Supporting Information

Synthesis of lipo-chitooligosaccharide analogues and evaluation of their ability to interact with the LysM receptor-like kinase LYR3, a high affinity binding protein for Nod factors and Myc-LCOs

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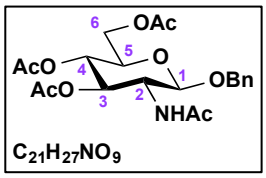
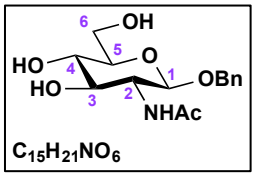
Products preparations and descriptions:

Benzyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside[1] (10).



To a mixture of **9**[2†] (1.00 g, 2.57 mmol, 1.00 equiv.) and benzyl alcohol (347 µL, 3.35 mmol, 1.30 equiv.) in anhydrous CH_2Cl_2 (19 mL) was added $Fe(OTf)_3$ (194 mg, 0.39 mmol, 0.15 equiv.) under an argon atmosphere. The reaction mixture was stirred at room temperature for 24 hours. The mixture was diluted in CH_2Cl_2 (30 mL), and washed with a saturated $NaHCO_3$ solution (100 mL). The aqueous layer was extracted with CH_2Cl_2 (5 x 30 mL). The organic layers were washed with H_2O (200 mL), dried over Na_2SO_4, filtered and concentrated. The residue was purified by silica gel column chromatography (cyclohexane/EtOAc 25:75) to give product **10** (1.01 g, 93%) as a white amorphous solid. **Rf:** 0.53 (EtOAc). **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 7.35-7.15 (m, 5H, C**H arom.**); 5.35 (d, 1H, $J_{NH,2}$ 8.7 Hz, N**H**); 5.18 (dd, 1H, $J_{2,3}$ 10.5, $J_{3,4}$ 9.7 Hz, **H-3**); 5.07 (dd, 1H, $J_{4,5}$ 9.6, $J_{3,4}$ 9.7 Hz, **H-4**); 4.87 (d, 1H, $^2J_{HCH}$ 12.2 Hz, C**H**HPh); 4.61 (d, 1H, $J_{1,2}$ 8.5 Hz, **H-1**); 4.58 (d, 1H, $^2J_{HCH}$ 12.2 Hz, CH**H**Ph); 4.25 (dd, 1H, $^2J_{6a,6b}$ 12.2, $J_{5,6a}$ 4.6 Hz, **H-6a**); 4.15 (dd, 1H, $^2J_{6a,6b}$ 12.2, $J_{5,6b}$ 245 Hz, **H-6b**); 3.95 (ddd, 1H, $J_{2,3}$ 10.5, $J_{2,NH}$ 8.7, $J_{2,1}$ 8.5 Hz, **H-2**); 3.65 (ddd, 1H, $J_{4,5}$ 9.6, $J_{5,6a}$ 4.6, $J_{5,6b}$ 2.4 Hz, **H-5**); 2.08, 1.99, 1.88 (4 s, 12H, 4 **Ac**). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 171.2, 171.0, 170.3, 169.6 (4 **C**OCH_3); 137.1, 128.7, 128.3 (**C arom.**); 99.6 (**C-1**); 72.6 (**C-3**); 72.1 (**C-5**); 70.9 (**C**H_2Ph); 68.8 (**C-4**); 62.3 (**C-6**); 54.8 (**C-2**); 23.5 (NCO**C**H_3); 21.0, 20.9, 20.8 (OCO**C**H_3). Analyses are in accordance with the literature.[1]

Benzyl 2-acetamido-2-deoxy-β-D-glucopyranoside[3] (11).

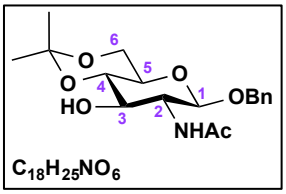


To a mixture of **10** (500 mg, 1.18 mmol, 1.0 equiv.) in dry CH_3OH (7.3 mL) was added $NaOCH_3$ (590 µL, 0.2 mol/L in CH_3OH, 0.12 mmol, 0.1 equiv.) under an argon atmosphere. The reaction mixture was stirred at room temperature for 30 min. A white precipitate formed rapidly within 10 min. The mixture was diluted in CH_2Cl_2/CH_3OH until dissolution of the precipitate, neutralized with Dowex® 50WX8 H^+ resin, filtrated and concentrated to give product **11** (339 mg, 92%) as a white amorphous solid. **Rf:** 0.08 (CH_2Cl_2/CH_3OH 9:1). **^{1}H NMR (500 MHz, CD_3OD)** δ: 7.36-7.23 (m, 5H, C**H arom.**); 4.88 (d, 1H, $^2J_{HCH}$ 12.3 Hz, C**H**HPh); 4.61 (d, 1H, $^2J_{HCH}$ 12.3 Hz, CH**H**Ph); 5.33 (d, 1H, $J_{1,2}$ 8.4 Hz, **H-1**); 3.91 (dd, 1H, $^2J_{6a,6b}$ 12.0, $J_{5,6a}$ 1.9 Hz, **H-6a**); 3.72 (dd, 1H, $J_{2,3}$ 10.0, $J_{2,1}$ 8.4 Hz, **H-2**); 3.71 (dd, 1H, $^2J_{6a,6b}$ 12.0, $J_{5,6b}$ 5.7 Hz, **H-6b**); 3.45 (dd, 1H, $J_{2,3}$ 10.0, $J_{3,4}$ 8.9 Hz, **H-3**); 3.34 (dd, 1H, $J_{4,5}$ 9.7, $J_{3,4}$ 8.9 Hz, **H-4**); 3.27 (ddd, 1H, $J_{4,5}$ 9.7, $J_{5,6b}$ 5.7, $J_{5,6a}$ 1.9 Hz, **H-5**); 1.95 (s, 3H, **Ac**). **^{13}C NMR (125 MHz, CD_3OD)** δ:

† Commercially available.

173.9 (**C**OCH_3); 139.4, 129.5, 129.0, 128.8 (**C arom.**); 102.0 (**C-1**); 78.2 (**C-5**); 76.1 (**C-3**); 72.4 (**C-4**); 71.7 (**C**H_2Ph); 63.0 (**C-6**); 57.5 (**C-2**); 23.1 (CO**C**H_3). Analyses are in accordance with the literature.[3]

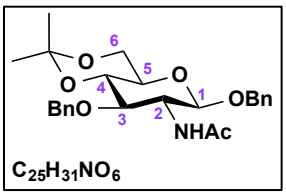
Benzyl 2-acetamido-2-deoxy-4,6-*O*-isopropylidene-β-D-glucopyranoside[4] (12).



$C_{18}H_{25}NO_6$

To a solution of **11** (1.61 g, 5.16 mmol, 1.0 equiv.) and 2,2-dimethoxypropane (9.5 mL, 77.4 mmol, 25.0 equiv.) in dry DMF (20.6 mL) was added PTSA (98 mg, 0.52 mmol, 0.1 equiv.) under an argon atmosphere. The reaction mixture was stirred at 40 °C and 250 mbar for 1 hour, and the acid was then quenched with triethylamine and the mixture concentrated to give crude isopropylidene product **12** as a yellowish solid used in the next step without further purification. An analytical sample of pure product **12**, as a white amorphous solid, was obtained by silica gel column chromatography of an aliquot (CH_2Cl_2/CH_3OH 100:0 to 90:10) and characterized. **Rf:** 0.30 (CH_2Cl_2/CH_3OH 95:5). **$[\alpha]_D^{20}$** = –103.40 (*c* = 1.00, $CHCl_3$) (–110.2 (*c* = 1, $CHCl_3$) in literature[4]). **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 7.40-7.22 (m, 5H, C**H arom.**); 5.65 (d, 1H, $J_{NH,2}$ 5.3 Hz, N**H**); 4.86 (d, 1H, $^2J_{HCH}$ 12.0 Hz, C**H**HPh); 4.59 (d, 1H, $J_{1,2}$ 8.3 Hz, **H-1**); 4.55 (d, 1H, $^2J_{HCH}$ 12.0 Hz, CH**H**Ph); 4.27 (s, 1H, O**H**); 3.93 (dd, 1H, $^2J_{6a,6b}$ 10.8, $J_{5,6a}$ 5.3 Hz, **H-6a**); 3.83 (dd, 1H, $J_{2,3}$ 9.6, $J_{3,4}$ 9.0 Hz, **H-3**); 3.80 (dd, 1H, $^2J_{6a,6b}$ 10.8, $J_{5,6b}$ 10.5 Hz, **H-6b**); 3.58 (dd, 1H, $J_{4,5}$ 9.8, $J_{3,4}$ 9.0 Hz, **H-4**); 3.51 (ddd, 1H, $J_{2,3}$ 9.6, $J_{1,2}$ 8.3, $J_{NH,2}$ 5.3 Hz, **H-2**); 3.27 (ddd, 1H, $J_{5,6b}$ 10.5, $J_{4,5}$ 9.8, $J_{5,6a}$ 5.3 Hz, **H-5**); 1.93 (s, 3H, **Ac**); 1.50 (s, 3H, C**H$_3$**CCH_3); 1.41 (s, 3H, CH_3CC**H$_3$**). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 172.1 (**C**OCH_3); 137.1, 128.9, 128.5, 128.4 (**C arom.**); 100.1 (CH_3**C**CH_3); 99.8 (**C-1**); 74.5 (**C-4**); 72.3 (**C-3**); 71.2 (**C**H_2Ph); 67.5 (**C-5**); 62.2 (**C-6**); 59.1 (**C-2**); 29.3 (**C**H_3CCH_3); 23.7 (CO**C**H_3); 19.3 (CH_3**C**CH_3). **HRMS (ESI^+):** calculated for $C_{18}H_{26}NO_6^+$ 352.1755 [$M+H^+$]; found 352.1740. **IR:** υ (cm^{-1}) = 3600-3100, 2881, 1652, 1554, 1374, 1200, 1118, 1082, 1042, 857, 754. Analyses are in accordance with the literature.[4]

Benzyl 2-acetamido-3-*O*-benzyl-2-deoxy-4,6-*O*-isopropylidene-β-D-glucopyranoside[5] (13).

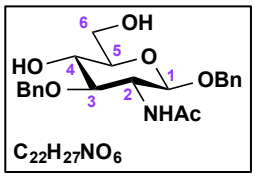


$C_{25}H_{31}NO_6$

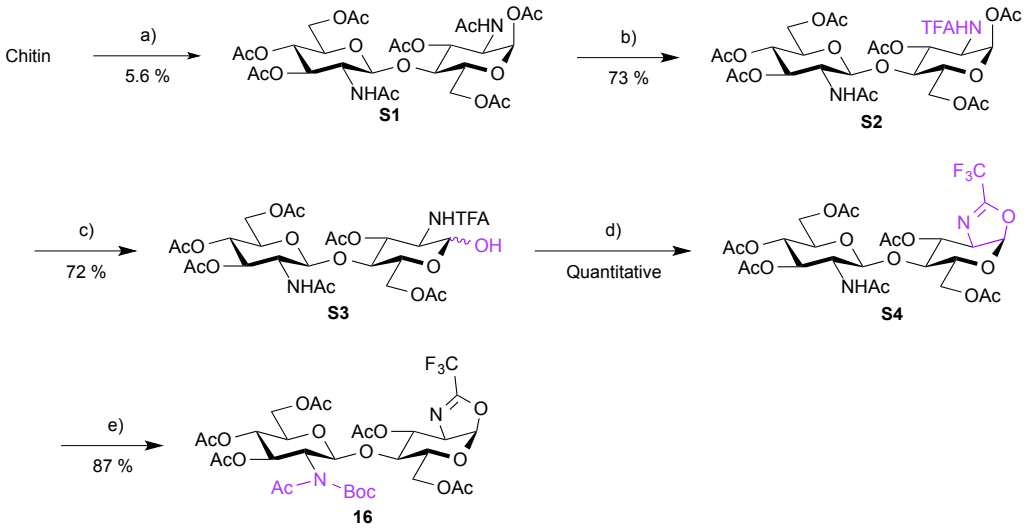
To a solution of crude **12** in dry DMF (25 mL) were added BaO (2.38 g, 15.52 mmol, 3.0 equiv.) and $Ba(OH)_2.8H_2O$ (814 mg, 2.58 mmol, 0.5 equiv.) under an argon atmosphere. The mixture was stirred at room temperature for 1 hour. Benzyl bromide (925 μL, 7.73 mmol, 1.5 equiv.) was then added and the mixture was stirred at room temperature for 19 hours. The mixture was diluted in CH_2Cl_2/CH_3OH, filtered over Celite® plug and concentrated. The residue was purified by silica gel column chromatography (CH_2Cl_2/CH_3OH 99:1) to give product **13** (1.99 g, 87% over 2 steps) as yellow crystalline solid. **Rf:** 0.18 (CH_2Cl_2/CH_3OH 99:1). **$[\alpha]_D^{20}$** = –21 (*c* = 1, $CHCl_3$) (–21.00 (*c* = 1.10, $CHCl_3$) in literature[5]). **^{1}H NMR (300 MHz, $CDCl_3$)** δ: 7.36-7.21 (m, 10H, C**H arom.**); 5.36 (d, 1H, $J_{NH,2}$ 7.8 Hz, N**H**);

4.89 (d, 1H, $J_{1,2}$ 8.3 Hz, **H-1**); 4,83 (d, 1H, $^{2}J_{HCH}$ 11.9 Hz, C**H**HPh-1); 4.80 (d, 1H, $^{2}J_{HCH}$ 11.9 Hz, C**H**HPh-3); 4.57 (d, 1H, $^{2}J_{HCH}$ 11.9 Hz, CH**H**Ph-3); 4.53 (d, 1H, $^{2}J_{HCH}$ 11.9 Hz, CH**H**Ph-1); 3.98 (dd, 1H, $J_{2,3}$ 9.9, $J_{3,4}$ 9.0 Hz, **H-3**); 3.94 (dd, 1H, $^{2}J_{6a,6b}$ 10.8, $J_{5,6a}$ 5.5 Hz, **H-6a**); 3.79 (dd, 1H, $^{2}J_{6a,6b}$ 10.8, $J_{5,6b}$ 10.2 Hz, **H-6b**); 3.70 (dd, 1H, $J_{4,5}$ 9.5, $J_{3,4}$ 9.0 Hz, **H-4**); 3.35 (ddd, 1H, $J_{2,3}$ 9.9, $J_{1,2}$ 8.3, $J_{NH,2}$ 7.8 Hz, **H-2**); 3.32 (ddd, 1H, $J_{5,6b}$ 10.2, $J_{4,5}$ 9.5, $J_{5,6a}$ 5.5 Hz, **H-5**); 1.81 (s, 3H, **Ac**); 1.48 (s, 3H, C**H**$_3$CCH$_3$); 1.41 (s, 3H, CH$_3$CC**H**$_3$). **^{13}C NMR (125 MHz, CDCl$_3$)** δ: 170.4 (**C**OCH$_3$); 138.9, 137.5, 128.6, 128.5, 128.3, 128.2, 128.1, 127.9 (**C arom.**); 99.9 (**C-1**); 99.5 (CH$_3$**C**CH$_3$); 77.2 (**C-3**); 75.6 (**C-4**); 74.2 (**C**H$_2$Ph-**3**); 71.4 (**C**H$_2$Ph-**1**); 67.1 (**C-5**); 62.5 (**C-6**); 57.7 (**C-2**); 29.4 (**C**H$_3$CCH$_3$); 23.7 (CO**C**H$_3$); 19.3 (CH$_3$**C**CH$_3$). **HRMS (ESI$^+$):** calculated for $C_{25}H_{32}NO_6^+$ 442.2224 [M+H$^+$]; found 442.2211. **IR:** υ (cm^{-1}) = 3277, 3100-2800, 1654, 1563, 1374, 1201, 1117, 1084, 859, 737, 697.

Benzyl 2-acetamido-3-*O*-benzyl-2-deoxy-β-D-glucopyranoside (14).

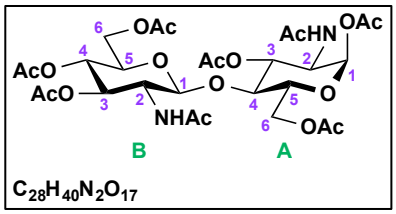


To a solution of **13** (1.7 g, 3.8 mmol, 1 equiv.) in CH_2Cl_2 (5.8 mL) was added a solution of trifluoroacetic acid (50% in water, 5.8 mL, 37.9 mmol, 10 equiv.) at 0 °C. The mixture was stirred at room temperature for 2 hours. The reaction mixture was then diluted with H_2O, cooled at 0 °C and the acid was quenched with triethylamine (5.3 mL, 10 equiv.). A white precipitate was filtered off, yielding a first crop of product **14**. Sodium chloride was added to the filtrate and the layers separated. The aqueous layer was then extracted with CH_2Cl_2 (3 x 50 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated yielding a second crop. The two samples were combined and purified by silica gel column chromatography (CH_2Cl_2/CH_3OH 96:4) to give product **14** (1.3 g, 88%) as a white amorphous solid. **Rf:** 0.30 (CH_2Cl_2/CH_3OH 95:5). **$[\alpha]_D^{20}$** = –24.00 (*c* = 1.00, CH_3OH) (–20 (*c* = 0.5, EtOH) in literature[6]). **^{1}H NMR (300 MHz, CD$_3$OD)** δ: 7.36-7.20 (m, 10H, C**H arom.**); 4,88 (d, 1H, $^{2}J_{HCH}$ 12.2 Hz, C**H**HPh-1); 4.87 (d, 1H, $^{2}J_{HCH}$ 11.3 Hz, C**H**HPh-3); 4.63 (d, 1H, $^{2}J_{HCH}$ 11.3 Hz, CH**H**Ph-3); 4.61 (d, 1H, $^{2}J_{HCH}$ 12.2 Hz, CH**H**Ph-1); 4.50 (d, 1H, $J_{1,2}$ 8.4 Hz, **H-1**); 3.93 (dd, 1H, $^{2}J_{6a,6b}$ 12.0, $J_{5,6a}$ 2.0 Hz, **H-6a**); 3.82 (dd, 1H, $J_{2,3}$ 10.1, $J_{1,2}$ 8.4 Hz, **H-2**); 3.72 (dd, 1H, $^{2}J_{6a,6b}$ 12.0, $J_{5,6b}$ 6.0 Hz, **H-6b**); 3.57-3.45 (m, 2H, **H-3** and **H-4**); 3.34-3.26 (m, 1H, **H-5**); 1.85 (s, 3H, **Ac**). **^{13}C NMR (125 MHz, CD$_3$OD)** δ: 173.5 (**C**OCH$_3$); 140.4, 139.3, 129.5, 129.4, 129.0, 128.9, 128.8, 128.6 (**C arom.**); 101.8 (**C-1**); 84.3 (**C-3**); 78.2 (**C-5**); 78.8 (**C**H$_2$Ph-**3**); 72.2 (**C-4**); 71.7 (**C**H$_2$Ph-**1**); 62.9 (**C-6**); 56.5 (**C-2**); 23.2 (CO**C**H$_3$). **HRMS (ESI$^+$):** calculated for $C_{22}H_{28}NO_6^+$ 402.1911 [M+H$^+$]; found 402.1899. **IR:** υ (cm^{-1}) = 3400-3100, 2867, 1654, 1551, 1373, 1111, 1074, 1053, 737, 699.



Preparation of compound 16 from chitin. (a) Ac_2O, H_2SO_4, 55 °C, then r.t. then 55 °C ; (b) $(CF_3CO)_2O$, CH_3CN, 135 °C, then CH_3OH, r.t. ; (c) ethylenediamine, AcOH, THF, r.t. ; (d) $(CH_3SO_2)O$, CH_3CN, r.t. then Et_3N, r.t. ; (e) Boc_2O, 4-DMAP, THF, 85 °C.

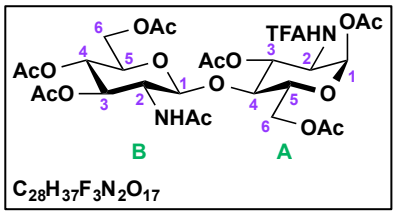
2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-1,3,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranoside[7] (S1).



To an ice-cold mixture of acetic anhydride (400 mL) and sulfuric acid (40 mL) was added chitin (80 g) portion-wise. The suspension was stirred at 55°C for 3 hours to give a heterogeneous brown mixture, kept at room temperature for 14 hours and then heated at 55°C for 1 hour to give a homogenous solution. This mixture was then poured into an ice-cold solution of sodium acetate in water (1.6 L, 100 g/L). The resulting solid was filtered off. The filtrate was extracted with CH_2Cl_2 (3 x 2 L). The combined organic layers were washed with an ice-cold saturated $NaHCO_3$ solution (6 L), dried over Na_2SO_4, filtered and concentrated to afford a yellow solid (73 g). The residue was purified by silica gel chromatography (CH_2Cl_2/acetone: from 9:1 to 1:9) to afford four fractions. After concentration, the first three fractions were recrystallized from CH_3OH/Et_2O. The second fraction was identified as peracetylated α-GlcNAc **S1** (7.5 g, 5.6%) obtained as a white solid. The first and third fractions were respectively identified as peracetylated α-chitose (3.8 g, 2.5%) and peracetylated α-chitotriose (5.8 g, 4.6%). The highly impure fourth fraction contained longer chitooligosaccharides. **Rf:** 0.60 (CH_2Cl_2/acetone 1:1). **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 6.07 (d, 1H, $J_{1^A,2^A}$ 3.5 Hz, **H-1^A**); 6.00 (d, 1H, $J_{NH^B,2^B}$ 9.2 Hz, N**H^B**); 5.64 (d, 1H, $J_{NH^A,2^A}$ 9.0 Hz, N**H^A**); 5.20 (dd, 1H, $J_{2^A,3^A}$ 10.8, $J_{3^A,4^A}$ 9.3 Hz, **H-3^A**); 5.10 (dd, 1H, $J_{2^B,3^B}$ 10.1, $J_{3^B,4^B}$ 9.6 Hz, **H-3^B**); 5.03 (dd, 1H, $J_{3^B,4^B}$ 9.6, $J_{4^B,5^B}$ 9.6 Hz, **H-4^B**); 4.44 (d, 1H, $J_{1^B,2^B}$ 8.6 Hz, **H-1^B**); 4.42 (dd, 1H, $^2J_{6a^A,6b^A}$ 12.2, $J_{5^A,6a^A}$ 3.5 Hz, **H-6a^A**); 4.36 (dd, 1H, $^2J_{6a^B,6b^B}$ 12.4, $J_{5^B,6a^B}$ 4.4 Hz, **H-6a^B**); 4.34 (ddd, 1H, $J_{2^A,3^A}$

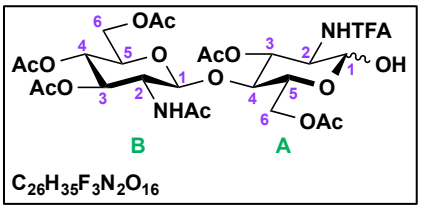
10.8, $J_{NH}^{A},_{2}^{A}$ 9.0, $J_{1}^{A},_{2}^{A}$ 3.5 Hz, **H-2^{A}**); 4.16 (dd, 1H, $^{2}J_{6a}^{A},_{6b}^{A}$ 12.2, $J_{5}^{A},_{6b}^{A}$ 1.5 Hz, **H-6b^{A}**); 4.00 (dd, 1H, $^{2}J_{6a}^{B},_{6b}^{B}$ 12.4, $J_{5}^{B},_{6b}^{B}$ 1.7 Hz, **H-6b^{B}**); 3.94 (ddd, 1H, $J_{2}^{B},_{3}^{B}$ 10.1, $J_{NH}^{B},_{2}^{B}$ 9.2, $J_{1}^{B},_{2}^{B}$ 8.6 Hz, **H-2^{B}**); 3.87 (ddd, 1H, $J_{4}^{A},_{5}^{A}$ 9.8, $J_{5}^{A},_{6a}^{A}$ 3.5, $J_{5}^{A},_{6b}^{A}$ 1.5 Hz, **H-5^{A}**); 3.71 (dd, 1H, $J_{3}^{A},_{4}^{A}$ 9.8, $J_{4}^{A},_{5}^{A}$ 9.3 Hz, **H-4^{A}**); 3.60 (ddd, 1H, $J_{4}^{B},_{5}^{B}$ 9.6, $J_{5}^{B},_{6a}^{B}$ 4.4, $J_{5}^{B},_{6b}^{B}$ 1.7 Hz, **H-5^{B}**); 2.16-1.90 (8 s, 24H, 8 **Ac**). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 171.7-169.1 (8 **C**OCH_3); 102.0 (**C-1^{B}**); 90.7 (**C-1^{A}**); 76.1 (**C-4^{A}**); 72.8 (**C-3^{B}**); 72.2 (**C-5^{B}**); 71.0 (**C-5^{A}**); 70.9 (**C-3^{A}**); 68.1 (**C-4^{B}**); 61.9 (**C-6^{B}**); 61.7 (**C-6^{A}**); 54.7 (**C-2^{B}**); 51.4 (**C-2^{A}**); 23,4-20.8 (8 CO**C**H_3). Analyses are in accordance with the literature.[7]

2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl-(1→4)-1,3,6-tri-*O*-acetyl-2-deoxy-2-trifluoroacetamido-α-D-glucopyranoside[7] (S2).



To a solution of peracetylated α-chitobiose **S1** (800 mg, 1.18 mmol, 1.0 equiv.) in dry CH_3CN (220 mL) was added trifluoroacetic anhydride (1.15 mL, 8.28 mmol, 7.0 equiv.) under an argon atmosphere. The reaction mixture was stirred at 135°C for 7 min in a sealed tube, then allowed to cool to room temperature, diluted with CH_3OH and stirred for 1 hour. After concentration, the residue was purified by silica gel column chromatography (CH_2Cl_2/methyl *tert*-butyl ether/CH_3OH 100:0:0 to 70:28:2) to give product **S2** (631 mg, 73%) as a white amorphous solid. **Rf:** 0.36 (CH_2Cl_2/acetone 4:1). **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 6.72 (d, 1H, $J_{NH}^{A},_{2}^{A}$ 8.7 Hz, N**H^{A}**); 6.16 (d, 1H, $J_{1}^{A},_{2}^{A}$ 3.6 Hz, **H-1^{A}**); 5.97 (d, 1H, $J_{NH}^{B},_{2}^{B}$ 9.2 Hz, N**H^{B}**); 5.28 (dd, 1H, $J_{2}^{A},_{3}^{A}$ 10.9, $J_{3}^{A},_{4}^{A}$ 9.2 Hz, **H-3^{A}**); 5.12 (dd, 1H, $J_{2}^{B},_{3}^{B}$ 10.2, $J_{3}^{B},_{4}^{B}$ 9.5 Hz, **H-3^{B}**); 5.02 (dd, 1H, $J_{3}^{B},_{4}^{B}$ 9.7, $J_{4}^{B},_{5}^{B}$ 9.5 Hz, **H-4^{B}**); 4.48 (d, 1H, $J_{1}^{B},_{2}^{B}$ 8.4 Hz, **H-1^{B}**); 4.42 (dd, 1H, $^{2}J_{6a}^{A},_{6b}^{A}$ 12.2, $J_{5}^{A},_{6a}^{A}$ 3.7 Hz, **H-6a^{A}**); 4.37 (dd, 1H, $^{2}J_{6a}^{B},_{6b}^{B}$ 12.5, $J_{5}^{B},_{6a}^{B}$ 4.2 Hz, **H-6a^{B}**); 4.31 (ddd, 1H, $J_{2}^{A},_{3}^{A}$ 10.9, $J_{NH}^{A},_{2}^{A}$ 8.7, $J_{1}^{A},_{2}^{A}$ 3.6 Hz, **H-2^{A}**); 4.19 (dd, 1H, $^{2}J_{6a}^{A},_{6b}^{A}$ 12.2, $J_{5}^{A},_{6b}^{A}$ 1.5 Hz, **H-6b^{A}**); 4.00 (dd, 1H, $^{2}J_{6a}^{B},_{6b}^{B}$ 12.5, $J_{5}^{B},_{6b}^{B}$ 2.2 Hz, **H-6b^{B}**); 3.92 (ddd, 1H, $J_{4}^{A},_{5}^{A}$ 9.7, $J_{5}^{A},_{6a}^{A}$ 3.7, $J_{5}^{A},_{6b}^{A}$ 1.5 Hz, **H-5^{A}**); 3.91 (ddd, 1H, $J_{2}^{B},_{3}^{B}$ 10.2, $J_{NH}^{B},_{2}^{B}$ 9.2, $J_{1}^{B},_{2}^{B}$ 8.4 Hz, **H-2^{B}**); 3.75 (dd, 1H, $J_{3}^{A},_{4}^{A}$ 9.7, $J_{4}^{A},_{5}^{A}$ 9.2 Hz, **H-4^{A}**); 3.62 (ddd, 1H, $J_{4}^{B},_{5}^{B}$ 9.7, $J_{5}^{B},_{6a}^{B}$ 4.2, $J_{5}^{B},_{6b}^{B}$ 2.2 Hz, **H-5^{B}**); 2.18-1.94 (7 s, 21H, 7 **Ac**). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 171.8-168.8 (7 **C**OCH_3); 157.7 ($^{2}J_{C,F}$ 38.0 Hz, **C**OCF3); 115.6 ($^{1}J_{C,F}$ 288 Hz, CO**C**F3); 102.0 (**C-1^{B}**); 89.7 (**C-1^{A}**); 75.9 (**C-4^{A}**); 72.7 (**C-3^{B}**); 72.3 (**C-5^{B}**); 71.1 (**C-5^{A}**); 70.3 (**C-3^{A}**); 68.1 (**C-4^{B}**); 61.9 (**C-6^{B}**); 61.5 (**C-6^{A}**); 54.8 (**C-2^{B}**); 52.2 (**C-2^{A}**); 23,4-20.6 (7 CO**C**H_3). Analyses are in accordance with the literature.[7]

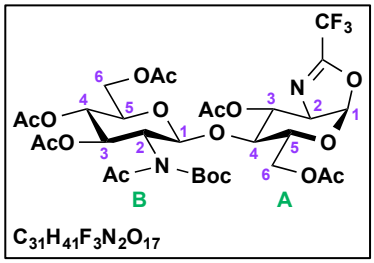
2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-acetyl-2-deoxy-2-trifluoroacetamido-D-glucopyranose[7] (S3).



$C_{26}H_{35}F_3N_2O_{16}$

To a solution of ethylenediamine (52 μL, 0.78 mmol, 1.2 equiv.) in dry THF (500 μL) was added acetic acid (45 μL, 0.78 mmol, 1.2 equiv.) at 0°C. The reaction mixture was stirred at room temperature for 30 min. A white salt was formed and a suspension of **S2** (465 mg, 0.64 mmol, 1.0 equiv.) in dry THF (3 mL) was added. The reaction mixture was stirred at room temperature for 22 hours. The mixture was concentrated and the residue was purified by silica gel column chromatography (CH_2Cl_2/CH_3OH 10:0 to 9:1) to give product **S3** (317 mg, α/β mixture, 72%) as a white amorphous solid. **Rf α isomer:** 0.34 (CH_2Cl_2/CH_3OH 95:5), **Rf β isomer:** 0.21 (CH_2Cl_2/CH_3OH 95:5). α/β mixture 4:1 (H_2O + CH_3CN + εHCO_2H, UPLC analysis). **^{1}H NMR α isomer (500 MHz, $CDCl_3$)** δ: 8.11 (d, 1H, $J_{NH^A,2^A}$ 9.7 Hz, N**H^A**); 6.00 (d, 1H, $J_{NH^B,2^B}$ 8.6 Hz, N**H^B**); 5.75 (dd, 1H, $J_{2^A,3^A}$ 10.9, $J_{3^A,4^A}$ 9.3 Hz, **H-3^A**); 5.42 (brd, 1H, $J_{OH,1^A}$ 2.8 Hz, **OH**); 5.27 (brdd, 1H, $J_{1^A,2^A}$ 3.6, $J_{OH,1^A}$ 2.8 Hz, **H-1^A**); 5.05 (dd, 1H, $J_{4^B,5^B}$ 9.7, $J_{3^B,4^B}$ 9.5 Hz, **H-4^B**); 4.94 (dd, 1H, $J_{2^B,3^B}$ 10.0, $J_{3^B,4^B}$ 9.5 Hz, **H-3^B**); 4.41 (dd, 1H, $^2J_{6a^B,6b^B}$ 12.4, $J_{5^B,6a^B}$ 4.2 Hz, **H-6a^B**); 4.32 (dd, 1H, $^2J_{6a^A,6b^A}$ 11.9, $J_{5^A,6a^A}$ 3.7 Hz, **H-6a^A**); 4.29 (ddd, 1H, $J_{2^A,3^A}$ 10.9, $J_{NH^A,2^A}$ 9.7, $J_{1^A,2^A}$ 3.1 Hz, **H-2^A**); 4.12 (dd, 1H, $^2J_{6a^A,6b^A}$ 11.9, $J_{5^A,6b^A}$ 1.8 Hz, **H-6b^A**); 4.11-4.04 (m, 2H, **H-2^B** and **H-1^B**); 4.05 (ddd, 1H, $J_{4^A,5^A}$ 9.8, $J_{5^A,6a^A}$ 3.7, $J_{5^A,6b^A}$ 1.8 Hz, **H-5^A**); 4.00 (dd, 1H, $^2J_{6a^B,6b^B}$ 12.4, $J_{5^B,6b^B}$ 1.7 Hz, **H-6b^B**); 3.60 (dd, 1H, $J_{4^A,5^A}$ 9.8, $J_{3^A,4^A}$ 9.3 Hz, **H-4^A**); 3.55 (ddd, 1H, $J_{4^B,5^B}$ 9.7, $J_{5^B,6a^B}$ 4.2, $J_{5^B,6b^B}$ 1.7 Hz, **H-5^B**); 2.14-1.92 (6 s, 18H, 6 **Ac**). **^{13}C NMR α isomer (125 MHz, $CDCl_3$)** δ: 172.1-169.4 (6 **C**OCH_3); 102.6 (**C-1^B**); 91.4 (**C-1^A**); 77.0 (**C-4^A**); 72.4 (**C-3^B**); 72.1 (**C-5^B**); 69.8 (**C-3^A**); 68.8 (**C-5^A**); 67.8 (**C-4^B**); 62.2 (**C-6^A**); 61.7 (**C-6^B**); 54.5 (**C-2^B**); 52.9 (**C-2^A**); 23,4-20.2 (6 CO**C**H_3). **HRMS (ESI$^+$):** calculated for $C_{26}H_{36}F_3N_2O_{16}^+$ 689.2011 [M+H$^+$]; found 689.1989. **IR:** ν (cm^{-1}) = 3300, 1741, 1714, 1663, 1371, 1227, 1181, 1160, 1040.

2-Trifluoromethyl-{[2-(*N*-acetyl-*tert*-butyloxycarbonylamino)-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl]-(1→4)-3,6-di-*O*-acetyl-1,2-dideoxy-α-D-glucopyranoso}[2,1-*d*]oxazoline[7] (16).

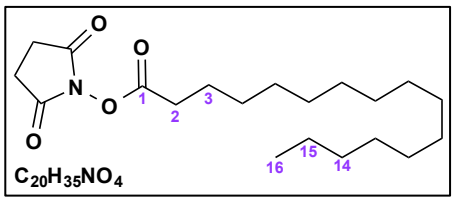


$C_{31}H_{41}F_3N_2O_{17}$

To a solution of compound **S3** (314 mg, 0.46 mmol, 1 equiv.) in dry CH_3CN (7.5 mL) was added methanesulfonic anhydride (238 mg, 1.4 mmol, 3 equiv.) under an argon atmosphere. The reaction mixture was stirred at room temperature for 35 min to form a mesyl intermediate. Triethylamine (1.3 mL, 9.1 mmol, 20 equiv.) was then added and the reaction mixture was stirred at room temperature for 2 hours. The mixture was

diluted with CH_2Cl_2 and washed with saturated $NaHCO_3$ solution (50 mL). The aqueous layer was then extracted with CH_2Cl_2 (3 x 50 mL). The combined organic layers were washed with brine (50 mL), dried over Na_2SO_4, filtered and concentrated to give oxazoline **S4** product (325 mg, quantitative yield) as a yellow solid. A solution of this solid **S4** in dry THF (3.1 mL) was then treated with di-*tert*-butyl dicarbonate (Boc_2O) (524 μL, 2.3 mmol, 5.0 equiv.) and 4-dimethylaminopyridine (4-DMAP) (11 mg, 0.091 mmol, 0.2 equiv.) under an argon atmosphere. The reaction mixture was stirred at room temperature for 30 min and then concentrated. The residue was purified by silica gel column chromatography (CH_2Cl_2/CH_3OH 100:0 to 98:2) to give product **16** (306 mg, 87%) as a yellow oil. **Rf:** 0.56 (Heptane/EtOAc 3:7). **$[\alpha]_D^{20}$** = -6.20 (*c* = 1.00, $CHCl_3$). **^{1}H NMR (500 MHz, CD_3CN, 70 °C)** δ: 6.27 (d, 1H, $J_{1^A,2^A}$ 7.5 Hz, **H-1^A**); 5.63 (dd, 1H, $J_{2^B,3^B}$ 10.6, $J_{3^B,4^B}$ 8.8 Hz, **H-3^B**); 5.62 (dd, 1H, $J_{2^A,3^A}$ 2.5, $J_{3^A,4^A}$ 1.5 Hz, **H-3^A**); 5.40 (brs, 1H, **H-1^B**); 4.99 (dd, 1H, $J_{4^B,5^B}$ 10.1, $J_{3^B,4^B}$ 8.8 Hz, **H-4^B**); 4.41 (ddd, 1H, $J_{1^A,2^A}$ 7.5, $J_{2^A,3^A}$ 2.5 Hz, **H-2^A**); 4.24 (dd, 1H, $^2J_{6a^B,6b^B}$ 12.2, $J_{5^B,6a^B}$ 4.7 Hz, **H-6a^B**); 4.19 (brd, 1H, $^2J_{6a^A,6b^A}$ 12.4 Hz, **H-6a^A**); 4.13 (dd, 1H, $^2J_{6a^B,6b^B}$ 12.2, $J_{5^B,6b^B}$ 2.7 Hz, **H-6b^B**); 4.01 (dd, 1H, $^2J_{6a^A,6b^A}$ 12.4, $J_{5^A,6b^A}$ 6.2 Hz, **H-6b^A**); 3.82 (ddd, 1H, $J_{4^B,5^B}$ 10.1, $J_{5^B,6a^B}$ 4.7, $J_{5^B,6b^B}$ 2.7 Hz, **H-5^B**); 3.79 (dd, 1H, $J_{4^A,5^A}$ 9.1, $J_{3^A,4^A}$ 1.5 Hz, **H-4^A**); 3.42 (ddd, 1H, $J_{4^A,5^A}$ 9.1, $J_{5^A,6b^A}$ 6.2, $J_{5^A,6a^A}$ 1.9 Hz, **H-5^A**); 2.30-1.93 (6 s, 18H, 6 **Ac**); 1.54 (s, 9H, **Boc**). **^{13}C NMR (125 MHz, CD_3CN, 70 °C)** δ: 172.1-171.1(6 **C**OCH_3); 157.4 (q, $^2J_{C,F}$ 40.0 Hz, O**C**NCF3); 118.2 (q, $^1J_{C,F}$ 274 Hz, OCN**C**F3); 104.4 (**C-1^A**); 103.3 (**C-1^B**); 86.8 (brs, **C**$(CH_3)_3$); 78.6 (**C-4^A**); 73.9 (**C-5^B**); 72.4 (brs, **C-3^B**); 71.8 (**C-4^B**); 71.5 (**C-3^A**); 70.9 (**C-5^A**); 66.2 (**C-2^A**); 65.1 (**C-6^A**); 64.0 (**C-6^B**); 29.1 (3C, C(**C**$H_3)_3$); 27.9 (brs, CO**C**H_3 NAc); 21,9-21.5 (5 CO**C**H_3 OAc). **HRMS (ESI$^+$):** calculated for $C_{26}H_{34}F_3N_2O_{15}^+$ 671.1906 [M-Boc+H$^+$]; found 671.1925. **IR:** ν (cm^{-1}) = 2980, 1744, 1690, 1370, 1227, 1154, 1043. Analyses are in accordance with the literature.[7]

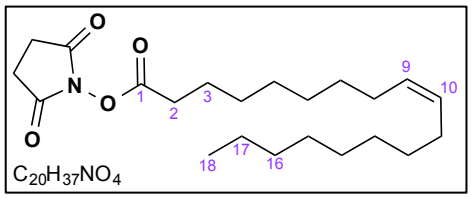
2,5-Dioxopyrrolidin-1-yl palmitate[8] (21).



Solutions of palmitic acid (100 mg, 0.39 mmol, 1.0 equiv.) in dry THF (600 μL), *N*-hydroxysuccinimide (63 mg, 0.55 mmol, 1.4 equiv.) in dry THF (900 μL) and *N*,*N'*-dicyclohexylcarbodiimide (129 mg, 0.62 mmol, 1.6 equiv.) in dry THF (700 μL) were mixed and stirred a room temperature under an argon atmosphere for 2 days. The mixture was then filtered and concentrated. The residue was resuspended in EtOAc and left overnight at 4°C. The precipitate was filtered again and the filtrate was concentrated. The crude residue was purified by silica gel column chromatography (CH_2Cl_2/CH_3OH 100:0 to 96:4) to afford product **21** (113 mg, 82%) as a white amorphous solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 2.81 (brs, 4H, 2 C**H**$_2$succi); 2.58 (t, 2H, $J_{2,3}$ 7.5 Hz, **H-2**); 1.72 (tt, 2H, $J_{2,3}$ 7.5, $J_{3,4}$ 7.5 Hz, **H-3**); 1.38 (brtt, 2H, $J_{3,4}$ 7.5, $J_{4,5}$ 7.5 Hz, **H-4**); 1.33-1.19 (m, 22H, **H-5** to **H-15**); 0.86 (t, 3H, $J_{15,16}$ 6.8 Hz, **H-16**). **^{13}C NMR (125 MHz,**

$CDCl_3$) δ: 169.4, 168.9 (**C**=Osucci and **C-1**); 32.2 (**C-14**); 31.2 (**C-2**); 30.0-29.0 (**C-4** to **C-13**); 25.8 (**C**H_2succi); 24.8 (**C-3**); 22.9 (**C-15**); 14.3 (**C-16**). Analyses are in accordance with the literature.[8]

2,5-Dioxopyrrolidin-1-yl oleate[9] (22).



To a mixture of oleic acid (112 μL, 0.35 mmol, 1.0 equiv.), *N*,*N'*-dicyclohexylcarbodiimide (80 mg, 0.39 mmol, 1.1 equiv.) and 4-pyrolydinopyridine (5 mg, 0.035 mmol, 0.1 equiv.) in dry THF (1.0 mL) was added, at 0°C, under an argon atmosphere, a solution of *N*-hydroxysuccinimide (81 mg, 0.71 mmol, 2.0 equiv.) in dry THF (0.4 mL). The reaction mixture was stirred at 0°C for 2 hours and then at room temperature for 2 days. The mixture was then filtered and concentrated. The residue was resuspended in EtOAc and left overnight at 4°C. The precipitate was filtered again and the filtrate was concentrated. The crude residue was purified by silica gel column chromatography (CH_2Cl_2/CH_3OH 100:0 to 98:2) to afford product **22** (108 mg, 81%) as a colorless gel. **Rf:** 0.89 (CH_2Cl_2/EtOAc 9:1). **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 5.37-5.27 (m, 2H, **H-9** and **H-10**); 2.81 (brs, 4H, 2 C**H**$_2$succi); 2.58 (t, 2H, $J_{2,3}$ 7.5 Hz, **H-2**); 2.03-1.95 (m, 4H, **H-8** and **H-11**); 1.72 (tt, 2H, $J_{2,3}$ 7.5, $J_{3,4}$ 7.5 Hz, **H-3**); 1.43-1.35 (m, 2H, **H-4**); 1.35-1.20 (m, 18H, **H-5** to **H-7** and **H-12** to **H-17**); 0.86 (t, 3H, $J_{17,18}$ 6.9 Hz, **H-18**). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 169.3, 168.9 (**C**=Osucci and **C-1**); 130.3, 129.9 (**C-9** and **C-10**); 32.1 (**C-16**); 31.2 (**C-2**); 30.0-29.0 (**C-4** to **C-7** and **C-12** to **C-15**); 27.5, 27.4 (**C-8** and **C-11**); 25.8 (**C**H_2succi); 24.8 (**C-3**); 22.9 (**C-17**); 14.3 (**C-18**). Analyses are in accordance with the literature.[9]

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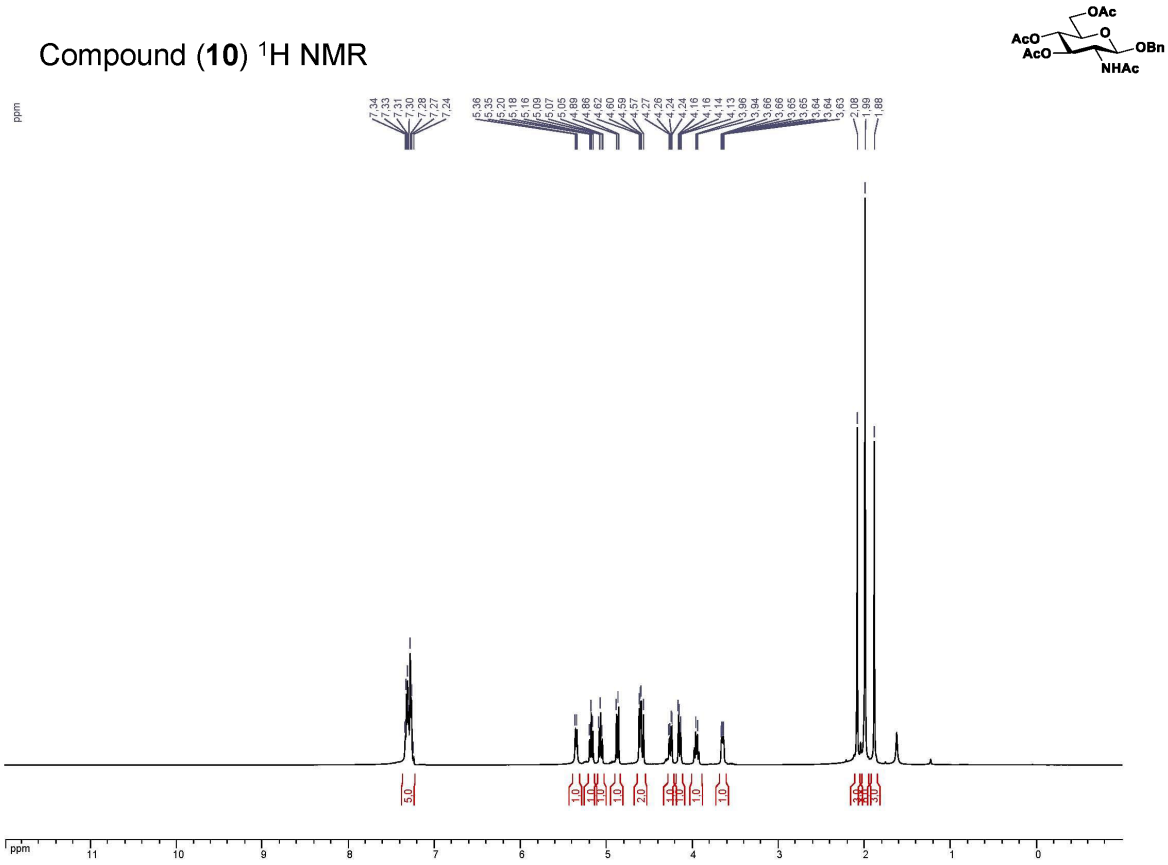
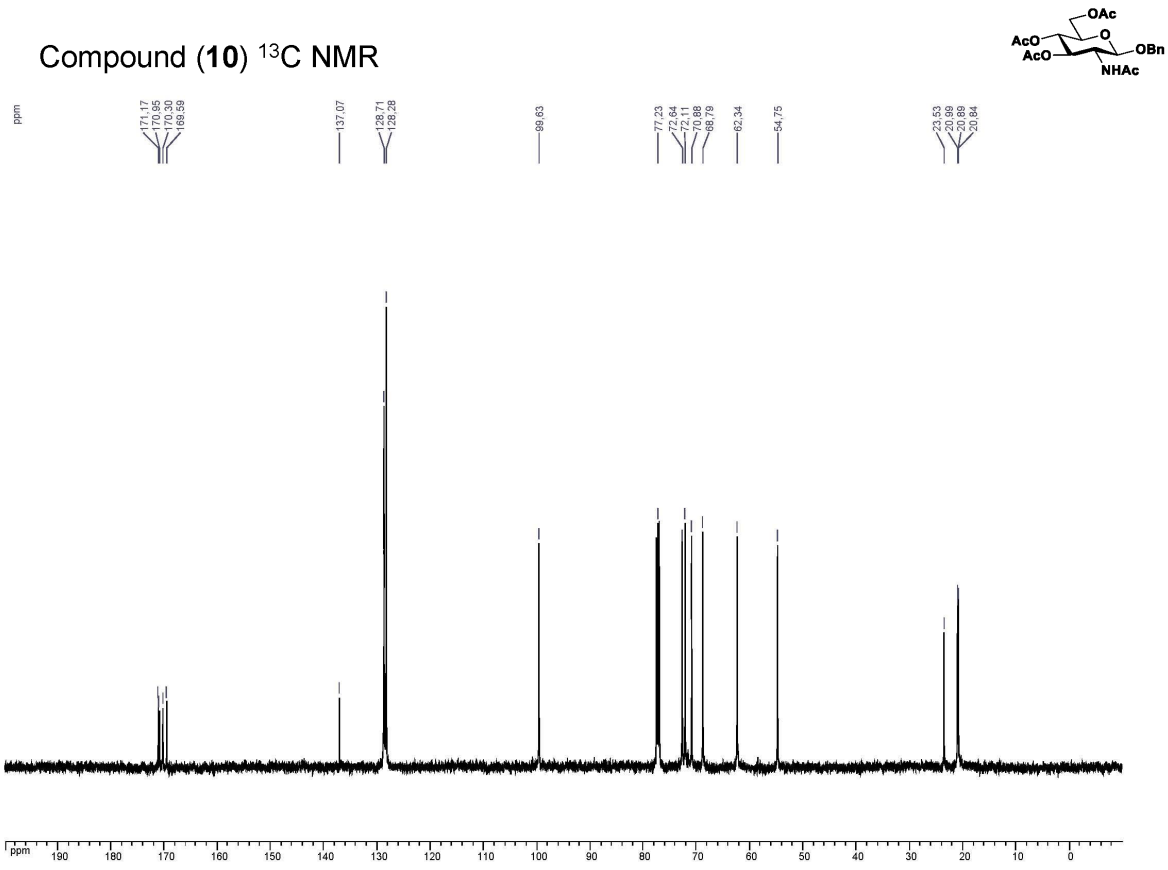
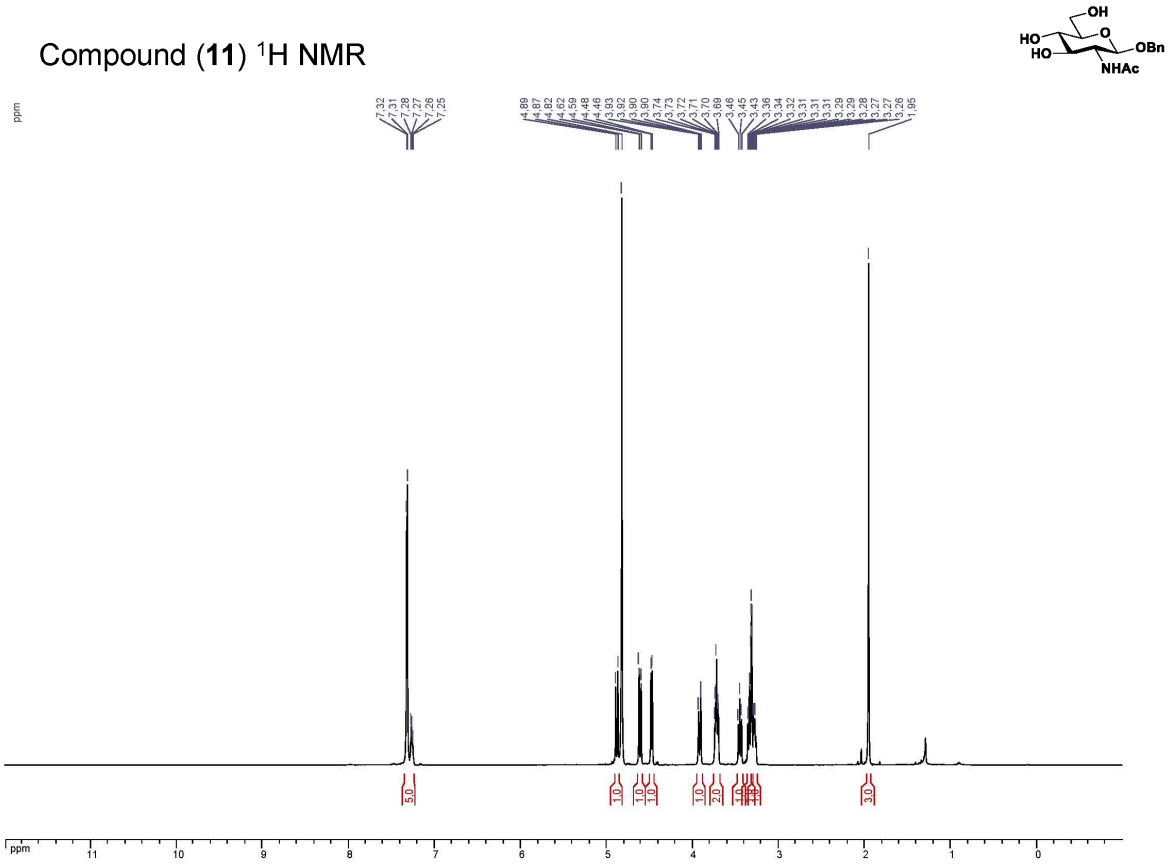
Compound (**10**) ^{1}H NMR



