

# **Solvent- and catalyst-free transamidations of unprotected glycosyl carboxamides**

Fouzia Ouadah Bensalah,<sup>a,b</sup> Abed Bil,<sup>a</sup> Karlo Wittine,<sup>c</sup> Salima Bellahouel,<sup>b</sup> David Lesur,<sup>a</sup>  
Dean Markovic,<sup>c</sup> and Sylvain Laclef,<sup>\*a</sup>

## **Supporting information**

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## I. General methods - Chemicals and Instruments.

All purchased materials were used without further purification. Dichloromethane was distilled from calcium hydride. Analytical thin-layer chromatography (TLC) was carried out using Merck D.C.-Alufolien Kieselgel 60 F<sub>254</sub>. Flash chromatography (FC) was performed on a Reveleris iES System supplied by Grace (USA) using silica cartridges and ELSD/UV detection. <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectra were respectively recorded at 400 and 75 MHz using a Bruker DRX-400 spectrometer. Chemical shifts are reported in parts per million relative to a residual solvent peak for CDCl<sub>3</sub> (<sup>1</sup>H: δ=7.26 ppm, <sup>13</sup>C: δ=77.16 ppm) and pyridine-d<sub>5</sub> (<sup>1</sup>H: δ=8.74, 7.58 and 7.22 ppm, <sup>13</sup>C: δ=150.35, 135.91 and 123.87 ppm). For D<sub>2</sub>O, MeOH was used as standard for <sup>13</sup>C (<sup>1</sup>H: δ=4.79 ppm, <sup>13</sup>C: δ=49.50 ppm). Peak multiplicity is reported as: singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), sextuplet (s<sup>x</sup>), septuplet (s<sup>p</sup>), multiplet (m), doublet of doublet (dd), doublet of doublet of doublet (ddd), doublet of triplet (dt) and broad (br). High-resolution mass spectra HRMS were obtained by electrospray ionization (ESI) using a Micromass-Waters Q-TOF Ultima Global instrument. Infra-Red spectra were obtained by a Shimadzu FTIR-84005 spectrometer (reported in cm<sup>-1</sup>). Optical rotations were measured using a 343 Perkin–Elmer instrument at 20°C in a 1 cm cell in the stated solvent; [α]<sub>D</sub> values are given in 10<sup>-1</sup> deg.cm<sup>-1</sup>g<sup>-1</sup> (concentration *c* given as g.100 mL<sup>-1</sup>). Melting points were measured in a Büchi 535 (maximum temperature 275 °C).

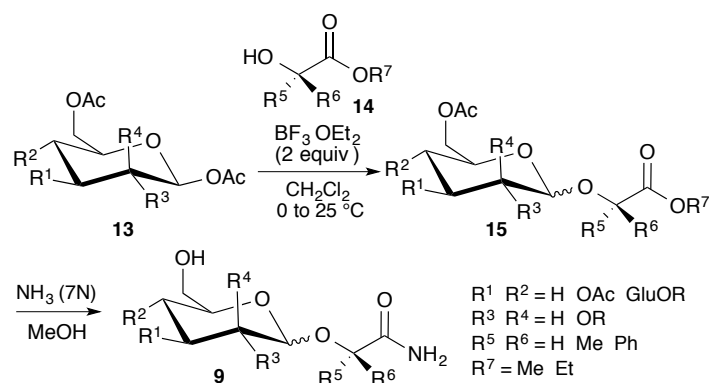
## II. Experimental part

### A. Synthesis of starting primary amides

The starting primary amides were obtained easily in a two step sequence starting from the corresponding acetate protected sugars (Table 1). In the case of glucose pentaacetates (**13a**) cellobiose octaacetate (**13c**) and lactose octaacetate (**13d**), the glycosylation reaction with methyl glycolate provided the β anomer in a pure form. In the case of mannose pentaacetate, the glycosylation with methyl glycolate provided only the α anomer in a pure form. In every other case (Entries 2-4), the major isomer was obtained in a pure form by recrystallisation in *i*-

PrOH or by column chromatography. In every cases, we were able to carry out the deprotection step and the formation of primary amides quantitatively in a single step by treatment with a solution of ammonia in MeOH. Products **9** were obtained directly in a pure form by triturating products **9a-f** with AcOEt in order to eliminate the acetamide, side product formed during the reaction.

**Table 1.** Synthesis of starting primary amides.

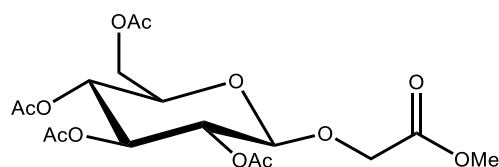


Entry	13 (R = Ac)	14	R <sup>5</sup>	R <sup>6</sup>	R <sup>7</sup>	Ratio β/α for 15	15 (yield) (R = Ac)	9 (yield) (R = H)
1	13a	14a	H	H	OMe	β (only)	15a (83%)	9a (98%)
2		14b	H	H	OEt	5.8/1	β : 15b (71%)	9a (96%)
3		14c	Me	Me	OMe	4.5/1	15c (54%)	9b (91%)
4		14d	H	Ph	OMe	8.3/1	β : 15d (76%)	9c (94%)
5	13b	14a	H	H	OMe	α (only)	15e (62%)	9d (93%)
6	13c	14a	H	H	OMe	β (only)	15f (69%)	9e (94%)
7	13d	14a	H	H	OMe	β (only)	15g (72%)	9f (96%)

## B. General procedure for glycosidation reactions and characterization of the products resulting from glycosidation.

To a solution of acetate protected glycosides (**13**) (20 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (40 mL) was added the glycolate derivative (**14**) (2 equiv., 40 mmol). The temperature was decreased at 0 °C and BF<sub>3</sub>.OEt<sub>2</sub> (5.0 mL, 2 equiv., 40 mmol) was added. The temperature was allowed to slowly warm to 25 °C and the reaction was stirred for 12 h at 25 °C. The reaction mixture was added to a saturated solution of NaHCO<sub>3</sub> (200 mL). The water phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 100 mL). The combined organic phases were dried using Na<sub>2</sub>SO<sub>4</sub>, filtered and rotary evaporated.

### Methyl 2-[(2,3,4,6-tetra-*O*-acetyl- $\beta$ -D-glucopyranosyl)oxy]-acetate (**15a**).



The reaction was carried out using methyl glycolate (2 equiv.). The reaction is providing methyl 1-*O*-(2-carboxy)methyl-2,3,4,6-tetra-*O*-acetyl- $\beta$ -D-glucopyranose as only diastereoisomer. The product was purified by recrystallization in *i*-PrOH.

The product was obtained as white solid (7.0 g, 83%, m.p. 70-71 °C.).

R<sub>f</sub>=0.48 (AcOEt : Cyclohexan, 1:1)

$[\alpha]_{589}^{25} = -38.2$ , ( $c = 1.0$ , CHCl<sub>3</sub>).

IR (film)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 2961, 1748, 1436, 1376, 1308, 1219, 1170, 1097, 1065, 1042, 982, 908.

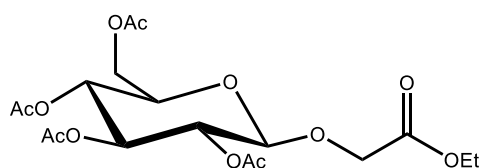
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C, 400 MHz):  $\delta_{\text{H}}$  5.23 (t,  $J = 9.5$  Hz, 1H, H-C(3)), 5.08 (t,  $J = 9.5$  Hz, 1H, H-C(4)), 5.04 (dd,  $J = 9.5, 7.9$  Hz, 1H, H-C(2)), 4.66 (d,  $J = 7.9$  Hz, 1H, H-C(1)), 4.28 (s, 2H, CH<sub>2</sub>), 4.25 (dd,  $J = 12.4, 4.7$  Hz, 1H, Ha-C(6)), 4.13 (dd,  $J = 12.4, 2.8$  Hz, 1H, Hb-C(6)), 3.74 (s, 3H, COOCH<sub>3</sub>), 3.69 (ddd,  $J = 9.50, 4.7, 2.8$  Hz, 1H, H-C(5)), 2.09 (s, 3H, Ac), 2.08 (s, 3H, Ac), 2.02 (s, 3H, Ac), 2.00 (s, 3H, Ac).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 25 °C, 100 MHz):  $\delta_{\text{C}}$  170.6 (Ac), 170.1 (Ac), 169.6 (Ac), 169.5 (Ac), 169.3 (COOMe), 100.1 (C1), 72.4 (C5), 71.9 (C3), 70.9 (C2), 68.2 (C4), 64.9 (CH<sub>2</sub>), 61.7 (C6), 51.9 (COOCH<sub>3</sub>), 20.5 (4 x Ac).

HRMS (ESI<sup>+</sup>) : Calcd for C<sub>17</sub>H<sub>24</sub>O<sub>12</sub>Na<sup>+</sup> [M + Na]<sup>+</sup>: 444.1165; Found: 443.1179.



**Ethyl 2-[(2,3,4,6-tetra-*O*-acetyl- $\beta$ -D-glucopyranosyl)oxy]-acetate (15b).**



The reaction was carried out using ethyl glycolate (2 equiv.). The reaction is providing a mixture 5.8 : 1 respectively of ethyl 1-*O*-(2-carboxy)methyl-2,3,4,6-tetra-*O*-acetyl- $\beta$ -D-glucopyranose and ethyl 1-*O*-(2-carboxy)methyl-2,3,4,6-tetra-*O*-acetyl- $\beta$ -D-glucopyranose. The major isomer was obtained in a pure form by recrystallization of the reaction mixture using *i*-PrOH.

Only the  $\beta$  anomer was obtained as white solid (6.2 g, 71%, m.p. 80 °C.).

R<sub>f</sub>=0.51 (AcOEt : Cyclohexan, 1:1)

$[\alpha]_{589}^{25} = -39$ , ( $c = 1.0$ , CHCl<sub>3</sub>).

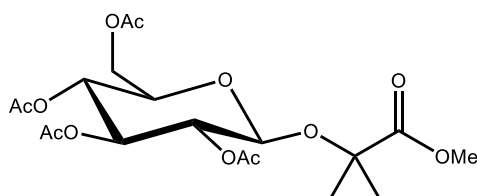
IR (film)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 1740, 1435, 1369, 1312, 1219, 1173, 1132, 1090, 1067, 1036, 988, 937, 910, 858.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C, 400 MHz):  $\delta_{\text{H}}$  5.24 (t,  $J = 9.7$  Hz, 1H, H-C(3)), 5.09 (t,  $J = 9.7$  Hz, 1H, H-C(4)), 5.04 (dd,  $J = 9.3, 7.8$  Hz, 1H, H-C(2)), 4.67 (d,  $J = 7.8$  Hz, 1H, H-C(1)), 4.27 (s, 2H, CH<sub>2</sub>), 4.25 (dd,  $J = 12.3, 4.6$  Hz, 1H, Ha-C(6)), 4.22 (q,  $J = 7.2$  Hz, 1H, CH<sub>2</sub>CH<sub>3</sub>), 4.20 (q,  $J = 7.2$  Hz, 1H, CH<sub>2</sub>CH<sub>3</sub>), 4.13 (dd,  $J = 12.3, 2.4$  Hz, 1H, Hb-C(6)), 3.69 (ddd,  $J = 9.7, 4.6, 2.4$  Hz, 1H, H-C(5)), 2.09 (s, 3H, Ac), 2.08 (s, 3H, Ac), 2.02 (s, 3H, Ac), 2.01 (s, 3H, Ac), 1.28 (t,  $J = 7.2$  Hz, CH<sub>2</sub>CH<sub>3</sub>).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 25 °C, 100 MHz):  $\delta_{\text{C}}$  170.6 (Ac), 170.2 (Ac), 169.6 (Ac), 169.4 (Ac), 169.1 (COOEt), 100.1 (C1), 72.5 (C5), 71.9 (C3), 70.9 (C2), 68.3 (C4), 65.0 (CH<sub>2</sub>), 61.8 (C6), 61.1 (CH<sub>2</sub>CH<sub>3</sub>), 20.7 (2 x Ac), 20.6 (2 x Ac), 14.2 (CH<sub>2</sub>CH<sub>3</sub>).

HRMS (ESI<sup>+</sup>) : Calcd for C<sub>18</sub>H<sub>26</sub>NO<sub>12</sub>Na<sup>+</sup> [M + Na]<sup>+</sup>: 457.1322; Found: 457.1342.

**Methyl 2-methyl-2-[(2,3,4,6-tetra-*O*-acetyl- $\beta$ -D-glucopyranosyl)oxy]-propanoate (15c).**



The reaction was carried out using methyl 2-hydroxyisobutyrate. The reaction is providing a mixture 4.5 :1 respectively of methyl 2-methyl-2-[(2,3,4,6-tetra-*O*-acetyl- $\beta$ -D-

glucopyranosyl)oxy]-propanoate and methyl 2-methyl-2-[(2,3,4,6-tetra-O-acetyl- $\alpha$ -D-glucopyranosyl)oxy]-propanoate. Only the major isomer was isolated in a pure form by crystallisation of the reaction mixture in *i*-PrOH. The minor isomer was then purified by column chromatography (AcOEt/cyclohexan, 3 : 7).

The  $\beta$  anomer was obtained as white solid (4.8 g, 54%, m.p. 96 °C).

R<sub>f</sub> = 0.46 (AcOEt : Cyclohexan, 1:1)

$[\alpha]_{589}^{25} = -7.6$ , ( $c = 1.0$ , CHCl<sub>3</sub>).

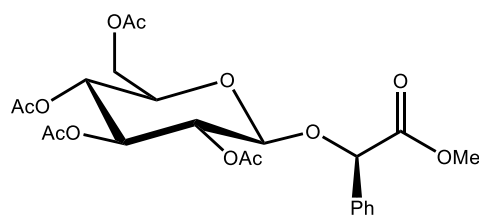
IR (film)  $\nu$  max/cm<sup>-1</sup>: 3565, 3350, 3298, 2913, 1663, 1547, 1447, 1352, 1250, 1161, 1082, 1044, 905.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C, 400 MHz):  $\delta_H$  5.22 (t,  $J = 9.5$  Hz, 1H, H-C(3)), 5.04-4.97 (m, 2H, H-C(4), H-C(2)), 4.70 (d,  $J = 7.9$  Hz, 1H, H-C(1)), 4.18 (dd,  $J = 12.2, 5.7$  Hz, 1H, Ha-C(6)), 4.08 (dd,  $J = 12.2, 2.4$  Hz, 1H, Hb-C(6)), 3.72 (s, 3H, COOCH<sub>3</sub>), 3.65 (ddd,  $J = 10, 5.7, 2.4$  Hz, 1H, H-C(5)), 2.07 (s, 3H, Ac), 2.05 (s, 3H, Ac), 2.02 (s, 3H, Ac), 2.00 (s, 3H, Ac), 1.47 (s, 3H, CH<sub>3</sub>), 1.43 (s, 3H, CH<sub>3</sub>).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 25 °C, 100 MHz):  $\delta_C$  173.5 (COOMe), 170.6 (Ac), 170.2 (Ac), 169.5 (Ac), 169.3 (Ac), 96.7 (C1), 78.8 (C), 72.8 (C5), 71.7 (C3), 71.3 (C2), 68.6 (C4), 62.2 (C6), 52.3 (COOCH<sub>3</sub>), 25.2 (CH<sub>3</sub>), 24.8 (CH<sub>3</sub>), 20.7 (2 x Ac), 20.6 (2 x Ac).

HRMS (ESI<sup>+</sup>) : Calcd for C<sub>19</sub>H<sub>28</sub>O<sub>12</sub>Na<sup>+</sup> [M + Na]<sup>+</sup>: 471.1478; Found: 471.1494.

### Methyl (R)- $\alpha$ -[(2,3,4,6-tetra-O-acetyl- $\beta$ -D-glucopyranosyl)oxy]phenylacetate (15d).



The reaction was carried out using methyl (*R*)-mandelate (2 equiv.). The reaction is providing a mixture 8.3 : 1 respectively of methyl (R)- $\alpha$ -[(2,3,4,6-tetra-O-acetyl- $\beta$ -D-glucopyranosyl)oxy]phenylacetate and methyl (R)- $\alpha$ -[(2,3,4,6-tetra-O-acetyl- $\alpha$ -D-glucopyranosyl)oxy]phenylacetate. Only the major isomer was isolated in a pure form by crystallisation of the reaction mixture in *i*-PrOH.

The  $\beta$  anomer was obtained as white solid (7.5 g, 76%, m.p. 114 °C).

R<sub>f</sub> = 0.67 (AcOEt : Cyclohexan, 1:1)

$[\alpha]_{589}^{25} = -52.4$ , ( $c = 1.0$ , CHCl<sub>3</sub>).

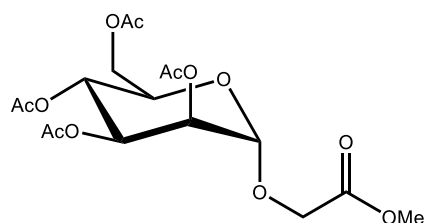
IR (film)  $\nu$  max/cm<sup>-1</sup>: 1746, 1437, 1370, 1221, 1146, 1094, 1049, 976, 895, 799.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C, 400 MHz):  $\delta_H$  7.28 (s, 5H, Ph), 5.11 (s, 1H, CHPh), 5.08-4.96 (m, 3H, H-C(3), H-C(4), H-C(2)), 4.37 (d,  $J$  = 7.6 Hz, 1H, H-C(1)), 4.12 (dd,  $J$  = 12.3, 5.0 Hz, 1H, Ha-C(6)), 4.03 (dd,  $J$  = 12.3, 2.5 Hz, 1H, Hb-C(6)), 3.59 (s, 3H, COOCH<sub>3</sub>), 3.65 (ddt,  $J$  = 7.4, 4.9, 2.4 Hz, 1H, H-C(5)), 2.01 (s, 3H, 1 x Ac), 1.90 (s, 9H, 3 x Ac).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 25 °C, 100 MHz):  $\delta_C$  170.6 (Ac), 170.2 (Ac), 169.8 (Ac), 169.3 (Ac), 168.1 (COOMe), 134.7 (C(Ph)), 129.2 (CH(Ph)), 128.8 (2 x CH(Ph)), 127.3 (2 x CH(Ph)), 98.5 (C1), 79.0 (CH-Ph), 72.7 (C5), 72.0 (C3), 71.1 (C2), 68.3 (C4), 61.8 (C6), 52.4 (COOCH<sub>3</sub>), 20.7 (1 x Ac), 20.6 (3 x Ac).

HRMS (ESI<sup>+</sup>) : Calcd for C<sub>23</sub>H<sub>28</sub>O<sub>12</sub>Na<sup>+</sup> [M + Na]<sup>+</sup>: 519.1478; Found: 519.1484.

### Methyl 2-[(2,3,4,6-tetra-*O*-acetyl- $\alpha$ -D-mannopyranosyl)oxy]-acetate (15e).



The reaction was carried out using methyl glycolate. The reaction is providing methyl 2-[(2,3,4,6-tetra-*O*-acetyl- $\alpha$ -D-mannopyranosyl)oxy]-acetate as only diastereoisomer.. The product was then purified by column chromatography (AcOEt/cyclohexan, 3 : 7) to provide only the desired  $\alpha$  anomer as colourless oil (5.2 g, 62%).

R<sub>f</sub>=0.32 (AcOEt : Cyclohexan, 1:1).

$[\alpha]_{589}^{25}$  = +58.000, ( $c$  = 0.5, CH<sub>3</sub>OH).

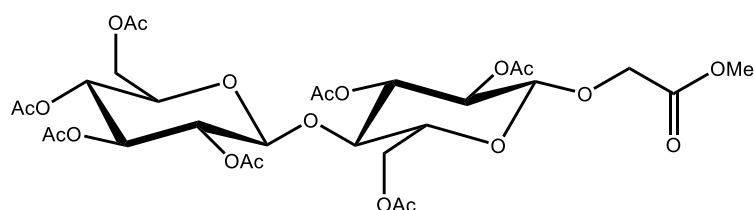
IR (film)  $\nu$  max/cm<sup>-1</sup>: 2359, 2338, 1746, 1437, 1369, 1221, 1144, 1049, 976, 895, 799.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C, 400 MHz):  $\delta_H$  5.39 (dd,  $J$ =9.3, 2.4 Hz, 1H, H-(C5)), 5.37 (d,  $J$ =2.4 Hz, 1H, H-(C3)), 5.30 (t,  $J$ =9.8 Hz, 1H, H-(C4)), 4.95 (d,  $J$ =1.3 Hz, 1H, H-(C1)), 4.28 (dd,  $J$ =13.3 Hz, 4.9 Hz, 1H, Ha-(C6)), 4.28/4.19 (dd,  $J$ =23.3, 16.3 Hz, Ha/Hb-(C7)), 4.10 (dd,  $J$ =12.1, 2.4 Hz, 1H, Hb-C(6)), 3.77 (s, 3H, Ac), 2.16 (s, 3H, Ac), 2.11 (s, 3H, Ac), 2.05 (s, 3H, Ac), 2.00 (s, 3H, Ac).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 25 °C, 100 MHz):  $\delta_C$  170.6 (Ac), 169.8 (Ac), 169.8 (Ac), 169.7 (Ac), 169.5 (COOMe), 97.9 (C1), 69.2 (C5), 69.2 (C3), 68.8 (C2), 65.9 (C4), 64.4 (CH<sub>2</sub>), 62.3 (C6), 52.1 (COOCH<sub>3</sub>), 20.8 (1x Ac), 20.7 (3x Ac).

HRMS (ESI<sup>+</sup>) : Calcd for C<sub>17</sub>H<sub>24</sub>O<sub>12</sub>Na<sup>+</sup> [M + Na]<sup>+</sup>: 443.1165; Found: 4806.1163.

**Methyl 2-[(2,2',3,3',4',6,6'-hepta-*O*-acetyl- $\beta$ -D-cellobiosyl)oxy]-acetate (15f).**



The reaction was carried out using methyl glycolate. The reaction is providing methyl 2-[(2,2',3,3',4',6,6'-hepta-*O*-acetyl- $\beta$ -D-cellobiosyl)oxy]-acetate as only diastereoisomer. The product was purified by recrystallization in *i*-PrOH.

The product was obtained as white solid (9.82 g, 69%, m.p. 164 °C).

$R_f$ =0.21 (AcOEt : Cyclohexan, 3:2)

$[\alpha]_{589}^{25} = -30,200$ , ( $c = 1.0$ , CHCl<sub>3</sub>).

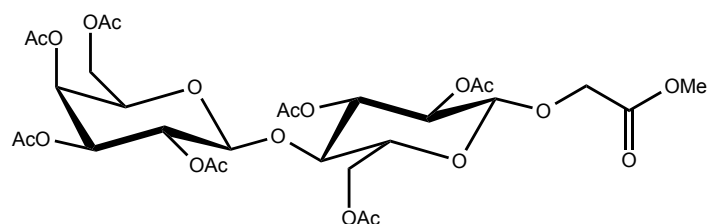
IR (film)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 1742, 1437, 1369.1223, 1169, 1132, 1044, 907, 689, 619.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C, 400 MHz):  $\delta_H$  5.18-4.96 (m, 3H, 3x CH), 4.92-4.82 (m, 2H, 2x CH), 4.54 (d,  $J=7.8$  Hz, 1H, H-(C1)), 4.47 (d,  $J=2.1$  Hz, 1H, CH), 4.45 (d,  $J=7.9$  Hz, 1H, H-(C1')), 4.30 (dd,  $J=12.4$ , 4.5 Hz, 1H, Ha-CH<sub>2</sub>-6), 4.19 (s, 2H, CH<sub>2</sub>-7), 4.02 (dd,  $J=12.1$ , 4.9 Hz, 1H, Hb-CH<sub>2</sub>-6), 3.98 (dd,  $J=13.7$ , 2.0 Hz, 1H, CH), 3.76-3.69 (m, 1H, CH), 3.67 (s, 3H, OCH<sub>3</sub>), 3.59 (ddd,  $J=9.8$ , 4.2, 2.2 Hz, 1H, CH), 3.53 (ddd,  $J=9.7$ , 4.6, 1.5 Hz, 1H, CH), 2.06 (s, 3H, Ac), 2.02 (s, 3H, Ac), 2.01 (s, 3H, Ac), 1.96 (s, 6H, 2x Ac), 1.94 s, 3H, Ac), 1.91 (s, 3H, Ac)

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 25 °C, 100 MHz):  $\delta_C$  170.5, 170.3, 170.2, 169.8, 169.7, 169.5 169.3, 169.0 (7x CH<sub>3</sub>COO, 1x CO<sub>2</sub>Me), 100.7 (C1'), 100.0 (C1), 76.3 (CH), 72.9 (CH), 72.8 (CH), 72.1 (CH), 72.0 (CH), 71.6 (CH), 71.2 (CH), 67.8 (CH), 65.1 (C7), 61.6 (C6'), 61.5 (C6), 52.0 (COOCH<sub>3</sub>), 20.8 (Ac), 20.7 (2x Ac), 20.5 (4x Ac).

HRMS (ESI<sup>+</sup>) : Calcd for C<sub>29</sub>H<sub>41</sub>O<sub>20</sub> [M + H]<sup>+</sup>: 731.2021; Found: 731.2028.

**Methyl 2-[(2,2',3,3',4',6,6'-hepta-*O*-acetyl- $\beta$ -D-lactosyl)oxy]-acetate (15g).**



The reaction was carried out using methyl glycolate. The reaction is providing methyl 2-[(2,2',3,3',4',6,6'-hepta-*O*-acetyl- $\beta$ -D-lactosyl)oxy]-acetate as only diastereoisomer. The product was purified by recrystallization in *i*-PrOH.

The product was obtained as white solid (10.2 g, 72%, m.p. 164°C).

R<sub>f</sub>=0.22 (AcOEt : Cyclohexan, 3:2).

[ $\alpha$ ]<sub>589</sub><sup>25</sup> = -29,4, (*c* = 1.0, CHCl<sub>3</sub>).

IR (film)  $\nu$  max/cm<sup>-1</sup>: 1753, 1738, 1437, 1373, 1227, 1165, 1130, 1065, 1044, 945, 914, 903, 746, 712.

<sup>1</sup>H NMR (CD<sub>3</sub>OD, 25 °C, 400 MHz):  $\delta_H$  5.37 (d, *J* = 3.4 Hz, 1H), 5.22 (t, *J* = 9.3 Hz, 1H), 5.13 (dd, *J* = 10.4, 3.5 Hz, 1H), 5.02 (dd, *J* = 10.4, 7.9 Hz, 1H), 4.91 (dd, *J* = 9.6, 8.0 Hz, 1H), 4.73 (dd, *J* = 7.9, 6.2 Hz, 2H), 4.53 (dd, *J* = 12.0, 2.0 Hz, 1H), 4.36-4.24 (m, 2H), 4.19-4.08 (m, 4H), 3.89 (t, *J* = 9.5 Hz, 1H), 3.75 (s, 3H, OCH<sub>3</sub>), 3.79-3.73 (m, 1H), 2.15 (s, 3H, Ac), 2.13 (s, 3H, Ac), 2.07 (2x s, 2x 3H, 2x Ac), 2.06 (s, 6H, 2x Ac), 1.95 (s, 3H, Ac).

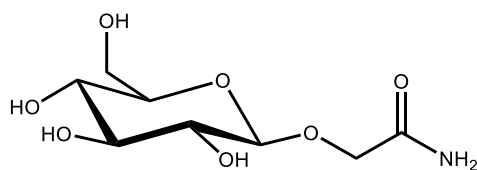
<sup>13</sup>C NMR (CD<sub>3</sub>OD, 25 °C, 100 MHz):  $\delta_C$  170.9, 170.6, 170.5, 170.3, 170.1, 170.0, 169.7 (7 x CH<sub>3</sub>COO, 1 x CO<sub>2</sub>Me), 100.6 (C1'), 100.0 (C1), 76.1 (CH), 72.8 (CH), 72.6 (CH), 71.4 (CH), 71.1 (CH), 70.4 (CH), 69.3 (CH), 67.2 (CH), 65.0 (C7), 62.0 (C6'), 60.9 (C6), 51.0 (COOCH<sub>3</sub>), 19.7, 19.5, 19.3, 19.3, 19.3, 19.2, 19.1 (7 x CH<sub>3</sub>COO).

HRMS (ESI<sup>+</sup>) : Calcd for C<sub>29</sub>H<sub>41</sub>O<sub>20</sub> [M + H]<sup>+</sup>: 731.2021; Found: 731.2020.

### **C. General procedure for the synthesis of deprotected carbohydrates containing primary carboxamides functionality and their characterization.**

Protected sugars obtained previously in part 1. (10 mmol) were treated with a solution of ammonia 7N in MeOH (20 mL) at 25 °C, until complete conversion. The solvent was then evaporated under reduced pressure and the crude residue was triturated 3 times with AcOEt (10 mL) to provide pure product.

### 2-( $\beta$ -D-Glucopyranosyloxy)-acetamide (9a).



The pure product 2-( $\beta$ -D-glucopyranosyloxy)-acetamide was obtained as white solid (2.3 g, 98%, m.p. 150 °C).

$R_f$ =0.32 ( $\text{CH}_2\text{Cl}_2$  : MeOH, 7:3).

$[\alpha]_{589}^{25} = -90,7$ , ( $c = 1.0$ , EtOH).

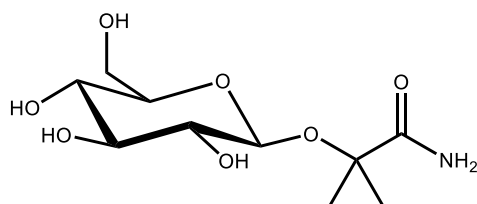
IR (film)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3360, 2884, 1676, 1423, 1364, 1076, 1036, 899, 781.

$^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ , 25 °C, 400 MHz):  $\delta_H$  4.36 (d,  $J = 7.8$  Hz, 1H, H-C(1)), 4.32 (d,  $J = 16.0$  Hz, 1H, Ha- $\text{CH}_2$ ), 4.15 (d,  $J = 16.0$  Hz, 1H, Hb- $\text{CH}_2$ ), 3.89 (dd,  $J = 11.9$ , 1.4 Hz, 1H, Ha-C(6)), 3.71 (dd,  $J = 11.9$ , 5.2 Hz, 1H, Hb-C(6)), 3.43-3.32 (m, 3H, H-C(3), H-C(4), H-C(5)), 3.29 (d,  $J = 9.0$ , 7.8 Hz, 1H, H-C(2)).

$^{13}\text{C}$  NMR ( $\text{CD}_3\text{OD}$ , 25 °C, 100 MHz):  $\delta_C$  175.4 ( $\text{COONH}_2$ ), 104.6 (C1), 78.2 (C3), 77.8 (C4), 74.9 (C2), 71.4 (C5), 69.1 ( $\text{CH}_2$ ), 62.5 (C6).

HRMS ( $\text{ESI}^+$ ) : Calcd for  $\text{C}_8\text{H}_{15}\text{NO}_7\text{Na}^+$   $[\text{M} + \text{Na}]^+$ : 260.0746; Found: 260.0740.

### 2-( $\beta$ -D-Glucopyranosyloxy)-2-methyl-propanamide (9b).



The pure product 2-( $\beta$ -D-glucopyranosyloxy)-acetamide was obtained as white solid (2.4 g, 91%, m.p. 149 °C).

$R_f$ =0.39 ( $\text{CH}_2\text{Cl}_2$  : MeOH, 7:3).

$[\alpha]_{589}^{25} = -21,2$  ( $c = 1.0$ , MeOH).

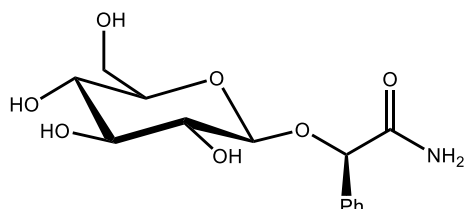
IR (film)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3289, 2918, 1672, 1441, 1369, 1254, 1165, 1072, 1038, 903, 785.

$^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ , 25 °C, 400 MHz):  $\delta_H$  5.15 (d,  $J=3.9$  Hz, 1H, H-(C1)), 3.81 (dd,  $J=11.4$ , 2.1 Hz, 1H, Ha-(C6)), 3.79-3.66 (m, 2H, Hb-(C6) + H-(C2)), 3.49 (dd,  $J=9.7$ , 3.9 Hz, 1H, H-(C3)), 3.36-3.29 (m, 2H, H-(C5) + H-(C4)), 1.54 (s, 3H,  $\text{CH}_3$ ), 1.46 (s, 3H,  $\text{CH}_3$ ).

$^{13}\text{C}$  NMR ( $\text{CD}_3\text{OD}$ , 25 °C, 100 MHz):  $\delta_{\text{C}}$  179.7 ( $\text{CONH}_2$ ), 94.97 (C1), 79.47 (C7), 73.5 (C3), 72.6 (C4), 71.9 (C2), 70.3 (C5), 61.2 (C6), 26.9 ( $\text{CH}_3$ ), 21.9 ( $\text{CH}_3$ ).

HRMS ( $\text{ESI}^+$ ) : Calcd for  $\text{C}_{10}\text{H}_{20}\text{NO}_7^+$  [ $\text{M} + \text{H}$ ] $^+$ : 266.1240; Found: 266.1228.

**(*R*)- $\alpha$ -( $\beta$ -D-Glucopyranosyloxy)phenylacetamide (9c).**



The pure product (*R*)- $\alpha$ -( $\beta$ -D-glucopyranosyloxy)phenylacetamide was obtained as white solid (2.9 g, 94%, m.p. 126 °C).

$R_f$ =0.56 ( $\text{CH}_2\text{Cl}_2$  : MeOH, 7:3).

$[\alpha]_{589}^{25} = -94.7$ , ( $c = 1.0$ , MeOH).

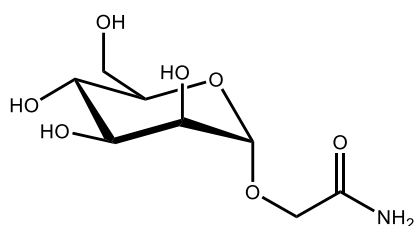
IR (film)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3358, 2918, 1665, 1398, 1614, 1398, 1258, 1194, 1076, 1040, 899, 762.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 25 °C, 400 MHz):  $\delta_{\text{H}}$  7.55 (dd,  $J=7.7$ , 1.9 Hz, 2H, Ph), 7.42-7.36 (m, 3H, Ph), 5.36 (s, 1H, H-(C7)), 4.09 (d,  $J=7.7$  Hz, 1H, H-(C1)), 3.88 (dd,  $J=12.0$ , 2.3 Hz, 1H, Ha-(C6)), 3.69 (dd,  $J=12.0$ , 2.3 Hz, 1H, Hb-(C6)), 3.36-3.23 (m, 3H, H-(C3,C4,C5)), 3.09 (ddd,  $J=9.4$ , 5.9, 2.3 Hz, 1H, H-(C2)).

$^{13}\text{C}$  NMR ( $\text{CD}_3\text{OD}$ , 25 °C, 100 MHz):  $\delta_{\text{C}}$  174.7 ( $\text{CONH}_2$ ), 135.9 ( $\text{Ph}_{\text{quaternary}}$ ), 128.5 (Ph), 128.2 (2x Ph), 128.0 (2x Ph), 98.7 (C1), 77.9 (C3), 76.8 (C4), 76.1 (C2), 73.6 (C5), 70.2 (C7), 61.2 (C6).

HRMS ( $\text{ESI}^+$ ) : Calcd for  $\text{C}_{14}\text{H}_{20}\text{NO}_7^+$  [ $\text{M} + \text{H}$ ] $^+$ : 314.1240; Found: 314.1238.

**2-( $\alpha$ -D-Mannopyranosyloxy)-acetamide (9d).**



The pure product 2-( $\alpha$ -D-mannopyranosyloxy)-acetamide was obtained as a colourless oil (2.2 g, 93%).

R<sub>f</sub>=0.33 (CH<sub>2</sub>Cl<sub>2</sub> : MeOH, 7:3).

[α]<sub>589</sub><sup>25</sup> = +63.125, (c = 1.6, MeOH).

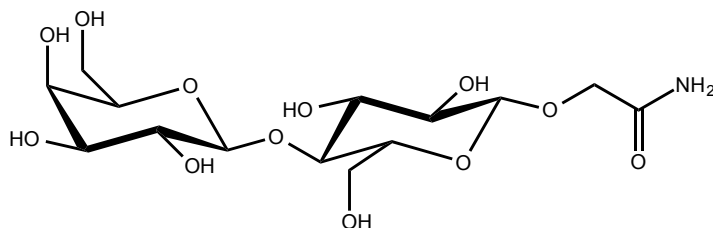
IR (film) ν max/cm<sup>-1</sup>: 3350, 2928, 1665, 1611, 1402, 1317, 1260, 1140, 1084, 1061, 968, 905, 878, 812.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C, 400 MHz): δ<sub>H</sub> 4.84 (d, *J*=1.8 Hz, H-(C1)), 4.19 (d, *J*=15.5 Hz, 1H, Ha-(C7)), 4.03 (d, *J*=15.5 Hz, 1H, Hb-(C7)), 3.97 (dd, *J*=11.8, 6.0 Hz, 1H, H-(C2)), 3.86 (dd, *J*=11.8, 2.3 Hz, 1H, Ha-(C6)), 3.78 (dd, *J*=9.3, 3.4 Hz, 1H, H-(C4)), 3.72 (dd, *J*=11.8, 6.0 Hz, 1H, Hb-(C6)), 3.64 (t, *J*=9.6 Hz, 1H, H-(C5)), 3.53 (ddd, *J*=9.7, 6.0, 2.3 Hz, 1H, H-(C3)).

<sup>13</sup>C NMR (CD<sub>3</sub>OD, 25 °C, 100 MHz): δ<sub>C</sub> 173.4 (CONH<sub>2</sub>), 100.3 (C1), 73.92 (C3), 71.0 (C4), 70.2 (C2), 67.1 (C5), 65.3 (C7), 61.4 (C6).

HRMS (ESI<sup>+</sup>) : Calcd for C<sub>8</sub>H<sub>15</sub>NO<sub>7</sub>Na<sup>+</sup> [M + Na]<sup>+</sup>: 260.0746; Found: 260.0749.

### 2-(β-D-Lactosyloxy)-acetamide (9e).



The pure product methyl 2-(β-D-lactosyloxy)-acetamide was obtained as white solid (3.7 g, 96%, m.p. 162 °C).

R<sub>f</sub>=0.32 (CH<sub>2</sub>Cl<sub>2</sub> : MeOH, 6:4).

[α]<sub>589</sub><sup>25</sup> = -3.9, (c = 1.0, H<sub>2</sub>O).

IR (film) ν max/cm<sup>-1</sup>: 3358, 1705, 1676, 1427, 1406, 1366, 1321, 1288, 1258, 1225, 1167, 1130, 1119, 1090, 1032, 991, 899, 877, 799, 704.

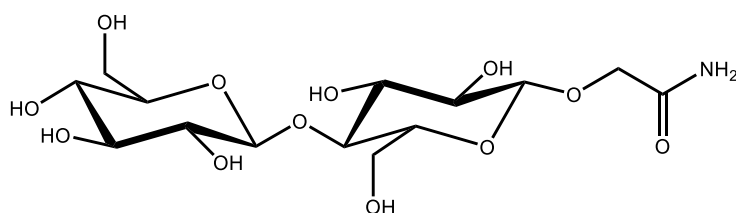
<sup>1</sup>H NMR (D<sub>2</sub>O, 25 °C, 400 MHz): δ<sub>H</sub> 4.48 (d, *J*=7.9 Hz, 1H, H-(C1')), 4.38 (d, *J*=7.8 Hz, 1H, H-(C1)), 4.31 (d, *J*=16.0 Hz, 1H, Ha-(C7)), 4.19 (d, *J*=16.0 Hz, 1H, Hb-(C7)), 3.90 (dd, *J*=12.3, 1.7 Hz, 1H, Ha-(C6)), 3.85 (d, *J*=3.2 Hz, 1H, H-(C4')), 3.75 (dd, *J*=13.1, 5.6 Hz, 2H, Hb-(C6), H-(C4)), 3.69 (d, *J*=4.3 Hz, 1H, Ha-(C6')), 3.65 (dd, *J*=8.7, 2.4 Hz, 1H, CH), 3.60 (dt, *J*=8.7, 3.8 Hz, 3H, Hb-(C6')) + 2x CH, 3.56-3.50 (m, 1H, CH), 3.47 (dd, *J*=9.8, 7.9 Hz, 1H, H-(C2)), 3.39-3.32 (m, 1H, CH).



$^{13}\text{C}$  NMR ( $\text{D}_2\text{O}$ , 25 °C, 100 MHz):  $\delta_{\text{C}}$  175.0 ( $\text{CONH}_2$ ), 102.9 ( $\text{C1}'$ ), 102.2 ( $\text{C1}$ ), 78.1 (CH), 75.3 (CH), 74.9 (CH), 74.2 (CH), 72.6 (CH), 72.5 (CH), 70.9 (CH), 68.5 (CH), 67.7 (C7), 61.0 ( $\text{C6}'$ ), 59.9 (C6).

HRMS ( $\text{ESI}^+$ ) : Calcd for  $\text{C}_{14}\text{H}_{25}\text{NO}_{12}\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$ : 422.1275; Found: 422.1287.

### 2-( $\beta$ -D-Cellobiosyloxy)-acetamide (9f).



The pure product methyl 2-( $\beta$ -D-cellobiosyloxy)-acetamide was obtained as white solid (3.6 g, 94%, m.p. 178 °C).

$R_f$ =0.29 ( $\text{CH}_2\text{Cl}_2$  : MeOH, 6:4).

$[\alpha]_{589}^{25}$  = -18.1, ( $c$  = 1.0,  $\text{H}_2\text{O}$ ).

IR (film)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3381, 3186, 2905, 2345, 1690, 1422, 1059, 897, 799.

$^1\text{H}$  NMR ( $\text{D}_2\text{O}$ , 25 °C, 400 MHz):  $\delta_{\text{H}}$  4.47 (d,  $J$  = 8.0 Hz, 1H, H-( $\text{C1}'$ )), 4.43 (d,  $J$  = 7.9 Hz, 1H, H-( $\text{C1}$ )), 4.30 (d,  $J$  = 16.0 Hz, 1H, Ha-(C7)), 4.19 (d,  $J$  = 16.0 Hz, 1H, Hb-(C7)), 3.90 (dd,  $J$  = 12.3, 2.1 Hz, 1H, Ha-( $\text{C6}'$ )), 3.84 (dd,  $J$  = 12.4, 2.0 Hz, 1H, Ha-(C6)), 3.75 (dd,  $J$  = 12.3, 4.8 Hz, 1H, Hb-( $\text{C6}'$ )), 3.66 (dd,  $J$  = 12.4, 5.7 Hz, 1H, Hb-(C6)), 3.61-3.49 (m, 3H, H-C3,  $\text{C3}'$ , C4), 3.41-3.38 (q,  $J$  = 8.2, 7.5 Hz, 1H + m, 1H, H-( $\text{C5}$ ,  $\text{C5}'$ )), 3.37-3.30 (m, 2H, H- $\text{C4}'$ ,  $\text{C2}'$ ), 3.28-3.20 (m, 1H, H-(C2)).

$^{13}\text{C}$  NMR ( $\text{D}_2\text{O}$ , 25 °C, 101 MHz):  $\delta_{\text{C}}$  175.0 ( $\text{CONH}_2$ ), 102.5 ( $\text{C1}'$ ), 100.2 (C1), 78.4 (CH), 76.0 (CH) 75.6 (CH) 74.8 (CH), 74.1 (CH) 73.1 (CH), 72.7 (CH), 69.4 (CH), 67.7 (C7), 60.6 ( $\text{C6}'$ ), 59.8 (C6).

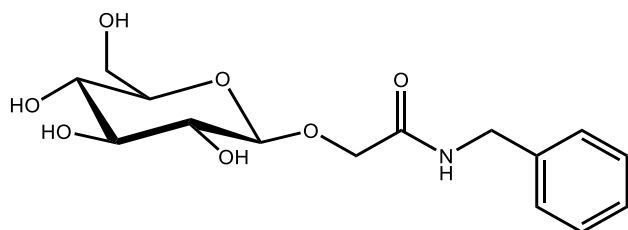
HRMS ( $\text{ESI}^+$ ) : Calcd for  $\text{C}_{14}\text{H}_{25}\text{NO}_{12}\text{Na}^+$  [ $\text{M} + \text{Na}$ ] $^+$ : 422.1274; Found: 422.1285.

### D. General procedure for the synthesis of sugars containing amides and their characterization.

A mixture of primary amide derived glycoside obtained previously in part 2. (1 mmol), and amine (3 mmol) was stirred in sealed tube at indicated temperature for 12 h. After being

cooled to room temperature the reaction mixture was dissolved in a minimum of hot methanol and the mixture was chromatographed using silica gel 200-400 mesh size (eluted using appropriate mixture DCM : MeOH). The pure product was obtained by rotary evaporation of the solvent.

**2-( $\beta$ -D-Glucopyranosyloxy)-*N*-(phenylmethyl)-acetamide (11a).**



The reaction was carried out at 100 °C with 2-( $\beta$ -D-glucopyranosyloxy)-acetamide (237 mg, 1 mmol) and benzylamine (321 mg, 3 mmol, 3 equiv.) in a sealed tube. The pure product 2-( $\beta$ -D-glucopyranosyloxy)-*N*-(phenylmethyl)-acetamide was obtained as white solid (301 mg, 92%, m.p. 139°C).

$R_f$ =0.54 (CH<sub>2</sub>Cl<sub>2</sub> : MeOH, 8:2).

$[\alpha]_{589}^{25} = -22.8$ , ( $c = 1.0$ , MeOH).

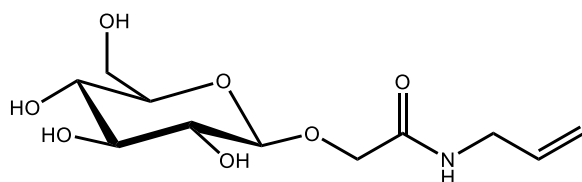
IR (film)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3460, 3372, 3306, 3121, 2897, 1638, 1576, 1449, 1366, 1331, 1300, 1231, 1163, 1107, 1069, 1051, 1036, 984, 897, 752.

<sup>1</sup>H NMR (CD<sub>3</sub>OD, 25 °C, 400 MHz):  $\delta_H$  7.28-7.20 (m, 5 H, Ph), 4.46 (d,  $J = 14.9$  Hz, 1H, Ha-CH<sub>2</sub>-Bn), 4.37 (d,  $J = 14.9$  Hz, 1H, Hb-CH<sub>2</sub>-Bn), 4.33 (d,  $J = 15.7$  Hz, 1H, Ha-CH<sub>2</sub>), 4.29 (d,  $J = 7.7$  Hz, H-C(1)), 4.16 (d,  $J = 15.7$  Hz, 1H, Hb-CH<sub>2</sub>), 3.89 (dd,  $J = 11.5, 1.2$  Hz, 1H, Ha-C(6)), 3.63 (dd,  $J = 11.5, 5.2$  Hz, 1H, Hb-C(6)), 3.35-3.25 (m, 3H, H-C(3), H-C(4), H-C(5)), 3.22 (dd,  $J = 9.0, 7.8$  Hz, 1H, H-C(2)).

<sup>13</sup>C NMR (CD<sub>3</sub>OD, 25 °C, 100 MHz):  $\delta_C$  172.2 (CONH<sub>2</sub>), 139.6 (C-Ph), 129.5 (2 x CH), 128.6 (2 x CH), 128.3 (CH), 104.6 (C1), 78.2 (C3), 77.8 (C4), 74.9 (C2), 71.3 (C5), 69.5 (CH<sub>2</sub>), 62.5 (C6), 43.6 (CH<sub>2</sub>(Bn)).

HRMS (ESI<sup>+</sup>) : Calcd for C<sub>15</sub>H<sub>21</sub>NO<sub>7</sub>Na<sup>+</sup> [M + Na]<sup>+</sup>: 350.1216; Found: 350.1208.

### 2-( $\beta$ -D-Glucopyranosyloxy)-*N*-2-propen-1-yl-acetamide (11b).



The reaction was carried out at 80 °C with 2-( $\beta$ -D-glucopyranosyloxy)-acetamide (237 mg, 1 mmol) and allylamine (171 mg, 3 mmol, 3 equiv.) in a sealed tube. The pure product 2-( $\beta$ -D-glucopyranosyloxy)-*N*-2-propen-1-yl-acetamide was obtained as white solid (261 mg, 94%, m.p. 158°C).

$R_f$ =0.58 (CH<sub>2</sub>Cl<sub>2</sub> : MeOH, 8:2).

$[\alpha]_{589}^{25} = -66.6$ , ( $c = 1.0$ , MeOH).

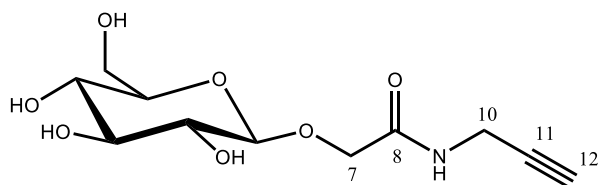
IR (film)  $\nu$  max/cm<sup>-1</sup>: 3316, 2932, 1705, 1659, 1553, 1449, 1343, 1254, 1167, 1076, 1044, 924, 880, 804.

<sup>1</sup>H NMR (CD<sub>3</sub>OD, 25 °C, 400 MHz):  $\delta_H$  5.86 (ddt,  $J = 17.2, 10.5, 5.5$  Hz, 1H, CH(allyl)), 5.21 (dq,  $J = 17.2, 1.5$  Hz, 1H, Ha-CH<sub>2</sub>(allyl)), 5.12 (dt,  $J = 10.5, 1.5$  Hz, 1H, Hb-CH<sub>2</sub>(allyl)), 4.33 (d,  $J = 15.7$  Hz, 1H, Ha-CH<sub>2</sub>), 4.32 d,  $J = 7.6$  Hz, H-C(1)), 4.16 (d,  $J = 15.7$  Hz, 1H, Hb-CH<sub>2</sub>), 3.94-3.82 (m, 3H, Ha-C(6), CH<sub>2</sub>(allyl)), 3.68 (dd,  $J = 11.9, 5.2$  Hz, 1H, Hb-C(6)), 3.40-3.30 (m, 3H, H-C(3), H-C(4), H-C(5)), 3.27 (dd,  $J = 9.1, 7.8$  Hz, 1H, H-C(2)).

<sup>13</sup>C NMR (CD<sub>3</sub>OD, 25 °C, 100 MHz):  $\delta_C$  172.1 (CONH<sub>2</sub>), 135.1 (CH), 116.4 (CH<sub>2</sub>), 104.7 (C1), 78.2 (C3), 77.8 (C4), 74.9 (C2), 71.4 (C5), 69.5 (CH<sub>2</sub>), 62.5 (C6).

HRMS (ESI<sup>+</sup>) : Calcd for C<sub>11</sub>H<sub>19</sub>NO<sub>7</sub>Na<sup>+</sup> [M + Na]<sup>+</sup>: 300.1059; Found: 300.1063.

### 2-( $\beta$ -D-Glucopyranosyloxy)-*N*-2-propyn-1-yl-acetamide (11c).



The reaction was carried out at 90 °C with 2-( $\beta$ -D-glucopyranosyloxy)-acetamide (237 mg, 1 mmol) and propargylamine (165 mg, 3 mmol, 3 equiv.) in a sealed tube. The pure product 2-( $\beta$ -D-glucopyranosyloxy)-*N*-2-propen-1-yl-acetamide was obtained as a yellow oil (248 mg, 90%).

$R_f$ =0.49 (CH<sub>2</sub>Cl<sub>2</sub> : MeOH, 8:2).

$[\alpha]_{589}^{25} = -24.0$ , ( $c = 1.0$ , MeOH)..

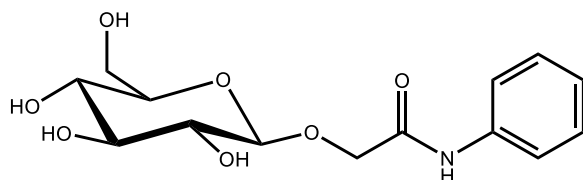
IR (film)  $\nu_{\max}/\text{cm}^{-1}$ : 3289, 2926, 1657, 1545, 1441, 1346, 1261, 1161, 1072, 1042.

$^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ , 25 °C, 400 MHz):  $\delta_{\text{H}}$  4.36 (d,  $J=15.7$  Hz, 1H, Ha-(C7)), 4.34 (d,  $J=7.7$  Hz, 1H, H-(C1)), 4.17 (d,  $J=15.7$  Hz, 1H, Ha-(C7)), 4.12-3.99 (m, 2H, H-(C10)), 3.89 (dd,  $J=11.9$  Hz, 1.8 Hz, 1H, Ha-(C6)), 3.70 (dd,  $J=11.9$  Hz, 5.2 Hz, 1H, Hb-(C6)), 3.43-3.26 (m, 4H, H-C2, C3, C4, C5), 2.62 (t,  $J=2.6$  Hz, 1H, H-(C12)).

$^{13}\text{C}$  NMR ( $\text{CD}_3\text{OD}$ , 25 °C, 100 MHz):  $\delta_{\text{C}}$  170.6 ( $\text{CONH}_2$ ), 103.2 (C1), 78.9 (C11), 76.8 (C3), 76.3 (C4), 73.5 (C2), 70.9 (C12), 70.0 (C5), 68.0 (C7), 61.1 (C6), 27.7 (C10).

HRMS (ESI<sup>+</sup>) : Calcd for  $\text{C}_{11}\text{H}_{17}\text{NO}_7\text{Na}^+$  [ $\text{M} + \text{Na}$ ]<sup>+</sup>: 298.0903; Found: 298.0913.

### 2-( $\beta$ -D-Glucopyranosyloxy)-*N*-phenyl-acetamide (11d).



The reaction was carried out at 130 °C with 2-( $\beta$ -D-glucopyranosyloxy)-acetamide (237 mg, 1 mmol) and aniline (279 mg, 3 mmol, 3 equiv.) in a sealed tube. The pure product 2-( $\beta$ -D-glucopyranosyloxy)-*N*-phenyl-acetamide was obtained as a yellow oil (213 g, 68%).

$R_f=0.29$  ( $\text{CH}_2\text{Cl}_2$  : MeOH, 7:3).

$[\alpha]_{589}^{25} = -44.7$ , ( $c = 1.0$ , MeOH).

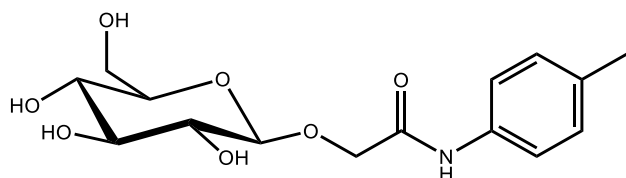
IR (film)  $\nu_{\max}/\text{cm}^{-1}$ : 3310, 2899, 1649, 1605, 1558, 1501, 1445, 1333, 1071, 1049, 1034, 901, 754.

$^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ , 25 °C, 400 MHz):  $\delta_{\text{H}}$  7.62 (d,  $J = 8.0$  Hz, 2H, Ph), 7.32 (t,  $J = 8.0$  Hz, 2H, Ar), 7.13 (t,  $J = 8.0$  Hz, 1H, Ph), 4.43 (d,  $J = 16.0$  Hz, 1H, Ha-CH<sub>2</sub>), 4.42 (d,  $J = 7.4$  Hz, 1H H-C(1)), 4.30 (d,  $J = 16.0$  Hz, 1H, Hb-CH<sub>2</sub>), 3.89 (dd,  $J = 11.9$ , 1.3 Hz, 1H, Ha-C(6)), 3.70 (dd,  $J = 11.9$ , 5.1 Hz, 1H, Hb-C(6)), 3.44-3.33 (m, 4H, H-C(3), H-C(4), H-C(5), H-C(2)).

$^{13}\text{C}$  NMR ( $\text{CD}_3\text{OD}$ , 25 °C, 100 MHz):  $\delta_{\text{C}}$  170.5 ( $\text{CONH}_2$ ), 138.9 (C(Ph)), 129.8 (2xCH(Ph)), 125.7 (CH(Ph)), 121.4 (2xCH(Ph)), 104.8 (C1), 78.3 (C3), 77.9 (C4), 74.9 (C2), 71.4 (C5), 69.7 (CH<sub>2</sub>), 62.5 (C6).

HRMS (ESI<sup>+</sup>) : Calcd for  $\text{C}_{14}\text{H}_{19}\text{NO}_7\text{Na}^+$  [ $\text{M} + \text{Na}$ ]<sup>+</sup>: 336.1059; Found: 336.1048.

### 2-( $\beta$ -D-glucopyranosyloxy)-*N*-(4-methylphenyl)-acetamide (11e).



The reaction was carried out at 130 °C with 2-(β-D-glucopyranosyloxy)-acetamide (237 mg, 1 mmol) and *p*-toluidine (321 mg, 3 mmol, 3 equiv.) in a sealed tube. The pure product 2-(β-D-glucopyranosyloxy)-*N*-(4-methylphenyl)-acetamide was obtained as a white solid (213 mg, 65%, m.p. 195°C).

$R_f$ =0.32 (CH<sub>2</sub>Cl<sub>2</sub> : MeOH, 7:3).

$[\alpha]_{589}^{25} = -42.2$ , ( $c = 1.0$ , MeOH).

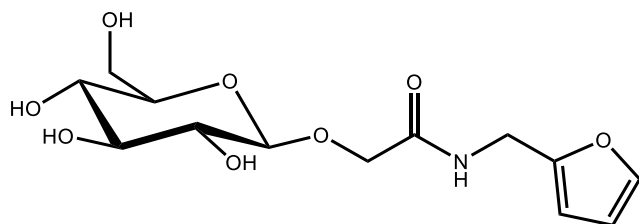
IR (film)  $\nu_{\max}/\text{cm}^{-1}$ : 3483, 3312, 2901, 1645, 1609, 1553, 1512, 1441, 1408, 1364, 1329, 1302, 1227, 1157, 1107, 1072, 1045, 1034, 988, 897, 864, 814, 723.

<sup>1</sup>H NMR (CD<sub>3</sub>OD, 25 °C, 400 MHz):  $\delta_H$  7.48 (d,  $J = 8.2$  Hz, 1H, Ar), 7.14 (d,  $J = 8.2$  Hz, 1H, Ar), 4.40 (d,  $J = 7.7$  Hz, 1H H-C(1)), 4.41 (d,  $J = 16.0$  Hz, 1H, Ha-CH<sub>2</sub>), 4.28 (d,  $J = 16.0$  Hz, 1H, Hb-CH<sub>2</sub>), 3.88 (dd,  $J = 11.8, 1.3$  Hz, 1H, Ha-C(6)), 3.69 (dd,  $J = 11.8, 4.6$  Hz, 1H, Hb-C(6)), 3.43-3.33 (m, 4H, H-C(3), H-C(4), H-C(5), H-C(2)), 2.31 (s, 3H, CH<sub>3</sub>).

<sup>13</sup>C NMR (CD<sub>3</sub>OD, 25 °C, 100 MHz):  $\delta_C$  170.4 (COONH<sub>2</sub>), 136.3 (C(Ar)), 135.5 (C(Ar)), 130.3 (2xCH(Ar)), 121.5 (2xCH(Ar)), 104.9 (C1), 78.3 (C3), 77.9 (C4), 75.0 (C2), 71.4 (C5), 69.7 (CH<sub>2</sub>), 62.6 (C6), 20.9 (CH<sub>3</sub>).

HRMS (ESI<sup>+</sup>) : Calcd for C<sub>15</sub>H<sub>22</sub>NO<sub>7</sub><sup>+</sup> [M + H]<sup>+</sup>: 328.1396; Found: 328.1396.

### 2-(β-D-glucopyranosyloxy)-*N*-(2-Furanylmethyl)-acetamide (11f).



The reaction was carried out at 130 °C with 2-(β-D-glucopyranosyloxy)-acetamide (237 mg, 1 mmol) and furfurylamine (291 mg, 3 mmol, 3 equiv.) in a sealed tube. The pure product 2-(β-D-glucopyranosyloxy)-*N*-(2-furanylmethyl) acetamide was obtained as a yellow oil (232 mg, 73%).

$R_f$ =0.28 (CH<sub>2</sub>Cl<sub>2</sub> : MeOH, 7:3).

$[\alpha]_{589}^{25} = -28.7$ , ( $c = 1.0$ , MeOH).

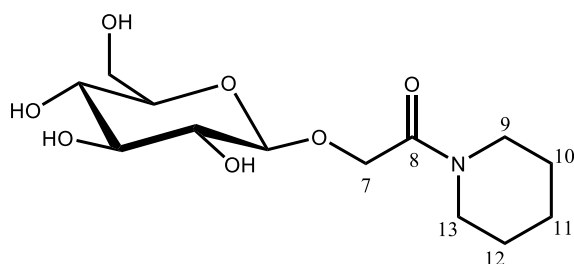
IR (film)  $\nu_{\max}/\text{cm}^{-1}$ : 3314, 2901, 1645, 1611, 1553, 1512, 1439, 1410, 1342, 1072, 1038, 926, 897, 814, 747.

$^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ , 25 °C, 400 MHz):  $\delta_{\text{H}}$  7.42 (dd,  $J = 1.8, 0.7$  Hz, 1H, Furan), 6.34 (dd,  $J = 3.2, 1.8$  Hz, 1H, Furan), 7.27 (dd,  $J = 3.2, 0.7$  Hz, 1H, Furan), 4.47 (d,  $J = 15.5$  Hz, 1H, Ha- $\text{CH}_2$ ), 4.39 (d,  $J = 15.5$  Hz, 1H, Hb- $\text{CH}_2$ ), 4.39 (d,  $J = 15.8$  Hz, 1H, Ha- $\text{CH}_2$ ), 4.31 (d,  $J = 7.9$  Hz, 1H H-C(1)), 4.16 (d,  $J = 15.8$  Hz, 1H, Ha- $\text{CH}_2$ ), 3.85 (dd,  $J = 11.9, 1.7$  Hz, 1H, Ha-C(6)), 3.66 (dd,  $J = 11.9, 5.2$  Hz, 1H, Hb-C(6)), 3.39-3.23 (m, 4H, H-C(3), H-C(4), H-C(5), H-C(2)).

$^{13}\text{C}$  NMR ( $\text{CD}_3\text{OD}$ , 25 °C, 100 MHz):  $\delta_{\text{C}}$  172.1 ( $\text{COONH}_2$ ), 152.7 (Cfuran), 143.4 (CHfuran), 111.4 (CHfuran), 108.3 (CHfuran), 104.6 (C1), 78.2 (C3), 77.8 (C4), 74.9 (C2), 71.4 (C5), 69.4 ( $\text{CH}_2$ ), 62.5 (C6), 36.6 ( $\text{CH}_2\text{NH}$ ).

HRMS (ESI<sup>+</sup>) : Calcd for  $\text{C}_{13}\text{H}_{19}\text{NO}_8\text{Na}^+$  [ $\text{M} + \text{Na}$ ]<sup>+</sup>: 340.1008; Found: 340.1010.

### 2-( $\beta$ -D-glucopyranosyloxy)-*I*-(piperidin-1-yl)-acetamide (11g).



The reaction was carried out at 100 °C with 2-( $\beta$ -D-glucopyranosyloxy)-acetamide (237 mg, 1 mmol) and piperidine (255 mg, 3 mmol, 3 equiv.) in a sealed tube. The pure product *I*-(piperidin-1-yl)-2-( $\beta$ -D-glucopyranosyloxy)-acetamide was obtained as a white solid (217 mg, 71%, m.p. = 187 °C).

$R_f$ =0.21 ( $\text{CH}_2\text{Cl}_2$  : MeOH, 7:3).

$[\alpha]_{589}^{25} = -37,2$  ( $c = 1.0$ , MeOH).

