Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting information

Influence of remote functional groups towards the formation of 1,2-*cis* glycosides: Special emphasis to the β-mannosylation

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Index

Spectral data of synthesized compounds:

Compound 32: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24-6.76 (m, 23 H, Ar-H), 5.56 (br s, 1 H, PhC*H*), 5.49 (d, *J* = 3.5 Hz, 1 H, H-1_A), 5.45 (dd, *J* = 9.0 Hz, 3.0 Hz, 1 H, H-3_A), 4.87-4.80 (m, 3 H, 2 PhCH_2, H-1_B), 4.72 (d, *J* =11.5 Hz, 1 H, PhCH_2), 4.60 (d, *J* = 11.5 Hz, 1 H, PhCH_2), 4.29-4.23 (m, 4 H, H-4_A, H-4_B, H-6_{aA}, PhCH_2), 4.18-4.15 (m, 1 H, H-5_B), 4.08 (t, *J* = 9.0 Hz, 1 H, H-3_B), 3.84-3.82 (m, 2 H, H-2_A, H-6_{bB}), 3.77 (br s, 3 H, OMe), 3.76 (br s, 3 H, OMe), 3.72 (t, *J* = 9.0 Hz, 1 H, H-6_{bA}), 3.61-3.59 (m, 1 H, H-5_A), 3.54-3.47 (m, 2 H, H-2_B, H-6_{bB}), 2.21 (s, 3 H, COCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.0 (*C*OCH_3), 150.1-113.7 (Ar-C), 101.3 (Ph*C*H), 99.9 (C-1_B), 98.3 (C-1_A), 82.7 (C-5_A), 79.3 (C-2_B), 78.3 (C-3_B), 75.0 (C-4_A), 74.9 (Ph*C*H_2), 74.3 (Ph*C*H_2), 72.9 (Ph*C*H_2), 69.9 (C-3_A), 69.8 (C-4_B), 69.1 (C-6_A), 67.7 (C-6_B), 63.2 (C-5_B), 57.7 (C-2_A), 55.4 (OMe), 55.1 (OMe), 21.1 (CO*C*H_3); ESI-MS: 926.3 $[M+Na]^+$; Anal. Calcd. for $C_{50}H_{53}N_3O_{13}$ (903.98): C, 66.43; H, 5.91; found: C, 66.25; H, 6.05.

Compound 33: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46-6.77 (m, 28 H, Ar-H), 5.82 (d, *J* = 4.0 Hz, 1 H, H-1_B), 5.51 (br s, 1 H, PhC*H*), 5.35 (d, *J* = 3.5 Hz, 1 H, H-1_A), 4.88-4.73 (m, 5 H, 5 PhC*H*), 4.47 (d, *J* = 11.0 Hz, 2 H, 2 PhC*H*), 4.35 (d, *J* = 11.0 Hz, 1 H, PhC*H*), 4.22-4.20 (m, 2 H, H-2_A, H-6_{aB}), 4.16-4.11 (m, 3 H, H-3_A, H-4_A, H-5_A), 4.03 (t, *J* = 8.5 Hz, 1 H, H-3_B), 4.00-3.97 (m, 1 H, H-5_B), 3.76 (br s, 3 H, OMe), 3.75 (br s, 3 H, OMe), 3.68 (t, *J* = 9.5 Hz, 1 H, H-6_{bB}), 3.54 (t, *J* = 9.5 Hz, 1 H, H-4_B), 3.47 (dd, *J* = 8,5 Hz, 3,0 Hz, 1 H, H-2_B), 1.41 (d, *J* = 3.5 Hz, 3 H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.4-113.6 (Ar-C), 101.1 (Ph*C*H), 97.3 (C-1_A), 97.2 (C-1_B), 82.0 (C-4_B), 79.5 (C-2_B), 79.3 (C-3_A), 77.9 (C-4_A), 76.5 (C-5_B), 75.0 (Ph*C*H_2), 74.4 (C-5_A), 74.1 (Ph*C*H_2), 72.9 (Ph*C*H_2), 72.2 (Ph*C*H_2), 68.9 (Ph*C*H_2), 67.1 (C-2_A), 63.0 (C-3_B), 55.4 (OMe), 55.1 (OMe), 17.7 (CH_3); ESI-MS: 933.3 $[M+Na]^+$; Anal. Calcd. for $C_{55}H_{58}O_{12}$ (911.06): C, 72.51; H, 6.42; found: C, 72.40; H, 6.65.

Compound 34: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47-6.77 (m, 33 H, Ar-H), 5.47 (d, *J* = 3.5 Hz, 1 H, H-1_A), 5.45 (br s, 1 H, PhC*H*), 5.25 (d, *J* = 3.5 Hz, 1 H, H-1_B), 5.19 (t, *J* = 9.5 Hz, 1 H, H-4_A), 4.84 (d, *J* =11.5 Hz, 1 H, PhC*H*), 4.70 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.64 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 4.58 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 4.36-4.31 (m, 2 H, H-3_A, H-6_{aA}), 4.17-4.09 (m, 3 H, H-2_B, H-4_B, H-6_{aB}), 4.05-4.01 (m, 4 H, H-3_B, H-5_A, H-6_{bA}, H-6_{bB}), 3.93 (br s, 1 H, H-5_B), 3.84 (OMe), 3.81 (OMe), 3.30 (dd, *J* = 10.0 Hz, 3.5 Hz, 1 H, H-2_A), 2.03 (s, 3 H, $COCH_3$), 1.83 (s, 3 H, $COCH_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.2 (*C*OCH_3), 169.2 (*C*OCH_3), 155.6-113.7 (Ar-C), 100.8 (Ph*C*H), 100.2 (C-1_B), 97.9 (C-1_A), 76.2 (C-3_B), 74.8 (C-2_B), 74.7 (C-4_B), 74.4 (C-3_A), 74.2 (Ph*C*H_2), 71.6 (Ph*C*H_2), 70.3 (C-4_A), 69.6 (C-6_A), 68.5 (C-5_A), 63.7 (C-5_B), 62.2 (C-2_A), 62.0 (C-6_B), 55.5 (OMe), 55.1 (OMe), 20.7 (CO*C*H_3); ESI-MS: 878.3 $[M+Na]^+$; Anal. Calcd. for $C_{45}H_{49}N_3O_{14}$ (855.89): C, 63.15; H, 5.77; found: C, 63.00; H, 5.94.

Compound 35: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47-6.77 (m, 33 H, Ar-H), 5.33 (br s, 1 H, PhC*H*), 5.08 (br s, 1 H, H-1_B), 5.01 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 4.93 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 4.87 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 4.83 (d, *J* = 7.5 Hz, 1 H, H-1_A), 4.75 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 4.69 (br s, 2 H, 2 PhC*H*), 4.65 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.61 (d, *J* = 12.0 Hz, 1

H, PhC*H*), 4.30 (d, *J* = 11.5 Hz, H-1, PhC*H*), 4.16 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.14 (d, *J* = 3.0 Hz, 1 H, H-2_B), 4.11 (br s, 2 H, H-4_B, H-5_B), 4.06 (br s, 1 H, H-4_A), 3.97 (t, *J* = 8.5 Hz, 1 H, H-6_{aB}), 3.96 (br s, 1 H, H-5_A), 3.85 (dd, *J* = 10.0 Hz, 3.5 Hz, 1 H, H-2_A), 3.75 (s, 3 H, OMe), 3.73 (s, 3 H, OMe), 3.61-3.53 (m, 3 H, H-3_B, H-6_{aA}, H-6_{bB}), 3.46-3.40 (m, 2 H, H-3_A, H-6_{bA}); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.1-113.7 (Ar-C), 103.4 (C-1_A), 100.8 (Ph*C*H, C-1_B), 80.7 (C-3_A), 77.9 (C-2_A), 75.7 (C-5_B), 75.4 (C-4_B), 74.9 (Ph*C*H_2), 74.7 (C-4_A), 73.9 (Ph*C*H_2), 73.7 (C-2_B, C-3_B), 73.1 (Ph*C*H_2), 72.3 (Ph*C*H_2), 71.2 (Ph*C*H_2), 69.2 (C-6_B), 67.5 (C-6_A), 62.9 (C-5_A), 55.5 (OMe), 55.0 (OMe); ESI-MS: 1039.4 $[M+Na]^+$; Anal. Calcd. for $C_{62}H_{64}O_{13}$ (1017.16): C, 73.21; H, 6.34; found: C, 73.05; H, 6.50.

Compound 36: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50-7.24 (m, 17 H, Ar-H), 6.98 (d, *J* = 9.0 Hz, 2 H, Ar-H), 6.84 (d, *J* = 9.0 Hz, 2 H, Ar-H), 6.80 (d, *J* = 9.0 Hz, 2 H, Ar-H), 5.81 (d, *J* = 2.5 Hz, 1 H, H-1_B), 5.41 (s, 1 H, PhC*H*), 5.30 (d, *J* = 3.5 Hz, 1 H, H-1_A), 4.92 (d, *J* = 11.0 Hz, 1 H, PhC*H*), 4.87 (d, *J* = 11.0 Hz, 1 H, PhC*H*), 4.79 (d, *J* = 11.0 Hz, 1 H, PhC*H*), 4.72-4.61 (m, 3 H, 3 PhC*H*), 4.31 (dd, *J* = 10.0, 3.5 Hz, 1 H, H-3_B), 4.22 (dd, *J* = 12.0, 2.0 Hz, 1 H, H-6_{aB}), 4.19-4.11 (m, 3 H, H-4_A, H-4_B, H-5_A), 4.03 (dd, *J* = 12.0, 2.0 Hz, 1 H, H-6_{bB}), 4.00-3.96 (m, 3 H, H-2_A, H-2_B, H-3_A), 3.78 (s, 3 H, OCH_3), 3.77 (s, 1 H, OCH_3), 3.74 (br s, 1 H, H-5_B), 1.12 (d, *J* = 6.5 Hz, 3 H, CCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.3-113.7 (Ar-C), 100.8 (Ph*C*H), 98.2 (C-1_B), 97.6 (C-1_A), 78.8 (C-2_A), 75.6 (C-3_B), 75.4 (C-3_A), 74.0 (C-4_A), 73.6 (Ph*C*H_2), 73.3 (Ph*C*H_2), 73.2 (C-4_B), 71.2 (Ph*C*H_2), 69.4 (C-6_B), 66.9 (C-5_A), 63.1 (C-5_B), 59.2 (C-2_B), 55.5 (O*C*H_3), 55.1 (O*C*H_3), 17.6 (C*C*H_3); ESI-MS: 868.3 $[M+Na]^+$; Anal. Calcd. for $C_{48}H_{51}N_3O_{11}$ (845.93): C, 68.15; H, 6.08; found: C, 68.00; H, 6.25.

Compound 37 (α/β = 1.5/1): ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48-6.71 (m, 82 H, Ar-H), 5.58 (d, *J* = 3.5 Hz, 1.5 H, H-$1_{B\alpha}$), 5.57 (s, 1 H, PhCH_β), 5.52 (br s, 1 H, H-$1_{A\beta}$), 5.46 (d, *J* = 1.5 Hz, H-$1_{A\alpha}$), 5.45 (s, 1.5 H, PhCH_α), 5.30-4.54 (m, 19 H, PhC*H*), 4.46-4.43 (m, 2 H, PhC*H*), 4.42 (d, *J* = 8.0 Hz, 1 H, H-$1_{B\beta}$), 4.40-4.28 (m, 9 H), 4.25-4.08 (m, 6.5 H), 4.04-3.90 (m, 8.5 H), 3.88-3.84 (m, 2.5 H), 3.79 (s, 7.5 H, OCH_3), 3.75 (s, 4 H, OCH_3), 3.72 (s, 5 H, OCH_3), 3.62-3.46 (m, 6 H), 3.40-3.35 (m, 1.5 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.0-113.6 (Ar-C), 103.6 (C-$1_{B\beta}$), 101.4 (PhCH_β), 101.3 (PhCH_α), 98.9 (C-$1_{A\alpha}$), 98.1 (C-$1_{B\alpha}$), 97.3 (C-$1_{A\beta}$), 82.1, 79.2, 79.1, 78.1, 77.9, 76.5, 76.4, 75.4, 75.3, 75.1, 74.7, 74.6 (2 C), 74.1, 73.9 (3 C), 73.6, 73.5, 73.3, 73.0, 72.8, 72.6, 71.5, 71.3, 70.2, 69.7, 68.8, 68.7, 68.6, 64.9, 64.7, 55.5 (2 C), 55.1 (2 C); ESI-MS: 1039.4 $[M+Na]^+$; Anal. Calcd. for $C_{62}H_{64}O_{13}$ (1017.16): C, 73.21; H, 6.34; found: C, 73.04; H, 6.50.

