Electronic Supplementary Information

Phenylenediamine catalysis of click glycosylations in water : Practical and direct access to unprotected neoglycoconjugates

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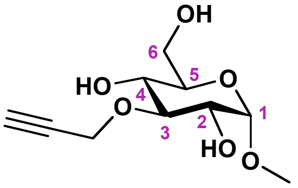
General Methods

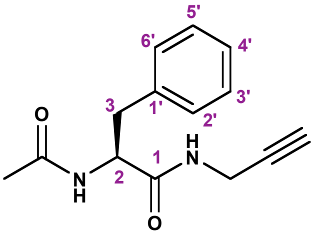
Thin layer chromatography was performed on Merck $60F_{254}$ sheets with detection by UV and by charring with 5% ethanolic H_2SO_4. Unless otherwise stated, TLC was eluted with ethyl acetate / isopropanol / water 3:2:1. Hygroscopic reagents were dried *in vacuo* immediately prior to weighing. NMR spectra were taken on Bruker DPX 250, AM 300, AV 360 or DRX 400 spectrometers, using the residual protonated solvent as internal standard. Chemical shifts δ are given in *parts per million* (ppm). Mass spectra were taken on a ThermoFinnigan Mat 95, with Electrospray ionization in the positive (ESI^+) or negative (ESI^-) mode of detection, or on a Jeol JMS-700, with Fast Atom Bombardment ionization in the positive mode of detection (FAB^+). Residual free copper was first estimated with Quantofic® Copper test sticks (Macherey-Nagel) and then quantified by CHEMets® Kit Copper K-3510 (CHEMetrics) colorimetric assay.

Methyl 3-O-propargyl-α-D-glucopyranoside:



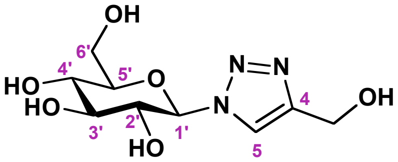
To a solution of methyl 4,6-*O*-benzylidene-3-*O*-propargyl-α-D-glucopyranoside[1] (500 mg, 1.56 mmol) in MeOH (20.0 ml) was added 2.1 g of Dowex 50WX8-H^+ resin. The suspension was stirred at 50°C overnight. The reaction mixture was filtered off, and neutralized with solid $NaHCO_3$, filtered and the solvent was evaporated. The residue was purified by column chromatography over silica gel (Petroleum Ether/EtOAc 1/4) to yield 356 mg (98%) of *methyl 3-O-propargyl-α-D-glucopyranoside* as a colourless oil. ^{1}*H NMR* (360 MHz, MeOD-d$_4$) δ: 4.65 (d, 1H, $J_{1,2}$ 4.0 Hz, *H-1*); 4.49 (d, 2H, ^{4}J 2.0 Hz, OC*H$_2$*CCH); 3.80 (dd, 1H, $J_{6a,6b}$ 12.0, $J_{6a,5}$ 2.0 Hz, *H-6a*); 3.67 (dd, 1H, $J_{6b,6a}$ 12.0, $J_{6b,5}$ 5.5 Hz, *H-6b*); 3.57 (dd, 1H, $J_{3,2}$ 9.5, $J_{3,4}$ 8.5 Hz, *H-3*); 3.54 (ddd, 1H, $J_{4,5}$ 10.0, $J_{5,6b}$ 5.5, $J_{5,6a}$ 2.0 Hz, *H-5*); 3.47 (dd, 1H, $J_{2,3}$ 9.5, $J_{2,1}$ 4.0 Hz, *H-2*); 3.41 (s, 3H, OC*H$_3$*); 3.36 (dd, 1H, $J_{4,5}$ 10.0, $J_{4,3}$ 8.5 Hz, *H-4*); 2.81 (t, 1H, ^{4}J 2.5 Hz, CH$_2$CC*H*). ^{13}*C NMR (90 MHz, DMSO-d$_6$)* δ: 99.7 (*C-1*); 81.4 (*C-3*); 81.3 (OCH$_2$*C*CH); 76.3 (OCH$_2$C*C*H); 72.6 (*C-5*); 71.6 (*C-2*); 69.4 (*C-4*); 60.7 (*C-6*); 59.2 (O*C*H$_2$CCH); 54.3 (O*C*H$_3$). *MS (ESI$^+$)* : *m/z* 255.2 [M+Na]$^+$. *HRMS (ESI$^+$)* : Calcd. for $C_{10}H_{16}O_6Na$ 255.0839, found 255.0834.

N-acetyl-L-phenylalanine propargylamide *:*



N-Acetyl-L-phenylalanine (324 mg, 1.56 mmol) was dissolved in dry CH$_2$Cl$_2$ (6.0 ml) with DMAP (19.0 mg, 0.16 mmol, 0.1 eq.) and EDC•HCl (449 mg, 2.34 mmol, 1.5 eq.). Propargylamine (100 μl, 86.0 mg, 1.56 mmol, 1.0 eq.) was added and the reaction mixture was stirred at room temperature overnight under an argon atmosphere until TLC (CH$_2$Cl$_2$/MeOH 9:1) showed complete conversion. The reaction mixture was washed three times with water, and the organic layer was dried over sodium sulfate, filtered and concentrated. The residue was purified by flash chromatography over silica gel (CH$_2$Cl$_2$ / MeOH 9/1) to give 99.0 mg (26 %) of *N*-acetyl-L-phenylalanine propargylamide as a white solid. ^{1}*H NMR* (300 MHz, CDCl$_3$) δ: 7.35-7.25 (m, 3H, *H-3', H-4', H-5'*); 7.20 (m, 2H, *H-2', H-6'*); 6.47 (t, 1H, ^{3}J 5.3 Hz, CON*H*CH$_2$); 6.41 (d, 1H, $J_{NH,2}$ 7.5 Hz, CH$_3$CON*H*); 4.69 (td, 1H, $J_{2,3}$ 7.5, $J_{2,NH}$ 7.5 Hz, *H-2*); 3.95 (dd, 2H, *J* 5.3, ^{4}J 2.5 Hz, C*H$_2$*CCH); 3.05 (d, 2H, $J_{3,2}$ 7.5 Hz, *H-3*); 2.19 (t, 1H, ^{4}J 2.5 Hz, CH$_2$CC*H*); 1.97 (s, 3H, C*H$_3$*). ^{13}*C NMR (75 MHz, CDCl$_3$)* δ: 170.9 (*C-1*); 170.4 (CH$_3$*C*ONH); 136.6 (*C-1'*); 129.5 (*C-2', C-6'*); 128.9 (*C-3', C-5'*); 127.3 (*C-4'*); 79.1 (CH$_2$*C*CH); 71.8 (CH$_2$C*C*H); 54.6 (*C-2*); 38.7 (*C-3*); 29.3 (*C*H$_2$CCH); 23.3 (*C*H$_3$). *MS (ESI$^+$)* : *m/z* 267.1 [M+Na]$^+$. *HRMS (ESI$^+$)* : Calcd. for $C_{14}H_{16}N_2O_2Na$ 267.11040, found 267.10907.

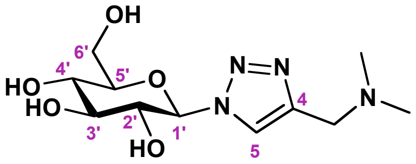
4-Hydroxymethyl-1-(β-D-glucopyranosyl)-1H-[1,2,3]-triazole (2) :



Procedure A :

To a solution of β-D-glucopyranosyl azide (53.0 mg, 260 μmol, 1 eq.) in H_2O (730 μl) were added propargyl alcohol (15 μl, 14.5 mg, 260 μmol, 1 eq.), *o*-phenylenediamine (104 μl, 40.5 mg per ml of H_2O, 4.2 mg, 39 μmol, 15 mol%), sodium ascorbate (104 μl, 49.5 mg per ml of H_2O, 5.1 mg, 26 μmol, 10 mol%) and copper sulfate pentahydrate (104 μl, 31.2 mg per ml of H_2O, 3.2 mg, 13 μmol, 5 mol%). The reaction mixture was stirred at room temperature under an argon atmosphere for 45 min. After this time, TLC showed complete conversion and activated charcoal (100 mg) was added to the reaction mixture, which was stirred overnight under an air atmosphere. The reaction mixture was then filtered through a celite plug and eluted with water. The solvent was evaporated to dryness to give 66.4 mg (98%) of *4-hydroxymethyl-1-(β-D-glucopyranosyl)-1H-[1,2,3]-triazole*[2] (**2**) as a colourless oil. *^{1}H NMR* (300 MHz, methanol-d4) δ: 8.13 (s, 1H, *H-5*); 5.61 (d, 1H, $J_{1',2'}$ 9.5 Hz, *H-1'*); 4.71 (s, 2H, CCH_2OH); 3.95-3.85 (m, 2H, *H-2'*, *H-6a'*); 3.72 (dd, 1H, $J_{6a',6b'}$ 12.0, $J_{5',6b'}$ 5.0 Hz, *H-6b'*); 3.62-3.45 (m, 3H, *H-3'*, *H-4'*, *H-5'*). *^{13}C NMR* (75 MHz, methanol-d4) δ: 149.1 (*C-4*); 123.4 (*C-5*); 89.5 (*C-1'*); 81.1 (*C-5'*); 78.5 (*C-3'*); 74.0 (*C-2'*); 70.9 (*C-4'*); 62.4 (*C-6'*); 59.4 (CCH_2OH). *Residual copper* ~ 0.10 mol%. *MS (ESI$^+$)* : *m/z* 284.1 $[M+Na]^+$. *HRMS (ESI$^+$)* : Calcd. for $C_9H_{15}N_5O_6Na$ 284.08531, found 284.08604.

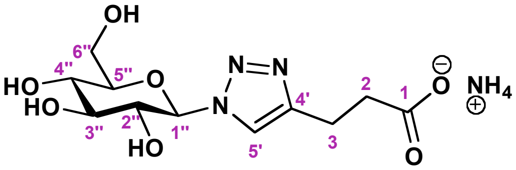
4-((Dimethylamino)methyl)-1-(β-D-glucopyranosyl)-1H-[1,2,3]-triazole (3) :



Following *Procedure A*, *4-((dimethylamino)methyl)-1-(β-D-glucopyranosyl)-1H-[1,2,3]-triazole* (**3**) was obtained from β-D-glucopyranosyl azide (51.3 mg, 250 μmol, 1 eq.) in H_2O (600 μl), dimethylaminopropyne (27 μl, 20.8 mg, 250 μmol, 1 eq.), *o*-phenylenediamine (200 μl, 20.3 mg per ml of H_2O, 4.0 mg, 37.5 μmol, 15 mol%), sodium ascorbate (100 μl, 49.5 mg per ml of H_2O, 4.9 mg, 25.0 μmol, 10 mol%) and copper sulfate pentahydrate (100 μl, 31.2

mg per ml of H_2O, 3.1 mg, 12.5 µmol, 5 mol%). The reaction mixture was stirred at room temperature for 45 min, and activated charcoal was added followed by 45 min of stirring under an air atmosphere. Purification by filtration and evaporation gave 53.7 mg (75%) of *4-((dimethylamino)methyl)-1-(β-D-glucopyranosyl)-1H-[1,2,3]-triazole* (**3**) as a white solid. ^{1}*H NMR* (300 MHz, methanol-d4) δ: 8.12 (s, 1H, *H-5*); 5.60 (d, 1H, $J_{1',2'}$ 9.0 Hz, *H-1’*); 3.89 (dd, 1H, $J_{2',1'}$ 9.0, $J_{2',3'}$ 9.0 Hz, *H-2’*); 3.88 (dd, 1H, $J_{6a',6b'}$ 12.0, $J_{6a',5'}$ 2.0 Hz, *H-6a’*); 3.71 (dd, 1H, $J_{6a',6b'}$ 12.0, $J_{5',6b'}$ 5.0 Hz, *H-6b’*); 3.66 (s, 2H, $CCH_2N(CH_3)_2$); 3.58 (ddd, 1H, $J_{5',4'}$ 9.0, $J_{5',6b'}$ 5.0, $J_{5',6a'}$ 2.0 Hz, *H-5’*); 3.56 (dd, 1H, $J_{3',4'}$ 9.0, $J_{3',2'}$ 8.5 Hz, *H-3’*); 3.49 (dd, 1H, $J_{4',3'}$ 9.0, $J_{4',5'}$ 9.0 Hz, *H-4’*); 2.29 (s, 6H, 2 CH_3). ^{13}*C NMR* (62.5 MHz, methanol-d4) δ: 144.7 (*C-4*); 124.8 (*C-5*); 89.7 (*C-1’*); 81.3 (*C-5’*); 78.7 (*C-3’*); 74.2 (*C-2’*); 71.0 (*C-4’*); 62.6 (*C-6’*); 54.4 ($CCH_2N(CH_3)_2$); 45.0 (2 CH_3). *Residual copper* ~ 0.16 mol%. *MS (ESI$^+$)* : *m/z* 311.1 [M+Na]$^+$. *HRMS (ESI$^+$)* : Calcd. for $C_{11}H_{20}N_5O_5Na$ 311.13259, found 311.13230.

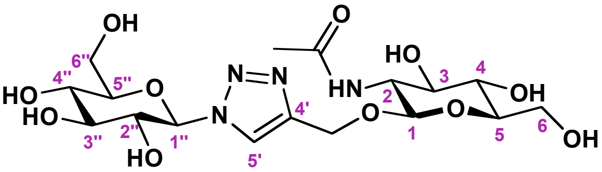
Ammonium 3-[1’-(β-D-glucopyranosyl)-1’H-[1’,2’,3’]-triazol-4’-yl]propanoate (4) :



Following *Procedure A*, *ammonium 3-[1’-(β-D-glucopyranosyl)-1’H-[1’,2’,3’]-triazol-4’-yl]propanoate* (**4**) was obtained from β-D-glucopyranosyl azide (51.3 mg, 250 µmol, 1 eq.) in H_2O (600 µl), ammonium 4-pentynoate (28.8 mg, 250 µmol, 1 eq.), *o*-phenylenediamine (200 µl, 20.3 mg per ml of H_2O, 4.0 mg, 37.5 µmol, 15 mol%), ammonium ascorbate (100 µl, 48.3 mg per ml of H_2O, 4.8 mg, 25.0 µmol, 10 mol%) and copper sulfate pentahydrate (100 µl, 31.2 mg per ml of H_2O, 3.1 mg, 12.5 µmol, 5 mol%). The reaction mixture was stirred at room temperature for 2 hours, and activated charcoal was added followed by 45 min of stirring under an air atmosphere. Purification by filtration and evaporation gave 62.5 mg (78%) of *ammonium 3-[1’-(β-D-glucopyranosyl)-1’H-[1’,2’,3’]-triazol-4’-yl]propanoate* (**4**) as a white solid. ^{1}*H NMR* (250 MHz, methanol-d4) δ: 7.95 (s, 1H, *H-5’*); 5.55 (d, 1H, $J_{1'',2''}$ 9.0 Hz, *H-1”*); 3.87 (dd, 1H, $J_{6a'',6b''}$ 12.0, $J_{5'',6a''}$ 1.5 Hz, *H-6a”*); 3.86 (dd, 1H, $J_{1'',2''}$ 9.0, $J_{2'',3''}$ 9.5 Hz, *H-2”*); 3.70 (dd, 1H, $J_{6a'',6b''}$ 12.0, $J_{5'',6b''}$ 5.0 Hz, *H-6b”*); 3.60-3.40 (m, 3H, *H-3”*, *H-4”*, *H-5”*); 3.00 (t, 2H, $J_{3,2}$ 7.0 Hz, *H-3*); 2.59 (t, 2H, $J_{2,3}$ 7.0 Hz, *H-2*). ^{13}*C NMR* (62.5 MHz, methanol-d4) δ: 148.8 (*C-4’*); 122.6 (*C-5’*); 89.7 (*C-1”*); 81.2 (*C-5”*); 78.6 (*C-3”*); 74.2 (*C-2”*); 71.0 (*C-4”*); 62.6 (*C-6”*); 36.9 (*C-2*); 23.0 (*C-3*). *Residual copper* ~ 0.04 mol%. *MS*

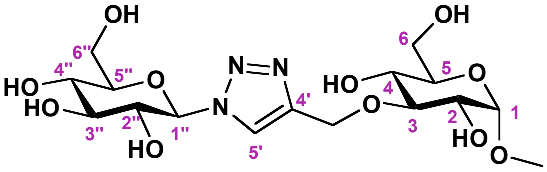
(ESI$^-$) : *m/z* 302.1 [M]$^-$. *HRMS (ESI$^-$)* : Calcd. for $C_{11}H_{16}N_3O_7Na$ 302.09937, found 302.09920.