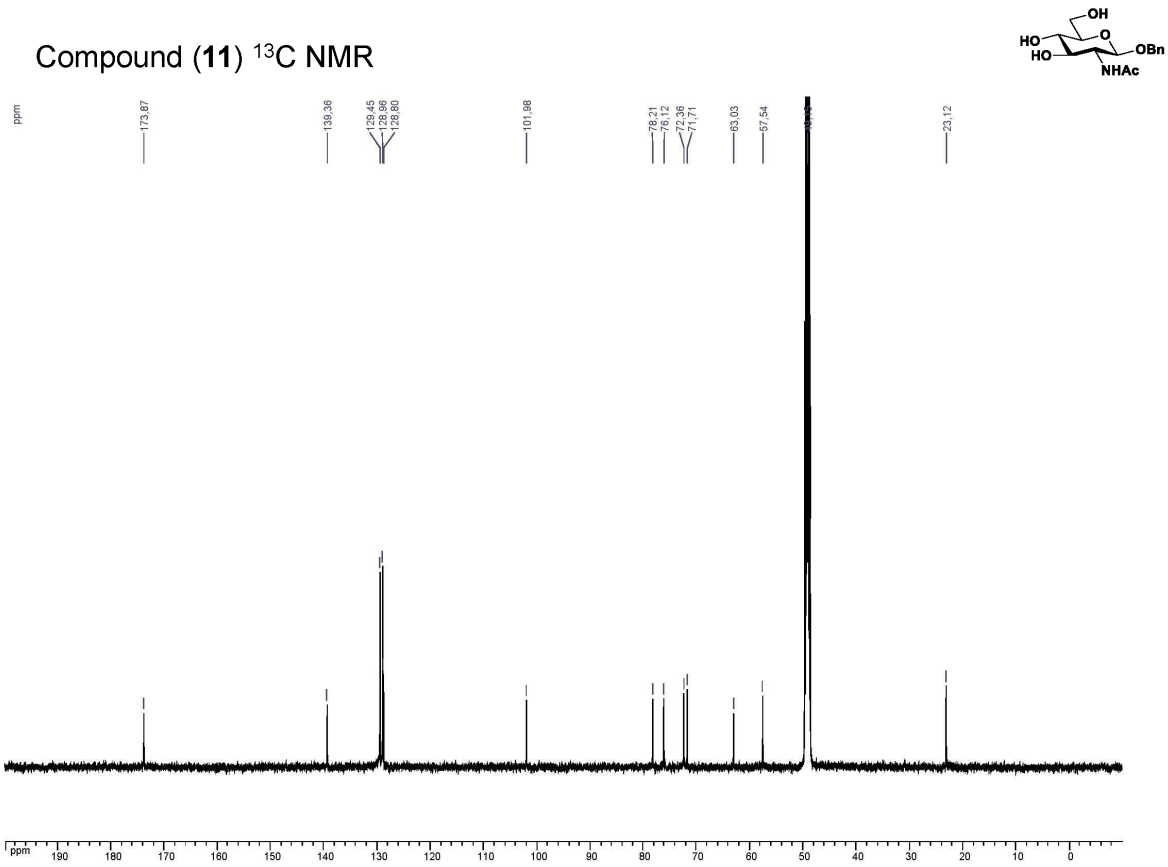
Compound (**10**) ^{13}C NMR



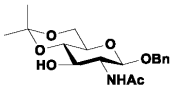
Compound (**11**) ^{1}H NMR

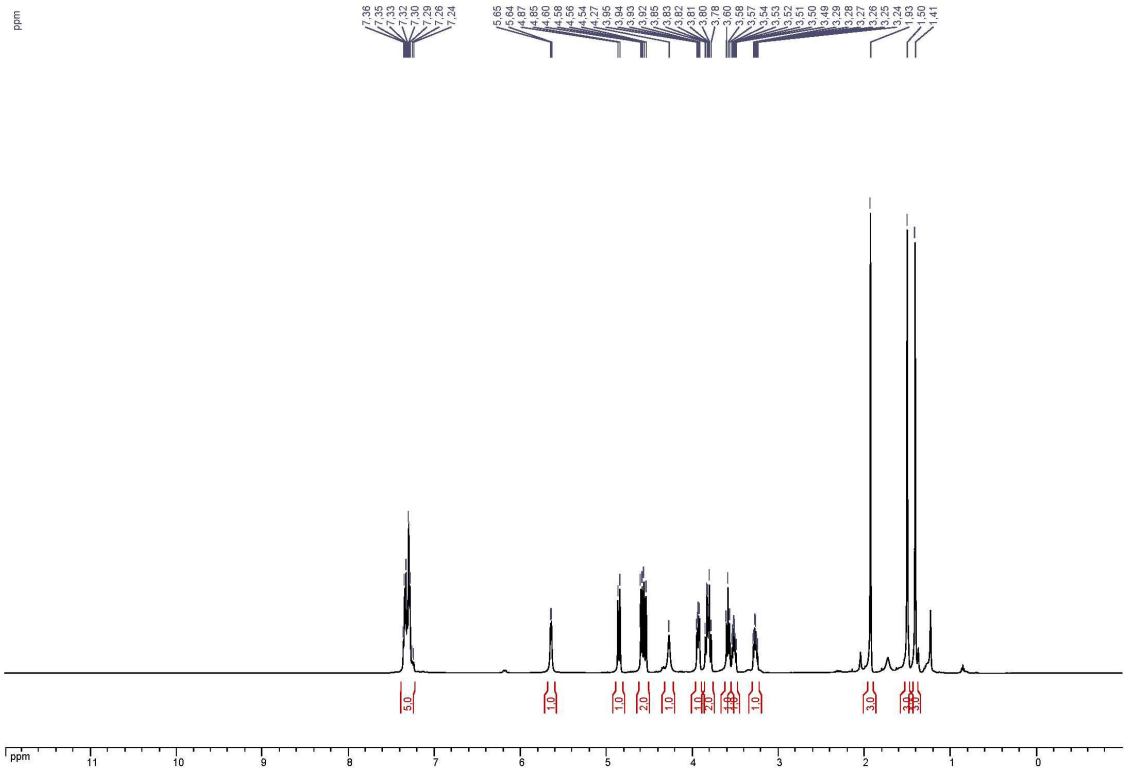


Compound (**11**) ^{13}C NMR

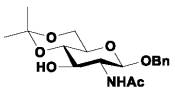


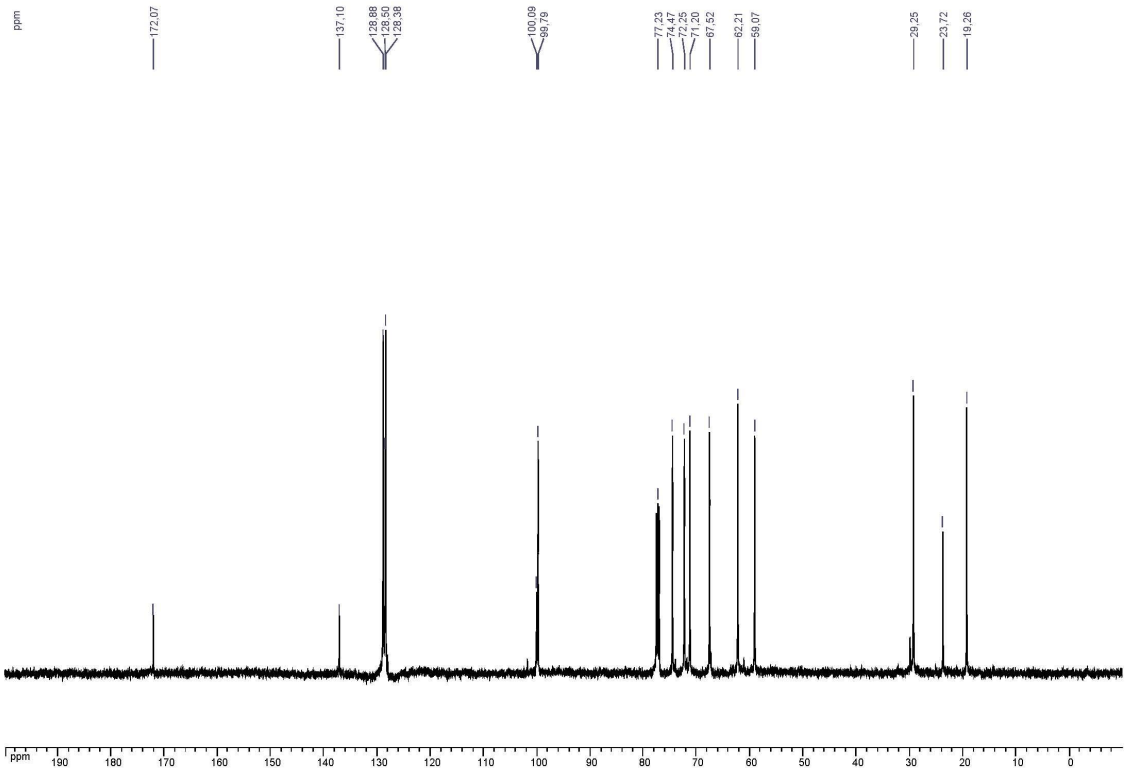
Compound (**12**) ^{1}H NMR



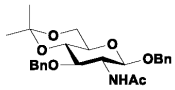


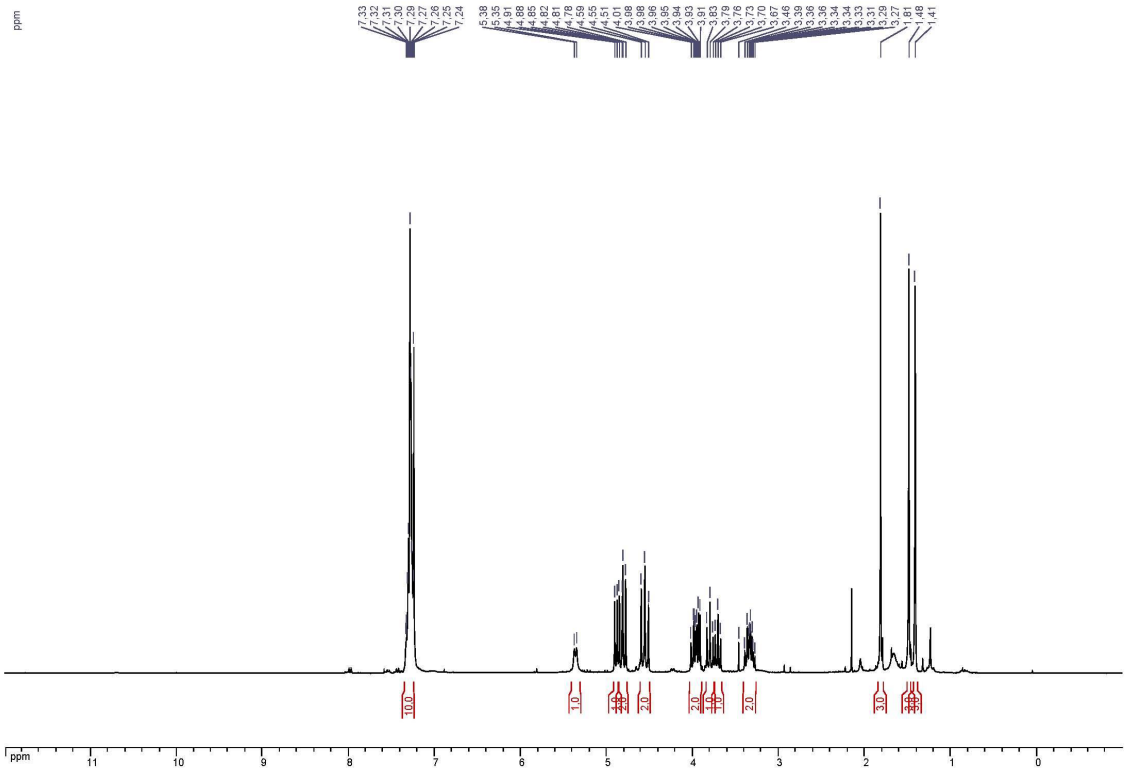
Compound (**12**) ^{13}C NMR



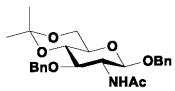


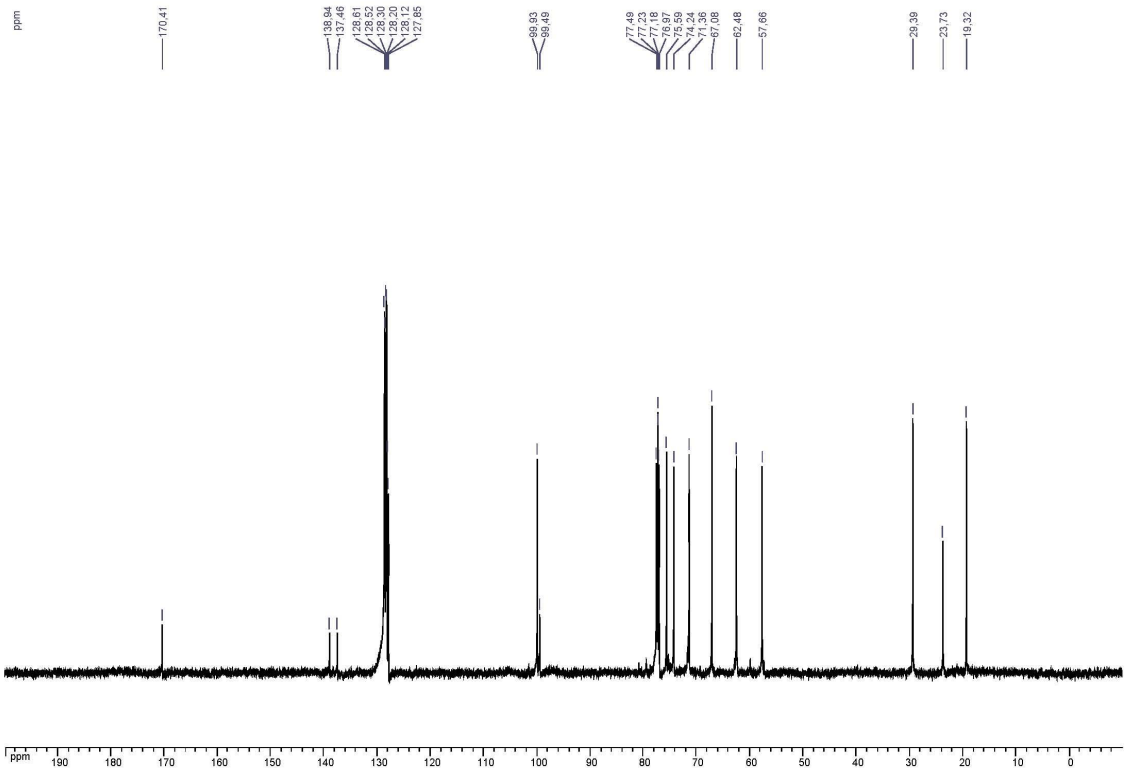
Compound (**13**) ^{1}H NMR



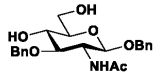


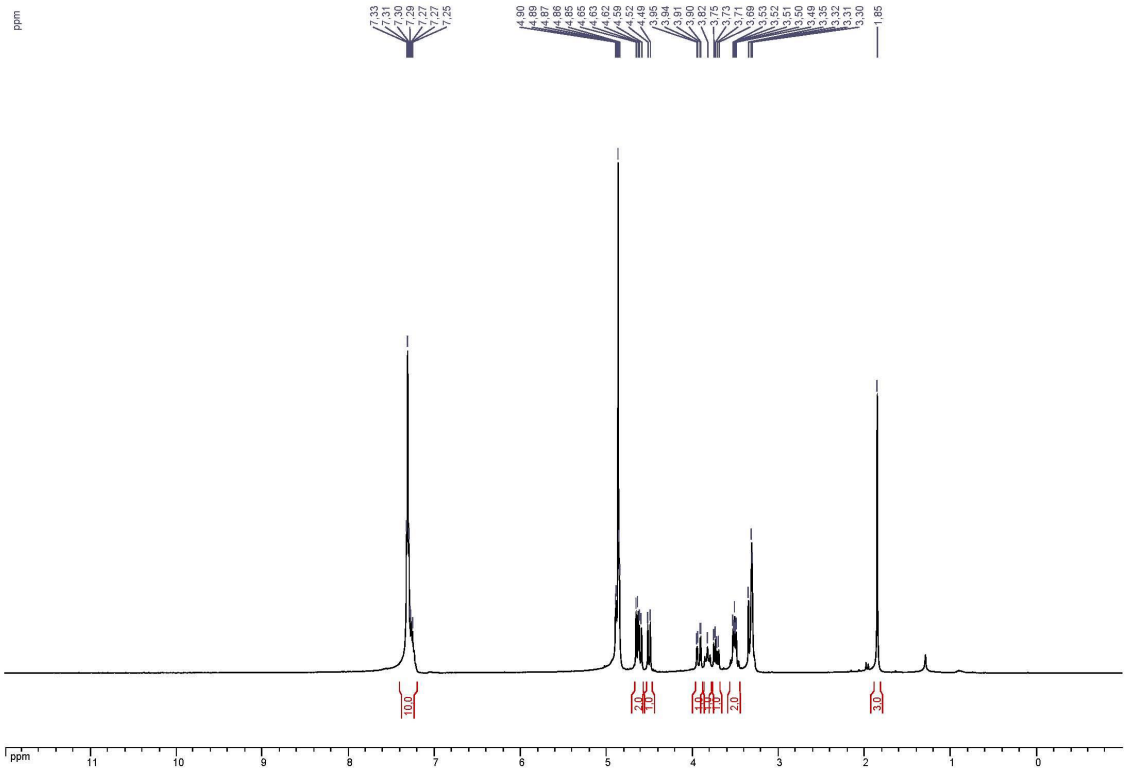
Compound (**13**) ^{13}C NMR



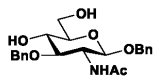


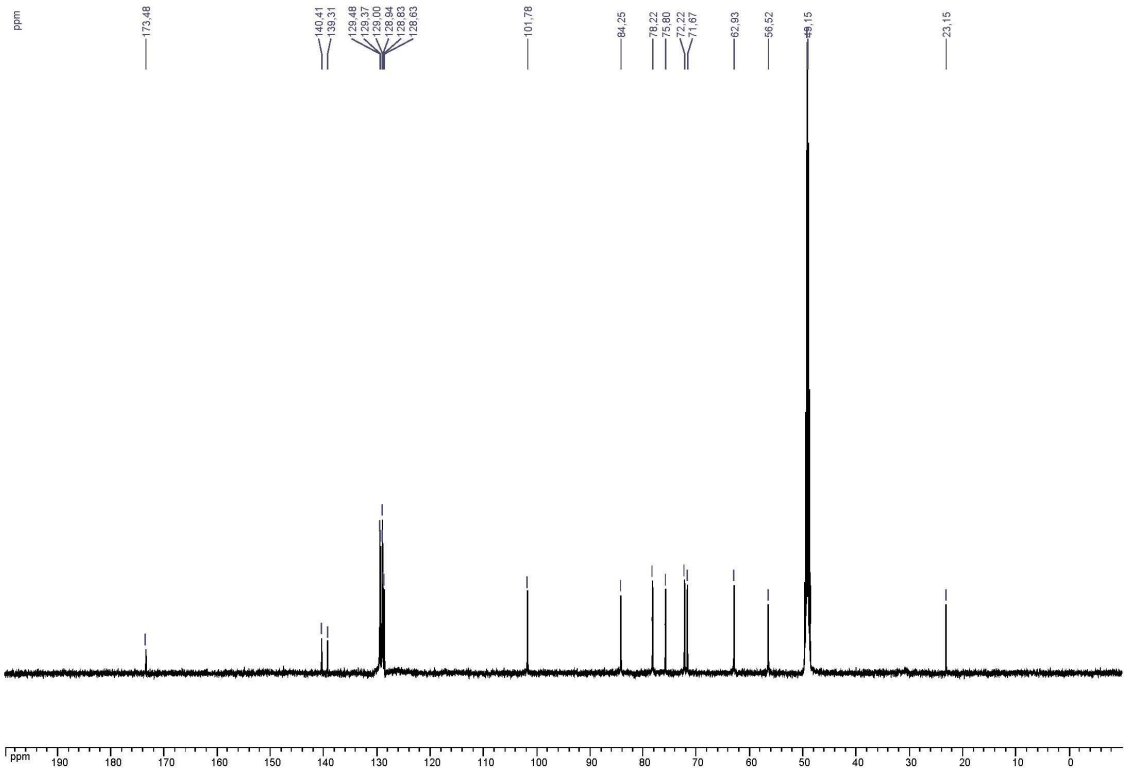
Compound (**14**) ^{1}H NMR



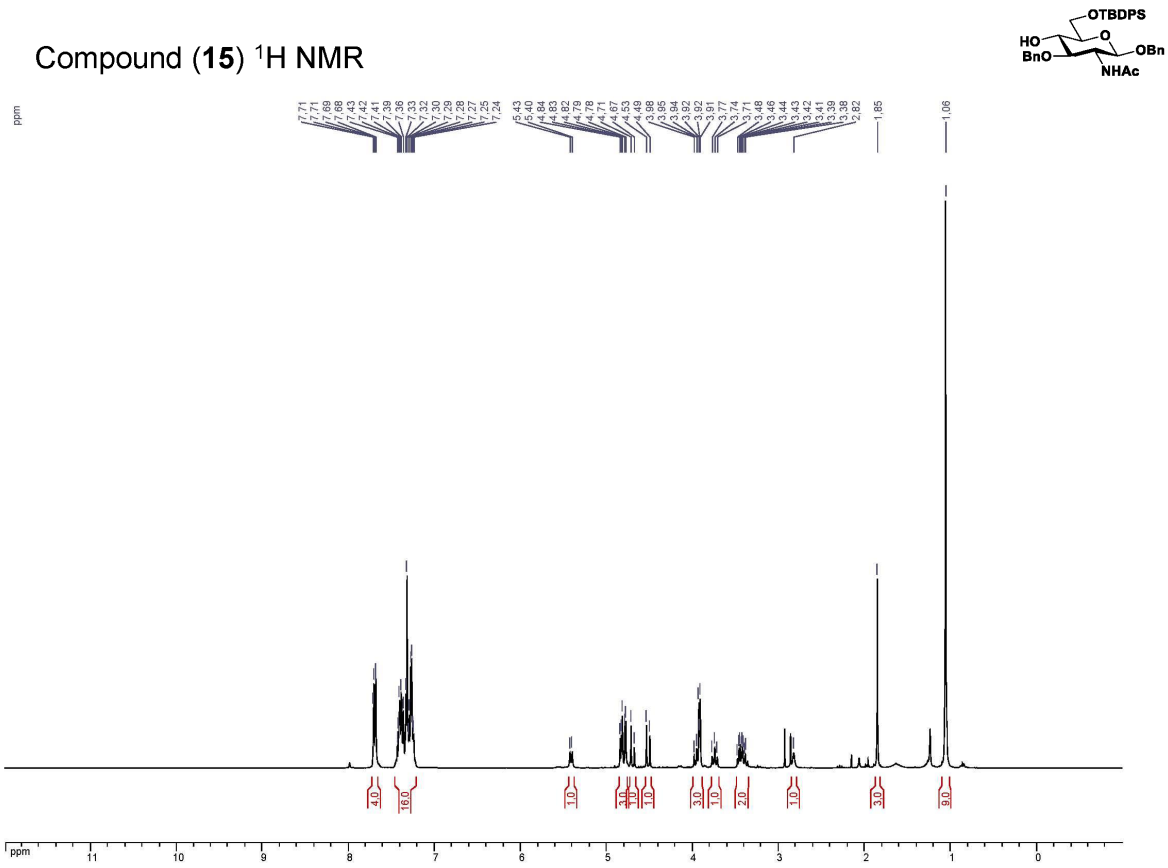


Compound (**14**) ^{13}C NMR

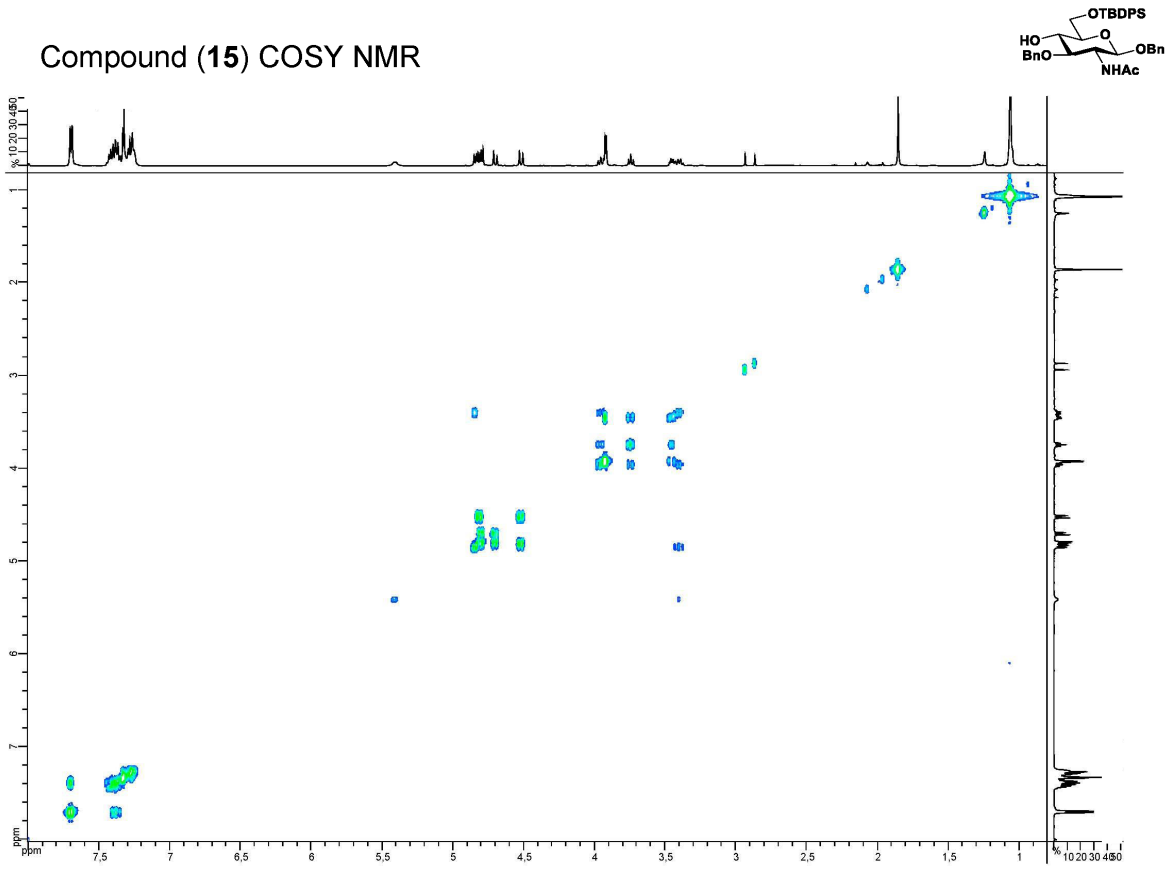




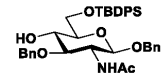
Compound (**15**) ^{1}H NMR

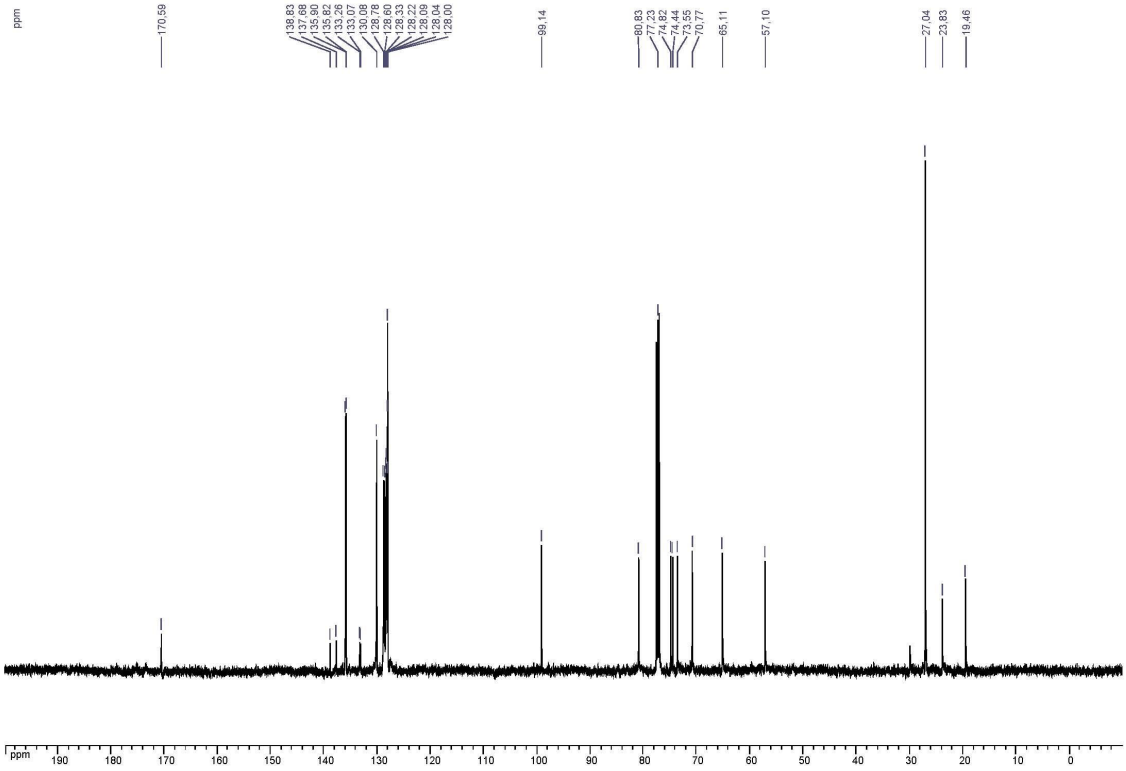


Compound (**15**) COSY NMR

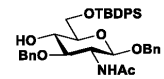


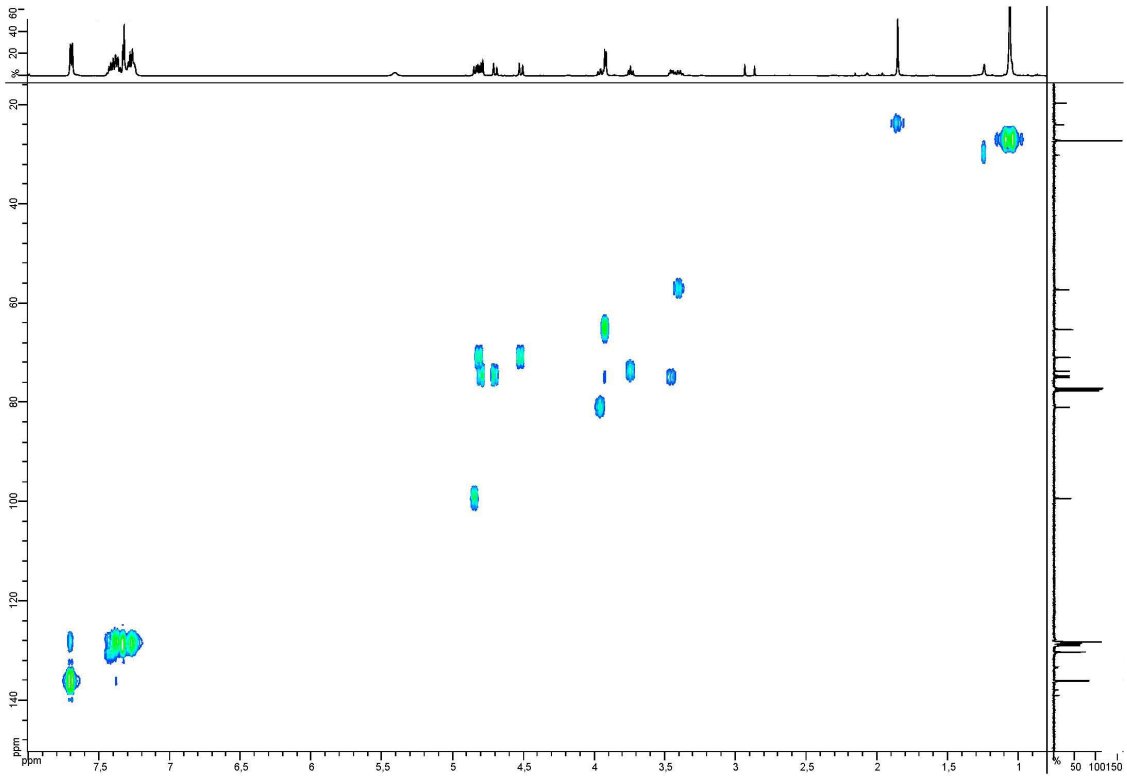
Compound (**15**) ^{13}C NMR



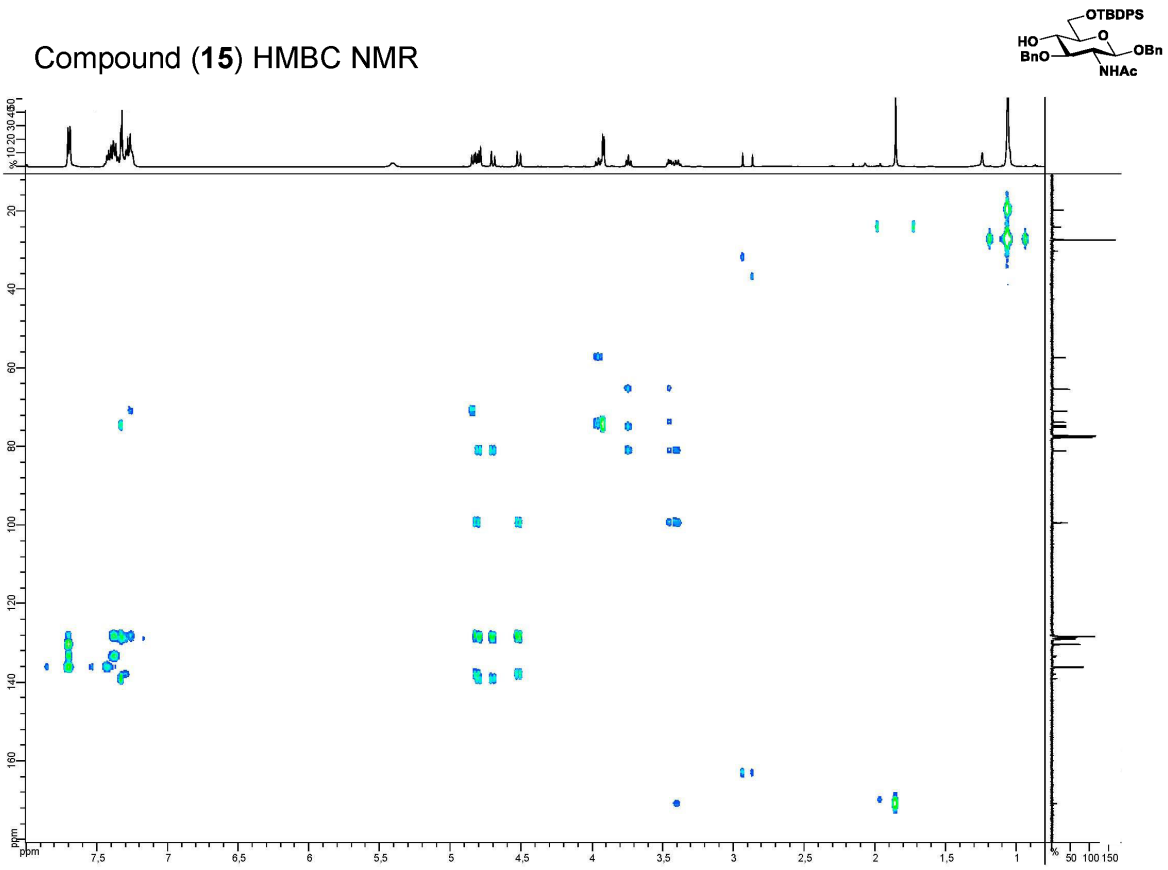


Compound (**15**) HSQC NMR

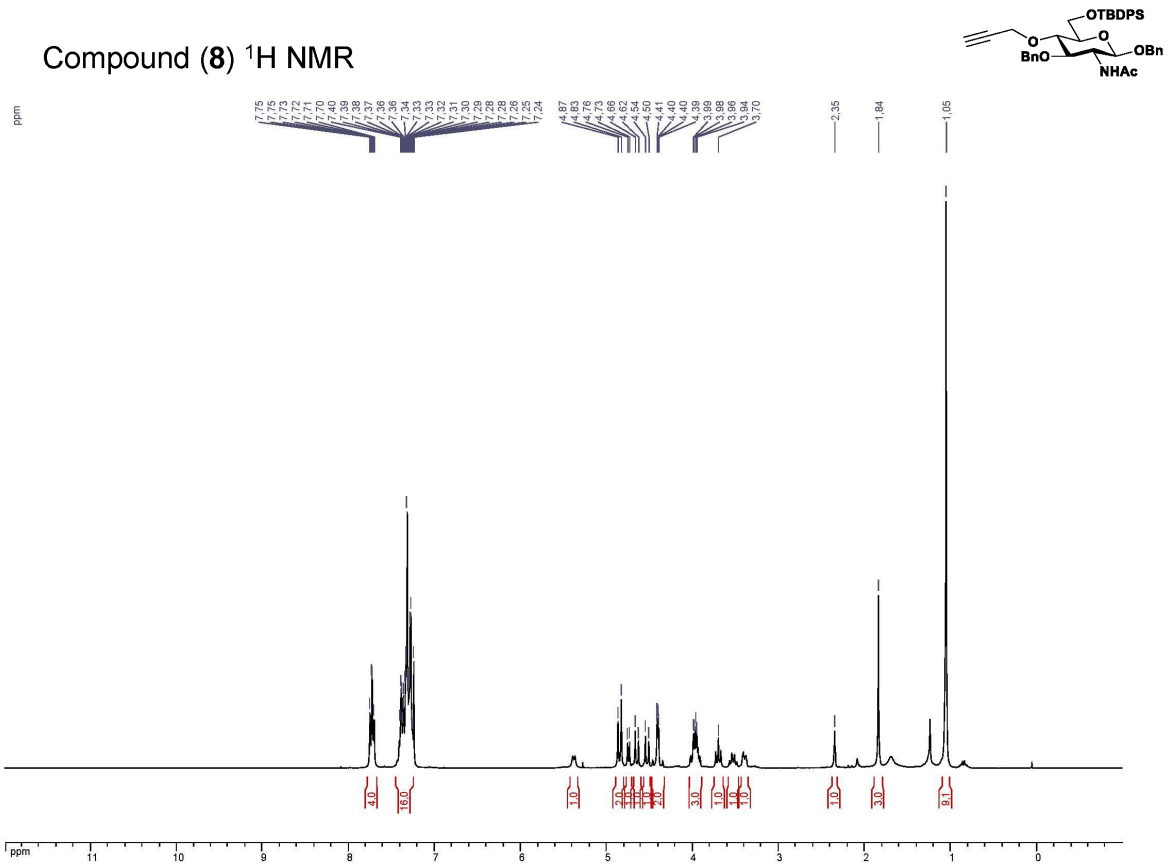




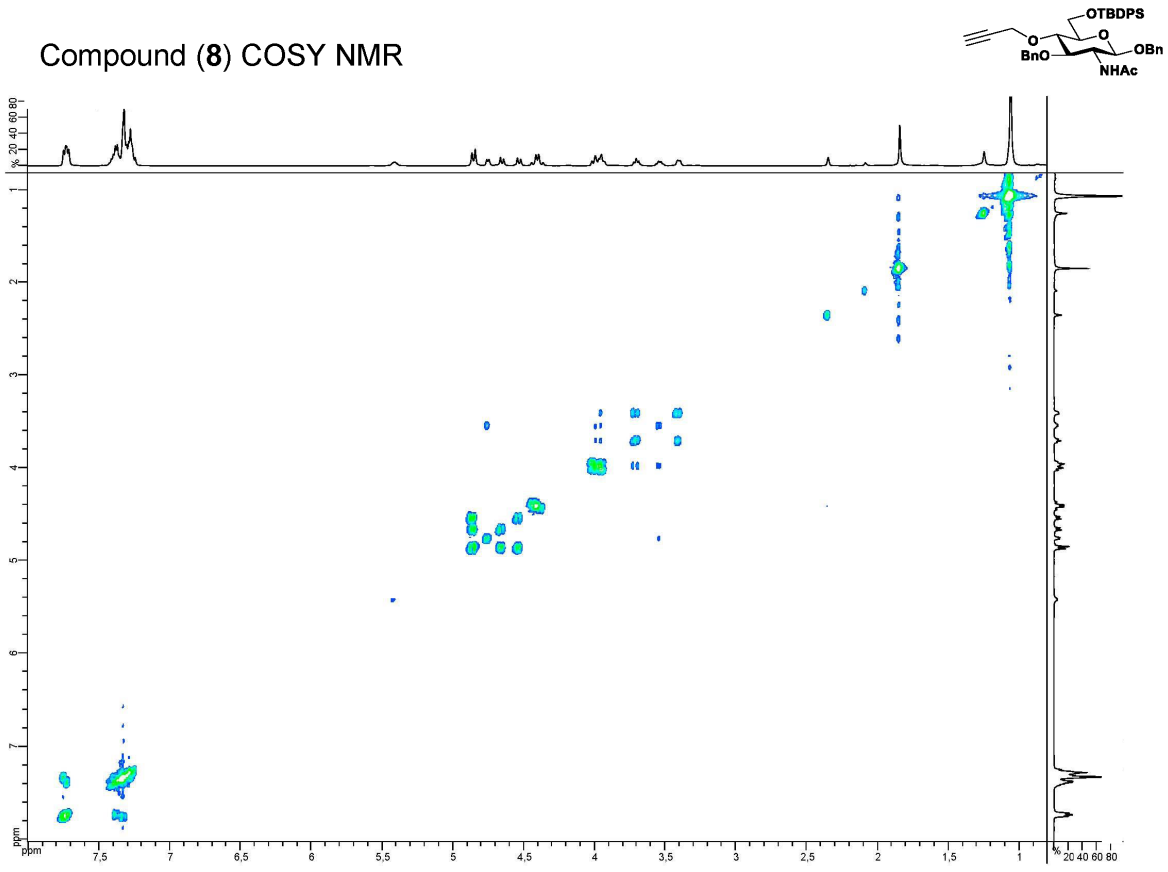
Compound (**15**) HMBC NMR



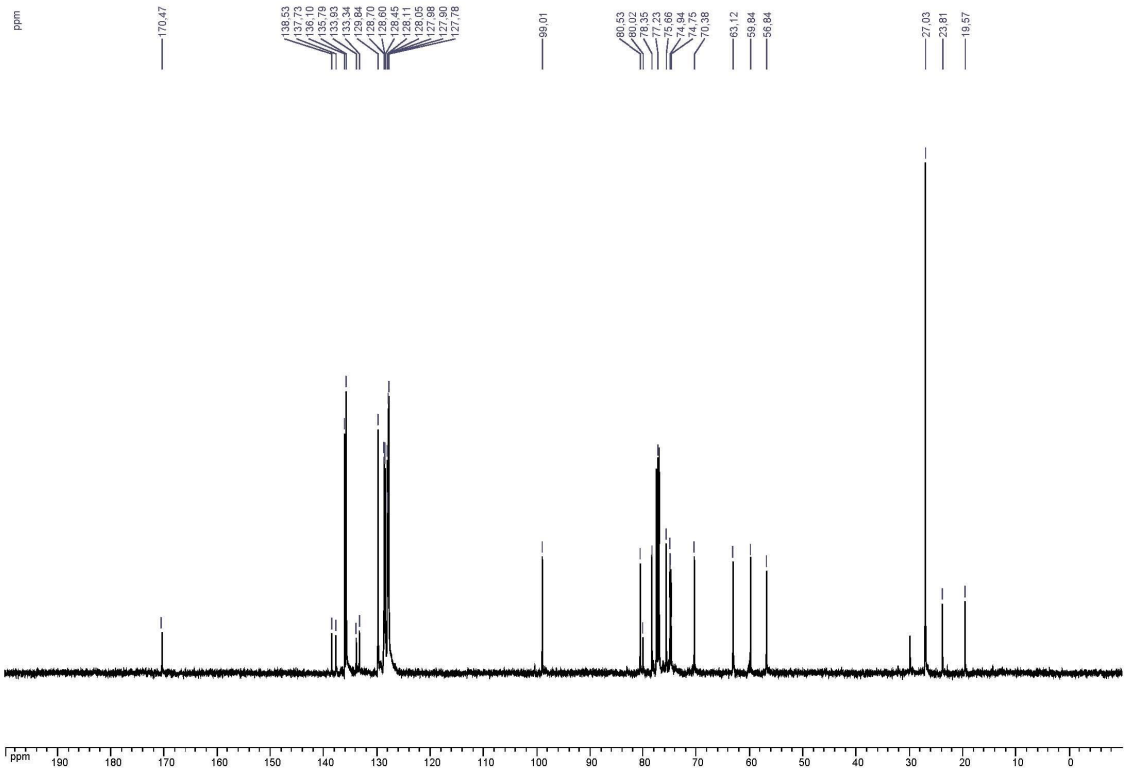
Compound (**8**) ^{1}H NMR



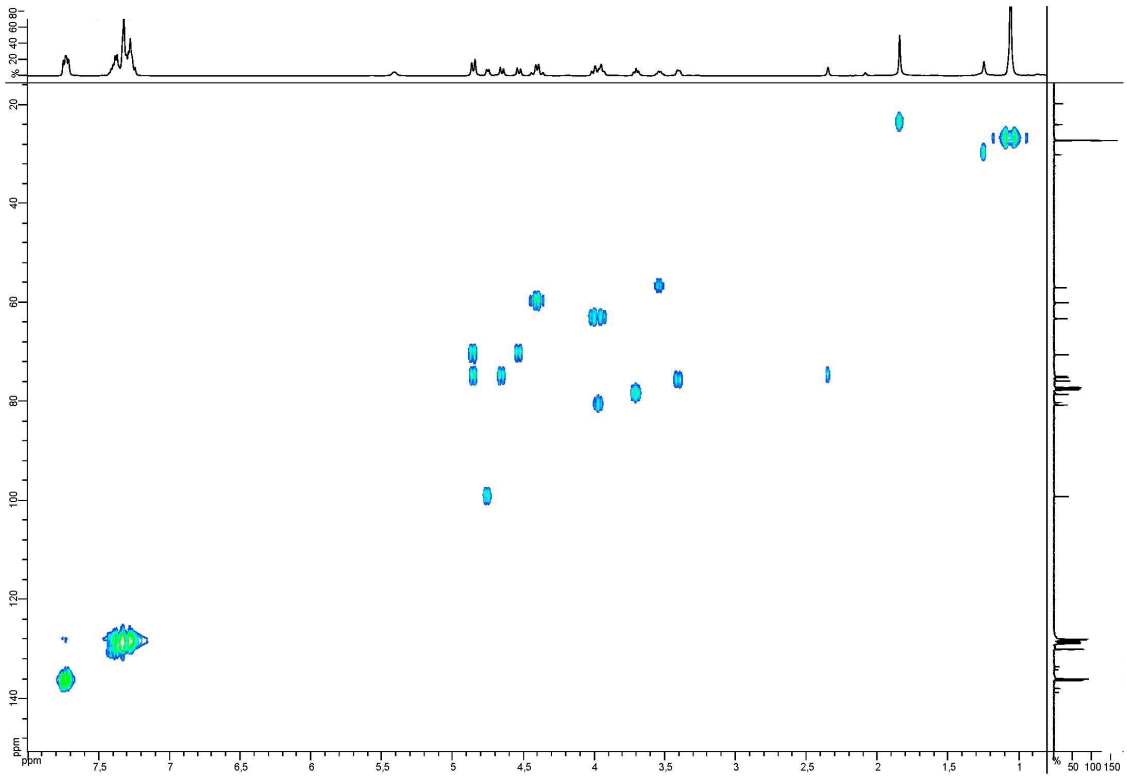
