wire	81% (43.7 mg, α : β = 1 : 1.6)
5	3	0.6 mm soldering wire, 45 min	86% (46.9 mg, α : β = 1 : 1.5)
6	3	0.6 mm soldering wire, 1 h	86% (46.7 mg, α : β = 1 : 1.4)
7	3	Reaction time = 45 min	88% (47.6 mg, α : β = 1 : 1.3)
8	**3**	**Reaction time = 1 h**	**90% (49 mg, α : β = 1 : 1.3)**
9	1	New Zn electrode	55% (30.1 mg, α : β = 1 : 1.2)
10	1	Reaction time = 1 h	73% (39.5 mg, α : β = 1 : 1.3)
11	1	Reaction time = 1.5 h	67% (36.3 mg, α : β = 1 : 1.2) Decomposition
12	0	Reaction time = 16 min (Voltage went above 30V)	57% (31 mg, α : β = 1 : 1.2)
13	0	New Zn electrode 15 mA 15.4V → 8 mA 30V	67% (36.1 mg, α : β = 1 : 1.2)

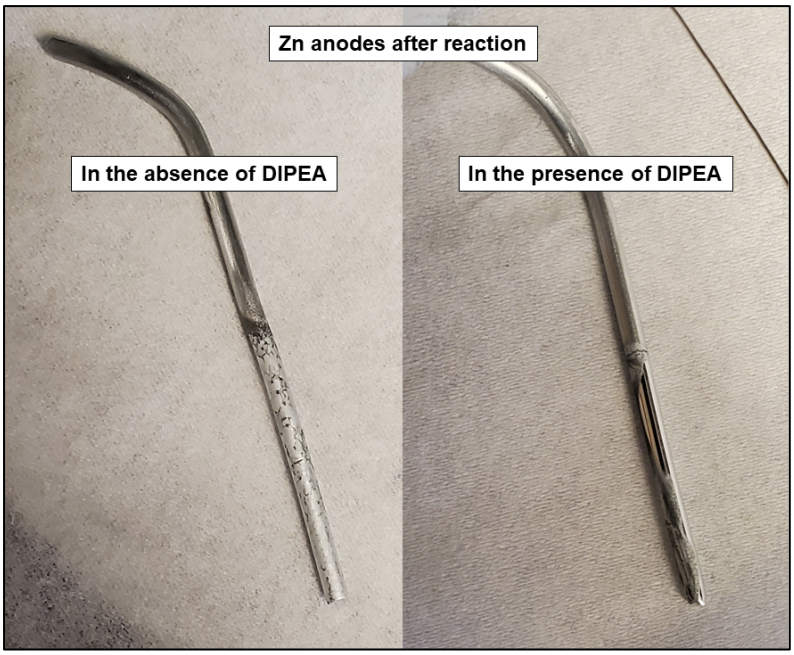
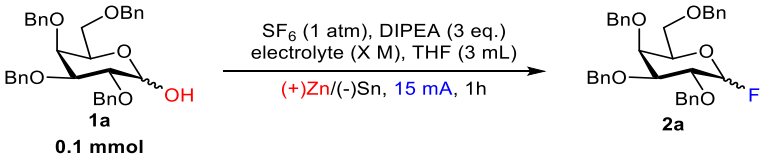


Figure S1. Amine base prevents the electrode passivation.

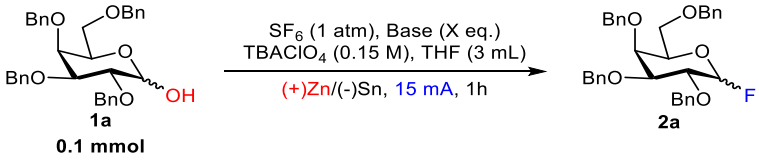
Table S4. Electrolyte Screening



Entry	Electrolyte	Concentration	Monitored V[a]	Comment	Yield (%)
1	**$TBAClO_4$**	**0.2 M**	**15-16 V**	**-**	**90% (49 mg) α : β = 1 : 1.3**
2	**$TBAClO_4$**	**0.15 M**	**22-23 V**	**-**	**93% (50.5 mg) α : β = 1 : 1.3**
3	$TBAClO_4$	0.1 M	30 V (13-14 mA)	-	74% (40 mg) α : β = 1 : 1.3
4	TBAOAc	0.2 M	30 V (0 mA)	electrolytes not dissolving	-
5	$TBAPF_6$	0.2 M	9-10 V	electrolytes extracted in organic layer	75% (40.9 mg) α : β = 1 : 1.4

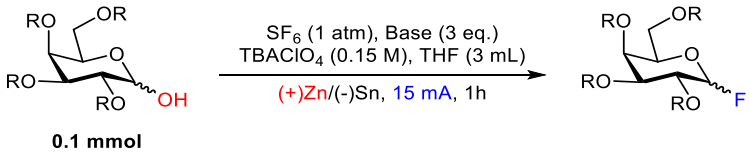
[a]Voltage applied to the electrolytic cell by DC power supply.

Table S5. Amine Base Screening



Entry	Base	Equiv. (X)	Comment	Yield (%)
1	DIPEA	3	-	93% (50.5 mg), α : β = 1 : 1.3
2	**TEA**	**3**	**22 V → 30V (13 mA)**	**93% (50.2 mg), α : β = 1 : 1.4**
3	Pyridine	3	30 V / 14 mA → 30 V / 1-2 mA	Crude NMR shows products and byproduct

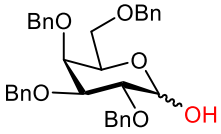
Table S6. TEA vs DIPEA



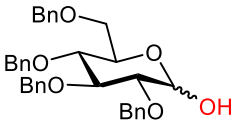
Base	R = Bn (1a)	R = Ac (1k)	R = PMB (1h)
TEA	**93% (50.2 mg, α : β = 1 : 1.4)**	**69% (24.3 mg, α : β = 1.6 : 1)**	**97% (64.1 mg, α : β = 1 : 1.2)**
DIPEA	93% (50.5 mg, α : β = 1 : 1.3)	59% (20.8 mg, α : β = 1.4 : 1)	87% (57.8 mg, α : β = 1 : 1.3)

III. Experimental Procedure

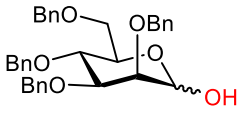
a. Synthesis of Substrates



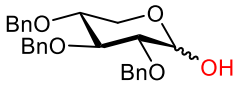
1a



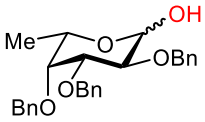
1b



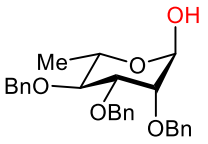
1c



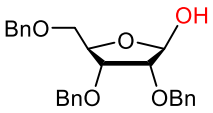
1d



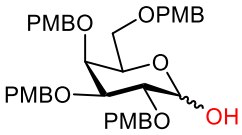
1e



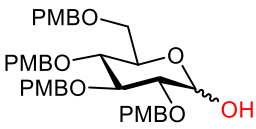
1f



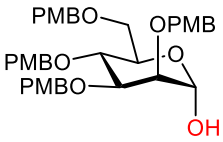
1g



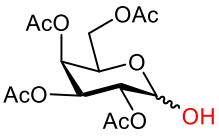
1h



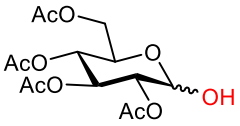
1i



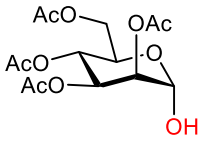
1j



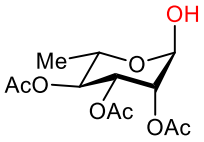
1k



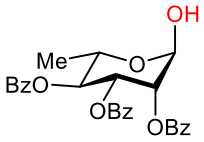
1l



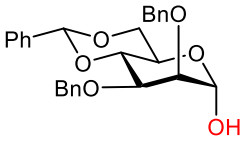
1m



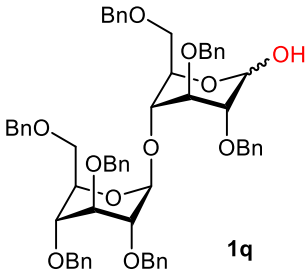
1n



1o

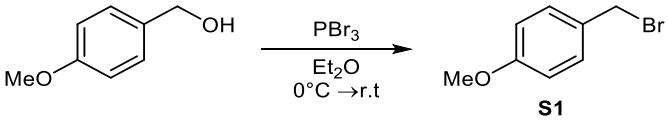


1p

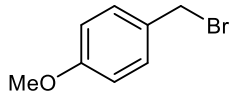


1q

Preparation of 4-Methoxybenzyl bromide (S1)



S1

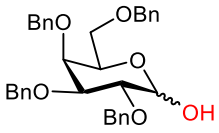


S1

4-Methoxybenzyl bromide (S1)

In a dry round-bottom flask, 4-methoxybenzyl alcohol (112 mmol, 2.8 equiv.) was dissolved with Et_2O (40 mL). After cooling the mixture by placing the flask in an ice bath, PBr_3 (40 mmol, 1 equiv.) was added dropwise into the reaction mixture. The reaction was stirred for 5 hours while it was gradually warmed up to room temperature and quenched by adding aqueous NaCl solution (50 mL). The crude mixture was washed with aqueous $NaHCO_3$ (saturated, 50 mL) and then aqueous NaCl solution (saturated, 50 mL). The organic layer is concentrated *in vacuo* to yield 4-methoxybenzyl bromide **S1** as colorless liquid. The product was confirmed by ^{1}H NMR and was subjected to the next synthesis without further purification. **^{1}H NMR** (700 MHz, Chloroform-*d*) δ 7.33 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 4.51 (s, 2H), 3.81 (s, 3H).

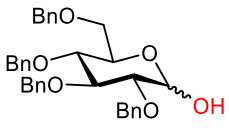
Preparation of 2,3,4,6-tetrakis-*O*-(phenylmethyl)-D-galactopyranoside (1a)



1a

Purchased from CarboSynth. Lot#: MT040861801.

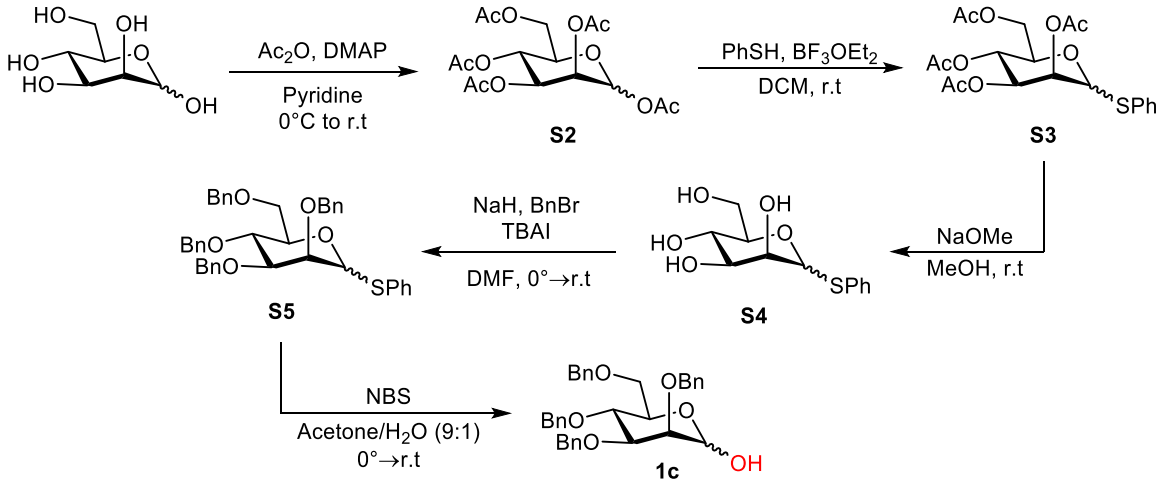
Preparation of 2,3,4,6-Tetrakis-*O*-(phenylmethyl)-D-glucopyranoside (1b)

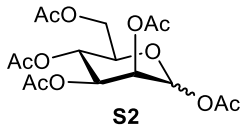


1b

Purchased from CarboSynth. Batch#: MT066911502.

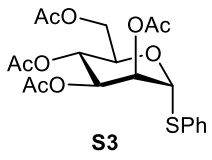
Preparation of 2,3,4,6-tetrakis-*O*-(phenylmethyl)-D-Mannopyranoside (1c)





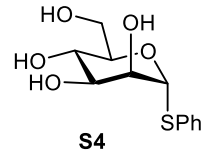
1,2,3,4,6-Penta-*O*-acetyl-D-mannopyranoside (S2)

In an oven dried round-bottom flask, D-mannose (27.8 mmol, 1.0 equiv.) and pyridine (40 mL) were added. The reaction mixture was stirred until the solution became homogeneous, and then the round-bottom flask was placed in an ice-bath. After the reaction was cooled down, acetic anhydride (166.8 mmol, 6.0 equiv.) and DMAP (1.35 mmol, 0.05 equiv.) were added in that order. The reaction was stirred overnight while it was gradually warmed up to the room temperature. The reaction was quenched by diluting with DCM (200 mL) followed by washing with 1N HCl (200 mL x 2), water (200 mL x 2), and then brine (200 mL). Extracted organic layer was dried with Na_2SO_4 and was concentrated *in vacuo* to yield 1,2,3,4,6-penta-*O*-acetyl-D-mannopyranoside **S2**. The product was subjected to the next synthesis without further purification. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.09 (d, *J* = 1.9 Hz, 1H (α-C_1-H)), 5.35 (d, *J* = 6.2 Hz, 2H), 5.30 (s, 1H), 5.27 – 5.26 (m, 1H), 4.29 (dd, *J* = 12.4, 4.9 Hz, 1H), 4.11 (dd, *J* = 12.4, 2.5 Hz, 1H), 4.06 (q, *J* = 6.9, 6.2 Hz, 1H), 2.18 (s, 3H), 2.17 (s, 3H), 2.10 (s, 3H), 2.06 (s, 3H), 2.01 (s, 3H).



Phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-α-D-mannopyranoside (S3)

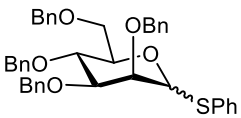
In an oven dried round-bottom flask, **S2** (27.8 mmol, 1.0 equiv.) and DCM (30 mL) were added. After the addition of thiophenol (41.7 mmol, 1.5 equiv.), the round-bottom flask was sealed with a rubber-septum cap and purged with nitrogen gas. The reaction mixture was stirred until it became homogeneous, and then $BF_3 \cdot OEt_2$ (83.4 mmol, 3.0 equiv.) was slowly injected into the flask. The reaction was stirred overnight at room temperature and quenched with aqueous $NaHCO_3$ (saturated, 50 mL). After extracting the mixture with DCM (100mL x 3), the combined organic layer was dried with Na_2SO_4 and concentrated *in vacuo*. The concentrated crude mixture was subjected to FCC (SiO_2, 20% EtOAc in hexane → 40% EtOAc in hexane) to afford phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-D-mannopyranoside **S3**.



S4

Phenyl 1-thio-α-D-mannopyranoside (S4)

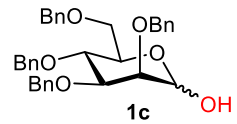
A dry round-bottom flask was filled with **S3** (26.5 mmol, 1.0 equiv.) and anhydrous methanol (50 mL). After the reaction mixture became homogeneous, a chip of sodium metal (2.7 mmol, 0.1 equiv.) was added. The reaction was stirred overnight at room temperature, and then quenched by adding acetic acid until the pH of the reaction became neutral. The crude mixture was concentrated *in vacuo* to yield **S4** as yellowish white solid. The product was subjected to the next synthesis without further purification.



S5

Phenyl 2,3,4,6-tetrakis-*O*-(phenylmethyl)-1-thio-D-mannopyranoside (S5)

An oven dried and nitrogen filled round-bottom flask was charged with **S4** (11 mmol, 1.0 equiv.) and DMF (30 mL). After cooling down the reaction in an ice bath, NaH (88 mmol, 8.0 equiv.) was added portion wise. Once H_2 gas stops generating, PMBBr (88 mmol, 8.0 equiv.) was added followed by TBAI (0.55 mmol, 0.05 equiv.). The reaction mixture was stirred at room temperature overnight and quenched by adding water. The mixture was extracted with EtOAc (100 mL x 3), and the organic layer was dried with Na_2SO_4 and concentrated *in vacuo*. The concentrated crude mixture was subjected to FCC (SiO_2, 20% EtOAc in hexane → 30% EtOAc in hexane) to afford phenyl 2,3,4,6-tetrakis-*O*-(phenylmethyl)-1-thio-D-mannopyranoside **S5** as product

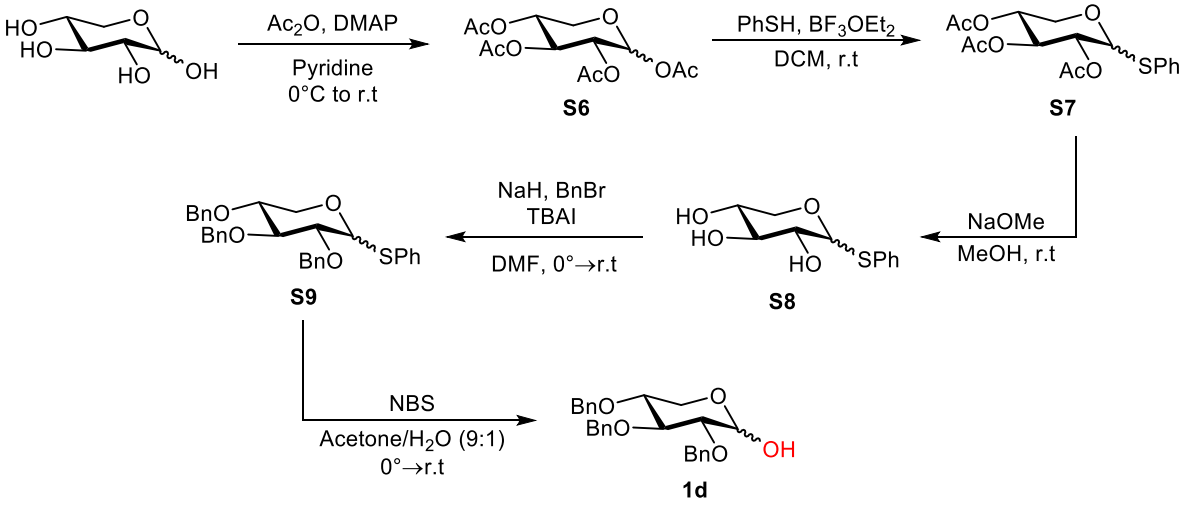


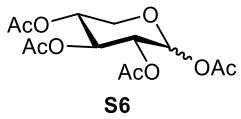
1c

2,3,4,6-Tetrakis-*O*-(phenylmethyl)-D-mannopyranoside (1c)

In a clean round-bottom flask, **S5** (10.9 mmol, 1.0 equiv.) was dissolved with acetone/water mixture (9:1, 55.5 mL). After cooling down the mixture in an ice bath, NBS (22.9 mmol, 2.1 equiv.) was added. The reaction was stirred overnight while it was gradually warmed up to the room temperature. Water (50 mL) was added to quench the reaction followed by the extraction with EtOAc (120 mL x 3). The combined organic layer was dried with Na_2SO_4 and concentrated *in vacuo*. The concentrated crude mixture was subjected to FCC (SiO_2, 40% EtOAc in hexane → 60% EtOAc in hexane) to afford 2,3,4,6-tetrakis-*O*-(phenylmethyl)-D-mannopyranoside **1c** as yellowish syrup.

Preparation of 2,3,4-tris-*O*-(phenylmethyl)-D-xylopyranoside (1d)

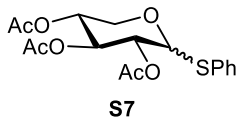




S6

1,2,3,4-Tetra-*O*-acetyl-D-xylopyranoside (S6)

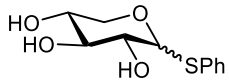
In an oven dried round bottom flask, D-xylopyranose (13 mmol, 1.0 equiv.) and anhydrous pyridine (40 mL) were added. After stirring the mixture until it became homogeneous, the round bottom flask was placed in an ice bath and was cooled down to 0°C. Into the cooled down reaction, acetic anhydride (65 mmol, 5.0 equiv.) and DMAP (0.65 mmol, 0.05 equiv.) were added in that order. The reaction was slowly warmed up to room temperature with stirring until starting materials are gone. The mixture was then diluted with DCM (150 mL) and washed with 1N HCl solution (2 x 120 mL). The organic layer was washed with water (2 x 120 mL) and then saturated brine (2 x 120 mL). The extracted organic layer was dried with Na_2SO_4 and concentrated *in vacuo*. The product 1,2,3,4-Tetra-*O*-acetyl-D-xylopyranose **S6** is subjected to the next synthesis without further purification.



S7

Phenyl 2,3,4-tri-*O*-acetyl-1-thio-D-xylopyranoside (S7)

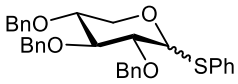
In an oven dried round-bottom flask, **S6** (13 mmol, 1.0 equiv.) and DCM (15 mL) were added. After the addition of thiophenol (19.5 mmol, 1.5 equiv.), the round-bottom flask was sealed with a rubber-septum cap and purged with nitrogen gas. The reaction mixture was stirred until it became homogeneous, and then $BF_3{\cdot}OEt_2$ (33 mmol, 3.0 equiv.) was slowly injected into the flask. The reaction was stirred overnight at room temperature and quenched with saturated $NaHCO_3$ solution (50 mL). After extracting the mixture with DCM (3 x 70mL), the combined organic layer was dried with Na_2SO_4 and concentrated *in vacuo*. The concentrated crude mixture was subjected to FCC (SiO_2, 20% EtOAc in hexane) to afford phenyl 2,3,4-tri-*O*-acetyl-1-thio-D-xylopyranose **S7** as yellowish oil.



S8

Phenyl 1-thio-D-xylopyranoside (S8)

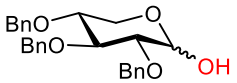
A dry round-bottom flask was filled with **S7** (13 mmol, 1.0 equiv.) and anhydrous methanol (40 mL). After the reaction mixture became homogeneous, a chip of sodium metal (1.3 mmol, 0.1 equiv.) was added. The reaction was stirred overnight at room temperature, and then quenched by adding acetic acid until the pH of the reaction became neutral. The crude mixture was concentrated *in vacuo* to yield yellowish white solid. The product phenyl 1-thio-D-xylopyranose **S8** was subjected to the next synthesis without further purification.



S9

Phenyl 2,3,4-tris-*O*-(phenylmethyl)-1-thio-D-xylopyranoside (S9)

An oven dried and nitrogen filled round-bottom flask was charged with **S8** (13 mmol, 1.0 equiv.) and DMF (60 mL). After cooling down the reaction in an ice bath, NaH (78 mmol, 6.0 equiv.) was added portion wise. Once H_2 gas stops generating, BnBr (78 mmol, 6.0 equiv.) was added followed by TBAI (0.65 mmol, 0.05 equiv.). The reaction mixture was stirred at room temperature overnight and quenched by adding water. The mixture was extracted with EtOAc (3 x 100 mL), and the organic layer was dried with Na_2SO_4 and concentrated *in vacuo*. The concentrated crude mixture was subjected to FCC (SiO_2, 20% EtOAc in hexane) to afford phenyl 2,3,4-tris-*O*-(phenylmethyl)-1-thio-D-xylopyranoside **S9** as yellowish oil.



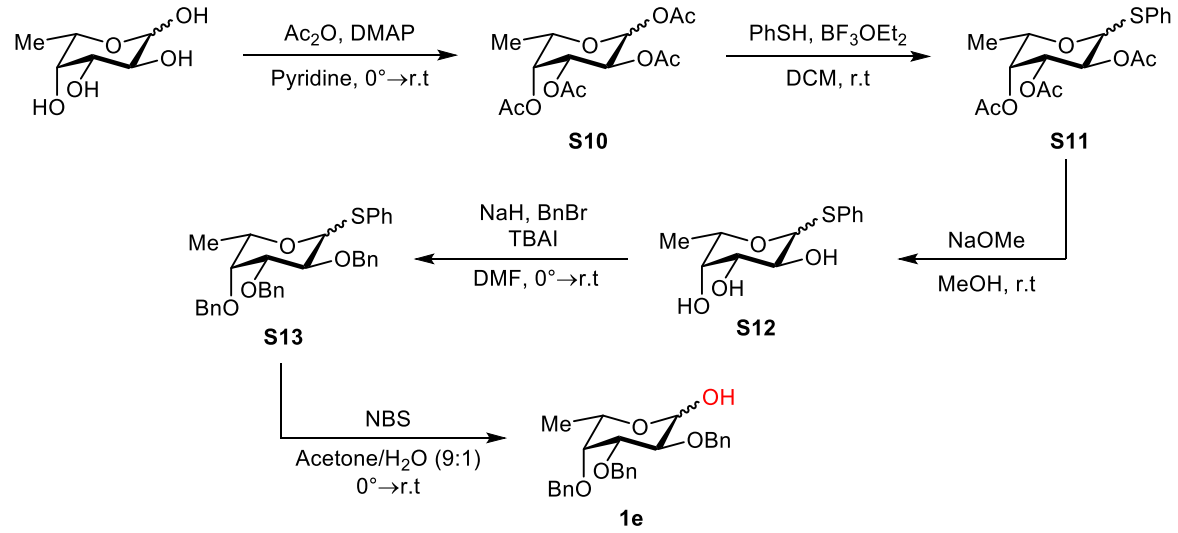
1d

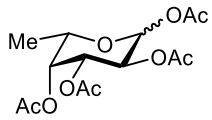
2,3,4-tris-*O*-(phenylmethyl)-D-xylopyranoside (1d)

In a clean round-bottom flask, **S9** (13 mmol, 1 equiv.) was dissolved with acetone/water mixture (9:1, 50 mL). After cooling down the mixture in an ice bath, NBS (26 mmol, 2 equiv.) was added. The reaction was stirred overnight while it was gradually warmed up to the room temperature. Water (50 mL) was added to quench the reaction followed by the extraction with EtOAc (3 x 120 mL). The combined organic layer was dried with Na_2SO_4 and concentrated *in vacuo*. The concentrated crude mixture was subjected to FCC (SiO_2, 10% EtOAc in DCM) to afford 2,3,4-tris-*O*-(phenylmethyl)-D-xylopyranose **1d** as white solid, which is confirmed by comparing with literature NMR spectra.[1]

[1]Zhang, J.; Fu, J.; Si, W.; Wang, X.; Wang, Z.; Tang, J. *Carbohydrate Research.* **2011**, 346, 2290-2293

Preparation of 2,3,4-tris-*O*-(phenylmethyl)-L-fucopyranoside (1e)

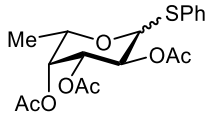




S10

1,2,3,4-Tetra-*O*-acetyl-L-fucopyranoside (S10)

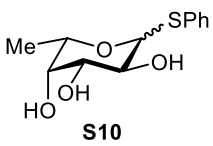
In an oven dried round bottom flask, L-fucose (3.05 mmol, 1.0 equiv.) and anhydrous pyridine (10 mL) were added. After stirring the mixture until it became homogeneous, the round bottom flask was placed in an ice bath and was cooled down to 0°C. Into the cooled down reaction, acetic anhydride (18.3 mmol, 6.0 equiv.) and DMAP (0.15 mmol, 0.05 equiv.) were added in that order. The reaction was slowly warmed up to room temperature with stirring until starting materials are gone. The mixture was then diluted with DCM (100 mL) and washed with 1N HCl solution (2 x 80 mL). The organic layer was washed with water (2 x 80 mL) and then saturated brine (2 x 80 mL). The extracted organic layer was dried with Na_2SO_4 and concentrated *in vacuo*. The product 1,2,3,4-tetra-*O*-acetyl-L-fucopyranoside **S10** is subjected to the next synthesis without further purification.



S11

Phenyl 2,3,4-tri-*O*-acetyl-1-thio-L-fucopyranoside (S11)

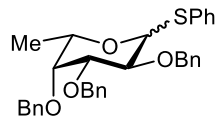
In an oven dried round bottom flask, **S8** (3.0 mmol, 1.0 equiv.) and anhydrous DCM (5 mL) were added. After stirring until the mixture became homogeneous, PhSH (4.5 mmol, 1.5 equiv.) and $BF_3{\cdot}OEt_2$ (9.0 mmol, 3.0 equiv.) were added. Then, the reaction mixture was stirred overnight and quenched with saturated $NaHCO_3$ solution (20 mL). The aqueous layer was extracted with DCM (3 x 35 mL) and dried with Na_2SO_4. The extracted organic layer was concentrated in vacuo and subjected to FCC (SiO_2, 30% EtOAc in hexane → 50% EtOAc in hexane) to afford phenyl 2,3,4-tri-*O*-acetyl-1-thio-L-fucopyranoside **S11**.



S10

Phenyl 1-thio-L-fucopyranoside (S12)

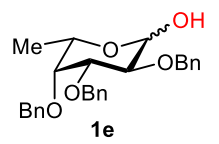
In an oven dried round bottom flask, **S9** (2.9 mmol, 1 equiv.) and MeOH (20 mL) were added. After stirring until the mixture became homogeneous, Na metal (0.29 mmol, 0.1 equiv.) was added and stirred at room temperature until all starting materials were consumed. Once all starting materials are gone, the reaction was neutralized with acetic acid and was concentrated *in vacuo* to afford phenyl 1-thio-L-fucopyranoside **S10** as yellowish syrup. The product was subjected to next reaction without further purification.



S11

Phenyl 2,3,4-tri-*O*-(phenylmethyl)-1-thio-L-fucopyranoside (S13)

An oven dried and nitrogen filled round-bottom flask was charged with **S10** (3.0 mmol, 1.0 equiv.) and DMF (23 mL). After cooling down the reaction in an ice bath, NaH (18 mmol, 6.0 equiv.) was added portion wise. Once H_2 gas stops generating, BnBr (18 mmol, 6.0 equiv.) was added followed by TBAI (0.15 mmol, 0.05 equiv.). The reaction mixture was stirred at room temperature overnight and quenched by adding water. The mixture was extracted with EtOAc (3 x 100 mL), and the organic layer was dried with Na_2SO_4 and concentrated *in vacuo*. The concentrated crude mixture was subjected to FCC (SiO_2, 20% EtOAc in hexane) to afford phenyl 2,3,4-tris-*O*-(phenylmethyl)-1-thio-D-fucopyranoside **S11** as yellowish oil.



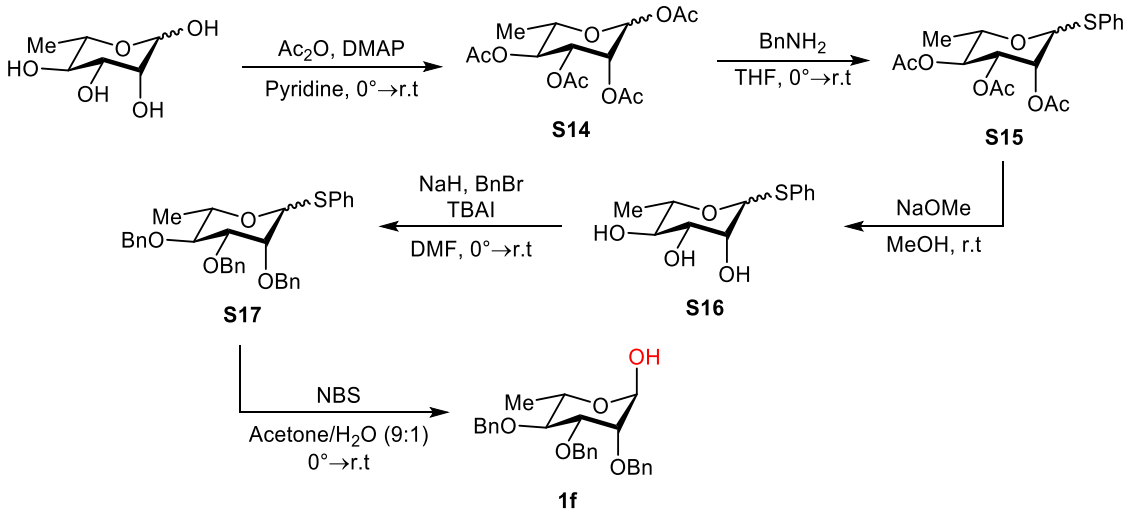
1e

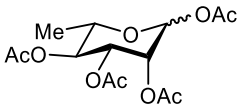
2,3,4-Tris-*O*-(phenylmethyl)-L-fucopyranoside (1e)

In a clean round-bottom flask, **S11** (2.6 mmol, 1 equiv.) was dissolved with acetone/water mixture (9:1, 25 mL). After cooling down the mixture in an ice bath, NBS (5.2 mmol, 2 equiv.) was added. The reaction was stirred overnight while it was gradually warmed up to the room temperature. Water (20 mL) was added to quench the reaction followed by the extraction with EtOAc (3 x 100 mL). The combined organic layer was dried with Na_2SO_4 and concentrated *in vacuo*. The concentrated crude mixture was subjected to FCC (SiO2, 30% EtOAc in hexane) to afford **1e** as white solid, which is confirmed by comparing with literature NMR spectra.[2]

[2]Nishi, Y.; Tanimoto, T. *Biosci. Biotechnol. Biochem.* **2009**, 73 (3), 562–569

Preparation of 2,3,4-tri-*O*-(phenylmethyl)-α-L-rhamnopyranoside (1f)

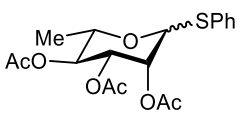




S14

1,2,3,4-Tetra-*O*-acetyl-L-rhamnopyranoside (S14)

An oven dried round bottom flask was charged with L-rhamnose (3.0 mmol, 1.0 equiv.) and anhydrous pyridine (10 mL). After stirring the mixture until it became homogeneous, the round bottom flask was placed in an ice bath and was cooled down to 0°C. Into the cooled down mixture, acetic anhydride (18 mmol, 6.0 equiv.) and DMAP (0.15 mmol, 0.05 equiv.) were added in that order. The reaction was slowly warmed up to room temperature with stirring until all starting materials were gone. The mixture was then diluted with DCM (100 mL) and washed with 1N HCl solution (2 x 80 mL). The organic layer was washed with water (2 x 80 mL) and then saturated brine (2 x 80 mL). The extracted organic layer was dried with Na_2SO_4 and concentrated *in vacuo* to afford 1,2,3,4-tetra-*O*-acetyl-L-rhamnopyranoside **S14** as yellowish syrup. The product was then subjected to the next synthesis without further purification.

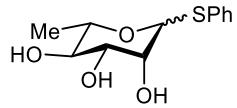


S15

Phenyl 2,3,4-tri-*O*-acetyl-1-thio-L-rhamnopyranoside (S15)

In an oven dried round bottom flask, **S14** (3.0 mmol, 1.0 equiv.) and anhydrous DCM (5 mL) were added. After stirring until the mixture became homogeneous, PhSH (4.5 mmol, 1.5 equiv.) and $BF_3{\cdot}OEt_2$ (9.0 mmol, 3.0 equiv.) were added. The reaction mixture was stirred overnight and quenched with saturated $NaHCO_3$ solution (20 mL). The aqueous layer was extracted with DCM (3 x 35 mL) and dried with Na_2SO_4. The extracted organic layer was concentrated *in vacuo* and subjected to FCC (SiO_2, 30% EtOAc in hexane) to afford phenyl 2,3,4-tri-*O*-acetyl-1-thio-L-rhamnopyranoside **S15** as white solid.

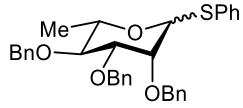
Phenyl 1-thio-L-rhamnopyranoside (S16)



S16

In an oven dried round bottom flask, **S15** (3.0 mmol, 1 equiv.) and MeOH (20 mL) were added. After stirring until the mixture became homogeneous, a chip of sodium metal (0.3 mmol, 0.1 equiv.) was added and stirred at room temperature until all starting materials were consumed. Once all starting materials are gone, the reaction was neutralized with acetic acid and was concentrated *in vacuo* to afford phenyl 1-thio-L-rhamnopyranoside **S16** as white syrup. The product was then subjected to next reaction without further purification.

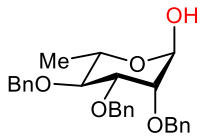
Phenyl 2,3,4-tri-*O*-(phenylmethyl)-1-thio-L-rhamnopyranoside (S17)



S17

An oven dried and nitrogen filled round-bottom flask was charged with **S16** (3.0 mmol, 1.0 equiv.) and DMF (20 mL). After cooling down the reaction in an ice bath, NaH (18 mmol, 6.0 equiv.) was added portion wise. Once H_2 gas stops generating, BnBr (18 mmol, 6.0 equiv.) was added followed by TBAI (0.15 mmol, 0.05 equiv.). The reaction mixture was stirred at room temperature overnight and quenched by adding water. The mixture was extracted with EtOAc (3 x 60 mL), and the organic layer was dried with Na_2SO_4 and concentrated *in vacuo*. The concentrated crude mixture was subjected to FCC (SiO_2, 5% EtOAc in hexane) to afford phenyl 2,3,4-tri-*O*-(phenylmethyl)-1-thio-L-rhamnopyranoside **S17** as yellowish oil.

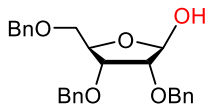
2,3,4-tri-*O*-(phenylmethyl)-α-L-rhamnopyranoside (1f)



1f

In a clean round-bottom flask, **S7** (2.5 mmol, 1 equiv.) was dissolved with acetone/water mixture (9:1, 22.2 mL). After cooling down the mixture in an ice bath, NBS (5.0 mmol, 2.0 equiv.) was added. The reaction was stirred overnight while it was gradually warmed up to the room temperature. Water (20 mL) was added to quench the reaction followed by the extraction with EtOAc (3 x 70 mL). The combined organic layer was dried with Na_2SO_4 and concentrated *in vacuo*. The concentrated crude mixture was subjected to FCC (SiO2, 30% EtOAc in hexane) to afford 2,3,4-tri-*O*-(phenylmethyl)-α-L-rhamnopyranoside **1f** as white solid, which is confirmed by comparing with literature NMR spectra.[3]

Preparation of 2,3,5-Tris-*O*-(phenylmethyl)-β-D-ribofuranose (1g)

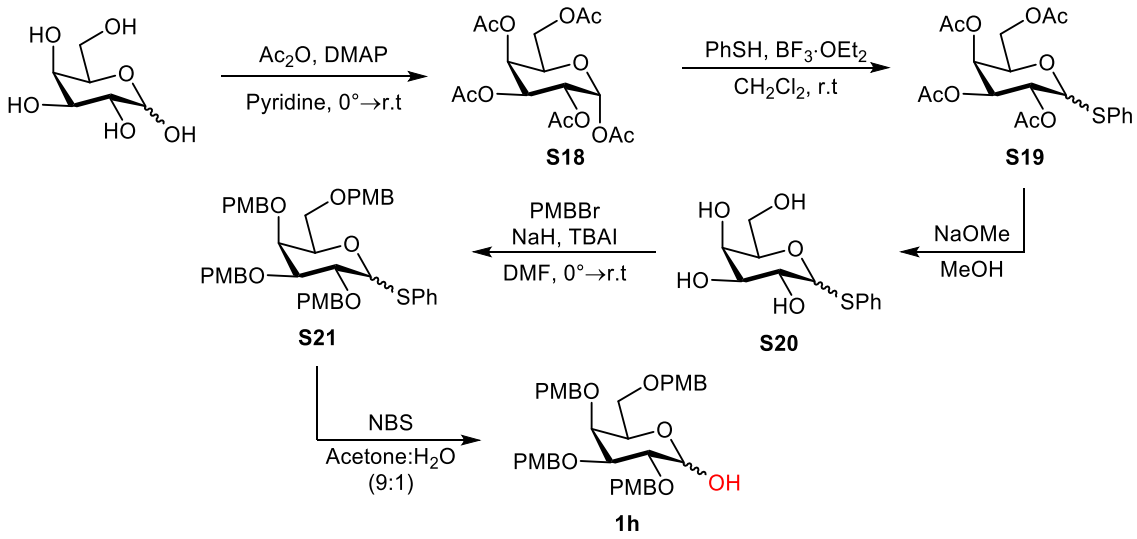


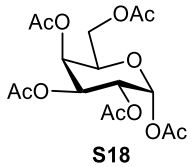
1g

Purchased from Combi-Blocks. Batch#: A98634.

[3]Zhang, J.; Fu, J.; Si, W.; Wang, X.; Wang, Z.; Tang, J. *Carbohydrate Research.* **2011**, 346, 2290-2293

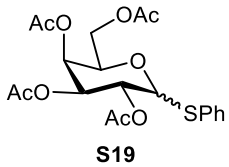
Preparation of 2,3,4,6-tetrakis-*O*-[(4-methoxyphenyl)methyl]-D-galactopyranose (1h)




S18

1,2,3,4,6-Penta-*O*-acetyl-α-D-galactopyranoside (S18)

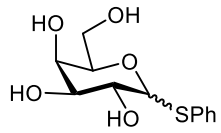
In an oven dried round-bottom flask, D-galactose (5.55 mmol, 1.0 equiv.) and pyridine (20 mL) were added. The reaction mixture was stirred until the solution became homogeneous, and then the round-bottom flask was placed in an ice-bath. After the reaction was cooled down, acetic anhydride (33.3 mmol, 6.0 equiv.) and DMAP (0.278 mmol, 0.05 equiv.) were added in that order. The reaction was stirred overnight while it was gradually warmed up to the room temperature. The reaction was quenched by diluting with DCM (150 mL) followed by washing with 1N HCl (2 x 150 mL), water (2 x 150 mL), and then brine (150 mL). Extracted organic layer was dried with Na_2SO_4 and was concentrated *in vacuo* to yield 1,2,3,4,6-penta-*O*-acetyl-α-D-galactopyranoside **S18** as yellowish syrup. The product was subjected to the next synthesis without further purification. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 6.38 (d, *J* = 1.8 Hz, 1H), 5.50 (d, *J* = 1.5 Hz, 1H), 5.36 – 5.32 (m, 2H), 4.34 (td, *J* = 6.6, 1.4 Hz, 1H), 4.14 – 4.05 (m, 2H), 2.16 (s, 3H), 2.16 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H).


S19

Phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-D-galactopyranoside (S19)

In an oven dried round-bottom flask, **S18** (11 mmol, 1.0 equiv.) and DCM (15 mL) were added. After the addition of thiophenol (16.5 mmol, 1.5 equiv.), the round-bottom flask was sealed with a rubber-septum cap and purged with nitrogen gas. The reaction mixture was stirred until it became homogeneous, and then $BF_3{\cdot}OEt_2$ (33 mmol, 3.0 equiv.) was slowly injected into the flask. The reaction was stirred overnight at room temperature and quenched with saturated $NaHCO_3$ solution (50 mL). After extracting the mixture with DCM (3 x 70mL), the combined organic layer was dried with Na_2SO_4 and concentrated *in vacuo*. The concentrated crude mixture was subjected to FCC (SiO_2, 20% EtOAc in hexane → 40% EtOAc in hexane) to afford phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-D-galactopyranoside **S19** as product. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.54 – 7.49 (m, 2H), 7.34 – 7.30 (m, 3H), 5.42 (dd, *J* = 3.4, 1.1 Hz, 1H), 5.24 (t, *J* = 10.0 Hz, 1H), 5.05 (dd, *J* = 9.9, 3.3 Hz, 1H), 4.72 (d, *J* = 10.0 Hz, 1H), 4.19 (dd, *J* = 11.3, 7.0 Hz, 1H), 4.12

(dd, *J* = 11.4, 6.3 Hz, 2H), 3.96 – 3.92 (m, 1H), 2.12 (s, 3H), 2.10 (s, 3H), 2.04 (s, 3H), 1.98 (s, 3H).

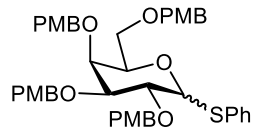


S22

Phenyl 1-thio-D-galactopyranoside (S20)

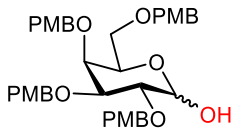
A dry round-bottom flask was filled with **S19** (11 mmol, 1.0 equiv.) and dry methanol (45 mL). After the reaction mixture became homogeneous, a chip of sodium metal (1.1 mmol, 0.1 equiv.) was added. The reaction was stirred overnight at room temperature, and then quenched by adding acetic acid until the pH of the reaction became neutral. The crude mixture was concentrated *in vacuo* to afford phenyl 1-thio-D-galactopyranoside **S20** as yellowish white solid. The product was subjected to the subsequent reaction without further purification.

Phenyl 2,3,4,6-tetrakis-*O*-[(4-methoxyphenyl)methyl]-1-thio-D-galactopyranoside (S21)



S21

An oven dried and nitrogen filled round-bottom flask was charged with **S20** (11 mmol, 1.0 equiv.) and DMF (60 mL). After cooling down the reaction in an ice bath, NaH (88 mmol, 8.0 equiv.) was added portion wise. Once H_2 gas stops generating, PMBBr (88 mmol, 8.0 equiv.) was added followed by TBAI (1.1 mmol, 0.1 equiv.). The reaction mixture was stirred at room temperature overnight and quenched by adding water. The mixture was extracted with EtOAc (3 x 100 mL), and the organic layer was dried with Na_2SO_4 and concentrated *in vacuo*. The concentrated crude mixture was subjected to FCC (SiO_2, 20% EtOAc in hexane → 30% EtOAc in hexane) to afford phenyl 2,3,4,6-tetrakis-*O*-[(4-methoxyphenyl)methyl]-1-thio-D-galactopyranoside **S21** as yellowish syrup.



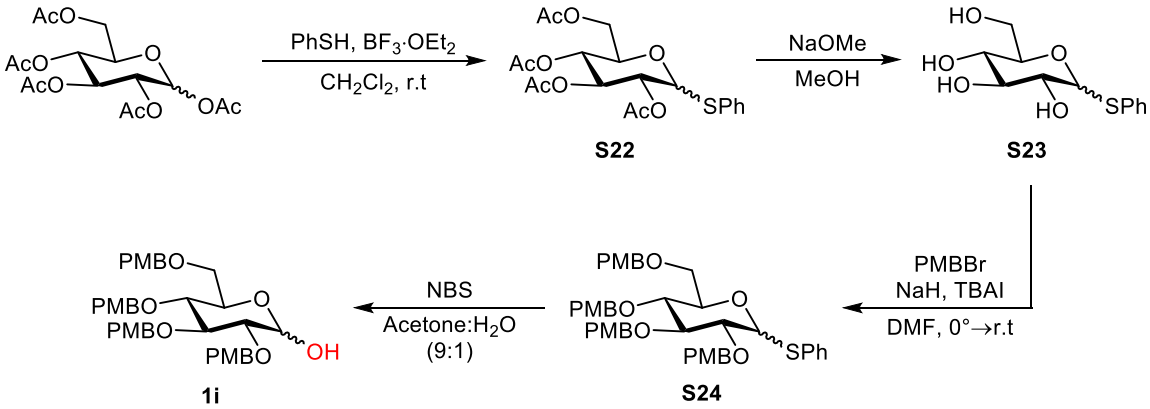
1h

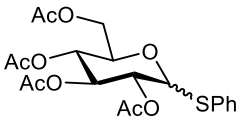
2,3,4,6-tetrakis-*O*-[(4-methoxyphenyl)methyl]-D-galactopyranoside (1h)

In a clean round-bottom flask, **S21** (10 mmol, 1.0 equiv.) was dissolved with acetone/water mixture (9:1, 55.5 mL). After cooling down the mixture in an ice bath, NBS (21 mmol, 2.1 equiv.) was added. The reaction was stirred overnight while it was gradually warmed up to the room temperature. Water (50 mL) was added to quench the reaction followed by the extraction with EtOAc (3 x 120 mL). The combined organic layer was dried with Na_2SO_4 and concentrated *in vacuo*. The concentrated crude mixture was subjected to FCC (SiO2, 30% EtOAc in hexane → 40% EtOAc in hexane) to afford 2,3,4,6-tetrakis-*O*-[(4-methoxyphenyl)methyl]-D-galactopyranoside **1h** as white solid product, which is confirmed by comparing with literature NMR spectra.[4]

[4]Whalen, L. J.; Halcomb, R. L. *Org. Lett.* **2004**, 6, 19, 3221-3224

Preparation of 2,3,4,6-tetrakis-*O*-[(4-methoxyphenyl)methyl]-α-D-glucopyranoside (1i)

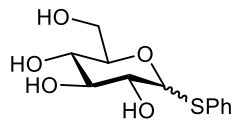




S22

Phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-D-glucopyranoside (S22)

In an oven dried round-bottom flask, 1,2,3,4,6-penta-*O*-acetyl-D-glucopyranoside (5.0 mmol, 1.0 equiv.) and DCM (5 mL) were added. After the addition of thiophenol (7.5 mmol, 1.5 equiv.), the round-bottom flask was sealed with a rubber-septum cap and purged with nitrogen gas. The reaction mixture was stirred until it became homogeneous, and then $BF_3 \cdot OEt_2$ (15 mmol, 3.0 equiv.) was slowly injected into the flask. The reaction was stirred overnight at room temperature and quenched with saturated $NaHCO_3$ solution (10 mL). After extracting the mixture with DCM (3 x 50mL), the combined organic layer was dried with Na_2SO_4 and concentrated *in vacuo*. The concentrated crude mixture was subjected to FCC (SiO_2, pure hexane → 30% EtOAc in hexane) to afford phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-D-glucopyranoside **S22** as white solid.

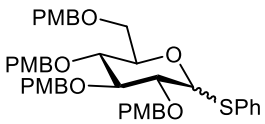


S23

Phenyl 1-thio-D-glucopyranoside (S23)

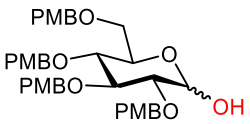
A dry round-bottom flask was filled with **S22** (5.0 mmol, 1.0 equiv.) and dry methanol (30 mL). After the reaction mixture became homogeneous, a chip of sodium metal (0.5 mmol, 0.1 equiv.) was added. The reaction was stirred overnight at room temperature, and then quenched by adding acetic acid until the pH of the reaction became neutral. The crude mixture was concentrated *in vacuo* to yield **S23** as yellowish white solid. The product was subjected to the subsequent reaction without further purification.

Phenyl 2,3,4,6-tetrakis-*O*-[(4-methoxyphenyl)methyl]-1-thio-D-glucopyranoside (S24)



S24

An oven dried and nitrogen filled round-bottom flask was charged with **S23** (5.0 mmol, 1.0 equiv.) and DMF (30 mL). After cooling down the reaction in an ice bath, NaH (25 mmol, 5.0 equiv.) was added portion wise. Once H_2 gas stops generating, PMBBr (25 mmol, 5.0 equiv.) was added followed by TBAI (0.5 mmol, 0.1 equiv.). The reaction mixture was stirred at room temperature overnight and quenched by adding water. The mixture was extracted with EtOAc (3 x 100 mL), and the organic layer was dried with Na_2SO_4 and concentrated *in vacuo*. The concentrated crude mixture was subjected to FCC (SiO_2, 40% EtOAc in hexane) to afford phenyl 2,3,4,6-tetrakis-*O*-[(4-methoxyphenyl)methyl]-1-thio-D-glucopyranoside **S24** as yellowish white syrup.



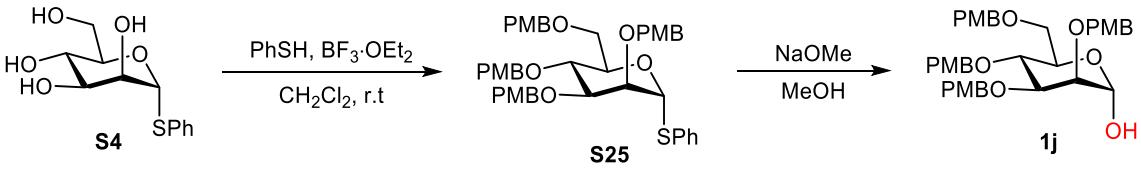
1i

2,3,4,6-Tetrakis-*O*-[(4-methoxyphenyl)methyl]-α-D-glucopyranoside (1i)

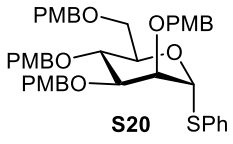
In a clean round-bottom flask, **S24** (5.0 mmol, 1.0 equiv.) was dissolved with acetone/water mixture (9:1, 33.3 mL). After cooling down the mixture in an ice bath, NBS (10 mmol, 2.0 equiv.) was added. The reaction was stirred overnight while it was gradually warmed up to the room temperature. Water (35 mL) was added to quench the reaction followed by the extraction with EtOAc (3 x 100 mL). The combined organic layer was dried with Na_2SO_4 and concentrated *in vacuo*. The concentrated crude mixture was subjected to FCC (SiO2, 40% EtOAc in hexane) to afford 2,3,4,6-tetrakis-*O*-[(4-methoxyphenyl)methyl]-α-D-glucopyranoside **1i** as white solid, which is confirmed by comparing with literature NMR spectra.[5]

[5]Lucchetti, N.; Gilmour, R. *Chem. Eur. J.* **2018**, 24,16266 –16270

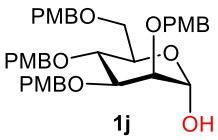
Preparation of 2,3,4,6-tetrakis-*O*-[(4-methoxyphenyl)methyl]-α-D-mannopyranoside (1j)



Phenyl 2,3,4,6-tetrakis-*O*-[(4-methoxyphenyl)methyl]-1-thio-α-D-mannopyranoside (S25)



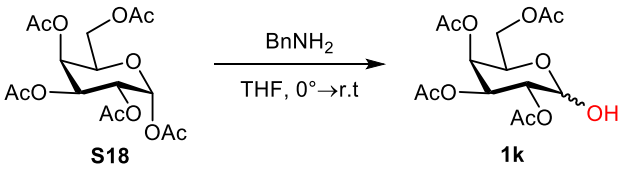
An oven dried and nitrogen filled round-bottom flask was charged with **S4** (9.5 mmol, 1.0 equiv.) and DMF (50 mL). After cooling down the reaction in an ice bath, NaH (52 mmol, 5.5 equiv.) was added portion wise. Once H_2 gas stops generating, PMBBr (47.5 mmol, 5.0 equiv.) was added followed by TBAI (0.95 mmol, 0.1 equiv.). The reaction mixture was stirred at room temperature overnight and quenched by adding water. The mixture was extracted with EtOAc (3 x 100 mL), and the organic layer was dried with Na_2SO_4 and concentrated *in vacuo*. The concentrated crude mixture was subjected to FCC (SiO_2, pure hexane → 40% EtOAc in hexane) to afford phenyl 2,3,4,6-tetrakis-*O*-[(4-methoxyphenyl)methyl]-1-thio-α-D-mannopyranoside **S25**.

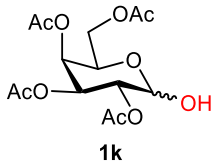


2,3,4,6-Tetrakis-*O*-[(4-methoxyphenyl)methyl]-α-D-mannopyranoside (1j)

In a clean round-bottom flask, **S25** (9.5 mmol, 1.0 equiv.) was dissolved with acetone/water mixture (9:1, 55.5 mL). After cooling down the mixture in an ice bath, NBS (20 mmol, 2.1 equiv.) was added. The reaction was stirred overnight while it was gradually warmed up to the room temperature. Water (50 mL) was added to quench the reaction followed by the extraction with EtOAc (3 x 120 mL). The combined organic layer was dried with Na_2SO_4 and concentrated *in vacuo*. The concentrated crude mixture was subjected to FCC (SiO_2, 50% EtOAc in hexane → 70% EtOAc in hexane) to afford 2,3,4,6-Tetrakis-*O*-[(4-methoxyphenyl)methyl]-α-D-mannopyranoside **1m** as white solid. **^{1}H NMR** (700 MHz, $CDCl_3$) δ 7.27 (d, *J* = 10.2 Hz, 6H), 7.06 (dd, *J* = 8.7, 2.6 Hz, 2H), 6.90 – 6.78 (m, 8H), 5.21 (d, *J* = 1.9 Hz, 1H), 4.77 (d, *J* = 10.4 Hz, 1H), 4.66 (d, *J* = 20.2 Hz, 2H), 4.55 (d, *J* = 3.8 Hz, 2H), 4.52 (d, *J* = 11.9 Hz, 1H), 4.48 (d, *J* = 11.9 Hz, 1H), 4.39 (d, *J* = 10.5 Hz, 1H), 3.96 (ddd, *J* = 8.9, 6.3, 2.0 Hz, 1H), 3.90 (dd, *J* = 9.5, 3.0 Hz, 1H), 3.81 (s, 3H), 3.80 (s, 3H), 3.79 (s, 3H), 3.79 (s, 3H), 3.76 (t, *J* = 2.5 Hz, 1H), 3.68 – 3.66 (m, 1H), 3.65 (d, *J* = 1.9 Hz, 1H), 3.62 (dd, *J* = 10.5, 6.4 Hz, 1H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 159.1, 159.1, 159.1, 159.1, 130.7, 130.6, 130.4, 130.1, 129.8, 129.7, 129.6, 129.6, 129.6, 129.5, 129.2, 129.2, 113.7, 113.7, 113.7, 113.6, 92.7, 79.4, 74.9, 74.6, 74.3, 72.8, 72.2, 71.8, 71.4, 69.1, 55.2, 55.2.

Preparation of 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranose (1k)



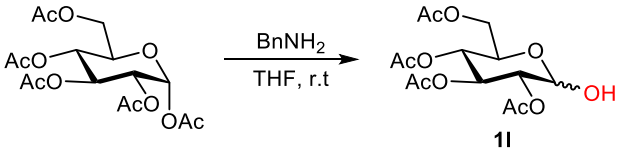


2,3,4,6-tetra-*O*-acetyl-D-galactopyranoside (1k)

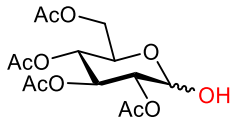
In an oven dried round-bottom flask, **S18** (5.55 mmol, 1.0 equiv.) and THF (20 mL) were added. The mixture was stirred until the solution became homogeneous, and then benzylamine (8.33 mmol, 1.5 equiv.) was added. The reaction was stirred at room temperate for 20 hours and quenched by evaporating the solvent under reduced pressure. The crude mixture was diluted with DCM (150 mL) and washed with 1N HCl (100 mL x 2), saturated $NaHCO_3$ solution (100 mL), and then water (100 mL). The organic layer was dried with Na_2SO_4 and was concentrated *in vacuo* to give amber-colored oil. This oil was subjected to FCC (SiO_2, 20% EtOAc in hexane → 60% EtOAc in hexane) to afford 2,3,4,6-tetra-*O*-acetyl-D-galactopyranoside **1k** as yellowish solid, which was confirmed by comparing with reported NMR spectra.[6]

[6]Cai, T. B.; Lu, D.; Tang, X.; Zhang, Y.; Landerholm, M.; Wang, P. G. *J. Org. Chem.* **2005**, 70, 9, 3518-3524

Preparation of 2,3,4,6-tetra-*O*-acetyl-D-glucopyranoside (1l)



1l



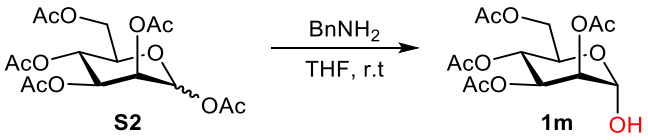
1l

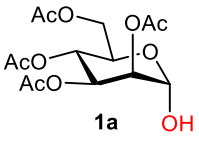
2,3,4,6-Tetra-*O*-acetyl-D-glucopyranoside (1l)

In an oven dried round-bottom flask, 1,2,3,4,6-penta-*O*-acetyl-α-D-glucopyranoside (5.12 mmol, 1.0 equiv.) and THF (20 mL) were added. The mixture was stirred until the solution became homogeneous, and then benzylamine (7.69 mmol, 1.5 equiv.) was added. The reaction was stirred at room temperate for 24 hours and quenched by evaporating the solvent under reduced pressure. The crude mixture was diluted with DCM (150 mL) and washed with 1N HCl (2 x 100 mL), saturated $NaHCO_3$ solution (100 mL), and then water (100 mL). The organic layer was dried with Na_2SO_4 and was concentrated *in vacuo* to give amber-colored oil. This oil was subjected to FCC (SiO_2, 60% EtOAc in hexane) to afford 2,3,4,6-tetra-*O*-acetyl-D-glucopyranoside **1l** as yellowish solid, which is confirmed by comparing with literature NMR spectra.[7]

[7]Ikeda, K.; Morimoto, T.; Kakiuchi, K. *J. Org. Chem.* **2010**, 75, 18, 6279–6282

Preparation of 2,3,4,6-tetra-*O*-acetyl-D-mannopyranose (1m)



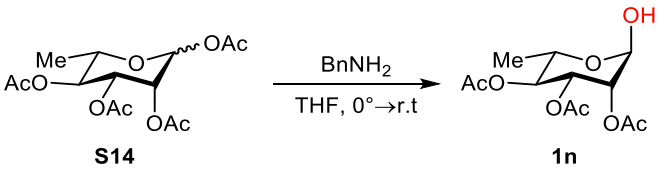


2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranoside (1m)

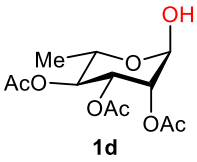
In an oven dried round-bottom flask, **S2** (2.17 g, 5.55 mmol) and THF (20 mL) were added. The mixture was stirred until the solution became homogeneous, and then benzylamine (0.91 mL, 8.33 mmol) was added. The reaction was stirred at room temperate for 20 hours and quenched by evaporating the solvent under reduced pressure. The crude mixture was diluted with DCM (150 mL) and washed with HCl (1.0 M, 100 mL x 2), $NaHCO_3$ (saturated, 100 mL), and then water (100 mL). The organic layer was dried with Na_2SO_4 and was concentrated *in vacuo* to give amber-colored oil. This oil was subjected to FCC (SiO_2, 20% EtOAc in hexane → 60% EtOAc in hexane) to afford 2,3,4,6-tetra-O-acetyl-D-mannopyranoside **1m** as yellowish solid, which was confirmed by comparing with reported NMR spectra.[8] **^{1}H NMR** (700 MHz, Chloroform-*d*) δ 5.42 (dd, *J* = 10.1, 3.4 Hz, 1H), 5.30 (t, *J* = 9.8 Hz, 1H), 5.28 – 5.24 (m, 2H), 4.27 – 4.22 (m, 2H), 4.12 (q, *J* = 7.4 Hz, 2H), 3.19 (br, 1H), 2.16 (s, 3H), 2.11 (s, 3H), 2.04 (s, 3H), 2.00 (s, 3H).

[8]Carcabal, P.; Hunig, I.; Gamblin, D. P.; Liu, B.; Jockusch, R. A.; Kroemer, R. T.; Snoek, L. C.; Fairbanks, A. J.; Davis, B. G.; Simons, J. P. *J. Am. Chem. Soc.* **2006**, 128, 6, 1976-1981

Preparation of 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranoside (1n)



S14 1n



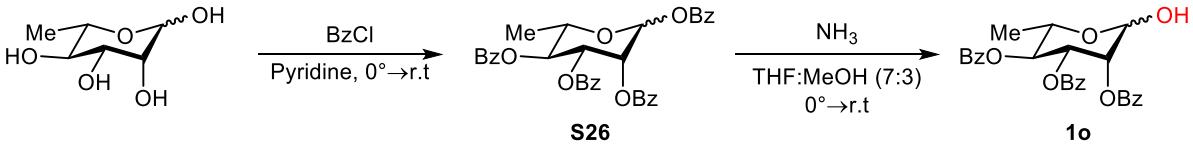
1d

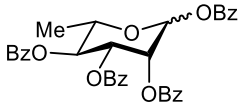
2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranoside (1n)

In an oven dried round-bottom flask, **S14** (3.0 mmol, 1.0 equiv.) and THF (15 mL) were added. The mixture was stirred until the solution became homogeneous, and then benzylamine (4.5 mmol, 1.5 equiv.) was added. The reaction was stirred at room temperate for 20 hours and quenched by evaporating the solvent under reduced pressure. The crude mixture was diluted with DCM (70 mL) and washed with 1N HCl (2 x 50 mL), saturated $NaHCO_3$ solution (50 mL), and then water (50 mL). The organic layer was dried with Na_2SO_4 and was concentrated *in vacuo* to give amber-colored oil. This oil was subjected to FCC (SiO_2, 20% EtOAc in hexane → 50% EtOAc in hexane) to afford 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranoside **1n** as yellowish solid, which is confirmed by comparing with literature NMR spectra.[9]

[9]Donahue, M. G.; Johnston, J. N. *Bioorg. Med. Chem. Lett.* **2006**, 16, 5602–5604

Preparation of 2,3,4-tri-*O*-benzoyl-L-rhamnopyranoside (1o)

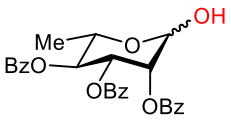




S26

1,2,3,4-Tetra-*O*-benzoyl-L-rhamnopyranoside (S26)

An oven dried round bottom flask was charged with L-rhamnose (5.5 mmol, 1.0 equiv.) and anhydrous pyridine (12 mL). After stirring the mixture until it became homogeneous, the round bottom flask was placed in an ice bath and was cooled down to 0°C. Into the cooled down mixture, benzoyl chloride (33 mmol, 6.0 equiv.) was added, and then the reaction was slowly warmed up to room temperature with stirring until all starting materials were gone. The mixture was then diluted with DCM (100 mL) and washed with 1N HCl solution (2 x 80 mL). The organic layer was washed with water (2 x 80 mL) and then saturated brine (2 x 80 mL). The extracted organic layer was dried with Na_2SO_4 and concentrated *in vacuo*. The worked-up mixture was then subjected to FCC (SiO_2, 20% EtOAc in hexane) to afford 1,2,3,4-tetra-*O*-benzoyl-L-rhamnopyranoside **S26** as white solid.

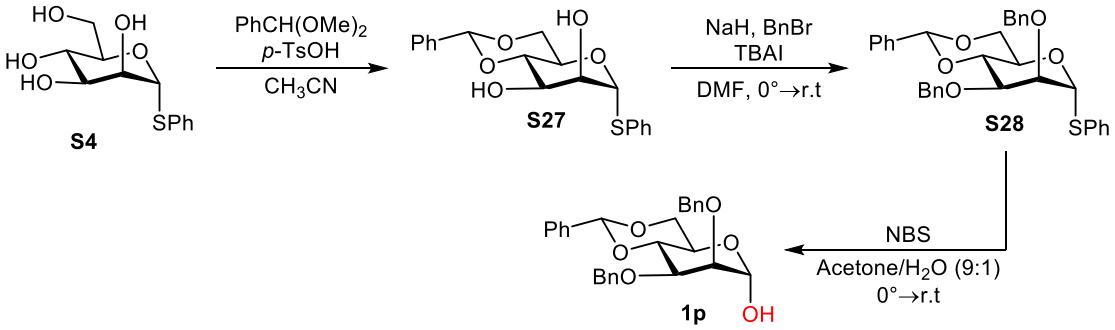


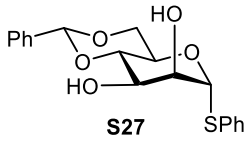
1o

2,3,4-tri-*O*-benzoyl-L-rhamnopyranoside (1o)

An oven dried round bottom flask was charged with 1,2,3,4-tetra-*O*-benzoyl-L-rhamnopyranoside **S26** (3.7 mmol, 1.0 equiv.) and THF:MeOH solution (7:3). After stirring the mixture until it became homogeneous, the round bottom flask was placed in an ice bath and was cooled down to 0°C. Into the cooled down mixture, ammonia gas was bubbled for 1 minute, and then the reaction was stirred for 10 hours while slowly warmed up to room temperature. The mixture was then concentrated *in vacuo,* and then was subjected to FCC (SiO_2, 30% EtOAc in hexane) to afford 2,3,4-tri-*O*-benzoyl-L-rhamnopyranoside **1o** as white solid.

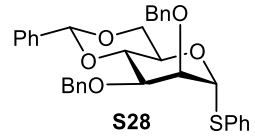
Preparation of 2,3-bis-*O*-(phenylmethyl)-4,6-*O*-[(R)-phenylmethylene]-α-D-mannopyranoside (1p)





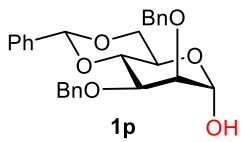
Phenyl 4,6-*O*-[(R)-phenylmethylene]-1-thio-α-D-manopyranoside (S27)

An oven dried and nitrogen filled round-bottom flask was charged with **S4** (4.5 mmol, 1.0 equiv.) and anhydrous acetonitrile (26 mL). $PhCH(OMe)_2$ (6.75 mmol, 1.5 equiv.) and p-TsOH (0.27 mmol, 0.06 equiv.) were added and the mixture was refluxed for 3 hours. Once all starting materials are consumed, the reaction was quenched with Et_3N (3 mL), diluted with EtOAc (50 mL), and then washed with brine. Collected organic layer was dried with $NaSO_4$ and concentrated *in vacuo*. The concentrated crude mixture was subjected to FCC (SiO_2, 5% EtOAc in hexane) to afford phenyl 4,6-*O*-[(R)-phenylmethylene]-1-thio-α-D-manopyranoside **S18** as white solid.



Phenyl 2,3-bis-*O*-(phenylmethyl)-4,6-*O*-[(R)-phenylmethylene]-1-thio-α-D-mannopyranoside (S28)

An oven dried and nitrogen filled round-bottom flask was charged with **S27** (3.0 mmol, 1.0 equiv.) and DMF (20 mL). After cooling down the reaction in an ice bath, NaH (18 mmol, 6.0 equiv.) was added portion wise. Once H_2 gas stops generating, BnBr (12 mmol, 4 equiv.) was added followed by TBAI (0.15 mmol, 0.05 equiv.). The reaction mixture was stirred at room temperature overnight and quenched by adding water. The mixture was extracted with EtOAc (3 x 60 mL), and the organic layer was dried with Na_2SO_4 and concentrated *in vacuo*.

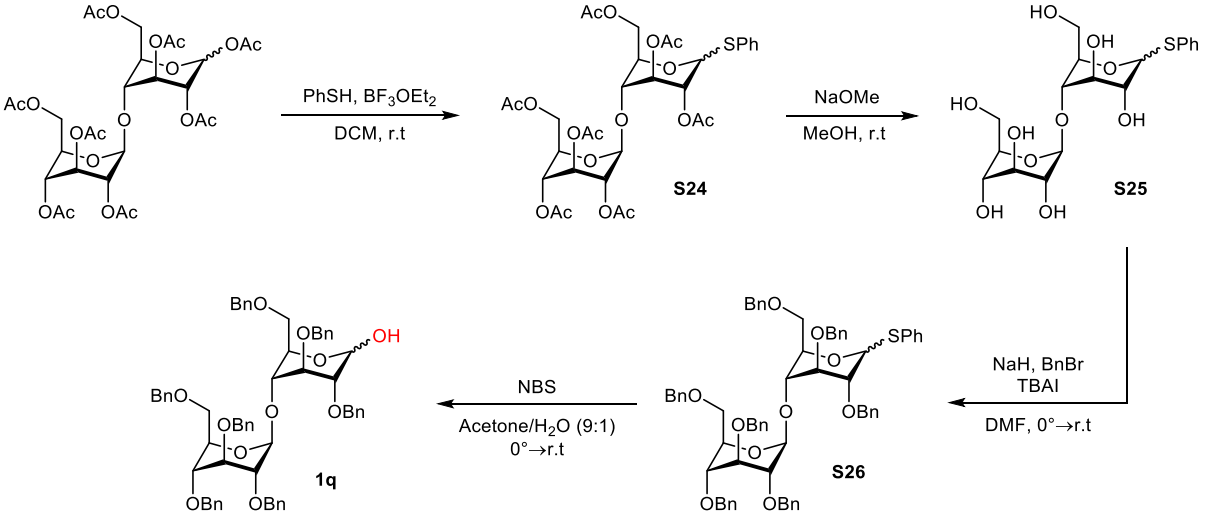


2,3-Bis-*O*-(phenylmethyl)-4,6-*O*-[(R)-phenylmethylene]-α-D-mannopyranoside (1p)

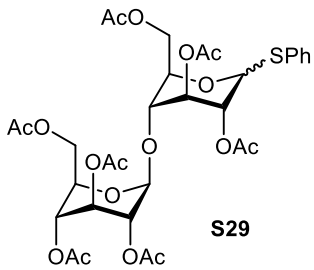
In a clean round-bottom flask, **S19** (3.0 mmol, 1.0 equiv.) was dissolved with acetone/water mixture (9:1, 22.2 mL). After cooling down the mixture in an ice bath, NBS (6.3 mmol, 2.1 equiv.) was added. The reaction was stirred overnight while it was gradually warmed up to the room temperature. Water (20 mL) was added to quench the reaction followed by the extraction with EtOAc (3 x 60 mL). The combined organic layer was dried with Na_2SO_4 and concentrated *in vacuo*. The concentrated crude mixture was subjected to FCC (SiO_2, 40% EtOAc in hexane) to afford 2,3-bis-*O*-(phenylmethyl)-4,6-*O*-[(R)-phenylmethylene]-α-D-mannopyranoside **1p** as white solid, which is confirmed by comparing with literature NMR spectra.[10]

[10]Codée, J. D. C.; Hossain, L. H.; Seeberger, P. H. *Org. Lett.* **2005**, 7, 15, 3251–3254

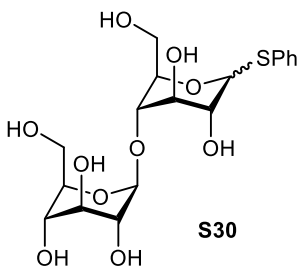
Preparation of 2,3,6-tris-*O*-(phenylmethyl)-4-*O*-[2,3,4,6-tetrakis-*O*-(phenylmethyl)-β-D-glucopyranosyl]-D-glucopyranoside (1q)



Phenyl 4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-1-thio-D-glucopyranoside 2,3,6-triacetate (S29)



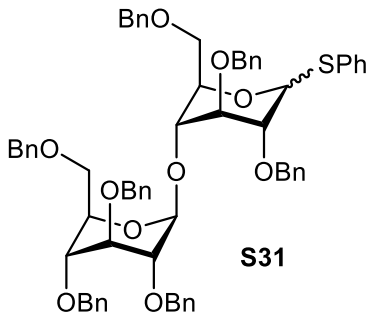
In an oven dried round-bottom flask, α-D-cellobiose octaacetate (3.0 mmol, 1.0 equiv.) and DCM (10 mL) were added. After the addition of thiophenol (4.5 mmol, 1.5 equiv.), the round-bottom flask was sealed with a rubber-septum cap and purged with nitrogen gas. The reaction mixture was stirred until it became homogeneous, and then $BF_3 \cdot OEt_2$ (9.0 mmol, 3.0 equiv.) was slowly injected into the flask. The reaction was stirred overnight at room temperature and quenched with saturated $NaHCO_3$ solution (10 mL). After extracting the mixture with DCM (3 x 70mL), the combined organic layer was dried with Na_2SO_4 and concentrated *in vacuo*. The concentrated crude mixture was subjected to FCC (SiO_2, 50% EtOAc in hexane) to afford phenyl 4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-1-thio-D-glucopyranoside 2,3,6-triacetate **S29** as fluffy white solid.



Phenyl 4-*O*-β-D-glucopyranosyl-1-thio-D-glucopyranoside (S30)

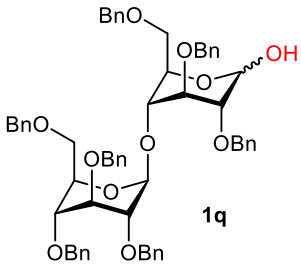
A dry round-bottom flask was filled with **S29** (3.0 mmol, 1.0 equiv.) and dry methanol (20 mL). After the reaction mixture became homogeneous, a chip of sodium metal (0.3 mmol, 0.1 equiv.) was added. The reaction was stirred overnight at room temperature, and then quenched by adding acetic acid until the pH of the reaction became neutral. The crude mixture was concentrated *in vacuo* to yield **S30** as yellowish white solid. The product was subjected to the subsequent reaction without further purification.

Phenyl 2,3,6-tris-*O*-(phenylmethyl)-4-*O*-[2,3,4,6-tetrakis-*O*-(phenylmethyl)-β-D-glucopyranosyl]-1-thio-D-glucopyranoside (S31)



An oven dried and nitrogen filled round-bottom flask was charged with **S30** (3.0 mmol, 1.0 equiv.) and DMF (30 mL). After cooling down the reaction in an ice bath, NaH (48 mmol, 16 equiv.) was added portion wise. Once H_2 gas stops generating, BnBr (42 mmol, 14 equiv.) was added followed by TBAI (0.15 mmol, 0.05 equiv.). The reaction mixture was stirred at room temperature overnight and quenched by adding water. The mixture was extracted with EtOAc (3 x 80 mL), and the organic layer was dried with Na_2SO_4 and concentrated *in vacuo*. The concentrated crude mixture was subjected to FCC (SiO_2, hexane → 20% EtOAc in hexane) to afford phenyl 2,3,6-tris-*O*-(phenylmethyl)-4-*O*-[2,3,4,6-tetrakis-*O*-(phenylmethyl)-β-D-glucopyranosyl]-1-thio-D-glucopyranoside **S31** as yellowish white solid.

