Electronic Supplementary Information

Stereoselective copper-catalyzed Chan-Lam-Evans *N*-arylation of glucosamines with arylboronic acids at room temperature

Alexandre Bruneau, Jean-Daniel Brion, Mouâd Alami* and Samir Messaoudi*

Univ. Paris-Sud, CNRS, BioCIS-UMR 8076, LabEx LERMIT, Laboratoire de Chimie Thérapeutique, Faculté de Pharmacie, 5 rue J.-B. Clément, Châtenay-Malabry, 92296 France.

samir.messaoudi@u-psud.fr, mouad.alami@u-psud.fr,
Phone: 33(0)1.46.83.58.28 ; Fax: 33(0)1.46.83.58.28

Contents

Experimental Section

General Experimental Methods

The compounds were all identified by usual physical methods, e.g., ^{1}H NMR,^{13}C NMR, IR, MS (ESI).^{1}H and ^{13}C NMR spectra were measured in $CDCl_3$, C_6D_6 and Acetone-d6 with a Bruker Avance-300. ^{1}H chemical shifts are reported in ppm from an internal standard TMS or of residual solvent peak. ^{13}C chemical shifts are reported in ppm from the residual solvent peak. IR spectra were measured on a Bruker Vector 22 spectrophotometer. MS were recorded on a Micromass spectrometer. Analytical TLC was performed on Merck precoated silica gel 60F plates. Merck silica gel 60 (0.015–0.040 mm) was used for column chromatography. Melting points were recorded on a Büchi B-450 apparatus and are uncorrected. High resolution mass spectra (HR-MS) were recorded on a Bruker MicroTOF spectrometer, using ESI with methanol as the carrier solvent. Nominal and exact m/z values are reported in Daltons. Aryl boronic acids are commercially available. Aminosaccharides **1a**[1] and **1e**,[1] **1b**,[2] **1c**,[3] **1d**,[4] **1f**[5] were synthesized as according to literature protocols.

Aminomannose **1g** is not enough stable for its characterization and was used immediately after its preparation.

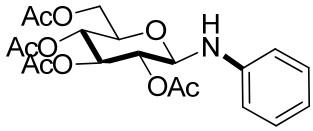
General Procedure for Copper-Catalyzed Coupling of Aminosugar 1a-g with Aryl boronic acids

A 50 mL round bottom flask was charged with $Cu(OAc)_2$ (20 mol%), aminosugar **1** (0.575 mmol), pyridine (0.575 mmol, 1 equiv) and CH_2Cl_2 (1 mL). Arylboronic acid **2** (2.5 equiv) was added in three portions at t = 0 (0.575 mmol, 1 equiv), 3 h30 (0.431 mmol, 0.75 equiv) and 7 h (0.431 mmol, 0.75 equiv). The reaction mixture was stirred under pressure of balloon of air. After 24h, the mixture was filtered through celite eluting with ethyl acetate and CH_2Cl_2. The filtrate was concentrated under vacuum and the residue purified by silica gel column chromatography gave the desired product **3** or **4**.

1 C. Badía, F. Souard, C. Vicent, *J. Org. Chem*, 2012, **77**, 10870.
2 A. D. Dorsey, J. E. Barbarow, D. Trauner, *Org. Lett*, 2003, **5**, 3237.
3 G. Zhou, P. Zhang, Y. Pan, J. Guo, *Org. Prep. Proc. Int.*, 2005, **37**, 65
4 Joseph, R.; Dyer, F. B.; Garner, P. *Org. Lett*, 2013, **15**, 732.
5 X. Zheng, J. Morgan, S. K. Pandey, Y. Chen, E. Tracy, H. Baumann, J. R. Missert, C. Batt, J. Jackson, D. A. Bellnier, B. W. Henderson, R. K. Pandey, *J. Med. Chem*., 2009, **52**, 4306.

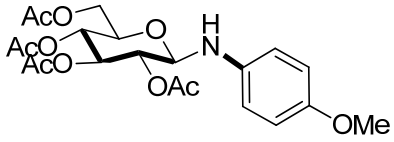
Characterization data of β-aryl *N*-glycoside 3a-p

(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(phenylamino)tetrahydro-2H-pyran-3,4,5-triyl triacetate **3a:**



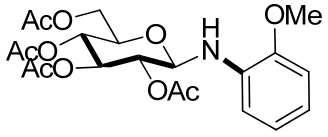
R_f = 0.49 (CH_2Cl_2; EtOAc, 92:8); white solid recrystallized from diisopropyl ether; m.p. = 93-95°C; $[\alpha]_D^{24}$ +18 (c,1.0 in $CHCl_3$); IR (neat): 3437, 3349, 3049, 1744, 1605, 1370, 1221, 1034 $cm^{-1.}$ ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 (t, *J* = 7.8 Hz, 2H), 6.83 (t, *J* = 7.4 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 2H), 5.37 (t, *J* = 9.4 Hz, 1H), 5.13 – 4.99 (m, 2H), 4.83 – 4.70 (m, 2H), 4.30 (dd, *J* = 12.2, 5.3 Hz, 1H), 4.09 (dd, *J* = 12.2, 2.2 Hz, 1H), 3.83 (ddd, *J* = 9.9, 5.2, 2.2 Hz, 1H), 2.05 (s, 3H), 2.04 (s, 3H), 2.03 (s, 6H). ^{13}C NMR (75 MHz, Acetone) δ 170.63(2C=O), 170.30(C=O), 170.11(C=O), 146.79(C), 129.80(2CH), 119.69(CH), 115.14(2CH), 84.01(CH), 74.27(CH), 72.95(CH), 72.22(CH), 69.82(CH), 63.06(CH_2), 20.68(CH_3), 20.62(3CH_3). HR-MS(ESI): m/z calculated for $C_{20}H_{25}NO_9Na$ 446.1427 obtained 446.1423

(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-((4-methoxyphenyl)amino)tetrahydro-2H-pyran-3,4,5-triyl triacetate **3b:**



R_f = 0.42 (CH_2Cl_2 ; EtOAc, 92:8) ; white solid recrystallized from diisopropyl ether; m.p. = 129-130°C; $[\alpha]_D^{24}$ –40 (c,1.0 in $CHCl_3$); IR (neat): 3457, 3415, 3246, 1755, 1514, 1366, 1232, 1209, 1109, 1032 $cm^{-1.}$ ^{1}H NMR (300 MHz, C_6D_6) δ = 6.77 (d, *J*=8.9 Hz, 2H), 6.49 (d, *J*=8.9 Hz, 2H), 5.50 (t, *J*=9.5 Hz, 1H), 5.29 (t, *J*=9.7 Hz, 1H), 5.10 (t, *J*=9.3 Hz, 1H), 4.48 (t, *J*=9.8 Hz, 1H), 4.32 (dd, *J*=12.2, 4.7 Hz, 1H), 4.17 (dd, *J*=10.4, 4.3 Hz, 1H), 3.92 (dd, *J*=12.3, 2.1 Hz, 1H), 3.35 (d, *J*=6.4 Hz, 3H), 3.28 – 3.11 (m, 1H), 1.72 (s, 3H), 1.72 (s, 3H), 1.70 (s, 3H), 1.63 (s, 3H). ^{13}C NMR (75 MHz, C_6D_6) δ 170.67(C=O), 170.34(C=O), 170.11(C=O), 169.63(C=O), 154.79(C), 139.27(C), 117.00(2CH), 115.35(2CH), 85.72(CH), 74.01(CH), 73.04(CH), 72.06(CH), 69.46(CH), 62.35(CH_2), 55.57(CH_3), 20.55(4CH_3). HR-MS(ESI): m/z calculated for $C_{21}H_{27}NO_{10}Na$ 476.1533 obtained 476.1533

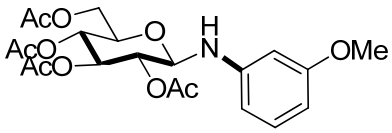
(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-((2-methoxyphenyl)amino)tetrahydro-2H-pyran-3,4,5-triyl triacetate **3c:**



R_f = 0.60 (CH_2Cl_2; EtOAc, 92:8); colorless oil; $[\alpha]_D^{24}$ -3 (c,0.25 in $CHCl_3$); IR (neat): 3445, 3398, 1742, 1604, 1521, 1367, 1226, 1032 $cm^{-1.}$ ^{1}H NMR (300 MHz, C_6D_6) δ = 6.95 (td, *J*=7.7, 1.2 Hz, 1H), 6.78 (td, *J*=8.0, 1.8 Hz, 2H), 6.49 (d, *J*=8.0 Hz, 1H), 5.63 – 5.43 (m, 2H), 5.26 (t, *J*=9.9 Hz, 1H), 5.18 (t, *J*=9.3 Hz, 1H), 4.64 (t, *J*=9.4 Hz, 1H), 4.28 (dd, *J*=12.2, 4.8 Hz, 1H), 3.91 (dd, *J*=12.2, 2.3 Hz, 1H), 3.29 – 3.19 (m, 4H), 1.71 (s, 3H), 1.69 (s, 3H), 1.68 (s, 3H), 1.60 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.97(C=O), 169.71(C=O), 169.48(C=O), 168.96(C=O), 147.52(C), 134.94(C), 121.00(CH), 119.05(CH), 111.87(CH), 110.27(CH), 83.64(CH), 73.29(CH), 72.40(CH), 71.32(CH), 68.88(CH), 61.73(CH_2),

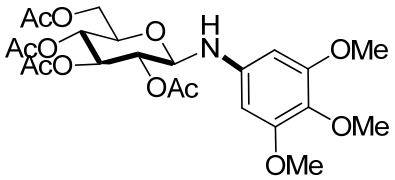
54.85(CH_3), 19.95($4CH_3$). HR-MS(ESI): m/z calculated for $C_{21}H_{27}NO_{10}Na$ 476.1533 obtained 476.1539

(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-((3-methoxyphenyl)amino)tetrahydro-2H-pyran-3,4,5-triyl triacetate **3d:**



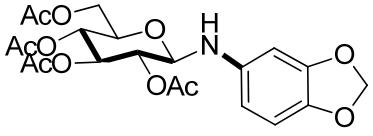
R_f = 0.30 (CH_2Cl_2; EtOAc, 92:8); white solid recrystallized from diisopropyl ether; m.p. = 114-115°C; $[\alpha]_D^{24}$ –31 (c,0.5 in $CHCl_3$); IR (neat): 3469, 3404, 3164, 1756, 1603, 1525, 1497, 1434, 1377, 1367, 1212, 1162, 1034 $cm^{-1.}$ ^{1}H NMR (300 MHz, C_6D_6) δ = 7.03 (t, *J*=8.1 Hz, 1H), 6.38 (dd, *J*=8.2 Hz, 1.7, 1H), 6.30 (t, *J*=2.2 Hz, 1H), 6.20 (dd, *J*=8.0, 1.5 Hz, 1H), 5.47 (t, *J*=9.5 Hz, 1H), 5.27 (t, *J*=9.7 Hz, 1H), 5.14 – 5.04 (m, 1H), 4.55 (d, *J*=5.3 Hz, 2H), 4.29 (dd, *J*=12.2, 4.8 Hz, 1H), 3.91 (dd, *J*=12.2, 2.2 Hz, 1H), 3.34 (s, 3H), 3.19 – 3.09 (m, 1H), 1.73 (s, 3H), 1.71 (s, 6H), 1.59 (s, 3H). ^{13}C NMR (75 MHz, C_6D_6) δ 170.15(C=O), 169.67(C=O), 169.38(C=O), 168.94(C=O), 161.09(C), 146.29(C), 129.86(CH), 107.50(CH), 104.74(CH), 101.19(CH), 83.85(CH), 73.22(CH), 72.31(CH), 71.35(CH), 68.65(CH), 61.59(CH_2), 54.41(CH_3), 19.88($2CH_3$), 19.83($2CH_3$). HR-MS(ESI): m/z calculated for $C_{21}H_{27}NO_{10}Na$ 476.1533 obtained 476.1539

(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-((3,4,5-trimethoxyphenyl)amino)tetrahydro-2H-pyran-3,4,5-triyl triacetate **3e:**



R_f = 0.59 (CH_2Cl_2; EtOAc, 92:8) ; red solid ; m.p. = 111-115 °C ; $[\alpha]_D^{24}$ -11 (c,0.5 in $CHCl_3$); IR (neat): 3426, 3378, 3304, 1741, 1510, 1366, 1212, 1127, 103 $cm^{-1.}$ ^{1}H NMR (300 MHz, Acetone) δ 6.16 (s, 2H), 5.39 (dd, *J* = 19.7, 10.2 Hz, 2H), 5.14 (t, *J* = 9.4 Hz, 1H), 5.01 (dd, *J* = 11.1, 8.2 Hz, 1H), 4.96 (d, *J* = 9.2 Hz, 1H), 4.26 – 4.16 (m, 1H), 4.13 – 4.04 (m, 2H), 3.77 (s, 6H), 3.62 (s, 3H), 2.01 (s, 3H), 1.99 (s,3H), 1.97 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (75 MHz, Acetone) δ 170.69(C=O), 170.59(C=O), 170.32(C=O), 170.11(C=O), 154.91(2C), 143.19(C), 132.53(C), 93.46(2CH), 84.22(CH), 74.24(CH), 73.00(CH), 72.04(CH), 69.88(CH), 63.27(CH_2), 60.64(CH_3), 56.30($2CH_3$), 20.71(CH_3), 20.62($2CH_3$), 20.58(CH_3). HR-MS(ESI): m/z calculated for $C_{23}H_{31}NO_{12}Na$ 536.1744 obtained 536.1749

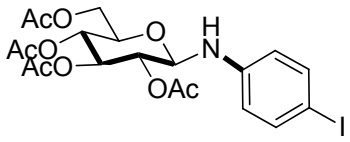
(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(benzo[d][1,3]dioxol-5-ylamino)tetrahydro-2H-pyran-3,4,5-triyl triacetate **3f:**



R_f = 0.39 (CH_2Cl_2; EtOAc, 92:8); white solid recrystallized from diisopropyl ether; m.p. = 134-135°C; $[\alpha]_D^{24}$ -37 (c,1;0 in $CHCl_3$); IR (neat): 3339, 3296, 1753, 1742, 1492, 1367, 1220, 1201, 1035 $cm^{-1.}$ ^{1}H NMR (300 MHz, C_6D_6) δ 6.58 (d, *J* = 8.3 Hz, 1H), 6.25 (d, *J* = 2.2 Hz, 1H), 5.93 (dd, *J* = 8.3, 2.2 Hz, 1H), 5.46 (t, *J* = 9.4 Hz, 1H), 5.34 (dd, *J* = 6.2, 1.2 Hz, 2H), 5.25 (t, *J* = 9.7 Hz, 1H), 5.04 (t, *J* = 9.2 Hz, 1H),

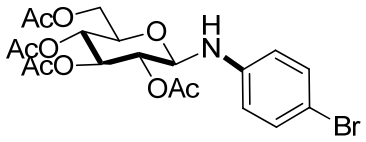
4.44 – 4.32 (m, 1H), 4.32 – 4.18 (m, 2H), 3.91 (dd, *J* = 12.2, 2.1 Hz, 1H), 3.21 – 3.06 (m, 1H), 1.74 (s, 3H), 1.71 (s, 6H), 1.61 (s, 3H). ^{13}C NMR (75 MHz, C_6D_6) δ 169.98(C=O), 169.62(C=O), 169.38(C=O), 168.92(C=O), 148.54(C), 141.46(C), 140.22(C), 108.42(CH), 107.29(CH), 100.49(CH_2), 97.79(CH), 84.91(CH), 73.26(CH), 72.33(CH), 71.30(CH), 68.73(CH), 61.65(CH_2), 19.85($4CH_3$). HR-MS(ESI): m/z calculated for $C_{21}H_{25}NO_{11}Na$ 490.1325 obtained 490.1323

(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-((4-iodophenyl)amino)tetrahydro-2H-pyran-3,4,5-triyl triacetate **3g:**



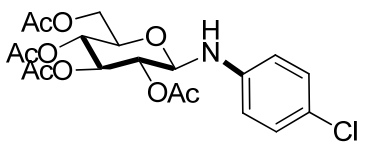
R_f = 0.68 (CH_2Cl_2; EtOAc, 92:8); white solid recrystallized from diisopropyl ether; m.p. = 176-178 °C ; $[\alpha]_D^{24}$ -47 (c,1.0 in $CHCl_3$); IR (neat): 3482, 3448, 3418, 1740, 1593, 1513, 1487, 1429, 1366, 1315, 1292, 1245, 1212, 1062, 1033 $cm^{-1.}$ ^{1}H NMR (300 MHz, C_6D_6) δ 7.37 (d, *J* = 8.8 Hz, 2H), 6.06 (d, *J* = 8.8 Hz, 2H), 5.44 (t, *J* = 9.5 Hz, 1H), 5.23 (t, *J* = 9.7 Hz, 1H), 5.07 – 4.92 (m, 1H), 4.49 – 4.19 (m, 3H), 3.91 (dd, *J* = 12.2, 2.2 Hz, 1H), 3.13 (ddd, *J* = 10.0, 4.9, 2.3 Hz, 1H), 1.71 (s, 3H), 1.71 (s, 3H), 1.68 (s, 3H), 1.58 (s, 3H). ^{13}C NMR (75 MHz, C_6D_6) δ 170.49(C=O), 169.97(C=O), 169.73(C=O), 169.29(C=O), 144.86(C), 138.18(2CH), 117.06(2CH), 83.78(CH), 81.44(C), 73.42(CH), 72.75(CH), 71.61(CH), 69.03(CH), 61.97(CH_2), 20.23($2CH_3$), 20.19($2CH_3$). HR-MS(ESI): m/z calculated for $C_{20}H_{24}NO_9NaI$ 572.0394 obtained 572.0398

(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-((4-bromophenyl)amino)tetrahydro-2H-pyran-3,4,5-triyl triacetate **3h:**



R_f = 0.60 (CH_2Cl_2 ; EtOAc, 92:8) ; white solid recrystallized from diisopropyl ether; m.p. = 161-162°C; $[\alpha]_D^{24}$ -49 (c,1.0 in $CHCl_3$); IR (neat): 3469, 3369, 1745, 1597, 1220, 1035 $cm^{-1.}$ ^{1}H NMR (300 MHz, C_6D_6) δ 7.18 (d, *J* = 8.8 Hz, 2H), 6.15 (d, *J* = 8.8 Hz, 2H), 5.44 (t, *J* = 9.5 Hz, 1H), 5.22 (t, *J* = 9.7 Hz, 1H), 5.00 (t, *J* = 9.1 Hz, 1H), 4.50 – 4.17 (m, 3H), 3.90 (dd, *J* = 12.2, 2.2 Hz, 1H), 3.29 – 3.01 (m, 1H), 1.70 (s, 3H), 1.70 (s, 3H), 1.67 (s, 3H), 1.57 (s, 3H). ^{13}C NMR (75 MHz, C_6D_6) δ 170.49(C=O), 169.97(C=O), 169.73(C=O), 169.30(C=O), 144.23(C), 132.28(2CH), 116.55(2CH), 112.09(C), 83.96(CH), 73.43(CH), 72.77(CH), 71.62(CH), 69.05(CH), 61.99(CH_2), 20.23($2CH_3$), 20.19($2CH_3$). HR-MS(ESI): m/z calculated for $C_{20}H_{24}NO_9NaBr$ 524.0532 obtained 524.0527

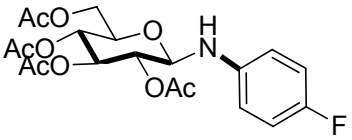
(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-((4-chlorophenyl)amino)tetrahydro-2H-pyran-3,4,5-triyl triacetate **3i:**



R_f = 0.53 (CH_2Cl_2; EtOAc, 92:8); white solid recrystallized from diisopropyl ether; m.p. = 149-150°C; $[\alpha]_D^{24}$ -55 (c,1.0 in $CHCl_3$); IR (neat): 3487, 3391, 3286, 1741, 1600, 1512, 1492, 1368, 1213, 1088,

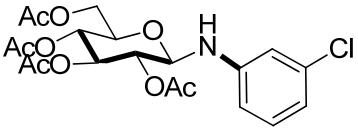
1031, 1003 $cm^{-1.}$ ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.14 (d, *J*=8.8 Hz, 2H), 6.59 (d, *J*=8.8 Hz, 2H), 5.36 (t, *J*=9.5 Hz, 1H), 5.09 (t, *J*=9.9 Hz, 1H), 5.01 (t, *J*=9.1 Hz, 1H), 4.85 – 4.62 (m, 2H), 4.29 (dd, *J*=12.2, 5.4 Hz, 1H), 4.08 (dd, *J*=12.2, 2.2 Hz, 1H), 3.91 – 3.75 (m, 1H), 2.05 (s, 3H), 2.04 (s, 6H), 2.03 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.13(C=O), 170.54(C=O), 169.97(C=O), 169.51(C=O), 143.02(C), 129.16(2CH), 124.71(C), 115.41(2CH), 84.37(CH), 72.83(CH), 72.45(CH), 71.16(CH), 68.79(CH), 62.12(CH_2), 20.72(CH_3), 20.68(CH_3), 20.58($2CH_3$). HR-MS(ESI): m/z calculated for $C_{20}H_{25}NO_9Cl$ 458.1218 obtained 458.1211

(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-((4-fluorophenyl)amino)tetrahydro-2H-pyran-3,4,5-triyl triacetate **3j:**



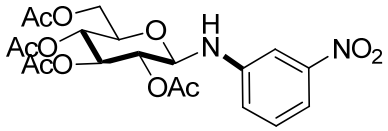
R_f = 0.53 (CH_2Cl_2 ; EtOAc, 92:8) ; light brown solid recrystallized from diisopropyl ether; m.p. = 128-130 °C; $[\alpha]_D^{24}$ -54 (c,1.0 in $CHCl_3$); IR (neat): 3469,3355,3180,1753,1740,1511,1366,1215,1033 $cm^{-1.}$ ^{1}H NMR (300 MHz, C_6D_6) δ 6.79 (t, *J* = 8.7 Hz, 2H), 6.41 – 6.32 (m, 2H), 5.48 (t, *J* = 9.5 Hz, 1H), 5.24 (t, *J* = 9.7 Hz, 1H), 5.14 – 5.02 (m, 1H), 4.59 – 4.38 (m, 2H), 4.30 (dd, *J* = 12.2, 5.2 Hz, 1H), 3.96 (dd, *J* = 12.2, 2.3 Hz, 1H), 3.30 (ddd, *J* = 10.0, 5.2, 2.3 Hz, 1H), 1.74 (s, 3H), 1.70 (s, 3H), 1.64 (s, 3H), 1.60 (s, 3H). ^{13}C NMR (75 MHz, C_6D_6) δ 170.05 (C=O), 169.66 (C=O), 169.44 (C=O), 169.00 (C=O), 157.19 (d, *J* = 237.1 Hz,C), 141.17 (d, *J* = 1.2 Hz,C), 115.74 (d, *J* = 7.9 Hz,CH), 115.53 (d, *J* = 24.0 Hz, CH), 84.31 (CH), 73.21 (CH), 72.36 (CH), 71.28 (CH), 68.84 (CH), 61.81 (CH_2), 19.85 ($4CH_3$). ^{19}F NMR (188 MHz, C_6D_6) δ = 122.90. HR-MS(ESI): m/z calculated for $C_{20}H_{24}NO_9NaF$ 464.1333 obtained 464.1331

(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-((3-chlorophenyl)amino)tetrahydro-2H-pyran-3,4,5-triyl triacetate **3k:**



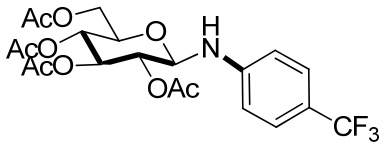
R_f = 0.58 (CH_2Cl_2 ; EtOAc, 92:8) ; light brown solid recrystallized from diisopropyl ether; m.p. = 133-135 °C ; $[\alpha]_D^{24}$ -70 (c,1.0 in $CHCl_3$); IR (neat): 3365, 3320, 1736, 1600, 1520, 1484, 1432, 1366, 1207, 1092, 1062, 1032 $cm^{-1.}$ ^{1}H NMR (300 MHz, C_6D_6) δ 6.88 – 6.71 (m, 2H), 6.65 (d, *J* = 1.7 Hz, 1H), 6.24 (dt, *J* = 6.7, 2.4 Hz, 1H), 5.43 (t, *J* = 9.5 Hz, 1H), 5.20 (t, *J* = 9.7 Hz, 1H), 5.03 (t, *J* = 9.3 Hz, 1H), 4.70 (d, *J* = 9.7 Hz, 1H), 4.37 (t, *J* = 9.4 Hz, 1H), 4.23 (dd, *J* = 12.2, 5.6 Hz, 1H), 3.93 (dd, *J* = 12.2, 2.1 Hz, 1H), 3.14 (ddd, *J* = 10.0, 5.5, 2.1 Hz, 1H), 1.76 (s, 3H), 1.73 (s, 6H), 1.60 (s, 3H). ^{13}C NMR (75 MHz, C_6D_6) δ 170.18(C=O), 169.69(C=O), 169.39(C=O), 168.98(C=O), 146.23(C), 134.98(C), 130.05(CH), 119.50(CH), 114.13(CH), 113.16(CH), 83.29(CH), 73.05(CH), 72.39(CH), 71.21(CH), 68.70(CH), 61.72(CH_2), 19.91(CH_3), 19.84(CH_3), 19.79($2CH_3$). HR-MS(ESI): m/z calculated for $C_{20}H_{24}NO_9NaCl$ 480.1037 obtained 480.1035

(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-((3-nitrophenyl)amino)tetrahydro-2H-pyran-3,4,5-triyl triacetate **3m:**



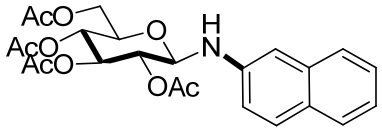
R_f = 0.47 (CH_2Cl_2; EtOAc, 92:8); yellow solid recrystallized from diisopropyl ether; m.p. = 136-137°C; $[\alpha]_D^{24}$ -74 (c,1.0 in $CHCl_3$); IR (neat): 3459, 3027, 1787, 1756, 1532, 1370, 1247, 1038 $cm^{-1.}$ ^{1}H NMR (300 MHz, C_6D_6) δ 7.51 – 7.45 (m, 1H), 7.39 (t, *J* = 2.2 Hz, 1H), 6.64 (t, *J* = 8.1 Hz, 1H), 6.22 (dd, *J* = 8.1, 1.7 Hz, 1H), 5.40 (t, *J* = 9.5 Hz, 1H), 5.22 – 5.10 (m, 1H), 4.96 (t, *J* = 9.3 Hz, 1H), 4.62 (d, *J* = 9.2 Hz, 1H), 4.27 (t, *J* = 9.2 Hz, 1H), 4.15 (dd, *J* = 12.3, 5.6 Hz, 1H), 3.96 (dd, *J* = 12.3, 2.1 Hz, 1H), 3.11 – 3.00 (m, 1H), 1.76 (s, 3H), 1.71 (s, 3H), 1.71 (s, 3H), 1.59 (s, 3H). ^{13}C NMR (75 MHz, C_6D_6) δ 170.21(C=O), 169.64(C=O), 169.31(C=O), 168.80(C=O), 149.49(C), 145.62(C), 129.28(CH), 120.44(CH), 114.14(CH), 107.95(CH), 82.91(CH), 72.80(CH), 72.57(CH), 71.21(CH), 68.50(CH), 61.58(CH_2), 19.81(CH_3), 19.75(CH_3). HR-MS(ESI): m/z calculated for $C_{20}H_{24}N_2O_{11}Na$ 491.1278 obtained 491.1279

(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-((4-(trifluoromethyl)phenyl)amino)tetrahydro-2H-pyran-3,4,5-triyl triacetate **3n:**



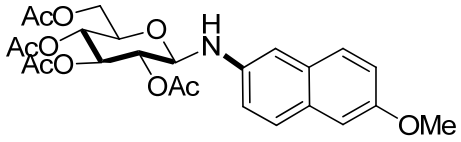
R_f = 0.71 (CH_2Cl_2; EtOAc, 92:8); white solid recrystallized from diisopropyl ether; m.p. = 185-187°C; $[\alpha]_D^{24}$ -70 (c,1.0 in $CHCl_3$); IR (neat): 3476, 3264, 1744, 1617, 1533, 1382, 1332, 1220, 1108, 1066 $cm^{-1.}$ ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.33 (d, *J*=8.5 Hz, 2H), 6.24 (d, *J*=8.5 Hz, 2H), 5.45 (t, *J*=9.5 Hz, 1H), 5.23 (t, *J*=9.7 Hz, 1H), 4.99 (t, *J*=9.3 Hz, 1H), 4.65 (d, *J*=9.5 Hz, 1H), 4.35 (t, *J*=9.3 Hz, 1H), 4.28 (dd, *J*=12.3, 4.9 Hz, 1H), 3.93 (dd, *J*=12.3, 2.3 Hz, 1H), 3.20 – 3.09 (m, 1H), 1.72 (s, 3H), 1.71 (s, 3H), 1.68 (s, 3H), 1.58 (s, 3H). ^{13}C NMR (75 MHz, Acetone) δ = 170.79 (C=O), 170.70 (C=O), 170.48 (C=O), 170.25 (C=O), 150.38 (C), 129.75 (d, *J*=269.3 Hz, *C*F_3), 127.31 (d, *J*=3.6 Hz, 2*C*-C-CF_3), 120.94 (d, *J*=32.4 Hz, C-CF_3), 114.90 (2CH), 83.36 (CH), 74.37 (CH), 73.35 (CH), 72.24 (CH), 69.79 (CH), 63.13 (CH_2), 20.78 (4CH_3). ^{19}F NMR (188 MHz, C_6D_6) δ = 58.98. HR-MS(ESI): m/z calculated for $C_{21}H_{24}NO_9NaF_3$ 514.1301 obtained 514.1307

(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(naphthalen-2-ylamino)tetrahydro-2H-pyran-3,4,5-triyl triacetate **3o:**



R_f = 0.68 (CH_2Cl_2; EtOAc, 92:8); white solid recrystallized from diisopropyl ether; m.p. = 174-176°C; $[\alpha]_D^{24}$ -39 (c,0.5 in $CHCl_3$); IR (neat): 3448, 3284, 1741, 1633, 1604, 1532, 1434, 1366, 1227, 1034 $cm^{-1.}$ ^{1}H NMR (300 MHz, C_6D_6) δ = 7.64 (dd, *J*=16.4, 8.2 Hz, 2H), 7.48 (d, *J*=8.8 Hz, 1H), 7.33 (t, *J*=7.6 Hz, 1H), 7.19 (d, *J*=7.1 Hz, 1H), 6.89 (s, 1H), 6.62 (dd, *J*=8.7, 2.1 Hz, 1H), 5.52 (t, *J*=9.5 Hz, 1H), 5.29 (t, *J*=9.7 Hz, 1H), 5.13 (t, *J*=9.1 Hz, 1H), 4.62 (d, *J*=6.6 Hz, 2H), 4.29 (dd, *J*=12.2, 5.1 Hz, 1H), 3.93 (d, *J*=12.2 Hz, 1H), 3.31 – 3.14 (m, 1H), 1.73 (s, 6H), 1.69 (s, 3H), 1.61 (s, 3H). ^{13}C NMR (75 MHz, Acetone) δ 170.64(2C=O), 170.31(C=O), 170.13(C=O), 144.62(C), 135.90(C), 129.59(CH), 129.31(C), 128.42(CH), 127.02(2CH), 123.37(CH), 118.93(CH), 108.21(CH), 84.03(CH), 74.32(CH), 73.13(CH), 72.25(CH), 69.87(CH), 63.13(CH_2), 20.70(2CH_3), 20.64(2CH_3). HR-MS(ESI): m/z calculated for $C_{24}H_{27}NO_9Na$ 496.1584 obtained 496.1578

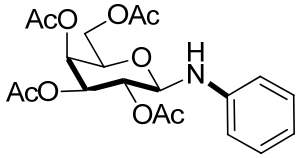
(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-((6-methoxynaphthalen-2-yl)amino)tetrahydro-2H-pyran-3,4,5-triyl triacetate **3p:**



R_f = 0.58 (CH_2Cl_2 ; EtOAc, 92:8); white solid recrystallized from diisopropyl ether; m.p. = 150-152°C; $[\alpha]_D^{24}$ 25 (c,1.0 in $CHCl_3$); IR (neat): 3478, 3087, 1755, 1611, 1225, 1032 $cm^{-1.}$ ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.54 (d, *J*=9.0 Hz, 1H), 7.47 (d, *J*=8.8 Hz, 1H), 7.24 (dd, *J*=8.9 Hz, 2.5, 1H), 6.95 (d, *J*=2.4 Hz, 1H), 6.89 (d, *J*=2.0 Hz, 1H), 6.72 (dd, *J*=8.7, 2.3 Hz, 1H), 5.54 (t, *J*=9.5 Hz, 1H), 5.29 (t, *J*=9.7 Hz, 1H), 5.20 – 5.11 (m, 1H), 4.70 – 4.55 (m, 2H), 4.35 – 4.25 (m, 1H), 3.96 (dd, *J*=12.2, 2.2 Hz, 1H), 3.45 (s, 3H), 3.32 – 3.24 (m, 1H), 1.74 (s, 3H), 1.74 (s, 3H), 1.70 (s, 3H), 1.64 (s, 3H). ^{13}C NMR (75 MHz, C_6D_6) δ 170.56(C=O), 170.03(C=O), 169.81(C=O), 169.36(C=O), 156.50(C), 141.28(C), 130.68(C), 130.12(C), 128.15(2CH), 119.75(CH), 118.75(CH), 109.34(CH), 106.51(CH), 84.61(CH), 73.65(CH), 72.79(CH), 71.82(CH), 69.29(CH), 62.18(CH_2), 54.86(CH_3), 20.29($2CH_3$), 20.23($2CH_3$). HR-MS(ESI): m/z calculated for $C_{25}H_{30}NO_{10}$ 504.1870 obtained 504.1873

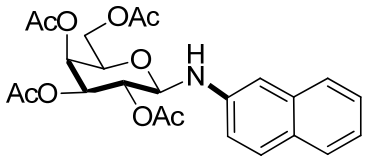
Characterization data of β-aryl *N*-glycoside 4a-l

(2R,3S,4S,5R,6R)-2-(acetoxymethyl)-6-(phenylamino)tetrahydro-2H-pyran-3,4,5-triyl triacetate **4a:**



