Supplementary Information

Synthesis of Glycosyl Fluorides by Photochemical Fluorination with Sulfur(VI) Hexafluoride

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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 500 (500 MHz), or Varian INOVA 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) 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 either 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}).

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 products was confirmed again by comparing with them.

Information of the light equipment:

a. Kessil H160 Tuna Flora LED (Blue LED) – Link to the website

- Peak Wavelength: 452 nm

b. Waveform lighting realUV™ LED Strip Lights (365nm) (UV-A LED) – Link to the website

- Peak Wavelength: 369.0 nm
- UV Output: 0.75 W
- Radiometric Efficiency: 15%
- Emission Angle: 120 degree

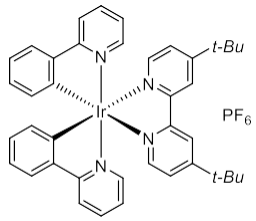
c. Waveform lighting realUV™ LED Flood Light (365nm) (UV-A Flood Lamp) – Link to the website

- Peak Wavelength: 368.5 nm
- UV Output: 8.0 W
- Radiometric Efficiency: 40%
- Emission Angle: 120 degree

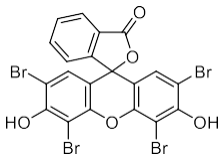
Detailed information of the light sources can be found on the website through the link

II. Optimization

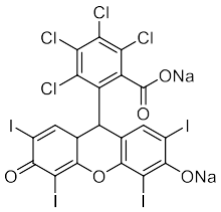
a. Photocatalyst Screening



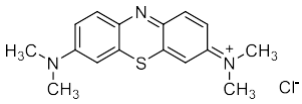
[Ir(dtbbpy)(ppy)$_2$]PF$_6$



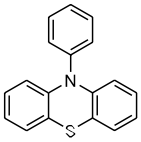
Eosin Y



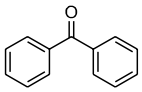
Rose Bengal



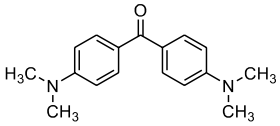
Methylene Blue



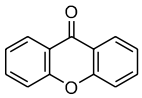
N-Phenylphenothiazine



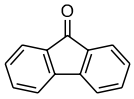
Benzophenone



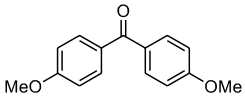
Michler's Ketone



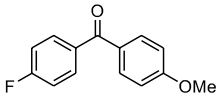
Xanthone



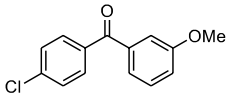
9-Fluorenone



4,4'-Dimethoxybenzophenone

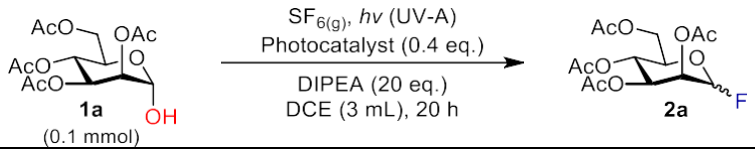


4-Fluoro-4'-methoxybenzophenone



4-Chloro-3'-methoxybenzophenone

Table SI-1. Photocatalyst Screening

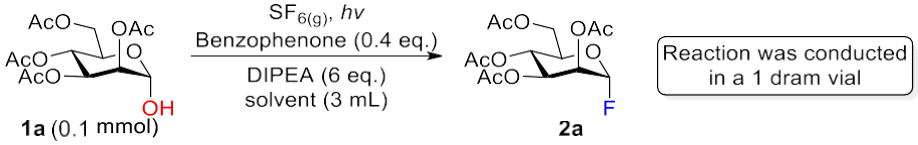


Entry	Photocatalyst	Light Source	NMR Yield[a]
1[b]	Ir(ppy)$_2$(dtbbpy)PF$_6$	Blue LED	38%
2	Eosin Y	Blue LED	7%
3	Eosin Y	UV-A Flood Lamp	9%
4	Rose Bengal	UV-A Flood Lamp	-
5	Methylene Blue	UV-A Flood Lamp	33%
6	*N*-Phenylphenothiazine	UV-A Flood Lamp	43%
7	Benzophenone	Blue LED	26%
8	Benzophenone	UV-A Flood Lamp	33%
9	Michler's Ketone	UV-A Flood Lamp	47%
10	Xanthone	UV-A Flood Lamp	25%
11	9-Fluorenone	UV-A Flood Lamp	7%
12	4,4'-Dimethoxybenzophenone	Blue LED	45%
13	**4,4'-Dimethoxybenzophenone**	**UV-A Flood Lamp**	**60%**
14	4-Fluoro-4'-methoxybenzophenone	UV-A Flood Lamp	56%
15	4-Chloro-3'-methoxybenzophenone	UV-A Flood Lamp	29%

[a] Determined by ^{19}F NMR with α,α,α-trifluorotoluene as an internal standard.
[b] 5 mol% of Ir(ppy)$_2$(dtbbpy)PF$_6$ and 3 eq. of DIPEA were used.

b. Reaction Condition Optimization

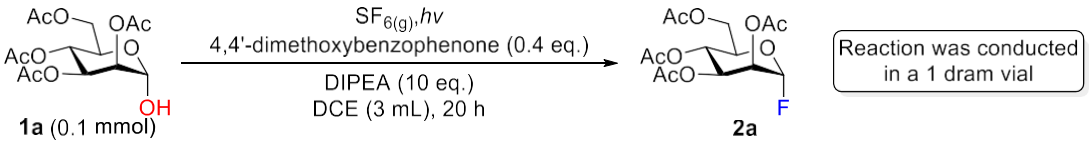
Table SI-2. Solvent Optimization



Entry	Light Source	Solvent	NMR Yield[a]
1	UV-A LED	DCE	After 16 h: 40% / 26 h: 47% / 40 h: 55%
2	UV-A Flood Lamp	Toluene	After 20 h: 21% / 33 h: 25% / 57 h: 36%
3	UV-A Flood Lamp	EtOAc	After 20 h: 12% / 33 h: 14% / 57 h: 16%

[a] Determined by ^{19}F NMR with α,α,α-trifluorotoluene as an internal standard.

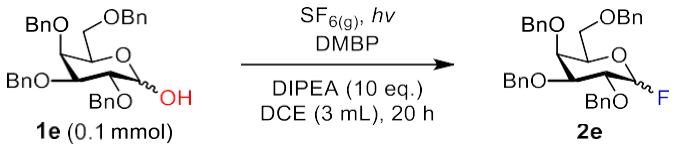
Table SI-3. Reaction Condition Optimization



Entry	Light Source	Modification	NMR Yield[a]
1	UV-A LED	Reaction was run for 40 hours	53%
2	UV-A LED	Oxygen balloon was added alongside SF_6 balloon	41%
3	UV-A Flood Lamp	5 eq. of DIPEA	43%
4	UV-A Flood Lamp	10 eq. of DIPEA	61%
5	UV-A Flood Lamp	20 eq. of DIPEA	59%
6	UV-A Flood Lamp	40 eq. of DIPEA	25%
7	UV-A Flood Lamp	10 eq. of triethylamine	52%
8	UV-A Flood Lamp	10 eq. of quinuclidine	5.5%

[a] Determined by ^{19}F NMR with α,α,α-trifluorotoluene as an internal standard.

Table SI-4. Light Source Optimization

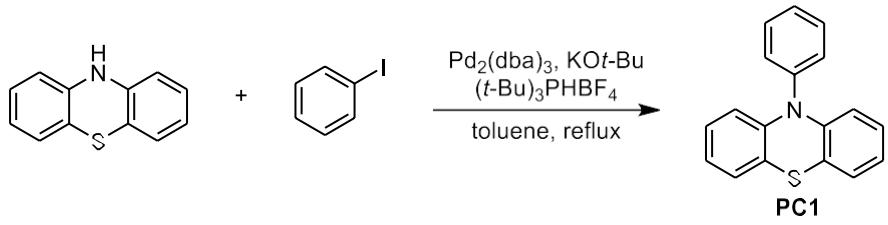


Entry	Photocatalyst Loading	Light Source	Reaction Vessel	Yield
1	0.1 eq.	Two UV-A Flood Lamps	60 mL syringe	84% (46 mg)
2	0.2 eq.	Two UV-A Flood Lamps	60 mL syringe	77% (42 mg)
3	0.2 eq.	One UV-A Flood Lamp	60 mL syringe	80% (44 mg)
4	0.4 eq.	One UV-A Flood Lamp	1 dram vial	59%[a]

[a] Determined by ^{19}F NMR with α,α,α-trifluorotoluene as an internal standard.

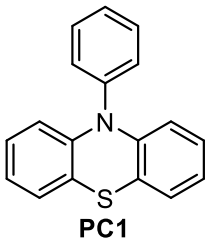
III. Experimental Procedure

a. Synthesis of Photocatalysts



Synthesis of *N*-phenylphenothiazine

In an oven dried round bottom flask, phenothiazine (4.06 mmol, 1.0 equiv.) was dissolved in anhydrous toluene (10 mL). Iodobenzene (4.95 mmol, 1.2 equiv.), KO*t*-Bu (5.28 mmol, 1.3 equiv.), and (t-Bu)$_3$PHBF$_4$ (0.24 mmol, 0.06 equiv.) were added, followed by the addition of Pd$_2$(dba)$_3$ (0.24 mmol, 0.06 equiv.). The reaction mixture was stirred under reflux for 20 h. After cooling the reaction to room temperature, EtOAc (100 mL) and water (50 mL) were added to the reaction mixture. The aqueous layer was extracted with EtOAc (100 mL x 3). The collected organic phase was dried with Na_2SO_4 and concentrated *in vacuo*. The product was purified by FCC (SiO_2, pure hexanes) and confirmed by comparing with literature NMR spectra.[1]

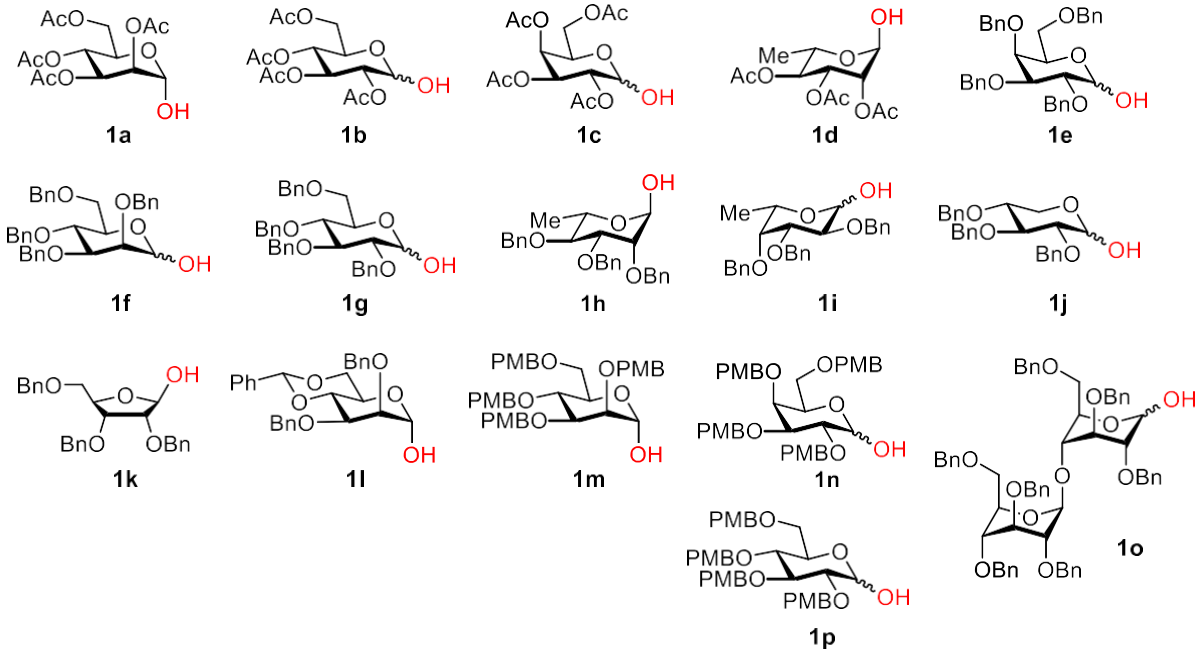


***N*-Phenylphenothiazine (PC1)**

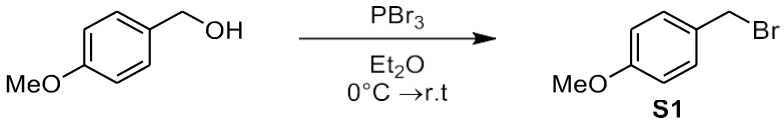
^{1}H NMR (700 MHz, CD_3CN) δ 7.64 (t, J = 7.7 Hz, 2H), 7.52 (td, J = 7.5, 1.1 Hz, 1H), 7.39 (dt, J = 7.2, 1.1 Hz, 2H), 7.04 (dt, J = 7.5, 1.2 Hz, 2H), 6.90 (ddd, J = 8.4, 7.1, 1.3 Hz, 2H), 6.84 (tt, J = 7.4, 1.1 Hz, 2H), 6.22 (dt, J = 8.3, 1.1 Hz, 2H); **^{13}C NMR** (176 MHz, CD_3CN) δ 145.6, 142.4, 132.3, 131.8, 129.7, 128.6, 128.4, 124.1, 121.5, 117.7; **IR** (thin film, cm^{-1}): 2921, 1584, 1569, 1489, 1459, 1442, 1301, 1254, 1237, 1126, 1070, 1042, 1022, 1003, 969, 935, 898, 854, 774, 751, 740, 704, 693, 631, 617; **HRMS (ESI-TOF)** (m/z): $[M]^+$ calcd for $C_{18}H_{13}NS$ 275.0769, found 275.0767.

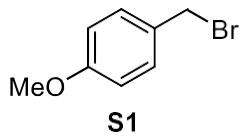
[1]Speck, F.; Rombach, D.; Wagenknecht, H-A. *Beilstein J. Org. Chem.* **2019**, 15, 52–59.

b. Synthesis of Substrates



Preparation of 4-Methoxybenzyl bromide (S1)

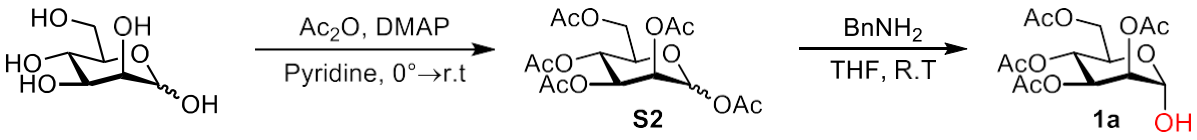


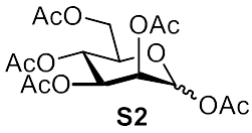


4-Methoxybenzyl bromide (S1)

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 h 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, $CDCl_3$) 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).

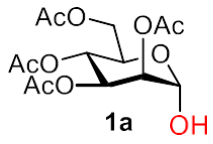
Preparation of 2,3,4,6-tetra-*O*-acetyl-*D*-mannopyranose (1a)





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

In an oven dried round-bottom flask, *D*-mannose (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 (150 mL x 2), water (150 mL x 2), 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-D-mannopyranoside **S2** (α:β = 6.2:1) as yellowish gum. 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).

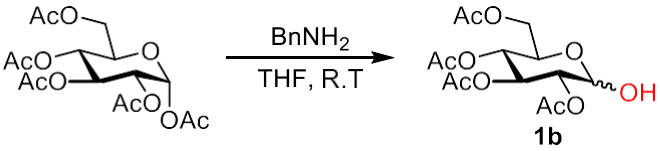


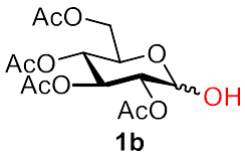
2,3,4,6-Tetra-*O*-acetyl-α-*D*-mannopyranoside (1a)

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 hexanes → 60% EtOAc in hexanes) to afford 2,3,4,6-tetra-O-acetyl-D-mannopyranoside **1a** as yellowish solid, which was confirmed by comparing with reported NMR spectra.[2] **^{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).

[2]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 2,3,4,6-tetra-*O*-acetyl-*D*-glucopyranoside (1b)



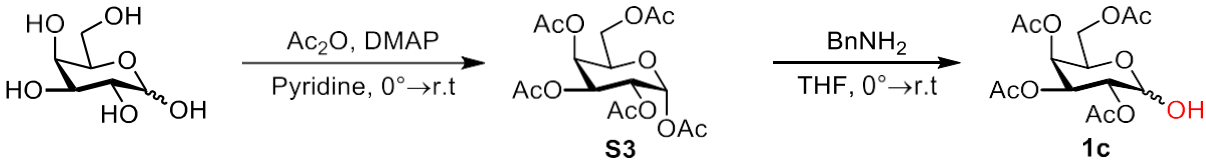


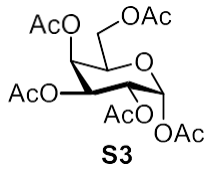
2,3,4,6-Tetra-*O*-acetyl-*D*-glucopyranoside (1b)

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 **1b** as yellowish solid, which is confirmed by comparing with literature NMR spectra.[3]

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

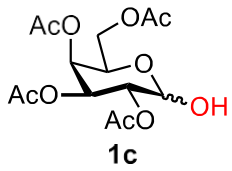
Preparation of 2,3,4,6-tetra-*O*-acetyl-*α*-*D*-galactopyranose (1c)





1,2,3,4,6-Penta-*O*-acetyl-*α*-*D*-galactopyranoside (S3)

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 **S3** as yellowish gum. 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).

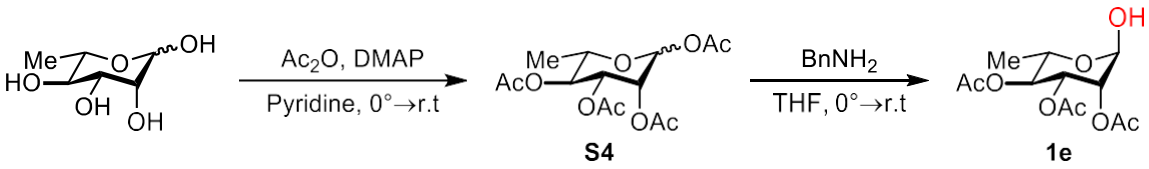


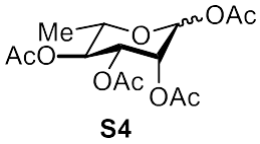
2,3,4,6-tetra-*O*-acetyl-*D*-galactopyranoside (1c)

In an oven dried round-bottom flask, **S3** (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 hexanes → 60% EtOAc in hexanes) to afford 2,3,4,6-tetra-*O*-acetyl-*D*-galactopyranoside **1c** as yellowish solid, which was confirmed by comparing with reported NMR spectra.[4]

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

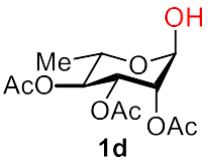
Preparation of 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranoside (1d)





1,2,3,4-Tetra-*O*-acetyl-*L*-rhamnopyranoside (S4)

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 yield 1,2,3,4-tetra-*O*-acetyl-*L*-rhamnopyranoside **S4** as yellowish gum. The product was then subjected to the next synthesis without further purification.

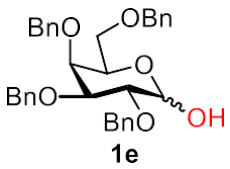


2,3,4-Tri-*O*-acetyl-α-*L*-rhamnopyranoside (1d)

In an oven dried round-bottom flask, **S4** (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 hexanes → 50% EtOAc in hexanes) to afford 2,3,4-tri-*O*-acetyl-α-*L*- rhamnopyranoside **1d** as yellowish solid, which is confirmed by comparing with literature NMR spectra.[5]

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

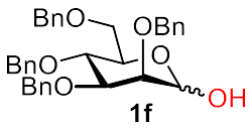
Preparation of 2,3,4,6-tetrakis-*O*-(phenylmethyl)-*D*-galactopyranoside (1e)



1e

Purchased from Alfa Aesar. Lot#: E28Z019.

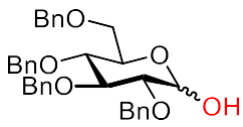
Preparation of 2,3,4,6-tetrakis-*O*-(phenylmethyl)-*D*-Mannopyranoside (1f)



1f

Purchased from Chem-Impex. Lot#: 001684-20150326.

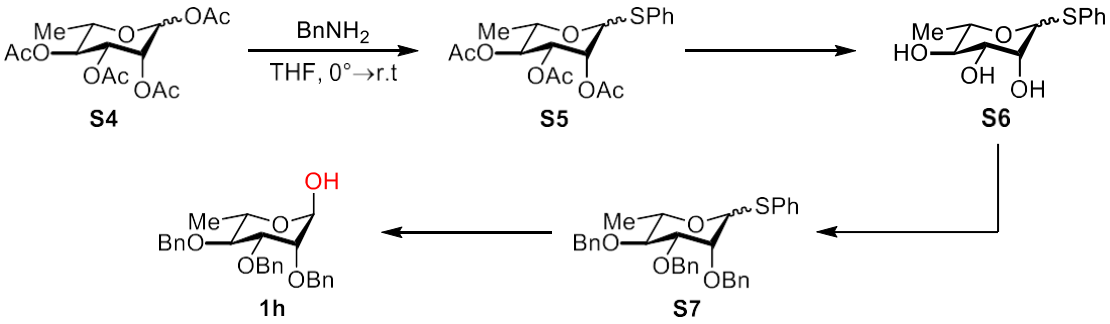
Preparation of 2,3,4,6-Tetrakis-*O*-(phenylmethyl)-*D*-glucopyranoside (1g)

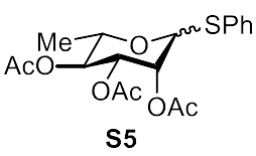


1g

Purchased from CarboSynth. Batch#: MT066911502.

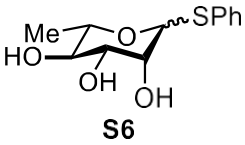
Preparation of 2,3,4-tri-*O*-(phenylmethyl)-α-*L*-rhamnopyranoside (1h)





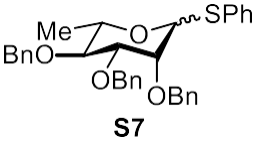
Phenyl 2,3,4-tri-*O*-acetyl-1-thio-*L*-rhamnopyranoside (S5)

In an oven dried round bottom flask, **S4** (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 hexanes) to afford phenyl 2,3,4-tri-*O*-acetyl-1-thio-*L*-rhamnopyranoside **S5** as white solid.



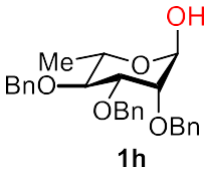
Phenyl 1-thio-*L*-rhamnopyranoside (S6)

In an oven dried round bottom flask, **S5** (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 yield phenyl 1-thio-*L*-rhamnopyranoside **S6** as white gum. The product was then subjected to next reaction without further purification.



Phenyl 2,3,4-tri-*O*-(phenylmethyl)-1-thio-*L*-rhamnopyranoside (S7)

An oven dried and nitrogen filled round-bottom flask was charged with **S6** (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 hexanes) to afford phenyl 2,3,4-tri-*O*-(phenylmethyl)-1-thio-*L*-rhamnopyranoside **S7** as yellowish oil.



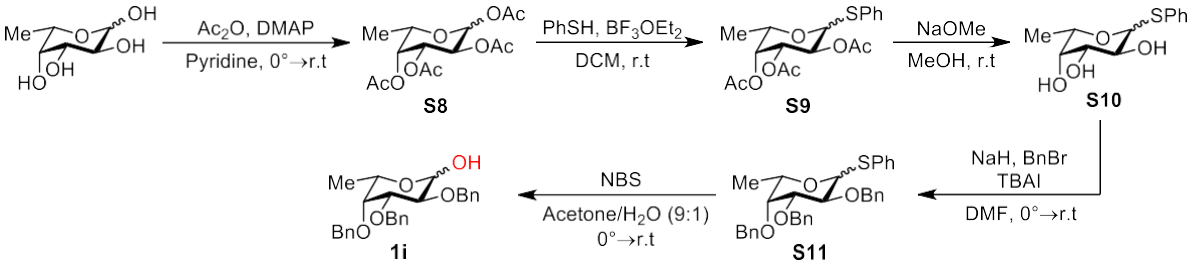
1h

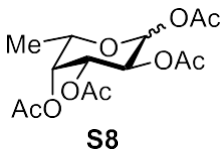
2,3,4-tri-*O*-(phenylmethyl)-*α*-*L*-rhamnopyranoside (1h)

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 hexanes) to afford 2,3,4-tri-*O*-(phenylmethyl)-α-*L*-rhamnopyranoside **1h** as white solid, which is confirmed by comparing with literature NMR spectra.[6]

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

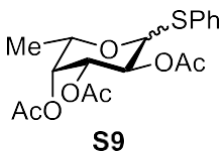
Preparation of 2,3,4-tris-*O*-(phenylmethyl)-*L*-fucopyranoside (1i)





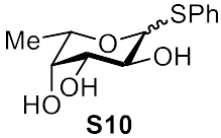
1,2,3,4-Tetra-*O*-acetyl-*L*-fucopyranoside (S8)

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 **S8** is subjected to the next synthesis without further purification.



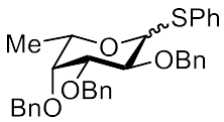
Phenyl 2,3,4-tri-*O*-acetyl-1-thio-*L*-fucopyranoside (S9)

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 **S9** as white solid.



Phenyl 1-thio-*L*-fucopyranoside (S10)

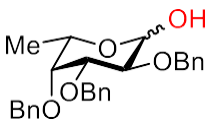
In an oven dried round bottom flask, **S9** (2.9 mmol, 1 equiv.) and MeOH (20 mL) were added. After stirring until the mixture became homogeneous, Na metal (0.29 mmol, 0.1 equiv.) was added and stirred at room temperature until all starting materials were consumed. Once all starting materials are gone,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



S11

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

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 hexanes) to afford phenyl 2,3,4-tris-*O*-(phenylmethyl)-1-thio- *L*-fucopyranoside **S11** as yellowish oil.



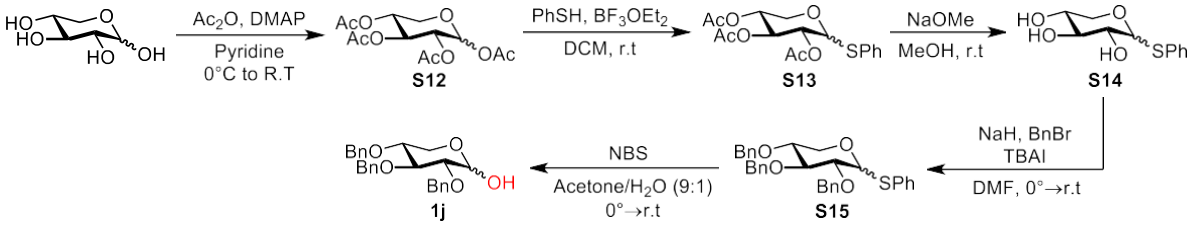
1i

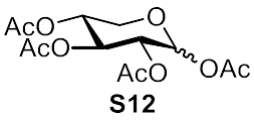
2,3,4-Tris-*O*-(phenylmethyl)-*L*-fucopyranoside (1i)

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 (SiO_2, 30% EtOAc in hexanes) to afford **1i** as white solid, which is confirmed by comparing with literature NMR spectra.[7]

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

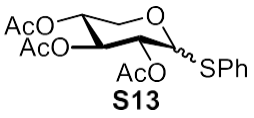
Preparation of 2,3,4-tris-*O*-(phenylmethyl)-*D*-xylopyranoside (1j)





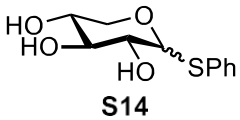
1,2,3,4-Tetra-*O*-acetyl-*D*-xylopyranoside (S12)

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 **S12** is subjected to the next synthesis without further purification.



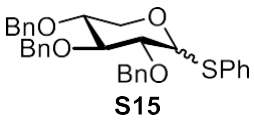
Phenyl 2,3,4-tri-*O*-acetyl-1-thio-D-xylopyranoside (S13)

In an oven dried round-bottom flask, **S12** (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 **S14** as yellowish oil.



Phenyl 1-thio-*D*-xylopyranoside (S14)

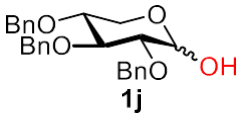
A dry round-bottom flask was filled with **S14** (13 mmol, 1.0 equiv.) and anhydrous methanol (40 mL). After the reaction mixture became homogeneous, a chip of sodium metal (1.3 mmol, 0.1 equiv.) was added. The reaction was stirred overnight at room temperature, and then quenched by adding acetic acid 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 **S14** was subjected to the next synthesis without further purification.



S15

Phenyl 2,3,4-tris-*O*-(phenylmethyl)-1-thio-*D*-xylopyranoside (S15)

An oven dried and nitrogen filled round-bottom flask was charged with **S14** (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 **S15** as yellowish oil.

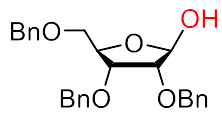


1j

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

In a clean round-bottom flask, **S15** (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 (SiO2, 10% EtOAc in DCM) to afford 2,3,4-tris-*O*-(phenylmethyl)-*D*-xylopyranose **1j** as white solid, which is confirmed by comparing with literature NMR spectra.[8]

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

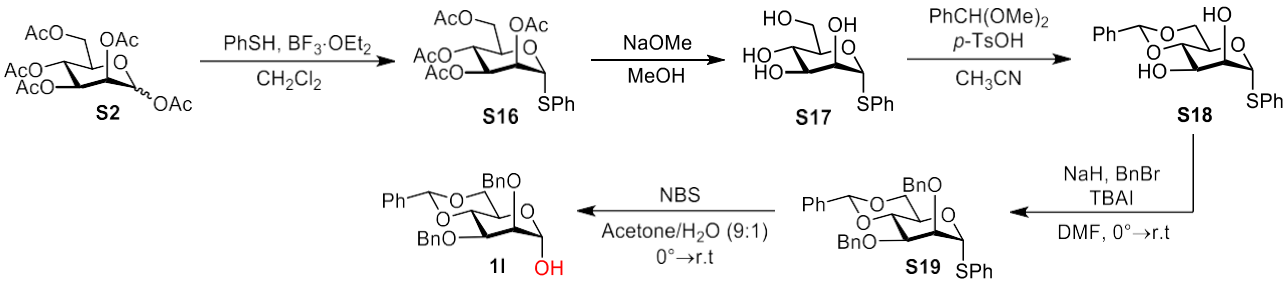


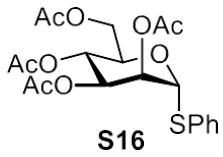
1k

Purchased from Combi-Blocks. Batch#: A98634.

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

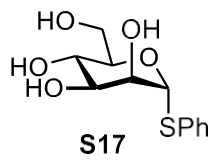
Preparation of 2,3-bis-*O*-(phenylmethyl)-4,6-*O*-[(*R*)-phenylmethylene]-α-*D*-mannopyranoside (1l)





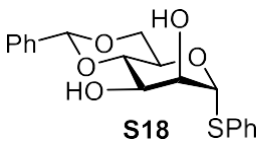
Phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-α-*D*-mannopyranoside (S16)

In an oven dried round-bottom flask, **S2** (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 aqueous $NaHCO_3$ (saturated, 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 hexanes → 40% EtOAc in hexanes) to afford phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-*D*-mannopyranoside **S16** as yellowish oil.



Phenyl 1-thio-α-*D*-mannopyranoside (S17)

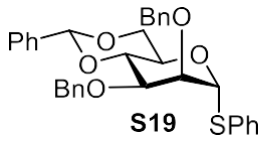
A dry round-bottom flask was filled with **S16** (9.5 mmol, 1.0 equiv.) and anhydrous methanol (40 mL). After the reaction mixture became homogeneous, a chip of sodium metal (0.95 mmol, 0.1 equiv.) was added. The reaction was stirred overnight at room temperature, and then quenched by adding acetic acid until the pH of the reaction became neutral. The crude mixture was concentrated *in vacuo* to yield yellowish white solid. The product was subjected to the next synthesis without further purification.



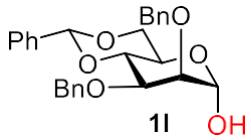
Phenyl 4,6-*O*-[(*R*)-phenylmethylene]-1-thio-α-*D*-manopyranoside (S18)

An oven dried and nitrogen filled round-bottom flask was charged with **S17** (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 hexanes) 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 (S19)



An oven dried and nitrogen filled round-bottom flask was charged with **S18** (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*.

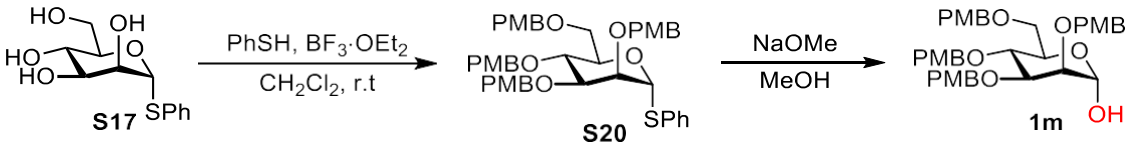


2,3-Bis-*O*-(phenylmethyl)-4,6-*O*-[(*R*)-phenylmethylene]-α-*D*-mannopyranoside (1l)

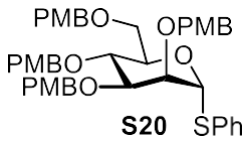
In a clean round-bottom flask, **S19** (3.0 mmol, 1.0 equiv.) was dissolved with acetone/water mixture (9:1, 22.2 mL). After cooling down the mixture in an ice bath, NBS (6.3 mmol, 2.1 equiv.) was added. The reaction was stirred overnight while it was gradually warmed up to the room temperature. Water (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 hexanes) to afford 2,3-bis-*O*-(phenylmethyl)-4,6-*O*-[(*R*)-phenylmethylene]-α-*D*-mannopyranoside **1l** as white solid, which is confirmed by comparing with literature NMR spectra.[9]

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

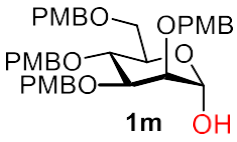
Preparation of 2,3,4,6-tetrakis-*O*-[(4-methoxyphenyl)methyl]-α-*D*-mannopyranoside (1m)



Phenyl 2,3,4,6-tetrakis-*O*-[(4-methoxyphenyl)methyl]-1-thio-α-*D*-mannopyranoside (S20)



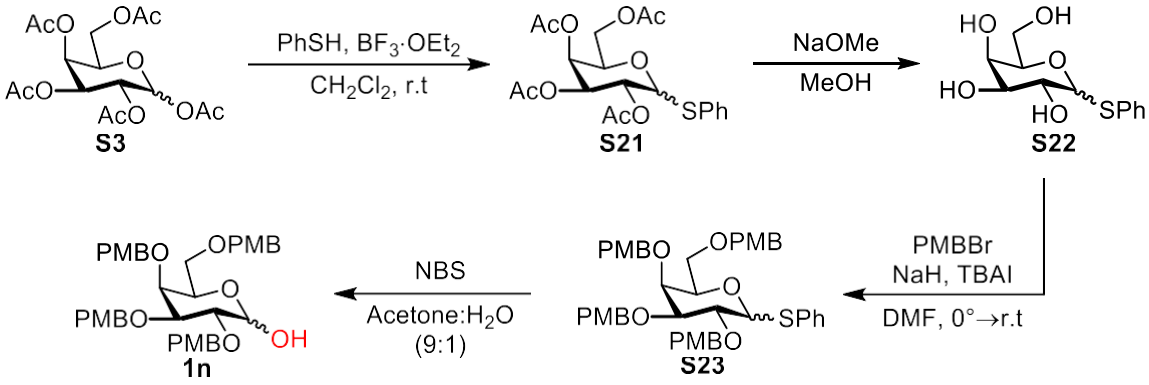
An oven dried and nitrogen filled round-bottom flask was charged with **S17** (9.5 mmol, 1.0 equiv.) and DMF (50 mL). After cooling down the reaction in an ice bath, NaH (52 mmol, 5.5 equiv.) was added portion wise. Once H_2 gas stops generating, PMBBr (47.5 mmol, 5.0 equiv.) was added followed by TBAI (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, hexanes → 40% EtOAc in hexanes) to afford phenyl 2,3,4,6-tetrakis-*O*-[(4-methoxyphenyl)methyl]-1-thio-α-*D*-mannopyranoside **S20**.

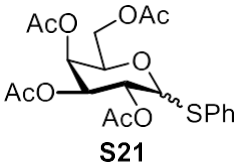


2,3,4,6-Tetrakis-*O*-[(4-methoxyphenyl)methyl]-α-*D*-mannopyranoside (1m)

In a clean round-bottom flask, **S20** (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 hexanes → 70% EtOAc in hexanes) 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; **HRMS (ESI-TOF)** (m/z): $[M+Na]^+$ calcd for $C_{38}H_{44}NaO_{10}$ 683.2832, found 683.2810

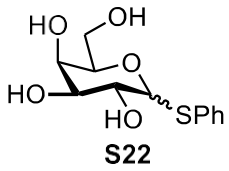
Preparation of 2,3,4,6-tetrakis-*O*-[(4-methoxyphenyl)methyl]-*D*-galactopyranose (1n)





Phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-*D*-galactopyranoside (S21)

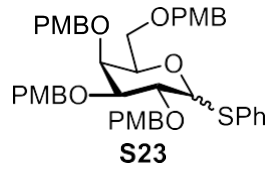
In an oven dried round-bottom flask, **S3** (11 mmol, 1.0 equiv.) and DCM (15 mL) were added. After the addition of thiophenol (16.5 mmol, 1.5 equiv.), the round-bottom flask was sealed with a rubber-septum cap and purged with nitrogen gas. The reaction mixture was stirred until it became homogeneous, 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 hexanes → 40% EtOAc in hexanes) to afford phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-*D*-galactopyranoside **S21** as product. **^{1}H NMR** (500 MHz, $CDCl_3$) 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).



Phenyl 1-thio-*D*-galactopyranoside (S22)

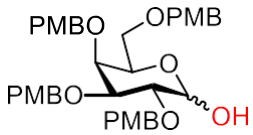
A dry round-bottom flask was filled with **S21** (11 mmol, 1.0 equiv.) and dry methanol (45 mL). After the reaction mixture became homogeneous, a chip of sodium metal (1.1 mmol, 0.1 equiv.) was added. The reaction was stirred overnight at room temperature, and then quenched by adding acetic acid until the pH of the reaction became neutral. The crude mixture was concentrated *in vacuo* to yield 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 (S23)



S23

An oven dried and nitrogen filled round-bottom flask was charged with S22 (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 hexanes → 30% EtOAc in hexanes) to afford phenyl 2,3,4,6-tetrakis-*O*-[(4-methoxyphenyl)methyl]-1-thio-*D*-galactopyranoside **S23** as yellowish gum.



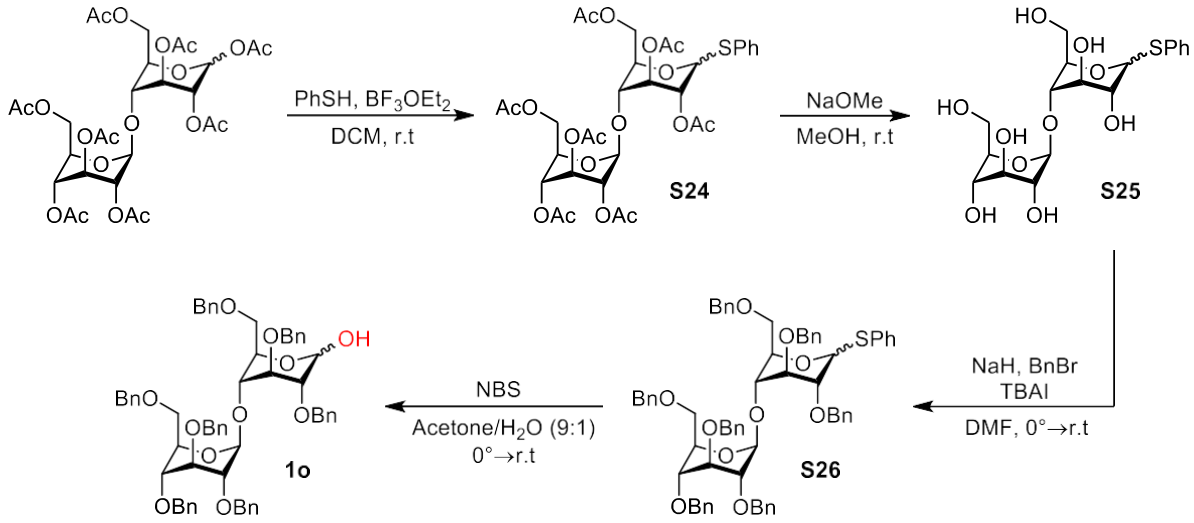
1n

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

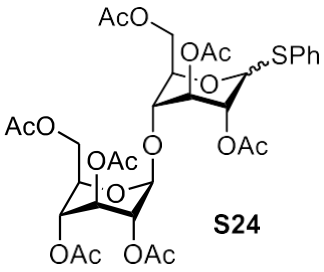
In a clean round-bottom flask, **S23** (10 mmol, 1.0 equiv.) was dissolved with acetone/water mixture (9:1, 55.5 mL). After cooling down the mixture in an ice bath, NBS (21 mmol, 2.1 equiv.) was added. The reaction was stirred overnight while it was gradually warmed up to the room temperature. Water (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 hexanes → 40% EtOAc in hexanes) to afford 2,3,4,6-tetrakis-*O*-[(4-methoxyphenyl)methyl]-*D*-galactopyranoside **1n** as white solid product, which is confirmed by comparing with literature NMR spectra.[10]

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

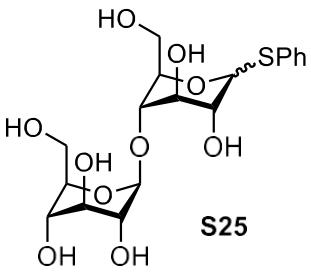
Preparation of 2,3,6-tris-*O*-(phenylmethyl)-4-*O*-[2,3,4,6-tetrakis-*O*-(phenylmethyl)-β-*D*-glucopyranosyl]-*D*-glucopyranoside (1o)



Phenyl 4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-1-thio-*D*-glucopyranoside 2,3,6-triacetate (S24)



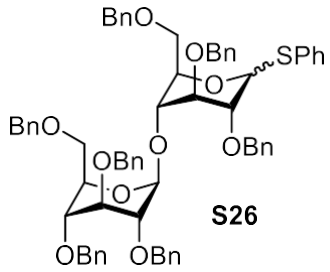
In an oven dried round-bottom flask, α-D-cellobiose octaacetate (3.0 mmol, 1.0 equiv.) and DCM (10 mL) were added. After the addition of thiophenol (4.5 mmol, 1.5 equiv.), the round-bottom flask was sealed with a rubber-septum cap and purged with nitrogen gas. The reaction mixture was stirred until it 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 hexanes) to afford phenyl 4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl)-1-thio-*D*-glucopyranoside 2,3,6-triacetate **S24** as fluffy white solid.



Phenyl 4-*O*-β-D-glucopyranosyl-1-thio-*D*-glucopyranoside (S25)

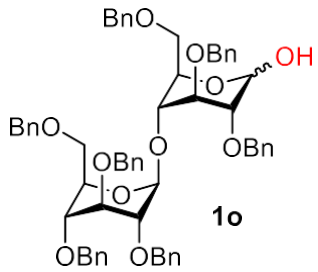
A dry round-bottom flask was filled with **S24** (3.0 mmol, 1.0 equiv.) and dry methanol (20 mL). After the reaction mixture became homogeneous, a chip of sodium metal (0.3 mmol, 0.1 equiv.) was added. The reaction was stirred overnight at room temperature, and then quenched by adding acetic acid until the pH of the reaction became neutral. The crude mixture was concentrated *in vacuo* to yield **S25** 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 (S26)



An oven dried and nitrogen filled round-bottom flask was charged with **S25** (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, hexanes → 20% EtOAc in hexanes) 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 **S26** as yellowish white solid.

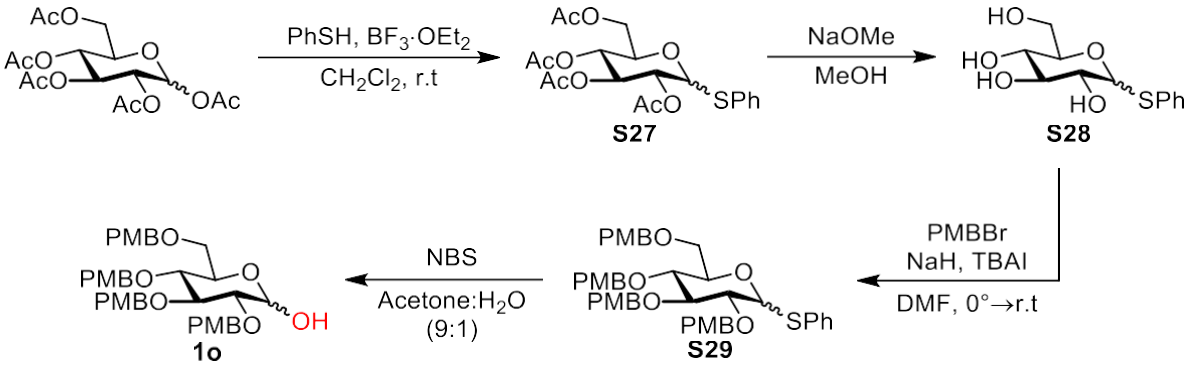
2,3,6-Tris-*O*-(phenylmethyl)-4-*O*-[2,3,4,6-tetrakis-*O*-(phenylmethyl)-β-D-glucopyranosyl]-*D*-glucopyranoside (1o)

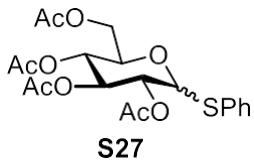


In a clean round-bottom flask, **S26** (2.0 mmol, 1.0 equiv.) was dissolved with acetone/water mixture (9:1, 22 mL). After cooling down the mixture in an ice bath, NBS (4.2 mmol, 2.1 equiv.) was added. The reaction was stirred overnight while it was gradually warmed up to the room temperature. Water (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 (SiO_2, 30% EtOAc in hexanes) to afford 2,3,6-tris-*O*-(phenylmethyl)-4-*O*-[2,3,4,6-tetrakis-*O*-(phenylmethyl)-β-*D*-glucopyranosyl]-*D*-glucopyranoside **1o** 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

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

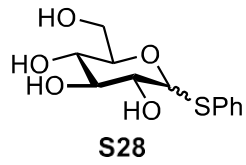




S27

Phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-*D*-glucopyranoside (S27)

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 hexanes) to afford phenyl 2,3,4,6-tetra-*O*-acetyl-1- thio-*D*-glucopyranoside **S27** as white solid.

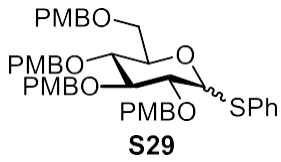


S28

Phenyl 1-thio-*D*-glucopyranoside (S28)

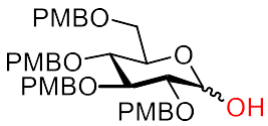
A dry round-bottom flask was filled with **S27** (5.0 mmol, 1.0 equiv.) and dry methanol (30 mL). After the reaction mixture became homogeneous, a chip of sodium metal (0.5 mmol, 0.1 equiv.) was added. The reaction was stirred overnight at room temperature, and then quenched by adding acetic acid until the pH of the reaction became neutral. The crude mixture was concentrated *in vacuo* to yield **S28** 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 (S29)



S29

An oven dried and nitrogen filled round-bottom flask was charged with **S28** (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 hexanes) to afford phenyl 2,3,4,6-tetrakis-*O*-[(4-methoxyphenyl)methyl]-1-thio-*D*-glucopyranoside **S29** as yellowish white gum.



1o

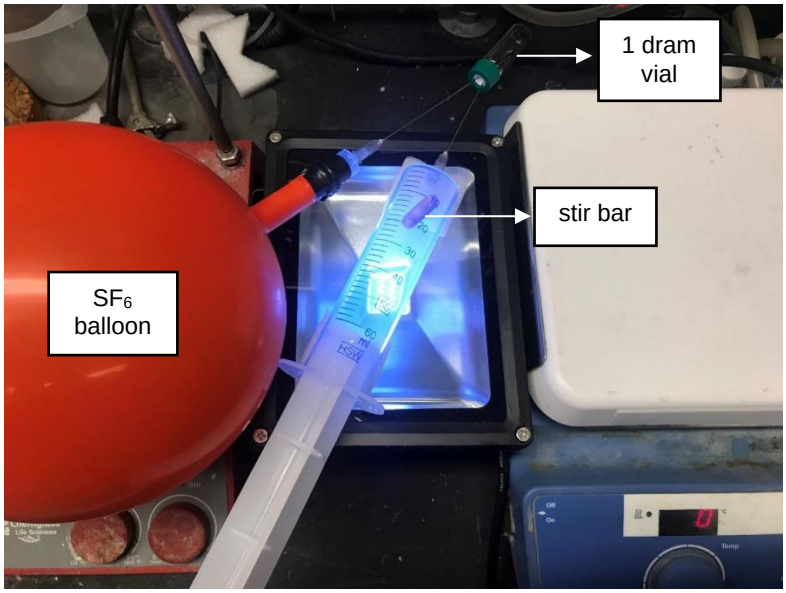
2,3,4,6-Tetrakis-*O*-[(4-methoxyphenyl)methyl]-α-*D*-glucopyranoside (1o)

In a clean round-bottom flask, **S26** (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 hexanes) to afford 2,3,4,6-tetrakis-*O*-[(4-methoxyphenyl)methyl]-α-D-glucopyranoside **1o** as white solid, the structure of which was confirmed by the comparison with the reported in literature NMR spectra.[12]

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

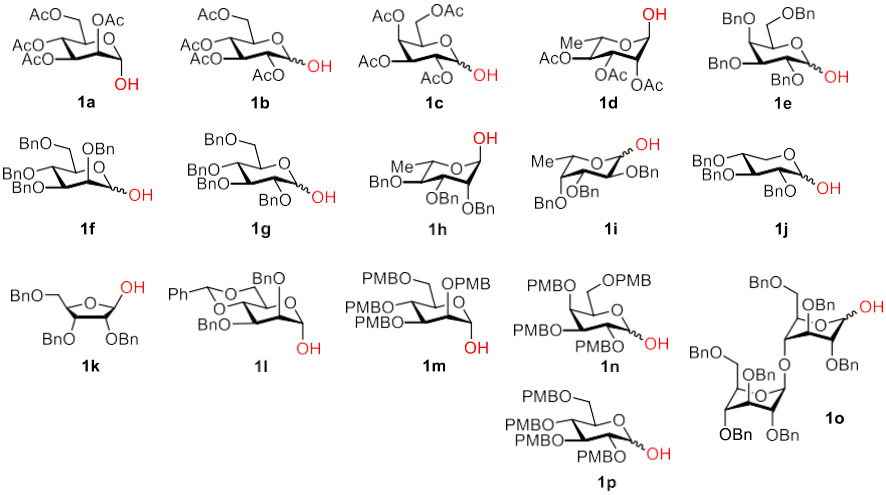
c. Synthesis of Glycosyl Fluorides

General Procedure: An oven-dried 1 dram vial was charged with the sugar substrate (0.1 mmol, 1 equiv.) and 4,4'-dimethoxybenzophenone (0.02 mmol, 0.2 equiv.). 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, DCE (3 mL) and DIPEA (1 mmol, 10 equiv.) were added, and the vial was sonicated 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 outlet needle was removed followed by transfer of the reaction mixture into a 60 mL plastic syringe containing a stir bar. The syringe containing the mixture was placed on UV-A Flood Light lamp (distance between the lamp and the syringe = 1cm) and the reaction was stirred for 20 h, and then stopped by turning off the UV-A lamp.



The resultant reaction mixture was diluted with 30 mL of DCM, and then washed with 1N HCl (20 mL x 3), $NaHCO_3$ (20 mL), water (20 mL), and brine (25 mL). The extracted organic layer was dried with Na_2SO_4 and concentrated *in vacuo* to give red-brown oil, which was subjected to FCC (SiO_2) to afford a pure product.

Procedure for acetylated glycosides: Similar to the general procedure except 0.03 mmol (0.3 equiv.) of 4,4'-dimethoxybenzophenone was used instead of 0.02 mmol (0.2 equiv.). For the substrates **1b** and **1c**, two UV-A lamps were used instead of one.


1a
1b
1c
1d
1e
1f
1g
1h
1i
1j
1k
1l
1m
1n
1o
1p

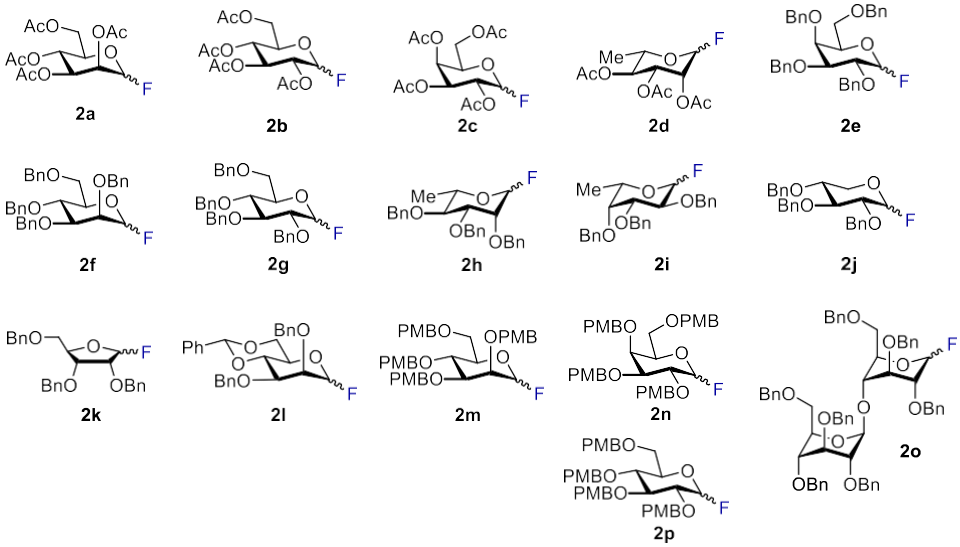
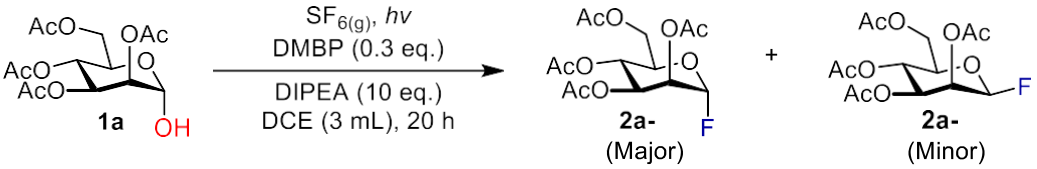

2a
2b
2c
2d
2e
2f
2g
2h
2i
2j
2k
2l
2m
2n
2o
2p

Table SI-5. Initial and final *a*:*b* ratios of the starting materials **1** used in the reactions and products **2**

Substrate	Initial dr (*a*:*b* ratio) of the starting substrate 1 determined by ^{1}H NMR	Product fluoride (2) dr (*a*:*b* ratio) Determined by ^{19}F NMR
1a	alpha only	13:1
1b	5:1	1:4.8
1c	4.2:1	1:3.1
1d	alpha only	6.7:1
1e	1.4:1	1:2.9
1f	2.5:1	19:1
1g	4.75:1	1:3.7
1h	alpha only	5:1
1i	2.7:1	1:3.6
1j	5.5:1	1:4.3
1k	beta only	1:13
1l	alpha only	7.8:1
1m	alpha only	36:1
1n	3.35:1	1:2.4
1o	1.86:1	1:3.4
1p	3:1	1.3.7

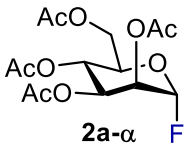
Table SI-6. Summary of the previous methods for the synthesis of glycosyl fluoride products **2**

product	method	yield	d.r. (*a*:*b*)	link to the paper
2a	Xtalfluor-E, DCE, reflux	94%	alpha only	Link
2b	DAST, DCM, microreactor	89%	5:4	Link
2c	DAST, DCE, 70°C	38%	1:2.4	Link
	DAST, DMTST, DCM, 25°C	100%	1:9.1	
2d	AgF. I_2	80%	alpha only	Link
2e	DAST (1.2 eq.), THF, -30°C, N_2	91%	3:5	Link
2f	DAST (1.2 eq.), THF, -30°C, N_2	91%	alpha only	Link
2g	DAST, DCM, microreactor	100%	1:4	Link
2h	–	–	–	–
2i	DAST, NBS, DCM, -15°C	98%	1:2	Link
2j	HF, DCM, -70°C	~ 100%	alpha only	Link
2k	DAST (1.2 eq.), THF, -30°C, N_2	90%	10:1	Link
2l	DAST, -78°C to 0°C, 2h	91%	beta only	Link
2m	-	–	–	–
2n	NBS, DAST	93%	not provided	Link
2o	–	–	–	–
2p	–	–	–	–



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

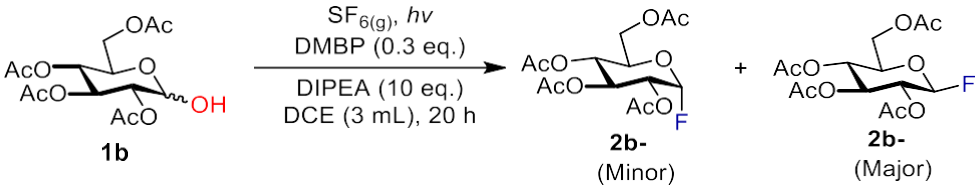
The product was synthesized employing a procedure for acetylated glycosides. After a work-up, the reaction mixture was subjected to FCC (SiO_2, pure hexanes → 40% EtOAc in hexane) to afford pure **2a** (25.1 mg, α : β = 13 : 1) in 72% yield as yellow oil. Stereochemistry of the products was confirmed by comparing with previously reported NMR spectra.[13]



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

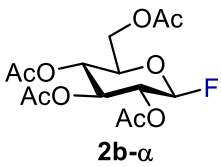
^{1}H NMR (700 MHz, $CDCl_3$) δ 5.58 (d, *J* = 48.6 Hz, 1H), 5.40 (s, 1H), 5.35 (d, *J* = 5.0 Hz, 2H), 4.32 – 4.27 (m, 1H), 4.16 (dd, *J* = 14.7, 4.4 Hz, 2H), 2.17 (s, 3H), 2.11 (s, 3H), 2.06 (s, 3H), 2.01 (s, 3H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 170.5, 169.7, 169.6, 169.5, 104.7 (d, $^{1}J_{C\text{-}F}$ = 223.7 Hz, β-C_1), 70.9 (d, $^{3}J_{C\text{-}F}$ = 2.7 Hz), 68.2, 67.7 (d, $^{2}J_{C\text{-}F}$ = 39.5 Hz), 65.0, 61.8, 20.7, 20.6, 20.6; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -138.36 (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-TOF)** (m/z): $[M+Na]^+$ calcd for $C_{14}H_{19}FNaO_9$ 373.0911, found 373.0905; **[α]$_D^{24}$** = +11.2 (c = 0.5, CH_2Cl_2).

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



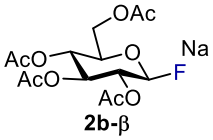
Synthesis of 2,3,4,6-Tetra-*O*-acetyl-*D*-glucopyranosyl fluoride (2b)

The product was synthesized employing a procedure for acetylated glycosides. After a work-up, the reaction mixture was subjected to FCC (SiO_2, pure hexanes → 40% EtOAc in hexanes) to afford **2b** as amber colored oil (14.1 mg, α : β = 1 : 4.8) in 53% yield.



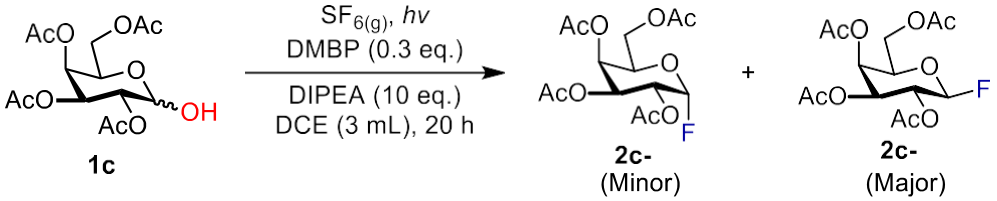
2,3,4,6-Tetra-*O*-acetyl-α-*D*-glucopyranosyl fluoride (Minor product)

^{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, $^1J_{C\text{-}F}$ = 229.5 Hz, α-C_1), 70.2 (d, $^2J_{C\text{-}F}$ = 24.5 Hz), 69.8 (d, $^3J_{C\text{-}F}$ = 4.3 Hz), 69.4, 67.3, 61.2, 20.7, 20.6, 20.5; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -149.75 (dd, *J* = 52.8, 24.3 Hz, α-C_1-F); **IR** (thin film, cm^{-1}): 2918, 1743, 1434, 1367, 1208, 1160, 1103, 1033, 904, 779; **HRMS (ESI-TOF)** (m/z): $[M+Na]^+$ calcd for $C_{14}H_{19}FNaO_9$ 373.0911, found 373.0899



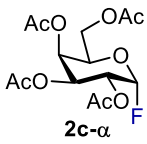
2,3,4,6-Tetra-*O*-acetyl-β-*D*-glucopyranosyl fluoride (Major product)

^{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, $^1J_{C\text{-}F}$ = 219.6 Hz, β-C_1), 72.0 (d, $^3J_{C\text{-}F}$ = 3.8 Hz), 71.8 (d, $^3J_{C\text{-}F}$ = 8.3 Hz), 71.2 (d, $^2J_{C\text{-}F}$ = 28.8 Hz), 67.4, 61.7, 20.7, 20.6; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -137.07 (dd, *J* = 51.9, 10.4 Hz, β-C_1-F); **IR** (thin film, cm^{-1}): 2918, 1743, 1434, 1367, 1208, 1160, 1103, 1033, 904, 779; **HRMS (ESI-TOF)** (m/z): $[M+Na]^+$ calcd for $C_{14}H_{19}FNaO_9$ 373.0911, found 373.0899; **$[\alpha]_D^{24}$** = +13.6 (c = 0.5, CH_2Cl_2)



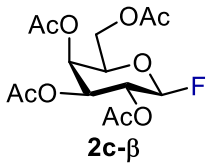
Synthesis of 2,3,4,6-Tetra-*O*-acetyl-*D*-galactopyranosyl fluoride (2c)

The product was synthesized employing a procedure for acetylated glycosides. After a work-up, the reaction mixture was subjected to FCC (SiO_2, pure hexanes → 40% EtOAc in hexanes) to afford **2c** as amber colored oil (15.6 mg, α : β = 1 : 3.1) in 45% yield.



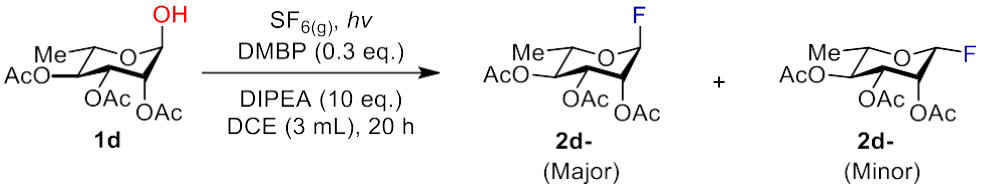
2,3,4,6-Tetra-*O*-acetyl-α-*D*-galactopyranosyl fluoride (Minor product).

^{1}H NMR (700 MHz, $CDCl_3$) 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, $^1J_{C\text{-}F}$ = 228.4 Hz, α-C_1), 68.9 (d, $^3J_{C\text{-}F}$ = 3.5 Hz), 67.5, 67.3, 67.0, 61.3, 20.7, 20.6, 20.6; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -150.77 (dd, *J* = 53.1, 24.0 Hz); **IR** (thin film, cm^{-1}): 2921, 2851, 1744, 1369, 1212, 1167, 1104, 1042, 951, 899; **HRMS (ESI-TOF)** (m/z): $[M+Na]^+$ calcd for $C_{14}H_{19}FNaO_9$ 373.0911, found 373.0905; **$[\alpha]_D^{25}$** = +28.1 (c = 0.4, CH_2Cl_2)



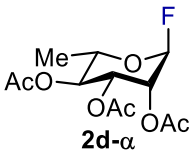
2,3,4,6-Tetra-*O*-acetyl-β-*D*-galactopyranosyl fluoride (Major product).

^{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 170.4, 170.0, 169.9, 169.3, 107.1 (d, $^1J_{C\text{-}F}$ = 218.6 Hz, β-C_1), 71.2 (d, $^3J_{C\text{-}F}$ = 4.7 Hz), 70.0 (d, $^3J_{C\text{-}F}$ = 10.6 Hz), 68.8 (d, $^2J_{C\text{-}F}$ = 24.9 Hz), 66.4, 61.3, 20.7, 20.6, 20.5; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -141.42 (dd, *J* = 50.7, 13.2 Hz); **IR** (thin film, cm^{-1}): 2921, 2851, 1744, 1369, 1212, 1167, 1104, 1042, 951, 899; **HRMS (ESI-TOF)** (m/z): $[M+Na]^+$ calcd for $C_{14}H_{19}FNaO_9$ 373.0911, found 373.0905; **$[\alpha]_D^{25}$** = +6.0 (c = 0.4, CH_2Cl_2)



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

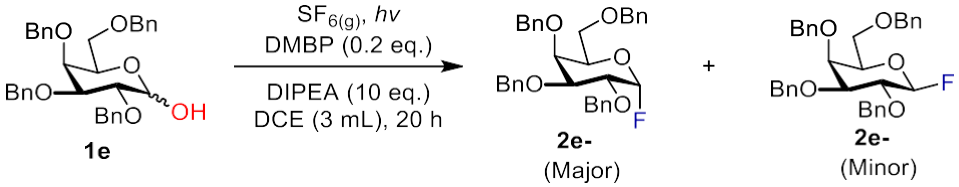
The product was synthesized employing a procedure for acetylated glycosides. After a work-up, the reaction mixture was purified by FCC (SiO_2, pure hexanes → 10% EtOAc in hexanes) to afford **2d** as amber colored oil (21.3 mg, α : β = 6.7 : 1) in 73% yield. Stereochemistry of the products was confirmed by comparing with previously reported NMR spectra.[14]



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

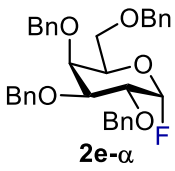
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.49 (dd, *J* = 48.6, 1.9 Hz, 1H), 5.38 (ddd, *J* = 3.2, 1.9, 0.9 Hz, 1H), 5.29 (ddd, *J* = 10.2, 3.6, 1.7 Hz, 1H), 5.12 (t, *J* = 10.0 Hz, 1H), 4.04 (dq, *J* = 9.9, 6.2 Hz, 1H), 2.16 (s, 3H), 2.06 (s, 3H), 2.00 (s, 3H), 1.27 (d, *J* = 6.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.8, 169.8, 169.7, 104.8 (d, $^1J_{C\text{-}F}$ = 221.9 Hz), 70.0, 68.9 (d, $^3J_{C\text{-}F}$ = 3.0 Hz), 68.2 (d, $^3J_{C\text{-}F}$ = 1.7 Hz), 70.0 (d, $^2J_{C\text{-}F}$ = 40.3 Hz), 20.7, 20.7, 20.6, 17.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -137.47 (d, *J* = 48.9 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, 640

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



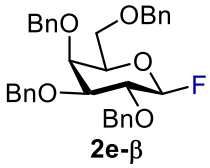
Synthesis of 2,3,4,6-tetrakis-*O*-(phenylmethyl)-*D*-galactopyranosyl fluoride (2e)

The product was synthesized employing the general procedure. After a work-up, the reaction mixture was subjected to FCC (SiO_2, pure hexanes → 30% EtOAc in hexanes) to afford pure **2e** (46.4 mg, α : β = 1 : 2.9) in 85% yield as cloudy oil.



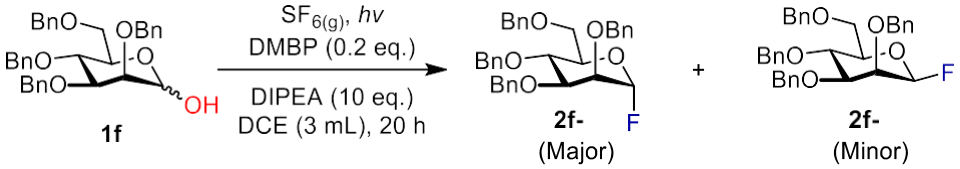
2,3,4,6-Tetrakis-*O*-(phenylmethyl)-α-*D*-galactopyranosyl fluoride (minor product).

^{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, 138.4, 138.0, 137.7, 128.4, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.8, 127.7, 127.7, 127.5, 106.2 (d, $^1J_{C\text{-}F}$ = 226.1 Hz, α-C_1), 78.4, 75.7 (d, $^2J_{C\text{-}F}$ = 23.8 Hz), 74.8, 74.3, 73.7, 73.5, 73.1, 71.7 (d, $^3J_{C\text{-}F}$ = 2.8 Hz), 68.2; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -150.10 (dd, *J* = 53.7, 25.2 Hz); **IR** (thin film, cm^{-1}): 3030, 2870, 1496, 1453, 1363, 1302, 1208, 1099, 1053, 1027, 910, 820, 732, 695, 632; **HRMS (ESI-TOF)** (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)



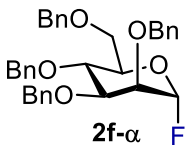
2,3,4,6-Tetrakis-*O*-(phenylmethyl)-β-*D*-galactopyranosyl fluoride (major product).