Compound 38: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37-6.76 (m, 64 H, Ar-H), 5.85 (d, *J* = 3.5 Hz, H-$1_{A\alpha}$), 5.34 (br s, 1.8 H, H-$1_{B\beta}$, H-$1_{B\alpha}$), 5.08 (d, *J* = 11.0 Hz, 1 H), 5.00 (d, *J* = 11.0 Hz, 1 H), 4.97 (d, *J* = 11.0 Hz, 0.8 H), 4.88-4.66 (m, 11 H), 4.60-4.56 (m, 2 H), 4.54 (d, *J* = 7.5 Hz, 1 H), 4.50-4.40 (m, 4 H), 4.39-4.30 (m, 3.3 H), 4.23-4.07 (m, 5.9 H), 4.05-3.96 (m, 3.9 H), 3.77-3.75 (m, 11.8 H), 3.67-3.57 (m, 5.2 H), 3.52-3.44 (m, 4.8 H), 1.36-1.32 (m, 4.2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.9-113.7 (Ar-C), 104.1, 97.9, 97.2, 96.2, 84.7, 82.3, 81.2, 79.9, 79.5, 77.9, 77.6, 76.7, 76.5, 75.7, 75.4, 75.3, 74.9 (2 C), 74.8, 74.1, 74.0, 73.5, 73.4, 73.3, 72.9, 71.7, 70.8,

70.8, 69.7, 68.8, 67.3, 66.9, 55.5, 55.1, 17.9, 17.0; ESI-MS: 1025.4 $[M+Na]^+$; Anal. Calcd. for $C_{62}H_{66}O_{12}$ (1002.45): C, 74.23; H, 6.63; found: C, 74.16; H, 6.80.

Compound 39: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47-6.80 (m, 29 H, Ar-H), 5.56 (s, 1 H, PhC*H*), 5.01 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.89 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.82 (d, *J* = 11.0 Hz, 1 H, PhC*H*), 4.79 (d, *J* = 11.0 Hz, 1 H, PhC*H*), 4.77 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.76 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.69 (d, *J* = 3.5 Hz, 1 H, H-1_A), 4.66 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.65 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.55 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.48 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.23-4.20 (dd, *J* = 10.5 Hz, 5.5 Hz, 1 H, H-6_{aB}), 4.15 (t, *J* = 9.5 Hz, 1 H, H-4_B), 4.02-3.98 (m, 2 H, H-4_A, H-6_{aA}), 3.95 (br s, 1 H, H-1_B), 3.87 (t, *J* = 9.5 Hz, 1 H, H-6_{bB}), 3.77 (s, 3 H, OMe), 3.76-3.73 (m, 2 H, H-5_A, OC*H*), 3.57 (d, *J* = 2.5 Hz, 1 H, H-2_B), 3.49-3.35 (m, 7 H, H-2_A, H-3_A, H-3_B, H-6_{bA}, OC*H*, NCH_2), 3.29-3.27 (m, 1 H, H-5_B); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.5-114.4 (Ar-C), 101.8 ($J_{C1/H1}$ = 156 Hz; C-1_B), 101.4 (Ph*C*H), 97.0 (C-1_A), 81.8 (C-4_A), 79.8 (C-4_B), 78.7 (C-3_B), 77.4 (C-2_B), 76.9 (2 C, C-2_A, C-3_A), 75.6 (Ph*C*H_2), 74.5 (Ph*C*H_2), 74.3 (Ph*C*H_2), 73.1 (Ph*C*H_2), 72.2 (Ph*C*H_2), 69.9 (C-5_A), 68.5 (C-6_A), 67.9 (C-6_B), 67.6 (C-5_B), 66.5 (O*C*H_2), 55.1 (OMe), 50.5 (NCH_2); ESI-MS: 1002.4 $[M+Na]^+$; Anal. Calcd. for $C_{57}H_{61}N_3O_{12}$ (980.12): C, 69.85; H, 6.27; found: C, 69.70; H, 6.48.

Compound 40: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47-6.76 (m, 23 H, Ar-H), 5.57 (s, 1 H, PhC*H*), 5.48 (dd, *J* = 11 Hz, 2.5 Hz, 1 H, H-3_A), 5.40 (d, *J* = 3.5 Hz, 1 H, H-1_A), 4.88-4.87 (m, 2 H, 2 Ph*C*H), 4.74 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 4.61 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.46 (br s, 2 H, 2 PhCH), 4.42 (br s, 1 H, H-1_B), 4.27-4.25 (m, 1 H, H-5_A), 4.24 (d, *J* = 2.5 Hz, 1 H, H-4_A), 4.16 (t, *J* = 9.5 Hz, 1 H, H-4_B), 4.05 (dd, *J* = 12.0 Hz, 4.5 Hz, 1 H, H-6_{aA}), 3.89 (d, *J* = 3.0 Hz, 1 H, H-2_B), 3.81-3.74 (m, 8 H, H-6_{bA}, H-6_{aB}, 2 OMe), 3.68 (dd, *J* = 12.0 Hz, 6.5 Hz, 1 H, H-6_{bB}), 3.50 (dd, *J* = 9.0 Hz, 3.0 Hz, 1 H, H-3_B), 3.38 (dd, *J* = 9.5 Hz, 3.0 Hz, 1 H, H-2_A), 3.22-3.18 (m, 1 H, H-5_B), 1.97 (s, 3 H, $COCH_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.2 (*C*OCH_3), 159.3-113.7 (Ar-C), 102.5 ($J_{C1/H1}$ = 158 Hz; C-1_B), 101.5 (Ph*C*H), 98.5 (C-1_A), 78.6 (C-4_B), 77.4 (C-3_B), 76.4 (C-2_B), 74.8 (Ph*C*H_2), 74.3 (C-4_A), 73.1 (Ph*C*H_2), 72.4 (Ph*C*H_2), 70.6 (C-3_A), 69.9 (C-5_A), 69.1 (C-6_A), 68.3 (C-6_B), 67.9 (C-5_B), 57.7 (C-2_A), 55.5 (OMe), 55.1 (OMe), 20.6 (CO*C*H_3); ESI-MS: 926.3 $[M+Na]^+$; Anal. Calcd. for $C_{50}H_{53}N_3O_{13}$ (903.98): C, 66.43; H, 5.91; found: C, 66.26; H, 6.07.

Compound 41: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49-7.47 (m, 2 H, Ar-H), 6.97 (d, *J* = 9.0 Hz, 2 H, Ar-H), 6.78 (d, *J* = 9.0 Hz, 4 H, Ar-H), 5.53 (s, 1 H, PhC*H*), 5.25 (d, *J* = 3.5 Hz, 1 H, H-1_A), 5.04 (d, *J* = 11.0 Hz, 1 H, PhC*H*), 4.85 (d, *J* = 11.0 Hz, 1 H, PhC*H*), 4.82 (d, *J* = 11.0 Hz, 1 H, PhC*H*), 4.78 (d, *J* = 11.0 Hz, 1 H, PhC*H*), 4.56 (d, *J* = 11.0 Hz, 1 H, PhC*H*), 4.54 (br s, 1 H, H-1_B), 4.51 (d, *J* = 11.0 Hz, 1 H, PhC*H*), 4.20 (t, *J* = 9.0 Hz each, 1 H, H-4_B), 4.15 (dd, *J* = 12.0 Hz, 5.0 Hz, 1 H, H-6_{aB}), 4.10-4.06 (m, 3 H, H-3_A, H-4_A, H-5_A), 3.96 (d, *J* = 4.0 Hz, 1 H, H-2_B), 3.94 (dd, *J* = 10.0 Hz, 3.5 Hz, 1 H, H-2_B), 3.78 (s, 3 H, OMe), 3.76 (s, 3 H, OMe), 3.71 (t, *J* = 10.0 each, 1 H, H-6_{bB}), 3.51 (dd, *J* = 10.0 Hz, 3.0 Hz, 1 H, H-3_B), 3.29-3.22 (m, 1 H, H-5_B), 1.17 (d, *J* = 6.5 Hz, 3 H, CCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.1-113.6 (Ar-C), 103.4 (C-1_B), 101.3 (Ph*C*H), 97.7 (C-1_A), 78.7 (C-4_B), 77.5 (C-3_B), 77.3 (C-4_A), 76.7 (C-3_A), 75.9 (C-2_A), 75.3

(C-2_B), 74.7 (Ph*C*H_2), 73.7 (Ph*C*H_2), 71.9 (Ph*C*H_2), 71.4 (Ph*C*H_2), 68.4 (C-6_B), 67.8 (C-5_B), 66.6 (C-5_A), 55.5 (OMe), 55.1 (OMe), 17.8 (*C*CH_3); ESI-MS: 933.3 $[M+Na]^+$; Anal. Calcd. for $C_{55}H_{58}O_{12}$ (911.04): C, 72.51; H, 6.42; found: C, 72.40; H, 6.56.

Compound 42: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48-6.79 (m, 18 H, Ar-H), 5.58 (s, 1 H, PhC*H*), 5,42 (d, *J* = 3.5 Hz, 1 H, H-1_A), 5.08 (t, *J* = 9.0 Hz, 1 H, H-4_A), 4.82 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 4.71 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 4.69 (br s, 1 H, H-1_B), 4.65 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.50 (d, *J* =12.0 Hz, 1 H, PhC*H*), 4.35 (dd, *J* = 10.5 Hz, 5 Hz, 1 H, H-6_{aB}), 4.24 (t, *J* = 10.0 Hz, 1 H, H-4_B), 4.22-4.20 (m, 1 H, H-6_{aA}), 4.14-4.06 (m, 3 H, H-3_A, H-5_A, H-6_{bA}), 3.92 (d, *J* = 2.0 Hz, 1 H, H-2_B), 3.83 (t, *J* = 10.5 Hz, 1 H, H-6_{bB}), 3.78 (s, 3 H, OMe), 3.76 (s, 3 H, OMe), 3.58 (dd, *J* = 10.0 Hz, 3.5 Hz, 1 H, H-3_A), 3.39-3.37 (m, 1 H, H-5_B), 2.05 (s, 3 H, COC*H*$_3$), 2.01 (s, 3 H, $COCH_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.1 (*C*OCH_3), 169.2 (*C*OCH_3), 159.2-113.7 (Ar-C), 102.0 ($J_{C1/H1}$ = 158 Hz; C-1_B), 101.5 (Ph*C*H), 97.4 (C-1_A), 78.5 (C-4_B), 77.3 (C-3_B), 76.6 (C-2_B), 76.3 (C-3_A), 75.0 (Ph*C*H_2), 72.0 (Ph*C*H_2), 68.7 (C-2_A), 68.6 (C-6_A), 68.1 (C-4_A), 67.7 (C-5_A), 63.3 (C-5_B), 62.0 (C-6_B), 55.5 (OMe), 55.1 (OMe), 20.8 (CO*C*H_3), 20.7 (CO*C*H_3); ESI-MS: 878.3 $[M+Na]^+$; Anal. Calcd. for $C_{45}H_{49}N_3O_{14}$ (855.89): C, 63.15; H, 5.77; found: C, 63.00; H, 5.90.