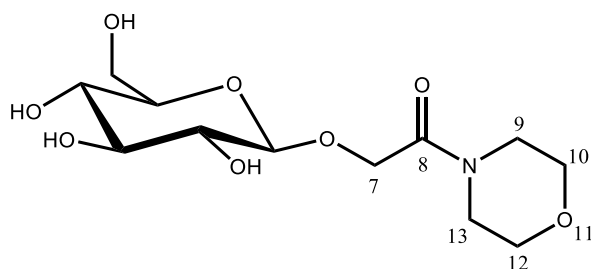
IR (film)  $\nu_{\max}/\text{cm}^{-1}$ : 3499, 3310, 2932, 1624, 1439, 1341, 1254, 1161, 1090, 899.

$^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ , 25 °C, 100 MHz):  $\delta_{\text{H}}$  4.53 (d,  $J=14.6$  Hz, 1H, Ha-(C7)), 4.24 (d,  $J=14.4$  Hz, 1H, Hb-(C7)), 4.22 (d,  $J=7.6$  Hz, 1H, H-(C1)), 3.78 (dd,  $J=11.9, 1.9$  Hz, 1H, Ha-(C6)), 3.54 (dd,  $J=11.8, 5.8$  Hz, 1H, Hb-(C6)), 3.45 (t,  $J=5.6$  Hz, 2H,  $\text{CH}_2$  pip), 3.33-3.25 (m, 3H,  $\text{CH}_2$  pip + H-(C5)), 3.23-3.13 (m, 3H, H-C2, C3, C4), 1.64-1.61 (m, 6H, 3x  $\text{CH}_2$  pip).

$^{13}\text{C}$  NMR ( $\text{CD}_3\text{OD}$ , 25 °C, 400 MHz):  $\delta_{\text{H}}$  168.25 ( $\text{CONH}_2$ ), 103.1 (C1), 76.8 (C3), 76.3 (C4), 73.6 (C2), 70.2 (C5), 66.8 (C7), 61.5 (C6), 45.4 (C-pip), 42.7 (C-pip), 25.9 (C-pip), 25.2 (C-pip), 24.0 (C-pip).

HRMS (ESI<sup>+</sup>) : Calcd for  $\text{C}_{13}\text{H}_{23}\text{NO}_7\text{Na}^+$  [ $\text{M} + \text{Na}$ ]<sup>+</sup>: 328.1372; Found: 328.1384.

### 2-( $\beta$ -D-glucopyranosyloxy)-*I*-morpholino-acetamide (11h).



The reaction was carried out at 130 °C with 2-( $\beta$ -D-glucopyranosyloxy)-acetamide (237 mg, 1 mmol) and morpholine (321 mg, 3 mmol, 3 equiv.) in a sealed tube. The pure product 2-( $\beta$ -D-glucopyranosyloxy)-*I*-morpholino-acetamide was obtained as a white solid (240 mg, 78%, m.p. = 162 °C).

$[\alpha]_{589}^{25} = -574,5$  ( $c = 1.0$ , MeOH).

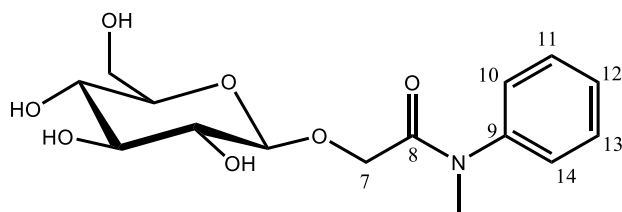
IR (film)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3354, 2874, 1630, 1443, 1364, 1319, 1277, 1246, 1165, 1069, 1034, 891, 851, 785.

$^1\text{H}$  NMR (DMSO- $d_6$ , 25 °C, 400 MHz):  $\delta_{\text{H}}$  4.43 (d,  $J=13.9$  Hz, 1H, Ha-(C7)), 4.29 (d,  $J=13.9$  Hz, 1H, Hb-(C7)), 4.21 (d,  $J=7.8$  Hz, 1H, H-(C1)), 3.66 (dd,  $J=11.8$ ; 2.0 Hz, 1H, Ha-(C6)), 3.60-3.55, m, 4H, 2x  $\text{CH}_2$  morf.), 3.55-3.52 (m, 2H, Hb-(C6) + H-(C3)), 3.46-3.40 (m, 4H, 2x  $\text{CH}_2$  morf.), 3.17-2.96 (m, 3H, H-C4, C5, C2).

$^{13}\text{C}$  NMR (DMSO- $d_6$ , 25 °C, 100 MHz):  $\delta_{\text{C}}$  168.17 ( $\text{CONH}_2$ ), 103.3 (C1), 77.5 (C3), 77.1 (C4), 73.9 (C2), 70.3 (C5), 67.5 (C7), 67.32 (C6), 66.4 (C-morf), 61.5 (C-morf), 45.4 (C-morf), 42.1 (C-morf).

HRMS (ESI $^+$ ) : Calcd for  $\text{C}_{12}\text{H}_{21}\text{NO}_8\text{Na}^+$  [ $\text{M} + \text{Na}$ ] $^+$ : 330.1165; Found: 330.1164

### 2-( $\beta$ -D-Glucopyranosyloxy)-*N*-phenylaniline-acetamide (11i).



The reaction was carried out at 130 °C with 2-( $\beta$ -D-glucopyranosyloxy)-acetamide (237 mg, 1 mmol) and *N*-methylaniline (321 mg, 3 mmol, 3 equiv.) in a sealed tube. The pure product 2-( $\beta$ -D-Glucopyranosyloxy)-*N*-phenylaniline-acetamide was obtained as a white solid (190 mg, 58%, m.p. = 183 °C).

$[\alpha]_{589}^{25} = -24.000$ , ( $c = 0.1$ , DMSO).

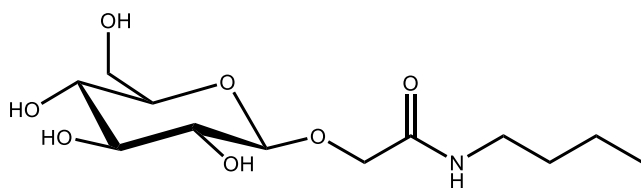
IR (film)  $\nu_{\max}/\text{cm}^{-1}$ : 3364, 2920, 2853, 2527, 2384, 1649, 1545, 1460, 1368, 1298, 1263, 1078, 903, 791, 733.

$^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ , 25 °C, 400 MHz):  $\delta_{\text{C}}$  7.40-7.12 (m, 5H, Ph), 4.48 (d,  $J=14.8$  Hz, 1H, Ha-(C7)), 4.33 (d,  $J=14.8$  Hz, 1H, Hb-(C7)), 4.27 (d,  $J=7.7$  Hz, 1H, H-(C1)), 3.78 (dd,  $J=11.8$ , 1.6 Hz, 1H, Ha-(C6)), 3.56 (dd,  $J=11.8$ , 1.6 Hz, 1H, Hb-(C6)), 3.32-3.12 (m, 4H, H-C3, C4, C5, C2), 2.82 (m, 3H, N-CH<sub>3</sub>).

$^{13}\text{C}$  NMR ( $\text{CD}_3\text{OD}$ , 25 °C, 100 MHz):  $\delta_{\text{H}}$  170.0 (CONH<sub>2</sub>), 136.7 (C9), 129.4 (Ph), 128.9 (Ph), 128.3 (Ph), 127.6 (Ph), 127.2 (Ph), 103.1 (C1), 76.9 (C3), 76.3 (C4), 73.6 (C2), 70.2 (C5), 66.6 (C7), 61.4 (C6), 32.7 (N-CH<sub>3</sub>).

HRMS (ESI<sup>+</sup>) : Calcd for  $\text{C}_{15}\text{H}_{21}\text{NO}_7\text{Na}^+$   $[\text{M} + \text{Na}]^+$ : 364.1372; Found: 364.1370.

#### ***N*-Butyl-2-( $\beta$ -D-glucopyranosyloxy)-acetamide (11j).**



The reaction was carried out at 100 °C with 2-( $\beta$ -D-glucopyranosyloxy)-acetamide (237 mg, 1 mmol) and butylamine (219 mg, 3 mmol, 3 equiv.) in a sealed tube. The pure product *N*-butyl-2-( $\beta$ -D-glucopyranosyloxy)-acetamide was obtained as a white solid (267 mg, 91%, m.p. = 142 °C).

$R_f=0.48$  ( $\text{CH}_2\text{Cl}_2$  : MeOH, 8:2).

$[\alpha]_{589}^{25} = -100.4$ , ( $c = 1.0$ , MeOH).

IR (film)  $\nu_{\max}/\text{cm}^{-1}$ : 3453, 3343, 3248, 2930, 1638, 1568, 1443, 1406, 1358, 1304, 1161, 1130, 1072, 1061, 1038, 995, 893, 797.

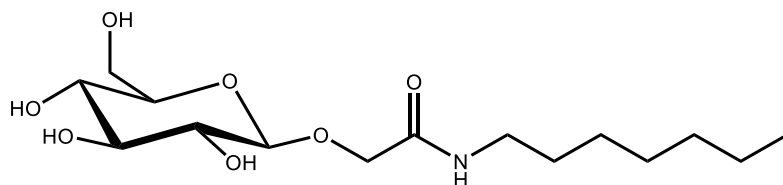
$^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ , 25 °C, 400 MHz):  $\delta_{\text{H}}$  4.32 (d,  $J = 7.7$  Hz, 1H H-C(1)), 4.31 (d,  $J = 15.8$  Hz, 1H, Ha-CH<sub>2</sub>), 4.15 (d,  $J = 15.7$  Hz, 1H, Hb-CH<sub>2</sub>), 3.88 (dd,  $J = 10.5$ , 1.7 Hz, 1H, Ha-C(6)), 3.70 (dd,  $J = 11.9$ , 5.1 Hz, 1H, Hb-C(6)), 3.42-3.22 (m, 6H, H-C(3), H-C(4), H-C(5), CH<sub>2</sub>NH, H-C(2)), 1.58-1.51 (m, 2H, CH<sub>2</sub>), 1.44-1.35 (m, 2H, CH<sub>2</sub>), 0.94-0.91 (t,  $J = 7.3$  Hz, 3H, CH<sub>3</sub>).

$^{13}\text{C}$  NMR ( $\text{CD}_3\text{OD}$ , 25 °C, 100 MHz):  $\delta_{\text{C}}$  172.1 (COONH<sub>2</sub>), 104.7 (CH(1)), 78.2 (CH(3)), 77.8 (CH(4)), 74.9 (CH(2)), 71.4 (CH(5)), 69.4 (CH<sub>2</sub>), 62.5 (CH<sub>2</sub>(6)), 39.8 (CH<sub>2</sub>NH), 32.5 (CH<sub>2</sub>), 21.1 (CH<sub>2</sub>), 14.1 (CH<sub>3</sub>).



HRMS (ESI<sup>+</sup>) : Calcd for C<sub>12</sub>H<sub>23</sub>NO<sub>7</sub>Na<sup>+</sup> [M + Na]<sup>+</sup>: 316.1372; Found: 316.1372.

**2-(β-D-Glucopyranosyloxy)-N-heptyl-acetamide (11k).**



The reaction was carried out at 100 °C with 2-(β-D-glucopyranosyloxy)-acetamide (237 mg, 1 mmol) and heptylamine (346 mg, 3 mmol, 3 equiv.) in a sealed tube. The pure product 2-(β-D-glucopyranosyloxy)-N-heptyl-acetamide was obtained as a white solid (319 mg, 95%, m.p. = 149 °C).

R<sub>f</sub>=0.38 (CH<sub>2</sub>Cl<sub>2</sub> : MeOH, 9:1).

[α]<sub>589</sub><sup>25</sup> = -325.9, (c = 1.0, MeOH).

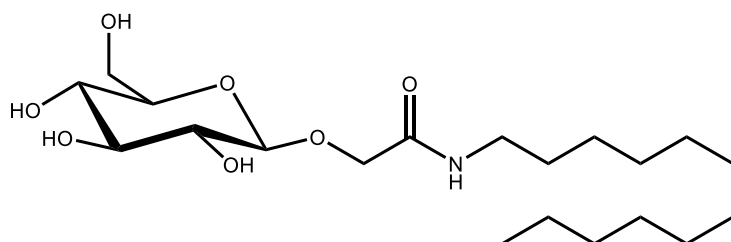
IR (film) ν max/cm<sup>-1</sup>: 3472, 3318, 3217, 2926, 2895, 1640, 1572, 1443, 1362, 1335, 1298, 1238, 1159, 1103, 1078, 1051, 1036, 984, 899, 727.

<sup>1</sup>H NMR (CD<sub>3</sub>OD, 25 °C, 400 MHz): δ<sub>H</sub> 4.32 (d, *J* = 7.7 Hz, 1H H-C(1)), 4.31 (d, *J* = 15.7 Hz, 1H, Ha-CH<sub>2</sub>), 4.15 (d, *J* = 15.7 Hz, 1H, Hb-CH<sub>2</sub>), 3.88 (dd, *J* = 11.9, 1.5 Hz, 1H, Ha-C(6)), 3.64 (dd, *J* = 11.9, 5.2 Hz, 1H, Hb-C(6)), 3.42-3.21 (m, 6H, H-C(3), H-C(4), H-C(5), CH<sub>2</sub>NH, H-C(2)), 1.60-1.53 (m, 2H, CH<sub>2</sub>), 1.34-1.32 (s, 8H, CH<sub>2</sub>), 0.94-0.91 (t, *J* = 7.3 Hz, 3H, CH<sub>3</sub>).

<sup>13</sup>C NMR (CD<sub>3</sub>OD, 25 °C, 100 MHz): δ<sub>C</sub> 172.1 (CONH<sub>2</sub>), 104.7 (C1), 78.2 (C3), 77.8 (C4), 74.9 (C2), 71.4 (C5), 69.4 (CH<sub>2</sub>), 62.5 (C6), 40.1 (CH<sub>2</sub>NH), 33.0 (CH<sub>2</sub>), 32.9 (CH<sub>2</sub>), 30.4 (CH<sub>2</sub>), 30.1 (CH<sub>2</sub>), 28.0 (CH<sub>2</sub>), 23.7 (CH<sub>2</sub>), 14.4 (CH<sub>3</sub>).

HRMS (ESI<sup>+</sup>) : Calcd for C<sub>15</sub>H<sub>29</sub>NO<sub>7</sub>Na<sup>+</sup> [M + Na]<sup>+</sup>: 358.1842; Found: 358.1834.

**N-dodecyl-2-(β-D-glucopyranosyloxy)-acetamide (11l).**



The reaction was carried out at 120 °C with 2-(β-D-glucopyranosyloxy)-acetamide (237 mg, 1 mmol) and dodecylamine (556 mg, 3 mmol, 3 equiv.) in a sealed tube. The pure product 2-(β-

D-glucopyranosyloxy)-*N*-heptyl-acetamide was obtained as a white solid (381 mg, 94%, m.p. 149°C).

R<sub>f</sub>=0.46 (CH<sub>2</sub>Cl<sub>2</sub> : MeOH, 9:1).

[α]<sub>589</sub><sup>25</sup> = -385,9, (*c* = 1.0, MeOH).

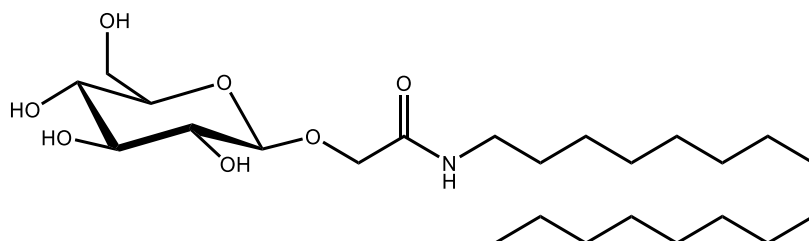
IR (film) ν max/cm<sup>-1</sup>: 3472, 3314, 2922, 2851, 1641, 1580, 1470, 1443, 1331, 1300, 1234, 1161, 1098, 1074, 1038, 1017, 984, 897, 721.

<sup>1</sup>H NMR (CD<sub>3</sub>OD, 25 °C, 400 MHz): δ<sub>H</sub> 4.26 (d, *J* = 7.7 Hz, 1H H-C(1)), 4.25 (d, *J* = 15.7 Hz, 1H, Ha-CH<sub>2</sub>), 4.09 (d, *J* = 15.7 Hz, 1H, Hb-CH<sub>2</sub>), 3.82 (dd, *J* = 11.0, 1.8 Hz, 1H, Ha-C(6)), 3.64 (dd, *J* = 11.0, 5.1 Hz, 1H, Hb-C(6)), 3.29-3.16 (m, 6H, H-C(3), H-C(4), H-C(5), CH<sub>2</sub>NH, H-C(2)), 1.52-1.48 (m, 2H, CH<sub>2</sub>), 1.25 (s, 18H, CH<sub>2</sub>), 0.89-0.83 (m, 3H, CH<sub>3</sub>).

<sup>13</sup>C NMR (CD<sub>3</sub>OD, 25 °C, 100 MHz): δ<sub>C</sub> 172.1 (CONH<sub>2</sub>), 104.7 (C1), 78.2 (C3), 77.8 (C4), 74.9 (C2), 71.4 (C5), 69.4 (CH<sub>2</sub>), 62.5 (C6), 40.1 (CH<sub>2</sub>NH), 33.1 (CH<sub>2</sub>), 30.8 (4 x CH<sub>2</sub>), 30.5 (CH<sub>2</sub>), 30.4 (2 x CH<sub>2</sub>), 28.0 (CH<sub>2</sub>), 23.7 (CH<sub>2</sub>), 14.4 (CH<sub>3</sub>).

HRMS (ESI<sup>+</sup>) : Calcd for C<sub>20</sub>H<sub>39</sub>NO<sub>7</sub>Na<sup>+</sup> [*M* + Na]<sup>+</sup>: 428.2624; Found: 428.2624.

### 2-(β-D-Glucopyranosyloxy)-*N*-hexadecyl-acetamide (11m).



The reaction was carried out at 150 °C with 2-(β-D-glucopyranosyloxy)-acetamide (237 mg, 1 mmol) and hexadecylamine (725 mg, 3 mmol, 3 equiv.) in a sealed tube. The pure product 2-(β-D-glucopyranosyloxy)-*N*-hexadecyl-acetamide was obtained as a white solid (411 mg, 89%, m.p. 153°C).

R<sub>f</sub>=0.54 (CH<sub>2</sub>Cl<sub>2</sub> : MeOH, 9:1).

[α]<sub>589</sub><sup>25</sup> = -24,000 (*c* = 0.2, DMSO).

IR (film) ν max/cm<sup>-1</sup>: 3475, 3316, 2920, 2851, 1641, 1578, 1470, 1331, 1300, 1234, 1163, 1096, 1078, 1038, 1017, 897, 721.

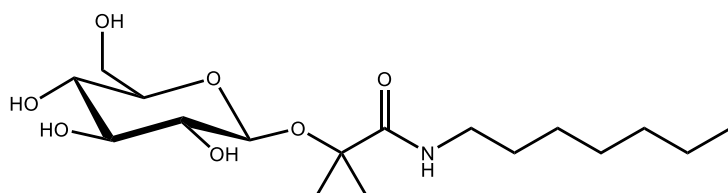
<sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>SO, 25 °C, 400 MHz): δ<sub>H</sub> 7.83 (t, 1H, *J* = 5.7 Hz, NH), 5.54 (bs, 1H, OH), 5.02 (bs, 1H, OH), 4.95 (bs, 1H, OH), 4.52 (bs, 1H, OH), 4.15 (d, *J* = 8.0 Hz, 1H H-C(1)), 4.12 (d, *J* = 15.7 Hz, 1H, Ha-CH<sub>2</sub>), 3.96 (d, *J* = 15.7 Hz, 1H, Hb-CH<sub>2</sub>), 3.77-3.64 (m, 1H, Ha-

C(6)), 3.45-3.42 (m, 1H, Hb-C(6)), 3.18-3.02 (m, 6H, H-C(3), H-C(4), H-C(5), CH<sub>2</sub>NH, H-C(2)), 1.43-1.40 (m, 2H, CH<sub>2</sub>), 1.24 (s, 26H, CH<sub>2</sub>), 0.85 (m, 3H, CH<sub>3</sub>).

<sup>13</sup>C NMR ((CD<sub>3</sub>)<sub>2</sub>SO, 25 °C, 100 MHz):  $\delta_C$  168.7 (C=O), 103.2 (C1), 77.1 (C3), 76.2 (C4), 73.3 (C2), 69.9 (C5), 68.0 (CH<sub>2</sub>), 60.9 (C6), 38.2 (CH<sub>2</sub>NH), 31.3 (CH<sub>2</sub>), 29.1 (9 x CH<sub>2</sub>), 29.0 (CH<sub>2</sub>), 28.8 (CH<sub>2</sub>), 28.7 (CH<sub>2</sub>), 26.4 (CH<sub>2</sub>), 22.1 (CH<sub>3</sub>).

HRMS (ESI<sup>+</sup>) : Calcd for C<sub>24</sub>H<sub>47</sub>NO<sub>7</sub>Na<sup>+</sup> [M + Na]<sup>+</sup>: 484.3250; Found: 484.3260.

### 2-( $\beta$ -D-Glucopyranosyloxy)-2-methyl-N-heptyl-propanamide (11n).



The reaction was carried out with at 150 °C with 2-( $\beta$ -D-Glucopyranosyloxy)-2-methyl-propanamide (**9b**) (265 mg, 1 mmol) and heptylamine (346 mg, 3 mmol, 3 equiv.) in a sealed tube. The pure product 2-( $\beta$ -D-glucopyranosyloxy)-2-methyl-N-heptyl-propanamide was obtained as a white solid (280 mg, 77%, m.p. = 126 °C).

R<sub>f</sub>=0.45 (CH<sub>2</sub>Cl<sub>2</sub> : MeOH, 9:1).

$[\alpha]_{589}^{25} = -38.800$ , ( $c = 0.5$ , CH<sub>3</sub>OH).

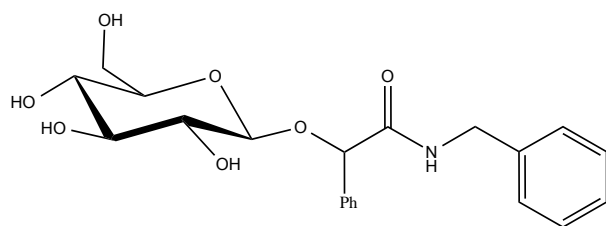
IR (film)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3323, 2928, 2860, 1641, 1549, 1460, 1369, 1171, 1076, 1042, 895, 664, 625.

<sup>1</sup>H NMR (CD<sub>3</sub>OD, 25 °C, 400 MHz):  $\delta_H$  4.50 (d,  $J=7.8$  Hz, 1H, H-(C1)), 3.84 (dd,  $J=11.9, 2.2$  Hz, 1H, Ha-(C6)), 3.67 (dd,  $J=11.9, 5.4$  Hz, 1H, Hb-(C6)), 3.38 (q,  $J=9.7$  Hz, 1H, H-(C3 or C4), 3.34-3.25 (m, 3H, H-(C2) H-(C5), and H-(C3 or C4), 2.68-2.61 (t, 2H,  $J=7.1$  Hz, CH<sub>2</sub>NH), 1.40-1.28 (m, 10 H, 5x CH<sub>2</sub>), 0.93 (t,  $J=6.8$  Hz, 3H, CH<sub>3</sub>).

<sup>13</sup>C NMR (CD<sub>3</sub>OD, 25 °C, 100 MHz):  $\delta_C$  176.1 (C=O), 98.2 (C1), 80.1 (CCH<sub>3</sub>), 77.0 (C3), 76.5 (C4), 73.8 (C2), 70.1 (C5), 61.2 (C6), 41.2 (CH<sub>2</sub>NH), 32.4 (CH<sub>2</sub>), 31.6 (CH<sub>2</sub>), 28.9 (CH<sub>2</sub>), 28.8 (CH<sub>2</sub>), 28.7 (CH<sub>2</sub>), 22.4 (CCH<sub>3</sub>), 22.3 (CCH<sub>3</sub>), 13.0 (CH<sub>2</sub>CH<sub>3</sub>).

HRMS (ESI<sup>+</sup>) : Calcd for C<sub>17</sub>H<sub>33</sub>NO<sub>7</sub>Na [M + Na]<sup>+</sup>: 386.2155; Found: 386.2162.

**$\alpha$ -( $\beta$ -D-Glucopyranosyloxy)phenyl-*N*-(phenylmethyl)-acetamide (11o).**



The reaction was carried out with at 150 °C with (*R*)- $\alpha$ -( $\beta$ -D-glucopyranosyloxy)phenylacetamide (**9c**) (313 mg, 1 mmol) and benzylamine (321 mg, 3 mmol, 3 equiv.) in a sealed tube. The  $\alpha$ -( $\beta$ -D-glucopyranosyloxy)phenyl-*N*-(phenylmethyl)-acetamide was obtained as a colourless oil (315 mg, 78%).

R<sub>f</sub>=0.28 (CH<sub>2</sub>Cl<sub>2</sub> : MeOH, 9:1).

IR (film)  $\nu$  max/cm<sup>-1</sup>: 3318, 3061, 2913, 2357, 2326, 15659, 1537, 1501, 1452, 1391, 1354, 1306, 1256, 1074, 824, 748.

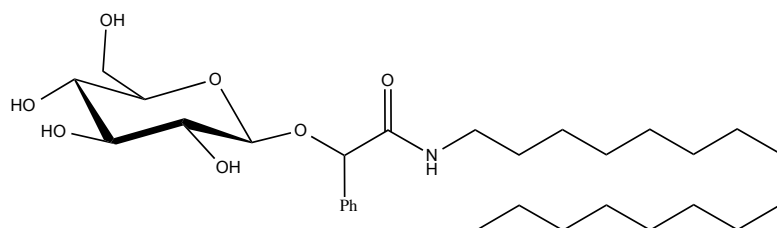
Isomer 1 / Isomer 2 = 1 / 1

<sup>1</sup>H NMR (MeOD, 25 °C, 400 MHz):  $\delta_H$  **Isomer 1**: 7.23-7.09 (m, 10H, Ph), 5.25 (s, H-(C5)), 4.43-4.22 (m, 3H, CH<sub>2</sub>-10 + H-(C1)), 3.73 (dd, *J* = 12.0, 2.0 Hz, 1H, Ha-(C6)), 3.59-3.50 (dd, *J* = 12.4, 5.2 Hz, 1H, Hb-(C6)), 3.33-3.12 (m, 4H, H-C2, C3, C4, C5). **Isomer 2**: 7.40-7.10 (m, Ph), 5.32 (s, H-(C5)), 4.43-4.22 (m, CH<sub>2</sub>-10), 4.00 (d, *J* = 7.7 Hz, H-(C1)), 3.73 (dd, *J* = 12.0, 2.0 Hz, Ha-(C6)), 3.59-3.50 (dd, *J* = 12.4, 5.2 Hz, Hb-(C6)), 3.33-3.12 (m, 4H, H-C2, C3, C4), 2.98-2.94 (m, H-(C5)).

<sup>13</sup>C NMR (MeOD, 25 °C, 100 MHz):  $\delta_C$  **Isomer 1**: 171.9 (CONH), 140.9 (C<sub>quater</sub>Ph), 137.6 (C<sub>quater</sub>Ph), 128.3 (Ph), 128.2 (2x Ph), 128.0 (2x Ph), 102.2 (C1), 80.1 (C1), 77.0 (C5), 76.7 (C3), 73.7 (C2), 70.0 (C4), 61.2 (C6), 45.0 (C10). **Isomer 2**: 171.67 (CONH), 138.2 (C<sub>quater</sub>Ph), 136.0 (C<sub>quater</sub>Ph), 127.3 (Ph), 127.2 (2x Ph), 127.1, 127.0 (Ph), 126.9 (Ph), 98.9 (C1), 78.2 (C1), 76.8 (C5), 76.2 (C3), 73.6 (C2), 70.2 (C4), 61.2 (C6), 42.5 (C10).

HRMS (ESI<sup>+</sup>) : Calcd for C<sub>12</sub>H<sub>25</sub>O<sub>7</sub>Na [M + Na]<sup>+</sup>: 426.1529; Found: 426.1537.

**$\alpha$ -( $\beta$ -D-Glucopyranosyloxy)phenyl-*N*-hexadecyl-acetamide (11p).**



The reaction was carried out with at 150 °C with (*R*)- $\alpha$ -( $\beta$ -D-glucopyranosyloxy)phenylacetamide (**9c**) (313 mg, 1 mmol) and hexadecylamine (725 mg, 3 mmol, 3 equiv.) in a sealed tube. The  $\alpha$ -( $\beta$ -D-glucopyranosyloxy)phenyl-*N*-(phenylmethyl)-acetamide was obtained as a white solid (333 mg, 62%, m.p. = 112 °C).

R<sub>f</sub>=0.61 (CH<sub>2</sub>Cl<sub>2</sub> : MeOH, 9:1).

IR (film)  $\nu$  max/cm<sup>-1</sup>: 3325, 2920, 2851, 2361, 1641, 1545, 1466 1373, 1263, 1080, 1034, 895, 721.

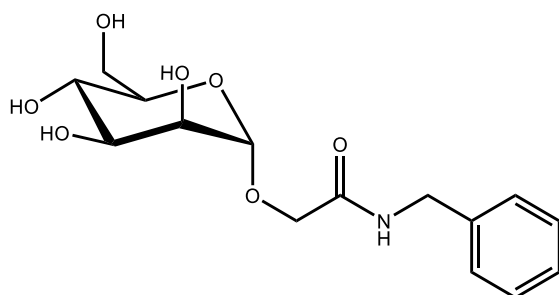
Isomer1 / Isomer 2 = 1 / 1

<sup>1</sup>H NMR (CD<sub>3</sub>OD, 25 °C, 400 MHz):  $\delta_H$  **Isomer 1**: 7.52-7.28 (m, 10H, Ph), 5.30 (s, 1H, H-(C7)), 4.46 (d, *J* = 7.7 Hz, 1H, H-(C1)), 3.88 (d, *J* = 12.0 Hz, 1H, Ha-(C6)), 3.68 (m, 1H, Hb-(C6)), 3.45-2.88 (m, 4H, H-C2, C3, C4, C5), 1.96 (s, 2H, NHCH<sub>2</sub>), 1.31 (s, 28H, 14x CH<sub>2</sub>), 0.91 (t, *J* = 6.6 Hz, 3H, CH<sub>3</sub>). **Isomer 2**: 7.52-7.28 (m, Ph), 5.35 (s, H-(C7)), 4.09 (d, *J* = 7.7 Hz, 1H, H-(C1)), 3.88 (d, *J* = 12.0 Hz, Ha-(C6)), 3.68 (m, Hb-(C6)), 3.45-2.88 (m, H-C2, C3, C4, C5), 1.94 (s, NHCH<sub>2</sub>), 1.31 (s, 28H, 14x CH<sub>2</sub>), 0.91 (t, *J* = 6.6 Hz, 3H, CH<sub>3</sub>).

<sup>13</sup>C NMR (CD<sub>3</sub>OD, 25 °C, 100 MHz):  $\delta_C$  **Isomer 1**: 171.80 (CONH), 137.6 (C<sub>quater</sub> Ph), 127.0 (2x Ph), 127.9 (3x Ph), 102.2 (C1), 80.1 (C7), 77.0 (C5), 76.7 (C3), 73.7 (C2), 70.0 (C4), 61.2 (C6), 38.8 (NHCH<sub>2</sub>), 31.7 (CH<sub>2</sub>), 29.4-28.2 (9x CH<sub>2</sub>), 26.6 (CH<sub>2</sub>), 22.4 (CH<sub>2</sub>CH<sub>3</sub>), 13.1 (CH<sub>3</sub>). **Isomer 2**: 171.6 (CONH), 136.1 (C<sub>quater</sub> Ph), 128.2 (2x Ph), 127.9 (3x Ph), 98.7 (C1), 78.1 (C7), 76.8 (C5), 76.2 (C3), 73.6 (C2), 70.2 (C4), 61.2 (C6), 38.8 (NHCH<sub>2</sub>), 31.7 (CH<sub>2</sub>), 29.4-28.2 (9x CH<sub>2</sub>), 26.6 (CH<sub>2</sub>), 22.4 (CH<sub>2</sub>CH<sub>3</sub>), 13.1 (CH<sub>3</sub>).

HRMS (ESI<sup>+</sup>) : Calcd for C<sub>12</sub>H<sub>25</sub>O<sub>7</sub>Na [M + Na]<sup>+</sup>: 560.3563; Found: 560.3561.

## 2-( $\alpha$ -D-Mannopyranosyloxy)-*N*-(phenylmethyl)-acetamide (**11q**).



The reaction was carried out at 150 °C with 2-( $\alpha$ -D-mannopyranosyloxy)-acetamide (**9d**) (237 mg, 1 mmol) and benzylamine (321 mg, 3 mmol, 3 equiv.) in a sealed tube. The pure product 2-( $\alpha$ -D-Mannopyranosyloxy)-*N*-(phenylmethyl)-acetamide was obtained as colourless oil (259 mg, 79%).

R<sub>f</sub>=0.43 (CH<sub>2</sub>Cl<sub>2</sub> : MeOH, 8:2).

$[\alpha]_{589}^{25} = -305.1$ , ( $c = 1.0$ , CH<sub>3</sub>OH).

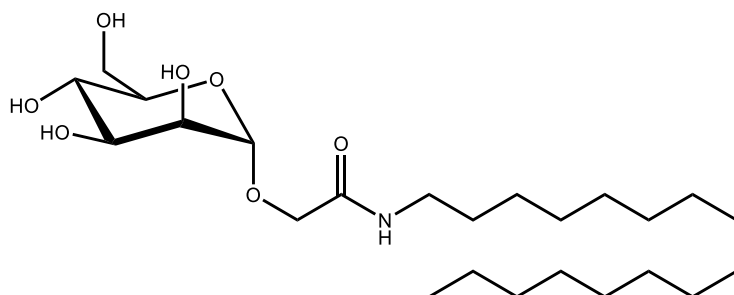
IR (film)  $\nu$  max/cm<sup>-1</sup>: 3347, 2926, 2860. 2361, 2336, 1742, 1663, 1543, 1452, 1422, 1258, 1196, 1136, 1076, 810.

<sup>1</sup>H NMR (MeOD, 25 °C, 400 MHz):  $\delta_H$  7.24-7.17 (m, 5H), 4.72 (d,  $J = 1.5$  Hz, 1H, H-(C1)), 4.31 (s, 2H, CH<sub>2</sub>-10), 4.10 (d,  $J = 15.2$  Hz, 1H, Ha-(C7)), 3.96 (d,  $J = 15.2$  Hz, 1H, Hb-(C7)), 3.87 (d,  $J = 5.1$  Hz, 1H, H-(C2)), 3.75-3.66 (m, 4H, Ha-(C6) + H-(C4)), 3.63-3.51 (m, 2H, Hb-(C6) + H-(C5)), 3.41 (ddd,  $J = 9.6, 5.9, 2.2$  Hz, 1H, H-(C3)).

<sup>13</sup>C NMR (MeOD, 25 °C, 100 MHz):  $\delta_C$  170.4 (CONH), 138.5 (C<sub>quater</sub>Ph), 128.3 (2x Ph), 127.4 (Ph), 127.2 (Ph), 100.4 (C1), 73.9 (C3), 71.0 (C4), 70.2 (C2), 67.1 (C5), 65.8 (C7), 61.4 (C6), 44.8 (C10).

HRMS (ESI<sup>+</sup>) : Calcd for C<sub>15</sub>H<sub>21</sub>NO<sub>7</sub>Na [M + Na]<sup>+</sup>: 350.1216; Found: 350.1214.

### 2-( $\alpha$ -D-Mannopyranosyloxy)-*N*-hexadecyl-acetamide (11r).



The reaction was carried out at 150 °C with 2-( $\alpha$ -D-mannopyranosyloxy)-acetamide (**9d**) (237 mg, 1 mmol) and hexadecylamine (725 mg, 3 mmol, 3 equiv.) in a sealed tube. The pure product 2-( $\alpha$ -D-Mannopyranosyloxy)-*N*-hexadecyl-acetamide was obtained as a white solid (319 mg, 69%, m.p. 163°C).

R<sub>f</sub>=0.58 (CH<sub>2</sub>Cl<sub>2</sub> : MeOH, 9:1).

$[\alpha]_{589}^{25} = -36.8$ , ( $c = 1.0$ , CH<sub>3</sub>OH).

IR (film)  $\nu$  max/cm<sup>-1</sup>: 3410, 2918, 2851, 2357, 1655, 1622, 1553, 1470, 1433, 1375, 1325, 1263, 1213, 1142, 1098, 1071, 966, 883, 818, 721.

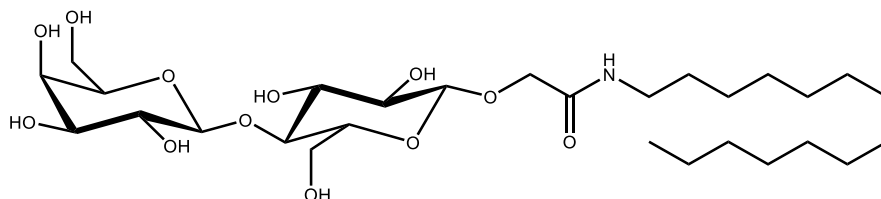
<sup>1</sup>H NMR (CD<sub>3</sub>OD, 25 °C, 400 MHz):  $\delta_H$  4.70 (d,  $J = 1.5$  Hz, 1H, H-(C1)), 4.05 (d,  $J = 15.1$  Hz, 1H, Ha-(C7)), 3.91 (d,  $J = 15.1$  Hz, 1H, Hb-(C7)), 3.86 (dd,  $J = 3.4, 1.7$  Hz, 1H, H-(C2)), 3.74 (dd,  $J = 11.8, 2.2$  Hz, 1H, Ha-(C6)), 3.67 (dd,  $J = 9.3, 3.4$  Hz, 1H, H-(C3)), 3.60 (dd,  $J =$

11.8, 6.0 Hz, 1H, Hb-(C6)), 3.52 (t,  $J = 9.6$  Hz, 1H, H-(C4)), 3.43-3.36 (m, 1H, H-(C5)), 1.49-1.37 (m, 2H, NHCH<sub>2</sub>), 1.21 (m, 28H, 14x CH<sub>2</sub>), 0.85-0.75 (m, 3H, CH<sub>3</sub>).

<sup>13</sup>C NMR (DMSO, 25 °C, 101 MHz):  $\delta_C$  168.8 (CONH), 100.2 (C1), 74.8 (C3), 71.2 (C4), 70.2 (C2), 67.5 (C5), 65.8 (C7), 61.7 (C6), 42.1 (NHCH<sub>2</sub>), 38.9 (CH), 38.7 (CH), 33.7 (CH), 31.8 (CH), 29.5 (5x CH), 29.3 (CH), 29.2 (CH), 26.9 (CH), 23.1 (CH), 22.6 (CH<sub>2</sub>CH<sub>3</sub>), 14.4 (CH<sub>3</sub>).

HRMS (ESI<sup>+</sup>) : Calcd for C<sub>24</sub>H<sub>47</sub>NO<sub>7</sub>Na [M + Na]<sup>+</sup>: 484.3250; Found: 484.3250.

## 2-( $\beta$ -D-Cellobiosyloxy)-*N*-tetradecyl-acetamide (1).



The reaction was carried out with at 150 °C with 2-( $\beta$ -D-lactosyloxy)-acetamide (**9f**) (399 mg, 1 mmol) and tetradecylamine (640 mg, 3 mmol, 3 equiv.) in a sealed tube. The 2-( $\beta$ -D-lactosyloxy)-*N*-hexadecyl-acetamide was obtained as a white solid (471 mg, 79%, m.p. 164 °C).

R<sub>f</sub>=0.33 (CH<sub>2</sub>Cl<sub>2</sub> : MeOH, 7:3).

$[\alpha]_{589}^{25} = +28.000$ , ( $c = 0.5$ , DMSO).

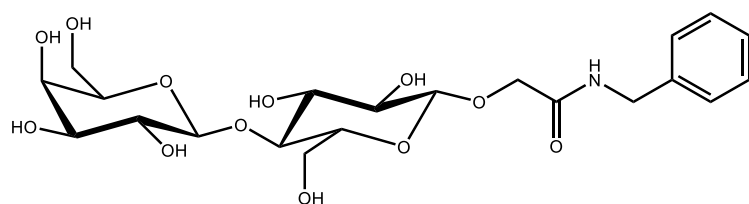
IR (film)  $\nu$  max/cm<sup>-1</sup>: 3350, 2922, 2853, 2344, 1724, 1643, 1557, 1466, 1410, 1373, 1343, 1263, 1074, 893, 781, 725.

<sup>1</sup>H NMR (CD<sub>3</sub>OD, 25 °C, 400 MHz):  $\delta_H$  4.37 (t,  $J=7.4$  Hz, 2H, H-(C1') + H-(C1)), 4.30 (d,  $J=15.7$  Hz, 1H, Ha-(C7)), 4.14 (d,  $J=15.7$  Hz, 1H, Hb-(C7)), 3.95-3.85 (m, 2H, Ha-(C6) + Hb-(C6)), 3.84 (d,  $J=3.2$  Hz, 1H, H-(C5) or H-(C5')), 3.82-3.77 (m, 1H, Ha-(C6')), 3.72 (dd,  $J=11.4$ , 4.6 Hz, 1H, Hb-(C6')), 3.66-3.53 (m, 4H, H-(C2',C3,C3') and H-(C5) or H-(C5')), 3.50 (dd,  $J=9.7$ , 3.2 Hz, 1H, H-(C4)), 3.46 (dt,  $J=9.7$ , 3.2 Hz, 1H, H-(C4')), 3.37 (t,  $J=4.0$  Hz, 1H, H-(C2)), 1.60-1.51 (m, 2H, CH<sub>2</sub>-NH), 1.33 (s, 24H, 12x CH<sub>2</sub>), 0.95-0.89 (m, 3H, CH<sub>3</sub>).

<sup>13</sup>C NMR (CD<sub>3</sub>OD, 25 °C, 100 MHz):  $\delta_C$  170.6 (CONH), 103.7 (C1'), 103.1 (C1), 78.9 (CH), 75.7 (CH), 75.3 (CH), 74.8 (CH), 73.4 (CH), 73.2 (CH), 71.2 (CH), 68.9 (CH), 68.0 (C7), 61.1 (C6'), 60.3 (C6), 38.7 (NHCH<sub>2</sub>), 31.7 (CH<sub>2</sub>), 29.4 (5x CH<sub>2</sub>), 29.3 (CH<sub>2</sub>), 29.1 (CH<sub>2</sub>), 29.0 (2x CH<sub>2</sub>), 26.6 (CH<sub>2</sub>), 22.3 (CH<sub>2</sub>), 13.0 (CH<sub>3</sub>).

HRMS (ESI<sup>+</sup>) : Calcd for C<sub>28</sub>H<sub>53</sub>NO<sub>12</sub>Na [M + Na]<sup>+</sup>: 618.3465; Found: 618.3478.

### 2-( $\beta$ -D-Lactosyloxy)-*N*-(phenylmethyl)-acetamide (**11s**).



The reaction was carried out with at 150 °C with 2-( $\beta$ -D-lactosyloxy)-acetamide (**9f**) (399 mg, 1 mmol) and benzylamine (321 mg, 3 mmol, 3 equiv.) in a sealed tube. The 2-( $\beta$ -D-lactosyloxy)-*N*-(phenylmethyl)-acetamide was obtained as a white solid (333 mg, 68%, m.p. 178 °C).

$R_f$ =0.38 (CH<sub>2</sub>Cl<sub>2</sub> : MeOH, 7:3).

$[\alpha]_{589}^{25} = +16,500.1$ , ( $c = 0.2$ , DMSO).

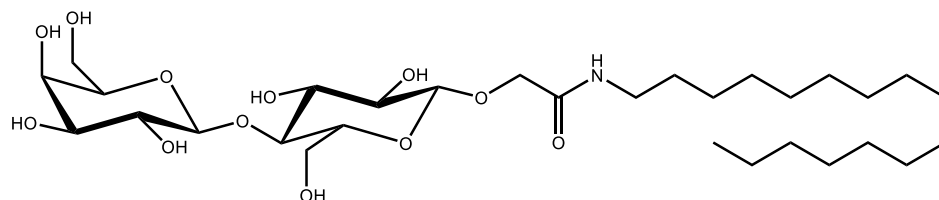
IR (film)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3341, 1722, 1659, 1551, 1454, 1343, 1271, 1157, 1074, 989, 893, 781, 758, 727.

<sup>1</sup>H NMR (D<sub>2</sub>O, 25 °C, 400 MHz):  $\delta_H$  4.43 (d,  $J = 7.9$  Hz, 1H, H-(C1')), 4.41 (d,  $J = 15.2$  Hz, 1H, Ha-(C9)), 4.35 (d,  $J = 7.8$  Hz, 1H, H-(C1)), 4.34 (d,  $J = 15.4$  Hz, 1H, Hb-(C9)), 4.32 (d,  $J = 16.2$  Hz, 1H, Ha-(C7)), 4.23 (d,  $J = 15.7$  Hz, 1H, Hb-(C7)), 3.82 (dd,  $J = 11.2, 2.7$  Hz, 2H, Ha-(C6)), 3.72-3.60 (m, 4H, Hb-(C6) + 2x  $\underline{\text{CH}}$ ), 3.60-3.53 (m, 3H, H-(C3) + 2x  $\underline{\text{CH}}$ ), 3.51-3.43 (m, 2H, 2x  $\underline{\text{CH}}$ ), 3.36-3.29 (m, 1H, H-(C2 or 2')).

<sup>13</sup>C NMR (D<sub>2</sub>O, 25 °C, 100 MHz):  $\delta_C$  171.9 ( $\underline{\text{CONH}}$ ), 141.1 (C<sub>quater</sub> Ph), 128.8 (Ph), 127.5 (Ph), 127.3 (Ph), 102.9 (C1), 102.5 (C1), 78.1 (CH), 75.3 (CH), 74.8 (CH), 74.1 (CH), 72.7 (CH), 72.5 (CH), 70.9 (CH), 68.5 (CH), 68.3 (C7), 61.0 (C6'), 59.9 (C6), 42.6 (C-10).

HRMS (ESI<sup>+</sup>) : Calcd for C<sub>21</sub>H<sub>31</sub>NO<sub>12</sub>Na [ $\text{M} + \text{Na}$ ]<sup>+</sup>: 512.1744; Found: 512.1753.

### 2-( $\beta$ -D-Cellobiosyloxy)-*N*-hexadecyl-acetamide (**11t**).



The reaction was carried out with at 150 °C with 2-( $\beta$ -D-lactosyloxy)-acetamide (**9f**) (399 mg, 1 mmol) and hexadecylamine (725 mg, 3 mmol, 3 equiv.) in a sealed tube. The 2-( $\beta$ -D-



lactosyloxy)-*N*-hexadecyl-acetamide was obtained as a white solid (443 mg, 71%, m.p. 184 °C).

$R_f=0.39$  ( $\text{CH}_2\text{Cl}_2$  : MeOH, 7:3).

$[\alpha]_{589}^{25} = +110.0$ , ( $c = 0.1$ , DMSO).

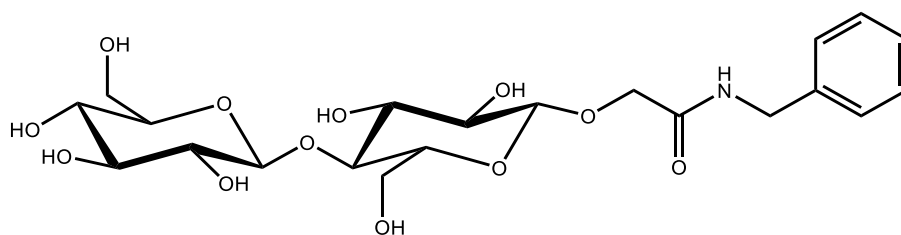
IR (film)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3358, 2920, 2853, 1722, 1645, 1555, 1466, 1410, 1373, 1341, 1261, 1094, 893, 876, 727.

$^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ , 25 °C, 400 MHz):  $\delta_H$  4.37 (t,  $J=7.4$  Hz, 2H, H-(C1') + H-(C1)), 4.30 (d,  $J=15.7$  Hz, 1H, Ha-(C7)), 4.14 (d,  $J=15.7$  Hz, 1H, Hb-(C7)), 3.94-3.85 (m, 2H, Ha-(C6) + Hb-(C6)), 3.83 (d,  $J=3.2$  Hz, 1H, H-(C5 or C5')), 3.82-3.77 (m, 1H, Ha-(C6')), 3.72 (dd,  $J=11.4$ , 4.6 Hz, 1H, Hb-(C6')), 3.65-3.53 (m, 4H, H-(C2', C3, C3') and H-(C5 or C5')), 3.50 (dd,  $J=9.7$ , 3.2 Hz, 1H, H-(C4)), 3.48-3.35 (dt,  $J=9.7$ , 3.2 Hz, 1H, H-(C4')), 3.39-3.35 (m, 1H, H-(C2)), 1.61-1.51 (m, 2H,  $\underline{\text{CH}_2\text{-NH}}$ ), 1.31 (s, 28H, 14x  $\underline{\text{CH}_2}$ ), 0.92 (t,  $J=6.8$  Hz, 3H,  $\underline{\text{CH}_3}$ ).

$^{13}\text{C}$  NMR ( $\text{CD}_3\text{OD}$ , 25 °C, 100 MHz):  $\delta_C$  170.6 ( $\underline{\text{CONH}}$ ), 103.7 (C1'), 103.1 (C1), 78.9 (CH), 75.5 (CH), 75.3 (CH), 74.8 (CH), 73.4 (CH), 73.2 (CH), 71.1 (CH), 68.9 (CH), 68.0 (C7), 61.1 (C6'), 60.3 (C6), 38.7 ( $\text{NH}\underline{\text{CH}_2}$ ), 31.7 ( $\underline{\text{CH}_2}$ ), 29.4 (7x  $\underline{\text{CH}_2}$ ), 29.3 ( $\underline{\text{CH}_2}$ ), 29.1 ( $\underline{\text{CH}_2}$ ), 29.0 ( $\underline{\text{CH}_2}$ ), 29.0 ( $\underline{\text{CH}_2}$ ), 26.6 ( $\underline{\text{CH}_2}$ ), 22.3 ( $\underline{\text{CH}_2}$ ), 13.0 ( $\underline{\text{CH}_3}$ ).

HRMS (ESI<sup>+</sup>) : Calcd for  $\text{C}_{30}\text{H}_{57}\text{NO}_{12}\text{Na}$  [ $\text{M} + \text{Na}$ ]<sup>+</sup>: 646.3778; Found: 646.3784.

### 2-( $\beta$ -D-Cellobiosyloxy)-*N*-(phenylmethyl)-acetamide (11u).



The reaction was carried out with at 150 °C with 2-( $\beta$ -D-cellobiosyloxy)-acetamide (**9e**) (399 mg, 1 mmol) and benzylamine (321 mg, 3 mmol, 3 equiv.) in a sealed tube. The 2-( $\beta$ -D-cellobiosyloxy)-*N*-(phenylmethyl)-acetamide was obtained as a white solid (284 mg, 58%, m.p. 159 °C).

$R_f=0.57$  ( $\text{CH}_2\text{Cl}_2$  : MeOH, 7:3).

$[\alpha]_{589}^{25} = -6,3$  ( $c = 1.0$ , MeOH). Yield: 63%.

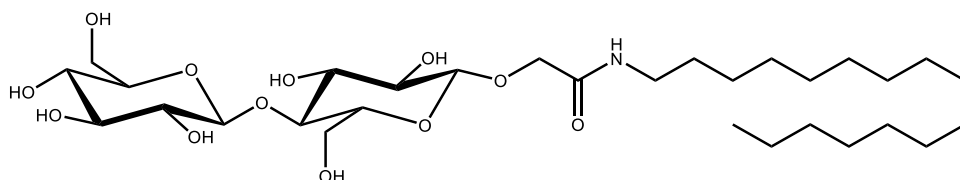
IR (film)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3564, 3350, 3298, 2913, 1663, 1547, 1447, 1352, 1250, 1161, 1082, 1044, 905.

$^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ , 25 °C, 400 MHz):  $\delta_{\text{H}}$  7.27-7.11 (m, 5H), 4.40 (d,  $J=14.9$  Hz, 1H, Ha- $\text{CH}_2\text{-Bn}$ ), 4.33-4.23 (m, 4H, Hb- $\text{CH}_2\text{-Bn}$ , Ha-(C7), H-(C1), H-(C1')), 4.10 (d,  $J=15.7$  Hz, 1H, Hb-(C7), 3.80-3.75 (dd,  $J=12.8, 2.5$  Hz, 1H, Ha-(C6), Ha-(C6')), 3.59-3.52 (m, 1H, Hb-(C6)), 3.50 (d,  $J=8.9$  Hz, 1H, H-(C3) or H-(C3')), 3.46 (d,  $J=5.7$  Hz, 1H, H-(C5) or H-(C5')), 3.42 (d,  $J=8.8$  Hz, 1H, H-(C2) or H-(C2')), 3.33 (dt,  $J=9.4$  Hz, 3.1 Hz, 1H, H-(C4) or H-(C4')), 3.30-3.17 (m, 5H, H-(C3, C4, C5) or H-(C3', C4', C5')), 3.16-3.09 (m, 1H, H-(C2) or H-(C2')).

$^{13}\text{C}$  NMR ( $\text{CD}_3\text{OD}$ , 25 °C, 100 MHz):  $\delta_{\text{C}}$  170.7 ( $\text{CONH}$ ), 138.3 (C-Ph), 128.2 (2xCH Ph), 127.2 (2xCH Ph), 126.9 (CH Ph), 103.2 (C1'), 103.1 (C1), 79.0 (CH), 76.7 (CH), 76.5 (CH), 75.3 (CH), 74.7 (CH), 73.5 (CH), 73.2 (CH), 69.7 (CH), 68.1 (C7), 61.1 (C6), 60.2 (C6'), 45.3 (C9).

HRMS (ESI $^+$ ) : Calcd for  $\text{C}_{21}\text{H}_{31}\text{NO}_{12}\text{Na}^+$  [ $\text{M} + \text{Na}$ ] $^+$ : 512.1744; Found: 512.1738.

### 2-( $\beta$ -D-Cellobiosyloxy)-*N*-hexadecyl-acetamide (11v).



The reaction was carried out with at 150 °C with 2-( $\beta$ -D-cellobiosyloxy)-acetamide (**9e**) (399 mg, 1 mmol) and hexadecylamine (725 mg, 3 mmol, 3 equiv.) in a sealed tube. The 2-( $\beta$ -D-cellobiosyloxy)-*N*-hexadecyl-acetamide was obtained as a white solid (449 mg, 72%, m.p. 176 °C).

$R_f=0.46$  ( $\text{CH}_2\text{Cl}_2$  : MeOH, 7:3).

$[\alpha]_{589}^{25} = -5,9$  ( $c = 1.0$ , MeOH).

IR (film)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3343, 2920, 2851, 2361, 1649, 1562, 1468, 1373, 1263, 1159, 1076, 897, 719.

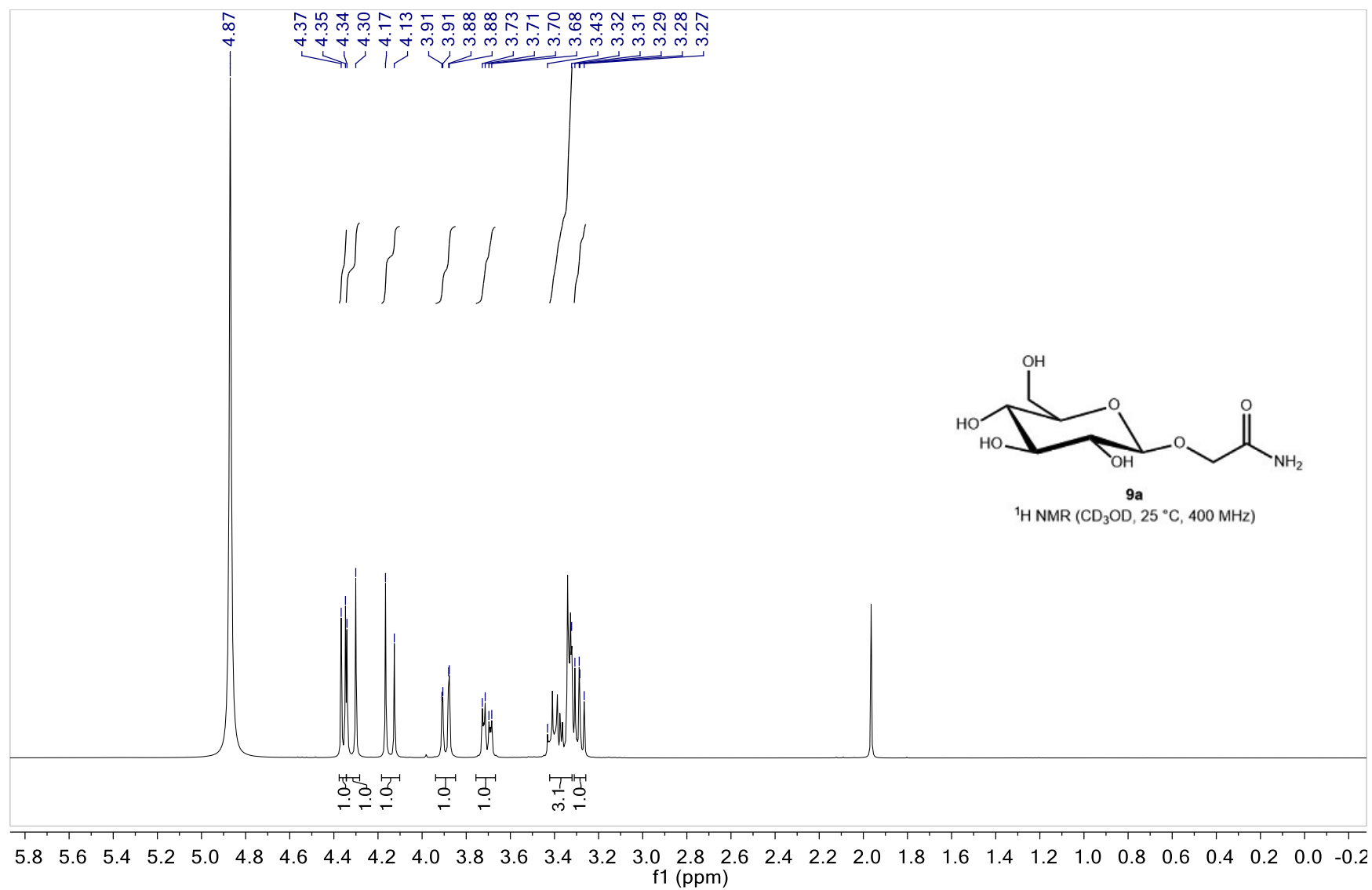
$^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ , 25 °C, 400 MHz):  $\delta_{\text{H}}$  4.31 (d,  $J=7.8$  Hz, 1H, H-(C1')), 4.24 (d,  $J=7.8$  Hz, 1H, H-(C1)), 4.18 (d,  $J=15.7$  Hz, 1H, Ha-(C7)), 4.03 (d,  $J=15.7$  Hz, 1H, Hb-(C7)), 3.82-3.76 (m, 1H, Ha-(C6)), 3.56 (dd,  $J=11.8$  Hz, 5.6 Hz, 1H, Hb-(C6)), 3.51 (d,  $J=8.8$  Hz, 1H, Ha- $\text{CH}_2$ ), 3.47 (d,  $J=5.3$  Hz, 1H, H-(C4) or H-(C4')), 3.43 (d,  $J=8.7$  Hz, 1H, Hb- $\text{CH}_2$ ), 3.33 (dt,  $J=9.3, 3.1$  Hz, 1H, H-(C5) or H-(C5')), 3.30-3.19 (m, 5H, H-(C2, C5, C3),  $\text{CH}_2\text{-NH}$ ), 3.19-3.08 (m, 3H, H-C2', C3', C4'), 1.48-1.39 (m, 2H,  $\text{CH}_2\text{NH}$ ), 1.19 (s, 26H, 14x  $\text{CH}_2$ ), 0.80 (t, 3H,  $\text{CH}_3$ ).

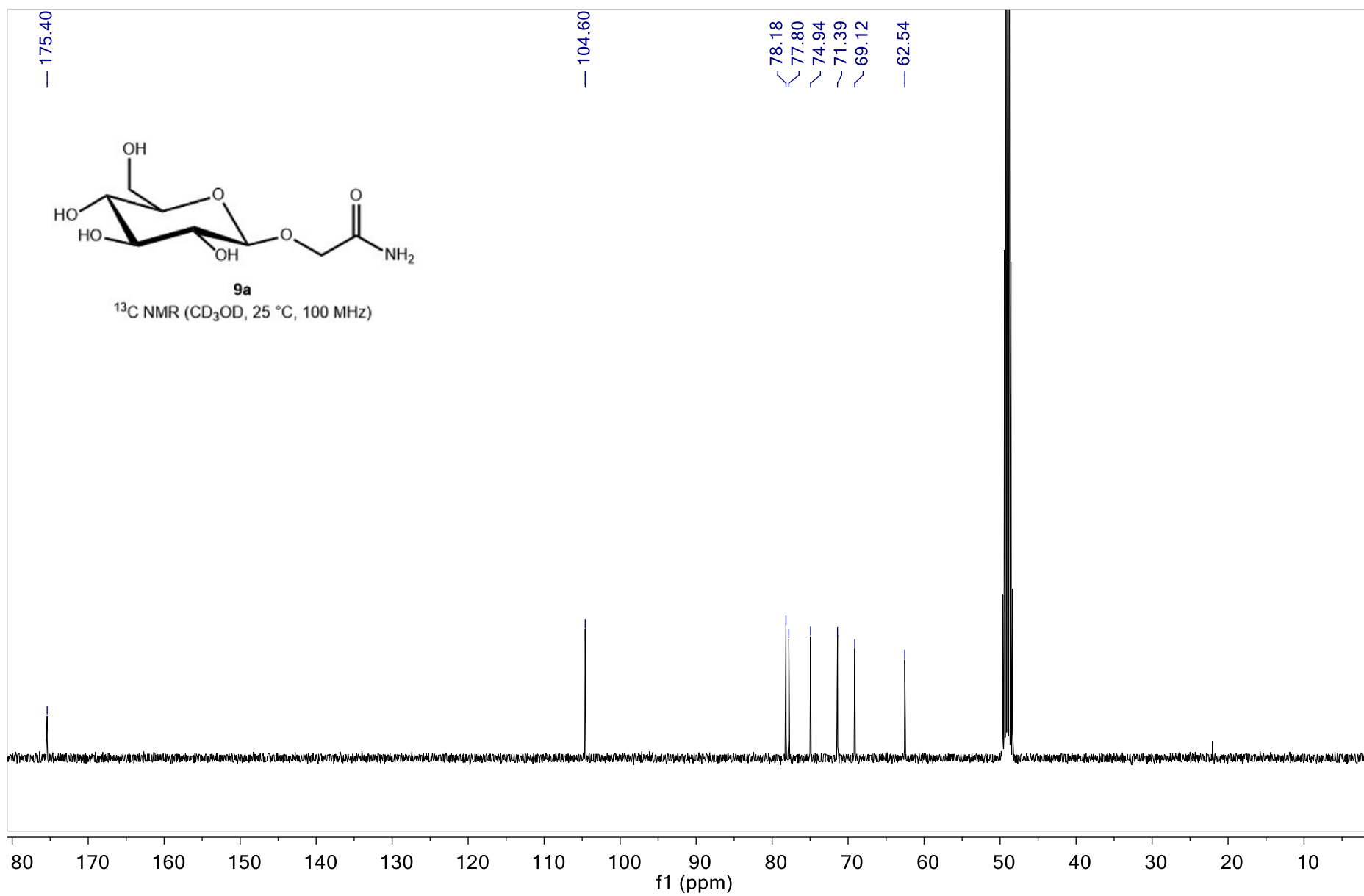
$^{13}\text{C}$  NMR ( $\text{CD}_3\text{OD}$ , 25 °C, 100 MHz):  $\delta_{\text{C}}$  170.6 ( $\text{CONH}$ ), 103.2 (C1'), 103.1 (C1), 79.0 (CH), 76.7 (CH), 76.5 (CH), 75.3 (CH), 74.8 (CH), 73.5 (CH), 73.2 (CH), 70.0 (CH), 68.0 (C7), 61.1 (C6'), 60.2 (C6), 38.7 ( $\text{CH}_2\text{NH}$ ), 31.7 ( $\text{CH}_2$ ), 29.4 (9x  $\text{CH}_2$ ), 29.4 ( $\text{CH}_2$ ), 29.3 ( $\text{CH}_2$ ), 29.1 ( $\text{CH}_2$ ), 29.0 ( $\text{CH}_2$ ), 29.0 ( $\text{CH}_2$ ), 26.6 ( $\text{CH}_2$ ), 13.1 ( $\text{CH}_3$ ).