^{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, 138.1, 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, $^1J_{C\text{-}F}$ = 215.4 Hz, β-C_1), 81.0 (d, $^3J_{C\text{-}F}$ = 11.3 Hz), 79.1 (d, $^2J_{C\text{-}F}$ = 20.8 Hz), 75.0, 75.0, 74.6, 73.6, 73.6, 73.1, 73.0, 68.3; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -139.13 (d, *J* = 53.4 Hz); **IR** (thin film, cm^{-1}): 3030, 2870, 1496, 1453, 1363, 1302, 1208, 1099, 1053, 1027, 910, 820, 732, 695, 632; **HRMS (ESI-TOF)** (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-tetraki-O-(phenylmethyl)-*D*-mannopyranosyl fluoride (2f)

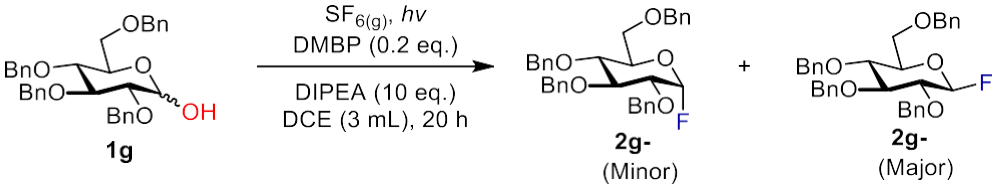
The product was synthesized employing the general procedure. After a work-up, the reaction mixture was subjected to FCC (SiO_2, pure hexanes → 30% EtOAc in hexanes) to afford **2f** as cloudy oil (37.6 mg, α : β = 19 : 1) in 69% yield. Stereochemistry of products was confirmed by comparing with previously reported NMR spectra.[15]



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

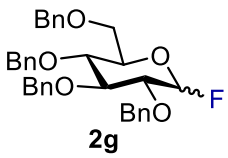
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 18H), 7.20 – 7.17 (m, 2H), 5.61 (d, *J* = 50.8 Hz, 1H), 4.89 (d, *J* = 10.8 Hz, 1H), 4.81 (d, *J* = 12.3 Hz, 1H), 4.72 – 4.64 (m, 4H), 4.55 (d, *J* = 12.4 Hz, 2H), 4.09 (t, *J* = 9.5 Hz, 1H), 3.93 (ddd, *J* = 10.1, 4.7, 1.8 Hz, 1H), 3.89 (d, *J* = 8.9 Hz, 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, 106.44 (d, $^1J_{C\text{-}F}$ = 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** (471 MHz, $CDCl_3$) δ -138.01 (d, *J* = 50.6 Hz); **IR** (thin film, cm^{-1}): 3030, 2863, 1496, 1453, 1363, 1311, 1183, 1094, 1026, 952, 801, 733, 695; **HRMS (ESI-TOF)** (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)

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



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

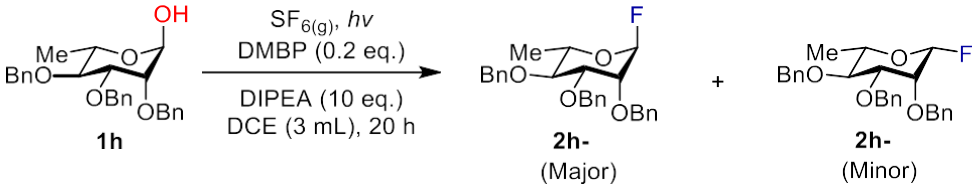
The product was synthesized employing the general procedure. After a work-up, the reaction mixture was subjected to FCC (SiO_2, pure hexanes → 20% EtOAc in hexanes) to afford **2g** as cloudy oil (44.1 mg, α : β = 1 : 3.7) in 81% yield.



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

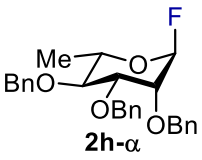
(Isolated as α : β = 1 : 3.7)

^{1}H NMR (700 MHz, Chloroform-*d*) δ 7.41 – 7.28 (m, 24.2H), 7.18 (dd, *J* = 7.3, 2.3 Hz, 2.65H), 5.59 (dd, *J* = 53.2, 2.6 Hz, 0.27H, α-C_1-H), 5.29 (dd, *J* = 52.9, 6.8 Hz, 1H, β-C_1-H), 4.99 (d, *J* = 10.9 Hz, 0.29H), 4.93 (d, *J* = 11.0 Hz, 1H), 4.90 – 4.86 (m, 1.61H), 4.85 – 4.80 (m, 2.32H), 4.74 (d, *J* = 11.2 Hz, 1.40H), 4.66 (d, *J* = 12.1 Hz, 1H), 4.63 (d, *J* = 12.1 Hz, 0.36H), 4.57 (dd, *J* = 11.5, 3.0 Hz, 2H), 4.55 (d, *J* = 10.8 Hz, 0.35H), 4.51 (d, *J* = 12.2 Hz, 0.33H), 4.02 (t, *J* = 9.4 Hz, 0.28H), 4.00 – 3.96 (m, 0.28H), 3.80 – 3.74 (m, 3.68H), 3.73 – 3.68 (m, 1.37H), 3.66 – 3.57 (m, 2.40H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 138.4, 138.2, 138.0, 137.8, 137.8, 137.7, 137.6, 137.6, 128.5, 128.4, 128.4, 128.4, 128.4, 128.11, 128.0, 128.0, 127.9, 127.9, 127.8, 127.8, 127.8, 127.8, 127.7, 127.7, 127.7, 109.8 (d, $^1J_{C\text{-}F}$ = 215.9 Hz, β-C_1), 105.5 (d, $^1J_{C\text{-}F}$ = 226.8 Hz, α-C_1), 83.4 (d, $^3J_{C\text{-}F}$ = 11.2 Hz), 81.5, 81.4, 81.4, 79.3 (d, $^2J_{C\text{-}F}$ = 24.8 Hz), 76.6, 75.8, 75.4, 75.1, 74.9, 74.8 (d, $^3J_{C\text{-}F}$ = 4.9 Hz), 74.4 (d, $^3J_{C\text{-}F}$ = 2.1 Hz), 73.5, 73.5 (d, $^3J_{C\text{-}F}$ = 3.4 Hz), 72.6 (d, *J* = 3.9 Hz), 68.3, 67.8; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -137.93 (dd, *J* = 53.4, 11.8 Hz), -149.47 (dd, *J* = 53.5, 25.5 Hz); **IR** (thin film, cm^{-1}): 3030, 2867, 1496, 1453, 1360, 1308, 1208, 1155, 1088, 1062, 909, 821, 733. 695; **HRMS (ESI-TOF)** (m/z): $[M+Na]^+$ calcd for $C_{34}H_{35}FNaO_5$ 565.2392, found 565.2353



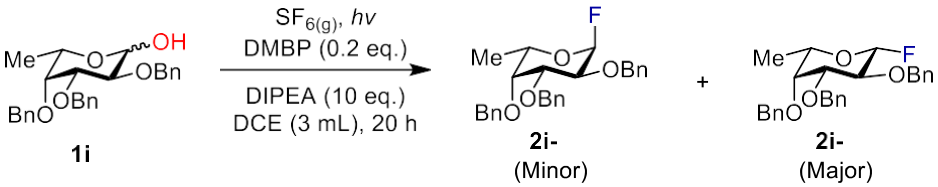
Synthesis of 2,3,4-tris-*O*-(phenylmethyl)-L-rhamnopyranosyl fluoride (2h)

The product was synthesized employing the general procedure. The product was purified by FCC (SiO_2, pure hexanes → 20% EtOAc in hexanes) and was obtained as amber colored oil (29.7 mg, α : β = 5 : 1) in 68% yield. The structure of the product was confirmed by comparing with previously reported data.



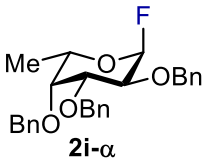
2,3,4-Tris-*O*-(phenylmethyl)-α-L-rhamnopyranosyl fluoride (Major product)

^{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, $^1J_{C\text{-}F}$ = 221.1 Hz), 79.6, 79.2, 75.4, 73.7 (d, $^2J_{C\text{-}F}$ = 35.2 Hz), 73.4, 72.6, 70.6 (d, $^3J_{C\text{-}F}$ = 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-TOF)** (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)



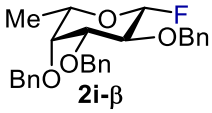
Synthesis of 2,3,4-tris-*O*-(phenylmethyl)-L-fucopyranosyl fluoride (2i)

The product was synthesized employing the general procedure. The product was purified by FCC (SiO_2, pure hexanes → 20% EtOAc in hexanes) and was obtained as amber colored oil (35 mg, α : β = 1 : 3.6) in 80% yield.



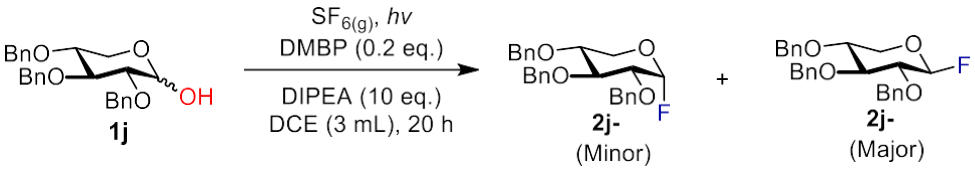
2,3,4-Tris-*O*-(phenylmethyl)-α-L-fucopyranosyl fluoride (minor product).

^{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, $^1J_{C\text{-}F}$ = 224.5 Hz, α-C_1), 78.8, 75.6 (d, $^2J_{C\text{-}F}$ = 23.9 Hz), 74.9, 73.7, 73.2, 69.1 (d, $^3J_{C\text{-}F}$ = 3.2 Hz), 16.5; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -149.66 (dd, *J* = 54.1, 25.3 Hz); **IR** (thin film, cm^{-1}): 3030, 2872, 1496, 1453, 1361, 1307, 1208, 1100, 1056, 1027, 912, 801, 732, 695, 629 ; **HRMS (ESI-TOF)** (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)



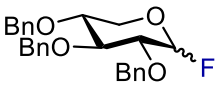
2,3,4-tris-*O*-(phenylmethyl)-β-L-fucopyranosyl fluoride (major product).

^{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, $^1J_{C\text{-}F}$ = 213.5 Hz, β-C_1), 81.4 (d, $^3J_{C\text{-}F}$ = 11.7 Hz), 79.0 (d, $^2J_{C\text{-}F}$ = 20.6 Hz), 75.8, 74.9, 74.7, 73.3, 70.8 (d, $^3J_{C\text{-}F}$ = 4.9 Hz), 16.6; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -139.10 (dd, *J* = 53.2, 13.1 Hz); **IR** (thin film, cm^{-1}): 3030, 2872, 1496, 1453, 1361, 1307, 1208, 1100, 1056, 1027, 912, 801, 732, 695, 629 ; **HRMS (ESI-TOF)** (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)-D-xylopyranosyl fluoride (2j)

The product was synthesized employing the general procedure. The product was purified by FCC (SiO_2, pure hexanes → 20% EtOAc in hexanes) and was obtained as amber colored oil (33.7 mg, α : β = 1 : 4.3) in 80% yield.

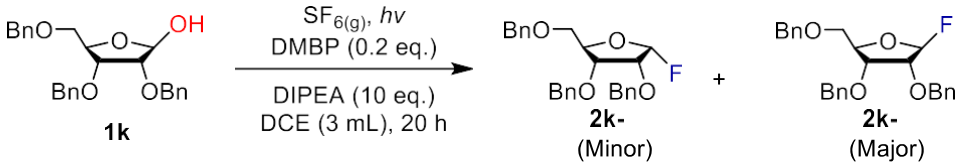


2j

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

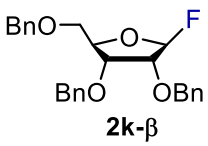
(Isolated as α : β = 1 : 4.3 mixture).

^{1}H NMR (700 MHz, $CDCl_3$) δ 7.40 – 7.30 (m, 19.57H), 5.48 (dd, *J* = 53.1, 2.7 Hz, 0.23H, α-C_1-H), 5.35 (dd, *J* = 54.0, 5.6 Hz, 1H, β-C_1-H), 4.93 (s, 0.45H), 4.84 – 4.76 (m, 3.49H), 4.73 – 4.68 (m, 2.45H), 4.67 – 4.60 (m, 1.56H), 4.06 (ddd, *J* = 12.2, 4.2, 1.6 Hz, 1H), 3.93 (t, *J* = 9.3 Hz, 0.25H), 3.79 (dd, *J* = 11.3, 5.8 Hz, 0.38H), 3.74 – 3.66 (m, 2.32H), 3.63 (ddd, *J* = 10.8, 9.0, 5.7 Hz, 0.33H), 3.60 – 3.52 (m, 2H), 3.48 (ddd, *J* = 25.7, 9.6, 2.7 Hz, 0.34H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 138.2, 137.8, 137.7, 128.5, 128.5, 128.4, 128.4, 128.3, 128.3, 128.0, 128.0, 128.0, 127.9, 127.9, 127.9, 127.9, 127.8, 127.8, 127.8, 127.7, 127.7, 127.7, 110.1 (d, $^1J_{C\text{-}F}$ = 218.6 Hz, β-C_1), 105.6 (d, $^1J_{C\text{-}F}$ = 227.4 Hz, α-C_1), 80.8, 80.6 (d, $^3J_{C\text{-}F}$ = 9.1 Hz), 79.7 (d, $^2J_{C\text{-}F}$ = 25.1 Hz), 79.1 (d, $^2J_{C\text{-}F}$ = 24.8 Hz), 76.7, 75.8, 74.7, 74.1, 74.1, 73.6 (d, $^2J_{C\text{-}F}$ = 18.3 Hz), 72.7, 71.0 (d, $^3J_{C\text{-}F}$ = 9.7 Hz), 63.2 (d, $^3J_{C\text{-}F}$ = 4.4 Hz), 61.9 (d, $^3J_{C\text{-}F}$ = 4.7 Hz); **^{19}F NMR** (471 MHz, $CDCl_3$) δ -134.11 (dd, *J* = 53.9, 11.6 Hz), -151.07 (dd, *J* = 53.1, 25.7 Hz); **IR** (thin film, cm^{-1}): 3030, 2869, 1496, 1453, 1361, 1257, 1208, 1162, 1088. 1027, 942, 733, 695, 618; **HRMS (ESI-TOF)** (m/z): $[M+Na]^+$ calcd for $C_{26}H_{27}FNaO_4$ 445.1792, found 445.1780.



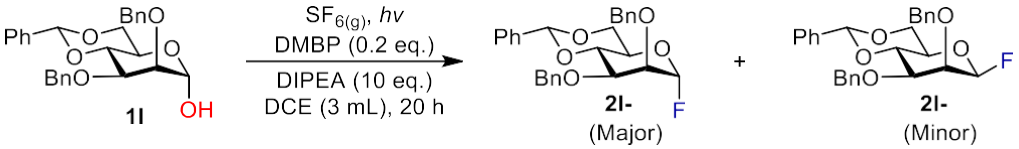
Synthesis of 2,3,5-Tris-*O*-(phenylmethyl)-D-ribofuranosyl fluoride (2k)

The product was synthesized employing the general procedure. The product was purified by FCC (SiO_2, pure hexanes → 30% EtOAc in hexanes) and was obtained as amber colored oil (33.5 mg, α : β = 1 : 13) in 79% yield.



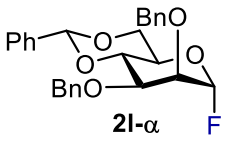
2,3,5-Tris-*O*-(phenylmethyl)-β-D-ribofuranosyl fluoride (Major porduct).

^{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, $^{1}J_{C\text{-}F}$ = 224.4 Hz, β-C_1), 82.3 (d, $^{3}J_{C\text{-}F}$ = 2.6 Hz), 78.9 (d, $^{2}J_{C\text{-}F}$ = 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-TOF)** (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)



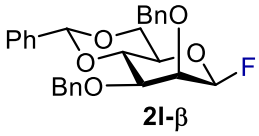
Synthesis of 2,3-bis-*O*-(phenylmethyl)-4,6-*O*-[(R)-phenylmethylene]-D-mannopyranosyl fluoride (2l)

The product was synthesized employing the general procedure. The product was purified by FCC (SiO_2, pure hexanes → 40% EtOAc in hexanes) and was obtained as amber colored oil (29.5 mg, α : β = 7.8 : 1) in 66% yield. Stereochemistry of the products was determined by comparing with previously reported NMR spectra.[16]



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

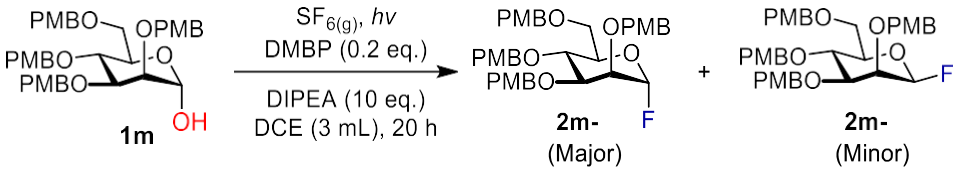
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.1 Hz, 2H), 7.41 – 7.28 (m, 13H), 5.65 (s, 1H), 5.50 (d, *J* = 49.6 Hz, 1H), 4.89 (d, *J* = 12.0 Hz, 2H), 4.74 – 4.68 (m, 2H), 4.33 – 4.27 (m, 2H), 3.99 – 3.92 (m, 3H), 3.87 (td, *J* = 10.3, 2.0 Hz, 1H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 138.3, 137.6, 137.4, 128.9, 128.5, 128.4, 128.2, 128.1, 128.1, 127.7, 127.6, 126.1, 107.0 (d, $^1J_{C\text{-}F}$ = 223.7 Hz), 101.6, 78.3, 75.5 (d, $^3J_{C\text{-}F}$ = 2.5 Hz), 75.0, 74.8, 74.2, 73.5, 68.3, 66.1 (d, $^3J_{C\text{-}F}$ = 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, 641; **HRMS (ESI-TOF)** (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).



2,3-Bis-*O*-(phenylmethyl)-4,6-*O*-[(R)-phenylmethylene]-β-D-mannopyranosyl fluoride (minor product, isolated as α : β = 1 : 7 mixture).

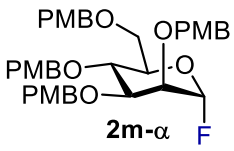
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.2 Hz, 2H), 7.44 (d, *J* = 7.5 Hz, 2H), 7.40 – 7.28 (m, 11H), 5.62 (s, 1H), 5.30 (d, *J* = 49.2 Hz, 1H), 4.93 – 4.80 (m, 2H), 4.71 (ddd, *J* = 84.0, 12.3, 2.2 Hz, 2H), 4.38 – 4.34 (m, 1H), 4.25 (td, *J* = 9.8, 2.1 Hz, 1H), 4.01 (t, *J* = 3.3 Hz, 1H), 3.95 (td, *J* = 10.4, 1.9 Hz, 1H), 3.67 (dt, *J* = 9.8, 2.8 Hz, 1H), 3.41 (td, *J* = 10.3, 9.6, 2.9 Hz, 1H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 138.0, 137.8, 137.2, 129.0, 128.4, 128.3, 128.2, 127.8, 127.8, 127.7, 126.0, 107.6 (d, $^1J_{C\text{-}F}$ = 217.5 Hz), 101.5, 78.2, 75.0 (d, $^2J_{C\text{-}F}$ = 17.0 Hz), 74.7 (d, $^4J_{C\text{-}F}$ = 1.6 Hz), 72.8, 68.3, 66.8 (d, $^3J_{C\text{-}F}$ = 5.3 Hz); **^{19}F NMR** (471 MHz, $CDCl_3$) δ -142.75 (d, *J* = 49.3 Hz); **IR** (thin film, cm^{-1}): 2919, 1454, 1372, 1313, 1214, 1166, 1099, 1054, 1006, 965, 925, 799, 735, 696, 641; **HRMS (ESI-TOF)** (m/z): $[M+Na]^+$ calcd for $C_{27}H_{27}FNaO_5$ 473.1692, found 473.1729; **$[\alpha]_D^{23}$** = -35.4 (c = 0.1, CH_2Cl_2).

[16]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 2,3,4,6-Tetrakis-*O*-[(4-methoxyphenyl)methyl]-D-mannopyranosyl fluoride (2m)

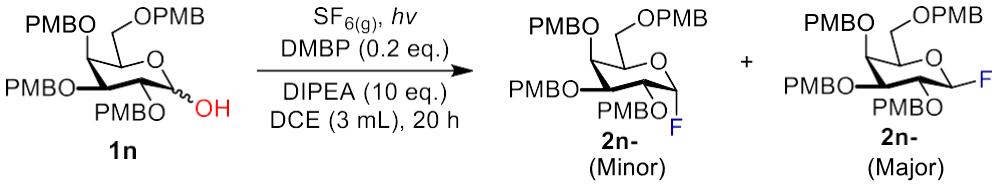
The product was synthesized employing the general procedure. The product was purified by FCC (SiO_2, pure hexanes → 10% EtOAc in hexanes) and was obtained as cloudy oil (49.2 mg, α : β = 36 : 1) in 74% yield



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

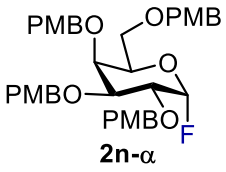
(Major Product)

^{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, $^1J_{C\text{-}F}$ = 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, 636; **HRMS (ESI-TOF)** (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).



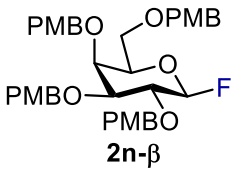
Synthesis of 2,3,4,6-tetrakis-*O*-[(4-methoxyphenyl)methyl]-D-galactopyranosyl fluoride (2n)

The product was synthesized employing the general procedure. The product was purified by FCC (SiO_2, pure hexanes → 30% EtOAc in hexanes) and was obtained as cloudy oil (37.5 mg, α : β = 1 : 2.4) in 72% yield



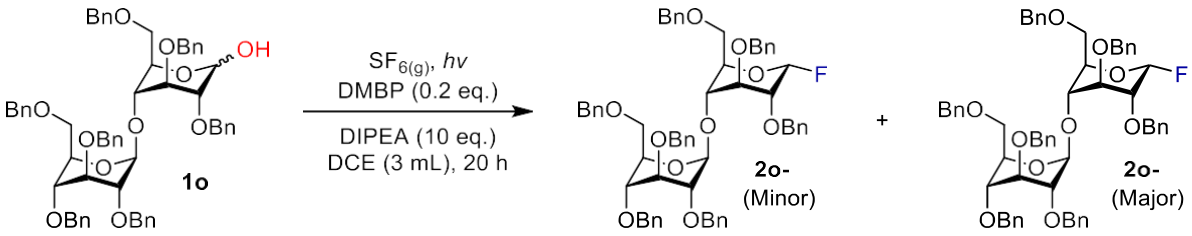
2,3,4,6-Tetrakis-*O*-[(4-methoxyphenyl)methyl]-α-D-galactopyranosyl fluoride (minor product).

^{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, $^1J_{C\text{-}F}$ = 225.8 Hz), 78.2, 75.3 (d, $^2J_{C\text{-}F}$ = 23.5 Hz), 74.4, 73.8, 73.4, 73.1, 72.7, 71.8 (d, $^3J_{C\text{-}F}$ = 2.7 Hz), 68.0, 55.3, 55.3, 55.2; **IR** (thin film, cm^{-1}): 2912, 2835, 1611, 1585, 1512, 1463, 1442, 1422, 1362, 1301, 1244, 1172, 1096, 1031, 817, 757, 710, 665, 637, 621; **HRMS (ESI-TOF)** (m/z): $[M+Na]^+$ calcd for $C_{38}H_{43}FNaO_9$ 685.2783, found 685.2716; **$[\alpha]_D^{23.3}$** = +26.9 (c = 0.13, CH_2Cl_2).



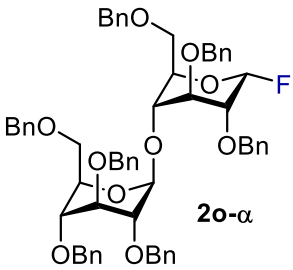
2,3,4,6-Tetrakis-*O*-[(4-methoxyphenyl)methyl]-β-D-galactopyranosyl fluoride (major product).

^{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, $^1J_{C\text{-}F}$ = 215.3 Hz, β-C_1), 80.7 (d, $^3J_{C\text{-}F}$ = 11.3 Hz), 78.8 (d, $^2J_{C\text{-}F}$ = 20.7 Hz), 74.7, 74.6, 74.1, 73.7 (d, $^3J_{C\text{-}F}$ = 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, 637, 622; **HRMS (ESI-TOF)** (m/z): $[M+Na]^+$ calcd for $C_{38}H_{43}FNaO_9$ 685.2783, found 685.2716; **$[\alpha]_D^{24}$** = +39.8 (c = 0.19, CH_2Cl_2).



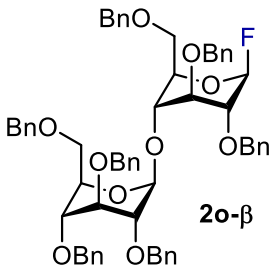
Synthesis of 2,3,6-Tris-O-(phenylmethyl)-4-O-[2,3,4,6-tetrakis-O-(phenylmethyl)-β-D-glucopyranosyl]-D-glucopyranosyl fluoride (2o)

The product was synthesized employing the general procedure.. The product was purified by FCC (SiO_2, pure hexanes → 20% EtOAc in hexanes) to afford **2o** as cloudy oil (68 mg, α : β = 1 : 3.4) in 70% yield.



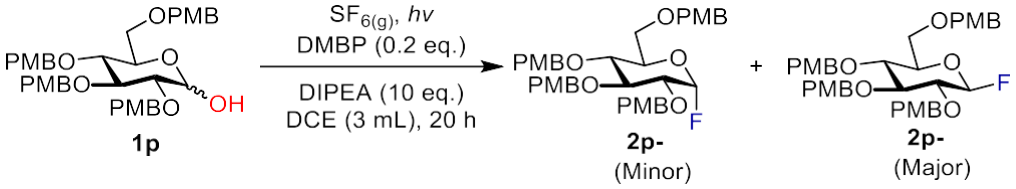
2,3,6-Tris-O-(phenylmethyl)-4-O-[2,3,4,6-tetrakis-O-(phenylmethyl)-β-D-glucopyranosyl]-α-D-glucopyranosyl fluoride (minor product).

^{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, $^1J_{C\text{-}F}$ = 226.8 Hz, α-C_1), 102.5, 84.9, 82.7, 79.8, 78.2 (d, $^2J_{C\text{-}F}$ = 24.3 Hz), 78.0, 75.6, 75.6, 75.4, 75.2, 75.0, 74.8, 73.8, 73.3, 72.6 (d, $^3J_{C\text{-}F}$ = 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, 635, 619, 611; **HRMS (ESI-TOF)** (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)



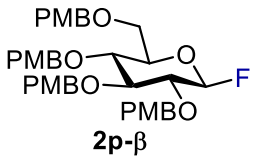
2,3,6-Tris-O-(phenylmethyl)-4-O-[2,3,4,6-tetrakis-O-(phenylmethyl)-β-D-glucopyranosyl]-β-D-glucopyranosyl fluoride (major product).

^{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, $^{1}J_{C\text{-}F}$ = 215.9 Hz, β-C_1), 102.3, 84.9, 82.7, 81.3 (d, $^{3}J_{C\text{-}F}$ = 10.3 Hz), 80.5 (d, $^{2}J_{C\text{-}F}$ = 23.0 Hz), 77.9, 75.8, 75.6, 75.0, 74.9 (d, $^{3}J_{C\text{-}F}$ = 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, 635, 619, 611; **HRMS (ESI-TOF)** (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)



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

The product was synthesized employing the general procedure. The product was purified by FCC (SiO_2, pure hexanes → 30% EtOAc in hexanes) to afford **2p** as cloudy oil (47.2 mg, α : β = 1 : 3.7) in 71% yield

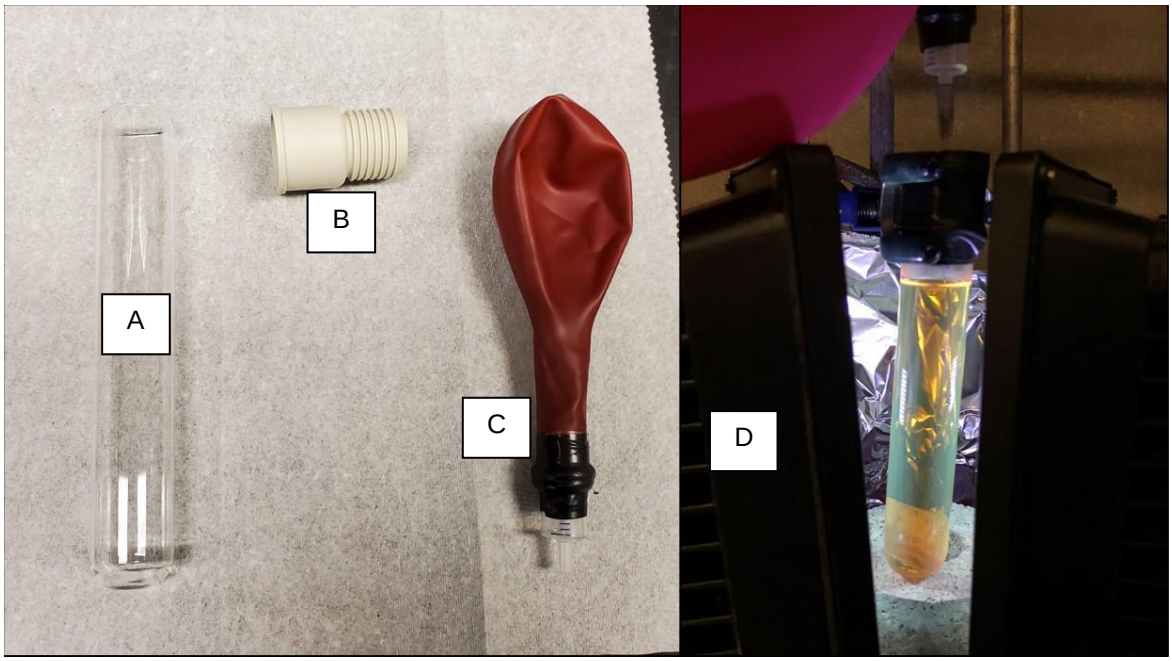


2,3,4,6-Tetrakis-*O*-[(4-methoxyphenyl)methyl]-β-D-glucopyranosyl fluoride

(Major product, Isolated as α : β = 1 : 9.4 mixture).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.21 (m, 6H), 7.03 (d, *J* = 8.6 Hz, 2H), 6.86 (dd, *J* = 8.6, 3.2 Hz, 6H), 6.80 (d, *J* = 8.6 Hz, 2H), 5.21 (dd, *J* = 52.9, 6.7 Hz, 1H), 4.79 (dd, *J* = 19.8, 10.7 Hz, 2H), 4.70 (dd, *J* = 10.6, 1.4 Hz, 2H), 4.63 (d, *J* = 10.8 Hz, 1H), 4.56 (d, *J* = 11.8 Hz, 1H), 4.47 (d, *J* = 11.8 Hz, 1H), 4.41 (d, *J* = 10.4 Hz, 1H), 3.80 (s, 6H), 3.79 (s, 6H), 3.70 – 3.64 (m, 2H), 3.64 – 3.57 (m, 2H), 3.56 – 3.50 (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.4, 159.3, 159.3, 159.2, 130.6, 130.1, 129.9, 129.8, 129.7, 129.6, 129.5, 113.9, 113.8, 109.9 (d, $^1J_{C\text{-}F}$ = 215.9 Hz), 83.2 (d, $^3J_{C\text{-}F}$ = 11.4 Hz), 81.2 (d, $^2J_{C\text{-}F}$ = 21.4 Hz), 75.1, 74.8 (d, $^3J_{C\text{-}F}$ = 5.0 Hz), 74.6, 74.1, 74.1, 73.2, 68.0, 55.3; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -138.15 (dd, *J* = 53.0, 11.9 Hz).; **IR** (thin film, cm^{-1}): 2907, 2835, 1611, 1585, 1512, 1463, 1441, 1359, 1302, 1244, 1172, 1083, 1031, 816, 758, 712, 637; **HRMS (ESI-TOF)** (m/z): $[M+Na]^+$ calcd for $C_{38}H_{43}FNaO_9$ 685.2792, found 685.2772; **$[\alpha]_D^{24}$** = +20.7 (c = 0.34, CH_2Cl_2).

d. Large Scale Batch Synthesis



A. Fisherbrand™ Disposable Borosilicate Glass Tube (25x150mm)

B. Suba-Seal® septum (24/40 joint)

C. Norm-Ject™ Syringe (5 mL) + 2 Balloons

D. Waveform lighting realUV™ LED Flood Light (365nm)

An oven-dried glass tube was charged with 2,3,4,6-tetrakis-*O*-(phenylmethyl)-*D*-glucopyranoside **1g** (1.85 mmol, 1.0 equiv.), 4,4'-dimethoxybenzophenone (0.37 mmol, 0.2 equiv.), and a stir bar. After sealing the glass tube with a rubber septum, the tube was left under high vacuum for 5 minutes. Once the tube is taken off from the vacuum line, dichloroethane (42 mL) and DIPEA (18.5 mmol, 10 equiv.) were injected into the tube and the mixture was stirred until it became homogeneous. Then, the mixture was sparged with SF_6 filled balloon for 30 seconds. Once the sparging was done, the tube was irradiated with two UV-A Lamps until all starting material was consumed (166 h). The reaction mixture was worked up following the general procedure and purified by FCC (SiO_2, pure hexanes → 20% EtOAc in hexanes) and 2,3,4,6-tetrakis-*O*-(phenylmethyl)-*D*-glucopyranosyl fluoride **2g** was obtained in 93% yield (0.93 gram, $\alpha : \beta = 1 : 3.4$).

IV. Continuous Flow Synthesis

a. Information of the flow equipment:

a. NE-1010 Higher Pressure Syringe Pump (Serial No. 296019) – Link to the website

b. 8 ml Stainless Steel Syringe with 1/16 inch SWAGELOK® (70-2267) – Link to the website

c. Upchurch Scientific™ Low Pressure Y Connectors (P-512) – Link to the website

d. Upchurch Scientific™ Micro-Metering and Micro-Splitter Valves: Needle Valves (P445) – Link to the website

e. Upchurch Scientific NUT SHT ML LITETCH 1/16IN 10PK (LT115X) – Link to the website

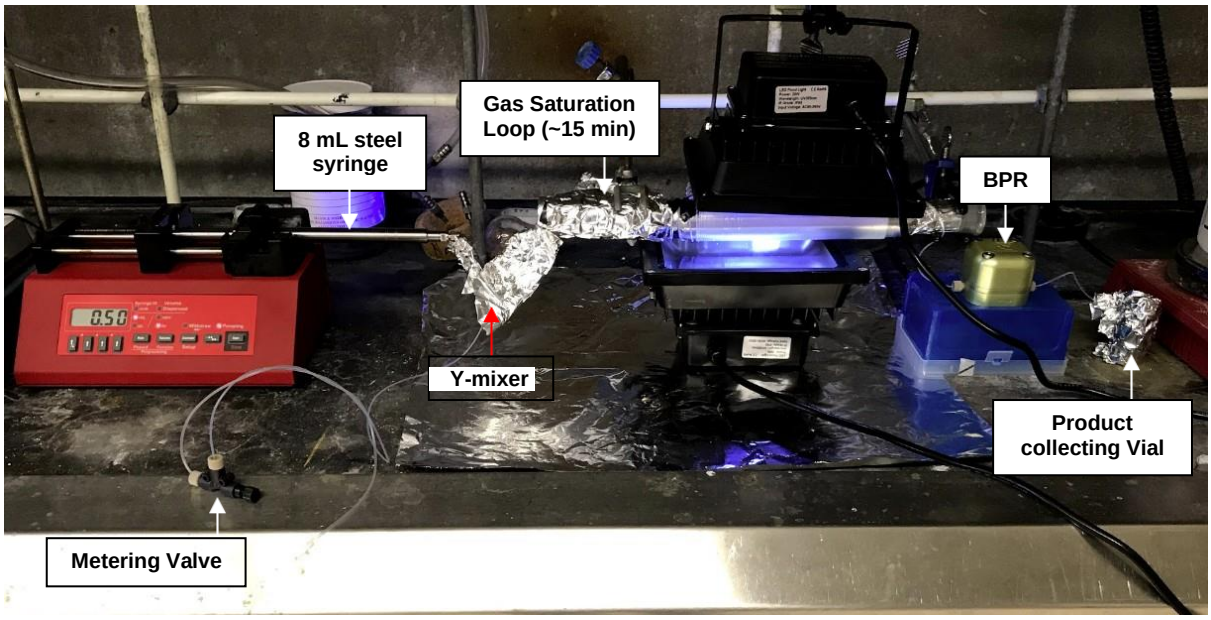
f. Upchurch Scientific™ Flangeless Fittings: Ferrules, PEEK (P250X) – Link to the webstie

g. Upchurch Scientific™ Low-Pressure Unions: PEEK (P-702) – Link to the website

h. Zaiput Flow Back Pressure Regulator (BPR-100) – Link to the website

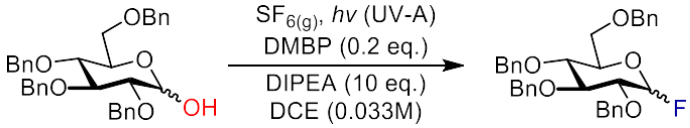
i. Waters Prep LC 4000 Preparative Chromatography System – Link to the website

b. Small Scale Continuous Flow Setup with a Steel Syringe



Into an oven dried vial, 2,3,4,6-tetrakis-*O*-(phenylmethyl)-*D*-glucopyranose **1g** (0.2 mmol, 1.0 equiv.) and 4,4'-dimethoxybenzophenone (0.04 mmol, 0.2 equiv.) were added. Followed by addition of 1,2-dichloroethane (6 mL) and DIPEA (2.0 mmol, 10 equiv.), the reaction mixture was sonicated until it became homogeneous. The prepared reaction mixture was transferred into 8 mL steel syringe, which was then connected to the flow system. The flow rate of syringe pump and SF_6 gas were adjusted for desired residence time of the reaction mixture inside the flow tube that was irradiated by UV-A Flood Lamp. From the collecting vial, 3.2 mL (equivalent to one standard-scale reaction) of the reaction mixture was collected and then analyzed.

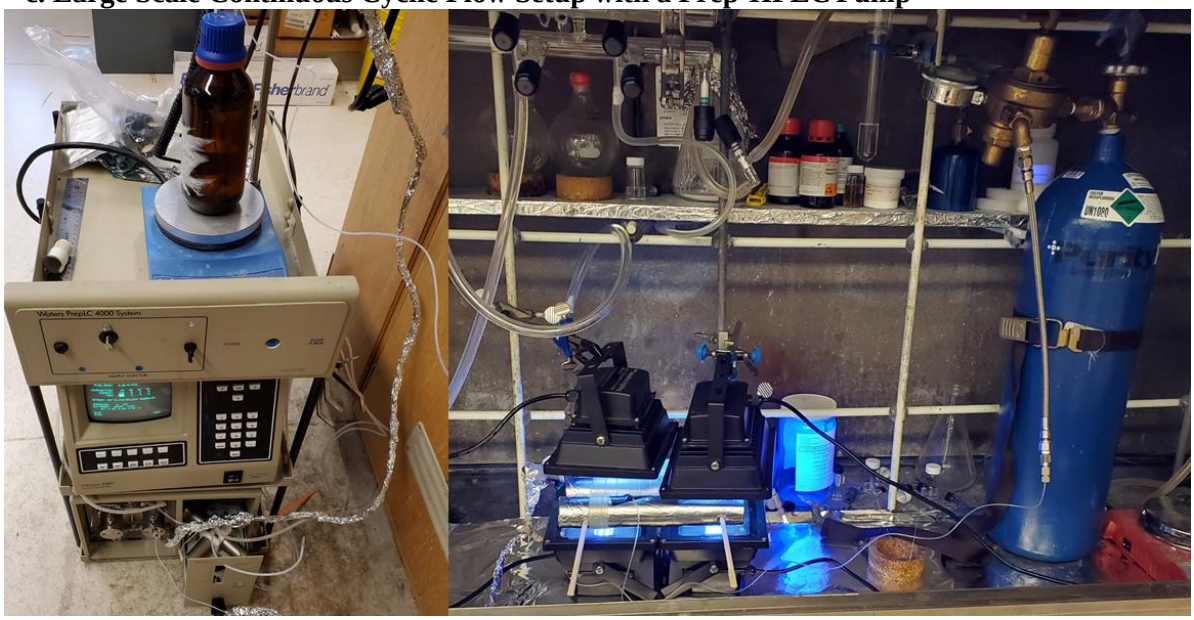
Table SI-7. Small Scale Synthesis of Glycosyl Fluoride with a Continuous Flow Setup

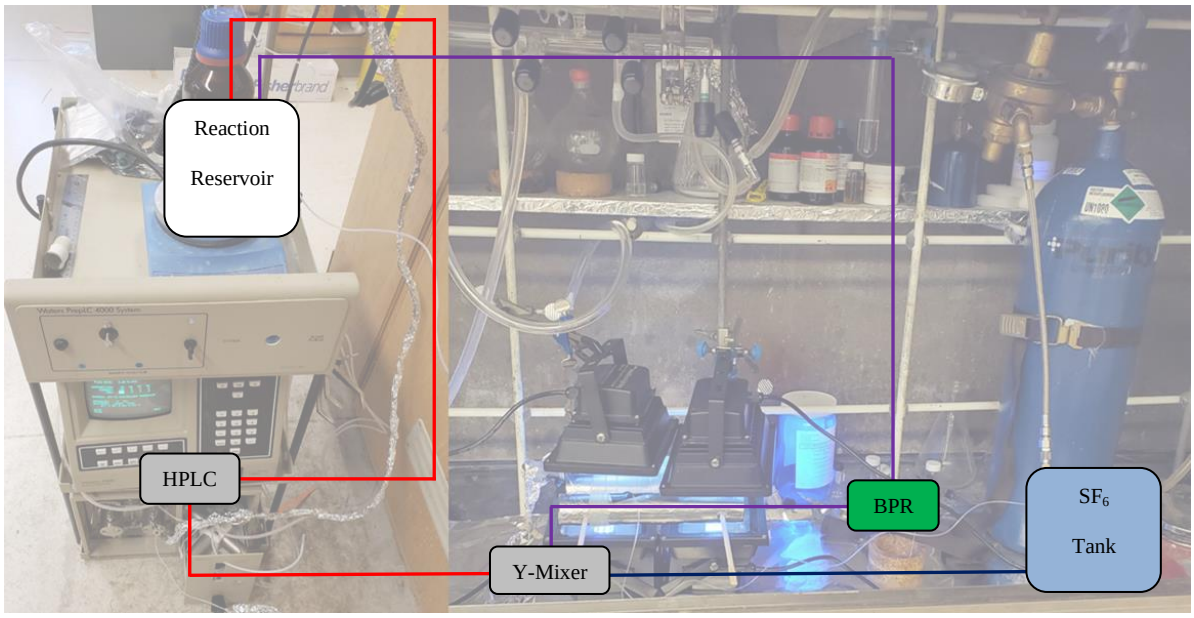


Entry	BPR Pressure	Residence Time (h)	NMR Yield[a]	Yield[b]	BRSM
1	50 psi	9	64%	62% (33.7 mg)	84%
2	90 psi	8.5	81%	78% (42.1 mg)	91%

[a] Determined by ^{19}F NMR with α,α,α-trifluorotoluene as an internal standard.
[b] Determined from 3.2 mL of the reaction mixture collected, which is equivalent to one standard reaction

c. Large Scale Continuous Cyclic Flow Setup with a Prep-HPLC Pump





Number of UV-A lamps: 4
Length of flow tube irradiated by the lamps: approximately 100 feet
Pressure of BPR: 100 psi

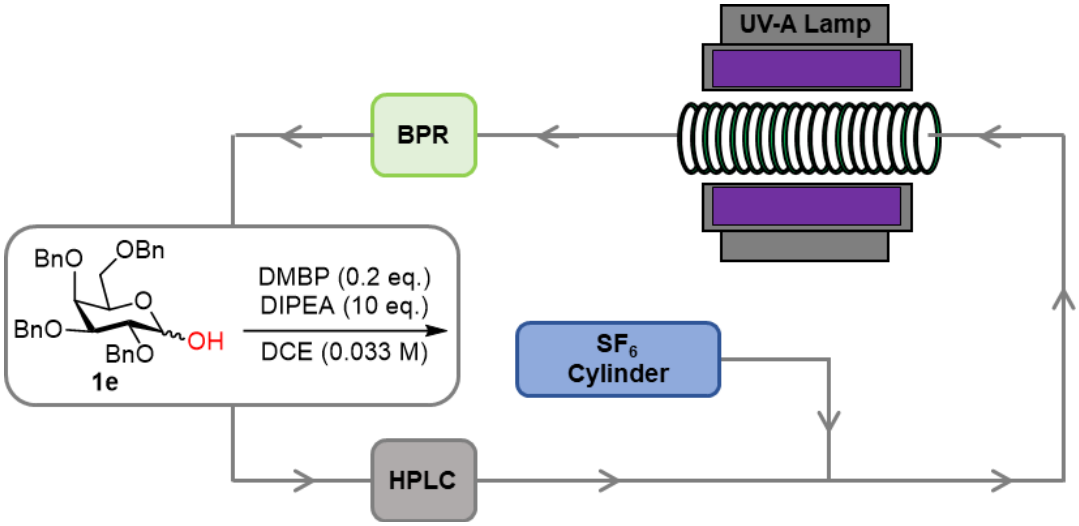


Table SI-8. Large Scale Synthesis of Glycosyl Fluoride with a Continuous Flow Setup

Total Volume (mL)	Collected Volume (mL)	BPR Pressure	Cycling Time (h)	Yield	BRSM
475	455	100 psi	120	93% (7.17 g)	99.8% (0.5 g)

Into a clean 500 mL glass bottle, 2,3,4,6-tetrakis-O-(phenylmethyl)-*D*-galactopyranose **1e** (14.8 mmol, 1.0 equiv.) and 4,4'dimethoxybenzophenone (2.96 mmol, 0.2 equiv.) were dissolved into DCM (444 mL). After adding DIPEA (140.8 mmol, 10 equiv.), the mixture was shaken until it became homogeneous. The reservoir bottle containing the reaction mixture was then connected to HPLC pump and stirred with a magnetic stir bar while the reaction was running. After connecting flow tubes and priming, the HPLC pump was turned on and the flow rate was adjusted to 2 mL/min, which maintained the pressure at 114 psi with an occasional fluctuation of ± 20 psi. The regulator of SF_6 tank was adjusted between 120-130 psi for a steady flow of the reaction mixture. The reaction was cycled through the flow tube until almost all the starting material was consumed, which was monitored by TLC. After turning off the pump, 455 mL of the reaction mixture in the reservoir bottle was collected (corresponds to 7.66 g of starting material and 7.69 g of the product) and worked up following the standard procedure. Purification of crude mixture by FCC gave 7.17 g of 2,3,4,6-tetrakis-*O*-(phenylmethyl)-*D*-galactopyranosyl fluoride **2e** as product in 93% yield (α : β = 1 : 2.7), and 0.50 g of starting material was recovered (99.8% BRSM).

V. UV-Vis Study of Photocatalysts

UV absorbance of photocatalysts was measured with UV-Vis detector (Shimadzu SPD-M20A) by injecting 20 microliter of 1 mM samples (0.01 mmol of photocatalyst in 10 mL of acetonitrile) into a reverse-phase HPLC (Shimadzu CTO-20A). All photocatalysts were eluted with 97% acetonitrile/ 3% water mixture except for Methylene Blue (30% acetonitrile/ 70% water).

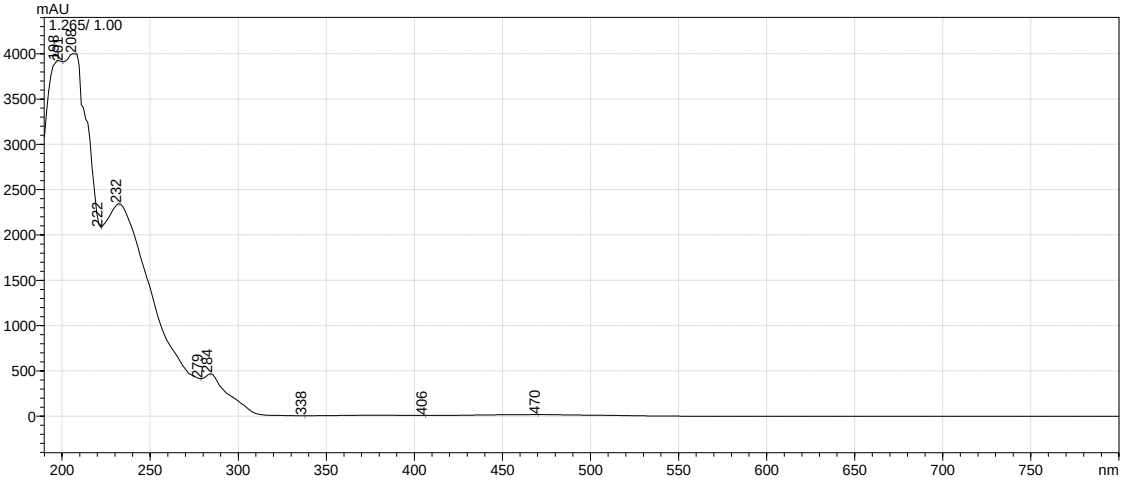


Figure SI-1. Eosin Y

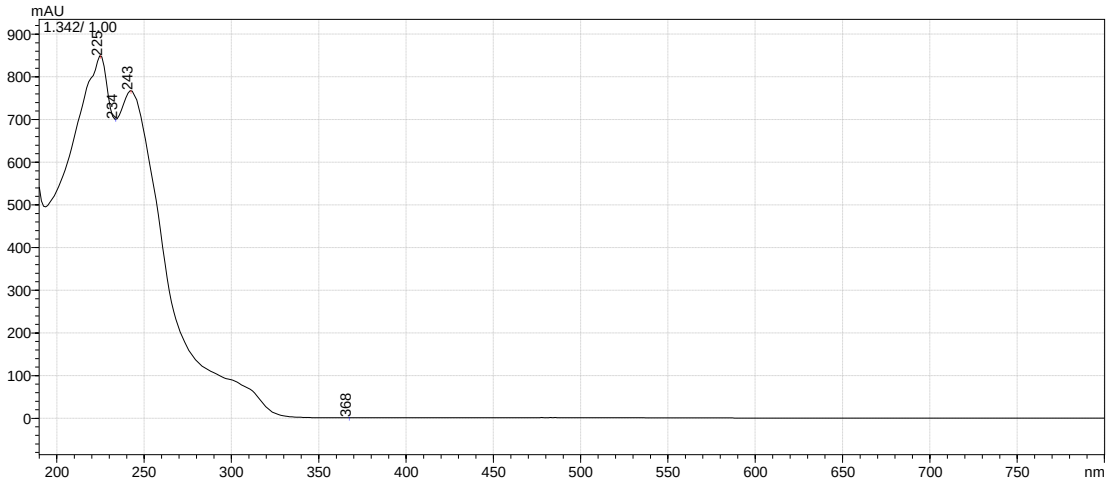


Figure SI-2. Rose Bengal

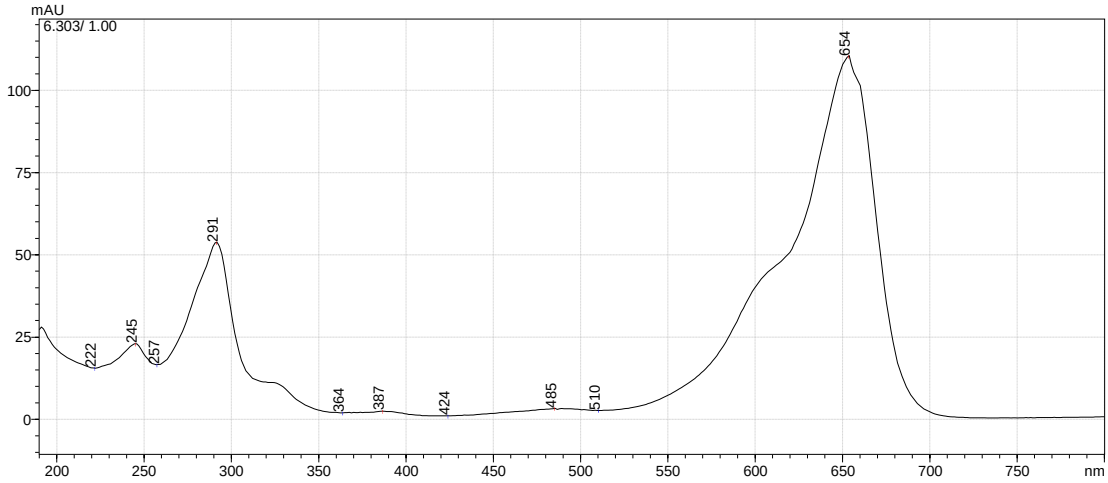


Figure SI-3. Methylene Blue

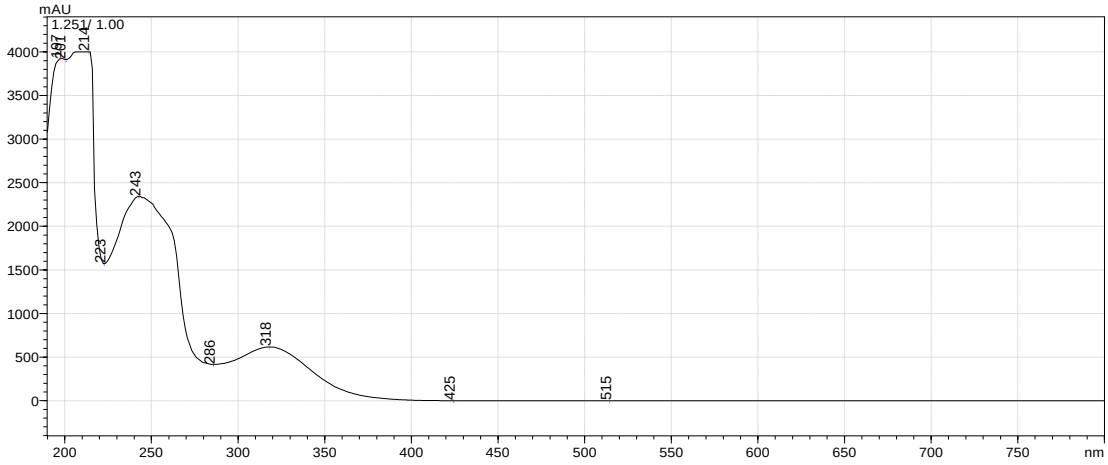


Figure SI-4. *N*-Phenylphenothiazine

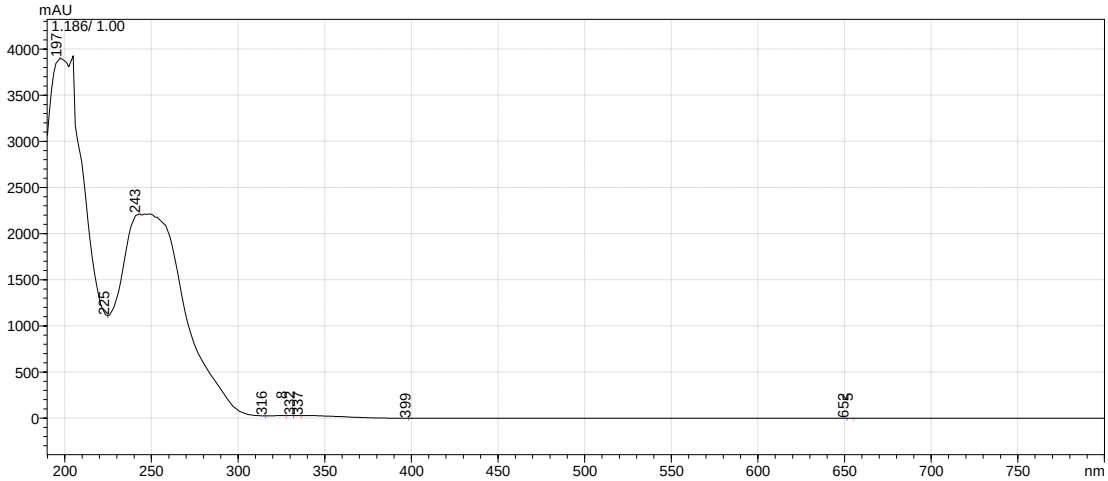


Figure SI-5. Benzophenone

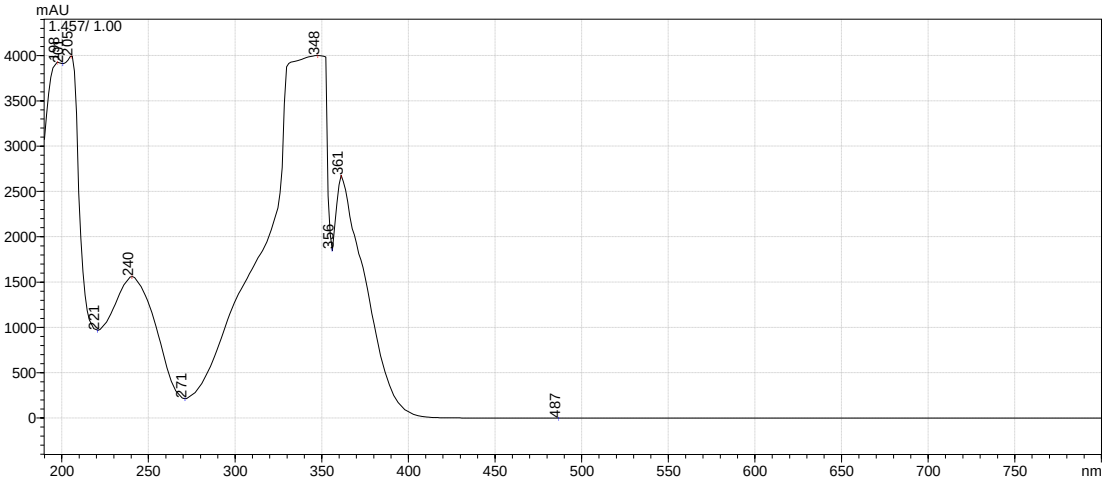


Figure SI-6. Michler's Ketone

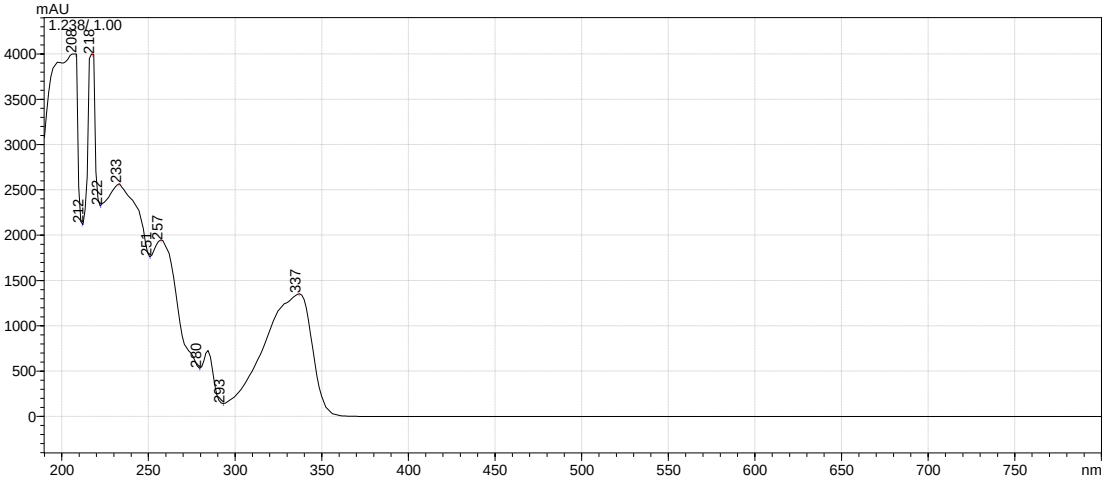


Figure SI-7. Xanthone

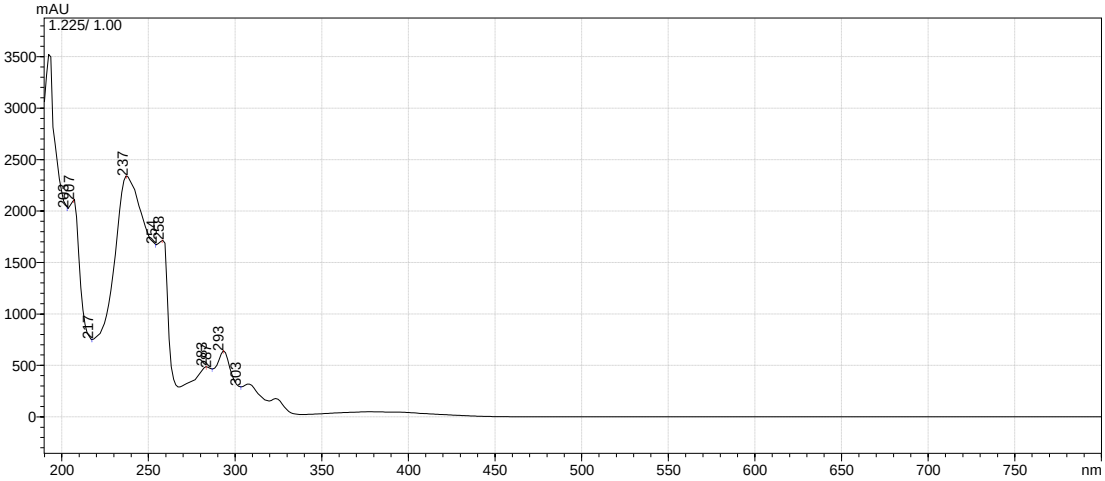


Figure SI-8. 9-Fluorenone

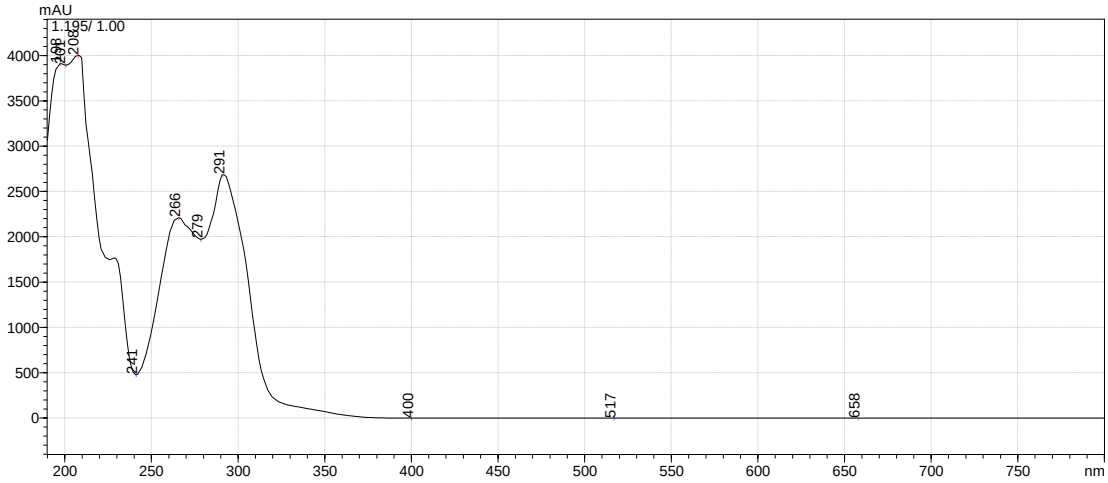


Figure SI-9. 4,4’-Dimethoxybenzophenone

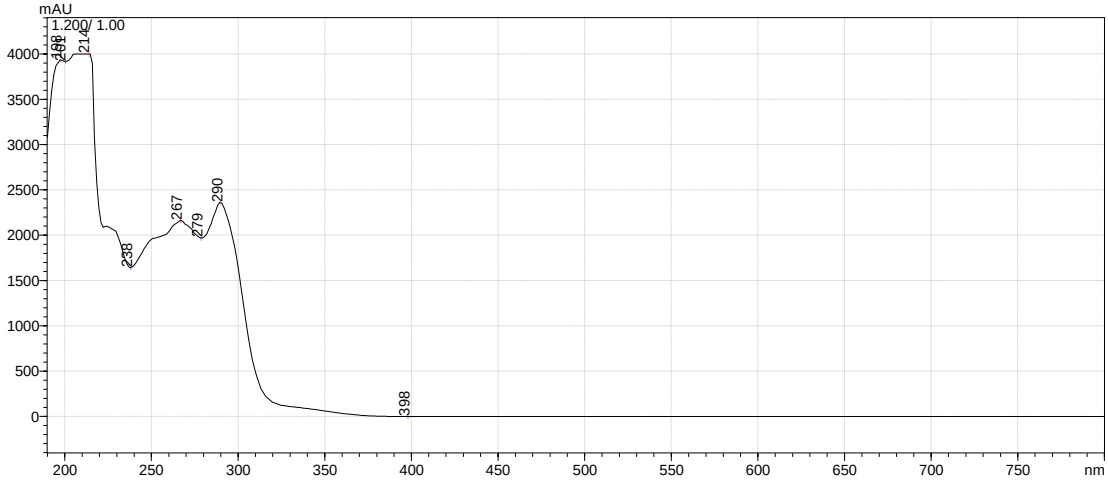


Figure SI-10. 4-Fluoro-4’-methoxybenzophenone

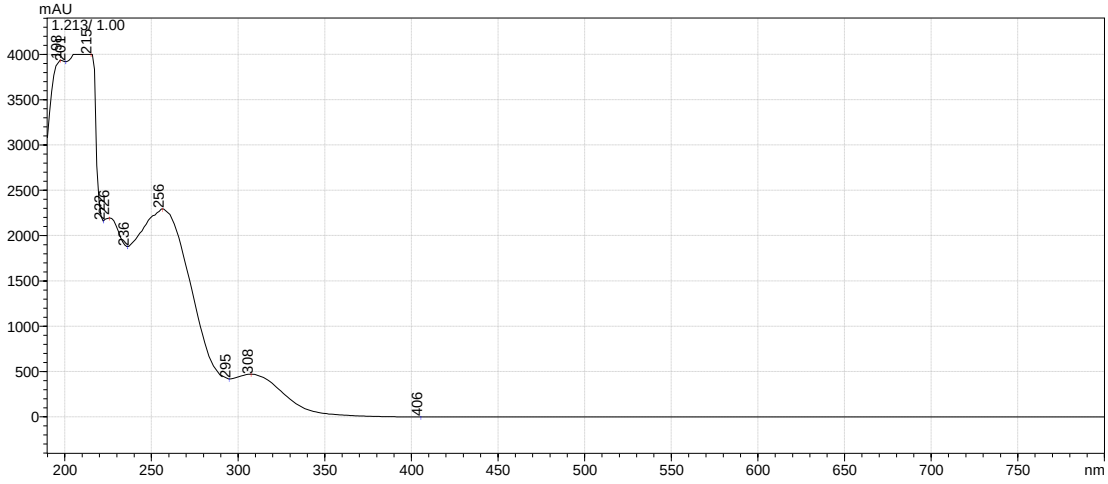
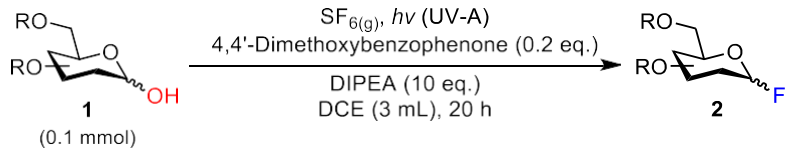


Figure SI-11. 4-Chloro-3’-methoxybenzophenone

VI. Additional Experiment

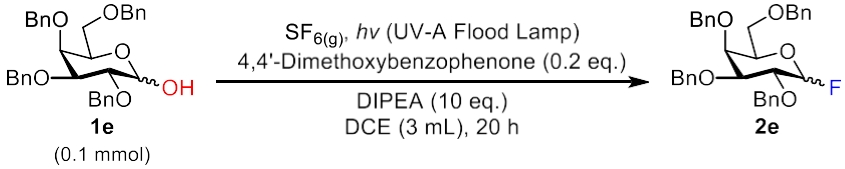
a. Control Experiment

Table SI-9. Result of Control Experiment



Entry	Substrate	Control	Conversion
1	**1a**	No catalyst	13%
2	**1e**	No catalyst	16%
3	**1k**	No catalyst	18%
4	**1e**	No light	–
5	**1e**	No DIPEA	–

b. Light On/Off Experiment



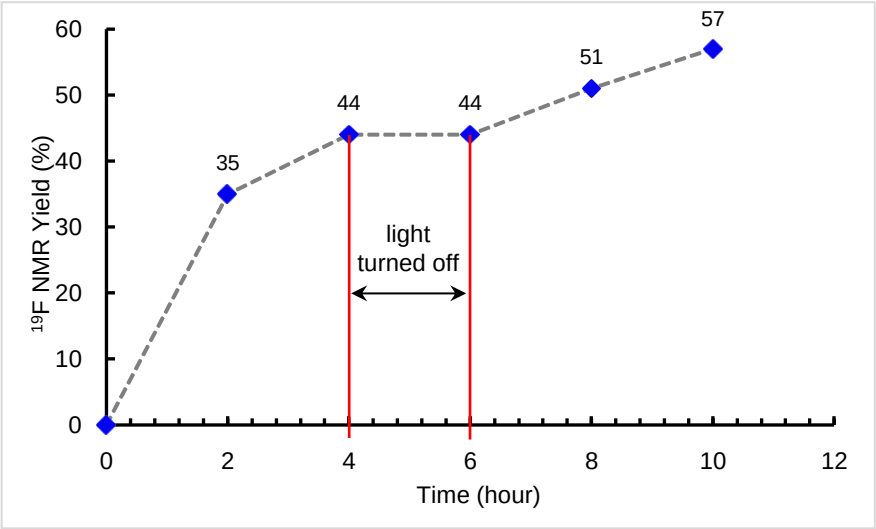


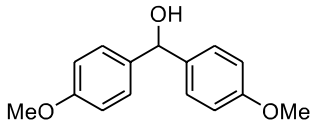
Figure SI-12. Light On/Off Experiment

The reaction was setup in a 1 dram vial following the general procedure outlined above. The yield was measured by ^{19}F NMR with α,α,α-trifluorotoluene as an internal standard. From the vial, 0.2 mL of reaction mixture was taken out every 2 h to monitor the progression of the reaction. After 4 h from setting up a reaction, the light was turned off for 2 h, and then turned back on. This result is implying that the reaction proceeds via a non-chain mechanism, that the active fluorinating reagent (SF_4) is quickly consumed after it is generated *in situ*, does not build up in the reaction and requires light to be regenerated from SF_6.

c. Identification of the Decomposed Photocatalyst

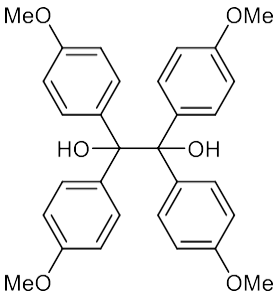
Identified side-products resulting from the catalyst decomposition that are typically observed in variable quantities while executing the standard fluorination protocol (24 h):

4,4'-Dimethoxybenzhydrol[17]



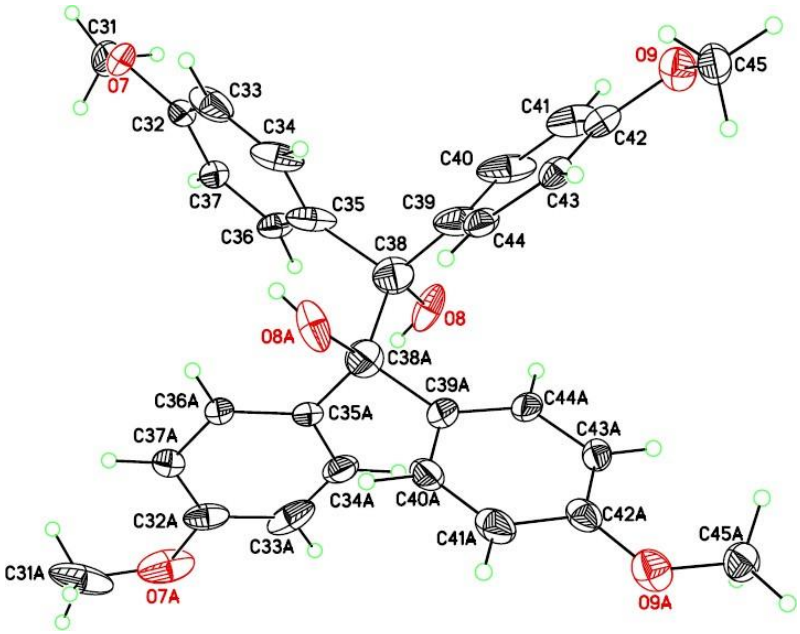
(Minor decomposed catalyst, isolated as 1:8.8 = minor:major mixture) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.7 Hz, 4H, Ar**H**), 6.87 (d, *J* = 8.7 Hz, 4H, Ar**H**), 5.78 (s, 1H, Ar_2CHOH), 3.79 (s, 6H, $ArOCH_3$), 2.38 (s, 1H, Ar_2CHOH); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.0, 136.7, 127.7, 113.8, 75.4(Ar_2CHOH), 55.27($ArOCH_3$).

