The ESI for Org. Biomol. Chem., 2007, 5, 2756-2757 was updated on 11th May 2020. Some of the NMR spectra included in the original submission were inadvertently cropped and have been replaced.

# Simple, Efficient Route to *O*- and *S*-Linked Carbohydrate Functionalized *N*-Carboxyanhydrides (GlycoNCAs)

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## General Experimental Details

All chemicals were used as supplied unless otherwise stated. *N*-Boc-L-threonine (>98%), *N*-Boc-L-serine (>98%) and *N*-Boc-L-cysteine were purchased from Fluka. Acetobromo-α-D-glucose (>95%), acetobromo-α-D-galactose (>95%), iodine (>99.8%), potassium carbonate (>99%), trifloroacetic acid (>98%), sulfuric acid (95-98%) and potassium carbonate (>99.5%) were purchased from Aldrich. Triphosgene (>96%) and triethylamine (>98%) were purchased from Lancaster synthesis. THF, MeCN and DCM (>99.5%) were purchased from Fischer Scientific and dried by passage through two alumina columns using an Innovative Technology Inc. solvent purification system and stored under $N_2$. Anhydrous ethyl acetate (>99.8%, <0.005% $H_2O$) was purchased from Aldrich. Hexane (Fischer Scientific >99%) was dried over

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3A molecular sieves. 3A molecular sieves (Aldrich) were activated in an oven at 200$^{o}$C before use. Glass-backed silica plates (Biotage) were used for TLC with 5wt % phosphomolybdic acid in ethanol, developed at 80$^{o}$C as the visualising agent. Column chromatography was undertaken on a Biotage SP1 flash chromatography unit using UV detectors at 200 and 236nm. Gradients were calculated the on-board software using $R_f$ values from TLC.

NMR spectroscopy ($^{1}$H, $^{13}$C, COSY, NOESY, HSQC) was conducted on a Varian Inova-500 at 500Mhz. Mass spectral analyses were preformed on a Micromass LCT using positive or negative electrospray mode. Infrared spectroscopy was conducted on a Nicolet Nexus FT-IR as a KBr disc. Liquid samples were analysed by direct injection of the reaction medium into a liquid cell with KBr windows. Elemental analyses were conducted on an Exeter Analytical E-440 elemental analyser.

## GENERAL EXPERIMENTAL PROCEDURE

The same methodology was applied for the synthesis of each glycosylated NCA, with only the carbohydrate or *N*-Boc amino acid varying in each case. The full procedure for the synthesis of Thr(GluAc) NCA is detailed below.

**Synthesis of *N*$_{\alpha}$-(Butoxycarbonyl)-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-L-threonine - BocThr(GluAc) – 2(a)**

*N*-Boc-L- threonine (3.0g, 13.6mmol), potassium carbonate (1.41g, 10.2mmol) and acetobromoglucose (2.79g, 6.8mmol) were dissolved in 40 ml of dry acetonitrile under an $N_2$ atmosphere with stirring for 5 minutes to ensure dissolution. Iodine (2.59g, 10.2mmol) was then added in a single portion against a flow of $N_2$. The vessel was sealed and allowed to stir at ambient temperature with the exclusion of light for 5 hours.

To the still stirring solution, saturated sodium thiosulfate (aqueous) was added until the deep red colouration had disappeared, to leave a slightly yellow solution. The insoluble components (residual potassium carbonate) were removed by filtration and the filtrate concentrated to ¼ of its original volume under reduced pressure on a rotorary evaporator. 40 mL of dichloromethane were then added, and the solution extracted with sodium bicarbonate (aqueous 5% w/v, 50 mL) followed by brine (2 x 50mL), and the organic layer dried over magnesium sulphate. Separation by column chromatography (Hexane/THF 10:1 → 2:8) yielded the title product as a white solid. Isolated yield 2.05 g, 55%.

**Synthesis of 3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-L-threonine acetic acid salt – Thr(GluAc) – 2(b)**

BocThr(GluAc) (1g, 1.82 mmol) was dissolved in 10 mL of DCM under $N_2$. TFA (0.7 ml, 9.11 mmol) was then added dropwise and allowed to stir at ambient temperature for 90 minutes. The solution was then concentrated under reduced pressure on a rotorary evaporator to give a thick syrup. The syrup was taken up in 20 mL of 10% w/v acetic acid(aq) solution and extracted 3 times with 20 mL portions of n-hexane. The aqueous solution was freeze dried, and re-precipitated from $CHCl_3$ to di-ethyl ether to afford the title product without further purification as an off-white solid: 0.90 g, 97% yield.

**Synthesis of 3-*O*-(2,3,4,6-tetraacetyl)-β-D-glucopyranose)-L-threonine-*N*-carboxyanhydride - Thr(GluAc)NCA – 2(c)**

Thr(GluAc) (100mg, 0.20 mmol) was taken up in 5 mL of EtOAc under $N_2$. Triphosgene (39mg, 0.13 mmol) was added in a single portion, against the flow of $N_2$ followed by α-pinene (0.37mL, 2.34 mmol) and allowed to stir at ambient temperature for 20 hours then concentrated to ½ of its original volume on a rotary evaporator under reduced pressure, with the water bath below 30°C. The concentrate was precipitated into hexane at -20°C. This was re-precipitated from ethyl acetate into hexane at -20°C three times. The white solid was obtained by centrifugation following each precipitation, and finally dried under vacuum to give a white solid. Yield 81mg, 87% yield.

## CHARACTERISATION

As indicated in the main text, NCA polymerisation is often complicated by residual amino acid or acidic impurities remaining from the synthetic procedure[1]. Here acidic impurities were removed by the HCl scavenger α-pinene. In the $^{1}$H NMR spectra of the NCAs, trace amounts of amino acid residues (appearing slightly shifted relative to the main peaks) can be seen. Additional purification is possible (by an aqueous extraction) but this should only be conducted prior to polymerisation, as further degradation reactions will occur rapidly negating any increase in purity[2]. This purification was not undertaken, allowing comparison with other published glycoNCA synthetic procedures.

***N$_{\alpha}$*-(Butoxycarbonyl)-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galatopyranosyl)-L-threonine - BocThr(GalAc) – 1(a)**

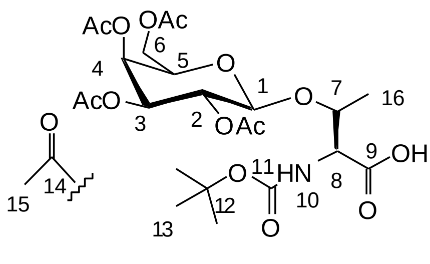
**$^{1}$H NMR** ($CDCl_3$) $\delta_{ppm}$; 5.73 (1H, d, $J_{1\text{-}2}$ = 8.26Hz, $H_1$), 5.42 (1H, dd, $J_{4\text{-}3}$ = 3.41Hz, $J_{4\text{-}5}$ = 0.94, $H_4$), 5.33 (1H, dd, $J_{2\text{-}1}$ = 8.26Hz, $J_{2\text{-}3}$ = 10.44Hz, $H_2$), 5.08 (1H, dd, $J_{3\text{-}4}$ = 3.41Hz, $J_{3\text{-}2}$ = 10.44Hz, $H_3$), 4.22 (1H, d, $J_{7\text{-}16}$ = 9.2 Hz, $H_7$), 4.35 (1H, m, $H_8$), 4.20 (1H, dd, $J_{6a\text{-}5}$ = 6.40Hz, $J_{6a\text{-}6b}$ = 10.86Hz, $H_{6a}$), 4.07 (1H, dd, $J_{6b\text{-}5}$ = 6.14Hz, $J_{6b\text{-}6a}$ = 10.89Hz, $H_{6b}$), 4.04 (1H, td, $J_{5\text{-}4}$ = 0.74Hz, $J_{5\text{-}6a}$ = $J_{5\text{-}6b}$ = 6.47Hz, $H_5$), 1.99 – 2.06 (12H, m, $H_{15}$), 1.26 (3H, d, $J_{16\text{-}7}$ = 6.38Hz, $H_{16}$).

**$^{13}$C NMR** ($CDCl_3$) $\delta_{ppm}$: 170.6 ($C_9$), 169.9-170.1 (4x $C_{14}$), 156.0 ($C_{11}$), 92.9 ($C_1$), 80.1 ($C_{12}$), 72.3, ($C_5$), 71.4 ($C_3$), 67.9 ($C_2$), 67.2 ($C_4$), 62.3 ($C_8$), 60.8 ($C_6$), 59.0 ($C_7$), 28.2 ($C_{13}$), 20.5-20.7 (4x$C_{15}$), 19.9 ($C_{16}$),

**IR** (KBr disc) cm$^{-1}$: 3447 (br., N-H), 2981 (C-H), 1757 (C=O Ac), 1718 (C=O Boc).

**MS** (ES+) m/z = 572.2 [M+Na]$^{+}$ 100%.

**Elemental** (Found %) C, 50.48; H, 6.54; N, 2.36 (Expected %) C, 50.27; H, 6.42; N, 2.55.



***N$_α$*-(Butoxycarbonyl)-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-L-threonine BocThr(GluAc) – 2(a)**

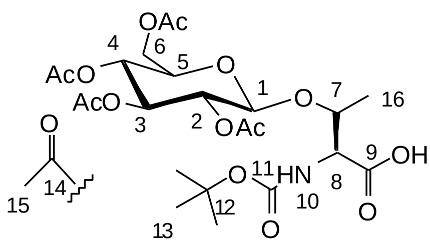
**$^1$H NMR** ($CDCl_3$) $δ_{ppm}$; 5.75 (1H, d, $J_{1-2}$ = 8.17Hz, $H_1$), 5.30 (1H, d, $J_{8-7}$ = 9.6Hz, $H_8$), 5.26 (1H, t, $J$ = 9.47Hz, $H_3$), 5.15 (1H, dd, $J_{2-1}$ = 8.18Hz, $J_{2-3}$ = 9.60Hz, $H_2$), 5.10 (1H, t, $J$ = 9.70Hz, $H_4$), 4.33 (1H, m, $H_8$), 4.30 (1H, dd, $J_{6b-5}$ = 5.02Hz, $J_{6b-6a}$ = 12.44Hz, $H_{6b}$), 4.23 (1H, dd, $J_{7-9}$ = 6.36Hz, $J_{7-8}$ = 9.7Hz, $H_7$), 4.09 (1H, dd, $J_{6a-5}$ = 2.19Hz, $J_{6a-6b}$ = 12.36Hz, $H_{6a}$), 3.82 (1H, ddd, $J_{5-6a}$ = 2.20Hz, $J_{5-6b}$ = 4.96Hz, $J_{5-4}$ = 10.07Hz, $H_5$), 2.01 – 2.06 (12H, m, $H_{15}$), 1.25 (3H, d, $J_{16-7}$ = 6.39Hz, $H_{16}$).

**$^{13}$C NMR** ($CDCl_3$) $δ_{ppm}$; 170.9 ($C_9$), 169.4-167.0 (4x$C_{14}$), 156.0 ($C_{11}$), 92.4 ($C_1$), 80.1 ($C_{12}$), 72.9 ($C_5$), 72.5 ($C_3$), 70.0 ($C_2$), 67.8 ($C_4$), 67.5 ($C_8$), 61.3 ($C_6$), 58.9 ($C_7$), 28.2 ($C_{16}$), 20.5 - 20.7 (4x$C_{15}$), 19.9 ($C_{16}$).

**IR** (KBr disc) $cm^{-1}$: 3447 (br., N-H), 2980 (C-H), 1757 (C=O Ac), 1718 (C=O Boc).

**MS** (ES+) m/z = 572.2 $[M+Na]^+$ 100%.

**Elemental** (Found %) C, 50.16; H, 6.38; N, 2.35 (Expected %) C, 50.27; H, 6.42; N, 2.55.




***N$_α$*-(Butoxycarbonyl)-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-L-serine - BocSer(GalAc) – 3(a)**

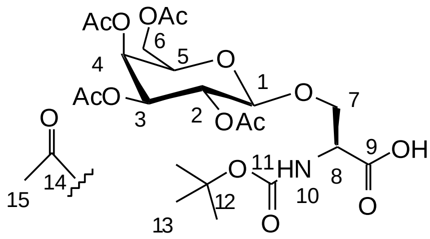
**$^1$H NMR** ($CDCl_3$) $δ_{ppm}$; 5.73 (1H, d, $J_{1-2}$ = 8.21Hz, $H_1$), 5.46 (1H, dd, $J_{4-5}$ = 1.08Hz, $J_{4-3}$ = 3.35Hz, $H_4$), 5.31(1H, dd, $J_{2-1}$ = 8.28Hz, $J_{2-3}$ = 10.43Hz, $H_2$), 5.08 (1H, dd, $J_{3-4}$ = 3.45Hz, $J_{3-2}$ = 10.45Hz, $H_3$), 1.99 – 2.06 (12H, m, $H_{15}$), 1.43 (9H, s, $H_{13}$).

**$^{13}$C NMR** ($CDCl_3$) $δ_{ppm}$; 169.2 – 170.5 (4x $C_{14}$ and $C_9$), 155.0 ($C_{11}$), 89.8 ($C_1$), 80.3 ($C_{12}$), 72.1 ($C_4$), 70.8 ($C_2$), 67.5 ($C_3$), 66.7 ($C_5$), 62.0 ($C_8$), 61.0 ($C_6$), 57.7 ($C_7$), 29.2 ($C_{13}$), 20.4 – 20.7 (4x $C_{15}$).

