Electronic Supplementary Information

Regenerative Labeling of Saccharides

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Determination of the *E*/*Z* isomers of oxime ether (Glc-a)Ac_5

The condensation product of D-glucose with reagent **a** using method A was treated with Ac_2O to give peracetyl-D-glucose *O*-(naphth-2-ylmethyl)oxime (Glc-**a**)Ac_5 as a mixture of *E*/*Z* isomers in a ratio of 4:1 in $CDCl_3$ solution according to the ^1H NMR analysis. The proton at the C=N double bond of *E*-isomer appeared at δ 7.36, whereas that of *Z*-isomer displayed at δ 6.59.[s1, s2] The signals of the naphthyl-C$\underline{H}_2$ protons occurred at δ 5.20 (*E*-form) and δ 5.27 (*Z*-form).

References:

s1 P. M. Collins, *Chem. Commun.*, 1966, 164–165.

s2 A. Kampf and E. Dimant, *Carbohydr. Res.*, 1971, **16**, 212–214.

Determination of the β-pyranoside structure of Glc-b

The condensation reaction of D-glucose with reagent **b** using method C gave exclusively *N*-methyl-*N*-(naphth-2-ylmethoxy)glucosylamine (**Glc-b**) as a single isomer. The pyranoside structure of **Glc-b** with β-configuration was deduced from the large coupling constant (8 Hz) of its anomeric proton (doublet at δ_H 3.91). The characteristic anomeric carbon occurred at δ_C 93.3 in the ^{13}C NMR spectrum. The condensation reactions of xylose, lactose, maltohexaose and maltoheptaose with reagent **b** also proceeded smoothly to give exclusively the corresponding glycopyranosylamines Xyl-**b**, Lac-**b**, Glc_6-**b** and Glc_7-**b** in β-configuration.

Mechanistic study for regeneration of saccharides by the one-pot hydrogenolysis–hydrolysis reaction

In the absence of $Pd(OH)_2$, our study showed that peracetyl-glycosylamines (Glc-**b**)Ac_4 and (Lac-**b**)Ac_7 were inert in a methanolic solution containing 1–5 equiv of $HCl_{(aq)}$ at room temperature. In contrast, (Glc-**b**)Ac_4 and (Lac-**b**)Ac_7 were subject to one-pot hydrogenolysis–hydrolysis by catalysis of $Pd(OH)_2/HCl_{(aq)}$, giving 2,3,4,6-tetra-*O*-acetyl-D-glucopyranose[s3] and 2,3,6,2',3',4',6'-hepta-*O*-acetyl-lactose[s4], respectively.

As shown in the main text, treatment of (Glc-**a**)Ac_5 with catalytic amounts of $Pd(OH)_2$ and $HCl_{(aq)}$ in MeOH under an atmosphere of H_2 afforded the corresponding peracetylglucose oxime (Glc-oxime)Ac_5 by hydrogenolysis of the $ArCH_2$–O bond. The peracetylated saccharides (Xyl-**a**)Ac_4, (Fru-**a**)Ac_5 and (Lac-**a**)Ac_8 were also converted to the corresponding oximes (Xyl-oxime)Ac_4, (Fru-oxime)Ac_5 and (Lac-oxime)Ac_8 on treatment with $Pd(OH)_2/HCl_{(aq)}$ in MeOH under an atmosphere of H_2. The naphthylmethyl group appeared to play an essential role in the initial hydrogenolysis.

References:

s3 T. Ren and D. Liu, *Tetrahedron Lett.*, 1999, **40**, 7621–7625.

s4 H. Kondo, S. Aoki, Y. Ichikawa, R. L. Halcomb, H. Ritzen and C.-H. Wong, *J. Org. Chem.*, 1994, **59**, 864–877.

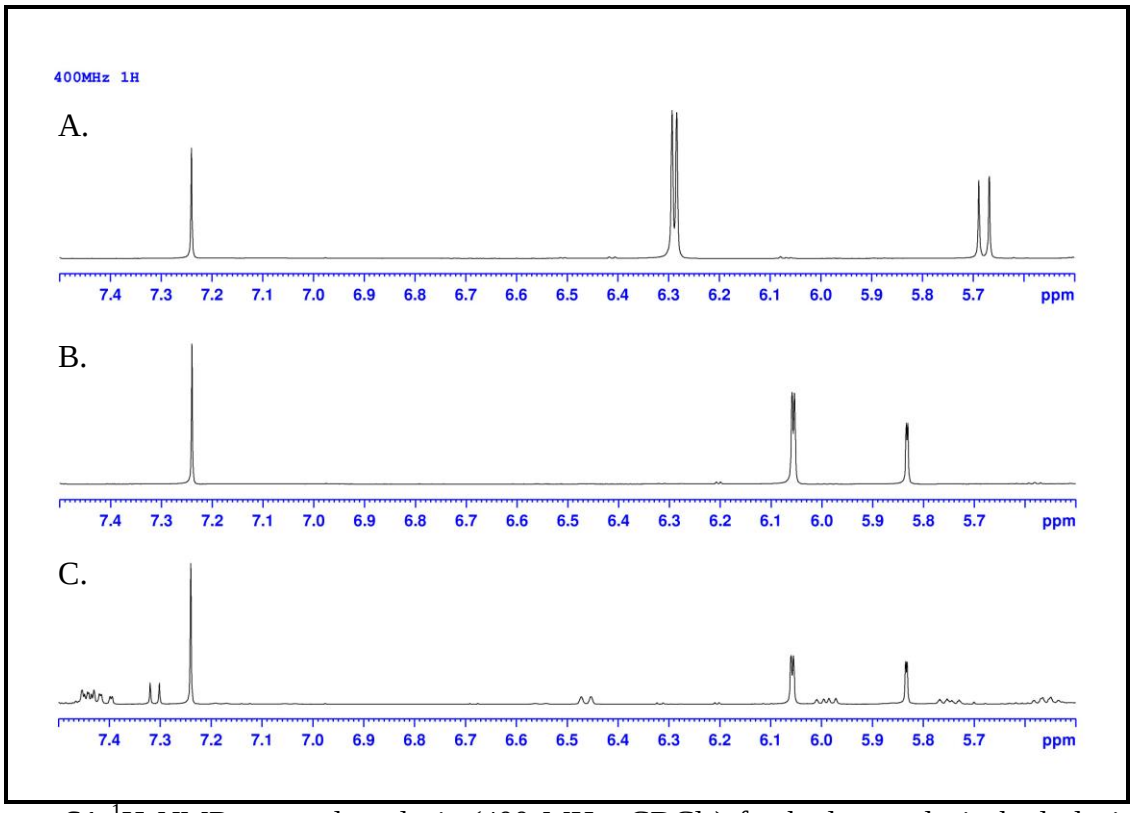


Figure S1 ^{1}H NMR spectral analysis (400 MHz, $CDCl_3$) for hydrogenolysis–hydrolysis of Man-**a**. (A) glucose pentaacetate showing H-1 at δ 6.29 (β-anomer) and δ 5.68 (α-anomer); (B) mannose pentaacetate showing H-1 at δ 6.06 (β-anomer) and δ 5.83 (α-anomer); (C) The crude product from hydrogenolysis–hydrolysis of Man-**a** followed by peracetylation gave mannose pentaacetate without epimerization at the C-2 position.

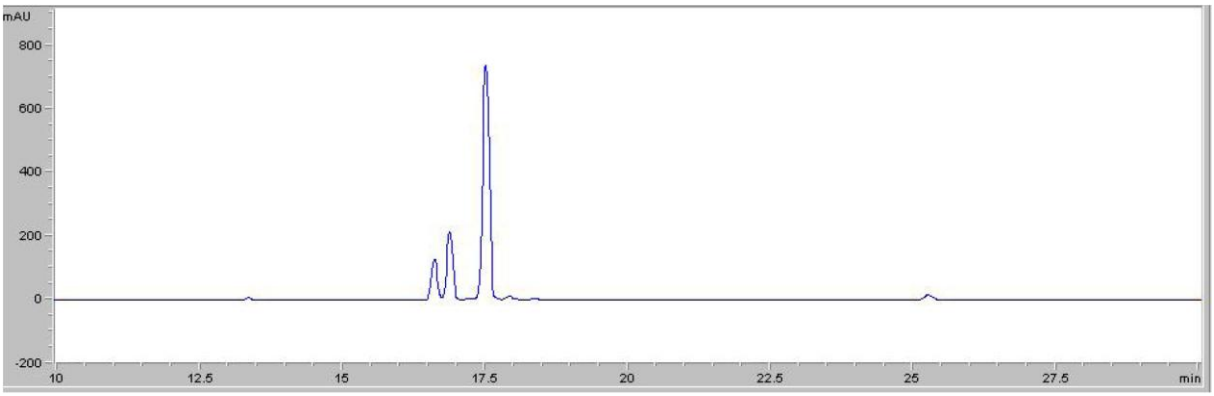


Figure S2 HPLC analysis of the labeling product of maltoheptaose with reagent **a** shows three isomers. Loading: 1.5×10^{-5} mol of each component in 20 μL solution on Agilent reversed-phase HC-C18 column (5 μm porosity, 4.6 mm inner diameter, 250 mm length). Flow rate: 1 mL/min; elution gradients: 0–20% CH_3CN/H_2O for 10 min; 20–70% CH_3CN/H_2O for 20 min; and 100% CH_3CN for 15 min. UV detection at 260-nm wavelength. (*Note*: Although the saccharide derivative bearing a naphthyl group is fluorogenic, the UV detection was applied in this study because there was no fluorescence detector coupled with our HPLC instrument.)

Synthesis and characterization of compounds

2,3,4,5,6-*O*-Pentaacetyl-D-glucose *O*-(naphth-2-ylmethyl)oxime [(Glc-a)Ac$_5$]. Treatment of D-glucose with reagent **a** (method A), followed by acetylation (Ac_2O, 25 ^oC, 4 h) afforded (Glc-**a**)Ac_5 (92%). $[\alpha]^{27}_D$ +58.7 (*c* 0.5, EtOAc); IR (neat) 1750 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, *E*/*Z* isomers = 4:1) δ 7.80–7.75 (4 H, m), 7.44–7.37 (3 H, m), 7.36 (0.8 H, d, *J* = 5.3 Hz), 6.59 (0.2 H, d, *J* = 5.6 Hz), 6.09 (0.2 H, t, *J* = 5.2 Hz) 5.62 (0.2 H, t, *J* = 4.8 Hz), 5.51–5.47 (1.6 H, m), 5.41–5.39 (0.2 H, m), 5.38–5.35 (0.8 H, m), 5.20 (1.6 H, s), 5.27 (0.4 H, s), 5.08–5.01 (1 H, m), 4.20–4.14 (0.8 H, m), 4.07–4.03 (0.4 H, m), 4.00–3.97 (0.8 H, m), 2.09 (0.6 H, s), 2.04 (2.4 H, s), 2.02 (2.4 H, s), 2.01 (0.6 H, s), 1.99 (0.6 H, s), 1.98 (2.4 H, s), 1.97 (2.4 H, s), 1.96 (0.6 H, s), 1.95 (2.4 H, s), 1.92 (0.6 H, s); ^{13}C NMR (100 MHz, $CDCl_3$, *E*-oxime) δ 170.3, 169.6, 169.5, 169.2 (2 ×), 144.1, 134.2, 133.0, 132.9, 128.0, 127.8, 127.5, 127.2, 126.0 (2 ×), 125.9, 76.5, 69.2, 69.0, 68.3, 68.1, 61.6, 20.5 (2 ×), 20.4 (2 ×), 20.2; ESI-TOF-HRMS calcd for $C_{27}H_{31}NNaO_{11}$: 568.1795, found: *m*/*z* 568.1806 $[M + Na]^+$.

***N*-Methyl-*O*-(naphth-2-ylmethyl)-β-D-glucosylamine (Glc-b).** Treatment of D-glucose with reagent **b** (method C) afforded Glc-**b** (83%) after chromatography (RP-C18, H_2O/MeOH (20:1 to 1:1)) and lyophilization. ^1H NMR (400 MHz, D_2O) δ 7.32 (1 H, s), 7.20 (2 H, t, *J* = 8.4 Hz), 7.08 (2 H, m), 6.82–6.72 (2 H, m), 4.56 (2 H, s, CH_2ON), 3.91 (1 H, d, *J* = 8.0 Hz), 3.66 (1 H, d, *J* = 11.2 Hz), 3.56 (1 H, d, *J* = 8.0 Hz), 3.50–3.40 (2 H, m), 3.31 (1 H, t, *J* = 9.6 Hz), 3.1 (1 H, d, *J* = 8.0 Hz), 2.41 (3 H, s); ^{13}C NMR (100 MHz, D_2O) δ 133.8, 132.7, 132.6, 127.8, 127.7 (2 ×), 127.2, 126.7, 125.7 (2 ×), 93.3, 77.1 (2 ×), 75.2, 70.0, 69.2, 60.7, 38.9; ESI-TOF-HRMS calcd for $C_{18}H_{24}NO_6$: 350.1604, found: *m*/*z* 350.1602 $[M + H]^+$.

***N*-Methyl-*N*-(naphth-2-ylmethoxy)-β-2,3,4,6-tetraacetyl-D-glucosylamine [(Glc-b)Ac$_4$].** Acetylation of Glc-**b** afforded (Glc-**b**)Ac_4 (98%). $[\alpha]^{23}_D$ –29.6 (*c* 0.5, CH_2Cl_2); IR (neat) 1735 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.80–7.77 (3 H, m), 7.72 (1 H, s), 7.48–7.42 (3 H, m), 5.20 (1 H, t, *J* = 9.2 Hz), 5.09–5.00 (2 H, m), 4.72 (2 H, s), 4.32 (1 H, d, *J* = 9.6 Hz), 4.25 (1 H, dd, *J* = 12.3, 4.4 Hz), 4.13 (1 H, dd, *J* = 12.3, 2.4 Hz), 3.67–3.62 (1 H, m), 2.65 (3 H, s), 2.01 (3 H, s), 1.98 (3 H, s) 1.97 (3 H, s), 1.93 (3 H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 170.1, 169.4 (2 ×), 134.4, 133.1, 133.0, 127.9 (2 ×), 127.8, 127.6, 126.7, 126.0, 125.9, 92.4, 75.1, 73.8, 73.2, 68.4 (2 ×), 62.0, 37.5, 20.61, 20.58, 20.52, 20.48; ESI-TOF-HRMS calcd for $C_{26}H_{31}NO_{10}$: 518.2040, found: *m*/*z* 518.2060 $[M + H]^+$.

***N*-Methyl-*N*-methoxy-β-2,3,4,6-tetraacetyl-D-glucosylamine.** Treatment of D-glucose with (*N*-methoxy)methanamine hydrochloride (method C), followed by acetylation, afforded the title compound (85%). $[\alpha]^{24}_D$ +44.11 (*c* 0.7, EtOAc); IR (neat) 1752 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.22 (1 H, t, *J* = 9.2 Hz), 5.11 (1 H, t, *J* = 9.2 Hz), 5.04 (1 H, t, *J* = 9.6 Hz), 4.29–4.22 (2 H, m), 4.13 (1 H, dd, *J* = 12, 2.4 Hz), 3.67–3.63 (1 H, m), 3.41 (3 H, s), 2.68 (3 H, s), 2.05 (3 H, s), 2.03 (3 H, s) 2.00 (3 H, s), 1.99 (3 H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 170.3, 169.5, 169.4, 92.1, 73.9, 73.3, 68.5, 68.4, 62.2, 60.2, 37.3, 20.78, 20.72, 20.62, 20.58; ESI-TOF-HRMS calcd for $C_{16}H_{26}NO_{10}$: 392.1557, found: *m*/*z* 392.1554 $[M + H]^+$.

2,3,4,5,6-*O*-Pentaacetyl-D-glucose oxime [(Glc-oxime)Ac$_5$]. Hydrogenolysis–hydrolysis of (Glc-**a**)Ac$_5$ afforded (Glc-oxime)Ac$_5$ (73%) after chromatography (silica gel, EtOAc/hexane (1:3 to 1:1)). $[\alpha]^{28}_D$ +41.7 (*c* 0.6, EtOAc); IR (neat) 3403, 1749 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$, *E*/*Z* isomers = 7:3) δ 8.93 (0.3 H, s), 8.51 (0.7 H, s), 7.31 (0.7 H, d, *J* = 5.7 Hz), 6.56 (0.3 H, d, *J* = 5.4 Hz), 6.09 (0.3 H, t, *J* = 5.4 Hz), 5.59 (0.3 H, t, *J* = 5.2 Hz), 5.47–5.46 (1.4 H, m), 5.39–5.34 (1 H, m), 5.09–5.04 (1 H, m), 4.27–4.19 (1 H, m), 4.10–4.01 (1 H, m), 2.11 (0.9 H, s), 2.09 (2.1 H, s), 2.07 (0.9 H, s), 2.05 (4.2 H, s), 2.04 (0.9 H, s), 2.03 (0.9 H, s), 2.02 (2.1 H, s), 2.01 (3 H, s); ^{13}C NMR (100 MHz, CDCl$_3$, *E*/*Z*-isomers) δ 170.6, 169.80 169.7, 169.4, 146.2, 145.2, 69.3, 69.1, 69.0, 68.8, 68.4, 68.3, 65.5, 61.7, 61.5, 20.7, 20.62, 20.57, 20.46; ESI-TOF-HRMS calcd for $C_{16}H_{23}NNaO_{11}$: 428.1169, found: *m*/*z* 428.1164 $[M + Na]^+$.

2,3,4,5,6-*O*-Pentaacetyl-D-mannose *O*-(naphth-2-ylmethyl)oxime [(Man-a)Ac$_5$]. Treatment of D-mannose with reagent **a** (method A), followed by acetylation (Ac$_2$O, 25 °C, 4 h) afforded (Man-**a**)Ac$_5$ (90%). $[\alpha]^{23}_D$ +19.5 (*c* 0.5, EtOAc); IR (neat) 1752 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$, *E*/*Z* isomers = 4:1) δ 7.80–7.74 (4 H, m), 7.46–7.39 (3 H, m), 7.32 (0.8 H, d, *J* = 7.2 Hz), 6.69 (0.2 H, d, *J* = 6.4 Hz), 6.14 (0.2 H, t, *J* = 6.4 Hz), 5.50–5.48 (0.2 H, m), 5.48–5.45 (0.8 H, m), 5.43–5.40 (1 H, m), 5.28–5.27 (0.8 H, m), 5.20 (2 H, s), 5.13–5.09 (0.2 H, m), 5.08–5.04 (0.8 H, m), 4.18–4.14 (1 H, m), 4.10–4.08 (0.2 H, m), 4.05–4.01 (0.8 H, m), 2.02–1.94 (12 H, m), 1.76 (3 H, s); ^{13}C NMR (100 MHz, CDCl$_3$, *E*-oxime) δ 170.4, 169.7, 169.6, 169.4, 169.1, 145.3, 134.4, 133.1, 133.0, 128.1, 127.9, 127.5, 127.2, 126.1, 126.0, 125.9, 76.5, 68.3, 68.1, 67.7, 67.0, 61.7, 20.6 (2 ×), 20.5, 20.4, 20.2; ESI-TOF-HRMS calcd for $C_{27}H_{31}NNaO_{11}$: 568.1795, found: *m*/*z* 568.1799 $[M + Na]^+$.

***N*-Methyl-*N*-(naphth-2-ylmethoxy)-2,3,4,6-tetraacetyl-D-mannosylamine [(Man-b)Ac$_4$].** Treatment of D-mannose with reagent **b** (method C), followed by acetylation (Ac$_2$O, 25 °C, 4 h) afforded (Man-**b**)Ac$_4$ (62%). IR (neat) 1748 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$, α/β anomers = 2:1) δ 7.85–7.77 (4 H, m), 7.53–7.42 (3 H, m), 5.80 (0.67 H, t, *J* = 3.0 Hz), 5.59 (0.33 H, dd, *J* = 6.4, 4.8 Hz), 5.51 (0.67 H, dd, *J* = 4.8, 3.2 Hz), 5.47 (0.67 H, d, *J* = 3.2 Hz), 5.30 (0.33 H, t, , *J* = 9.6 Hz), 5.24–5.20 (0.33 H, m), 4.98 (1.34 H, s, α-form CH$_2$ON), 4.81 (0.66 H, s, β-form CH$_2$ON), 4.68 (0.34 H, d, *J* = 6.4 Hz), 4.47 (0.33 H, dd, *J* = 12, 2 Hz), 4.32 (0.33 H, dd, *J* = 12, 2.8 Hz), 4.23–4.04 (3 H, m), 2.67 (1 H, s, β-form CH$_3$NO), 2.62 (2 H, s, α-form CH$_3$NO), 2.11 (2 H, s), 2.03 (3 H, s), 2.02 (2 H, s), 2.00 (2 H, s), 1.95 (1 H, s), 1.94 (1 H, s), 1.93 (1 H, s); ^{13}C NMR (100 MHz, CDCl$_3$, α/β anomers = 2:1) δ 170.4, 170.1, 169.8, 169.5, 169.4, 133.7, 133.1, 133.0, 128.1, 128.0, 127.9, 127.8, 127.5, 126.7, 126.0, 125.93, 125.89, 96.5 (β-form anomeric), 91.8 (α-form anomeric), 77.0, 75.6, 75.5, 71.7, 71.1, 70.9, 69.9, 68.0, 65.9, 62.9, 62.7, 40.9 (α-form CH$_3$NO), 40.2 (β-form CH$_3$NO), 20.7, 20.54, 20.51, 20.48, 20.3, 20.2; ESI-TOF-HRMS calcd for $C_{26}H_{31}NNaO_{10}$: 540.1840, found: *m*/*z* 540.1835 $[M + Na]^+$.

2,3,4,5-*O*-Tetraacetyl-D-xylose *O*-(naphth-2-ylmethyl)oxime [(Xyl-a)Ac$_4$]. Treatment of D-xylose with reagent **a** (method A), followed by acetylation, afforded (Xyl-**a**)Ac$_4$ (93%).

$[\alpha]^{27}_{D}$ +56.8 (*c* 0.7, EtOAc); IR (neat) 1749 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, *E*/*Z* isomers = 4:1) δ 7.81–7.75 (4 H, m), 7.48–7.40 (3 H, m), 7.35 (0.8 H, d, *J* = 6 Hz), 6.64 (0.2 H, d, *J* = 5.4 Hz), 6.08 (0.2 H, t, *J* = 5.2 Hz), 5.57 (0.2 H, dd, *J* = 6, 1.7 Hz), 5.57 (0.8 H, t, *J* = 6.2 Hz), 5.44 (0.8 H, dd, *J* = 6.7, 4.2 Hz), 5.31–5.25 (1 H, m), 5.20 (2 H, s), 4.30–4.26 (0.2 H, m), 4.27–4.22 (0.8 H, m), 4.09–4.04 (0.2 H, m), 3.97–3.92 (0.8 H, m), 2.08 (0.6 H, s), 2.03 (3 H, s), 2.01 (2.4 H, s), 1.97 (2.4 H, s), 1.96 (2.4 H, s), 1.91 (0.6 H, s), 1.78 (0.6 H, s); ^{13}C NMR (100 MHz, $CDCl_3$, *E*/*Z* isomers) δ 170.1, 169.6, 169.41, 169.37, 169.33, 169.32, 169.1, 146.0, 144.3, 134.2, 134.1, 133.1, 133.0, 132.9, 128.02, 127.96, 127.83, 127.79, 127.4, 127.2, 126.8, 126.0, 125.9, 125.6, 76.8, 76.5, 69.6, 69.03, 68.99, 68.9, 68.5, 65.9, 61.5, 61.3, 20.5, 20.42, 20.35, 20.2, 20.1; ESI-TOF-HRMS calcd for $C_{24}H_{27}NNaO_9$: 496.1584, found: *m*/*z* 496.1568 $[M + Na]^+$.

***N*-Methyl-*N*-(naphth-2-ylmethoxy)-β-D-xylosylamine (Xyl-b).** Treatment of D-xylose with reagent **b** (method C) afforded Xyl-**b** (91%). Mp 174–175 °C; $[\alpha]^{18}_{D}$ –43.3 (*c* 0.5, MeOH); ^{1}H NMR (400 MHz, CD_3OD) δ 7.86–7.83 (4 H, m), 7.53–7.46 (3 H, m), 4.92 (2 H, s), 3.98 (1 H, d, *J* = 9.0 Hz), 3.89 (1 H, dd, *J* = 11.5, 5.2 Hz), 3.51 (1 H, t, *J* = 9.0 Hz), 3.49–3.43 (1 H, m), 3.31 (1 H, H-3), 3.16 (1 H, t, *J* = 11.5 Hz), 2.71 (3 H, s, N-Me); ^{13}C NMR (100 MHz, CD_3OD) δ 136.2, 134. 9, 134.8, 129.1 (3 ×), 128.8, 127.3, 127.2, 96.6, 79.6, 76.6, 71.9, 71.3, 69.0, 39.5; ESI-TOF-HRMS calcd for $C_{17}H_{22}NO_5$: 320.1498, found: *m*/*z* 320.1494 $[M + H]^+$.