R_f = 0.30 (CH_2Cl_2; EtOAc, 92:8); white solid recrystallized from diisopropyl ether; m.p. = 121-124°C; $[\alpha]_D^{24}$ -18 (c,1.0 in $CHCl_3$); IR (neat): 3469, 3393, 1738, 1605, 1522, 1501, 1368, 1250, 1212, 1085, 1050, 1011 $cm^{-1.}$ ^{1}H NMR (300 MHz, C_6D_6) δ = 7.09 (t, *J*=7.9 Hz, 2H), 6.78 (t, *J*=7.3 Hz, 1H), 6.54 (d, *J*=7.6 Hz, 2H), 5.58 – 5.42 (m, 2H), 5.30 (dd, *J*=10.3, 3.5 Hz, 1H), 4.67 – 4.53 (m, 2H), 4.17 – 4.02 (m, 2H), 3.41 (t, *J*=6.8 Hz, 1H), 1.75 (s, 3H), 1.70 (s, 3H), 1.62 (s, 3H), 1.61 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.54(C=O), 169.78(C=O), 169.36(2C=O), 145.04(C), 129.19(2CH), 119.70(CH), 114.57(2CH), 84.39(CH), 71.41(CH), 71.08(CH), 69.06(CH), 67.49(CH), 61.08(CH_2), 19.99($2CH_3$), 19.83(CH_3), 19.78(CH_3). HR-MS(ESI): m/z calculated for $C_{20}H_{25}NO_9Na$ 446.1427 obtained 446.1423

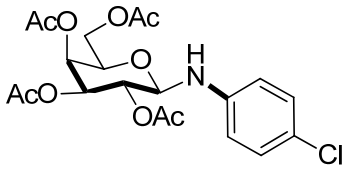
(2R,3S,4S,5R,6R)-2-(acetoxymethyl)-6-(naphthalen-2-ylamino)tetrahydro-2H-pyran-3,4,5-triyl triacetate **4b:**



R_f = 0.72 (CH_2Cl_2 ; EtOAc, 92:8); white solid ; m.p. = °C; $[\alpha]_D^{24}$ -26 (c,1.0 in $CHCl_3$); IR (neat): 1748, 1600, 1369, 1226, 1050, 1030 $cm^{-1.}$ ^{1}H NMR (300 MHz, Acetone) δ 7.74 – 7.68 (m, 2H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.25 – 7.12 (m, 3H), 5.83 (d, *J* = 8.3 Hz, 1H), 5.48 (d, *J* = 3.3 Hz, 1H), 5.36 – 5.21 (m, 3H), 4.41 (t, *J* = 6.6 Hz, 1H), 4.18 – 4.06 (m, 2H), 2.14 (s, 3H), 1.99 (s, 3H), 1.96 (s, 3H), 1.95 (s, 3H). ^{13}C NMR (75 MHz, Acetone) δ 170.92(C=O), 170.76(C=O), 170.54(C=O), 170.23(C=O),

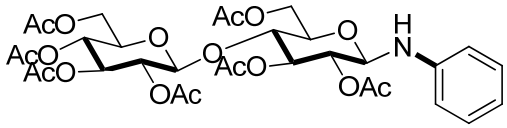
144.66(C), 135.90(C), 129.55(CH), 129.27(C), 128.41(C), 126.98(2CH), 123.32(CH), 118.99(CH), 108.10(CH), 84.36(CH), 72.43(CH), 72.07(CH), 69.73(CH), 68.75(CH), 62.45(CH_2), 20.75(CH_3), 20.62(2CH_3), 20.57(CH_3). HR-MS(ESI): m/z calculated for $C_{24}H_{27}NO_9Na$ 496.1584 obtained 496.1588

(2R,3S,4S,5R,6R)-2-(acetoxymethyl)-6-((4-chlorophenyl)amino)tetrahydro-2H-pyran-3,4,5-triyl triacetate **4c:**



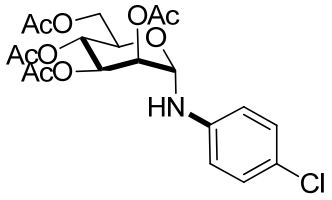
R_f = 0.50 (CH_2Cl_2 ; EtOAc, 92:8); brown solid recrystallized from diisopropyl ether; m.p. = 142-145°C; $[\alpha]_D^{24}$ -13 (c,1.0 in $CHCl_3$); IR (neat): 3479, 3359, 3200, 3105, 1745, 1494, 1369, 1222, 1081, 1057 $cm^{-1.}$ ^{1}H NMR (300 MHz, C_6D_6) δ 7.05 (d, *J* = 8.8 Hz, 2H), 6.29 (d, *J* = 8.9 Hz, 2H), 5.54 (dd, *J* = 3.4, 0.9 Hz, 1H), 5.43 (dd, *J* = 10.3, 8.8 Hz, 1H), 5.27 (dd, *J* = 10.3, 3.5 Hz, 1H), 4.67 (d, *J* = 9.9 Hz, 1H), 4.45 (dd, *J* = 9.8, 9.0 Hz, 1H), 4.14 – 4.04 (m, 2H), 3.43 (td, *J* = 6.6, 0.9 Hz, 1H), 1.75 (s, 3H), 1.73 (s, 3H), 1.62 (s, 6H). ^{13}C NMR (75 MHz, C_6D_6) δ 170.86(C=O), 170.11(C=O), 169.77(C=O), 169.71(C=O), 143.94(C), 129.37(2CH), 124.77(C), 116.05(2CH), 84.44(CH), 71.62(CH), 71.55(CH), 69.25(CH), 67.82(CH), 61.53(CH_2), 20.31(CH_3), 20.27(CH_3), 20.18(CH_3), 20.11(CH_3). HR-MS(ESI): m/z calculated for $C_{20}H_{24}NO_9NaCl$ 480.1037 obtained 480.1035

(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-(((2R,3R,4S,5R,6R)-4,5-diacetoxy-2-(acetoxymethyl)-6-(phenylamino)tetrahydro-2H-pyran-3-yl)oxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate **4d:**



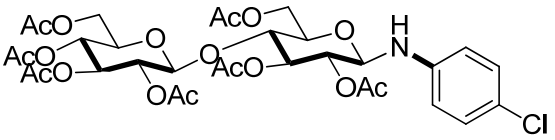
R_f = 0.21 (CH_2Cl_2 ; EtOAc, 92:8); white solid recrystallized from diisopropyl ether, CH_2Cl_2, 95:5; m.p. = 230-231°C; $[\alpha]_D^{24}$ -30 (c,0.5 in $CHCl_3$); IR (neat): 3465, 1746, 1607, 1376, 1240, 1225, 1036 $cm^{-1.}$ ^{1}H NMR (300 MHz, Acetone) δ 7.15 (dd, *J* = 8.4, 7.4 Hz, 2H), 6.81 (d, *J* = 7.7 Hz, 2H), 6.74 (t, *J* = 7.3 Hz, 1H), 5.55 (d, *J* = 9.3 Hz, 1H), 5.36 – 5.27 (m, 1H), 5.23 (ddd, *J* = 9.4, 5.6, 3.9 Hz, 1H), 5.06 (td, *J* = 9.4, 4.2 Hz, 2H), 4.96 – 4.89 (m, 1H), 4.87 (dd, *J* = 7.1, 3.5 Hz, 2H), 4.48 (dd, *J* = 11.9, 1.8 Hz, 1H), 4.39 (dd, *J* = 12.4, 4.4 Hz, 1H), 4.17 (dd, *J* = 11.9, 5.8 Hz, 1H), 4.09 (dd, *J* = 12.4, 2.3 Hz, 1H), 4.04 – 3.94 (m, 2H), 3.94 – 3.86 (m, 1H), 2.06 (s, 3H), 2.05 (s, 6H), 2.04 (s, 3H), 1.98 (s, 3H), 1.98 (s, 3H), 1.93 (s, 3H). ^{13}C NMR (75 MHz, Acetone) δ 170.78(2C=O), 170.71(C=O), 170.30(C=O), 170.17(C=O), 169.90(C=O), 169.65(C=O), 146.85(C), 129.76(2CH), 119.61(C), 115.11(2CH), 101.30(CH), 83.88(CH), 77.92(CH), 74.07(CH), 74.04(CH), 73.71(CH), 72.47(CH), 72.44(CH), 72.42(CH), 69.02(CH), 63.35(CH_2), 62.56(CH_2), 20.79(CH_3), 20.75(2CH_3), 20.67(CH_3), 20.58(2CH_3), 20.51(CH_3). HR-MS(ESI): m/z calculated for $C_{32}H_{41}NO_{17}Na$ 734.2272 obtained 734.2270

(2R,3R,4S,5S,6S)-2-(acetoxymethyl)-6-((4-chlorophenyl)amino)tetrahydro-2H-pyran-3,4,5-triyl triacetate **4e:**



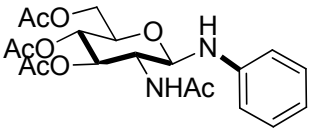
Compound **4e** is contaminated with a small amount of unknow byproduct. This compound is not enough stable for more purifications and it degrade during its successive purifications. R_f = 0.48 (CH_2Cl_2; EtOAc, 92:8); colorless oil; IR (neat): 3436, 3399, 1740, 1602, 1516, 1494, 1368, 1245, 1213, 1091, 1048 $cm^{-1.}$ ^{1}H NMR (300 MHz, C_6D_6) δ = 7.14 (d, *J*=8.9, 2H), 6.82 (d, *J*=8.9, 2H), 5.86 (d, *J*=15, 1H), 5.50 (d, *J*=3, 1H), 5.40 (m, 1H), 5.37-5.21 (m, 2H), 4.20 (dd, *J*=12.2, 4.7, 1H), 4.08 (m, 2H), 2.16 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H), 1.87 (s, 3H). ^{13}C NMR (75 MHz, Acetone) δ 171.15(C=O), 170.68(C=O), 170.32(C=O), 170.19(C=O), 145.54(C), 129.55(2CH), 123.77(C), 116.65(2CH), 81.42(CH), 73.63(CH), 72.69(CH), 71.03(CH), 67.12(CH), 63.44(CH_2), 20.93(CH_3), 20.69(CH_3), 20.64(CH_3), 20.54(CH_3). HR-MS(ESI): m/z calculated for $C_{20}H_{24}NO_9NaCl$ 480.1037 obtained 480.1041

(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-(((2R,3R,4S,5R,6R)-4,5-diacetoxy-2-(acetoxymethyl)-6-((4-chlorophenyl)amino)tetrahydro-2H-pyran-3-yl)oxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate **4f**:



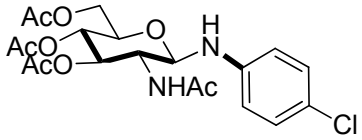
R_f = 0.34 (CH_2Cl_2; EtOAc, 92:8); white solid recrystallized from diisopropyl ether, CH_2Cl_2, 95:5; m.p. = 251-252 °C ; $[\alpha]_D^{24}$ -50 (c,1.0 in $CHCl_3$); IR (neat): 3432, 3269, 3208, 1757, 1739, 1495, 1367, 1231, 1213, 1037 $cm^{-1.}$ ^{1}H NMR (300 MHz, Acetone) δ 7.15 (d, *J* = 8.9 Hz, 2H), 6.82 (d, *J* = 8.9 Hz, 2H), 5.76 (d, *J* = 9.3 Hz, 1H), 5.35 – 5.16 (m, 2H), 5.04 (td, *J* = 9.3, 2.5 Hz, 2H), 4.92 (d, *J* = 9.3 Hz, 1H), 4.89 – 4.78 (m, 2H), 4.48 (dd, *J* = 11.9, 1.7 Hz, 1H), 4.38 (dd, *J* = 12.4, 4.4 Hz, 1H), 4.15 (dd, *J* = 11.9, 5.8 Hz, 1H), 4.07 (dd, *J* = 12.4, 2.3 Hz, 1H), 4.04 – 3.85 (m, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 2.02 (s, 6H), 1.97 (s, 3H), 1.96 (s, 3H), 1.92 (s, 3H). ^{13}C NMR (75 MHz, Acetone) δ 170.79(C=O), 170.70(C=O), 170.68(C=O), 170.30(C=O), 170.18(C=O), 169.90(C=O), 169.64(C=O), 145.85(C), 129.56(2CH), 123.80(C), 116.53(2CH), 101.31(CH), 83.71(CH), 77.82(CH), 74.12(CH), 74.06(CH), 73.70(CH), 72.47(CH), 72.41(CH), 72.30(CH), 69.02(CH), 63.31(CH_2), 62.55(CH_2), 20.77($2CH_3$), 20.71(CH_3), 20.67(CH_3), 20.58($2CH_3$), 20.51(CH_3). HR-MS(ESI): m/z calculated for $C_{32}H_{40}NO_{17}NaCl$ 768.1882 obtained 768.1888.

(2R,3S,4R,5R,6R)-5-acetamido-2-(acetoxymethyl)-6-(phenylamino)tetrahydro-2H-pyran-3,4-diyl diacetate **4g:**



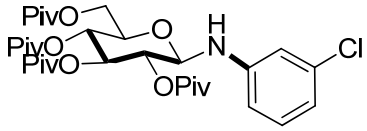
R_f = 0.18 (CH_2Cl_2; EtOAc, 92:8); white solid ; m.p. = 183-185 °C ; $[\alpha]_D^{24}$ -62 (c,1.0 in $CHCl_3$); IR (neat): 3485, 3280, 1743, 1660, 1605, 1530, 1368, 1229, 1042 $cm^{-1.}$ ^{1}H NMR (300 MHz, Acetone) δ 7.25 (d, *J* = 8.6 Hz, 1H), 7.13 (t, *J* = 7.0 Hz, 2H), 6.77 – 6.65 (m, 3H), 5.81 (d, *J* = 7.6 Hz, 1H), 5.30 (dd, *J* = 10.4, 9.3 Hz, 1H), 5.03 – 4.96 (m, 1H), 4.89 (dd, *J* = 9.4, 7.7 Hz, 1H), 4.24 (dd, *J* = 12.1, 5.5 Hz, 1H), 4.18 – 4.03 (m, 2H), 3.97 (ddd, *J* = 10.0, 5.5, 2.5 Hz, 1H), 2.00 (s, 3H), 1.99 (s, 3H), 1.98 (s, 3H), 1.87 (s, 3H). ^{13}C NMR (75 MHz, Acetone) δ 171.78(C=O), 170.84(C=O), 170.67(C=O), 170.13(C=O), 147.24(C), 129.78(2CH), 119.17(C), 114.56(2CH), 86.16(CH), 74.15(CH), 72.72(CH), 70.31(CH), 63.26(CH), 54.47(CH_2), 22.96(CH_3), 20.68($3CH_3$). HR-MS(ESI): m/z calculated for $C_{20}H_{26}N_2O_8Na$ 445.1587 obtained 446.1587

(2R,3S,4R,5R,6R)-5-acetamido-2-(acetoxymethyl)-6-((4-chlorophenyl)amino)tetrahydro-2H-pyran-3,4-diyl diacetate **4h:**



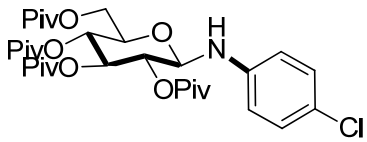
R_f = 0.14 (CH_2Cl_2; EtOAc, 92:8); white solid ; m.p. = 184-185 °C ; $[\alpha]_D^{24}$ -62 (c,1.0 in $CHCl_3$); IR (neat): 3490, 3471, 3453, 3250, 3234, 3116, 1696, 1369, 1247, 1031 cm^{-1}. ^{1}H NMR (300 MHz, Acetone) δ 7.29 (d, *J* = 8.7 Hz, 1H), 7.14 (d, *J* = 8.8 Hz, 2H), 6.75 (d, *J* = 8.9 Hz, 2H), 6.03 (d, *J* = 7.7 Hz, 1H), 5.29 (dd, *J* = 10.3, 9.4 Hz, 1H), 4.99 (t, *J* = 9.7 Hz, 1H), 4.91 (dd, *J* = 9.3, 7.8 Hz, 1H), 4.23 (dd, *J* = 12.1, 5.5 Hz, 1H), 4.16 – 4.03 (m, 2H), 3.98 (ddd, *J* = 10.0, 5.5, 2.4 Hz, 1H), 2.00 (s, 3H), 1.99 (s, 3H), 1.97 (s, 3H), 1.86 (s, 3H). ^{13}C NMR (75 MHz, Acetone) δ 171.78(C=O), 170.83(C=O), 170.67(C=O), 170.12(C=O), 146.18(C), 129.58(2CH), 123.34(C), 115.99(2CH), 85.91(CH), 74.09(CH), 72.81(CH), 70.22(CH), 63.21(CH), 54.44(CH_2), 22.95(CH_3), 20.67(3CH_3). HR-MS(ESI): m/z calculated for $C_{20}H_{25}N_2O_8NaCl$ 479.1197 obtained 479.1199

(2R,3R,4S,5R,6R)-2-((3-chlorophenyl)amino)-6-((pivaloyloxy)methyl)tetrahydro-2H-pyran-3,4,5-triyl tris(2,2-dimethylpropanoate) **4i:**



R_f = 0.45 (cyclohexane; EtOAc, 9:1); white solid ; m.p. = 182-186 °C ; $[\alpha]_D^{24}$ -47 (c,1.0 in $CHCl_3$); IR (neat): 3390, 3342, 3275, 3179, 1743, 1724, 1600, 1524, 1480, 1399, 1368, 1279, 1144, 1034 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07 (t, *J* = 8.0 Hz, 1H), 6.79 (dd, *J* = 7.9, 1.1 Hz, 1H), 6.64 (t, *J* = 2.0 Hz, 1H), 6.52 (dd, *J* = 8.2, 1.5 Hz, 1H), 5.48 (t, *J* = 9.4 Hz, 1H), 5.15 – 5.00 (m, 2H), 4.78 – 4.66 (m, 2H), 4.20 (dd, *J* = 12.1, 1.7 Hz, 1H), 4.05 (dd, *J* = 12.2, 6.8 Hz, 1H), 3.88 (ddd, *J* = 9.8, 6.7, 1.7 Hz, 1H), 1.20 (s, 9H), 1.18 (s, 9H), 1.13 (s, 9H), 1.11 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.00(C=O), 178.25(C=O), 177.10(C=O), 176.79(C=O), 146.07(C), 135.24(C), 130.44(CH), 120.04(CH), 113.99(CH), 112.84(CH), 84.63(CH), 73.40(CH), 72.24(CH), 71.15(CH), 68.52(CH), 62.60(CH_2), 39.10(C), 38.98(2C), 38.89(C), 27.30(5CH_3), 27.23(4CH_3), 27.15(3CH_3). HR-MS(ESI): m/z calculated for $C_{32}H_{48}NO_9NaCl$ 648.2915 obtained 648.2917

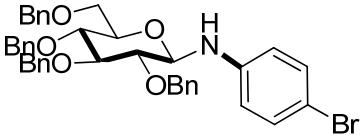
(2R,3R,4S,5R,6R)-2-((4-chlorophenyl)amino)-6-((pivaloyloxy)methyl)tetrahydro-2H-pyran-3,4,5-triyl tris(2,2-dimethylpropanoate) **4j:**



R_f = 0.39 (cyclohexane; EtOAc, 9:1); white solid ; m.p. = 211-214 °C ; $[\alpha]_D^{24}$ -33 (c,1,0 in $CHCl_3$); IR (neat): 3464, 3392, 1739, 1723, 1603, 1514, 1478, 1398, 1367, 1280, 1266, 1180, 1147, 1079, 1032, 1005 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.6 Hz, 2H), 6.59 (d, *J* = 8.7 Hz, 2H), 5.48 (t, *J* = 9.4 Hz, 1H), 5.15 – 5.01 (m, 2H), 4.73 – 4.63 (m, 2H), 4.20 (dd, *J* = 12.1, 1.4 Hz, 1H), 4.05 (dd, *J* = 12.1, 6.8 Hz, 1H), 3.85 (ddd, *J* = 9.4, 6.6, 1.4 Hz, 1H), 1.20 (s, 9H), 1.18 (s, 9H), 1.13 (s, 9H), 1.11 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.97(C=O), 178.17(C=O), 177.11(C=O), 176.78(C=O), 143.49(C), 129.34(2CH), 124.89(C), 115.65(2CH), 85.10(CH), 73.36(CH), 72.28(CH), 71.18(CH), 68.53(CH), 62.59(CH_2), 39.10(C),

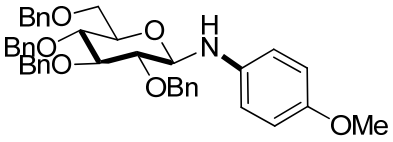
38.98(2C), 38.89(C), 27.27(5CH_3), 27.23(4CH_3), 27.15(3CH_3). HR-MS(ESI): m/z calculated for $C_{32}H_{48}NO_9Cl$ 648.2915 obtained 648.2909

(2R,3R,4S,5R,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)-N-(4-bromophenyl)tetrahydro-2H-pyran-2-amine **4k:**



R_f = 0.39 (cyclohexane; EtOAc, 9:1); white solid recrystallized from diisopropyl ether, CH_2Cl_2, 95:5; m.p. = 166-168 °C ; $[\alpha]_D^{24}$ -18 (c,0.25 in $CHCl_3$); IR (neat): 3401, 3381, 3319, 3288, 3218, 3196,3168, 3062, 1630, 1365, 1062 $cm^{-1.}$ ^{1}H NMR (300 MHz, Acetone) δ 7.42 – 7.21 (m, 22H), 6.79 (d, *J* = 8.9 Hz, 2H), 5.88 (d, *J* = 9.4 Hz, 1H), 4.99 – 4.76 (m, 6H), 4.68 (d, *J* = 11.1 Hz, 1H), 4.56 (d, *J* = 12.0 Hz, 1H), 4.50 (d, *J* = 11.9 Hz, 1H), 3.85 – 3.50 (m, 6H). ^{13}C NMR (75 MHz, Acetone) δ 147.14(C), 140.06(C), 139.91(C), 139.77(C), 139.71(C), 132.51(2CH), 129.07(8CH), 128.74(2CH), 128.64(2CH), 128.51(4CH), 128.31(2CH), 128.18(2CH), 117.02(2CH), 110.28(C), 86.89(CH), 85.44(CH), 82.84(CH), 79.38(CH), 76.51(CH), 76.03(CH_2), 75.33(CH_2), 75.25(CH_2), 73.76(CH_2), 70.12(CH_2). HR-MS(ESI): m/z calculated for $C_{40}H_{40}NO_5NaBr$ 716.1988 obtained 716.1989.

(2R,3R,4S,5R,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)-N-(4-methoxyphenyl)tetrahydro-2H-pyran-2-amine **4l:**

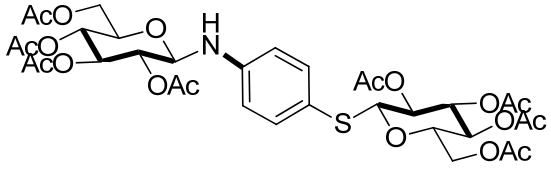


R_f = 0.31 (cyclohexane; EtOAc, 9:1) ; white solid recrystallized from diisopropyl ether, CH_2Cl_2, 95:5; m.p. = 148-149 °C ; $[\alpha]_D^{24}$ -18 (c,0.5 in $CHCl_3$); IR (neat): 3478, 3458, 3340, 3284, 1513, 1453, 1353, 1246, 1133, 1060, 1027 $cm^{-1.}$ ^{1}H NMR (300 MHz, Acetone) δ 7.40 – 7.21 (m, 20H), 6.82 – 6.77 (m, 2H), 6.77 – 6.72 (m, 2H), 5.30 (d, *J* = 9.6 Hz, 1H), 5.05 – 4.79 (m, 5H), 4.76 – 4.64 (m, 2H), 4.56 (d, *J* = 12.0 Hz, 1H), 4.51 (d, *J* = 12.0 Hz, 1H), 3.83 – 3.57 (m, 8H), 3.52 (t, *J* = 8.7 Hz, 1H). ^{13}C NMR (75 MHz, Acetone) δ 153.88(C), 141.58(C), 140.14(C), 140.06(C), 139.82(C), 139.77(C), 129.04(8CH), 128.80(2CH), 128.63(2CH), 128.51(4CH), 128.27(2CH), 128.15(2CH), 116.58(2CH), 115.35(2CH), 86.97(CH), 86.89(CH), 83.00(CH), 79.48(CH), 76.48(CH), 76.00(CH_2), 75.30(CH_2), 75.19(CH_2), 73.76(CH_2), 70.22(CH_2), 55.79(CH_3). HR-MS(ESI): m/z calculated for $C_{41}H_{39}NO_6Na$ 668.2988 obtained 668.2990

General procedure for Palladium-catalyzed coupling of β-thioglycosides with 3g:
Typical procedure: A flame-dried resealable Schlenk tube was charged with $Pd(OAc)_2$ (5 mol %), Xantphos (2.5 mol%), thiosugar (0.375 mmol), **3g** (0.25 mmol), and Et_3N (0.25 mmol). The Schlenk tube was capped with a rubber septum, evacuated and backfilled with argon; then, dioxane (1.5 mL) was added through the septum. The septum was replaced with a teflon screwcap. The Schlenk tube was sealed, and the mixture was stirred at 100 °C for 1 h. The resulting suspension was cooled to room temperature and filtered through celite eluting with ethyl acetate. The filtrate was concentrated and purification of the residue by silica gel column chromatography gave the desired product **5a-c**.

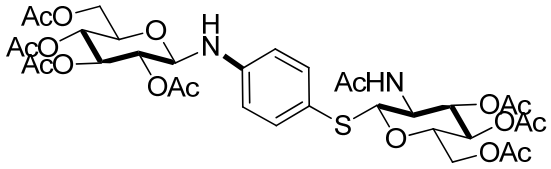
Characterization data of β-aryl *N*-glycoside 5a-c

(2S,3S,4R,5S,6R)-2-(acetoxymethyl)-6-((4-(((2R,3R,4S,5R,6R)-3,4,5-triacetoxy-6-(acetoxymethyl)tetrahydro-2H-pyran-2-yl)amino)phenyl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate **5a:**



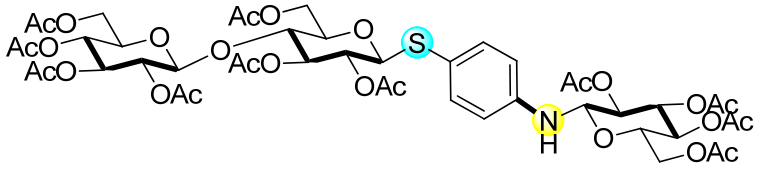
R_f = 0.16 (cyclohexane; EtOAc, 6:4); white solid recrystallized from diisopropyl ether; m.p. = 184-185 °C ; $[\alpha]_D^{24}$ -47 (c,1.0 in $CHCl_3$); IR (neat): 3450, 3150, 1755, 1746, 1739, 1599, 1514, 1366, 1212, 1034 cm^{-1}. ^{1}H NMR (300 MHz, Acetone) δ 7.41 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 6.00 (d, *J* = 9.2 Hz, 1H), 5.44 (t, *J* = 9.4 Hz, 1H), 5.33 (t, *J* = 8.6 Hz, 1H), 5.23 (t, *J* = 9.3 Hz, 1H), 5.10 (d, *J* = 10.5 Hz, 1H), 5.04 (d, *J* = 7.8 Hz, 1H), 4.99 (t, *J* = 9.1 Hz, 1H), 4.94 – 4.81 (m, 2H), 4.34 – 4.08 (m, 5H), 3.99 (ddd, *J* = 10.2, 5.0, 2.7 Hz, 1H), 2.10 (s, 3H), 2.08 (s, 3H), 2.07 (s, 3H), 2.05 (s, 3H), 2.03 (s, 6H), 2.02 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (75 MHz, Acetone) δ 170.69(C=O), 170.65(C=O), 170.57(C=O), 170.30(C=O), 170.24(C=O), 170.10(C=O), 169.96(C=O), 169.65(C=O), 147.71(C), 136.81(2CH), 119.80(C), 115.35(2CH), 86.28(CH), 83.55(CH), 76.18(CH), 74.61(CH), 74.24(CH), 73.04(CH), 72.14(CH), 70.91(CH), 69.76(CH), 69.25(CH), 63.06(CH_2), 62.88(CH_2), 20.76($2CH_3$), 20.68($2CH_3$), 20.62(CH_3), 20.57($2CH_3$), 20.53(CH_3). HR-MS(ESI): m/z calculated for $C_{34}H_{43}NO_{18}NaS$ 808.2099 obtained 808.2098.

(2R,3R,4S,5R,6R)-2-((4-(((2R,3S,4S,5R,6S)-3-acetamido-4,5-diacetoxy-6-(acetoxymethyl)tetrahydro-2H-pyran-2-yl)thio)phenyl)amino)-6-(acetoxymethyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate **5b:**

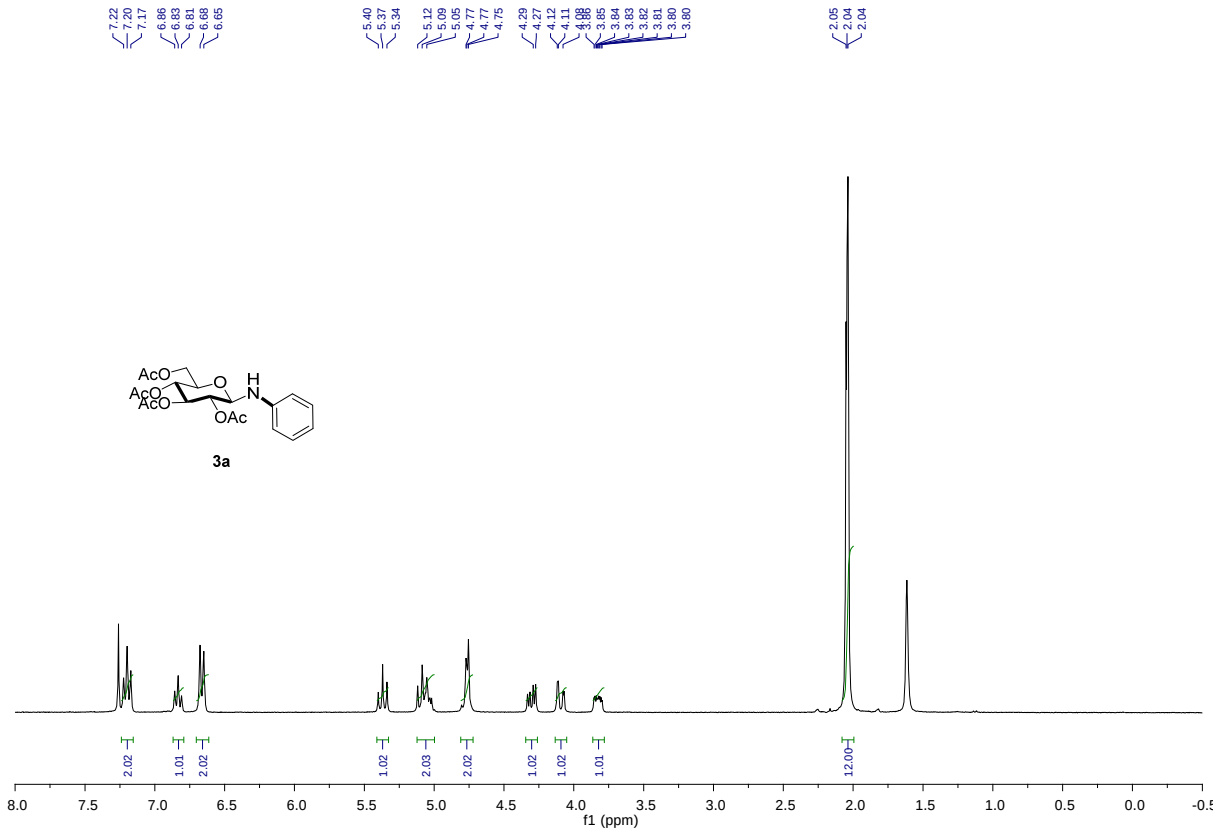


R_f = 0.16 (cyclohexane ; EtOAc, 6:4); white solid recrystallized from diisopropyl ether; m.p. = 219-221 °C; $[\alpha]_D^{24}$ -18 (c,0.375 in $CHCl_3$); IR (neat): 3493, 3318, 3278, 1743, 1650, 1600, 1553, 1512, 1435, 1367, 1294, 1213, 1083, 1031 cm^{-1}. ^{1}H NMR (300 MHz, Acetone) δ 7.38 (d, *J* = 8.6 Hz, 2H), 7.22 (d, *J* = 9.2 Hz, 1H), 6.81 (d, *J* = 8.6 Hz, 2H), 5.89 (d, *J* = 9.4 Hz, 1H), 5.39 (t, *J* = 9.4 Hz, 1H), 5.25 (t, *J* = 9.8 Hz, 1H), 5.17 (t, *J* = 9.2 Hz, 1H), 5.09 – 4.95 (m, 2H), 4.94 – 4.83 (m, 2H), 4.31 – 4.03 (m, 5H), 3.88 (dd, *J* = 19.7, 10.0 Hz, 1H), 3.76 (ddd, *J* = 9.7, 5.2, 2.3 Hz, 1H), 2.01 (s, 6H), 1.99 (s, 3H), 1.98 (s, 3H), 1.96 (s, 6H), 1.91 (s, 3H), 1.87 (s, 3H). ^{13}C NMR (75 MHz, Acetone) δ 170.68(2C=O), 170.57(C=O), 170.51(C=O), 170.30(C=O), 170.10(C=O), 169.99(C=O), 169.90(C=O), 147.40(C), 136.64(2CH), 120.85(C), 115.29(2CH), 87.49(CH), 83.62(CH), 76.30(CH), 74.75(CH), 74.23(CH), 73.02(CH), 72.14(CH), 69.75(2CH), 63.09(CH), 63.04(CH_2), 53.92(CH_2), 23.12(CH_3), 20.77(CH_3), 20.68($2CH_3$), 20.62($4CH_3$). HR-MS(ESI): m/z calculated for $C_{34}H_{44}N_2O_{17}NaS$ 807.2258 obtained 807.2260