**IR** (KBr disc) $cm^{-1}$: 3411 (br., N-H), 2976 (C-H), 1760 (C=O Ac), 1714 (C=O Boc).

**MS (**ES+) m/z = 558.2 (85%) $[M+Na]^+$, 599.2 (100%) $[M+Na+CH_3CN]^+$.

**Elemental** (Found %) C, 49.12; H, 6.30; N, 2.30 (Expected %) C, 49.34; H, 6.21; N, 2.62.



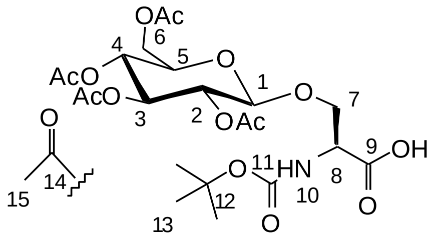
***N*α-(Butoxycarbonyl)-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-L-serine - (BocSer(GluAc) – 4(a)**

**$^{1}$H NMR** (CDCl$_3$) $\delta_{ppm}$; 5.75 (1H, d, $J_{1\text{-}2}$ = 8.13Hz, H$_1$), 5.40 (1H, dd, $J_{8\text{-}7a}$ = 2.79Hz, $J_{8\text{-}7b}$ = 6.67Hz, H$_8$), 5.26 (1H, t, $J$ = 9.38Hz, H$_3$), 5.14 (1H, dd, $J_{2\text{-}1}$ = 8.15Hz, $J_{2\text{-}3}$ = 9.47Hz, H$_2$), 5.11 (1H, t, $J$ = 9.90Hz , H$_4$), 4.35 (1H, m, H$_{7b}$), 4.28 (1H, dd, $J_{6b\text{-}5}$ = 4.81Hz, $J_{6b\text{-}6a}$ = 12.45Hz, H$_{6b}$), 4.10 (1H, dd, $J_{6a\text{-}5}$ = 2.20Hz, $J_{6a\text{-}6b}$ = 12.48Hz, H$_{6a}$), 4.02 (1H, m, H$_{7a}$), 3.83 (1H, ddd, $J_{5\text{-}6a}$ = 2.15Hz, $J_{5\text{-}6b}$ = 4.65Hz, $J_{5\text{-}4}$ = 9.95Hz, H$_5$), 1.99 – 2.07 (12H, m, H$_{15}$), 1.43 (9H, s, H$_{13}$).

**$^{13}$C NMR** (CDCl$_3$) $\delta_{ppm}$: 170.8 (C$_9$), 169.2 – 170.0 (4x C$_{14}$), 155.1 (C$_{11}$), 92.4 (C$_1$), 72.8 (C$_5$), 72.4 (C$_3$), 71.1 (C$_{12}$), 70.0 (C$_2$), 67.6 (C$_4$), 62.3 (C$_8$), 61.0 (C$_6$), 56.2 (C$_7$), 28.0 (C$_{13}$), 20.5 – 20.7 (4xC$_{15}$).

**IR** (KBr disc) cm$^{-1}$: 3447 (br., N-H), 2979 (C-H), 1753 (C=O Ac), 1717 (C=O Boc).**MS** (ES+) m/z = 558.2 (100%) [M+Na]$^{+}$.

**Elemental** (Found %) C, 49.52; H, 6.25; N, 2.10 (Expected %) C, 49.34; H, 6.21; N, 2.62.



***N*α-(Butoxycarbonyl)-3-*O*-(2,3,4,6-tetraacetyl-β-D-galactopyranosyl-(1-4)-1,2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranose)-L-serine - BocSer(LacAc) – 5(a)**

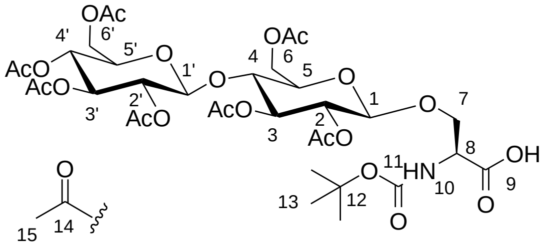
**$^{1}$H NMR** (CDCl$_3$) $\delta_{ppm}$: 5.77 (1H, d, $J_{1\text{-}2}$ 7.50Hz, H$_1$), 5.72 (1H, d, $J_{1'\text{-}2'}$ = 9.00Hz, H$_{1'}$), 5.54 (1H, t, $J$ = 9.68Hz, H$_{4'}$), 5.41 (1H, t, $J$ = 3.5Hz, H$_4$), 5.30 (1H, d, $J_{3'\text{-}2'}$ = 9.52 Hz, H$_{3'}$), 5.25 (1H, t, $J$ = 9.00 Hz, H$_3$), 5.07-5.15 (2H, m, H$_{2'}$,H$_2$), 4.24-4.31 (1H, m, H$_{6b}$), 4.01-4.17 (4H, m, H$_{6'a}$, H$_{6'b}$, H$_{6a}$, H$_{5'}$), 3.88 (1H, td $J_{5\text{-}6}$ = 6.0Hz, $J_{5\text{-}4}$ = 1.5Hz, H$_5$), 3.72 (1H, t, $J_{3\text{-}4}$ = 6.00 Hz, H$_3$), 1.96 - 2.16 (21H, m, H$_{15}$), 1.41 - 1.44 (9H, s(b), H$_{13}$).

$^{13}$**C NMR** ($CDCl_3$) $\delta_{ppm}$: 171.1 ($C_9$), 166.5-170.3 ( 4 x $C_{14}$), 157 ($C_{11}$), 94.0 ($C_{1'}$), 92.6 ($C_1$), 73.1 ($C_4$), 72.6 ($C_5$), 72.1 ($C_{3'}$), 71.4 ($C_{5'}$), 70.7 ($C_{2'}$), 70.3 ($C_3$), 68.3 ($C_{2'}$), 66.9 ($C_{4'}$), 61.8 ($C_6$), 61.1 ($C_{6'}$), 30.2 ($C_{13}$), 20.7-20.9 (4x$C_{15}$).

**MS (**ES+) m/z = 887.7 [M+Na+$CH_3CN$]$^+$.

**Elemental** Found (%) C 49.39, H 6.33, N 2.22, Expected (%)C 49.57; H 6.00; N 1.70

**IR** (KBr disc) cm$^{-1}$: 3450 (br., N-H), 2970 (CH), 1755 (C=O Ac), 1717 (C=O Boc).



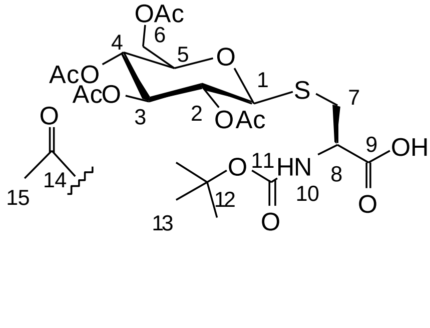

***N$\alpha$*-(Butoxycarbonyl)-3-*S*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-L-cysteine - BocCys(GluAc) – 6(a)**

$^1$**H NMR** ($CDCl_3$) $\delta_{ppm}$: 6.25 (1H, d, $J_{1-2}$ = 9.11Hz, $H_1$), 5.49 (1H, d, $J_{4-3}$ = 3.50Hz, $H_4$), 5.29 (1H, t, $J_{2-1}$ = 9.00 Hz, $H_2$), 5.10 -5.20 (4H, m, $H_{7a}$, $H_{7b}$, $H_8$, $H_3$), 4.93 (1H, dd, $J_{5-4}$ = 3.5Hz, $J_{5-6}$ = 6.50Hz, $H_5$), 4.88 (1H, dd, $J_{6a-5}$ = 8.00Hz, $J_{6a-6b}$ 2.00Hz, $H_{6a}$3.91 (1H, dd, $J_{6a-6b}$ = 4.00Hz, $J_{6b-5}$, 9.50Hz, $H_{6b}$), 2.04 - 2.11 (12H, m, $H_{15}$), 1.36 -1.38 (9H, s(b), $H_{13}$).

$^{13}$**C NMR** ($CDCl_3$) $\delta_{ppm}$: 171.5 ($C_9$), 169.5-170.5 (4 x $C_{14}$), 158 ($C_{11}$), 90.1 ($C_1$), 70.1 ($C_5$), 69.8 ($C_3$), 68.7 ($C_2$), 67.7 ($C_4$), 67.3 ($C_8$), 62.2 ($C_6$), 61.8 ($C_7$), 32.9 ($C_{13}$), 20.8 - 21.2 (4x$C_{15}$).

**MS (**ES+) m/z = 615.4 [M+Na+$CH_3CN$]$^+$ 100%.

**IR** (KBr disc) cm$^{-1}$: 3450 (br., N-H), 2980 (C-H), 1757 (br., C=O Ac), 1715 (C=O Boc).



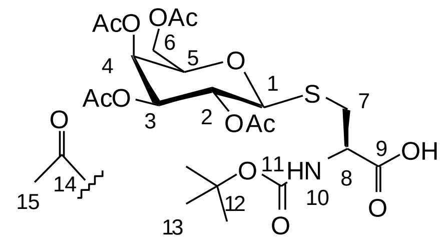

***N$\alpha$*-(Butoxycarbonyl)-3-*S*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-L-cysteine - BocCys(GalAc) – 7(a)**

$^{1}$**H NMR** ($CDCl_3$) $\delta_{ppm}$: 6.04 (1H, d, $J_{1-2}$ = 6.00Hz, $H_1$), 5.46 (1H, dd, $J_{4-3}$ = 2.50Hz, $J_{4-5}$ = 6.00Hz, $H_4$), 5.15-5.23 (2H, m, $H_2$, $H_3$), 4.99 (1H, dd, $J_{6b-6a}$ = 3.50Hz, $J_{6b-5}$ = 4.50Hz, $H_{6b}$) 4.69 (1H, dd, $J_{6a-6b}$ = 2.50Hz, $J_{6a-5}$ = 7.50Hz, $H_{6a}$), 4.39 (1H, d, $J_{4-5}$ = 6.50Hz, $H_4$), 4.14 (1H, ddd, $J_{5-6a}$ = 3.00Hz, $J_{5-6b}$ 3.60Hz, $J_{5-4}$ = 7.06Hz, $H_5$), 2.05 - 2.15 (12H, m, $H_{15}$), 1.42 - 1.44 (9H, s(b), $H_{13}$).

$^{13}$**C NMR** ($CDCl_3$) $\delta_{ppm}$; 171.1 ($C_9$), 169.2 -170.4 (4 x $C_{14}$), 154.0 ($C_{11}$), 91.1 ($C_1$), 70.1 ($C_5$), 69.6 ($C_3$), 68.8 ($C_2$), 68.3 ($C_4$), 67.3 ($C_8$), 62.2 ($C_6$), 61.7 ($C_7$), 33.2 ($C_{13}$), 20.7 - 21.1 (4x$C_{15}$).

**IR** (KBr disc) $cm^{-1}$: 3450 (br., N-H), 2985 (C-H), 1754 (br., C=O Ac), 1713 (C=O Boc).

**MS (**ES+) m/z = 574.9 $[M+Na]^+$.

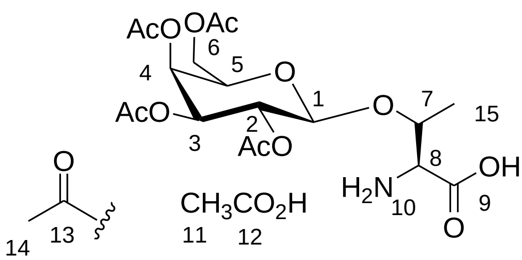



**3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-L-threonine acetic acid salt - Thr(GalAc) – 1(b)**

$^{1}$**H NMR** ($CDCl_3$) $\delta_{ppm}$; 5.96 (1H, d, $J_{1-2}$ = 8.07Hz, $H_1$), 5.45 (1H, d, $J_{4-3}$ = 2.89Hz, $H_4$), 5.31 (1H, dd, $J_{2-1}$ = 8.25Hz, $J_{2-3}$ = 10.10Hz, $H_2$), 5.22 (1H, dd, $J_{3-2}$ = 10.44Hz, $J_{3-4}$ = 3.04Hz, $H_3$), 4.39 (1H, q, $J_{7-15}$ = $J_{7-8}$ = 6.27Hz, $H_7$), 4.19 (1H, dd, $J_{6b-6a}$ = 10.31Hz, $J_{6b-5}$ = 5.91Hz, $H_{6b}$), (1H, dd, $J_{6a-6b}$ = 10.84Hz, $J_{6a-5}$ = 5.92Hz, $H_{6a}$), 4.08 (1H, dd, $J_{5-6a}$ = 6.62Hz, $J_{5-6b}$ = 7.88Hz, $H_5$), 3.97 (1H, m, $H_8$), 1.95 – 2.06 (15H, m, $H_{11}$ + $H_{13}$), 1.41 (1H, d, $J_{15-7}$ = 5.88, $H_{15}$).

