Factors Affecting Stereocontrol during Glycosidation of 2,3-Oxazolidinone Protected Derivatives of 1-Tolylthio-*N*-Acetyl-D-Glucosamine

*Peng Wei and Robert J. Kerns**

Division of Medicinal & Natural Product Chemistry, University of Iowa, Iowa City, Iowa 52242

robert-kerns@uiowa.edu

Supporting Information

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General Experiment Details.

^{1}H and ^{13}C NMR spectra were recorded using 300 MHz and 400 MHz instruments. Chemical shifts are downfield from tetramethylsilane in $CDCl_3$ unless otherwise noted. Mass spectra were obtained by ESI (electron spray ionization) technique. Analytical thin layer chromatography (TLC) was performed using silica gel 60 F254 precoated plates. Detection was examined by UV (254 nm) or heating with stain (8% sulfuric acid, 5% ammonium molybdate(VI), 2% ammonium cerium(IV) sulfate in water). Flash chromatography was performed using silica gel 60 (230-400 mesh). All reactions were carried out under anhydrous, inert atmosphere (nitrogen or argon) with dry, freshly distilled, solvents unless otherwise noted.

Tolyl 4,6-di-*O*-acetyl-2-deoxy-2-*N*-acetyl-1-thio-*β*-D-glucopyranosid[2,3-*d*]-1,3-oxazolidin-2-one (2). To a stirred solution of tolyl 4,6-di-*O*-acetyl-2-deoxy-1-thio-*β*-d-glucopyranosid[2,3-*d*]-1,3-oxazolidin-2-one **1** (0.395 g, 1 mmol),[8] in pyridine (4 mL) containing catalytic 4-(dimethylamino)pyridine was added acetic anhydride (0.5 mL). The reaction mixture was stirred at room temperature for 2h, quenched by the addition of saturated aqueous $NaHCO_3$ (10 mL), and extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layer was dried, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (Ethyl acetate/Hexanes, 2:3) to give **2** (0.432 g, 99%): ^{1}H NMR ($CDCl_3$) δ 7.40 (d, 2H, Ar-H), 7.14 (d, 2H, Ar-H), 5.28 (t, 1H, H-4), 4.82 (d, 1H, H-1), 4.22 (m, 4H, H-2, H-3, H-6_a, H-6_b), 3.69 (m, 1H, H-5), 2.55 (s, 3H, -$COCH_3$), 2.32 (s, 3H, -CH_3), 2.10 (s, 3H, -$COCH_3$), 2.05 (s, 3H, -$COCH_3$); ^{13}C NMR ($CDCl_3$) δ 172.7, 170.5, 169.1, 153.3, 138.5, 133.31, 129.8, 129.6, 87.8, 79.2, 77.2, 67.8, 62.3, 58.8, 24.7, 21.1, 20.7, 20.6; HRESI MS calcd for $C_{20}H_{23}NO_8S$ $[M + Na]^+$: 460.1042, found : 460.1054.

Separation and characterization details for glycosylation reactions and glycoside products listed in table 1 that were not presented as examples in the text.

Coupling of **2** with **3b** to give **4,6-di-*O*-acetyl-1-*O*-(*N*-carbobenzyloxy-L-threonine methyl ester)-2-deoxy-2-*N*-acetyl-β-D-glucopyranosid[2,3-*d*]-1,3-oxazolidin-2-one (4b).** The reaction was quenched after 1 hour and separated by flash chromatography (Ethyl acetate:Hexanes, 1:1.5), yield = 83%. R_f = 0.16 (Ethyl acetate:Hexanes = 1:1.5); ^{1}H NMR ($CDCl_3$) δ7.41-7.30 (m, 5H, Ar-H), 6.29 (d, 1H, -NH), 5.16 (m, 3H, -CH_2, H-1, *J* = 6.6 Hz), 5.09 (dd, 1H, H-4), 4.62 (m, 1H, -CH), 4.45 (dd, 1H, H-6_a), 4.38 (dd, 1H, -CH), 4.24 (dd, 1H, H-3), 4.08 (dd, 1H, H-6_b), 4.02 (m, 1H, H-5), 3.88 (dd, 1H, H-2), 3.72 (s, 3H, -$COOH_3$), 2.52 (s, 3H, -$COCH_3$), 2.15 (s, 3H, -$COCH_3$), 1.34 (d, 3H, -CH_3); ^{13}C NMR ($CDCl_3$) δ 170.9, 170.6, 169.4, 157.1, 152.9, 136.7, 128.4, 127.9, 127.6, 97.0, 77.2, 74.7, 73.6, 70.6, 69.9, 66.8, 63.8, 60.4, 58.9, 52.5, 24.6, 20.8, 20.7, 15.44; HRESI MS calcd for $C_{26}H_{32}N_2O_{13}$ $[M + Na]^+$: 603.1802, found : 603.1784.

Coupling of **2** with **3c** to give **4,6-di-*O*-acetyl-2-deoxy-2-*N*-acetyl-β-D-glucopyranosid[2,3-*d*]-1,3-oxazolidin-2-one-(1-3)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (4c).** The reaction was quenched after 1 hour and separated by flash chromatography (Ethyl acetate:Hexanes, 1:1.5), yield = 95%. Rf = 0.26 (Ethyl acetate:Hexanes = 1:1.5); ^{1}H NMR ($CDCl_3$) δ 6.04 (d, 1H), 5.33 (d, 1H, H-1, 6.8Hz), 5.19 (dd, 1H, H-4), 4.71 (d, 1H), 4.50 (d, 2H, H-6), 4.44 (d, 1H), 4.38 (m, 1H), 4.30 (dd, 1H, H-3), 4.14 (m, 1H, H-5), 4.12 (m, 2H), 4.10 (m, 1H), 4.03 (dd, 1H, H-2), 2.56 (s, 3H, -$COCH_3$), 2.15 (s, 3H, -$COCH_3$), 2.10 (s, 3H, -$COCH_3$), 1.56 (s, 3H), 1.42 (s, 3H), 1.38 (s, 3H), 1.28 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 170.5, 170.4, 169.4, 152.8, 111.8, 109.3, 105.2, 98.0, 81.2, 80.8, 79.9, 76.6, 74.8, 71.6, 70.1, 67.7, 63.6, 60.5, 26.8, 26.3, 25.1, 24.5, 20.8, 20.7; HRESI MS calcd for $C_{25}H_{35}NO_{14}$ $[M + Na]^+$: 596.1955, found : 596.1963.

Coupling of **2** with **3d** to give **Methyl (4,6-di-*O*-acetyl-2-deoxy-2-*N*-acetyl-β-D-gluco-pyranosid[2,3-*d*]-1,3-oxazolidin-2-one)-(1-6)-2-*O*-allyl-3,4-di-*O*-benzyl-α-D-mannopyranoside (4d).** The reaction was quenched after 4 hours and separated by flash chromatography (Ethyl acetate:Hexanes, 1:1.5), yield = 90%. Rf = 0.47 (Ethyl acetate:Hexanes = 1:1); ^{1}H NMR ($CDCl_3$) δ 7.41-7.21 (m, 10H, Ar-H), 5.98-5.86 (m, 1H, -CH=), 5.34-5.28 (dd, 1H, =C$\underline{H}_2$), 5.24-5.16 (m, 2H, =C$\underline{H}_2$, H-4), 5.12 (d, 1H, H-1, 6.8Hz), 4.94 (d, 1H, -C$\underline{H}_2$Ph), 4.74-4.66 (m, 4H, -CH_2Ph, C$\underline{H}_2$Ph, H-1'), 4.48-4.44 (dd, 1H, H-6_a), 4.40-4.36 (dd, 1H, H-6_b), 4.28-4.22 (dd, 2H, H-3), 4.18-4.14 (dd, 2H, -OCH_2), 4.08-3.98 (m, 3H, H-2, H-6_a', H-5), 3.94-3.82 (m, 3H, H-4', H-6_b', H-3'), 3.78-3.72 (m, 2H, H-5', H-2'), 3.35 (s, 3H, -OCH_3), 2.50 (s, 3H, -$COCH_3$), 2.15 (s, 3H, -$COCH_3$), 2.08 (s, 3H, -$COCH_3$); ^{13}C NMR ($CDCl_3$) δ 170.6, 170.0, 169.5, 152.8, 138.8, 138.4, 135.1, 128.4, 128.3, 127.9, 127.7, 127.6, 127.5, 117.5, 100.6, 99.00, 80.0, 75.4, 74.8, 74.6, 74.5, 72.1, 71.2, 69.9, 68.2, 63.8, 60.4, 54.7, 24.5, 20.8, 20.7; HRESI MS calcd for $C_{37}H_{45}NO_{14}$ $[M + Na]^+$: 750.2738, found : 750.2763.

Coupling of **2** with **3e** to give **Methyl (4,6-di-*O*-acetyl-2-deoxy-2-*N*-acetyl-β-D-glucopyranosid[2,3-*d*]-1,3-oxazolidin-2-one)-(1-3)-2-*O*-allyl-4,6-*O*-benzylidene-α-D-mannopyranoside (4e).** The reaction was quenched after 12 hour and glycosides separated by flash chromatography (Ethyl acetate:Hexanes, 1:1.5), yield = 82% (α:β = 1:20). Rf β-isomer = 0.56, Rf α-isomer = 0.52 (TLC Ethyl acetate:Hexanes = 1:1); Major isomer **β-4e** ^{1}H NMR ($CDCl_3$) δ 7.58-7.52 (m, 2H, Ar-H), 7.39-7.33(m, 3H, Ar-H), 6.02-5.88 (m, 1H, -CH=), 5.64 (s, 1H, -CH-Ph), 5.35-5.28 (m, 2H, H-1, 6.4Hz, =C$\underline{H}_2$), 5.22-5.18 (m, 2H, H-4, =C$\underline{H}_2$), 4.76 (d, 1H, H-1'), 4.56 (dd, 1H, H-3'), 4.33-4.22 (m, 3H, H-6_a', H-3, H-6_a), 4.18-4.10 (m, 3H, H-6_b', H-6_b, -OC$\underline{H}_2$), 4.08-3.98 (m, 3H, H-2', H-2, -OC$\underline{H}_2$), 3.92-3.86 (m, 2H, H-4', H-5), 3.82 (m, 1H, H-5'), 3.42 (s, 3H, -OCH_3), 2.52 (s, 3H, -$COCH_3$), 2.12 (s, 3H, -$COCH_3$), 2.08 (s, 3H, -$COCH_3$); ^{13}C

NMR ($CDCl_3$) δ 170.5, 170.2, 169.4, 153.1, 137.7, 135.0, 128.8, 128.2, 126.1, 117.3, 101.6, 100.8, 100.4, 78.2, 77.6, 76.8, 75.1, 72.9, 70.2, 68.9, 64.0, 63.9, 61.6, 54.9, 24.5, 20.9, 20.7; Minor isomer **α-4e** (H-1, 5.98ppm, $J_{1,2}$ = 2.7Hz); HRESI MS calcd for $C_{30}H_{37}NO_{14}$ $[M + Na]^+$: 658.2112, found : **β-4e** = 658.2097, found : **α-4e** = 658.2088.

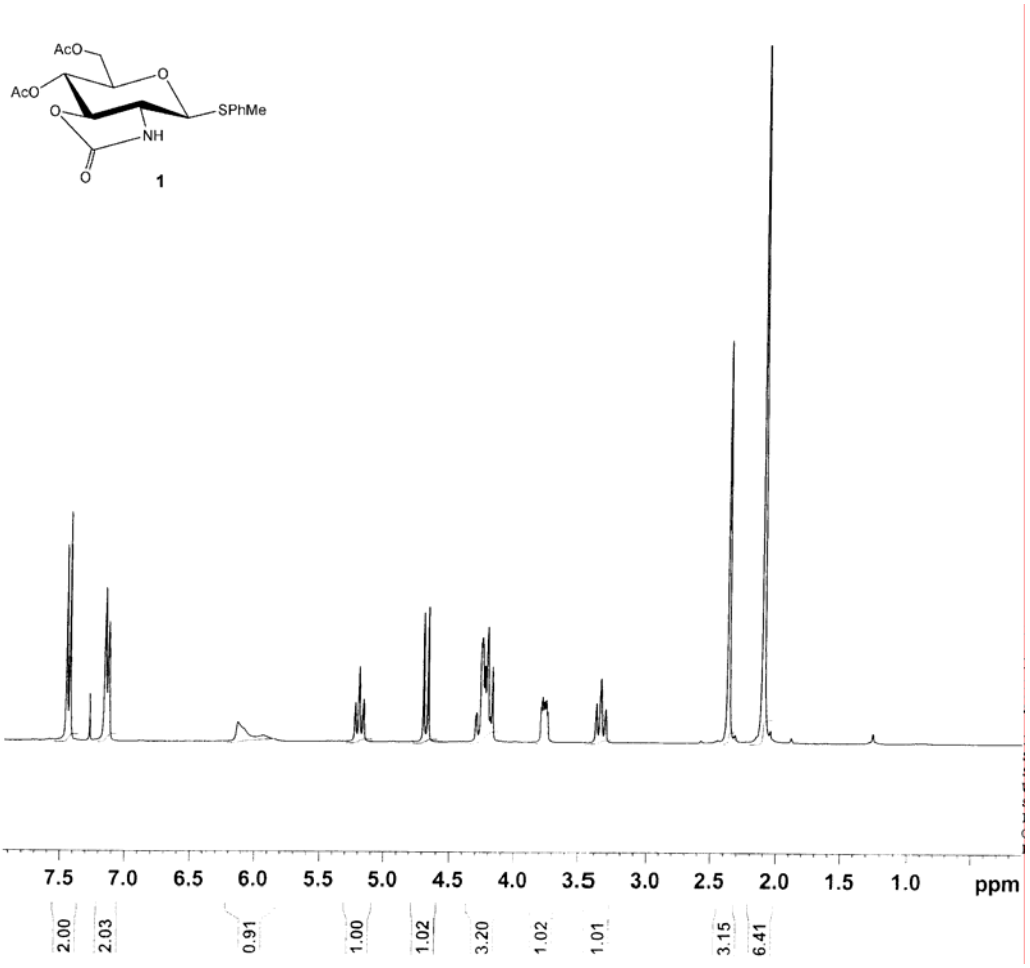
Coupling of **2** with **3f** to give **Methyl (4,6-di-*O*-acetyl-2-deoxy-2-*N*-acetyl-β-D-glucopyranosid[2,3-*d*]-1,3-oxazolidin-2-one)-(1-4)-2,3-*O*-benzyl-α-D-methylglucoronate (4f).** The reaction was quenched after 12 hour and separated by flash chromatography (Ethyl acetate:Hexanes, 1:1), yield = 75% (α:β = 1:7). Rf β-isomer = 0.41, Rf α-isomer = 0.44 (Ethyl acetate:Hexanes = 1:1); Major isomer **β-4f** ^{1}H NMR ($CDCl_3$) δ 7.40-7.22 (m, 10H, Ar-H), 5.36 (d, 1H, H-1, 6.9Hz), 5.17 (dd, 1H, H-4), 4.96 (s, 2H, -CH_2), 4.75 (d, 1H, -C$\underline{H}_2$), 4.61 (m, 2H, -C$\underline{H}_2$, H-1'), 4.31-4.23 (m, 2H, H-6_a, H-4'), 4.20-4.16 (m, 2H, H-3, H-6_b), 4.02-3.95 (m, 2H, H-3', H-5'), 3.88-3.82(m, 2H, H-5, H-2), 3.74 (s, 3H, $COOCH_3$), 3.57-3.53 (m, 1H, H-2'), 3.43 (s, 3H, OCH_3), 2.52 (s, 3H, -$COCH_3$), 2.12 (s, 3H, -$COCH_3$), 2.08 (s, 3H, -$COCH_3$); ^{13}C NMR ($CDCl_3$) δ 170.5, 170.4, 169.6, 169.5, 153.2, 139.2, 137.8, 128.5, 128.2, 128.1, 128.0, 127.4, 127.3, 100.1, 98.3, 79.4, 75.6, 75.0, 73.4, 69.8, 68.9, 63.2, 61.2, 60.4, 55.8, 52.4, 29.7, 24.5, 21.1, 20.8, 14.2; Minor isomer **α-4f** (H-1, 6.26ppm, $J_{1,2}$ = 2.7Hz); HRESI MS calcd for $C_{35}H_{41}NO_{15}$ $[M + Na]^+$: 738.2374, found : **β-4f** = 738.2376, found : **α-4f** = 738.2382.