(2S,3S,4R,5S,6R)-2-(acetoxymethyl)-6-(((2S,3S,4R,5S,6R)-4,5-diacetoxy-2-(acetoxymethyl)-6-((4-(((2R,3R,4S,5R,6R)-3,4,5-triacetoxy-6-(acetoxymethyl)tetrahydro-2H-pyran-2-yl)amino)phenyl)thio)tetrahydro-2H-pyran-3-yl)oxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate **5c:**



R_f = 0.18 (cyclohexane ; EtOAc, 6:4) ; white solid recrystallized from diisopropyl ether; m.p. = 220-222 °C ; $[\alpha]_D^{24}$ -31 (c,1.0 in $CHCl_3$); IR (neat): 3449, 3315, 3289, 1756, 1749, 1366, 1229, 1212, 1035 cm^{-1}. ^1H NMR (300 MHz, Acetone) δ 7.39 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.01 (d, *J* = 9.3 Hz, 1H), 5.45 (t, *J* = 9.4 Hz, 1H), 5.31 – 5.19 (m, 1H), 5.07 (ddd, *J* = 14.4, 9.6, 4.6 Hz, 1H), 4.96 – 4.74 (m, 2H), 4.61 (d, *J* = 11.3 Hz, 1H), 4.41 (dd, *J* = 12.4, 4.3 Hz, 1H), 4.34 – 4.12 (m, 2H), 4.13 – 3.93 (m, 1H), 3.84 (d, *J* = 7.0 Hz, 1H), 2.10 (s, 1H), 2.09 (s, 1H), 2.07 (s, 1H), 2.06 (s, 2H), 2.05 (s, 1H), 2.03 (s, 1H), 2.02 (s, 1H), 2.01 (s, 1H), 1.96 (s, 1H). ^{13}C NMR (75 MHz, Acetone) δ 170.78(C=O), 170.70(C=O), 170.69(C=O), 170.55(C=O), 170.30(C=O), 170.13(C=O), 169.99(C=O), 169.88(C=O), 169.77(C=O), 169.74(C=O), 169.61(C=O), 147.68(C), 137.09(2CH), 125.52(C), 115.23(2CH), 101.25(2CH), 85.69(CH), 83.51(CH), 77.32(CH), 77.23(CH), 74.34(CH), 74.24(CH), 73.71(CH), 73.05(CH), 72.42(CH), 72.13(CH), 71.09(CH), 69.77(CH), 68.94(CH), 63.09(CH_2), 62.97(CH_2), 62.42(CH_2), 20.93(CH_3), 20.70(4CH_3), 20.64(3CH_3), 20.57(3CH_3). HR-MS(ESI): m/z calculated for $C_{46}H_{59}NO_{26}NaS$ 1096.2944 obtained 1096.2947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6.65
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5.34
5.12
5.09
5.05
4.77
4.77
4.75
4.29
4.27
4.12
4.11
3.85
3.84
3.83
3.82
3.81
3.80
3.80
2.05
2.04
2.04
AcO
AcO
AcO
O
H
N
OAc
3a
2.02
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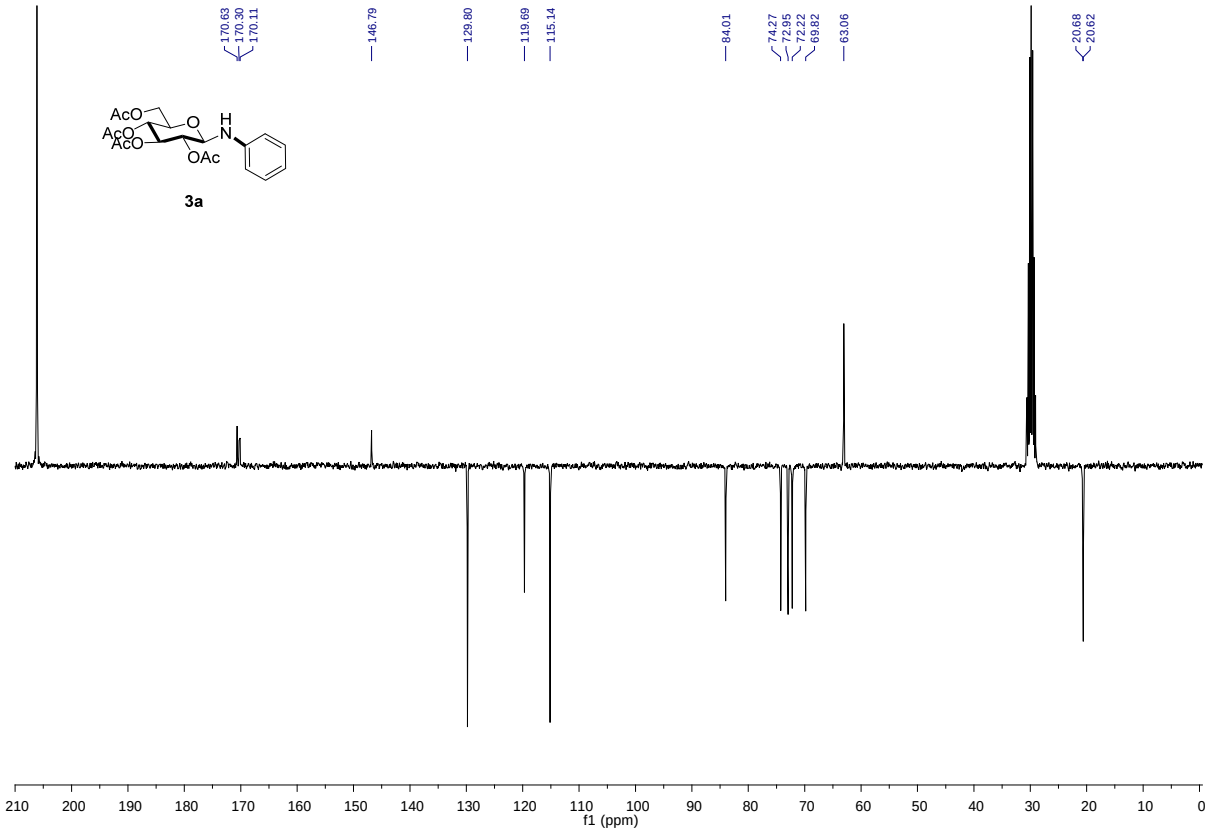
2.02
1.02
2.03
2.02
1.02
1.02
1.01
12.00
f1 (ppm)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84.01
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72.95
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20.68
20.62
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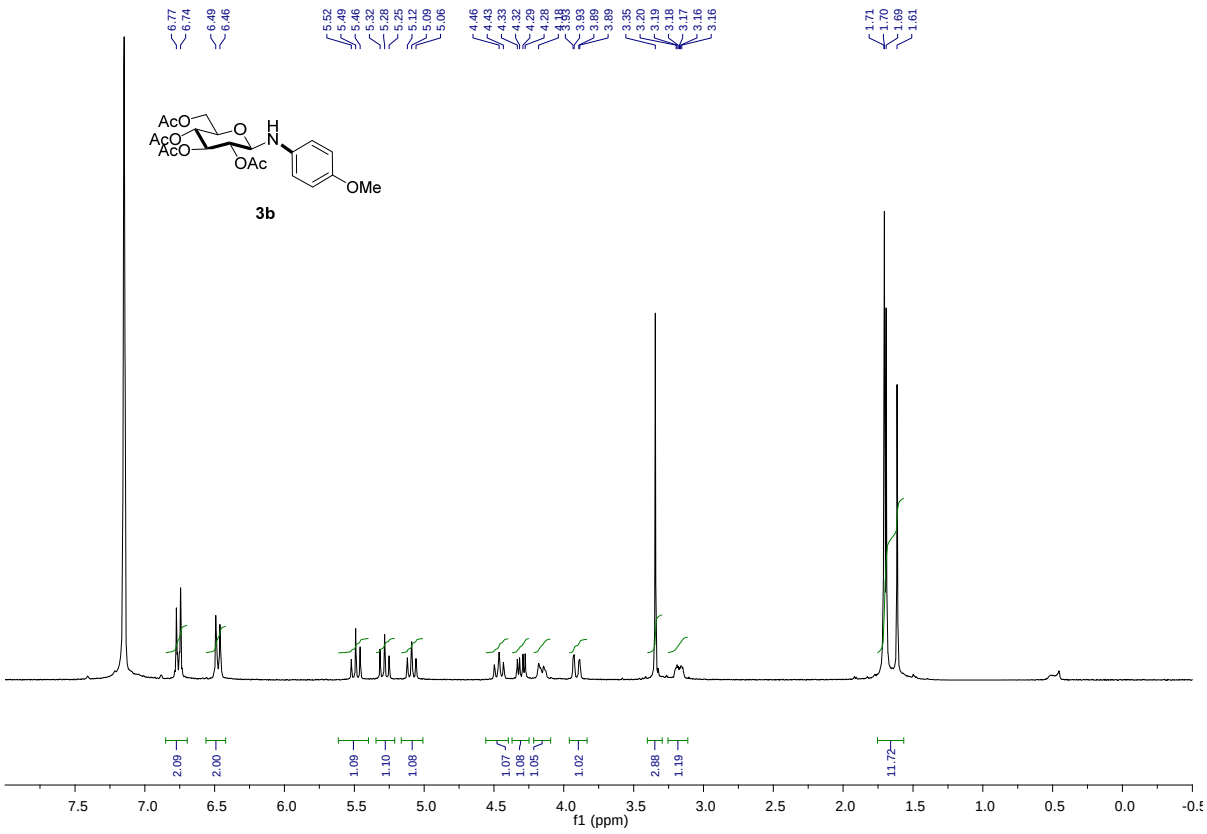
AcO
AcO
O
H
N
OAc
3a
f1 (ppm)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6.74
6.49
6.46
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5.49
5.46
5.32
5.28
5.25
5.12
5.09
5.06
4.46
4.43
4.33
4.32
4.29
4.28
4.18
4.03
3.93
3.89
3.89
3.35
3.20
3.19
3.18
3.17
3.16
3.16
1.71
1.70
1.69
1.61
AcO
AcO
AcO
O
H
N
OAc
OMe
3b
2.09
2.00
1.09
1.10
1.08
1.07
1.08
1.05
1.02
2.88
1.19
11.72
7.5
7.0
6.5
6.0
5.5
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3.0
2.5
2.0
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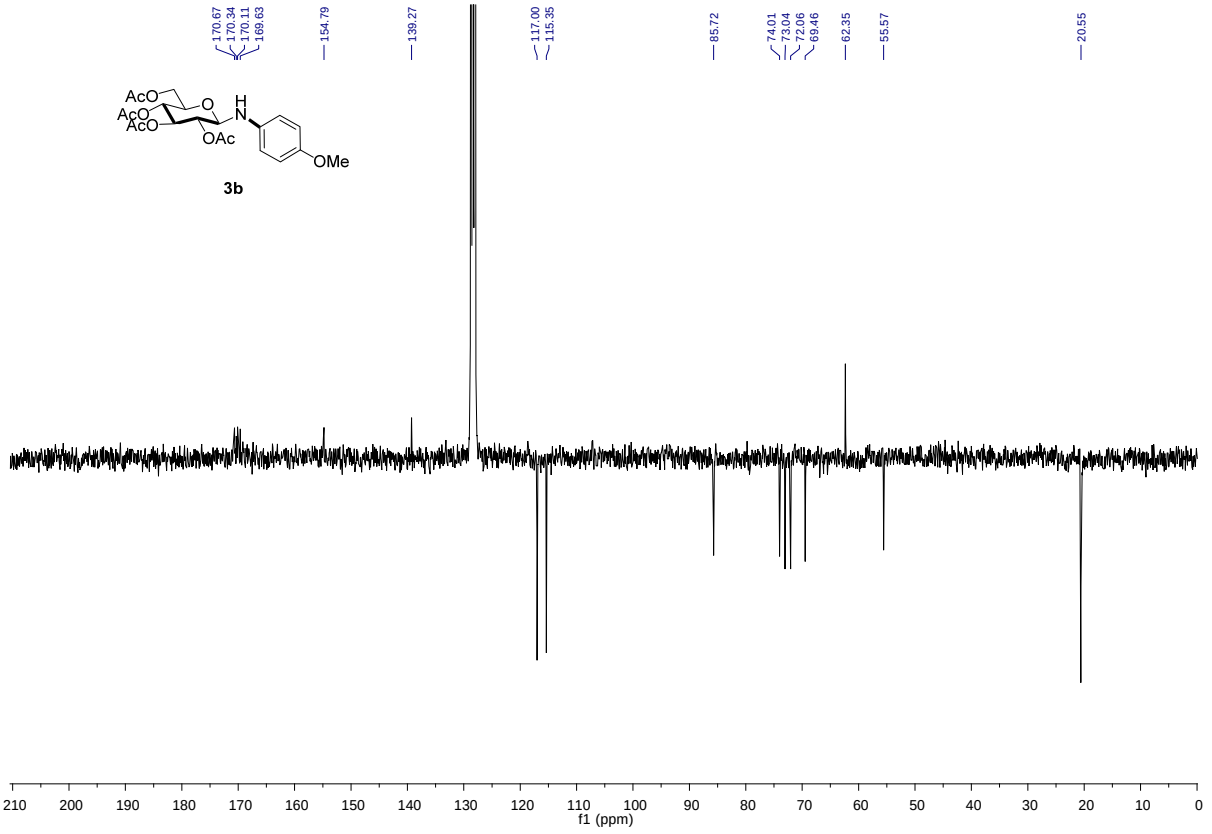
0.0
f1 (ppm)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139.27
117.00
115.35
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74.01
73.04
72.06
69.46
62.35
55.57
20.55
AcO
AcO
AcO
O
H
N
OAc
OMe
3b
210
200
190
180
170
160
150
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130
120
110
100
90
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70
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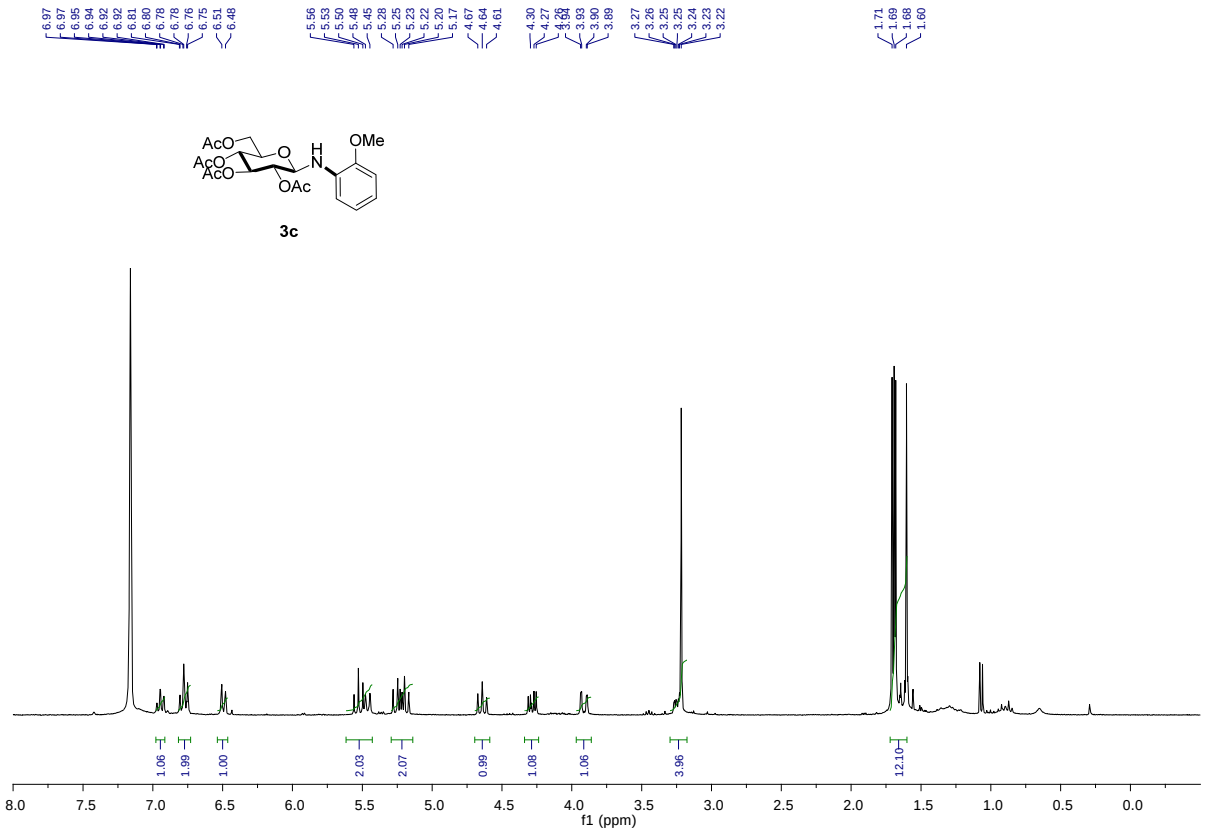
50
40
30
20
10
0
f1 (ppm)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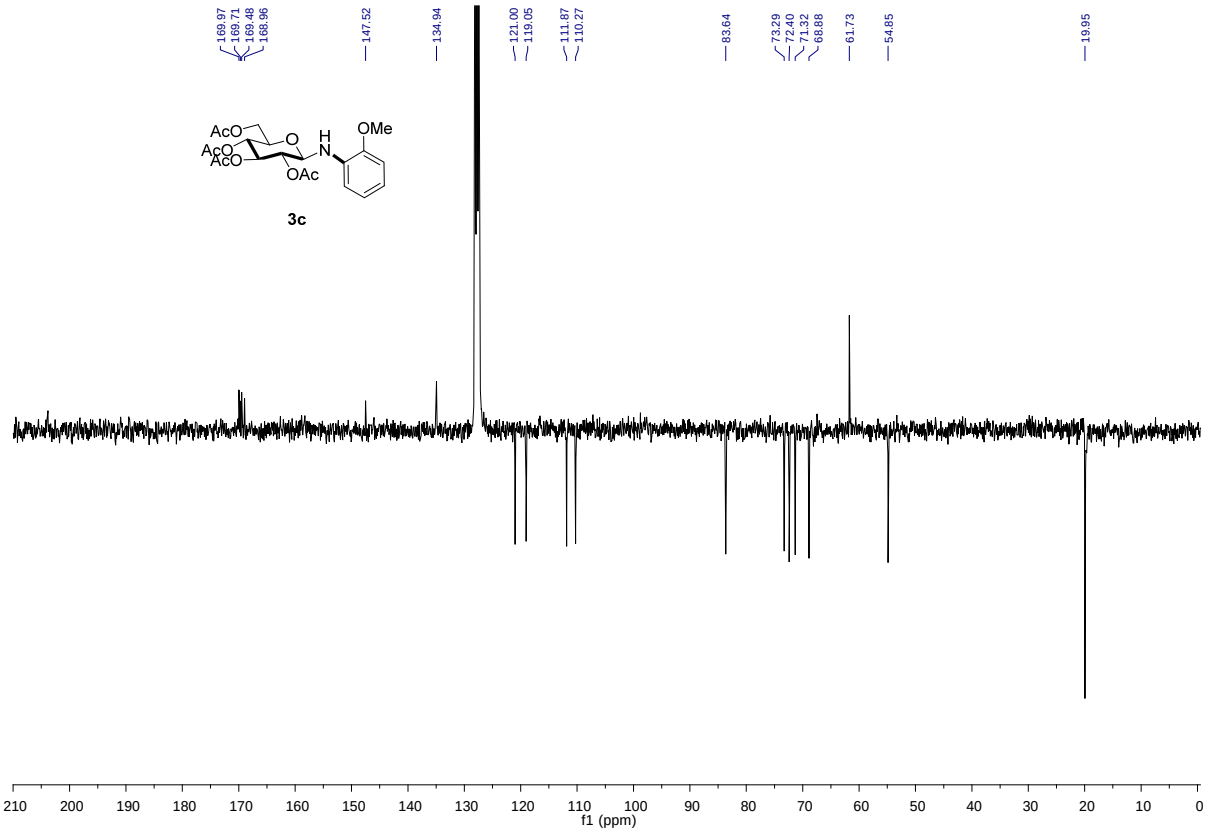
5.56 5.53 5.50 5.48 5.45 5.28 5.25 5.23 5.22 5.20 5.17 4.67 4.64 4.61
4.30 4.27 3.93 3.90 3.89
3.27 3.26 3.25 3.25 3.24 3.23 3.22
1.71 1.69 1.68 1.60
AcO AcO AcO O H N OMe OAc
3c
1.06 1.99 1.00 2.03 2.07 0.99 1.08 1.06 3.96 12.10
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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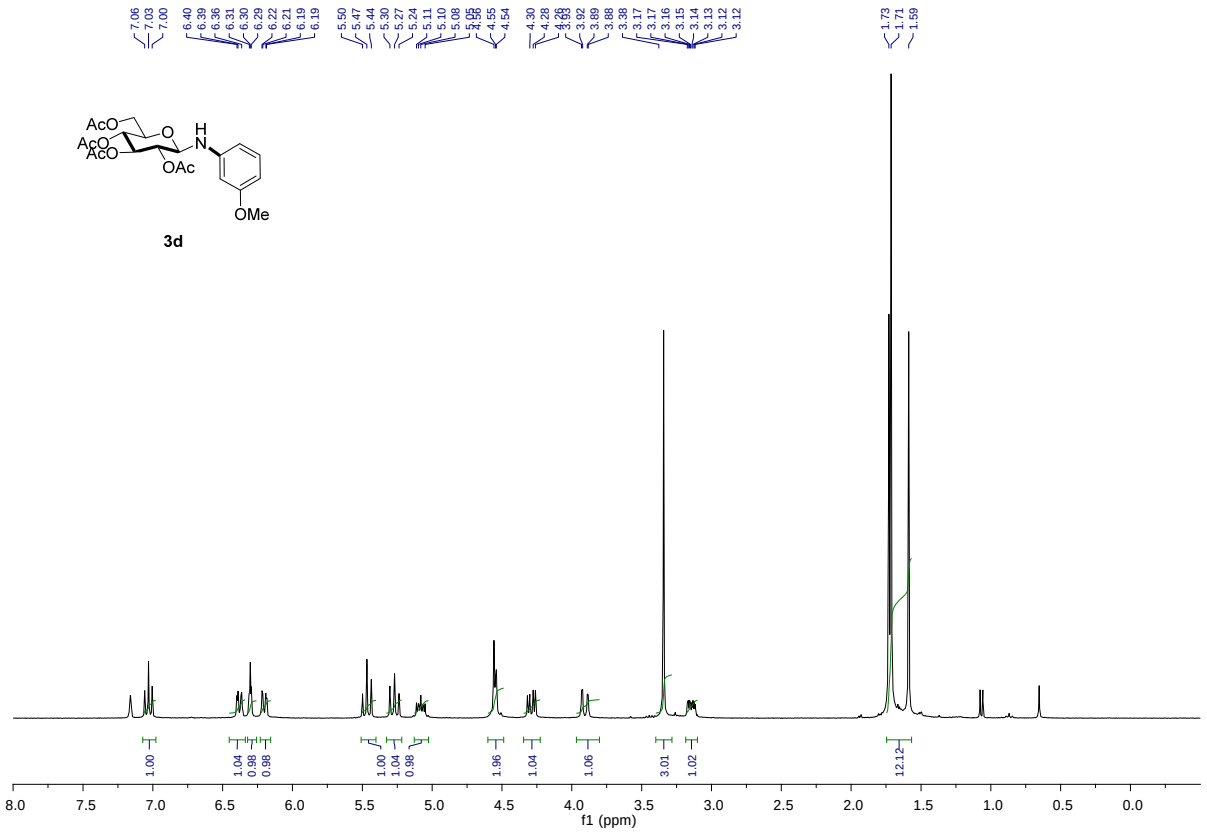
121.00 119.05
111.87 110.27
83.64
73.29 72.40 71.32 68.88
61.73
54.85
19.95
AcO AcO AcO O H N OMe OAc
3c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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6.21
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6.19
5.50
5.47
5.44
5.30
5.27
5.24
5.11
5.10
5.08
4.55
4.54
4.30
4.28
3.92
3.89
3.88
3.38
3.17
3.17
3.16
3.15
3.14
3.13
3.12
3.12
1.73
1.71
1.59
AcO
AcO
AcO
O
H
N
OAc
OMe
3d
1.00
1.04
0.98
0.98
1.00
1.04
0.98
1.96
1.04
1.06
3.01
1.02
12.12
8.0
7.5
7.0
6.5
6.0
5.5
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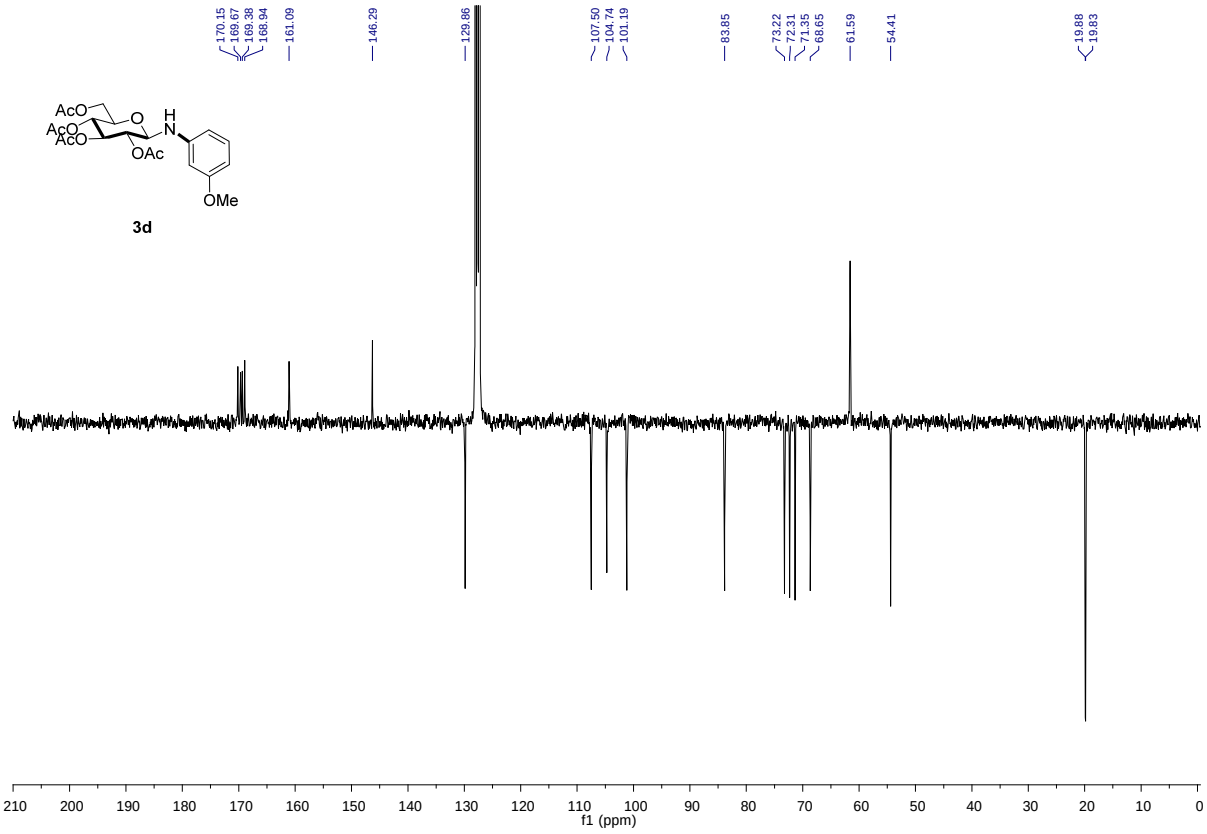
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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101.19
83.85
73.22
72.31
71.35
68.65
61.59
54.41
19.88
19.83
AcO
AcO
AcO
O
H
N
OAc
OMe
3d
210
200
190
180
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130
120
110
100
90
80
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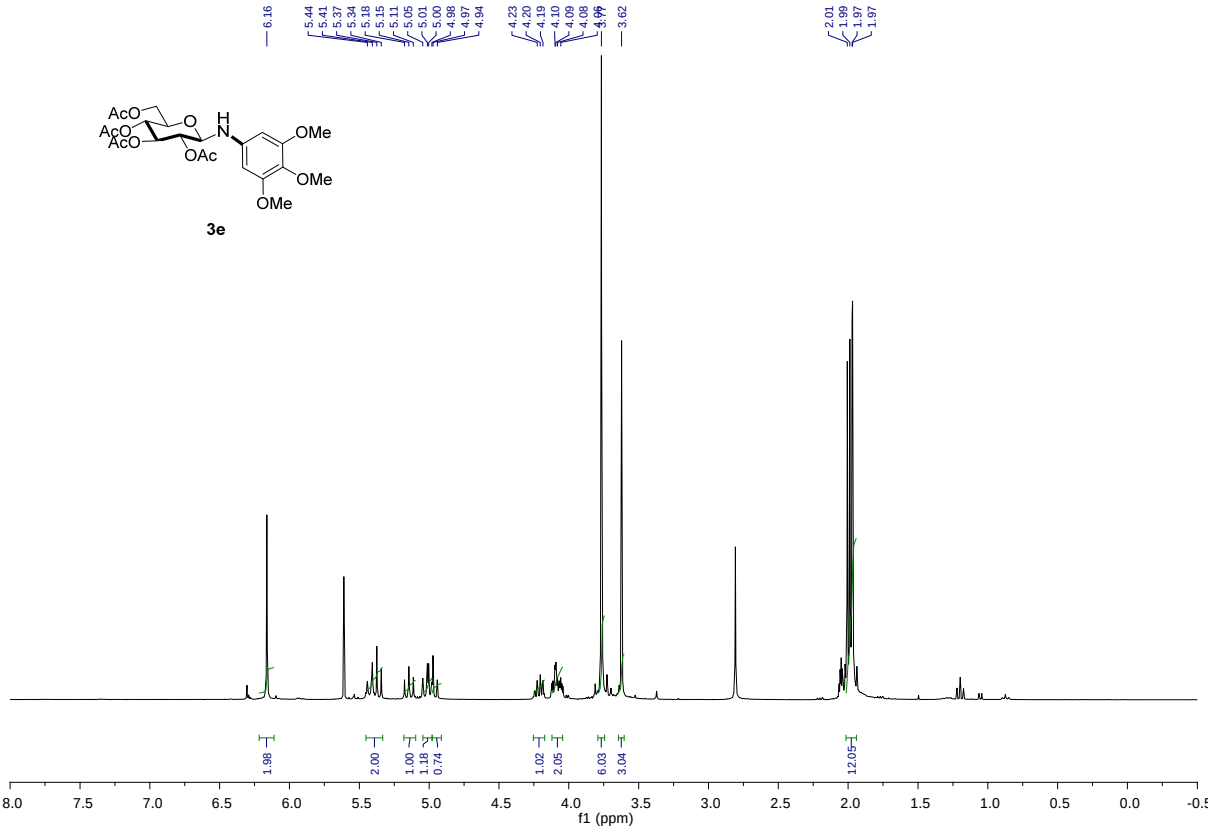
50
40
30
20
10
0
f1 (ppm)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5.11
5.05
5.01
5.00
4.98
4.97
4.94
4.23
4.20
4.19
4.10
4.09
4.08
3.62
2.01
1.99
1.97
1.97
AcO
AcO
AcO
O
H
N
OAc
OMe
OMe
OMe
3e
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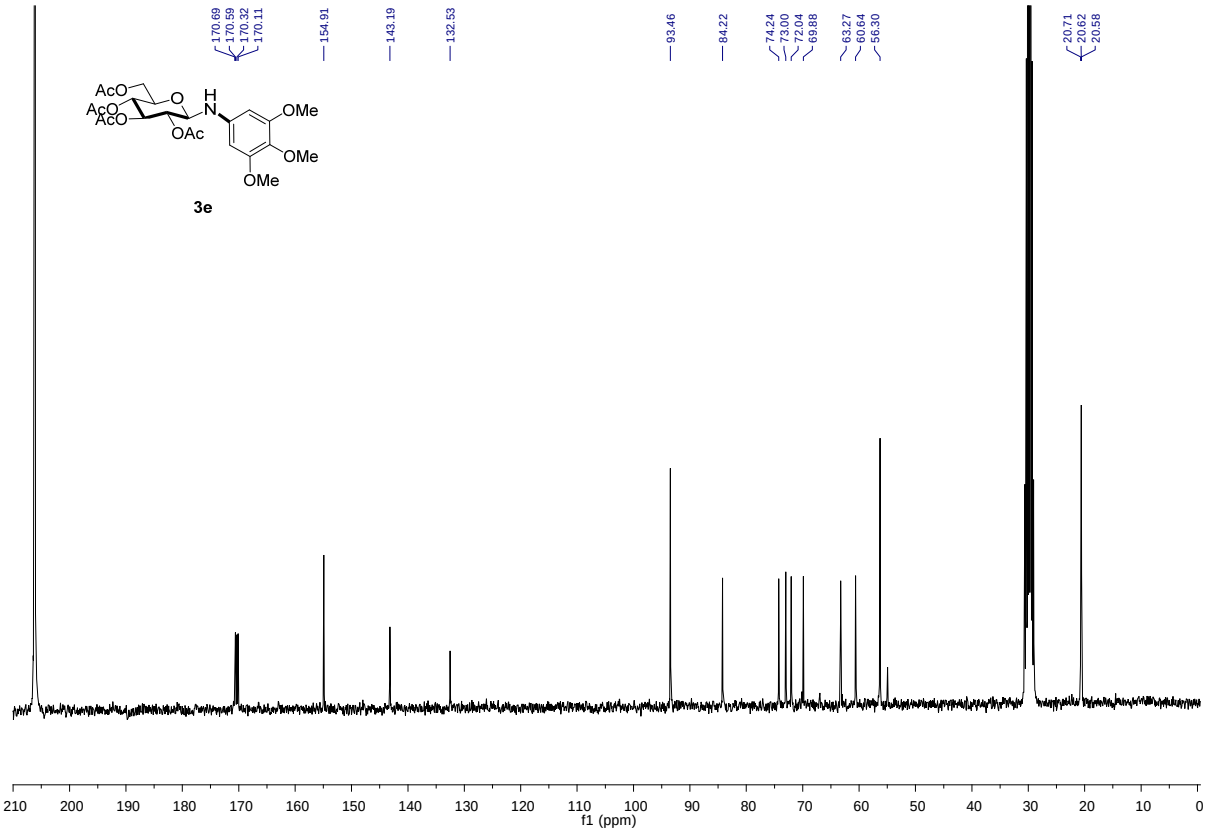
1.00
1.18
0.74
1.02
2.05
6.03
3.04
12.05
f1 (ppm)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84.22
74.24
73.00
72.04
69.88
63.27
60.64
56.30
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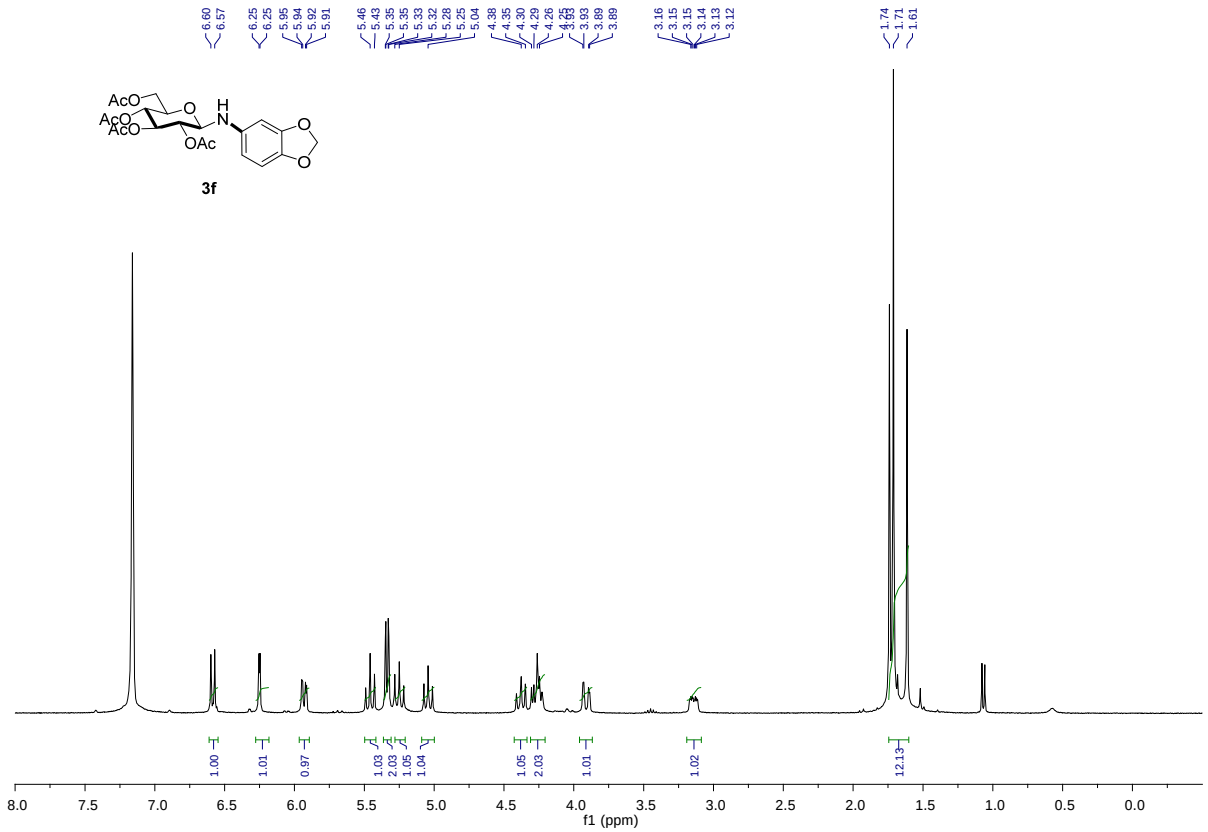
20.58
AcO
AcO
AcO
O
H
N
OAc
OMe
OMe
OMe
3e
f1 (ppm)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5.33
5.32
5.28
5.25
5.04
4.38
4.35
4.30
4.29
4.26
3.93
3.89
3.89
3.16
3.15
3.15
3.14
3.13
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1.74
1.71
1.61
AcO
AcO
AcO
O
H
N
OAc
O
O
3f
1.00
1.01
0.97
1.03
2.03
1.05
1.04
1.05
2.03
1.01
1.02
12.13
8.0
7.5
7.0
6.5
6.0
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1.0
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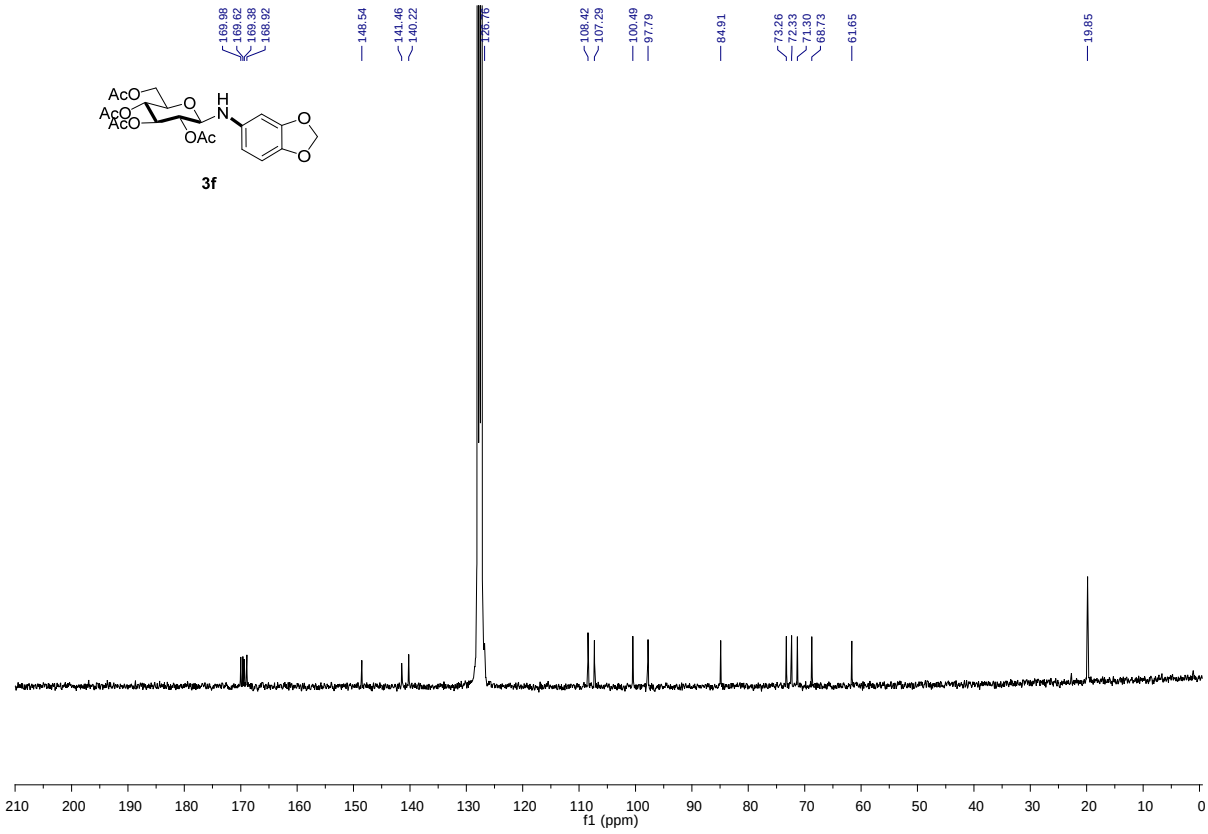
0.0
f1 (ppm)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100.49
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84.91
73.26
72.33
71.30
68.73
61.65
19.85
AcO
AcO
AcO
O
H
N
OAc
O
O
3f
210
200
190
180
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90
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50
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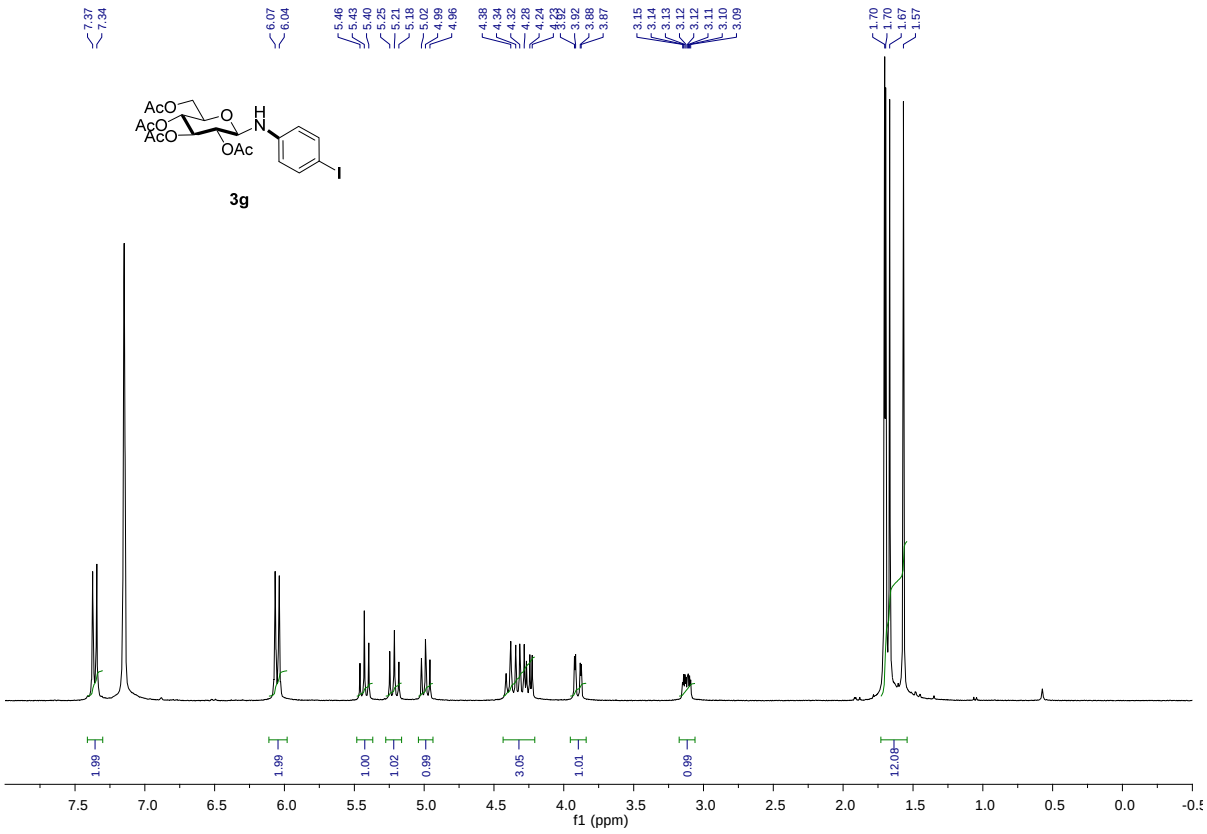
f1 (ppm)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4.28
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3.12
3.12
3.11
3.10
3.09
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1.57
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AcO
AcO
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H
N
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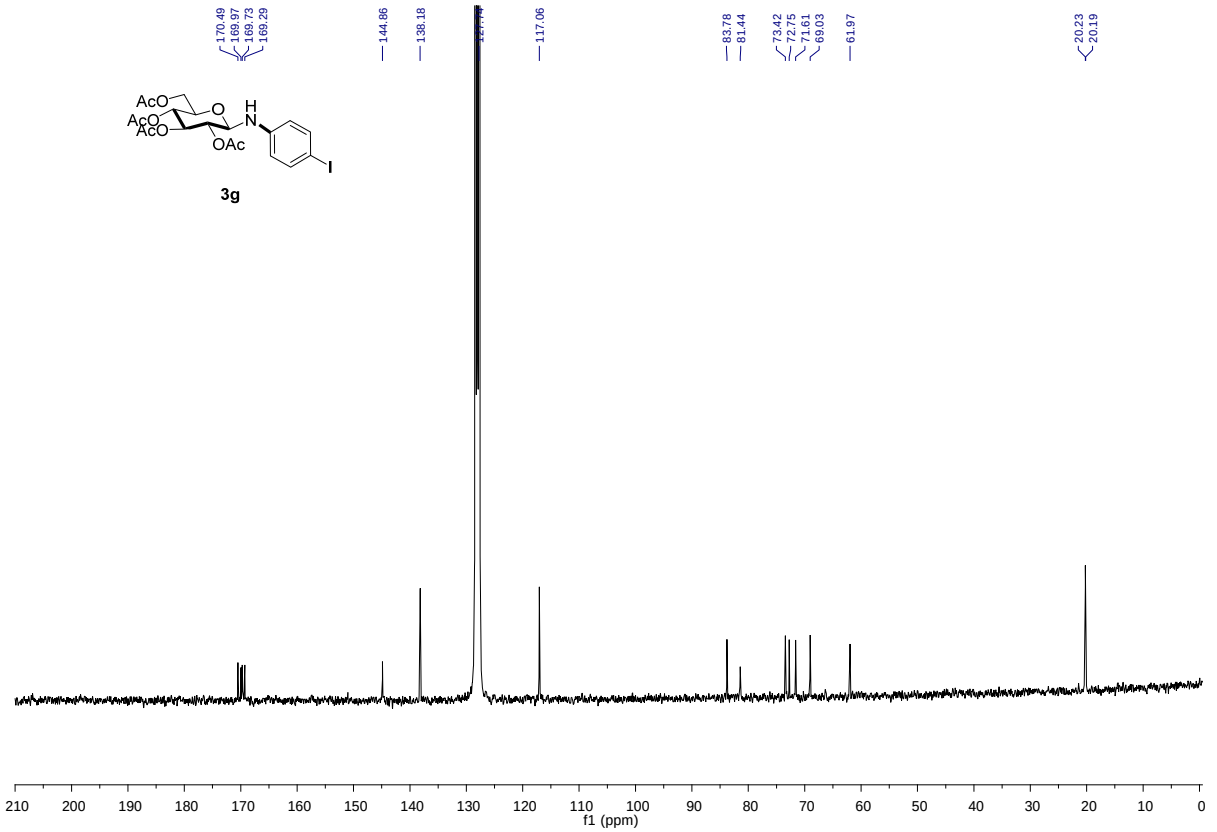
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AcO
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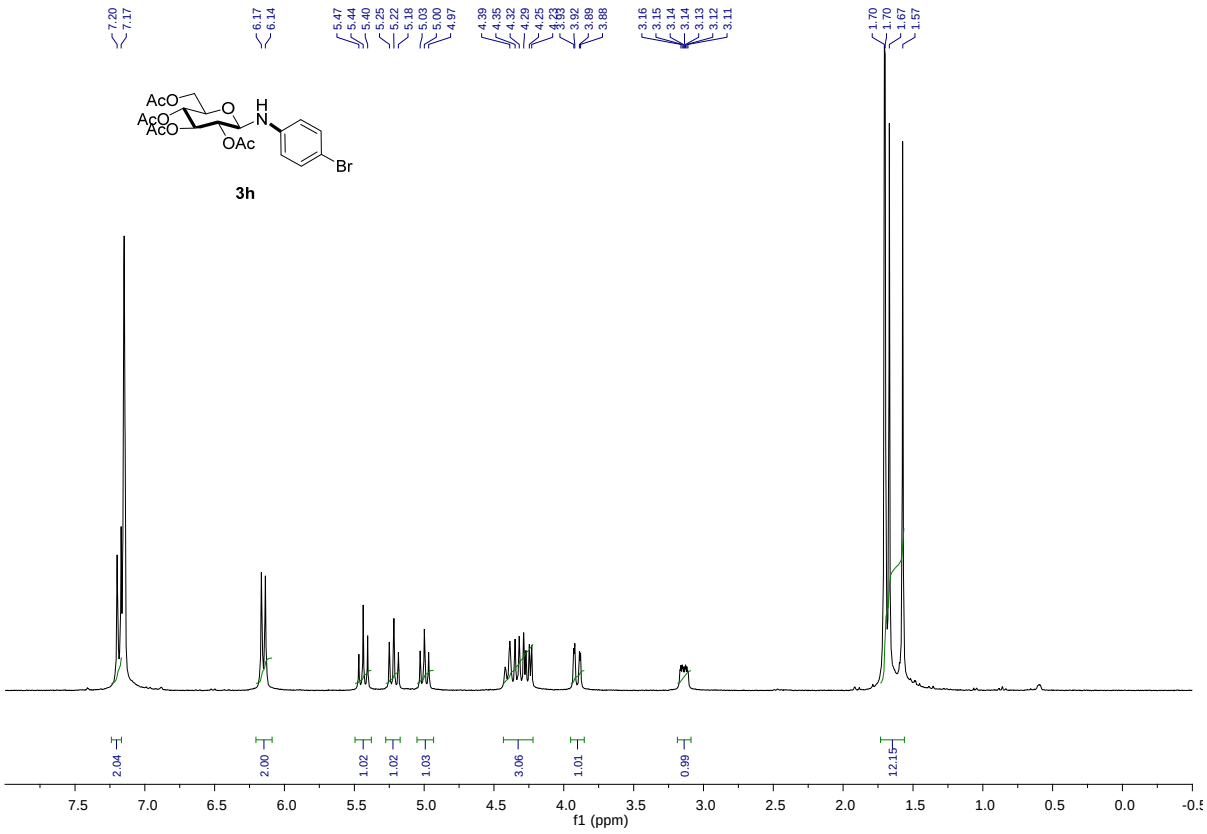
H
N
OAc
I
3g
f1 (ppm)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3.88
3.16
3.15
3.14
3.13
3.12
3.11
1.70
1.70
1.67
1.57
AcO
AcO
AcO
O
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N
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1.02
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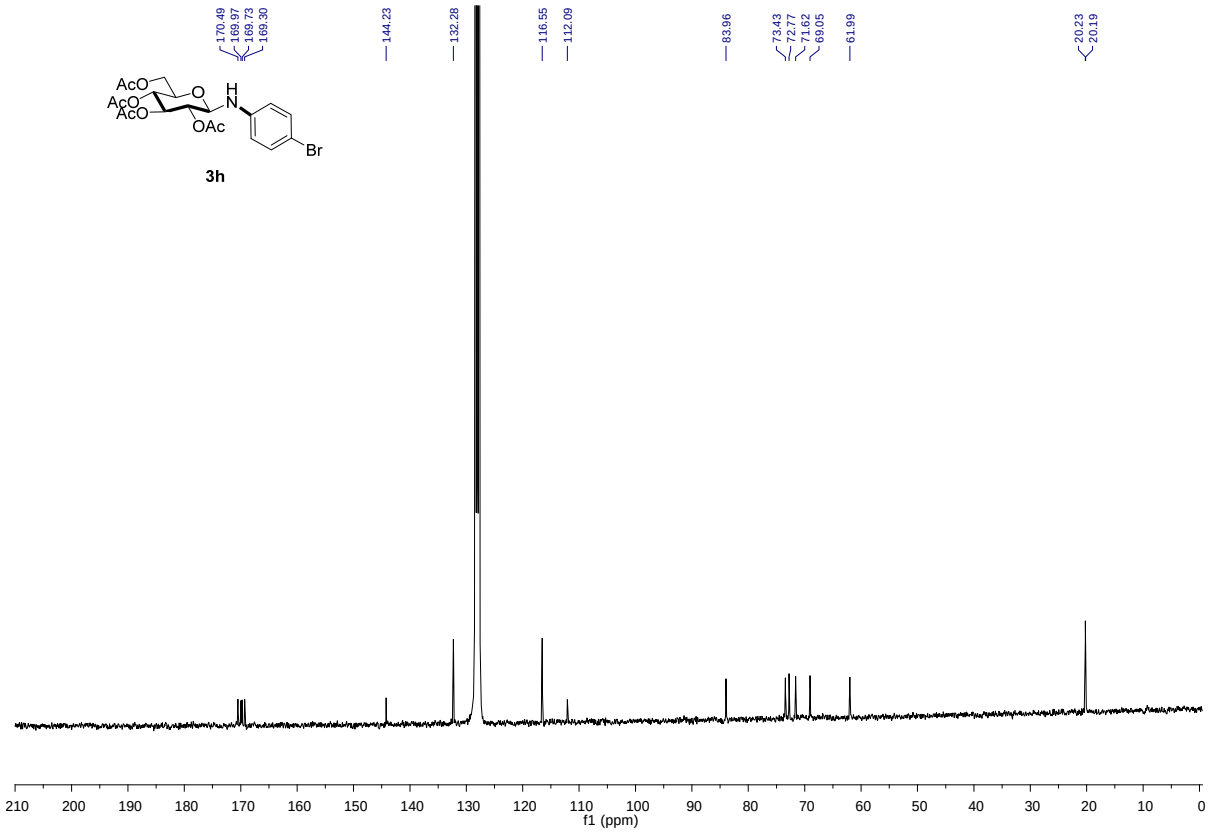
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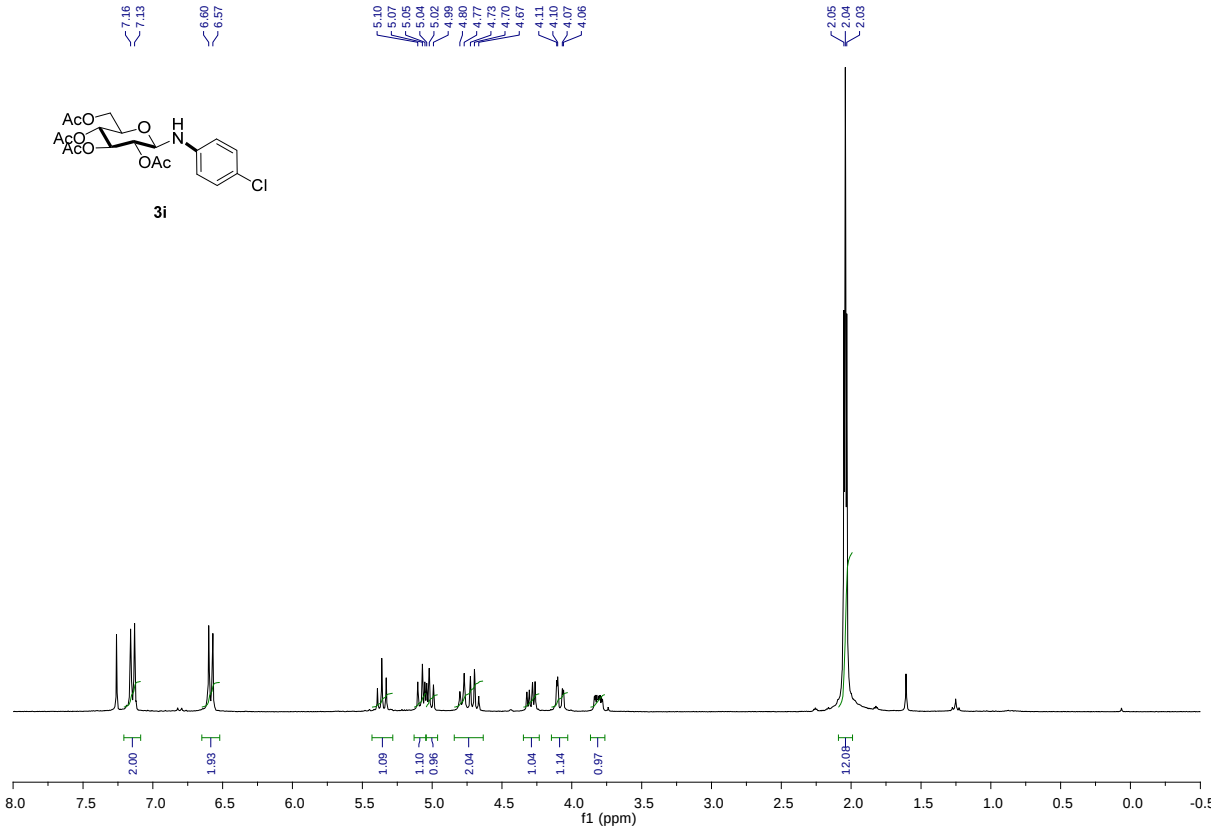
3h
f1 (ppm)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4.10
4.07
4.06
2.05
2.04
2.03
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Cl
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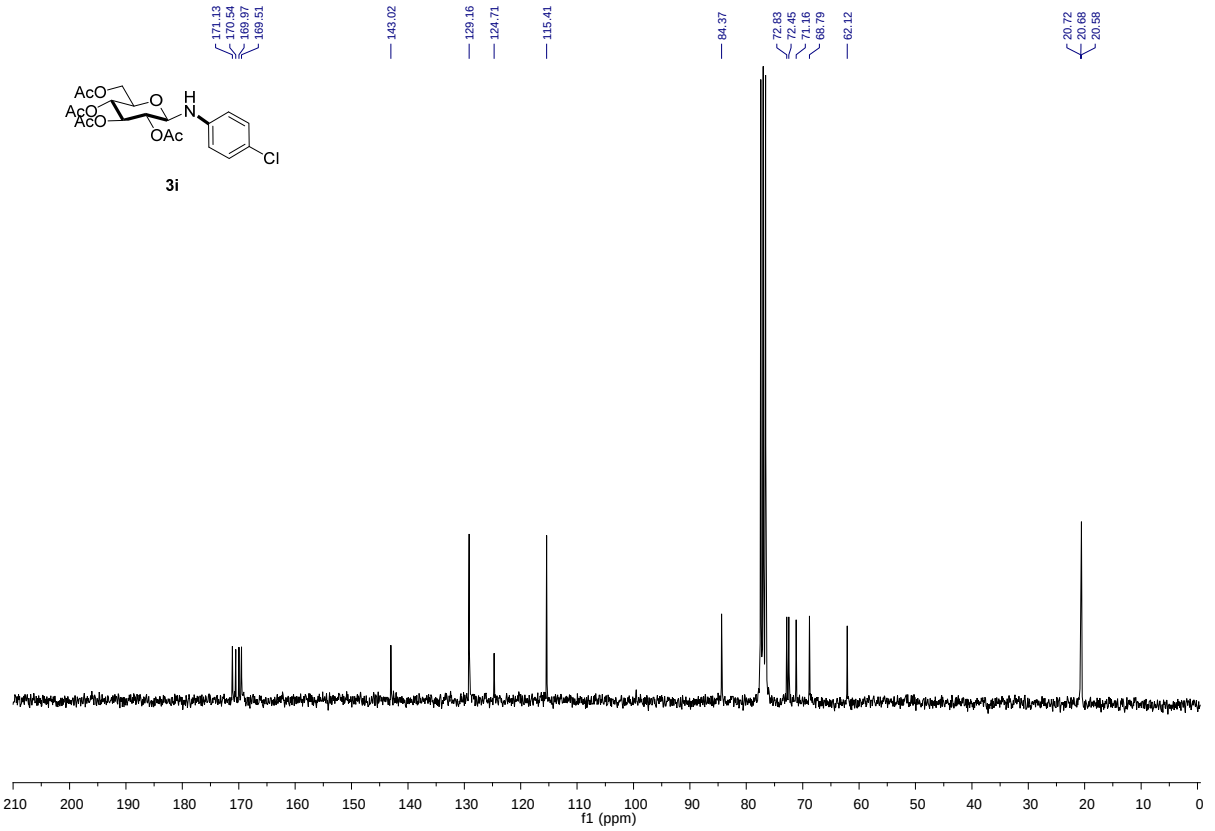
f1 (ppm)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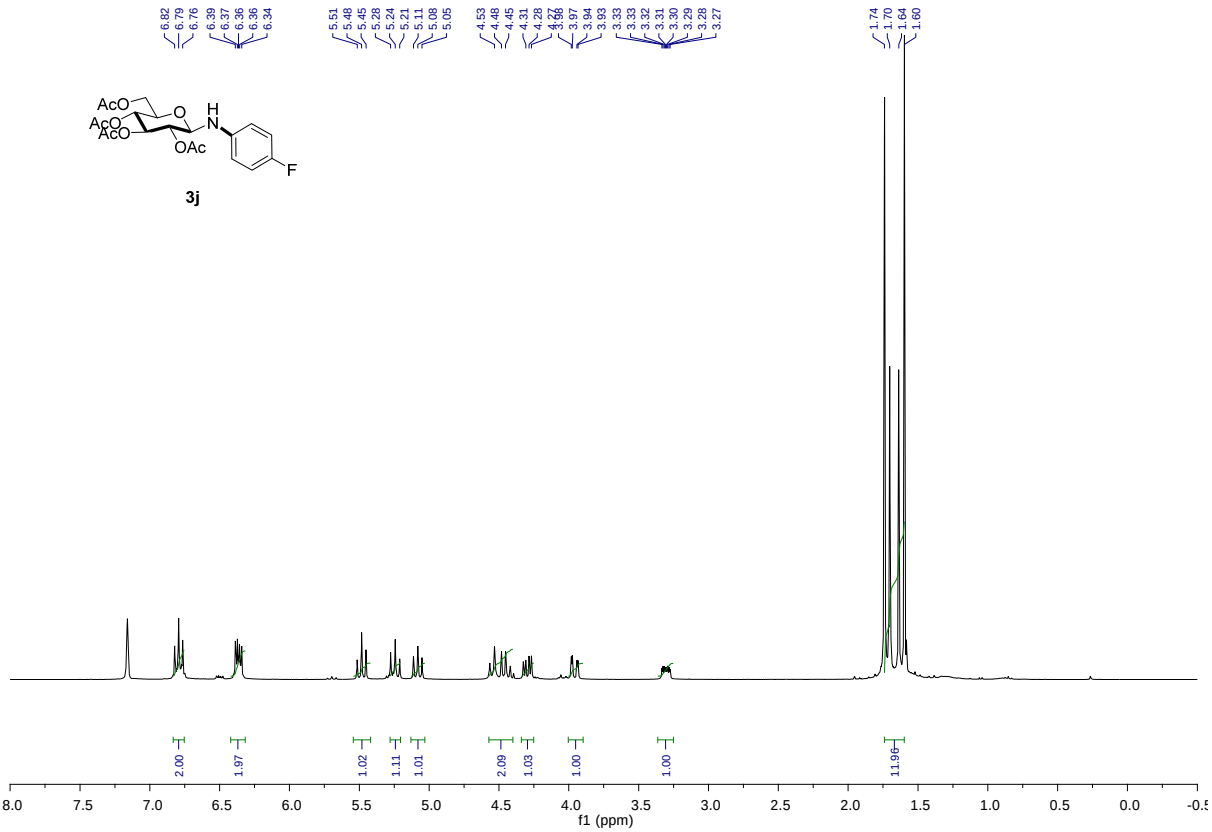
20.58
AcO
AcO
AcO
O
H
N
OAc
Cl
3i
f1 (ppm)