1,1,2,2-Tetrakis(*p*-methoxyphenyl)-1,2-ethanediol



(Major decomposed catalyst, crystallized) **^{1}H NMR** (700 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.9 Hz, 8H), 6.70 (d, *J* = 8.9 Hz, 8H), 3.76 (s, 12H), 2.87 (br, 2H); **^{13}C NMR** (176 MHz, $cdcl_3$) δ 158.2, 136.7, 129.8, 112.5, 82.7 (Ar_2COH), 55.1; **HRMS (ESI-TOF)** (m/z): $[2M+Na]^+$ calcd for $C_{60}H_{60}NaO12$ 995.3976, found 995.3975.

X-ray Crystal Structure Analysis of 1,1,2,2-tetrakis(*p*-methoxyphenyl)-1,2-ethanediol



Ellipsoid contour %probability level = 50%

[17]Denegri, B.; Kronja, O. *J. Org. Chem.* **2007**, 72, 22, 8427-8433

Structure Determination

Colorless blocks of 1,1,2,2-tetrakis(*p*-methoxyphenyl)-1,2-ethanediol were grown from a 20% ethyl acetate in hexaness solution of the compound at 25 deg. C. A crystal of dimensions 0.20 x 0.18 x 0.18 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (λ = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of 1.0° in *w*. The exposure times were 1 sec. for the low angle images, 4 sec. for high angle. Rigaku d*trek images were exported to CrysAlisPro for processing and corrected for absorption. The integration of the data yielded a total of 74249 reflections to a maximum 2θ value of 138.87° of which 9005 were independent and 8968 were greater than 2σ(I). The final cell constants (Crystal Data and Structure Refinement) were based on the xyz centroids of 43167 reflections above 10σ(I). Analysis of the data showed negligible decay during data collection. The structure was solved and refined with the Bruker SHELXTL (version 2018/3) software package, using the space group P2(1)2(1)2 with Z = 4 for the formula $C_{30}H_{30}O_6$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in a combination of refined and idealized positions. The structure was refined as a two-component inversion twin with the asymmetric unit consisting of four independent half-molecules located on two-fold rotation axes. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0578 and wR2 = 0.1586 [based on I > 2sigma(I)], R1 = 0.0580 and wR2 = 0.1592 for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.

G.M. Sheldrick (2015) "Crystal structure refinement with SHELXL", Acta Cryst., C71, 3-8 (Open Access).
CrystalClear Expert 2.0 r16, Rigaku Americas and Rigaku Corporation (2014), Rigaku Americas, 9009, TX, USA 77381-5209, Rigaku Tokyo, 196-8666, Japan.

CrysAlisPro 1.171.38.41 (Rigaku Oxford Diffraction, 2015).

Table SI-10. Crystal Data and Structure Refinement

Empirical formula	C30 H30 O6
Formula weight	486.54
Temperature	85(2) K
Wavelength	1.54184 A
Crystal system, space group	Orthorhombic, P2(1)2(1)2
Unit cell dimensions	a = 16.08990(10) A alpha = 90 deg.
	b = 16.48600(10) A beta = 90 deg.
	c = 18.20870(10) A gamma = 90 deg.
Volume	4830.01(5) A^3
Z, Calculated density	8, 1.338 Mg/m^3
Absorption coefficient	0.752 mm^-1
F(000)	2064
Crystal size	0.200 x 0.180 x 0.180 mm
Theta range for data collection	2.427 to 69.435 deg.
Limiting indices	-19<=h<=18, -20<=k<=19, -22<=l<=21
Reflections collected / unique	74249 / 9005 [R(int) = 0.0566]
Completeness to theta = 67.684	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.92602
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9005 / 2 / 674
Goodness-of-fit on F^2	0.998
Final R indices [I>2sigma(I)]	R1 = 0.0578, wR2 = 0.1586
R indices (all data)	R1 = 0.0580, wR2 = 0.1592
Absolute structure parameter	0.4(2)
Extinction coefficient	0.00079(15)
Largest diff. peak and hole	1.596 and -0.522 e.A^-3

Table SI-11. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	7945(2)	6480(2)	10835(1)	27(1)
O(2)	9153(2)	4250(2)	8353(2)	31(1)
O(3)	8529(2)	6839(2)	5782(2)	42(1)
O(4)	6862(2)	6947(2)	7257(1)	25(1)
O(5)	4230(2)	5795(2)	4931(1)	24(1)
O(6)	6611(2)	6383(2)	2207(2)	32(1)
O(7)	6331(3)	7790(2)	9422(2)	54(1)
O(8)	5937(2)	10634(2)	7040(2)	36(1)
O(9)	6672(2)	8471(2)	4366(2)	35(1)
O(10)	7983(2)	8326(2)	2982(2)	28(1)
O(11)	10745(2)	9192(2)	643(1)	22(1)
O(12)	8370(2)	8194(2)	-1959(2)	27(1)
C(1)	8379(3)	6950(2)	11366(2)	27(1)
C(2)	8389(2)	6186(2)	10251(2)	20(1)
C(3)	9247(2)	6233(2)	10188(2)	22(1)
C(4)	9638(2)	5894(2)	9581(2)	26(1)
C(5)	9184(3)	5509(2)	9030(2)	27(1)
C(6)	8320(3)	5483(3)	9106(2)	30(1)
C(7)	7927(2)	5812(2)	9703(2)	26(1)
C(8)	9513(3)	5061(3)	8354(2)	33(1)
C(9)	9269(3)	5553(3)	7654(2)	31(1)
C(10)	9351(2)	6397(3)	7592(2)	30(1)
C(11)	9108(2)	6810(3)	6965(2)	29(1)
C(12)	8762(2)	6384(3)	6377(2)	26(1)
C(13)	8667(2)	5550(3)	6436(2)	27(1)
C(14)	8925(3)	5149(3)	7066(2)	30(1)
C(15)	8034(3)	6457(4)	5251(3)	53(1)
C(16)	7210(2)	6493(2)	7846(2)	23(1)
C(17)	6450(2)	6530(2)	6725(2)	18(1)
C(18)	6376(2)	5692(2)	6695(2)	20(1)
C(19)	5942(2)	5338(2)	6118(2)	22(1)
C(20)	5576(2)	5794(2)	5565(2)	22(1)
C(21)	5667(2)	6638(2)	5606(2)	26(1)
C(22)	6088(2)	7004(2)	6173(2)	24(1)
C(23)	5065(2)	5471(2)	4914(2)	22(1)
C(24)	5483(2)	5731(2)	4190(2)	23(1)
C(25)	6343(2)	5703(2)	4084(2)	24(1)
C(26)	6702(2)	5925(2)	3421(2)	25(1)
C(27)	6210(2)	6179(2)	2844(2)	22(1)
C(28)	5354(2)	6213(2)	2930(2)	23(1)
C(29)	5006(2)	5983(2)	3601(2)	22(1)
C(30)	6106(3)	6679(3)	1618(2)	36(1)
C(31)	6876(4)	8093(4)	9976(3)	65(2)
C(32)	6118(3)	8318(3)	8877(2)	33(1)
C(33)	5725(3)	7984(3)	8264(3)	43(1)
C(34)	5498(3)	8463(3)	7676(3)	39(1)

C(35)	5631(3)	9294(3)	7678(3)	38(1)
C(36)	5990(3)	9620(2)	8309(2)	27(1)
C(37)	6244(2)	9149(2)	8903(2)	24(1)
C(38)	5476(3)	9872(3)	6986(3)	38(1)
C(39)	5705(4)	9411(3)	6295(3)	43(1)
C(40)	6557(3)	9416(3)	6134(3)	47(1)
C(41)	6852(3)	9095(3)	5507(3)	40(1)
C(42)	6306(3)	8754(2)	4993(2)	27(1)
C(43)	5464(2)	8729(2)	5140(2)	23(1)
C(44)	5169(3)	9044(2)	5794(2)	28(1)
C(45)	6141(3)	8106(3)	3832(2)	32(1)
C(46)	8388(3)	7891(3)	3553(2)	33(1)
C(47)	8477(2)	8663(2)	2454(2)	19(1)
C(48)	9335(2)	8714(2)	2490(2)	19(1)
C(49)	9776(2)	9039(2)	1901(2)	20(1)
C(50)	9384(2)	9292(2)	1265(2)	24(1)
C(51)	8516(2)	9266(2)	1249(2)	24(1)
C(52)	8062(2)	8961(2)	1836(2)	23(1)
C(53)	9913(2)	9529(2)	584(2)	24(1)
C(54)	9459(2)	9232(2)	-111(2)	26(1)
C(55)	9461(2)	8402(2)	-240(2)	26(1)
C(56)	9081(2)	8078(2)	-848(2)	25(1)
C(57)	8693(2)	8579(2)	-1357(2)	20(1)
C(58)	8655(2)	9412(2)	-1235(2)	22(1)
C(59)	9035(2)	9725(2)	-610(2)	24(1)
C(60)	7932(2)	8672(2)	-2487(2)	24(1)

Table SI-12. Bond lengths [A] and angles [deg]

O(1)-C(2)	1.370(4)
O(1)-C(1)	1.422(5)
O(2)-C(8)	1.457(5)
O(2)-H(2A)	0.83(3)
O(2)-H(2B)	0.84(3)
O(3)-C(12)	1.370(5)
O(3)-C(15)	1.403(6)
O(4)-C(17)	1.360(4)
O(4)-C(16)	1.423(4)
O(5)-C(23)	1.446(4)
O(5)-H(5)	0.87(6)
O(6)-C(27)	1.370(4)
O(6)-C(30)	1.431(5)
O(7)-C(32)	1.364(5)
O(7)-C(31)	1.428(8)
O(8)-C(38)	1.462(5)
O(8)-H(8)	0.81(6)
O(9)-C(42)	1.367(5)
O(9)-C(45)	1.428(5)
O(10)-C(47)	1.366(4)
O(10)-C(46)	1.422(5)
O(11)-C(53)	1.454(5)
O(11)-H(11)	0.86(5)
O(12)-C(57)	1.370(4)
O(12)-C(60)	1.428(4)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(2)-C(3)	1.387(5)
C(2)-C(7)	1.388(5)
C(3)-C(4)	1.390(5)
C(3)-H(3)	0.9500
C(4)-C(5)	1.395(6)
C(4)-H(4)	0.9500
C(5)-C(6)	1.398(6)
C(5)-C(8)	1.529(6)
C(6)-C(7)	1.370(6)
C(6)-H(6)	0.9500
C(7)-H(7)	0.9500
C(8)-C(9)	1.562(6)
C(8)-C(8)#1	1.579(8)
C(9)-C(14)	1.377(6)
C(9)-C(10)	1.403(6)
C(10)-C(11)	1.385(6)
C(10)-H(10)	0.9500
C(11)-C(12)	1.397(6)
C(11)-H(11A)	0.9500
C(12)-C(13)	1.387(6)
C(13)-C(14)	1.388(6)

C(13)-H(13)	0.9500
C(14)-H(14)	0.9500
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-C(18)	1.389(5)
C(17)-C(22)	1.401(5)
C(18)-C(19)	1.390(5)
C(18)-H(18)	0.9500
C(19)-C(20)	1.387(5)
C(19)-H(19)	0.9500
C(20)-C(21)	1.401(5)
C(20)-C(23)	1.538(5)
C(21)-C(22)	1.375(5)
C(21)-H(21)	0.9500
C(22)-H(22)	0.9500
C(23)-C(24)	1.542(5)
C(23)-C(23)#2	1.566(7)
C(24)-C(29)	1.383(5)
C(24)-C(25)	1.397(6)
C(25)-C(26)	1.389(5)
C(25)-H(25)	0.9500
C(26)-C(27)	1.380(5)
C(26)-H(26)	0.9500
C(27)-C(28)	1.387(6)
C(28)-C(29)	1.397(5)
C(28)-H(28)	0.9500
C(29)-H(29)	0.9500
C(30)-H(30A)	0.9800
C(30)-H(30B)	0.9800
C(30)-H(30C)	0.9800
C(31)-H(31A)	0.9800
C(31)-H(31B)	0.9800
C(31)-H(31C)	0.9800
C(32)-C(37)	1.387(6)
C(32)-C(33)	1.396(7)
C(33)-C(34)	1.379(7)
C(33)-H(33)	0.9500
C(34)-C(35)	1.387(7)
C(34)-H(34)	0.9500
C(35)-C(36)	1.394(5)
C(35)-C(38)	1.598(7)
C(36)-C(37)	1.393(5)
C(36)-H(36)	0.9500
C(37)-H(37)	0.9500
C(38)-C(39)	1.516(6)
C(38)-C(38)#3	1.589(9)
C(39)-C(44)	1.394(6)

C(39)-C(40)	1.402(8)
C(40)-C(41)	1.345(7)
C(40)-H(40)	0.9500
C(41)-C(42)	1.401(6)
C(41)-H(41)	0.9500
C(42)-C(43)	1.381(6)
C(43)-C(44)	1.383(5)
C(43)-H(43)	0.9500
C(44)-H(44)	0.9500
C(45)-H(45A)	0.9800
C(45)-H(45B)	0.9800
C(45)-H(45C)	0.9800
C(46)-H(46A)	0.9800
C(46)-H(46B)	0.9800
C(46)-H(46C)	0.9800
C(47)-C(48)	1.385(5)
C(47)-C(52)	1.398(5)
C(48)-C(49)	1.393(5)
C(48)-H(48)	0.9500
C(49)-C(50)	1.383(5)
C(49)-H(49)	0.9500
C(50)-C(51)	1.397(6)
C(50)-C(53)	1.555(5)
C(51)-C(52)	1.389(5)
C(51)-H(51)	0.9500
C(52)-H(52)	0.9500
C(53)-C(54)	1.540(5)
C(53)-C(53)#4	1.579(7)
C(54)-C(55)	1.388(6)
C(54)-C(59)	1.398(6)
C(55)-C(56)	1.374(6)
C(55)-H(55)	0.9500
C(56)-C(57)	1.389(5)
C(56)-H(56)	0.9500
C(57)-C(58)	1.393(5)
C(58)-C(59)	1.392(5)
C(58)-H(58)	0.9500
C(59)-H(59)	0.9500
C(60)-H(60A)	0.9800
C(60)-H(60B)	0.9800
C(60)-H(60C)	0.9800

C(2)-O(1)-C(1)	117.7(3)
C(8)-O(2)-H(2A)	108(9)
C(8)-O(2)-H(2B)	108(8)
C(12)-O(3)-C(15)	117.0(4)
C(17)-O(4)-C(16)	117.6(3)
C(23)-O(5)-H(5)	110(3)
C(27)-O(6)-C(30)	116.8(3)
C(32)-O(7)-C(31)	116.4(4)
C(38)-O(8)-H(8)	110(5)

C(42)-O(9)-C(45)	117.0(3)
C(47)-O(10)-C(46)	117.0(3)
C(53)-O(11)-H(11)	106(3)
C(57)-O(12)-C(60)	118.1(3)
O(1)-C(1)-H(1A)	109.5
O(1)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
O(1)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
O(1)-C(2)-C(3)	124.3(3)
O(1)-C(2)-C(7)	115.8(3)
C(3)-C(2)-C(7)	119.9(3)
C(2)-C(3)-C(4)	119.6(3)
C(2)-C(3)-H(3)	120.2
C(4)-C(3)-H(3)	120.2
C(3)-C(4)-C(5)	121.2(4)
C(3)-C(4)-H(4)	119.4
C(5)-C(4)-H(4)	119.4
C(4)-C(5)-C(6)	117.6(4)
C(4)-C(5)-C(8)	128.1(4)
C(6)-C(5)-C(8)	114.2(4)
C(7)-C(6)-C(5)	121.7(4)
C(7)-C(6)-H(6)	119.1
C(5)-C(6)-H(6)	119.1
C(6)-C(7)-C(2)	119.9(4)
C(6)-C(7)-H(7)	120.0
C(2)-C(7)-H(7)	120.0
O(2)-C(8)-C(5)	107.8(3)
O(2)-C(8)-C(9)	112.0(3)
C(5)-C(8)-C(9)	108.6(3)
O(2)-C(8)-C(8)#1	106.2(4)
C(5)-C(8)-C(8)#1	113.9(3)
C(9)-C(8)-C(8)#1	108.4(3)
C(14)-C(9)-C(10)	117.1(4)
C(14)-C(9)-C(8)	119.0(4)
C(10)-C(9)-C(8)	123.9(4)
C(11)-C(10)-C(9)	121.8(4)
C(11)-C(10)-H(10)	119.1
C(9)-C(10)-H(10)	119.1
C(10)-C(11)-C(12)	119.9(4)
C(10)-C(11)-H(11A)	120.1
C(12)-C(11)-H(11A)	120.1
O(3)-C(12)-C(13)	125.0(4)
O(3)-C(12)-C(11)	116.1(4)
C(13)-C(12)-C(11)	118.9(4)
C(12)-C(13)-C(14)	120.2(4)
C(12)-C(13)-H(13)	119.9
C(14)-C(13)-H(13)	119.9
C(9)-C(14)-C(13)	122.2(4)
C(9)-C(14)-H(14)	118.9

C(13)-C(14)-H(14)	118.9
O(3)-C(15)-H(15A)	109.5
O(3)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
O(3)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
O(4)-C(16)-H(16A)	109.5
O(4)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
O(4)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
O(4)-C(17)-C(18)	124.9(3)
O(4)-C(17)-C(22)	115.6(3)
C(18)-C(17)-C(22)	119.5(3)
C(19)-C(18)-C(17)	119.4(3)
C(19)-C(18)-H(18)	120.3
C(17)-C(18)-H(18)	120.3
C(18)-C(19)-C(20)	122.3(3)
C(18)-C(19)-H(19)	118.8
C(20)-C(19)-H(19)	118.8
C(19)-C(20)-C(21)	117.1(3)
C(19)-C(20)-C(23)	126.8(3)
C(21)-C(20)-C(23)	116.1(3)
C(22)-C(21)-C(20)	121.9(3)
C(22)-C(21)-H(21)	119.1
C(20)-C(21)-H(21)	119.1
C(21)-C(22)-C(17)	119.9(3)
C(21)-C(22)-H(22)	120.0
C(17)-C(22)-H(22)	120.0
O(5)-C(23)-C(20)	110.6(3)
O(5)-C(23)-C(24)	108.7(3)
C(20)-C(23)-C(24)	109.2(3)
O(5)-C(23)-C(23)#2	104.0(4)
C(20)-C(23)-C(23)#2	114.5(3)
C(24)-C(23)-C(23)#2	109.5(2)
C(29)-C(24)-C(25)	117.0(4)
C(29)-C(24)-C(23)	120.3(3)
C(25)-C(24)-C(23)	122.7(3)
C(26)-C(25)-C(24)	121.5(3)
C(26)-C(25)-H(25)	119.3
C(24)-C(25)-H(25)	119.3
C(27)-C(26)-C(25)	120.2(4)
C(27)-C(26)-H(26)	119.9
C(25)-C(26)-H(26)	119.9
O(6)-C(27)-C(26)	116.7(3)
O(6)-C(27)-C(28)	123.6(3)
C(26)-C(27)-C(28)	119.8(3)
C(27)-C(28)-C(29)	119.0(4)
C(27)-C(28)-H(28)	120.5

C(29)-C(28)-H(28)	120.5
C(24)-C(29)-C(28)	122.5(4)
C(24)-C(29)-H(29)	118.8
C(28)-C(29)-H(29)	118.8
O(6)-C(30)-H(30A)	109.5
O(6)-C(30)-H(30B)	109.5
H(30A)-C(30)-H(30B)	109.5
O(6)-C(30)-H(30C)	109.5
H(30A)-C(30)-H(30C)	109.5
H(30B)-C(30)-H(30C)	109.5
O(7)-C(31)-H(31A)	109.5
O(7)-C(31)-H(31B)	109.5
H(31A)-C(31)-H(31B)	109.5
O(7)-C(31)-H(31C)	109.5
H(31A)-C(31)-H(31C)	109.5
H(31B)-C(31)-H(31C)	109.5
O(7)-C(32)-C(37)	124.7(4)
O(7)-C(32)-C(33)	116.3(4)
C(37)-C(32)-C(33)	118.9(4)
C(34)-C(33)-C(32)	120.9(4)
C(34)-C(33)-H(33)	119.5
C(32)-C(33)-H(33)	119.5
C(33)-C(34)-C(35)	121.6(4)
C(33)-C(34)-H(34)	119.2
C(35)-C(34)-H(34)	119.2
C(34)-C(35)-C(36)	116.5(4)
C(34)-C(35)-C(38)	124.3(4)
C(36)-C(35)-C(38)	119.0(4)
C(37)-C(36)-C(35)	123.2(4)
C(37)-C(36)-H(36)	118.4
C(35)-C(36)-H(36)	118.4
C(32)-C(37)-C(36)	118.8(4)
C(32)-C(37)-H(37)	120.6
C(36)-C(37)-H(37)	120.6
O(8)-C(38)-C(39)	111.3(4)
O(8)-C(38)-C(38)#3	105.2(4)
C(39)-C(38)-C(38)#3	111.6(3)
O(8)-C(38)-C(35)	112.4(4)
C(39)-C(38)-C(35)	108.5(4)
C(38)#3-C(38)-C(35)	108.0(3)
C(44)-C(39)-C(40)	118.0(4)
C(44)-C(39)-C(38)	127.7(5)
C(40)-C(39)-C(38)	114.1(4)
C(41)-C(40)-C(39)	121.4(4)
C(41)-C(40)-H(40)	119.3
C(39)-C(40)-H(40)	119.3
C(40)-C(41)-C(42)	120.3(4)
C(40)-C(41)-H(41)	119.9
C(42)-C(41)-H(41)	119.9
O(9)-C(42)-C(43)	125.1(4)
O(9)-C(42)-C(41)	115.1(4)

C(43)-C(42)-C(41)	119.8(4)
C(42)-C(43)-C(44)	119.6(4)
C(42)-C(43)-H(43)	120.2
C(44)-C(43)-H(43)	120.2
C(43)-C(44)-C(39)	120.9(4)
C(43)-C(44)-H(44)	119.5
C(39)-C(44)-H(44)	119.5
O(9)-C(45)-H(45A)	109.5
O(9)-C(45)-H(45B)	109.5
H(45A)-C(45)-H(45B)	109.5
O(9)-C(45)-H(45C)	109.5
H(45A)-C(45)-H(45C)	109.5
H(45B)-C(45)-H(45C)	109.5
O(10)-C(46)-H(46A)	109.5
O(10)-C(46)-H(46B)	109.5
H(46A)-C(46)-H(46B)	109.5
O(10)-C(46)-H(46C)	109.5
H(46A)-C(46)-H(46C)	109.5
H(46B)-C(46)-H(46C)	109.5
O(10)-C(47)-C(48)	124.8(3)
O(10)-C(47)-C(52)	115.6(3)
C(48)-C(47)-C(52)	119.6(3)
C(47)-C(48)-C(49)	119.6(3)
C(47)-C(48)-H(48)	120.2
C(49)-C(48)-H(48)	120.2
C(50)-C(49)-C(48)	121.9(3)
C(50)-C(49)-H(49)	119.1
C(48)-C(49)-H(49)	119.1
C(49)-C(50)-C(51)	117.7(3)
C(49)-C(50)-C(53)	119.6(3)
C(51)-C(50)-C(53)	122.6(3)
C(52)-C(51)-C(50)	121.4(3)
C(52)-C(51)-H(51)	119.3
C(50)-C(51)-H(51)	119.3
C(51)-C(52)-C(47)	119.6(3)
C(51)-C(52)-H(52)	120.2
C(47)-C(52)-H(52)	120.2
O(11)-C(53)-C(54)	112.1(3)
O(11)-C(53)-C(50)	110.4(3)
C(54)-C(53)-C(50)	108.4(3)
O(11)-C(53)-C(53)#4	102.3(4)
C(54)-C(53)-C(53)#4	113.4(2)
C(50)-C(53)-C(53)#4	110.1(3)
C(55)-C(54)-C(59)	117.7(4)
C(55)-C(54)-C(53)	116.8(3)
C(59)-C(54)-C(53)	125.5(4)
C(56)-C(55)-C(54)	121.3(4)
C(56)-C(55)-H(55)	119.4
C(54)-C(55)-H(55)	119.4
C(55)-C(56)-C(57)	120.4(4)
C(55)-C(56)-H(56)	119.8

C(57)-C(56)-H(56)	119.8
O(12)-C(57)-C(56)	115.5(3)
O(12)-C(57)-C(58)	124.5(3)
C(56)-C(57)-C(58)	120.1(3)
C(59)-C(58)-C(57)	118.4(3)
C(59)-C(58)-H(58)	120.8
C(57)-C(58)-H(58)	120.8
C(58)-C(59)-C(54)	122.1(4)
C(58)-C(59)-H(59)	119.0
C(54)-C(59)-H(59)	119.0
O(12)-C(60)-H(60A)	109.5
O(12)-C(60)-H(60B)	109.5
H(60A)-C(60)-H(60B)	109.5
O(12)-C(60)-H(60C)	109.5
H(60A)-C(60)-H(60C)	109.5
H(60B)-C(60)-H(60C)	109.5

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,-y+1,z #2 -x+1,-y+1,z #3 -x+1,-y+2,z #4 -x+2,-y+2,z

Table SI-13. Anisotropic displacement parameters (A^2 x 10^3)

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(1)	25(1)	33(2)	22(1)	-4(1)	1(1)	2(1)
O(2)	34(2)	26(1)	33(2)	-3(1)	0(1)	-14(1)
O(3)	40(2)	60(2)	25(2)	15(2)	2(1)	9(2)
O(4)	31(1)	22(1)	23(1)	-2(1)	-5(1)	1(1)
O(5)	23(1)	22(1)	27(1)	5(1)	4(1)	6(1)
O(6)	28(1)	47(2)	20(1)	4(1)	3(1)	5(1)
O(7)	79(3)	36(2)	46(2)	24(2)	31(2)	23(2)
O(8)	38(2)	38(2)	32(2)	16(1)	-15(1)	-23(1)
O(9)	21(1)	48(2)	35(2)	4(1)	1(1)	-4(1)
O(10)	22(1)	39(2)	23(1)	8(1)	5(1)	1(1)
O(11)	24(1)	18(1)	25(1)	4(1)	2(1)	8(1)
O(12)	38(2)	22(1)	21(1)	-4(1)	-6(1)	3(1)
C(1)	37(2)	22(2)	22(2)	-3(2)	0(2)	5(2)
C(2)	23(2)	19(2)	18(2)	2(1)	0(1)	3(1)
C(3)	22(2)	18(2)	26(2)	-3(1)	-3(2)	-2(1)
C(4)	24(2)	20(2)	33(2)	3(2)	-1(2)	5(2)
C(5)	33(2)	29(2)	21(2)	1(2)	-4(2)	16(2)
C(6)	30(2)	33(2)	26(2)	-8(2)	-10(2)	13(2)
C(7)	25(2)	26(2)	28(2)	-3(2)	-6(2)	4(2)
C(8)	32(2)	29(2)	38(2)	-1(2)	-3(2)	2(2)
C(9)	29(2)	39(2)	24(2)	-7(2)	-2(2)	21(2)
C(10)	22(2)	40(2)	28(2)	-15(2)	-8(2)	13(2)
C(11)	19(2)	31(2)	37(2)	-5(2)	1(2)	2(2)
C(12)	21(2)	37(2)	21(2)	2(2)	3(1)	6(2)
C(13)	25(2)	33(2)	23(2)	-9(2)	-3(2)	6(2)
C(14)	31(2)	27(2)	32(2)	-5(2)	2(2)	9(2)
C(15)	43(3)	93(4)	23(2)	10(3)	-4(2)	-1(3)
C(16)	23(2)	24(2)	22(2)	0(1)	-4(1)	1(2)
C(17)	19(2)	18(2)	19(2)	1(1)	2(1)	1(1)
C(18)	20(2)	20(2)	21(2)	3(1)	1(1)	0(1)
C(19)	26(2)	19(2)	21(2)	4(1)	-1(2)	-5(1)
C(20)	21(2)	29(2)	17(2)	4(1)	1(1)	-7(2)
C(21)	28(2)	27(2)	22(2)	8(2)	-1(2)	2(2)
C(22)	29(2)	17(2)	25(2)	2(1)	1(2)	3(2)
C(23)	21(2)	23(2)	23(2)	1(2)	-1(1)	2(1)
C(24)	28(2)	18(2)	22(2)	2(1)	-4(2)	-4(2)
C(25)	28(2)	24(2)	22(2)	2(2)	-6(2)	0(2)
C(26)	25(2)	25(2)	25(2)	2(2)	-2(2)	3(2)
C(27)	30(2)	18(2)	19(2)	1(1)	2(2)	6(2)
C(28)	28(2)	21(2)	20(2)	1(1)	-2(2)	4(2)
C(29)	27(2)	18(2)	21(2)	2(1)	-2(2)	0(1)
C(30)	36(2)	55(3)	17(2)	10(2)	3(2)	9(2)
C(31)	58(3)	85(4)	51(3)	47(3)	24(3)	46(3)
C(32)	33(2)	25(2)	41(2)	10(2)	19(2)	9(2)

C(33)	35(2)	24(2)	70(3)	-17(2)	23(2)	-7(2)
C(34)	26(2)	31(2)	60(3)	-23(2)	-8(2)	7(2)
C(35)	36(2)	33(2)	43(2)	-18(2)	-17(2)	20(2)
C(36)	33(2)	20(2)	27(2)	-4(2)	-8(2)	8(2)
C(37)	24(2)	23(2)	26(2)	2(2)	1(2)	3(2)
C(38)	39(3)	33(2)	41(2)	-3(2)	-3(2)	0(2)
C(39)	61(3)	32(2)	37(2)	-15(2)	-20(2)	23(2)
C(40)	50(3)	29(2)	61(3)	-19(2)	-37(3)	17(2)
C(41)	34(2)	24(2)	60(3)	-7(2)	-24(2)	2(2)
C(42)	30(2)	21(2)	31(2)	5(2)	-7(2)	1(2)
C(43)	30(2)	16(2)	22(2)	0(1)	-5(2)	-2(1)
C(44)	43(2)	18(2)	23(2)	-1(1)	-4(2)	9(2)
C(45)	32(2)	39(2)	25(2)	2(2)	4(2)	1(2)
C(46)	33(2)	39(2)	26(2)	12(2)	6(2)	2(2)
C(47)	22(2)	16(2)	19(2)	-3(1)	3(1)	0(1)
C(48)	25(2)	19(2)	14(2)	0(1)	-1(1)	2(1)
C(49)	24(2)	18(2)	18(2)	-2(1)	0(1)	-4(1)
C(50)	30(2)	20(2)	21(2)	3(1)	-3(2)	-7(2)
C(51)	28(2)	20(2)	24(2)	5(2)	-6(2)	1(2)
C(52)	22(2)	19(2)	27(2)	1(2)	-2(2)	2(1)
C(53)	24(2)	23(2)	24(2)	1(2)	1(2)	0(2)
C(54)	25(2)	31(2)	21(2)	5(2)	1(2)	-10(2)
C(55)	24(2)	30(2)	23(2)	9(2)	-2(2)	-3(2)
C(56)	25(2)	25(2)	26(2)	1(2)	2(2)	1(2)
C(57)	21(2)	24(2)	16(2)	-3(1)	1(1)	-1(1)
C(58)	24(2)	22(2)	19(2)	0(1)	1(1)	2(2)
C(59)	27(2)	25(2)	22(2)	-2(1)	2(2)	-6(2)
C(60)	27(2)	26(2)	20(2)	-2(2)	-7(2)	0(2)

Table SI-14. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3)

	x	y	z	U(eq)
H(2A)	9530(50)	3920(60)	8270(60)	46
H(2B)	9290(70)	4020(70)	7960(40)	46
H(5)	4240(30)	6310(30)	4820(30)	36
H(8)	5760(40)	10910(40)	7370(30)	54
H(11)	10690(30)	8680(30)	640(30)	34
H(1A)	8814	6619	11592	41
H(1B)	7989	7134	11745	41
H(1C)	8631	7421	11126	41
H(3)	9565	6494	10559	26
H(4)	10226	5926	9540	31
H(6)	7996	5230	8734	36
H(7)	7339	5784	9743	31
H(10)	9578	6694	7992	36
H(11A)	9176	7381	6936	35
H(13)	8424	5252	6044	32
H(14)	8863	4576	7092	36
H(15A)	8375	6078	4966	79
H(15B)	7796	6866	4922	79
H(15C)	7585	6158	5494	79
H(16A)	6765	6215	8114	35
H(16B)	7505	6860	8180	35
H(16C)	7600	6091	7650	35
H(18)	6620	5363	7066	25
H(19)	5893	4764	6102	27
H(21)	5430	6966	5232	31
H(22)	6134	7578	6190	29
H(25)	6689	5527	4476	29
H(26)	7288	5903	3364	30
H(28)	5009	6390	2538	28
H(29)	4419	6001	3655	26
H(30A)	5679	6276	1499	54
H(30B)	6455	6776	1186	54
H(30C)	5839	7187	1767	54
H(31A)	7351	8364	9744	97
H(31B)	7075	7642	10280	97
H(31C)	6577	8482	10286	97
H(33)	5612	7418	8251	52
H(34)	5245	8218	7261	47
H(36)	6065	10191	8335	32
H(37)	6500	9393	9318	29
H(40)	6934	9651	6474	56
H(41)	7432	9100	5412	47
H(43)	5091	8497	4795	28
H(44)	4592	9010	5902	34
H(45A)	5881	7621	4042	48
H(45B)	6468	7954	3399	48
H(45C)	5709	8494	3687	48

H(46A)	8747	7473	3339	49
H(46B)	7971	7635	3870	49
H(46C)	8726	8266	3845	49
H(48)	9622	8529	2915	23
H(49)	10363	9087	1937	24
H(51)	8231	9462	828	29
H(52)	7472	8955	1817	27
H(55)	9730	8051	99	31
H(56)	9083	7507	-921	30
H(58)	8375	9758	-1571	26
H(59)	9005	10292	-520	29
H(60A)	7460	8940	-2248	36
H(60B)	7729	8322	-2883	36
H(60C)	8307	9083	-2691	36

Table SI-15. Torsion angles [deg]

C(1)-O(1)-C(2)-C(3)	8.2(5)
C(1)-O(1)-C(2)-C(7)	-172.8(3)
O(1)-C(2)-C(3)-C(4)	178.2(3)
C(7)-C(2)-C(3)-C(4)	-0.8(6)
C(2)-C(3)-C(4)-C(5)	0.1(6)
C(3)-C(4)-C(5)-C(6)	0.7(6)
C(3)-C(4)-C(5)-C(8)	-175.8(4)
C(4)-C(5)-C(6)-C(7)	-0.9(6)
C(8)-C(5)-C(6)-C(7)	176.1(4)
C(5)-C(6)-C(7)-C(2)	0.3(6)
O(1)-C(2)-C(7)-C(6)	-178.5(3)
C(3)-C(2)-C(7)-C(6)	0.6(6)
C(4)-C(5)-C(8)-O(2)	125.9(4)
C(6)-C(5)-C(8)-O(2)	-50.7(5)
C(4)-C(5)-C(8)-C(9)	-112.5(4)
C(6)-C(5)-C(8)-C(9)	70.9(5)
C(4)-C(5)-C(8)-C(8)#1	8.3(7)
C(6)-C(5)-C(8)-C(8)#1	-168.3(4)
O(2)-C(8)-C(9)-C(14)	-14.0(5)
C(5)-C(8)-C(9)-C(14)	-133.0(4)
C(8)#1-C(8)-C(9)-C(14)	102.9(5)
O(2)-C(8)-C(9)-C(10)	163.6(4)
C(5)-C(8)-C(9)-C(10)	44.6(5)
C(8)#1-C(8)-C(9)-C(10)	-79.6(5)
C(14)-C(9)-C(10)-C(11)	-0.9(6)
C(8)-C(9)-C(10)-C(11)	-178.5(4)
C(9)-C(10)-C(11)-C(12)	0.8(6)
C(15)-O(3)-C(12)-C(13)	11.4(6)
C(15)-O(3)-C(12)-C(11)	-167.6(4)
C(10)-C(11)-C(12)-O(3)	179.2(3)
C(10)-C(11)-C(12)-C(13)	0.2(6)
O(3)-C(12)-C(13)-C(14)	-180.0(4)
C(11)-C(12)-C(13)-C(14)	-1.0(6)
C(10)-C(9)-C(14)-C(13)	0.0(6)
C(8)-C(9)-C(14)-C(13)	177.7(4)
C(12)-C(13)-C(14)-C(9)	1.0(6)
C(16)-O(4)-C(17)-C(18)	-3.1(5)
C(16)-O(4)-C(17)-C(22)	177.5(3)
O(4)-C(17)-C(18)-C(19)	-179.6(3)
C(22)-C(17)-C(18)-C(19)	-0.2(5)
C(17)-C(18)-C(19)-C(20)	0.1(6)
C(18)-C(19)-C(20)-C(21)	0.4(6)
C(18)-C(19)-C(20)-C(23)	-178.3(3)
C(19)-C(20)-C(21)-C(22)	-0.8(6)
C(23)-C(20)-C(21)-C(22)	178.0(3)
C(20)-C(21)-C(22)-C(17)	0.8(6)
O(4)-C(17)-C(22)-C(21)	179.3(3)
C(18)-C(17)-C(22)-C(21)	-0.3(5)
C(19)-C(20)-C(23)-O(5)	119.3(4)

C(21)-C(20)-C(23)-O(5)	-59.5(4)
C(19)-C(20)-C(23)-C(24)	-121.0(4)
C(21)-C(20)-C(23)-C(24)	60.2(4)
C(19)-C(20)-C(23)-C(23)#2	2.2(6)
C(21)-C(20)-C(23)-C(23)#2	-176.6(4)
O(5)-C(23)-C(24)-C(29)	-19.2(5)
C(20)-C(23)-C(24)-C(29)	-140.0(4)
C(23)#2-C(23)-C(24)-C(29)	93.9(4)
O(5)-C(23)-C(24)-C(25)	162.9(3)
C(20)-C(23)-C(24)-C(25)	42.0(5)
C(23)#2-C(23)-C(24)-C(25)	-84.1(5)
C(29)-C(24)-C(25)-C(26)	0.6(6)
C(23)-C(24)-C(25)-C(26)	178.7(3)
C(24)-C(25)-C(26)-C(27)	-0.3(6)
C(30)-O(6)-C(27)-C(26)	-177.5(4)
C(30)-O(6)-C(27)-C(28)	2.8(6)
C(25)-C(26)-C(27)-O(6)	-179.6(3)
C(25)-C(26)-C(27)-C(28)	0.1(6)
O(6)-C(27)-C(28)-C(29)	179.3(3)
C(26)-C(27)-C(28)-C(29)	-0.4(6)
C(25)-C(24)-C(29)-C(28)	-0.9(6)
C(23)-C(24)-C(29)-C(28)	-179.0(3)
C(27)-C(28)-C(29)-C(24)	0.8(6)
C(31)-O(7)-C(32)-C(37)	-14.1(6)
C(31)-O(7)-C(32)-C(33)	167.8(4)
O(7)-C(32)-C(33)-C(34)	-178.7(4)
C(37)-C(32)-C(33)-C(34)	3.0(6)
C(32)-C(33)-C(34)-C(35)	-1.7(7)
C(33)-C(34)-C(35)-C(36)	-1.2(7)
C(33)-C(34)-C(35)-C(38)	173.1(4)
C(34)-C(35)-C(36)-C(37)	2.9(7)
C(38)-C(35)-C(36)-C(37)	-171.7(4)
O(7)-C(32)-C(37)-C(36)	-179.5(4)
C(33)-C(32)-C(37)-C(36)	-1.3(6)
C(35)-C(36)-C(37)-C(32)	-1.7(6)
C(34)-C(35)-C(38)-O(8)	-158.9(4)
C(36)-C(35)-C(38)-O(8)	15.3(6)
C(34)-C(35)-C(38)-C(39)	-35.5(6)
C(36)-C(35)-C(38)-C(39)	138.7(4)
C(34)-C(35)-C(38)-C(38)#3	85.6(5)
C(36)-C(35)-C(38)-C(38)#3	-100.2(5)
O(8)-C(38)-C(39)-C(44)	-133.6(5)
C(38)#3-C(38)-C(39)-C(44)	-16.5(7)
C(35)-C(38)-C(39)-C(44)	102.3(5)
O(8)-C(38)-C(39)-C(40)	41.6(5)
C(38)#3-C(38)-C(39)-C(40)	158.7(5)
C(35)-C(38)-C(39)-C(40)	-82.5(5)
C(44)-C(39)-C(40)-C(41)	1.5(7)
C(38)-C(39)-C(40)-C(41)	-174.2(4)
C(39)-C(40)-C(41)-C(42)	0.8(7)
C(45)-O(9)-C(42)-C(43)	-1.4(6)

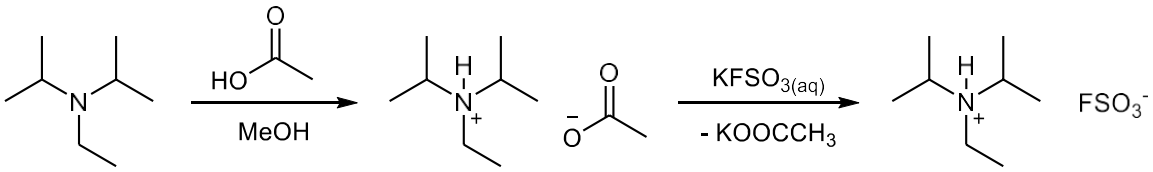
C(45)-O(9)-C(42)-C(41)	179.0(4)
C(40)-C(41)-C(42)-O(9)	177.9(4)
C(40)-C(41)-C(42)-C(43)	-1.7(6)
O(9)-C(42)-C(43)-C(44)	-179.3(3)
C(41)-C(42)-C(43)-C(44)	0.2(6)
C(42)-C(43)-C(44)-C(39)	2.2(6)
C(40)-C(39)-C(44)-C(43)	-3.0(6)
C(38)-C(39)-C(44)-C(43)	172.0(4)
C(46)-O(10)-C(47)-C(48)	-9.8(5)
C(46)-O(10)-C(47)-C(52)	169.2(3)
O(10)-C(47)-C(48)-C(49)	177.0(3)
C(52)-C(47)-C(48)-C(49)	-2.0(5)
C(47)-C(48)-C(49)-C(50)	-2.0(5)
C(48)-C(49)-C(50)-C(51)	4.4(5)
C(48)-C(49)-C(50)-C(53)	-171.0(3)
C(49)-C(50)-C(51)-C(52)	-3.1(6)
C(53)-C(50)-C(51)-C(52)	172.2(3)
C(50)-C(51)-C(52)-C(47)	-0.7(6)
O(10)-C(47)-C(52)-C(51)	-175.8(3)
C(48)-C(47)-C(52)-C(51)	3.3(5)
C(49)-C(50)-C(53)-O(11)	19.0(5)
C(51)-C(50)-C(53)-O(11)	-156.2(3)
C(49)-C(50)-C(53)-C(54)	142.2(4)
C(51)-C(50)-C(53)-C(54)	-33.0(5)
C(49)-C(50)-C(53)-C(53)#4	-93.2(4)
C(51)-C(50)-C(53)-C(53)#4	91.6(4)
O(11)-C(53)-C(54)-C(55)	49.6(4)
C(50)-C(53)-C(54)-C(55)	-72.5(4)
C(53)#4-C(53)-C(54)-C(55)	164.8(4)
O(11)-C(53)-C(54)-C(59)	-131.7(4)
C(50)-C(53)-C(54)-C(59)	106.1(4)
C(53)#4-C(53)-C(54)-C(59)	-16.5(6)
C(59)-C(54)-C(55)-C(56)	1.9(6)
C(53)-C(54)-C(55)-C(56)	-179.3(3)
C(54)-C(55)-C(56)-C(57)	0.9(6)
C(60)-O(12)-C(57)-C(56)	177.3(3)
C(60)-O(12)-C(57)-C(58)	-2.7(5)
C(55)-C(56)-C(57)-O(12)	177.0(3)
C(55)-C(56)-C(57)-C(58)	-3.0(6)
O(12)-C(57)-C(58)-C(59)	-177.9(3)
C(56)-C(57)-C(58)-C(59)	2.1(5)
C(57)-C(58)-C(59)-C(54)	0.8(6)
C(55)-C(54)-C(59)-C(58)	-2.8(6)
C(53)-C(54)-C(59)-C(58)	178.6(3)

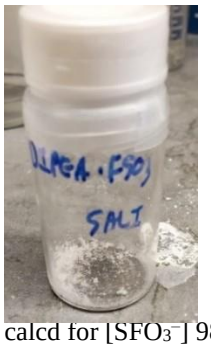
Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,z #2 -x+1,-y+1,z #3 -x+1,-y+2,z #4 -x+2,-y+2,z

d. Determination of SF_6 Decomposition Side Products. Validation of FSO_3^-

Synthesis of [DIPEA-H^+][FSO_3^-]

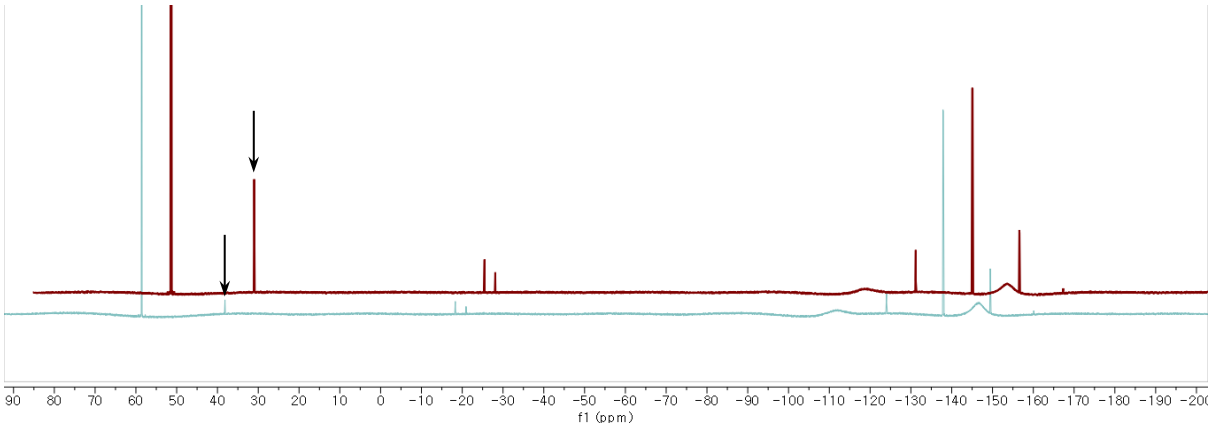




In a clean vial, DIPEA (2.0 mmol, 1 equiv.) was dissolved in methanol (1 mL). After adding acetic acid (2.0 mmol, 1 equiv.), the mixture was vigorously shaken and then concentrated *in vacuo*. The dried residue was then dissolved in 20 mL of DCM and transferred into a separatory funnel. After adding an aqueous solution of KSO_3F prepared from commercially available salt (1.8 mmol in 20 mL of H_2O), the separatory funnel was vigorously shaken. The resulting organic layer was then dried with $NaSO_4$ and concentrated *in vacuo* to give [DIPEA-H^+][SO_3F^-] as white solid. **^{19}F NMR** (471 MHz, $CDCl_3$) δ 38.52; **HRMS (ESI$^-$)** (m/z): [M]$^-$ calcd for [SFO_3^-] 98.9552, found 98.9564.

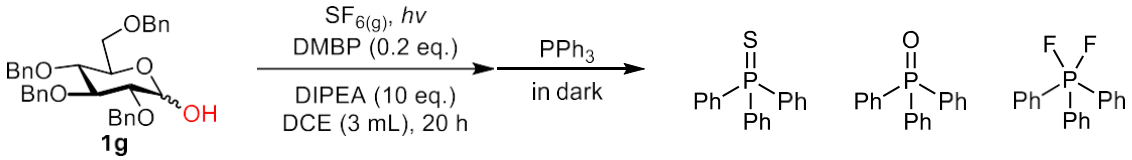
[DIPEA-H^+][FSO_3^-] Addition Experiment

Substrate **1g** was fluorinated under the standard reaction condition and after removing the light source analyzed by HRMS to contain molecular ion [SO_3F^-] with m/z =98.9552 Da (ESI$^-$). An aliquot (0.2 mL) of the crude reaction was taken out, followed by addition of [DIPEA-H^+][FSO_3^-] solution from above (2 mg in 0.5 mL $CDCl_3$). The reaction was then stirred in dark for 5 minutes, and another aliquot (0.2 mL) of sample was taken out. Both samples were subjected to ^{19}F NMR and compared.

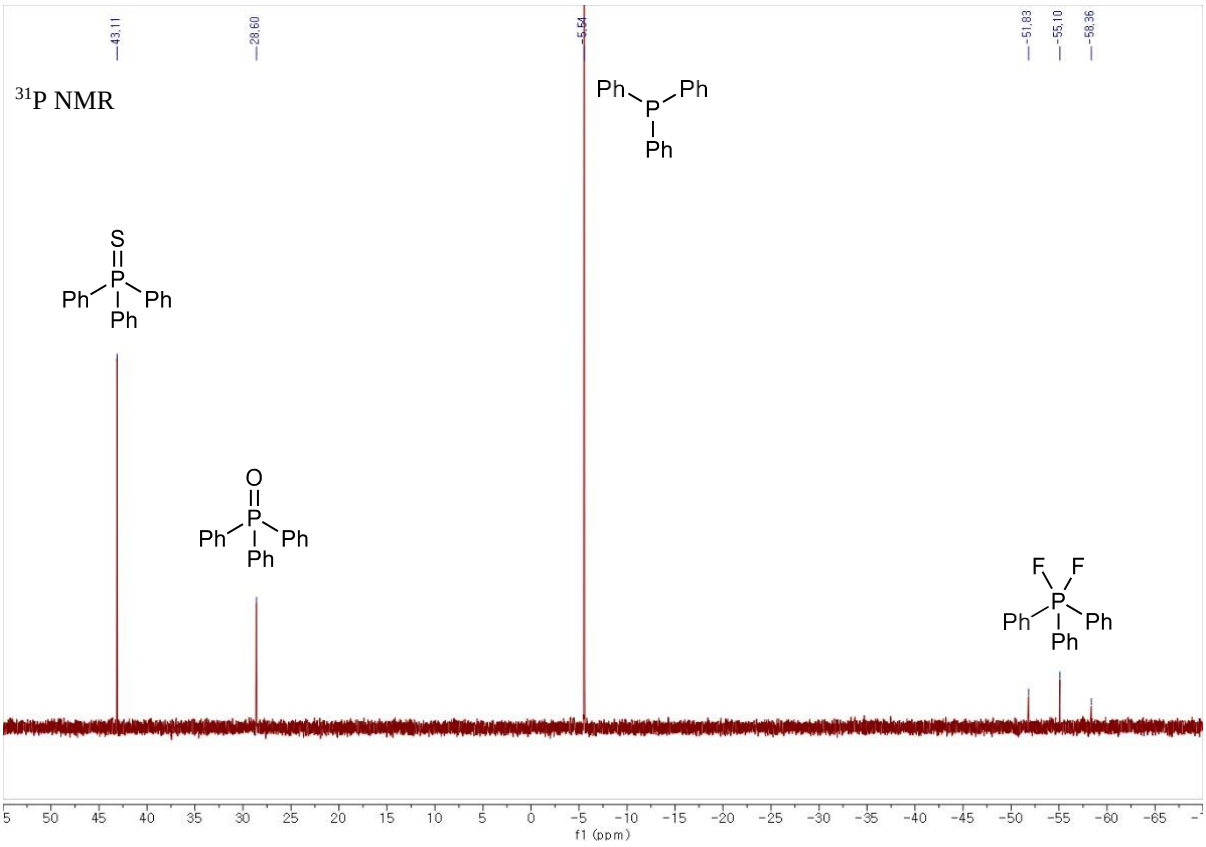


After the addition of [DIPEA-H^+][FSO_3^-], the intensity of the peak at 38.15 ppm was significantly enhanced, which verifies the formation of FSO_3^- as side product.

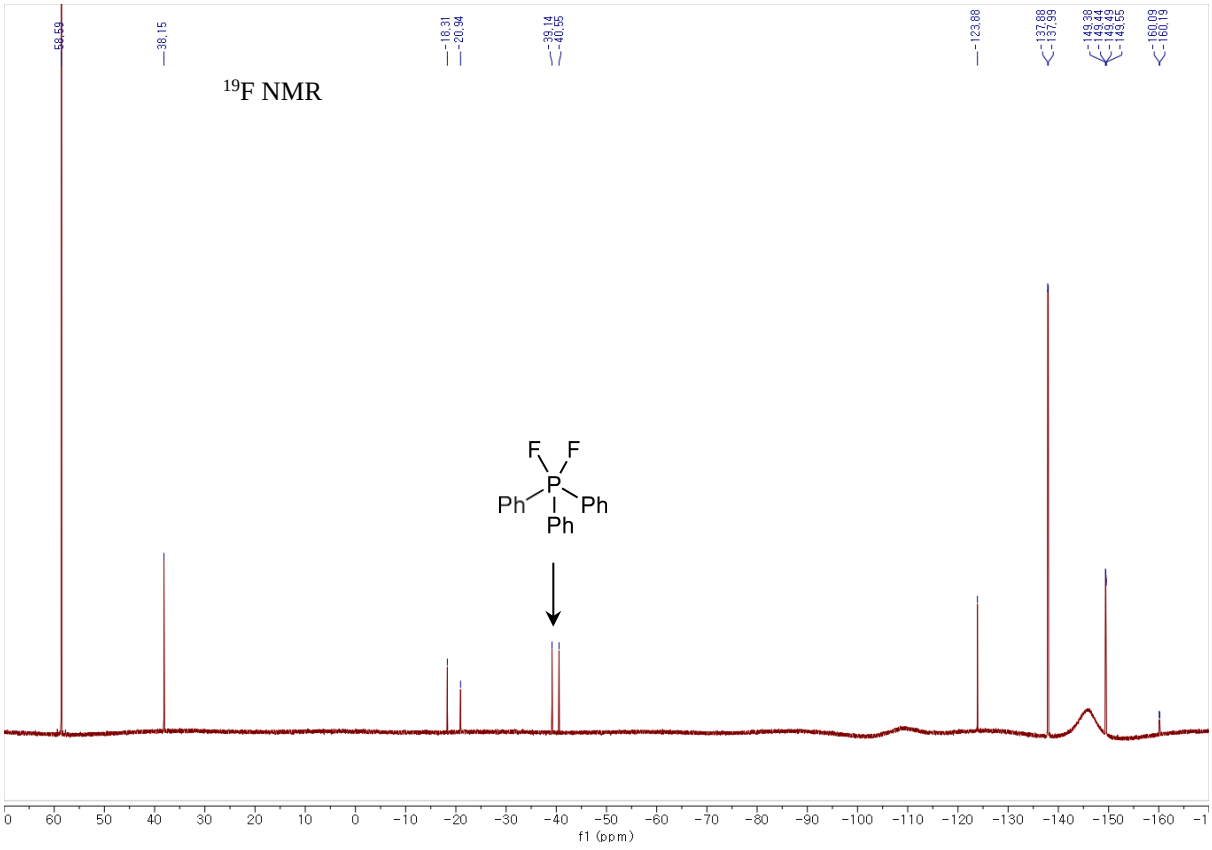
e. PPh_3 Quenching Experiment



Substrate **1g** was subjected to a standard reaction. After removing the light source, an aliquot of crude reaction was taken out, and then PPh_3 solution (0.1 mmol in 0.5 mL of $CDCl_3$) was injected into the reaction vial. The mixture was stirred in dark, and samples were taken out after 3 hours and after 23 hours. All samples were subjected to ^{19}F and ^{31}P NMR experiments. Formation of $Ph_3P{=}S$, and Ph_3PF_2 (as well as $Ph_3P{=}O$) was confirmed by the direct comparison of the resultant and published spectral data.

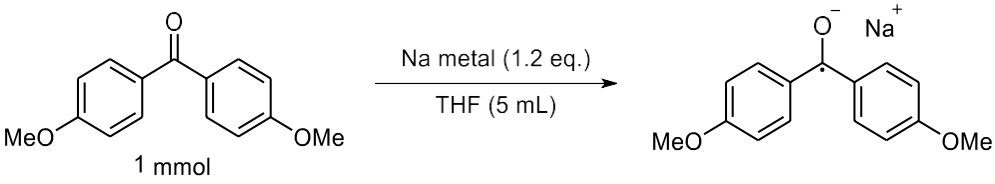


^{19}F NMR


58.59
38.15
18.31
20.94
39.14
40.55
123.88
137.88
137.99
149.38
149.44
149.49
149.55
160.09
160.19
F
F
P
Ph
Ph
Ph
f1 (ppm)

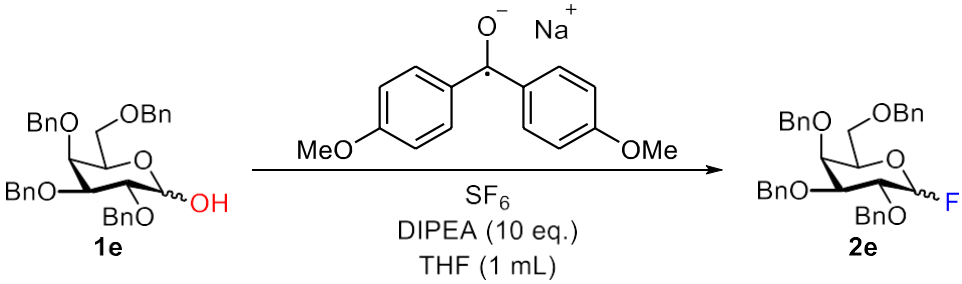
f. Ketyl Radical Experiment

Synthesis of Ketyl Radical Solution



Into an oven dried 2 dram vial, 4,4'-dimethoxybenzophenone (1.0 mmol, 1 equiv.) and sodium metal (1.2 mmol, 1.2 equiv.) were added. The vial was sealed and connected to high vacuum. After drying the content in the vial for 10 minutes, the vial was disconnected from the vacuum line, and dry THF (5 mL) was injected to the vial. The mixture was stirred for 1 hour to give a deep blue solution.

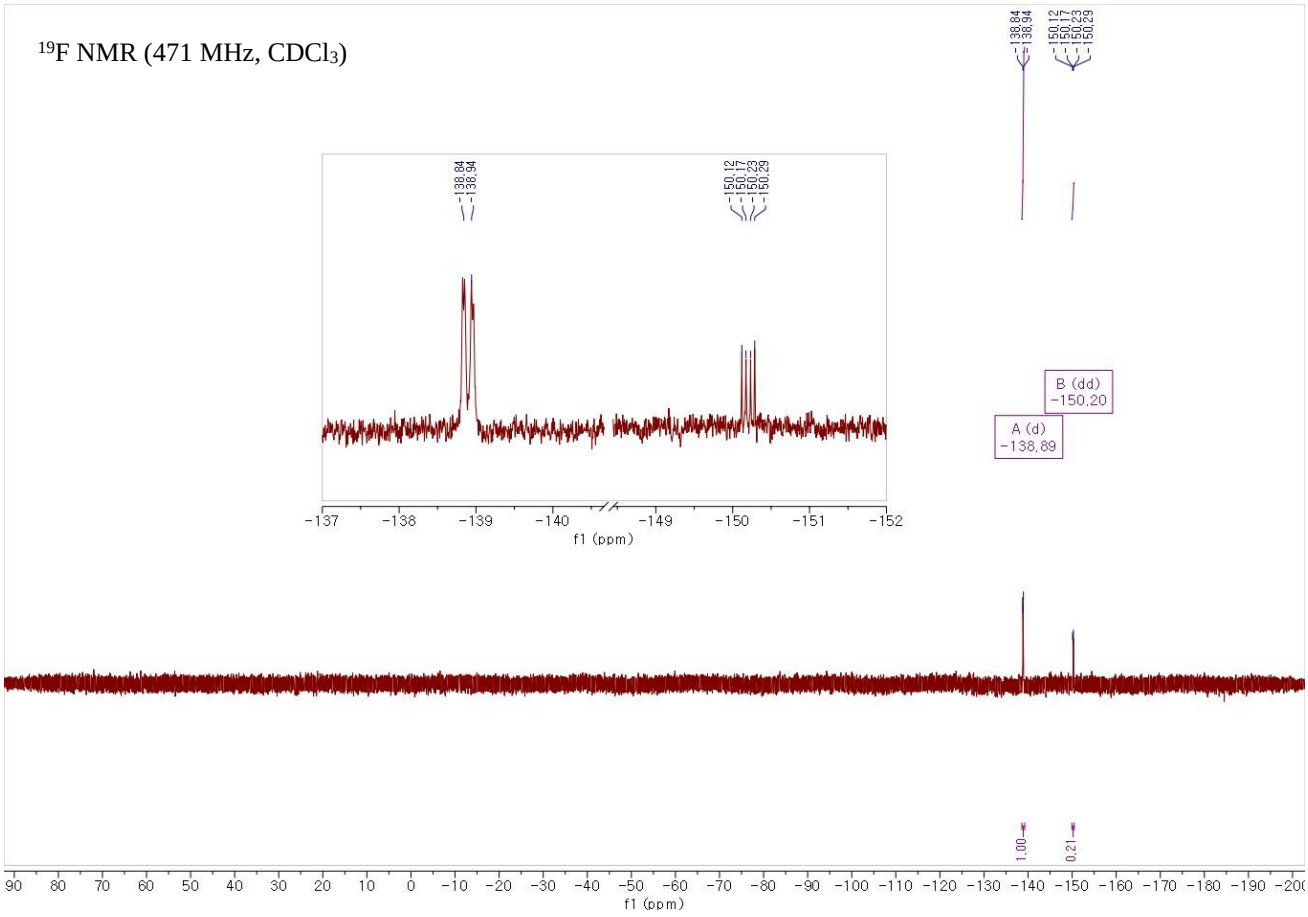
Fluorination of Glycoside with the Ketyl Radical Solution



Into an oven dried 1 dram vial, 2,3,4,6-tetrakis-*O*-(phenylmethyl)-*D*-galactopyranose **1e** (0.1 mmol, 1.0 equiv.) was added and sealed. The vial was connected to the vacuum line and the content was dried for 10 min. After disconnecting the vial, DIPEA (1.0 mmol,10 equiv.) and dry THF (1 mL) were added and stirred until the mixture became homogeneous. A balloon containing SF_6 was then plugged into the vial and the solution was sparged.

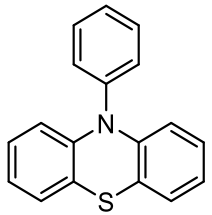
Into the 2 mL of the ketyl radical solution prepared before, a balloon containing SF_6 was plugged followed by the addition of 1 mL mixture containing **1e**. The reaction mixture was stirred in dark for 20 h and concentrated *in vacuo*. The crude mixture was then purified by FCC (SiO_2, 30% EtOAc in hexaness) to yield **2e** in 1% yield (~0.5 mg).