[1'-(β-D-Glucopyranosyl)-1'H-[1',2',3']-triazol-4'-yl]-methyl 2-acetamido-2-deoxy-β-D-glucopyranoside (5) :



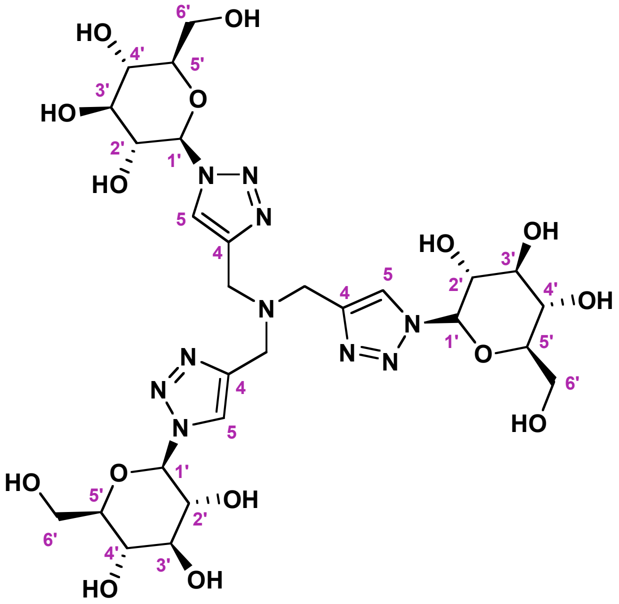
Following *Procedure A*, *[1'-(β-D-glucopyranosyl)-1'H-[1',2',3']-triazol-4'-yl]-methyl 2-acetamido-2-deoxy-β-D-glucopyranoside* (**5**) was obtained from β-D-glucopyranosyl azide (115 mg, 560 µmol, 1 eq.) in H_2O (1570 µl), propargyl 2-acetamido-2-deoxy-β-D-glucopyranoside[3] (145 mg, 560 µmol, 1 eq.), *o*-phenylenediamine (224 µl, 40.5 mg per ml of H_2O, 9.1 mg, 84.0 µmol, 15 mol%), sodium ascorbate (224 µl, 49.5 mg per ml of H_2O, 11.1 mg, 56.0 µmol, 10 mol%) and copper sulfate pentahydrate (224 µl, 31.2 mg per ml of H_2O, 7.0 mg, 28.0 µmol, 5 mol%). The reaction mixture was stirred at room temperature for 2 hours, and activated charcoal was added followed by overnight stirring under an air atmosphere. Purification by filtration and evaporation gave 247.4 mg (95%) of *[1'-(β-D-glucopyranosyl)-1'H-[1',2',3']-triazol-4'-yl]-methyl-2-acetamido-2-deoxy-β-D-glucopyranoside* (**5**) as a white solid. *^{1}H NMR* (360 MHz, methanol-d4) δ: 8.18 (s, 1H, *H-5'*); 5.61 (d, 1H, $J_{1'',2''}$ 9.0 Hz, *H-1"*); 4.91 (d, 1H, *J* 12.5 Hz, CCH_aH_bO); 4.78 (d, 1H, *J* 12.5 Hz, CCH_aH_bO); 4.57 (d, 1H, $J_{1,2}$ 8.5 Hz, *H-1*); 3.91 (dd, 1H, ^2J 12.0, ^3J 1.5 Hz, *H-6a or H-6a"*); 3.88 (dd, 1H, ^2J 12.0, ^3J 2.0 Hz, *H-6a* or *H-6a"*); 3.88 (dd, 1H, $J_{2'',1''}$ 9.0, $J_{2'',3''}$ 9.0 Hz, *H-2"*); 3.71 (dd, 1H, ^2J 12.0, ^3J 5.5 Hz, *H-6b* or *H-6b"*); 3.70 (dd, 1H, ^2J 12.0, ^3J 5.0 Hz, *H-6b* or *H-6b"*); 3.60 (dd, 1H, $J_{3,4}$ 10.0, $J_{3,2}$ 8.5 Hz, *H-3*); 3.59 (dd, 1H, $J_{2,1}$ 8.5, $J_{2,3}$ 8.5 Hz, *H-2*); 3.58 (dd, 1H, $J_{3'',2''}$ 9.0, $J_{3'',4''}$ 9.0 Hz, *H-3"*); 3.50 (dd, 1H, $J_{4'',3''}$ 9.0, $J_{4'',5''}$ 9.5 Hz, *H-4"*); 3.49 (dd, 1H, $J_{4,3}$ 10.0, $J_{4,5}$ 8.0 Hz, *H-4*); 3.42-3.26 (m, 2H, *H-5*, *H-5"*); 1.92 (s, 3H, CH_3). *^{13}C NMR* (90 MHz, methanol-d4) δ: 174.1 (*C*=O); 145.9 (*C-4'*); 124.8 (*C-5'*); 101.6 (*C-1*); 89.8 (*C-1"*); 81.3 (*C-3*); 78.5 (*C-3"*); 78.2 (*C-5*); 75.9 (*C-4*); 74.3 (*C-2"*); 72.3 (*C-5"*); 71.1 (*C-4"*); 63.0 (*C-6* or *C-6"*); 62.8 (CCH_2O); 62.5 (*C-6* or *C-6"*); 57.6 (*C-2*); 23.1 (CH_3). *Residual copper* ~ 0.31 mol%. *MS (ESI$^+$)* : *m/z* 487.0 [M+Na]$^+$. *HRMS (ESI$^+$)* : Calcd. for $C_{17}H_{28}N_4O_{11}Na$ 487.16468, found 487.16533.

Methyl 3-O-[1'-(β-D-glucopyranosyl)-1'H-[1',2',3']-triazol-4'-yl]-methyl-α-D-glucopyranoside (6):



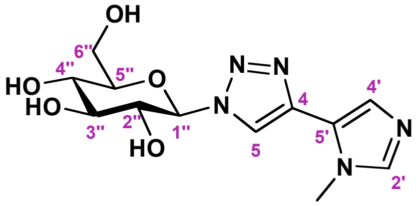
Following *Procedure A*, *methyl 3-O-[1'-(β-D-glucopyranosyl)-1'H-[1',2',3']-triazol-4'-yl]-methyl-α-D-glucopyranoside* (**6**) was obtained from β-D-glucopyranosyl azide (114 mg, 555 µmol, 1 eq.) in H_2O (1560 µl), methyl 3-*O*-propargyl-α-D-glucopyranoside (129 mg, 555 µmol, 1 eq.), *o*-phenylenediamine (220 µl, 40.5 mg per ml of H_2O, 8.9 mg, 82.5 µmol, 15 mol%), sodium ascorbate (220 µl, 49.5 mg per ml of H_2O, 10.9 mg, 55.5 µmol, 10 mol%) and copper sulfate pentahydrate (220 µl, 31.2 mg per ml of H_2O, 6.9 mg, 27.5 µmol, 5 mol%). The reaction mixture was stirred at room temperature for 45 min, and activated charcoal was added followed by overnight stirring under an air atmosphere. Purification by filtration and evaporation gave 239.1 mg (98%) of *methyl 3-O-[1'-(β-D-glucopyranosyl)-1'H-[1',2',3']-triazol-4'-yl]-methyl-α-D-glucopyranoside* (**6**) as a white solid. *^{1}H NMR* (360 MHz, methanol-d4) δ: 8.18 (s, 1H, *H-5'*); 5.60 (d, 1H, $J_{1'',2''}$ 9.0 Hz, *H-1''*); 5.00 (d, 1H, *J* 12.0 Hz, CCH_aH_bOC); 4.95 (d, 1H, *J* 12.0 Hz, CCH_aH_bOC); 4.67 (d, 1H, $J_{1,2}$ 3.5 Hz, *H-1*); 3.92-3.84 (m, 2H, *H-2''*, *H-6a''*); 3.81 (dd, 1H, $J_{6a,6b}$ 12.0, $J_{6a,5}$ 2.5 Hz, *H-6a*); 3.71 (dd, 1H, $J_{6b'',6a''}$ 11.5, $J_{6b'',5''}$ 5.5 Hz, *H-6b''*); 3.68 (dd, 1H, $J_{6b,6a}$ 12.0, $J_{6b,5}$ 5.5 Hz, *H-6b*); 3.65-3.45 (m, 5H, *H-3''*, *H-4*, *H-4''*, *H-5*, *H-5''*); 3.61 (dd, 1H, $J_{3,2}$ 9.5, $J_{3,4}$ 9.0 Hz, *H-3*); 3.51 (dd, 1H, $J_{2,3}$ 9.5, $J_{2,1}$ 3.5 Hz, *H-2*); 3.42 (s, 3H, CH_3). *^{13}C NMR* (90 MHz, methanol-d4) δ: 147.1 (*C-4'*); 124.2 (*C-5'*); 101.5 (*C-1*); 89.8 (*C-1''*); 84.3 (*C*H); 81.3 (*C*H); 78.6 (*C*H); 74.3 (*C-2'*); 73.7 (2 *C*H); 71.5 (*C*H); 71.1 (*C*H); 67.0 (CCH_2OC); 62.7, 62.6 (*C-6, C-6''*); 55.8 (CH_3). *Residual copper* ~ 0.40 mol%. *MS (ESI$^+$)* : *m/z* 460.1 $[M+Na]^+$. *HRMS (ESI$^+$)* : Calcd. for $C_{16}H_{27}N_3O_{11}Na$ 460.15378, found 460.15485.

Tris((1-(β-D-glucopyranosyl)-1H-[1,2,3]-triazol-4-yl)methyl)amine (7):



Following procedure A, *tris((1-β-D-glucopyranosyl)-1H-[1,2,3]-triazol-4-yl)methyl)amine* (**7**) was obtained from triprop-2-ynylamine (22 µl, 20.3 mg, 154.5 µmol), β-D-glucopyranosyl azide (95 mg, 463.5 µmol, 3 eq.), sodium ascorbate (185 µl, 49.5 mg per ml of H_2O, 9.2 mg, 46.4 µmol, 0.30 eq.), copper sulfate pentahydrate (185 µl, 31.2 mg per ml of H_2O, 5.8 mg, 23.2 µmol, 0.15 eq.) and *o*-phenylenediamine (370 µl, 20.3 mg per ml of H_2O, 7.5 mg, 69.5 µmol, 0.45 eq.) in H_2O (1110 µl). The reaction mixture was stirred at room temperature for 45 min, then activated charcoal was added followed by overnight stirring under an air atmosphere. Purification by filtration through an alumina plug and evaporation gave 106.2 mg (92%) of *tris((1-β-D-glucopyranosyl)-1H-[1,2,3]-triazol-4-yl)methyl)amine* as white powder. ^{1}*H NMR* (300 MHz, D_2O/methanol-d4 1:1) δ: 8.22 (s, 3H, 3 *H-5*); 5.68 (d, 3H, $J_{1',2'}$ 9.0 Hz, 3 *H-1'*); 3.97 (dd, 3H, $J_{2',1'}$ 9.0, $J_{2',3'}$ 9.0 Hz, 3 *H-2'*); 3.90 (dd, 3H, $J_{6a',6b'}$ 12.5, $J_{6a',5'}$ 2.0 Hz, 3 *H-6a'*); 3.83 (s, 6H, 3 NCH_2C); 3.76 (dd, 3H, $J_{6a',6b'}$ 12.5, $J_{5',6b'}$ 5.0 Hz, 3 *H-6b'*); 3.67 (ddd, 3H, $J_{5',4'}$ 9.5, $J_{5',6b'}$ 5.0, $J_{5',6a'}$ 2.0 Hz, 3 *H-5'*); 3.66 (dd, 3H, $J_{3',2'}$ 9.0, $J_{3',4'}$ 9.0 Hz, 3 *H-3'*); 3.58 (dd, 3H, $J_{4',3'}$ 9.0, $J_{4',5'}$ 9.5 Hz, 3 *H-4'*);. ^{13}*C NMR* (75 MHz, D_2O/ methanol-d4 1:1) δ: 145.1 (3 *C-4*); 125.3 (3 *C-5*); 89.1 (3 *C-1'*); 80.5 (3 *C-5'*); 77.8 (3 *C-3'*); 73.8 (3 *C-2'*); 70.5 (3 *C-4'*); 62.0 (3 *C-6'*); 48.4 (3 NCH_2C). *Residual copper below detection limit. MS (ESI$^+$)* : *m/z* 769.3 $[M+Na]^+$. *HRMS (ESI$^+$)* : Calcd. for $C_{27}H_{42}N_{10}O_{15}Na$ 1273.39911, found 1273.40023.

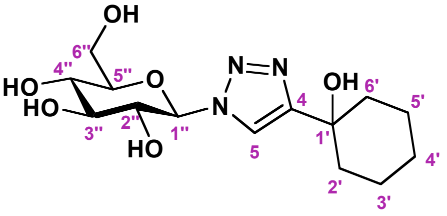
4-(1’-Methyl-1H-imidazol-5’-yl)-1-(β-D-glucopyranosyl)-1H-[1,2,3]-triazole (8) :



Procedure B :

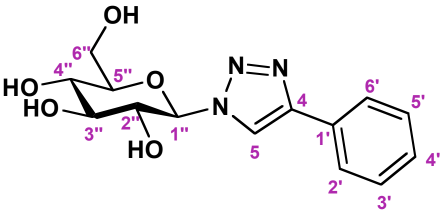
To a solution of β-D-glucopyranosyl azide (64.5 mg, 314 μmol, 1 eq.) in H_2O (253 μl) and tBuOH (628 μl), were added 5-ethynyl-1-methyl-1H-imidazole (32.9 μl, 33.4 mg, 314 μmol, 1 eq.), *o*-phenylenediamine (125 μl, 40.5 mg per ml of H_2O, 5.1 mg, 47.1 μmol, 15 mol%), sodium ascorbate (125 μl, 49.5 mg per ml of H_2O, 6.2 mg, 31.4 μmol, 10 mol%) and copper sulfate pentahydrate (125 μl, 31.2 mg per ml of H_2O, 3.9 mg, 15.7 μmol, 5 mol%). The reaction mixture was stirred at room temperature under an argon atmosphere for one hour. After this time, TLC showed complete conversion. The solvents were evaporated and the residue was dissolved in MeOH/H_2O, (1/1), (5 ml), activated charcoal (~150 mg) was added and the suspension was stirred under an air atmosphere overnight. The reaction mixture was then filtered through a celite plug and eluted with MeOH/H_2O (1/1). The solvent were evaporated to dryness to give 86.6 mg (89%) of *4-(1’-methyl-1H-imidazol-5’-yl)-1-(β-D-glucopyranosyl)-1H-[1,2,3]-triazole* (**8**) as a white solid. *^{1}H NMR* (360 MHz, methanol-d4) δ: 8.48 (s, 1H, *H-5*); 7.75 (s, 1H, *H-2’*); 7.31 (s, 1H, *H-4’*); 5.73 (d, 1H, $J_{1'',2''}$ 9.0 Hz, *H-1”*); 4.00 (dd, 1H, $J_{2'',1''}$ 9.0, $J_{2'',3''}$ 9.0 Hz, *H-2”*); 3.91 (dd, 1H, $J_{6a'',6b''}$ 12.0, $J_{6a'',5''}$ 2.0 Hz, *H-6a”*); 3.84 (s, 3H, NCH_3); 3.7 (dd, 1H, $J_{6a'',6b''}$ 12.0, $J_{6b'',5''}$ 5.0 Hz, *H-6b”*); 3.68 (ddd, 1H, $J_{5'',4''}$ 9.5, $J_{5'',6b''}$ 5.0, $J_{5'',6a''}$ 2.0 Hz, *H-5”*); 3.67 (dd, 1H, $J_{3'',4''}$ 9.0, $J_{3'',2''}$ 9.0 Hz, *H-3”*); 3.59 (dd, 1H, $J_{4'',3''}$ 9.0, $J_{4'',5''}$ 9.5 Hz, *H-4”*). *^{13}C NMR* (75 MHz, methanol-d4) δ: 141.3 (*C-2’*); 138.6 (*C-4*); 129.0 (*C-4’*); 124.3 (*C-5’*); 123.3 (*C-5*); 89.0 (*C-1”*); 80.4 (*C-5*”); 77.5 (*C-3”*); 73.6 (*C-2”*); 70.3 (*C-4”*); 61.7 (*C-6”*); 33.7 (CH_3). *Residual copper* ~ 0.05 mol%. *MS (ESI$^+$)* : *m/z* 334.1 $[M+Na]^+$. *HRMS (ESI$^+$)* : Calcd. for $C_{12}H_{17}N_5O_5Na$ 334.11219, found 334.11288.

4-(1’-Hydroxycyclohexyl)-1-(β-D-glucopyranosyl)-1H-[1,2,3]-triazole (9) :



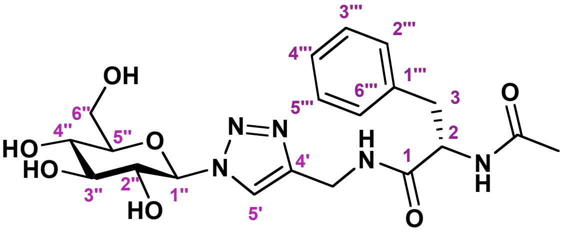
Following *Procedure B*, *4-(1'-hydroxycyclohexyl)-1-(β-D-glucopyranosyl)-1H-[1,2,3]-triazole* (**9**) was obtained from β-D-glucopyranosyl azide (55.3 mg, 270 µmol, 1 eq.) in H_2O (107 µl) and tBuOH (539 µl), 1-ethynylcyclohexanol (34.6 µl, 33.5 mg, 270 µmol, 1 eq.), *o*-phenylenediamine (216 µl, 20.3 mg per ml of H_2O, 4.4 mg, 40.5 µmol, 15 mol%), sodium ascorbate (108 µl, 49.5 mg per ml of H_2O, 5.3 mg, 27.0 µmol, 10 mol%) and copper sulfate pentahydrate (108 µl, 31.2 mg per ml of H_2O, 3.4 mg, 13.5 µmol, 5 mol%). The reaction mixture was stirred at room temperature for 45 min, and solvents were evaporated. The residue was dissolved in MeOH/H_2O (1/1), and activated charcoal was added followed by overnight stirring under an air atmosphere. Purification by filtration and evaporation gave 87.4 mg (98%) of *4-(1'-hydroxycyclohexyl)-1-(β-D-glucopyranosyl)-1H-[1,2,3]-triazole* (**9**) as a white solid. *^1H NMR* (300 MHz, methanol-d4) δ: 8.04 (s, 1H, *H-5*); 5.58 (d, 1H, $J_{1'',2''}$ 9.0 Hz, *H-1''*); 3.91 (dd, 1H, $J_{2'',1''}$ 9.0, $J_{2'',3''}$ 9.0 Hz, *H-2''*); 3.88 (dd, 1H, $J_{6a'',6b''}$ 12.0, $J_{6a',5'}$ 1.5 Hz, *H-6a''*); 3.71 (dd, 1H, $J_{6b'',6a''}$ 12.0, $J_{6b'',5''}$ 5.5 Hz, *H-6b''*); 3.61-3.50 (m, 1H, *H-5''*); 3.56 (dd, 1H, $J_{3'',4''}$ 9.0, $J_{3'',2''}$ 9.0 Hz, *H-3''*); 3.49 (dd, 1H, $J_{4'',3''}$ 9.0, $J_{4'',5''}$ 8.5 Hz, *H-4''*); 2.10-1.20 (m, 10H, *H-2',3',4',5',6'*). *^{13}C NMR* (75 MHz, methanol-d4) δ: 157.1 (*C-4*); 121.8 (*C-5*); 89.7 (*C-1''*); 81.2 (*C-5*''); 78.7 (*C-3''*); 74.1 (*C-2''*); 71.0 (*C-4''*); 70.4 (*C-1'*); 62.5 (*C-6''*); 70.4 (2 CH_2); 26.7 (*C-4'*); 23.2 (2 CH_2). *Residual copper* ~ 0.07 mol%. *MS (ESI^+)* : *m/z* 352.2 $[M+Na]^+$. *HRMS (ESI^+)* : Calcd. for $C_{14}H_{23}N_3O_6Na$ 352.14791, found 352.14832.