2,3,4,5-*O*-Tetraacetyl-D-xylose oxime [(Xyl-oxime)Ac_4]. Hydrogenolysis–hydrolysis of (Xyl-**a**)Ac_4 afforded (Xyl-oxime)Ac_4 (91%) after chromatography (silica gel, EtOAc/hexane (1:4 to 1:1)). $[\alpha]^{28}_{D}$ (*E*/*Z* isomers) +38.5 (*c* 1.575, EtOAc); IR (neat) 3426, 1750 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, *E*/*Z* isomers = 7:3) δ 9.63 (0.3 H, s), 9.26 (0.7 H, s), 7.20 (0.7 H, d, *J* = 5.9 Hz), 6.46 (0.3 H, d, *J* = 5.6 Hz), 5.99 (0.3 H, t, *J* = 5.9 Hz), 5.49–5.43 (1 H, m), 5.35–5.32 (0.7 H, m), 5.21–5.17 (0.7 H, m), 5.16–5.12 (0.3 H, m), 4.20–4.16 (1 H, m), 3.94–3.85 (1 H, m), 2.01 (0.9 H, s), 1.99 (2.1 H, s), 1.97 (6 H, s), 1.95 (0.9 H, s), 1.92 (2.1 H, s); ^{13}C NMR (100 MHz, $CDCl_3$, *E*/*Z*-isomers) δ 170.4, 170.0, 169.9, 169.64, 169.57, 169.5, 169.4, 145.8, 144.8, 69.7, 69.0, 68.9, 68.5, 65.3, 61.5, 61.42, 20.5, 20.4, 20.34, 20.32, 20.29, 20.21, 20.18; ESI-TOF-HRMS calcd for $C_{13}H_{19}NNaO_9$: 356.0958, found: *m*/*z* 356.0957 $[M + Na]^+$.

1,3,4,5,6-*O*-Pentaacetyl-D-fructose *O*-(naphth-2-ylmethyl)oxime [(Fru-a)Ac_5]. Treatment of D-fructose with reagent **a** (method A), followed by acetylation, afforded (Fru-**a**)Ac_5 (91%). $[\alpha]^{27}_{D}$ +12.7 (*c* 0.9, EtOAc); IR (neat) 1748 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, *E*/*Z* isomers = 3:2) δ 7.82–7.68 (4 H, m), 7.47–7.34 (3 H, m), 6.24 (0.6 H, d, *J* = 3.2 Hz), 5.90 (0.6 H, dd, *J* = 8.6, 3.2 Hz), 5.67 (0.4 H, d, *J* = 4.2 Hz), 5.55 (0.4 H, dd, *J* = 7.5, 4.2 Hz), 5.29 (1 H, m), 5.21–5.14 (1.8 H, m), 4.95 (1 H, d, *J* = 1.2 Hz), 4.77 (0.6 H, d, *J* = 12.8 Hz), 4.47 (0.6 H, d, *J* = 12.8 Hz), 4.25–4.16 (1 H, m), 4.13–4.01 (1 H, m), 2.06 (1.2 H, s), 2.05 (1.8 H, s), 2.04 (1.8 H, s), 1.98 (1.2 H, s), 1.97 (3 H, s), 1.93 (1.2 H, s), 1.91 (1.8 H, s),

1.82 (1.8 H, s), 1.79 (1.2 H, s); ^{13}C NMR (100 MHz, $CDCl_3$, *E*/*Z* isomers) δ 170.2, 170.1, 169.59, 169.54, 169.4, 169.34, 169.28, 169.23, 168.8, 150.8, 150.7, 134.4, 133.9, 133.0, 132.9, 132.78, 132.75, 127.84, 127.82, 127.72, 127.70, 127.4, 126.7, 126.5, 125.9, 125.8, 125.5, 125.4, 76.9, 76.7, 68.7, 68.58, 68.56, 67.99, 67.91, 66.8, 61.5, 61.3, 61.0, 57.7, 20.38, 20.35, 20.31, 20.24, 20.17, 20.1, 20.0; ESI-TOF-HRMS calcd for $C_{27}H_{31}NNaO_{11}$: 568.1795, found: *m*/*z* 568.1805 $[M + Na]^+$.

1,3,4,5,6-*O*-Pentaacetyl-D-fructose oxime [(Fru-oxime)Ac$_5$]. Hydrogenolysis–hydrolysis of (Fru-**a**)Ac_5 afforded (Fru-oxime)Ac_5 (275 mg, 81%) after chromatography (silica gel, EtOAc/hexane (1:4 to 1:2)). $[\alpha]^{28}_D$ +25.1 (*c* 1.4, EtOAc); IR (neat) 3400, 1749 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, *E*/*Z* isomers = 3:2) δ 9.84 (0.6 H, s), 9.64 (0.4 H, s), 6.13 (0.6 H, d, *J* = 3.3 Hz), 5.72 (0.6 H, dd, *J* = 8.5, 3.3 Hz), 5.56 (0.4 H, d, *J* = 3.9 Hz), 5.42 (0.4 H, dd, *J* = 7.9, 3.9 Hz), 5.11–5.07 (1 H, m), 4.83 (0.8 H, d, *J* = 5.6 Hz), 4.65 (0.6 H, d, *J* = 13 Hz), 4.35 (0.6 H, d, *J* = 13 Hz), 4.19–4.11 (1 H, m), 4.09–3.97 (1 H, m), 2.01 (1.2 H, s), 1.97 (1.8 H, s), 1.96 (1.8 H, s), 1.94 (3 H, s), 1.92 (4.2 H, s), 1.91 (1.2 H, m), 1.90 (1.8 H, s); ^{13}C NMR (100 MHz, $CDCl_3$, *E*/*Z*-isomers) δ 170.6, 170.5, 169.94, 169.87, 169.8, 169.7, 169.6, 169.5, 169.4, 169.2, 150.8, 150.5, 68.6, 68.5, 68.4, 68.1, 68.0, 66.4, 61.8, 61.5, 61.1, 57. 3, 20.41, 20.39, 20.31, 20.29, 20.22, 20.16, 20.12, 20.11; ESI-TOF-HRMS calcd for $C_{16}H_{23}NNaO_{11}$: 428.1169, found: *m*/*z* 428.1168 $[M + Na]^+$.

D-Glucuronic acid *O*-(naphtha-2-ylmethyl)oxime (GlcA-a). Treatment of D-glucuronic acid with reagent **a** (method A) afforded GlcA-**a** (67%) after chromatography (RP-C18, MeOH/H_2O (1:9 to 1:3)). Mp 163–166 ^{o}C; $[\alpha]^{23}_D$ –8.2 (*c* 0.5, MeOH); IR (neat) 3356, 1780 cm^{-1}; ^{1}H NMR (400 MHz, CD_3OD) δ 7.85–7.83 (4 H, m), 7.60 (1 H, d, *J* = 5.2 Hz), 7.50–7.46 (3 H, m), 5. 25 (2 H, s), 4.60 (1 H, dd, *J* = 8.0, 5.2 Hz), 4.48 (1 H, d, *J* = 4.8 Hz), 4.43 (1 H, dd, *J* = 8.0, 2.8 Hz), 4.36 (1 H, dd, *J* = 4.8, 2.8 Hz); ^{13}C NMR (100 MHz, CD_3OD) δ 177.9, 149.7, 136.7, 134.9, 134.7, 129.2, 129.1, 128.8, 128.3, 127.4, 127.3, 127.2, 87.8, 77.3, 72.2, 71.1, 68.9; ESI-TOF-HRMS (negative mode) calcd for $C_{17}H_{18}NO_7$: 348.1083, found: *m*/*z* 348.1067 $[M – H]^–$.

***O*-Peracetyl-D-lactose *O*-(naphth-2-ylmethyl)oxime [(Lac-a)Ac$_8$].** Treatment of D-lactose with reagent **a** (method A), followed by acetylation, afforded (Lac-**a**)Ac_8 (92%). Mp 77.5–80 ^{o}C; $[\alpha]^{25}_D$ +50.8 (*c* 0.5, EtOAc); IR (neat) 1748 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, *E*/*Z* isomers = 4:1) δ 7.85–7.79 (4 H, m), 7.49–7.45 (3.8 H, m), 6.65 (0.2 H, d, *J* = 5.0 Hz), 6.04 (0.2 H, t, *J* = 4.6 Hz), 5.77–5.73 (0.8 H, m), 5.66–5.62 (0.2 H, m), 5.50–5.47 (0.8 H, m), 5.33–5.30 (0.4 H, m), 5.27 (0.2 H, s), 5.23 (1.6 H, s), 5.20 (0.8 H, d, *J* = 3.2 Hz), 5.11–5.05 (1 H, m), 5.03–4.99 (0.8 H, m), 4.96–4.92 (0.2 H, m), 4.69–4.65 (0.8 H, m), 4.53 (0.2 H, d, *J* = 7.9 Hz), 4.47–4.41 (0.2 H, m), 4.36–4.33 (0.8 H, m), 4.31–4.27 (0.2 H, m), 4.13–4.00 (4 H, m), 3.90–3.79 (1 H, m), 3.47 (0.8 H, m), 2.11 (0.6 H, s), 2.08 (2.4 H, s), 2.05–1.95 (18 H, m), 1.93 (2.4 H, s), 1.88 (0.6 H, s); ^{13}C NMR (100 MHz, $CDCl_3$, *E*-oxime) δ 170.4, 170.3, 170.2, 170.0, 169.9, 169.7, 169.6, 169.2, 146.2, 135.0, 133.2, 133.0, 128.3, 125.9, 127.8, 127.5, 126.5, 126.4, 126.3, 101.5, 76.4, 70.9, 70. 8, 69.3, 69.1, 68.9, 68.7, 66.7 (2 ×), 62.1, 61.3, 20.8,

20.7, 20.62 (2 ×), 20.59 (3 ×), 20.5; ESI-TOF-HRMS calcd for $C_{39}H_{47}NNaO_{19}$: 856.2640, found: *m*/*z* 856.2653 $[M + Na]^+$.

***N*-Methyl-*N*-(naphth-2-ylmethoxy)-β-2,2',3,3',4',6,6'-heptaacetyl-D-lactosylamine [(Lac-b)Ac$_7$].** Treatment of D-lactose with reagent **b** (method C), followed by acetylation, afforded (Lac-**b**)Ac_7 (85%). $[\alpha]^{23}_D$ –11.6 (*c* 1.0, CH_2Cl_2); IR (neat) 1752 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.77–7.70 (4 H, m), 7.44–7.40 (3 H, m), 5.32–5.29 (1 H, m), 5.23–5.15 (1 H, m), 5.07–5.00 (2 H, m), 4.96–4.88 (1 H, m), 4.71–4.64 (2 H, m), 4.49–4.41 (2 H, m), 4.30–4.16 (2 H, m), 4.09–3.96 (2 H, m), 3.83–3.80 (1 H, m), 3.72–3.68 (1 H, m), 3.56–3.46 (1 H, m), 2.61–2.60 (3 H, s), 2.09 (3 H.s), 2.02–1.98 (12 H, m), 1.93–1.90 (6 H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 170.21, 170.16, 170.1, 170.0, 169.8, 169.7, 169.61, 169.57, 169.3, 168.8, 134.3, 134.2, 132.91, 132.87, 127.92,127.85, 127.76, 127.69, 127.67, 127.5, 126.8, 126. 7, 125.9, 125.82, 125.79, 125.76, 101.7, 100.8, 91.96, 91.92, 82.3, 76.1, 75.0, 74.1, 74.0, 73.7, 73.0, 71.1, 70.8, 70.6, 70.4, 69.4, 68.9, 68.5, 68.4, 66.6, 66. 5, 62.6, 62.0, 61.5, 60.6, 37.8, 37.7, 20.7, 20.58, 20.55, 20.53, 20.37, 20.35, 20.3; ESI-TOF-HRMS calcd for $C_{38}H_{47}NNaO_{18}$: 828.2691, found: *m*/*z* 828.2653 $[M + Na]^+$.

***O*-Peracetyl-D-lactose oxime [(Lac-oxime)Ac$_8$].** Hydrogenolysis–hydrolysis of (Lac-**a**)Ac_8 afforded (Lac-oxime)Ac_8 (72%) after chromatography (silica gel, CH_2Cl_2/MeOH (25:1 to 19:1)). Mp 78–80.4 °C; $[\alpha]^{26}_D$ +38.7 (*c* 0.7, EtOAc); IR (neat) 3460, 1748 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, *E*/*Z* isomers = 4:1) δ 9.03 (0.2 H, s), 8.64 (0.8 H, s), 7.39 (0.8 H, d, *J* = 5.7 Hz), 6.57 (0.2 H, d, *J* = 4.9 Hz), 6.05 (0.2 H, t, *J* = 4.3 Hz), 5.77–5.73 (0.8 H, m), 5.56 (0.2 H, t, *J* = 5.5 Hz), 5.47–5.44 (1 H, m), 5.32–5.31 (0.8 H, m), 5.17–5.12 (0.8 H, m), 5.06–5.02 (0.8 H, m), 4.97–4.92 (1 H, m), 4.58–4.54 (1 H, m), 4.48–4.42 (1 H, m), 4.40–4.36 (0.2 H, m), 4.26–4.21 (1 H, m), 4.17–3.99 (3 H, s), 3.86 (0.8 H, t, *J* = 6.3 Hz), 3.81 (0.2 H, t, *J* = 5.3 Hz), 3.61 (0.2 H, t, *J* = 5.3 Hz), 2.13 (2.4 H, s), 2.11 (0.6 H, s), 2.10 (0.6 H, s), 2.03 (6 H, s), 2.02 (6 H, s), 2.00 (5.4 H, s), 1.92 (3 H, s); ^{13}C NMR (100 MHz, $CDCl_3$, *E*-oxime) δ 170.8, 170.4, 170.3, 170.1, 169.8, 169.7, 169.5, 169.3, 146.3, 101.4, 76.0, 71.0 (2 ×), 69.6, 69.5, 68.92, 68.89, 66.9, 61.8, 61.4, 20.73, 20.66, 20.61, 20.56 (4 ×), 20.4; ESI-TOF-HRMS calcd for $C_{28}H_{39}NNaO_{19}$: 716.2014, found: *m*/*z* 716.2012 $[M + Na]^+$.

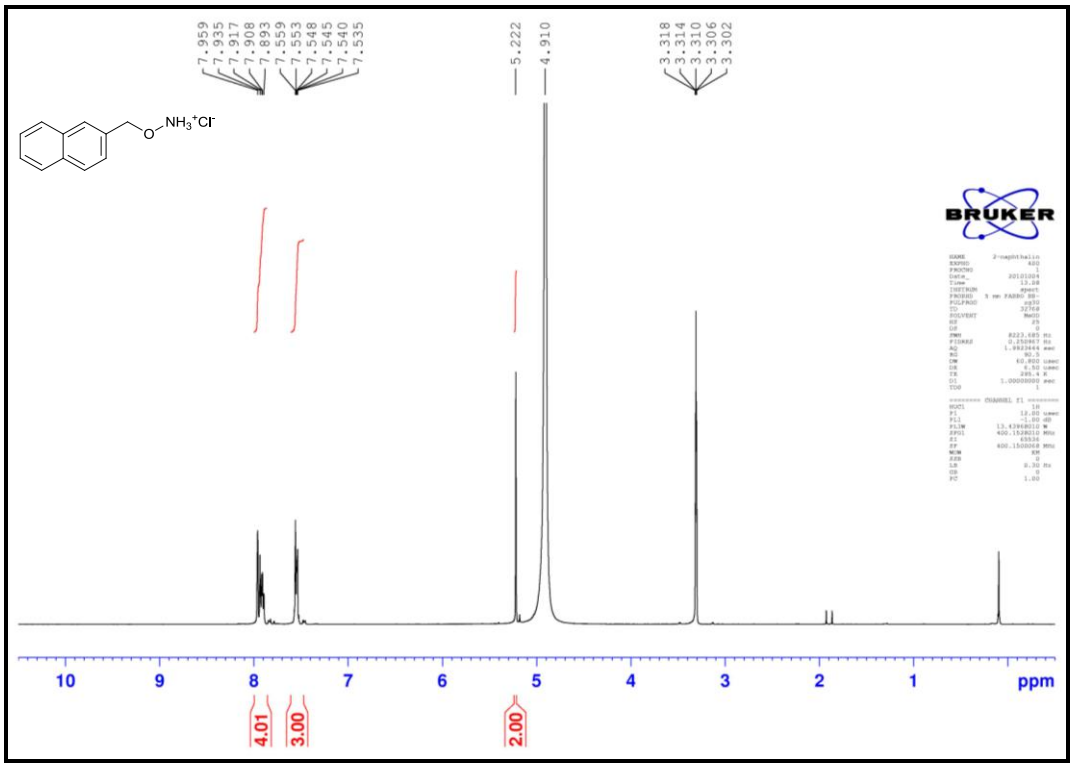
Mannobiose *O*-(naphth-2-ylmethyl)oxime (Man$_2$-a). Treatment of D-mannobiose with reagent **a** (method B) afforded Man_2-**a** (75%) after chromatography (RP-C18, MeOH/H_2O (1:9 to 1:1)) and lyophilization. Mp 102.5–104 °C; ^1H NMR (400 MHz, D_2O, *E*-oxime) δ 7.62 (1 H, d, *J* = 6.4 Hz), 7.18–7.15 (3 H, m) 7.13 (1 H, d, *J* = 7.9 Hz), 7.02 (1 H, d, *J* = 6.7 Hz), 6.90–6.82 (2 H, m), 4.86 (2 H, s), 4.68 (1 H, s), 4.54 (1 H, dd, *J* = 8.9, 6.8 Hz), 4.06–4.03 (2 H, m), 3.90–3.80 (4 H, m), 3.67–3.58 (3 H, m), 3.54–3.50 (1 H, m), 3.29–3.25 (1 H, m); ^{13}C NMR (100 MHz, D_2O, *E*-oxime) δ 152.6, 133.8, 132.7, 132.5, 127.9, 127.7, 127.3, 127.1, 125.9, 125.8 (2 ×), 100.0, 76.9, 75.9, 75.6, 72.9, 70.8, 70.7, 70.6, 68.0, 67.0, 62.3, 61.2; ESI-TOF-HRMS (negative mode) calcd for $C_{23}H_{30}NO_{11}$: 496.1819, found: *m*/*z* 496.1814 $[M – H]^-$.

Mannopentaose *O*-(naphtha-2-ylmethyl)oxime (Man_5-a). Treatment of D-mannopentaose with reagent **a** (method B) afforded Man_5-**a** (64%). Mp 168–170.3 °C; ^{1}H NMR (400 MHz, D_2O) δ 7.74–7.66 (5 H, m), 7.41–7.38 (3 H, m), 5.16 (2 H, s), 4.73 (2 H, s), 4.67 (1 H, s), 4.57 (1 H, s), 4.53 (1 H, t, *J* = 7.4 Hz), 4.13–3.25 (29 H, m); ^{13}C NMR (100 MHz, D_2O) δ 153.2, 134.7, 133.0, 132.9, 128.4, 128.1, 127.8, 127.4, 126.7 (2 ×), 126.3, 100.4, 100.3, 100.2, 99. 9, 77.3, 76.83, 76.79, 76.6, 76.5, 75.8, 75.2, 75.1, 74.8, 72.9, 71.7, 71.64, 71.59, 70.8 (2 ×), 70.7 (2 ×) 70.3, 70.1, 68.4, 66.9, 62.5, 61.2, 60.8, 60.7, 60.6; HRMS-ESI (negative mode) calcd for $C_{41}H_{60}NO_{26}$: 982.3404, found: *m*/*z* 982.3437 $[M - H]^-$.

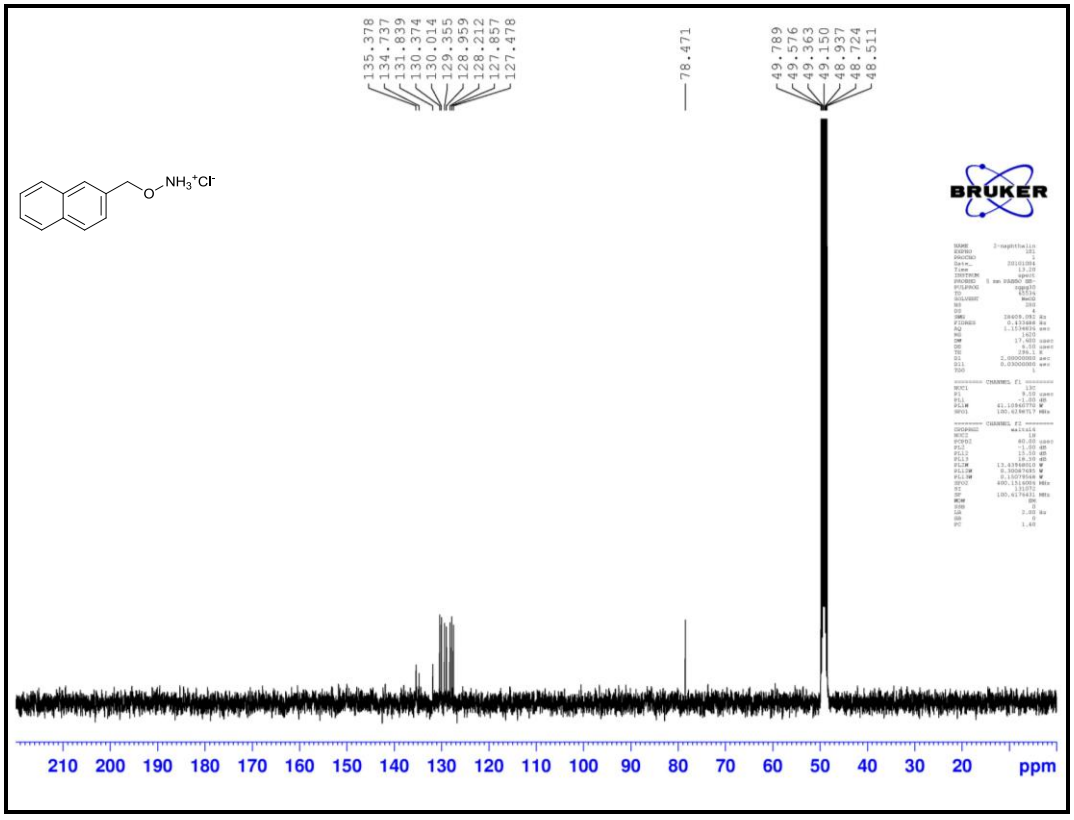
***N*-Methyl-*N*-(naphth-2-ylmethoxy)maltohexaosylamine (Glc_6-b).** Treatment of D-maltohexaose with reagent **b** (method D) afforded Glc_6-**b** (76%) after chromatograpy (RP-C18, H_2O/MeOH (20:1 to 1:1)) and lyophilization. Mp 188.5–192 °C; ^{1}H NMR (400 MHz, D_2O) δ 7.97–7.95 (4 H, m), 7.61–7.58 (3 H, m), 5.38–5.35 (5 H, m), 4.97 (2 H, s,), 4.12 (1 H, d, *J* = 8 Hz), 4.01–3.55 (33 H, m), 3.42 (1 H, t, *J* = 8 Hz), 3.35–3.33 (1 H, m), 2.81 (3 H); ^{13}C NMR (100 MHz, D_2O) δ 133.6, 132.91, 132.85, 128.4, 128.3, 128.0, 127.7, 127.1, 126.7, 126.6, 99.8 (3 ×), 99.6 (2 ×), 93.0, 77.4, 77.2 (3 ×), 76.9 (2 ×), 75.7 (2 ×), 75.3 (2 ×), 73.3 (3 ×), 72.9 (2 ×), 72.7 (2 ×), 71.7 (2 ×), 71.5 (2 ×), 71.1 (2 ×), 69.7, 69.3, 60.3 (6 ×), 38.8; ESI-TOF-HRMS calcd for $C_{48}H_{73}NNaO_{31}$: 1182.4064, found: *m*/*z* 1182.4084 $[M + Na]^+$.

