Supporting information for

Protecting group-free approach towards synthesizing *C*-glycosides through glycosyl dithiocarbamates

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1. General experimental and procedures

Commercially available compounds were used without further purification unless otherwise stated. The exact reaction conditions are given in the respective procedure. Flash silica gel column chromatography was performed with E. Merck silica gel 60. Reactions were monitored by analytical thin-layer chromatography on silica gel 60 F254 precoated on aluminum plates (E. Merck). NMR spectra were recorded on Bruker AV-400 or Bruker DRX-500 spectrometer at room temperature. Chemical shifts δ are given in ppm on a scale downfield from TMS, and the coupling constants *J* are in Hz. The signal patterns are indicated as follows: s, singlet; d, doublet; t, triplet; dd, doublet of doublet; m, multiplet. Assignments of ^{1}H and ^{13}C NMR spectra were performed by H-H COSY and HSQC experiments. ESI-MS spectra were recorded on Bruker solariX 9.4T. The product yields by NMR analysis in D_2O were determined by using sodium mesitylenesulfonate as an internal standard. NMR results in $CDCl_3$ were obtained by using 1,3,5-trimethoxybenzene as an internal standard.

General procedure A

-Synthesis of C-glycosides by the reaction of GDTC and alkenes (AIBN-Bu_3SnH system)-

To a solution of glycosyl dithiocarbamate (GDTC) (0.1 mmol), alkene (0.5 mmol) and tributyltin hydride (0.2 mmol, 48 μL) was added AIBN (8.2 mg, 0.05 mmol). The reaction mixture was heated to 75 ºC under argon atmosphere. TLC indicated the formation of a major product and consumption of starting substrate. The reaction mixture was cooled to room temperature and concentrated *in vacuo*. The residue was purified by flash column chromatography (eluent: chloroform/methanol). Freeze-drying gave the desired product as a white solid.

General procedure B

-Synthesis of allyl C-glycosides by the reaction of GDTC and allyltributyltin-

To a solution of a GDTC (0.1 mmol) and allyltributyltin (1.0 mmol, 310 μL) was added AIBN (8.2 mg, 0.05 mmol). The reaction mixture was heated to 75 ºC under argon. TLC indicated the formation of a major product and consumption of starting substrate. The reaction mixture was cooled to room temperature and concentrated *in vacuo*. The residue was purified by flash column chromatography (eluent: chloroform/methanol). Freeze-drying gave the desired product as a white solid. Stereoselectivity was confirmed by comparing the corresponding spectra data with that reported in the literature. The isolated product would be *O*-acetylated if required.

General procedure C

-C-Glycosylation with protected GDTCs-

To a solution of protected GDTC (0.1 mmol) and allyltributyltin (0.5 mmol, 155 μL) in toluene (1.0 mL) was added AIBN (8.2 mg, 0.05 mmol). The reaction mixture was heated to 75 ºC under argon. TLC indicated the formation of a major product and consumption of starting substrate. The reaction mixture was cooled to room temperature and concentrated in vacuo. The reaction mixture was subjected to the NMR analysis directly.

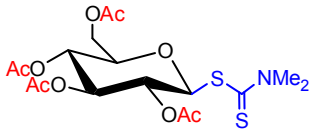
2. Experimental data

Synthesis of unprotected glycosyl dithiocarbamates (GDTC)

The unprotected glycosyl dithiocarbamates **1** was prepared according to our reported method. [1]

Synthesis of protected glycosyl dithiocarbamate

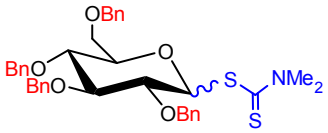
2,3,4,6-tetra-*O*-acetyl *N,N*-dimethyl *S*-β-glucopyranosyl dithiocarbamate (**Ac-GDTC, 12**)



Acetic anhydride (4 mmol, 378 μL) was added to a solution of *N,N*-dimethyl *S*-β-glucopyranosyl dithiocarbamate **1** (141 mg, 0.5 mmol) in pyridine (3 mL) at 0 ºC under argon. The resulting mixture was stirred for 3.5 hours at room temperature. Upon completion, the reaction mixture was diluted with CH_2Cl_2 and washed with sodium bicarbonate solution and brine. After concentration *in vacuo*, the residual was purified by silica gel column chromatography (eluent: hexane/ethyl acetate=1/1) to give 2,3,4,6-tetra-*O*-acetyl *N,N*-dimethyl *S*-β-glucopyranosyl dithiocarbamate (180 mg, 0.4 mmol, 80%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.79 (1H, d, *J*=10.1 Hz, H-1), 5.34-5.27 (m, 2H, H-2, H-3), 5.09 (1H, t, *J*=9.6×2 Hz, H-4), 4.23 (1H, dd, *J*=12.3, 4.7 Hz, H-6a), 4.11-4.08 (1H, m, H-6b), 3.88-3.85 (1H, m, H-5), 3.50 (3H, s, -NMe), 3.31 (3H, s, -NMe), 2.03-1.98 (12H, m, -Ac × 4). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.4 (C=S), 170.7, 170.0, 169.6, 169.5 (4C, C=O), 87.5 (C-1), 76.4, 74.5, 68.7, 68.3, 61.8 (5C, sugar), 45.7, 41.7 (2C, -NMe), 20.7, 20.6 (-Ac).

2,3,4,6-tetra-*O*-benzyl *N,N*-dimethyl *S*-glucopyranosyl dithiocarbamate (**Bn-GDTC, 16**)



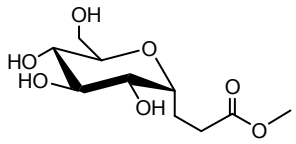
2-Chloro-1,3-dimethylimidazolinium chloride (DMC) (138 mg, 0.8 mmol) was added to a mixture of 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (216 mg, 0.4 mmol), triethylamine (342 μL, 2.4 mmol), and sodium dimethyldithiocarbamate dihydrate (116 mg, 0.8 mmol) in DMF/Water/CH_2Cl_2 (4 mL/2 mL/2 mL), and the resulting mixture was stirred for 1.0 h at 0 ºC. DMC (69 mg, 0.4 mmol) was added to the reaction mixture, and the solution was stirred for another one hour at 0 ºC. Thereafter, the reaction mixture was diluted with CH_2Cl_2 and washed with water and brine. After concentration *in vacuo*, the residue was purified by silica gel column chromatography (eluent: hexane/ethyl acetate=4/1) to give 2,3,4,6-tetra-*O*-benzyl *N,N*-dimethyl *S*-glucopyranosyl dithiocarbamate (142 mg, 0.22 mmol, 55%, α/β=1/9).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.11 (20H, m, -Ph×4), 6.99 (0.1H, d, *J*=5.5 Hz, H-1α), 5.72 (0.9H, d, *J*=10.3 Hz, H-1β), 5.02-4.45 (8H, m, -C*H*$_2$Ph×4), 4.03 (0.1H, dd, *J*=9.8, 5.5 Hz, H-2α), 3.88-3.63 (5.9H, m, sugar-H), 3.58 (0.3H, s, -Me), 3.54 (2.7H, s, -Me), 3.42 (0.3H, s, -Me), 3.33 (2.7H, s, -Me). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0 (C=S), 138.7-127.7 (-Ph×4), 90.7 (C-1α), 89.3 (C-1β), 87.2, 84.1, 79.8, 79.3, 78.7, 77.8, 75.9, 75.2, 75.0, 74.6, 73.6, 73.5, 72.3,

68.6, 45.6 (Me), 41.7 (Me).

Preparation of *C*-alkyl glycosides

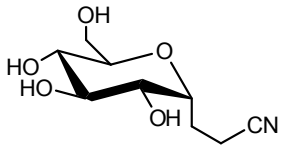
methyl 3-(α-D-glucopyranosyl)-propanoate (MA-α-Glc, 2)



This compound was prepared according to the general procedure **A** using *N,N*-dimethyl β-D-glucopyranosyl dithiocarbamate (0.1 mmol, 28.3 mg) and methyl acrylate (0.5 mmol, 45μL). Silica gel column chromatography (eluent: chloroform/methanol=5/1) and freeze-drying gave the desired product as a white solid (15 mg, 0.06 mmol).

^{1}H NMR (400 MHz, D_2O) δ 3.90 (1H, ddd, *J*=11.0, 6.1, 4.4 Hz, H-1), 3.79-3.76 (1H, m, H-6a), 3.71-3.65 (5H, m, H-2, -OC$\underline{H}_3$, H-6b), 3.63-3.58 (1H, m, H-3), 3.49-3.44 (1H, m, H-5), 3.35-3.30 (1H, m, H-4), 2.55-2.39 (2H, m, $CH_2C\underline{H}_2C$=O), 2.04-1.89 (2H, m, C$\underline{H}_2CH_2C$=O). ^{13}C NMR (100 MHz, D_2O) δ 176.6 (C=O), 75.2 (C-1), 73.1 (C-3), 72.5 (C-5), 71.0 (C-2), 70.1 (C-4), 60.9 (C-6), 52.2 (O$\underline{C}H_3$), 29.9 ($CH_2\underline{C}H_2C$=O), 19.4 ($\underline{C}H_2CH_2C$=O). The stereochemistry of the anomeric center was confirmed by detecting the signal derived from H-2 (5.09 ppm, $J_{2,1}$=5.7 Hz) of 2,3,4,6-tetra-*O*-acetylated product in $CDCl_3$.[2]

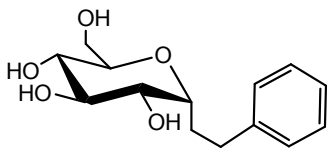
3-(α-D-glucopyranosyl)-propionitrile (AN-α-Glc, 4)



This compound was prepared according to the general procedure **A** using *N,N*-dimethyl β-D-glucopyranosyl dithiocarbamate (0.1 mmol, 28.3 mg) and acrylonitrile (0.5 mmol, 33 μL). Preparative HPLC (column: ODS-3; eluent: H_2O; flow rate: 6 mL/min; column temperature: 30 ° C; detection: RI) and freeze-drying gave the desired product as a white solid (15 mg, 0.069 mmol).

^{1}H NMR (400 MHz, D_2O) δ 4.10-4.04 (1H, m, H-1), 3.85-3.81 (1H, m, H-6a), 3.76-3.68 (2H, m, H-2, H-6b), 3.61-3.65 (1H, m, H-3), 3.51-3.46 (1H, m, H-5), 3.39-3.34 (1H, m, H-4), 2.65-2.49 (2H, m, -$CH_2C\underline{H}_2$CN), 2.15-1.96 (2H, m, -C$\underline{H}_2CH_2$CN). ^{13}C NMR (100 MHz, D_2O) δ 121.1 (C≡N), 74.6 (C-1), 73.0 (C-3), 72.6 (C-5), 70.7 (C-2), 70.0 (C-4), 60.7 (C-6), 20.0 ($\underline{C}H_2CH_2$CN), 13.0 ($CH_2\underline{C}H_2$CN). The stereochemistry of the anomeric center was confirmed by detecting the signal derived from H-2 (5.10 ppm, $J_{2,1}$=5.3 Hz) of per-*O*-acetylated product.[3]

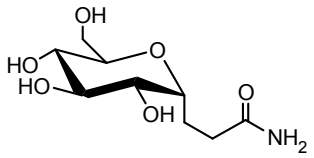
1-(α-D-glucopyranosyl)-2-phenyl ethane (St-α-Glc, 5)



This compound was prepared according to the general procedure **A** in 1,4-dioxane (1.0 mL) using *N,N*-dimethyl β-D-glucopyranosyl dithiocarbamate (0.1 mmol, 28.3 mg) and styrene (0.5 mmol, 58 μL). Silica gel column chromatography (eluent: chloroform/methanol=5/1) and freeze-drying gave the desired product as a white solid (6.5 mg, 0.025 mmol).

^{1}H NMR (400 MHz, D_2O) δ 7.37-7.23 (5H, m, Ph), 3.99-3.94 (1H, ddd, *J*=11.7, 5.6, 3.5 Hz, H-1), 3.82-3.78 (1H, m, H-6a), 3.69-3.59 (3H, m, H-6b, H-2, H-3), 3.57-3.53 (1H, m, H-5), 3.35-3.30 (1H, m, H-4), 2.81-2.58 (2H, m, $CH_2C\underline{H}_2Ph$), 2.05-1.86 (2H, m, $C\underline{H}_2CH_2Ph$). ^{13}C NMR (100 MHz, D_2O) δ 142.0 (Ph), 128.6 (Ph), 126.1 (Ph), 75.1 (C-1), 73.3 (C-3), 72.4 (C-5), 71.2 (C-2), 70.3 (C-4), 61.0 (C-6), 30.7 ($CH_2\underline{C}H_2Ph$), 25.5 ($\underline{C}H_2CH_2Ph$). The stereochemistry of the anomeric center was confirmed by detecting the signal derived from the H-2 (5.09 ppm, $J_{2,1}$=5.8 Hz) of per-*O*-acetylated product.[4]

3-(α-D-glucopyranosyl)-propanamide (AA-α-Glc, 6)

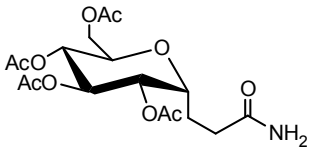


This compound was prepared according to the general procedure **A** in dimethylformamide (DMF, 1.0 mL) using *N,N*-dimethyl β-D-glucopyranosyl dithiocarbamate (0.1 mmol, 28.3 mg) and acrylamide (0.5 mmol, 36 mg). Silica gel column chromatography (eluent: acetonitrile/water=5/1) and freeze-drying gave the desired product as a white solid (14 mg, 0.06 mmol, purity: 88%).

^{1}H NMR (400 MHz, D_2O) δ 4.00-3.94 (1H, m, H-1), 3.83-3.79 (1H, m, H-6a), 3.72-3.59 (3H, m, H-2, H-6b, H-3), 3.52-3.47 (1H, m, H-5), 3.35-3.30 (1H, m, H-4), 2.44-2.25 (2H, m, $CH_2C\underline{H}_2C$=O), 2.04-1.86 (2H, m, $C\underline{H}_2CH_2C$=O). ^{13}C NMR (100 MHz, D_2O) δ 179.1 (C=O), 75.2 (C-1), 73.1 (C-3), 72.5 (C-5), 71.0 (C-2), 70.2 (C-4), 60.9 (C-6), 31.1($CH_2\underline{C}H_2C$=O), 20.1 ($\underline{C}H_2CH_2C$=O).

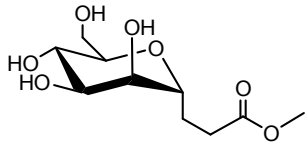
ESI-MS; calcd for $C_9H_{17}NO_6$ $[M+Na]^+$: 258.0954, found: 258.0948.

Since the resulting unprotected AA-*C*-Glc was hard to isolate, all the hydroxy groups were acetylated to give 2,3,4,6-tetra-*O*-acetyl 3-(α-D-glucopyranosyl)-propanamide (Ac-AA-α-Glc). The resulting *O*-acetylated product was purified by silica gel column chromatography (eluent: $CHCl_3$/MeOH=30/1→15/1).



^{1}H NMR (400 MHz, $CDCl_3$) δ 5.57, 5.47 (2H, NH_2), 5.32 (1H, t, *J*=8.8× (2) Hz, H-3), 5.08 (1H, dd, $J_{2,3}$=9.5, $J_{2,1}$=5.8 Hz, H-2), 5.00 (1H, t, *J*=9.4×(2) Hz, H-4), 4.25-4.16 (2H, m, H-6a, H-1), 4.08 (1H, dd, *J*=12.3, 2.8 Hz, H-6b), 3.90-3.86 (1H, m, H-5), 2.36-1.85 (16H, m, CH_2×2, Ac×4). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 170.8, 170.2, 170.0, 169.7, 72.4 (C-1), 70.4 (C-3), 70.3 (C-2), 69.0 (C-5), 68.8 (C-4), 62.4 (C-6), 31.3, 21.1, 21.1-20.8 (5C).

methyl 3-(α-D-mannopyranosyl)-propanoate (MA-α-Man, 7)



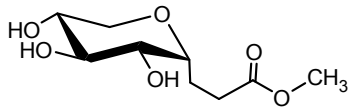
This compound was prepared according to the general procedure **A** using *N,N*-dimethyl β-D-mannopyranosyl dithiocarbamate (0.1 mmol, 28.3 mg) and methyl acrylate (0.5 mmol, 45μL). Silica gel column chromatography (eluent: chloroform/methanol=5/1) and freeze-drying gave the desired product as a colorless oil (12.5 mg, 0.05 mmol).

^{1}H NMR (400 MHz, D_2O) δ 3.92-3.86 (2H, m, H-1, H-2), 3.81-3.78 (2H, m, H-6a, H-3), 3.72-3.63 (4H, m, H-6b, -OC$\underline{H}_3$), 3.62 (1H, t, *J*=9.5×(2) Hz, H-4), 3.50-3.46 (1H, m, H-5), 2.55-2.41 (2H, m, $CH_2C\underline{H}_2C$=O), 2.14-2.04 (1H, m, C$\underline{H}_2CH_2C$=O), 1.98-1.75 (1H, m, C$\underline{H}_2CH_2C$=O). ^{13}C NMR (100 MHz, D_2O) δ 176.4 (C=O), 77.5 (C-1), 73.6 (C-5), 71.3 (C-2), 70.7 (C-3), 67.2 (C-4), 61.1 (C-6), 52.2 (O$\underline{C}H_3$), 30.1 ($CH_2\underline{C}H_2C$=O), 22.8 ($\underline{C}H_2CH_2C$=O). The stereochemistry of the anomeric center was confirmed by the ^{1}H NMR and NOESY spectra of 2,3,4,6-tetra-*O*-acetylated product in $CDCl_3$.[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.25-5.23 (1H, m, H-3), 5.20-5.16 (1H, m, H-4), 5.15 (1H, t, *J*=3.5×(2) Hz, H-2), 4.37 (1H, dd, *J*=6.4, 12.2 Hz, H-6a), 4.05 (1H, dd, *J*=3.0, 12.3 Hz, H-6b), 3.98 (1H, dt, *J*=11.2, 3.6×(2) Hz, H-1), 3.90-3.86 (1H, m, H-5), 3.68 (3H, s, OMe), 2.50-2.35 (2H, m, CH_2-C=O), 2.18-1.86 (14H, m, Ac, CH_2).

methyl 3-(D-xylopyranosyl)-propanoate (MA-Xyl, 8)

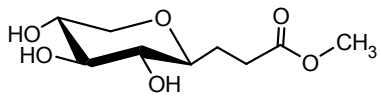
This compound was prepared according to the general procedure **A** using *N,N*-dimethyl β-D-xylopyranosyl dithiocarbamate (0.1 mmol, 25.3 mg) and methyl acrylate (0.5 mmol, 45μL). Silica gel column chromatography (eluent: chloroform/methanol=7/1) and freeze-drying gave the desired product as a white solid (11.5 mg, 0.052 mmol, α/β=3/2).

MA-α-Xyl



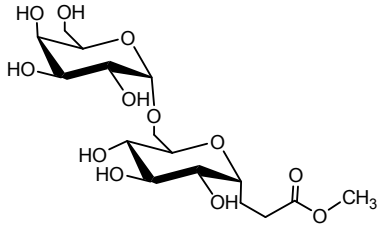
^{1}H NMR (400 MHz, D_2O) δ 3.81-3.76 (3H, m, sugar-H), 3.68 (3H, s, -OC$\underline{H}_3$), 3.65-3.57 (3H, m, sugar-H), 2.51-2.42 (2H, m, $CH_2C\underline{H}_2C$=O), 2.02-1.92 (1H, m, C$\underline{H}_2CH_2C$=O), 1.88-1.79 (1H, m, C$\underline{H}_2CH_2C$=O). ^{13}C NMR (100 MHz, D_2O) δ 176.7 (C=O), 74.8, 70.2, 69.7, 68.6, 65.7 (C-5), 52.2 (OCH_3), 30.0 ($CH_2\underline{C}H_2C$=O), 23.3 ($\underline{C}H_2CH_2C$=O). The stereochemistry of the anomeric center was confirmed by the ^{1}H NMR spectrum of 2,3,4-tri-*O*-acetylated product in $CDCl_3$.[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.01-4.99 (1H, m, H-3), 4.73 (1H, dd, *J*=3.3, 1.3 Hz, H-2), 4.67-4.66 (1H, m, H-4), 3.94 (1H, dt, *J*=13.1, 1.8×(2) Hz, H-5a), 3.79 (1H, dd, *J*=13.3, 2.3 Hz, H-5b), 3.75-3.72 (1H, m, H-1), 3.64 (3H, s, OMe), 2.52-2.33 (2H, m, CH_2C=O), 2.11-1.98 (9H, m, Ac), 1.93-1.85 (2H, m, CH_2).

MA-β-Xyl



^{1}H NMR (400 MHz, D_2O) δ 3.90 (1H, dd, *J*=11.3, 5.5 Hz, H-5a), 3.67 (3H, s, -OC<u>H</u>$_3$), 3.56-3.51 (1H, m, H-4), 3.35 (1H, t, *J*=8.8×(2) Hz, H-3), 3.25-3.13 (3H, m, H-1, H-5, H-2), 2.51-2.42 (2H, m, $CH_2C\underline{H}_2C$=O), 2.19-2.11 (1H, m, $C\underline{H}_2CH_2C$=O), 1.72-1.63 (1H, m, $C\underline{H}_2CH_2C$=O). ^{13}C NMR (100 MHz, D_2O) δ 176.7 (C=O), 79.3 (C-1), 77.3 (C-3), 73.2 (C-2), 69.5 (C-4), 68.9 (C-5), 52.2 (OCH_3), 30.0 ($CH_2\underline{C}H_2C$=O), 26.4 ($\underline{C}H_2CH_2C$=O). The stereochemistry of the anomeric center was confirmed by the ^{1}H NMR spectrum of 2,3,4-tri-*O*-acetylated product in $CDCl_3$. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.12 (1H, t, *J*=9.8×(2) Hz, H-3), 4.95-4.88 (1H, m, H-4), 4.78 (1H, t, *J*=9.3×(2) Hz, H-2), 4.04 (1H, dd, *J*=11.0, 5.8 Hz, H-5a), 3.63 (3H, s, OMe), 3.37-3.30 (1H, m, H-1), 3.19 (1H, t, *J*=10.8× (2) Hz, H-5b), 2.52-2.33 (2H, m, CH_2C=O), 2.11-1.98 (9H, m, Ac), 1.73-1.60 (2H, m, CH_2).

methyl 3-(α-D-melibiosyl)-propanoate (MA-α-melibiose, 9)

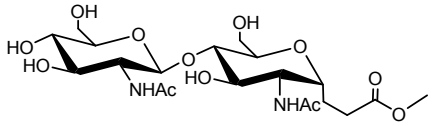


This compound was prepared according to the general procedure **A** in ethanol (1.0 mL) using *N,N*-dimethyl β-D-melibiosyl dithiocarbamate (0.1 mmol, 45 mg) and methyl acrylate (0.5 mmol, 45μL). Silica gel column chromatography (eluent: chloroform/methanol=2/1), preparative HPLC (column: ODS-3; eluent: H_2O; flow rate: 10 mL/min; column temperature: 30 °C; detection: RI) and freeze-drying gave the desired product as a white solid (15 mg, 0.041 mmol)

^{1}H NMR (400 MHz, D_2O) δ 4.94 (1H, d, *J*=3.5, H-1'), 4.04-3.99 (1H, m, H-1), 3.98-3.42 (15H, m, sugar-H, OCH_3), 2.57-2.41 (2H, m, $CH_2C\underline{H}_2C$=O), 2.07-1.91 (2H, m, -$C\underline{H}_2CH_2C$=O). ^{13}C NMR (100 MHz, D_2O) δ 176.6 (C=O), 98.1 (C-1'), 75.3 (C-1), 75.2, 73.3, 71.1, 70.9, 70.7, 70.0, 69.5, 69.2, 68.4, 66.0, 52.2 (OCH_3), 29.7 ($CH_2\underline{C}H_2C$=O), 19.3 (-$\underline{C}H_2CH_2C$=O). The stereochemistry of the anomeric center was confirmed by the signal derived from H-2 (5.05 ppm, $J_{2,1}$=5.9 Hz) of *O*-acetylated product in $CDCl_3$.