Compound 43: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52-6.78 (m, 33 H, Ar-H), 5.57 (s, 1 H, PhC*H*), 5.00 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.92 (d, *J* = 11.5 Hz, 1 H, PhCH), 4.87 (d, *J* = 11.5 Hz, 1 H, PhCH), 4.80 (d, *J* = 7.5 Hz, 1 H, H-1_A), 4.78-4.74 (m, 4 H, 4 PhC*H*), 4.61-4.54 (m, 2 H, 2 PhC*H*), 4.51-4.48 (m, 2 H, PhC*H*, H-1_B), 4.16-4.13 (m, 3 H, H-4_A, H-6_{aA}, H-6_{aB}), 3.97 (d, *J* = 3.5 Hz, 1 H, H-2_B), 3.90 (dd, *J* = 8.5 Hz, 2.5 Hz, 1 H, H-2_A), 3.86-3.80 (m, 2 H, H-4_B, H-6_{bB}), 3.79 (s, 3 H, OMe), 3.78 (s, 3 H, OMe), 3.73-3.70 (m, 1 H, H-6_{bA}), 3.66-3.64 (m, 1 H, H-5_A), 3.56 (dd, *J* = 9.5 Hz, 3.0 Hz, 1 H, H-3_A), 3.40 (dd, *J* = 10.0 Hz, 3.0 Hz, 1 H, H-3_B), 3.19-3.14 (m, 1 H, H-5_B); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.1-113.7 (Ar-C), 103.1 ($J_{C1/H1}$ = 158 Hz; C-1_B), 102.2 (Ph*C*H), 101.3 (C-1_A), 81.7 (C-3_A), 79.1 (C-2_A), 78.5 (C-4_B), 78.1 (C-3_B), 75.5 (C-2_B), 75.2 (Ph*C*H_2), 74.6 (Ph*C*H_2), 73.9 (C-4_A), 73.6 (Ph*C*H_2), 73.5 (Ph*C*H_2), 72.8 (C-5_A), 72.0 (Ph*C*H_2), 69.4 (C-6_A), 68.5 (C-6_B), 67.7 (C-5_B), 55.5 (OMe), 55.1 (OMe); ESI-MS: 1039.4 $[M+Na]^+$; Anal. Calcd. for $C_{62}H_{64}O_{13}$ (1017.18): C, 73.21; H, 6.34; found: C, 73.10; H, 6.50.

Compound 44: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47-6.80 (m, 23 H, Ar-H), 5.54 (s, 1 H, PhCH), 5.44 (d, *J* = 3.5 Hz, 1 H, H-1_A), 5.41-5.36 (m, 2 H, N*H*, H-3_A), 4.76 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.70-4.61 (m, 4 H, 4 PhC*H*), 4.60-4.58 (m, 1 H, H-6_{aA}), 4.50 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.31 (brs, 1 H, H-1_B), 4.29-4.25 (m, 2 H, H-6_{bA}, H-6_{aB}), 4.11-4.07 (m, 1 H, H-2_A), 4.04 (t, *J* = 9.5 Hz, 1 H, H-4_B), 3.99 (t, *J* = 9.0 Hz, 1 H, H-4_A), 3.80-3.76 (m, 8 H, H-5_A, H-6_{bB}, 2 OMe), 3.52 (d, *J* = 2.5 Hz, 1 H, H-2_B), 3.49-3.42 (m, 2 H, C*H*$_2$CCl_3), 3.13-3.11 (m, 1 H, H-5_B), 2.05 (s, 3 H, $COCH_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.7 (*C*OCH_3), 159.1 (*C*OCH_2CCl_3), 155.4-113.7 (Ar-C), 101.6 (Ph*C*H), 101.4 ($J_{C1/H1}$ = 156 Hz; C-1_B), 96.8 (C-1_A), 78.7 (C-4_B), 77.7 (C-3_B), 76.6 (C-2_B), 75.2 (C-4A), 74.7 (Ph*C*H_2), 74.5 (Ph*C*H_2), 73.6 (Ph*C*H_2), 72.2 (C-6_A), 71.1 (C-3_A), 70.6 (C-5_A), 68.6 (*C*H_2CCl_3), 67.9 (C-6_B), 67.4 (C-5_B), 55.5 (OMe), 55.1 (OMe), 54.3 (C-2_A), 20.9

(CO*C*H$_3$); ESI-MS: 1074.2 [M+Na]$^+$; Anal. Calcd. for $C_{53}H_{56}Cl_3NO_{15}$ (1053.37): C, 60.43; H, 5.36; found: C, 60.28; H, 5.50.

Compound 45: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53-6.80 (m, 28 H, Ar-H), 5.57 (s, 1 H, PhC*H*), 5.52 (br s, 1 H, H-1$_A$), 5.02 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.92-4.89 (m, 2 H, PhC*H*$_2$), 4.84 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 4.66 (d, *J* = 12.0 Hz, 2 H, PhC*H*$_2$), 4.56 (d, J=12.0 Hz, 1 H, PhCH), 4.54 (brs, 1 H, H-1$_B$), 4.50 (d, J=12.0 Hz, 1 H, PhCH), 4.24 (dd, *J* = 10.5 Hz, 5.0 Hz, 1 H, H-6$_{aB}$), 4.17-4.08 (m, 3 H, H-2$_B$, H-3$_A$, H-4$_B$), 4.00 (d, *J* = 1.5 Hz, 1 H, H-2$_A$), 3.91-3.81 (m, 2 H, H-5$_A$, H-6$_{bB}$), 3.79 (s, 3 H, OMe), 3.76 (s, 3 H, OMe), 3.55 (t, *J* = 9.5 Hz, 1 H, H-4$_A$), 3.43 (dd, *J* = 10.0 Hz, 3.0 Hz, 1 H, H-3$_B$), 3.21-3.15 (m, 1 H, H-5$_B$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.2-113.7 (Ar-C), 103.3 ($J_{C1/H1}$ = 156.5 Hz; C-1$_B$), 101.3 (Ph*C*H), 97.8 (C-1$_A$), 80.5 (C-4$_B$), 80.1 (C-3$_B$), 78.3 (C-2$_B$), 77.5 (C-4$_A$), 77.2 (C-3$_A$), 75.9 (C-2$_A$), 75.6 (Ph*C*H$_2$), 75.4 (Ph*C*H$_2$), 72.9 (Ph*C*H$_2$), 71.9 (Ph*C*H$_2$), 68.5 (C-6$_B$), 68.4 (C-5$_A$), 67.7 (C-5$_B$), 55.6 (OMe), 55.3 (OMe), 18.2 (Me); ESI-MS: 933.3 [M+Na]$^+$; Anal. Calcd. for $C_{55}H_{58}O_{12}$ (911.06): C, 72.51; H, 6.42; found: C, 72.40; H, 6.65.

Compound 46: ^{1}H NMR (500 MHz $CDCl_3$): δ 8.01-6.76 (m, 38 H, Ar-H), 5.53 (s, 1 H, PhC*H*), 5.31 (t, *J* = 9.5 Hz, 1 H, H-2$_B$), 4.96-4.90 (m, 3 H, H-3$_B$, 2 PhC*H*), 4.84 (d, *J* = 7.0 Hz, 1 H, H-1$_A$), 4.77-4.66 (m, 5 H, 5 PhC*H*), 4.65 (d, *J* = 7.5 Hz, 1 H, H-2$_B$), 4.64 (dd, *J* = 10.0 Hz, 6.0 Hz, 1 H, H-6$_{aA}$), 4.49-4.44 (m, 2 H, 2 PhC*H*), 4.42 (br s, 1 H, H-1$_C$), 4.40 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.28 (dd, *J* = 11.0 Hz, 5.5 Hz, 1 H, H-6$_{bA}$), 4.14 (d, *J* = 2.5 Hz, 1 H, H-4$_B$), 4.09 (t, *J* = 9.5 Hz, 1 H, H-4c), 4.00 (t, *J* = 9.0 Hz, 1 H, H-4$_A$), 3.94 (d, *J* = 2.5 Hz, 1 H, H-2$_C$), 3.85 (dd, *J* = 10.0 Hz, 5.5 Hz, 1 H, H-6$_{aC}$), 3.78- 3.77 (m, 5 H, H-6$_{abB}$, OMe), 3.76-3.62 (m, 3 H, H-2$_A$, H-3$_A$, H-6$_{bC}$), 3.60 (m, 1 H, H-5$_A$), 3.38 (dd, *J* = 10.0 Hz, 3.0 Hz, 1 H, H-3$_C$), 3.01 (m, 1 H, H-5$_C$), 2.05 (s, 3 H, COCH$_3$), 1.93 (s, 3 H, COCH$_3$), 20.7 (2 C, 2 CO*C*H$_3$); ^{13}C NMR (125MHz, $CDCl_3$): δ 169.8 (*C*OCH$_3$), 169.2 (*C*OCH$_3$), 165.7 (COPh), 155.3-113.6 (Ar-C), 103.0 ($J_{C1/H1}$ = 158 Hz; C-1$_C$), 102.6 (C-1$_A$), 101.3 (Ph*C*H), 100.5 (C-1$_B$), 82.5 (C-3$_A$), 81.6 (C-2$_A$), 78.0 (C-4$_C$), 77.4 (C-3$_C$), 76.9 (C-4$_A$), 75.1 (C-5$_A$), 75.0 (2 C, C-4$_B$, C-2$_C$), 74.5 (C-3$_B$), 74.3 (Ph*C*H$_2$), 73.6 (Ph*C*H$_2$), 73.4 (Ph*C*H$_2$), 73.3 (Ph*C*H$_2$), 72.0 (Ph*C*H$_2$), 71.6 (C-5$_B$), 70.2 (C-2$_B$), 68.2 (C-6$_B$), 67.9 (C-6$_C$), 67.8 (C-5$_C$), 62.6 (C-6$_A$), 55.6 (OMe), 55.2 (OMe); ESI-MS: 1341.5 [M+Na]$^+$; Anal. Calcd. for $C_{74}H_{78}O_{22}$ (1319.42): C, 67.36; H, 5.96; found: C, 67.20; H, 6.10.

Compound 47: ^{1}H NMR (500 MHz $CDCl_3$): δ 7.50-6.81 (m, 38 H, Ar-H), 5.63 (s, 1 H, PhC*H*), 5.52 (s, 1 H, PhC*H*), 5.42 (s, 1 H, PhC*H*), 5.35 (br s, 1 H, H-1$_A$), 5.12 (br s, 1 H, H-1$_B$), 4.96 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.89 (d, *J* = 11.5 Hz, 2 H, 2 PhC*H*), 4.83 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.76 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.62 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.58 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.52 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 4.24-4.13 (m, 6 H, H-2$_A$, H-2$_B$, H-4$_C$, H-6$_{Aa}$, H-6$_{aB}$, H-6$_{aC}$), 4.12-4.04 (m, 2 H, H-4$_A$, H-4$_B$), 4.05 (br s, 1 H, H-1$_C$), 4.02-3.98 (m, 2 H, H-2$_C$, H-3$_B$), 3.91-3.84 (m, 2 H, H-5$_A$, H-5$_B$), 3.79 (s, 3 H, OMe), 3.77 (s, 3 H, OMe), 3.75-3.70 (m, 4 H, H-3$_A$, H-6$_{bA}$, H-6$_{bB}$, H-6$_{bC}$), 3.24 (dd, *J* = 10.0 Hz, 3.0 Hz, 1 H, H-3$_C$), 2.98-2.93 (m, 1 H, H-5$_C$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.0-113.7 (Ar-C), 101.4 (2 C, 2 Ph*C*H), 101.3 (Ph*C*H), 100.5 (2 C, C-1$_B$, C-1$_C$ ($J_{C1/H1}$ = 158 Hz)), 98.6 (C-1$_A$), 79.5 (C-3$_B$), 78.7 (C-4$_A$), 77.1 (C-3$_C$), 76.8 (C-

3_A), 76.5 (C-2_A), 76.3 (C-2_B), 75.4 (C-4_C), 74.6 (Ph*C*H_2), 74.4 (Ph*C*H_2), 73.5 (C-2_C), 71.7 (Ph*C*H_2), 71.6 (Ph*C*H_2), 68.8 (C-6_C), 68.6 (C-6_B), 68.5 (C-6_A), 67.0 (C-5_C), 64.9 (C-5_B), 64.3 (C-5_A), 55.5 (OMe), 55.1 (OMe); ESI-MS: 1287.5 $[M+Na]^+$; Anal. Calcd. for $C_{75}H_{76}O_{18}$ (1265.42): C, 71.19; H, 6.05; found: C, 71.00; H, 6.15.