^{19}F NMR (471 MHz, $CDCl_3$)

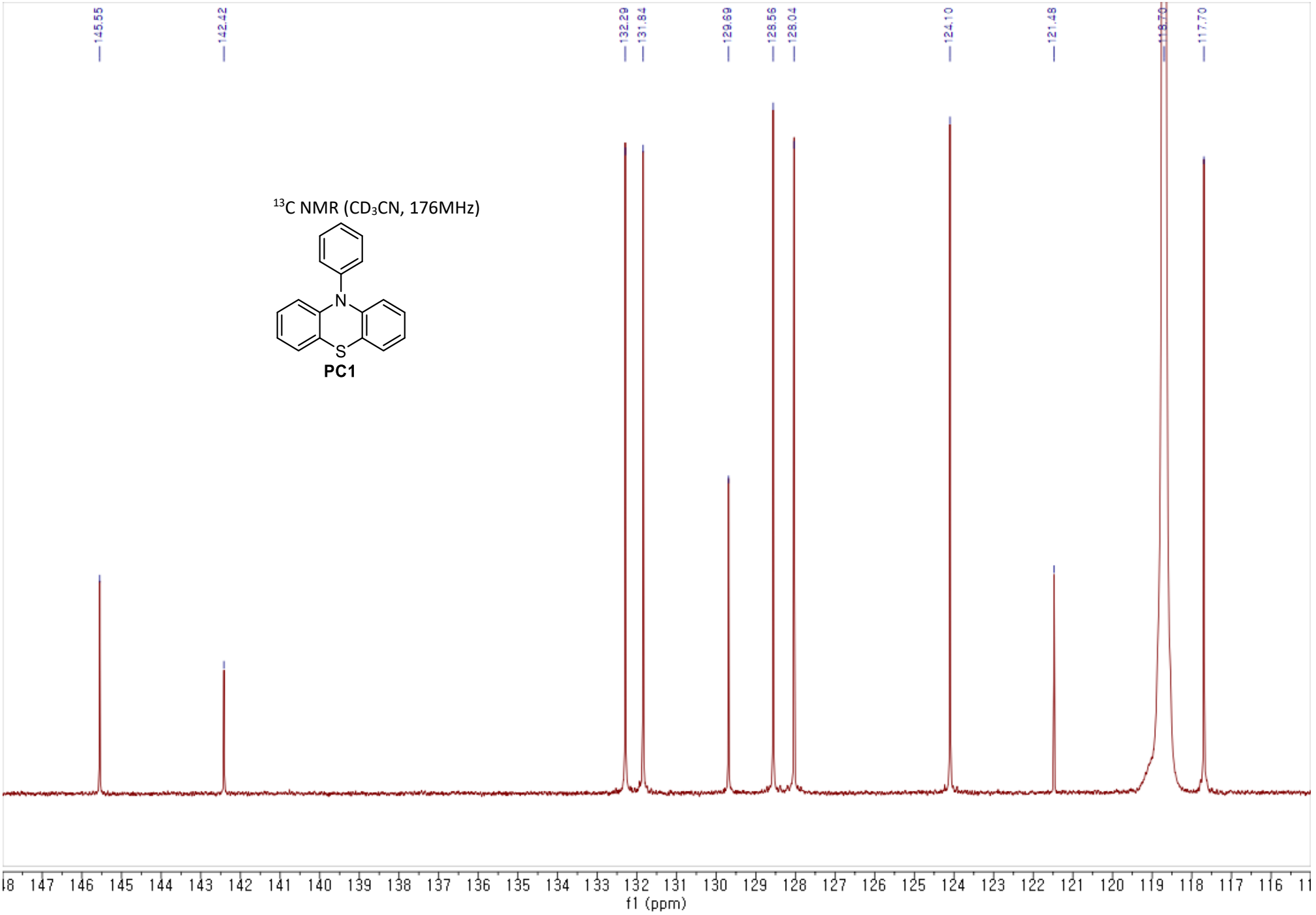


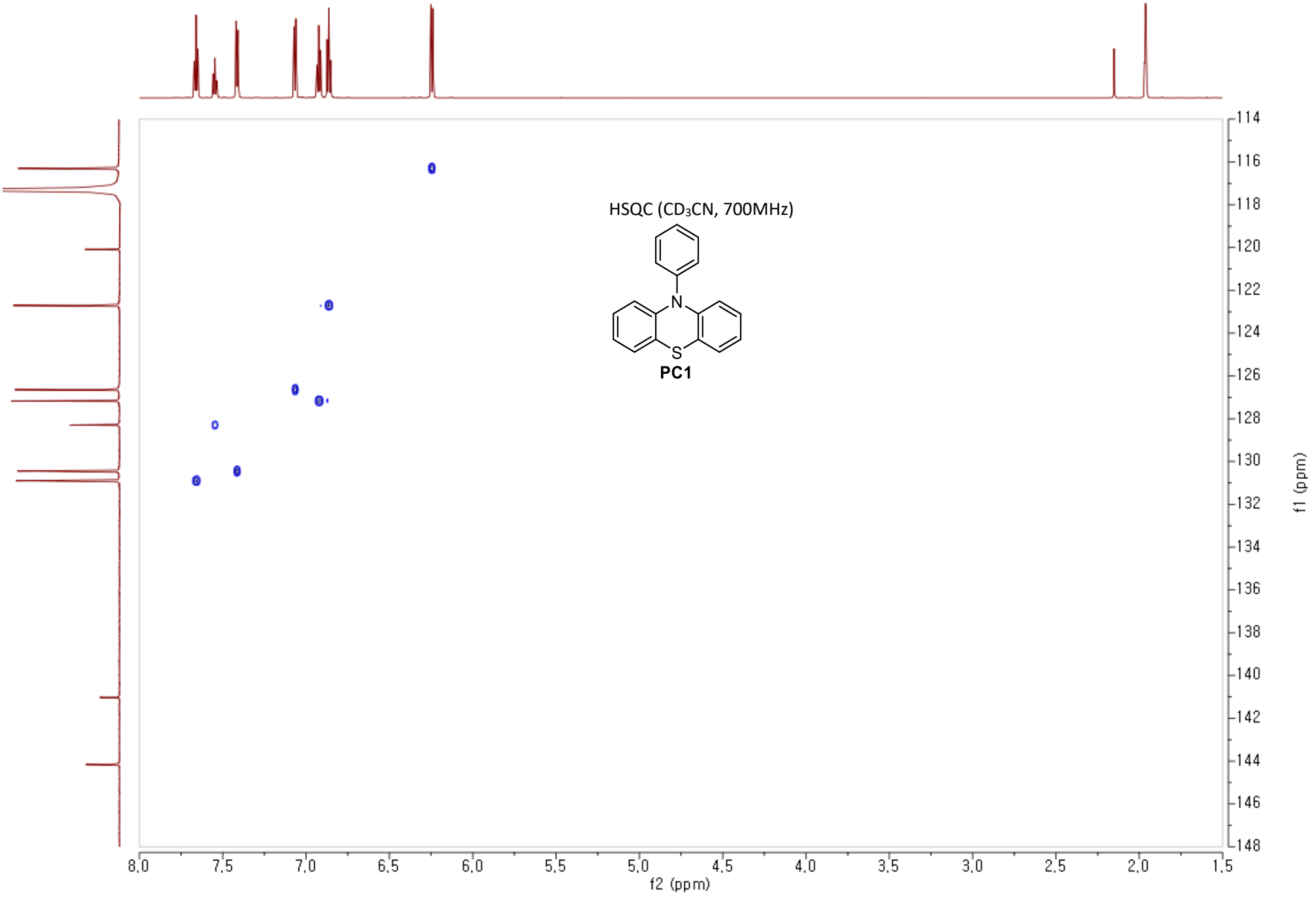
N-Phenylphenothiazine (PC1)

^{1}H NMR (CD_3CN, 700MHz)

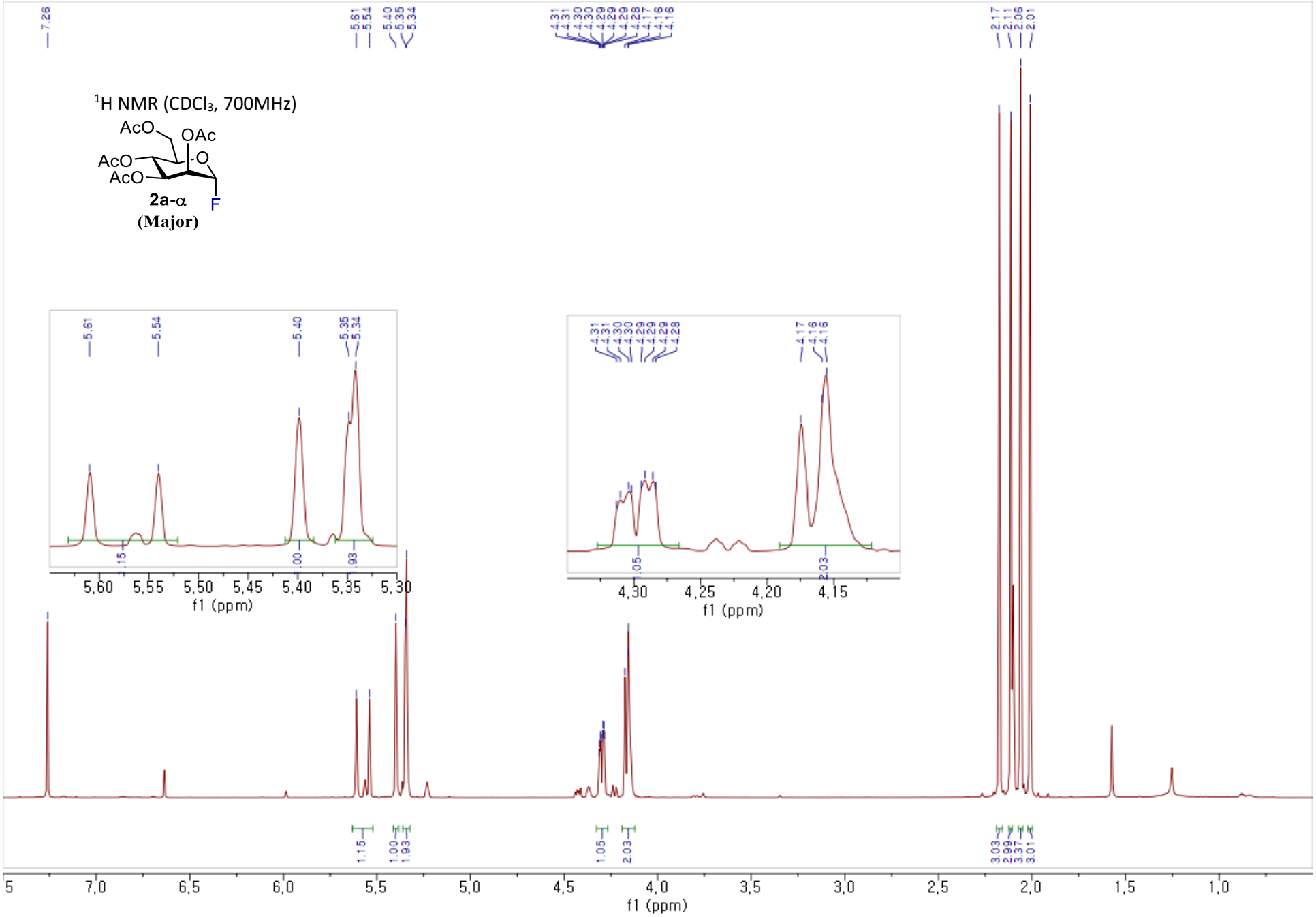


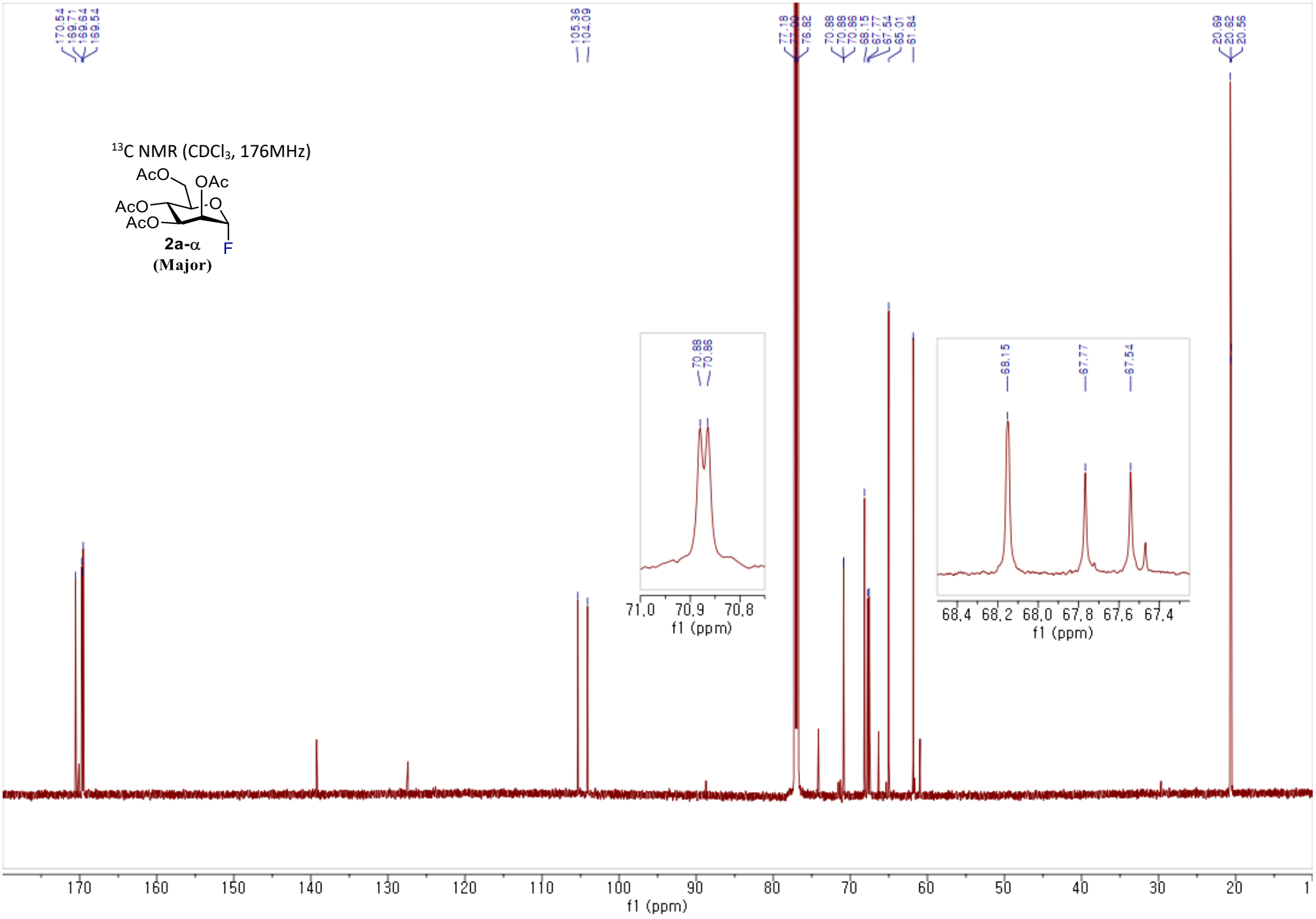
PC1

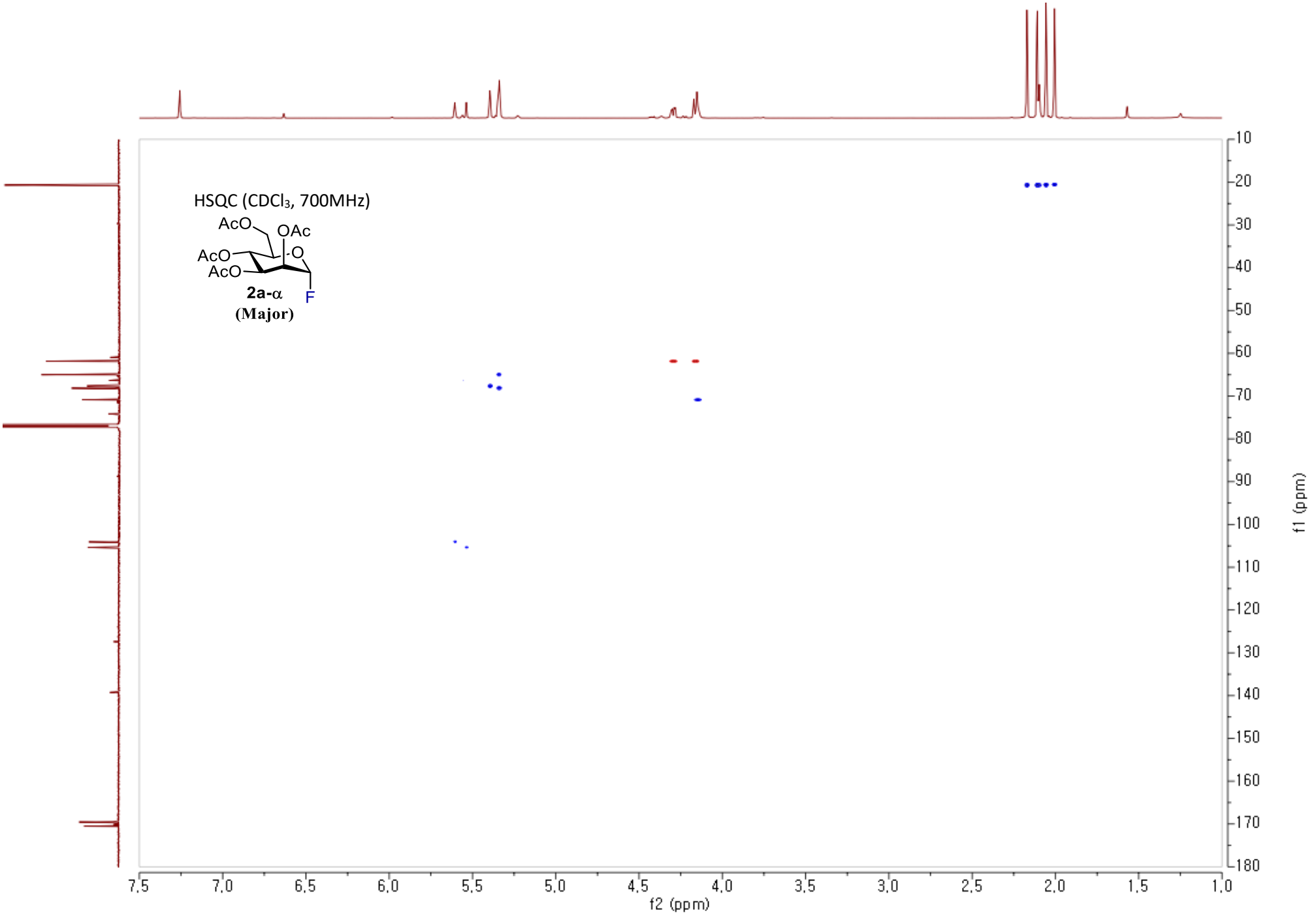

145.55
142.42
132.29
131.84
129.69
128.56
128.04
124.10
121.48
118.70
117.70
^{13}C NMR (CD_3CN, 176MHz)
N
S
PC1
f1 (ppm)


HSQC (CD_3CN, 700MHz)
N
S
PC1
f2 (ppm)
f1 (ppm)

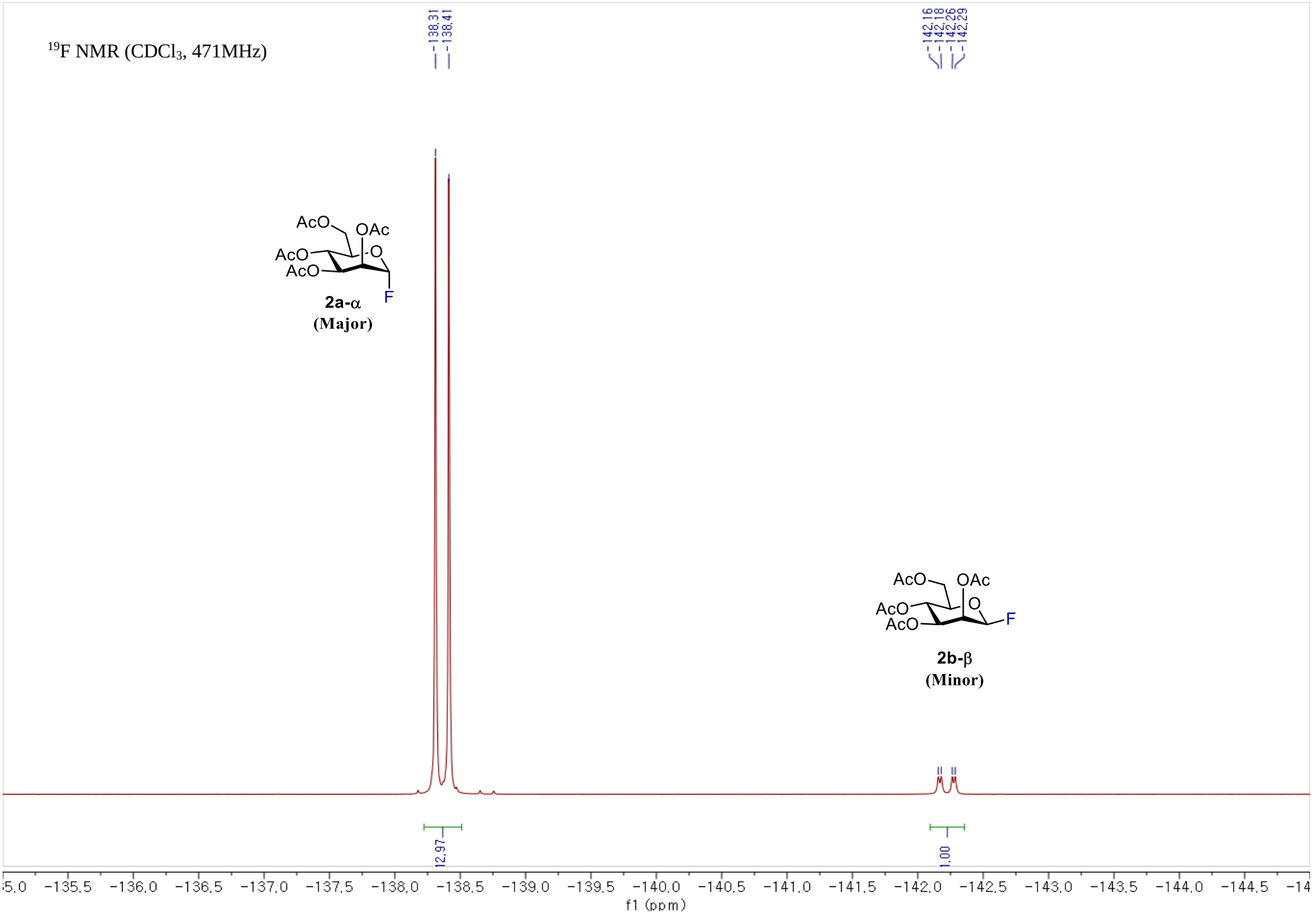
2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranosyl fluoride (2a-α, Major diastereomer)

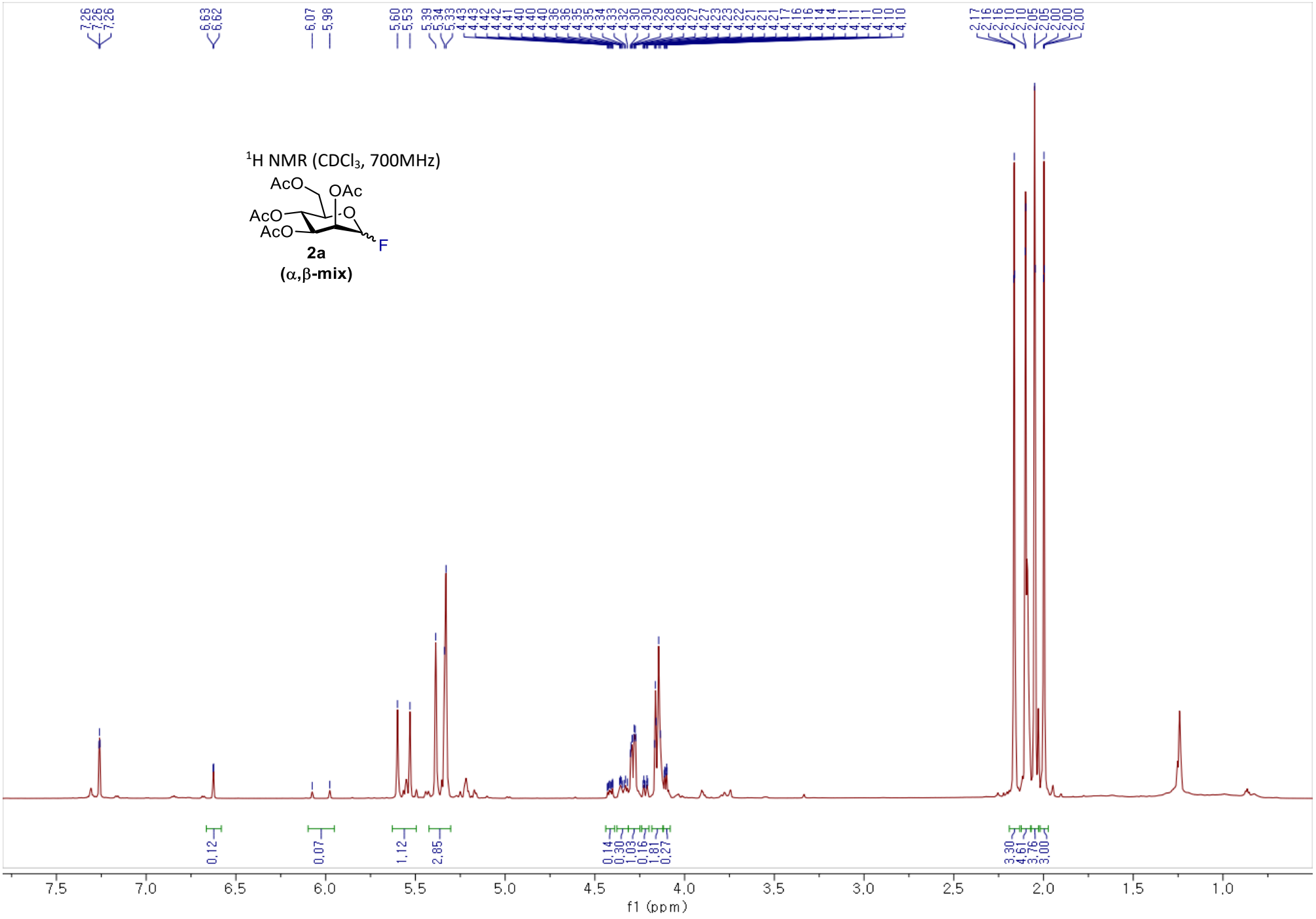



170.54
169.71
169.64
169.54
105.36
104.09
77.18
77.00
76.82
70.88
70.86
68.15
67.77
67.54
65.01
61.84
20.69
20.62
20.56
^{13}C NMR ($CDCl_3$, 176MHz)
AcO
OAc
AcO
O
AcO
F
2a-α
(Major)
70.88
70.86
71.0
70.9
70.8
f1 (ppm)
68.15
67.77
67.54
68.4
68.2
68.0
67.8
67.6
67.4
f1 (ppm)
170
160
150
140
130
120
110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

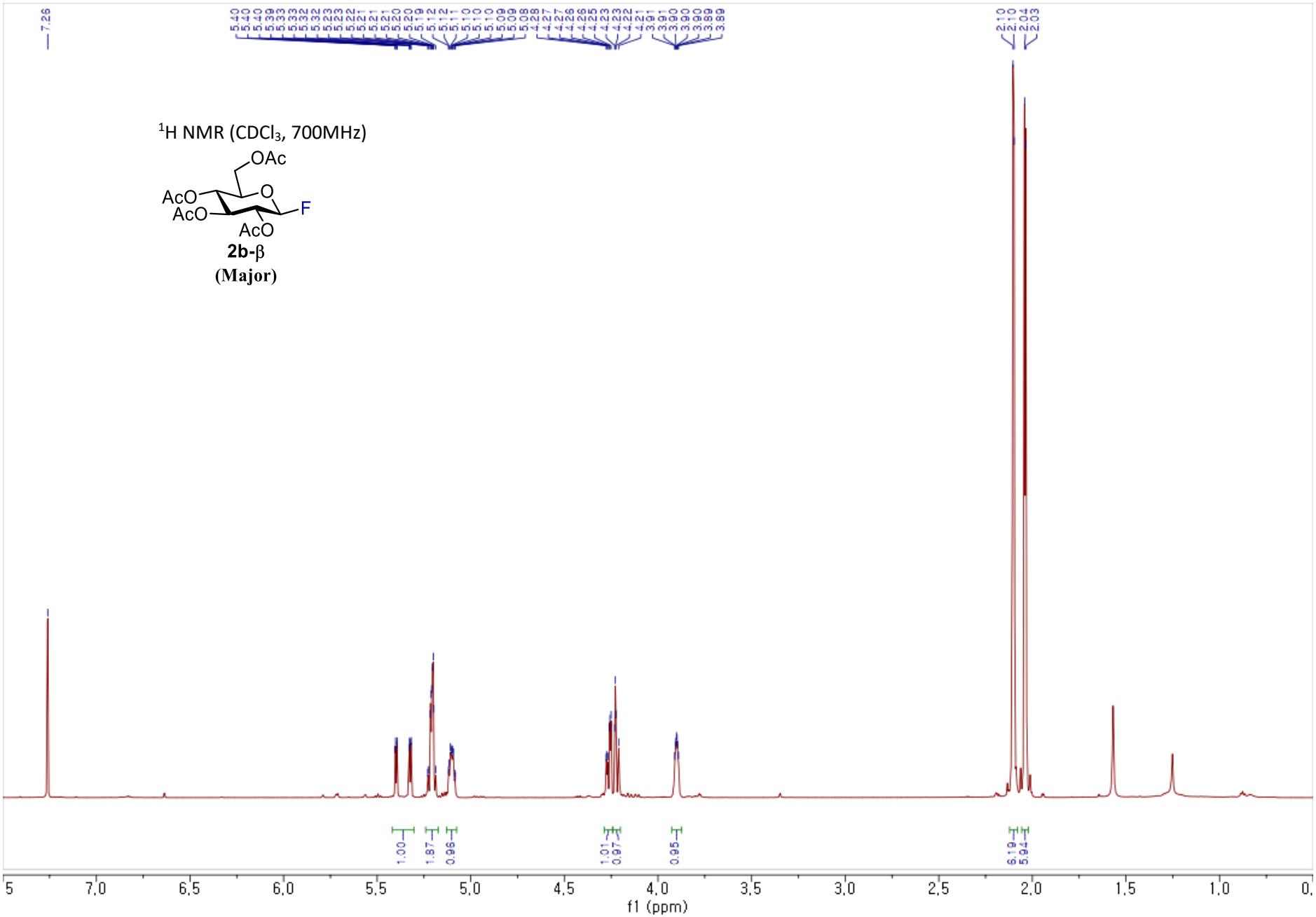

HSQC (CDCl3, 700MHz)
AcO
OAc
AcO
O
AcO
F
2a-α
(Major)
f2 (ppm)
f1 (ppm)

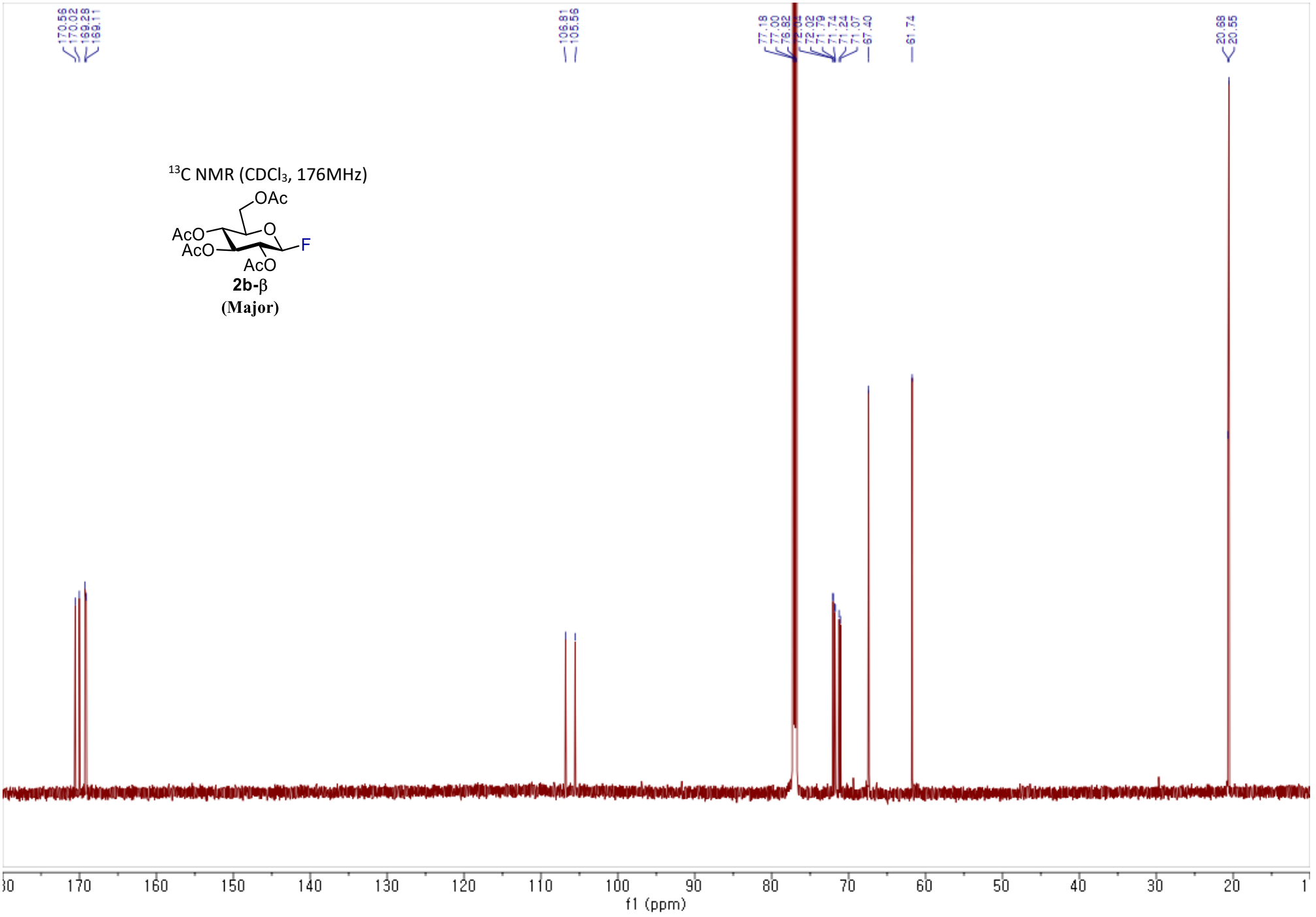
^{19}F NMR ($CDCl_3$, 471MHz)

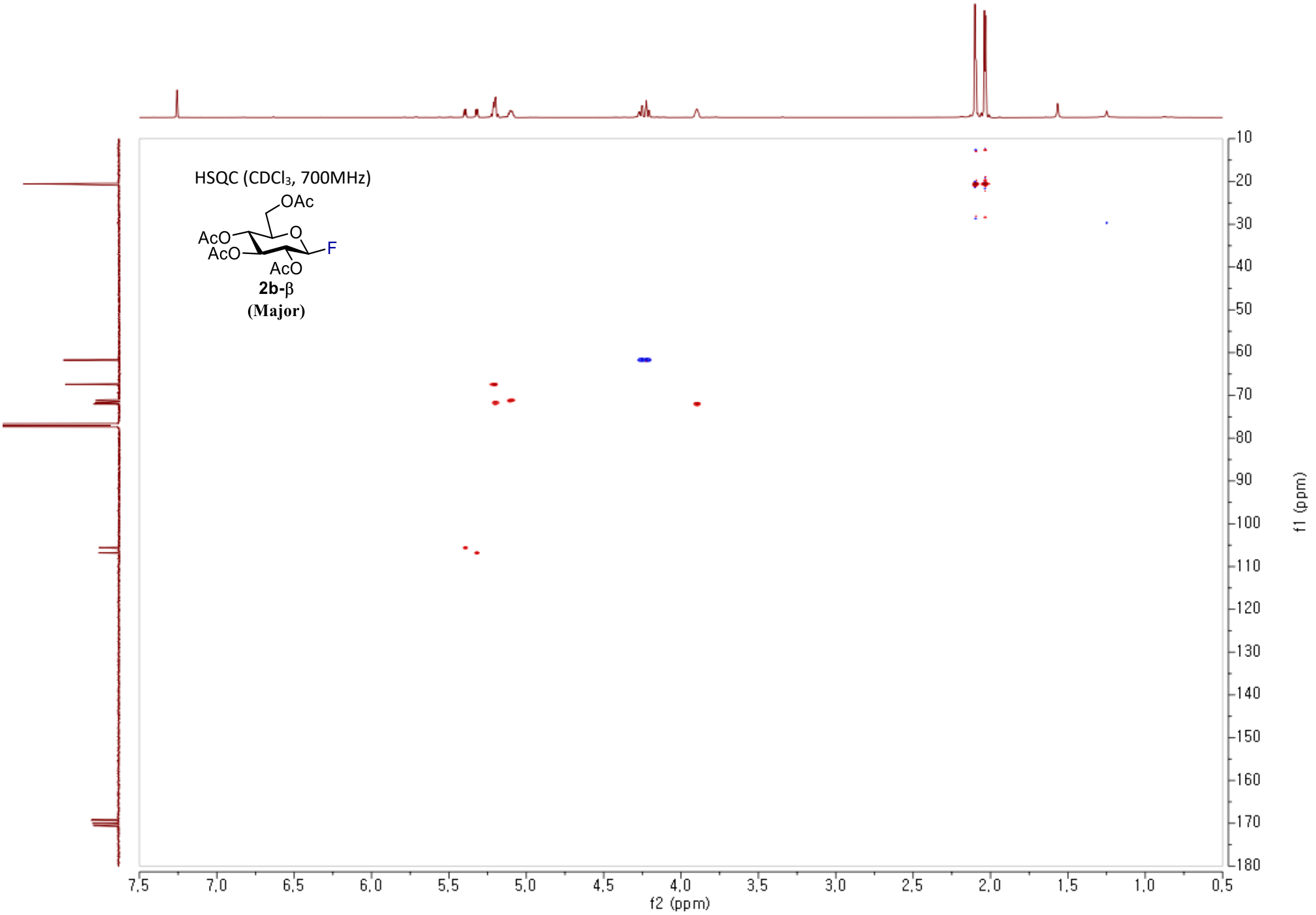



7.26
7.26
7.26
6.63
6.62
6.07
5.98
5.60
5.53
5.39
5.34
5.33
4.43
4.42
4.42
4.41
4.40
4.40
4.40
4.36
4.36
4.35
4.35
4.34
4.33
4.32
4.30
4.30
4.29
4.28
4.28
4.27
4.27
4.23
4.22
4.21
4.21
4.21
4.17
4.16
4.16
4.14
4.14
4.11
4.11
4.10
4.10
4.10
2.17
2.16
2.16
2.10
2.10
2.05
2.00
2.00
2.00
1H NMR (CDCl3, 700MHz)
AcO
OAc
AcO
O
AcO
F
2a
(α,β-mix)
0.12
0.07
1.12
2.85
0.14
0.30
1.03
0.16
1.81
0.27
3.30
4.61
3.76
3.00
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
f1 (ppm)

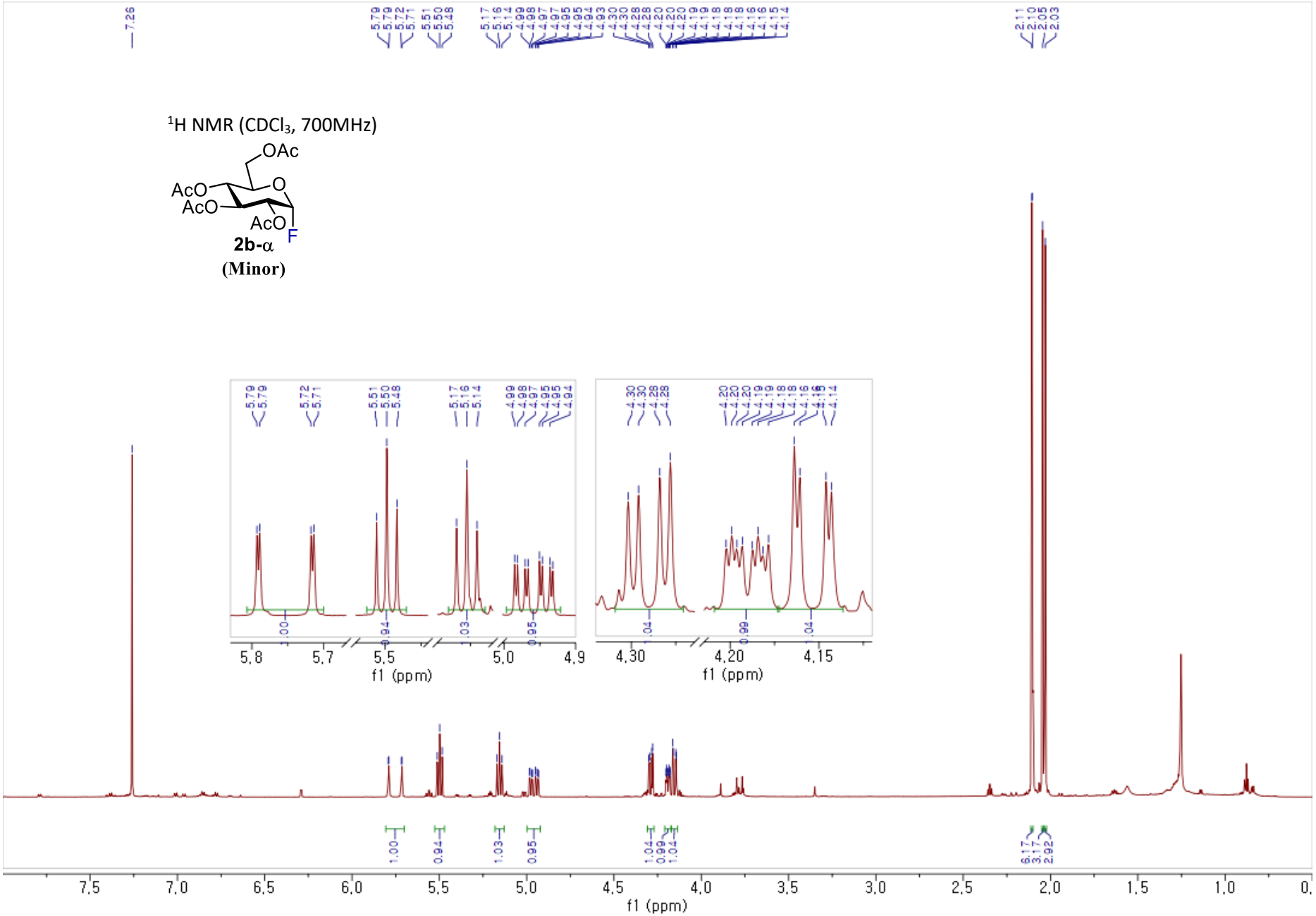
2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl fluoride (2b-β, Major diastereomer)

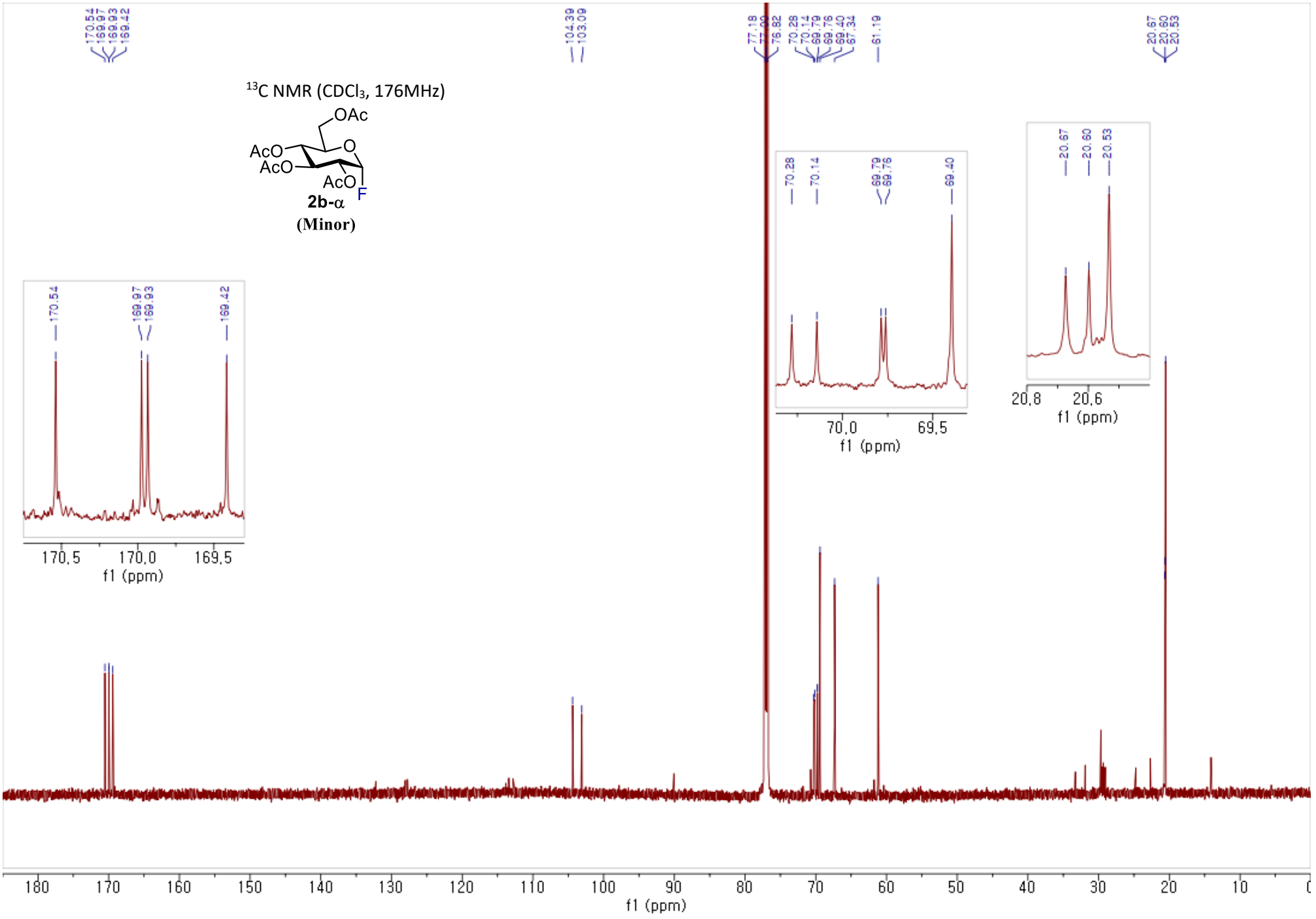


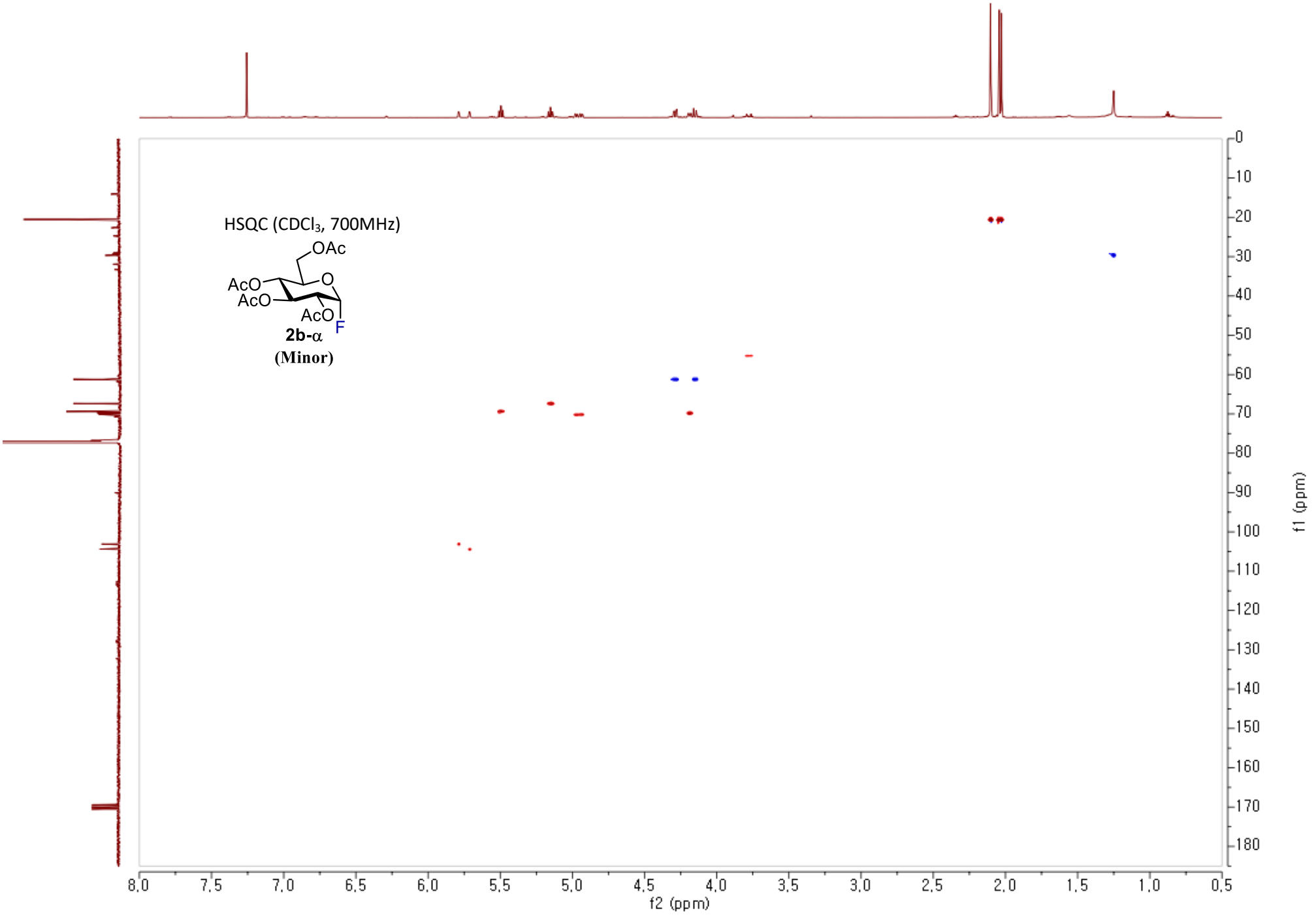

170.56
170.02
169.28
169.11
106.81
105.56
77.18
77.00
76.82
72.02
71.79
71.74
71.24
71.07
67.40
61.74
20.68
20.55
^{13}C NMR ($CDCl_3$, 176MHz)
OAc
AcO
AcO
O
F
AcO
2b-β
(Major)
f1 (ppm)


HSQC ($CDCl_3$, 700MHz)
OAc
AcO
AcO
AcO
O
F
2b-β
(Major)
f2 (ppm)
f1 (ppm)

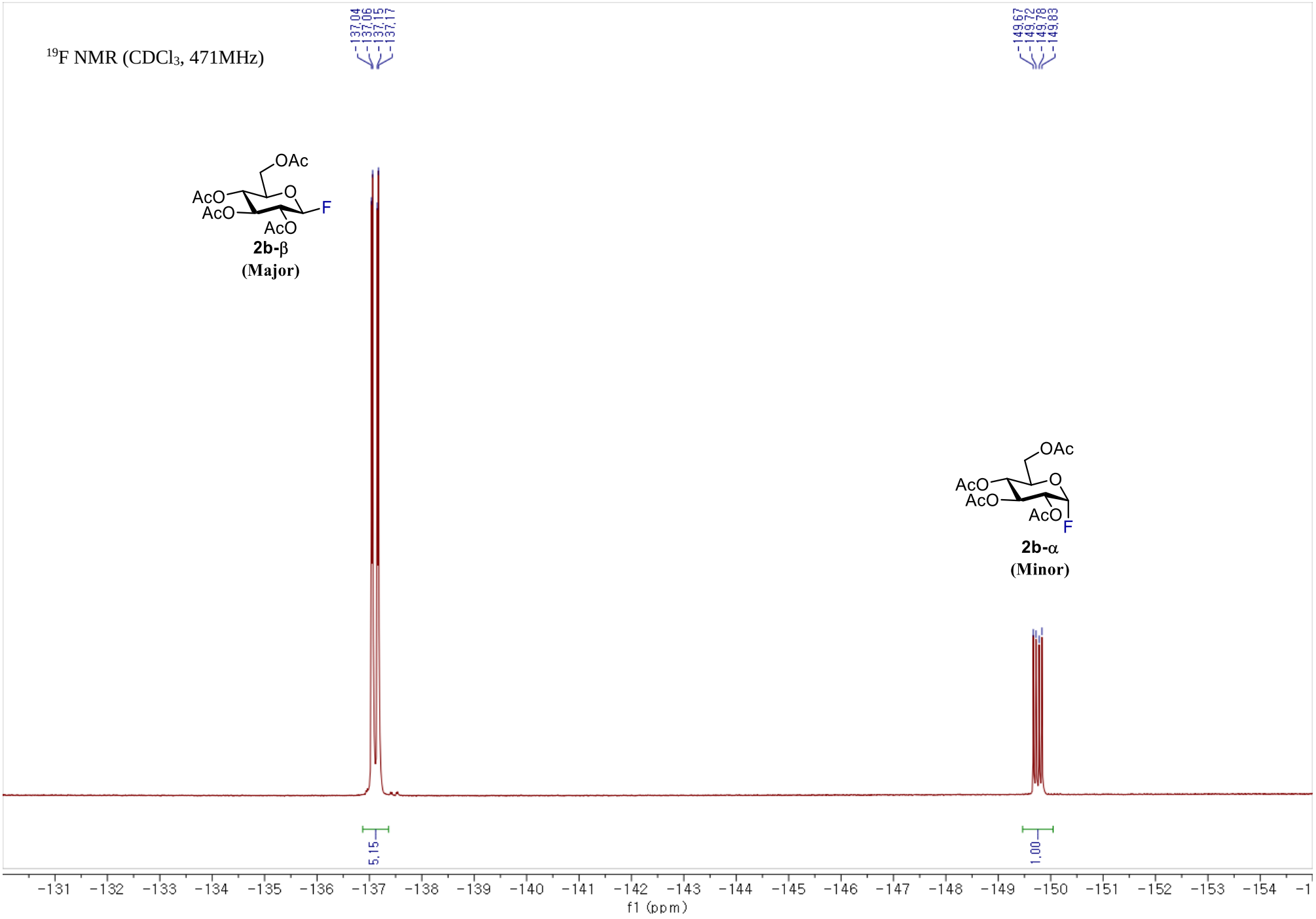
2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl fluoride (2b-α, Minor diastereomer)

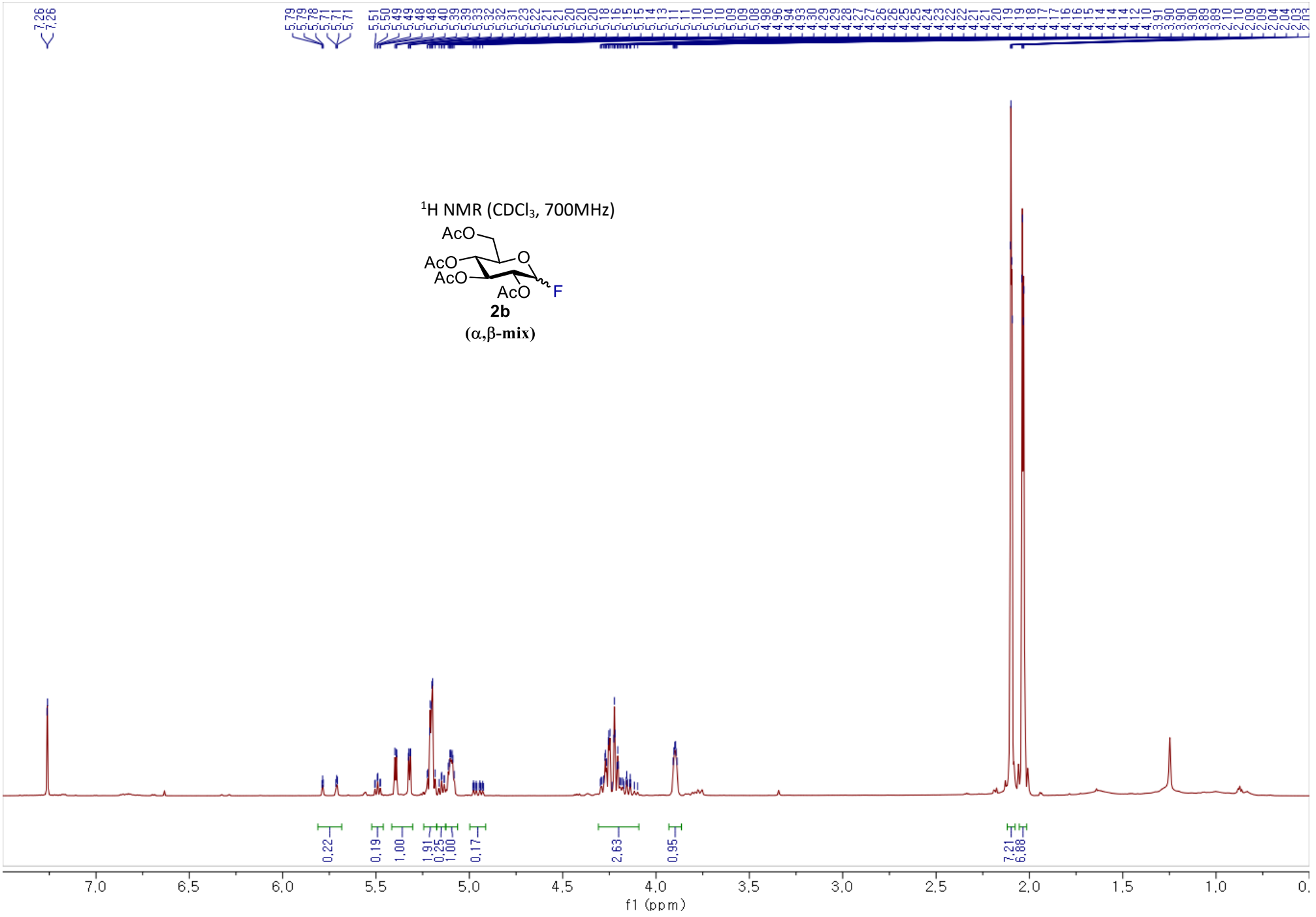



170.54
169.97
169.93
169.42
104.39
103.09
77.18
76.82
70.28
70.14
69.79
69.76
69.40
67.34
61.19
20.67
20.60
20.53
^{13}C NMR ($CDCl_3$, 176MHz)
OAc
AcO
AcO
AcO
O
F
2b-α
(Minor)
170,5
170,0
169,5
f1 (ppm)
70,0
69,5
f1 (ppm)
20,8
20,6
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

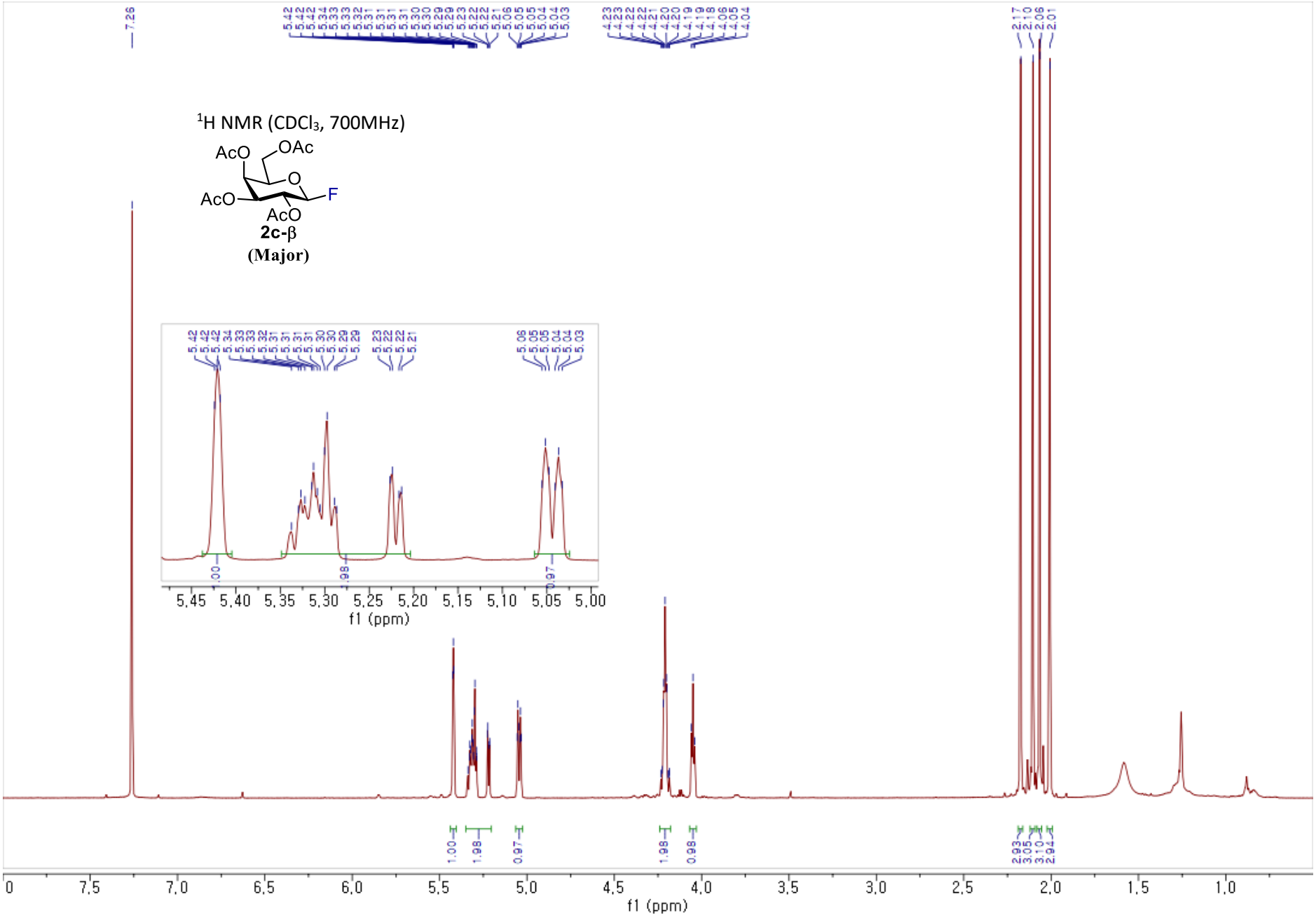

HSQC ($CDCl_3$, 700MHz)
OAc
AcO
AcO
O
AcO
F
2b-α
(Minor)
f2 (ppm)
f1 (ppm)

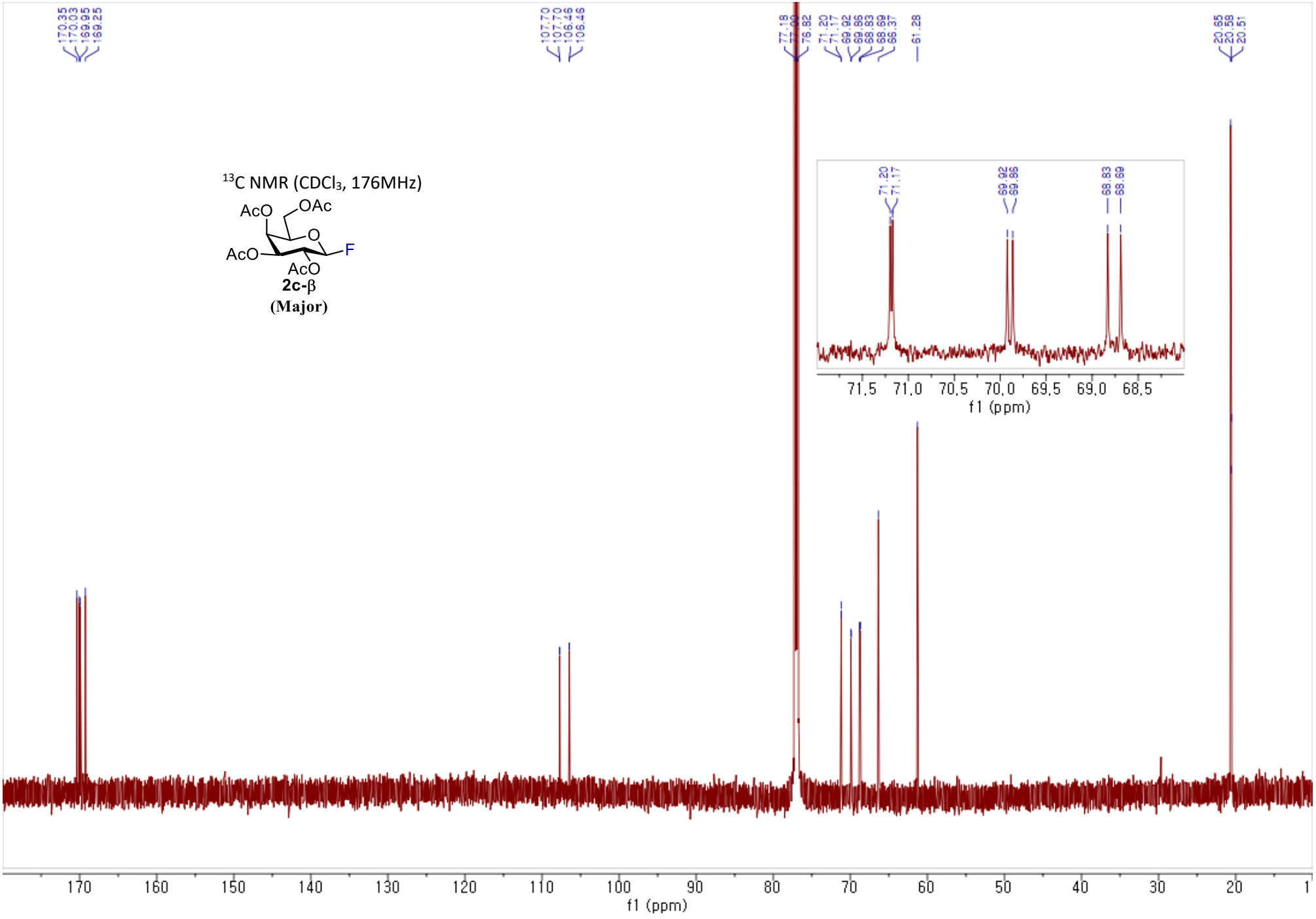
^{19}F NMR ($CDCl_3$, 471MHz)

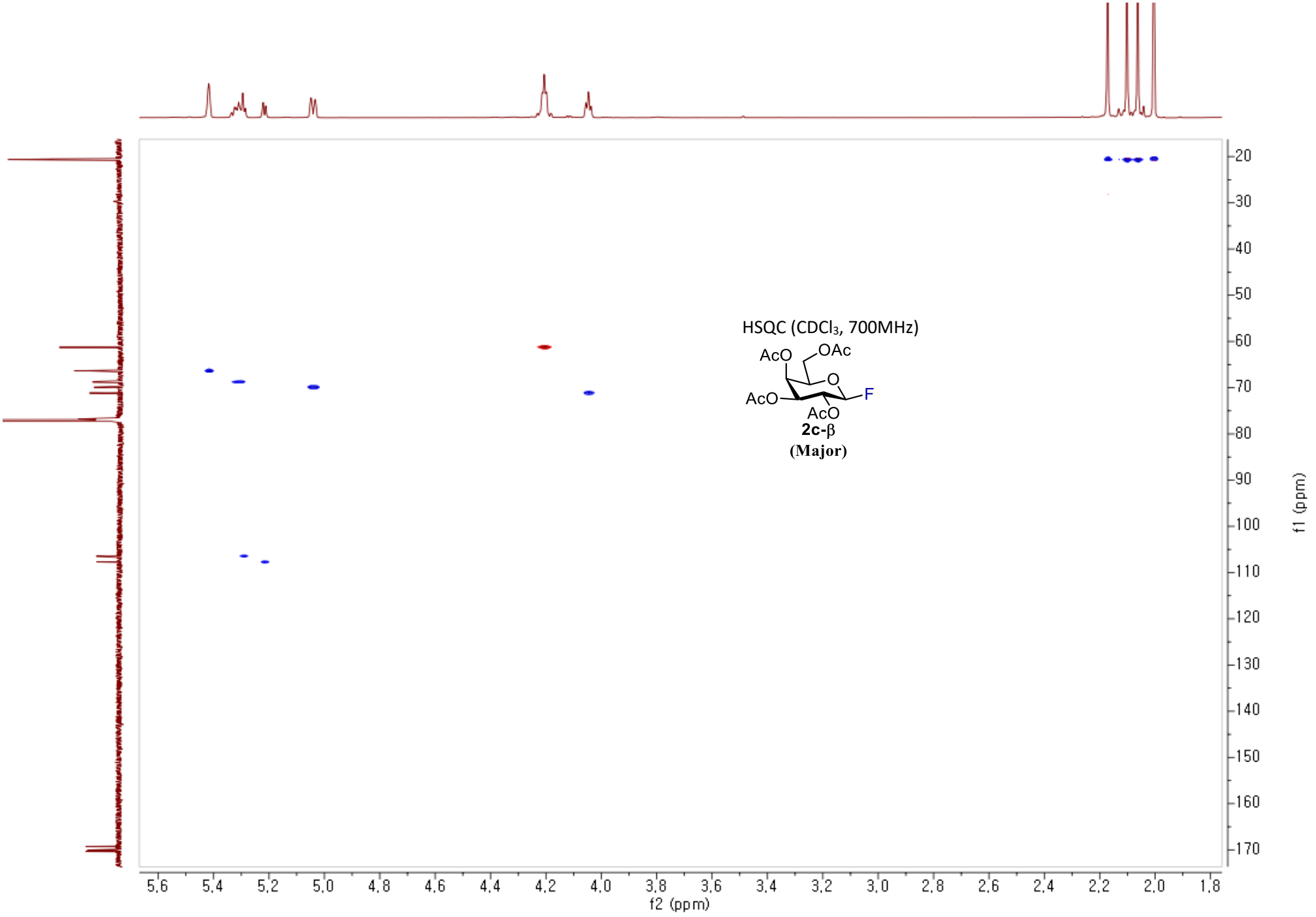



^{1}H NMR (CDCl$_3$, 700MHz)
AcO
AcO
AcO
AcO
O
F
2b
(α,β-mix)
0.22
0.19
1.00
1.91
0.25
1.00
0.17
2.63
0.95
7.21
6.88
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

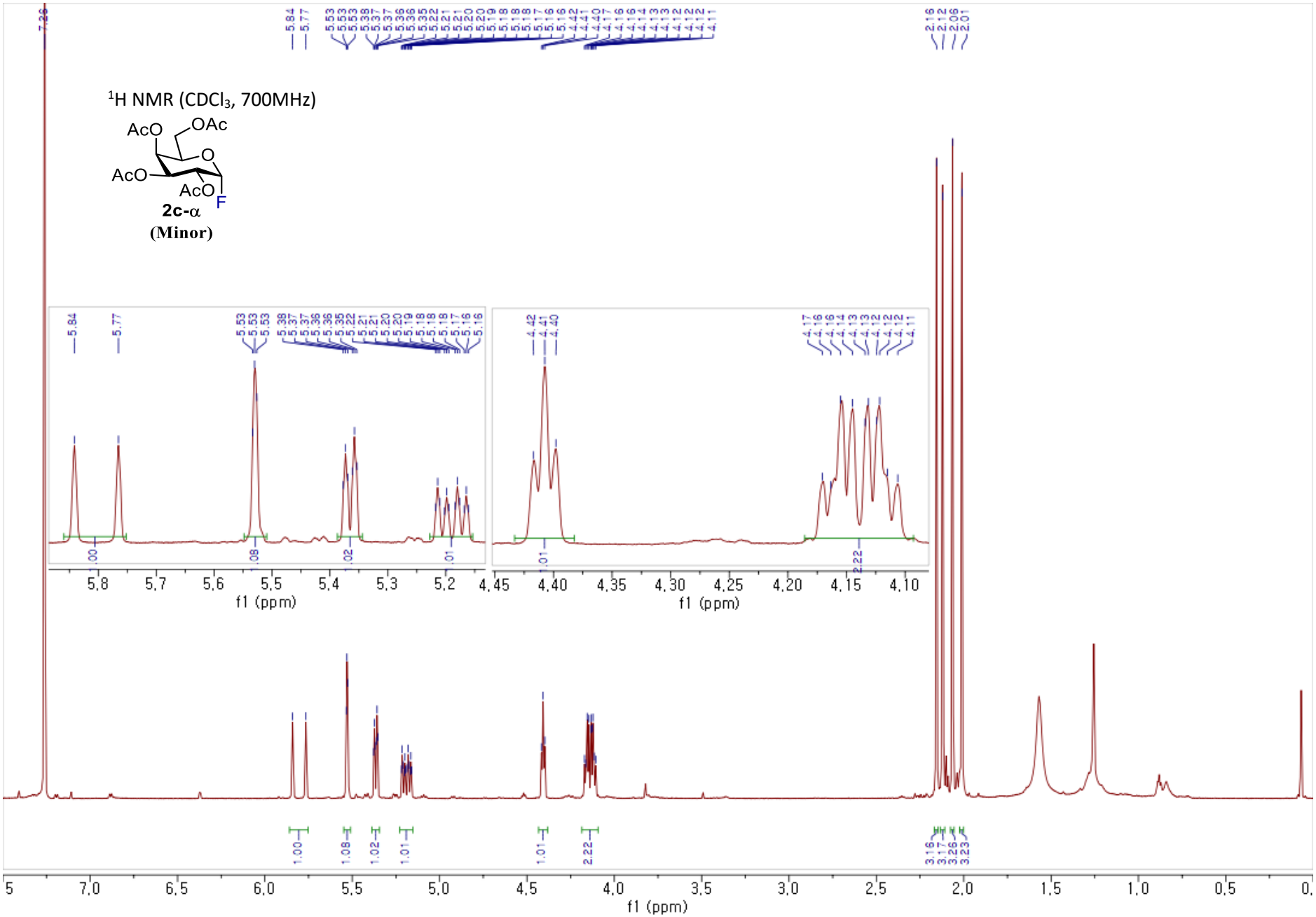
2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl fluoride (2c-β, Major diastereomer)

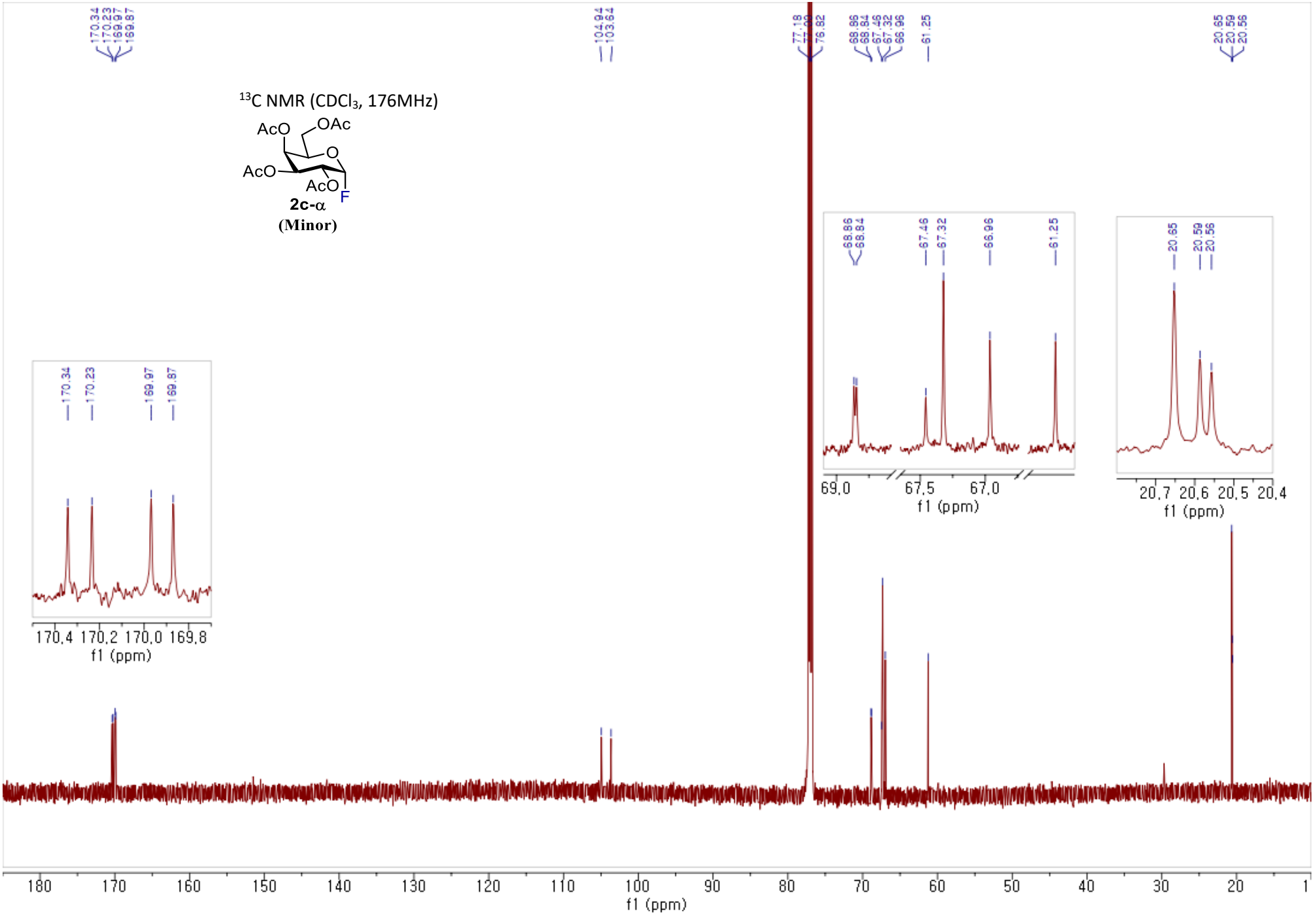


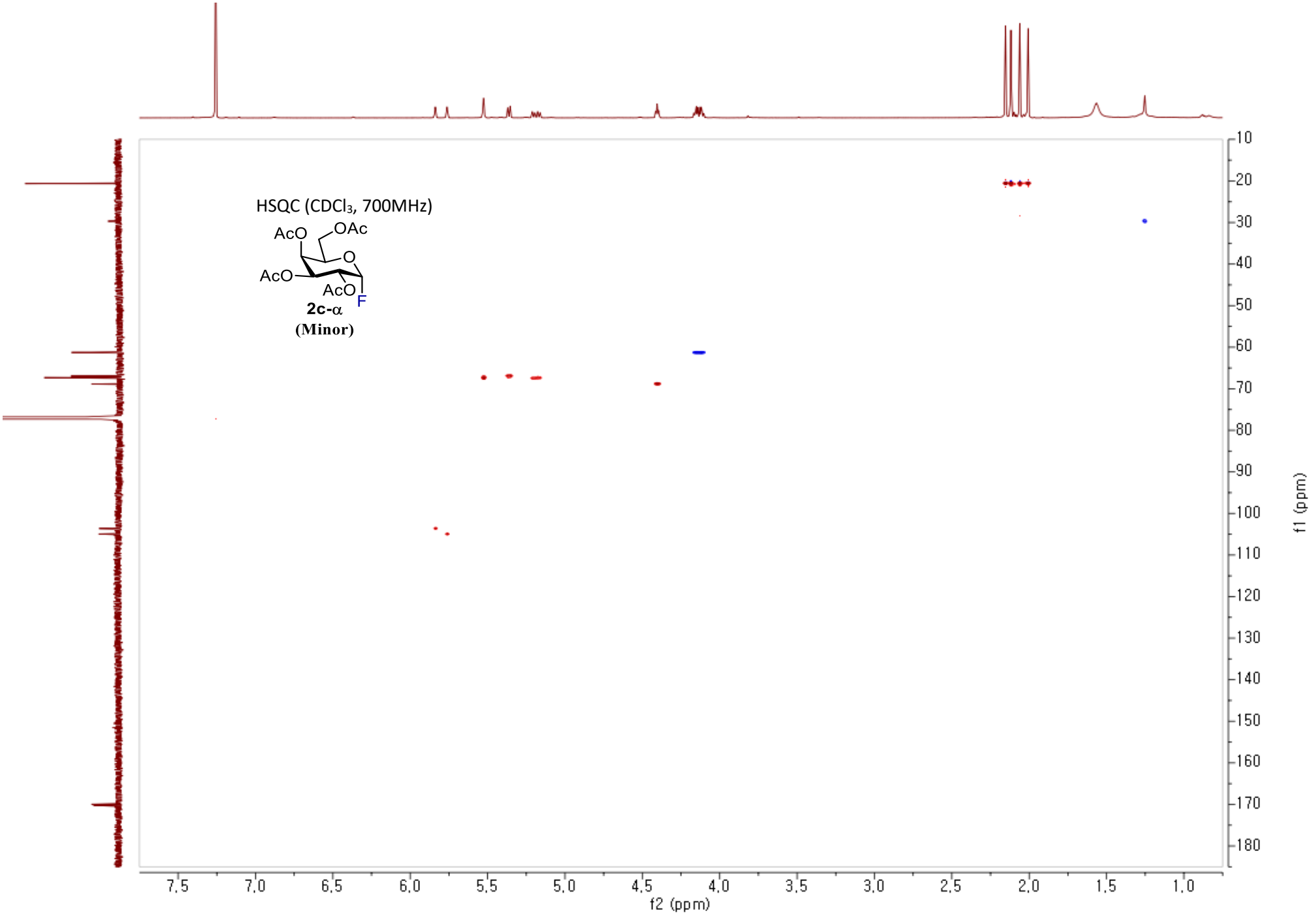

170.35
170.03
169.95
169.25
107.70
107.70
106.46
106.46
77.18
77.00
76.82
71.20
71.17
69.92
69.86
68.83
68.69
66.37
61.28
20.65
20.58
20.51
^{13}C NMR ($CDCl_3$, 176MHz)
AcO
OAc
O
F
AcO
AcO
2c-β
(Major)
71.20
71.17
69.92
69.86
68.83
68.69
71,5 71,0 70,5 70,0 69,5 69,0 68,5
f1 (ppm)
170 160 150 140 130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


