Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

for

Stereoselective Synthesis of α-Glycosyl Azides: Allyl Glycosyl Sulfones as Radical Precursors

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1. General Information

Flash column chromatography was performed using silica gel (300–400 mesh) purchased from Qindao Haiyang. The mixtures of petroleum ether/ethyl acetate as eluting solvents. Reaction solvents (e.g., DCM and DMSO) were purchased from Energy Chemicals and used as received. Glycosyl substrates, tosyl azide and photosensitizers were purchased from Adamas or Energy Chemicals and used as received.

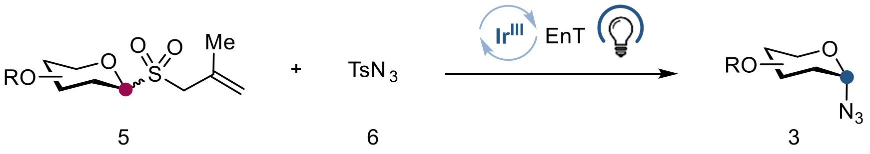
NMR yields were determined using 1,3,5-trimethoxybenzene as an internal standard. All new compounds were characterized by NMR spectroscopy, high-resolution mass spectroscopy (HRMS), and melting point (if solids). NMR spectra were recorded on a Bruker AMX 400 spectrometer and were calibrated using TMS or residual deuterated solvent as an internal reference [$CDCl_3$: 7.26 ppm or 0.00 ppm (TMS) for ^{1}H NMR and 77.16 ppm for ^{13}C NMR; CD_3OD: 3.31 ppm for ^{1}H NMR and 49.00 ppm for ^{13}C NMR; DMSO: 2.50 ppm for ^{1}H NMR and 39.52 ppm for ^{13}C NMR], and the tabulated data were reported in ppm. HRMS spectra were recorded on a Waters Q-TOF Premier. All IR spectra were taken on a Thermo Scientific Nicolet iS5 spectrometer (iD5 ATR, diamond). Melting points (m.p.) were recorded on an INESA SGW X-4 melting point apparatus. Optical rotations were measured on a Rudolph Research Analytical Autopol VI polarimeter with $[\alpha]_D$ values reported in degrees; concentration (c) is in 10 mg/1 mL. Light resource was use 452 nm blue LED purchased from IKA.

Photoreactor Reaction vial (8 mL)

Figure S1. Photoreactor and reaction vials used in this study

2. General Procedure for Synthesis of α-Glycosyl Azides

General Procedure A



To an oven dried screw-capped vial, allyl glycosyl sulfones **5** (0.05 mmol, 1.0 equiv.) and [Ir(dFMeppy)$_2$(dtbbpy)]PF$_6$ (0.001 mmol, 2 mol% equiv.) were added, then the vial was transferred to the N_2-filled glovebox. DMSO (0.5 mL, 0.1 M) and tosyl azide **6** (0.10 mmol, 2.0 equiv.) were added to the reaction. The vial was transferred out of the N_2-filled glovebox, stirred at room temperature under blue LED for 8 h.

The reaction was diluted with ethyl acetate (10 mL) and washed with water (10 mL×3). The organic layer was dried over Na_2SO_4 and concentrated. The resulting crude residue was purified by silica gel chromatography to give compound **3**.

3. Synthesis and Characterization Data of Allyl Glycosyl Sulfones

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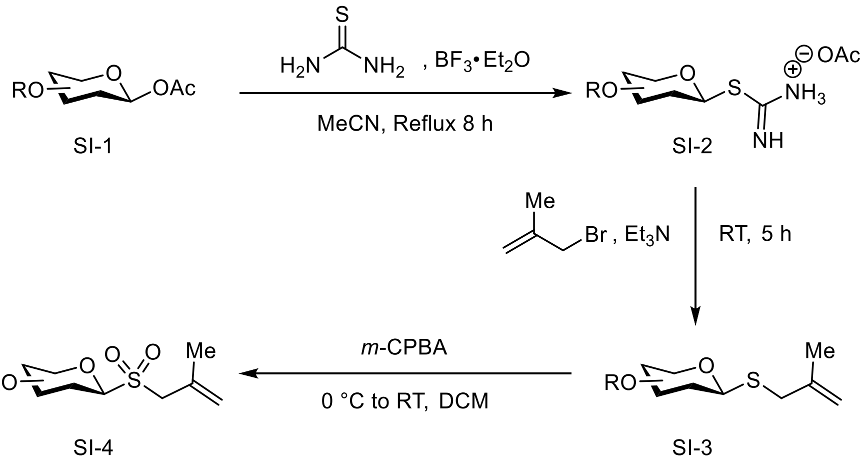
General Procedure B:

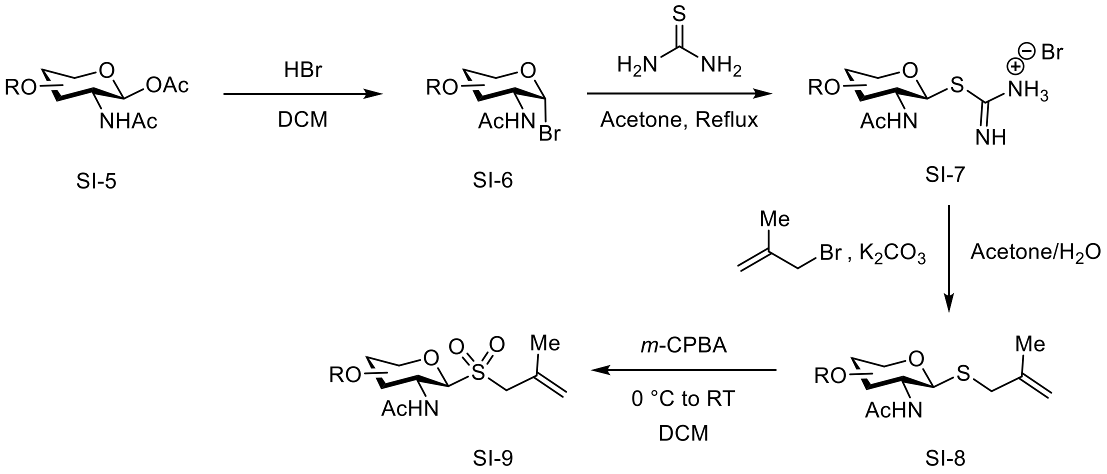


Step I: To a flask with **SI-1** (10 mmol, 1.0 equiv.), thiourea (15 mmol, 1.5 equiv.), boron trifluoride etherate (30 mmol, 3.0 equiv.), and MeCN (20 mL) were added. The reaction mixture was heated reflux about 8 hours to afford **SI-2**, until SI-1 was consumed completely monitored by TLC.

Step II: Without further operation, Et_3N (60 mmol, 6.0 equiv.) and 3-bromo-2-methylpropene (15 mmol, 1.5 equiv.) were added to the reaction mixture, stirred at room temperature about 5 hours until **SI-2** was consumed completely monitored by TLC. The reaction mixture was concentrated, dissolved in ethyl acetate (20 mL), washed with water (15 mL×3). The organic layer was dried with anhydrous Na_2SO_4. The resulting crude residue was purified by flash chromatography to afford **SI-3**.

Step III: To a flask with **SI-3** (1.0 equiv.) and DCM (1 M), *m*-CPBA (2.5 equiv.) was added slowly at 0 °C. The reaction mixture was stirred for 10 minutes at 0 °C, then warmed to room temperature, stirred overnight. The reaction mixture was filtered and the organic layer was washed with water, dried with anhydrous Na_2SO_4. The resulting crude residue was purified by flash chromatography to give compound **SI-4**.

General Procedure C:



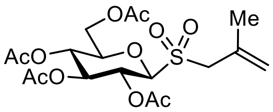
Step I: **SI-5** (10 mmol, 1.0 equiv.) was dissolved in DCM (25 mL), then hydrogen bromide (33 wt.% in acetic acid) was added slowly into the reaction at 0 °C. The reaction mixture was stirred at 0 °C overnight. The reaction was quenched with ice water (30 mL), extracted with DCM (20 mL×3). Organic layer was neutralized with ice water solution of K_2CO_3, dried with anhydrous Na_2SO_4, concentrated under low temperature to give **SI-6**.

Step II: **SI-6** (10 mmol, 1.0 equiv.) was dissolved in acetone (15 mL), then thiourea (15 mmol, 1.5 equiv.) was added. The reaction mixture was heated reflux for 5 hours to obtain **SI-7**, which was directly used for next step without purification.

Step III: To the reaction, H_2O (15 mL), K_2CO_3 (30 mmol, 3.0 equiv.), and 3-bromo-2-methylpropene (15 mmol, 1.5 equiv.) were added, stirred at room temperature, monitored by TLC. The solvent was removed under vacuum, then the residue was extracted with DCM. Organic layer was washed with water, NH_4Cl (aq.), dried over Na_2SO_4, concentrated to afford the crude **SI-8**.

Step IV: To a flask with **SI-8** (1.0 equiv.) and DCM (1M), *m*-CPBA (2.5 equiv.) was added slowly at 0 °C. The reaction mixture was stirred for 10 minutes at 0 °C, then warmed to room temperature, stirred overnight. The reaction mixture was filtered and the organic layer was washed with water, dried with anhydrous Na_2SO_4. The resulting crude residue was purified by flash chromatography to give the desired product **SI-9**.

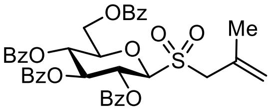
Characterization Data of Allyl Glycosyl Sulfones:



1-((2-Methylallyl)sulfonyl)-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (5a)

Compound **5a** was prepared following **General Procedure B** from peracetylated glucose (10 mmol, 3.9 g) and was obtained as a white solid (2.3 g, 59% total yield). The ^{1}H NMR data is in agreement with that reported in literature.[1]

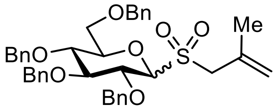
^{1}H NMR (CDCl$_3$, 400 MHz) δ: 5.53 (dd, *J* = 9.6, 9.6 Hz, 1H), 5.32 (dd, *J* = 9.3, 9.3 Hz, 1H), 5.27 (s, 1H), 5.20 (s, 1H), 5.10 (dd, *J* = 9.8, 9.8 Hz, 1H), 4.59 (d, *J* = 9.9 Hz, 1H), 4.34 – 4.17 (m, 2H), 3.98 (d, *J* = 13.6 Hz, 1H), 3.81 (ddd, *J* = 10.1, 5.0, 2.7 Hz, 1H), 3.66 (d, *J* = 13.6 Hz, 1H), 2.09 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), and1.98 (s, 3H).



1-((2-Methylallyl)sulfonyl)-2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (5b)

Compound **5b** was prepared following **General Procedure B** from 2,3,4,6-Tetra-O-benzoyl-D-glucopyranose (10 mmol, 6.4 g) and was obtained as a white solid (3.6 g, 52% total yield). The ^{1}H NMR data is in agreement with that reported in literature.[2]

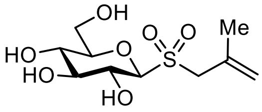
^{1}H NMR (CDCl$_3$, 400 MHz) δ: 8.06 – 7.98 (m, 2H), 7.96 – 7.88 (m, 4H), 7.86 – 7.80 (m, 2H), 7.61 – 7.22 (m, 12H), 6.07 (d, *J* = 9.4, 9.4 Hz, 1H), 5.99 (dd, *J* = 9.3, 9.3 Hz, 1H), 5.69 (dd, *J* = 9.6, 9.6 Hz, 1H), δ 5.21 (s, 1H), 5.17 (s, 1H), 4.94 (d, *J* = 9.6 Hz, 1H), 4.73 (dd, *J* = 12.5, 2.8 Hz, 1H), 4.53 (dd, *J* = 12.4, 5.7 Hz, 1H), 4.28 (ddd, *J* = 9.5, 5.7, 2.8 Hz, 1H), 4.04 (d, *J* = 13.5 Hz, 1H), 3.71 (d, *J* = 13.6 Hz, 1H), and 1.93 (s, 3H).



1-((2-Methylallyl)sulfonyl)-2,3,4,6-tetra-*O*-benzyl-D-glucopyranoside (5c)

Compound **5c** was prepared following **General Procedure B** from 2,3,4,6-Tetra-O-benzyl-D-glucopyranose (20 mmol, 10.8 g) and was obtained as a white solid (7.7 g, 60% total yield). The ^{1}H NMR data is in agreement with that reported in literature.[2]

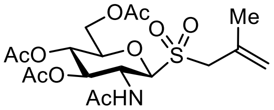
^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.40–7.24 (m, 18H), 7.20–7.12 (m, 2H), 5.21 (s, 0.3H), 5.17 (dd, *J* = 1.6, 1.6 Hz, 1H), 5.09 (s, 0.7H), 5.04 (d, *J* = 6.0 Hz, 0.7H), 4.90–4.81 (m, 2H), 4.80–4.67 (m, 3H), 4.58–4.37 (m, 5H), 4.15–4.07 (m, 1H), 4.05 (d, *J* = 13.5 Hz, 0.3H), 3.95 (d, *J* = 13.5 Hz, 0.7H), 3.81–3.50 (m, 5H), 1.97 (s, 0.9H), and 1.95 (s, 2.1H).



1-((2-Methylallyl)sulfonyl)-β-D-glucopyranoside (5d)

Compound **5d** was prepared by hydrolysis from **5a** (2 mmol, 780 mg), treated with LiOH (1.6 mmol, 19 mg) in MeOH at 0 °C. **5d** was obtained as a white solid (423 mg, 75% total yield). The ^{1}H NMR data is in agreement with that reported in literature.[1]

^{1}H NMR (CD$_3$OD, 400 MHz) δ 5.20 (m, 2H), 4.43 (d, *J* = 9.6 Hz, 1H), 4.11 (d, *J* = 13.6 Hz, 1H), 3.87 (dd, *J* = 12.5, 2.1 Hz, 1H), 3.80 (d, *J* = 13.5 Hz, 1H), 3.77 (dd, *J* = 9.2, 9.2 Hz, 1H), 3.64 (dd, *J* = 12.5, 6.2 Hz, 1H), 3.42 (dd, *J* = 8.9, 8.9 Hz, 1H), 3.36 (ddd, *J* = 9.2, 6.2, 2.0 Hz, 1H), 3.27 (dd, *J* = 9.4, 9.4 Hz, 1H), and 1.93 (s, 3H).



1-((2-Methylallyl)sulfony)-2-deoxy-2-N-acetyl-3,4,6-tri-*O*-acetyl-β-D-glucopyranoside (5e)

Compound **5e** was prepared following **General Procedure C** from peracetylated glucose (10 mmol, 3.9 g) and was obtained as a white solid (0.9 g, 20% total yield).

^{1}H NMR (CDCl$_3$, 400 MHz) δ: 6.14 (d, *J* = 8.0 Hz, 1H), 5.71 (dd, *J* = 9.7, 9.7 Hz, 1H), 5.33 – 5.14 (m, 3H), 5.05 (dd, *J* = 9.7, 9.7 Hz, 1H), 4.25 (dd, *J* = 12.6, 2.4 Hz, 1H), 4.20 (dd, *J* = 12.6, 5.1 Hz, 1H), 4.12 – 4.03 (m, 1H), 4.00 (d, *J* = 13.6 Hz, 1H), 3.90 (ddd, *J* = 10.4, 5.4, 2.4 Hz, 1H), 3.70 (d, *J* = 13.6 Hz, 1H), 2.09 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 1.96 (s, 3H), and 1.94 (s, 3H).

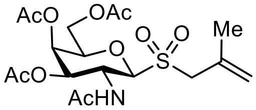
^{13}C NMR (CDCl$_3$, 101 MHz) δ 171.60, 170.55, 170.40, 169.54, 132.57, 121.34, 85.05, 76.51, 71.82, 68.44, 62.03, 57.61, 50.40, 23.37, 23.13, 20.81, 20.76, and 20.70.

$[\alpha]_D^{14}$ = 5.7 (c = 0.16, CHCl$_3$).

m.p.: 219– 221 ^{o}C.

IR (thin film, cm^{-1}): 3326, 2952, 1745, 1665, 1533, 1376, 1321, 1224, 1113, 1038, 920, 749 and 590.

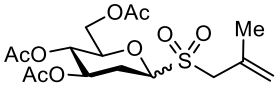
HRMS (DART-TOF) calculated for $C_{15}H_{27}NNaO_{10}S^+$ [M+Na]$^+$ m/z 472.1248, found 472.1250.



1-((2-Methylallyl)sulfonyl)-2-deoxy-2-N-acetyl-3,4,6-tri-*O*-acetyl-β-D-galactopyranoside (5f)

Compound **5f** was prepared following **General Procedure C** from peracetylated galactocose (3.33 mmol, 1.3 g) and was obtained as a white solid (148 mg, 10% total yield). The ^{1}H NMR data is in agreement with that reported in literature.[1]

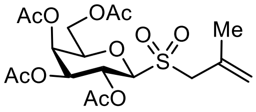
^{1}H NMR (CDCl$_3$, 400 MHz) δ: 6.18 (d, *J* = 8.0 Hz, 1H), 5.72 (dd, *J* = 10.8, 3.3 Hz, 1H), 5.46 (d, *J* = 3.3 Hz, 1H), 5.25 (s, 1H), 5.20 (s, 1H), 5.18 (d, *J* = 10.2 Hz, 1H). 4.28 – 4.12 (m, 4H), 4.02 (d, *J* = 13.5 Hz, 1H), 3.72 (d, *J* = 13.5 Hz, 1H), 2.17 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H), 1.96 (s, 3H), and 1.94 (s, 3H).



1-((2-Methylallyl)sulfonyl)-2-deoxy-3,4,6-tri-*O*-acetyl-D-glucopyranoside (5g)

Compound **5g** was prepared following **General Procedure B** from peracetylated 2-deoxy-glucose (10 mmol, 3.2 g) and was obtained as a colorless oil (0.6 g, 15% total yield). The ^{1}H NMR data is in agreement with that reported in literature.[1]

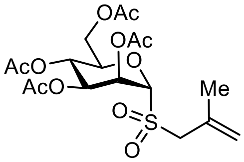
^{1}H NMR (CDCl$_3$, 400 MHz) (major isomer) δ: 5.47 (ddd, *J* = 9.7, 7.7, 5.1 Hz, 0.69H), 5.24 (dd, *J* = 1.5, 1.5 Hz, 1H), 5.18 (s, 1H), 5.15 – 4.92 (m, 2H), 4.69 – 4.57 (m, 1H), 4.32 – 4.18 (m, 1.25H), 4.15 (dd, *J* = 12.4, 2.5 Hz, 0.73H), 4.01 (dd, *J* = 20.1, 13.8 Hz, 1H), 3.71 (ddd, *J* = 9.6, 5.5, 2.7 Hz, 0.33H), 3.63 (dd, *J* = 19.8, 13.8 Hz, 1H), 2.82 (ddd, *J* = 14.8, 5.1, 3.4 Hz, 0.71H), 2.56 (ddd, *J* = 12.8, 5.1, 2.2 Hz, 0.34H), 2.18 – 2.11 (m, 1H), 2.10 (s, 2H), 2.09 (s, 1H), 2.06 (s, 2H), 2.06 (s, 1H), 2.05 (s, 3H), 1.98 (d, *J* = 1.3 Hz, 3H). (minor isomer) δ: 5.26 – 5.23 (m, 1H), 5.18 (s, 1H), 5.13 – 5.06 (m, 1H), 5.06 – 4.93 (m, 1H), 4.68 – 4.58 (m, 1H), 4.30 – 4.20 (m, 2H), 4.03 (d, *J* = 13.9 Hz, 1H), 3.71 (ddd, *J* = 9.6, 5.5, 2.7 Hz, 1H), 3.60 (d, *J* = 13.8 Hz, 1H), 2.56 (ddd, *J* = 12.8, 5.1, 2.2 Hz, 1H), 2.18 – 2.11 (m, 1H), 2.09 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), and 1.98 (s, 3H).



1-((2-Methylallyl)sulfonyl)-2,3,4,6-tetra-O-acetyl-β-D-Galactopyranoside (5h)

Compound **5h** was prepared following **General Procedure B** from peracetylated galactose (10 mmol, 3.9 g) and was obtained as a white solid (1.8 g, 40% total yield). The ^{1}H NMR data is in agreement with that reported in literature.[1]

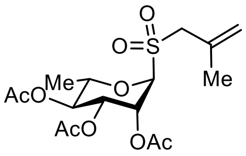
^{1}H NMR (CDCl$_3$, 400 MHz) δ: 5.72 (dd, *J* = 9.9, 9.9 Hz, 1H), 5.47 (d, *J* = 3.4 Hz, 1H), 5.27 (dd, *J* = 1.6, 1.6 Hz, 1H), 5.20 (s, 1H), 5.15 (dd, *J* = 10.0, 3.3 Hz, 1H), 4.55 (d, *J* = 9.9 Hz, 1H), 4.28 – 4.14 (m, 2H), 4.07 – 4.03 (m, 1H), 3.98 (d, *J* = 13.6 Hz, 1H), 3.68 (d, *J* = 13.5 Hz, 1H), 2.19 (s, 3H), 2.06 (s, 3H), 2.06 (s, 3H), and 1.98 (s, 3H).



1-((2-Methylallyl)sulfonyl)-2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranoside (5i)

Compound **5i** was prepared following **General Procedure B** from peracetylated mannose (10 mmol, 3.9 g) and was obtained as a white solid (2.3 g, 50% total yield). The ^{1}H NMR data is in agreement with that reported in literature.[1]

^{1}H NMR (CDCl$_3$, 400 MHz) δ: 5.94 (dd, *J* = 3.8, 2.1 Hz, 1H), 5.58 (dd, *J* = 9.3, 3.8 Hz, 1H), 5.34 – 5.23 (m, 2H), 5.19 (s, 1H), 4.99 (d, *J* = 2.1 Hz, 1H), 4.70 (ddd, *J* = 9.8, 5.9, 2.5 Hz, 1H), 4.27 (dd, *J* = 12.4, 5.8 Hz, 1H), 4.18 (dd, *J* = 12.5, 2.5 Hz, 1H), 4.00 (d, *J* = 13.9 Hz, 1H), 3.68 (d, *J* = 13.9 Hz, 1H), 2.17 (s, 3H), 2.11 (s, 3H), 2.07 (s, 3H), 2.01 (s, 3H), and 1.98 (s, 3H).



1-((2-Methylallyl)sulfonyl)-2,3,4-tri-*O*-acetyl-β-L-rhamnopyranosid (**5j**)

Compound **5j** was prepared following **General Procedure B** from peracetylated rhamnose (10 mmol, 3.3 g) and was obtained as a white solid (1.7 g, 42% total yield).

^{1}H NMR (CDCl$_3$, 400 MHz) δ: 5.93 (dd, *J* = 3.8, 2.0 Hz, 1H), 5.53 (dd, *J* = 9.4, 3.8 Hz, 1H), 5.25 (s, 1H), 5.17 (s, 1H), 5.10 (dd, *J* = 9.5, 9.5 Hz, 1H), 4.94 (d, *J* = 2.1 Hz, 1H), 4.55 (dq, *J* = 9.5, 6.1 Hz, 1H), 3.97 (d, *J* = 14.0 Hz, 1H), 3.66 (d, *J* = 13.9 Hz, 1H), 2.16 (s, 3H), 2.06 (s, 3H), 2.00 (s, 3H), 1.98 (s, 3H), and 1.29 (d, *J* = 6.0 Hz, 3H).

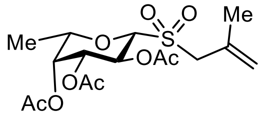
^{13}C NMR (CDCl$_3$, 101 MHz) δ: 169.96, 169.45, 169.40, 133.13, 121.35, 86.53, 71.71, 70.19, 68.98, 65.18, 58.67, 22.95, 20.80, 20.76, 20.60, and 18.11.

$[\alpha]_D^{14}$ = -83.9 (c = 0.08, CHCl$_3$).

m.p.: 92– 94 °C.

IR (thin film, cm^{-1}): 2922, 2940, 1745, 1370, 1314, 1212, 1112, 1050, 911 and 603.

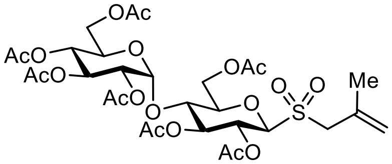
HRMS (DART-TOF) calculated for $C_{16}H_{26}O_{10}S$ [M+H_2O] m/z 410.1247, found 410.1496.



1-((2-Methylallyl)sulfonyl)-2,3,4-tri-*O*-acetyl-β-L-fucopyranoside (**5k**)

Compound **5k** was prepared following **General Procedure B** from peracetylated L-fucose (10 mmol, 3.3 g) and was obtained as a white solid (1.9 g, 48% total yield). The ^{1}H NMR data is in agreement with that reported in literature.[1]

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 5.68 (dd, *J* = 9.9, 9.9 Hz, 1H), 5.34 – 5.30 (m, 1H), 5.27 (s, 1H), 5.18 – 5.07 (m, 2H), 4.49 (d, *J* = 9.9 Hz, 1H), 4.01 – 3.90 (m, 2H), 3.74 (d, *J* = 13.5 Hz, 1H), 2.20 (s, 3H), 2.06 (s, 3H), 2.00 (s, 3H), 1.98 (s, 3H), and 1.28 (d, *J* = 6.3 Hz, 3H).



1-((2-Methylallyl)sulfonyl)-2,3,6-tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)- β-D-glucopyranoside (5l)

Compound **5l** was prepared following **General Procedure B** from peracetylated maltose (10 mmol, 6.8 g) and was obtained as a white solid (1.6 g, 22% total yield).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 5.41 (d, *J* = 4.1 Hz, 1H), 5.39 – 5.30 (m, 3H), 5.28 – 5.24 (m, 1H), 5.21 (s, 1H), 5.05 (dd, *J* = 9.9, 9.9 Hz, 1H), 4.87 (dd, *J* = 10.5, 4.1 Hz, 1H), 4.70 – 4.67 (m, 1H), 4.64 (dd, *J* = 12.5, 2.6 Hz, 1H), 4.27 (dd, *J* = 12.5, 4.2 Hz, 1H), 4.21 (dd, *J* = 12.4, 5.1 Hz, 1H), 4.08 (dd, *J* = 12.4, 2.3 Hz, 1H), 4.02 – 3.93 (m, 3H), 3.79 (ddd, *J* = 9.6, 5.0, 2.5 Hz, 1H), 3.59 (d, *J* = 13.7 Hz, 1H), 2.14 (s, 3H), 2.11 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H), and 1.97 (s, 3H);

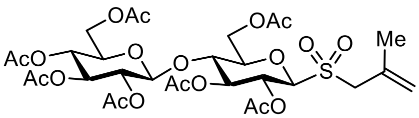
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 170.63, 170.59, 170.33, 170.21, 170.04, 169.49, 169.46, 133.18, 121.10, 96.02, 84.93, 75.46, 72.31, 70.09, 69.33, 68.87, 68.15, 66.79, 62.34, 61.69, 57.87, 22.92, 20.93, 20.84, 20.78, 20.68, and 20.66.

$[\alpha]_D^{14}$ = 21.3 (c = 0.14, $CHCl_3$).

m.p.: 79– 81 °C .

IR (thin film, cm^{-1}): 2995, 1747, 1325, 1224, 1034, 920, 750 and 610.

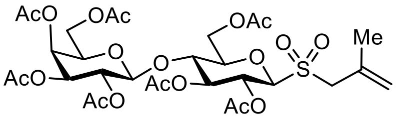
HRMS (DART-TOF) calculated for $C_{30}H_{42}NaO_{19}S^+$ $[M+Na]^+$ m/z 761.1933, found 761.1936.



(1-((2-Methylallyl)sulfonyl)-2,3,6-tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)- β-D-glucopyranoside (5m)

Compound **5m** was prepared following **General Procedure B** from peracetylated cellobiose (5.0 mmol, 3.4 g) and was obtained as a white solid (1.5 g, 40% total yield). The ^{1}H NMR data is in agreement with that reported in literature.[1]

^{1}H NMR (CDCl$_3$, 400 MHz) δ: 5.49 (dd, *J* = 9.4, 9.4 Hz, 1H), 5.29 (dd, *J* = 9.1, 9.1 Hz, 1H), 5.25 (s, 1H), 5.18 (s, 1H), 5.15 (d, *J* = 9.4 Hz, 1H), 5.06 (dd, *J* = 9.7, 9.7 Hz, 1H), 4.92 (dd, *J* = 9.4, 7.9 Hz, 1H), 4.66 – 4.61 (m, 1H), 4.61 – 4.54 (m, 2H), 4.37 (dd, *J* = 12.5, 4.4 Hz, 1H), 4.13 – 4.08 (m, 1H), 4.08 – 4.03 (m, 1H), 3.98 (d, *J* = 13.7 Hz, 1H), 3.81 (t, *J* = 9.4 Hz, 1H), 3.75 – 3.67 (m, 2H), 3.58 (d, *J* = 13.7 Hz, 1H), 2.12 (s, 3H), 2.09 (s, 3H), 2.04 (s, 3H), 2.04 (s, 6H), 2.01 (s, 3H), 1.98 (s, 3H), and 1.97 (s, 3H).



(1-((2-Methylallyl)sulfonyl)-2,3,6-tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)- β-D-glucopyranoside (5n)

Compound **5n** was prepared following **General Procedure B** from peracetylated lactose (5.0 mmol, 3.4 g) and was obtained as a white solid (1.1 g, 30% total yield).

^{1}H NMR (CDCl$_3$, 400 MHz) δ: 5.48 (dd, *J* = 9.4, 9.4 Hz, 1H), 5.38 – 5.31 (m, 1H), 5.31 (dd, *J* = 9.0, 9.0 Hz, 1H), 5.27 – 5.24 (m, 1H), 5.19 (s, 1H), 5.11 (ddd, *J* = 10.4, 7.6, 2.6 Hz, 1H), 4.98 (dd, *J* = 10.4, 3.2 Hz, 1H), 4.66 – 4.57 (m, 2H), 4.53 (d, *J* = 7.8 Hz, 1H), 4.18 – 4.05 (m, 3H), 3.98 (d, *J* = 13.8 Hz, 1H), 3.91 (dd, *J* = 6.7, 6.7 Hz, 1H), 3.83 (dd, *J* = 9.3, 9.3 Hz, 1H), 3.72 (ddd, *J* = 9.8, 5.7, 2.0 Hz, 1H), 3.58 (d, *J* = 13.7 Hz, 1H), 2.16 (s, 3H), 2.12 (s, 3H), 2.08 (s, 3H), 2.07 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), and 1.97 (s, 3H).

^{13}C NMR (CDCl$_3$, 101 MHz) δ: 170.48, 170.27, 170.21, 170.13, 169.78, 169.36, 169.19, 133.23, 121.02, 101.20, 84.91, 77.26, 75.52, 73.16, 70.97 (d, *J* = 2.1 Hz), 69.23, 66.74, 66.17, 61.61, 60.98, 57.78, 22.95, 20.86, 20.81, 20.76, 20.73, 20.70, and 20.60.

$[\alpha]_D^{14}$ = -10.1 (c = 0.13, CHCl$_3$).

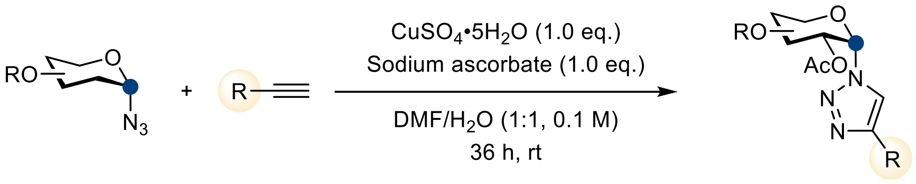
m.p.: 132– 134 ^{o}C.

IR (thin film, cm^{-1}): 2984, 1748, 1372, 1258, 1219, 1133, 1058, 908, and 750.

HRMS (DART-TOF) calculated for $C_{30}H_{42}NaO_{19}S^+$ $[M+Na]^+$ m/z 761.1933, found 761.1936.