ESI-MS; calcd for $C_{16}H_{28}O_{12}$ $[M+Na]^+$: 435.1479, found: 435.1473.

methyl 3-(α-chitobiosyl)-propanoate (MA-α-chitobiose, 10)



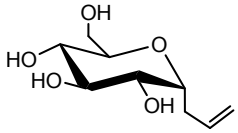
This compound was prepared according to the general procedure **A** in DMF (1.0 mL) using *N,N*-dimethyl chitobiosyl dithiocarbamate (0.1 mmol, 53 mg), methyl acrylate (1.0 mmol, 90 μL), tributyltin hydride (0.6 mmol, 144 μL) and AIBN (0.1 mmol, 16.4 mg). The reaction mixture was stirred for 48 hours at 75 ºC under argon. Silica gel column chromatography (eluent: chloroform/methanol=2/1), preparative HPLC (column: ODS-3; eluent: MeCN/H_2O=4/96; flow rate: 15 mL/min; column temperature: 40 ºC; detection: UV) and freeze-drying gave the desired product as a white solid (24 mg, 0.049mmol)

^{1}H NMR (400 MHz, D_2O): δ 4.53 (1H, d, *J*=8.5 Hz, H-1'), 4.05-4.00 (1H, m, H-1), 3.94-3.42 (15H, m, sugar-H, OCH_3),

2.50-2.35 (2H, m, $CH_2C\underline{H}_2C$=O), 2.05 (3H, s, Ac), 2.02 (3H, s, Ac), 2.01-1.74 (2H, m, -$C\underline{H}_2CH_2C$=O). ^{13}C NMR (100 MHz, D_2O) δ 176.4 (C=O), 174.7(Ac), 174.3(Ac), 101.3 (C-1'), 79.4, 75.8, 73.4, 72.0, 71.5 (C-1), 69.7, 68.6, 60.5, 60.0, 55.5, 52.3, 52.2 (OCH_3), 29.8 ($CH_2\underline{C}H_2C$=O), 22.1 (Ac), 21.8 (Ac), 20.8 ($\underline{C}H_2CH_2C$=O). The stereochemistry of the anomeric center was confirmed by the signal of H-2 (3.73 ppm, $J_{2,1}$=4.0 Hz) of *O*-acetylated product in CD_3OD.
ESI-MS; calcd for $C_{20}H_{34}N_2O_{12}$ $[M+Na]^+$: 517.2010, found: 517.2004.

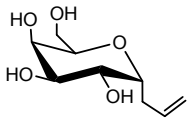
Preparation of *C*-allyl glycosides

1-(α-D-glucopyranosyl)-2-propene (11) [6]



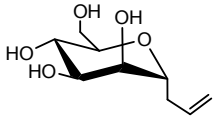
This compound was prepared according to the general procedure **B** in 1,4-dioxane using *N,N*-dimethyl β-glucopyranosyl dithiocarbamate (0.1 mmol, 28 mg). Silica gel column chromatography (eluent: chloroform/methanol=5/1) and freeze-drying gave the desired product as a white solid (10 mg, 0.05 mmol).
^{1}H NMR (400 MHz, CD_3OD) δ 5.93-5.83 (1H, m, C*H*=CH_2), 5.15-5.02 (2H, m, CH=CH_2), 3.95 (1H, dt, *J*=10.5, 5×(2) Hz), 3.76-3.72 (1H, m, H-6a), 3.67-3.51 (3H, m, H-6b, H-2, H-3), 3.47-3.43 (1H, ddd, *J*=9.5, 5.3, 2.5 Hz, H-5), 3.29-3.24 (1H, m, H-4), 2.51-2.38 (2H, m, CH_2CH=CH_2). ^{13}C NMR (100 MHz, CD_3OD) δ 136.6(*C*H=CH2), 116.9 (CH=*C*H_2), 77.1 (C-1), 75.2 (C-3), 74.5 (C-5), 72.9 (C-2), 72.2 (C-4), 62.9 (C-6), 30.6 (*C*H_2CH=CH_2).

1-(α-D-galactopyranosyl)-2-propene (20)[7]



This compound was prepared according to the general procedure **B** in ethanol using *N,N*-diethyl β-galactopyranosyl dithiocarbamate (0.1 mmol, 31.1 mg). Silica gel column chromatography (eluent: chloroform/methanol=5/1), preparative HPLC (column: ODS-3; eluent: H_2O; flow rate: 8 mL/min; column temperature: 30°C; detection: RI)and freeze-drying gave the desired product as a colorless oil (10 mg, 0.05 mmol).
^{1}H NMR (400 MHz, D_2O): δ 5.88-5.77 (1H, m, C$\underline{H}$=CH_2), 5.19-5.09 (2H, m, CH=C$\underline{H_2}$), 4.11-4.06 (1H, m, H-1), 3.99-3.95 (2H, m, H-4, H-2), 3.83-3.78 (2H, m, H-5, H-3), 3.66 (2H, d, *J*=6.0 Hz, H-6), 2.53-2.33 (2H, m, C$\underline{H_2}$-CH=CH_2). ^{13}C NMR (100 MHz, D_2O): δ 134.9 ($\underline{C}$H=CH_2), 117.3 (CH=$\underline{C}H_2$), 74.9 (C-1), 71.6 (C-5), 69.6 (C-3), 69.0 (C-2), 68.2 (C-4), 60.9 (C-6), 28.7 ($\underline{C}H_2$-CH=CH_2).

1-(α-D-mannopyranosyl)-2-propene (21)[6]

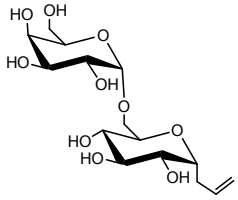


This compound was prepared according to the general procedure **B** in 1,4-dioxane using *N,N*-dimethyl β-

mannopyranosyl dithiocarbamate (0.1 mmol, 29 mg). Silica gel column chromatography (eluent: chloroform/methanol=5/1) and freeze-drying gave the desired product as a colorless oil (10 mg, 0.05 mmol).

^{1}H NMR (400 MHz, D_2O): δ 5.86-5.76 (1H, m, C<u>H</u>=CH_2), 5.19-5.10 (2H, m, CH=C<u>H_2</u>), 3.99-3.95 (1H, m, H-1), 3.90-3.88 (1H, m, H-2), 3.84-3.78 (2H, m, H-3, H-6a), 3.72-3.67 (1H, m, H-6b), 3.63 (1H, t, *J*=9.3×(2) Hz, H-4), 3.58-3.53 (1H, m, H-5), 2.56-2.48 (1H, m, C<u>H_2</u>-CH=CH_2), 2.37-2.30 (1H, m, C<u>H_2</u>-CH=CH_2). ^{13}C NMR (100 MHz, D_2O): δ 134.1 (<u>C</u>H=CH_2), 117.6 (CH=<u>C</u>H_2), 77.6 (C-1), 73.7 (C-5), 70.7 (C-2), 70.5 (C-3), 67.2 (C-4), 61.1 (C-6), 32.5 (<u>C</u>H_2-CH=CH_2).

1-(α-melibiosyl)-2-propene (22)

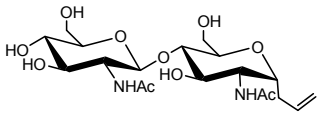


This compound was prepared according to the general procedure **B** in ethanol using *N,N*-dimethyl β-melibiosyl dithiocarbamate (0.1 mmol, 45 mg). Silica gel column chromatography (eluent: chloroform/methanol=2/1) and freeze-drying gave the desired product as a white solid (21 mg, 0.057 mmol).

^{1}H NMR (400 MHz, D_2O): δ 5.88-5.78 (1H, m, C<u>H</u>=CH_2), 5.22-5.12 (2H, m, CH=C<u>H_2</u>), 4.92 (1H, d, *J*=3.8 Hz, H-1'), 4.12-4.06 (1H, m, H-1), 3.97-3.44 (12H, m, sugar-H), 2.54-2.39 (2H, m, C<u>H_2</u>-CH=CH_2). ^{13}C NMR (100 MHz, D_2O): δ 134.5 (<u>C</u>H=CH_2), 117.5 (CH=<u>C</u>H_2), 98.0 (C-1'), 75.5 (C-1), 73.3, 71.1, 71.0, 70.9, 70.0, 69.5, 69.2, 68.4, 65.9, 61.0, 28.7 (<u>C</u>H_2-CH=CH_2). The stereochemistry of the anomeric center was confirmed by detecting the signal derived from H-2 (5.02 ppm, $J_{2,1}$=5.8 Hz) of *O*-acetylated product in $CDCl_3$.

ESI-MS; calcd for $C_{15}H_{26}O_{10}$ $[M+Na]^+$: 389.1424, found: 389.1418.

1-(α-chitobiosyl)-2-propene (23)



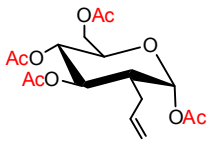
This compound was prepared according to the general procedure **B** in ethanol/DMF (Vol. 1/1, 2.0 mL) using *N,N*-dimethyl chitobiosyl dithiocarbamate (0.1 mmol, 53 mg). After 5 hours reaction, another portion of AIBN (0.05 mmol, 8.2 mg) was added, and heating continued for a further 4 hours. Silica gel column chromatography (eluent: chloroform/methanol=2/1), preparative HPLC (column: ODS-3; eluent: MeCN/H_2O=4/96; flow rate: 15 mL/min; column temperature: 40°C; detection: UV) and freeze-drying gave the desired product as a white solid (22 mg, 0.048 mmol).

^{1}H NMR (400 MHz, D_2O): δ 5.81-5.70 (1H, m, C<u>H</u>=CH_2), 5.16-5.08 (2H, m, CH=C<u>H_2</u>), 4.54 (1H, d, *J*=8.3 Hz, H-1'), 4.15-4.10 (1H, m, H-1), 3.92-3.44 (12H, m, sugar-H), 2.49-2.24 (2H, m, C<u>H_2</u>-CH=CH_2), 2.05 (3H, s, -Me), 2.01 (3H. s, -Me). ^{13}C NMR (100 MHz, D_2O): δ 174.7 (Ac), 174.2 (Ac), 134.0 (<u>C</u>H=CH_2), 117.5 (CH=<u>C</u>H_2), 101.2 (C-1'), 79.2, 75.8, 73.4, 72.1, 71.4 (C-1), 69.7, 68.8, 60.5, 59.8, 55.5, 52.2, 30.8 (<u>C</u>H_2-CH=CH_2), 22.1 (Me), 21.8 (Me). The

stereochemistry of the anomeric center was confirmed by detecting the signal derived from H-2 (3.73 ppm, $J_{2,1}$=4.0 Hz) of *O*-acetylated product in CD_3OD.[8]

ESI-MS; calcd for $C_{19}H_{32}N_2O_{10}$ $[M+Na]^+$: 471.1955, found: 471.1949.

1,3,4,6-tetra-*O*-acetyl-2-*C*-allyl-2-deoxy D-glucopyranose (**15**)[9]



Column chromatography on silica gel with hexane/EtOAc (2/1) as the eluent was used to give **8** in 55% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.09 (1H, m, H-1), 5.77-5.67 (1H, m, C*H*=CH_2), 5.38 (1H, dd, *J*=9.7, 5.1 Hz, H-3), 5.23-5.11 (3H, m, H-4, CH=C*H*$_2$), 4.22-4.08 (2H, m, H-6), 4.04-3.99 (1H, m, H-5), 2.52-2.46 (1H, m, C*H*$_2$CH=CH_2), 2.35-2.29 (1H, m, H-2), 2.24-2.18 (1H, m, C*H*$_2$CH=CH_2), 2.14-2.03 (12H, m, OAc). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7 (OAc), 169.7 (OAc), 169.0 (OAc), 135.0 (*C*H=CH2), 118.1 (CH=*C*H_2), 92.9 (C-1), 70.4-70.3 (2C, C-3, C-5), 65.9 (C-4), 62.3 (C-6), 41.5 (C-2), 29.6 (*C*H_2CH=CH_2), 21.1-20.7 (4C, OAc).

The structures of acetylated allyl *C*-glucoside **13** and acetylated 2-deoxy glucose **14** were identified by comparison of NMR spectra with those reported in the literatures.[10,11] The structures of benzylated allyl *C*-glucoside **17** and benzylated 1-deoxy glucose **18** were identified by comparison of with those reported in the literatures.[12,13]

3. Reference

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4. NMR spectra

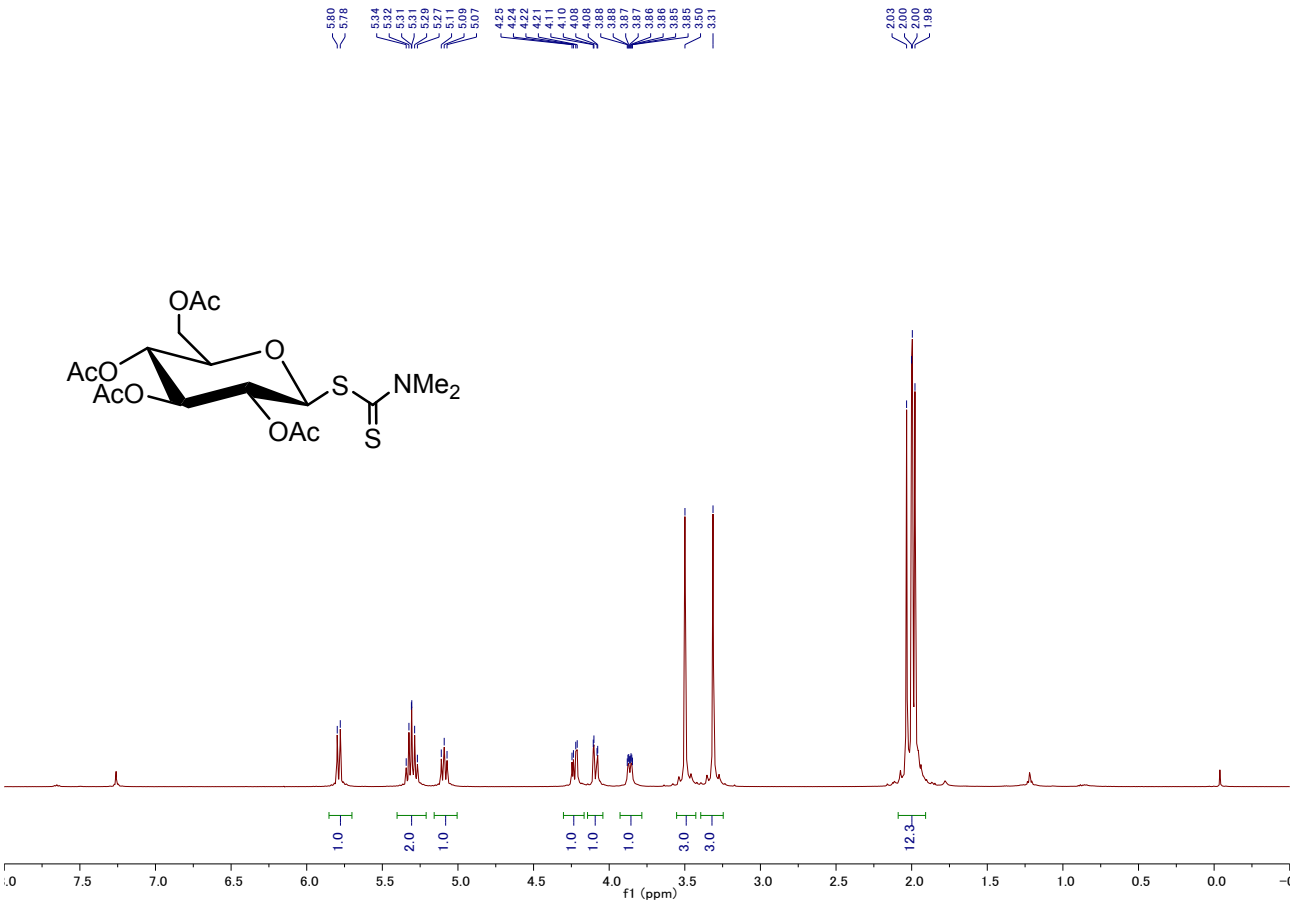


Fig. S1 ^{1}H NMR of 2,3,4,6-tetra-*O*-acetyl *N,N*-dimethyl *S*-β-glucopyranosyl dithiocarbamate (**Ac-GDTC, 12**) in $CDCl_3$

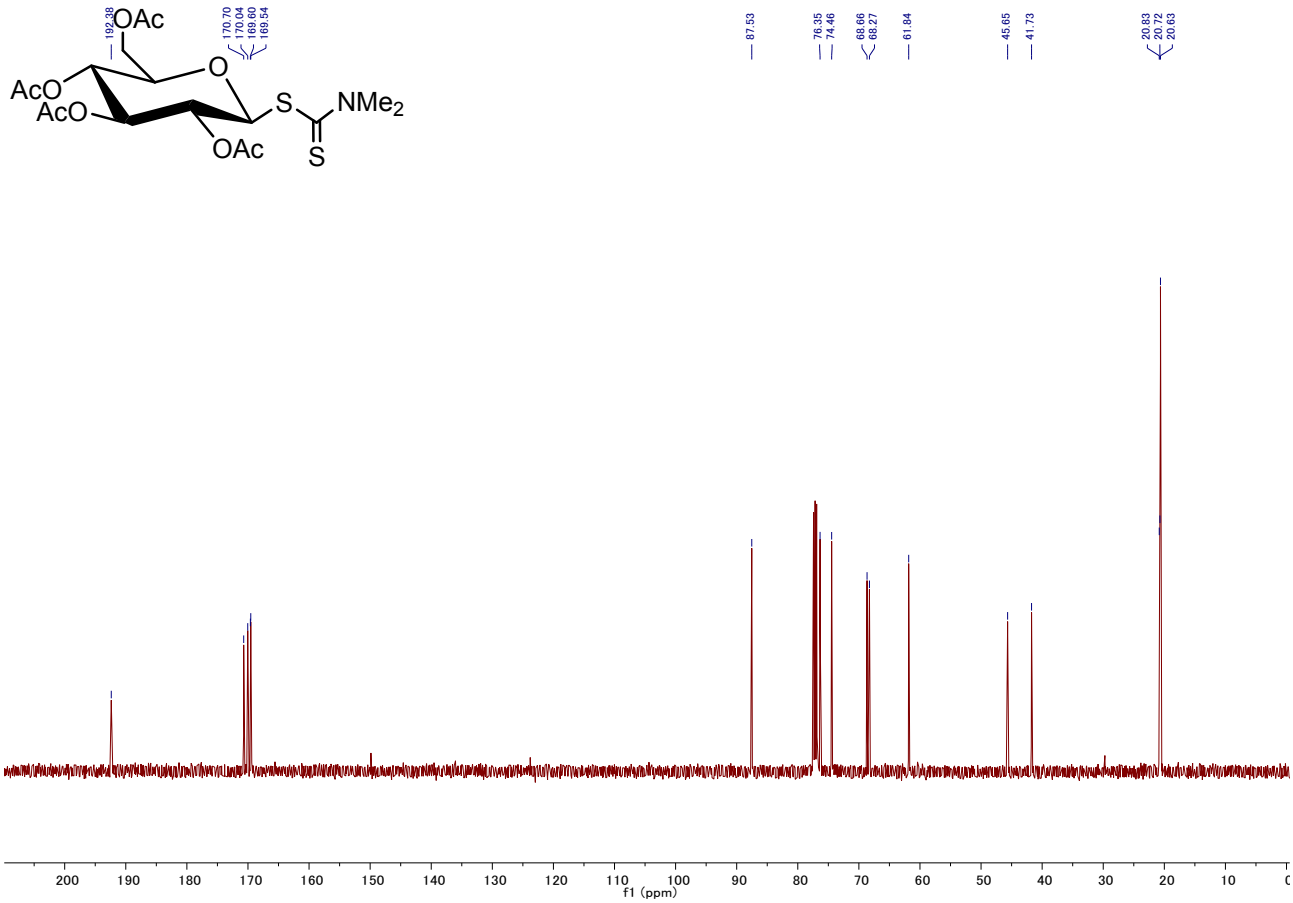


Fig. S2 ^{13}C NMR of 2,3,4,6-tetra-*O*-acetyl *N,N*-dimethyl *S*-β-glucopyranosyl dithiocarbamate (**Ac-GDTC, 12**) in $CDCl_3$

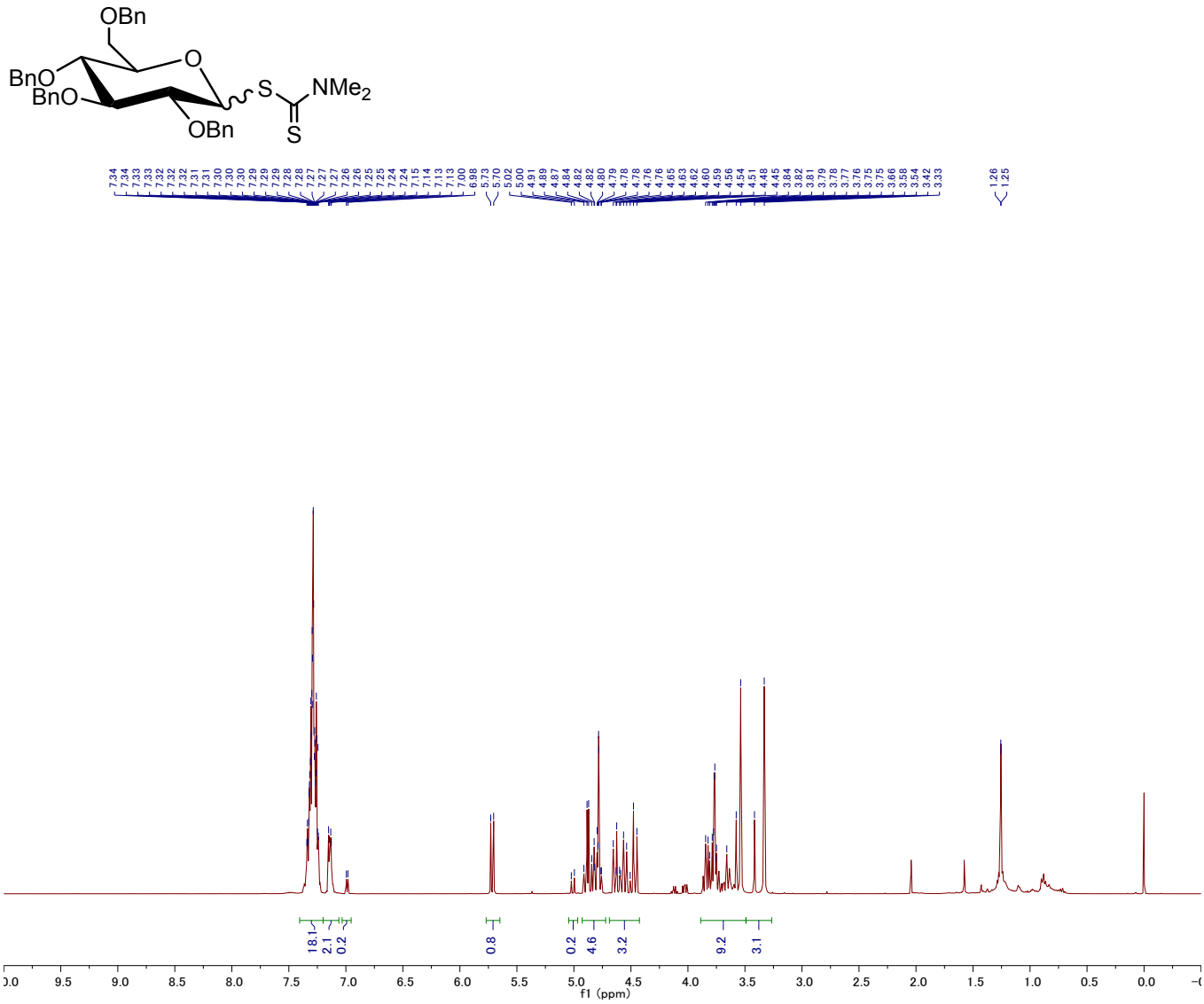


Fig. S3 ^{1}H NMR of 2,3,4,6-tetra-*O*-benzyl *N,N*-dimethyl *S*-glucopyranosyl dithiocarbamate (**Bn-GDTC, 16**) in $CDCl_3$