4-Phenyl-1-(β-D-glucopyranosyl)-1H-[1,2,3]-triazole (10) :



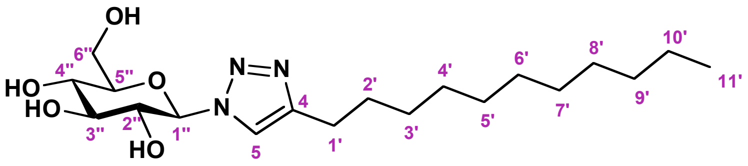
Following *Procedure B*, *4-phenyl-1-(β-D-glucopyranosyl)-1H-[1,2,3]-triazole* (**10**) was obtained from β-D-glucopyranosyl azide (64.1 mg, 312 µmol, 1 eq.) in H_2O (125 µl) and tBuOH (625 µl), ethynylbenzene (35.0 µl, 31.9 mg, 312 µmol, 1 eq.), *o*-phenylenediamine (250 µl, 20.3 mg per ml of H_2O, 5.1 mg, 46.8 µmol, 15 mol%), sodium ascorbate (125 µl, 49.5 mg per ml of H_2O, 6.2 mg, 31.2 µmol, 10 mol%) and copper sulfate pentahydrate (125 µl, 31.2 mg per ml of H_2O, 3.9 mg, 15.6 µmol, 5 mol%). The reaction mixture was stirred at room temperature for 45 min, and solvents were evaporated. The residue was dissolved in MeOH/H_2O (1/1), and activated charcoal was added followed by overnight stirring under an air atmosphere. Purification by filtration and evaporation gave 93.0 mg (97%) of *4-phenyl-1-(β-*D*-glucopyranosyl)-1H-[1,2,3]-triazole*[4] (**10**) as a white solid. *^{1}H NMR* (250 MHz, methanol-d4*)* δ: 8.57 (s, 1H, *H-5*); 7.84 (dd, 2H, ^3J 7.0, ^4J 1.5 Hz, *H-2', H-6'*); 7.44 (tt, 2H, ^3J 7.0, ^4J 1.5 Hz, *H-3', H-5'*); 7.35 (tt, 1H, ^3J 7.0, ^4J 1.5 Hz, *H-4'*); 5.66 (d, 1H, $J_{1'',2''}$ 9.0 Hz, *H-1''*); 3.96 (dd, 1H, $J_{2'',1''}$ 9.0, $J_{2'',3''}$ 9.0 Hz, *H-2''*); 3.91 (dd, 1H, $J_{6a'',6b''}$ 12.0, $J_{6a',5'}$ 1.5 Hz, *H-6a''*); 3.74 (dd, 1H, $J_{6b'',6a''}$ 12.0, $J_{6b'',5''}$ 5.0 Hz, *H-6b''*); 3.61 (ddd, 1H, $J_{5'',4''}$ 9.0, $J_{5'',6b''}$ 5.0, $J_{5'',6a''}$ 1.5 Hz, *H-5''*); 3.61 (dd, 1H, $J_{3'',4''}$ 8.5, $J_{3'',2''}$ 9.0 Hz, *H-3''*); 3.53 (dd, 1H, $J_{4'',3''}$ 8.5, $J_{4'',5''}$ 9.0 Hz, *H-4''*). *^{13}C NMR* (62.5 MHz, methanol-d4) δ: 149.0 (*C-4*); 131.7 (*C-1'*); 130.1 (*C-3',5'*); 129.6 (*C-4'*); 126.9 (*C-2',6'*); 121.5 (*C-5*); 89.9 (*C-1''*); 81.3 (*C-5*''); 78.6 (*C-3''*); 74.2 (*C-2''*); 71.0 (*C-4''*); 62.5 (*C-6''*). *Residual copper* ~ 0.07 mol%. *MS (ESI$^+$)* : *m/z* 330.0 [M+Na]$^+$. *HRMS (ESI$^+$)* : Calcd. for $C_{14}H_{17}N_3O_5Na$ 330.10604, found 330.10775.

N-acetyl-L-phenylalanine (1'-(β-D-glucopyranosyl)-1'H-[1',2',3']-triazol-4-yl)methylamide (11) :



Following *Procedure B*, *N-acetyl-*L*-phenylalanine (1'-(β-*D*-glucopyranosyl)-1'H-[1',2',3']-triazol-4-yl)methylamide* was obtained from β-D-glucopyranosyl azide (53.2 mg, 259 µmol, 1 eq.) in H_2O (103 µl) and tBuOH (518 µl), *N*-acetyl-L-phenylalanine propargylamide (63.6 mg, 259 µmol, 1 eq.), *o*-phenylenediamine (207 µl, 20.3 mg per ml of H_2O, 4.2 mg, 38.9 µmol, 15 mol%), sodium ascorbate (104 µl, 49.5 mg per ml of H_2O, 5.1 mg, 26.0 µmol, 10 mol%) and copper sulfate pentahydrate (104 µl, 31.2 mg per ml of H_2O, 3.2 mg, 13.0 µmol, 5 mol%). The reaction mixture was stirred at room temperature for 45 min, and solvents were evaporated. The residue was dissolved in MeOH/H_2O, and activated charcoal was added followed by overnight stirring under an air atmosphere. Purification by filtration and evaporation gave 98.2 mg (84%) of *N-acetyl-*L*-phenylalanine (1'-(β-*D*-glucopyranosyl)-1'H-[1',2',3']-triazol-4-yl)methylamide* (**11**) as a slightly beige solid. *^{1}H NMR* (360 MHz, dimethylsulfoxide-d6*)* δ: 7.85 (s, 1H, *H-5'*); 7.30-7.15 (m, 5H, *H-Ar*); 5.48 (d, 1H, $J_{1'',2''}$ 9.5 Hz, *H-1''*); 4.48 (dd, 1H, $J_{2,3b}$ 9.5, $J_{2,3a}$ 5.0 Hz, *H-2*); 4.31 (s, 2H, C*H$_2$*NH); 3.73-3.63 (m, 1H, *H-6a’’);* 3.70 (dd, 1H, $J_{2'',1''}$ 9.5, $J_{2'',3''}$ 9.0 Hz, *H-2’’*); 3.50-3.40 (m, 2H, *H-6b’’*, *H-5’’*); 3.38 (dd, 1H, $J_{3'',2''}$ 9.0, $J_{3'',4''}$ 9.0 Hz, *H-3’’*); 3.23 (dd, 1H, $J_{4'',3''}$ 9.0, $J_{4'',5''}$ 9.0 Hz, *H-4’’*); 2.99 (dd, 1H, $^2J_{3a,3b}$ 13.5, $J_{3a,2}$ 5.0 Hz, *H-3a*); 2.75 (dd, 1H, $^2J_{3a,3b}$ 13.5, $J_{3b,2}$ 9.5 Hz, *H-3b*); 1.76 (s, 3H, CH_3). ^{13}*C NMR* (75 MHz, methanol-d4) δ: 173.9 (*C-1*); 173.4 (CH_3C=O); 146.4 (*C-4’*); 138.5 (*C-1’’’*); 130.4 (*C-2’’’*, *C-6’’’*); 129.6 (*C-3’’’*, *C-5’’’*); 128.0 (*C-4’’’*); 123.5 (*C-5’*); 89.7 (*C-1’’*); 81.3 (*C-5’’*); 78.6 (*C-3’’*); 74.2 (*C-2’’*); 71.1 (*C-4’’*); 62.6 (*C-6’’*); 56.6 (*C-2*); 39.0 (*C-3*); 35.9 (CH_2NH); 22.6 (CH_3). *Residual copper* ~ 0.08 mol%. *HRMS (FAB$^+$)* : Calcd. for $C_{20}H_{27}N_5O_7Na$ 472.1803, found 472.1816.

4-Undecyl-1-(β-D-glucopyranosyl)-1H-[1,2,3]-triazole (12) **:**



Procedure C :

To a solution of β-D-glucopyranosyl azide (140.3 mg, 684 µmol, 1 eq.) in H_2O (546 µl) and tBuOH (1370 µl), were added tridec-1-yne (163 µl, 123.3 mg, 684 µmol, 1 eq.), *o*-phenylenediamine (274 µl, 40.5 mg per ml of H_2O, 11.1 mg, 102.6 µmol, 15 mol%), sodium ascorbate (274 µl, 49.5 mg per ml of H_2O, 13.6 mg, 68.4 µmol, 10 mol%) and copper sulfate pentahydrate (274 µl, 31.2 mg per ml of H_2O, 8.5 mg, 34.2 µmol, 5 mol%). The reaction mixture was stirred at room temperature under an argon atmosphere for 2 hours. After this time, TLC showed complete conversion. The reaction mixture was stirred one hour under an air atmosphere, and activated charcoal (~150 mg) was added and the suspension was stirred under an air atmosphere overnight. The reaction mixture was then filtered through a celite plug and washed with H_2O/tBuOH (1/1). Elution with ACN/H_2O gave after concentration to dryness, 224.1 mg (85%) of *4-undecyl-1-(β-D-glucopyranosyl)-1H-[1,2,3]-triazole* (**12**) as a white solid. ^{1}*H NMR* (250 MHz, methanol-d4) δ: 7.94 (s, 1H, *H-5*); 5.56 (d, 1H, $J_{1'',2''}$ 9.0 Hz, *H-1”*); 3.88 (dd, 1H, $J_{2'',1''}$ 9.0, $J_{2'',3''}$ 8.5 Hz, *H-2”*); 3.88 (dd, 1H, $J_{6a'',6b''}$ 12.0, $J_{6a',5'}$ 1.5 Hz, *H-6a”*); 3.71 (dd, 1H, $J_{6b'',6a''}$ 12.0, $J_{6b'',5''}$ 5.0 Hz, *H-6b”*); 3.56 (ddd, 1H, $J_{5'',4''}$ 9.0, $J_{5'',6b''}$ 5.0, $J_{5'',6a''}$ 1.5 Hz, *H-5”*); 3.56 (dd, 1H, $J_{3'',4''}$ 9.0, $J_{3'',2''}$ 8.5 Hz, *H-3”*); 3.48 (dd, 1H, $J_{4'',3''}$ 9.0, $J_{4'',5''}$ 9.0 Hz, *H-4”*); 2.71 (t, 2H, $J_{1',2'}$ 7.5 Hz, *H-1’*); 1.67 (tt, 2H, $J_{2',1'} = J_{2',3'}$ 7.2 Hz, *H-2’*); 1.37-1.25 (m, 16H, *H-3’,4’,5’,6’,7’,8’,9’,10’*); 0.90 (t, 3H, $J_{11',10'}$ 6.7 Hz, *H-11’*). ^{13}*C NMR* (62.5 MHz, methanol-d4) δ: 149.4 (*C-4*); 122.5 (*C-5*); 89.7 (*C-1”*); 81.3 (*C-5”*); 78.7 (*C-3”*); 74.1

(*C-2”*); 71.0 (*C-4”*); 62.5 (*C-6”*); 33.2 (*C*H$_2$); 30.9 (2 *C*H$_2$); 30.8 (*C*H$_2$); 30.7 (*C*H$_2$); 30.6 (2 *C*H$_2$); 30.4 (*C*H$_2$); 26.4 (*C*H$_2$); 23.9 (*C*H$_2$); 14.6 (*C-11’*). *Residual copper* ~ 0.06 mol%. *MS (ESI$^+$)* : *m/z* 408.2 [M+Na]$^+$. *HRMS (ESI$^+$)* : Calcd. for $C_{19}H_{35}N_3O_5Na$ 408.24689, found 408.24681.

Kinetic effect of added *o*-phenylenediamine

Reaction of β-glucosyl azide (0.25 M) with propargyl alcohol (0.25 M) in the presence of copper sulfate (5.0 mol%, 12.5 mM) and sodium ascorbate (10.0 mol%, 25.0 mM) was performed with or without added *o*-phenylemenediamine (15.0 mol%, 37.5 mM). The conversion was followed by ^{1}H-NMR spectroscopy (400 MHz) in D_2O under Ar, and estimated by integration of the H-2 signal of the starting material (δ 3.25 ppm) and anomeric signal of the product (δ 5.75 ppm). The reactions were initiated by copper sulfate addition.