$^{13}$**C NMR** ($CDCl_3$) $\delta_{ppm}$; 175.6 ($C_{14}$), 179.8 – 171.0 (4x$C_{12}$), 166.6 ($C_9$), 93.7 ($C_1$), 71.6 ($C_5$), 70.3 ($C_3$), 67.5 ($C_2$), 66.6 ($C_4$), 65.8 ($C_7$), 61.9 ($C_5$), 60.6 ($C_6$), 59.2 ($C_8$), 19.5 – 20.9 (4x$C_{11}$, $C_{13}$, $C_{15}$).

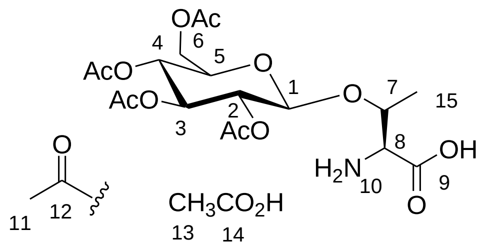
**MS (**ES+) m/z = 449.9 $[M]^+$ (100%).




**3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-L-threonine acetic acid salt - Thr(GluAc) – 2(b)**

$^{1}$**H NMR** ($CDCl_3$) $\delta_{ppm}$; 6.00 (1H, d, $J_{1-2}$ = 8.12Hz, $H_1$). 5.35 (1H, t, J = 9.41Hz, $H_3$), 5.12 (2H, t, 9.24Hz, $H_2$ + $H_4$), 4.35 (1H, q, $J_{7-8}$ = $J_{7-15}$ = 6.14Hz, $H_7$), 4.25 (1H, dd, $J_{6a-6b}$ = 12.37Hz, $J_{6a-5}$ = 2.74Hz, $H_{6a}$), 4.15 – 4.22 (2H, m, $H_8$ + $H_{6b}$), 4.06 (1H, d(b), J= 9.95Hz, $H_5$), 1.99 – 2.14 (12H, m, $H_{11}$ + $H_{13}$), 1.49 (3H, d, $J_{15-7}$ = 6.08Hz, $H_{15}$).

**MS (**ES+) m/z = 449.9 $[M]^+$ (100%).

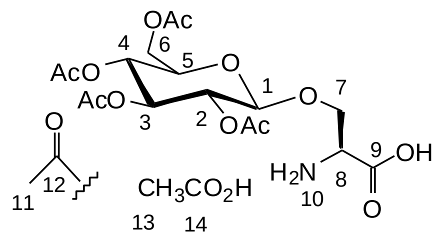



**3-*O*-((2,3,4,6-tetra-*O*-acetyl)-β-D-glucopyranosyl)-L-serine acetic acid salt - Ser(GluAc) – 3(b)**

$^{1}$**H NMR** ($CDCl_3$) $\delta_{ppm}$; 5.90 (1H, d, $J_{1-2}$ = 8.58Hz, $H_1$). 5.33 (1H, td, $J_{2-3}$ = 2.00Hz, $J_{2-1}$ = 8.5Hz, $H_2$), 5.29 (1H, t, $J_{3-4}$ = $J_{3-2}$ = 5.00Hz, $H_3$), 5.21 (1H, dd, $J_{4-5}$ = 7.45Hz, $J_{4-3}$ = 3.50Hz, $H_4$), 4.22 (1H, t, $J_{8-7}$ = 4.50Hz, $H_8$), 4.02-4.14 (4H, m, $H_{6a}$, $H_{6b}$, $H_{7b}$, $H_5$), 3.86 (1H, dd, $J_{7a-7b}$ = 3.63Hz, $J_{7a-8}$ = 4.43Hz, $H_{7a}$), 1.98- 2.18 (15H, m, $H_{11}$, $H_{13}$)

$^{13}$**C NMR** ($CDCl_3$) $\delta_{ppm}$; 166.6 - 171 ($C_9$, 4x$C_{12}$, $C_{14}$), 98.9 ($C_1$), 72.2 ($C_5$), 71.0 ($C_3$), 69.8 ($C_2$), 67.4 ($C_4$), 66.2 ($C_8$), 60.3 ($C_8$), 59.1 ($C_6$), 58.9 ($C_7$), 18.4 - 21.4 (4x$C_{11}$, $C_{13}$).

**MS (**ES+) m/z = 435.0[$M^+$] 80%, 458.7$[M+Na]^+$ 20%.

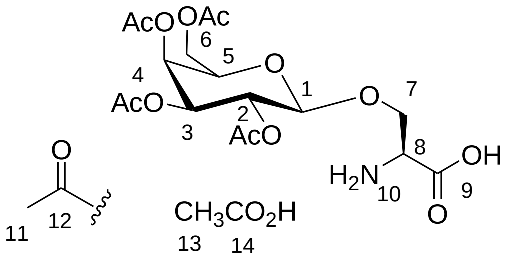



**3-*O*-((2,3,4,6-tetra-*O*-acetyl)-β-D-galactopyranosyl))-L-serine acetic acid salt - Ser(GalAc) – 4(b)**

$^{1}$**H NMR** ($CDCl_3$) $\delta_{ppm}$; 6.04 (1H, d, $J_{1-2}$ = 6.00Hz, $H_1$), 5.05 (1H, dd, $J_{3-4}$ = 3.5Hz, $J_{3-2}$ = 4.5Hz, $H_3$), 5.46 (1H, m, $H_{6b}$), 4.91 (1H, t, J = 4.50Hz, $H_2$), 4.80 (1H, m, $H_{6a}$), 4.69 (1H, dd, $J_{7a-7b}$ = 2.50Hz, $J_{7a-8}$ = 7.5Hz, $H_{7a}$), 4.39 (1H, t, $J_{4-5}$ = $J_{4-3}$ = 6.5Hz, $H_4$), 4.14 (1H, ddd, $J_{5-6a}$ = 3.00Hz, $J_{5-6b}$ = 3.60Hz $J_{5-4}$ = 7.06Hz, $H_5$), 2.05 - 2.15 (12H, m, $H_{11}$).

$^{13}$**C NMR** ($CDCl_3$) $\delta_{ppm}$; 174.8 ($C_{14}$), 168.2-170.6 ($C_9$, 4x$C_{12}$), 99.1 ($C_1$), 72.6 ($C_5$), 72.3 ($C_4$), 71.0 ($C_3$), 69.1 ($C_2$), 65.2 ($C_8$), 60.2 ($C_8$), 59.3 ($C_6$), 59.0 ($C_7$), 20.5 - 21.2 (4x$C_{11}$).

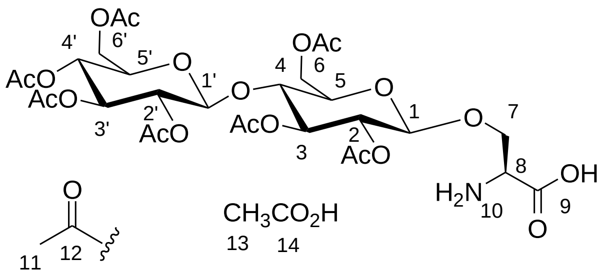
**MS** (ES+): m/z = 435.1[$M^+$] 100%.



**3-*O*-((2,3,4,6-tetra-*O*-acetyl)-β-D-galactopyranosyl-(1-4)-(2,3,4,6-tetra-*O*-acetyl)-β-D-glucopyranose)-L-serine acetic acid salt - Ser(LacAc) – 5(b)**

**$^1$H NMR** ($CDCl_3$) $\delta_{ppm}$: 5.77 (1H, d, $J_{1\text{-}2}$ 7.50Hz, $H_1$), 5.72 (1H, d, $J_{1'\text{-}2'}$ 9.00Hz, $H_{1'}$), 5.54 (1H, t, J = 9.68Hz, $H_{4'}$), 5.41 (1H, t, J = 3.5Hz, $H_4$), 5.30 (1H, t, $J_{2',3'}$ = 9.52Hz, $H_{3'}$), 5.25 (1H, t, $J_{2\text{-}3}$ = 9.00Hz, $H_3$), 5.07-5.15 (2H, m, $H_{2'}$, $H_2$), 4.24 - 4.31 (1H, m, $H_{6b}$), 4.01-4.17 (4H, m, $H_{6'a}$, $H_{6'b}$, $H_{6a}$, $H_{5'}$), 3.88 (1H, td, $J_{4\text{-}5}$ = 6.0Hz, $J_{5\text{-}6}$ 1.5Hz, $H_5$), 3.72 (1H, t, $J_{4\text{-}5}$ = 6.00Hz, $H_4$), 1.96 - 2.16 (24H, m, $H_{11}$).

**$^{13}$C NMR** ($CDCl_3$) $\delta_{ppm}$; 166.5 - 171.1 ($C_9$, 4 x $C_{12}$, $C_{14}$), 94.0 ($C_{1'}$), 92.6 ($C_1$), 73.1 ($C_4$), 72.6 ($C_5$), 72.1 ($C_{3'}$), 71.4 ($C_5$), 70.7 ($C_{2'}$), 70.3 ($C_3$), 68.3 ($C_{2'}$), 66.9 ($C_{4'}$), 61.6 ($C_6$), 61.1 ($C_{6'}$), 20.7-20.9 (4 x $C_{11}$, $C_{13}$). **MS (**ES+) m/z = 723.6 (100%), $[M]^+$.

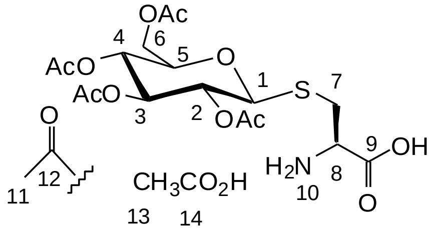


**3-*S*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-L-cysteine acetic acid salt - Cys(GluAc) – 6(b)**

**$^1$H NMR** ($CDCl_3$) $\delta_{ppm}$: 6.12 (1H, d, $J_{1\text{-}2}$ = 6Hz, $H_1$), 5.38 (1H, d, $J_{2\text{-}3}$ = 3.5Hz, $H_2$), 5.29 (1H, t, $J_{4\text{-}5}$ = 9.0Hz, $H_4$) 5.29 (1H, t, $J_{4\text{-}5}$ = 9.0Hz, $H_4$) 5.06 (4H, m, $H_{6a}$ , $H_{6b}$ , $H_{7a}$ , $H_8$), 4.90 (1H, dd, $J_{7b\text{-}7a}$ = 3.5Hz, $J_{7b\text{-}8}$ 6.5Hz, $H_{7b}$ ), 4.79 (1H, dd, $J_{1\text{-}2}$ 8.00Hz, $J_{3\text{-}4}$ = 2.0Hz, $H_3$ ), 3.93 (1H, dd, $J_{5\text{-}6}$ = 4.00Hz, $J_{4\text{-}5}$ = 9.5Hz, $H_5$ ), 1.99 - 2.10 (15H, m, $H_{11}$, $H_{13}$).

**$^{13}$C NMR** ($CDCl_3$) $\delta_{ppm}$: 169.5-171.5 (4x$C_{12}$, $C_{14}$), 166.4 ($C_9$), 90.1 ($C_1$), 70.1 ($C_5$), 69.8 ($C_3$), 68.7 ($C_2$), 67.7 ($C_4$), 67.3 ($C_8$), 62.2 ($C_6$), 61.8 ($C_7$), 20.8 - 21.2 (4x$C_{11}$, $C_{13}$).

**MS (**ES+) m/z = 451.1 $[M]^+$.

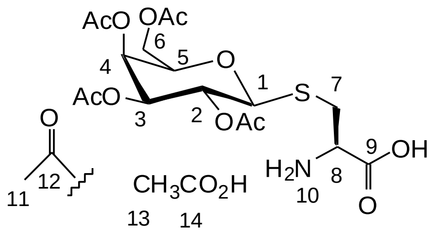


**3-*S*-((2,3,4,6-tetra-*O*-acetyl)-β-D-galactopyranosyl)-L-cysteine acetic acid salt - Cys(GalAc) – 7(b)**

**$^1$H NMR** ($CDCl_3$) $\delta_{ppm}$: 6.02 (1H, d, $J_{1\text{-}2}$ = 6.00Hz, $H_1$), 5.33 (1H, dd, $J_{2\text{-}1}$ = 6.10Hz, $J_{2\text{-}3}$ = 2.50Hz, $H_2$), 5.05 (1H, dd, $J_{3\text{-}4}$ 3.50Hz, $J_{2\text{-}3}$ = 4.50Hz, $H_3$), 4.61- 4.81 (3H, m, $H_{6a}$, $H_{6b}$, $H_8$), 4.55 (1H, dd, $J_{7a\text{-}7b}$ = 2.50Hz, $J_{7\text{-}8}$ = 7.50Hz, $H_{7a}$), 4.38 (1H, t, $J_{3\text{-}4}$ = 6.5Hz, $H_4$), 4.12 (1H, ddd, $J_{5\text{-}6a}$ = 3.00Hz, $J_{5\text{-}6b}$ = 3.60Hz, $J_{5\text{-}4}$ = 7.06Hz, $H_5$), 1.99 - 2.15 (15H, m, $H_{11}$, $H_{13}$).