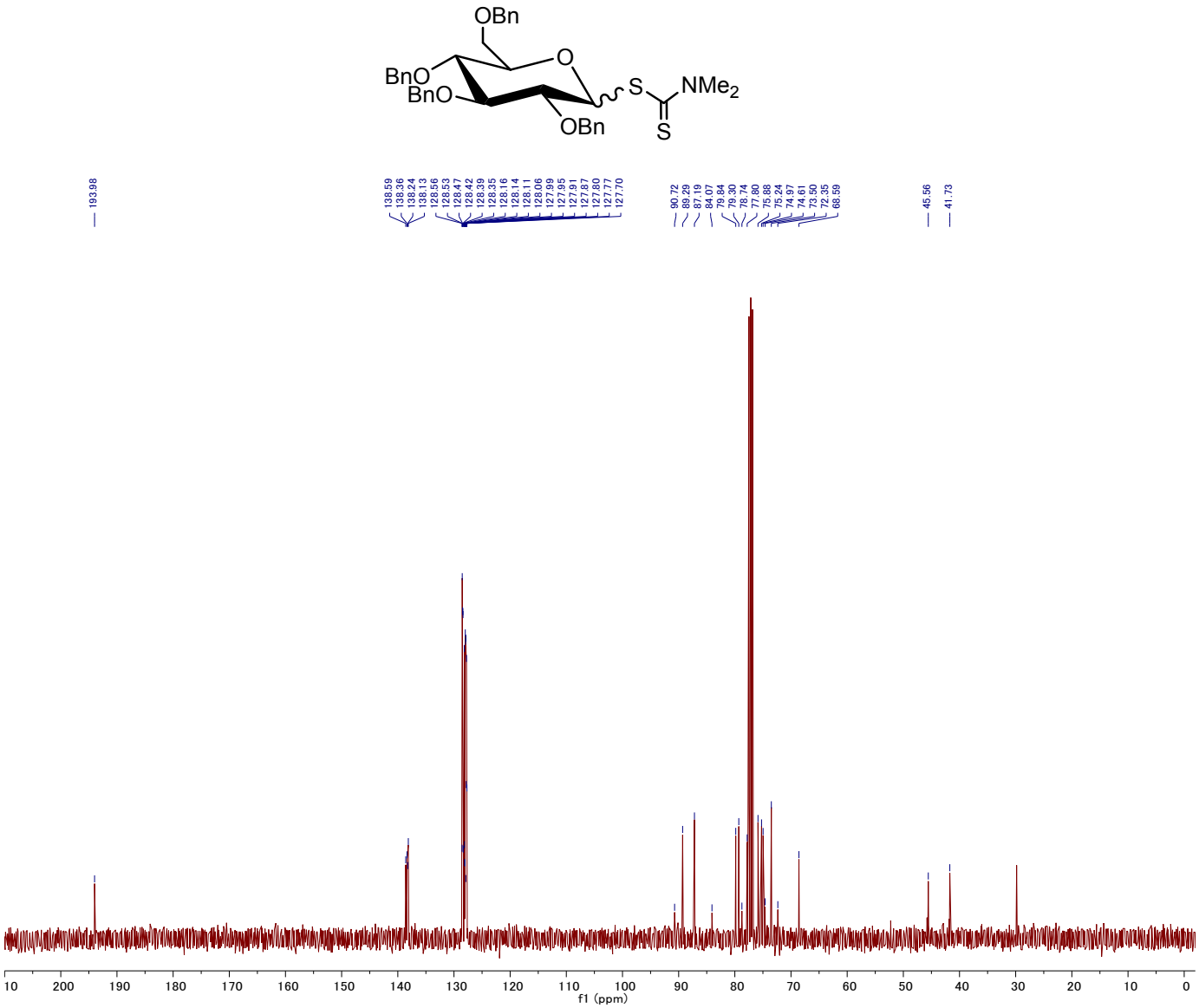


Fig. S4 ^{13}C NMR of 2,3,4,6-tetra-*O*-benzyl *N,N*-dimethyl *S*-glucopyranosyl dithiocarbamate (**Bn-GDTC, 16**) in $CDCl_3$

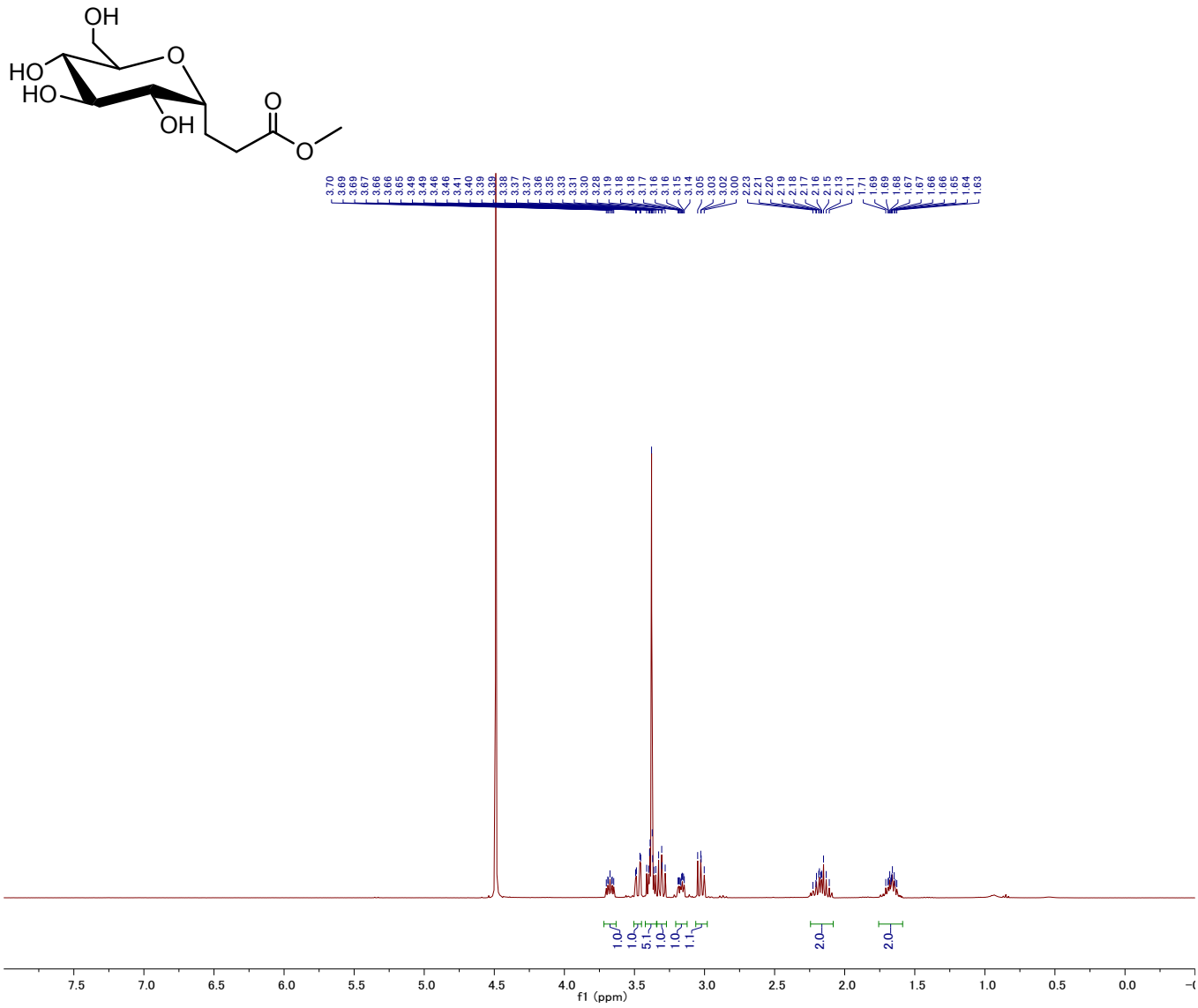


Fig. S5 ^{1}H NMR of methyl 3-(α-D-glucopyranosyl)-propanoate **(MA-α-Glc, 2)** in D_2O

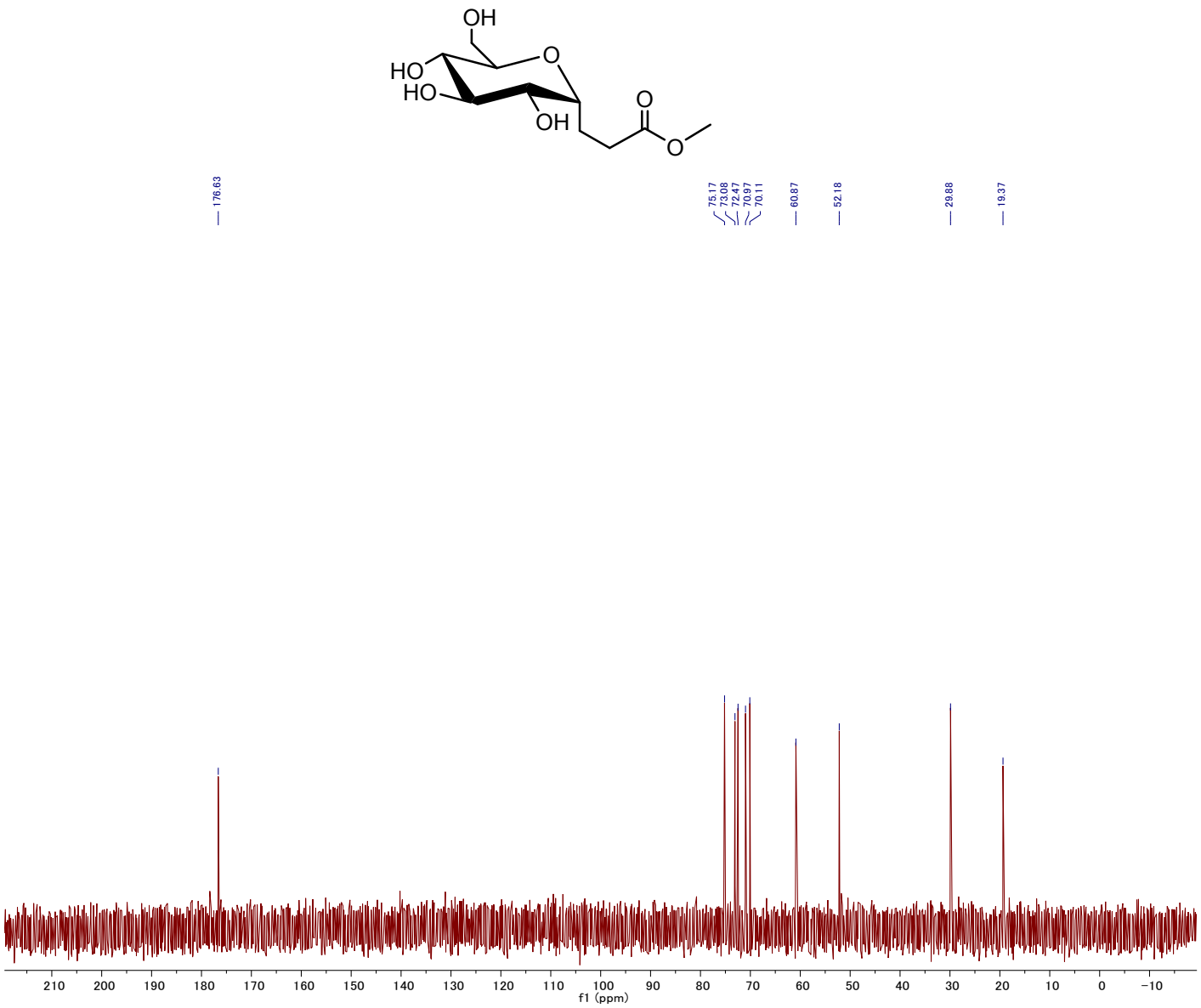


Fig. S6 ^{13}C NMR of methyl 3-(α-D-glucopyranosyl)-propanoate **(MA-α-Glc, 2)** in D_2O

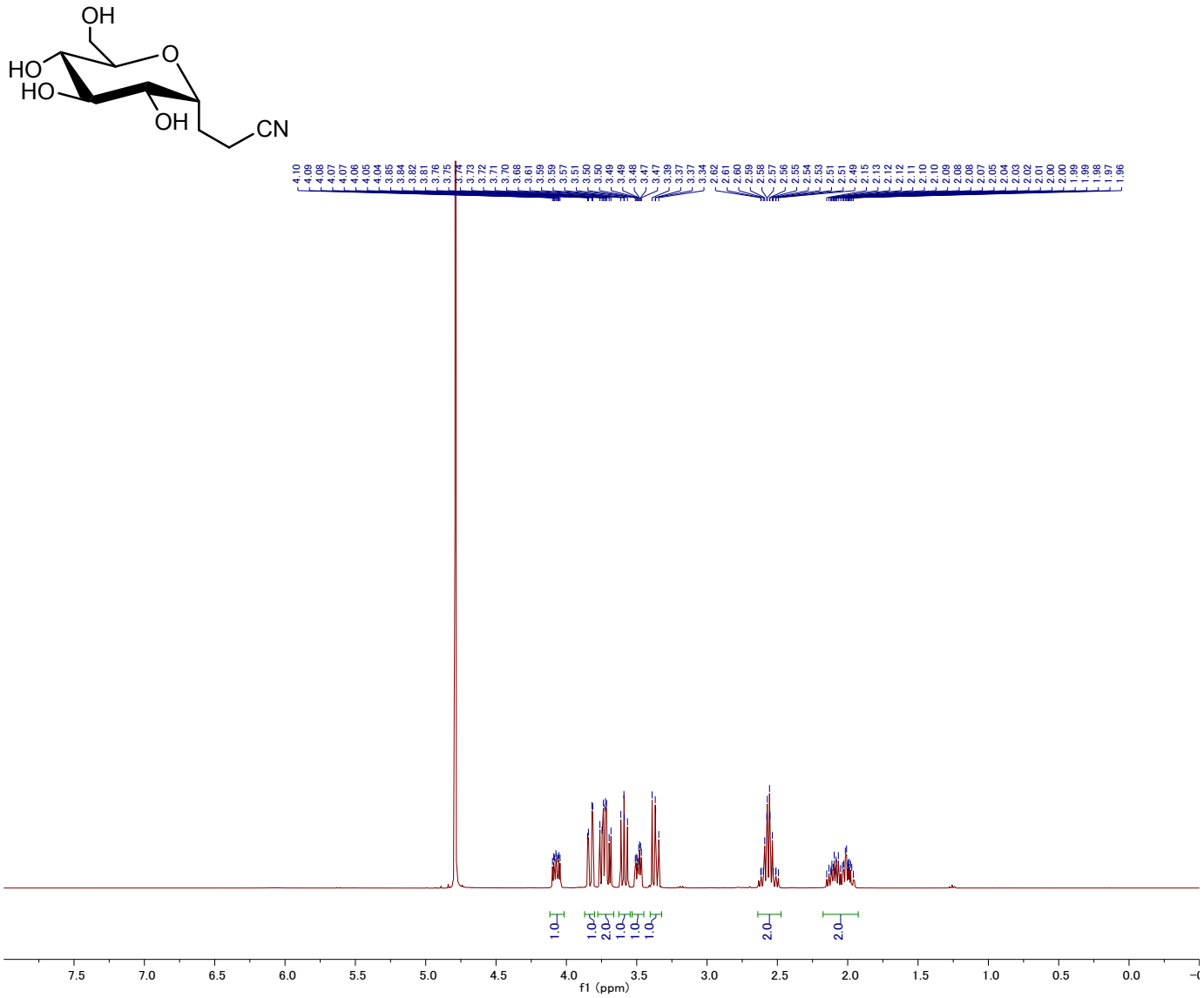


Fig. S7 ^{1}H NMR of 3-(α-D-glucopyranosyl)-propionitrile **(AN-α-Glc, 4)** in D_2O

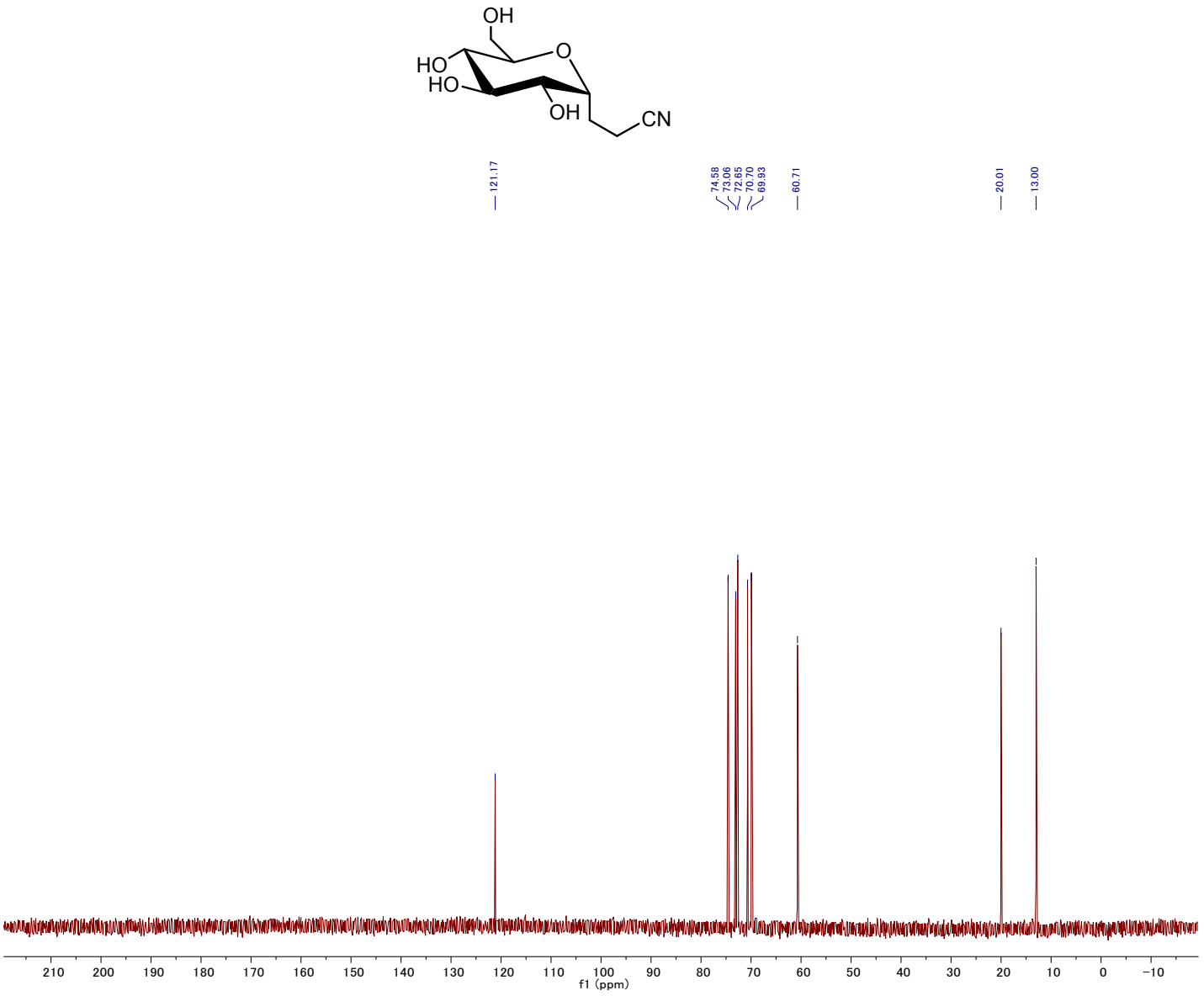


Fig. S8 ^{13}C NMR of 3-(α-D-glucopyranosyl)-propionitrile **(AN-α-Glc, 4)** in D_2O

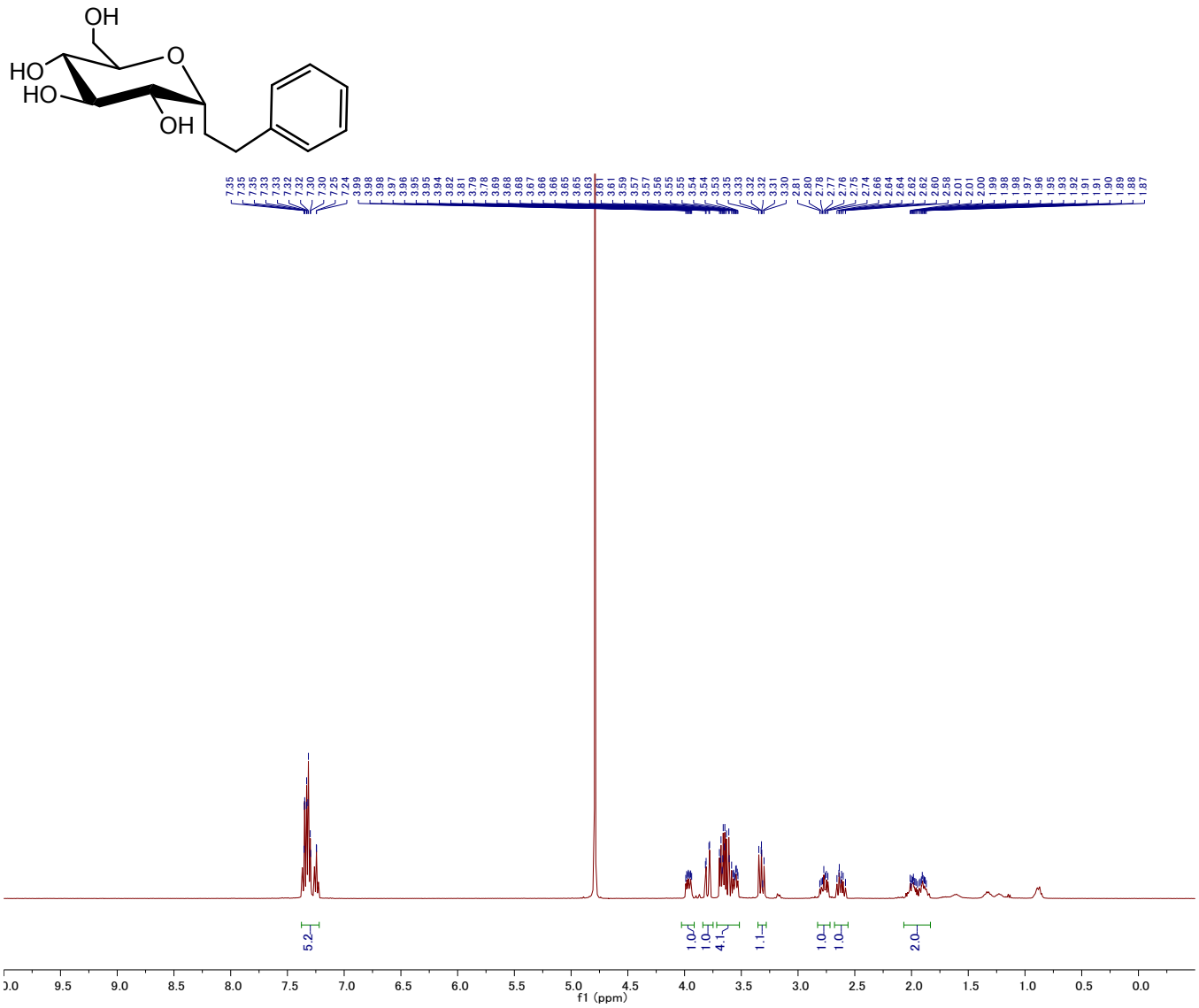


Fig. S9 ^{1}H NMR of 1-(α-D-glucopyranosyl)-2-phenyl ethane (St-α-Glc, **5**) in D_2O