2,3,6-Tris-*O*-(phenylmethyl)-4-*O*-[2,3,4,6-tetrakis-*O*-(phenylmethyl)-β-D-glucopyranosyl]-D-glucopyranoside (1q)



In a clean round-bottom flask, **S31** (2.0 mmol, 1.0 equiv.) was dissolved with acetone/water mixture (9:1, 22 mL). After cooling down the mixture in an ice bath, NBS (4.2 mmol, 2.1 equiv.) was added. The reaction was stirred overnight while it was gradually warmed up to the room temperature. Water (20 mL) was added to quench the reaction followed by the extraction with EtOAc (3 x 70 mL). The combined organic layer was dried with Na_2SO_4 and concentrated *in vacuo*. The concentrated crude mixture was subjected to FCC (SiO2, 30% EtOAc in hexane) to afford 2,3,6-tris-*O*-(phenylmethyl)-4-*O*-[2,3,4,6-tetrakis-*O*-(phenylmethyl)-β-D-glucopyranosyl]-D-glucopyranoside **1q** as white solid, which is confirmed by comparing with literature NMR spectra.[11]

[11]Liu, B.; Mechelen, J.; Berg, R.; Nieuwendijk, A.; Aerts, J.; Marel, G.; Codée, J. Overkleeft, H. S. *Eur. J. Org. Chem.* **2019**, 118–129

b. List of components for the experimental setup

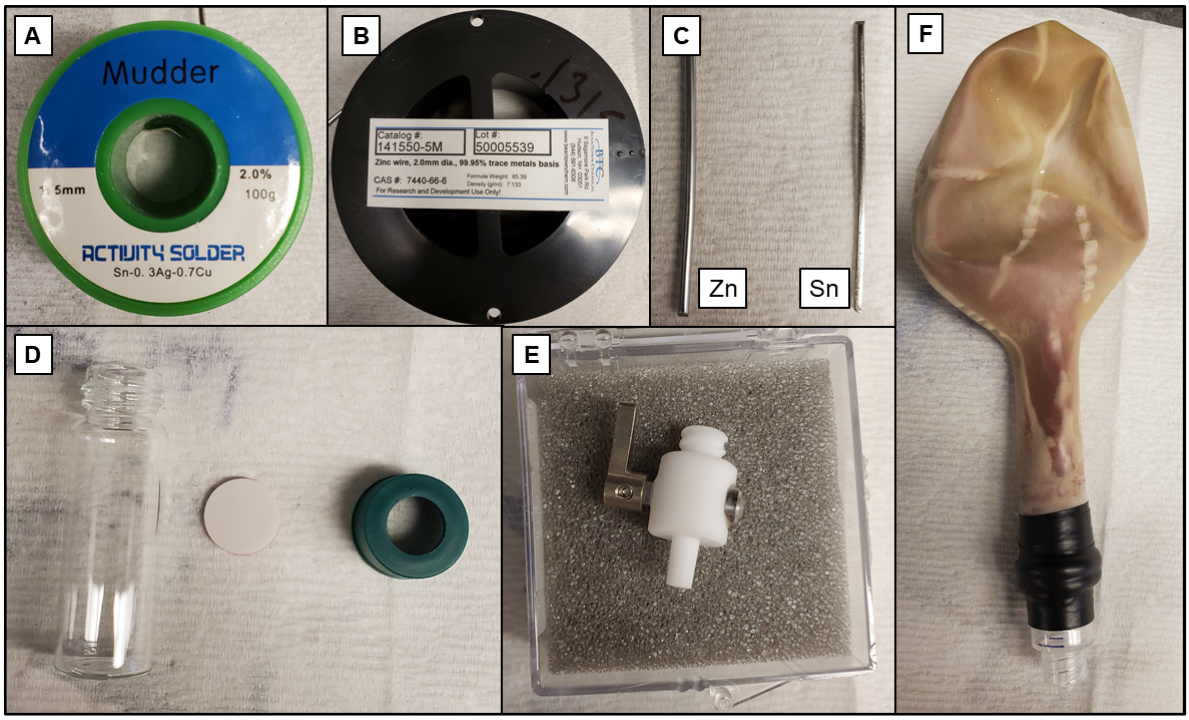


Figure S2. Components of experimental setup.

A) Mudder soldering tin wire (1.5 mm diameter) – Amazon
Content parameter: Lead-free, Sn 99% / Ag 0.3% / Cu 0.7%
Flux 2% (washed away by sonicating in acetone)

B) Zinc wire (2.0 mm diameter) – Beantown Chemical

C) 5 cm zinc and tin wire

D) 1 dram vial – Sigma and PTFE/Silicon seal with a cap – Fisher Scientific

E) Hamilton MTB valve – Thomas Scientific

F) Balloon for SF_6

c. Synthesis of glycosyl fluorides

General Procedure

An oven-dried 1 dram vial was charged with a glycosyl substrate (0.1 mmol, 1 equiv.) and tetrabutylammonium perchlorate (0.45 mmol, 0.15 M). The vial containing the mixture was sealed with PTFE/Silicone septum cap and was further dried under high vacuum for 5 minutes. Into the sealed vial, THF (3 mL) and triethylamine (0.3 mmol, 3 equiv.) were added, and the vial was stirred until the mixture became homogeneous. After plugging in the electrodes (2.3 cm submerged in the solution), the mixture was sparged with a balloon containing SF_6 gas for 30 seconds. Once the sparging was done, the valve of the balloon was adjusted to sparge small bubbles and left open until the reaction was stopped.

The reaction was stirred at high rpm while the electric current was applied to cathode and anode for 1 hour. The reaction mixture was then diluted with 30 mL of ethyl acetate, and then washed with 1N HCl (25 mL x 3), saturated $NaHCO_3$ (25 mL), water (25 mL), and brine (25 mL). The extracted organic layer was dried with Na_2SO_4 and concentrated *in vacuo*. The worked-up reaction mixture was then subjected to FCC (SiO_2) for purification.

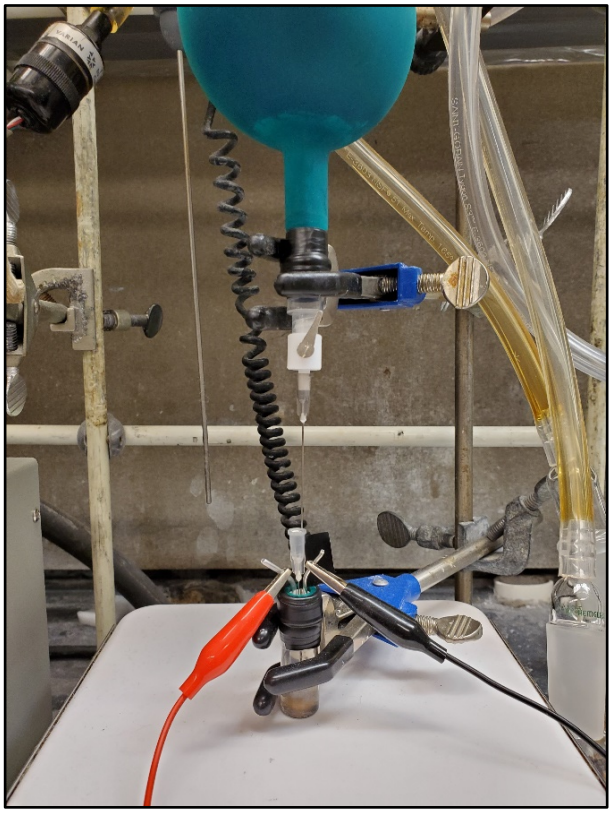
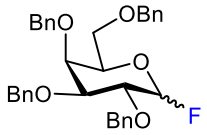


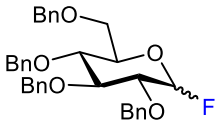
Figure S3. Experimental setup for substrate screening

Cleaning Procedure for the Electrodes

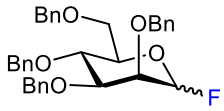
Before each use, the surface of electrodes is polished with 1000 grit sandpaper and sonicated in acetone. After wiping the surface with a paper towel, the electrodes are dried and kept under high vacuum.



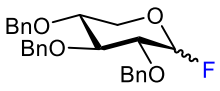
2a



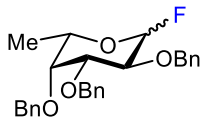
2b



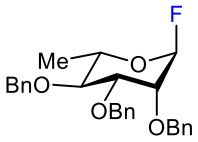
2c



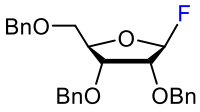
2d



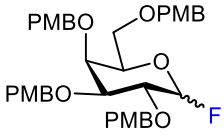
2e



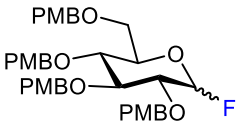
2f



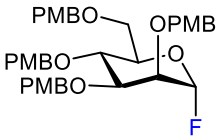
2g



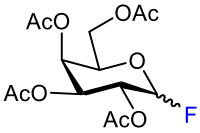
2h



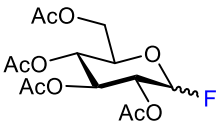
2i



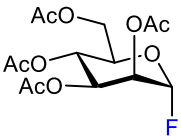
2j



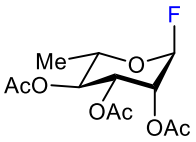
2k



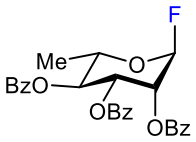
2l



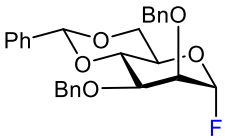
2m



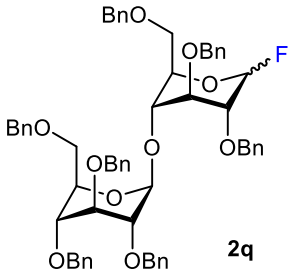
2n



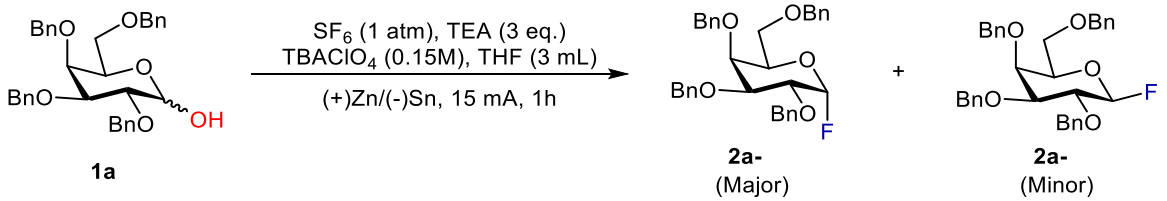
2o



2p



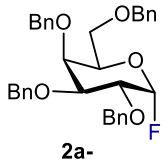
2q



Synthesis of 2,3,4,6-tetrakis-*O*-(phenylmethyl)-D-galactopyranosyl fluoride (2a)

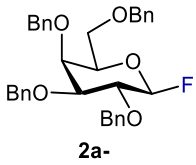
The product was synthesized employing the general procedure. After a work-up, the reaction mixture was subjected to FCC (SiO_2, pure hexane → 20% EtOAc in hexane) to afford **2a** in average of 94% yield as yellowish cloudy syrup ($R_{f\text{-}\alpha}$ = 0.36 (20% EtOAc/Hex), $R_{f\text{-}\beta}$ = 0.30 (20% EtOAc/Hex)).

	1st Run	2nd Run
Isolated Yield	93% (50.5 mg) α : β = 1 : 1.6	94% (51.3 mg) α : β = 1 : 1.6



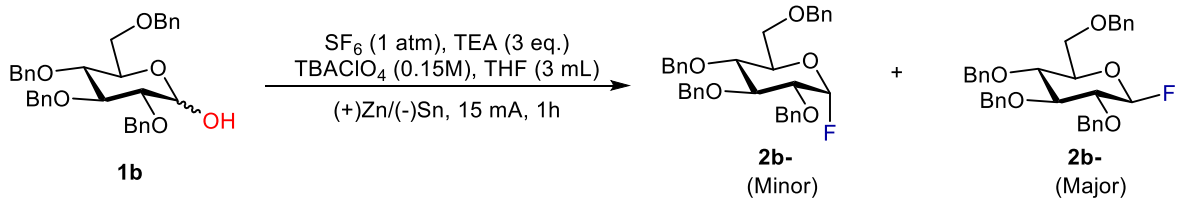
2,3,4,6-Tetrakis-*O*-(phenylmethyl)-α-D-galactopyranosyl fluoride (minor product).

^{1}H NMR (700 MHz, $CDCl_3$) δ 7.39 – 7.26 (m, 20H), 5.59 (dd, *J* = 53.7, 2.7 Hz, 1H), 4.94 (d, *J* = 11.3 Hz, 1H), 4.83 (dd, *J* = 23.1, 11.7 Hz, 2H), 4.74 (dd, *J* = 20.8, 11.8 Hz, 2H), 4.57 (d, *J* = 11.3 Hz, 1H), 4.48 (d, *J* = 11.8 Hz, 1H), 4.42 (d, *J* = 11.8 Hz, 1H), 4.13 – 4.09 (m, 1H), 4.08 – 4.01 (m, 2H), 3.95 (dd, *J* = 10.1, 2.7 Hz, 1H), 3.55 (d, *J* = 5.9 Hz, 2H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 138.4, 138.3, 138.0, 137.7, 128.4, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.8, 127.7, 127.6, 127.5, 106.2 (d, *J* = 226.1 Hz, α-C_1), 78.4, 75.7 (d, *J* = 23.8 Hz), 74.8, 74.3, 73.7, 73.5, 73.1, 71.7 (d, *J* = 2.8 Hz), 68.2; **^{19}F NMR** (564 MHz, $CDCl_3$) δ -150.13 (dd, *J* = 53.7, 25.3 Hz); **IR** (thin film, cm^{-1}): 3030, 2870, 1496, 1453, 1363, 1302, 1208, 1099, 1053, 1027, 910, 820, 732, 695; **HRMS (ESI+)** (m/z): $[M+Na]^+$ calcd for $C_{34}H_{35}FNaO_5$ 565.2392, found 565.2353; **$[\alpha]_D^{23}$** = +26.2 (c = 0.4, CH_2Cl_2)



2,3,4,6-Tetrakis-*O*-(phenylmethyl)-β-D-galactopyranosyl fluoride (major product).

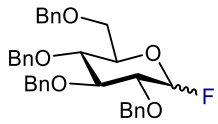
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 20H), 5.19 (dd, *J* = 53.1, 7.0 Hz, 1H), 4.95 (d, *J* = 11.5 Hz, 1H), 4.86 (d, *J* = 11.0 Hz, 1H), 4.80 – 4.71 (m, 3H), 4.61 (d, *J* = 11.5 Hz, 1H), 4.50 (d, *J* = 11.8 Hz, 1H), 4.43 (d, *J* = 11.8 Hz, 1H), 3.99 – 3.91 (m, 2H), 3.69 – 3.61 (m, 3H), 3.56 (ddd, *J* = 9.6, 2.9, 0.9 Hz, 1H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 138.3, 138.1, 138.0, 137.6, 128.4, 128.4, 128.3, 128.2, 128.1, 128.1, 127.9, 127.9, 127.7, 127.7, 127.6, 127.5, 110.2 (d, *J* = 215.4 Hz, β-C_1), 81.0 (d, *J* = 11.3 Hz), 79.1 (d, *J* = 20.8 Hz), 75.0, 75.0, 74.6, 73.6, 73.6, 73.1, 73.0, 68.3; **^{19}F NMR** (564 MHz, $CDCl_3$) δ -138.91 (dd, *J* = 54.0, 12.8 Hz); **IR** (thin film, cm^{-1}): 3030, 2870, 1496, 1453, 1363, 1302, 1208, 1099, 1053, 1027, 910, 820, 732, 695; **HRMS (ESI+)** (m/z): $[M+Na]^+$ calcd for $C_{34}H_{35}FNaO_5$ 565.2392, found 565.2353; **$[\alpha]_D^{23}$** = +29.8 (c = 1.1, CH_2Cl_2)



Synthesis of 2,3,4,6-tetrakis-*O*-(phenylmethyl)-D-glucopyranosyl fluoride (2b)

The product was synthesized employing the general procedure. After a work-up, the reaction mixture was subjected to FCC (SiO_2, pure hexane → 20% EtOAc in hexane) to afford **2b** as yellowish cloudy syrup in average of 98% yield (R_f = 0.38 (20% EtOAc/Hex)). The NMR spectrum of the product is in a good agreement with our previously published NMR data.[12]

	1st Run	2nd Run
Isolated Yield	96% (52.3 mg) α : β = 1 : 1.4	99% (54 mg) α : β = 1 : 1.5

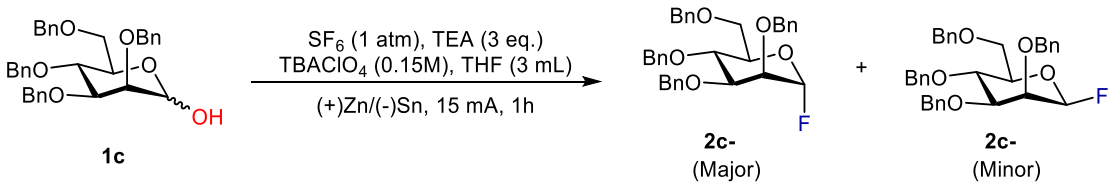


2b

2,3,4,6-Tetrakis-*O*-(phenylmethyl)-D-glucopyranosyl fluoride

(Isolated as α : β = 1 : 1.4) **^{1}H NMR** ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.42 – 7.28 (m, 41.4H), 7.21 – 7.14 (m, 4.8H), 5.59 (dd, *J* = 53.2, 2.6 Hz, 1H, C_1-H_α), 5.29 (dd, *J* = 52.8, 6.8 Hz, 1.4H, C_1-H_β), 4.99 (d, *J* = 10.9 Hz, 1H), 4.93 (d, *J* = 11.0 Hz, 1.4H), 4.91 – 4.80 (m, 7.3H), 4.74 (d, *J* = 11.3 Hz, 2.5H), 4.64 (dd, *J* = 16.1, 12.1 Hz, 2.5H), 4.60 – 4.54 (m, 3.4H), 4.54 – 4.48 (m, 1.6H), 4.02 (t, *J* = 9.4 Hz, 1H), 3.98 (dt, *J* = 10.2, 2.6 Hz, 1H), 3.81 – 3.73 (m, 6.3H), 3.73 – 3.67 (m, 2.5H), 3.66 – 3.57 (m, 3.9H); **^{19}F NMR** (564 MHz, $CDCl_3$) δ -138.06 (dd, *J* = 52.9, 11.9 Hz, C_1-F_β), -149.49 (dd, *J* = 53.1, 25.6 Hz, C_1-F_α); **IR** (thin film, cm^{-1}): 3030, 2867, 1496, 1453, 1360, 1308, 1208, 1155, 1088, 1062, 909, 821, 733, 695; **HRMS (ESI+)** (m/z): $[M+Na]^+$ calcd for $C_{34}H_{35}FNaO_5$ 565.2392, found 565.2353

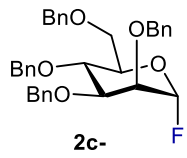
[12]Kim, S.; Khomutnyk, Y.; Bannykh, A.; Nagorny, P. *Org. Lett*. **2021**, 23, 1, 190-194



Synthesis of 2,3,4,6-tetraki-O-(phenylmethyl)-D-mannopyranosyl fluoride (2c)

The product was synthesized employing the general procedure. After a work-up, the reaction mixture was subjected to FCC (SiO_2, pure hexane → 30% EtOAc in hexane) to afford **2c** as cloudy syrup in average of 95% yield ($R_{f\text{-}\alpha}$ = 0.57 (30% EtOAc/Hex), $R_{f\text{-}\beta}$ = 0.5 (30% EtOAc/Hex)). Stereochemistry of the product was confirmed by comparing with previously reported NMR spectra.[13]

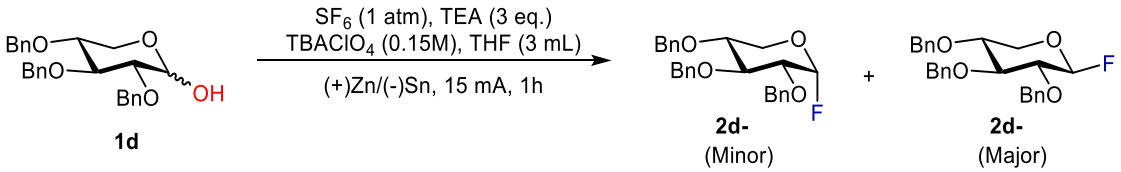
	1st Run	2nd Run
Isolated Yield	92% (50.1 mg) α : β = 23 : 1	97% (52.6 mg) α : β = 20 : 1



2,3,4,6-Tetrakis-*O*-(phenylmethyl)-α-D-Mannopyranosyl fluoride (major product)

^{1}H NMR (700 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 18H), 7.20 – 7.17 (m, 2H), 5.61 (d, *J* = 50.8 Hz, 1H), 4.89 (d, *J* = 10.8 Hz, 1H), 4.81 (d, *J* = 12.3 Hz, 1H), 4.72 – 4.64 (m, 4H), 4.55 (d, *J* = 12.4 Hz, 2H), 4.09 (t, *J* = 9.5 Hz, 1H), 3.93 (ddd, *J* = 10.1, 4.7, 1.8 Hz, 1H), 3.89 (d, *J* = 8.9 Hz, 2H), 3.79 (dd, *J* = 11.0, 4.7 Hz, 1H), 3.73 (dd, *J* = 11.1, 1.9 Hz, 1H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 138.2, 138.1, 138.1, 137.8, 128.4, 128.3, 128.3, 127.9, 127.9, 127.8, 127.7, 127.7, 127.6, 106.4 (d, *J* = 222.0 Hz), 79.2, 75.1, 74.2, 74.2, 74.0, 73.6, 73.4, 73.4, 73.2, 72.6, 68.6; **^{19}F NMR** (564 MHz, $CDCl_3$) δ -138.01 (d, *J* = 50.5 Hz); **IR** (thin film, cm^{-1}): 3030, 2863, 1496, 1453, 1363, 1311, 1183, 1094, 1026, 952, 801, 733, 695; **HRMS (ESI+)** (m/z): $[M+Na]^+$ calcd for $C_{34}H_{35}FNaO_5$ 565.2366, found 565.2358; **$[\alpha]_D^{24}$** = +12.0 (c = 1.1, CH_2Cl_2)

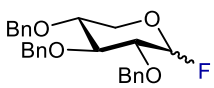
[13]Zeng, J.; Vedachalam, S.; Xiang, S.; Liu, X-W. *Org. Lett.* **2011**, 13, 1, 42-45



Synthesis of 2,3,4-tris-*O*-(phenylmethyl)-D-xylopyranosyl fluoride (2d)

The product was synthesized employing the general procedure. The product was purified by FCC (SiO_2, pure hexane → 20% EtOAc in hexane) to afford **2d** as yellowish white solid in average of 98% yield (R_f = 0.45(20% EtOAc/Hex)). The NMR spectrum of the product is in a good agreement with our previously published NMR data.[14]

	1st Run	2nd Run
Isolated Yield	96% (40.4 mg) α : β = 1 : 2.4	100% (42.1 mg) α : β = 1 : 2.7

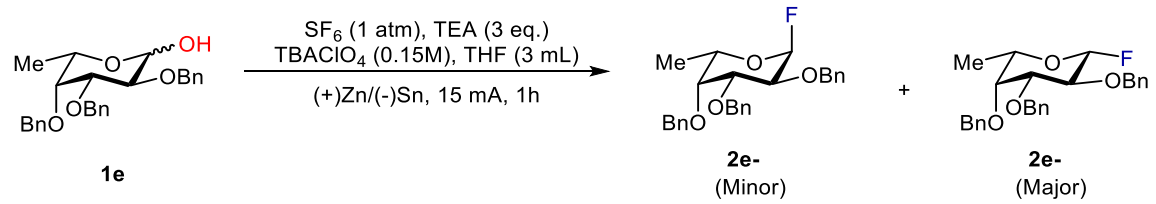


2d

2,3,4-Tris-*O*-(phenylmethyl)-D-xylopyranosyl fluoride

(Isolated as α : β = 1 : 2.4 mixture) **^{1}H NMR** ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 – 7.28 (m, 46.8H), 5.48 (dd, *J* = 53.1, 2.7 Hz, 1H, C_1-H_α), 5.35 (dd, *J* = 53.9, 5.6 Hz, 2.4H, C_1-H_β), 4.94 (s, 2H), 4.86 – 4.76 (m, 8.9H), 4.75 – 4.60 (m, 9.5H), 4.10 – 4.03 (m, 2.4H), 3.94 (t, *J* = 9.2 Hz, 1H), 3.80 (dd, *J* = 11.1, 5.6 Hz, 1H), 3.75 – 3.61 (m, 6.7H), 3.61 – 3.44 (m, 5.6H); **^{19}F NMR** (564 MHz, $CDCl_3$) δ -134.41 (dd, *J* = 54.0, 12.6 Hz, 2.4F, C_1-F_β), -151.04 (dd, *J* = 53.1, 25.7 Hz, 1F, C_1-F_α); **IR** (thin film, cm^{-1}): 3030, 2869, 1496, 1453, 1361, 1257, 1208, 1162, 1088. 1027, 942, 733, 695; **HRMS (ESI+)** (m/z): $[M+Na]^+$ calcd for $C_{26}H_{27}FNaO_4$ 445.1792, found 445.1780.

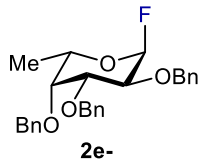
[14]Kim, S.; Khomutnyk, Y.; Bannykh, A.; Nagorny, P. *Org. Lett*. **2021**, 23, 1, 190-194



Synthesis of 2,3,4-tris-*O*-(phenylmethyl)-L-fucopyranosyl fluoride (2e)

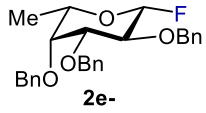
The product was synthesized employing the general procedure. The product was purified by FCC (SiO_2, pure hexane → 30% EtOAc in hexane) to afford **2e** as cloudy syrup in average of 91% yield ($R_{f\text{-}\alpha}$ = 0.6 (30% EtOAc/Hex), $R_{f\text{-}\beta}$ = 0.53 (30% EtOAc/Hex)).

	1st Run	2nd Run
Isolated Yield	90% (39.4 mg) α : β = 2.5 : 1	91% (39.8 mg) α : β = 2 : 1



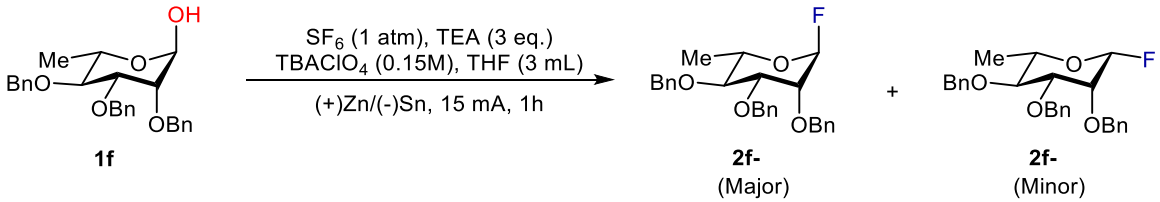
2,3,4-Tris-*O*-(phenylmethyl)-α-L-fucopyranosyl fluoride (major product).

^{1}H NMR (700 MHz, Chloroform-*d*) δ 7.41 – 7.27 (m, 15H), 5.57 (dd, *J* = 54.0, 2.8 Hz, 1H), 4.99 (d, *J* = 11.5 Hz, 1H), 4.85 (dd, *J* = 11.8, 3.9 Hz, 2H), 4.75 (dd, *J* = 19.1, 11.8 Hz, 2H), 4.66 (d, *J* = 11.5 Hz, 1H), 4.08 – 4.00 (m, 2H), 3.94 (dd, *J* = 10.1, 2.7 Hz, 1H), 3.70 (dd, *J* = 2.8, 1.2 Hz, 1H), 1.17 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 138.5, 138.3, 138.1, 128.5, 128.4, 128.4, 128.3, 128.0, 127.8, 127.7, 127.7, 127.5, 106.4 (d, *J* = 224.5 Hz, α-C_1), 78.8, 75.6 (d, *J* = 23.9 Hz), 74.9, 73.7, 73.2, 69.1 (d, *J* = 3.2 Hz), 16.5; **^{19}F NMR** (564 MHz, $CDCl_3$) δ -149.68 (dd, *J* = 54.0, 25.3 Hz); **IR** (thin film, cm^{-1}): 3030, 2872, 1496, 1453, 1361, 1307, 1208, 1100, 1056, 1027, 912, 801, 732, 695; **HRMS (ESI+)** (m/z): $[M+Na]^+$ calcd for $C_{27}H_{29}FNaO_4$ 459.1892, found 459.1917; **$[\alpha]_D^{24}$** = -41.9 (c=0.5, CH_2Cl_2)



2,3,4-tris-*O*-(phenylmethyl)-β-L-fucopyranosyl fluoride (minor product).

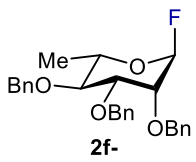
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.41 – 7.28 (m, 15H), 5.16 (dd, *J* = 53.3, 7.1 Hz, 1H), 5.00 (d, *J* = 11.6 Hz, 1H), 4.87 (d, *J* = 10.9 Hz, 2H), 4.80 (d, *J* = 11.7 Hz, 1H), 4.79 (d, *J* = 10.8 Hz, 1H), 4.74 (d, *J* = 11.8 Hz, 1H), 4.69 (d, *J* = 11.6 Hz, 1H), 3.94 (ddd, *J* = 13.3, 9.7, 7.0 Hz, 1H), 3.60 (m, 2H), 3.55 (dd, *J* = 9.8, 2.9 Hz, 1H), 1.26 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 138.2, 138.2, 138.2, 128.4, 128.3, 128.3, 128.2, 128.1, 127.7, 127.7, 127.6, 110.3 (d, *J* = 213.5 Hz, β-C_1), 81.4 (d, *J* = 11.7 Hz), 79.0 (d, *J* = 20.6 Hz), 75.8, 74.9, 74.7, 73.3, 70.8 (d, *J* = 4.9 Hz), 16.6; **^{19}F NMR** (564 MHz, $CDCl_3$) δ -139.13 (dd, *J* = 53.4, 13.2 Hz); **IR** (thin film, cm^{-1}): 3030, 2872, 1496, 1453, 1361, 1307, 1208, 1100, 1056, 1027, 912, 801, 732, 695; **HRMS (ESI+)** (m/z): $[M+Na]^+$ calcd for $C_{27}H_{29}FNaO_4$ 459.1892, found 459.1917; **$[\alpha]_D^{24}$** = -54.2 (c=0.7, CH_2Cl_2)



Synthesis of 2,3,4-tris-*O*-(phenylmethyl)-L-rhamnopyranosyl fluoride (2f)

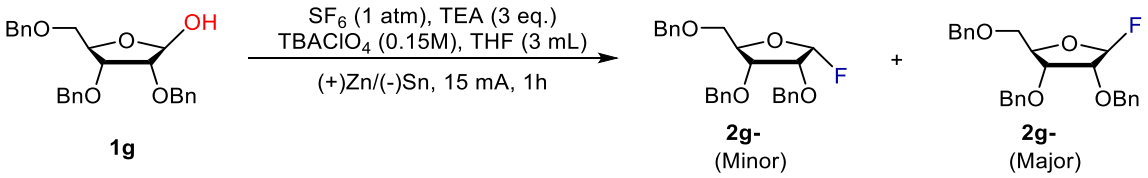
The product was synthesized employing the general procedure. The product was purified by FCC (SiO_2, pure hexane → 20% EtOAc in hexane) to afford **2f** as yellowish syrup in average of 93% yield ($R_{f\text{-}\alpha}$ = 0.57 (20% EtOAc/Hex), $R_{f\text{-}\beta}$ = 0.43 (20% EtOAc/Hex)).

	1st Run	2nd Run
Isolated Yield	93% (40.8 mg) α : β = 20 : 1	93% (40.5 mg) α : β = 18 : 1



2,3,4-Tris-*O*-(phenylmethyl)-α-L-rhamnopyranosyl fluoride (Major product)

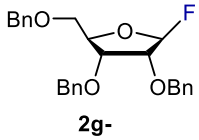
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 15H), 5.49 (dd, *J* = 50.6, 2.0 Hz, 1H), 4.95 (d, *J* = 10.9 Hz, 1H), 4.81 (d, *J* = 12.2 Hz, 1H), 4.72 – 4.64 (m, 4H), 3.89 – 3.82 (m, 3H), 3.67 (t, *J* = 9.4 Hz, 1H), 1.36 (d, *J* = 6.2 Hz, 3H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 138.3, 138.2, 137.8, 128.5, 128.4, 128.4, 128.0, 128.0, 127.9, 127.7, 127.7, 127.7, 106.4 (d, *J* = 221.1 Hz), 79.6, 79.2, 75.4, 73.7 (d, *J* = 35.2 Hz), 73.4, 72.6, 70.6 (d, *J* = 2.3 Hz), 17.9; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -137.07 (d, *J* = 50.6 Hz); **IR** (thin film, cm^{-1}): 3030, 2922, 1721, 1496, 1453, 1363, 1248, 1207, 1184, 1074, 1027, 911, 841, 734, 695; **HRMS (ESI+)** (m/z): $[M+Na]^+$ calcd for $C_{27}H_{29}FNaO_4$ 459.1948, found 459.1948; **$[\alpha]_D^{23.6}$** = +7.66 (c = 1.1, CH_2Cl_2)



Synthesis of 2,3,5-Tris-*O*-(phenylmethyl)-D-ribofuranosyl fluoride (2g)

The product was synthesized employing the general procedure. The product was purified by FCC (SiO_2, pure hexane → 30% EtOAc in hexane) to afford **2g** as yellowish oil in average of 94% yield ($R_{f\text{-}\alpha}$ = 0.31 (20% EtOAc/Hex), $R_{f\text{-}\beta}$ = 0.43 (20% EtOAc/Hex)).

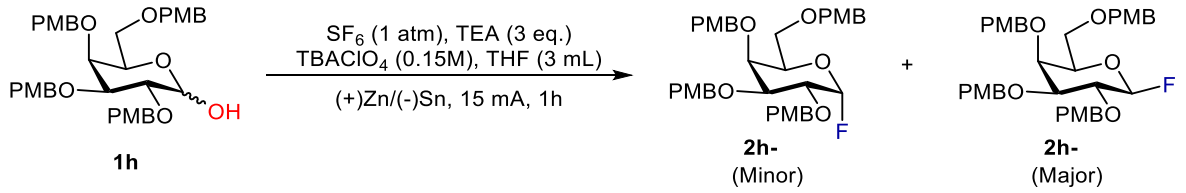
	1st Run	2nd Run
Isolated Yield	90% (37.9 mg) α : β = 1 : 17	98% (41.3 mg) α : β = 1 : 16



2g-

2,3,5-Tris-*O*-(phenylmethyl)-β-D-ribofuranosyl fluoride (Major porduct).

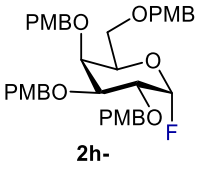
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 15H), 5.69 (d, *J* = 63.4 Hz, 1H, β-C_1-H), 4.67 (s, 2H), 4.61 (d, *J* = 12.1 Hz, 1H), 4.56 (d, *J* = 13.6 Hz, 2H), 4.48 (d, *J* = 11.8 Hz, 1H), 4.44 (dtd, *J* = 8.1, 5.1, 2.7 Hz, 1H), 4.14 (ddd, *J* = 7.4, 4.5, 2.4 Hz, 1H), 4.00 (t, *J* = 4.2 Hz, 1H), 3.70 (dd, *J* = 11.0, 3.4 Hz, 1H), 3.60 (dd, *J* = 11.0, 5.3 Hz, 1H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 138.1, 137.4, 137.3, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.6, 127.6, 112.5 (d, *J* = 224.4 Hz, β-C_1), 82.3 (d, *J* = 2.6 Hz), 78.9 (d, *J* = 30.1 Hz), 73.3, 72.8, 72.8, 70.2; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -115.29 (dt, *J* = 63.1, 5.5 Hz, β-C_1-F); **IR** (thin film, cm^{-1}): 3030, 2862, 1726, 1496, 1454, 1358, 1308, 1257, 1208, 1096, 1026, 784, 735, 696; **HRMS (ESI+)** (m/z): $[M+Na]^+$ calcd for $C_{26}H_{27}FNaO_4$ 445.1792, found 445.1782; **$[\alpha]_D^{24}$** = +63.9 (c=0.7, CH_2Cl_2)



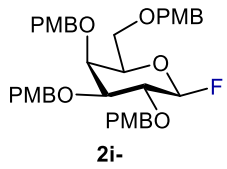
Synthesis of 2,3,4,6-tetrakis-*O*-[(4-methoxyphenyl)methyl]-D-galactopyranosyl fluoride (2h)

The product was synthesized employing the general procedure. The product was purified by FCC (SiO_2, pure hexane → 30% EtOAc in hexane) to afford **2h** as cloudy oil in average of 96% yield ($R_{f\text{-}\alpha}$ = 0.35 (30% EtOAc/Hex), $R_{f\text{-}\beta}$ = 0.33 (30% EtOAc/Hex)).

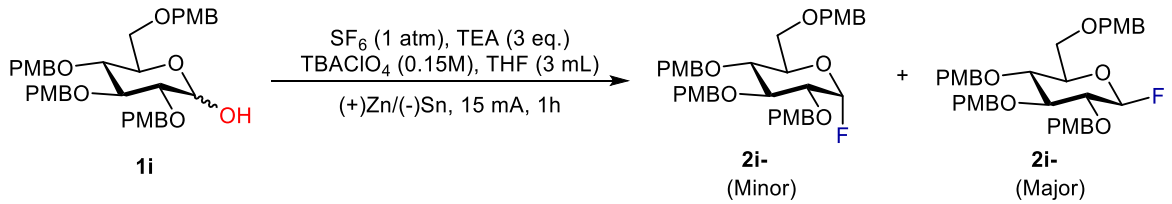
	1st Run	2nd Run
Isolated Yield	97% (64.1 mg) α : β = 1 : 1.2	96% (63.7 mg) α : β = 1 : 1.1



2,3,4,6-Tetrakis-*O*-[(4-methoxyphenyl)methyl]-α-D-galactopyranosyl fluoride (minor product). **^{1}H NMR** (700 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 4H), 7.22 – 7.15 (m, 4H), 6.92 – 6.79 (m, 8H), 5.51 (dd, J = 53.7, 2.8 Hz, 1H), 4.84 (d, J = 11.0 Hz, 1H), 4.77 (d, J = 11.5 Hz, 1H), 4.72 (d, J = 11.3 Hz, 1H), 4.65 (dd, J = 13.8, 11.4 Hz, 2H), 4.49 (d, J = 11.0 Hz, 1H), 4.42 (d, J = 11.5 Hz, 1H), 4.34 (d, J = 11.5 Hz, 1H), 4.04 (t, J = 6.5 Hz, 1H), 4.01 – 3.93 (m, 2H), 3.88 (dd, J = 10.1, 2.7 Hz, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 3.80 (s, 3H), 3.79 (s, 3H), 3.51 – 3.44 (m, 2H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 159.3, 159.3, 159.2, 159.2, 130.6, 130.6, 130.2, 129.8, 129.6, 129.5, 129.2, 113.8, 113.7, 106.4 (d, *J* = 225.8 Hz), 78.2, 75.3 (d, *J* = 23.5 Hz), 74.4, 73.8, 73.4, 73.1, 72.7, 71.8 (d, *J* = 2.7 Hz), 68.0, 55.3, 55.3, 55.2; **^{19}F NMR** (564 MHz, $CDCl_3$) δ -150.14 (dd, *J* = 53.7, 25.5 Hz);**IR** (thin film, cm^{-1}): 2912, 2835, 1611, 1585, 1512, 1463, 1442, 1422, 1362, 1301, 1244, 1172, 1096, 1031, 817, 757, 710, 665; **HRMS (ESI+)** (m/z): $[M+NH_4]^+$ calcd for $C_{38}H_{47}FNO_9$ 680.3229, found 680.3281; **$[\alpha]_D^{23.3}$** = +26.9 (c = 0.13, CH_2Cl_2).



2,3,4,6-Tetrakis-*O*-[(4-methoxyphenyl)methyl]-β-D-galactopyranosyl fluoride (major product). **^{1}H NMR** (700 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.6 Hz, 2H), 7.26 (d, *J* = 6.1 Hz, 2H), 7.20 (dd, *J* = 8.5, 5.5 Hz, 4H), 6.87 – 6.85 (m, 6H), 6.83 (d, *J* = 8.6 Hz, 2H), 5.13 (dd, *J* = 53.2, 7.0 Hz, 1H), 4.83 (d, *J* = 11.2 Hz, 1H), 4.76 (d, *J* = 10.7 Hz, 1H), 4.69 (d, *J* = 10.6 Hz, 1H), 4.64 (q, *J* = 11.4 Hz, 2H), 4.52 (d, *J* = 11.3 Hz, 1H), 4.42 (d, *J* = 11.4 Hz, 1H), 4.34 (d, *J* = 11.4 Hz, 1H), 3.91 – 3.85 (m, 1H), 3.82 (d, *J* = 2.7 Hz, 1H), 3.81 (s, 3H), 3.80 (s, 3H), 3.80 (s, 3H), 3.79 (s, 3H), 3.61 – 3.57 (m, 2H), 3.56 – 3.52 (m, 1H), 3.49 – 3.46 (m, 1H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 159.4, 159.3, 159.2, 159.2, 130.5, 130.3, 130.3, 129.8, 129.8, 129.6, 129.2, 113.8, 113.8, 113.8, 113.6, 110.3 (d, *J* = 215.3 Hz, β-C_1), 80.7 (d, *J* = 11.3 Hz), 78.8 (d, *J* = 20.7 Hz), 74.7, 74.6, 74.1, 73.7 (d, *J* = 4.8 Hz), 73.2, 72.7, 72.5, 68.1, 55.3, 55.3, 55.2; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -138.96 (dd, *J* = 53.0, 13.4 Hz); **IR** (thin film, cm^{-1}): 2912, 2835, 1611, 1585, 1512, 1463, 1442, 1422, 1362, 1301, 1244, 1172, 1096, 1031, 817, 756, 710, 664; **HRMS (ESI+)** (m/z): $[M+NH_4]^+$ calcd for $C_{38}H_{47}FNO_9$ 680.3229, found 680.3281; **$[\alpha]_D^{24}$** = +39.8 (c = 0.19, CH_2Cl_2).

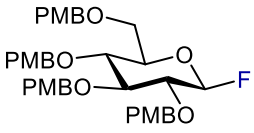


1i **2i-** (Minor) **2i-** (Major)

Synthesis of 2,3,4,6-Tetrakis-*O*-[(4-methoxyphenyl)methyl]-D-glucopyranosyl fluoride (2i)

The product was synthesized employing the general procedure. The product was purified by FCC (SiO_2, pure hexane → 30% EtOAc in hexane) to afford **2i** as clear oil in average of 96% yield (R_f = 0.33 (30% EtOAc/Hex)). The NMR spectrum of the product is in a good agreement with our previously published NMR data.[15]

	1st Run	2nd Run
Isolated Yield	99% (65.4 mg) α : β = 1 : 1.4	94% (62.3 mg) α : β = 1 : 1.4

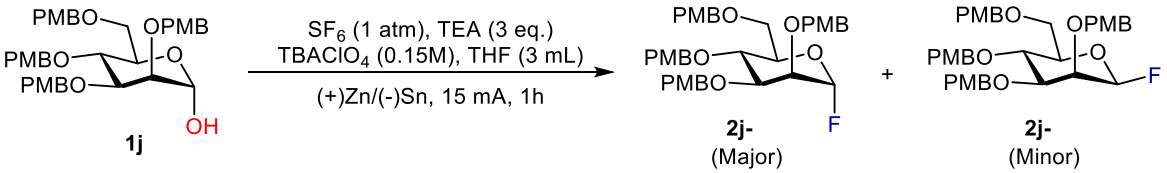


2i-

2,3,4,6-Tetrakis-*O*-[(4-methoxyphenyl)methyl]-β-D-glucopyranosyl fluoride (Major product, Isolated as α : β = 1 : 1.4 mixture).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 – 7.20 (m, 14H), 7.10 – 7.01 (m, 4.6H), 6.93 – 6.77 (m, 18.3H), 5.49 (dd, *J* = 53.2, 2.6 Hz, 1H, C_1-H_α), 5.23 (dd, *J* = 52.8, 6.8 Hz, 1.4H, C_1-H_β), 4.88 (d, *J* = 10.5 Hz, 1H), 4.83 (d, *J* = 10.7 Hz, 1.4H), 4.81 – 4.70 (m, 7H), 4.65 (dd, *J* = 11.1, 4.8 Hz, 2.4H), 4.58 (dd, *J* = 11.8, 3.3 Hz, 2.4H), 4.48 (d, *J* = 11.8 Hz, 1.4H), 4.45 – 4.37 (m, 3.3H), 3.96 – 3.88 (m, 2.4H), 3.84 – 3.77 (m, 27.6H), 3.73 – 3.59 (m, 8.6H), 3.59 – 3.49 (m, 3.7H); **^{19}F NMR** (564 MHz, $CDCl_3$) δ -138.29 (dd, *J* = 53.0, 12.0 Hz, 1.4F, C_1-F_β), -149.54 (dd, *J* = 53.3, 25.7 Hz, 1F, C_1-F_α); **IR** (thin film, cm^{-1}): 2907, 2835, 1611, 1585, 1512, 1463, 1441, 1359, 1302, 1244, 1172, 1083, 1031, 816, 758, 712, 637; **HRMS (ESI+)** (m/z): $[M+Na]^+$ calcd for $C_{38}H_{43}FNaO_9$ 685.2783, found 685.2772; **$[\alpha]_D^{24}$** = +20.7 (c = 0.34, CH_2Cl_2).

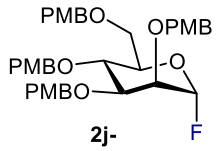
[15]Kim, S.; Khomutnyk, Y.; Bannykh, A.; Nagorny, P. *Org. Lett*. **2021**, 23, 1, 190-194



Synthesis of 2,3,4,6-Tetrakis-*O*-[(4-methoxyphenyl)methyl]-D-mannopyranosyl fluoride (2j)

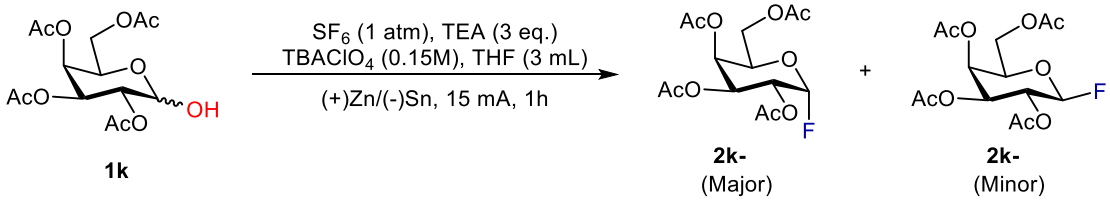
The product was synthesized employing the general procedure. The product was purified by FCC (SiO_2, pure hexane → 10% EtOAc in hexane) to afford **2j** as cloudy oil in average of 96% yield ($R_{f\text{-}\alpha}$ = 0.53 (40% EtOAc/Hex), $R_{f\text{-}\beta}$ = 0.45 (40% EtOAc/Hex)).

	1st Run	2nd Run
Isolated Yield	97% (64.6 mg) α : β = 25 : 1	95% (62.9 mg) α : β = 23 : 1



2,3,4,6-Tetrakis-*O*-[(4-methoxyphenyl)methyl]-α-D-mannopyranosyl fluoride

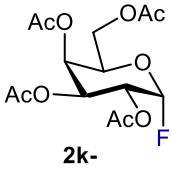
(Major Product) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.29 – 7.24 (m, 6H), 7.06 (d, *J* = 8.6 Hz, 2H), 6.90 – 6.79 (m, 8H), 5.53 (dd, *J* = 50.6, 1.6 Hz, 1H), 4.75 (dd, *J* = 24.8, 11.2 Hz, 2H), 4.64 – 4.53 (m, 4H), 4.44 (dd, *J* = 21.7, 11.1 Hz, 2H), 4.00 – 3.95 (m, 1H), 3.86 (ddd, *J* = 10.0, 4.8, 1.8 Hz, 1H), 3.80 (dd, *J* = 10.6, 4.1 Hz, 14H), 3.71 (dd, *J* = 11.0, 4.7 Hz, 1H), 3.66 (dd, *J* = 10.9, 2.0 Hz, 1H); **^{13}C NMR** (126 MHz, $cdcl_3$) δ 159.4, 159.2, 159.2, 159.2, 130.4, 130.4, 130.2, 129.9, 129.6, 129.6, 129.3, 113.8, 113.7, 106.5 (d, *J* = 221.9 Hz), 78.8, 74.7, 74.2, 74.2, 73.7, 73.1, 73.0, 72.9, 72.8, 72.2, 68.2, 55.3, 55.2, 55.2; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -137.88 (d, *J* = 50.6 Hz); **IR** (thin film, cm^{-1}): 2908, 2835, 1611, 1585, 1512, 1463, 1442, 1422, 1361, 1301, 1244, 1172, 1090, 1030, 950, 816, 756, 711, 667; **HRMS (ESI+)** (m/z): $[M+Na]^+$ calcd for $C_{38}H_{43}FNaO_9$ 685.2783, found 685.2753; **$[\alpha]_D^{24}$** = +7.45 (c = 0.88, CH_2Cl_2).



Synthesis of 2,3,4,6-Tetra-*O*-acetyl-D-galactopyranosyl fluoride (2k)

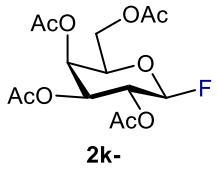
The product was synthesized employing a procedure for acetylated glycosides. After a work-up, the reaction mixture was subjected to FCC (SiO_2, pure hexane → 40% EtOAc in hexane) to afford **2k** as yellowish oil in average of 73% yield ($R_{f\text{-}\alpha}$ = 0.38 (40% EtOAc/Hex), $R_{f\text{-}\beta}$ = 0.30 (40% EtOAc/Hex)).

	1st Run	2nd Run
Isolated Yield	73% (25.6 mg) α : β = 1.9 : 1	73% (25.6 mg) α : β = 1.8 : 1



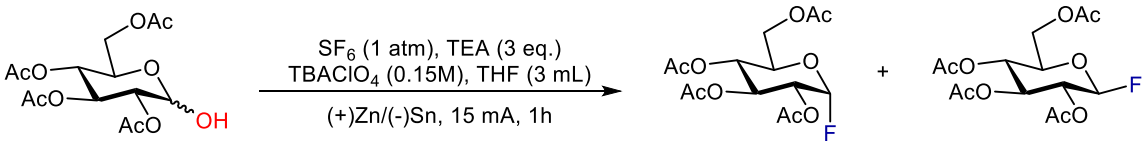
2,3,4,6-Tetra-*O*-acetyl-α-D-galactopyranosyl fluoride (Minor product).

^{1}H NMR (700 MHz, Chloroform-*d*) δ 5.80 (d, *J* = 53.3 Hz, 1H), 5.53 (t, *J* = 2.5 Hz, 1H), 5.37 (dt, *J* = 10.8, 2.8 Hz, 1H), 5.19 (ddt, *J* = 23.8, 10.9, 2.6 Hz, 1H), 4.41 (t, *J* = 6.7 Hz, 1H), 4.18 – 4.09 (m, 2H), 2.16 (s, 3H), 2.12 (s, 3H), 2.06 (s, 3H), 2.01 (s, 3H); **^{13}C NMR** (176 MHz, cdcl$_3$) δ 170.3, 170.2, 170.0, 169.9, 104.3 (d, *J* = 228.4 Hz, α-C_1), 68.9 (d, *J* = 3.5 Hz), 67.5, 67.3, 67.0, 61.3, 20.7, 20.6, 20.6; **^{19}F NMR** (564 MHz, $CDCl_3$) δ -150.78 (dd, *J* = 53.3, 23.9 Hz); **IR** (thin film, cm^{-1}): 2921, 2851, 1744, 1369, 1212, 1167, 1104, 1042, 951, 899; **HRMS (ESI+)** (m/z): [M+Na]+ calcd for $C_{14}H_{19}FNaO_9$ 373.0911, found 373.0905; **[α]$_D^{25}$** = +28.1 (c = 0.4, CH_2Cl_2)



2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl fluoride (Major product).

^{1}H NMR (700 MHz, Chloroform-*d*) δ 5.44 – 5.40 (m, 1H), 5.35 – 5.21 (m, 2H), 5.04 (dt, *J* = 10.5, 2.8 Hz, 1H), 4.24 – 4.18 (m, 2H), 4.05 (t, *J* = 6.6 Hz, 1H), 2.17 (s, 3H), 2.10 (s, 3H), 2.06 (s, 3H), 2.01 (s, 3H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 170.6, 170.0, 170.0, 169.3, 107.1 (d, *J* = 218.6 Hz, β-C_1), 71.2 (d, *J* = 4.7 Hz), 69.9 (d, *J* = 10.6 Hz), 68.8 (d, *J* = 24.9 Hz), 66.4, 61.3, 20.7, 20.6, 20.5; **^{19}F NMR** (564 MHz, $CDCl_3$) δ -141.49 (dd, *J* = 51.0, 12.9 Hz); **IR** (thin film, cm^{-1}): 2921, 2851, 1744, 1369, 1212, 1167, 1104, 1042, 951, 899; **HRMS (ESI+)** (m/z): [M+Na]+ calcd for $C_{14}H_{19}FNaO_9$ 373.0911, found 373.0905; **[α]$_D^{25}$** = +6.0 (c = 0.4, CH_2Cl_2)

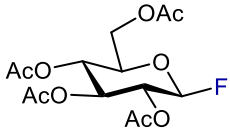


1l **2l-** (Minor) **2l-** (Major)

Synthesis of 2,3,4,6-Tetra-*O*-acetyl-D-glucopyranosyl fluoride (2l)

The product was synthesized employing a procedure for acetylated glycosides. After a work-up, the reaction mixture was subjected to FCC (SiO_2, pure hexane → 50% EtOAc in hexane) to afford **2l** as colorless oil in average of 76% yield ($R_{f\text{-}\alpha}$ = 0.47 (50% EtOAc/Hex), $R_{f\text{-}\beta}$ = 0.43 (50% EtOAc/Hex)).

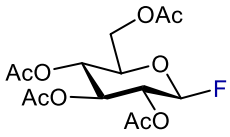
	1st Run	2nd Run
Isolated Yield	76% (26.7 mg) α : β = 1 : 2.3	75% (26.3 mg) α : β = 1 : 2.5



2l-

2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl fluoride (Minor product)

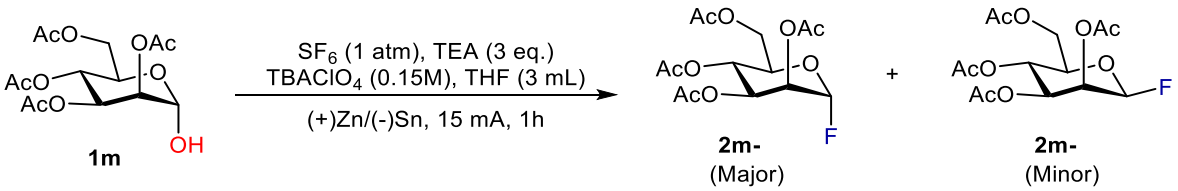
^{1}H NMR (700 MHz, $CDCl_3$) δ 5.75 (dd, *J* = 52.8, 2.8 Hz, 1H), 5.50 (t, *J* = 9.9 Hz, 1H), 5.16 (t, *J* = 10.0 Hz, 1H), 4.96 (ddd, *J* = 24.2, 10.2, 2.8 Hz, 1H), 4.29 (dd, *J* = 12.5, 4.1 Hz, 1H), 4.19 (ddd, *J* = 10.3, 4.2, 2.2 Hz, 1H), 4.15 (dd, *J* = 12.5, 2.2 Hz, 1H), 2.11 (s, 3H), 2.10 (s, 6H), 2.05 (s, 3H), 2.03 (s, 3H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 170.5, 170.0, 169.9, 169.4, 103.7 (d, *J* = 229.5 Hz, α-C_1), 70.2 (d, *J* = 24.5 Hz), 69.8 (d, *J* = 4.3 Hz), 69.4, 67.3, 61.2, 20.7, 20.6, 20.5; **^{19}F NMR** (564 MHz, $CDCl_3$) δ -149.76 (dd, *J* = 52.8, 24.2 Hz, α-C_1-F); **IR** (thin film, cm^{-1}): 2918, 1743, 1434, 1367, 1208, 1160, 1103, 1033, 904, 779; **HRMS (ESI+)** (m/z): $[M+Na]^+$ calcd for $C_{14}H_{19}FNaO_9$ 373.0892, found 373.0899



2l-

2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl fluoride (Major product)

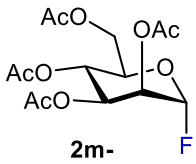
^{1}H NMR (700 MHz, $CDCl_3$) δ 5.36 (ddd, *J* = 52.0, 6.2, 1.8 Hz, 1H), 5.20 (tt, *J* = 9.4, 4.8 Hz, 2H), 5.12 – 5.08 (m, 1H), 4.29 – 4.24 (m, 1H), 4.24 – 4.20 (m, 1H), 3.90 (ddd, *J* = 7.5, 4.9, 2.5 Hz, 1H), 2.10 (s, 3H), 2.10 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 170.6, 170.0, 169.3, 169.1, 106.2 (d, *J* = 219.6 Hz, β-C_1), 72.0 (d, *J* = 3.8 Hz), 71.8 (d, *J* = 8.3 Hz), 71.2 (d, *J* = 28.8 Hz), 67.4, 61.7, 20.7, 20.6; **^{19}F NMR** (564 MHz, $CDCl_3$) δ -137.24 (dd, *J* = 52.0, 10.4 Hz, β-C_1-F), -149.76 (dd, *J* = 52.8, 24.2 Hz).; **IR** (thin film, cm^{-1}): 2918, 1743, 1434, 1367, 1208, 1160, 1103, 1033, 904, 779; **HRMS (ESI+)** (m/z): $[M+Na]^+$ calcd for $C_{14}H_{19}FNaO_9$ 373.0892, found 373.0899; **$[\alpha]_D^{24}$** = +13.6 (c = 0.5, CH_2Cl_2)



Synthesis of 2,3,4,6-Tetra-*O*-acetyl-D-mannopyranosyl fluoride (2m)

The product was synthesized employing the general procedure. After a work-up, the reaction mixture was subjected to FCC (SiO_2, pure hexane → 40% EtOAc in hexane) to afford pure **2m** in average of 81% yield as cloudy oil (Rf = 0.33 (40% EtOAc/Hex)). Stereochemistry of the products was confirmed by comparing with previously reported NMR spectra.[16]

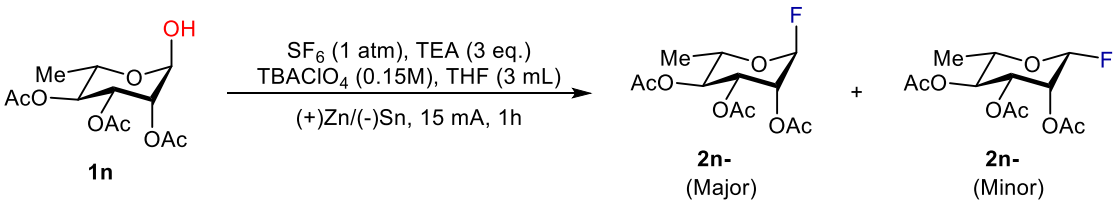
	1st Run	2nd Run
Isolated Yield	81% (28.4 mg) α : β = 20 : 1	80% (28.1 mg) α : β = 20 : 1



2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranosyl fluoride (Major product).

^{1}H NMR (700 MHz, Chloroform-*d*) δ 5.58 (d, *J* = 48.6 Hz, 1H), 5.40 (s, 1H), 5.35 (d, *J* = 5.0 Hz, 2H), 4.32 – 4.27 (m, 1H), 4.16 (dd, *J* = 14.7, 4.4 Hz, 2H), 2.17 (s, 3H), 2.11 (s, 3H), 2.06 (s, 3H), 2.01 (s, 3H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 170.5, 169.7, 169.6, 169.5, 104.7 (d, *J* = 223.7 Hz, β-C_1), 70.9 (d, *J* = 2.7 Hz), 68.2, 67.7 (d, *J* = 39.5 Hz), 65.0, 61.8, 20.7, 20.6, 20.6; **^{19}F NMR** (564 MHz, $CDCl_3$) δ -138.38 (d, *J* = 48.4 Hz); **IR** (thin film, cm^{-1}): 2960, 1742, 1434, 1368, 1211, 1172, 1087, 1051, 1019, 974, 916, 795, 685; **HRMS** (ESI+) (m/z): $[M+Na]^+$ calcd for $C_{14}H_{19}FNaO_9$ 373.0911, found 373.0905; **$[\alpha]_D^{24}$** = +11.2 (c = 0.5, CH_2Cl_2).

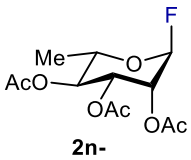
[16] Chambers, R. D.; Sandford, G.; Sparrowhawk, M. E.; Atherton, M. J. *J. Chem. Soc., Perkin Trans. 1*, **1996**, 1941-1944



Synthesis of 2,3,4-tri-*O*-acetyl-L-rhamnopyranosyl fluoride (2n)

The product was synthesized employing the general procedure. After a work-up, the reaction mixture was purified by FCC (SiO_2, pure hexane → 40% EtOAc in hexane) to afford **2n** as colorless oil in average of 79% yield (R_f = 0.37(30% EtOAc/Hex)). Stereochemistry of the products was confirmed by comparing with previously reported NMR spectra.[17]

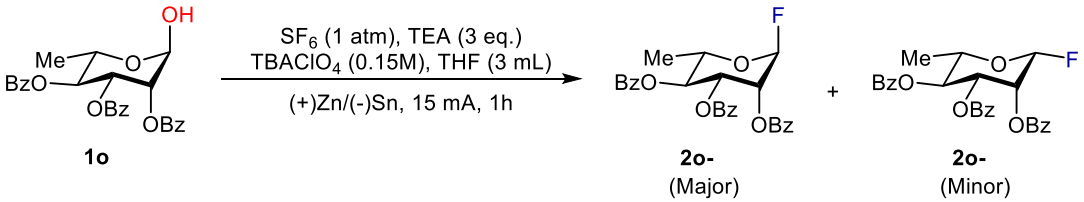
	1st Run	2nd Run
Isolated Yield	82% (23.8 mg) α : β = 22 : 1	77% (22.5 mg) α : β = 18 : 1



2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl fluoride (Major product)

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.49 (dd, *J* = 48.6, 1.9 Hz, 1H), 5.38 (ddd, *J* = 3.2, 1.9, 0.9 Hz, 1H), 5.29 (ddd, *J* = 10.2, 3.6, 1.7 Hz, 1H), 5.12 (t, *J* = 10.0 Hz, 1H), 4.04 (dq, *J* = 9.9, 6.2 Hz, 1H), 2.16 (s, 3H), 2.06 (s, 3H), 2.00 (s, 3H), 1.27 (d, *J* = 6.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.8, 169.8, 169.7, 104.8 (d, *J* = 221.9 Hz), 70.0, 68.9 (d, *J* = 3.0 Hz), 68.2 (d, *J* = 1.7 Hz), 68.0 (d, *J* = 40.3 Hz), 20.7, 20.7, 20.6, 17.3; **^{19}F NMR** (564 MHz, $CDCl_3$) δ -137.49 (d, *J* = 49.1 Hz); **IR** (thin film, cm^{-1}): 2925, 1748, 1605, 1509, 1457, 1369, 1293, 1242, 1214, 1173, 1038, 974, 929, 893, 830, 813, 793, 778, 684

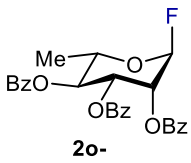
[17]Nishiyama, K.; Esaki, S.; Deguchi, I.; Sugiyama, N.; Kamiya, S. *Biosci. Biotechnol. Biochem.* **1993**, 57, 107–114



Synthesis of 2,3,4-tri-*O*-benzoyl-L-rhamnopyranosyl fluoride (2o)

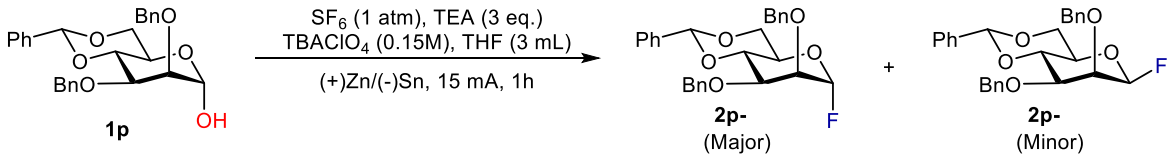
The product was synthesized employing the general procedure. After a work-up, the reaction mixture was purified by FCC (SiO_2, pure hexane → 30% EtOAc in hexane) to afford **2o** as cloudy syrup in average of 84% yield ($R_{f\text{-}\alpha}$ = 0.52 (30% EtOAc/Hex), $R_{f\text{-}\beta}$ = 0.46 (30% EtOAc/Hex)).

	1st Run	2nd Run
Isolated Yield	86% (41.2 mg) α : β = 20 : 1	82% (39.1 mg) α : β = 21 : 1



2,3,4-Tri-*O*-benzoyl-α-L-rhamnopyranosyl fluoride

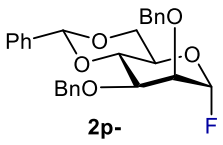
^{1}H NMR (700 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 8.3, 1.3 Hz, 2H), 8.00 – 7.97 (m, 2H), 7.83 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.63 (tt, *J* = 8.8, 1.3 Hz, 1H), 7.55 – 7.52 (m, 3H), 7.52 – 7.49 (m, 2H), 7.43 (tt, *J* = 7.4, 1.3 Hz, 1H), 7.42 – 7.38 (m, 2H), 5.87 – 5.81 (m, 2.5H, C_4-H + C_2-H + 1/2 C_1-H), 5.76 (d, *J* = 1.8 Hz, 0.5H, 1/2 C_1-H), 5.74 (t, *J* = 9.9 Hz, 1H, C_3-H), 4.39 (dq, *J* = 9.9, 6.2 Hz, 1H), 1.43 (d, *J* = 6.2 Hz, 3H); **^{13}C NMR** (176 MHz, cdcl$_3$) δ 165.6, 165.4, 165.3, 133.7, 133.5, 133.3, 130.0, 129.8, 129.7, 129.0, 128.9, 128.9, 128.7, 128.5, 128.3, 104.9 (d, *J* = 222.4 Hz, α-C_1-F), 70.7, 69.2 (d, *J* = 2.7 Hz), 69.1 (d, *J* = 1.0 Hz), 68.9 (d, *J* = 40.6 Hz), 17.6; **^{19}F NMR** (564 MHz, $CDCl_3$) δ -137.24 (d, *J* = 48.8 Hz); **IR** (thin film, cm^{-1}): 2985, 1724, 1601, 1584, 1451, 1315, 1276, 1258, 1173, 1091, 1068, 1026, 973, 910, 851, 793, 705, 685; **HRMS (ESI+)** (m/z): $[M\text{-}F]^+$ calcd for $C_{27}H_{23}O_7^+$ 459.1438, found 459.1427; **$[\alpha]_D^{23.9}$** = +166.9 (c (w/v%) = 4.15, CH_2Cl_2)



Synthesis of 2,3-bis-*O*-(phenylmethyl)-4,6-*O*-[(R)-phenylmethylene]-D-mannopyranosyl fluoride (2p)

The product was synthesized employing the general procedure. The product was purified by FCC (SiO_2, pure hexane → 20% EtOAc in hexane) to afford **2p** as cloudy oil in average of 96% yield ($R_{f\text{-}\alpha}$ = 0.44 (20% EtOAc/Hex)). Stereochemistry of the products was determined by comparing with previously reported NMR spectra.[18]

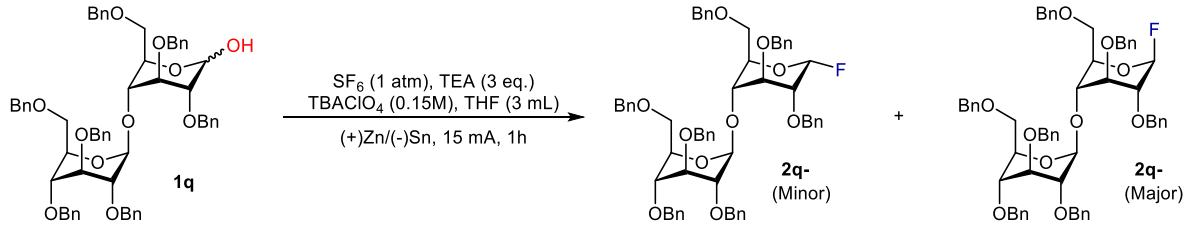
	1st Run	2nd Run
Isolated Yield	97% (43.9 mg) α : β = 24 : 1	94% (42.2 mg) α : β = 28 : 1



2,3-Bis-*O*-(phenylmethyl)-4,6-*O*-[(R)-phenylmethylene]-α-D-mannopyranosyl fluoride (major product).

^{1}H NMR (700 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.1 Hz, 2H), 7.41 – 7.28 (m, 13H), 5.65 (s, 1H), 5.50 (d, *J* = 49.6 Hz, 1H), 4.89 (d, *J* = 12.0 Hz, 2H), 4.74 – 4.68 (m, 2H), 4.33 – 4.27 (m, 2H), 3.99 – 3.92 (m, 3H), 3.87 (td, *J* = 10.3, 2.0 Hz, 1H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 138.3, 137.6, 137.4, 128.9, 128.5, 128.4, 128.2, 128.1, 128.1, 127.7, 127.6, 126.1, 107.0 (d, *J* = 223.7 Hz), 101.6, 78.3, 75.5 (d, *J* = 2.5 Hz), 75.0, 74.8, 74.2, 73.5, 68.3, 66.1 (d, *J* = 2.4 Hz); **^{19}F NMR** (471 MHz, $CDCl_3$) δ -137.06 (d, *J* = 49.7 Hz); **IR** (thin film, cm^{-1}): 2919, 1454, 1372, 1313, 1214, 1166, 1099, 1054, 1006, 965, 925, 799, 735, 696; **HRMS (ESI+)** (m/z): $[M+Na]^+$ calcd for $C_{27}H_{27}FNaO_5$ 473.1692, found 473.1729; **$[\alpha]_D^{23}$** = -17.4 (c = 0.6, CH_2Cl_2).

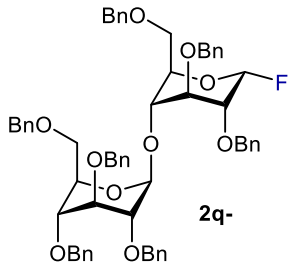
[18]Lee, Y. J.; Baek, J. Y.; Lee, B-Y.; Kang, S. S.; Park, H-S.; Jeon, H. B.; Kim, K. S. Carbohydrate Research. **2006**. 341(10). 1708-1716



Synthesis of 2,3,6-Tris-O-(phenylmethyl)-4-O-[2,3,4,6-tetrakis-O-(phenylmethyl)-β-D-glucopyranosyl]-D-glucopyranosyl fluoride (2q)

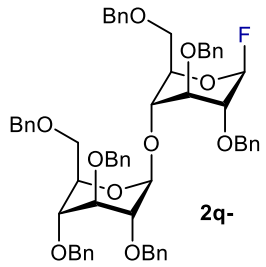
The product was synthesized employing the general procedure. The product was purified by FCC (SiO_2, pure hexane → 30% EtOAc in hexane) to afford **2q** as white solid in average of 84% yield ($R_{f\text{-}\alpha}$ = 0.58 (30% EtOAc/Hex), $R_{f\text{-}\beta}$ = 0.57 (30% EtOAc/Hex)).

	1st Run	2nd Run
Isolated Yield	80% (78.1 mg) α : β = 1 : 3.4	88% (85.8 mg) α : β = 1 : 3.2



2,3,6-Tris-O-(phenylmethyl)-4-O-[2,3,4,6-tetrakis-O-(phenylmethyl)-β-D-glucopyranosyl]-α-D-glucopyranosyl fluoride (minor product).

^{1}H NMR (700 MHz, $CDCl_3$) δ 7.40 (d, *J* = 6.5 Hz, 2H), 7.33 – 7.20 (m, 31H), 7.19 (d, *J* = 7.4 Hz, 2H), 5.48 (dd, *J* = 53.4, 2.7 Hz, 1H, α-C_1-H), 5.12 (dd, *J* = 11.4, 2.0 Hz, 1H), 4.89 – 4.86 (m, 1H), 4.83 – 4.72 (m, 6H), 4.63 (dd, *J* = 11.9, 2.0 Hz, 1H), 4.56 (d, *J* = 11.5 Hz, 2H), 4.44 (dd, *J* = 12.3, 2.0 Hz, 1H), 4.39 (ddd, *J* = 11.7, 6.9, 2.8 Hz, 3H), 4.07 – 4.03 (m, 1H), 3.90 – 3.84 (m, 2H), 3.80 (dd, *J* = 10.1, 2.2 Hz, 1H), 3.73 (d, *J* = 10.9 Hz, 1H), 3.61 (t, *J* = 8.8 Hz, 1H), 3.58 – 3.55 (m, 1H), 3.48 (ddd, *J* = 25.5, 19.6, 10.3 Hz, 4H), 3.39 – 3.35 (m, 1H), 3.33 – 3.29 (m, 1H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 139.2, 138.6, 138.5, 138.3, 138.3, 137.9, 137.6, 128.5, 128.4, 128.4, 128.4, 128.3, 128.2, 128.1, 128.0, 128.0, 127.9, 127.8, 127.8, 127.8, 127.8, 127.7, 127.6, 127.6, 127.3, 127.2, 105.8 (d, *J* = 226.8 Hz, α-C_1), 102.5, 84.9, 82.7, 79.8, 78.2 (d, *J* = 24.3 Hz), 78.0, 75.6, 75.6, 75.4, 75.2, 75.0, 74.8, 73.8, 73.3, 72.6 (d, *J* = 4.2 Hz), 69.0, 69.0, 67.1; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -149.55 (dd, *J* = 53.4, 25.8 Hz); **IR** (thin film, cm^{-1}): 1497, 1453, 1361, 1072, 1029, 1005, 908, 753, 731, 695, 665; **HRMS (ESI+)** (m/z): $[M+NH_4]^+$ calcd for $C_{61}H_{67}FNO_{10}$ 992.4738, found 992.4733; **$[\alpha]_D^{23.6}$** = +23.1 (c = 0.23, CH_2Cl_2)



2q-

2,3,6-Tris-O-(phenylmethyl)-4-O-[2,3,4,6-tetrakis-O-(phenylmethyl)-β-D-glucopyranosyl]-β-D-glucopyranosyl fluoride (major product).