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

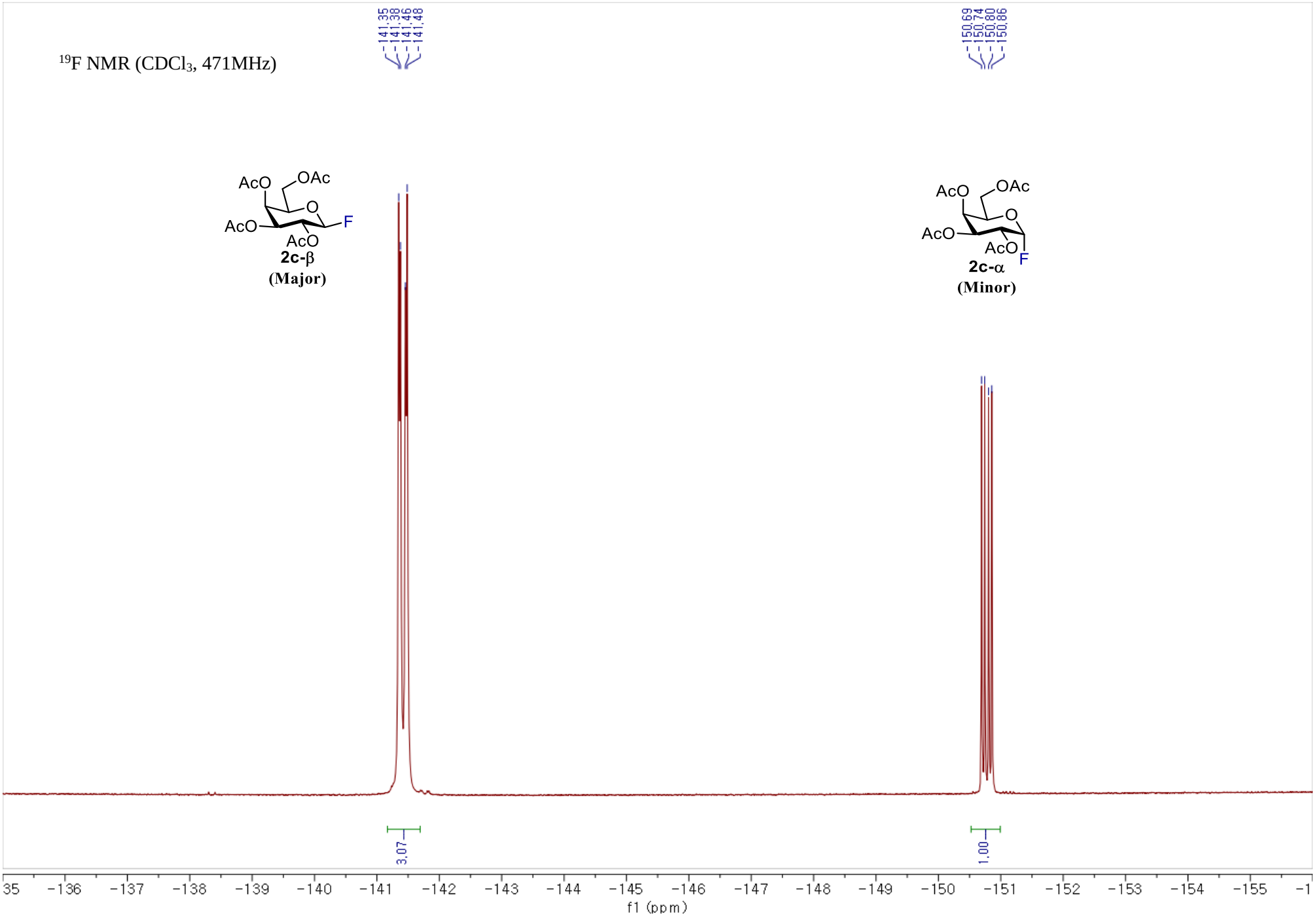
2,3,4,6-Tetra-*O*-acetyl-α-D-galactopyranosyl fluoride (2c-α, Minor diastereomer)



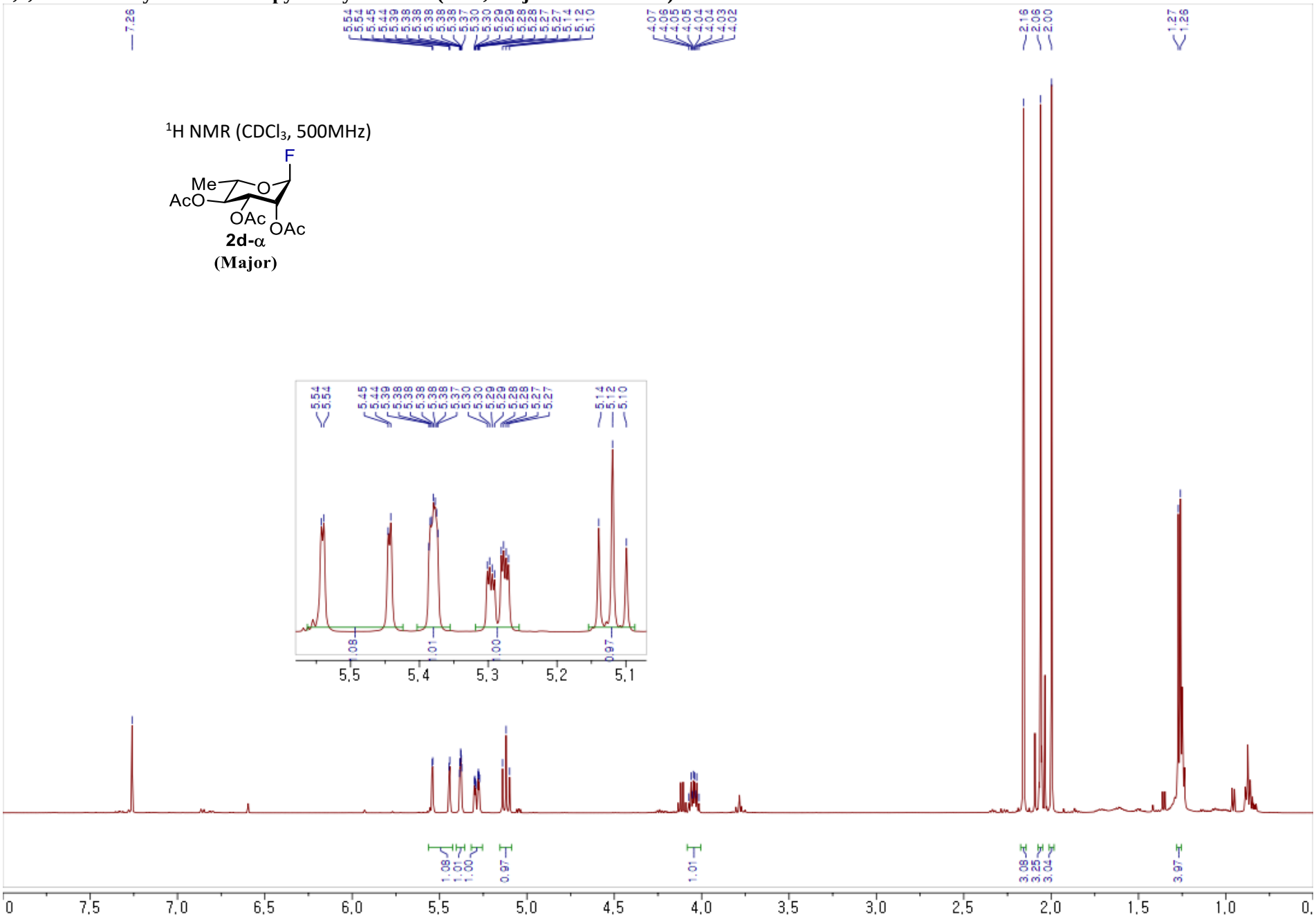

170.34
170.23
169.97
169.87
104.94
103.64
77.18
76.82
68.86
68.84
67.46
67.32
66.96
61.25
20.65
20.59
20.56
13C NMR (CDCl3, 176MHz)
AcO
OAc
O
AcO
AcO
F
2c-α
(Minor)
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
1

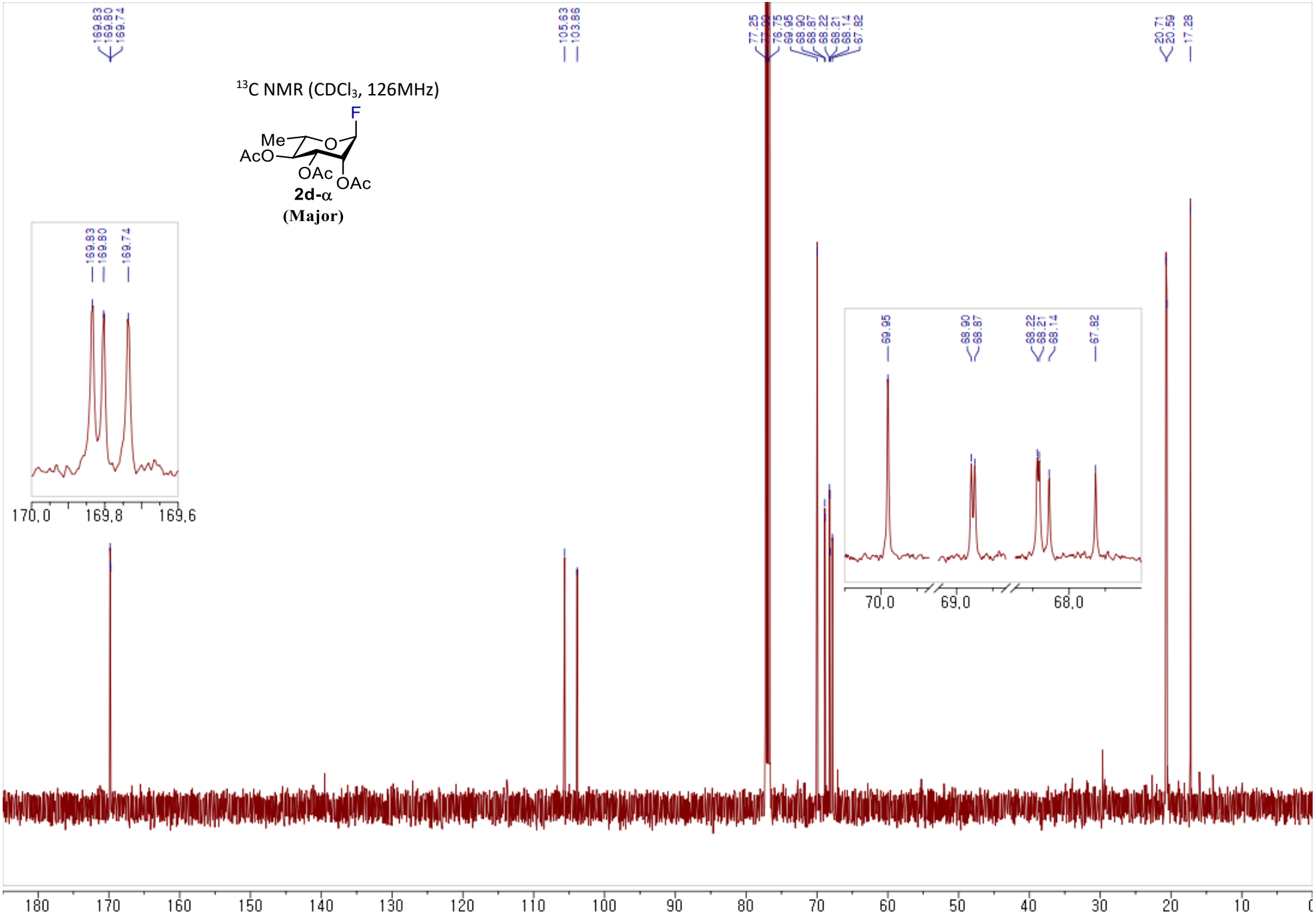

HSQC (CDCl3, 700MHz)
AcO
OAc
O
AcO
AcO
F
2c-α
(Minor)
f2 (ppm)
f1 (ppm)

^{19}F NMR ($CDCl_3$, 471MHz)

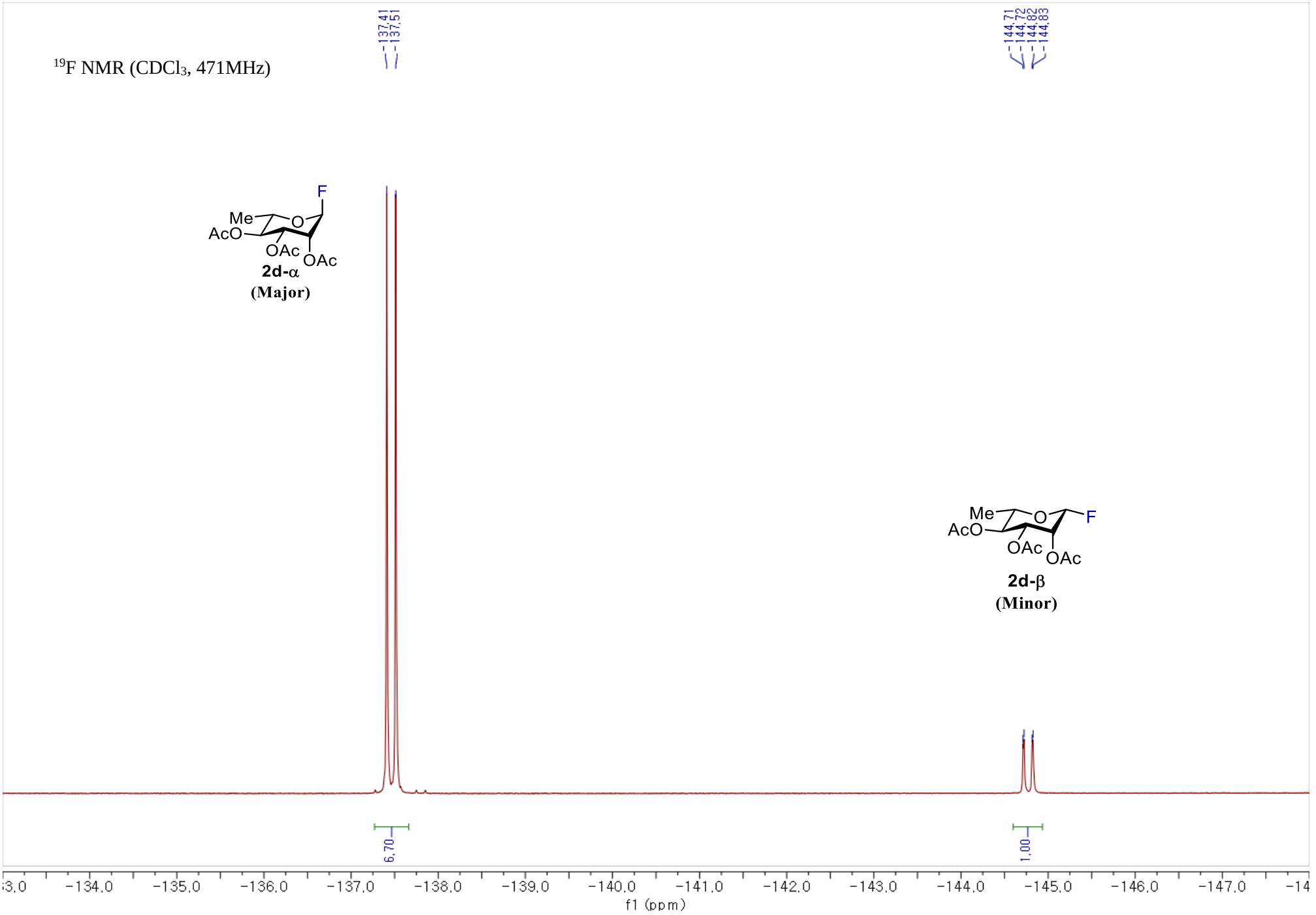


2,3,4-Tri-O-acetyl-α-L-rhamnopyranosyl fluoride (2d-α, Major diastereomer)

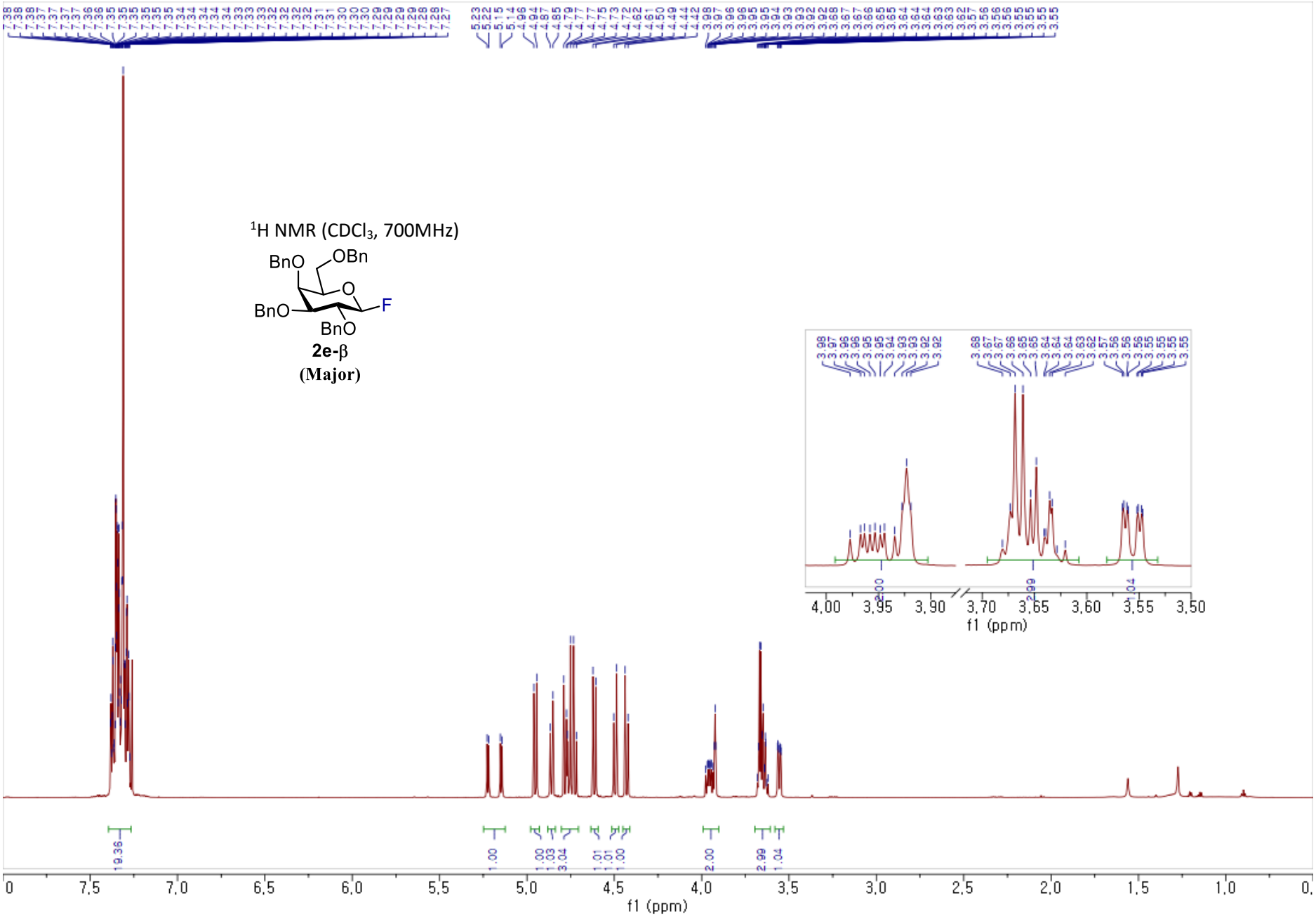


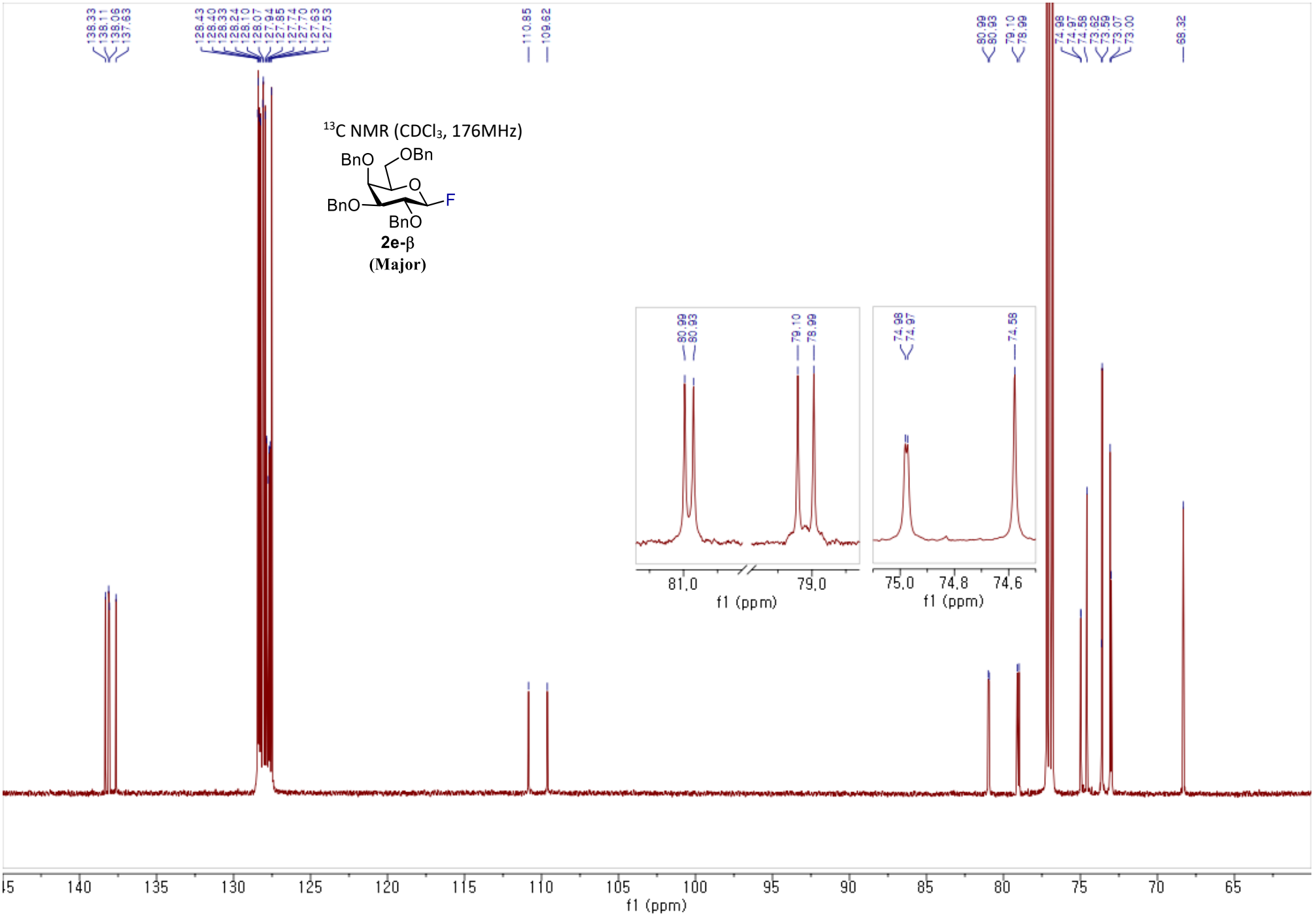

169.83
169.80
169.74
105.63
103.86
77.25
76.75
69.95
68.90
68.87
68.22
68.21
68.14
67.82
20.71
20.59
17.28
^{13}C NMR ($CDCl_3$, 126MHz)
F
Me
O
AcO
OAc
OAc
2d-α
(Major)
170.0
169.8
169.6
70.0
69.0
68.0
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

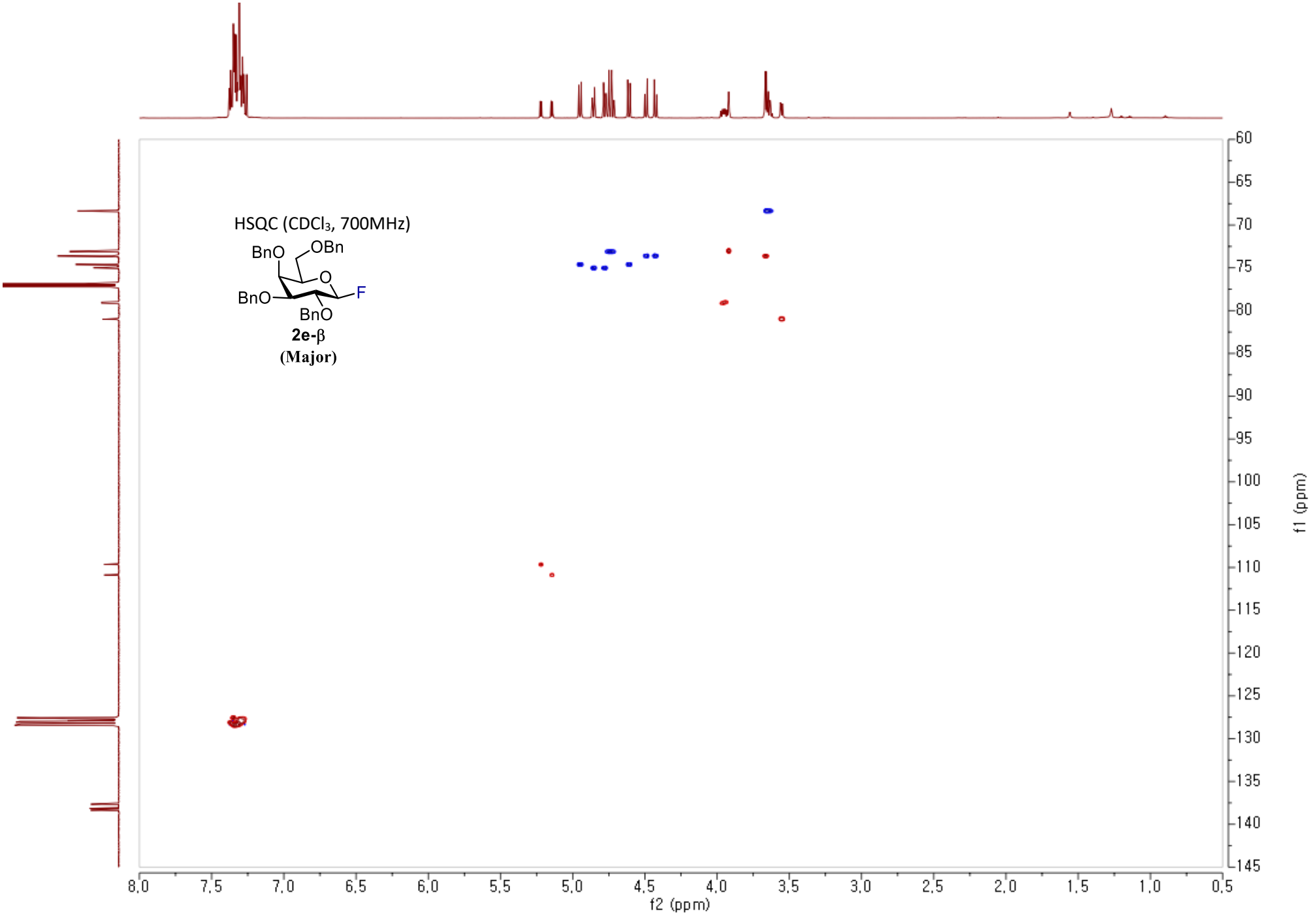
^{19}F NMR ($CDCl_3$, 471MHz)



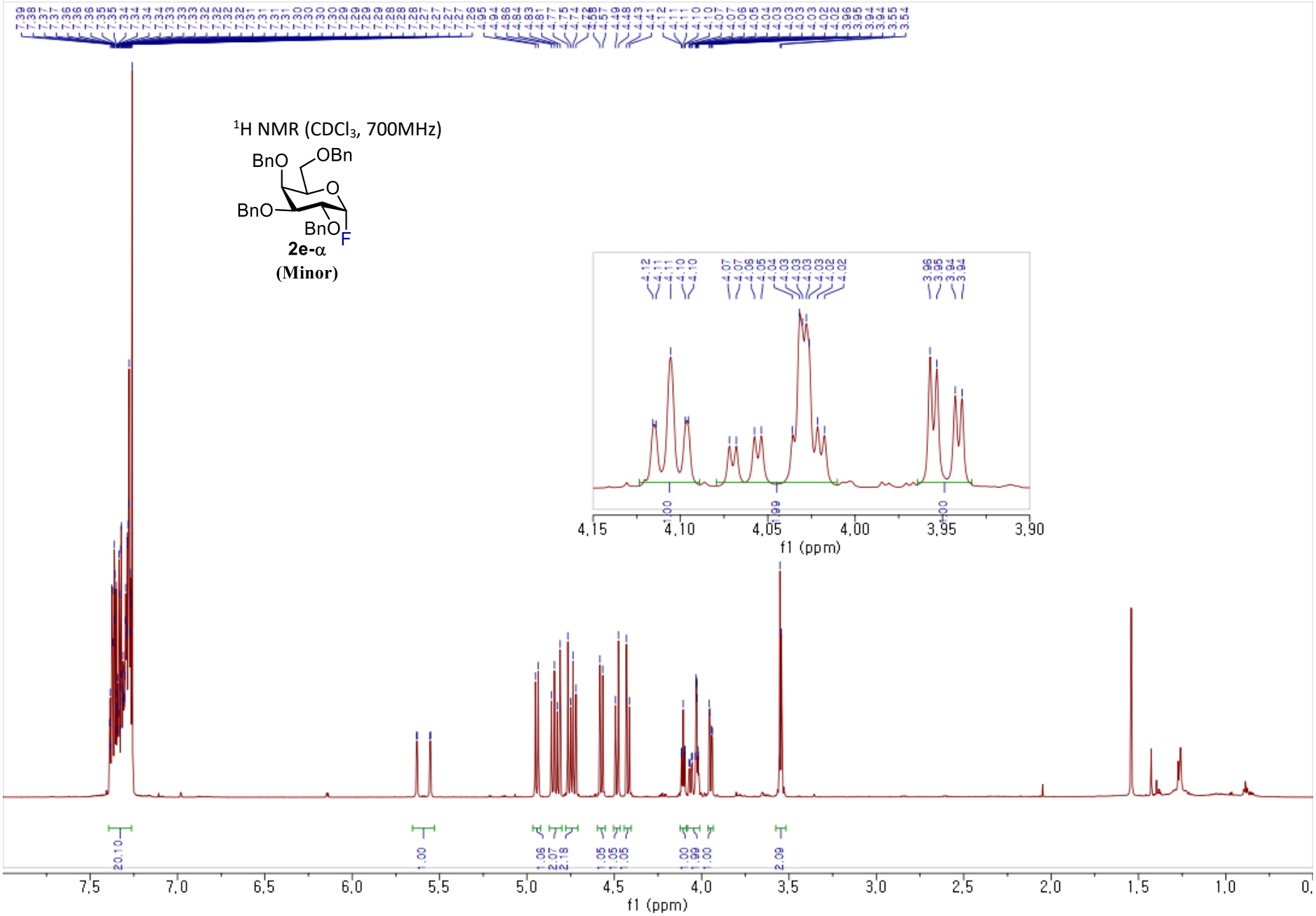
2,3,4,6-Tetrakis-*O*-(phenylmethyl)-β-D-galactopyranosyl fluoride (2e-β, Major diastereomer)

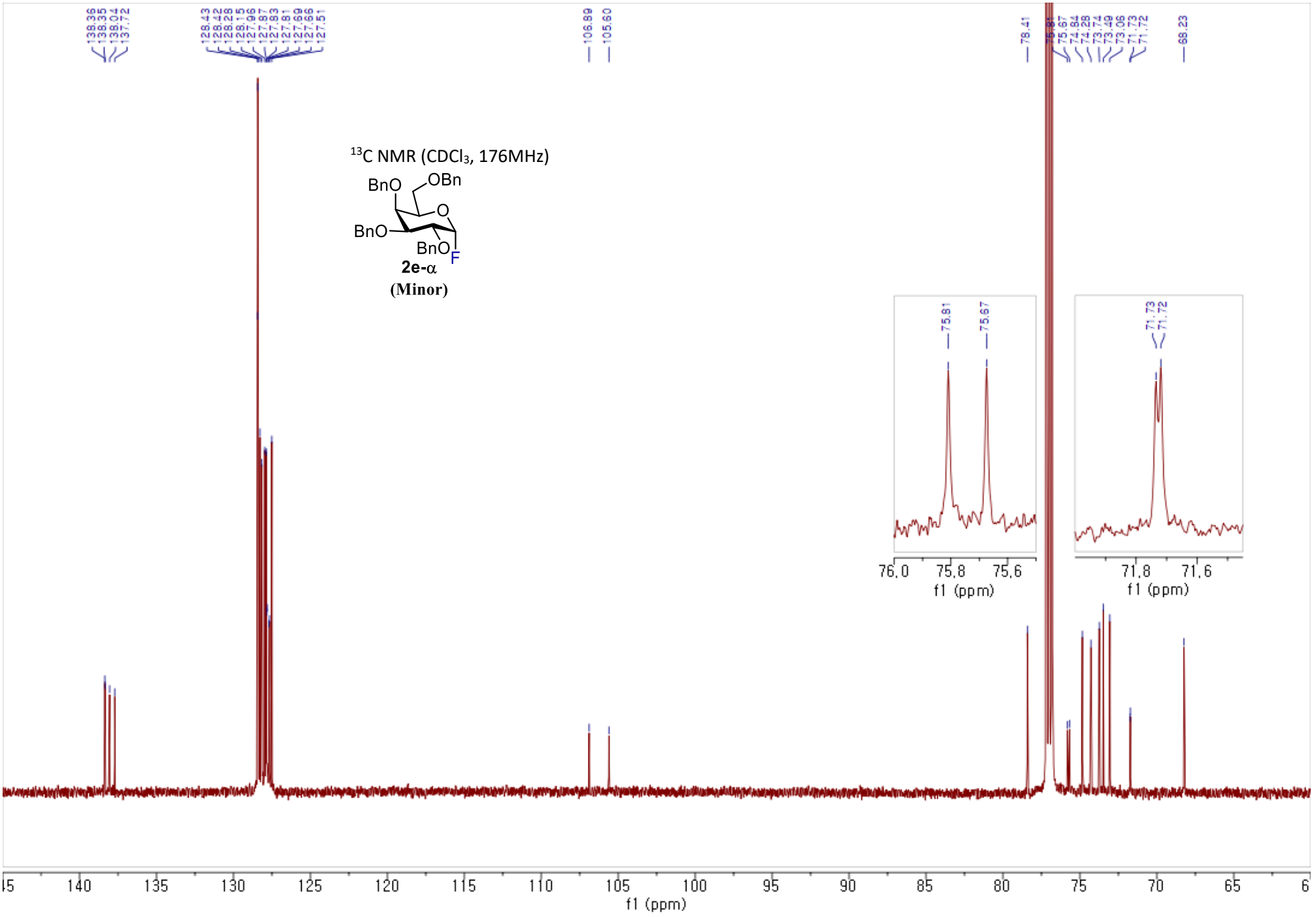


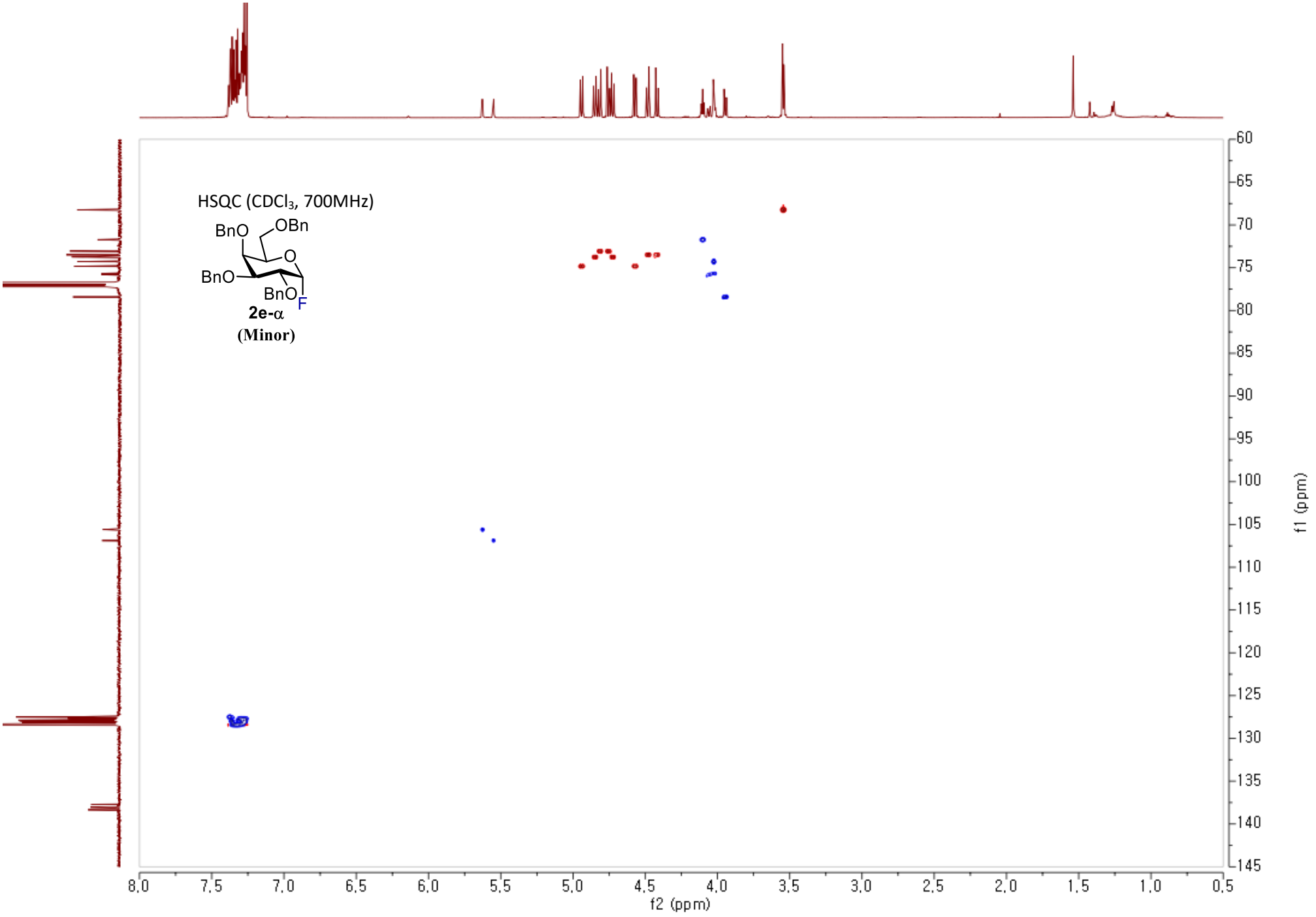

138.33
138.11
138.06
137.63
128.43
128.40
128.33
128.24
128.10
128.07
127.94
127.85
127.74
127.70
127.63
127.53
110.85
109.62
80.99
80.93
79.10
78.99
74.98
74.97
74.58
73.62
73.59
73.07
73.00
68.32
13C NMR (CDCl3, 176MHz)
BnO
OBn
O
F
BnO
BnO
2e-β
(Major)
81.0
79.0
f1 (ppm)
75.0
74.8
74.6
f1 (ppm)
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
f1 (ppm)


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

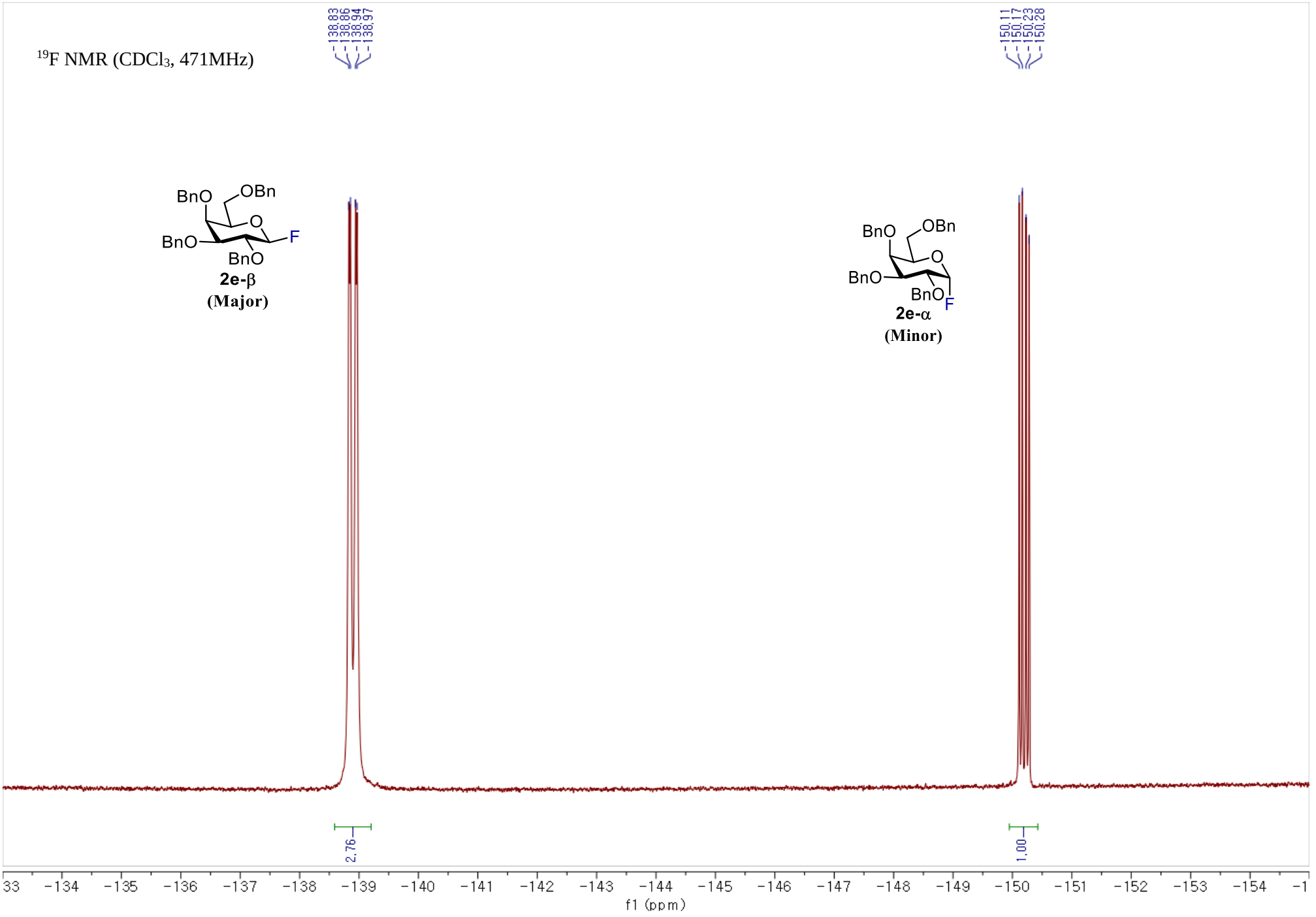
2,3,4,6-Tetrakis-*O*-(phenylmethyl)-α-D-galactopyranosyl fluoride (2e-α, Minor diastereomer)



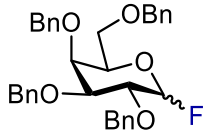

^{13}C NMR ($CDCl_3$, 176MHz)
BnO
OBn
O
BnO
BnO
F
2e-α
(Minor)
138.36
138.35
138.04
137.72
128.43
128.42
128.28
128.15
127.96
127.87
127.83
127.81
127.69
127.66
127.51
106.89
105.60
78.41
75.81
75.67
74.84
74.28
73.74
73.49
73.06
71.73
71.72
68.23
75.81
75.67
76.0
75.8
75.6
f1 (ppm)
71.73
71.72
71.8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


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

^{19}F NMR ($CDCl_3$, 471MHz)



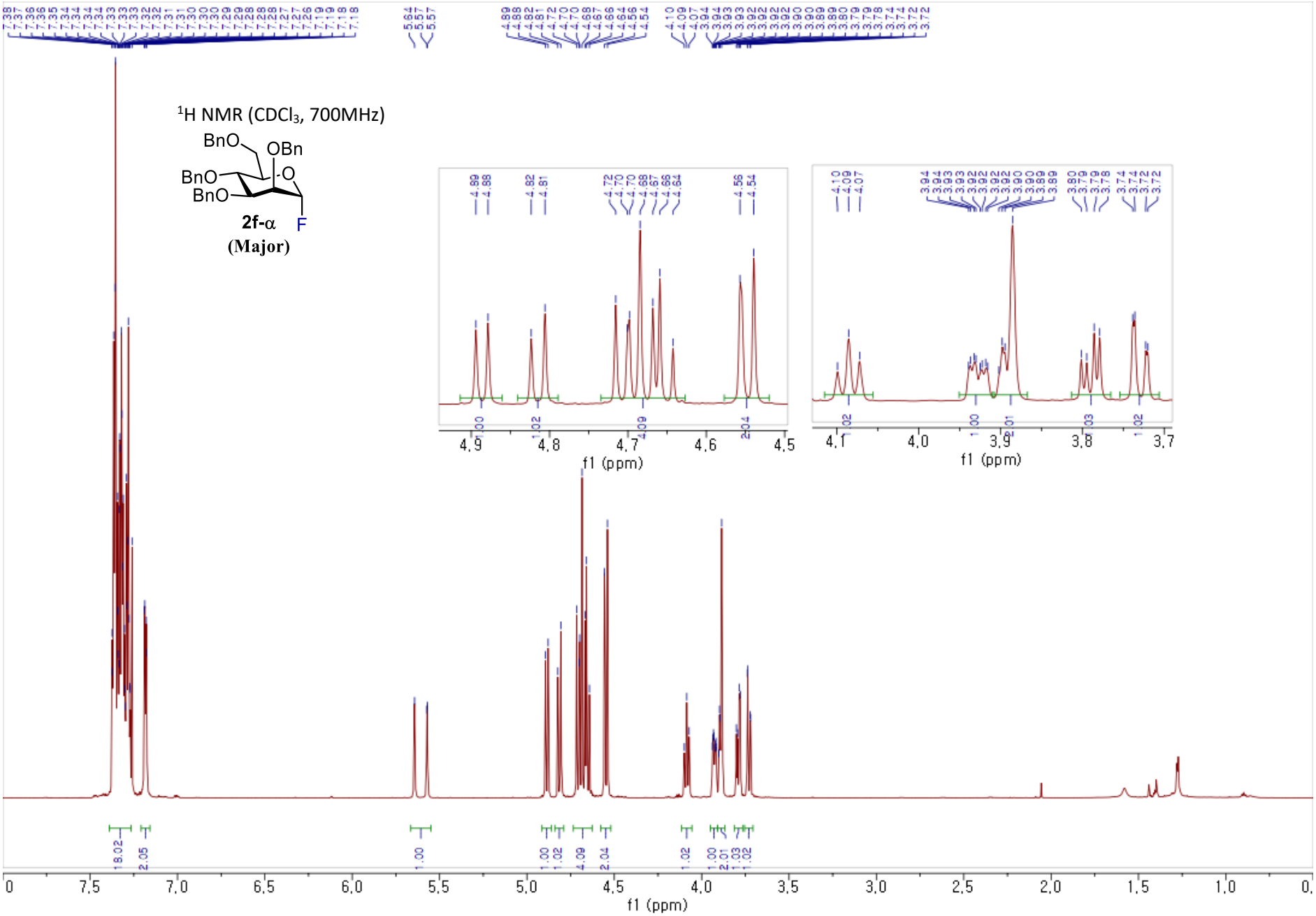
^{1}H NMR ($CDCl_3$, 700MHz)

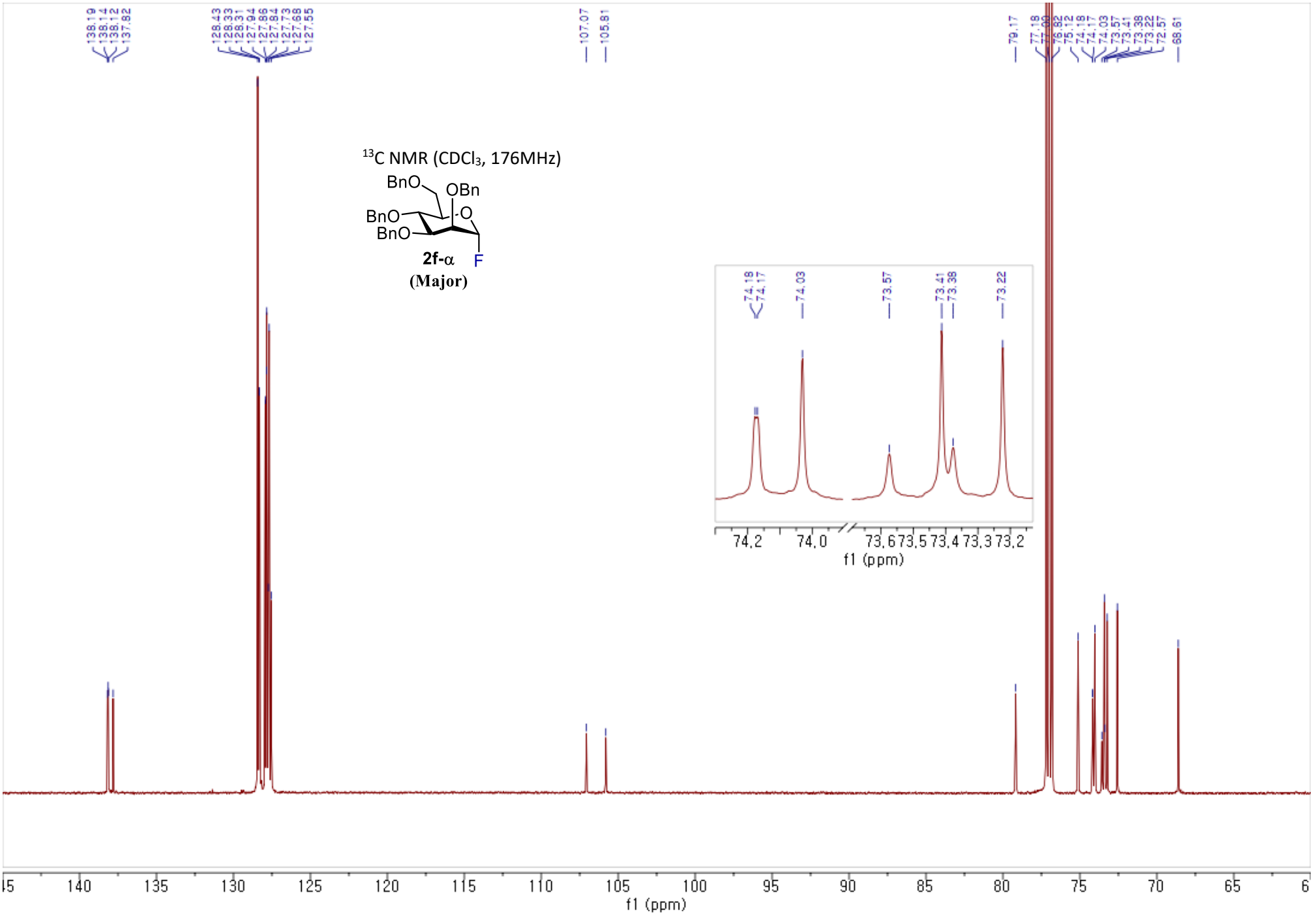


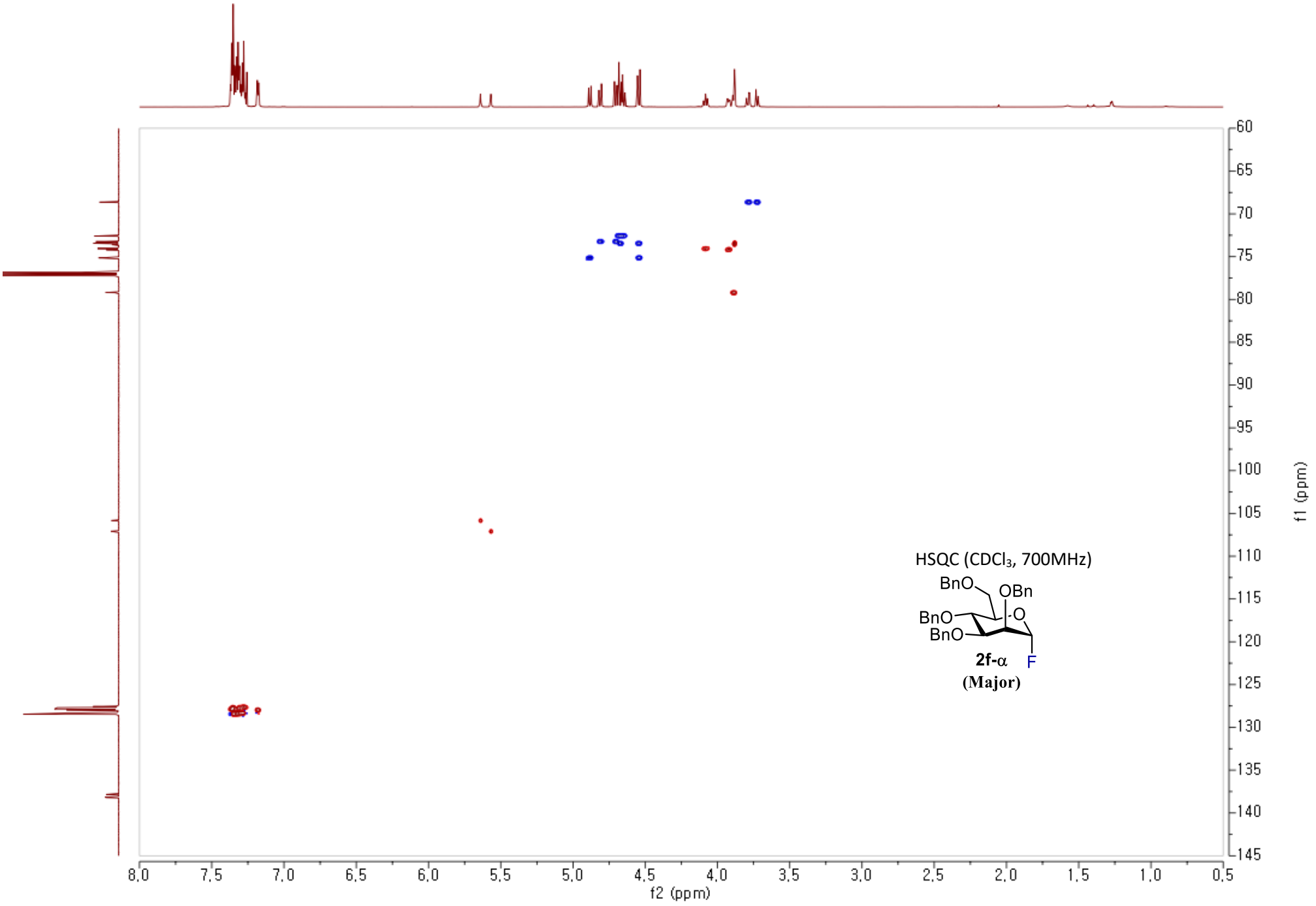
2e

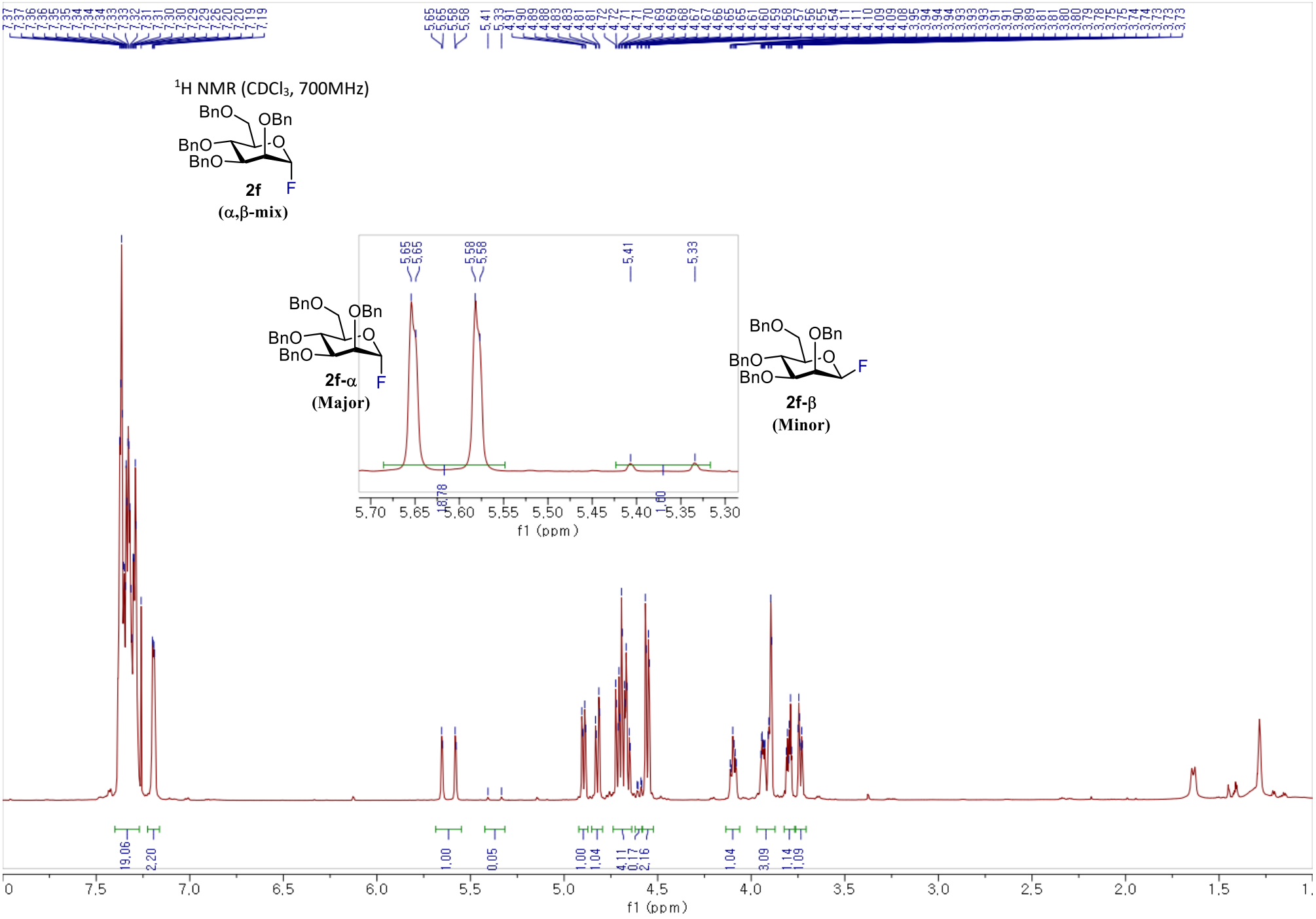
(α,β-mix)

2,3,4,6-Tetrakis-*O*-(phenylmethyl)-α-D-Mannopyranosyl fluoride (2f-α, Major diastereomer)

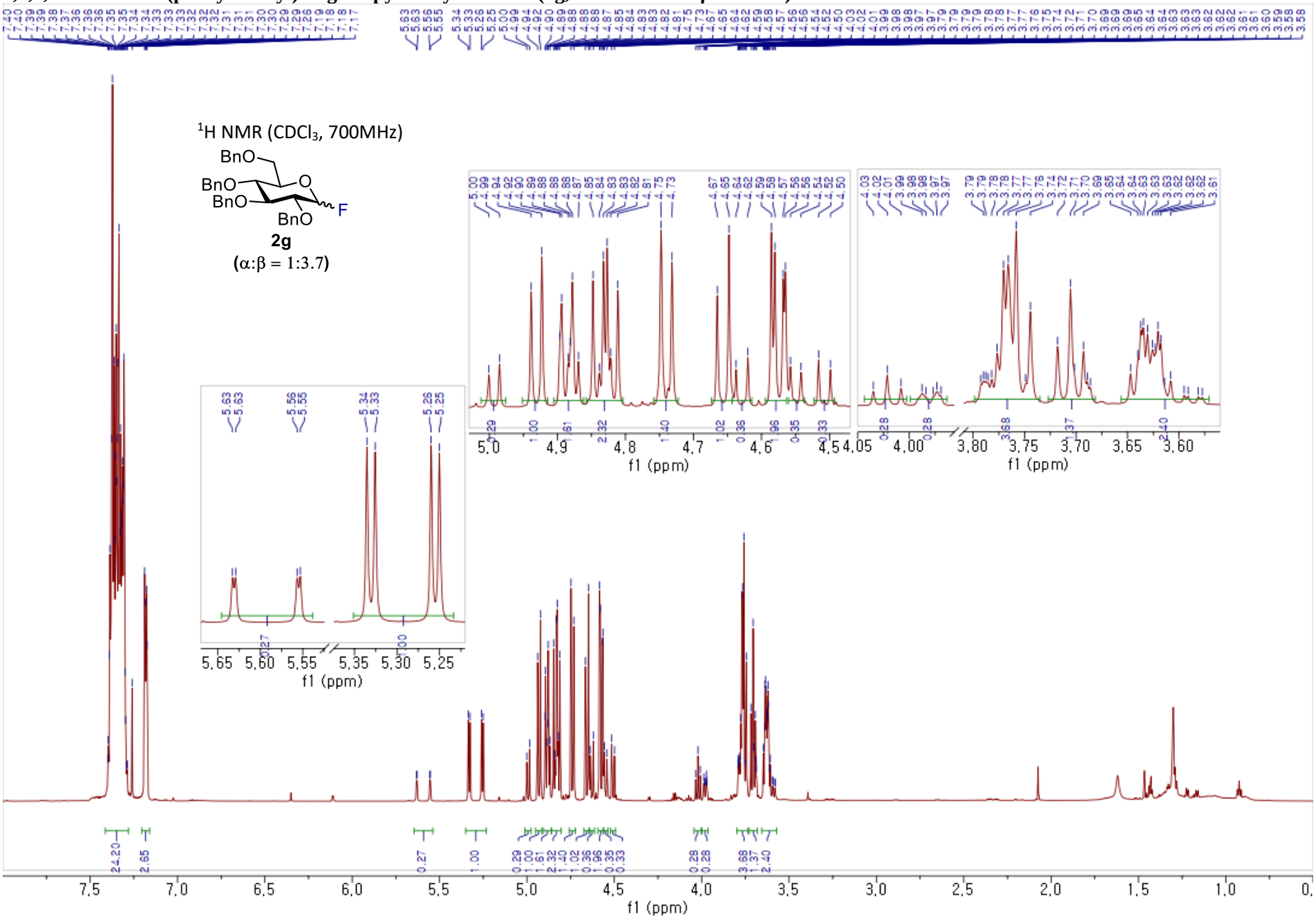


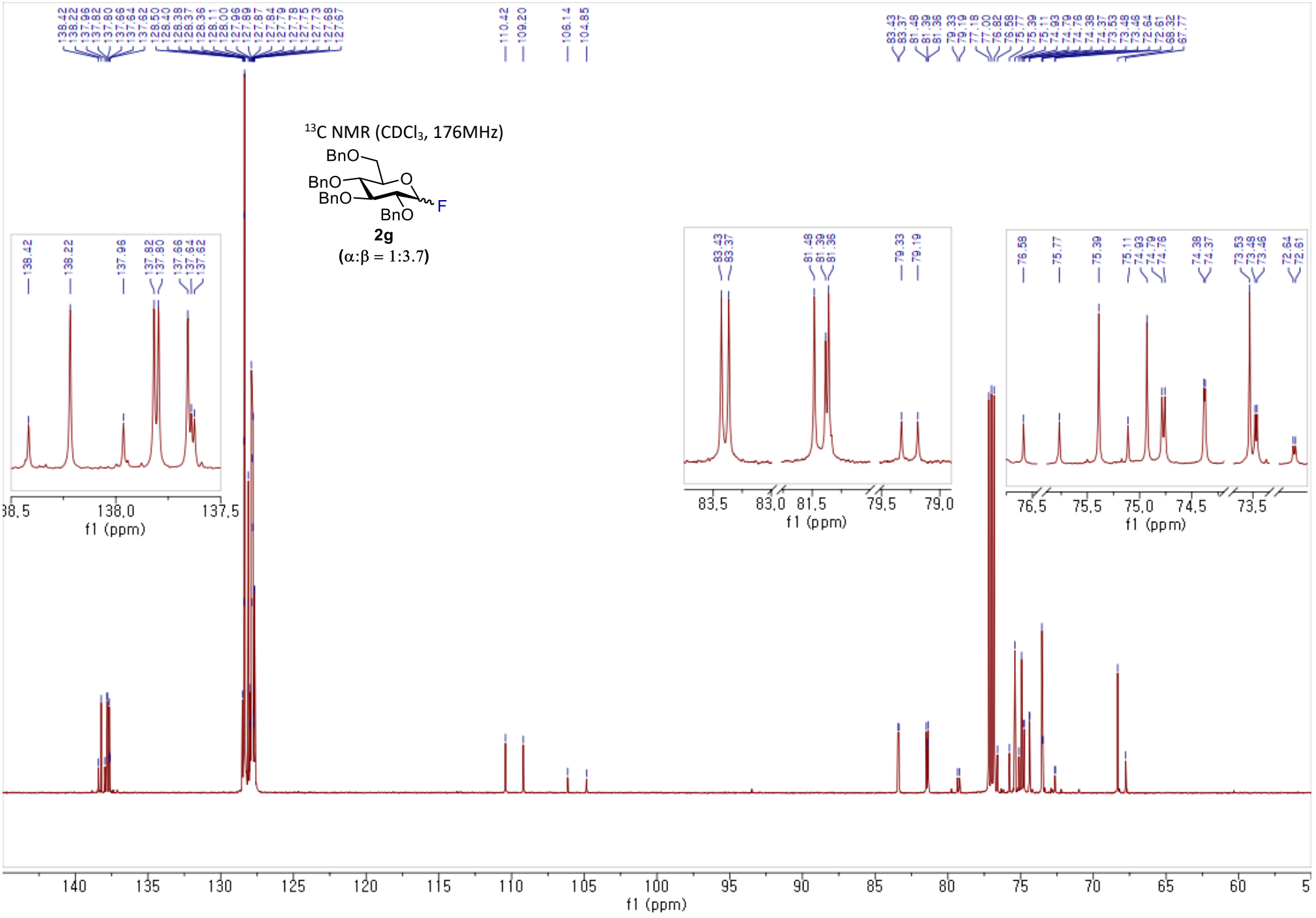

^{13}C NMR ($CDCl_3$, 176MHz)
BnO
OBn
BnO
O
BnO
F
2f-α
(Major)
f1 (ppm)