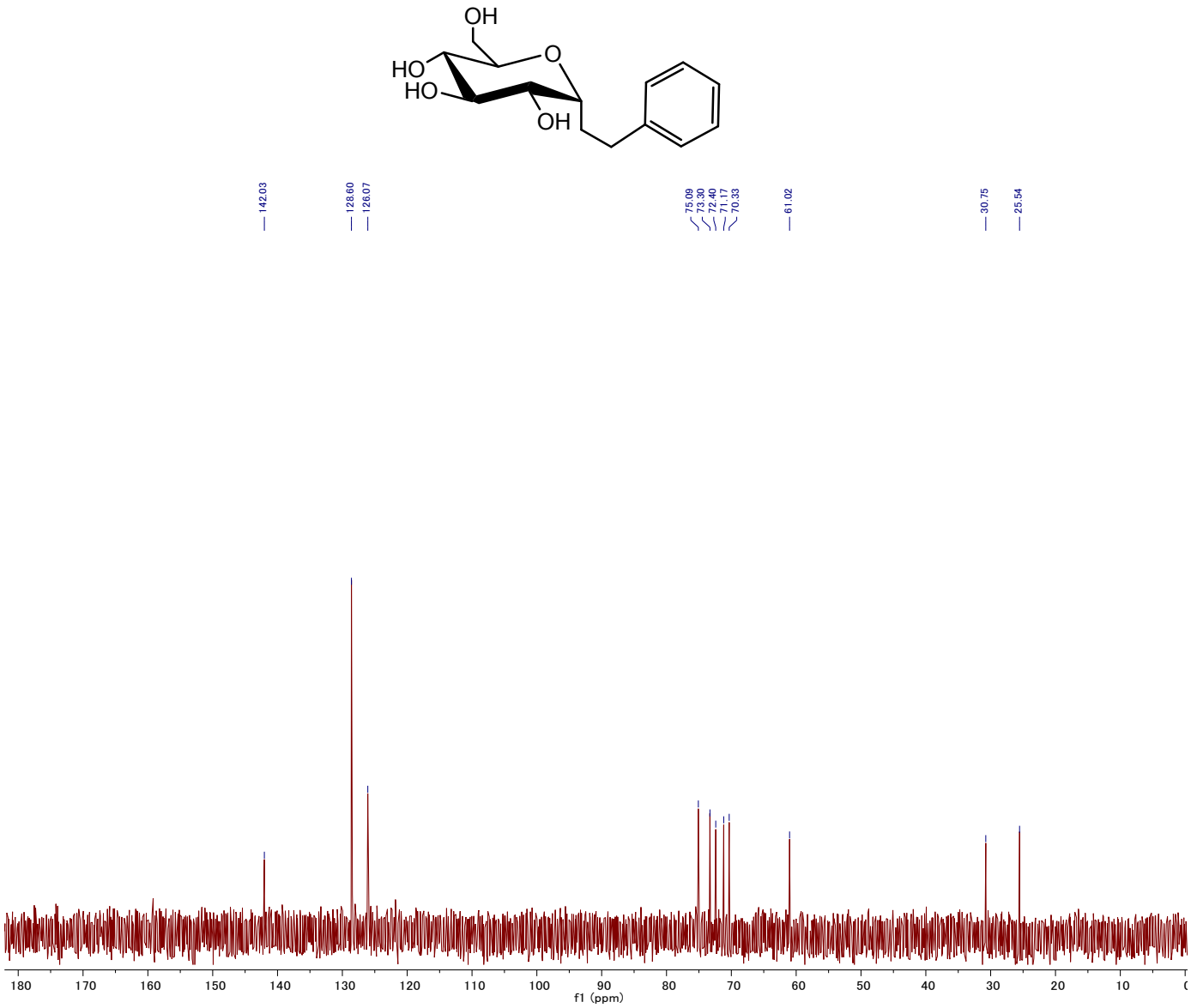


Fig. S10 ^{13}C NMR of 1-(α-D-glucopyranosyl)-2-phenyl ethane (St-α-Glc, **5**) in D_2O

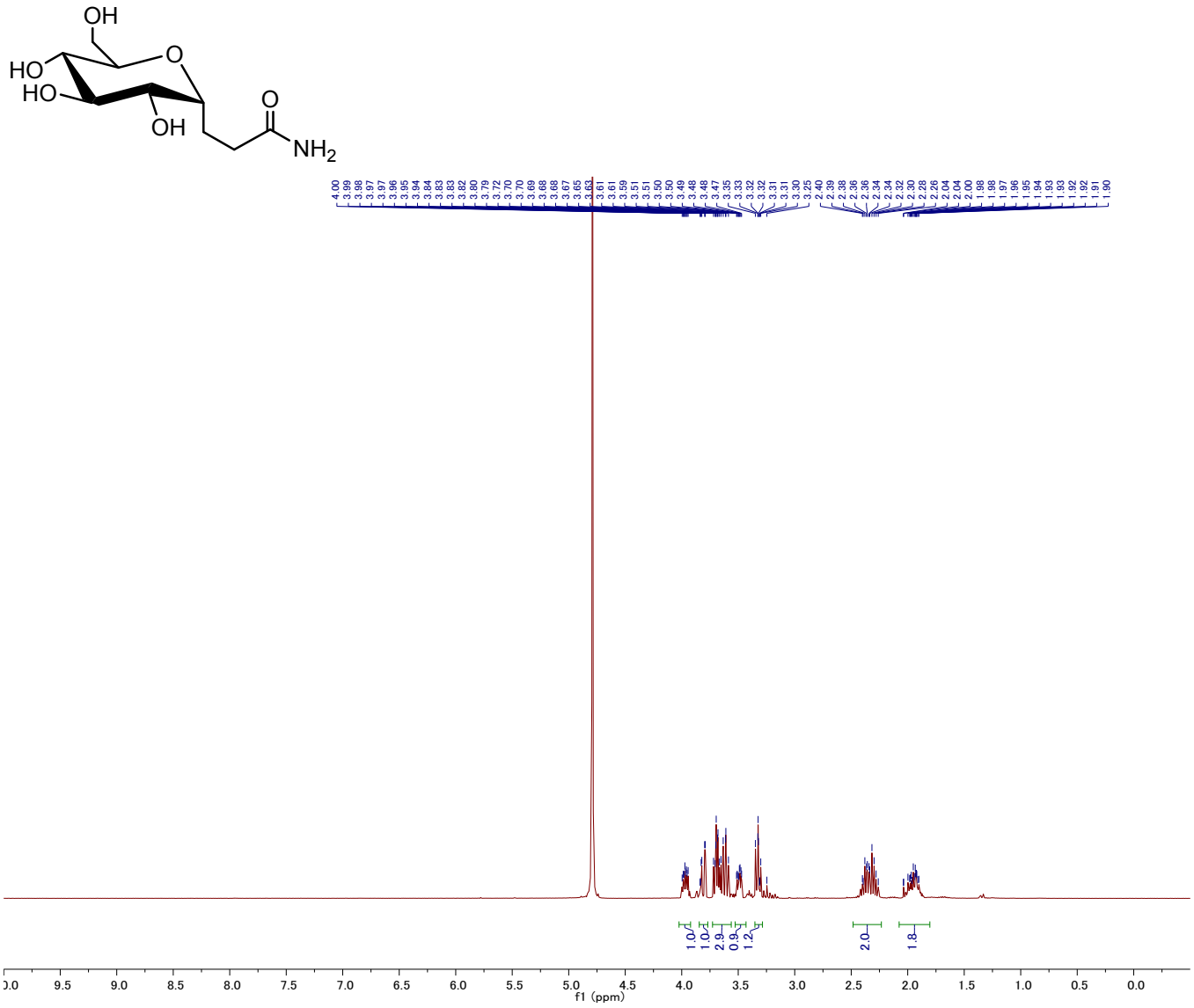


Fig. S11 ^{1}H NMR of 3-(α-D-glucopyranosyl)-propanamide **(AA-α-Glc, 6)** in D_2O

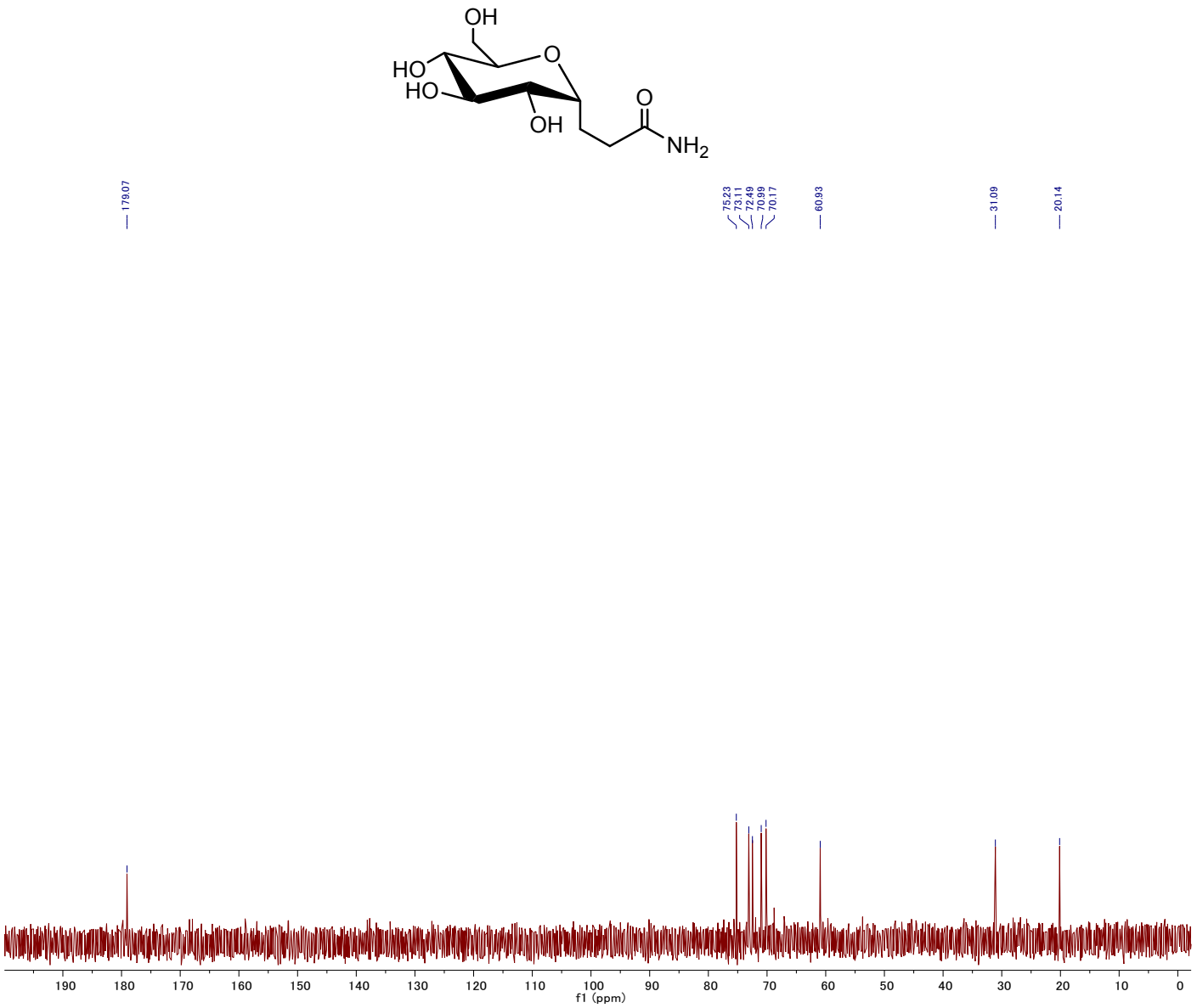


Fig. S12 ^{13}C NMR of 3-(α-D-glucopyranosyl)-propanamide **(AA-α-Glc, 6)** in D_2O

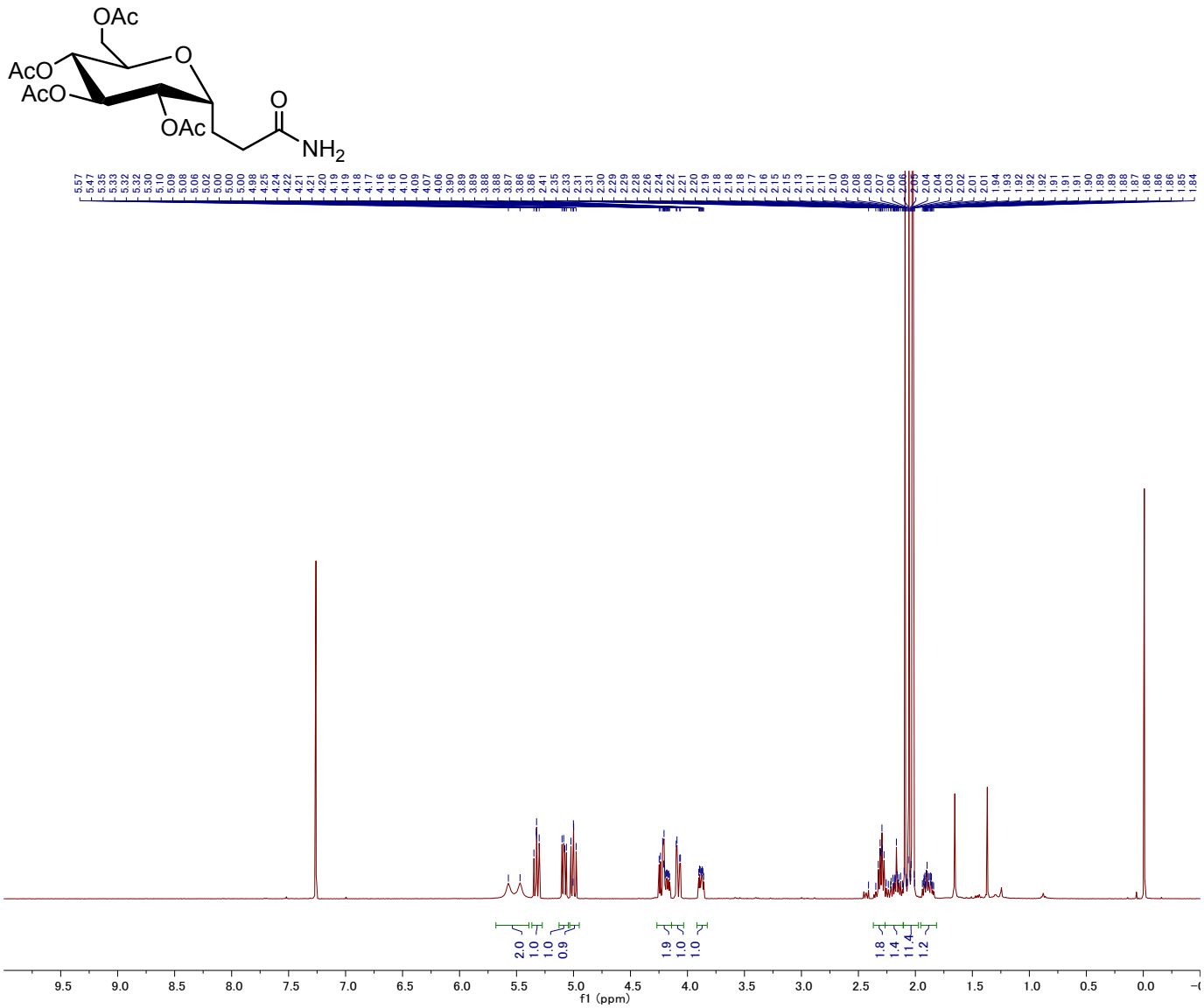


Fig. S13 ^{1}H NMR of 2,3,4,6-tetra-*O*-acetyl 3-(α-D-glucopyranosyl)-propanamide (**Ac-AA-α-Glc**) in $CDCl_3$

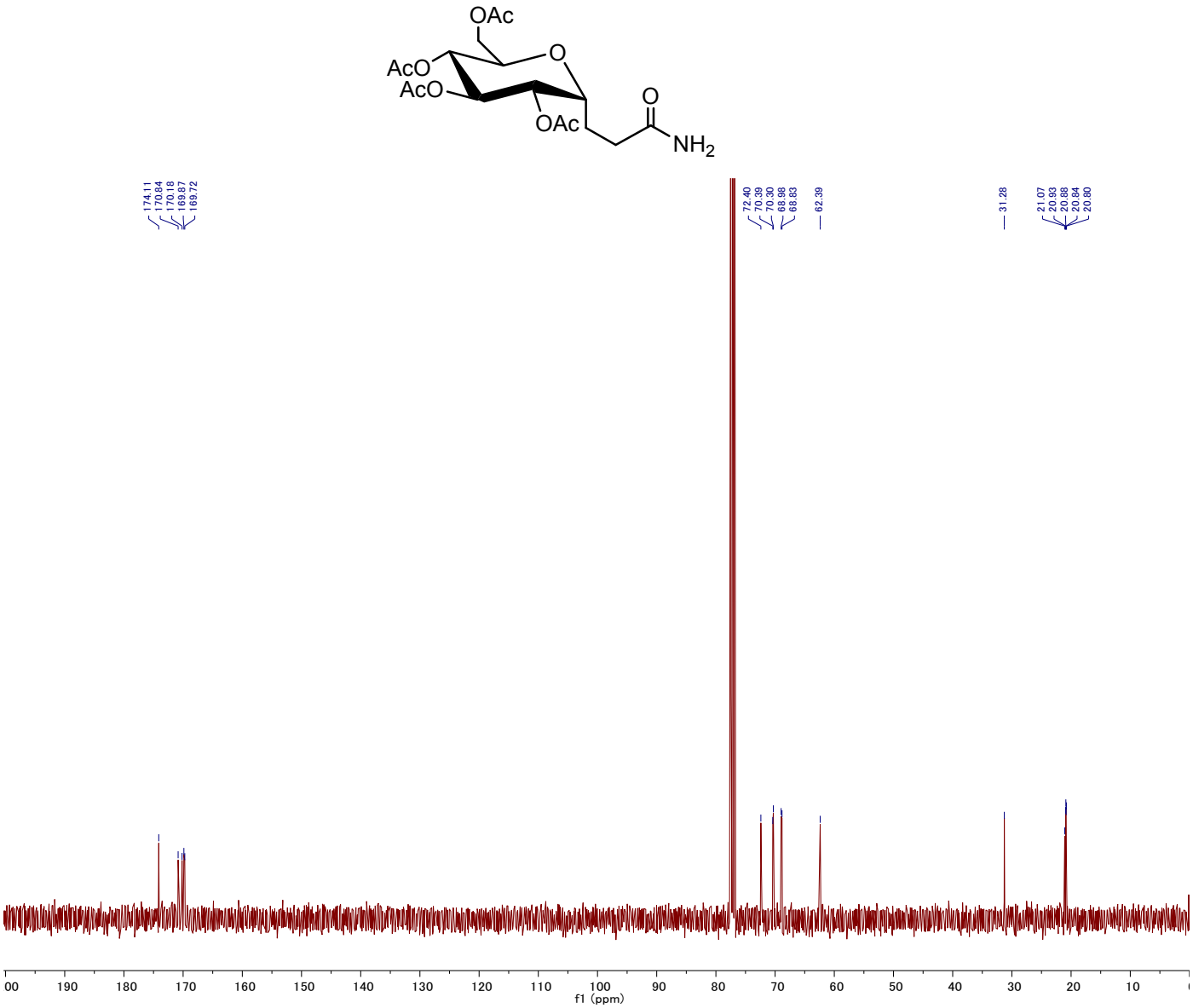


Fig. S14 ^{13}C NMR of 2,3,4,6-tetra-*O*-acetyl 3-(α-D-glucopyranosyl)-propanamide (**Ac-AA-α-Glc**) in $CDCl_3$

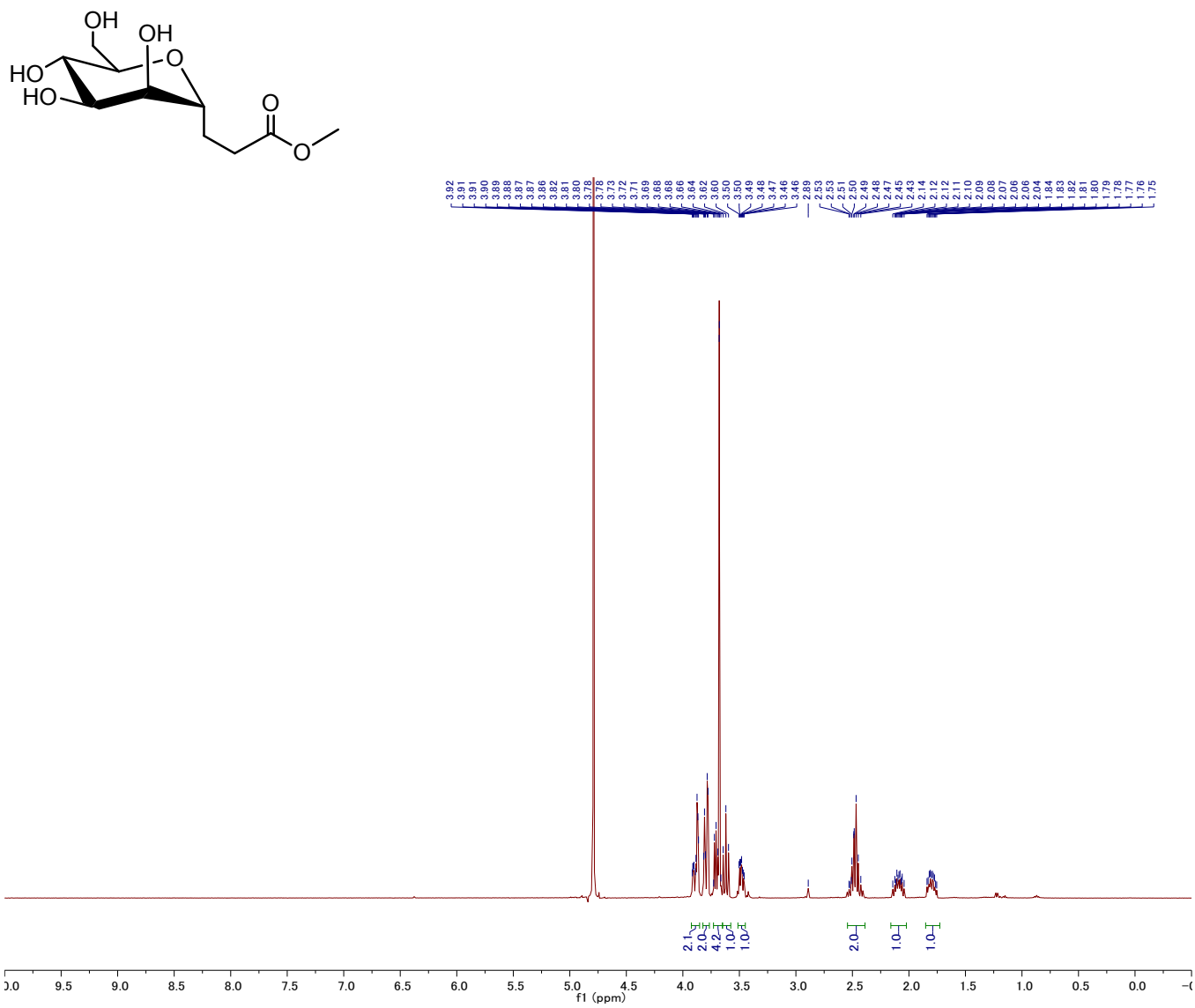


Fig. S15 ^{1}H NMR of methyl 3-(α-D-mannopyranosyl)-propanoate **(MA-α-Man, 7)** in D_2O