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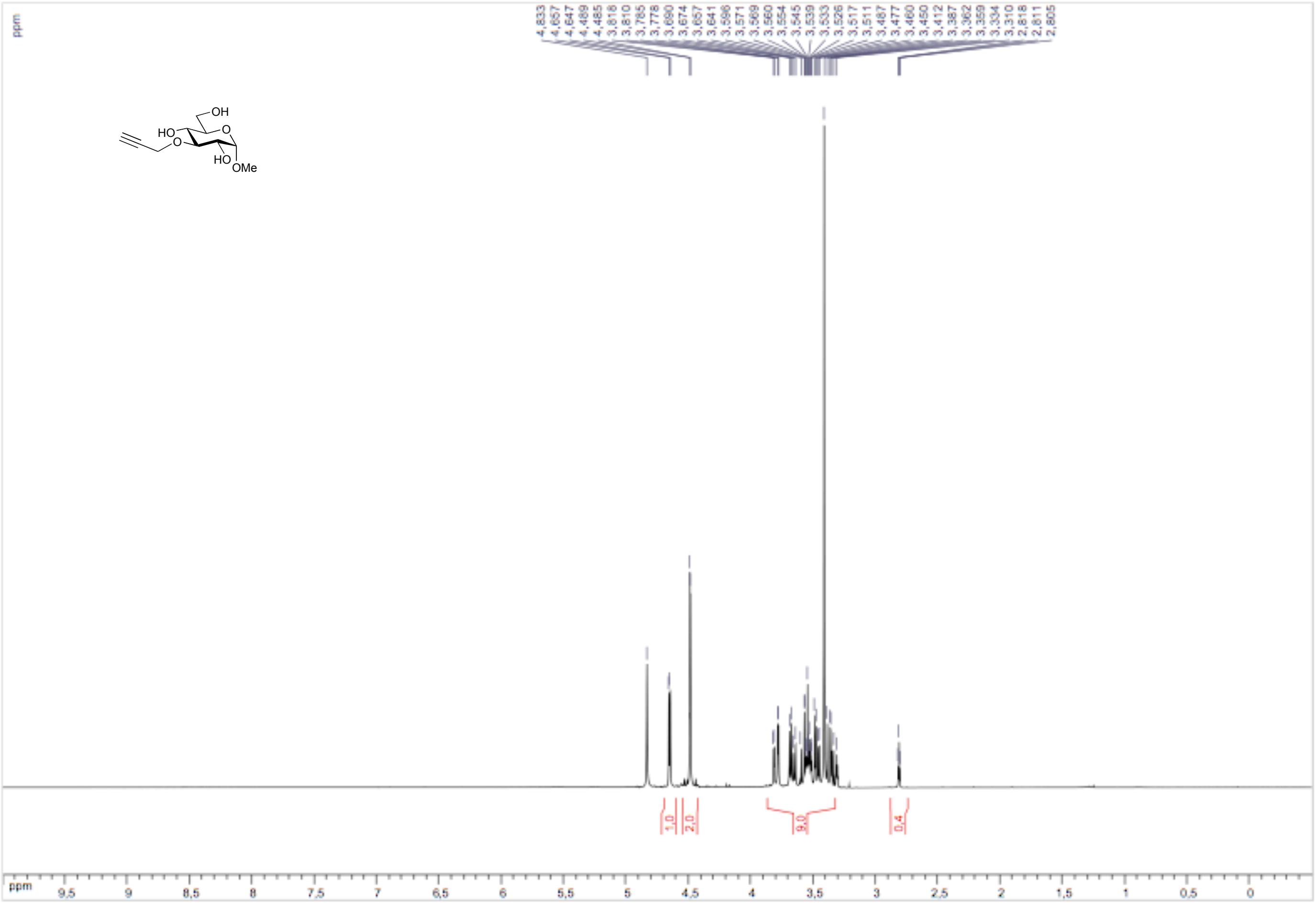
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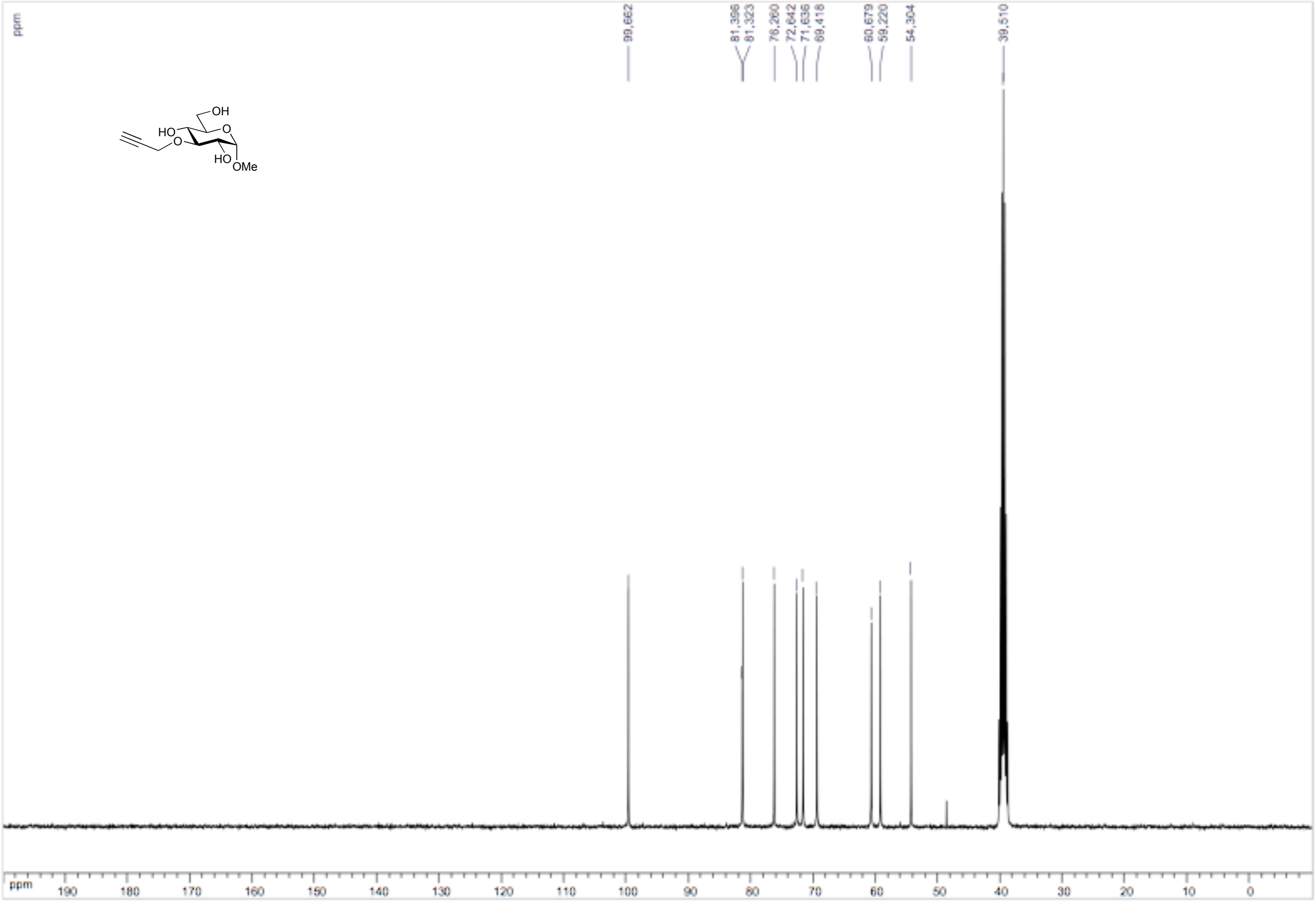
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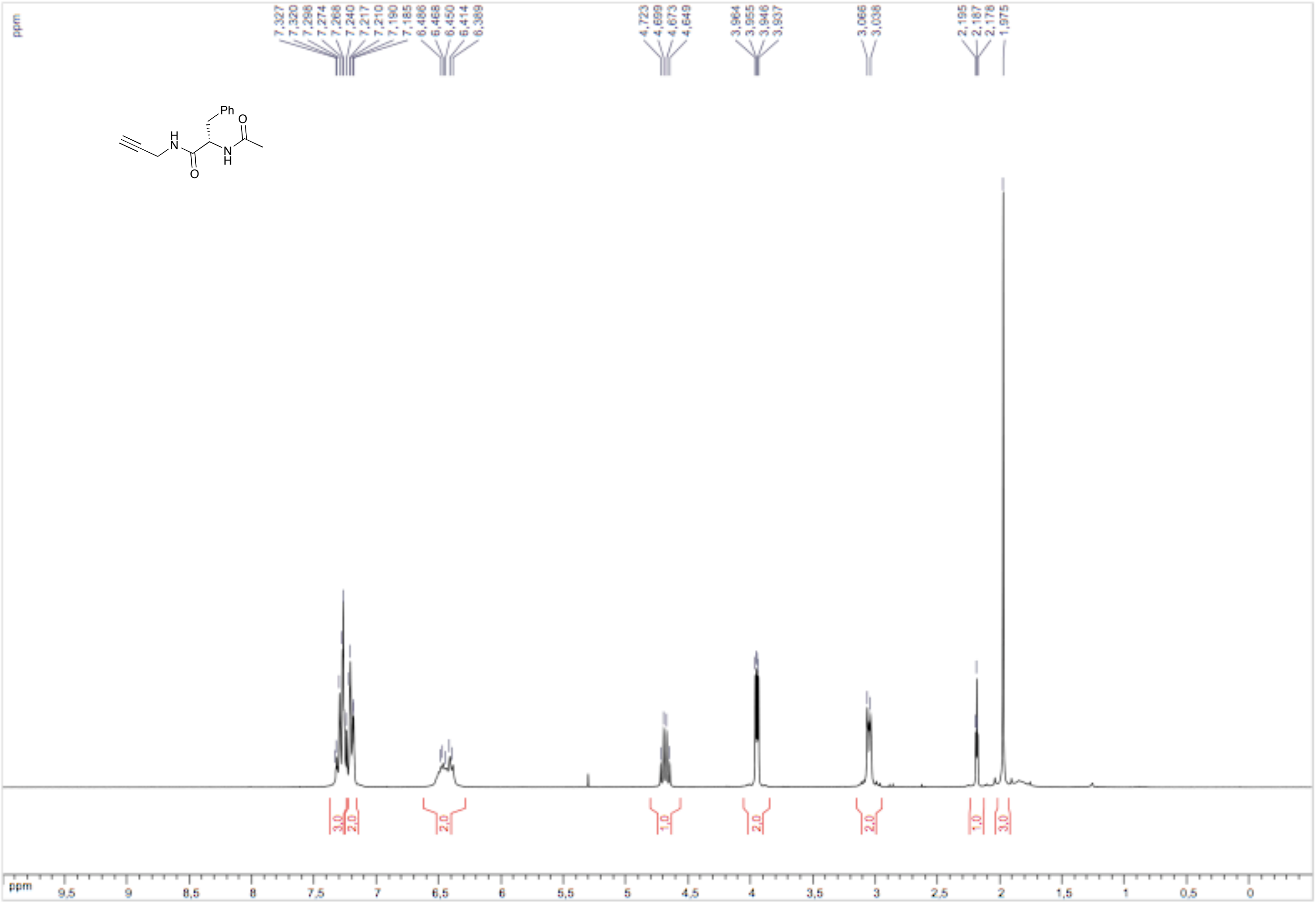
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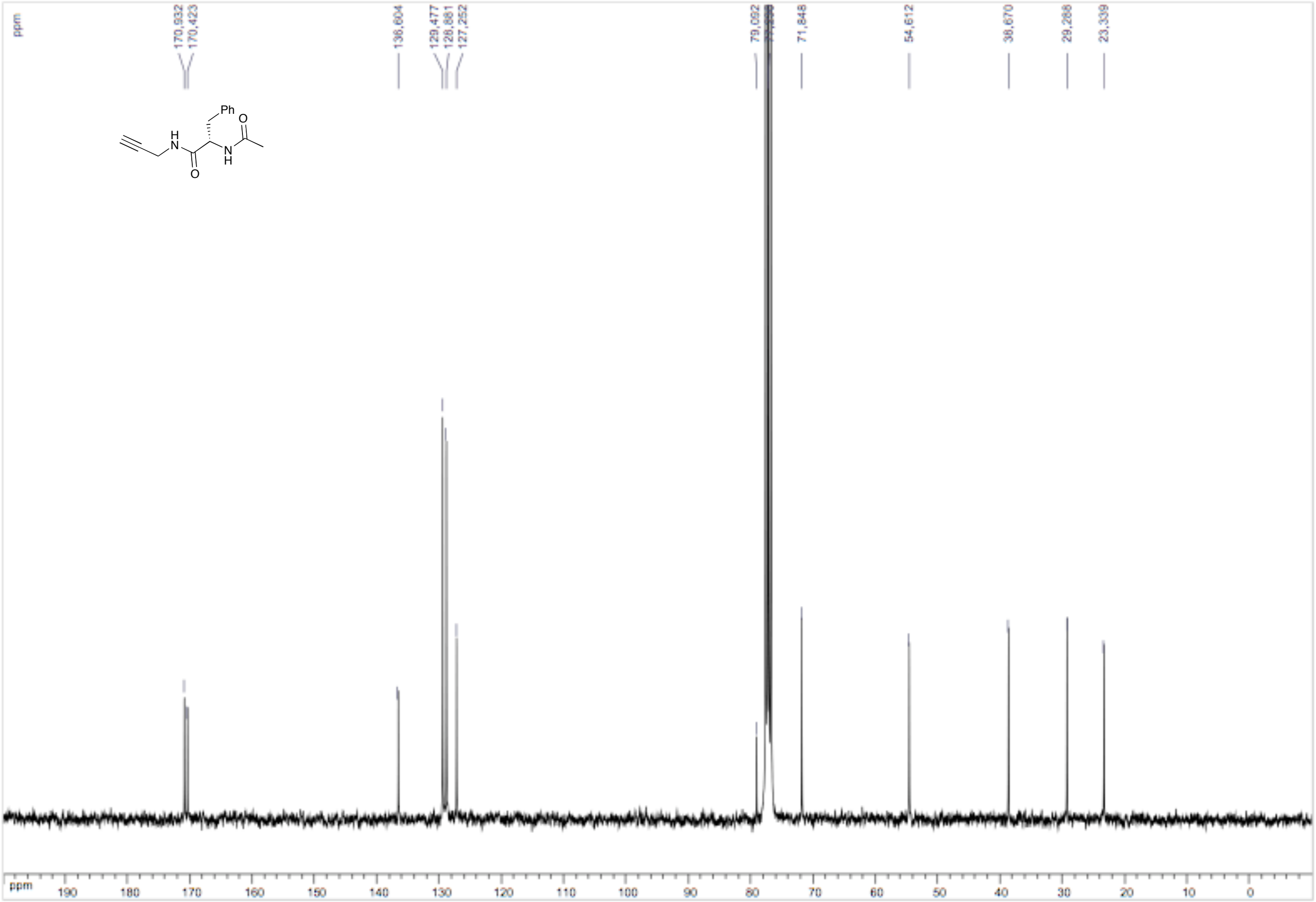
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170,423
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129,477
128,881
127,252
79,092
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54,612
38,670
29,288
23,339
Ph
O
H
N
N
H
O
ppm
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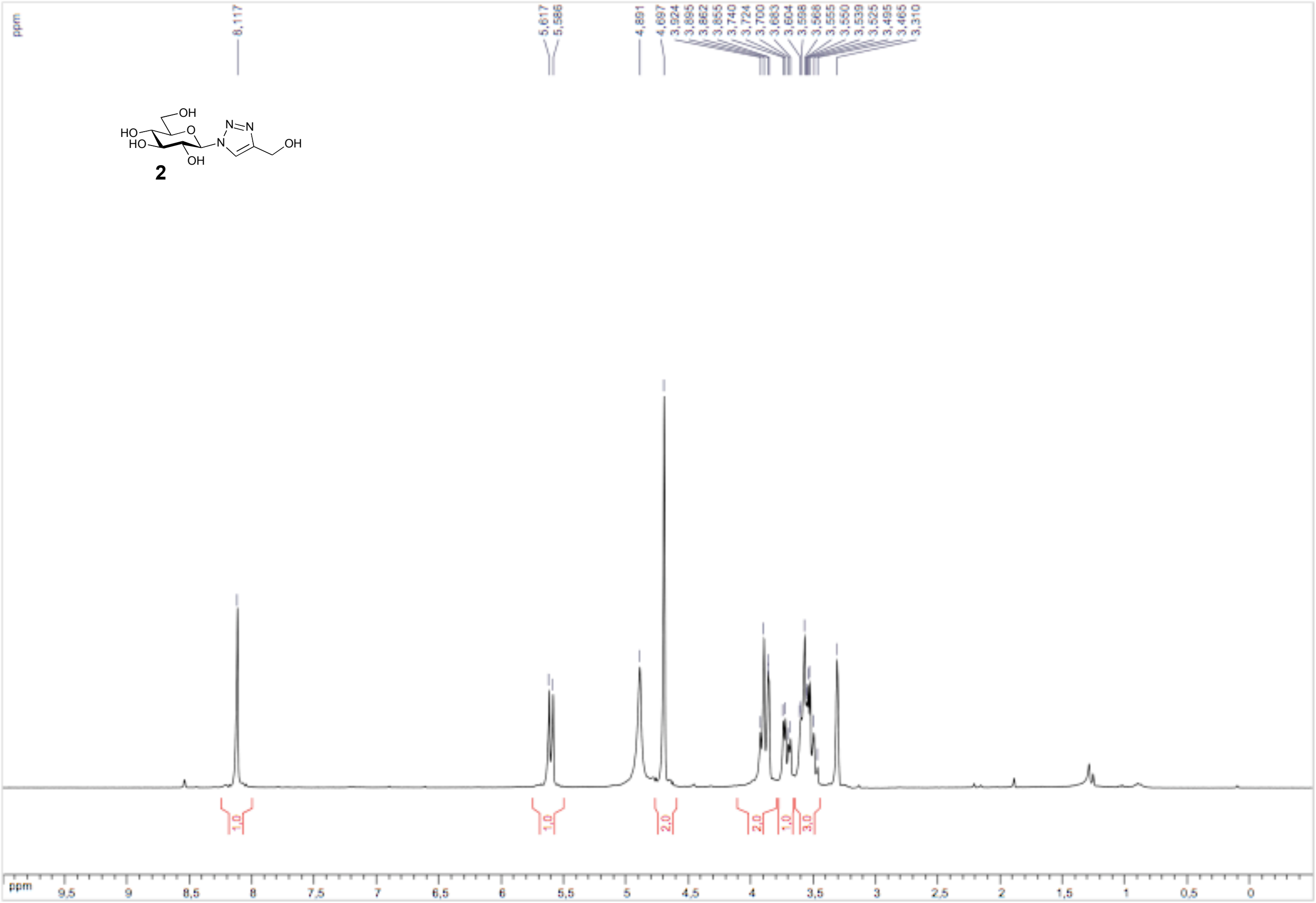
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5,586
4,891
4,697
3,924
3,895
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3,855
3,740
3,724
3,700
3,683
3,604
3,598
3,568
3,555
3,550
3,539
3,525
3,495
3,465
3,310
HO
HO
OH
OH
OH
O
N
N
N
OH
2
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1,0
2,0
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1,0
3,0
ppm
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8,5
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7,5
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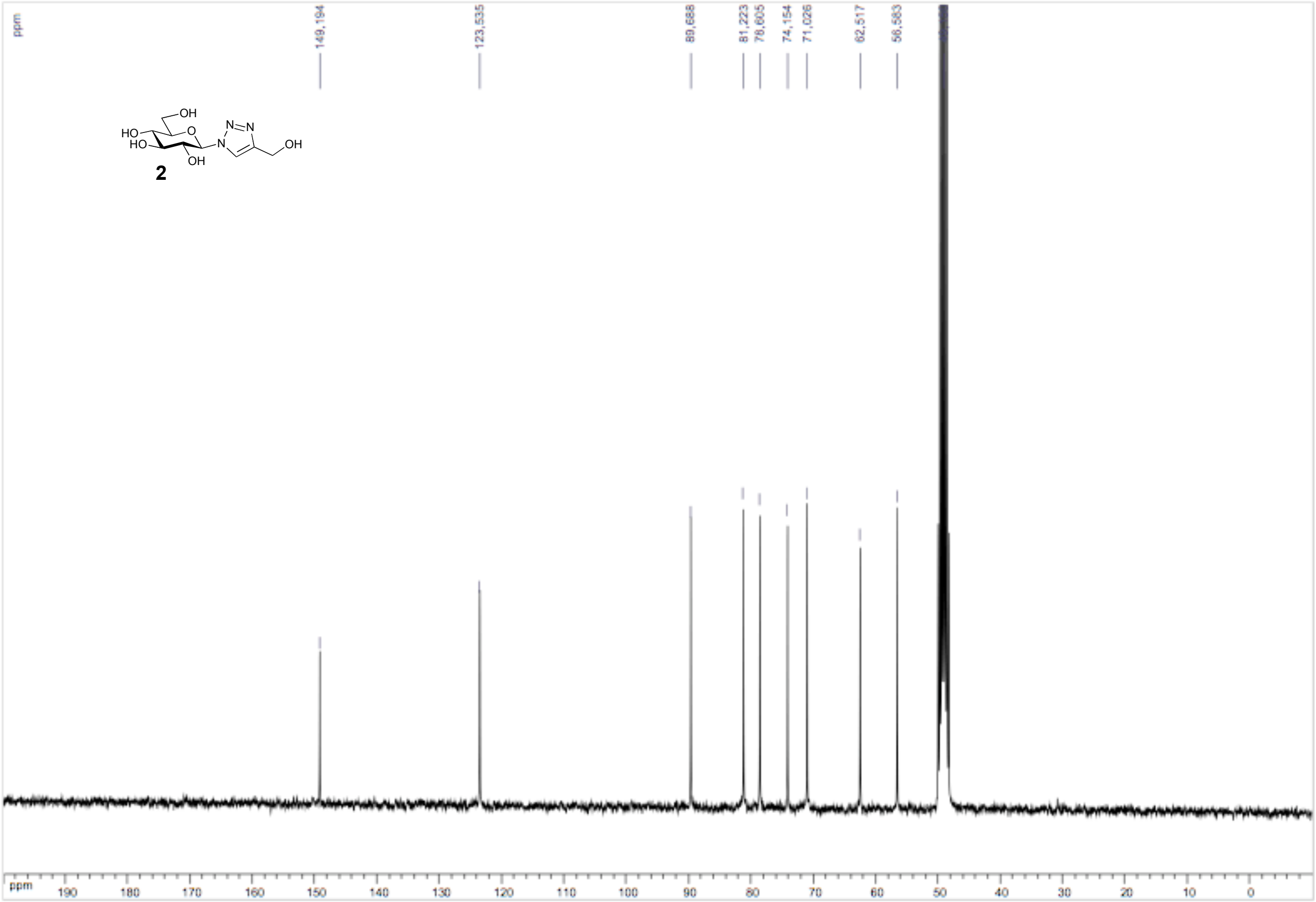
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74,154
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62,517
56,583
HO
HO
OH
OH
OH
O
N
N
N
OH
2
ppm
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150
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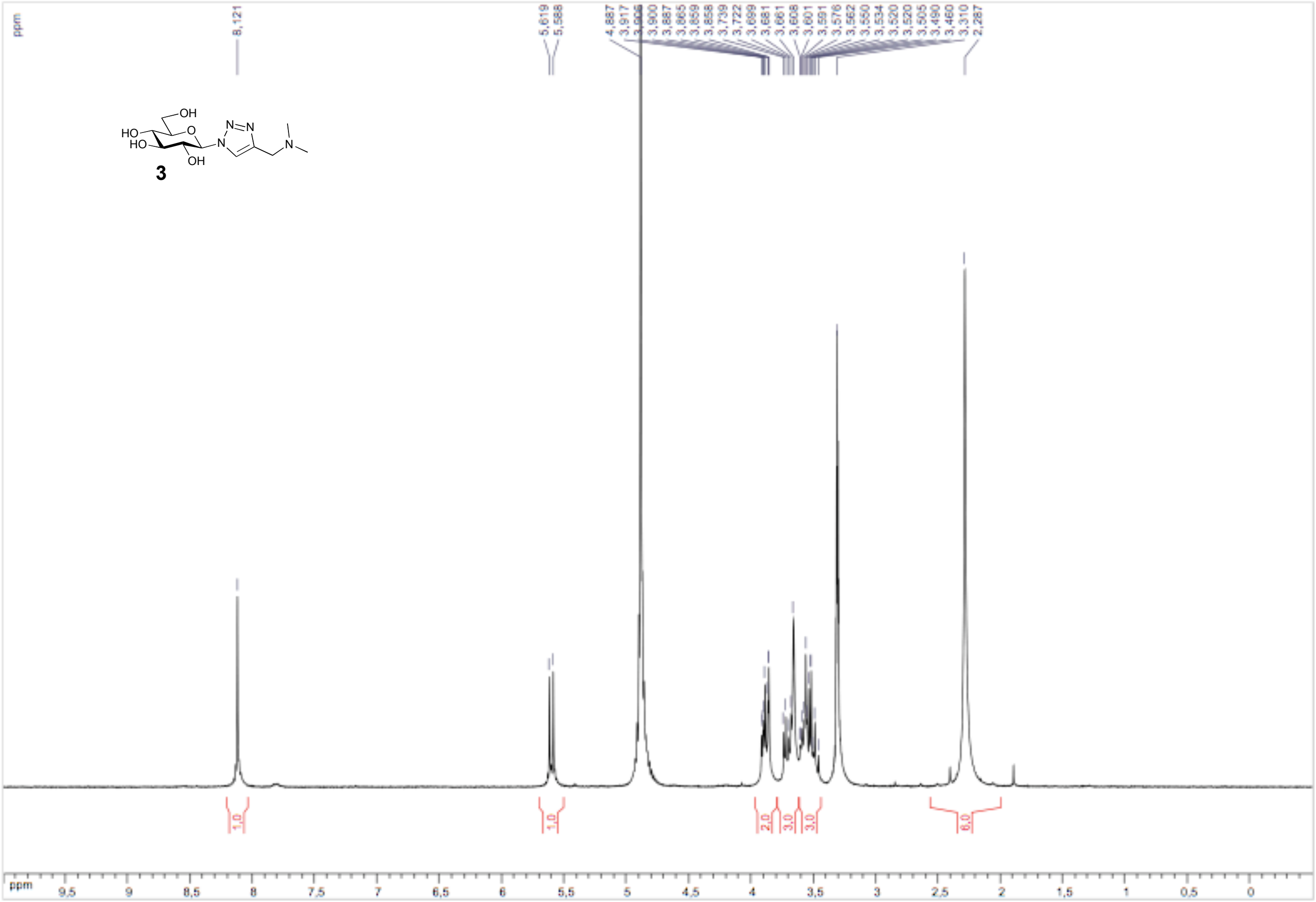
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3,550
3,534
3,520
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3,505
3,490
3,460
3,310
2,287
HO
HO
OH
O
OH
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N
N
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ppm
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7,5
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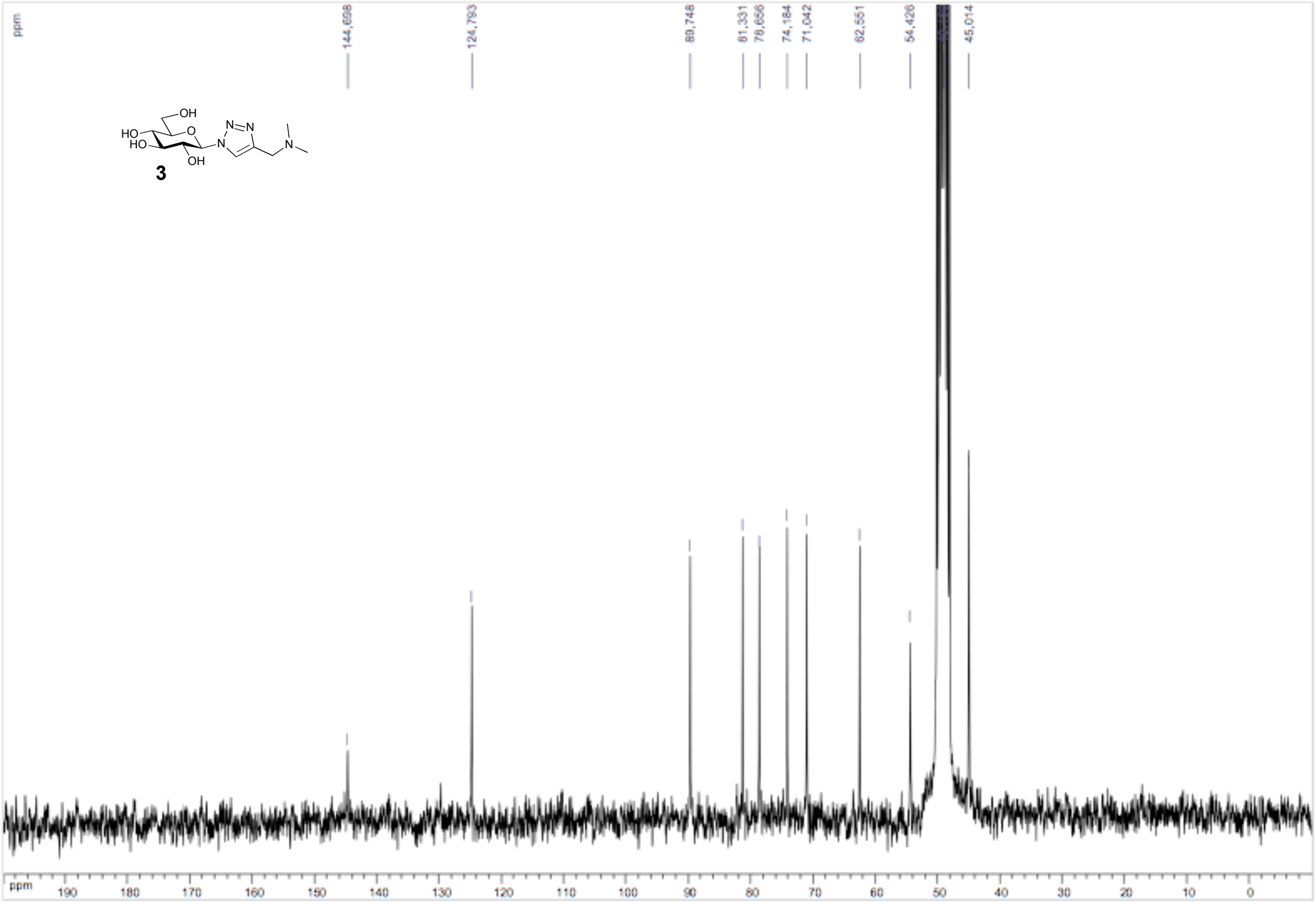
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O
OH
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N
N
N
3
ppm
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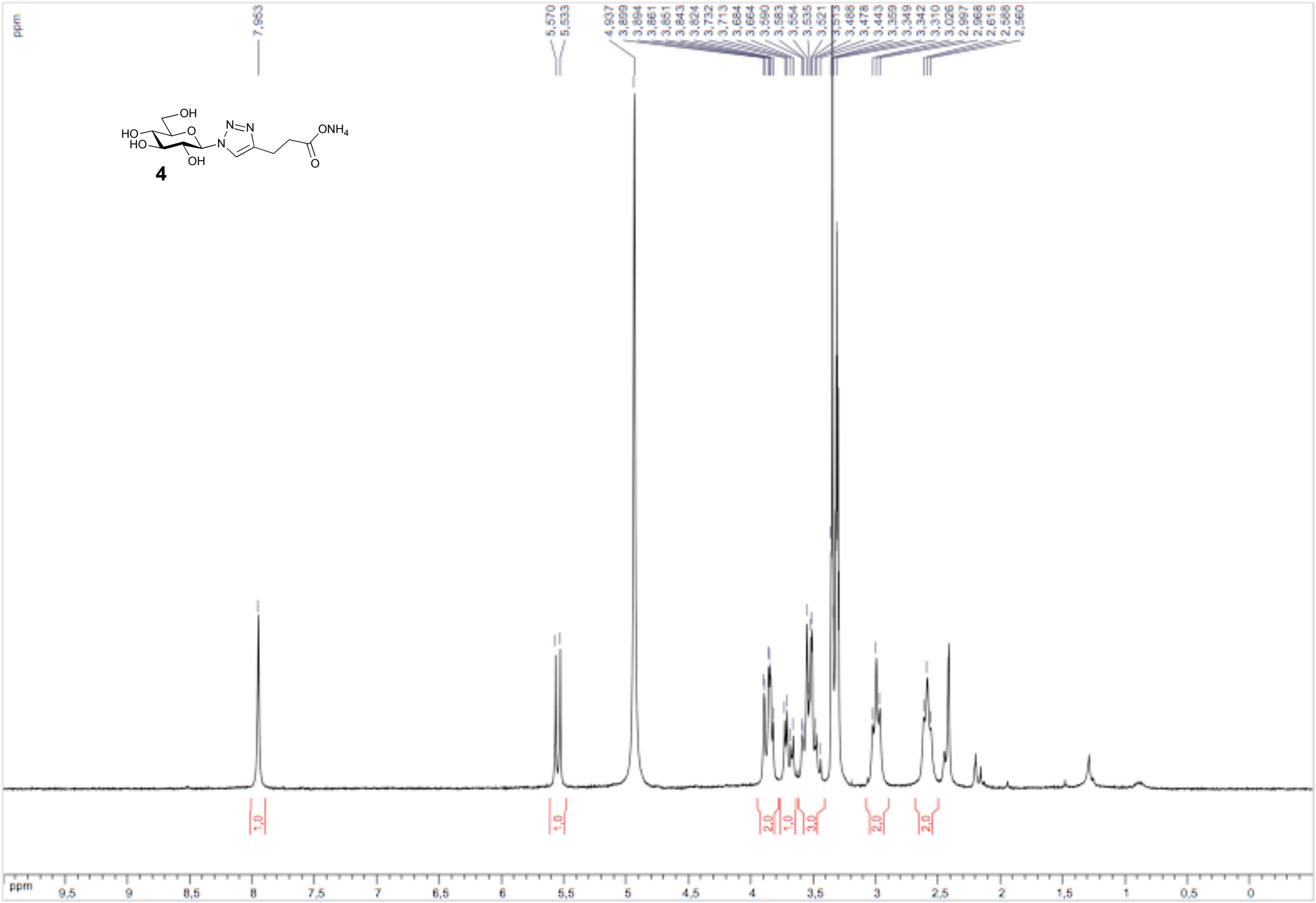