4. General Procedure for the Reactions of Derivatization

General Procedure D

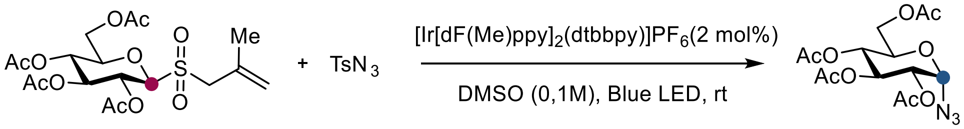


3 **11** **12**

To a screw-capped vial, sodium ascorbate (0.1 mmol, 1.0 equiv.), $CuSO_4 \cdot 5H_2O$ (0.1 mmol, 1.0 equiv.) and H_2O (0.5 mL) were added, stirring for 5 minutes. Glucosyl azide **3** (0.2 mmol, 2.0 equiv.), terminal alkyne **11** (0.1 mmol, 1.0 equiv.) and DMF (0.5 mL) were added. The vial was stirred for 36 h. The reaction was diluted with ethyl acetate (5 mL) and washed with water three times (total 15 mL). The organic layer was dried over Na_2SO_4 and concentrated. The resulting crude residue was purified by silica gel chromatography to afford the desired product **12**.

5. Optimization Tables

Table S1. Other Representative Conditions Not Listed in Table 1

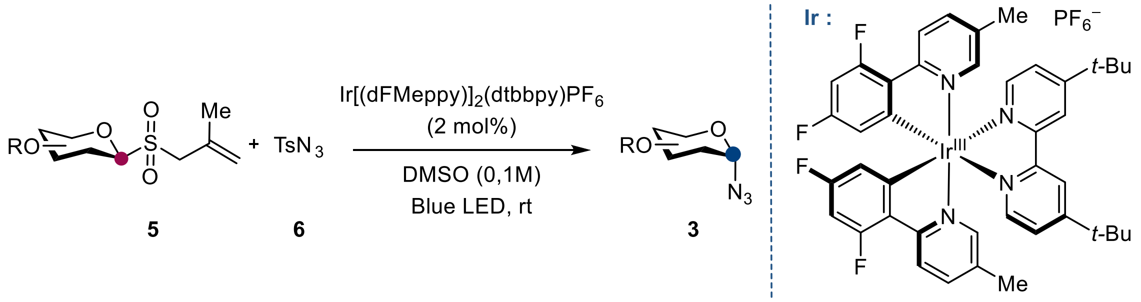


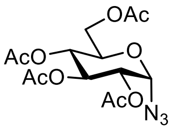
5a **6** **3a**

Entry	Variation from standard conditions	Yield (%)
1	Basic Red 1 instead of $[Ir[dF(Me)ppy]_2(dtbbpy)]PF_6$	41
2	fac-$Ir(ppy)_3$ instead of $[Ir[dF(Me)ppy]_2(dtbbpy)]PF_6$	62
3	Mes-$Acr^+ClO_4^-$ instead of $[Ir[dF(Me)ppy]_2(dtbbpy)]PF_6$	71
4	$Ir[(dFCF_3ppy)]_2(dtbbpy)]PF_6$ instead of $[Ir[dF(Me)ppy]_2(dtbbpy)]PF_6$	71
5	DMA instead of DMSO	78
6	DMF instead of DMSO	70
7	NMP instead of DMSO	66
8	THF instead of DMSO	60
9	MeOH instead of DMSO	42
10	*t*-BuOH instead of DMSO	40

Reactions in this **Table S1** were peformed under N_2 atmosphere with **5a** (22.5 mg, 0.05 mmol, 1.0 equiv.), tosyl azide **6** (19.7 mg, 0.1 mmol, 2.0 equiv.), $[Ir[dF(Me)ppy]_2(dtbbpy)]PF_6$ (1.0 mg, 0.001 mmol, 0.02 equiv.) in solvent (0.5 mL) for 8 h. Yields were determined by ^1H NMR analysis using 1,3,5-trimethoxy benzene as an internal standard.

6. Synthesis and Characterization Data for Products in Table 2





2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl azide (3a)

Compound **3a** was prepared following **General Reaction Procedure A** from glycosyl donor **5a** (90 mg, 0.2 mmol, 1.0 equiv.), tosyl azide **6** (79 mg, 0.4 mmol, 2.0 equiv.), and $[Ir[dF(Me)ppy]_2(dtbbpy)]PF_6$ (4 mg, 0.004 mml, 2 mol% equiv.). Flash chromatograph (SiO_2, petroleum ether: EtOAc = 3:1) afforded the desired product as a white solid (64 mg, 86% yield). Following a similar procedure, when the glycosyl donor 5a equivalent was increased to 2.5 mmol, the product was isolated with a separation yield of 78%.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 5.59 (d, *J* = 4.3 Hz, 1H), 5.37 (dd, *J* = 9.8, 9.8 Hz, 1H), 5.04 (dd, *J* = 9.9, 9.9Hz, 1H), 4.94 (dd, *J* = 10.1, 4.3 Hz, 1H), 4.25 (dd, *J* = 12.3, 4.5 Hz, 1H), 4.17 – 4.10 (m, 2H), 2.08 (s, 6H), 2.02 (s, 3H), and 2.00 (s, 3H).

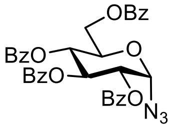
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 170.66, 170.00, 169.57, 86.31, 70.25, 69.74, 69.66, 68.04, 61.67, 20.77, 20.70, 20.64, and 20.62.

$[\alpha]_D^{15}$ = +152.5 (c = 0.30, $CHCl_3$).

m.p.: 91– 93 °C.

IR (thin film, cm^{-1}): 2119, 1753, 1369, 1222, 669, 605, and 563.

HRMS (DART-TOF) calculated for $C_{14}H_{19}NaN_3O_9^+[M+Na]^+$ m/z 396.1019, found 396.1012.



2,3,4,6-Tetra-*O*-benzoyl-α-D-glucopyranosyl azide (3b)

Compound **3b** was prepared following **General Reaction Procedure A** from glycosyl donor **5b** (128 mg, 0.2 mmol, 1.0 equiv.), tosyl azide **6** (79 mg, 0.4 mmol, 2.0 equiv.), and [Ir[dF(Me)ppy]$_2$(dtbbpy)]PF$_6$ (4 mg, 0.004 mml, 2 mol% equiv.). Flash chromatograph (SiO$_2$, petroleum ether: EtOAc = 6:1) afforded the desired product as a colorless oil (96 mg, 50% yield).

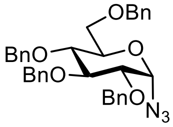
^{1}H NMR (CDCl$_3$, 400 MHz) δ: 8.10 – 8.04 (m, 2H), 8.02 – 7.96 (m, 2H), 7.96 – 7.91 (m, 2H), 7.89 – 7.84 (m, 2H), 7.60 – 7.48 (m, 4H), 7.47 – 7.27 (m, 8H), 6.09 (dd, *J* = 9.9, 9.9 Hz, 1H), 5.92 (d, *J* = 4.3 Hz, 1H), 5.70 (dd, *J* = 9.7, 9.7 Hz, 1H), 5.39 (dd, *J* = 10.1, 4.3 Hz, 1H), 4.70 – 4.59 (m, 2H), and 4.49 (dd, *J* = 11.7, 4.6 Hz, 1H).

^{13}C NMR (CDCl$_3$, 101 MHz) δ: 166.27, 165.80, 165.74, 165.31, 133.88, 133.70, 133.42, 133.35, 130.16, 130.03, 129.95, 129.86, 129.69, 129.05, 128.80, 128.70, 128.61, 128.58, 128.48, 86.66, 71.25, 70.25, 70.10, 69.02, and 62.77.

$[\alpha]_D^{22}$ = +63.4 (c = 0.19, CHCl$_3$).

IR (thin film, cm^{-1}): 2990, 2925, 1727, 1451, 1315, 1275, 1260, 1092, 1026, 801, 764, 750 and 707.

HRMS (DART-TOF) calculated for $C_{34}H_{27}NaN_3O_9^+$[M+Na]$^+$ m/z 644.1640, found 644.1646.



2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl azide (3c)

Compound **3c** was prepared following **General Reaction Procedure A** from glycosyl donor **5c** (128 mg, 0.2 mmol, 1.0 equiv.), tosyl azide **6** (79 mg, 0.4 mmol, 2.0 equiv.), and [Ir[dF(Me)ppy]$_2$(dtbbpy)]PF$_6$ (4 mg, 0.004 mml, 2 mol% equiv.). Flash chromatograph (SiO$_2$, petroleum ether: EtOAc = 6:1) afforded the desired product as a colorless oil (96 mg, 85% yield).

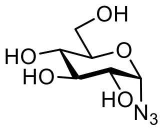
^{1}H NMR (CDCl$_3$, 400 MHz) δ: 7.38 – 7.21 (m, 18H), 7.15 – 7.11 (m, 2H), 5.22 (d, *J* = 4.1 Hz, 1H), 4.93 (d, *J* = 10.9 Hz, 1H), 4.84 – 4.76 (m, 3H), 4.65 (d, *J* = 12.0 Hz, 1H), 4.58 (d, *J* = 12.1 Hz, 1H), 4.48 (d, *J* = 10.8 Hz, 1H), 4.46 (d, *J* = 12.1 Hz, 1H), 3.85 (dd, *J* = 9.3, 9.3 Hz, 1H), 3.88 (dd, *J* = 10.2, 2.2 Hz, 1H), 3.72 (dd, *J* = 10.9, 3.5 Hz, 1H), and 3.67 – 3.56 (m, 3H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 138.66, 138.23, 137.87, 137.80, 128.77, 128.57, 128.55, 128.53, 128.31, 128.26, 128.09, 128.08, 127.96, 127.92, 127.89, 127.84, 88.24, 81.92, 79.62, 77.22, 75.97, 75.24, 73.94, 73.68, 72.69, and 68.29.

[α]$_D$^{15} = +32.2 (c = 0.58, $CHCl_3$).

IR (thin film, cm^{-1}): 2112, 1497, 1456, 1369, 1092, 1038, 735, and 697.

HRMS (DART-TOF) calculated for $C_{34}H_{35}NaN_3O_5^+[M+Na]^+$ m/z 588.2474, found 588.2468.



α-D-glucopyranosyl azide (3d)

Compound **3d** was prepared following **General Reaction Procedure A** from glycosyl donor **5d** (57mg, 0.2 mmol, 1.0 equiv.), tosyl azide **6** (79 mg, 0.4 mmol, 2.0 equiv.), and [Ir[dF(Me)ppy]$_2$(dtbbpy)]PF_6 (4 mg, 0.004 mml, 2 mol% equiv.). Flash chromatograph (SiO_2, DCM: MeOH = 6:1) afforded the desired product as a white solid (25 mg, 60% yield).

^{1}H NMR (CD_3OD, 400 MHz) δ: 5.33 (d, *J* = 3.6 Hz, 1H), 3.86 – 3.71 (m, 1H), 3.70 – 3.58 (m, 2H), 3.52 – 3.45 (m, 2H), and 3.27 (dd, *J* = 9.3, 9.3 Hz, 1H).

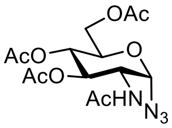
^{13}C NMR (CD_3OD, 101 MHz) δ: 91.64, 75.94, 74.65, 73.01, 71.13, and 62.36.

[α]$_D$^{15} = +238.2 (c = 0.20, $CHCl_3$).

m.p.: 163– 165 °C.

IR (thin film, cm^{-1}): 3680, 2972, 2864, 2116, 1652, 1346, 1054, 1032, and 1014.

HRMS (DART-TOF) calculated for $C_6H_{11}NaN_3O_5^+[M+Na]^+$ m/z 228.0591, found 228.0589.



3,4,6-Tri-*O*-acetyl-2-*N*-acetyl-2-deoxy-α-D-glucopyranosyl azide (3e)

Compound **3e** was prepared following **General Reaction Procedure A** from glycosyl donor **5e** (93 mg, 0.2 mmol, 1.0 equiv.), tosyl azide **6** (79 mg, 0.4 mmol, 2.0 equiv.), and [Ir[dF(Me)ppy]$_2$(dtbbpy)]PF_6 (4 mg, 0.004 mml, 2 mol% equiv.). Flash chromatograph (SiO_2, petroleum ether: EtOAc = 2:1) afforded the desired product as a white solid (49.8 mg, 67% yield).

^{1}H NMR (CDCl$_3$, 400 MHz) δ: 5.87 –5.81 (m, 1H) 5.48 (d, *J* = 4.2 Hz, 1H), 5.15 – 5.05 (m, 2H), 4.39 – 4.27 (m, 1H), 4.24 (dd, *J* = 12.4, 4.6 Hz, 1H), 4.14 (dd, *J* = 12.3, 2.3 Hz, 1H), 4.12 – 4.07 (m, 1H), 2.08 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H), and 1.96 (s, 3H).

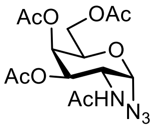
^{13}C NMR (CDCl$_3$, 101 MHz) δ: 171.58, 170.72, 170.27, 169.28, 88.14, 70.50, 69.92, 67.75, 61.80, 51.66, 23.14, 20.78, 20.77, and 20.65.

$[\alpha]_D^{15}$ = +178.5 (c = 0.32, CHCl$_3$).

m.p.: 141– 142 °C.

IR (thin film, cm^{-1}): 3388, 3282, 2921, 2849, 2120, 1746, 1659, 1527, 1365, 1229, 1106, and 1040.

HRMS (DART-TOF) calculated for $C_{14}H_{20}NaN_4O_8^+$[M+Na]$^+$ m/z 395.1173, found 395.1181.



3,4,6-Tri-*O*-acetyl-2-*N*-acetyl-2-deoxy-α-D-Galactopyranosyl azide (3f)

Compound **3f** was prepared following **General Reaction Procedure A** from glycosyl donor **5f** (90 mg, 0.2 mmol, 1.0 equiv.), tosyl azide **6** (79 mg, 0.4 mmol, 2.0 equiv.), and [Ir[dF(Me)ppy]$_2$(dtbbpy)]PF$_6$ (4 mg, 0.004 mml, 2 mol% equiv.). Flash chromatograph (SiO$_2$, petroleum ether: EtOAc = 2:1) afforded the desired product as a colorless oil (51 mg, 68% yield).

^{1}H NMR (CDCl$_3$, 400 MHz) δ: 5.75 (d, *J* = 8.9 Hz, 1H), 5.54 (d, *J* = 4.2 Hz, 1H), 5.37 (dd, *J* = 3.3, 1.4 Hz, 1H), 5.05 (dd, *J* = 11.4, 3.2 Hz, 1H), 4.62 – 4.53 (m, 1H), 4.36 – 4.27 (m, 1H), 4.15 (dd, *J* = 11.4, 5.9 Hz, 1H), 4.08 (dd, *J* = 11.4, 7.0 Hz, 1H), 2.14 (s, 3H), 2.04 (s, 3H), 1.98 (s, 3H), and 1.97 (s, 3H).

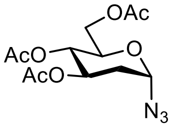
^{13}C NMR (CDCl$_3$, 101 MHz) δ: 171.01, 170.52, 170.41, 170.23, 88.70, 68.91, 67.76, 67.08, 61.81, 47.47, 23.25, 20.79, and 20.74.

$[\alpha]_D^{14}$ = +191.1 (c = 0.27, CHCl$_3$).

m.p.: 149- 151 °C.

IR (thin film, cm^{-1}): 2120, 1748, 1659, 1542, 1373, 1230, 1121, 1091, 1045, and 750.

HRMS (DART-TOF) calculated for $C_{11}H_{15}NaN_3O_7^+$[M+Na]$^+$ m/z 395.1173, found 395.1176.



3,4,6-Tri-*O*-acetyl-2-deoxy-α-D-glucopyranosyl azide (3g)

Compound **3g** was prepared following **General Reaction Procedure A** from glycosyl donor **5g** (78 mg, 0.2 mmol, 1.0 equiv.), tosyl azide **6** (79 mg, 0.4 mmol, 2.0 equiv.), and [Ir[dF(Me)ppy]$_2$(dtbbpy)]PF$_6$ (4 mg, 0.004 mml, 2 mol% equiv.). Flash chromatograph (SiO_2, petroleum ether: EtOAc = 4:1) afforded the desired product as a white solid (45 mg, 71% yield). The ^{1}H NMR data is in agreement with that reported in literature.[3]

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 5.53 (dd, *J* = 4.3, 1.4 Hz, 1H), 5.21 (ddd, *J* = 11.4, 9.4, 5.2 Hz, 1H), 5.00 (dd, *J* = 9.6, 9.6 Hz, 1H), 4.33 (dd, *J* = 12.8, 5.3 Hz, 1H), 4.20 – 4.04 (m, 2H), 2.18 (ddd, *J* = 13.2, 5.2, 1.5 Hz, 1H), 2.10 (s, 3H), 2.05 (s, 3H), 2.02 (s, 3H), and 1.86 (ddd, *J* = 13.2, 11.4, 4.3 Hz, 1H).

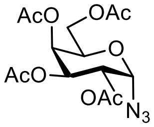
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 170.82, 170.18, 169.94, 86.79, 70.31, 68.90, 68.51, 62.19, 34.40, 21.02, 20.85, and 20.82.

$[\alpha]_D^{15}$ = +185 (c = 0.30, $CHCl_3$).

m.p.: 79– 81°C.

IR (thin film, cm^{-1}): 2947, 2113, 1741, 1437, 1367, 1224, 1077, 1044, 971, 749, and 649.

HRMS (DART-TOF) calculated for $C_{12}H_{17}NaN_3O_7^+$[M+Na]$^+$ m/z 338.0959, found 338.0957.



2,3,4,6-Tetra-*O*-acetyl-α-D-galactopyranosyl azide (3h)

Compound **3h** was prepared following **General Reaction Procedure A** from glycosyl donor **5h** (90 mg, 0.2 mmol, 1.0 equiv.), tosyl azide **6** (79 mg, 0.4 mmol, 2.0 equiv.), and [Ir[dF(Me)ppy]$_2$(dtbbpy)]PF$_6$ (4 mg, 0.004 mml, 2 mol% equiv.). Flash chromatograph (SiO_2, petroleum ether: EtOAc = 3:1) afforded the desired product as a colorless oil (63 mg, 85% yield).

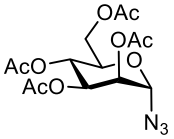
^{1}H NMR ($CDCl_3$, 400 MHz) δ: 5.65 (d, *J* = 3.9 Hz, 1H), 5.44 (dd, *J* = 3.1, 1.4 Hz, 1H), 5.23 (dd, *J* = 10.8, 3.0 Hz, 1H), 5.18 (dd, *J* = 10.8, 4.0 Hz, 1H), 4.39 – 4.30 (m, 1H), 4.19 – 4.02 (m, 2H), 2.13 (s, 3H), 2.09 (s, 3H), 2.05 (s, 3H), and 1.98 (s, 3H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 170.50, 170.26, 170.13, 169.92, 86.87, 68.70, 67.76, 67.50, 67.35, 61.60, 20.76, 20.74, and 20.69.

$[\alpha]_D^{15}$ = +109.6 (c = 0.40, $CHCl_3$).

IR (thin film, cm^{-1}): 2121, 1747, 1371, 1222, 1069, 955, and 895.

HRMS (DART-TOF) calculated for $C_{14}H_{19}NaN_3O_9^+$[M+Na]$^+$ m/z 396.1014, found 396.1014.



2,3,4,6-Tetra-*O*-acetyl-α-D-mannitopyranosyl azide (3i)

Compound **3i** was prepared following **General Reaction Procedure A** from glycosyl donor **5i** (90 mg, 0.2 mmol, 1.0 equiv.), tosyl azide **6** (79 mg, 0.4 mmol, 2.0 equiv.), and [Ir[dF(Me)ppy]$_2$(dtbbpy)]PF$_6$ (4 mg, 0.004 mml, 2 mol% equiv.). Flash chromatograph (SiO$_2$, petroleum ether: EtOAc = 3:1) afforded the desired product as a colorless oil (49 mg, 65% yield). The ^{1}H NMR data is in agreement with that reported in literature.[4]

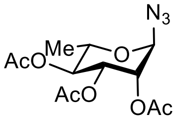
^{1}H NMR (CDCl$_3$, 400 MHz) δ: 5.38 (d, *J* = 2.0 Hz, 1H), 5.28 (dd, *J* = 9.5, 9.5 Hz, 1H), 5.24 (dd, *J* = 9.3, 2.9 Hz, 1H), 5.14 (dd, *J* = 3.0, 2.0 Hz, 1H), 4.30 (dd, *J* = 12.4, 5.6 Hz, 1H), 4.20 – 4.06 (m, 2H), 2.16 (s, 3H), 2.10 (s, 3H), 2.04 (s, 3H), and 1.99 (s, 3H).

^{13}C NMR (CDCl$_3$, 101 MHz) δ: 170.70, 169.96, 169.85, 169.75, 87.59, 70.77, 69.32, 68.38, 65.78, 62.28, 20.92, 20.81, 20.77, and 20.71.

$[\alpha]_D^{15}$ = +87.1 (c = 0.49, CHCl$_3$).

IR (thin film, cm^{-1}): 2917, 2847, 2121, 1747, 1437, 1370, 1220, 1124, 1085, 1051, 960, and 600.

HRMS (DART-TOF) calculated for $C_{14}H_{19}NaN_3O_9^+$[M+Na]$^+$ m/z396.1014, found 396.1018.



2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl azide (3j)

Compound **3j** was prepared following glycosyl donor **5j** (78 mg, 0.2 mmol, 1.0 equiv.), tosyl azide **6** (79 mg, 0.4 mmol, 2.0 equiv.), and [Ir[dF(Me)ppy)]$_2$(dtbbpy)]PF$_6$ (4 mg, 0.004 mml, 2 mol% equiv.). Flash chromatograph (SiO$_2$, petroleum ether: EtOAc = 4:1) afforded the desired product as a corlorless oil (42 mg, 66% yield). The ^{1}H NMR data is in agreement with that reported in literature.[5]

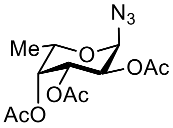
^{1}H NMR (CDCl$_3$, 400 MHz) δ: 5.29 (d, *J* = 1.9 Hz, 1H), 5.17 (dd, *J* = 10.2, 3.0 Hz, 1H), 5.12 (dd, *J* = 3.4, 1.9 Hz, 1H), 5.05 (dd, *J* = 9.9, 9.9Hz, 1H), 4.00 (dq, *J* = 12.3, 6.3 Hz, 1H), 2.13 (s, 3H), 2.03 (s, 3H), 1.96 (s, 3H), and 1.25 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (CDCl$_3$, 101 MHz) δ: 170.00, 169.95, 169.91, 87.59, 70.56, 69.56, 68.71, 68.40, 20.89, 20.82, 20.70, and 17.53.

$[\alpha]_D^{15}$ = -91.1 (c = 0.25, $CHCl_3$).

IR (thin film, cm^{-1}): 2930, 2118, 1747, 1437, 1437, 1370, 1220, 1124, 1054, 935, 785, and 535.

HRMS (DART-TOF) calculated for $C_{12}H_{17}NaN_3O_7^+[M+Na]^+$ m/z 338.0959, found 338.0959.



2,3,4-Tri-*O*-acetyl-α-L-fucopyranosyl azide (3k)

Compound **3k** was prepared following **General Reaction Procedure A** from glycosyl donor **5k** (79 mg, 0.2 mmol, 1.0 equiv.), tosyl azide **6** (79 mg, 0.4 mmol, 2.0 equiv.), and $[Ir[dF(Me)ppy]_2(dtbbpy)]PF_6$ (4 mg, 0.004 mml, 2 mol% equiv.). Flash chromatograph (SiO_2, petroleum ether: EtOAc = 4:1) afforded the desired product as a corlorless oil (54 mg, 85% yield). The ^{1}H NMR data is in agreement with that reported in literature.[6]

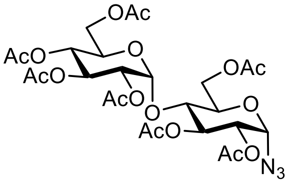
^{1}H NMR ($CDCl_3$, 400 MHz) δ: 5.61 (d, *J* = 4.0 Hz, 1H), 5.30 (dd, *J* = 3.1, 1.3 Hz, 1H), 5.25 (dd, *J* = 10.7, 3.1 Hz, 1H), 5.19 (dd, *J* = 10.6, 4.1 Hz, 1H), 4.32 – 4.24 (m, 1H), 2.17 (s, 3H), 2.11 (s, 3H), 1.99 (s, 3H), and 1.18 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR ($CDCl_3$, 101 M Hz) δ: 170.55, 170.36, 170.02, 87.16, 70.79, 67.81, 67.63, 67.02, 20.79, 20.76, 20.72, and 16.03.

$[\alpha]_D^{15}$ = -154.5 (c = 0.33, $CHCl_3$).

IR (thin film, cm^{-1}): 2989, 2924, 2849, 2117, 1744, 1432, 1371, 1217, 1130, 1069, 928, and 682.

HRMS (DART-TOF) calculated for $C_{12}H_{17}NaN_3O_7^+[M+Na]^+$ m/z 338.0959, found 338.0965.



Hepta-*O*-acetyl-α-maltosyl azide (3l)

Compound **3l** was prepared following **General Reaction Procedure A** from glycosyl donor **5l** (148 mg, 0.2 mmol, 1.0 equiv.), tosyl azide **6** (79 mg, 0.4 mmol, 2.0 equiv.), and $[Ir[dF(Me)ppy]_2(dtbbpy)]PF_6$ (4 mg, 0.004 mml, 2 mol% equiv.). Flash chromatograph (SiO_2, petroleum ether: EtOAc = 1:1) afforded the desired product as a white solid (87 mg, 66% yield).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 5.48 (d, *J* = 4.3 Hz, 1H), 5.45 – 5.31 (m, 3H), 5.05 (dd, *J* = 9.9, 9.9 Hz, 1H), 4.87 – 4.79 (m, 2H), 4.50 (dd, *J* = 12.3, 2.4 Hz, 1H), 4.26 – 4.20 (m, 2H), 4.18 – 4.11 (m, 1H), 4.04 (dd, *J* = 12.5, 2.4 Hz, 1H), 3.98 – 3.91 (m, 2H), 2.14 (s, 3H), 2.09 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 2.02 (s, 3H), 2.01 (s, 2H), and 1.99 (s, 3H).

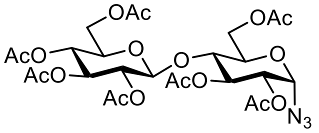
^{13}C NMR (CDCl$_3$, 101 MHz) δ: 170.76, 170.63, 170.53, 170.11, 169.98, 169.83, 169.56, 95.79, 86.16, 72.39, 72.12, 70.62, 70.15, 69.44, 68.72, 68.11, 62.53, 61.56, 21.00, 20.91, 20.80, 20.71, and 20.64.

[α]$_D$^{15} = +143.4 (c = 0.29, CHCl$_3$).

m.p.: 65– 66 °C.

IR (thin film, cm^{-1}): 2958, 2917, 2118, 1740, 1432, 1367, 1212, 1029, 898, 735, and 600.

HRMS (DART-TOF) calculated for $C_{26}H_{35}NaN_3O_{17}^+$[M+Na]$^+$ m/z 684.1859, found 684.1859.



Hepta-*O*-acetyl-α-cellobiosyl azide (3m)

Compound **3m** was prepared following **General Reaction Procedure A** from glycosyl donor **5m** (148 mg, 0.2 mmol, 1.0 equiv.), tosyl azide **6** (79 mg, 0.4 mmol, 2.0 equiv.), and [Ir[dF(Me)ppy]$_2$(dtbbpy)]PF$_6$ (4 mg, 0.004 mml, 2 mol% equiv.). Flash chromatograph (SiO$_2$, petroleum ether: EtOAc = 1:1) afforded the desired product as a white solid (86 mg, 65% yield).

^{1}H NMR (CDCl$_3$, 400 MHz) δ: 5.52 (d, *J* = 4.3 Hz, 1H), 5.36 (dd, *J* = 9.7, 9.7 Hz, 1H), 5.15 (dd, *J* = 9.3, 9.3 Hz, 1H), 5.09 (s, 1H), 4.99 – 4.80 (m, 2H), 4.57 – 4.47 (m, 2H), 4.36 (dd, *J* = 12.5, 4.4 Hz, 1H), 4.15 (dd, *J* = 12.1, 4.8 Hz, 1H), 4.08 – 4.00 (m, 2H), 3.73 (dd, *J* = 9.6, 9.6 Hz, 1H), 3.68 – 3.62 (m, 1H), 2.14 (s, 3H), 2.09 (s, 6H), 2.04 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), and 1.99 (s, 3H).

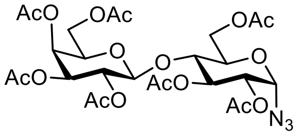
^{13}C NMR (CDCl$_3$, 101 MHz) δ: 170.58, 170.34, 170.20, 169.54, 169.39, 169.08, 100.79, 86.21, 76.15, 73.06, 72.13, 71.74, 70.66, 70.39, 69.21, 67.95, 61.74, 61.56, 20.93, 20.76, 20.68, and 20.66.

[α]$_D$^{15} = +66.0 (c = 0.26, CHCl$_3$).

m.p.: 198– 199 °C.

IR (thin film, cm^{-1}): 2924, 2117, 1739, 1367, 1210, 1032, 1904, and 735.

HRMS (DART-TOF) calculated for $C_{26}H_{35}NaN_3O_{17}^+$[M+Na]$^+$ m/z 684.1859, found 684.1865.



Hepta-O-acetyl-α-lactosyl azide (3n)

Compound **3n** was prepared following **General Reaction Procedure A** from glycosyl donor **5n** (148 mg, 0.2 mmol, 1.0 equiv.), tosyl azide **6** (79 mg, 0.4 mmol, 2.0 equiv.), and [Ir[dF(Me)ppy]$_2$(dtbbpy)]PF$_6$ (4 mg, 0.004 mml, 2 mol% equiv.).

Flash chromatograph (SiO_2, petroleum ether: EtOAc = 1:1) afforded the desired product as a white solid (67 mg, 50% yield).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 5.52 (d, *J* = 4.3 Hz, 1H), 5.45 – 5.31 (m, 2H), 5.11 (dd, *J* = 10.4, 7.9 Hz, 1H), 4.96 (dd, *J* = 10.4, 3.4 Hz, 1H), 4.88 (dd, *J* = 10.1, 4.3 Hz, 1H), 4.57 – 4.45 (m, 2H), 4.20 – 4.11 (m, 2H), 4.11 – 4.04 (m, 2H), 3.91 – 3.84 (m, 1H), 3.75 (dd, *J* = 9.6, 9.6 Hz, 1H), 2.16 (s, 3H), 2.14 (s, 3H), 2.09 (s, 3H), 2.06 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), and 1.97 (s, 3H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 170.45, 170.41, 170.26, 170.22, 170.18, 169.51, 169.09, 101.07, 86.23, 75.89, 71.13, 70.89, 70.65, 70.48, 69.44, 69.23, 66.78, 61.69, 61.01, 20.94, 20.92, 20.76, 20.70, and 20.62.

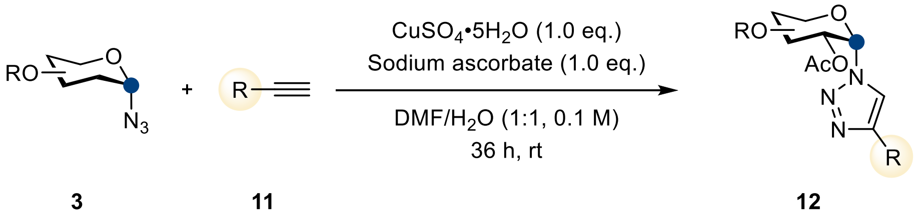
$[\alpha]_D^{15}$ = +60.9 (c = 0.21, $CHCl_3$).

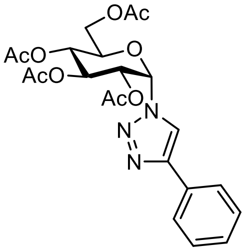
m.p.: 79– 81°C.

IR (thin film, cm^{-1}): 2119, 1747, 1433, 1369, 1219, 1079, 1045, 903, and 605.

HRMS (DART-TOF) calculated for $C_{26}H_{35}NaN_3O_{17}^+[M+Na]^+$ m/z 684.1859, found 684.1856.