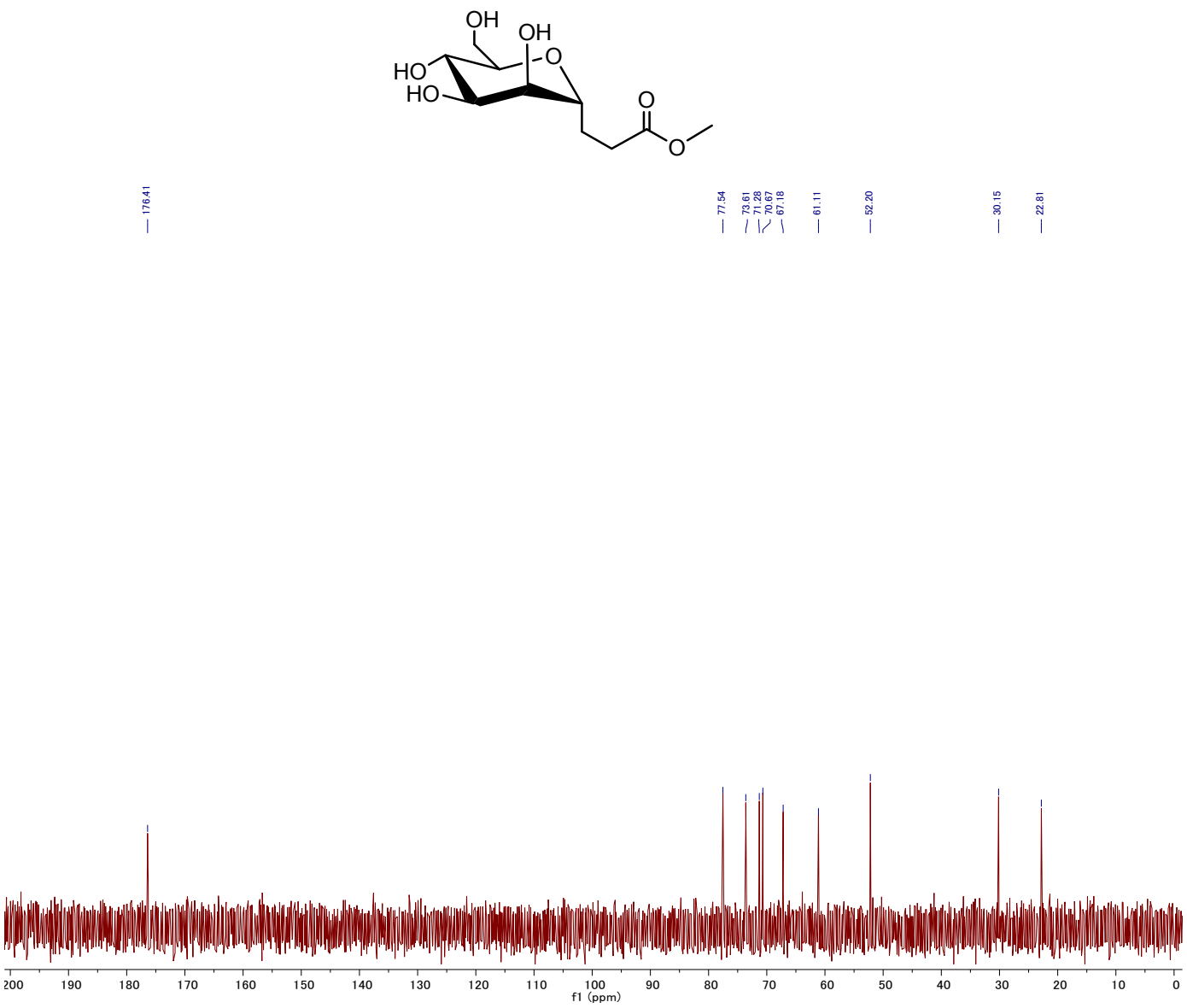
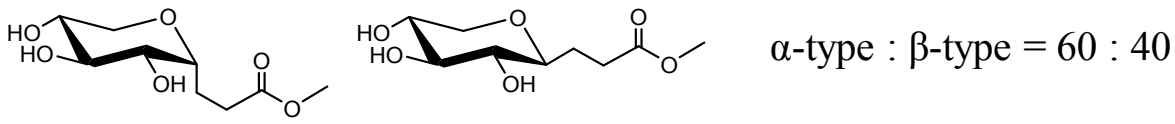


Fig. S16 ^{13}C NMR of methyl 3-(α-D-mannopyranosyl)-propanoate **(MA-α-Man, 7)** in D_2O



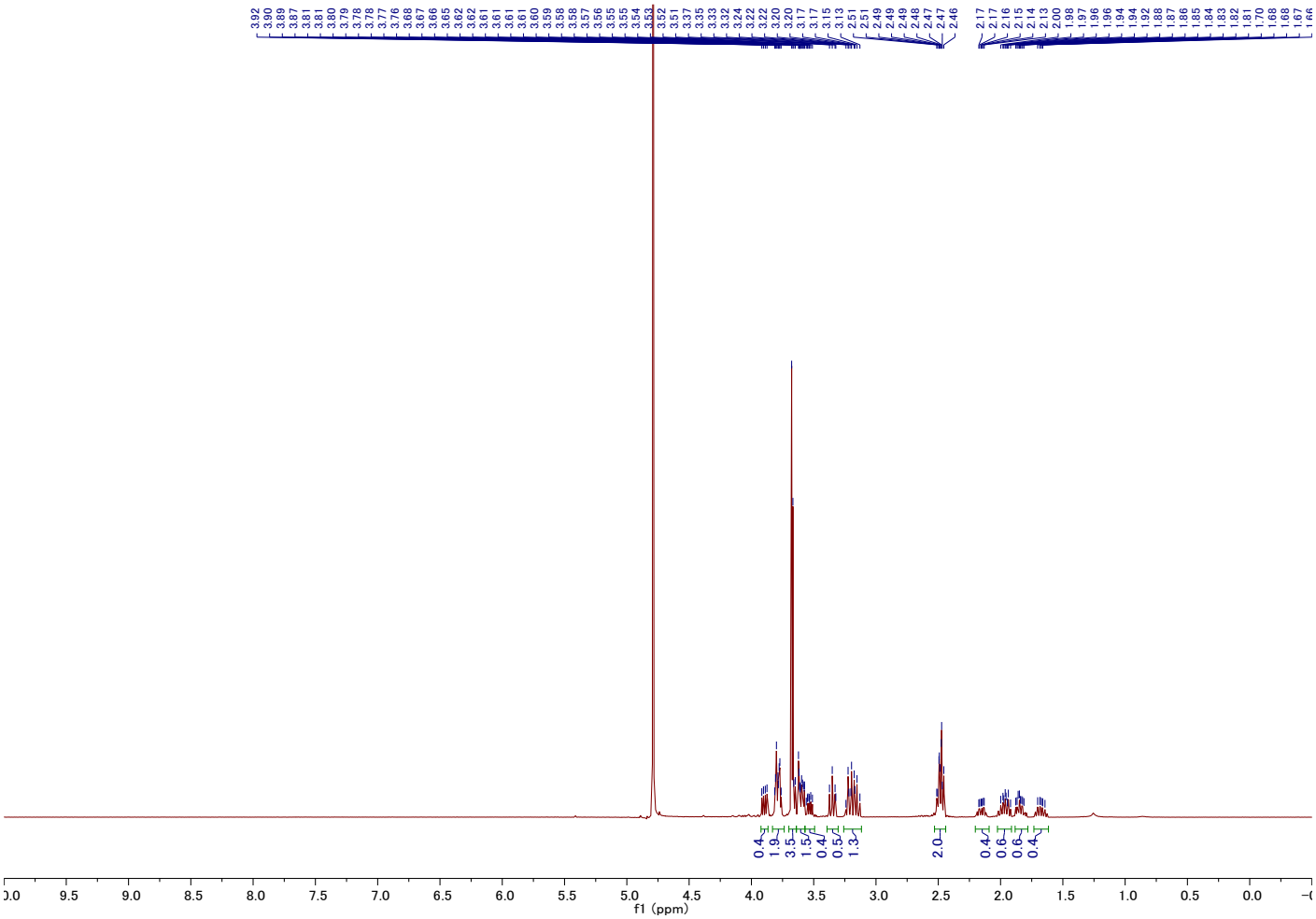


Fig. S17 ^{1}H NMR of methyl 3-(D-xylopyranosyl)-propanoate **(MA-Xyl, 8)** in D_2O

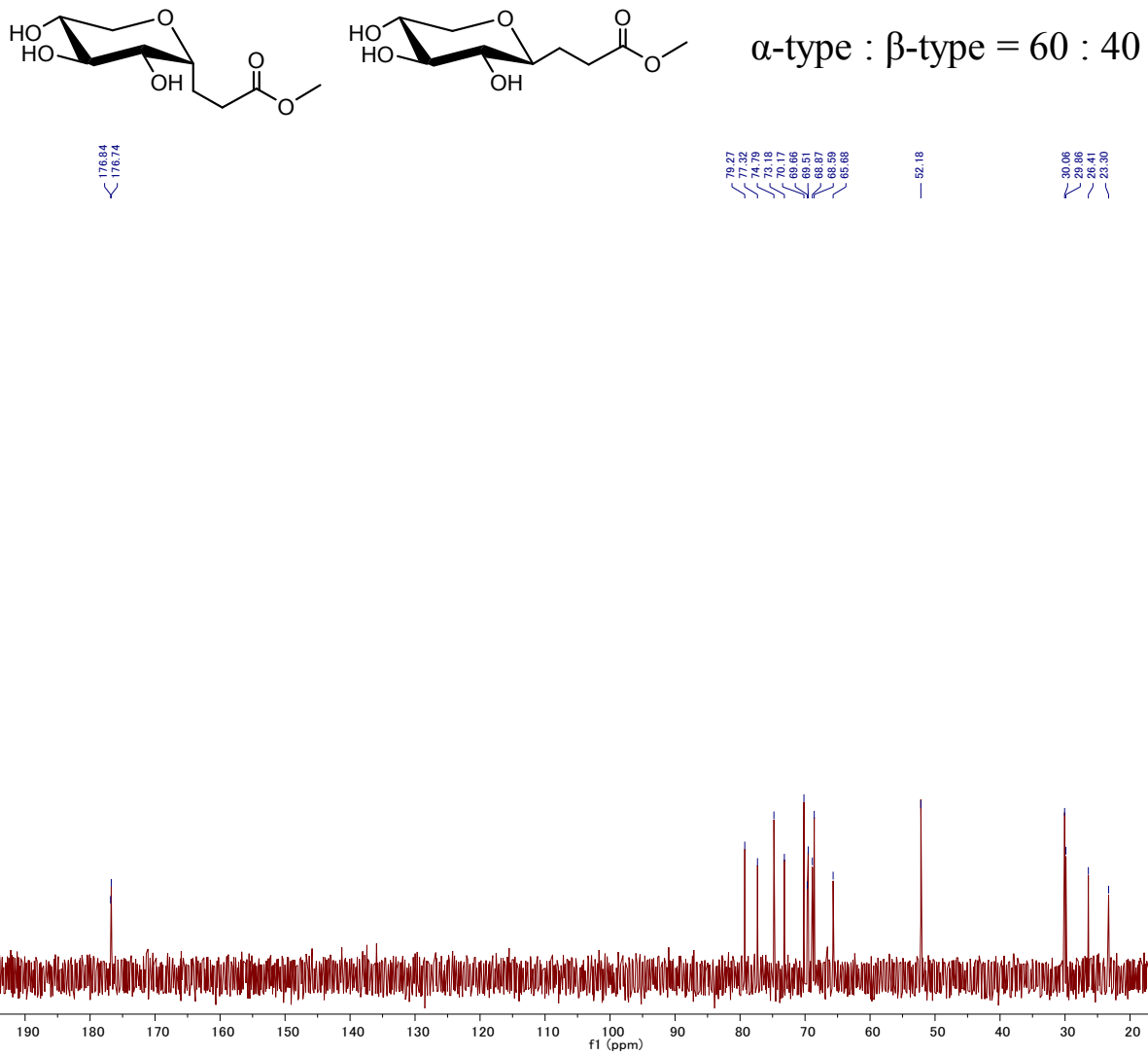


Fig. S18 ^{13}C NMR of methyl 3-(D-xylopyranosyl)-propanoate **(MA-Xyl, 8)** in D_2O

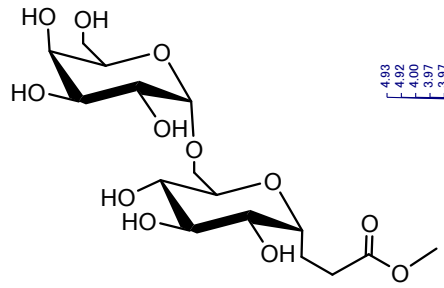


Fig. S19 ^{1}H NMR of methyl 3-(α-melibiosyl)-propanoate **(MA-α-melibiose, 9)** in D_2O

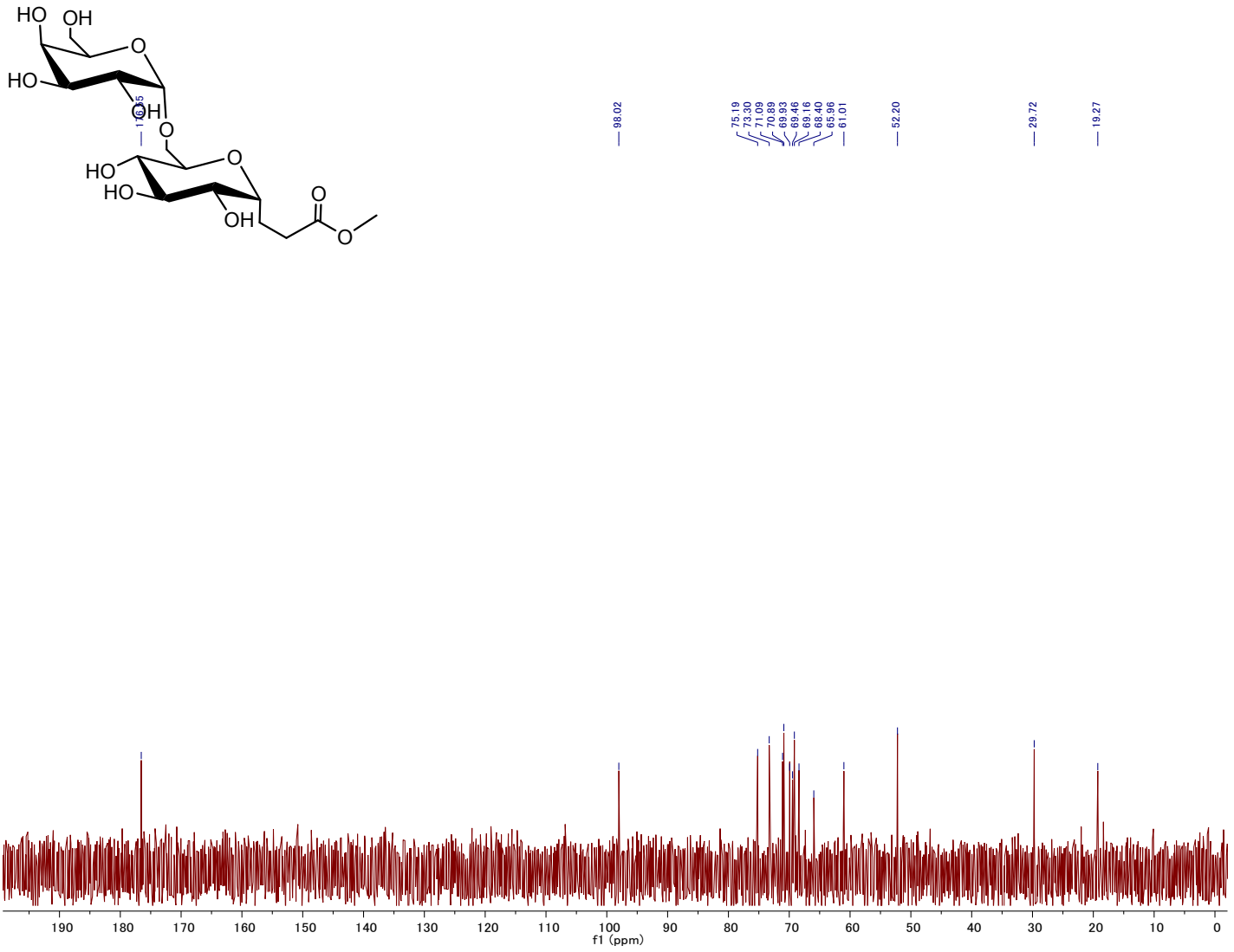


Fig. S20 ^{13}C NMR of methyl 3-(α-melibiosyl)-propanoate **(MA-α-melibiose, 9)** in D_2O

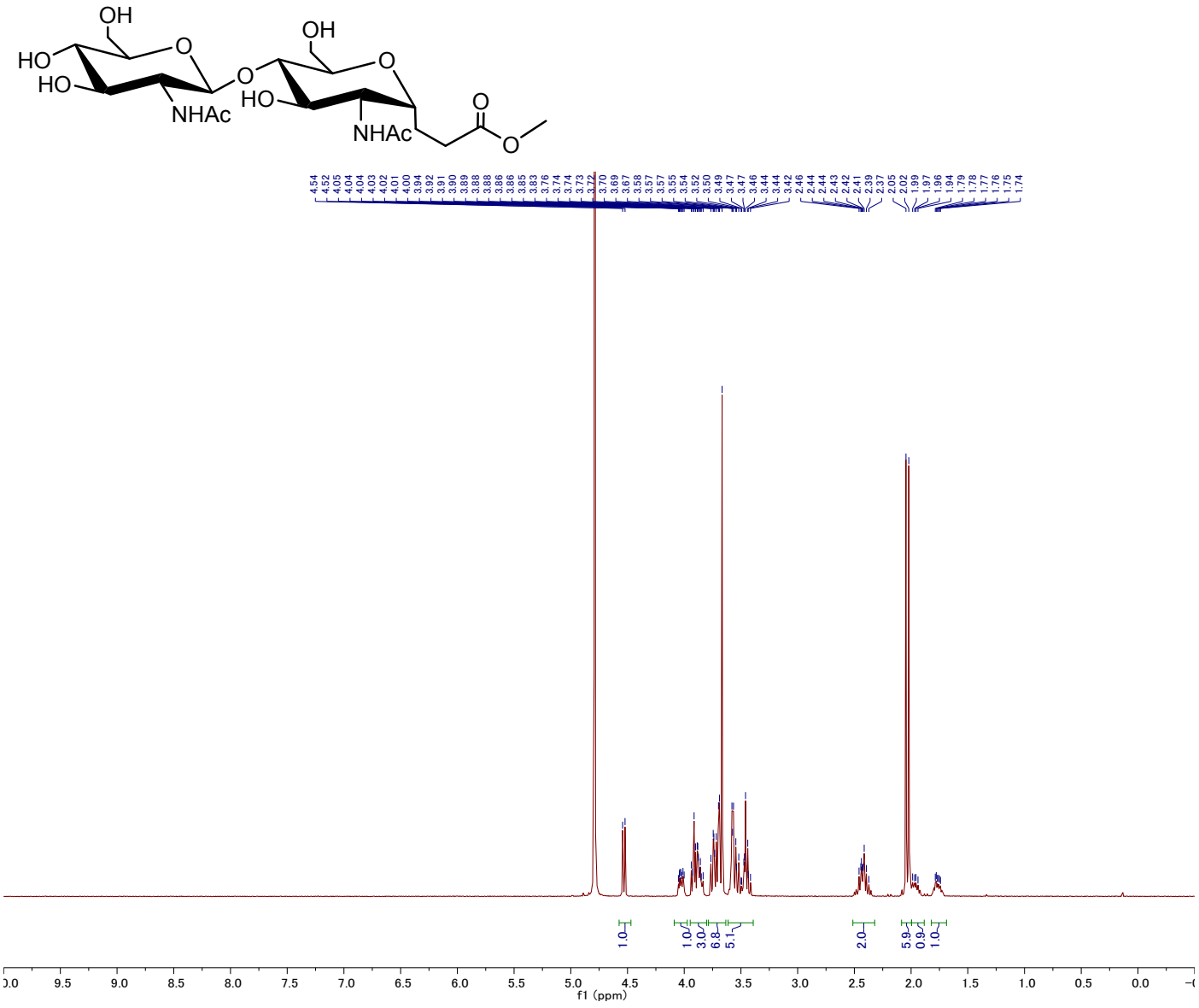


Fig. S21 ^{1}H NMR of methyl 3-(α-chitobiosyl)-propanoate **(MA-α-chitobiose, 10)** in D_2O

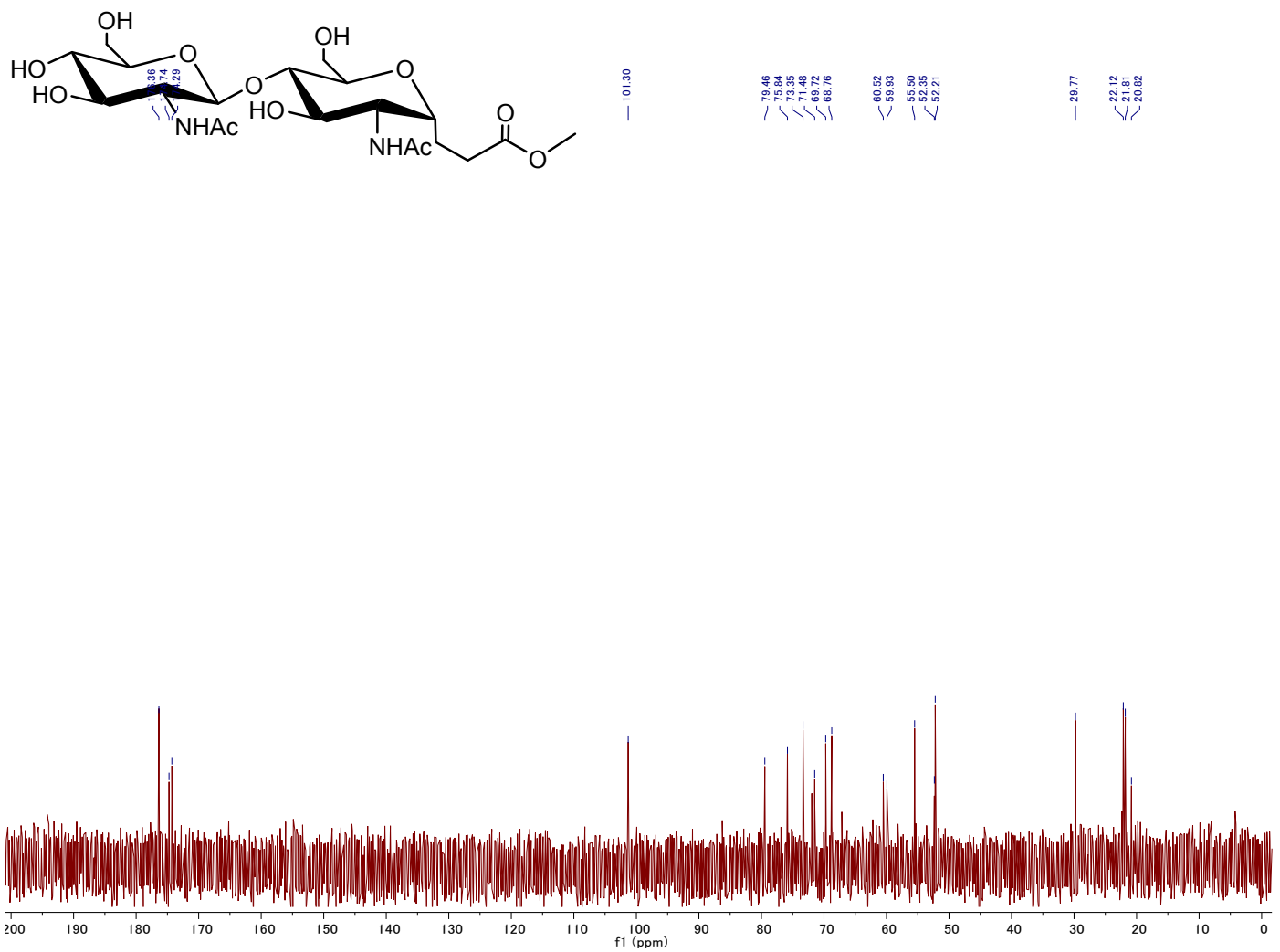


Fig. S22 ^{13}C NMR of methyl 3-(α-chitobiosyl)-propanoate **(MA-α-chitobiose, 10)** in D_2O