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3,894
3,861
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3,843
3,824
3,732
3,713
3,684
3,664
3,590
3,583
3,554
3,535
3,521
3,513
3,488
3,478
3,443
3,359
3,349
3,342
3,310
3,026
2,997
2,968
2,615
2,588
2,560
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HO
OH
OH
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O
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3,0
2,0
2,0
ppm
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7,5
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5,5
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2,5
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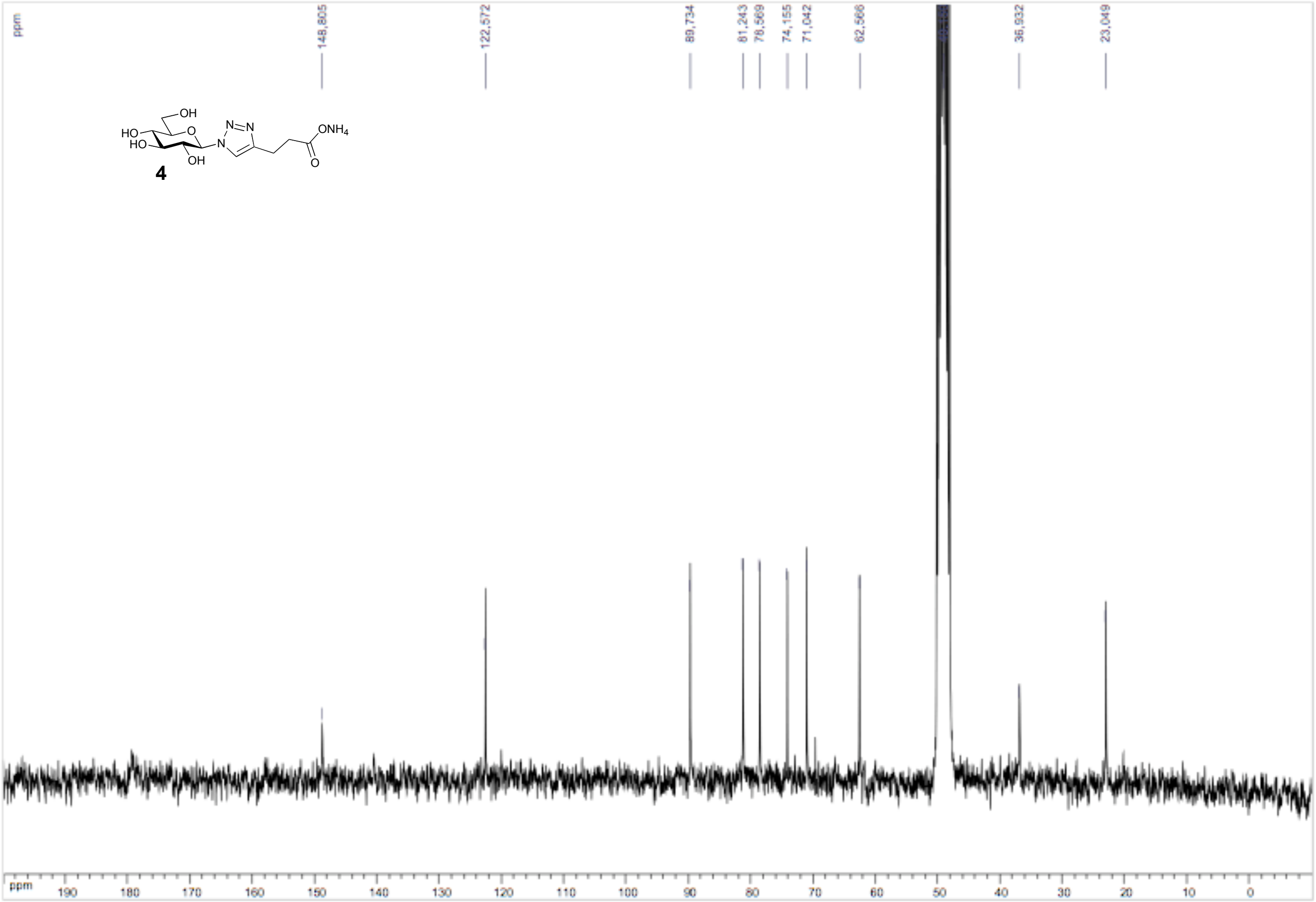
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78,569
74,155
71,042
62,566
36,932
23,049
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HO
HO
OH
OH
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N=N
ONH4
O
4
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150
140
130
120
110
100
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30
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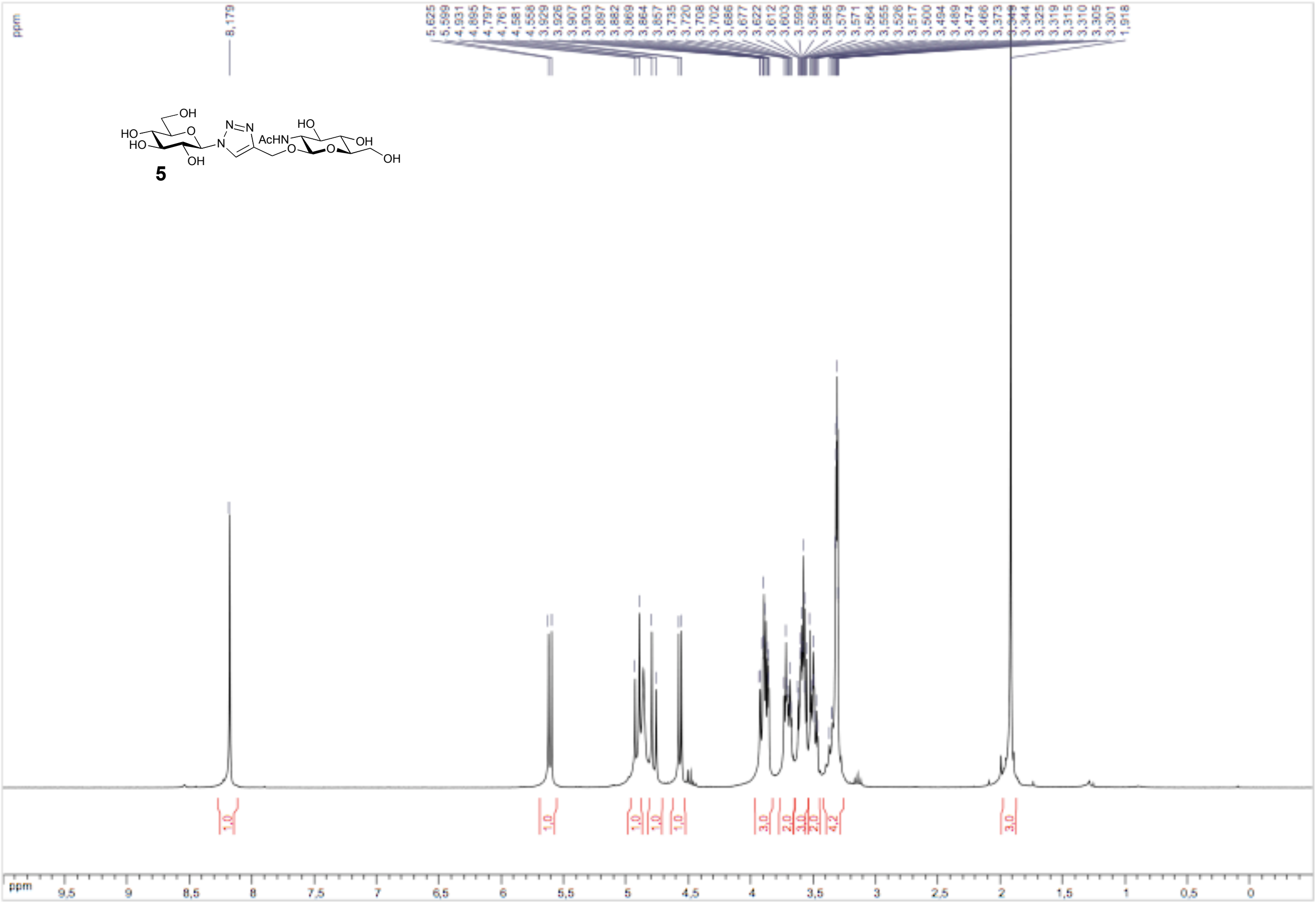
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5,599
4,931
4,895
4,797
4,761
4,581
4,558
3,929
3,926
3,907
3,903
3,897
3,882
3,869
3,864
3,857
3,735
3,720
3,708
3,702
3,686
3,677
3,622
3,612
3,603
3,599
3,594
3,585
3,579
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3,517
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3,466
3,373
3,349
3,344
3,325
3,319
3,315
3,310
3,305
3,301
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7,5
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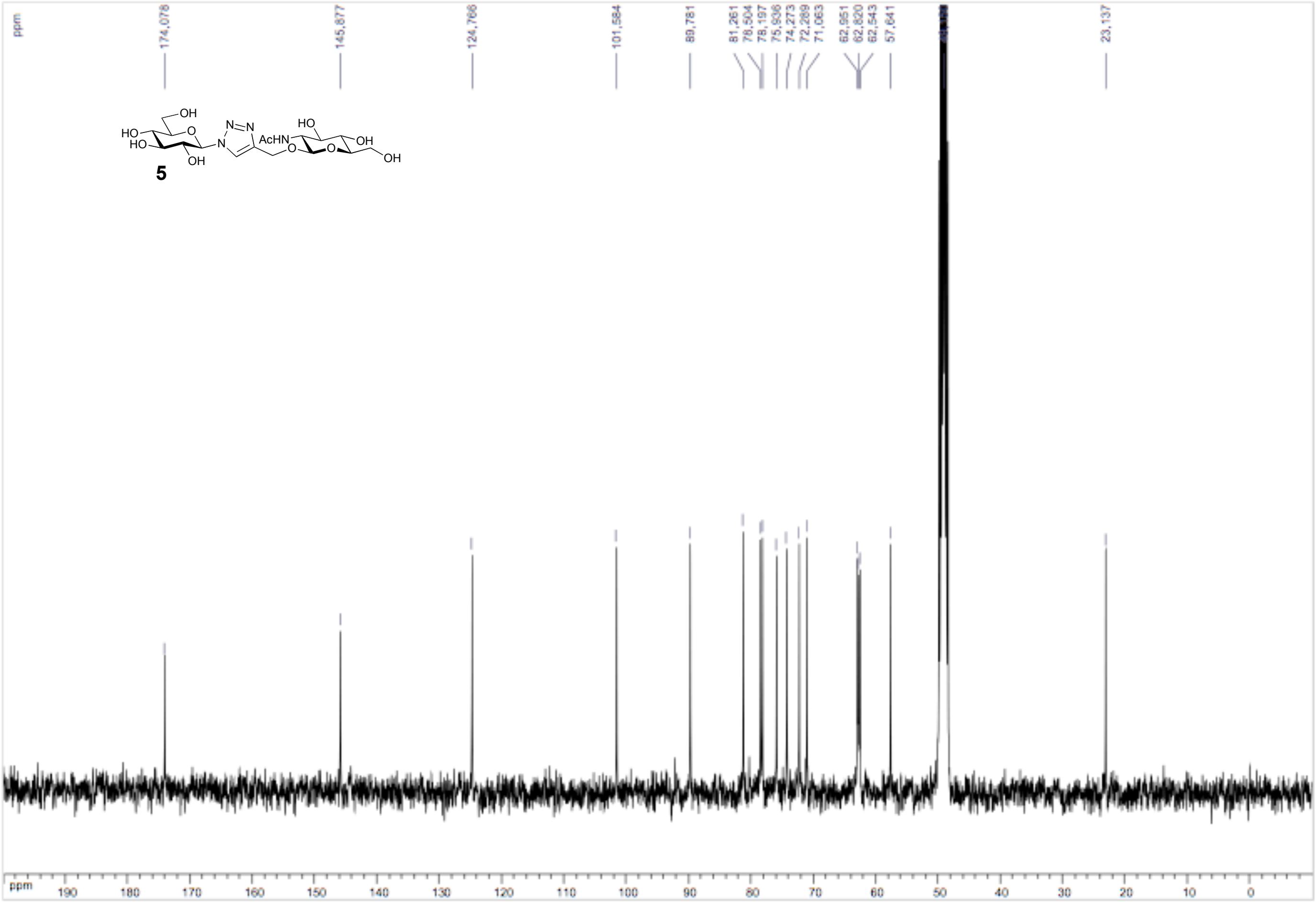
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101,584
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81,261
78,504
78,197
75,936
74,273
72,289
71,063
62,951
62,820
62,543
57,641
23,137
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150
140
130
120
110
100
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70
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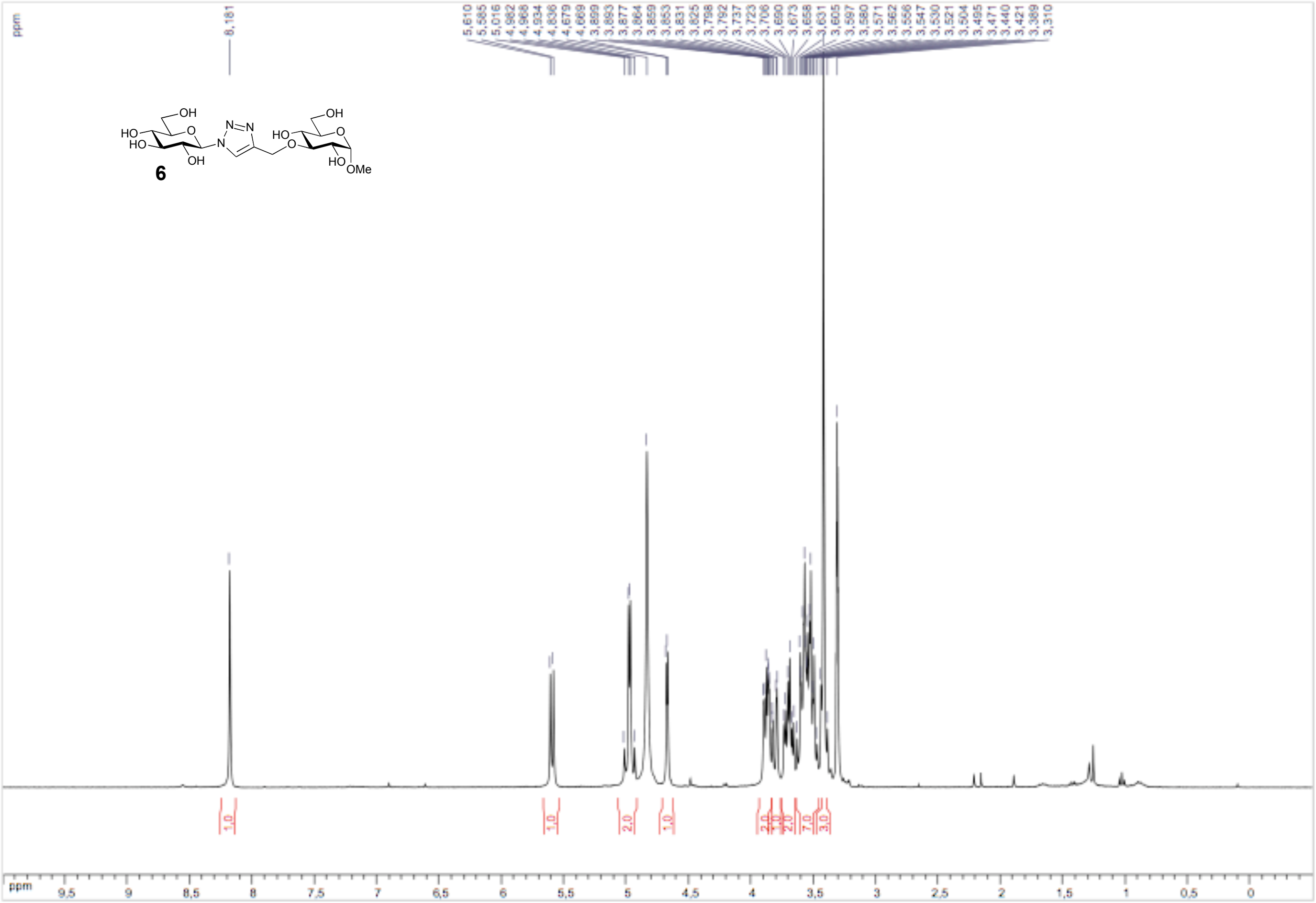