AcO
AcO
AcO
O
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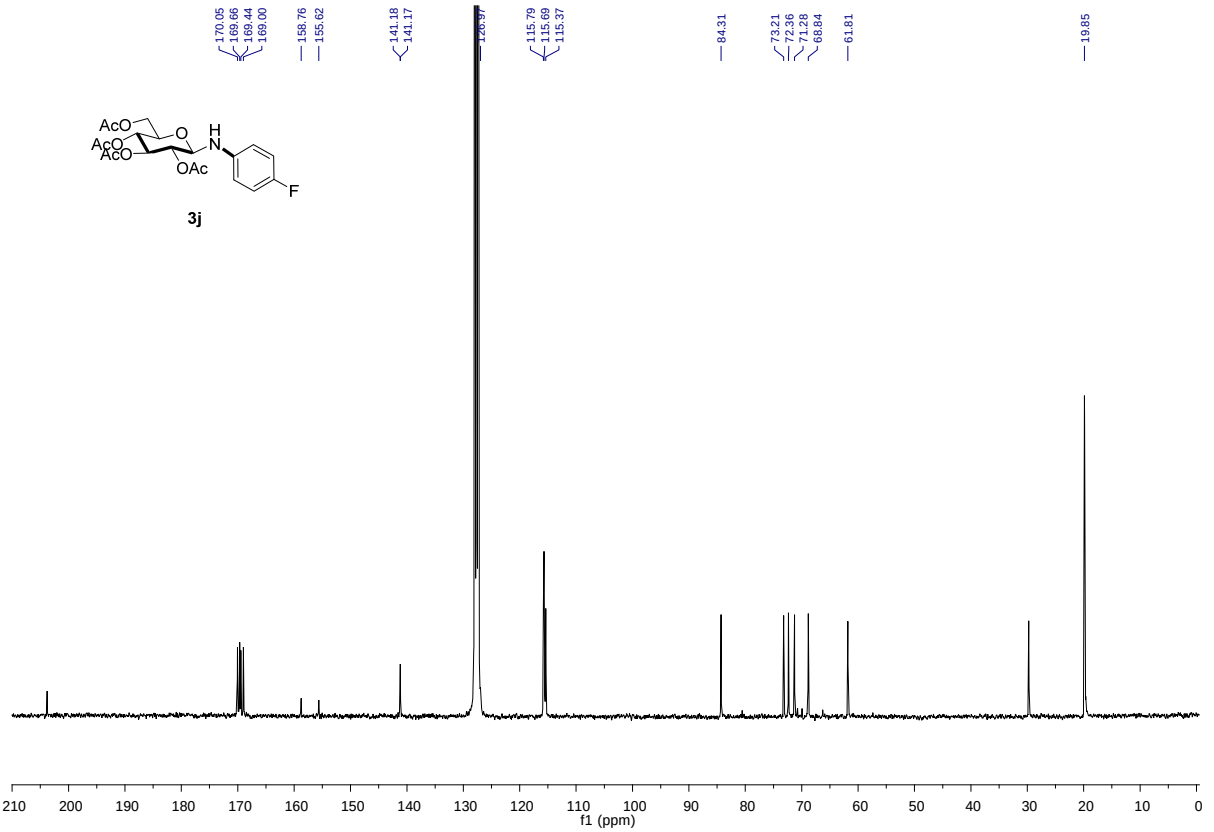
N
OAc
F
3j
f1 (ppm)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AcO
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N
OAc
F
3j
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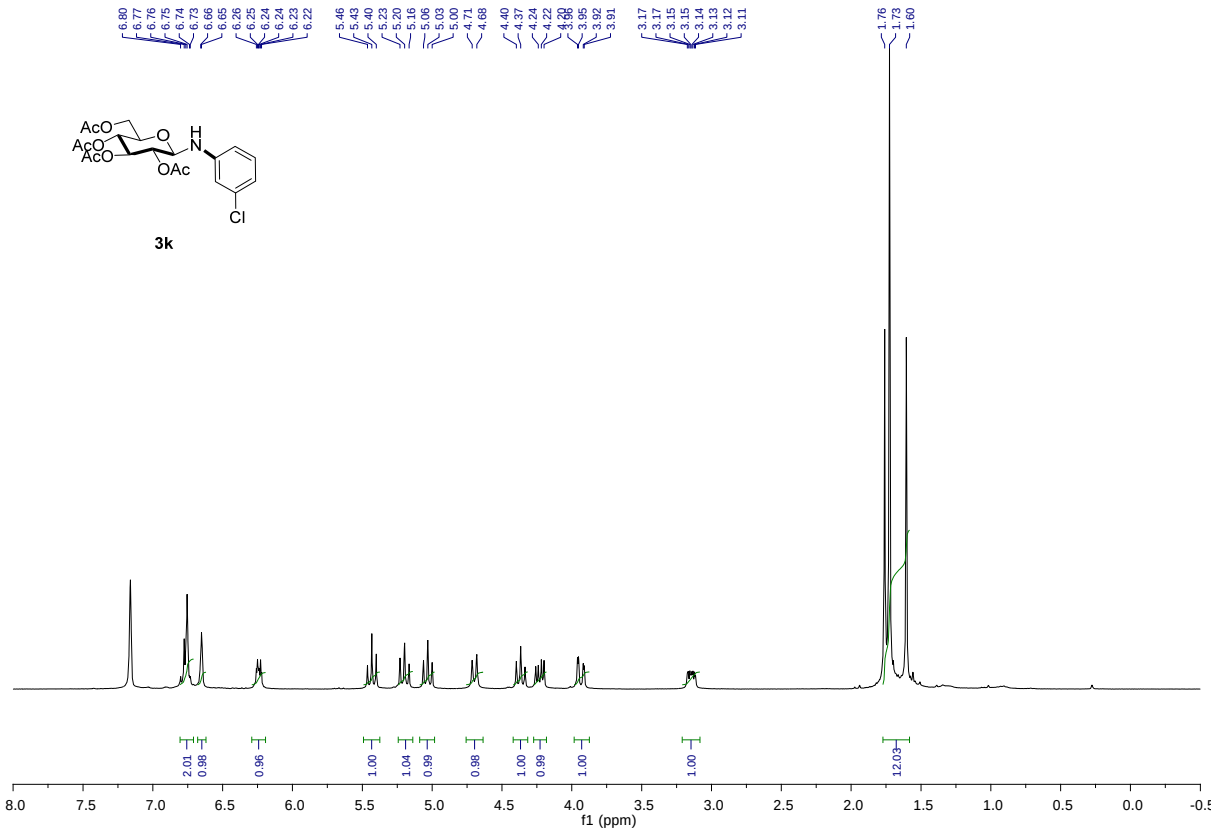
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Cl
3k
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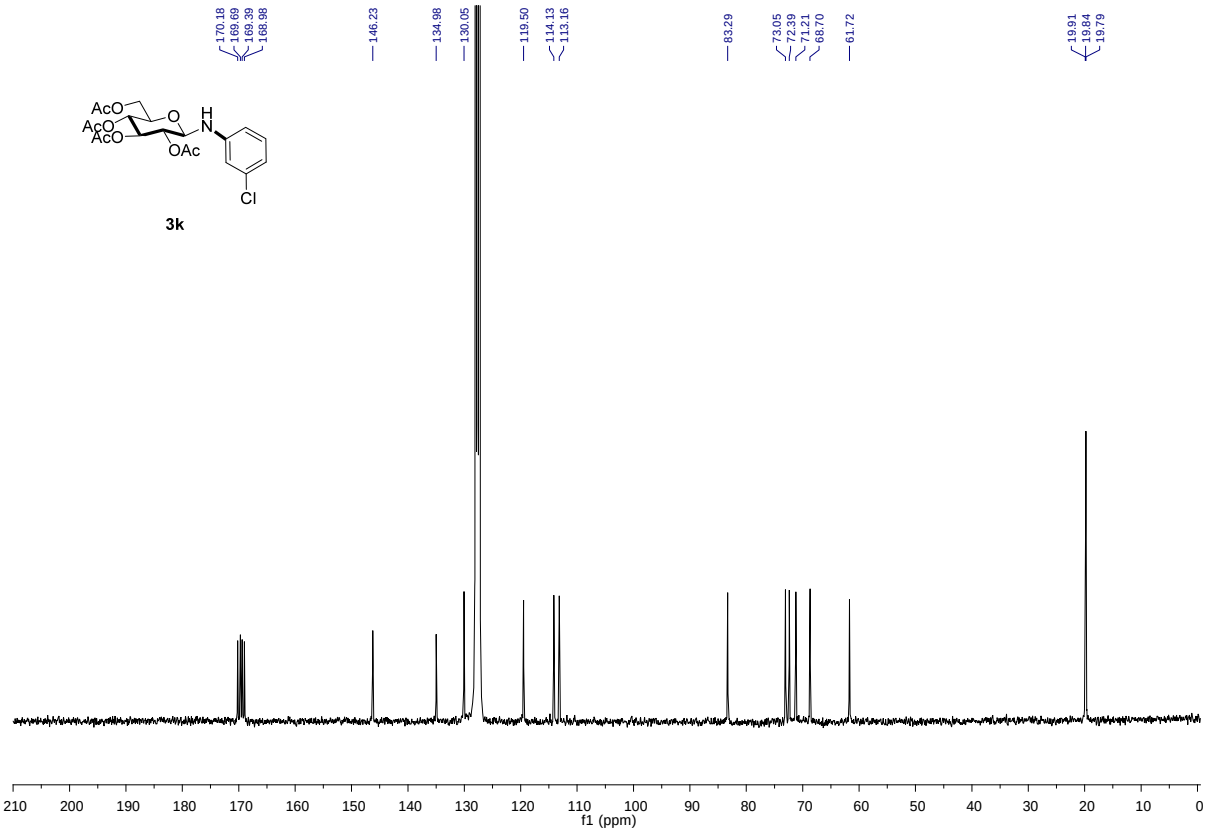
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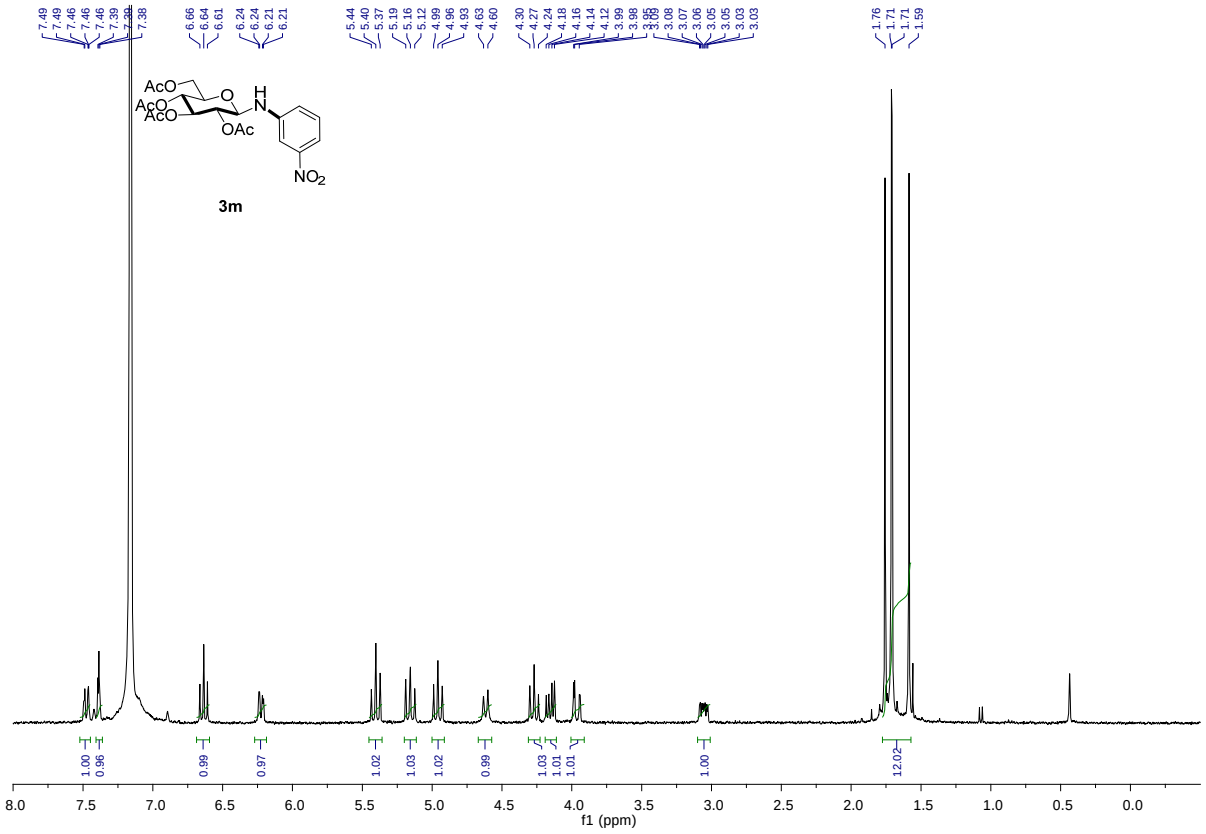
Cl
3k
f1 (ppm)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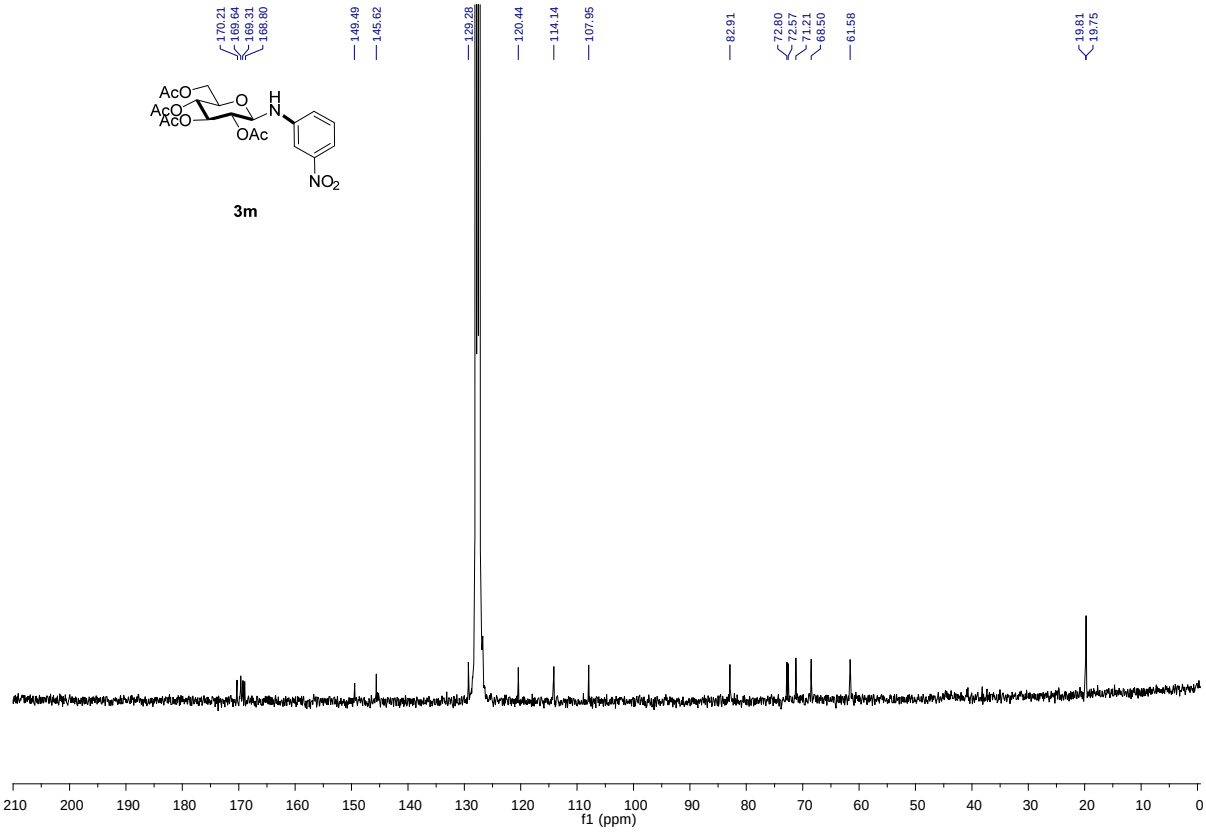
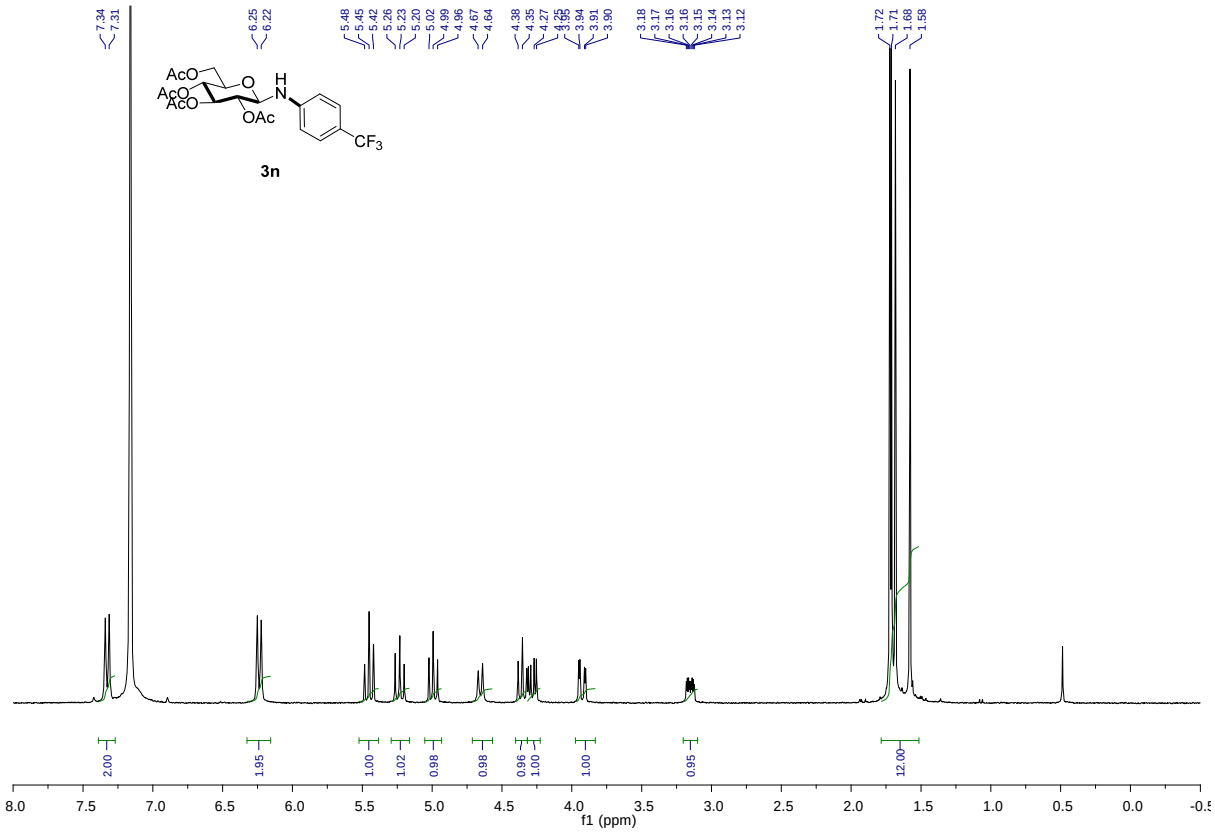
OAc
NO2
3m
f1 (ppm)