Compound 48: ^{1}H NMR (500 MHz $CDCl_3$): δ 7.49-6.84 (m, 34 H, Ar-H), 5.49 (s, 1 H, PhC*H*), 5.43 (s, 1 H, PhC*H*), 5.42 (s, 1 H, PhC*H*), 5.19 (br s, 1 H, H-1_B), 4.93 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.83 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.82 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.74 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.70 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.63 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.55 (d, *J* = 7.5 Hz, 1 H, H-1_A), 4.47 (br s, 2 H, 2 PhC*H*), 4.29 (dd, *J* = 10.0 Hz, 3.5 Hz, 1 H, H-6_{aB}), 4.19 (br s, 1 H, H-2_B), 4.17-4.07 (m, 4 H, H-5_B, H-6_{aA}, H-6_{aC}, OCH), 4.06 (br s, 1 H, H-1_C), 4.05-3.86 (m, 3 H, H-3_A, H-3_B, H-4_B), 3.80 (s, 3 H, OMe), 3.78-3.68 (m, 5 H, H-2_C, OCH, H-6_{bA}, H-6_{bB}, H-6_{bC}), 3.61-3.58 (m, 2 H, H-4_A, H-4_C), 3.47-3.45 (m, 2 H, NCH_2), 3.44-3.36 (m, 1 H, H-5_A), 3.35 (t, *J* = 9.5 Hz, 1 H, H-2_A), 2.90 (dd, *J* = 10.0 Hz, 2.5 Hz, 1 H, H-3_C), 2.45-2.35 (m, 1 H, H-5_C); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.0-113.7 (Ar-C), 104.5 (C-1_B), 102.3 (Ph*C*H), 101.5 (Ph*C*H), 101.3 (Ph*C*H), 99.8 ($J_{C1/H1}$ = 158 Hz; C-1_C), 98.2 (C-1_A), 81.8 (C-4_A), 79.2 (C-4_C), 78.5 (C-2_C), 78.1 (C-2_A), 76.8 (C-3_A), 76.5 (C-4_B), 75.7 (C-2_B), 75.2 (Ph*C*H_2), 74.6 (Ph*C*H_2), 71.3 (Ph*C*H_2), 70.9 (Ph*C*H_2), 68.7 (C-6_C), 68.6 (C-6_B), 68.5 (O*C*H_2), 68.4 (C-6_A), 66.8 (C-5_C), 65.6 (C-3_C), 64.1 (C-5_B), 55.2 (OMe), 50.9 (NCH_2); ESI-MS: 1250.4 $[M+Na]^+$; Anal. Calcd. for $C_{70}H_{73}N_3O_{17}$ (1228.36): C, 68.45; H, 5.99; found: C, 68.30; H, 6.15.

Compund 49: ^{1}H NMR (500 MHz $CDCl_3$): δ 7.92-6.72 (m, 52 H, Ar-H), 5.89 (dd, *J* = 9.0 Hz, 3.0 Hz, 1 H, H-3_C), 5.62 (br s, 1 H, PhC*H*), 5.39 (d, *J* = 2.5 Hz, 1 H, H-4_B), 4.92 (d, *J* = 11.0 Hz, 1 H, PhC*H*), 4.82-4.79 (m, 2 H, PhC*H*), 4.77 (d, *J* = 3.0 Hz, 1 H, H-1_C), 4.75-4.54 (m, 10 H, H-2C, 9 PhC*H*), 4.45 (d, *J* = 9.0 Hz, 1 H, H-1_A), 4.42 (br s, 1 H, H-1_D), 4.39 (d, *J* = 11.0 Hz, 1 H, PhC*H*), 4.30-4.27 (m, 3 H, H-4_C, H-6_{abD}), 4.21 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.11-4.08 (m, 3 H, H-5_B, H-6_{abC}), 3.95-3.91 (m, 3 H, H-5_B, H-6_{aA}, H-6_{aB}), 3.86 (t, *J* = 9.0 Hz, 1 H, H-4_D), 3.82 (d, *J* = 3.0 Hz, 1 H, H-4_A), 3.79-3.76 (m, 2 H, H-2_D, H-6_{bB}), 3.75 (br s, 6 H, 2 OMe), 3.69-3.68 (m, 1 H, H-6_{bA}), 3.51-3.49 (m, 2 H, H-5_A, H-5_C), 3.46-3.43 (m, 2 H, H-2_B, H-5_A), 3.31-3.24 (m, 3 H, H-2_A, H-3_A, H-3_B), 3.23-3.19 (m, 1 H, H-5_D), 2.10 (br s, 3 H, $COCH_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.3 (*C*OCH_3), 155.1 (*C*OPh), 151.3-113.7 (Ar-C), 102.3 ($J_{C1/H1}$ = 158 Hz; C-1_D), 102.1 (C-1_A), 101.4 (Ph*C*H), 98.7 (C-1_C), 97.7 (C-1_B), 81.9 (C-5_A), 79.0 (C-3_D), 78.5 (C-5_B), 77.5 (C-3_A), 76.5 (2 C, C-5_C, C-4_A), 75.5 (C-5_D), 75.2 (Ph*C*H_2), 75.1 (Ph*C*H_2), 75.0 (C-3_B), 74.1 (Ph*C*H_2), 73.6 (C-2_D), 73.3 (C-4_D), 73.2 (Ph*C*H_2), 73.1 (C-2_C), 73.0 (Ph*C*H_2), 72.9 (Ph*C*H_2), 72.0 (Ph*C*H_2), 71.1 (C-4_B), 70.6 (C-3_C), 68.8 (C-6_B), 68.4 (C-6_D), 67.8 (C-6_C), 67.5 (C-2_A), 67.4 (C-4_C), 67.0 (C-6_A), 66.3 (C-2_B), 20.9 (CO*C*H_3); ESI-MS: 1860.7 $[M+Na]^+$; Anal. Calcd. for $C_{107}H_{107}NO_{27}$ (1839.01): C, 69.88; H, 5.86; found: C, 69.70; H, 6.05.

Compound 50: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47-6.79 (m, 14 H, Ar-H), 5.58 (s, 1 H, PhCH), 4.92 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.83 (d, *J* = 12.5 Hz, 1 H, PhC*H*), 4.60 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.51 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.48 (br s, 1 H, H-1), 4.27 (dd, *J* = 10.5 Hz, 5.0 Hz, 1 H, H-6_a), 4.20-4.13 (m, 2 H, H-4, OCH), 3.91-3.87 (m, 2 H, H-2, H-6_b), 3.77 (s, 3 H, OMe),

3.75-3.74 (m, 1 H, OC*H*), 3.53 (dd, *J* = 10.0 Hz, 3.5 Hz, 1 H, H-3), 3.48-3.42 (m, 2 H, BrCH_2), 3.32-3.26 (m, 1 H, H-5); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.3-113.8 (Ar-C), 102.4 (C-1), 101.5 (PhCH), 78.7 (C-4), 77.4 (C-3), 75.9 (C-2), 74.9 (PhCH_2), 72.2 (PhCH_2), 69.7 (OCH_2), 68.5 (C-6), 67.8 (C-5), 55.1 (OMe), 30.0 (BrCH_2); ESI-MS: 607.1 $[M+Na]^+$; Anal. Calcd. for $C_{30}H_{33}BrO_7$ (585.48): C, 61.54; H, 5.68; found: C, 61.40; H, 5.80.

Compound 51: ^{1}H NMR (500 MHz $CDCl_3$): δ 7.45-6.80 (m, 19 H, Ar-H), 5.55 (s, 1 H, PhC*H*), 5.02 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.92 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 4.74 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 4.68 (br s, 1 H, H-1_B), 4.64-4.57 (m, 3 H, 3 PhC*H*), 4.44-4.36 (m, 2 H, OCH_2), 4.26 (dd, *J* = 10.5 Hz, 5. 0 Hz, 1 H, H-6_{aB}), 4.19 (d, *J* = 7.5 Hz, 1 H, H-1_A), 4.04 (t, *J* = 9.5 Hz, 1 H, H-4_B), 3.87-3.83 (m, 2 H, H-2_B, H-6_{bB}), 3.77 (s, 3 H, OMe), 3.72 (dd, *J* = 9.5 Hz, 7.5 Hz, 1 H, H-2_A), 3.63 (dd, *J* = 10.0 Hz, 3.0 Hz, 1 H, H-3_A), 3.54 (t, *J* = 9.5 Hz, 1 H, H-4_A), 3.53 (s, 3 H, OMe), 3.48-3.46 (m, 1 H, H-5_A), 3.38 (dd, *J* = 10.0 Hz, 3.0 Hz, 1 H, H-3_B), 3.22-3.19 (m, 1 H, H-5_B), 2.31 (br s, 1 H, C*H*), 1.14 (d, *J* = 6.5 Hz, 3 H, Me); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.2-113.7 (Ar-C), 104.7 (C-1_A), 103.0 ($J_{C1/H1}$ = 156 Hz; C-1_B), 101.4 (Ph*C*H), 82.1 (C-3_A), 79.6 (C-2_A), 78.5 (C-4_B), 77.8 (C-4_A), 77.4 (C-3_B), 75.7 (C-2_B), 75.0 (Ph*C*H_2), 74.2 (Ph*C*H_2), 72.2 (Ph*C*H_2), 70.2 (C-5_A), 67.4 (C-6_B), 65.1 (C-5_B), 60.0 (O*C*H_2), 56.7 (OMe), 55.0 (OMe), 16.6 (*C*H_3); ESI-MS: 789.3 $[M+Na]^+$; Anal. Calcd. for $C_{45}H_{50}O_{11}$ (766.88): C, 70.48; H, 6.57; found: C, 70.30; H, 6.65.

Compound 52: ^{1}H NMR (500 MHz $CDCl_3$): δ 7.48-6.75 (m, 14 H, Ar-H), 5.52 (s, 1 H, PhC*H*), 5.45 (d, *J* = 4.0 Hz, 1 H, H-1_A), 5.44 (t, *J* = 8.5 Hz, 1 H, H-3_A), 5.36 (br s, 1 H, NH), 4.79 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.68-4.59 (m, 4 H, CH_2CCl_3, 2 PhC*H*), 4.44-4.37 (m, 3 H, OCH_2, PhC*H*), 4.35 (br s, 1 H, H-1_B), 4.27 (dd, *J* = 10.5 Hz, 5.0 Hz, 1 H, H-6_{aB}), 4.09 (dd, *J* = 10.0 Hz, 3.0 Hz, 1 H, H-2_A), 4.03 (t, *J* = 9.5 Hz, 1 H, H-4_A), 3.95 (t, *J* = 9.5 Hz, 1 H, H-4_A), 3.93-3.91 (m, 1 H, H-5_A), 3.84 (d, *J* = 2.0 Hz, 1 H, H-2_B), 3.82-3.77 (m, 1 H, H-6_{bB}), 3.76 (s, 3 H, OMe), 3.75 (s, 3 H, OMe), 3.74-3.71 (m, 1 H, H-6_{aA}), 3.36 (dd, *J* = 10.0 Hz, 1.5 Hz, 1 H, H-6_{bA}), 3.10-3.08 (m, 1 H, H-5_B), 2.36 (br s, 1 H, C*H*), 2.05 (s, 3 H, $COCH_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.6 (*C*OCH_3), 159.2-113.7 (Ar-C), 101.7 (PhCH), 101.4 ($J_{C1/H1}$ = 156.2 Hz; C-1_B), 96.7 (C-1_A), 78.3 (C-4_A), 75.2 (C-3_B), 75.0 (C-4_B), 74.8 (C-2_B), 74.5 (Ph*C*H_2), 73.6 (Ph*C*H_2), 71.9 (*C*H_2CCl_3), 71.6 (C-5_A), 76.7 (C-3_A), 68.6 (C-6_B), 68.1 (C-6_A), 67.4 (C-5_B), 59.6 (O*C*H_2), 55.5 (OMe), 55.1 (OMe), 54.2 (C-2_A), 21.0 (CO*C*H_3); ESI-MS: 1022.2 $[M+Na]^+$; Anal. Calcd. for $C_{49}H_{52}Cl_3NO_{15}$ (1001.30): C, 58.78; H, 5.23; found: C, 58.62; H, 5.40.

Compound 53 (α/β = 5/9): ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52-6.77 (m, 106 H, Ar-H), 5.45 (br s, 1 H, H-$1_{B\alpha}$), 5.30 (d, *J* = 3.5 Hz, 1 H, H-$1_{A\alpha}$), 5.20 (d, *J* = 3.5 Hz, 1.76 H, H-$1_{A\beta}$), 5.15 (d, *J* = 11.5 Hz, 1.76 H, PhCH_β), 5.09 (d, *J* = 11.5 Hz, 1.76 H, PhCH_β), 4.90-4.60 (m, 13.6 H), 4.50 (br s, 1.76 H, H-$1_{B\beta}$), 4.49-4.21 (m, 22.1 H), 4.12-4.00 (m, 10.0 H), 3.96-3.80 (m, 8.30 H), 3.78-3.70 (m, 23 H), 3.68-3.60 (m, 12 H), 3.52-3.40 (m, 7.6 H), 1.24-1.22 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.7-113.7 (Ar-C), 102.4 (C-$1_{B\beta}$), 99.1 (C-$1_{B\alpha}$), 97.9 (C-$1_{A\beta}$), 97.1 (C-$1_{A\alpha}$), 82.2, 79.9, 79.0, 77.0, 76.9, 76.0, 75.9, 75.5, 75.4, 75.3, 75.2, 75.1, 74.2, 74.0, 73.9, 73.8, 73.7, 73.5, 73.4, 73.3, 73.2, 71.2, 71.0, 70.9, 70.8, 70.7, 69.9, 67.2, 67.0, 63.0, 62.9, 61.0, 55.7, 55.5, 17.5,

17.4; ESI-MS: 1025.4 $[M+Na]^+$; Anal. Calcd. for $C_{62}H_{66}O_{12}$ (1003.18): C, 74.23; H, 6.63; found: C, 74.05; H, 6.76.