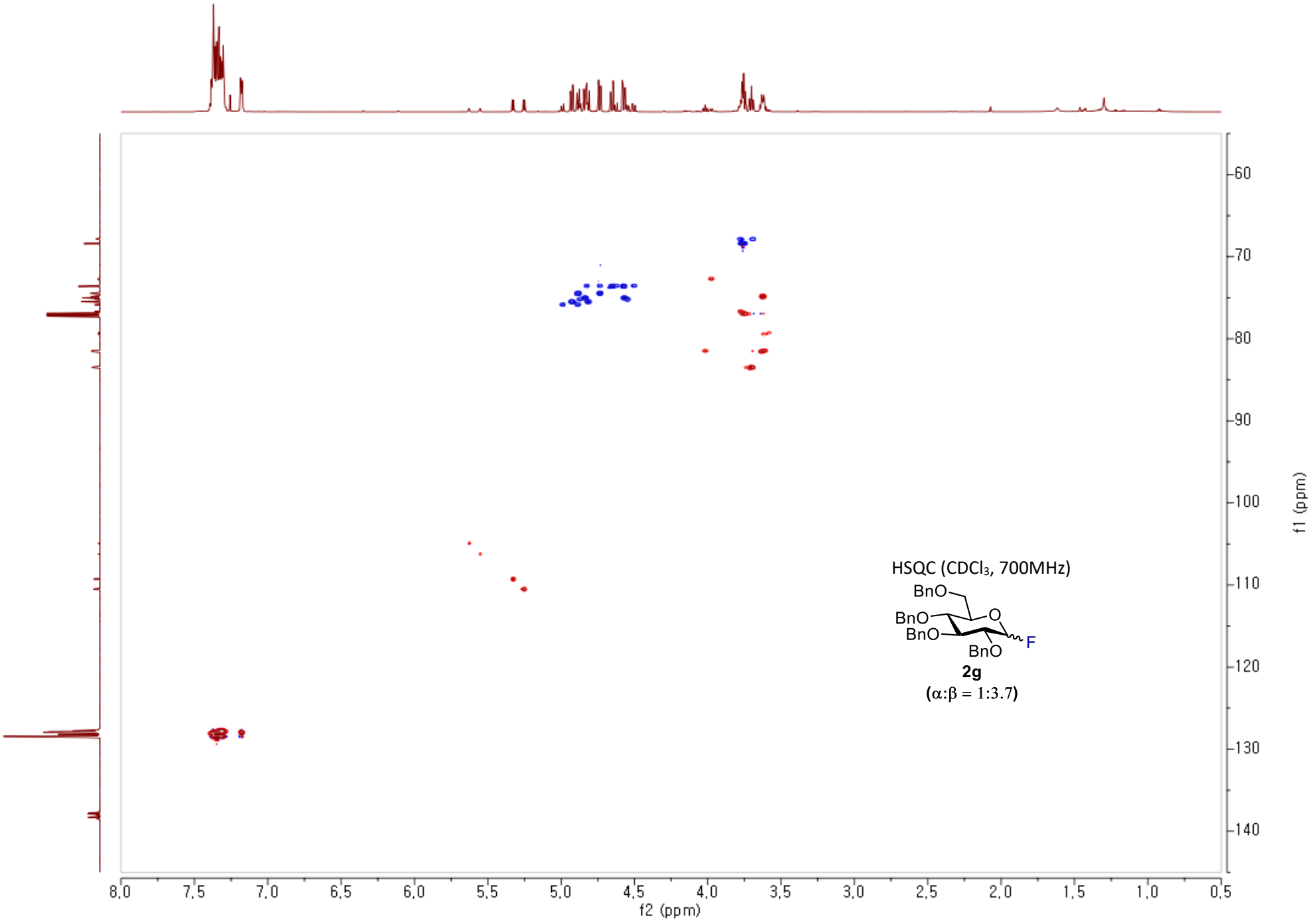

HSQC (CDCl3, 700MHz)
BnO
OBn
BnO
O
BnO
2f-α
(Major)
F
f1 (ppm)
f2 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
60
65
70
75
80
85
90
95
100
105
110
115
120
125
130
135
140
145


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

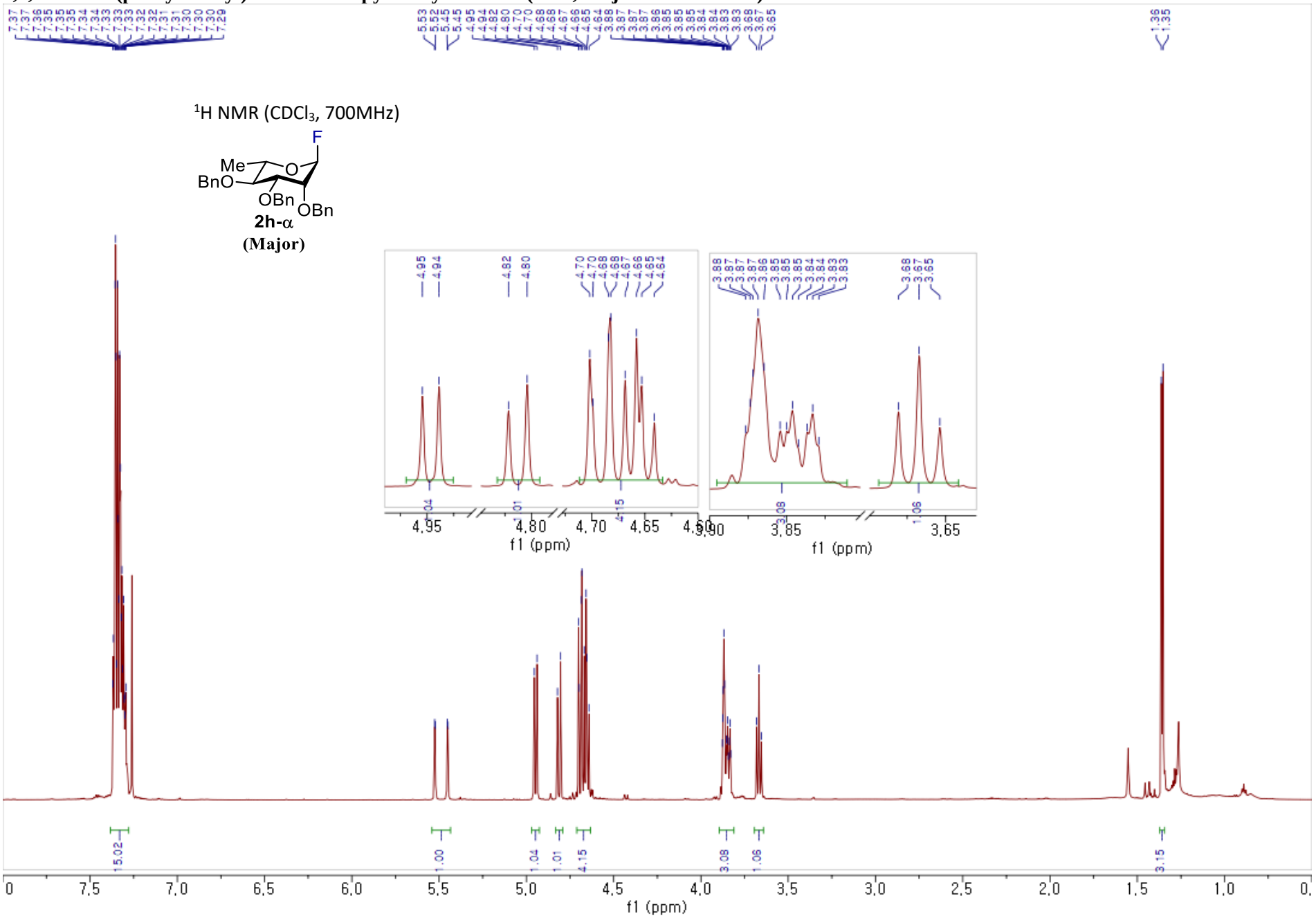
2,3,4,6-Tetrakis-*O*-(phenylmethyl)-D-glucopyranosyl fluoride (2g, Isolated as α : β = 1 : 3.7)

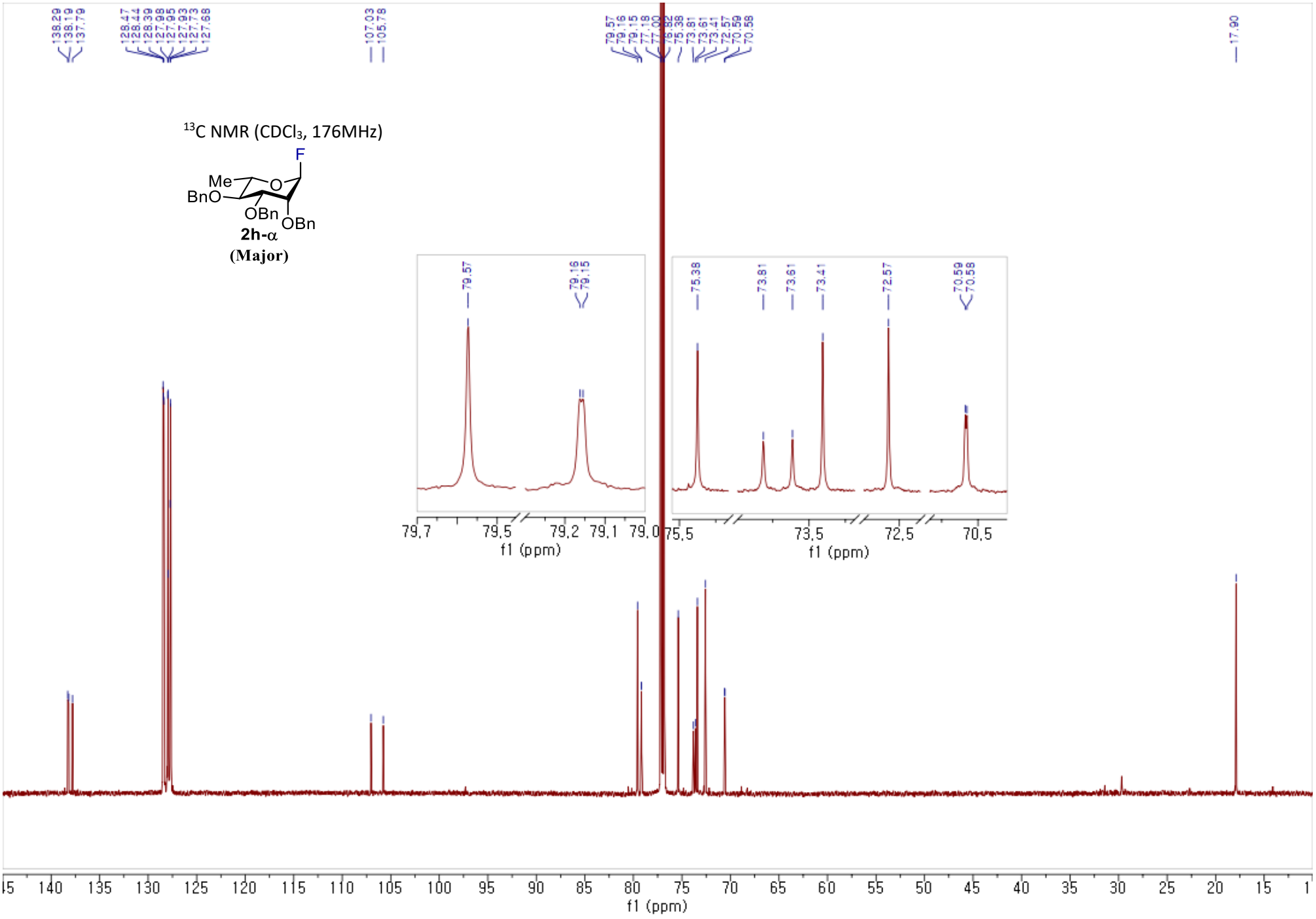


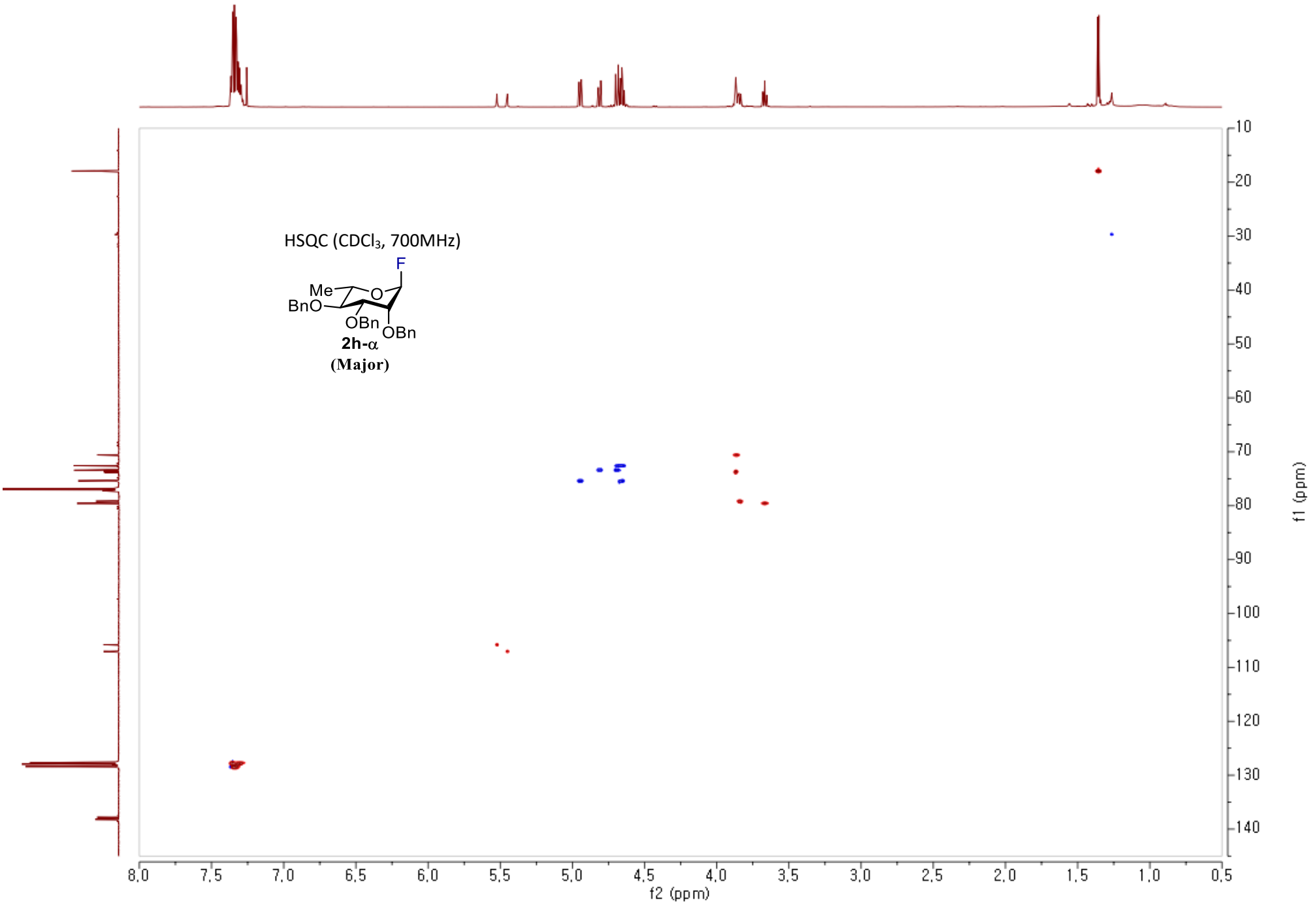

^{13}C NMR ($CDCl_3$, 176MHz)
BnO
BnO
BnO
BnO
O
F
2g
(α:β = 1:3.7)
f1 (ppm)


HSQC (CDCl3, 700MHz)
BnO
BnO
BnO
O
F
BnO
2g
(α:β = 1:3.7)
f2 (ppm)
f1 (ppm)

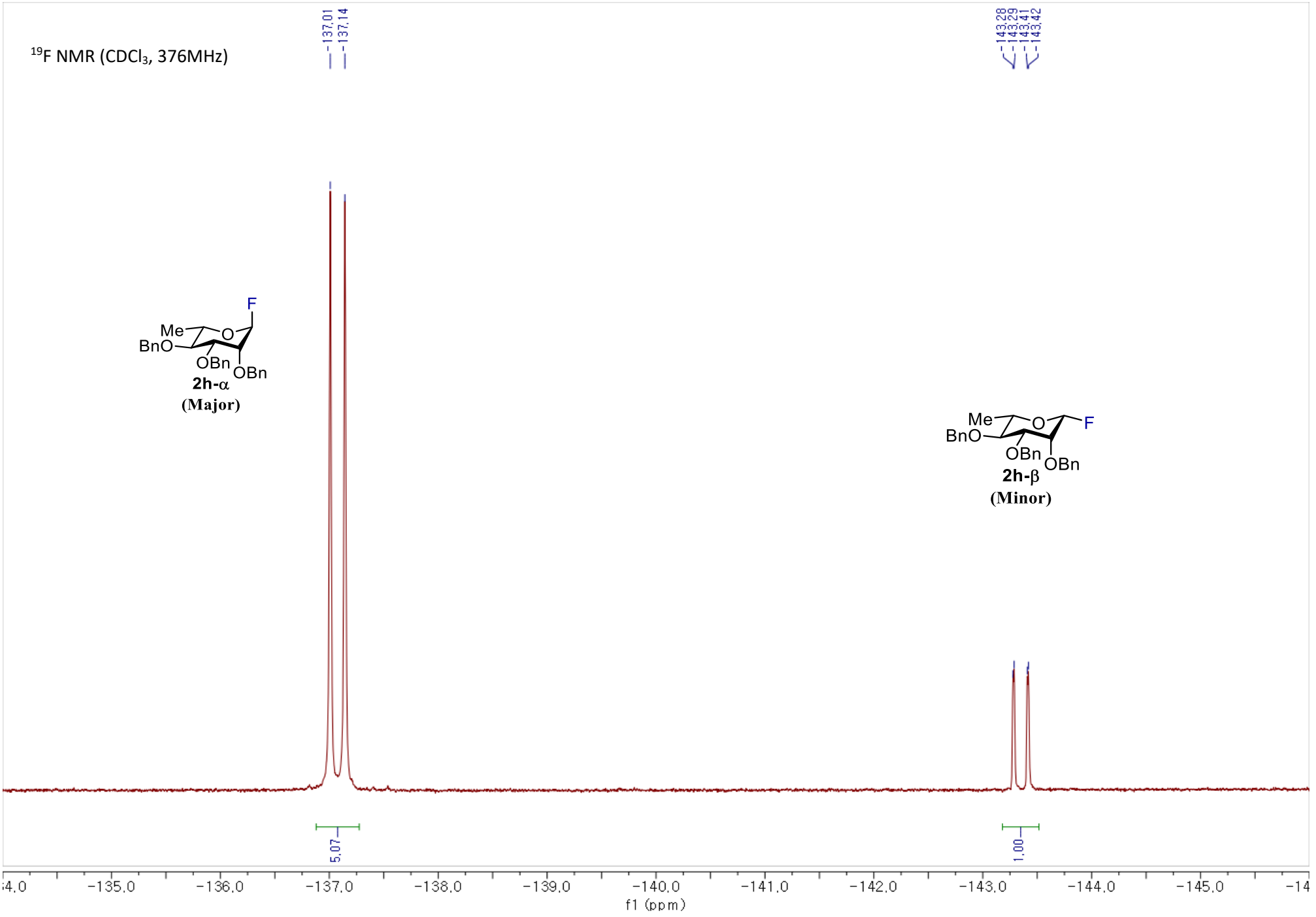
2,3,4-Tris-O-(phenylmethyl)-α-L-rhamnopyranosyl fluoride (2h-α, Major diastereomer)

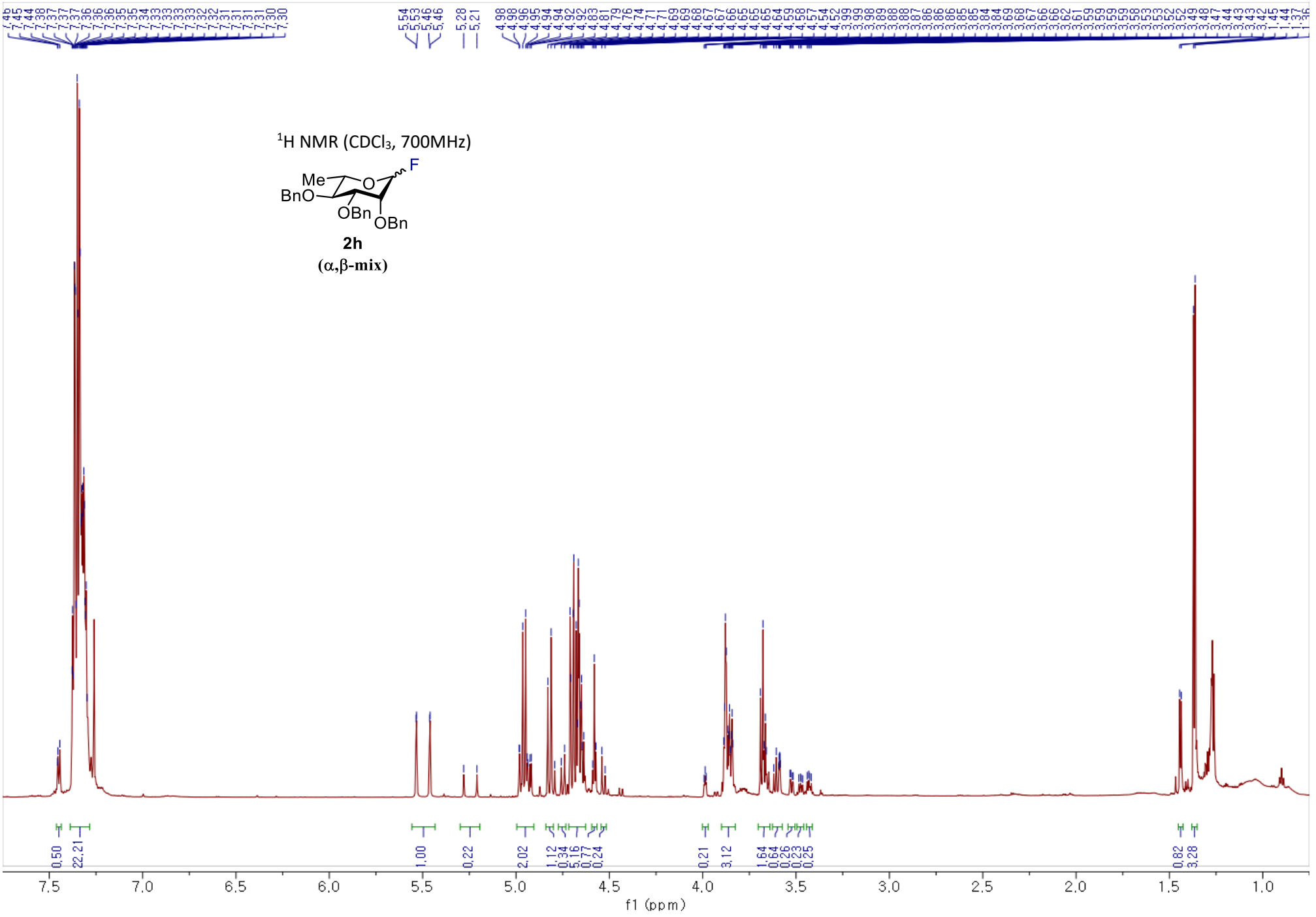



^{13}C NMR ($CDCl_3$, 176MHz)
F
Me
BnO
O
OBn
OBn
2h-α
(Major)
f1 (ppm)

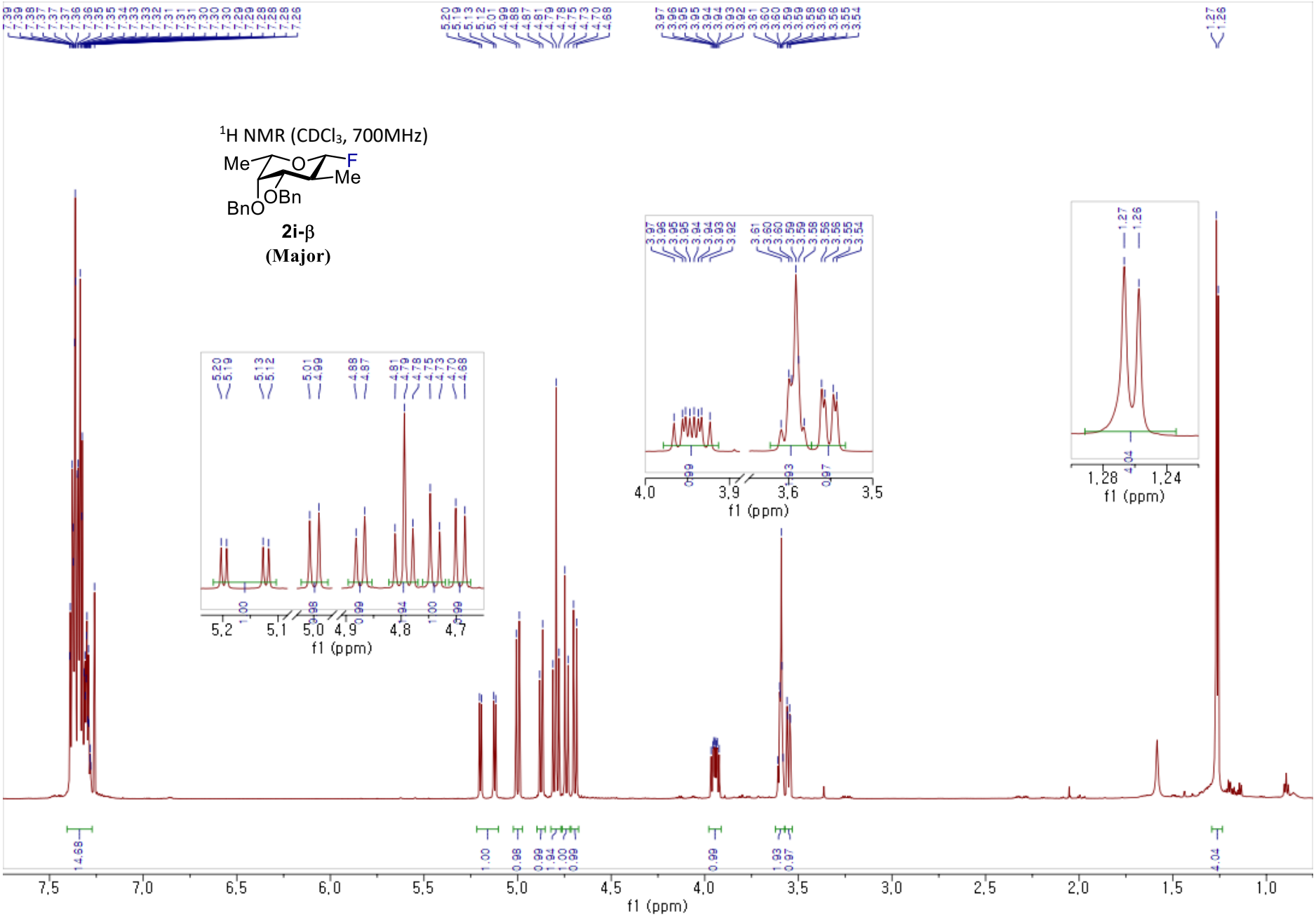

HSQC (CDCl3, 700MHz)
F
Me
O
BnO
OBn
OBn
2h-α
(Major)
f2 (ppm)
f1 (ppm)

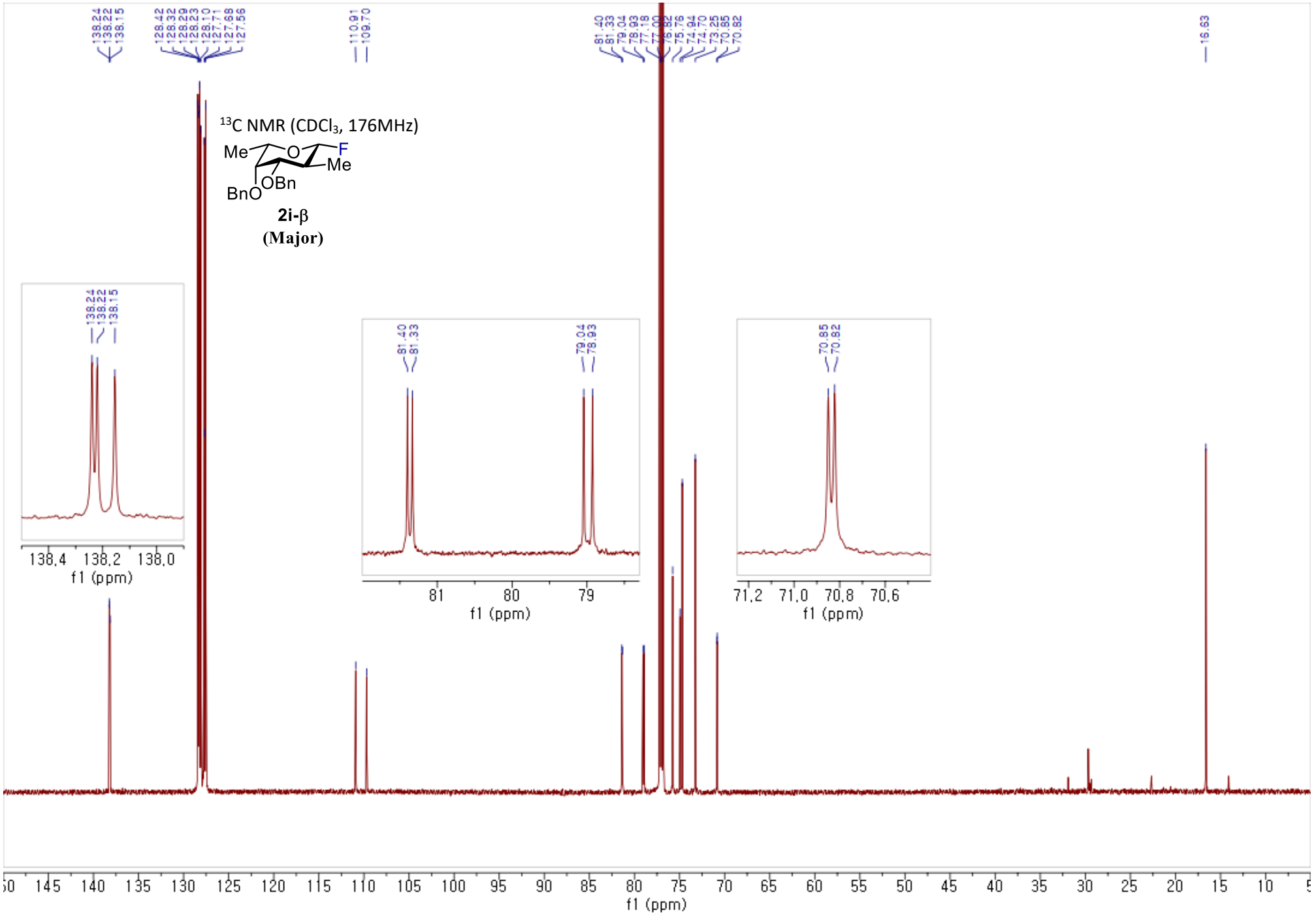
^{19}F NMR ($CDCl_3$, 376MHz)

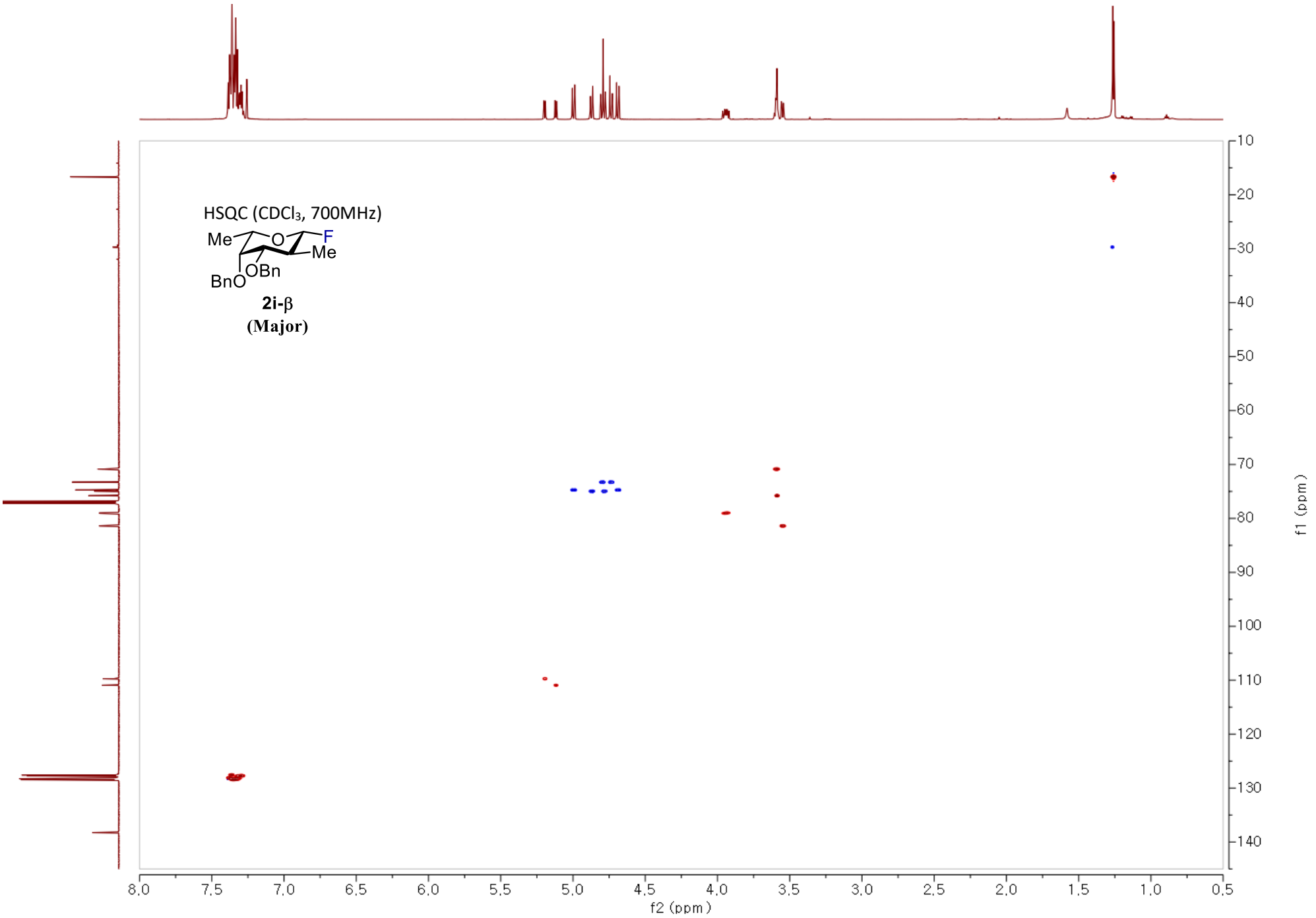



^{1}H NMR ($CDCl_3$, 700MHz)
Me
BnO
O
F
OBn
OBn
2h
(α,β-mix)
f1 (ppm)

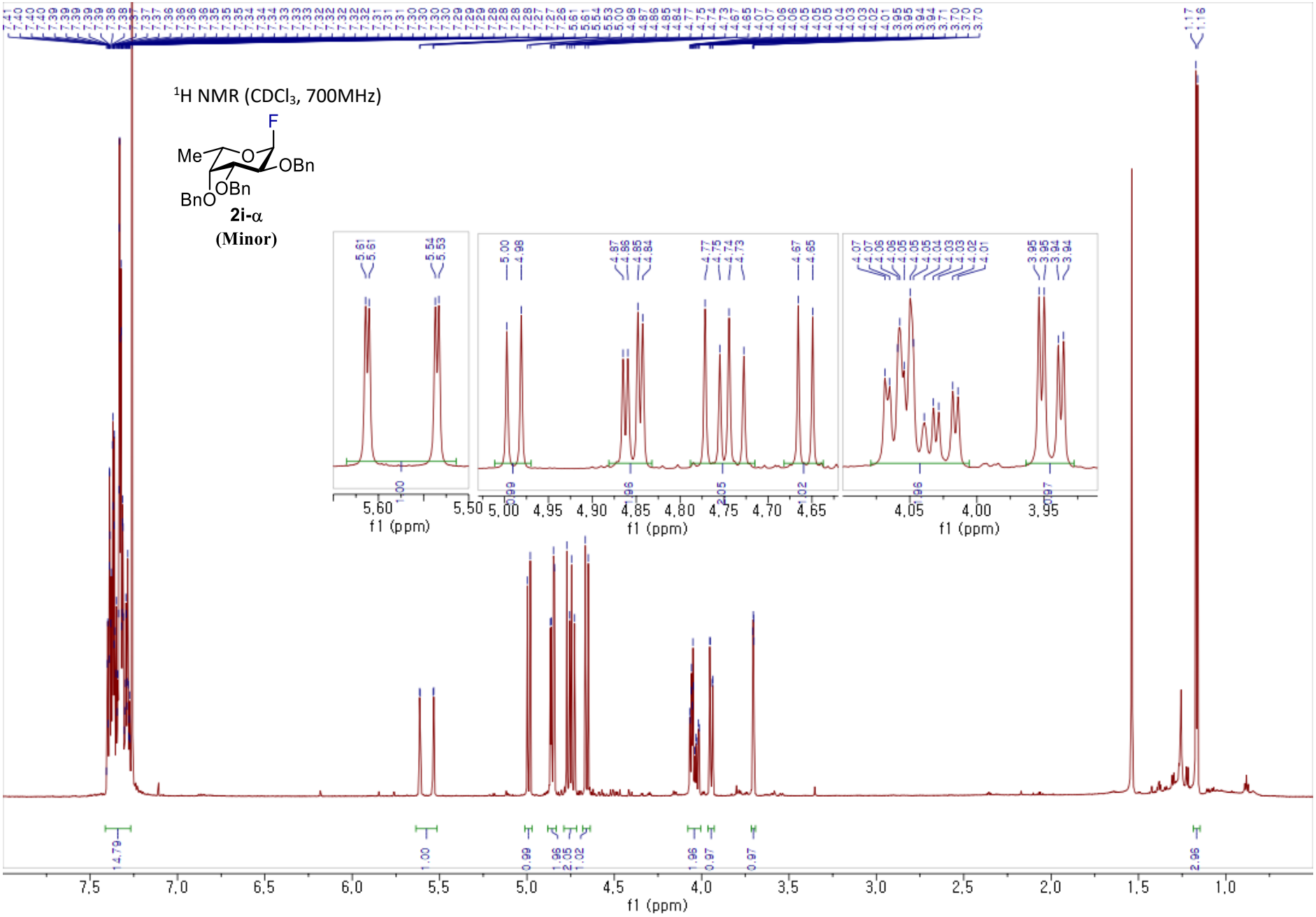
2,3,4-Tris-O-(phenylmethyl)-β-L-fucopyranosyl fluoride (2i-β, Major diastereomer)

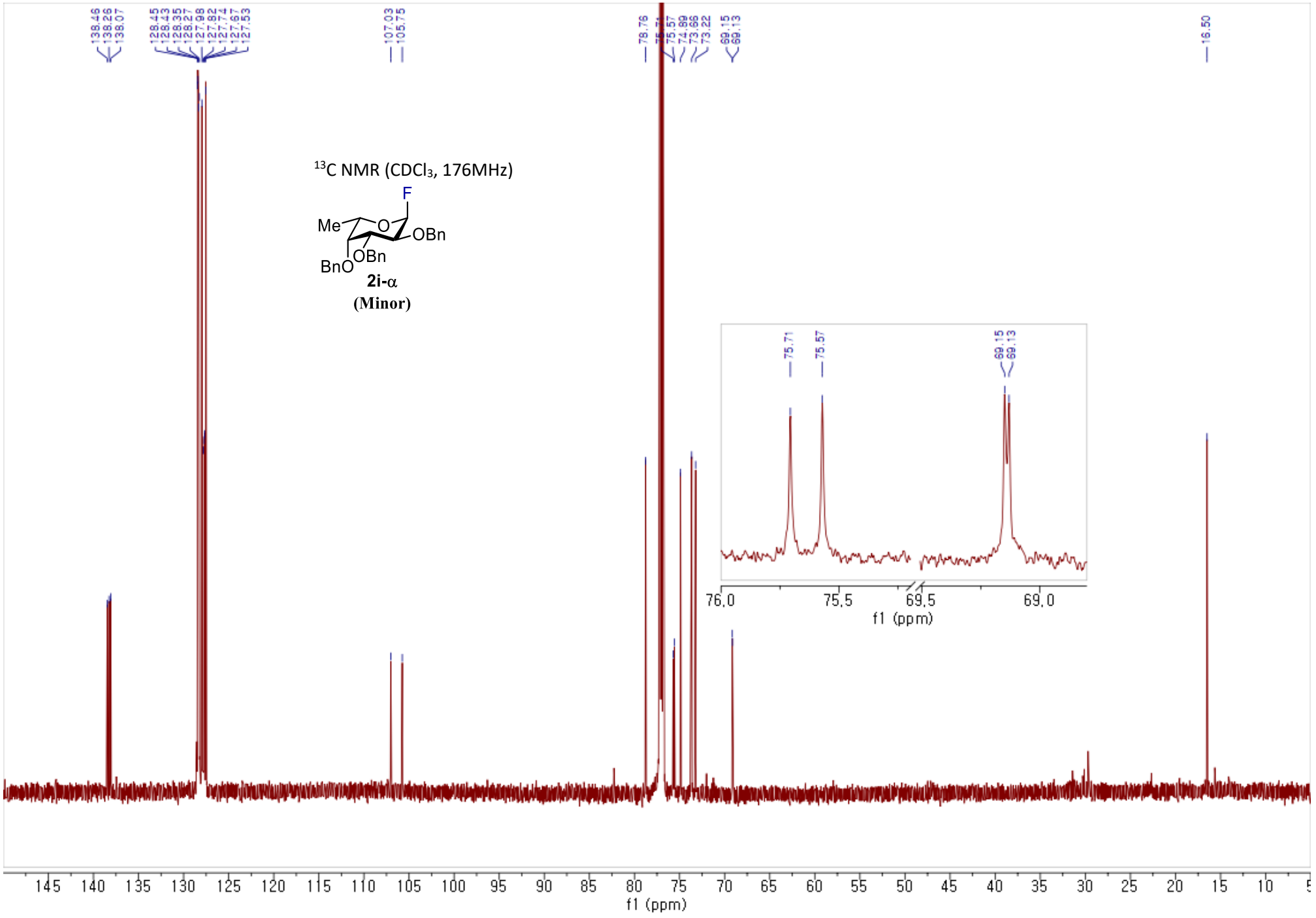


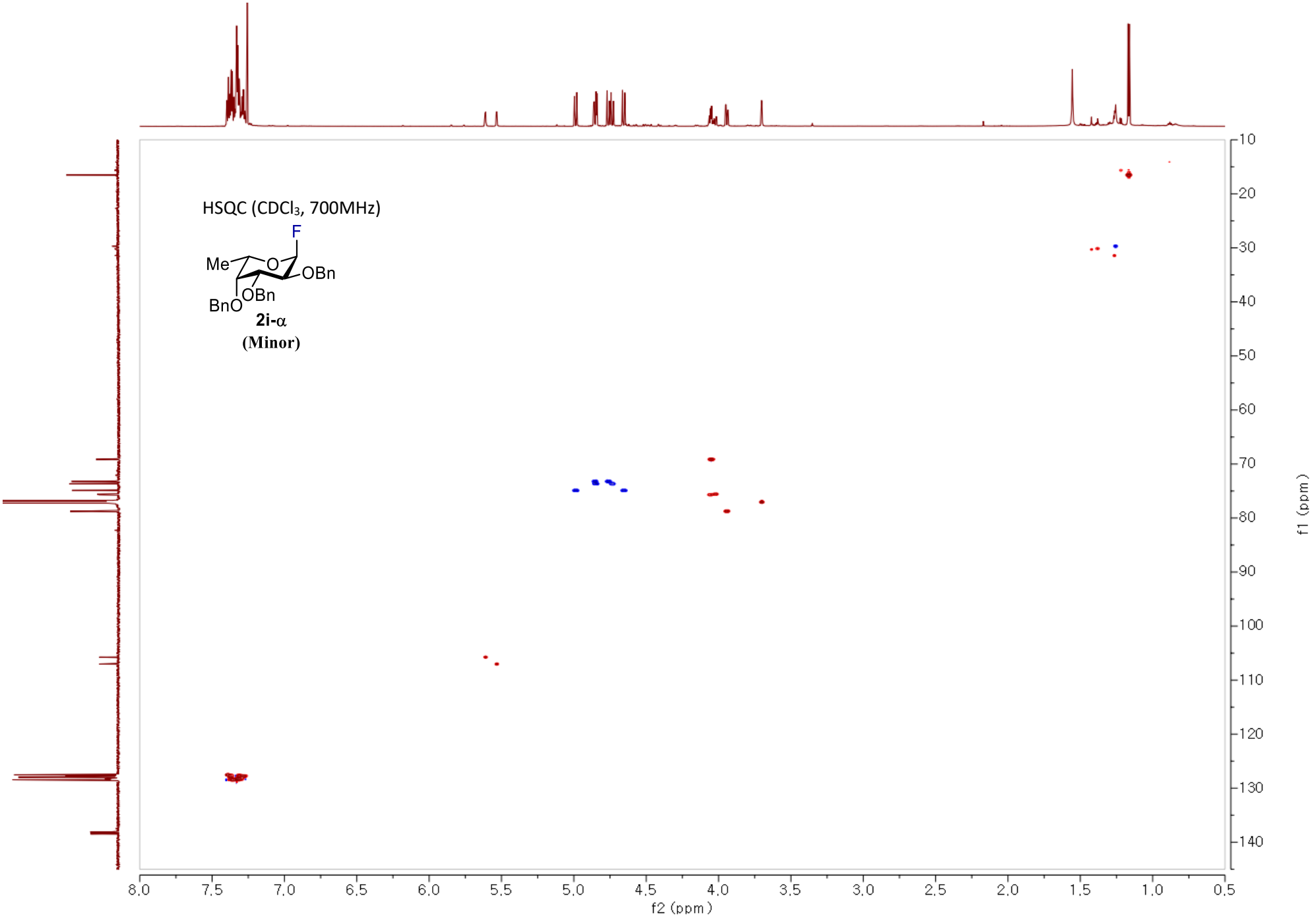

^{13}C NMR ($CDCl_3$, 176MHz)
Me
O
F
Me
BnO
OBn
2i-β
(Major)
f1 (ppm)

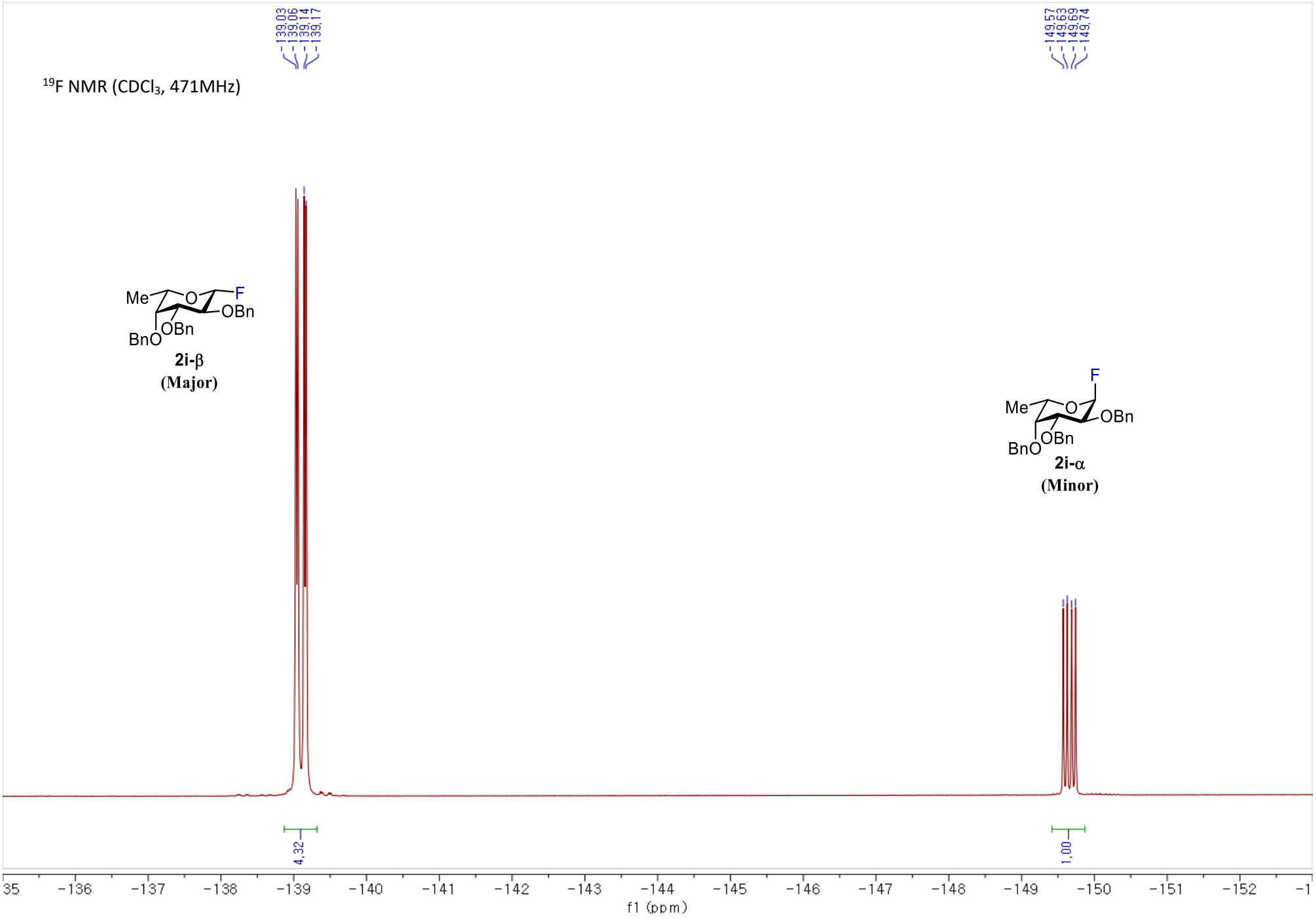

HSQC (CDCl3, 700MHz)
Me
O
F
Me
OBn
BnO
2i-β
(Major)
f2 (ppm)
f1 (ppm)

2,3,4-Tris-*O*-(phenylmethyl)-α-L-fucopyranosyl fluoride (2i-α, Minor diastereomer)

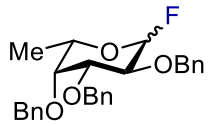



^{13}C NMR ($CDCl_3$, 176MHz)
F
Me
O
OBn
BnO
OBn
2i-α
(Minor)
138.46
138.26
138.07
128.45
128.43
128.35
128.27
127.98
127.82
127.74
127.67
127.53
107.03
105.75
78.76
75.71
75.57
74.89
73.66
73.22
69.15
69.13
16.50
75.71
75.57
69.15
69.13
76.0
75.5
69.5
69.0
f1 (ppm)
145 140 135 130 125 120 115 110 105 100 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
2i-α
(Minor)
f2 (ppm)
f1 (ppm)


19F NMR (CDCl3, 471MHz)
139.03
139.06
139.14
139.17
149.57
149.63
149.69
149.74
Me
O
F
OBn
BnO
OBn
2i-β
(Major)
F
Me
O
OBn
BnO
OBn
2i-α
(Minor)
4.32
1.00
-135
-136
-137
-138
-139
-140
-141
-142
-143
-144
-145
-146
-147
-148
-149
-150
-151
-152
f1 (ppm)

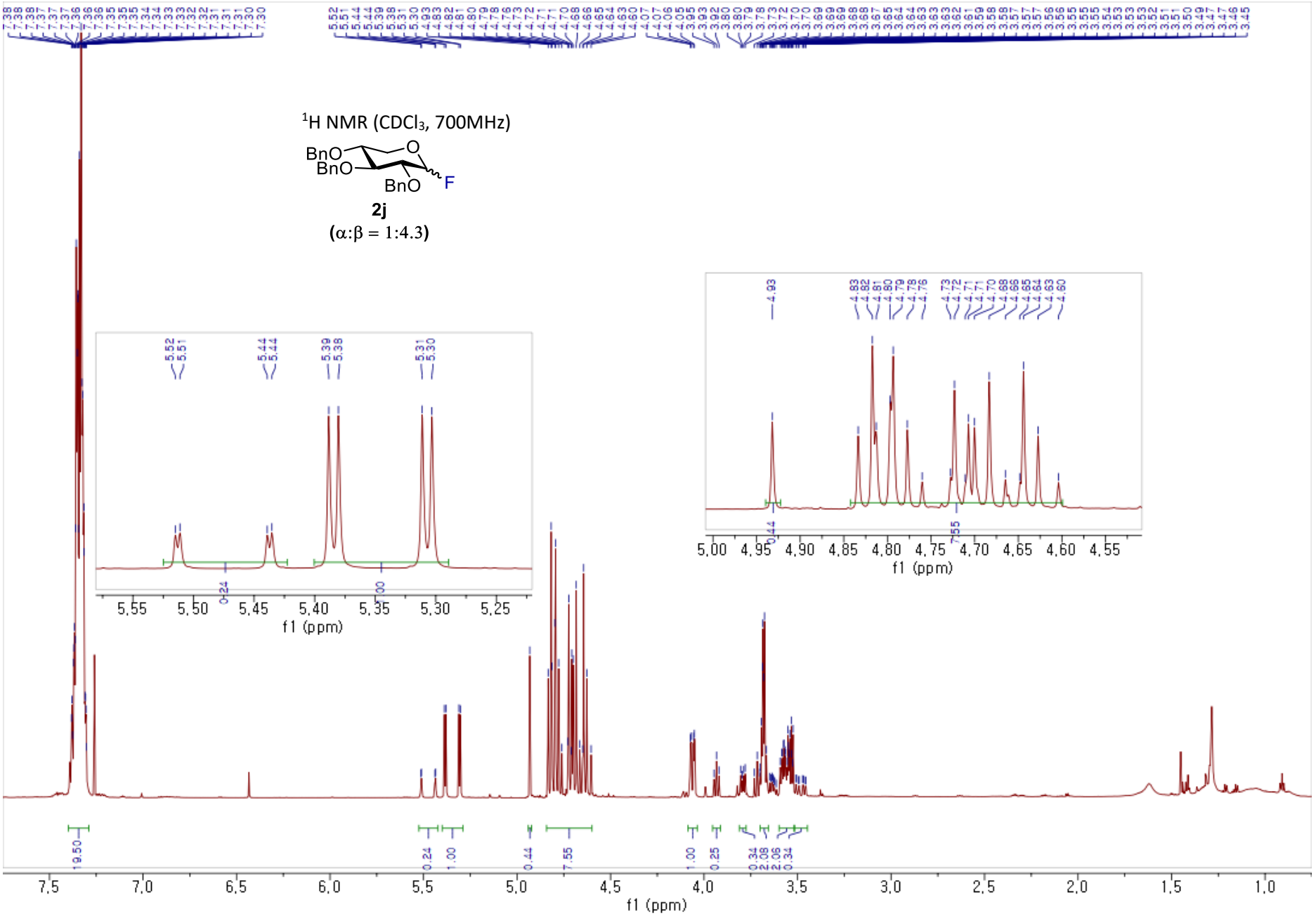
^{1}H NMR ($CDCl_3$, 700MHz)

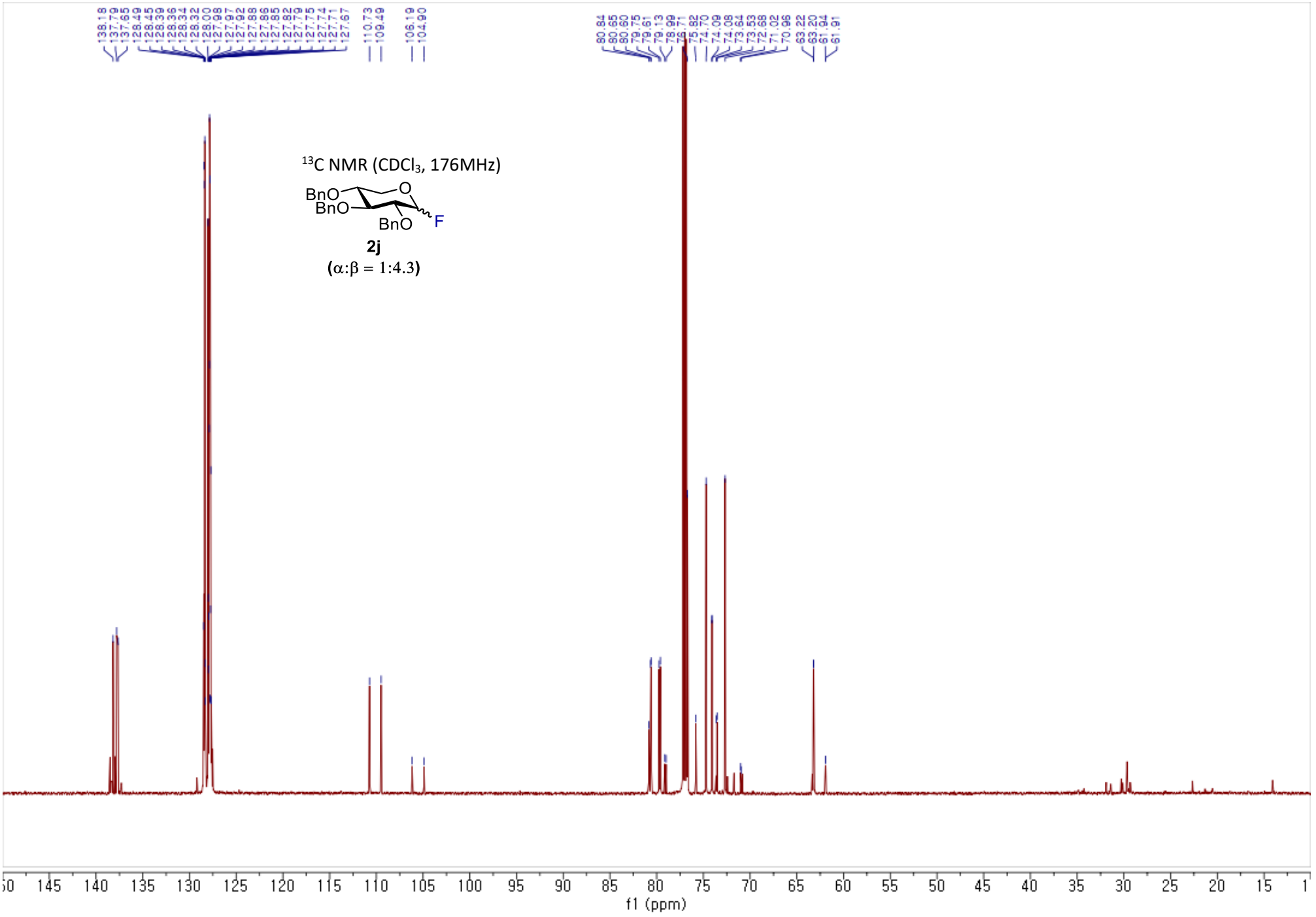


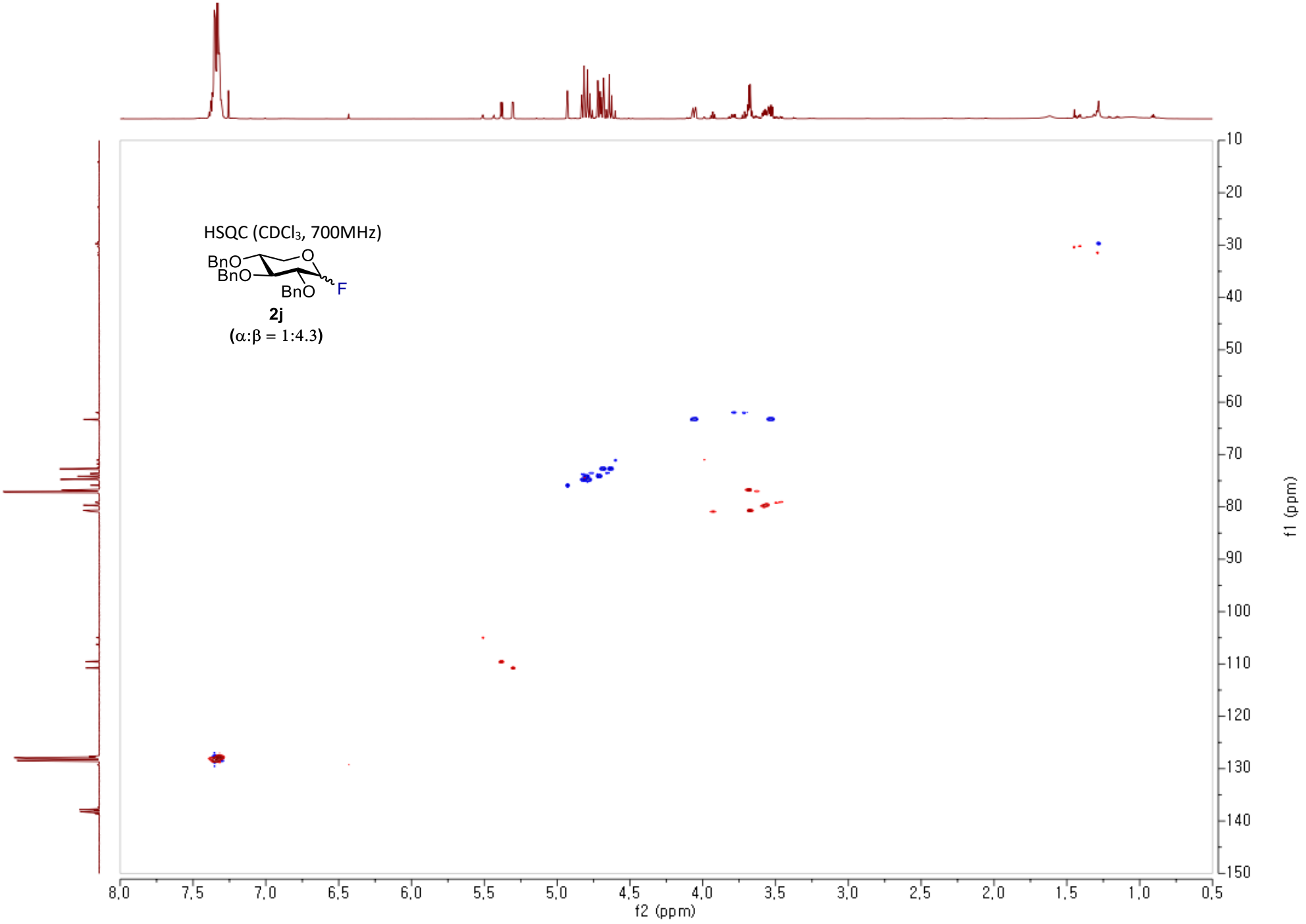
2i

(α,β-mix)

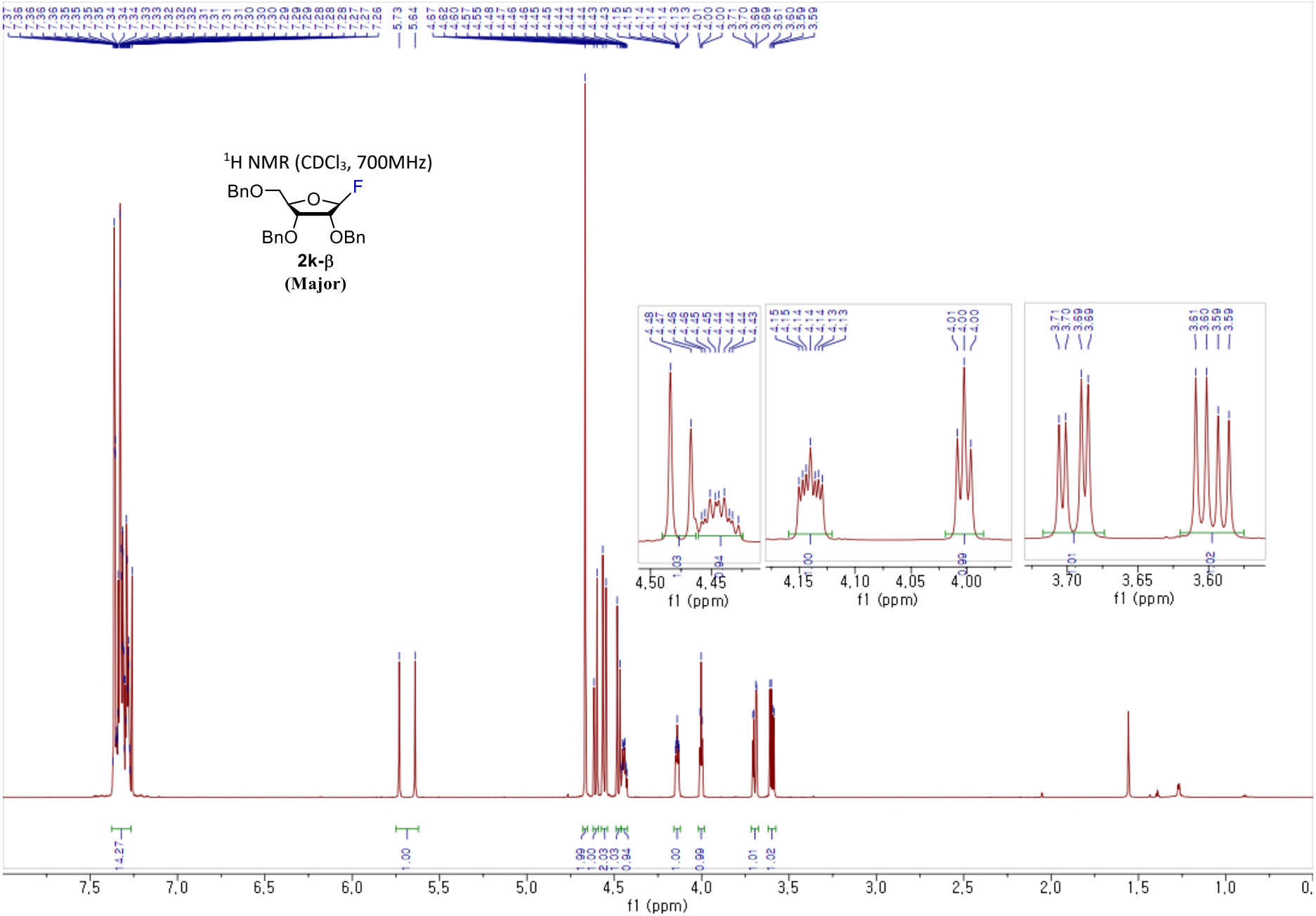
2,3,4-tris-O-(phenylmethyl)-D-xylopyranosyl fluoride (2j, Isolated as α : β = 1 : 4.3 mixture)

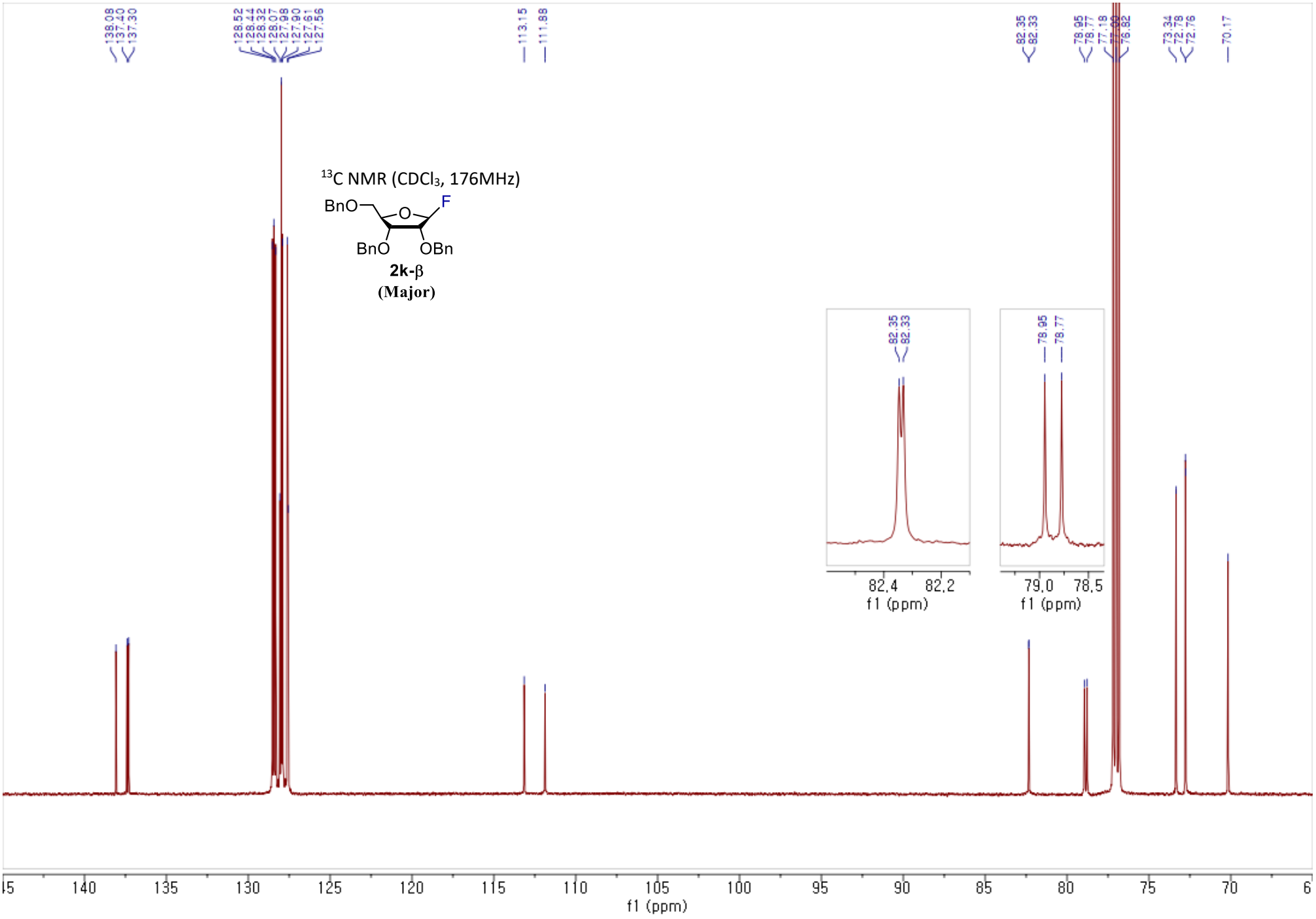


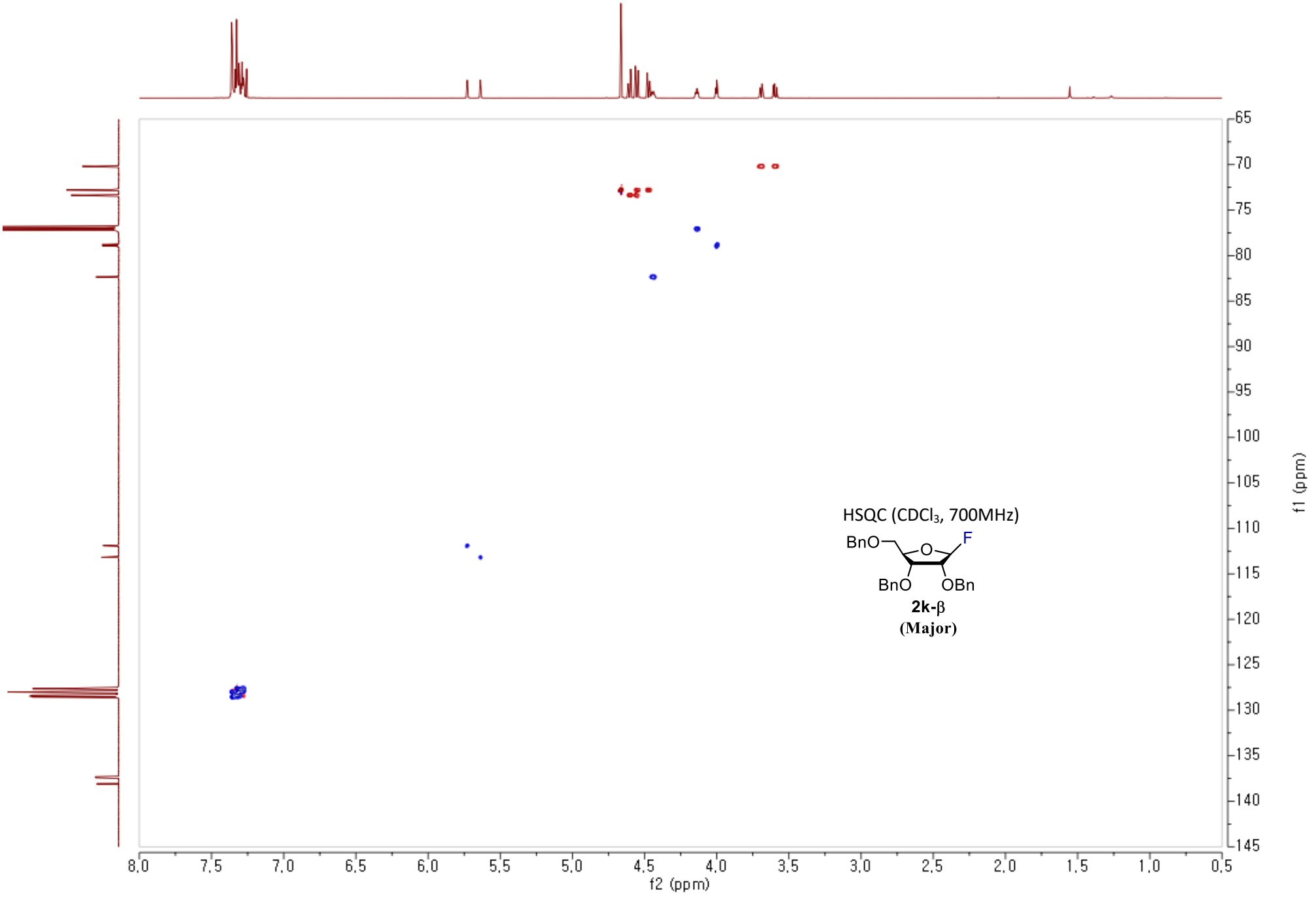

138.18
137.79
137.65
128.49
128.45
128.39
128.36
128.34
128.32
128.00
127.98
127.97
127.92
127.88
127.86
127.85
127.82
127.79
127.75
127.74
127.71
127.67
110.73
109.49
106.19
104.90
80.84
80.65
80.60
79.75
79.61
79.13
78.99
79.71
75.82
74.70
74.09
74.08
73.64
73.53
72.68
71.02
70.96
63.22
63.20
61.94
61.91
^{13}C NMR ($CDCl_3$, 176MHz)
BnO
BnO
BnO
O
F
2j
(α:β = 1:4.3)
f1 (ppm)