Compound (**8**) COSY NMR



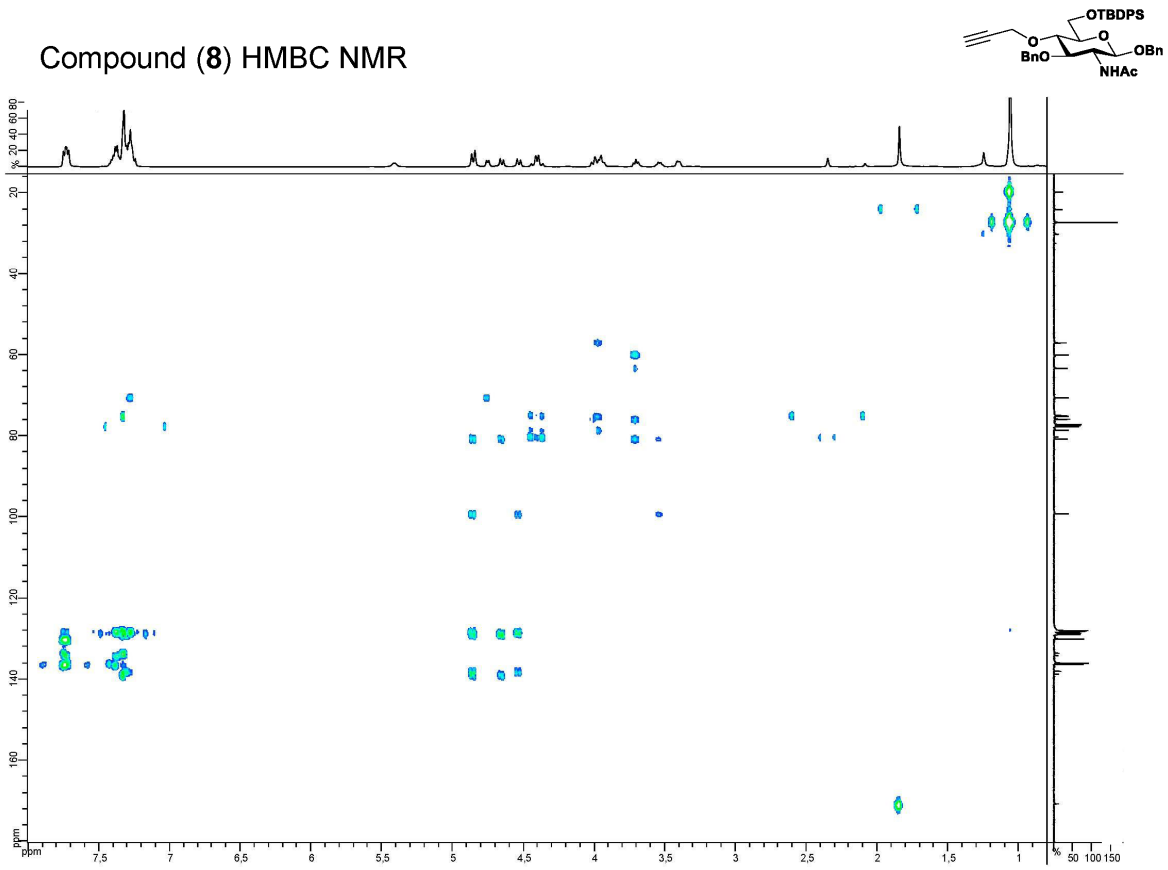
Compound (**8**) ^{13}C NMR



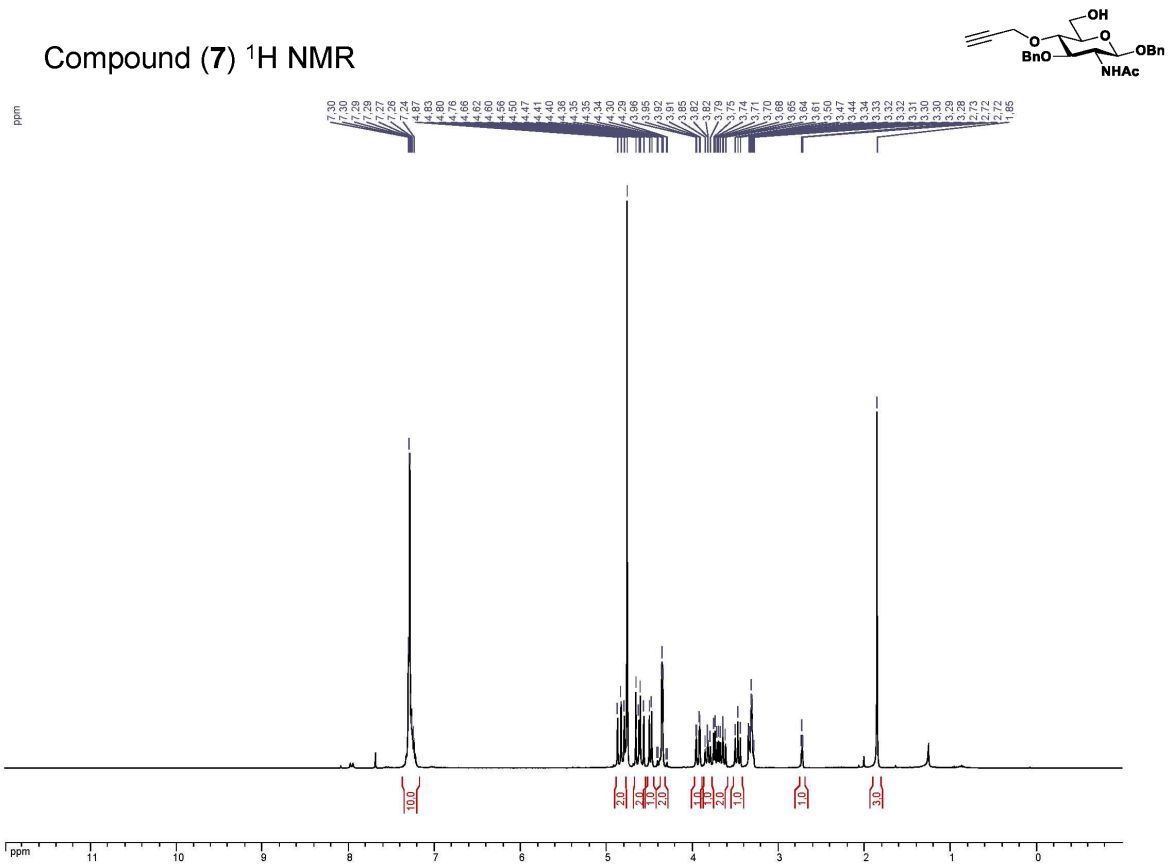
Compound (**8**) HSQC NMR



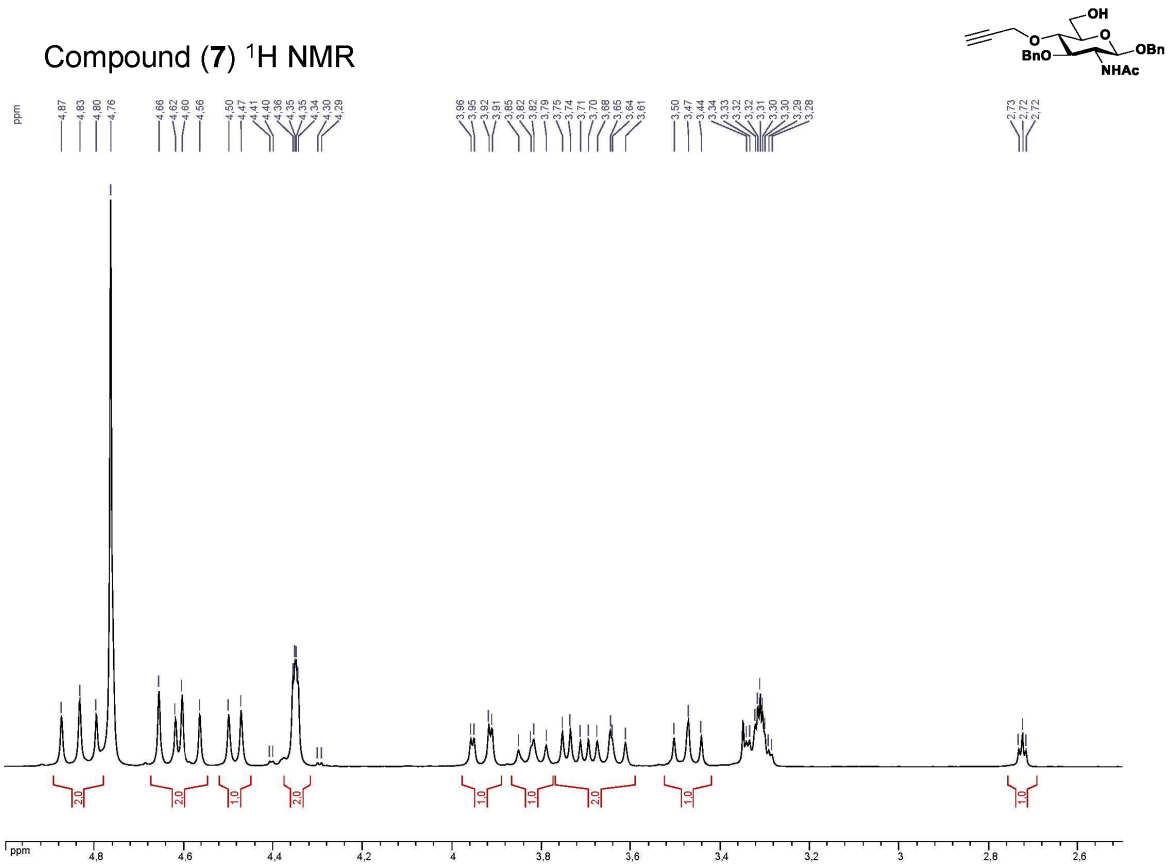
Compound (**8**) HMBC NMR



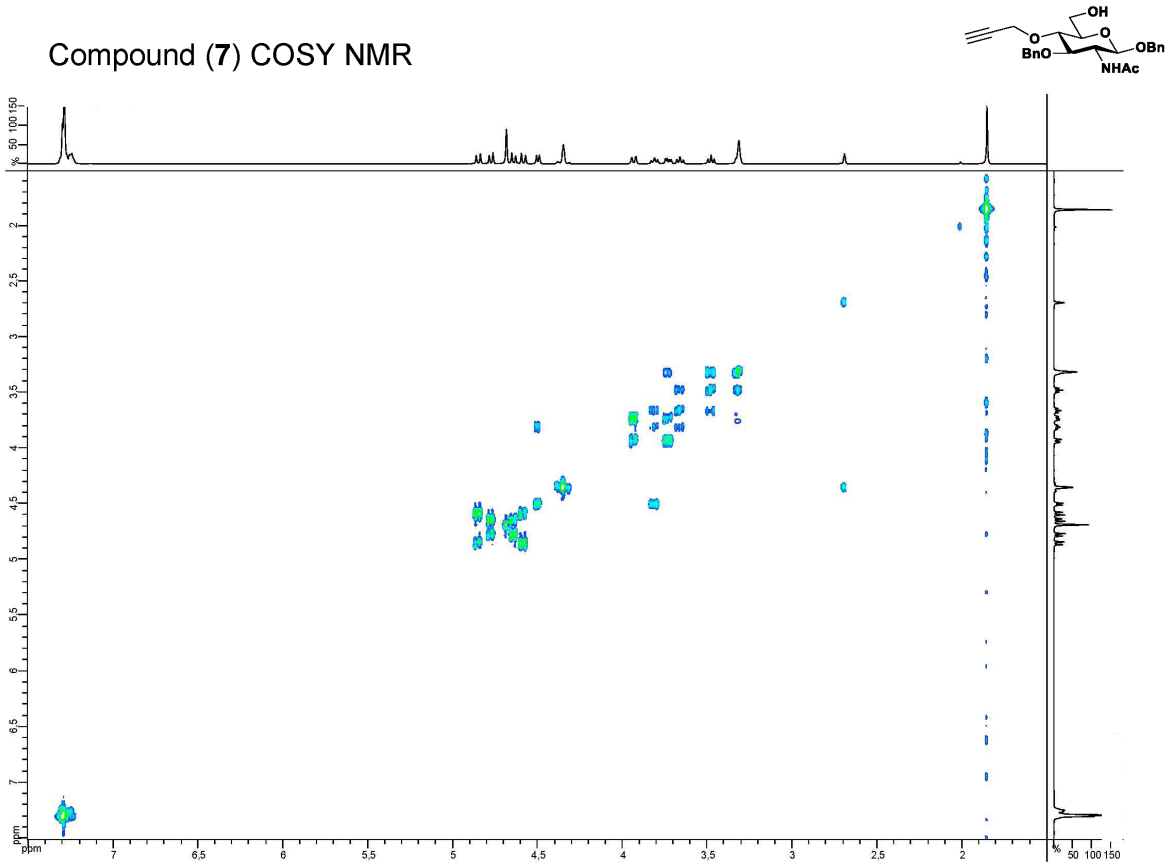
Compound (**7**) ^{1}H NMR



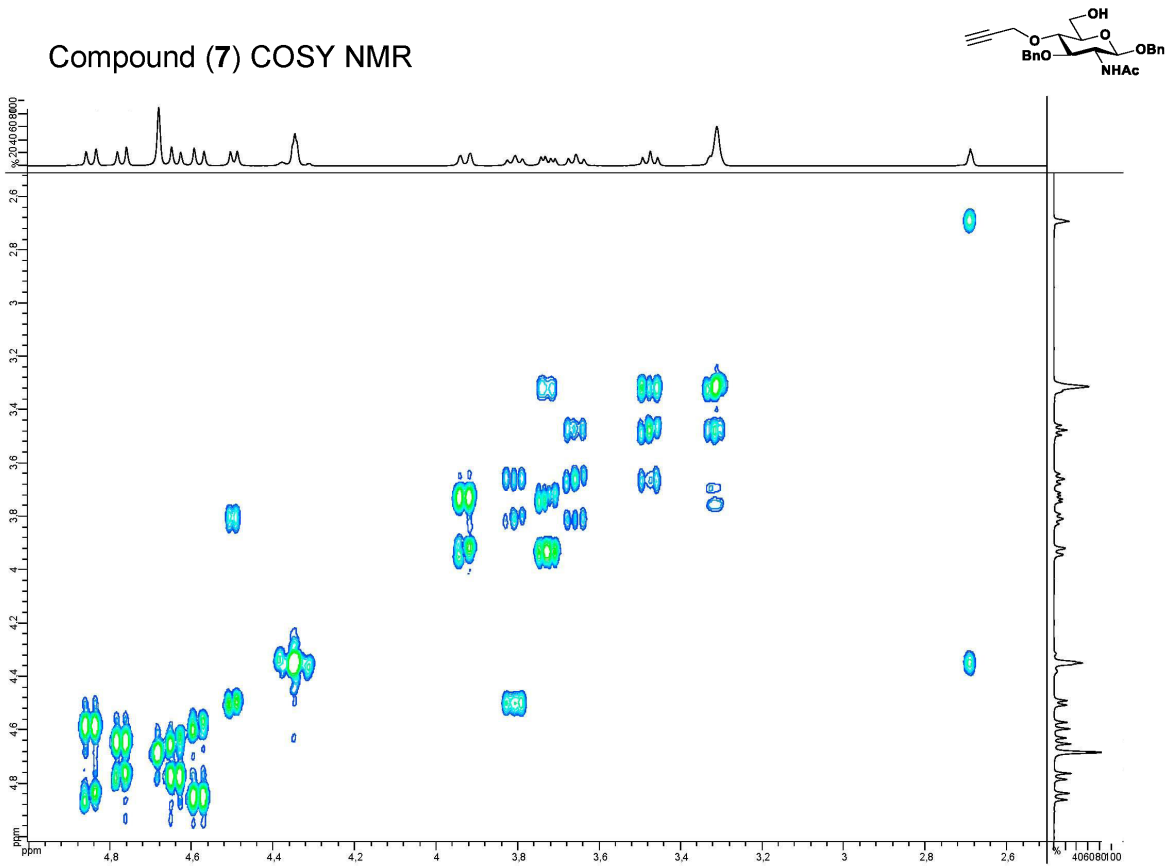
Compound (**7**) ^{1}H NMR



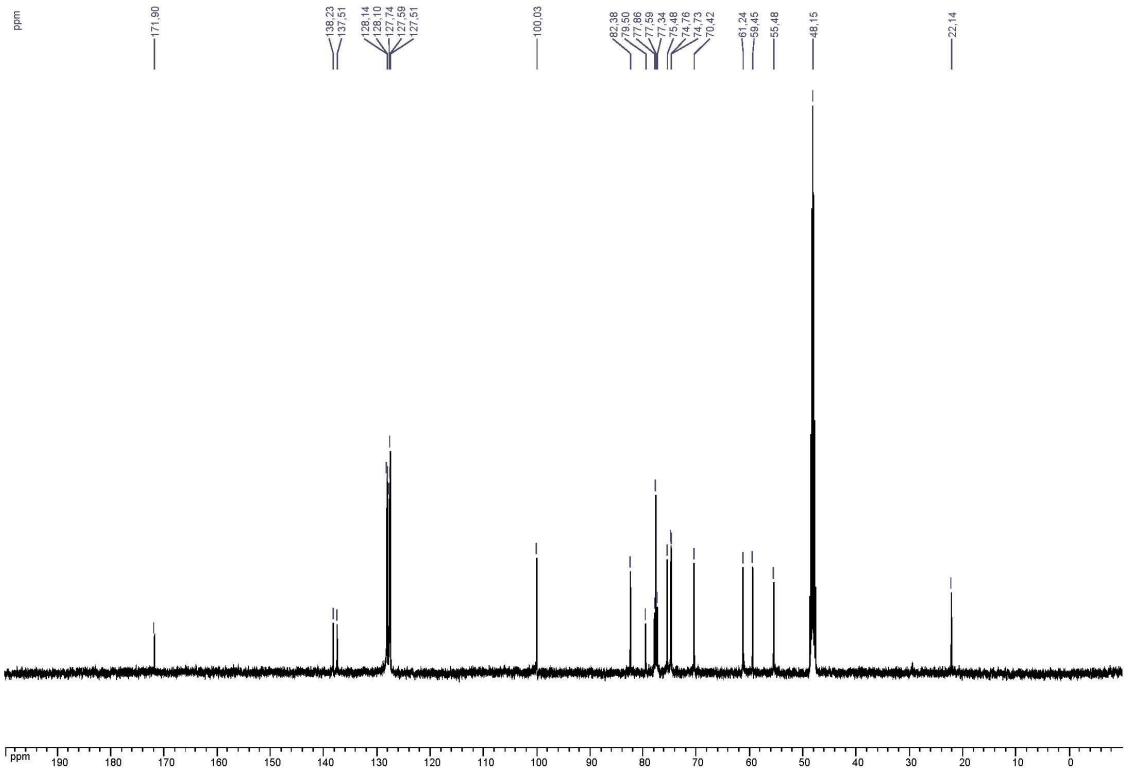
Compound (**7**) COSY NMR



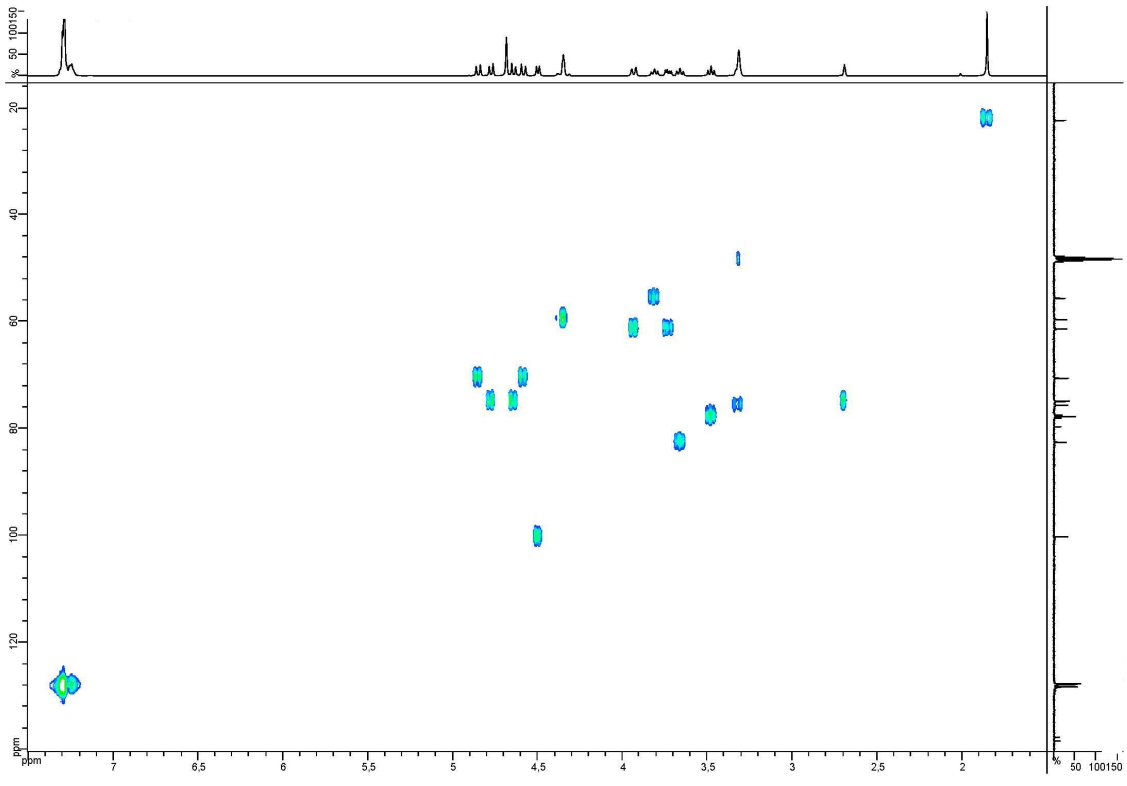
Compound (**7**) COSY NMR



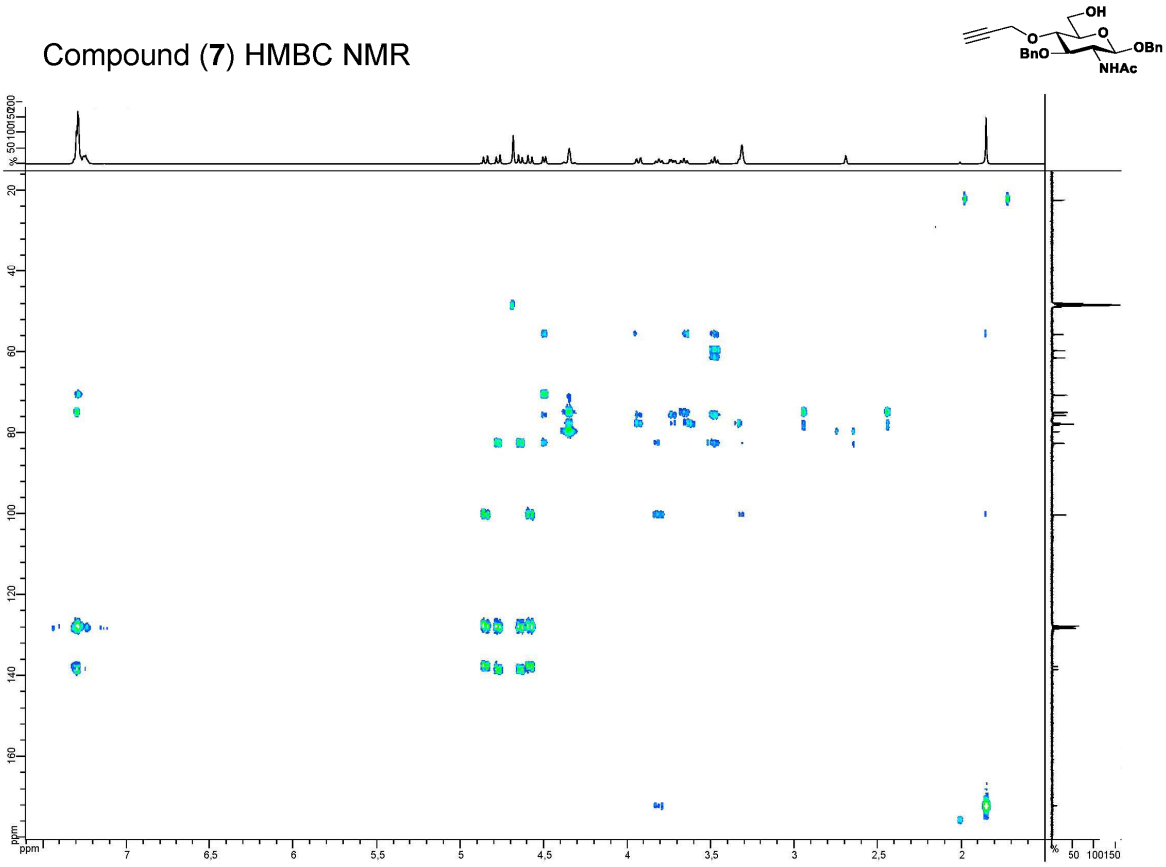
Compound (**7**) ^{13}C NMR



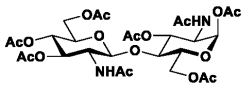
Compound (**7**) HSQC NMR

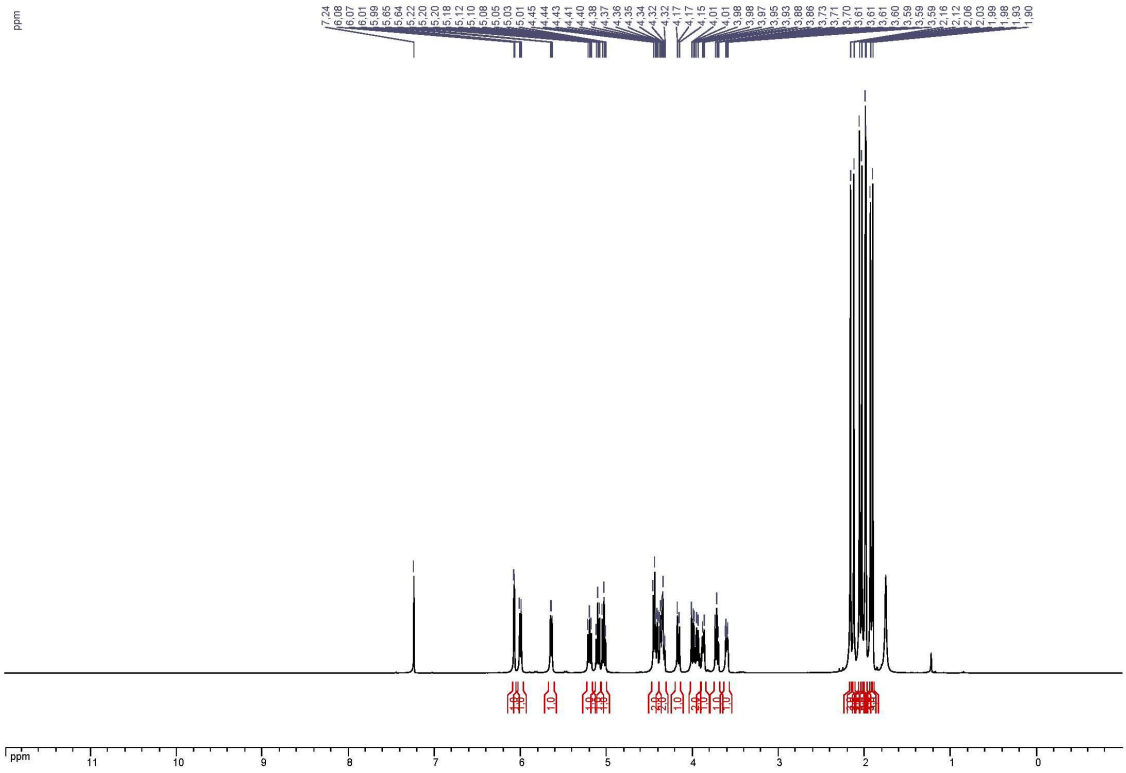


Compound (**7**) HMBC NMR

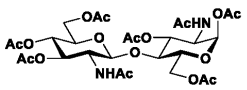


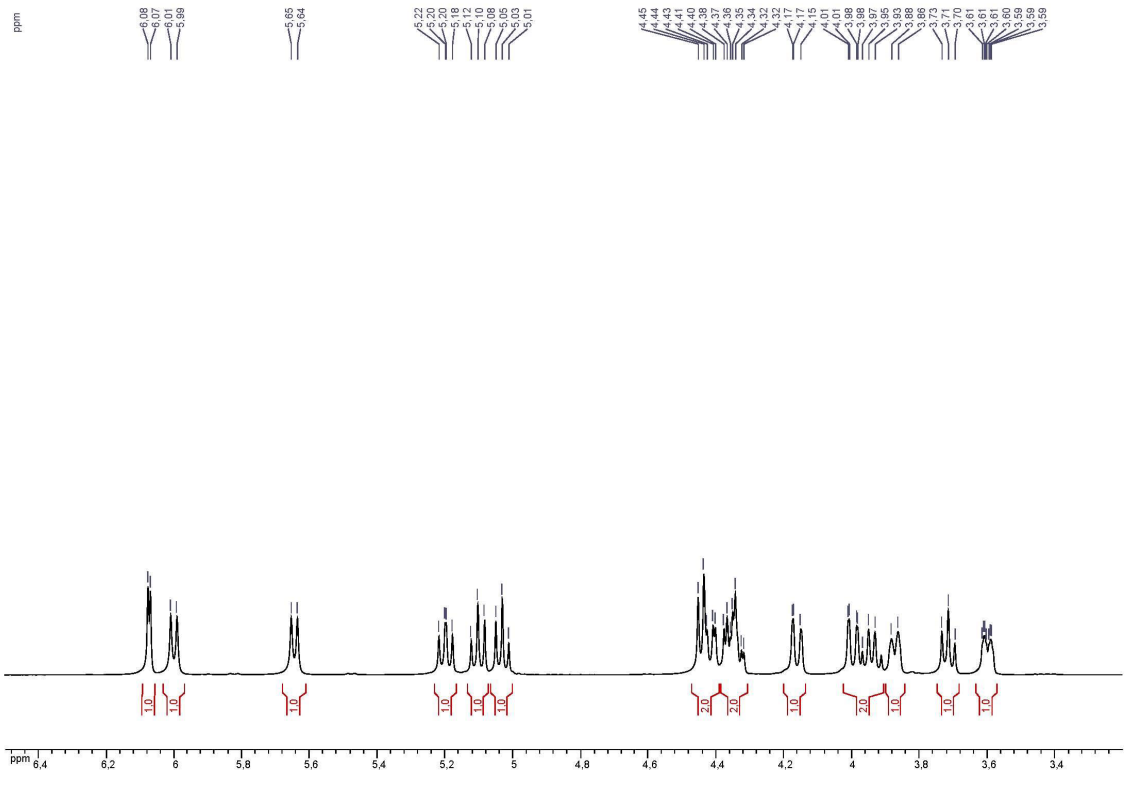
Compound (**S1**) ^{1}H NMR



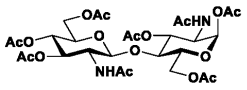


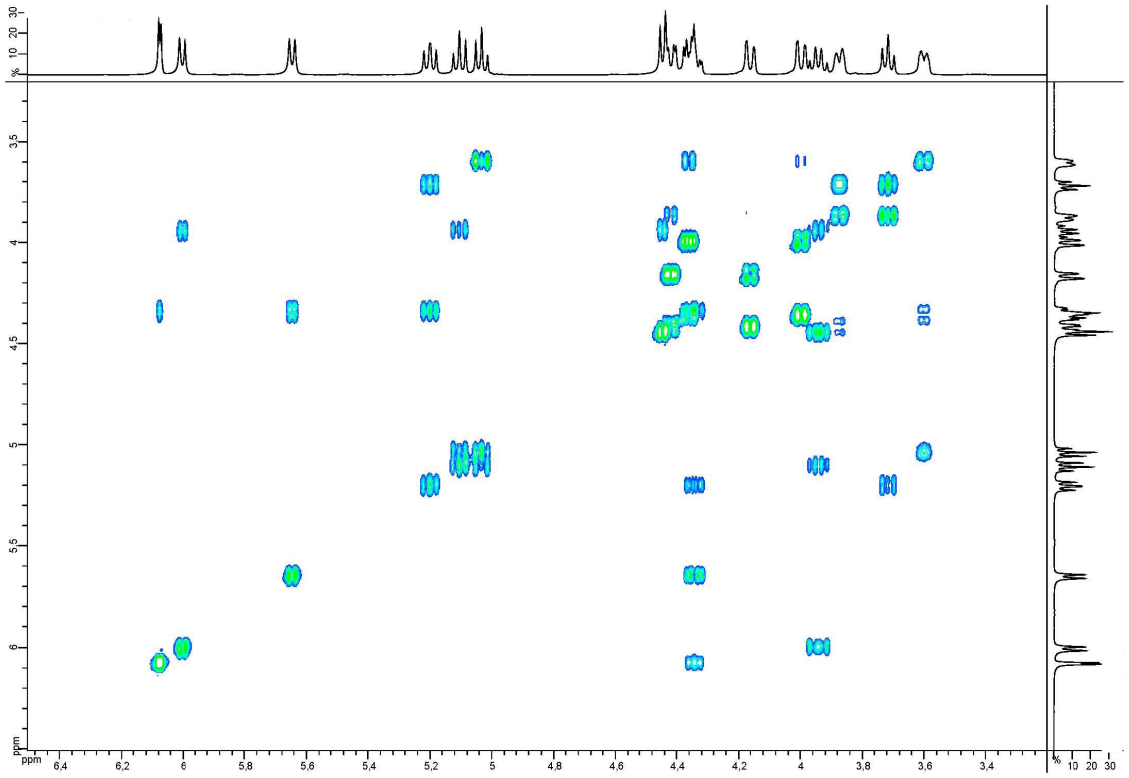
Compound (**S1**) ^{1}H NMR



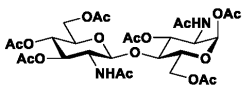


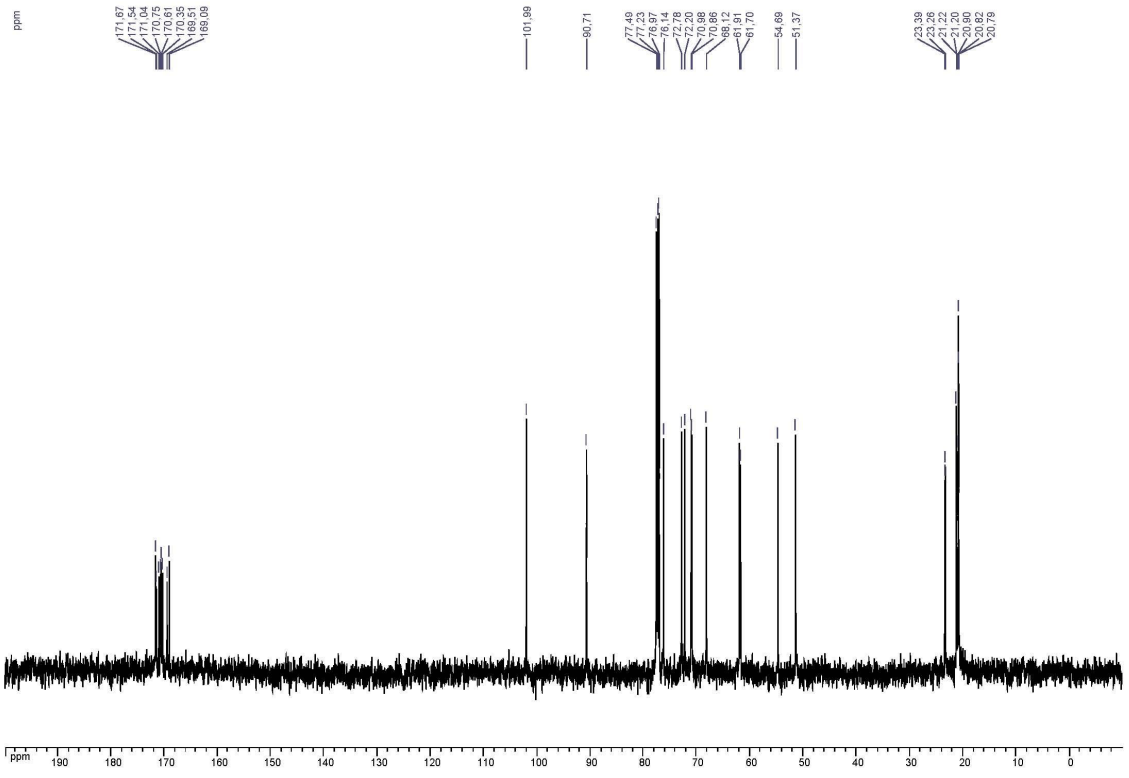
Compound (**S1**) COSY NMR



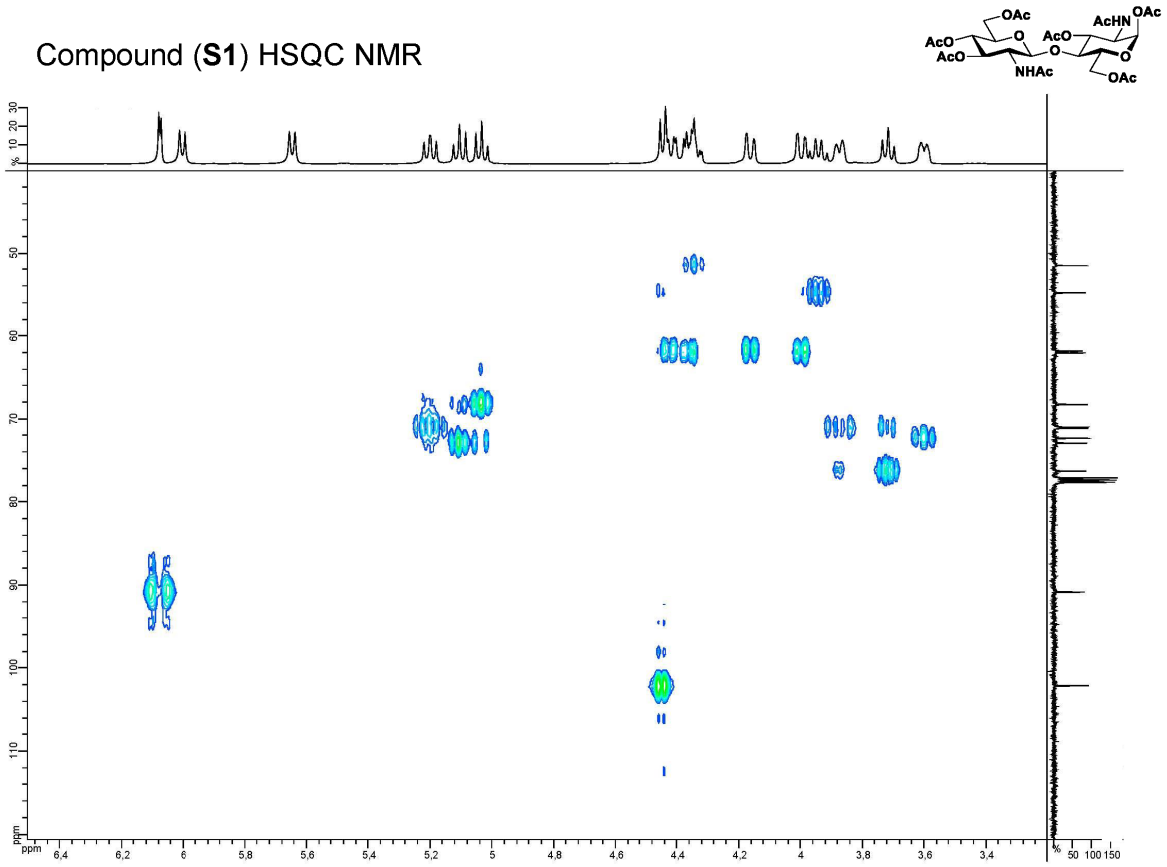


Compound (**S1**) ^{13}C NMR

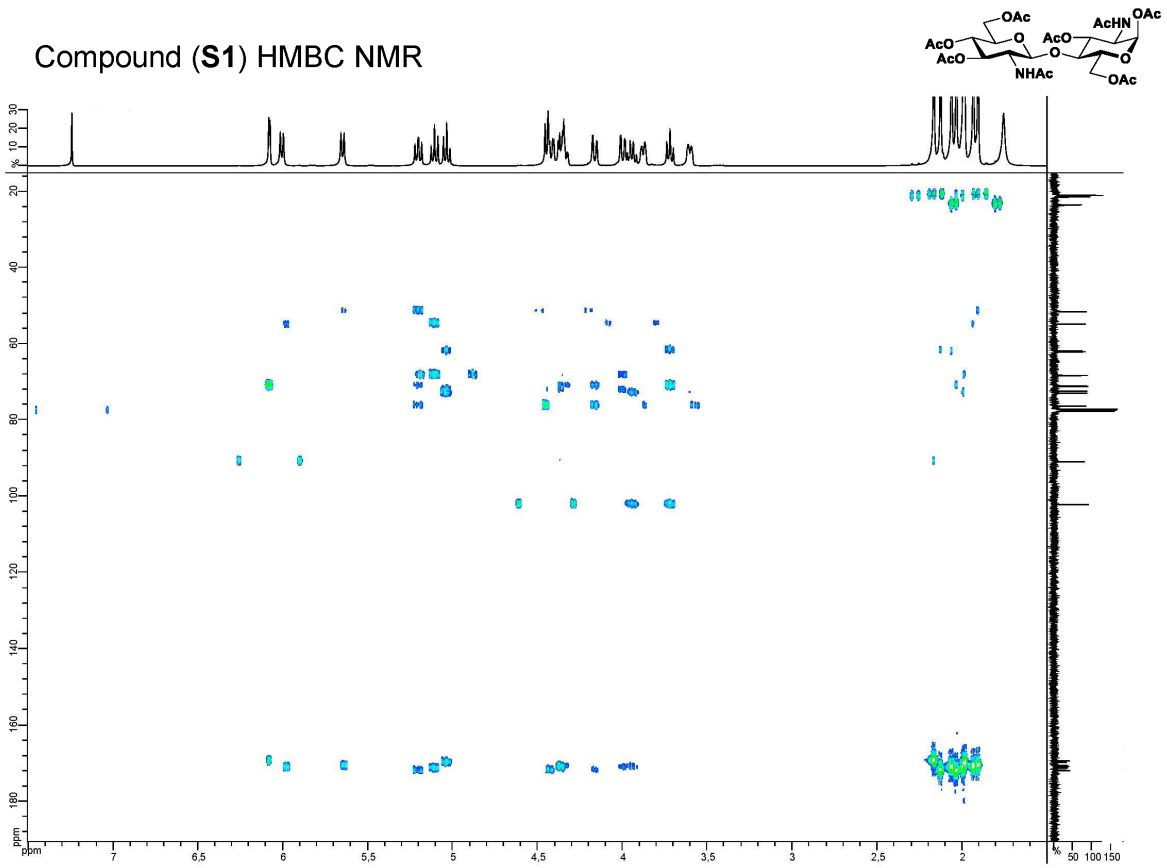




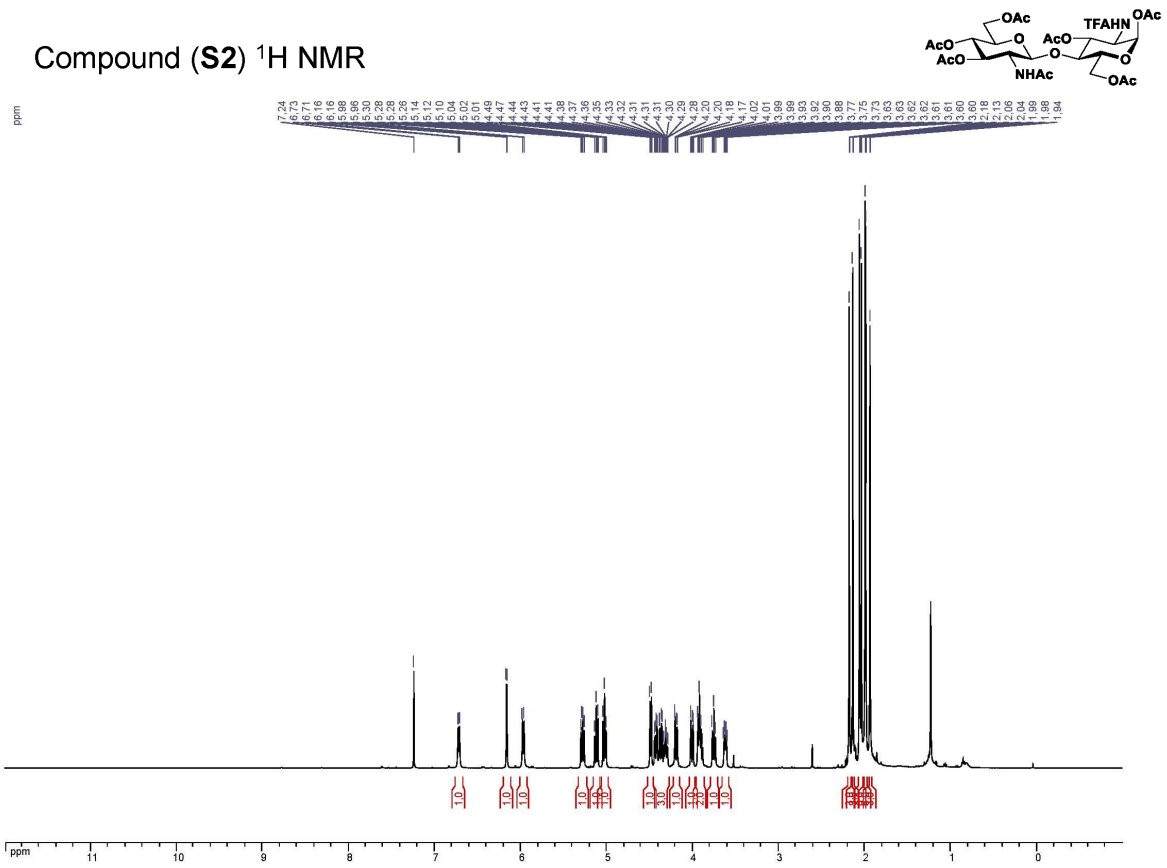
Compound (**S1**) HSQC NMR



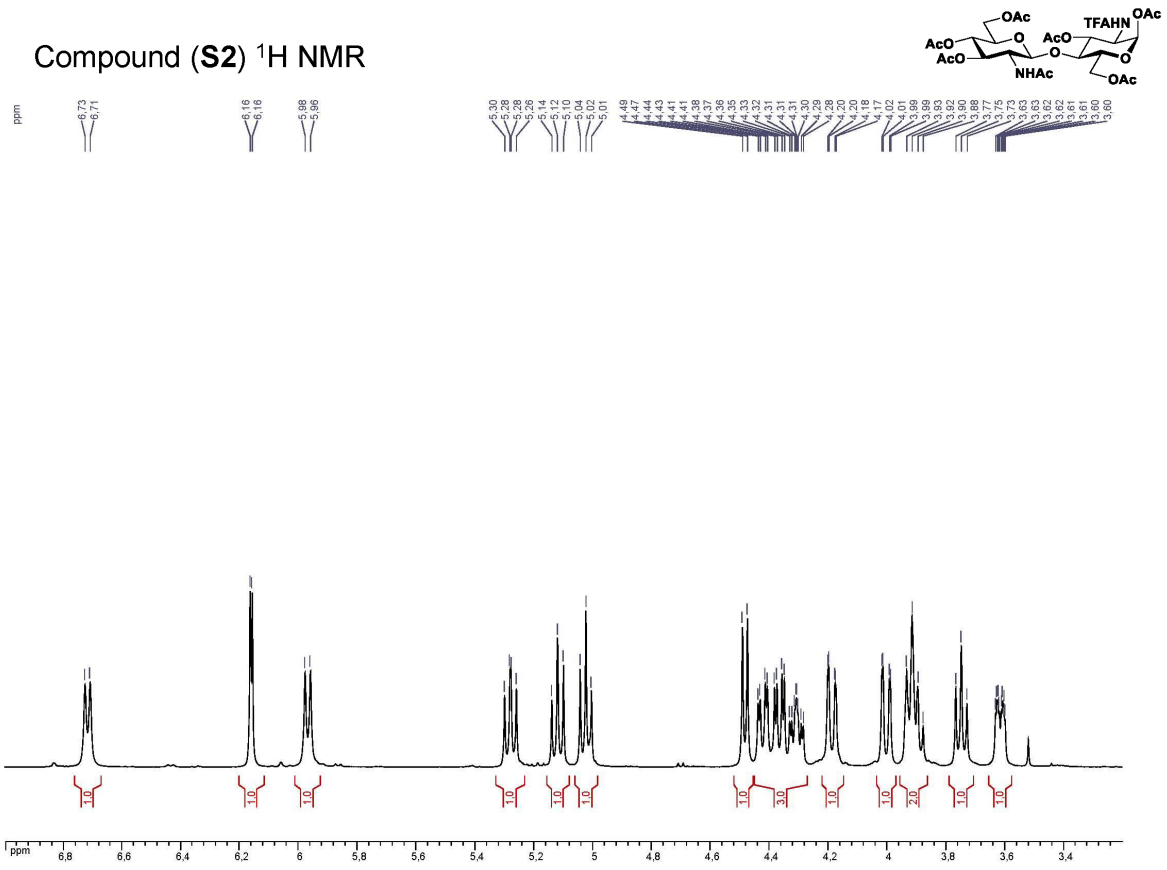
Compound (**S1**) HMBC NMR



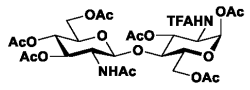
Compound (**S2**) ^{1}H NMR

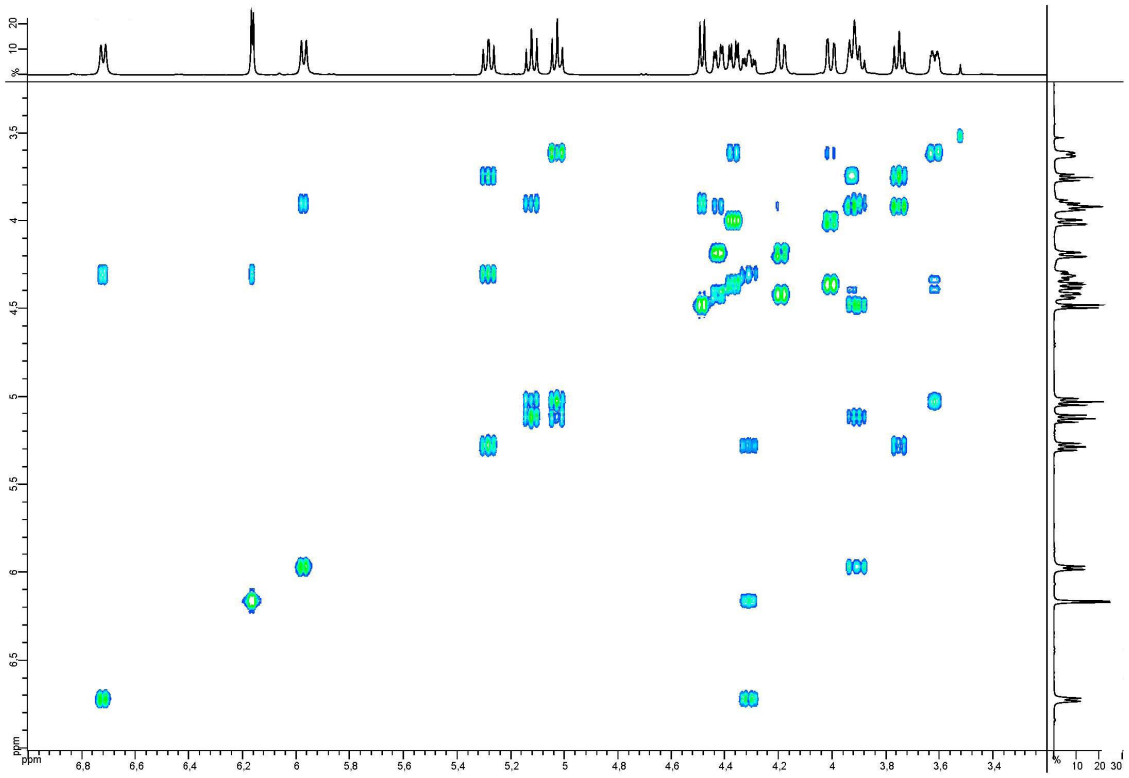


Compound (**S2**) ^{1}H NMR