Compound 54 (α/β = 4.4/10): ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51-6.76 (m, 51 H, Ar-H), 5.60 (s, 0.44 H, PhCH_α), 5.50 (br s, 0.44 H, H-$1_{A\alpha}$), 5.49 (s, 1 H, PhCH_β), 5.45 (br s, 1 H, H-$1_{A\beta}$), 5.21 (br s, 0.44 H, H-$1_{B\alpha}$), 5.08-4.85 (m, 6.9 H), 4.70-4.66 (m, 1.62 H), 4.62 (br s, 1 H, H-$1_{B\beta}$), 4.60-4.36 (m, 10 H), 4.22-4.10 (m, 6 H), 4.00-3.86 (m, 6.34 H), 3.78-3.65 (m, 14.6 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.8-113.9 (Ar-C), 101.7 (Ph*C*H$_\beta$), 101.5 (Ph*C*H$_\alpha$), 100.3 (C-$1_{B\alpha}$), 99.5 (C-$1_{B\beta}$), 98.6 (C-$1_{A\alpha}$), 97.1 (C-$1_{A\beta}$), 82.0, 79.4, 78.6, 77.0, 76.9, 76.5, 76.1, 76.0, 75.9, 75.7, 74.4, 74.3, 74.0, 73.9 (2 C), 73.0, 72.9, 72.2, 72.0, 71.8, 70.7, 70.6, 69.9, 69.8, 69.7, 69.6, 65.4, 65.3, 65.2, 55.4, 55.3; ESI-MS: 1039.4 $[M+Na]^+$; Anal. Calcd. for $C_{62}H_{64}O_{13}$ (1017.16): C, 73.21; H, 6.34; found: C, 73.02; H, 6.50.

Compound 55: ^{1}H NMR (500 MHz $CDCl_3$): δ 7.52-6.82 (m, 29 H, Ar-H), 5.62 (s, 1 H, PhC*H*), 4.97-4.92 (m, 3 H, 3 PhC*H*), 4.86-4.83 (m, 3 H, 3 PhC*H*), 4.76 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 4.64 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 4.56-4.54 (m, 2 H, 2 PhC*H*), 4.43 (d, *J* = 7.5 Hz, 1 H, H-1_A), 4.31-4.30 (m, 2 H, H-1_B, H-6_{aB}), 4.19-4.14 (m, 2 H, H-6_{aA}, H-4_B), 3.95-3.90 (m, 1 H, H-6_{bB}), 3.81 (s, 3 H, OMe), 3.78-3.77 (m, 1 H, H-2_B), 3.70 (t, *J* = 8.5 Hz, 1 H, H-3_A), 3.51-3.48 (m, 3 H, H-4_A, H-5_A, H-6_{bA}), 3.42-3.36 (m, 2 H, H-2_A, H-3_B), 3.26-3.25 (m, 1 H, H-5_B), 2.70-2.62 (m, 2 H, SCH_2), 1.24 (t, *J* = 7.5 Hz, 3 H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.6-113.7 (Ar-C), 102.6 ($J_{C1/H1}$ = 156 Hz; C-1_B), 101.4 (Ph*C*H), 86.7 (C-3_A), 84.8 (C-1_A), 81.8 (C-3_B), 78.8 (C-4_A), 78.7 (C-4_B), 78.0 (C-2_A), 77.3 (C-5_A), 75.8 (C-2_B), 75.7 (Ph*C*H$_2$), 75.4 (Ph*C*H$_2$), 74.8 (Ph*C*H$_2$), 74.6 (Ph*C*H$_2$), 72.1 (Ph*C*H$_2$), 69.3 (C-6_A), 68.5 (C-6_B), 67.5 (C-5_B), 55.1 (OMe), 24.8 (S*C*H$_2$), 14.9 (*C*H$_3$); ESI-MS: 977.4 $[M+Na]^+$; Anal. Calcd. for $C_{57}H_{62}O_{11}S$ (955.17): C, 71.68; H, 6.54; found: C, 71.54; H, 6.65.

Compound 56: ^{1}H NMR (500 MHz $CDCl_3$): δ 7.46-7.20 (m, 29 H, Ar-H), 6.02-5.95 (m, 1 H, CH$_2$=C*H*), 5.47 (s, 1 H, PhC*H*), 5.36-5.32 (m, 1 H, CH_2=CH), 5.23-5.20 (m, 1 H, CH_2=CH), 5.07 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 4.98-4,94 (m, 2 H, 2 PhC*H*), 4.88 (br s, 1 H, H-1_B), 4.80 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.69 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 4.64-4.60 (m, 2 H, 2 PhC*H*), 4.57-4.54 (m, 2 H, 2 PhC*H*), 4.43-4.42 (m, 1 H, H-6_{aB}), 4.41 (d, *J* = 8.0 Hz, 1 H, H-1_A), 4.33 (d, *J* = 11.0 Hz, 1 H, PhC*H*), 4.21-4.15 (m, 2 H, H-6_{aA}, H-6_{bB}), 3.68 (t, *J* = 9.0 Hz, 1 H, H-4_A), 3.78-3.69 (m, 3 H, H-3_B, OCH_2), 3.61 (t, *J* = 10.5 Hz, 1 H, H-6_{bB}), 3.51-3.44 (m, 5 H, H-2_A, H-3_A, H-2_B, H-4_B), 3,21-3.20 (m, 1 H, H-5_B); ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.46-126.2 (Ar-C), 133.9 (CH$_2$=*C*H), 117.3 (*C*H$_2$=CH), 102.5 ($J_{C1/H1}$ = 158.8 Hz; C-1_B), 102.3 (C-1_A), 101.9 (Ph*C*H), 82.7 (C-4_A), 82.2 (C-4_B), 79.3 (C-3_B), 78.5 (C-2_B), 76.1 (C-2_A), 75.5 (Ph*C*H$_2$), 74.8 (Ph*C*H$_2$), 74.4 (Ph*C*H$_2$), 74.5 (Ph*C*H$_2$), 74.4 (C-3_A), 73.4 (Ph*C*H$_2$), 70.8 (C-5_A), 70.2 (C-6_A), 68.7 (C-6_B), 68.5 (O*C*H$_2$), 66.8 (C-5_B), 55.1 (OMe); ESI-MS: 973.4 $[M+Na]^+$; Anal. Calcd. for $C_{58}H_{62}O_{12}$ (951.12): C, 73.24; H, 6.57; found: C, 73.10; H, 6.75.

Compound 57: ^{1}H NMR (500 MHz $CDCl_3$): δ 7.44-6.80 (m, 29 H, Ar-H), 5.91-5.81 (m, 1 H, C*H*=CH$_2$), 5.48 (s, 1 H, PhCH), 5.27-5.17 (m, 2 H, CH=CH_2), 4.86 (br s, 1 H, H-1_A), 4.83-4.49

(m, 9 H, 9 PhC*H*), 4.48 (br s, 1 H, H-1_B), 4.38 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.19-4.14 (m, 2 H, OC*H*, H-2_B), 4.04-3.93 (m, 3 H, H-4_B, H-6_{aB}, OC*H*), 3.87-3.86 (m, 1 H, H-3_A), 3.78 (s, 3 H, OMe), 3.75-3.74 (m, 2 H, H-2_A, H-6_{bB}), 3.68-3.64 (m, 2 H, H-5_A, H-6_{aA}), 3.60-3.57 (m, 2 H, H-4_A, H-6_{bA}), 3.37-3.35 (m, 1 H, H-3_B), 3.04-3.03 (m, 1 H, H-5_B); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.1-113.7 (Ar-C), 117.2 (*C*H=CH_2), 101.9 ($J_{C1/H1}$ = 160 Hz; C-1_B), 101.3 (Ph*C*H), 97.5 (C-1_A), 78.7 (C-4_B), 78.0 (C-3_B), 77.9 (C-2_B), 76.9 (C-3_A), 76.1 (C-4_A), 75.6 (C-2_A), 74.8 (Ph*C*H_2), 73.4 (Ph*C*H_2), 72.8 (Ph*C*H_2), 72.5 (Ph*C*H_2), 71.4 (Ph*C*H_2), 69.1 (C-6_A), 68.5 (C-6_B), 67.9 (O*C*H_2), 55.1 (OMe); ESI-MS: 973.4 $[M+Na]^+$; Anal. Calcd. for $C_{58}H_{62}O_{12}$ (951.12): C, 73.24; H, 6.57; found: C, 73.11; H, 6.68.

Compound 58: ^{1}H NMR (500 MHz $CDCl_3$): δ 7.79-6.82 (m, 29 H, Ar-H), 5.61 (s, 1 H, PhC*H*), 5.01 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.94 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 4.86-4.76 (m, 6 H, 6 PhC*H*), 4.71 (br s, 1 H, H-1_A), 4.67 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 4.51 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 4.25-4.05 (m, 2 H, H-3_B, H-6_{aB}), 4.04-4.02 (m, 3 H, H-1_B, H-4_A, H-6_{aA}), 3.91 (t, *J* = 12.0 Hz, 1 H, H-6_{bB}), 3.81-3.79 (m, 1 H, H-5_A), 3.73-3.71 (m, 1 H, OC*H*), 3.68 (br s, 1 H, H-2_A), 3.53-3.43 (m, 5 H, H-2_B, H-3_A, H-3_B, OCH, H-6_{bA}), 3.40-3.39 (m, 1 H, NC*H*), 3.36-3.35 (m, 1 H, NC*H*), 3.22-3.21 (m, 1 H, H-5_B); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.0-114.4 (Ar-C), 102.1 ($J_{C1/H1}$ = 157.5 Hz; C-1_B), 101.6 (Ph*C*H), 97.0 (C-1_A), 81.9 (C-4_A), 79.8 (C-4_B), 78.6 (C-3_B), 77.7 (2C, C-2_B, C-3_A), 75.8 (Ph*C*H_2), 75.6 (C-2_A), 74.9 (Ph*C*H_2), 74.6 (Ph*C*H_2), 73.2 (Ph*C*H_2), 72.5 (Ph*C*H_2), 69.9 (C-5_A), 68.5 (C-6_A), 68.0 (C-6_A), 67.5 (C-5_B), 66.4 (OCH_2), 50.5 (N*C*H_2); ESI-MS: 1022.4 $[M+Na]^+$; Anal. Calcd. for $C_{60}H_{61}N_3O_{11}$ (1000.16): C, 72.05; H, 6.15; found: C, 71.94; H, 6.25.

Compound 59: ^{1}H NMR (500 MHz $CDCl_3$): δ 7.81-6.80 (m, 31 H, Ar-H), 5.58 (s, 1 H, PhC*H*), 5.27 (d, *J* = 3.5 Hz, 1 H, H-1_A), 5.08 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 4.89-4.75 (m, 5 H, 5 PhC*H*), 4.70 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 4.58 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.56 (br s, 1 H, H-1_B), 4.26 (t, *J* = 10.0 Hz, 1 H, H-4_B), 4.16 (dd, *J* = 10.5 Hz, 5.0 Hz, 1 H, H-6_{aB}), 4.07-4.04 (m, 4 H, H-2_B, H-3_A, H-4_A, H-5_A), 3.98 (dd, *J* = 9.0 Hz, 3.5 Hz, 1 H, H-2_A), 3.76 (s, 3 H, OMe), 3.72 (t, *J* = 10.5 Hz, 1 H, H-6_{bB}), 3.60 (dd, *J* = 9.5 Hz, 2.5 Hz, 1 H, H-3_B), 3.28 (m, 1 H, H-5_B), 1.16 (d, *J* = 6.5 Hz, 3 H, Me); ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.9-114.5 (Ar-C), 103.4 ($J_{C1/H1}$ = 158.5 Hz; C-1_B), 101.4 (Ph*C*H), 97.7 (C-1_A), 78.5 (C-4_B), 77.7 (C-3_B), 77.3 (C-2_B), 76.7 (C-4_A), 75.7 (C-3_A), 75.3 (C-2_A), 74.7 (Ph*C*H_2), 73.7 (Ph*C*H_2), 72.1 (Ph*C*H_2), 71.1 (Ph*C*H_2), 68.4 (C-6_B), 67.8 (C-5_B), 66.6 (C-5_A), 55.5 (OMe), 17.0 (Me); ESI-MS: 953.4 $[M+Na]^+$; Anal. Calcd. for $C_{58}H_{58}O_{11}$ (931.09): C, 74.82; H, 6.28; found: C, 74.70; H, 6.45.