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4,968
4,934
4,836
4,679
4,669
3,899
3,893
3,877
3,864
3,859
3,853
3,831
3,825
3,798
3,792
3,737
3,723
3,706
3,690
3,673
3,658
3,631
3,605
3,597
3,580
3,571
3,562
3,556
3,547
3,530
3,521
3,504
3,495
3,471
3,440
3,421
3,389
3,310
HO
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OH
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O
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HO
OMe
6
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7,5
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5,5
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3,5
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2,5
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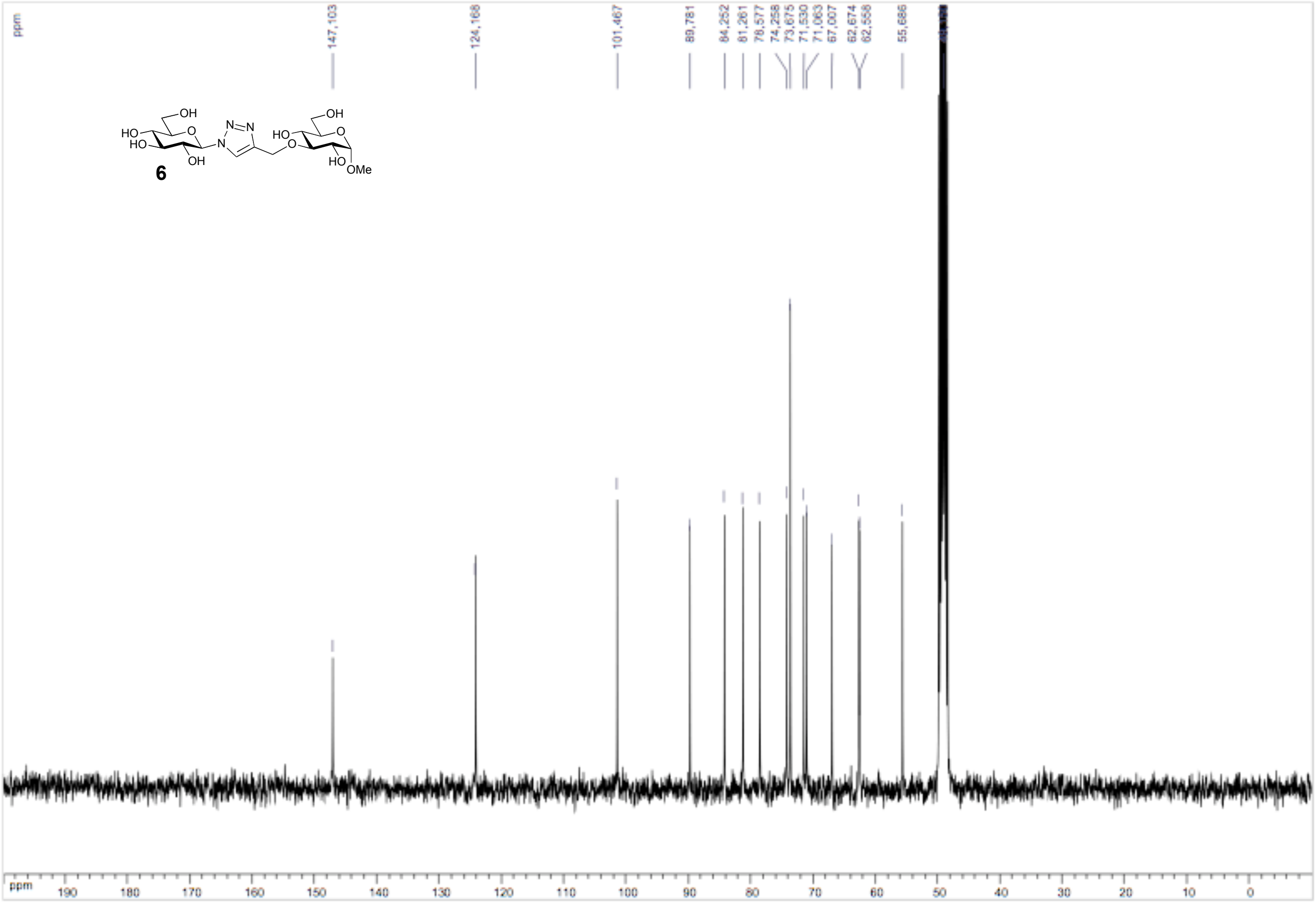
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101,467
89,781
84,252
81,261
78,577
74,258
73,675
71,530
71,063
67,007
62,674
62,558
55,686
HO
HO
OH
OH
N
N=N
HO
O
OH
HO
OMe
6
ppm
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180
170
160
150
140
130
120
110
100
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70
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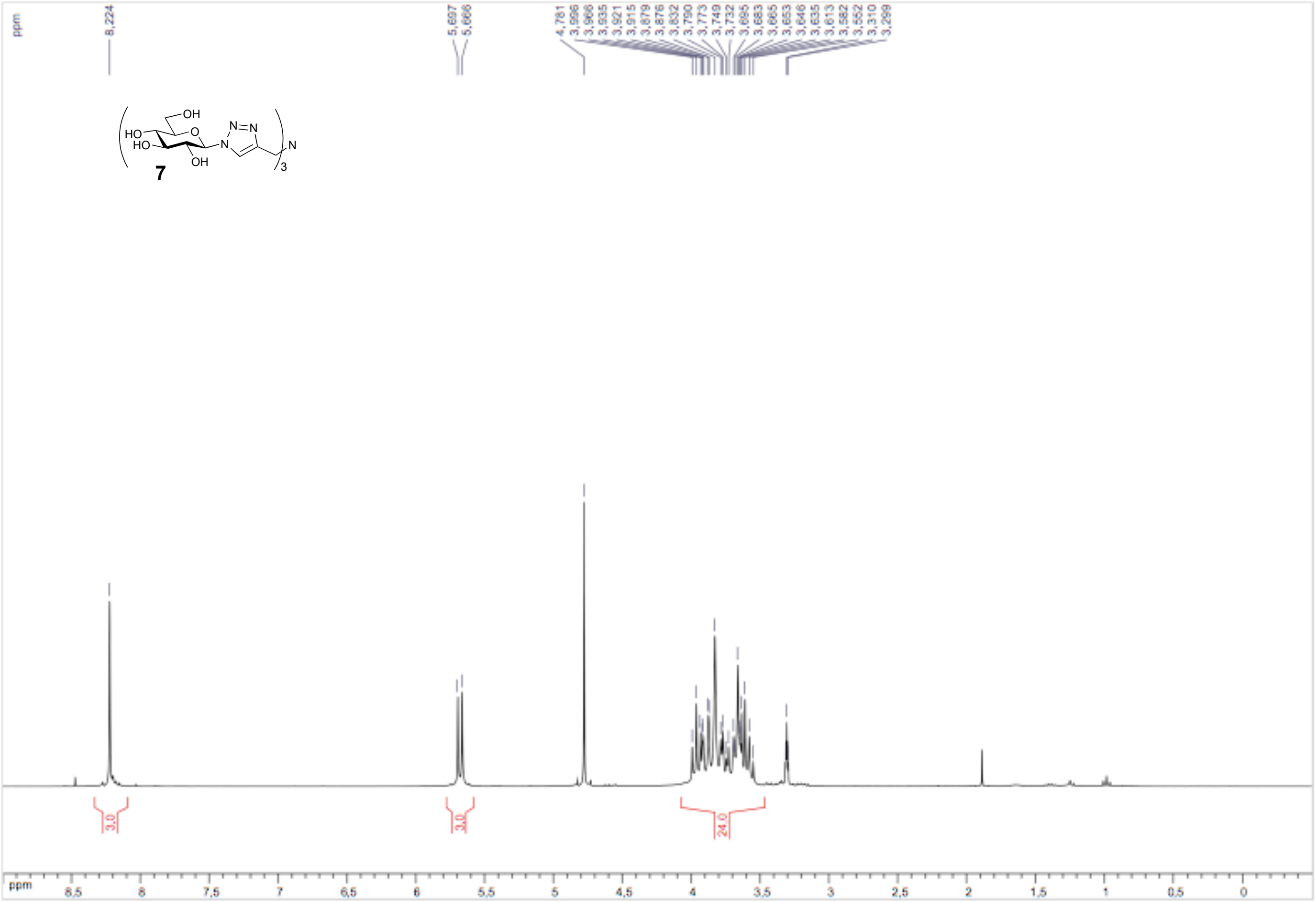
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5,666
4,781
3,996
3,966
3,935
3,921
3,915
3,879
3,876
3,832
3,790
3,773
3,749
3,732
3,695
3,683
3,665
3,653
3,646
3,635
3,613
3,582
3,552
3,310
3,299
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OH
HO
O
OH
N
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7,5
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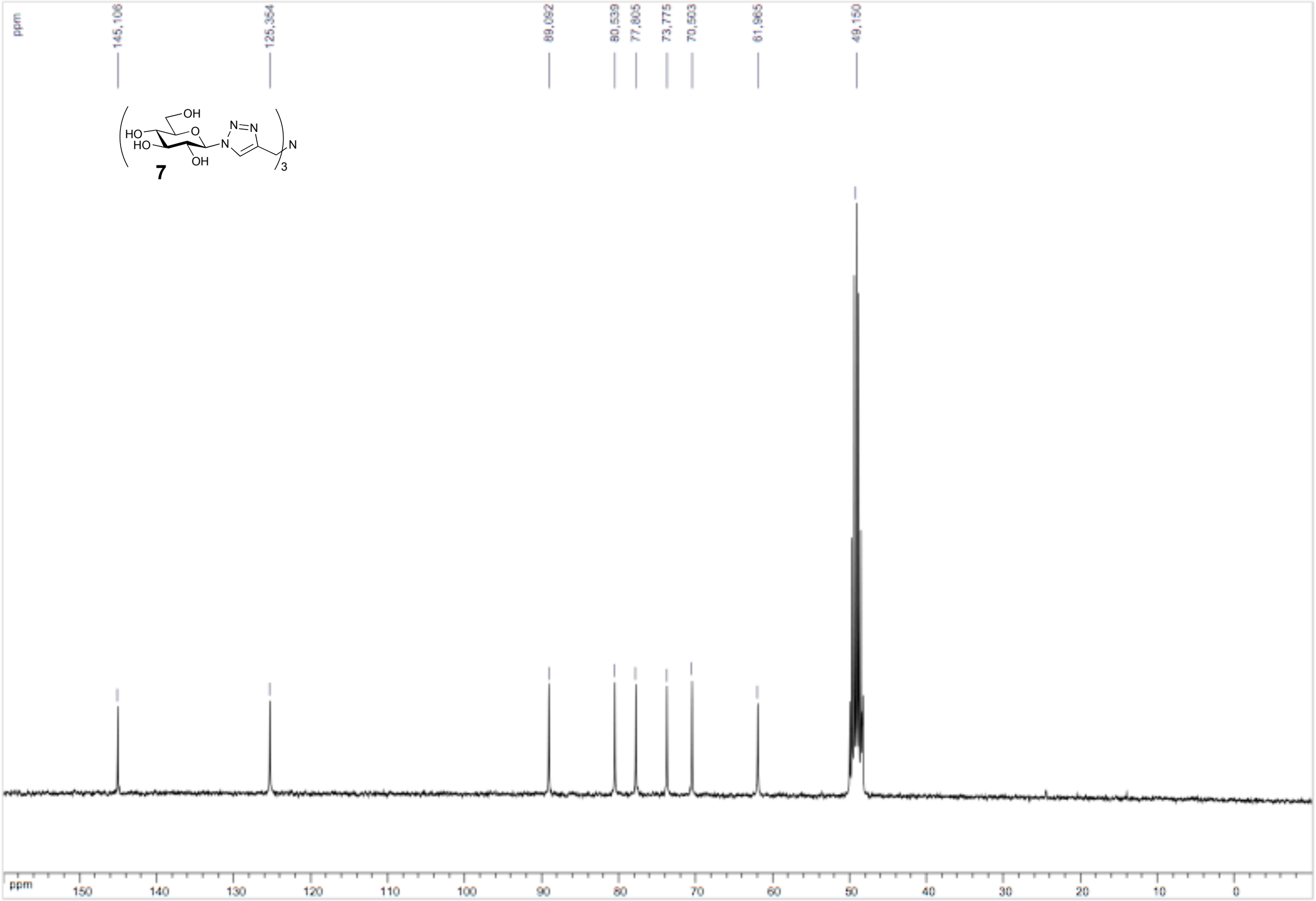
ppm
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89,092
80,539
77,805
73,775
70,503
61,965
49,150
HO
OH
HO
O
OH
N
N=N
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ppm
150
140
130
120
110
100
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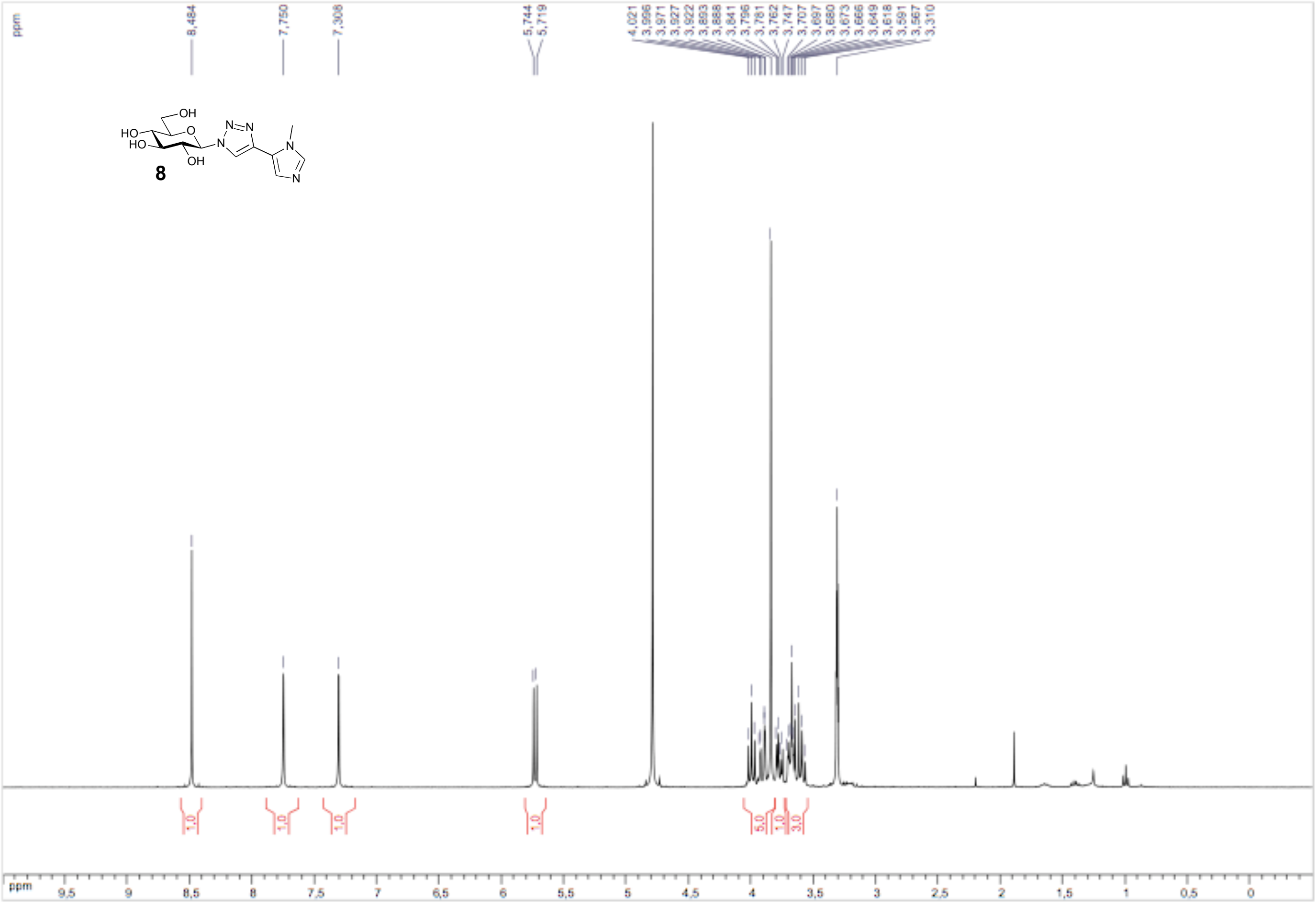
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7,308
5,744
5,719
4,021
3,996
3,971
3,927
3,922
3,893
3,888
3,841
3,796
3,781
3,762
3,747
3,707
3,697
3,680
3,673
3,666
3,649
3,618
3,591
3,567
3,310
OH
HO
HO
O
OH
N
N=N
N
N
8
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1,0
1,0
5,0
1,0
3,0
ppm
9,5
9
8,5
8
7,5