**$^{13}$C NMR** ($CDCl_3$) $\delta_{ppm}$: 169.2 -171.1 (4x$C_{12}$, $C_{14}$), 166.9 ($C_9$), 91.1 ($C_1$), 70.1 ($C_5$), 69.6 ($C_3$), 68.8 ($C_2$), 68.3 ($C_4$), 67.3 ($C_8$), 62.5 ($C_6$), 62.2 ($C_7$), 18.2 - 21.1 (4x$C_{11}$,$C_{13}$).

**MS (**ES+) m/z = 451.0 $[M + Na]^+$

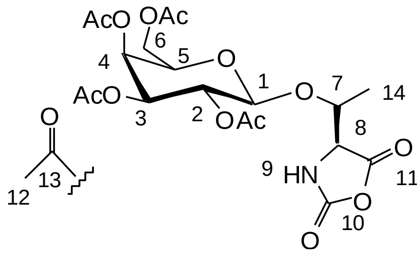


**3-*O*-((2,3,4,6-tetra-*O*-acetyl)-β-D-galactopyranose))-L-threonine-*N*-carboxyanhydride - (Thr(GalAc)NCA – 1(c)**

**$^1$H NMR** ($CDCl_3$) $\delta_{ppm}$; 6.16 (1H, s, $H_9$), 5.68 (1H, d, $J_{1\text{-}2}$ = 8.18Hz, $H_1$), 5.43 (1H, d, $J_{4\text{-}3}$ = 2.69 Hz, $H_4$), 5.29 (1H, dd, $J_{2\text{-}3}$ = 10.40Hz, $J_{2\text{-}1}$ = 8.22Hz, $H_2$), 5.11 (1H, dd, $J_{3\text{-}2}$ = 10.45Hz, $J_{3\text{-}4}$ = 3.38Hz, $H_3$), 4.80 (1H, m, $H_7$), 4.00 (1H, d, $J_{8\text{-}7}$ = 4.83Hz, $H_8$), 1.96 – 2.19 (12H, m, $H_{12}$), 1.55 (3H, d, $J_{14\text{-}7}$ = 6.32Hz, $H_{14}$).

**$^{13}$C NMR** ($CDCl_3$) $\delta_{ppm}$; 169.8 – 170.4 (4 x $C_{13}$), 168.0 ($C_{11}$), 157.9 ($C_{10}$), 93.3 ($C_1$), 75.4 ($C_7$), 72.2 ($C_5$), 70.5 ($C_3$), 67.9 ($C_2$), 66.8 ($C_4$), 61.1 ($C_6$), 60.2 ($C_8$), 20.5 – 21.0 (4 x $C_{12}$, $C_{14}$).

**HRMS** (ES+) m/z = 498.1230 $[M+Na]^+$; expected 498.1218

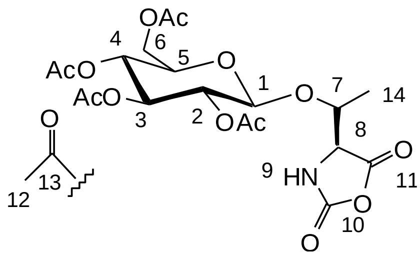


**3-*O*-((2,3,4,6-tetra-*O*-acetyl)-β-D-glucopyranose))-L-threonine-*N*-carboxyanhydride - Thr(GluAc)NCA – 2(c)**

**$^1$H NMR** ($CDCl_3$) $\delta_{ppm}$; 6.30 (1H, s, $H_9$), 5.72 (1H, d, $J_{1-2}$ = 8.14Hz, $H_1$), 5.26 (1H, t, J = 9.41Hz, $H_3$), 5.12 (2H, m, $H_2$ + $H_4$), 4.76 (1H, m, $H_7$), 4.28 (1H, dd, $J_{6b-6a}$ = 12.58Hz, $J_{6b-5}$ = 4.52Hz, $H_{6b}$), 4.09 (1H, dd, $J_{6a-6b}$ = 12.30Hz, $J_{6a-5}$ = 1.14Hz, $H_{6a}$), 4.00 (1H, d, $J_{8-7}$ = 4.85Hz, $H_8$), 3.87 (1H, dd, $J_{5-4}$= 10.09Hz, $J_{5-6}$ = 2.33Hz, $H_5$), 1.98 – 2.10 (12H, m, $H_{12}$), 1.54 (3H, d, $J_{14-7}$ = 6.24Hz, $H_{14}$).

**$^{13}$C NMR** ($CDCl_3$) $\delta_{ppm}$; 169.3 – 170.5 (4x$C_{13}$), 168.8 ($C_{11}$), 157.7 ($C_{10}$), 92.8 ($C_1$), 75.0 ($C_7$), 72.9 ($C_5$), 72.2 ($C_3$), 69.9 ($C_2$), 67.6 ($C_4$), 61.3 ($C_6$), 59.9 ($C_8$), 20.5 – 21.0 (4x$C_{12}$, $C_{14}$).

**HRMS (ES+)** m/z = 476.1396 $[M+H]^+$ ; Expected 476.1399.

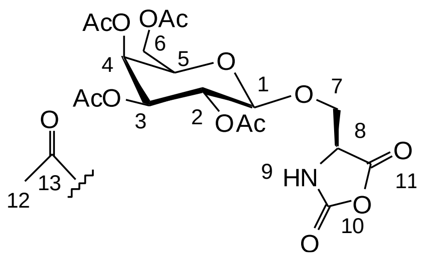


**((2,3,4,6-tetra-*O*-acetyl)-β-D-galactopyranosyl)-L-serine-*N*-carboxyanhydride - Ser(GalAc)NCA – 3(c)**

**$^1$H NMR** ($CDCl_3$) $\delta_{ppm}$; 6.71 (1H, s, $H_9$), 6.04 (1H, d, $J_{1,2}$ = 6Hz, $H_1$), 5.45 (1H, dd, $J_{3-2}$ 2.00Hz, $J_{3-4}$ = 3.50Hz, $H_3$), 5.07 (1H, dd, $J_{2-3}$ = 3.50Hz, $J_{1-2}$ = 4.50Hz, $H_2$ ), 4.35 - 4.48 (4H, m, $H_4$, $H_{6a}$, $H_{6b}$ $H_8$), 4.00 (1H, ddd, $J_{5-6a}$ = 3.00Hz, $J_{5-6b}$ = 3.60Hz, $J_{5-4}$ = 7.06Hz, $H_5$), 2.02 - 2.14 ($H_{13}$).

**$^{13}$C NMR** ($CDCl_3$) $\delta_{ppm}$; 167.2-170.1 (4x$C_{13}$), 164.7 ($C_{11}$), 155.8 ($C_{10}$), 99.1 ($C_1$), 72.6 ($C_5$), 72.2 ($C_4$), 71.0 ($C_3$), 69.2 ($C_2$), 60.4 ($C_8$), 59.3 ($C_6$), 59.0 ($C_7$), 20.5 - 21.2 (4x$C_{13}$).

**HRMS** (ES+) m/z = 484.1061 $[M+Na]^+$; expected 484.1062

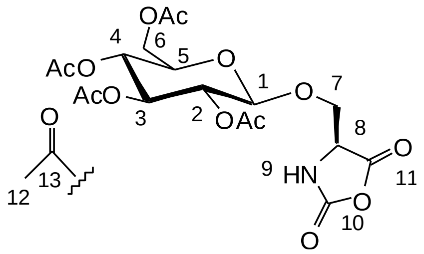


**3-*O*-((2,3,4,6-tetra-*O*-acetyl)-β-D-glucopyranosyl)-L-serine-*N*-carboxyanhydride - Ser(GluAc)NCA – 4(c)**

**$^{1}$H NMR** (CDCl$_3$) $\delta_{ppm}$; 6.07 (1H, s, H$_9$), 5.75 (1H, d, J$_{1\text{-}2}$ 8.00Hz, H$_1$), 5.25 (1H, td, J$_{2\text{-}3}$ = 2.00Hz, J$_{2\text{-}1}$ = 7.7Hz, H$_2$), 5.11 (1H, dd, J$_{4\text{-}5}$ = 7.50Hz, J$_{4\text{-}3}$ = 3.00Hz, H$_4$), 4.77 (1H, m, H$_5$), 4.21 (1H, t, J$_{3\text{-}4}$ = 4.50Hz, H$_3$), 4.06-4.19 (4H, m, H$_{6a}$, H$_{6b}$, H$_{7ba}$, H$_8$), 3.70 (1H, dd, J$_{7a\text{-}7b}$ = 3.50Hz, J$_{7a\text{-}8}$ = 4.00Hz, H$_{7a}$), 1.99 - 2.19 (12H, m, H$_{13}$).

**$^{13}$C NMR** (CDCl$_3$) $\delta_{ppm}$; 168.7 -171.0 (4xC$_{13}$), 165.3(C$_{11}$), 154.1(C$_{10}$), 98.6 (C$_1$), 72.2 (C$_5$), 71.0 (C$_3$), 69.8 (C$_2$), 66.2, 67.4 (C$_4$), 60.1 (C$_8$), 59.1 (C$_6$), 58.9 (C$_7$), 20.7 - 21.8 (4xC$_{12}$).

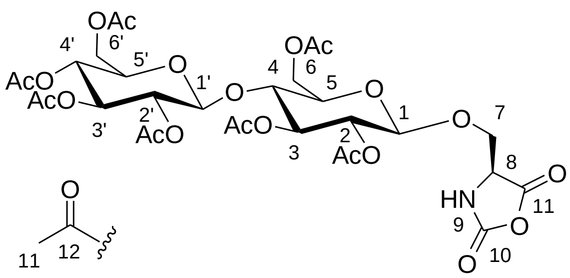
**HRMS** (ES+) m/z = 484.1066 [M+Na]$^+$; expected 484.1062.



**3-*O*-((2,3,4,6-tetra-*O*-acetyl)-β-D-galactopyranosyl-(1-4)-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranose)-L-serine–*N*-carboxyanhydride - Ser(LacAc)NCA – 5(c)**

**$^{1}$H NMR** (CDCl$_3$) $\delta_{ppm}$: 7.67 (1H, s, H$_9$), 5.82 (1H, d, J$_{1\text{-}2}$ = 7.50Hz, H$_1$), 5.76 (1H, d, J$_{1'\text{-}2'}$ = 9.00Hz, H$_{1'}$), 5.44 (1H, t, J$_{4\text{-}5}$ = 9.68Hz, H$_{4'}$), 5.22 – 5.37 (3H, m H$_3$, H$_{3'}$, H$_4$), 5.07-5.15 (2H, m, H$_{2'}$, H$_2$), 4.24 - 4.31 (1H, m, H$_{6b}$), 4.01-4.17 (4H, m, H$_{6'a}$, H$_{6'b}$, H$_{76a}$, H$_{5'}$), 3.70-3.82 (2H, m, H$_4$, H$_5$), 1.97-2.15 (21H, m, H$_{12}$).

**MS (**ES+) m/z =: 749.7 [M]$^+$.

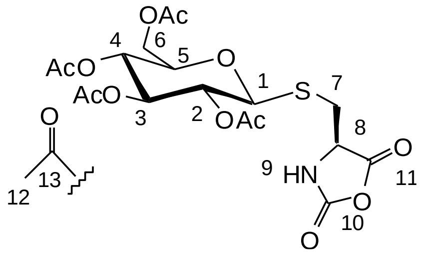


**3-*S*-((2,3,4,6-tetra-*O*-acetyl)-β-D-glucopyranosyl)-L-cysteine-*N*-carboxyanhydride - Cys(GluAc) NCA – 6(c)**

**$^{1}$H NMR** ($CDCl_3$) $\delta_{ppm}$: 6.32 (1H, d, $J_{1,2}$ = 6Hz, $H_9$), 6.05 (1H, d, $J_{1-2}$ = 6.2Hz), 5.38 (1H, d, $J_{2-3}$ = 3.5Hz, $H_2$), 5.29 (1H, t, $J_{3-4}$ = 9.0Hz, $H_3$), 5.06 (4H, m, $H_{6a}$, $H_{6b}$, $H_{7b}$, $H_8$), 4.90 (1H, dd, $J_{7a-7b}$ = 3.5Hz, $J_{7-8}$ = 6.5Hz, $H_{7a}$), 4.79 (1H, dd, $J_{4-5}$ = 8.00Hz, $J_{3-4}$ = 2.0Hz, $H_4$), 3.93 (1H, dd, $J_{5-6}$ = 4.00Hz, $J_{4-5}$ = 9.5Hz, $H_5$), 2.04 - 2.11 (12H, m, $H_{12}$).

**$^{13}$C NMR** ($CDCl_3$) $\delta_{ppm}$: 169.4 -171.5 (4 x $C_{13}$), 163.9 ($C_{11}$), 153.6 ($C_{10}$), 94.1($C_1$), 70.1 ($C_5$), 69.9 ($C_3$), 68.7 ($C_2$), 67.7 ($C_4$), 67.3 ($C_8$), 62.2 ($C_6$), 61.8 ($C_7$), 20.8 - 21.2 (4 x $C_{12}$).