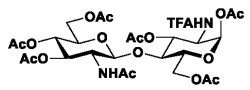


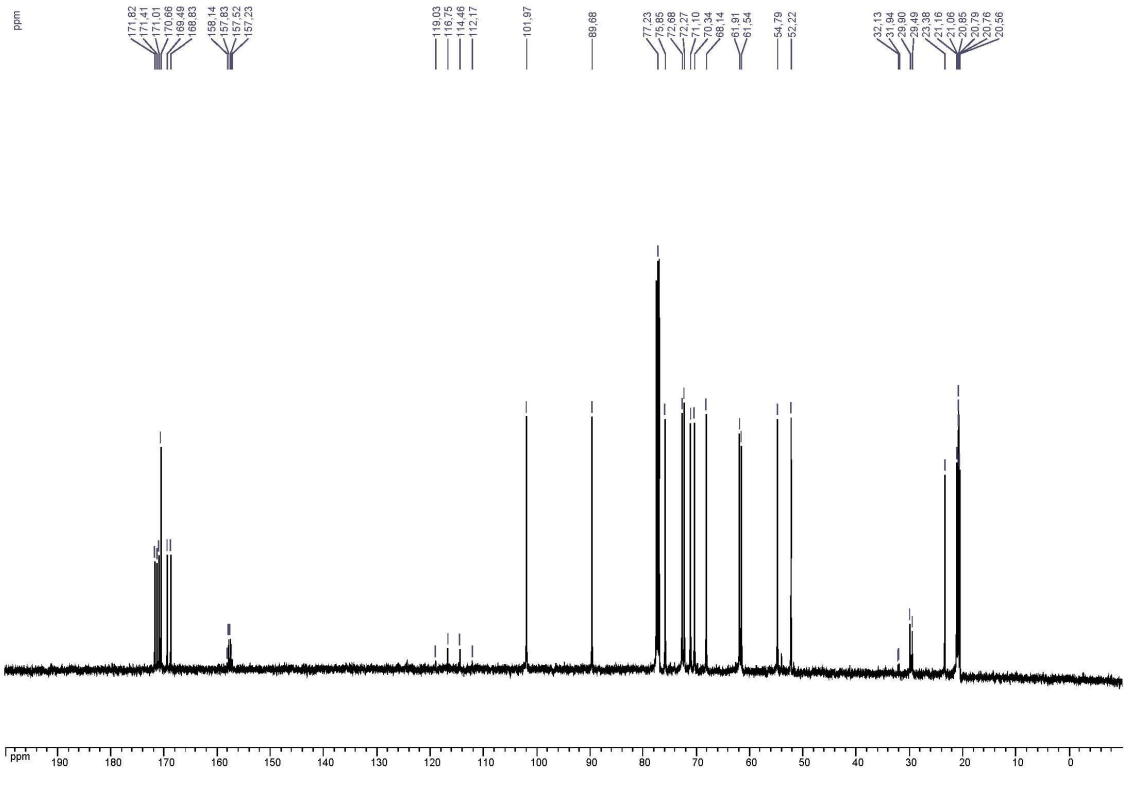
Compound (**S2**) COSY NMR



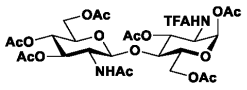


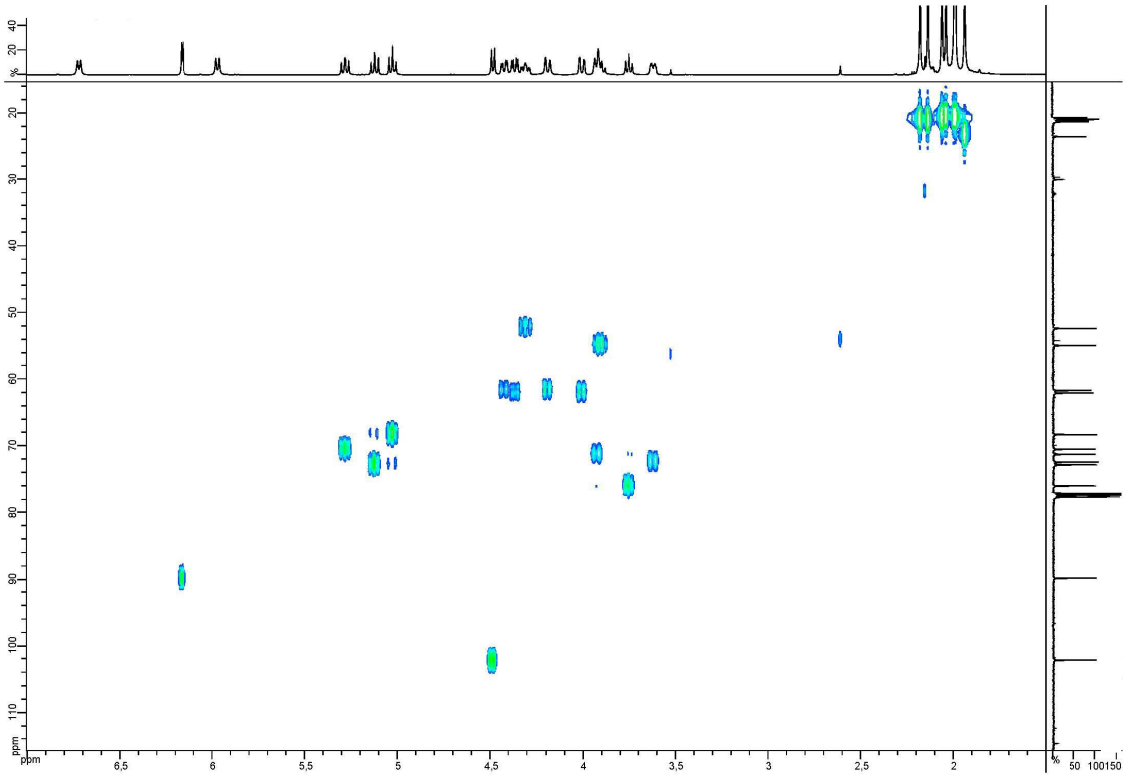
Compound (**S2**) ^{13}C NMR



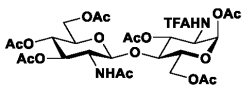


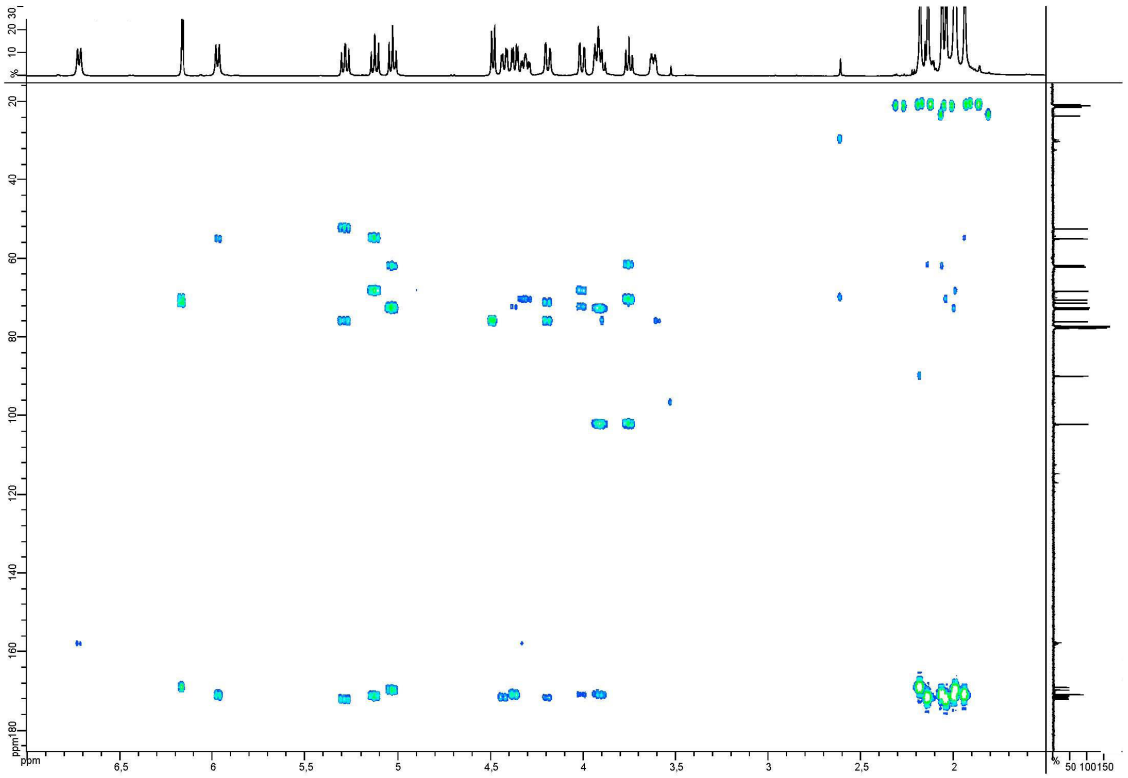
Compound (**S2**) HSQC NMR



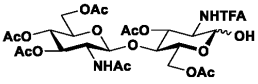


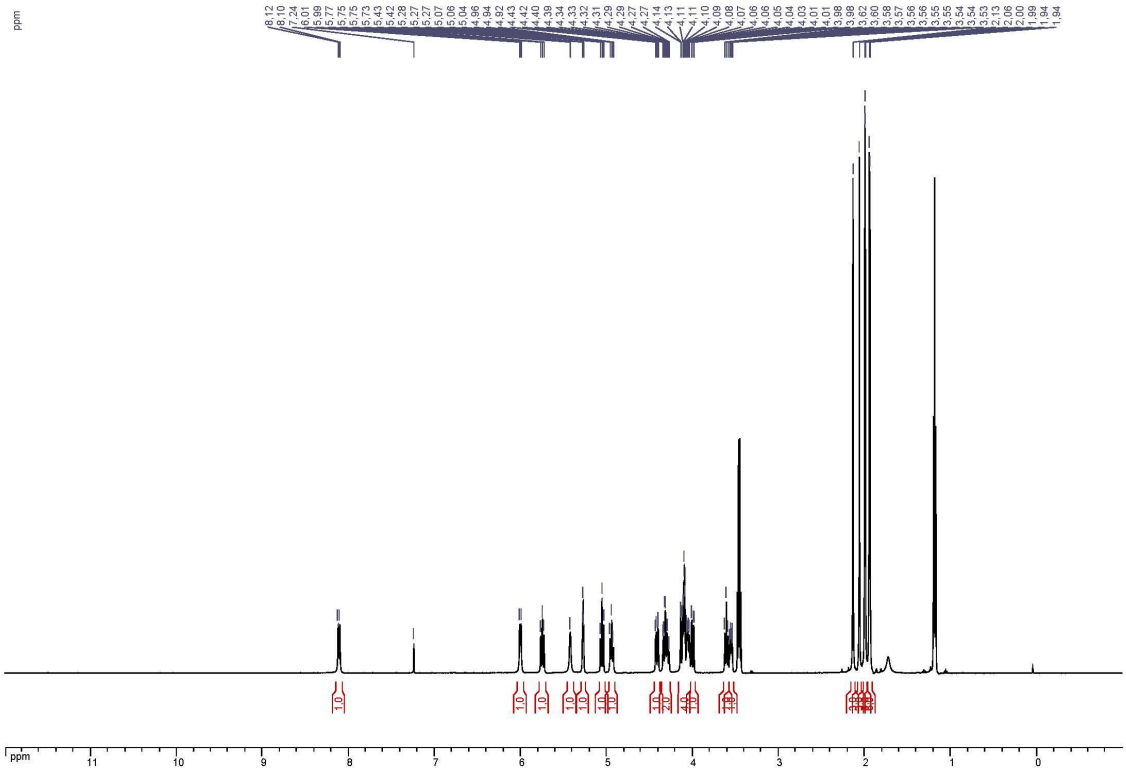
Compound (**S2**) HMBC NMR



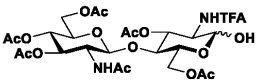


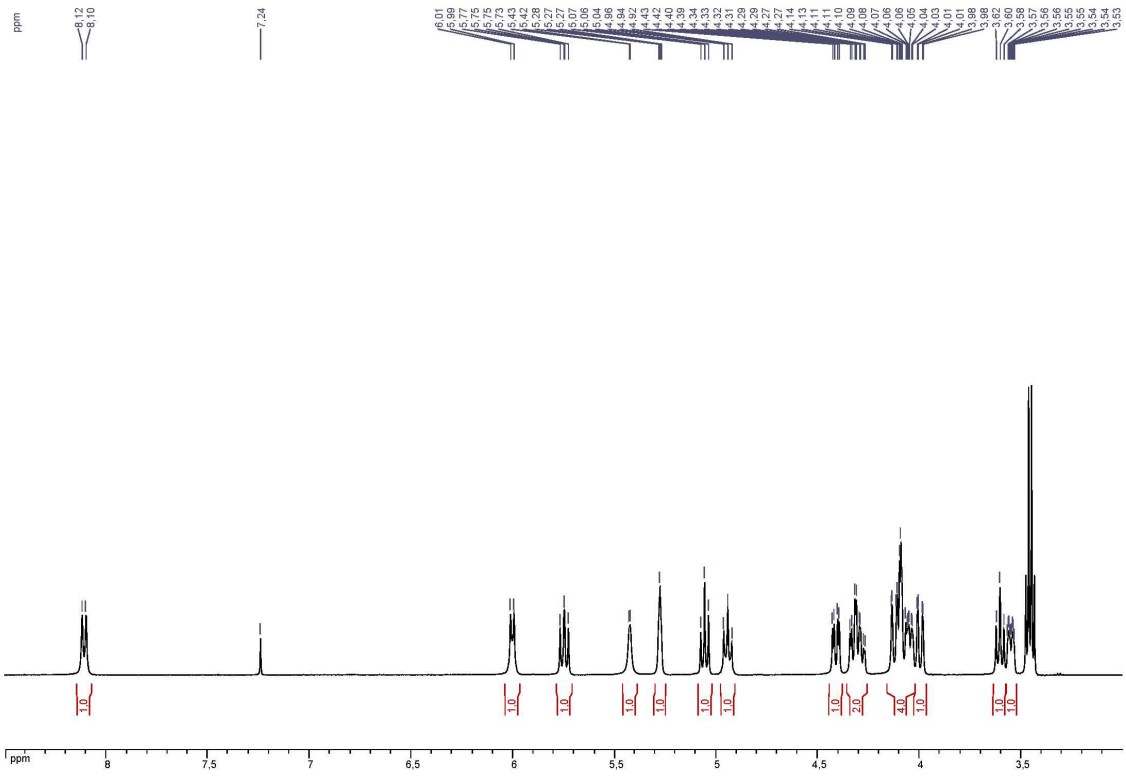
Compound (**S3**) ^{1}H NMR



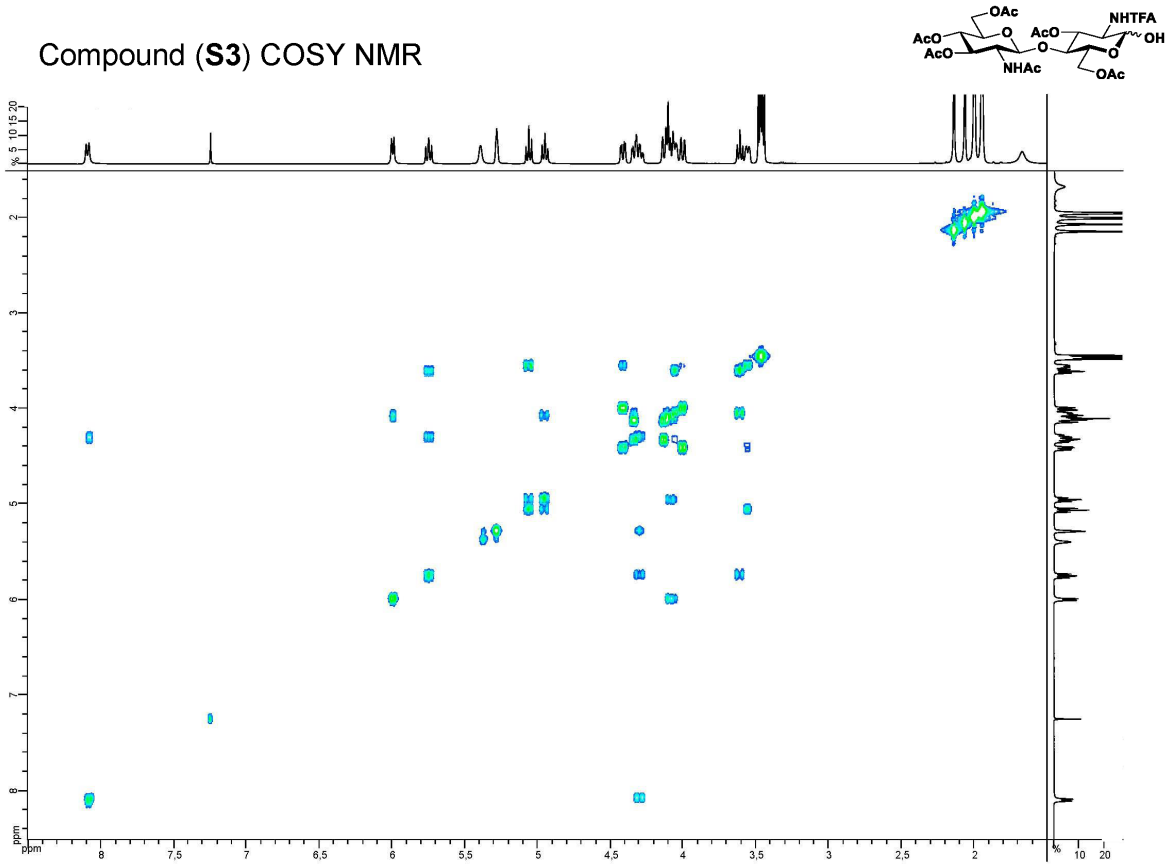


Compound (**S3**) ^{1}H NMR

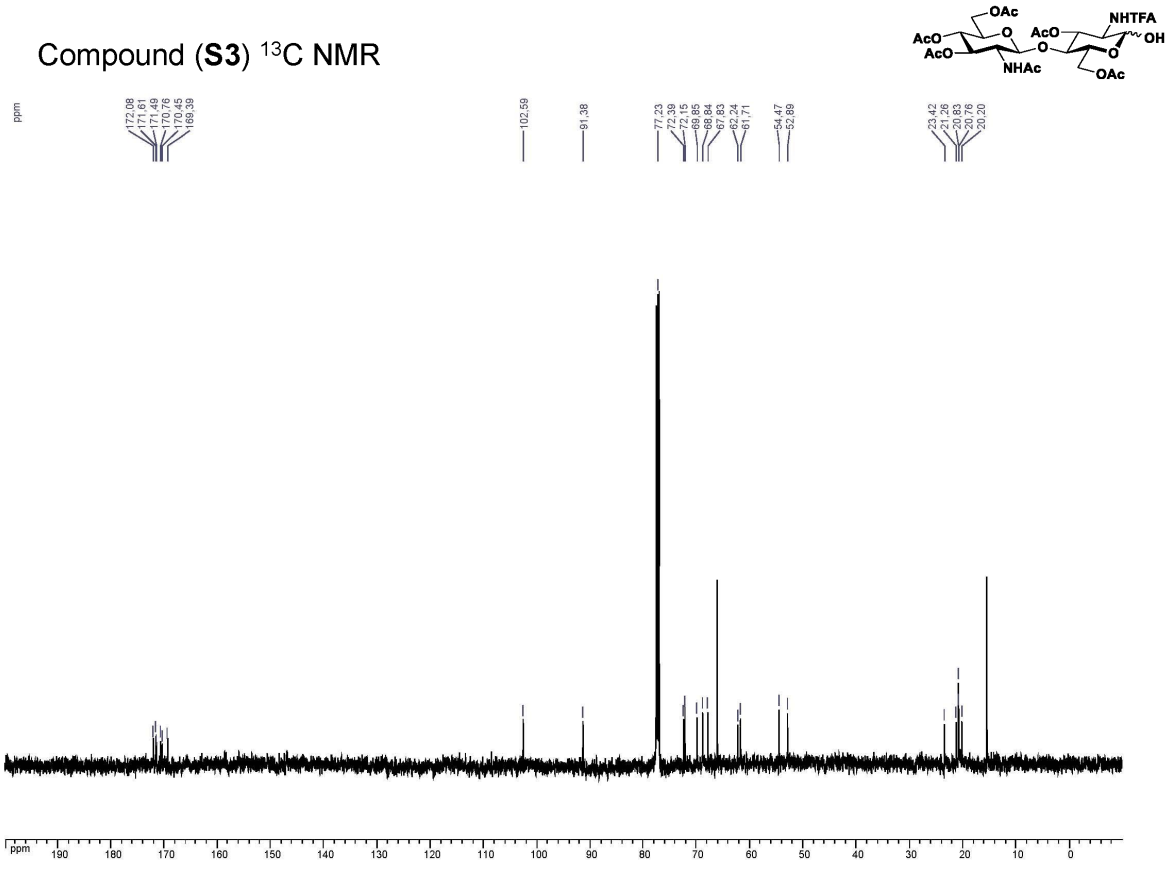




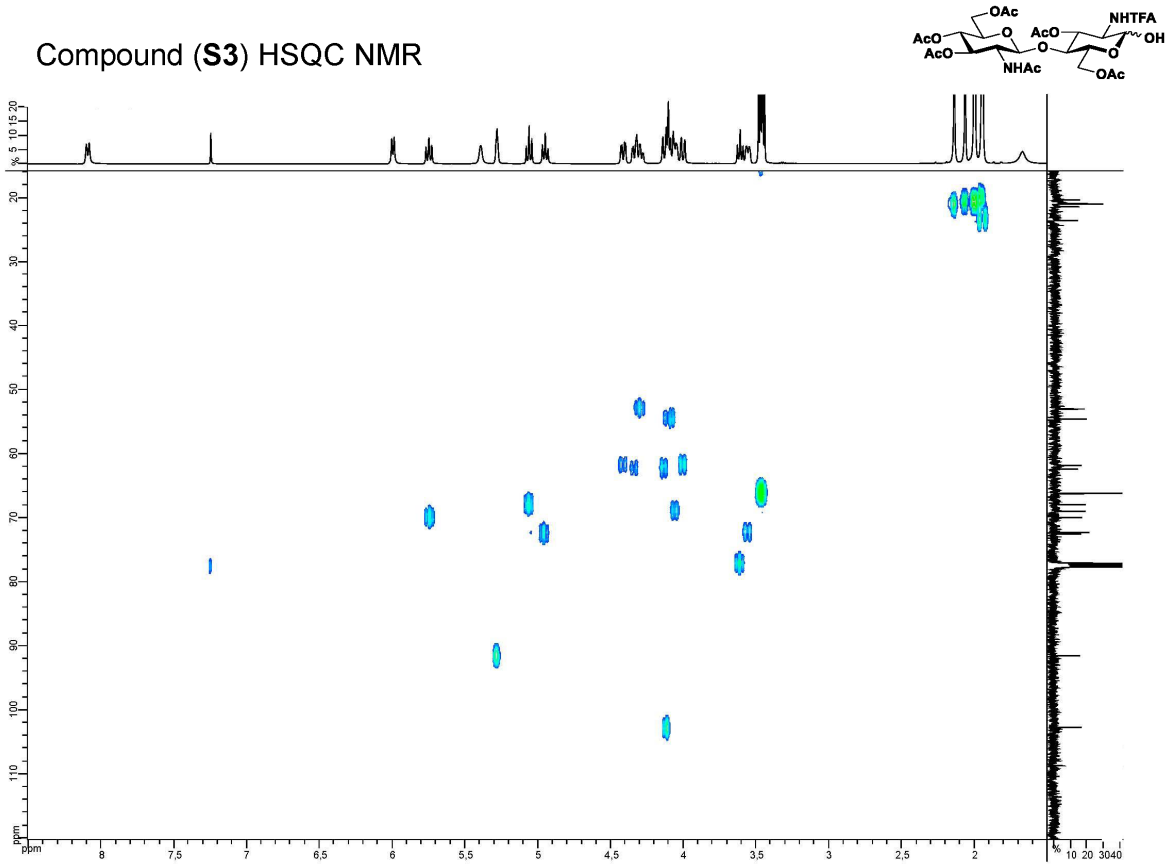
Compound (**S3**) COSY NMR



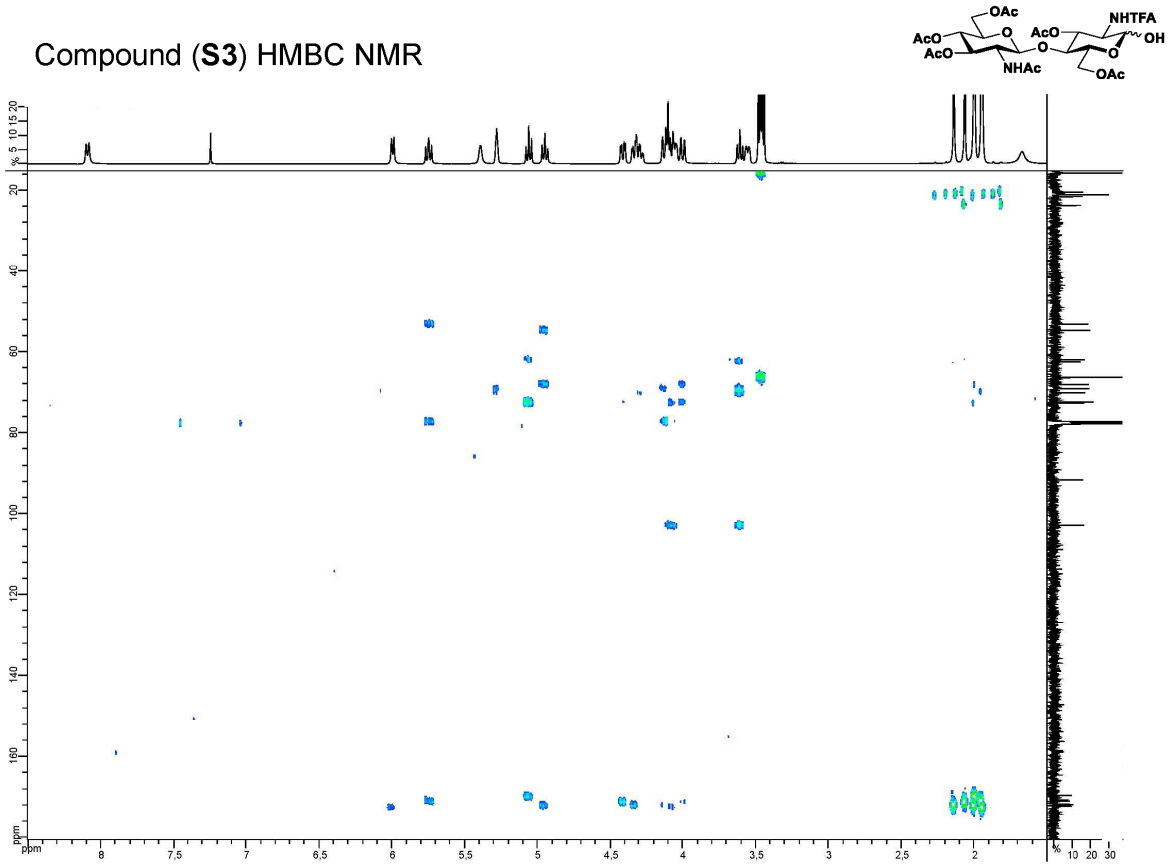
Compound (**S3**) ^{13}C NMR



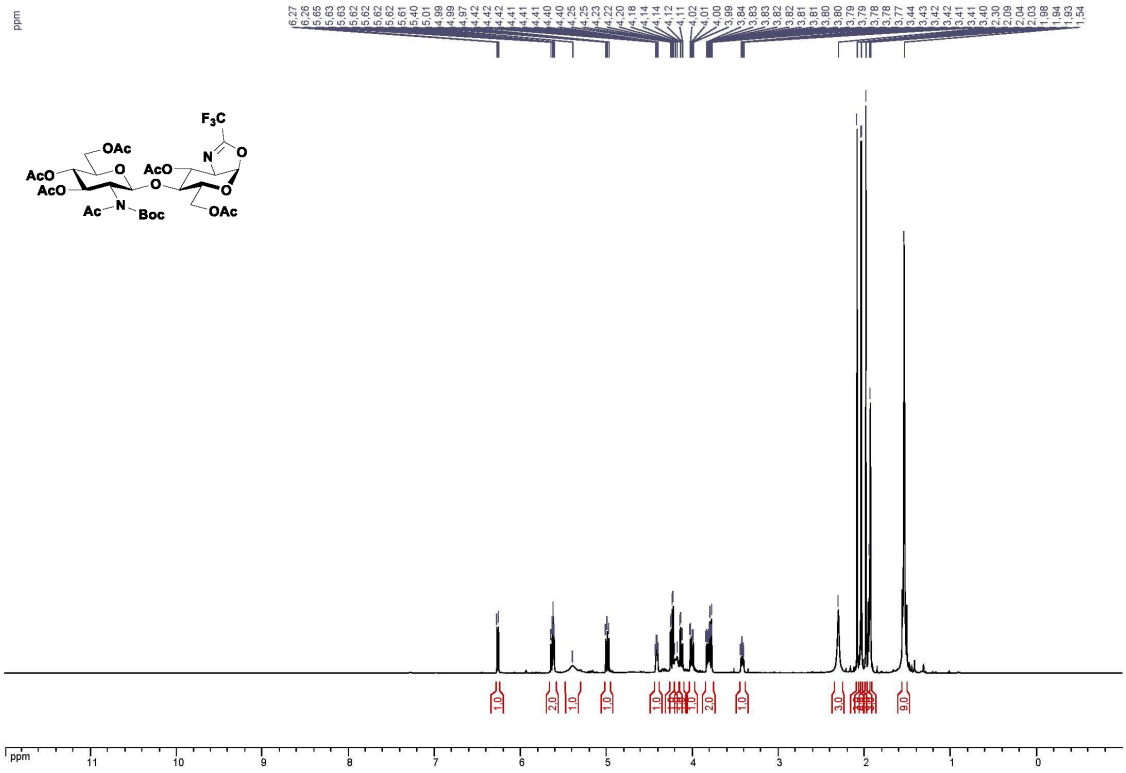
Compound (**S3**) HSQC NMR



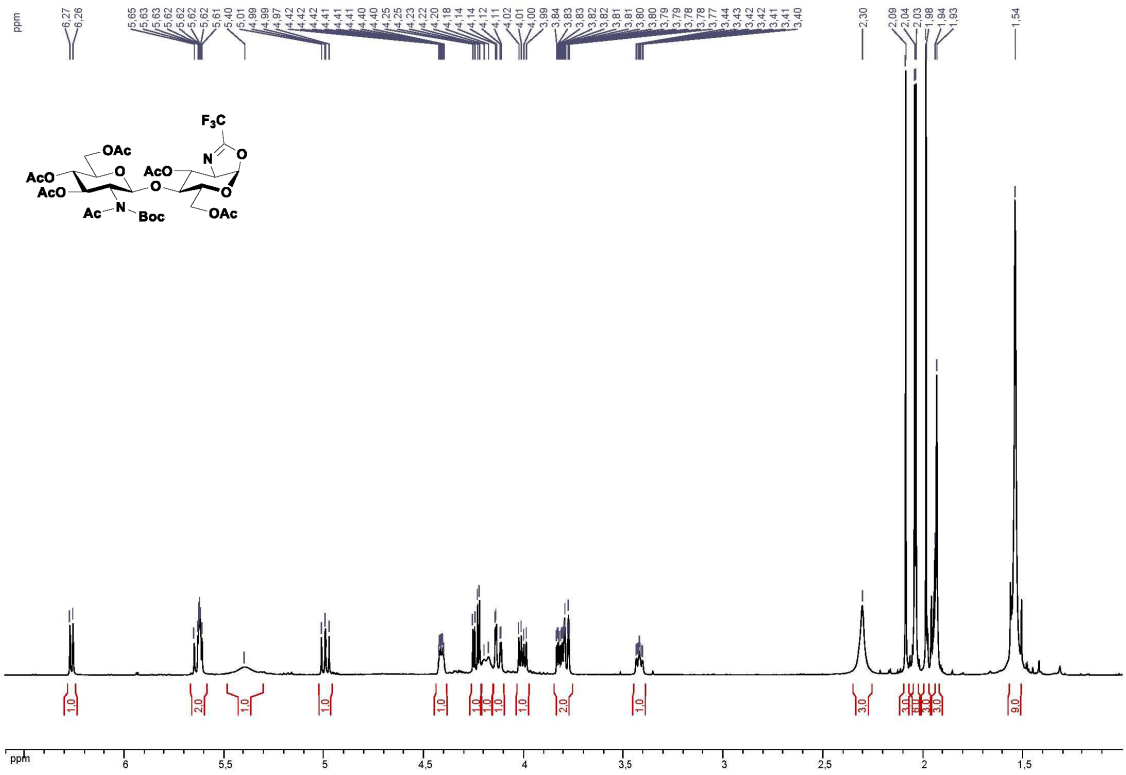
Compound (**S3**) HMBC NMR



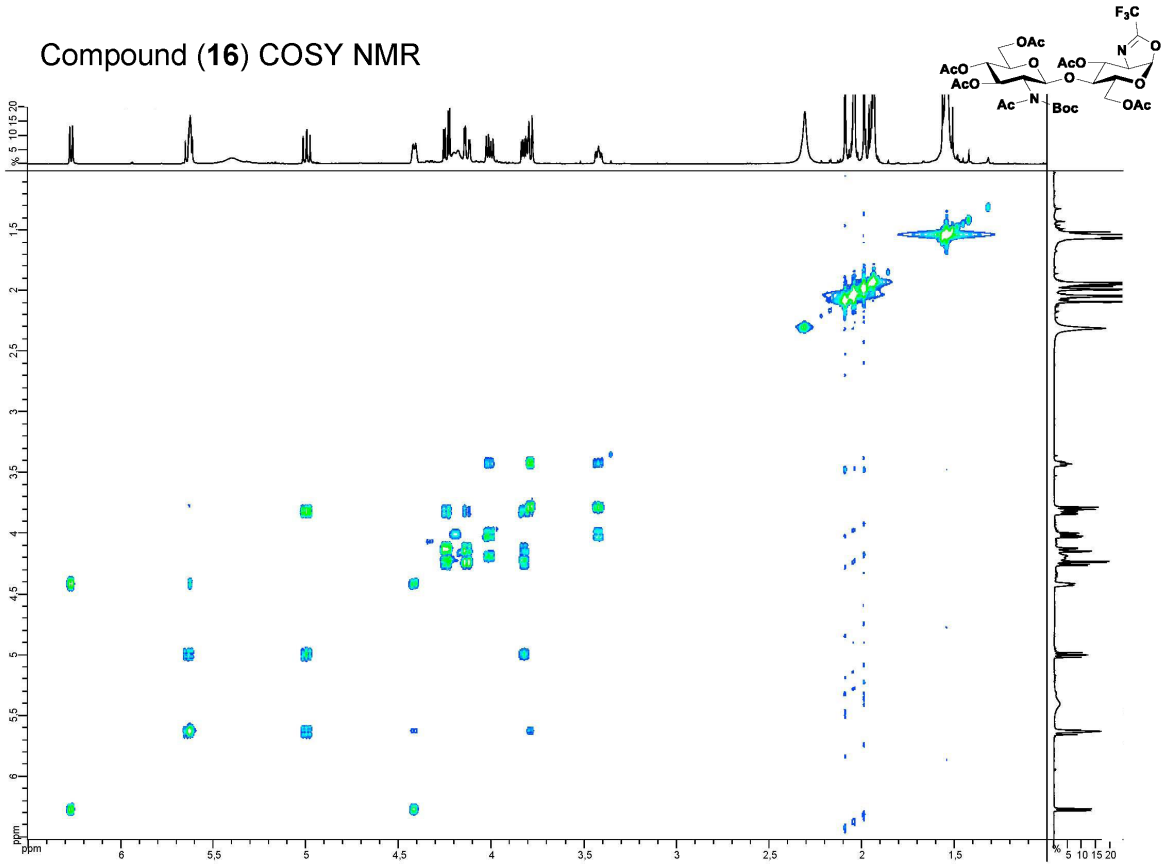
Compound (**16**) ^{1}H NMR



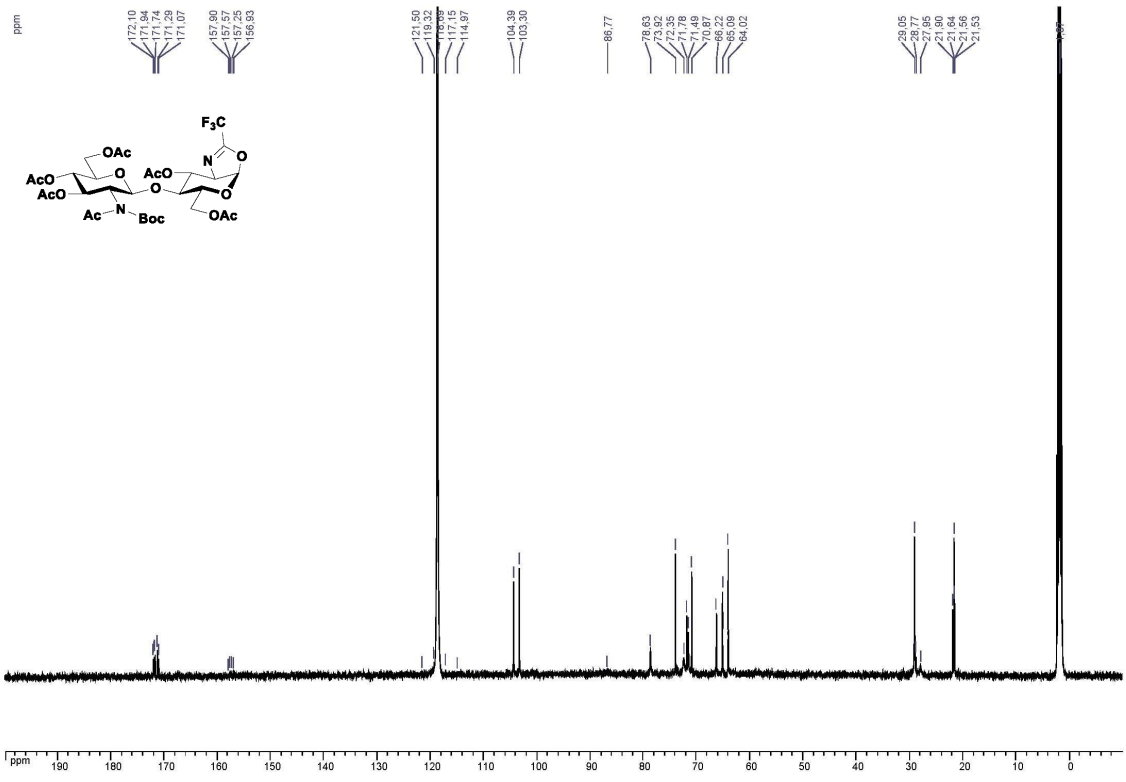
Compound (**16**) ^{1}H NMR



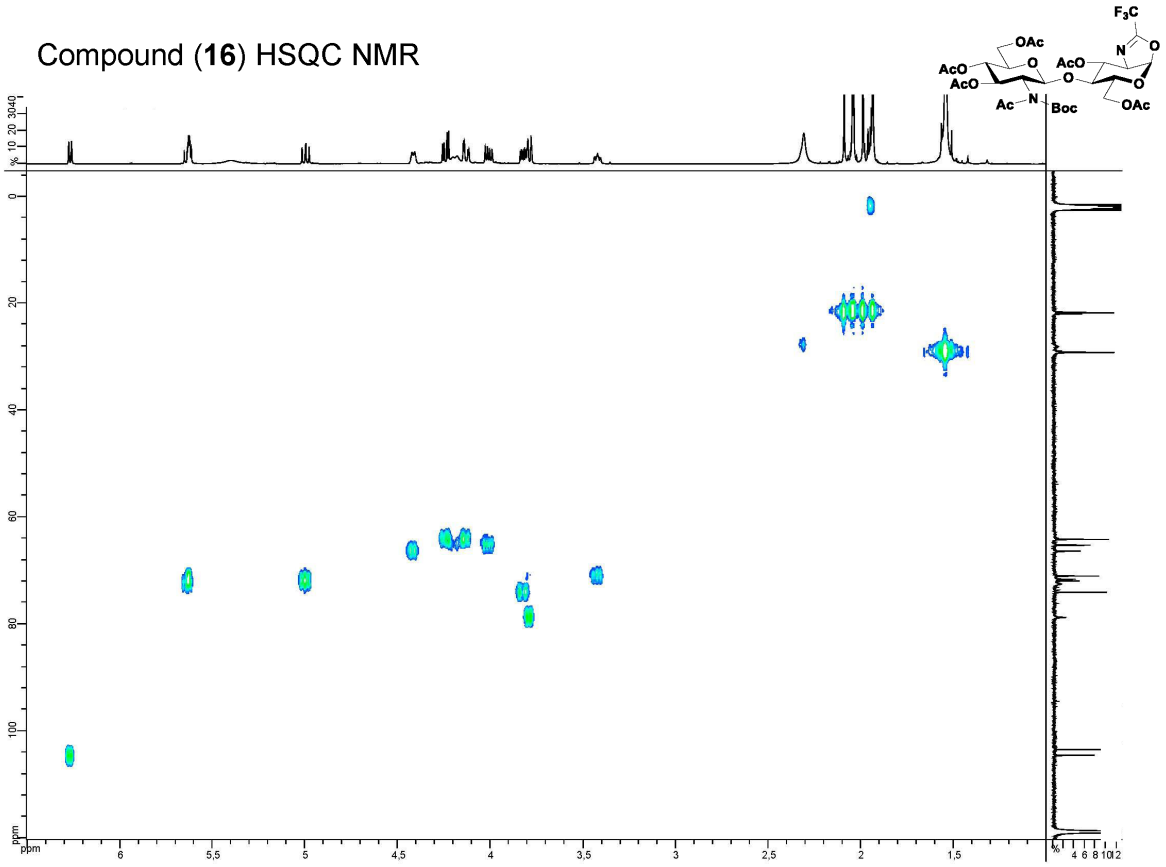
Compound (**16**) COSY NMR



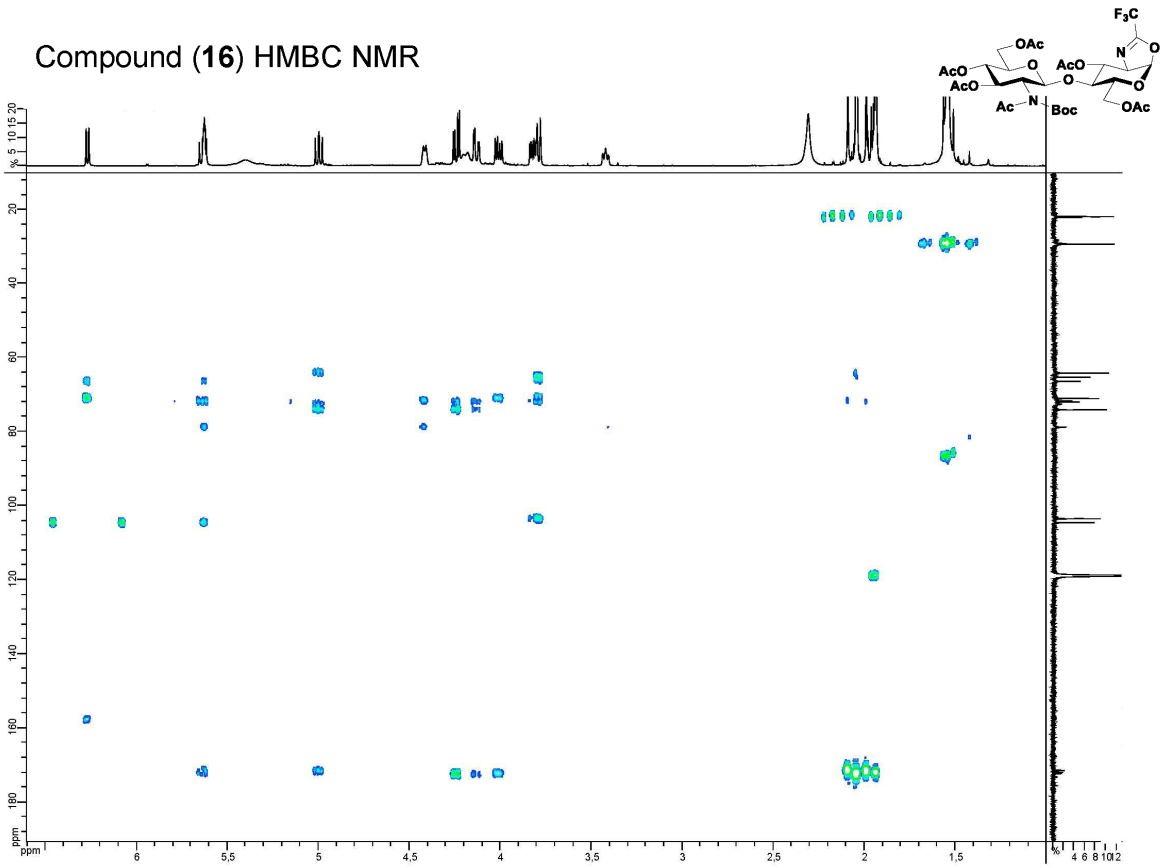
Compound (**16**) ^{13}C NMR



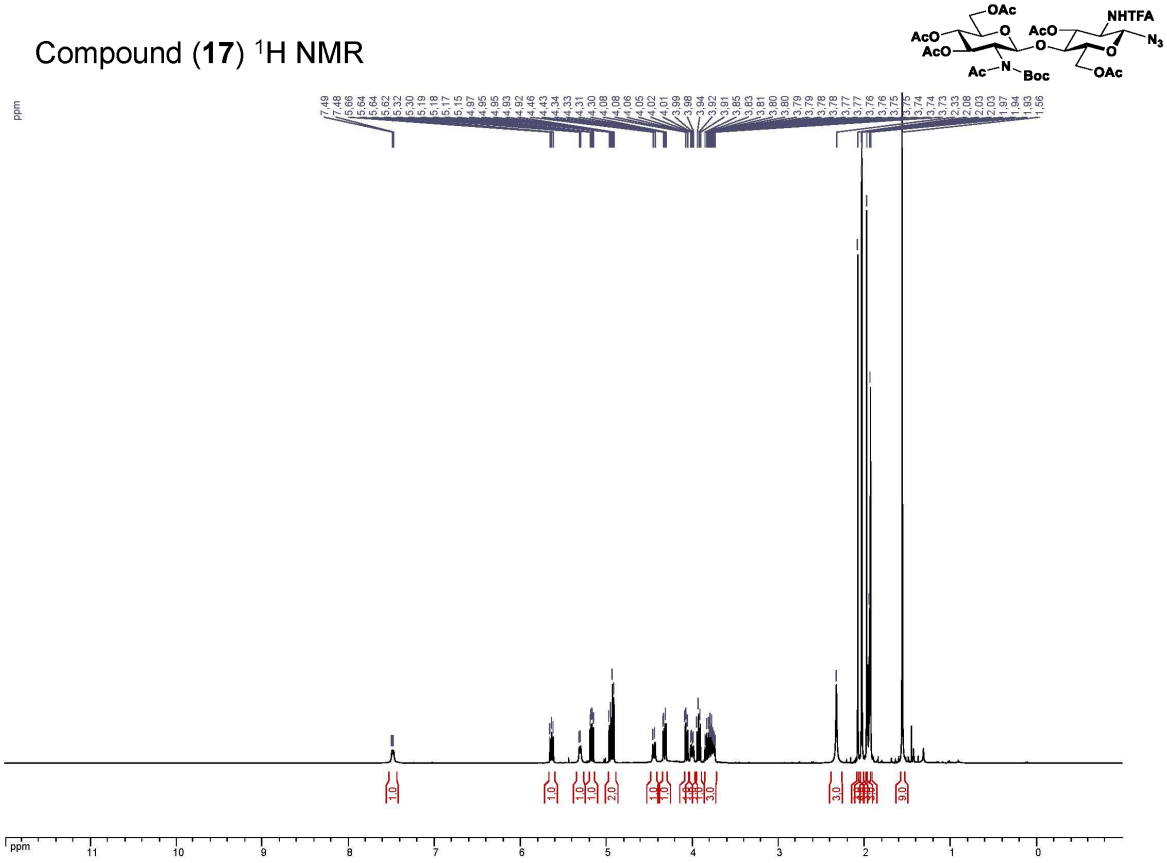
Compound (**16**) HSQC NMR



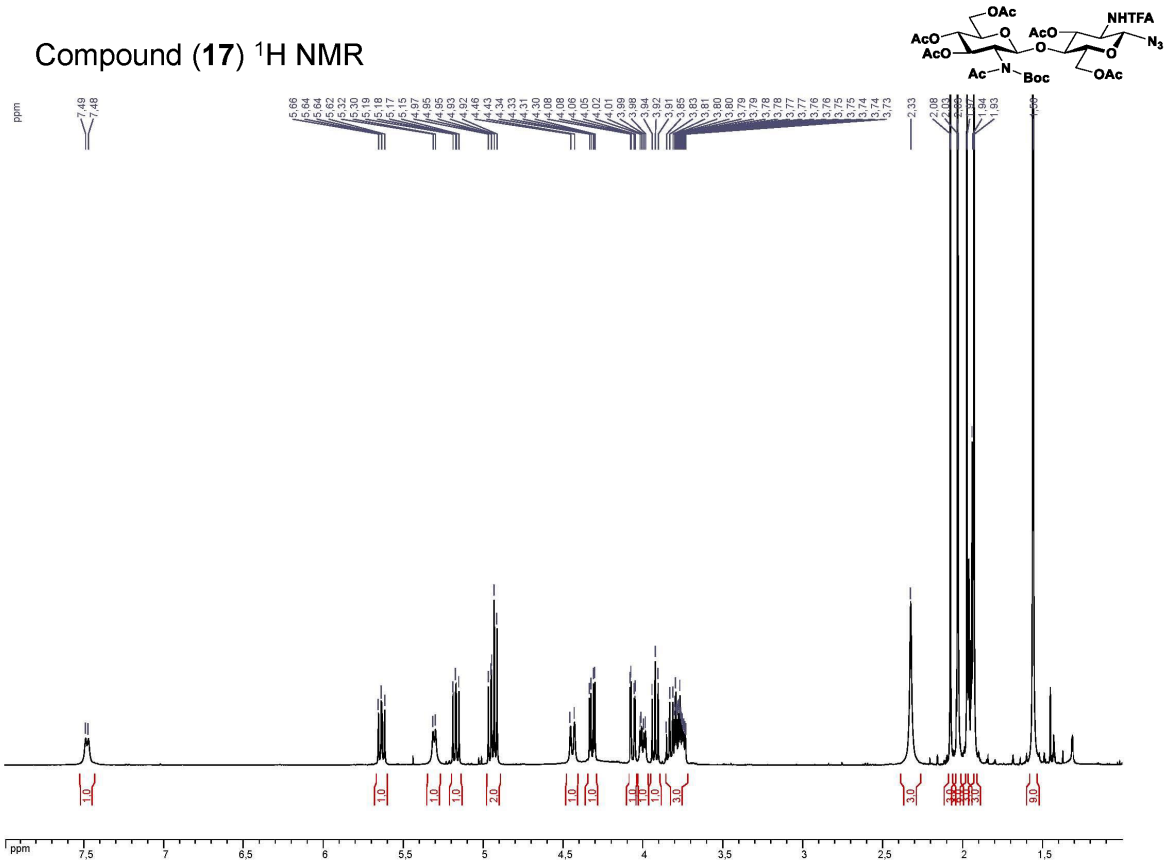
Compound (**16**) HMBC NMR



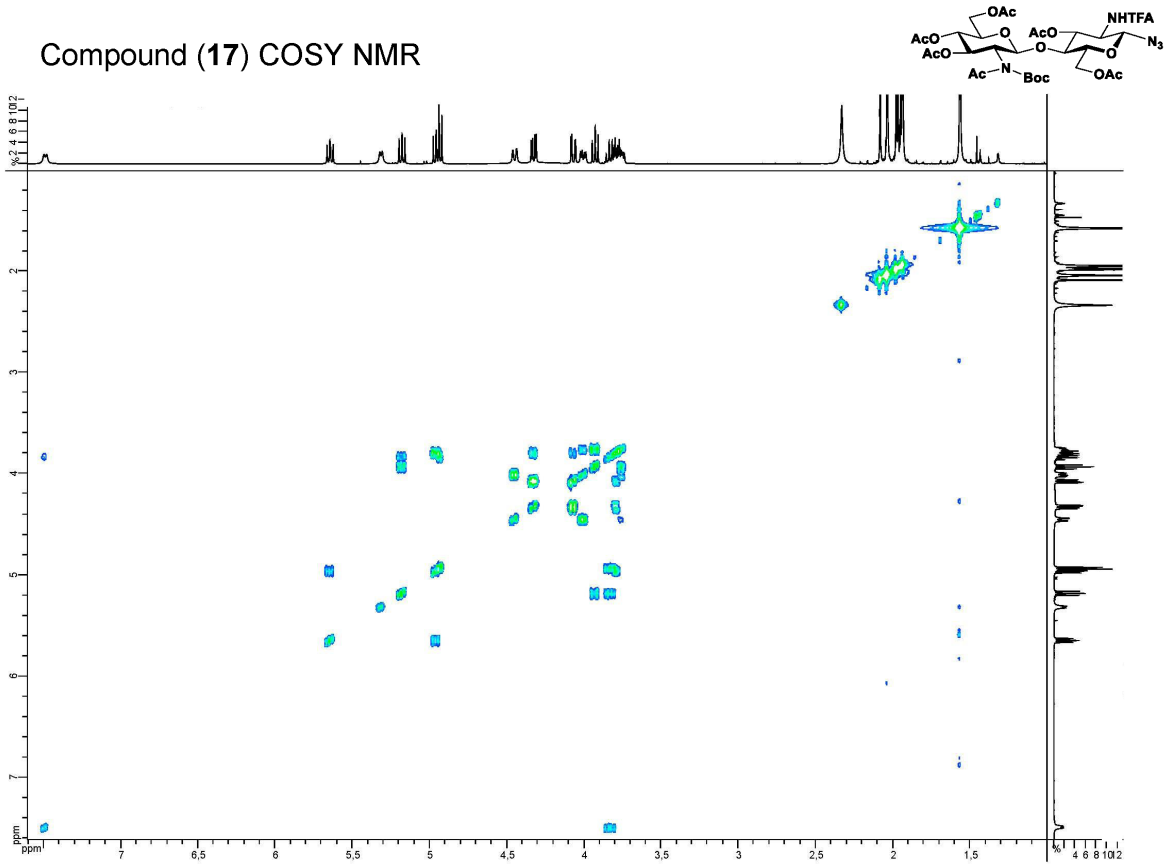