Maltoheptaose *O*-(naphth-2-ylmethyl)oxime (Glc_7-a). , Treatment of D-maltoheptaose with reagent **a** (method B) afforded Glc_7-**a** (73%). Mp 207–210 °C; $[\alpha]^{20}_D$ +137 (*c* 0.1, H_2O); ^{1}H NMR (600 MHz, D_2O, *E*/*Z*-isomers = 4:1) δ 7.98–7.93 (4 H, m), 7.69 (0.8 H, d, *J* = 5.2 Hz), 7.62–7.60 (3 H, m), 6.99 (0.2 H, d, *J* = 4 Hz), 5.39–5.37 (2 H, m), 5.34–5.32 (2 H, m), 5.30 (1 H, s), 5.28–5.27 (2 H, m), 5.26–5.24 (1 H, m), 4.57 (0.8 H, t, *J* = 2.4 Hz), 4.39 (1 H, t, *J* = 5.6 Hz), 4.27 (0.2 H, d, *J* = 6 Hz), 4.04–3.09 (40 H, m); ^{13}C NMR (100 MHz, D_2O, *E*/*Z*-isomers) δ 152.0/153.4, 135.3/134.2, 132.89, 132.86, 128.4, 128.0, 127.7, 127.5, 126.7, 126.6, 126. 5, 100.5, 100.4, 100.2, 100.12, 100.07, 99.8, 78.6, 78.5, 78.3, 78.0, 77.9, 77.4, 77.1, 76.9, 76.8, 76.7, 75.6, 75.5, 73.4, 73.3, 73.0, 72.8, 72.7, 71.8, 71.71, 71.65, 71.59, 71.54, 71.45, 71.31, 71.25, 71.20, 71.0, 70.9, 69.7, 69.3, 61.9, 60.5, 60.43, 60.36, 60.3, 60.2; ESI-TOF-HRMS calcd for $C_{53}H_{81}NNaO_{36}$: 1330.4436, found: *m*/*z* 1330.4446 $[M + Na]^+$.

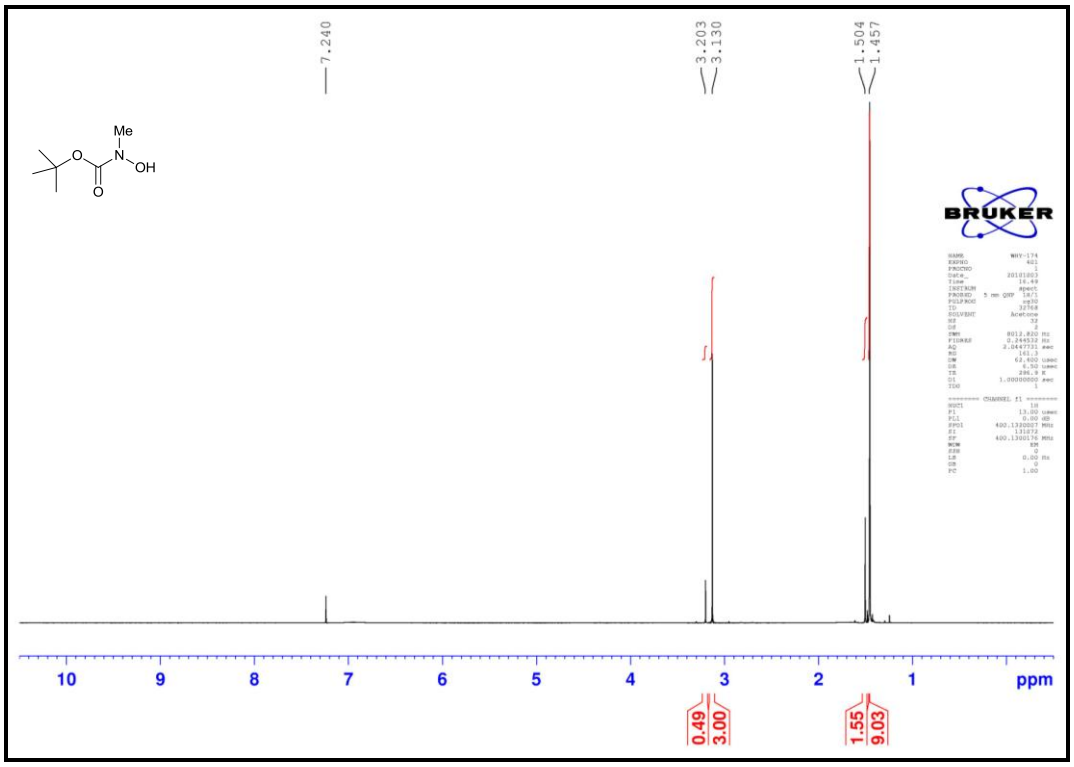
***N*-Methyl-*N*-(naphth-2-ylmethoxy)maltoheptaosylamine (Glc_7-b).** Treatment of D-maltoheptaose with reagent **b** (method D) afforded Glc_7-**b** (68%). Mp 206–209 °C; ^{1}H NMR (400 MHz, D_2O) δ 7.99–7.97 (4 H, m), 7.62–7.59 (3 H, m), 5.40–5.39 (6 H, m), 4.99 (2 H, s), 4.17 (1 H, d, *J* = 8 Hz), 4.01–3.37 (41 H, m), 2.82 (3 H); ^{13}C NMR (100 MHz, D_2O) δ 134.8, 133.7, 132.9, 128.4, 128.3, 127.9, 127. 7, 127.1, 126.7, 126.6, 99.72 (2 ×), 99.62 (4 ×), 93.1, 77.4, 76.9 (4 ×), 75.8 (3 ×), 75.3 (3 ×), 73.3 (3 ×), 72.8 (2 ×), 72.7 (2 ×), 71.5 (4 ×), 71.2 (3 ×), 69.8 (2 ×), 69.3 (2 ×), 60.4 (7 ×), 38.9; ESI-TOF-HRMS calcd for $C_{54}H_{83}NNaO_6$: 1344.4592, found: *m*/*z* 1344.4595 $[M + Na]^+$.



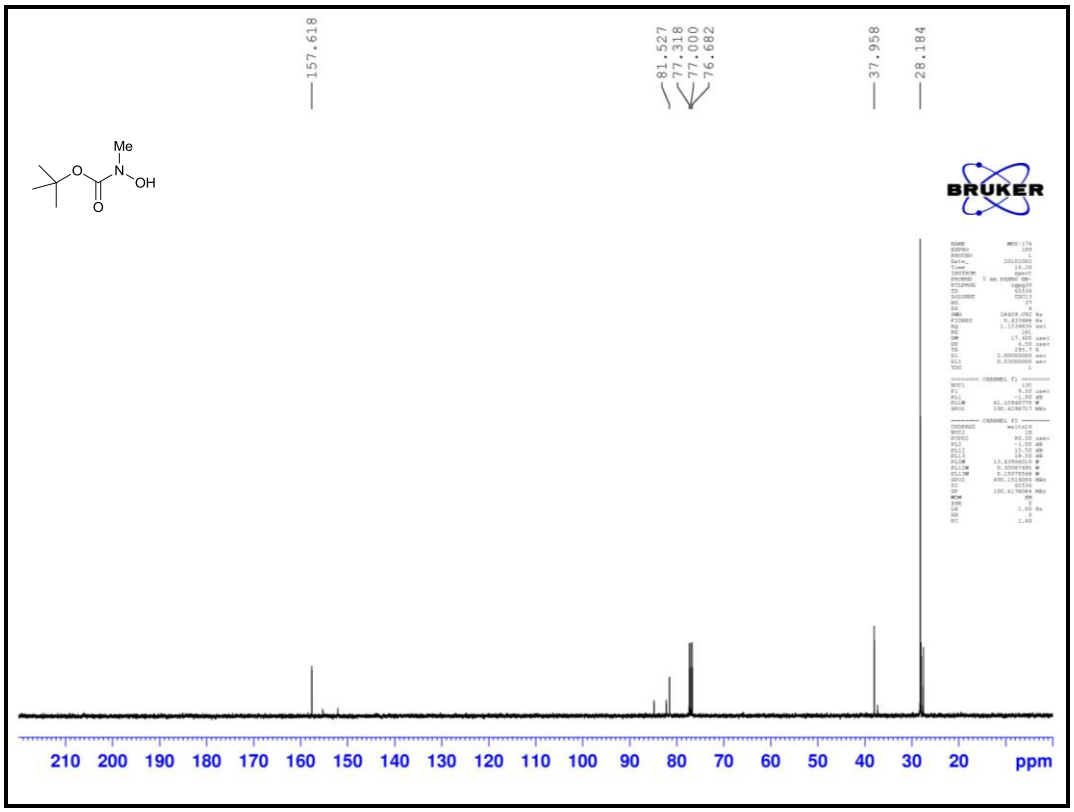
^{1}H NMR spectrum of reagent **a** (400 MHz, CD_3OD)



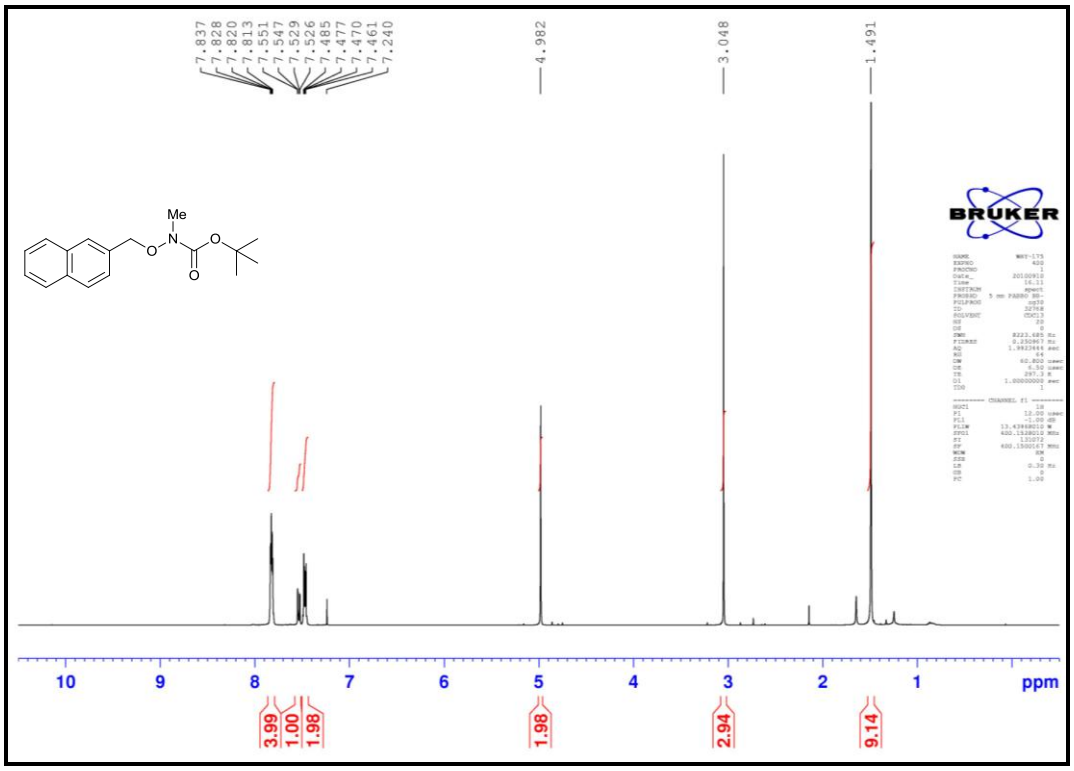
^{13}C NMR spectrum of reagent **a** (100 MHz, CD_3OD)



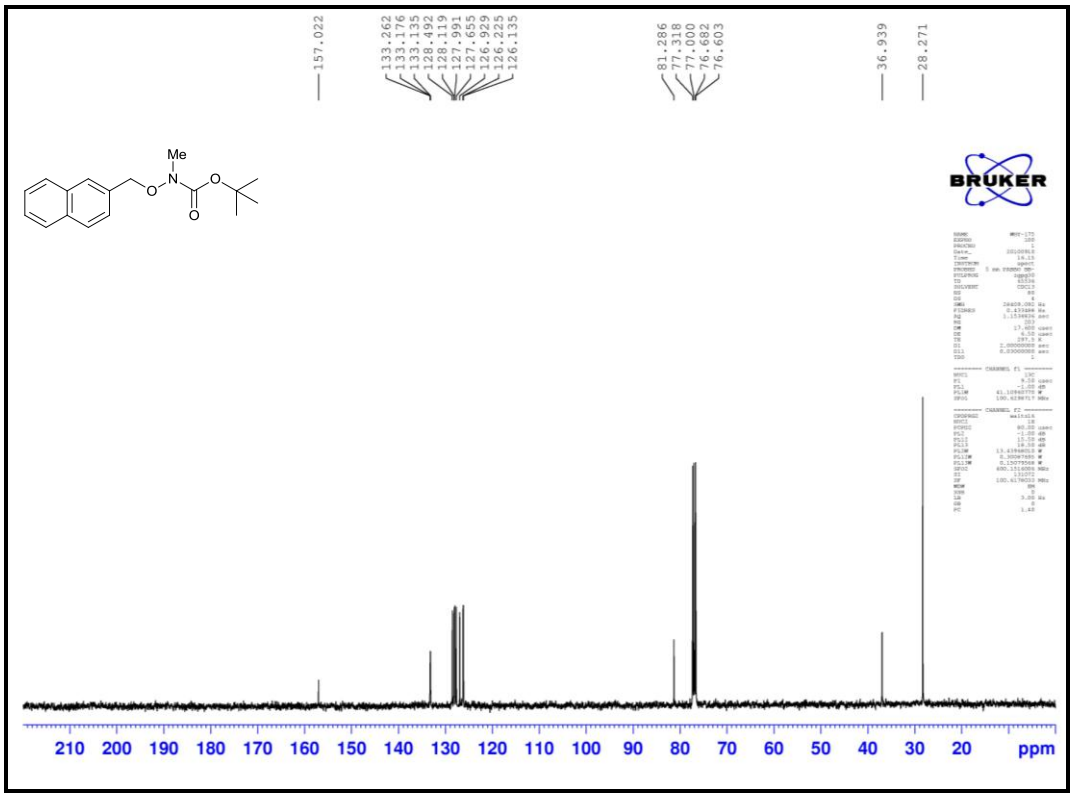
^{1}H NMR spectrum of *O*-(*tert*-butyl)-*N*-hydroxy-*N*-methyl carbamate (400 MHz, $CDCl_3$)



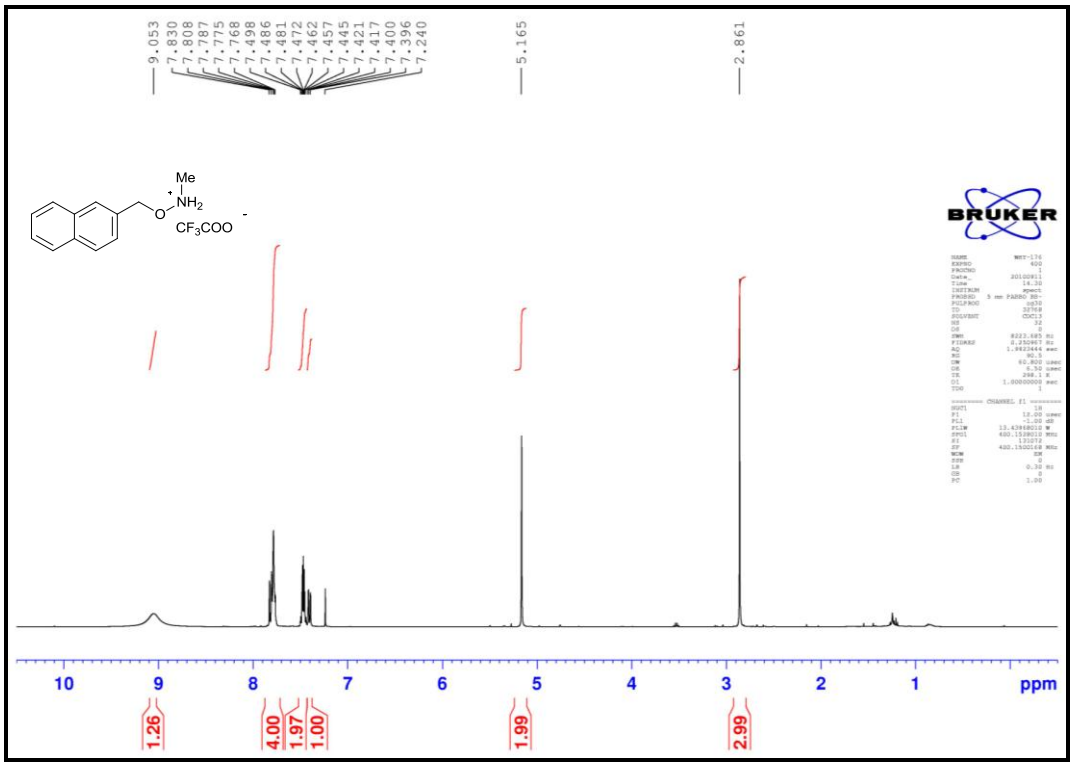
^{13}C NMR spectrum of *O*-(*tert*-butyl)-*N*-hydroxy-*N*-methyl carbamate (100 MHz, $CDCl_3$)



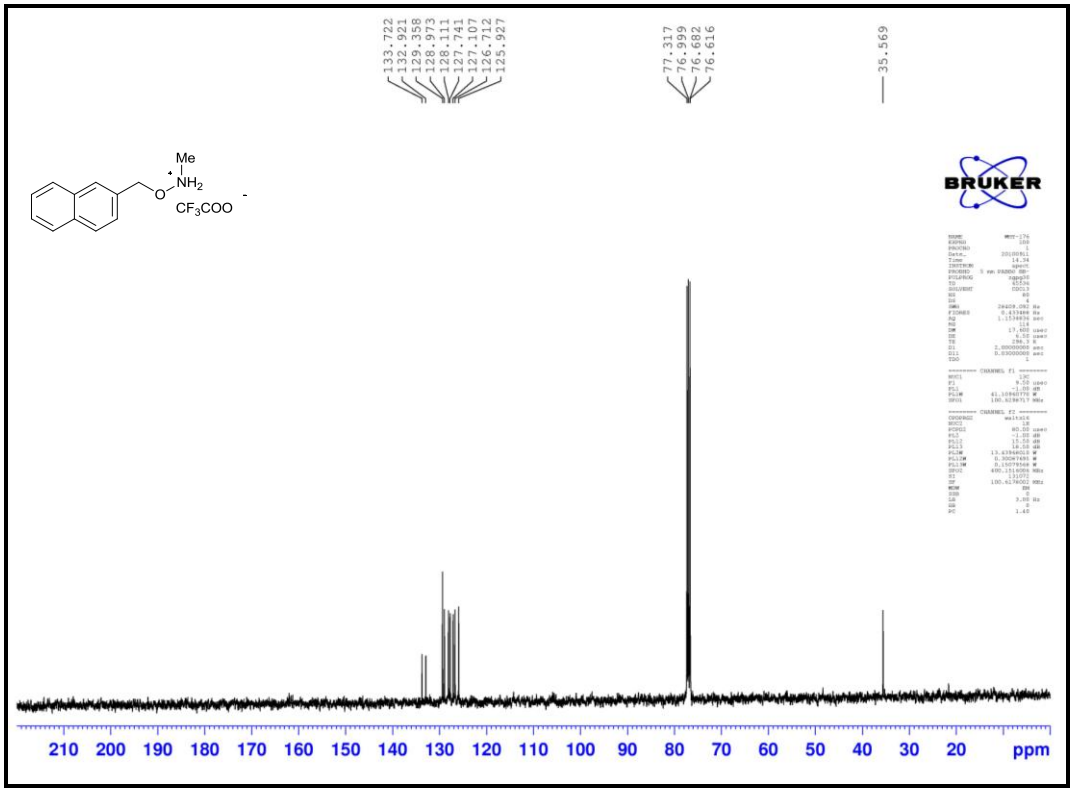
^{1}H NMR spectrum of *O*-(*tert*-butyl)-*N*-methyl-*N*-(naphtha-2-ylmethoxy) carbamate (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of *O*-(*tert*-butyl)-*N*-methyl-*N*-(naphtha-2-ylmethoxy) carbamate (100 MHz, $CDCl_3$)



^{1}H NMR spectrum of reagent **b** (400 MHz, $CDCl_3$)



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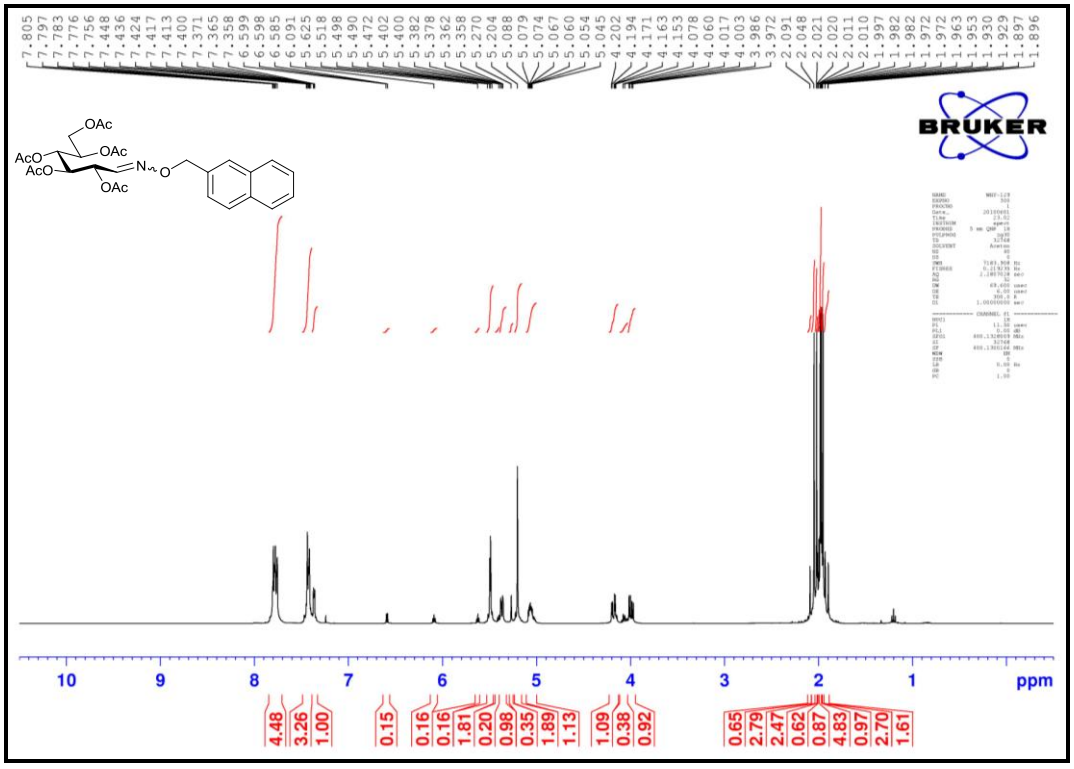
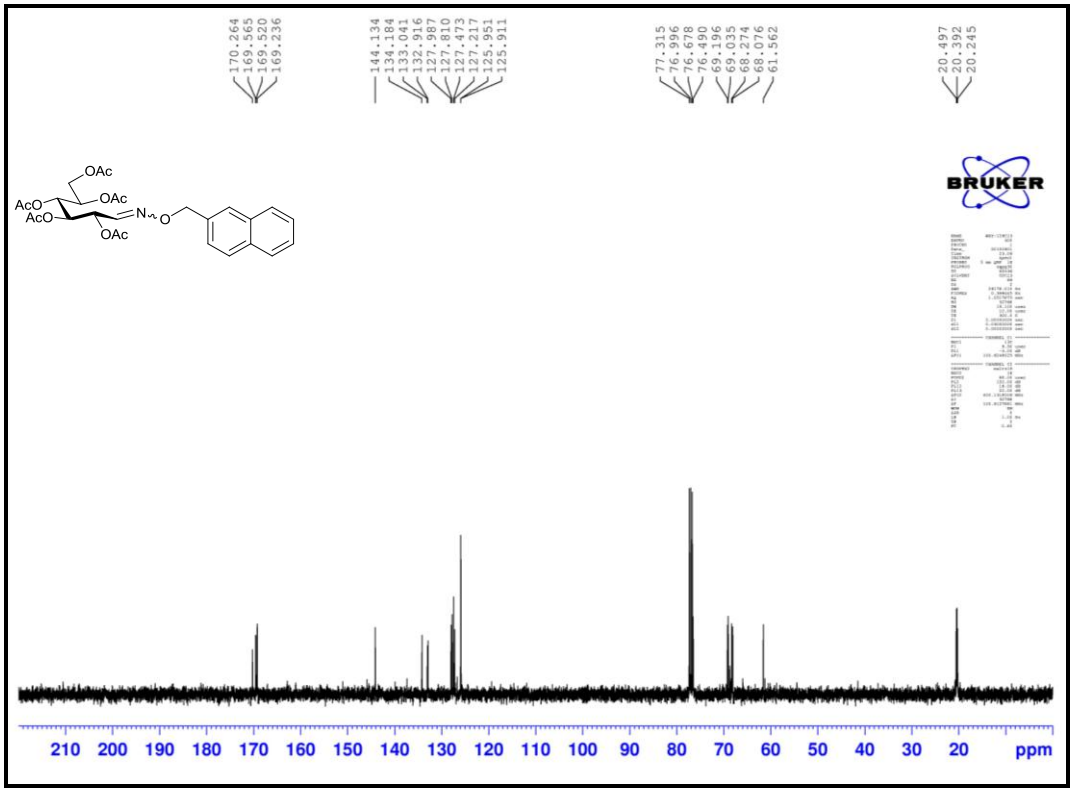
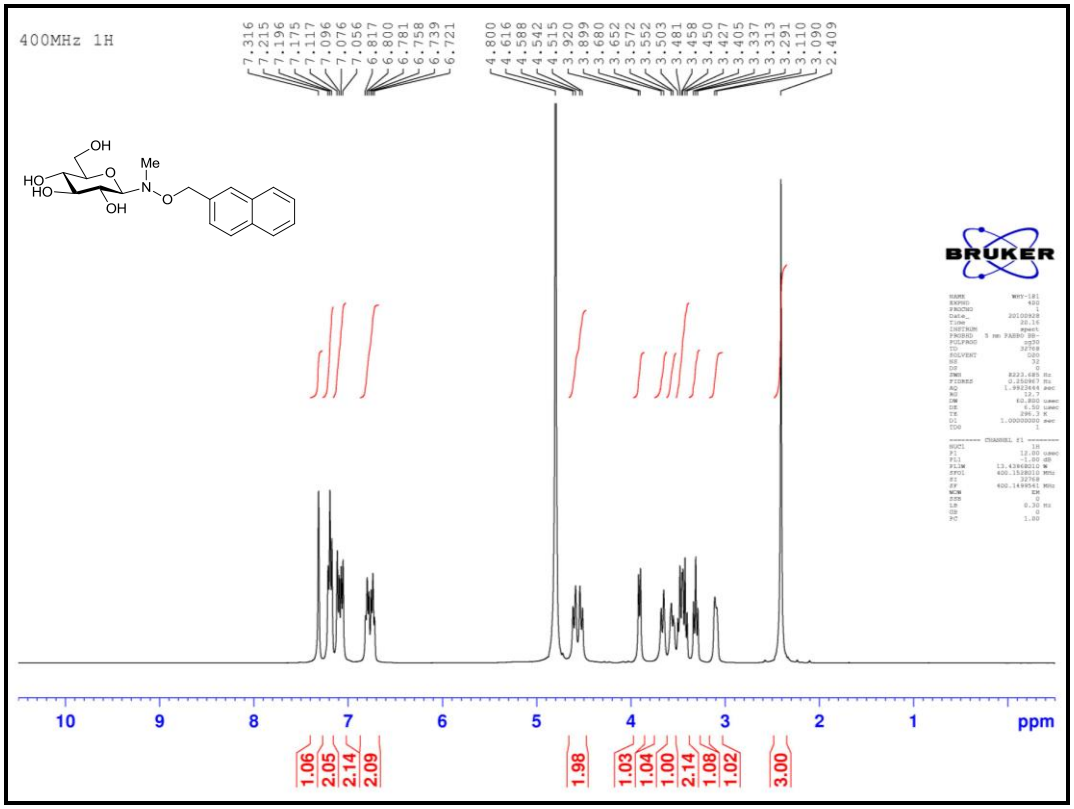