^{1}H NMR (700 MHz, $CDCl_3$) δ 7.37 (d, *J* = 5.2 Hz, 2H), 7.34 – 7.22 (m, 31H), 7.19 (d, *J* = 7.3 Hz, 2H), 5.25 (dd, *J* = 53.5, 6.5 Hz, 1H, β-C_1-H), 5.05 (d, *J* = 11.4 Hz, 1H), 4.89 (d, *J* = 10.9 Hz, 1H), 4.81 (d, *J* = 10.6 Hz, 2H), 4.75 (dd, *J* = 17.7, 9.3 Hz, 4H), 4.69 (d, *J* = 11.2 Hz, 1H), 4.58 (dd, *J* = 17.0, 11.4 Hz, 2H), 4.50 (d, *J* = 7.9 Hz, 1H), 4.47 – 4.39 (m, 3H), 4.13 (t, *J* = 8.9 Hz, 1H), 3.84 (dd, *J* = 11.1, 3.4 Hz, 1H), 3.72 – 3.48 (m, 8H), 3.39 (t, *J* = 8.5 Hz, 1H), 3.30 (dd, *J* = 10.4, 4.0 Hz, 1H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 138.9, 138.5, 138.4, 138.4, 138.2, 137.8, 137.8, 128.4, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 128.1, 127.9, 127.8, 127.8, 127.8, 127.8, 127.8, 127.7, 127.7, 127.6, 127.6, 127.5, 127.4, 127.3, 109.5 (d, *J* = 215.9 Hz, β-C_1), 102.3, 84.9, 82.7, 81.3 (d, *J* = 10.3 Hz), 80.5 (d, *J* = 23.0 Hz), 77.9, 75.8, 75.6, 75.0, 74.9 (d, *J* = 3.7 Hz), 74.8, 74.7, 74.3, 73.4, 73.3, 68.9, 67.7; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -135.75 (dd, *J* = 53.5, 12.3 Hz); **IR** (thin film, cm^{-1}): 1497, 1453, 1361, 1072, 1029, 1005, 908, 753, 731, 695, 665; **HRMS (ESI+)** (m/z): $[M+NH_4]^+$ calcd for $C_{61}H_{67}FNO_{10}$ 992.4738, found 992.4733; **$[\alpha]_D^{23}$** = +25.9 (c = 1.1, CH_2Cl_2)

d. Summary of α:β ratio for 1a-q and 2a-q

Table S7. Initial and final α:β ratios of the starting materials 1a-q and products 2a-q

Substrate	Initial dr of **1a-q** determined by ^{1}H NMR	dr of **2a-q** determined by ^{19}F NMR
a	alpha only	1:1.6
b	4.8:1	1:1.5
c	alpha only	22:1
d	5.5:1	1:2.6
e	2.7:1	2.3:1
f	alpha only	19:1
g	beta only	1:17
h	3.4:1	1:1.2
i	3:1	1:1.4
j	alpha only	24:1
k	4.2:1	1.9:1
l	5:1	1:2.4
m	alpha only	20:1
n	alpha only	20:1
o	6.8:1	21:1
p	alpha only	26:1
q	1.9:1	1:3.3

e. Comparison with DAST method

Product	Our method	DAST method	
		α:β of SM	Yield
2a	94% (α:β = 1:1.6)	α:β = 1.7:1	91% (α:β = 3:5)
2b	98% (α:β = 1:1.5)	α:β = 1.7:1	89% (α:β = 5:1)
2c	95% (α:β = 22:1)	α only	91% (α only)
2d	98% (α:β = 1:2.6)	-	-
2e	95% (α:β = 2.3:1)	α:β mixture	100% (α:β mixture)
2f	93% (α:β = 19:1)	-	-
2g	94% (α:β = 1:17)	α:β mixture	95% (α:β = 1:19 to 1:99)
2h	96% (α:β = 1:1.2)	α:β mixture	93% (α:β mixture)
2i	96% (α:β = 1:1.4)	-	-
2j	96% (α:β = 24:1)	-	-
2k	73% (α:β = 1.9:1)	-	-
2l	76% (α:β = 1:2.4)	α:β = 1:2	92% (α:β = 3:1)
2m	81% (α:β = 20:1)	-	-
2n	79% (α:β = 3:1)	-	-
2o	84% (α:β = 21:1)	-	-
2p	96% (α:β = 26:1)	-	-
2q	84% (α:β = 1:3.3)	-	-

References:

2a, 2b, 2c: Zeng, J.; Vedachalam, S.; Xiang, S.; Liu, X.-W. *Org. Lett.* **2011**, 13, 1, 42-45

2e: Guan, X.; Chaffey, P. K.; Zeng, C.; Greene, E. R.; Chen, L.; Drake, M. R.; Chen, C.; Groobman, A.; Resch, M. G.; Himmel, M. E.; Beckham, G. T.; Tan, Z. *Chem. Sci.* **2015**, 6, 7185

2g: Ginisty, M.; Gravier-Pelletier, C.; Merrer, Y. L. *Tetrahedron: Asymmetry.* **2006**, 17, 142-150

2h: Li, X.; Wu, P.; Cheng, S.; Lv, X. *J. Med. Chem.* **2021**, 55, 6, 2702-2710

2l: Zagrobelny, M.; Olsen, C. E.; Pentzold, S.; Fürstenberg-Hägg, J.; Jørgensen, K.; Bak, S.; Møller, B. L.; Motawia, M. S. *Insect Biochemistry and Molecular Biology.* **2014**, 44, 44-53

f. Large Scale Batch Synthesis

5 Gram Scale Synthesis

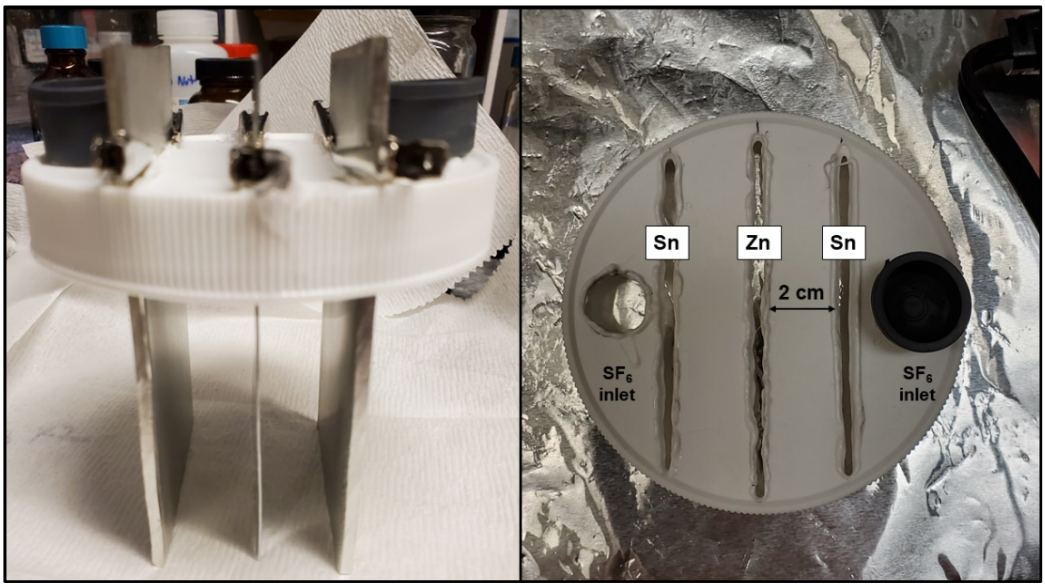


Figure S4. Experimental setup adopted from Baran Group's Work[19]

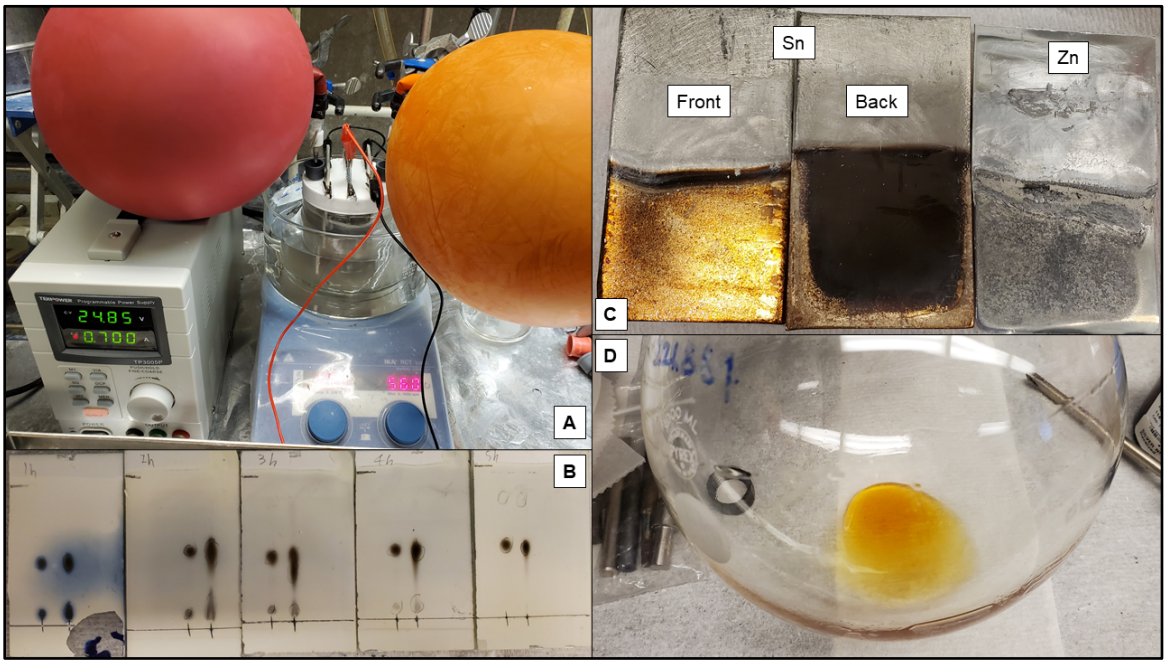
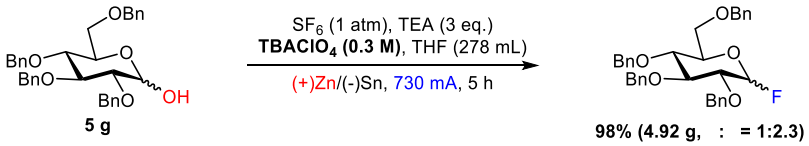


Figure S5. (A) Reaction setup (B) Reaction progress monitored by TLC (C) Electrodes after the reaction (D) Isolated product

[19]Hu, P.; Peters, B. K.; Malapit, C. A.; Vantourout, J. C.; Wang, P.; Li, J.; Mele, L.; Echeverria, P.-G.; Minteer, S. D.; Baran, P. S. *J. Am. Chem. Soc.* **2020**, 142, 50, 20979-20986



Applied Current	Surface Area	Current Density
730 mA	58 cm^2	12.6 mA/cm^2

To achieve high current density, the experimental setup was adopted from Baran group's large scale setup (**Fig. SI-4**).[19] Electrodes were prepared by cutting off tin plate (3.2 mm thickness, 5.8 cm x 10 cm x 2) and zinc plate (0.5 mm thickness, 6.0 cm x 10 cm) and 5.0 cm height of the electrodes were submerged in the solution. Due to the voltage limit (31 V) of the DC power supply, the concentration of electrolyte was doubled (0.3 M). Into an oven dried glass jar containing a stir bar, 2,3,4,6-tetrakis-*O*-(phenylmethyl)-D-glucopyranoside **1a** (9.25 mmol, 1.0 equiv.), tetrabutylammonium perchlorate (83.4 mmol, 0.3 M) were dissolved in dry THF (278 mL). After the addition of triethylamine (27.7 mmol, 3.0 equiv.), the reaction was placed inside a water bath (to relieve the heat generated during electrolysis) and stirred until the solution became homogeneous. The reaction was then sparged with SF_6 balloons for 1 minute before the electric current was applied, and then the rest of the reaction. The electric current was applied for 6 hours, and then the reaction mixture was diluted with 300 mL of ethyl acetate. The diluted mixture was then washed with 1N HCl (250 mL x 3), $NaHCO_3$ (250 mL x 1), water (250 mL x 5), and brine (250 mL x 1). The extracted organic layer was dried with Na_2SO_4 and concentrated *in vacuo*, which was subjected to FCC to afford 2,3,4,6-tetrakis-*O*-(phenylmethyl)-D-glucopyranosyl fluoride **2a** in 98 % yield (4.92 g, $\alpha : \beta = 1 : 2.3$) as yellow syrup.

IV. Cyclic Voltammetry Studies

General information

Cyclic voltammetry studies were performed with the Pine WaveNow[XV] Potentiostat/Galvanostat. All experiments were measured under slight argon stream. SF_6 was added by sparging SF_6 gas to the solution for 1 minute. Electrodes were polished with 1000-grit sandpaper and cleaned by sonicating in acetone, and they were dried under high vacuum before use. All electrolytes were dried under high vacuum before use. THF was prepared from Innovative Technology PureSolv solvent drying system and dry acetonitrile was purchased from Alfa Aesar. All solvents were degassed with argon before use.

a. Identifying half reduction potential of SF_6

Scan range: -3.0 V to 0.0 V (-3.1 V to -0.5 V is shown on the graph after voltage reference with Fc^+/Fc)
Scan rates: 20 mV/s
Electrolyte: $TBAClO_4$ (0.1M) / Solvent: acetonitrile (12 mL)
Working electrode: 0.635 mm diameter Pt wire (0.6 cm submerged)
Counter electrode: Pt plate (0.8 cm^2)
Reference electrode: Ag/AgCl (voltage is referenced to ferrocene [0.001 M])

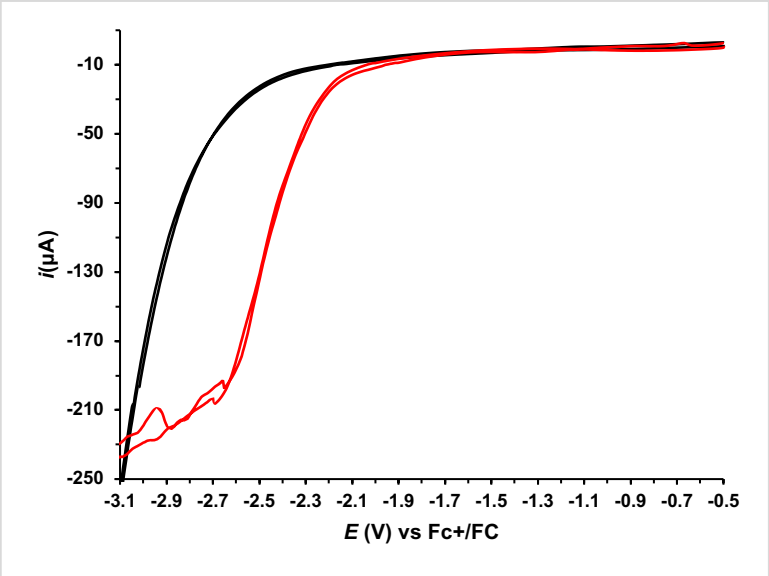


Figure S6. Blank is shown in black line and the reduction of SF_6 is shown in red line. Voltage was corrected by ferrocene (0.001 M)

We first attempted to measure the half reduction potential of SF_6 by adopting the CV experimental set-up from Magnier group.[20] The voltammogram shows $E_{red1/2}$ = -2.44 V (vs. Fc^+/Fc).

Half reduction potential of SF_6 reference to SCE: -1.99 V vs. SCE

[20]Bouvet, S.; Pegot, B.; Sengmany, S.; Gall, E. L.; Leonel, E.; Goncalves, A.-M.; Magnier, E. *Beilstein J. Org. Chem.* **2020**, 16, 2948-2953

b. SF_6 at multiple scan rate

Scan range: -2.0 V to 0.0 V

Scan rates (in chronological order):

1) 50 mV/s 2) 100 mV/s 3) 25 mV/s 4) 75 mV/s 5) 200 mV/s

Electrolyte: $TBAClO_4$ (0.15M) / Solvent: THF (12 mL)

Working electrode: 1.5 mm diameter Sn wire (0.6 cm submerged)

Counter electrode: 2.0 mm diameter Zn wire (1.5 cm submerged)

Reference electrode: Ag/AgCl

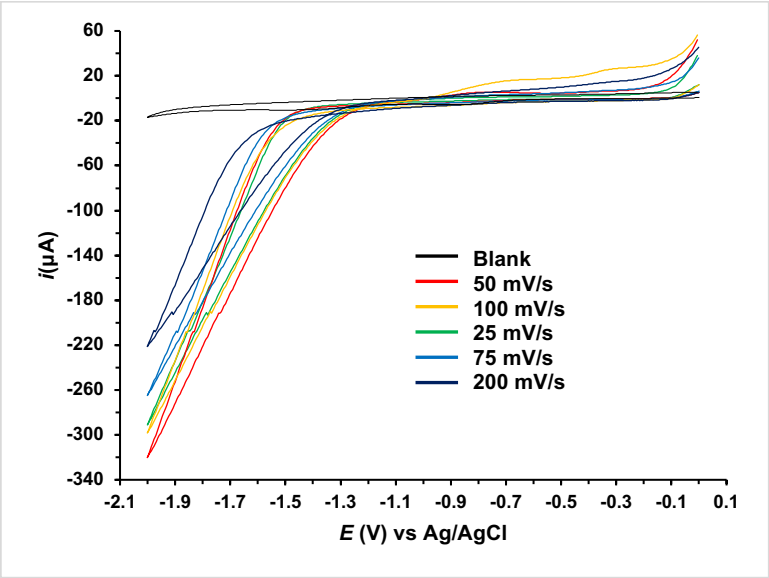


Figure S7. Reduction of SF_6 with Zn as sacrificial anode at multiple scan rates.

The voltammogram shows the decrease of cathodic current in the chronological order of the scans. It suggests the increased internal resistance from either a) electrode passivation or b) accumulation of salt formed from solvated Zn cation.

Scan range: -2.0 V to 0.0 V
Scan rates (in chronological order):
1) 50 mV/s 2) 100 mV/s 3) 25 mV/s 4) 75 mV/s 5) 200 mV/s
Electrolyte: $TBAClO_4$ (0.15M) / Solvent: THF (12 mL)
Working electrode: 1.5 mm diameter Sn wire (0.6 cm submerged)
Counter electrode: Pt plate (0.8 cm^2)
Reference electrode: Ag/AgCl

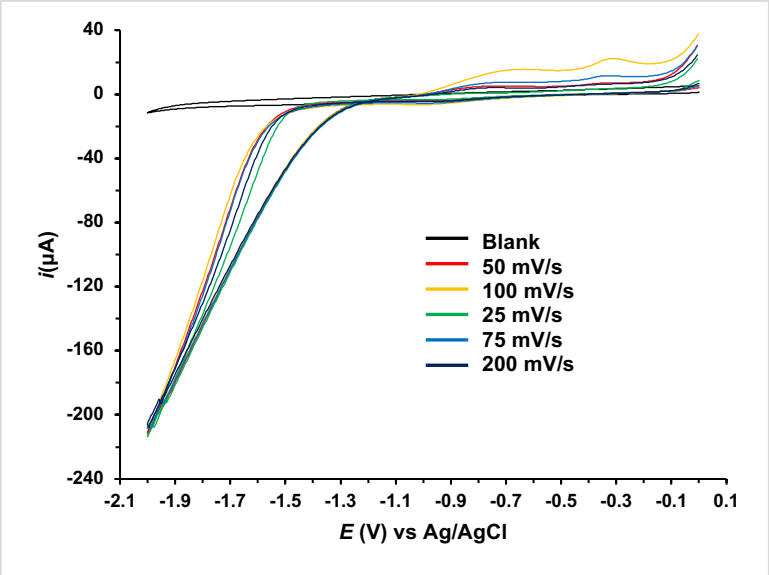


Figure S8. Reduction of SF_6 with Pt as anode at multiple scan rates.

Pt anode is resistant to galvanic corrosion and does not dissociate Pt cation under electric current. As expected with Pt as anode, the voltammogram shows consistent current throughout the entire CV experiment. This result supports that the decrease of cathodic current in previous CV experiment is caused by Zn sacrificial anode.

c. SF_6 + NEt_3 at multiple scan rate

Scan range: -2.0 V to 0.0 V

Scan rates (in chronological order):

1) 50 mV/s 2) 100 mV/s 3) 25 mV/s 4) 75 mV/s 5) 200 mV/s

Electrolyte: $TBAClO_4$ (0.15M) / Solvent: THF (12 mL)

Working electrode: 1.5 mm diameter Sn wire (0.6 cm submerged)

Counter electrode: 2.0 mm diameter Zn wire (1.5 cm submerged)

Reference electrode: Ag/AgCl

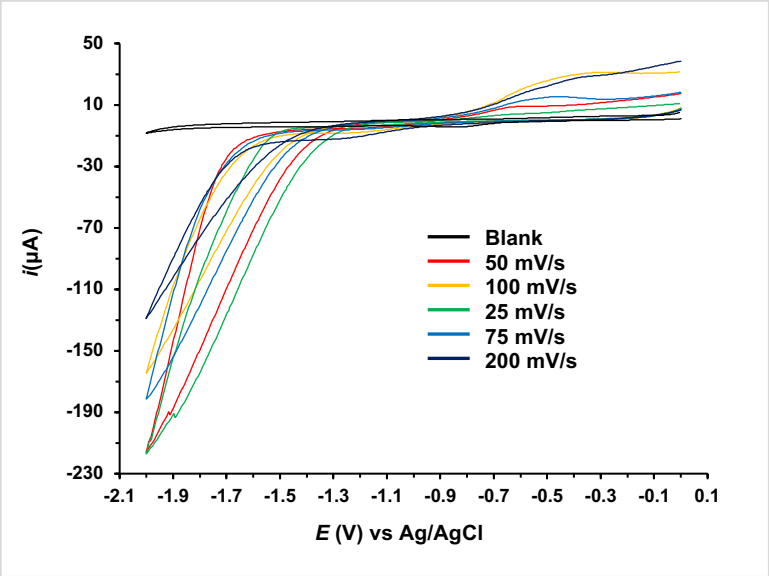


Figure S9. Reduction of SF_6 in the presence of NEt_3 with Zn as sacrificial anode at multiple scan rates. [NEt_3] = 99 mM

In the presence of triethylamine, the cathodic current is now dependent on the scan rate. Slower scan rate allows more diffusion time for amine base to either scavenge the reduced SF_6 material or promote the solvation of Zn cation. This maintains the internal resistance fairly stable, which enhances the cathodic current compared to faster scan rate.

Scan range: -2.0 V to 0.0 V
Scan rates (in chronological order):
1) 50 mV/s 2) 100 mV/s 3) 25 mV/s 4) 75 mV/s 5) 200 mV/s
Electrolyte: $TBAClO_4$ (0.15M) / Solvent: THF (12 mL)
Working electrode: 1.5 mm diameter Sn wire (0.6 cm submerged)
Counter electrode: Pt plate (0.8 cm^2)
Reference electrode: Ag/AgCl

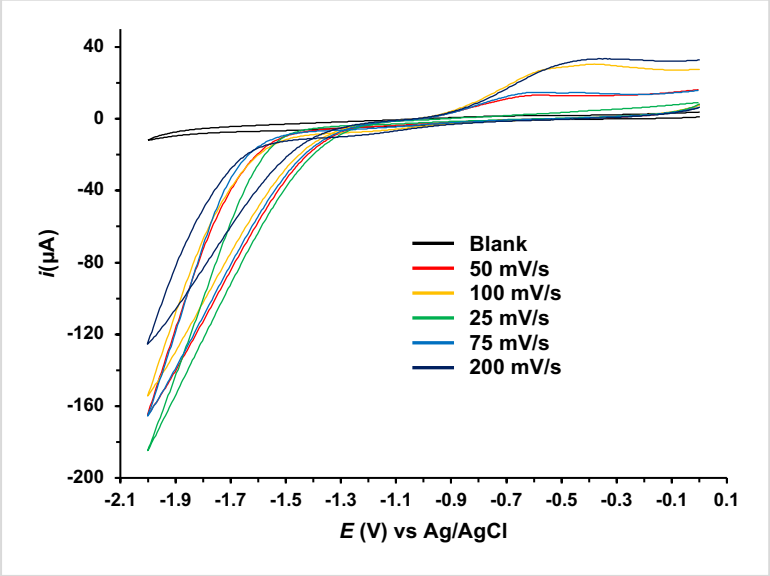


Figure S10. Reduction of SF_6 in the presence of NEt_3 with Pt as anode at multiple scan rates. [NEt_3] = 99 mM

With Pt as anode, the voltammogram still shows enhanced cathodic current under slower scan rate. The result supports that the amine base scavenges reduced SF_6 material (S_nF_m or F-), which can maintain the internal resistance stable.

d. SF_6 + glycoside at multiple scan rate

Glycoside: 2,3,4,6-tetrakis-*O*-(phenylmethyl)-D-glucopyranoside (**1b**)
Scan range: -2.0 V to 0.0 V
Scan rates (in chronological order):
1) 50 mV/s 2) 100 mV/s 3) 25 mV/s 4) 75 mV/s 5) 200 mV/s
Electrolyte: $TBAClO_4$ (0.15M) / Solvent: THF (12 mL)
Working electrode: 1.5 mm diameter Sn wire (0.6 cm submerged)
Counter electrode: 2.0 mm diameter Zn wire (1.5 cm submerged)
Reference electrode: Ag/AgCl

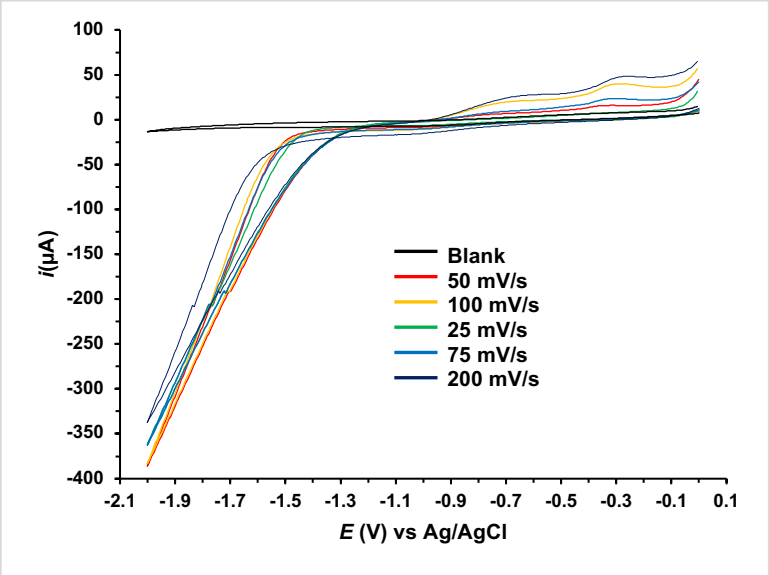


Figure S11. Reduction of SF_6 in the presence of glycoside substrate with Zn as sacrificial anode. [**1b**] = 33 mM.

In the presence of SF_6 and glycoside substrate, the voltammogram is consistently showing the decrease of cathodic current in chronological order of the scanning. This result suggests that deoxofluorination of glycoside is a chemical reaction process which is not catalyzed by electrolysis.

e. SF_6 + glycoside +NEt_3 at multiple scan rate

Glycoside: 2,3,4,6-tetrakis-*O*-(phenylmethyl)-D-glucopyranoside (**1b**)
Scan range: -2.0 V to 0.0 V
Scan rates (in chronological order):
1) 50 mV/s 2) 100 mV/s 3) 25 mV/s 4) 75 mV/s 5) 200 mV/s
Electrolyte: TBAClO4 (0.15M) / Solvent: THF (12 mL)
Working electrode: 1.5 mm diameter Sn wire (0.6 cm submerged)
Counter electrode: 2.0 mm diameter Zn wire (1.5 cm submerged)
Reference electrode: Ag/AgCl

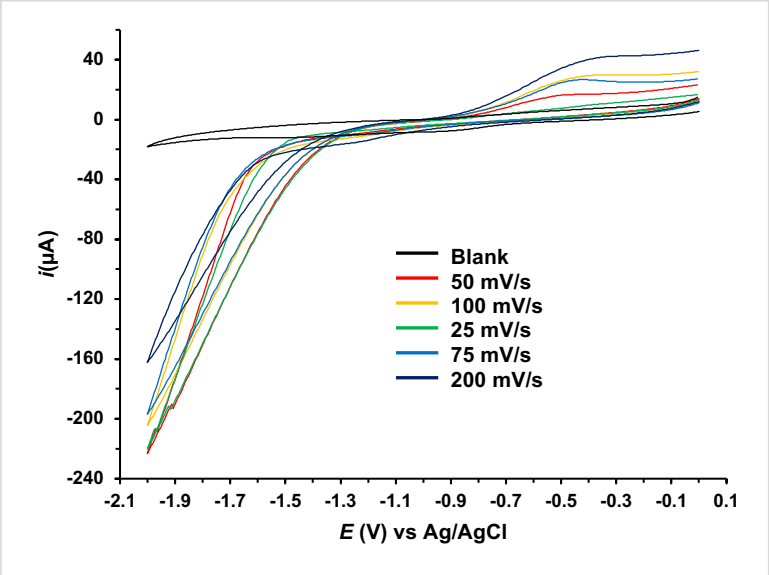


Figure S12. Reduction of SF_6 under standard reaction condition. [**1b**] = 33 mM, [NEt3] = 99 mM

The CV experiment under standard reaction condition shows the enhancement of cathodic current under slower scan rate again because the amine base is present in the solution.

V. Additional Experiments

a. Electric Current On/Off Experiment

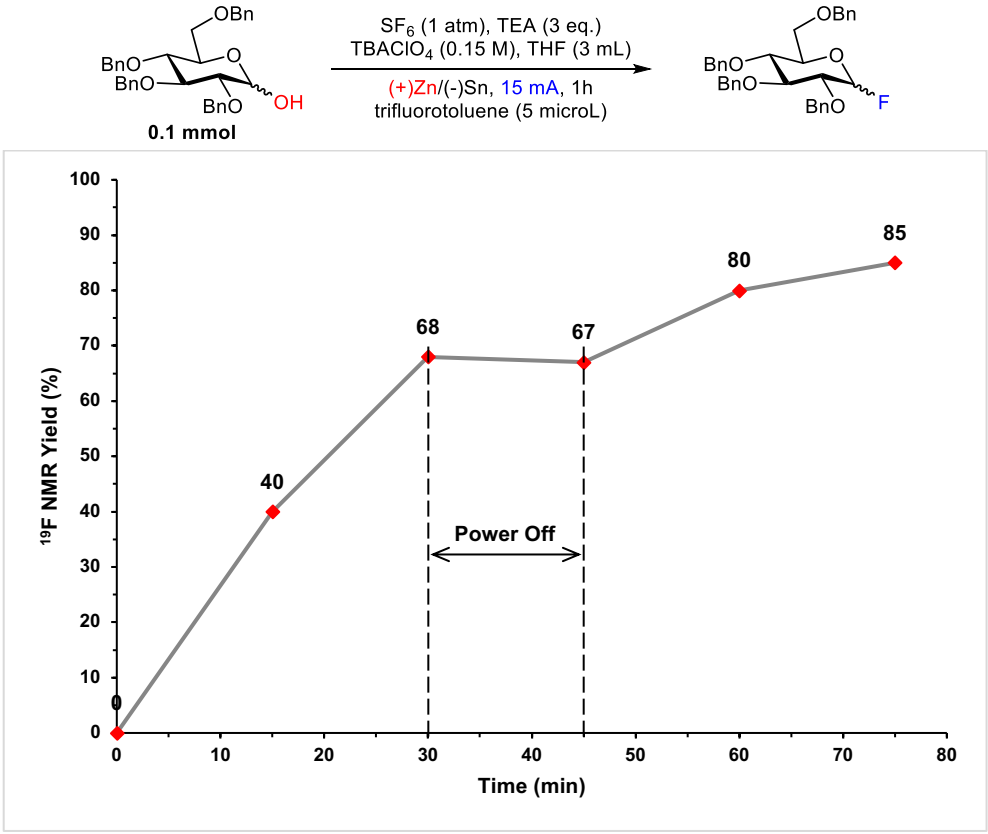


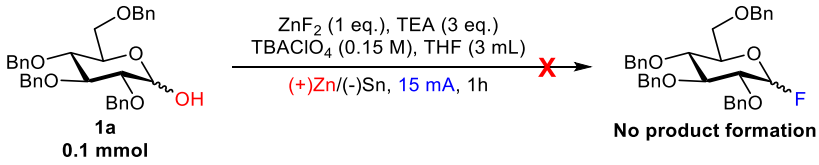
Figure S13. Electric current On/Off experiment

An oven-dried 1 dram vial was charged with 2,3,4,6-tetrakis-*O*-(phenylmethyl)-D-glucopyranoside **1a** (0.1 mmol, 1 equiv.) and tetrabutylammonium perchlorate (0.45 mmol, 0.15 M). The vial containing the mixture was sealed with PTFE/Silicone septum cap and was further dried under high vacuum for 5 minutes. Into the sealed vial, THF (3 mL), triethylamine (0.3 mmol, 3 equiv.), and α,α,α-trifluorotoluene (5 microL) were added, and the vial was stirred until the mixture became homogeneous. The mixture was sparged with a balloon containing SF_6 gas for 30 seconds. After the sparging was done, the valve of the balloon was adjusted to sparge small bubbles and left open until the reaction was stopped. Cathode and anode were connected to DC power supply and the reaction was stirred at high rpm. The reaction progress was monitored by taking an aliquot of sample (0.2 mL) every 15 minutes.

30 minutes after the start of reaction, the electric current was shut off and then a sample was taken out. 15 minutes after, another aliquot of sample was taken out, and then the electric current was applied again.

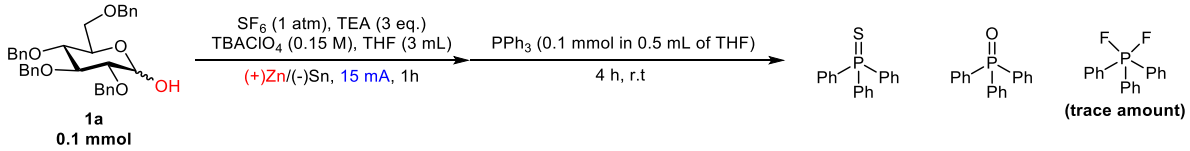
The result is showing that the reaction proceeds only when the electric current is applied, which means that the active fluorinating agent formed *in situ* is consumed right away and does not accumulate.

b. Control Experiment with ZnF_2



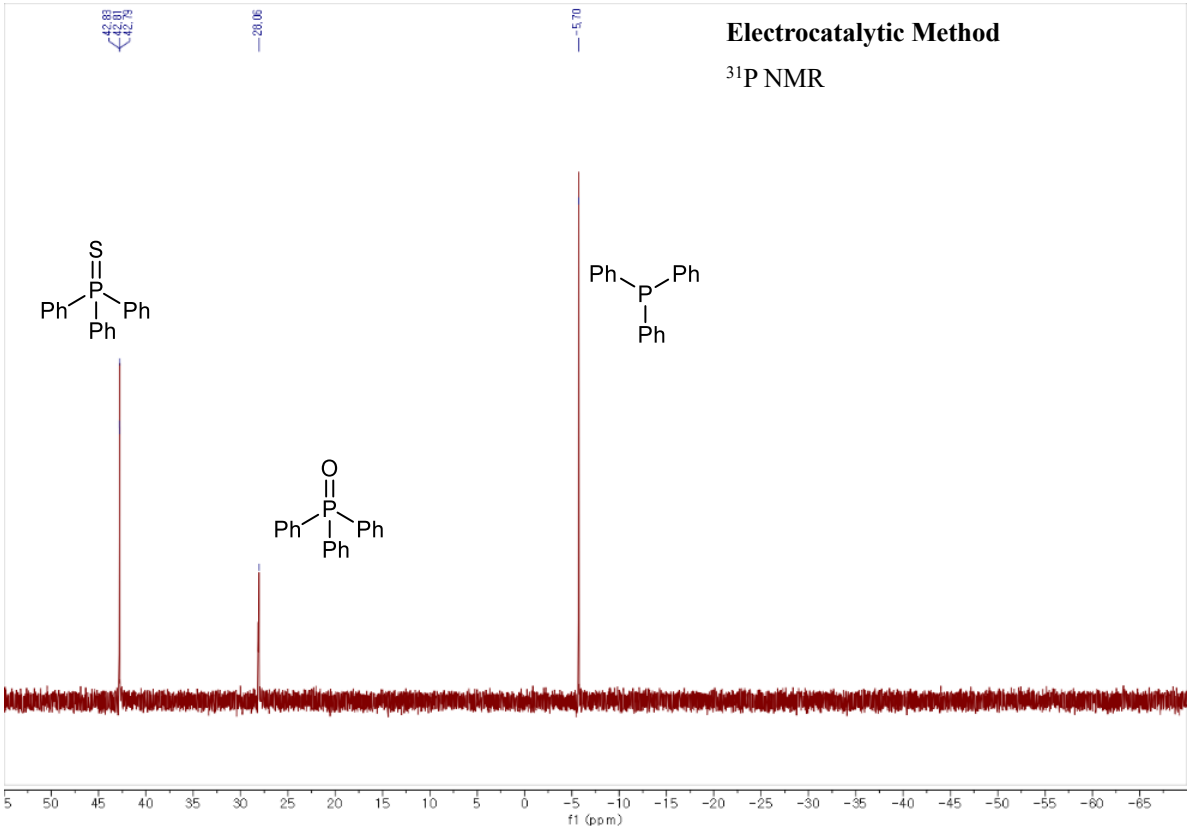
An oven-dried 1 dram vial was charged with 2,3,4,6-tetrakis-*O*-(phenylmethyl)-D-glucopyranoside **1a** (0.1 mmol, 1 equiv.), zinc(II) fluoride (0.1 mmol, 1 equiv.), and tetrabutylammonium perchlorate (0.45 mmol, 0.15 M). The vial containing the mixture was sealed with PTFE/Silicone septum cap and was further dried under high vacuum for 5 minutes. Into the sealed vial, THF (3 mL) and triethylamine (0.3 mmol, 3 equiv.) were added. The mixture was stirred until everything, except ZnF_2, became homogeneous. Sn cathode and Zn anode were connected to DC power supply and the reaction was stirred at high rpm for 1 hour. The color of the reaction turned from clear to black, and the electric current dropped from 15 mA to 3 mA after the voltage reached the limit of DC power supply (31 V). ^{1}H and ^{19}F NMR of crude and worked-up reaction did not show any formation of fluorinated product.

c. PPh_3 Quenching Experiment



2,3,4,6-tetrakis-*O*-(phenylmethyl)-D-glucopyranoside **1a** was subjected to a standard reaction. After the electric current was shut off, an aliquot of crude reaction was taken out, and then PPh_3 solution (0.1 mmol in 0.5 mL of THF) was injected into the reaction vial. The mixture was then stirred for 4 hours, and then the samples were taken out. All samples were subjected to ^{19}F and ^{31}P NMR experiments and were compared with each other and with the NMR spectra from our photocatalytic reaction.[21] Careful examination of ^{19}F and ^{31}P NMR spectrum of electrocatalytic reaction showed the formation of $S{=}PPh_3$ and $O{=}PPh_3$ just like photocatalytic reaction. However, F_2PPh_3 is formed in trace amount unlike photocatalytic reaction, which suggests that elemental fluorine or fluoride anion is scavenged by triethylamine or zinc cations.

[21]Kim, S.; Khomutnyk, Y.; Bannykh, A.; Nagorny, P. *Org. Lett*. **2021**, 23, 1, 190-194



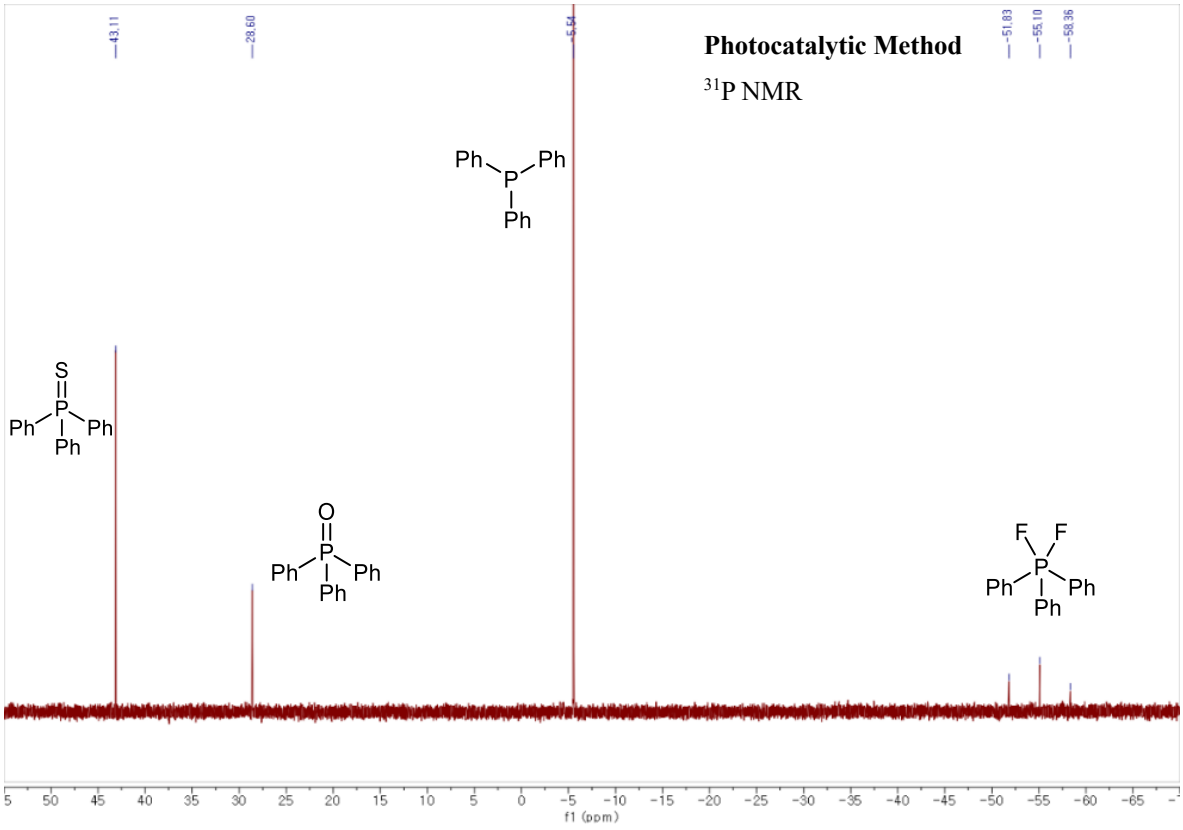


Figure S14. ^{31}P NMR spectra of PPh_3 quenching experiment.

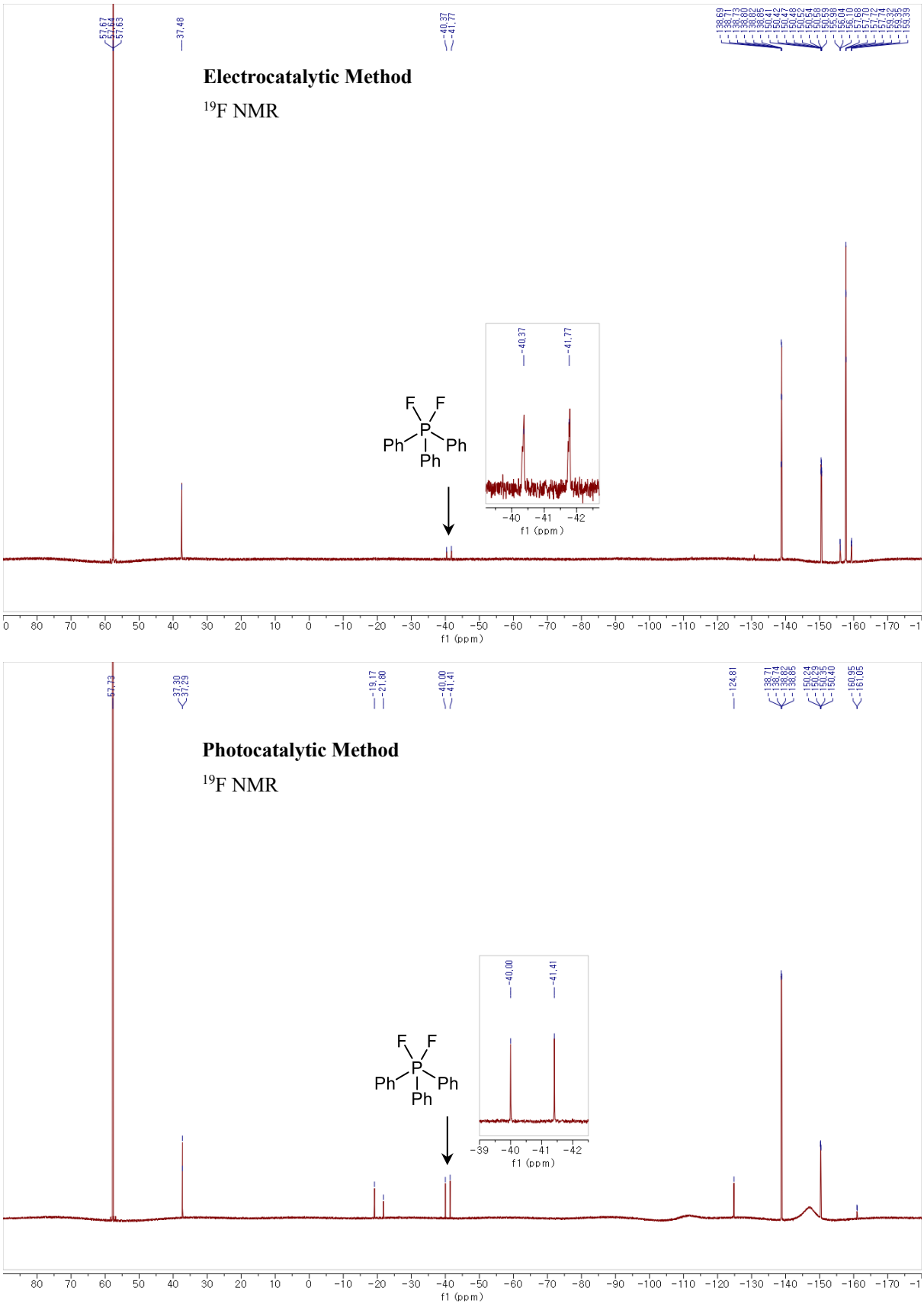
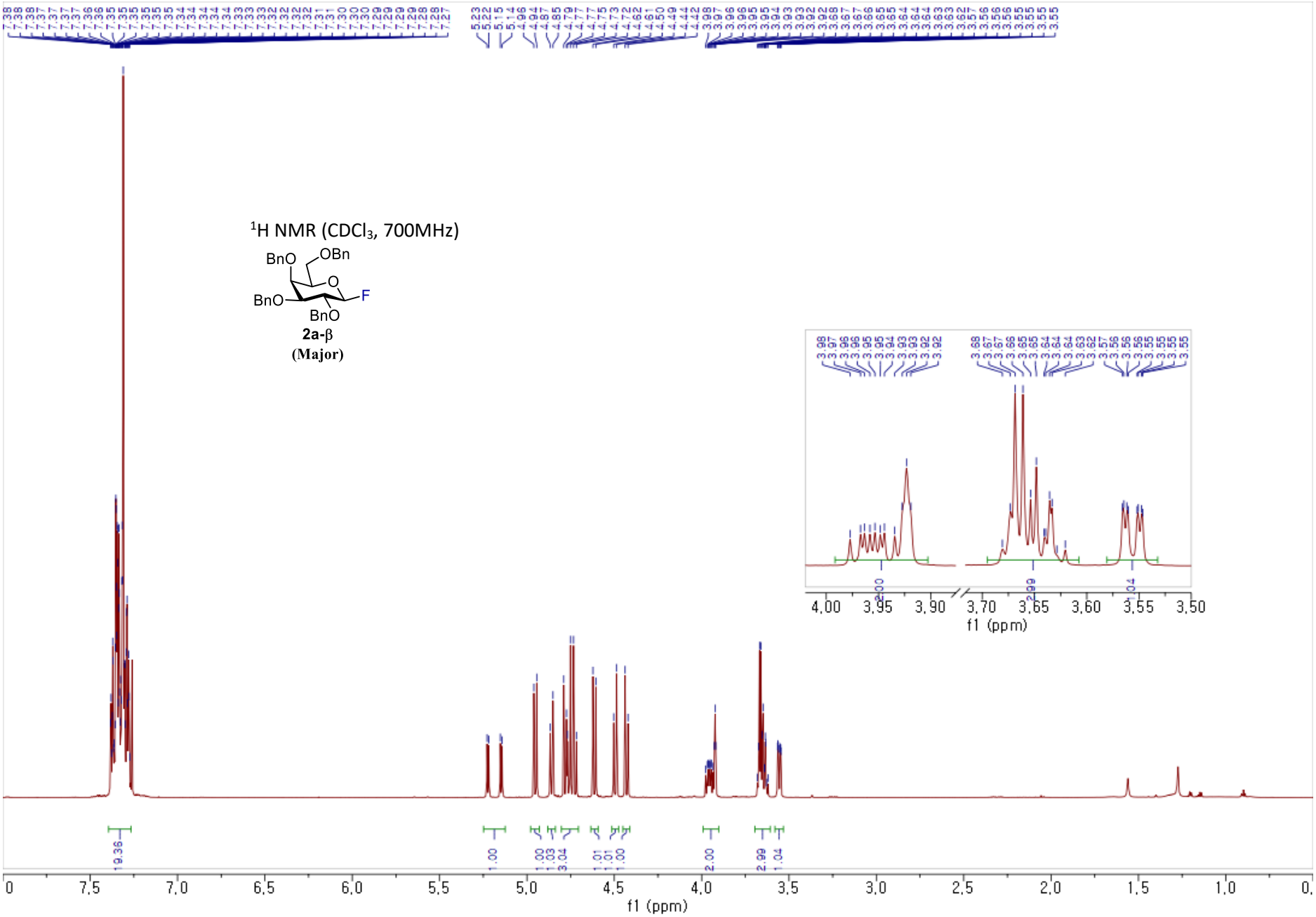
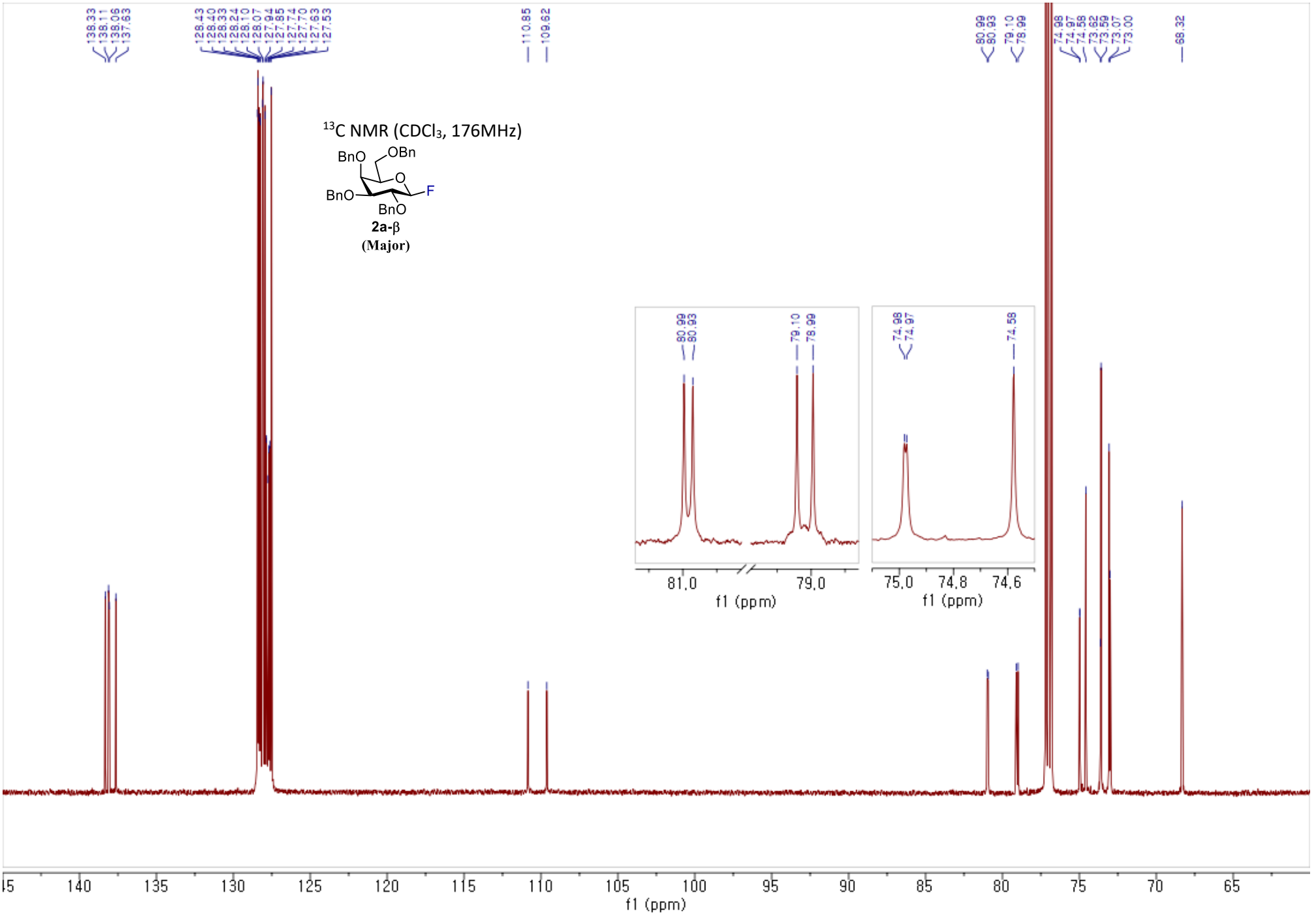
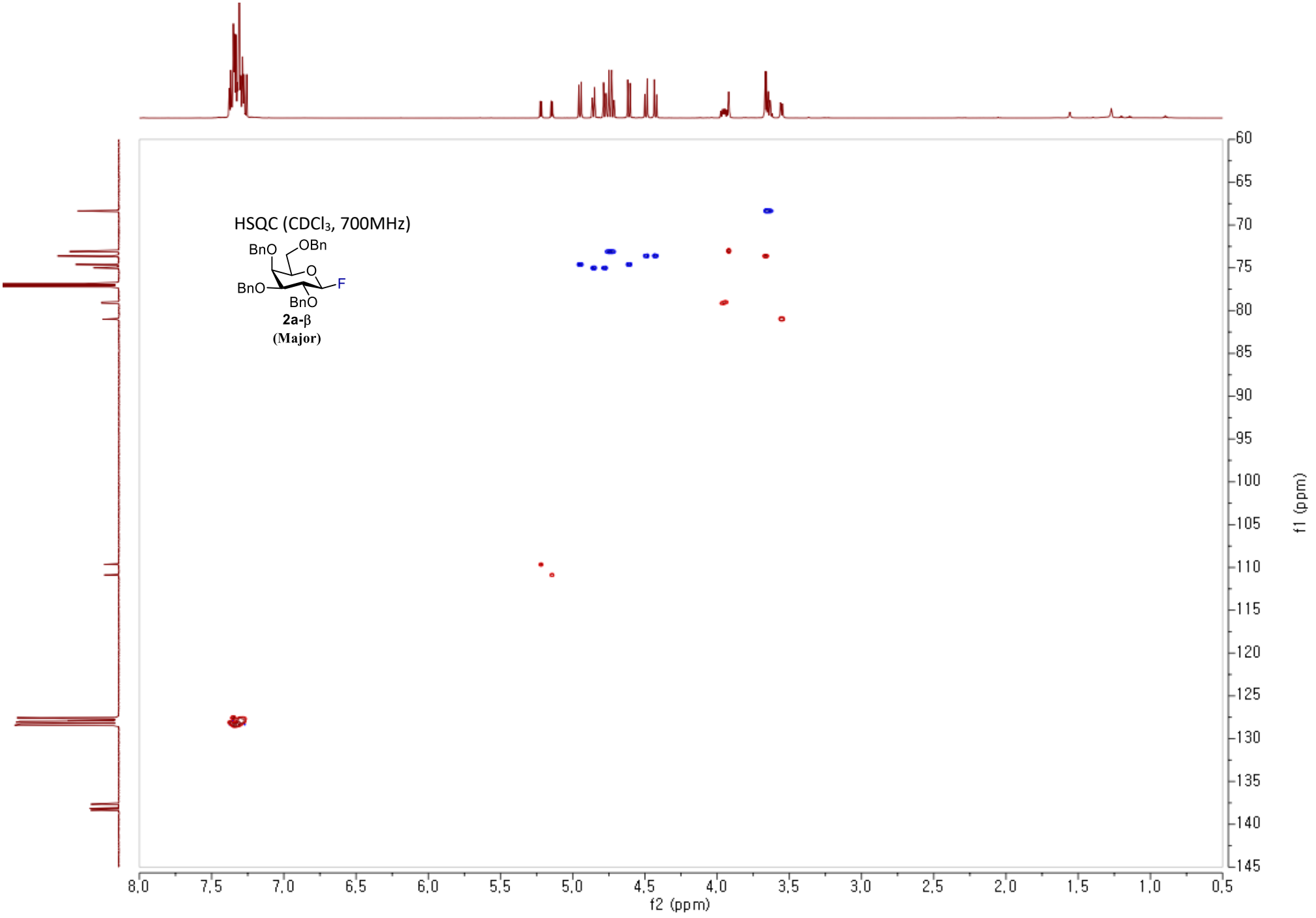


Figure S15. ^{19}F NMR spectra of PPh_3 quenching experiment.

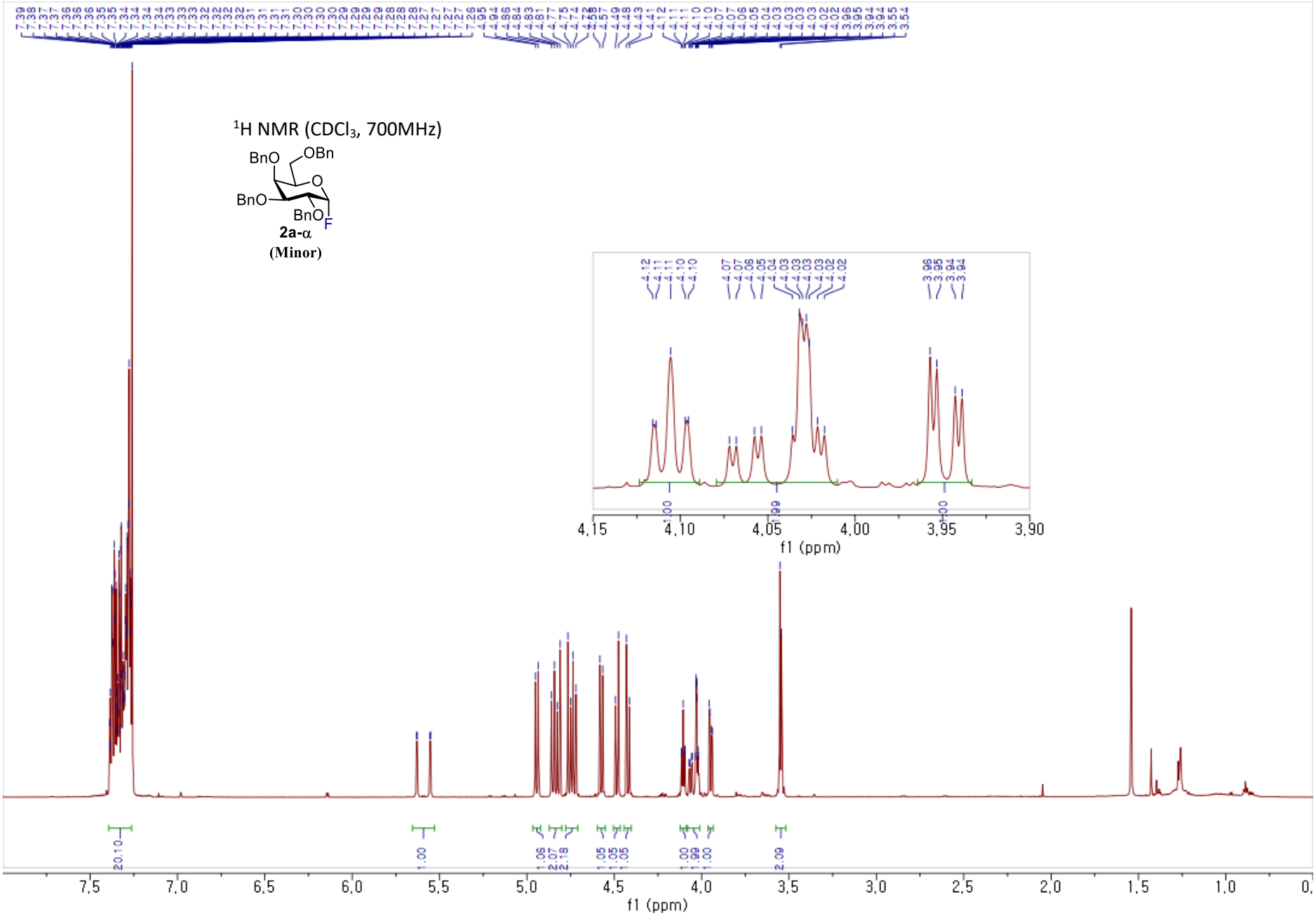
2,3,4,6-Tetrakis-*O*-(phenylmethyl)-β-D-galactopyranosyl fluoride (2a-β, Major diastereomer)

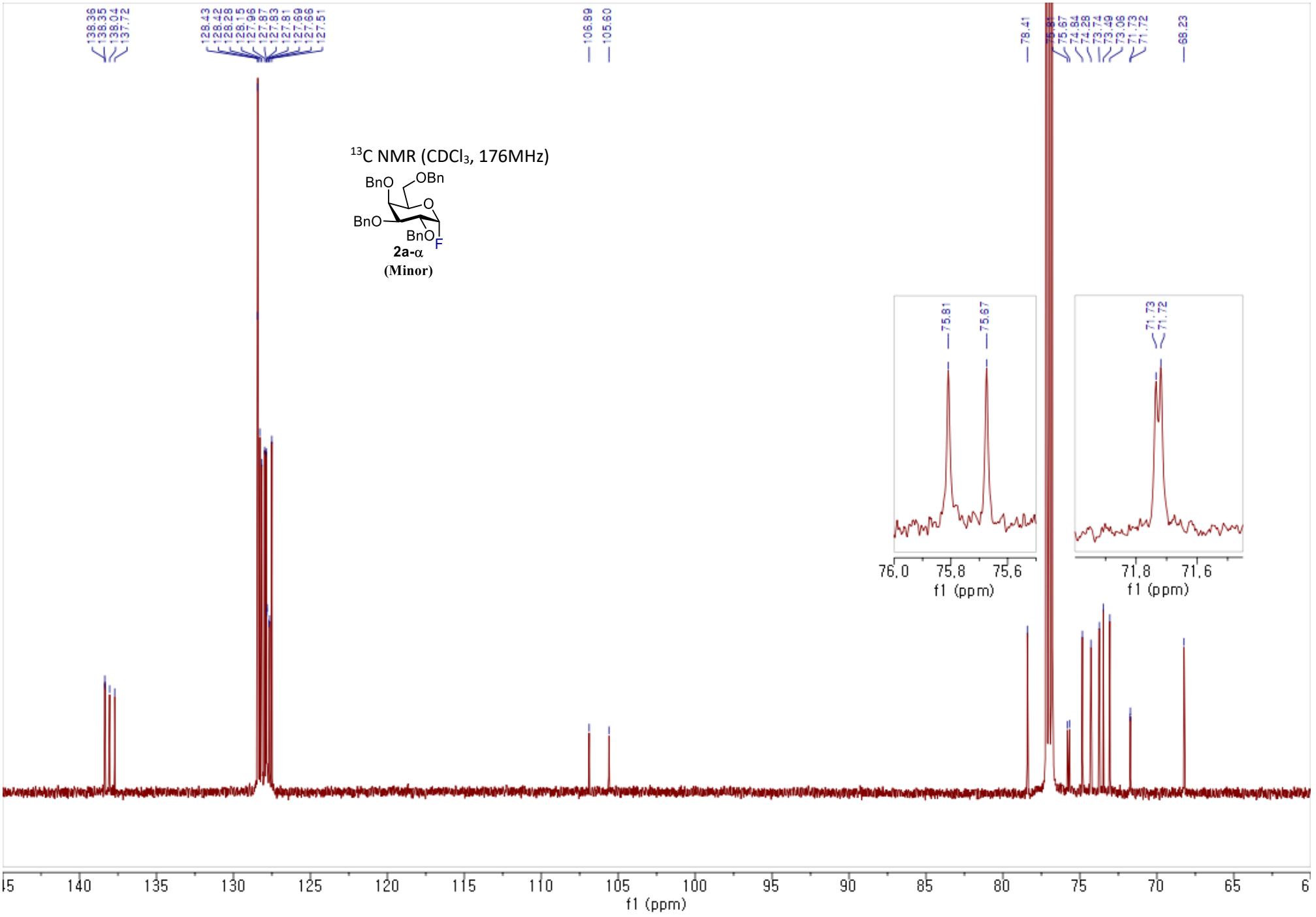


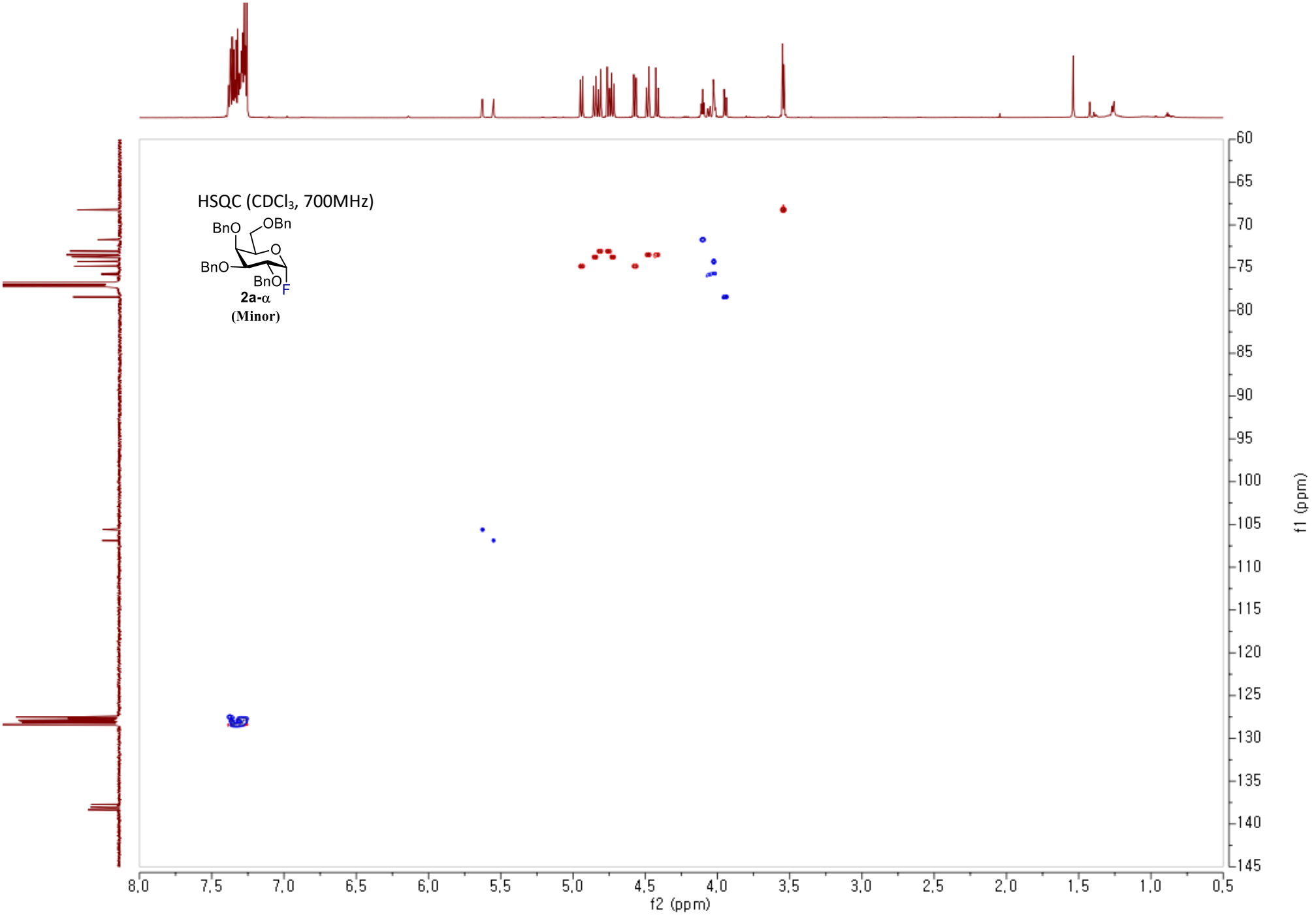

^{13}C NMR ($CDCl_3$, 176MHz)
BnO
OBn
O
F
BnO
BnO
2a-β
(Major)
f1 (ppm)
f1 (ppm)
f1 (ppm)


HSQC ($CDCl_3$, 700MHz)
BnO
OBn
O
F
BnO
BnO
2a-β
(Major)
f2 (ppm)
f1 (ppm)

2,3,4,6-Tetrakis-*O*-(phenylmethyl)-α-D-galactopyranosyl fluoride (2a-α, Minor diastereomer)

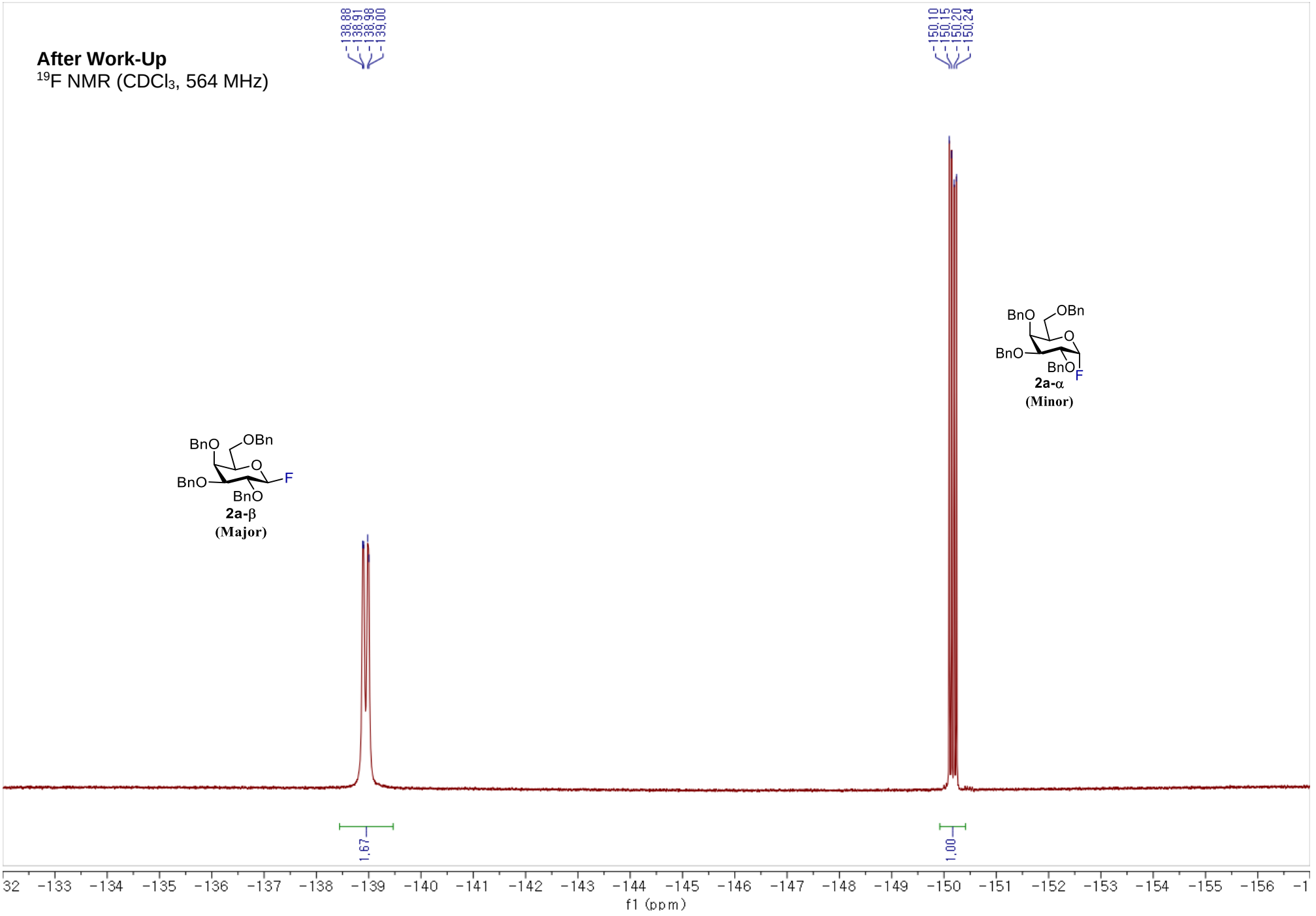



^{13}C NMR ($CDCl_3$, 176MHz)
BnO
OBn
O
BnO
BnO
F
2a-α
(Minor)
138.36
138.35
138.04
137.72
128.43
128.42
128.28
128.15
127.96
127.87
127.83
127.81
127.69
127.66
127.51
106.89
105.60
78.41
75.81
75.67
74.84
74.28
73.74
73.49
73.06
71.73
71.72
68.23
75.81
75.67
76.0
75.8
75.6
f1 (ppm)
71.73
71.72
71.8
71.6
f1 (ppm)
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
f1 (ppm)


HSQC (CDCl3, 700MHz)
BnO
OBn
O
BnO
BnO
F
2a-α
(Minor)
f2 (ppm)
f1 (ppm)

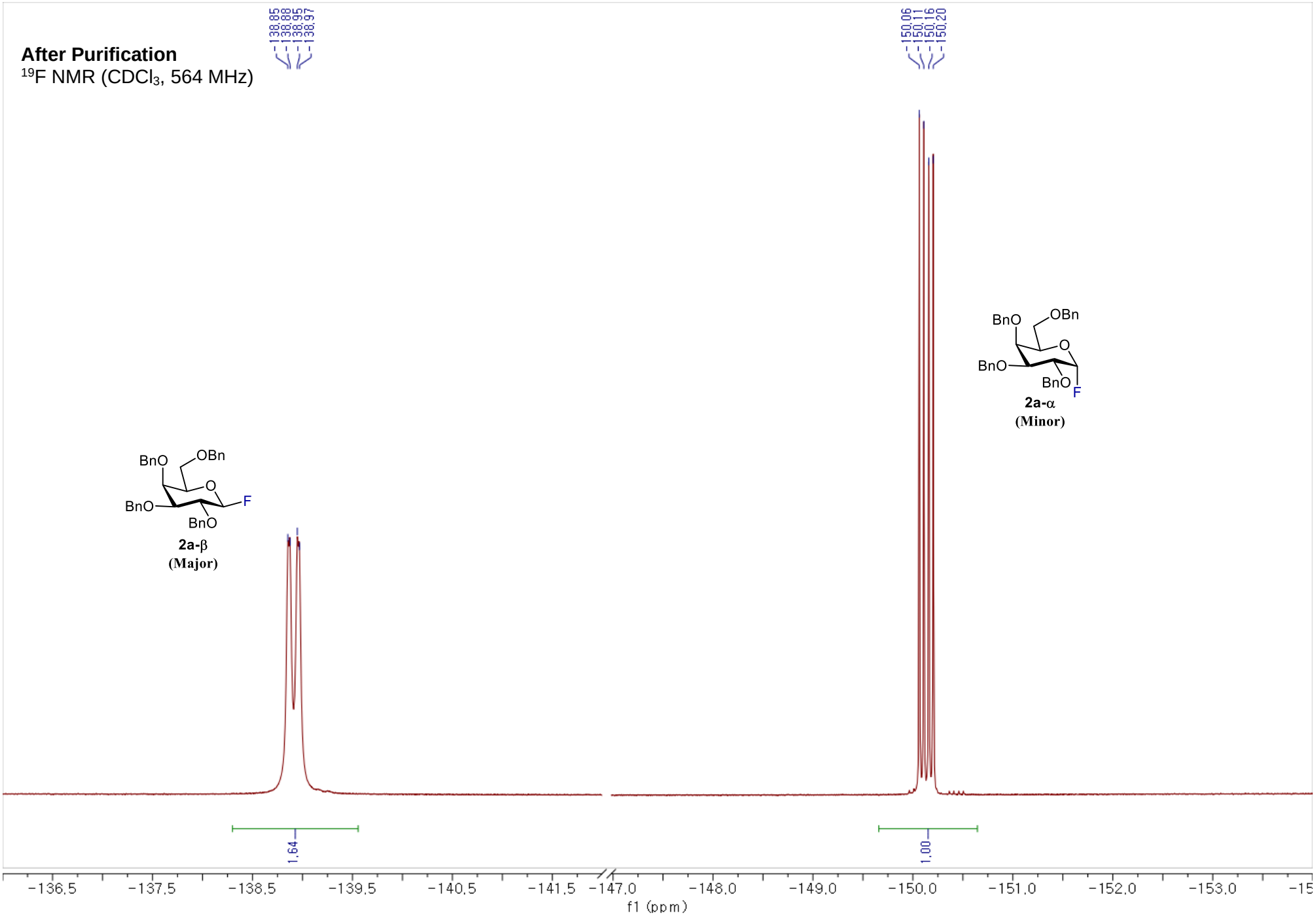
After Work-Up

^{19}F NMR ($CDCl_3$, 564 MHz)

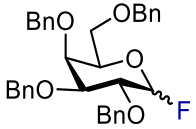


After Purification

^{19}F NMR ($CDCl_3$, 564 MHz)