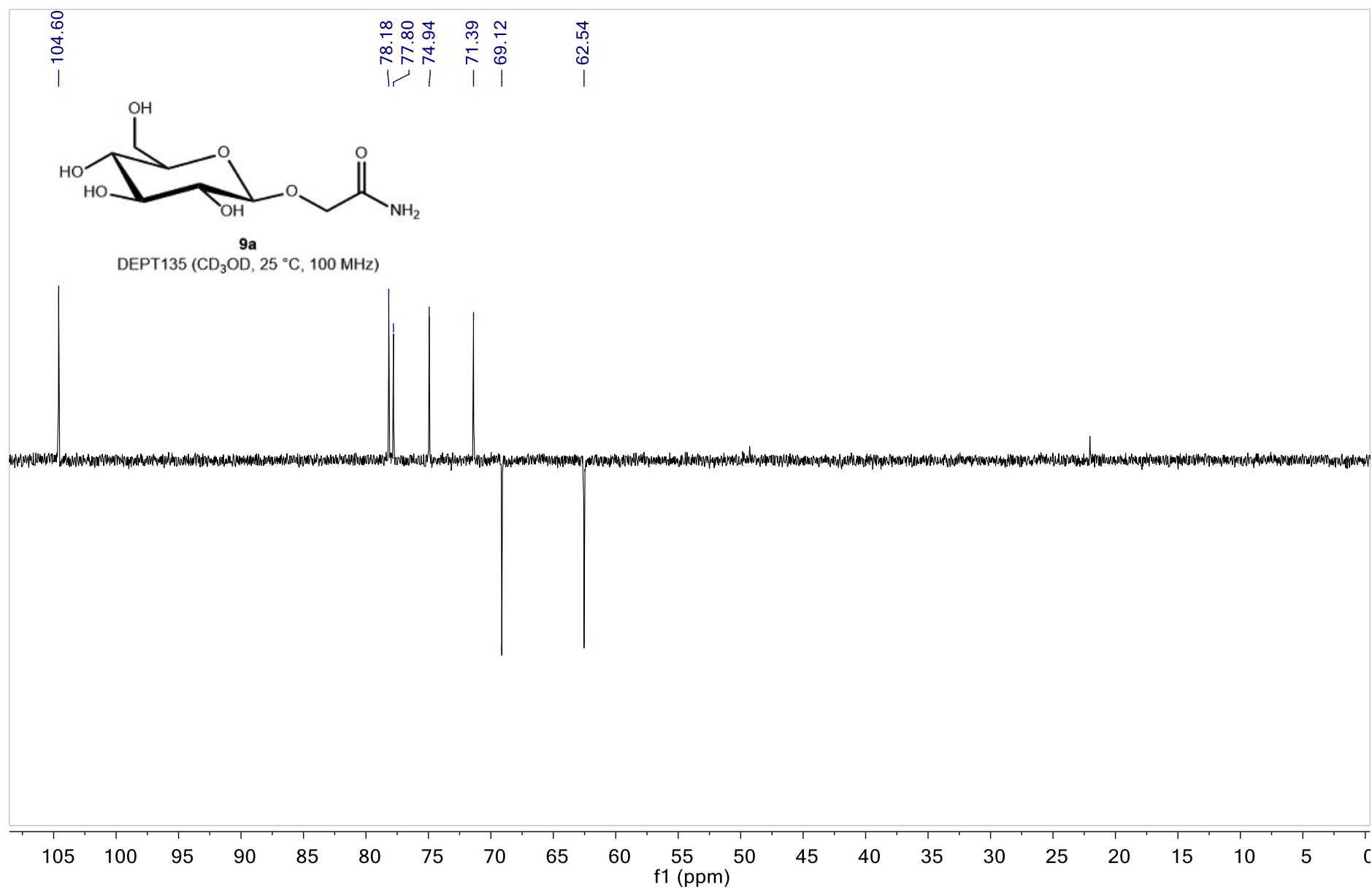
HRMS (ESI<sup>+</sup>) : Calcd for C<sub>30</sub>H<sub>57</sub>NO<sub>12</sub>Na<sup>+</sup> [M + Na]<sup>+</sup>: 646.3778; Found: 646.3779.

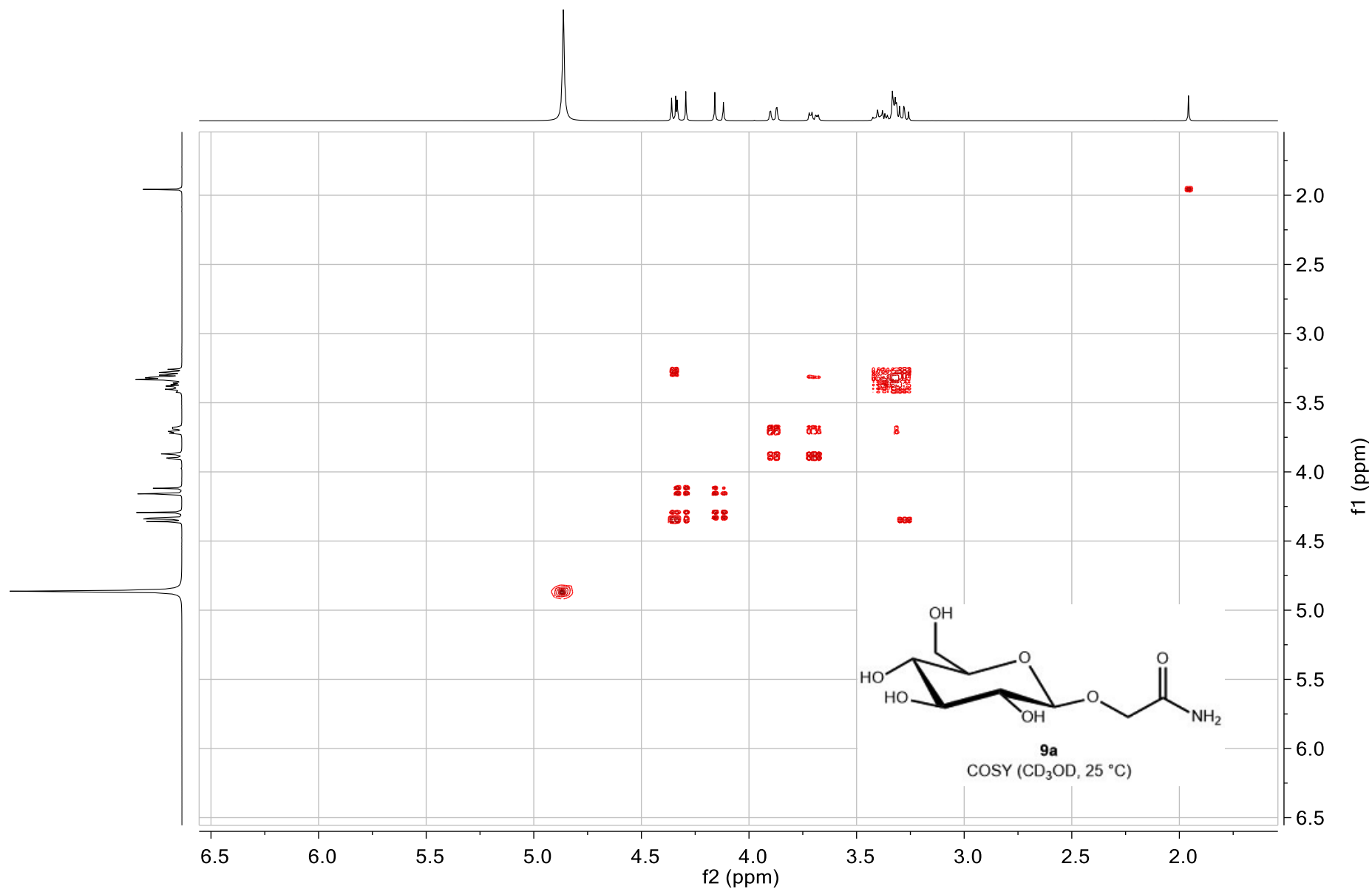
### **III. NMR spectra of synthesized compounds**

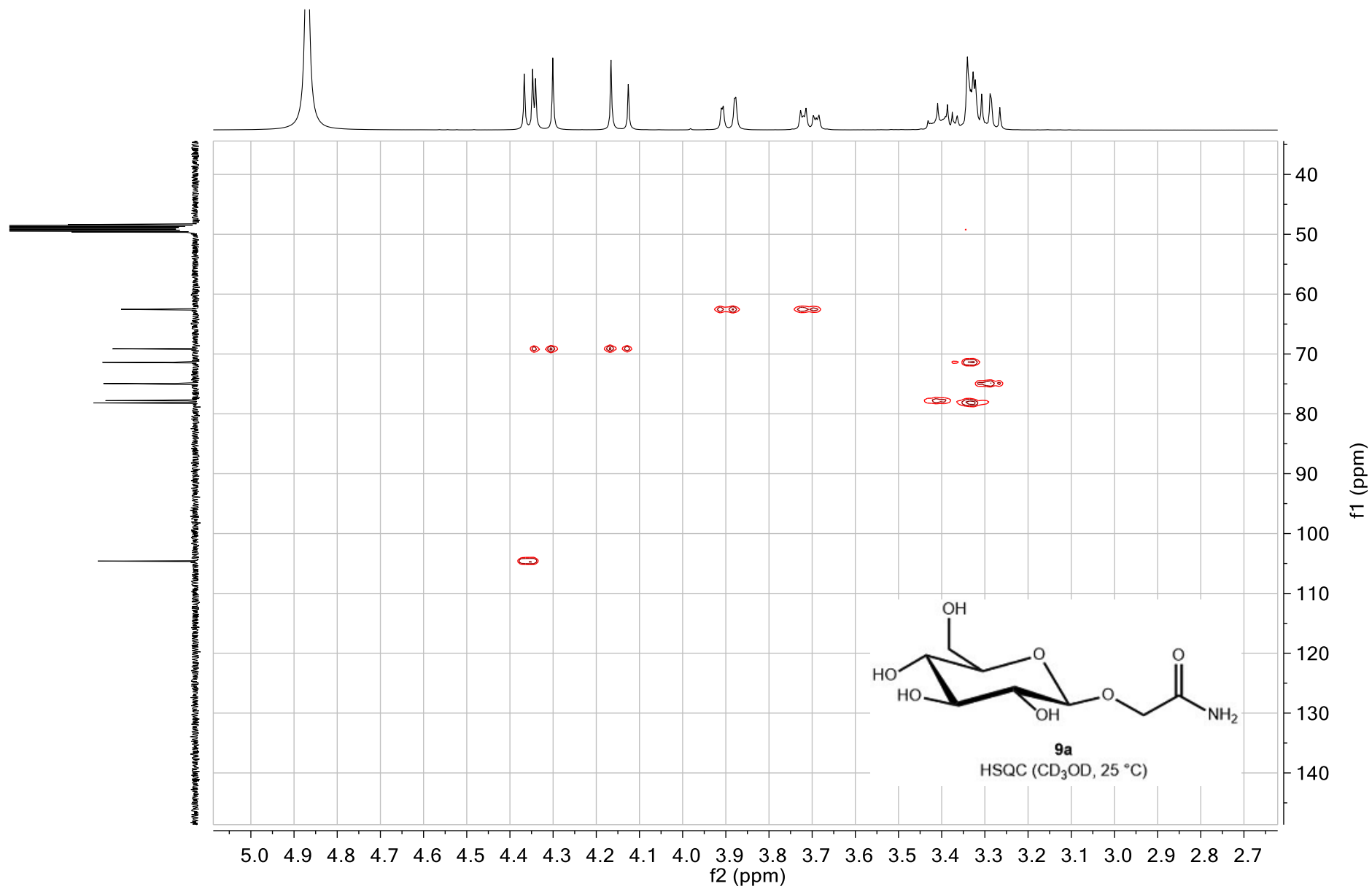
2-( $\beta$ -D-Glucopyranosyloxy)-acetamide (9a).





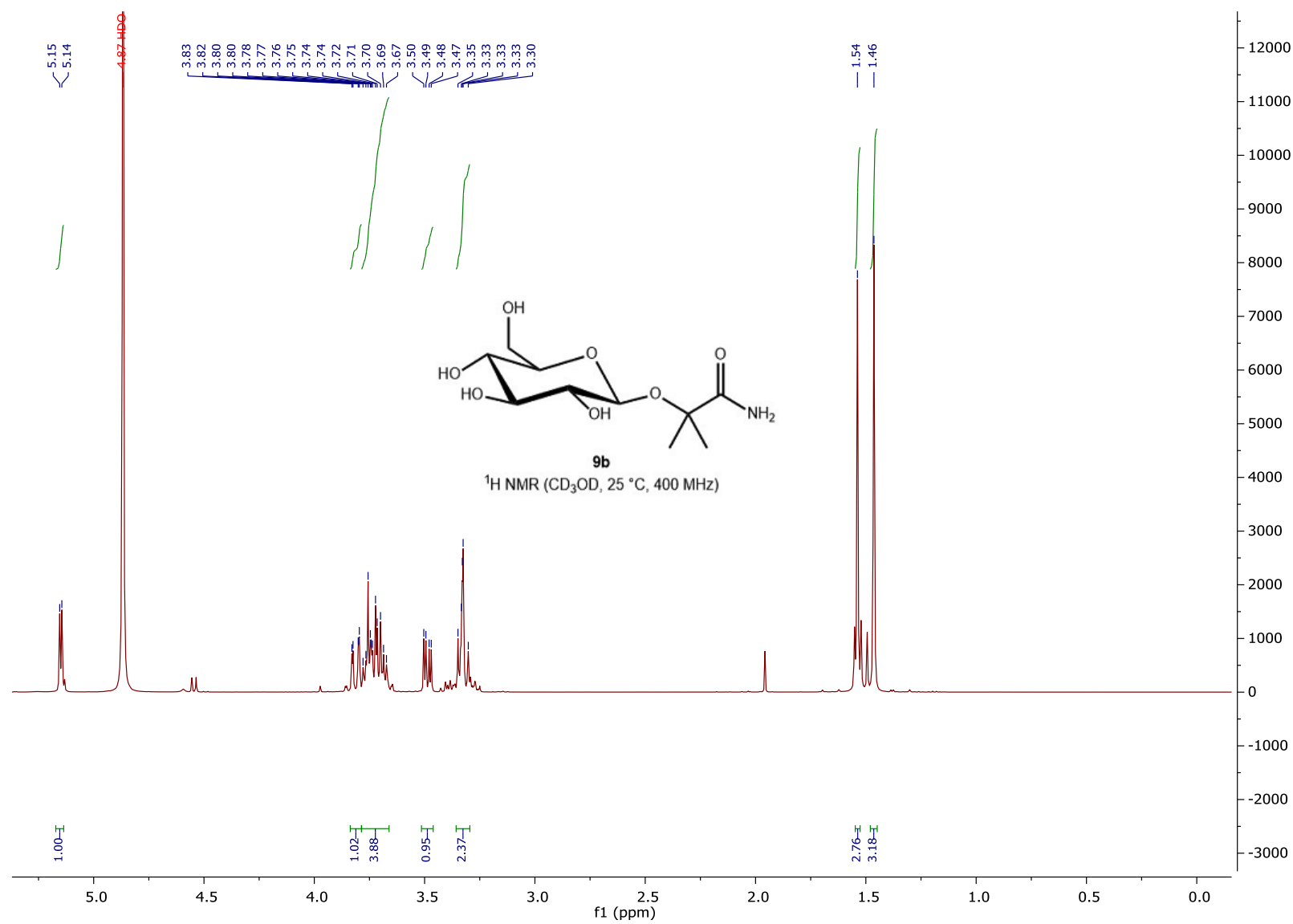


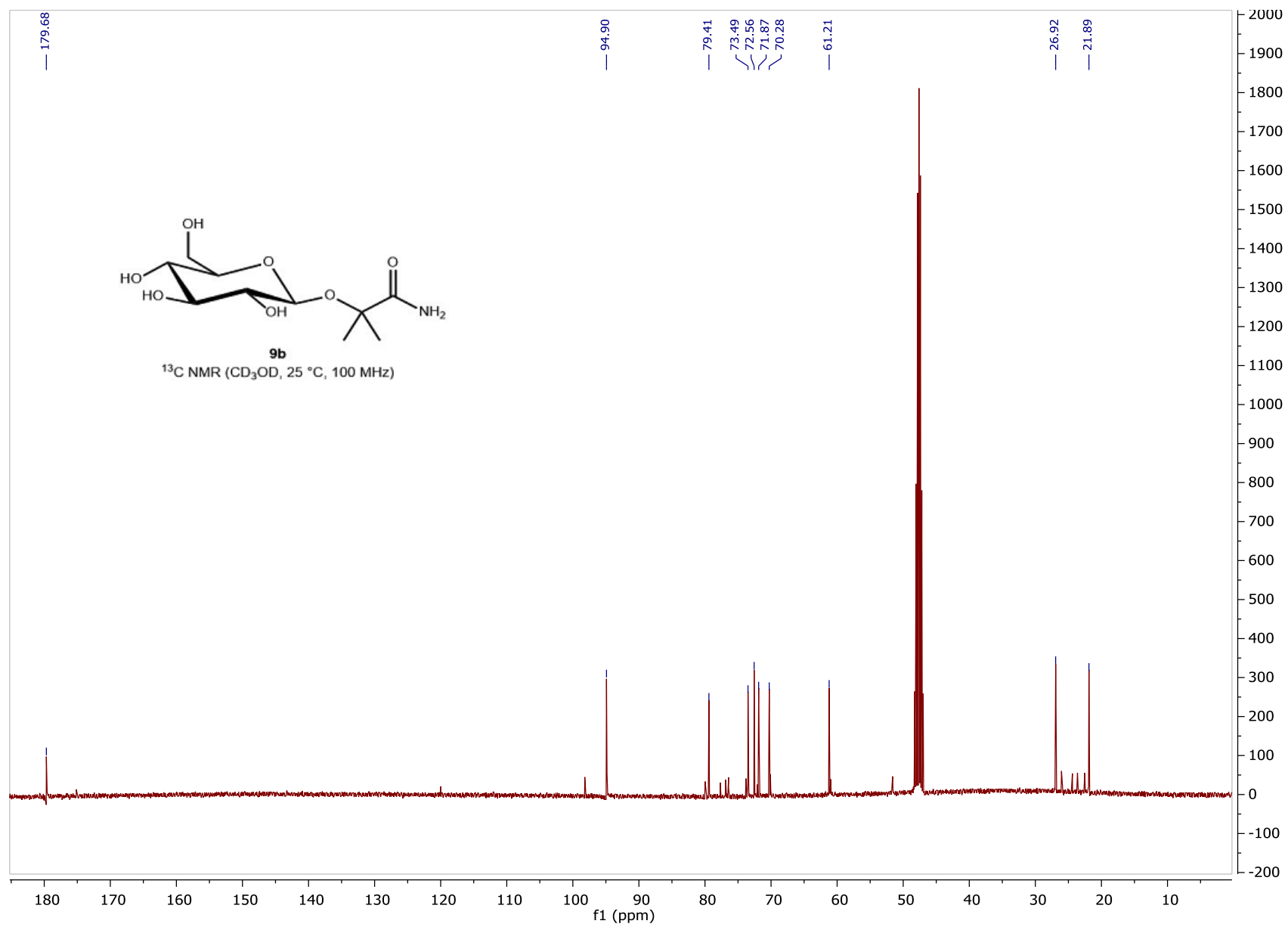


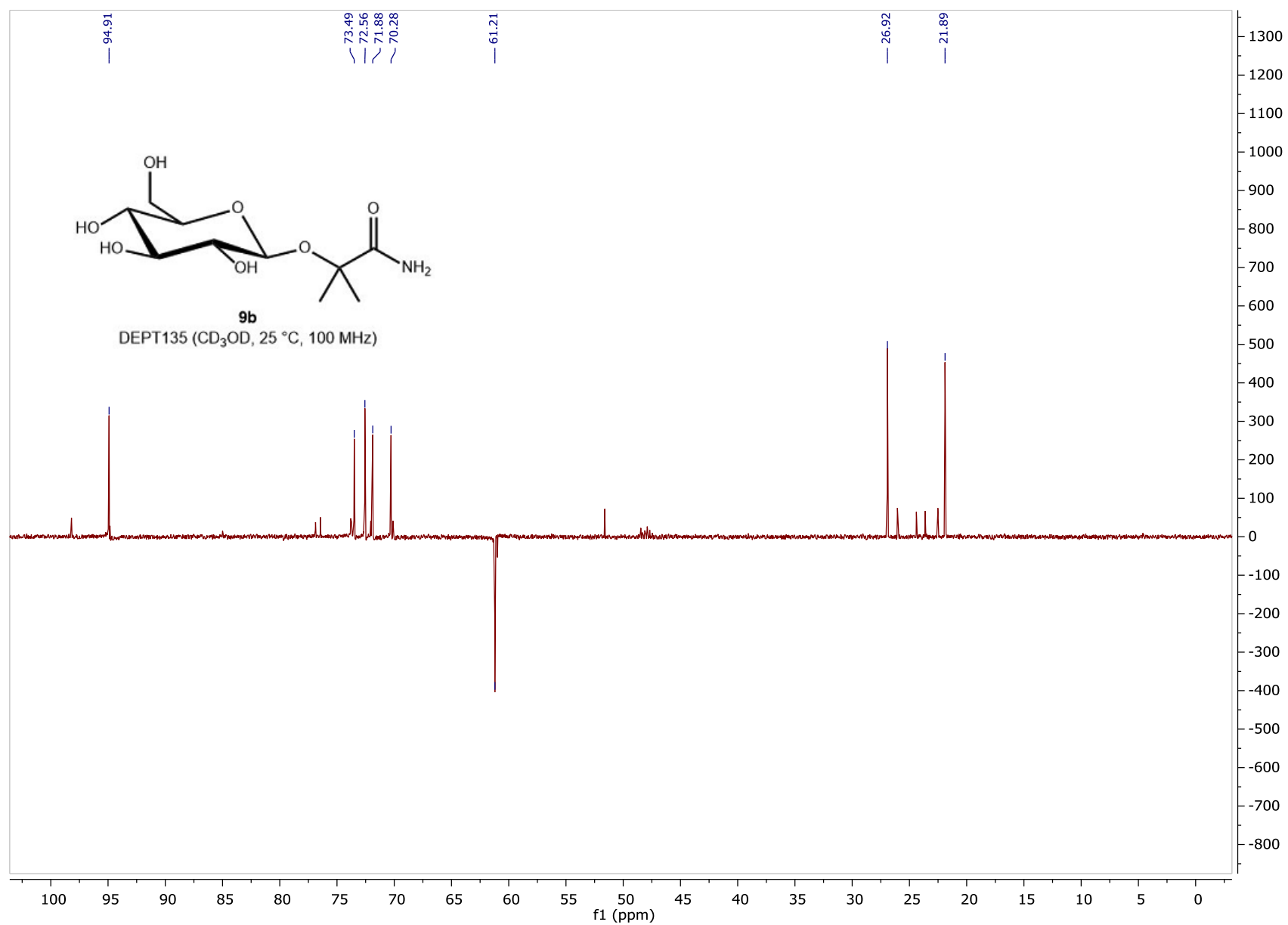




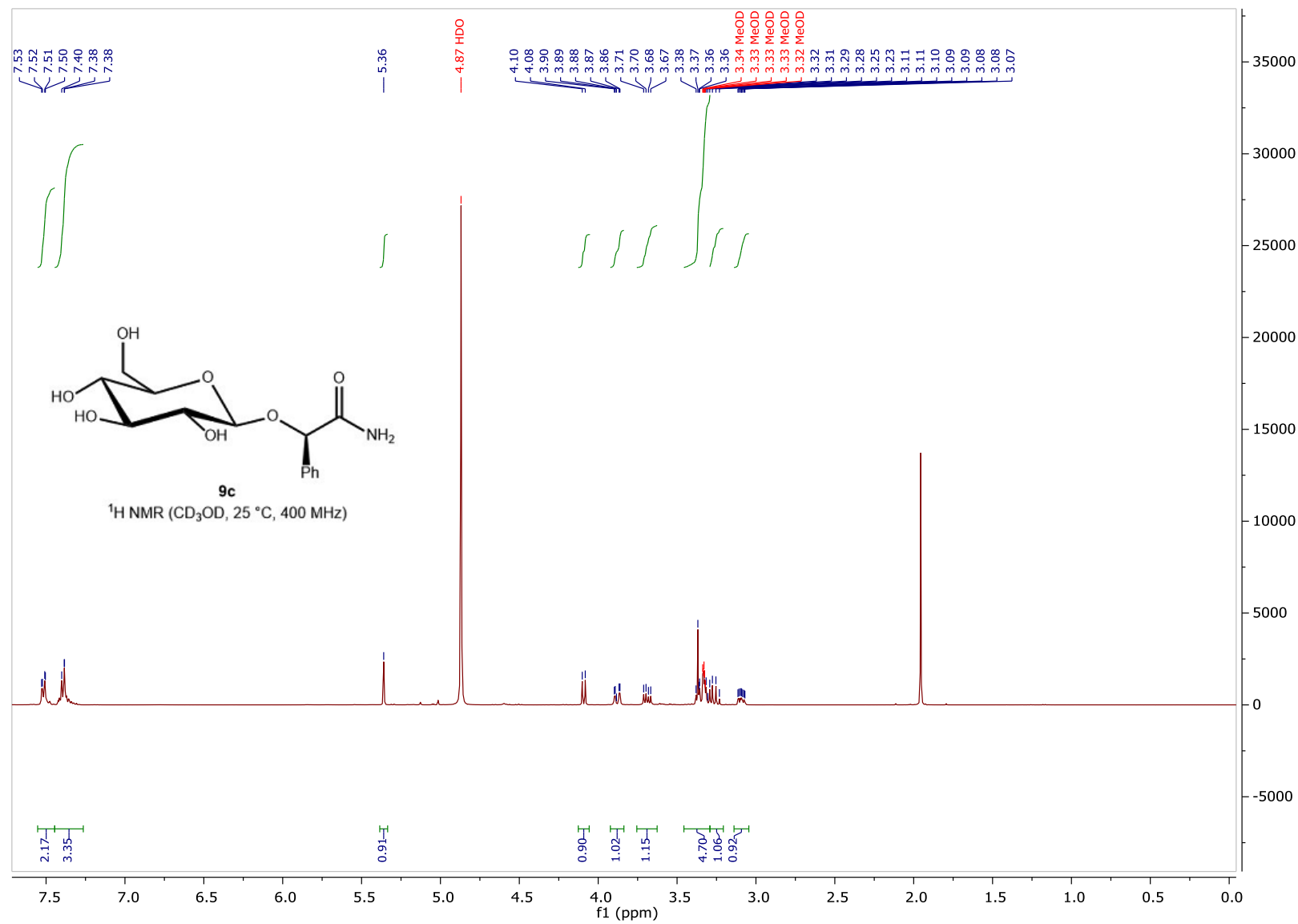
**2-( $\beta$ -D-Glucopyranosyloxy)-2-methyl-propanamide (9b).**

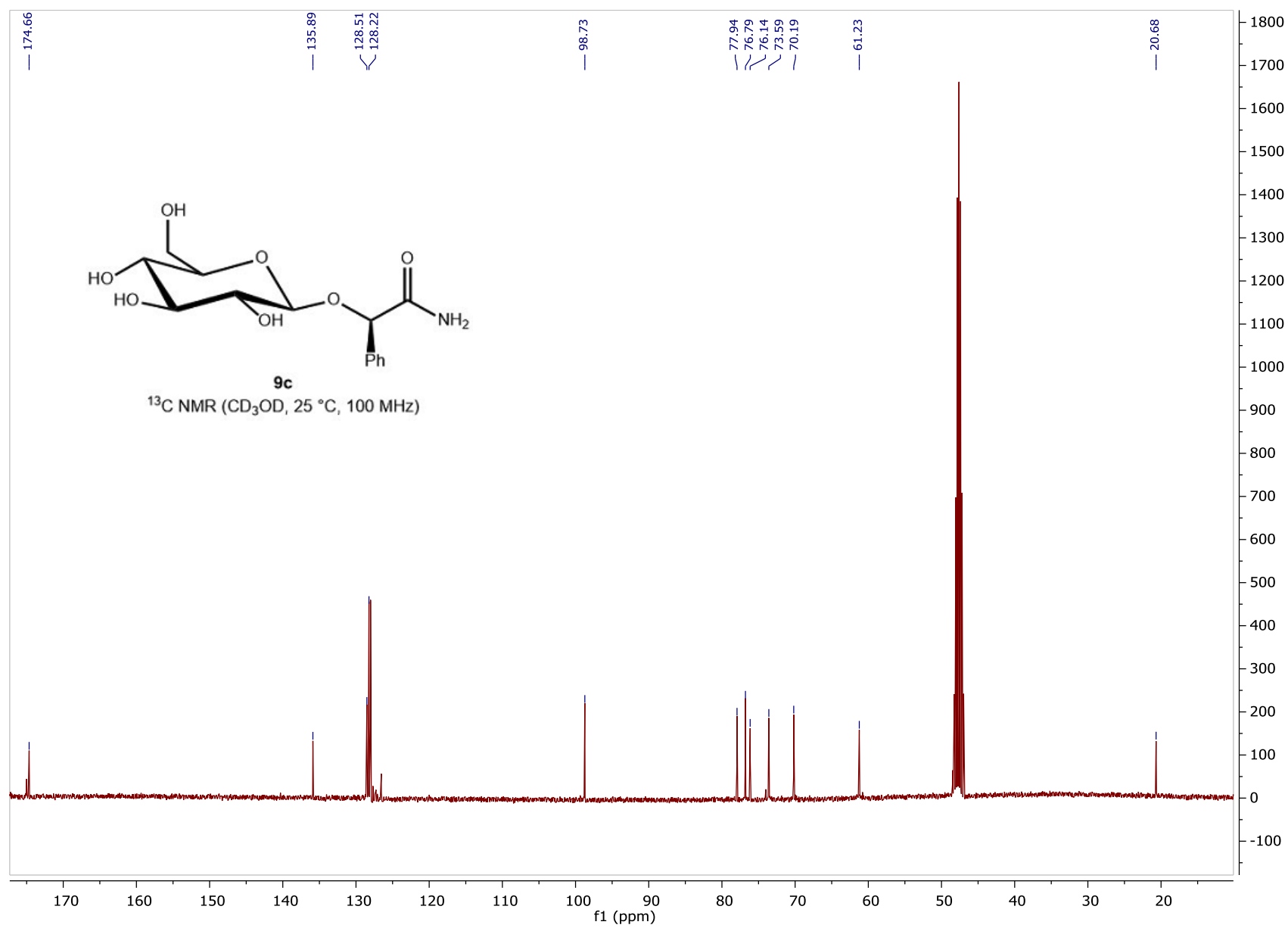


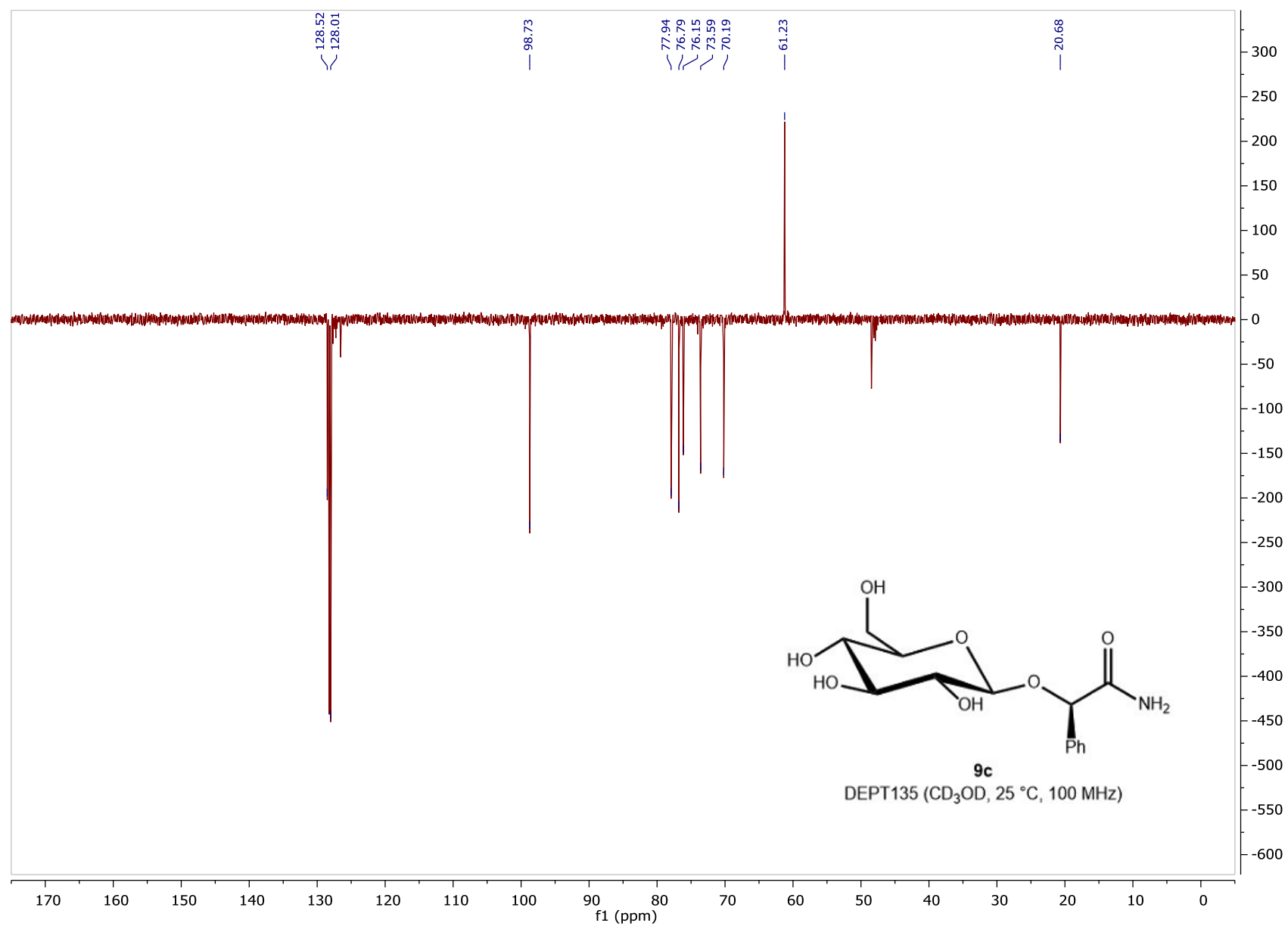




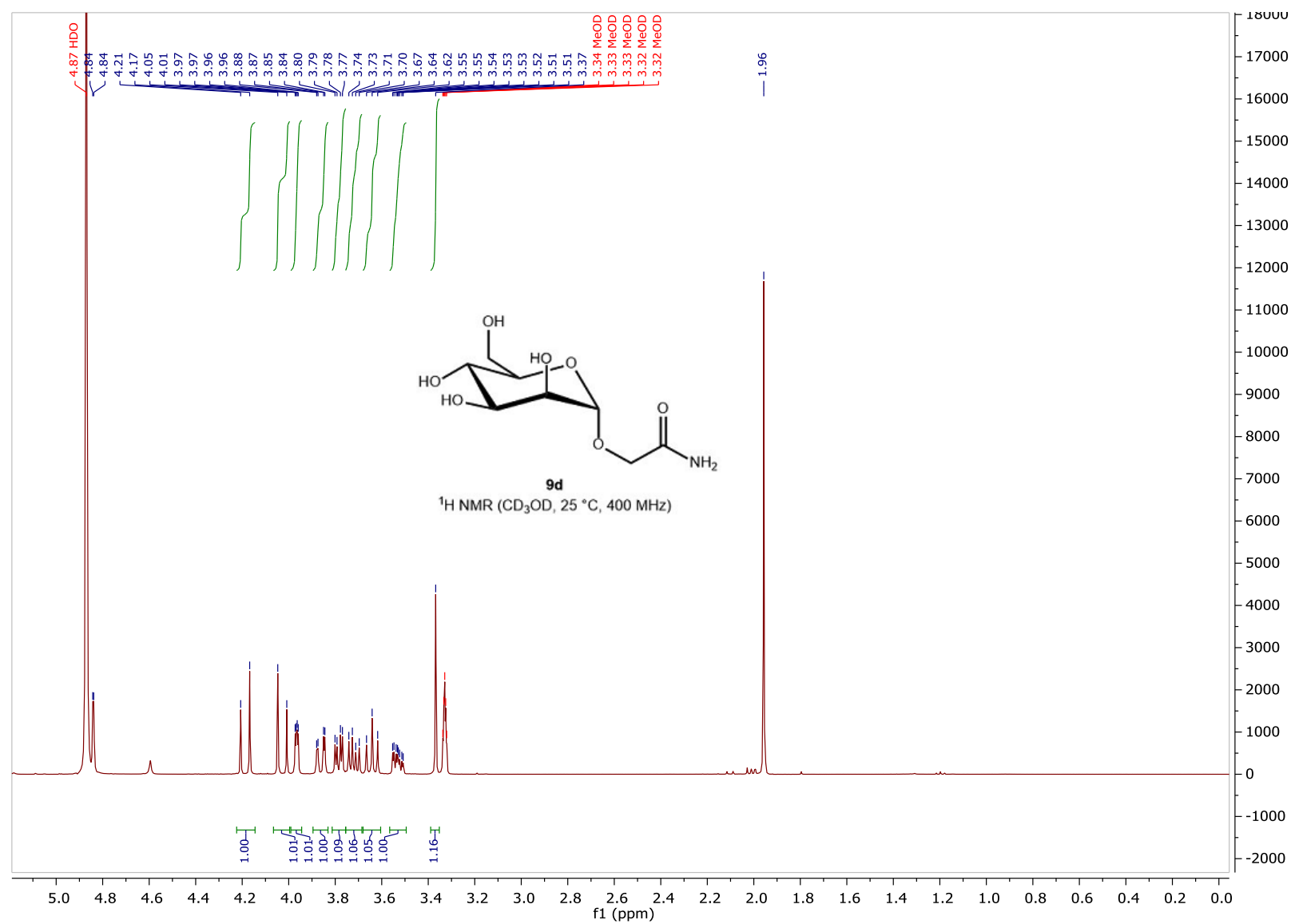
**(R)- $\alpha$ -( $\beta$ -D-Glucopyranosyloxy)phenylacetamide (9c).**

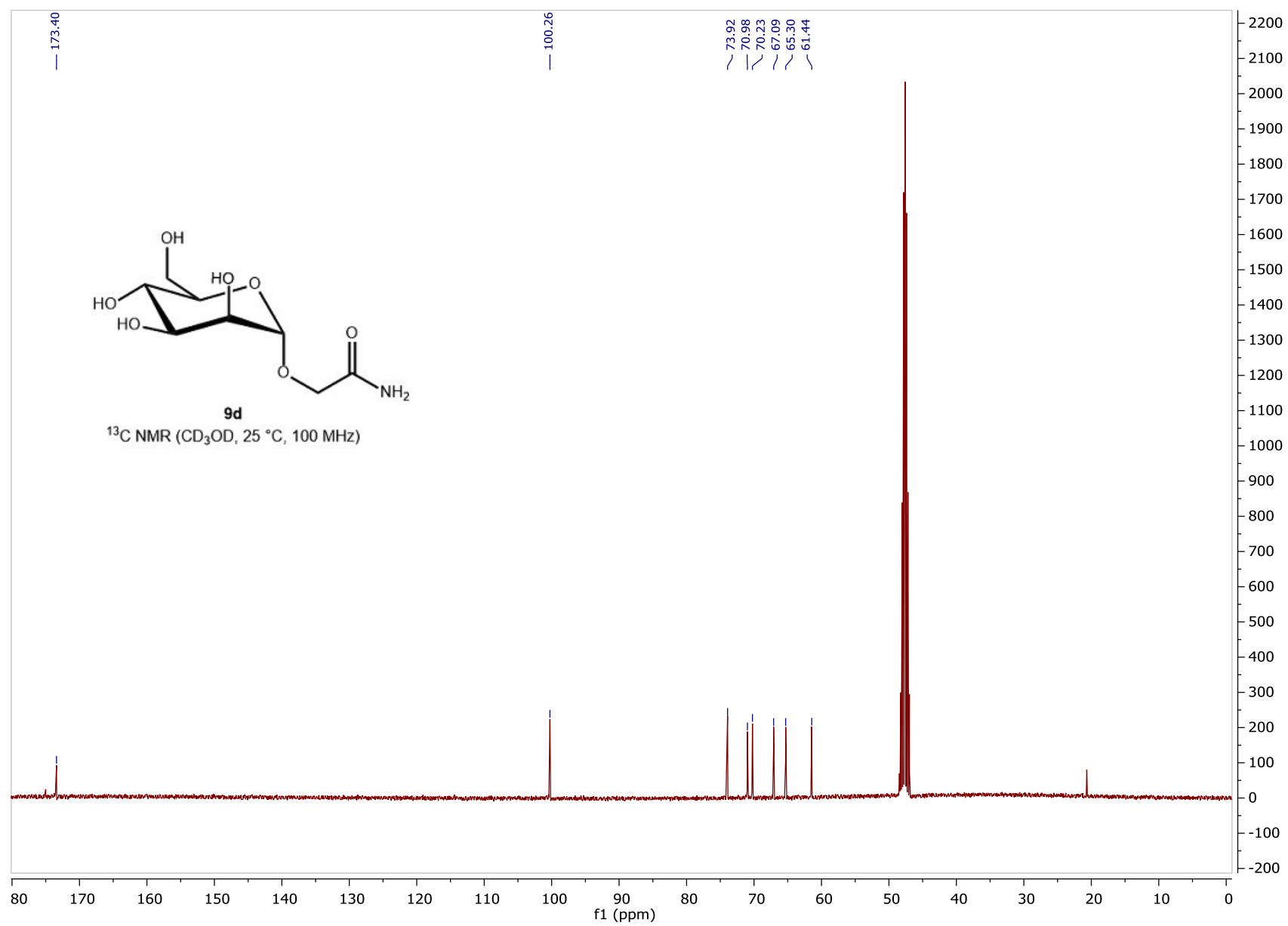




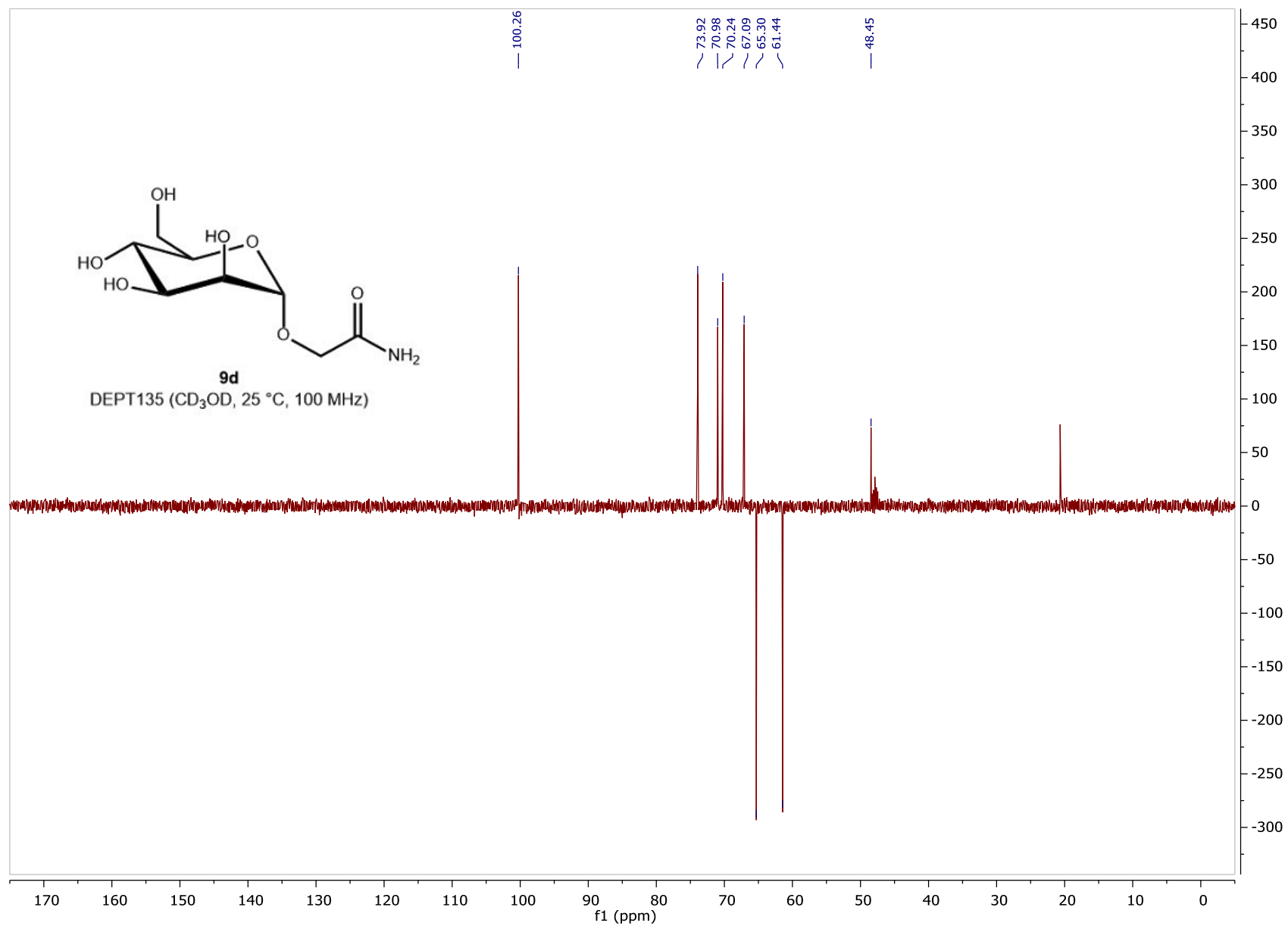


2-( $\alpha$ -D-Mannopyranosyloxy)-acetamide (9d).

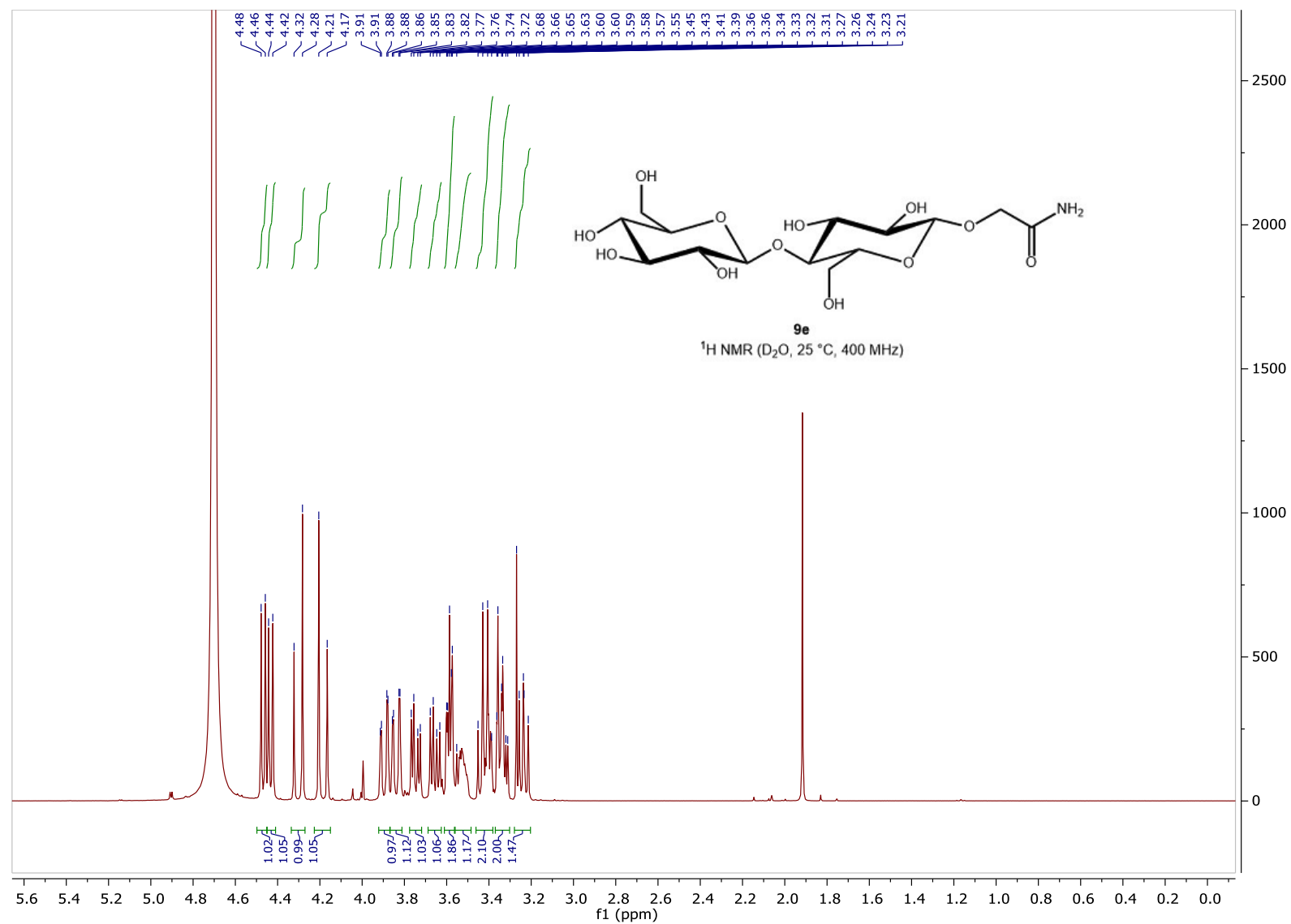


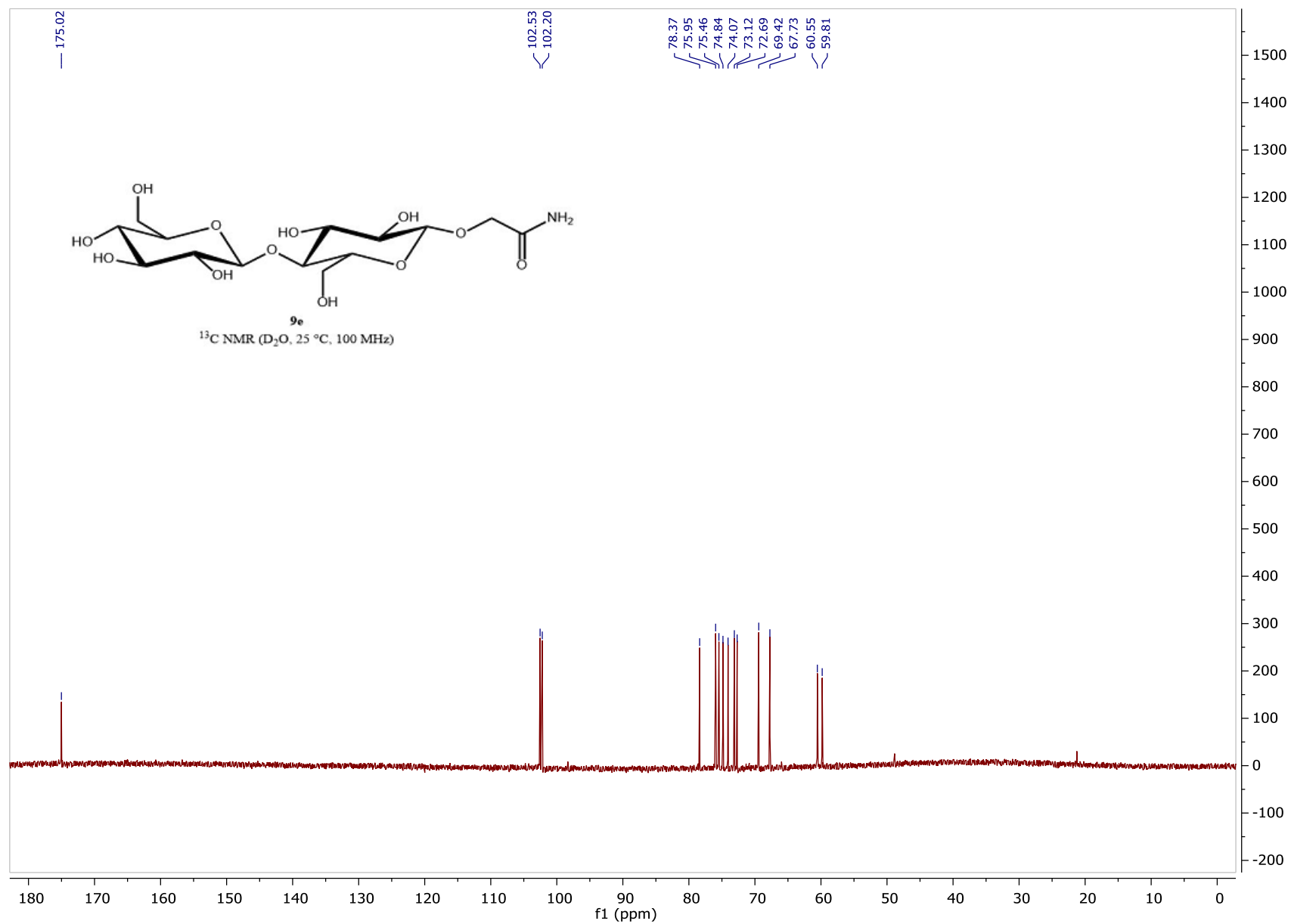


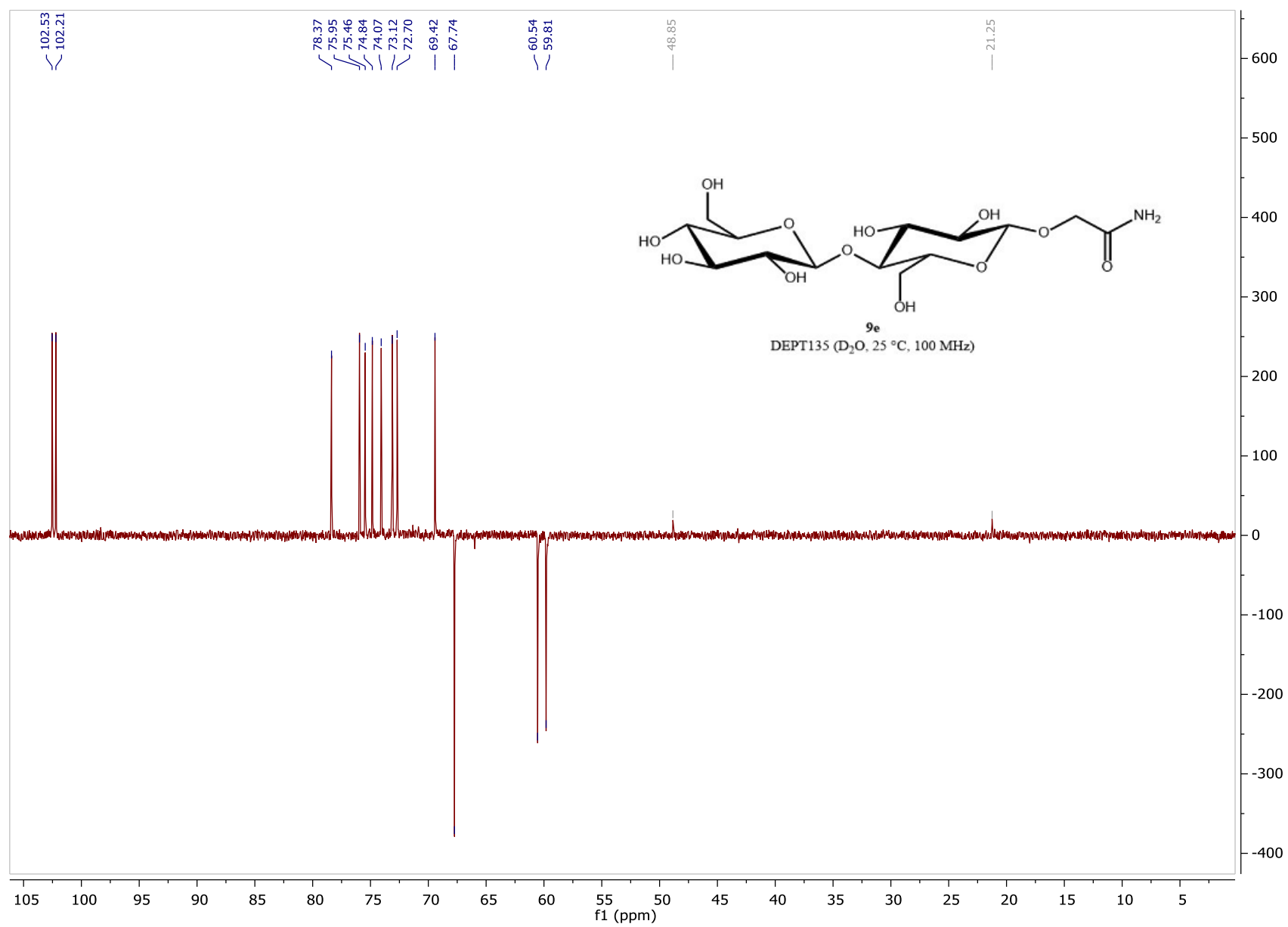




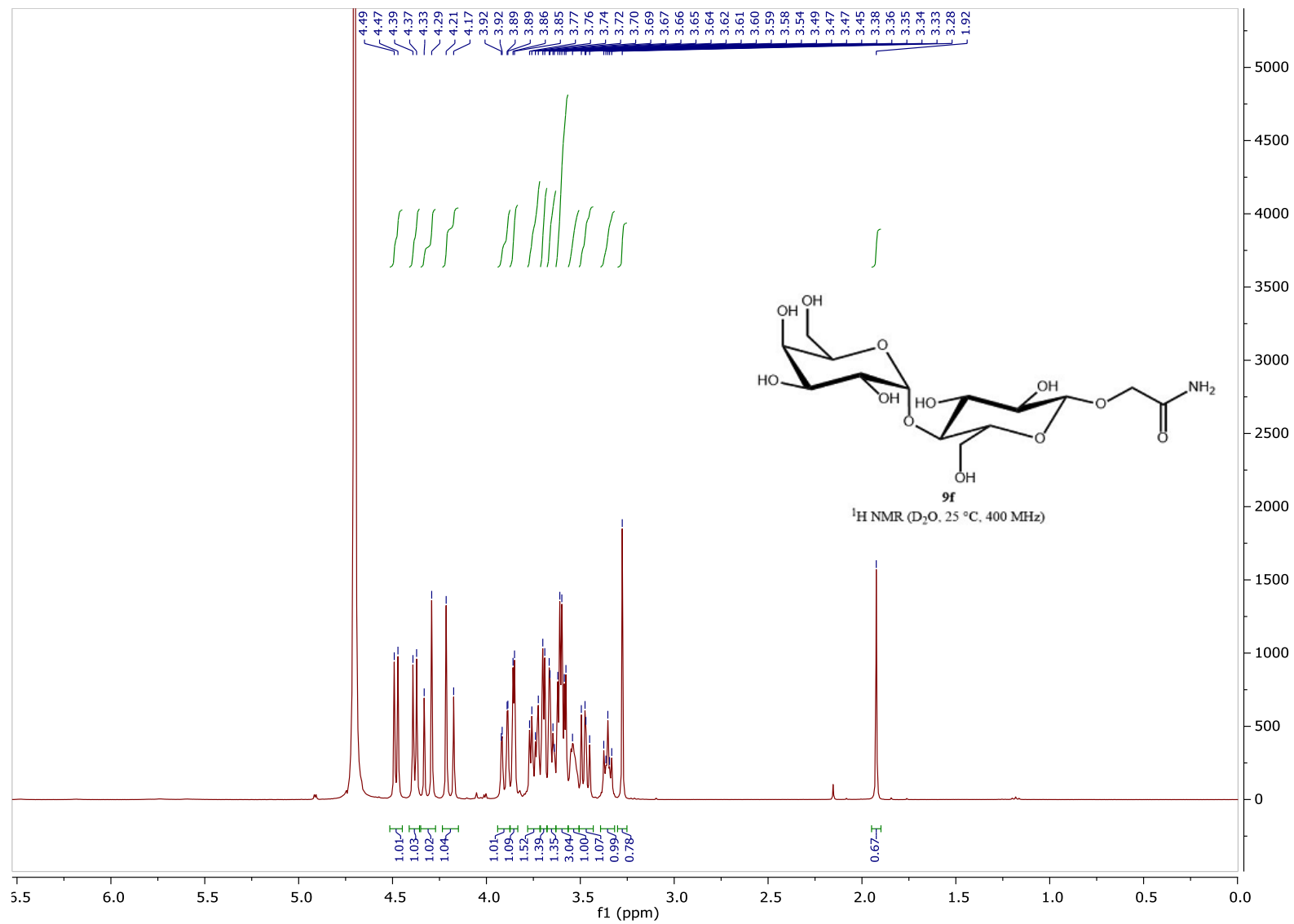
2-( $\beta$ -D-Cellobiosyloxy)-acetamide (9e).