Coupling of **2** with **3g** to give **Methyl (4,6-di-*O*-acetyl-2-deoxy-2-*N*-acetyl-β-D-glucopyranosid[2,3-*d*]-1,3-oxazolidin-2-one)-(1-3)-4,6-*O*-Benzylidene-2-*N*-phthalimido-β-D-glucopyranoside (4g).** The reaction was quenched after 24 hour and separated by flash chromatography (Ethyl acetate:Hexanes, 1:1.5), yield = 75% (α:β = 1:4.5). Rf β-isomer = 0.23, Rf α-isomer = 0.19 (Ethyl acetate:Hexanes = 1:1.5); Major isomer **β-4g** ^{1}H NMR ($CDCl_3$) δ 7.88

(m, 2H, Ar-H), 7.75 (m, 2H, Ar-H), 7.53 (m, 2H, Ar-H),7.40 (m, 3H, Ar-H), 5.62 (s, 1H, -CHPh), 5.34(d, 1H, H-1'), 5.22 (d, 1H, H-1, 6.4Hz), 5.06 (dd, 1H, H-4), 4.72 (dd, 1H, H-3'), 4.46(m, 2H, H-6_a', H-6_a), 4.26 (dd, 1H, H-2'), 4.18 (dd, 1H, H-6_b), 4.10 (dd, 1H, H-3), 3.95 (m, 2H, H-6_b', H-4'), 3.84 (m, 1H, H-5), 3.74 (m, 2H, H-5', H-2), 3.50 (s, 3H, -OCH_3), 2.20 (s, 3H, -$COCH_3$), 2.08 (s, 3H, -$COCH_3$)1.90 (s, 3H, -$COCH_3$); ^{13}C NMR ($CDCl_3$) δ 170.4, 169.5, 169.4, 152.8, 137.3, 133.7, 129.1, 128.3, 126.0, 123.1, 101.3, 99.6, 81.5, 75.2, 69.4, 68.9, 65.9, 63.6, 61.3, 57.1, 55.2, 29.7, 23.4, 21.0, 20.6; Minor isomer **α-4g** (H-1, 6.08ppm, $J_{1,2}$ = 2.7Hz); HRESI MS calcd for $C_{35}H_{36}N_2O_{15}$ $[M + Na]^+$: 747.2013, found : **β-4g** = 747.2021, found : **α-4g** = 747.2036.

Coupling of **2** with **3h** to give **Methyl (4,6-di-*O*-acetyl-2-deoxy-2-*N*-acetyl-α-D-glucopyranosid[2,3-*d*]-1,3-oxazolidin-2-one)-(1-4)-6-*p*-methoxybenzene-2,3-*O*-benzyl-α-D-glucopyranoside (4h).** The reaction was quenched after 48 hour and separated by flash chromatography (Ethyl acetate:Hexanes, 1:1.5), yield = 65% (α:β = 1.6:1). Rf β-isomer = 0.54, Rf α-isomer = 0.50 (Ethyl acetate:Hexanes = 1:1); Major isomer **α-4h** ^{1}H NMR ($CDCl_3$) δ 7.44-7.26 (m, 10H, Ar-H), 6.88-6.82 (m, 4H, Ar-H), 6.42 (d, 1H, H-1, 2.7Hz), 5.26 (t, 1H, H-4), 5.12 (d, 1H, -C$\underline{H}_2$Ph), 4.96 (d, 1H, -C$\underline{H}_2$Ph), 4.76 (d, 1H, -C$\underline{H}_2$Ph), 4.64 (d, 1H, H-1'), 4.60 (d, 1H, -C$\underline{H}_2$Ph), 4.54-4.48 (dd, 1H, H-3), 4.26-4.18 (m, 2H, H-4', H-6_a'), 4.12 (dd, H-6_b'), 4.00-3.92 (m, 3H, H-3', H-6_a, H-5'), 3.86-3.78 (m, 2H, H-6_b, H-2), 3.77 (s, 3H, PhOCH_3), 3.68-3.64 (dd, 2H, H-2', H-5), 3.41 (s, 3H, OCH_3), 2.38 (s, 3H, -OCH_3), 2.15 (s, 3H, -$COCH_3$), 2.08 (s, 3H, -$COCH_3$); Minor isomer **β-4h** (H-1, 5.50 ppm, $J_{1,2}$ = 6.6Hz); HRESI MS calcd for $C_{41}H_{47}NO_{15}$ $[M + Na]^+$: 816.2843, found : **β-4h** = 816.2849, found : **α-4h** = 816.2831.