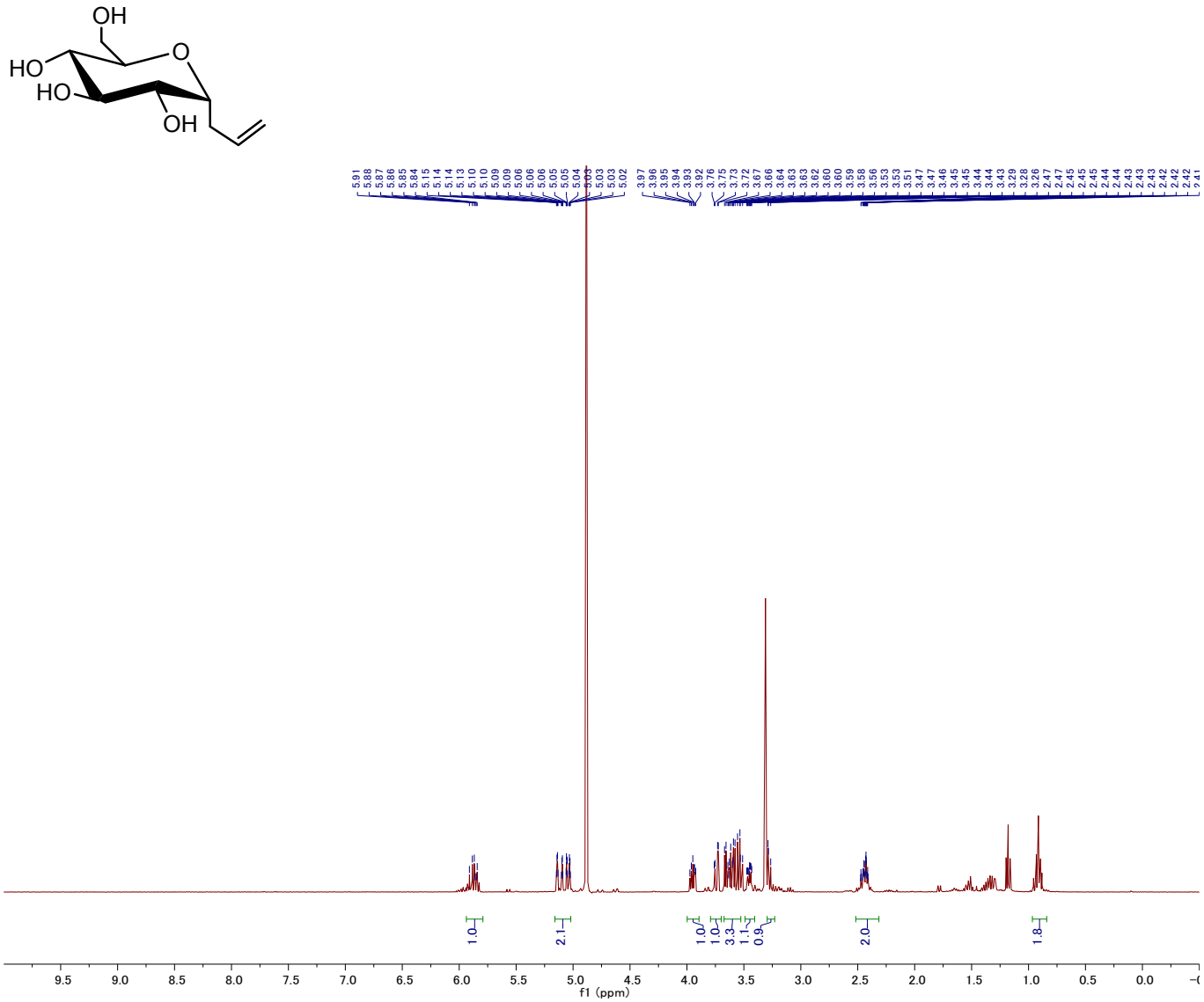


Fig. S23 ^{1}H NMR of 1-(α-D-glucopyranosyl)-2-propene (**11**) in CD_3OD

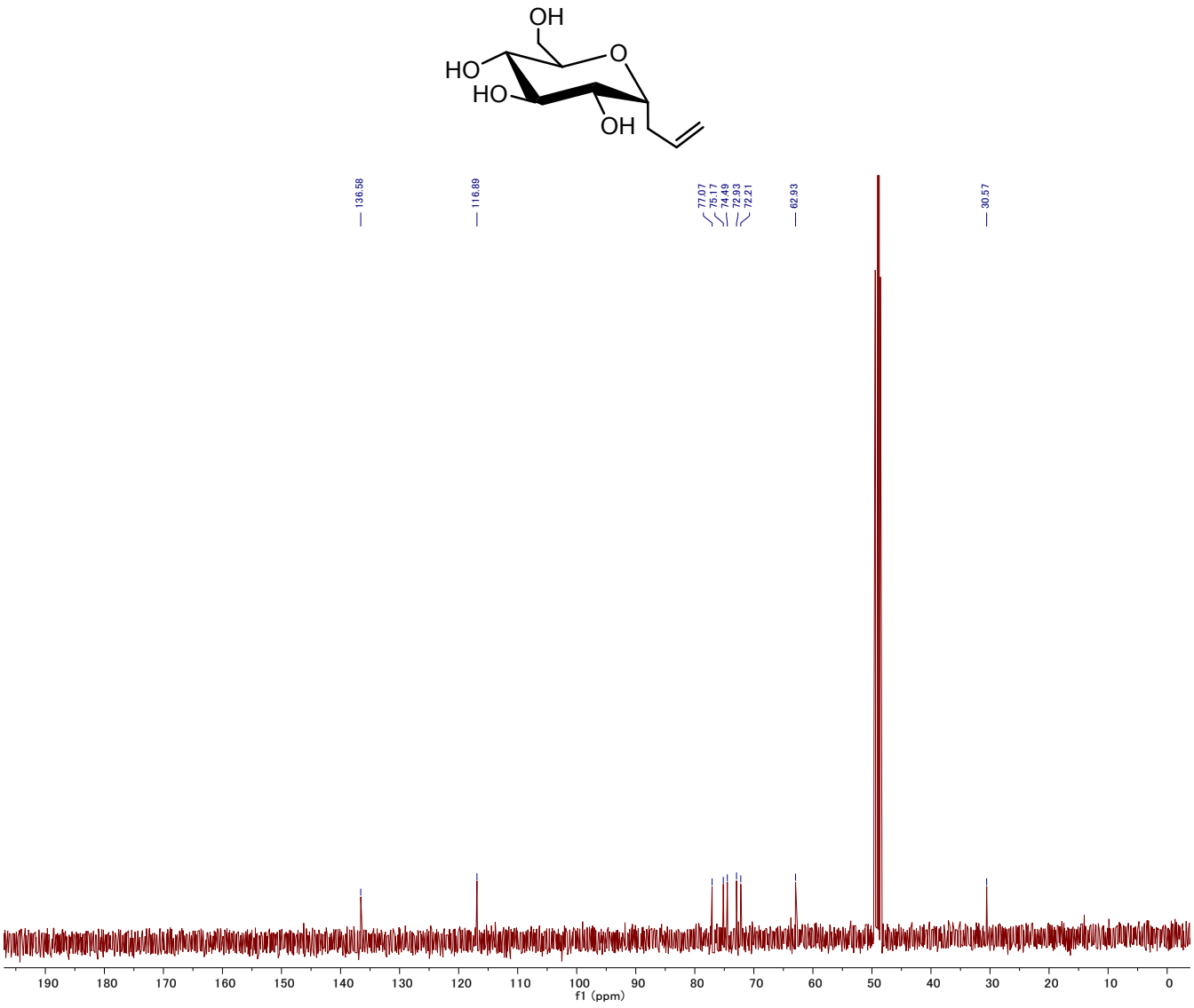


Fig. S24 ^{13}C NMR of 1-(α-D-glucopyranosyl)-2-propene (**11**) in CD_3OD

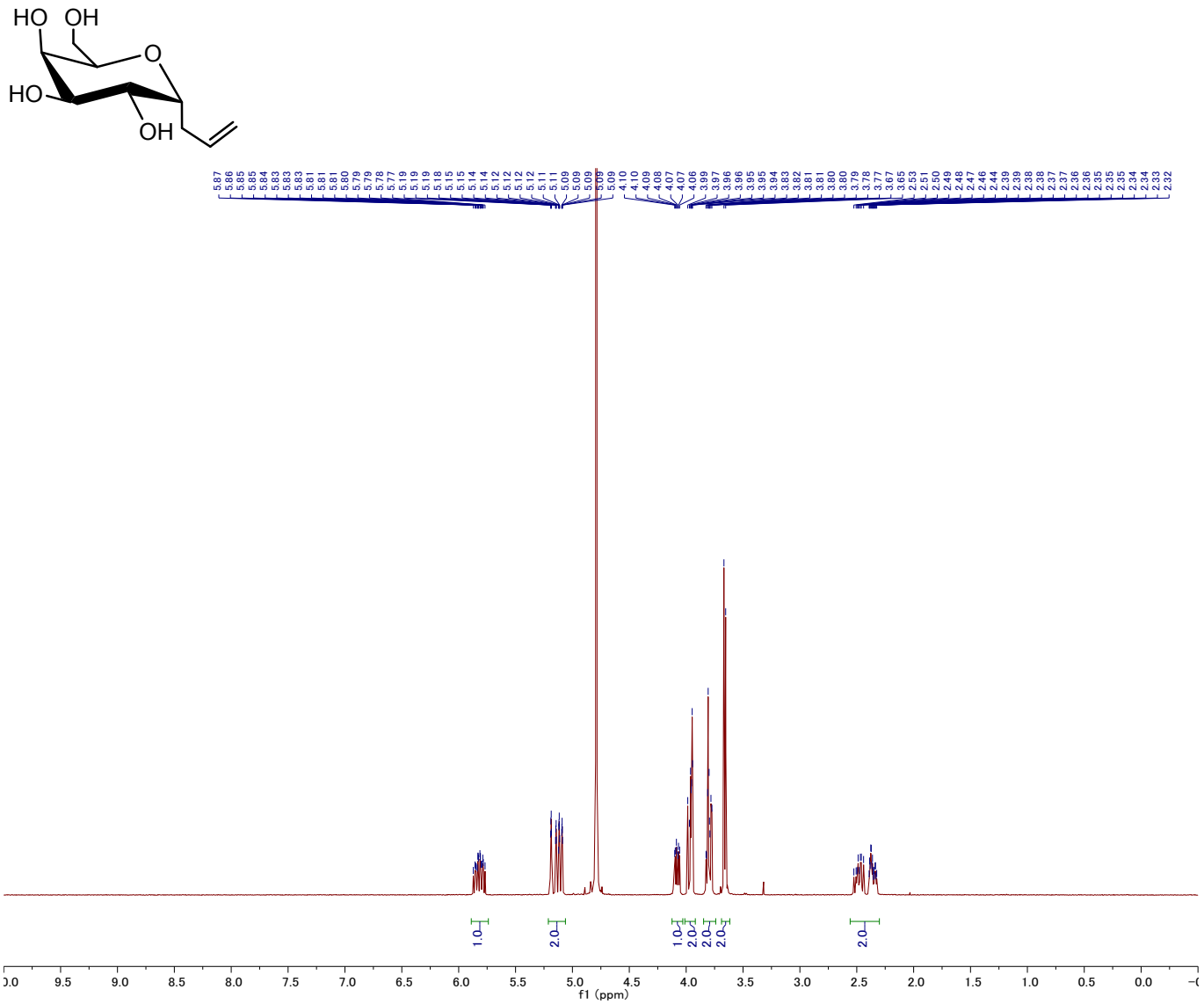


Fig. S25 ^{1}H NMR of 1-(α-D-galactopyranosyl)-2-propene (**20**) in D_2O

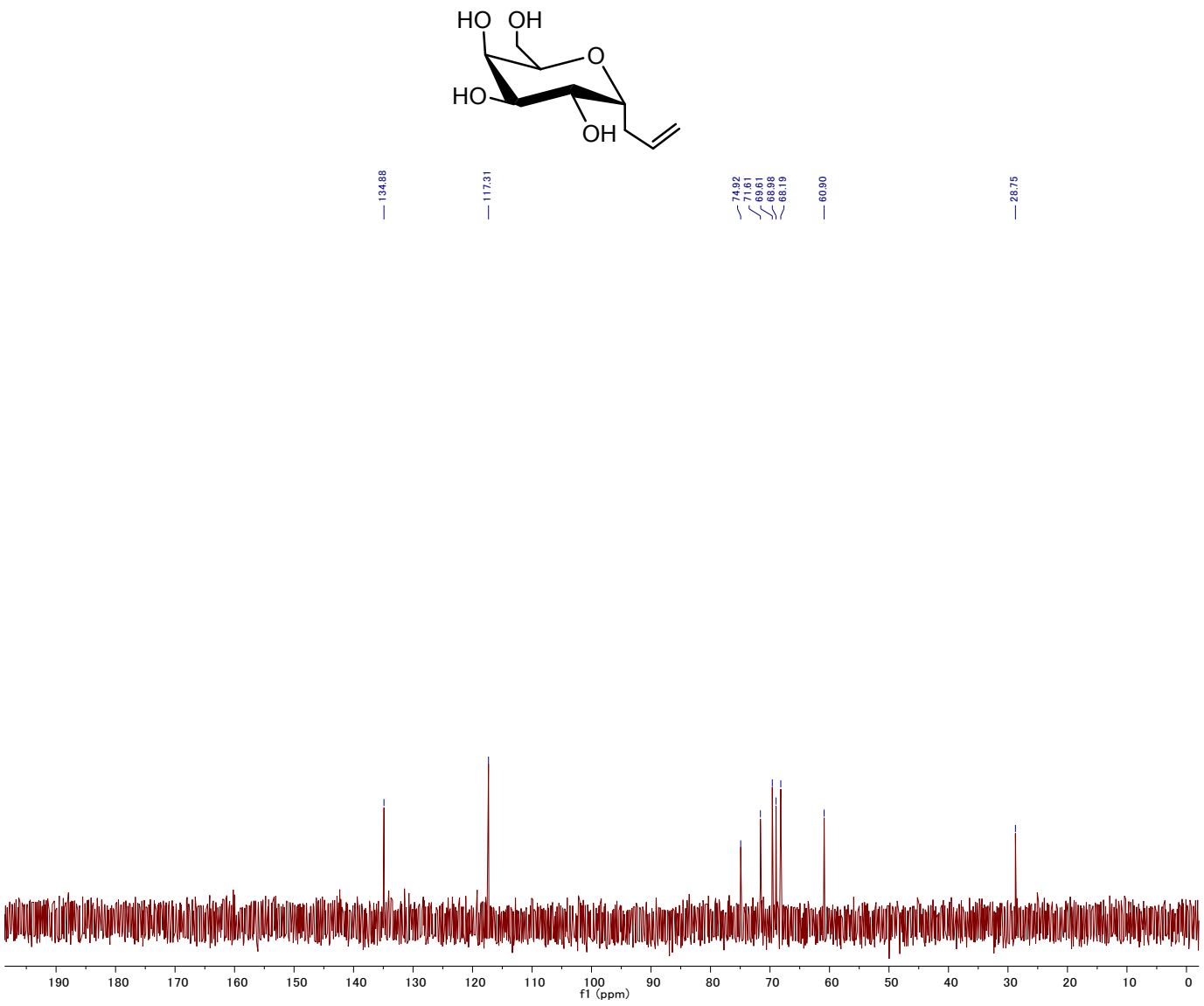


Fig. S26 ^{13}C NMR of 1-(α-D-galactopyranosyl)-2-propene (**20**) in D_2O

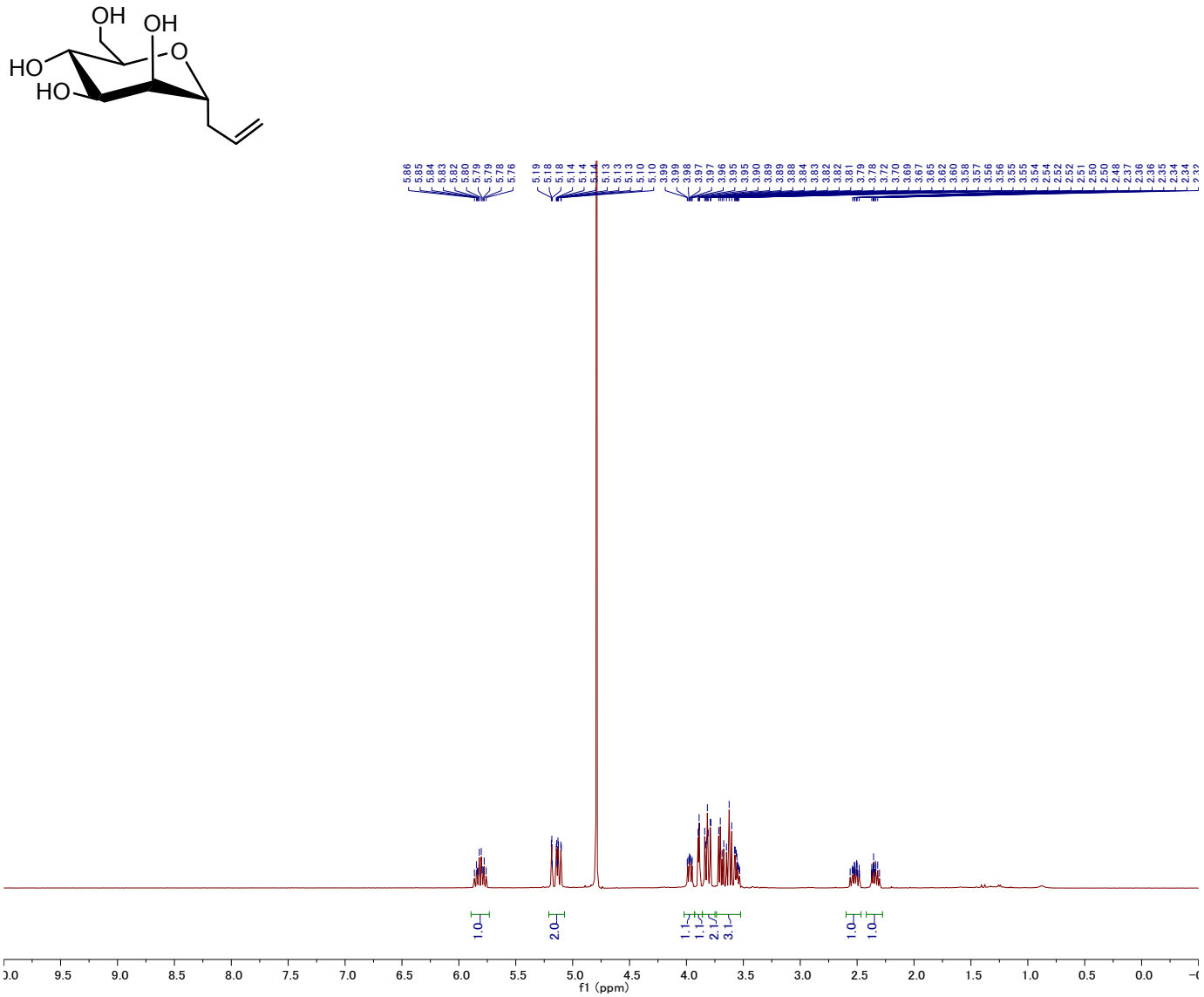


Fig. S27 ^{1}H NMR of 1-(α-D-mannopyranosyl)-2-propene (**21**) in D_2O

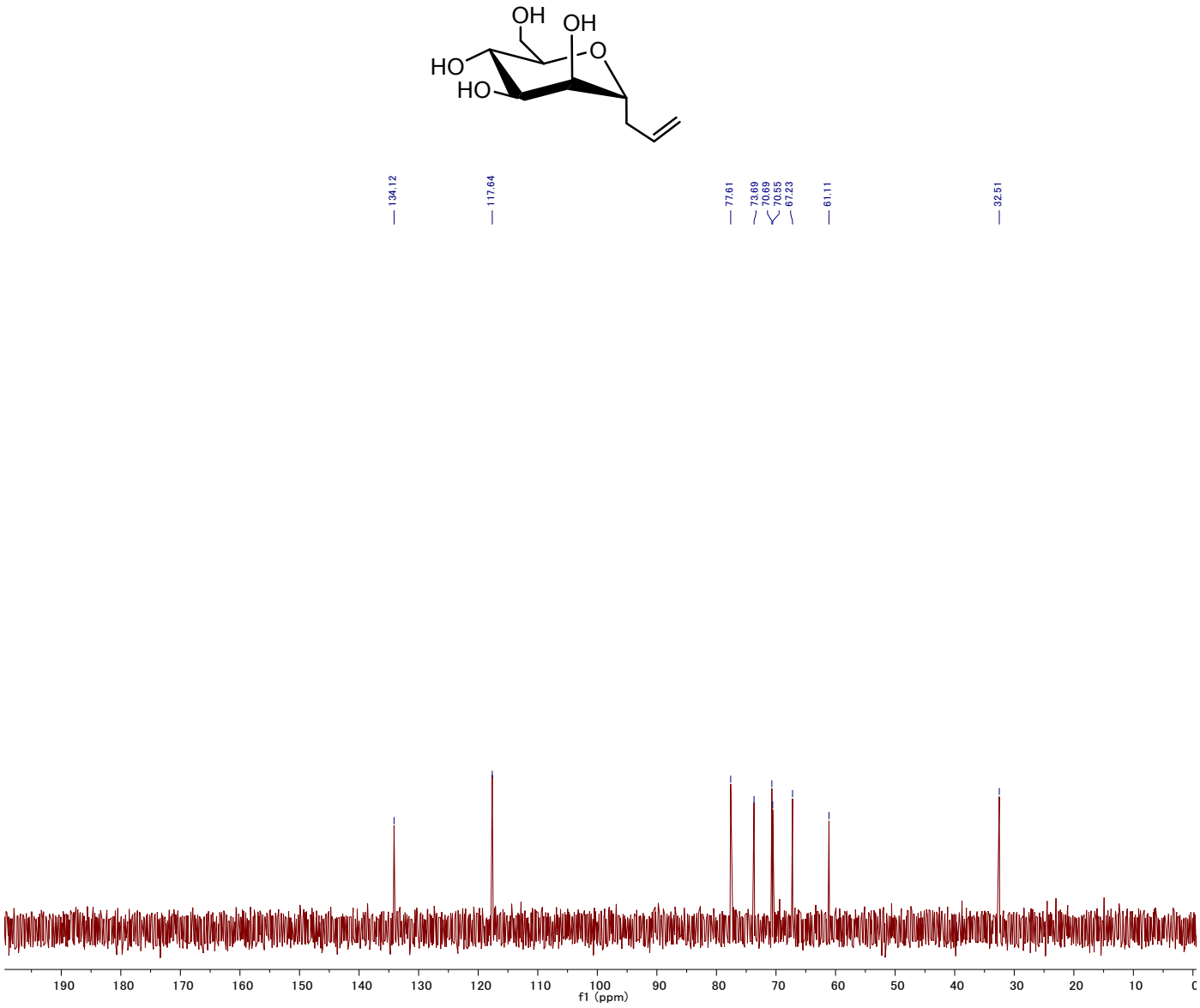


Fig. S28 ^{13}C NMR of 1-(α-D-mannopyranosyl)-2-propene (**21**) in D_2O

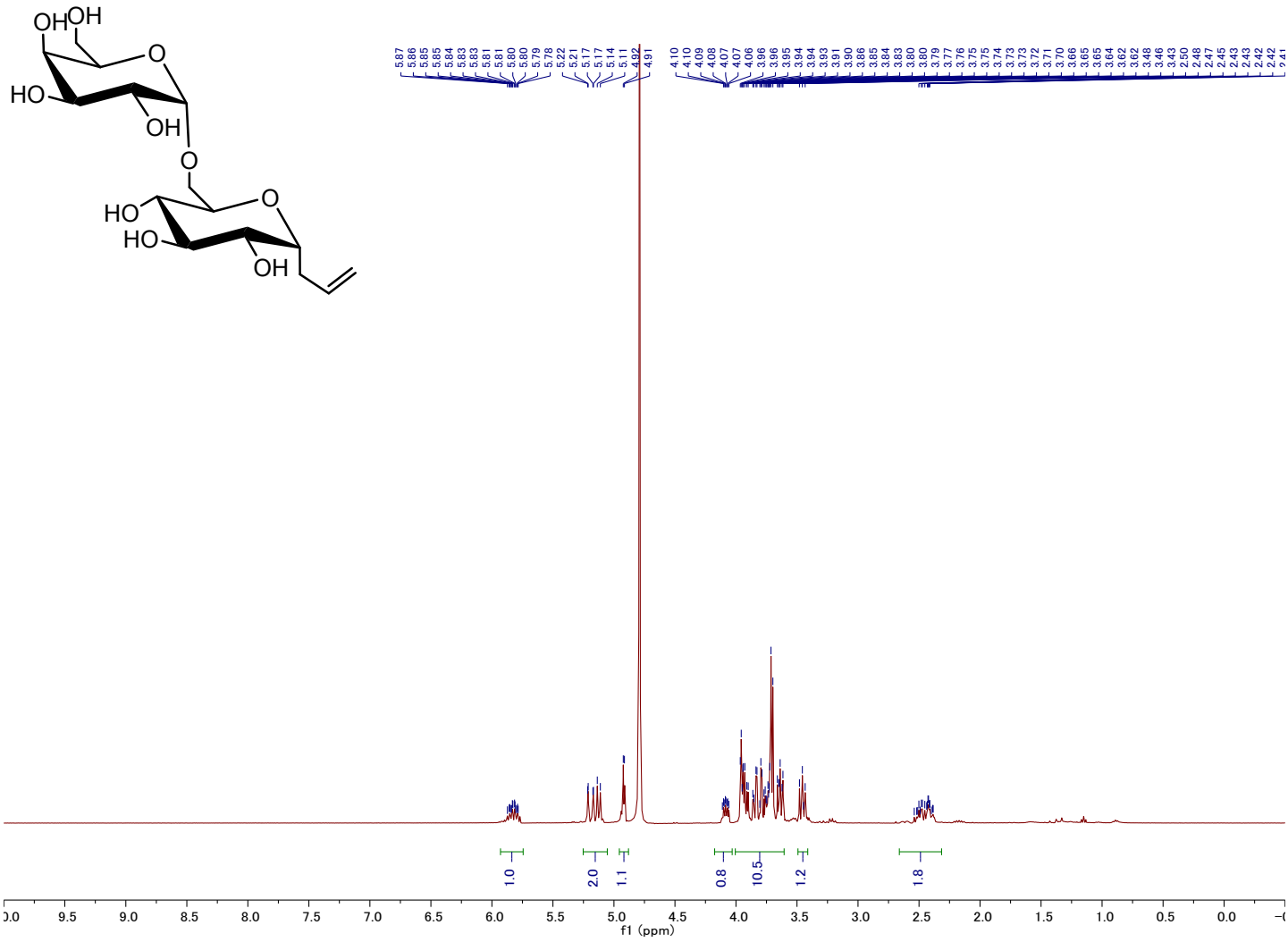