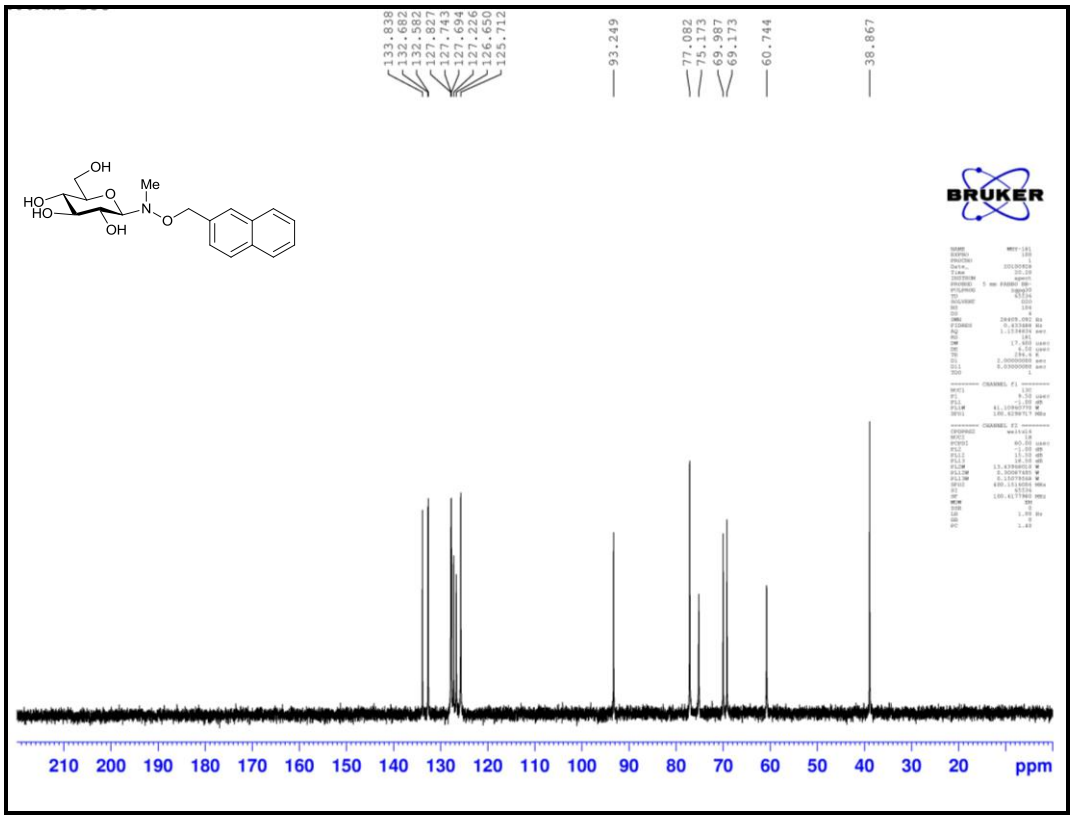
^{1}H NMR spectrum of (Glc-**a**)Ac$_5$ (400 MHz, $CDCl_3$, a mixture of *E*/*Z* isomers (4:1))



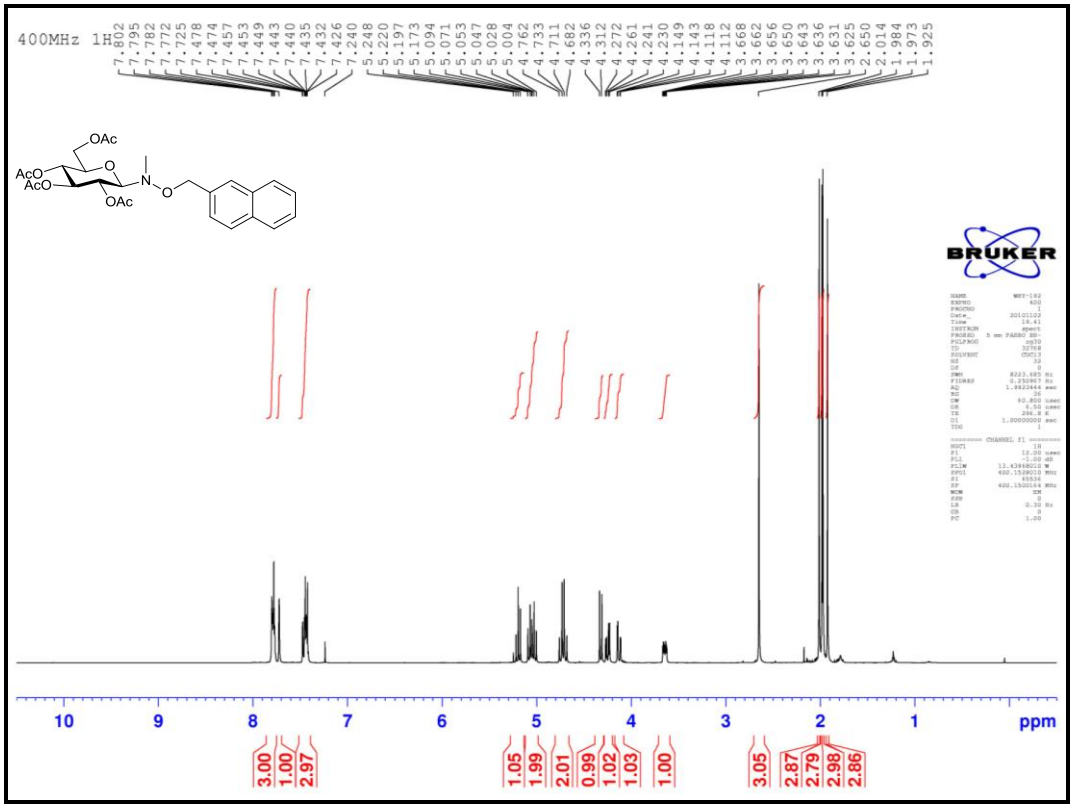
^{13}C NMR spectrum of (Glc-**a**)Ac$_5$ (100 MHz, $CDCl_3$, a mixture of *E*/*Z* isomers (4:1))



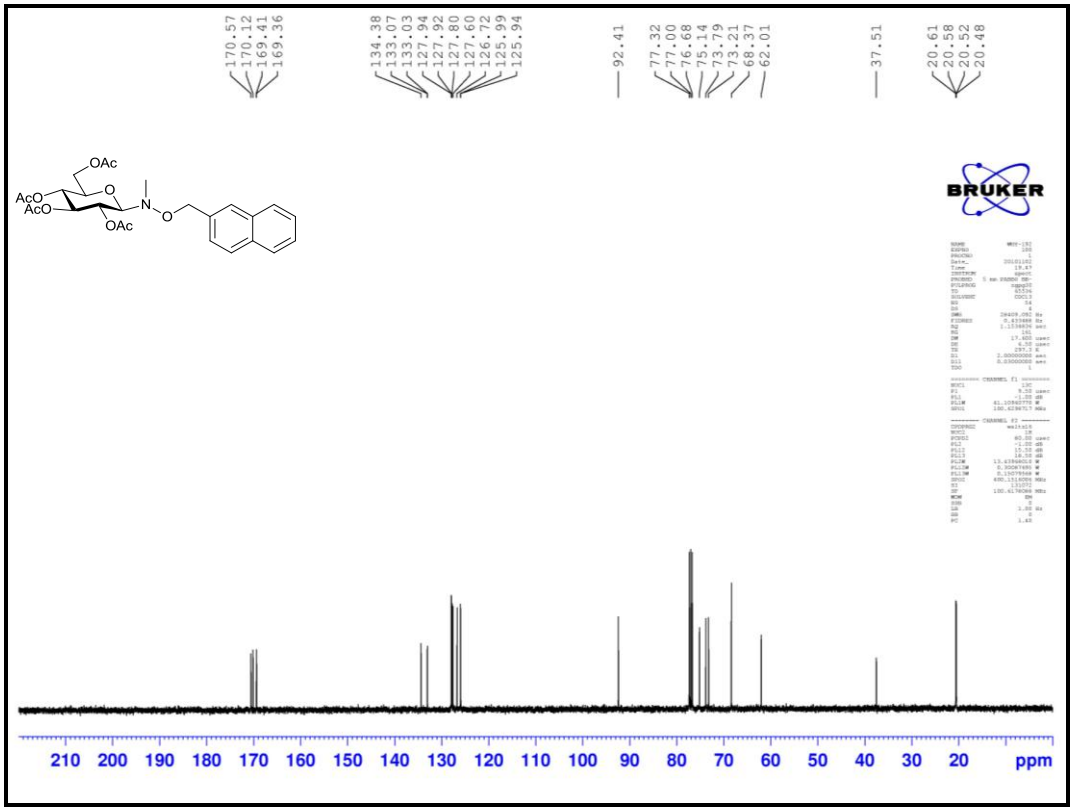
^{1}H NMR spectrum of Glc-**b** (400 MHz, D_2O)



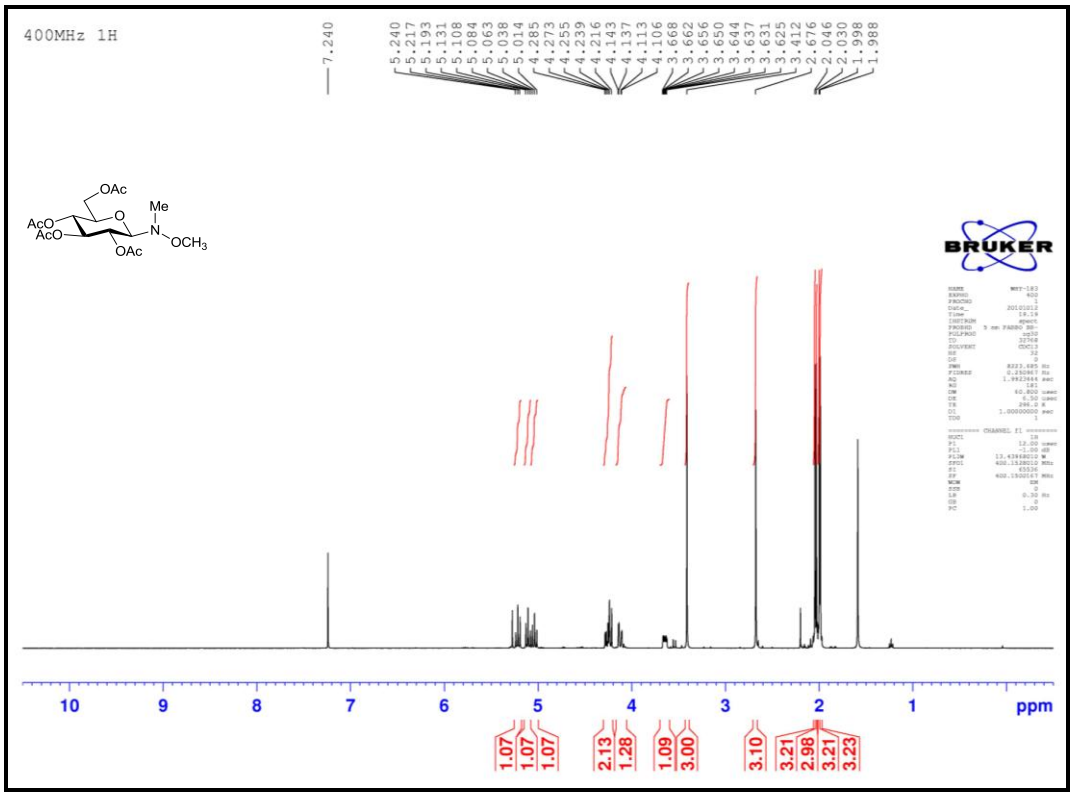
^{13}C NMR spectrum of Glc-**b** (100 MHz, D_2O)



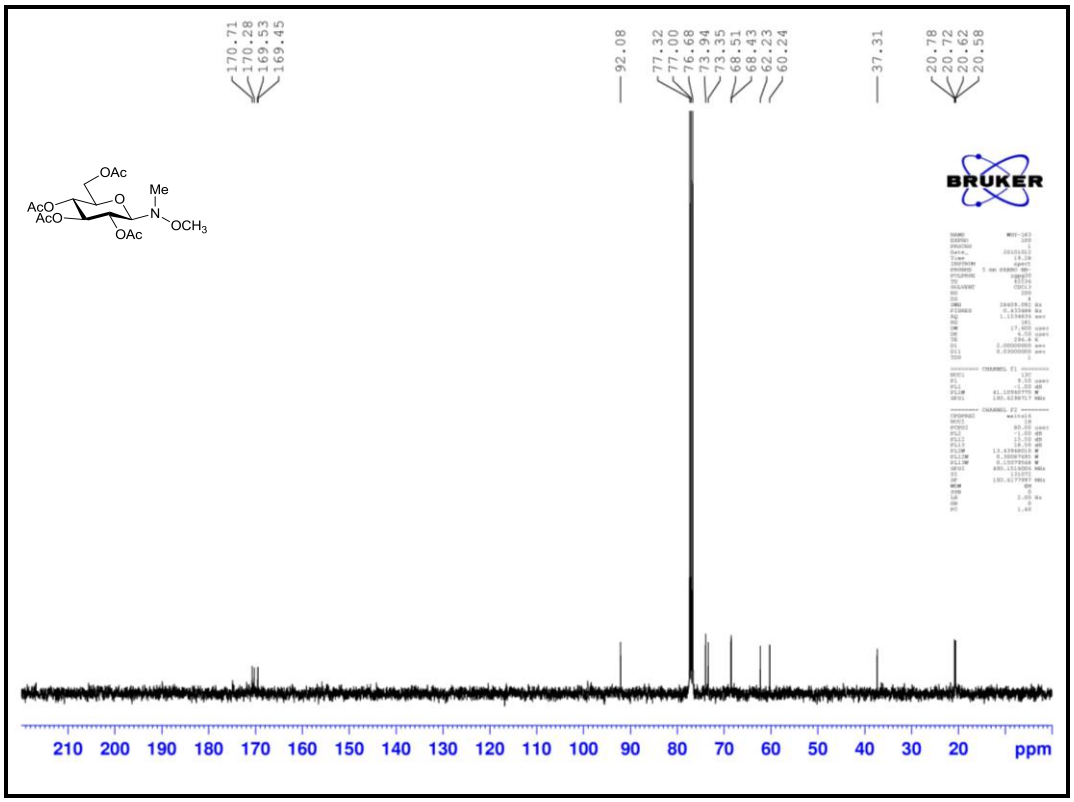
^{1}H NMR spectrum of (Glc-**b**)Ac$_4$ (400 MHz, $CDCl_3$)



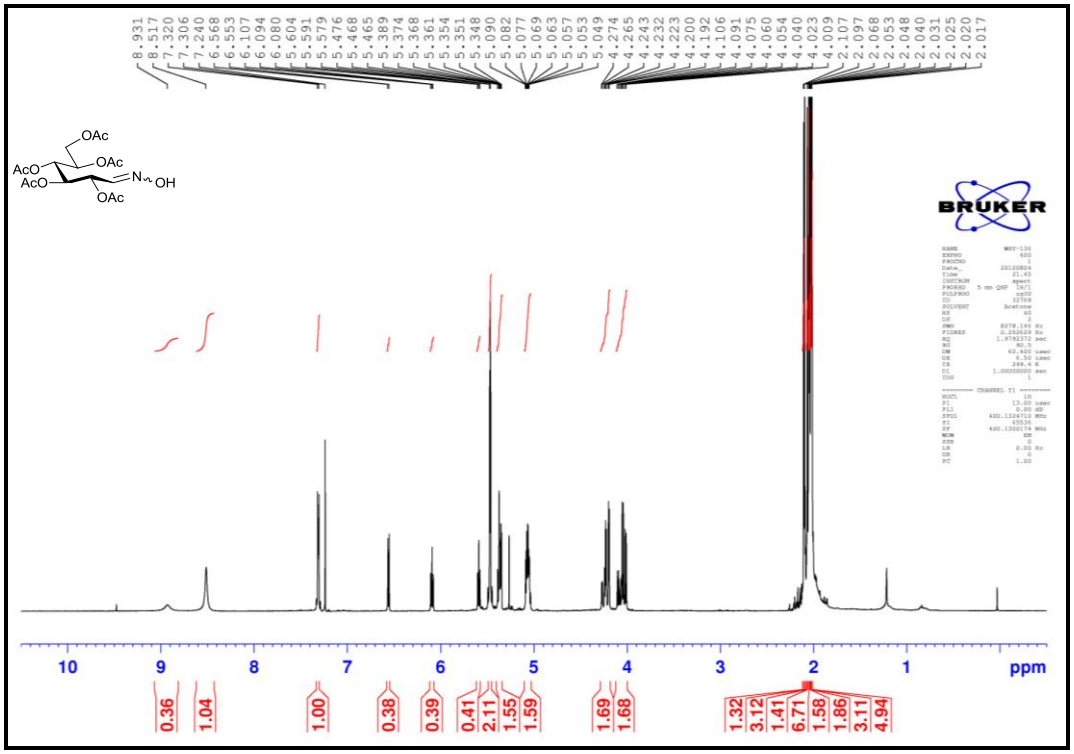
^{13}C NMR spectrum of (Glc-**b**)Ac$_4$ (100 MHz, $CDCl_3$)



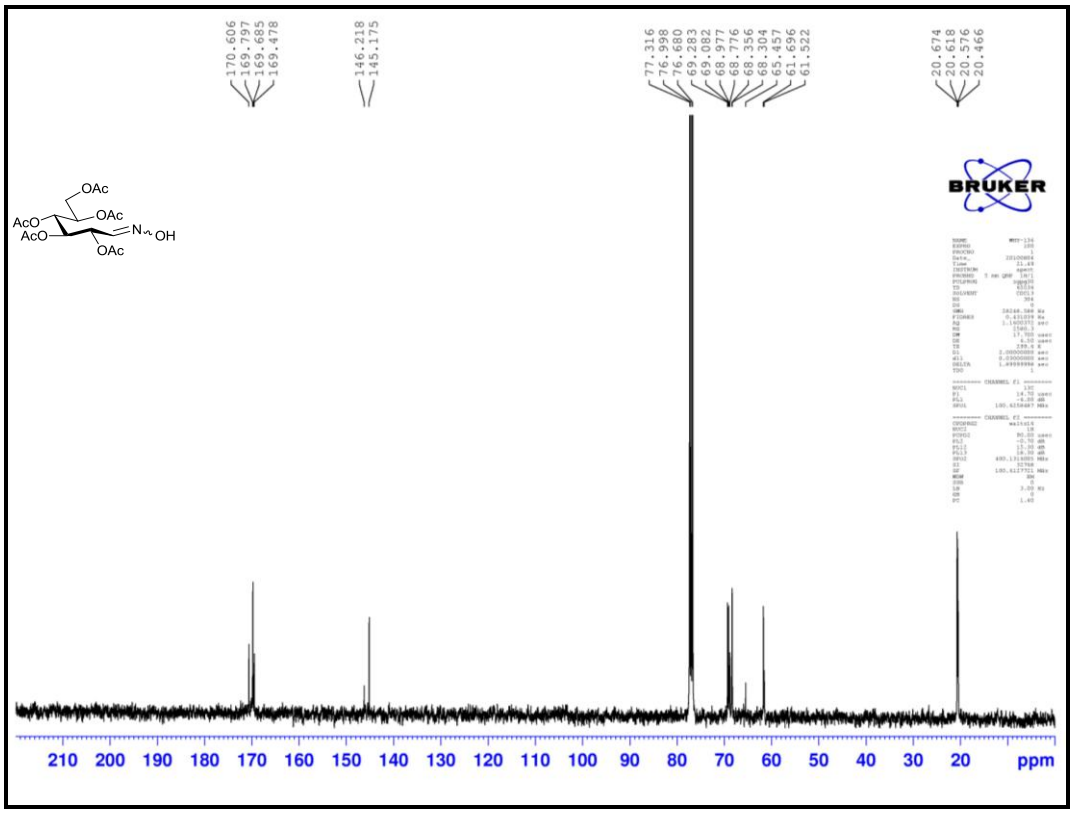
^{1}H NMR spectrum of *N*-Methyl-*N*-methoxy-β-2,3,4,6-tetraacetyl-D-glucosylamine (400 MHz, $CDCl_3$)



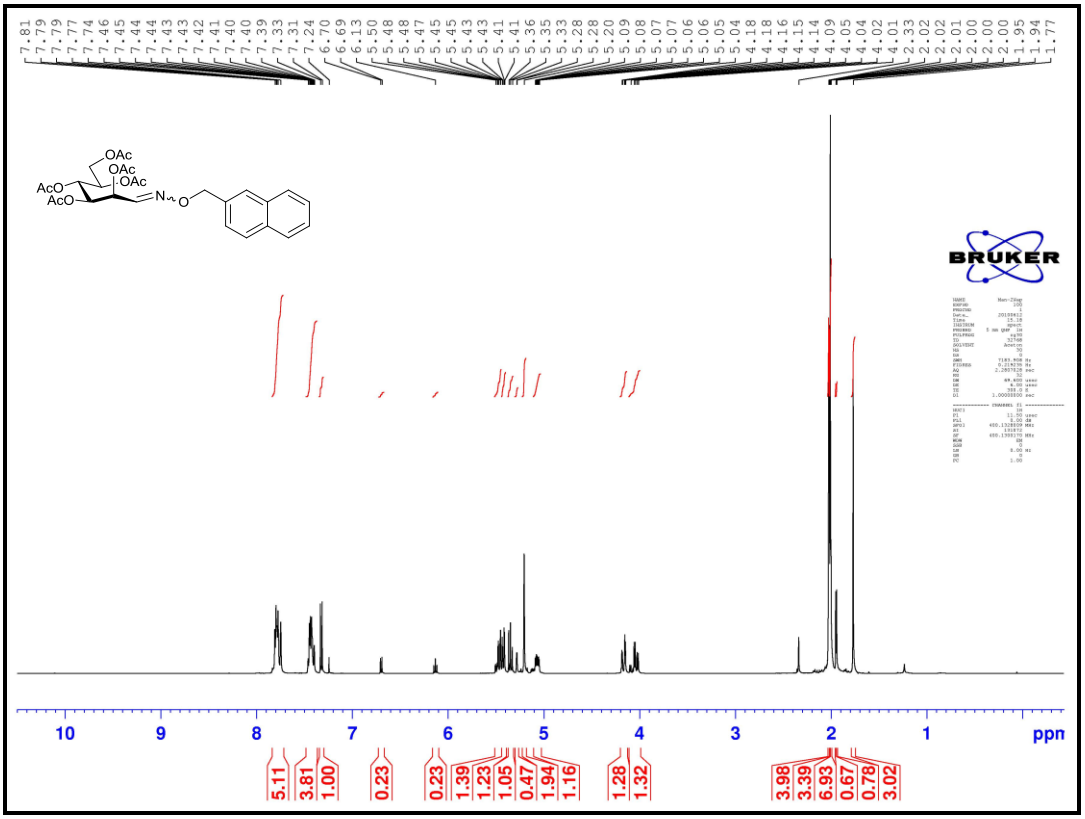
^{13}C NMR spectrum of *N*-Methyl-*N*-methoxy-β-2,3,4,6-tetraacetyl-D-glucosylamine (100 MHz, $CDCl_3$)