Coupling of **2** with **3i** to give **Methyl (4,6-di-*O*-acetyl-2-deoxy-2-*N*-acetyl-α-D-glucopyranosid[2,3-*d*]-1,3-oxazolidin-2-one)-(1-4)-2,3-*O*-benzoyl-β-D-methylglucoronate (4i).** The reaction was quenched after 48 hour and separated by flash chromatography (Ethyl acetate:Hexanes, 1:1), yield = 75% (α:β = 2.8:1). Rf β-isomer = 0.16, Rf α-isomer = 0.19 (Ethyl acetate:Hexanes = 1:1.5); Major isomer **α-4i** ^{1}H NMR ($CDCl_3$) δ 7.98-7.90 (m, 4H, Ar-H), 7.56-7.46 (m, 2H, Ar-H), 7.44-7.36 (m, 4H, Ar-H), 5.92 (d, 1H, H-1, 2.7Hz), 5.65 (t, 1H, H-3'), 5.42-5.36 (dd, 1H, H-2'), 5.28 (t, 1H, H-4), 4.68 (d, 1H, H-1'), 4.58 (dd, 1H, H-3), 4.48-4.44 (dd, 1H,H-4'), 4.20 (m, 2H, H-6_a, H-6_b), 4.15 (d, 1H, H-5'), 3.92-3.86 (m, 1H, H-5), 3.85 (s, 3H, -COOMe), 3.68-3.64 (dd, 1H, H-2), 3.53 (s, 3H, -OCH_3), 2.15 (s, 3H, -$COCH_3$), 2.08 (s, 3H, -$COCH_3$), 1.66 (s, 3H, -$COCH_3$); ^{13}C NMR ($CDCl_3$) δ 171.3, 170.6, 169.1, 167.5, 165.6, 165.0, 152.2, 133.6, 133.3, 130.0, 129.8, 129.0, 128.9, 128.6, 128.4, 75.4, 73.2, 72.6, 71.4, 71.0, 67.8, 61.1, 59.8, 57.4, 53.1, 29.7, 22.5, 20.7, 20.6; Minor isomer **β-4i** (H-1, 5.18 ppm, 6.4Hz); HRESI MS calcd for $C_{35}H_{37}NO_{17}$ $[M + Na]^+$: 766.1959, found : **α-4i** = 766.1943, found : **β-4i** = 766.1967.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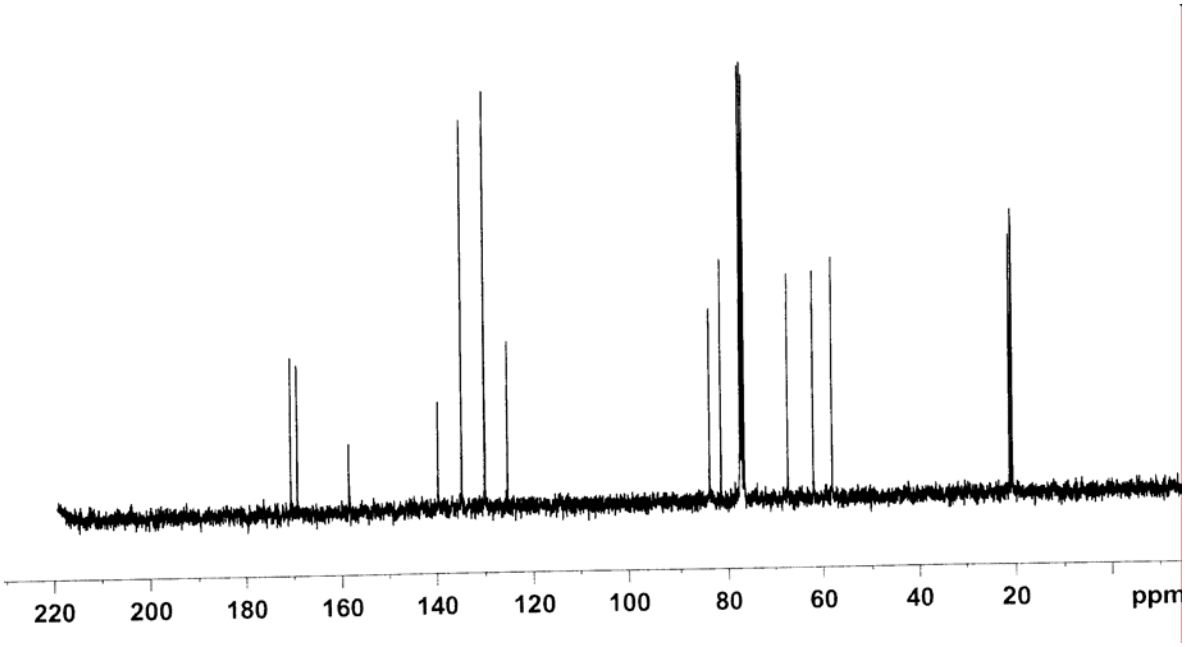