Fig. S29 ^{1}H NMR of 1-(α-melibiosyl)-2-propene (**22**) in D_2O

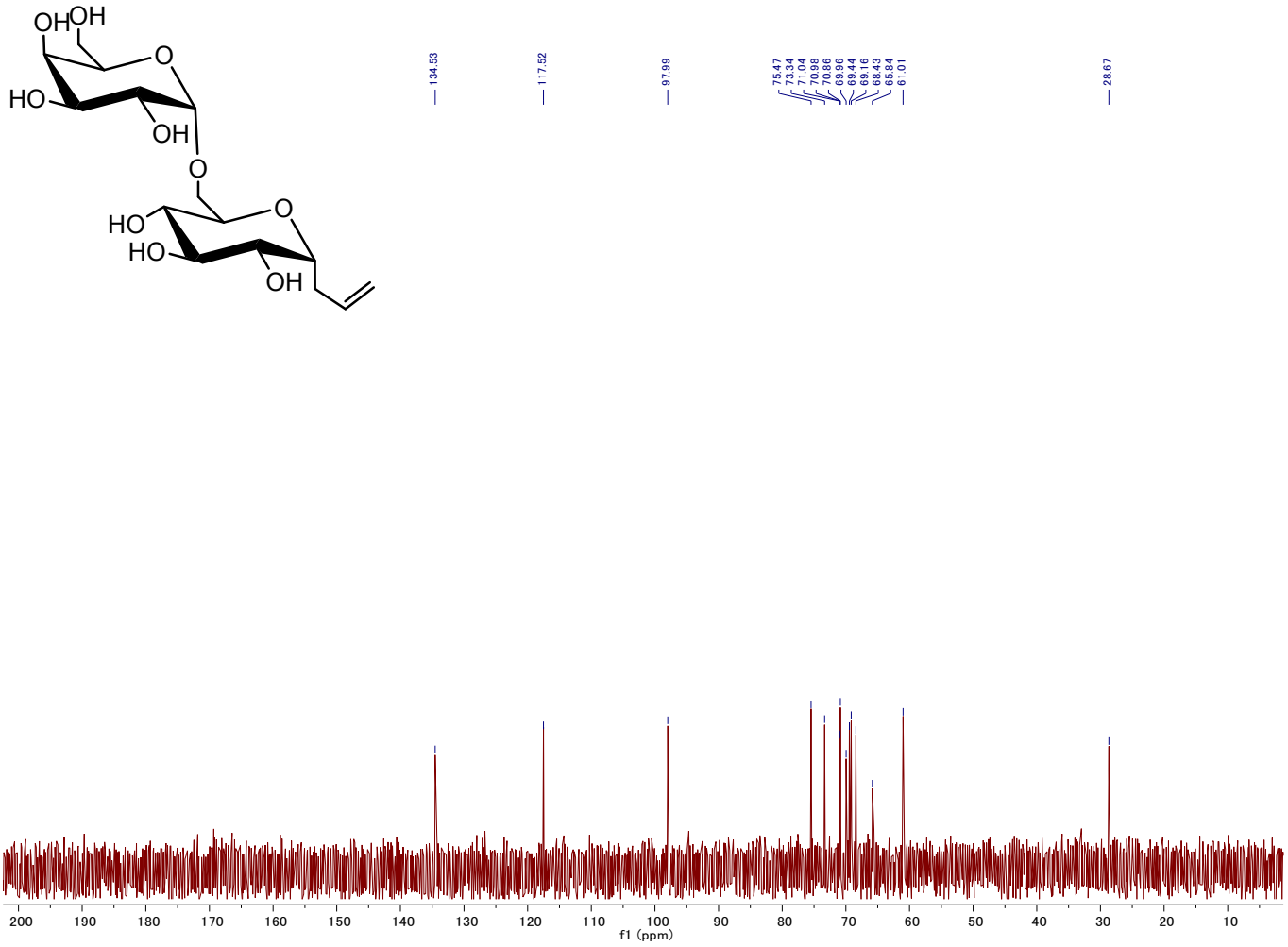


Fig. S30 ^{13}C NMR of 1-(α-melibiosyl)-2-propene (**22**) in D_2O

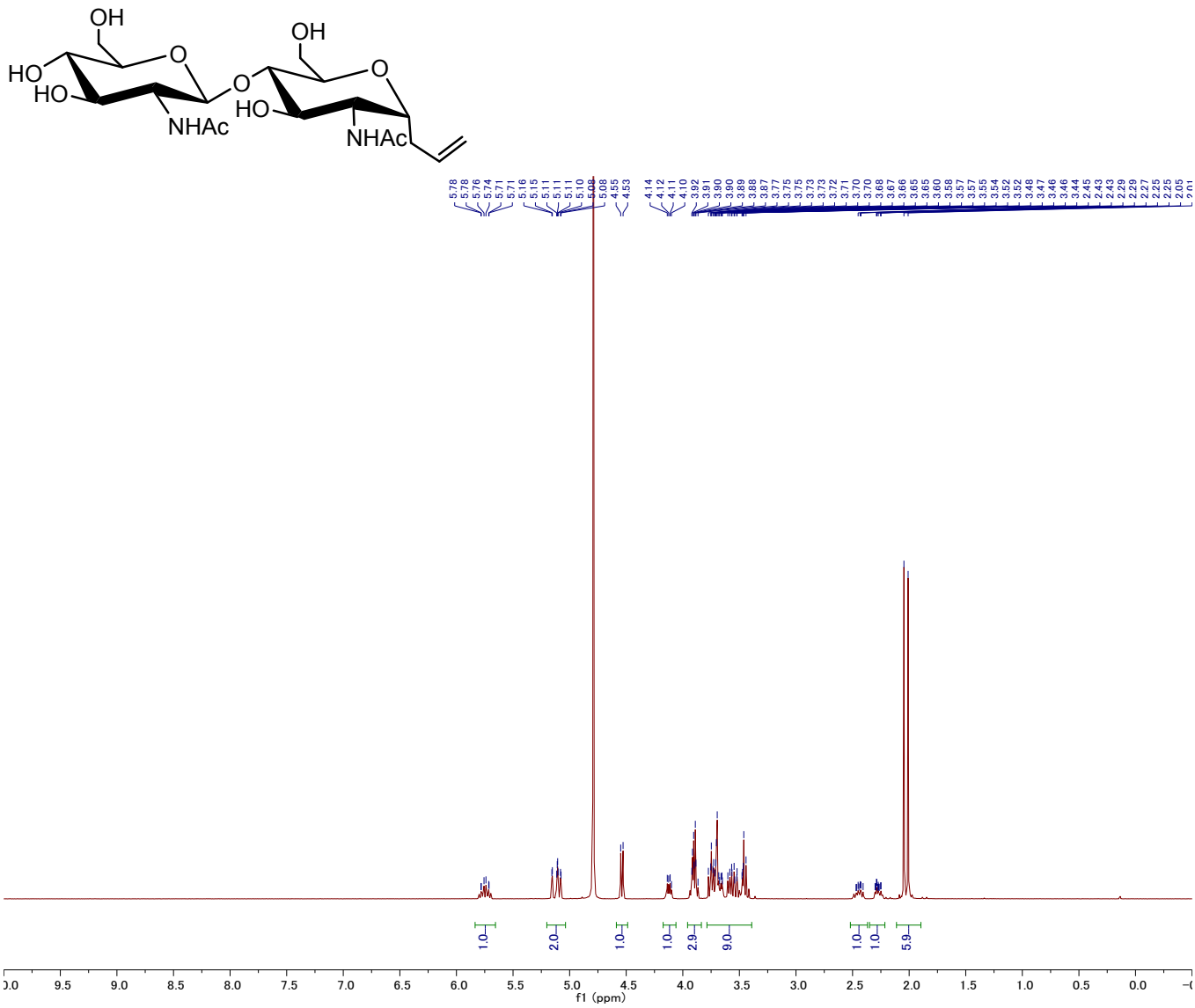


Fig. S31 ^{13}C NMR of 1-(α-chitobiosyl)-2-propene (**23**) in D_2O

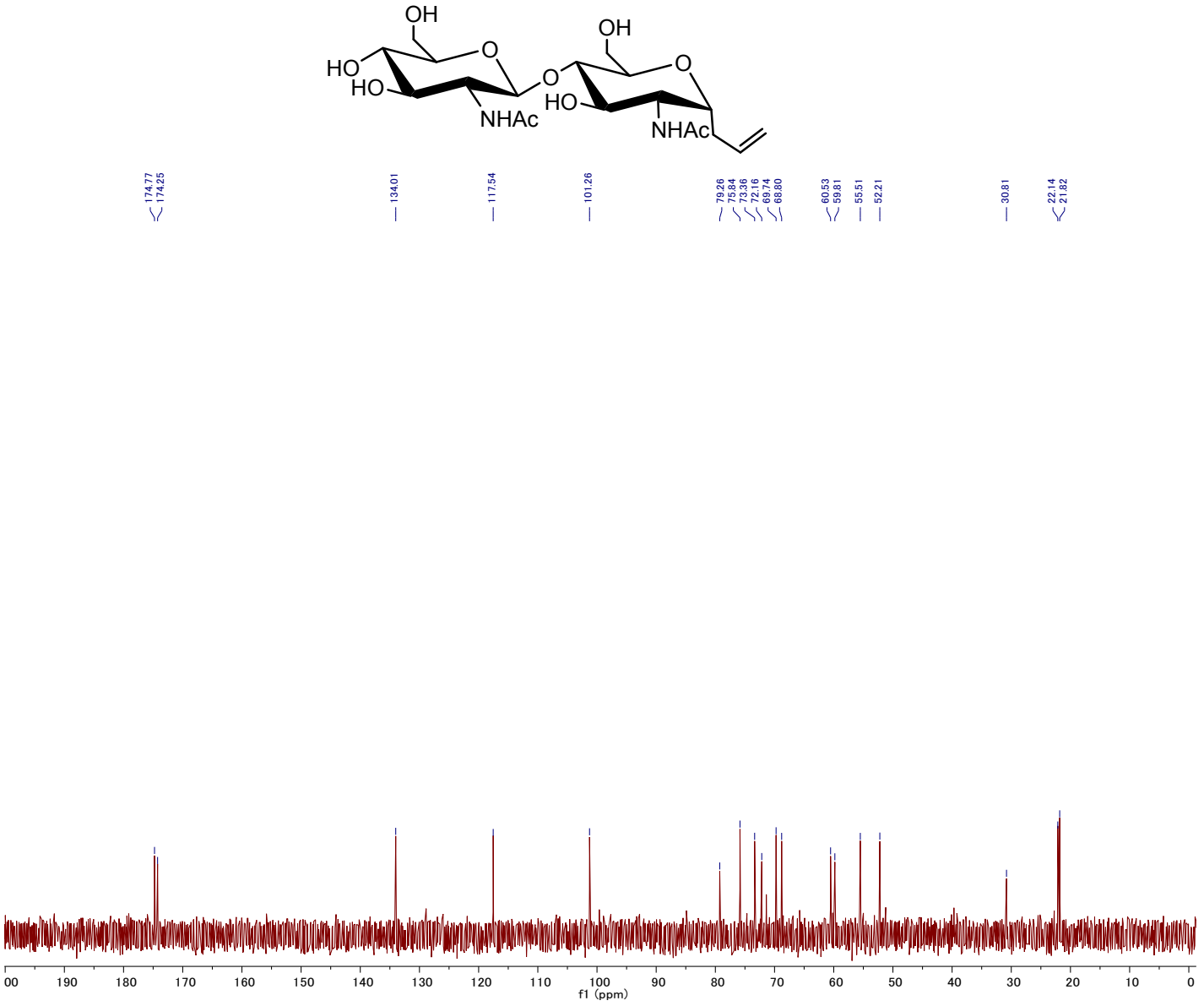


Fig. S32 ^{13}C NMR of 1-(α-chitobiosyl)-2-propene (**23**) in D_2O

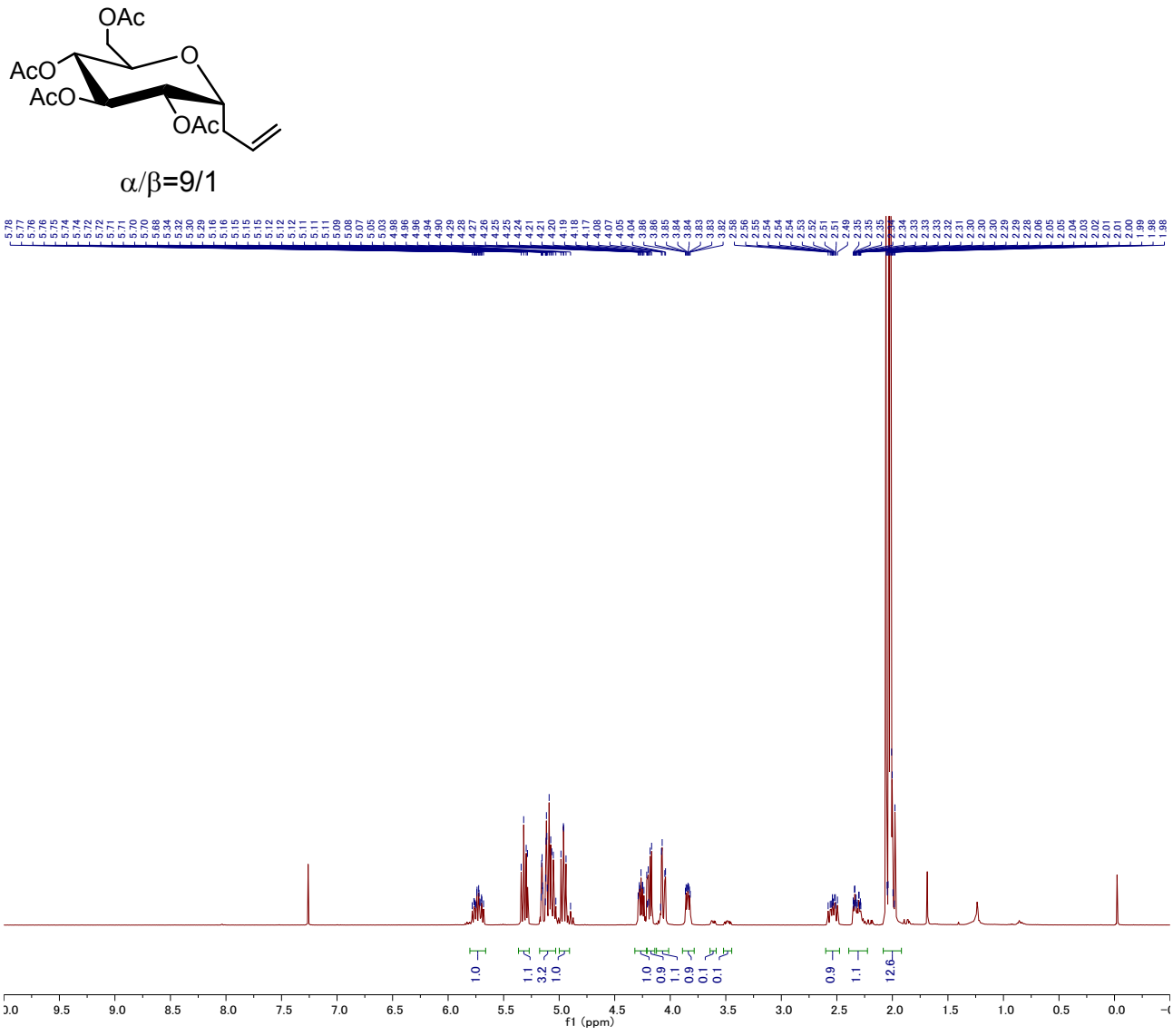


Fig. S33 ^{1}H NMR of tetra-*O*-acetyl 1-(D-glucopyranosyl)-2-propene (**13**) in $CDCl_3$ [10]

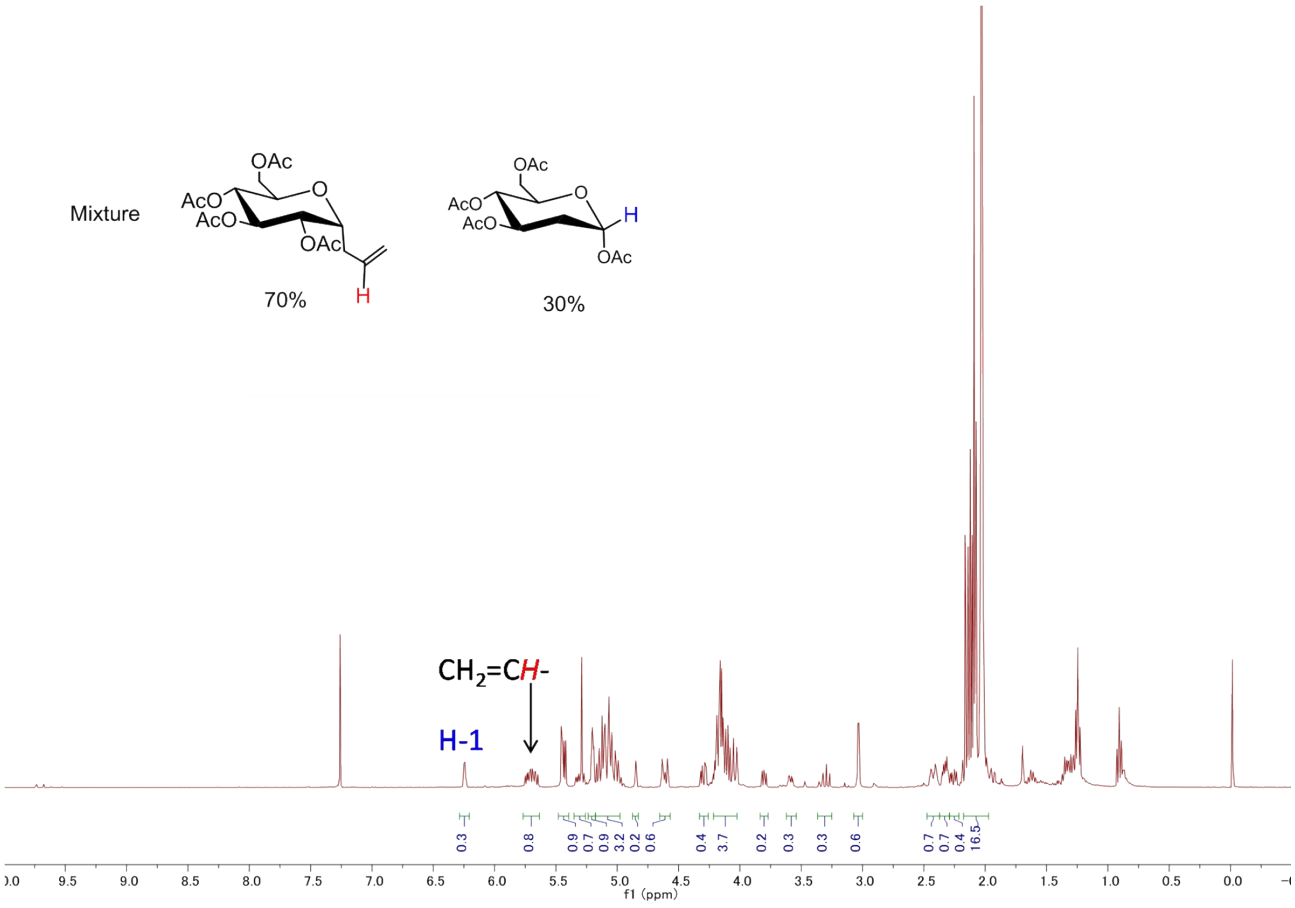


Fig. S34 ^{1}H NMR of mixture of **13** and **14** in $CDCl_3$ [11]

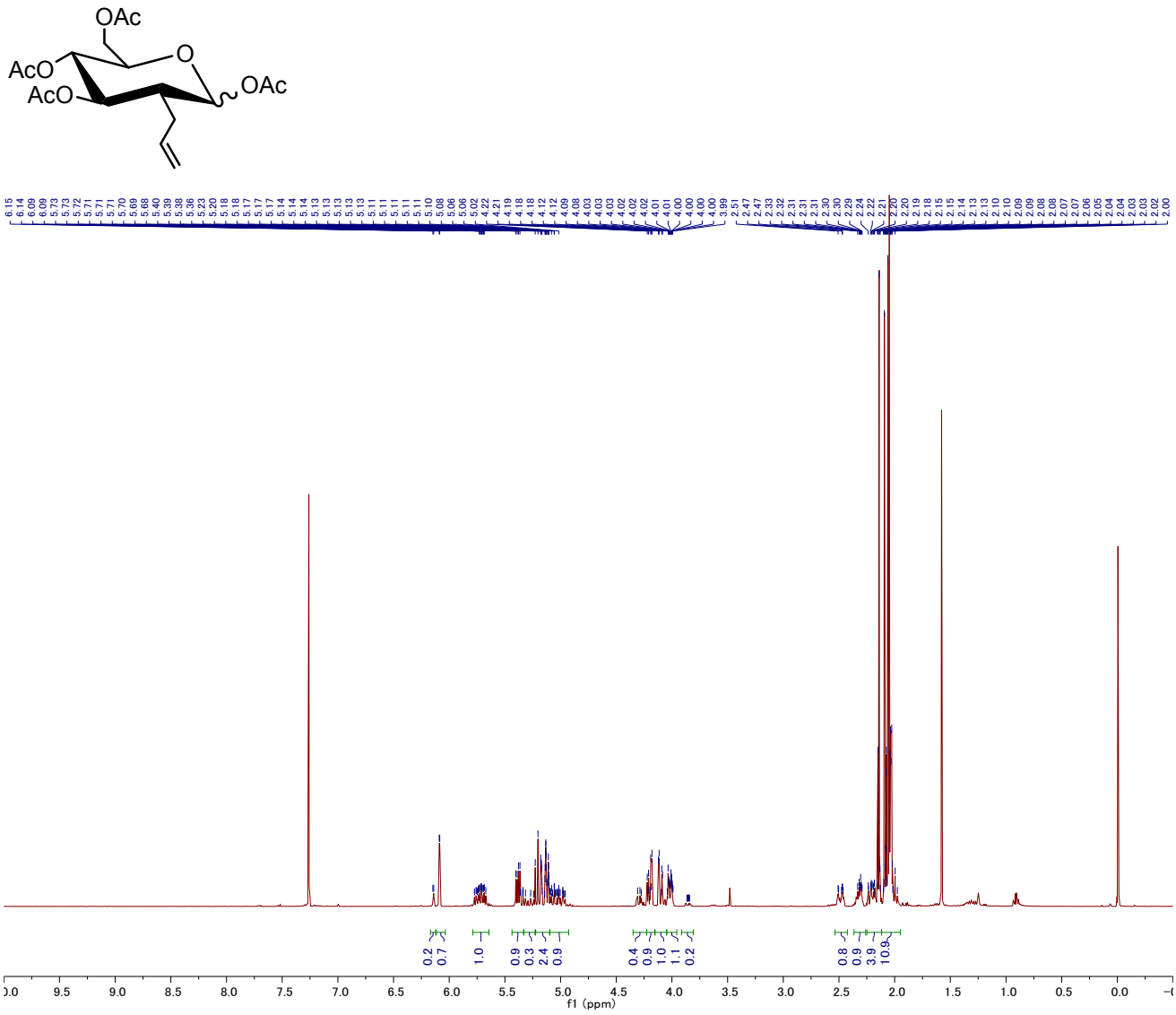


Fig. S35 ^{1}H NMR of 1,3,4,6-tetra-*O*-acetyl-2-*C*-allyl-2-deoxy D-glucopyranose (**15**) in $CDCl_3$