7. Synthesis and Characterization Data for Products in Table 3





(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(4-phenyl-1*H*-1,2,3-triazol-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (12a)

Compound **12a** was prepared following **General Reaction Procedure D** from 2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl azide **3a** (37 mg, 0.1 mmol, 1.0 equiv.), ethynylbenzene (10 mg, 0.1 mmol, 1.0 equiv.), sodium ascorbate (20 mg, 0.1 mmol, 1.0 equiv.), $CuSO_4$•$5H_2O$ (25 mg, 0.1 mmol, 1.0 equiv.), DMF (0.5 mL) and H_2O (0.5 mL). Flash chromatograph (SiO_2, petroleum ether: EtOAc = 1:1) afforded the desired product as a white solid (40 mg, 84% yield)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.90 – 7.86 (m, 2H), 7.87 – 7.83 (m, 1H), 7.49 – 7.42 (m, 2H), 7.41 – 7.33 (m, 1H), 6.43 (d, *J* = 6.1 Hz, 1H), 6.35 (dd, *J* = 9.6, 9.6 Hz, 1H), 5.35 (dd, *J* = 10.0, 6.1 Hz, 1H), 5.32 – 5.24 (m, 1H), 4.39 (ddd, *J* = 10.3, 4.0, 2.3 Hz, 1H), 4.27 (dd, *J* = 12.7, 4.0 Hz, 1H), 4.04 (dd, *J* = 12.6, 2.2 Hz, 1H), 2.07 (s, 6H), 2.05 (s, 3H), and 1.89 (s, 3H).

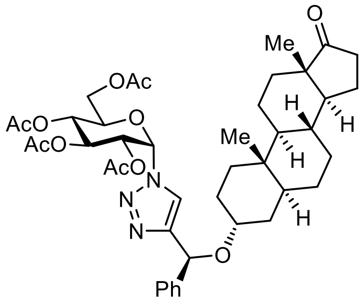
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 170.62, 170.46, 169.87, 169.76, 147.46, 129.80, 129.12, 128.81, 125.93, 121.79, 81.59, 71.27, 70.64, 70.06, 68.19, 61.44, 20.78, 20.73, and 20.48.

$[\alpha]_D^{14}$ = +53.7 (c = 0.10, $CHCl_3$).

m.p.: 187– 189 °C.

IR (thin film, cm^{-1}): 2925, 2850, 1748, 1367, 1219, 1033, 764, 749, and 704.

HRMS (DART-TOF) calculated for $C_{22}H_{25}NaN_3O_9^+$[M+Na]$^+$ m/z 498.1483, found 498.1486.



(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(4-((*S*)-(((3*R*,5*S*,8*R*,9*S*,10*S*,13*S*,14*S*)-10,13-dimethyl-17-oxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)(phenyl)methyl)-1*H*-1,2,3-triazol-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (12b)

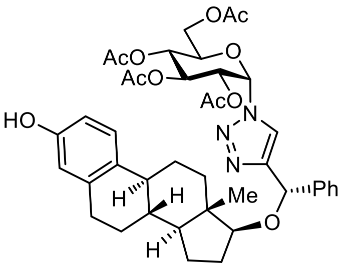
Compound **12b** was prepared following **General Reaction Procedure D** from 2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl azide **3a** (75 mg, 0.2 mmol, 2.0 equiv.), Androsterone derivative (40 mg, 0.1 mmol, 1.0 equiv.), sodium ascorbate (20 mg, 0.1 mmol, 1.0 equiv.), $CuSO_4 \bullet 5H_2O$ (25 mg, 0.1 mmol, 1.0 equiv.), DMF (0.5 mL) and H_2O (0.5 mL). Flash chromatograph (SiO_2, petroleum ether: EtOAc = 1:1) afforded the desired product as a yellow solid (66 mg, 85% yield).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.49 – 7.41 (m, 3H), 7.39 – 7.33 (m, 2H), 7.32 – 7.27(m, 1H), 6.38 – 6.16 (m, 2H), 5.72 (s, 1H), 5.40 – 5.11 (m, 2H), 4.33 (ddd, *J* = 10.4, 3.9, 2.2 Hz, 1H), 4.20 (dd, *J* = 12.7, 3.9 Hz, 1H), 4.00 (dd, *J* = 12.6, 2.3 Hz, 1H), 3.73 – 3.62 (m, 1H), 2.43 (dd, *J* = 19.1, 8.7 Hz, 1H), 2.03 (s, 6H), 2.02 (s, 3H). 1.98 – 1.89 (m, 1H), 1.87 (s, 3H), 1.85-1.75 (m, 3H), 1.71-1.58 (m, 2H), 1.57-1.46 (m, 5H), 1.43-1.20(m, 9H), 1.06 – 0.92 (m, 1H), 0.86 (s, 3H), and 0.80 (s, 3H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 170.51, 170.29, 169.77, 169.66, 150.69, 141.05, 128.59, 127.95, 126.82, 123.79, 81.36, 73.33, 71.88, 71.21, 70.47, 70.07, 68.08, 61.31, 54.50, 51.57, 47.88, 39.86, 36.19, 35.92, 35.13, 33.60, 32.92, 31.63, 28.29, 25.50, 21.82, 20.73, 20.70, 20.66, 20.45, 20.16, 13.91, and 11.50.

IR (thin film, cm^{-1}): 2924, 2853, 1744, 1452, 1367, 1219, 1109, 1037, 914, 749, 706, and 605.

HRMS (DART-TOF) calculated for $C_{42}H_{55}NaN_3O_{11}^+$[M+Na]$^+$ m/z 800.3731, found 800.3729.



(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(4-((*R*)-(((8*R*,9*S*,13*S*,14*S*,17*S*)-3-hydroxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-17-yl)oxy)(phenyl)methyl)-1*H*-1,2,3-triazol-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (12c)

Compound **12c** was prepared following **General Reaction Procedure D** from 2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl azide **3a** (75 mg, 0.2 mmol, 2.0 equiv.), β-Estradiol derivative (39 mg, 0.1 mmol, 1.0 equiv.), sodium ascorbate (20 mg, 0.1 mmol, 1.0 equiv.), $CuSO_4{\bullet}5H_2O$ (25 mg, 0.1 mmol, 1.0 equiv.), DMF (0.5 mL) and H_2O (0.5 mL). Flash chromatograph (SiO_2, petroleum ether: EtOAc = 1:1) afforded the desired product as a yellow solid (65 mg, 85% yield)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.45 – 7.39 (m, 3H), 7.38 – 7.32 (m, 2H), 7.31 – 7.25 (m, 1H), 7.12 (d, *J* = 8.5 Hz, 1H), 6.62 (dd, *J* = 8.4, 2.8 Hz, 1H), 6.55 (d, *J* = 2.7 Hz, 1H), 6.29 (d, *J* = 6.1 Hz, 1H), 6.21 (dd, *J* = 9.6, 9.6 Hz, 1H), 5.72 (s, 1H), 5.41 – 5.32 (m, 1H), 5.28 – 5.21 (m, 2H), 4.46 (ddd, *J* = 10.3, 3.8, 2.2 Hz, 1H), 4.25 (dd, *J* = 12.7, 3.9 Hz, 1H), 4.06 (dd, *J* = 12.6, 2.3 Hz, 1H), 3.56 (dd, *J* = 8.2, 8.2 Hz, 1H), 2.95 – 2.71 (m, 2H), 2.28 – 2.20 (m, 1H), 2.15 – 2.10 (m, 1H), 2.07 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H), 1.86 – 1.79(m, 1H), 1.71 (s, 3H), 1.68 – 1.60 (m, 2H), 1.54 – 1.36 (m, 3H), 1.33 – 1.21(m, 4H), 1.12 (td, *J* = 11.7, 6.9 Hz, 1H), and 0.86 (s, 3H).

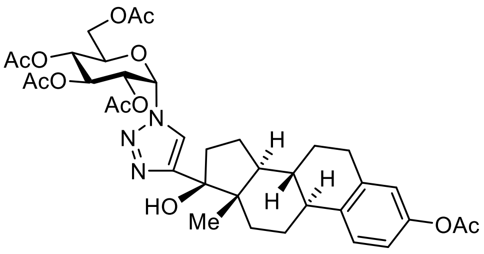
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 170.72, 170.38, 169.92, 169.74, 153.69, 150.91, 140.88, 138.29, 132.59, 128.63, 128.06, 126.81, 126.58, 123.76, 115.41, 112.85, 86.70, 81.42, 75.11, 71.38, 70.51, 70.13, 68.14, 61.43, 50.05, 44.06, 43.44, 38.69, 37.45, 29.72, 27.85, 27.29, 26.45, 23.33, 20.80, 20.77, 20.73, 20.25, and 12.11.

IR (thin film, cm^{-1}): 2924, 2857, 1749, 1614, 1499, 1449, 1367, 1220, 1037, 740, and 700.

$[\alpha]_D^{15}$ = +70.0 (c = 0.21, $CHCl_3$).

m.p.: 101– 103 °C.

HRMS (DART-TOF) calculated for $C_{41}H_{49}NaN_3O_{11}{}^+[M+Na]^+$ m/z 782.3259, found 782.3254.

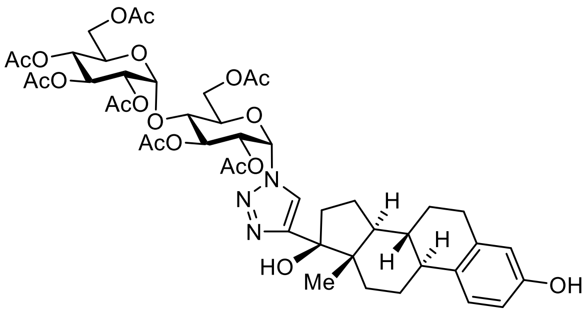


(2*R*,3*R*,4*S*,5*R*,6*R*)-2-(acetoxymethyl)-6-(((2*R*,3*R*,4*S*,5*R*,6*S*)-4,5-diacetoxy-2-(acetoxymethyl)-6-(4-((8*R*,9*S*,13*S*,14*S*)-3,17-dihydroxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-17-yl)-1*H*-1,2,3-triazol-1-yl)tetrahydro-2*H*-pyran-3-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate

Compound **12d** was prepared following **General Reaction Procedure D** from α-D-glucosyl azide **3d** (41 mg, 0.2 mmol, 1.0 equiv.), ethinyl estradiol (59 mg, 0.2 mmol, 1.0 equiv.), sodium ascorbate (40 mg, 0.2 mmol, 1.0 equiv.), $CuSO_4•5H_2O$ (50 mg, 0.2 mmol, 1.0 equiv.), DMF (1 mL) and H_2O (1 mL). The solvent was evaporated under reduced pressure, and the residue was dissolved with ethyl acetate (3 mL), followed by 4-Dimethylaminopyridine (5 mg, 0.04 mmol, 0.2 equiv.), acetic anhydride (184 mg, 1.8 mmol, 9.0 equiv.) and triethylamine (60 mg, 0.6 mmol, 3.0 equiv.) at room temperature, and stirred for 6 h. Flash chromatograph (SiO_2, petroleum ether: EtOAc = 3:1) afforded the desired product as a yellow solid (42 mg, 30% yield).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.55 (s, 1H), 7.16 (d, *J* = 8.2 Hz, 1H), 6.84 – 6.74 (m, 2H), 6.37 (d, *J* = 6.1 Hz, 1H), 6.28 (dd, *J* = 9.6, 9.6 Hz, 1H), 5.30 (dd, *J* = 10.1, 6.1 Hz, 1H), 5.27 (dd, *J* = 9.2, 9.2 Hz, 1H), 4.46 (ddd, *J* = 10.3, 3.8, 2.3 Hz, 1H), 4.25 (dd, *J* = 12.7, 3.8 Hz, 1H), 4.04 (dd, *J* = 12.7, 2.2 Hz, 1H), 2.90 – 2.82 (m, 2H), 2.54 (s, 1H), 2.49 (ddd, *J* = 14.6, 9.6, 5.9 Hz, 1H), 2.26 (s, 3H), 2.15 – 2.08 (m, 2H), 2.05 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 2.00 – 1.90 (m, 2H), 1.85 (s, 3H), 1.78 – 1.66 (m, 2H), 1.64 – 1.54 (m, 2H), 1.54 – 1.38 (m, 3H), 1.03 (s, 3H), 0.58 (td, *J* = 12.8, 4.1 Hz, 1H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 170.66, 170.29, 170.04, 169.91, 169.82, 153.31, 148.50, 138.46, 137.88, 126.25, 123.90, 121.61, 118.59, 82.60, 81.34, 71.30, 70.50, 70.12, 68.13, 61.37, 48.45, 47.39, 43.52, 39.14, 38.34, 32.98, 29.80, 29.56, 27.09, 26.10, 23.66, 21.25, 20.81, 20.73, 20.39, and 14.20.



(2*R*,3*R*,4*S*,5*R*,6*R*)-2-(acetoxymethyl)-6-(((2*R*,3*R*,4*S*,5*R*,6*S*)-4,5-diacetoxy-2-(acetoxymethyl)-6-(4-((8*R*,9*S*,13*S*,14*S*)-3,17-dihydroxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-17-yl)-1*H*-1,2,3-triazol-1-yl)tetrahydro-2*H*-pyran-3-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate

Compound **12e** was prepared following **General Reaction Procedure D** from Hepta-*O*-acetyl-α-maltosyl azide **3l** (132 mg, 0.2 mmol, 1.0 equiv.), ethinyl estradiol (59 mg, 0.2 mmol, 1.0 equiv.), sodium ascorbate (40 mg, 0.2 mmol, 1.0 equiv.), $CuSO_4•5H_2O$ (50 mg, 0.2 mmol, 1.0 equiv.), DMF (1 mL) and H_2O (1 mL). Flash chromatograph (SiO_2, petroleum ether: EtOAc = 1:1) afforded the desired product as a white solid (86 mg, 45% yield)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.58 (s, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.56 (dd, *J* = 8.3, 2.7 Hz, 1H), 6.53 (d, *J* = 2.6 Hz, 1H), 6.27 (d, *J* = 5.7 Hz, 1H), 6.12 (dd, *J* = 8.9, 7.6 Hz, 1H), 5.54 (s, 1H), 5.44 (d, *J* = 3.9 Hz, 1H), 5.35 (dd, *J* = 10.5, 9.5 Hz, 1H), 5.24 (dd, *J* = 8.9, 5.7 Hz, 1H), 5.07 (dd, *J* = 9.8, 9.8 Hz, 1H), 4.88 (dd, *J* = 10.5, 3.9 Hz, 1H), 4.46 (dd, *J* = 12.4, 2.5 Hz, 1H), 4.41 (dt, *J* = 9.5, 3.3 Hz, 1H), 4.28 – 4.15 (m, 2H), 4.12 – 4.02 (m, 2H), 3.99 (dt, *J* = 9.9, 3.2 Hz, 1H), 2.85 – 2.73 (m, 2H), 2.68 (s, 1H), 2.46 (ddd, *J* = 14.6, 9.4, 5.6 Hz, 1H), 2.15 – 2.12 (m, 1Hz), 2.10 (s, 3H), 2.08 (s, 3H), 2.08 (s, 3H), 2.04 (s, 3H), 2.03 – 2.01 (m, 1H), 2.01 (s, 3H), 1.99 (s, 3H), 1.97 – 1.89 (m, 2H), 1.86 (s, 3H), 1.85 – 1.83 (m, 1H), 1.72 – 1.62 (m, 1H), 1.62 – 1.50 (m, 2H), 1.49 – 1.31 (m, 3H), 1.03 (s, 3H), 0.60 (td, *J* = 12.8, 4.1 Hz, 1H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 170.91, 170.85, 170.55, 170.19, 170.03, 169.69, 169.62, 153.79, 153.39, 138.24, 132.15, 126.33, 123.30, 115.36, 112.72, 96.03, 82.58, 81.31, 72.97, 72.08, 71.99, 70.05, 69.90, 69.36, 68.58, 68.07, 62.27, 61.55, 48.45, 47.45, 43.28, 39.50, 38.20, 33.01, 29.66, 27.22, 26.27, 23.57, 20.99, 20.88, 20.78, 20.77, 20.68, 20.38, and 14.26.

8. Mechanistic Studies

8.1 Cyclic voltammetry experiments

Cyclic voltammetry (CV) experiments were conducted using a conventional three-electrode system on a CHI660E electrochemical workstation. The electrochemical measurements were made using a glassy carbon electrode as the working electrode, platinum wire as counter electrode, and a saturated calomel electrode (SCE, saturated KCl) as reference electrode. Experiments were performed in a solution of 0.1 M tetrabutylammonium hexafluorophosphate (n-Bu_4NPF_6) in MeCN, with a scan rate of 100 mV/s. The concentration of analyte was 2 mM. The reference values were calibrated to SCE by using the ferrocene (Fc/Fc^+ couple) as internal standard (+0.40 V in 0.1 M n-Bu_4NPF_6 in MeCN). [3]

To avoid oxidation effects, N_2 was bubbled through the samples for 10 minutes prior to measurements and an argon atmosphere was maintained for the whole process. The electrodes were carefully prepared before measurements: the working electrode (glassy carbon electrode) and counter electrode (platinum wire) were polished with 0.05 µm aluminum oxide and then sonicated in distilled water and ethanol, the reference electrode (SCE) was washed with water and ethanol.

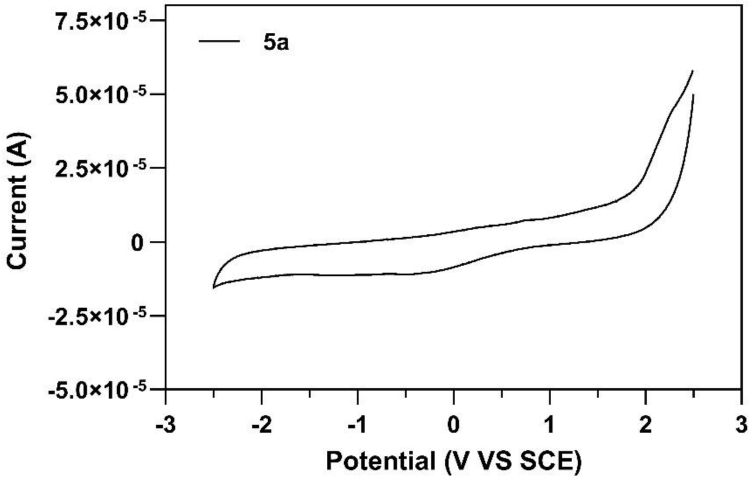


Figure S2. The CV of glycosyl donor 5a (2 mM) in n-Bu_4NPF_6 (0.1 M) in MeCN.

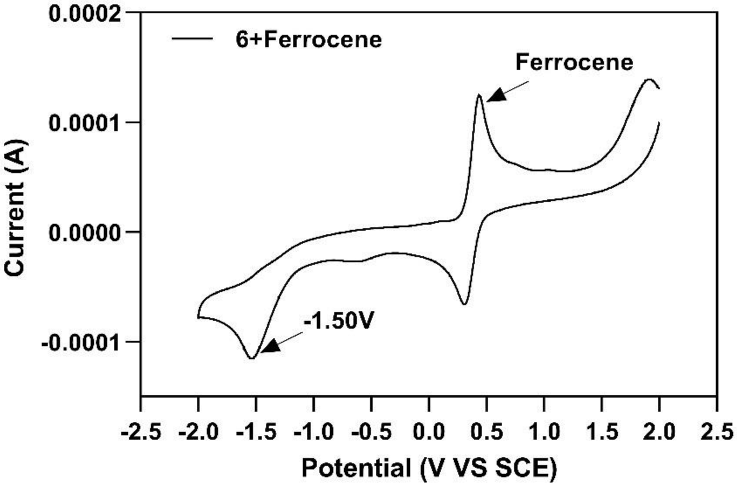


Figure S3. The CV of TsN_3 **6** (2 mM) in n-Bu_4NPF_6 (0.1 M) in MeCN using ferrocene as internal standard

The CV analysis revealed that glycosyl donor 5a did not show any significant oxidation or reduction peaks, suggesting that glycosyl donors were not prone to undergo facile electron transfer reactions under the conditions tested. The CV profile of compound 6 displayed a distinct reduction peak at -1.50 V vs. SCE during the cathodic scan, with no significant oxidation peak in the anodic scan. Considering the redox potential of the utilized photocatalyst $[Ir[dF(Me)ppy]_2(dtbbpy)]^+$ ($E^{0'*}IrL_3^{3+}/\ IrL_3^{4+}$ = -0.92 V vs SCE)[4] in comparison with compound 6, it became evident that compound 6 was not susceptible to single-electron reduction by the photocatalyst. This observation effectively excluded the possibility of a single-electron transfer pathway being operational for this reaction, as supported by Figures S2 and S3.

8.2 Stern-Volmer quenching studies

Stern-Volmer luminescence quenching experiments were run with freshly prepared solutions of 4.2 x 10^{-6} M $[Ir[dF(Me)ppy]_2(dtbbpy)]PF_6$ (PC) and varying concentrations of TsN_3 as quencher in degassed MeCN at room temperature under N_2 atmosphere. The solutions were irradiated at 400 nm and luminescence was measured at 495 nm. The following parameters were employed: excitation bandwidth = 5 nm, emission bandwidth = 10 nm, scan speed = 1000 nm/min. I_0 is the luminescence intensity without the quencher, I is the intensity in the presence of the quencher. The slow decrease of PC luminescence could be observed in the presence of TsN_3.

Table S2. Fluorescence quenching data with solutions of PC and TsN_3 (6).

Entry	Concentration of 6/ M	I / a.u.	I_0 / I[a]
1	0	117.82	1
2	0.06	108.86	1.08
3	0.12	99.11	1.19
4	0.18	90.41	1.30
5	0.24	82.84	1.42
6	0.30	76.41	1.54

[a] Given intensity values refer to the emission intensities at λ = 495 nm.

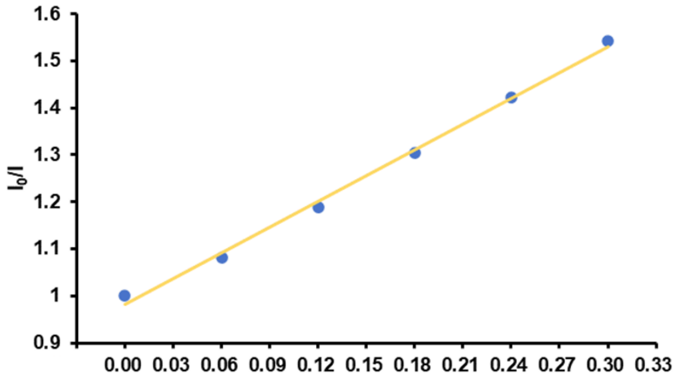


Figure S4. PC emission quenching by TsN_3 at various concentration

9. References

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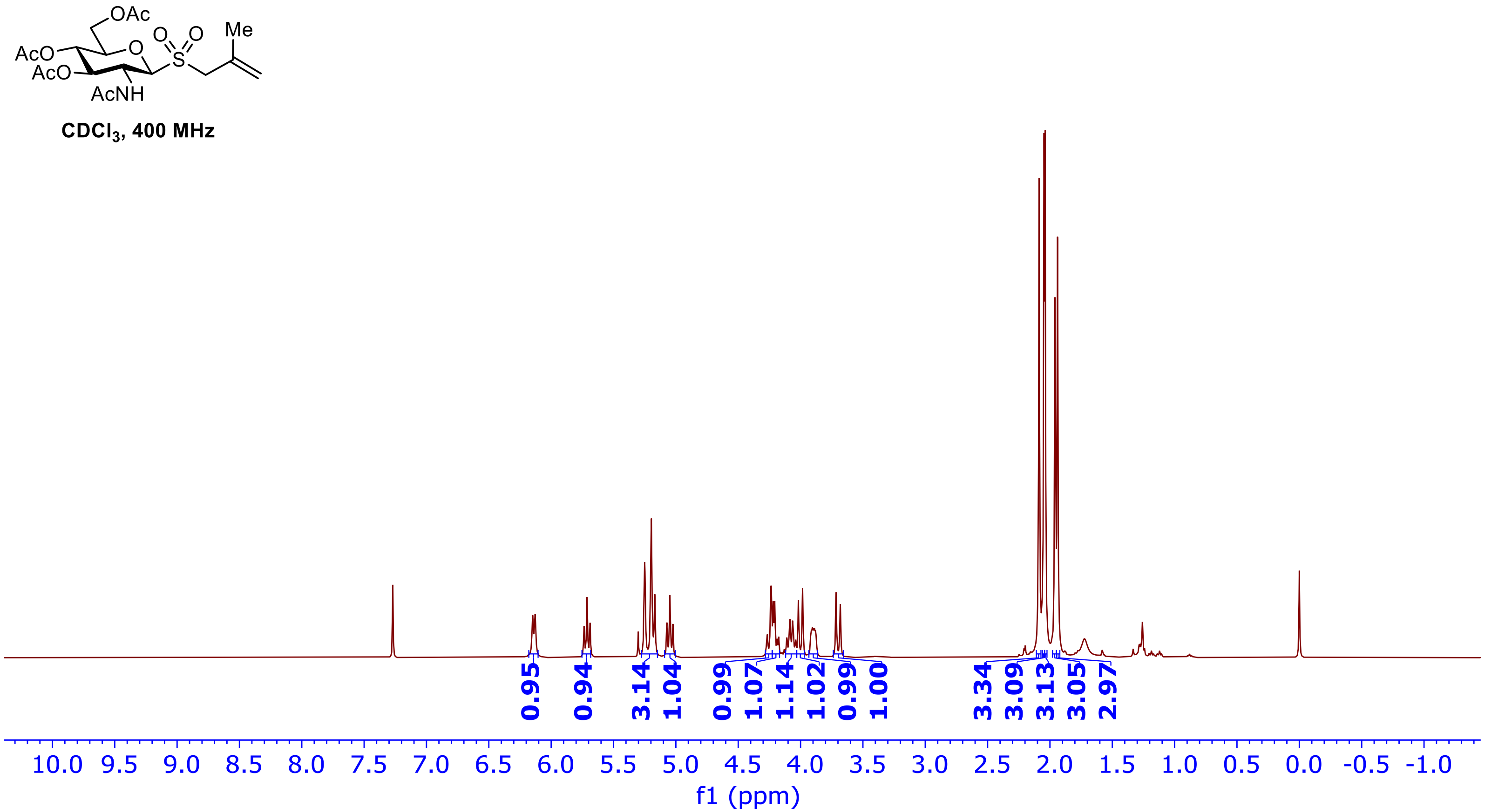
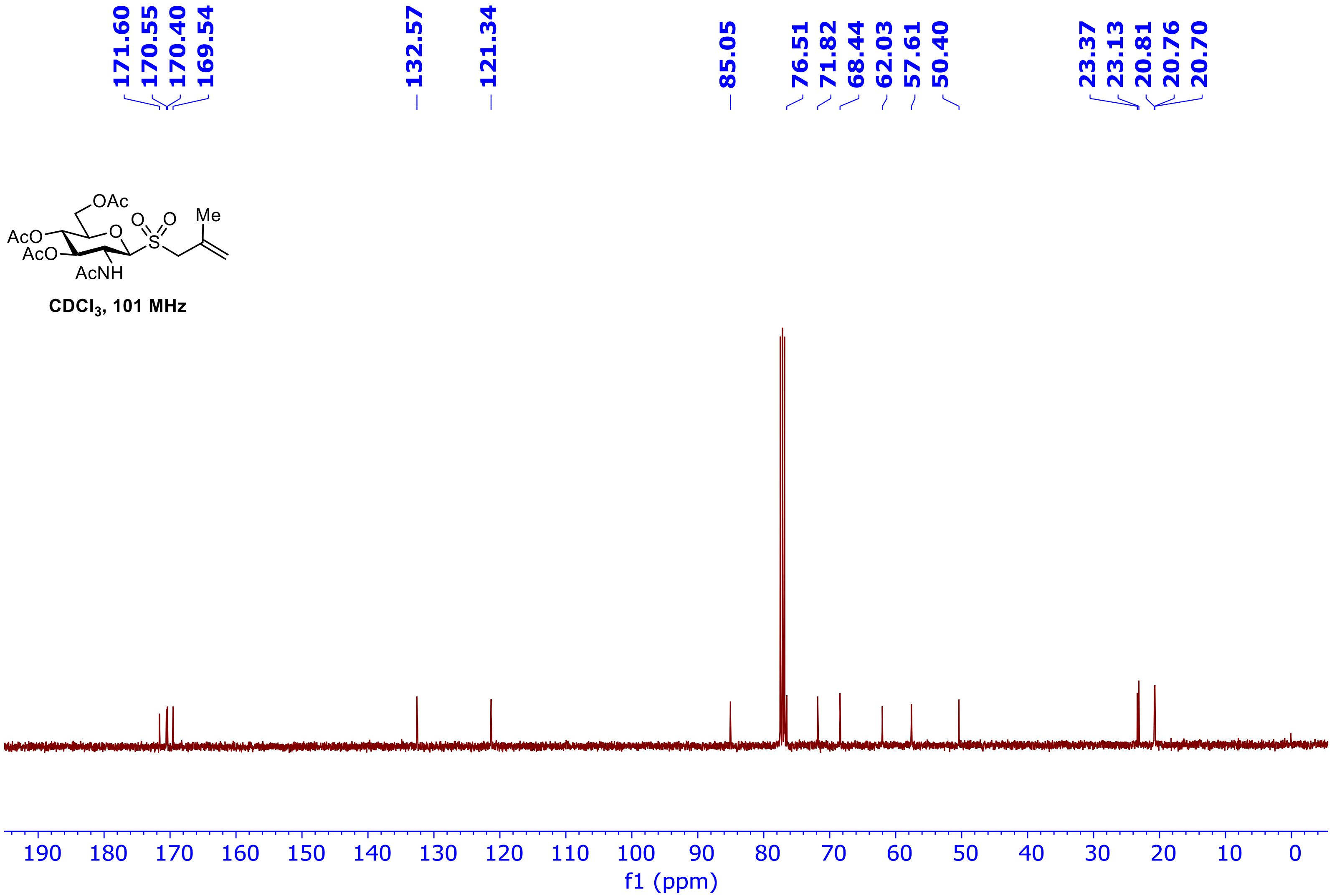
10. NMR Spectrum



^{1}H NMR spectrum of 5e



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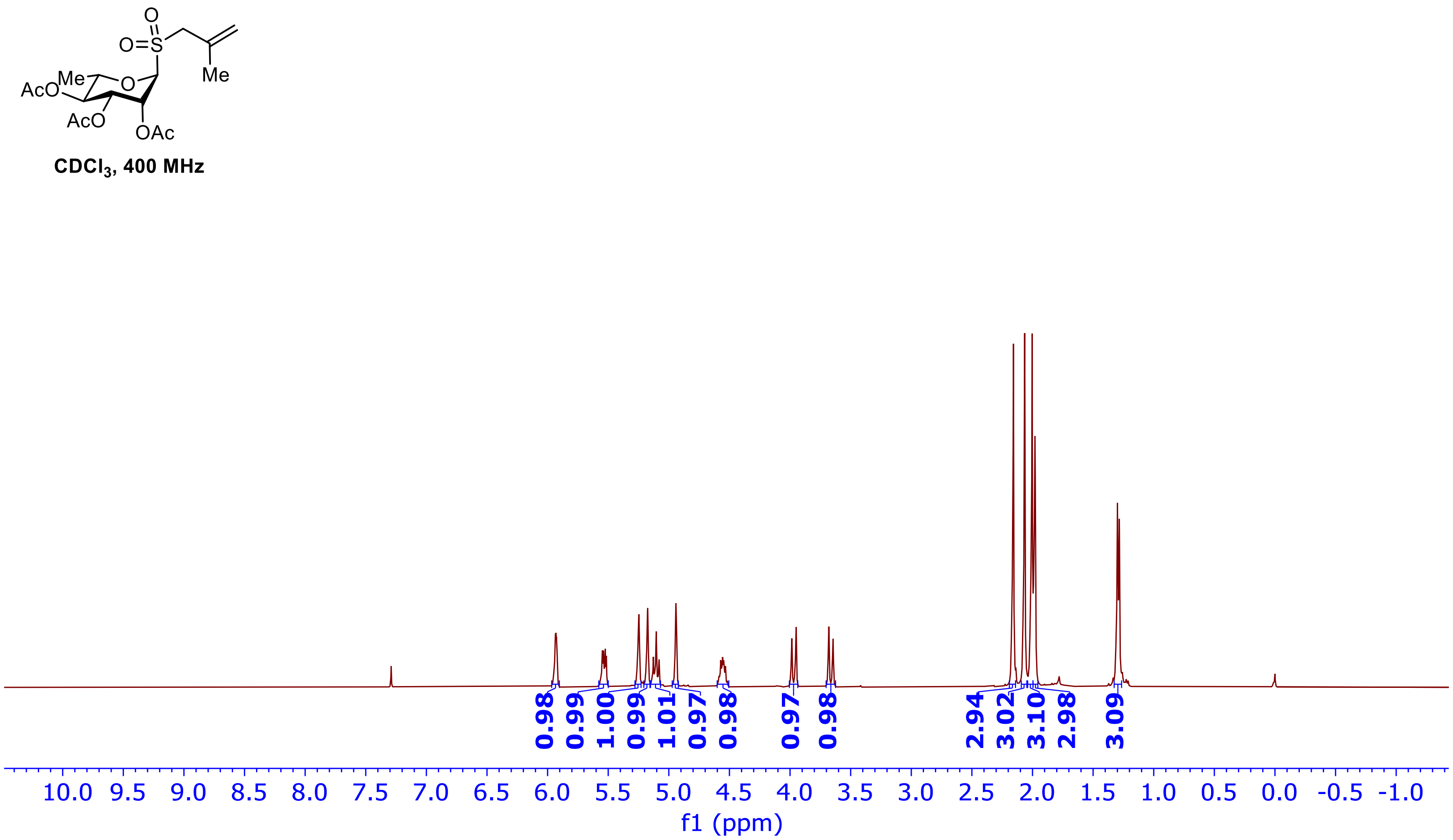