Compound (**17**) ^{1}H NMR



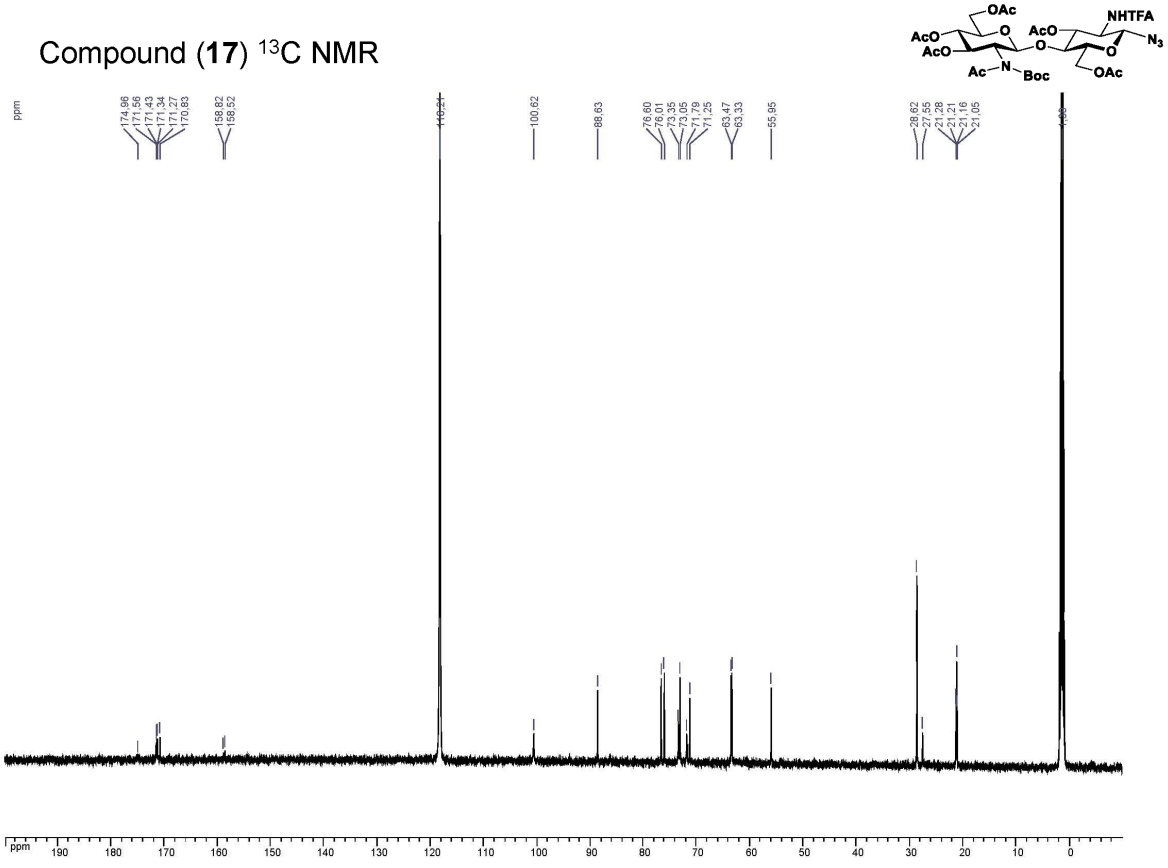
Compound (**17**) ^{1}H NMR



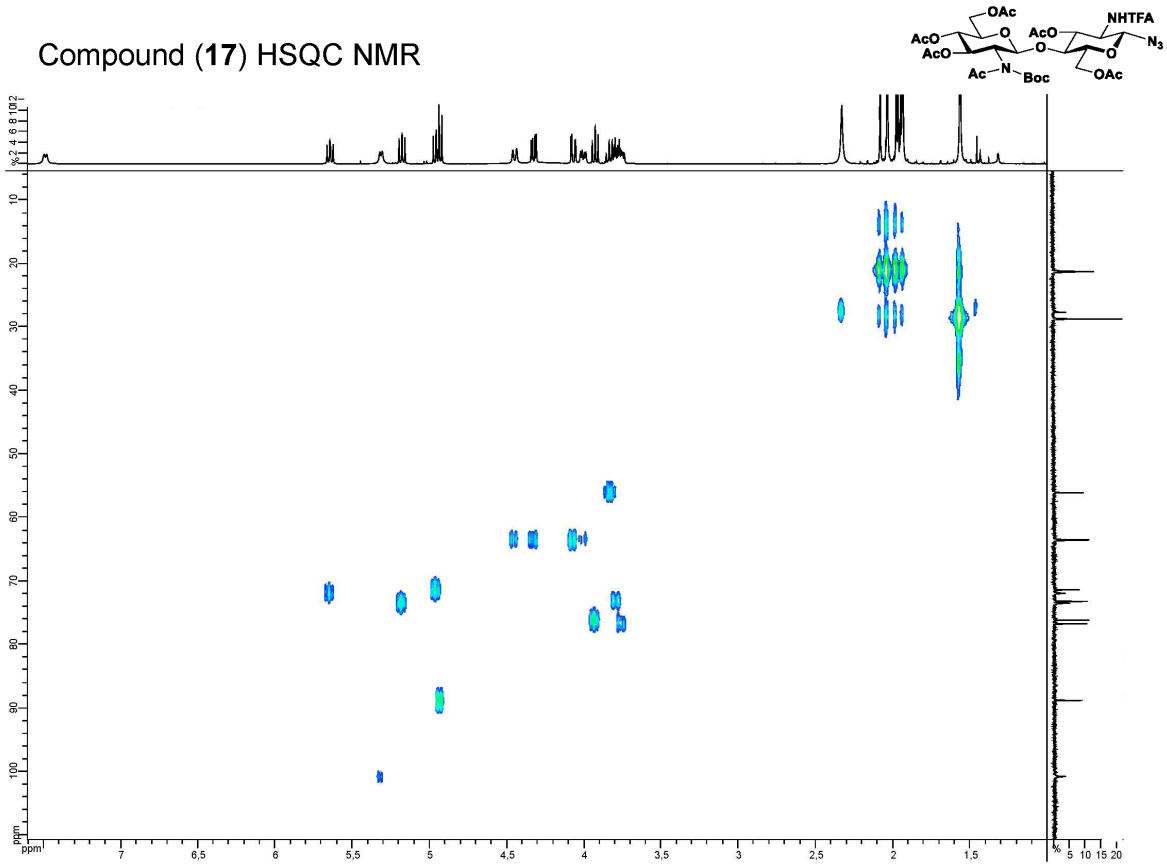
Compound (**17**) COSY NMR



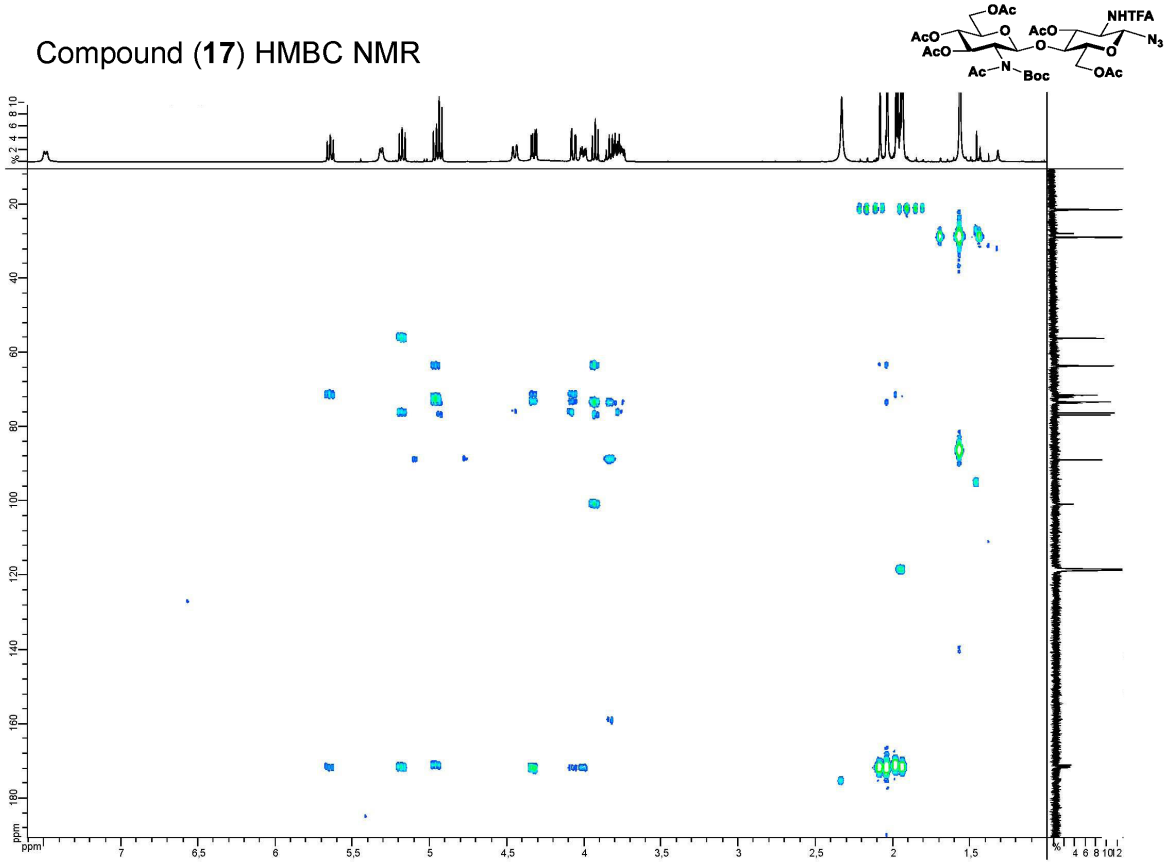
Compound (**17**) ^{13}C NMR



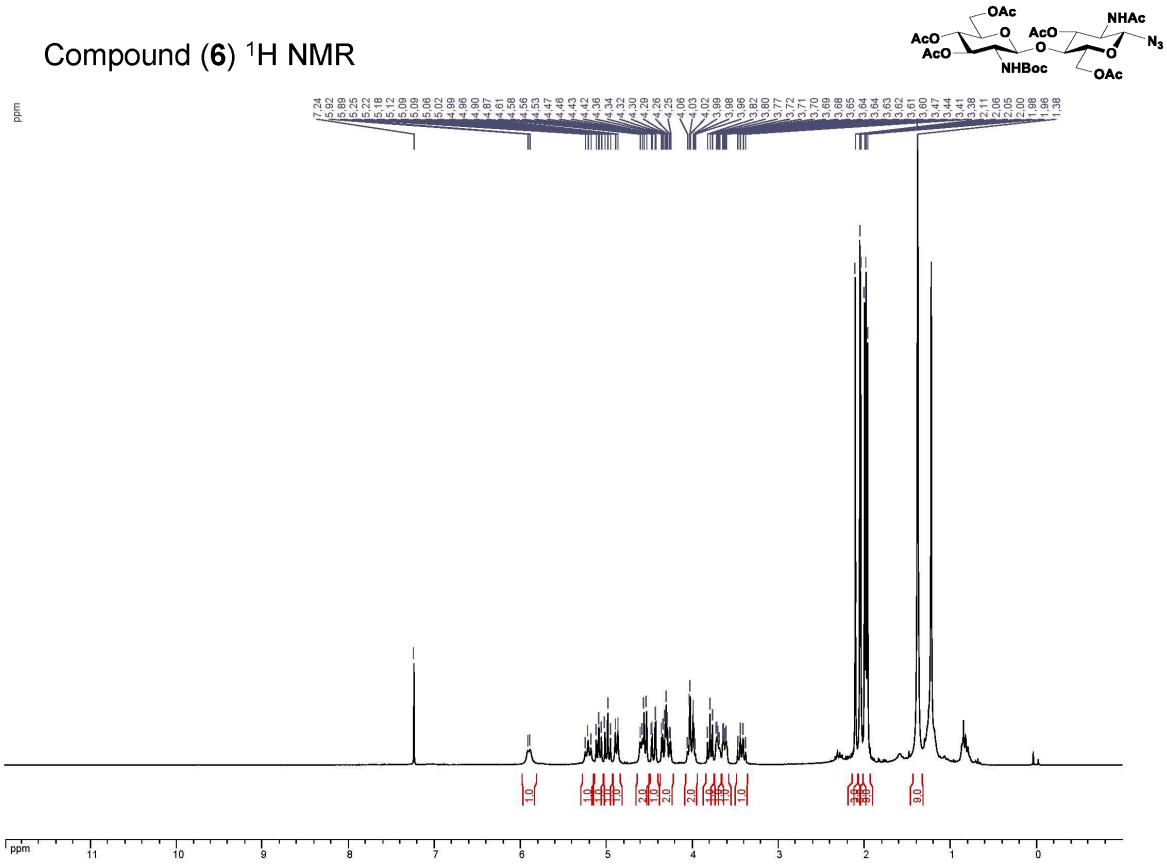
Compound (**17**) HSQC NMR



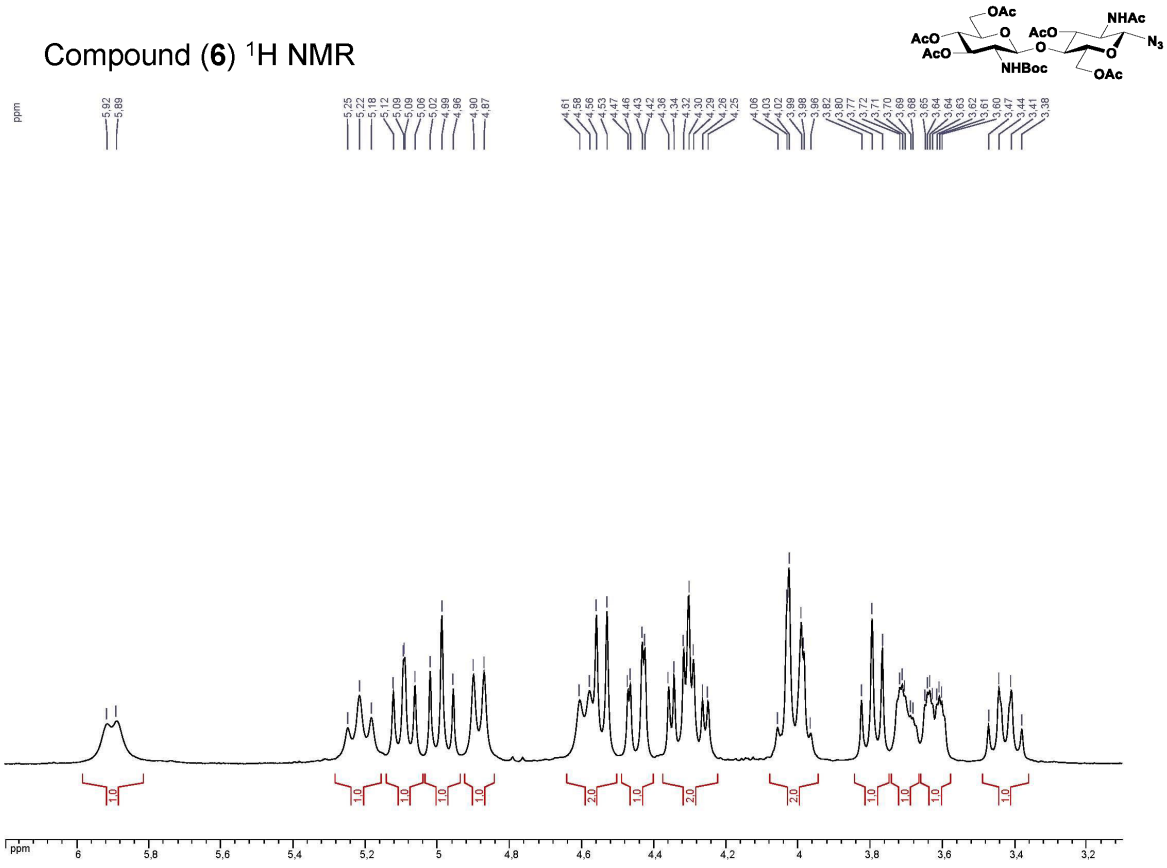
Compound (**17**) HMBC NMR



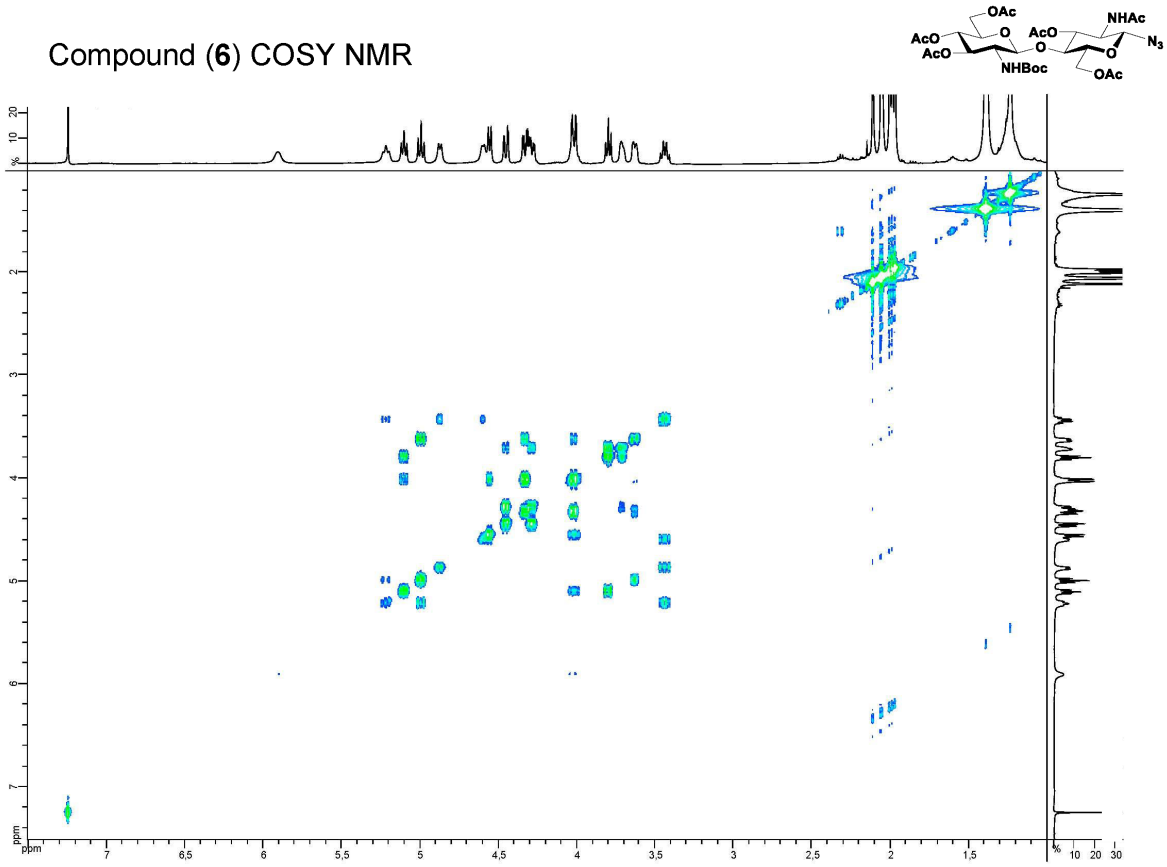
Compound (**6**) ^{1}H NMR



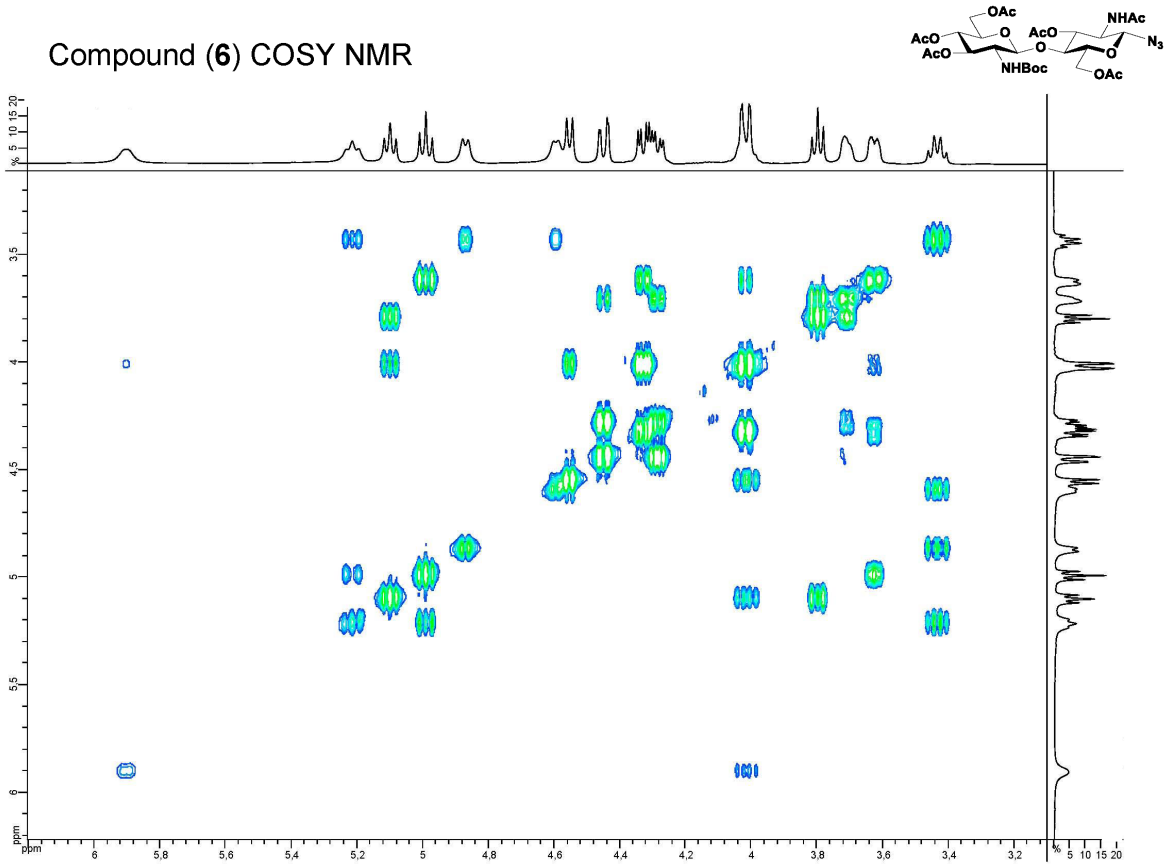
Compound (**6**) ^{1}H NMR



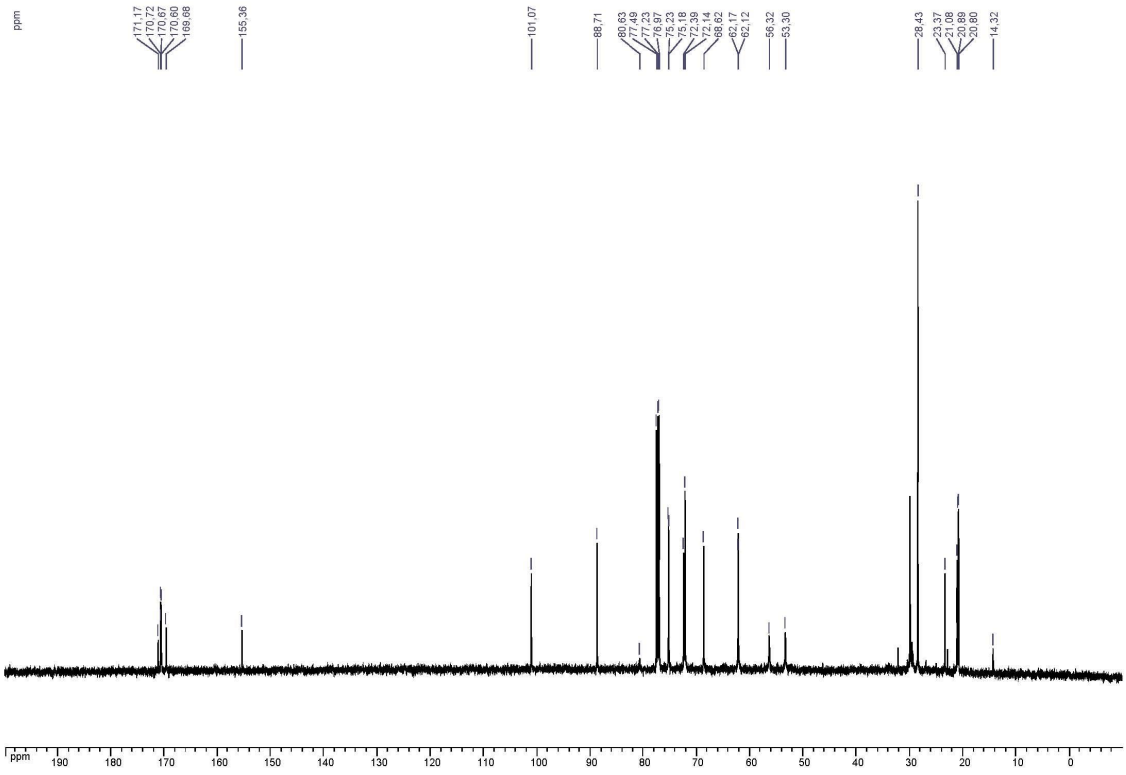
Compound (**6**) COSY NMR



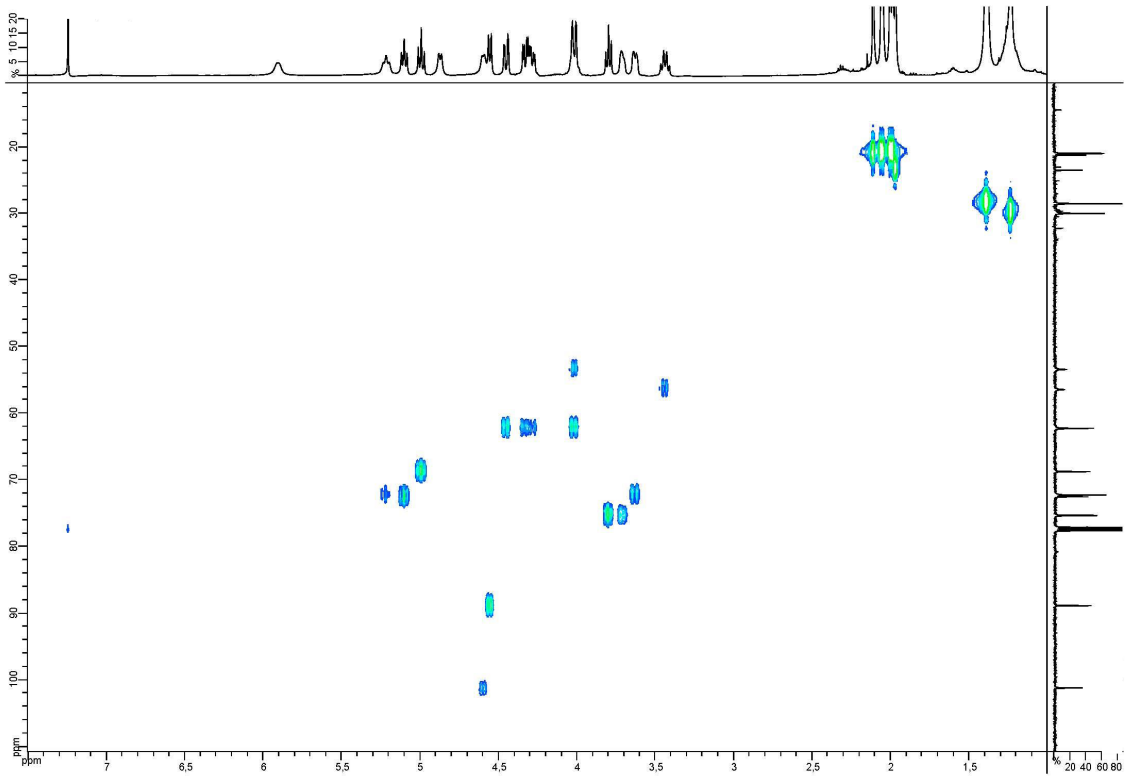
Compound (**6**) COSY NMR



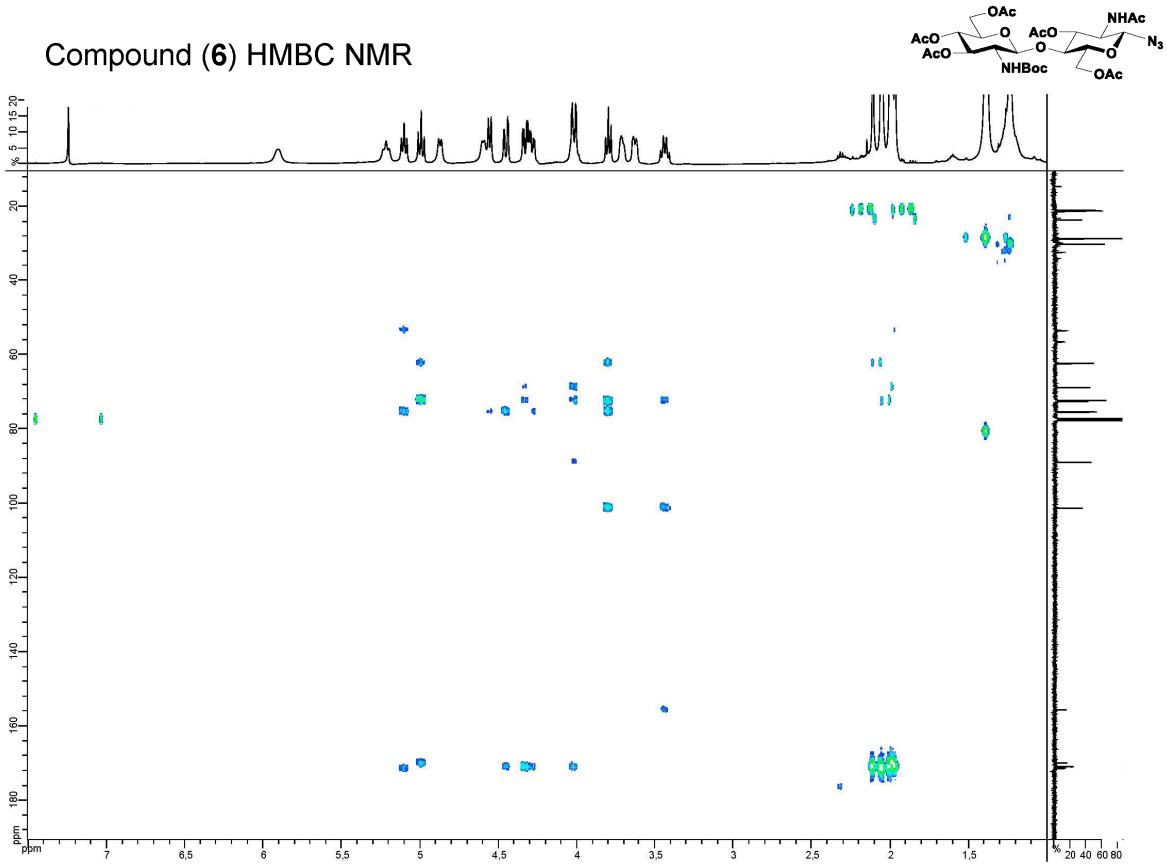
Compound (**6**) ^{13}C NMR



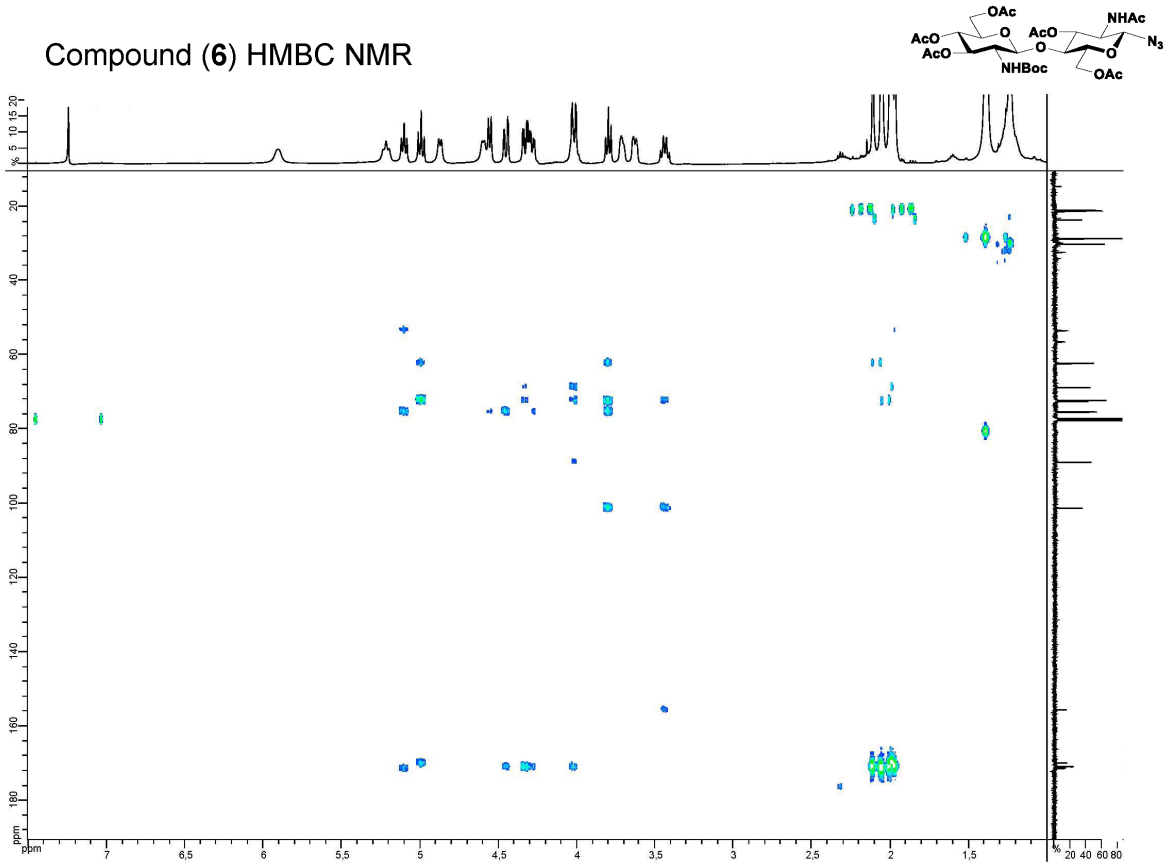
Compound (**6**) HSQC NMR



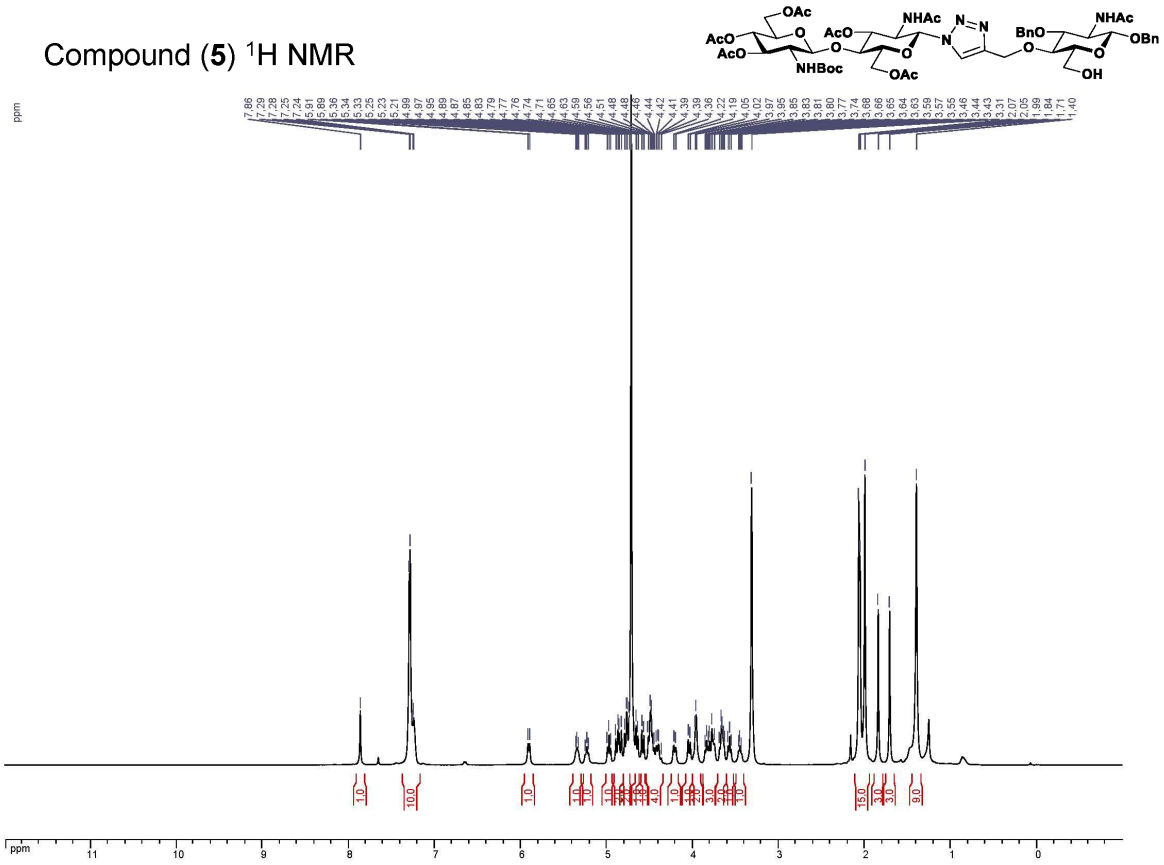
Compound (**6**) HMBC NMR



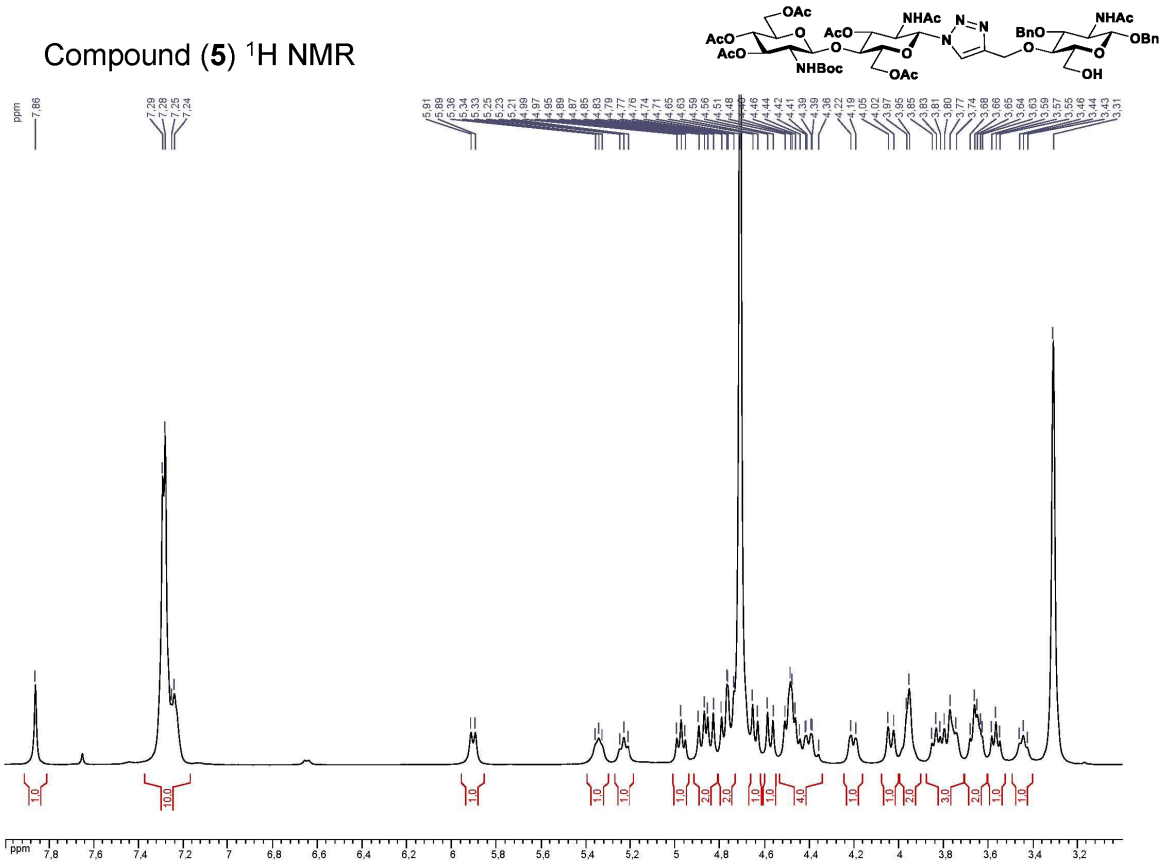
Compound (**6**) HMBC NMR



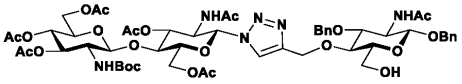
Compound (**5**) ^{1}H NMR

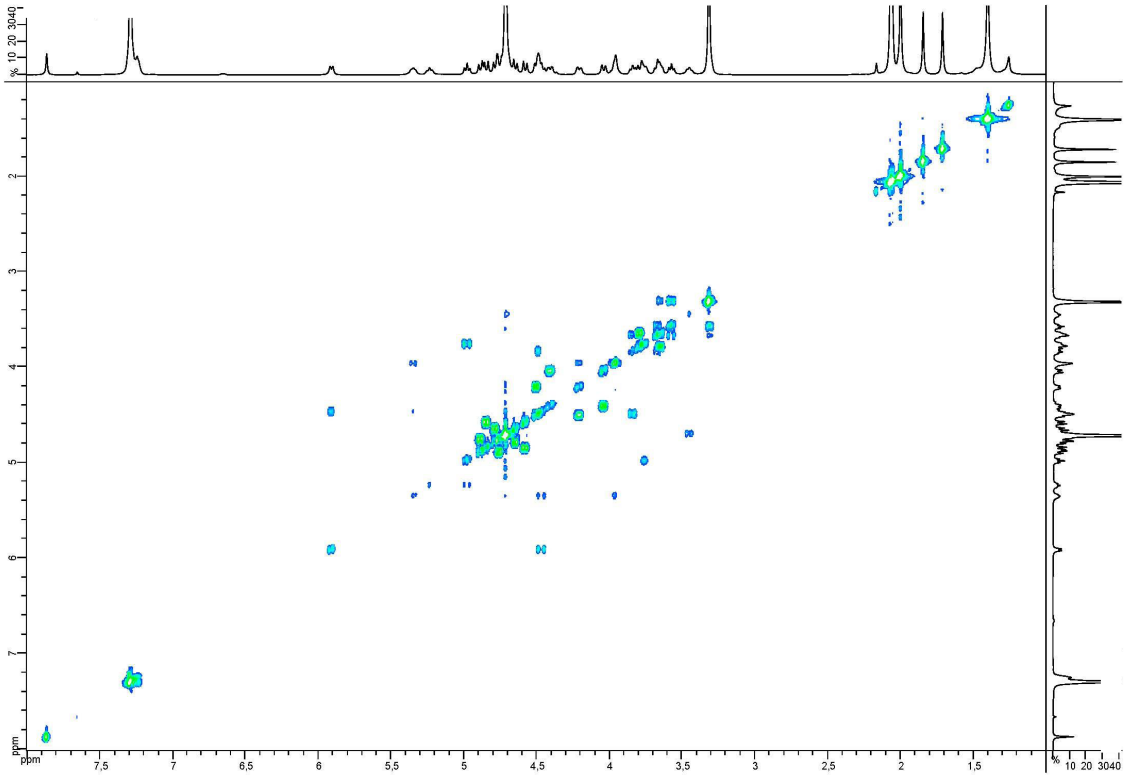


Compound (**5**) ^{1}H NMR

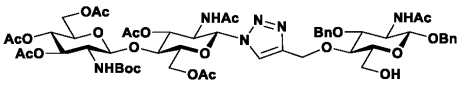


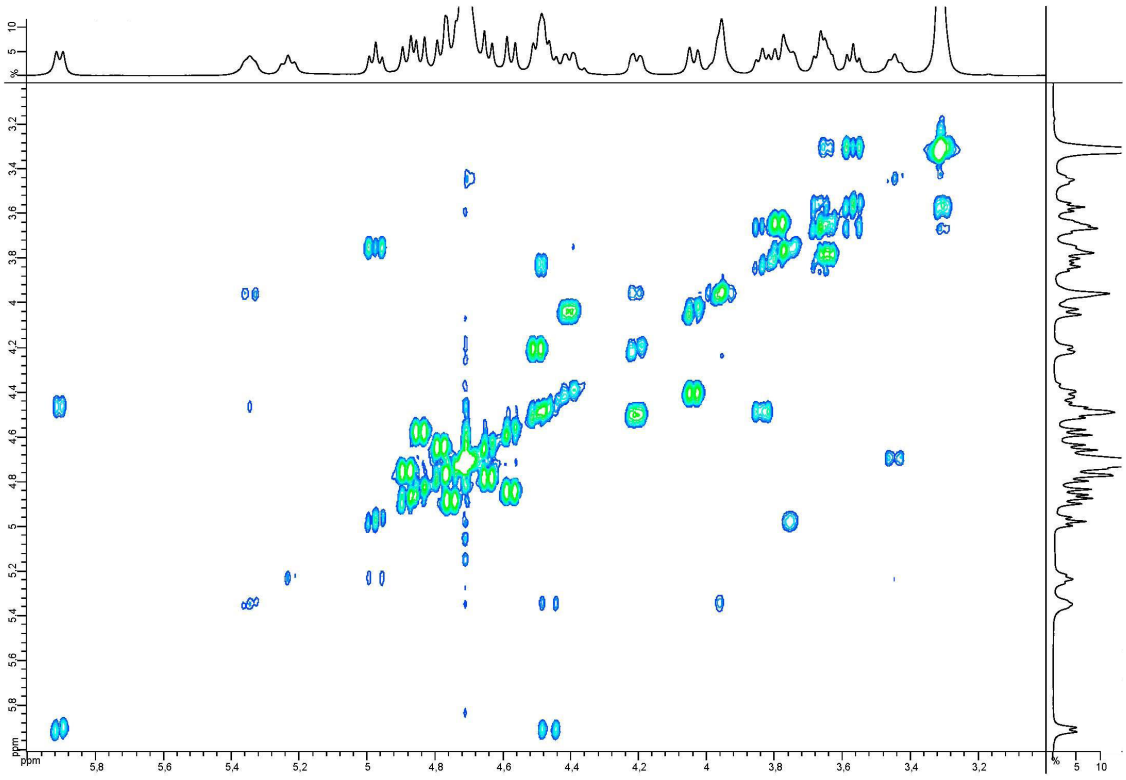
Compound (**5**) COSY NMR



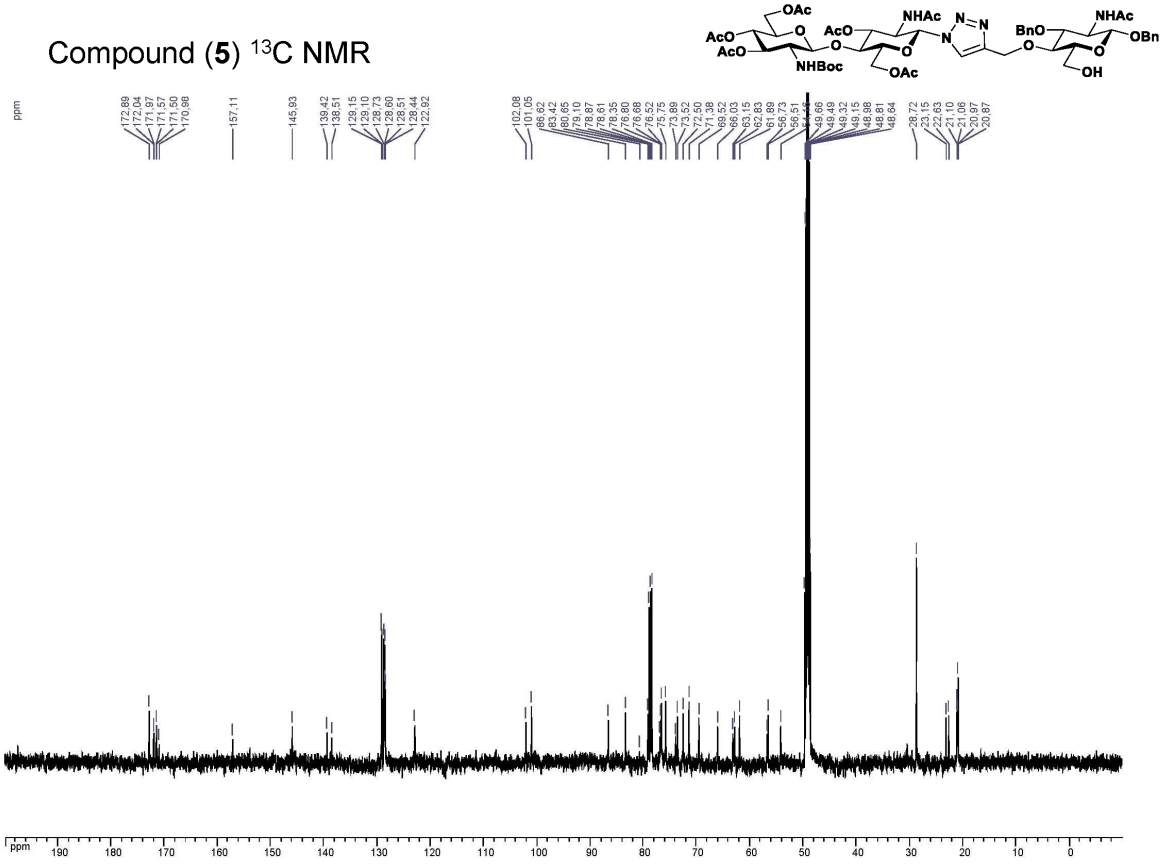


Compound (**5**) COSY NMR

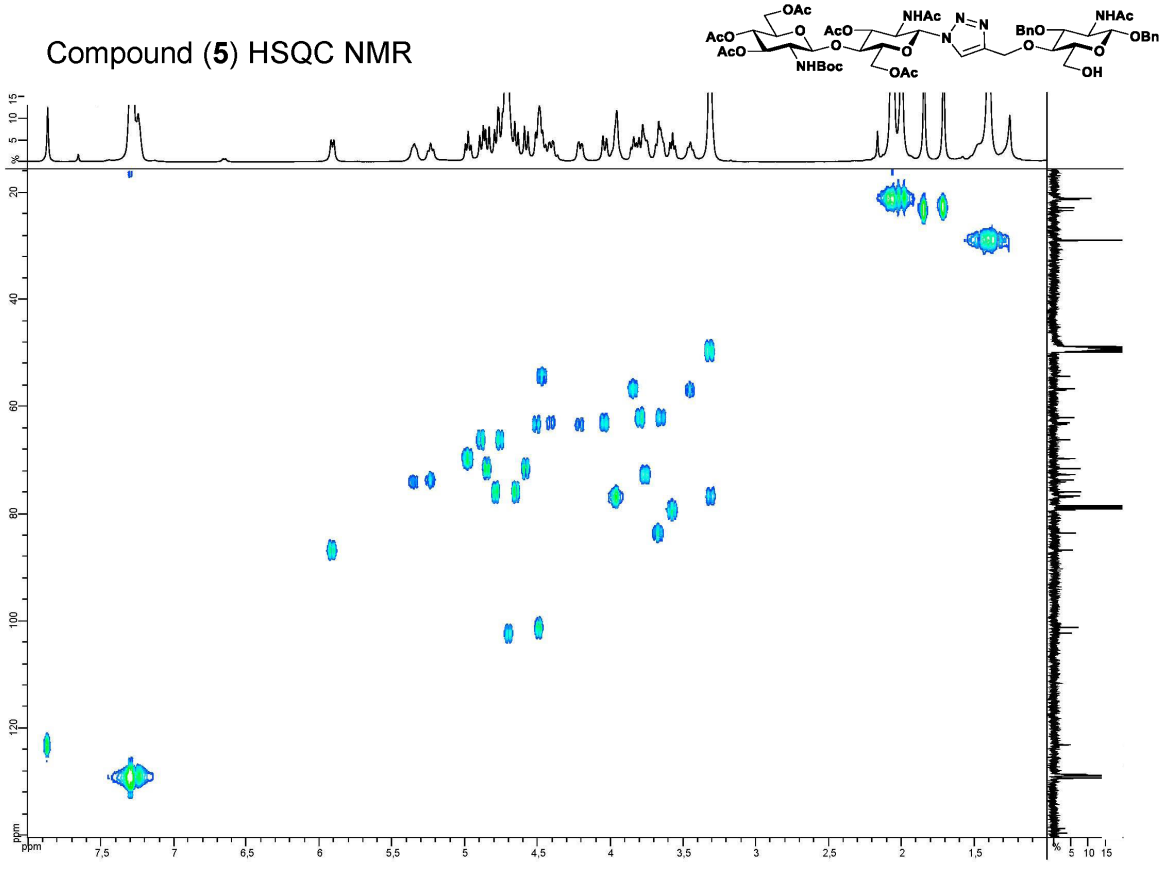




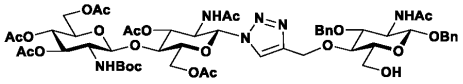
Compound (**5**) ^{13}C NMR

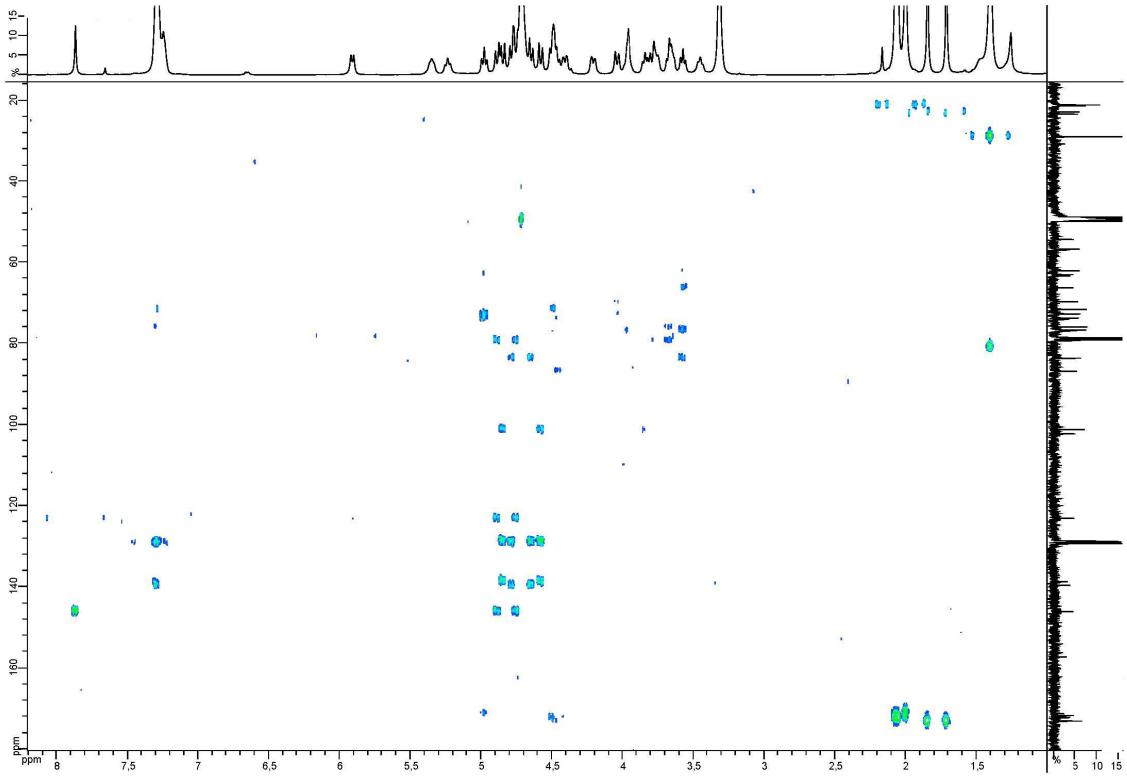


Compound (**5**) HSQC NMR