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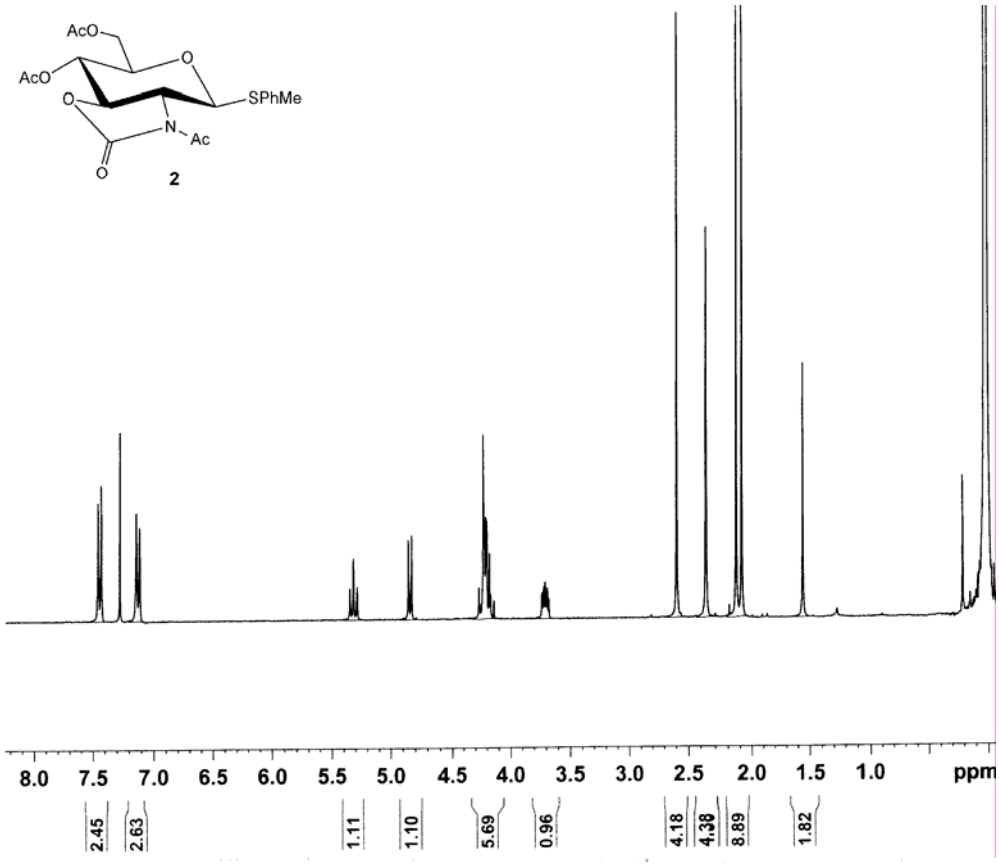
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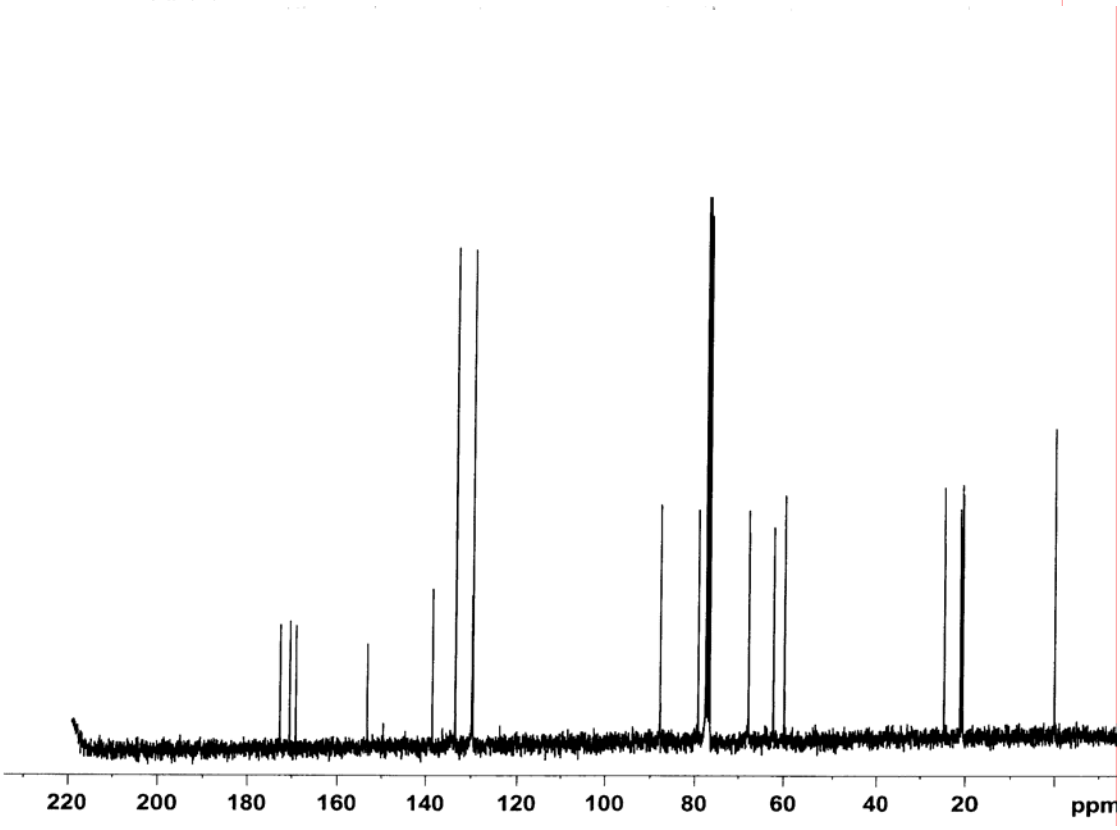
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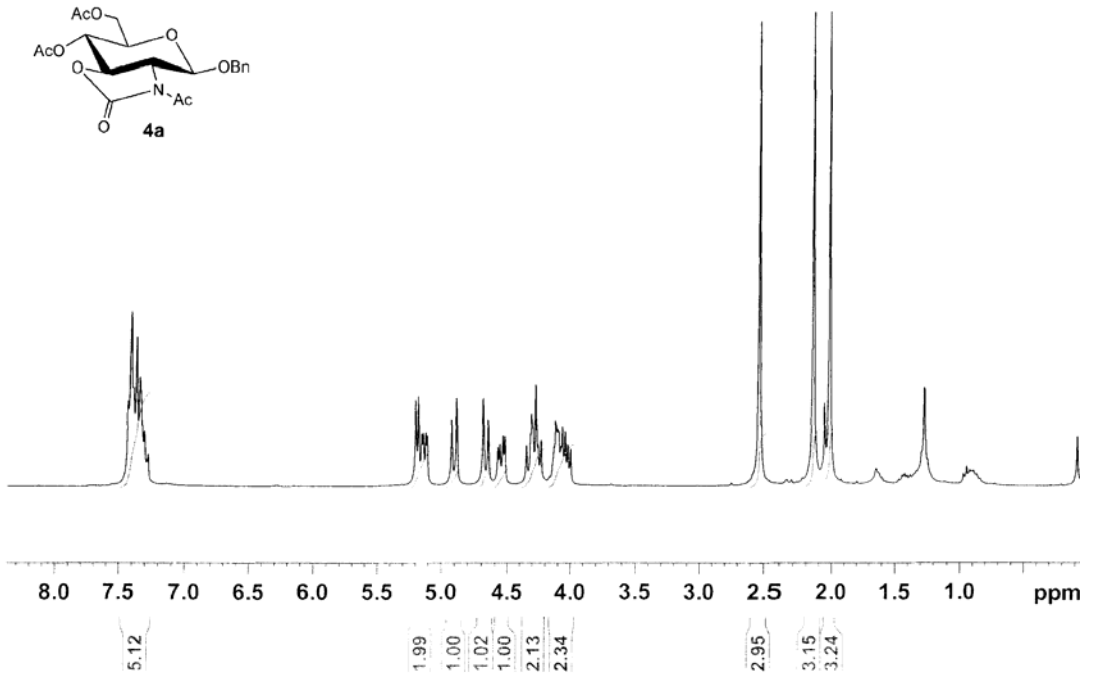
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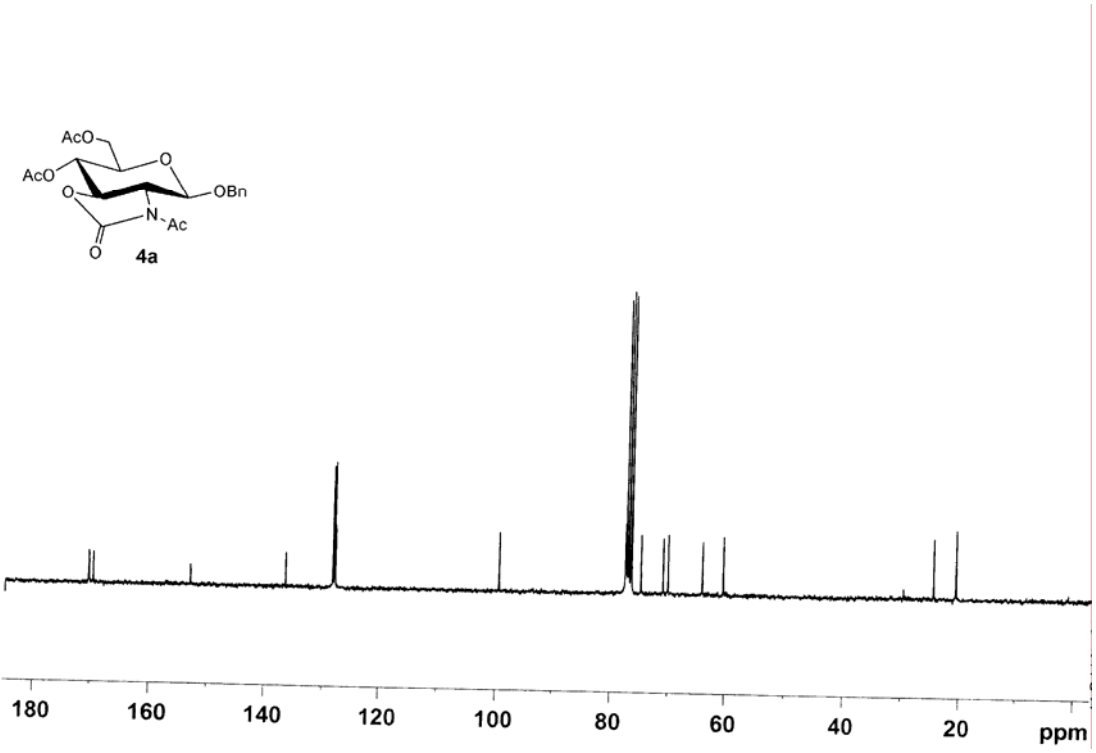
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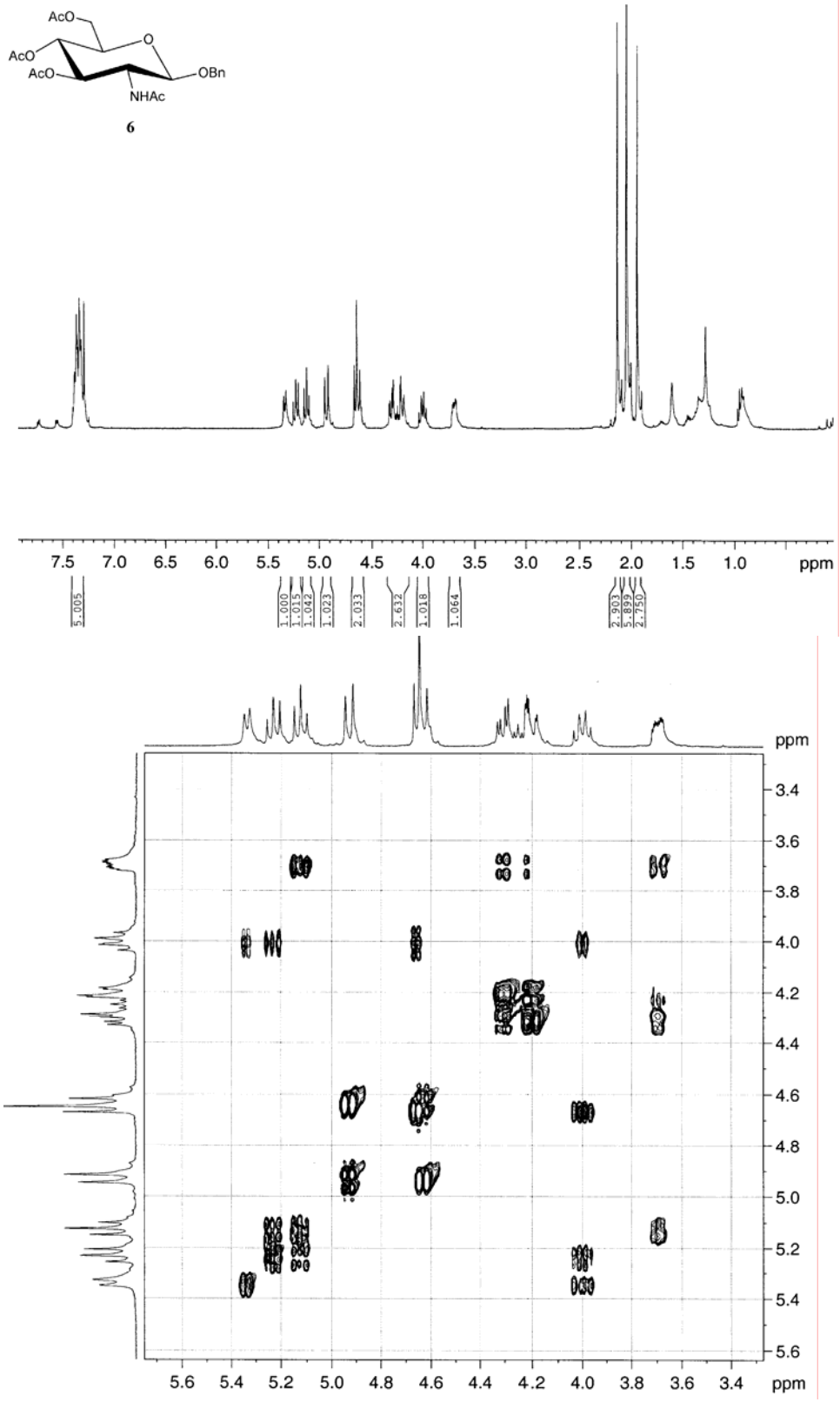
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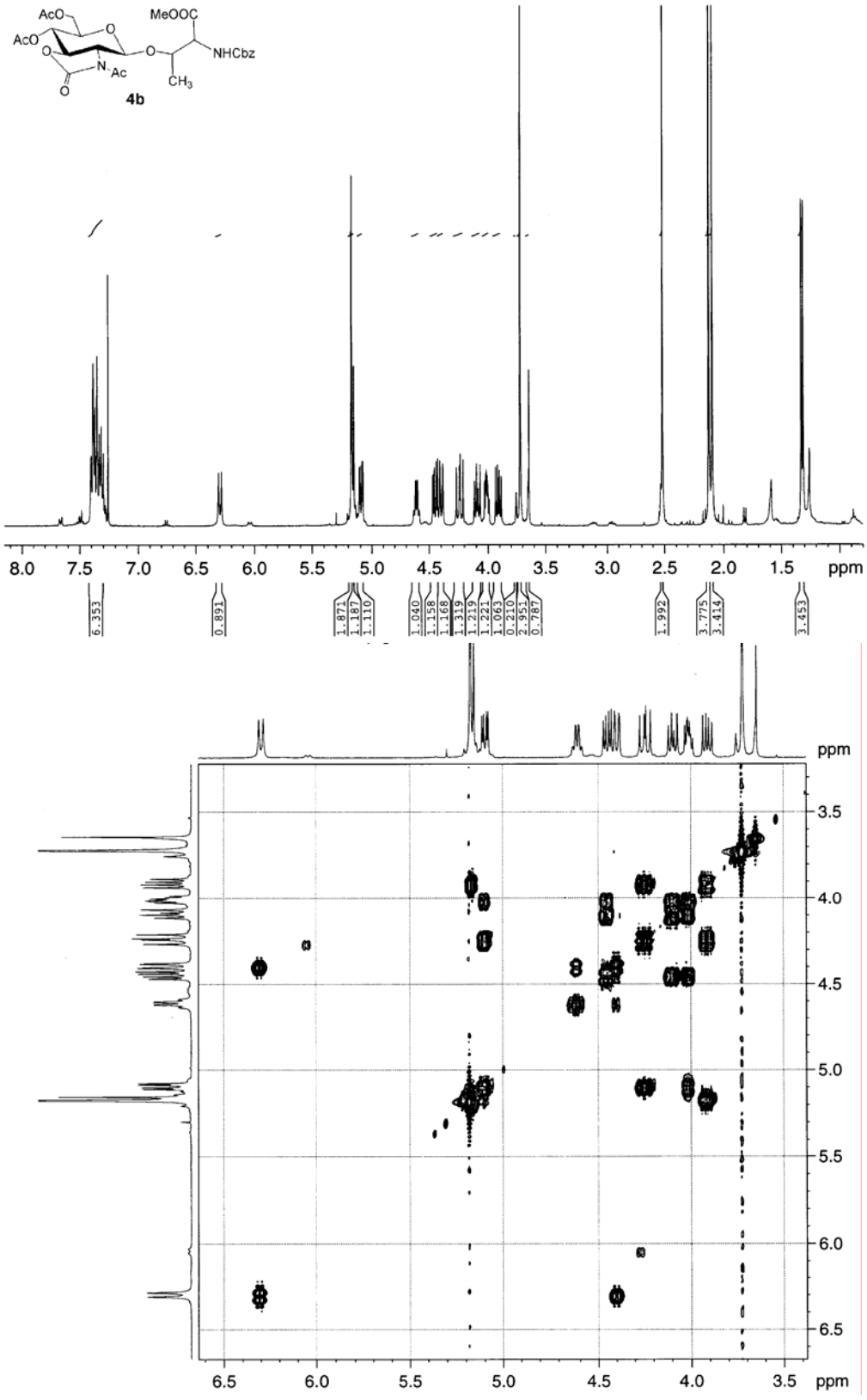
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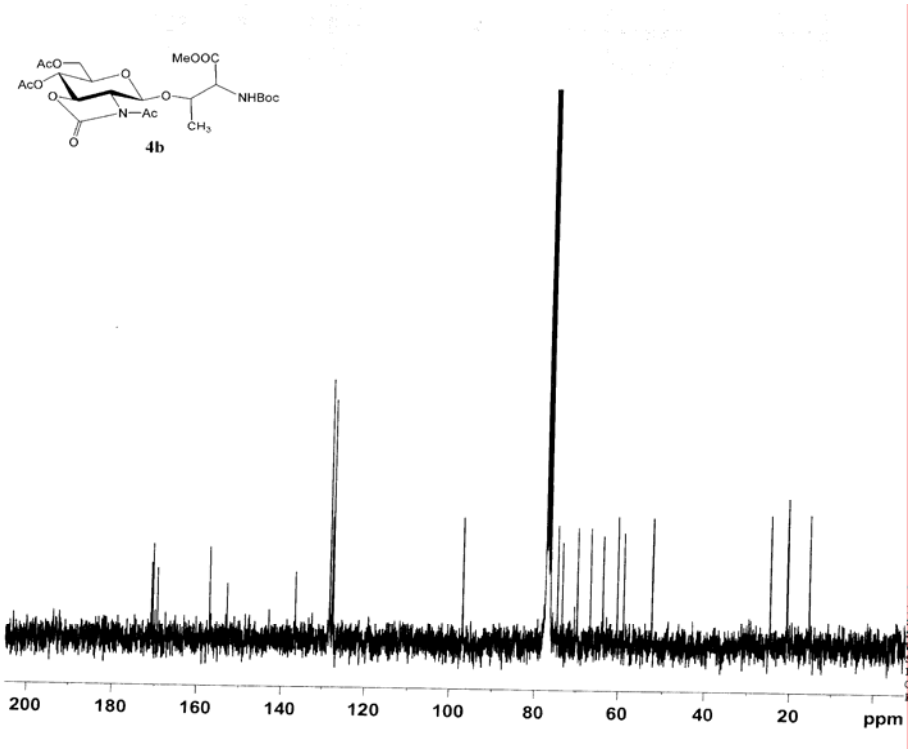
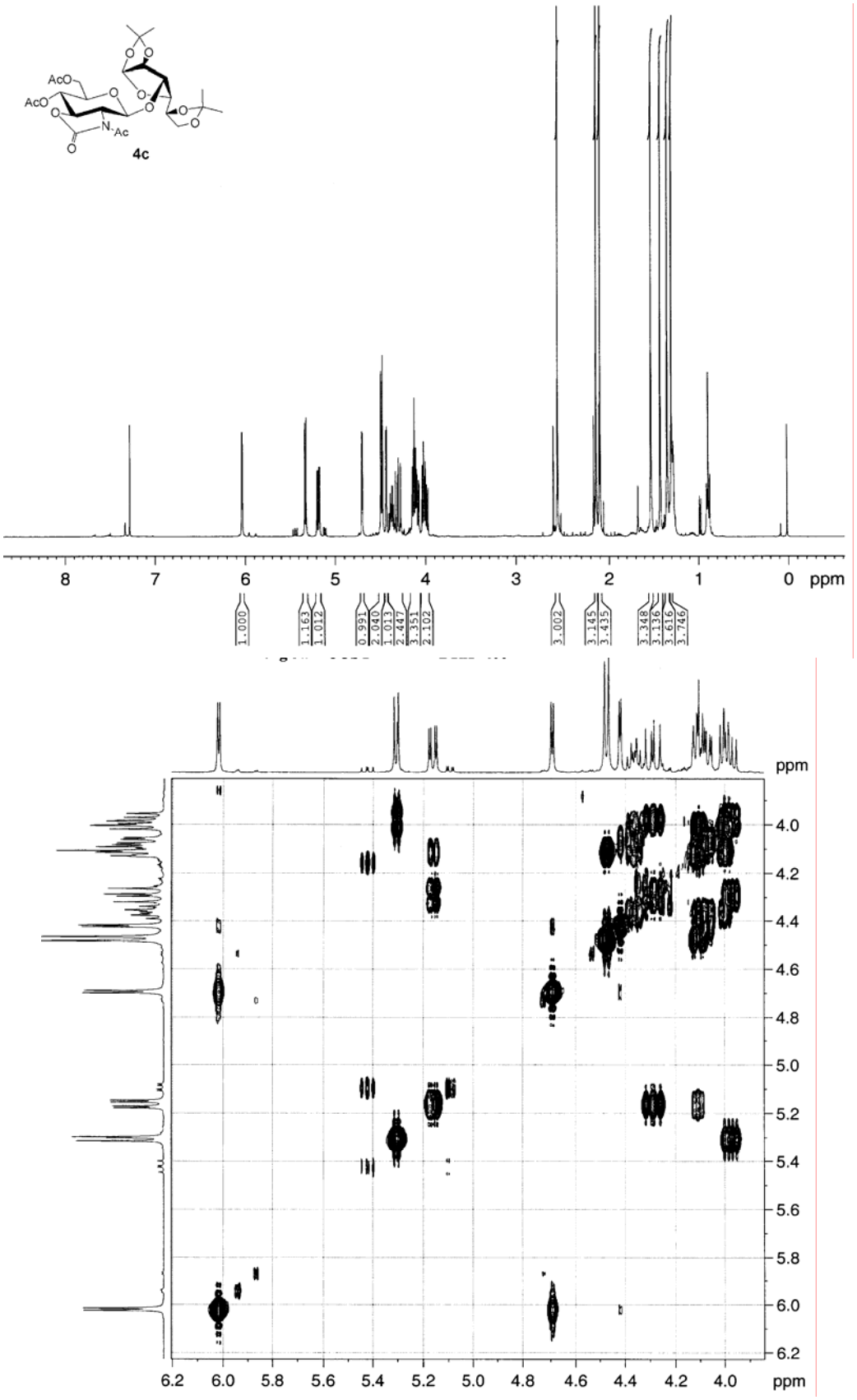
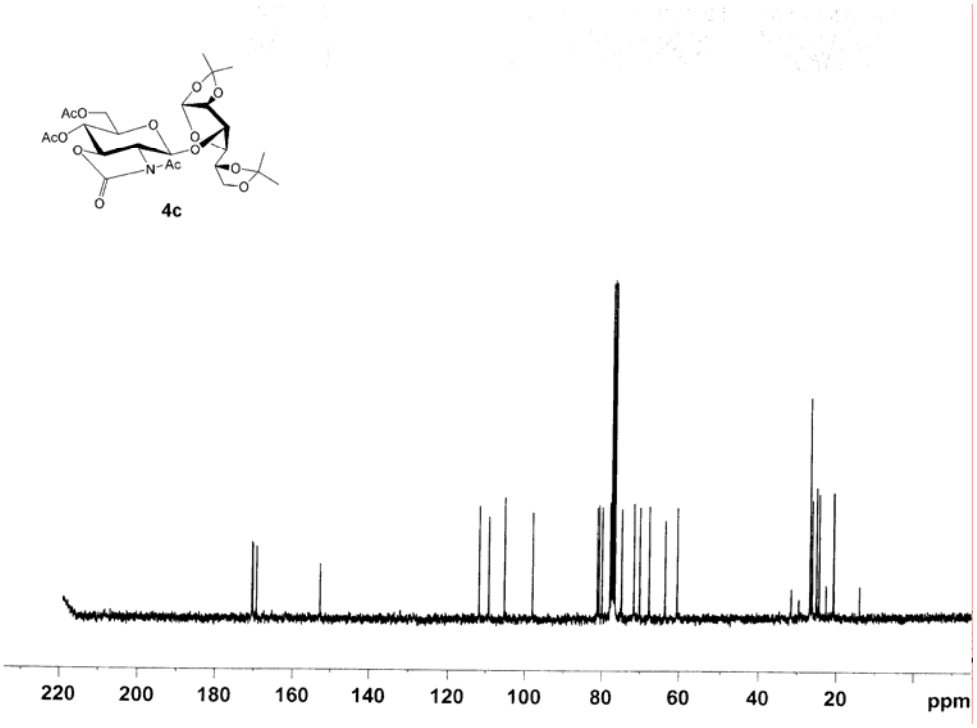
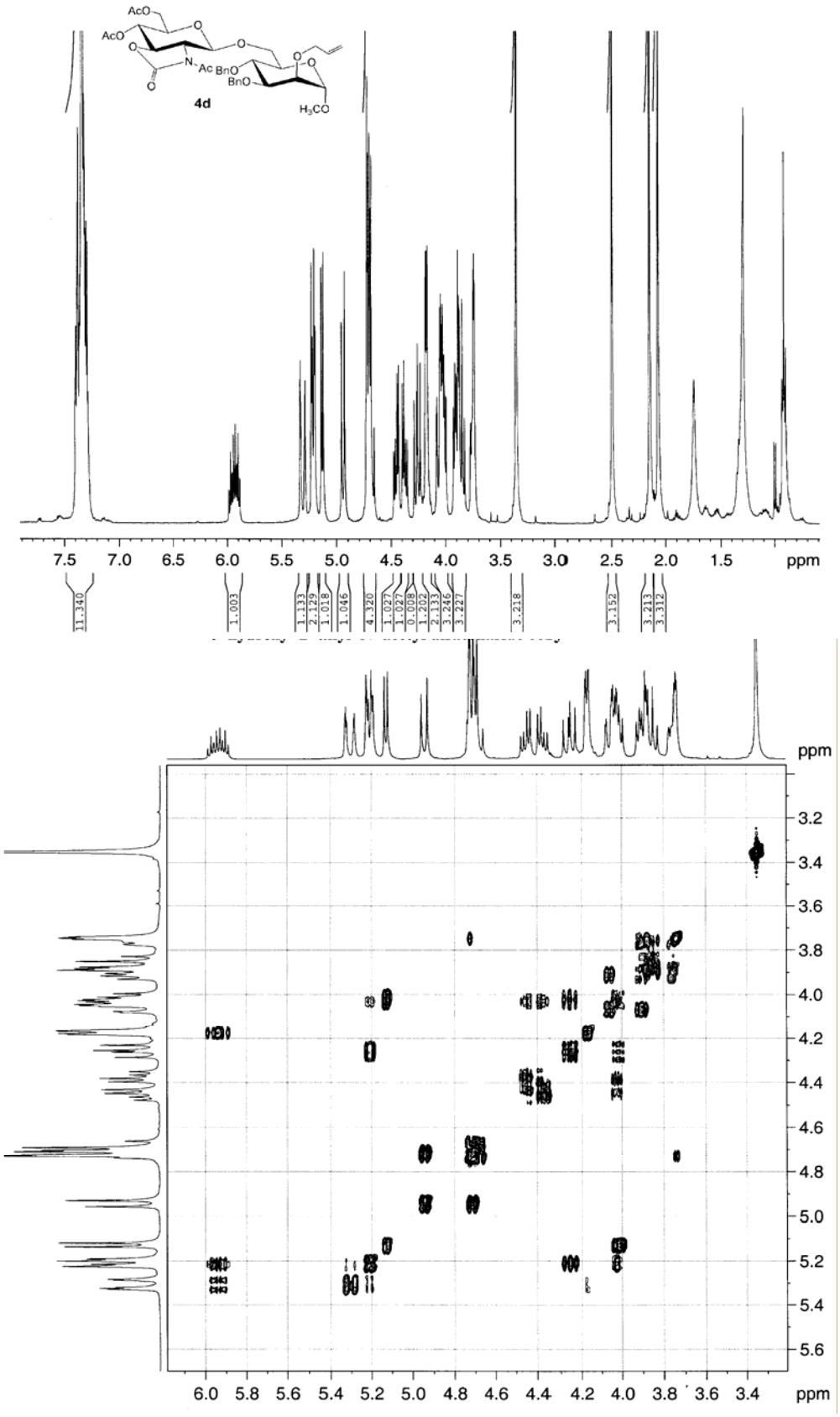
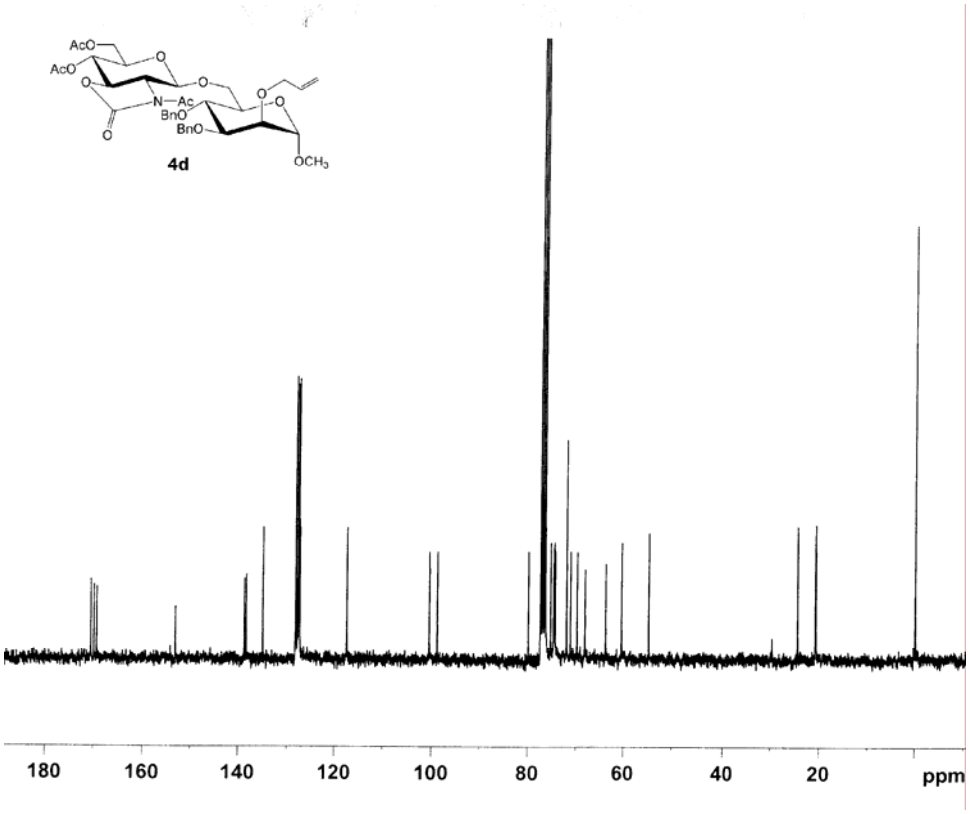
1.871
1.187
1.110
1.040
1.158
1.168
1.319
1.219
1.221
1.063
0.210
2.951
0.787
1.992
3.775
3.414
3.453
ppm
3.5
4.0
4.5
5.0
5.5
6.0
6.5
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm

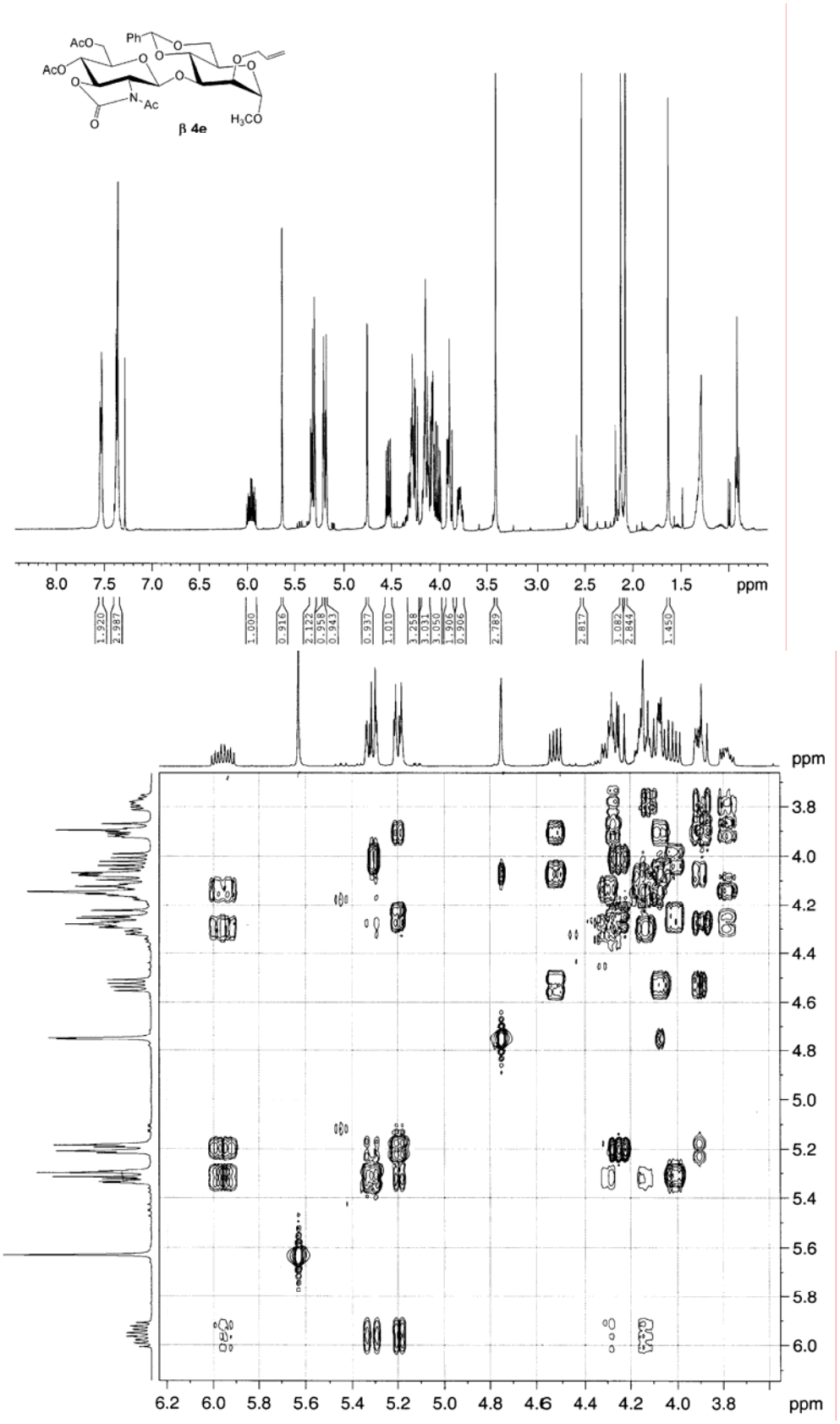

AcO
AcO
O
O
N—Ac
O
MeOOC
NHBoc
CH3
4b
200
180
160
140
120
100
80
60
40
20
ppm

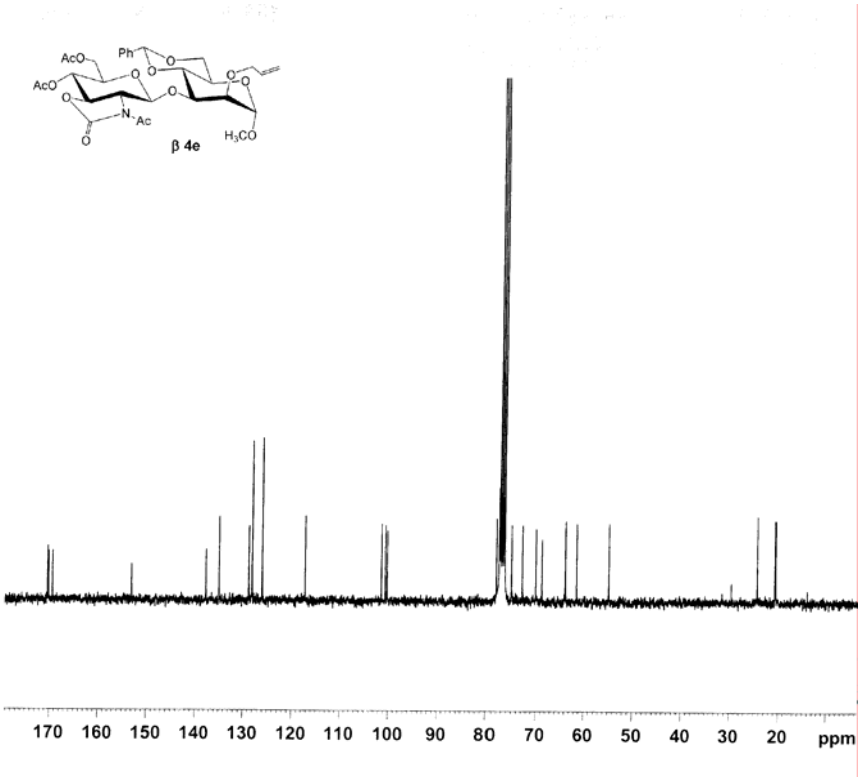

AcO
AcO
N
Ac
4c
8
7
6
5
4
3
2
1
0
ppm
1.000
1.163
1.012
0.991
2.040
1.013
2.447
3.351
2.102
3.002
3.145
3.435
3.348
3.136
3.616
3.746
ppm
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.2
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
ppm