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5,5
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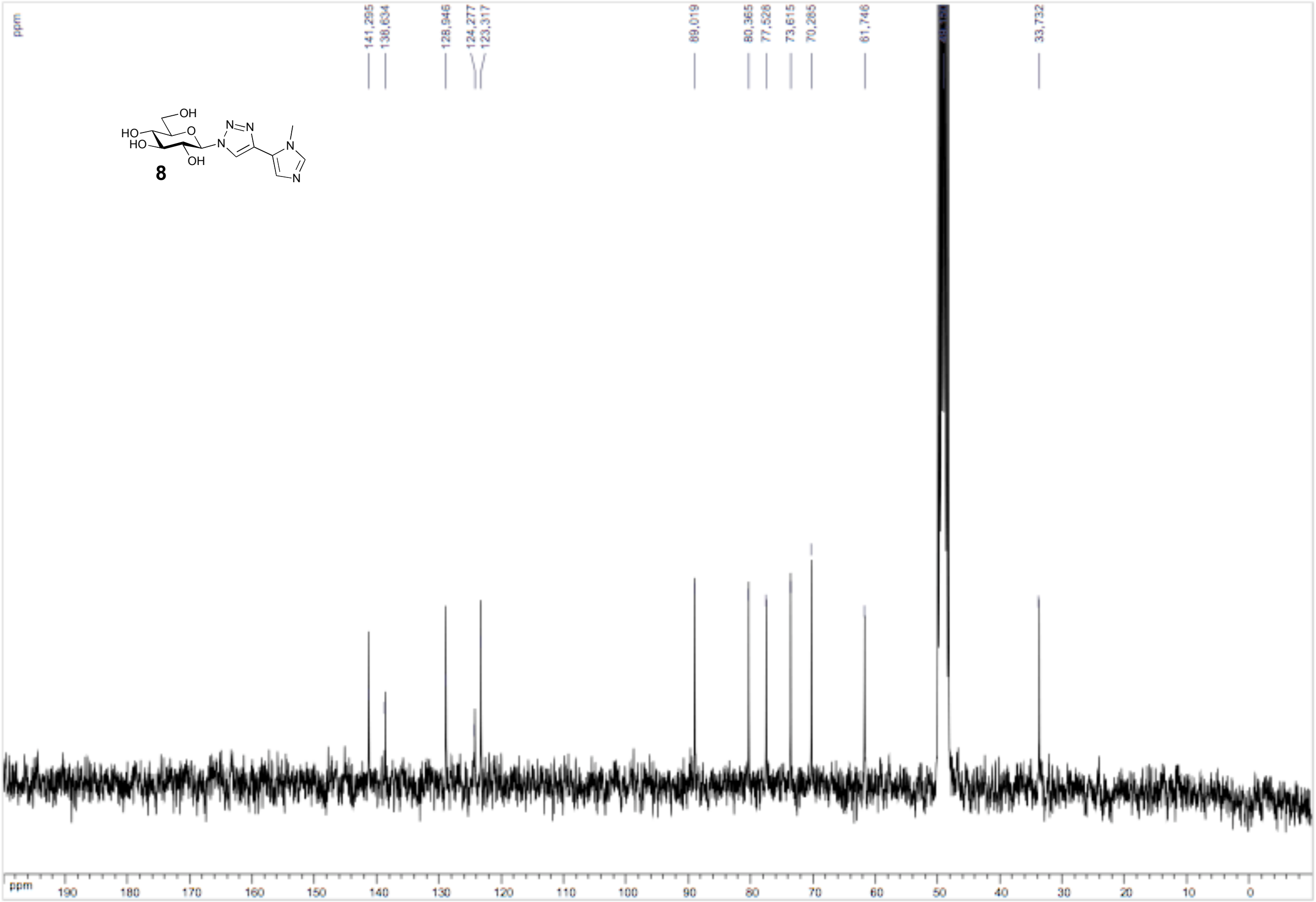
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80,365
77,528
73,615
70,285
61,746
33,732
OH
HO
HO
O
OH
N
N=N
N
N
8
ppm
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150
140
130
120
110
100
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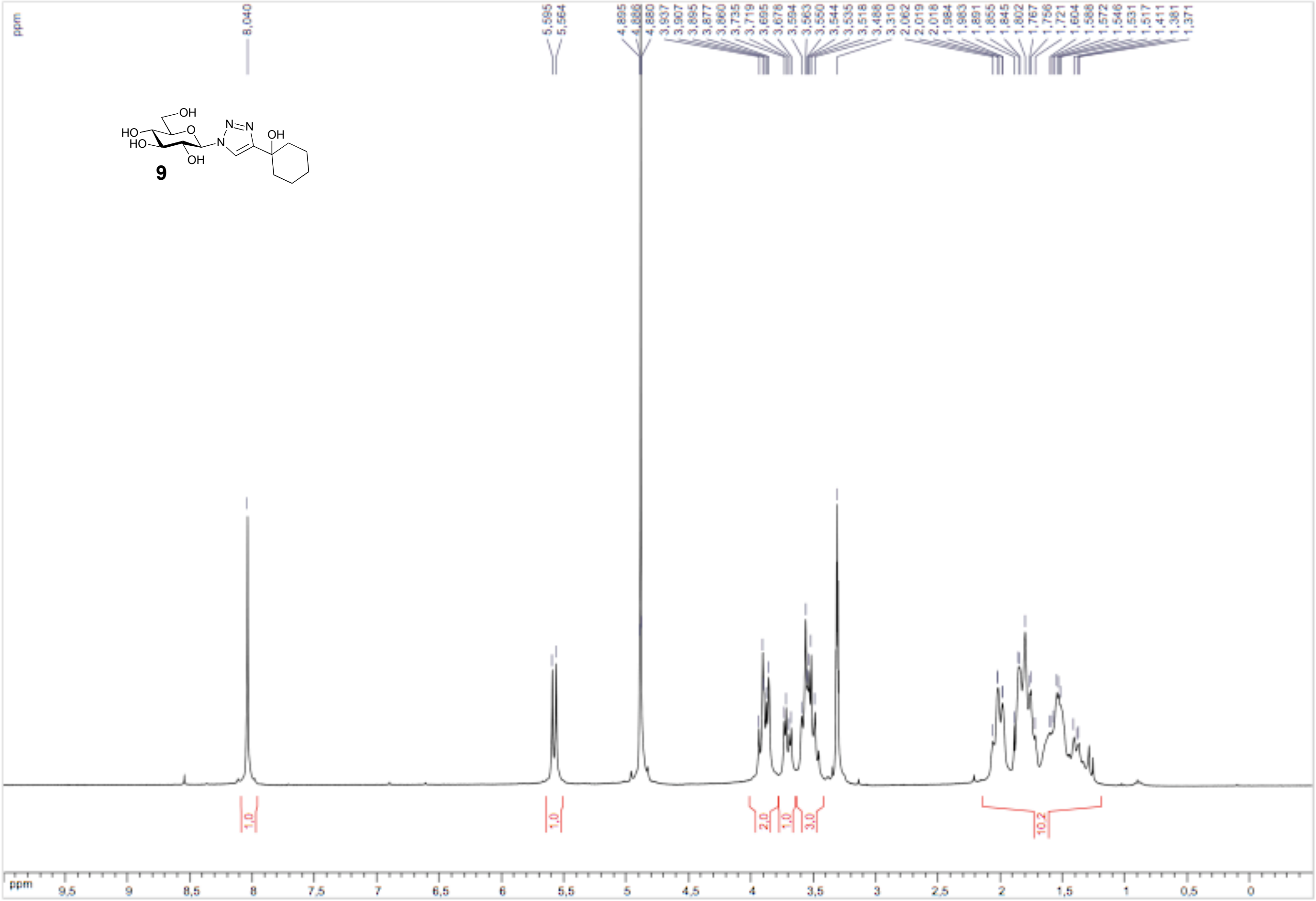
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4,888
4,880
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3,895
3,877
3,860
3,735
3,719
3,695
3,678
3,594
3,563
3,550
3,544
3,535
3,518
3,488
3,310
2,062
2,019
2,018
1,984
1,983
1,891
1,855
1,845
1,802
1,767
1,756
1,721
1,604
1,588
1,572
1,546
1,531
1,517
1,411
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HO
HO
OH
O
OH
N
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ppm
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8,5
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7,5
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5,5
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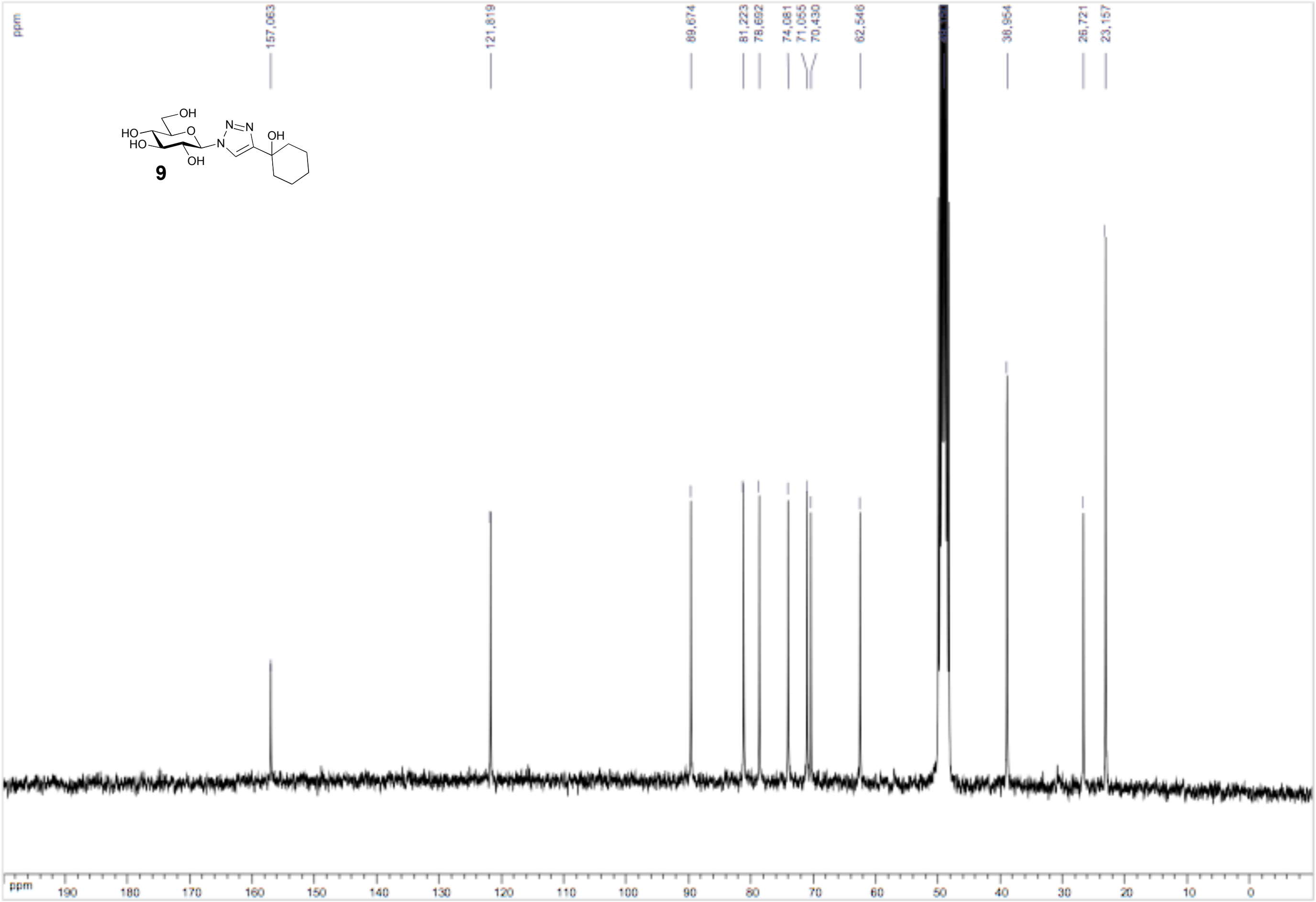
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62,546
38,954
26,721
23,157
HO
HO
OH
O
OH
N
N=N
OH
9
ppm
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150
140
130
120
110
100
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70
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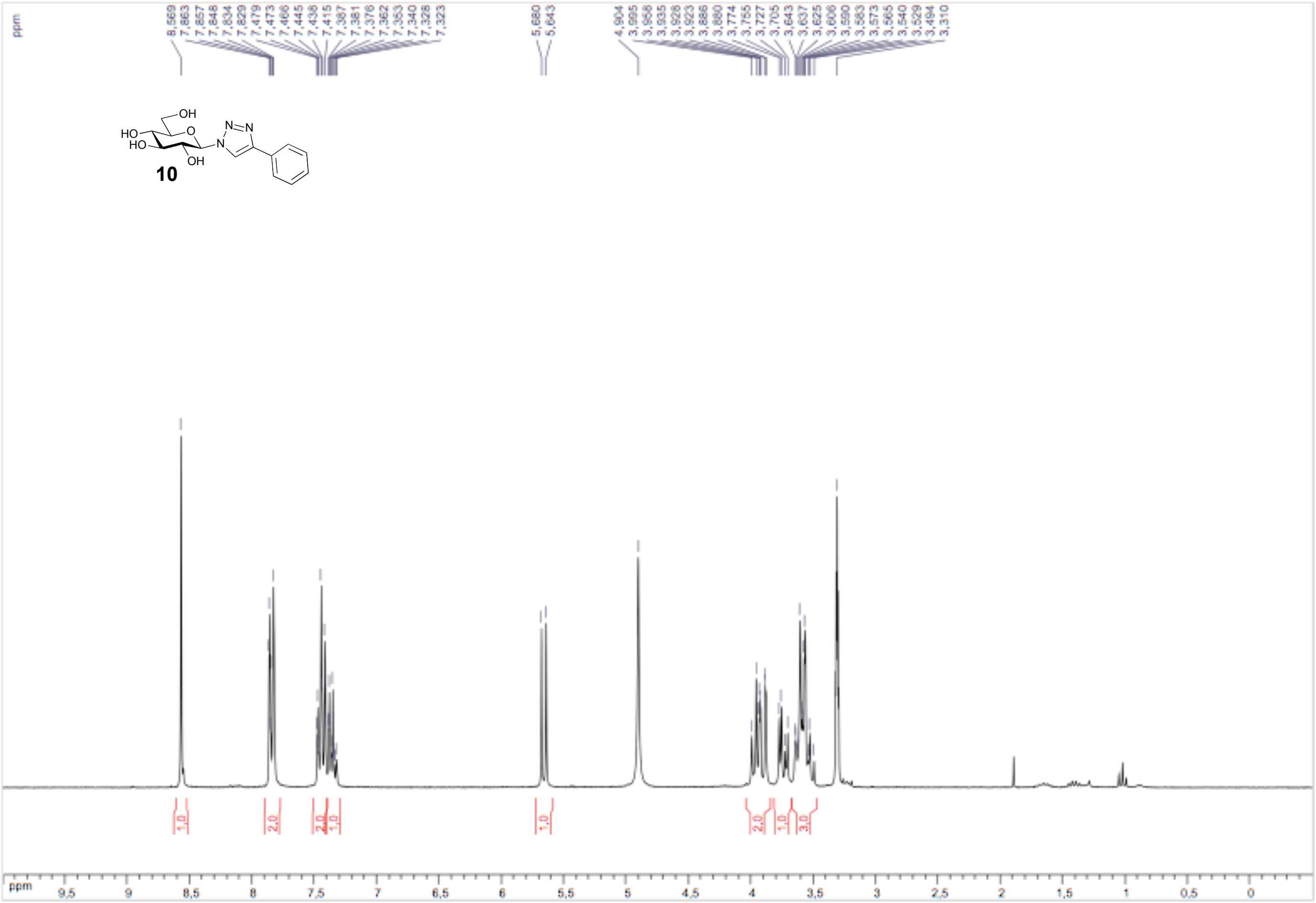
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7,466
7,445
7,438
7,415
7,387
7,381
7,376
7,362
7,353
7,340
7,328
7,323
5,680
5,643
4,904
3,995
3,958
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3,928
3,923
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3,880
3,774
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3,727
3,705
3,643
3,637
3,625
3,606
3,590
3,583
3,573
3,565
3,540
3,529
3,494
3,310
OH
HO
HO
O
OH
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N=N
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1,0
1,0
2,0
1,0
3,0
ppm
9,5
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8
7,5
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5,5