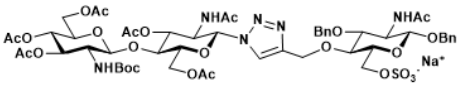


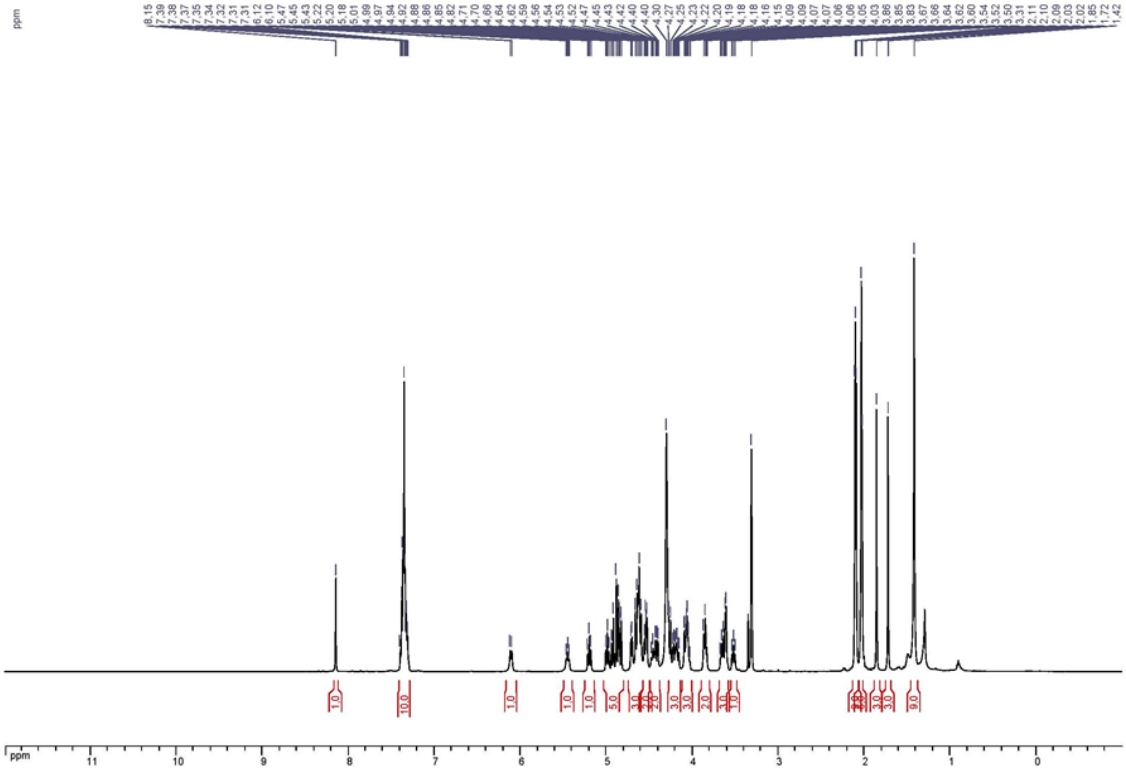
Compound (**5**) HMBC NMR



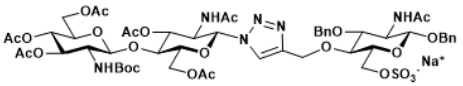


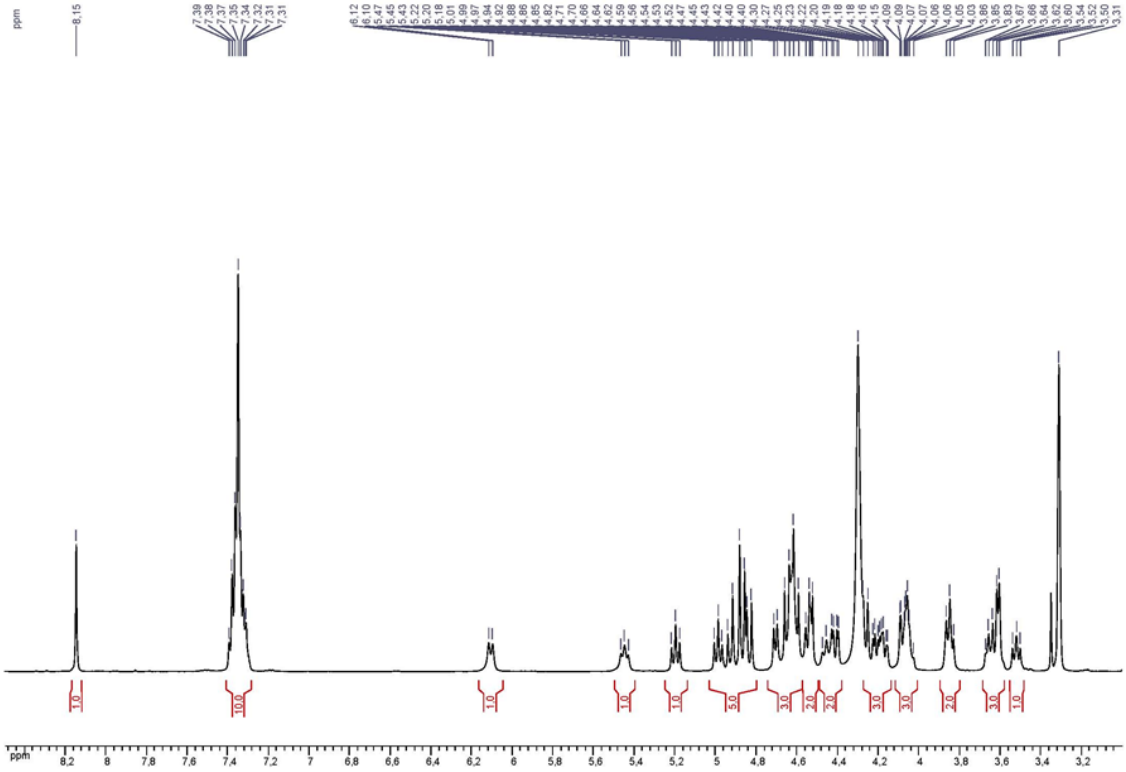
Compound (**18**) ^{1}H NMR



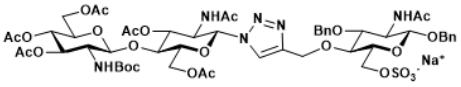


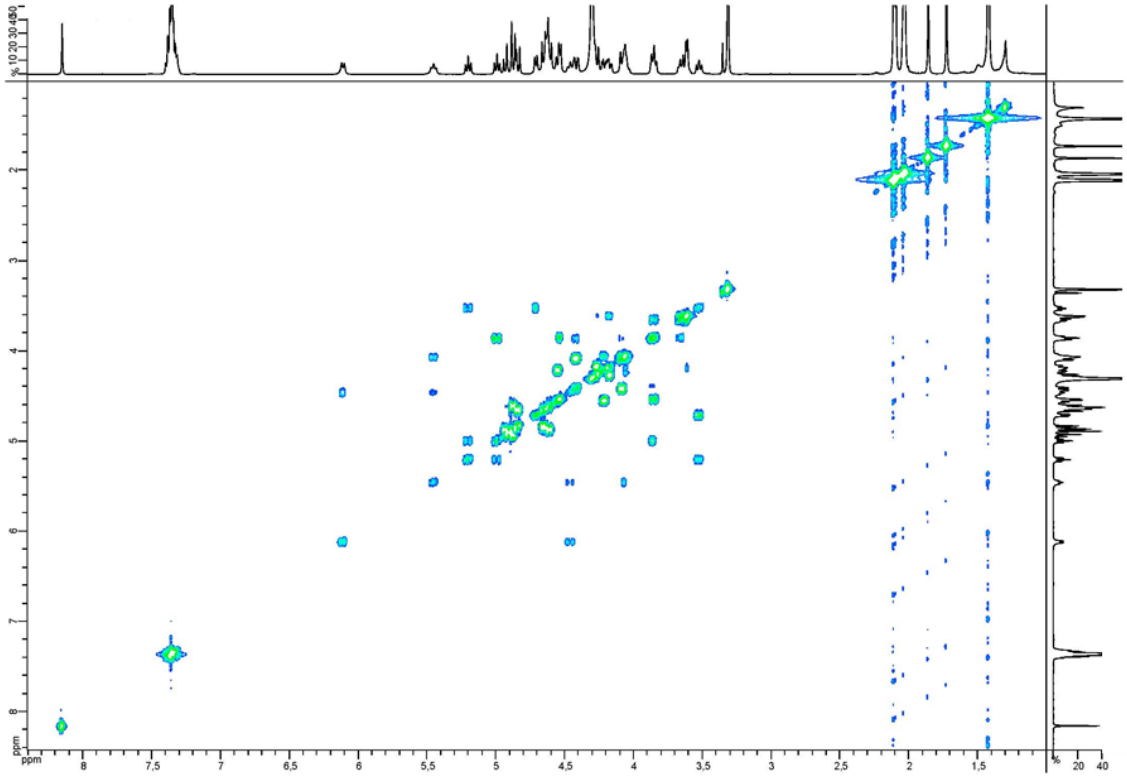
Compound (**18**) ^{1}H NMR



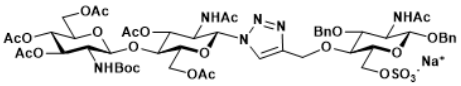


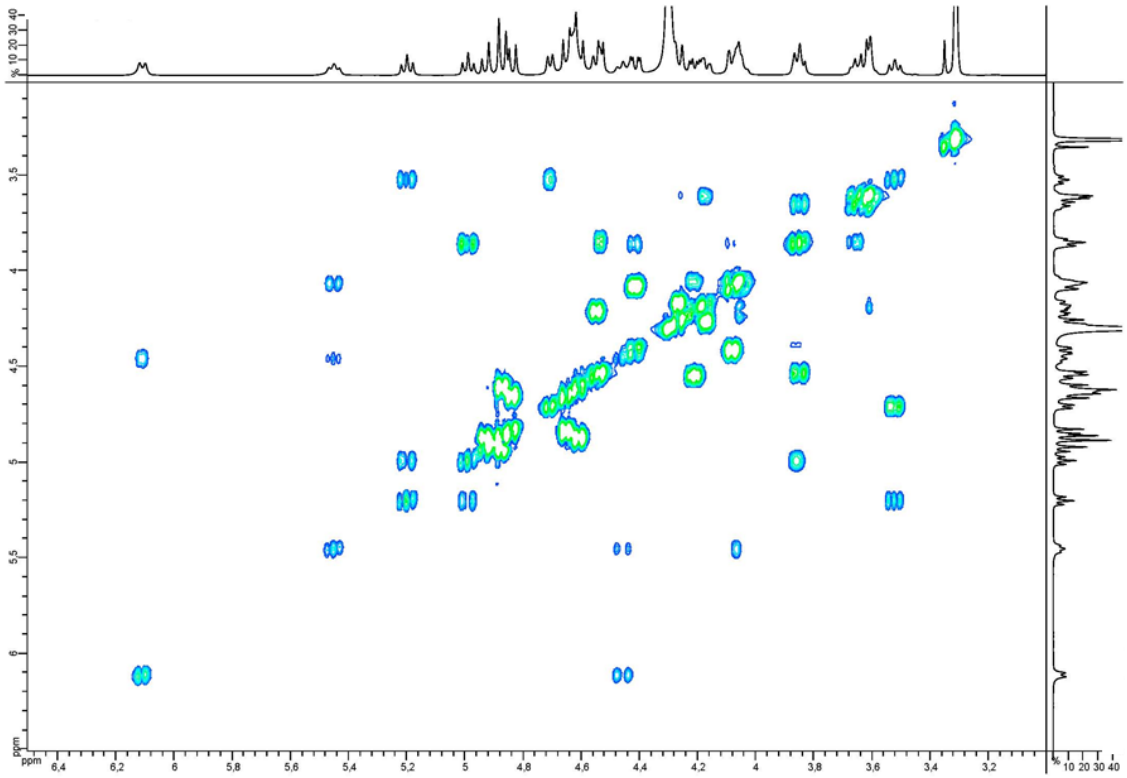
Compound (**18**) COSY NMR



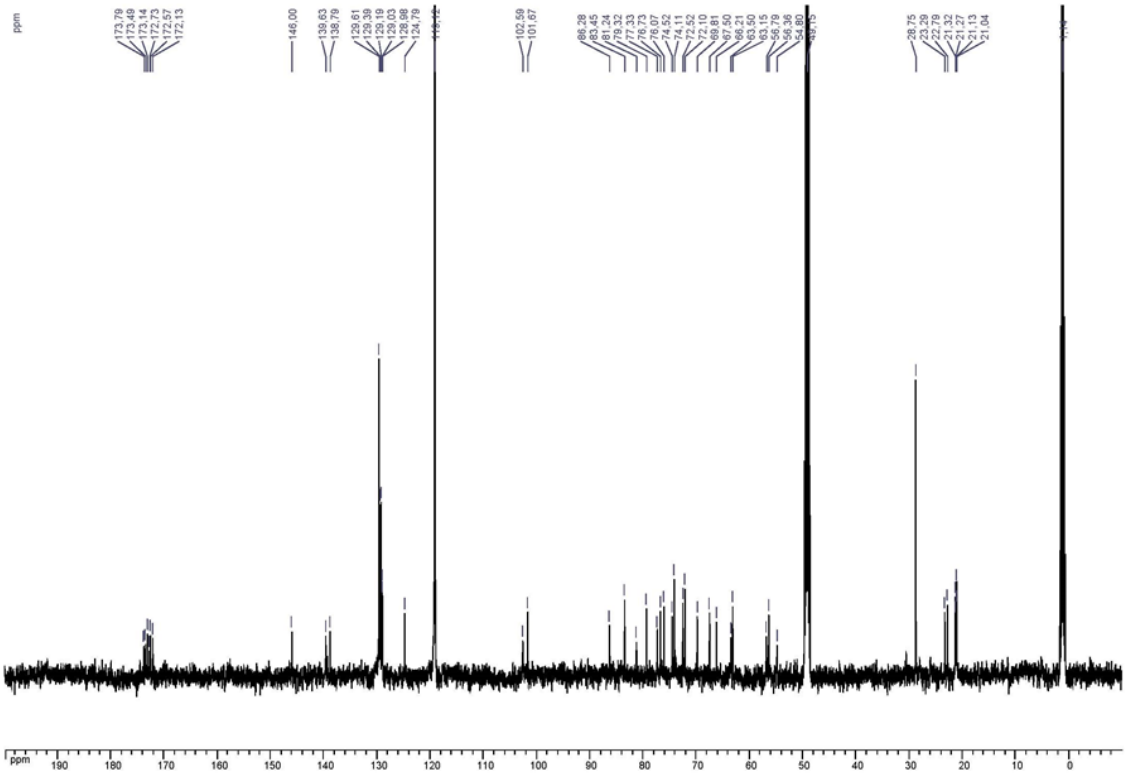


Compound (**18**) COSY NMR

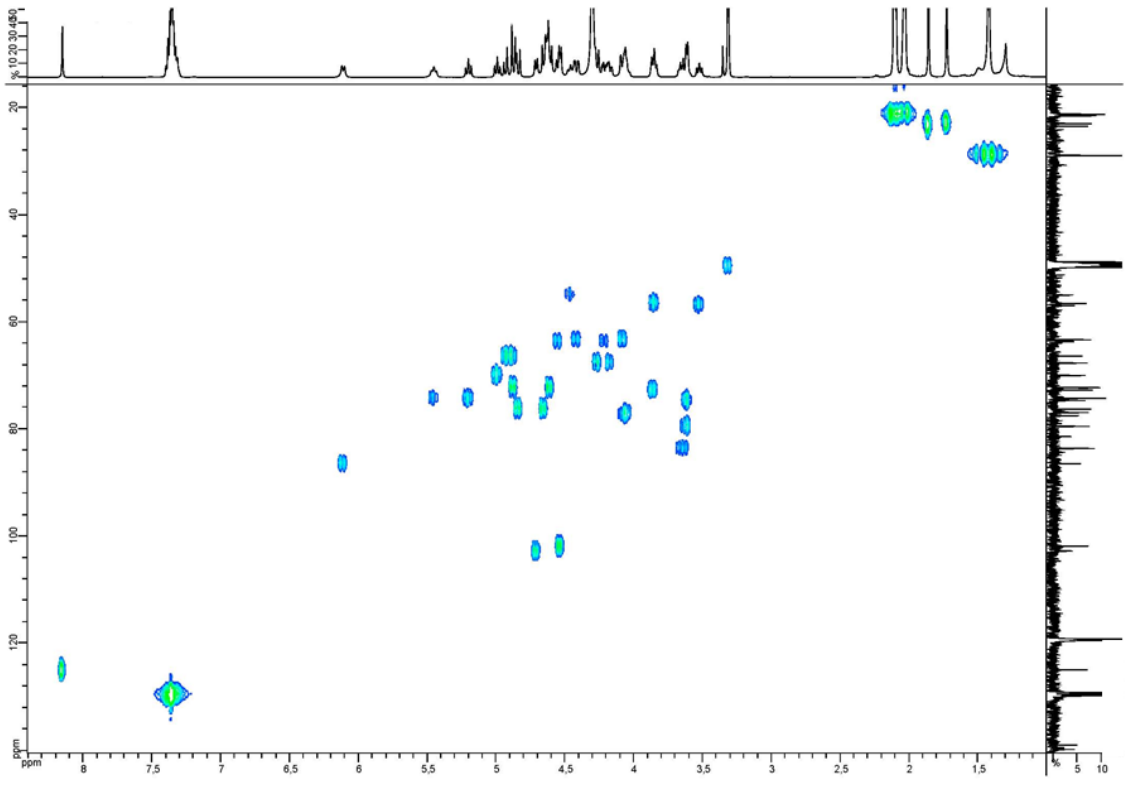




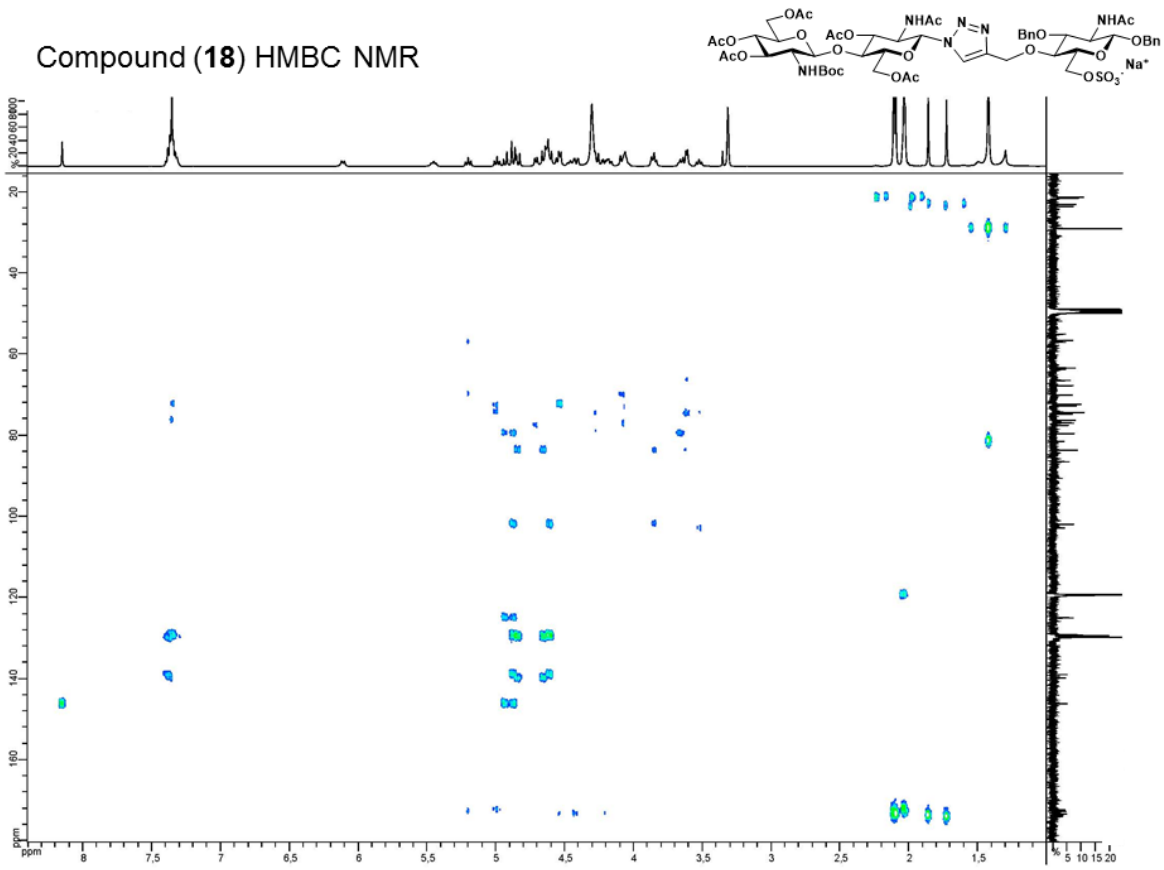
Compound (**18**) ^{13}C NMR



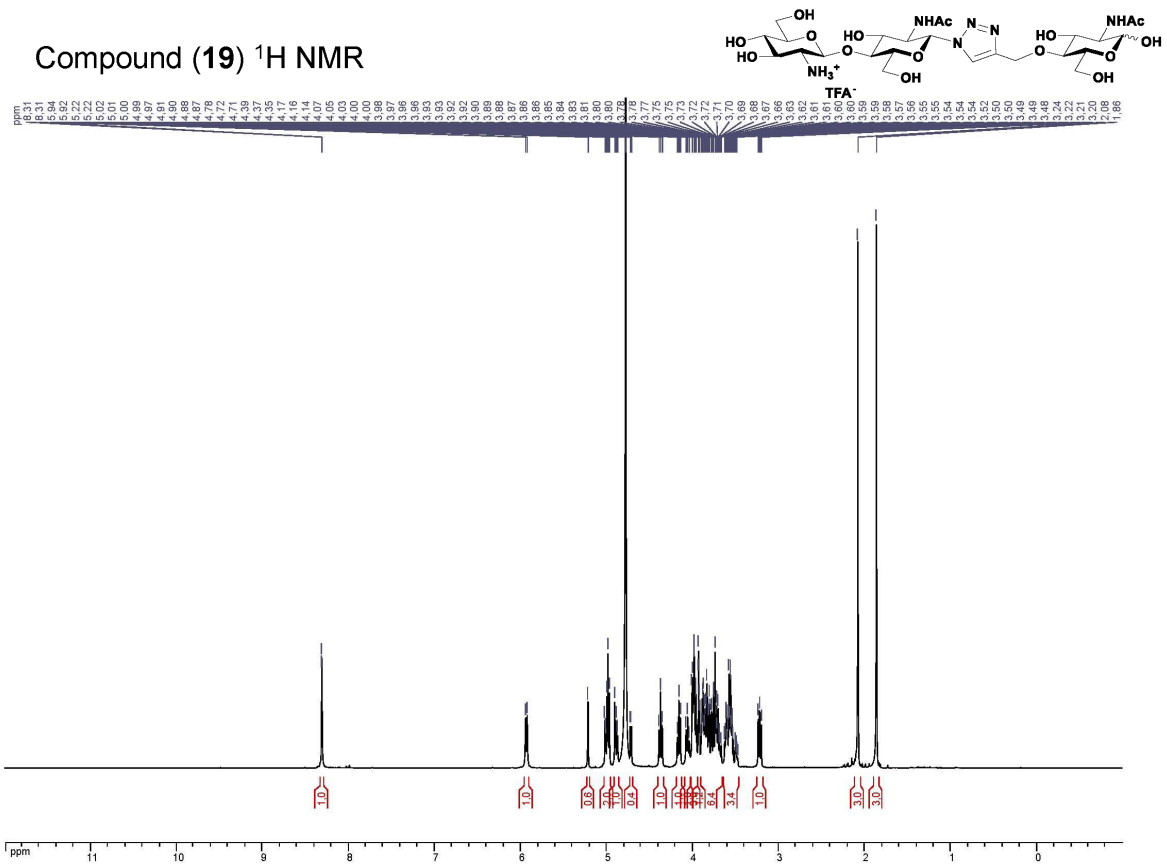
Compound (**18**) HSQC NMR



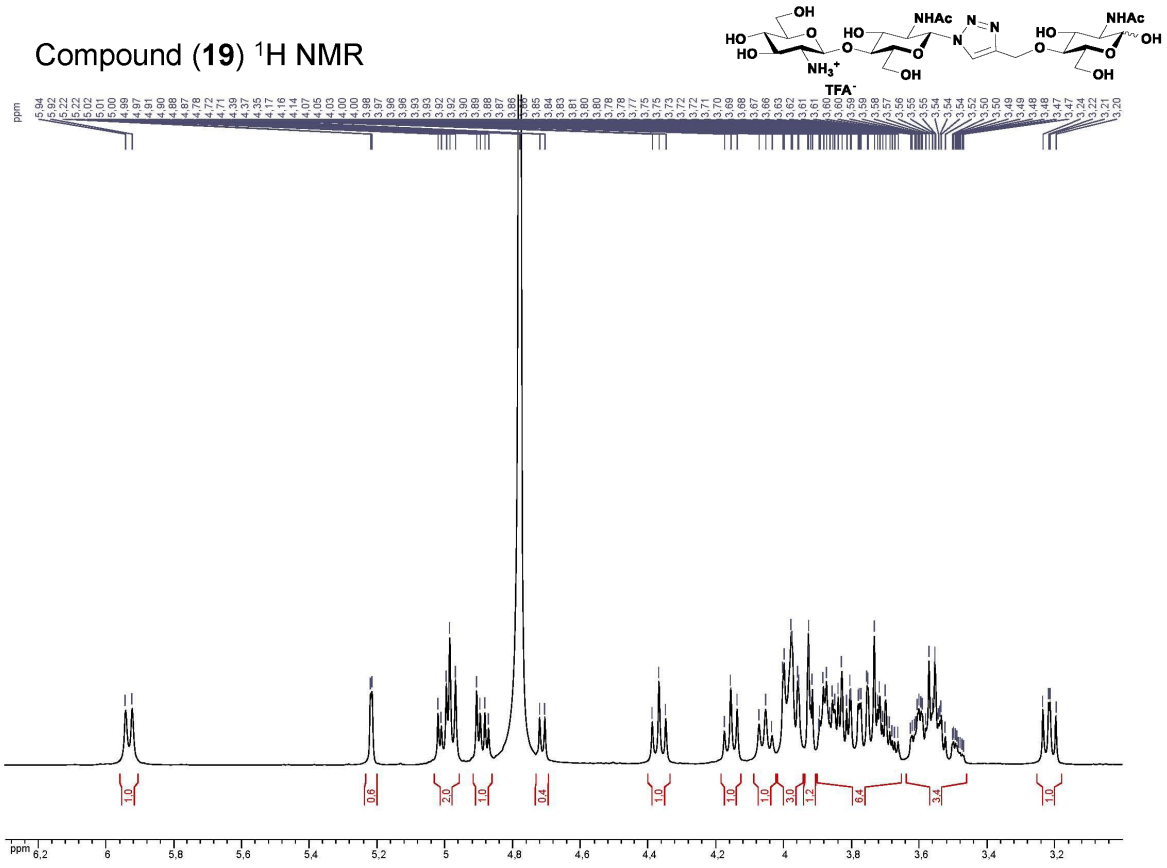
Compound (**18**) HMBC NMR



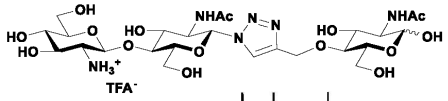
Compound (**19**) ^{1}H NMR

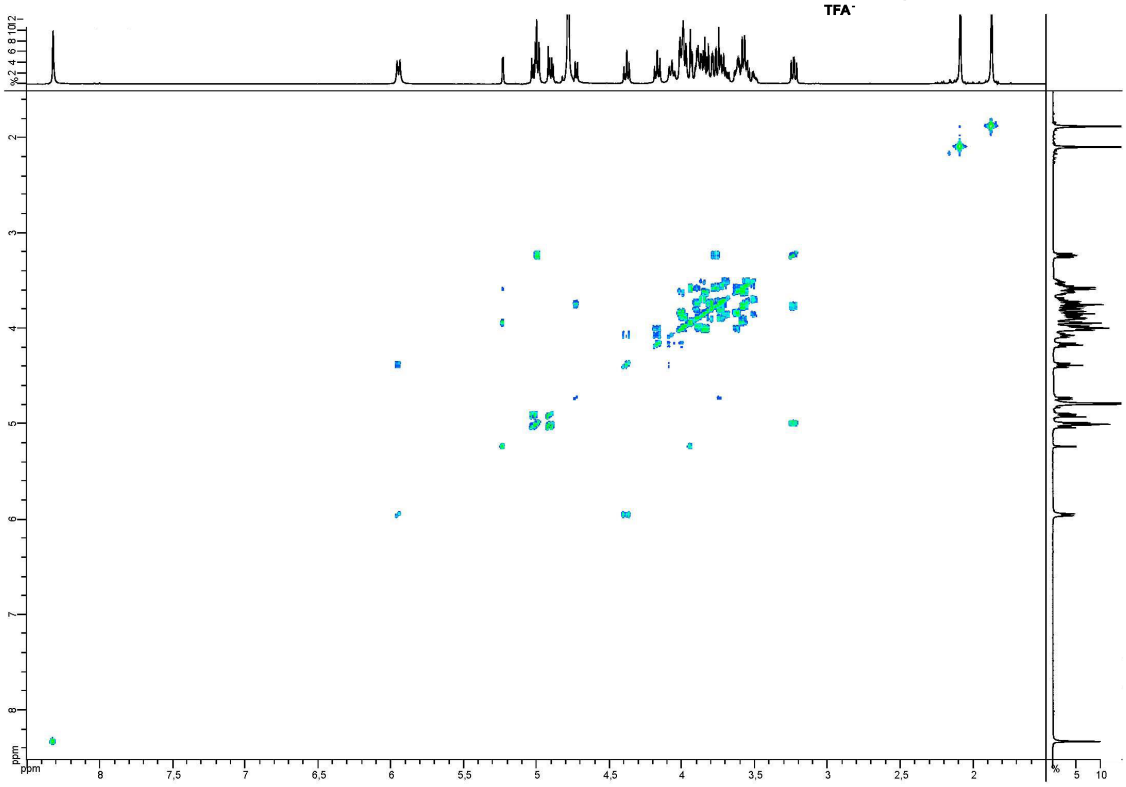


Compound (**19**) ^{1}H NMR

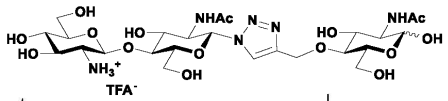


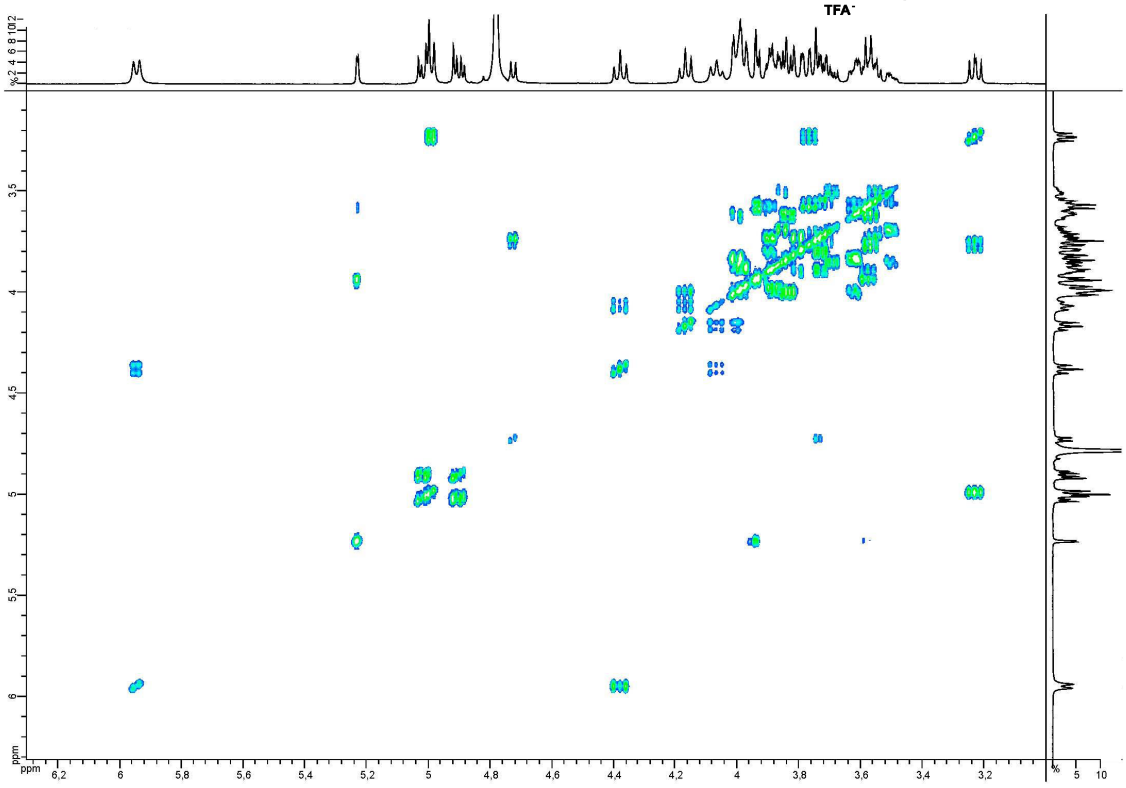
Compound (**19**) COSY NMR



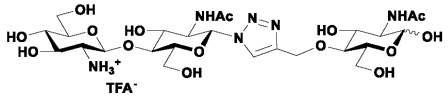


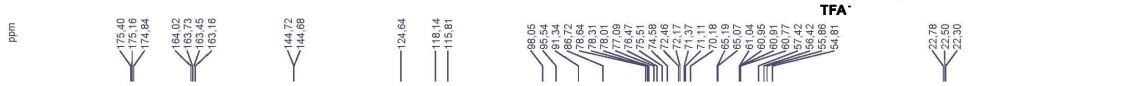
Compound (**19**) COSY NMR

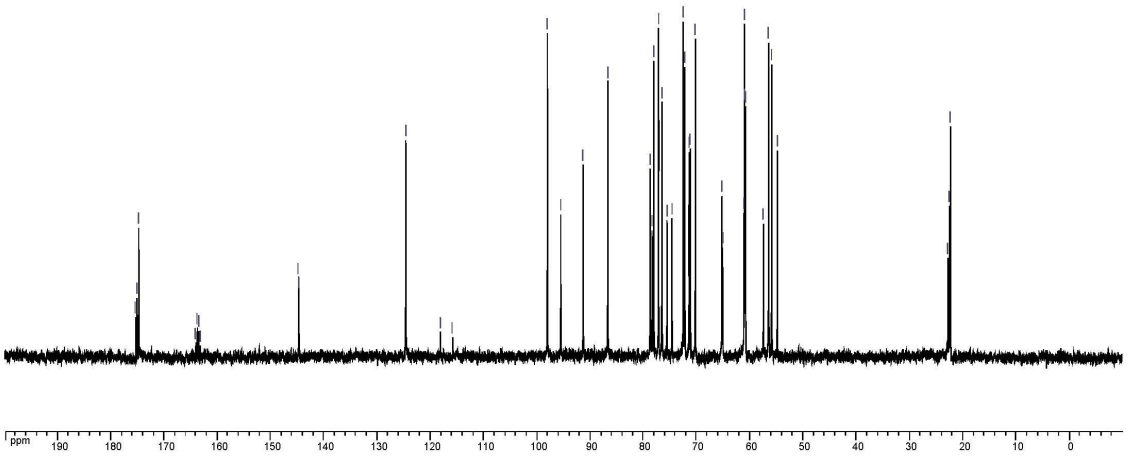




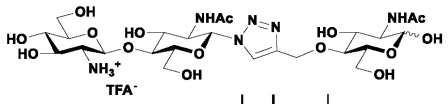
Compound (**19**) ^{13}C NMR

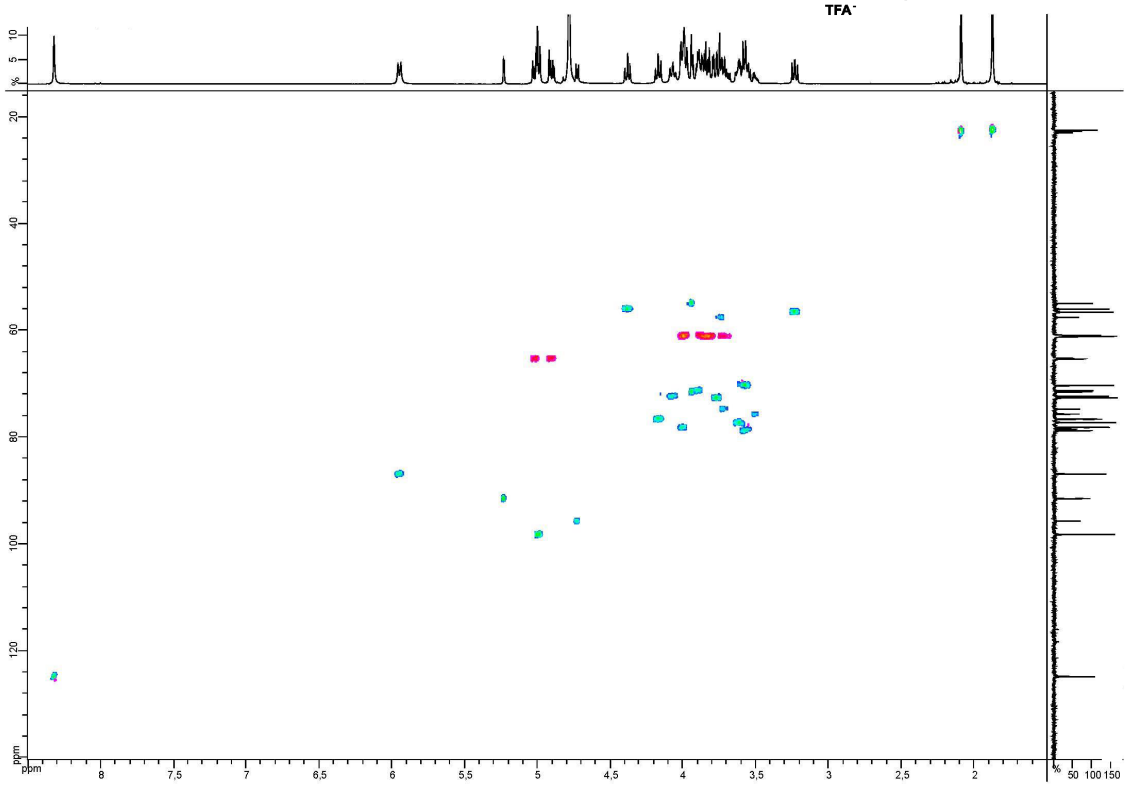




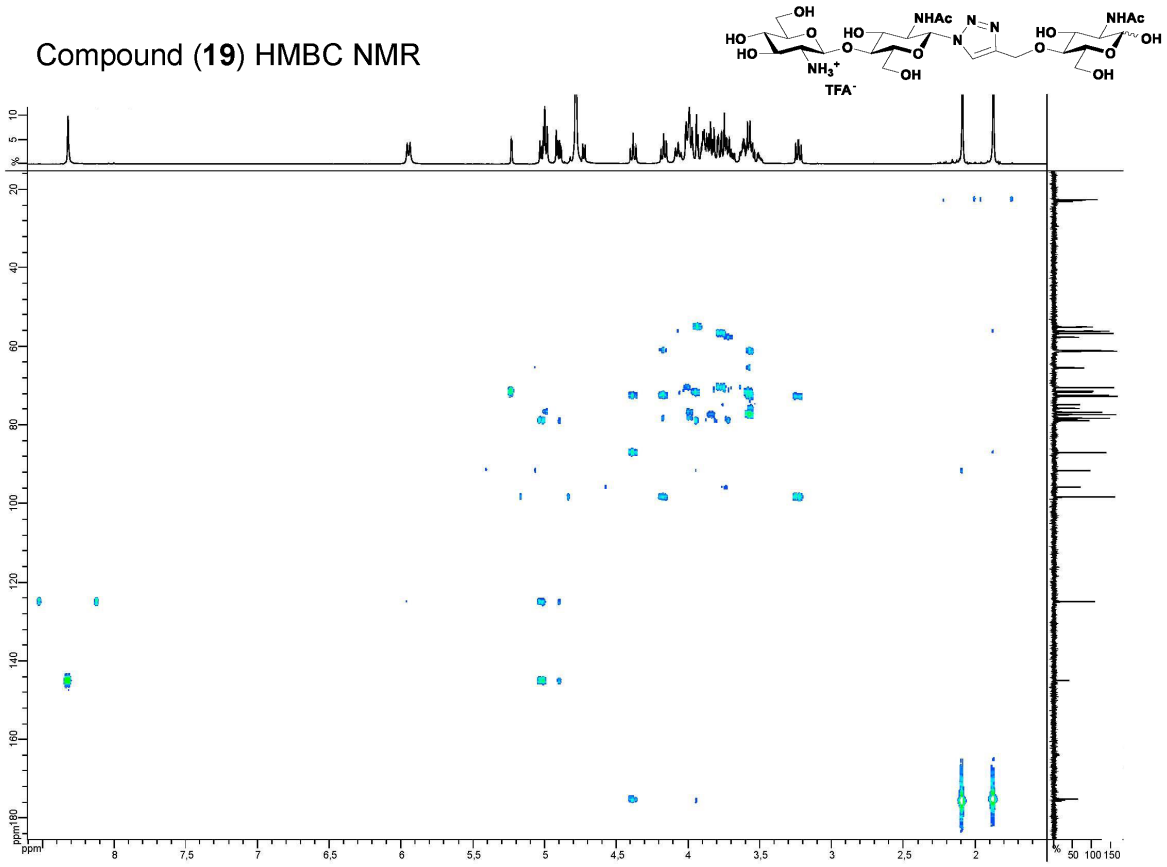


Compound (**19**) HSQC NMR

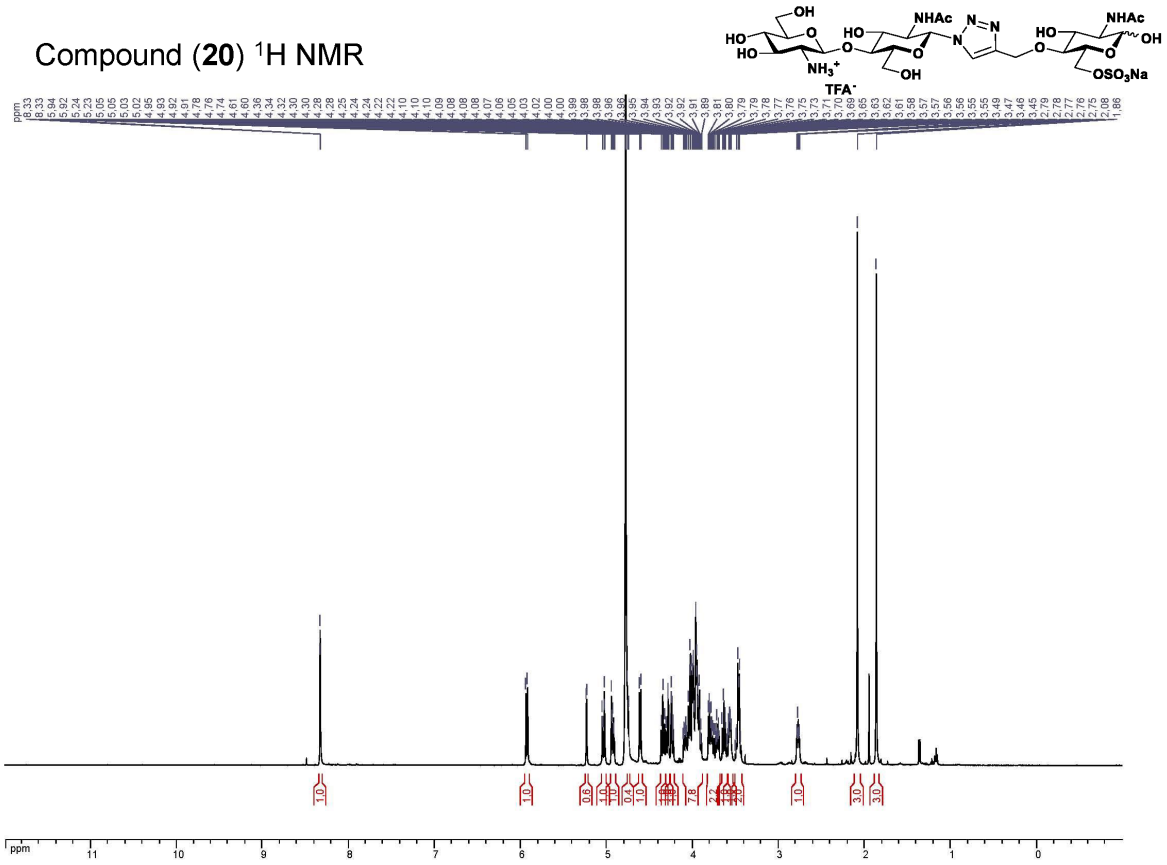




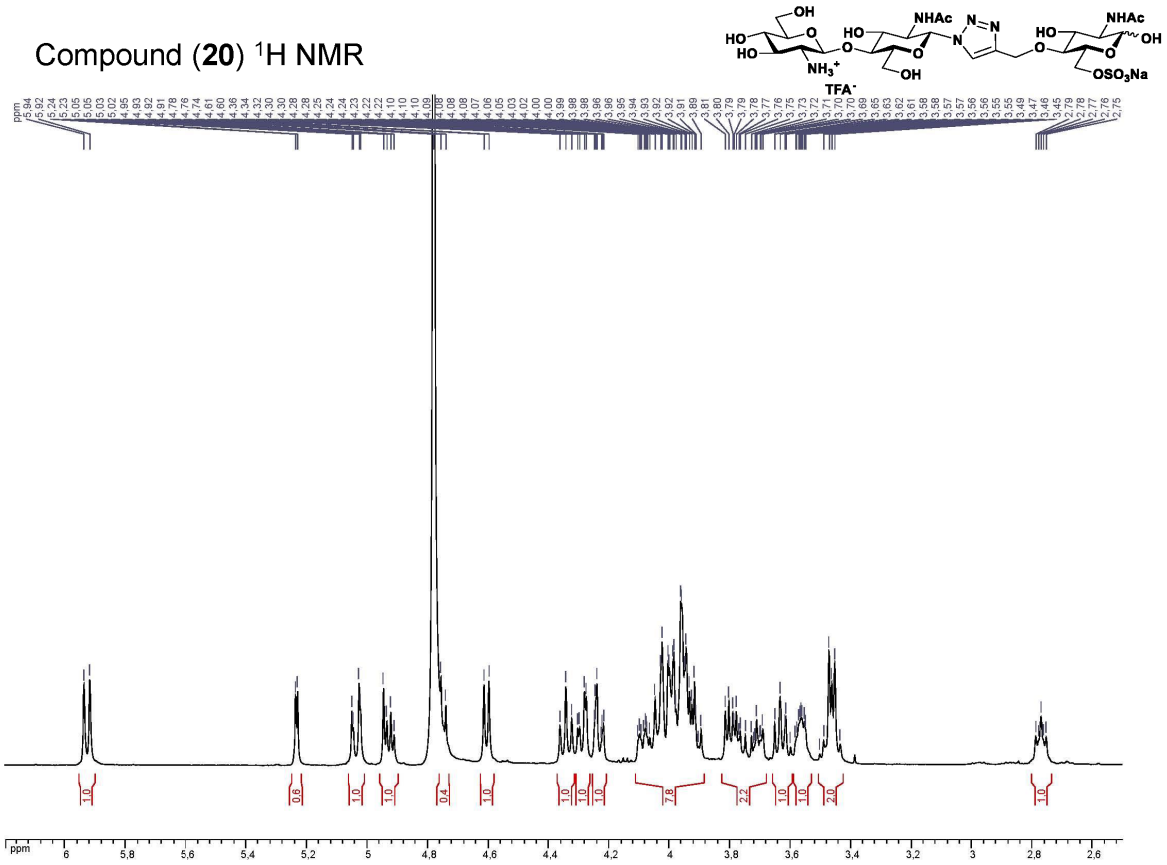