AcO
AcO
AcO
O
H
N
OAc
NO2
3m
f1 (ppm)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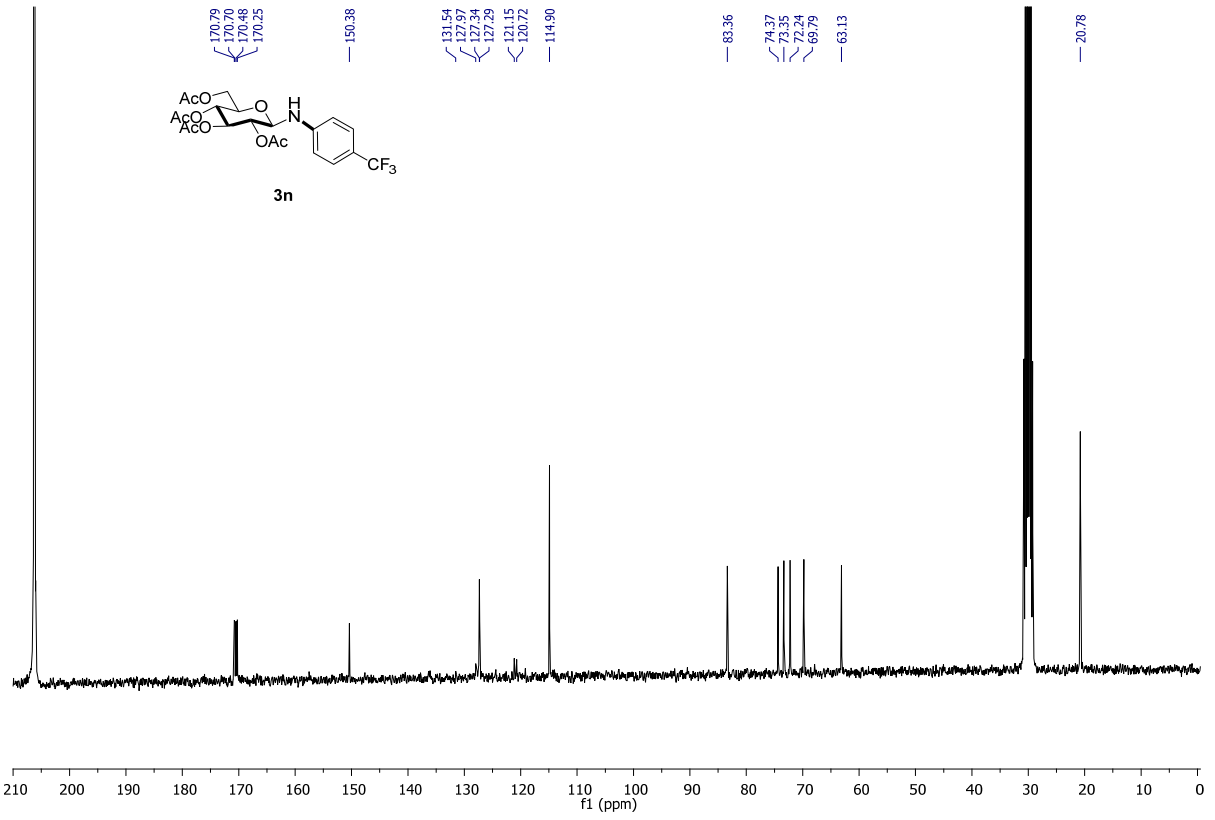
5.45
5.42
5.26
5.23
5.20
5.02
4.99
4.96
4.67
4.64
4.38
4.35
4.27
3.94
3.91
3.90
3.18
3.17
3.16
3.15
3.14
3.13
3.12
1.72
1.71
1.68
1.58
AcO
AcO
AcO
O
H
N
OAc
CF3
3n
2.00
1.95
1.00
1.02
0.98
0.98
0.96
1.00
1.00
0.95
12.00
f1 (ppm)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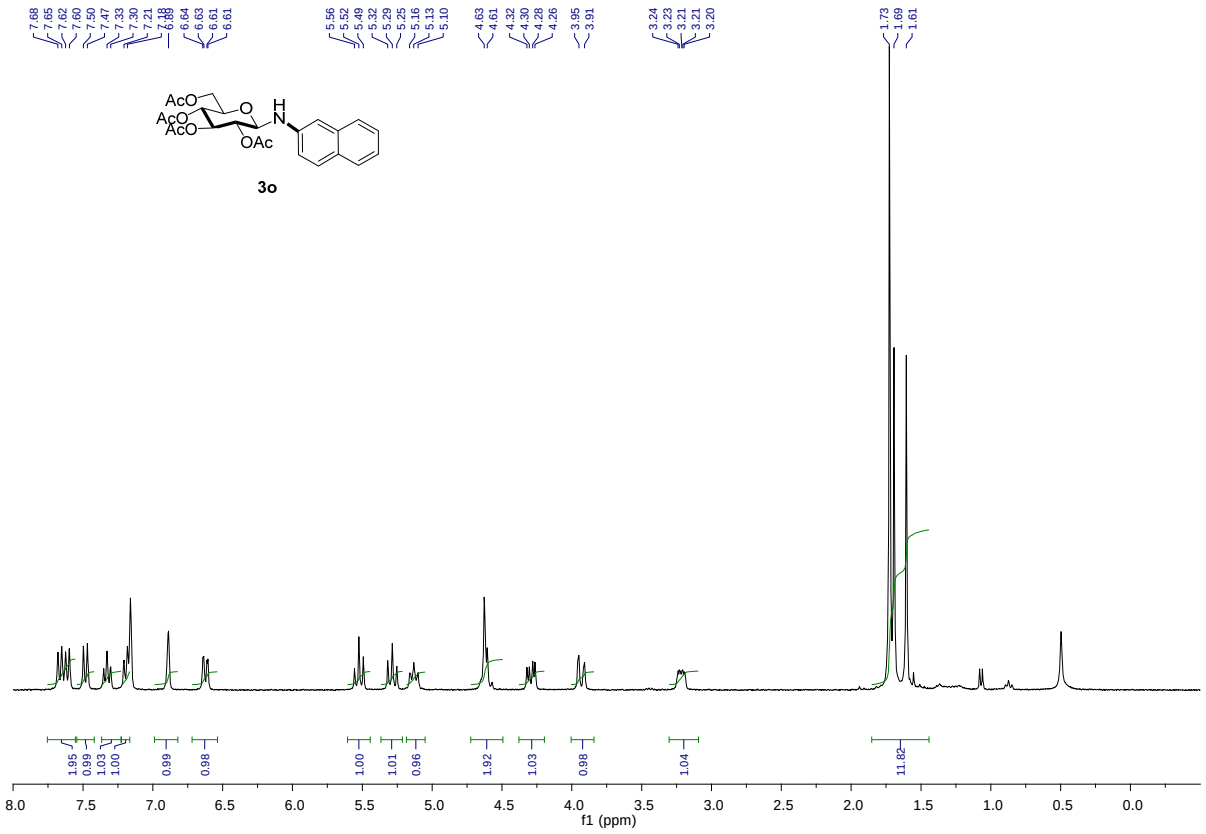
127.34
127.29
121.15
120.72
114.90
83.36
74.37
73.35
72.24
69.79
63.13
20.78
AcO
AcO
AcO
O
H
N
OAc
CF3
3n
f1 (ppm)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7.30
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6.63
6.61
6.61
5.56
5.52
5.49
5.32
5.29
5.25
5.16
5.13
5.10
4.63
4.61
4.32
4.30
4.28
4.26
3.95
3.91
3.24
3.23
3.21
3.21
3.20
1.73
1.69
1.61
AcO
AcO
AcO
O
H
N
OAc
3o
1.95
0.99
1.03
1.00
0.99
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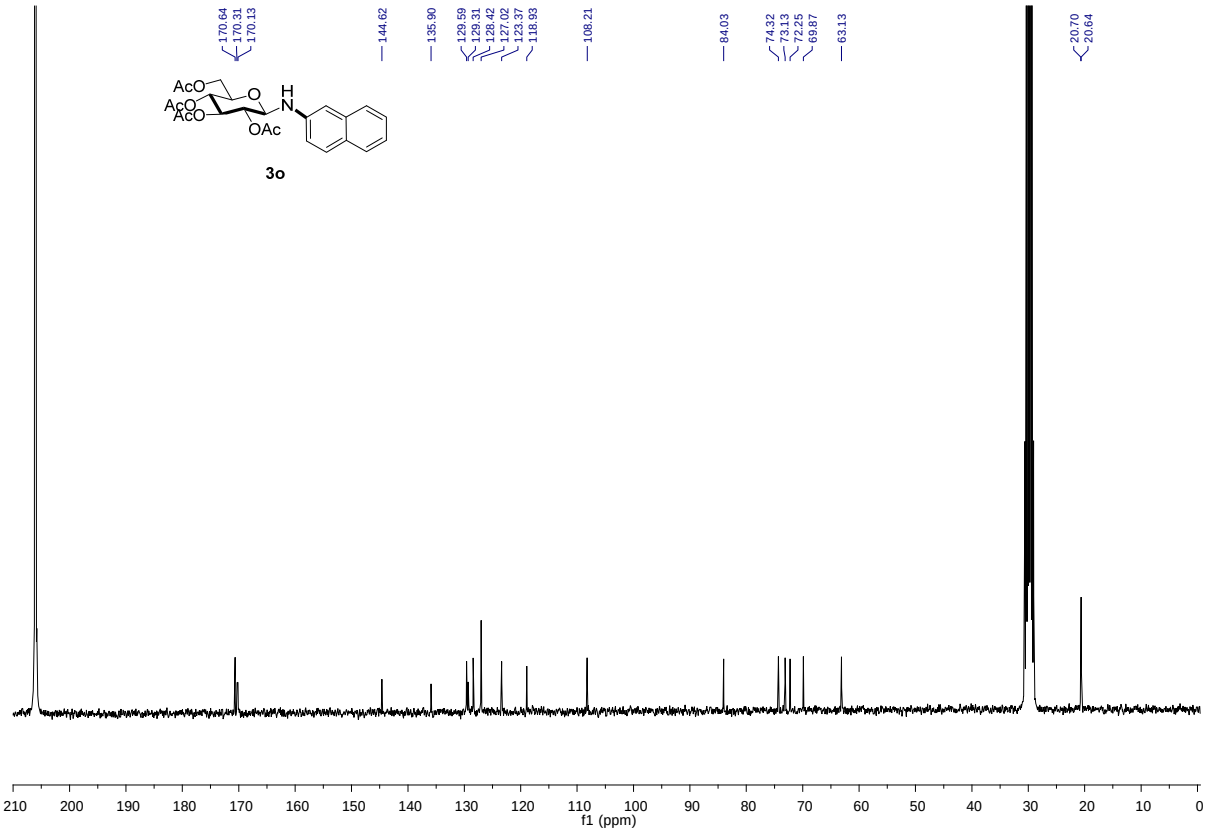
1.00
1.01
0.96
1.92
1.03
0.98
1.04
11.82
f1 (ppm)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170.13
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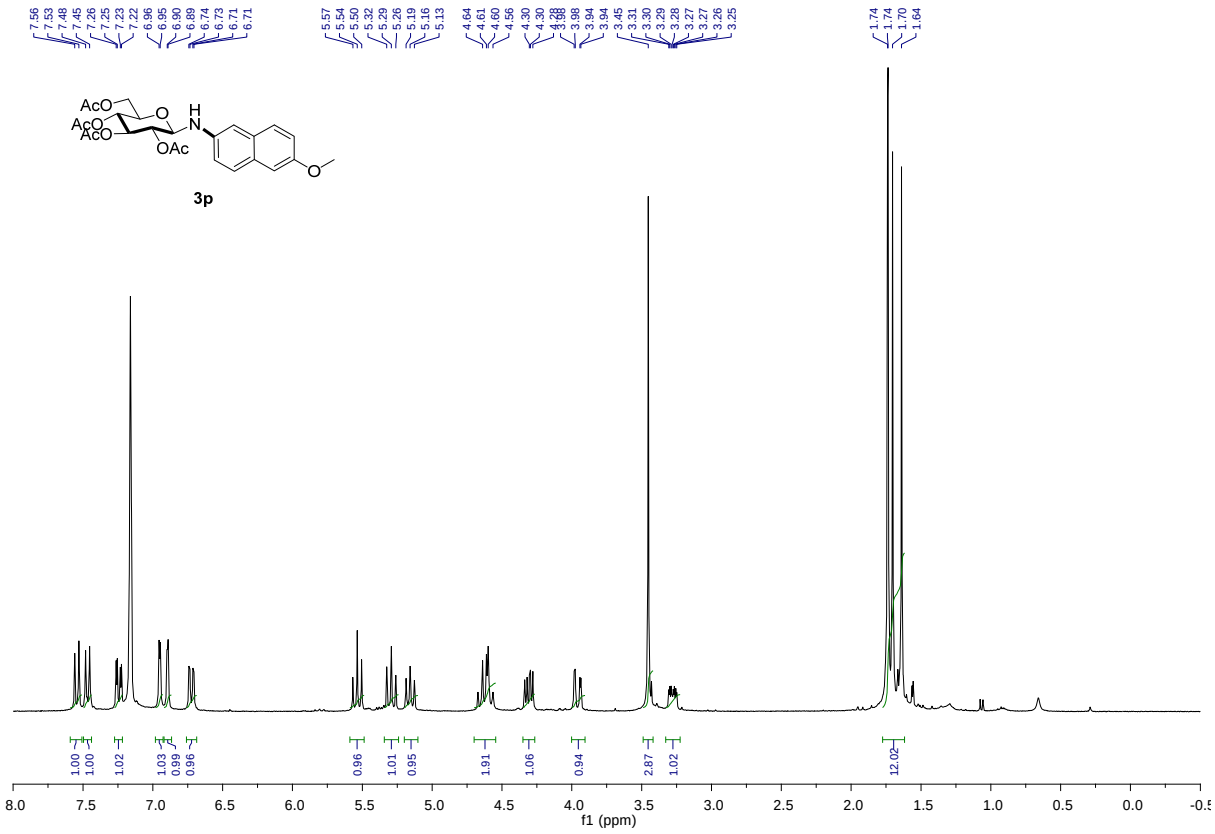
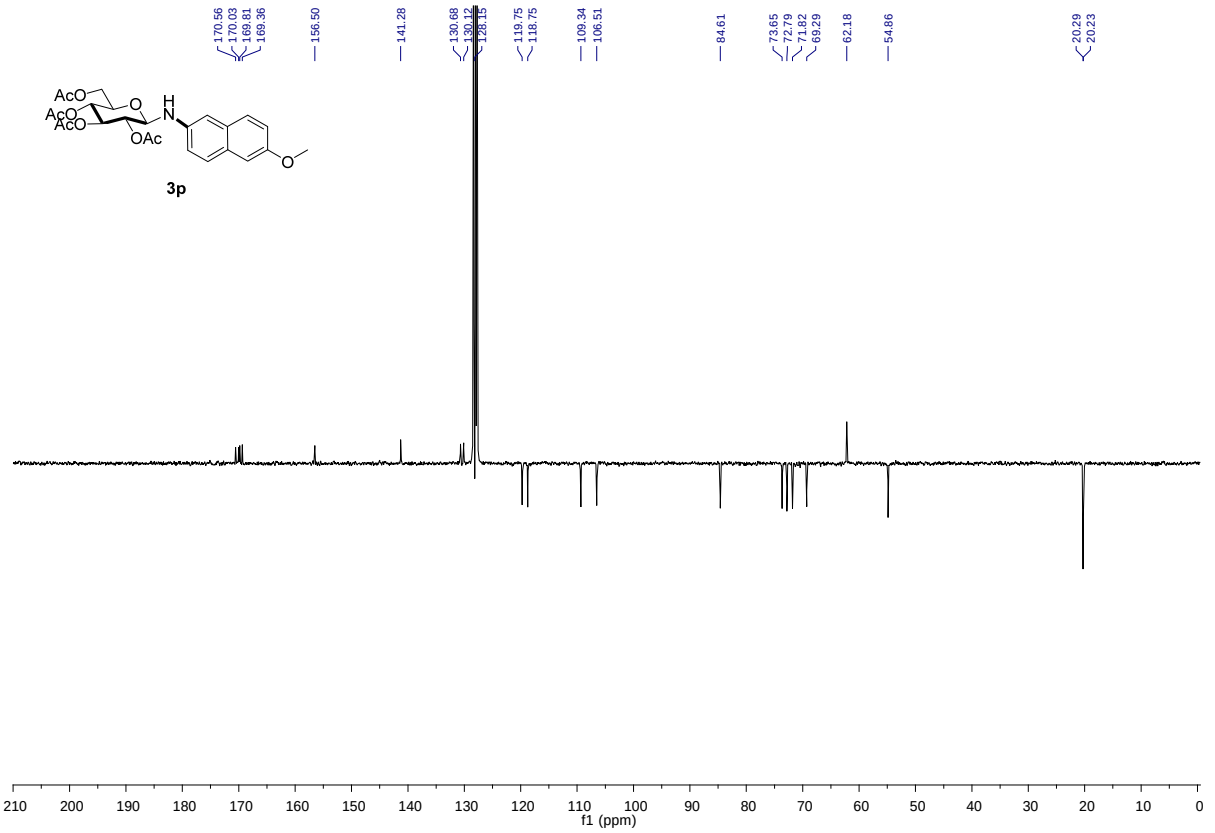
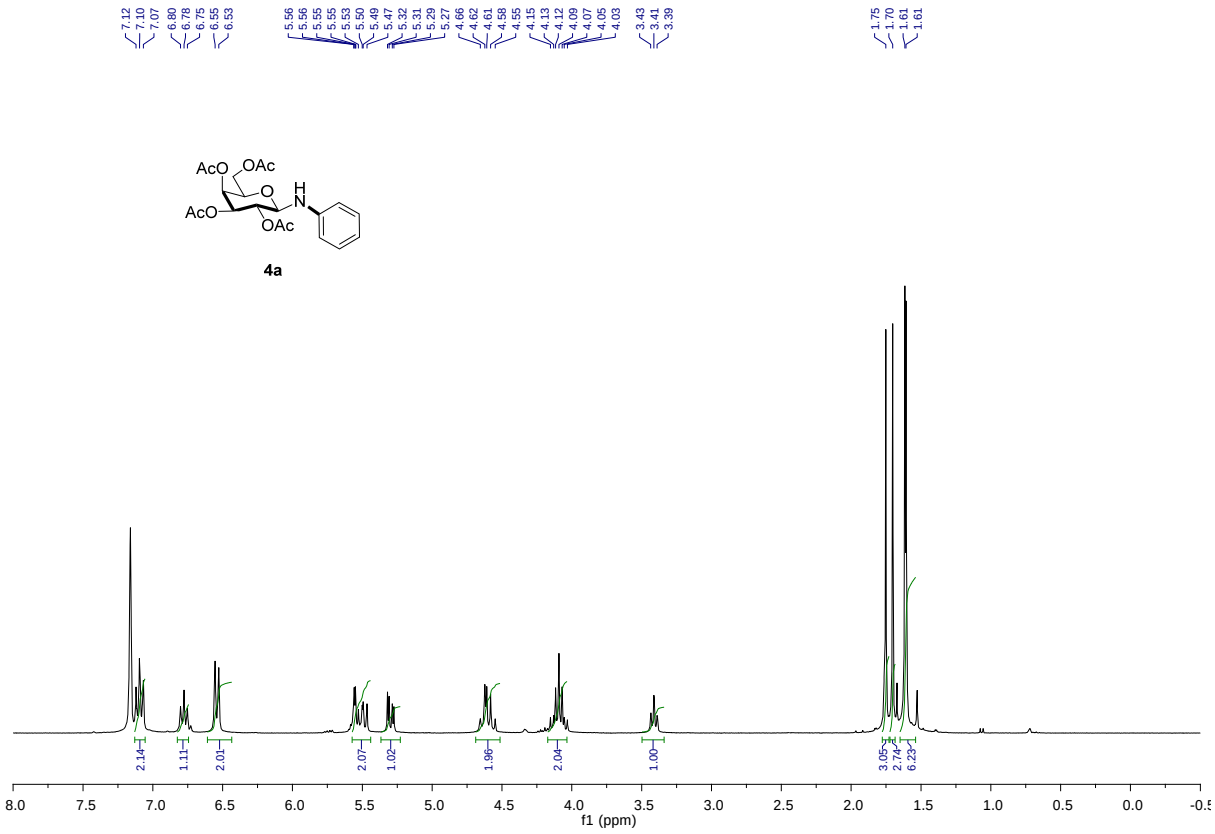
135.90
129.59
129.31
128.42
127.02
123.37
118.93
108.21
84.03
74.32
73.13
72.25
69.87
63.13
20.70
20.64
AcO
AcO
AcO
O
H
N
OAc
3o
f1 (ppm)