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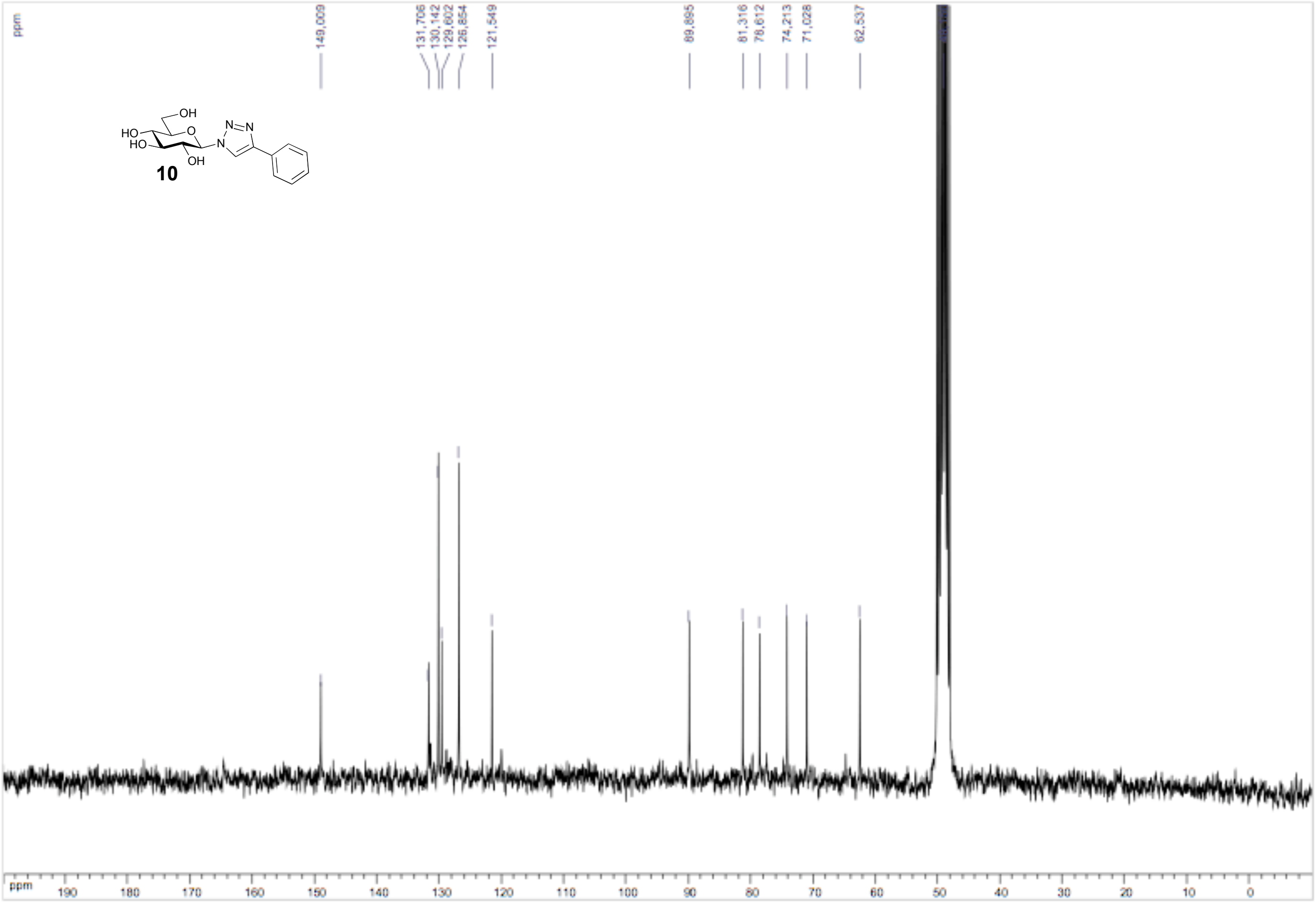
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78,612
74,213
71,028
62,537
OH
HO
HO
O
OH
N
N=N
10
ppm
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150
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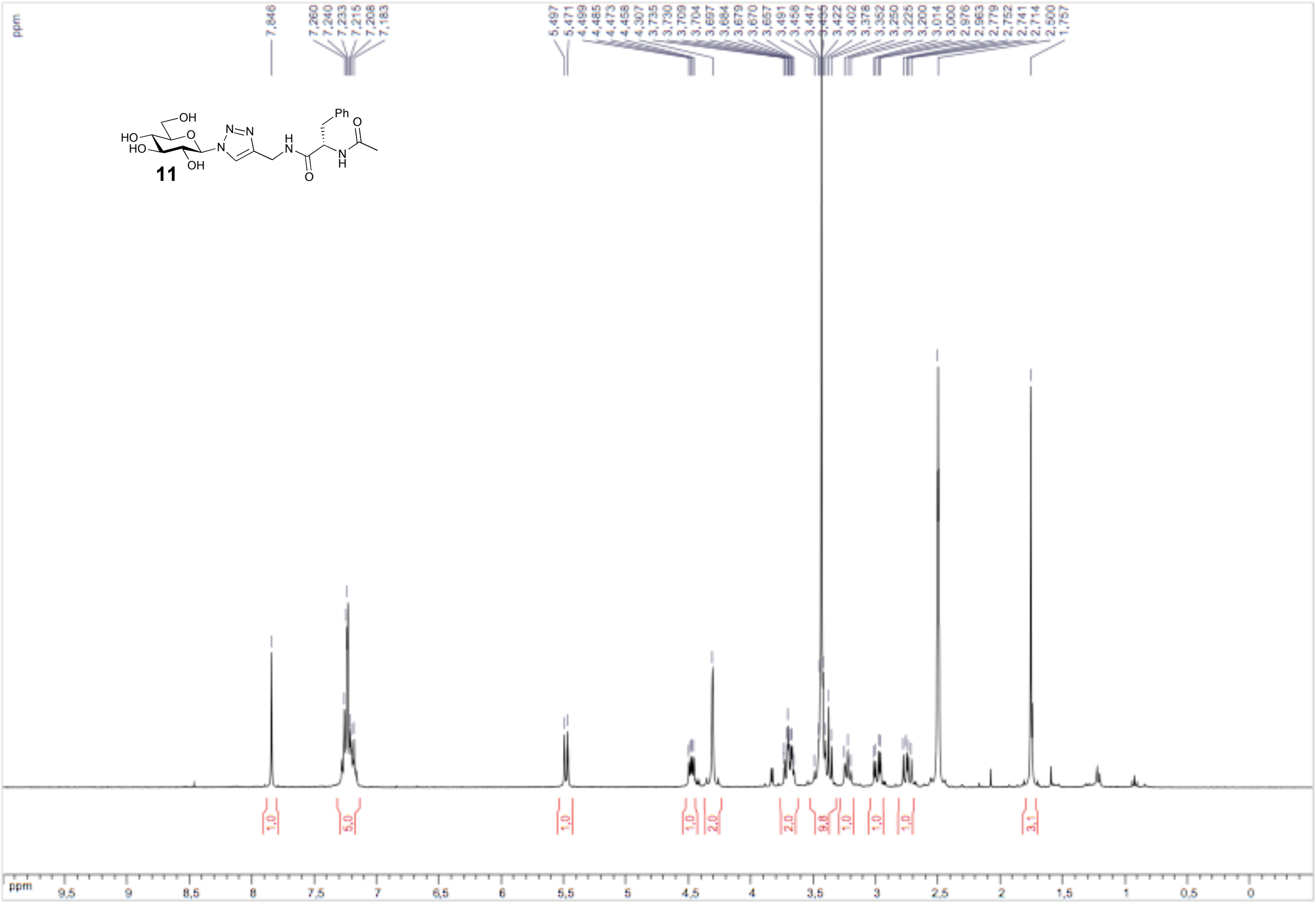
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4,485
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4,458
4,307
3,735
3,730
3,709
3,704
3,697
3,684
3,679
3,670
3,657
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3,000
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2,963
2,779
2,752
2,741
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HO
O
OH
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N
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Ph
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H
O
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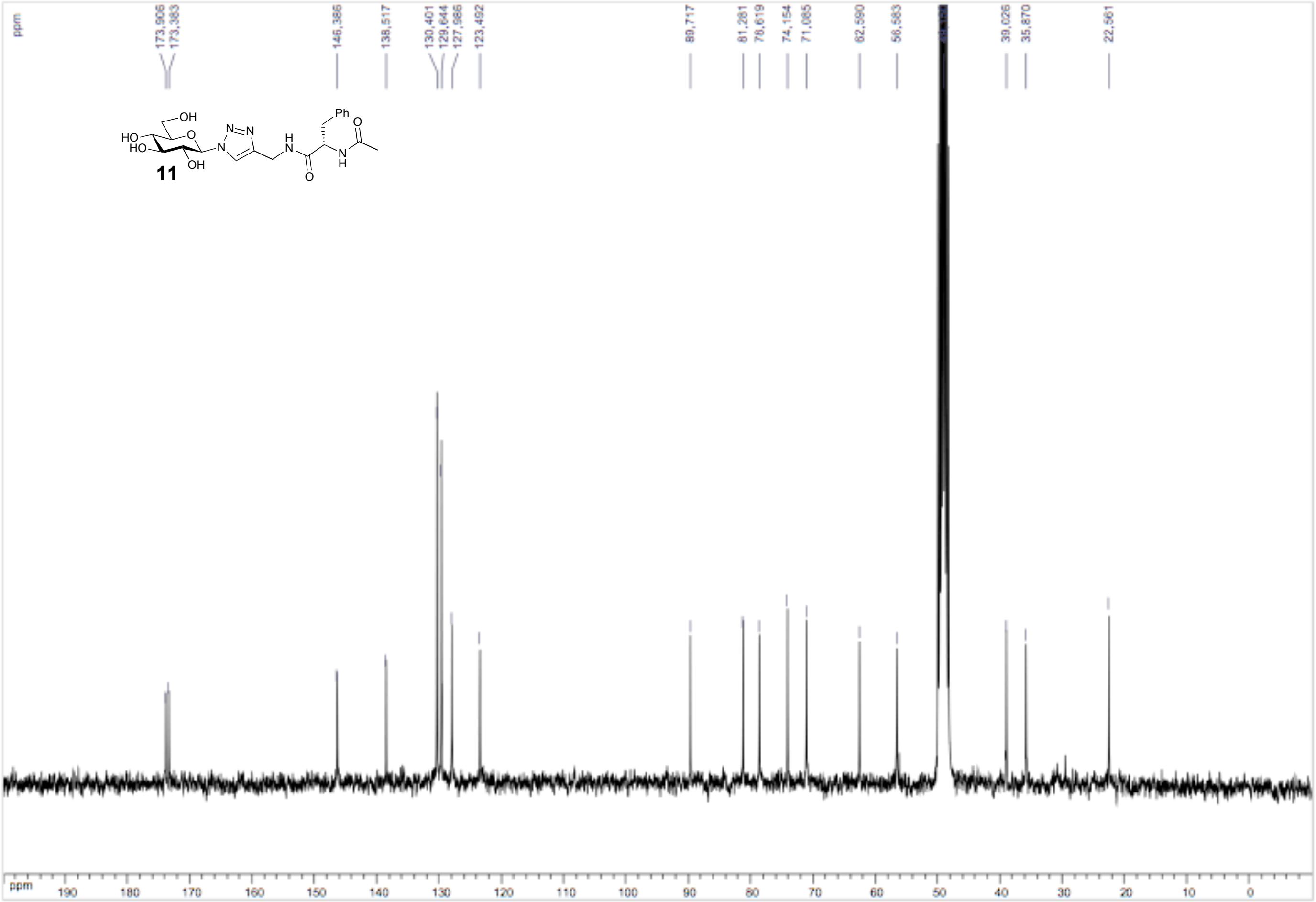
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89,717
81,281
78,619
74,154
71,085
62,590
56,583
39,026
35,870
22,561
OH
HO
HO
O
OH
N
N=N
H
N
O
Ph
N
H
O
11
ppm
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150
140
130
120
110
100
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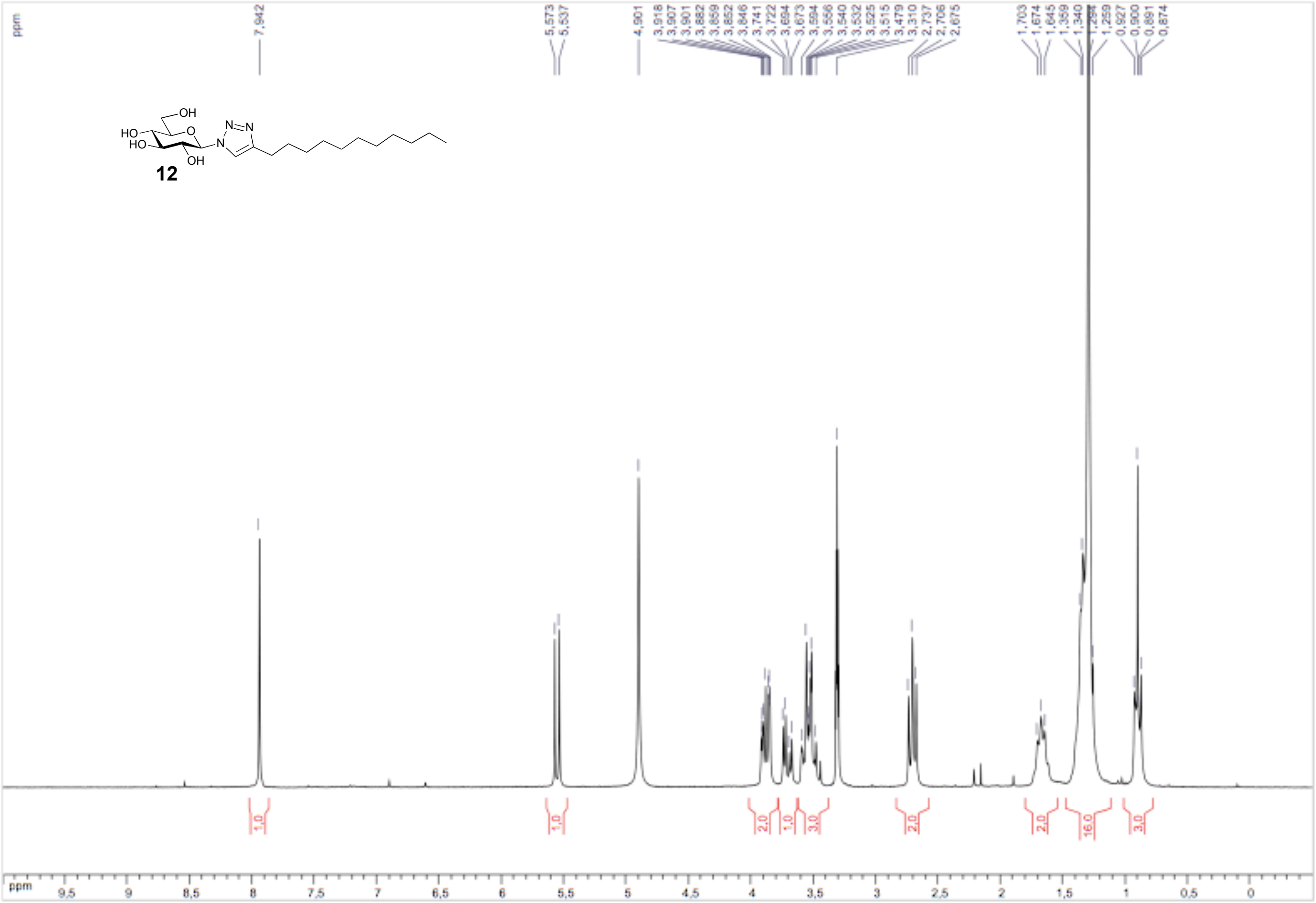
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3,852
3,846
3,741
3,722
3,694
3,673
3,594
3,556
3,540
3,532
3,525
3,515
3,479
3,310
2,737
2,706
2,675
1,703
1,674
1,645
1,359
1,340
1,294
1,259
0,927
0,900
0,891
0,874
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HO
O
OH
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2,0
1,0
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2,0
2,0
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ppm
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8,5
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7,5
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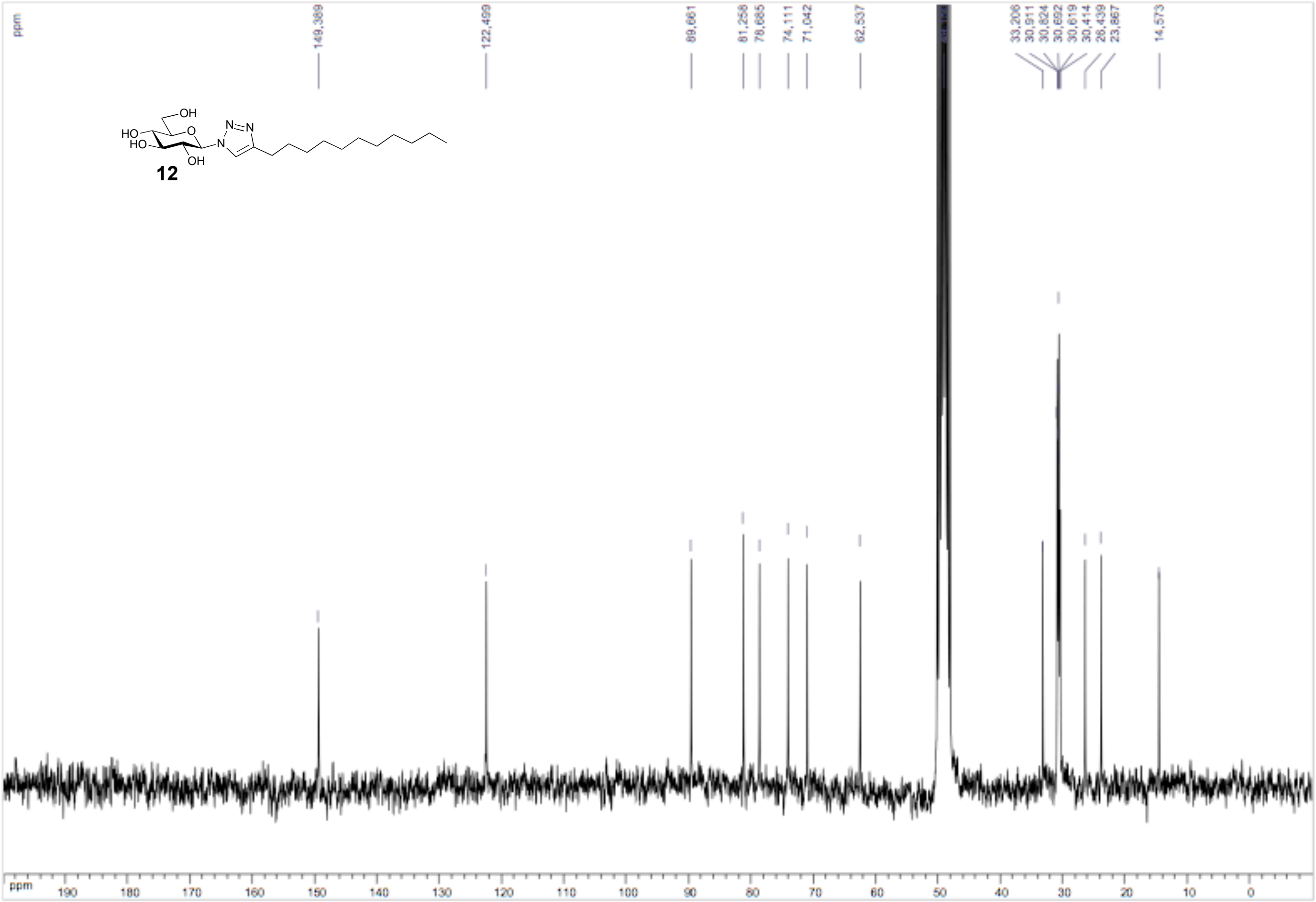
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71,042
62,537
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30,911
30,824
30,692
30,619
30,414
26,439
23,867
14,573
OH
HO
HO
O
OH
N
N=N
12
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0