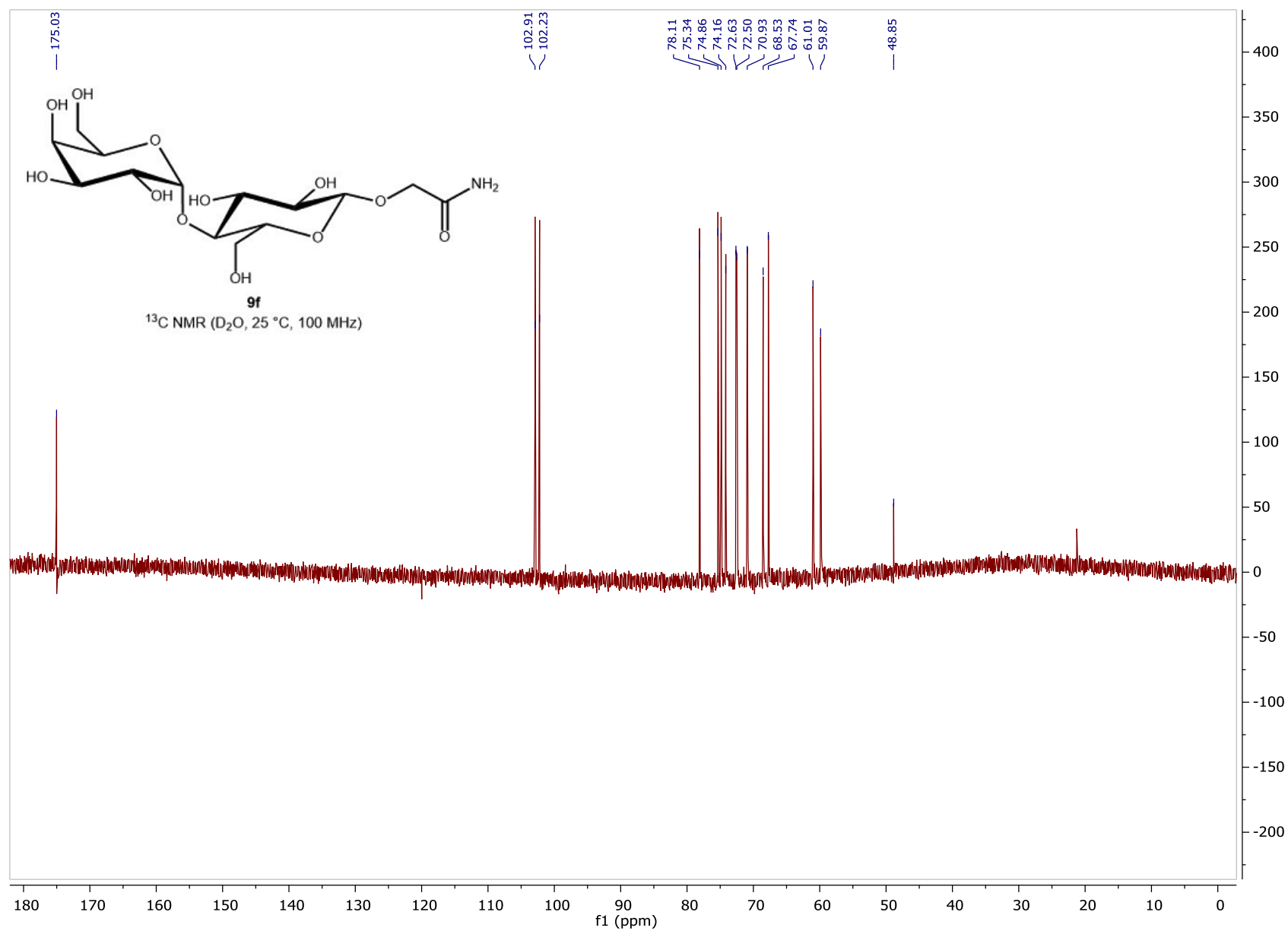


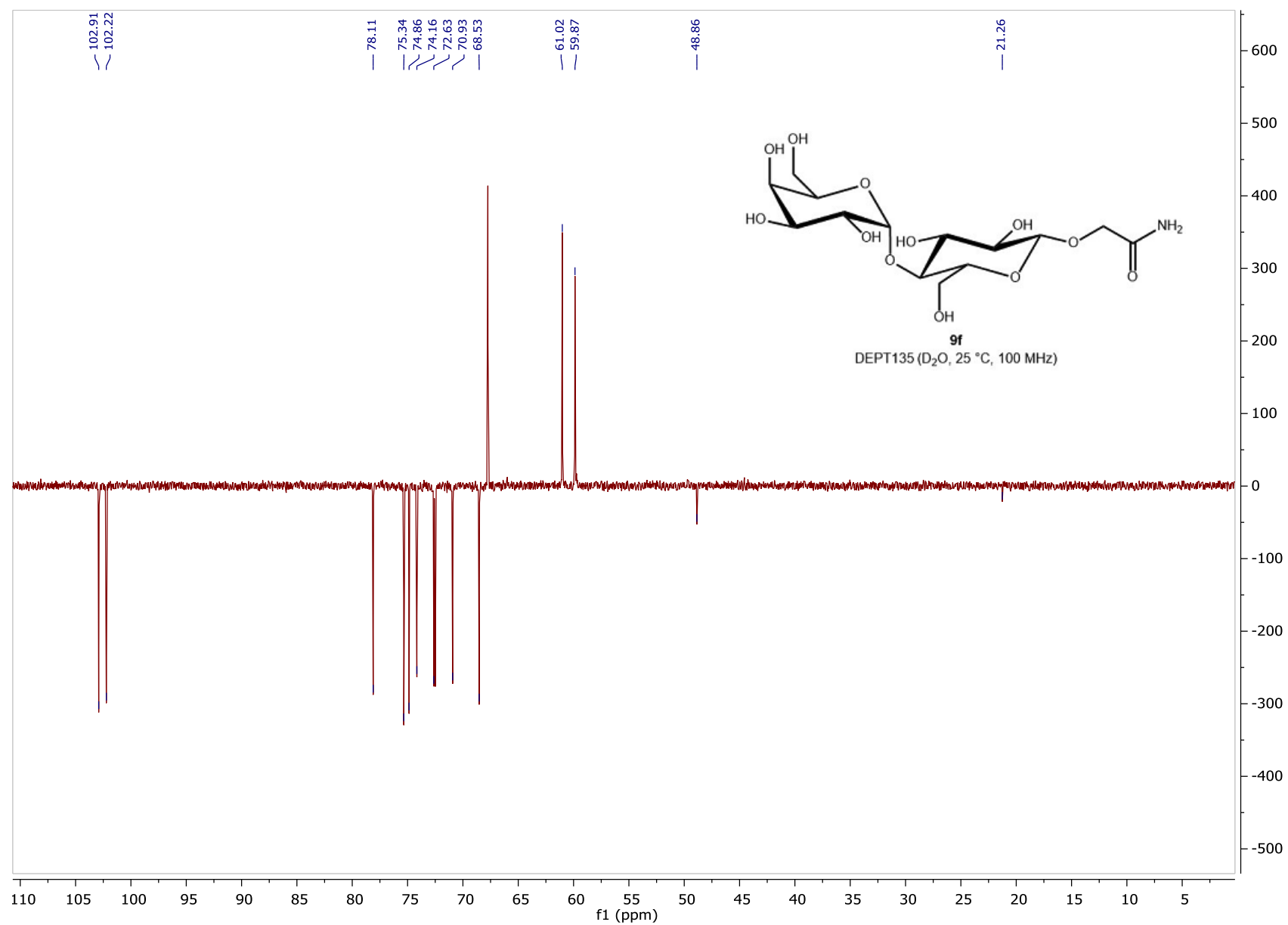




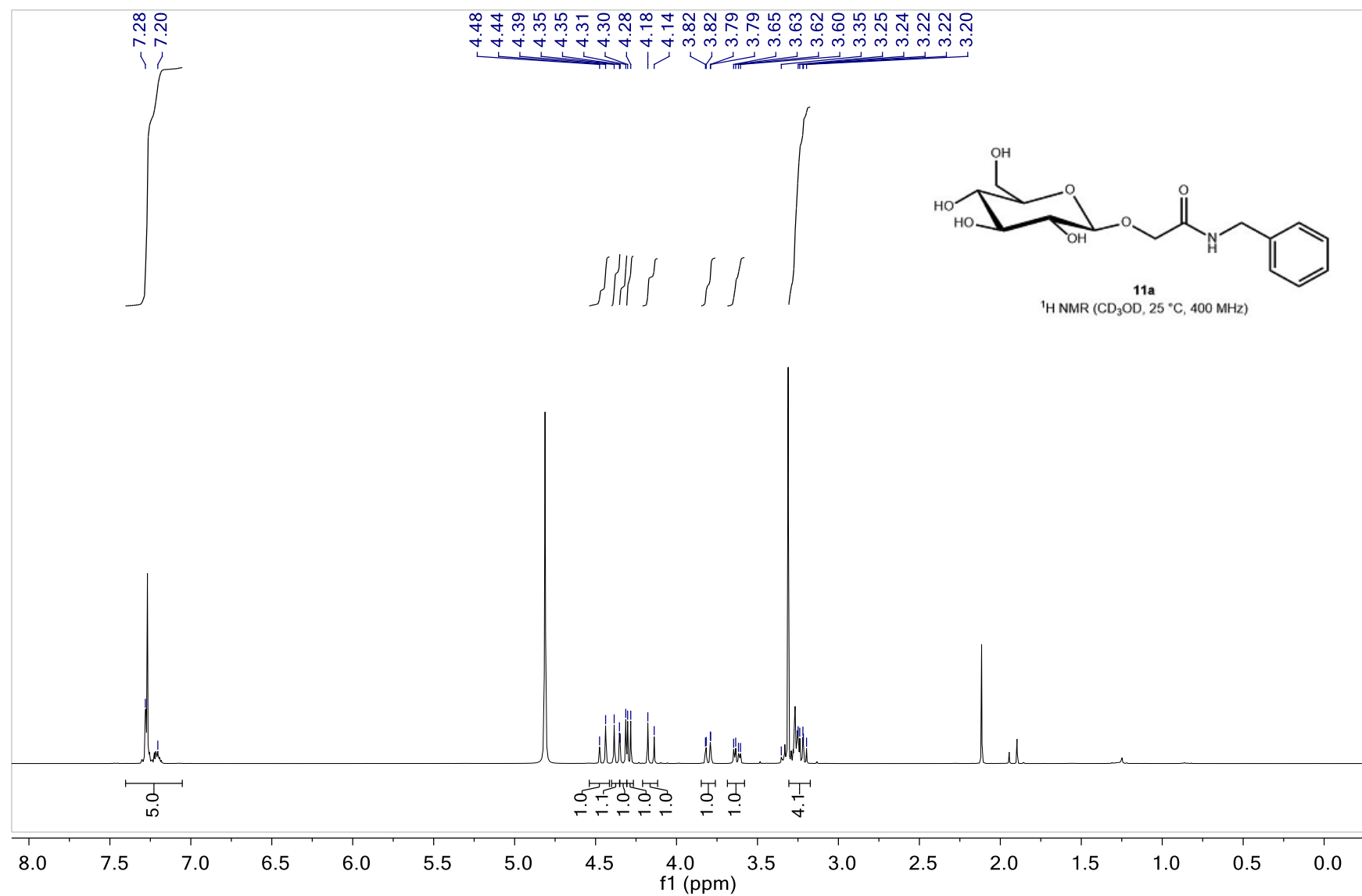
2-( $\beta$ -D-Lactosyloxy)-acetamide (9f).



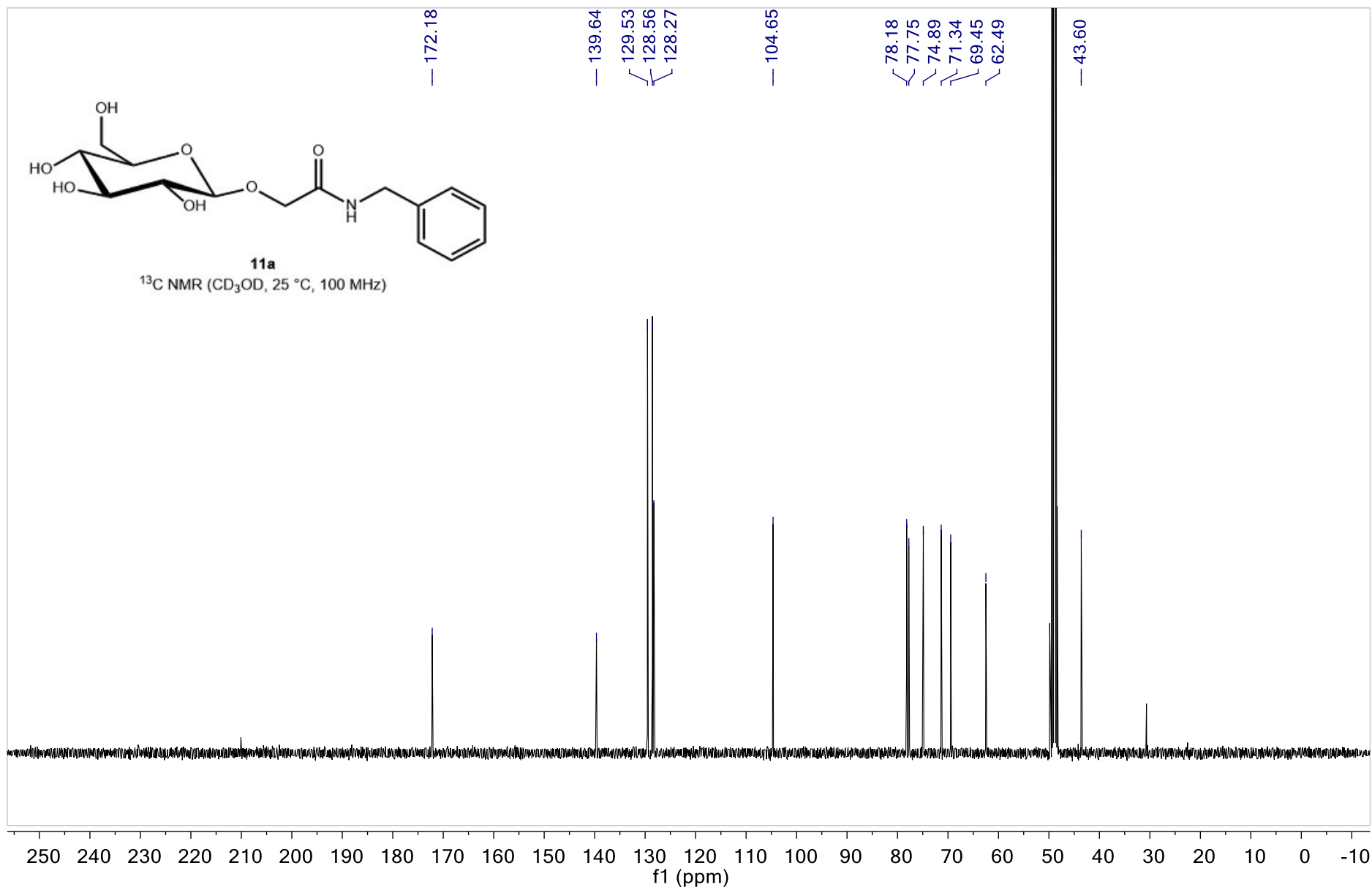


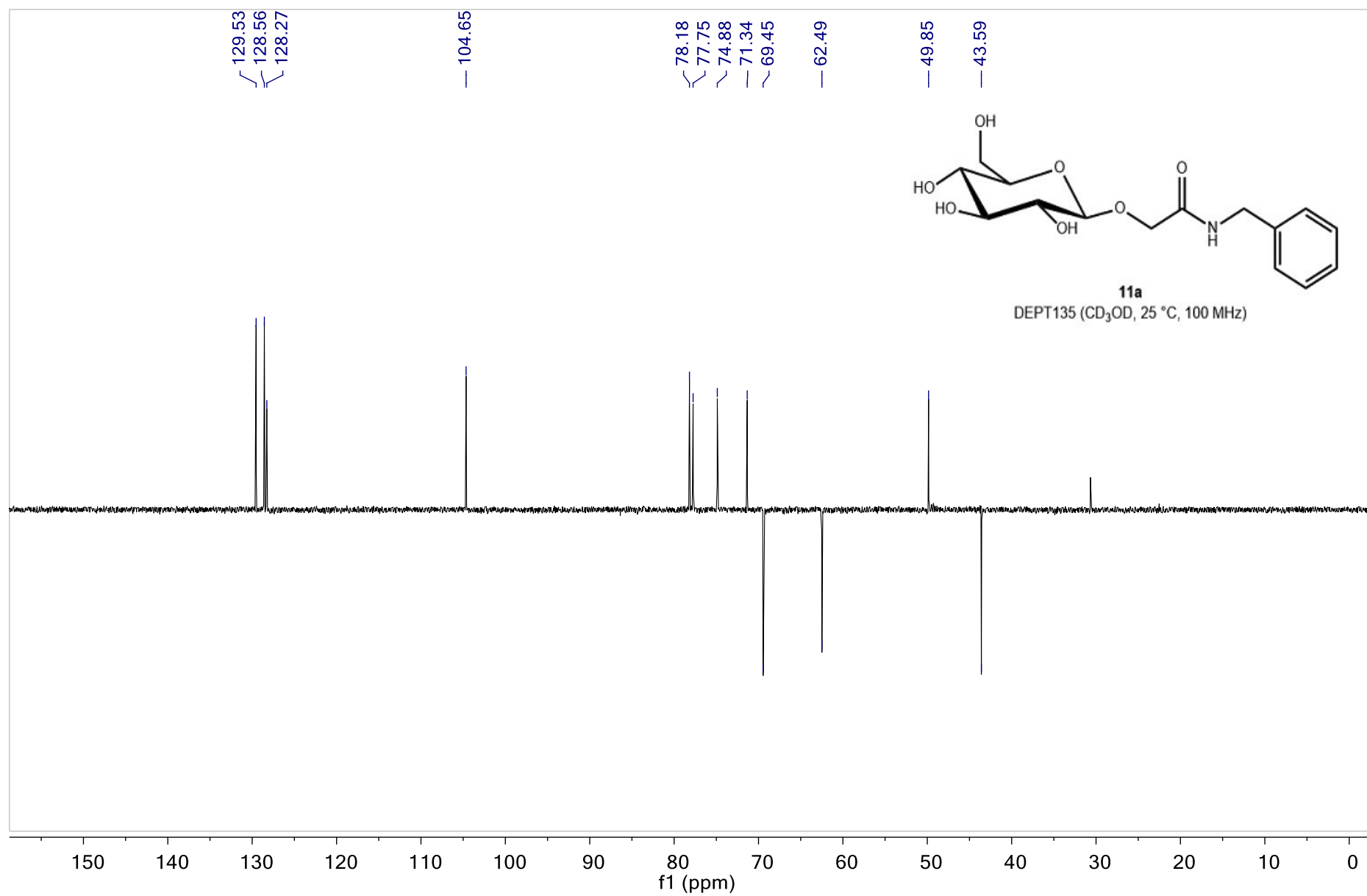


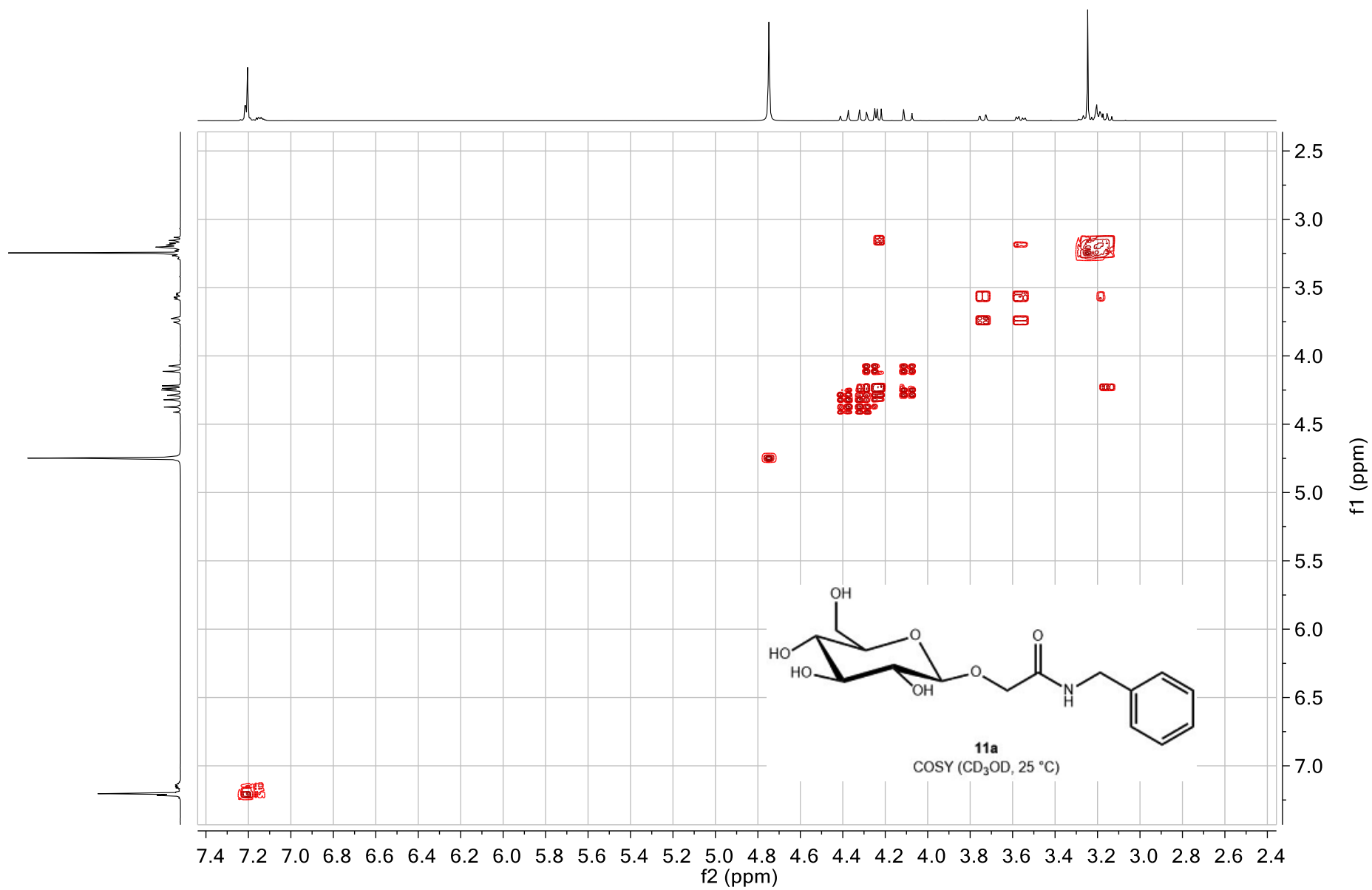
**2-( $\beta$ -D-Glucopyranosyloxy)-*N*-(phenylmethyl)-acetamide (11a).**

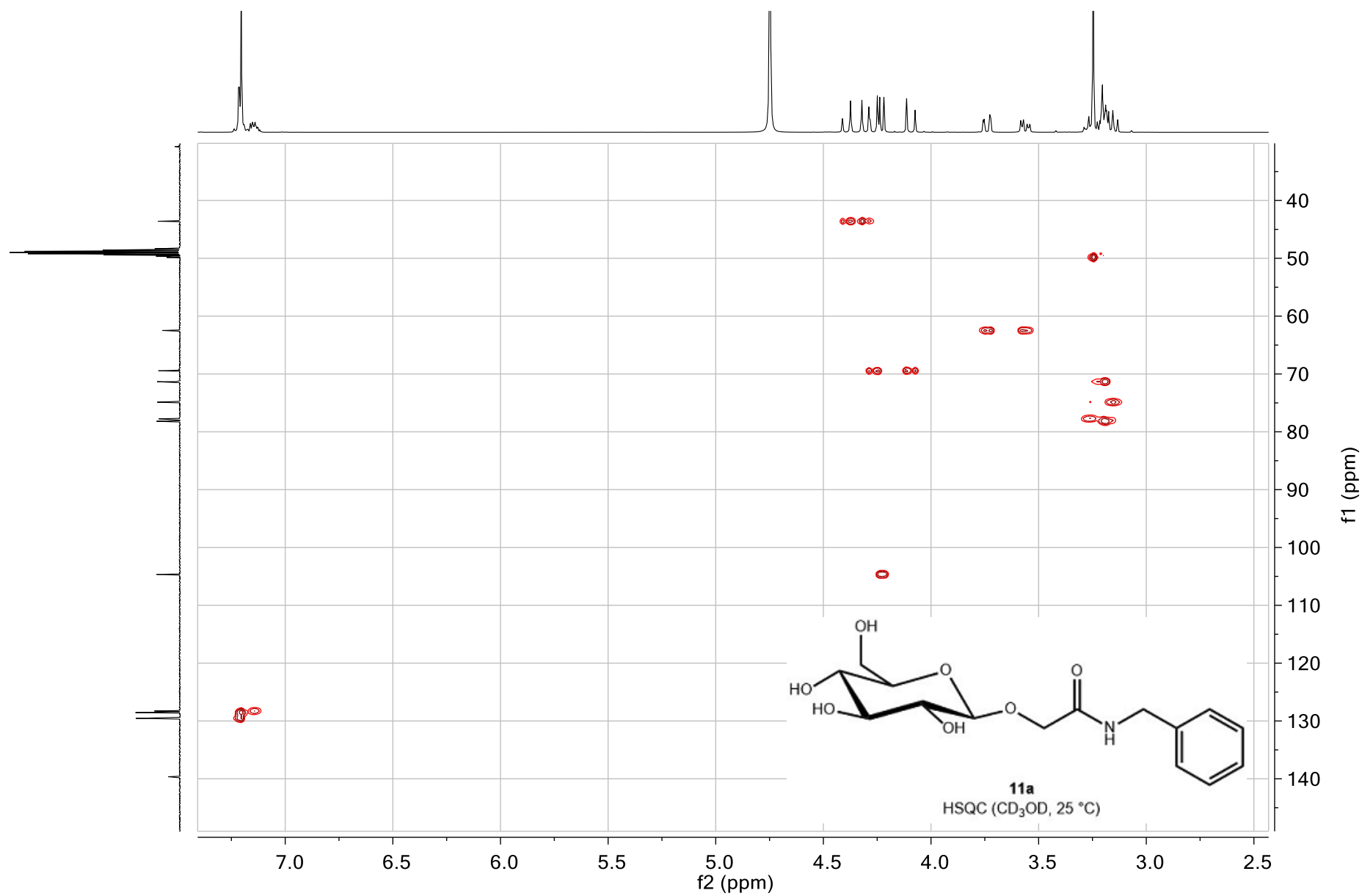




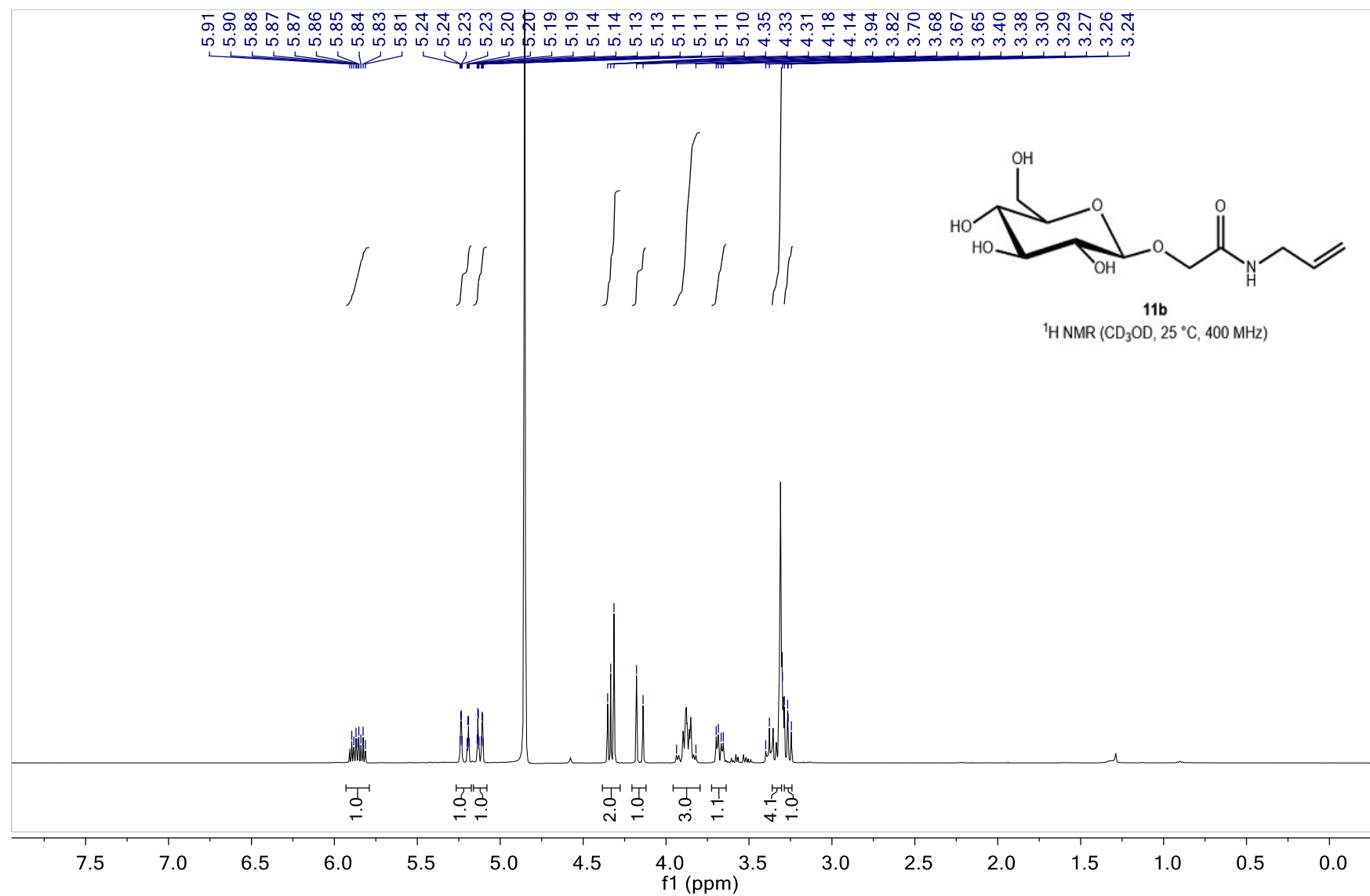


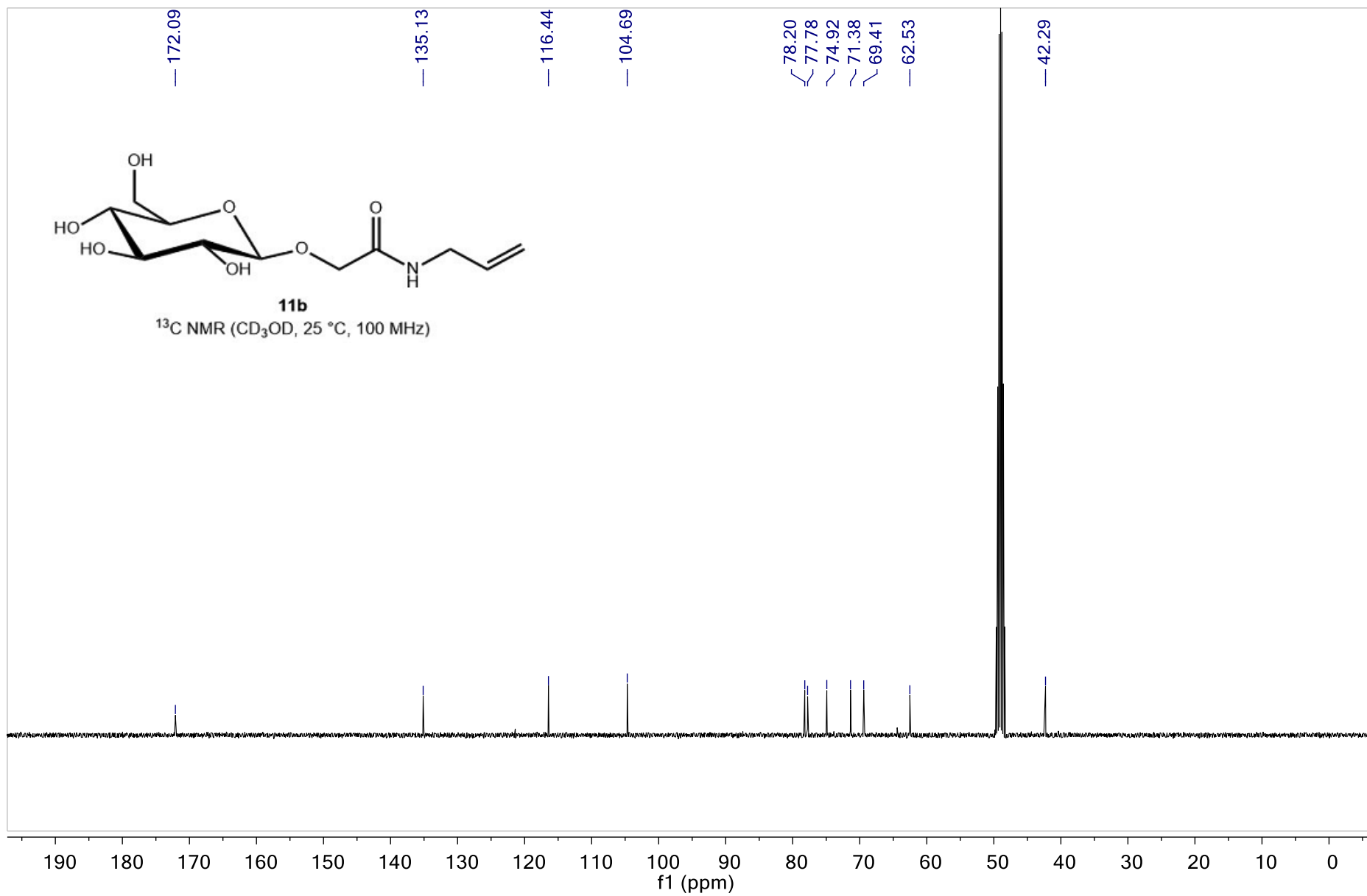


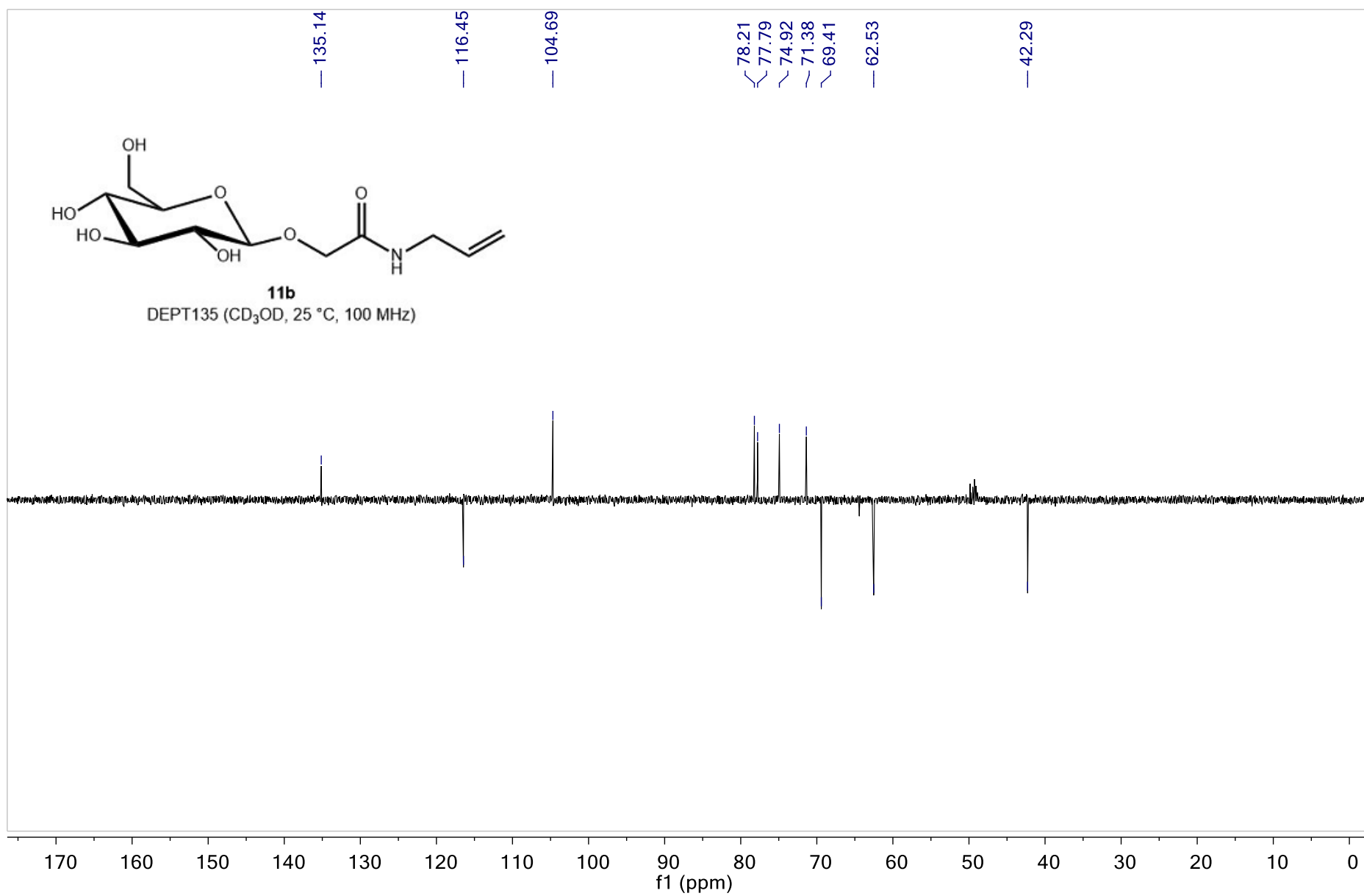


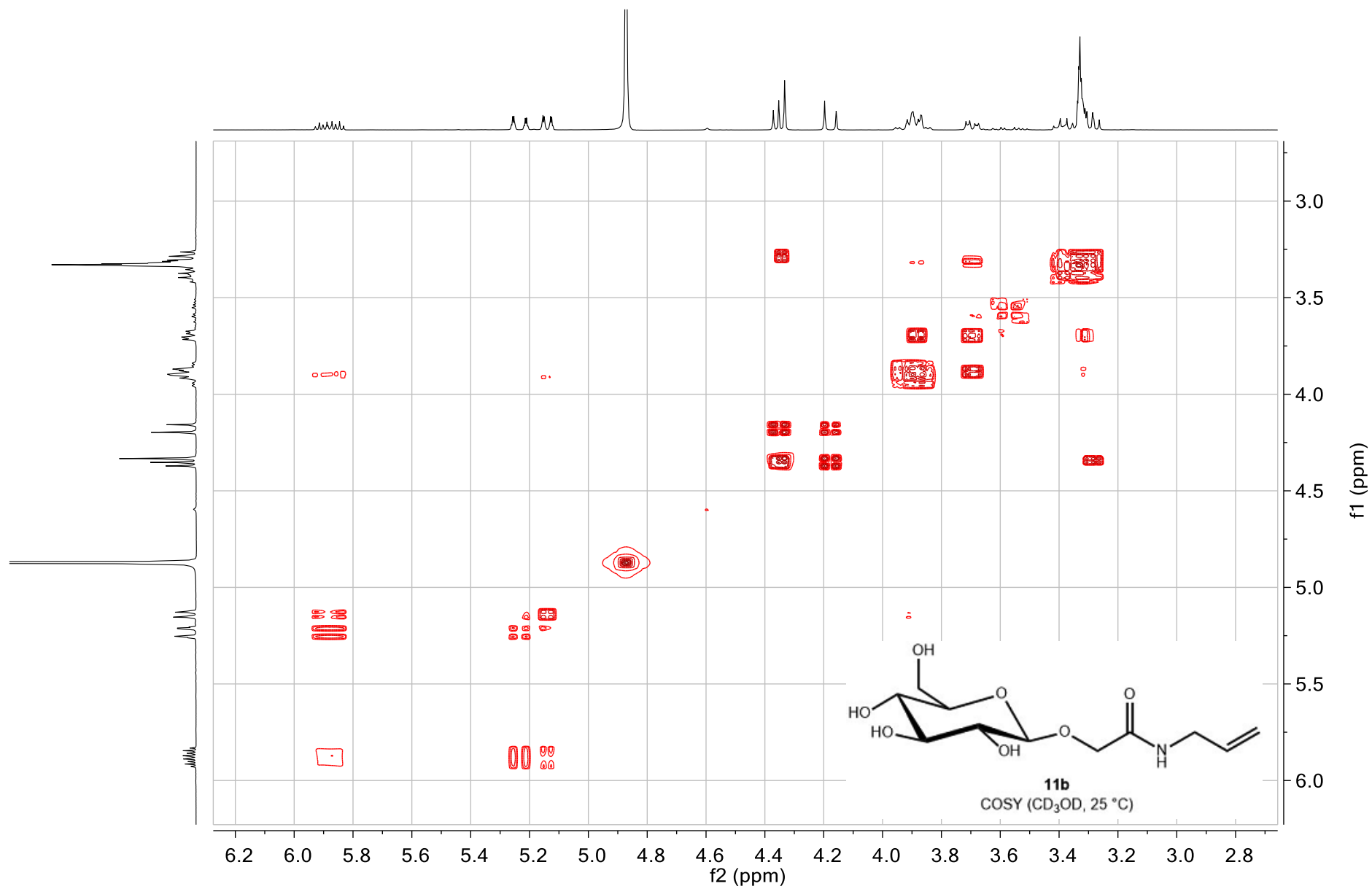


**2-( $\beta$ -D-Glucopyranosyloxy)-N-2-propen-1-yl-acetamide (11b).**

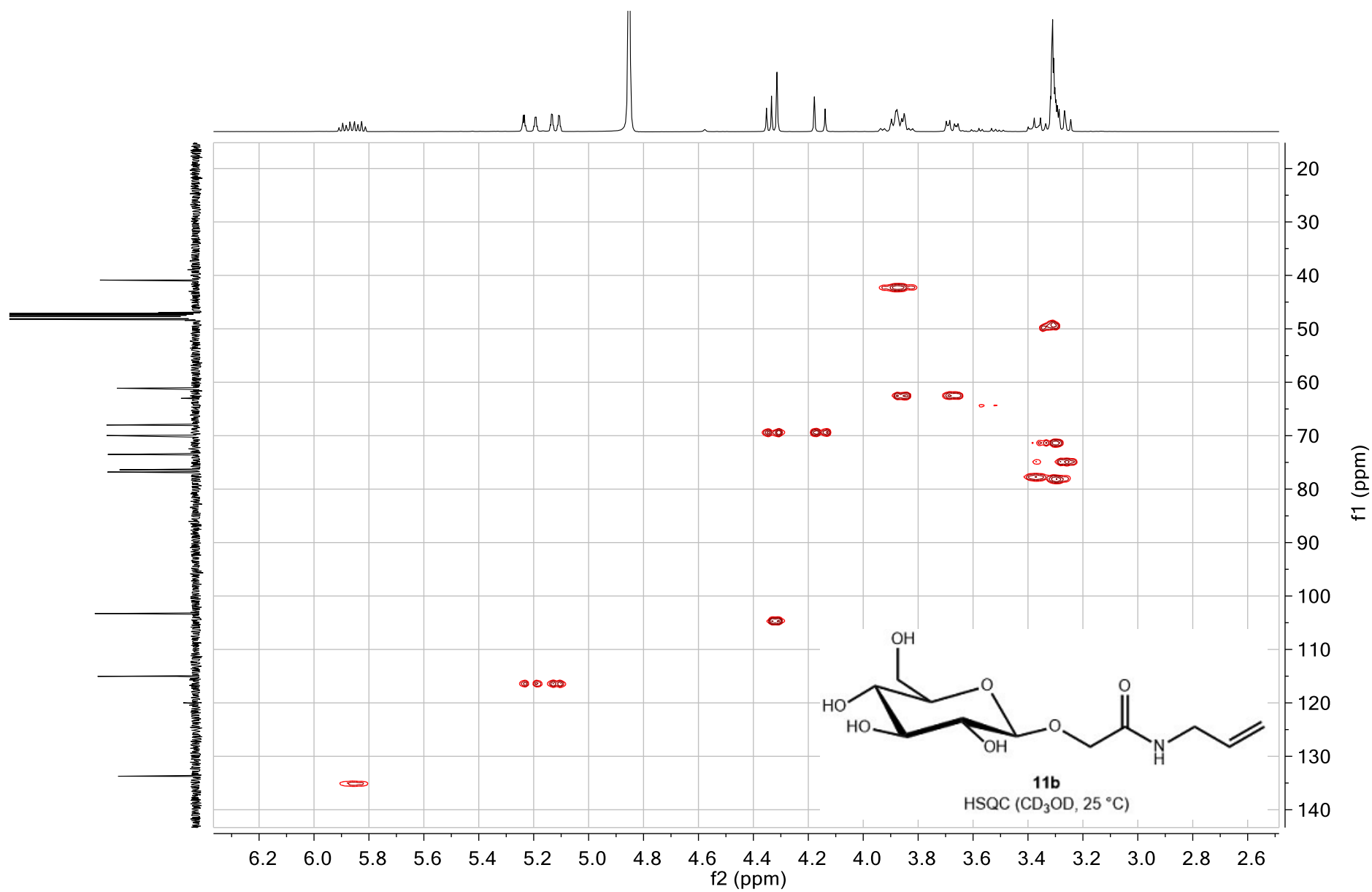




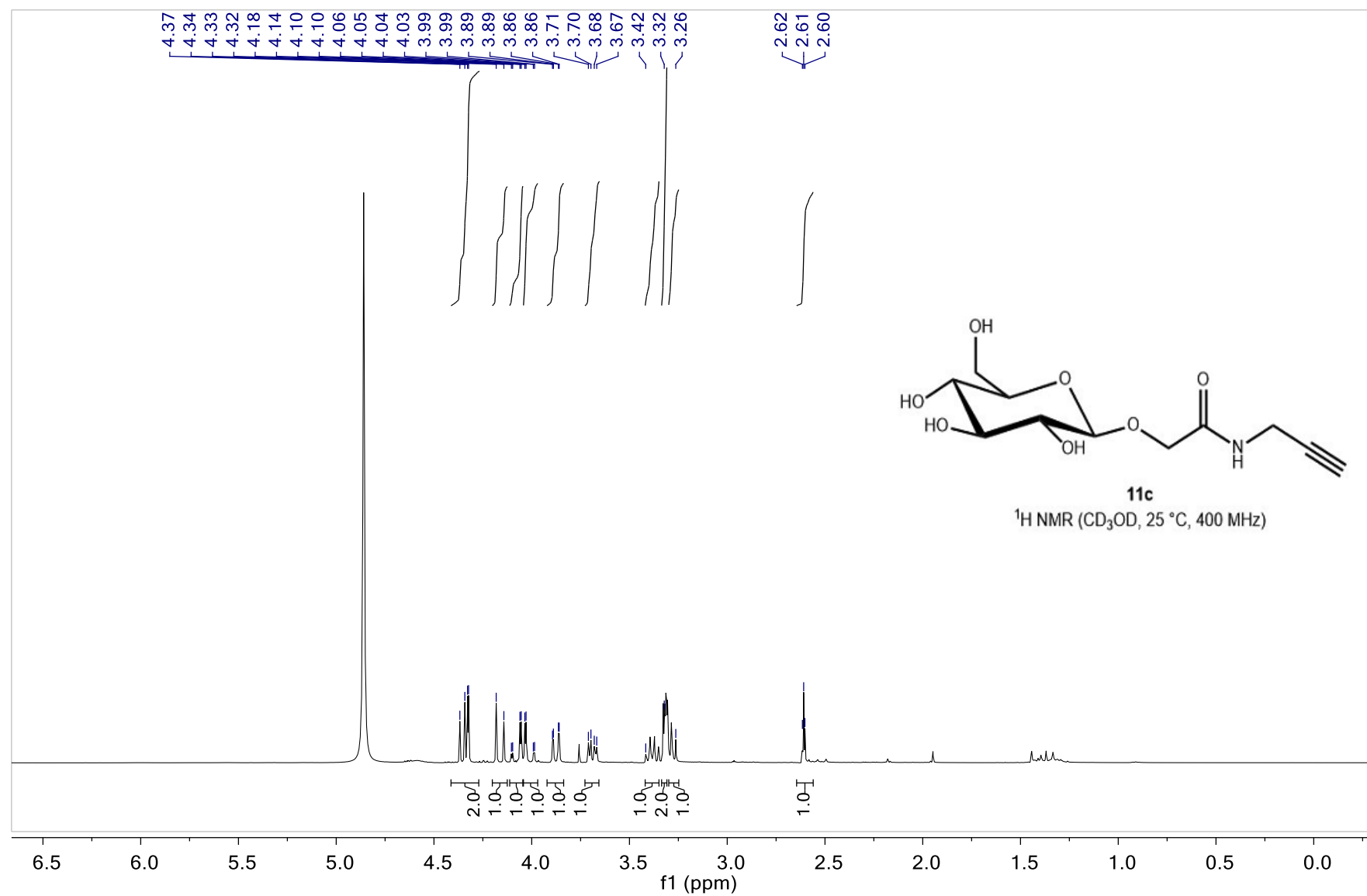


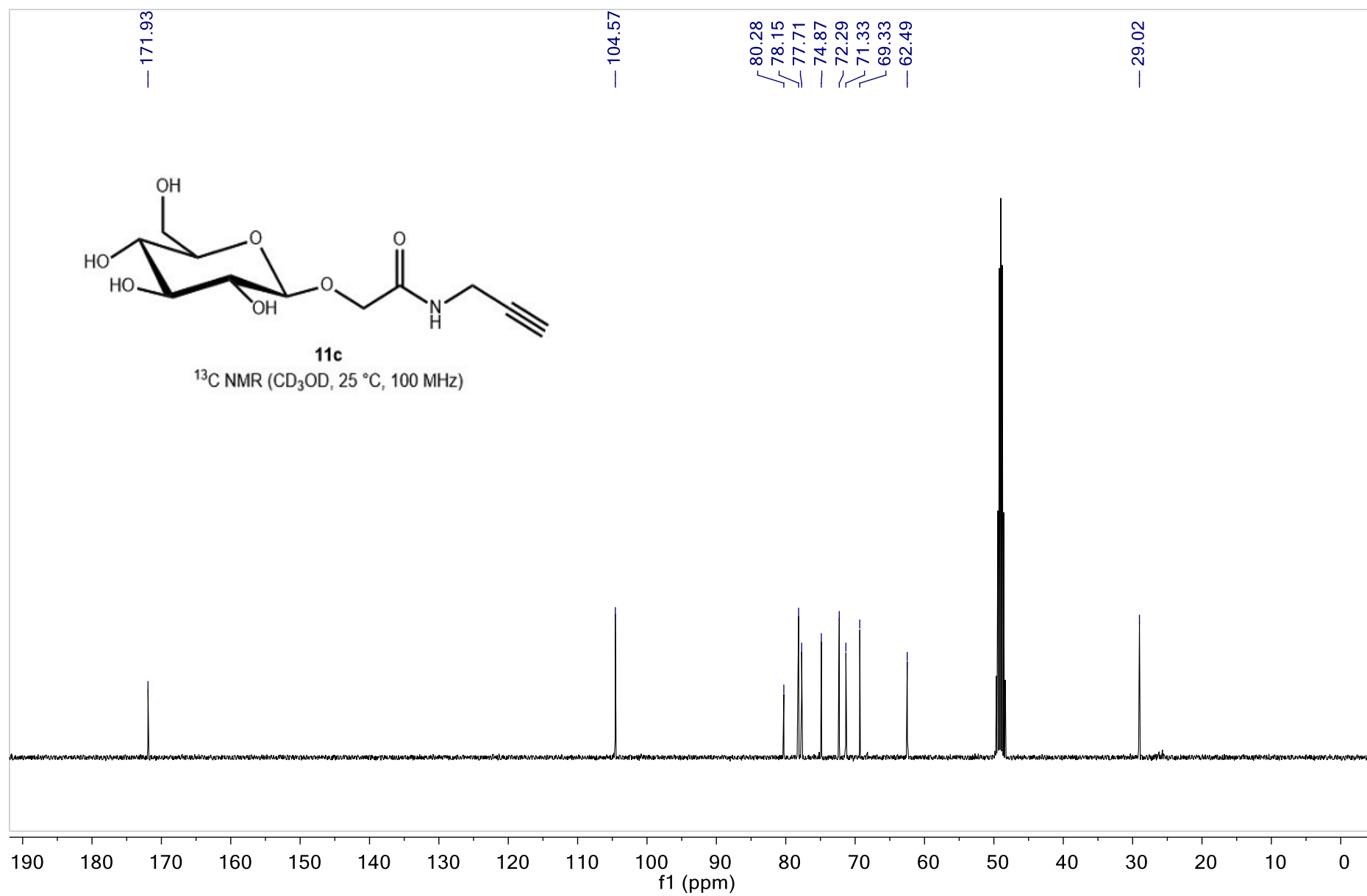


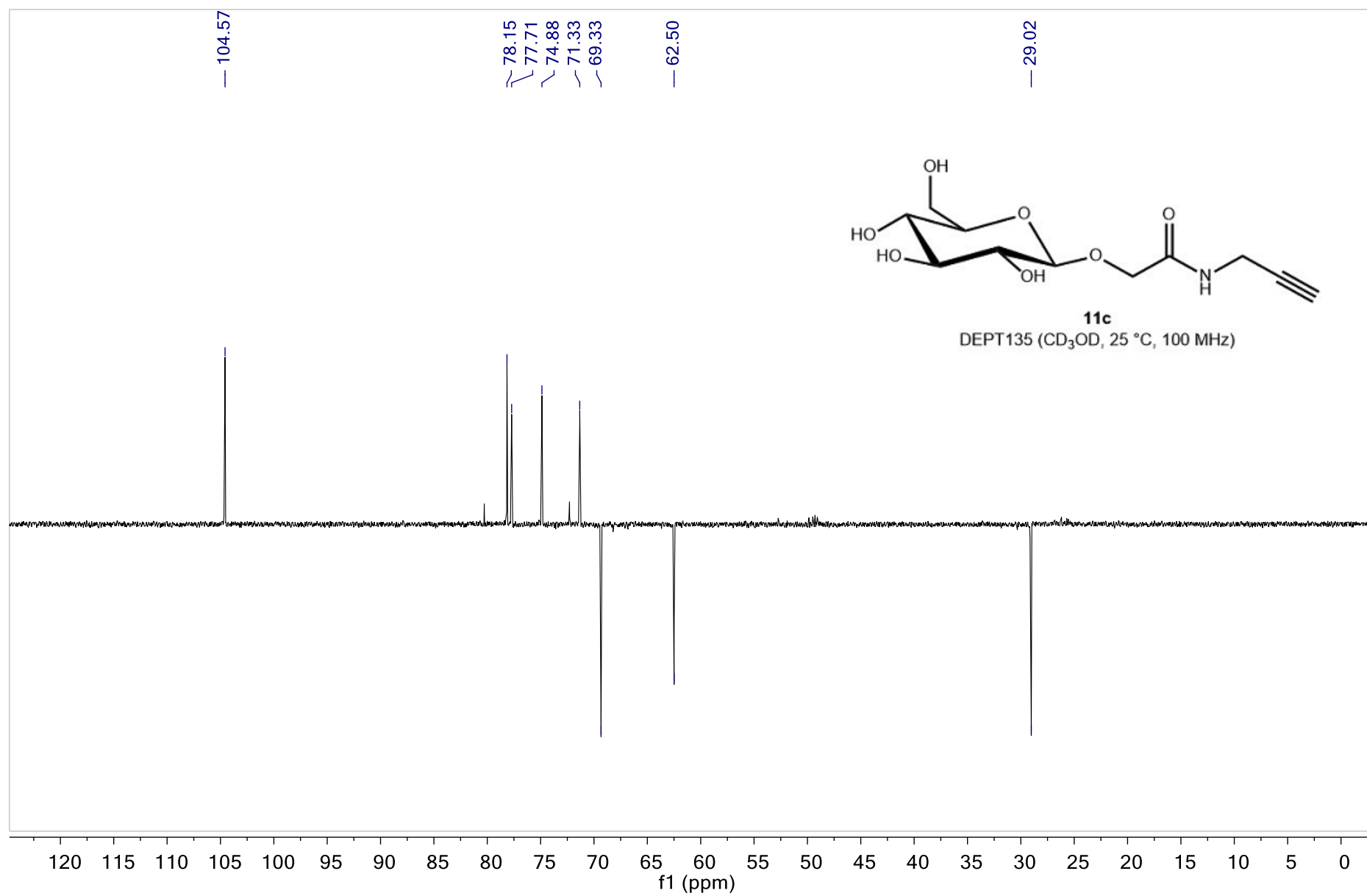


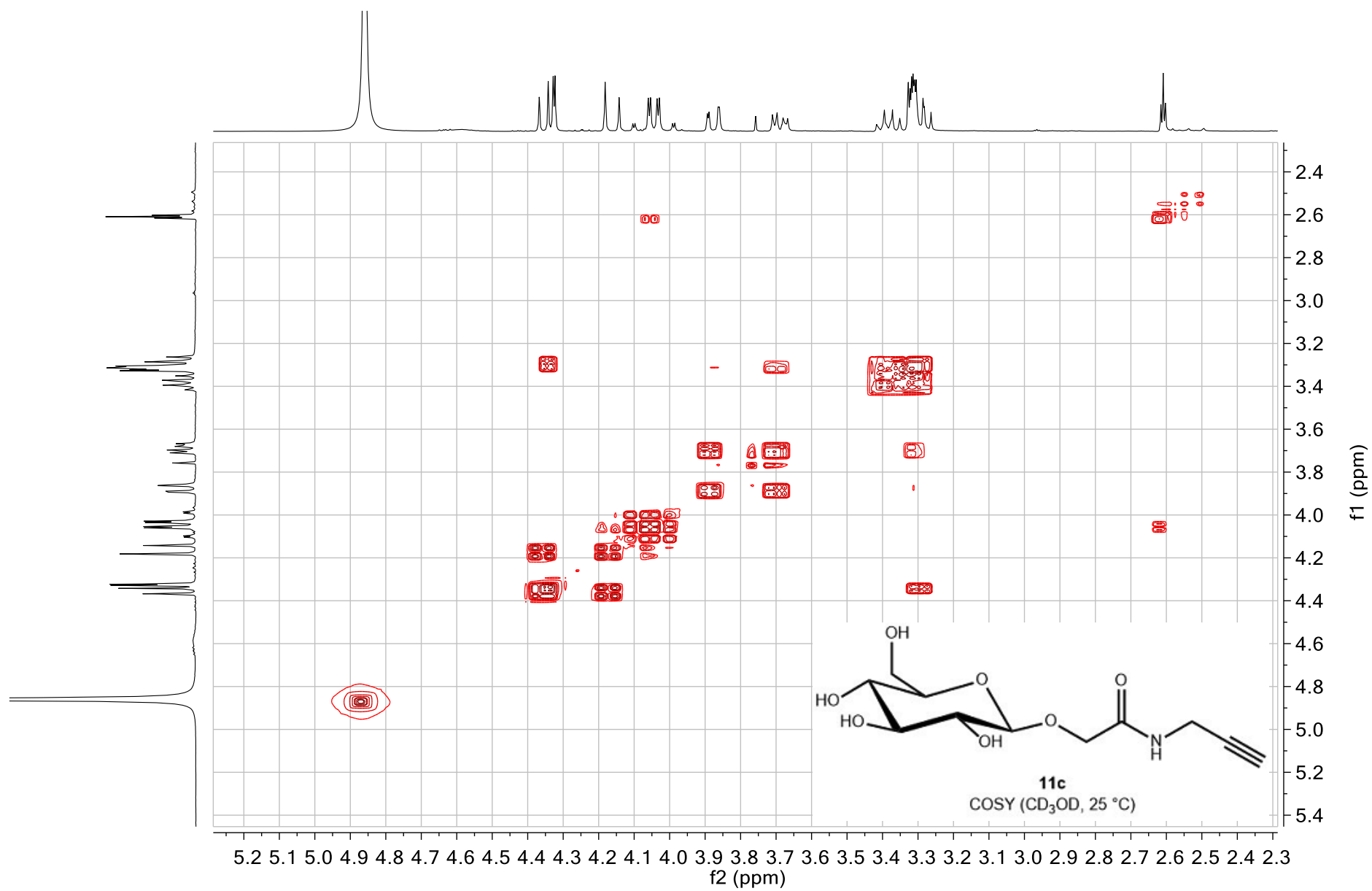


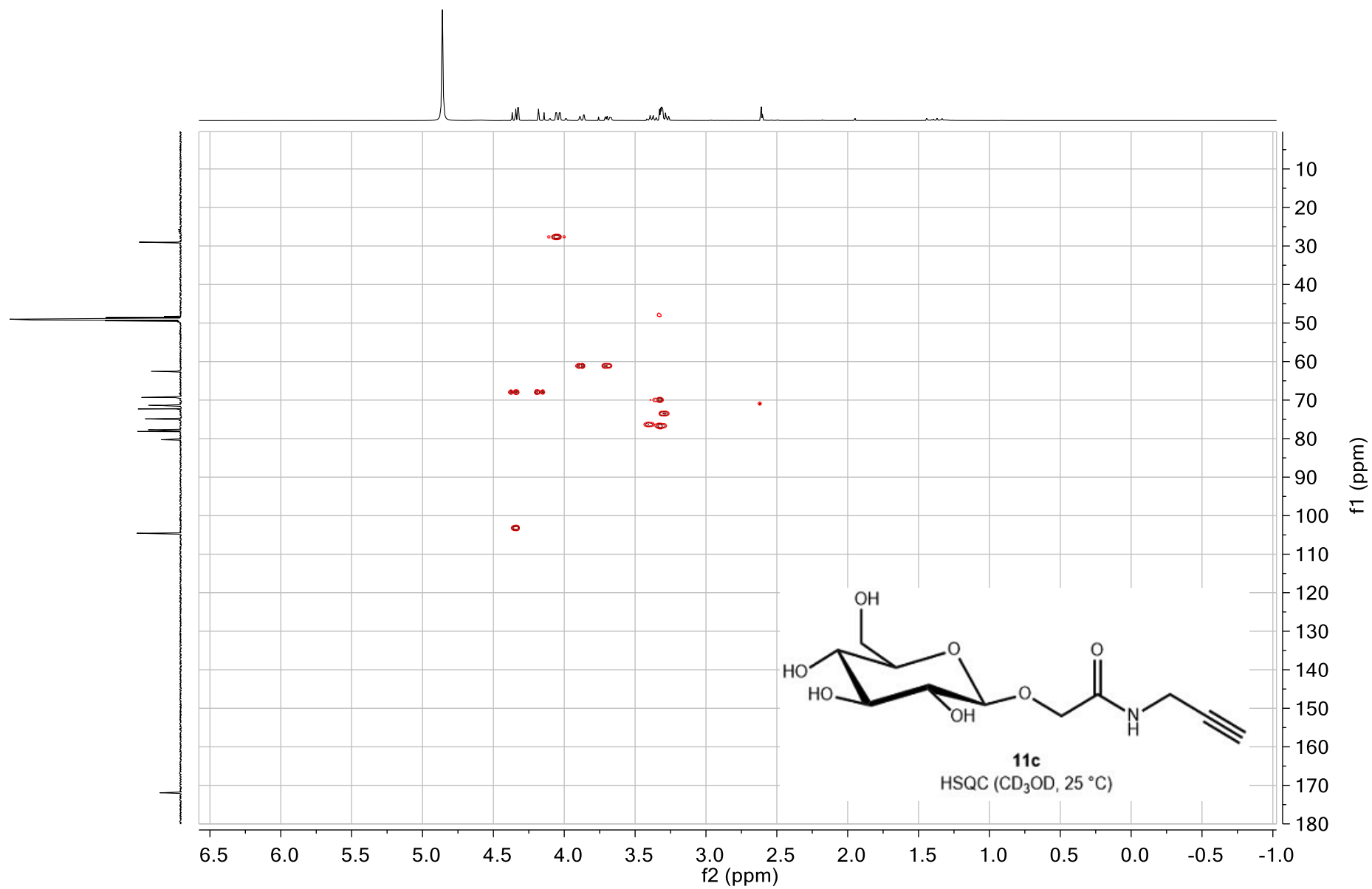
**2-( $\beta$ -D-Glucopyranosyloxy)-N-2-propyn-1-yl-acetamide (11c).**