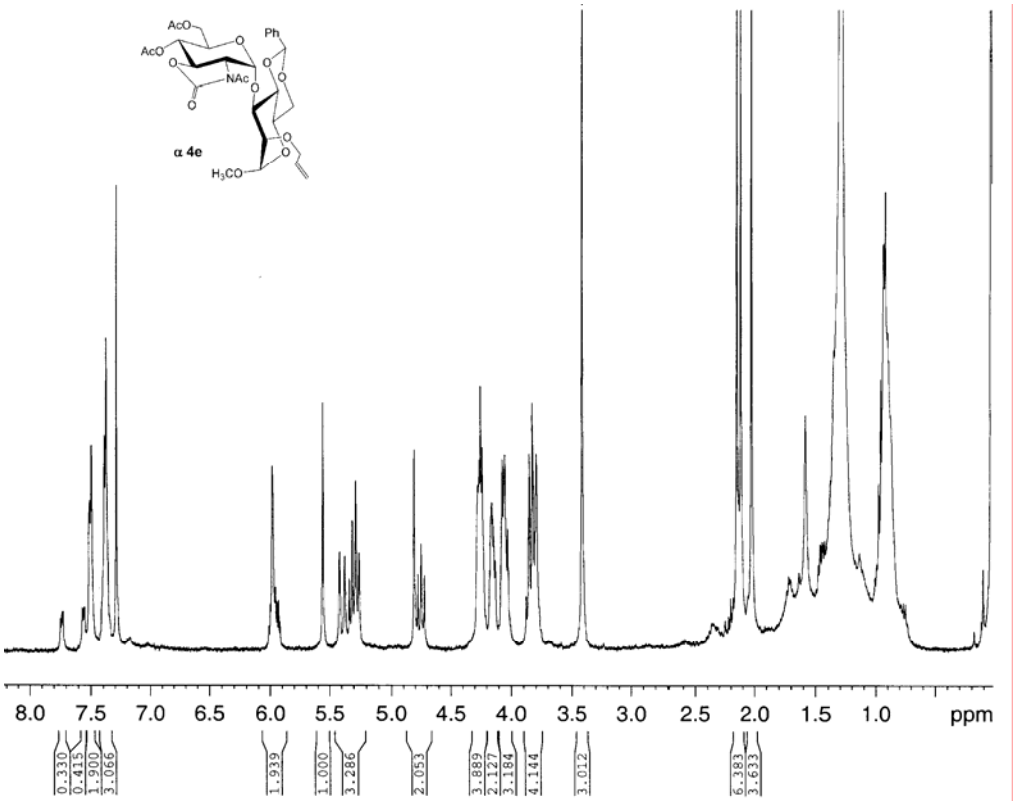

AcO
AcO
O
O
N-Ac
O
O
O
O
O
O
4c
220
200
180
160
140
120
100
80
60
40
20
ppm

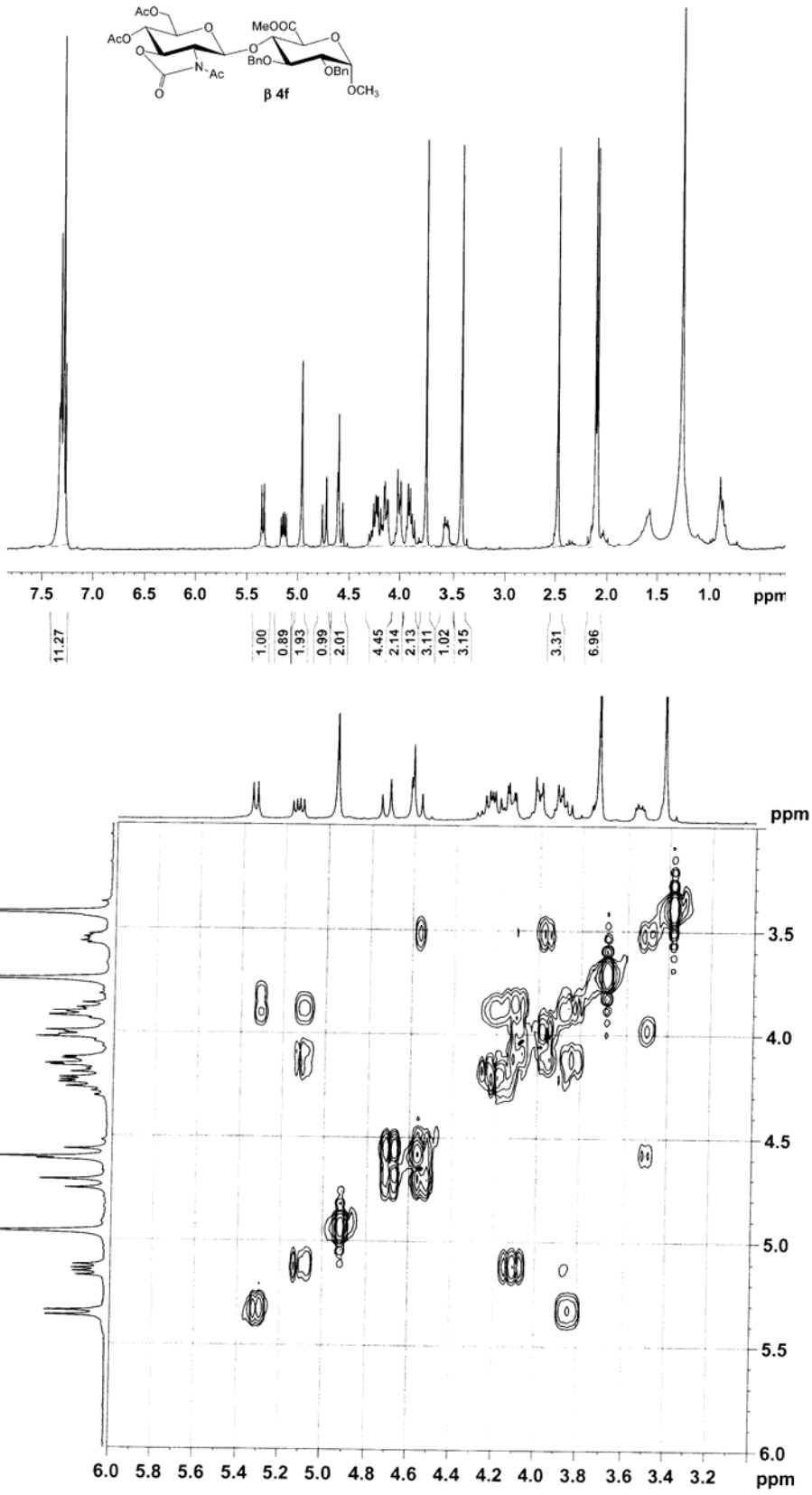

AcO
AcO
O
O
N
Ac
BnO
BnO
O
O
O
O
H3CO
4d
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
11.340
1.003
1.133
2.129
1.018
1.046
4.320
1.027
1.027
0.008
1.202
2.133
3.246
3.227
3.218
3.152
3.213
3.312
ppm
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
ppm

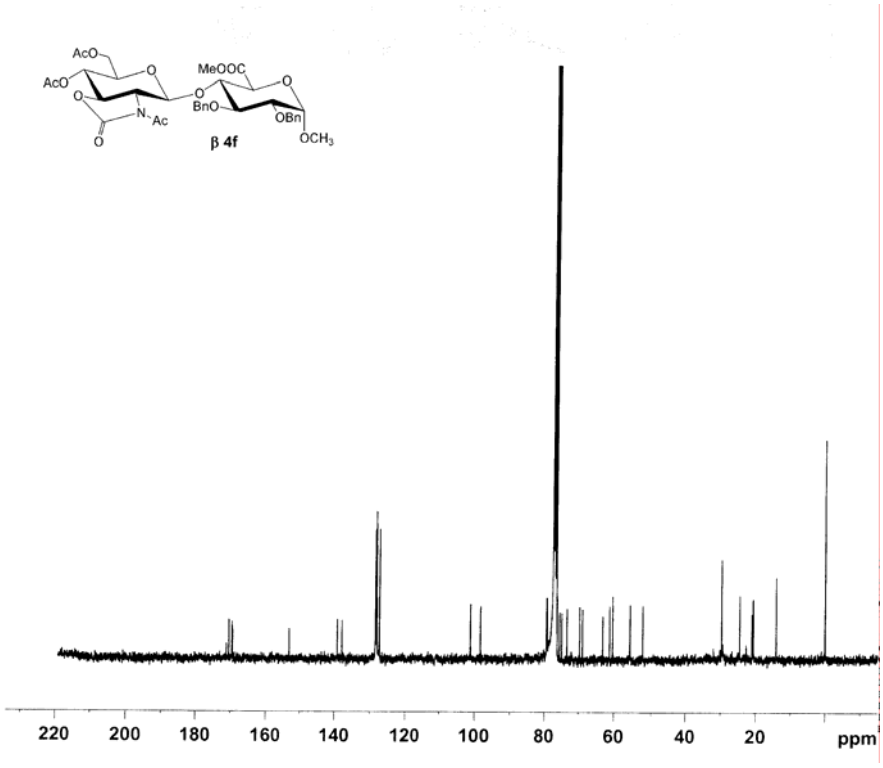

AcO
AcO
O
O
O
N
Ac
BnO
BnO
O
O
O
OCH3
4d
180
160
140
120
100
80
60
40
20
ppm

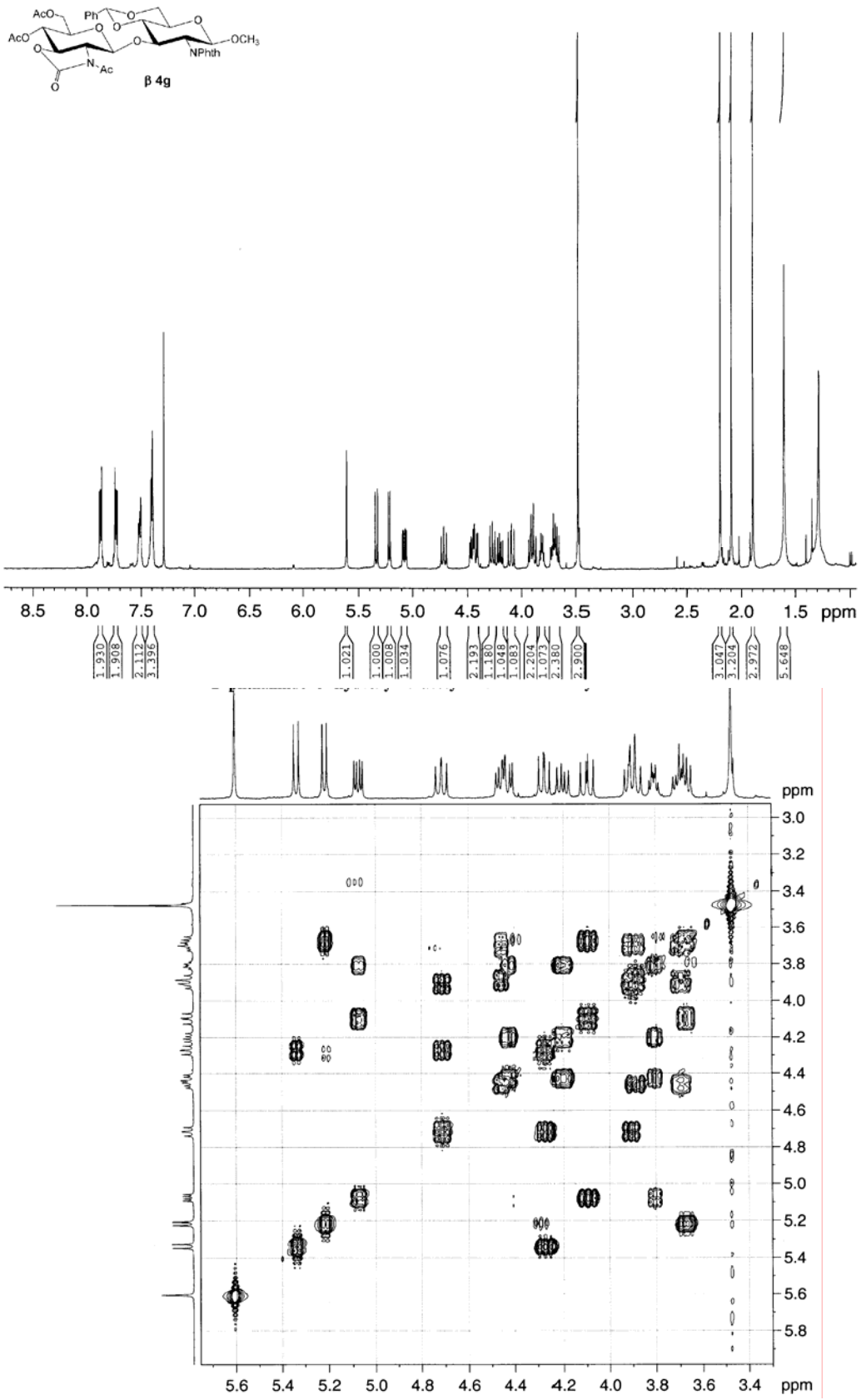

AcO
Ph
AcO
O
N
Ac
O
H3CO
β 4e
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm
1.920 2.987 1.000 0.916 2.122 0.958 0.943 0.937 1.010 3.258 3.031 3.050 1.906 0.906 2.789 2.817 3.082 2.844 1.450
ppm
3.8 4.0 4.2 4.4 4.6 4.8 5.0 5.2 5.4 5.6 5.8 6.0
6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 ppm

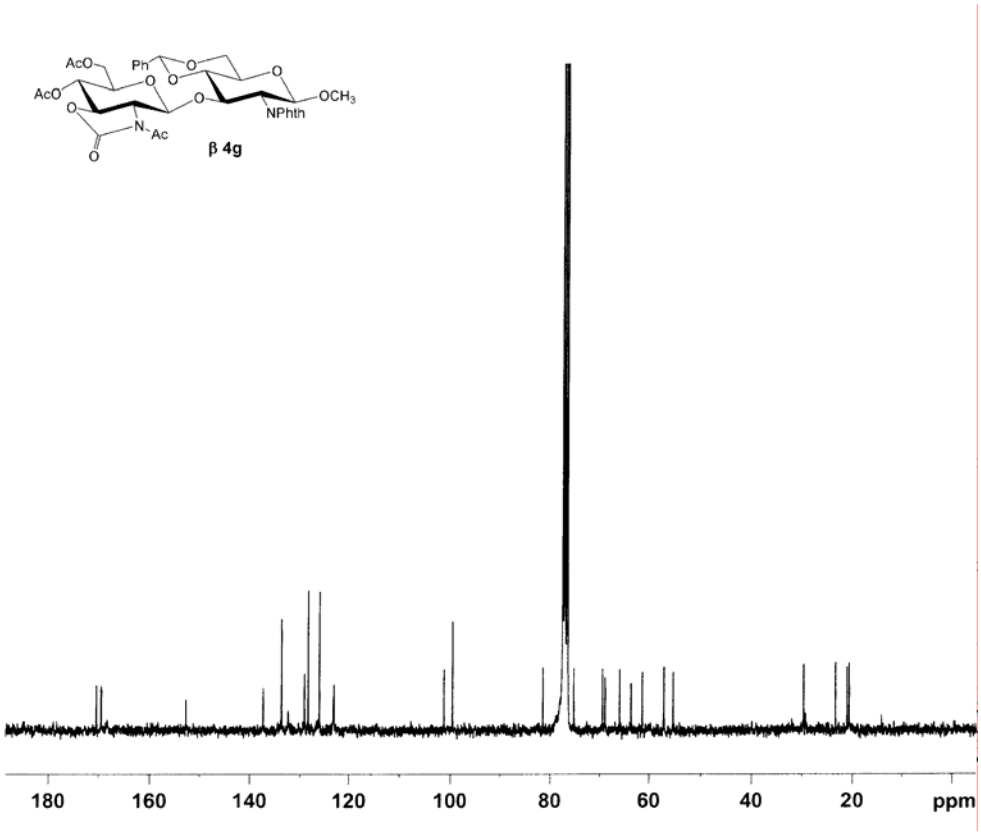

β 4e
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

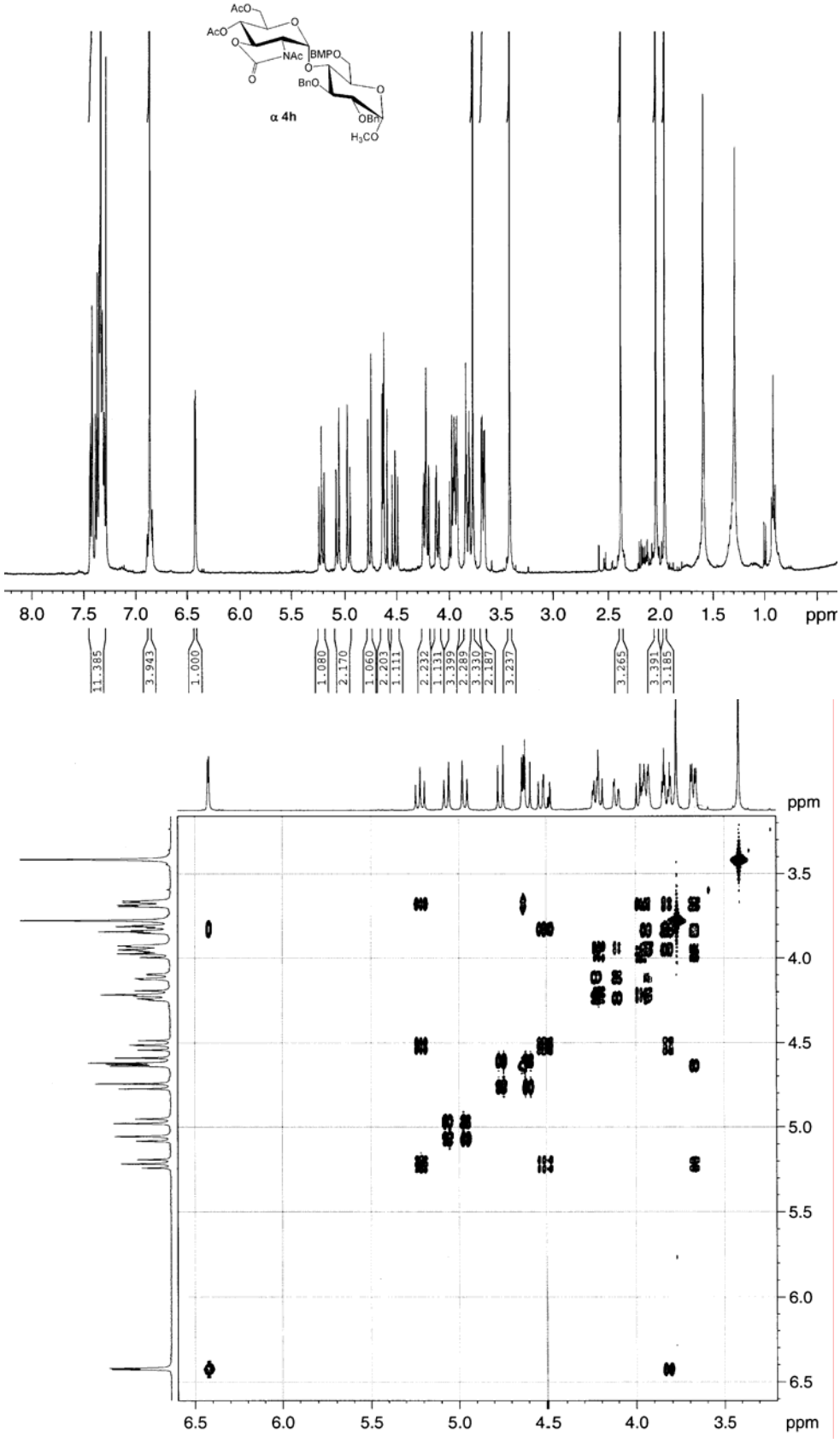

α 4e
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
0.330
0.415
1.900
3.066
1.939
1.000
3.286
2.053
3.889
2.127
3.184
4.144
3.012
6.383
3.633