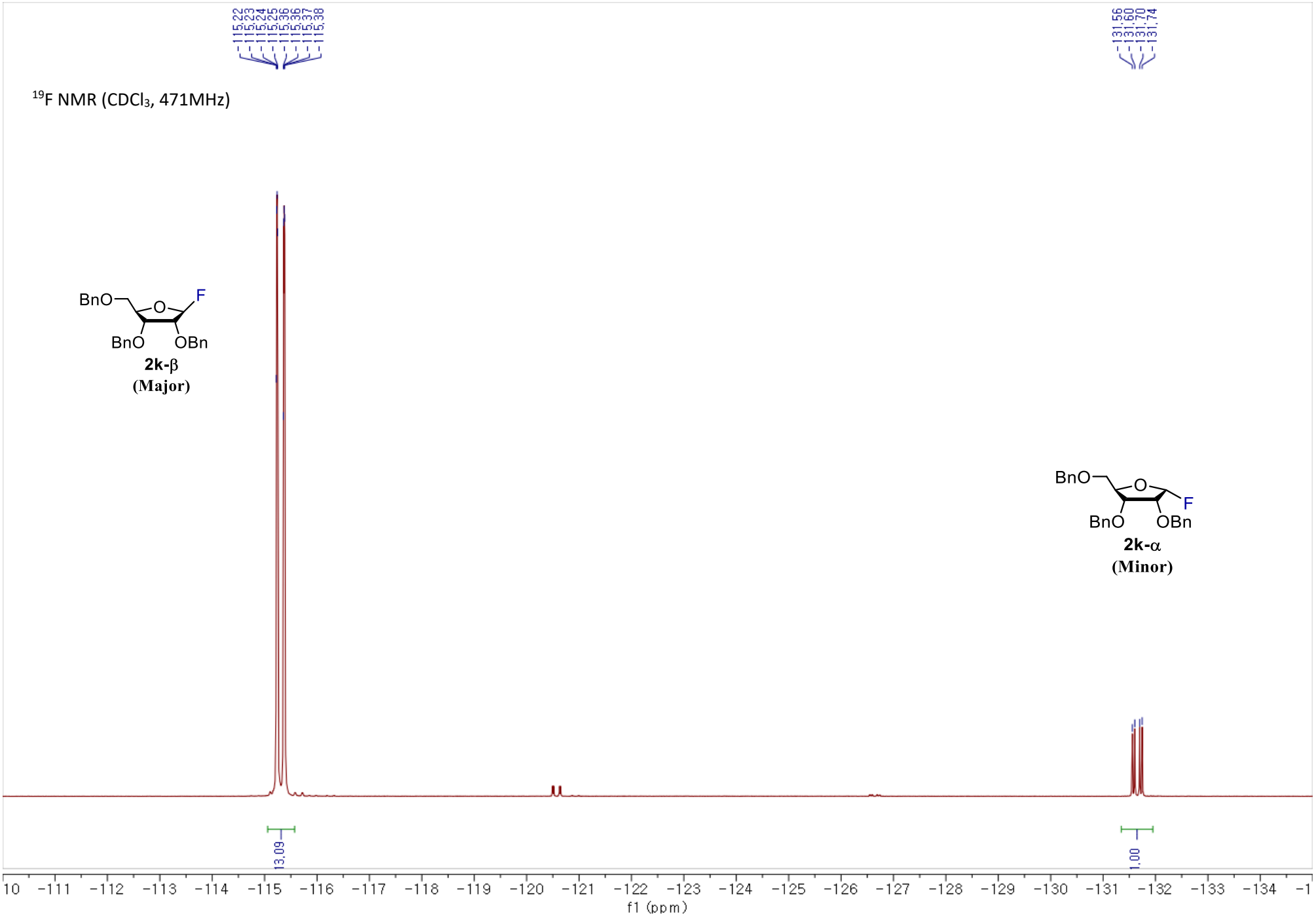

HSQC ($CDCl_3$, 700MHz)
BnO
BnO
BnO
O
F
2j
(α:β = 1:4.3)
f2 (ppm)
f1 (ppm)

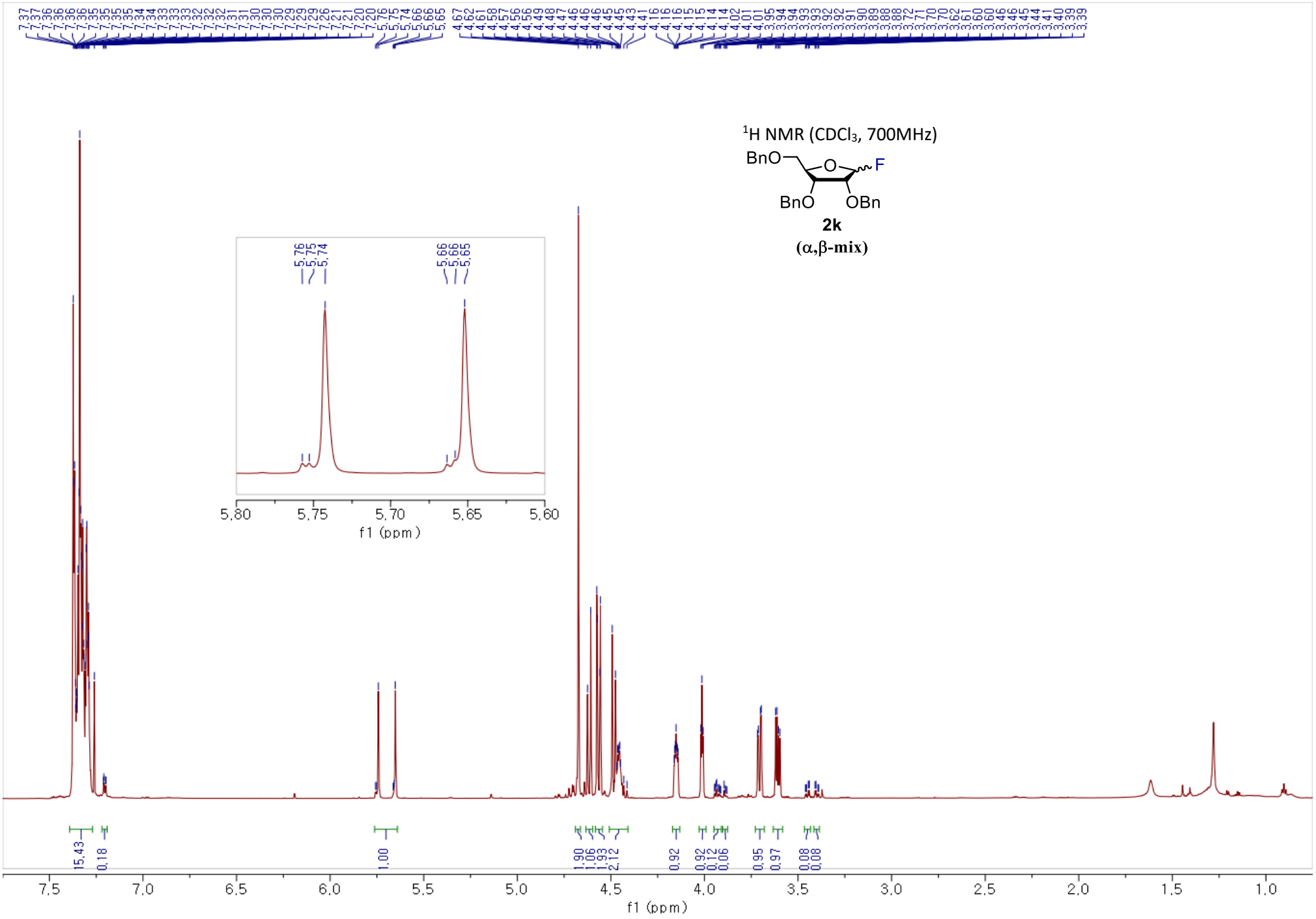
2,3,5-Tris-O-(phenylmethyl)-β-D-ribofuranosyl fluoride (2k- β, Major diastereomer)



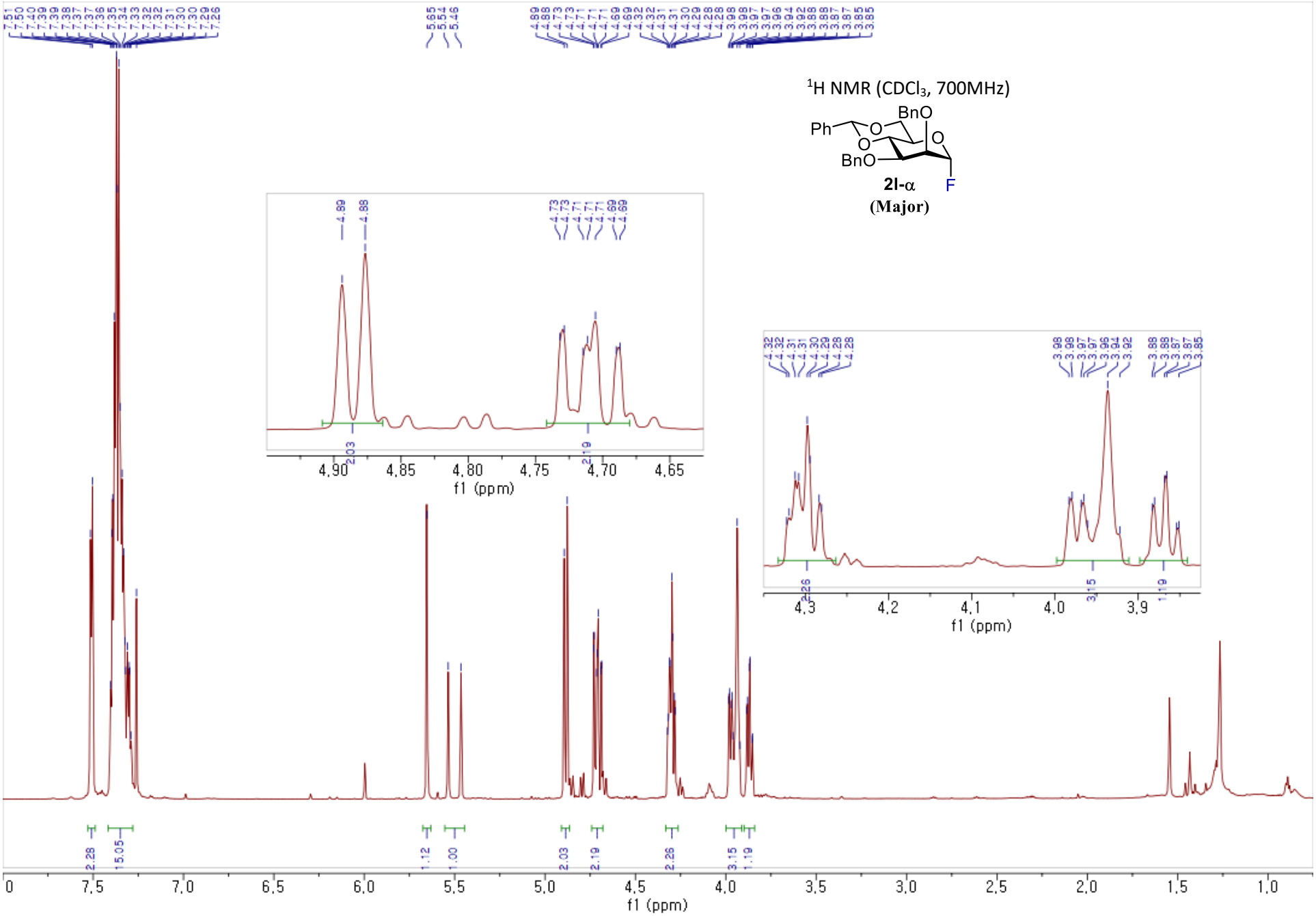

138.08
137.40
137.30
128.52
128.44
128.32
128.07
127.98
127.90
127.61
127.56
113.15
111.88
82.35
82.33
78.95
78.77
77.18
76.82
73.34
72.78
72.76
70.17
13C NMR (CDCl3, 176MHz)
BnO
O
F
BnO
OBn
2k-β
(Major)
82.35
82.33
82.4
82.2
f1 (ppm)
78.95
78.77
79.0
78.5
f1 (ppm)
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
f1 (ppm)

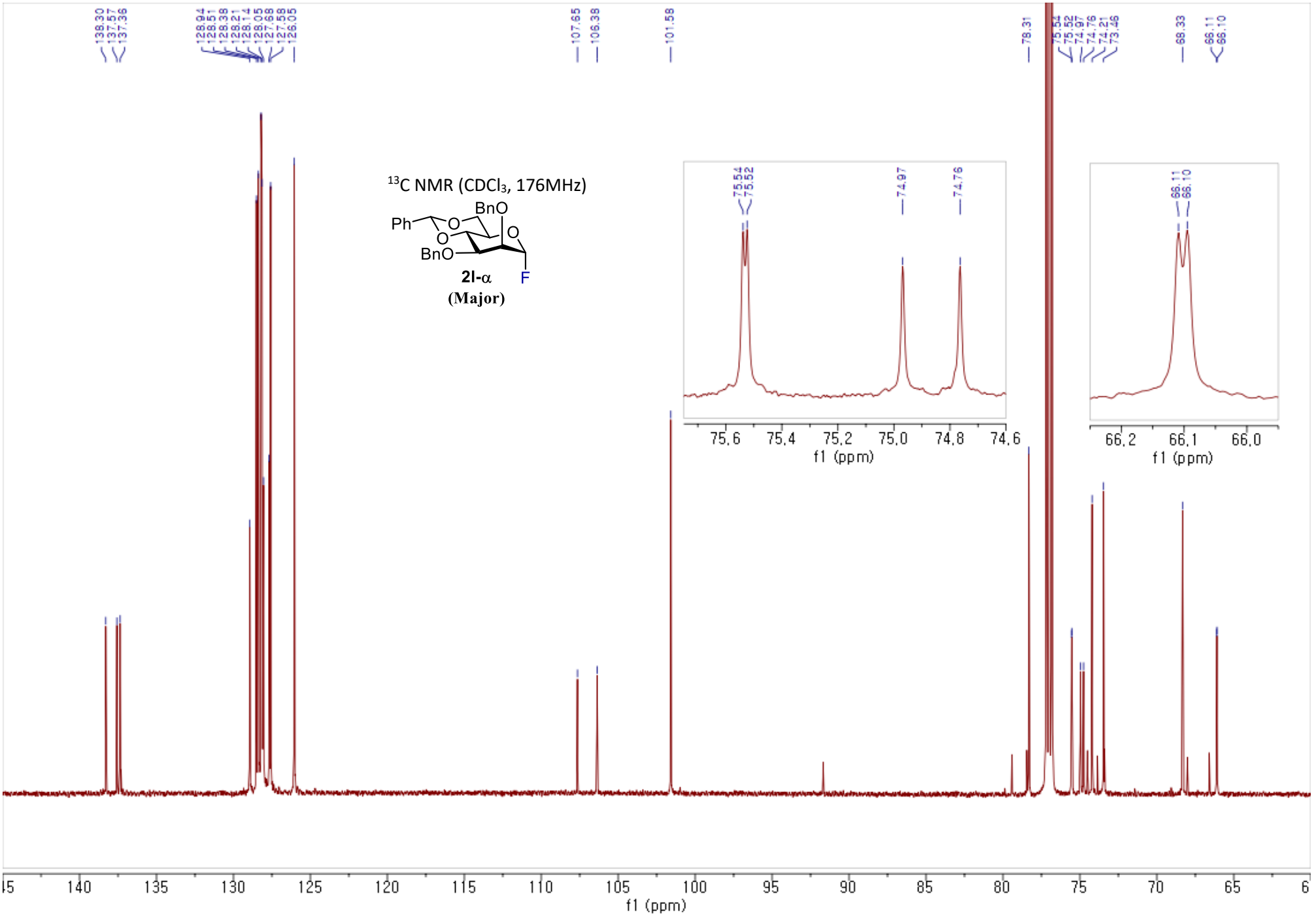

HSQC (CDCl3, 700MHz)
BnO
F
O
BnO
OBn
2k-β
(Major)
f2 (ppm)
f1 (ppm)

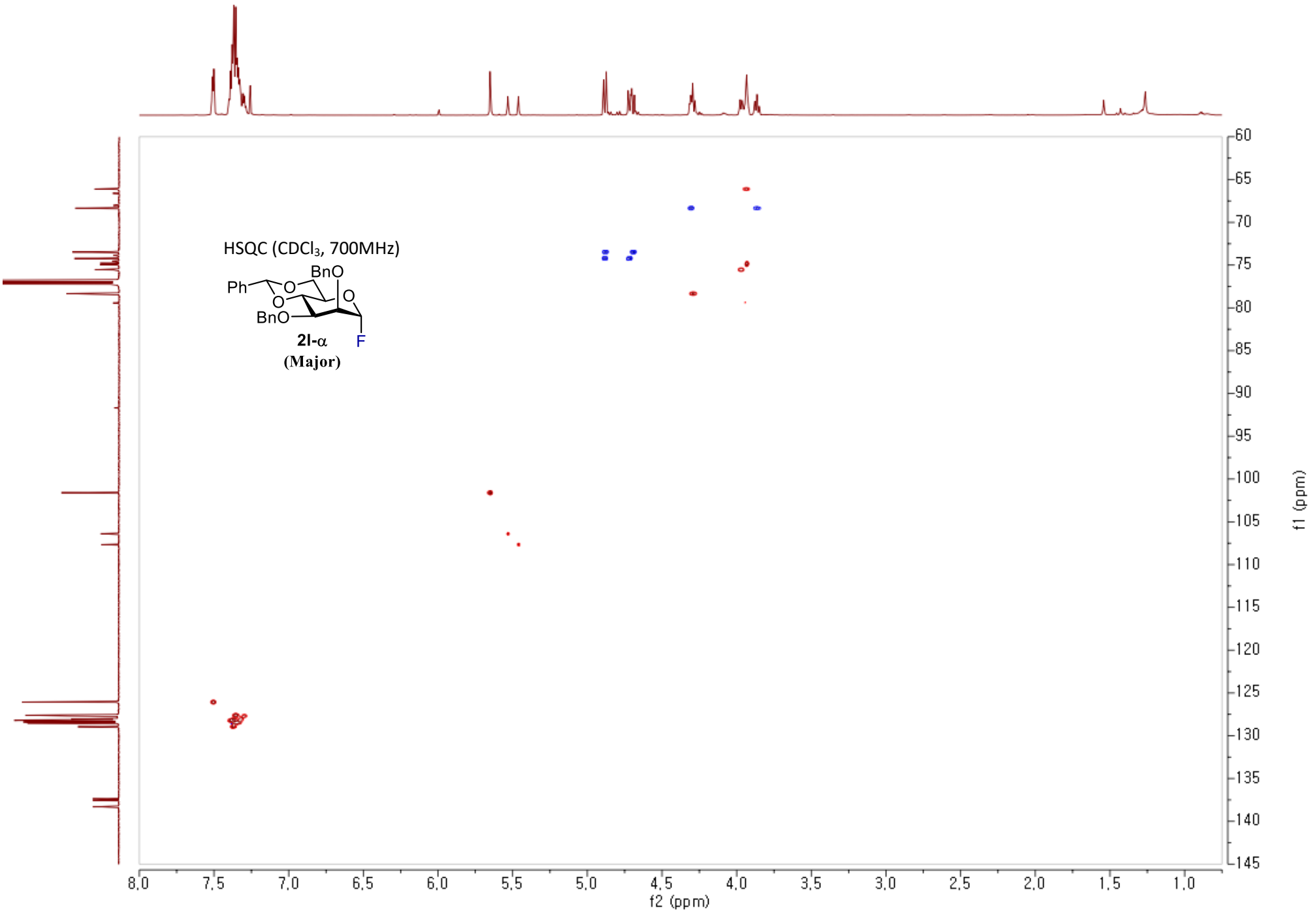

115.22
115.23
115.24
115.25
115.36
115.36
115.37
115.38
131.56
131.60
131.70
131.74
19F NMR (CDCl3, 471MHz)
BnO
O
F
BnO
OBn
2k-β
(Major)
BnO
O
F
BnO
OBn
2k-α
(Minor)
13.09
1.00
10 -111 -112 -113 -114 -115 -116 -117 -118 -119 -120 -121 -122 -123 -124 -125 -126 -127 -128 -129 -130 -131 -132 -133 -134 -1
f1 (ppm)


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

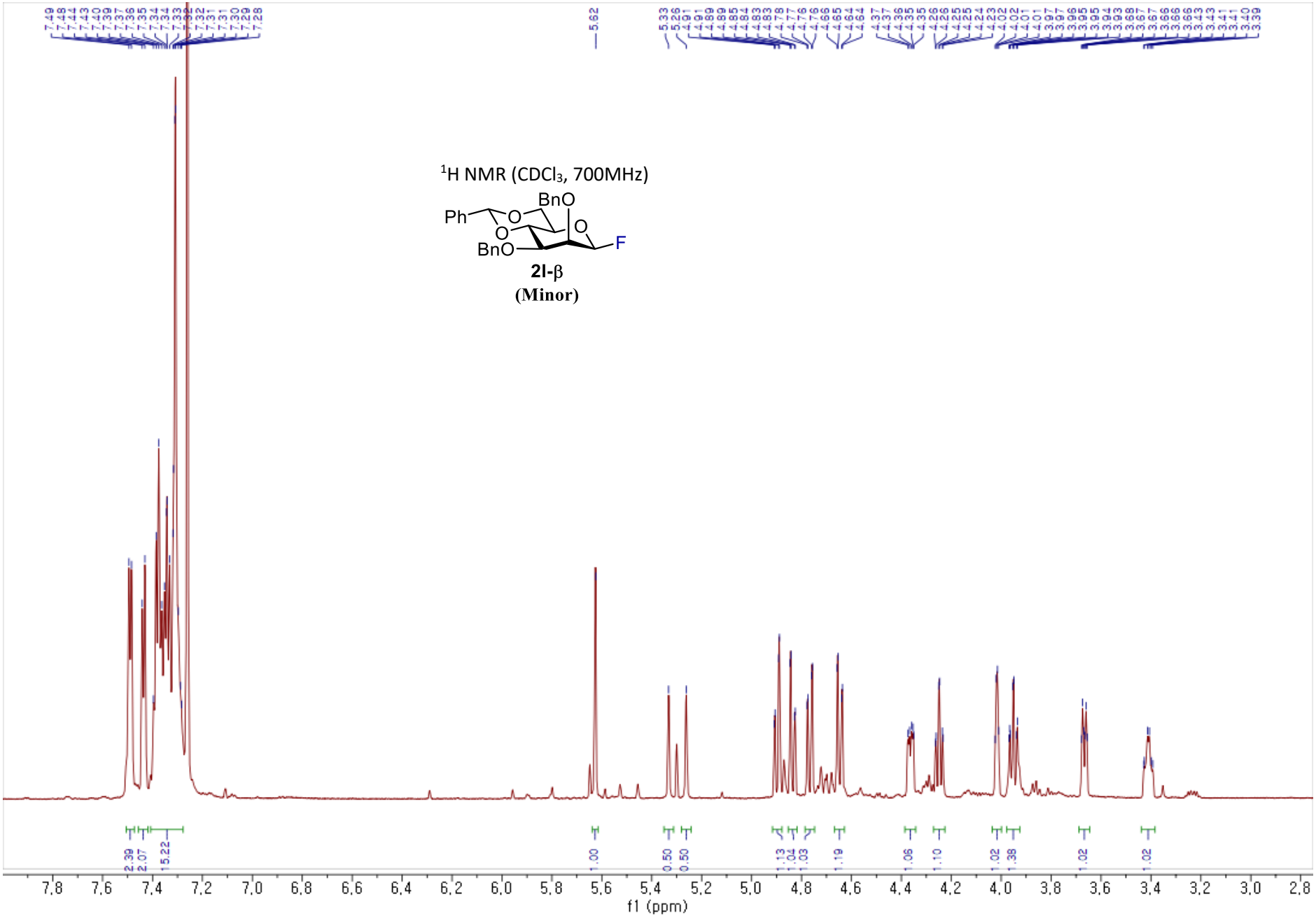
2,3-Bis-*O*-(phenylmethyl)-4,6-*O*-[(R)-phenylmethylene]-α-D-mannopyranosyl fluoride (2l-α, Major diastereomer)

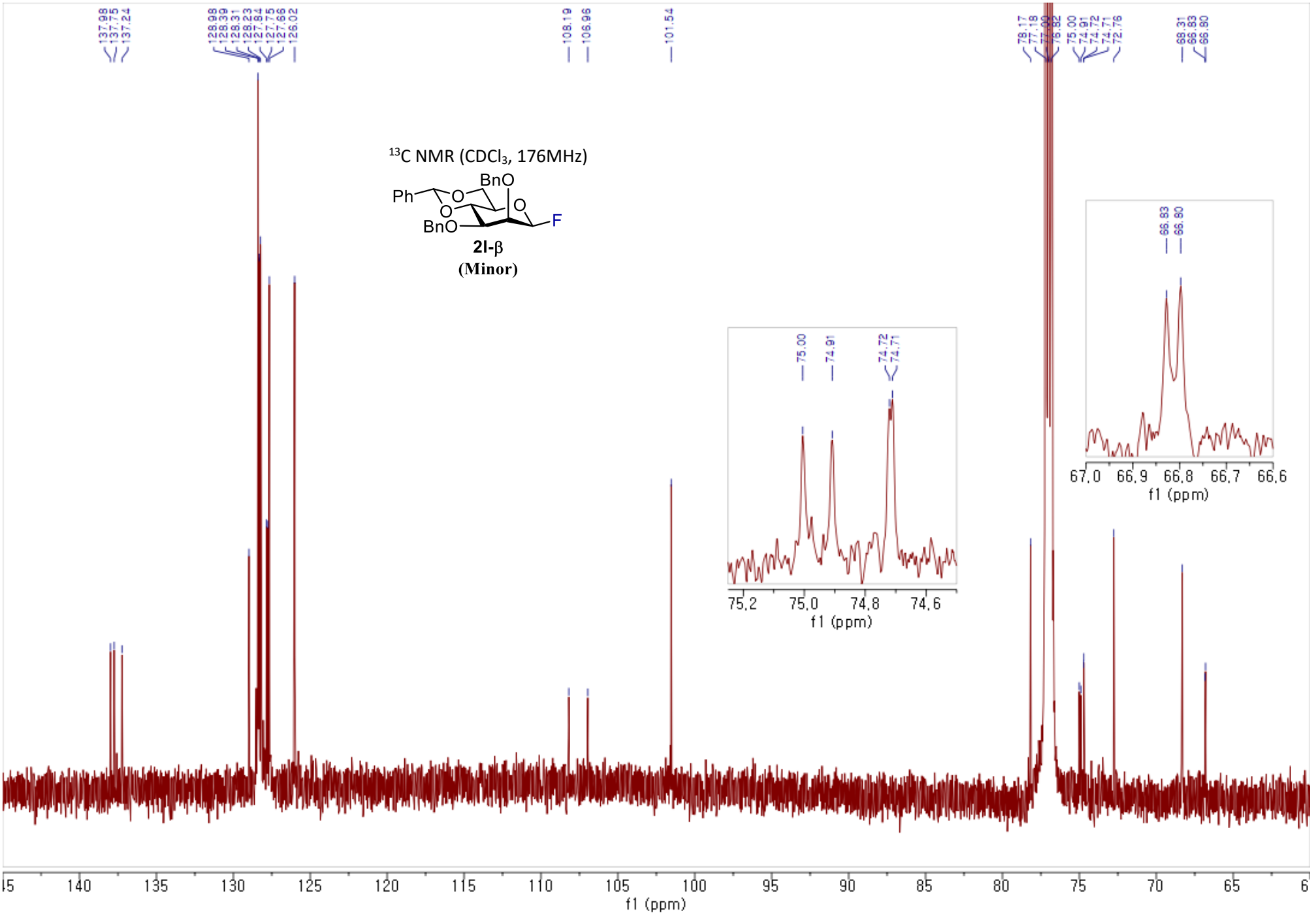


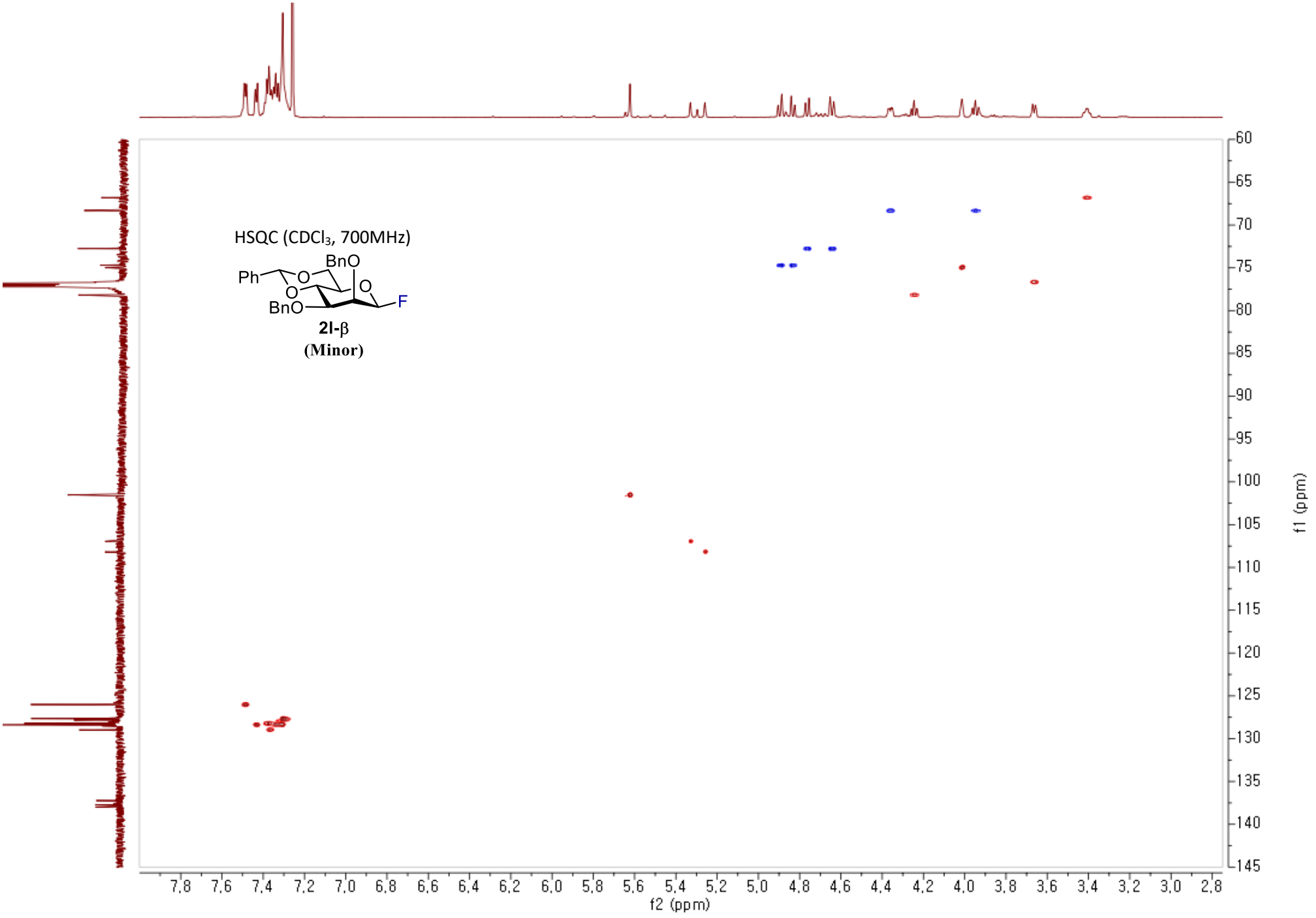

138.30
137.57
137.36
128.94
128.51
128.38
128.21
128.14
128.05
127.68
127.58
126.05
107.65
106.38
101.58
78.31
75.54
75.52
74.97
74.76
74.21
73.46
68.33
66.11
66.10
^{13}C NMR ($CDCl_3$, 176MHz)
Ph
BnO
BnO
O
O
O
F
2l-α
(Major)
75.6
75.4
75.2
75.0
74.8
74.6
f1 (ppm)
66.2
66.1
66.0
f1 (ppm)
140
135
130
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
2l-α
(Major)
f2 (ppm)
f1 (ppm)

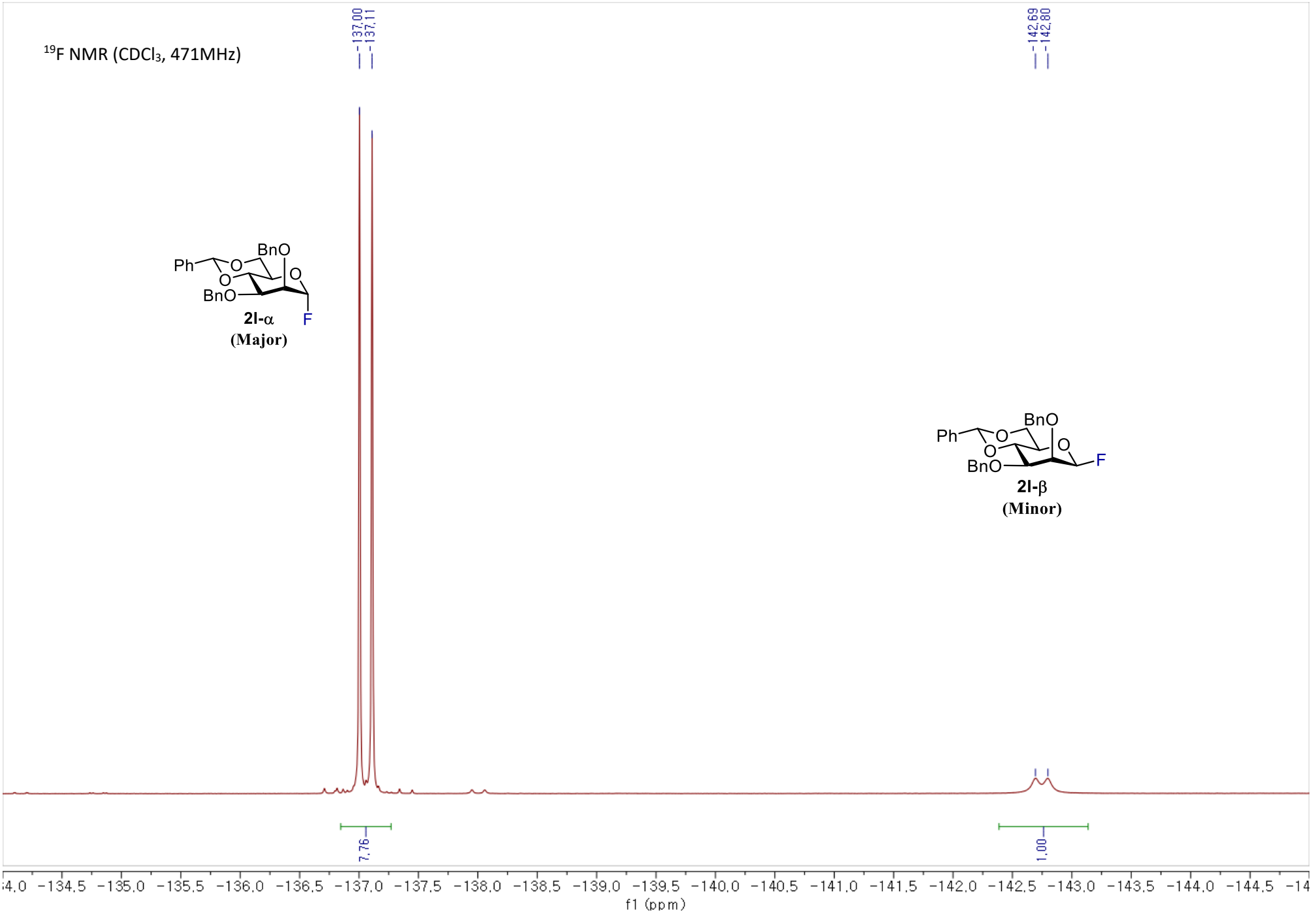
2,3-Bis-*O*-(phenylmethyl)-4,6-*O*-[(R)-phenylmethylene]-β-D-mannopyranosyl fluoride (2l-β, Minor diastereomer)



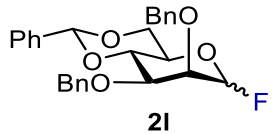

137.98
137.75
137.24
128.98
128.39
128.31
128.23
127.84
127.75
127.66
126.02
108.19
106.96
101.54
78.17
77.18
77.00
76.82
75.00
74.91
74.72
74.71
72.76
68.31
66.83
66.80
^{13}C NMR ($CDCl_3$, 176MHz)
BnO
Ph
O
O
O
BnO
F
2l-β
(Minor)
75.00
74.91
74.72
74.71
75.2
75.0
74.8
74.6
f1 (ppm)
66.83
66.80
67.0
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
2l-β
(Minor)
f2 (ppm)
f1 (ppm)

^{19}F NMR ($CDCl_3$, 471MHz)



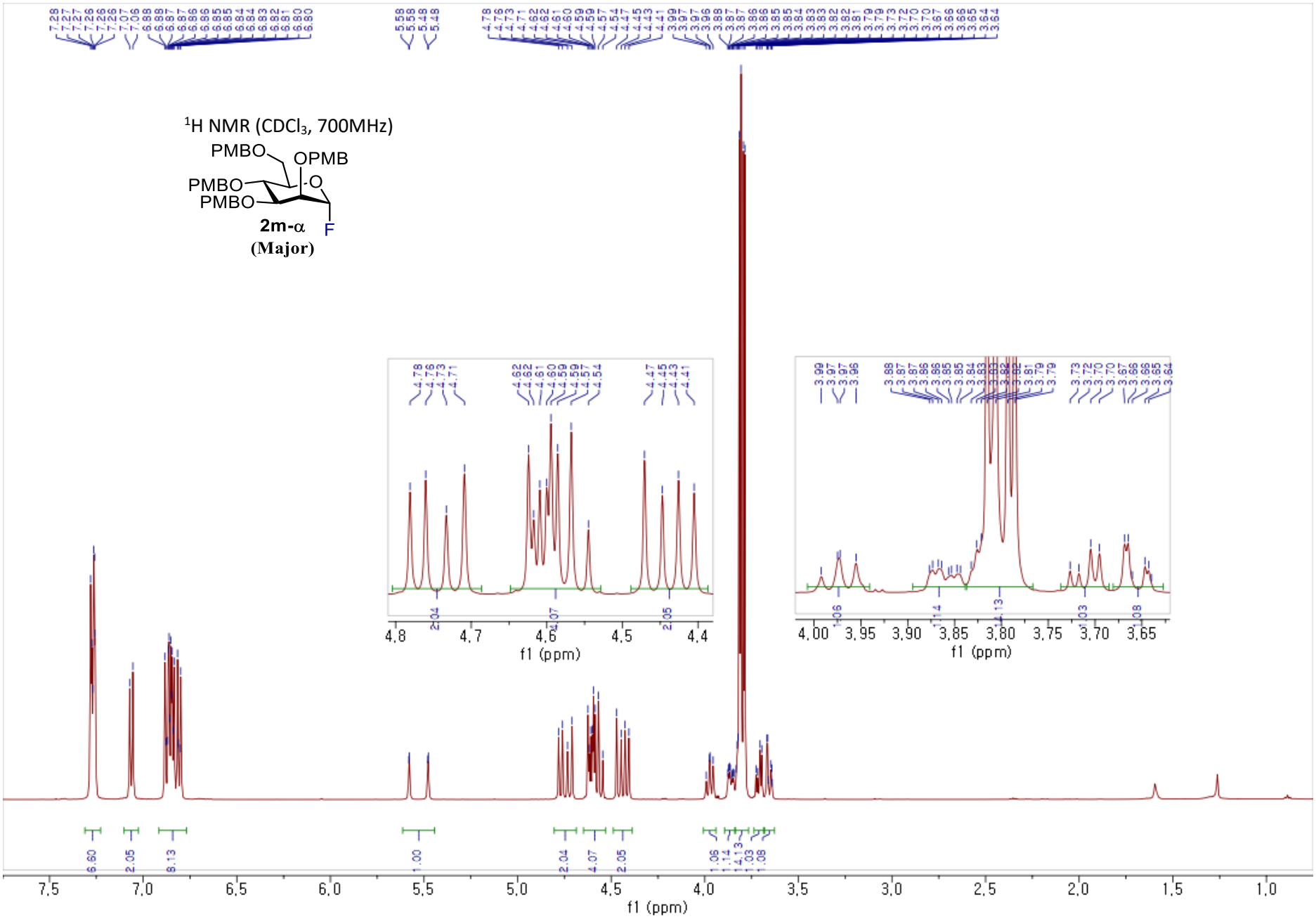
^{1}H NMR ($CDCl_3$, 700MHz)

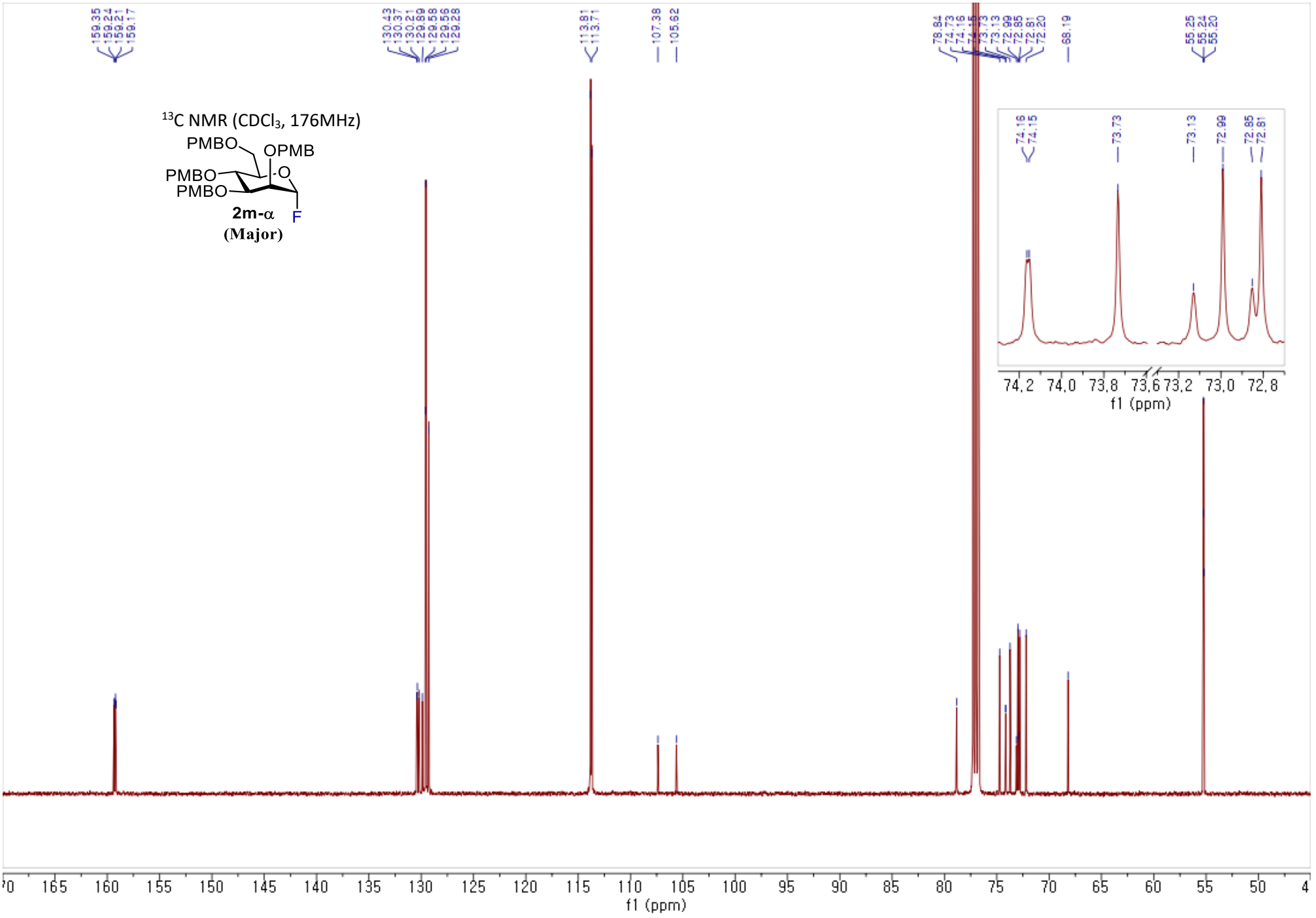


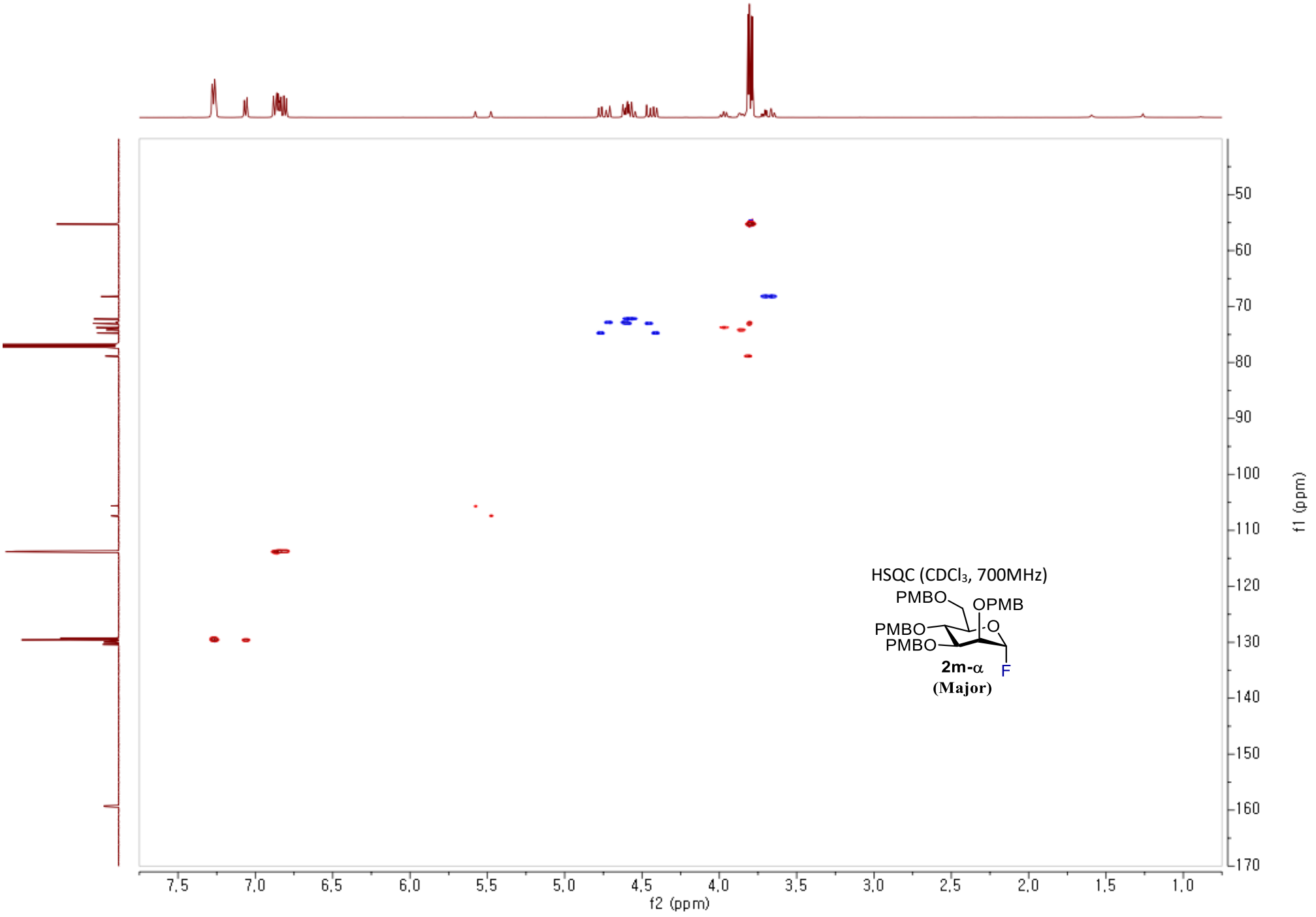
2l

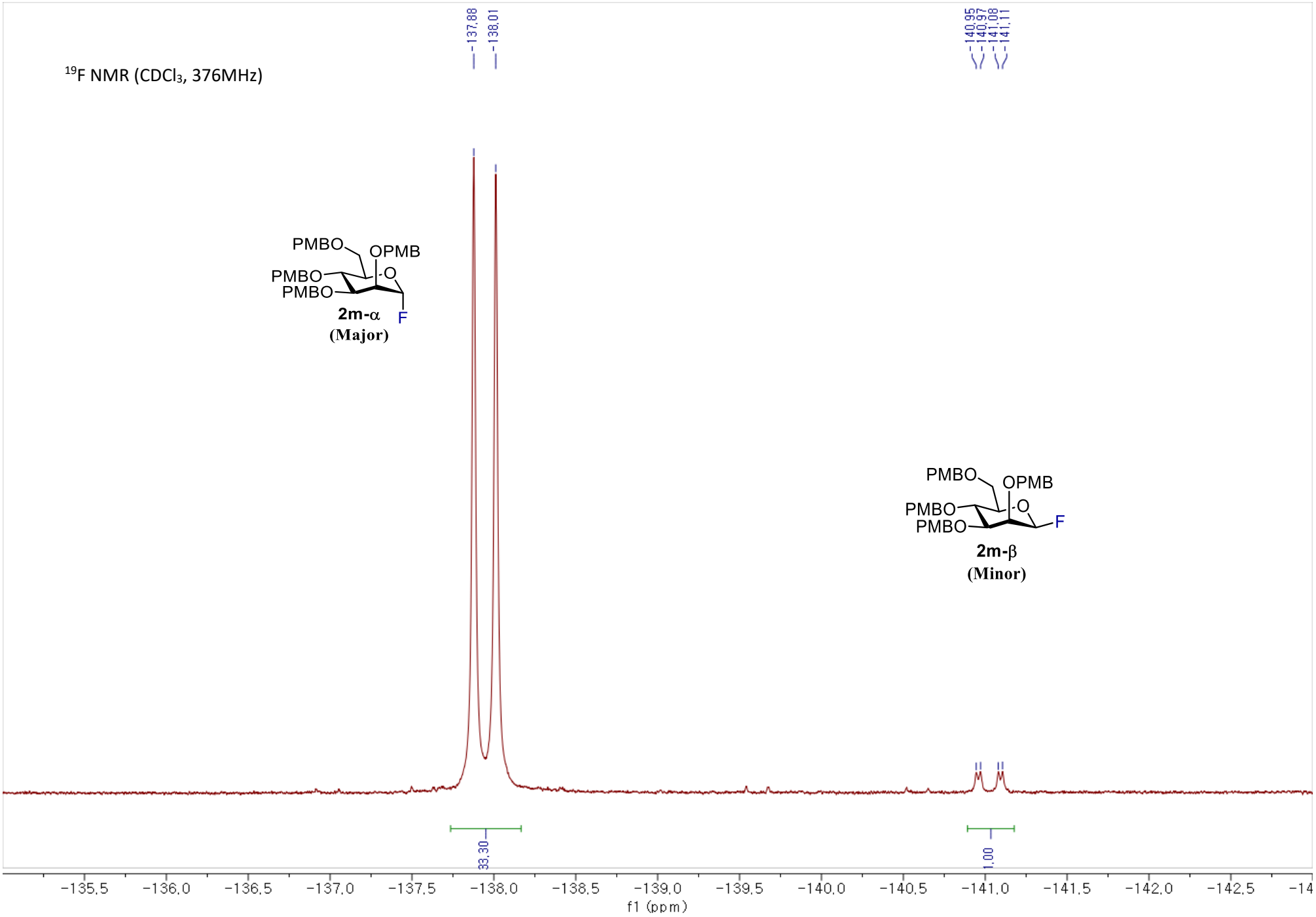
(α,β-mix)

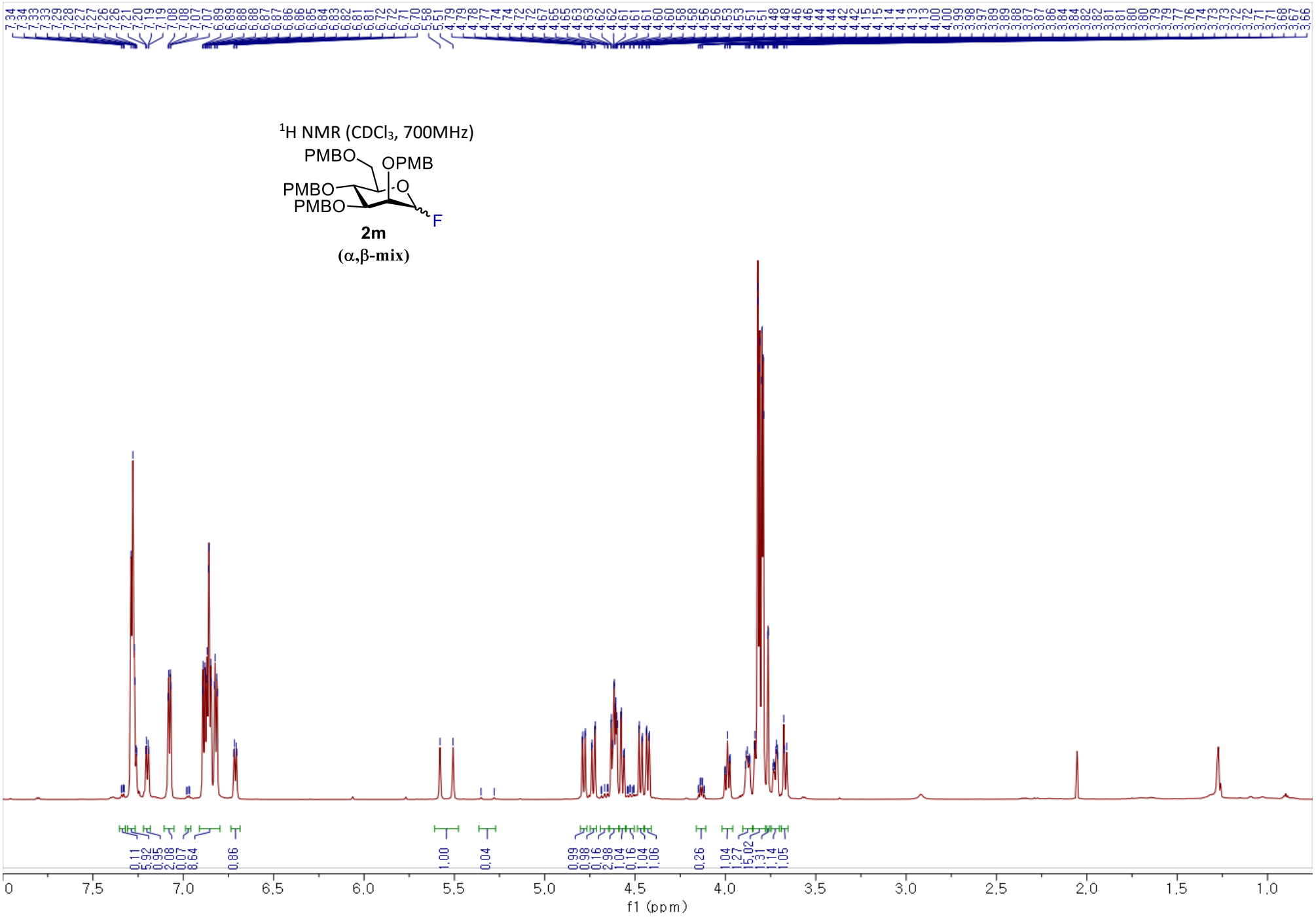
2,3,4,6-Tetrakis-O-[(4-methoxyphenyl)methyl]-α-D-mannopyranosyl fluoride (2m- α, Major diastereomer)



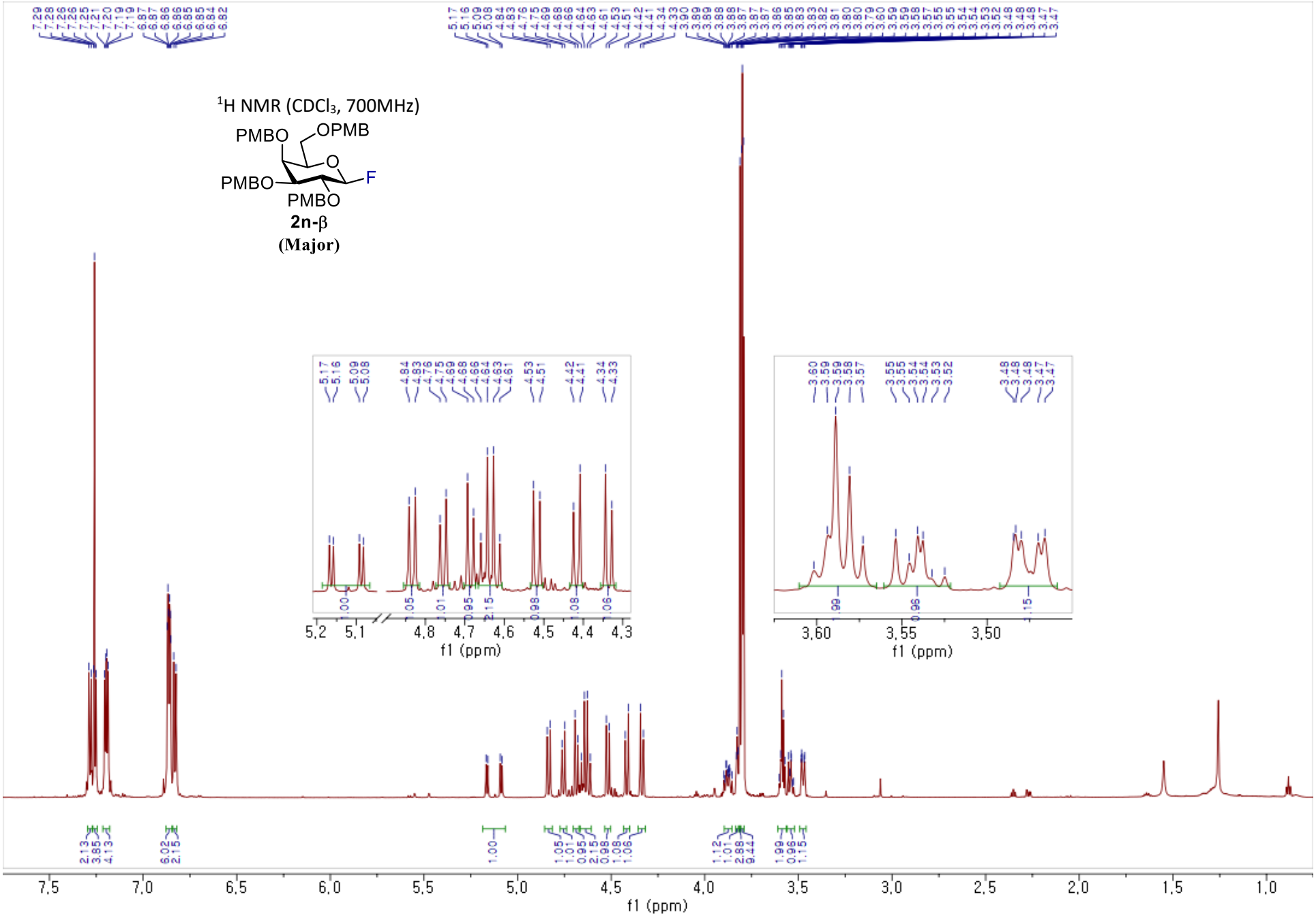

159.35
159.24
159.21
159.17
130.43
130.37
130.21
129.89
129.58
129.56
129.28
113.81
113.71
107.38
105.62
78.84
74.73
74.16
74.15
73.73
73.13
72.99
72.85
72.81
72.20
68.19
55.25
55.24
55.20
13C NMR (CDCl3, 176MHz)
PMBO
OPMB
PMBO
PMBO
O
F
2m-α
(Major)
74.16
74.15
73.73
73.13
72.99
72.85
72.81
74.2 74.0 73.8 73.6 73.2 73.0 72.8
f1 (ppm)
f1 (ppm)

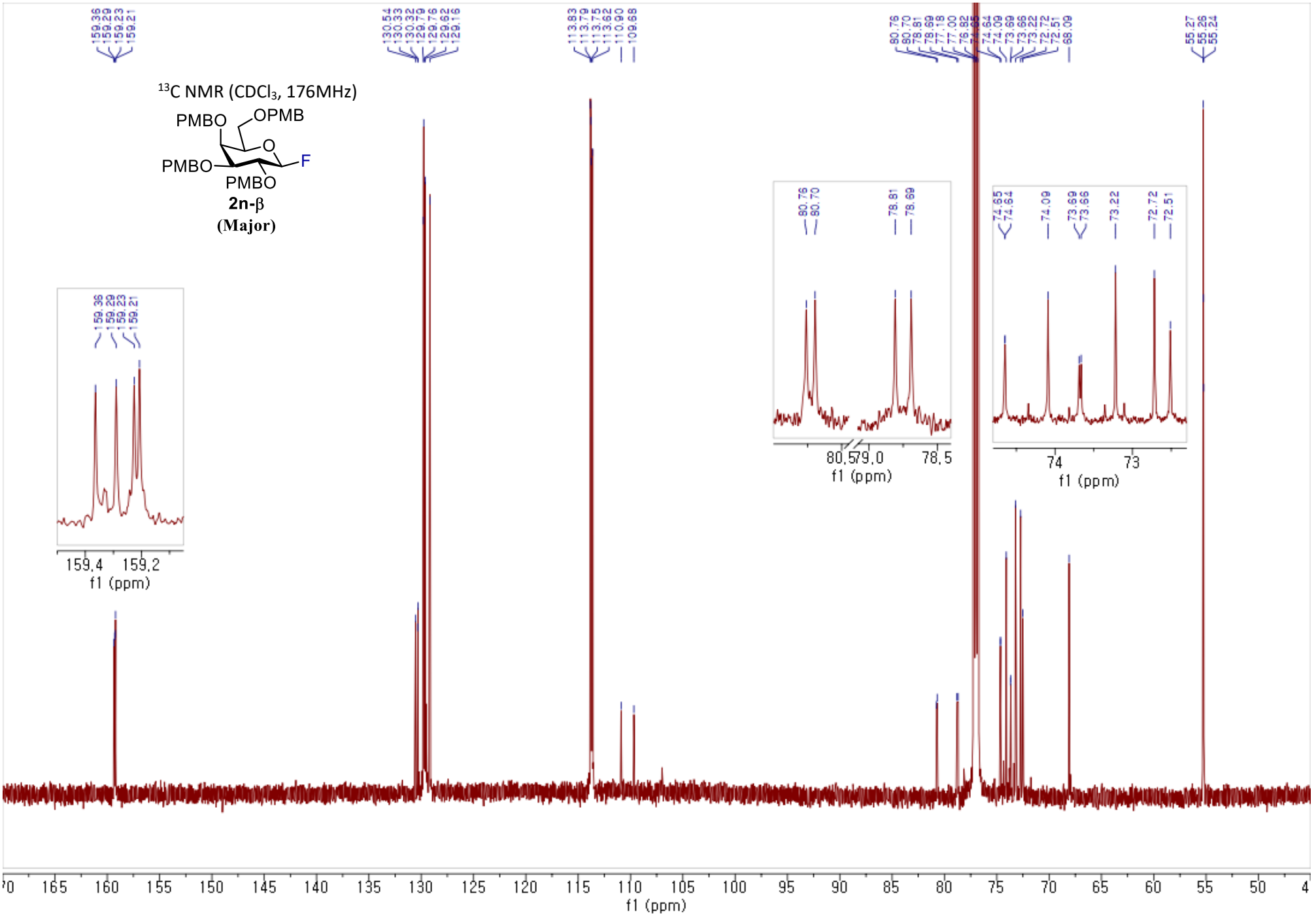

HSQC (CDCl3, 700MHz)
PMBO
OPMB
PMBO
O
PMBO
2m-α
(Major)
F
f2 (ppm)
f1 (ppm)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
50
60
70
80
90
100
110
120
130
140
150
160
170

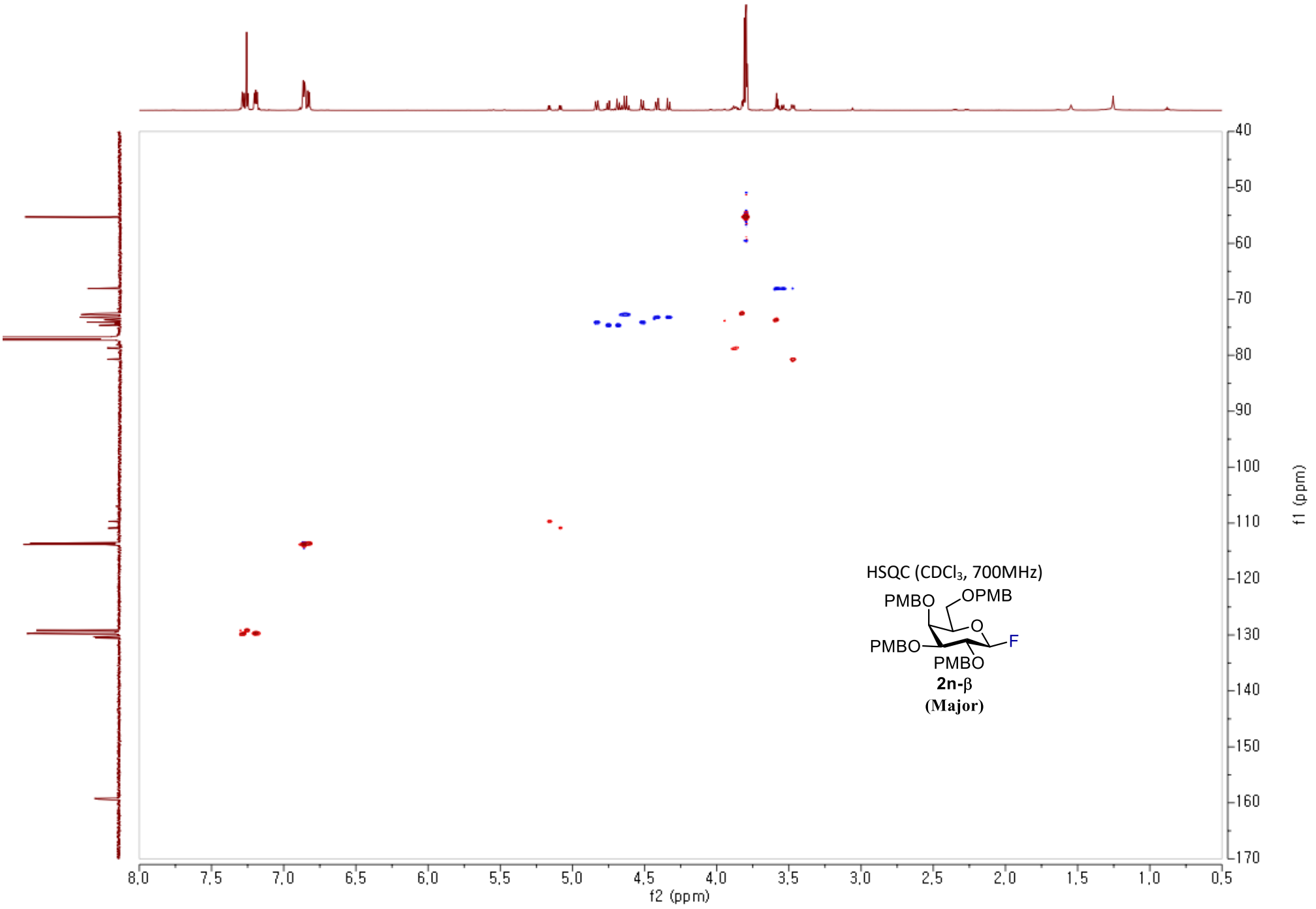

^{19}F NMR ($CDCl_3$, 376MHz)
-137.88
-138.01
-140.95
-140.97
-141.08
-141.11
PMBO
OPMB
PMBO
PMBO
O
F
2m-α
(Major)
PMBO
OPMB
PMBO
PMBO
O
F
2m-β
(Minor)
33.30
1.00
-135.5
-136.0
-136.5
-137.0
-137.5
-138.0
-138.5
-139.0
-139.5
-140.0
-140.5
-141.0
-141.5
-142.0
-142.5
f1 (ppm)


^{1}H NMR (CDCl$_3$, 700MHz)
PMBO
OPMB
PMBO
O
PMBO
F
2m
(α,β-mix)
f1 (ppm)