Compound (**19**) HMBC NMR



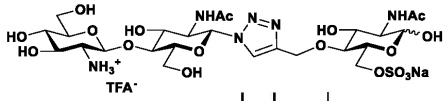
Compound (**20**) ^{1}H NMR

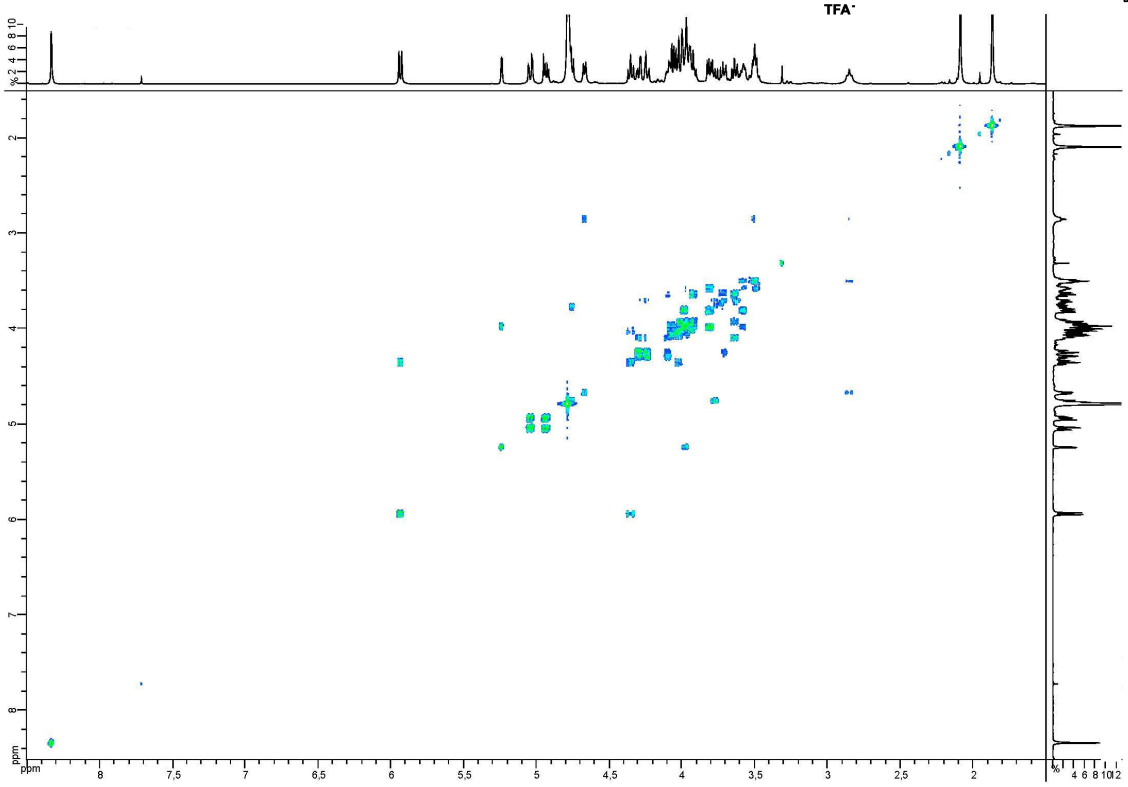


Compound (**20**) ^{1}H NMR

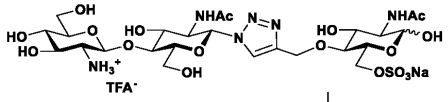


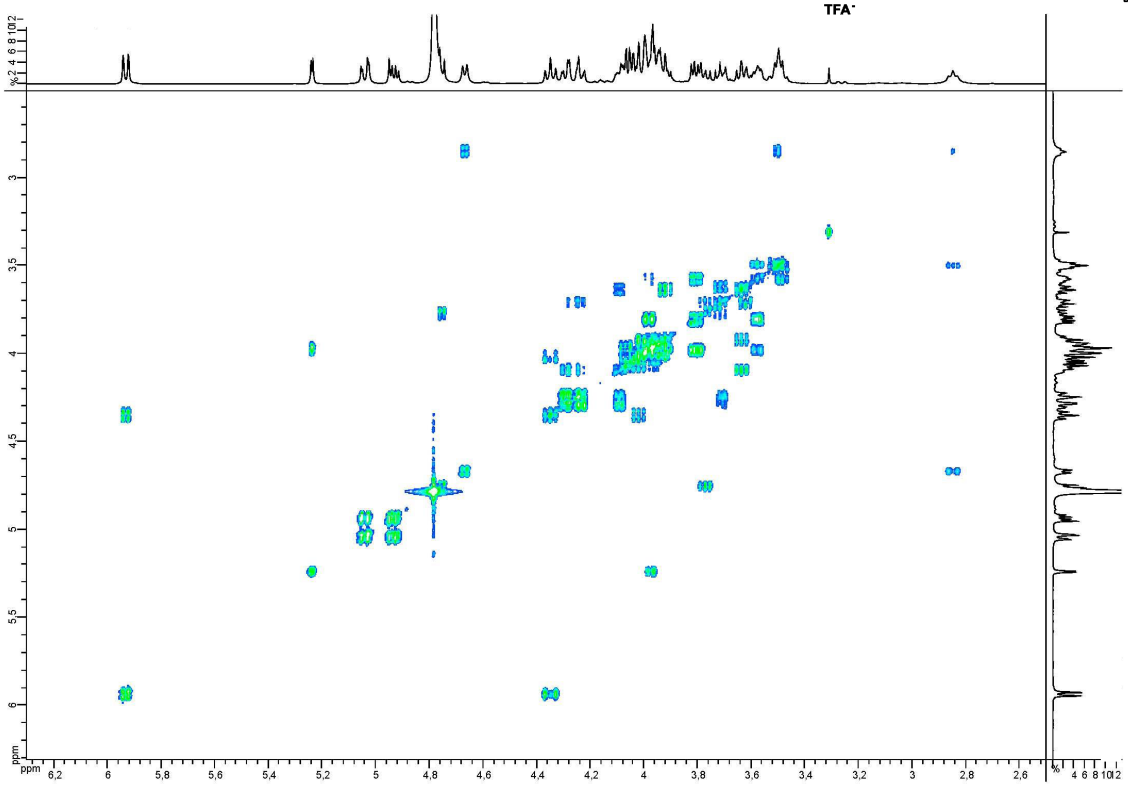
Compound (**20**) COSY NMR



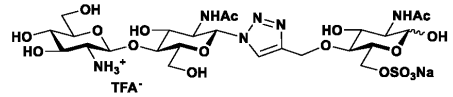


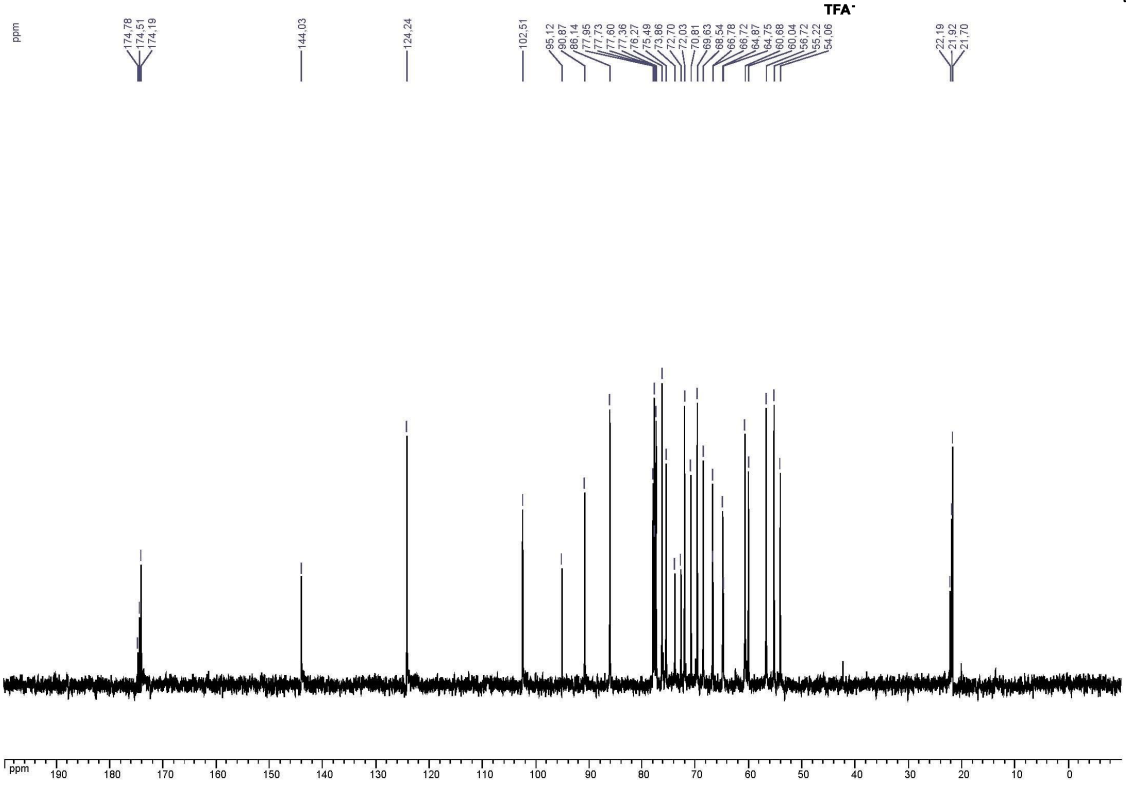
Compound (**20**) COSY NMR



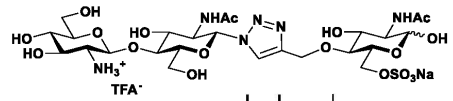


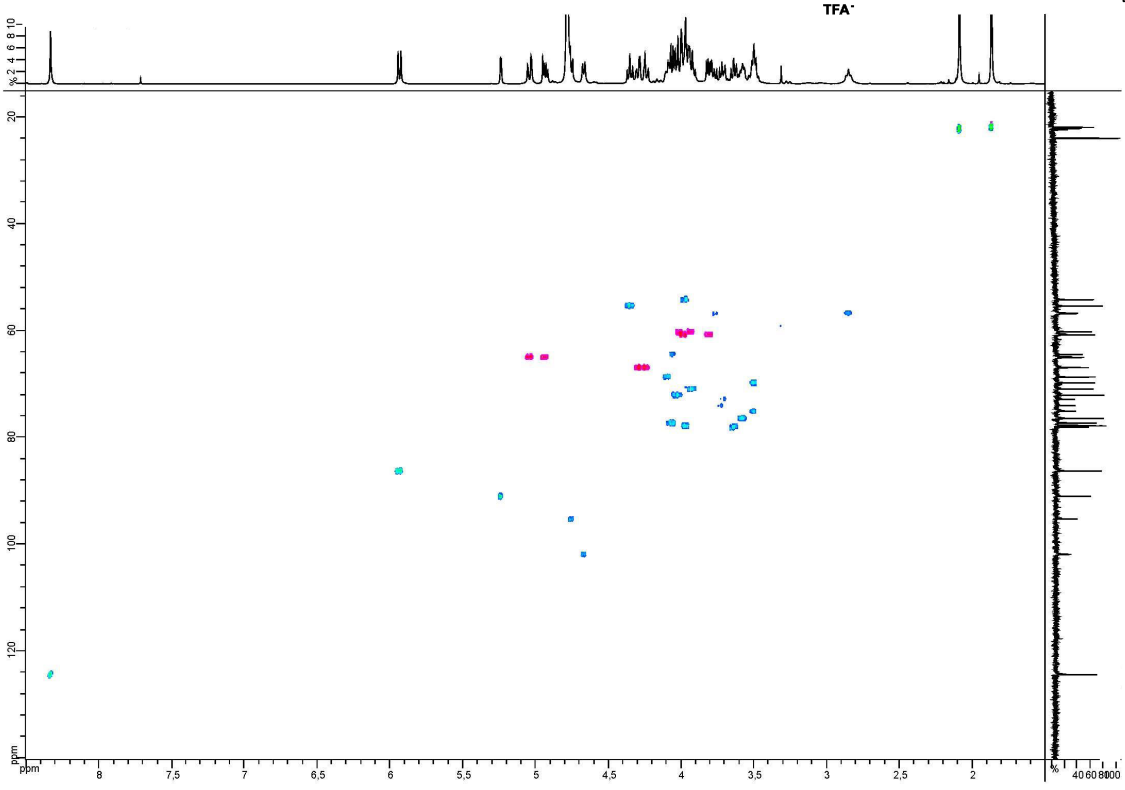
Compound (**20**) ^{13}C NMR



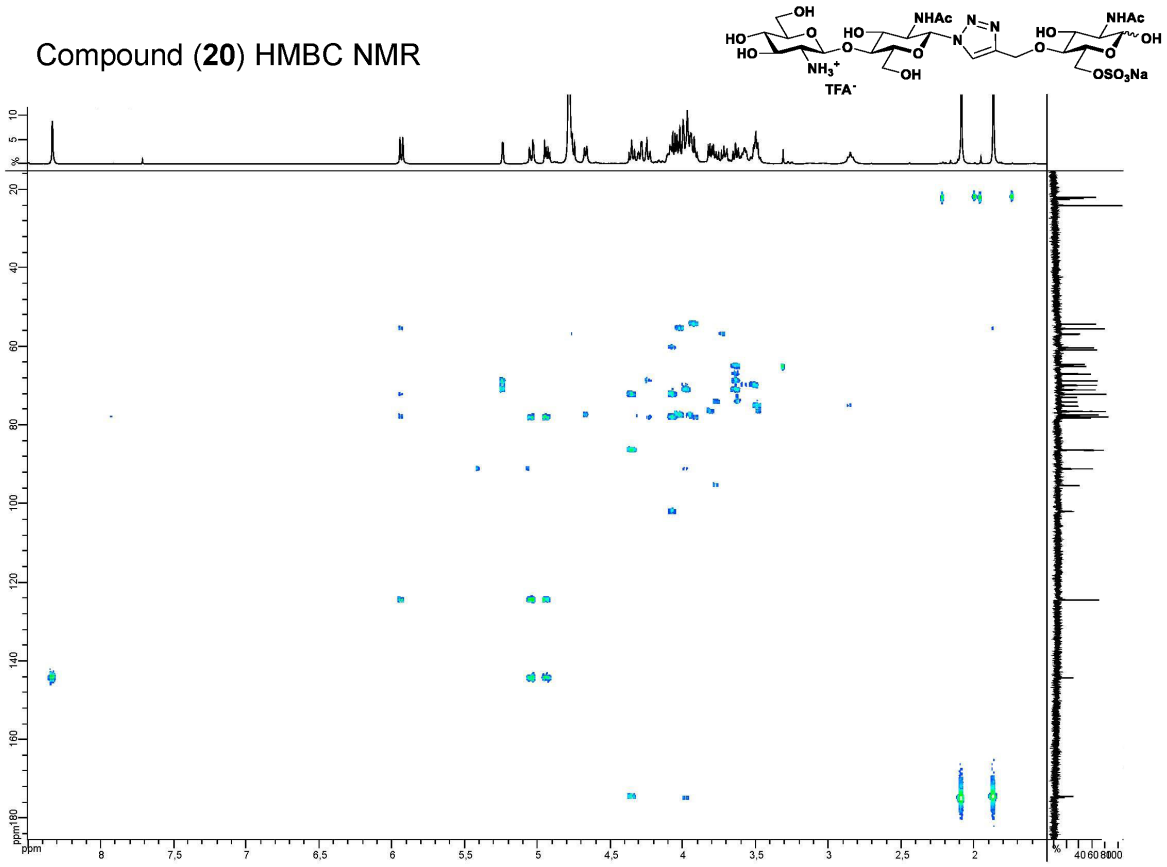


Compound (**20**) HSQC NMR

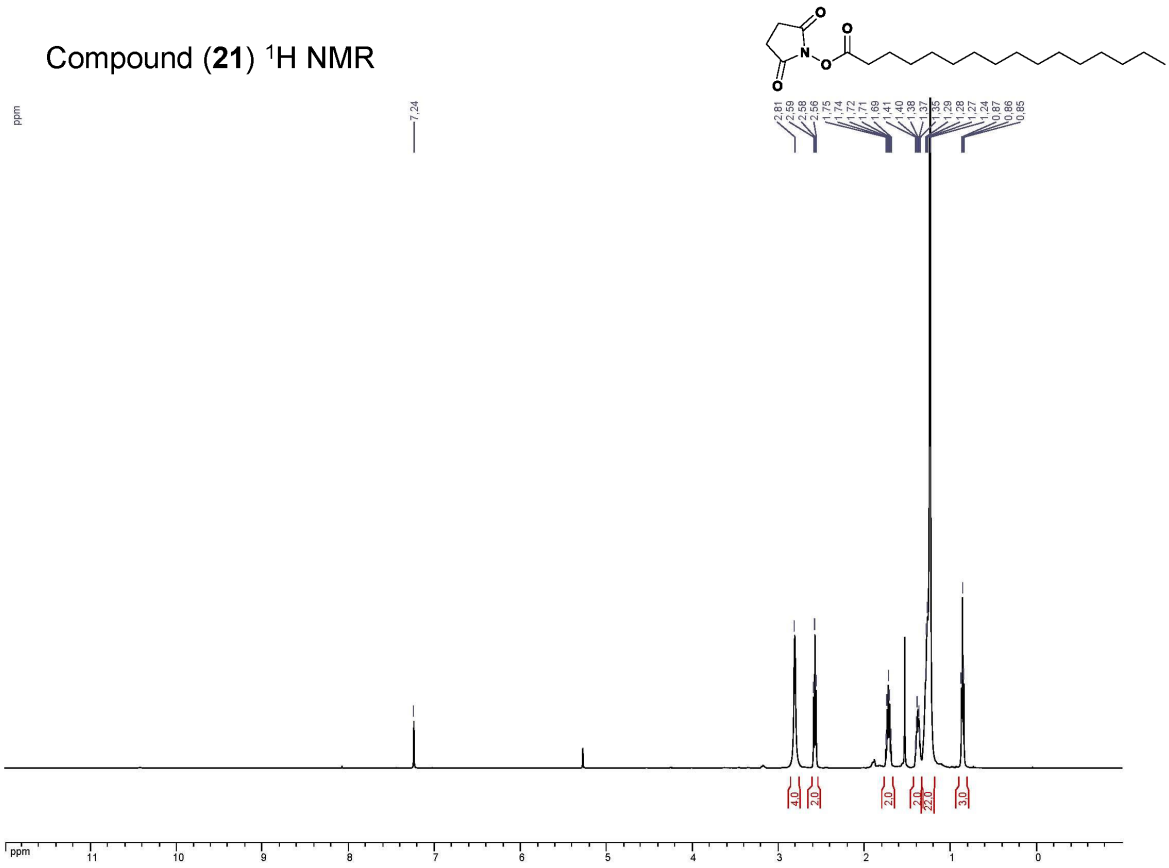




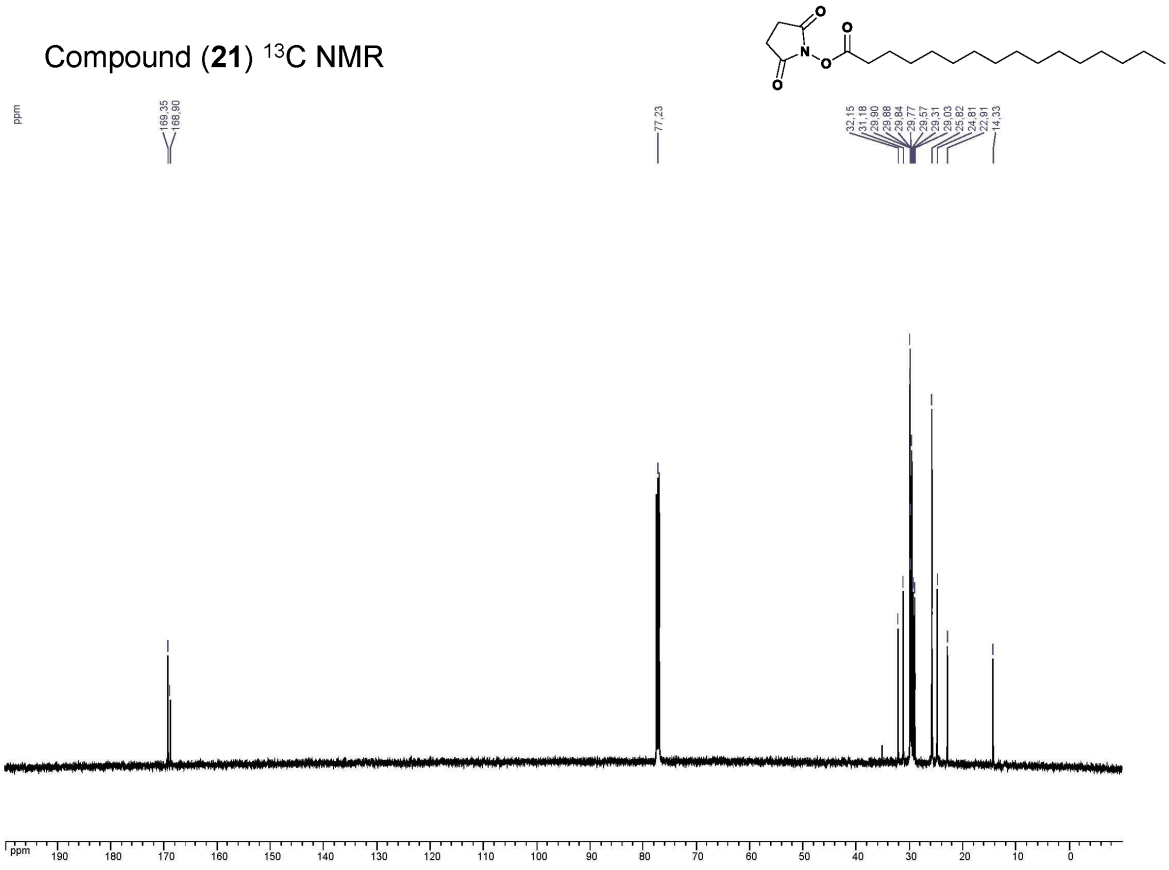
Compound (**20**) HMBC NMR



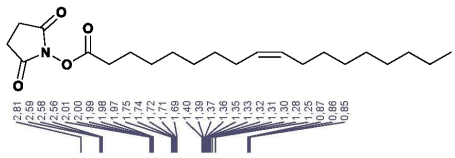
Compound (**21**) ^{1}H NMR

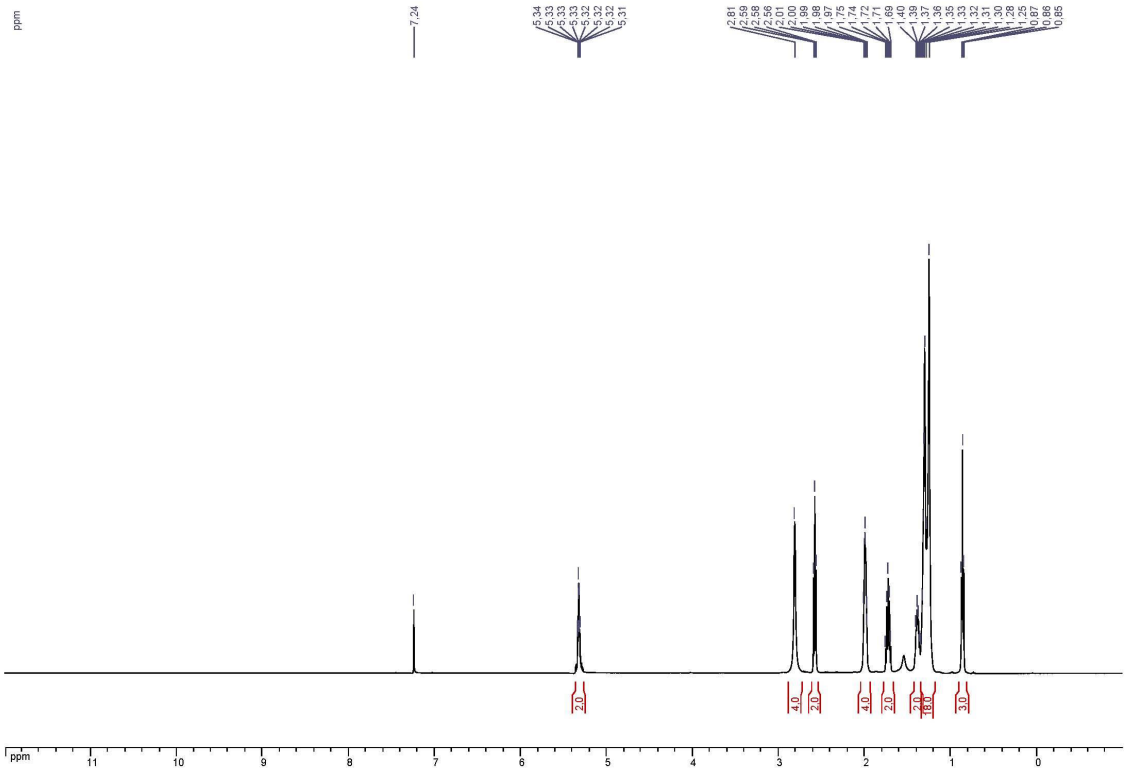


Compound (**21**) ^{13}C NMR

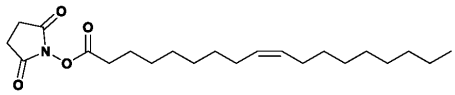


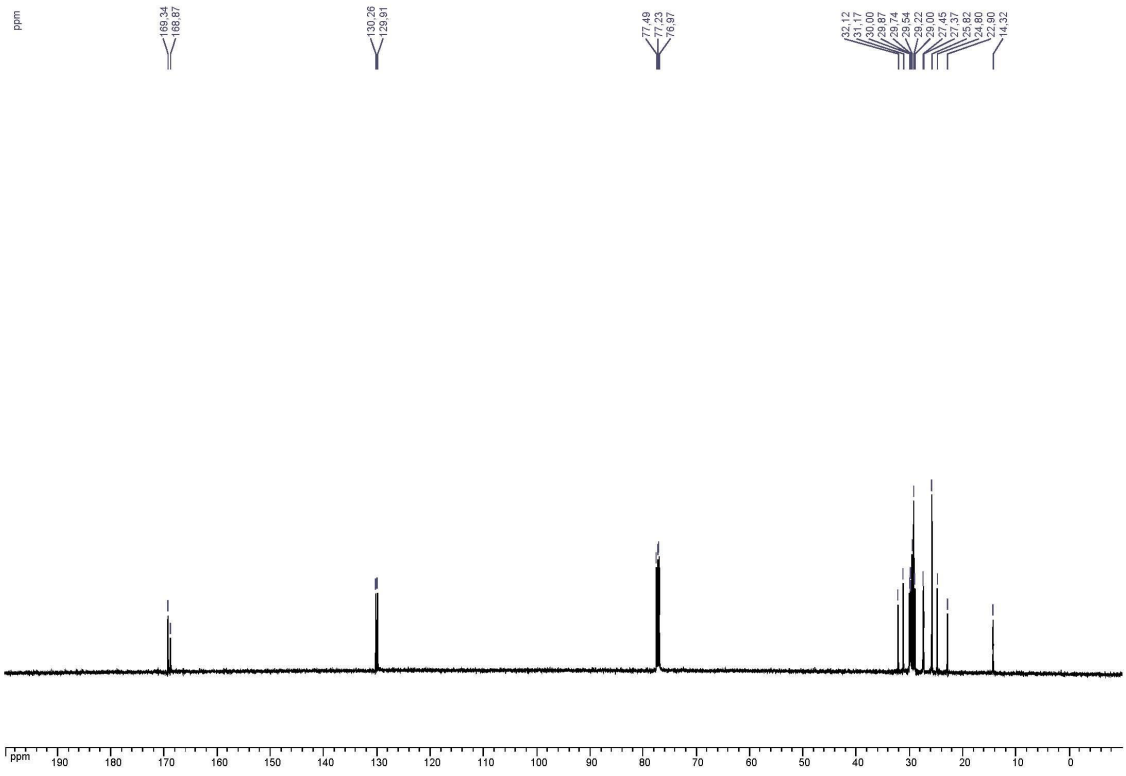
Compound (**22**) ^{1}H NMR



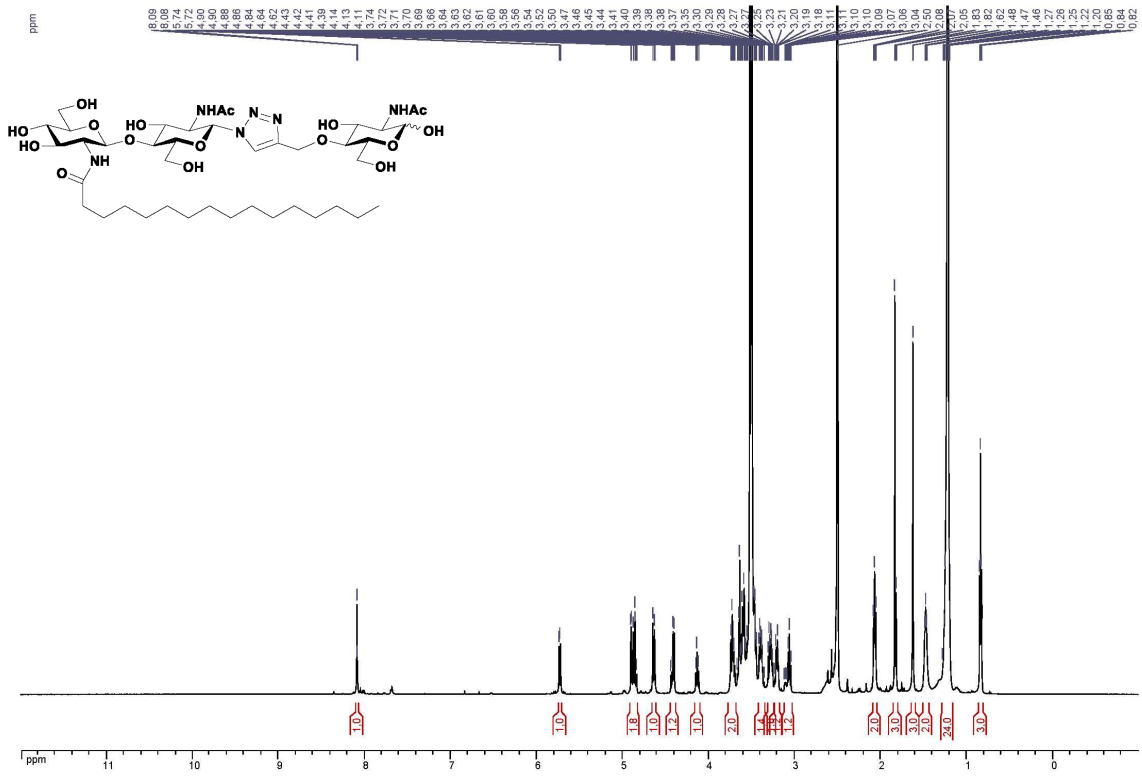


Compound (**22**) ^{13}C NMR

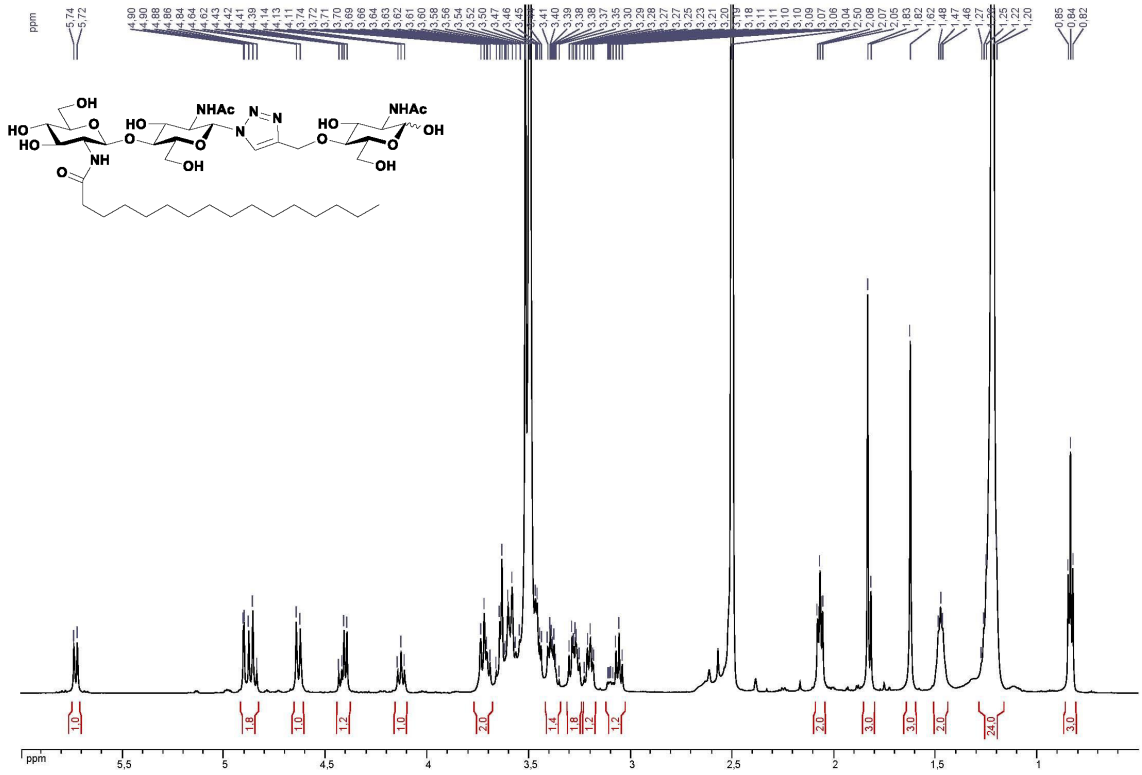




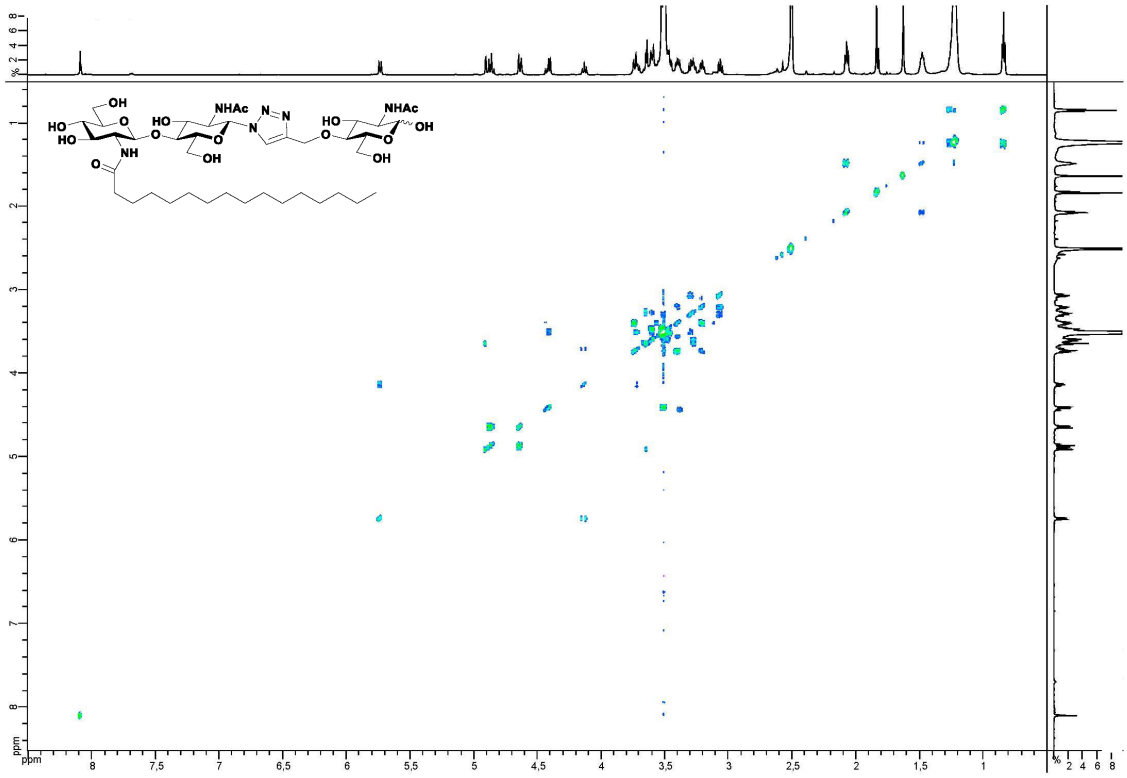
Compound (**3**) ^{1}H NMR



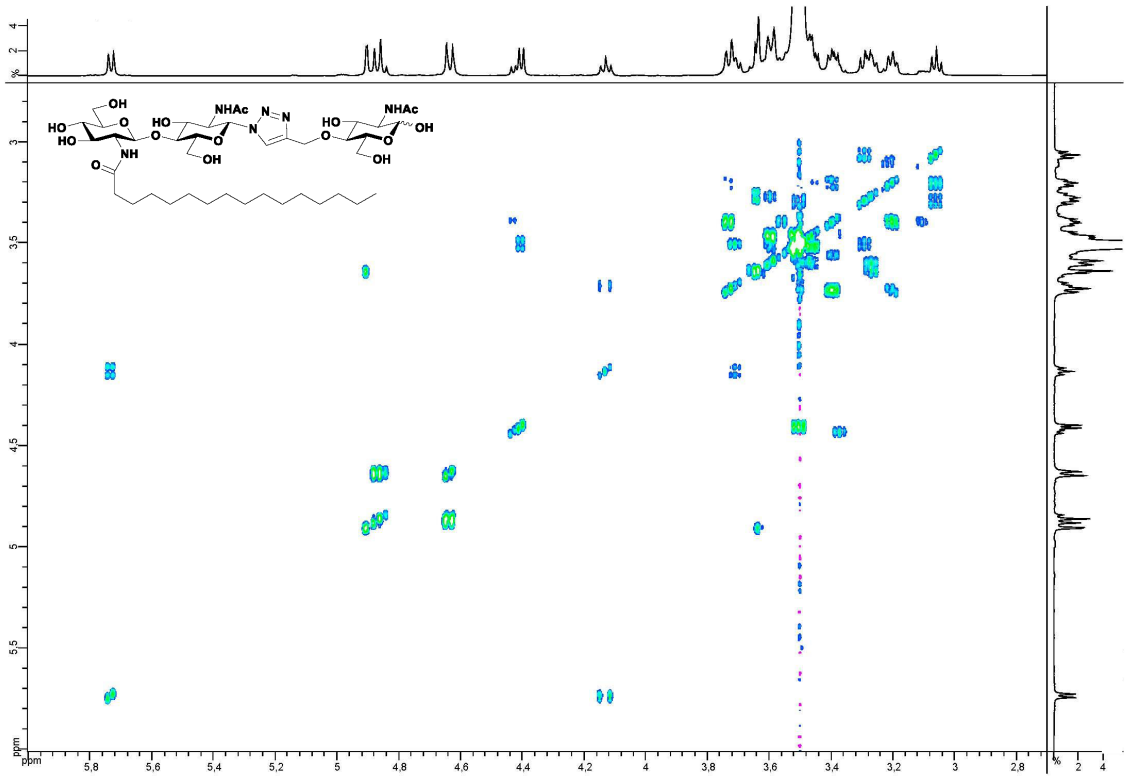
Compound (**3**) ^{1}H NMR



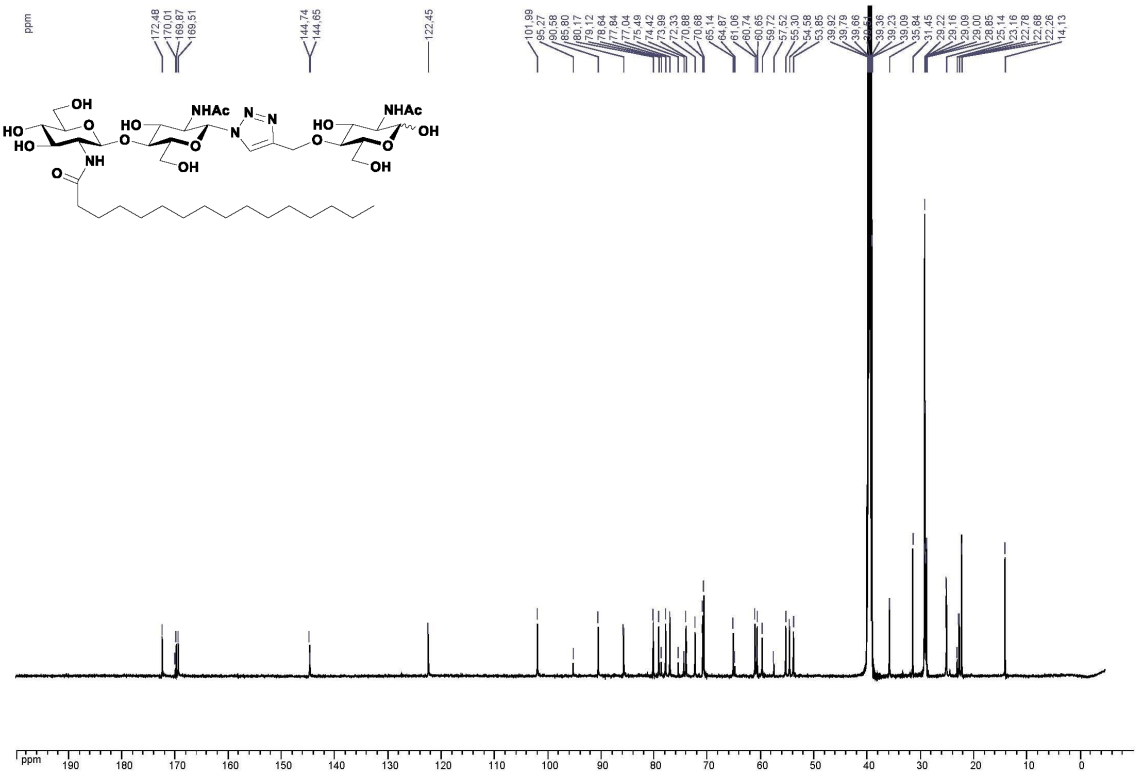
Compound (**3**) COSY NMR



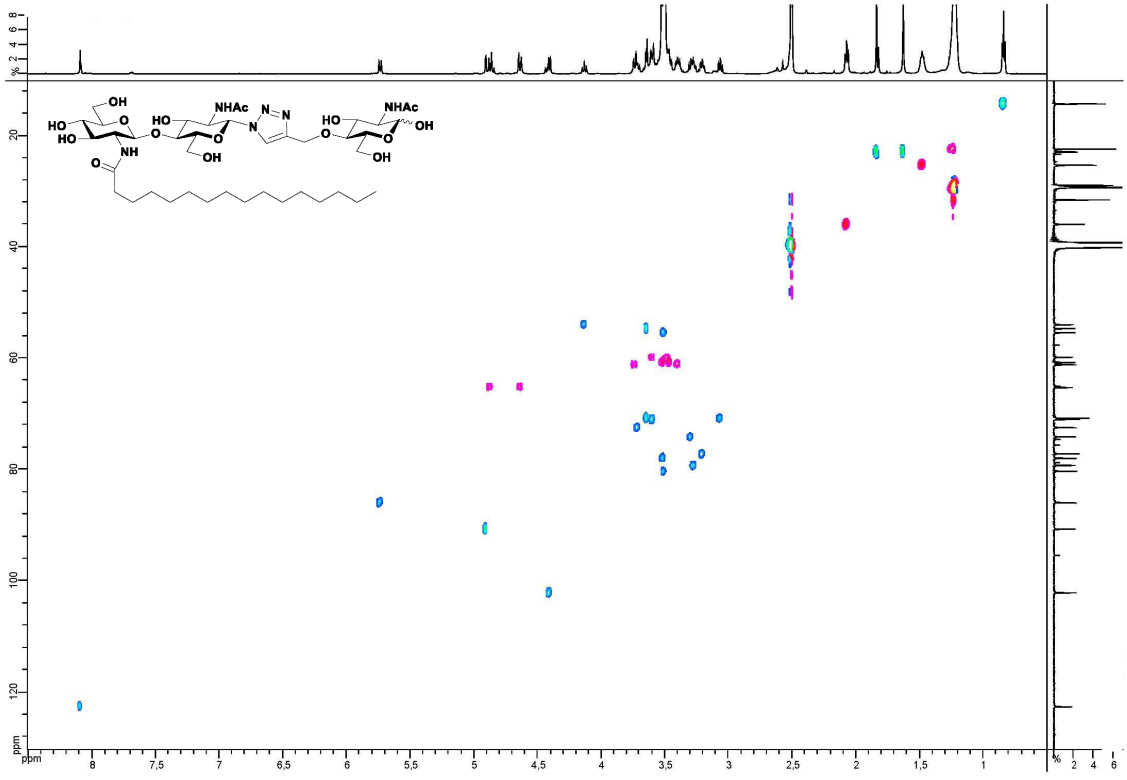
Compound (**3**) COSY NMR



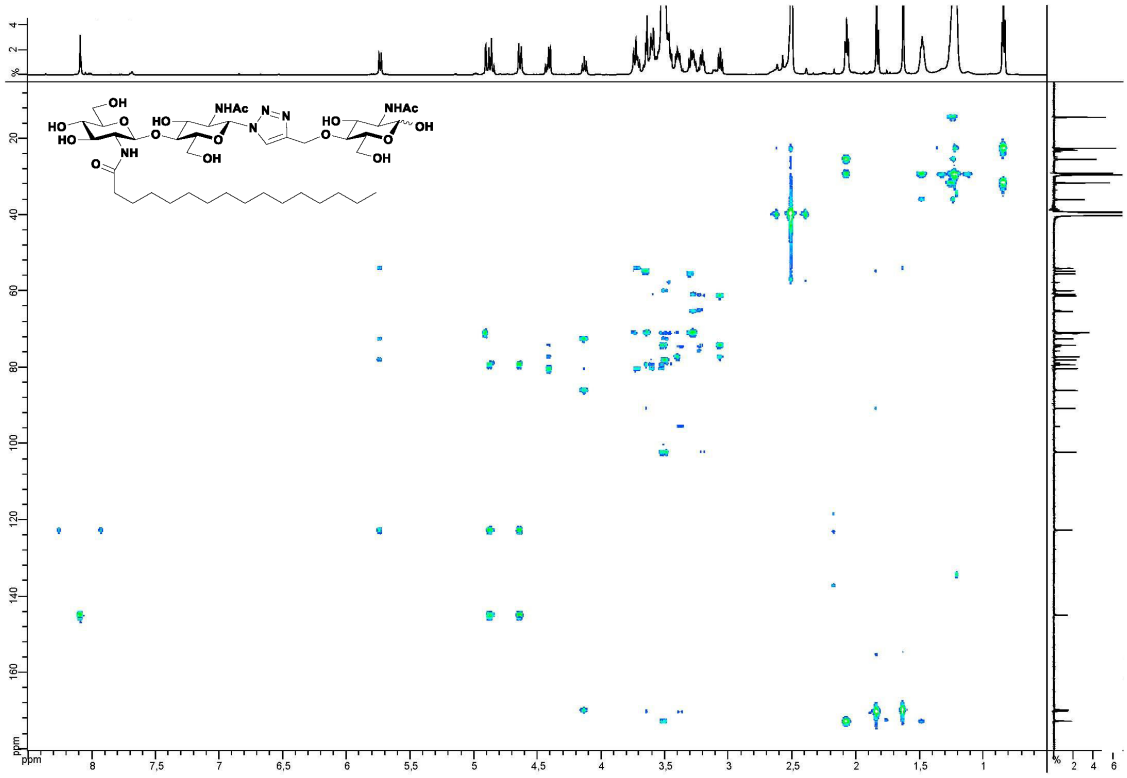
Compound (**3**) ^{13}C NMR



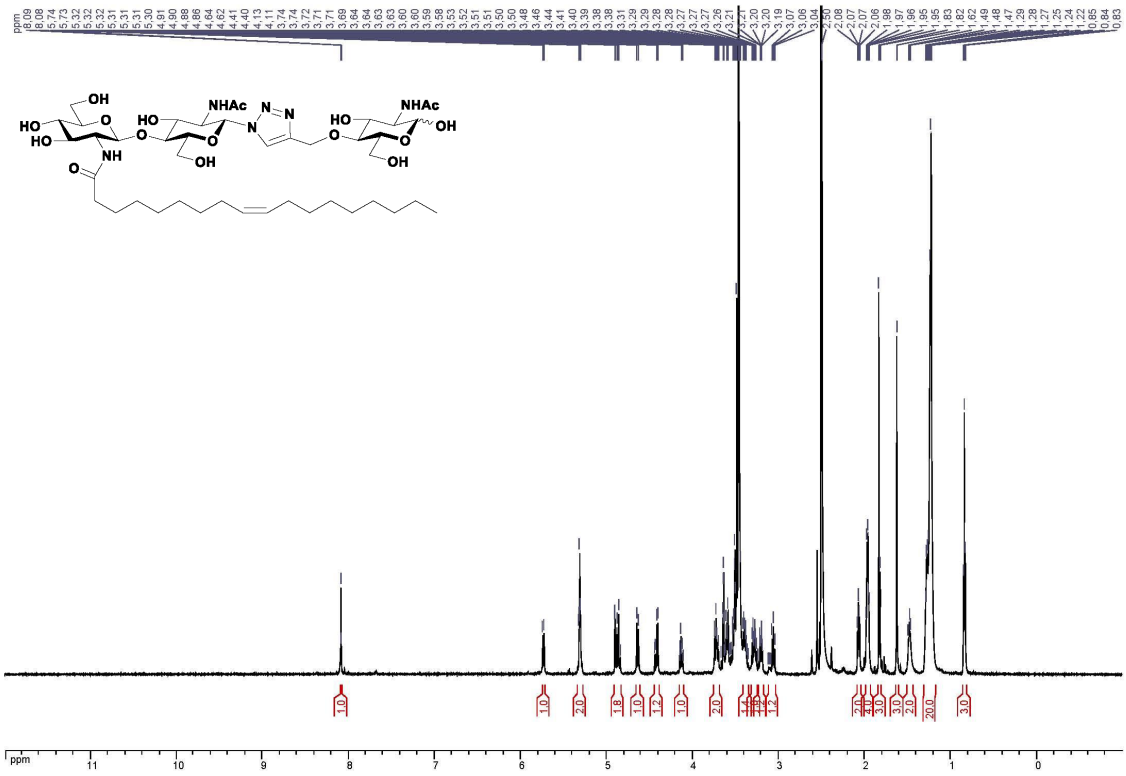