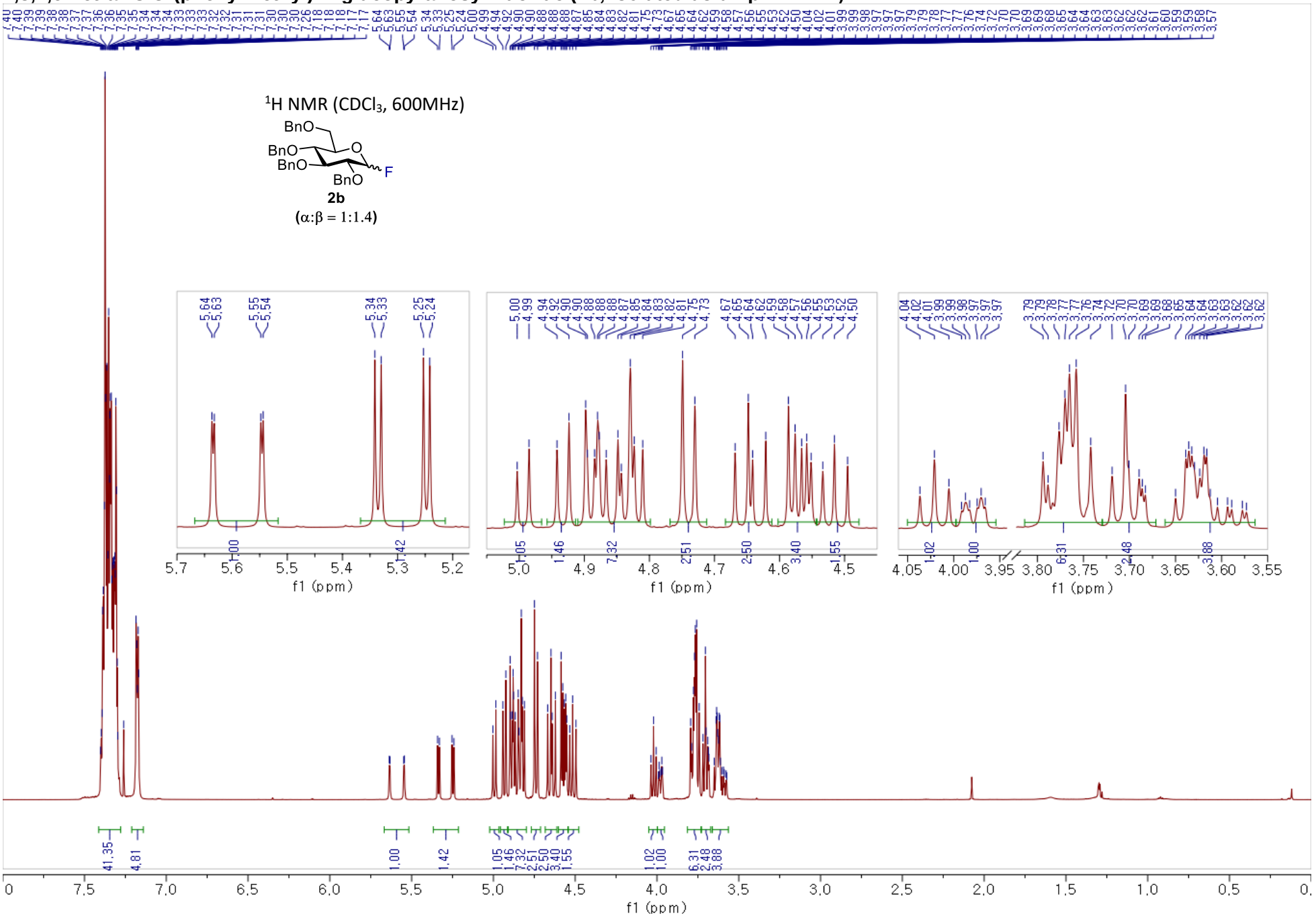
^{1}H NMR ($CDCl_3$, 600MHz)



2a

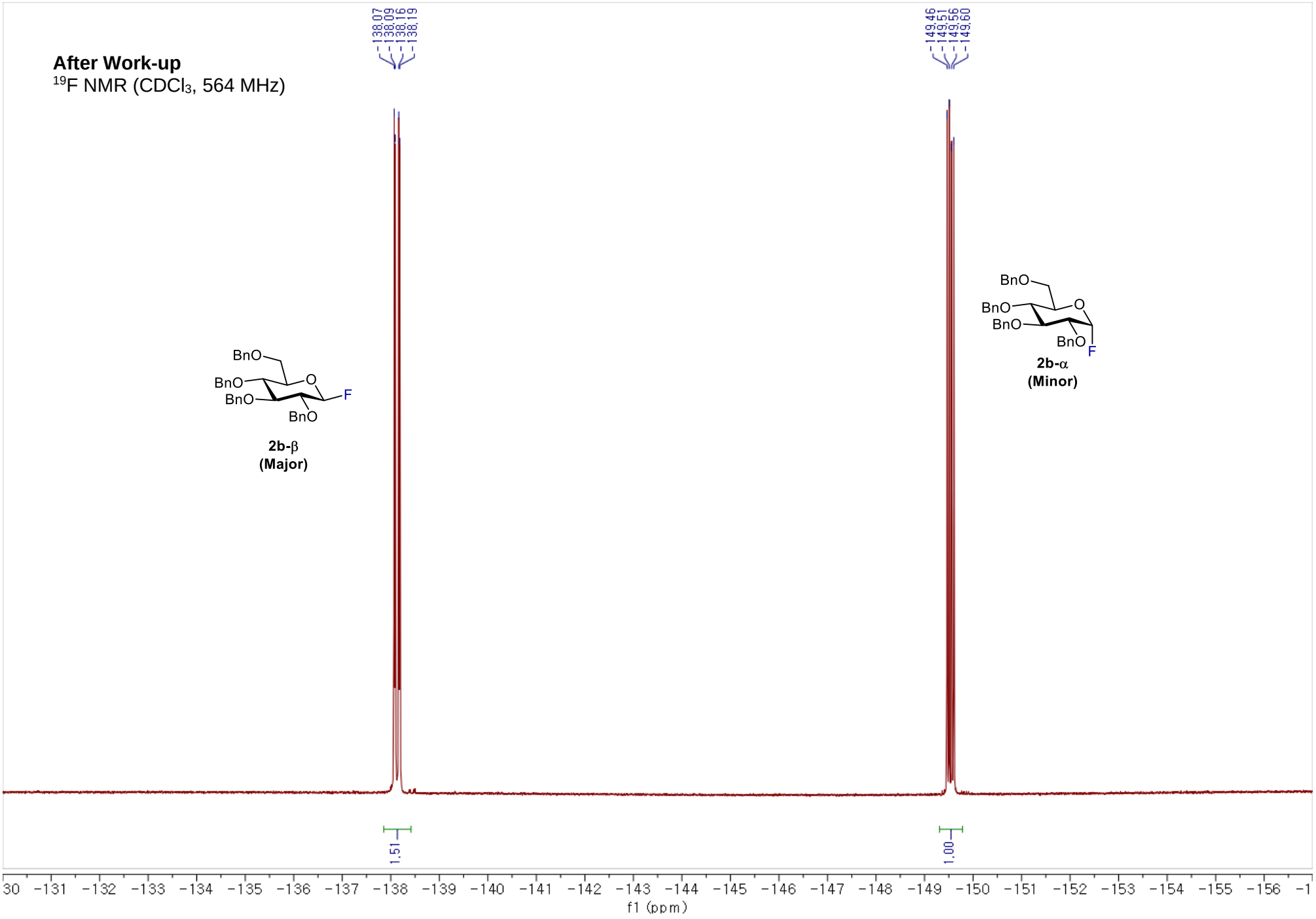
(α,β-mix)

2,3,4,6-Tetrakis-*O*-(phenylmethyl)-D-glucopyranosyl fluoride (2b, Isolated as α : β = 1 : 1.4)



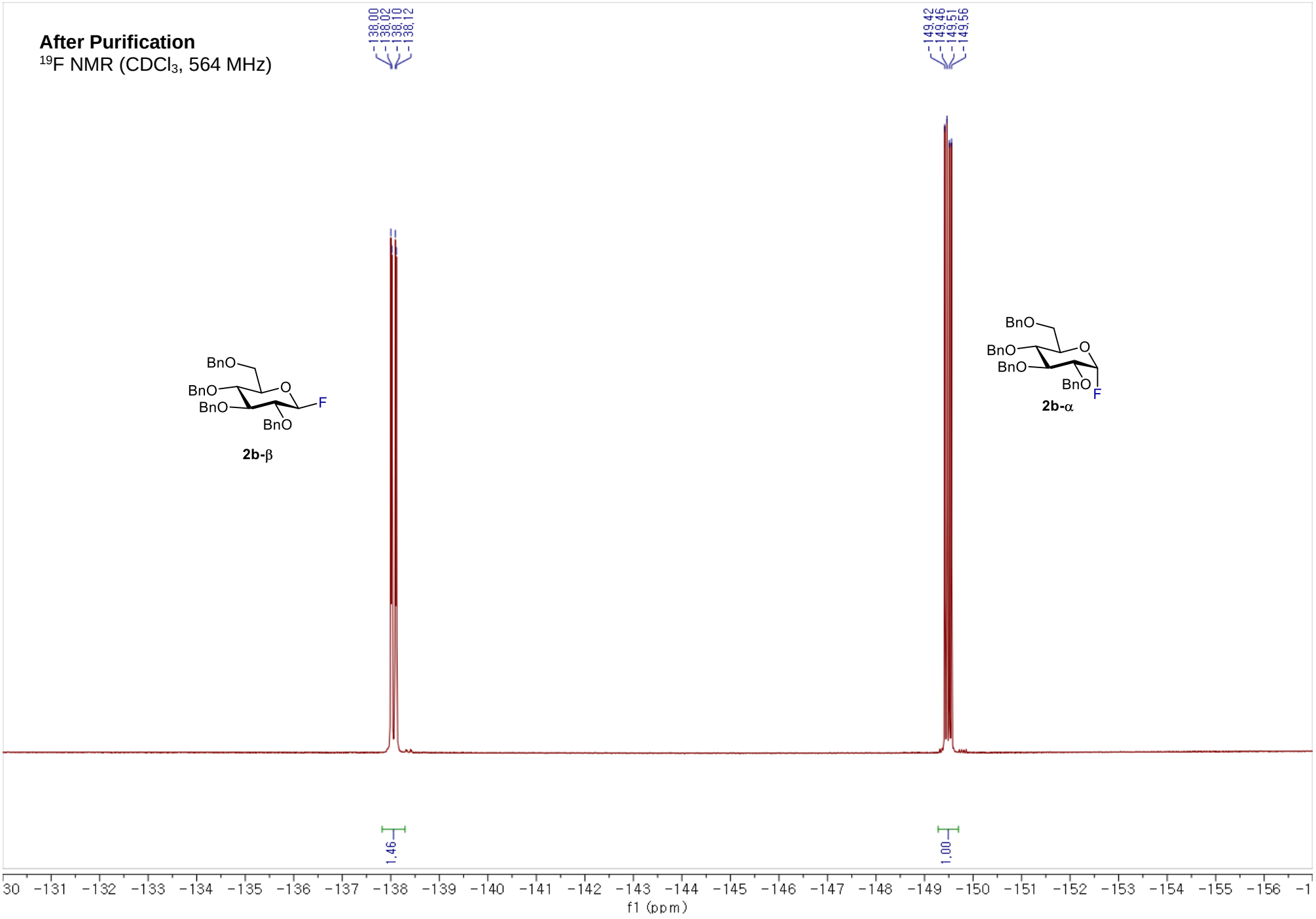
After Work-up

^{19}F NMR ($CDCl_3$, 564 MHz)

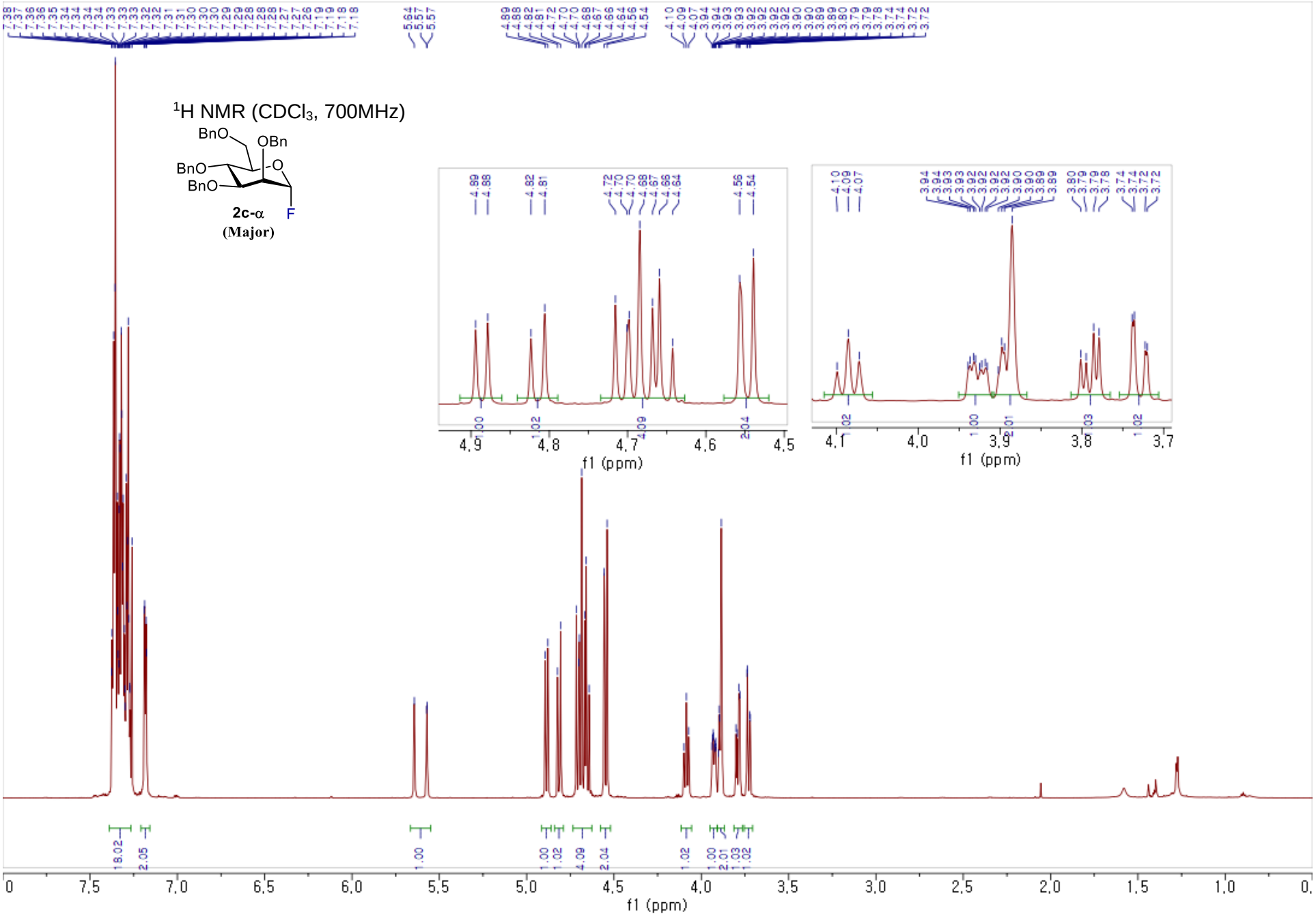


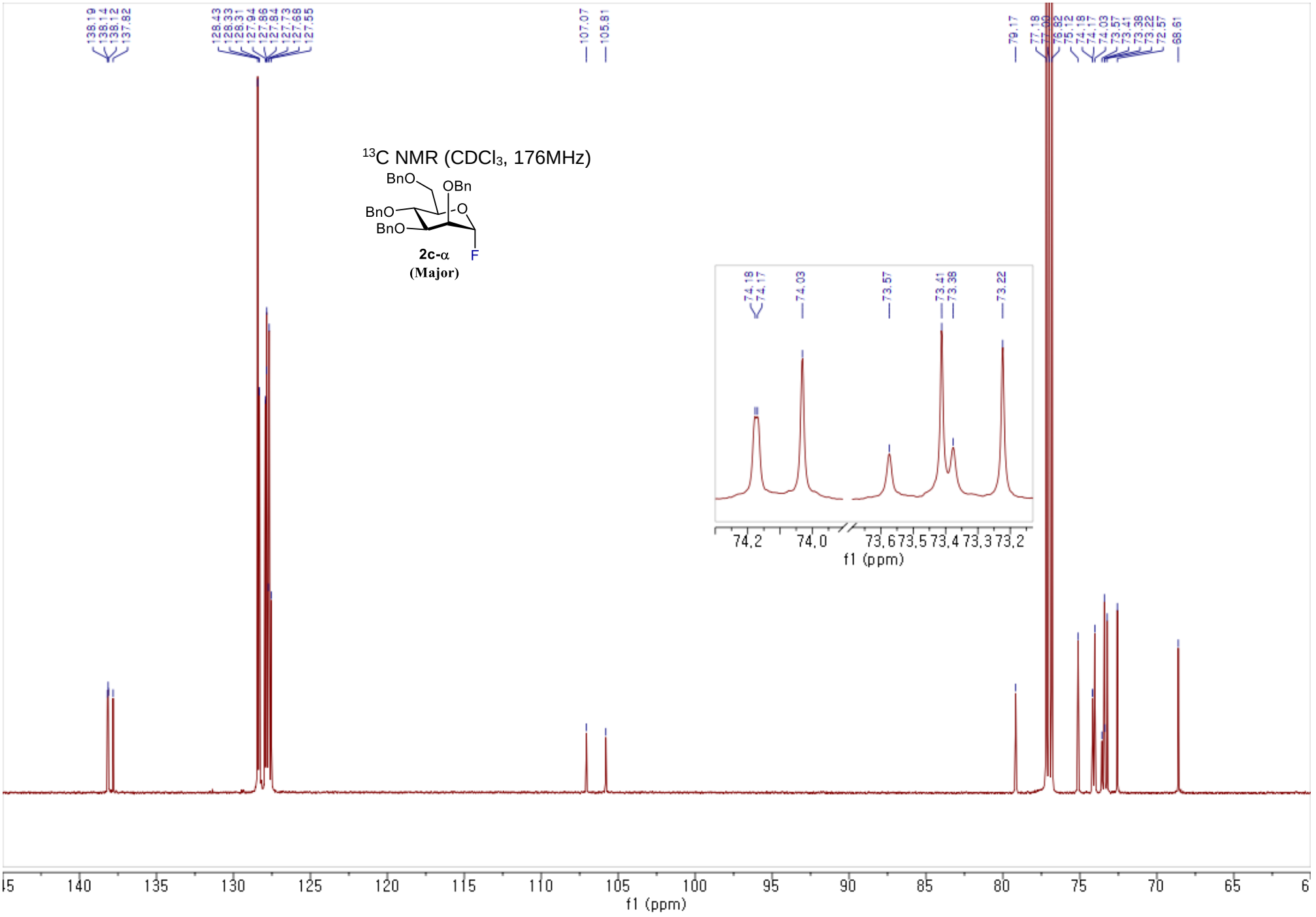
After Purification

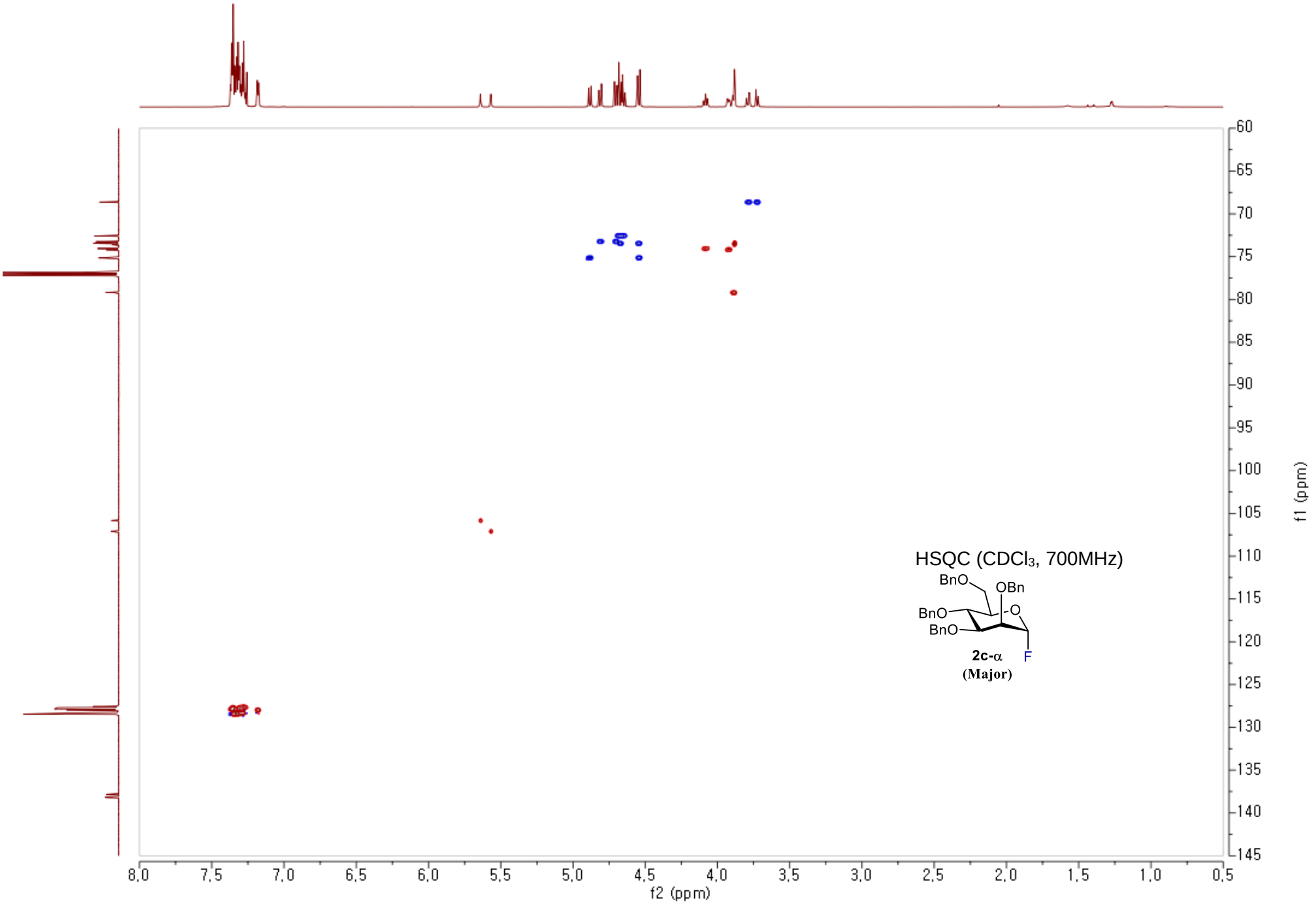
^{19}F NMR ($CDCl_3$, 564 MHz)



4,6-Tetrakis-*O*-(phenylmethyl)-α-D-Mannopyranosyl fluoride (2c-α, Major diastereomer)

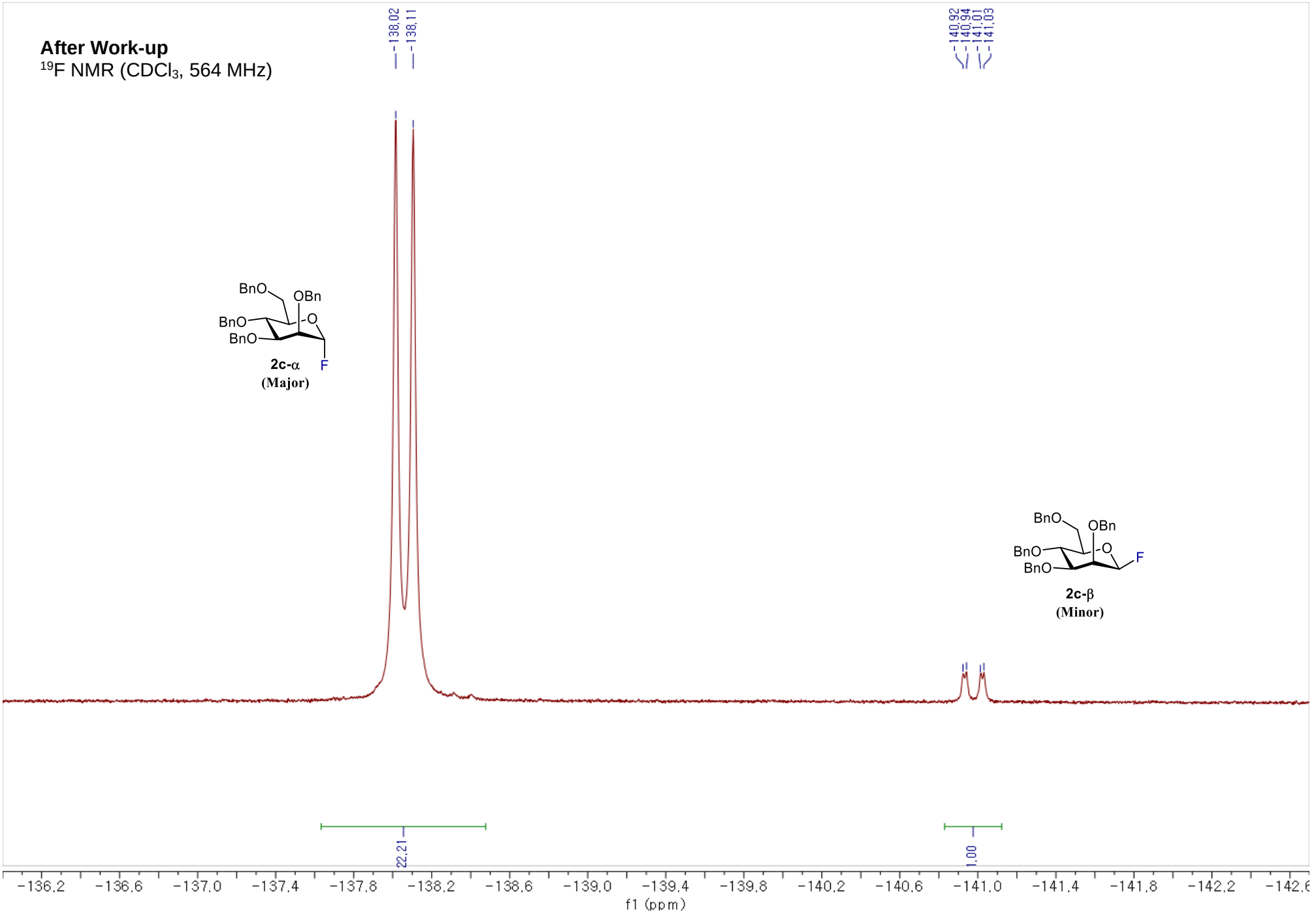



^{13}C NMR ($CDCl_3$, 176MHz)
BnO
OBn
BnO
O
BnO
F
2c-α
(Major)
138.19
138.14
138.12
137.82
128.43
128.33
128.31
127.94
127.86
127.84
127.73
127.68
127.55
107.07
105.81
79.17
77.18
77.00
76.82
75.12
74.18
74.17
74.03
73.57
73.41
73.38
73.22
72.57
68.61
74.18
74.17
74.03
73.57
73.41
73.38
73.22
74.2
74.0
73.6
73.5
73.4
73.3
73.2
f1 (ppm)
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
f1 (ppm)


HSQC (CDCl3, 700MHz)
BnO
OBn
BnO
O
BnO
F
2c-α
(Major)
f2 (ppm)
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
60
65
70
75
80
85
90
95
100
105
110
115
120
125
130
135
140
145

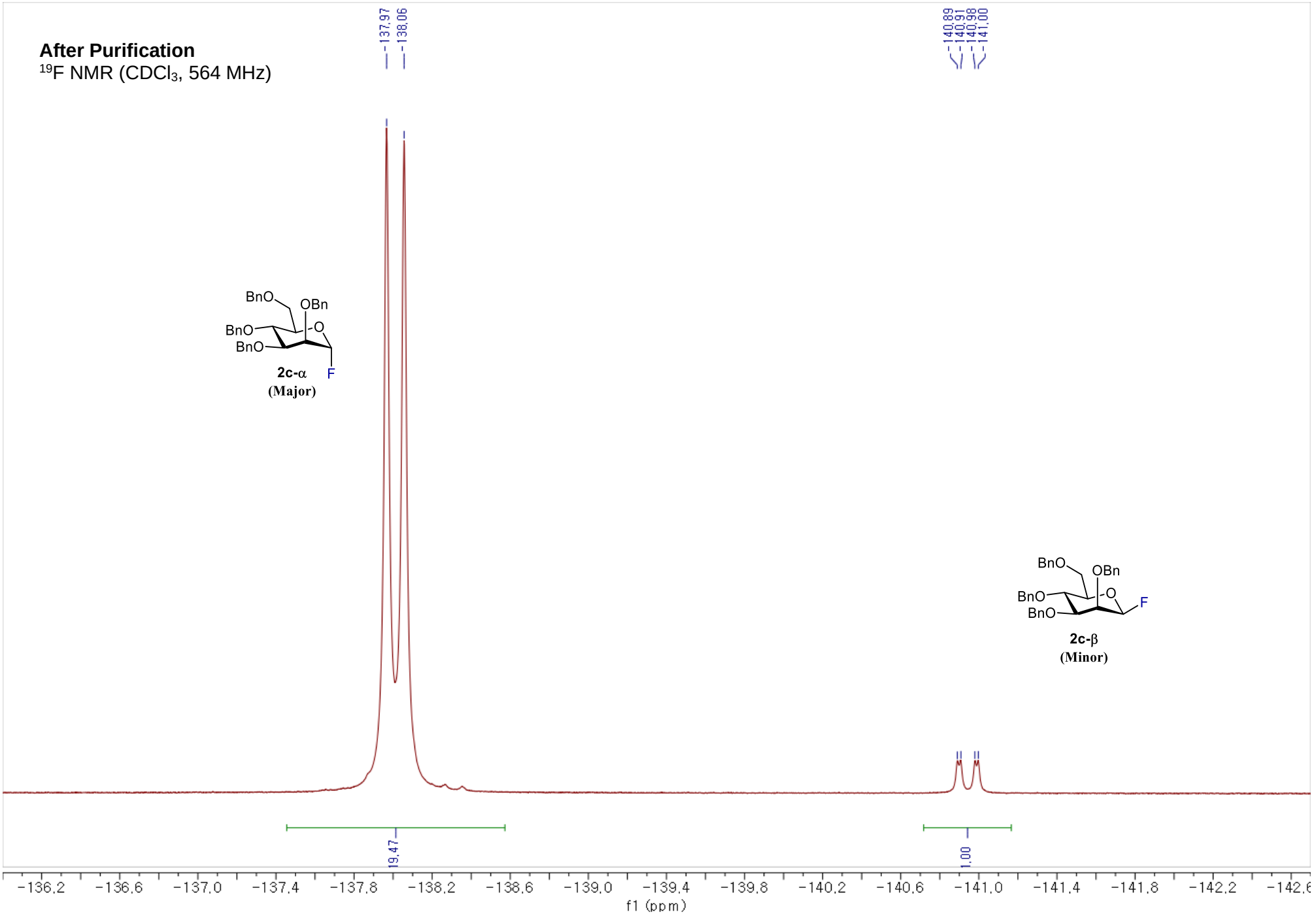
After Work-up

^{19}F NMR ($CDCl_3$, 564 MHz)

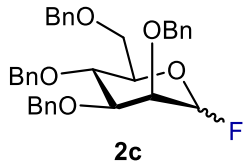


After Purification

^{19}F NMR ($CDCl_3$, 564 MHz)



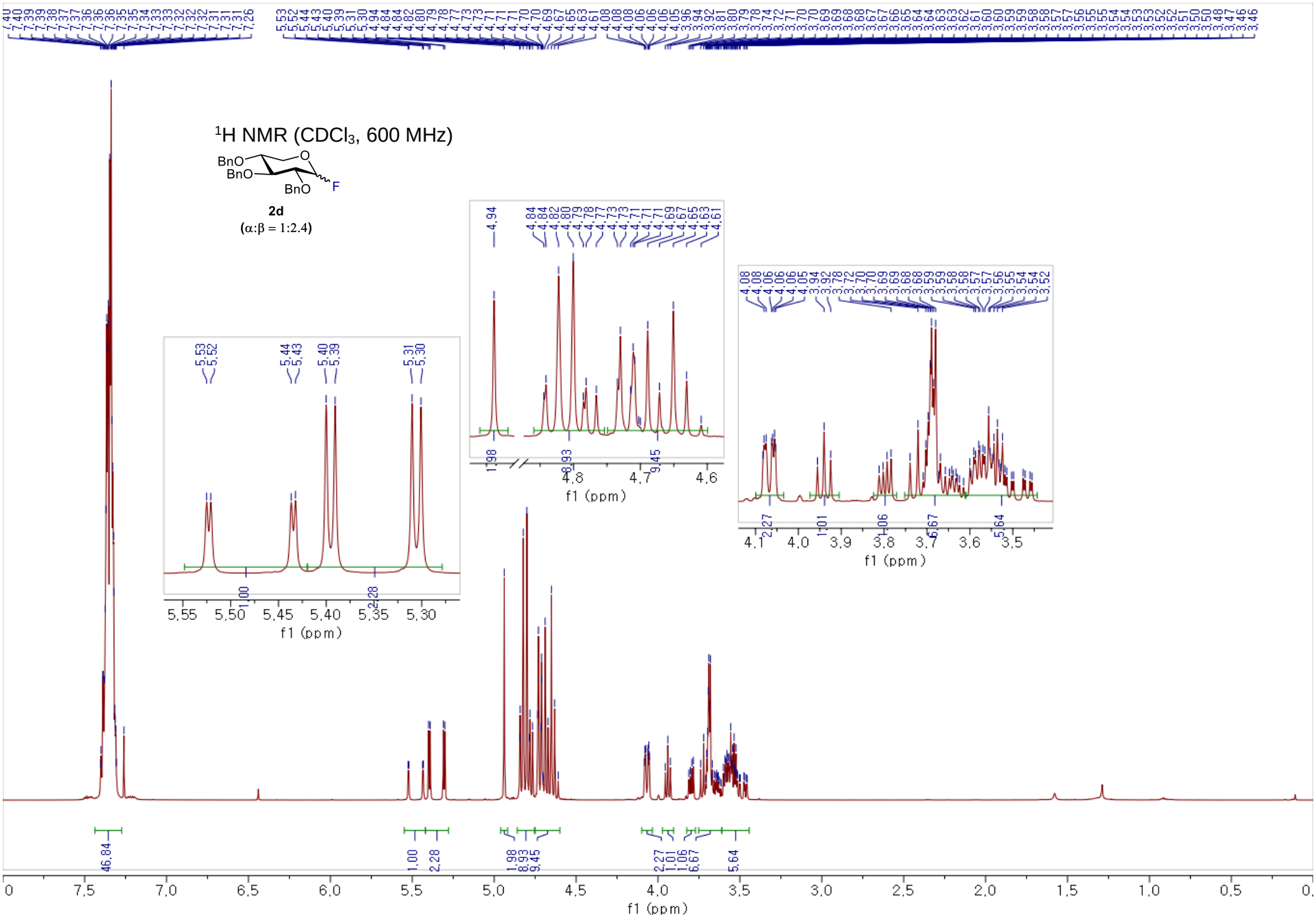
^{1}H NMR ($CDCl_3$, 600MHz)



2c

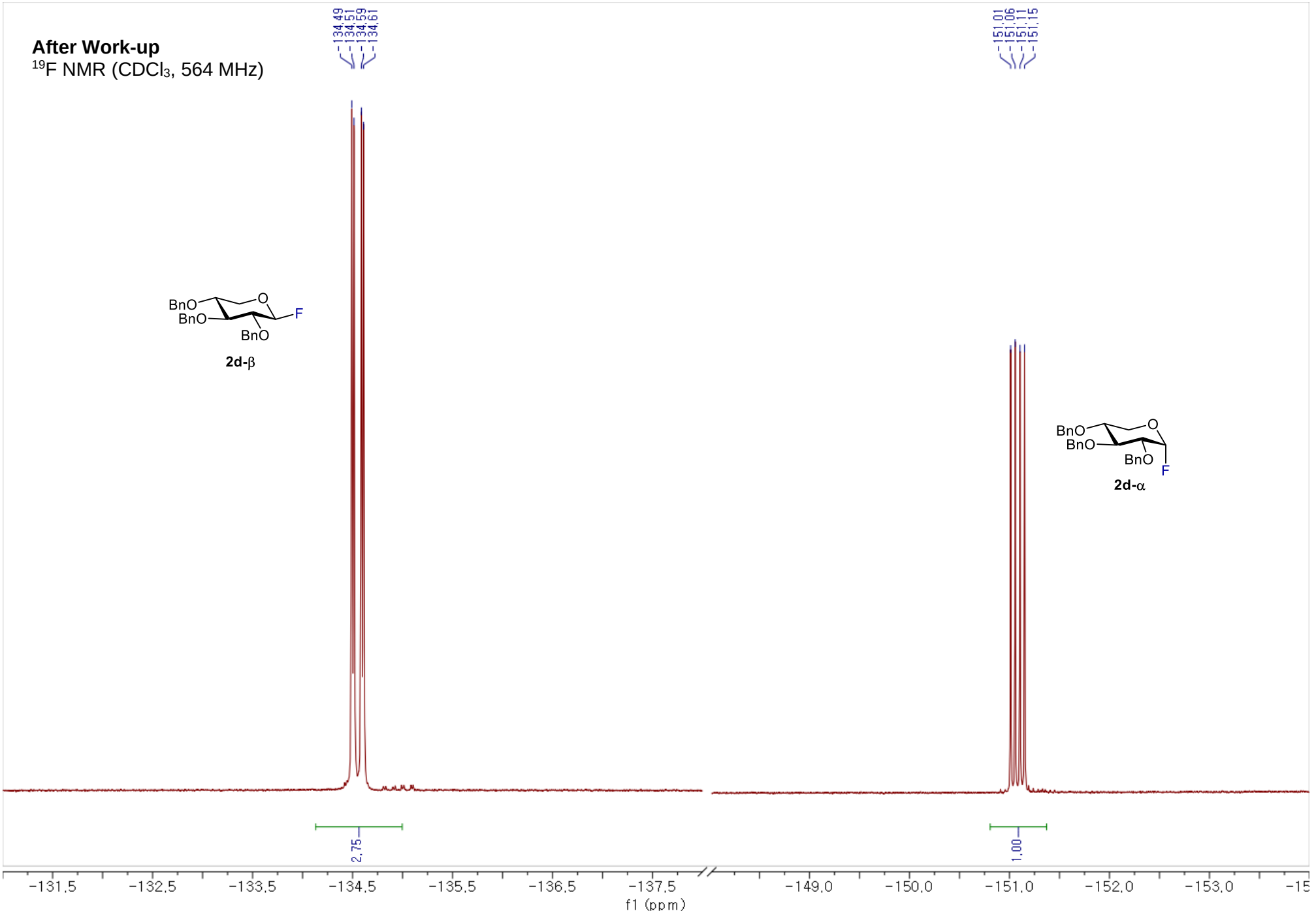
(α,β-mix)

2,3,4-tris-O-(phenylmethyl)-D-xylopyranosyl fluoride (2d, Isolated as α : β = 1 : 2.4 mixture)



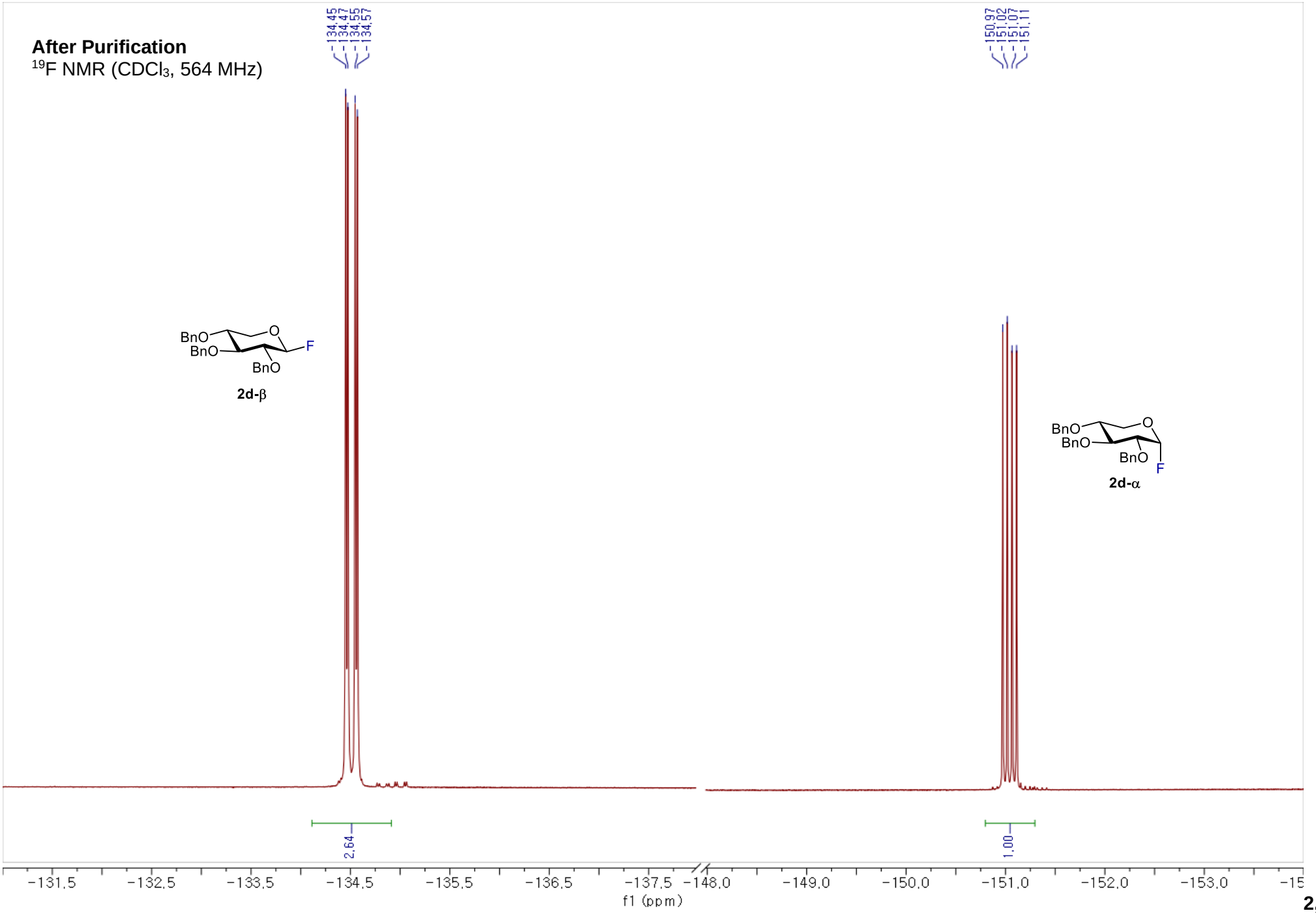
After Work-up

^{19}F NMR ($CDCl_3$, 564 MHz)



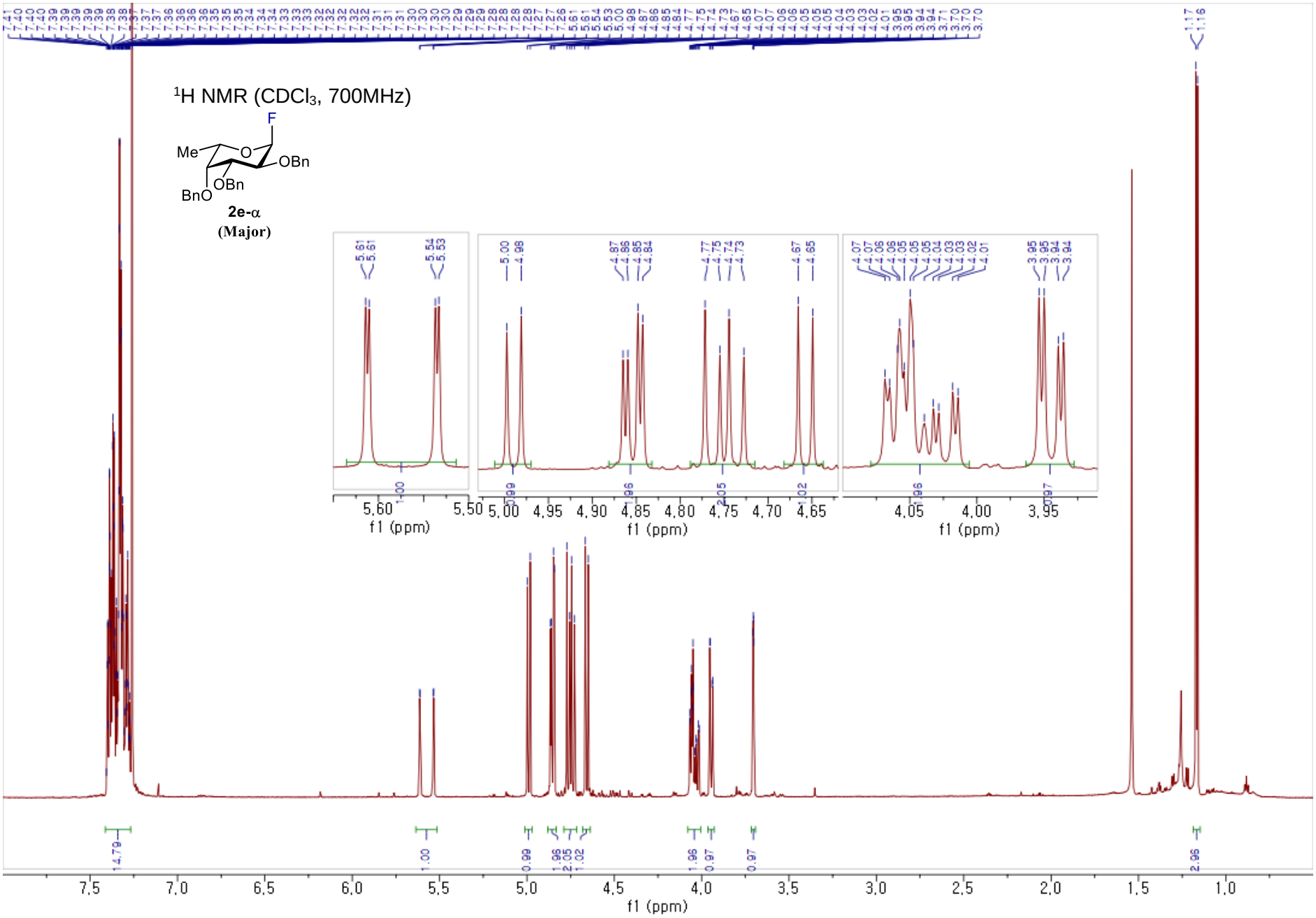
After Purification

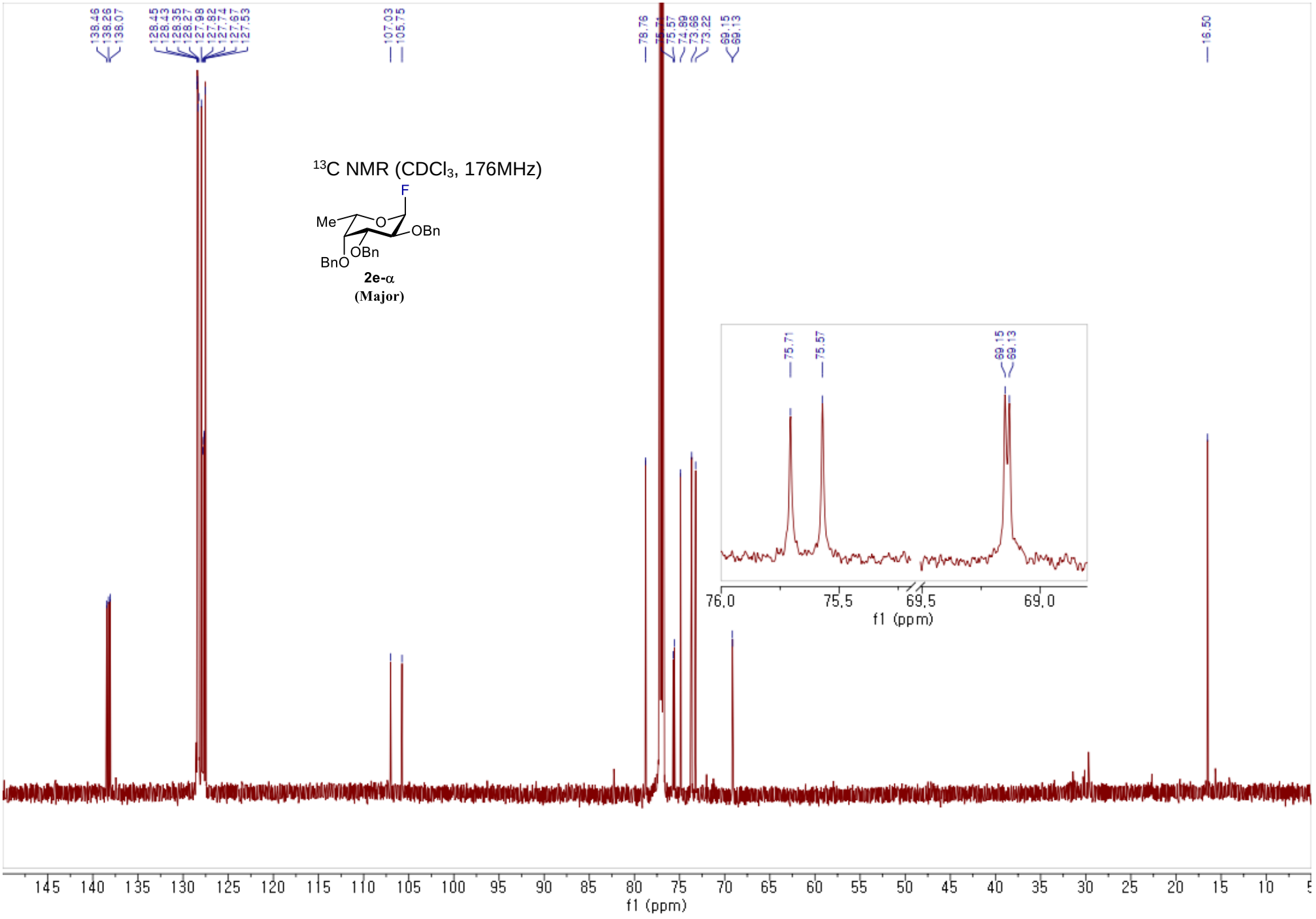
^{19}F NMR ($CDCl_3$, 564 MHz)

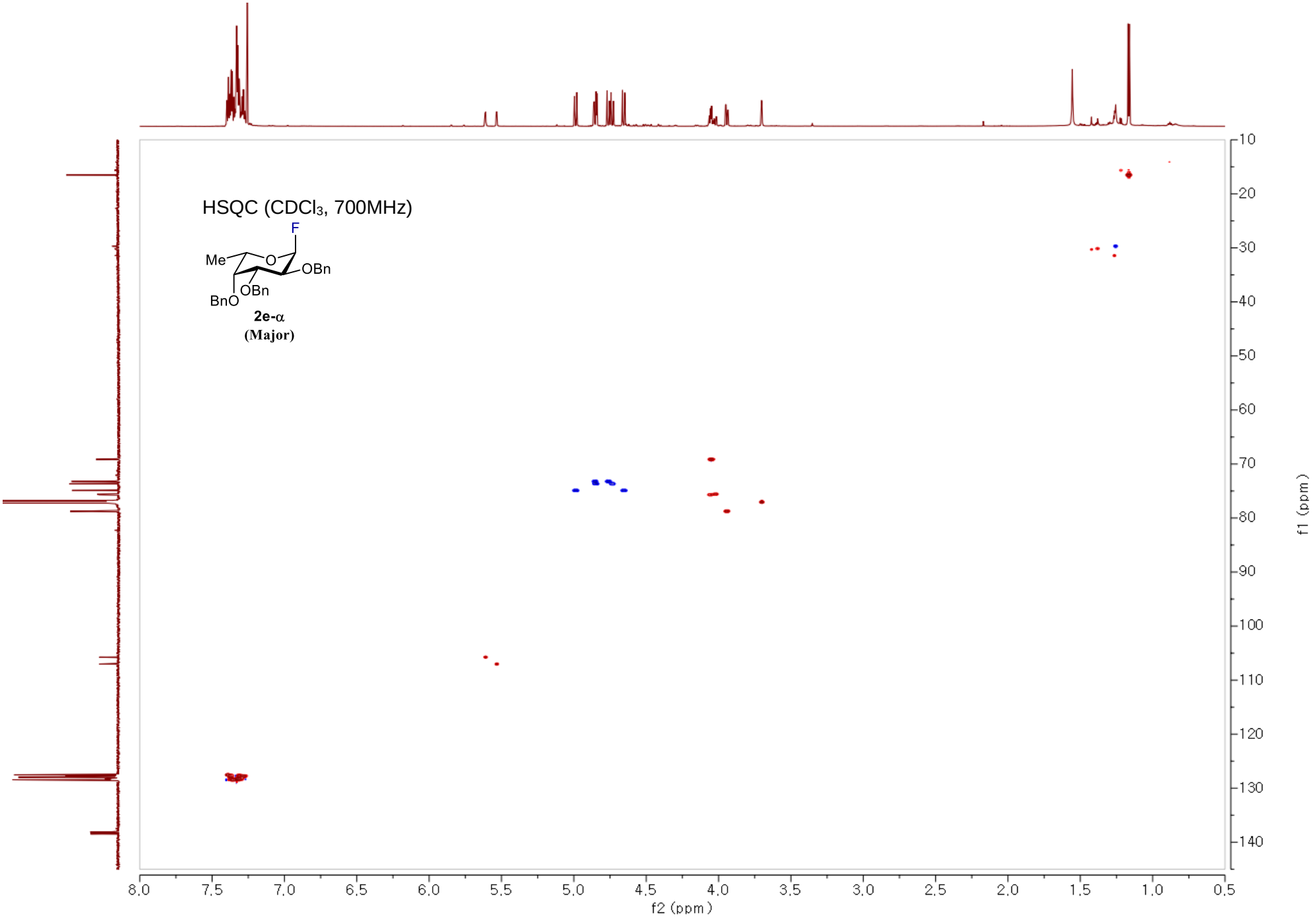


2,3,

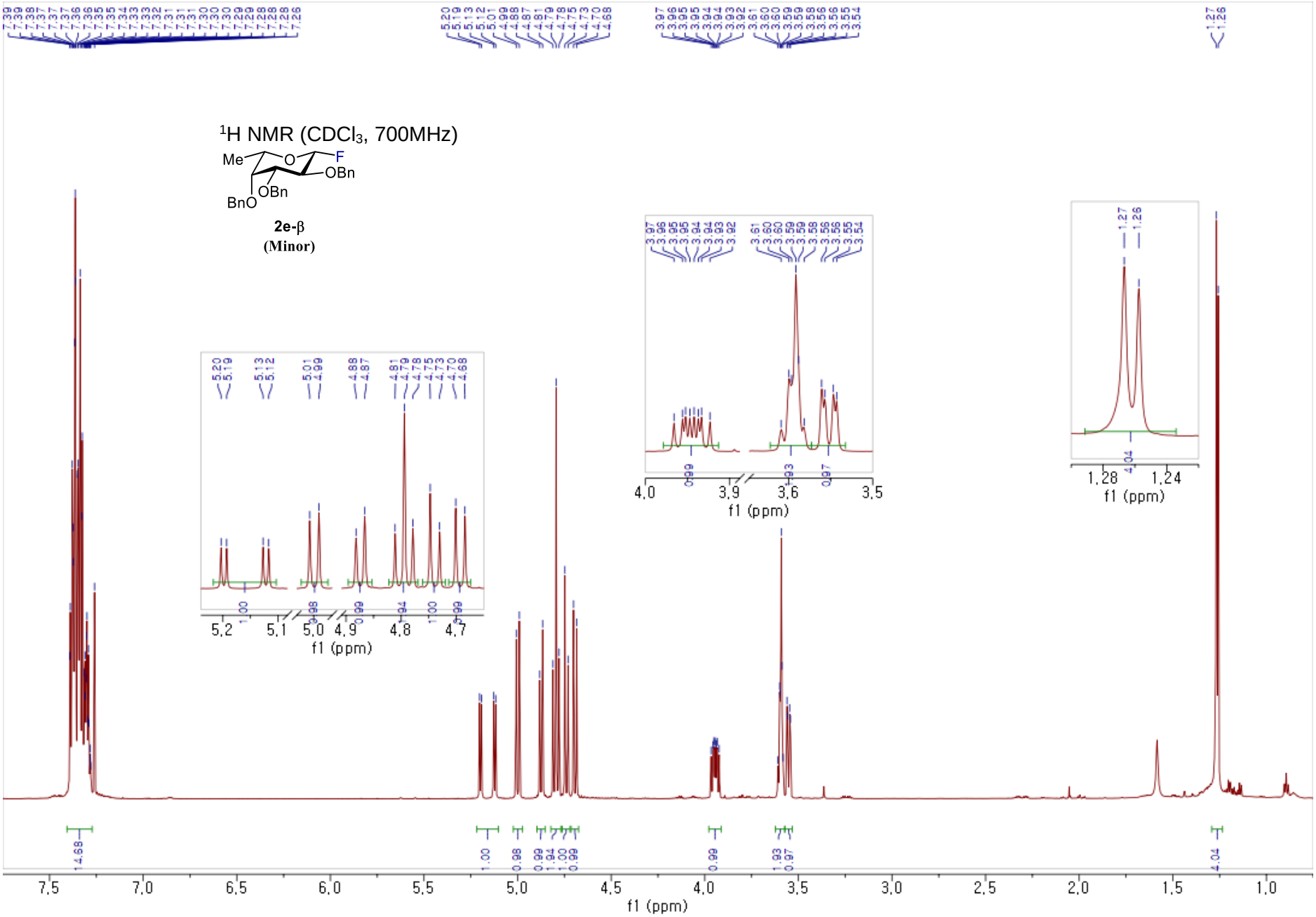
4-Tris-*O*-(phenylmethyl)-α-L-fucopyranosyl fluoride (2e-α, Major diastereomer)

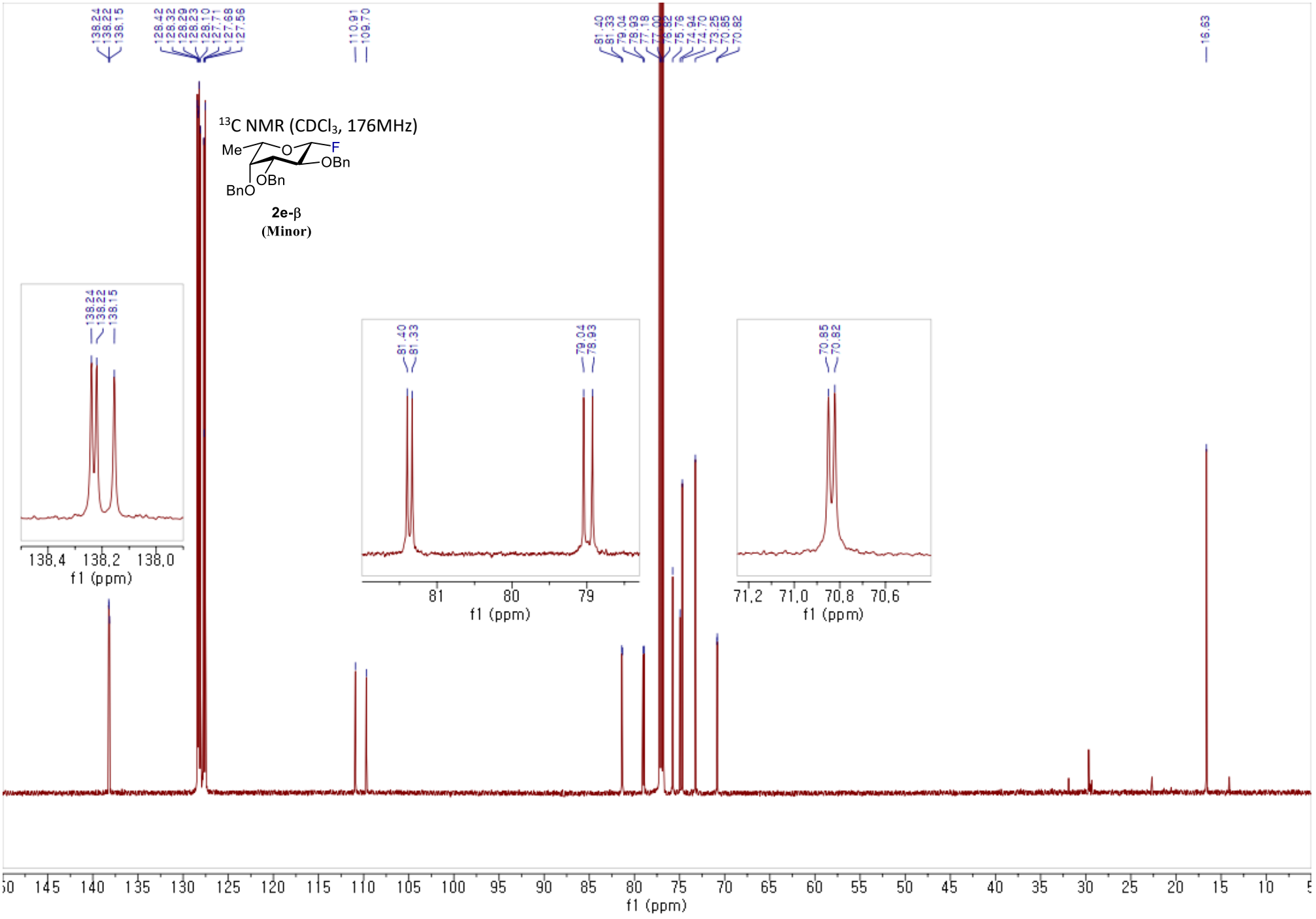


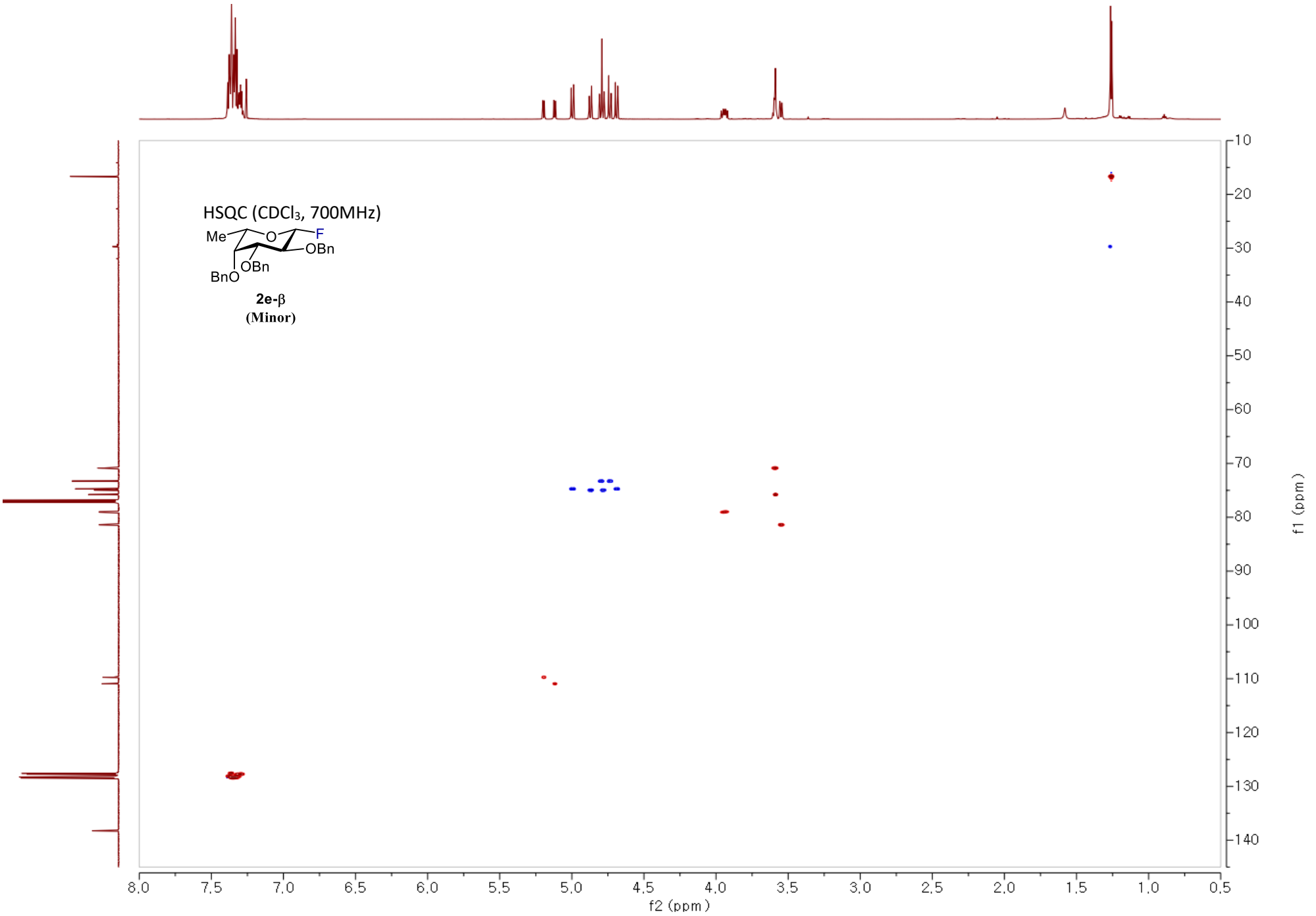

138.46
138.26
138.07
128.45
128.43
128.35
128.27
127.98
127.82
127.74
127.67
127.53
107.03
105.75
78.76
75.71
75.57
74.89
73.66
73.22
69.15
69.13
16.50
^{13}C NMR ($CDCl_3$, 176MHz)
F
Me
O
OBn
BnO
OBn
2e-α
(Major)
75.71
75.57
69.15
69.13
76.0
75.5
69.5
69.0
f1 (ppm)
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
f1 (ppm)


HSQC (CDCl3, 700MHz)
F
Me
O
OBn
BnO
OBn
2e-α
(Major)
f2 (ppm)
f1 (ppm)

2,3,4-Tris-O-(phenylmethyl)-β-L-fucopyranosyl fluoride (2e-β, Minor diastereomer)

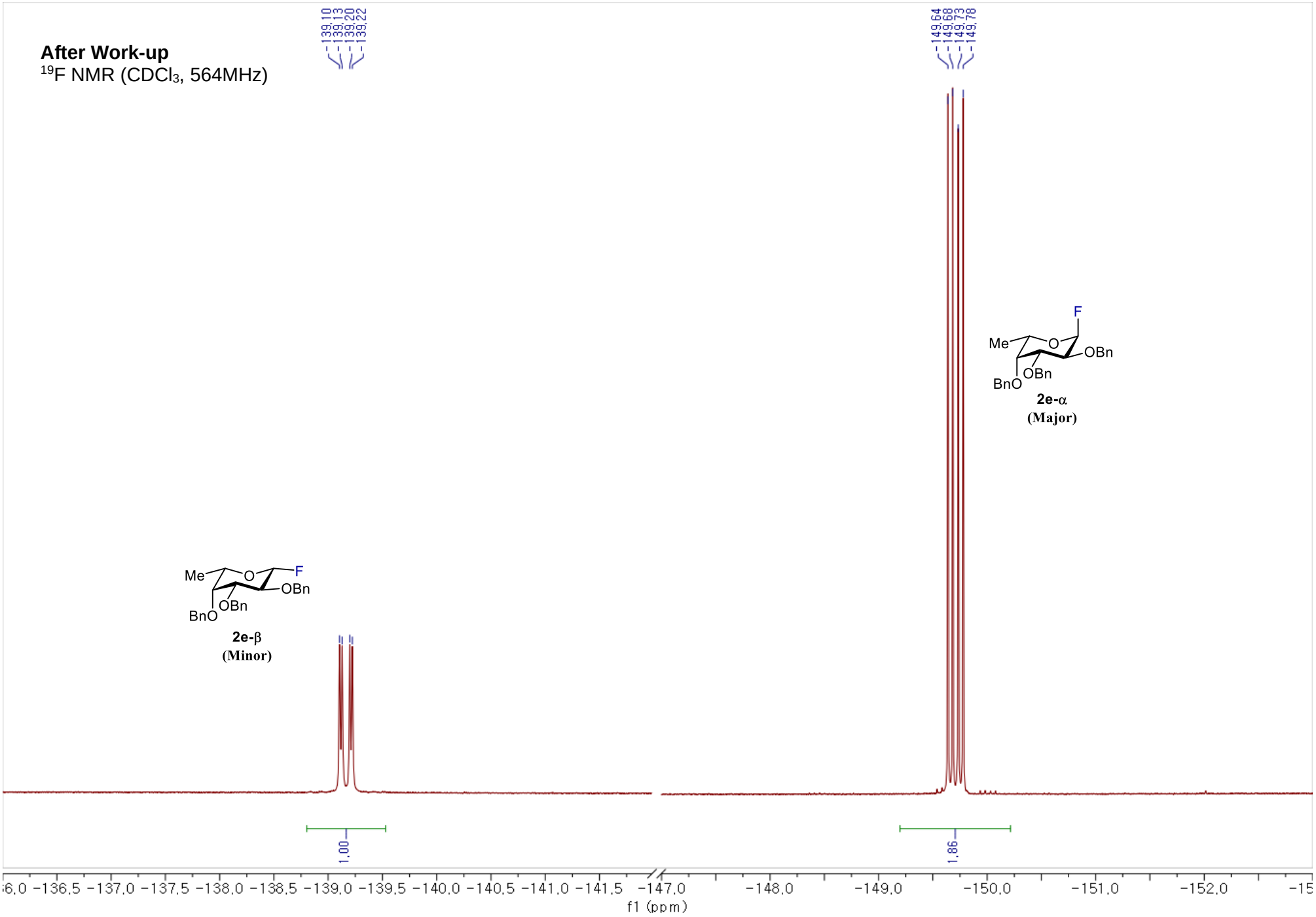



^{13}C NMR ($CDCl_3$, 176MHz)
Me
O
F
OBn
BnO
OBn
2e-β
(Minor)
138.24
138.22
138.15
128.42
128.32
128.29
128.23
128.10
127.71
127.68
127.56
110.91
109.70
81.40
81.33
79.04
78.93
77.18
77.00
76.82
75.76
74.94
74.70
73.25
70.85
70.82
16.63
f1 (ppm)


HSQC (CDCl3, 700MHz)
Me
O
F
OBn
OBn
BnO
2e-β
(Minor)
f2 (ppm)
f1 (ppm)

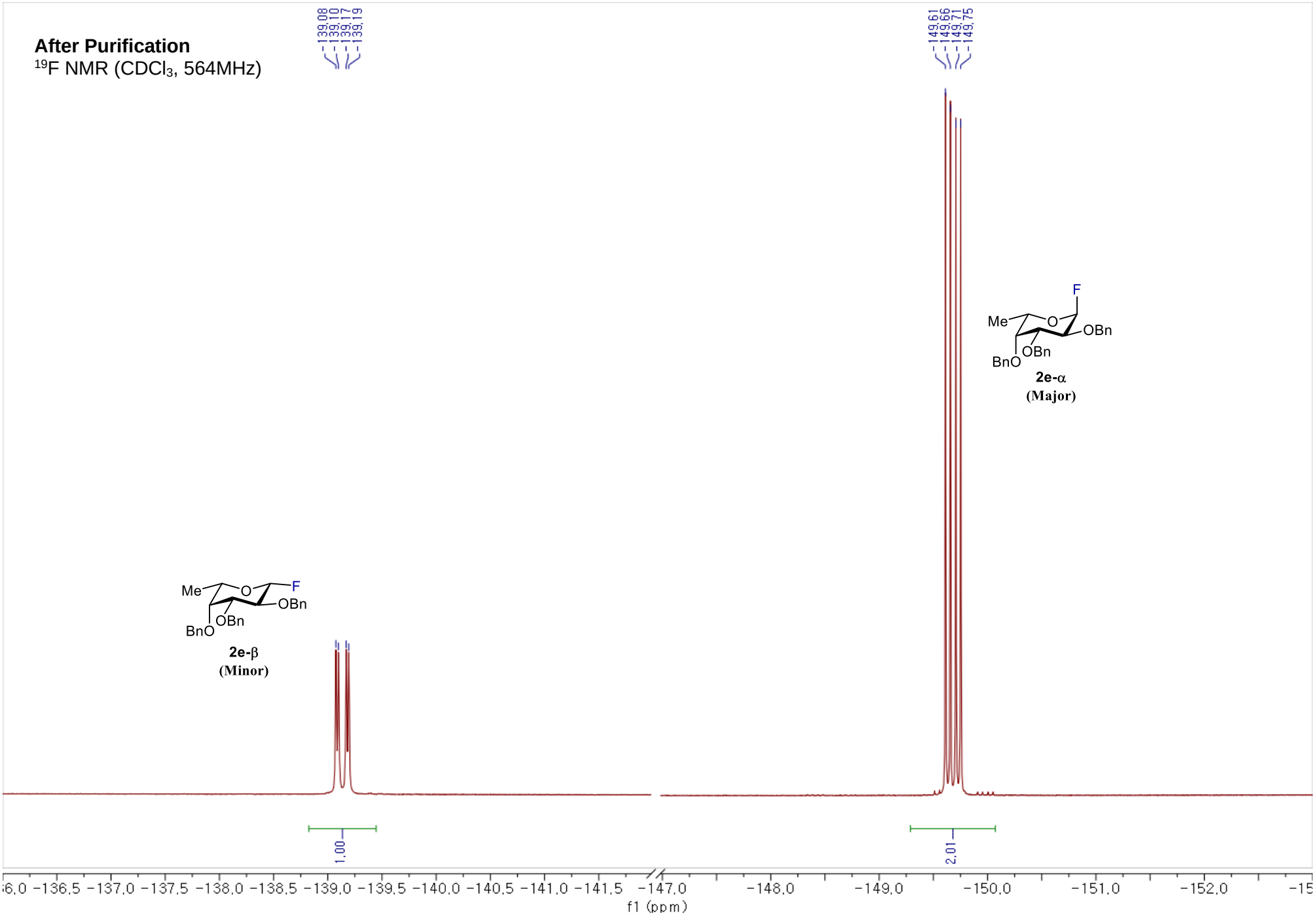
After Work-up

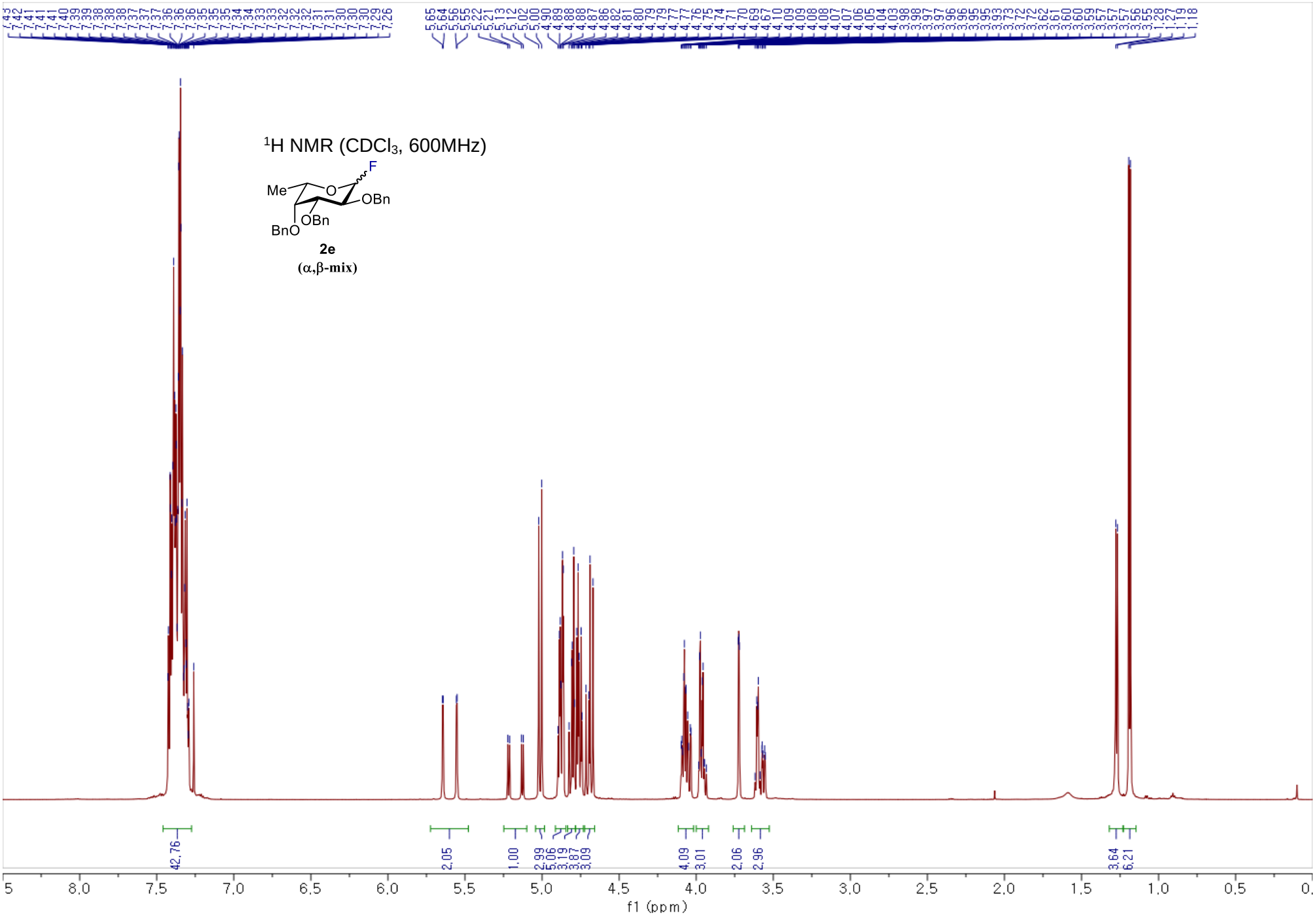
^{19}F NMR ($CDCl_3$, 564MHz)



After Purification

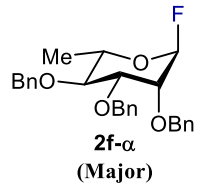
^{19}F NMR ($CDCl_3$, 564MHz)