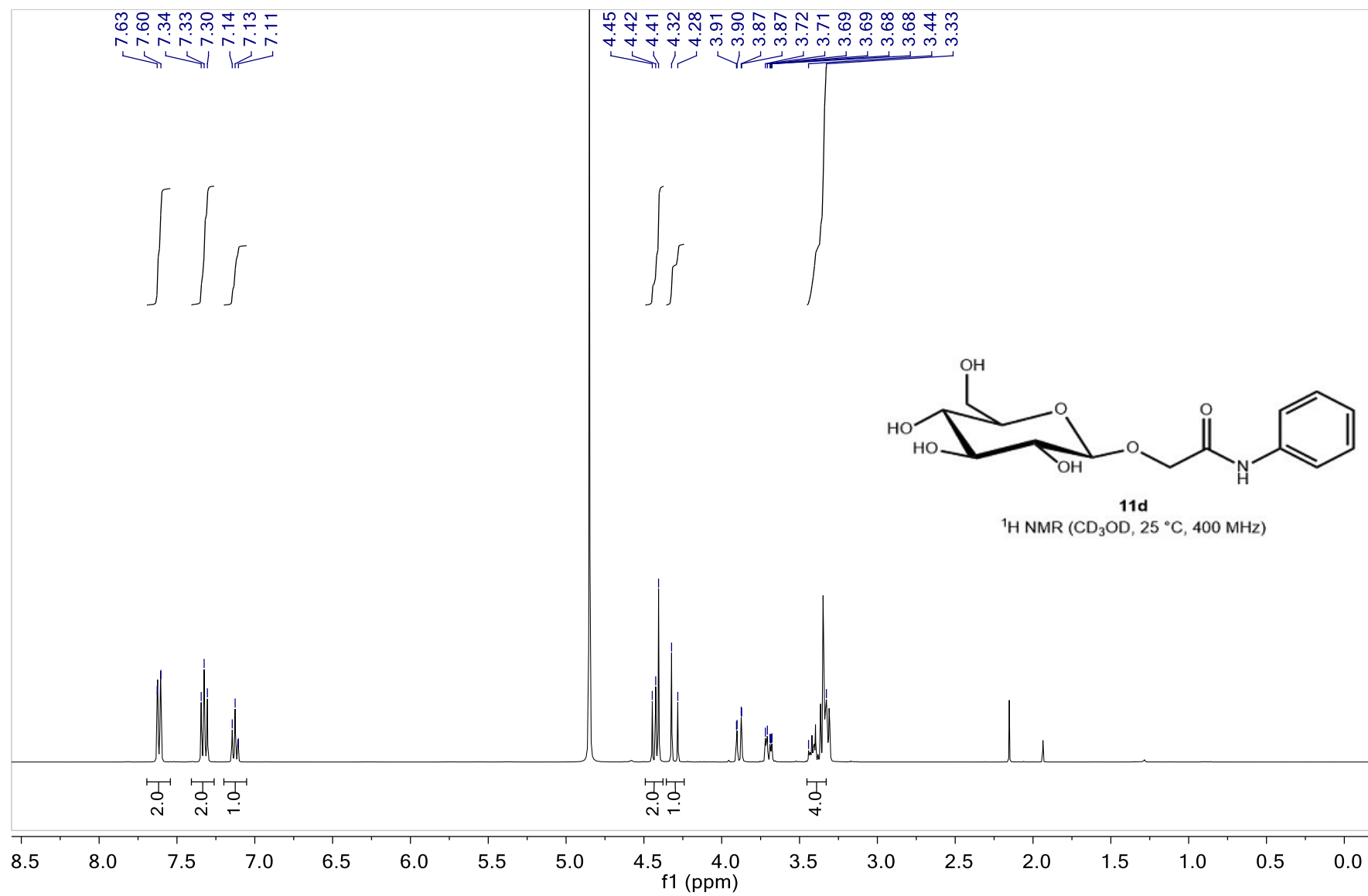


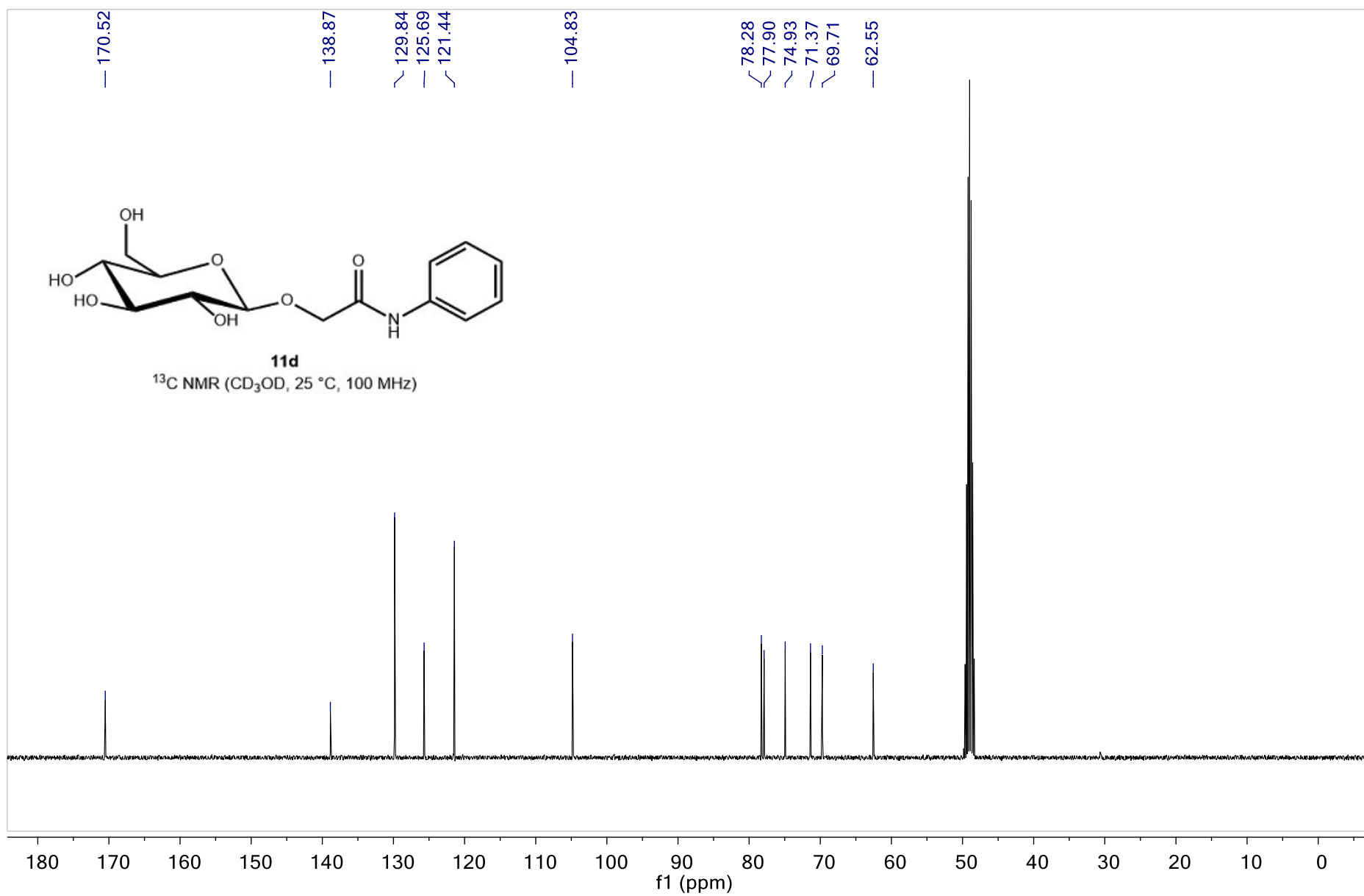




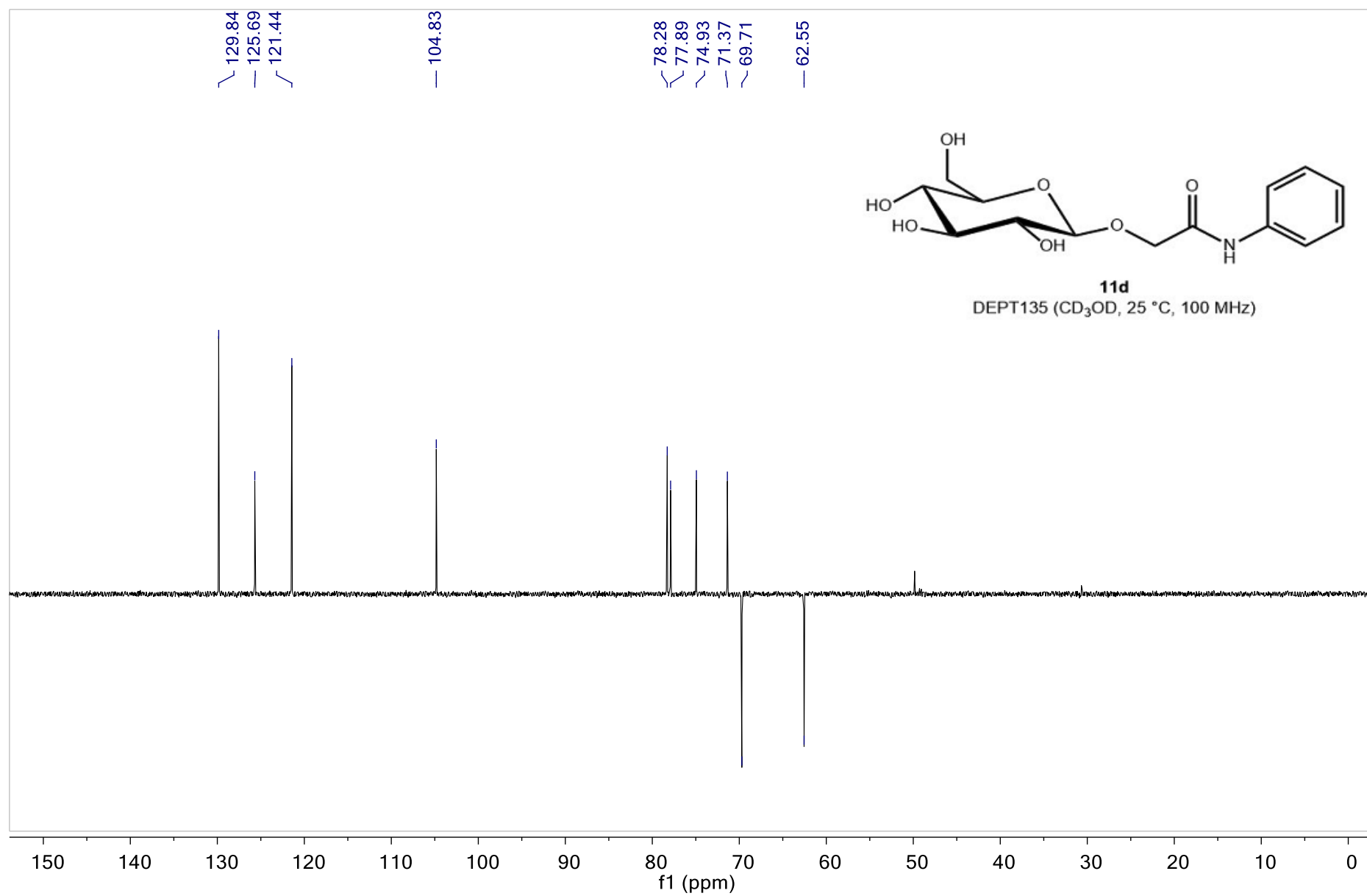


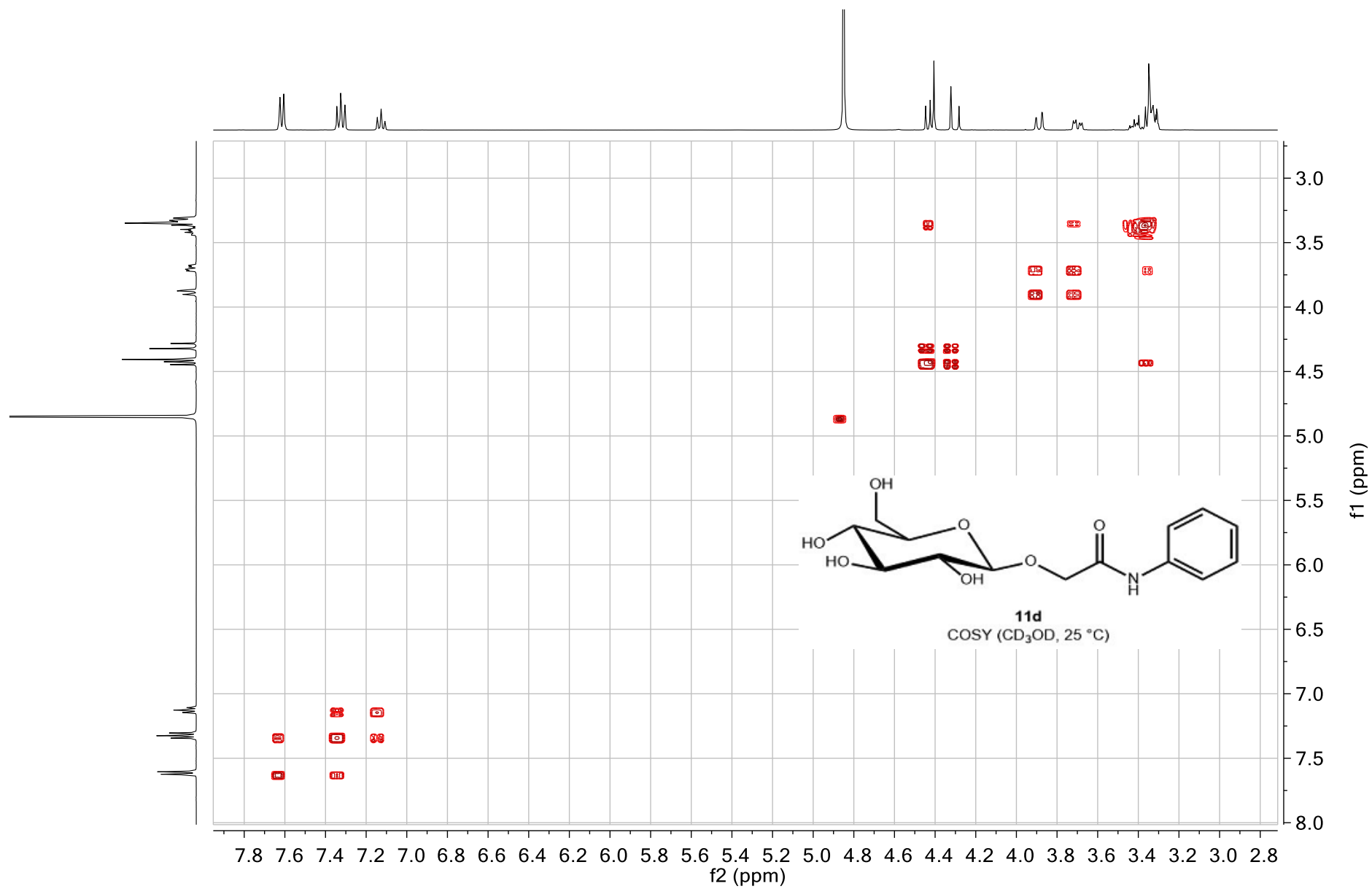
2-( $\beta$ -D-Glucopyranosyloxy)-*N*-phenyl-acetamide (**11d**).

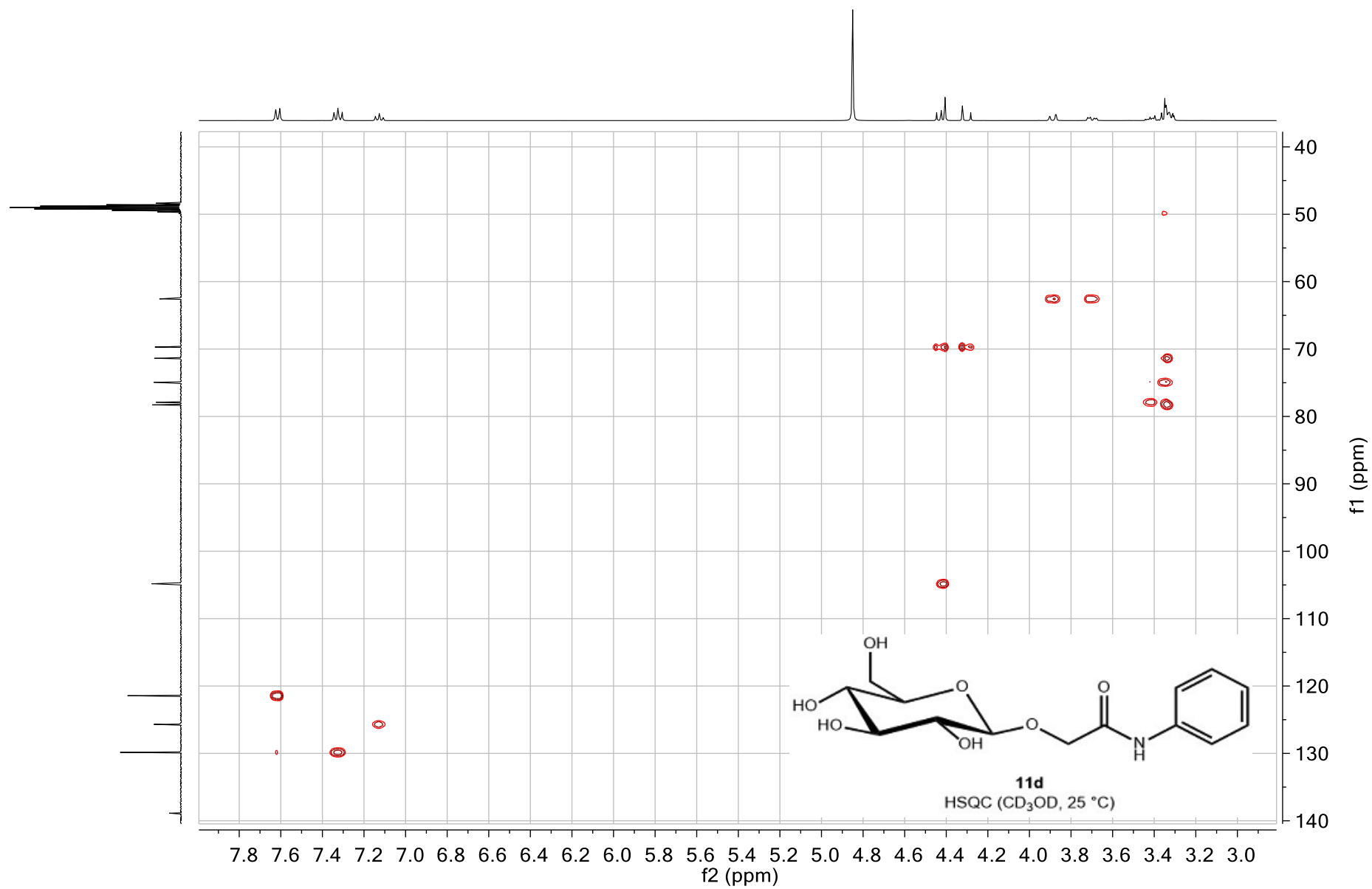


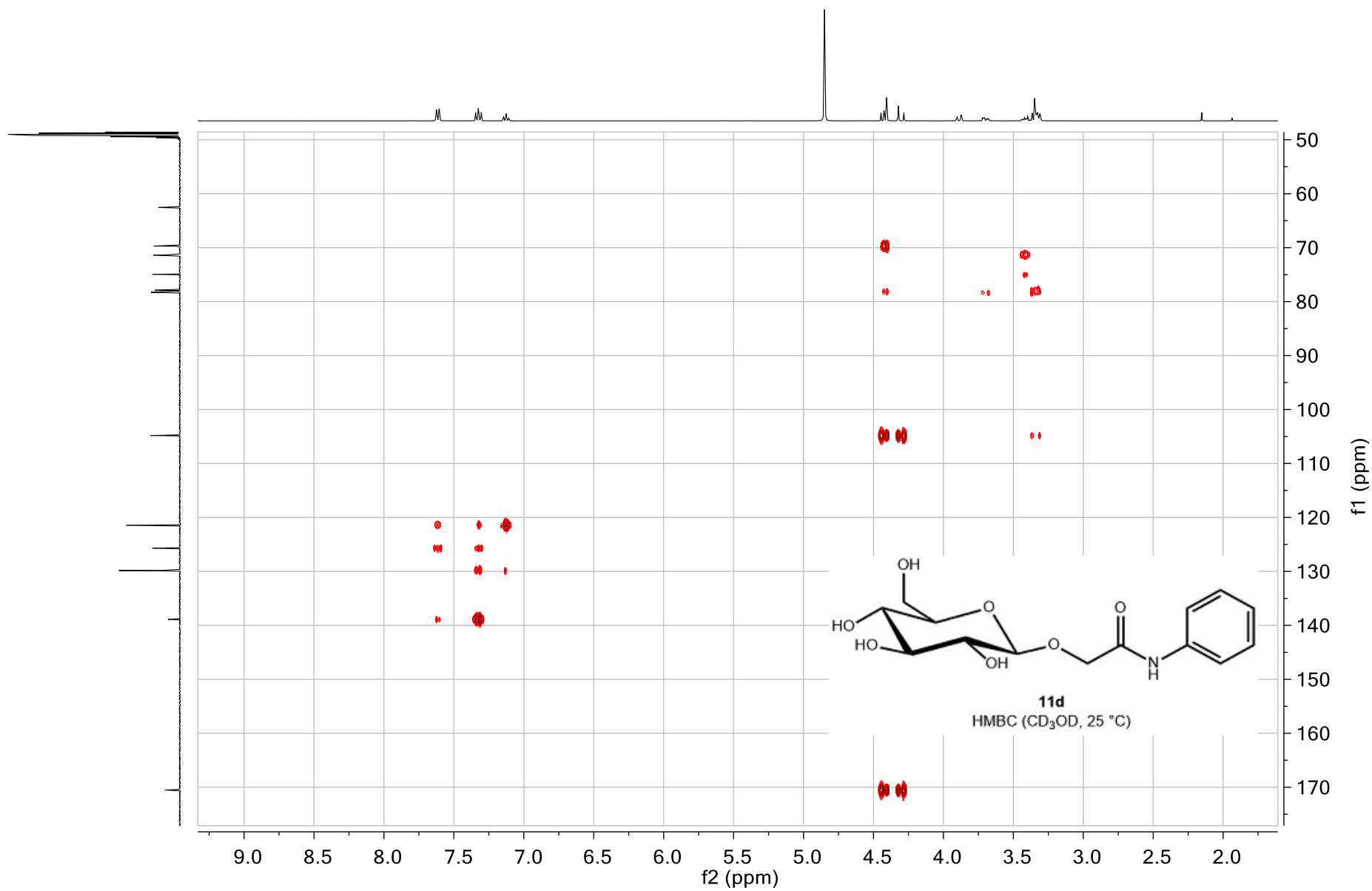




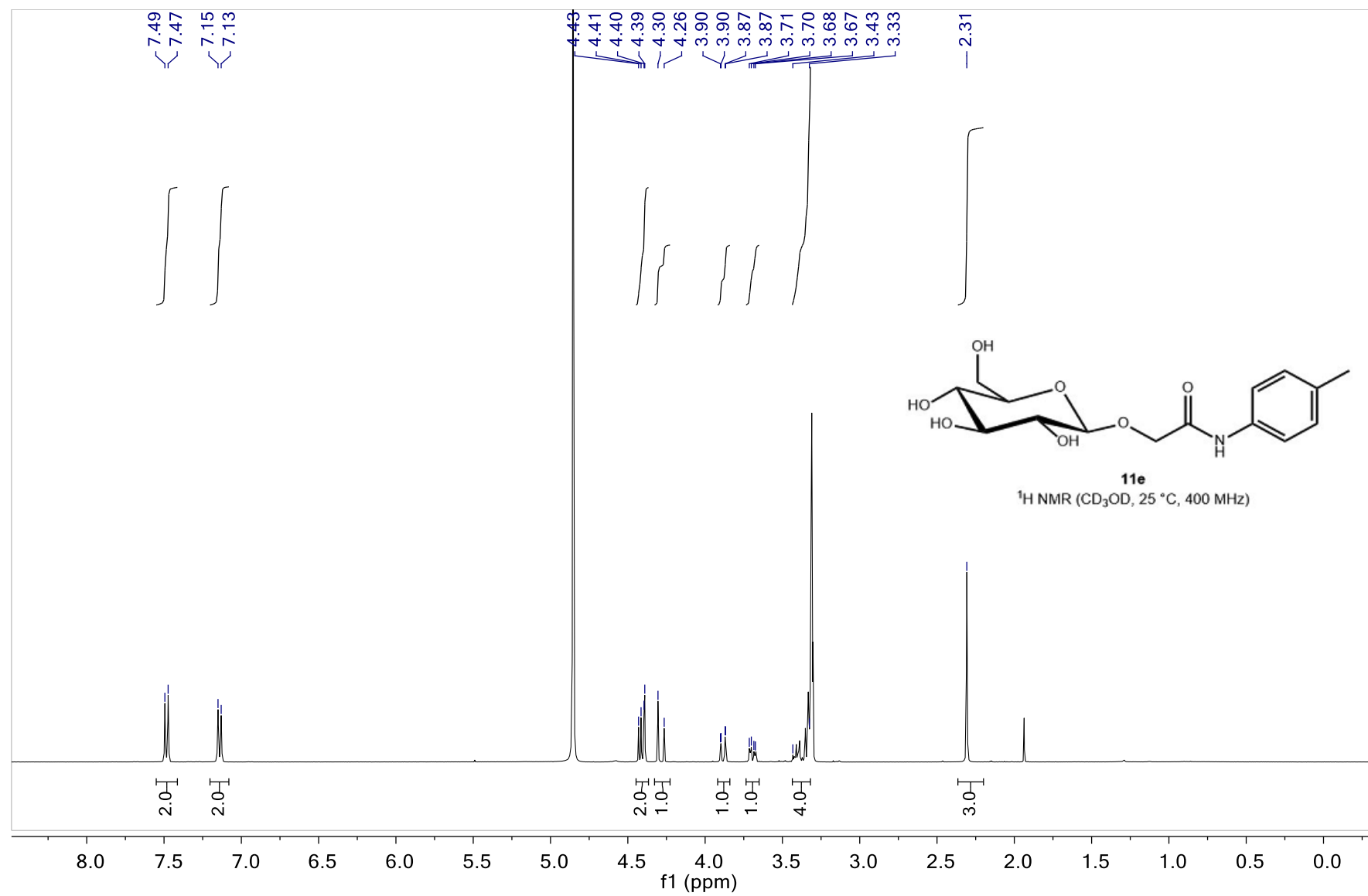


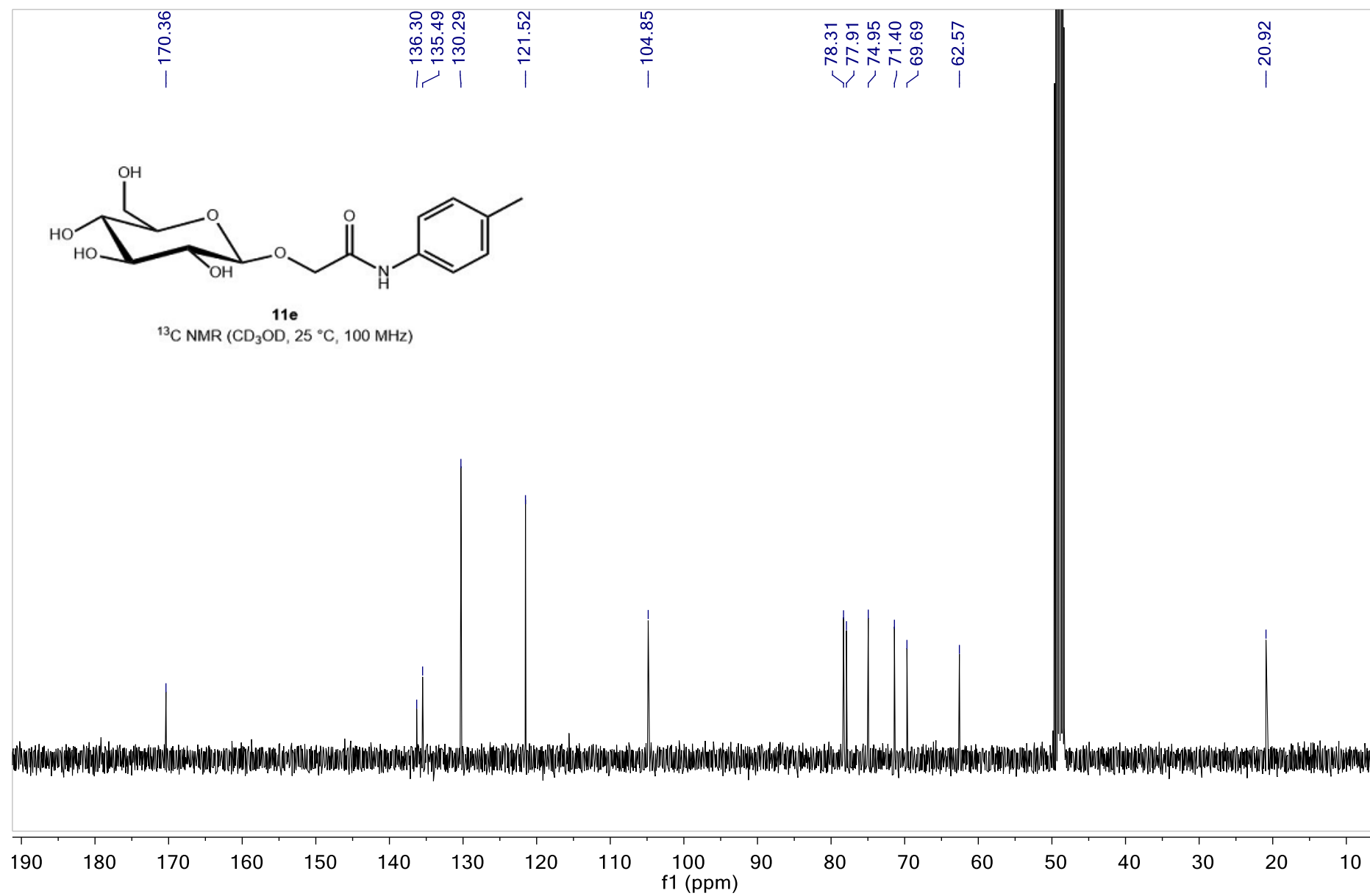


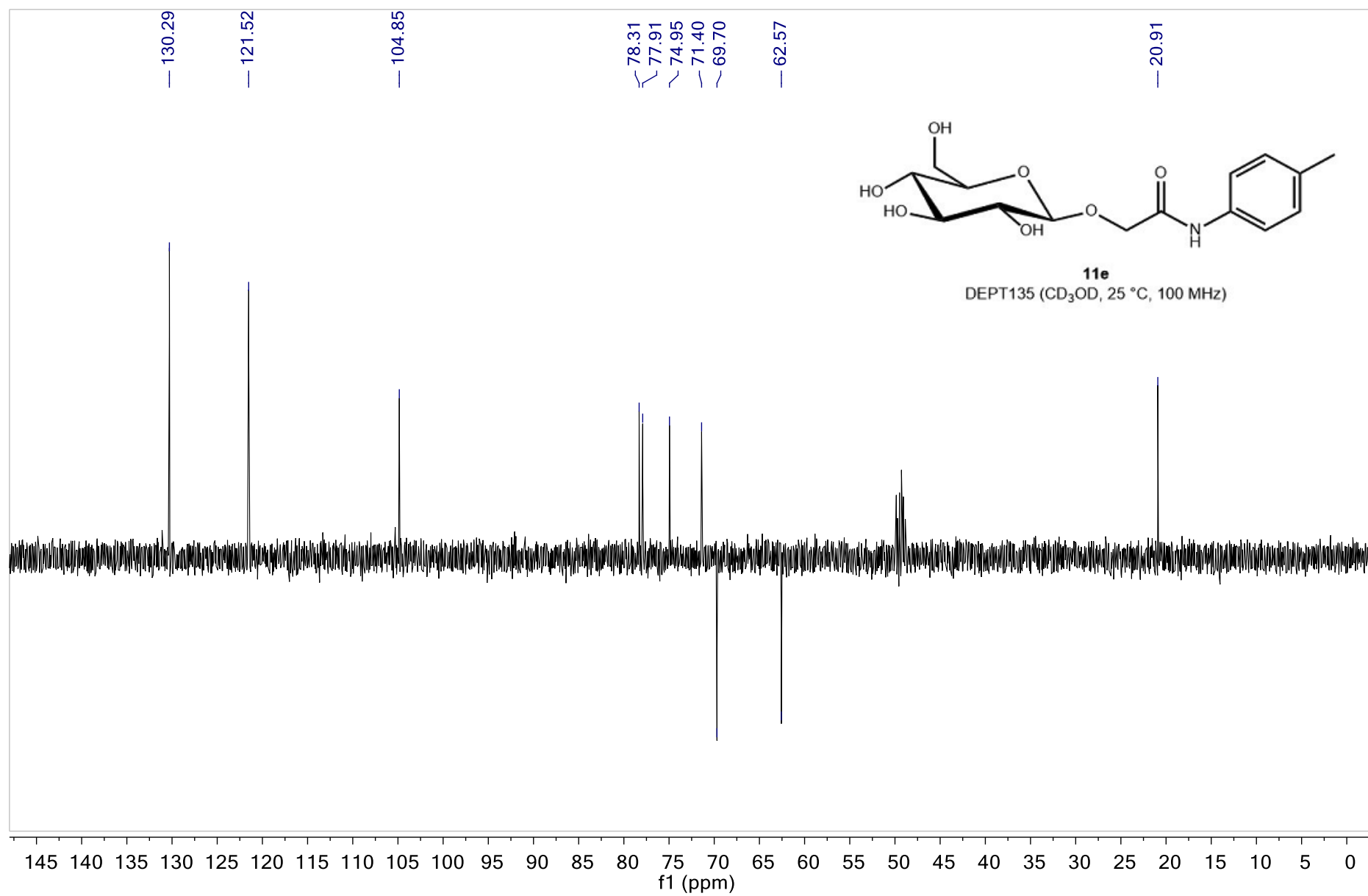


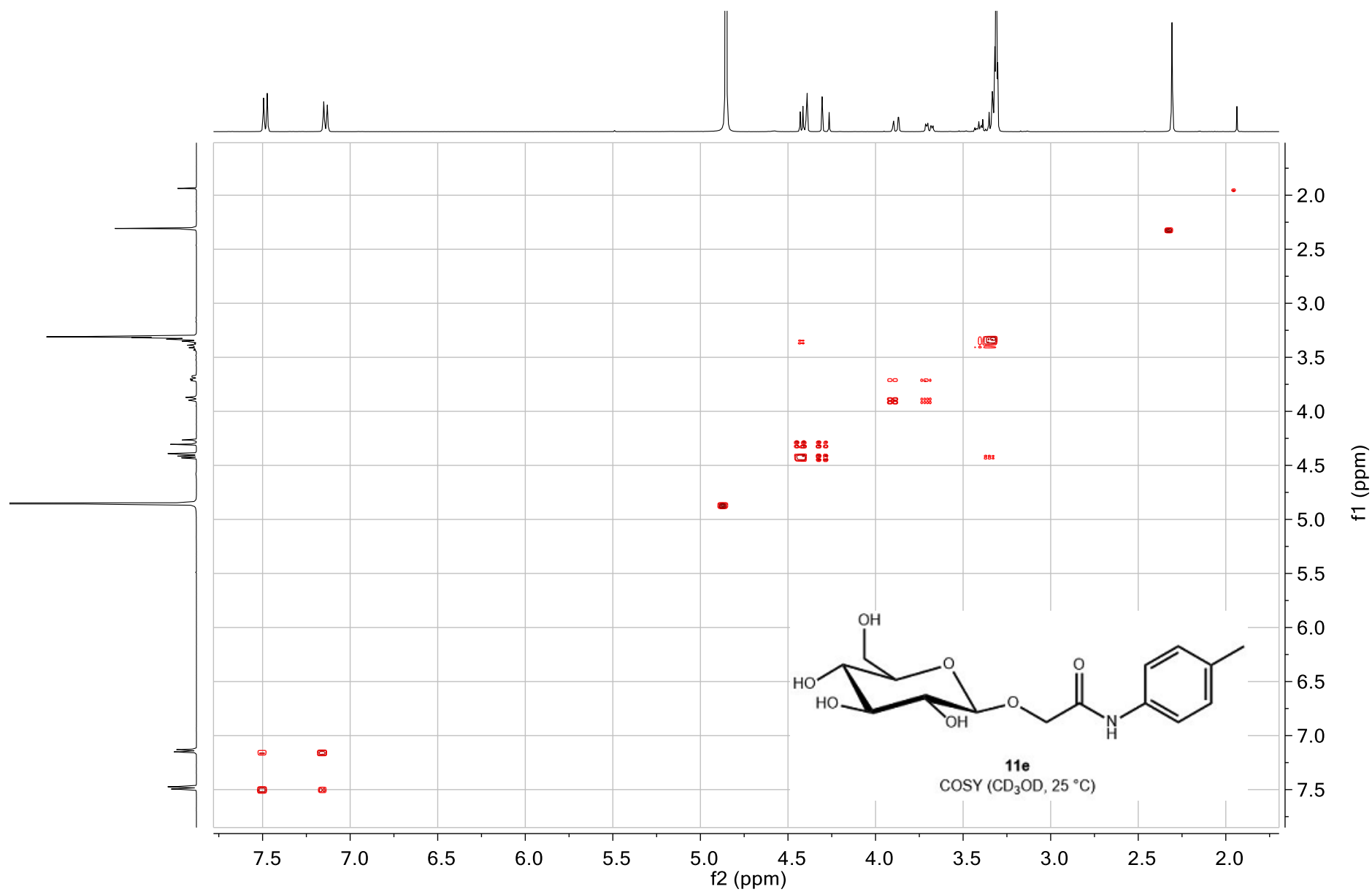


2-( $\beta$ -D-glucopyranosyloxy)-*N*-(4-methylphenyl)-acetamide (**11e**).