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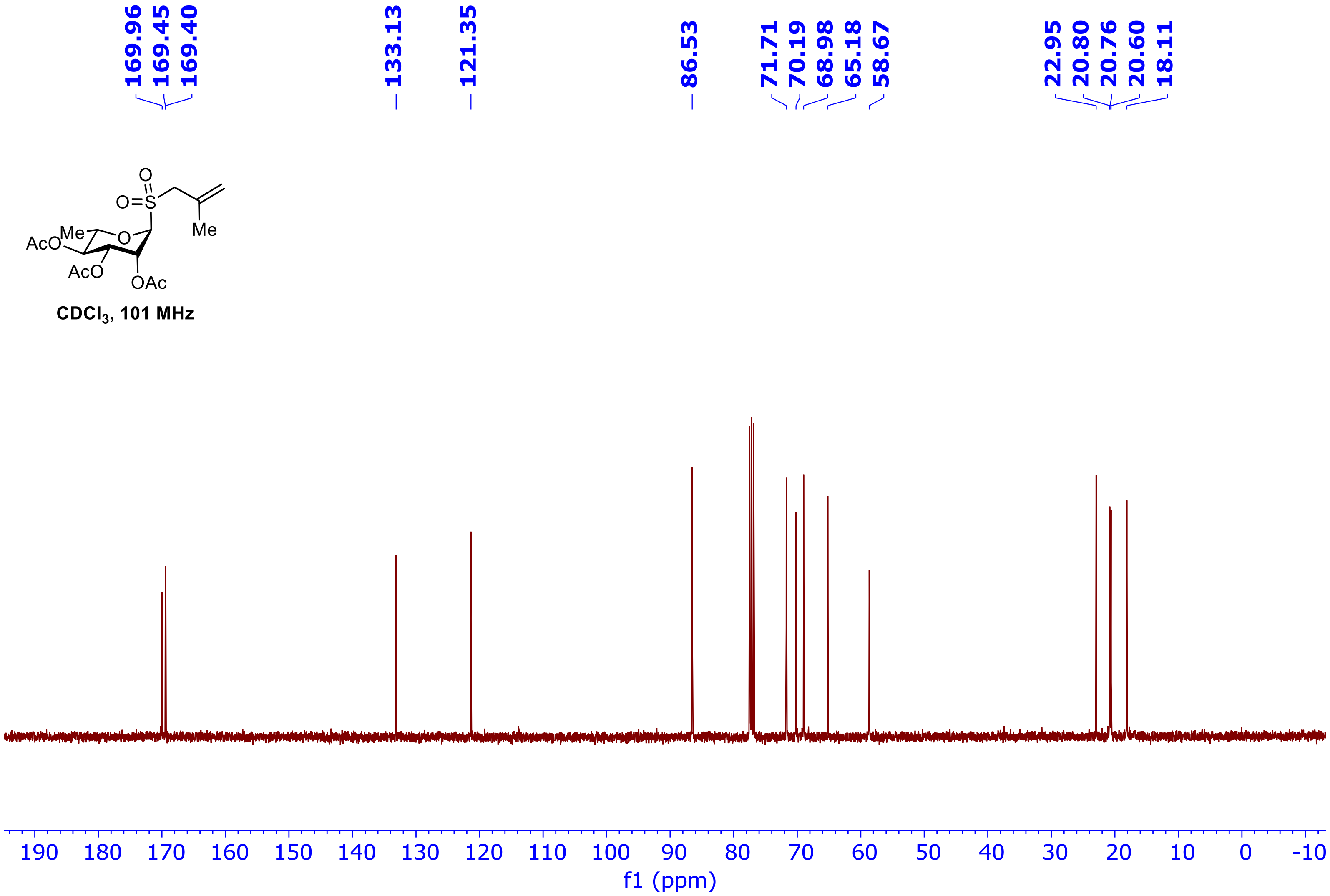

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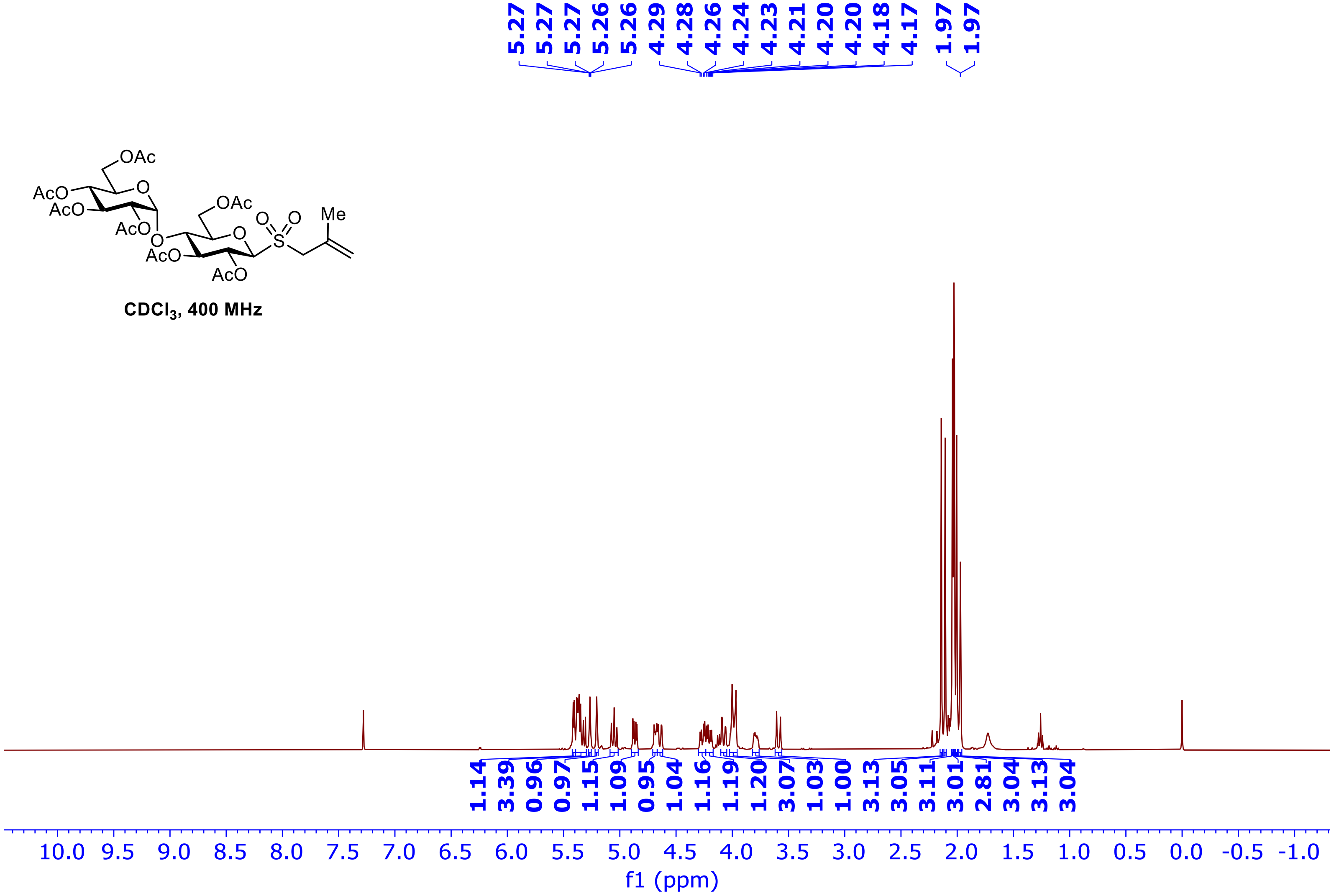
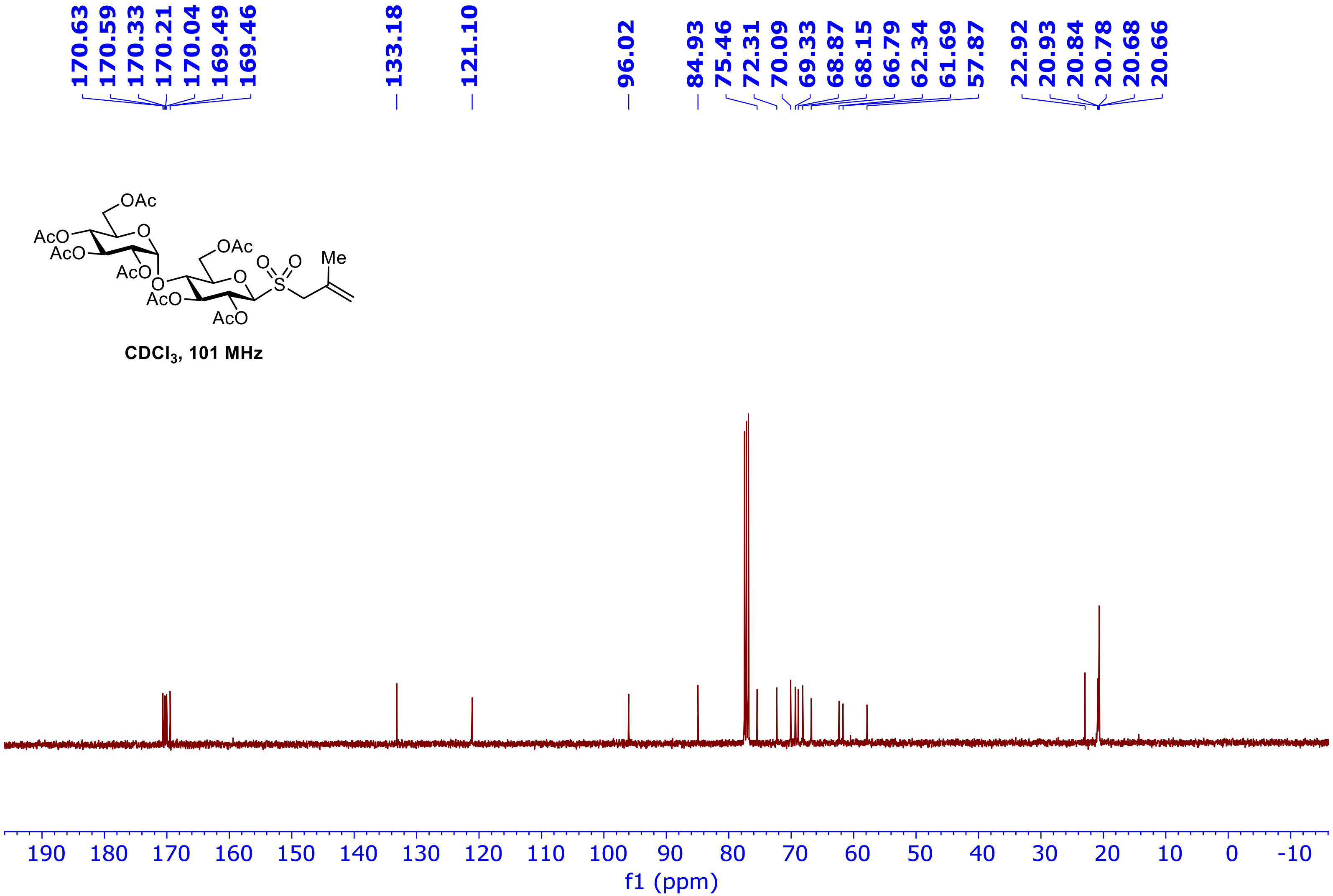


^{1}H NMR spectrum of 5l



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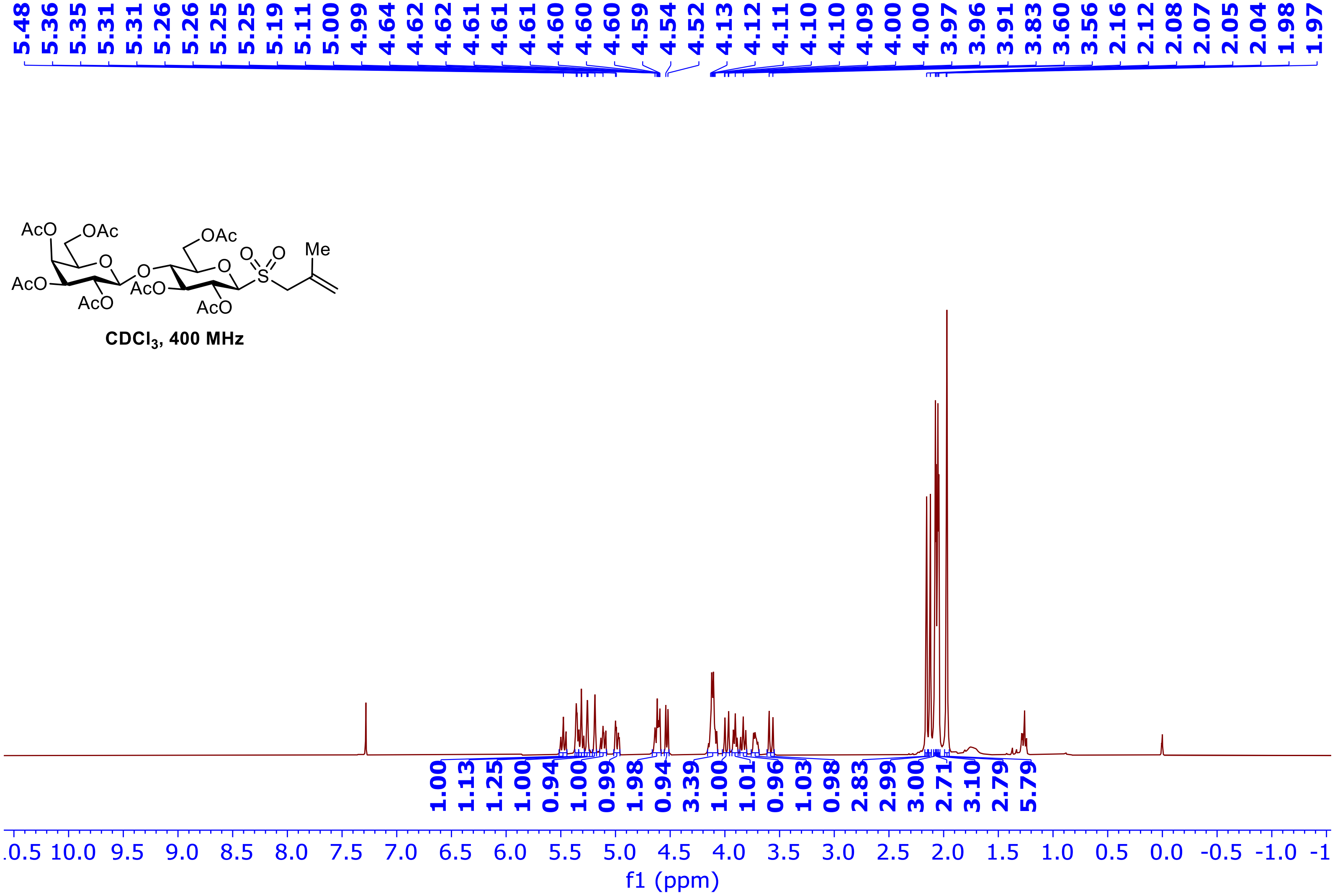

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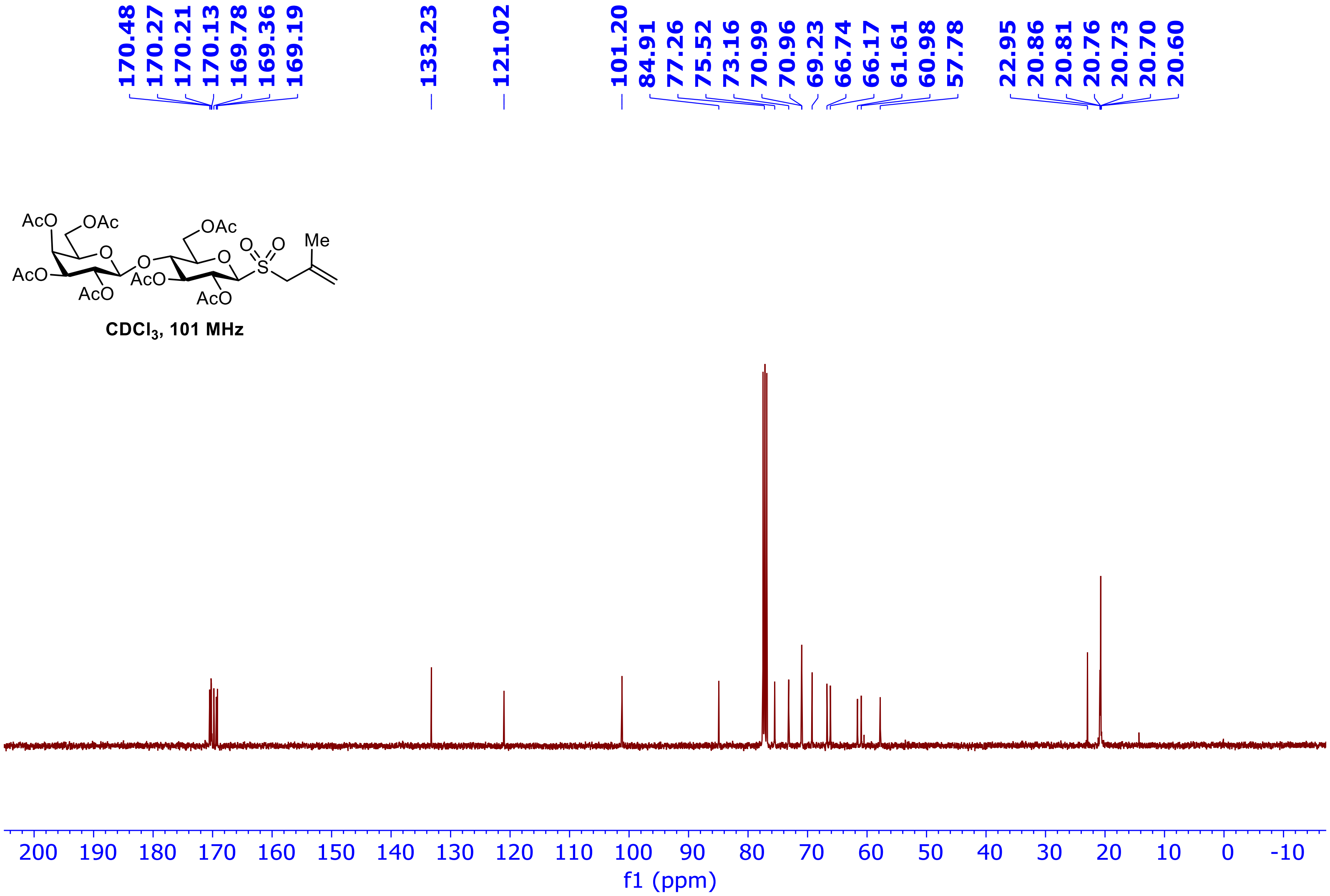

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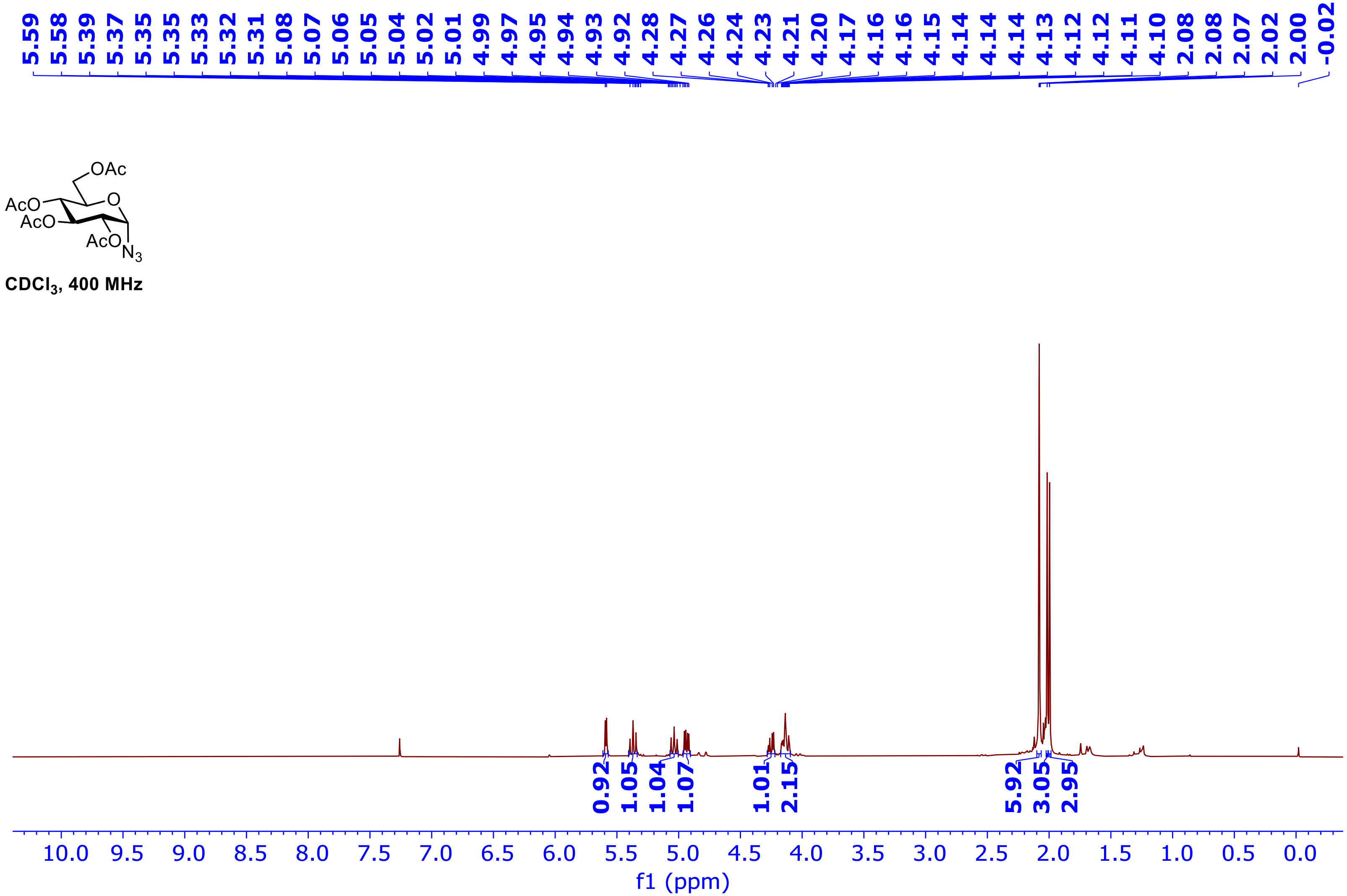

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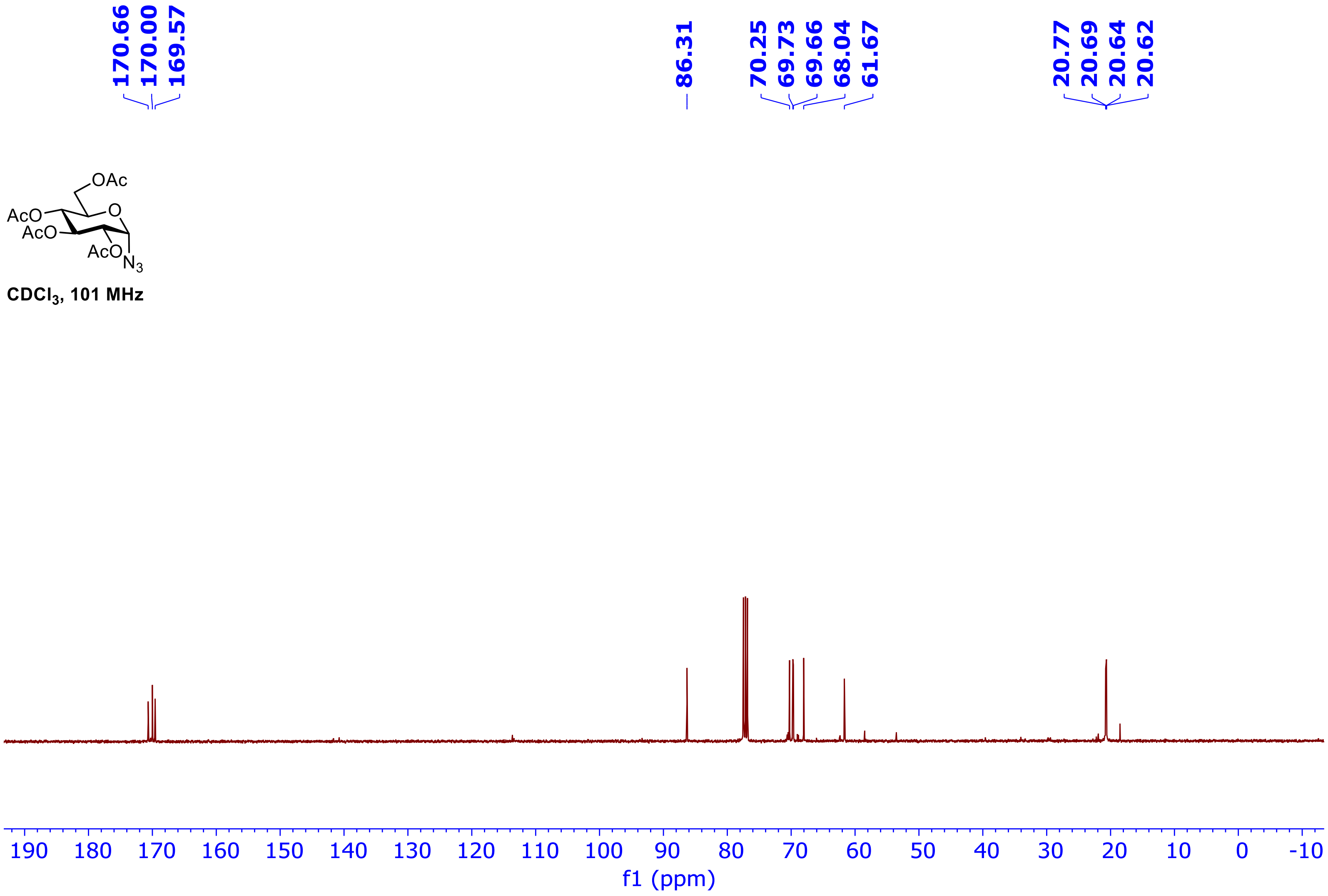

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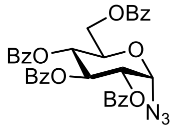
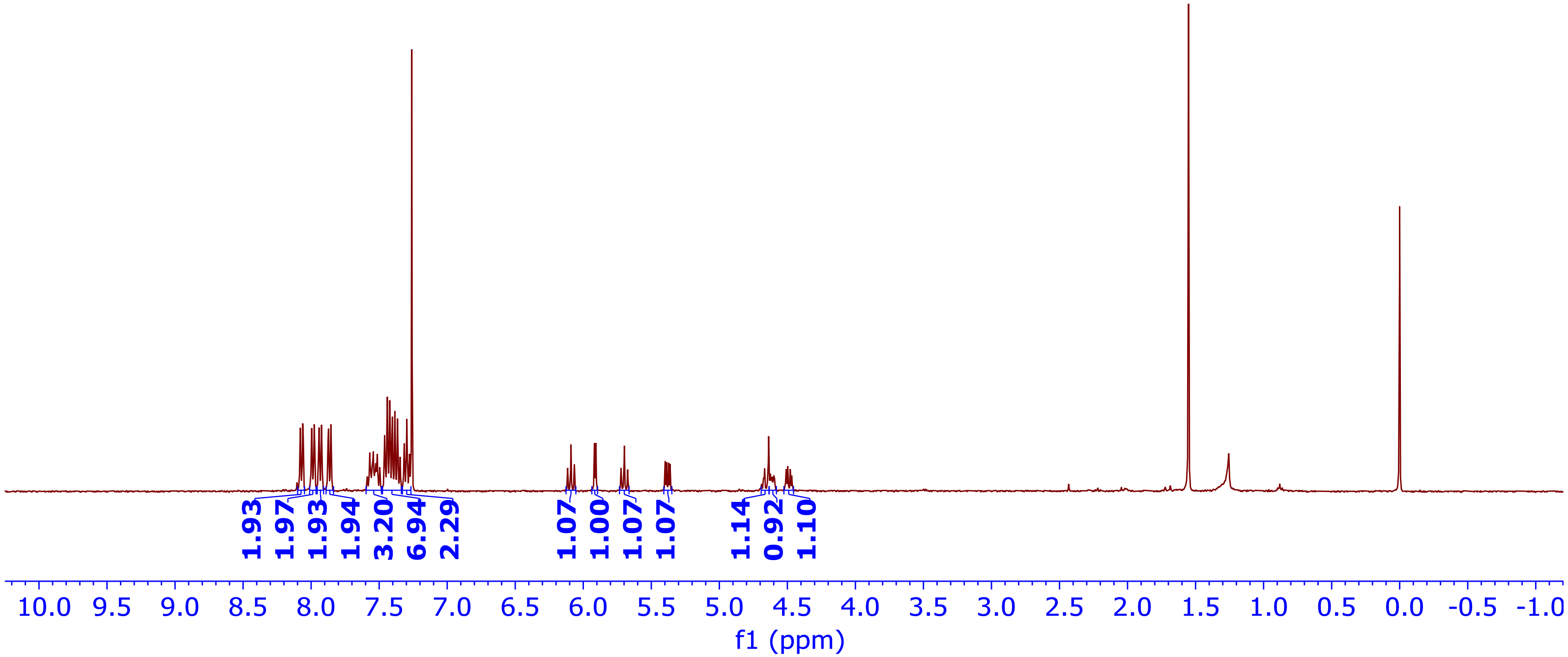