**MS (**ES+) m/z = 477.2 $[M]^+$.



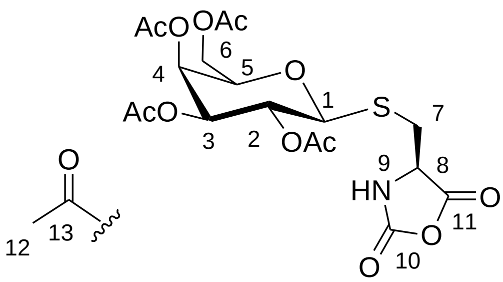

**3-*S*-((2,3,4,6-tetra-*O*-acetyl)-β-D-galactopyranosyl)-L-cysteine-*N*-carboxyanhydride - Cys(GalAc)NCA – 7Cc)**

**$^{1}$H NMR** ($CDCl_3$) $\delta_{ppm}$: 6.92 (1H, s, $H_9$), 6.02 (1H, d, $J_{1-2}$ = 6Hz, $H_1$), 5.41 (1H, d, $J_{2-1}$ = 3.5Hz, $H_2$), 5.33 (1H, dd, $J_{6b-6a}$ =1Hz, $J_{6b-5}$ = 2.5Hz, $H_{6b}$), 5.29 (1H, t, $J_{3-4}$ = 9.0Hz, $H_3$), 5.05 (1H, dd, $J_{6a-6b}$ = 3.5Hz, $J_{6a-5}$ = 4.5Hz, $H_{6a}$), 4.44 (1H, dd, $J_{7a-7b}$ = 2.5Hz, $J_{7-8}$ = 7.5Hz, $H_{7a}$), 4.17- 4.29 (2H, m, $H_4$ + $H_5$), 2.03 - 2.14 (12H, m, $H_{12}$).

**$^{13}$C NMR** ($CDCl_3$) $\delta_{ppm}$: 169.0 -171.1 (4x$C_{13}$), 164.1 ($C_{11}$), 155.0 ($C_{10}$), 91.7 ($C_1$), 70.1 ($C_5$), 69.6 ($C_3$), 69.3 ($C_2$), 68.9 ($C_4$), 66.7 ($C_8$), 61.5 ($C_6$), 60.2 ($C_7$), 21.0 - 21.4 (4x$C_{12}$).

**MS (**ES+) m/z = 477.4 (100%) $[M]^+$.

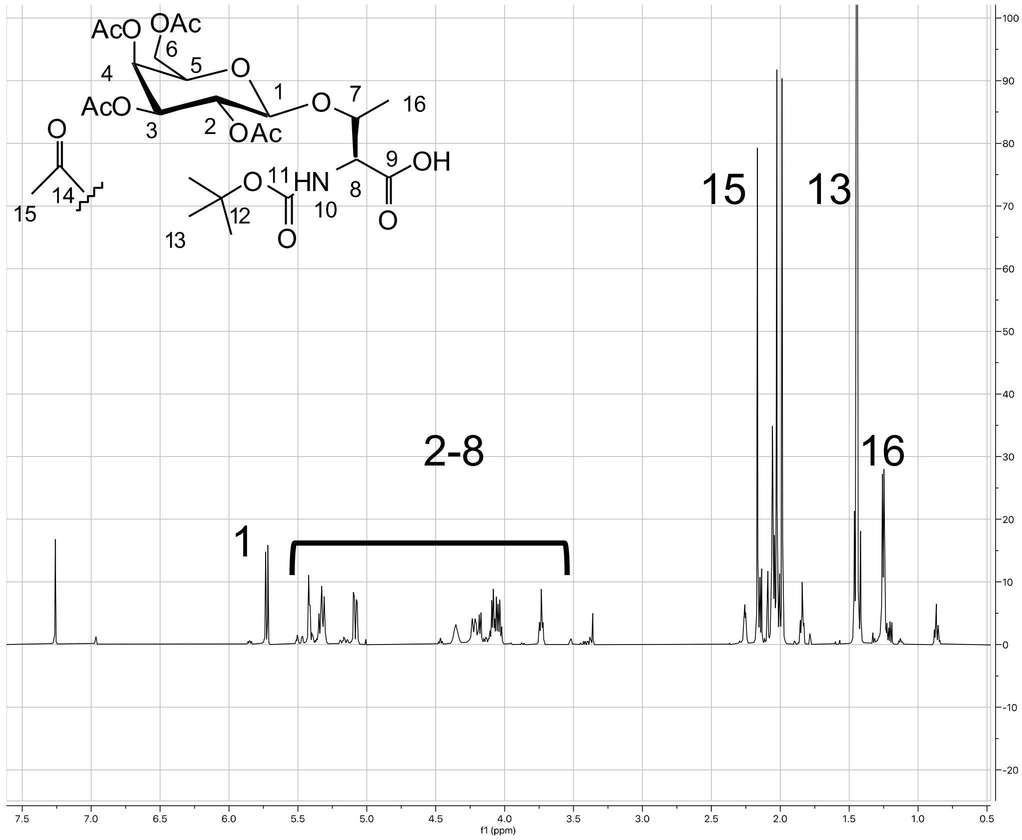
**Elemental** (Found %) C, 45.37; H, 4.66; N, 2.11 (Expected %) C, 45.28 H, 4.86 N, 2.53.

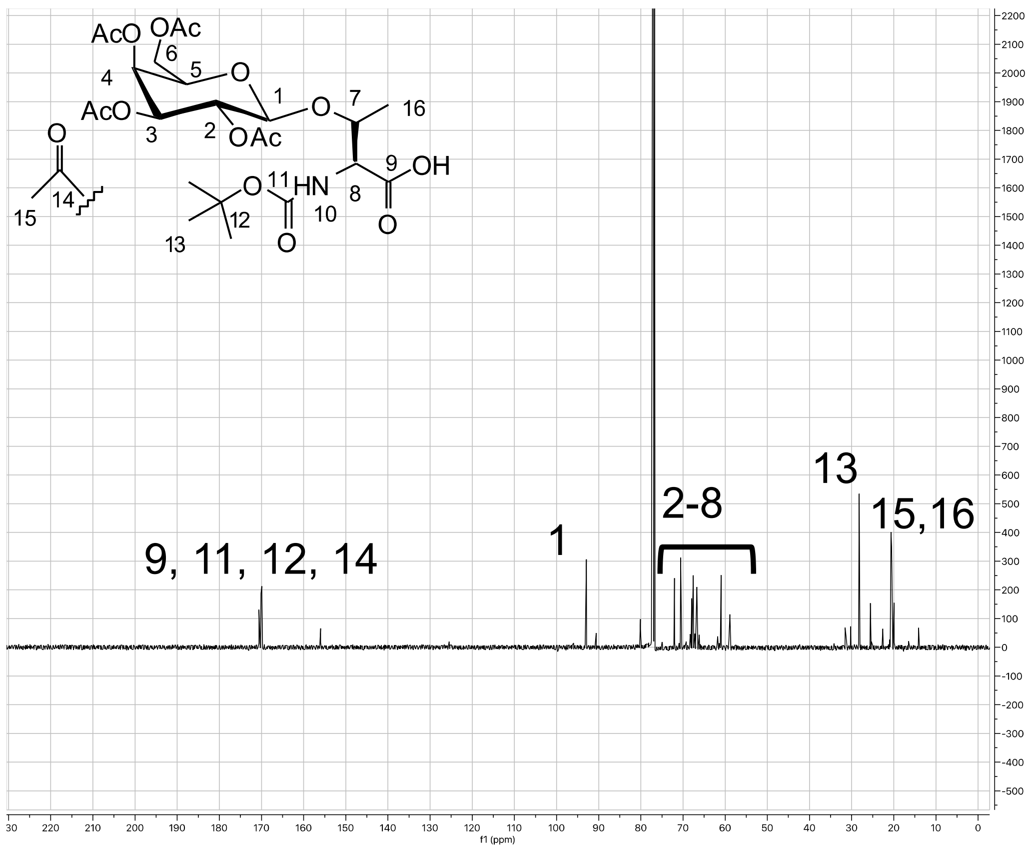


## NMR SPECTRA

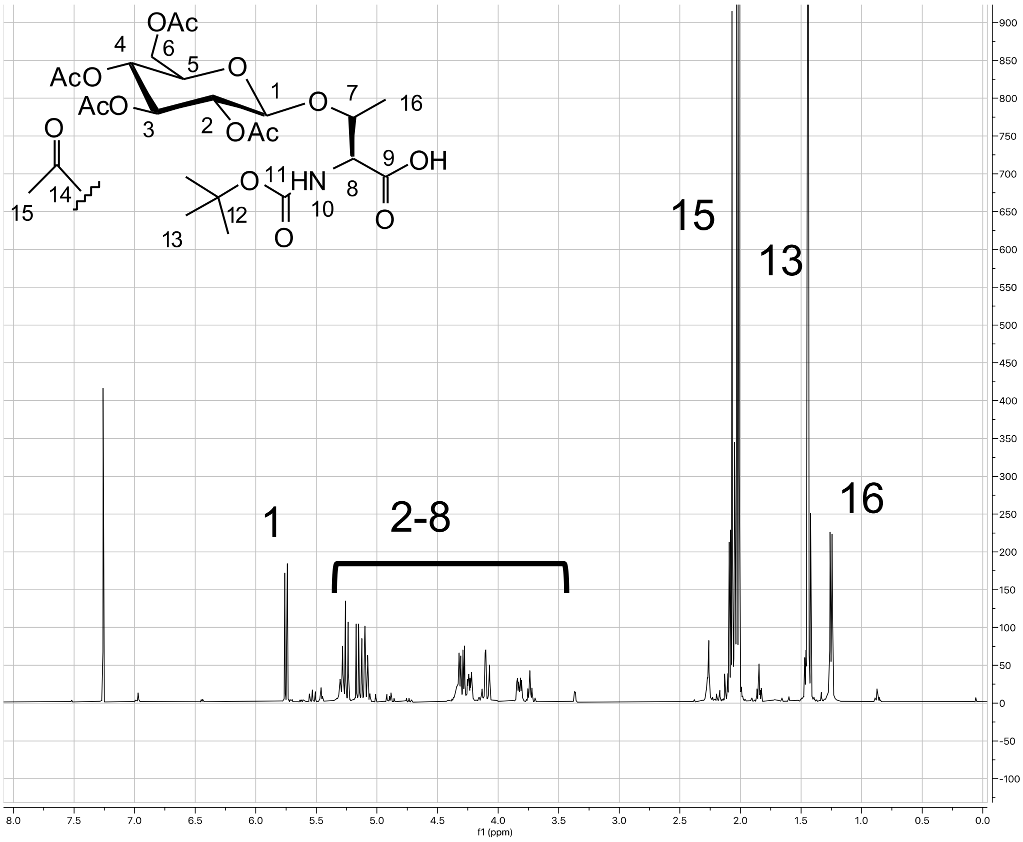
In this section $^{1}H$ and $^{13}C$ spectra for all new compounds are shown. (SerGalAc NCA and SerGluAc NCA have been described previously[3] and are not included here. The intermediate glycosylated amino acids, 1 (b) → 7 (b), were used without purification and were thus not 'analytically' pure and not included here. A single example, Thr(GluAc) - 1 (b) is shown for completeness.