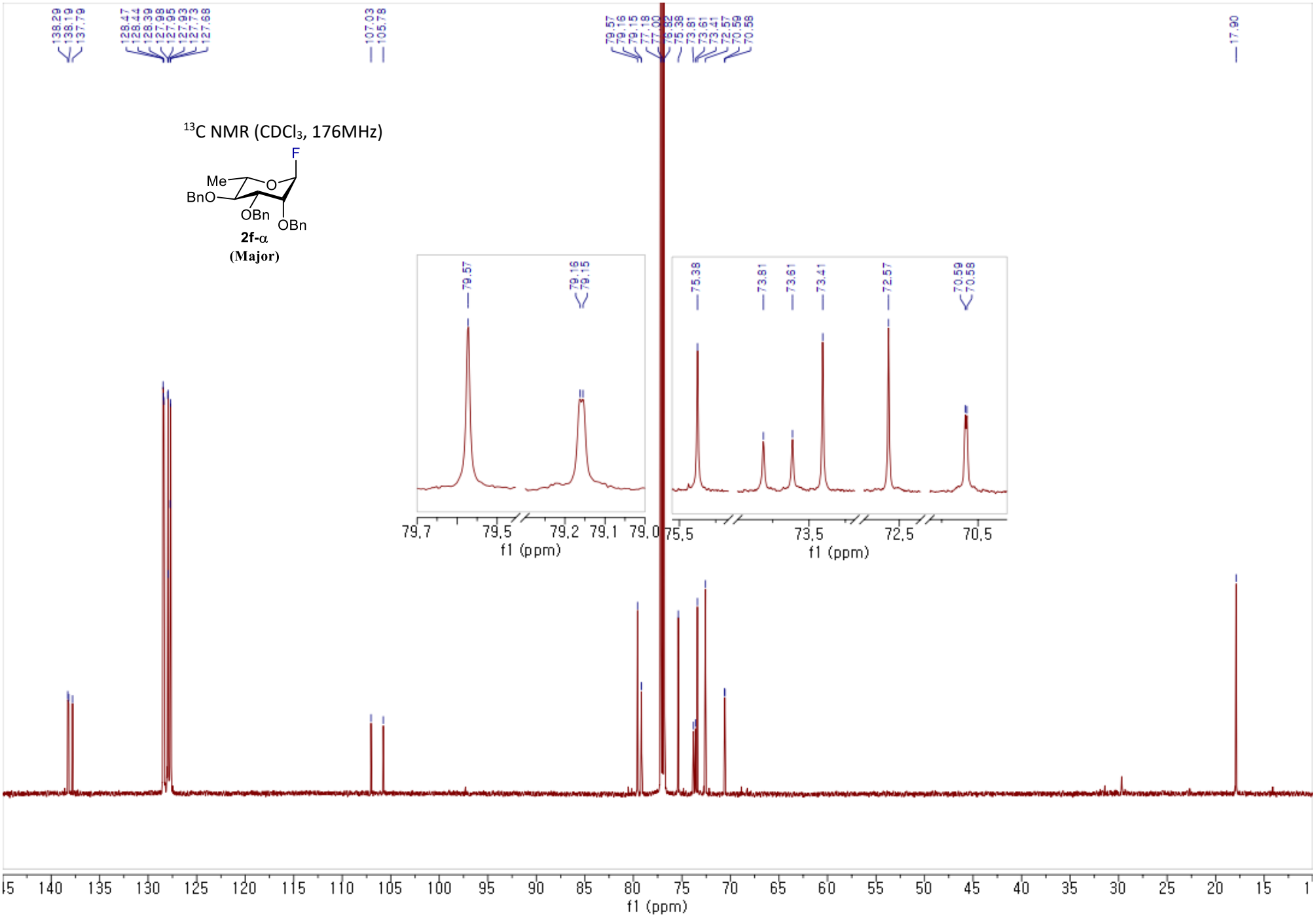

1H NMR (CDCl3, 600MHz)
F
Me
O
OBn
BnO
OBn
2e
(α,β-mix)
42.76
2.05
1.00
2.99
5.06
3.19
3.87
3.09
4.09
3.01
2.06
2.96
3.64
6.21
f1 (ppm)

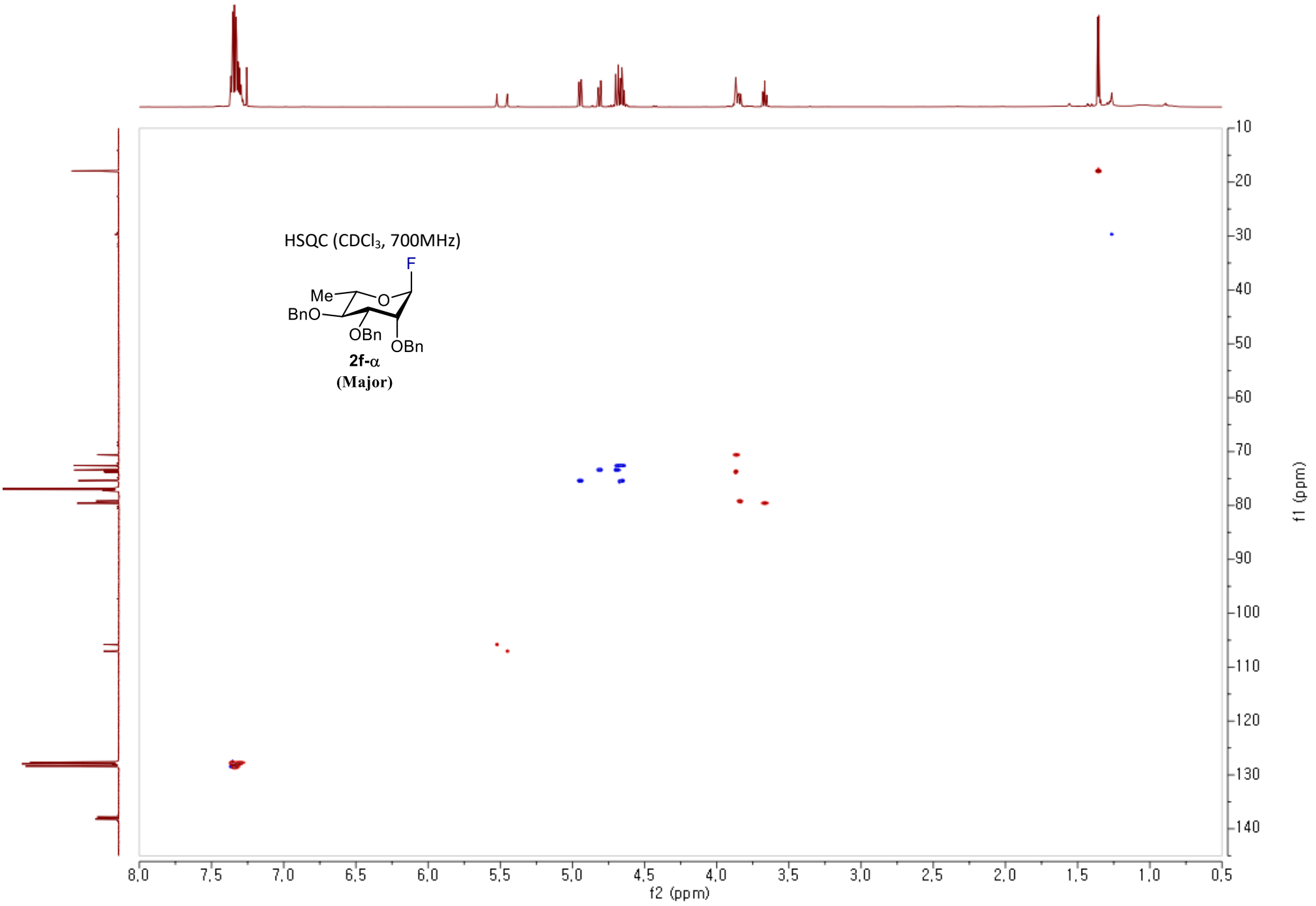
2,3,4-Tris-O-(phenylmethyl)-α-L-rhamnopyranosyl fluoride (2f-α, Major diastereomer)

^{1}H NMR ($CDCl_3$, 700MHz)



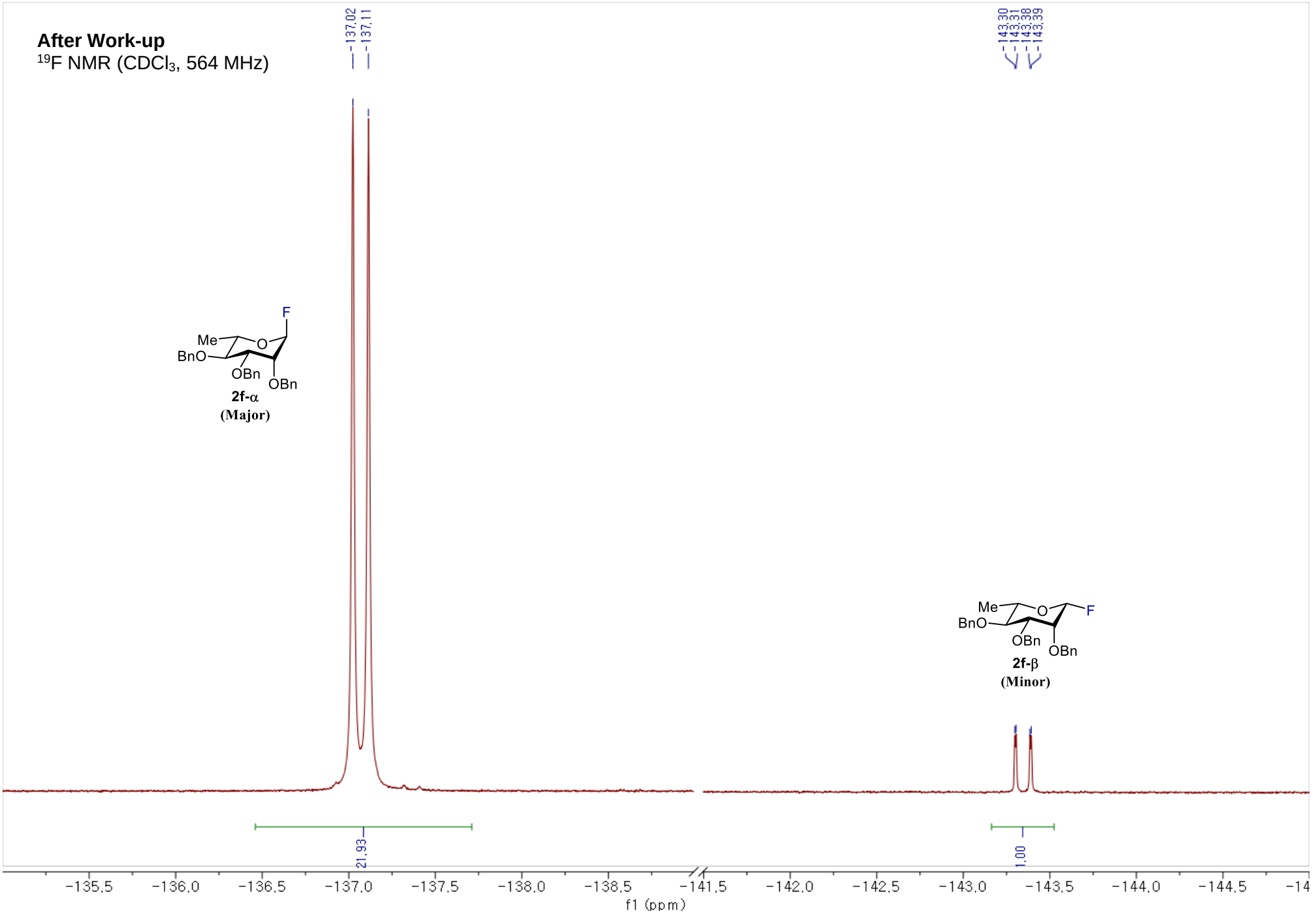
2f-α
(Major)


^{13}C NMR ($CDCl_3$, 176MHz)
F
Me
O
BnO
OBn
OBn
2f-α
(Major)
138.29
138.19
137.79
128.47
128.44
128.39
127.98
127.95
127.93
127.73
127.68
107.03
105.78
79.57
79.16
79.15
77.18
77.00
76.82
75.38
73.81
73.61
73.41
72.57
70.59
70.58
17.90
f1 (ppm)
f1 (ppm)
f1 (ppm)


HSQC (CDCl3, 700MHz)
F
Me
O
BnO
OBn
OBn
2f-α
(Major)
f2 (ppm)
f1 (ppm)

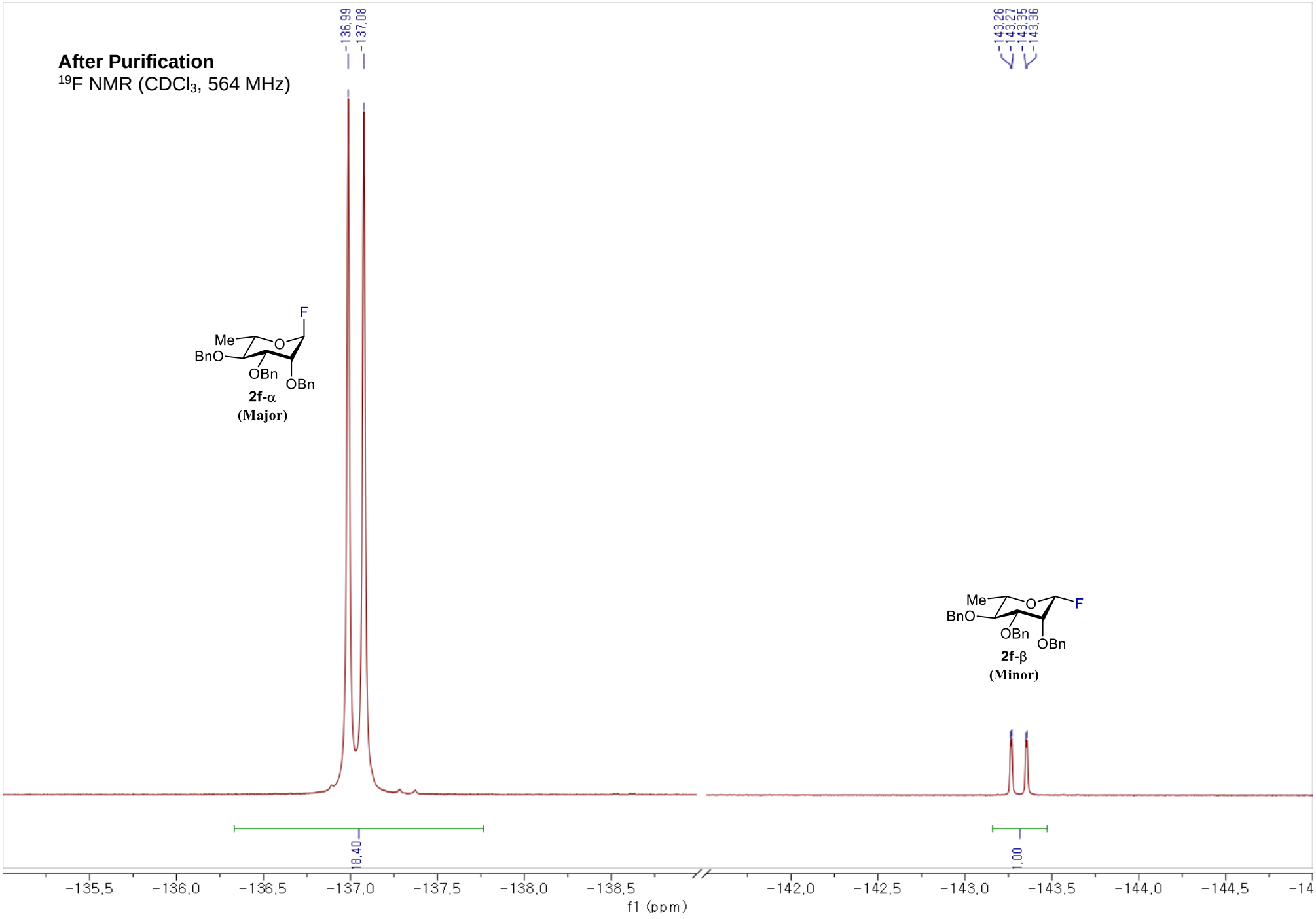
After Work-up

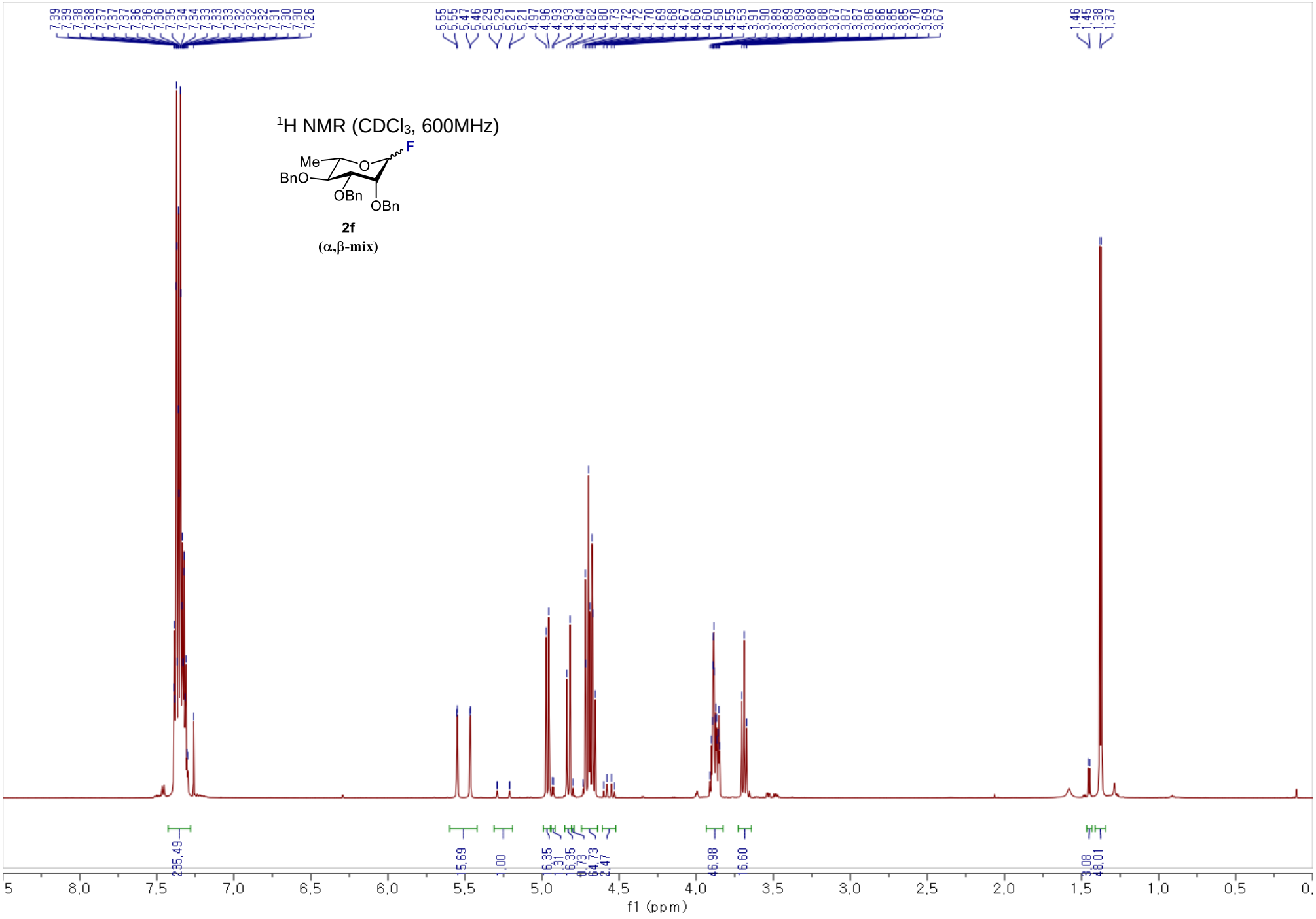
^{19}F NMR ($CDCl_3$, 564 MHz)



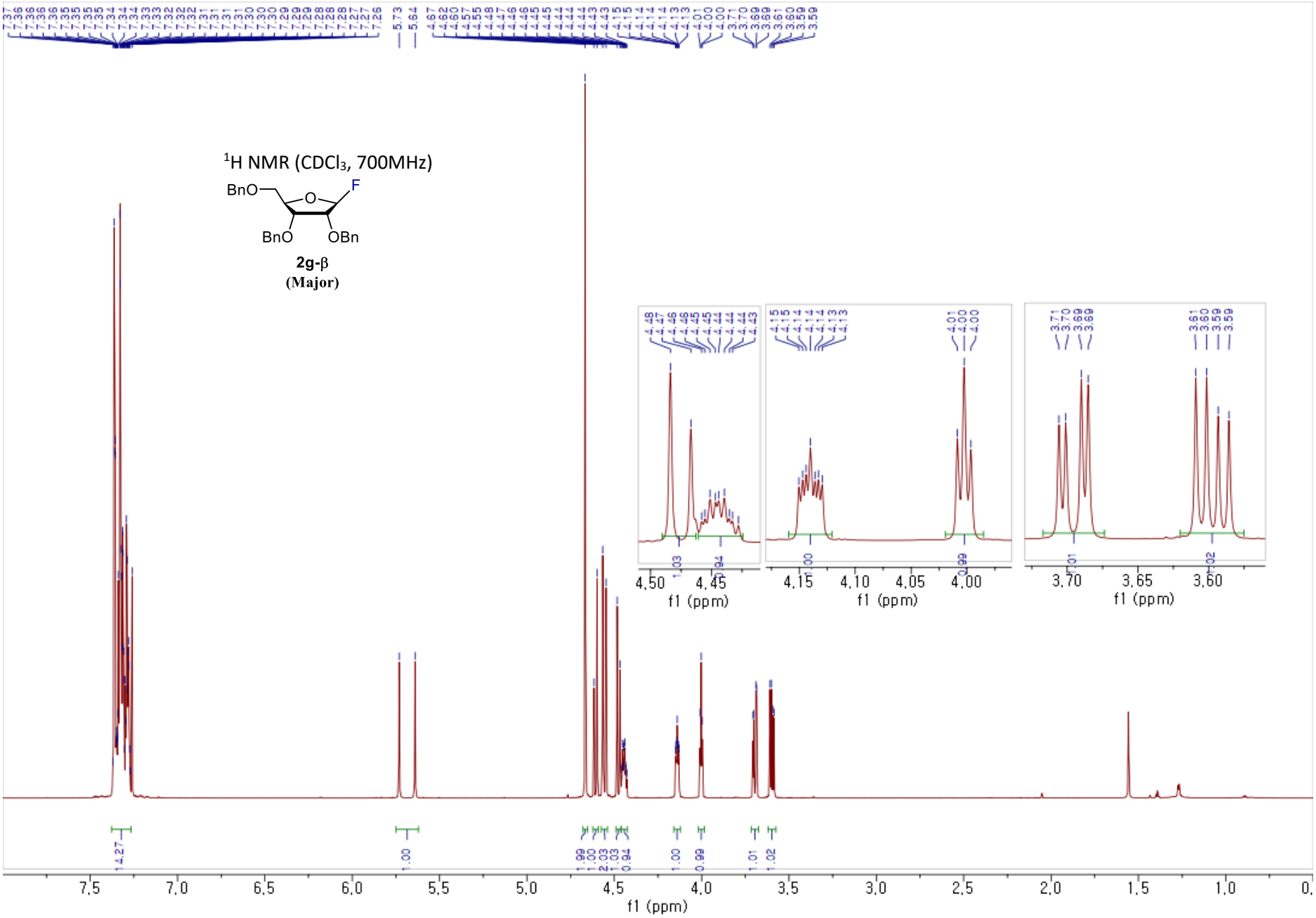
After Purification

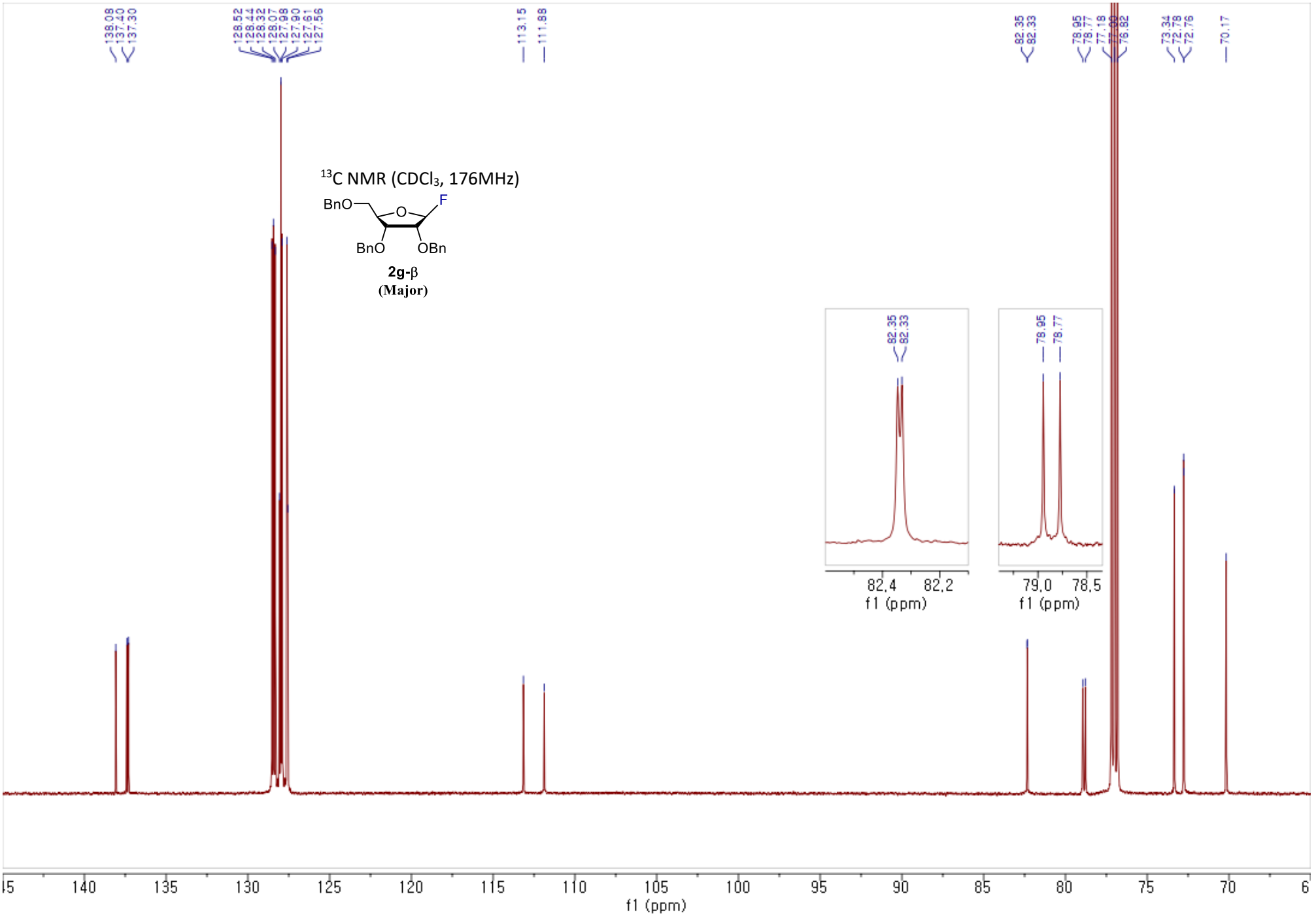
^{19}F NMR ($CDCl_3$, 564 MHz)

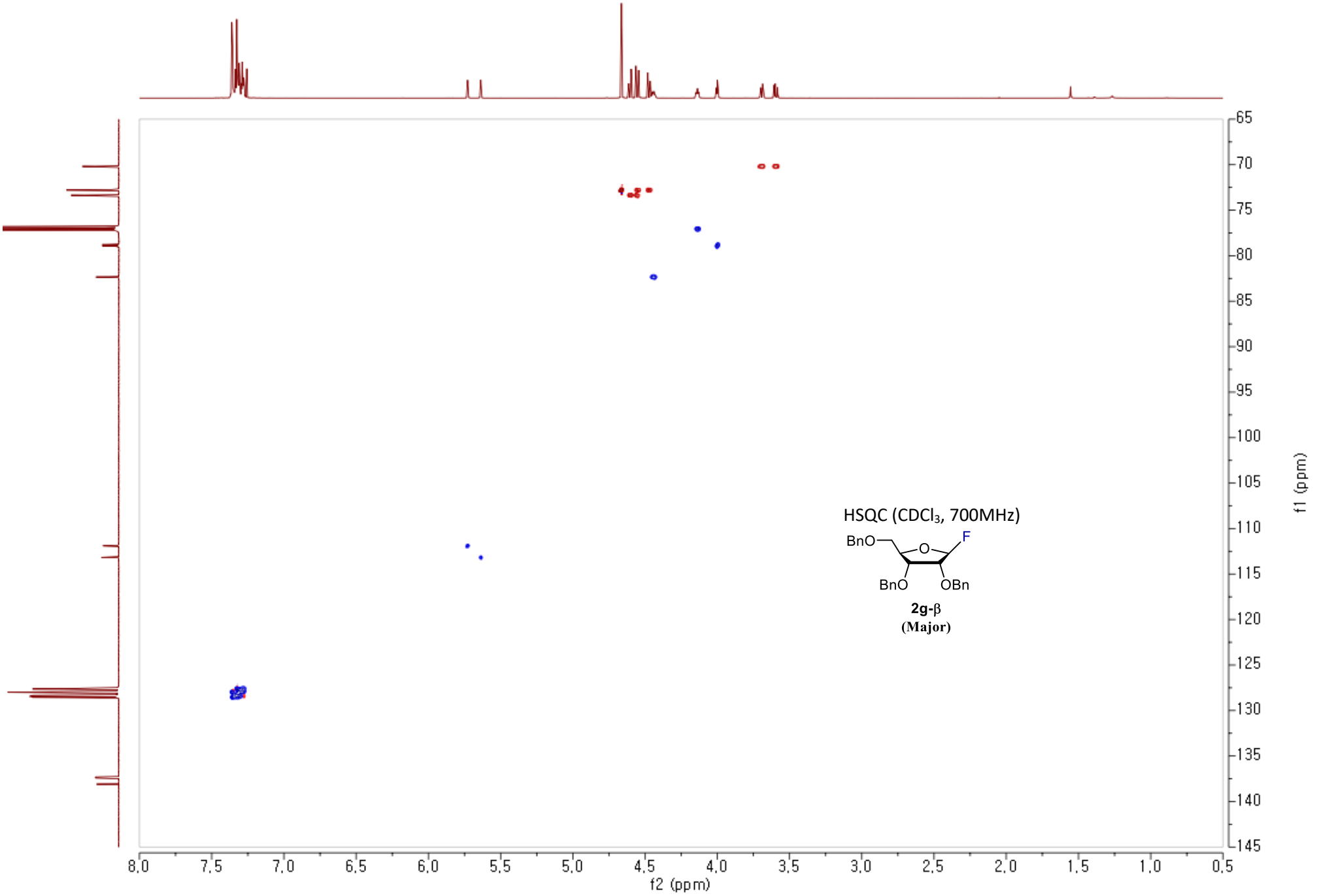



^{1}H NMR ($CDCl_3$, 600MHz)
Me
BnO
O
F
OBn
OBn
2f
(α,β-mix)
f1 (ppm)

2,3,5-Tris-O-(phenylmethyl)-β-D-ribofuranosyl fluoride (2g- β, Major diastereomer)

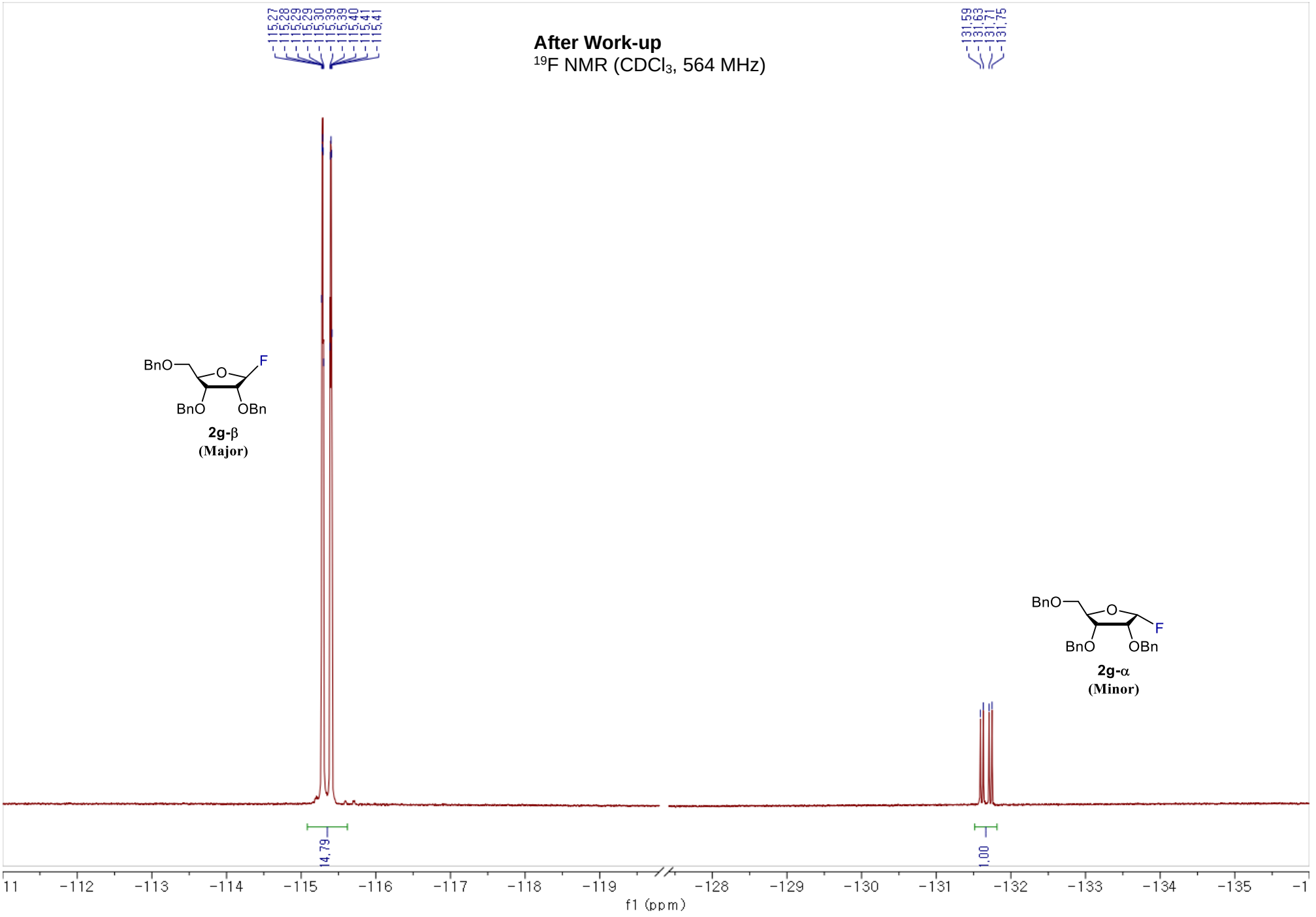



138.08
137.40
137.30
128.52
128.44
128.32
128.07
127.98
127.90
127.61
127.56
113.15
111.88
82.35
82.33
78.95
78.77
77.18
76.82
73.34
72.78
72.76
70.17
^{13}C NMR ($CDCl_3$, 176MHz)
BnO
O
F
BnO
OBn
2g-β
(Major)
82.35
82.33
82.4
82.2
f1 (ppm)
78.95
78.77
79.0
78.5
f1 (ppm)
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
f1 (ppm)


HSQC (CDCl3, 700MHz)
BnO
F
O
BnO
OBn
2g-β
(Major)
f2 (ppm)
f1 (ppm)

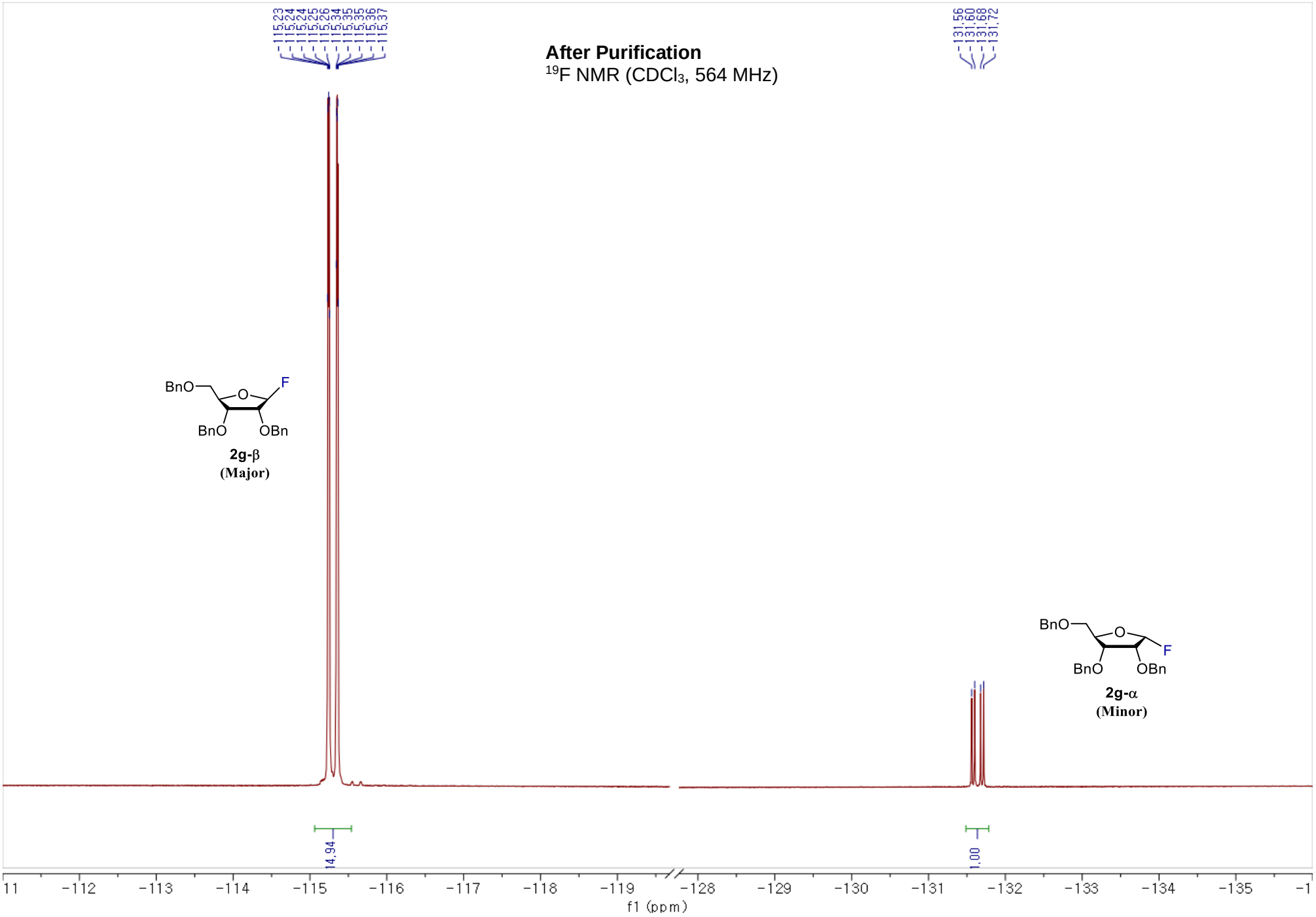
After Work-up

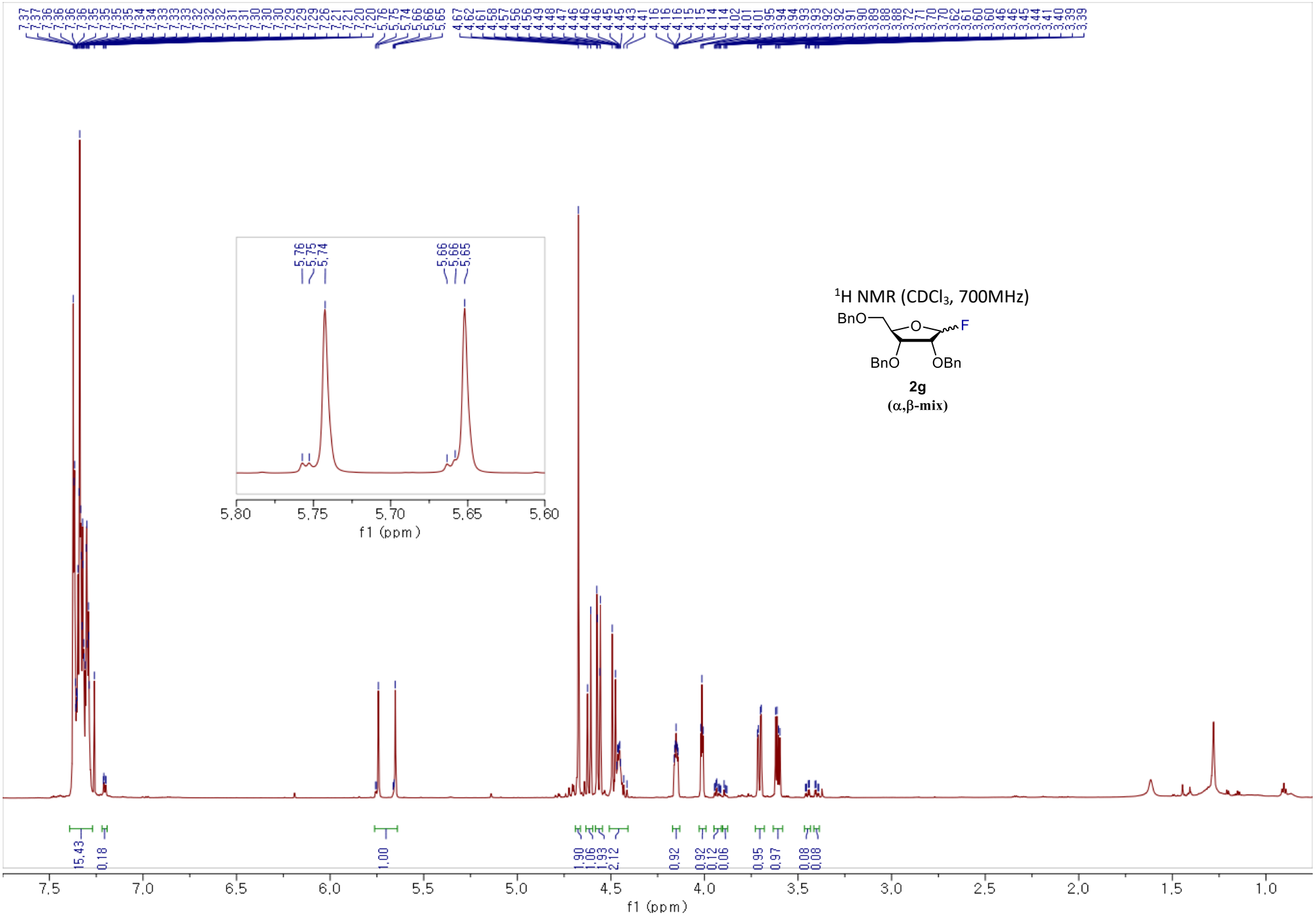
^{19}F NMR ($CDCl_3$, 564 MHz)



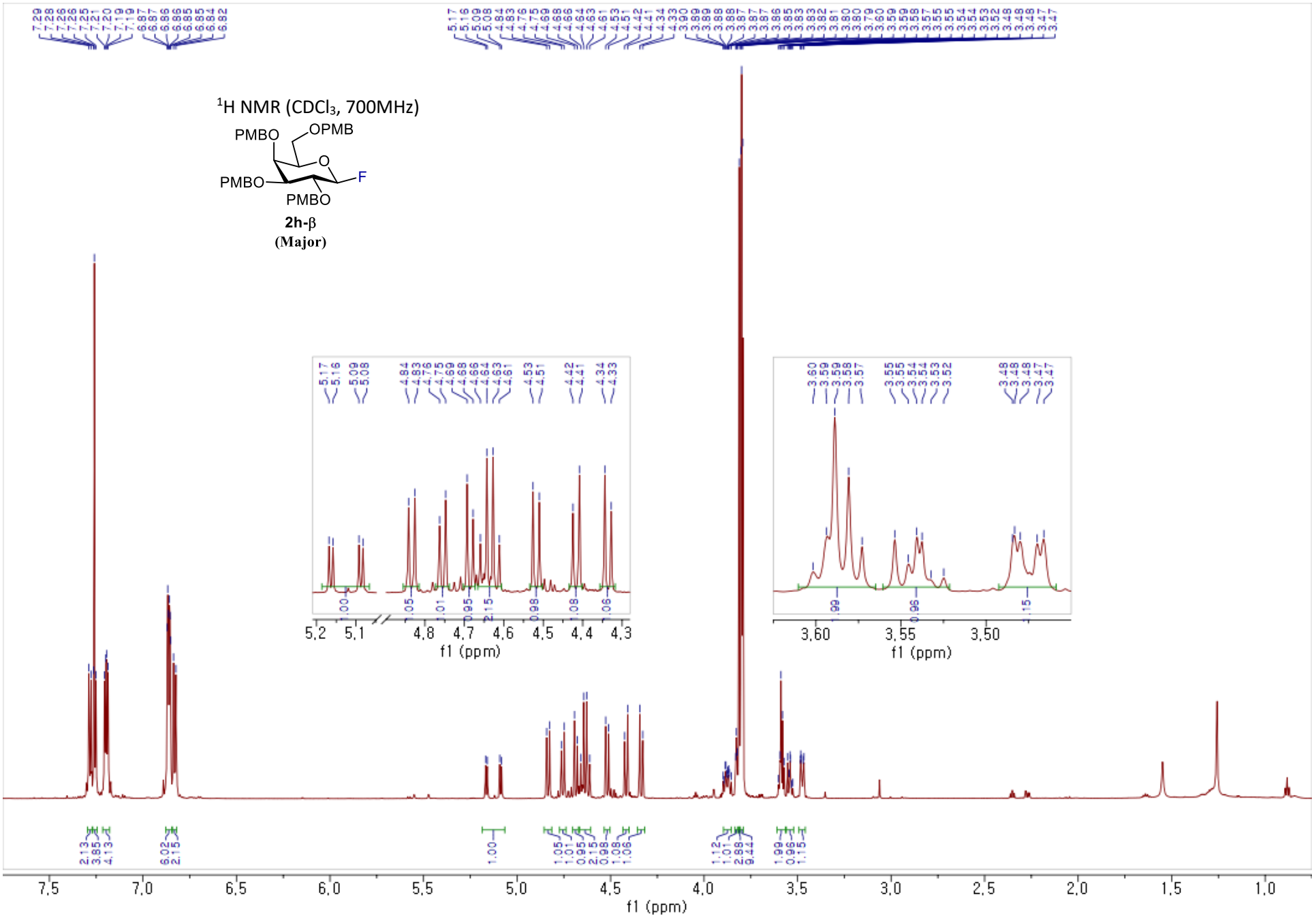
After Purification

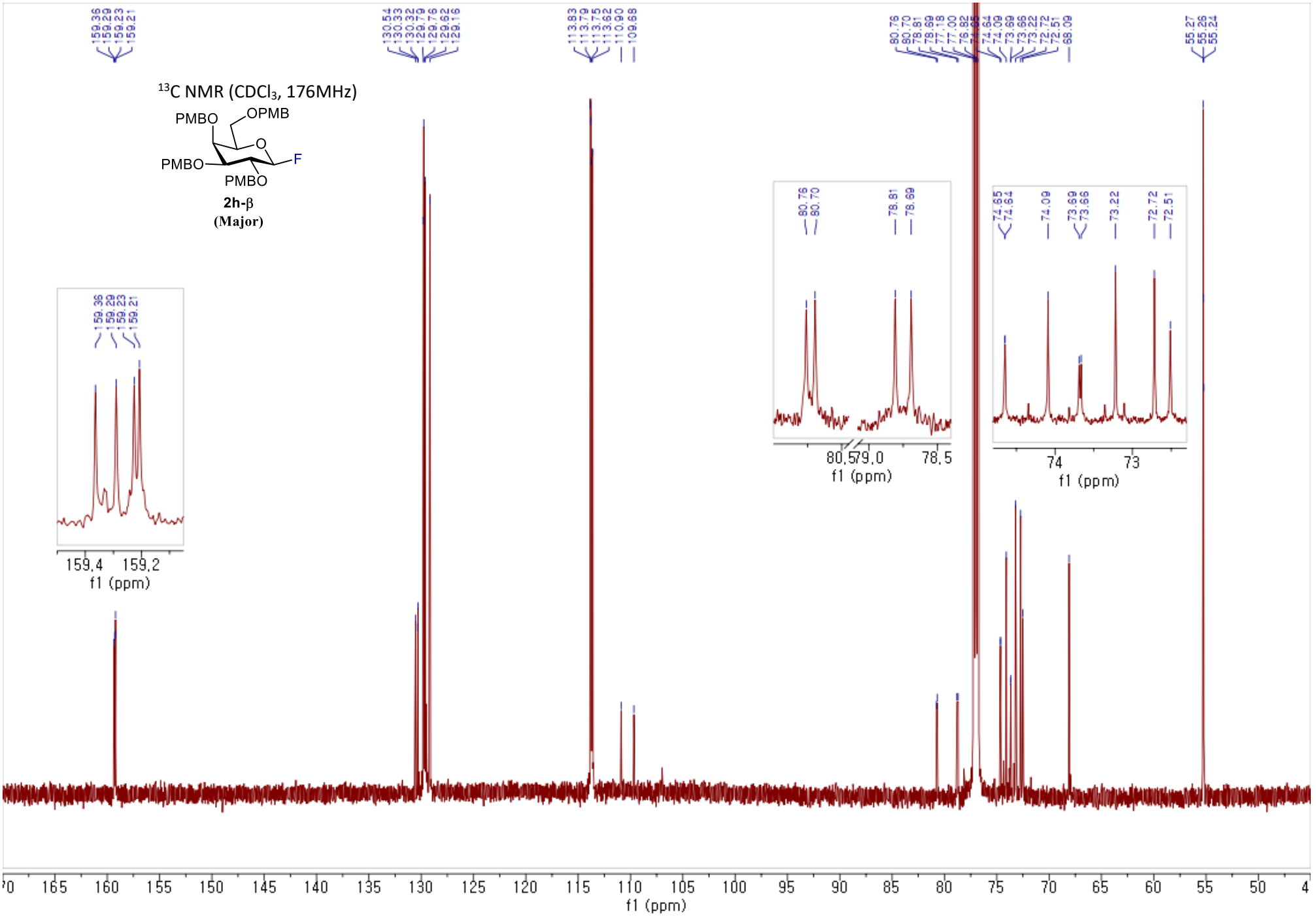
^{19}F NMR ($CDCl_3$, 564 MHz)

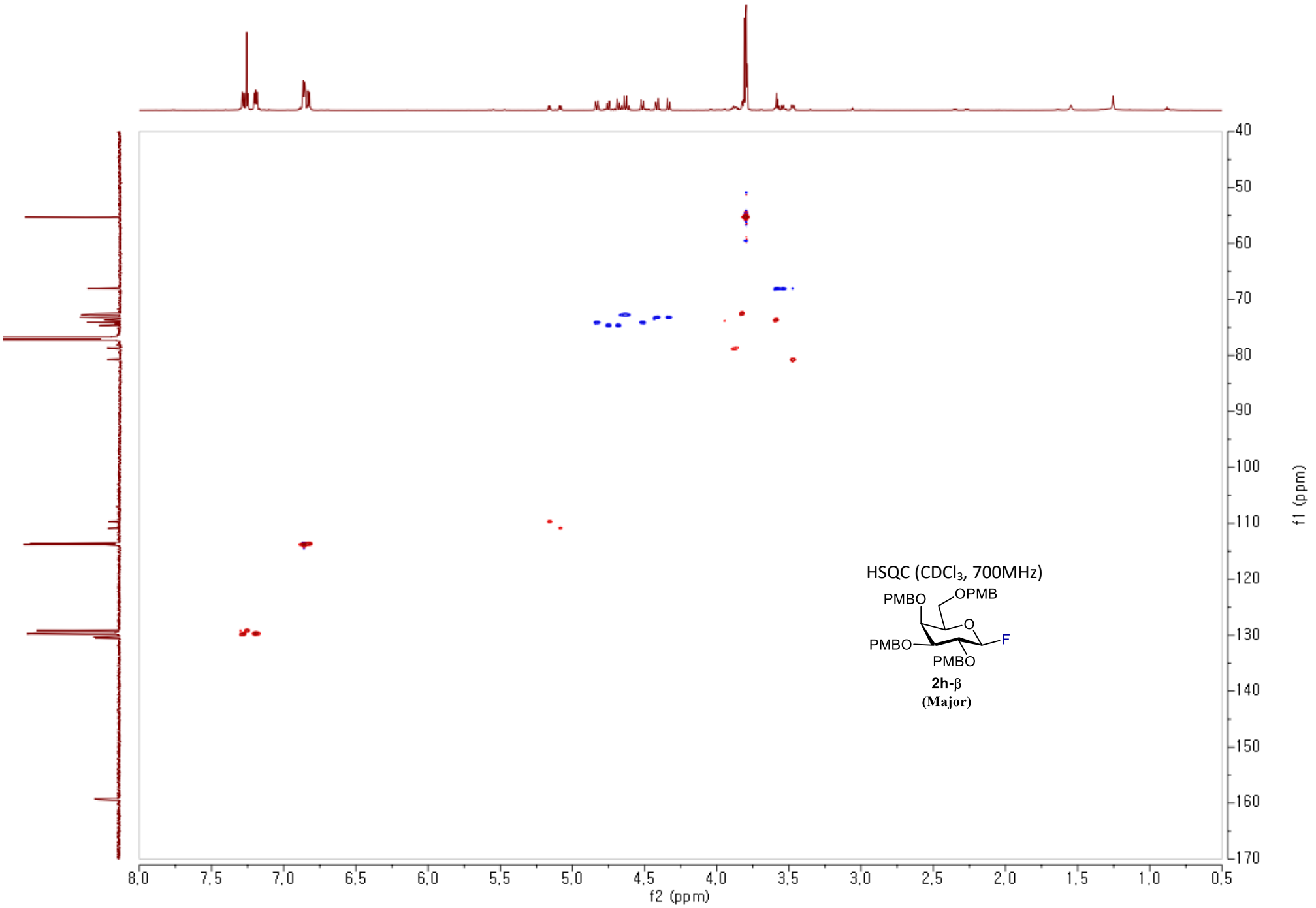



^{1}H NMR ($CDCl_3$, 700MHz)
BnO
O
F
BnO
OBn
2g
(α,β-mix)
f1 (ppm)
f1 (ppm)

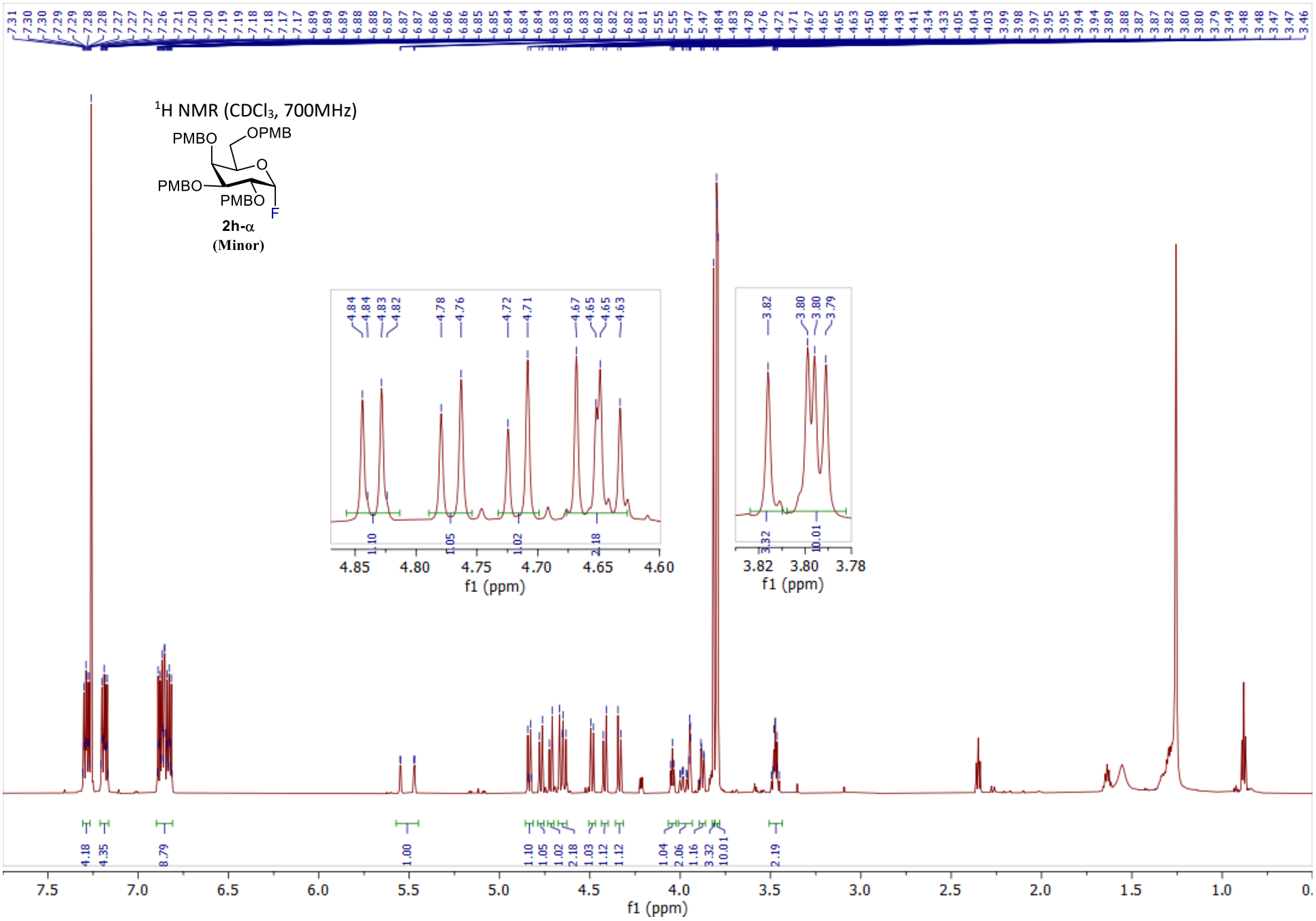
2,3,4,6-Tetrakis-O-[(4-methoxyphenyl)methyl]-β-D-galactopyranosyl fluoride (2h-β, Major diastereomer)

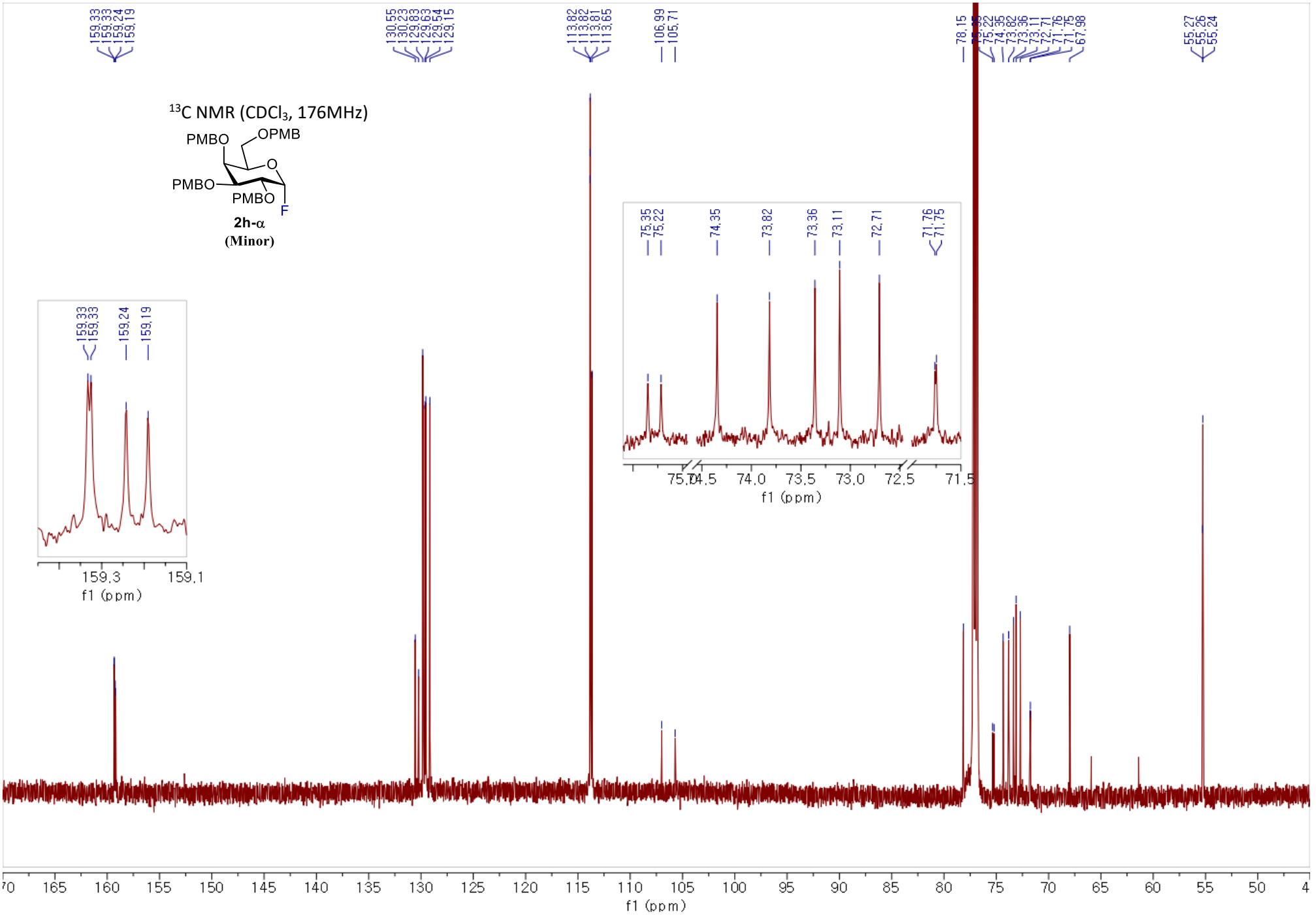


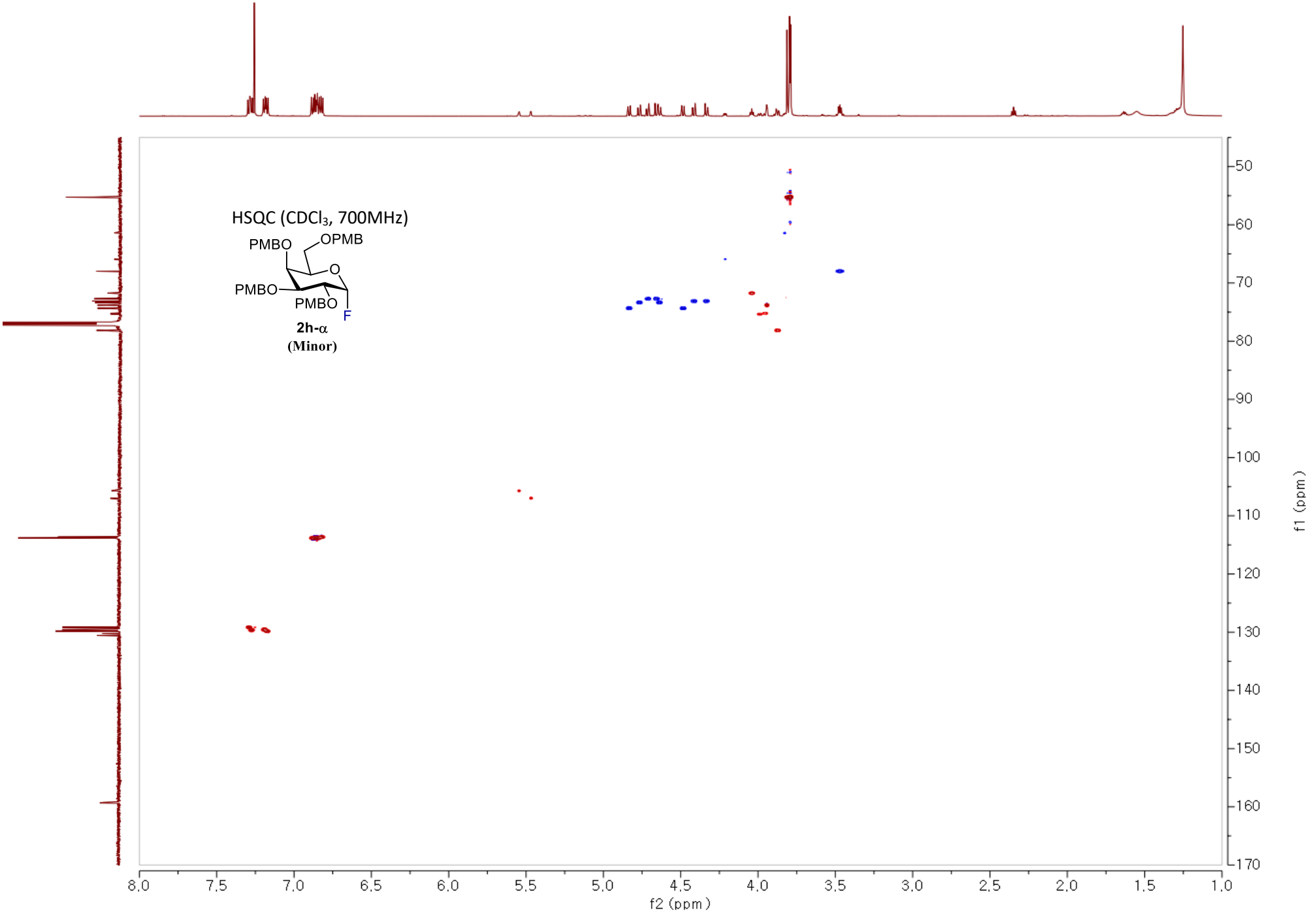

^{13}C NMR ($CDCl_3$, 176MHz)
PMBO
OPMB
O
F
PMBO
PMBO
2h-β
(Major)
159.36
159.29
159.23
159.21
130.54
130.33
130.32
129.79
129.76
129.62
129.16
113.83
113.79
113.75
113.62
110.90
109.68
80.76
80.70
78.81
78.69
77.18
77.00
76.82
74.65
74.64
74.09
73.69
73.66
73.22
72.72
72.51
68.09
55.27
55.26
55.24
159,4
159,2
f1 (ppm)
80,5
79,0
78,5
f1 (ppm)
74
73
f1 (ppm)
f1 (ppm)

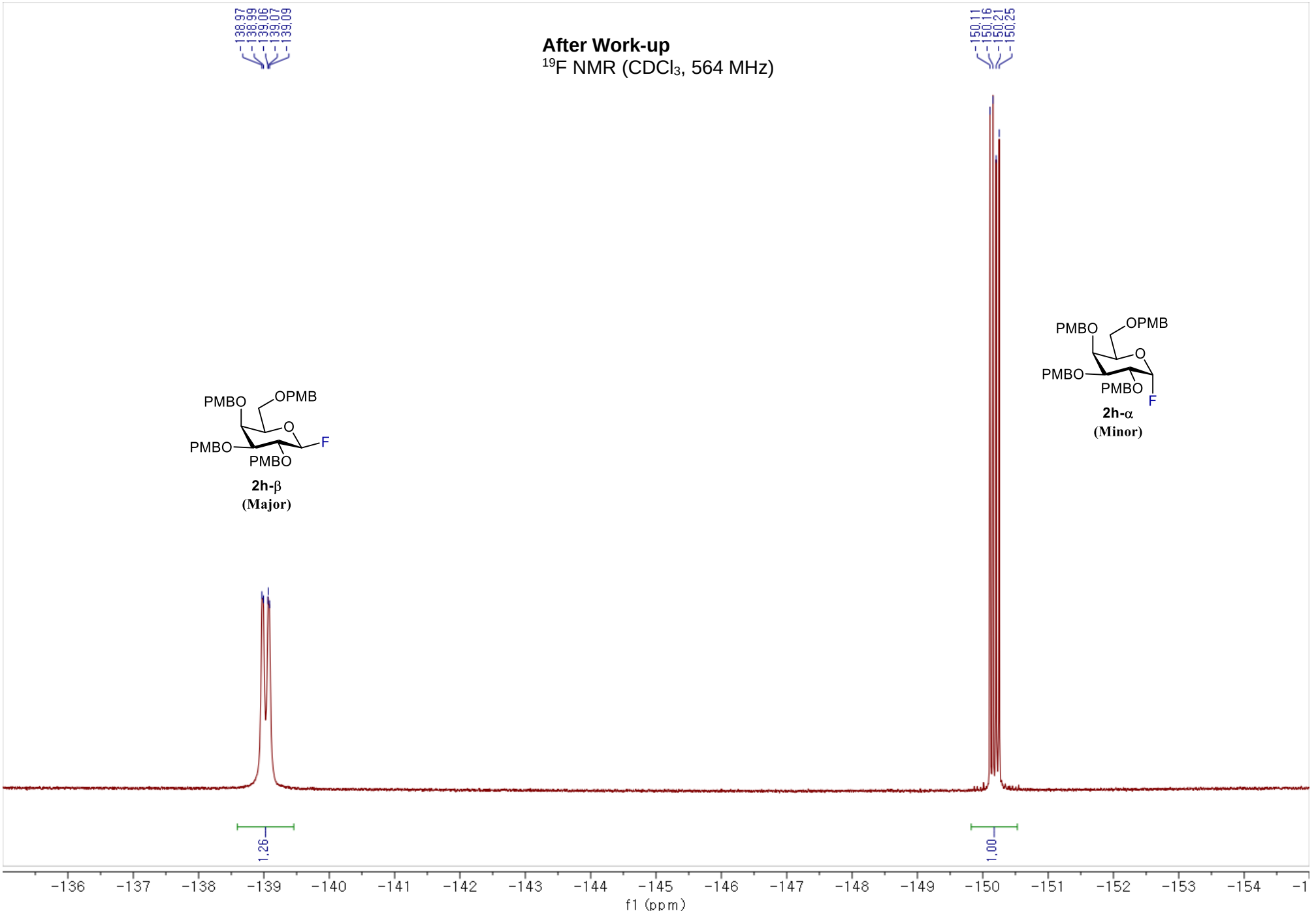

HSQC ($CDCl_3$, 700MHz)
PMBO
OPMB
O
F
PMBO
PMBO
2h-β
(Major)
f2 (ppm)
f1 (ppm)

2,3,4,6-Tetrakis-*O*-[(4-methoxyphenyl)methyl]-α-D-galactopyranosyl fluoride (2h-α, Minor diastereomer)



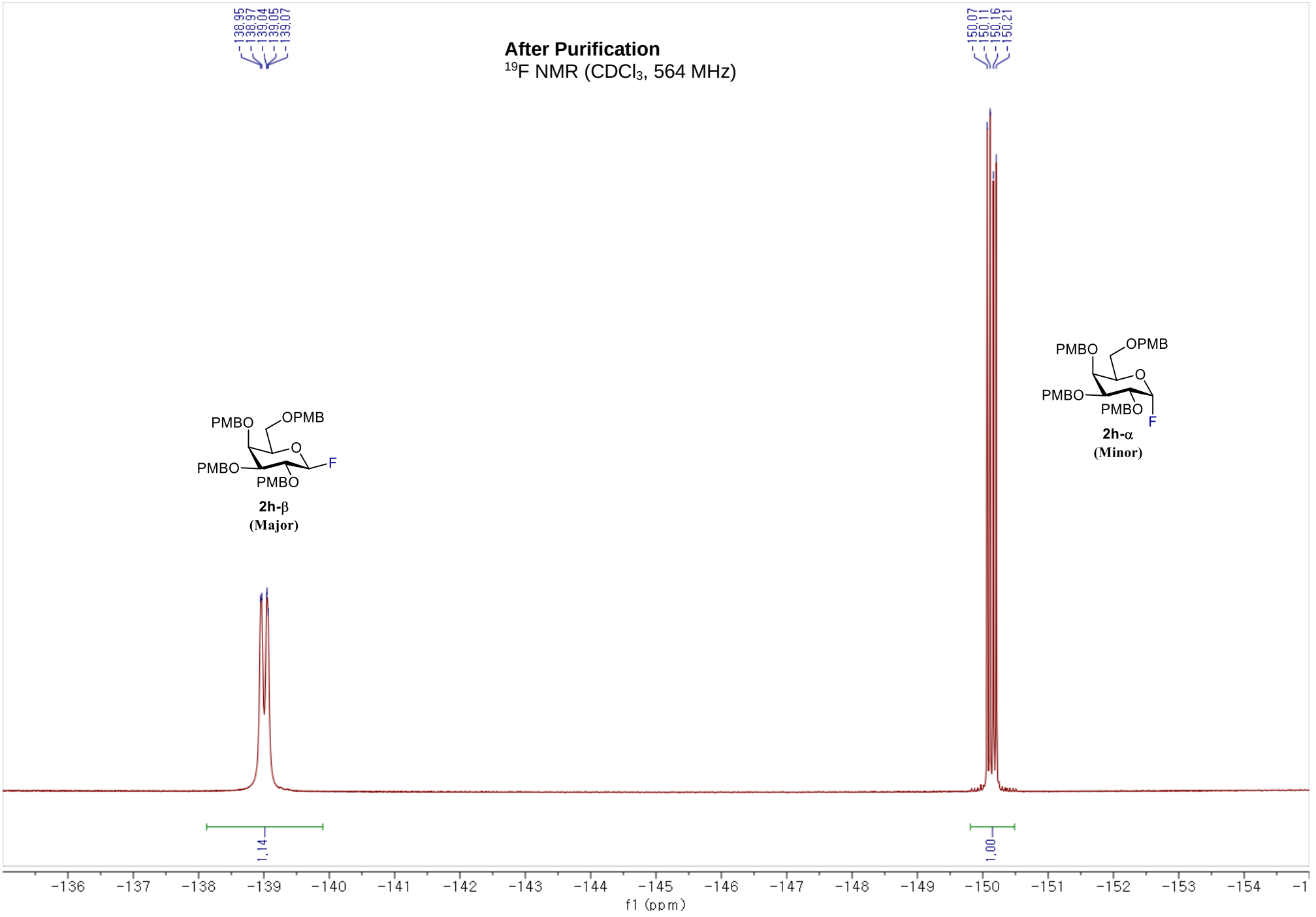

159.33
159.33
159.24
159.19
130.55
130.23
129.83
129.63
129.54
129.15
113.82
113.82
113.81
113.65
106.99
105.71
78.15
75.35
75.22
74.35
73.82
73.36
73.11
72.71
71.76
71.75
67.98
55.27
55.26
55.24
^{13}C NMR ($CDCl_3$, 176MHz)
PMBO
OPMB
O
PMBO
PMBO
F
2h-α
(Minor)
159.3
159.1
f1 (ppm)
75.0
74.5
74.0
73.5
73.0
72.5
71.5
f1 (ppm)
f1 (ppm)

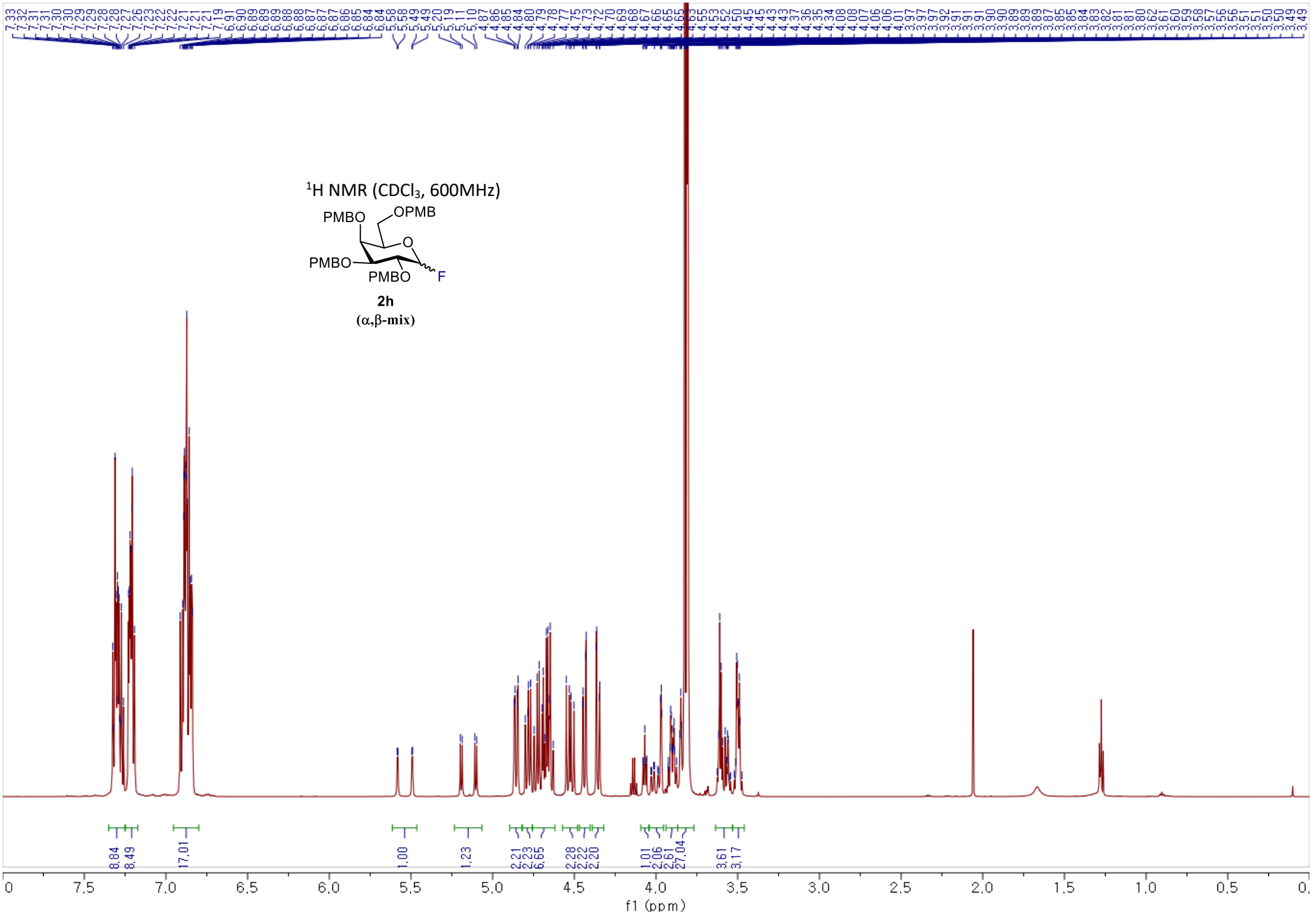

HSQC ($CDCl_3$, 700MHz)
PMBO
OPMB
O
PMBO
PMBO
F
2h-α
(Minor)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
50
60
70
80
90
100
110
120
130
140
150
160
170
f1 (ppm)