CDCl$_3$, 400 MHz



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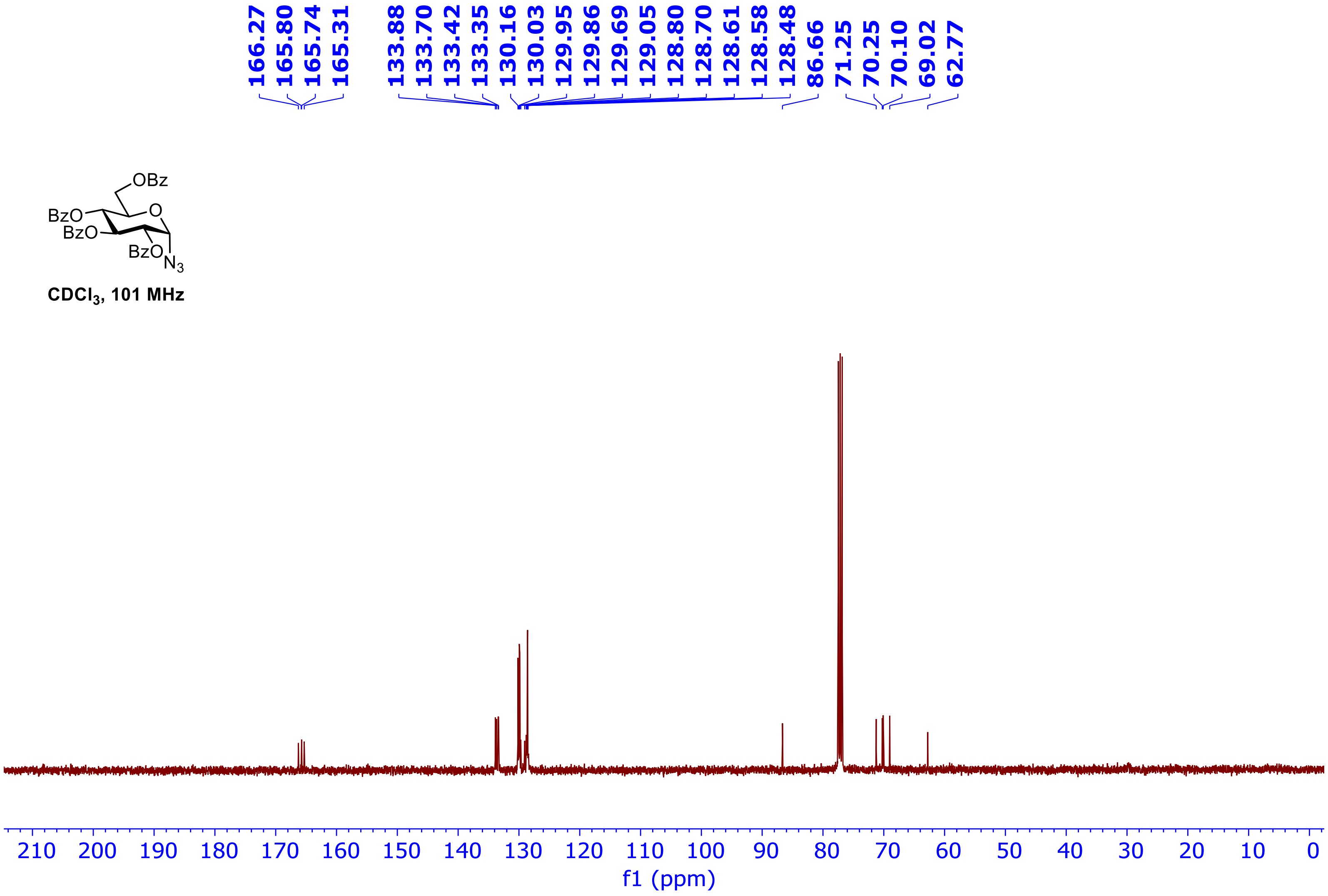
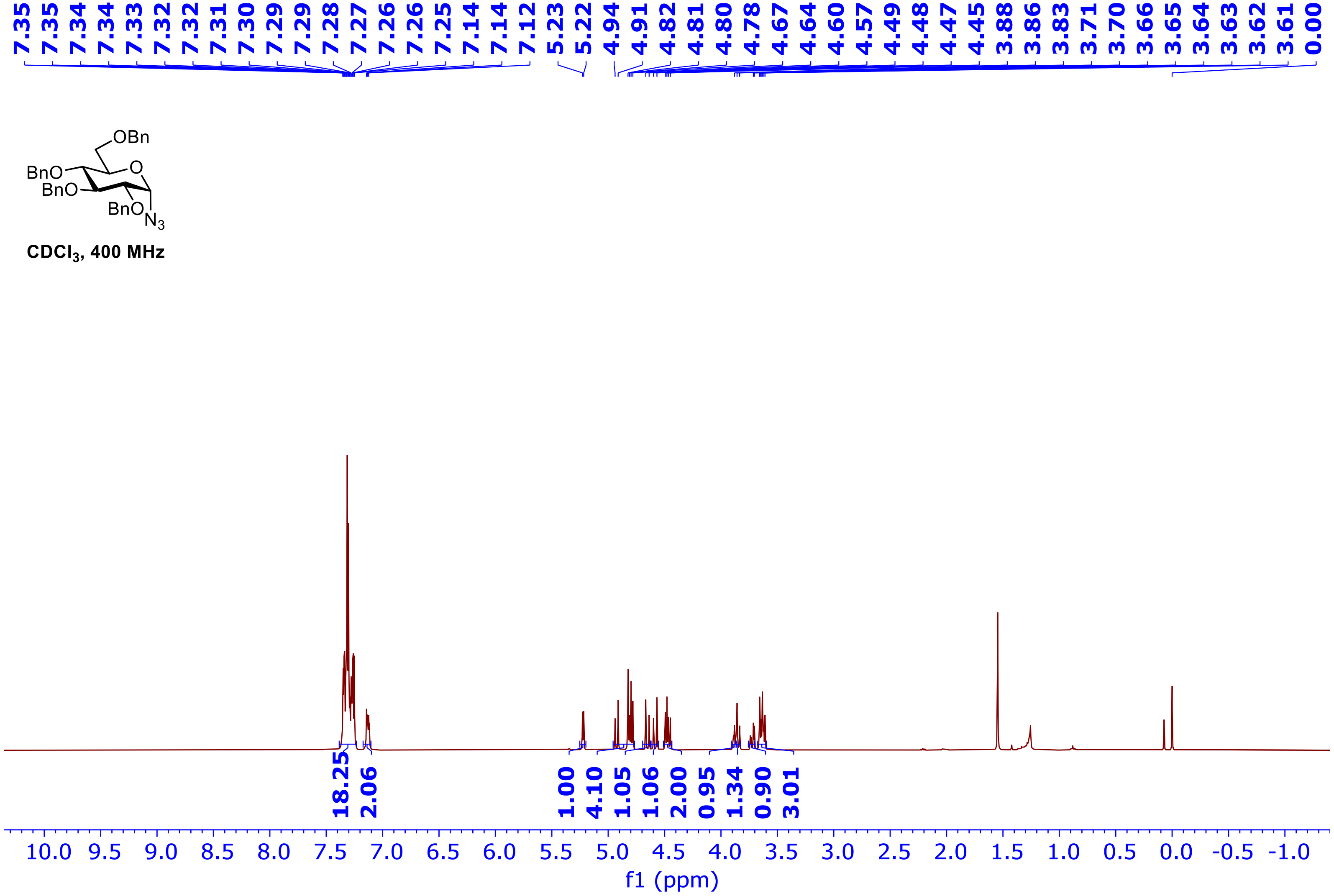
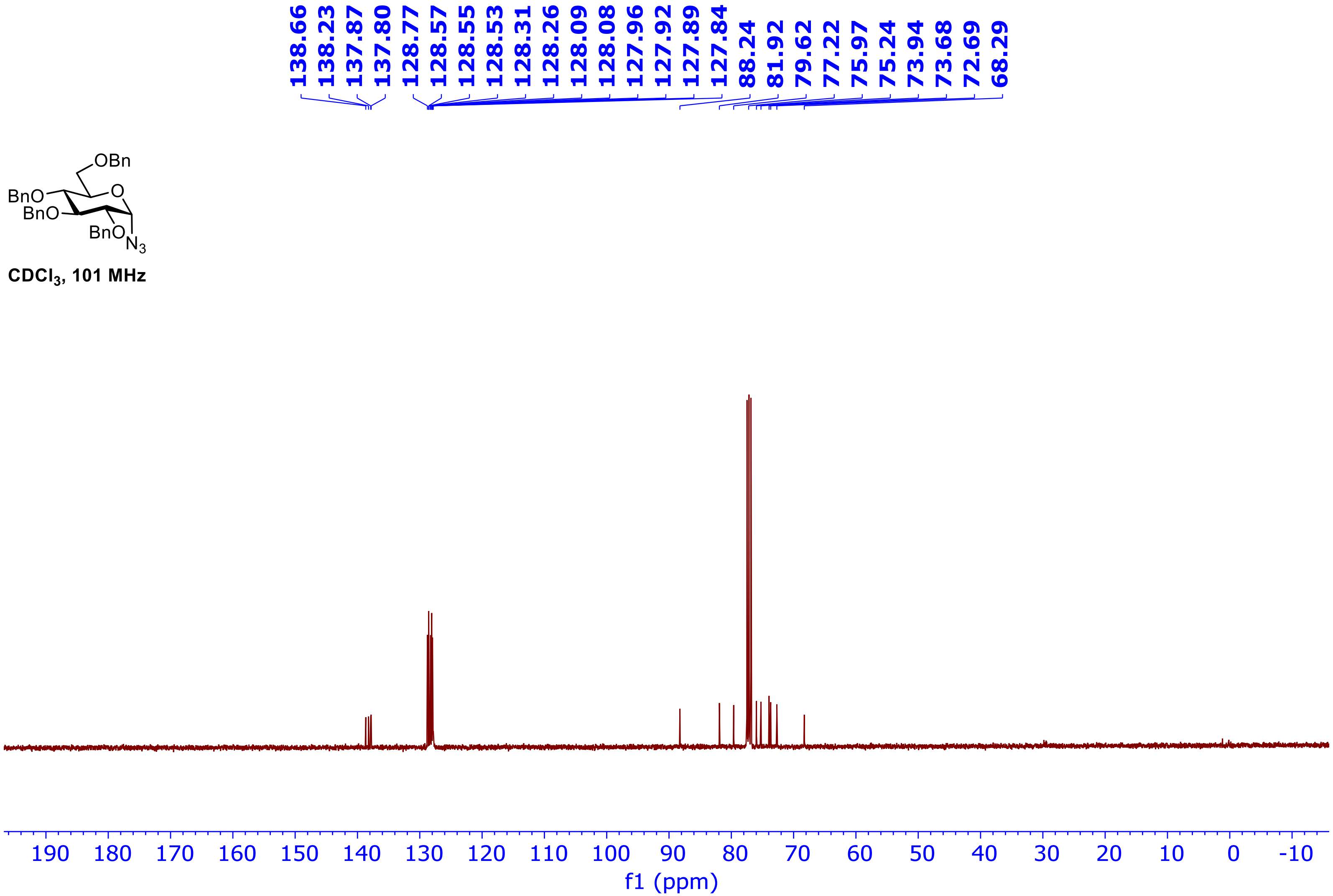


^{13}C NMR spectrum of 3b



^{1}H NMR spectrum of 3c



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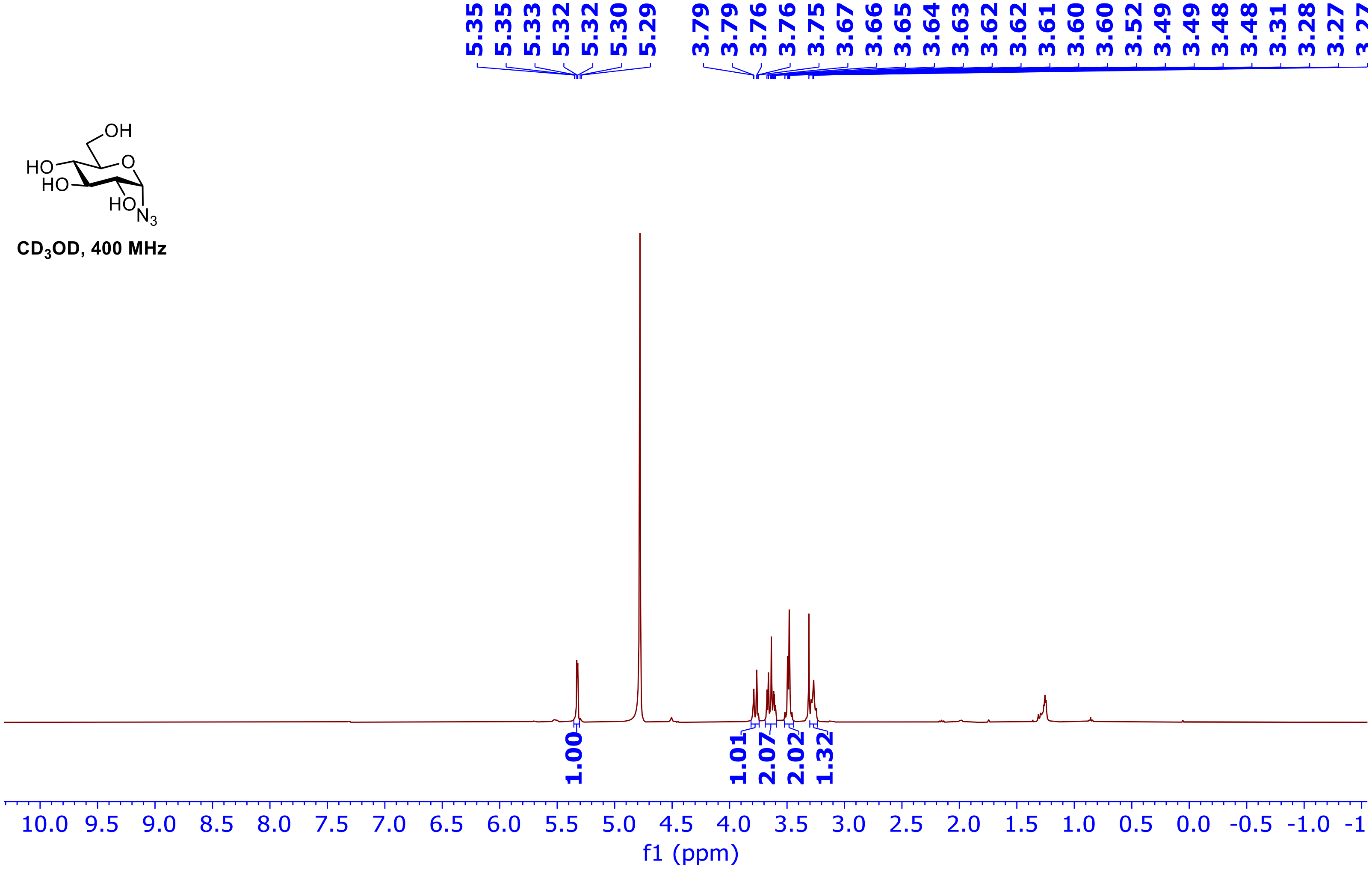

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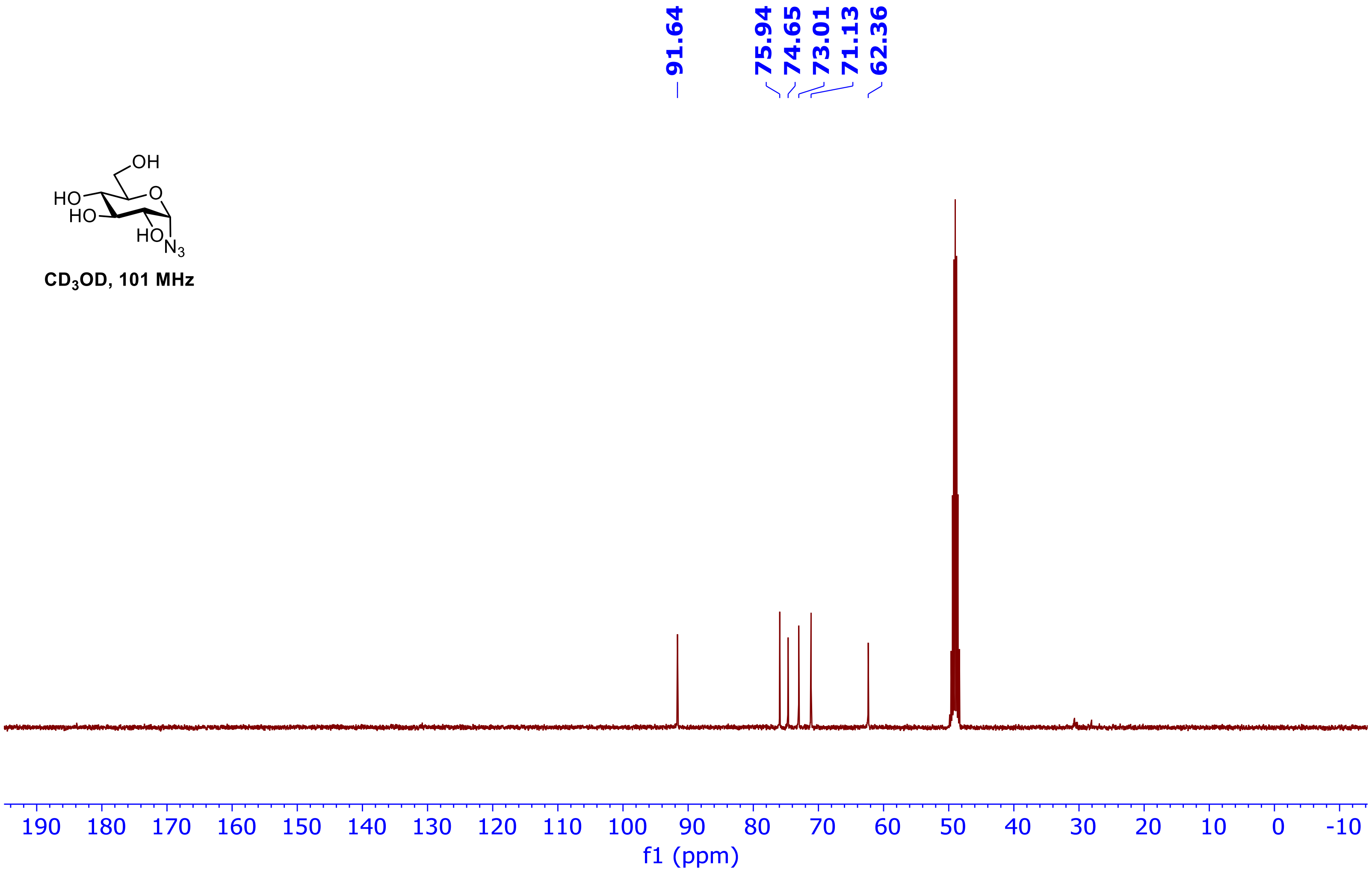

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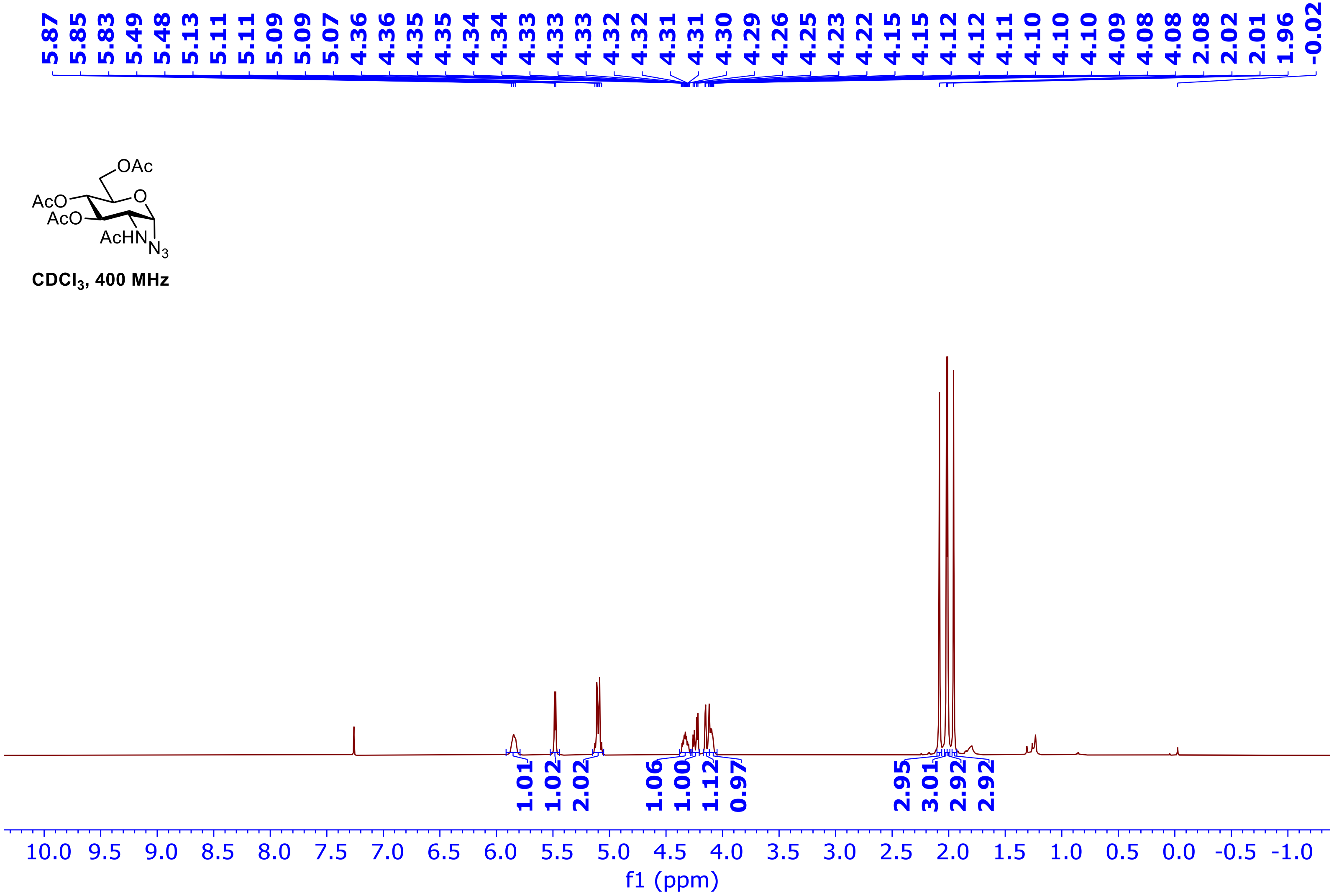

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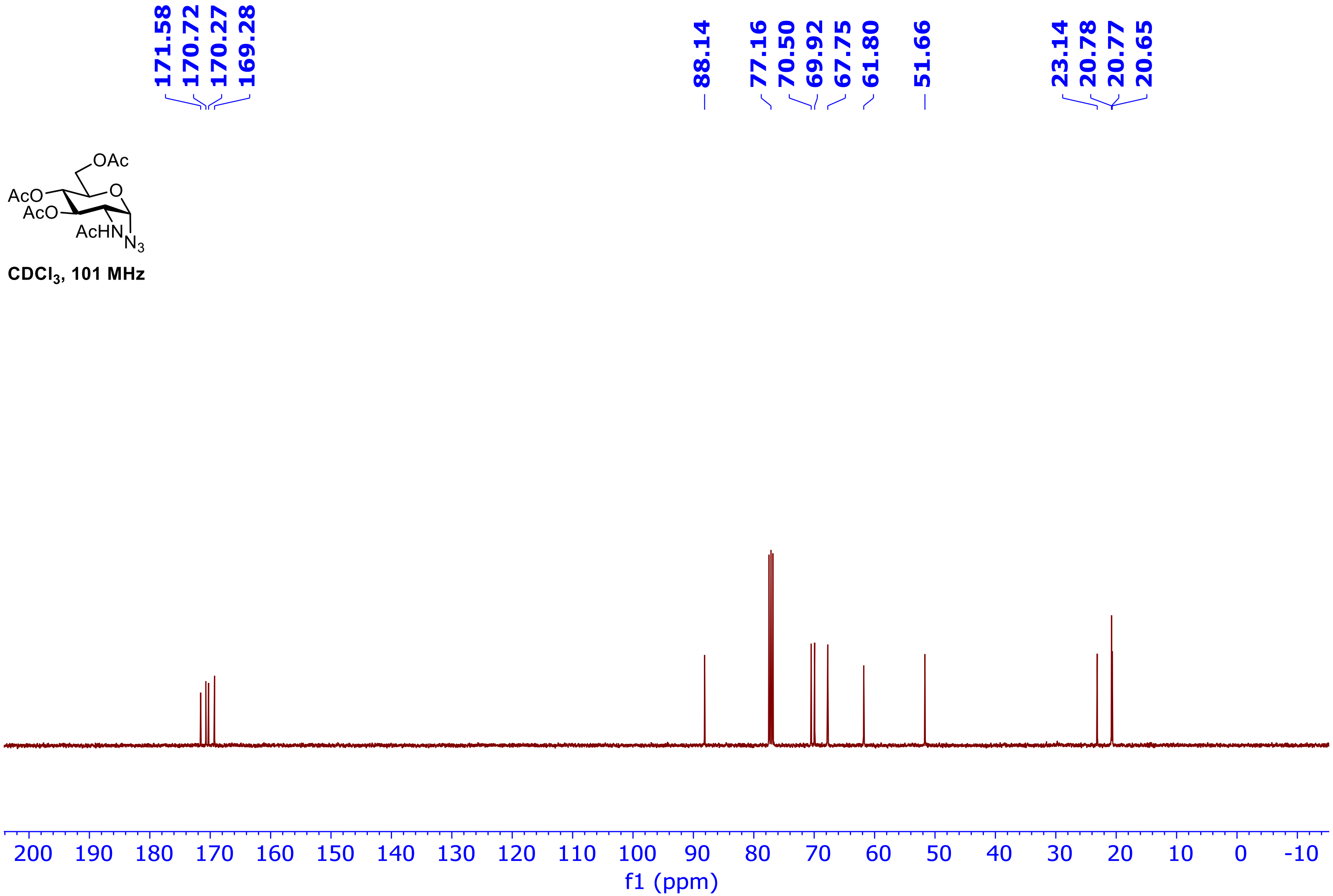

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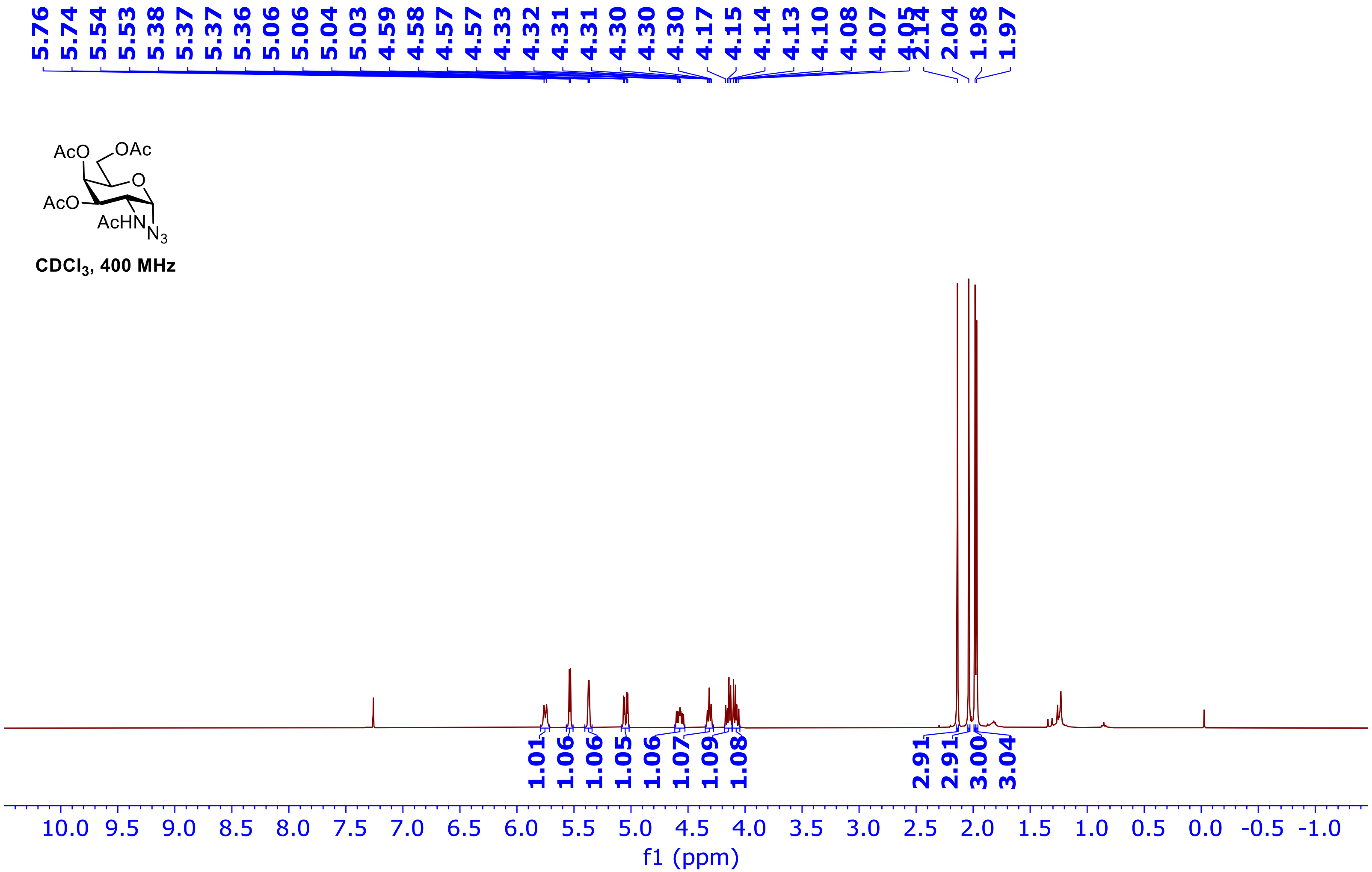
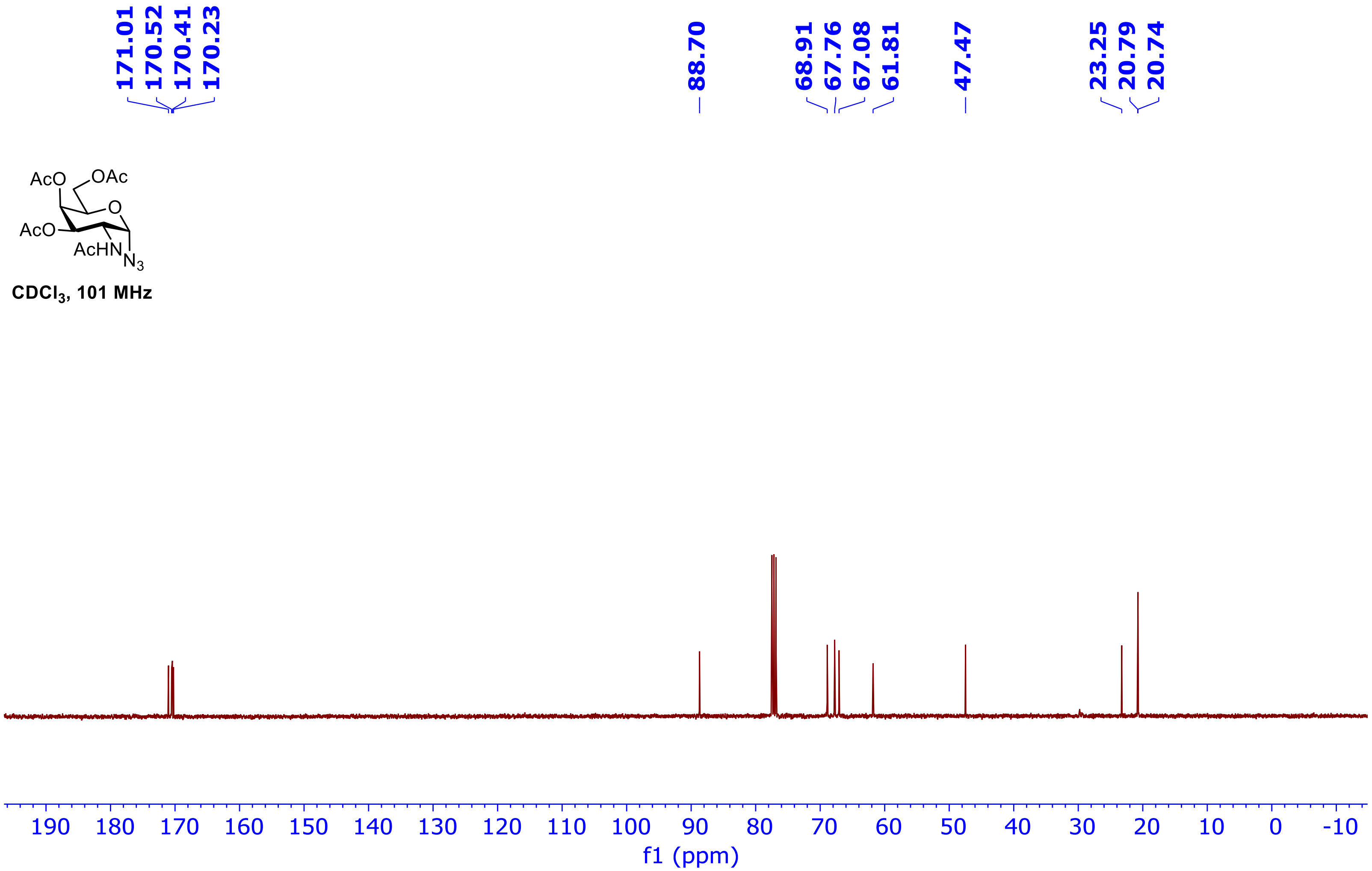
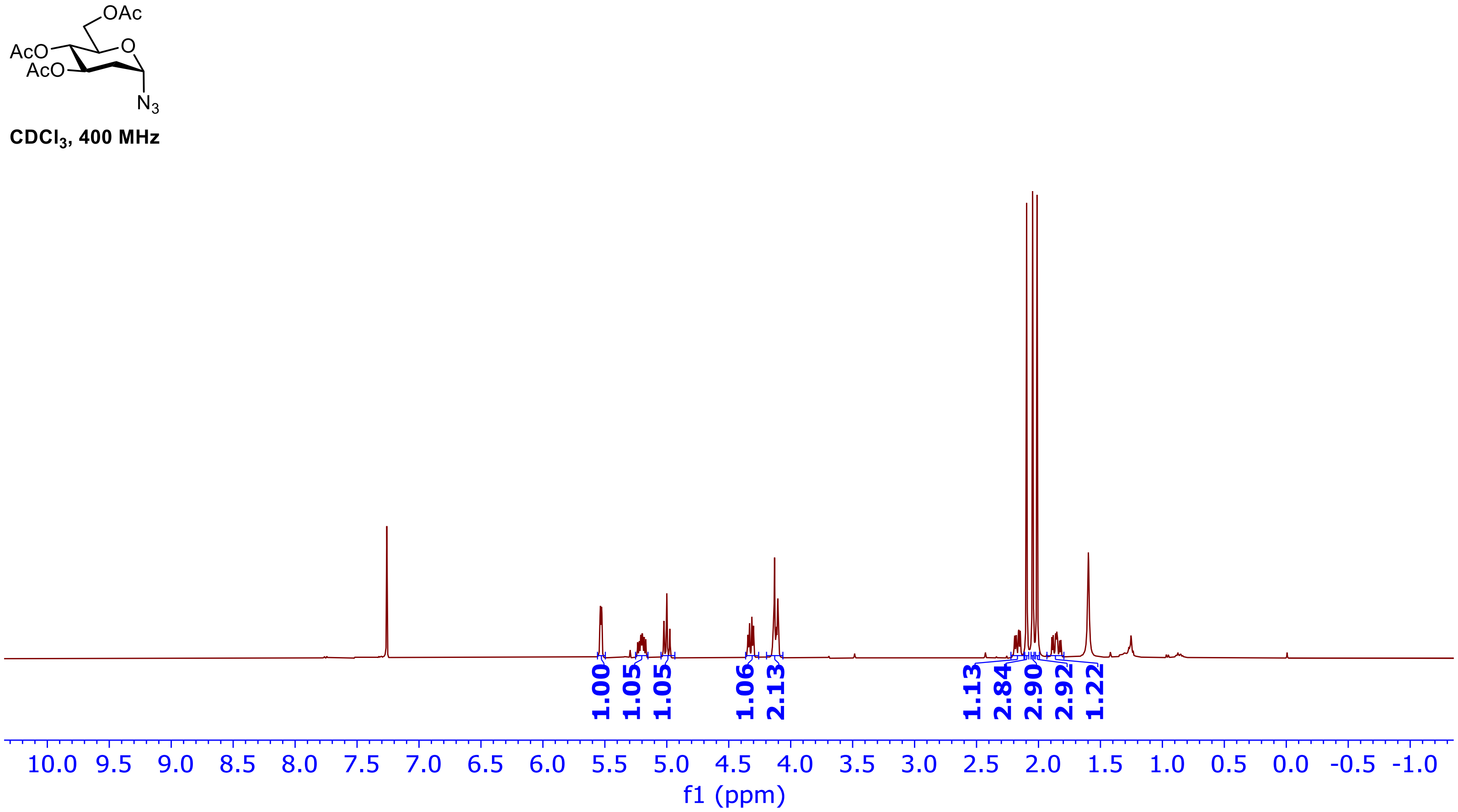