Compound (**3**) HSQC NMR



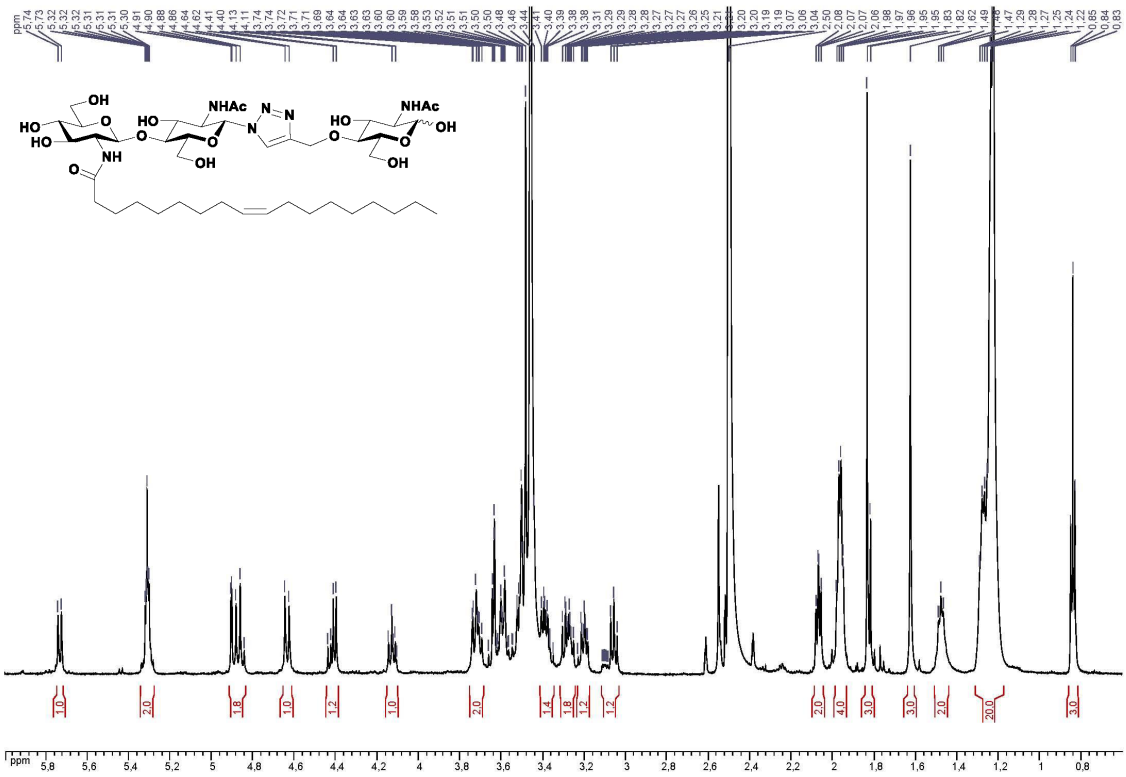
Compound (**3**) HMBC NMR



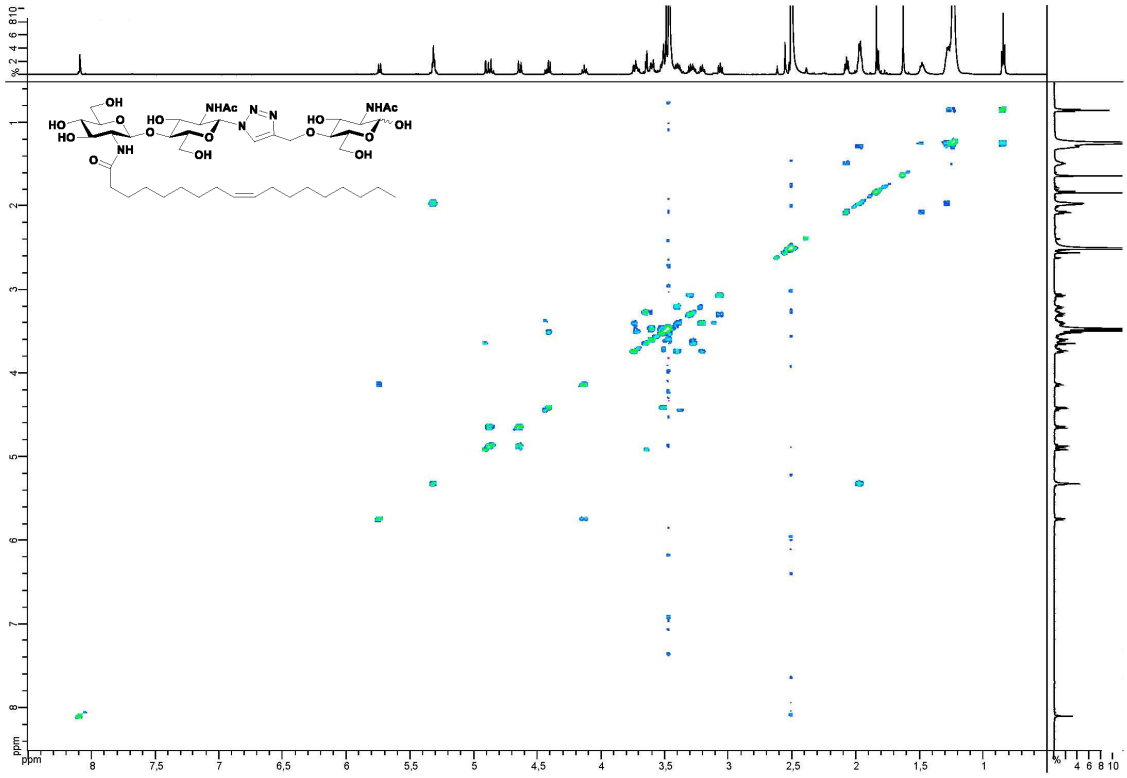
Compound (**4**) ^{1}H NMR



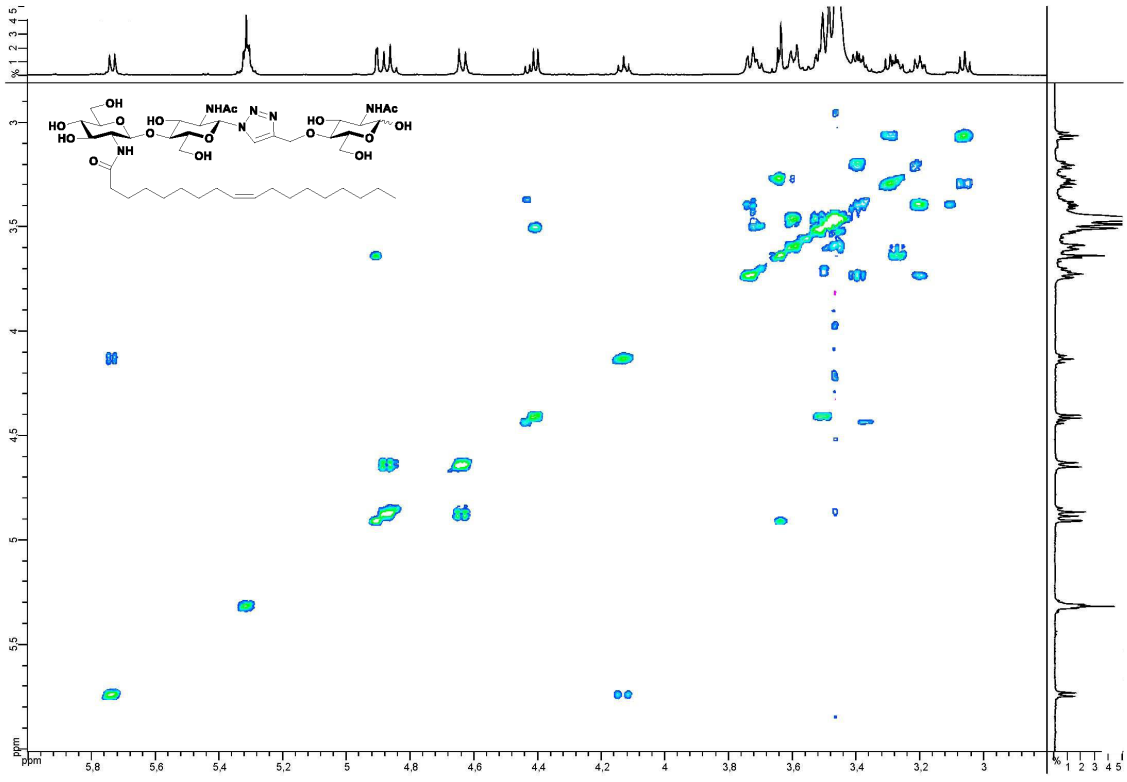
Compound (**4**) ^{1}H NMR



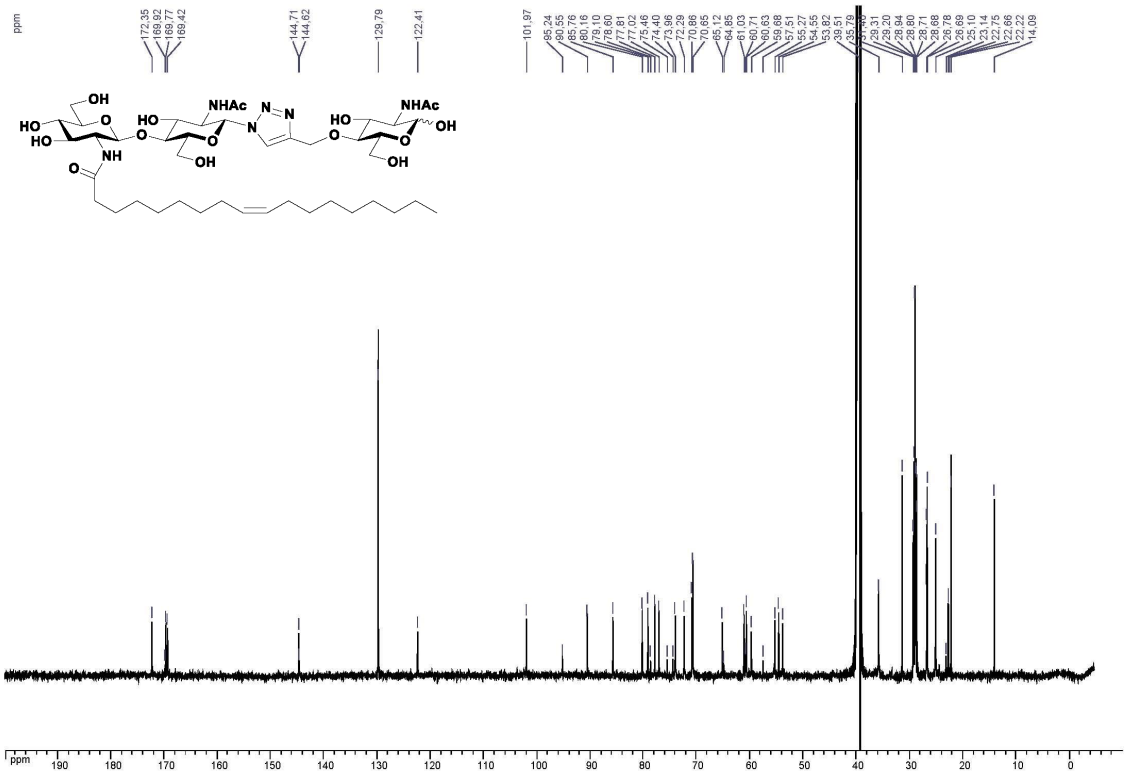
Compound (**4**) COSY NMR



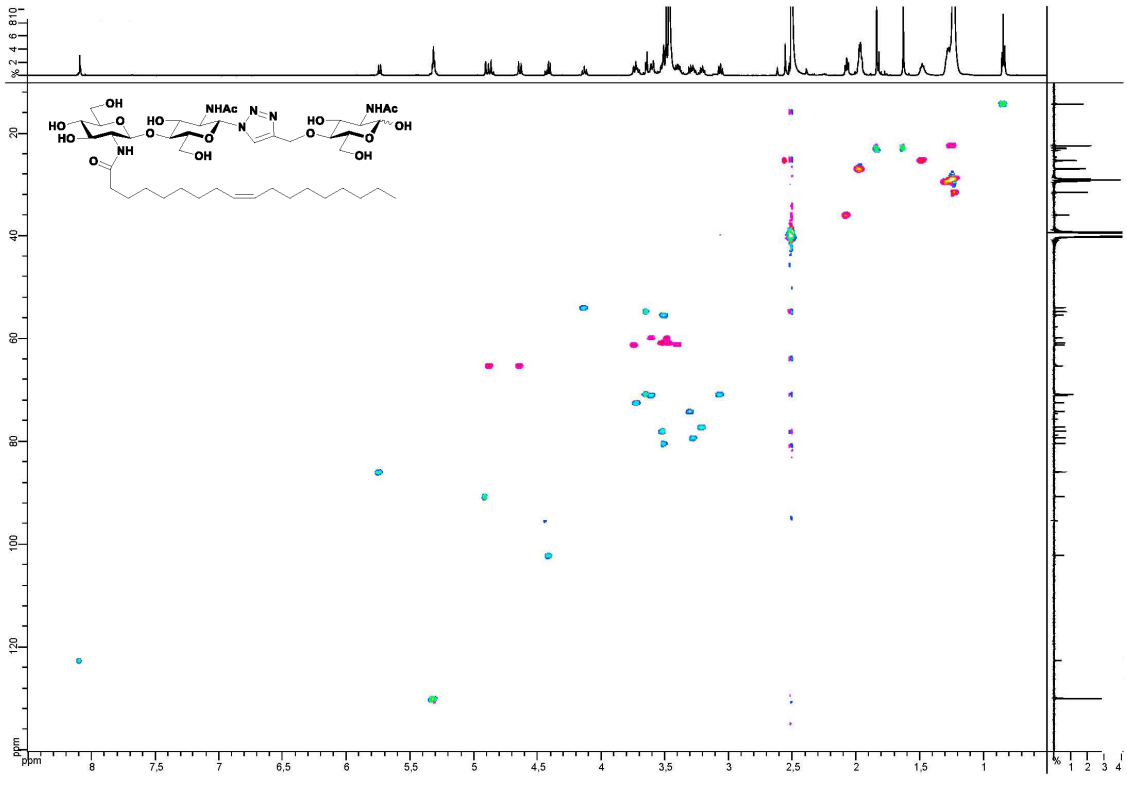
Compound (**4**) COSY NMR



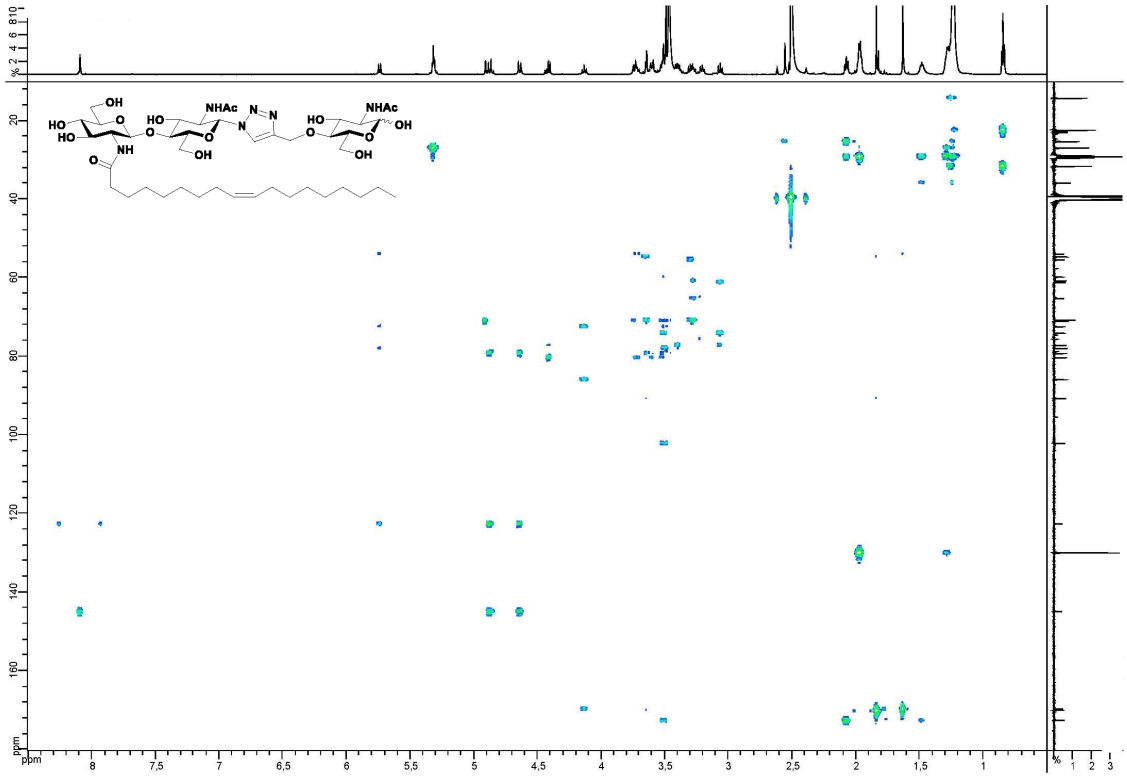
Compound (**4**) ^{13}C NMR



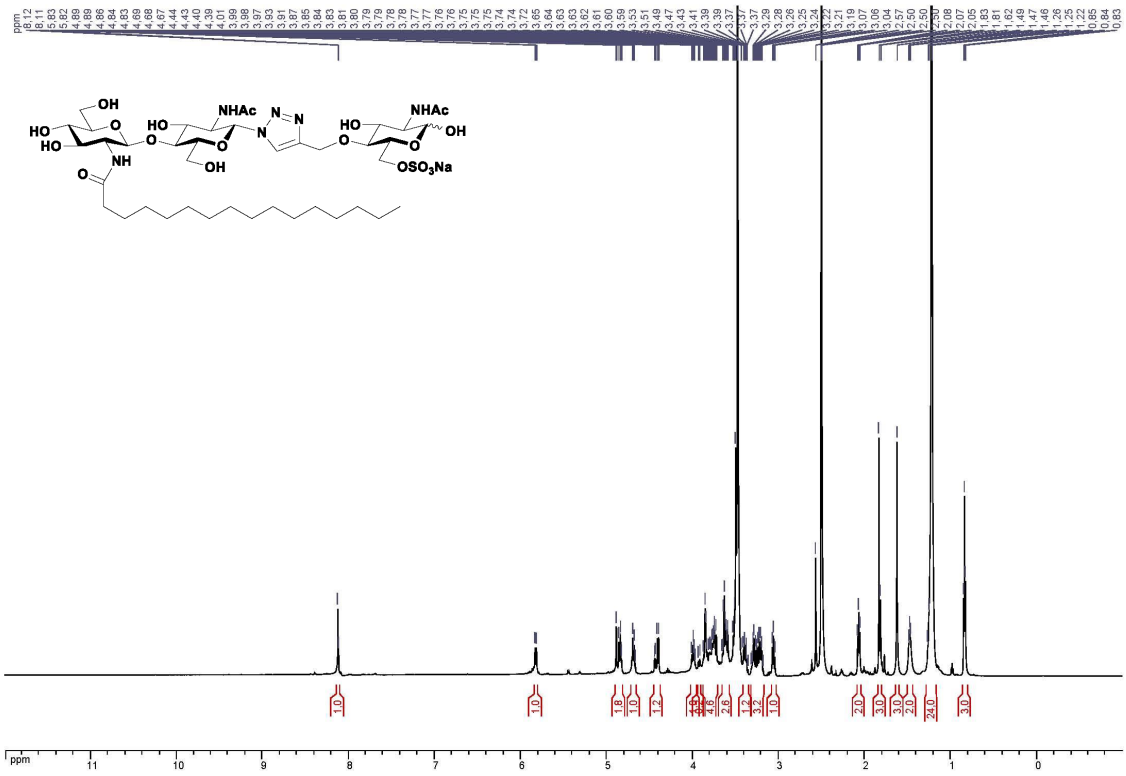
Compound (**4**) HSQC NMR



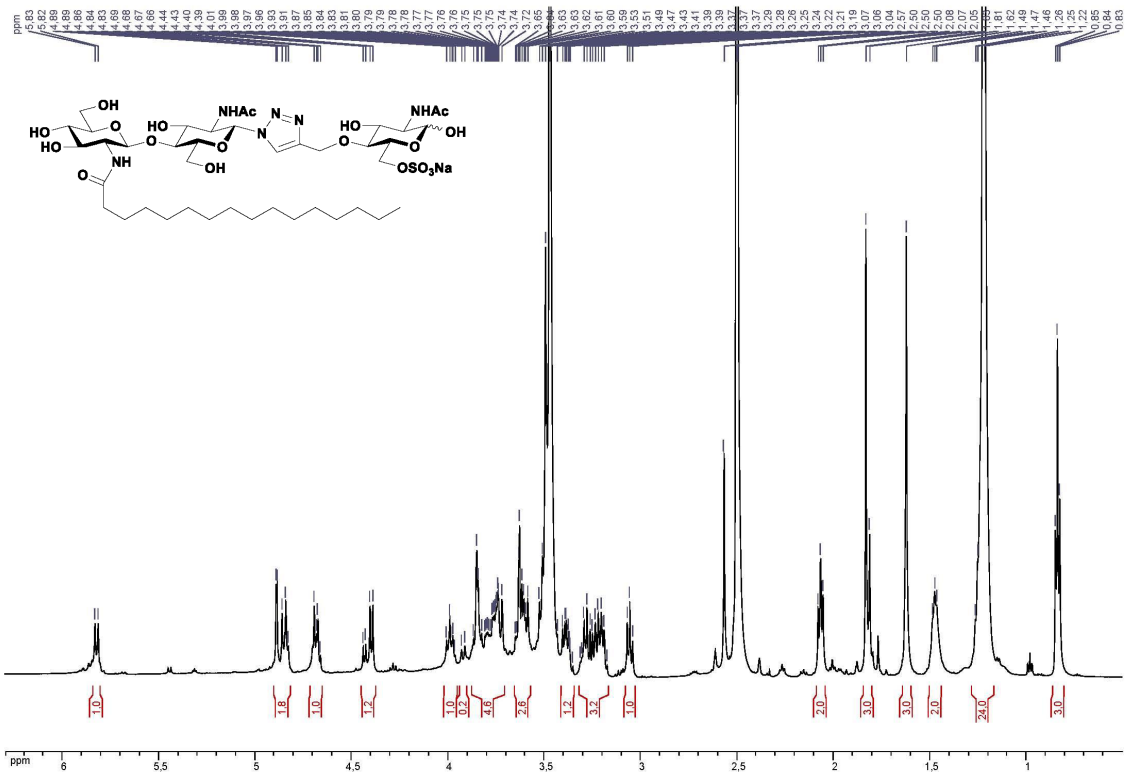
Compound (**4**) HMBC NMR



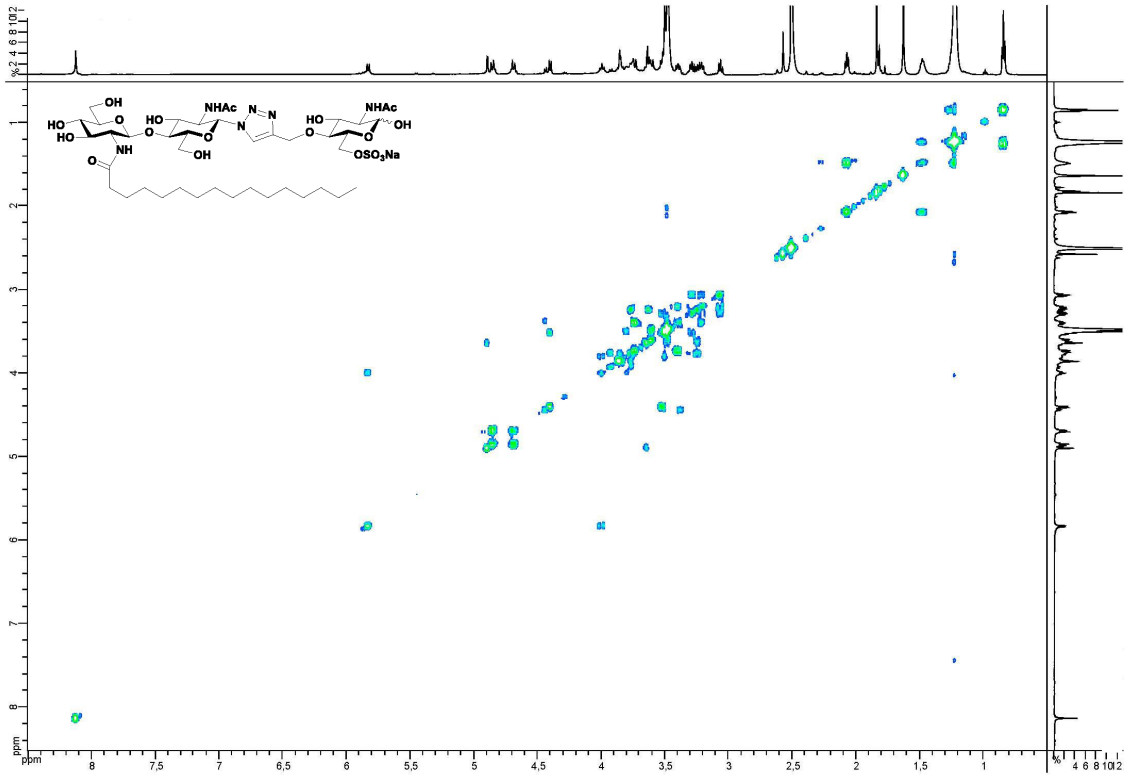
Compound (**3S**) ^{1}H NMR



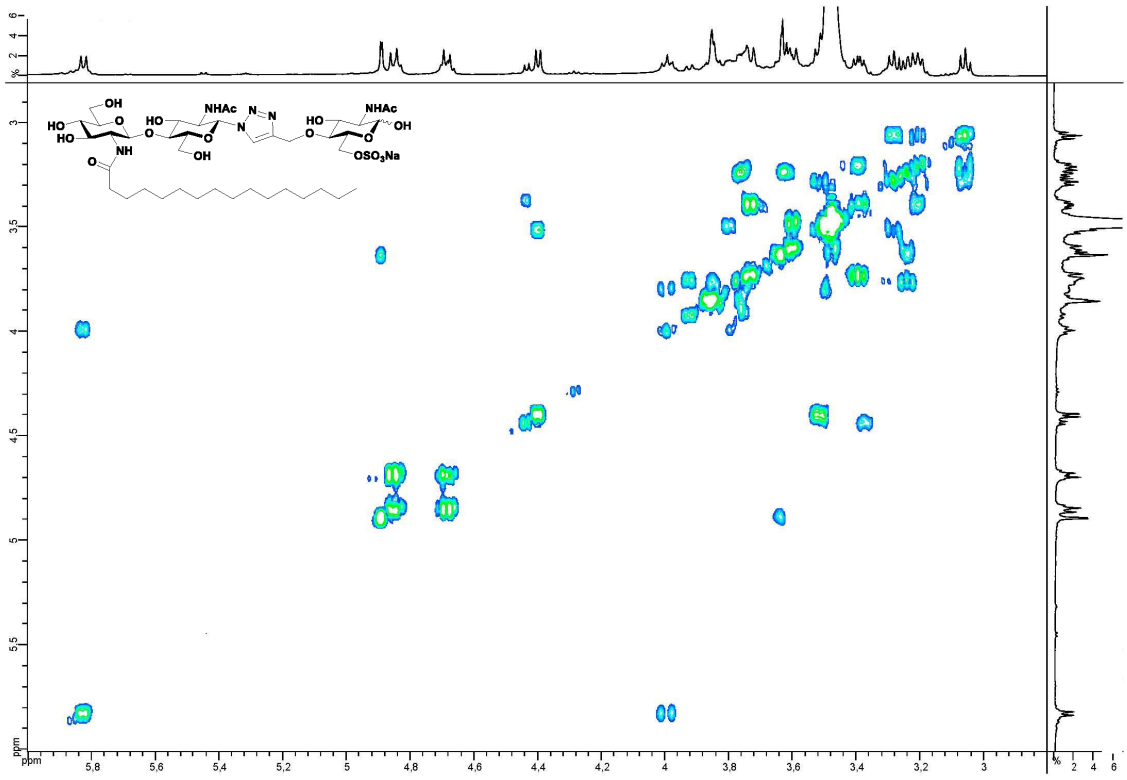
Compound (**3S**) ^{1}H NMR



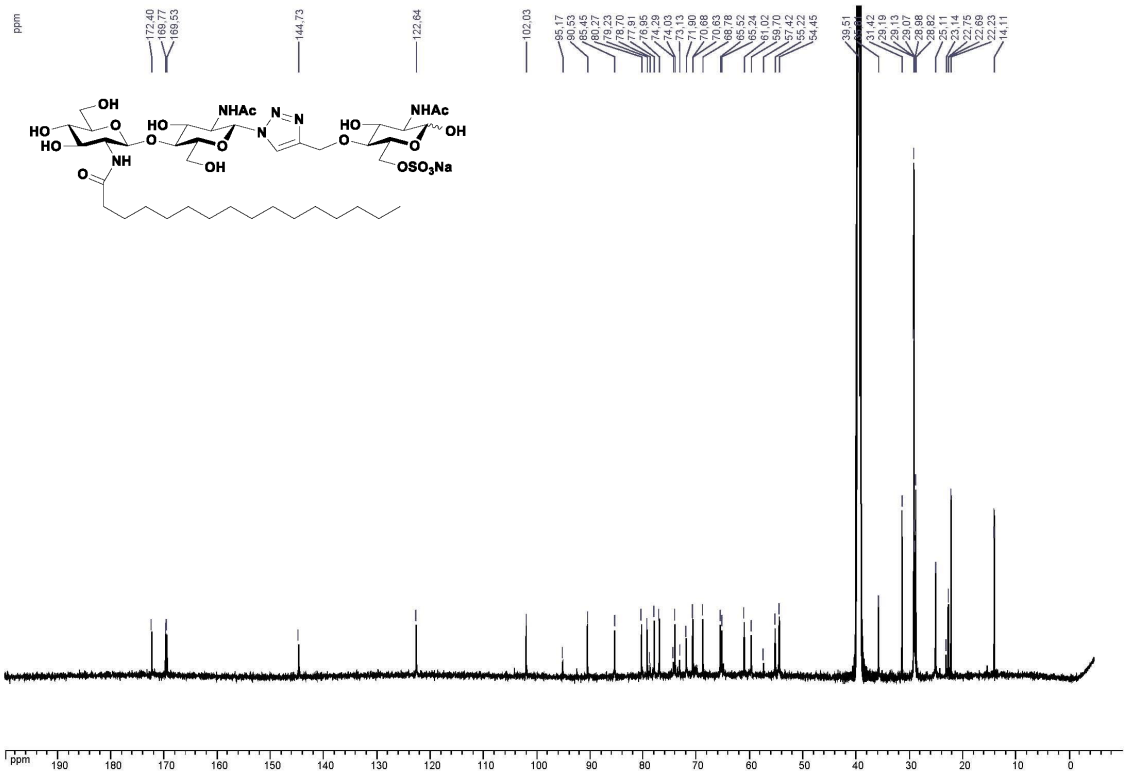
Compound (**3S**) COSY NMR



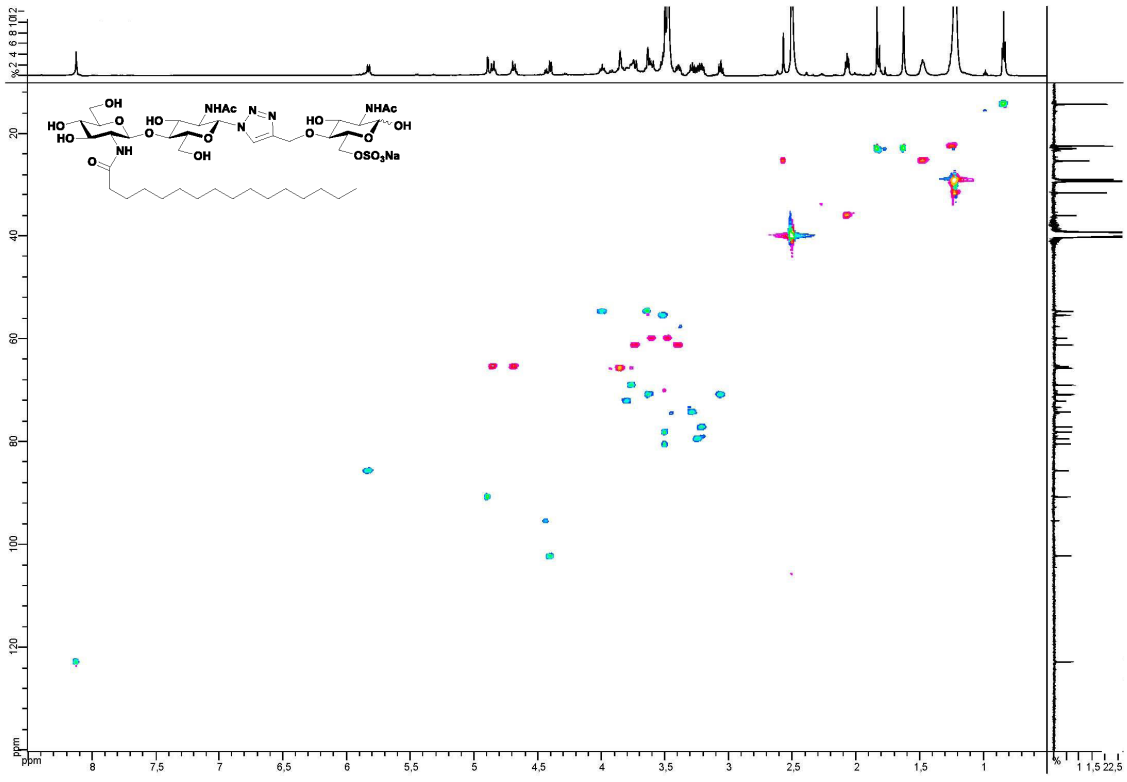
Compound (**3S**) COSY NMR



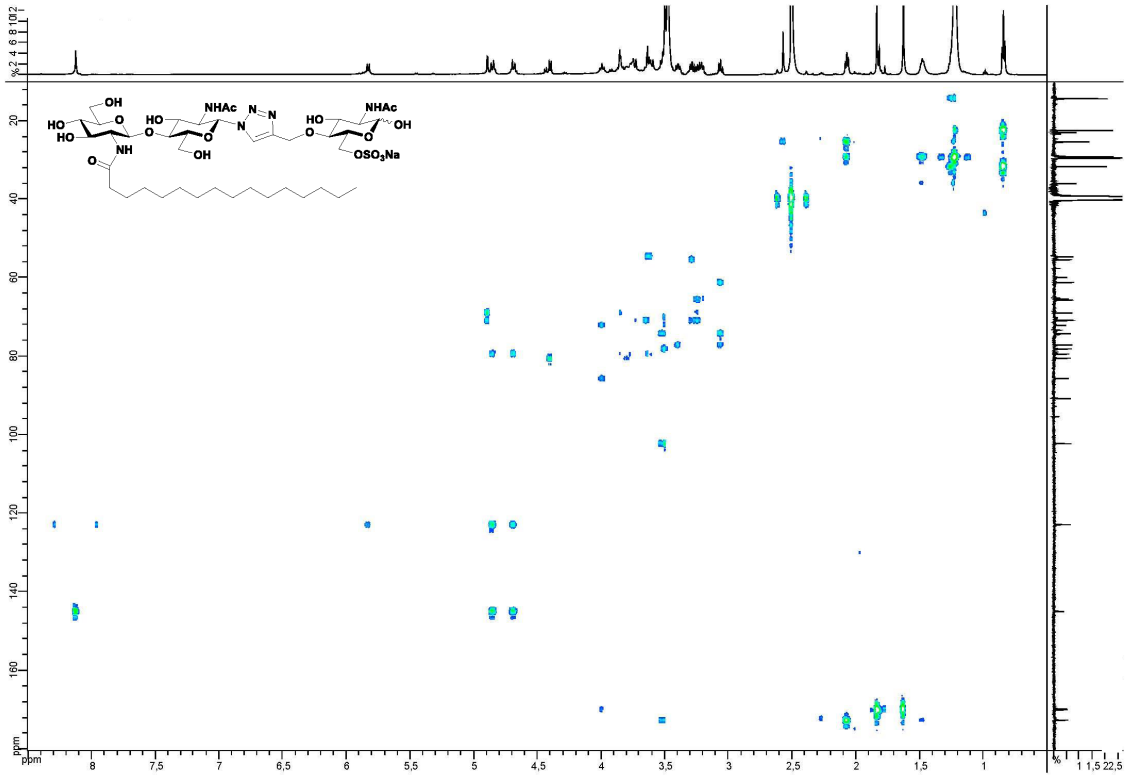
Compound (**3S**) ^{13}C NMR



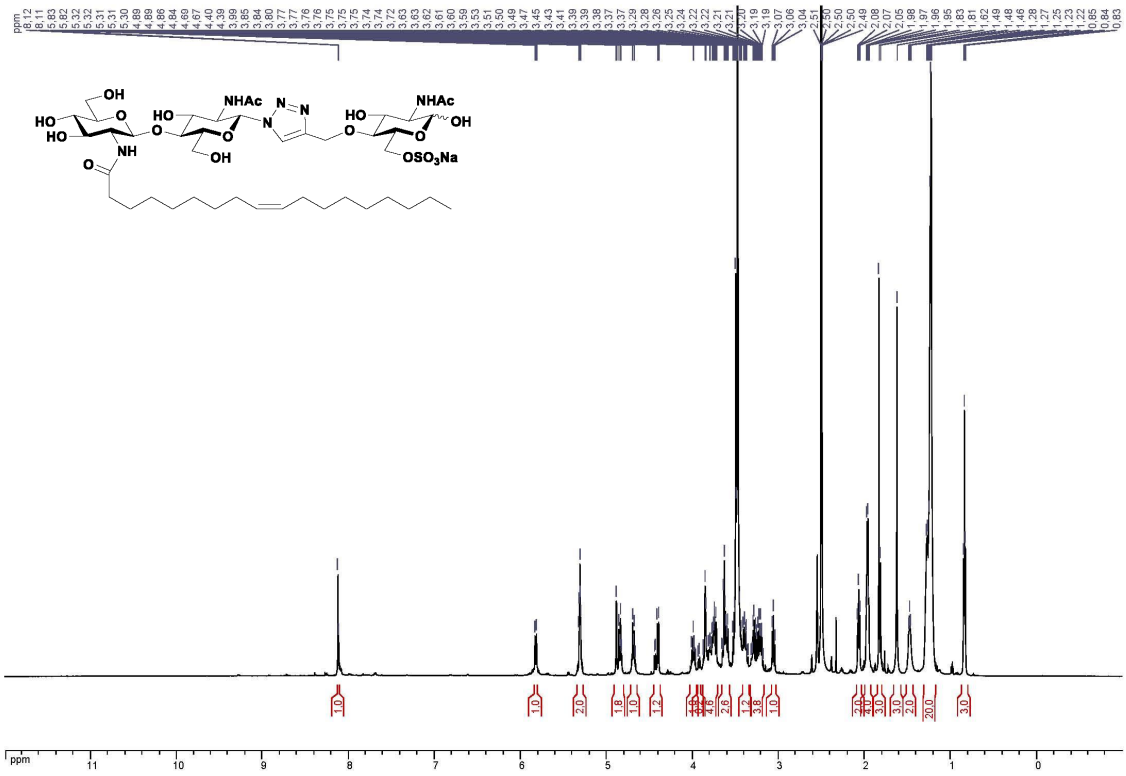
Compound (**3S**) HSQC NMR



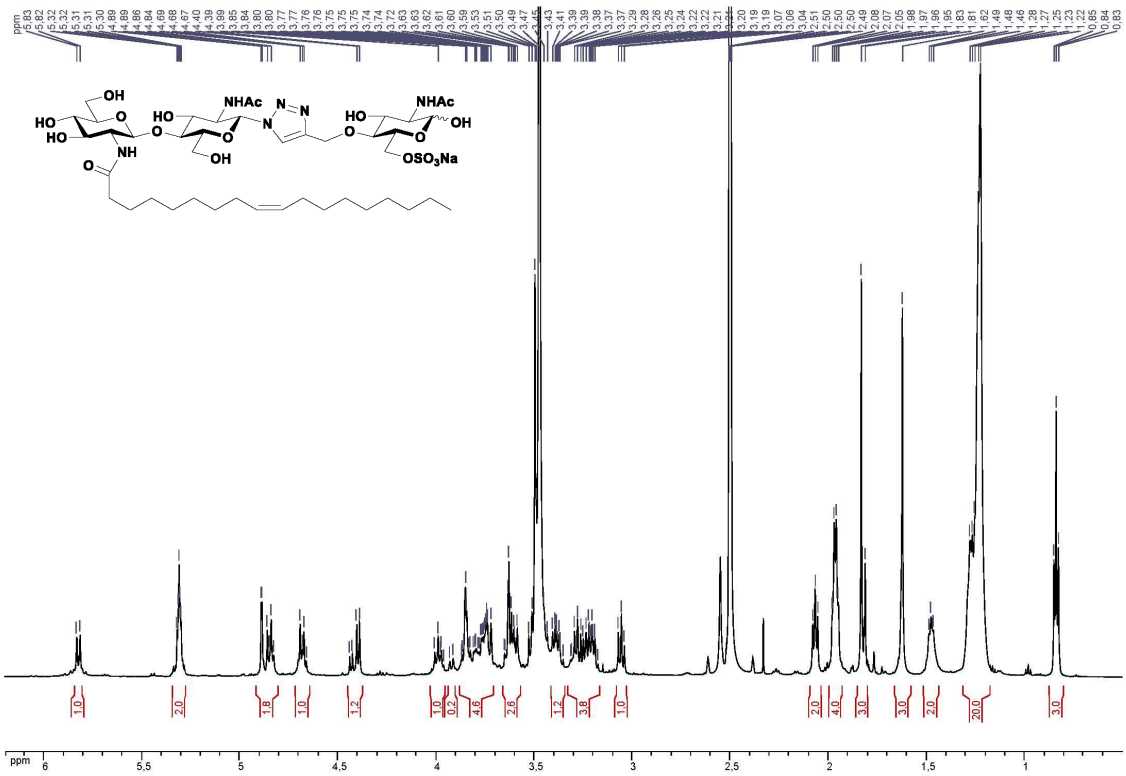
Compound (**3S**) HMBC NMR



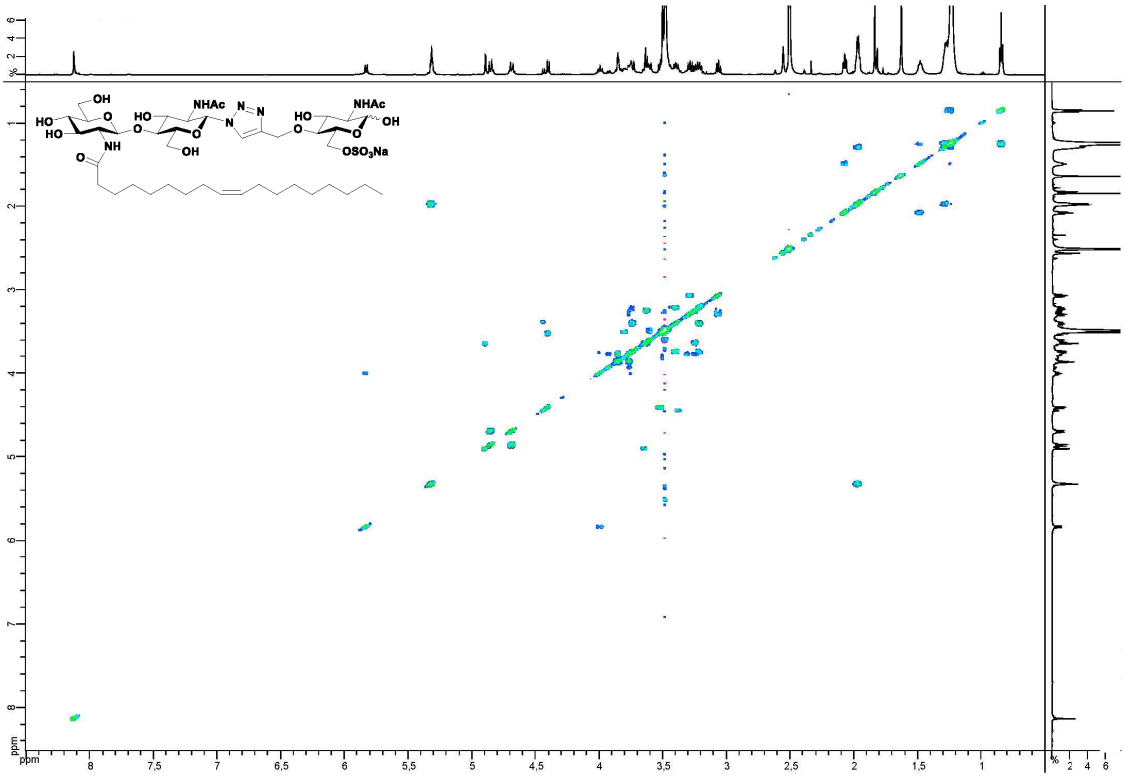
Compound (**4S**) ^{1}H NMR



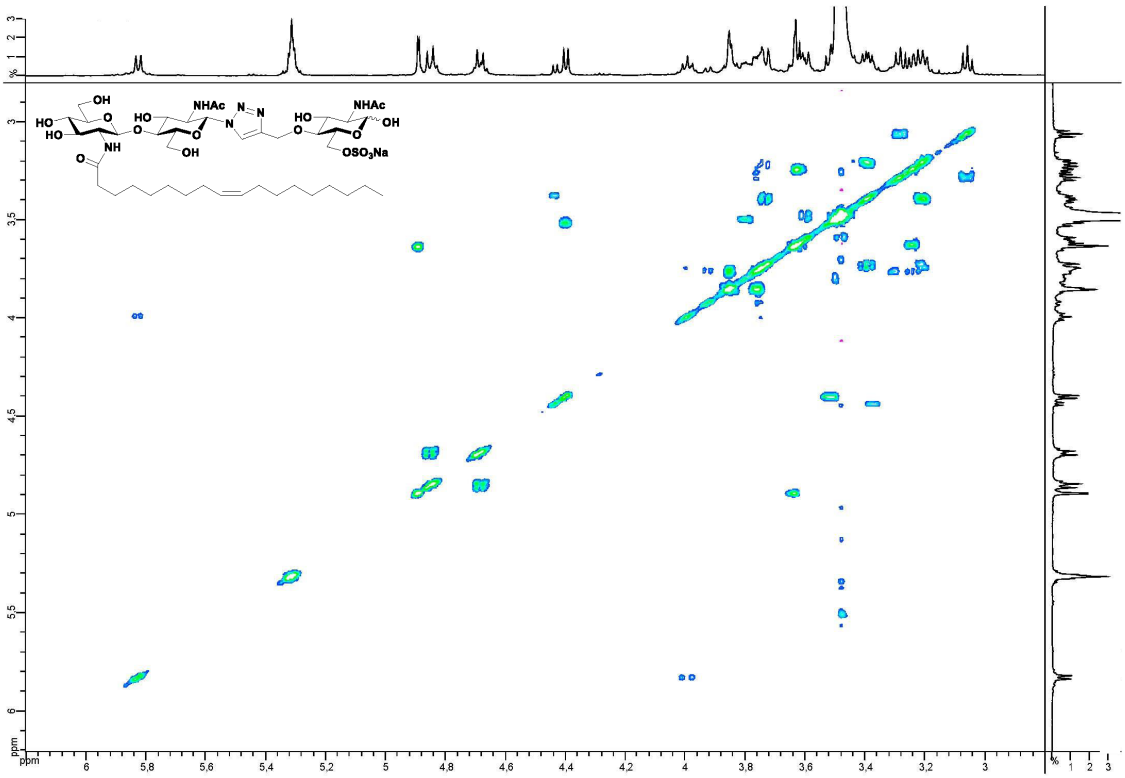
Compound (**4S**) ^{1}H NMR



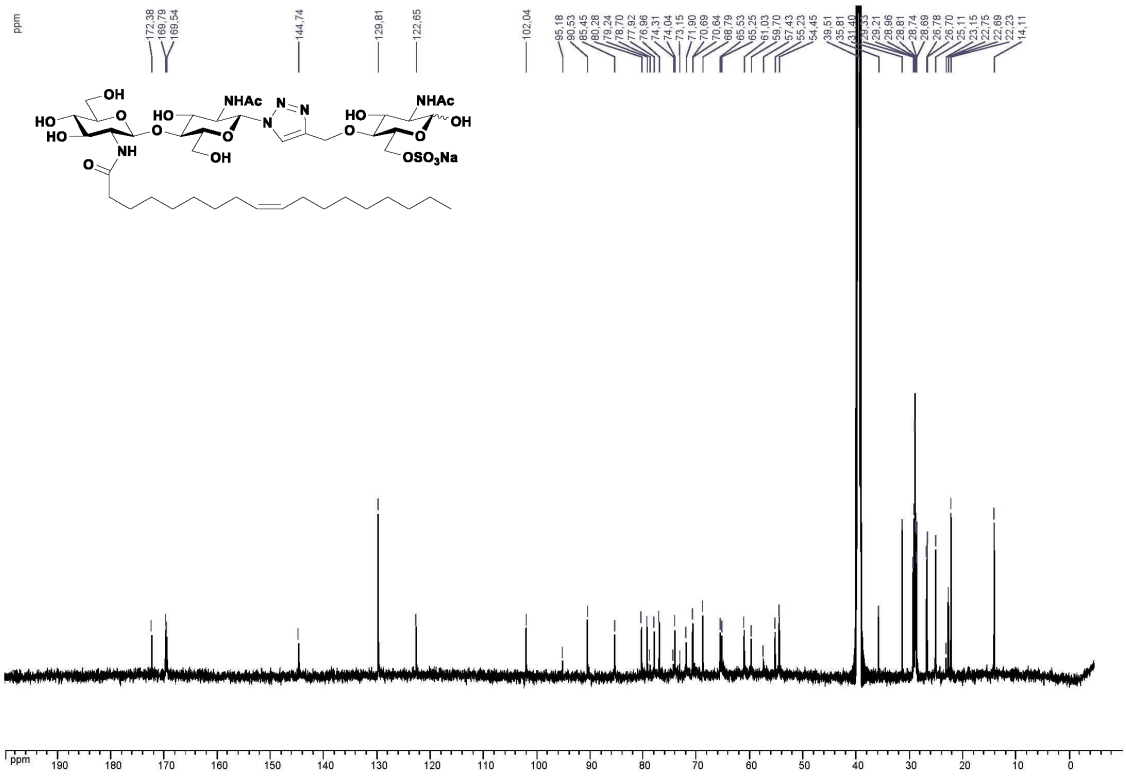
Compound (**4S**) COSY NMR



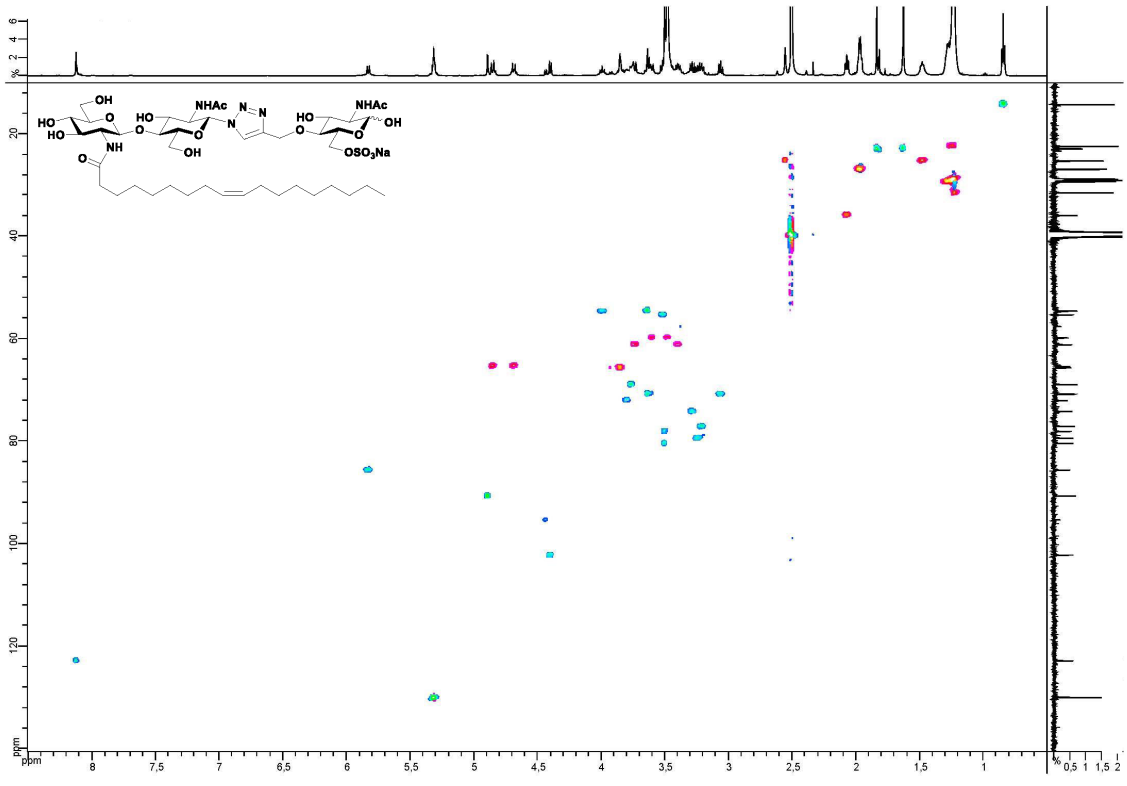
Compound (**4S**) COSY NMR



Compound (**4S**) ^{13}C NMR



Compound (**4S**) HSQC NMR



Compound (**4S**) HMBC NMR