Compound 60: ^{1}H NMR (500 MHz $CDCl_3$): δ 7.79-6.80 (m, 31 H, Ar-H), 5.61 (s, 1 H, PhCH), 5.07 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 4.95 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 4.91 (d, *J* = 11.5 Hz, 1 H, PhCH), 4.82 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 4.76-4.70 (m, 2 H, 2 PhC*H*), 4.66-4.60 (m, 2 H, 2 PhC*H*), 4.54 (br s, 1 H, H-1_B), 4.24 (dd, *J* = 10.5 Hz, 5.0 Hz, 1 H, H-6_{bB}), 4.21 (t, *J* = 9.5 Hz, 1 H, H-4_B), 4.12 (br s, 1 H, H-2_A), 4.10 (dd, *J* = 9.5 Hz, 3.0 Hz, 1 H, H-3_A), 4.06 (d, *J* = 2.5 Hz, 1 H, H-2_B), 3.90 (t, *J* = 10.5 Hz, 1 H, H-4_A), 3.85-3.82 (m, 1 H, H-5_A), 3.77 (s, 3 H, OMe), 3.55 (t, *J* = 9.5 Hz, 1 H, H-6_{bB}), 3.49 (dd, *J* = 10.0 Hz, 3.0 Hz, 1 H, H-3_B), 3.21-3.18 (m, 1 H, H-5_B), 1.30 (d, *J* = 6.5 Hz, 3 H, Me); ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.8-114.6 (Ar-C), 103.3 ($J_{C1/H1}$

= 158 Hz; C-1_B), 101.4 (Ph*C*H), 97.8 (C-1_A), 80.5 (C-4_B), 80.0 (C-3_B), 78.3 (C-2_B), 77.7 (C-4_A), 75.9 (C-3_A), 75.5 (C-2_A), 75.4 (Ph*C*H_2), 74.8 (Ph*C*H_2), 72.2 (Ph*C*H_2), 72.0 (Ph*C*H_2), 68.5 (C-6_B), 68.4 (C-5_A), 67.7 (C-5_B), 55.6 (OMe), 18.2 (Me); ESI-MS: 953.4 $[M+Na]^+$; Anal. Calcd. for $C_{58}H_{58}O_{11}$ (931.09): C, 74.82; H, 6.28; found: C, 74.67; H, 6.45.

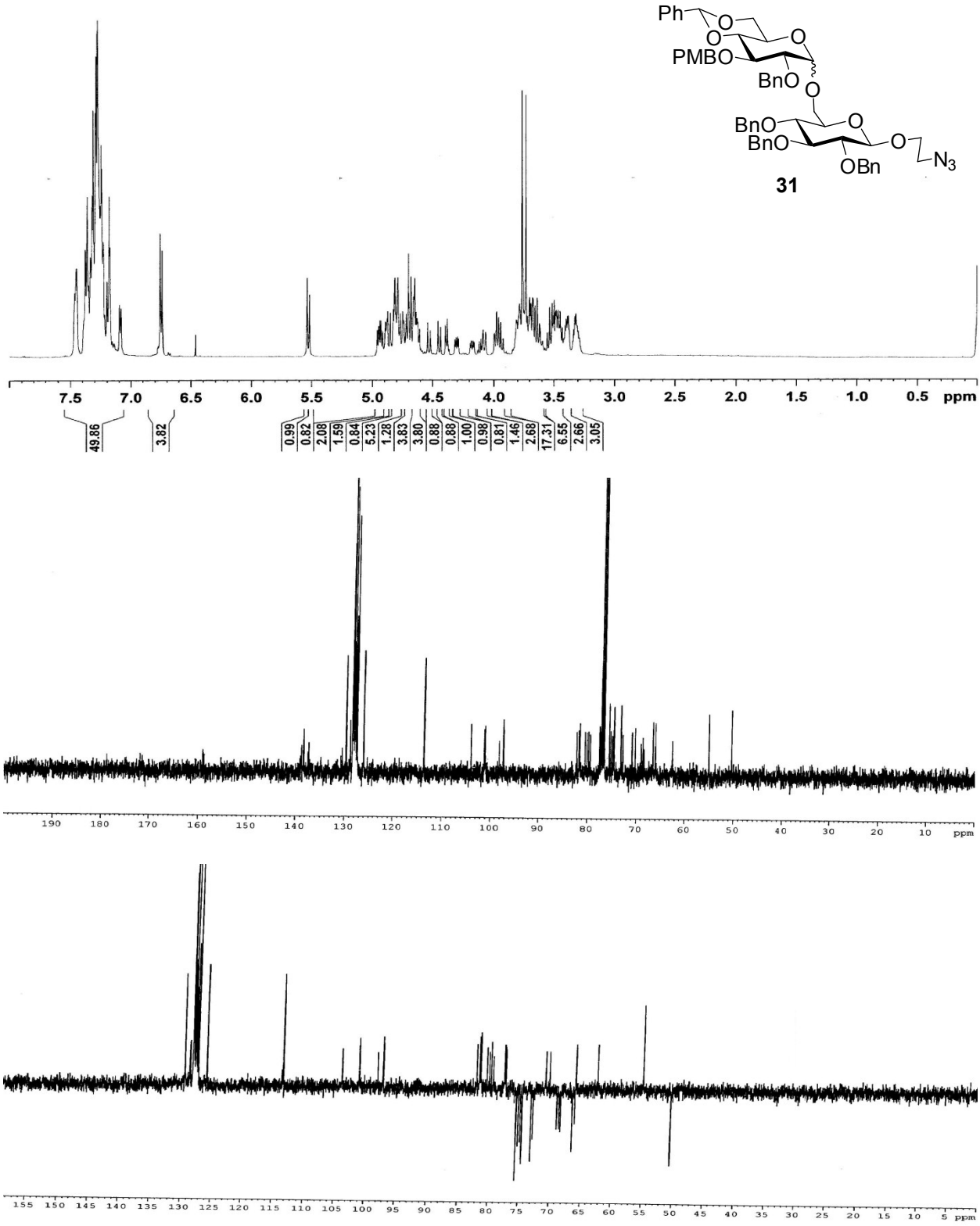
Compound 61: ^{1}H NMR (500 MHz $CDCl_3$): δ 7.71-7.26 (m, 17 H, Ar-H), 5.62 (s, 1 H, PhC*H*), 5.55 (d, *J* = 5.0 Hz, 1 H, H-1_A), 5.04 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.92 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.68 (br s, 2 H, 2 PhC*H*), 4.59 (dd, *J* = 7.5 Hz, 2.0 Hz, 1 H, H-3_A), 4.52 (br s, 1 H, H-1_B), 4.31-4.27 (m, 2 H, H-2_A, H-6_{aB}), 4.22-4.18 (m, 2 H, H-4_A, H-4_B), 4.14 (dd, *J* = 10.5 Hz, 2.0 Hz, 1 H, H-6_{aA}), 4.07-4.05 (m, 1 H, H-5_A), 4.03 (d, *J* = 10.5 Hz, 1 H, H-2_B), 3.89 (t, *J* = 10.5 Hz, 1 H, H-6_{bB}), 3.62-3.56 (m, 2 H, H-3_B, H-6_{bA}), 3.32-3.29 (m, 1 H, H-5_B), 1.49 (s, 3 H, CH_3), 1.42 (s, 3 H, CH_3), 1.33 (s, 3 H, CH_3), 1.30 (s, 3 H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.4-125.5 (Ar-C), 109.5 {*C*$(CH_3)_2$}, 108.7 {*C*$(CH_3)_2$}, 102.9 ($J_{C1/H1}$ = 160 Hz; C-1_B), 101.5 (Ph*C*H), 96.4 (C-1_A), 78.5 (C-4_B), 77.3 (C-3_B), 74.8 (C-2_B), 74.5 (Ph*C*H_2), 71.9 (Ph*C*H_2), 71.6 (C-4_A), 70.8 (C-3_A), 70.4 (C-2_A), 70.0 (C-6_A), 68.6 (C-6_B), 68.0 (C-5_A), 67.6 (C-5_B), 26.0 (2 C, 2 CH_3), 25.1 (*C*H_3), 24.4 (*C*H_3); ESI-MS: 763.3 $[M+Na]^+$; Anal. Calcd. for $C_{43}H_{48}O_{11}$ (740.85): C, 69.71; H, 6.53; found: C, 69.56; H, 6.70.

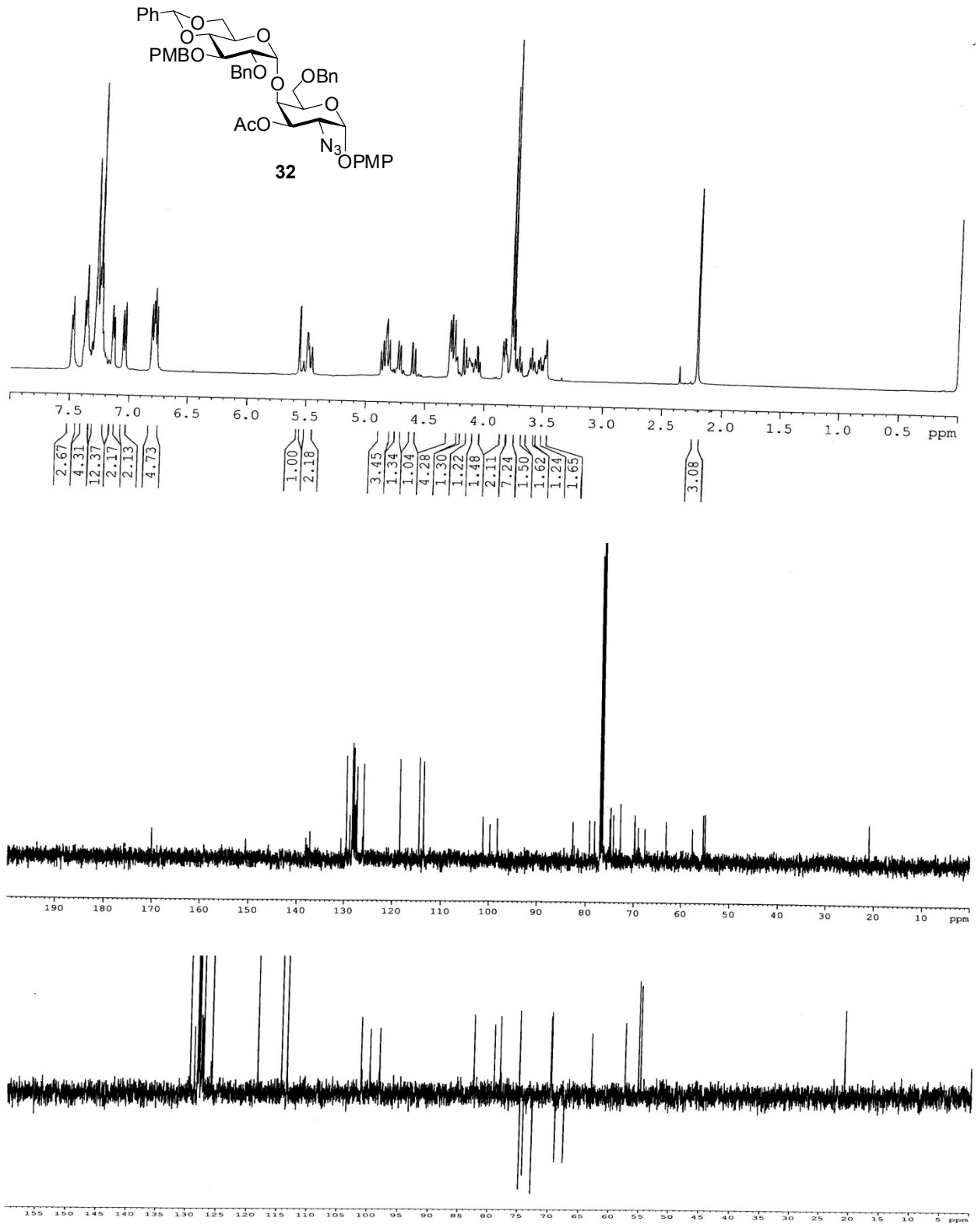
Compound 62: ^{1}H NMR (500 MHz $CDCl_3$): δ 7.79-6.79 (m, 19 H, Ar-H), 5.61 (s, 1 H, PhC*H*), 5.42 (d, *J* = 3.5 Hz, 1 H, H-1_A), 4.98 (t, *J* = 9.5 Hz, 1 H, H-4_A), 4.96-4.88 (m, 2 H, 2 PhC*H*), 4.56 (br s, 1 H, H-1_B), 4.33 (dd, *J* = 10.0 Hz, 4.5 Hz, 1 H, H-6_{aB}), 4.24 (d, *J* = 2.5 Hz, 1 H, H-2_B), 4.21-4.15 (m, 2 H, H-3_A, H-6_{aA}), 4.11-4.03 (m, 2 H, H-5_A, H-6_{bA}), 3.81 (t, *J* = 10.5 Hz, 1 H, H-6_{bB}), 3.76 (s, 3 H, OMe), 3.59 (dd, *J* = 10.0 Hz, 3.0 Hz, 1 H, H-3_B), 3.51 (dd, *J* = 10.0 Hz, 3.5 Hz, 1 H, H-2_A), 3.38-3.32 (m, 1 H, H-5_B), 2.02 (s, 6 H, 2 $COCH_3$), 0.12 (s, 3 H, CH_3), 0.10 (s, 3 H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.2 (*C*OCH_3), 168.7 (*C*OCH_3), 155.7-114.6 (Ar-C), 102.2 ($J_{C1/H1}$ = 158 Hz; C-1_B), 101.6 (Ph*C*H), 97.2 (C-1_A), 78.8 (C-4_B), 77.9 (C-3_B), 77.7 (C-3_A), 72.5 (Ph*C*H_2), 71.4 (C-2_B), 68.8 (C-5_A), 68.7 (C-6_B), 68.2 (C-4_A), 67.5 (C-5_B), 63.6 (C-2_A), 62.1 (C-6_A), 55.5 (OMe), 26.0 {3 C, (*C*H_3)$_3$}, 20.7 (CO*C*H_3), 20.6 (CO*C*H_3); ESI-MS: 922.3 $[M+Na]^+$; Anal. Calcd. for $C_{47}H_{57}N_3O_{13}Si$ (900.07): C, 62.72; H, 6.38; found: C, 62.60; H, 6.50.