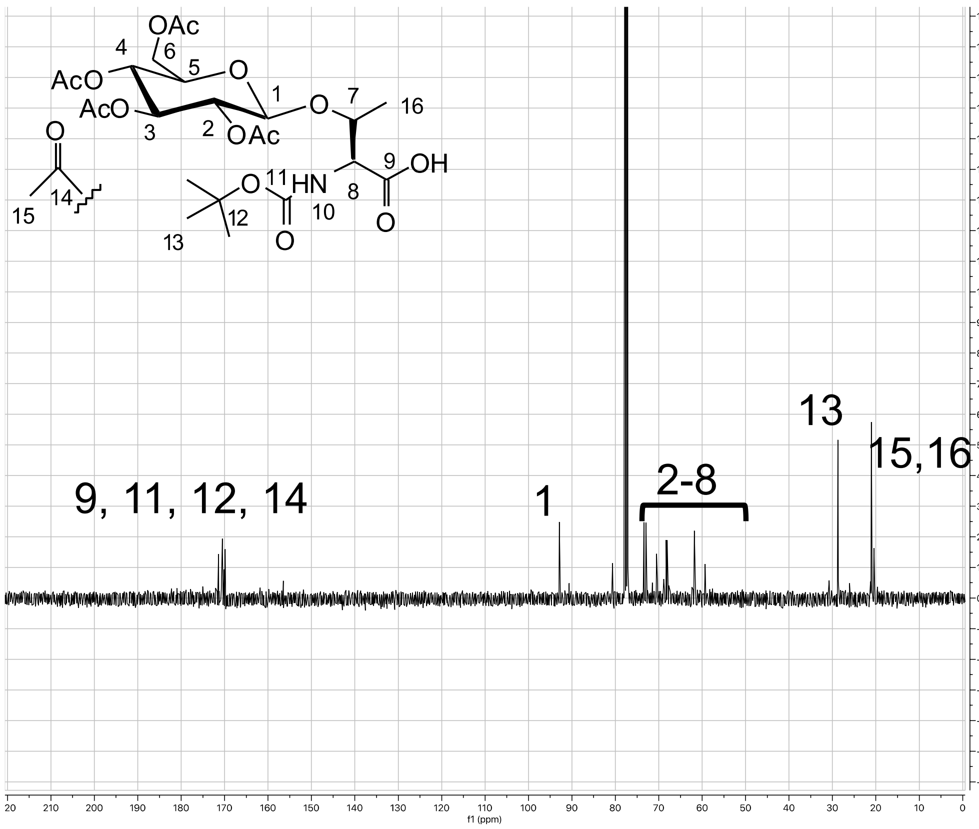
**BocThr(GalAc) – 1(a)**



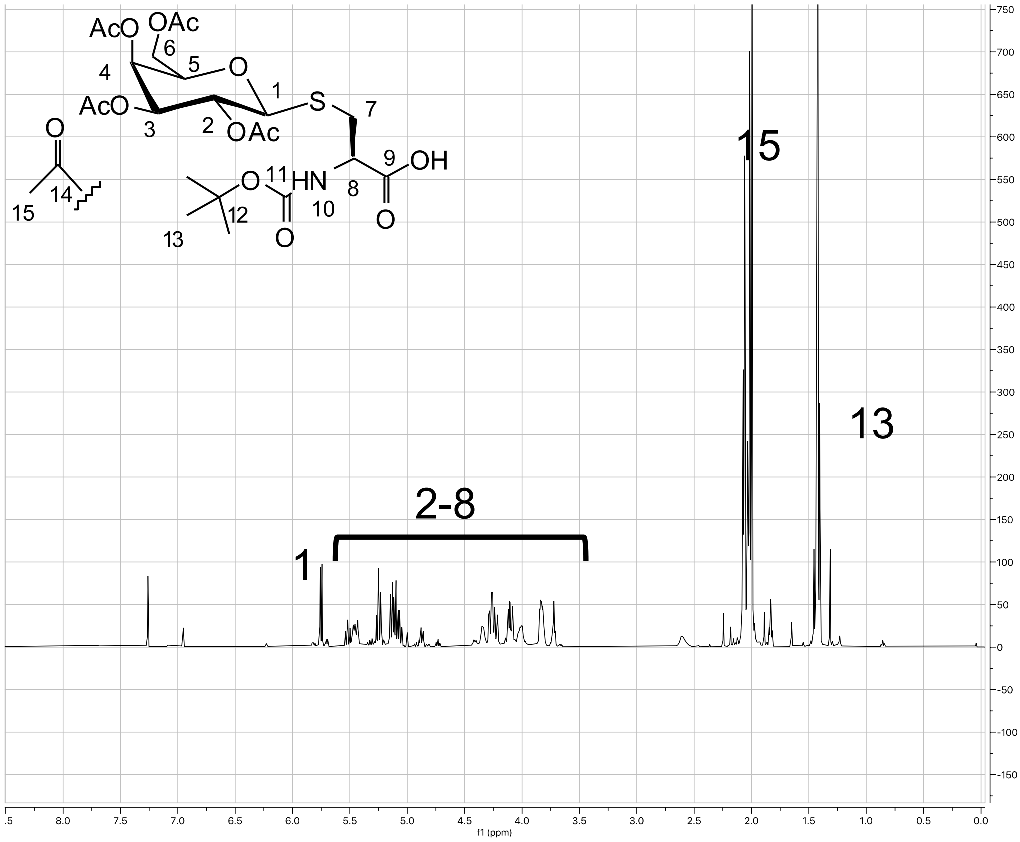



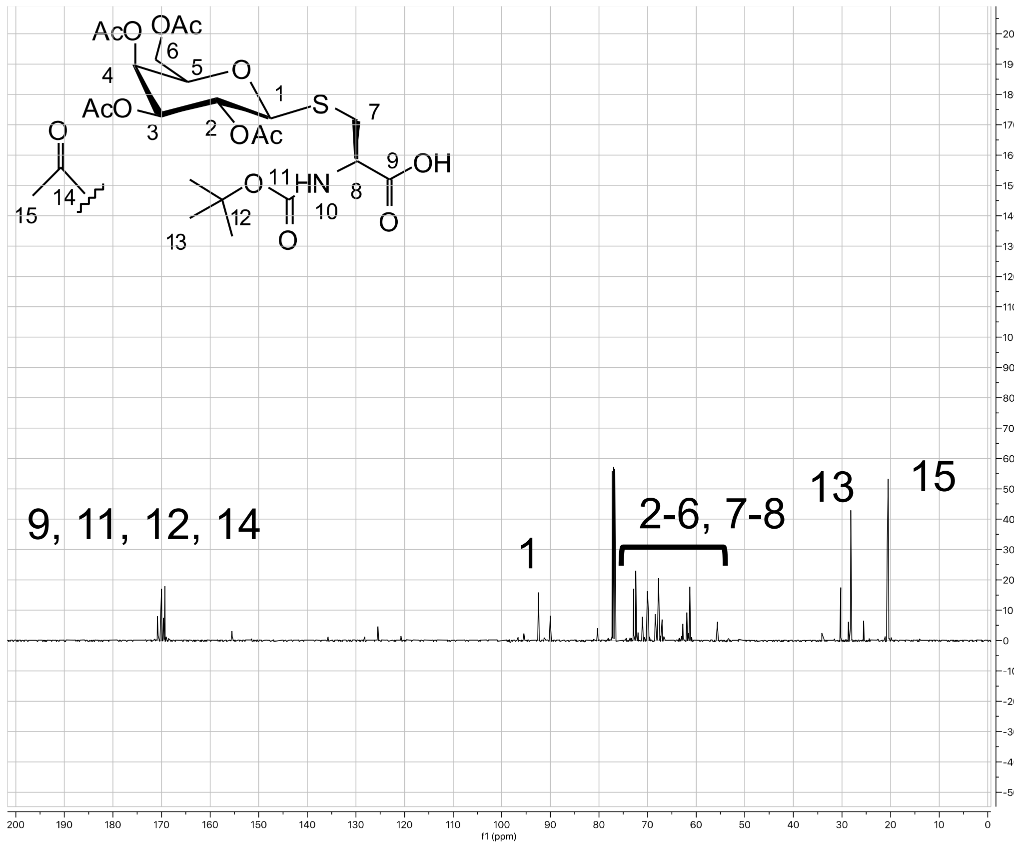
**BocThr(GluAc) – 2(a)**



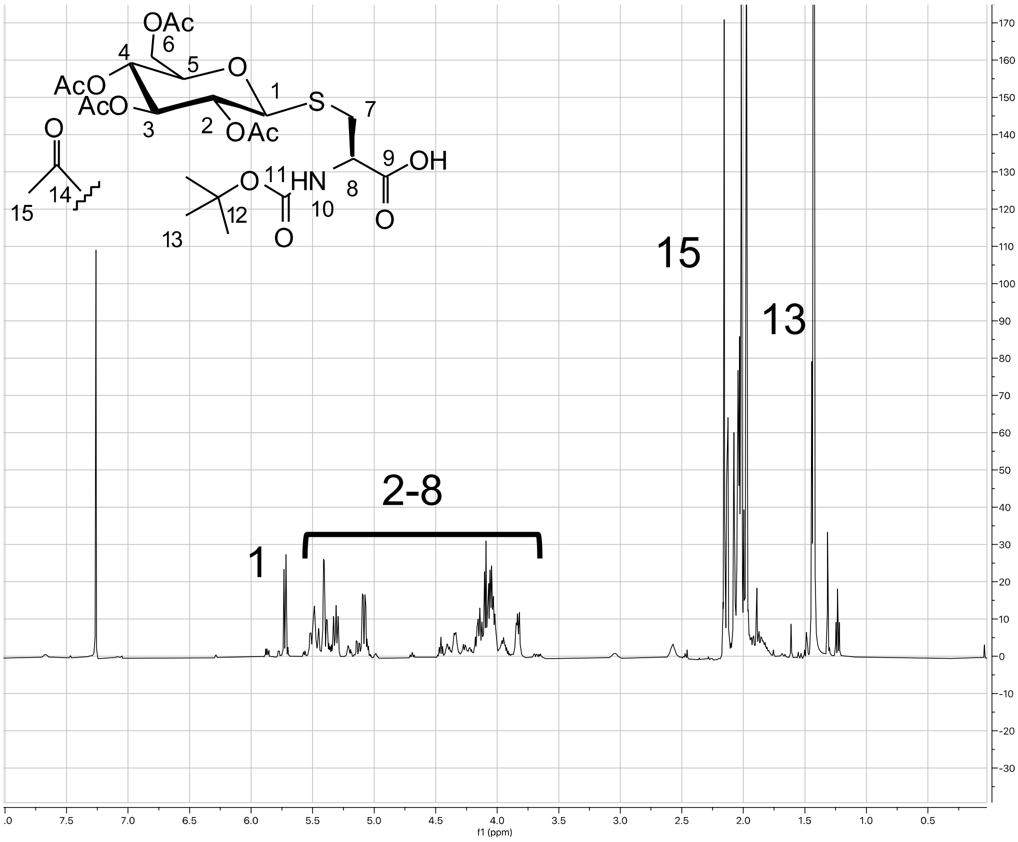



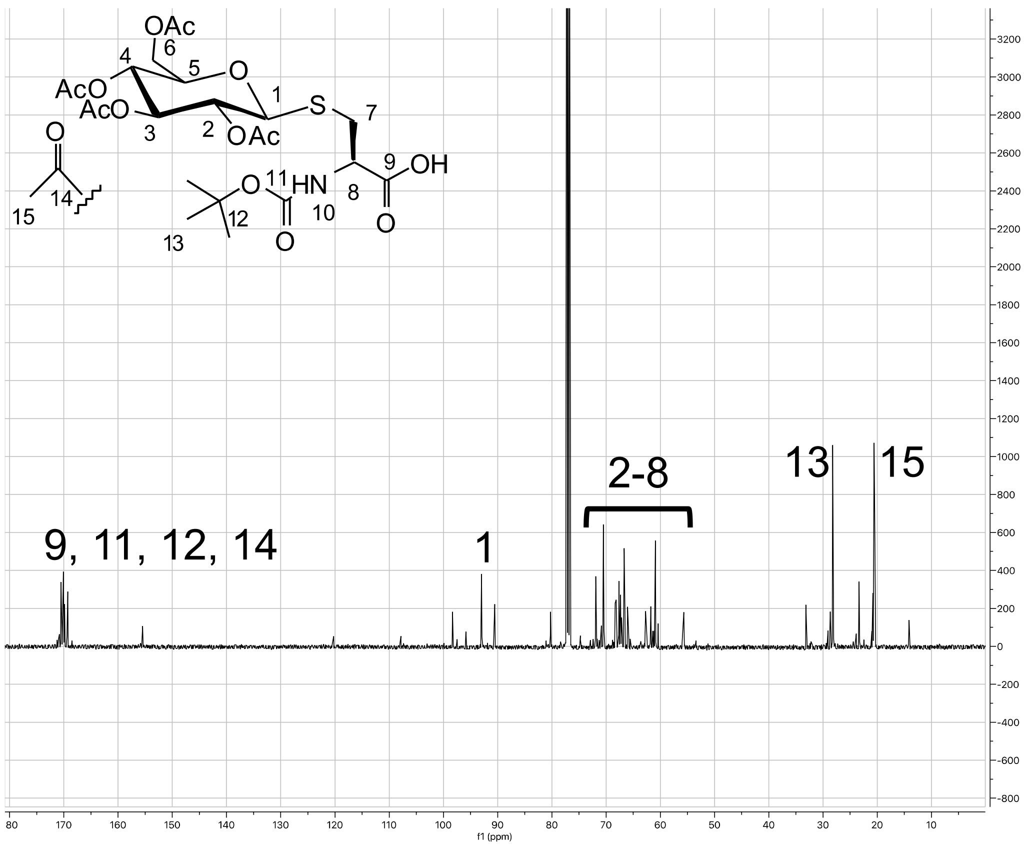
**BocCys(GalAc) – 7 (a)**



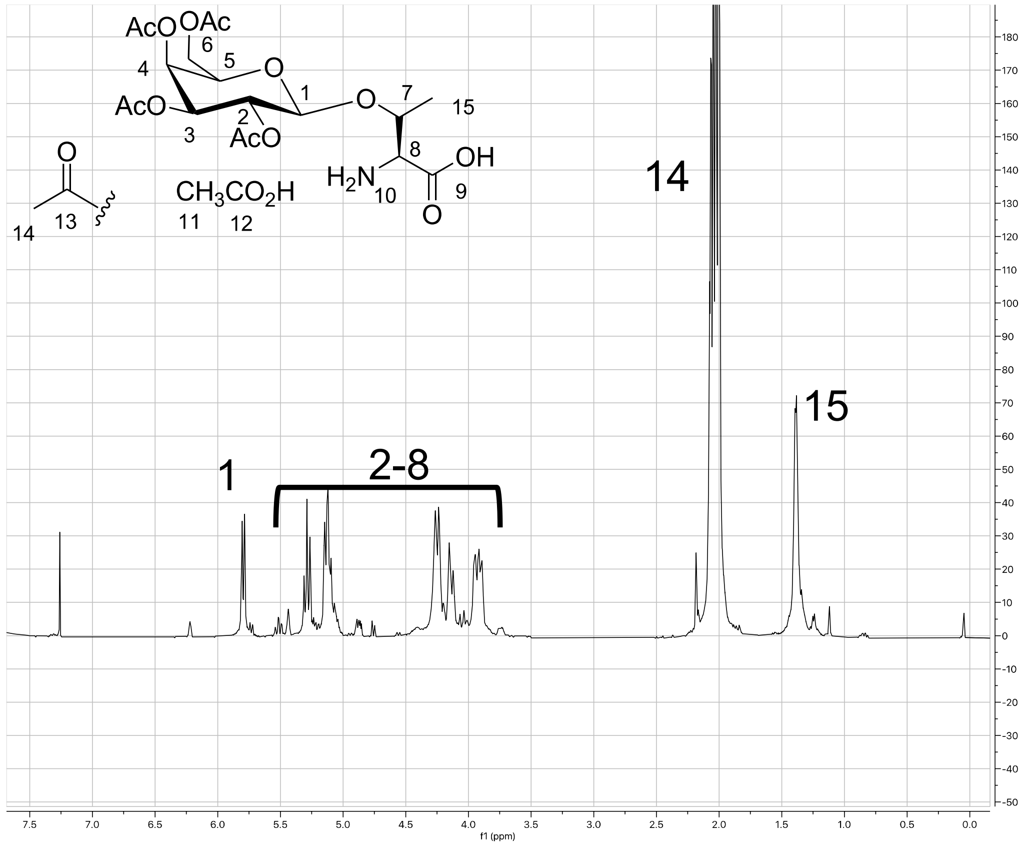



**BocCys(GluAc) – 6(b)**

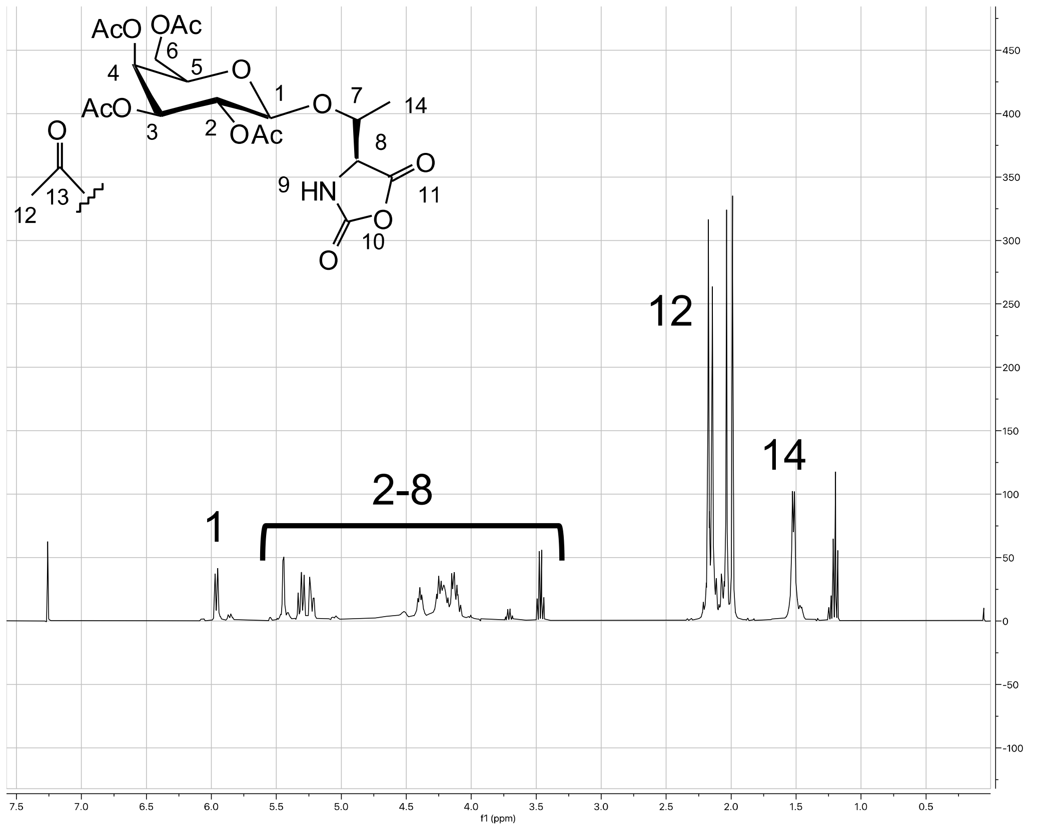


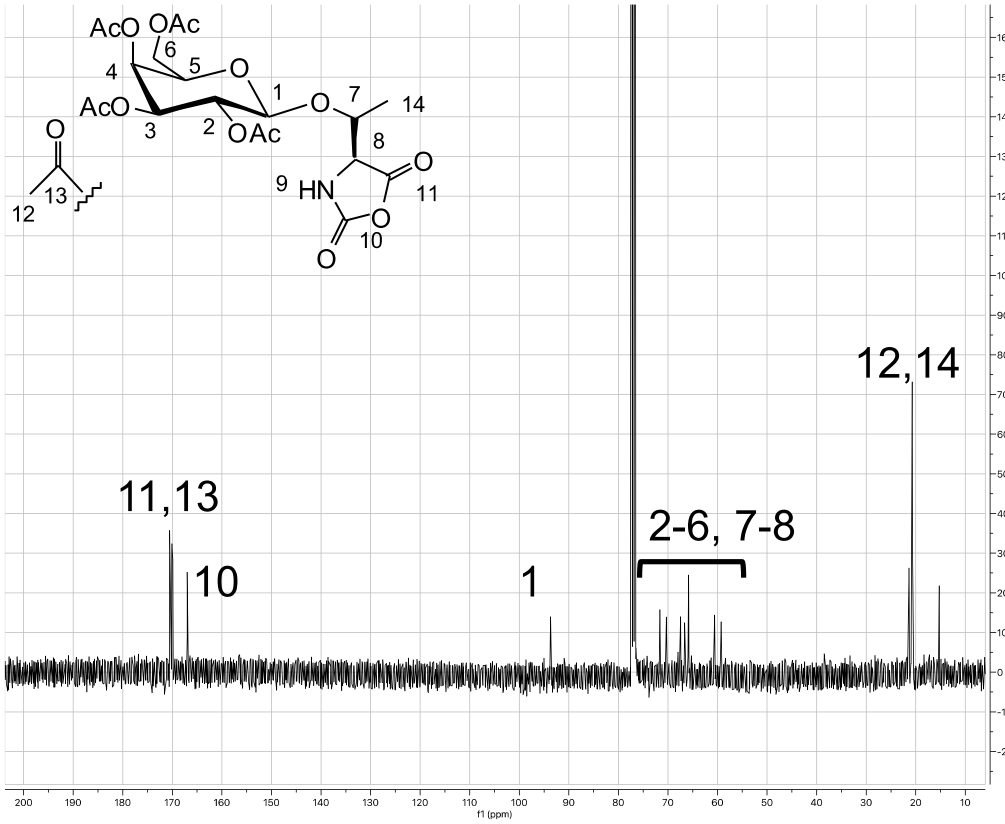