After Work-up
19F NMR (CDCl3, 564 MHz)
-138.97
-138.99
-139.06
-139.07
-139.09
-150.11
-150.16
-150.21
-150.25
PMBO
OPMB
O
PMBO
F
PMBO
2h-β
(Major)
PMBO
OPMB
O
PMBO
PMBO
F
2h-α
(Minor)
1.26
1.00
-136
-137
-138
-139
-140
-141
-142
-143
-144
-145
-146
-147
-148
-149
-150
-151
-152
-153
-154
f1 (ppm)

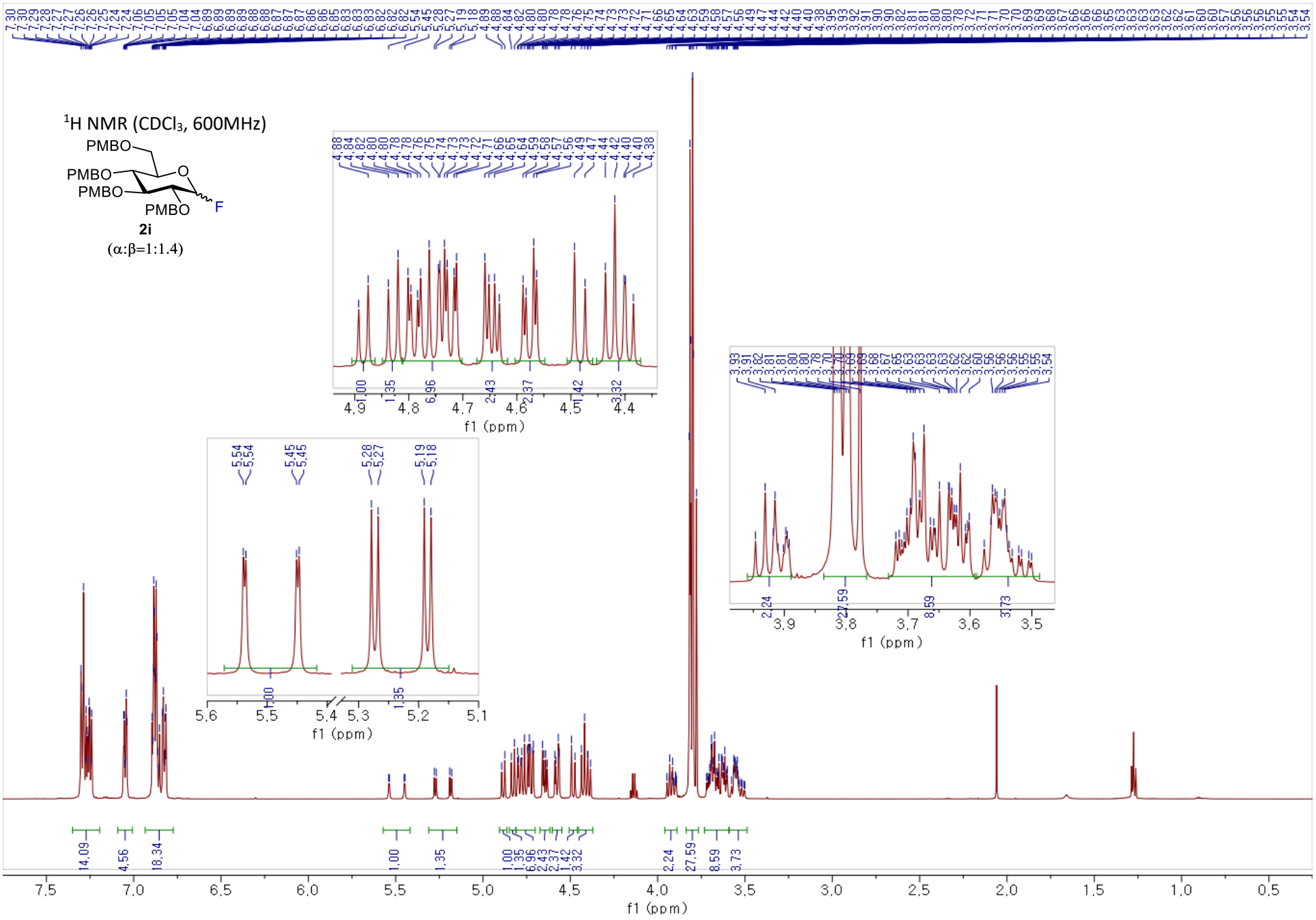
After Purification

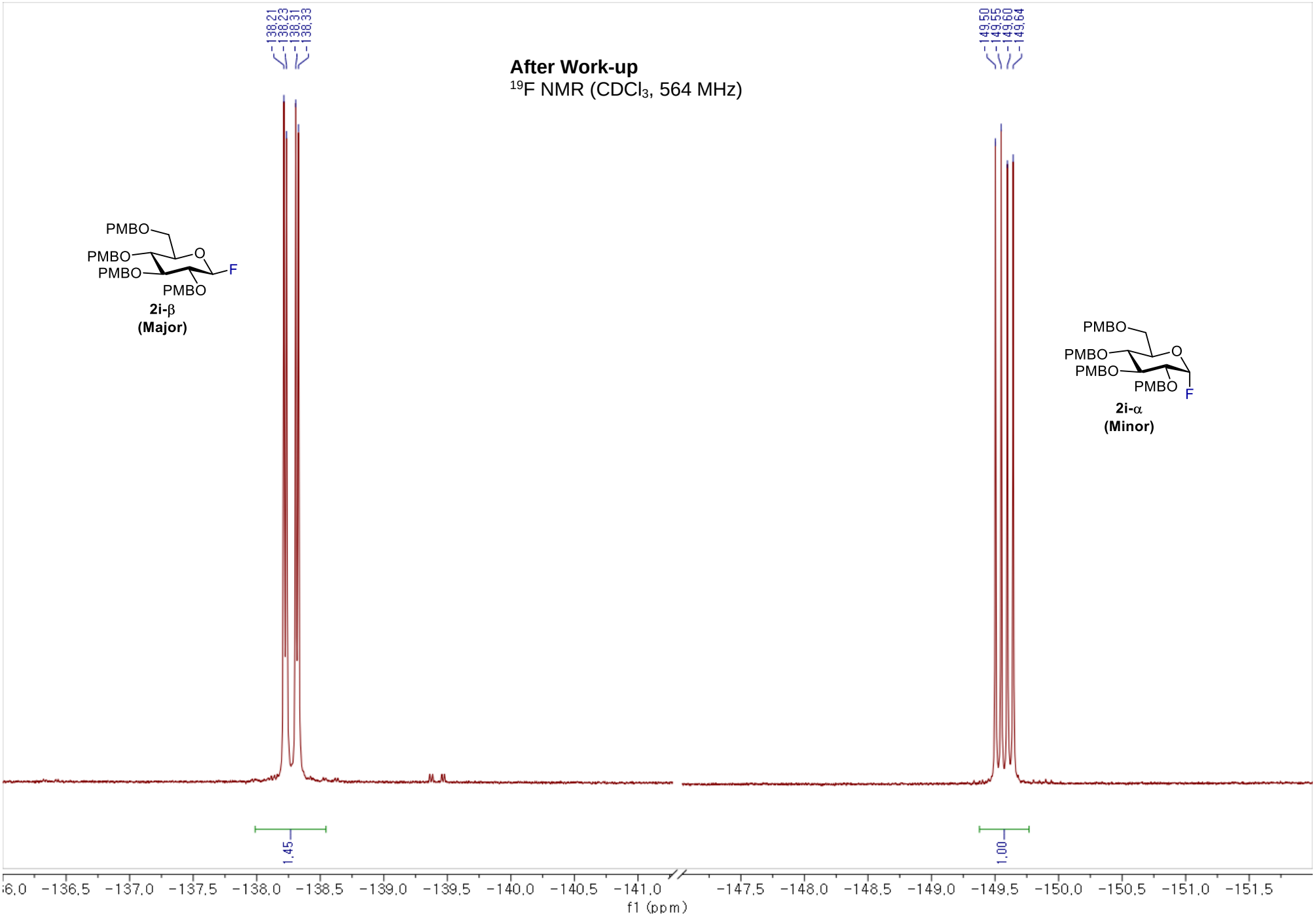
^{19}F NMR ($CDCl_3$, 564 MHz)




^{1}H NMR ($CDCl_3$, 600MHz)
PMBO
OPMB
O
PMBO
PMBO
F
2h
(α,β-mix)
8.84
8.49
17.01
1.00
1.23
2.21
2.23
6.65
2.28
2.22
2.20
1.01
2.06
2.61
27.04
3.61
3.17
f1 (ppm)

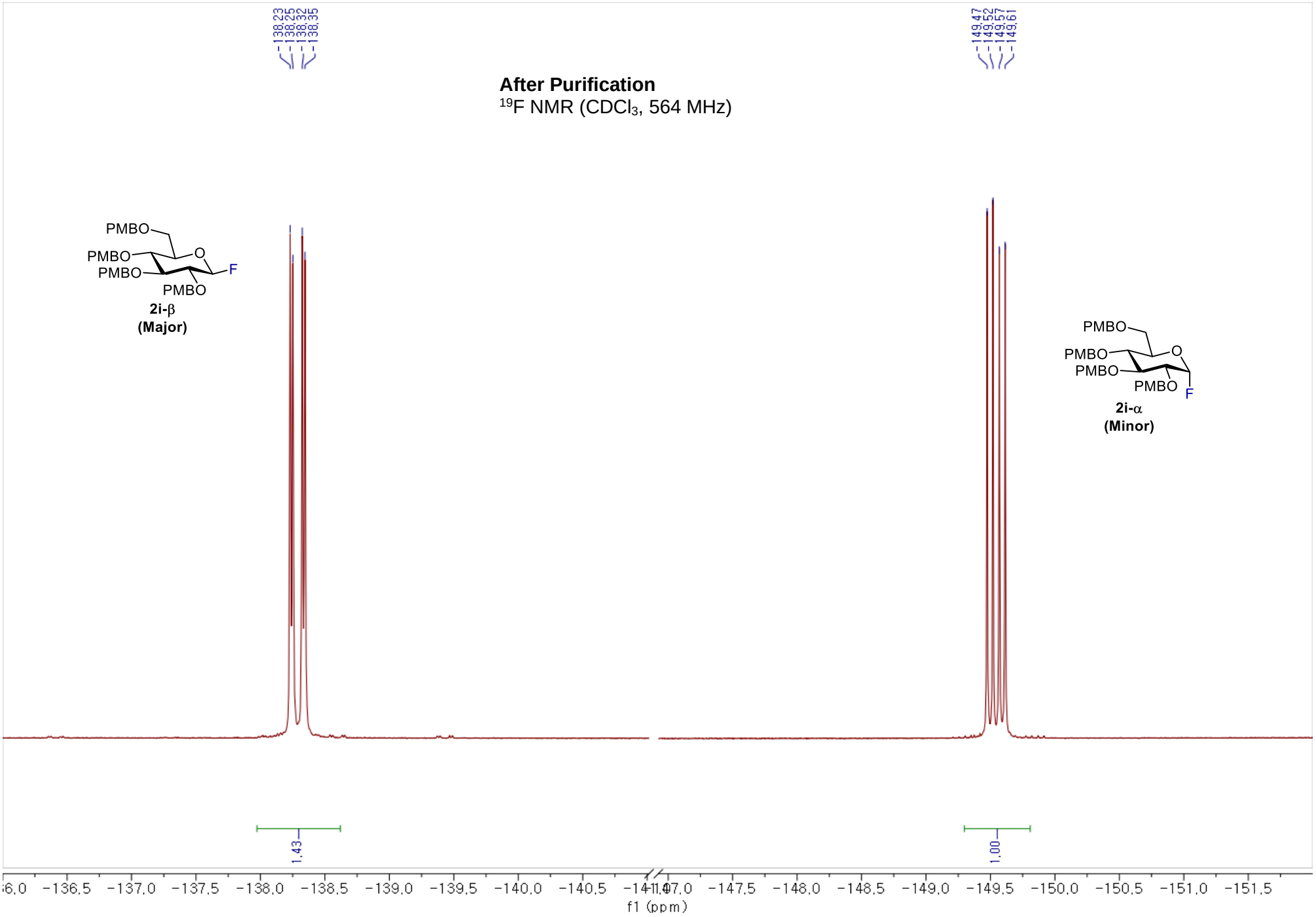
2,3,4,6-Tetrakis-O-[(4-methoxyphenyl)methyl]-β-D-glucopyranosyl fluoride (2i, Isolated as α : β = 1 : 1.4 mixture)



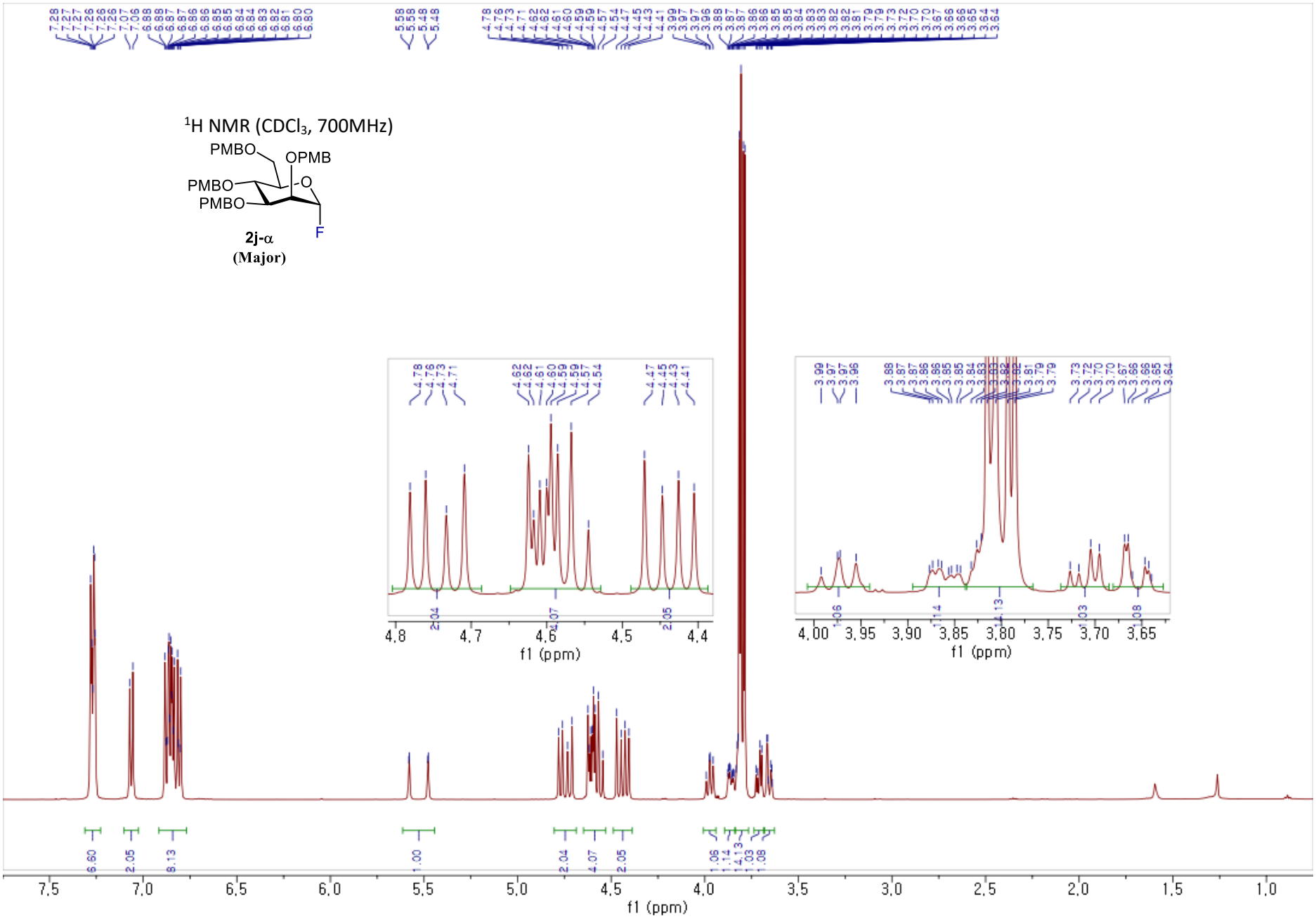

After Work-up
19F NMR (CDCl3, 564 MHz)
138.21
138.23
138.31
138.33
149.50
149.55
149.60
149.64
PMBO
PMBO
PMBO
PMBO
O
F
2i-β
(Major)
PMBO
PMBO
PMBO
PMBO
O
F
2i-α
(Minor)
1.45
1.00
-136.5
-137.0
-137.5
-138.0
-138.5
-139.0
-139.5
-140.0
-140.5
-141.0
-147.5
-148.0
-148.5
-149.0
-149.5
-150.0
-150.5
-151.0
-151.5
f1 (ppm)

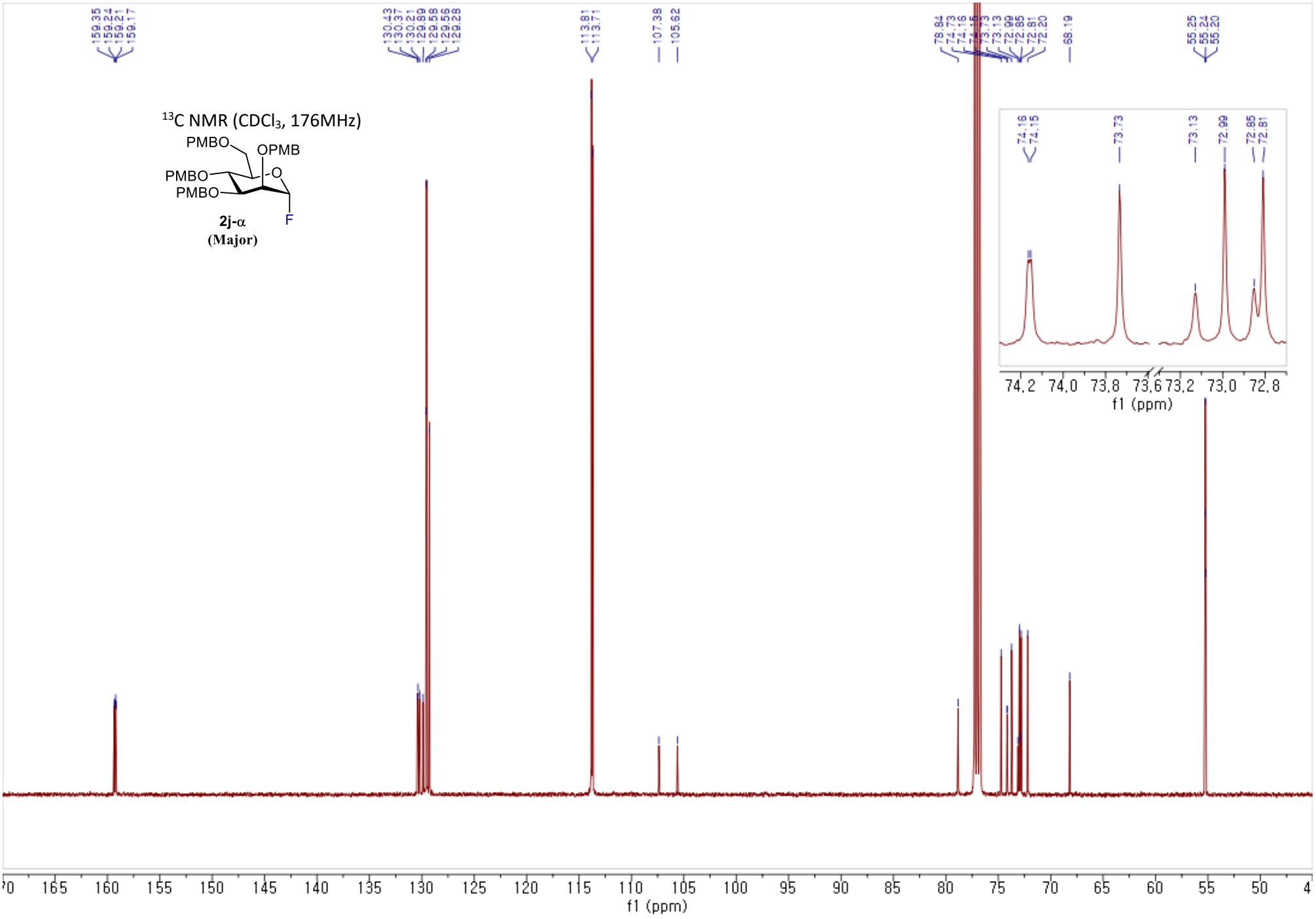
After Purification

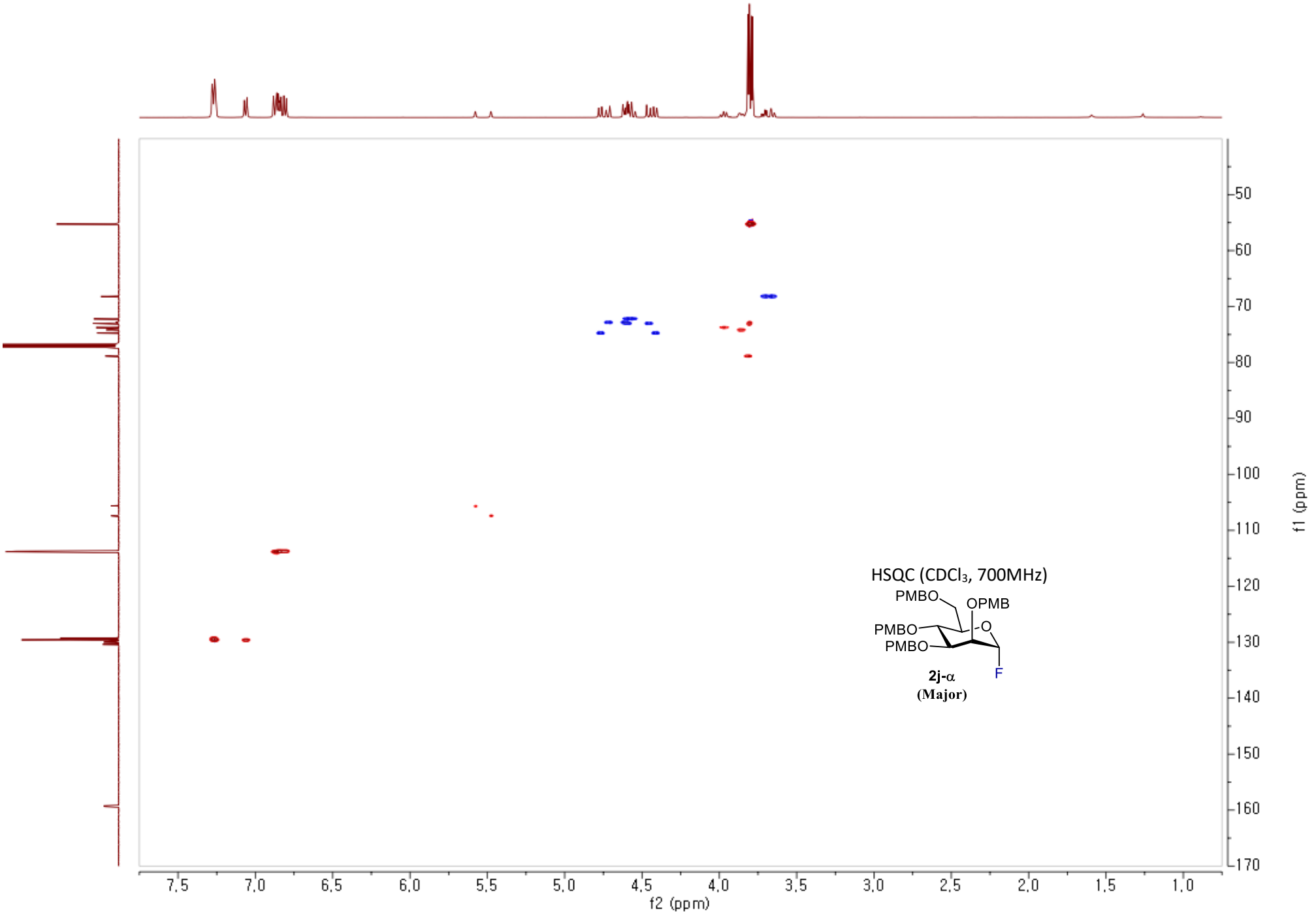
^{19}F NMR ($CDCl_3$, 564 MHz)

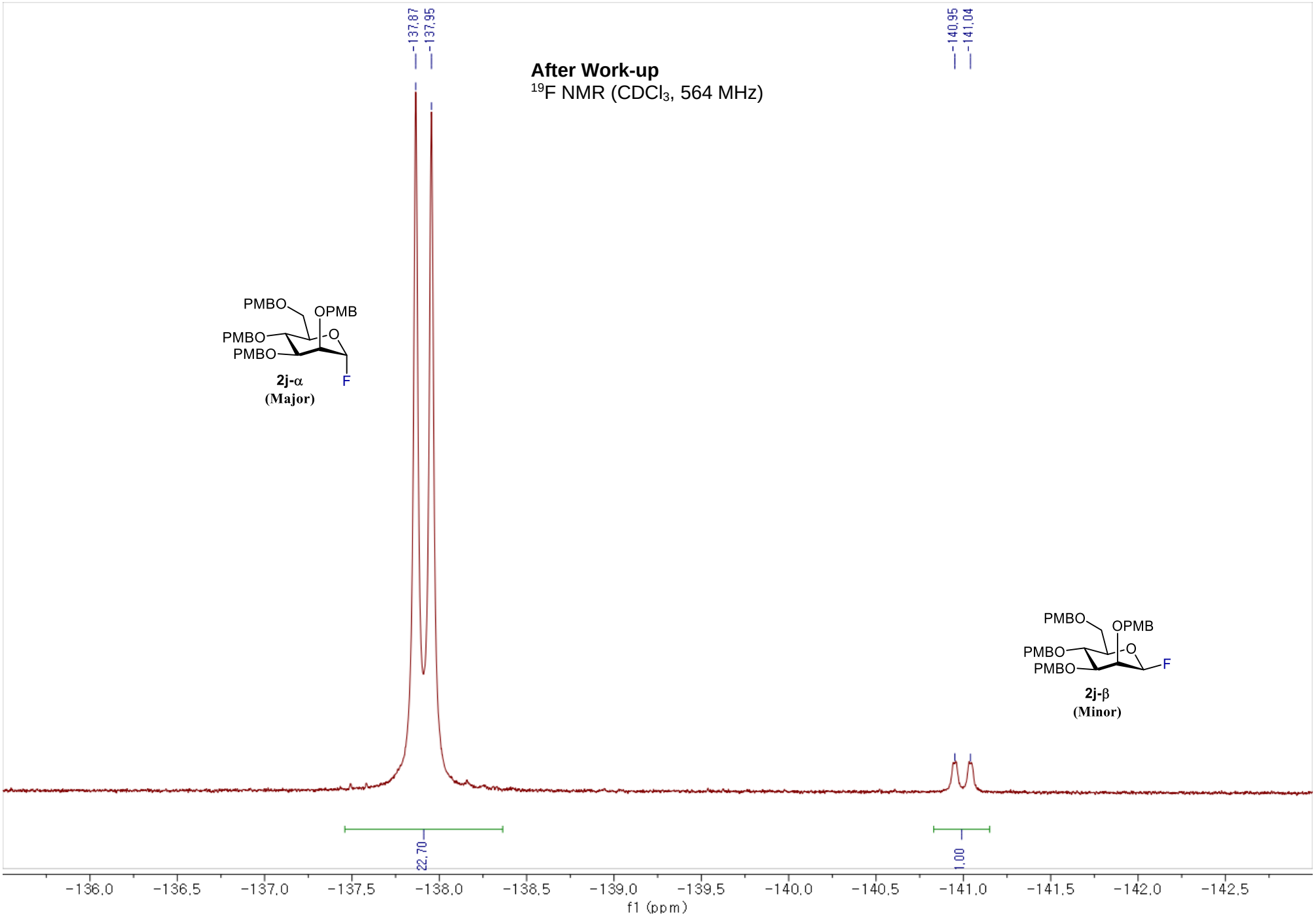


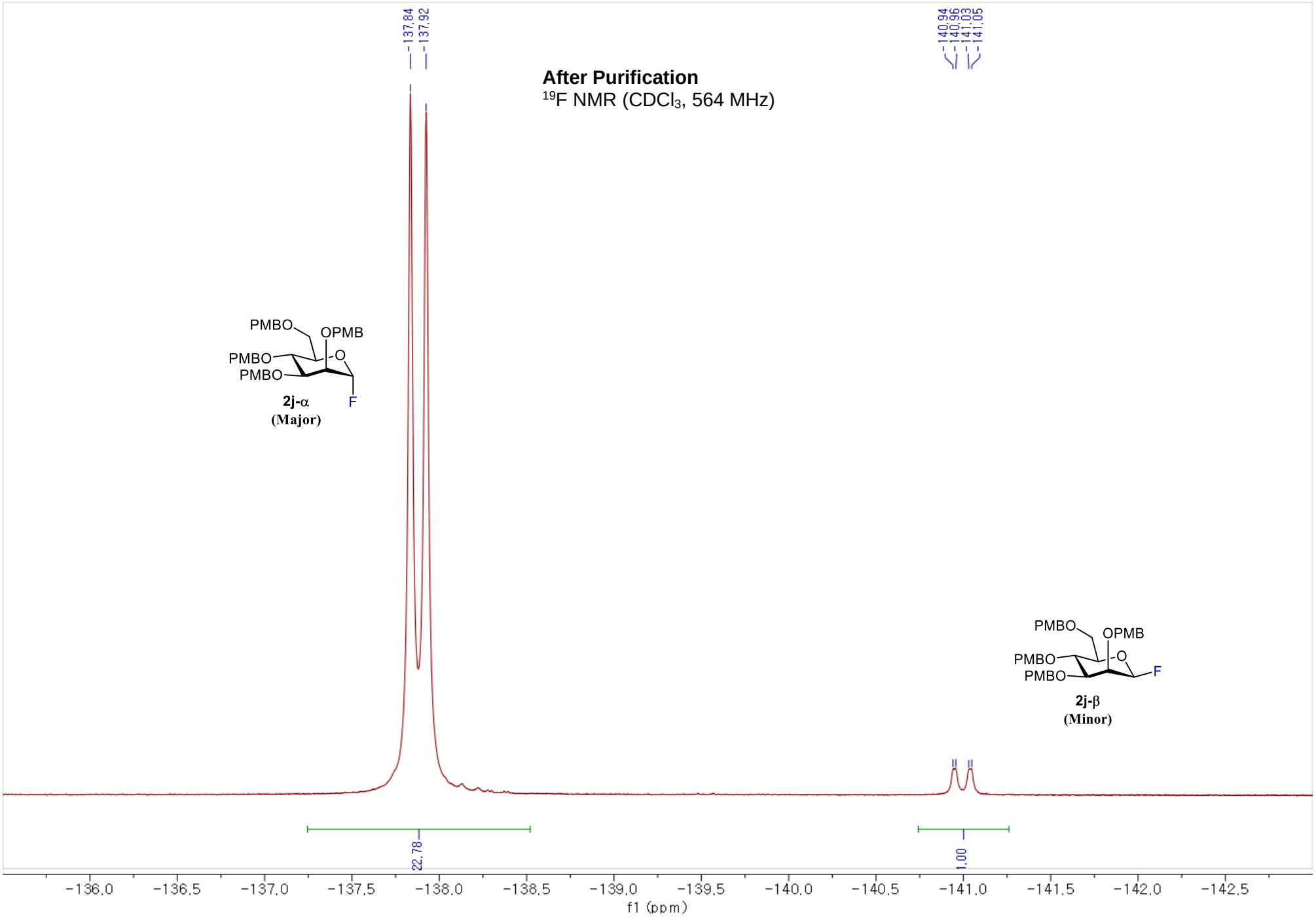
2,3,4,6-Tetrakis-O-[(4-methoxyphenyl)methyl]-α-D-mannopyranosyl fluoride (2j- α, Major diastereomer)

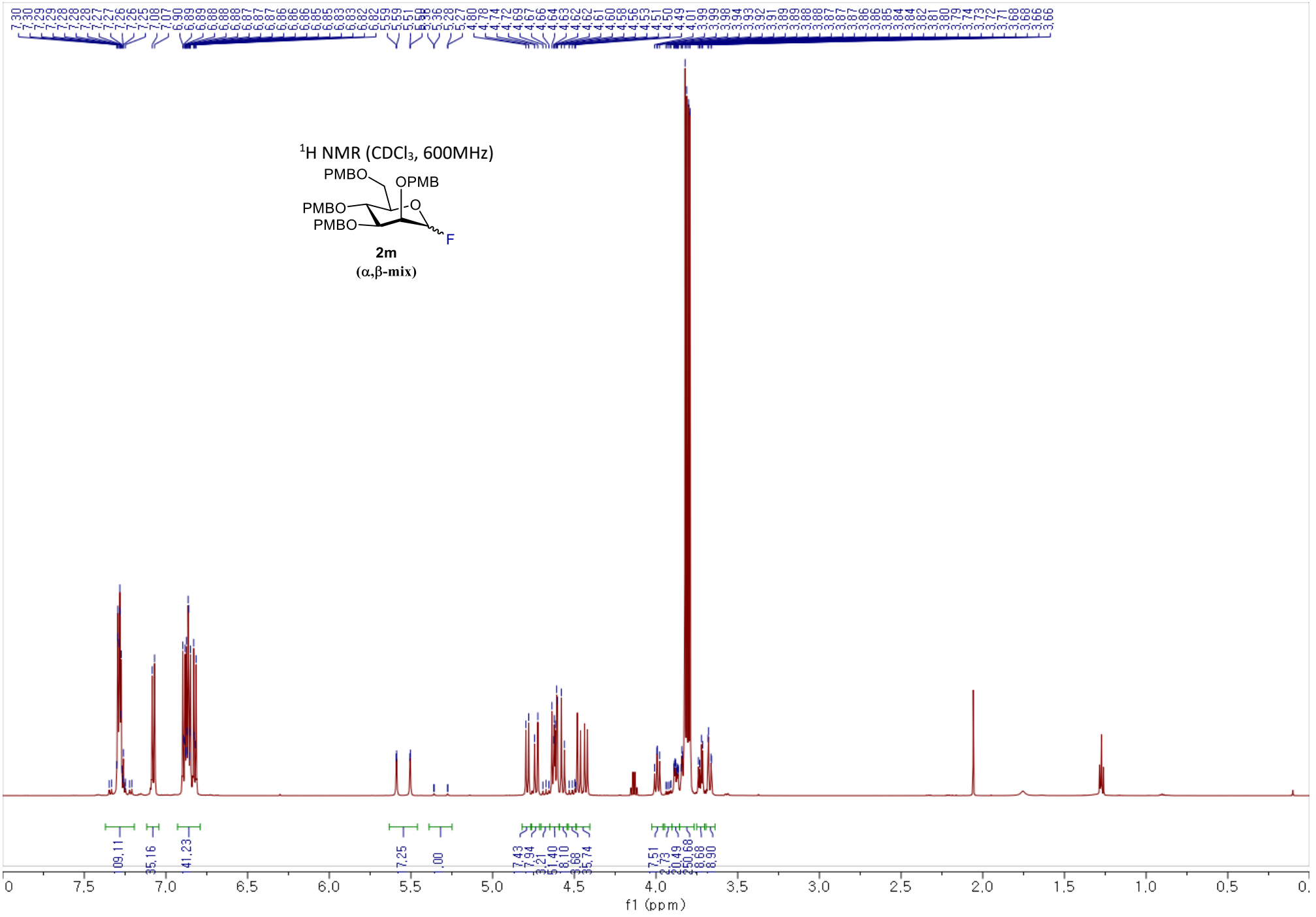



159.35
159.24
159.21
159.17
130.43
130.37
130.21
129.89
129.58
129.56
129.28
113.81
113.71
107.38
105.62
78.84
74.73
74.16
74.15
73.73
73.13
72.99
72.85
72.81
72.20
68.19
55.25
55.24
55.20
13C NMR (CDCl3, 176MHz)
PMBO
OPMB
PMBO
PMBO
O
F
2j-α
(Major)
74.16
74.15
73.73
73.13
72.99
72.85
72.81
74.2 74.0 73.8 73.6 73.2 73.0 72.8
f1 (ppm)
165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50
f1 (ppm)

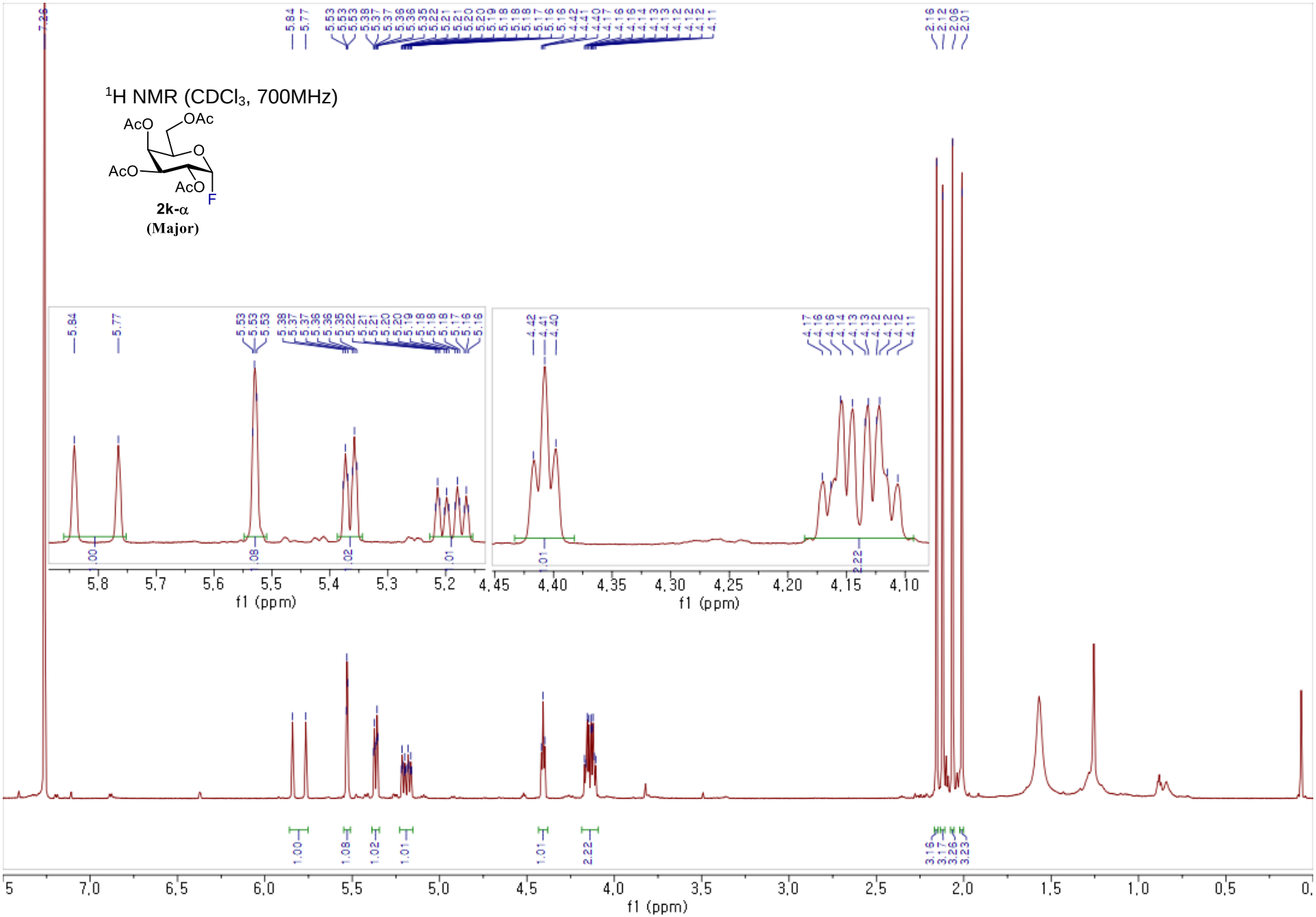

HSQC ($CDCl_3$, 700MHz)
PMBO
OPMB
PMBO
O
PMBO
F
2j-α
(Major)
f2 (ppm)
f1 (ppm)

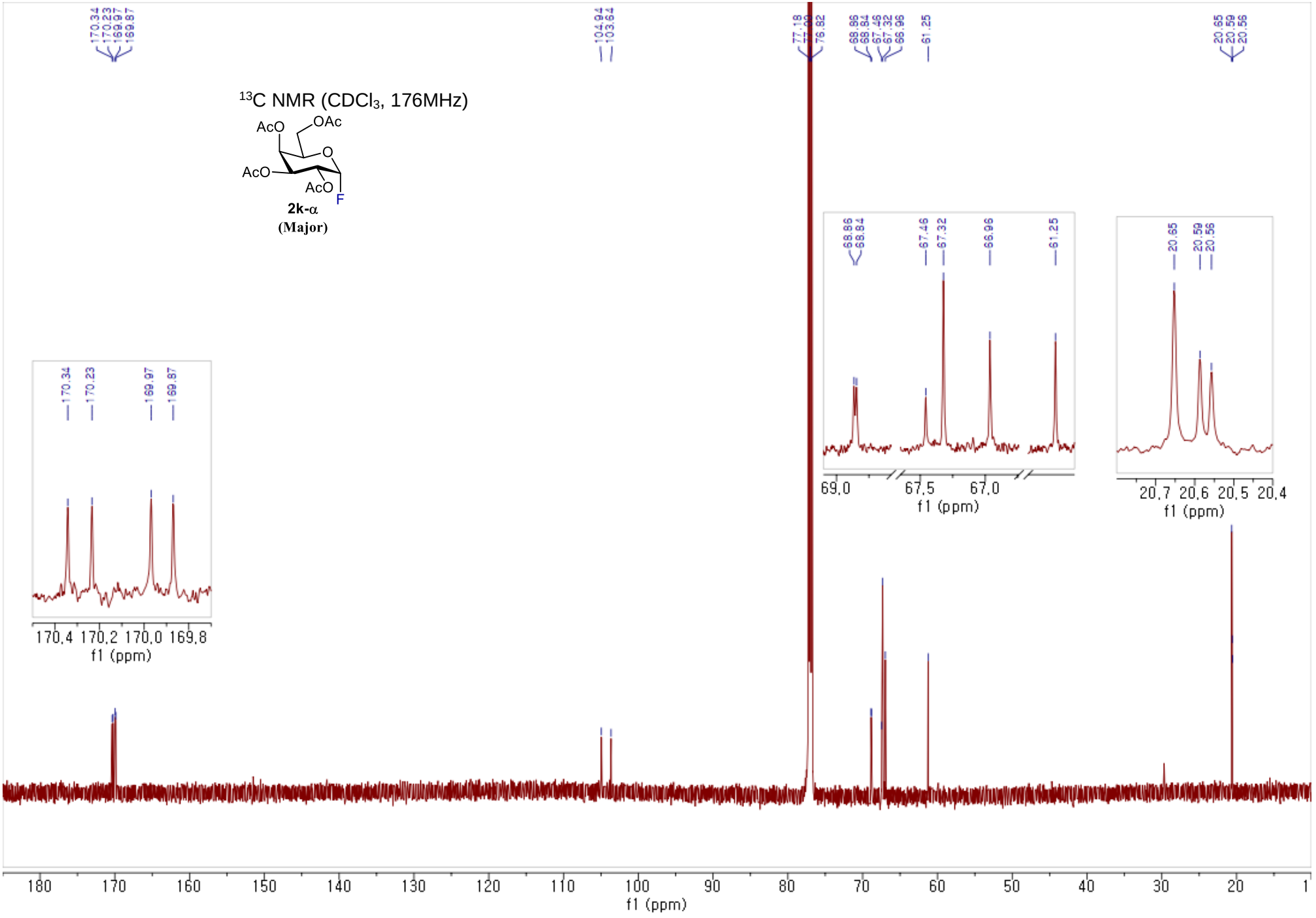

After Work-up
19F NMR (CDCl3, 564 MHz)
-137.87
-137.95
-140.95
-141.04
PMBO
OPMB
PMBO
PMBO
O
F
2j-α
(Major)
PMBO
OPMB
PMBO
PMBO
O
F
2j-β
(Minor)
22.70
1.00
-136.0
-136.5
-137.0
-137.5
-138.0
-138.5
-139.0
-139.5
-140.0
-140.5
-141.0
-141.5
-142.0
-142.5
f1 (ppm)

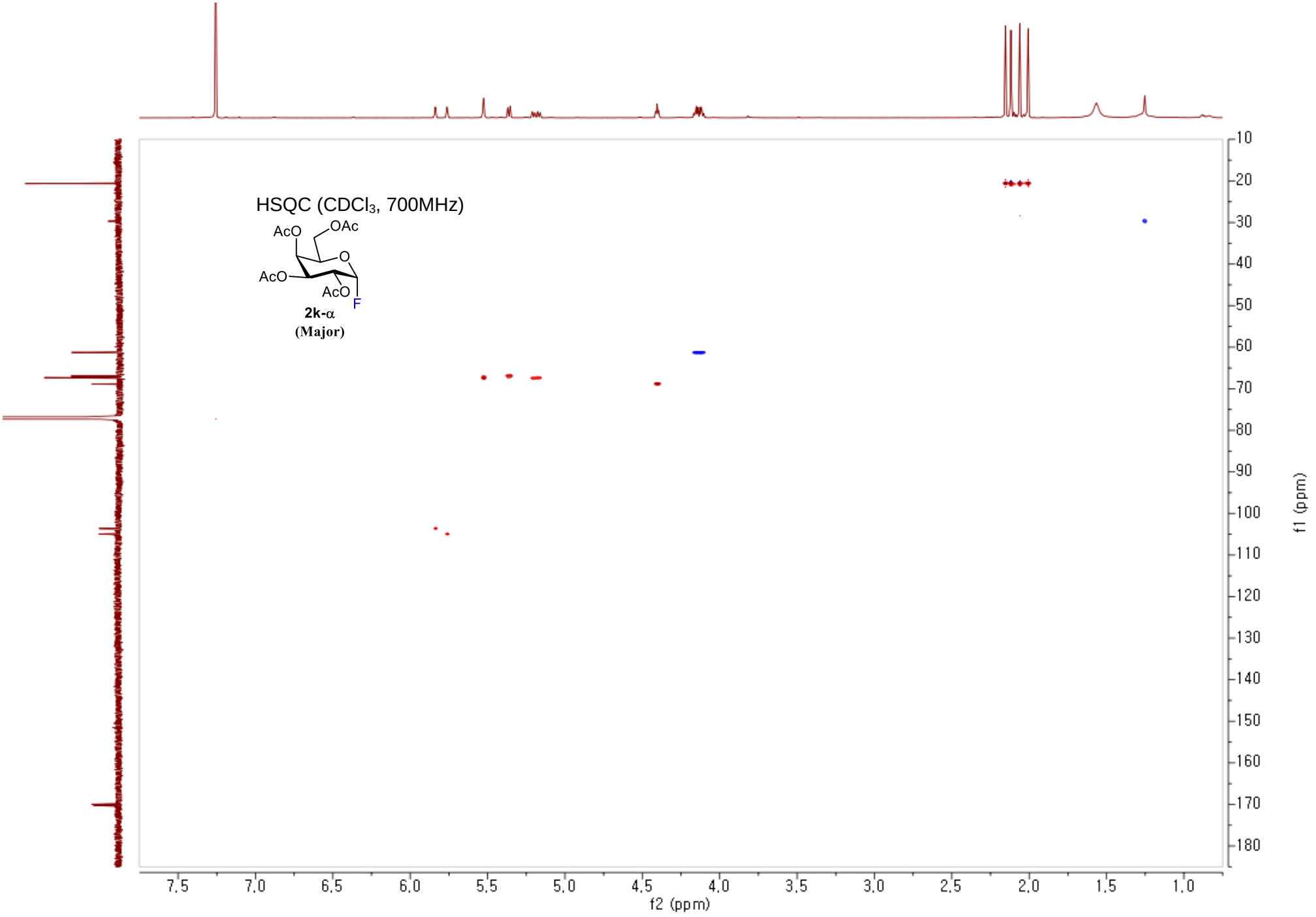

After Purification
19F NMR (CDCl3, 564 MHz)
-137.84
-137.92
-140.94
-140.96
-141.03
-141.05
PMBO
OPMB
PMBO
PMBO
O
F
2j-α
(Major)
PMBO
OPMB
PMBO
PMBO
O
F
2j-β
(Minor)
22.78
1.00
-136.0
-136.5
-137.0
-137.5
-138.0
-138.5
-139.0
-139.5
-140.0
-140.5
-141.0
-141.5
-142.0
-142.5
f1 (ppm)


^{1}H NMR ($CDCl_3$, 600MHz)
PMBO
OPMB
PMBO
O
PMBO
F
2m
(α,β-mix)
f1 (ppm)

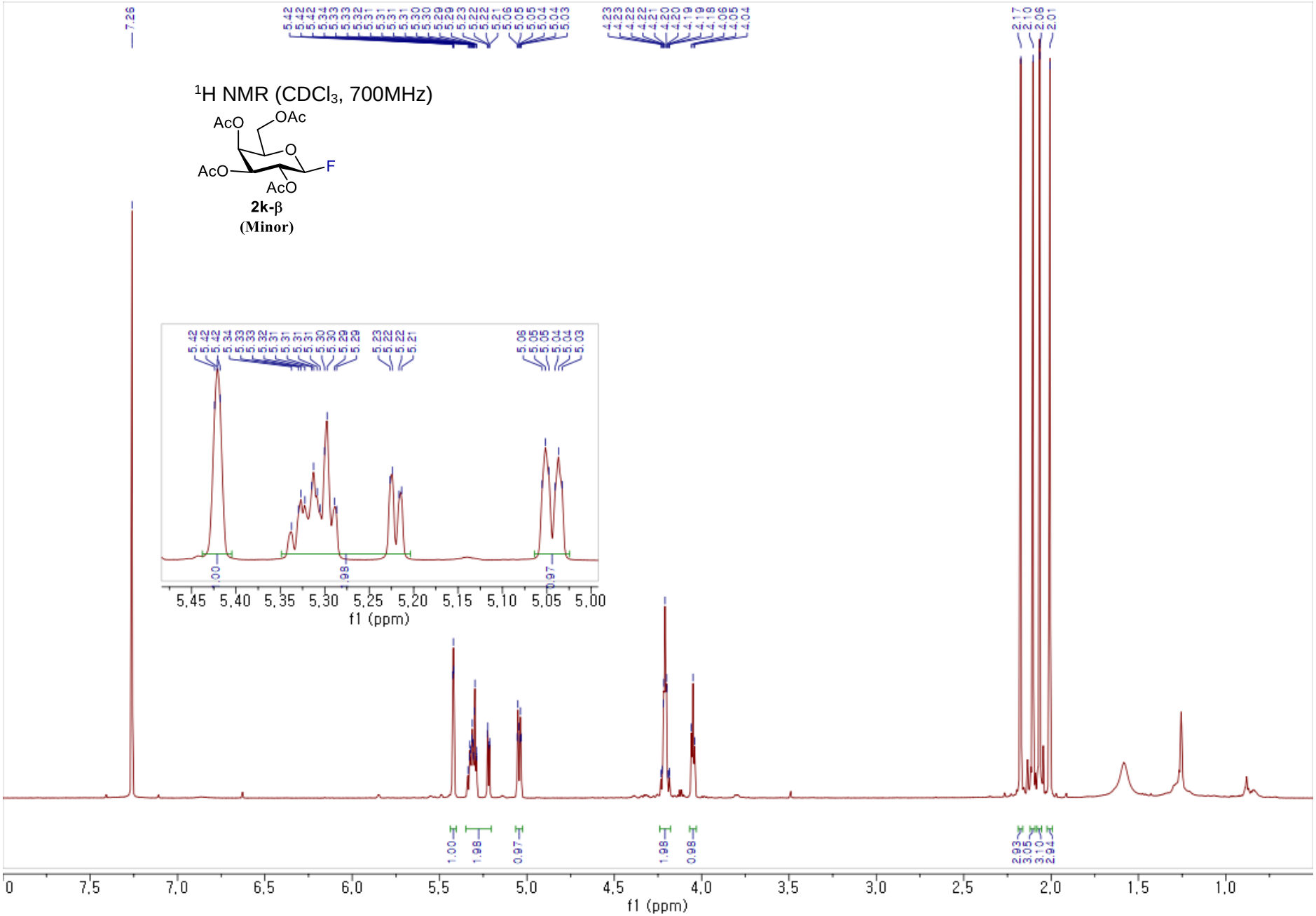
2,3,4,6-Tetra-*O*-acetyl-α-D-galactopyranosyl fluoride (2k-α, Major diastereomer)

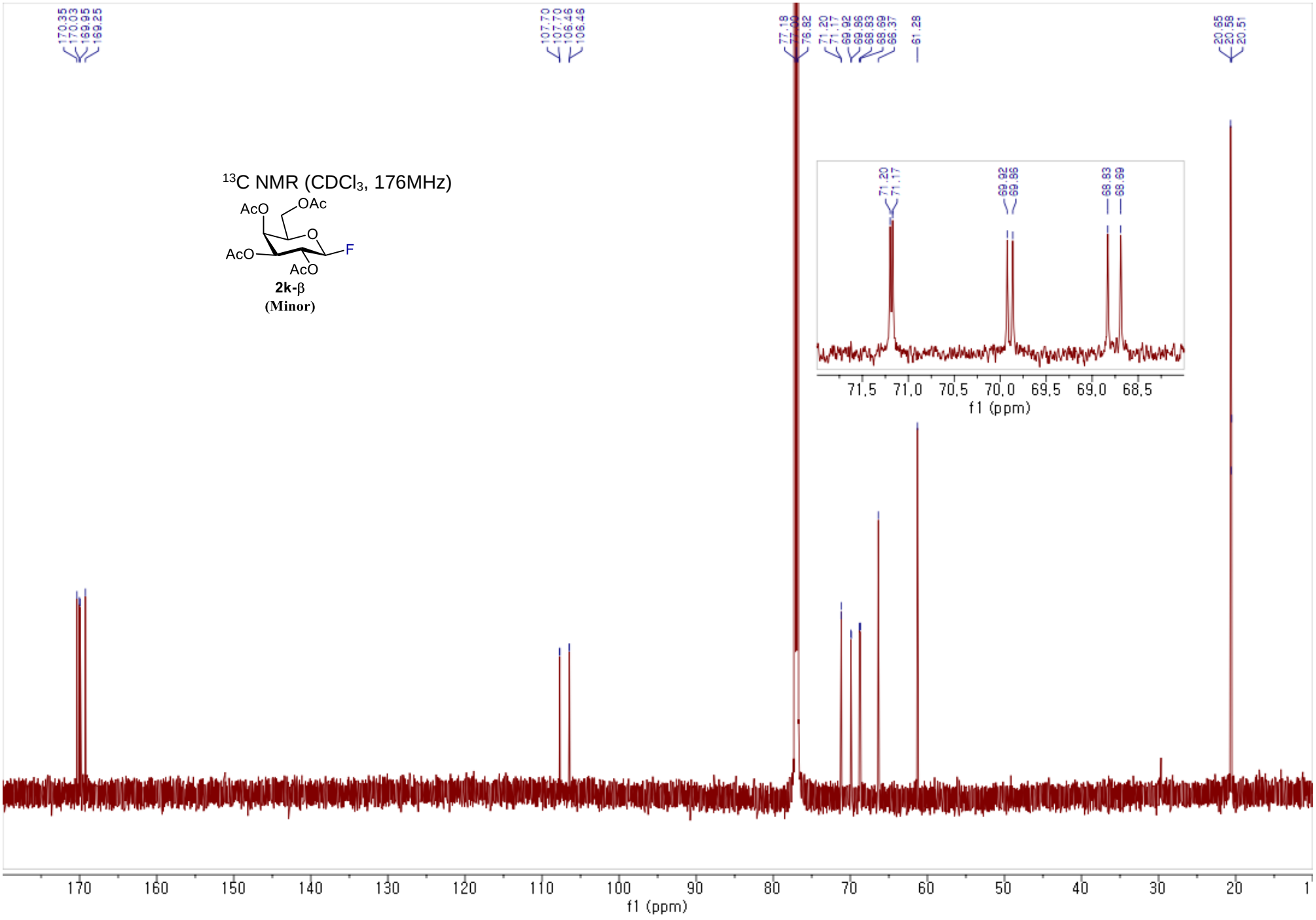


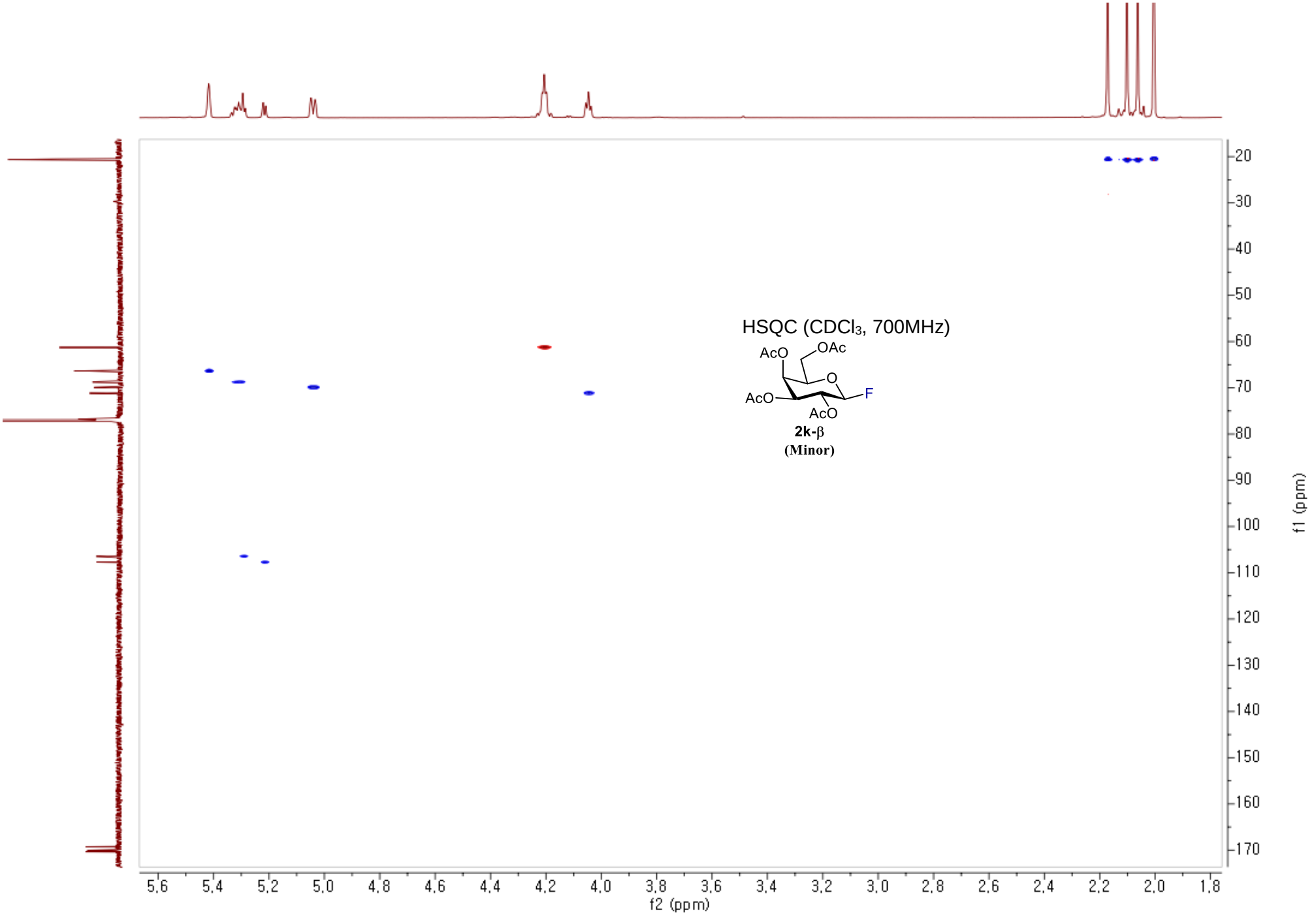

^{13}C NMR ($CDCl_3$, 176MHz)
AcO
OAc
O
AcO
AcO
F
2k-α
(Major)
170.34
170.23
169.97
169.87
104.94
103.64
77.18
76.82
68.86
68.84
67.46
67.32
66.96
61.25
20.65
20.59
20.56
170.4 170.2 170.0 169.8
f1 (ppm)
69.0 67.5 67.0
f1 (ppm)
20.7 20.6 20.5 20.4
f1 (ppm)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 1
f1 (ppm)


HSQC (CDCl3, 700MHz)
AcO
OAc
O
AcO
AcO
F
2k-α
(Major)
f2 (ppm)
f1 (ppm)

2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl fluoride (2k-β, Minor diastereomer)

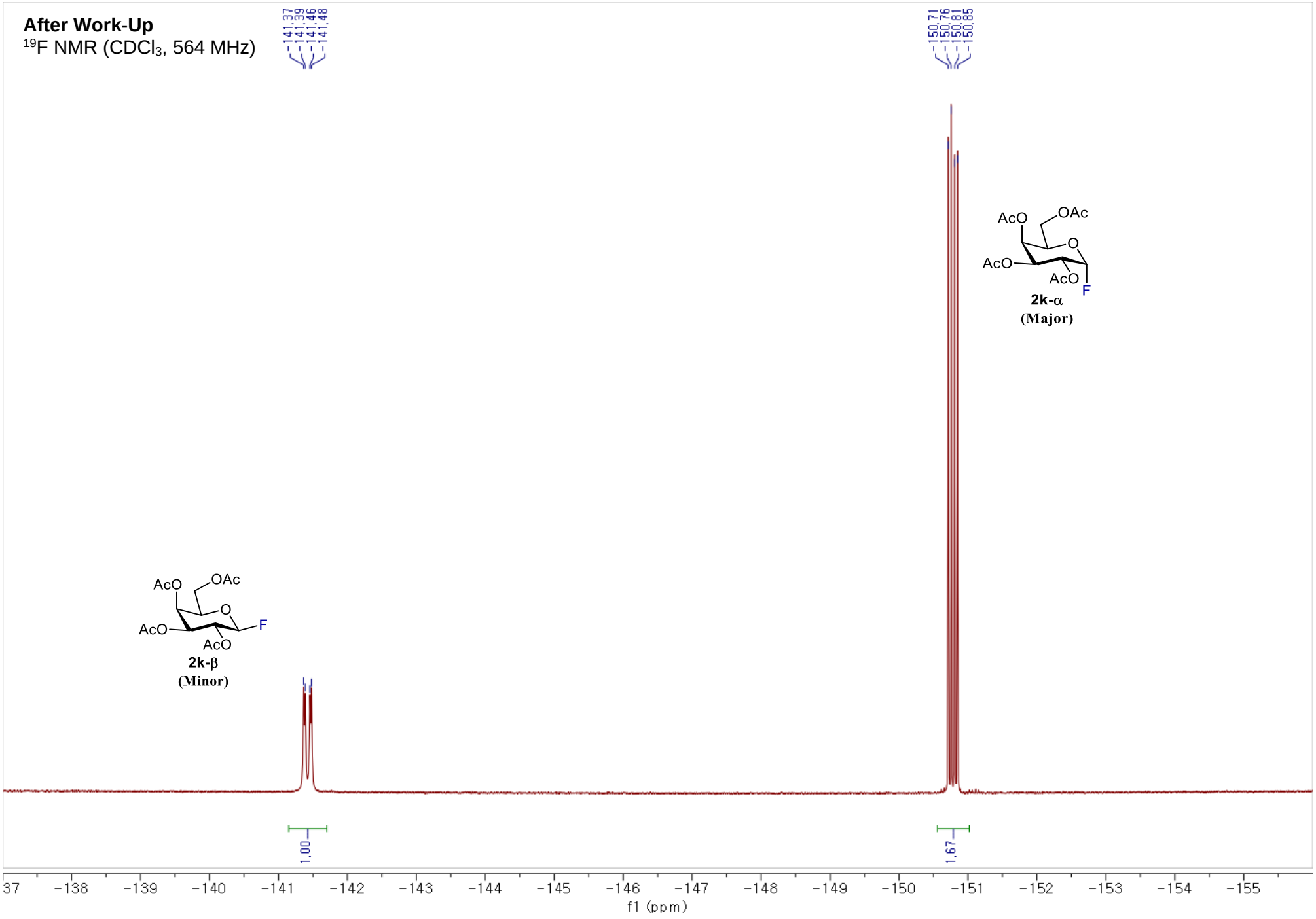



170.35
170.03
169.95
169.25
107.70
107.70
106.46
106.46
77.18
77.00
76.82
71.20
71.17
69.92
69.86
68.83
68.69
66.37
61.28
20.65
20.58
20.51
^{13}C NMR ($CDCl_3$, 176MHz)
AcO
OAc
O
F
AcO
AcO
2k-β
(Minor)
71.20
71.17
69.92
69.86
68.83
68.69
71,5 71,0 70,5 70,0 69,5 69,0 68,5
f1 (ppm)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 1
f1 (ppm)


HSQC (CDCl3, 700MHz)
AcO
OAc
O
AcO
F
AcO
2k-β
(Minor)
f2 (ppm)
f1 (ppm)

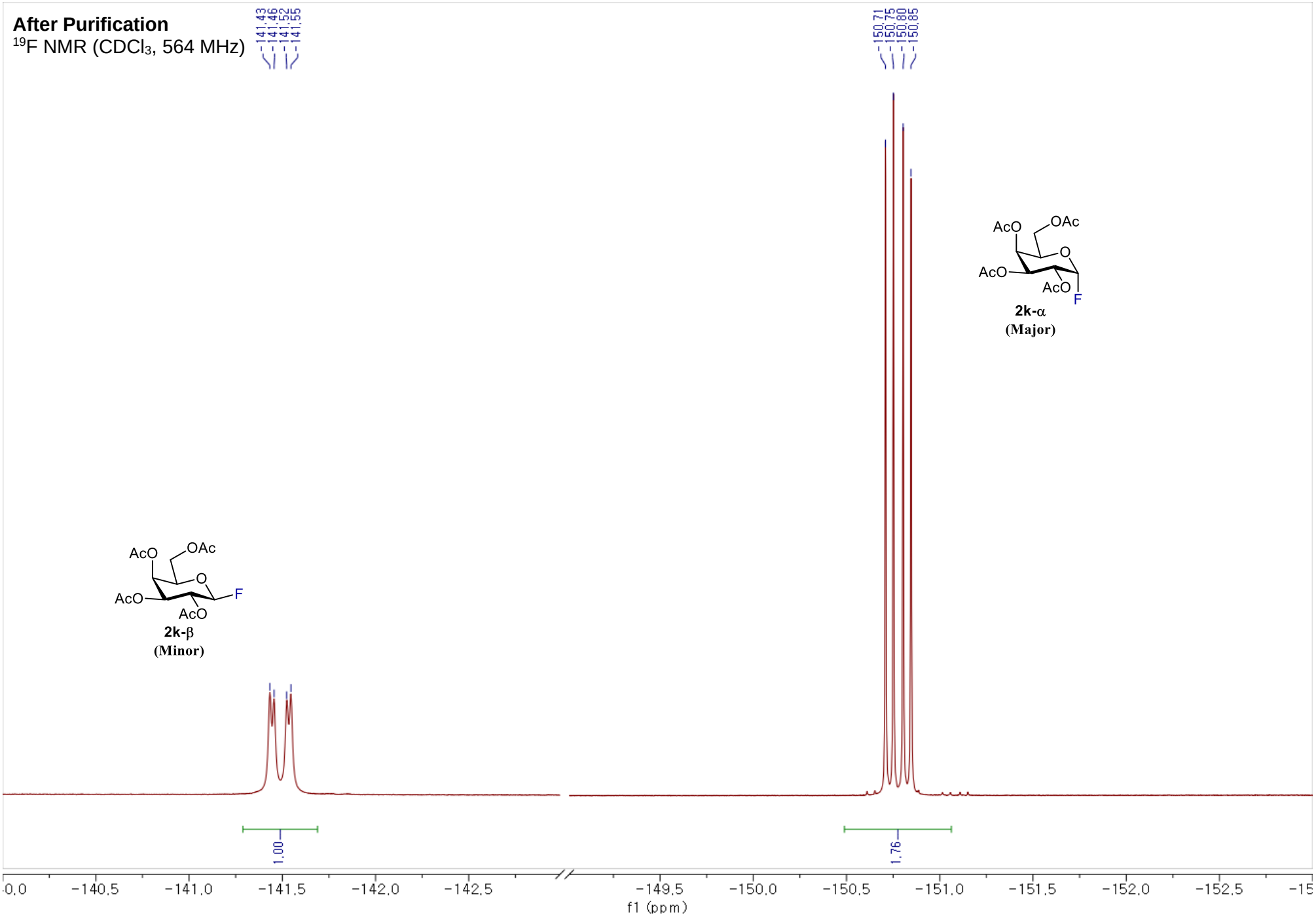
After Work-Up

^{19}F NMR ($CDCl_3$, 564 MHz)

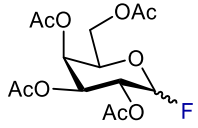


After Purification

^{19}F NMR ($CDCl_3$, 564 MHz)



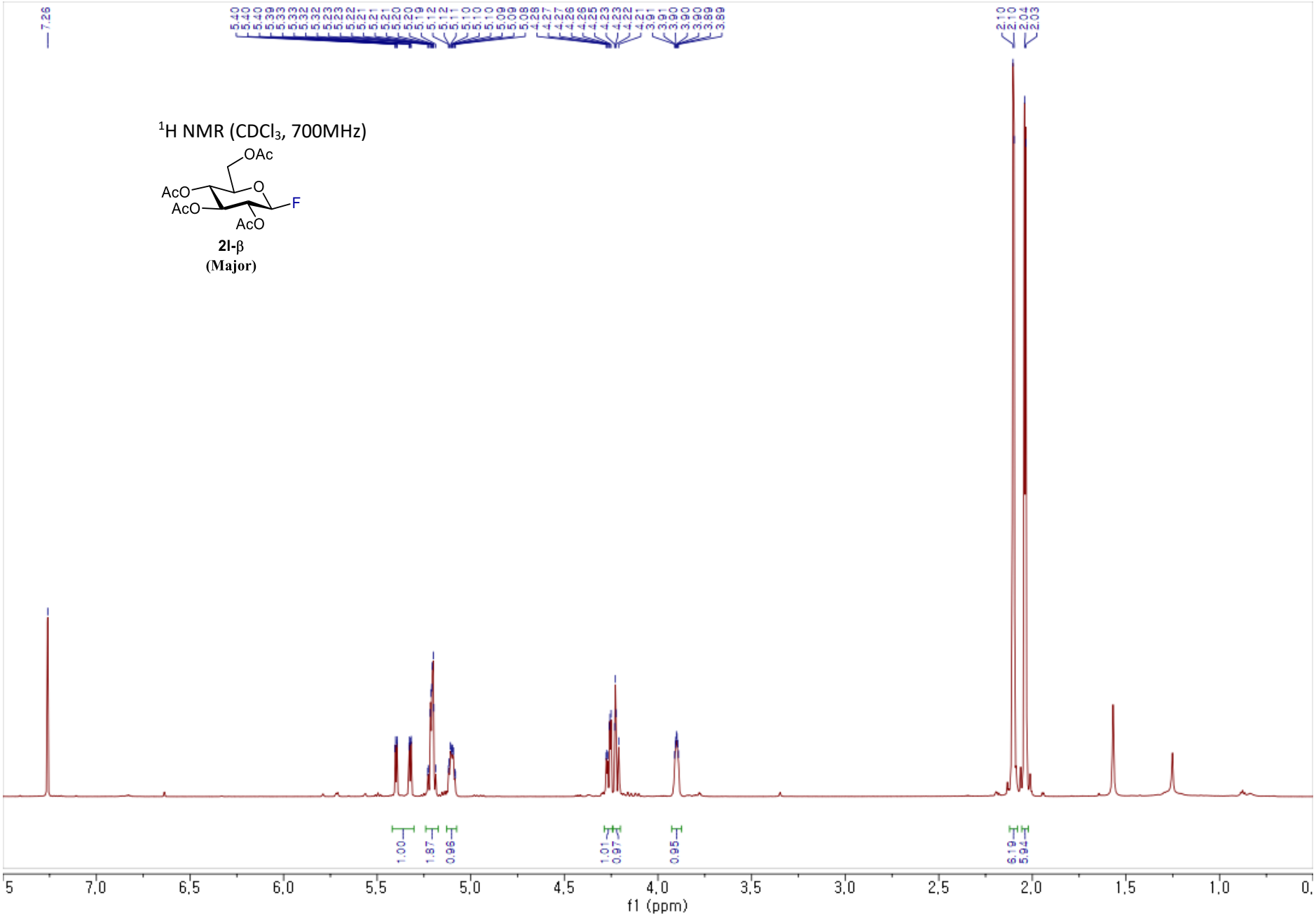
^{1}H NMR ($CDCl_3$, 600MHz)