Compound 63: ^{1}H NMR (500 MHz $CDCl_3$): δ 7.81-6.78 (m, 26 H, Ar-H), 5.62 (s, 1 H, PhC*H*), 5.55 (s, 1 H, PhC*H*), 5.37 (br s, 1 H, H-1_A), 4.93 (br s, 2 H, 2 PhC*H*), 4.82 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.74 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.46 (br s, 1 H, H-1_B), 4.35 (br s, 1 H, H-2_A), 4.25 (t, *J* = 10.0 Hz, 1 H, H-4_A), 4.20-4.16 (m, 4 H, H-2_B, H-4_B, H-6_{aA}, H-6_{aB}), 3.91 (dd, *J* = 10.0 Hz, 5.0 Hz, 1 H, H-3_A), 3.75-3.73 (m, 5 H, H-6_{bB}, H-6_{bA}, OMe), 3.56 (d, *J* = 9.5 Hz, 1 H, H-3_B), 3.30-3.27 (m, 1 H, H-5_B), 1.01 (br s, 9 H, C(*C*H_3)$_3$), 0.27 (s, 3 H, CH_3), 0.23 (s, 3 H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.0-114.5 (Ar-C), 101.6 (Ph*C*H), 101.5 (Ph*C*H), 100.8 ($J_{C1/H1}$ = 160 Hz; C-1_B), 97.4 (C-1_A), 78.7 (C-4_B), 78.0 (C-4_A), 76.9 (C-3_B), 75.4 (C-2_A), 73.7 (C-3_A), 72.2 (Ph*C*H_2), 71.8 (C-2_B), 71.0 (Ph*C*H_2), 68.6 (C-6_A), 68.5 (C-6_B), 67.7 (C-5_B), 64.6 (C-5_A), 55.5 (OMe), 26.2 {3 C, C$(CH_3)_3$}; ESI-MS: 991.4 $[M+Na]^+$; Anal. Calcd. for $C_{57}H_{64}O_{12}Si$ (969.21): C, 70.64; H, 6.66; found: C, 74.50; H, 6.75.

Compound 64 (α/β = 1.6/1): ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75-6.77 (m, 72 H, Ar-H), 5.48 (br s, 1 H, H-$1_{B\alpha}$), 5.24-5.23 (m, 1.66 H, H-$1_{A\alpha}$, H-$1_{A\beta}$), 5.18-5.08 (m, 1.42 H), 4.94-4.60 (m, 13.4 H), 4.58-4.50 (m, 6.64 H, H-$1_{B\beta}$, PhC*H*), 4.49-4.20 (m, 4.93 H), 4.14-4.02 (m, 5.8 H), 4.00-3.88 (m, 4.52 H), 3.85-3.40 (m, 15.1 H), 1.21 (d, *J* = 6.5 Hz, 3.8 H), 1.16 (d, *J* = 6.5 Hz, 2.34 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.7-113.7 (Ar-C), 102.5 (C-$1_{B\beta}$), 99.0 (C-$1_{B\alpha}$), 97.9 (C-$1_{A\alpha}$), 97.1 (C-$1_{A\beta}$), 82.2, 80.0, 79.1, 77.1, 77.0, 76.2, 76.0, 75.9, 75.8, 75.7, 75.6, 75.5, 75.4, 74.0, 73.9, 73.8 (2C), 73.7, 73.6, 73.5, 72.2, 72.0, 71.1, 71.0, 70.8, 70.0, 67.2, 67.0, 55.8 (2C), 18.2 (2 C); ESI-MS: 1045.4 $[M+Na]^+$; Anal. Calcd. for $C_{65}H_{66}O_{11}$ (1023.21): C, 76.30; H, 6.50; found: C, 76.14; H, 6.66.

NMR spectra of synthesized compounds:

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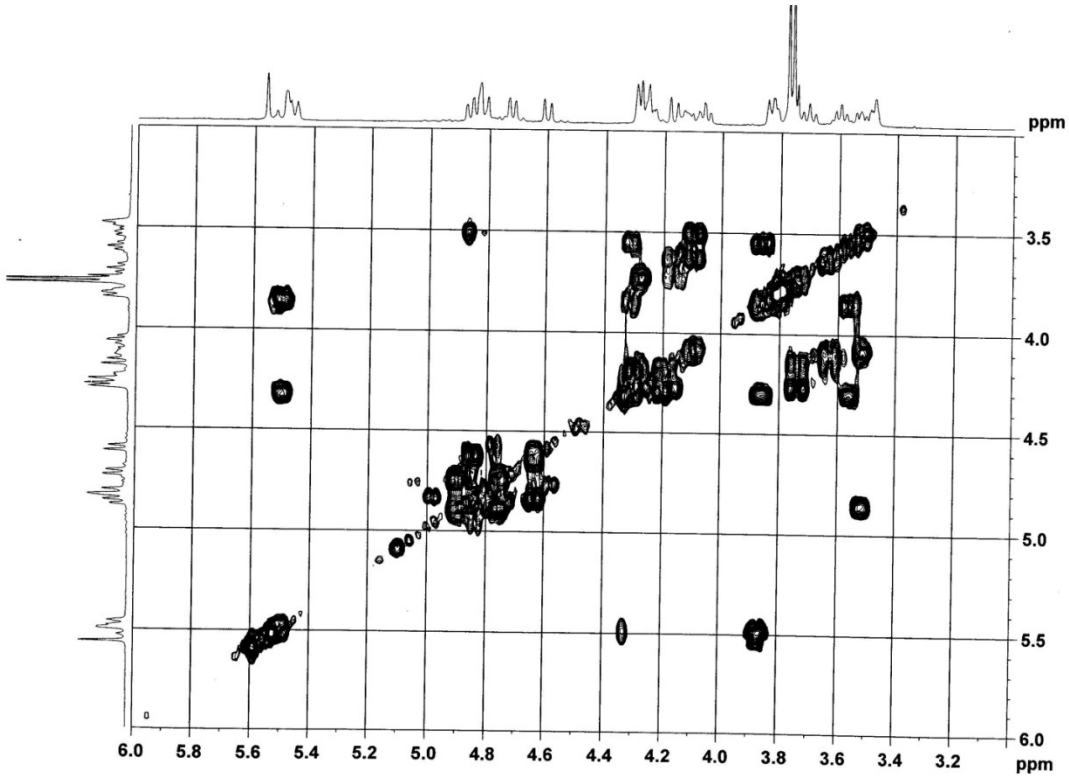
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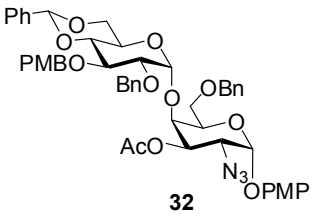
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N3
OPMP