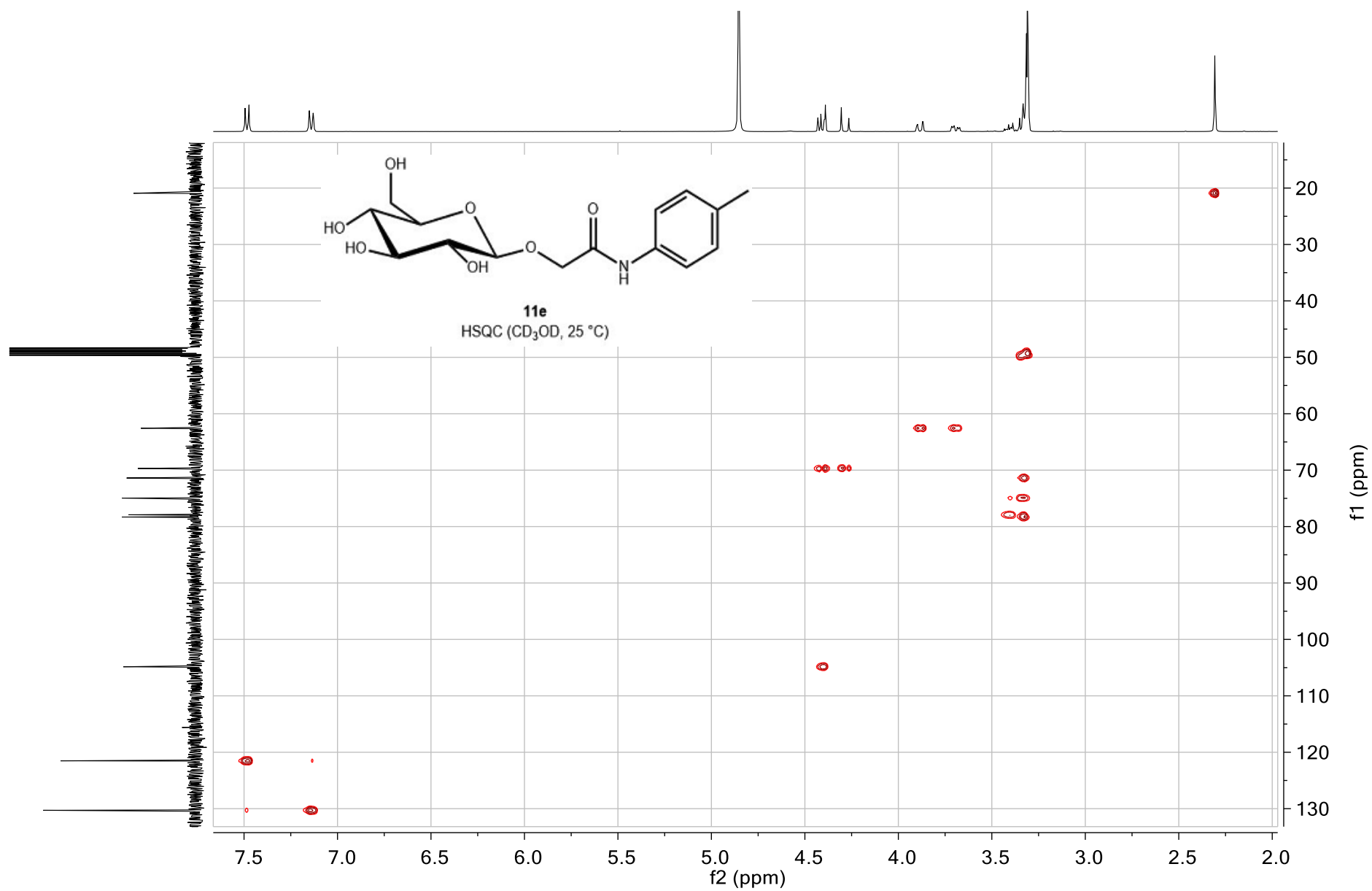


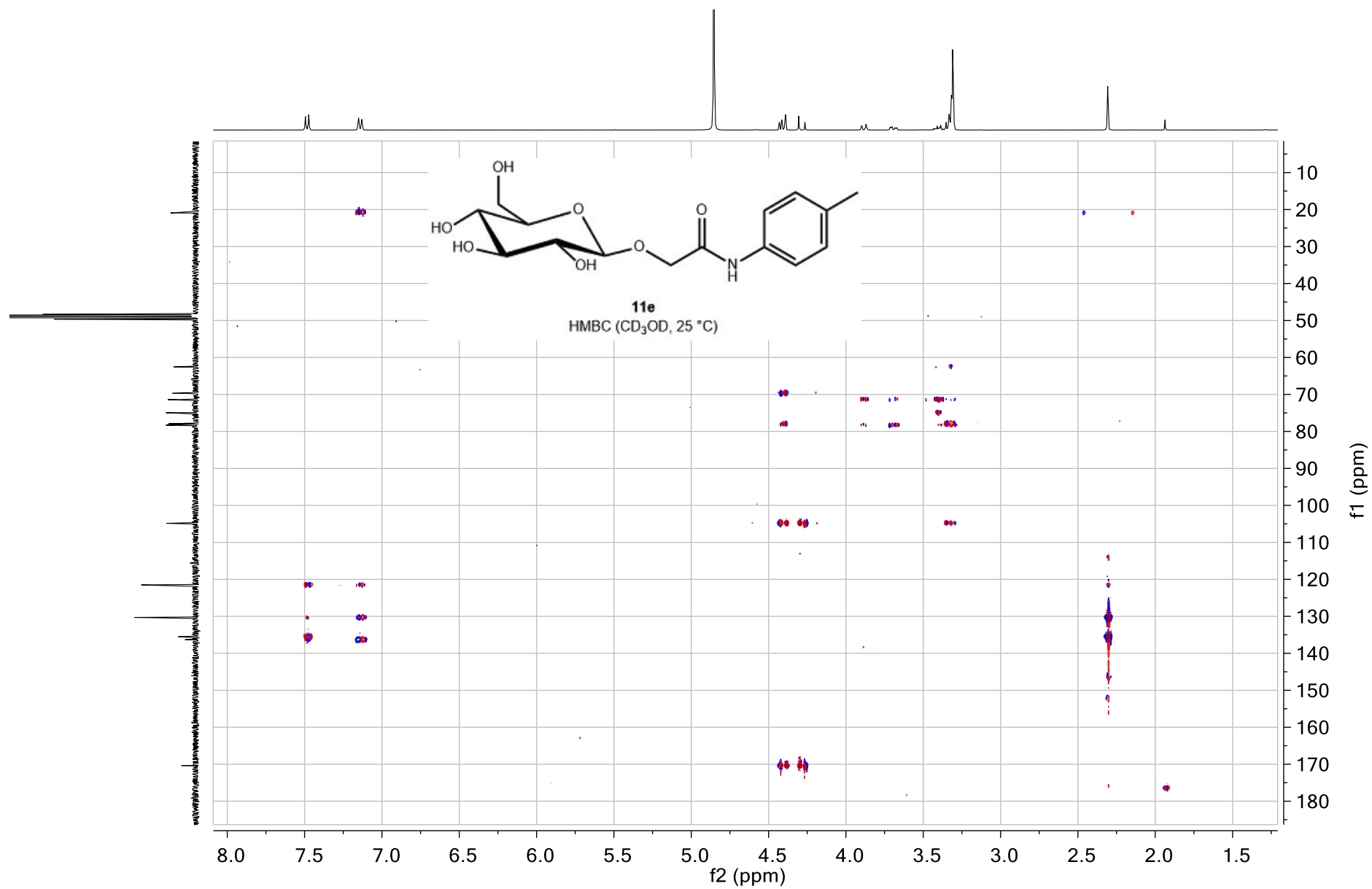




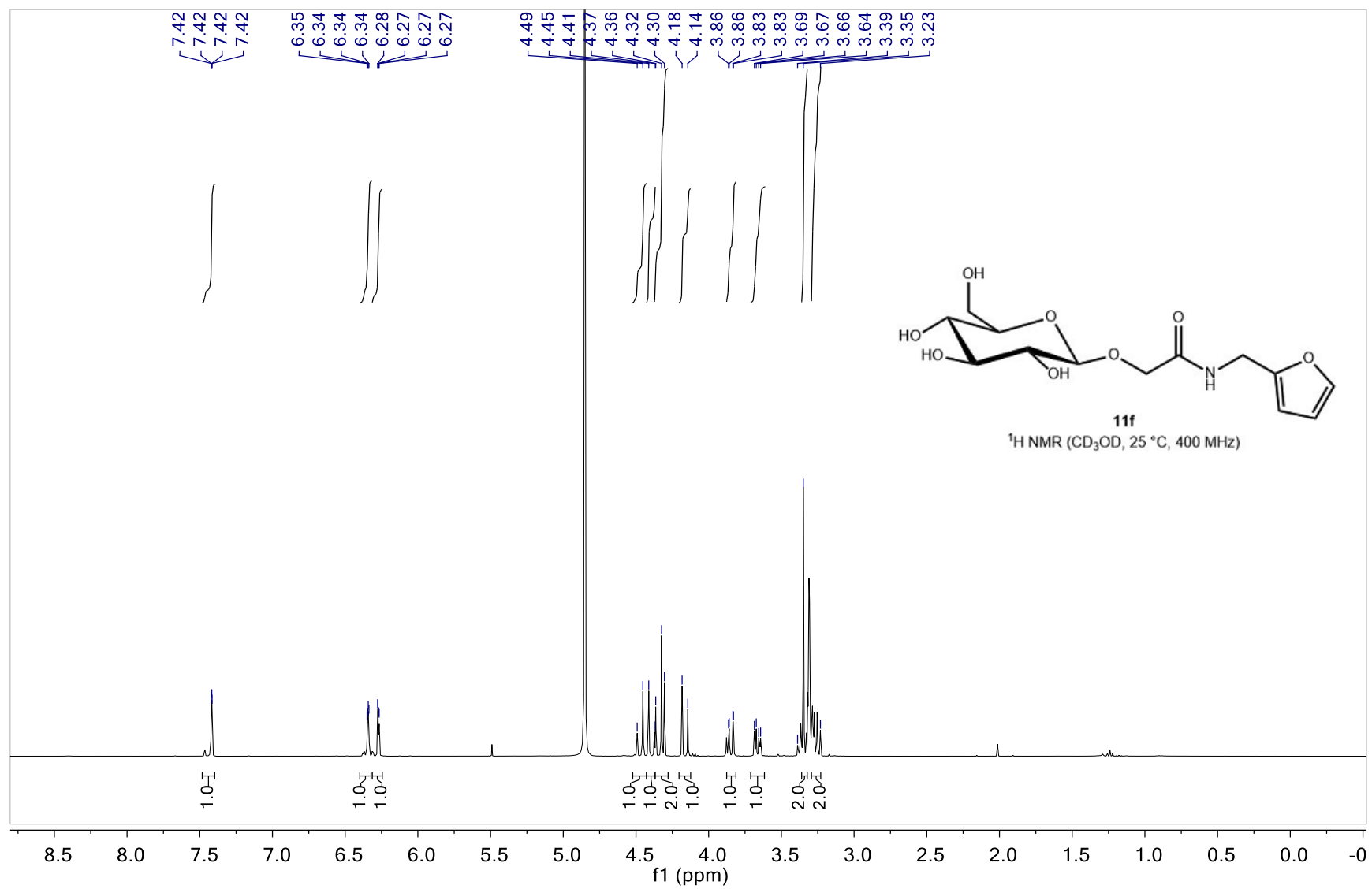


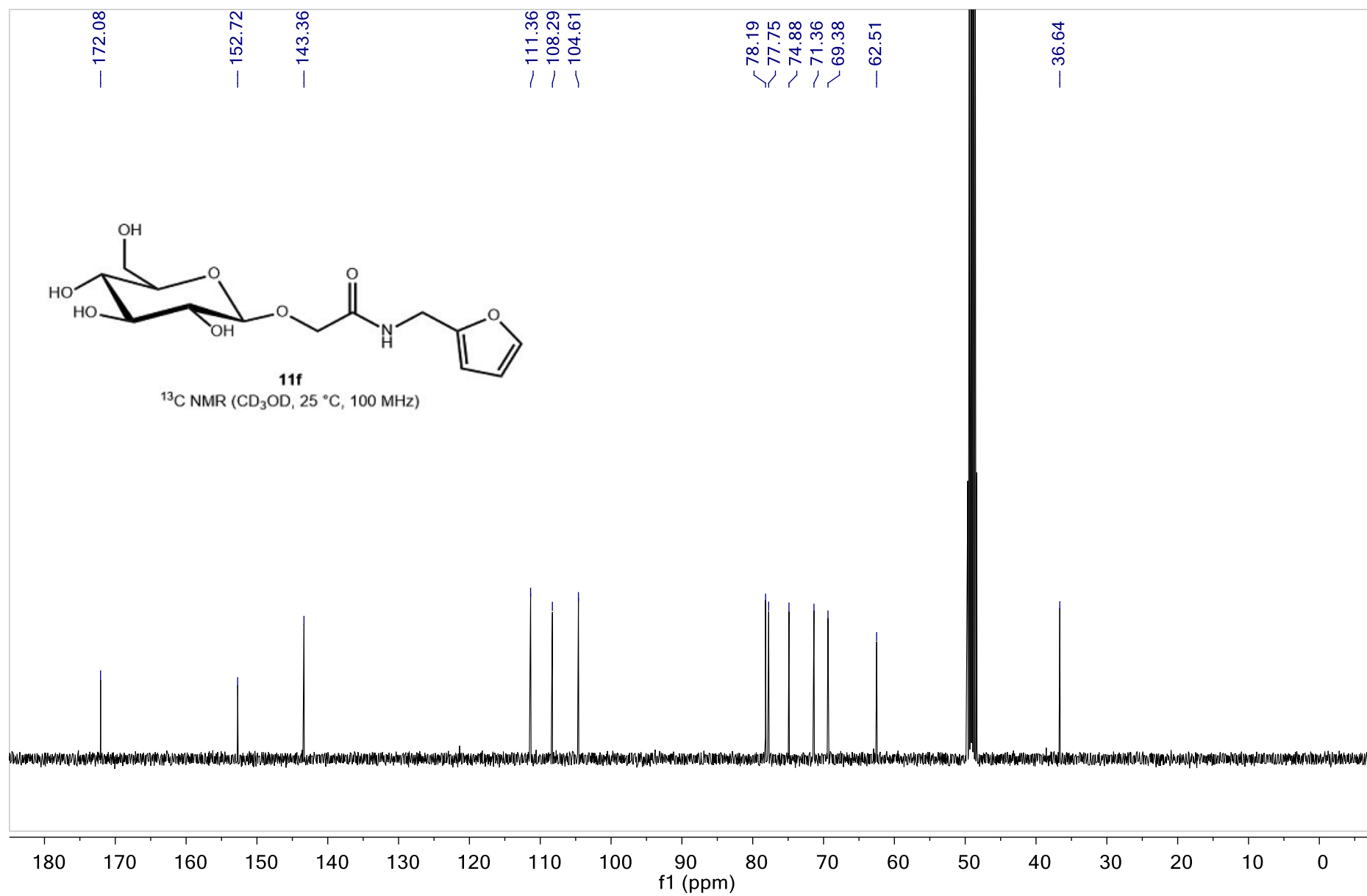


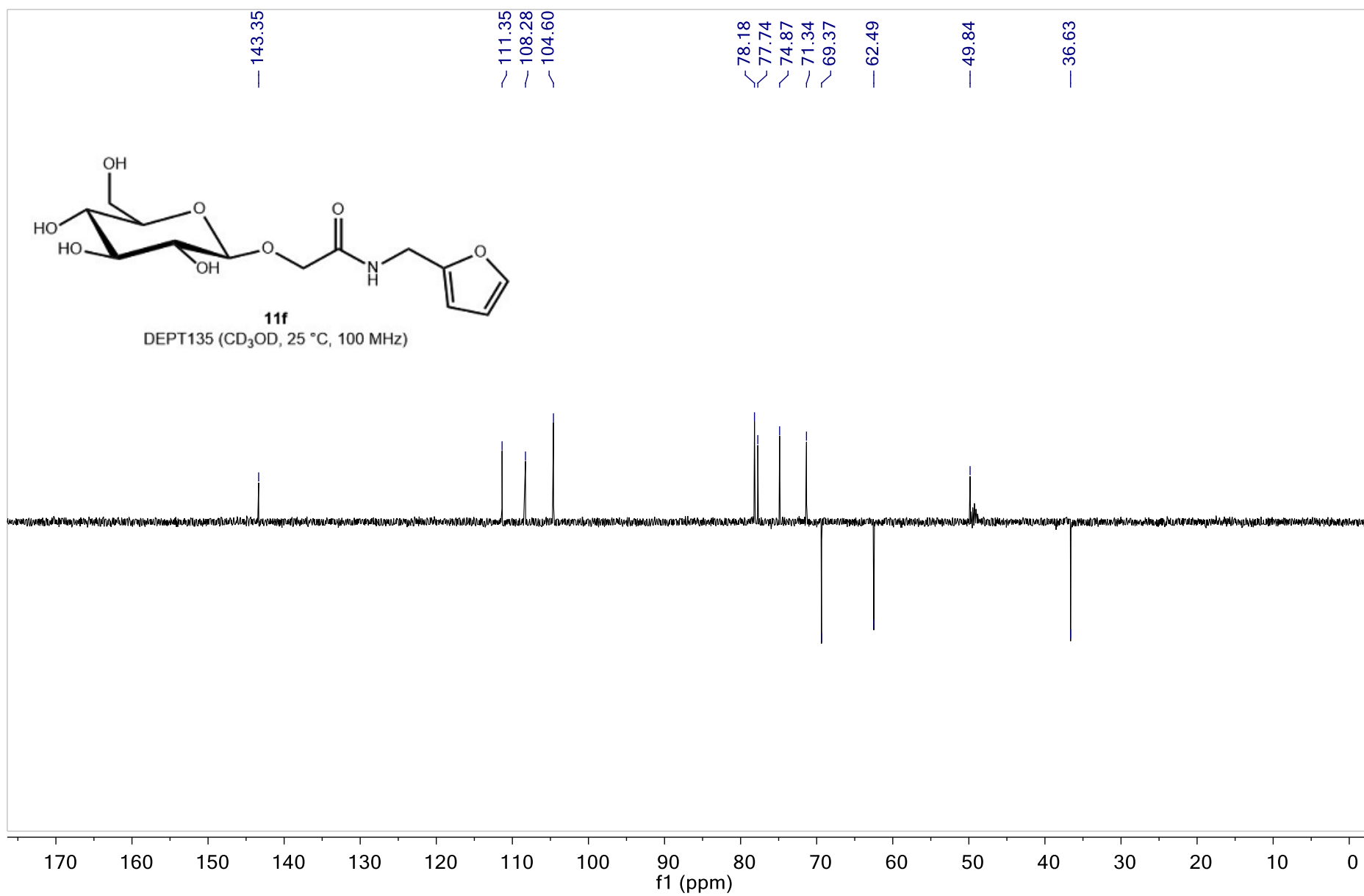


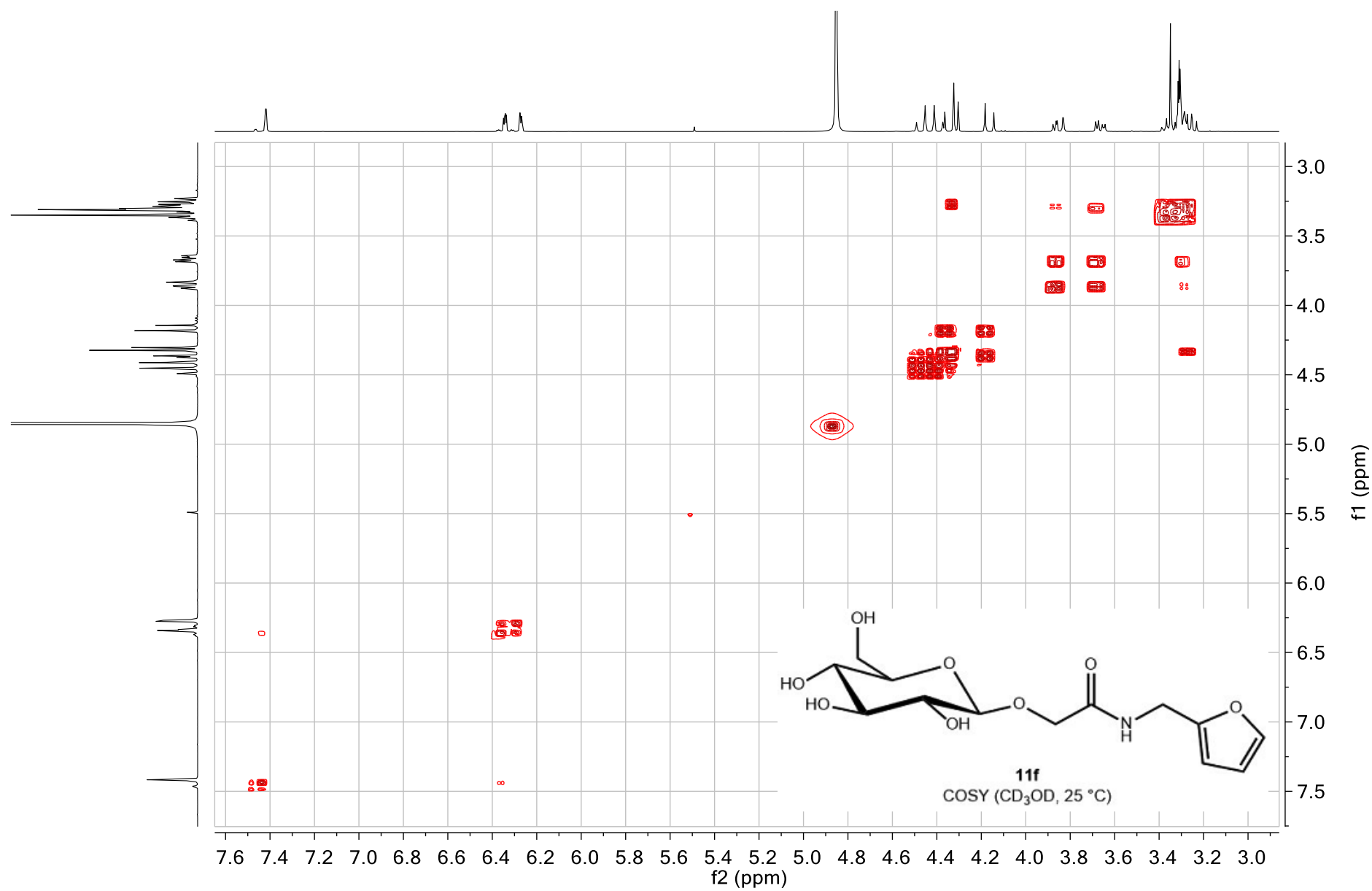


**2-( $\beta$ -D-glucopyranosyloxy)-N-(2-Furanylmethyl)-acetamide (11f).**

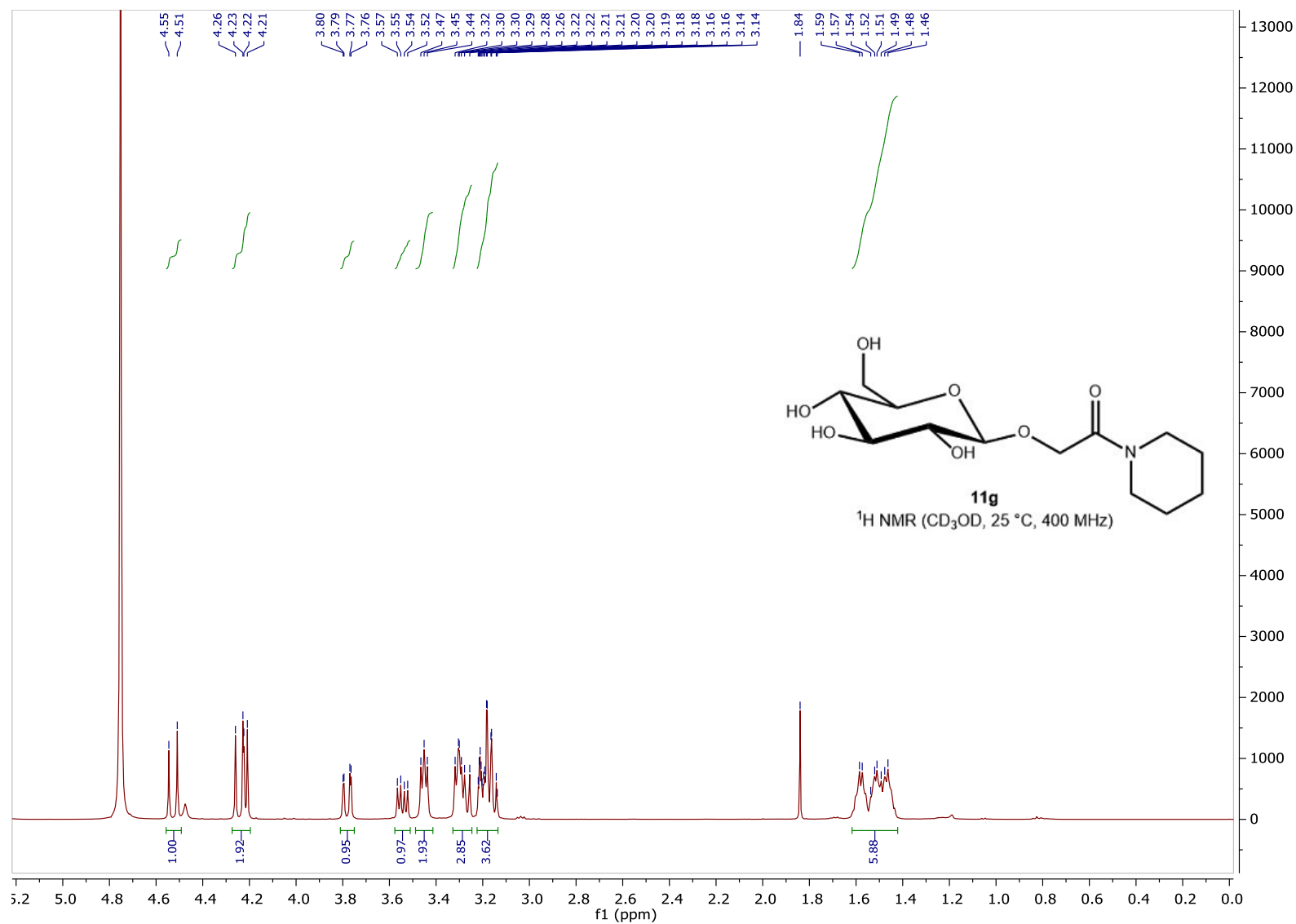


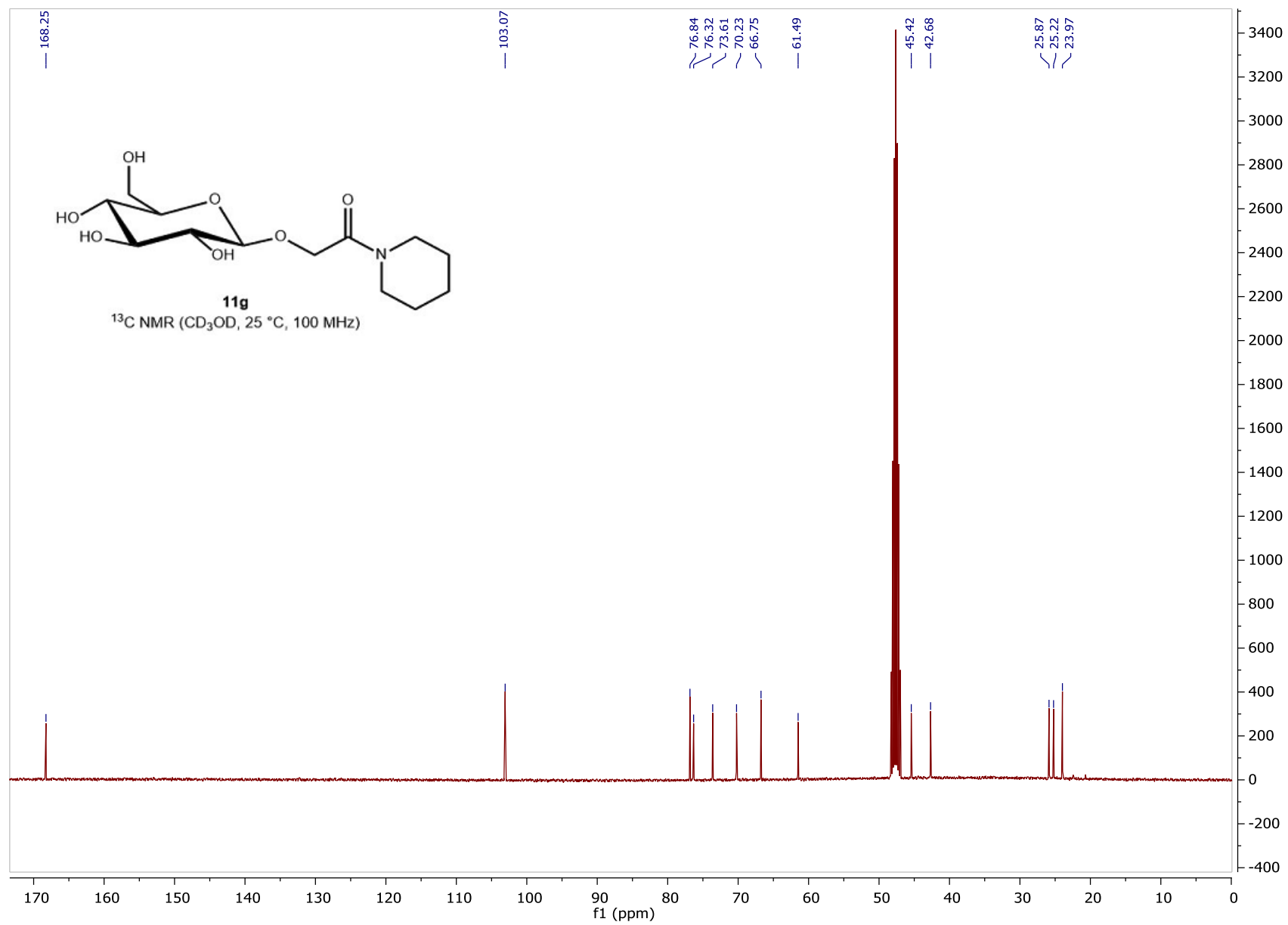






**2-( $\beta$ -D-glucopyranosyloxy)-1-(piperidin-1-yl)-acetamide (11g).**

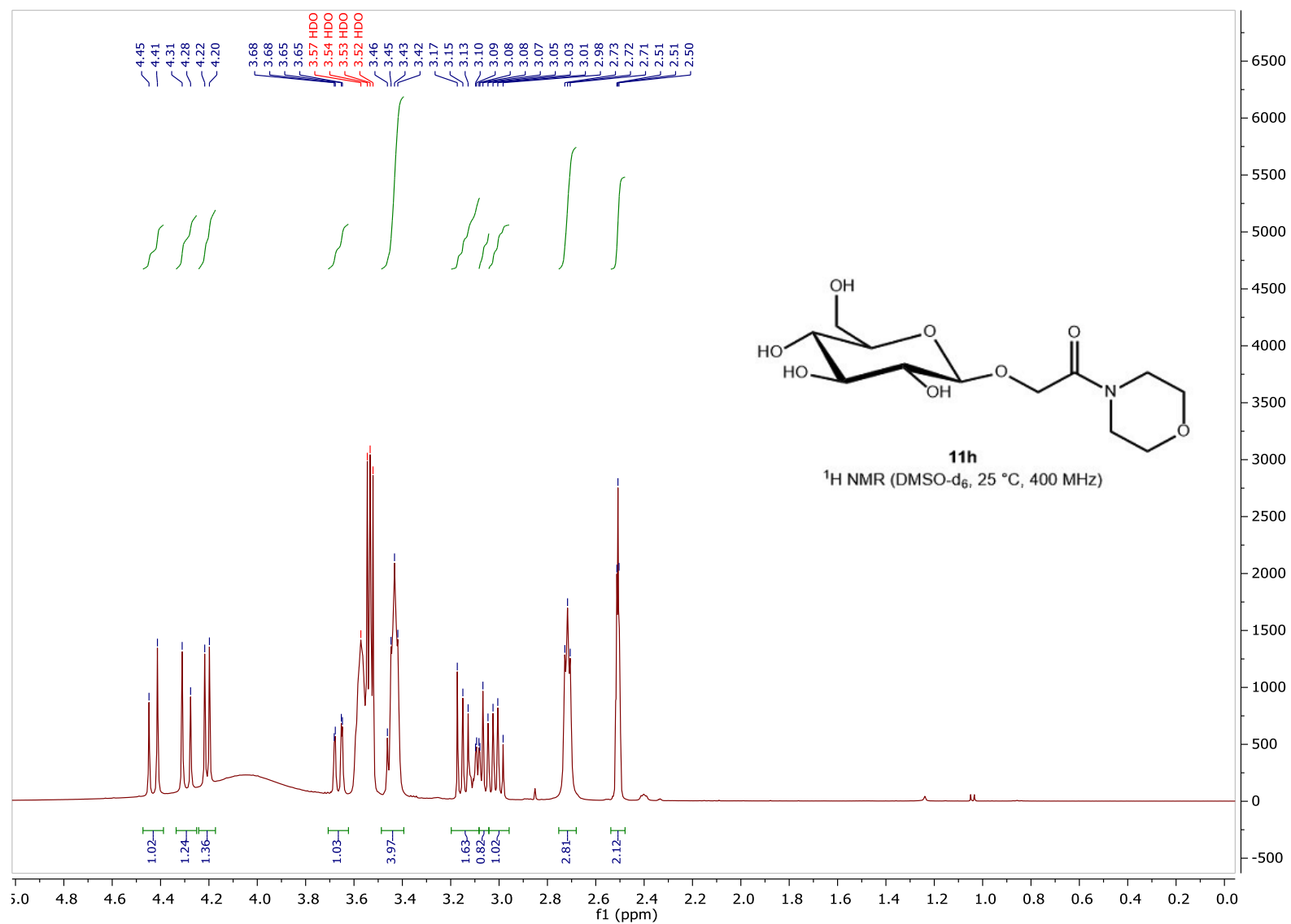


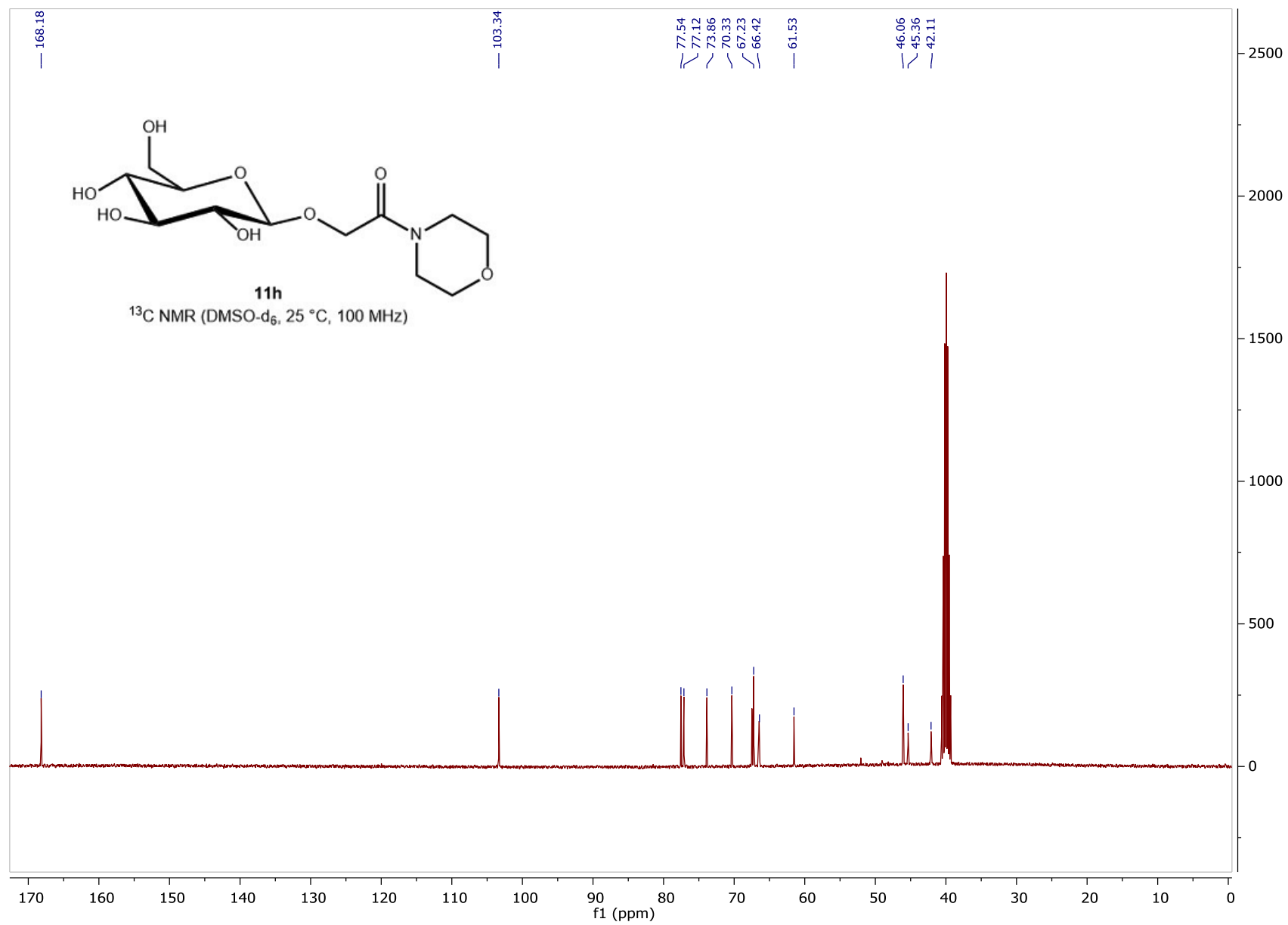


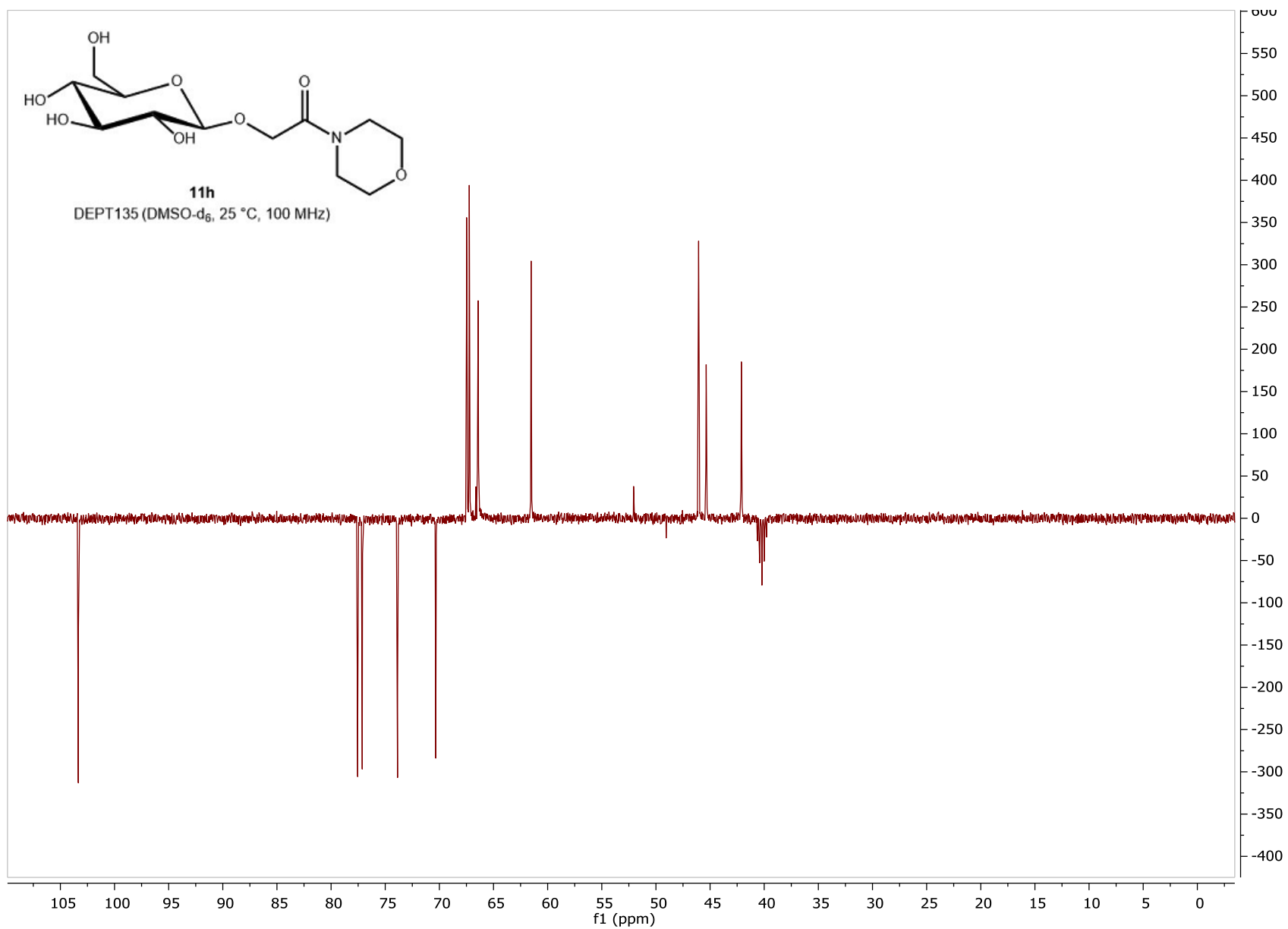




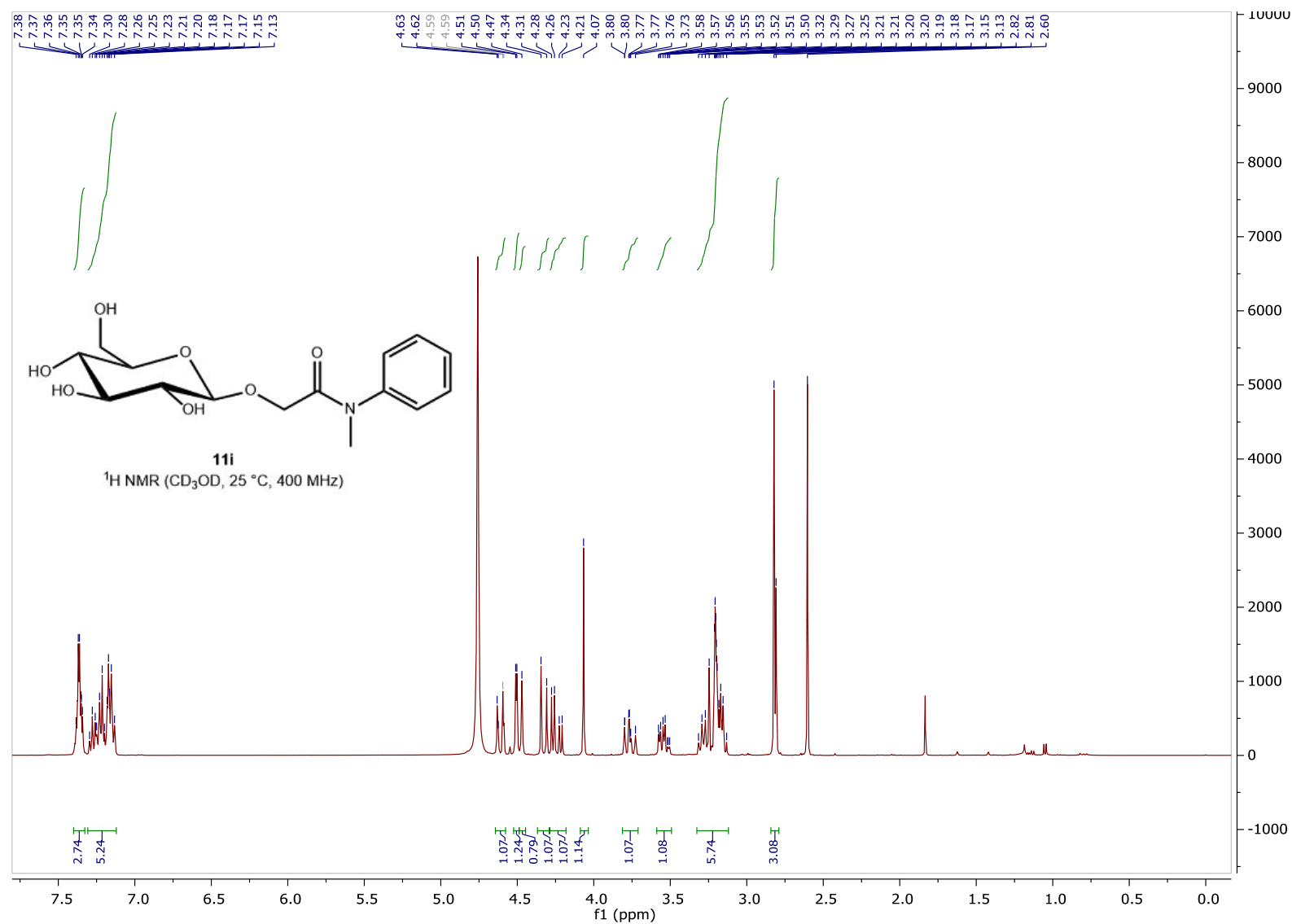
**2-( $\beta$ -D-glucopyranosyloxy)-1-morpholino-acetamide (11h).**

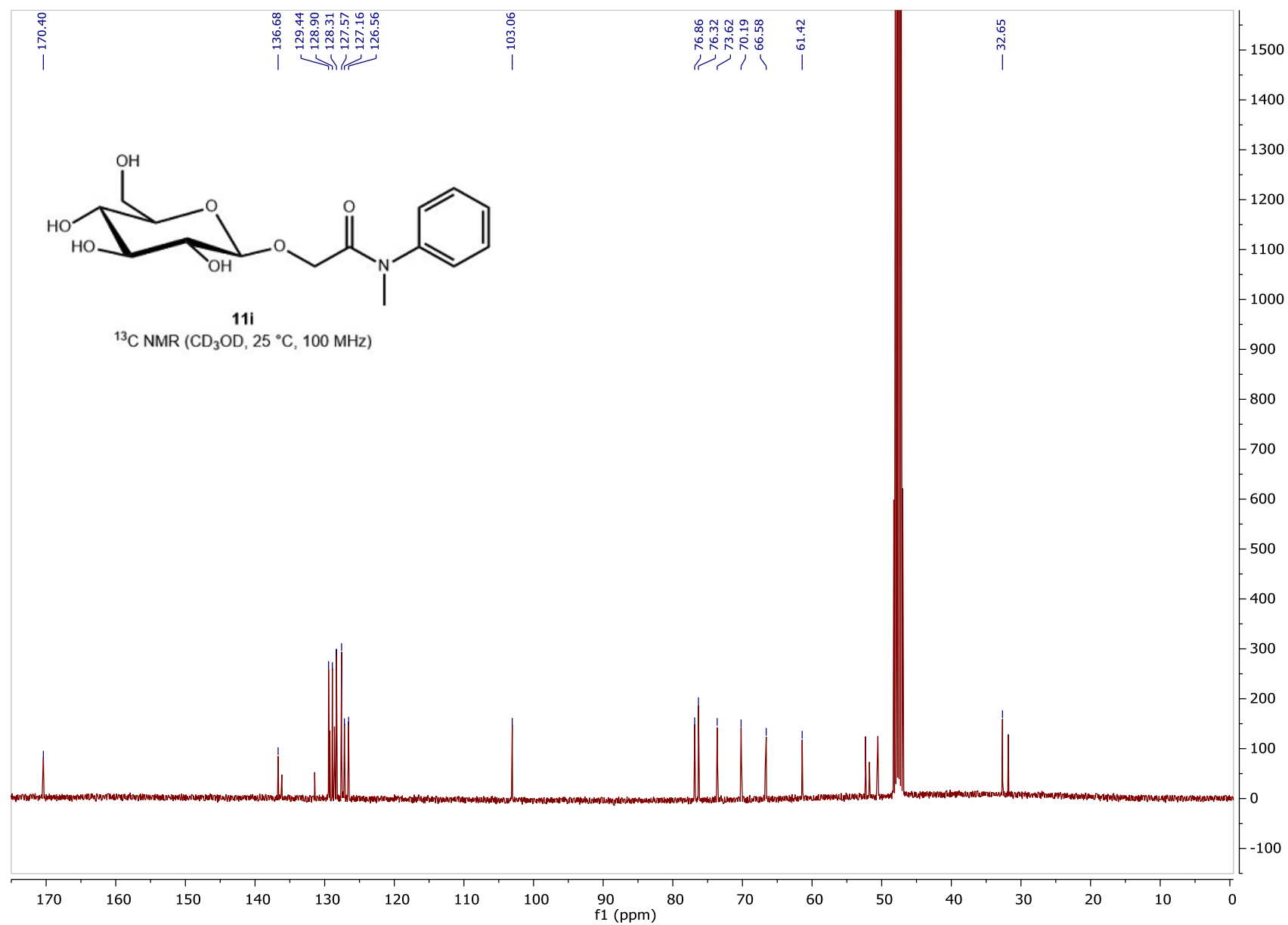




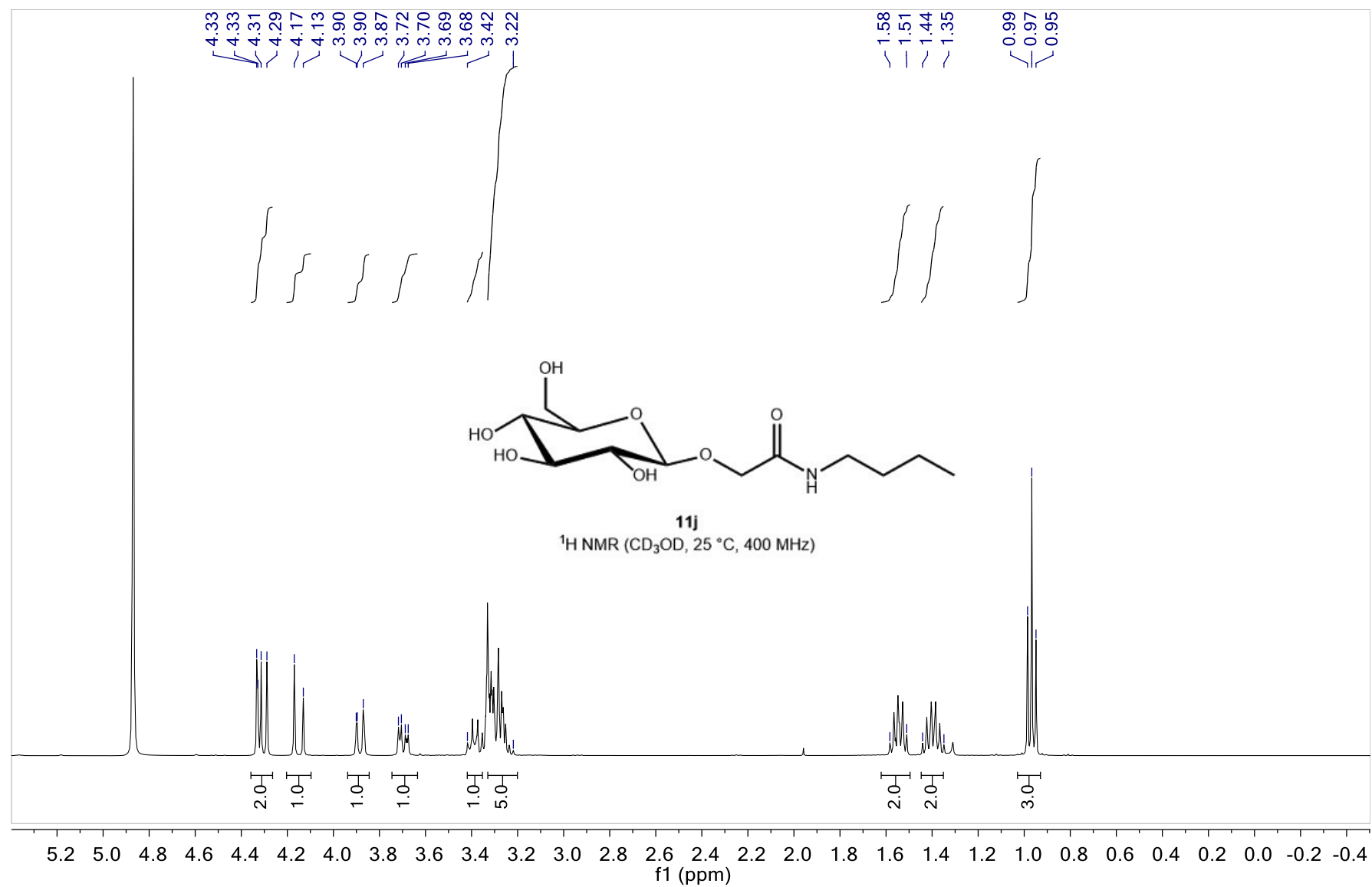


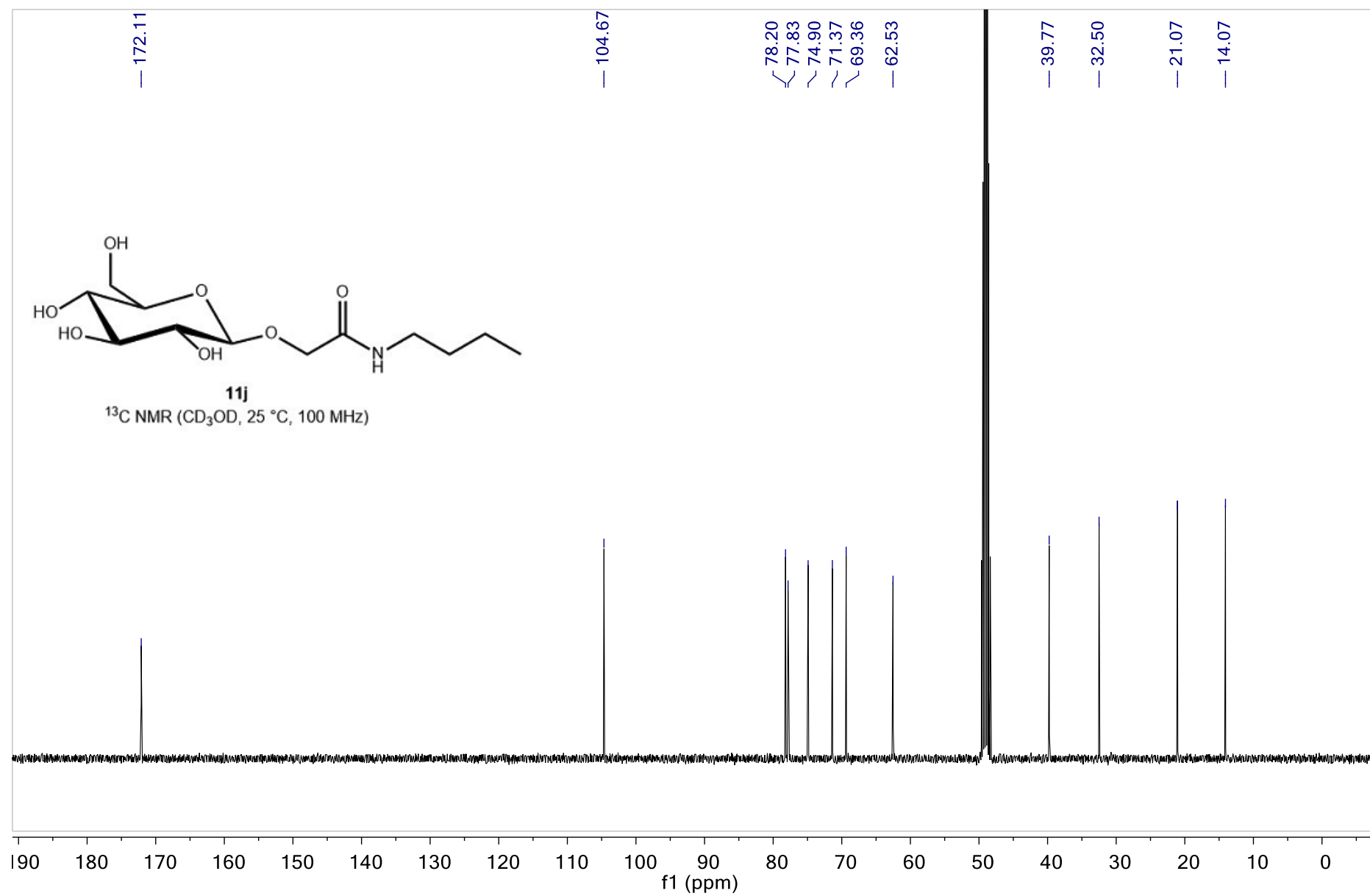
**2-( $\beta$ -D-Glucopyranosyloxy)-*N*-phenylaniline-acetamide (11i).**



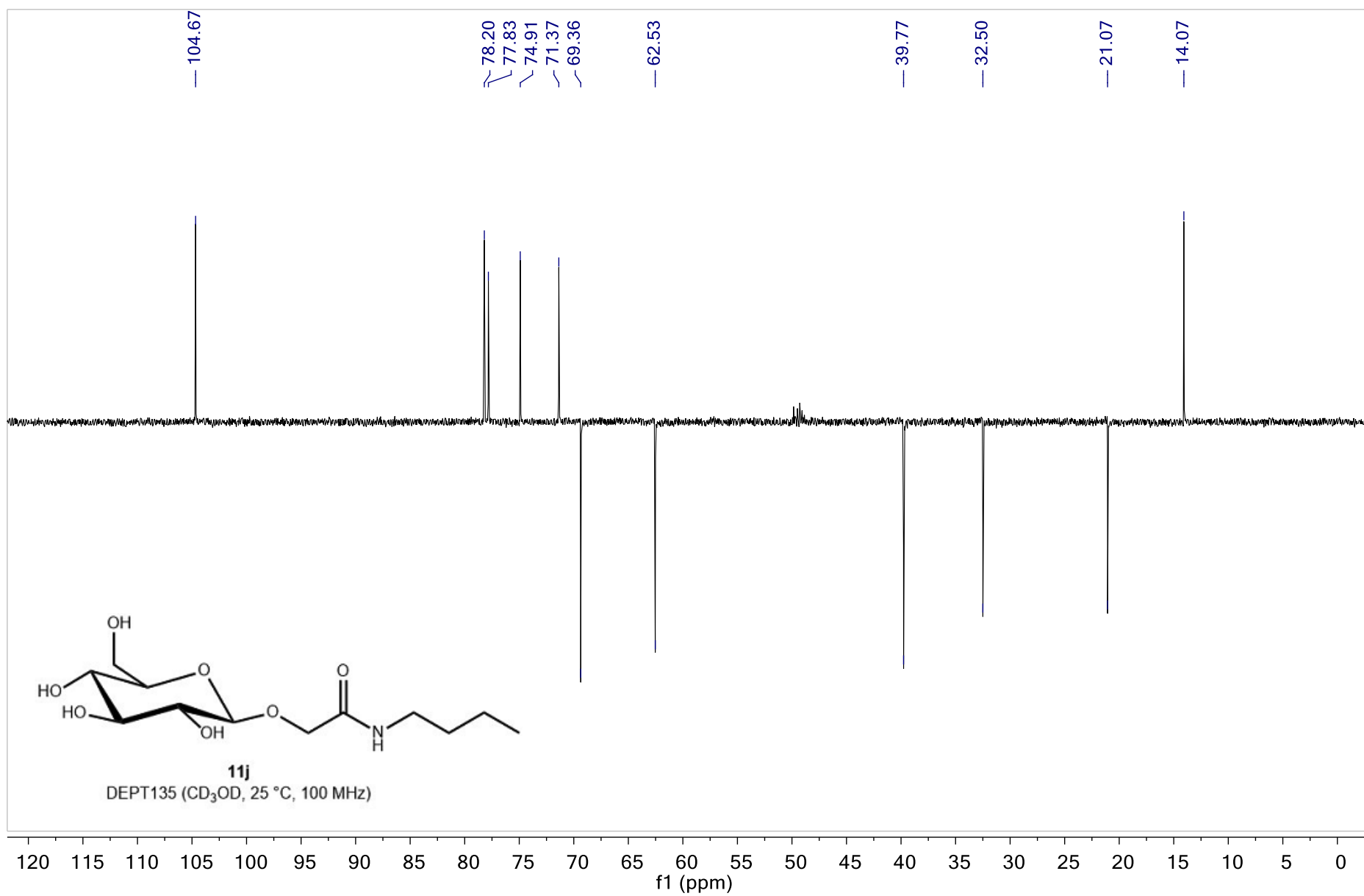


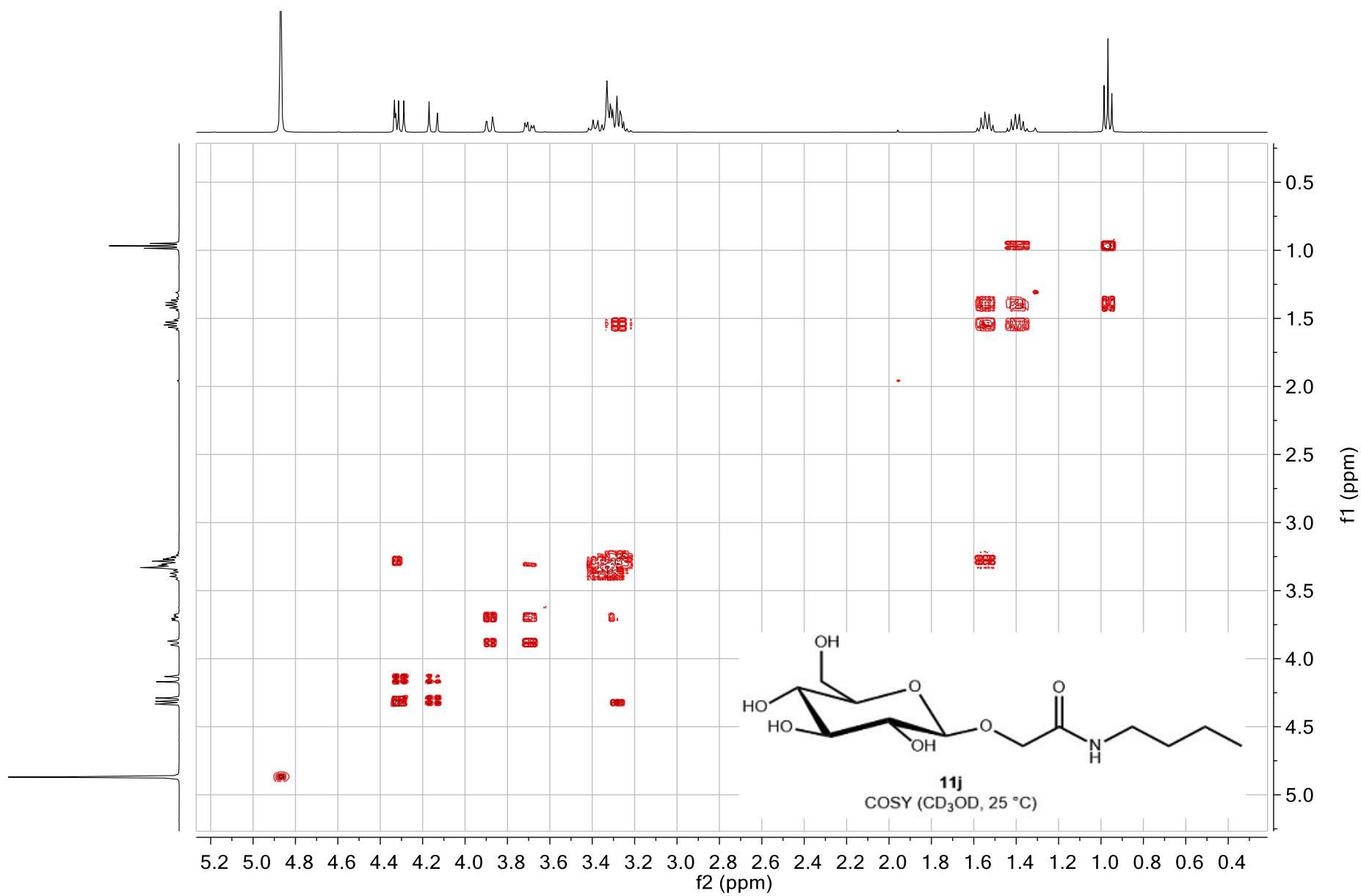
***N*-Butyl-2-( $\beta$ -D-glucopyranosyloxy)-acetamide (**11j**).**

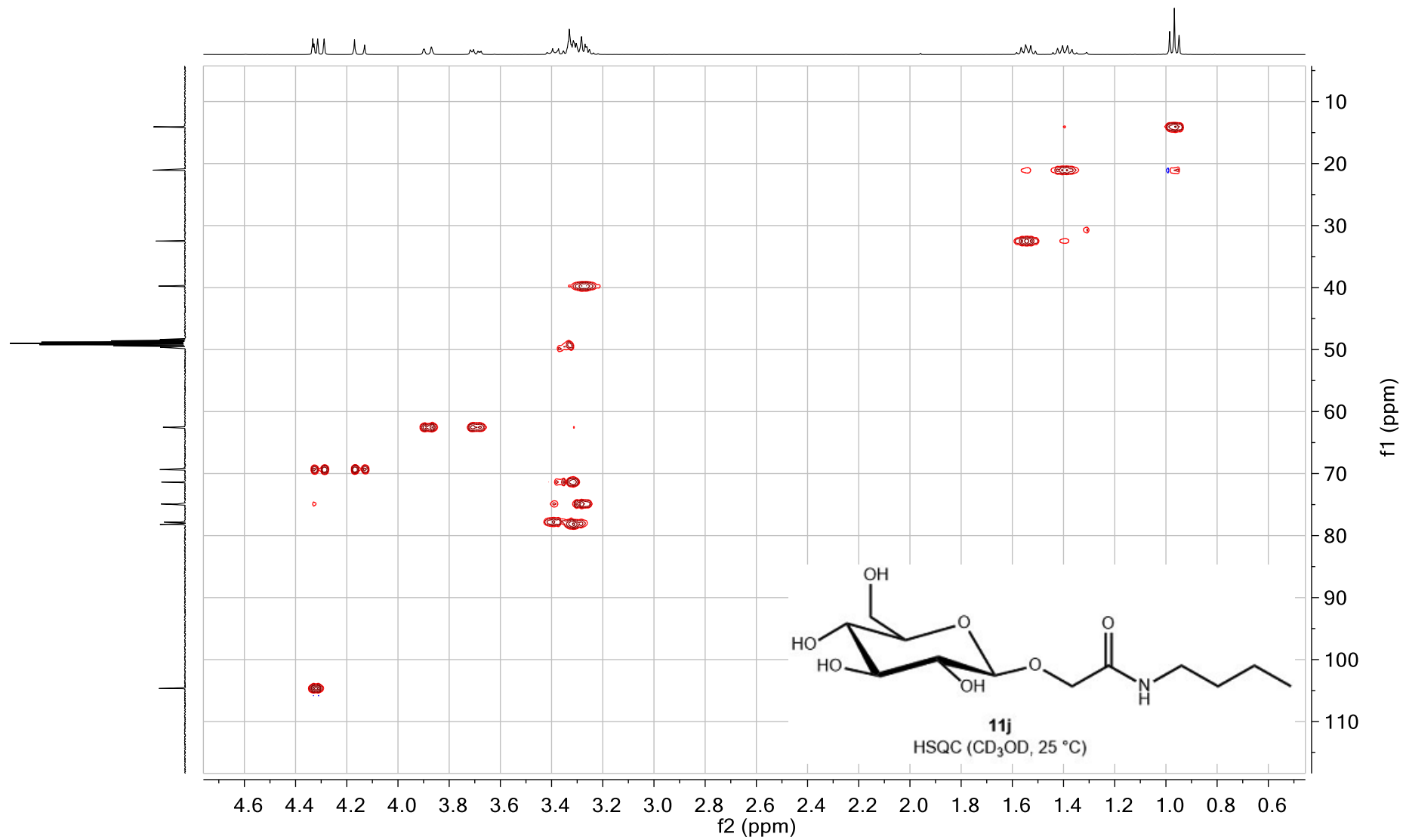


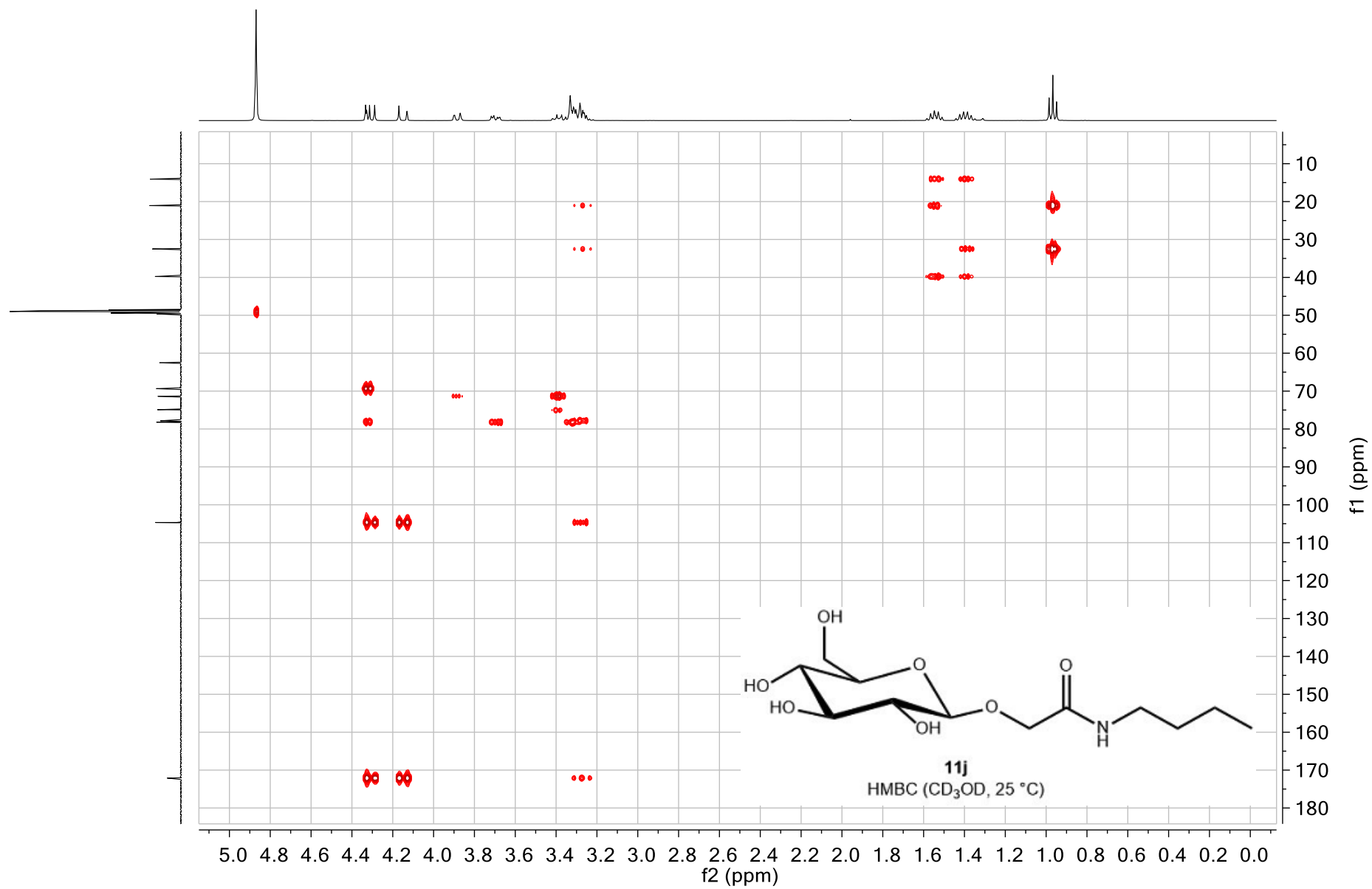




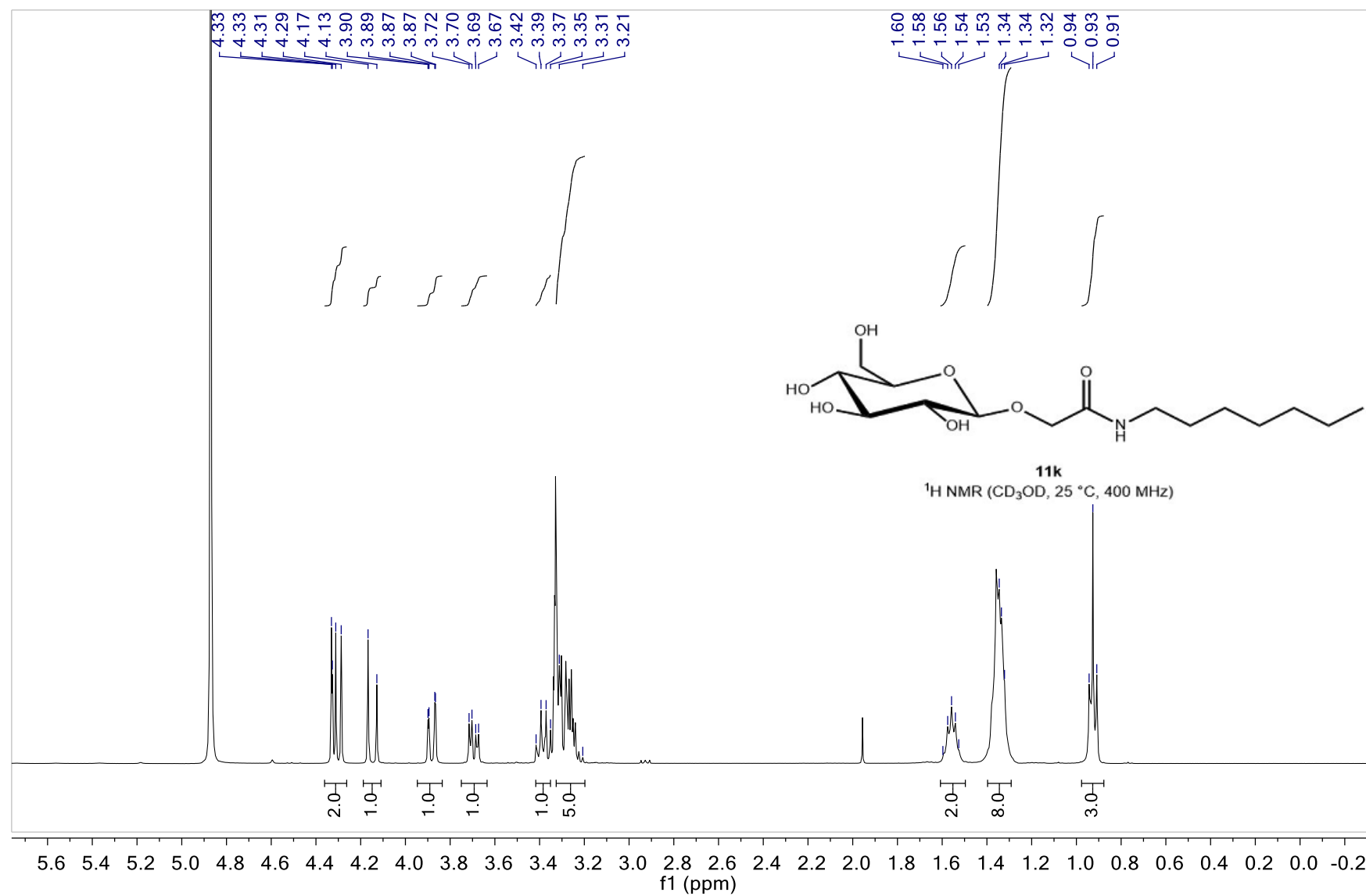


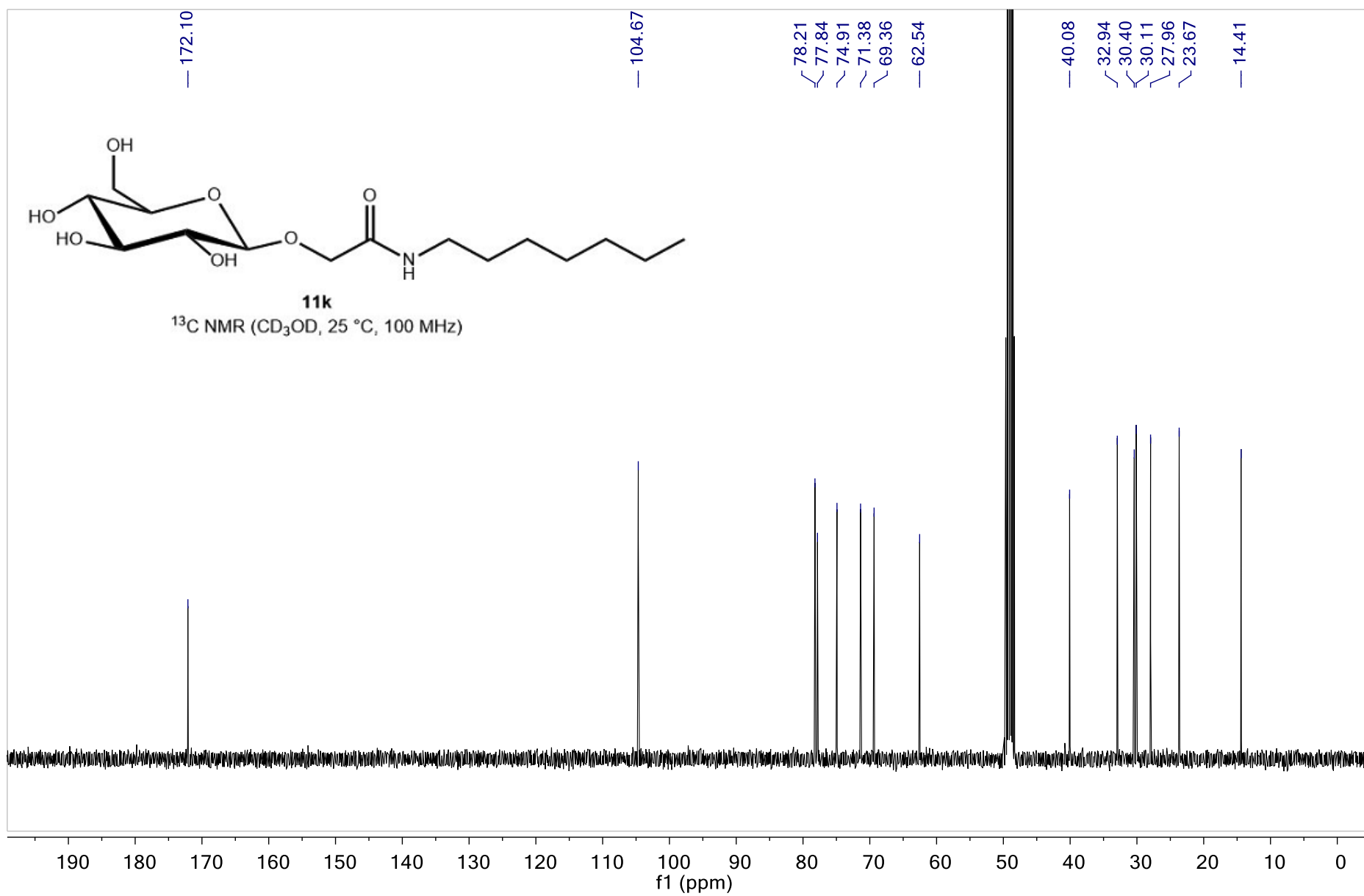


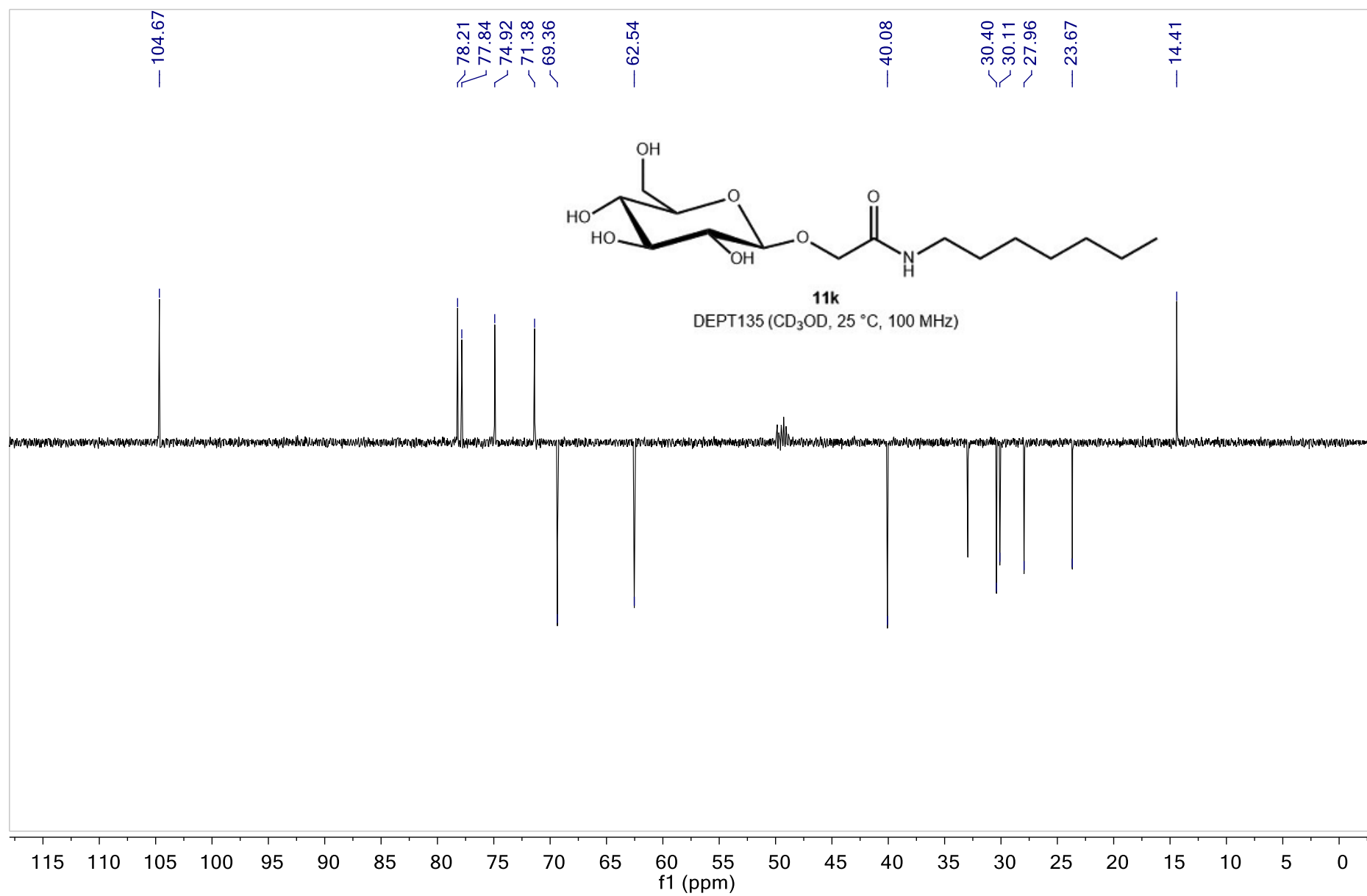


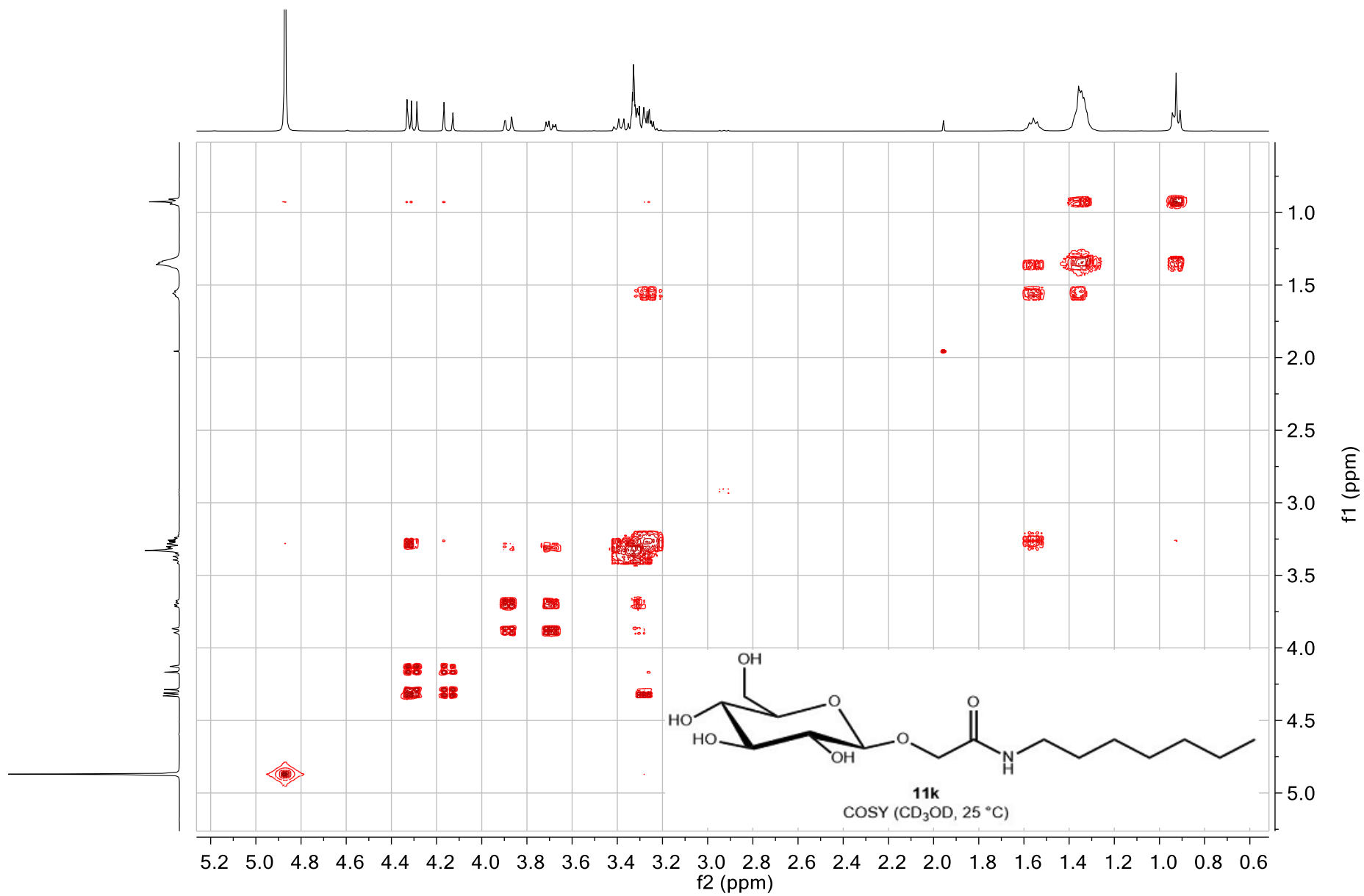


2-( $\beta$ -D-Glucopyranosyloxy)-*N*-heptyl-acetamide (**11k**).