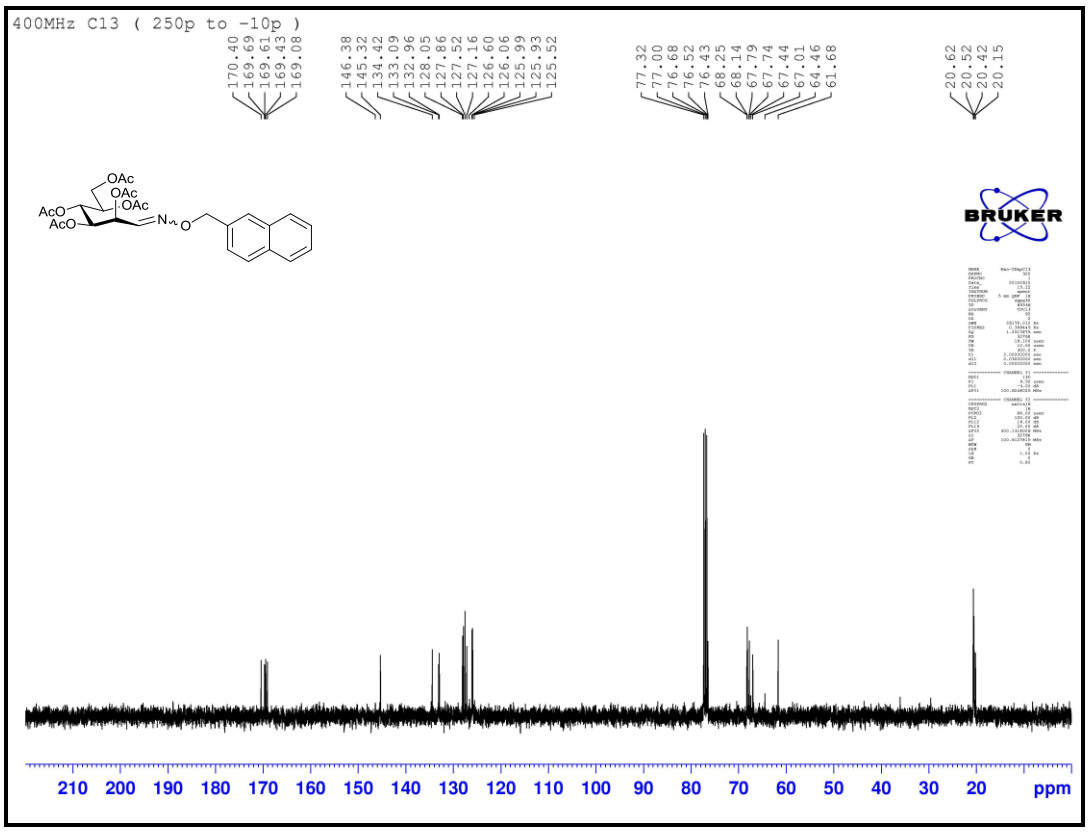
^{1}H NMR spectrum of (Glc-oxime)Ac$_5$ (400 MHz, $CDCl_3$, a mixture of *E*/*Z* isomers (7:3))



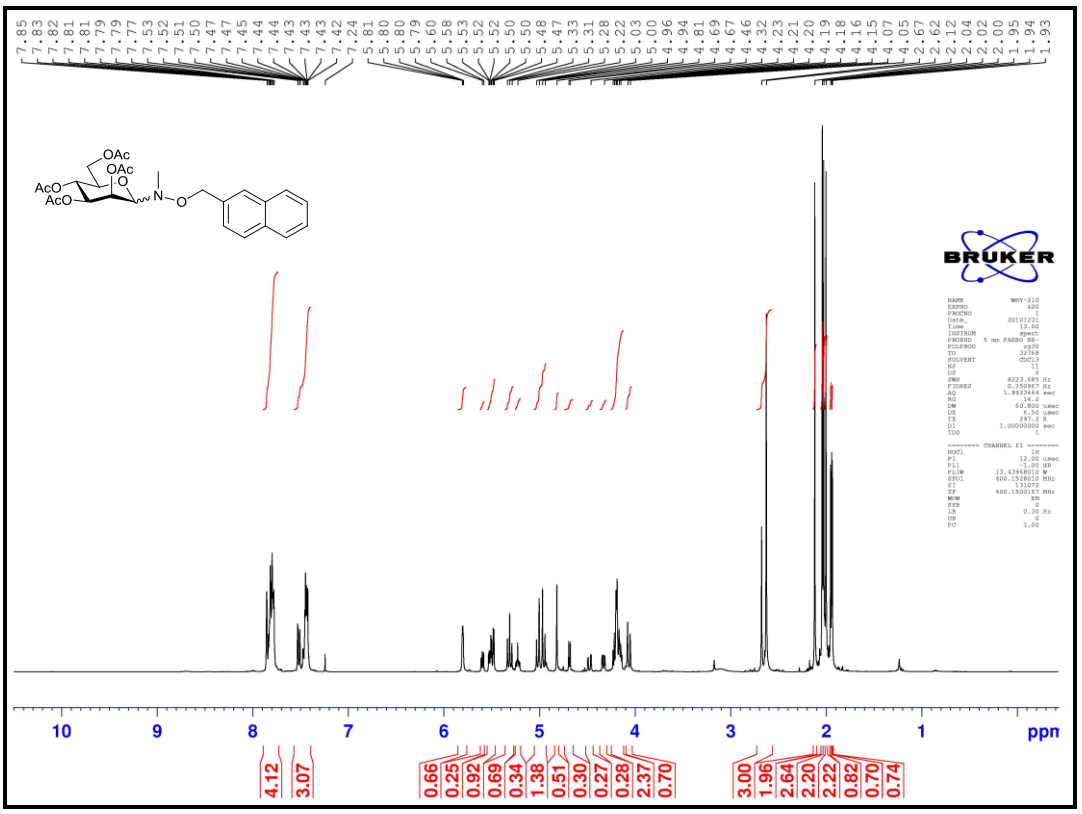
^{13}C NMR spectrum of (Glc-oxime)Ac$_5$ (100 MHz, $CDCl_3$, a mixture of *E*/*Z* isomers (7:3))



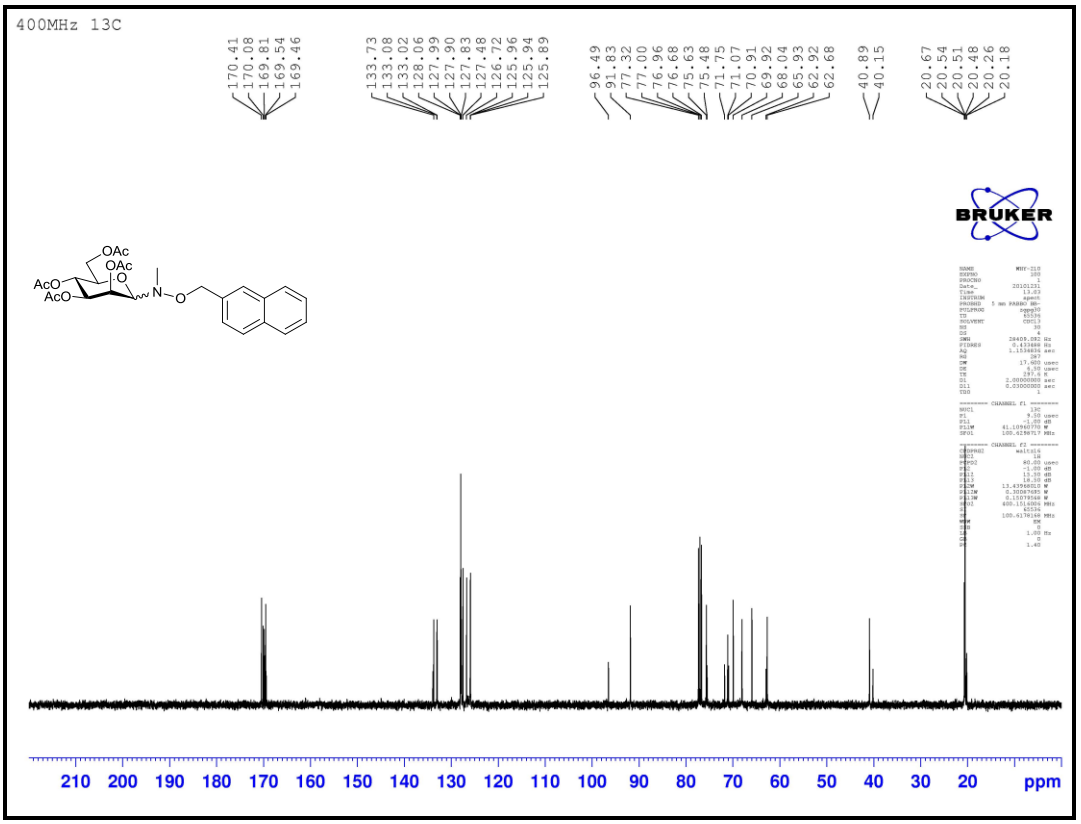
^{1}H NMR spectrum of (Man-**a**)Ac$_5$ (400 MHz, $CDCl_3$, a mixture of *E*/*Z* isomers (4:1))



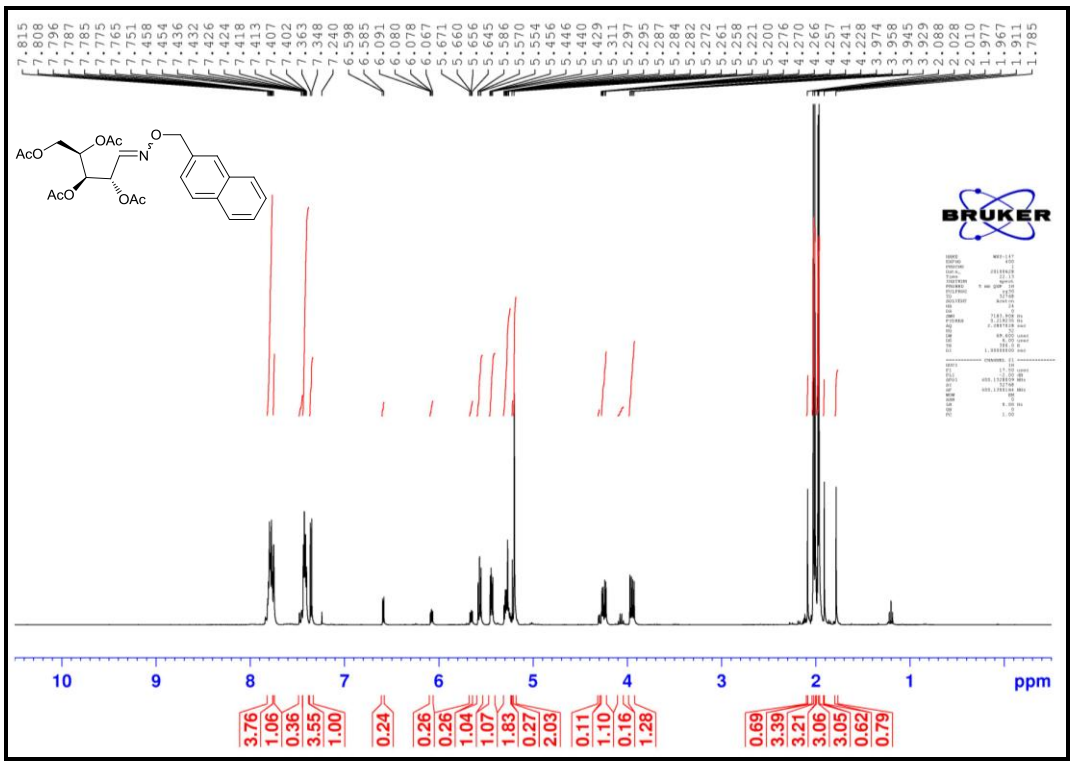
^{13}C NMR spectrum of (Man-**a**)Ac$_5$ (100 MHz, $CDCl_3$, a mixture of *E*/*Z* isomers (4:1))



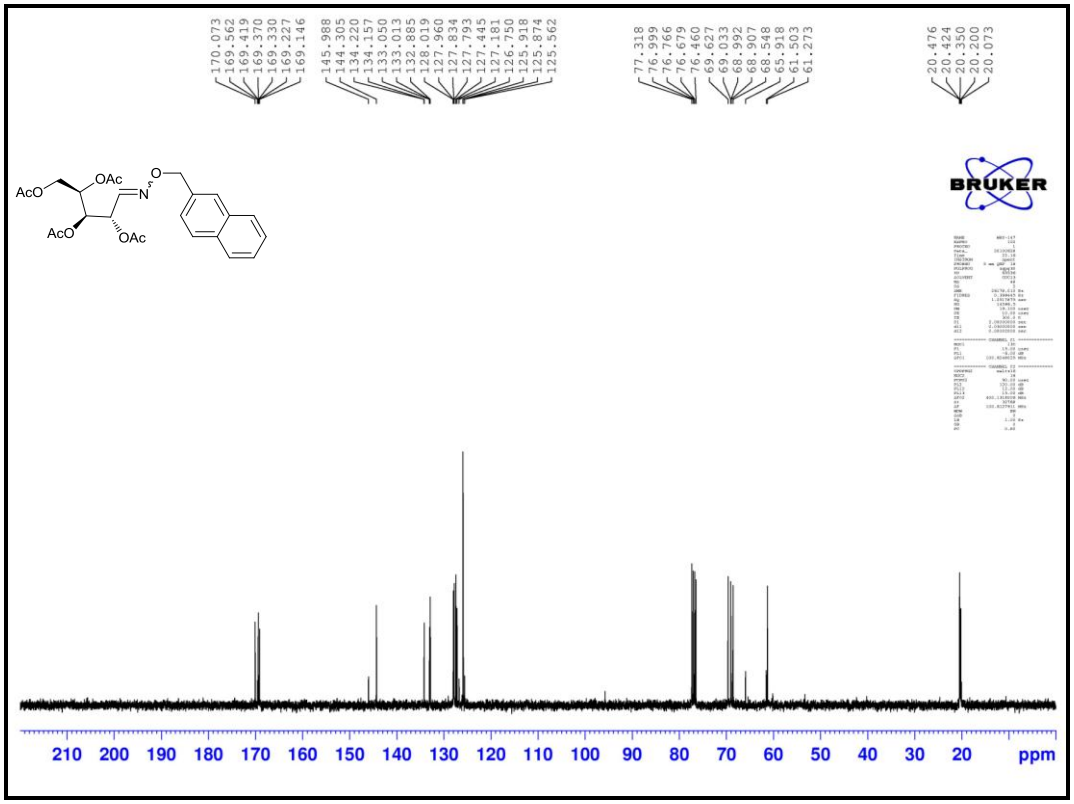
^{1}H NMR spectrum of (Man-**b**)Ac$_4$ (400 MHz, $CDCl_3$, α/β anomers (2:1))



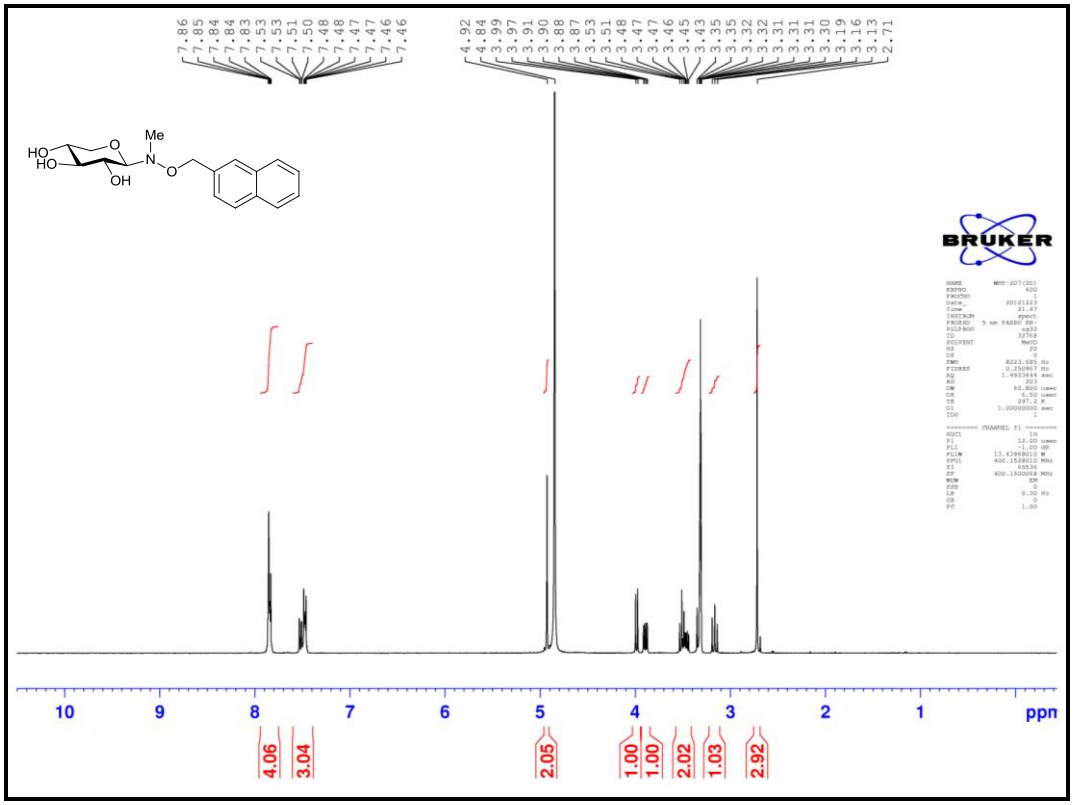
^{13}C NMR spectrum of (Man-**b**)Ac$_4$ (100 MHz, $CDCl_3$, α/β anomers (2:1))



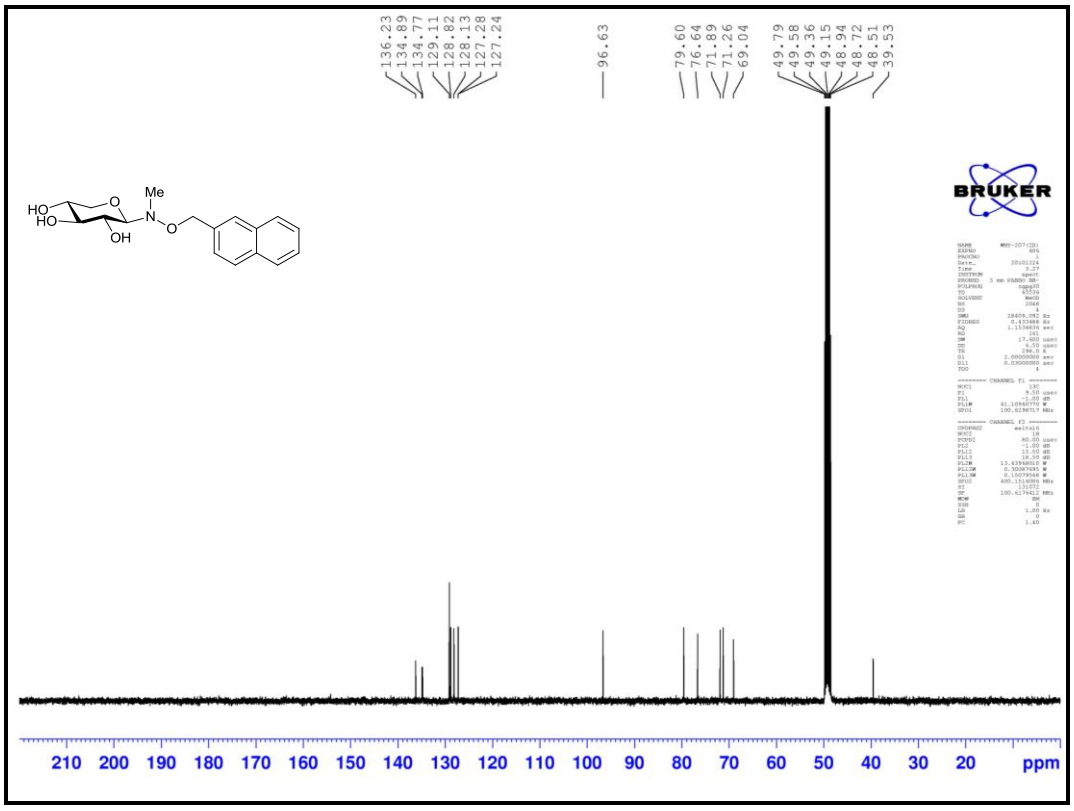
^{1}H NMR spectrum of (Xyl-**a**)Ac$_4$ (400 MHz, $CDCl_3$, a mixture of *E*/*Z* isomers (4:1))



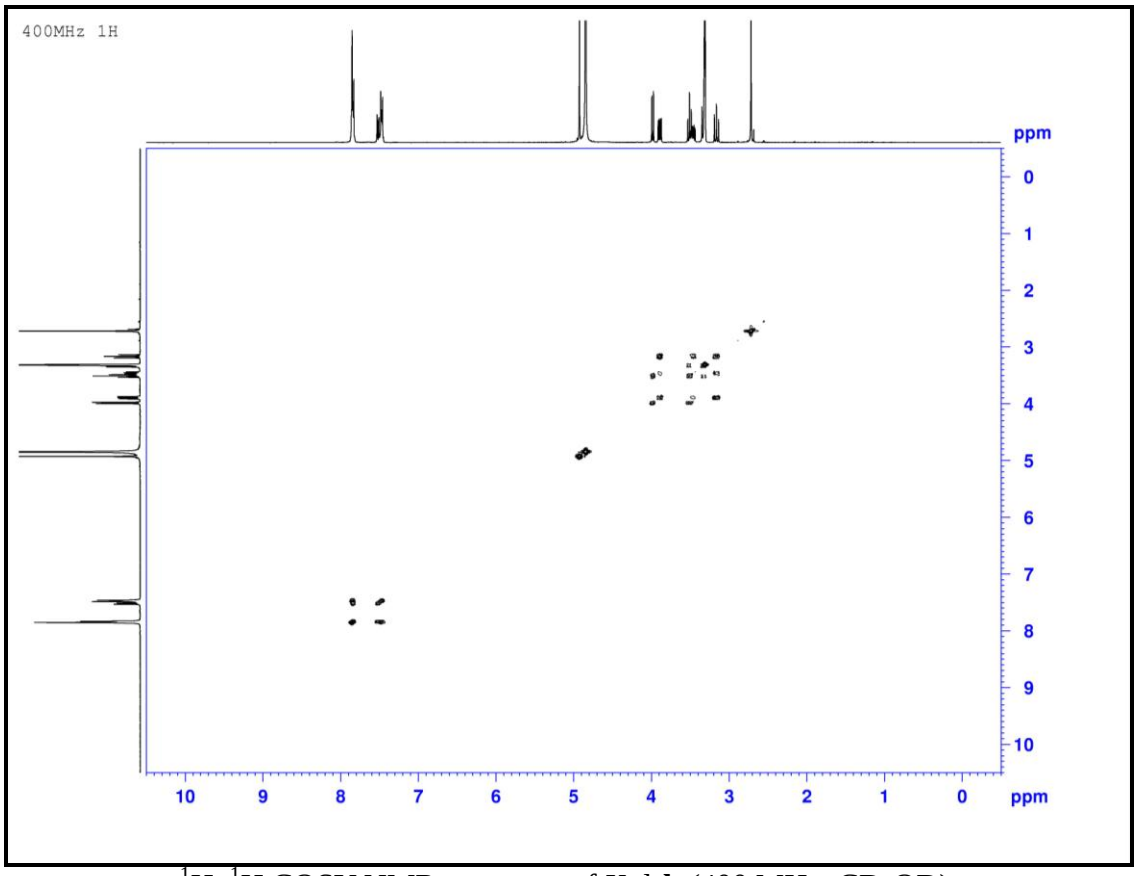
^{13}C NMR spectrum of (Xyl-**a**)Ac$_4$ (100 MHz, $CDCl_3$, a mixture of *E*/*Z* isomers (4:1))