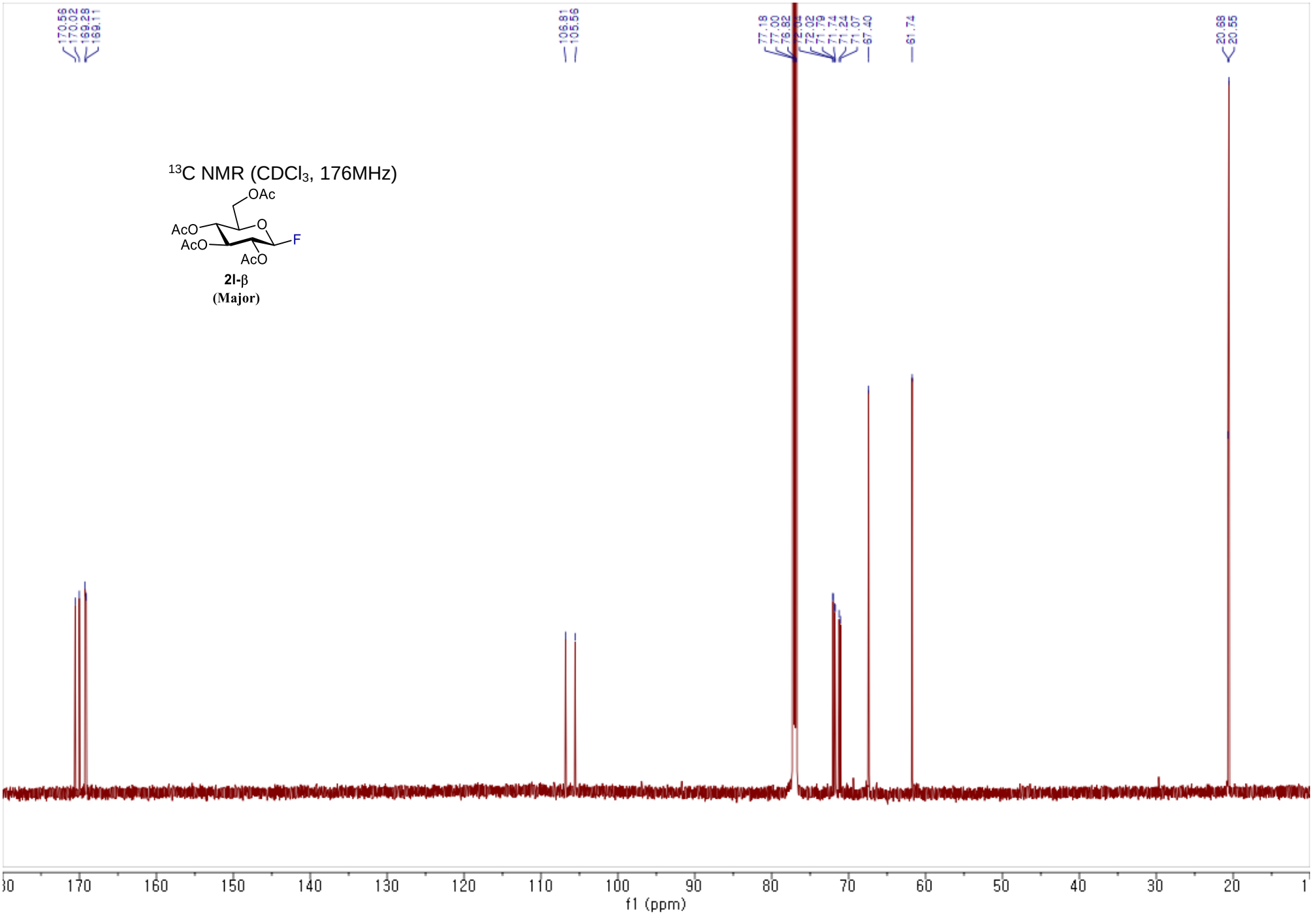


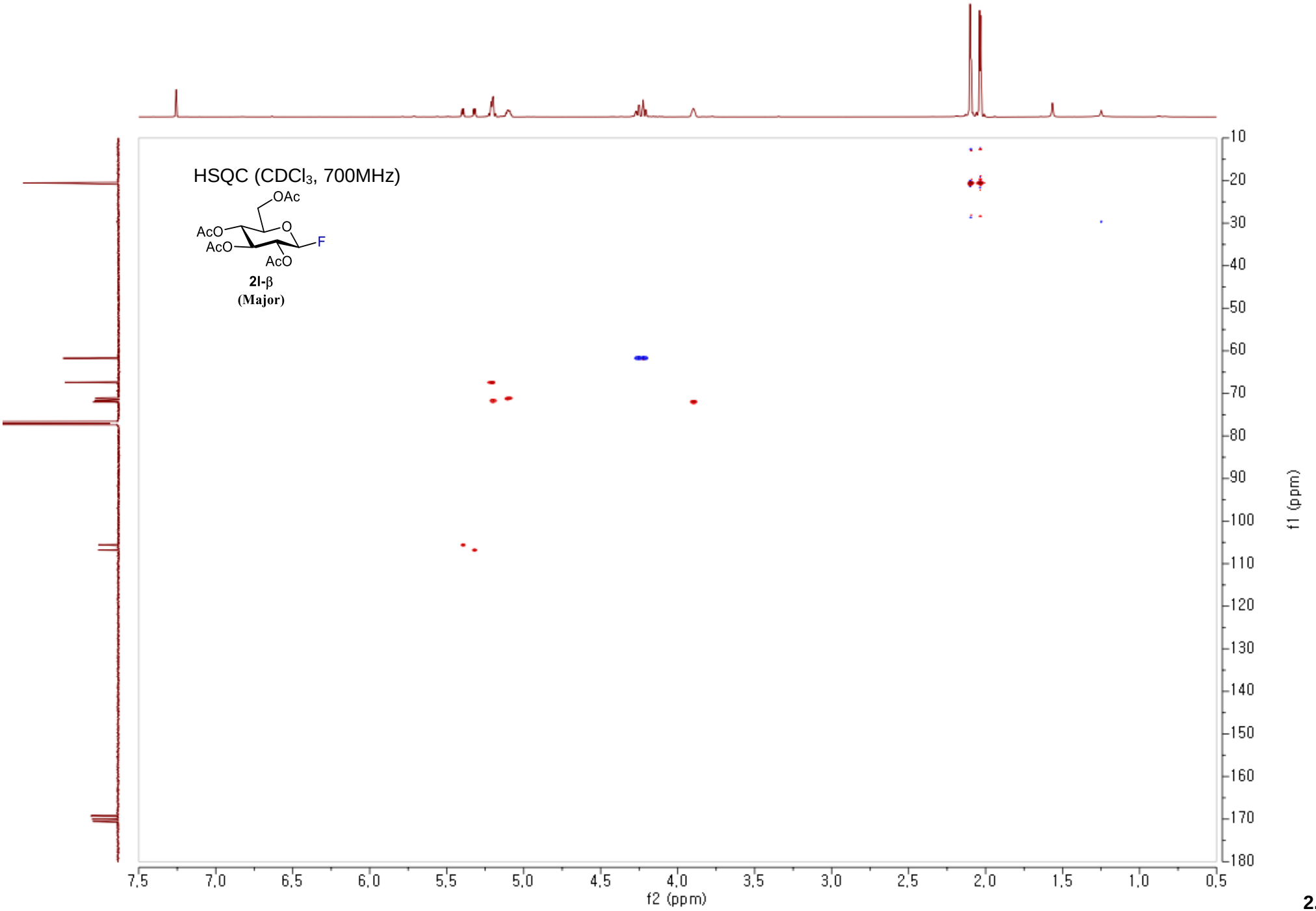
2k

(α,β-mix)

2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl fluoride (2l-β, Major diastereomer)

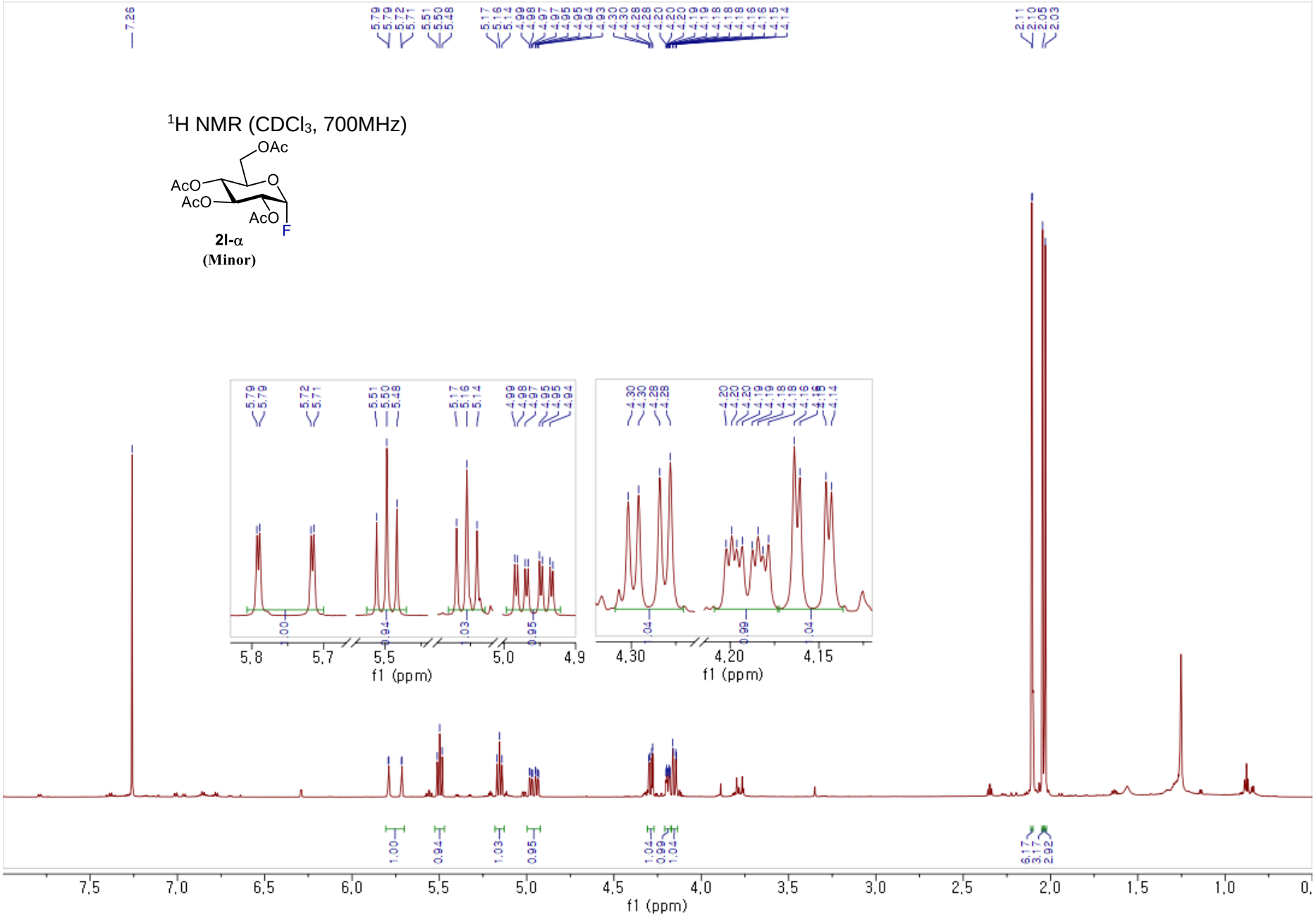


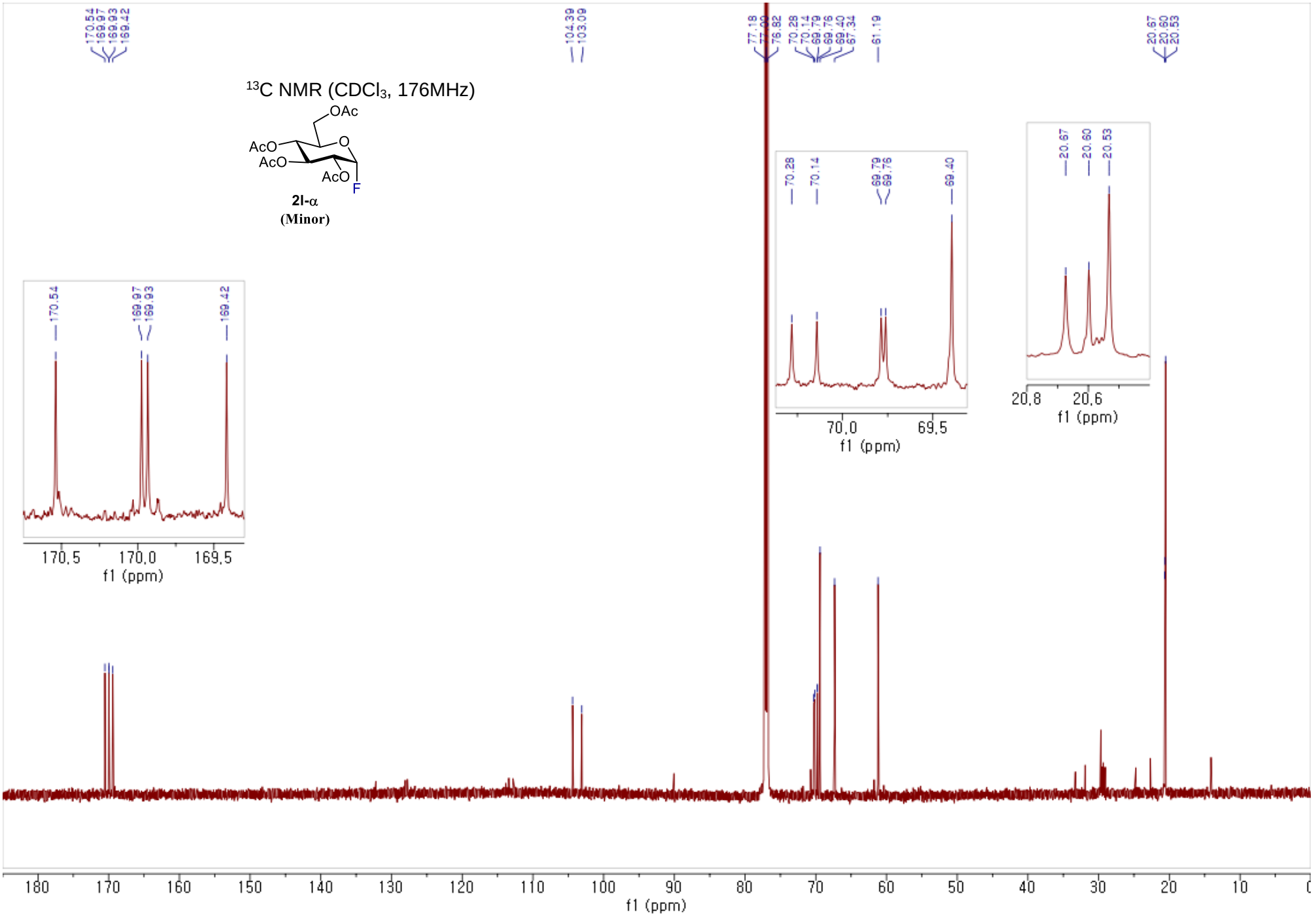

170.56
170.02
169.28
169.11
106.81
105.56
77.18
77.00
76.82
72.02
71.79
71.74
71.24
71.07
67.40
61.74
20.68
20.55
13C NMR (CDCl3, 176MHz)
OAc
AcO
AcO
AcO
O
F
2l-β
(Major)
f1 (ppm)

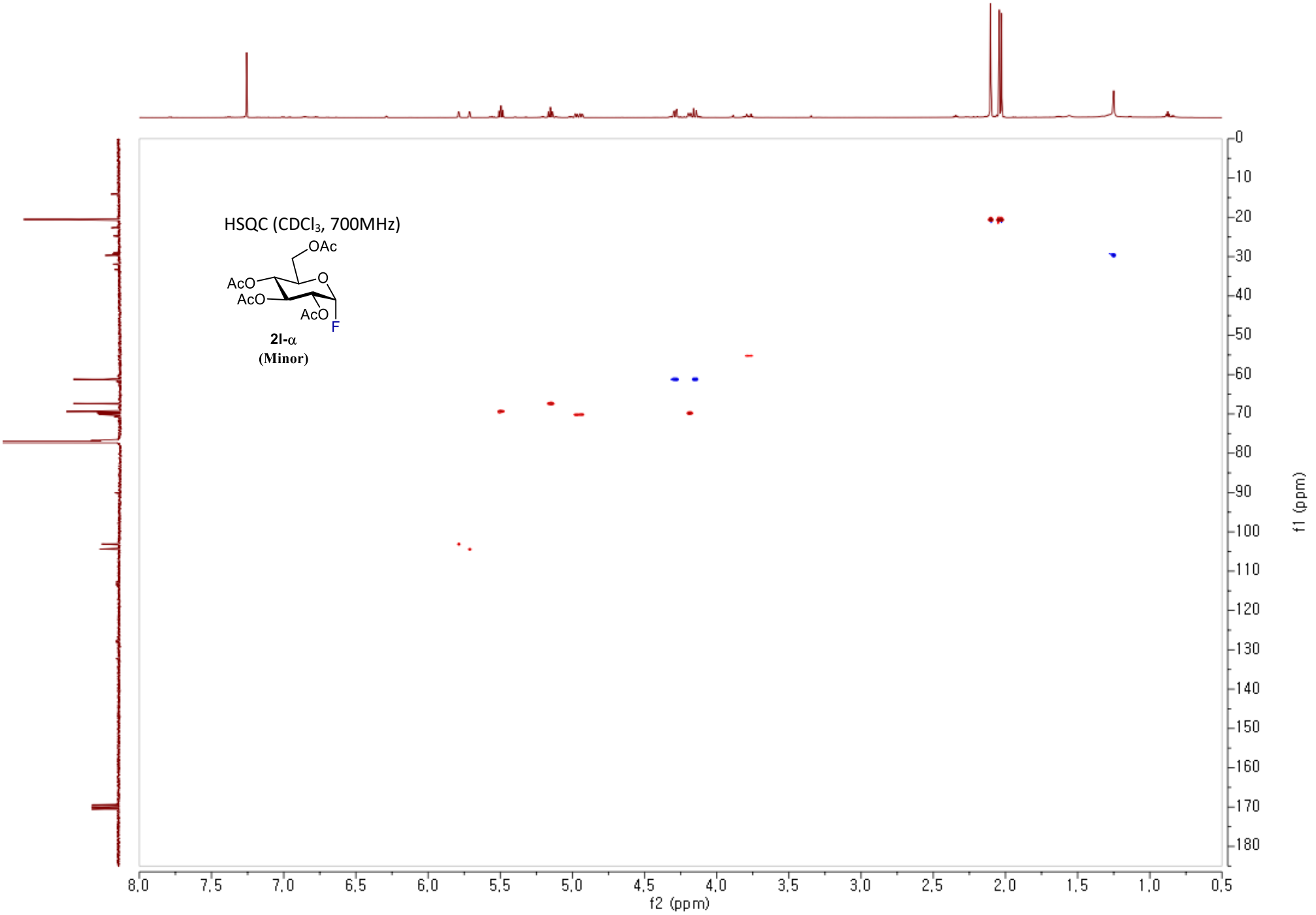


2,3,

2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl fluoride (2l-α, Minor diastereomer)

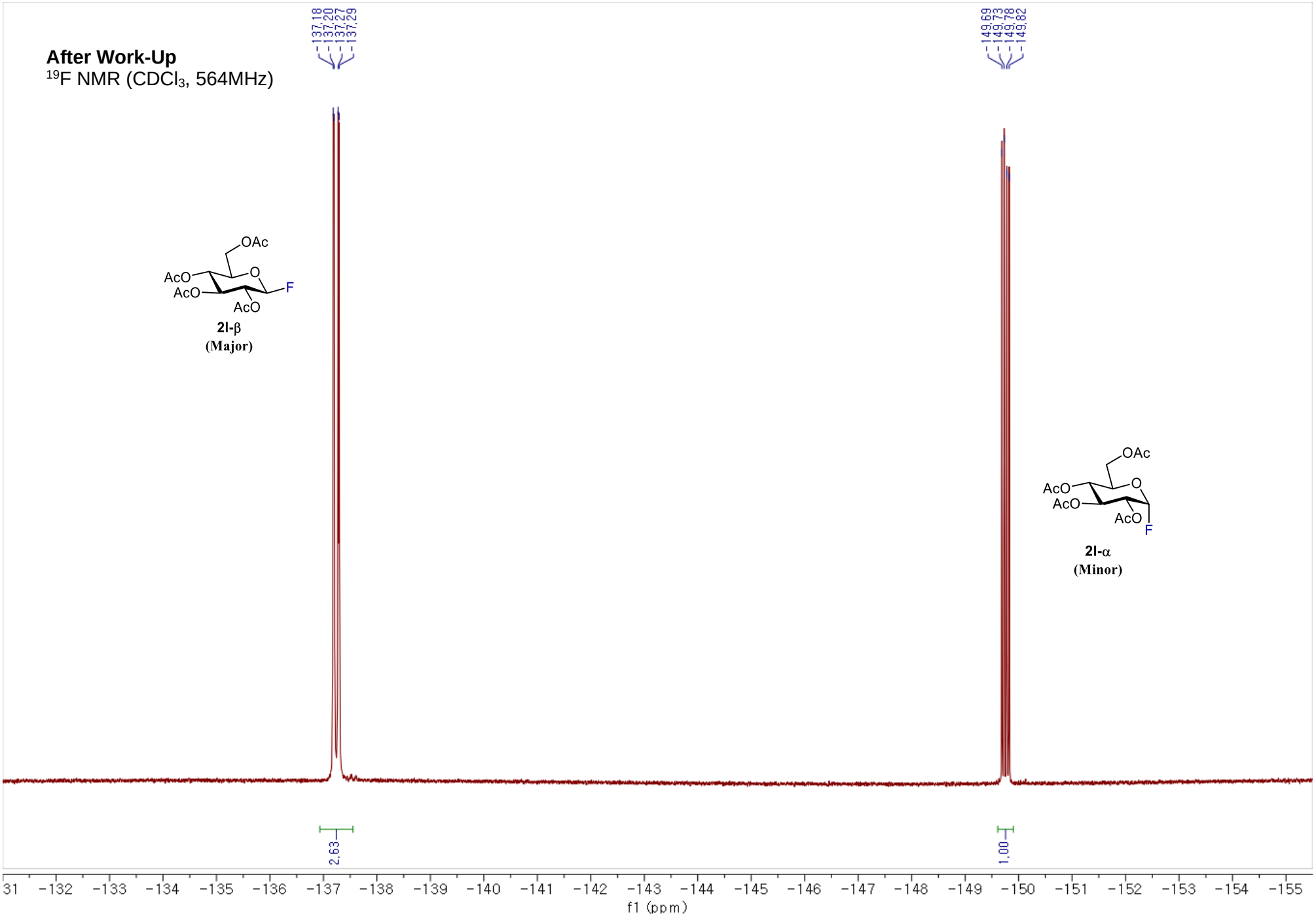



^{13}C NMR ($CDCl_3$, 176MHz)
OAc
AcO
AcO
AcO
O
F
2l-α
(Minor)
170.54
169.97
169.93
169.42
104.39
103.09
77.18
76.82
70.28
70.14
69.79
69.76
69.40
67.34
61.19
20.67
20.60
20.53
f1 (ppm)


HSQC ($CDCl_3$, 700MHz)
OAc
AcO
AcO
AcO
O
F
2l-α
(Minor)
f2 (ppm)
f1 (ppm)

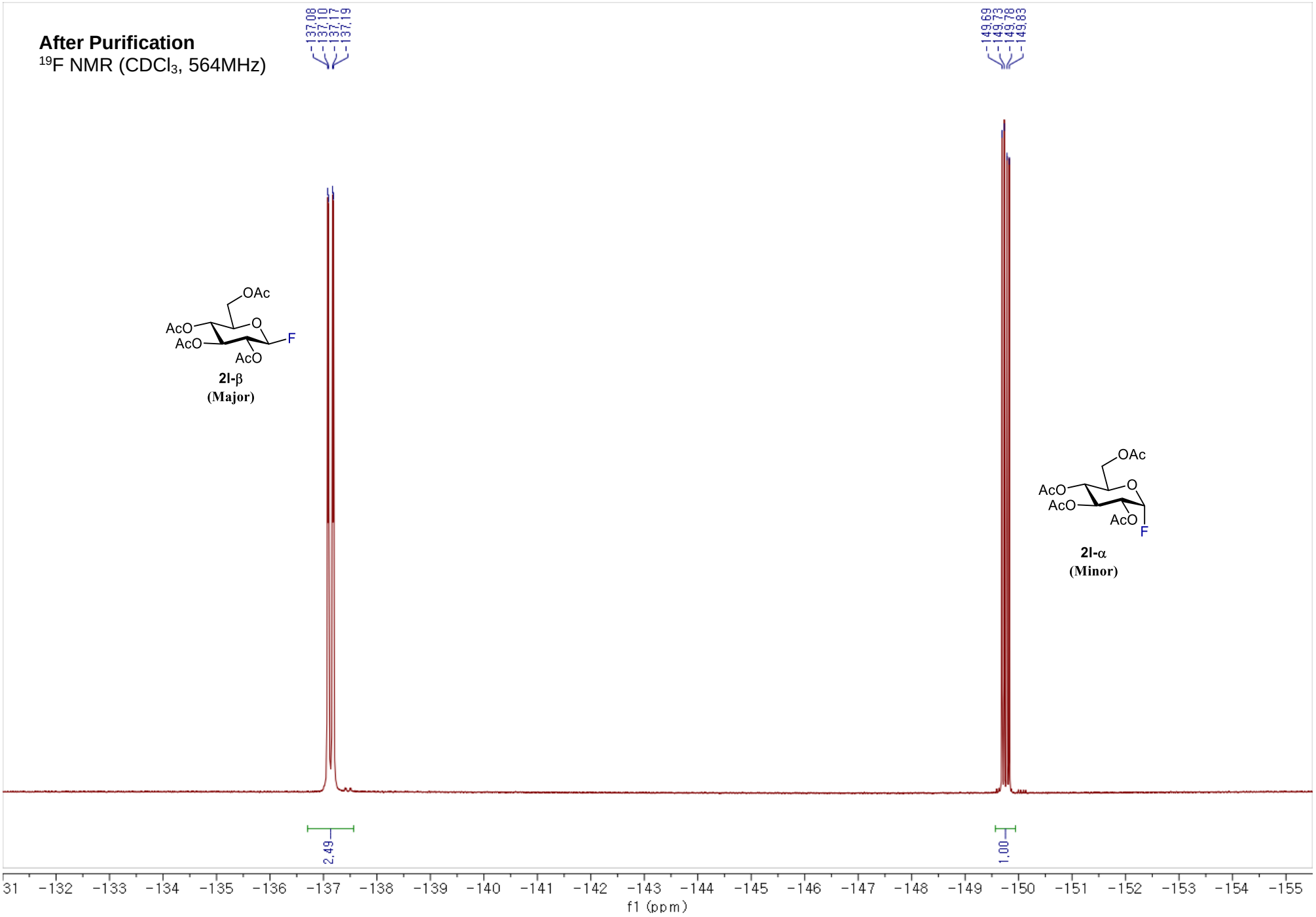
After Work-Up

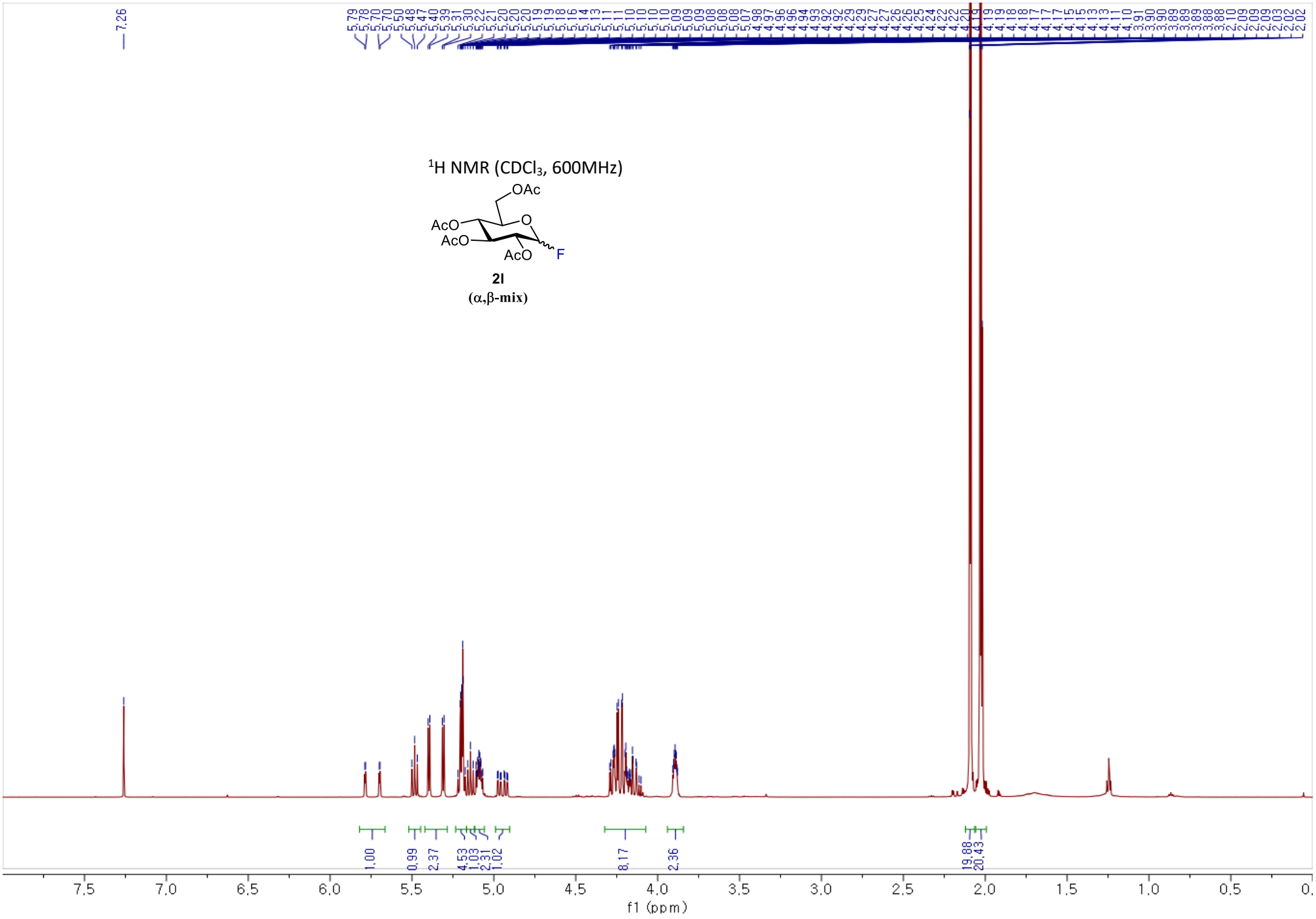
^{19}F NMR ($CDCl_3$, 564MHz)



After Purification

^{19}F NMR ($CDCl_3$, 564MHz)



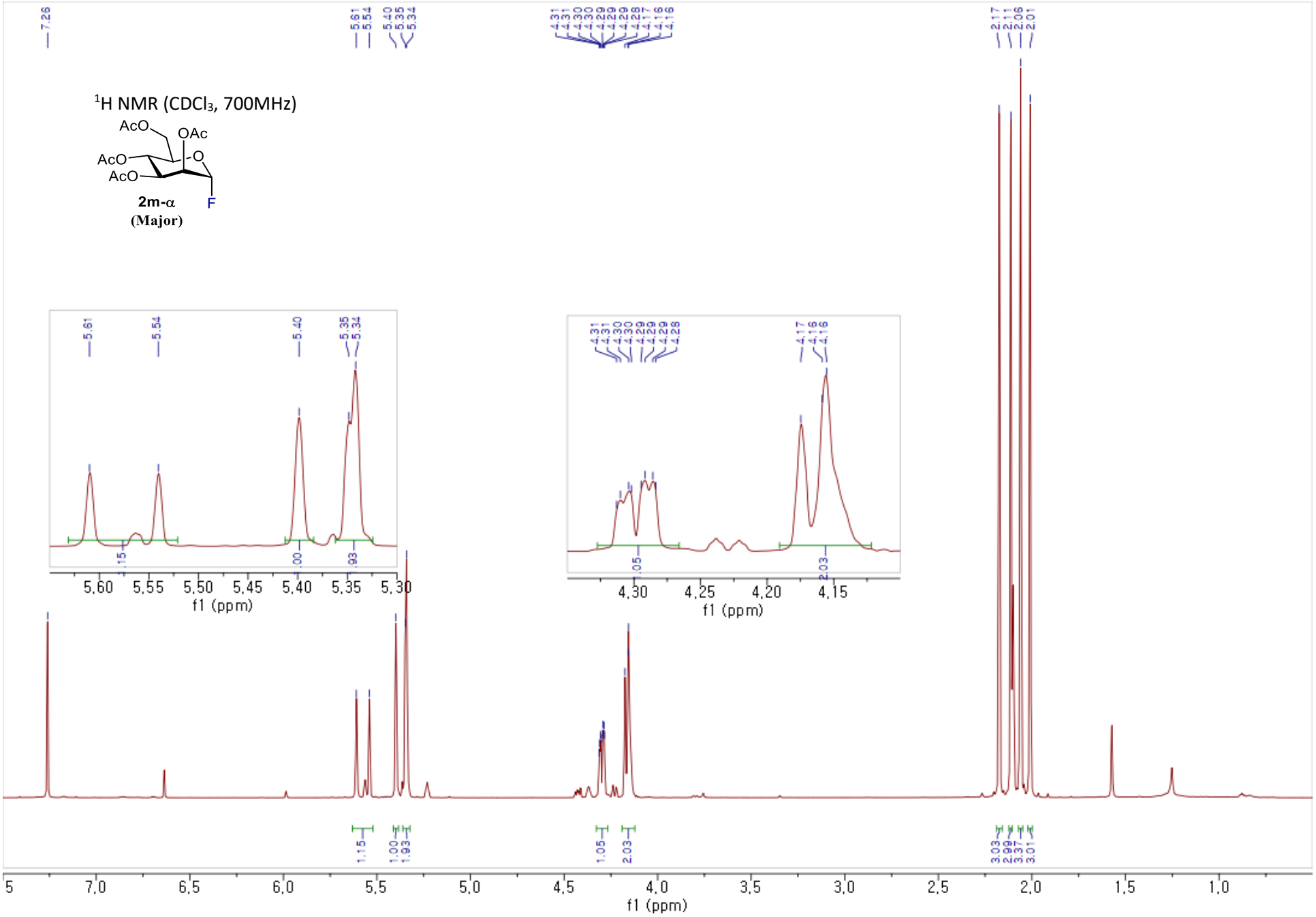


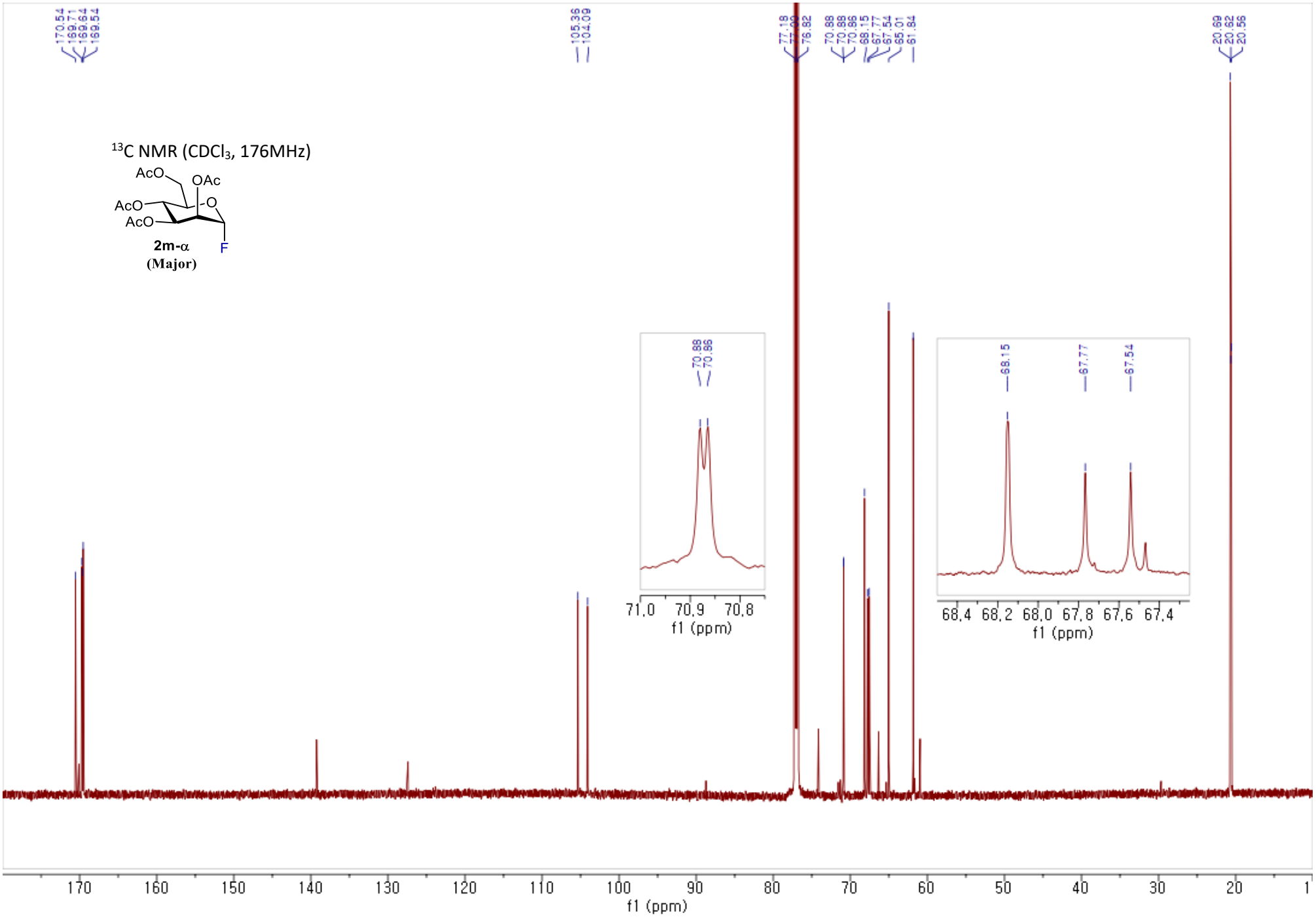
^{1}H NMR ($CDCl_3$, 600MHz)

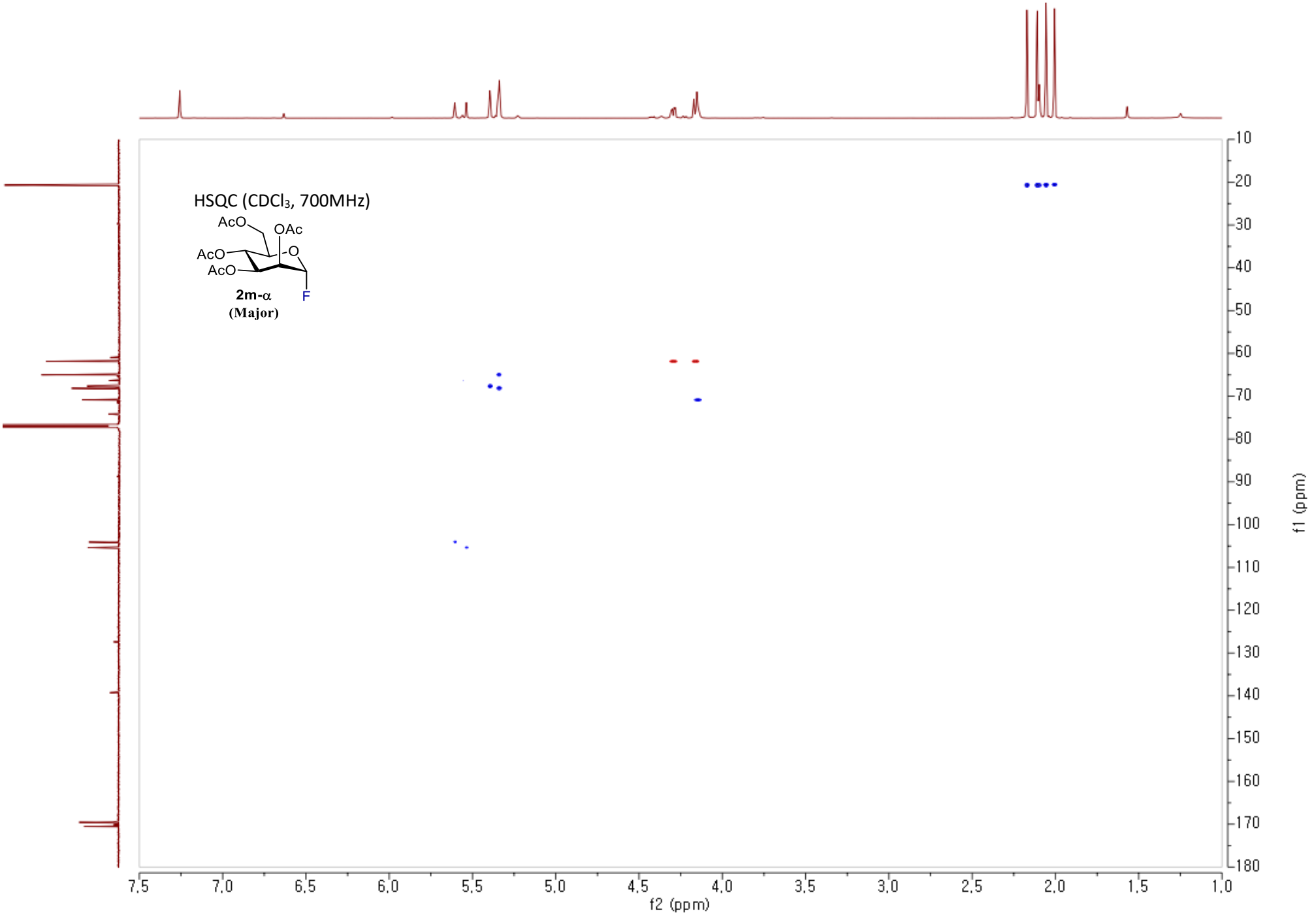
2l

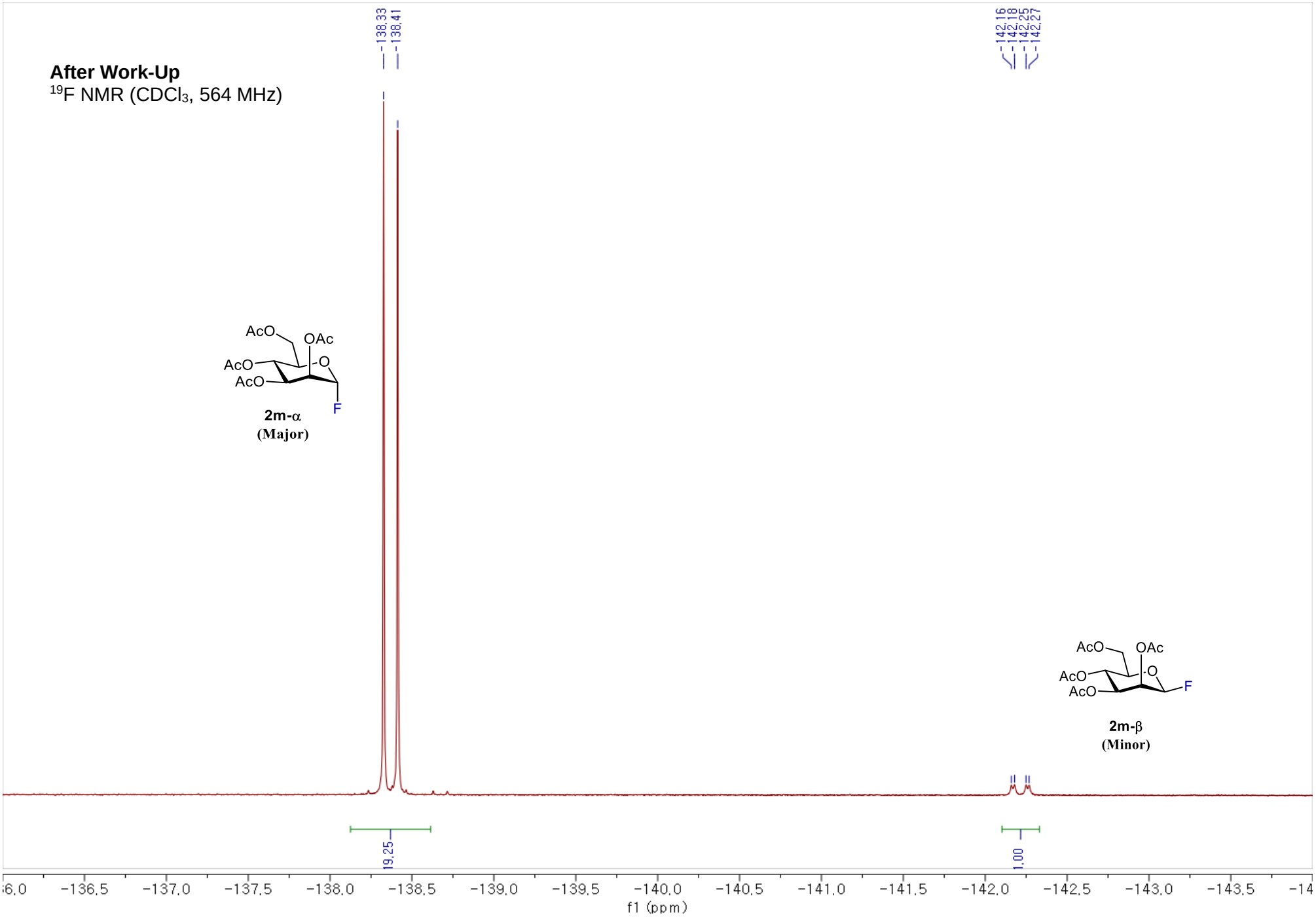
(α,β-mix)

2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranosyl fluoride (2m-α, Major diastereomer)



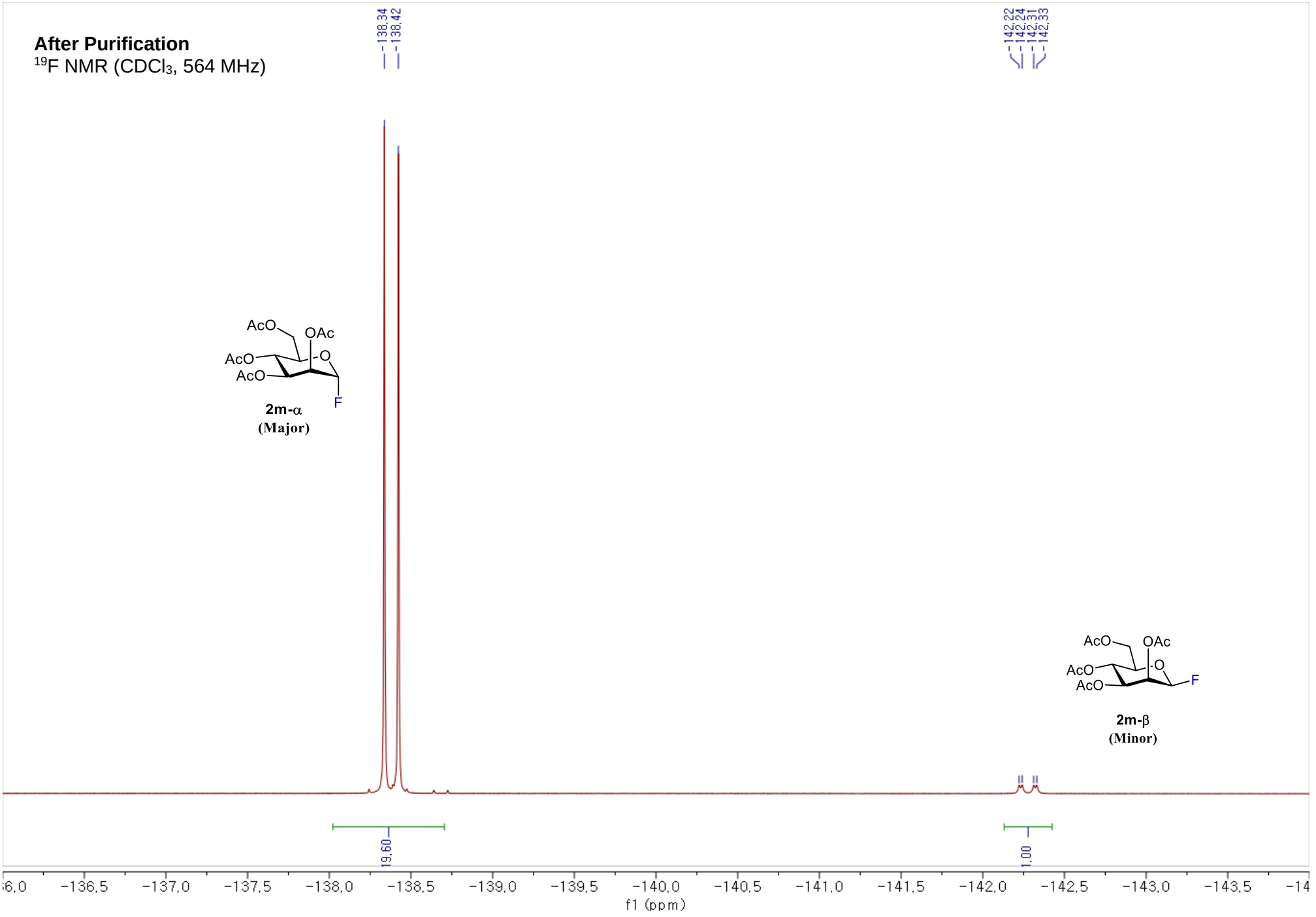

170.54
169.71
169.64
169.54
105.36
104.09
77.18
77.00
76.82
70.88
70.86
68.15
67.77
67.54
65.01
61.84
20.69
20.62
20.56
^{13}C NMR ($CDCl_3$, 176MHz)
AcO
OAc
AcO
O
AcO
F
2m-α
(Major)
70.88
70.86
71.0
70.9
70.8
f1 (ppm)
68.15
67.77
67.54
68.4
68.2
68.0
67.8
67.6
67.4
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
1
f1 (ppm)


HSQC (CDCl3, 700MHz)
AcO
OAc
AcO
O
AcO
F
2m-α
(Major)
f2 (ppm)
f1 (ppm)

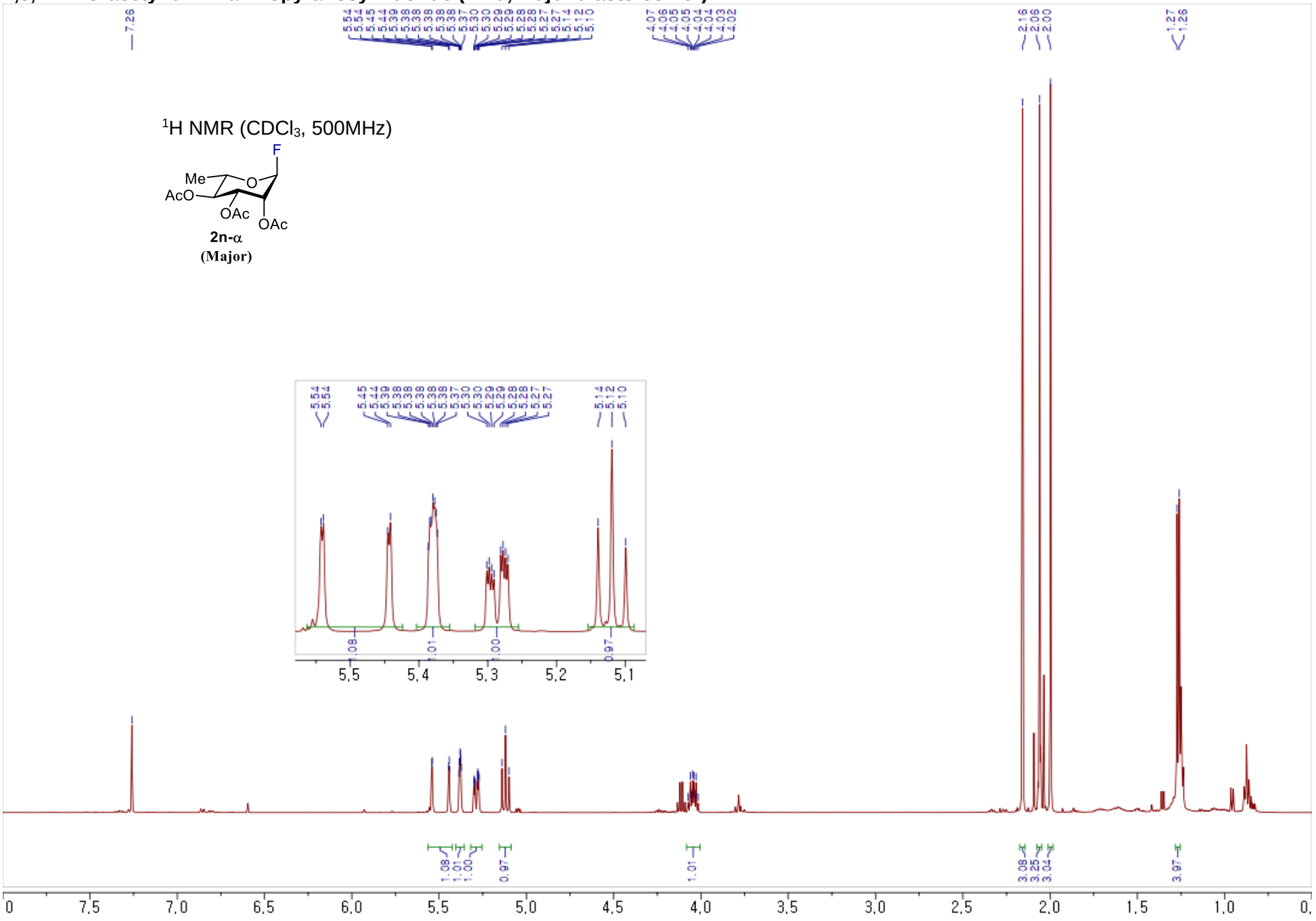

After Work-Up
19F NMR (CDCl3, 564 MHz)
-138.33
-138.41
-142.16
-142.18
-142.25
-142.27
AcO
OAc
AcO
O
AcO
F
2m-α
(Major)
AcO
OAc
AcO
O
AcO
F
2m-β
(Minor)
19.25
1.00
-136.5
-137.0
-137.5
-138.0
-138.5
-139.0
-139.5
-140.0
-140.5
-141.0
-141.5
-142.0
-142.5
-143.0
-143.5
f1 (ppm)

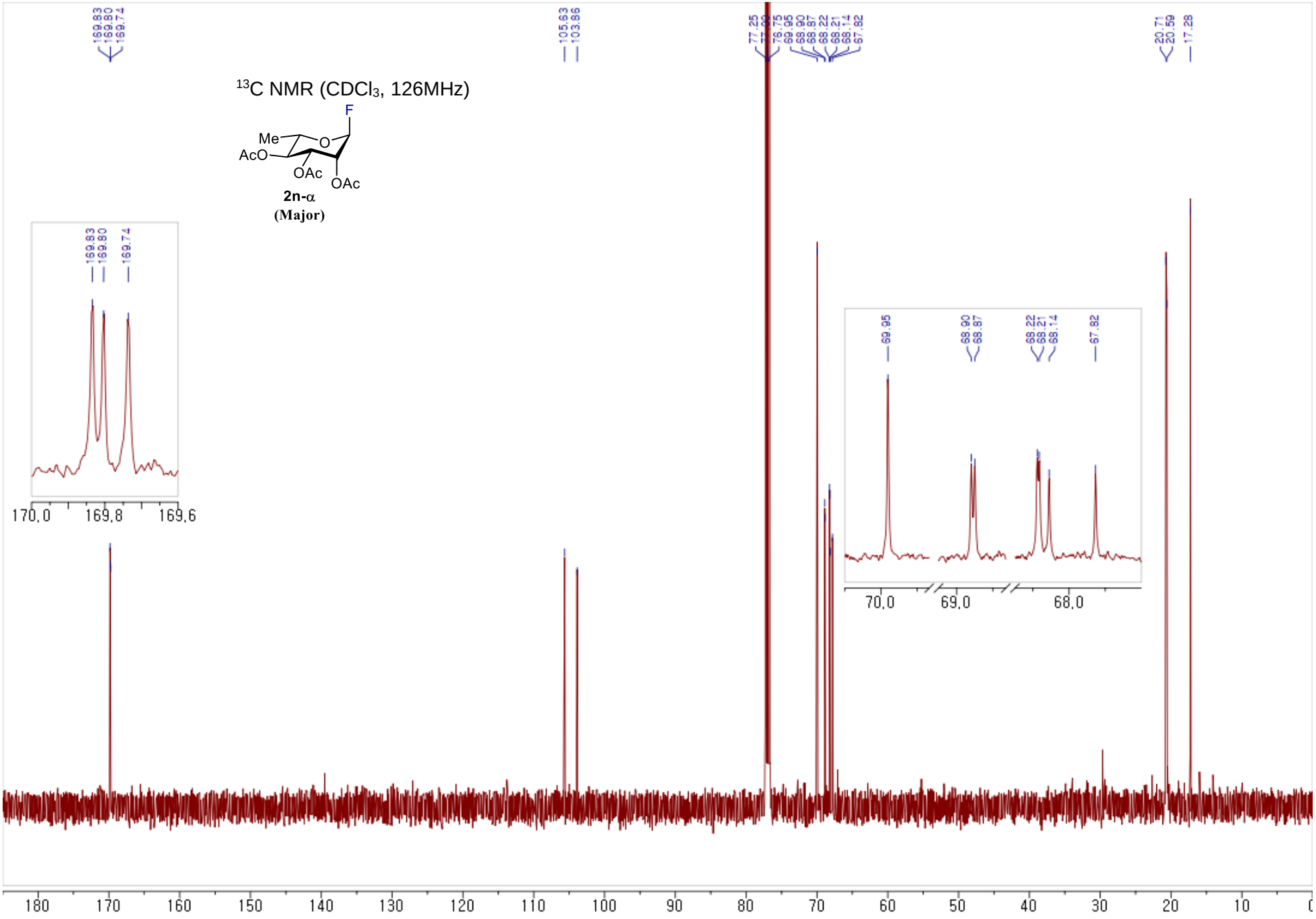
After Purification

^{19}F NMR ($CDCl_3$, 564 MHz)



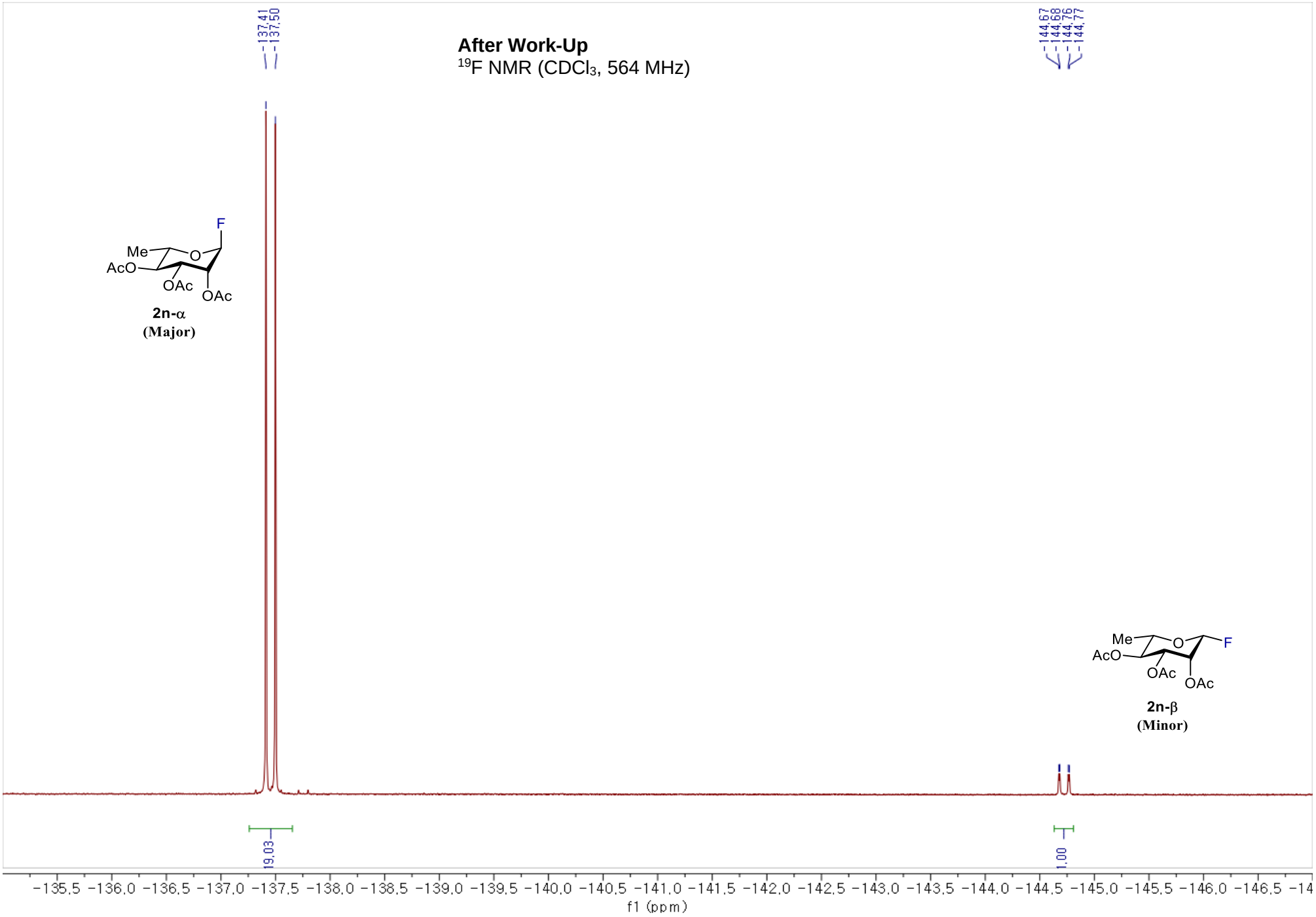
2,3,4-Tri-O-acetyl-α-L-rhamnopyranosyl fluoride (2n-α, Major diastereomer)




169.83
169.80
169.74
105.63
103.86
77.25
77.00
76.75
69.95
68.90
68.87
68.22
68.21
68.14
67.82
20.71
20.59
17.28
13C NMR (CDCl3, 126MHz)
F
Me
O
AcO
OAc
OAc
2n-α
(Major)
170.0
169.8
169.6
70.0
69.0
68.0
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

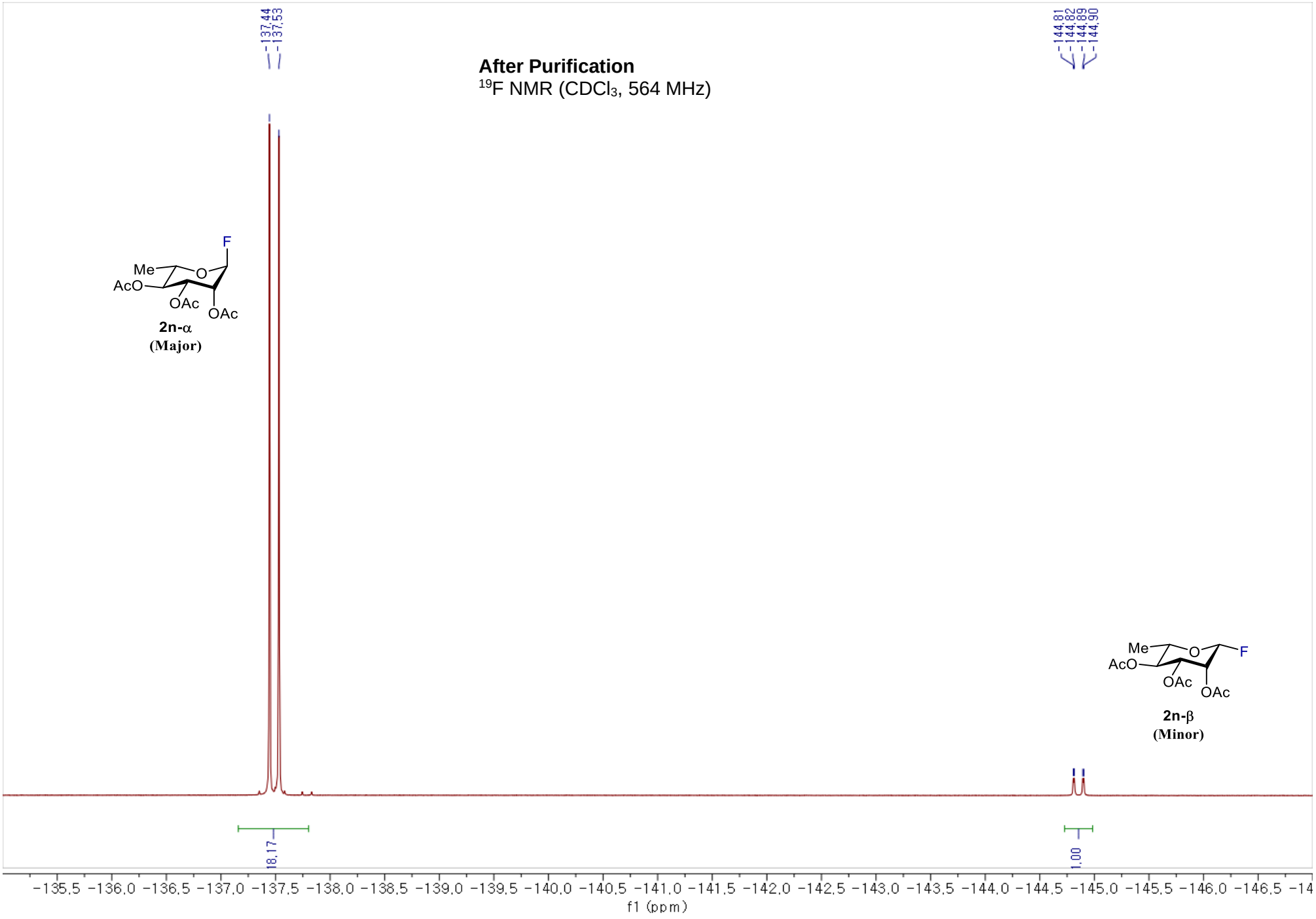
After Work-Up

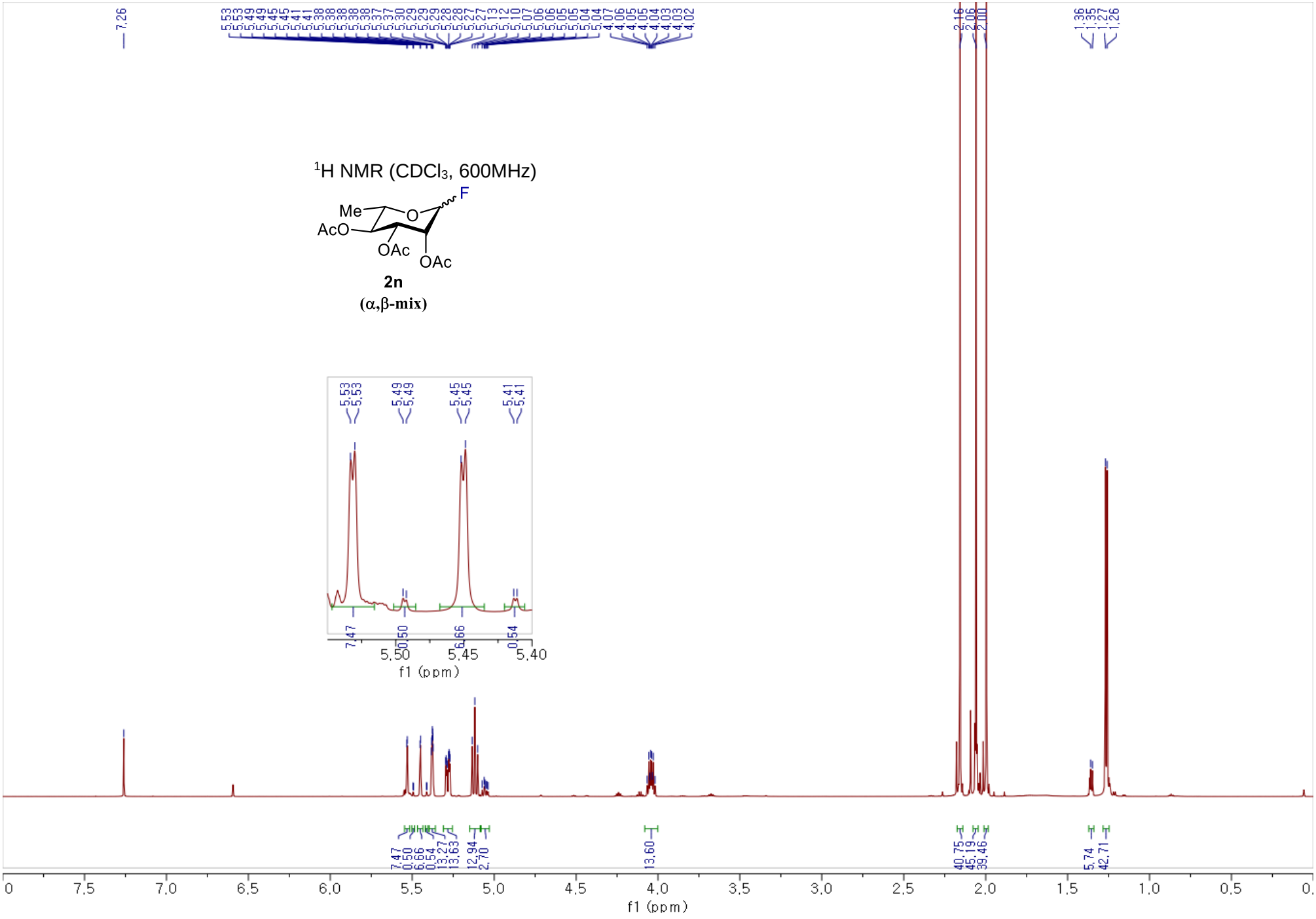
^{19}F NMR ($CDCl_3$, 564 MHz)



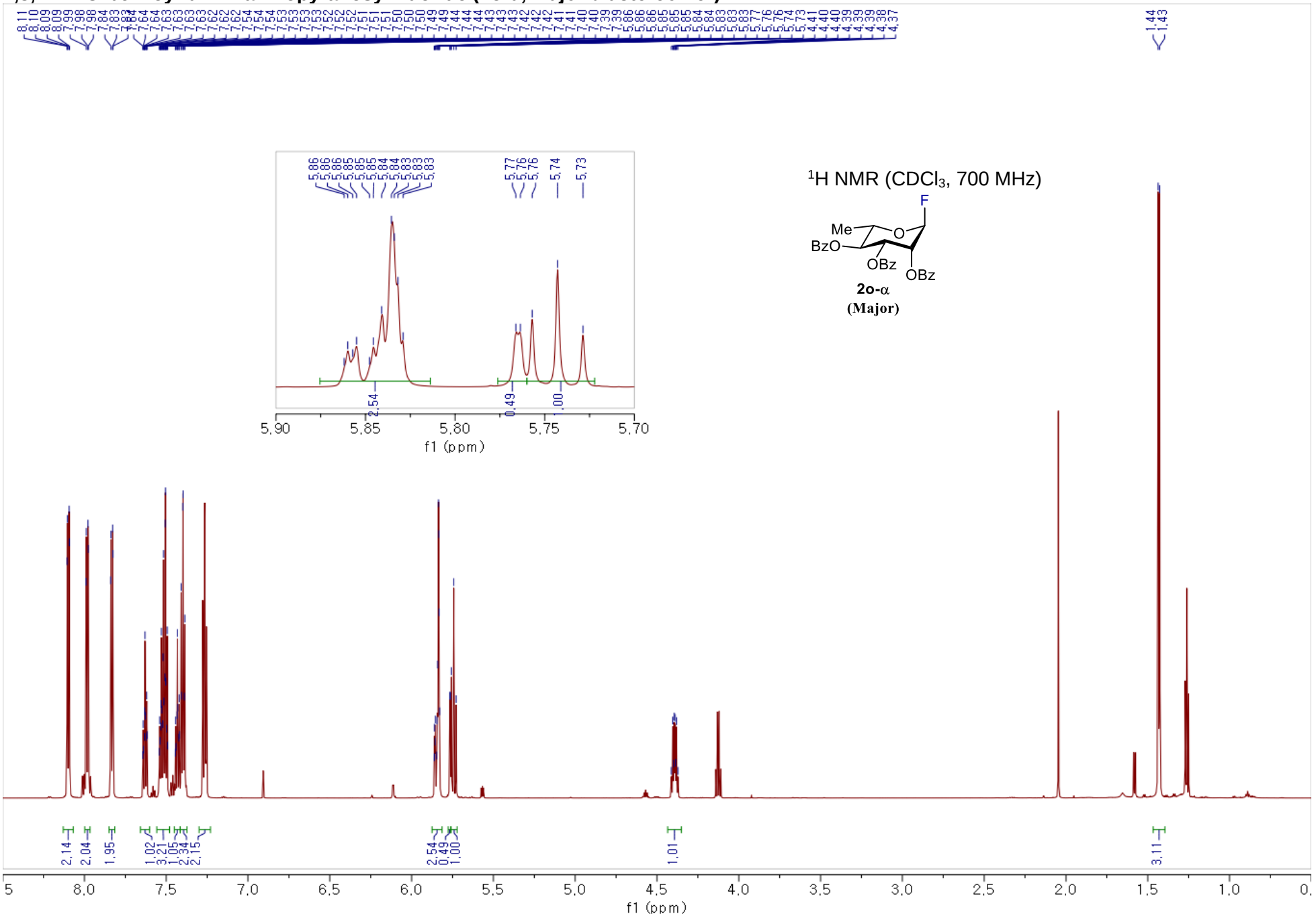
After Purification

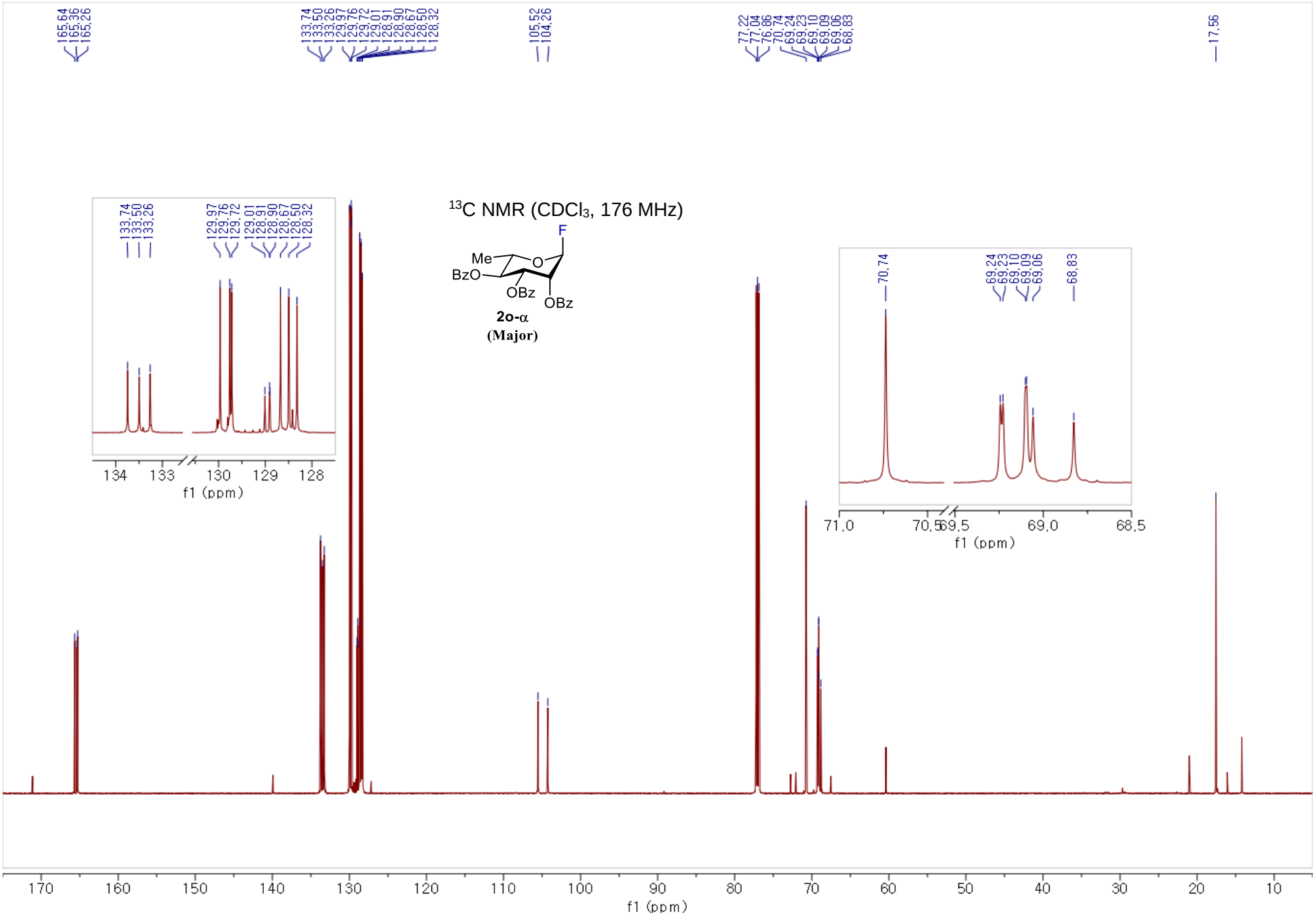
^{19}F NMR ($CDCl_3$, 564 MHz)