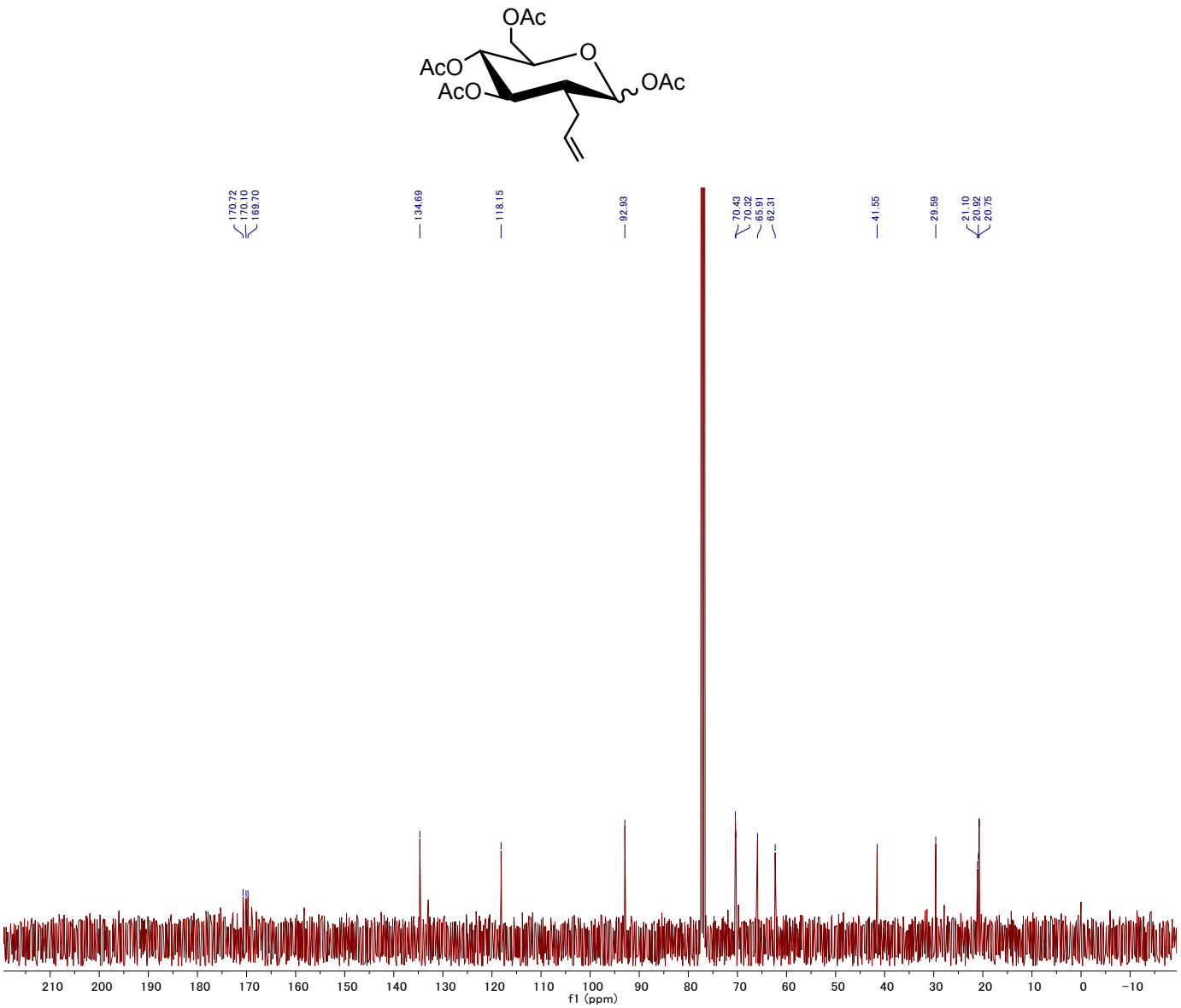


Fig. S36 ^{13}C NMR of 1,3,4,6-tetra-*O*-acetyl-2-*C*-allyl-2-deoxy D-glucopyranose (**15**) in $CDCl_3$

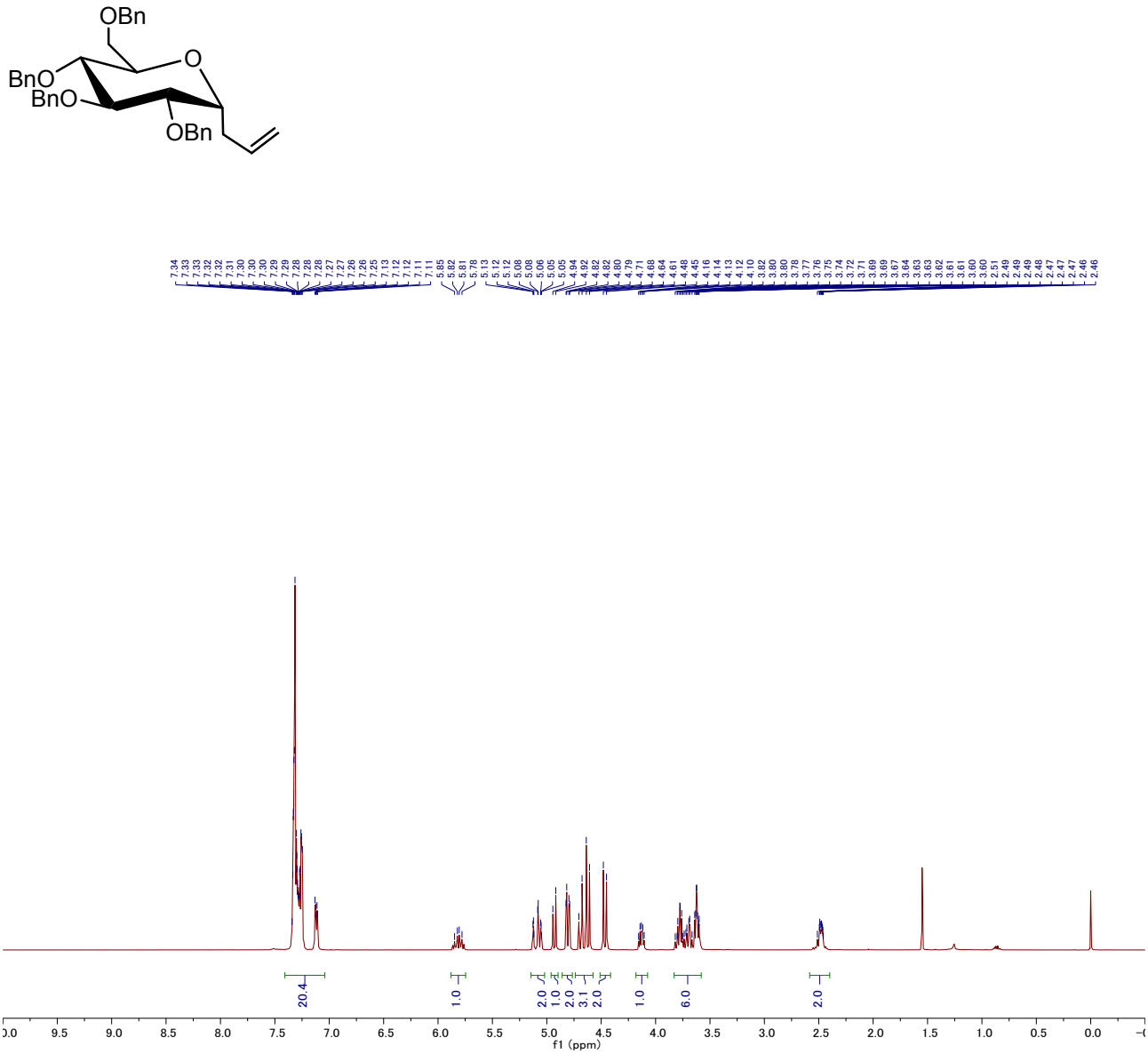


Fig. S37 ^{1}H NMR of tetra-*O*-benzyl 1-(D-glucopyranosyl)-2-propene (**17**) in $CDCl_3$ [12]

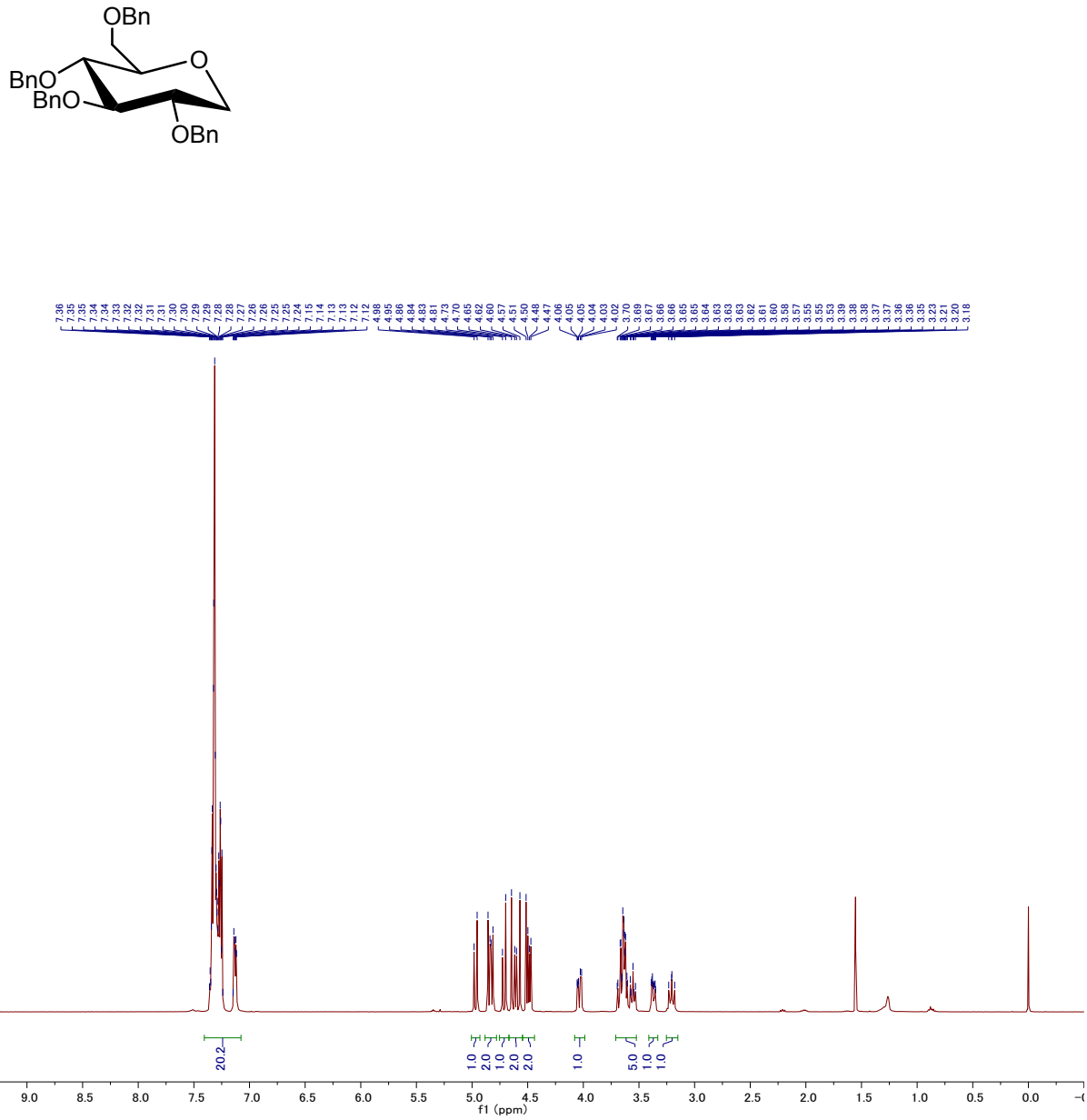
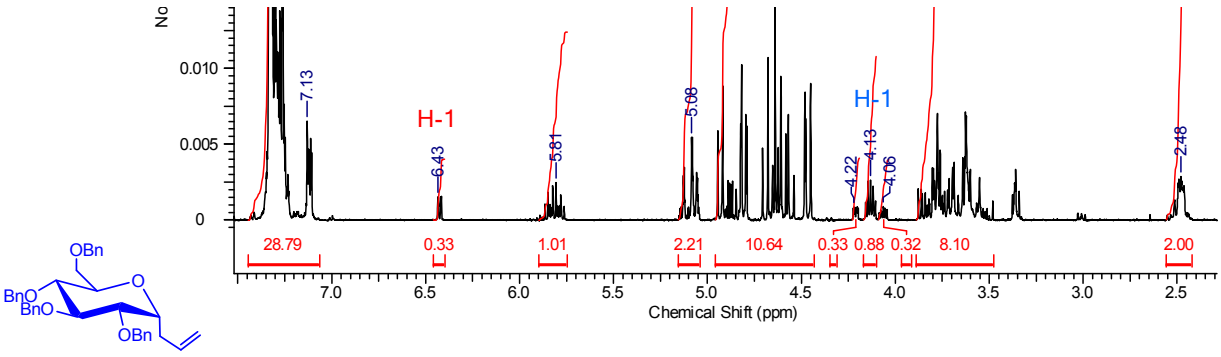


Fig. S38 ^{1}H NMR of 1,5-anhydro-2,3,4,6-tetra-*O*-benzyl-D-glucitol (**18**) in $CDCl_3$ [13]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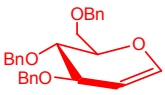
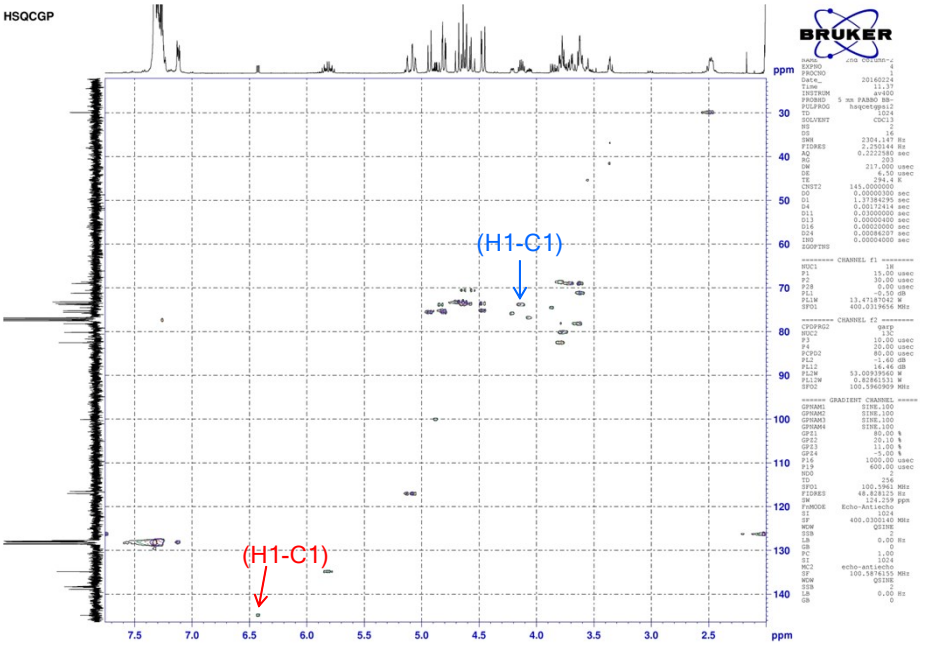
0.005
0
7.13
H-1
6.43
5.81
5.08
H-1
4.22
4.13
4.06
2.48
28.79
0.33
1.01
2.21
10.64
0.33
0.88
0.32
8.10
2.00
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
Chemical Shift (ppm)

OBn
BnO
BnO
O
OBn


OBn
BnO
BnO
O


HSQCGP
BRUKER
(H1-C1)
(H1-C1)
ppm
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5

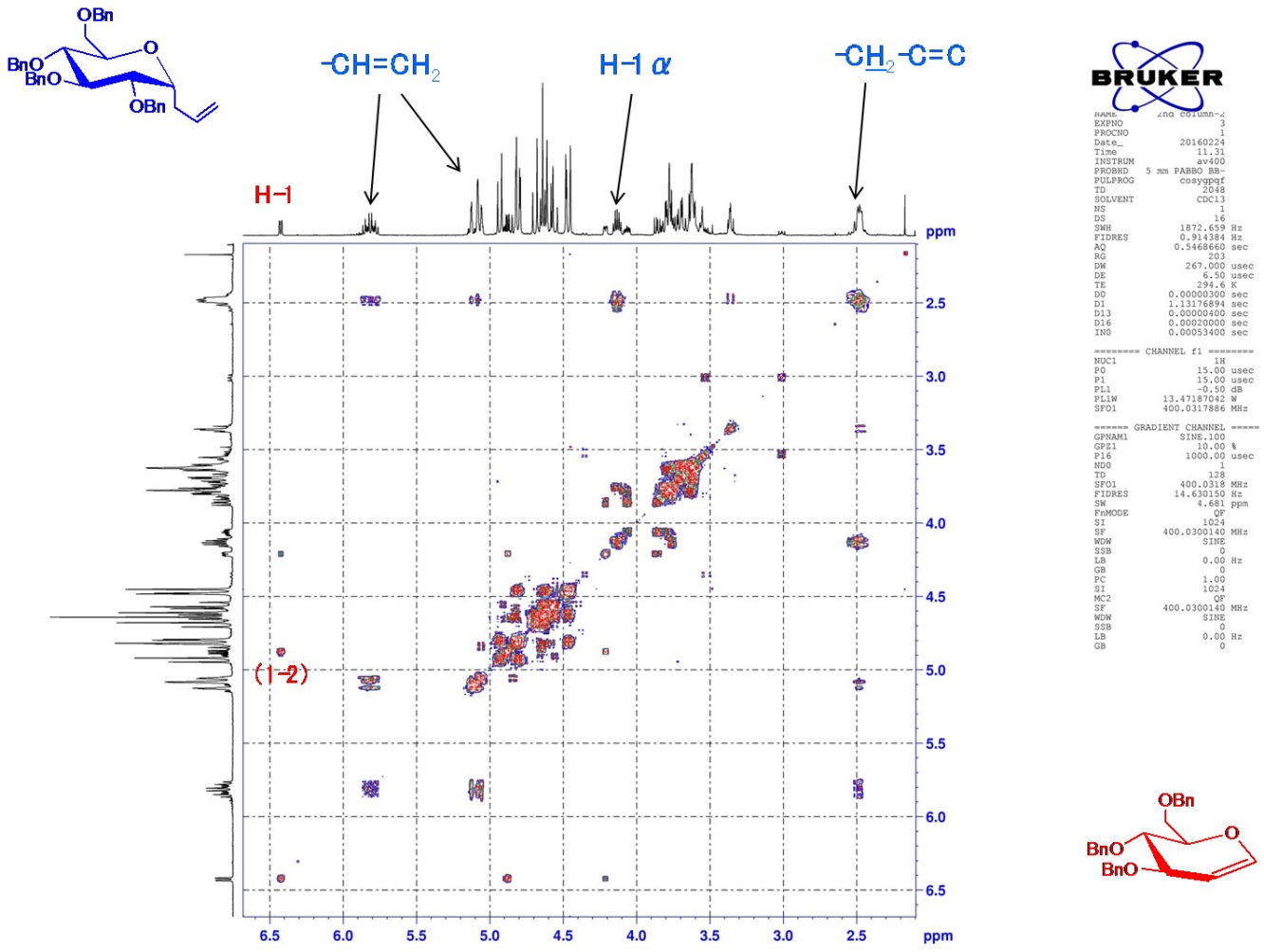

Fig. S39 NMR spectra of reaction mixture of 1-α-(2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl)-2-propene (product **17**) and 3,4,6-tri-*O*-benzylglucal (byproduct **19**) in CDCl3

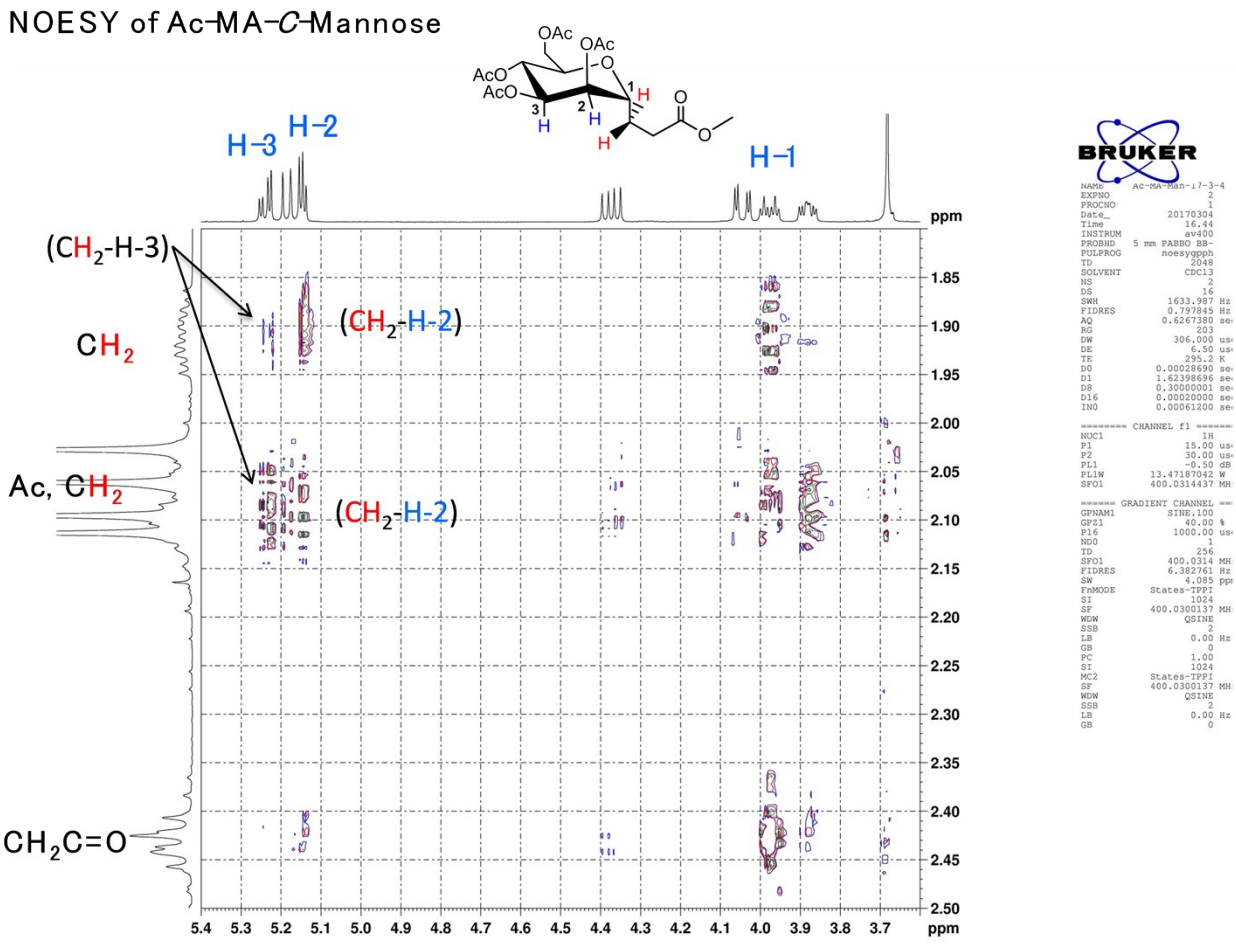

Fig. S40 NOESY of methyl 3-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-propanoate (Ac-MA-α-*C*-Man) in $CDCl_3$