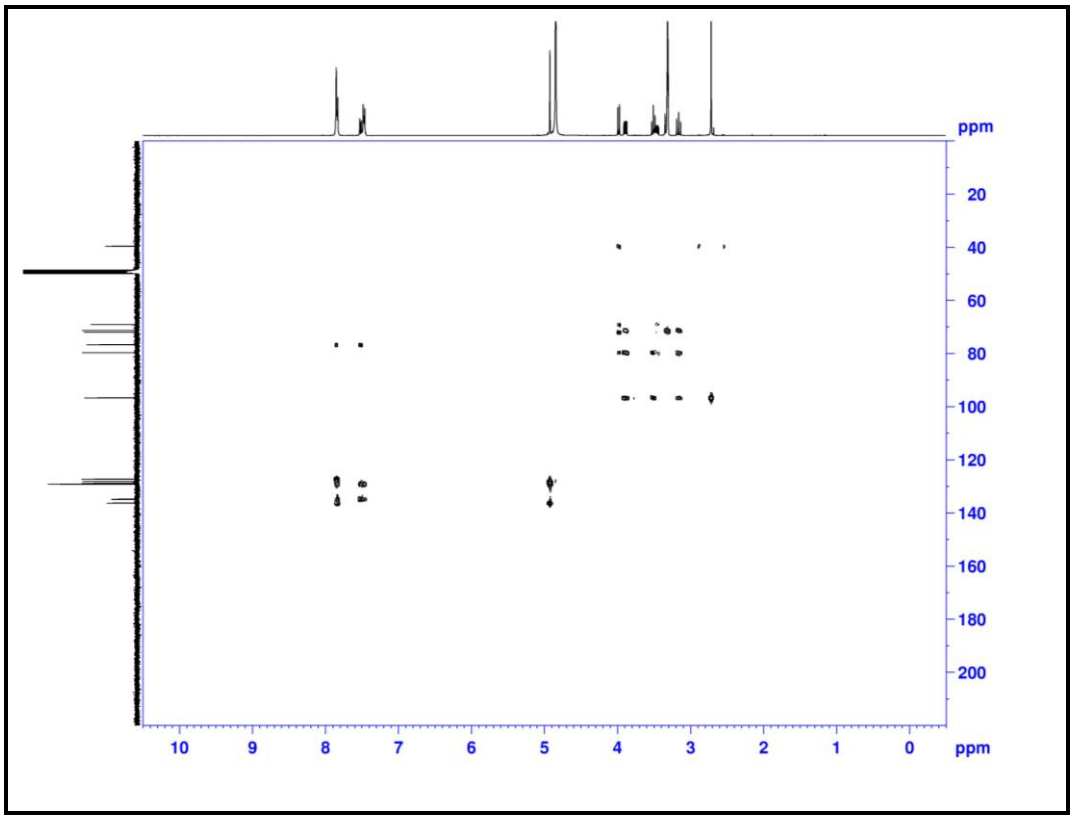
^{1}H NMR spectrum of Xyl-**b** (400 MHz, CD_3OD)



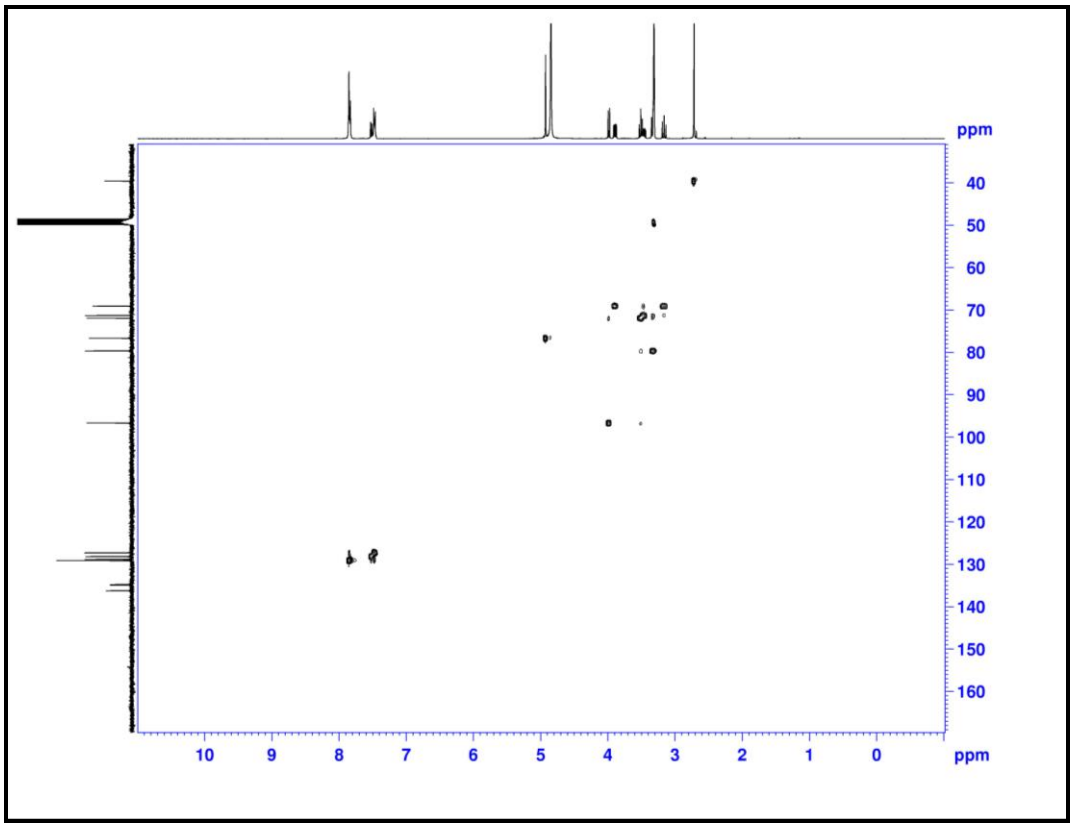
^{13}C NMR spectrum of Xyl-**b** (100 MHz, CD_3OD)



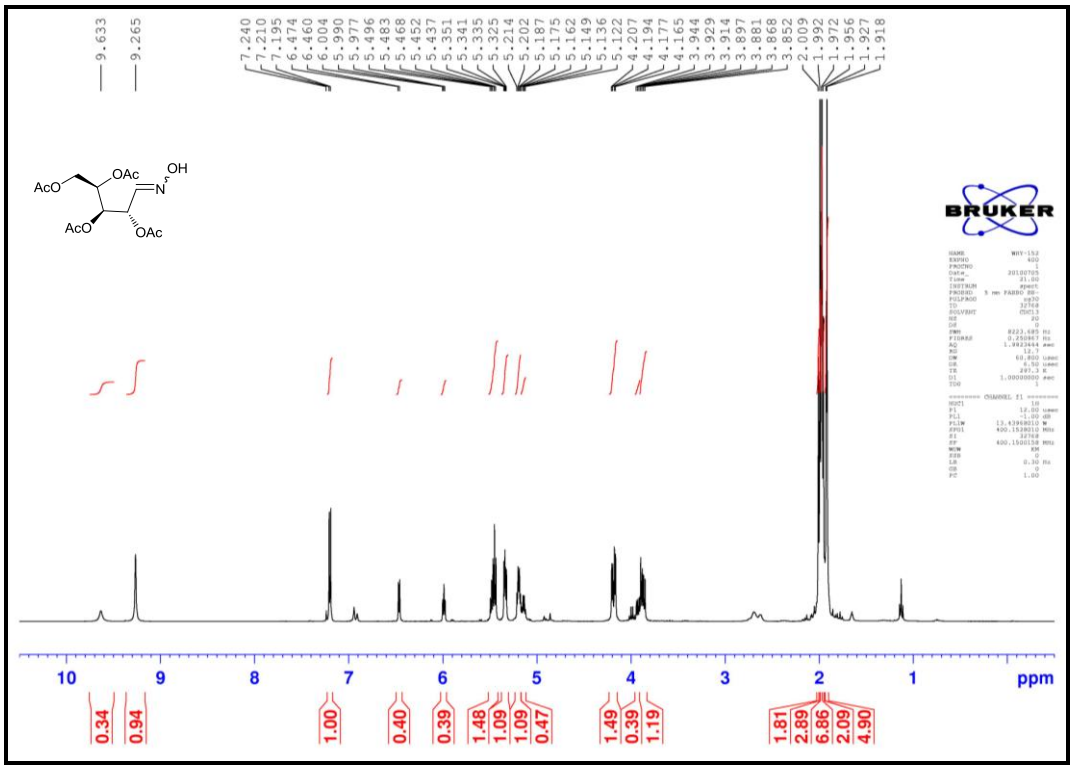
$^{1}H–^{1}H$ COSY NMR spectrum of Xyl-**b** (400 MHz, CD_3OD).



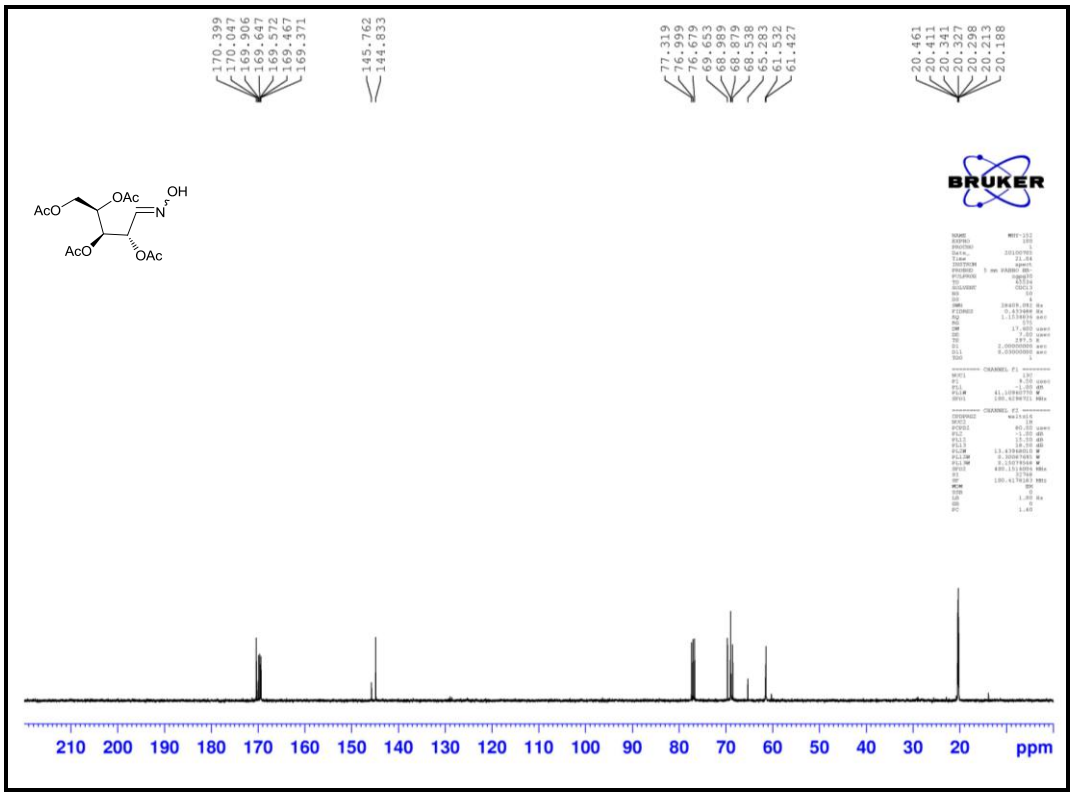
HMBC NMR spectrum of Xyl-**b** (400 MHz, CD_3OD).



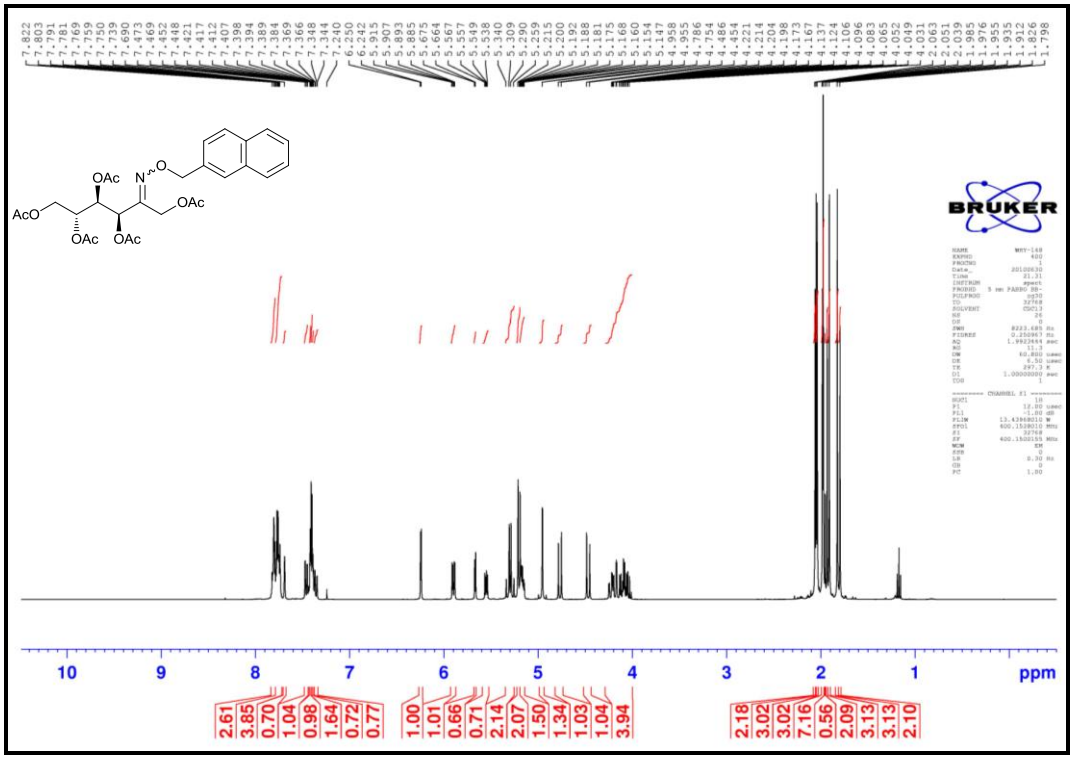
HSQC NMR spectrum of Xyl-**b** (400 MHz, CD_3OD).



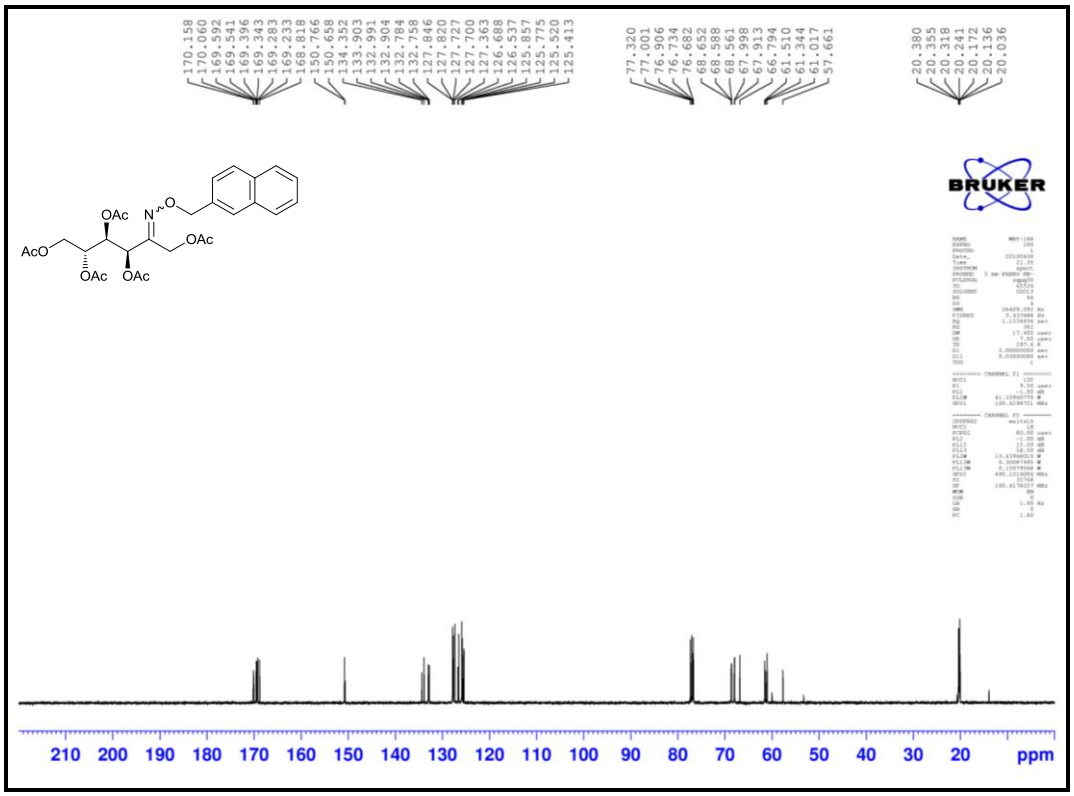
^{1}H NMR spectrum of (Xyl-oxime)Ac_4 (400 MHz, $CDCl_3$, a mixture of *E*/*Z* isomers (7:3))



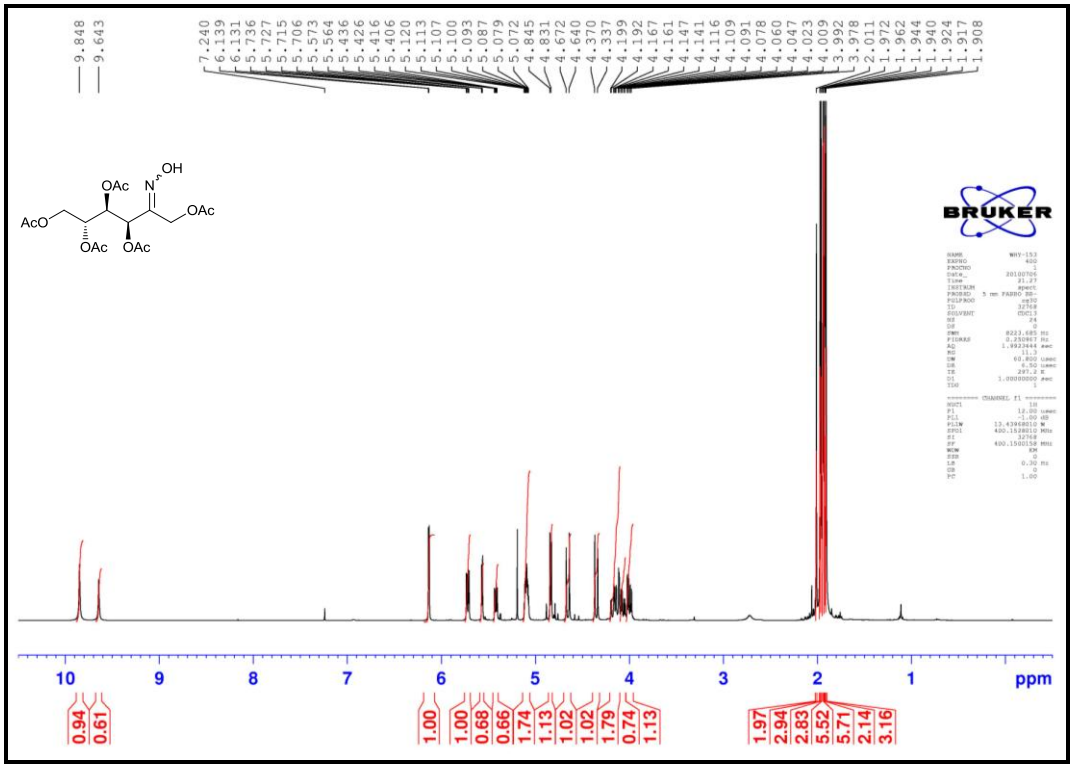
^{13}C NMR spectrum of (Xyl-oxime)Ac$_4$ (100 MHz, $CDCl_3$, a mixture of *E*/*Z* isomers (7:3))



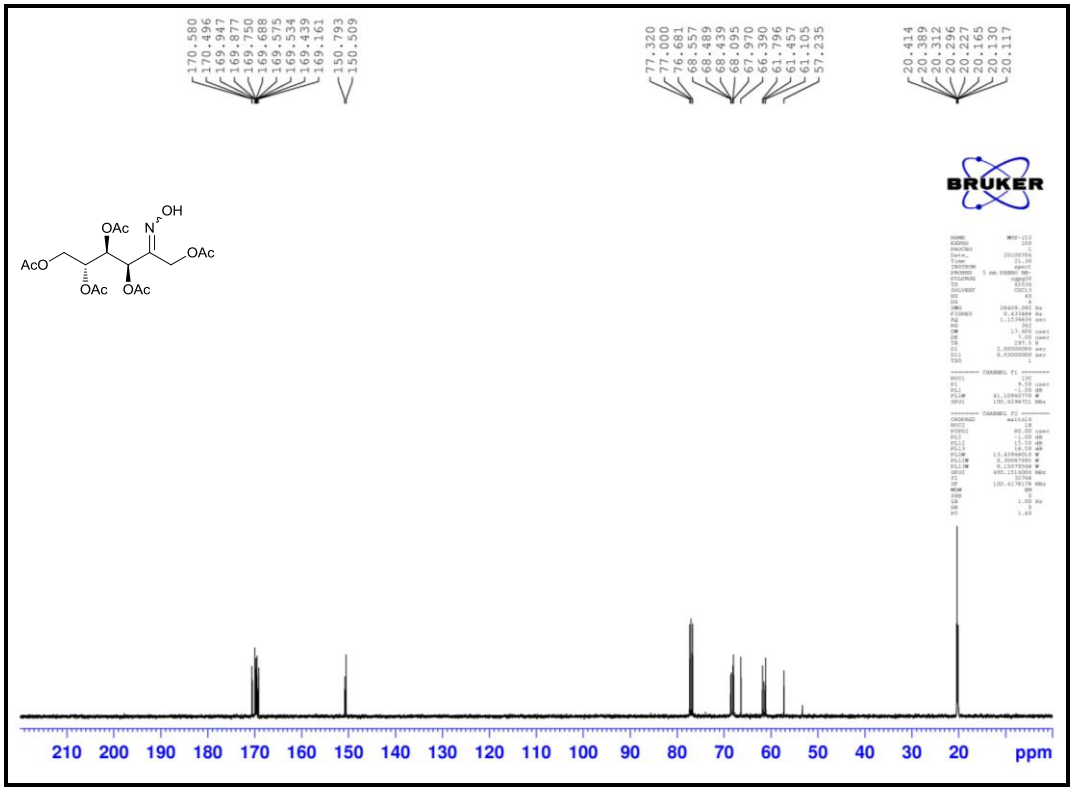
^{1}H NMR spectrum of (Fru-**a**)Ac$_5$ (400 MHz, $CDCl_3$, a mixture of *E*/*Z* isomers (3:2))



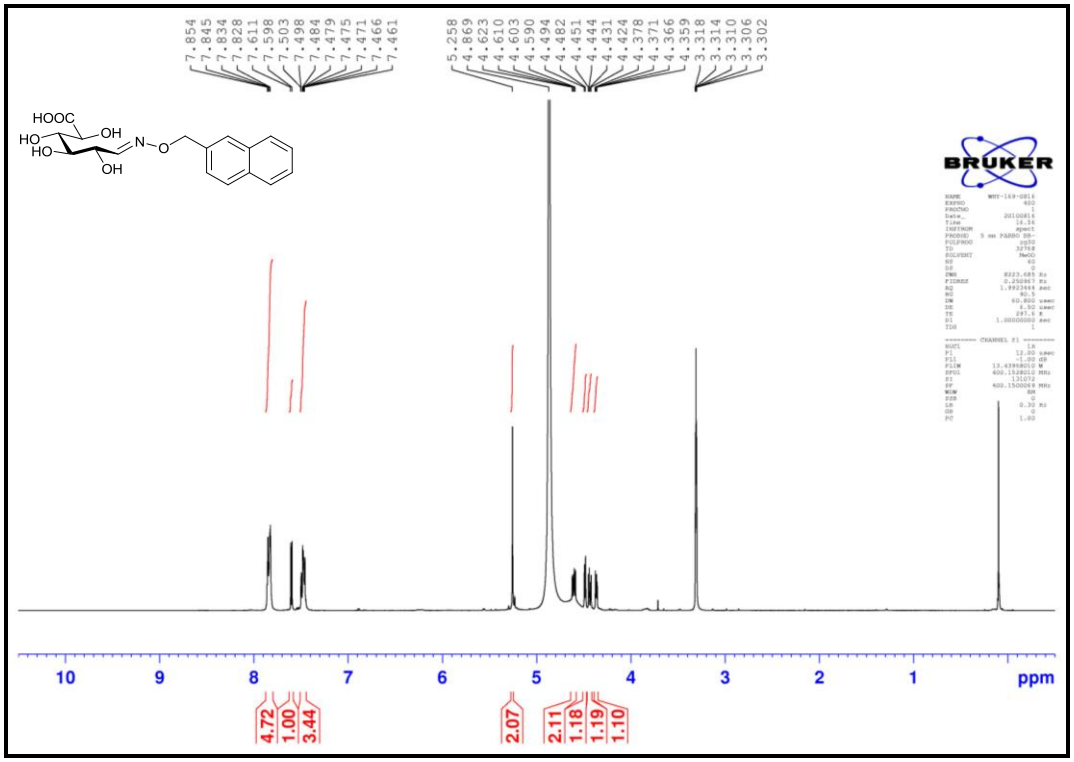
^{13}C NMR spectrum of (Fru-**a**)Ac$_5$ (100 MHz, $CDCl_3$, a mixture of *E*/*Z* isomers (3:2))