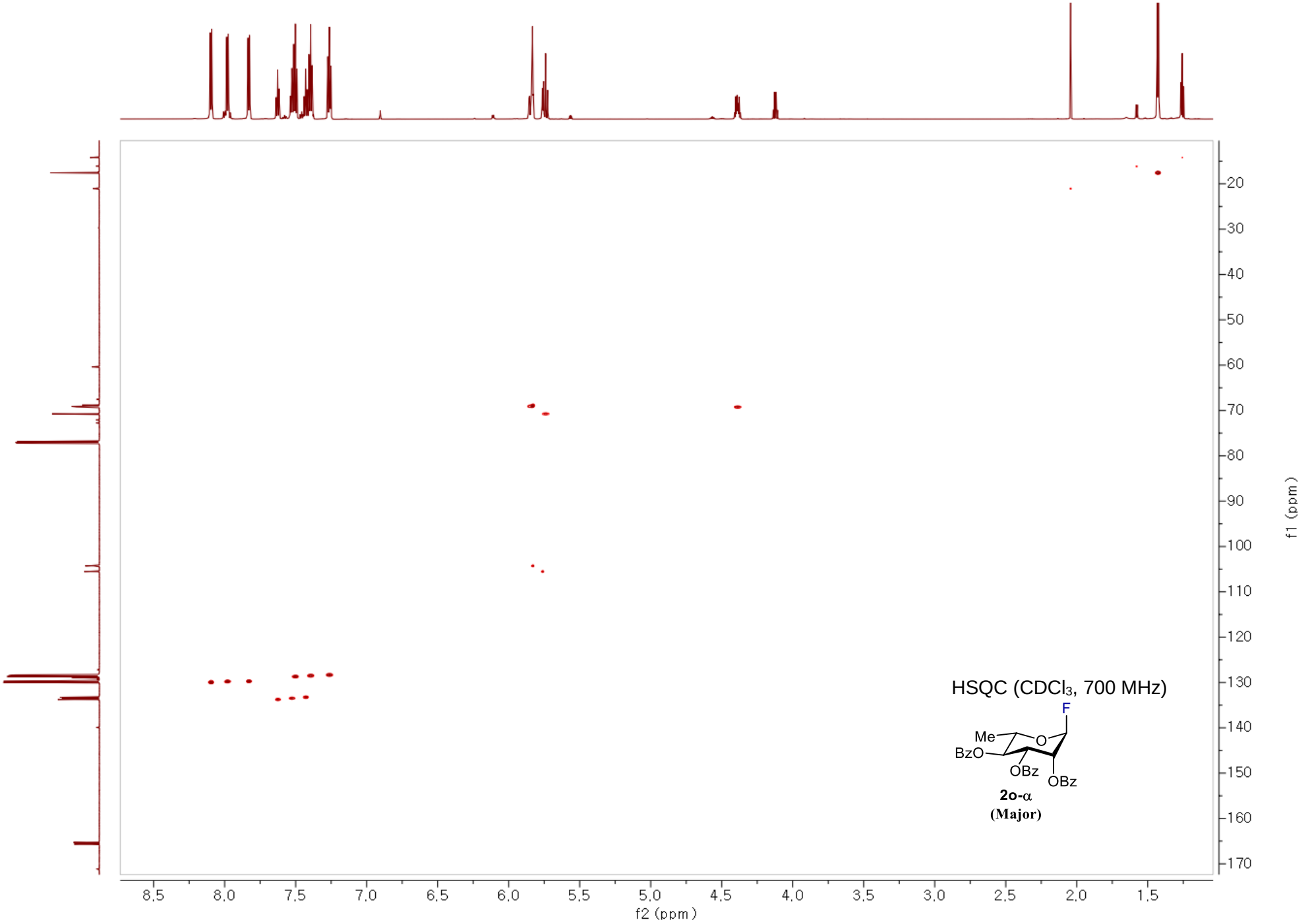


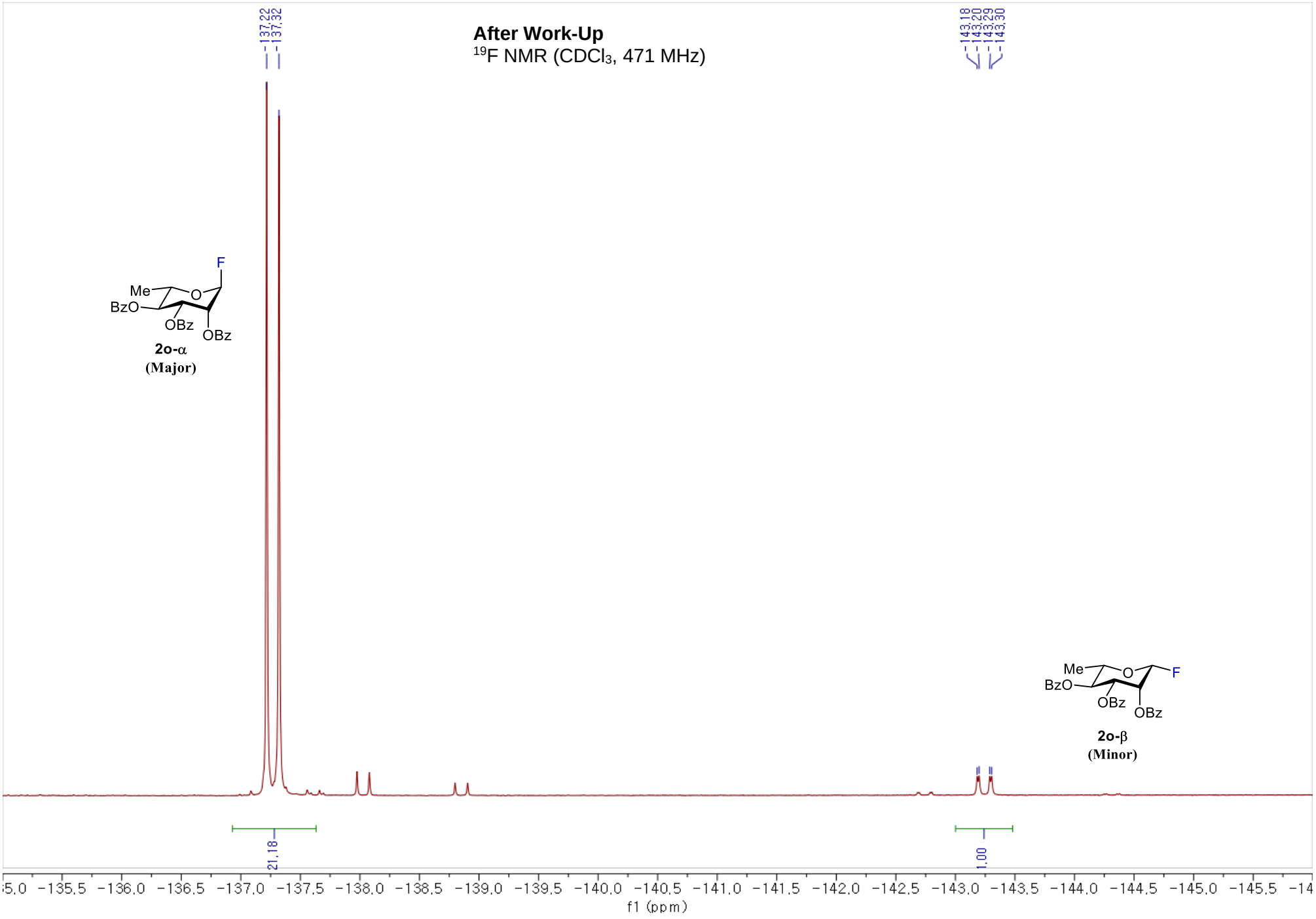

^{1}H NMR (CDCl$_3$, 600MHz)
Me
AcO
O
F
OAc
OAc
2n
(α,β-mix)
f1 (ppm)

2,3,4-Tri-O-benzoyl-α-L-rhamnopyranosyl fluoride (2o-α, Major diastereomer)



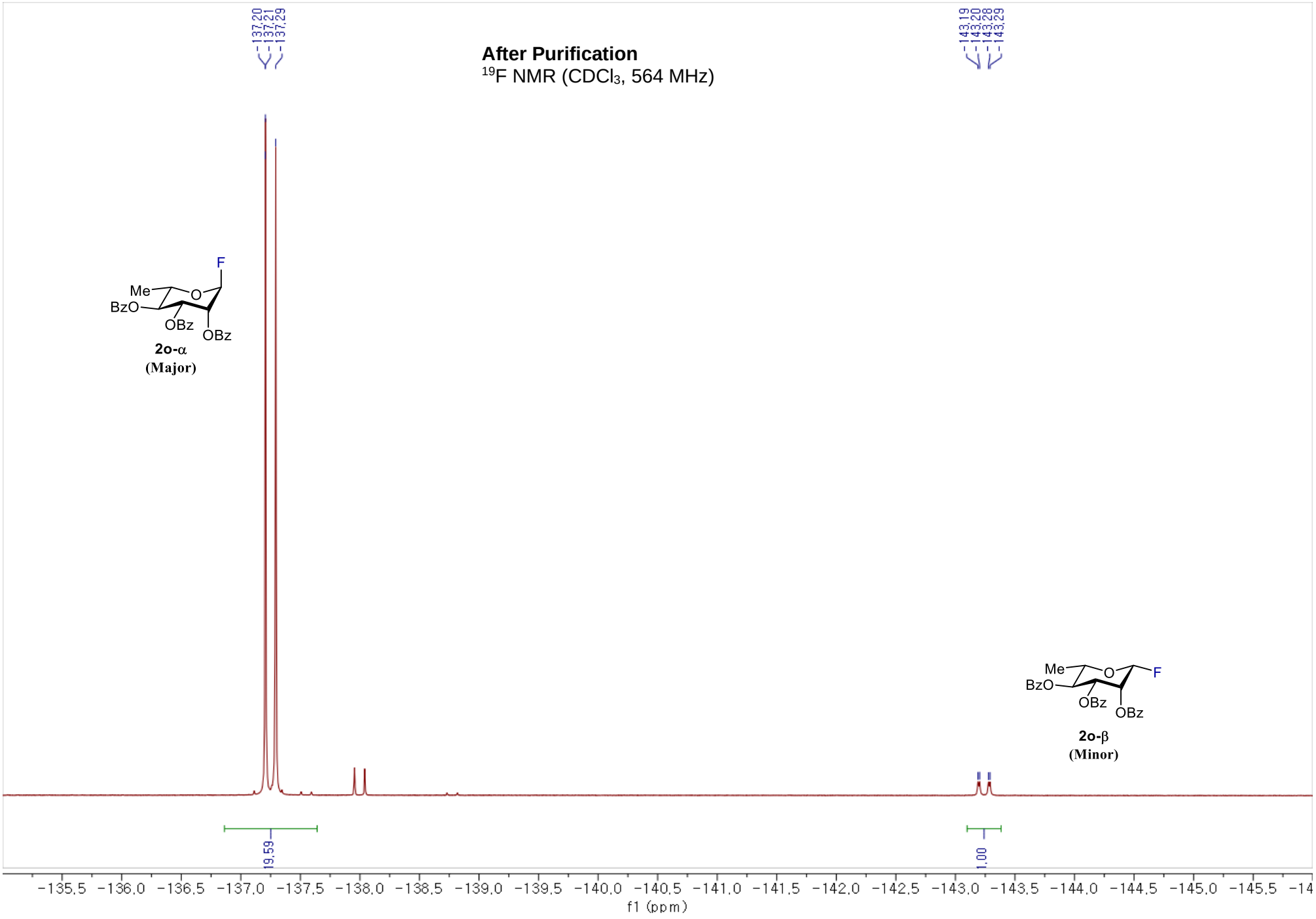

165.64
165.36
165.26
133.74
133.50
133.26
129.97
129.76
129.72
129.01
128.90
128.67
128.50
128.32
105.52
104.26
77.22
77.04
76.86
70.74
69.24
69.23
69.10
69.09
69.06
68.83
17.56
^{13}C NMR ($CDCl_3$, 176 MHz)
F
Me
O
BzO
OBz
OBz
2o-α
(Major)
f1 (ppm)
f1 (ppm)
f1 (ppm)


HSQC ($CDCl_3$, 700 MHz)
F
Me
O
BzO
OBz
OBz
2o-α
(Major)
f2 (ppm)
f1 (ppm)

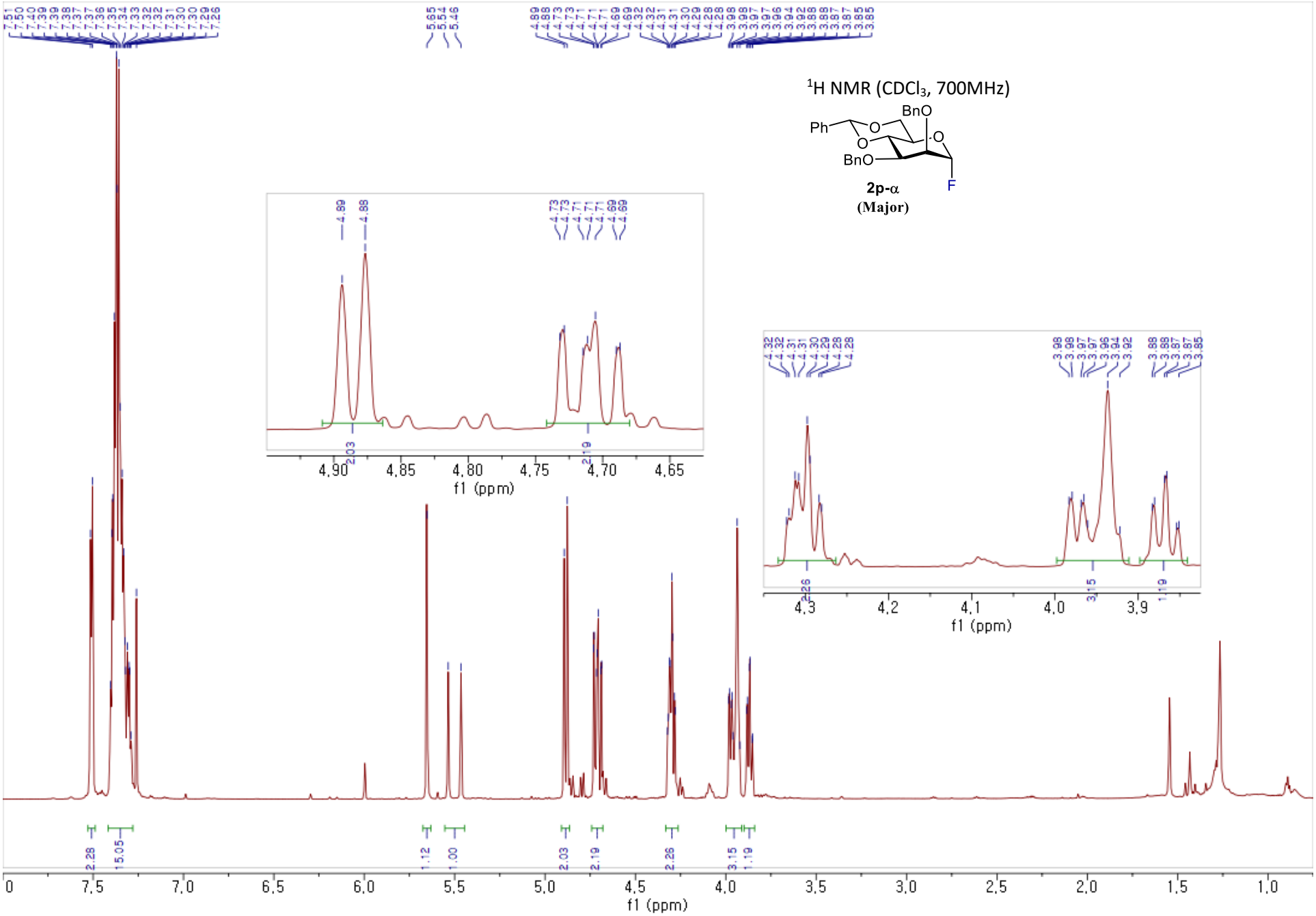

After Work-Up
19F NMR (CDCl3, 471 MHz)
-137.22
-137.32
-143.18
-143.20
-143.29
-143.30
F
Me
O
BzO
OBz
OBz
2o-α
(Major)
Me
O
F
BzO
OBz
OBz
2o-β
(Minor)
21.18
1.00
-135.5 -136.0 -136.5 -137.0 -137.5 -138.0 -138.5 -139.0 -139.5 -140.0 -140.5 -141.0 -141.5 -142.0 -142.5 -143.0 -143.5 -144.0 -144.5 -145.0 -145.5
f1 (ppm)

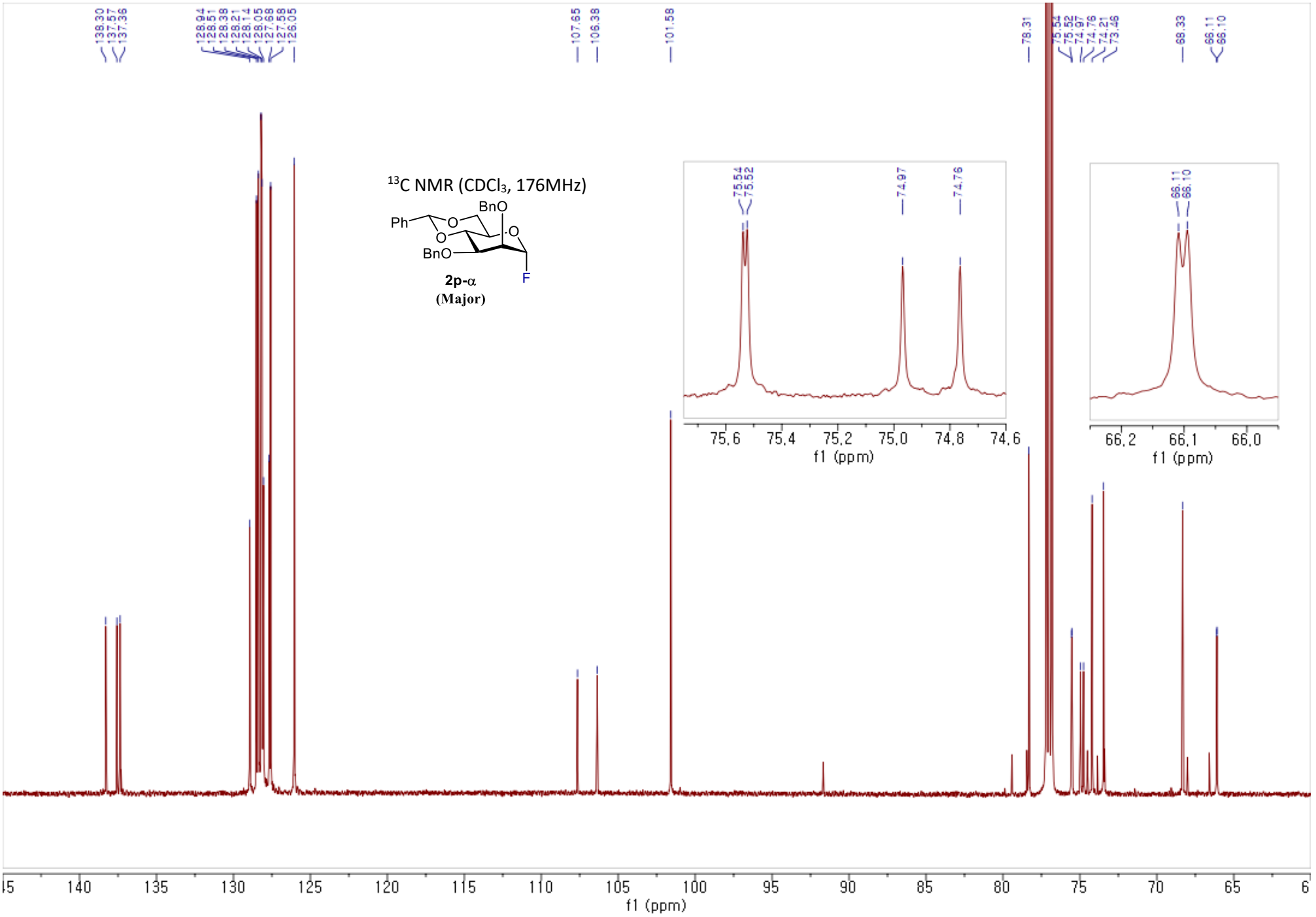
After Purification

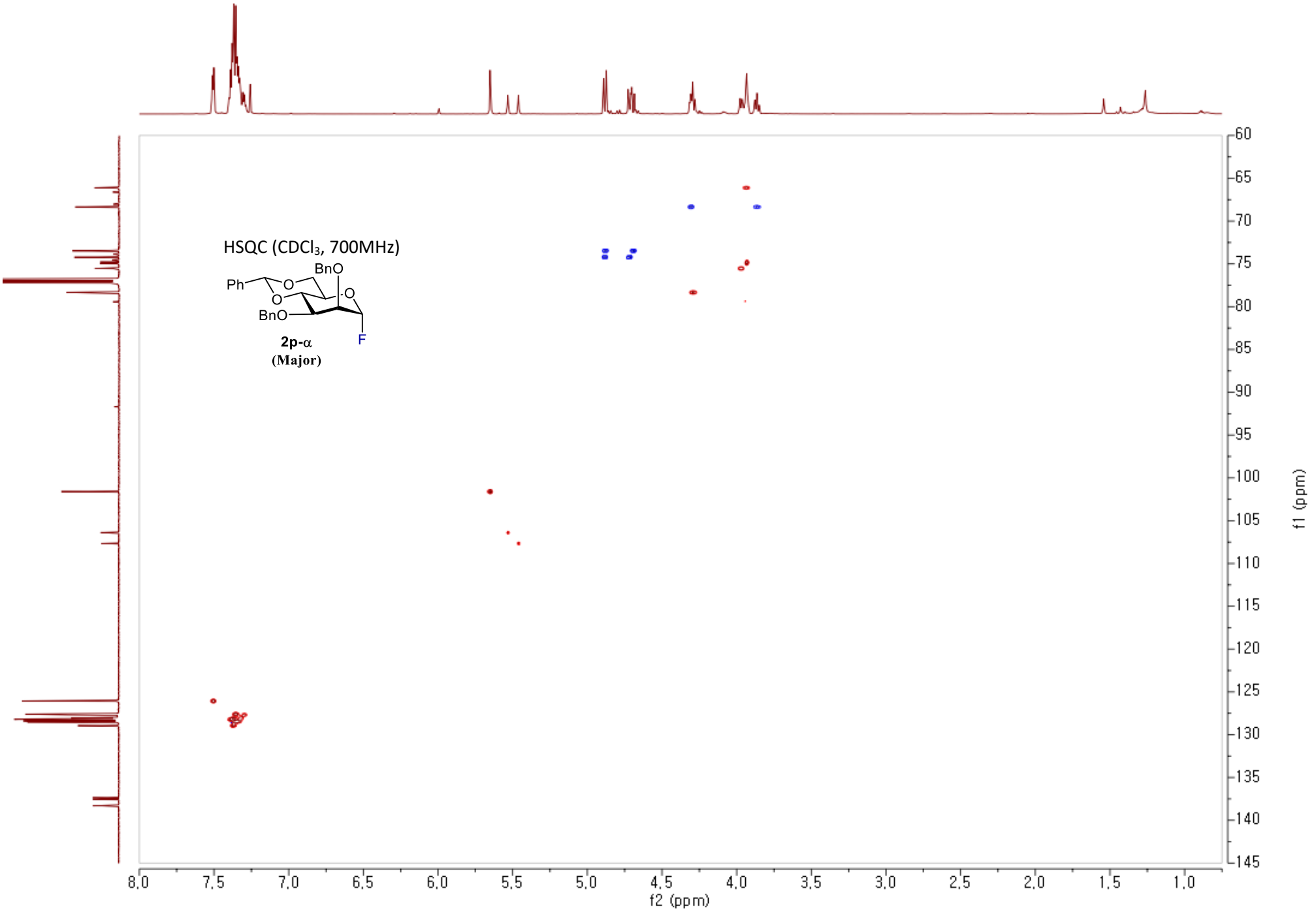
^{19}F NMR ($CDCl_3$, 564 MHz)



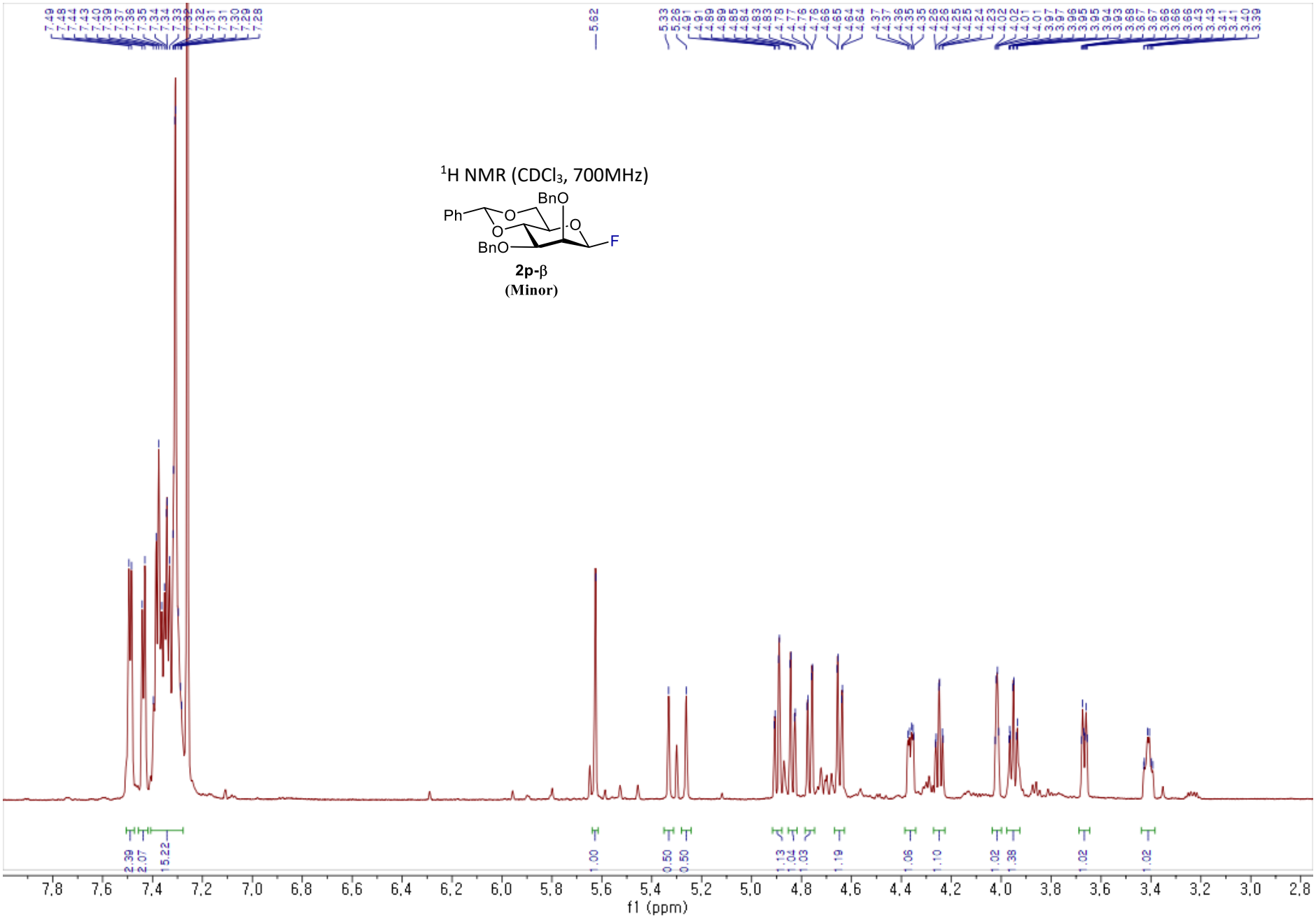
2,3-Bis-*O*-(phenylmethyl)-4,6-*O*-[(R)-phenylmethylene]-α-D-mannopyranosyl fluoride (2p-α, Major diastereomer)

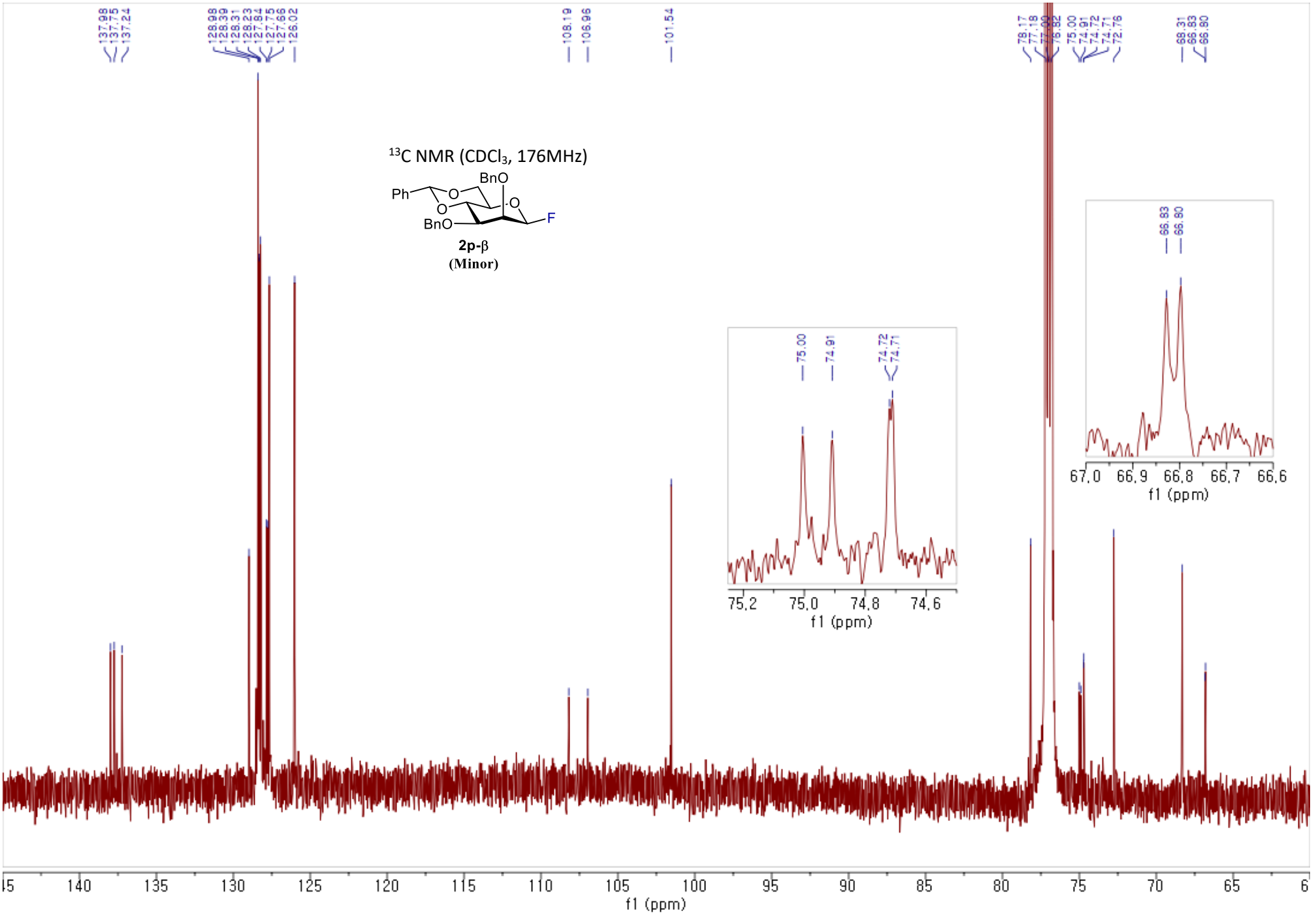


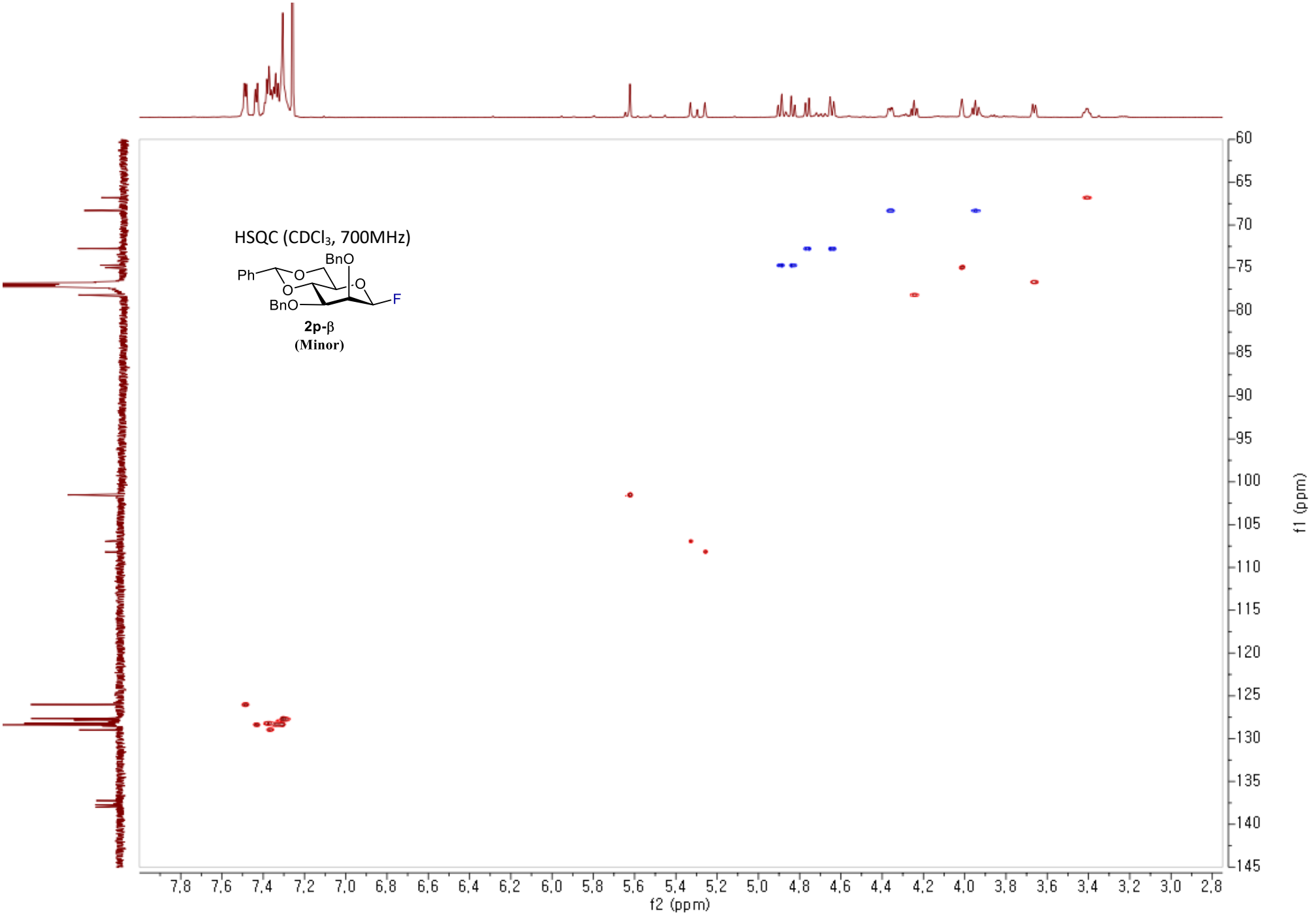

^{13}C NMR ($CDCl_3$, 176MHz)
BnO
Ph
O
O
O
BnO
F
2p-α
(Major)
138.30
137.57
137.36
128.94
128.51
128.38
128.21
128.14
128.05
127.68
127.58
126.05
107.65
106.38
101.58
78.31
75.54
75.52
74.97
74.76
74.21
73.46
68.33
66.11
66.10
f1 (ppm)


HSQC ($CDCl_3$, 700MHz)
BnO
Ph
O
O
O
BnO
F
2p-α
(Major)
f2 (ppm)
f1 (ppm)

2,3-Bis-*O*-(phenylmethyl)-4,6-*O*-[(R)-phenylmethylene]-β-D-mannopyranosyl fluoride (2p-β, Minor diastereomer)

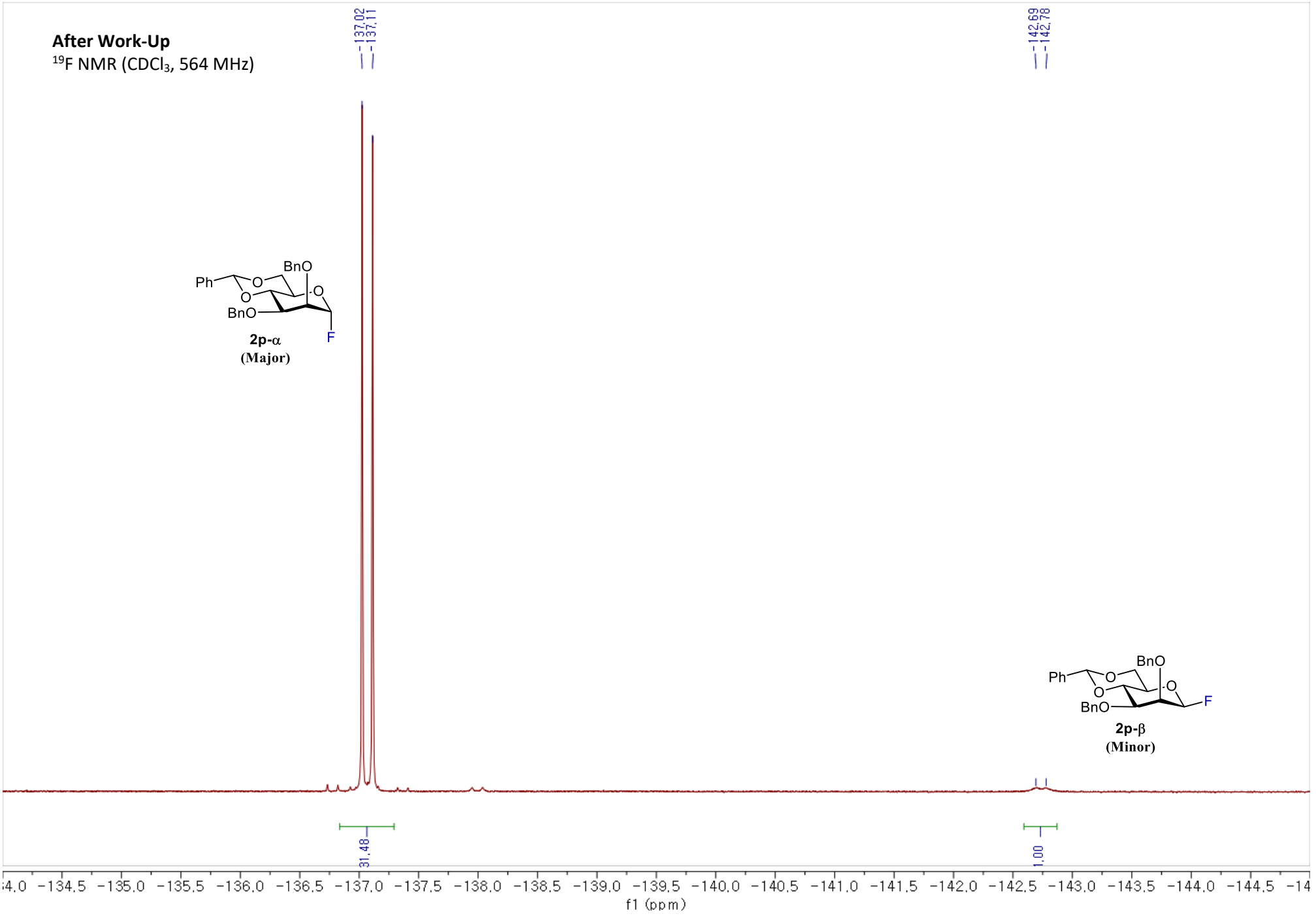



137.98
137.75
137.24
128.98
128.39
128.31
128.23
127.84
127.75
127.66
126.02
108.19
106.96
101.54
78.17
77.18
77.00
76.82
75.00
74.91
74.72
74.71
72.76
68.31
66.83
66.80
^{13}C NMR ($CDCl_3$, 176MHz)
BnO
Ph
O
O
O
BnO
F
2p-β
(Minor)
75.00
74.91
74.72
74.71
75.2
75.0
74.8
74.6
f1 (ppm)
66.83
66.80
67.0
66.9
66.8
66.7
66.6
f1 (ppm)
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
f1 (ppm)


HSQC (CDCl3, 700MHz)
BnO
Ph
O
O
O
BnO
F
2p-β
(Minor)
f2 (ppm)
f1 (ppm)

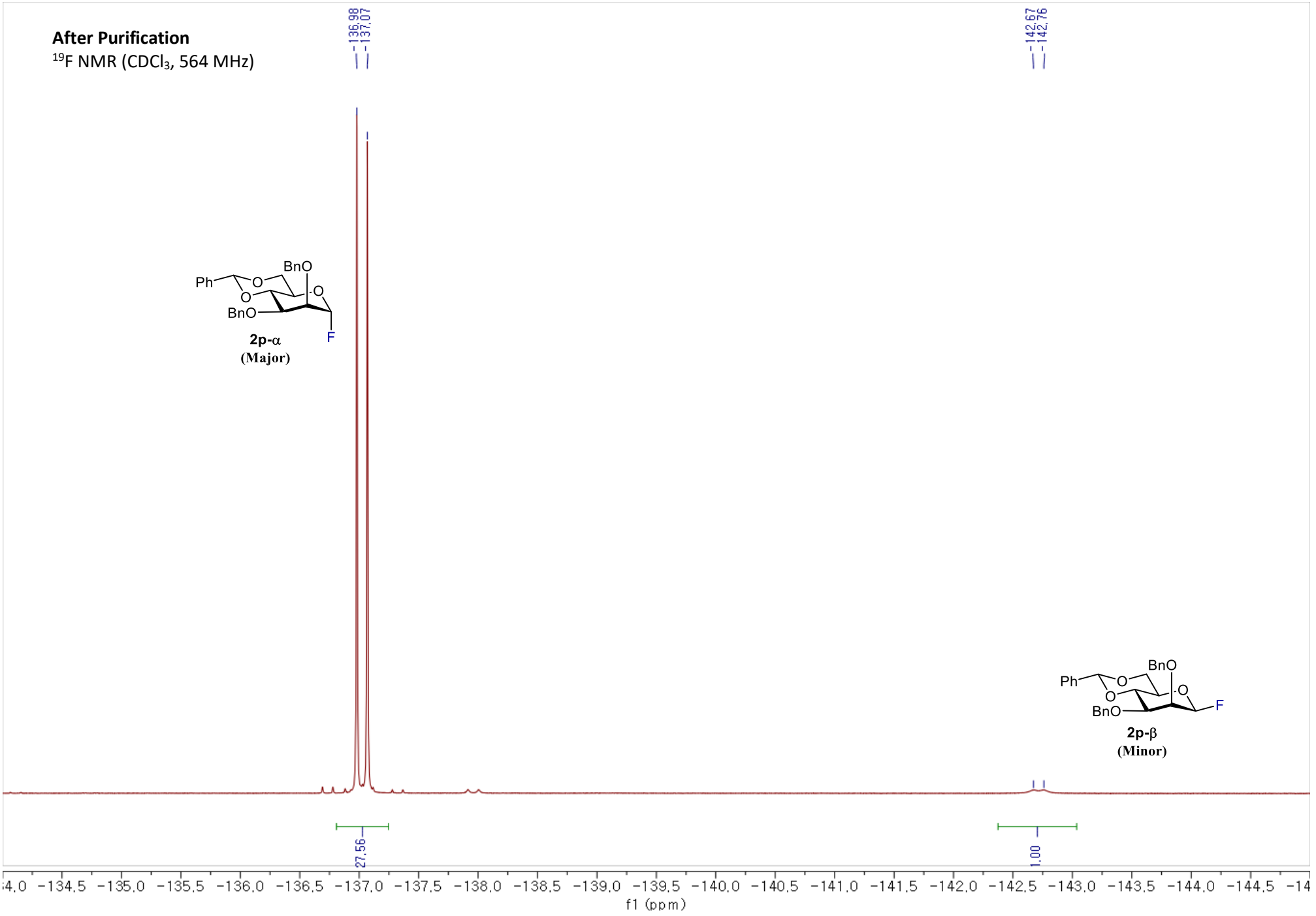
After Work-Up

^{19}F NMR ($CDCl_3$, 564 MHz)

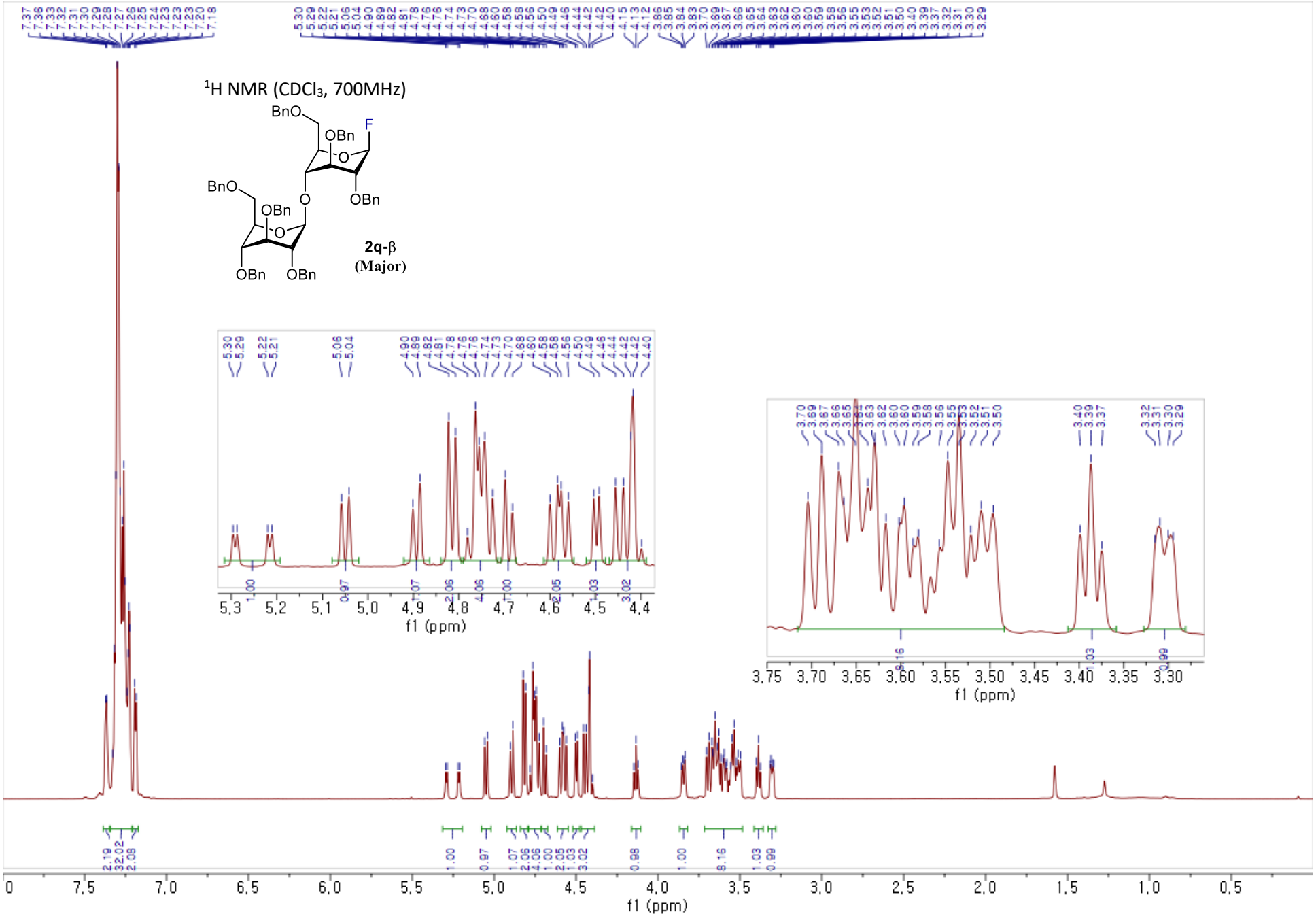


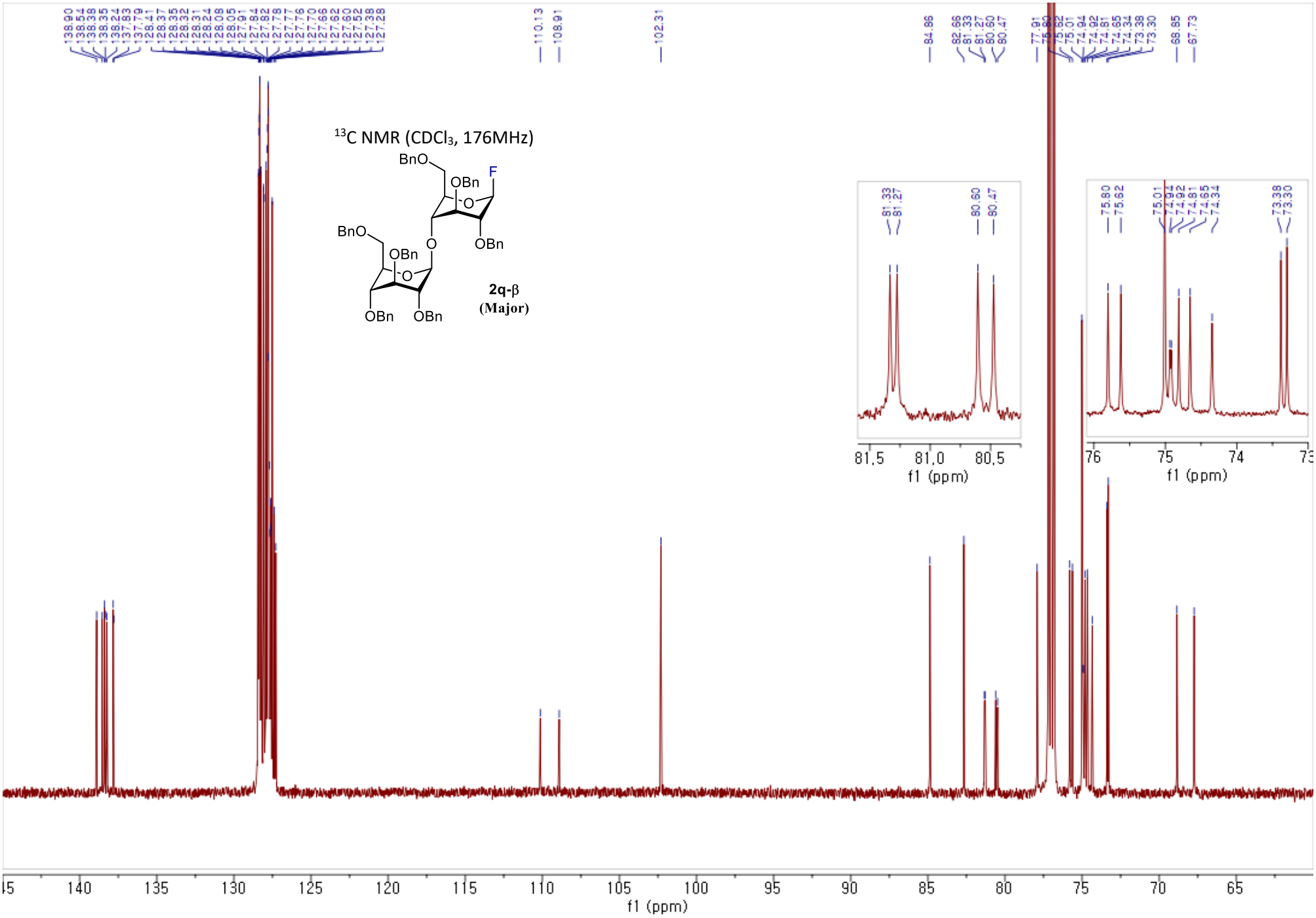
After Purification

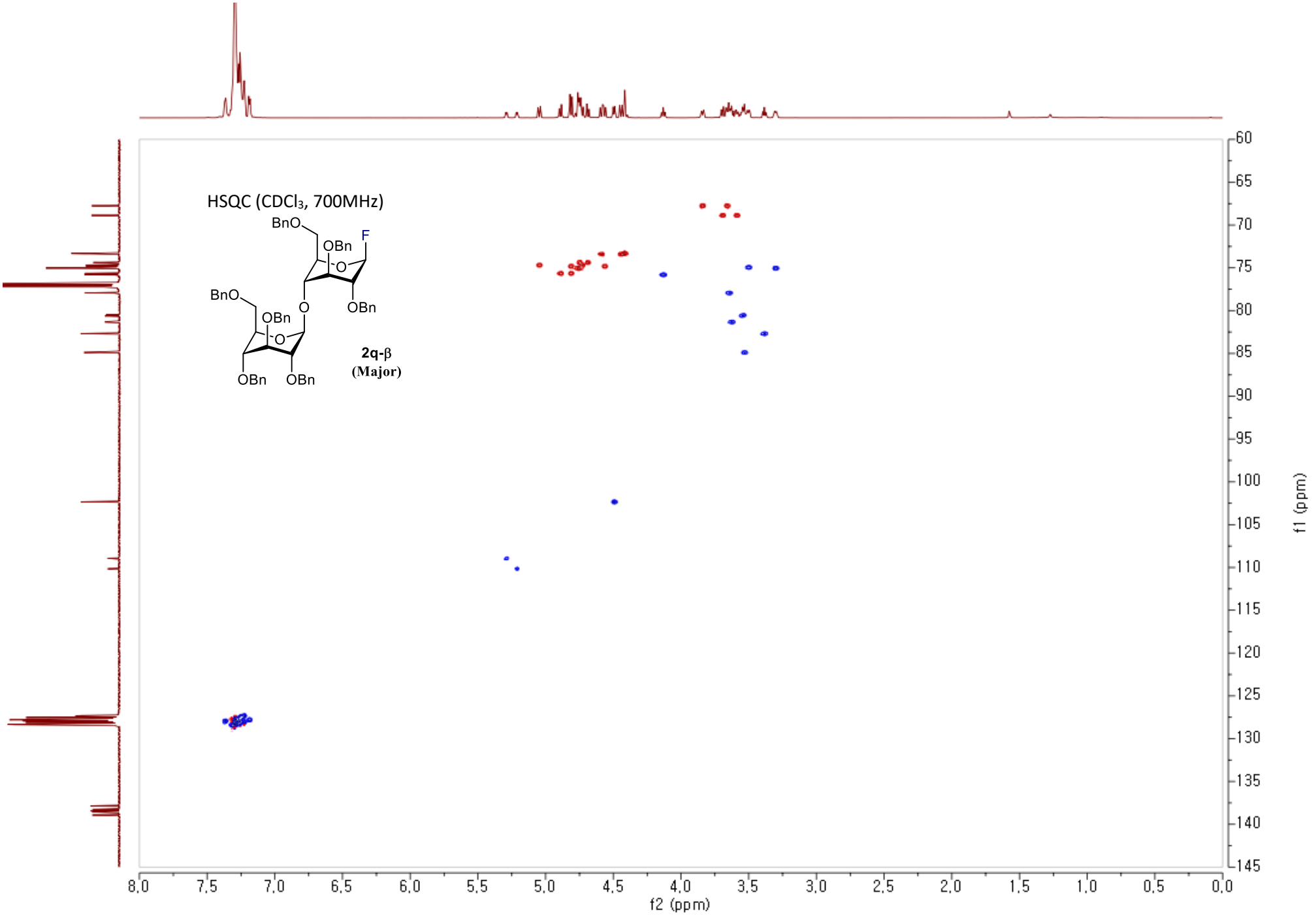
^{19}F NMR ($CDCl_3$, 564 MHz)



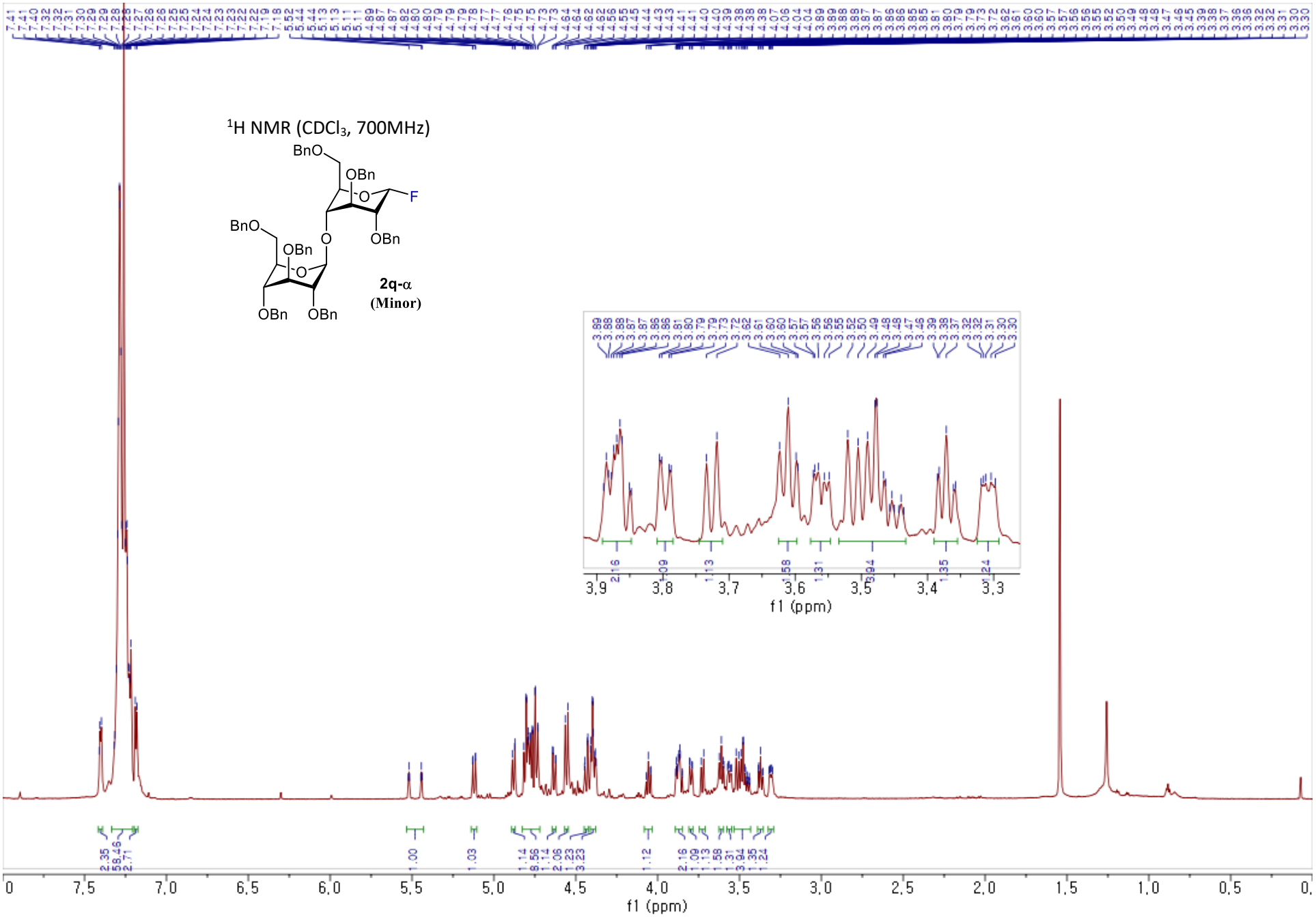
2,3,6-Tris-*O*-(phenylmethyl)-4-*O*-[2,3,4,6-tetrakis-*O*-(phenylmethyl)-β-D-glucopyranosyl]-β-D-glucopyranosyl fluoride (2q-β, Major diastereomer)

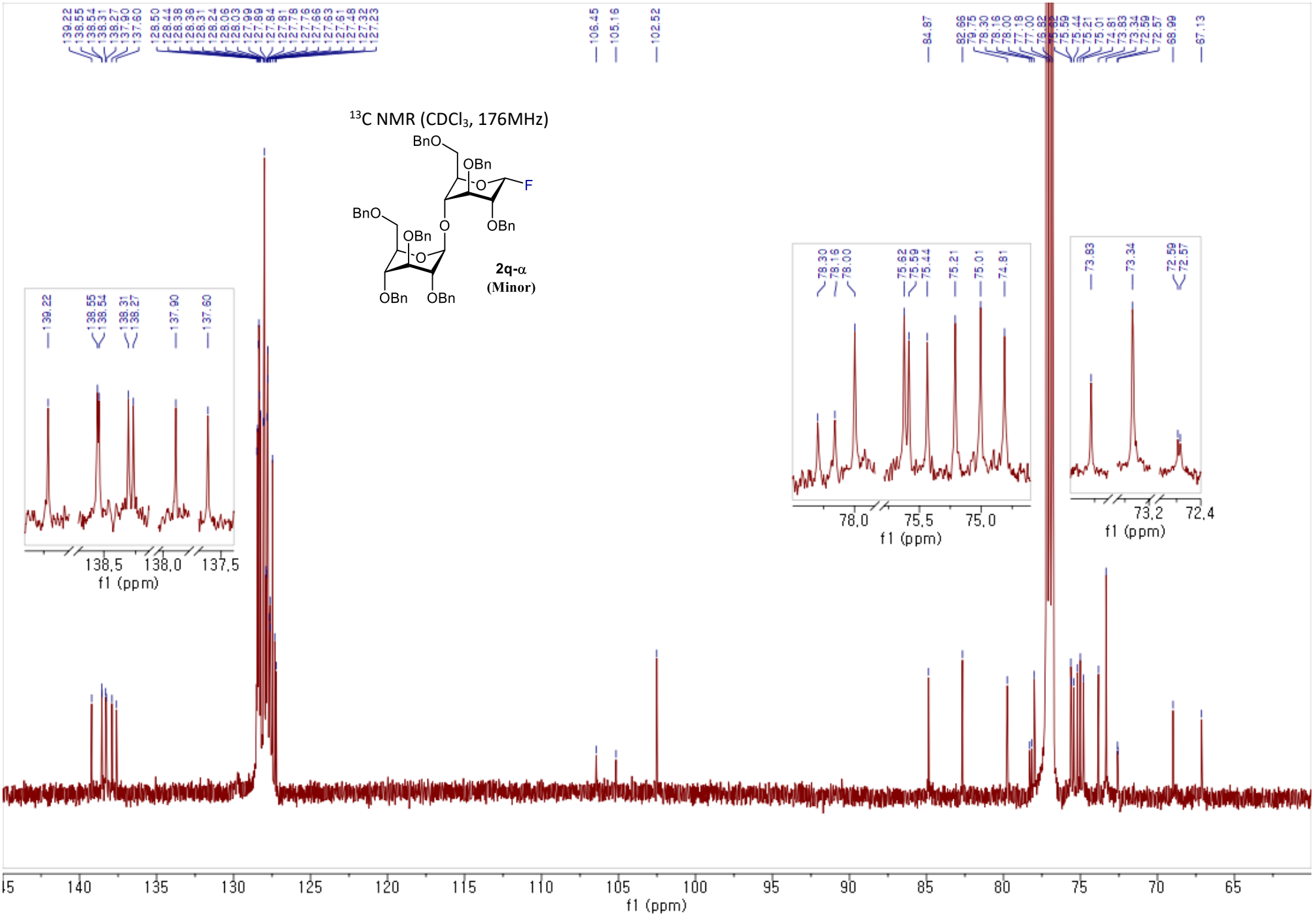


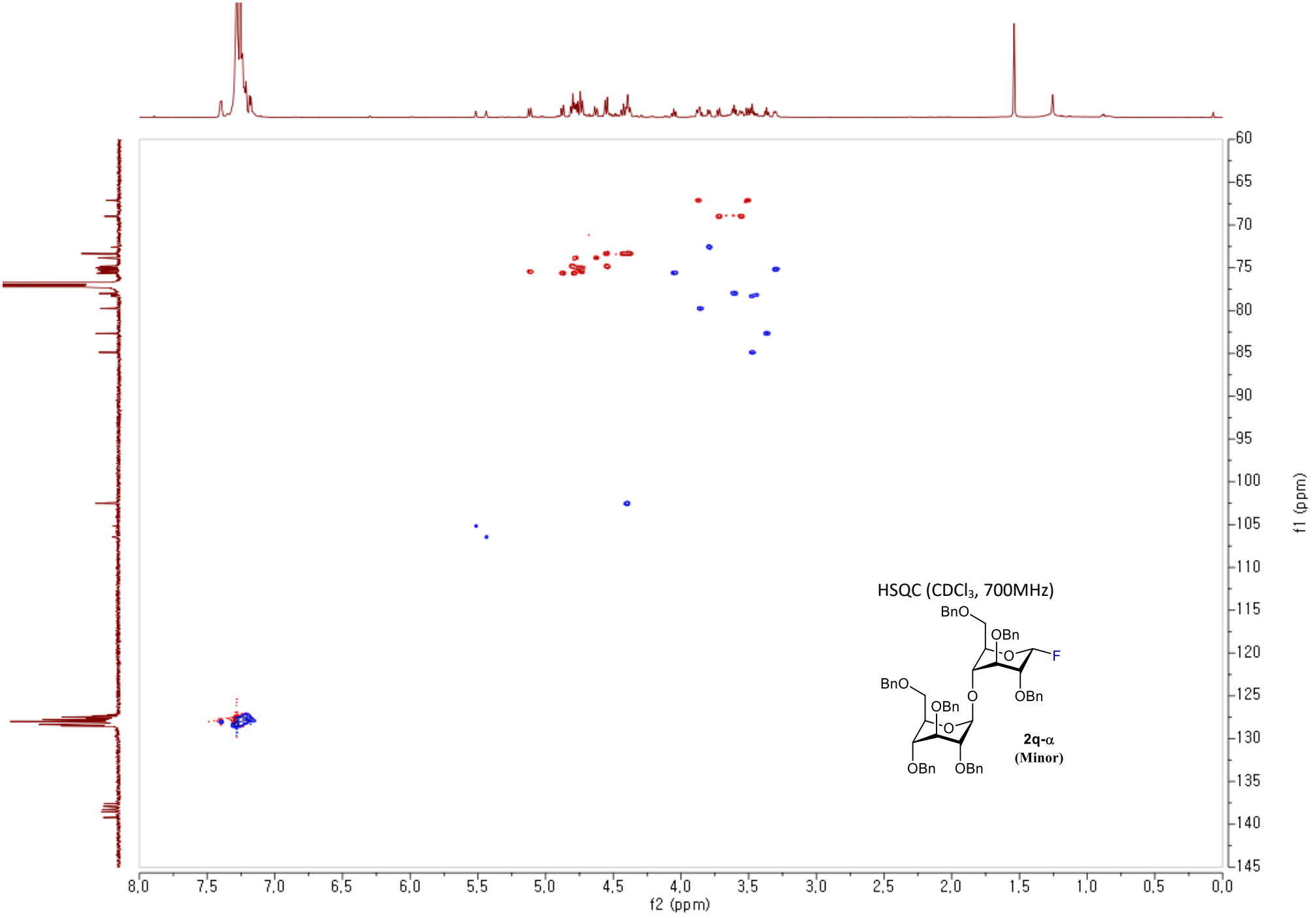

^{13}C NMR ($CDCl_3$, 176MHz)
BnO
OBn
F
O
OBn
BnO
OBn
O
OBn
OBn
OBn
2q-β
(Major)
f1 (ppm)
f1 (ppm)


HSQC (CDCl3, 700MHz)
BnO
OBn
F
BnO
O
OBn
OBn
OBn
OBn
2q-β
(Major)
f2 (ppm)
f1 (ppm)

2,3,6-Tris-*O*-(phenylmethyl)-4-*O*-[2,3,4,6-tetrakis-*O*-(phenylmethyl)-β-D-glucopyranosyl]-α-D-glucopyranosyl fluoride (2q-α, Minor diastereomer)

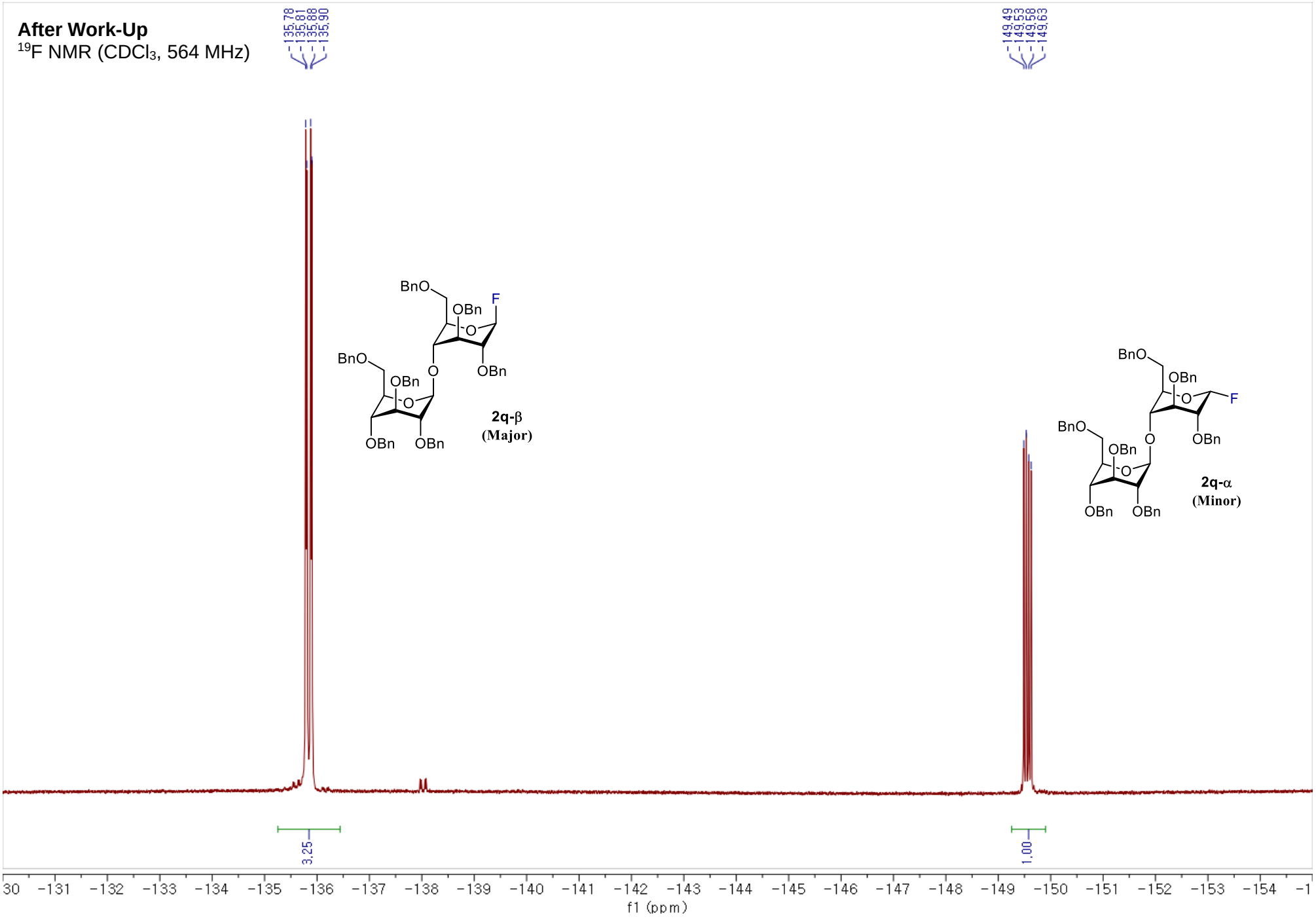



^{13}C NMR ($CDCl_3$, 176MHz)
BnO
OBn
O
F
OBn
BnO
OBn
O
OBn
OBn
OBn
2q-α
(Minor)
f1 (ppm)
f1 (ppm)
f1 (ppm)
f1 (ppm)


HSQC ($CDCl_3$, 700MHz)
BnO
OBn
O
F
OBn
BnO
OBn
O
O
OBn
OBn
2q-α
(Minor)
f2 (ppm)
f1 (ppm)

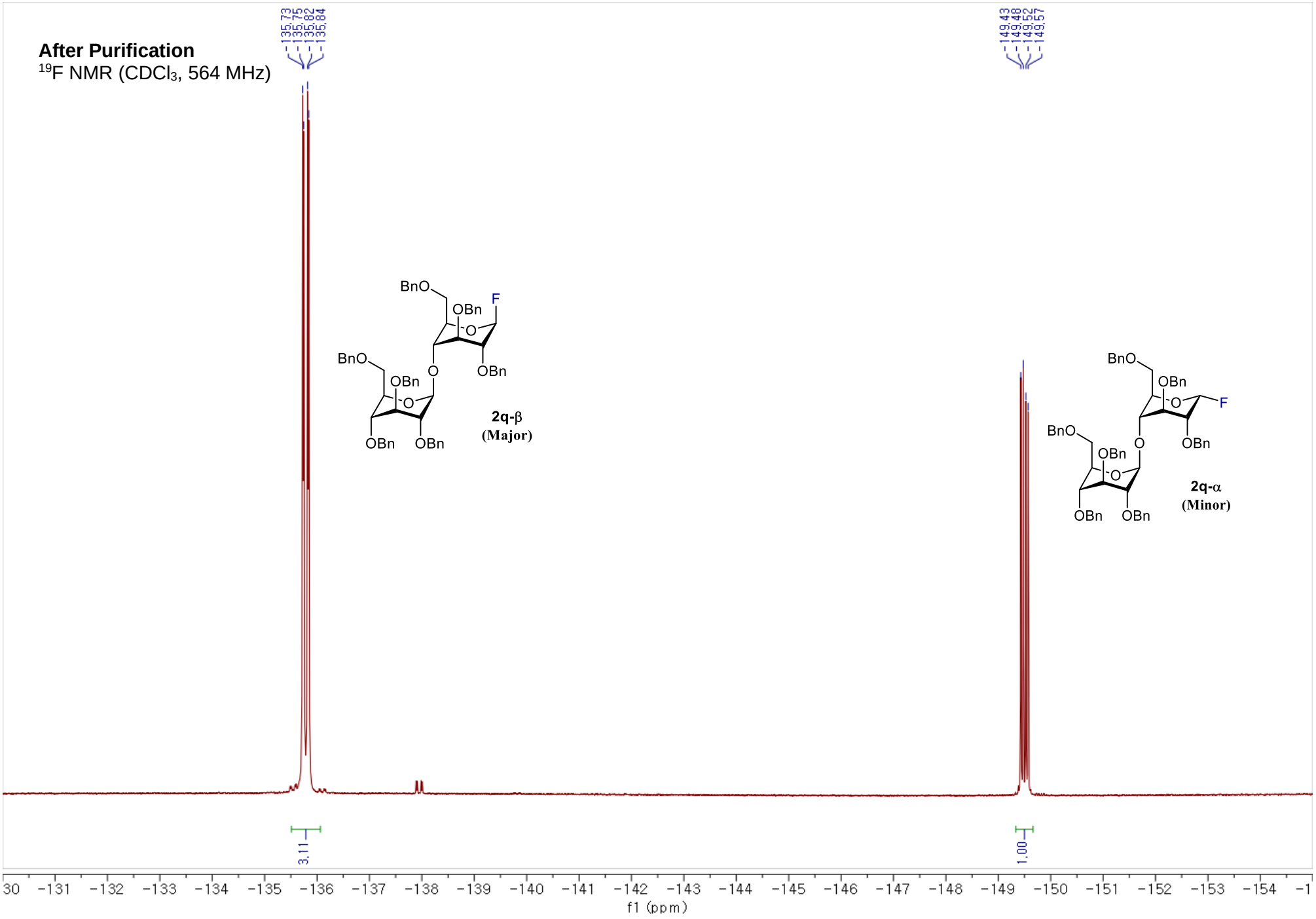
After Work-Up

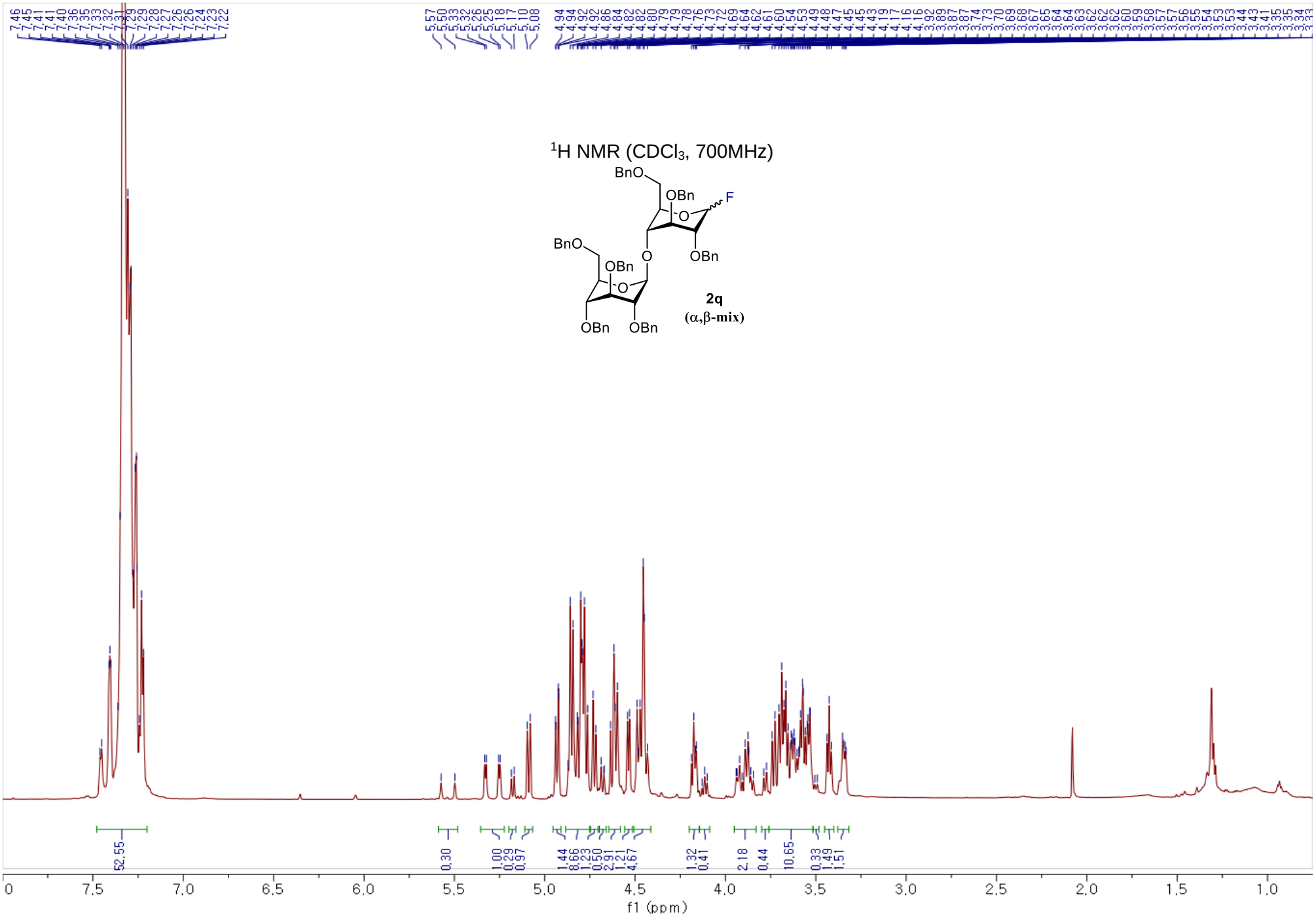
^{19}F NMR ($CDCl_3$, 564 MHz)



After Purification

^{19}F NMR ($CDCl_3$, 564 MHz)




^{1}H NMR ($CDCl_3$, 700MHz)
BnO
OBn
F
O
BnO
OBn
O
OBn
OBn
OBn
2q
(α,β-mix)
f1 (ppm)