7.56 7.53 7.48 7.45 7.26 7.25 7.23 7.22 6.96 6.95 6.90 6.89 6.74 6.73 6.71 6.71
5.57 5.54 5.50 5.32 5.29 5.26 5.19 5.16 5.13
4.64 4.61 4.60 4.56 4.30 4.30 3.98 3.98 3.94 3.94 3.45 3.31 3.30 3.29 3.28 3.27 3.27 3.26 3.25
1.74 1.74 1.70 1.64
AcO
AcO
AcO
O
H
N
OAc
O
3p
1.00 1.00 1.02 1.03 0.98 0.96 0.96 1.01 0.95 1.91 1.06 0.94 2.87 1.02 12.02
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 0.5 0.0
f1 (ppm)


170.56 170.03 169.81 169.36 156.50 141.28 130.68 130.12 128.15 119.75 118.75 109.34 106.51 84.61 73.65 72.79 71.82 69.29 62.18 54.86 20.29 20.23
AcO
AcO
AcO
O
H
N
OAc
O
3p
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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6.75
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6.53
5.56
5.56
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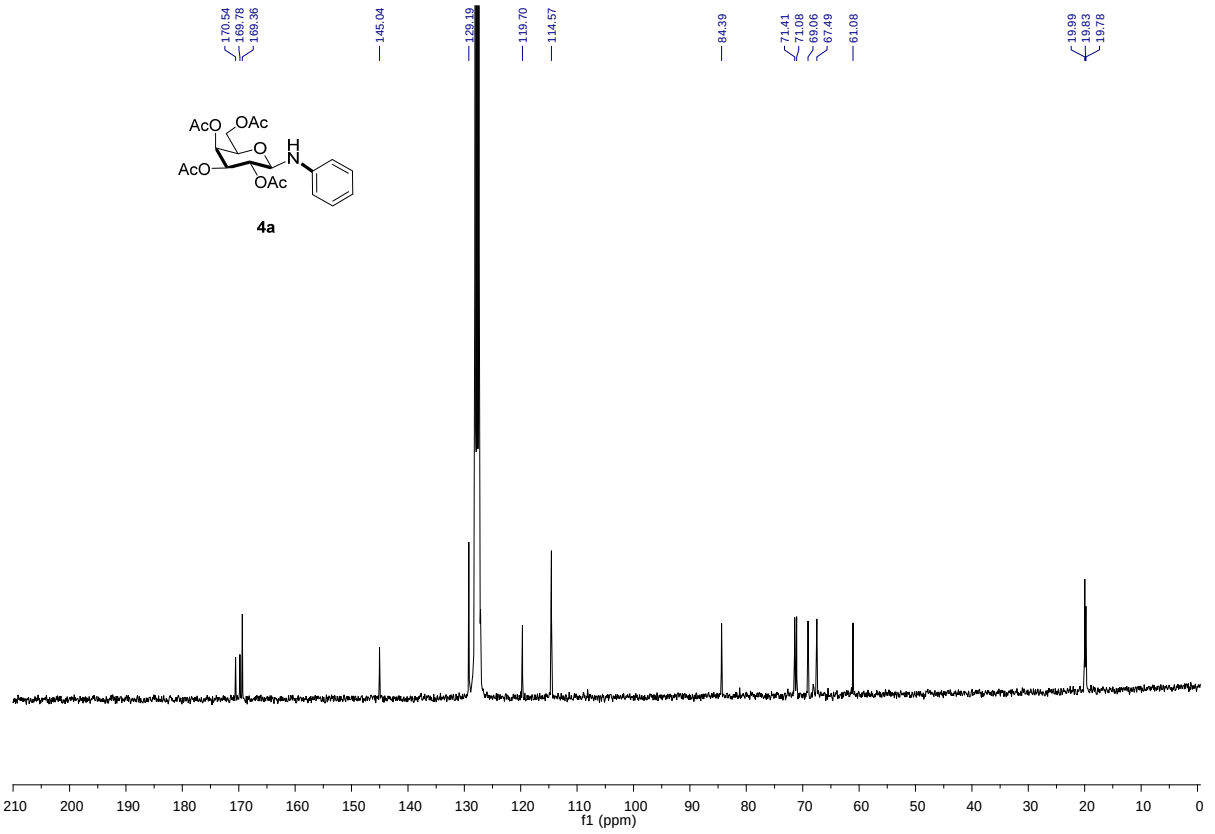
5.53
5.50
5.49
5.47
5.32
5.31
5.29
5.27
4.66
4.62
4.61
4.58
4.55
4.15
4.13
4.12
4.09
4.07
4.05
4.03
3.43
3.41
3.39
1.75
1.70
1.61
1.61
AcO
OAc
O
H
N
AcO
OAc
4a
2.14
1.11
2.01
2.07
1.02
1.96
2.04
1.00
3.05
2.74
6.23
f1 (ppm)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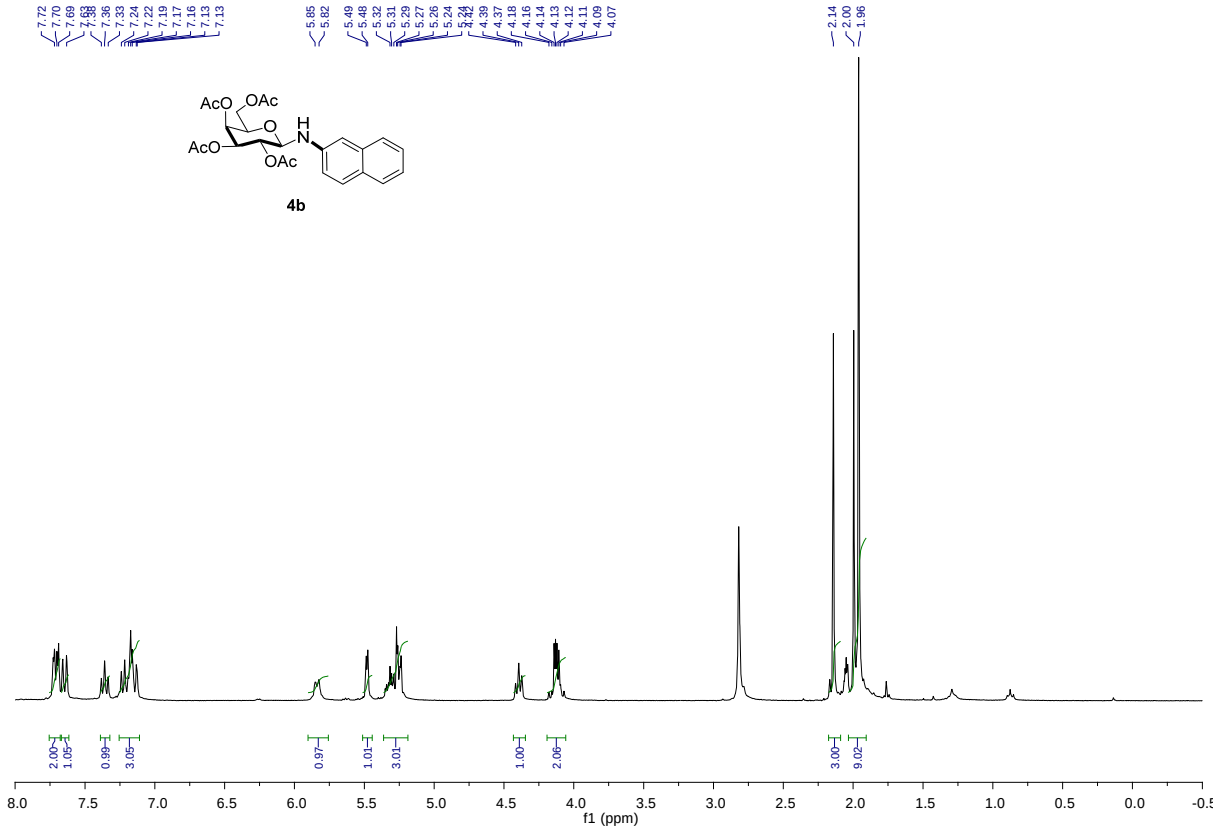
169.36
145.04
129.19
119.70
114.57
84.39
71.41
71.08
69.06
67.49
61.08
19.99
19.83
19.78
AcO
OAc
O
H
N
AcO
OAc
4a
f1 (ppm)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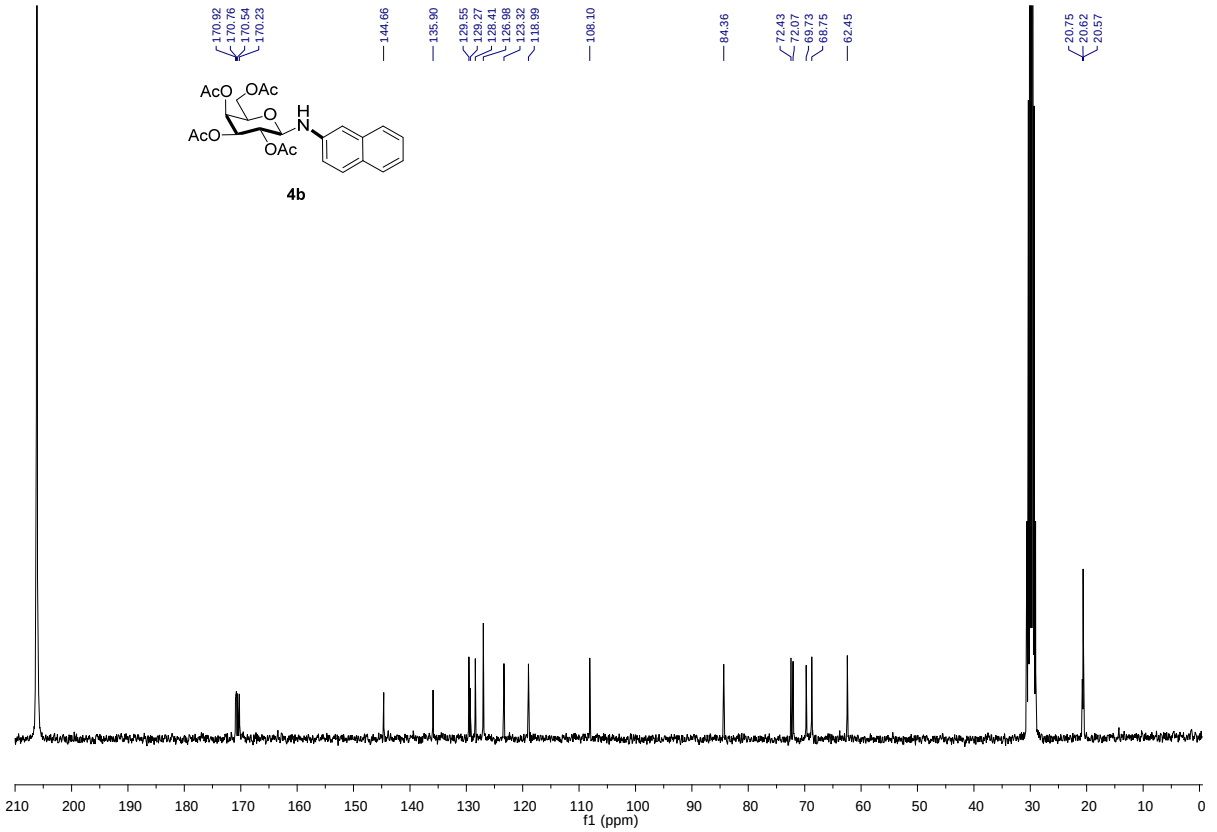
7.13
5.85
5.82
5.49
5.48
5.32
5.31
5.29
5.27
5.26
5.24
4.39
4.37
4.18
4.16
4.14
4.13
4.12
4.11
4.09
4.07
2.14
2.00
1.96
AcO
OAc
O
H
N
AcO
OAc
4b
2.00
1.05
0.99
3.05
0.97
1.01
3.01
1.00
2.06
3.00
9.02
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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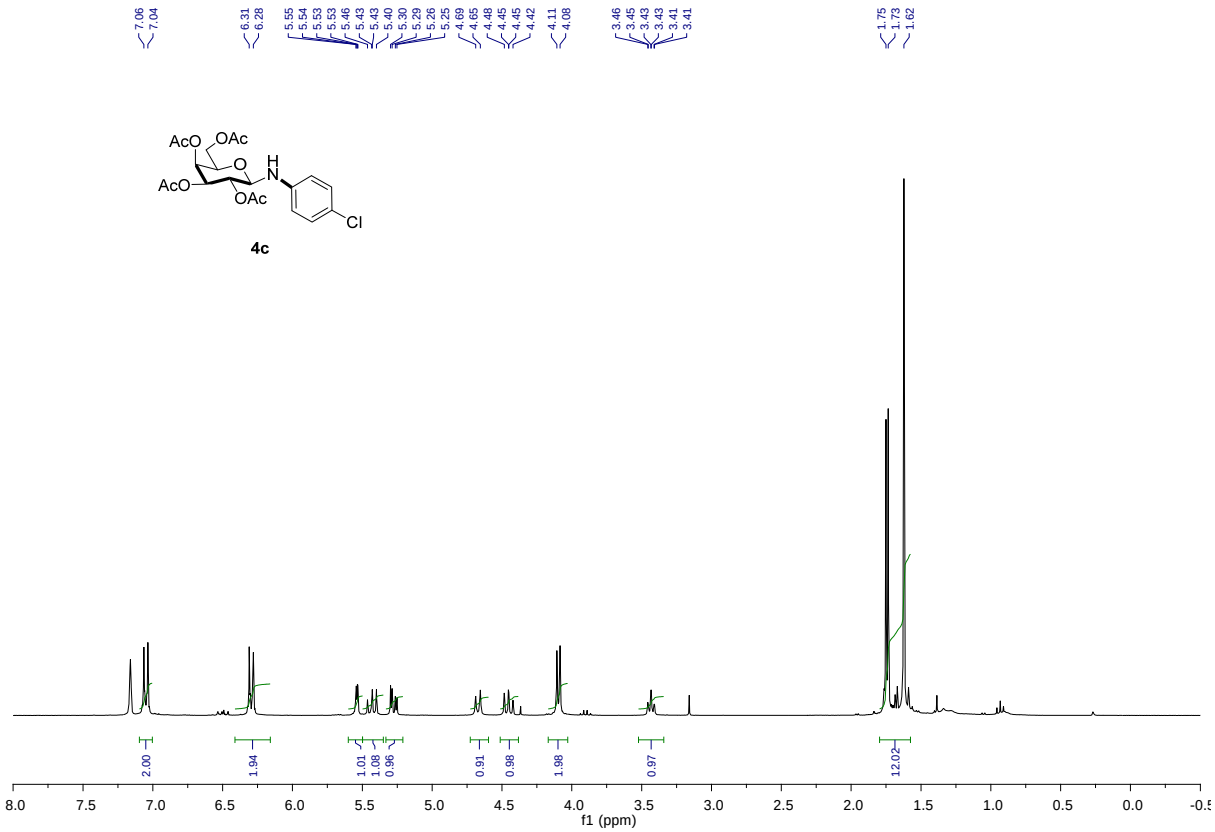
129.27
128.41
126.98
123.32
118.99
108.10
84.36
72.43
72.07
69.73
68.75
62.45
20.75
20.62
20.57
AcO
OAc
O
H
N
AcO
OAc
4b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.04
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6.28
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5.53
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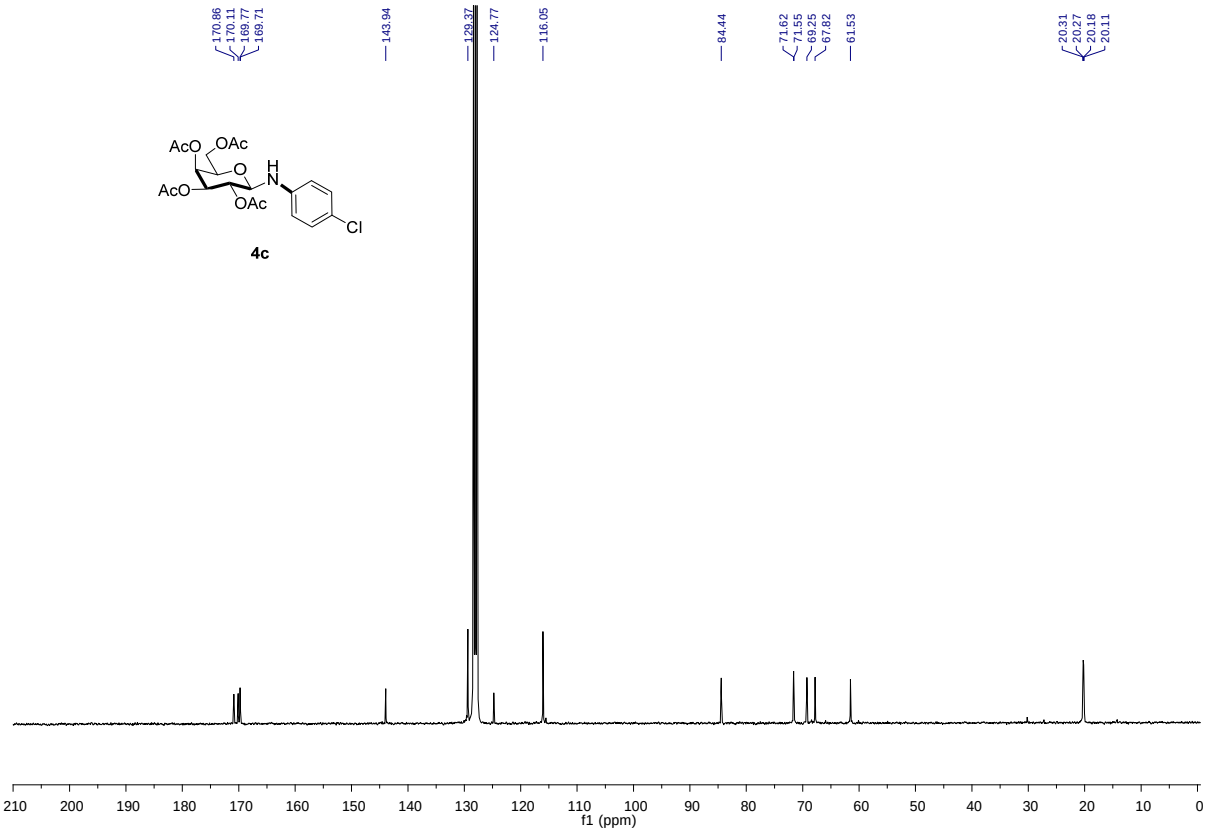
5.40
5.30
5.29
5.26
5.25
4.69
4.65
4.48
4.45
4.45
4.42
4.11
4.08
3.46
3.45
3.43
3.43
3.41
3.41
1.75
1.73
1.62
AcO
OAc
O
H
N
AcO
OAc
Cl
4c
2.00
1.94
1.01
1.08
0.96
0.91
0.98
1.98
0.97
12.02
f1 (ppm)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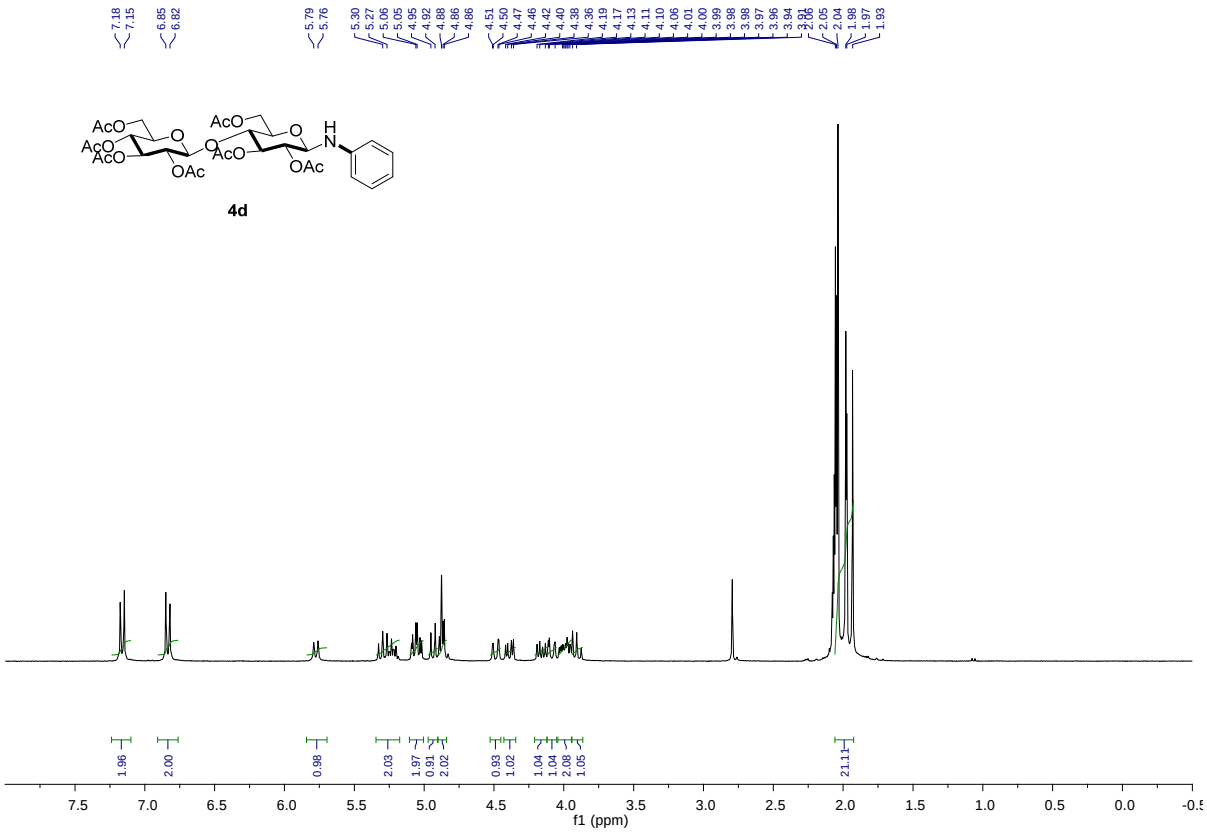
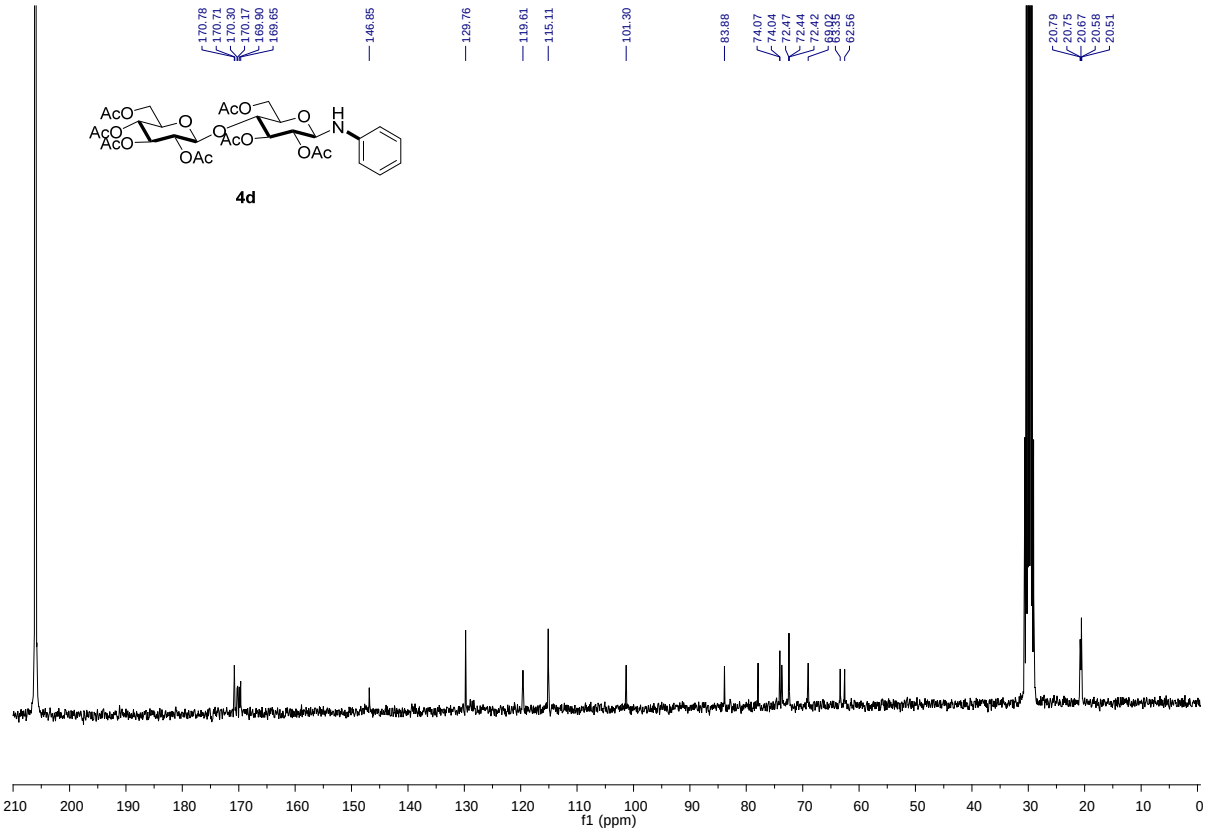
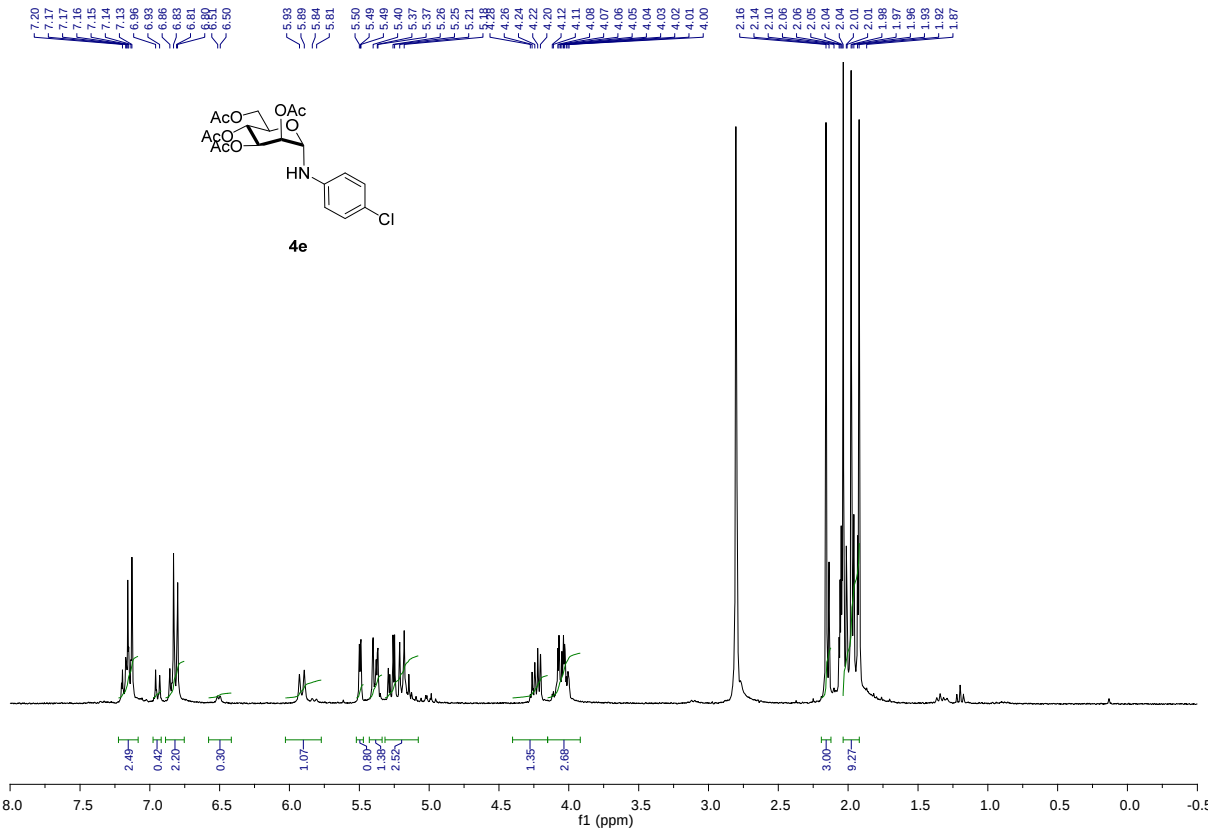
116.05
84.44
71.62
71.55
69.25
67.82
61.53
20.31
20.27
20.18
20.11
AcO
OAc
O
H
N
AcO
OAc
Cl
4c
f1 (ppm)


4d
f1 (ppm)