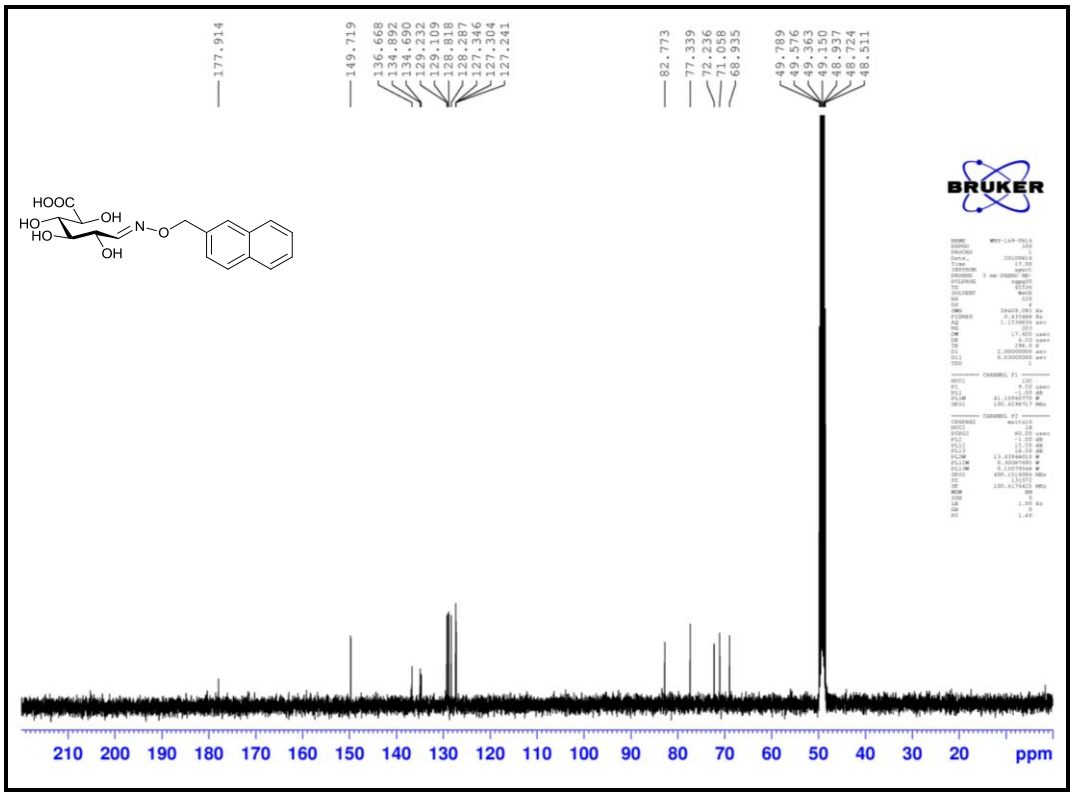
^{1}H NMR spectrum of (Fru-oxime)Ac$_5$ (400 MHz, $CDCl_3$, a mixture of *E*/*Z* isomers (3:2))



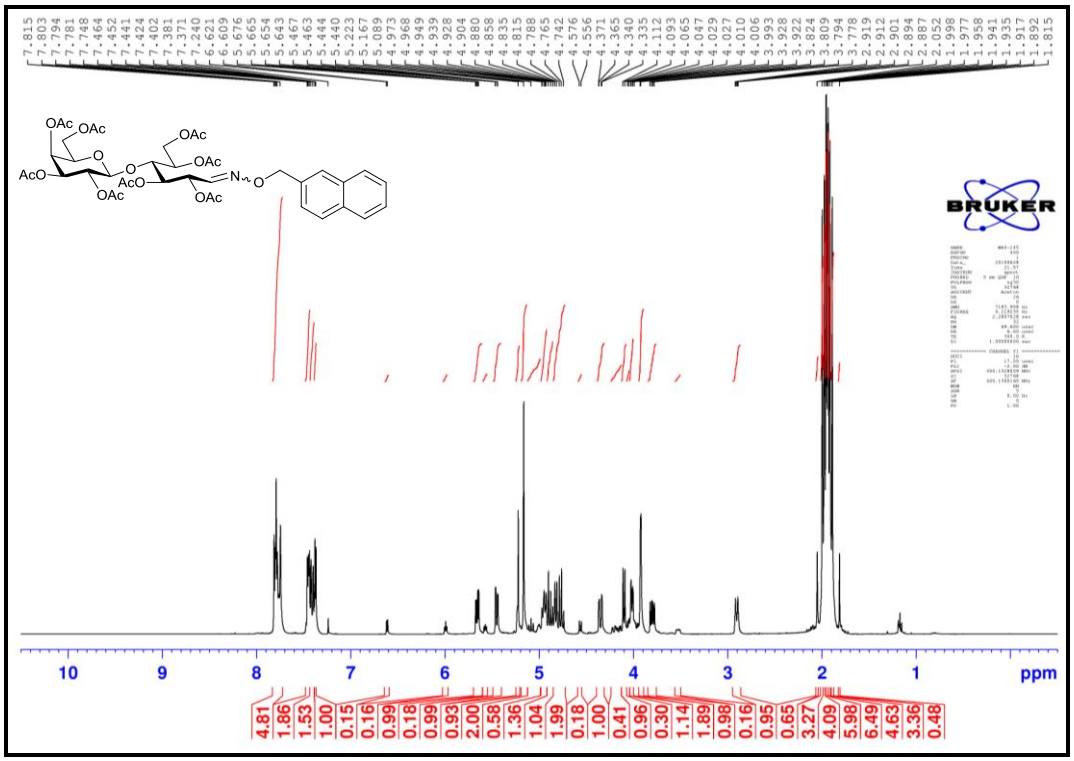
^{13}C NMR spectrum of (Fru-oxime)Ac$_5$ (100 MHz, $CDCl_3$, a mixture of *E*/*Z* isomers (3:2))



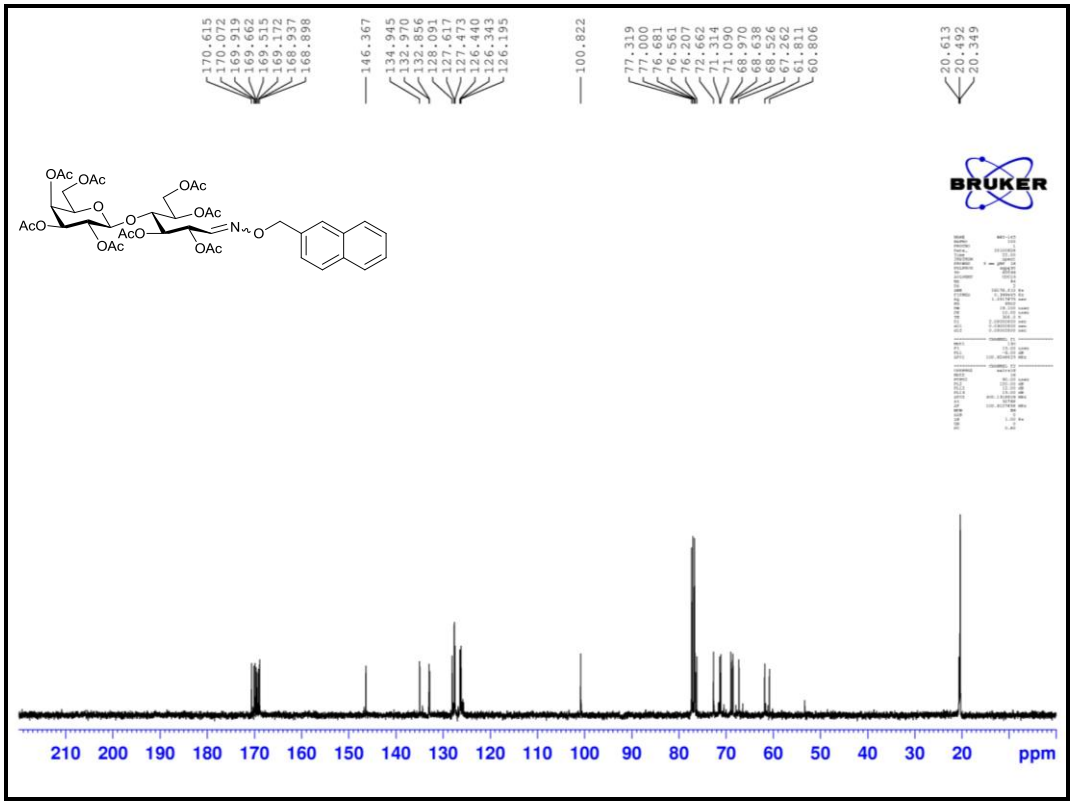
^{1}H NMR spectrum of GlcA-**a** (400 MHz, CD_3OD)



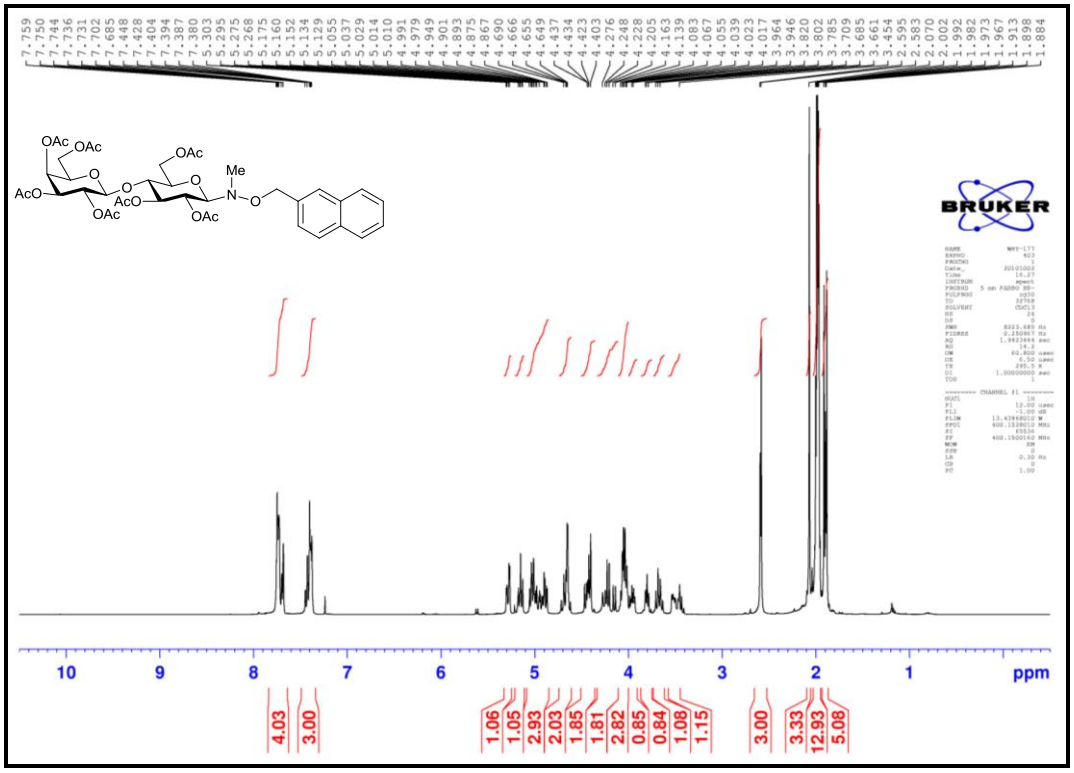
^{13}C NMR spectrum of GlcA-**a** (100 MHz, CD_3OD)



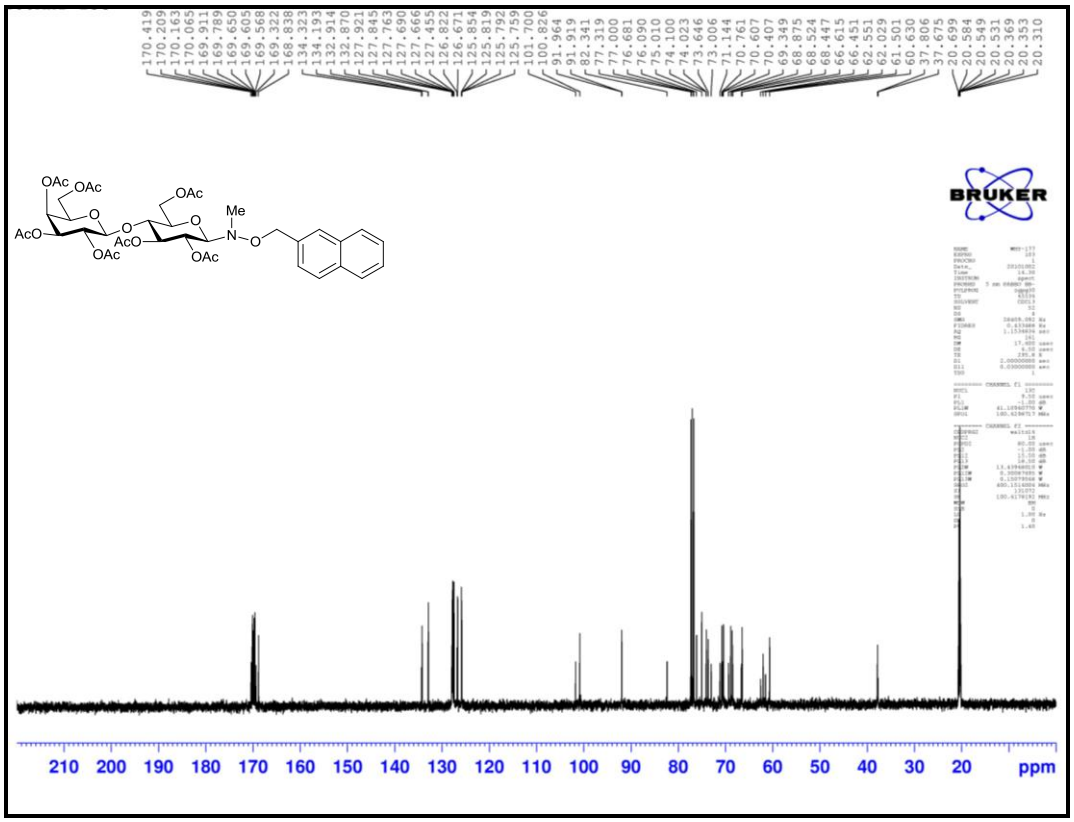
^{1}H NMR spectrum of (Lac-**a**)Ac_8 (400 MHz, $CDCl_3$, a mixture of *E*/*Z* isomers (4:1))



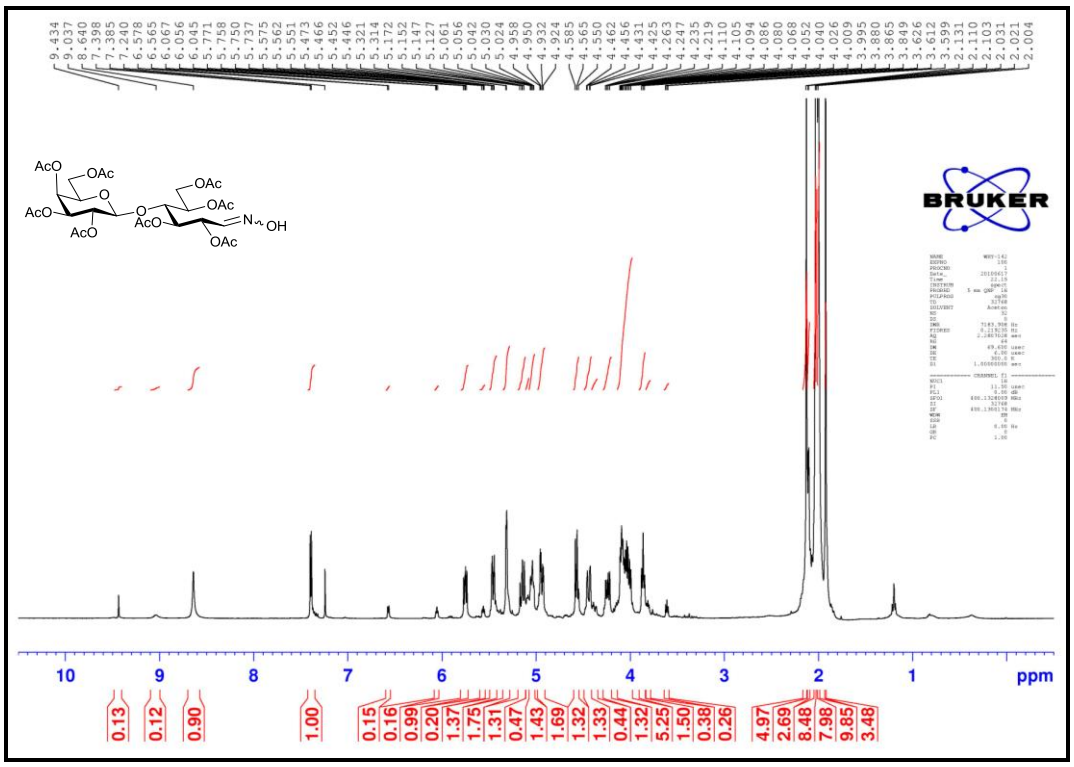
^{13}C NMR spectrum of (Lac-**a**)Ac$_8$ (100 MHz, CDCl$_3$, a mixture of *E*/*Z* isomers (4:1))



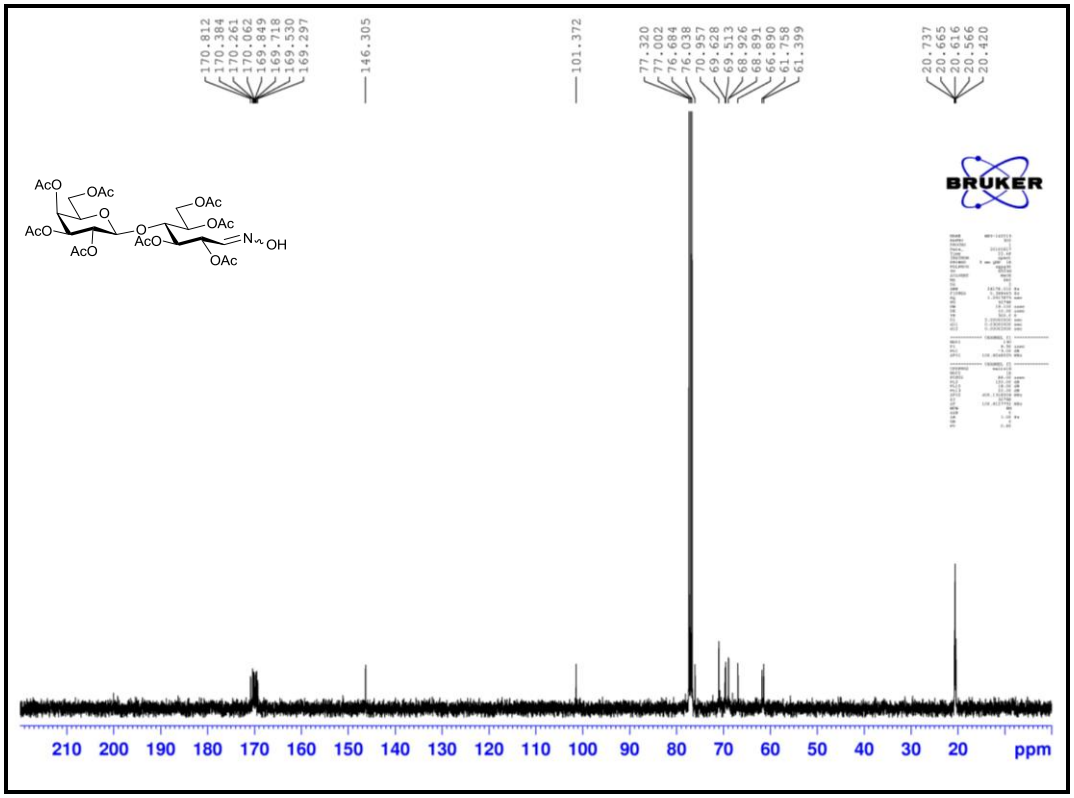
^{1}H NMR spectrum of (Lac-**b**)Ac$_7$ (400 MHz, CDCl$_3$)



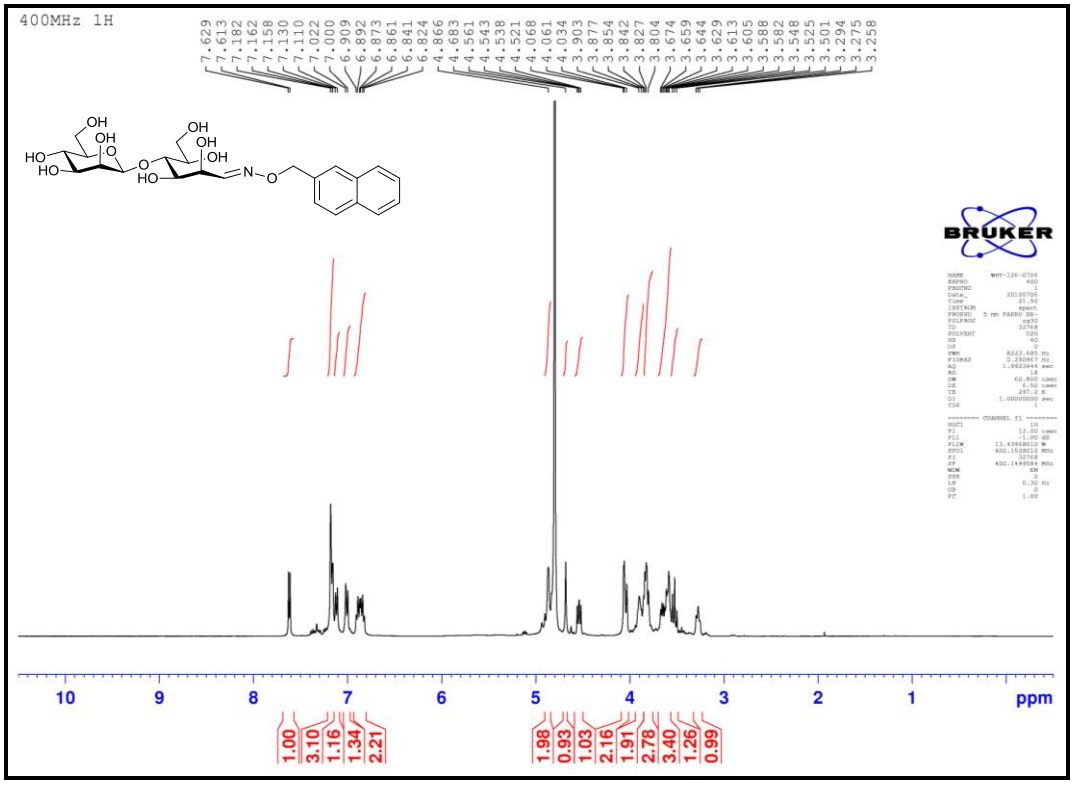
^{13}C NMR spectrum of (Lac-**b**)Ac$_7$ (400 MHz, $CDCl_3$, rotamer)