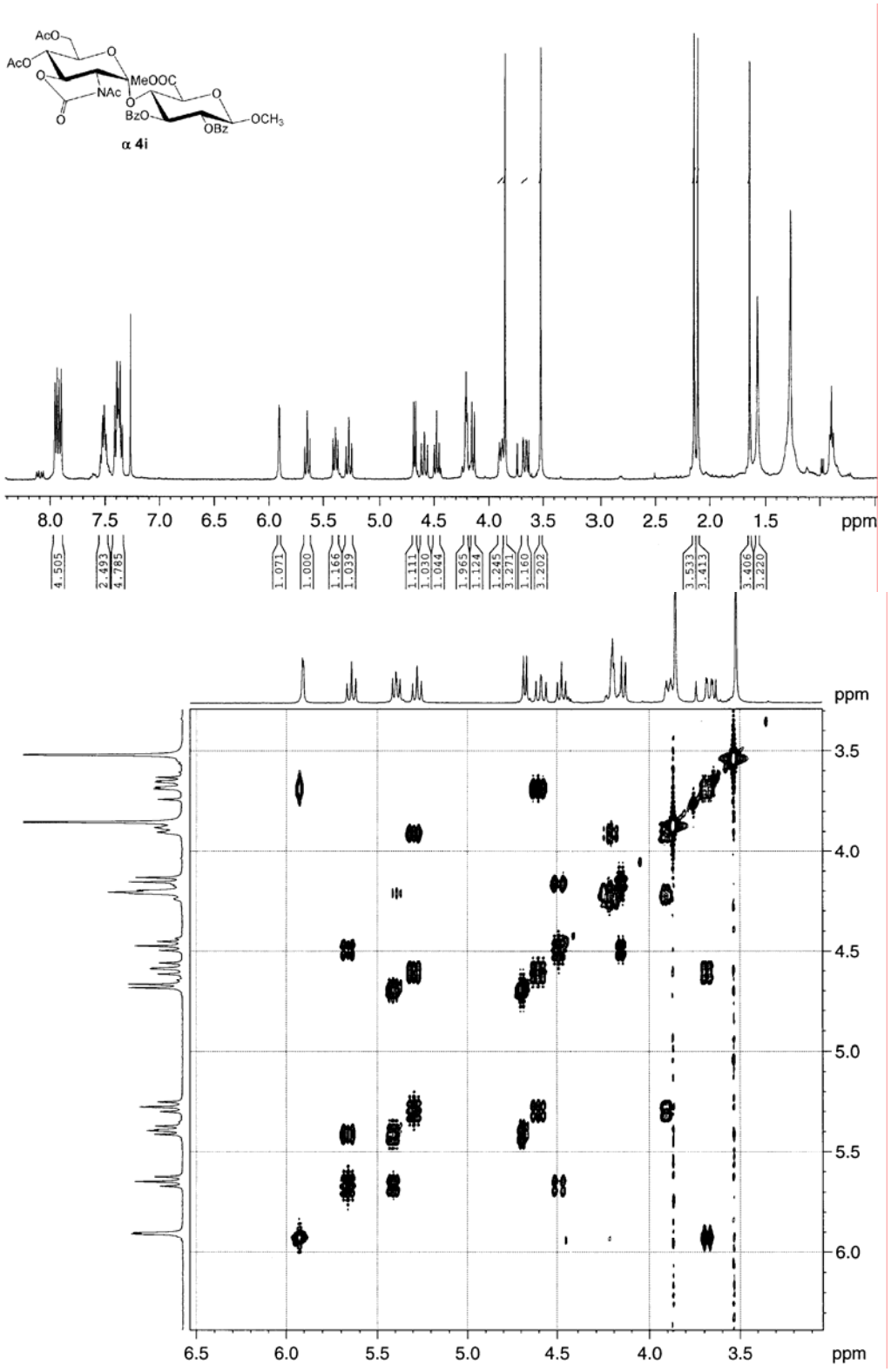

β 4f
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
11.27
1.00
0.89
1.93
0.99
2.01
4.45
2.14
2.13
3.11
1.02
3.15
3.31
6.96
ppm
3.5
4.0
4.5
5.0
5.5
6.0
6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 ppm

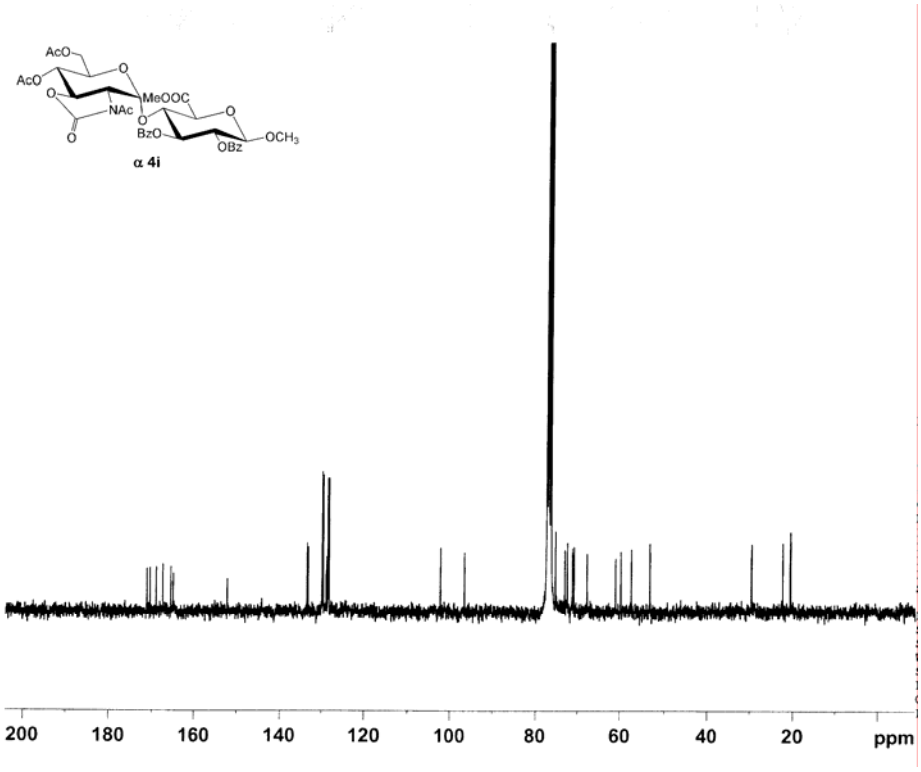

AcO
AcO
O
O
N
Ac
O
MeOOC
O
BnO
OBn
OCH3
β 4f
220
200
180
160
140
120
100
80
60
40
20
ppm

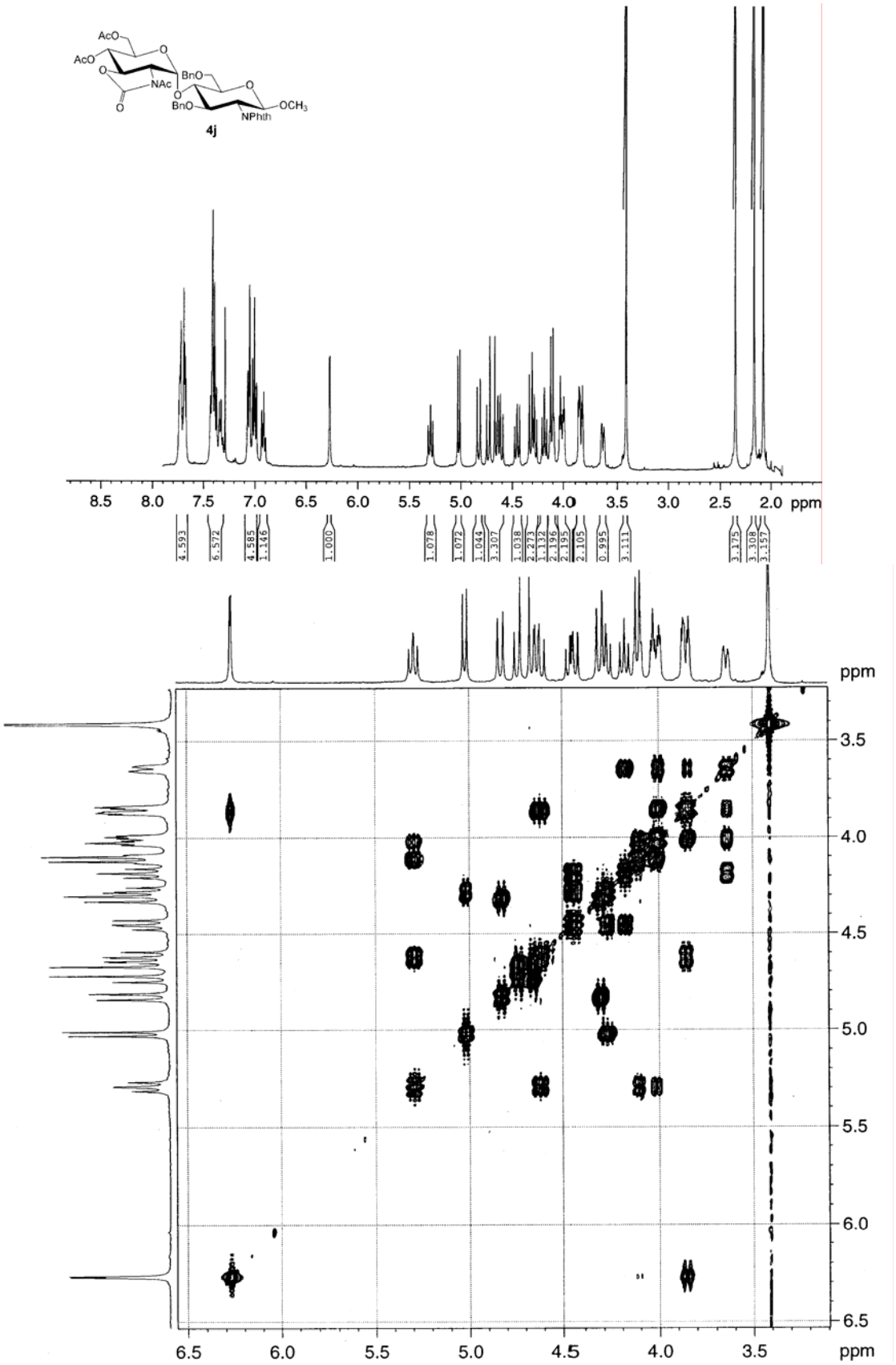

β 4g
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm
1.930 1.908 2.112 3.396 1.021 1.000 1.008 1.034 1.076 2.193 1.180 1.048 1.083 2.204 1.073 2.380 2.900 3.047 3.204 2.972 5.648
ppm
3.0 3.2 3.4 3.6 3.8 4.0 4.2 4.4 4.6 4.8 5.0 5.2 5.4 5.6 5.8
5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 ppm