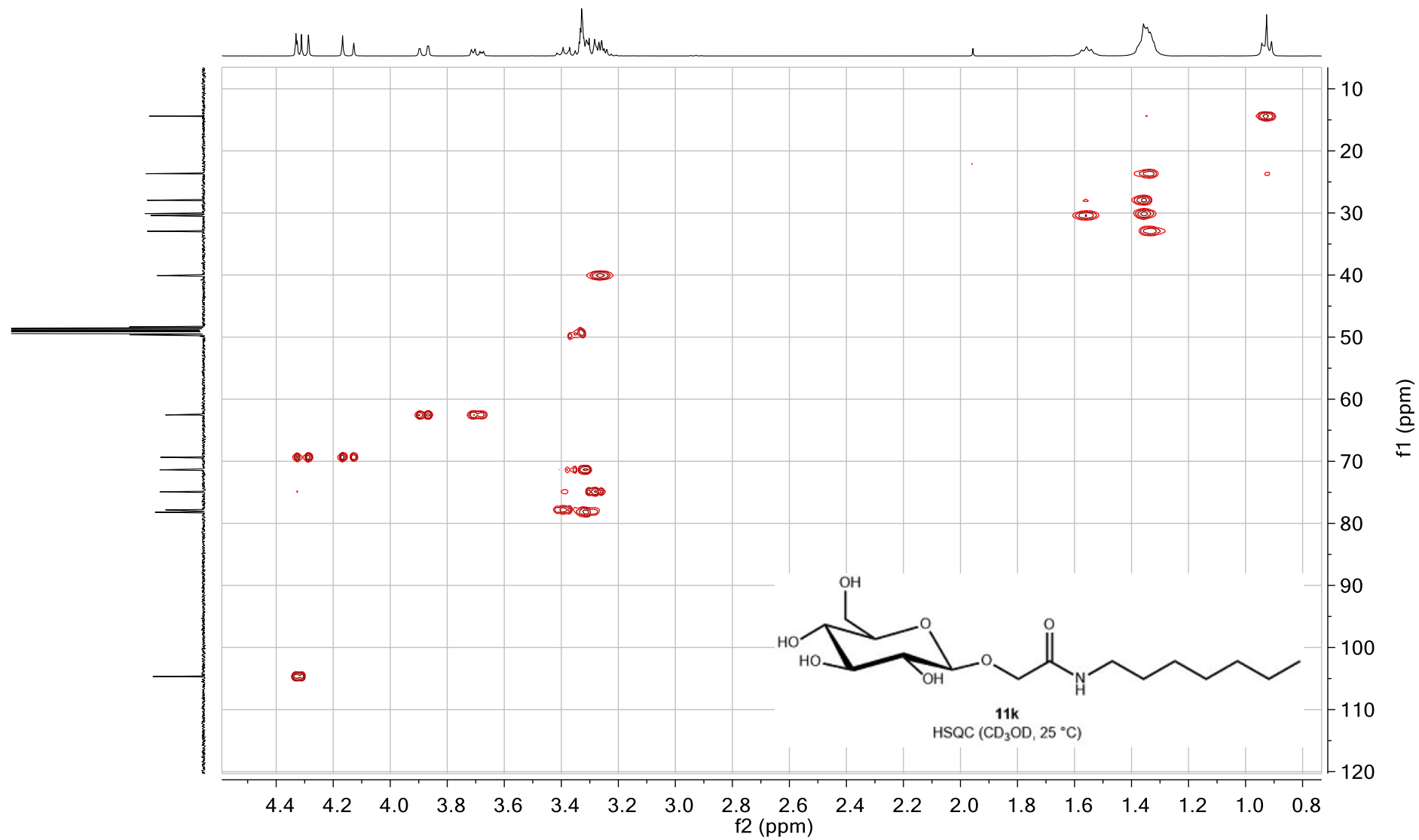


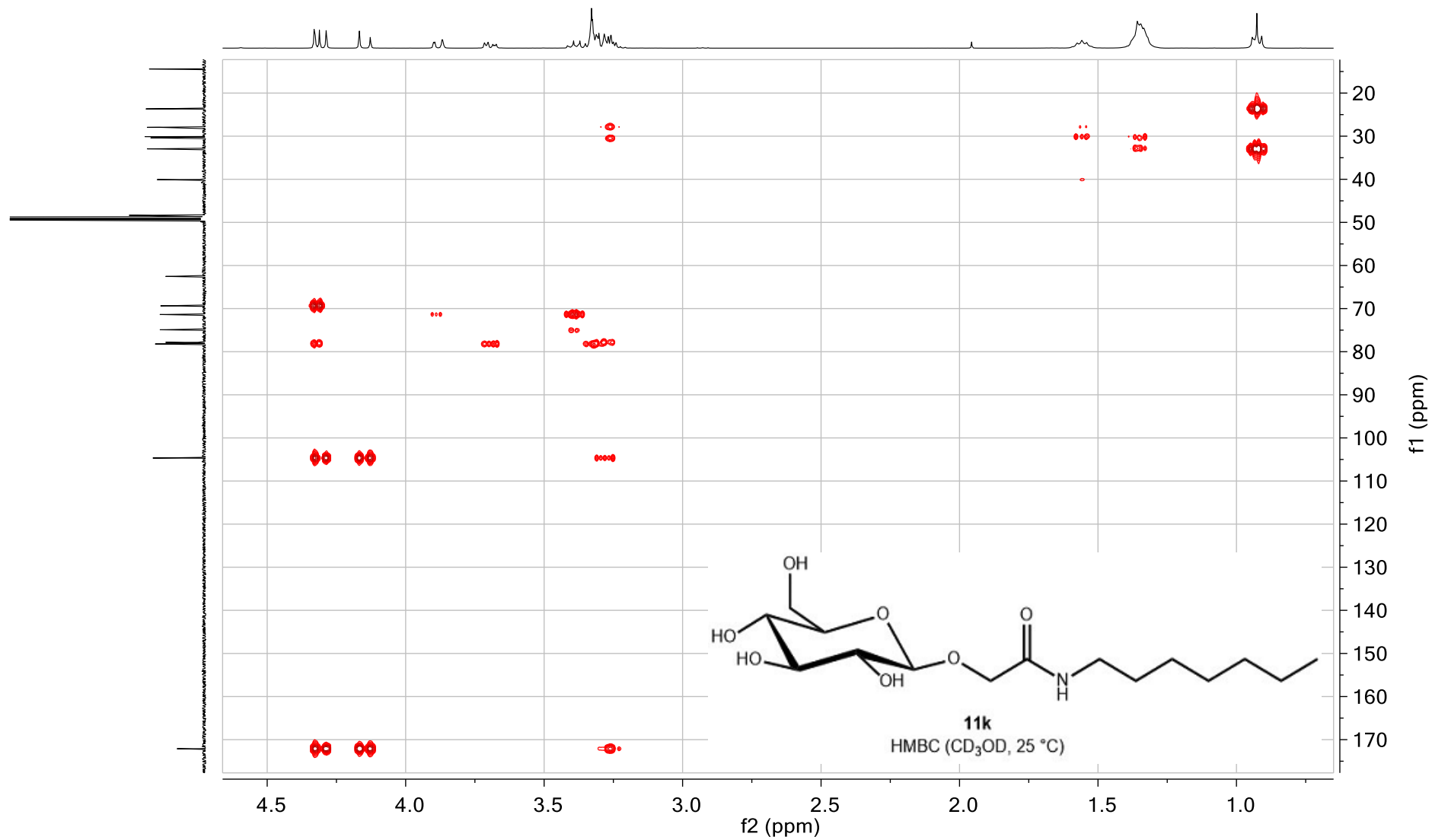




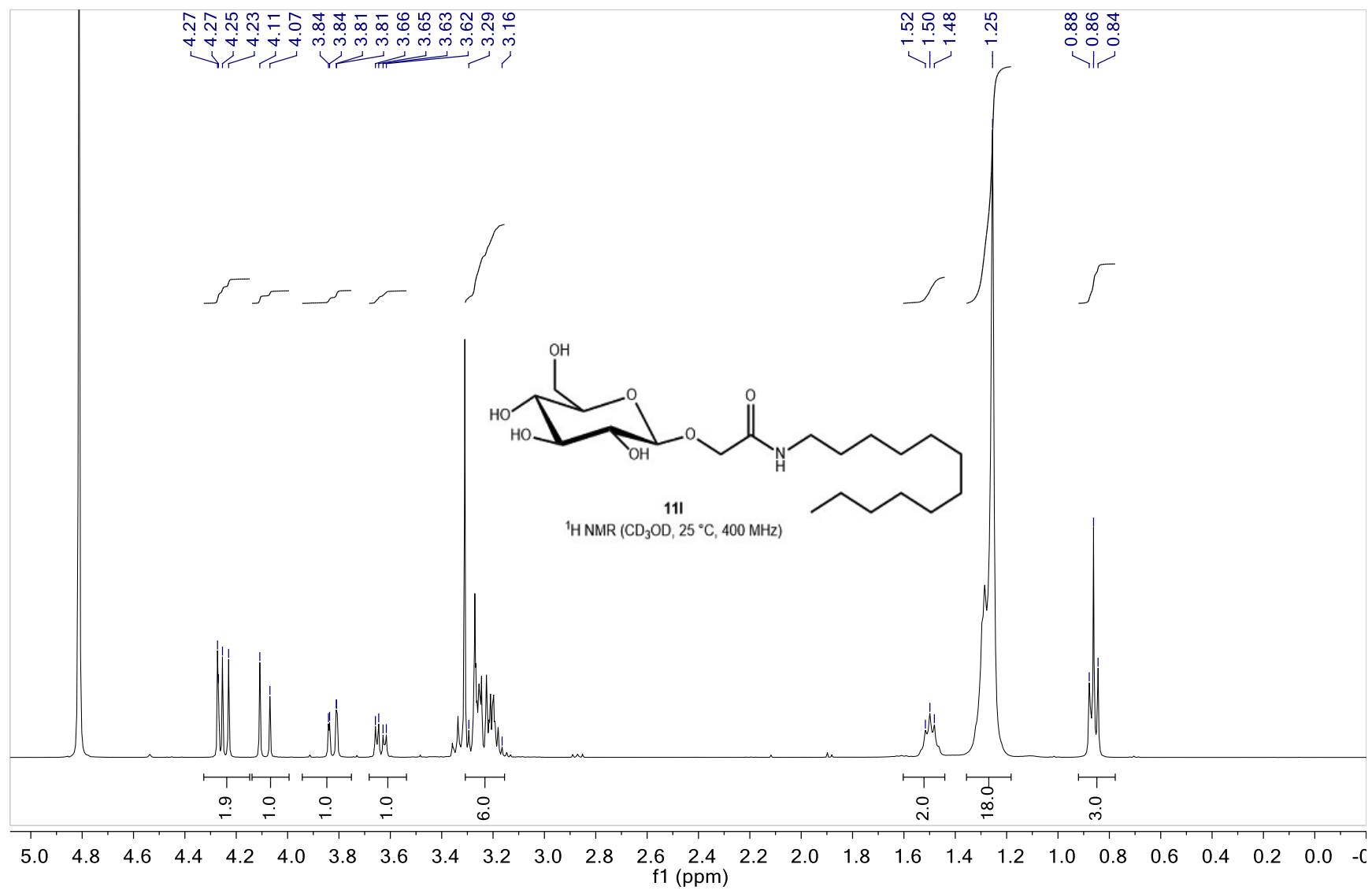


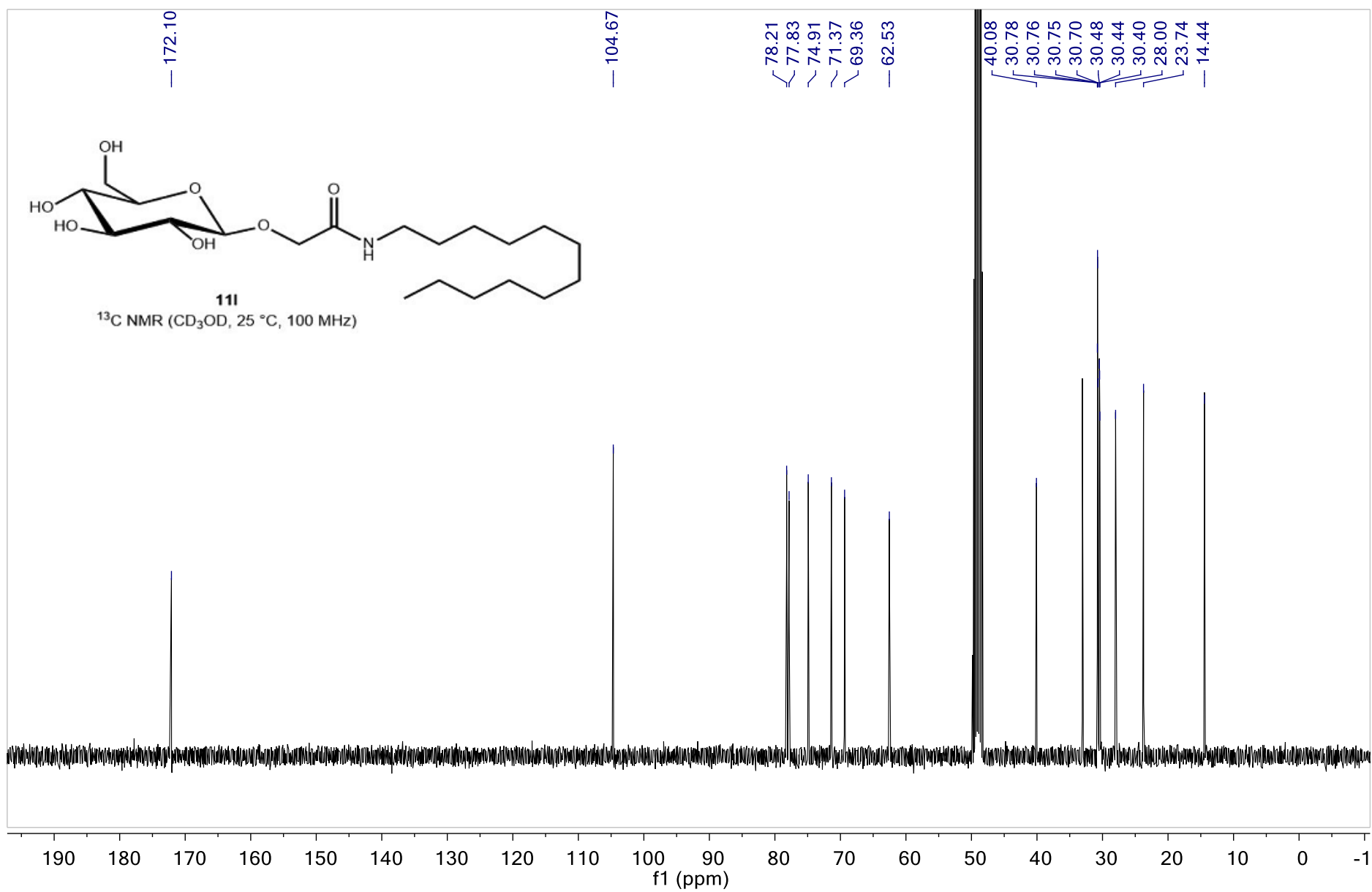


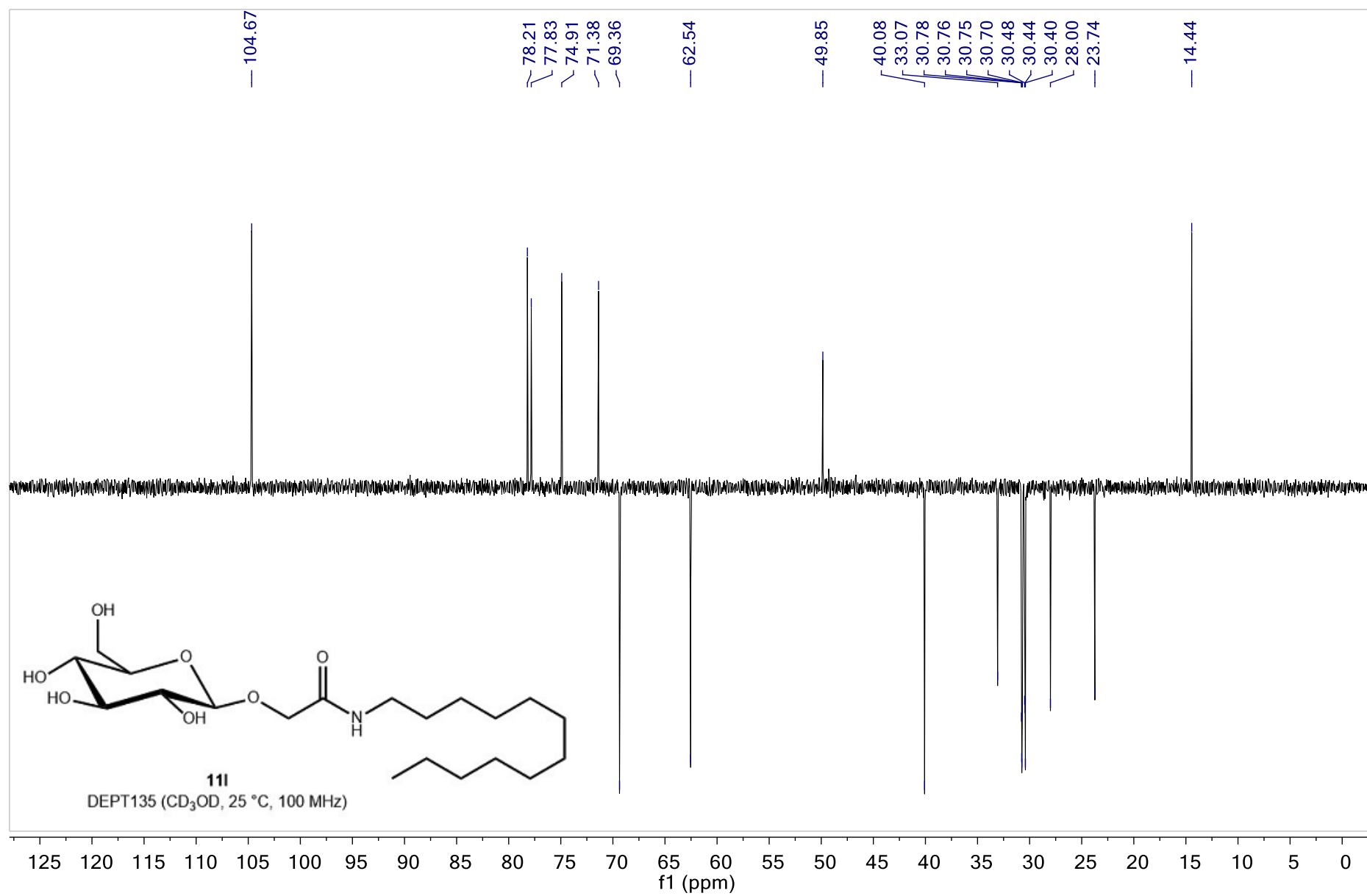


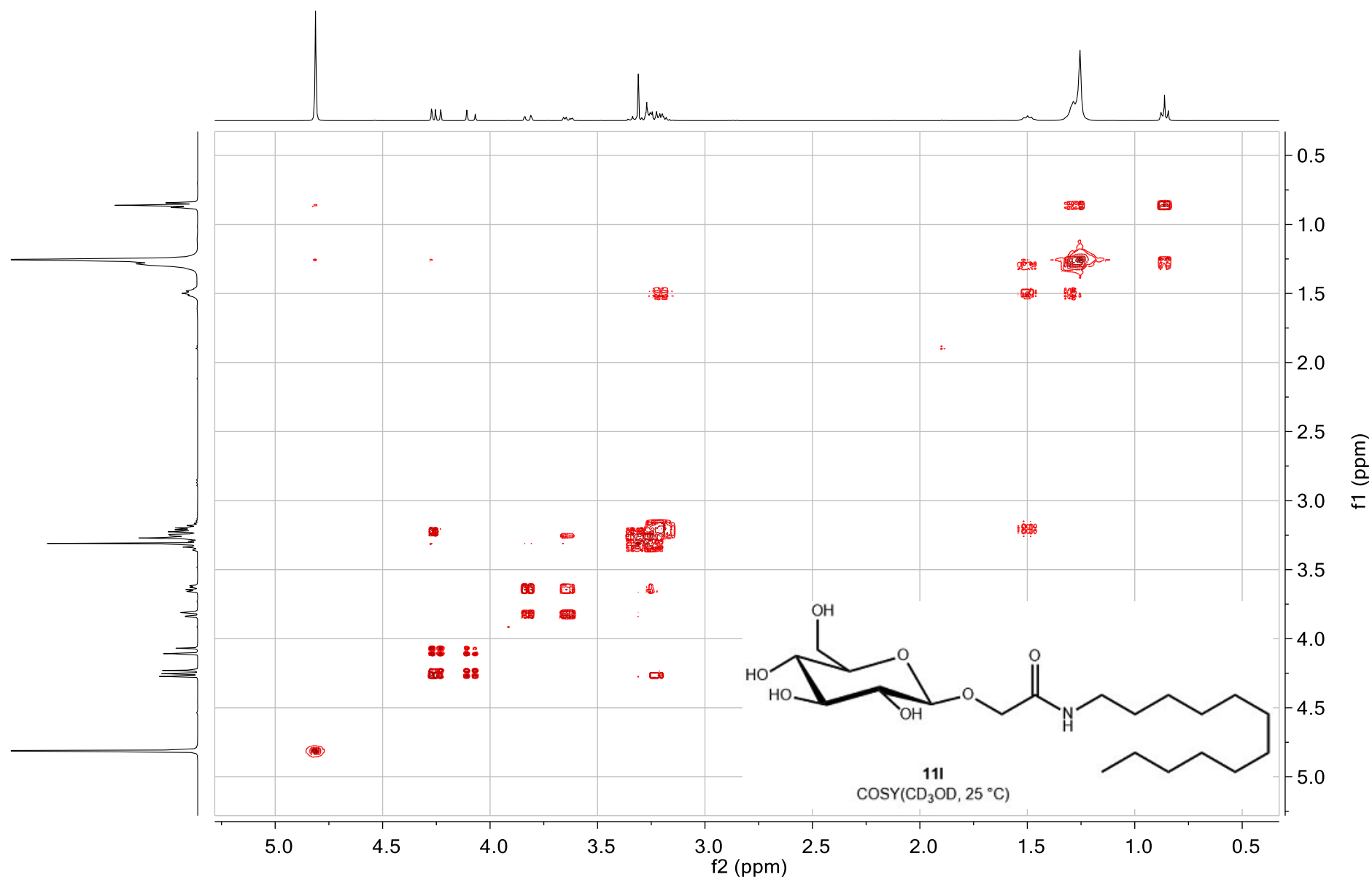


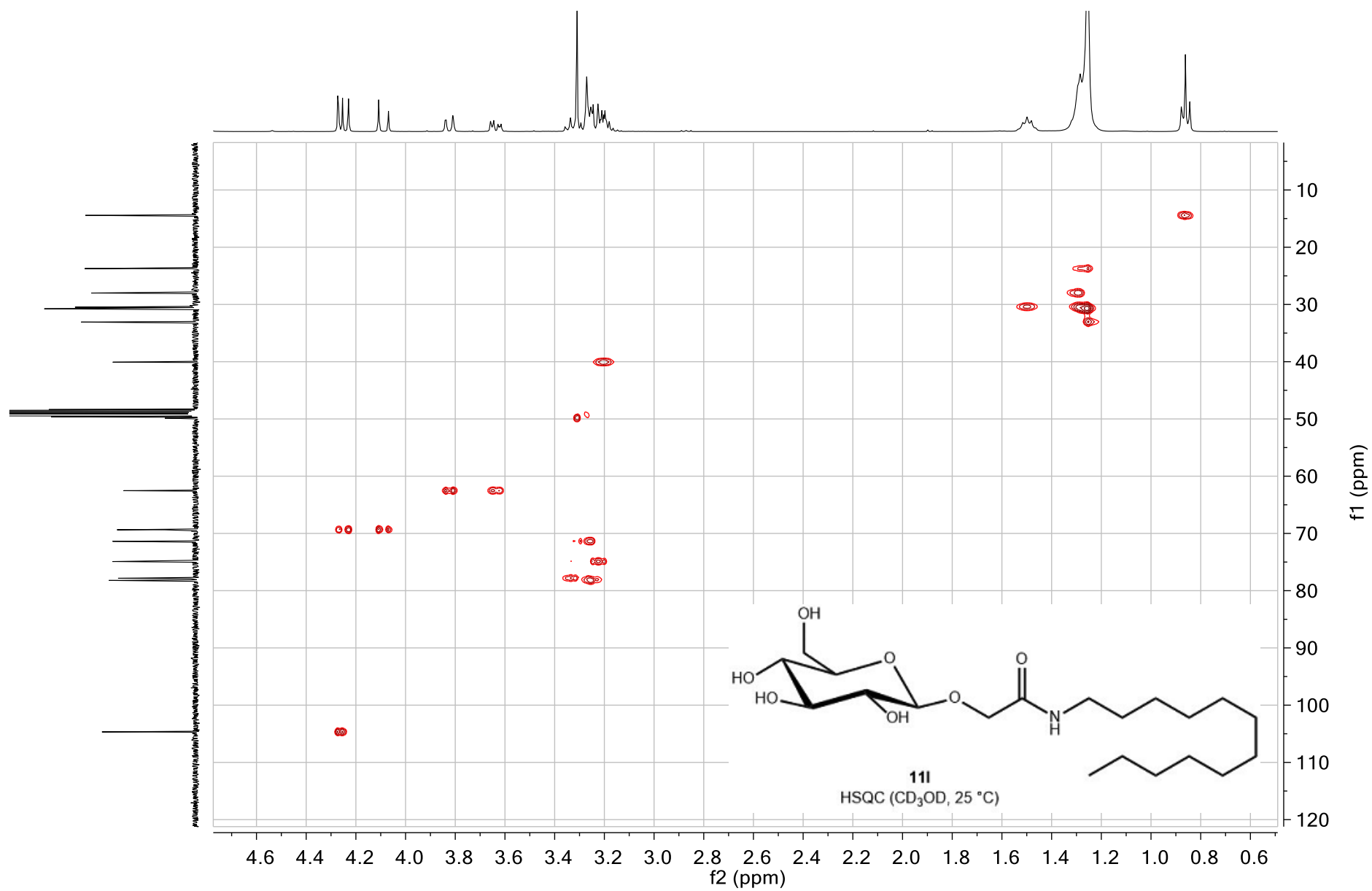
***N*-dodecyl-2-( $\beta$ -D-glucopyranosyloxy)-acetamide (11I).**

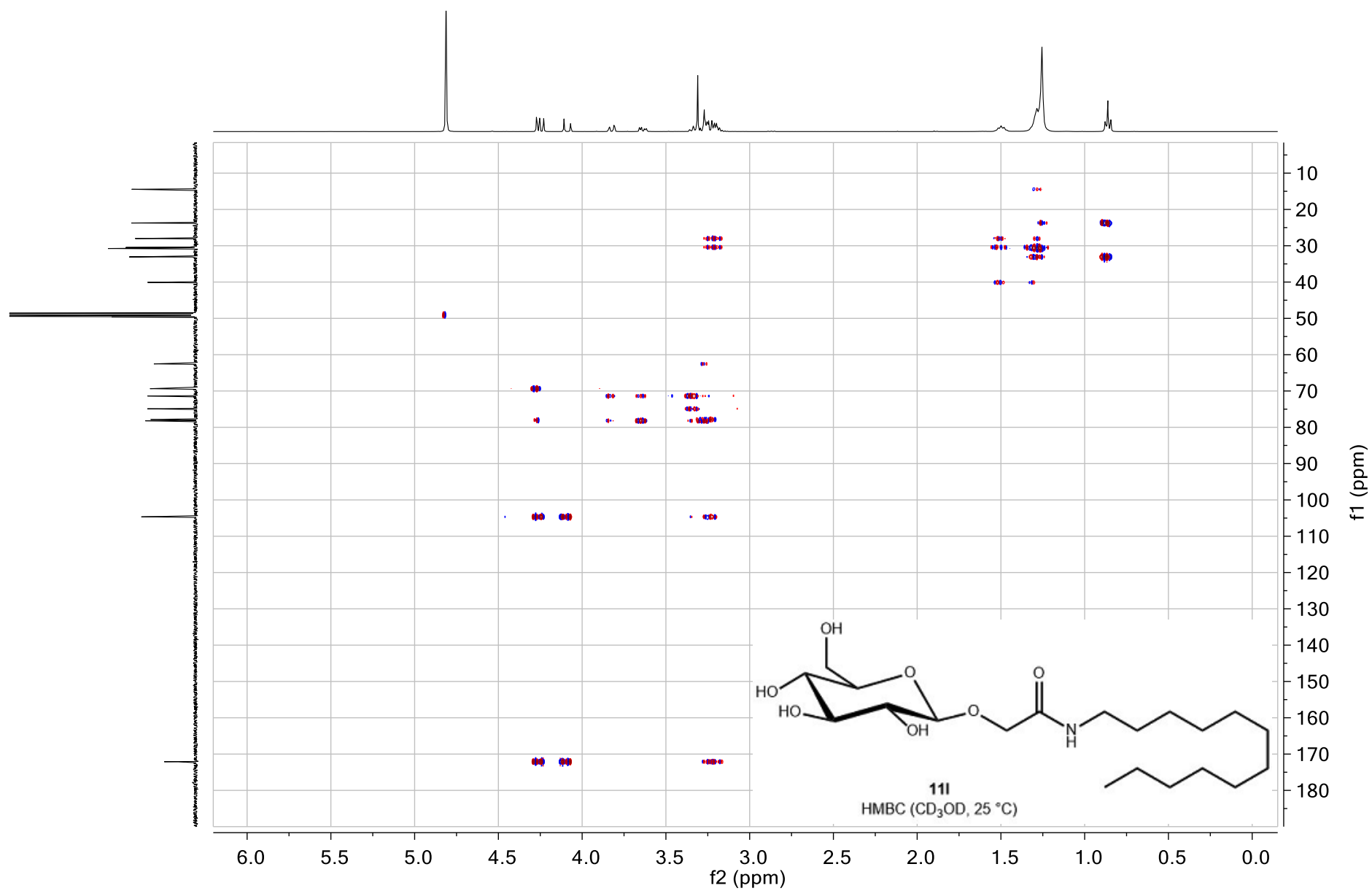






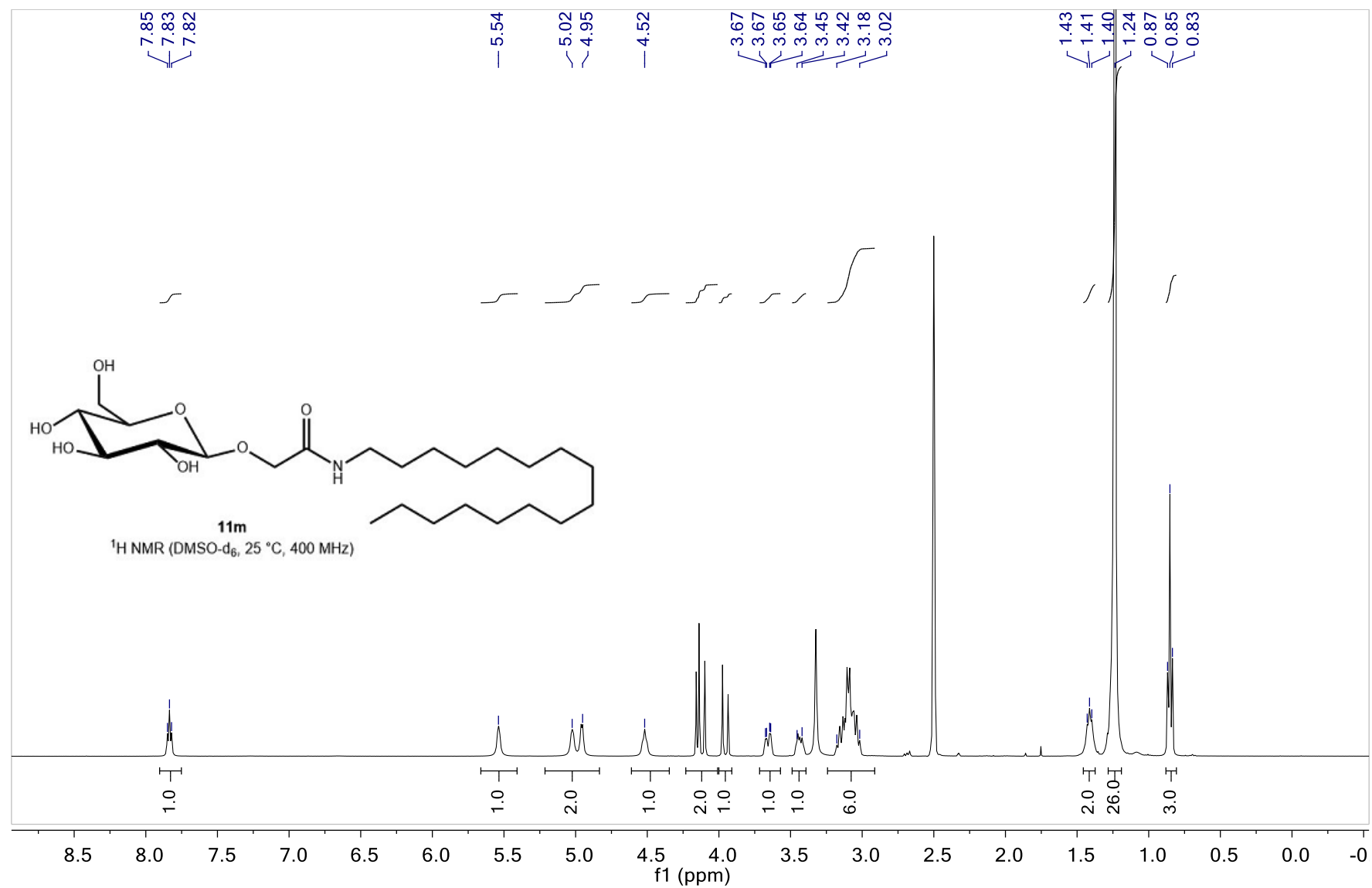


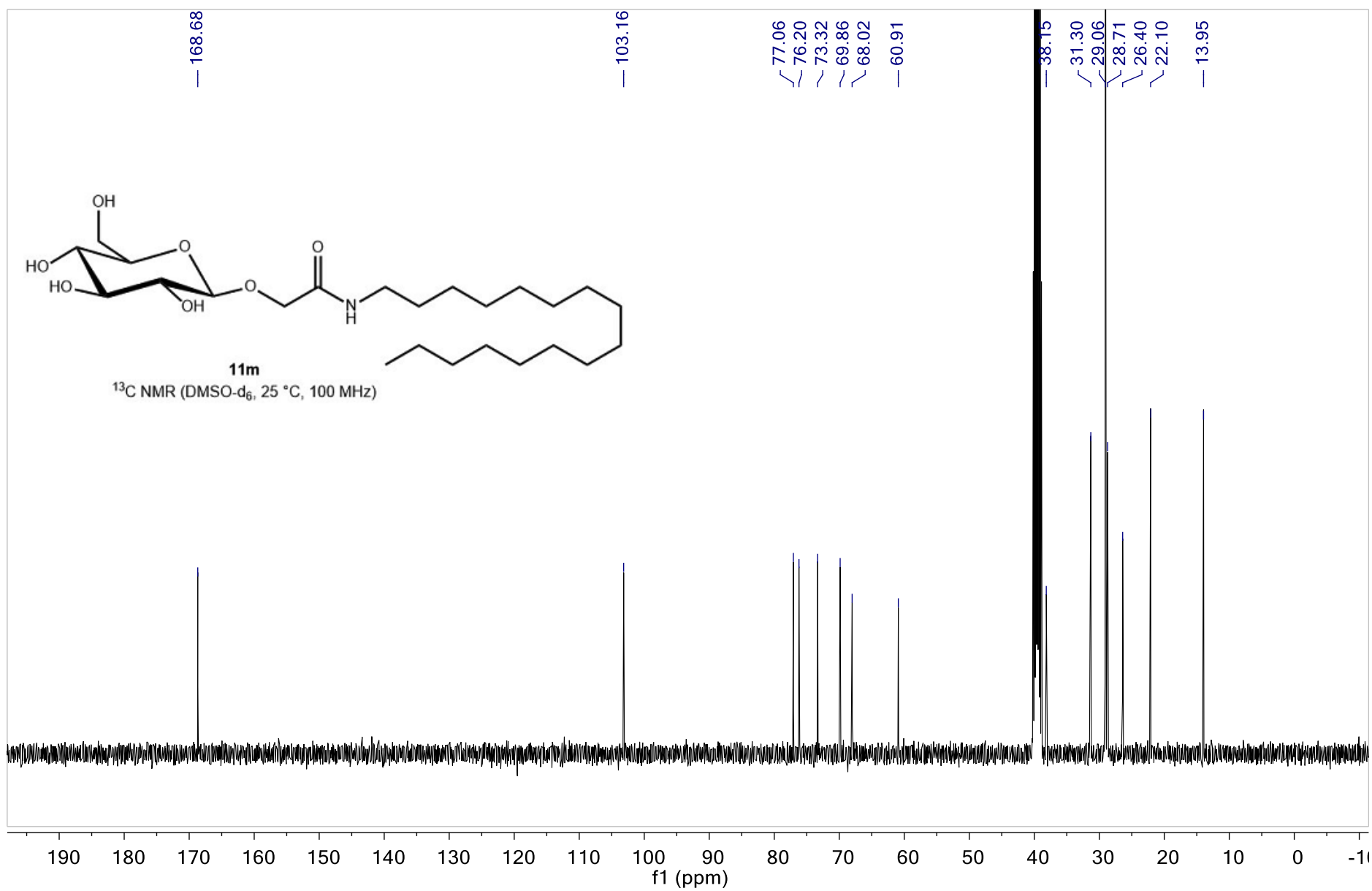


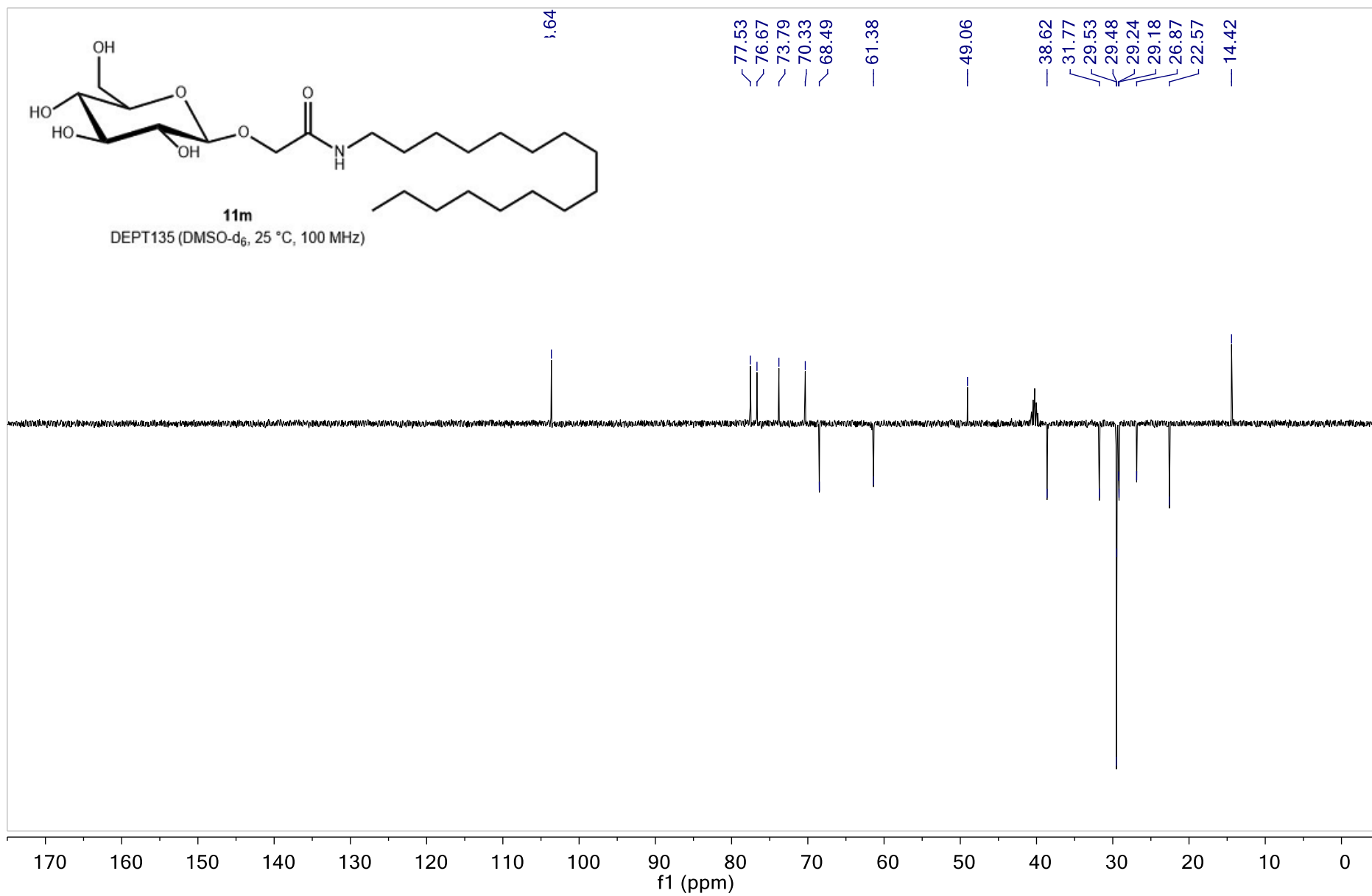


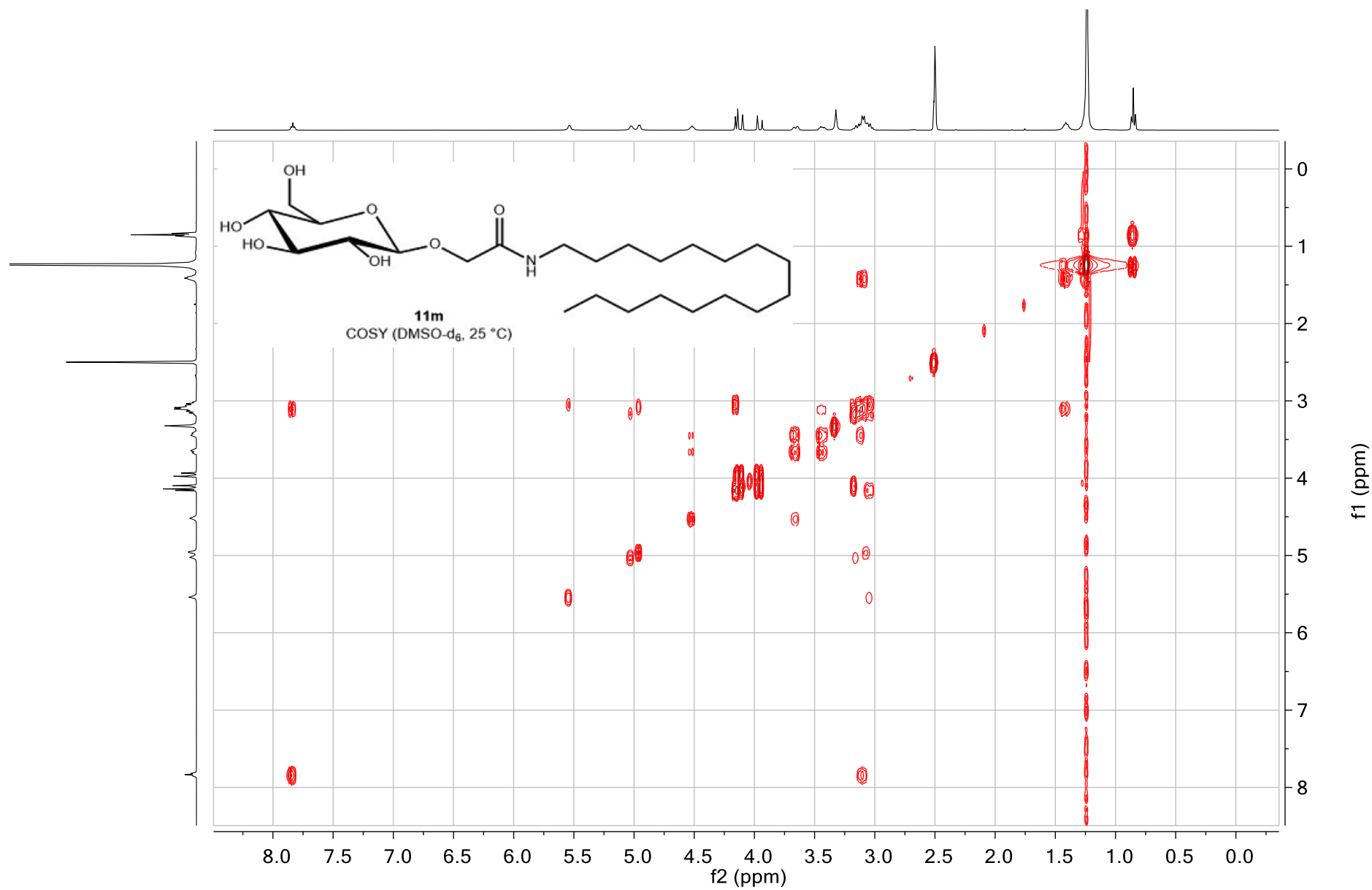


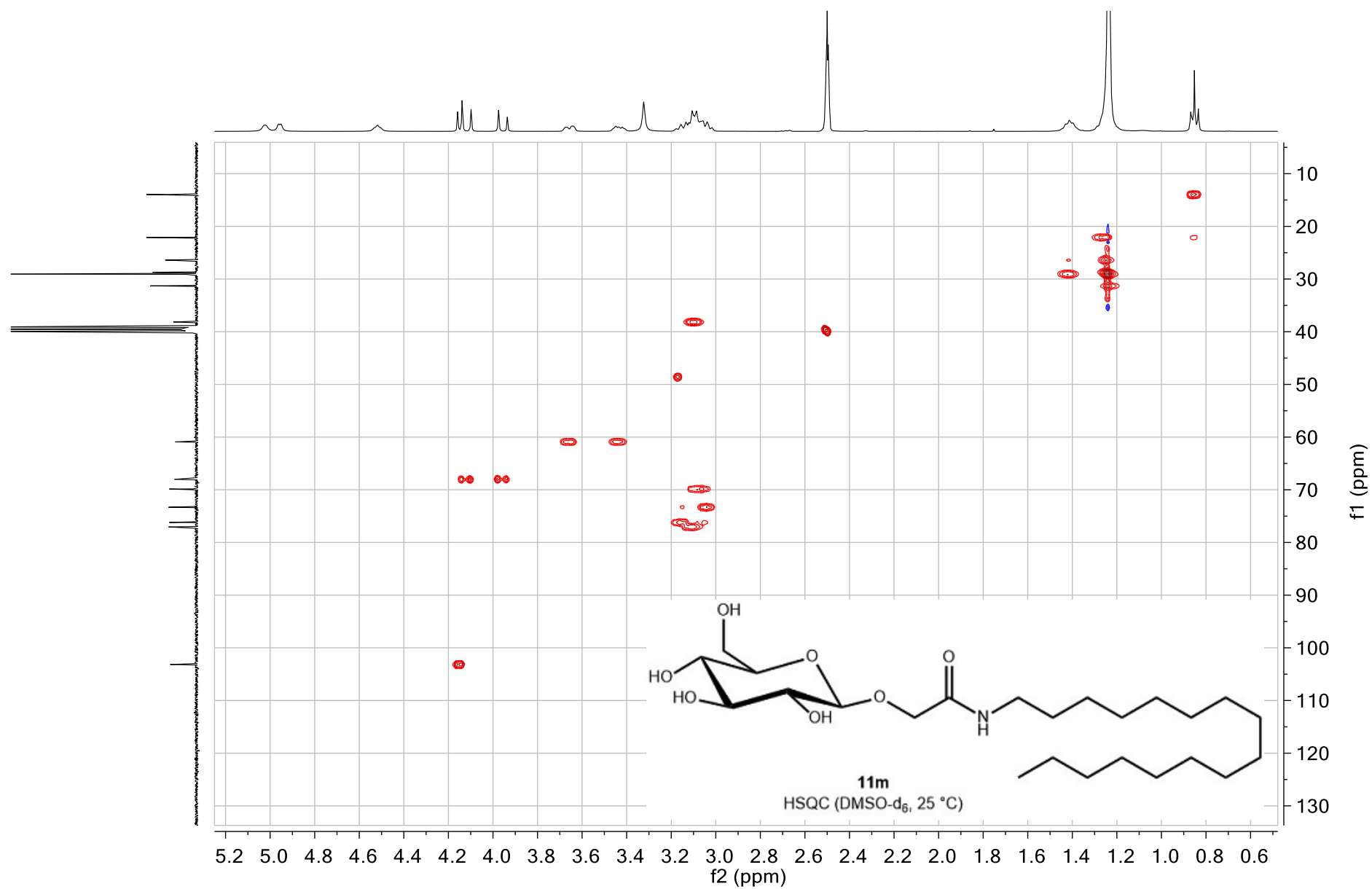
2-( $\beta$ -D-Glucopyranosyloxy)-*N*-hexadecyl-acetamide (11m).



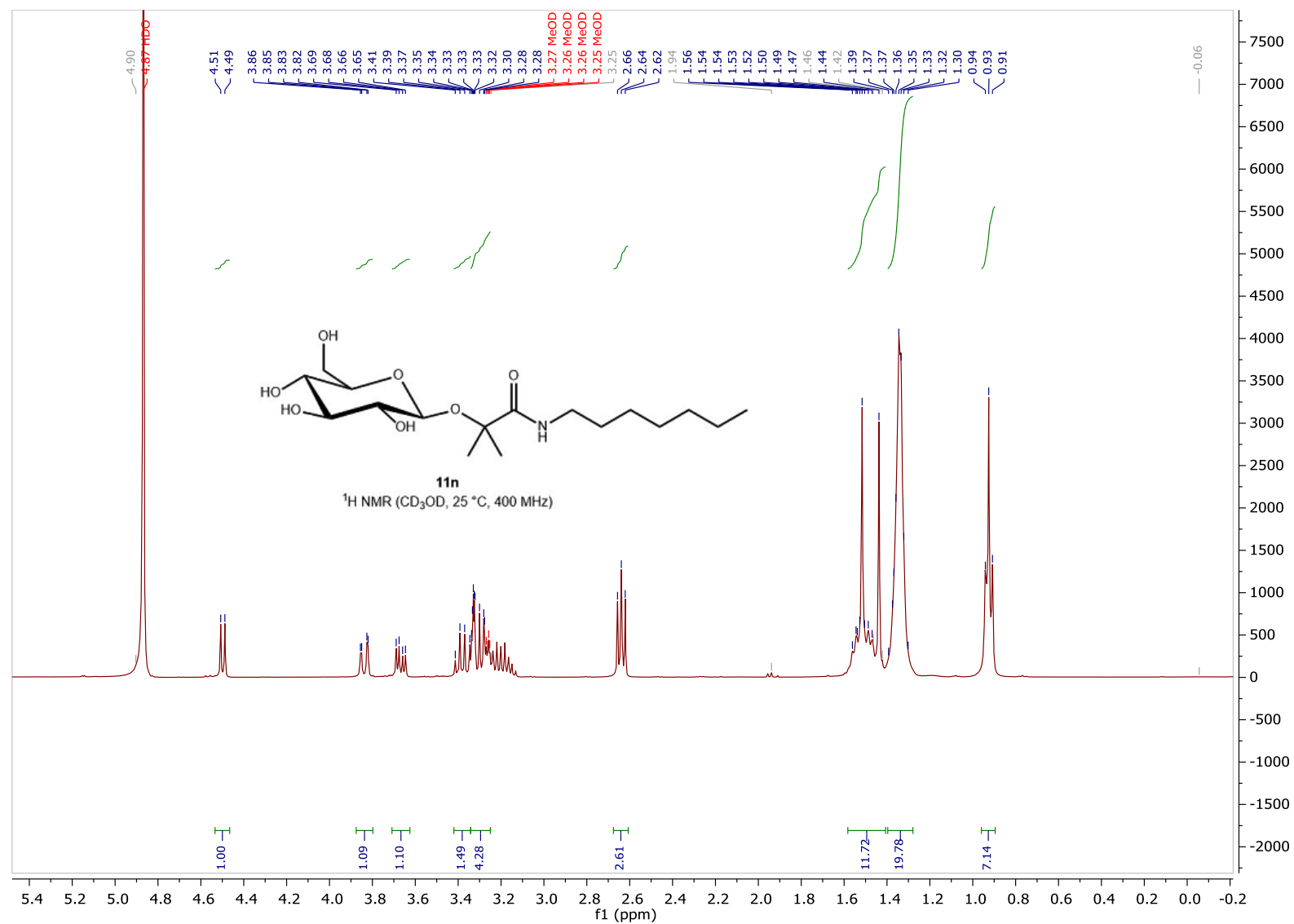


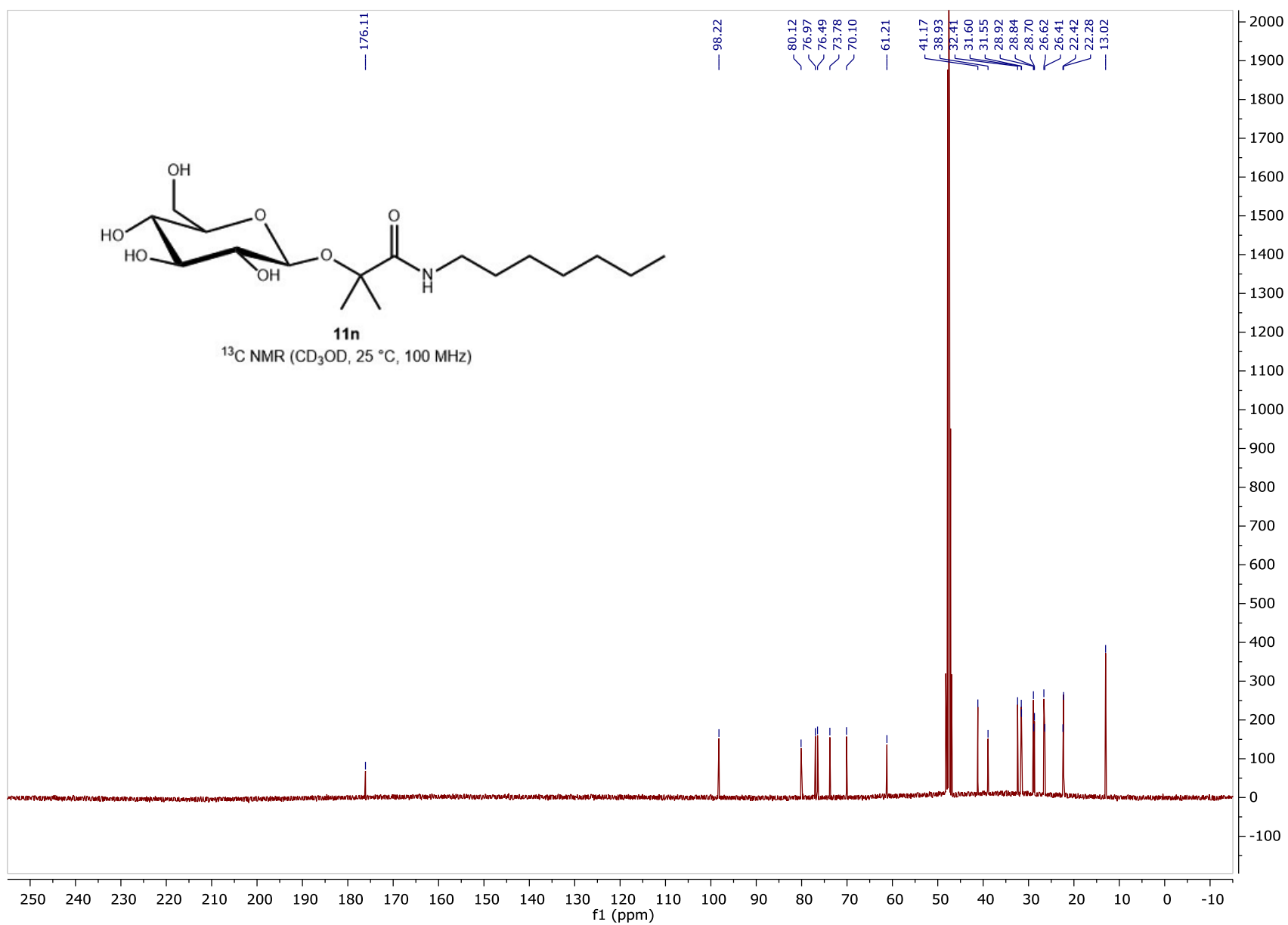


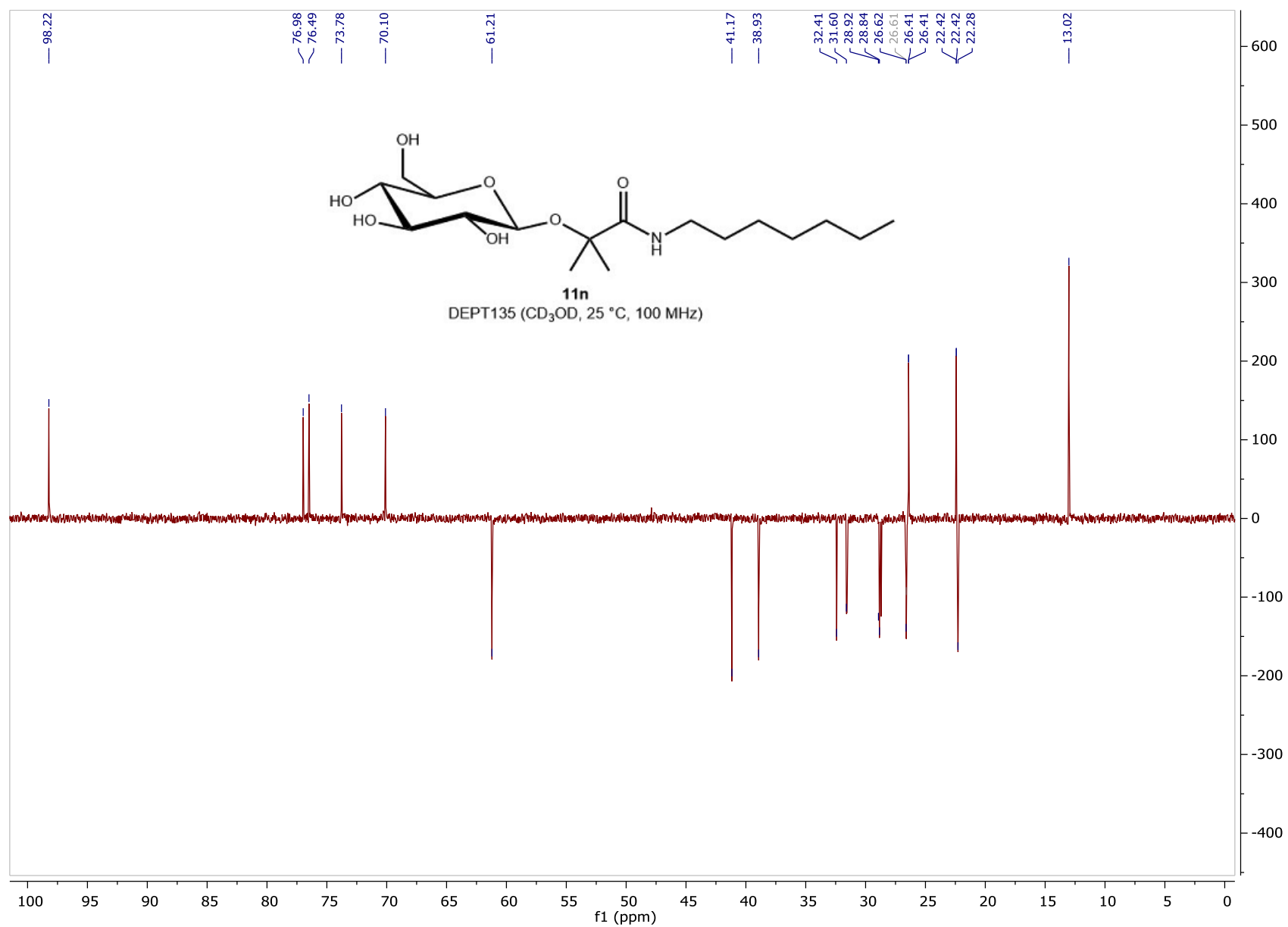




**2-( $\beta$ -D-Glucopyranosyloxy)-2-methyl-N-heptyl-propanamide (11n).**

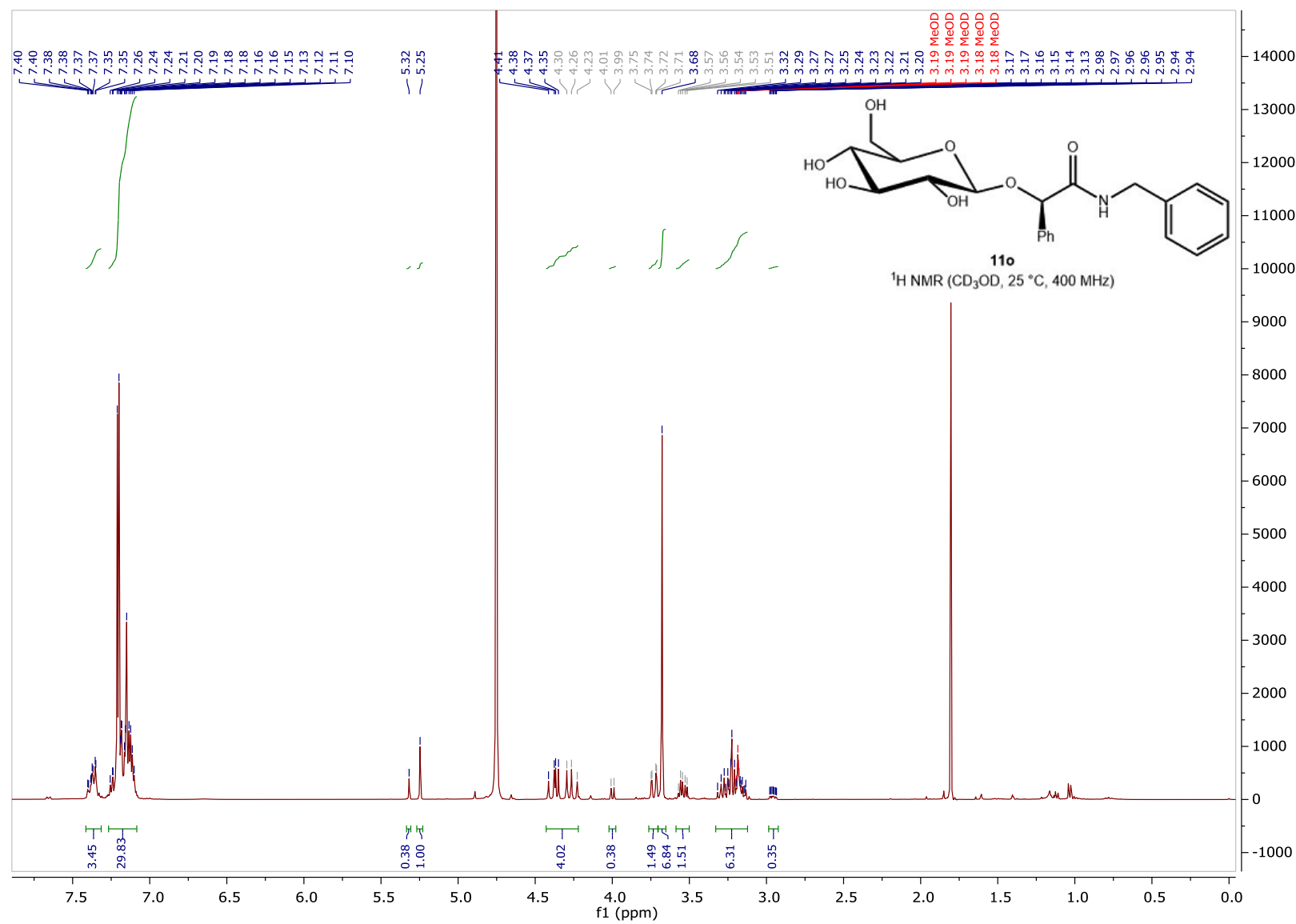


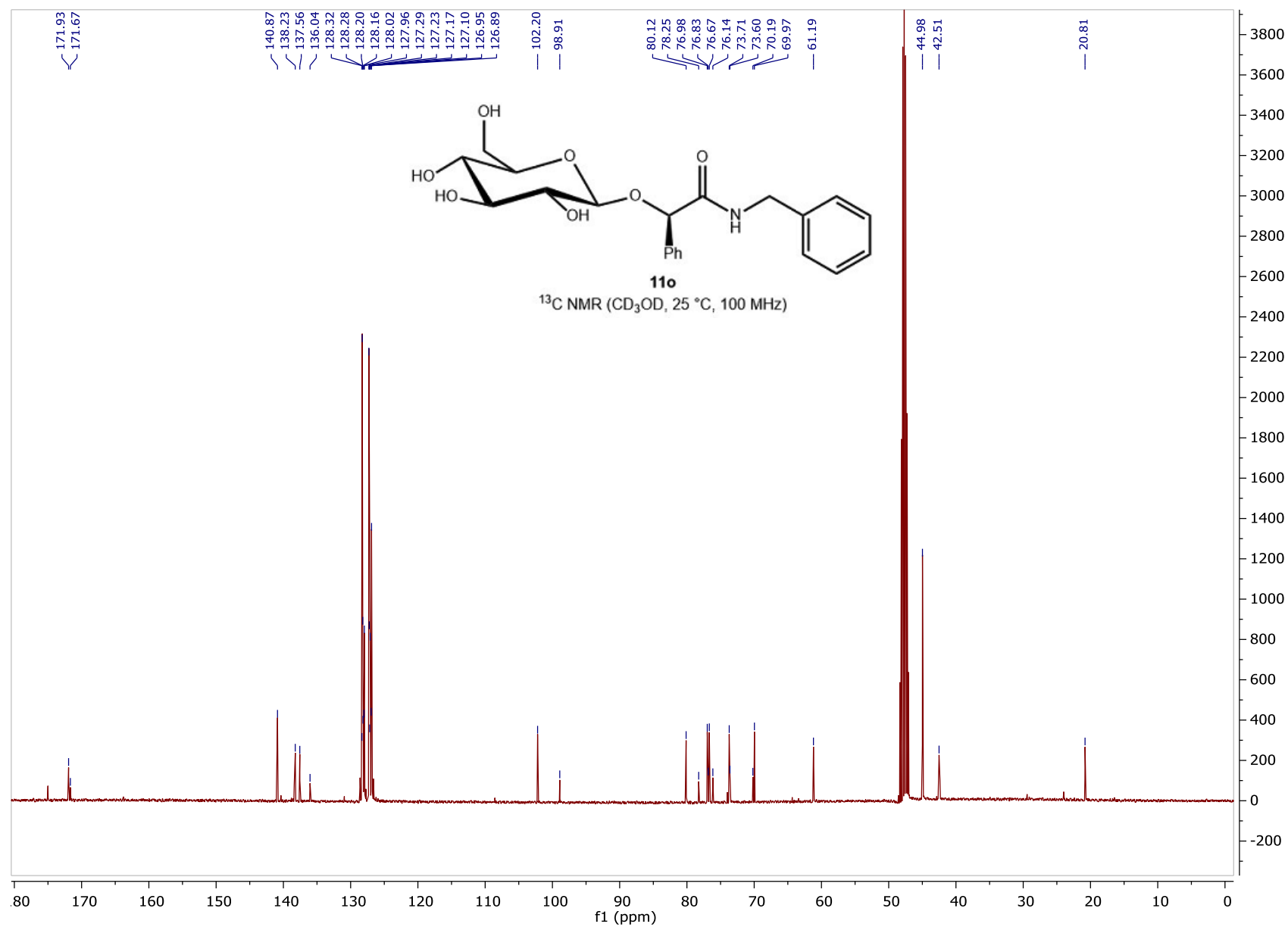




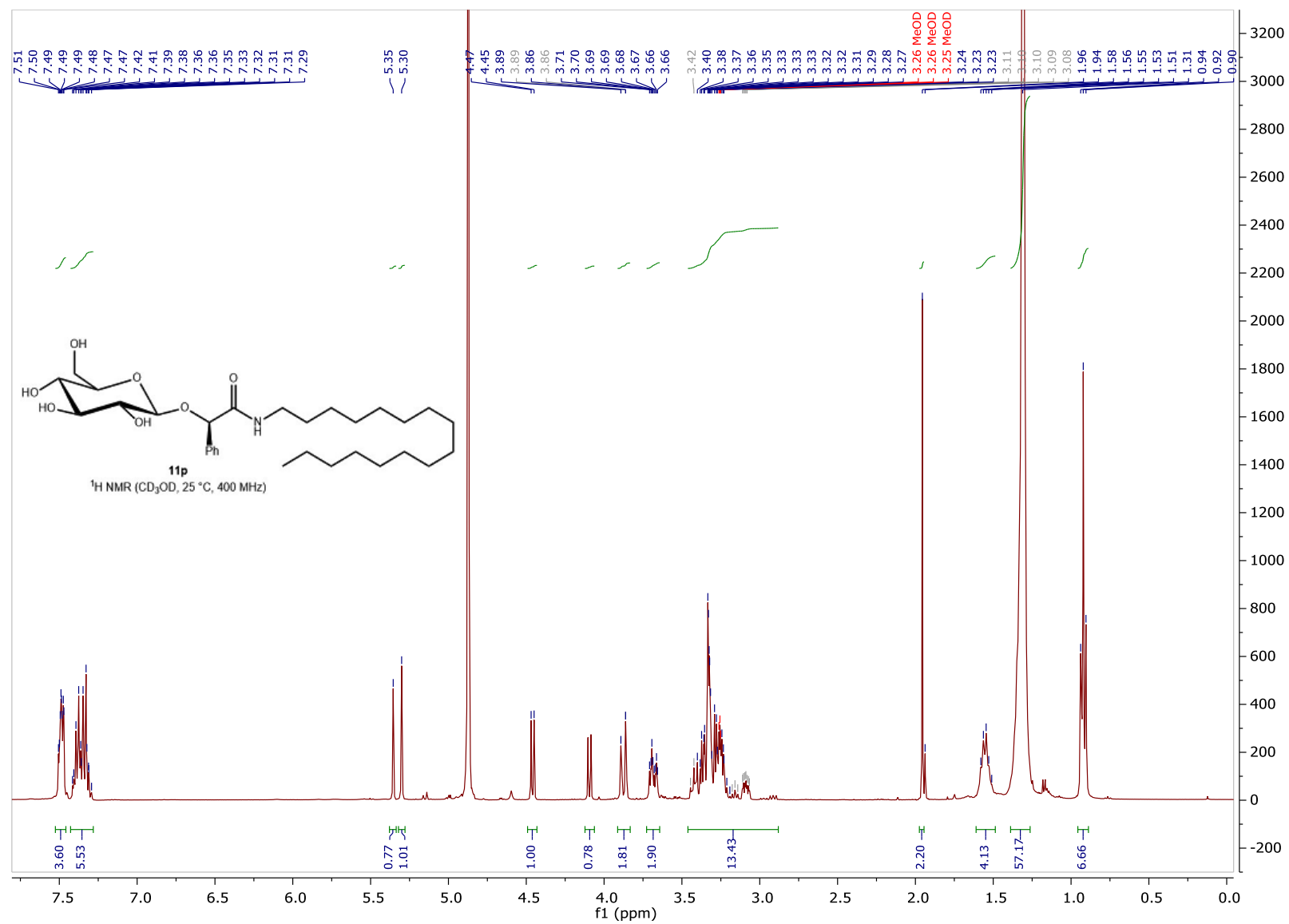


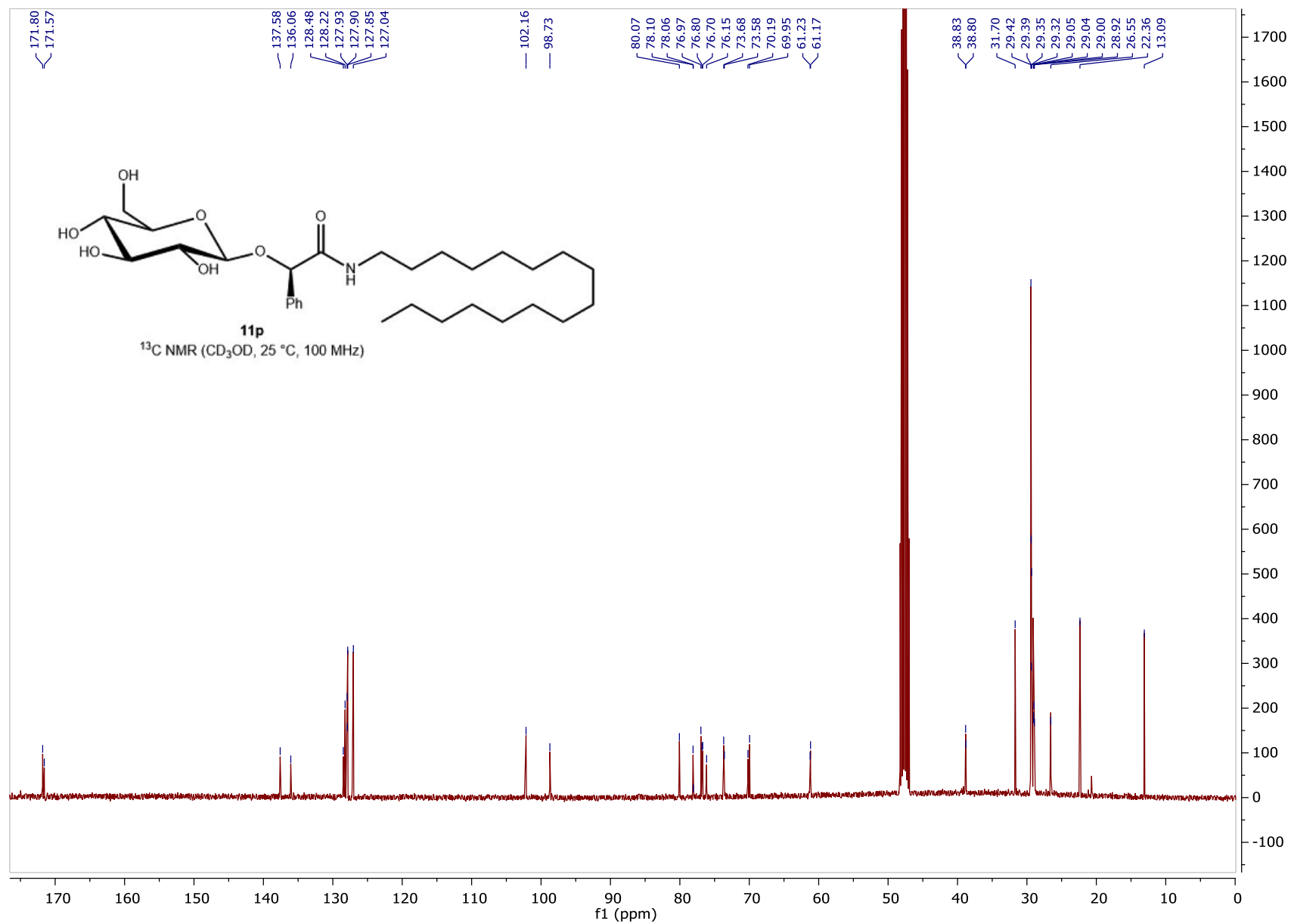
**$\alpha$ -( $\beta$ -D-Glucopyranosyloxy)phenyl-*N*-(phenylmethyl)-acetamide (**11o**).**