^{1}H NMR spectrum of 3f



^{13}C NMR spectrum of 3f



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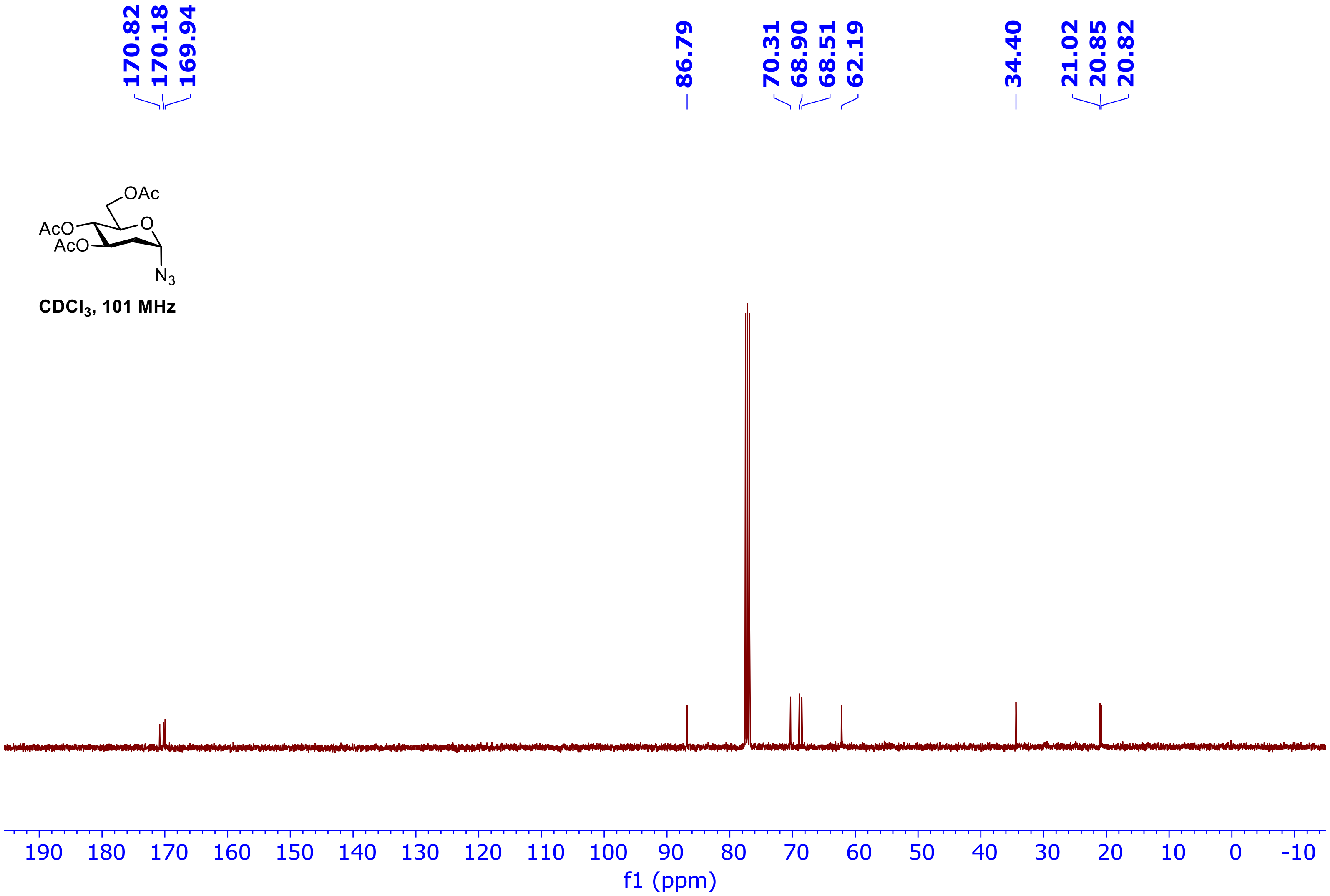
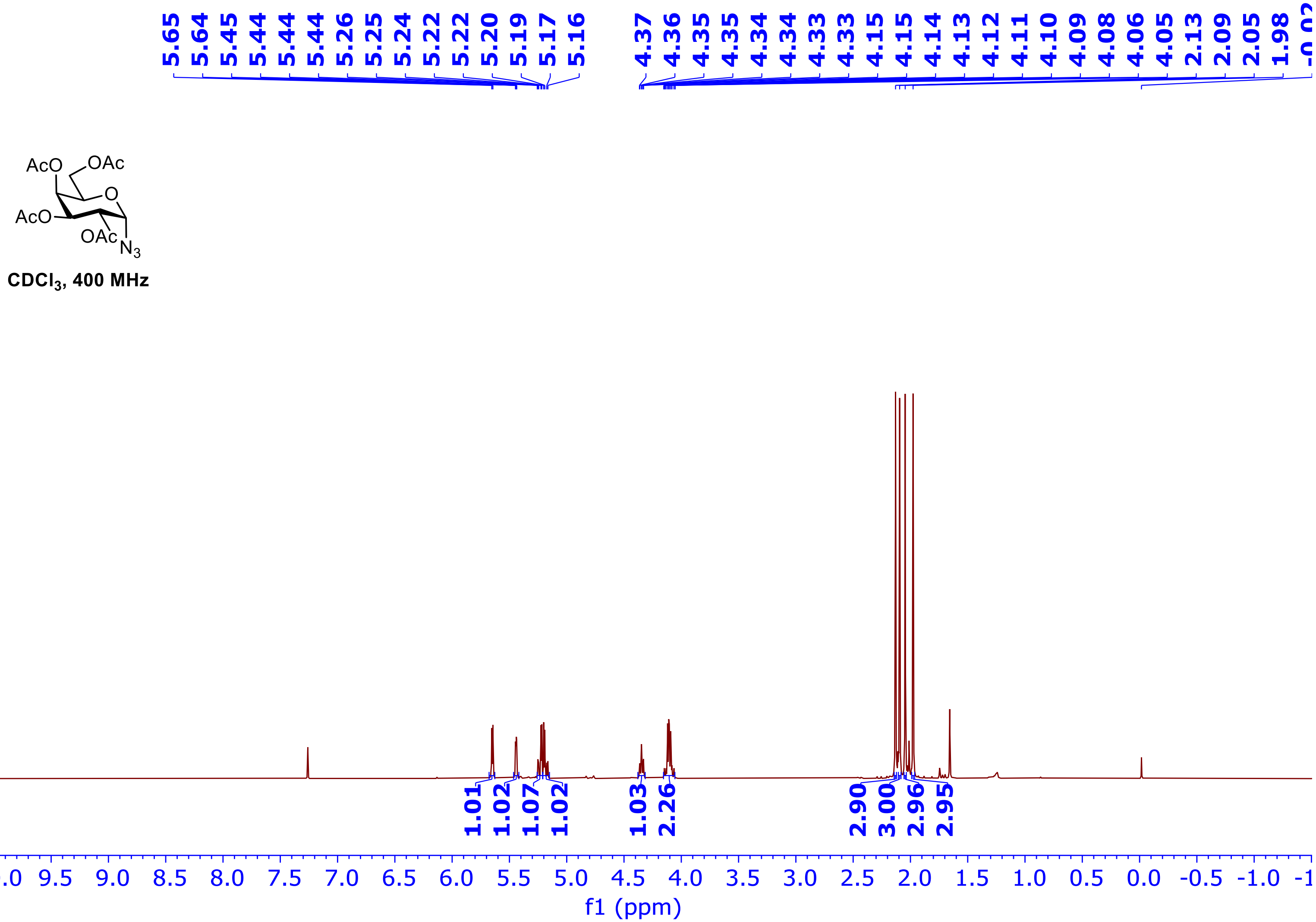


^{13}C NMR spectrum of 3g



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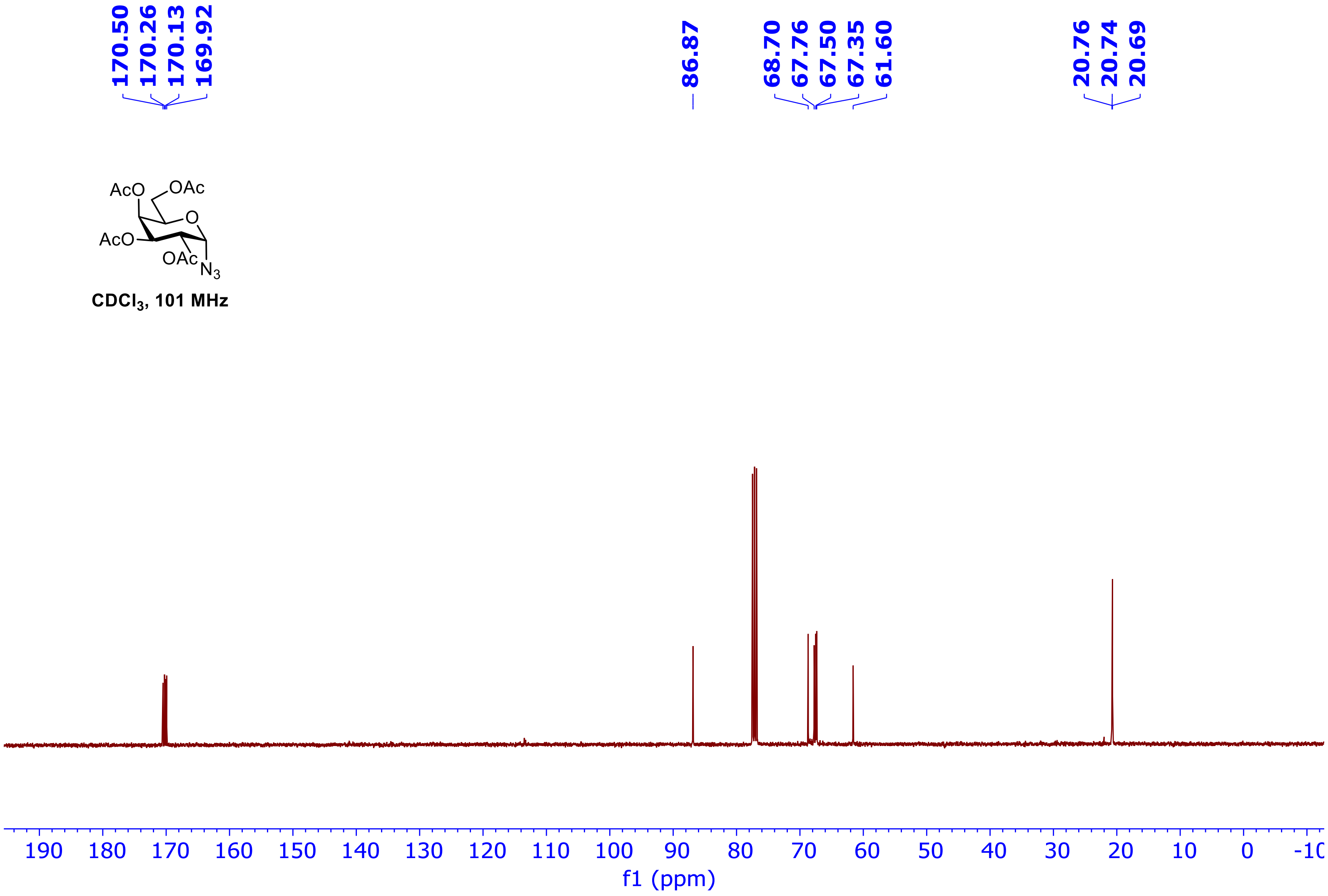

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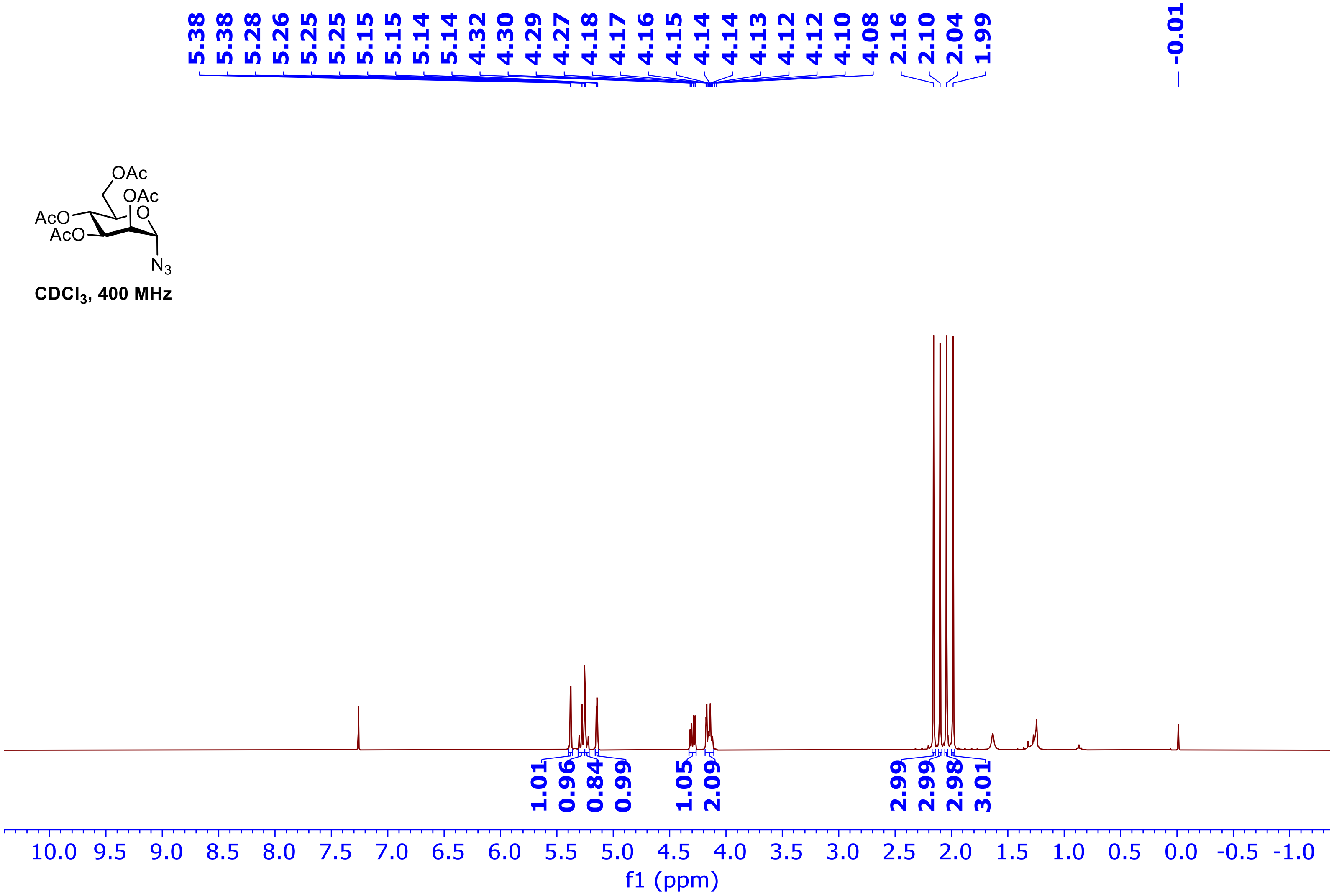
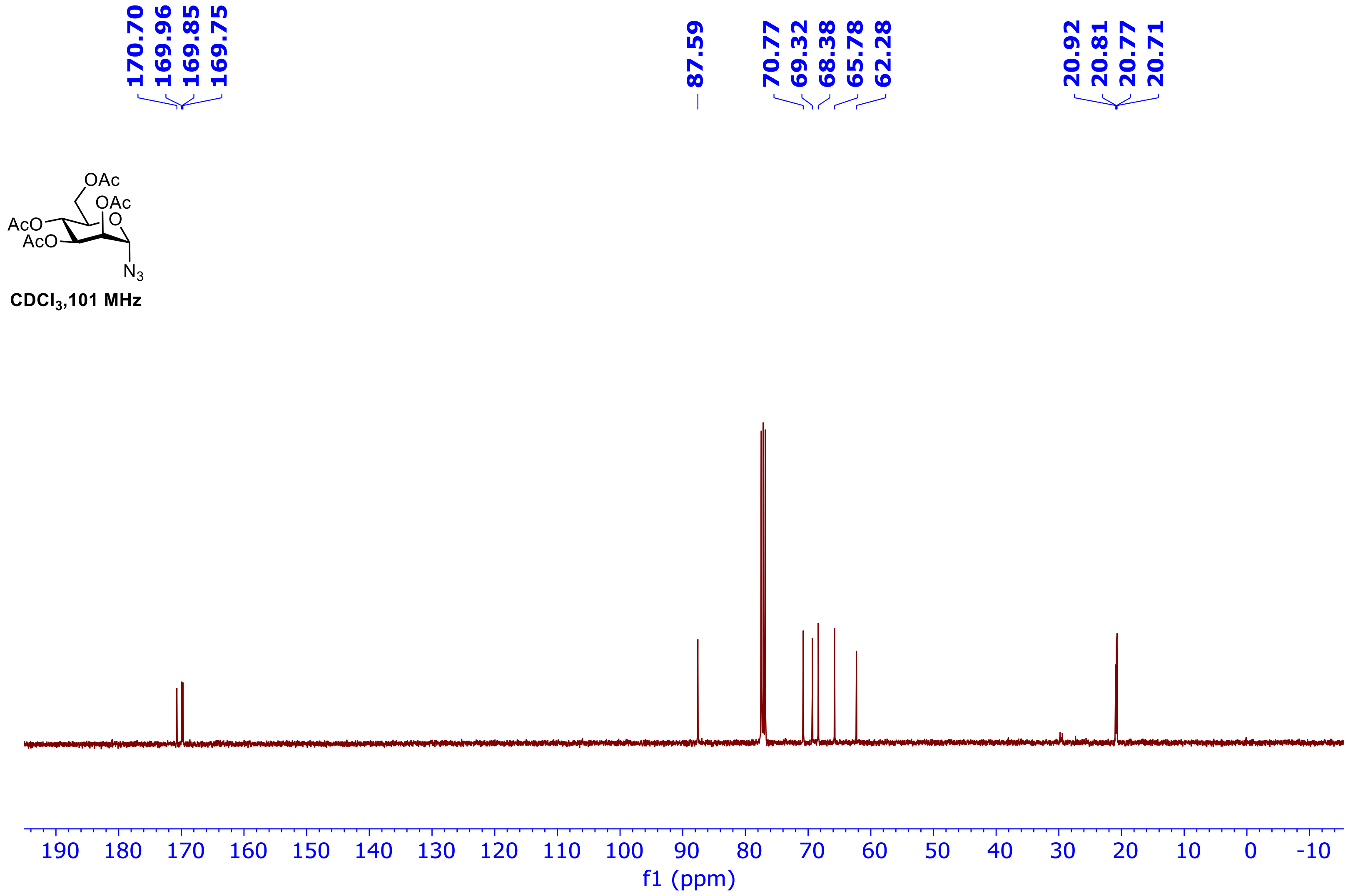


^{1}H NMR spectrum of 3i



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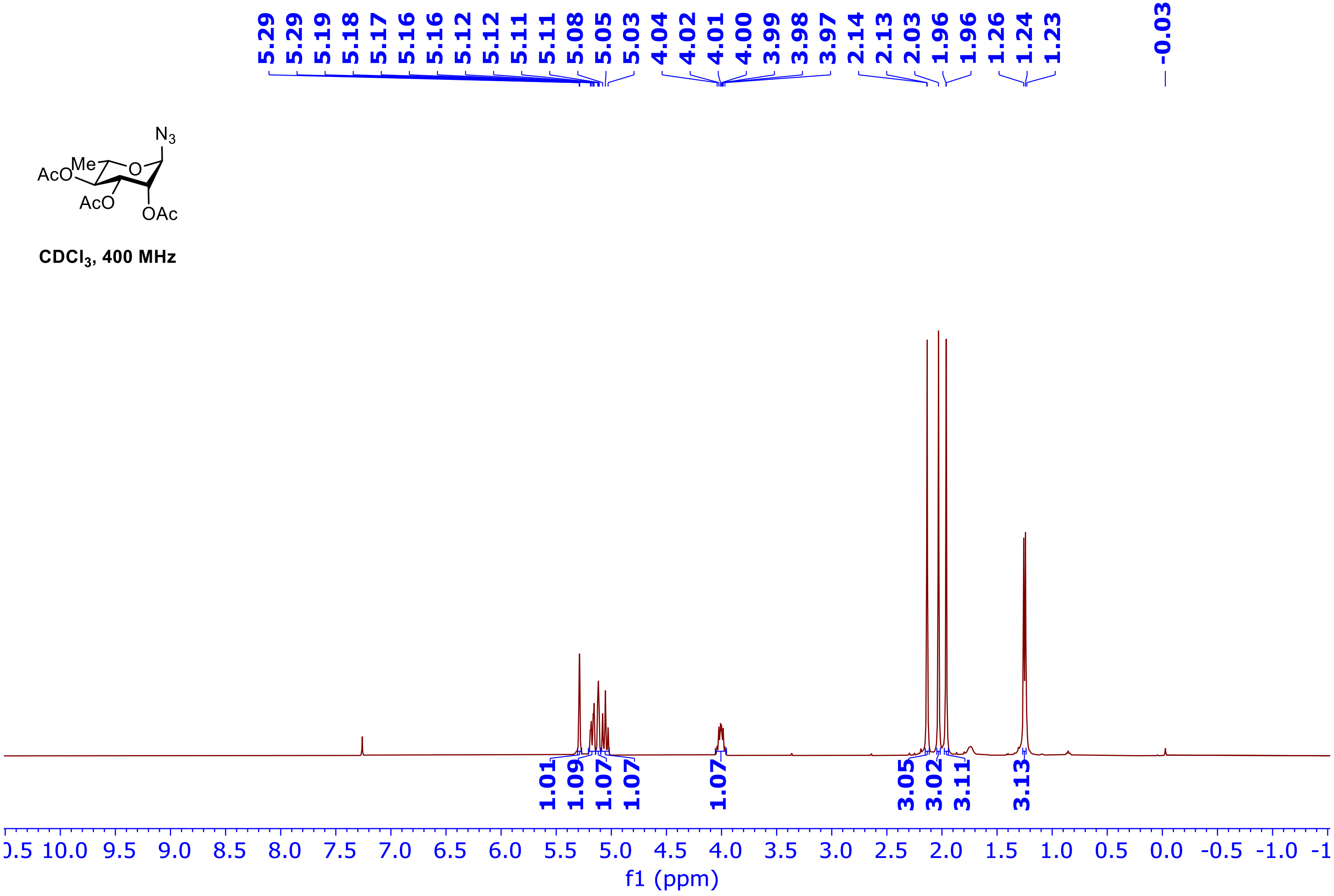

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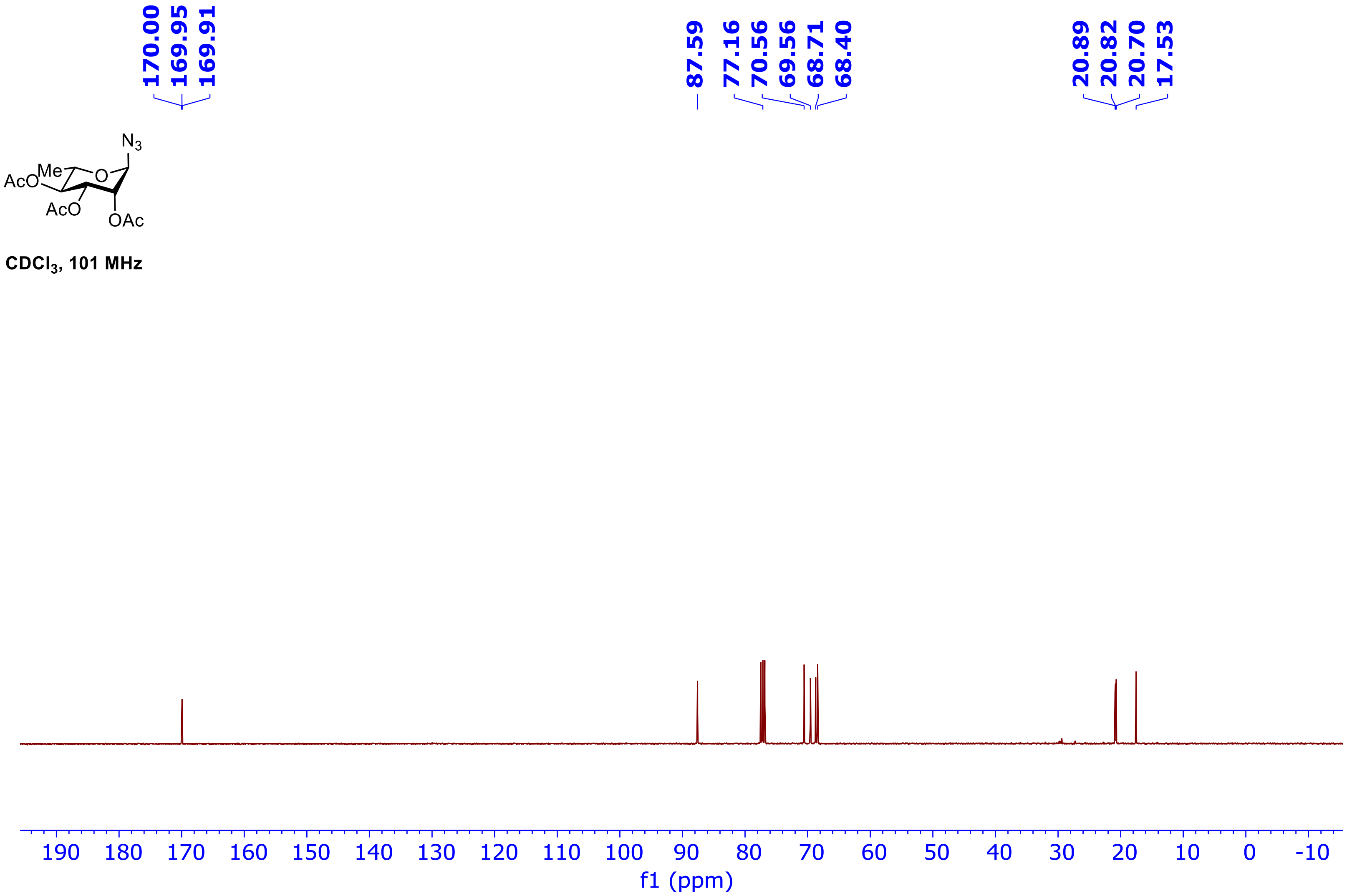

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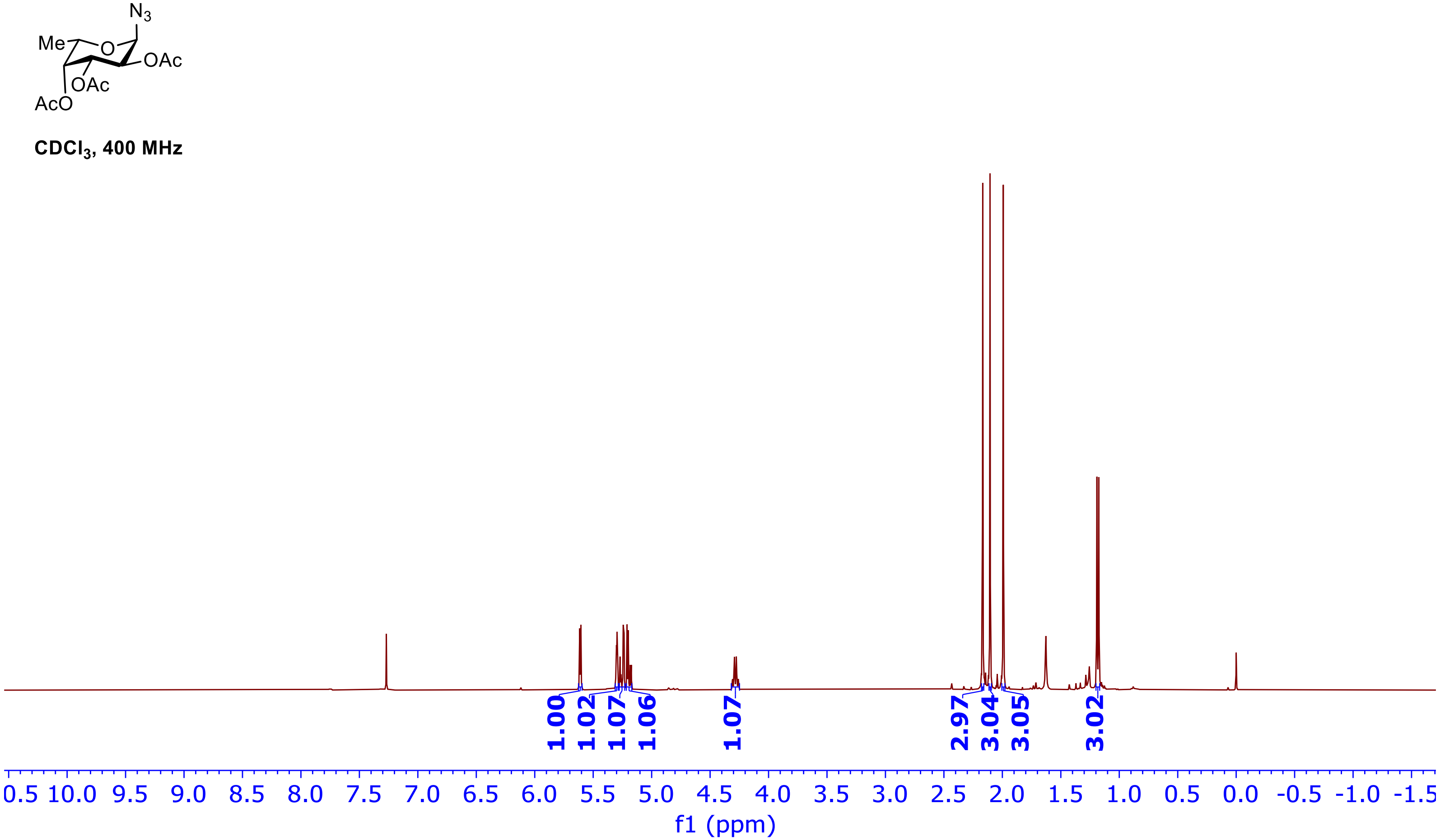