**ThrGal(Ac) – 1 (b)**

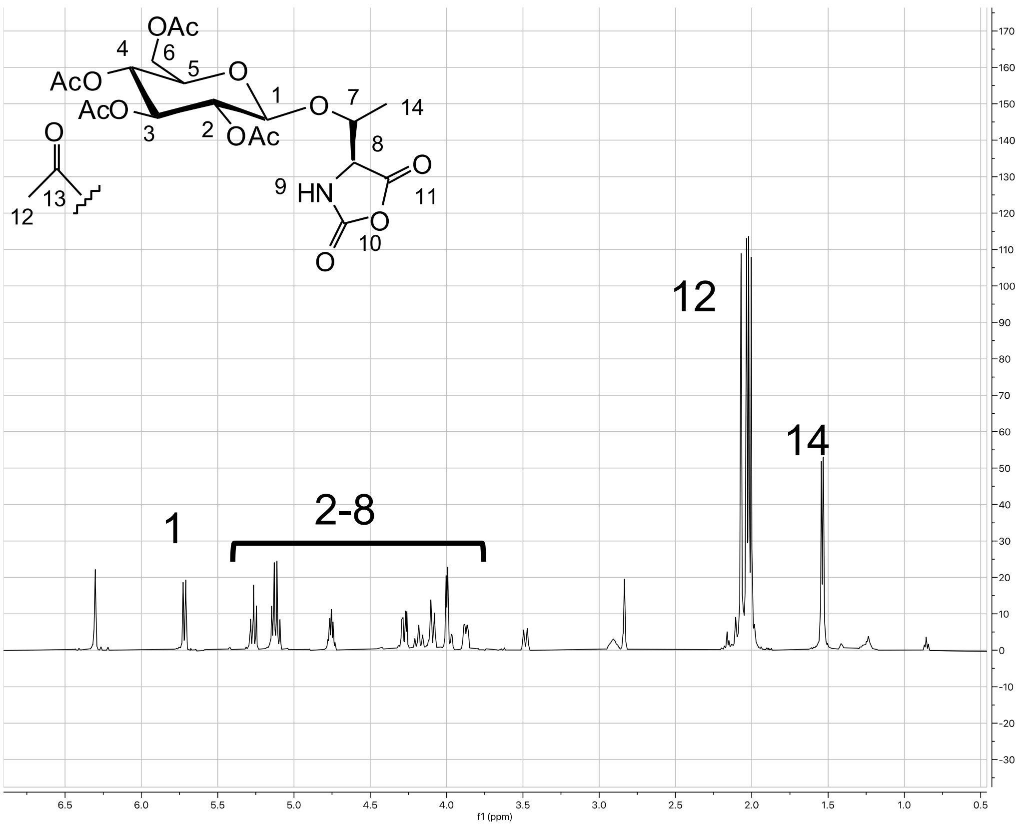


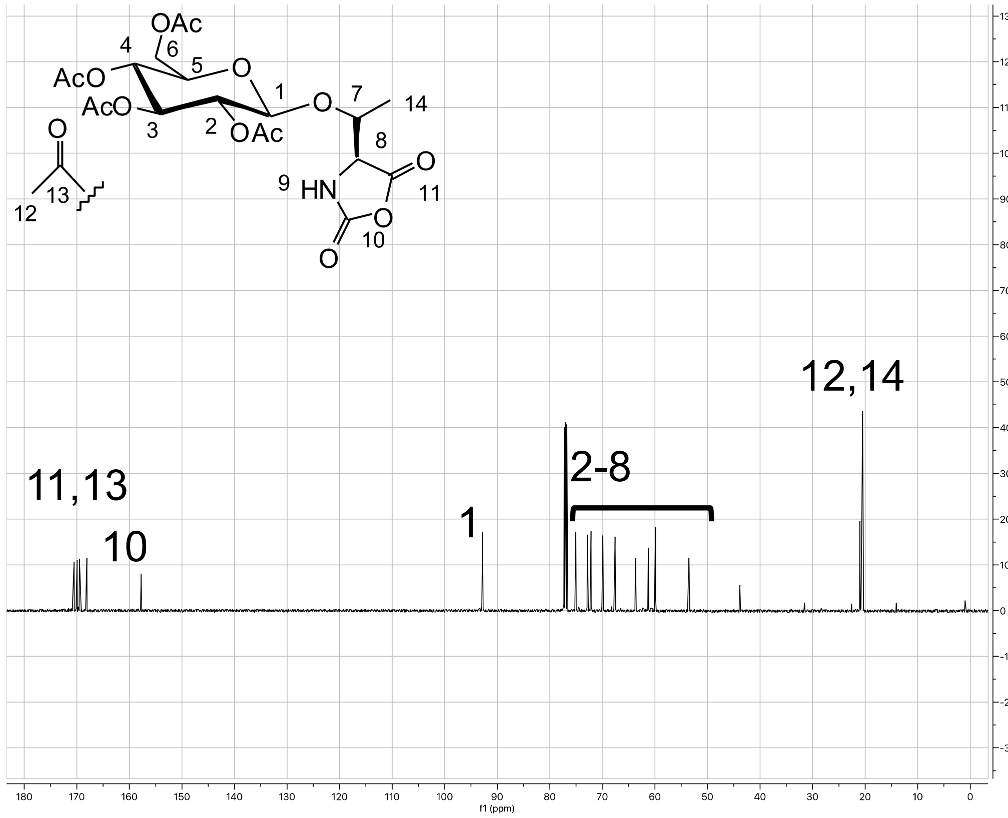

**ThrGalAc NCA – 1(c)**



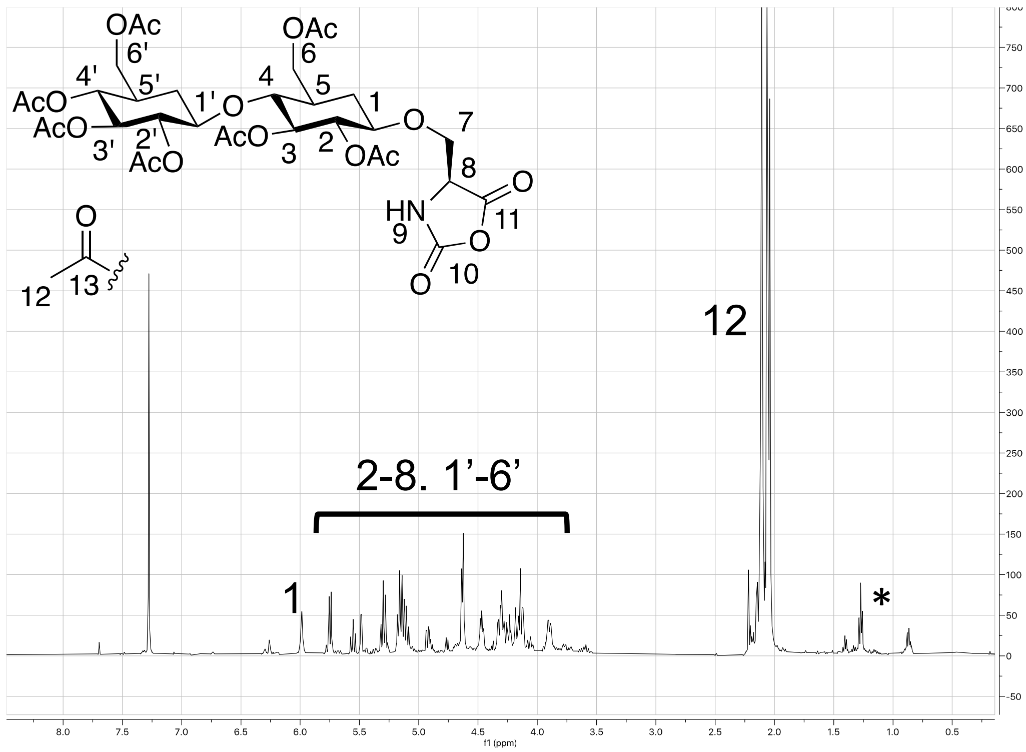


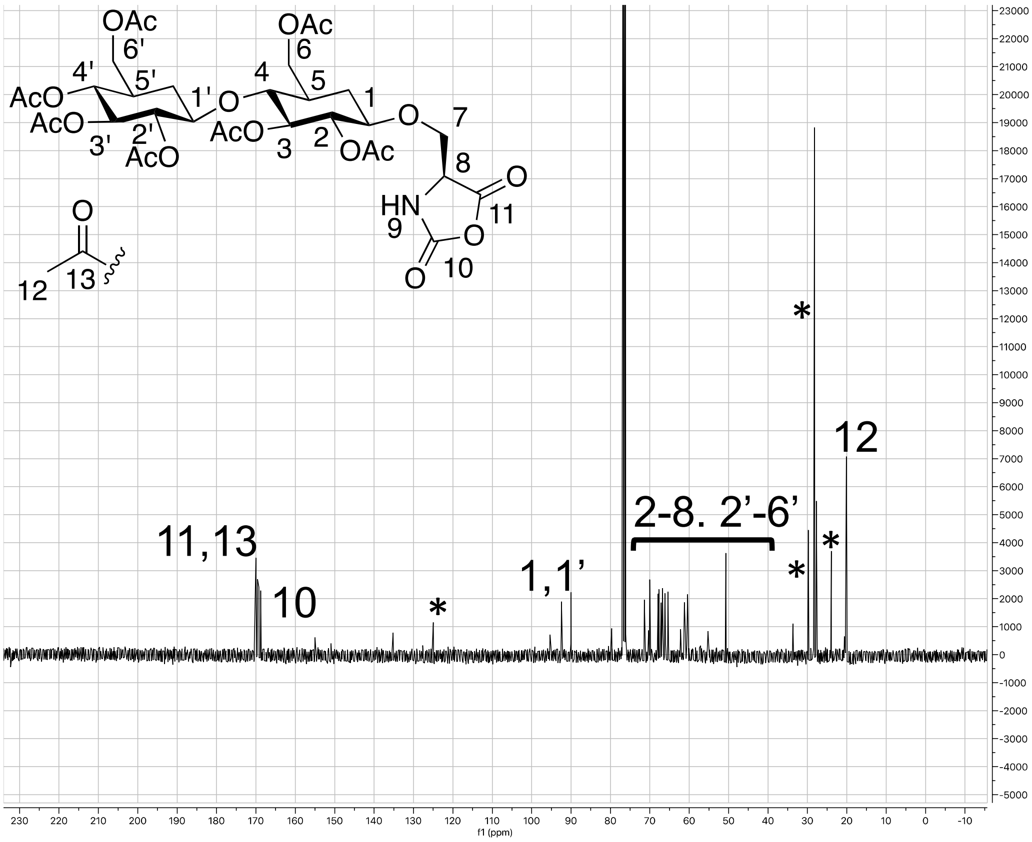

**ThrGluAc NCA – 2(c)**



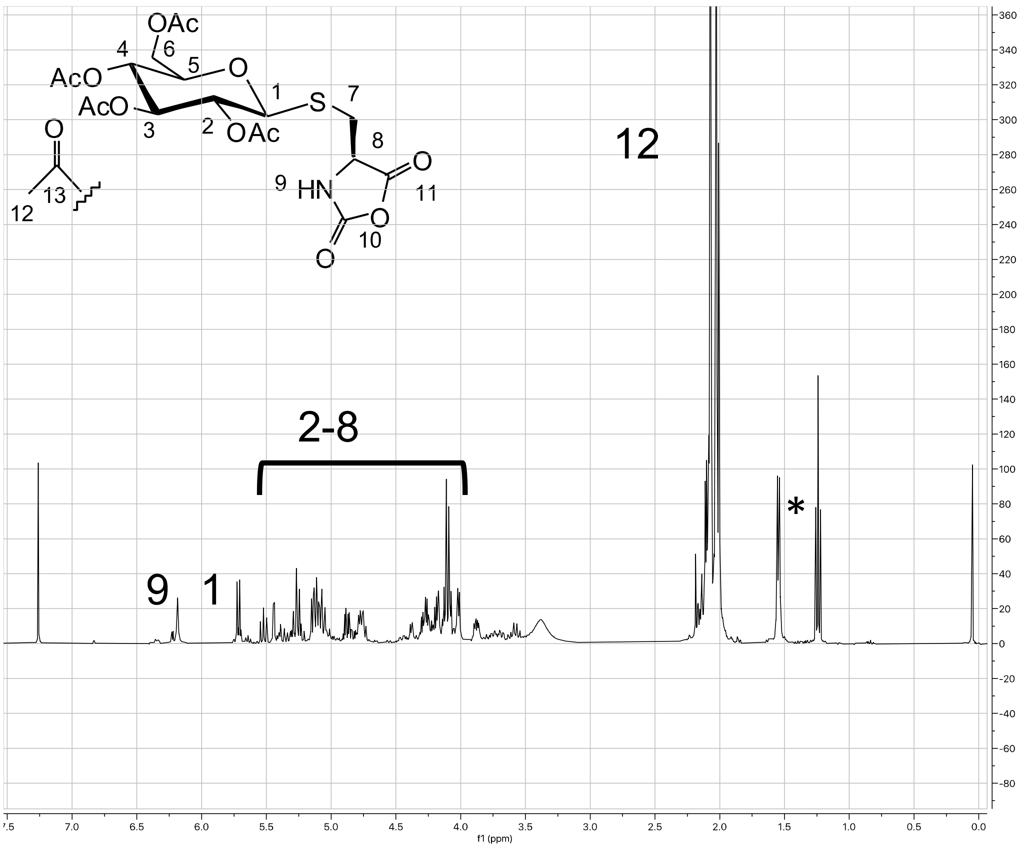


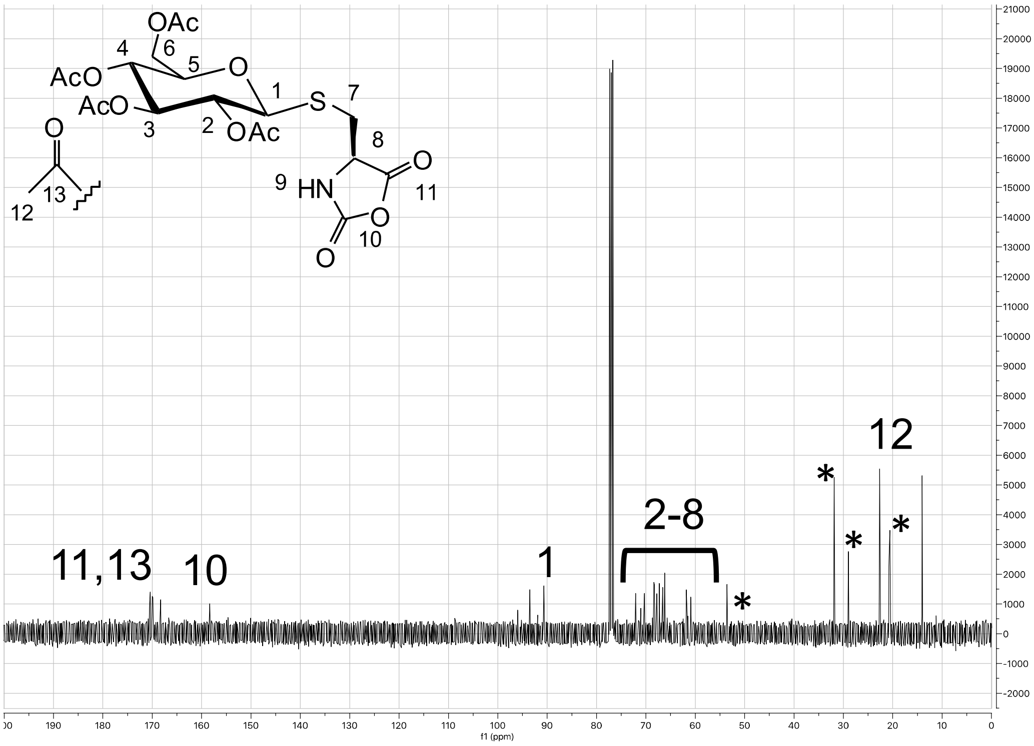

**SerLacAc NCA – 5(c)**



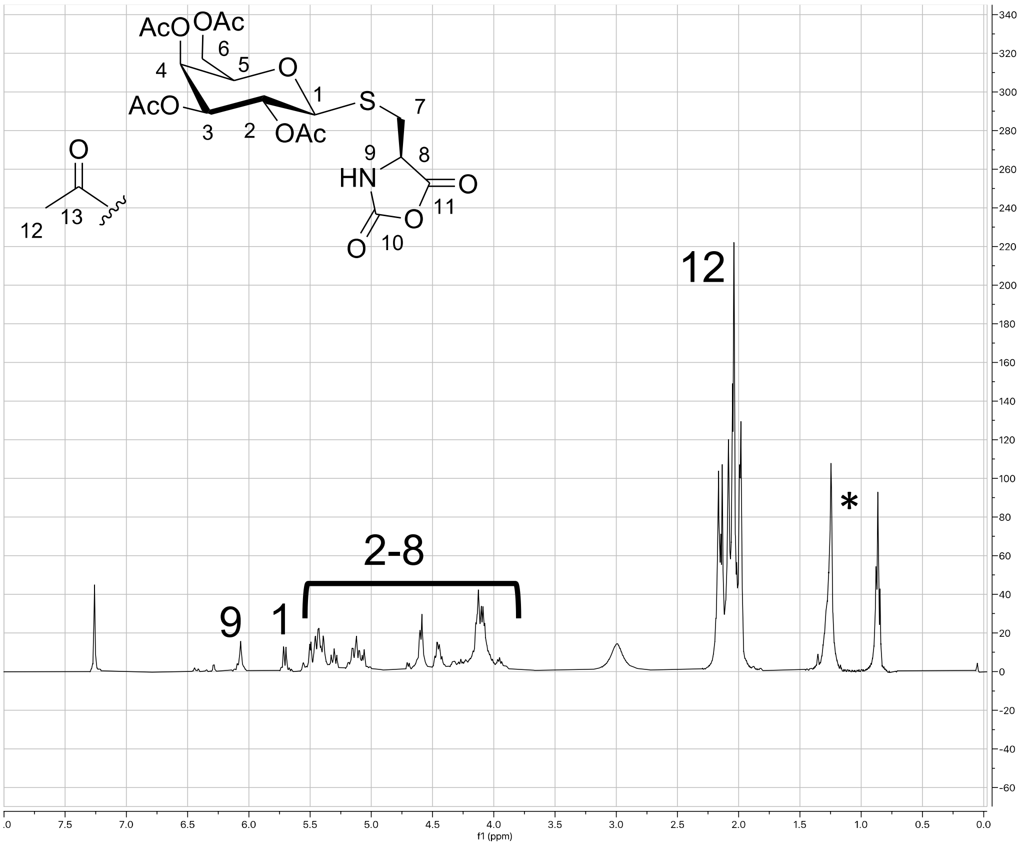



**CysGluAc NCA – 6(c)**






**CysGalAc NCA – 7(c)**




- Indicates pinene residues

# References

1. H. R. Kricheldorf, in *Alpha amino acid-N-CarboxyAnhydrides and Related Materials*, Springer-Verlag, New York, Editon edn., 1987, pp. 59-157.
2. D. Poche, M. J. Moore and J. L. Bowles, *Syn. Comm.*, 1999, **29**, 843-854.
3. Rude E, Westphal O, Hurwitz E, Fuchs S and Sela M, *Immuno Chem.*, 1966, **3**, 137-151; Rude.E and Meyer-Delius.M, *Car.Res*, 1968, **8**, 219-232; Aoi.K, Tsutsumiuchi.K and Okada.M, *Macromolecules*, 1994, **27**, 875-877.