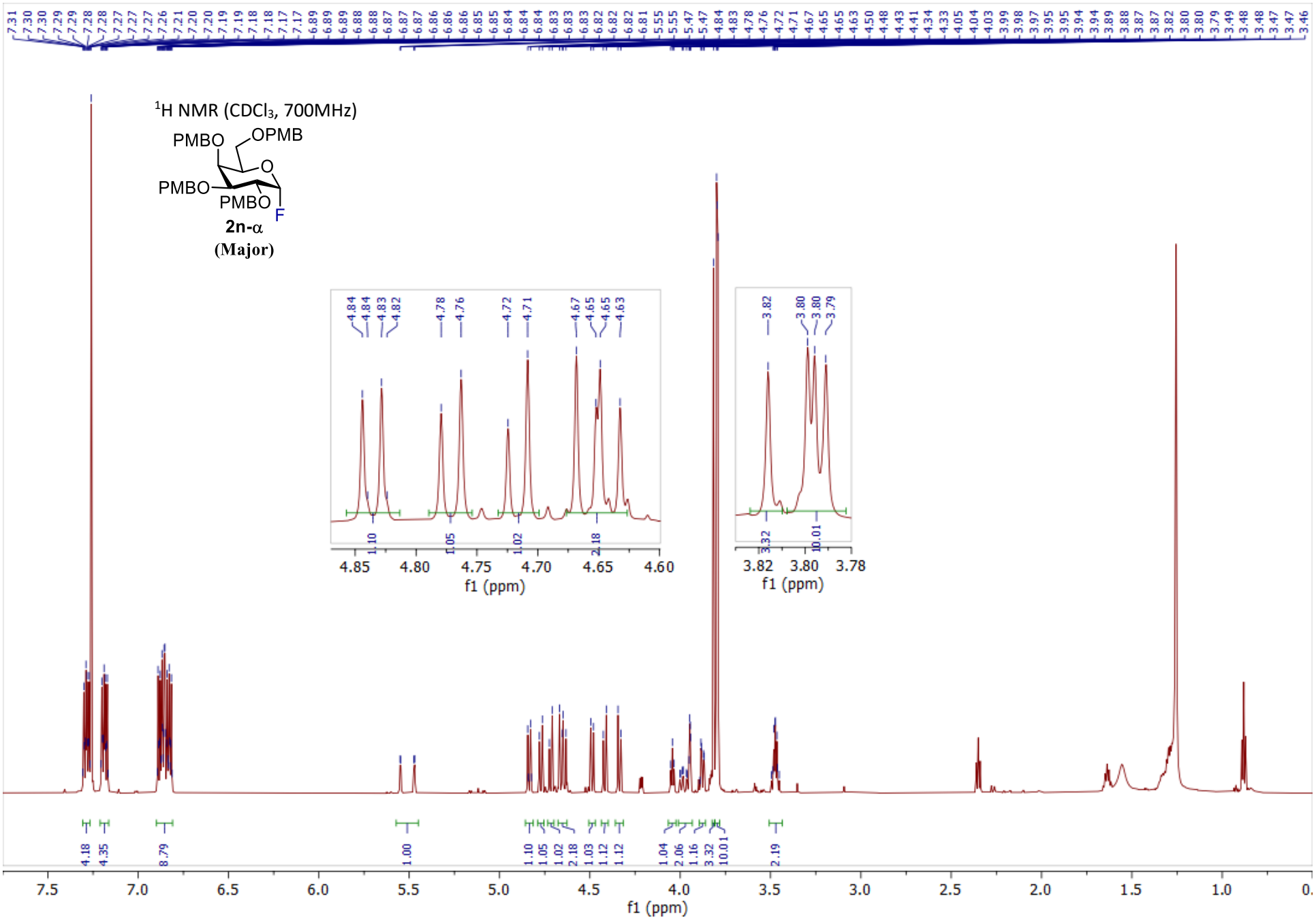
2,3,4,6-Tetrakis-O-[(4-methoxyphenyl)methyl]-β-D-galactopyranosyl fluoride (2n-β, Major diastereomer)

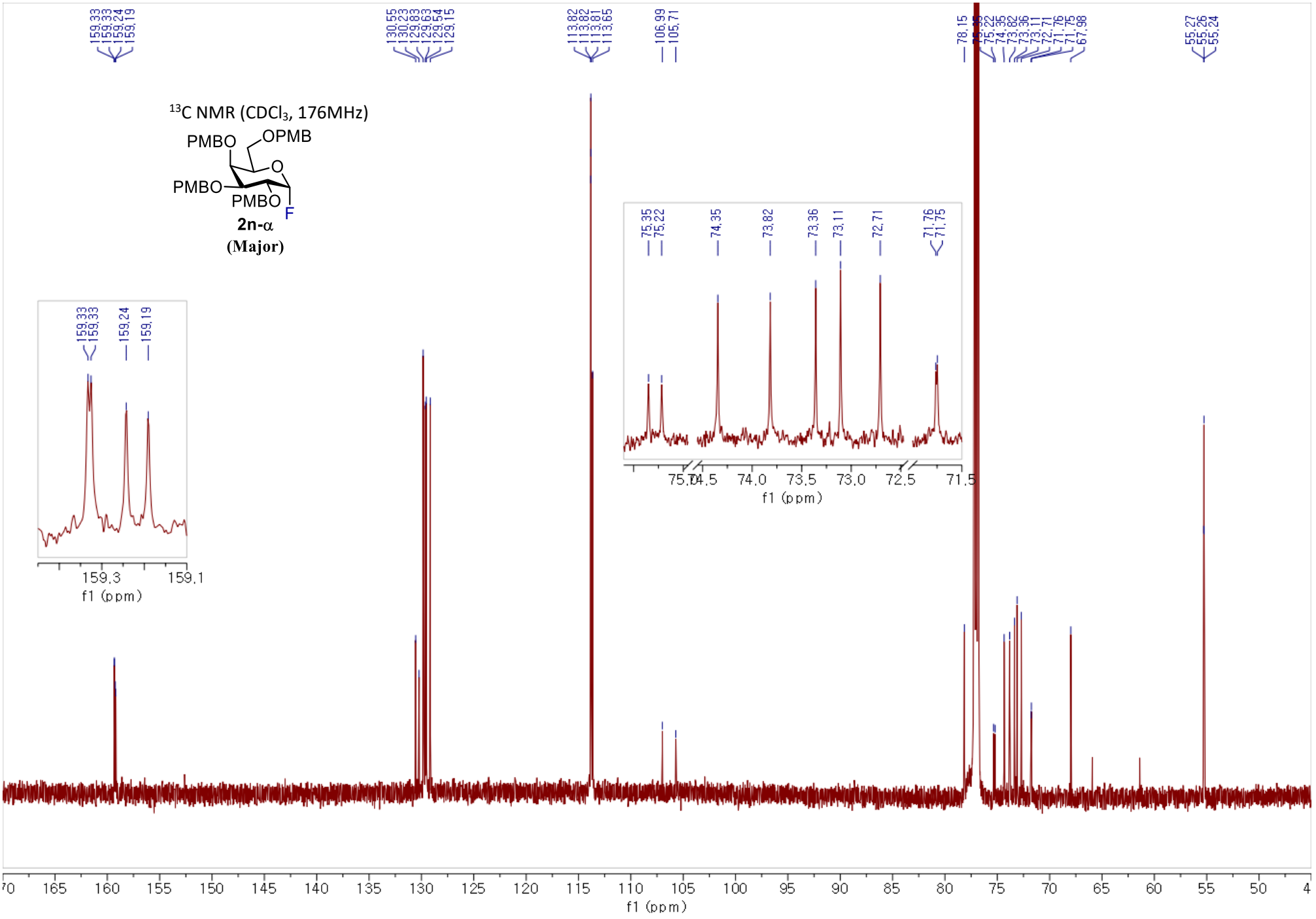


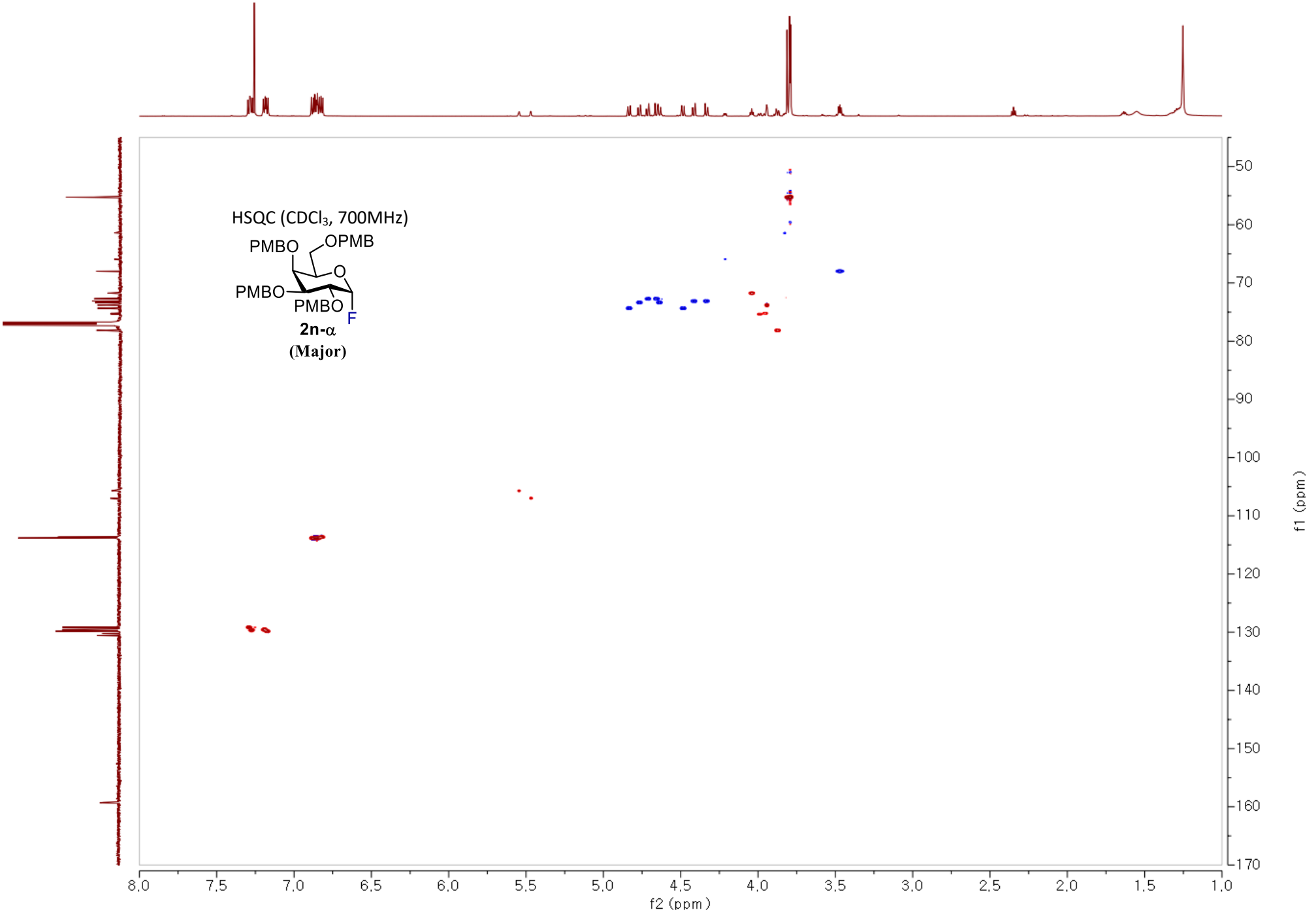

^{13}C NMR ($CDCl_3$, 176MHz)
PMBO
OPMB
O
F
PMBO
PMBO
2n-β
(Major)
159.36
159.29
159.23
159.21
130.54
130.33
130.32
129.79
129.76
129.62
129.16
113.83
113.79
113.75
113.62
110.90
109.68
80.76
80.70
78.81
78.69
77.18
77.00
76.82
74.65
74.64
74.09
73.69
73.66
73.22
72.72
72.51
68.09
55.27
55.26
55.24
159,4
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
2n-β
(Major)
f2 (ppm)
f1 (ppm)

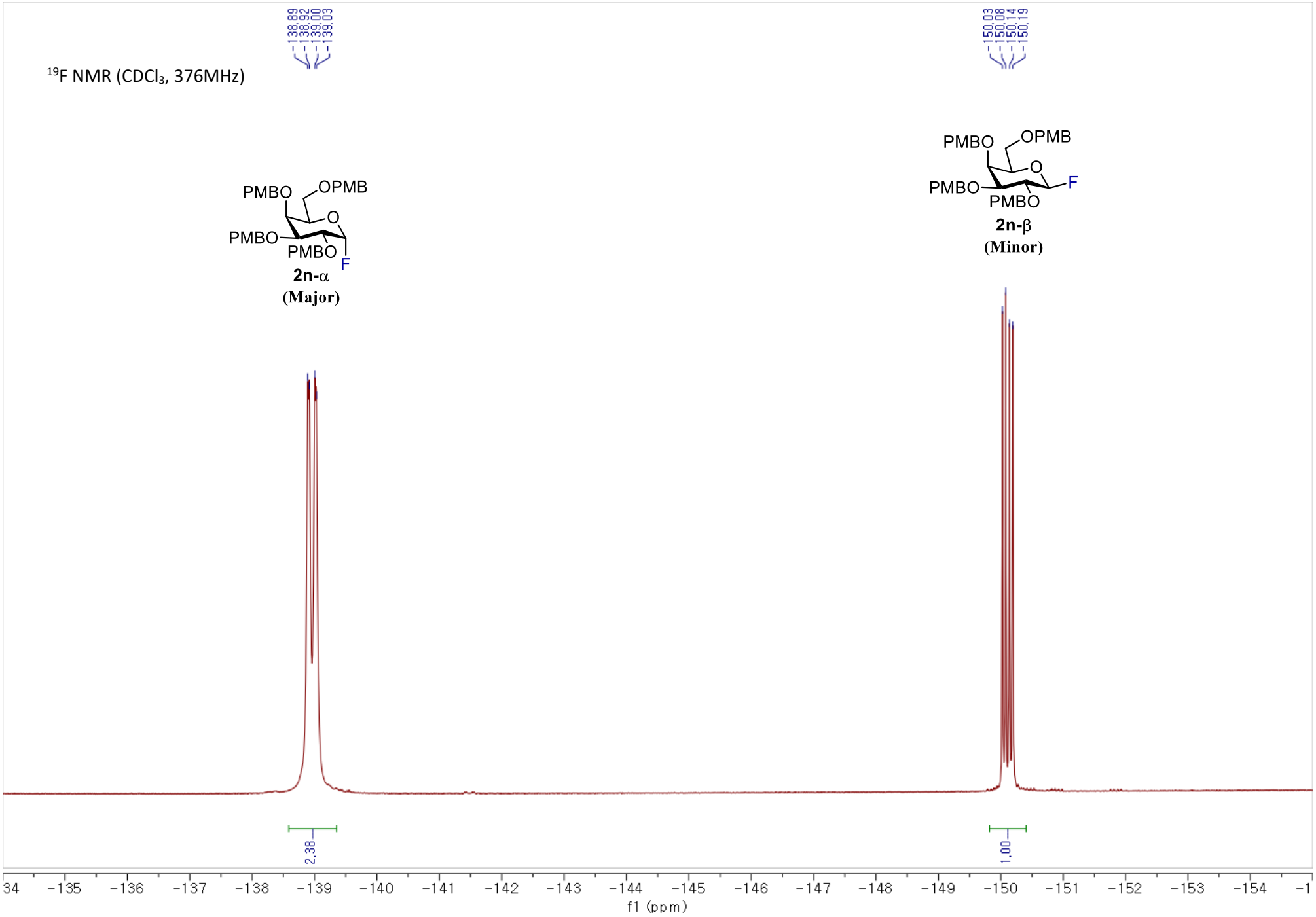
2,3,4,6-Tetrakis-*O*-[(4-methoxyphenyl)methyl]-α-D-galactopyranosyl fluoride (2n-α, Minor diastereomer)



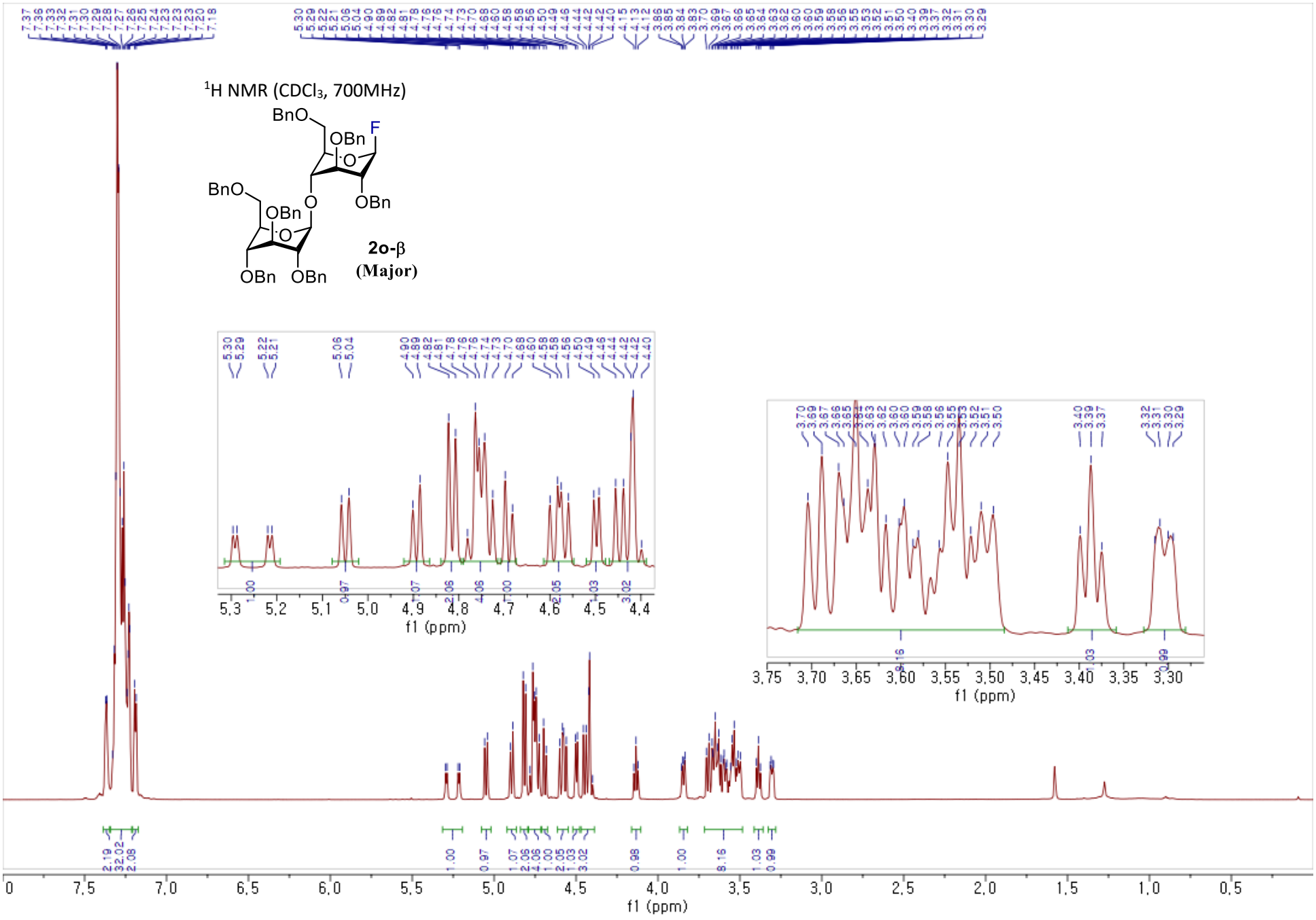

159.33
159.33
159.24
159.19
130.55
130.23
129.83
129.63
129.54
129.15
113.82
113.82
113.81
113.65
106.99
105.71
78.15
75.35
75.22
74.35
73.82
73.36
73.11
72.71
71.76
71.75
67.98
55.27
55.26
55.24
^{13}C NMR ($CDCl_3$, 176MHz)
PMBO
OPMB
O
PMBO
PMBO
F
2n-α
(Major)
159.3
159.1
f1 (ppm)
75.0
74.5
74.0
73.5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

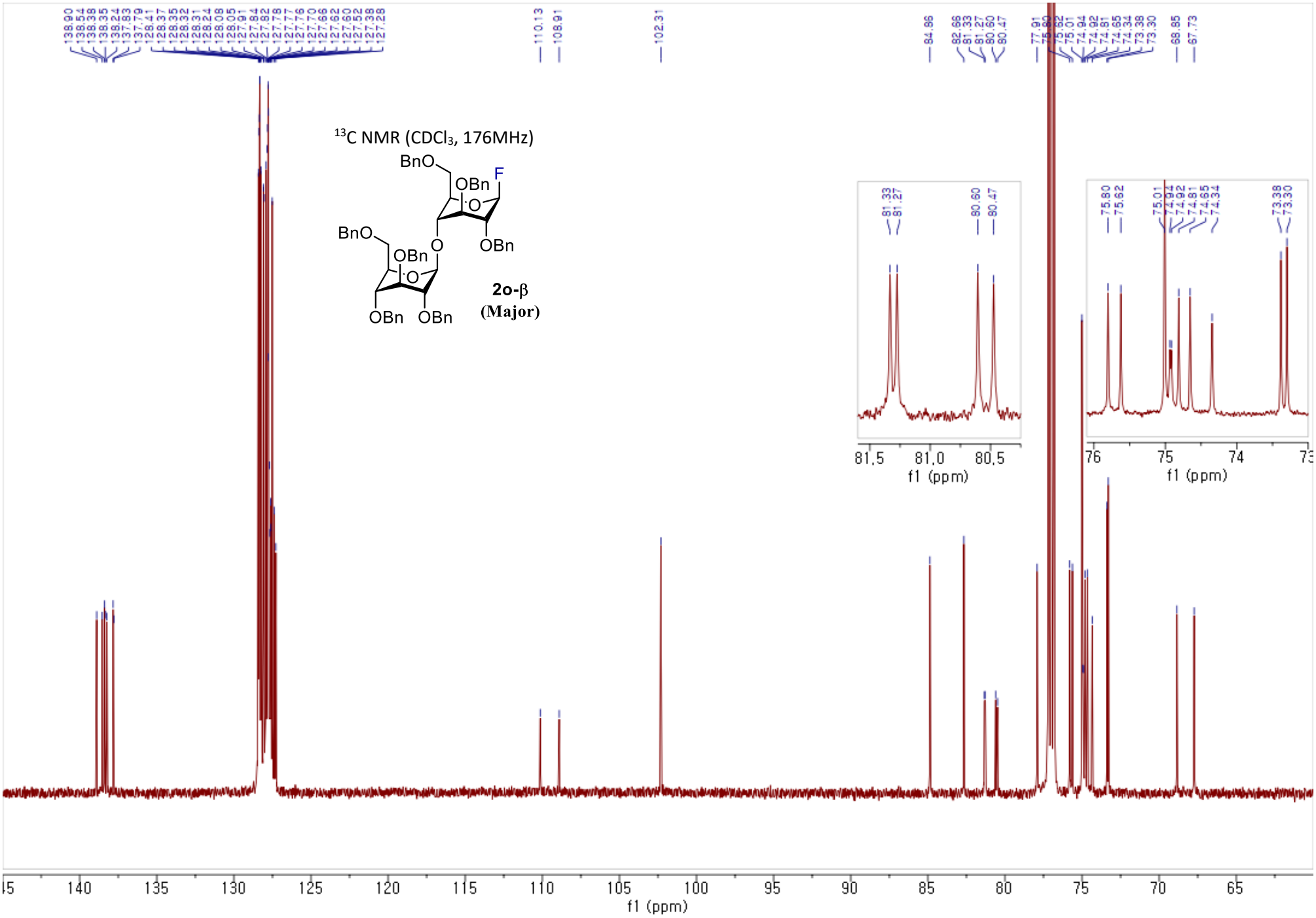

HSQC ($CDCl_3$, 700MHz)
PMBO
OPMB
O
PMBO
PMBO
F
2n-α
(Major)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
50
60
70
80
90
100
110
120
130
140
150
160
170
f1 (ppm)

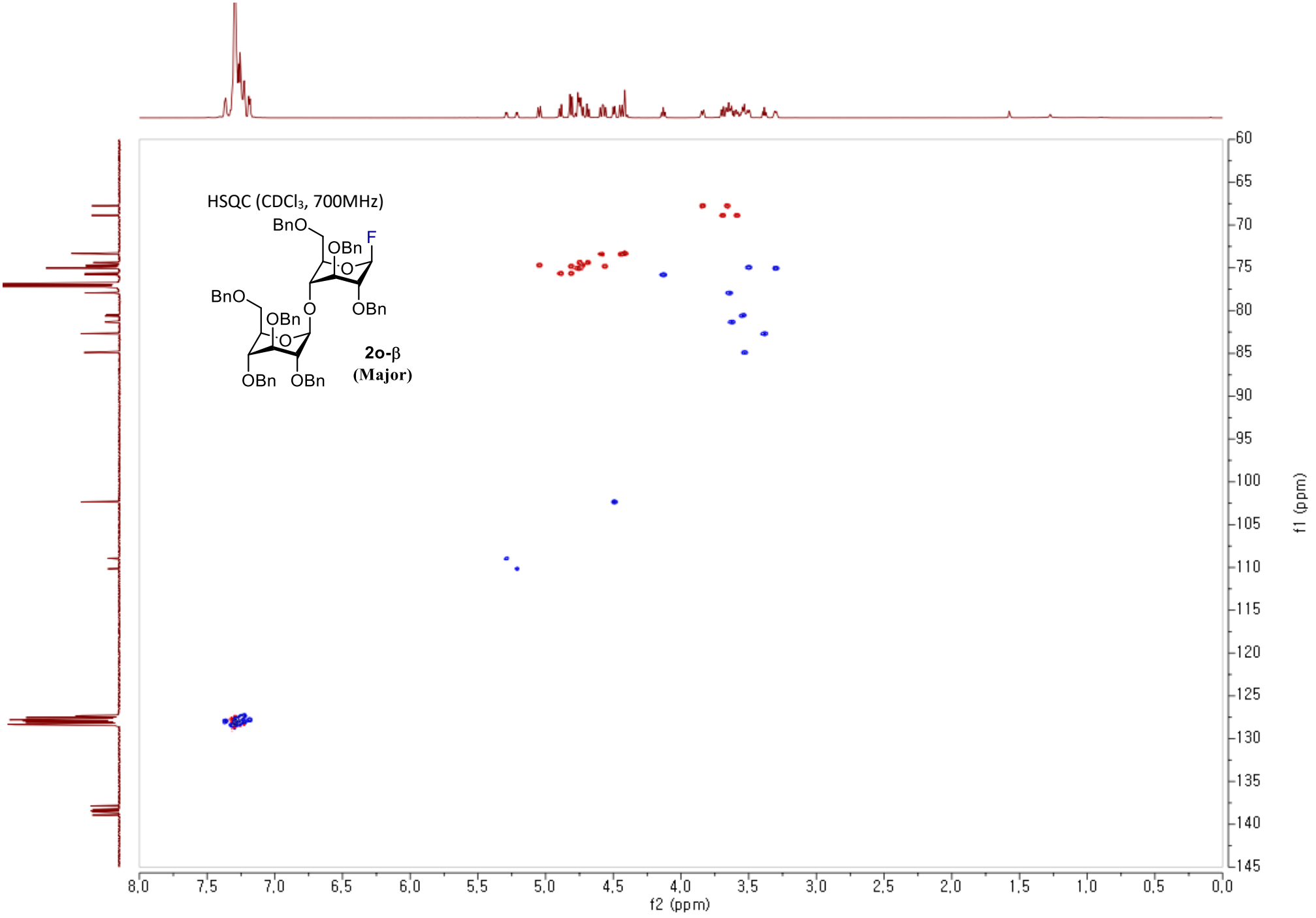
^{19}F NMR ($CDCl_3$, 376MHz)



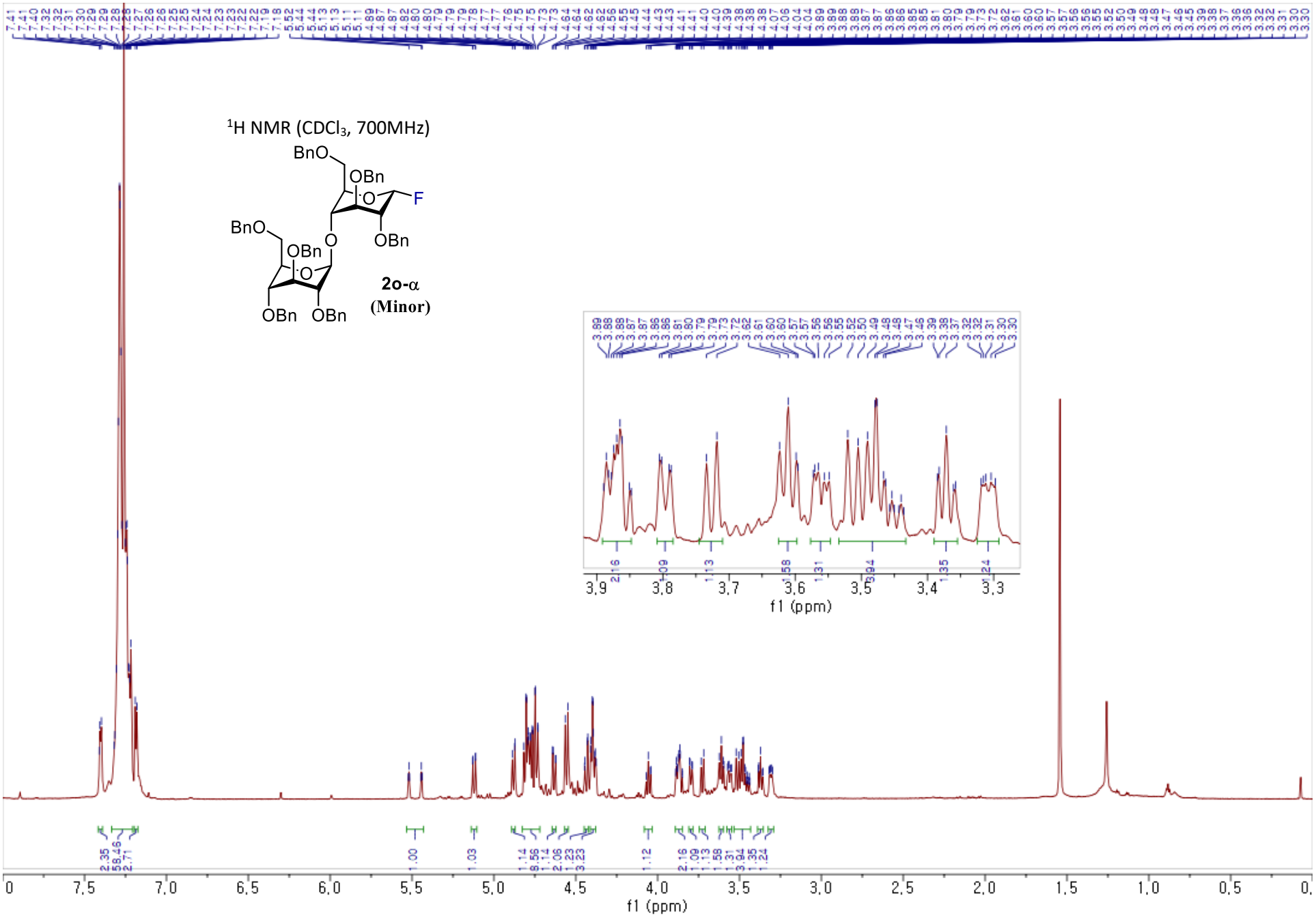
2,3,6-Tris-*O*-(phenylmethyl)-4-*O*-[2,3,4,6-tetrakis-*O*-(phenylmethyl)-β-D-glucopyranosyl]-β-D-glucopyranosyl fluoride (2o-β, Major diastereomer)

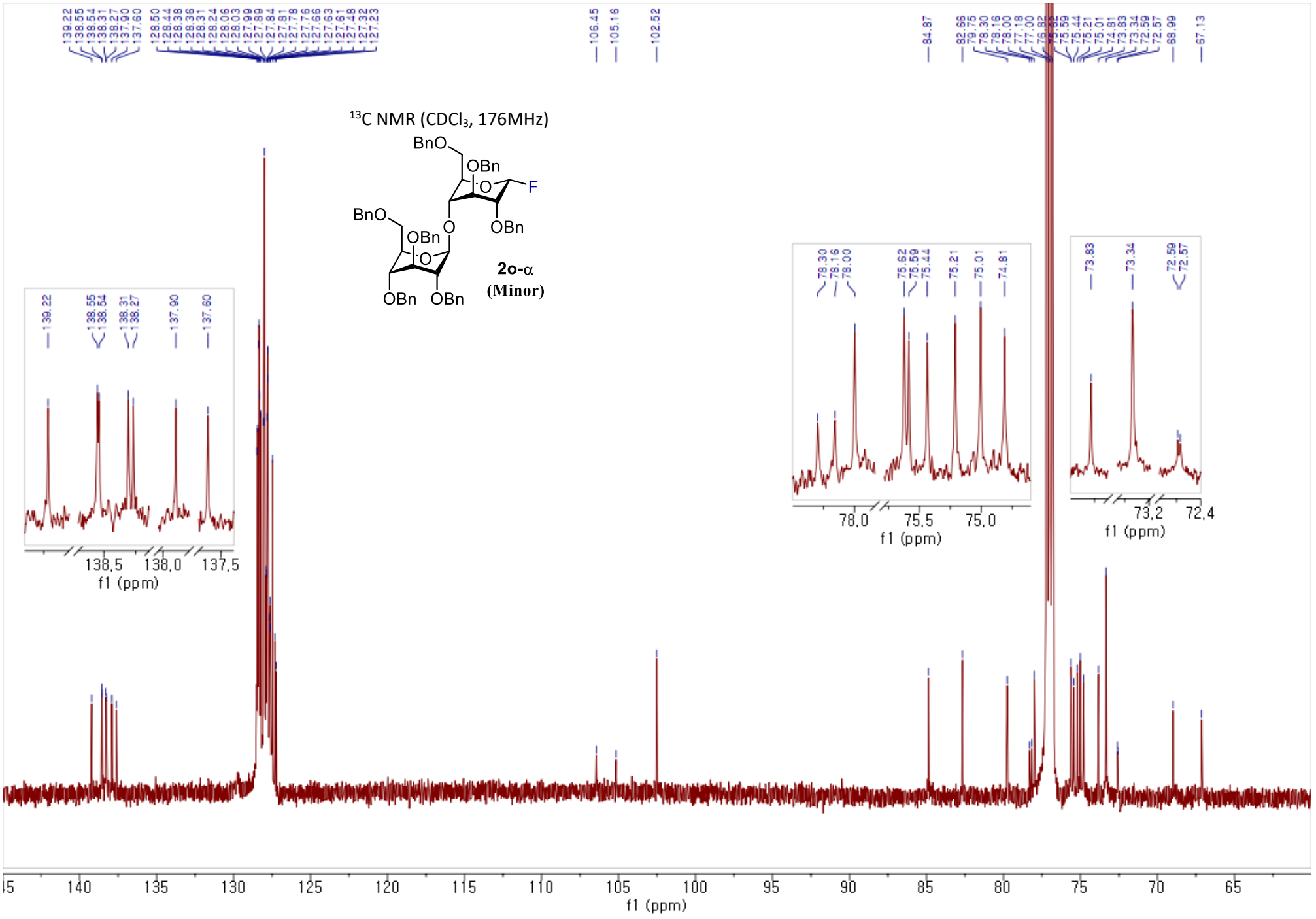


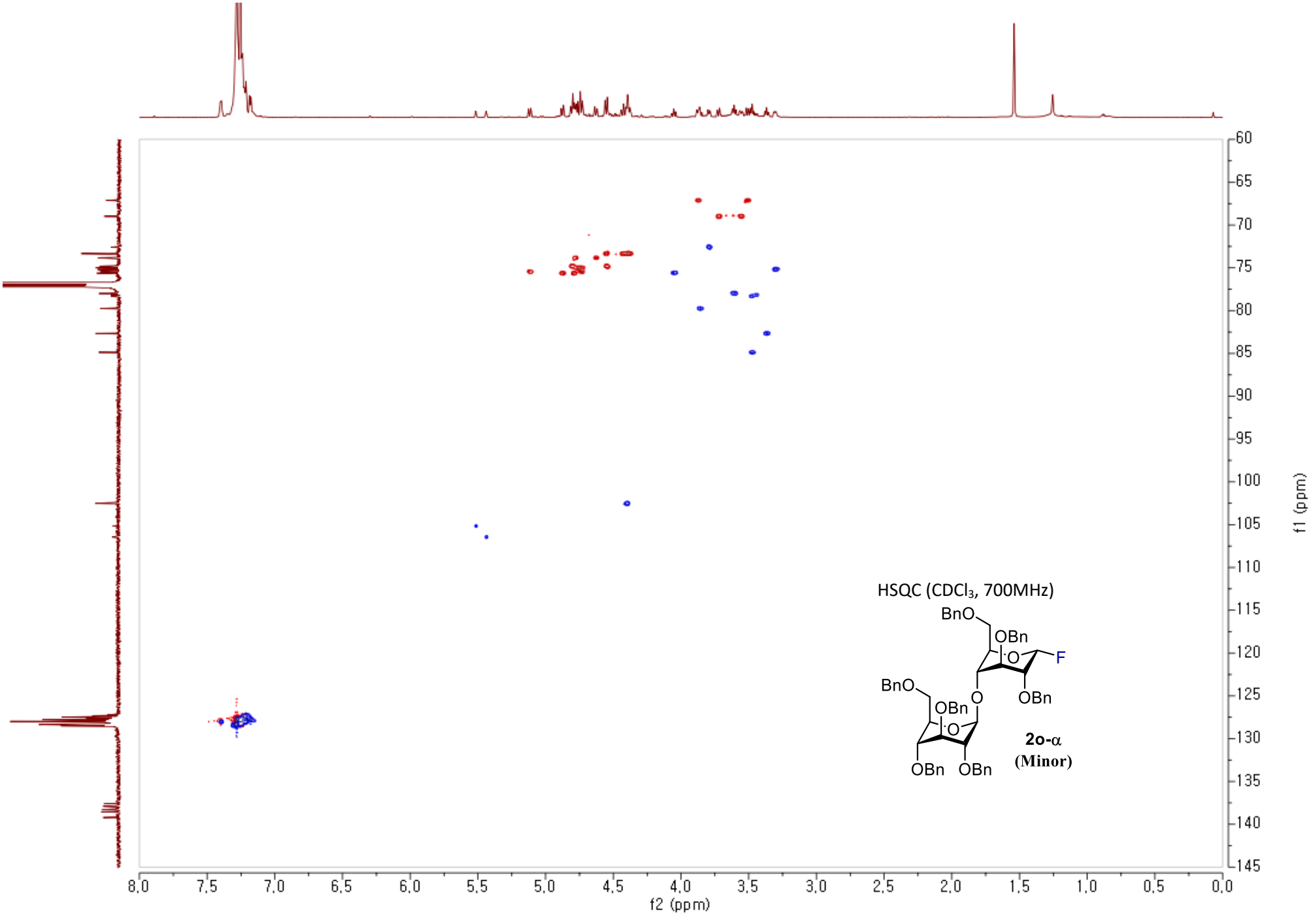

^{13}C NMR ($CDCl_3$, 176MHz)
BnO
OBn
F
O
OBn
BnO
OBn
O
OBn
OBn
OBn
2o-β
(Major)
f1 (ppm)
f1 (ppm)


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

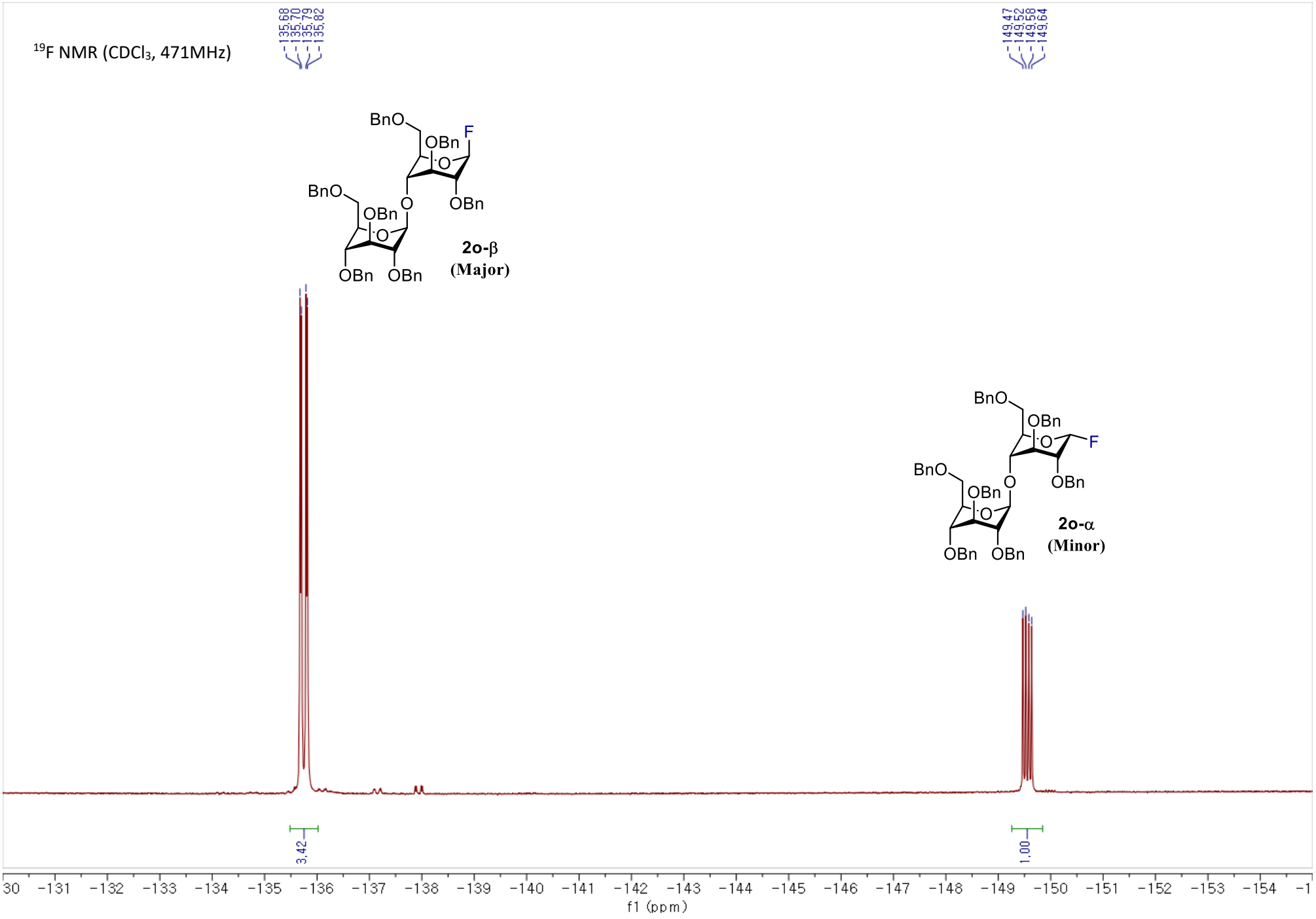
2,3,6-Tris-*O*-(phenylmethyl)-4-*O*-[2,3,4,6-tetrakis-*O*-(phenylmethyl)-β-D-glucopyranosyl]-α-D-glucopyranosyl fluoride (2o-α, Minor diastereomer)



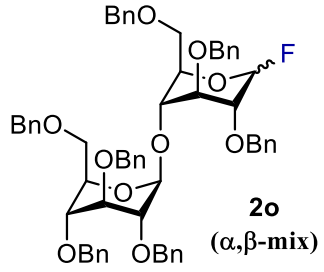

^{13}C NMR ($CDCl_3$, 176MHz)
BnO
OBn
F
BnO
OBn
O
OBn
OBn
OBn
2o-α
(Minor)
f1 (ppm)


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

^{19}F NMR ($CDCl_3$, 471MHz)

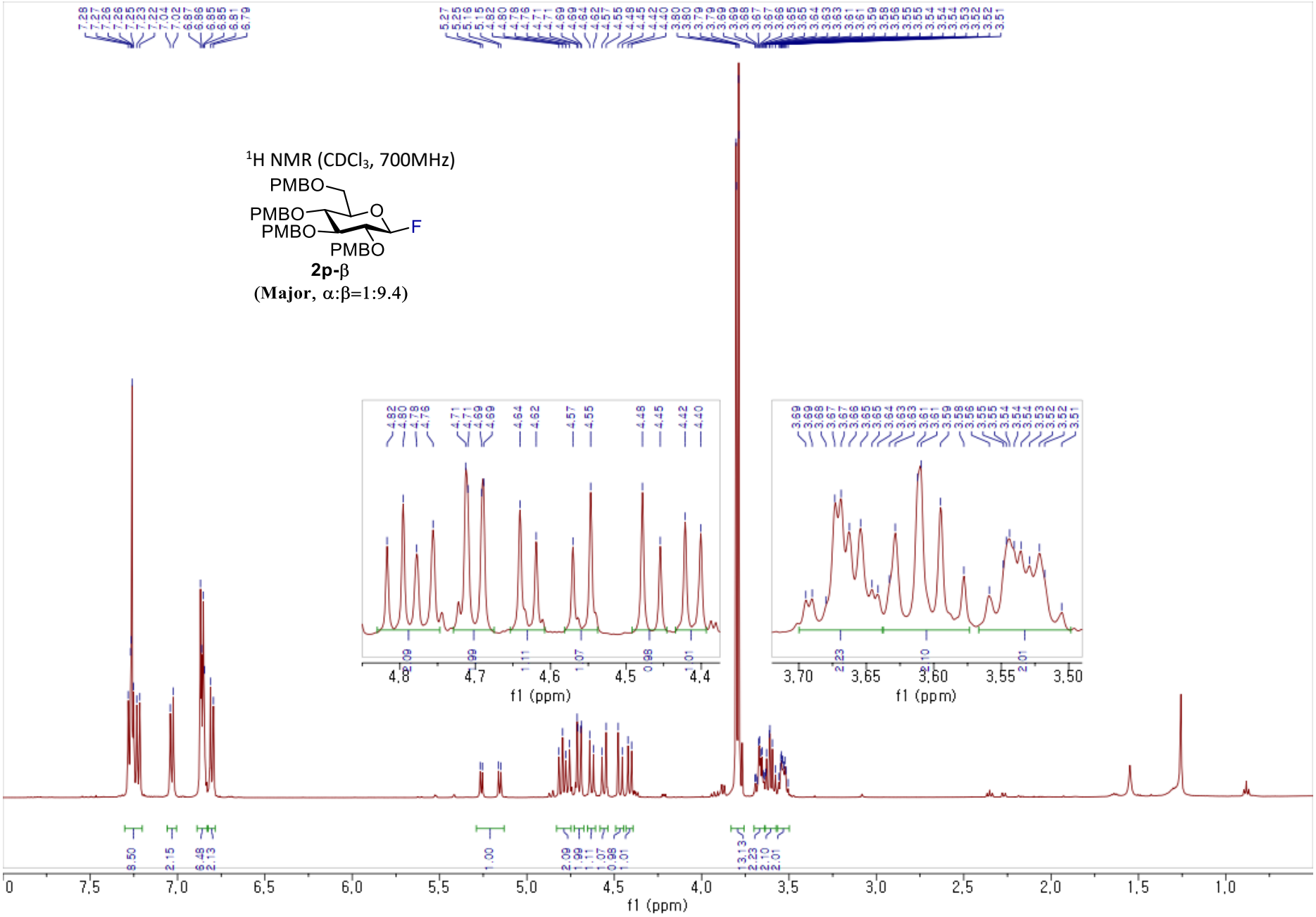


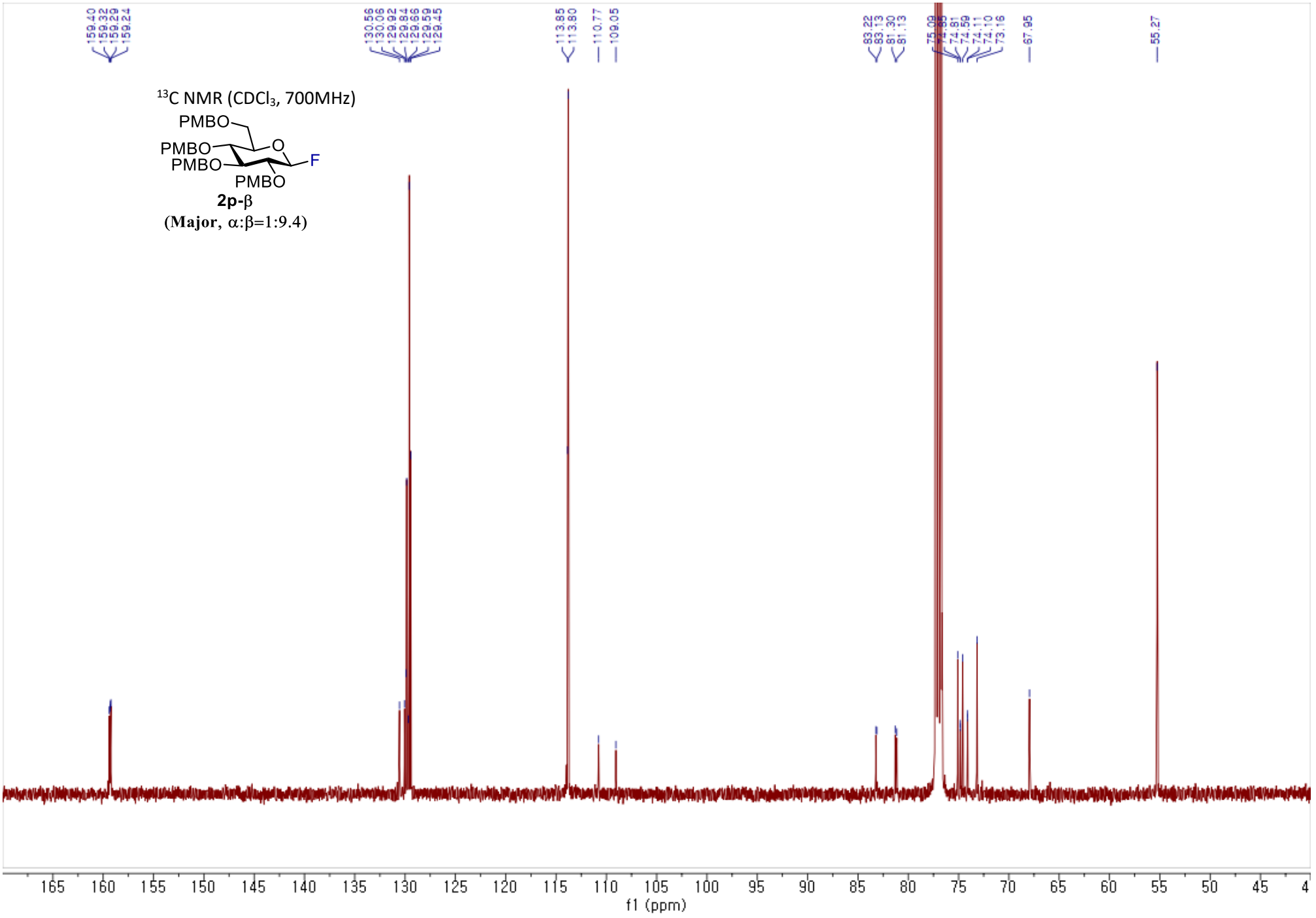
^{1}H NMR ($CDCl_3$, 700MHz)

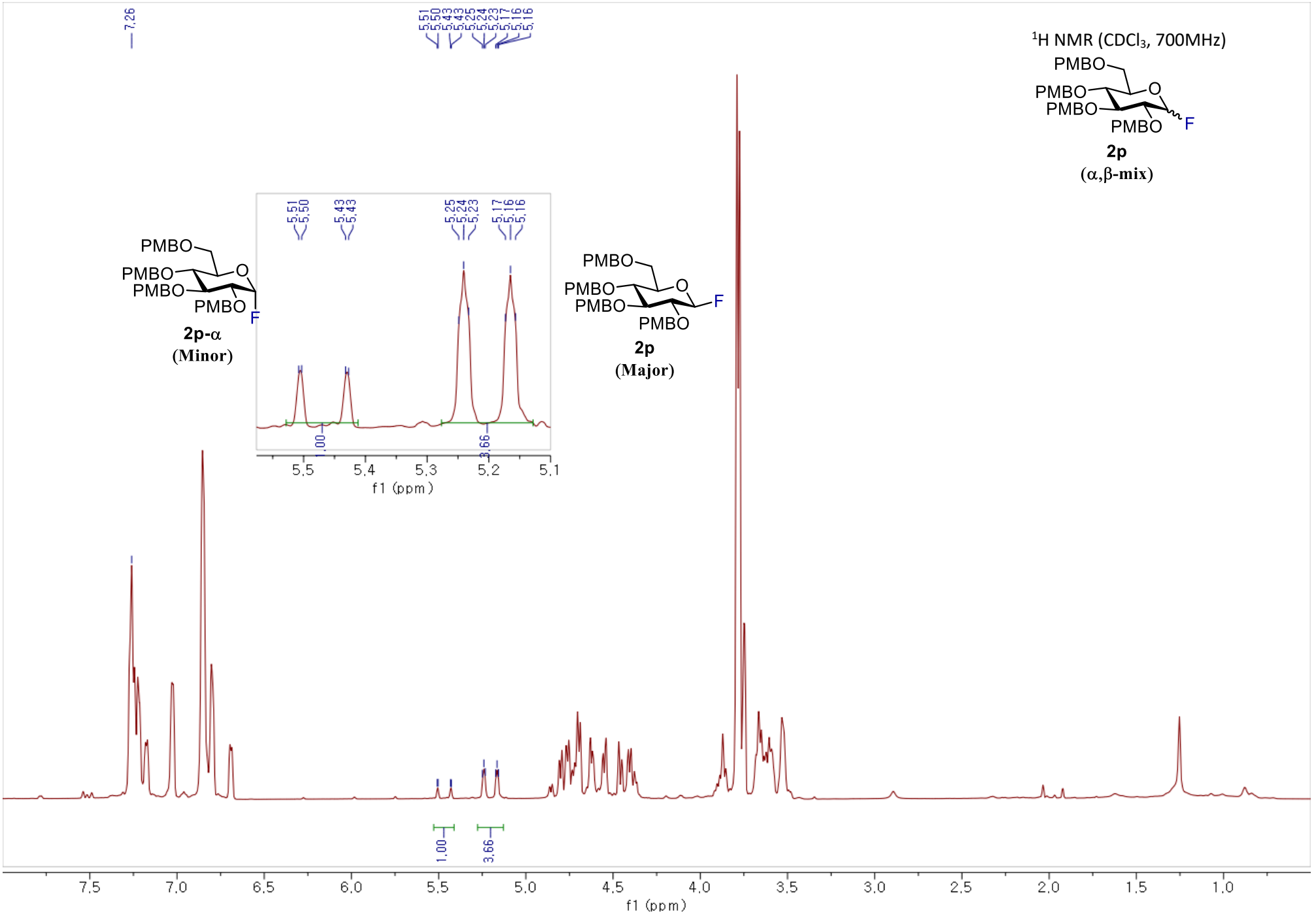


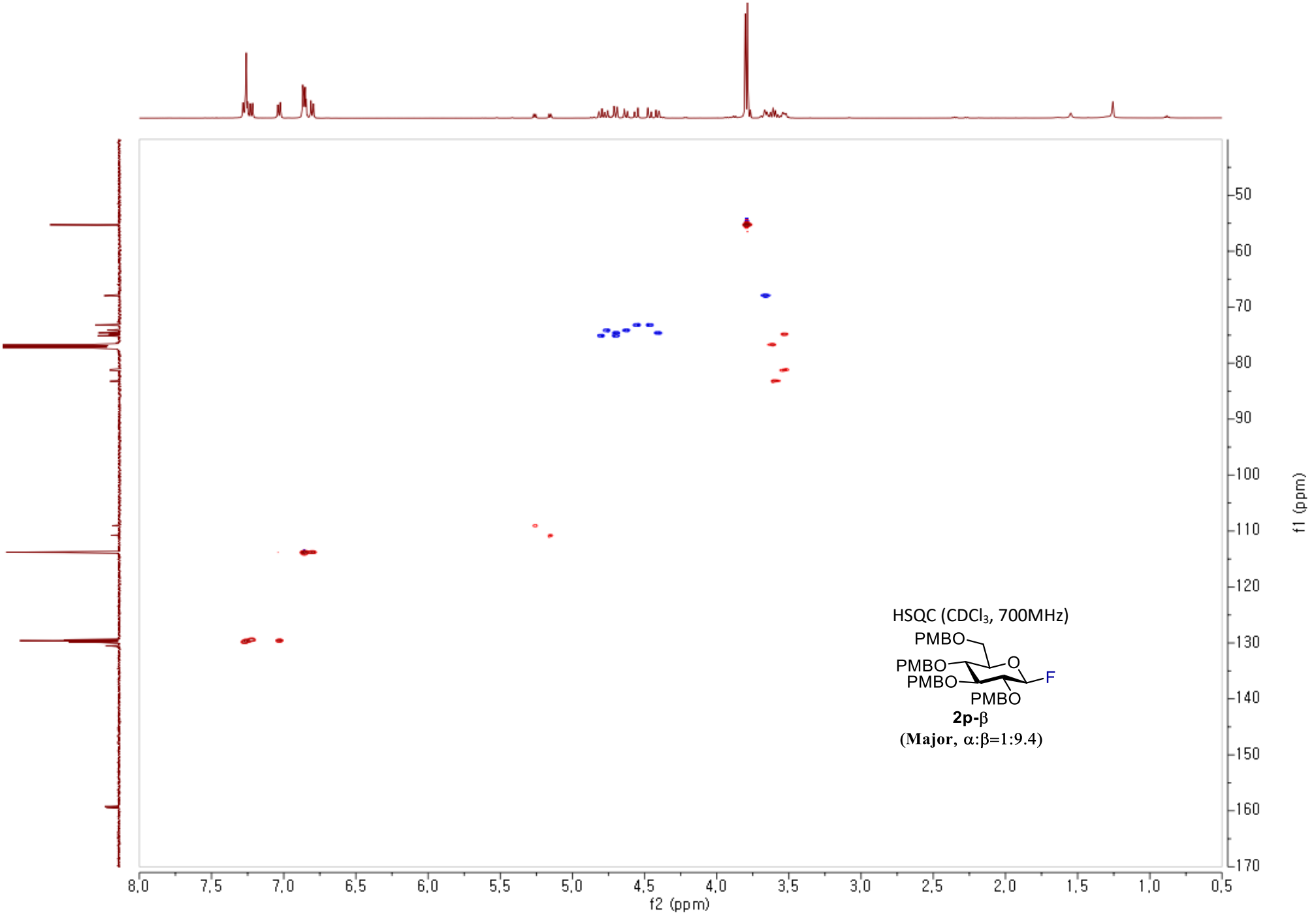
2o
(α,β-mix)

2,3,4,6-Tetrakis-O-[(4-methoxyphenyl)methyl]-β-D-glucopyranosyl fluoride (2p-β, Major product, Isolated as α : β = 1 : 9.4 mixture)

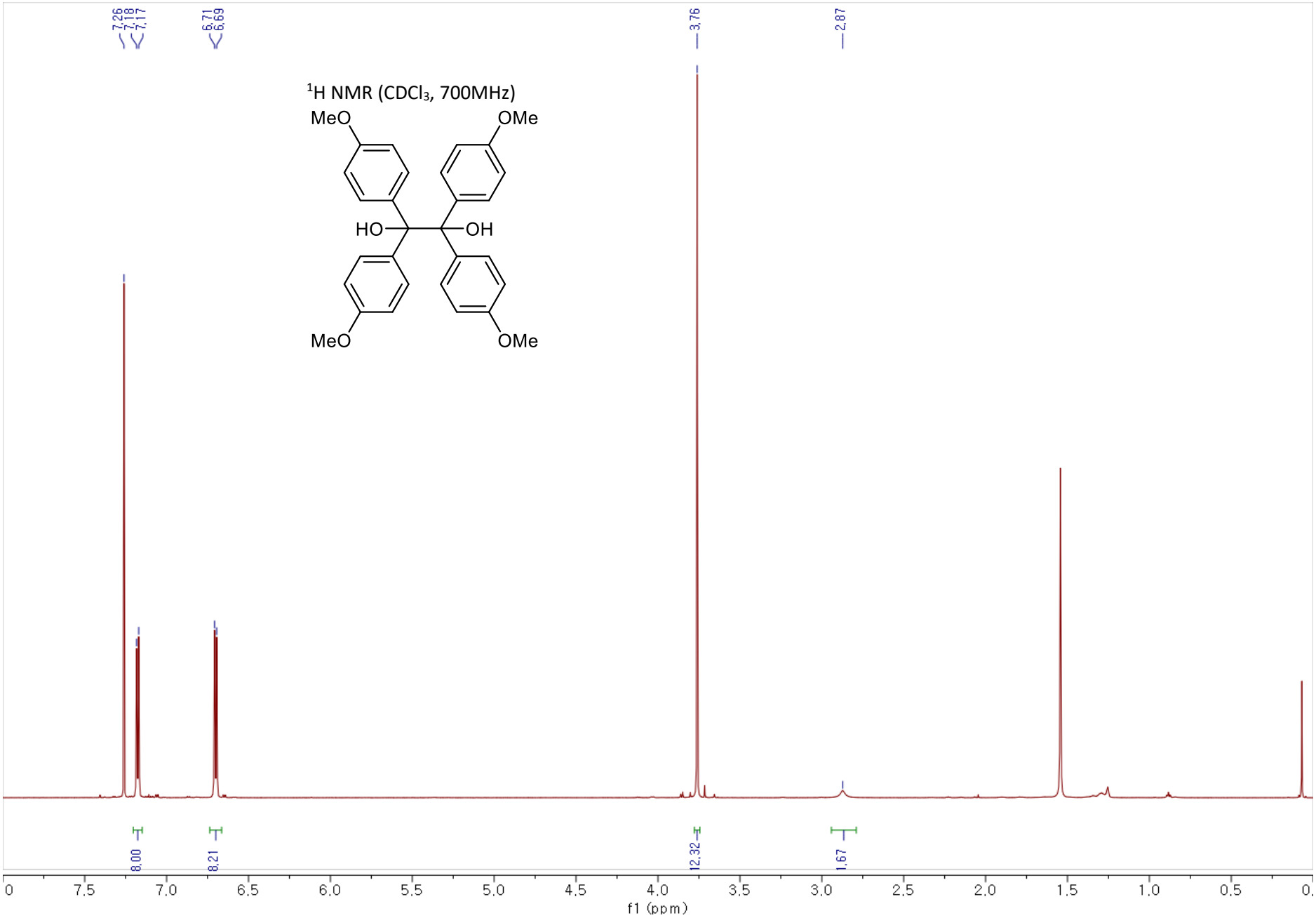


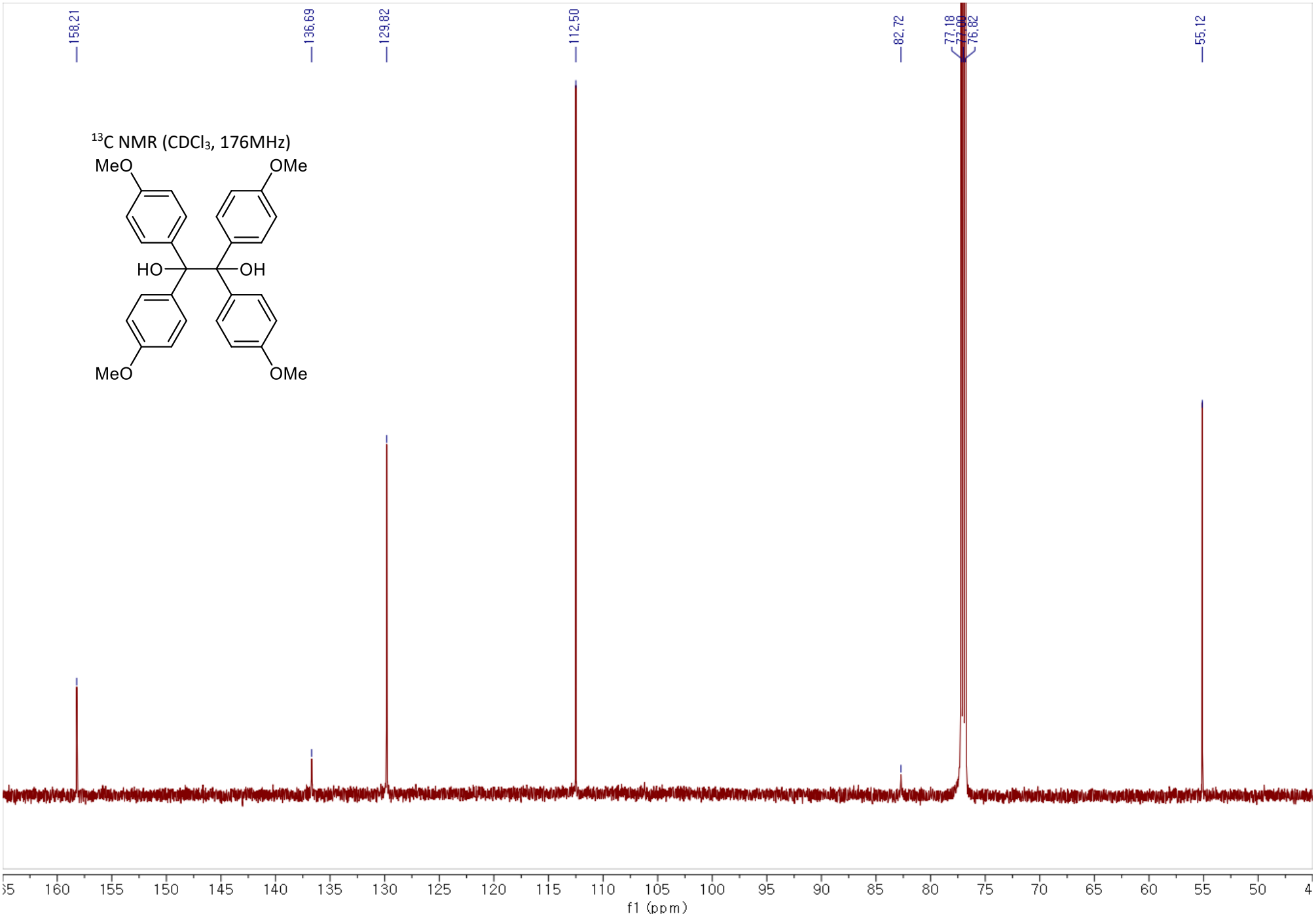

159.40
159.32
159.29
159.24
130.56
130.06
129.92
129.84
129.66
129.59
129.45
113.85
113.80
110.77
109.05
83.22
83.13
81.30
81.13
75.09
74.85
74.81
74.59
74.11
74.10
73.16
67.95
55.27
13C NMR (CDCl3, 700MHz)
PMBO
PMBO
PMBO
PMBO
O
F
2p-β
(Major, α:β=1:9.4)
165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 4
f1 (ppm)

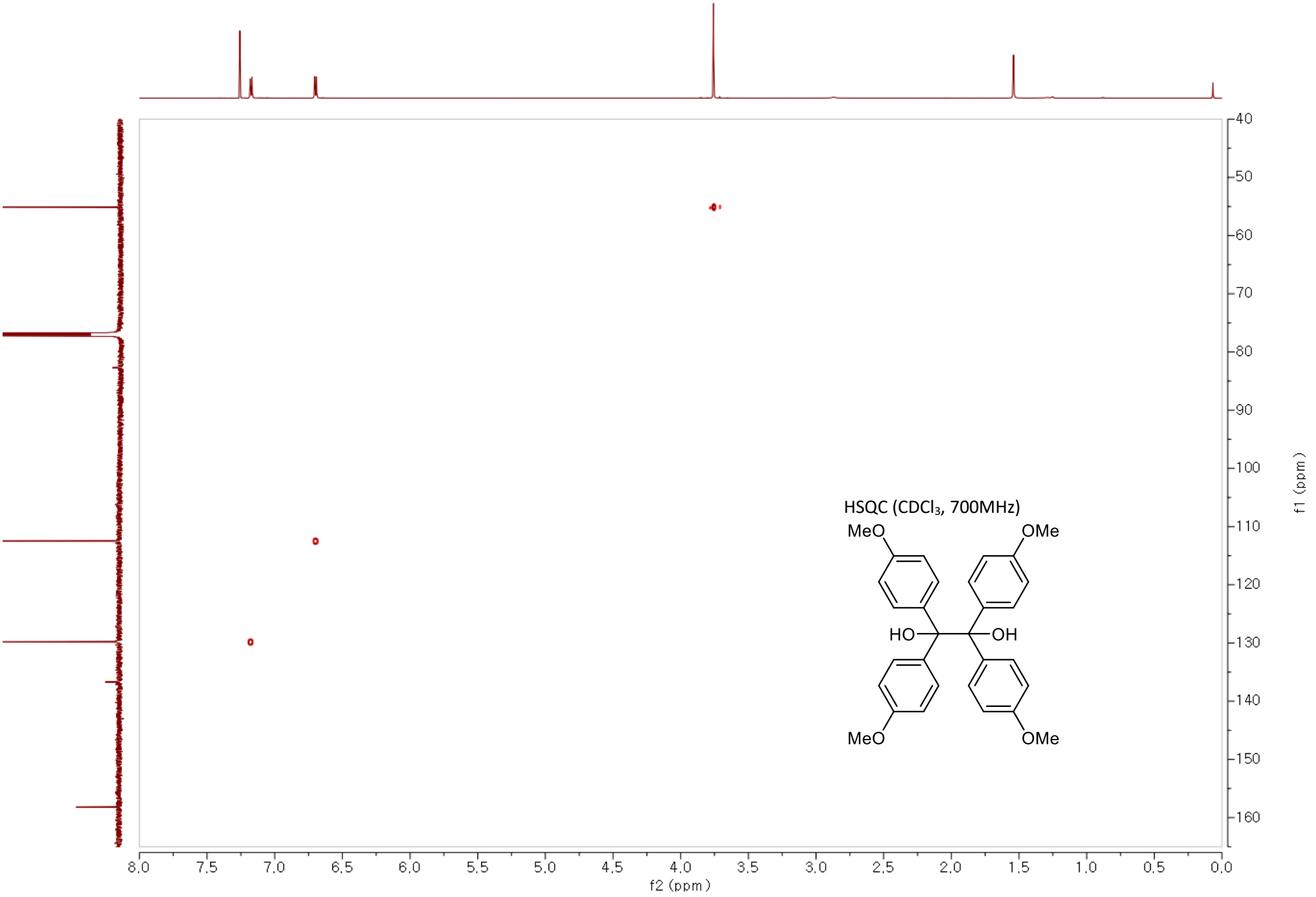

^{1}H NMR ($CDCl_3$, 700MHz)
PMBO
PMBO
PMBO
PMBO
O
F
2p
(α,β-mix)
2p-α
(Minor)
2p
(Major)
7.26
5.51
5.50
5.43
5.43
5.25
5.24
5.23
5.17
5.16
5.16
1.00
3.66
f1 (ppm)


HSQC ($CDCl_3$, 700MHz)
PMBO
PMBO
PMBO
O
F
PMBO
2p-β
(Major, α:β=1:9.4)
f2 (ppm)
f1 (ppm)

1,1,2,2-Tetrakis(*p*-methoxyphenyl)-1,2-ethanediol




158.21
136.69
129.82
112.50
82.72
77.18
77.00
76.82
55.12
^{13}C NMR ($CDCl_3$, 176MHz)
MeO
OMe
HO
OH
MeO
OMe
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)
MeO
OMe
HO
OH
MeO
OMe
f2 (ppm)
f1 (ppm)