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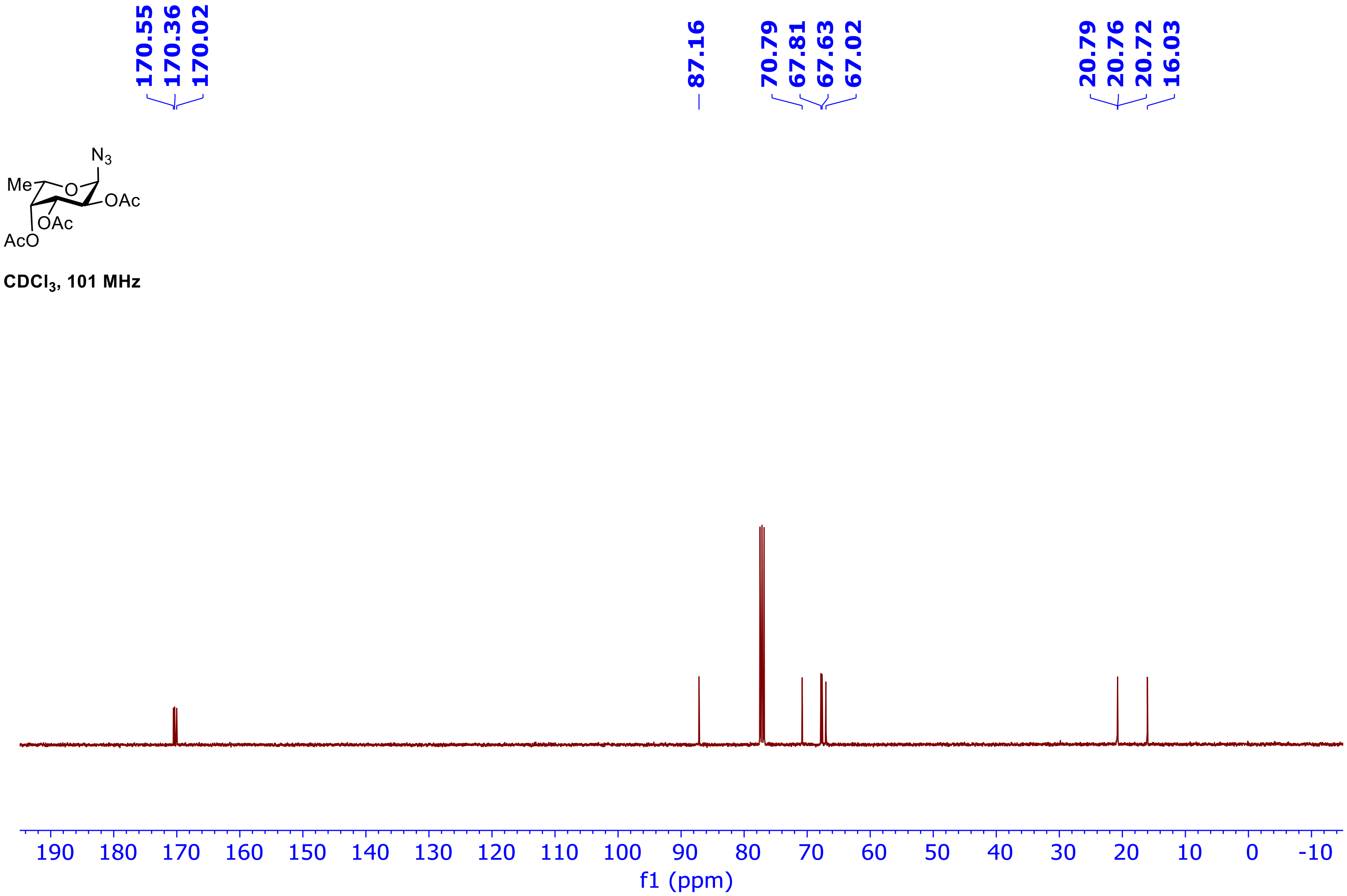

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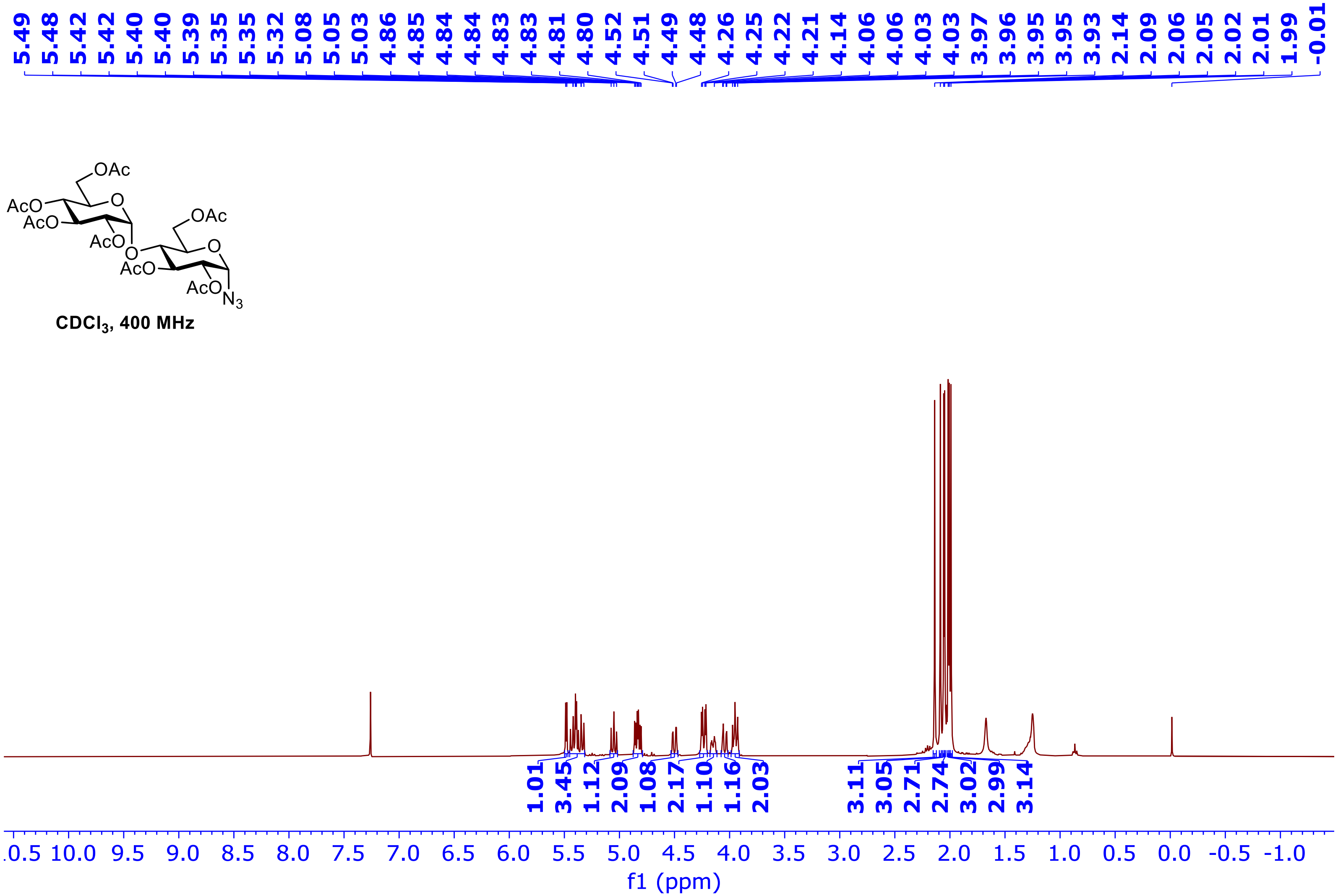

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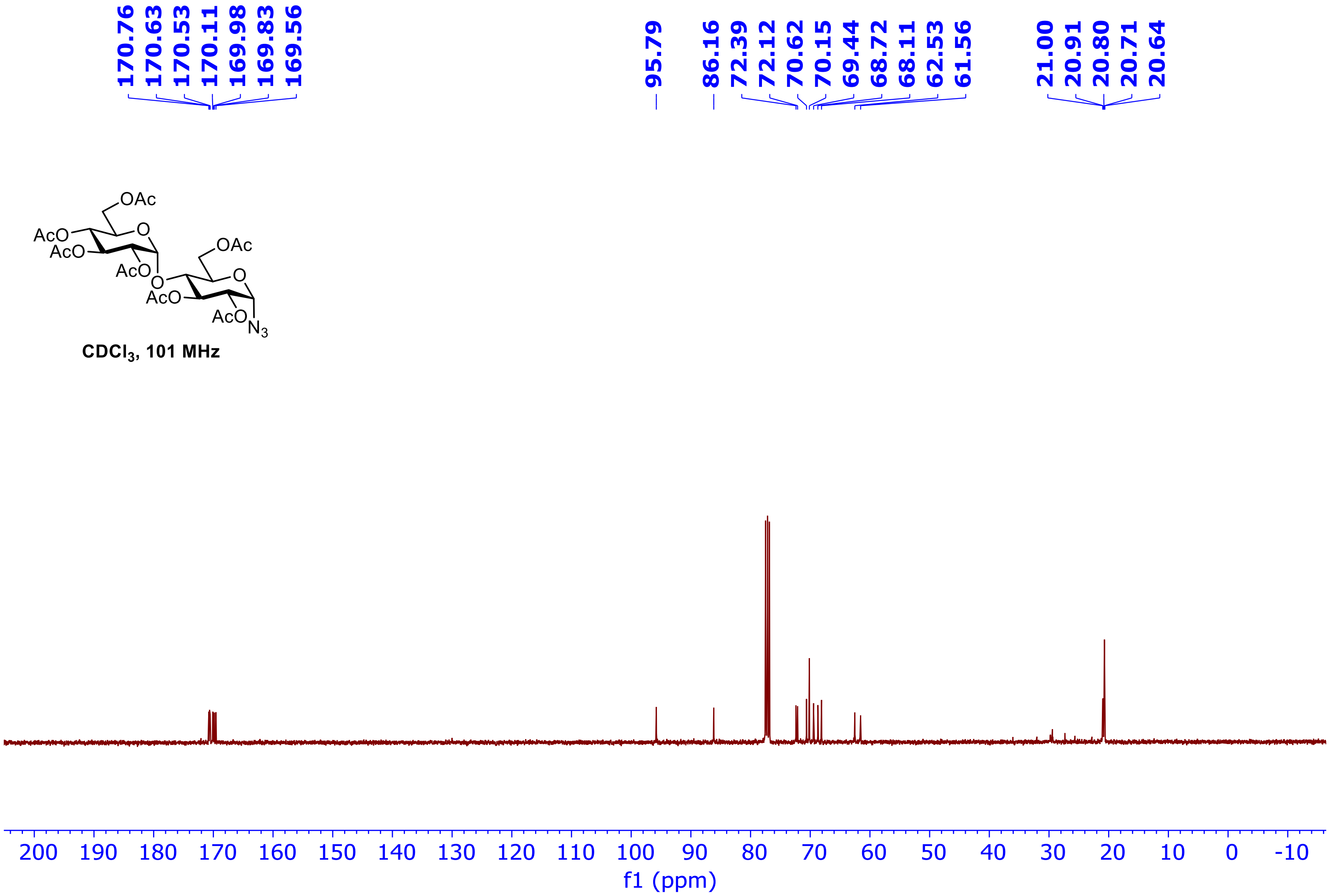

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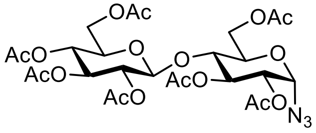
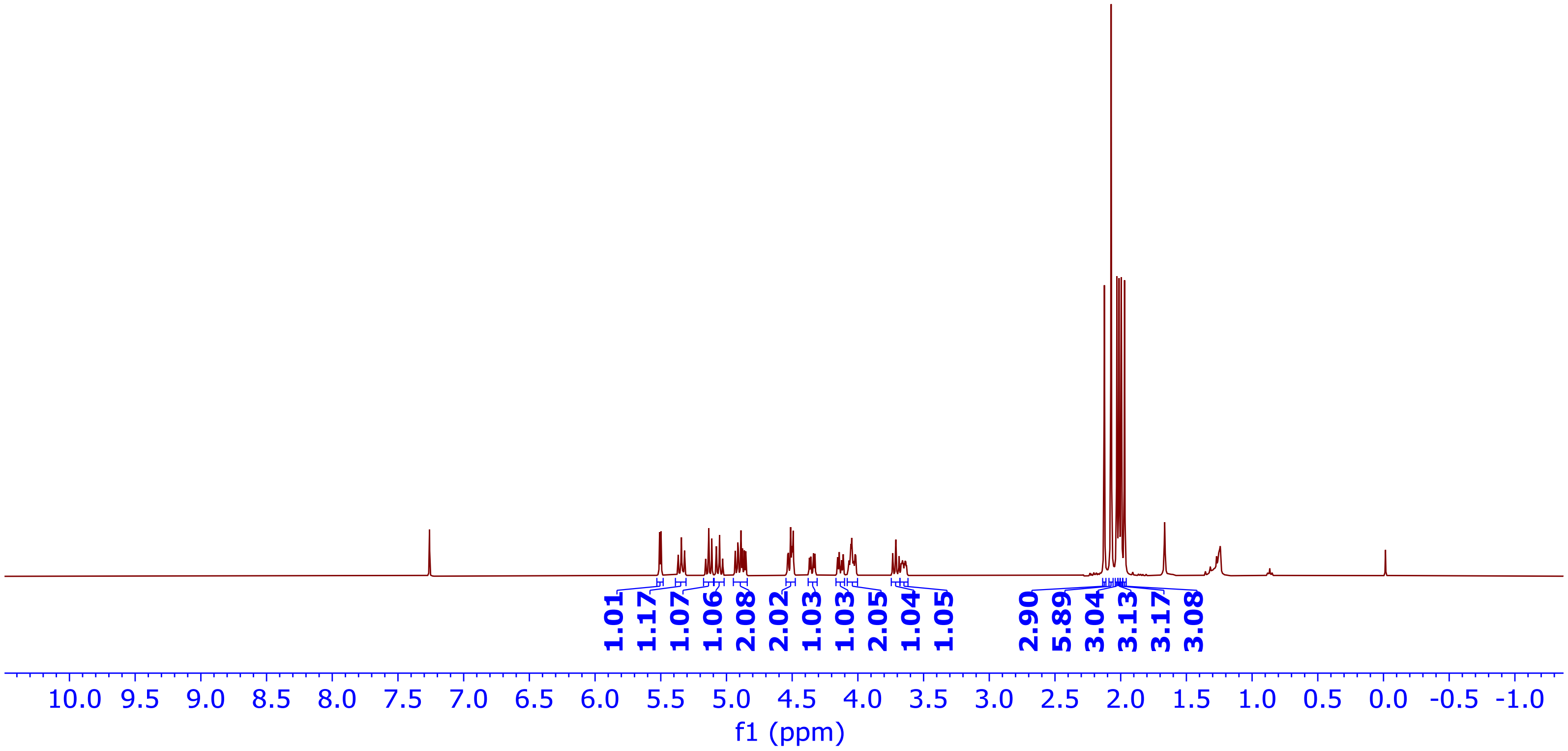
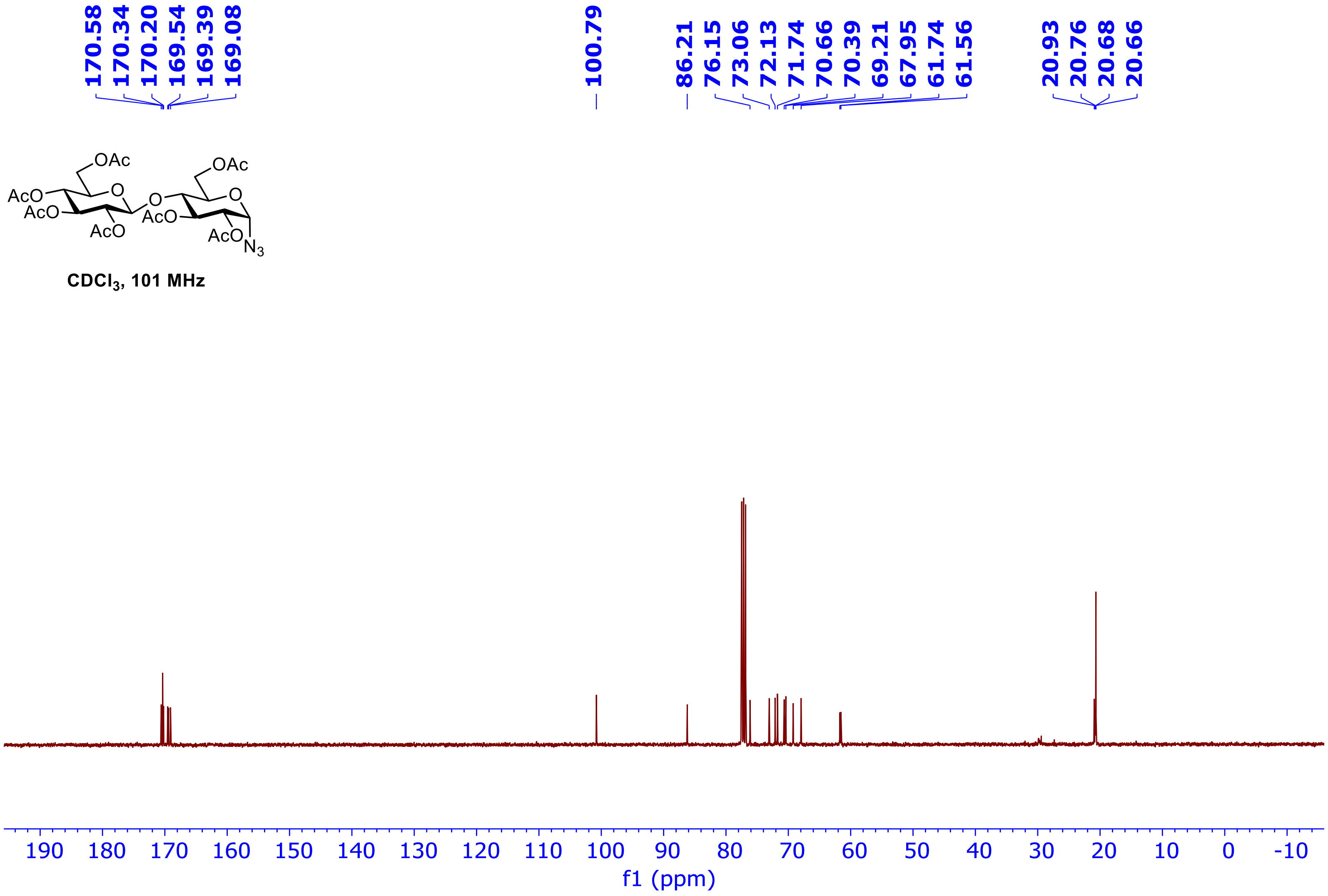