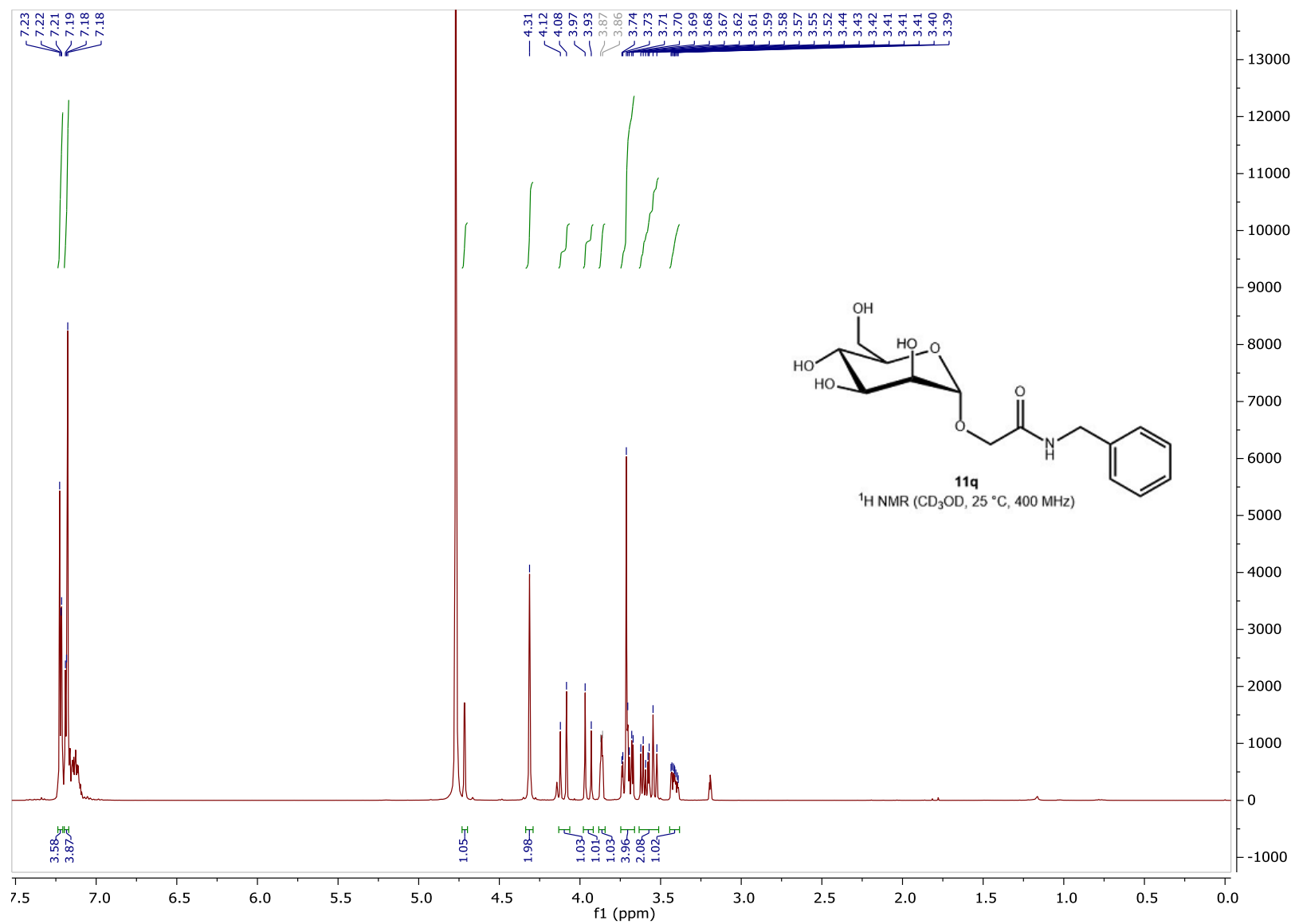


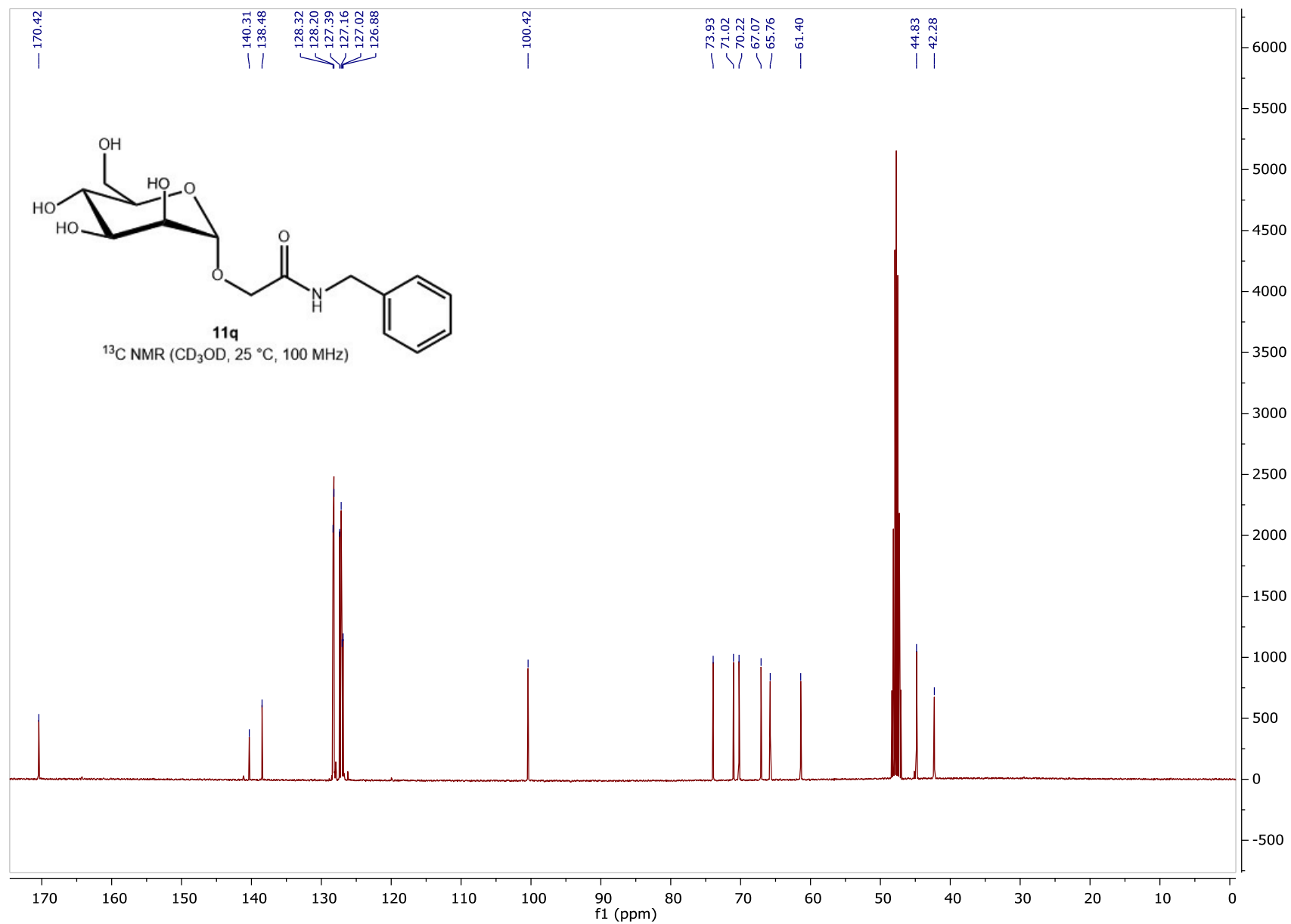
**$\alpha$ -( $\beta$ -D-Glucopyranosyloxy)phenyl-*N*-hexadecyl-acetamide (11p).**



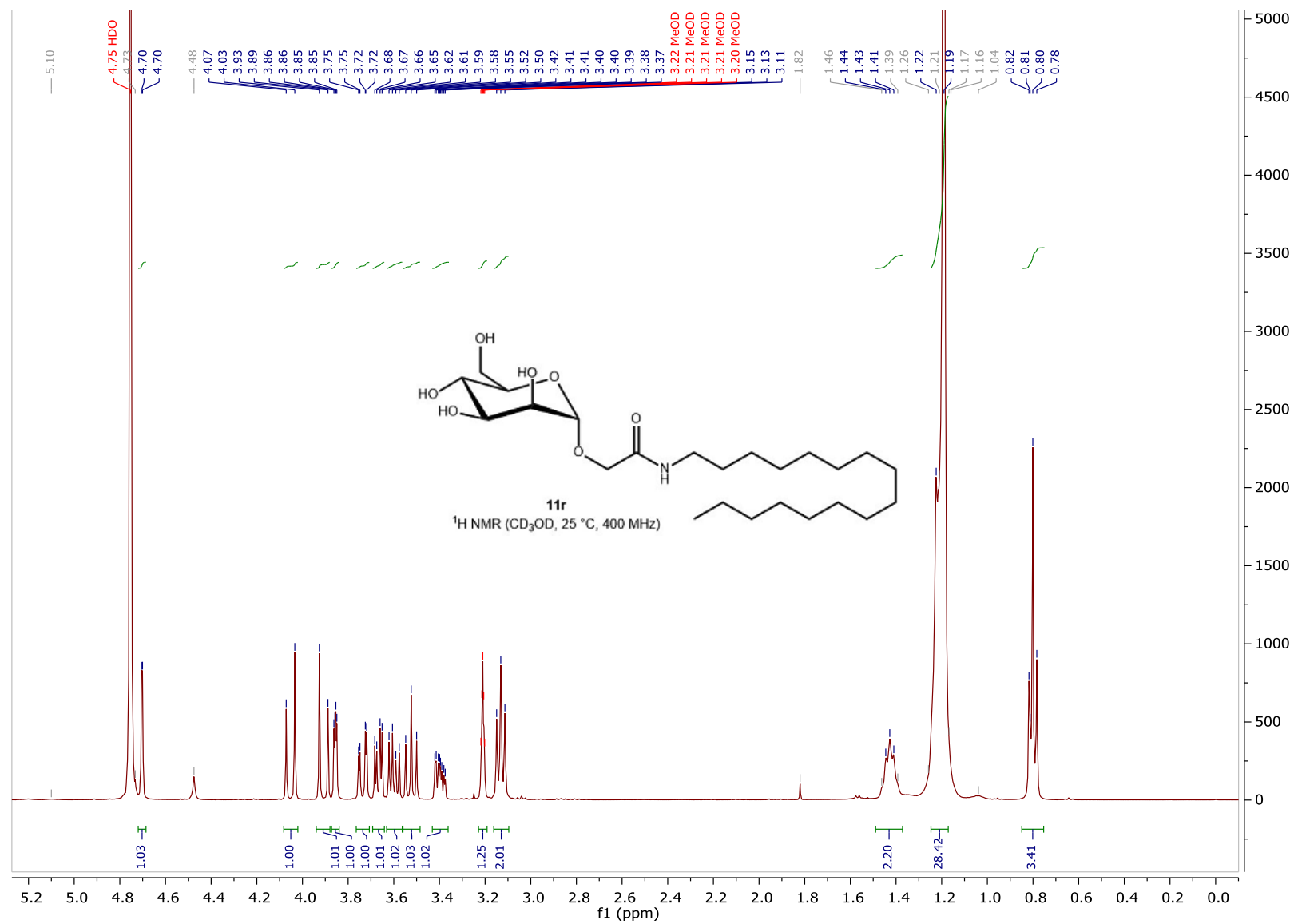


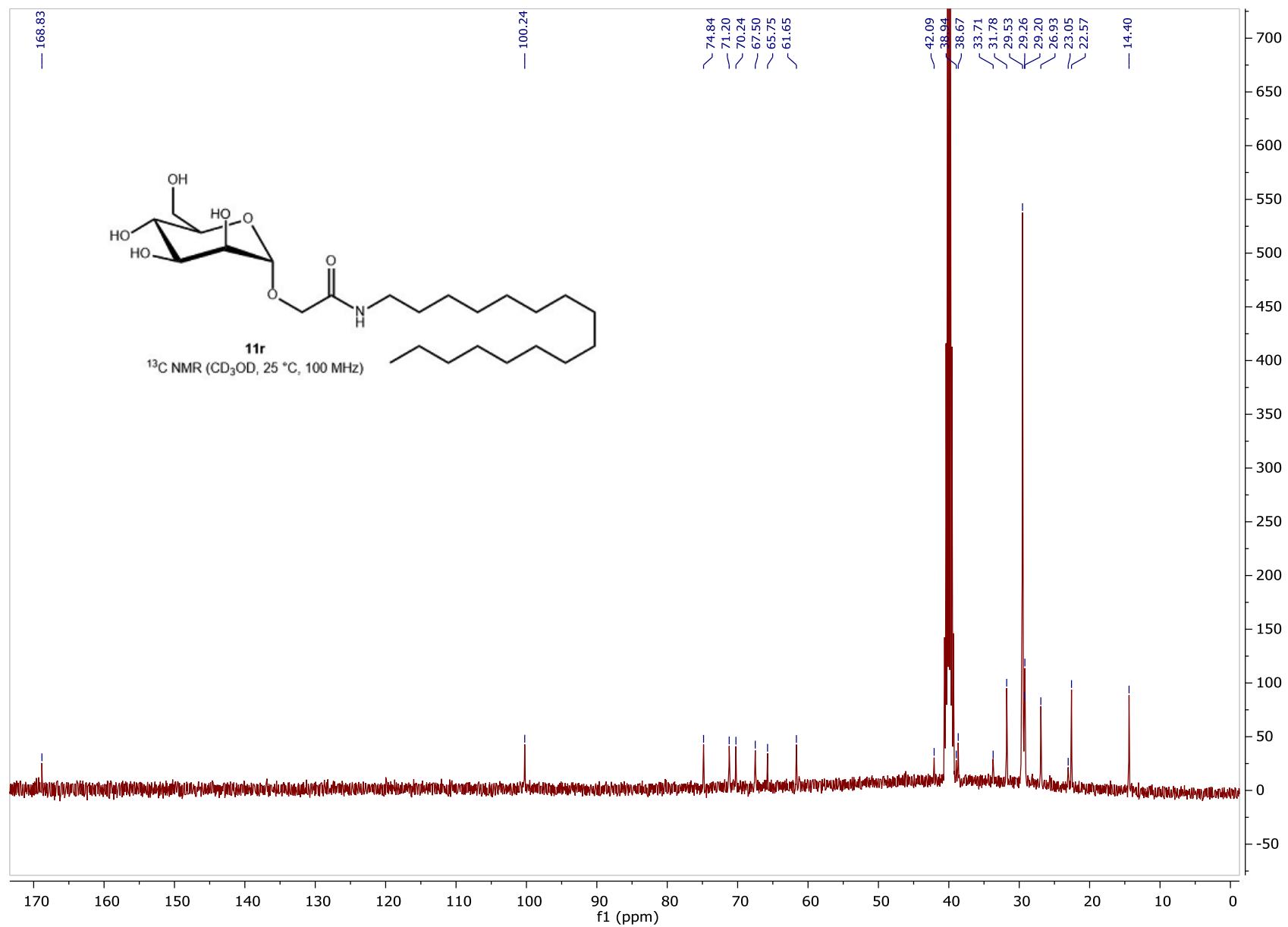
**2-( $\alpha$ -D-Mannopyranosyloxy)-*N*-(phenylmethyl)-acetamide (11q).**





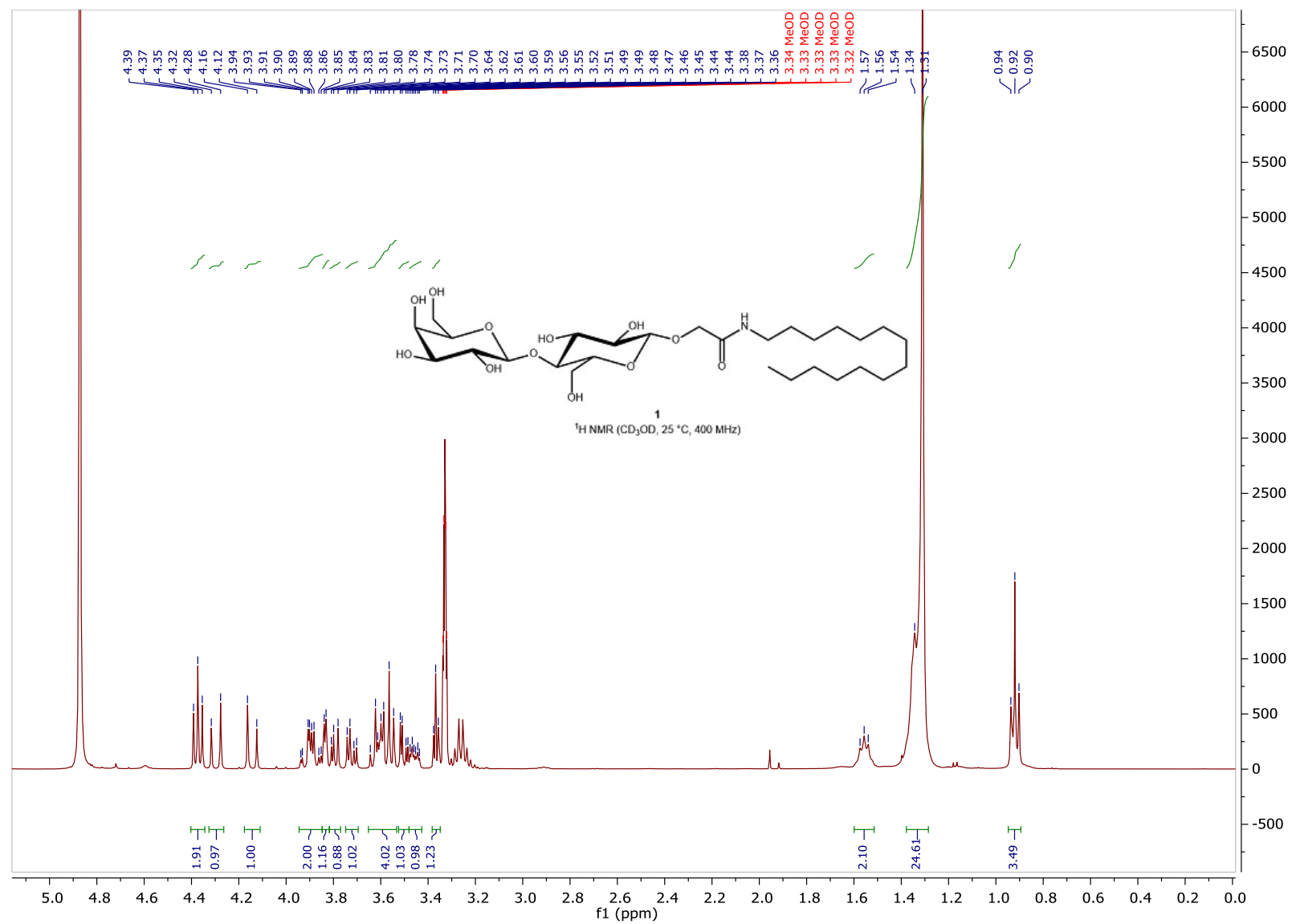
**2-( $\alpha$ -D-Mannopyranosyloxy)-N-hexadecyl-acetamide (11r).**

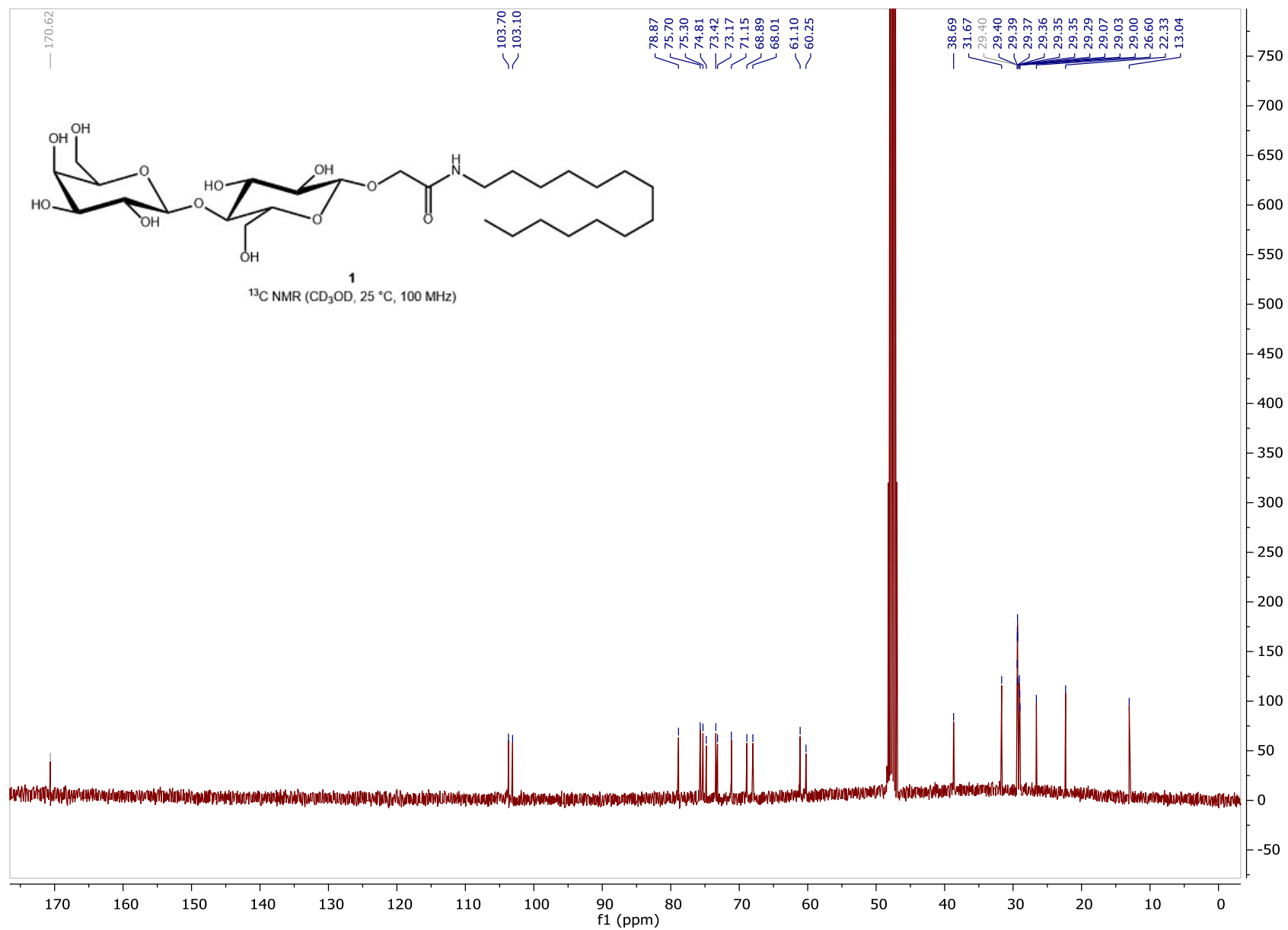


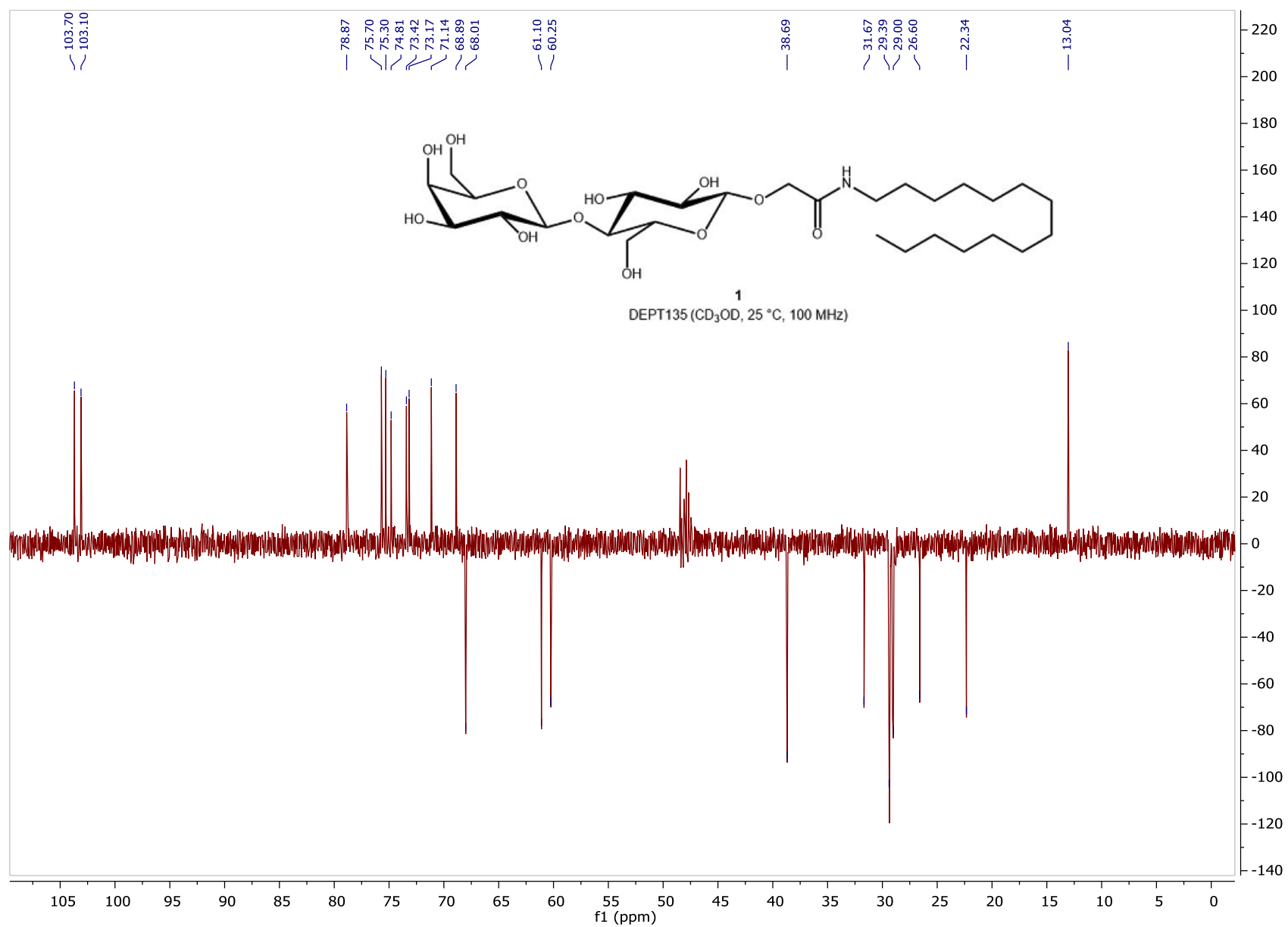




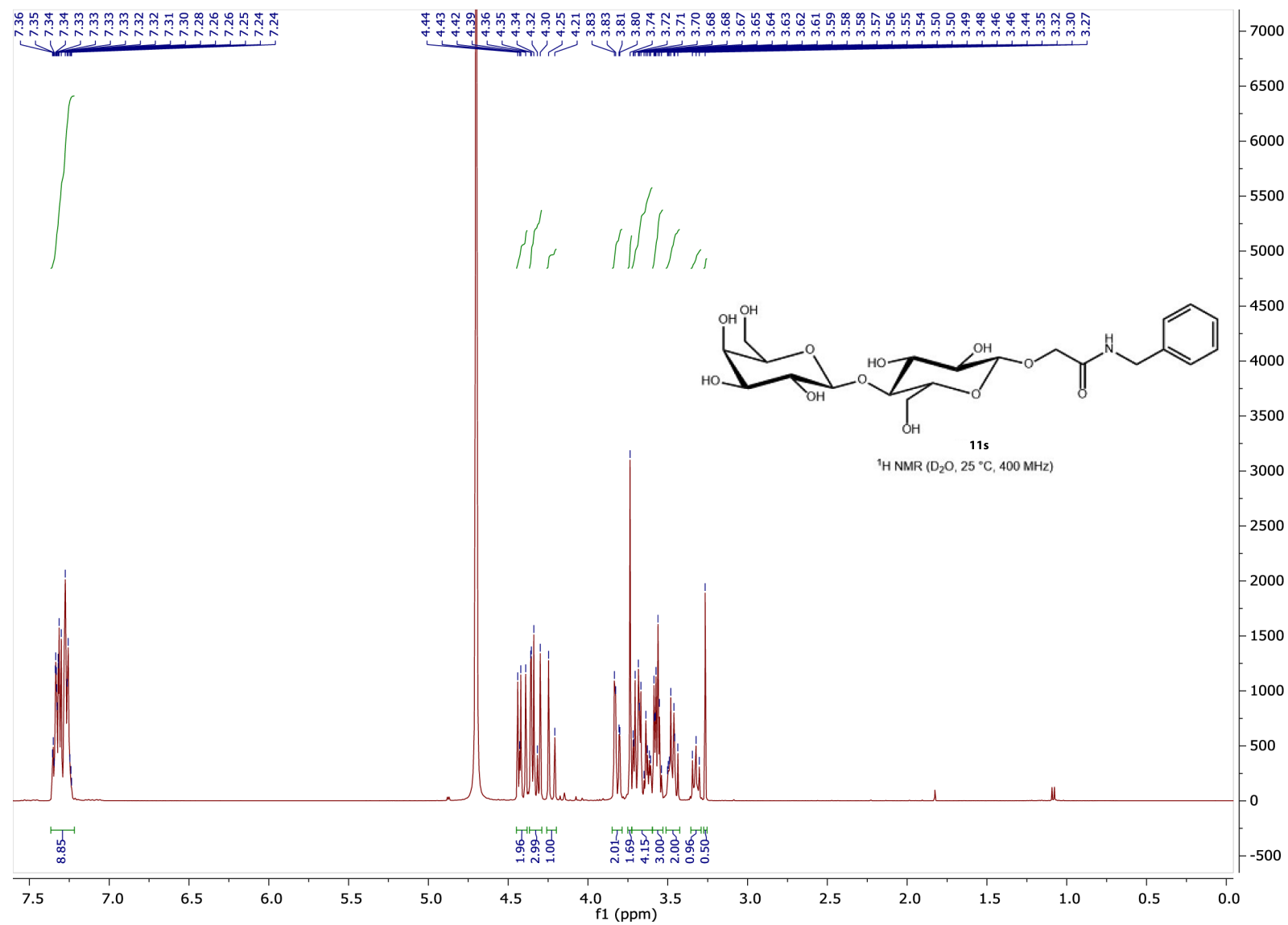
2-( $\beta$ -D-Cellobiosyloxy)-*N*-tetradecyl-acetamide (1).

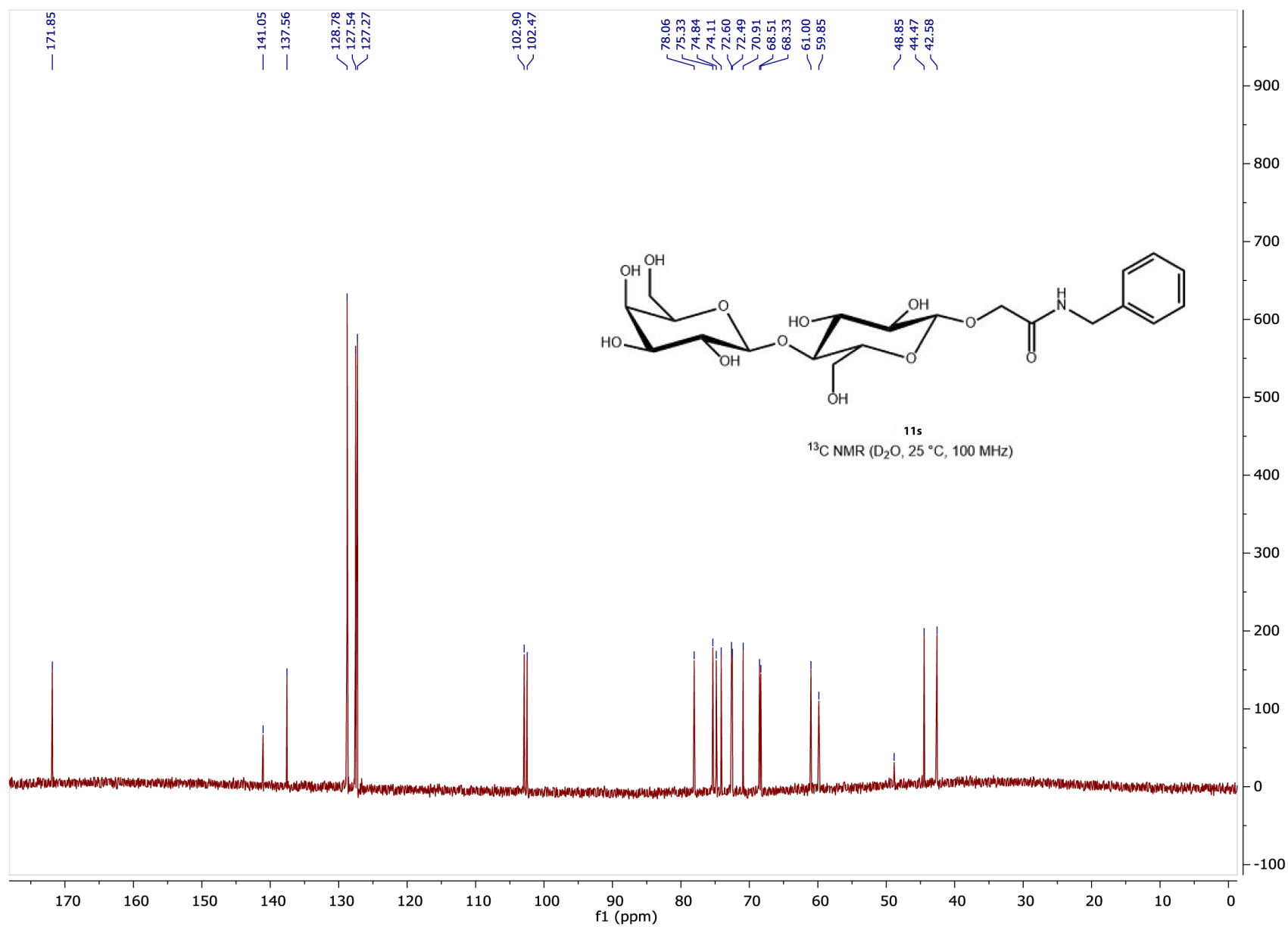


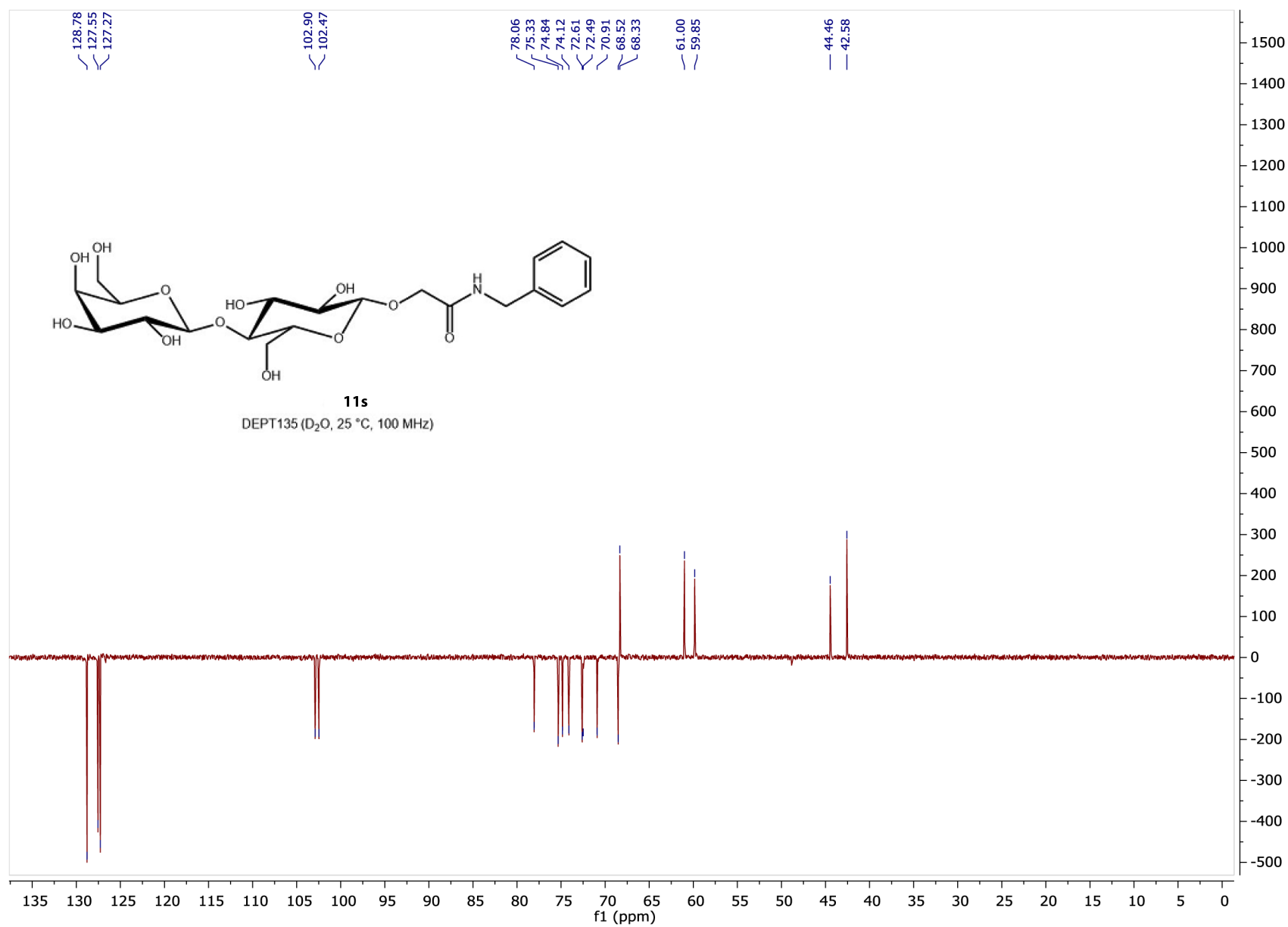




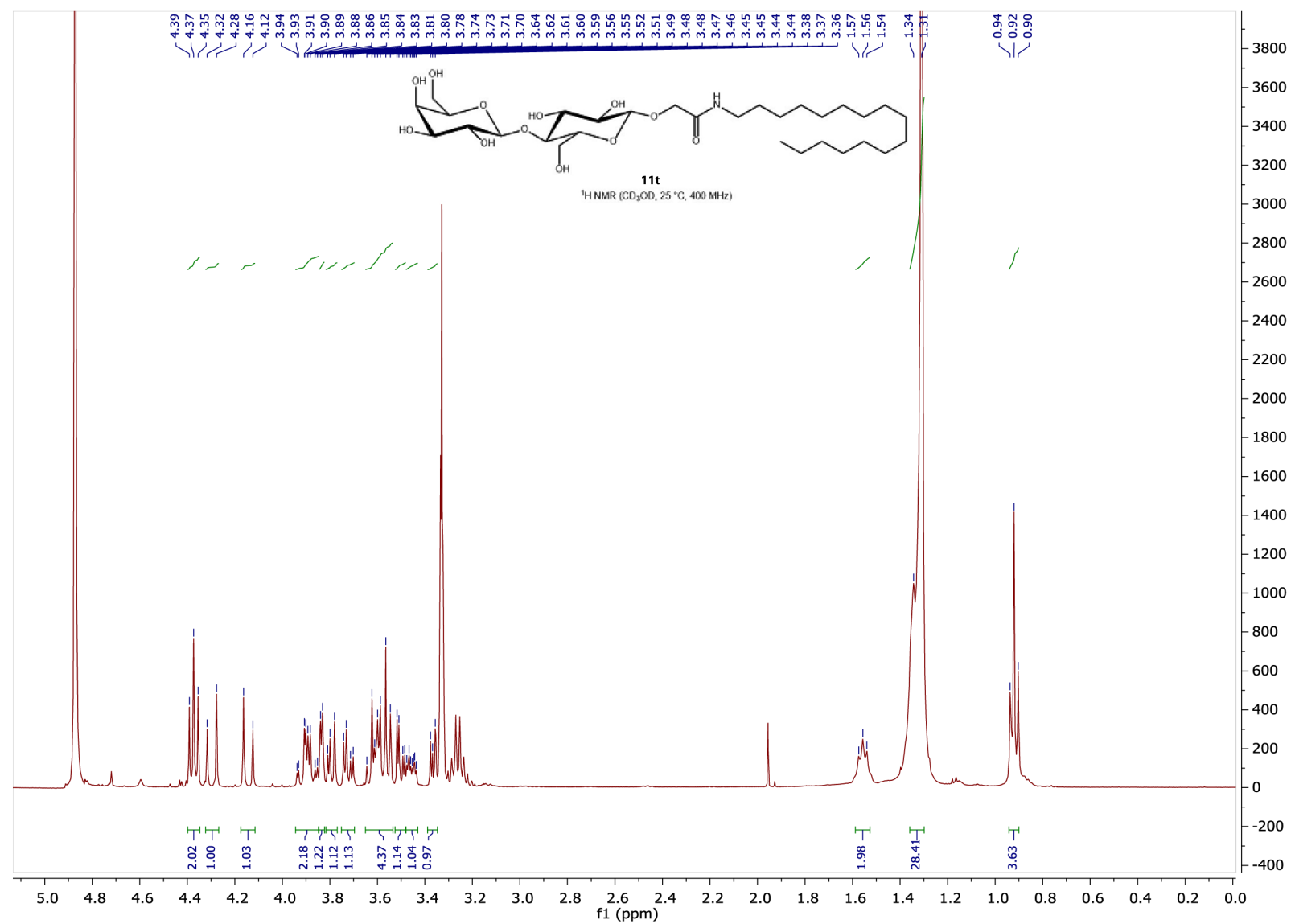
**2-( $\beta$ -D-Lactosyloxy)-*N*-(phenylmethyl)-acetamide (11s).**

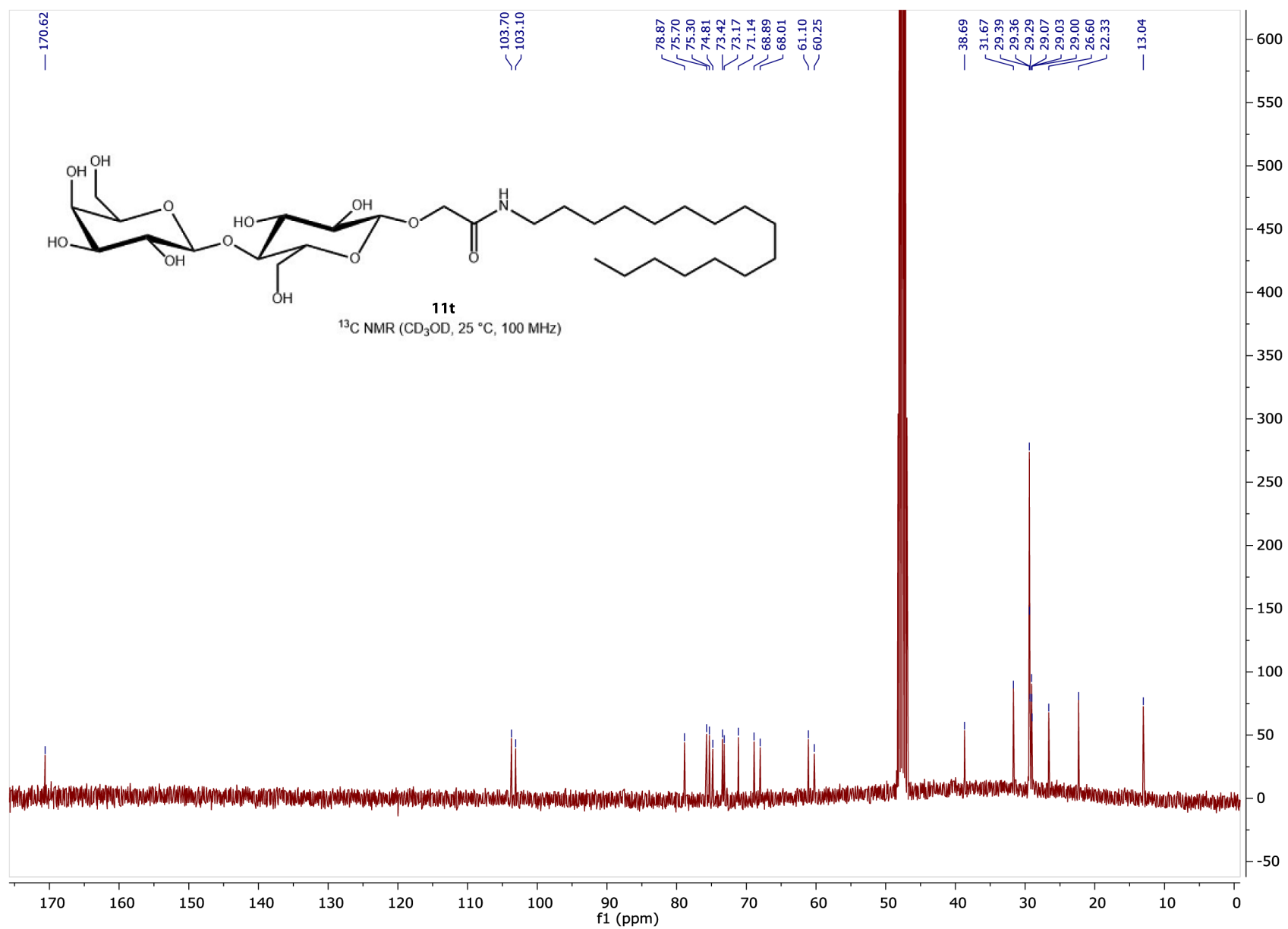




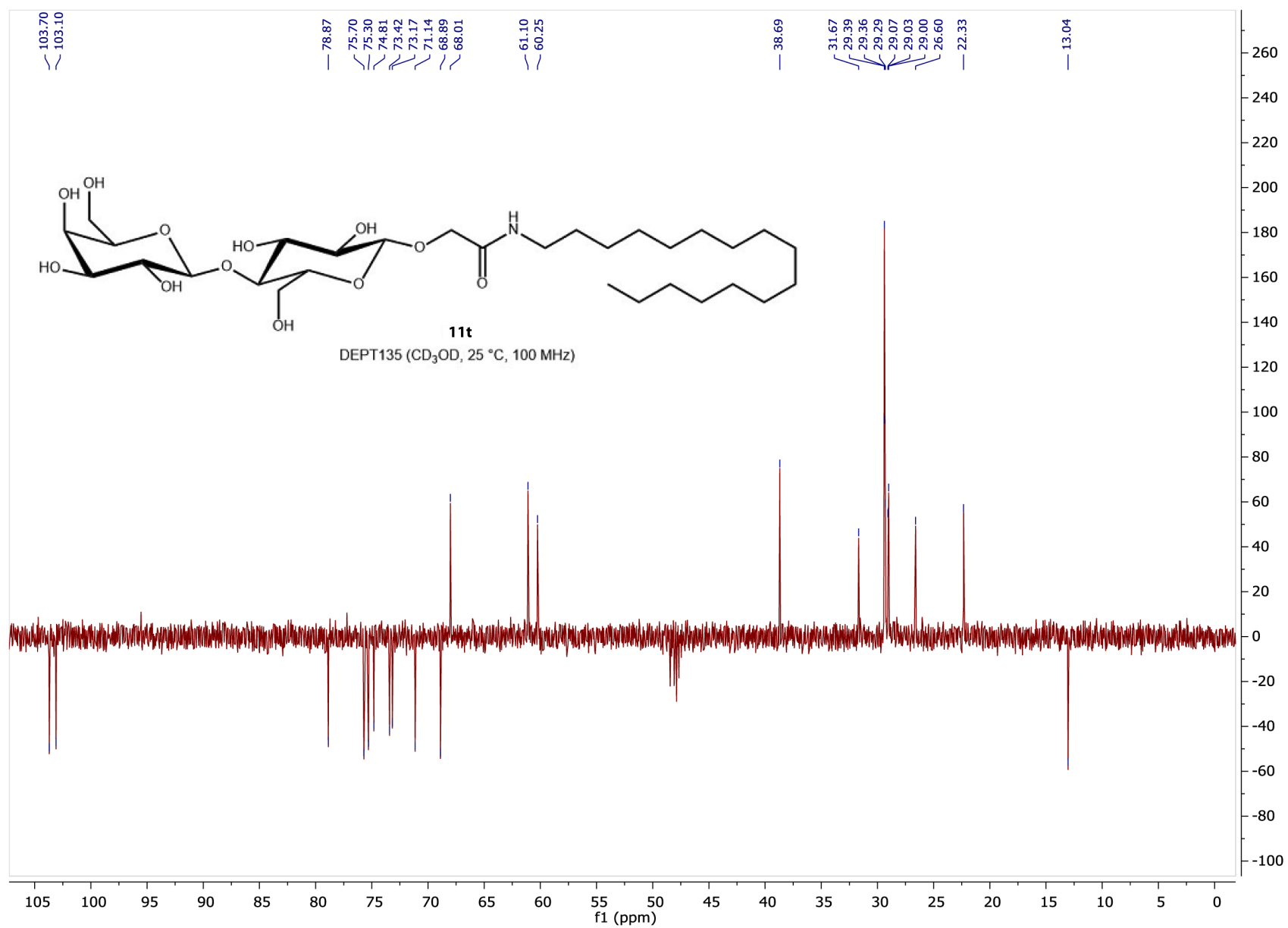


**2-( $\beta$ -D-Cellobiosyloxy)-*N*-hexadecyl-acetamide (11t).**

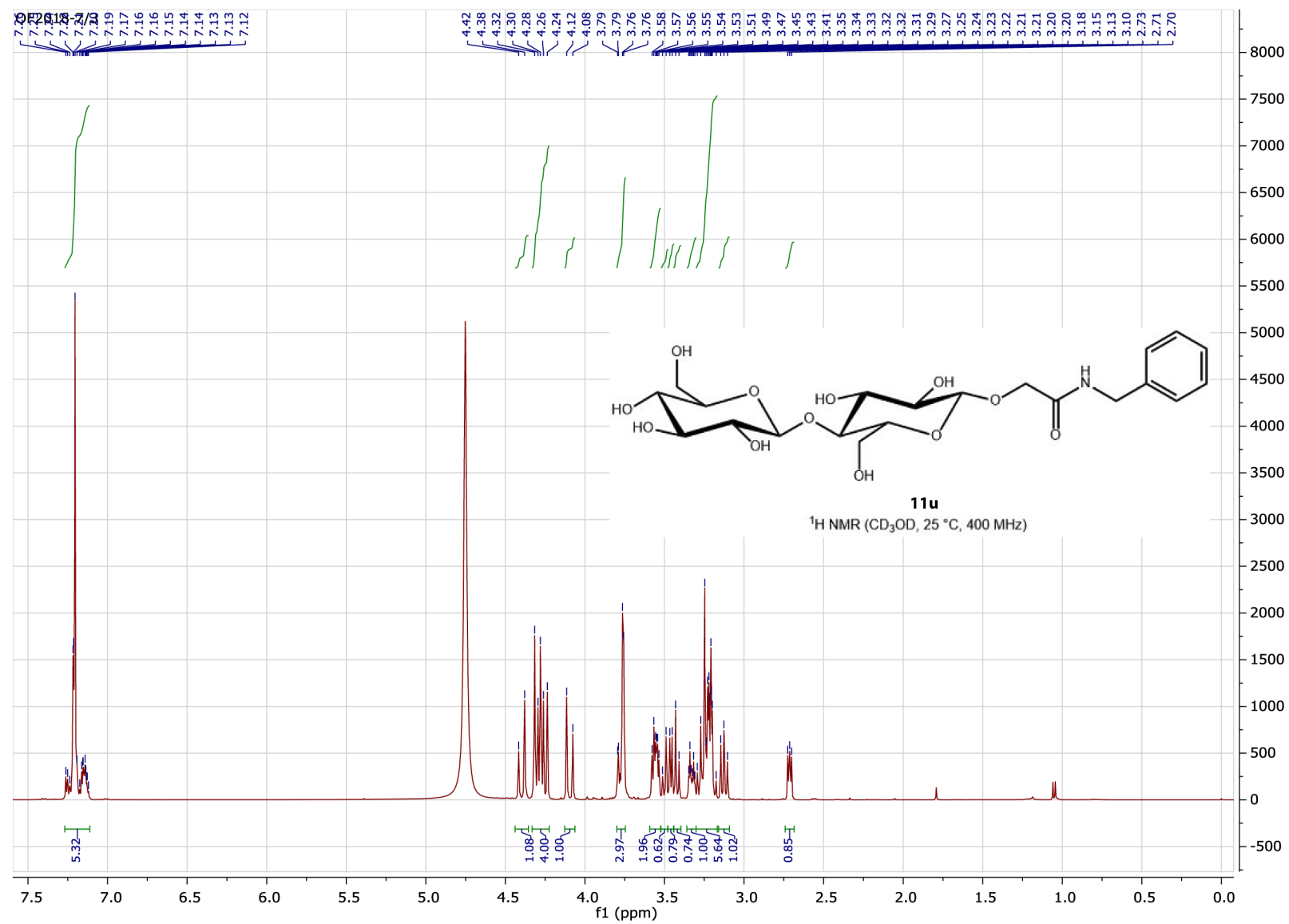




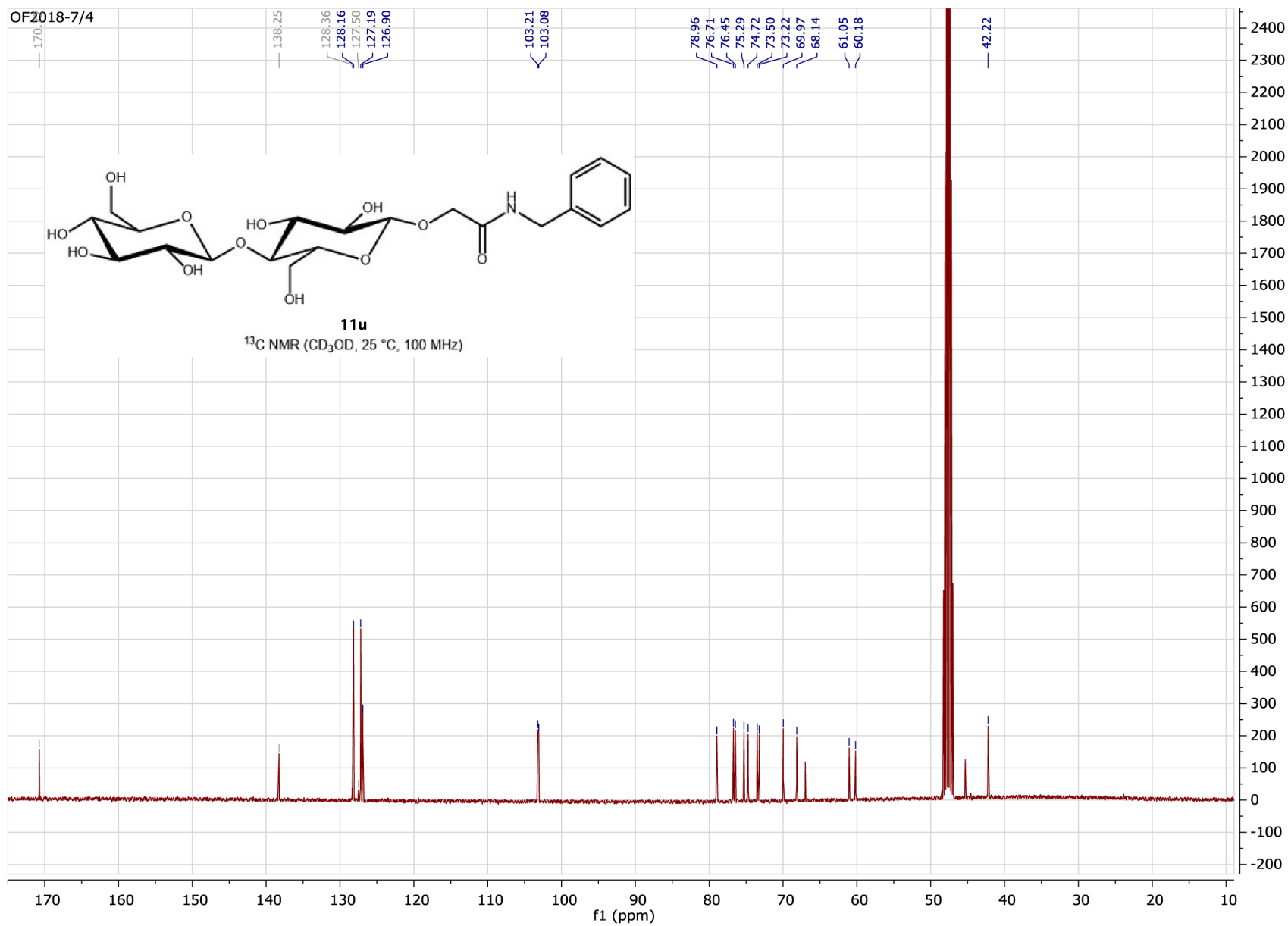




**2-( $\beta$ -D-Cellobiosyloxy)-*N*-(phenylmethyl)-acetamide (11u).**



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**2-( $\beta$ -D-Cellobiosyloxy)-*N*-hexadecyl-acetamide (11v).**