4d
f1 (ppm)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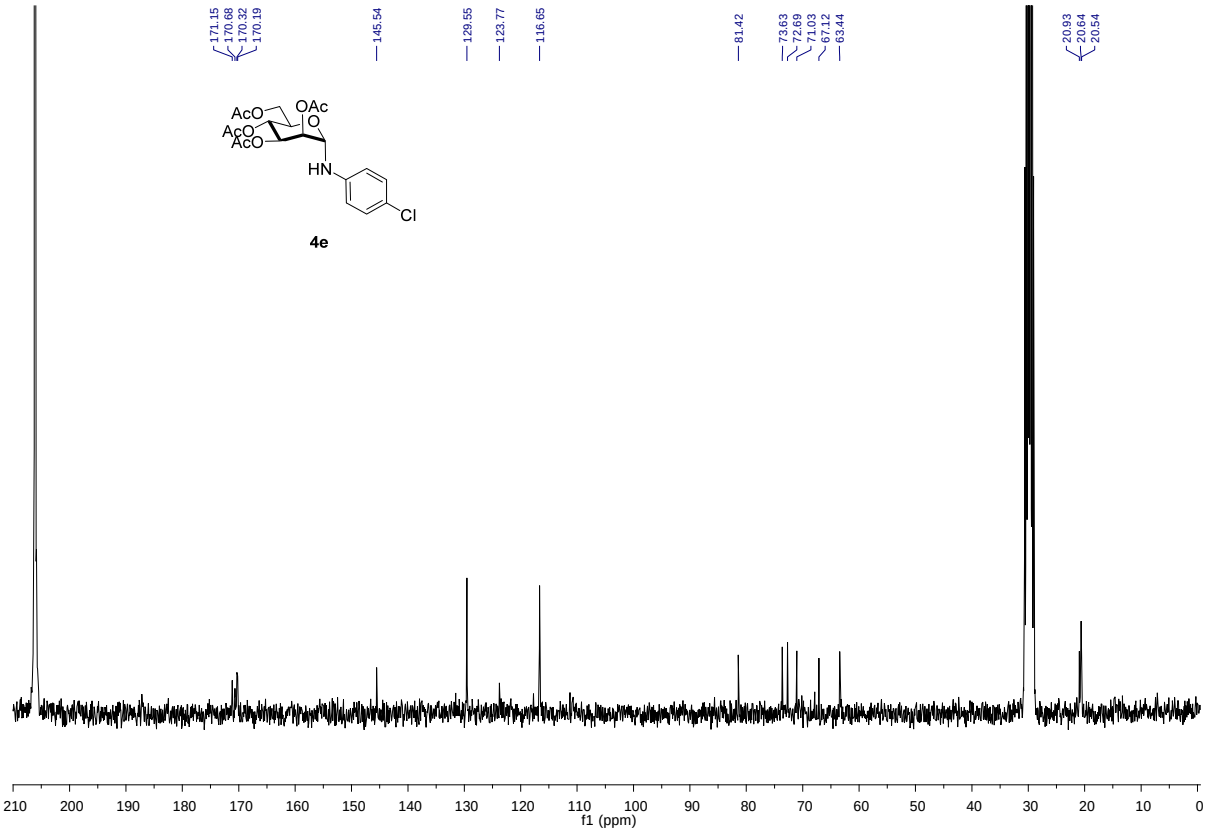
AcO
AcO
OAc
O
HN
Cl
4e
f1 (ppm)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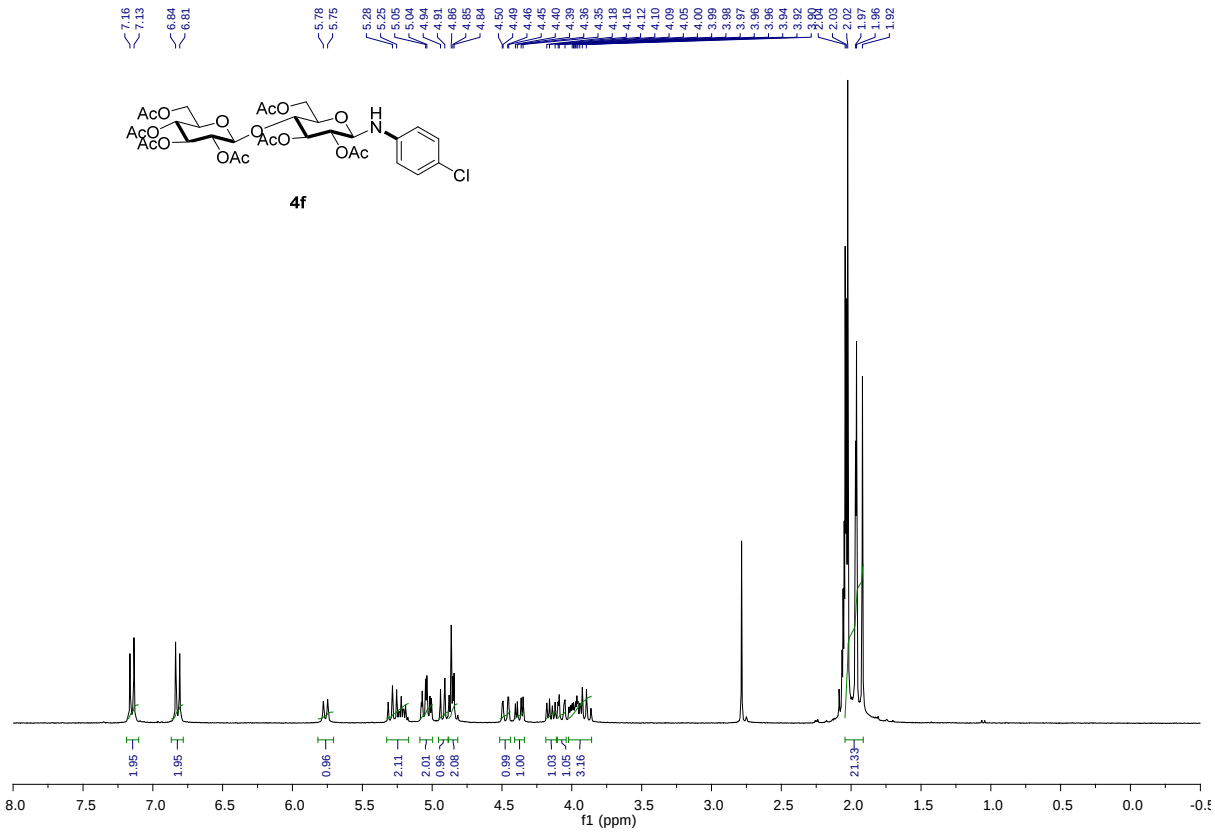
AcO
AcO
OAc
O
HN
Cl
4e
f1 (ppm)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5.04
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4.91
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3.98
3.97
3.96
3.96
3.94
3.92
2.03
2.02
1.97
1.96
1.92
AcO
AcO
AcO
O
OAc
O
AcO
AcO
O
OAc
H
N
Cl
4f
1.95
1.95
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2.11
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2.08
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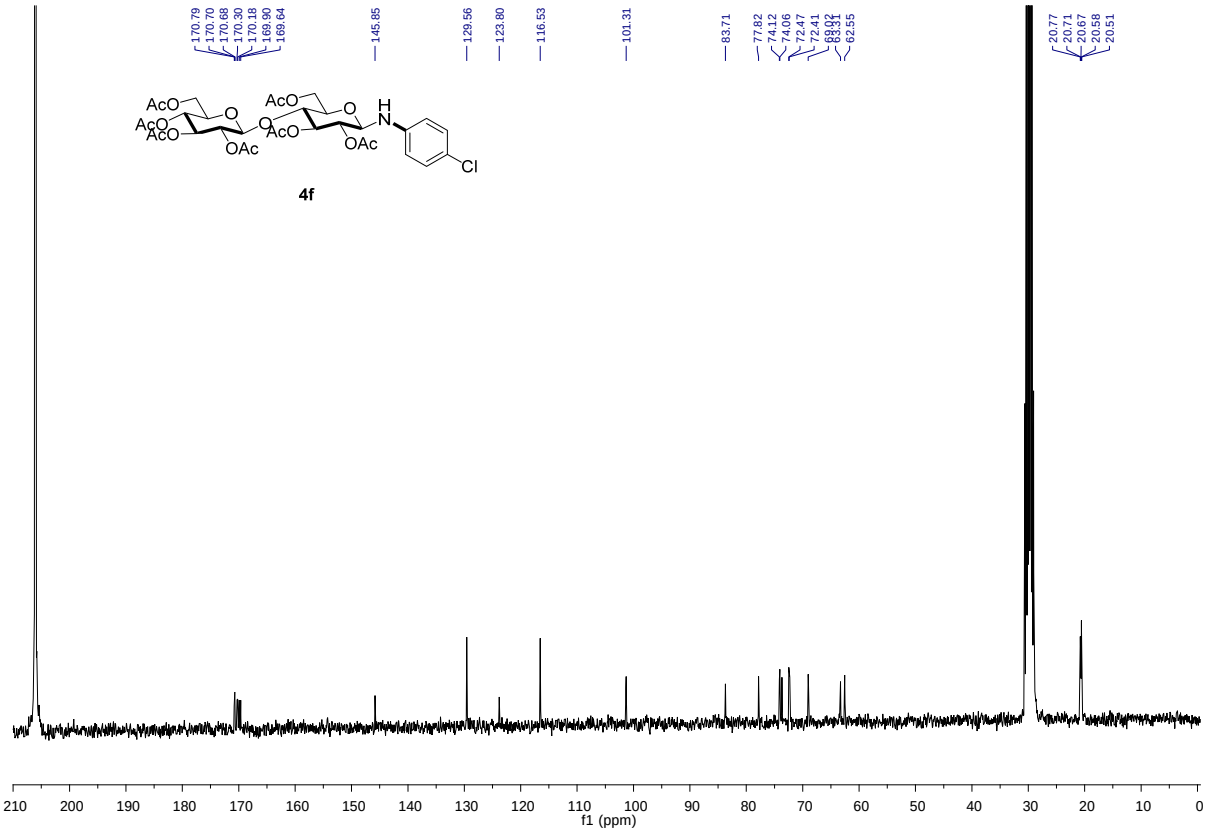
1.00
1.03
1.05
3.16
21.33
f1 (ppm)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101.31
83.71
77.82
74.12
74.06
72.47
72.41
69.02
68.91
62.55
20.77
20.71
20.67
20.58
20.51
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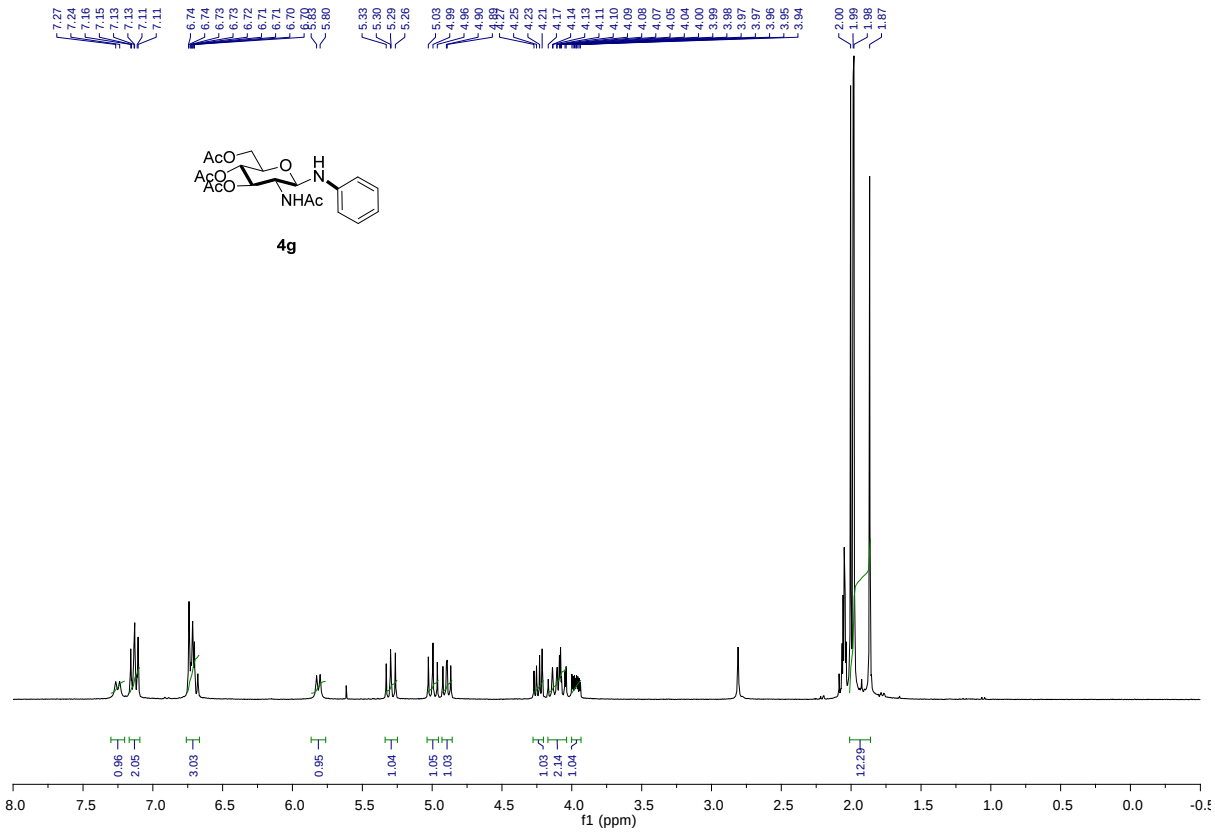
O
OAc
O
AcO
AcO
O
OAc
H
N
Cl
4f
f1 (ppm)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O
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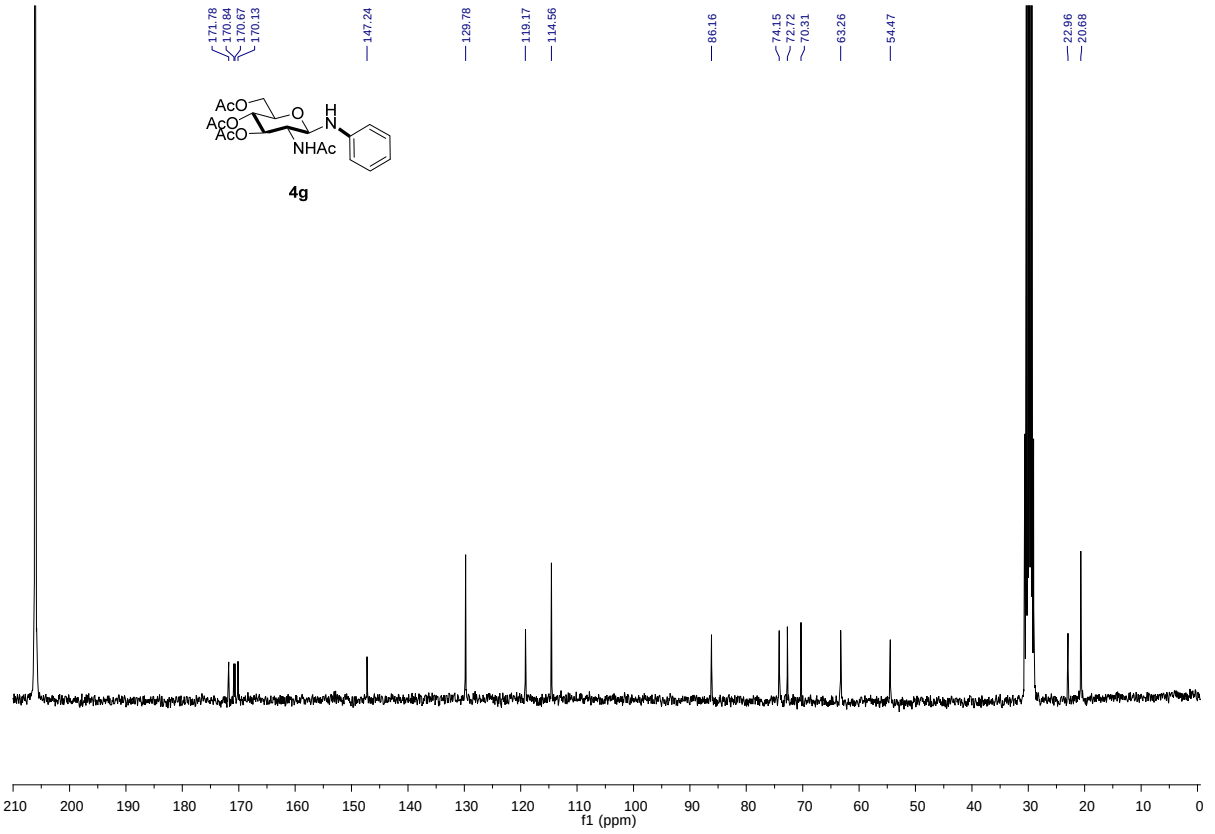
NHAc
4g
f1 (ppm)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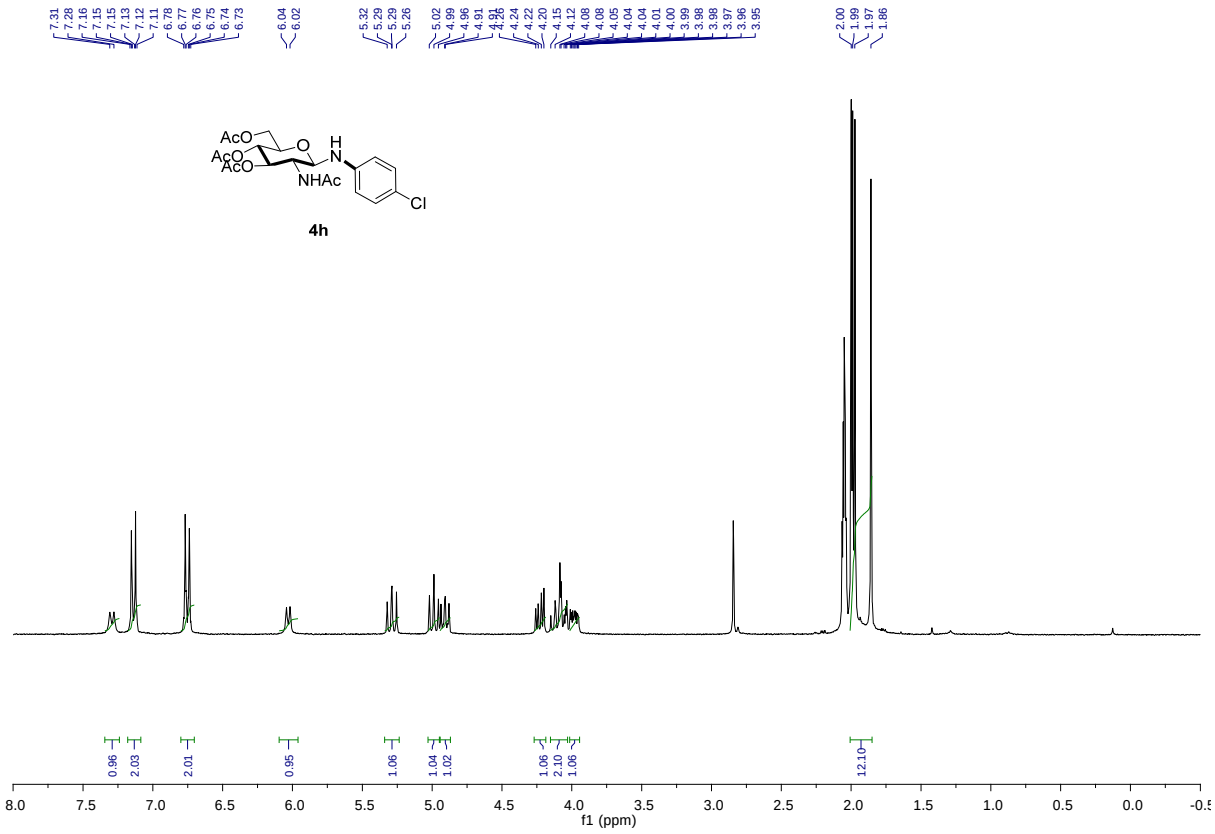
4g
f1 (ppm)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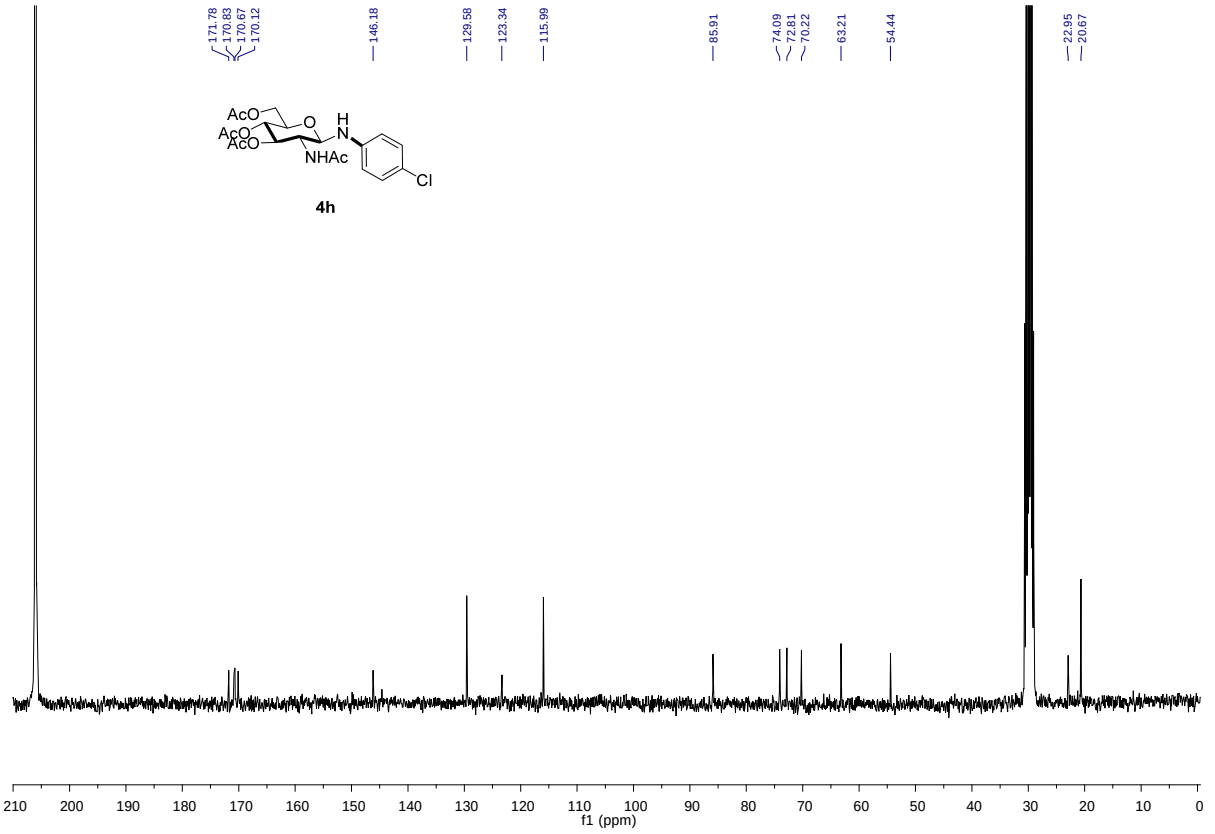
AcO
AcO
AcO
O
H
N
NHAc
Cl
4h
0.96 2.03 2.01 0.95 1.06 1.04 1.02 1.06 2.10 1.06 12.10
f1 (ppm)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AcO
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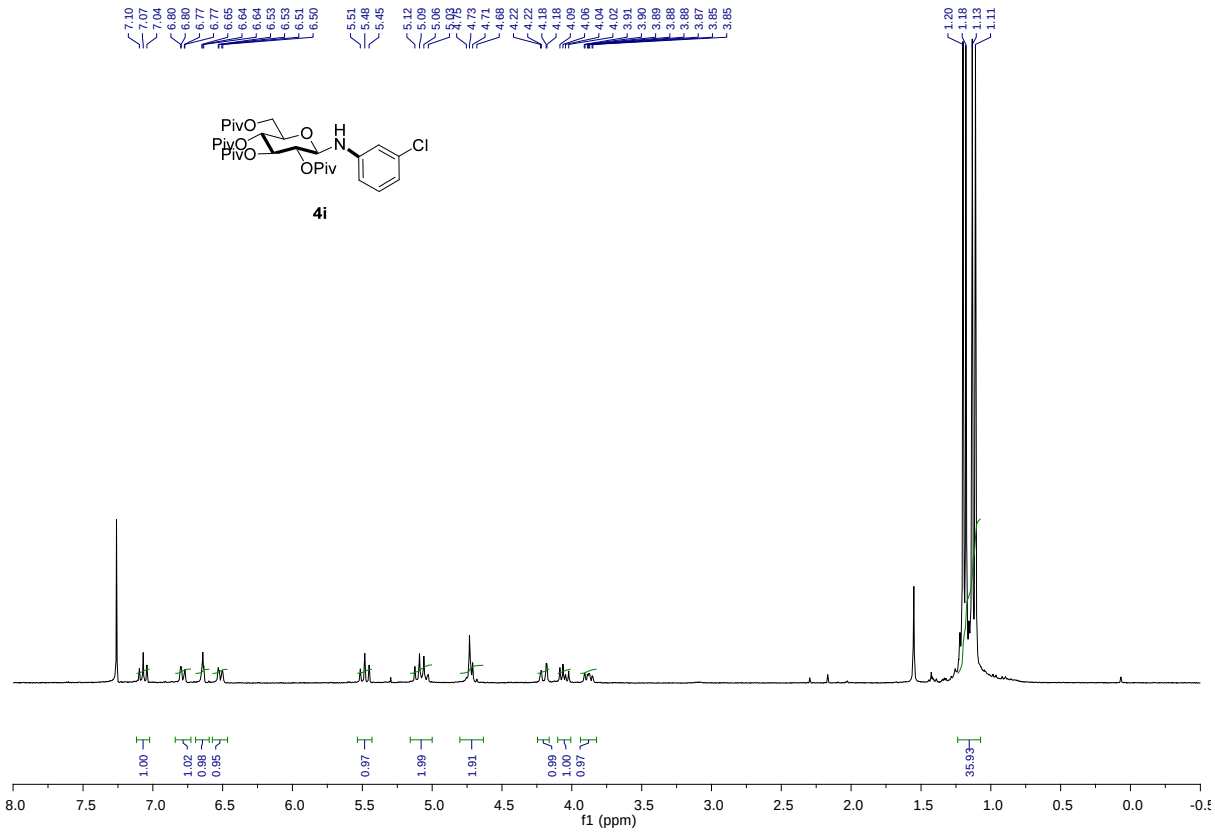
O
H
N
NHAc
Cl
4h
f1 (ppm)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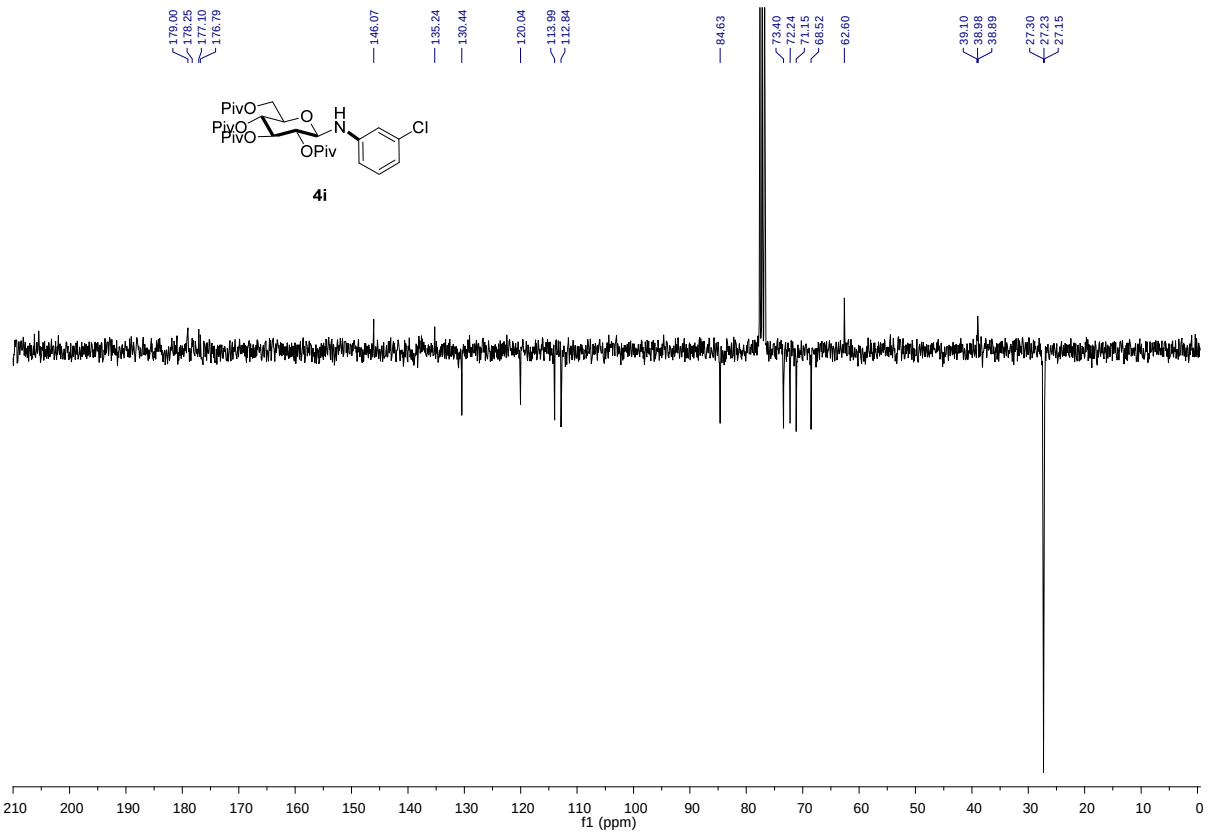
PivO
PivO
O
H
N
Cl
OPiv
4i
f1 (ppm)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PivO
PivO
O
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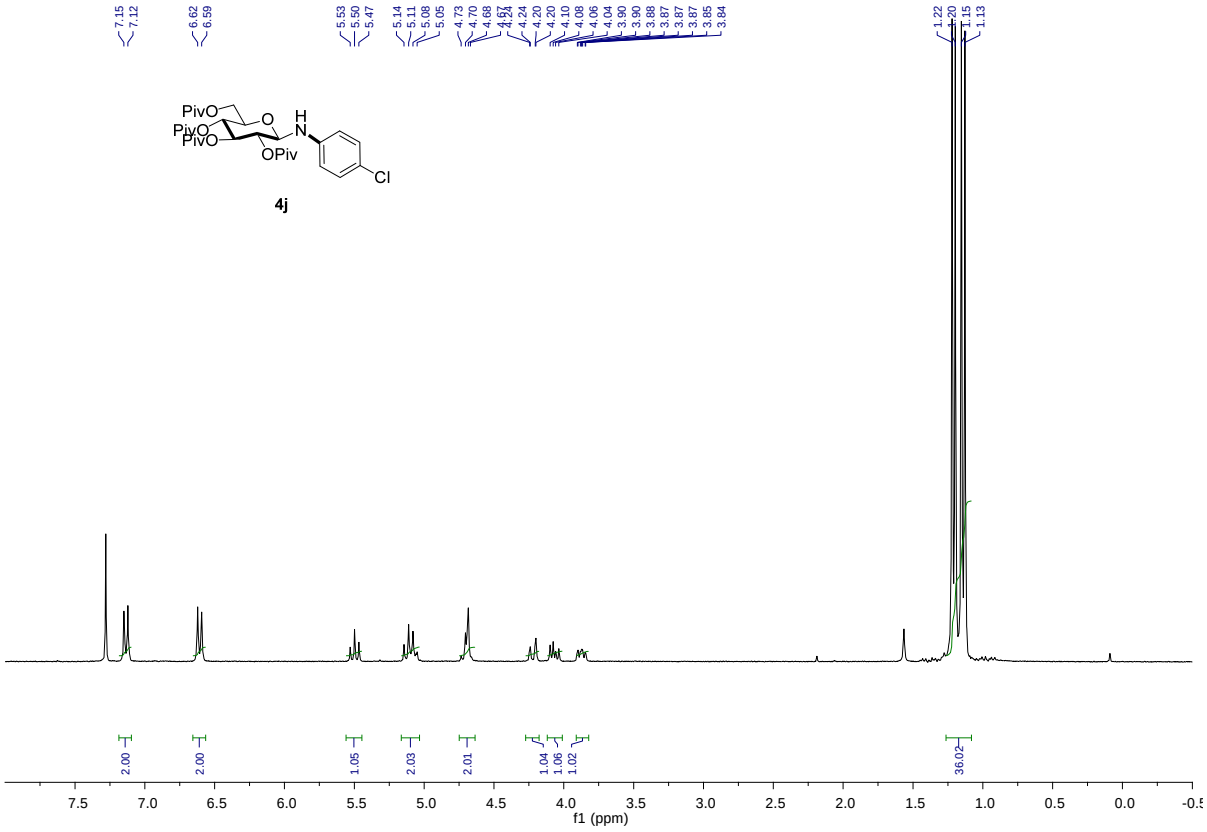
N
Cl
OPiv
4i
f1 (ppm)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4.67
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4.24
4.20
4.20
4.10
4.08
4.06
4.04
3.90
3.90
3.88
3.87
3.87
3.87
3.85
3.84
1.22
1.20
1.15
1.13
PivO
PivO
PivO
O
H
N
OPiv
Cl
4j
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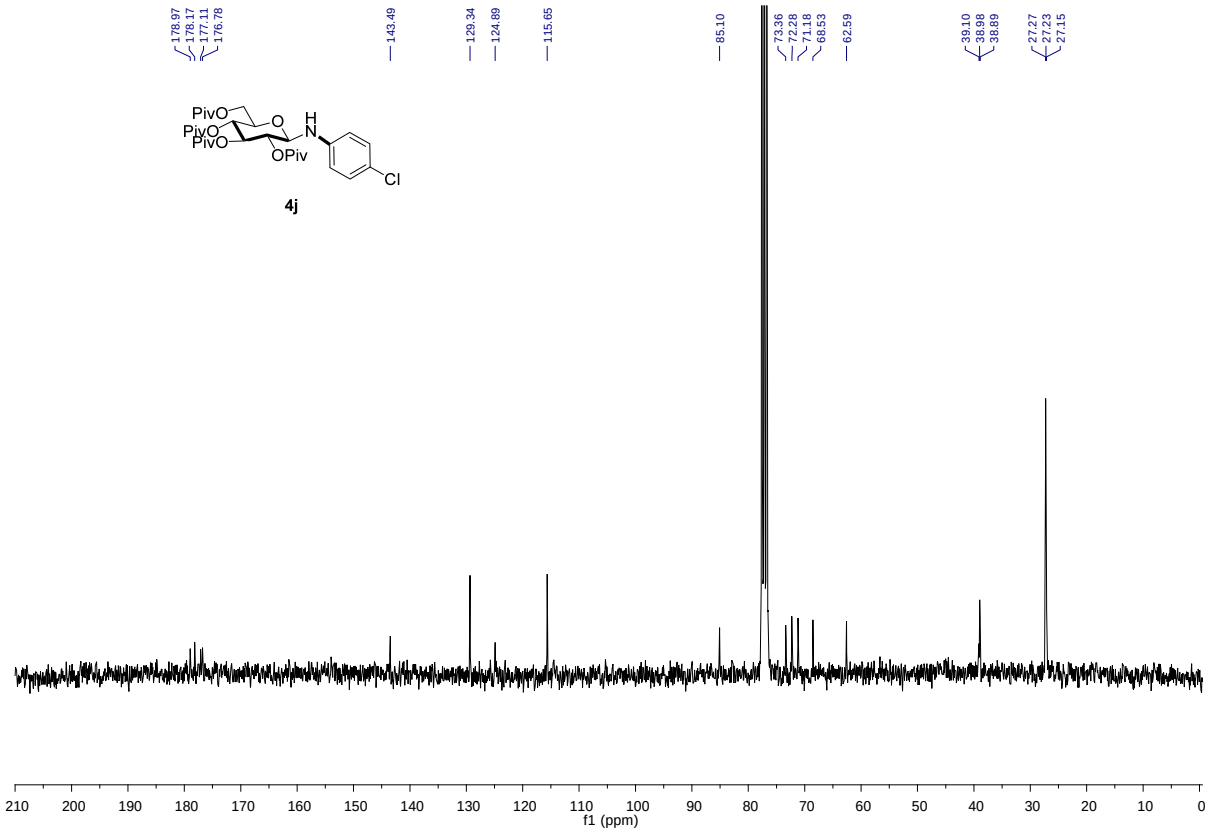
2.00
1.05
2.03
2.01
1.04
1.06
1.02
36.02
f1 (ppm)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72.28
71.18
68.53
62.59
39.10
38.98
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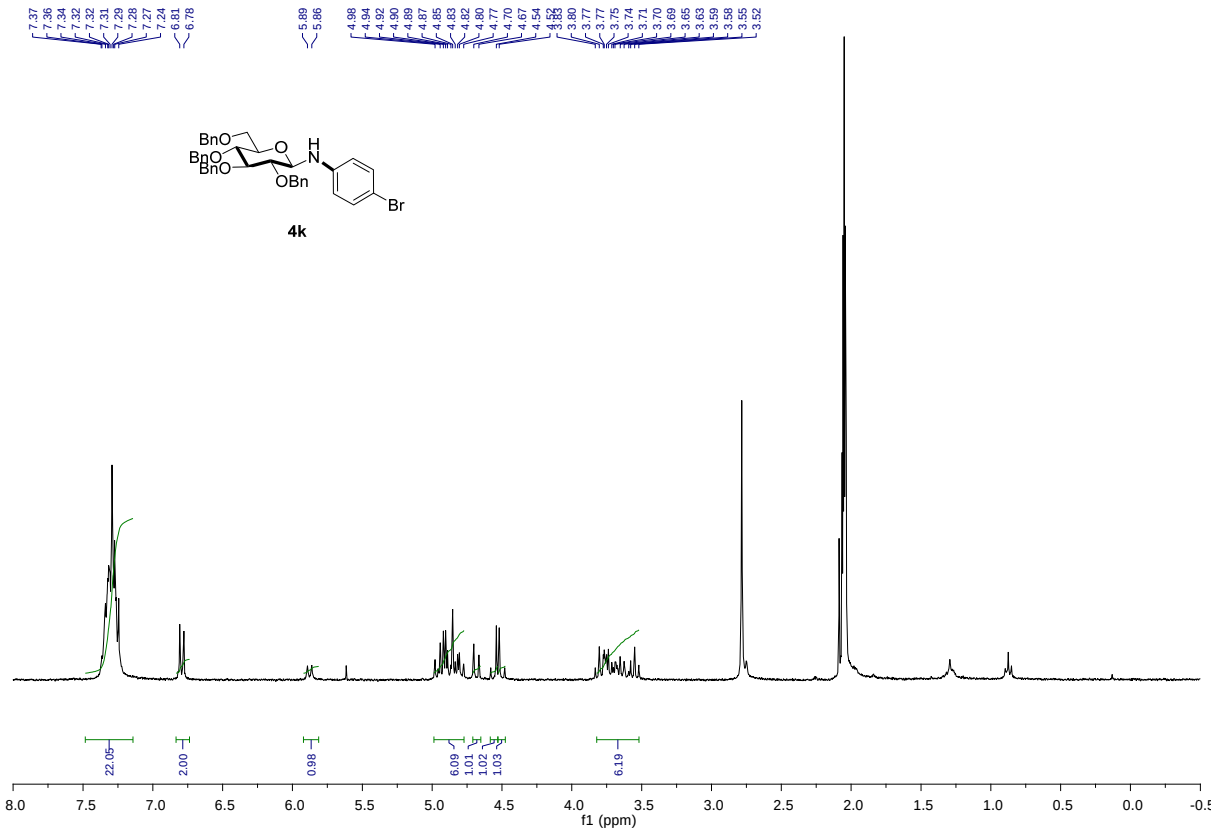
O
H
N
OPiv
Cl
4j
f1 (ppm)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7.31
7.29
7.28
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7.24
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3.58
3.55
3.52
BnO
BnO
BnO
O
H
N
OBn
Br
4k
22.05
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6.09
1.01
1.02
1.03
6.19
8.0
7.5
7.0
6.5
6.0
5.5
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3.0
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2.0
1.5
1.0
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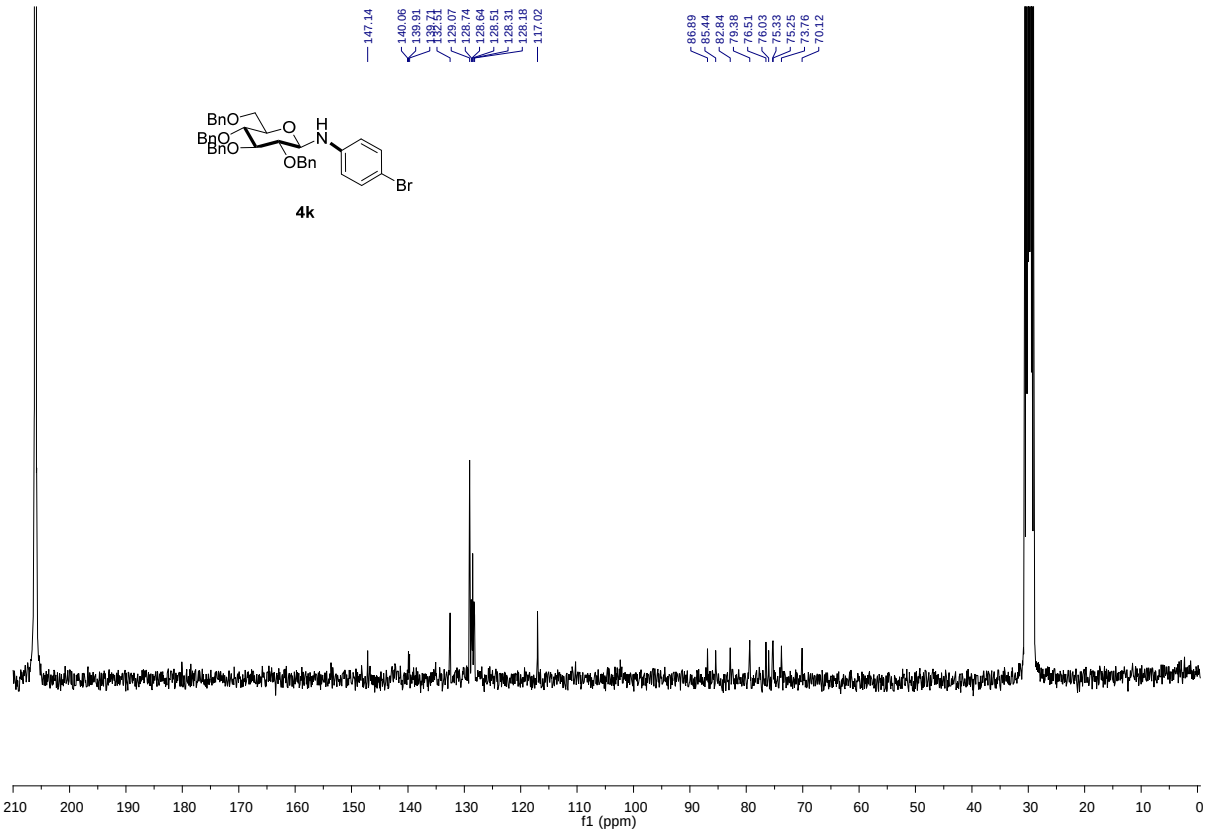
0.0
f1 (ppm)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129.07
128.74
128.64
128.51
128.31
128.18
117.02
86.89
85.44
82.84
79.38
76.51
76.03
75.33
75.25
73.76
70.12
BnO
BnO
BnO
O
H
N
OBn
Br
4k
210
200
190
180
170
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90
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50
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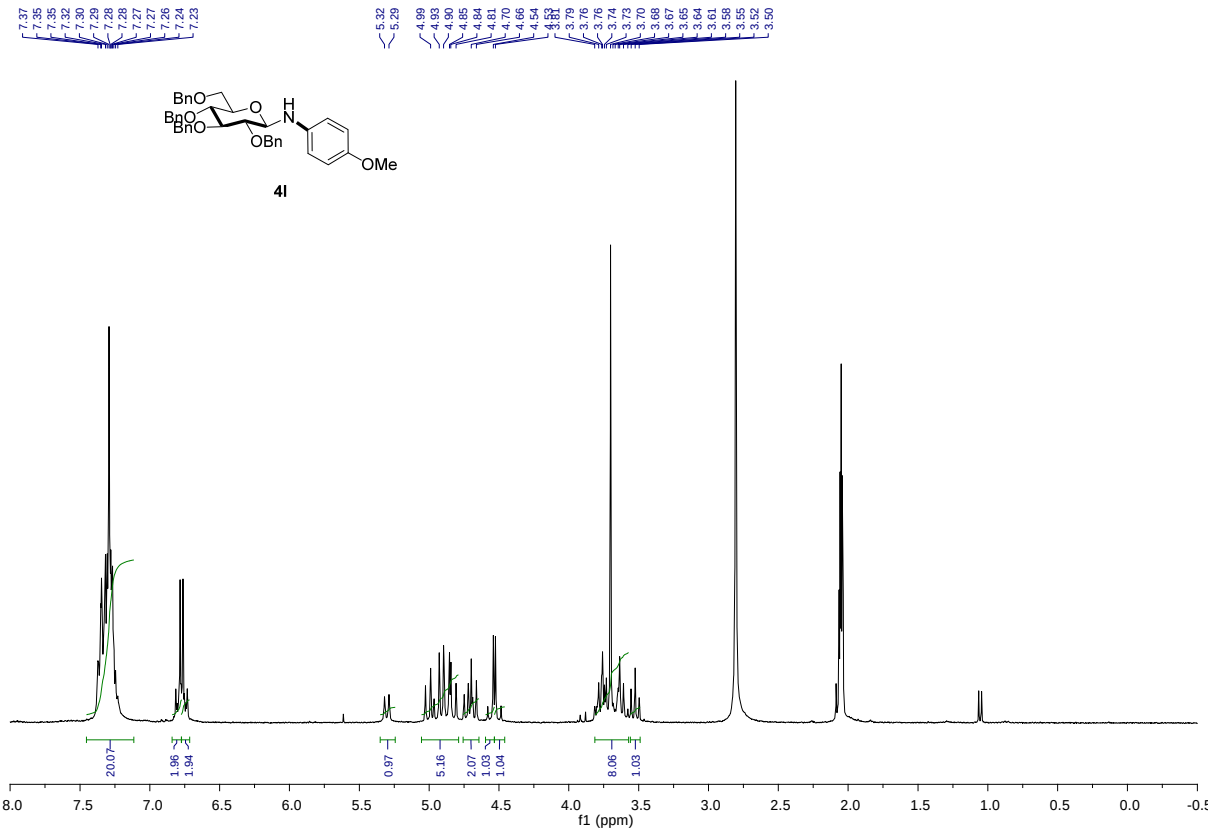
f1 (ppm)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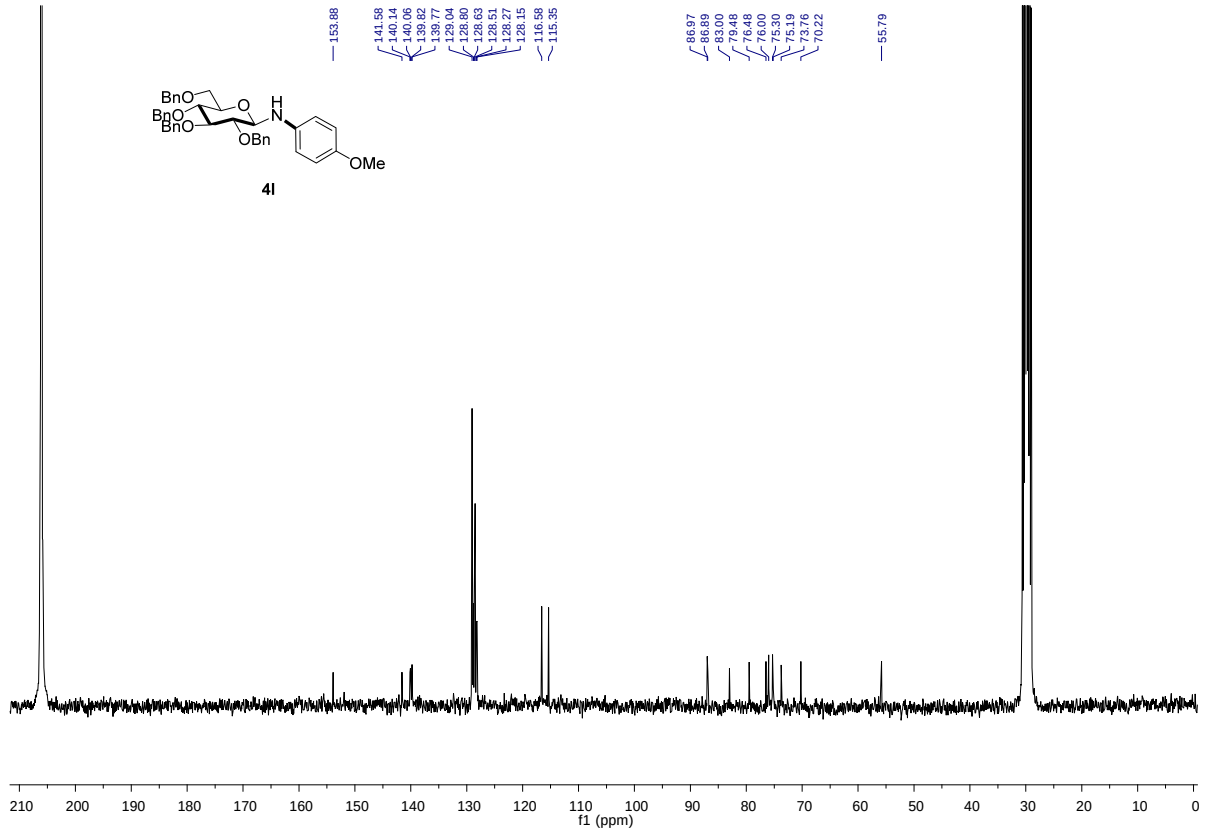
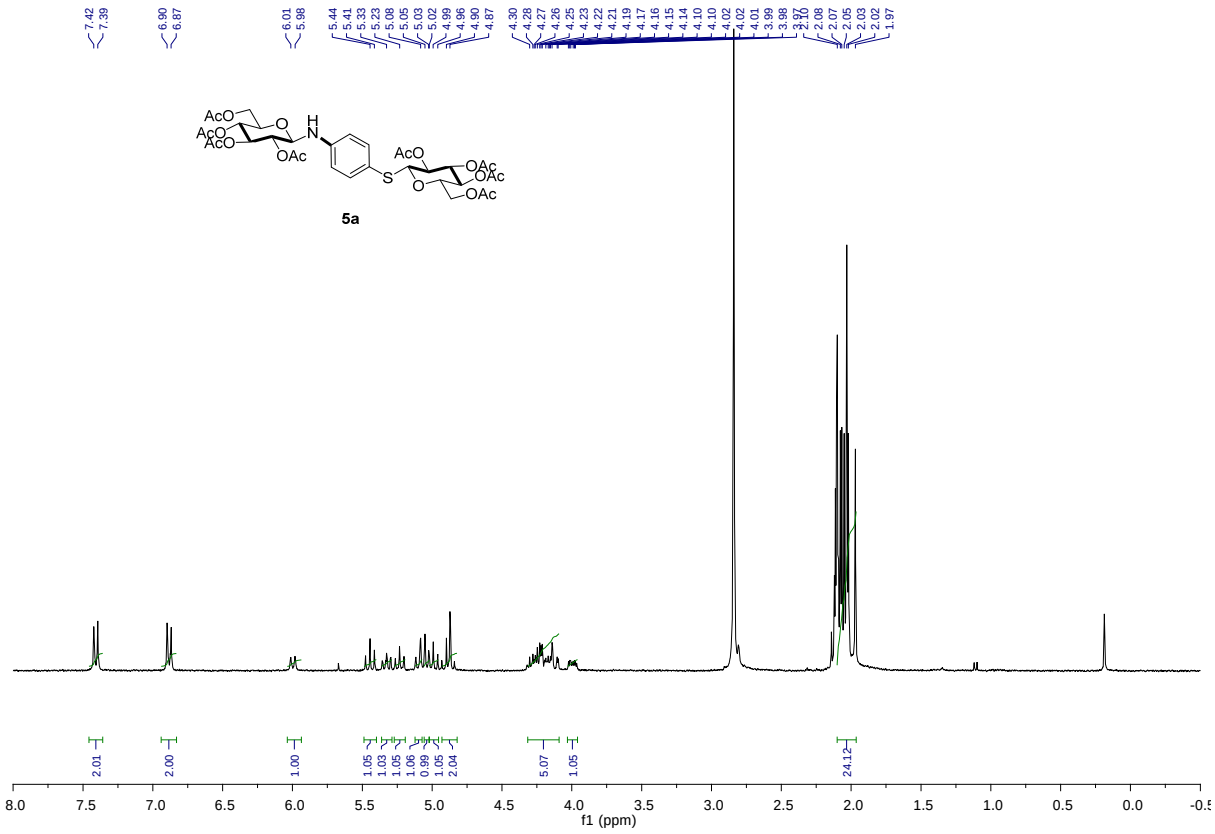
BnO
BnO
O
H
N
OBn
OMe
4l
f1 (ppm)