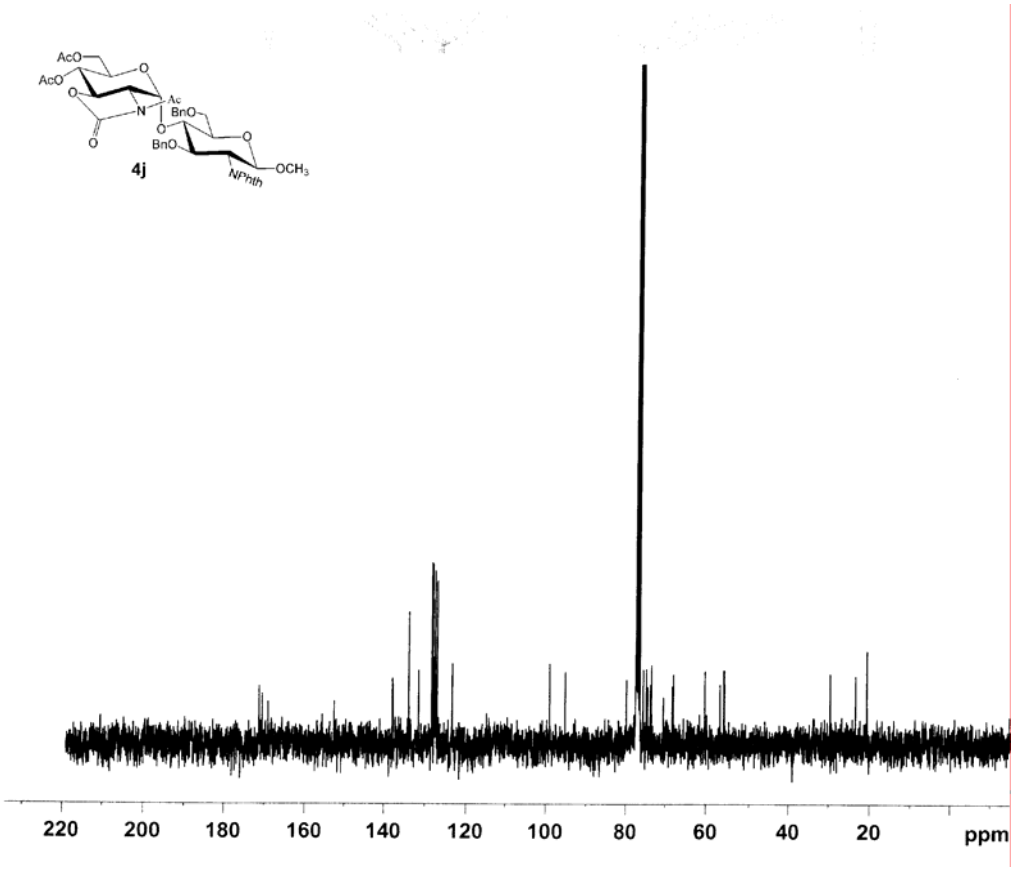

AcO
Ph
O
O
O
AcO
O
O
OCH3
NPhth
N
Ac
O
β 4g
180
160
140
120
100
80
60
40
20
ppm


AcO
AcO
NAc
BMPO
BnO
OBn
H3CO
α 4h
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
11.385
3.943
1.000
1.080
2.170
1.060
2.203
1.111
2.232
1.131
3.399
2.289
3.330
2.187
3.237
3.265
3.391
3.185
ppm
3.5
4.0
4.5
5.0
5.5
6.0
6.5
6.5 6.0 5.5 5.0 4.5 4.0 3.5 ppm


AcO
AcO
O
O
NAc
O
MeOOC
O
BzO
OBz
OCH3
α 4i
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
4.505
2.493
4.785
1.071
1.000
1.166
1.039
1.111
1.030
1.044
1.965
1.124
1.245
3.271
1.160
3.202
3.533
3.413
3.406
3.220
ppm
3.5
4.0
4.5
5.0
5.5
6.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm


AcO
AcO
O
O
NAc
O
MeOOC
O
BzO
OBz
OCH3
α 4i
200
180
160
140
120
100
80
60
40
20
ppm


AcO
AcO
O
NAc
O
BnO
BnO
O
OCH3
NPhth
4j
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 ppm
4.593
6.572
4.585
1.146
1.000
1.078
1.072
1.044
3.307
1.038
2.273
1.132
2.196
2.195
2.105
0.995
3.111
3.175
3.308
3.157
ppm
3.5
4.0
4.5
5.0
5.5
6.0
6.5
6.5 6.0 5.5 5.0 4.5 4.0 3.5 ppm

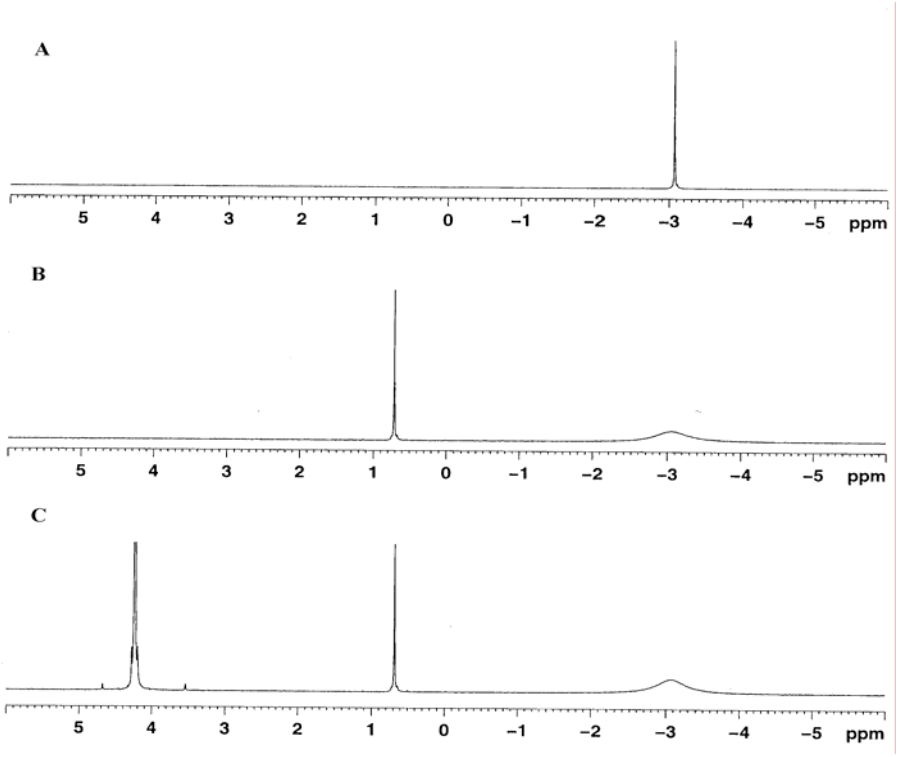

AcO
AcO
O
O
N
Ac
BnO
O
O
BnO
OCH3
NPhth
4j
220
200
180
160
140
120
100
80
60
40
20
ppm

Representative procedure for NMR-scale activation of thioglycoside 2 with BSP, TTBP and Tf_2O at -60 ^oC. To a solution of thioglycoside **2** (4.4 mg, 0.01 mmol), BSP (2.1 mg, 0.01 mmol) and TTBP (5.0 mg, 0.02 mmol) in CD_2Cl_2 (0.8 mL) in a 5 mm NMR tube at -60 ^oC, under an argon atmosphere, was added 1.1eq of Tf_2O (0.011 mmol, 1.9 μL). The NMR tube was immediately transferred to the pre-cooled NMR probe (-60 ^oC), and the ^1H and ^{19}F spectra recorded. The α-glucosyl triflate [major component, ^1H NMR δ 6.91 (H-1, d, $J_{1,2}$ = 2.4 Hz,); ^{19}F NMR δ 0.69] and β-glucosyl triflate [minor component, ^1H NMR δ 6.41 (H-1, d, $J_{1,2}$ = 7.2 Hz,); ^{19}F NMR δ 0.69] were formed immediately. Other signals at δ -3.08 ($TTBPH^+OTf^-$) and δ 4.26 (Tf_2O) were observed in the ^{19}F NMR spectrum. Homonuclear decoupling experiments were performed to confirm the anomeric proton of α- and β-glucosyl triflates.

Panel A: The ^{19}F spectrum of BSP and TTBP with 0.6eq of Tf_2O in CD_2Cl_2 at -60 ^oC.

Panel B: The ^{19}F spectrum of thioglycoside **2**, BSP and TTBP with 0.6eq of Tf_2O in CD_2Cl_2 at -60 ^oC.

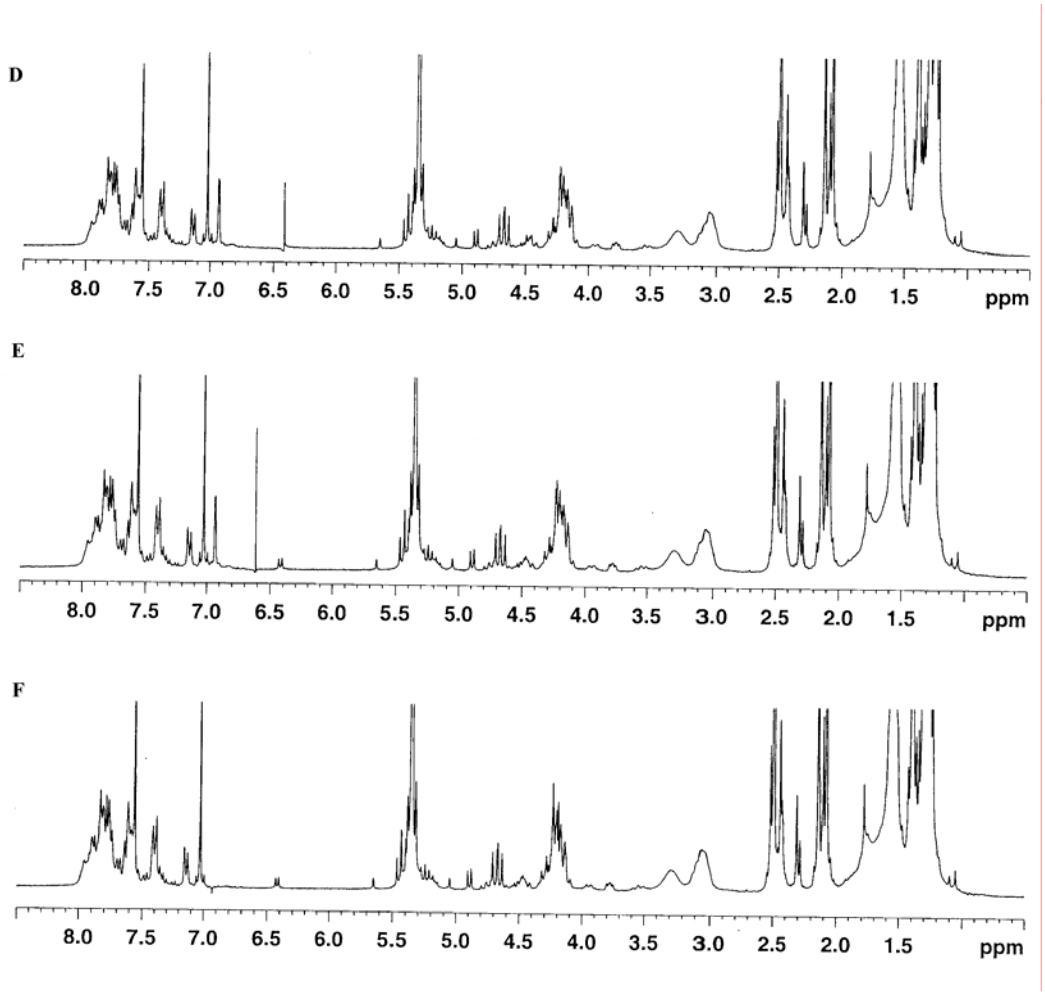
Panel C: The ^{19}F spectrum of thioglycoside **2**, BSP and TTBP with > 2eq of Tf_2O in CD_2Cl_2 at -60 ^oC.



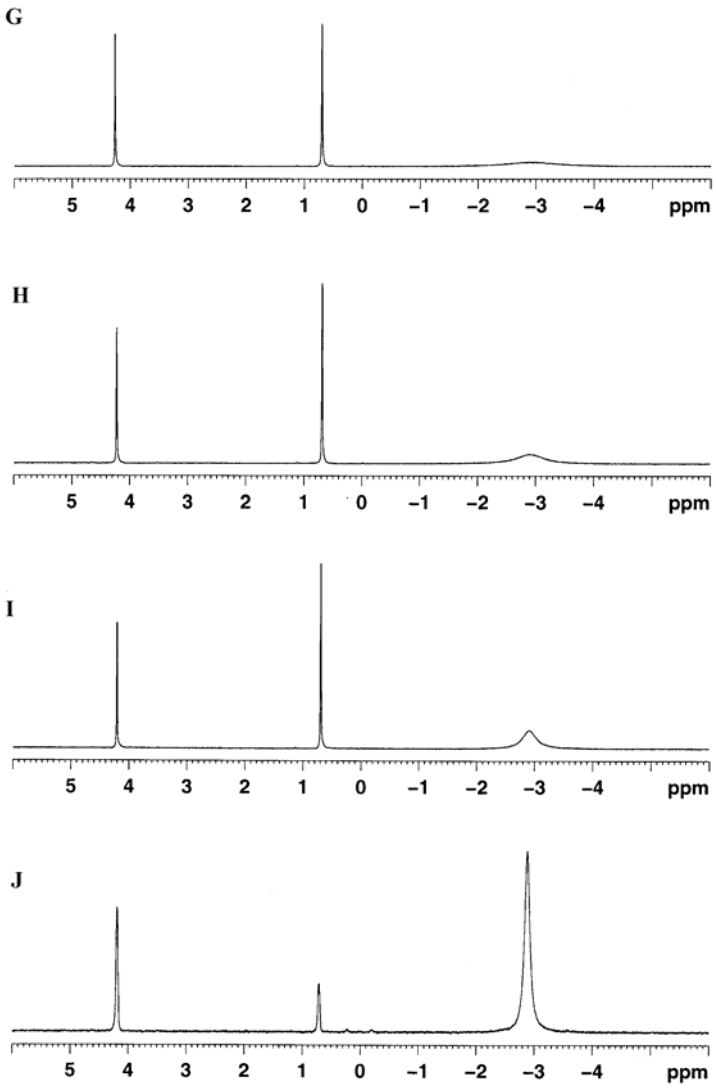
Panel D: Homonuclear decoupling at δ 6.4 (anomeric proton of β-glucosyl triflate), only signal change is observed at δ 4.5 (corresponding H-2 of β-glucosyl triflate intermediate).

Panel E: Control Homonuclear decoupling at δ 6.6 (blank area), no signal change observed.

Panel F: Homonuclear decoupling at δ 6.9 (anomeric proton of α-glucosyl triflate), only signal change is observed at δ 4.2 (corresponding H-2 of α-glucosyl triflate).



In a continuation of low temperature NMR experiments, the probe was gradually warmed with the acquisition of ^{1}H and ^{19}F NMR spectra at every 20^{o}C. The obvious decomposition of glucosyl triflate intermediate was detected at 0 ^{o}C (^{19}F NMR spectra shown below).



Panel G, H, I, J: The ^{19}F spectrum of thioglycoside **2**, BSP and TTBP with > 2eq of Tf_2O in CD_2Cl_2 at -60^{o}C, -40^{o}C, -20^{o}C and 0^{o}C respectively.