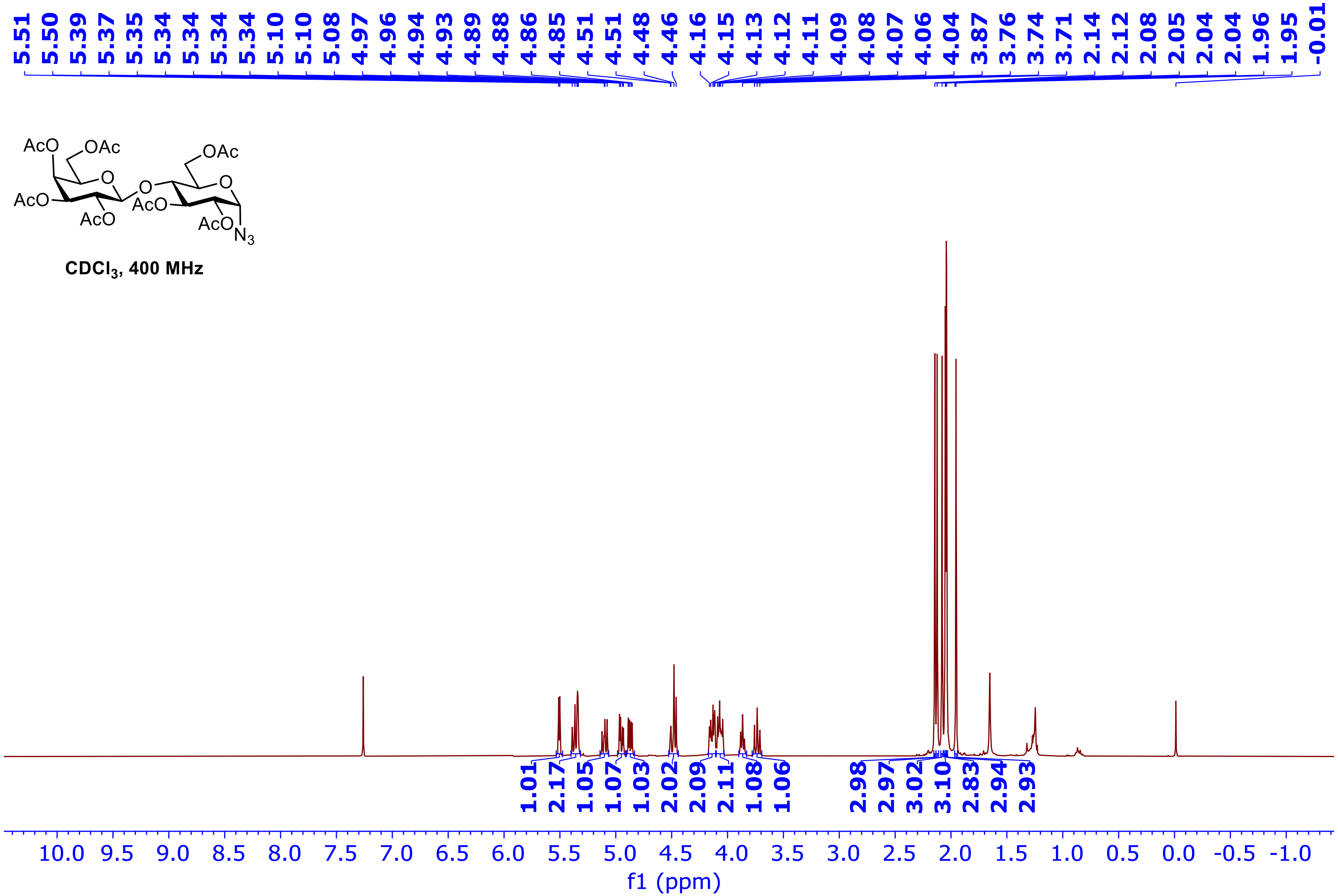
$CDCl_3$, 400 MHz



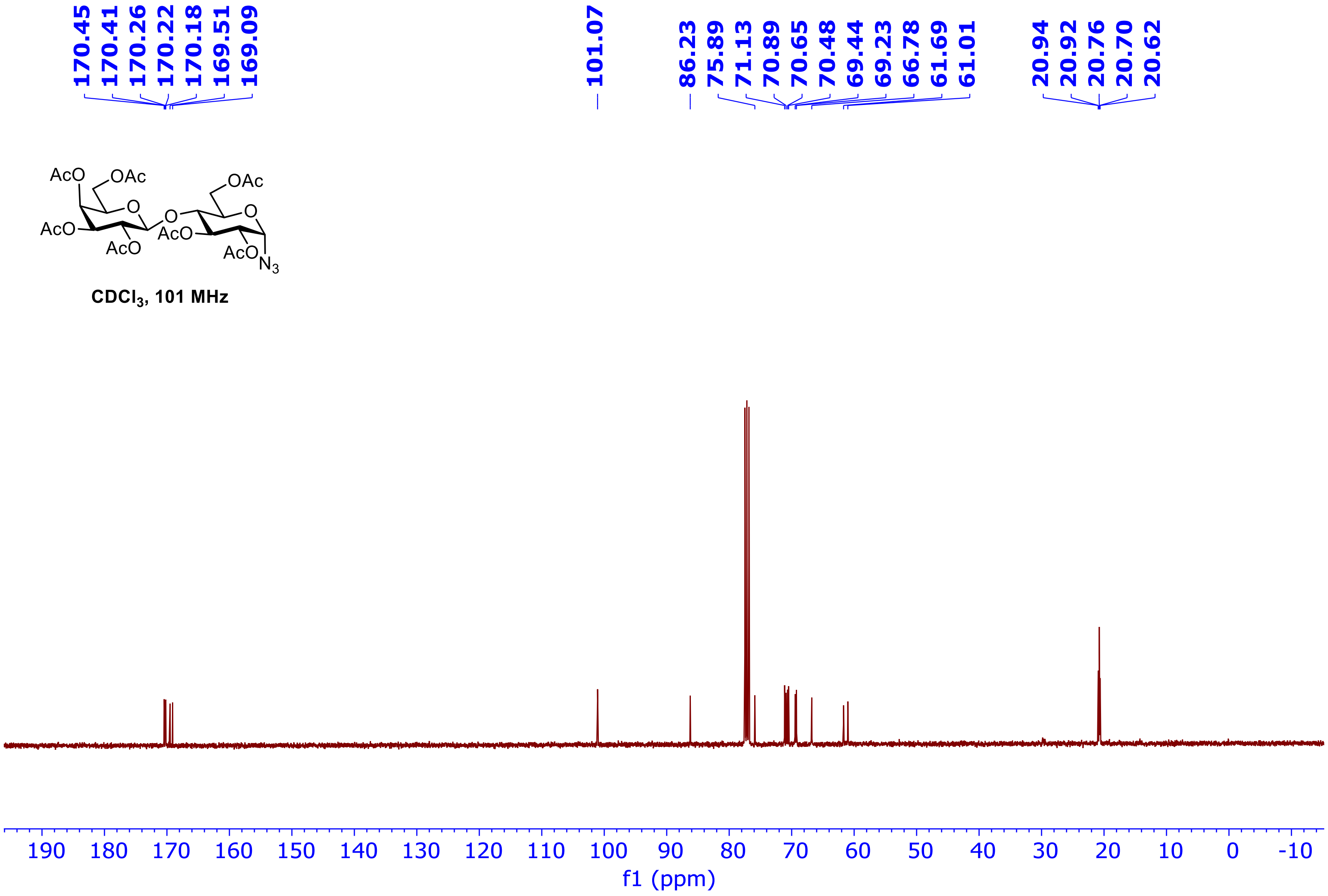
^{1}H NMR spectrum of 3m



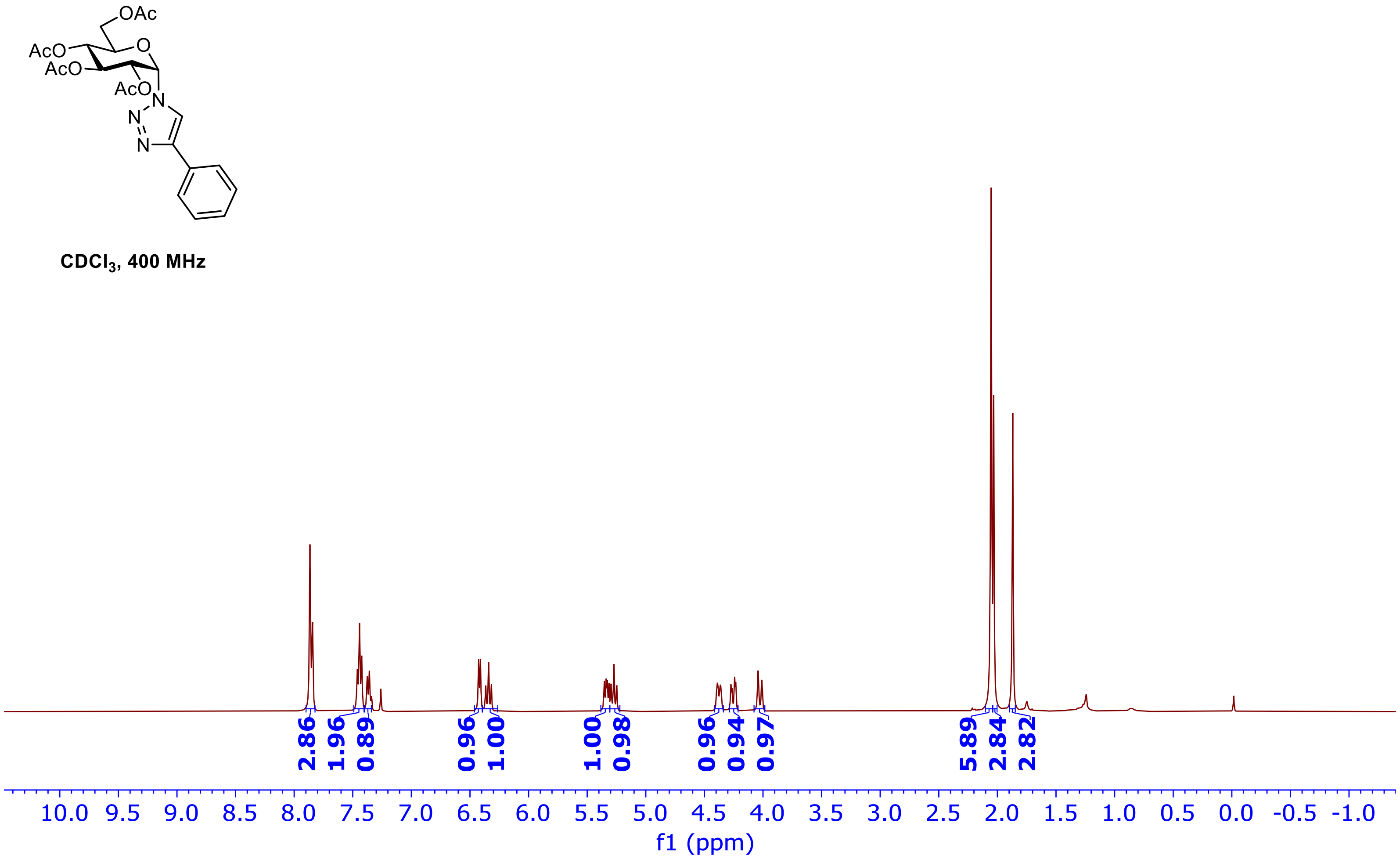
^{13}C NMR spectrum of 3m



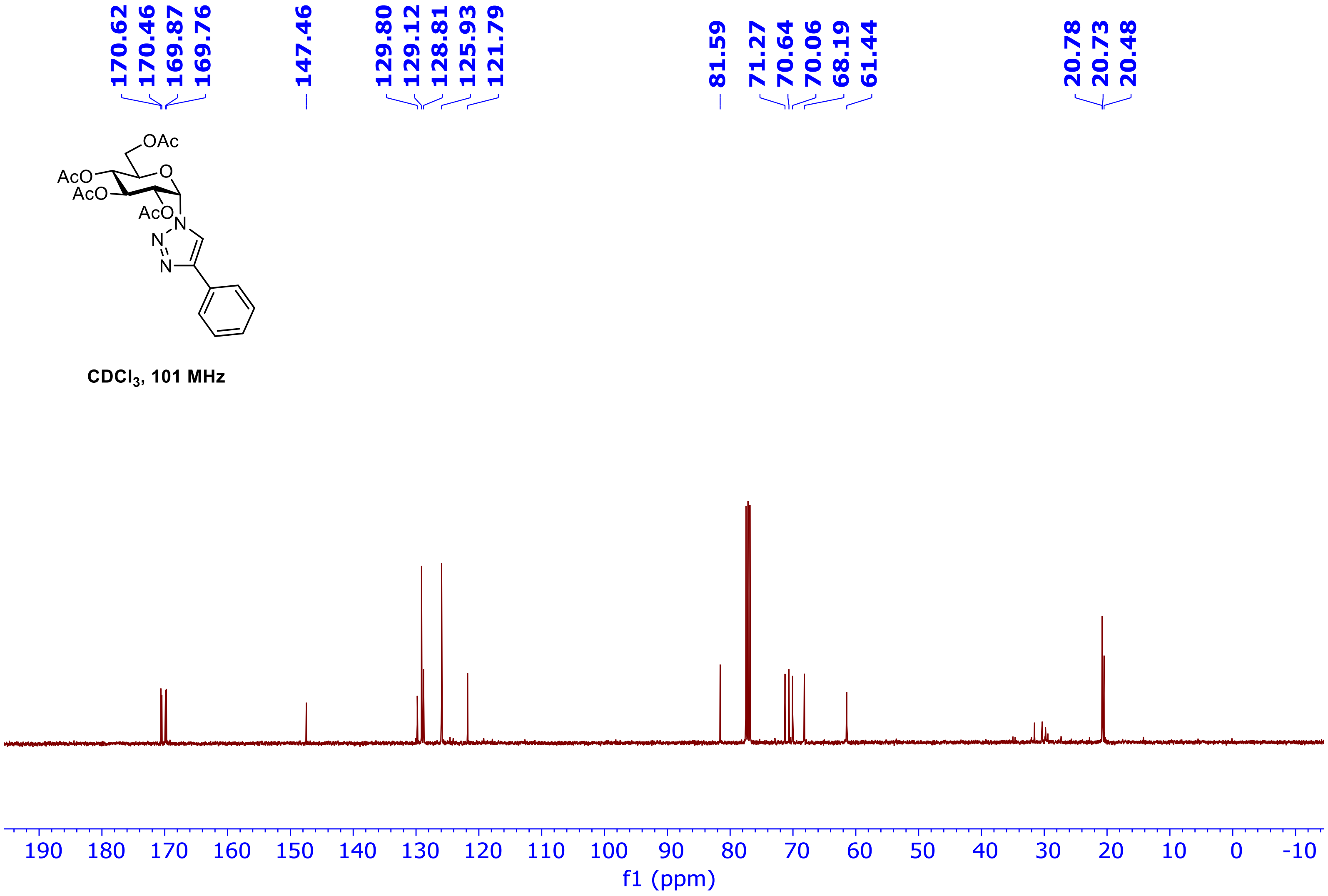
^{1}H NMR spectrum of 3n



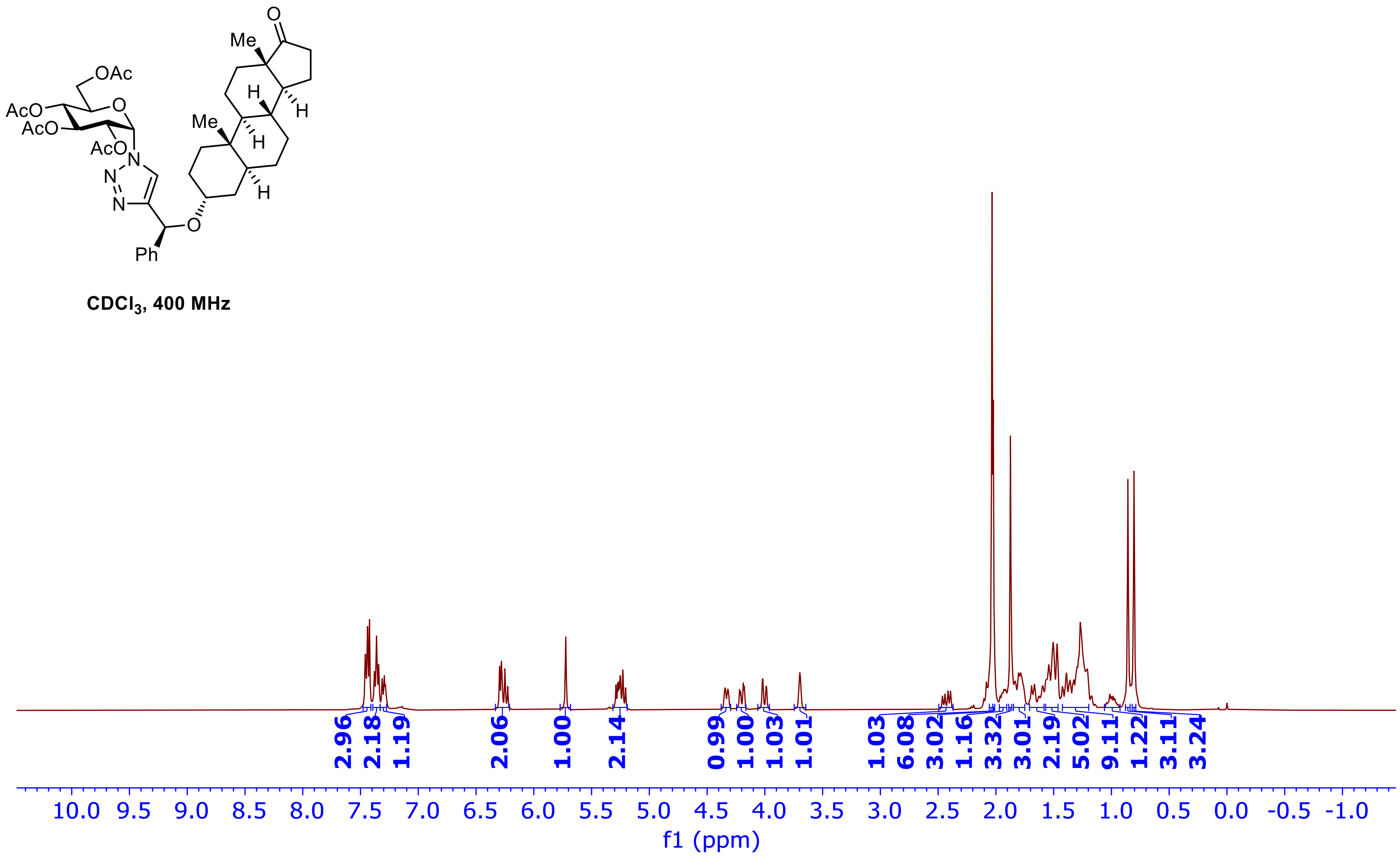
^{13}C NMR spectrum of 3n



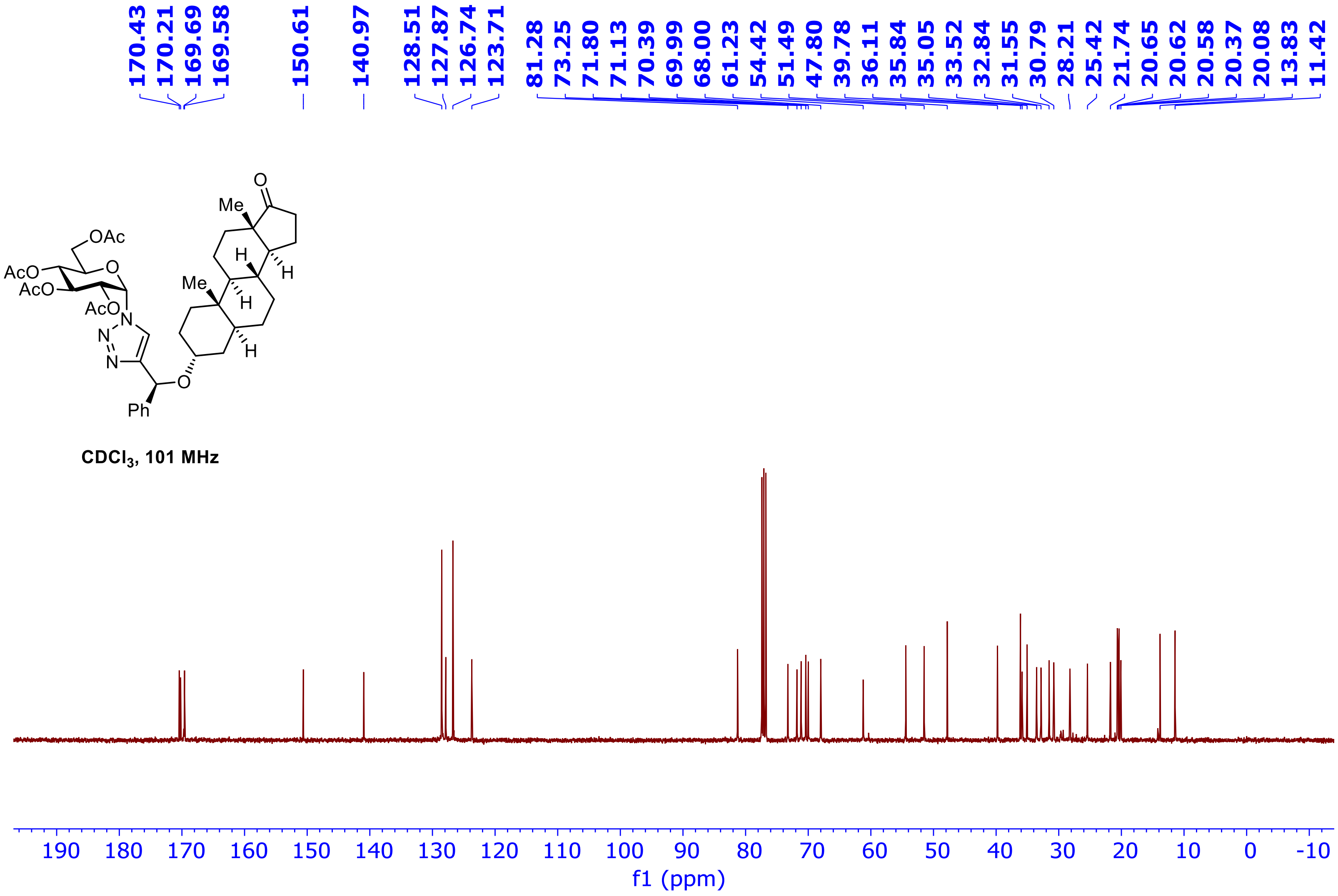
^{1}H NMR spectrum of 12a



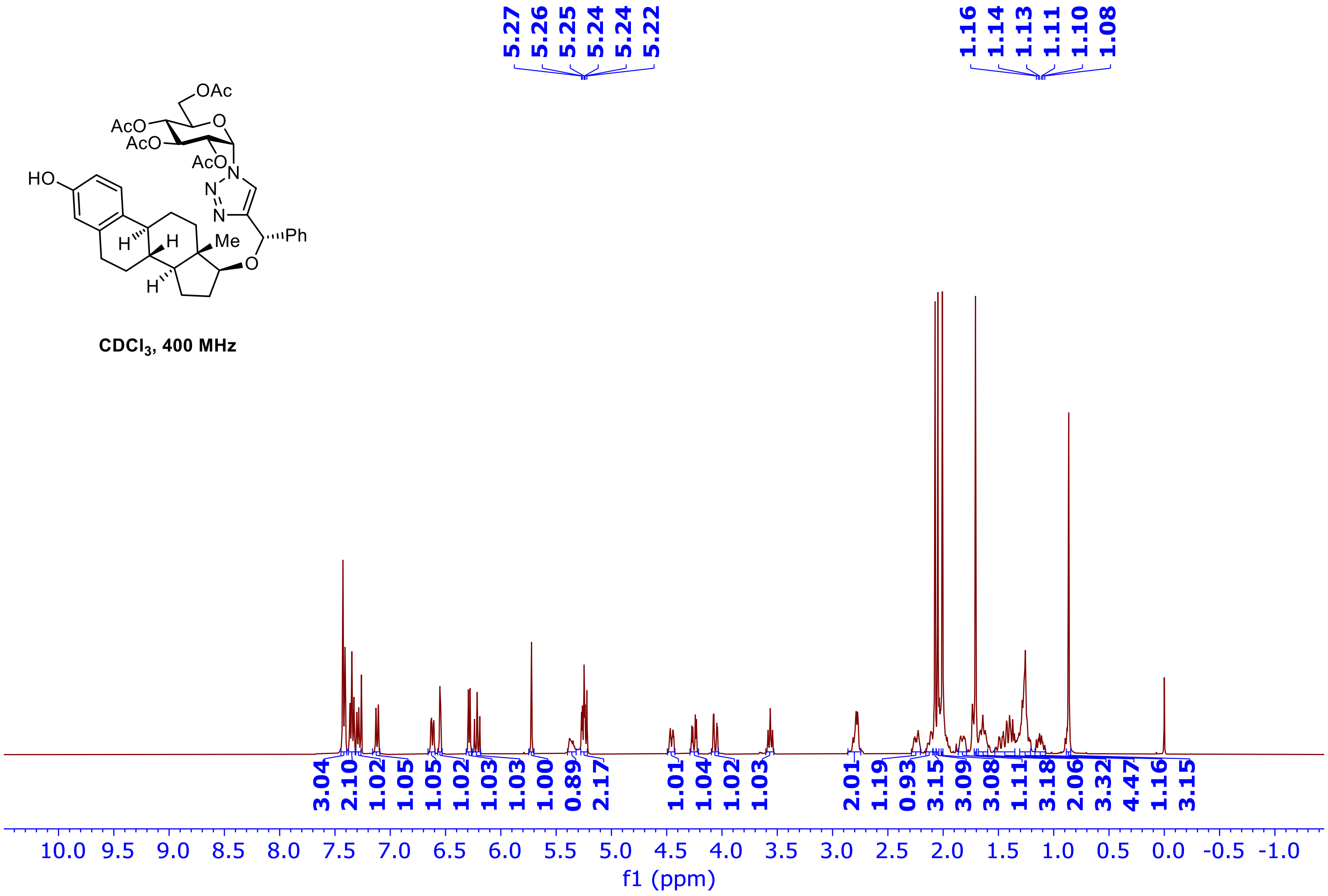
^{13}C NMR spectrum of 12a



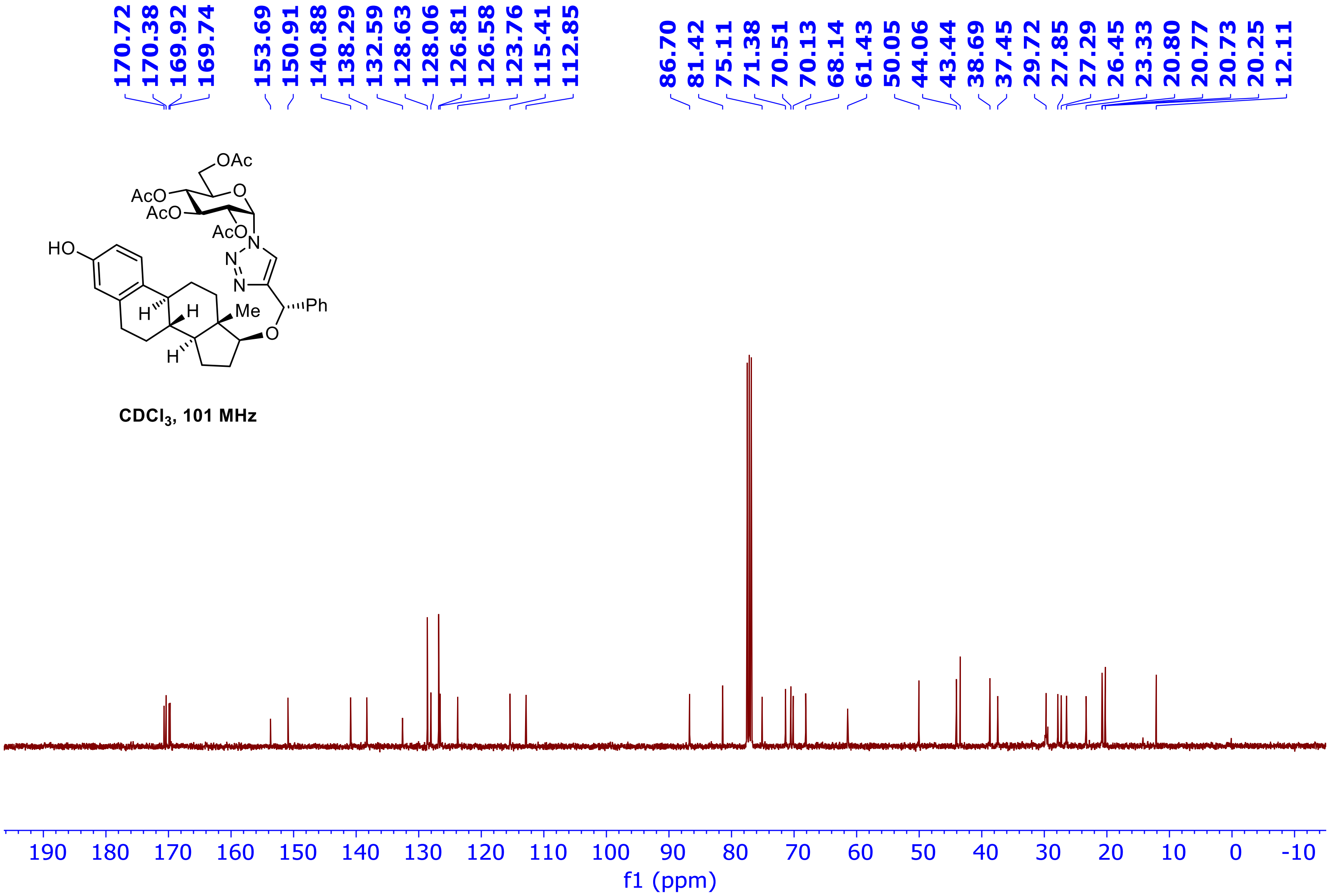
^{1}H NMR spectrum of 12b



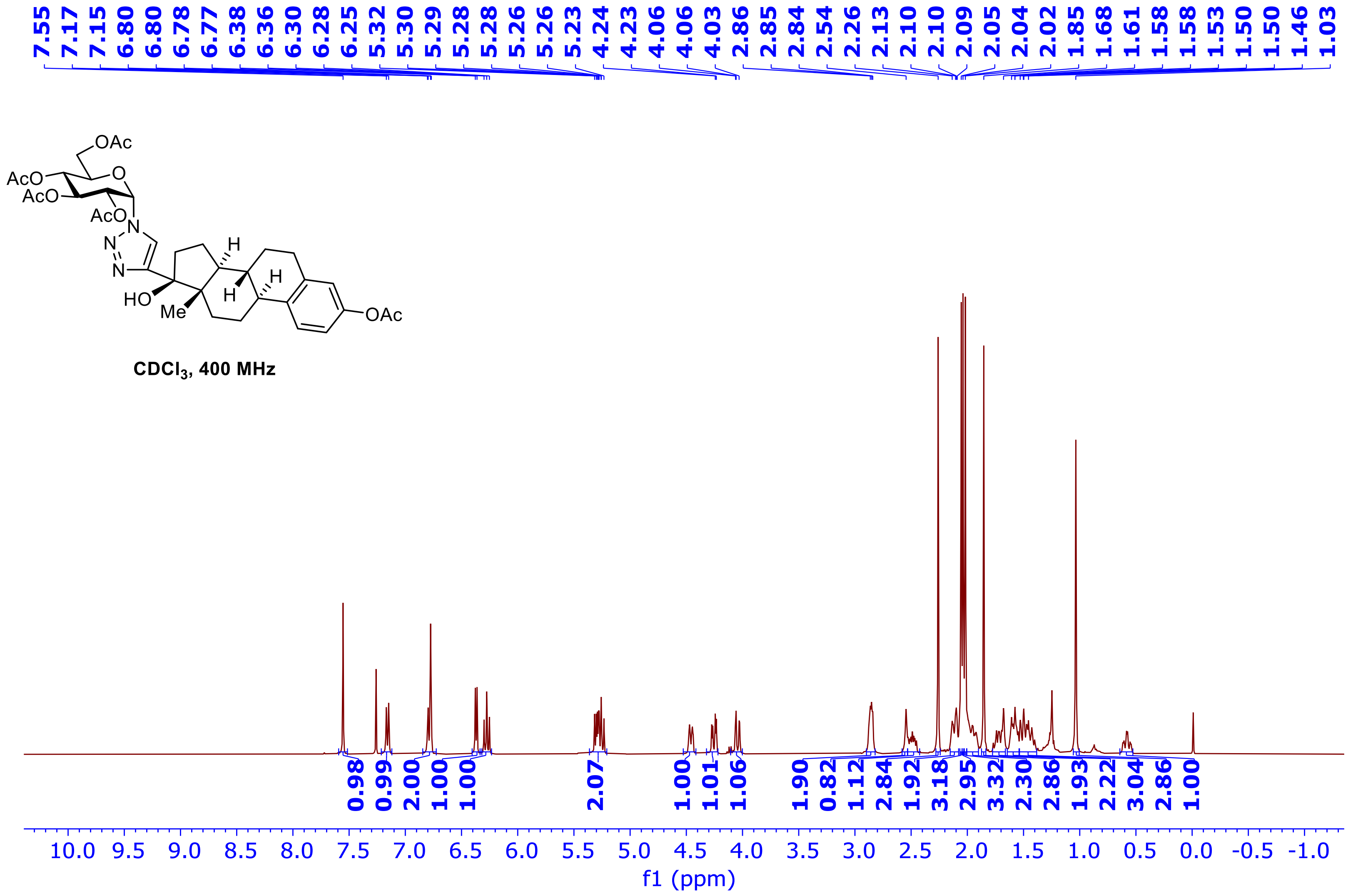
^{13}C NMR spectrum of 12b



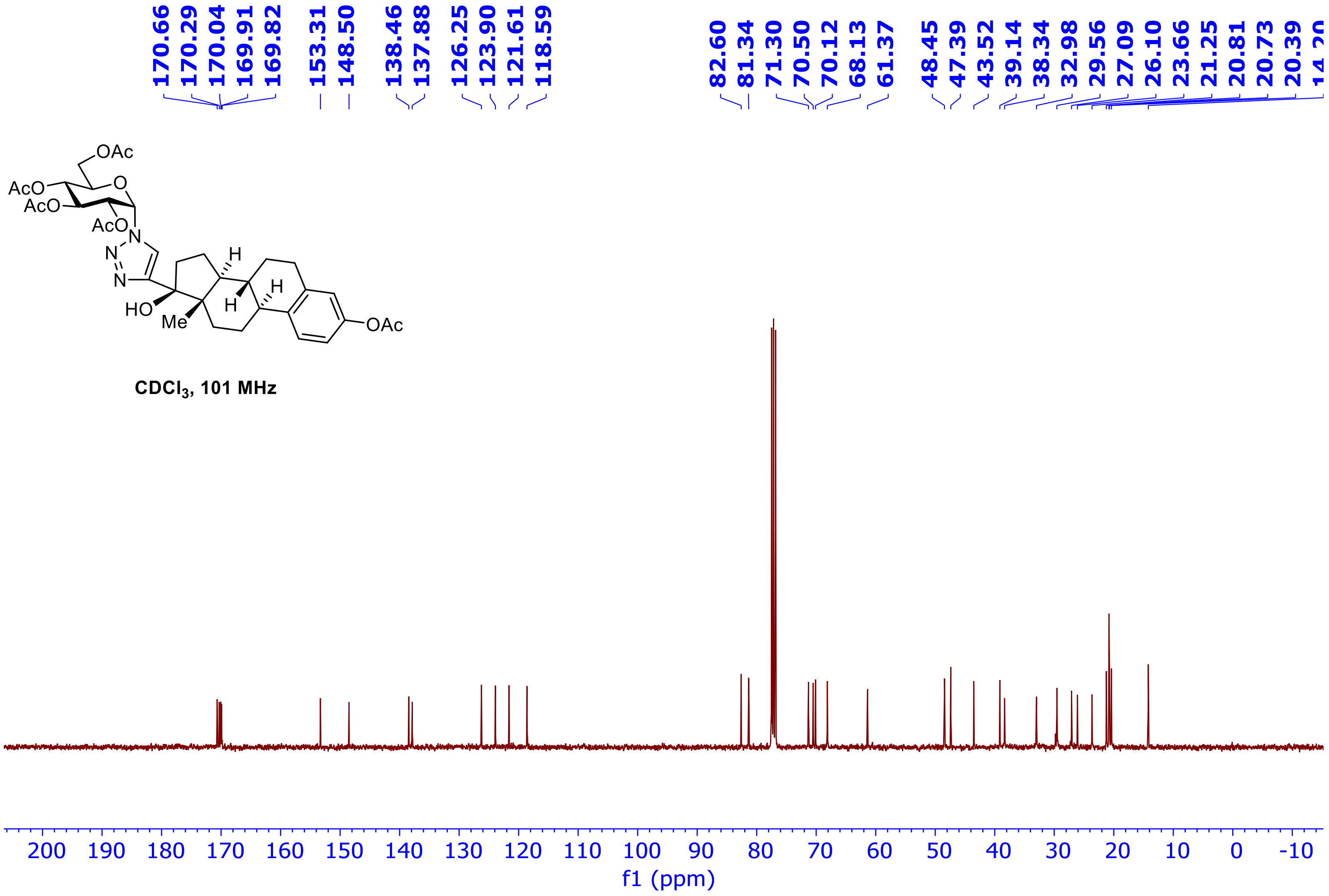
^{1}H NMR spectrum of 12c



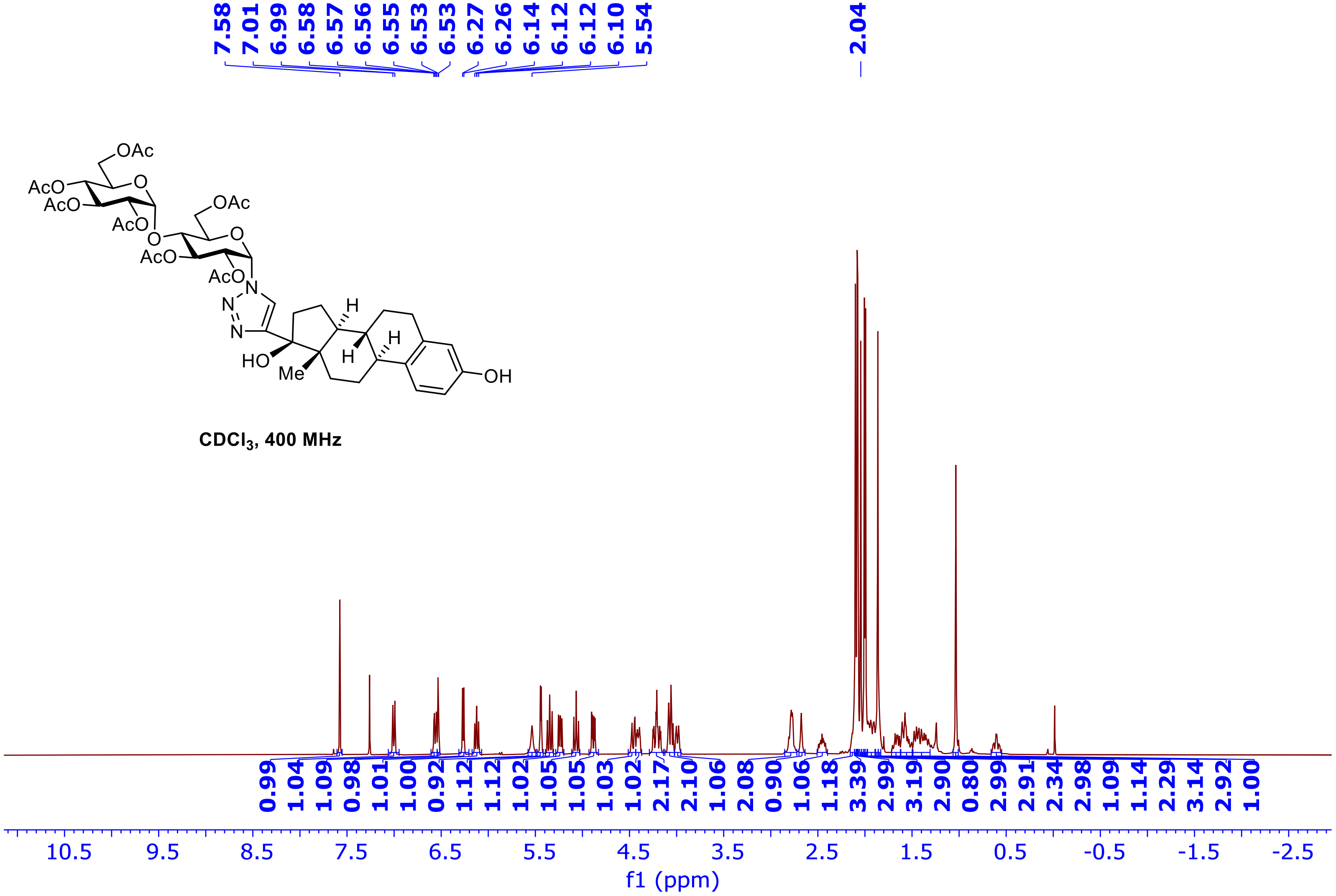
^{13}C NMR spectrum of 12c



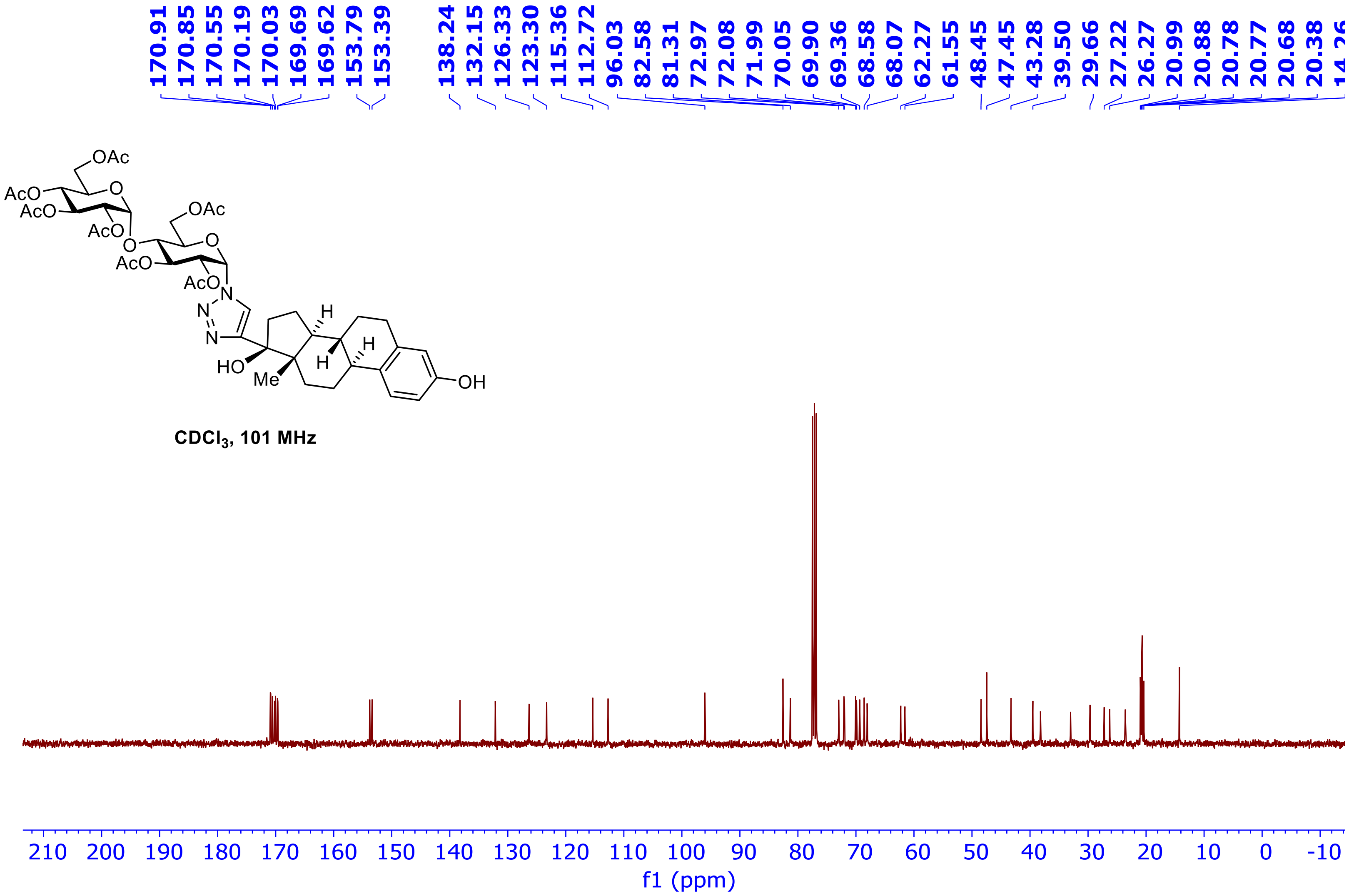
^{1}H NMR spectrum of 12d



^{13}C NMR spectrum of 12d



^{1}H NMR spectrum of 12e



^{13}C NMR spectrum of 12e