BnO
BnO
BnO
O
H
N
OBn
OMe
4l
f1 (ppm)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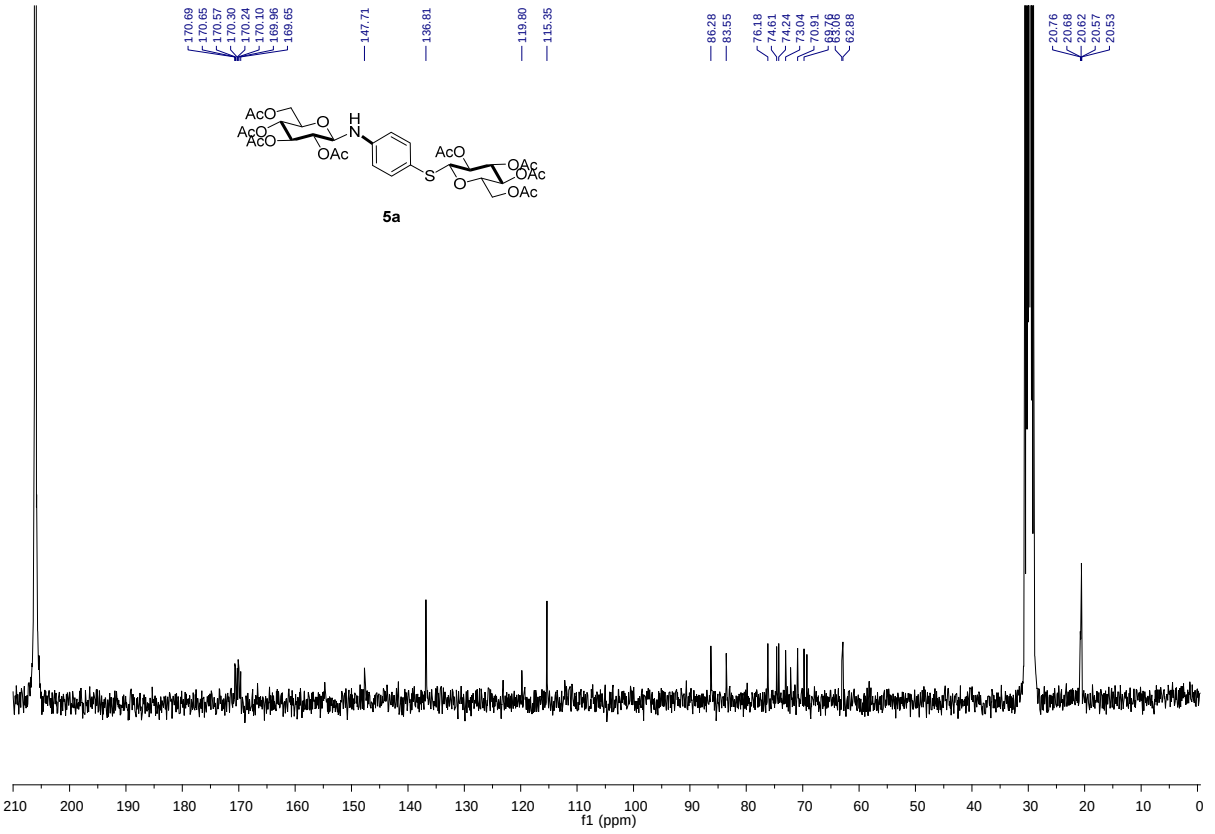
6.90
6.87
6.01
5.98
5.44
5.41
5.33
5.23
5.08
5.05
5.03
5.02
4.99
4.96
4.90
4.87
4.30
4.28
4.27
4.26
4.25
4.23
4.22
4.21
4.19
4.17
4.16
4.15
4.14
4.10
4.10
4.02
4.02
4.01
3.99
3.98
2.10
2.08
2.07
2.05
2.03
2.02
1.97
AcO
AcO
AcO
O
H
N
OAc
S
AcO
OAc
OAc
O
OAc
5a
2.01
2.00
1.00
1.05
1.03
1.05
1.06
0.99
1.05
2.04
5.07
1.05
24.12
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
0.5
0.0
f1 (ppm)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170.57
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170.24
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169.65
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136.81
119.80
115.35
86.28
83.55
76.18
74.61
74.24
73.04
70.91
68.76
68.08
62.88
20.76
20.68
20.62
20.57
20.53
AcO
AcO
AcO
O
H
N
OAc
S
AcO
OAc
OAc
O
OAc
5a
210
200
190
180
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160
150
140
130
120
110
100
90
80
70
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50
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30
20
10
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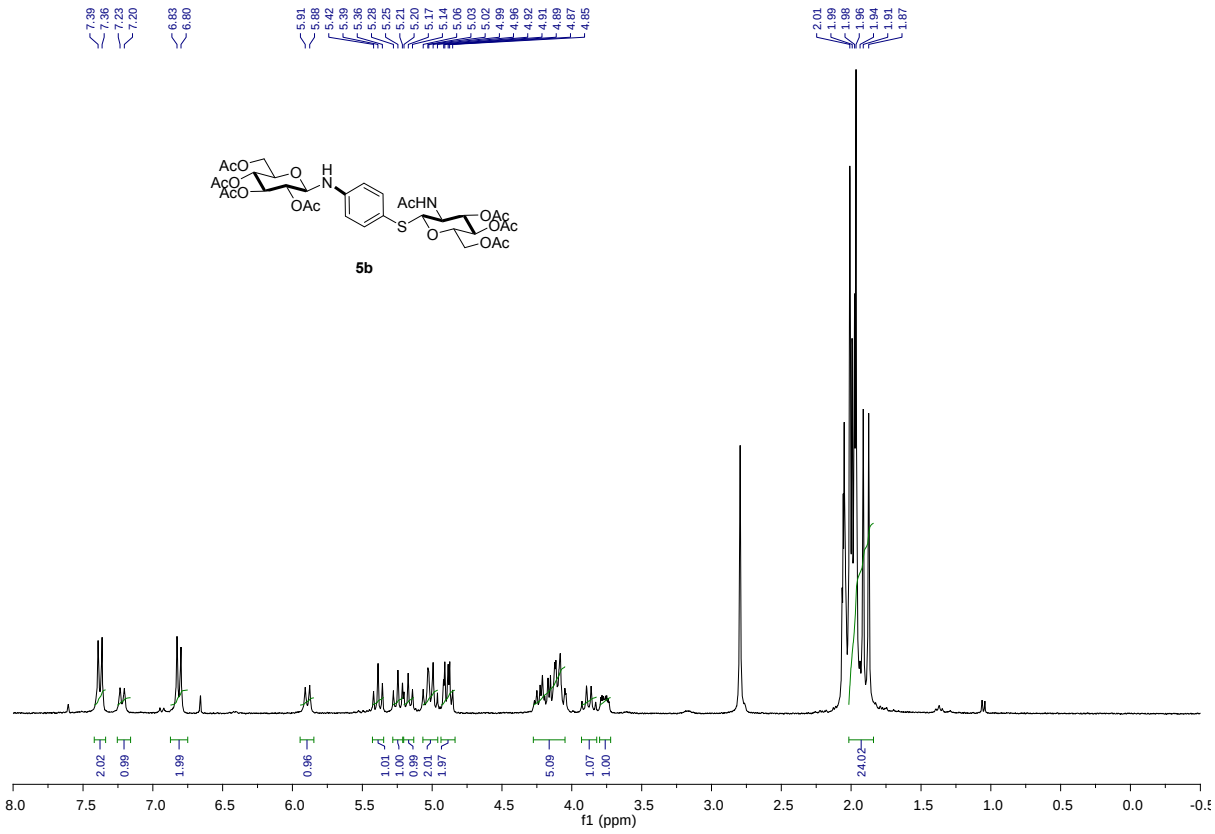
f1 (ppm)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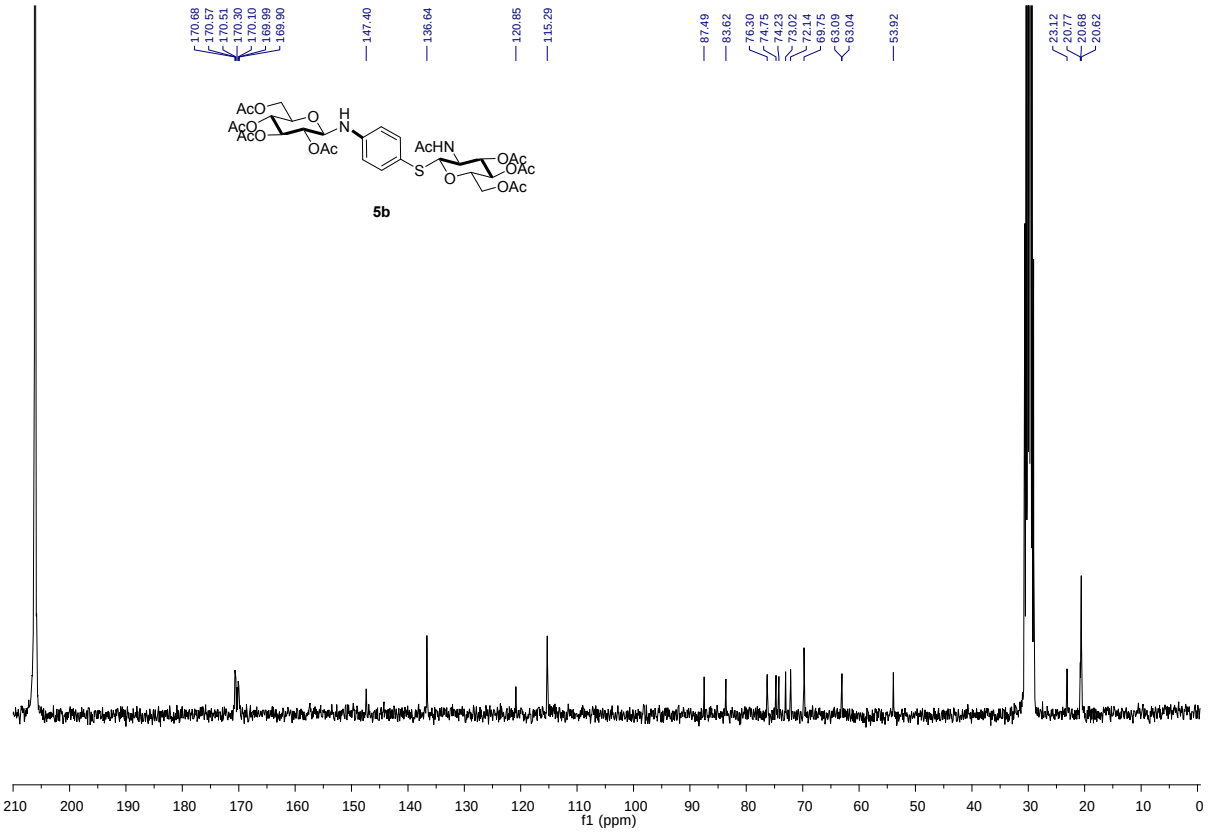
7.23
7.20
6.83
6.80
5.91
5.88
5.42
5.39
5.36
5.28
5.25
5.21
5.20
5.17
5.14
5.06
5.03
5.02
4.99
4.96
4.92
4.91
4.89
4.87
4.85
2.01
1.99
1.98
1.96
1.94
1.91
1.87
AcO
AcO
AcO
O
H
N
OAc
AcHN
S
O
OAc
OAc
OAc
5b
2.02
0.99
1.99
0.96
1.01
1.00
0.99
2.01
1.97
5.09
1.07
1.00
24.02
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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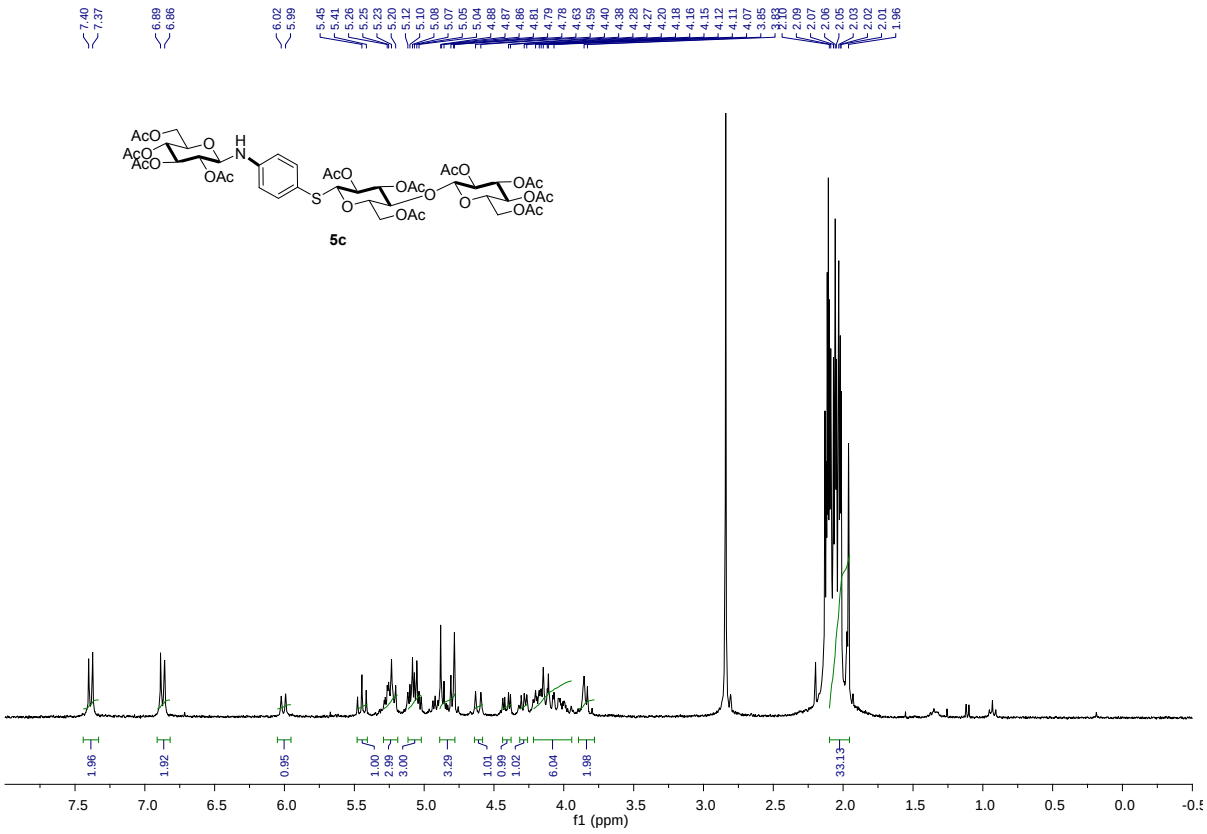
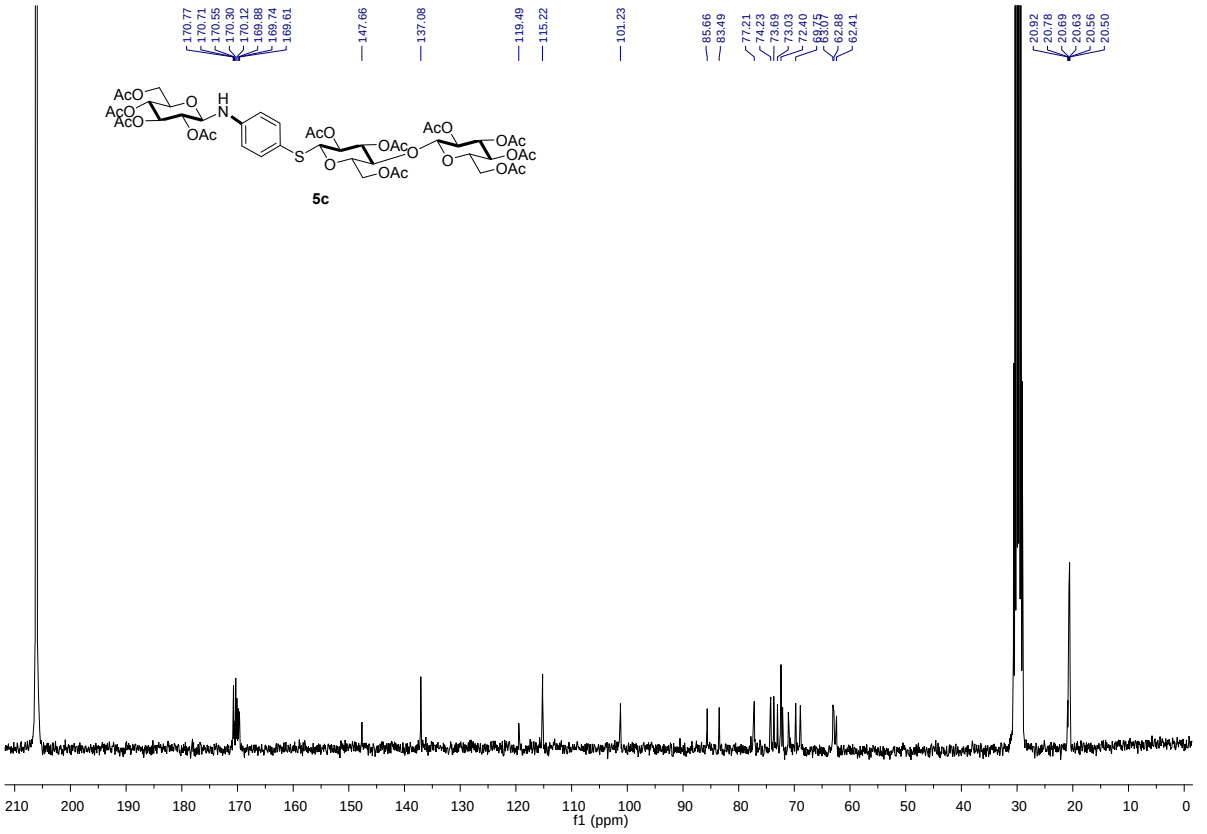
147.40
136.64
120.85
115.29
87.49
83.62
76.30
74.75
74.23
73.02
72.14
69.75
63.09
63.04
53.92
23.12
20.77
20.68
20.62
AcO
AcO
AcO
O
H
N
OAc
AcHN
S
O
OAc
OAc
OAc
5b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.40
7.37
6.89
6.86
6.02
5.99
5.45
5.41
5.26
5.25
5.23
5.20
5.12
5.10
5.09
5.07
5.05
5.04
4.88
4.87
4.86
4.81
4.79
4.78
4.63
4.59
4.40
4.38
4.28
4.27
4.20
4.18
4.16
4.15
4.12
4.11
4.07
3.85
2.09
2.07
2.06
2.05
2.03
2.02
2.01
1.96
AcO
AcO
AcO
O
H
N
OAc
S
AcO
OAc
O
O
OAc
AcO
OAc
O
OAc
OAc
O
OAc
5c
1.96
1.92
0.95
1.00
2.99
3.00
3.29
1.01
0.99
1.02
6.04
1.98
33.13
f1 (ppm)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170.55
170.30
170.12
169.88
169.74
169.61
147.66
137.08
119.49
115.22
101.23
85.66
83.49
77.21
74.23
73.69
73.03
72.40
68.75
68.07
62.88
62.41
20.92
20.78
20.69
20.63
20.56
20.50
AcO
AcO
AcO
O
H
N
OAc
S
AcO
OAc
O
O
OAc
AcO
OAc
O
OAc
OAc
O
OAc
5c
f1 (ppm)