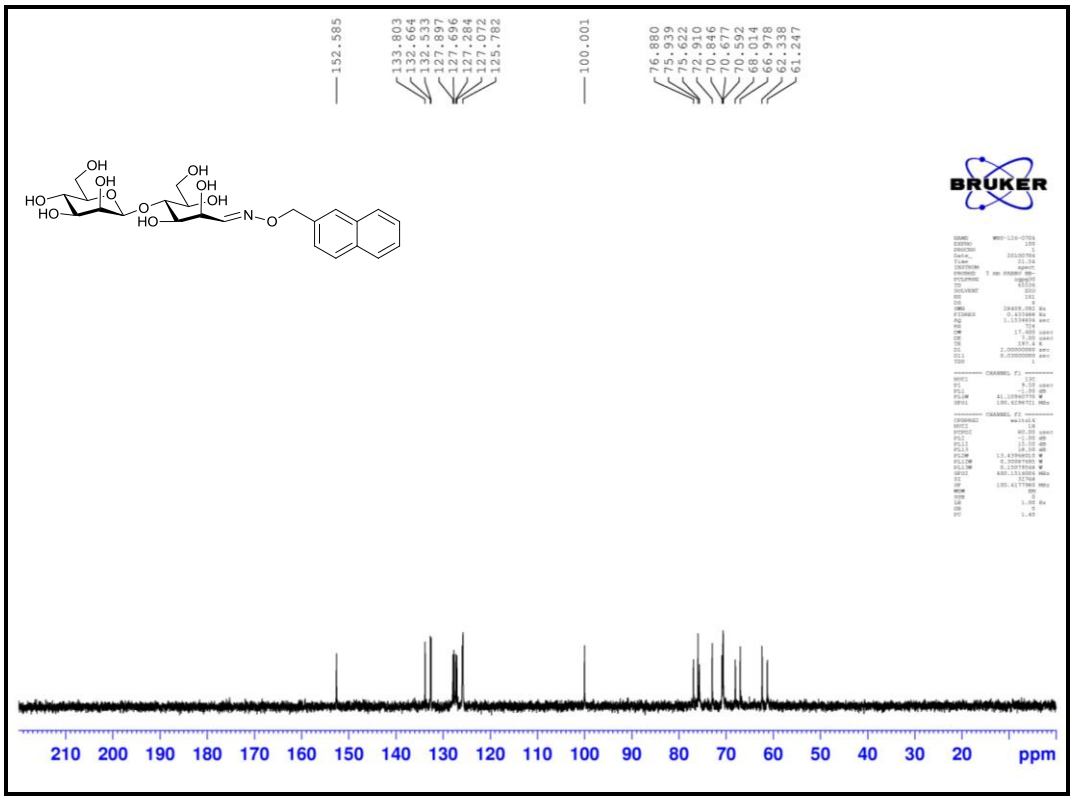
^{1}H NMR spectrum of (Lac-oxime)Ac$_8$ (400 MHz, $CDCl_3$, a mixture of *E*/*Z* isomers (4:1))



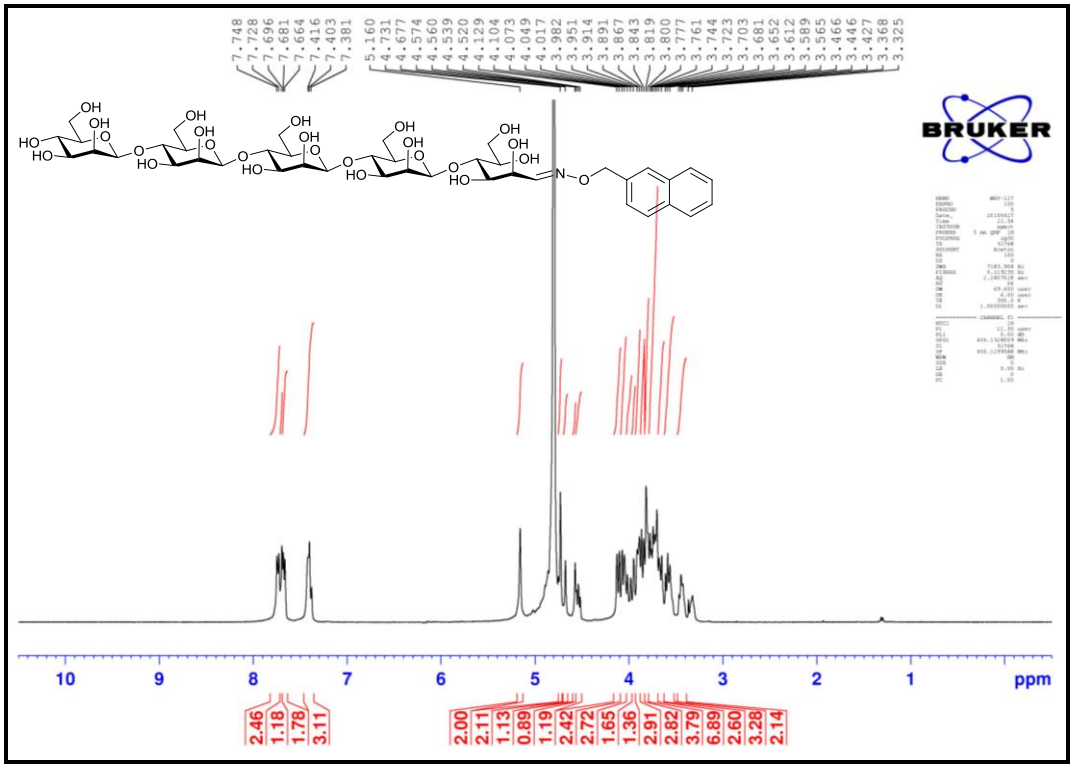
^{13}C NMR spectrum of (Lac-oxime)Ac$_8$ (100 MHz, $CDCl_3$, a mixture of *E*/*Z* isomers (4:1))



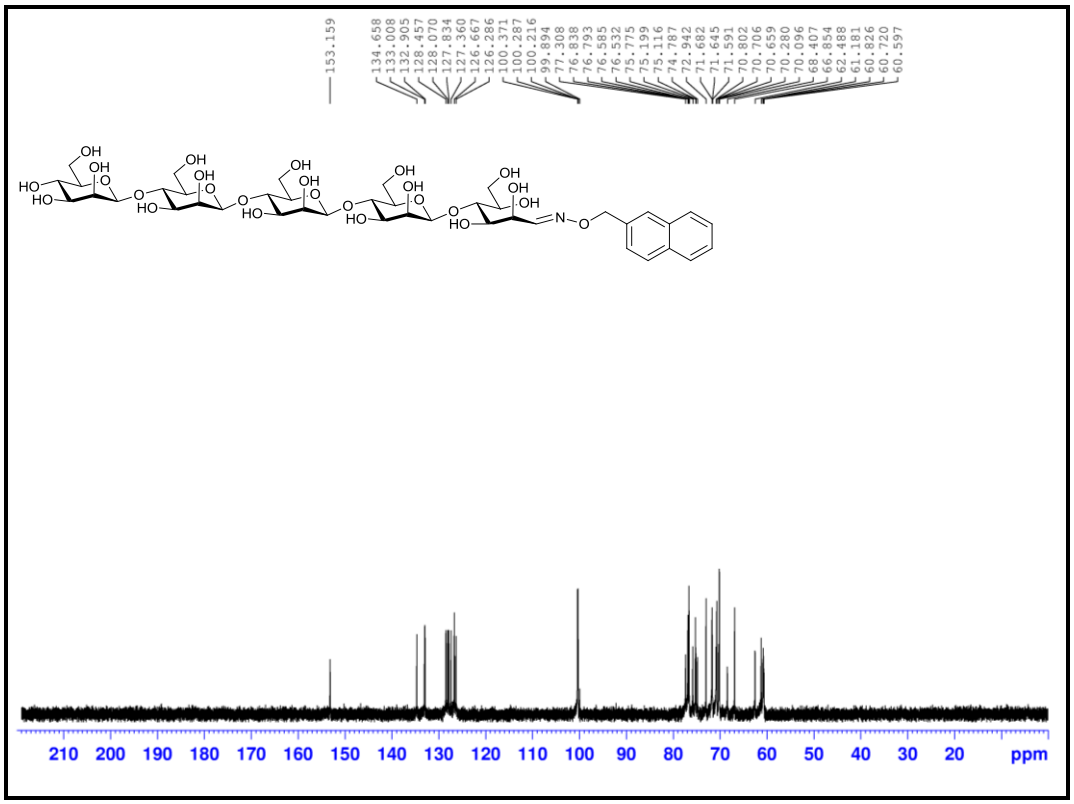
^{1}H NMR spectrum of Man$_2$-**a** (400 MHz, D_2O)



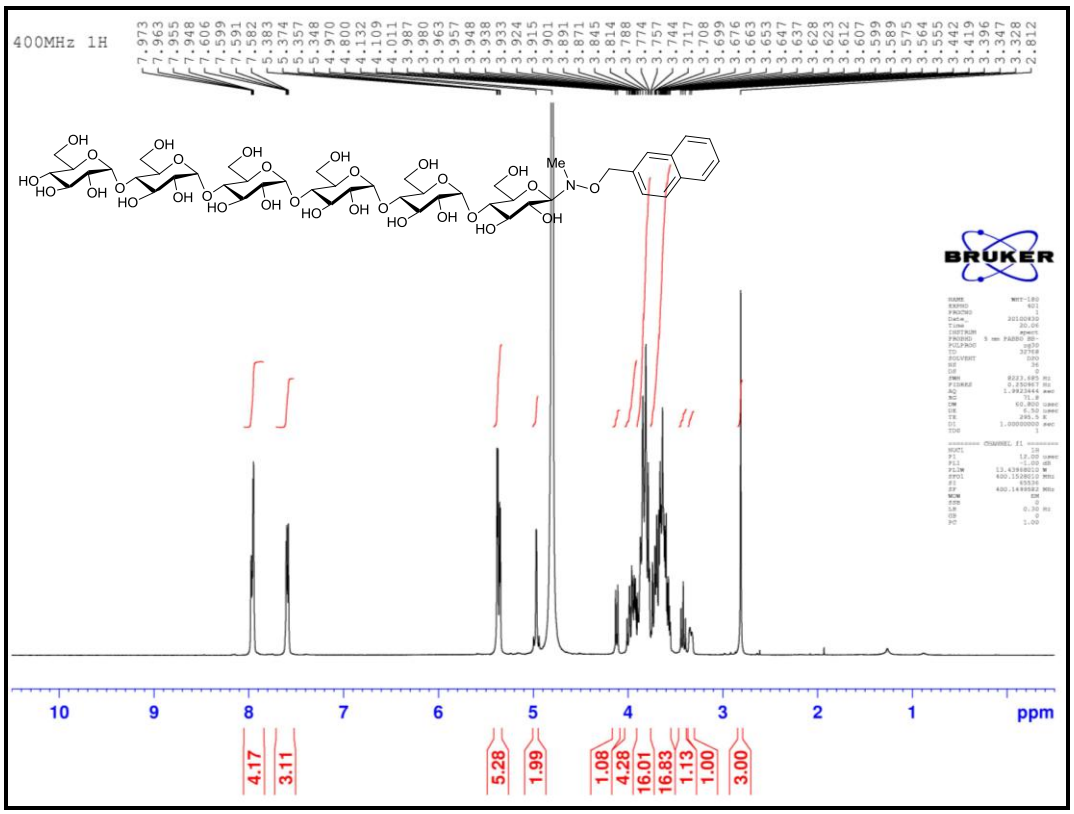
^{13}C NMR spectrum of Man_2-**a** (100 MHz, D_2O)



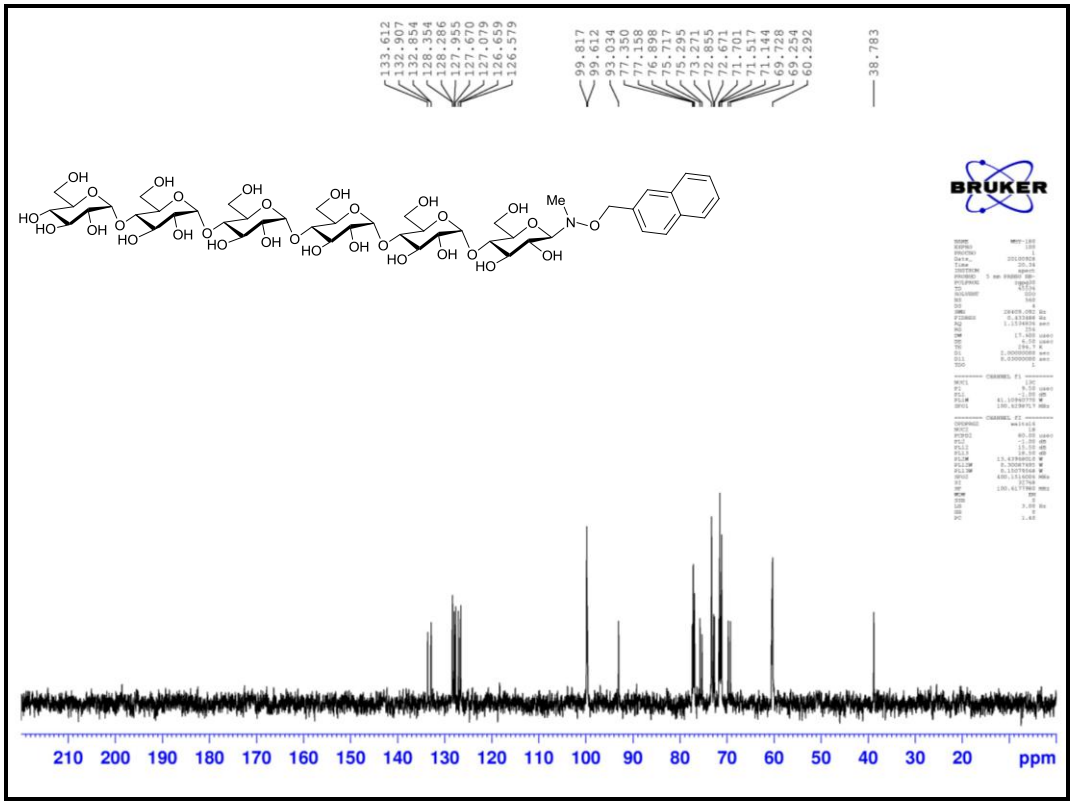
^{1}H NMR spectrum of Man_5-**a** (400 MHz, D_2O)



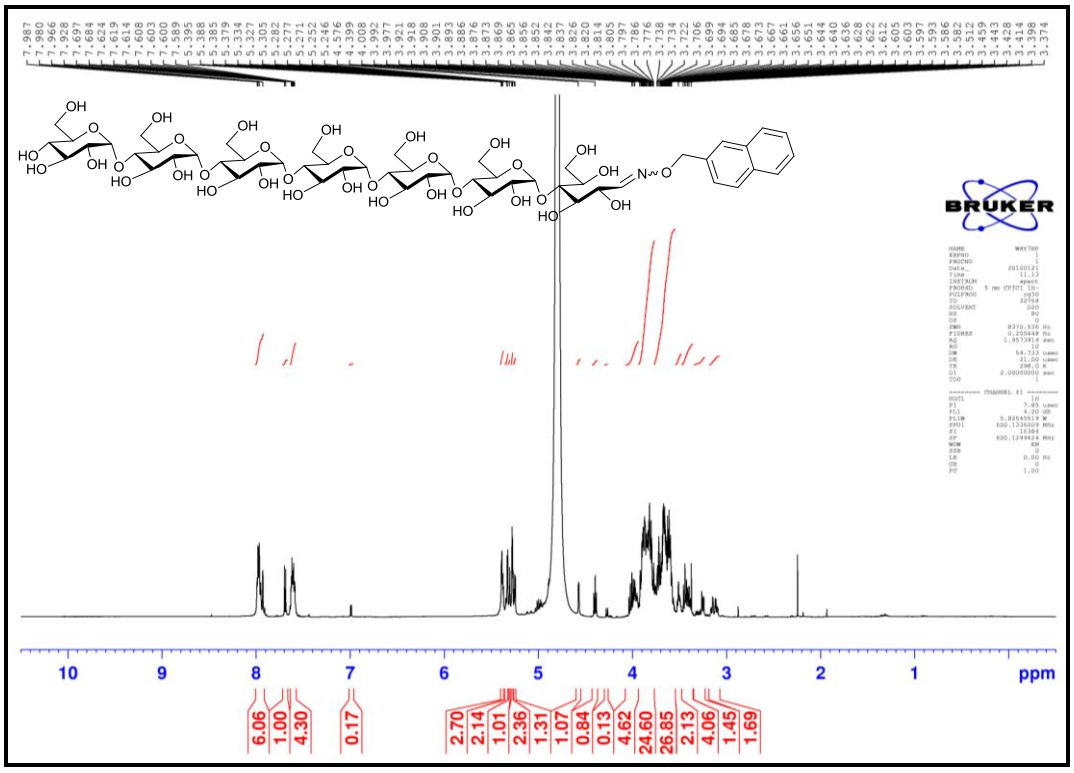
^{13}C NMR spectrum of Man$_5$-**a** (100 MHz, D_2O)



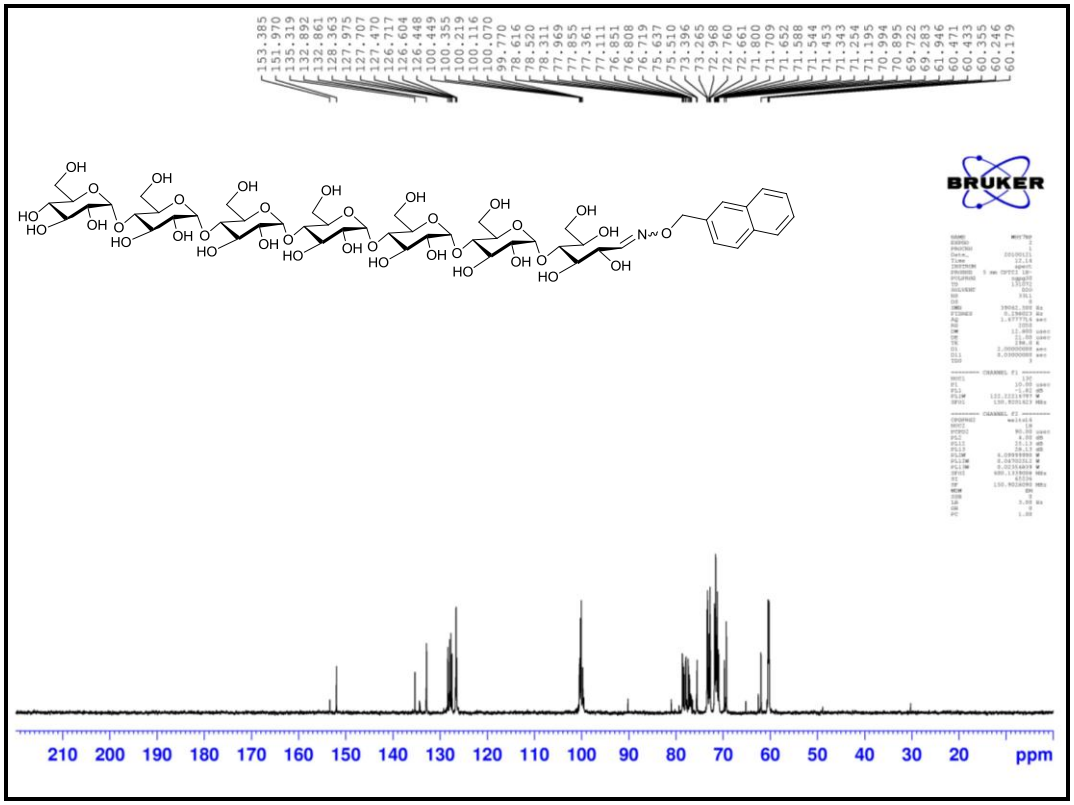
^{1}H NMR spectrum of Glc$_6$-**b** (400 MHz, D_2O)



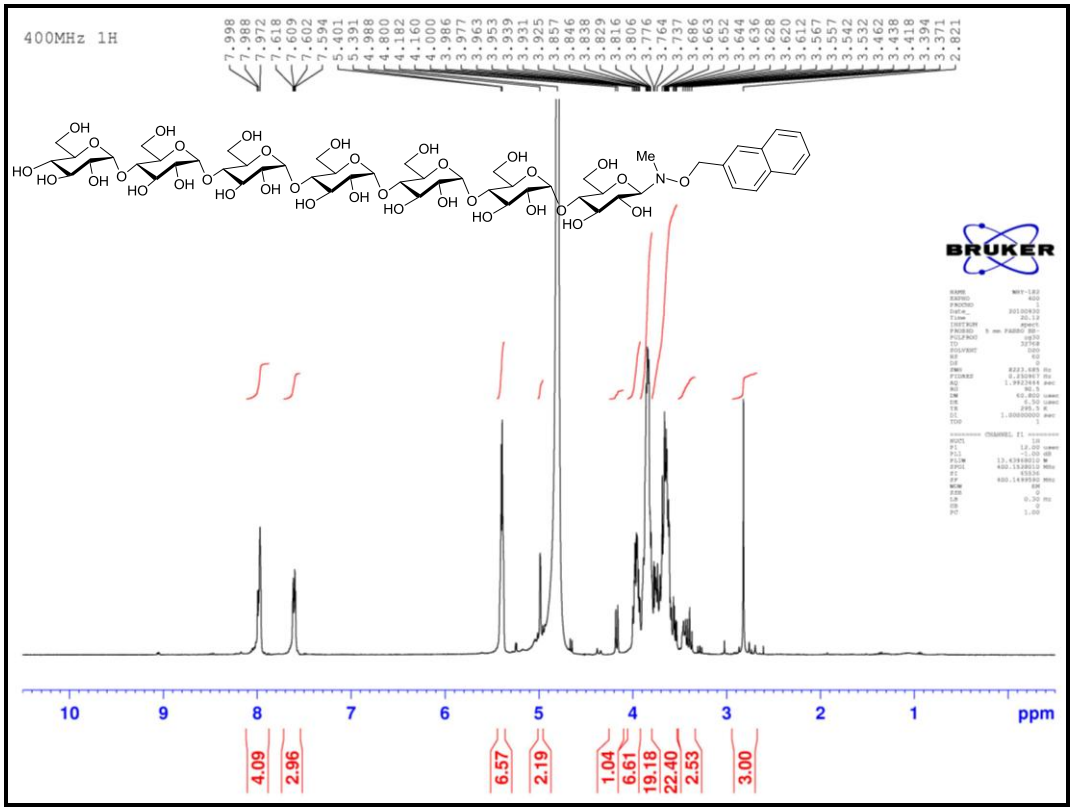
^{13}C NMR spectrum of Glc$_6$-**b** (100 MHz, D_2O)



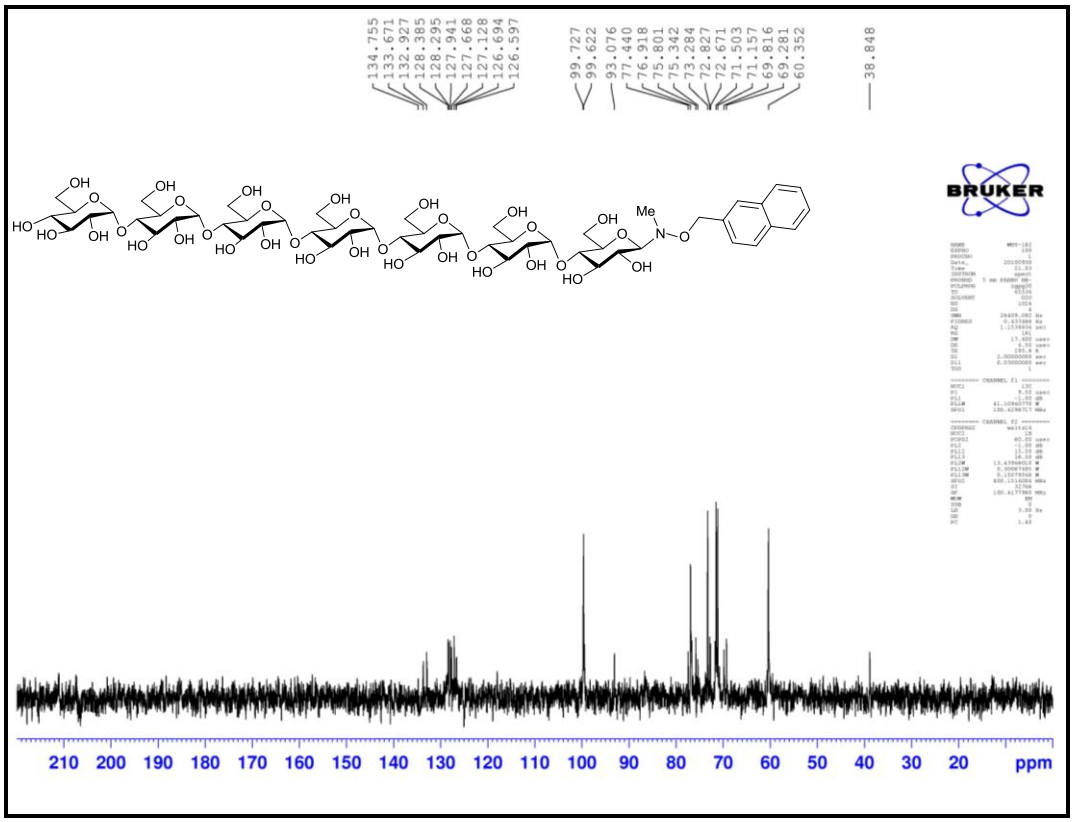
^{1}H NMR spectrum of Glc$_7$-**a** (600 MHz, D_2O, a mixture of *E*/*Z* isomers (4:1))



^{13}C NMR spectrum of Glc$_7$-**a** (150 MHz, D_2O, a mixture of *E*/*Z* isomers (4:1))



^{1}H NMR spectrum of Glc$_7$-**b** (400 MHz, D_2O)



^{13}C NMR spectrum of Glc$_7$-**b** (100 MHz, D_2O)