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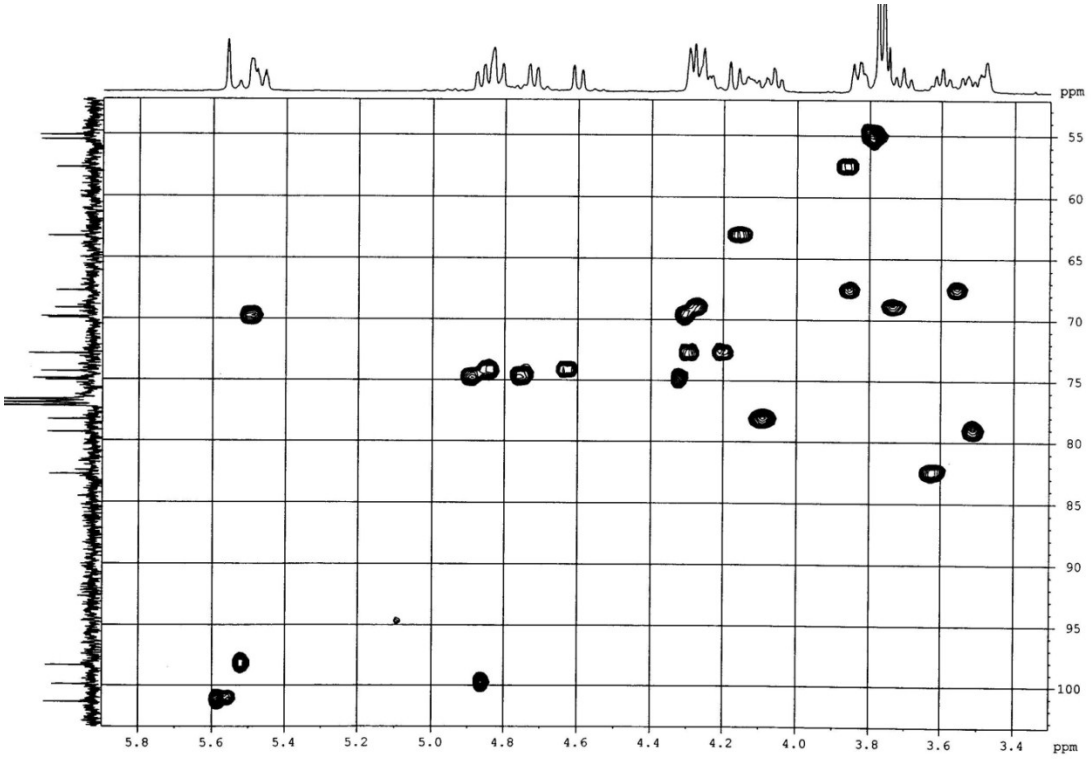
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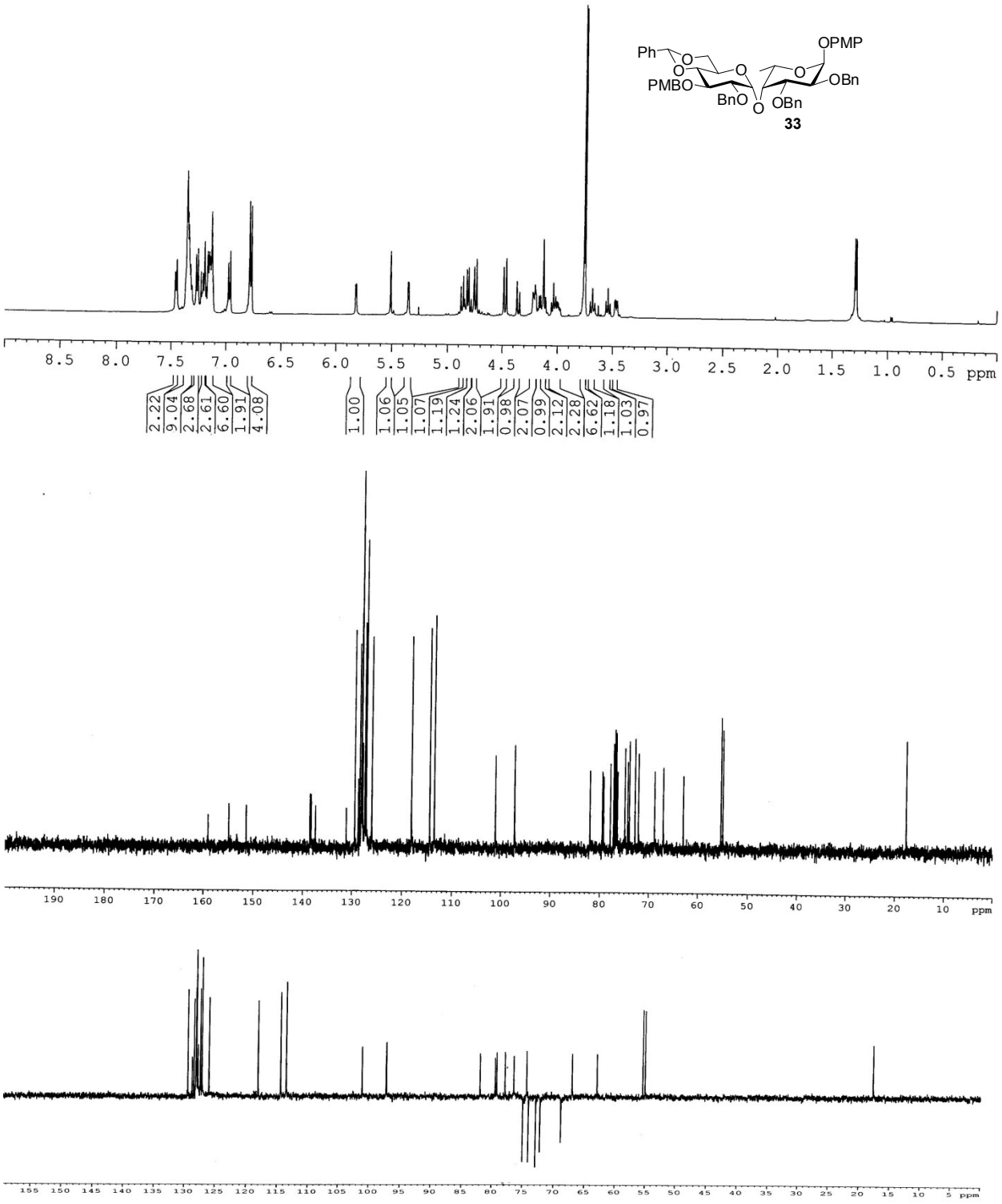
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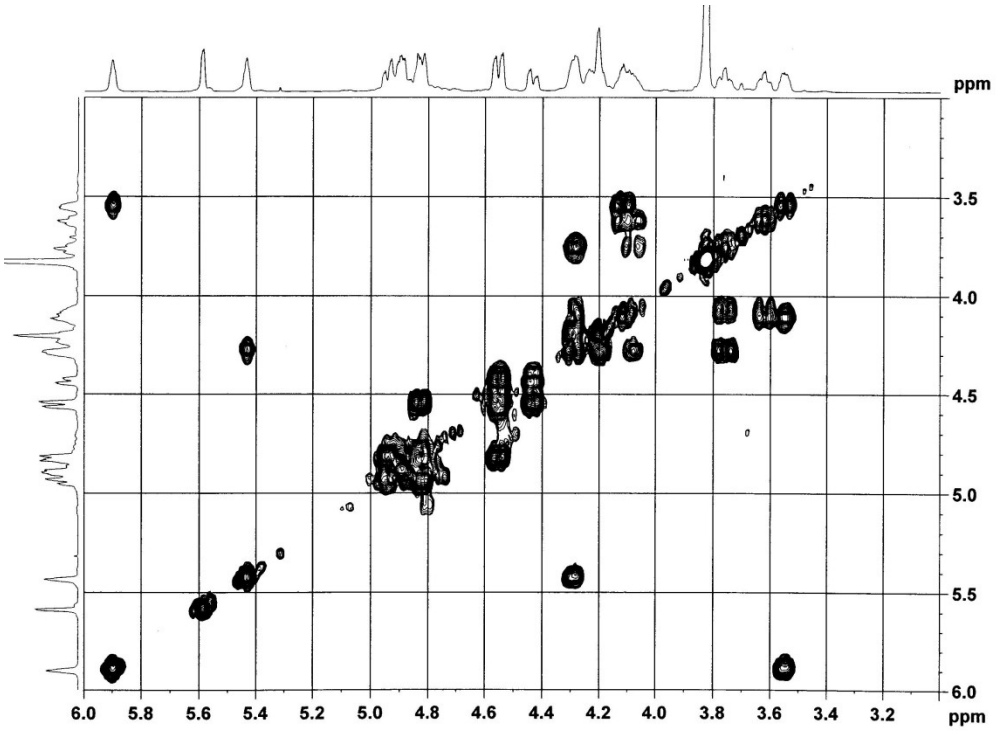
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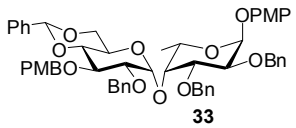
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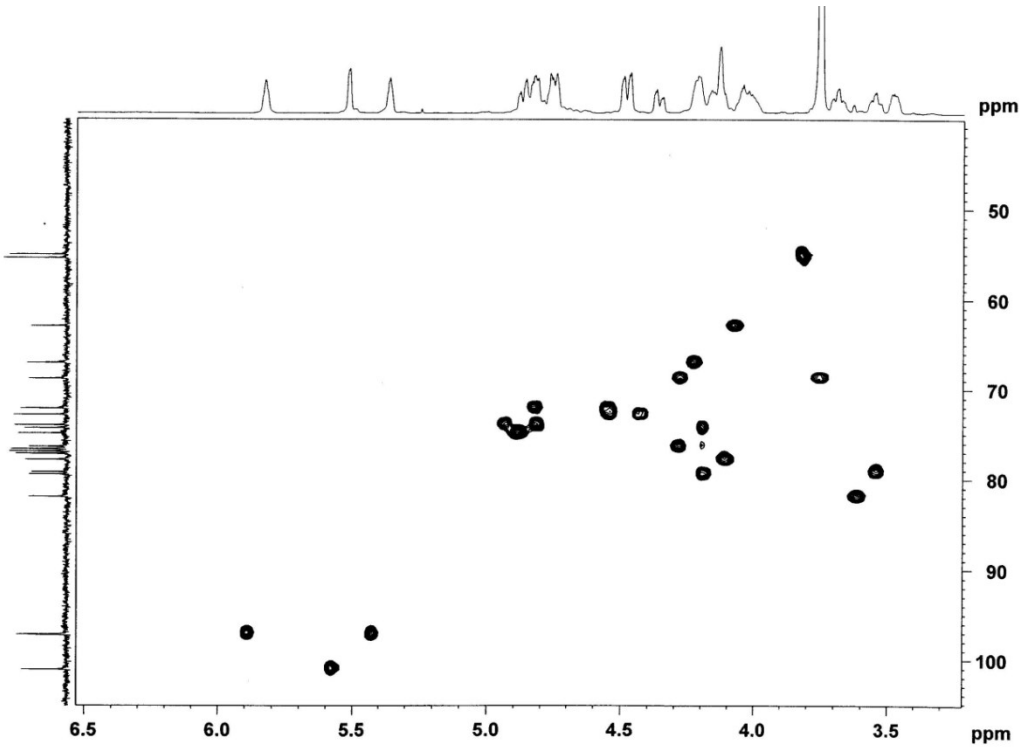
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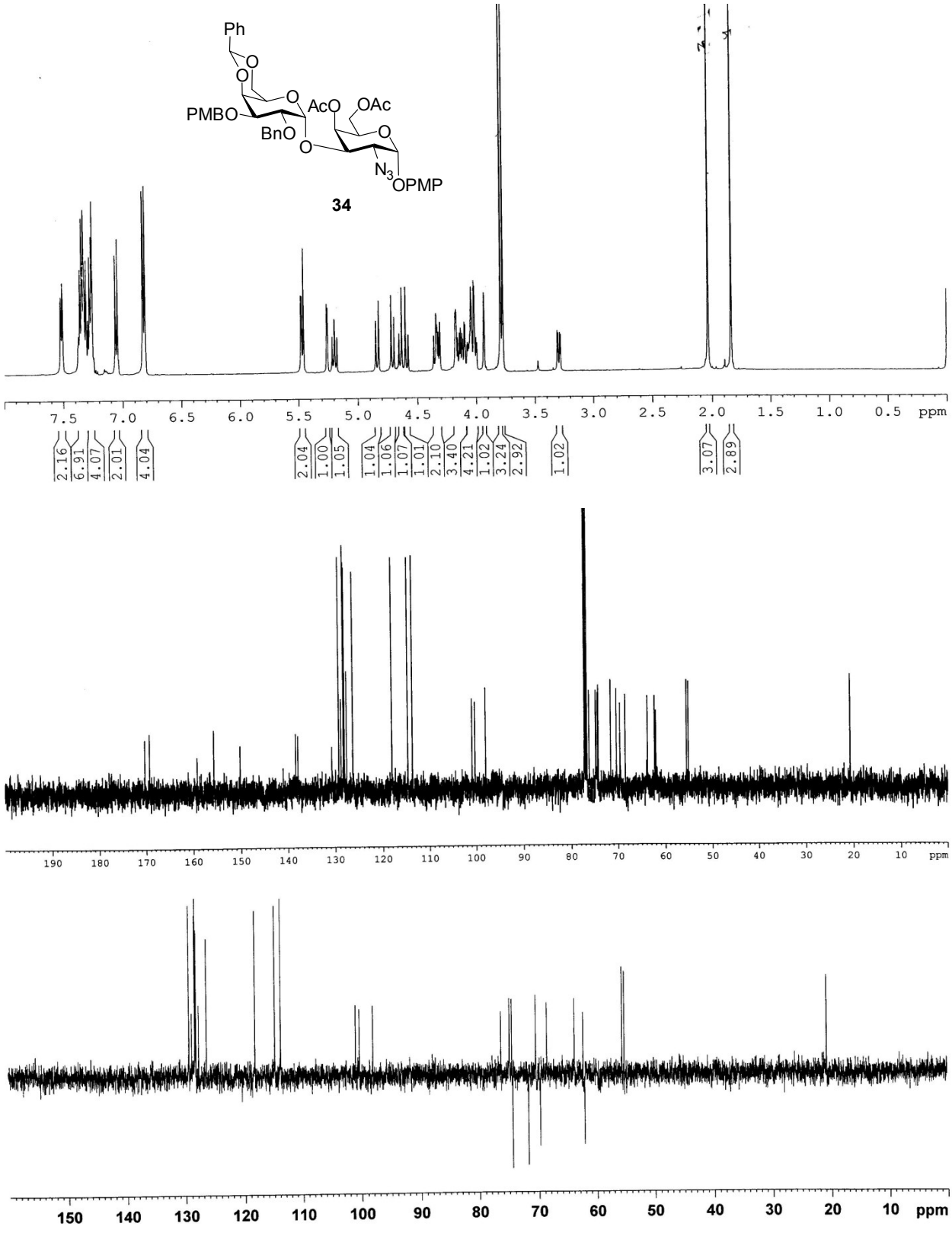
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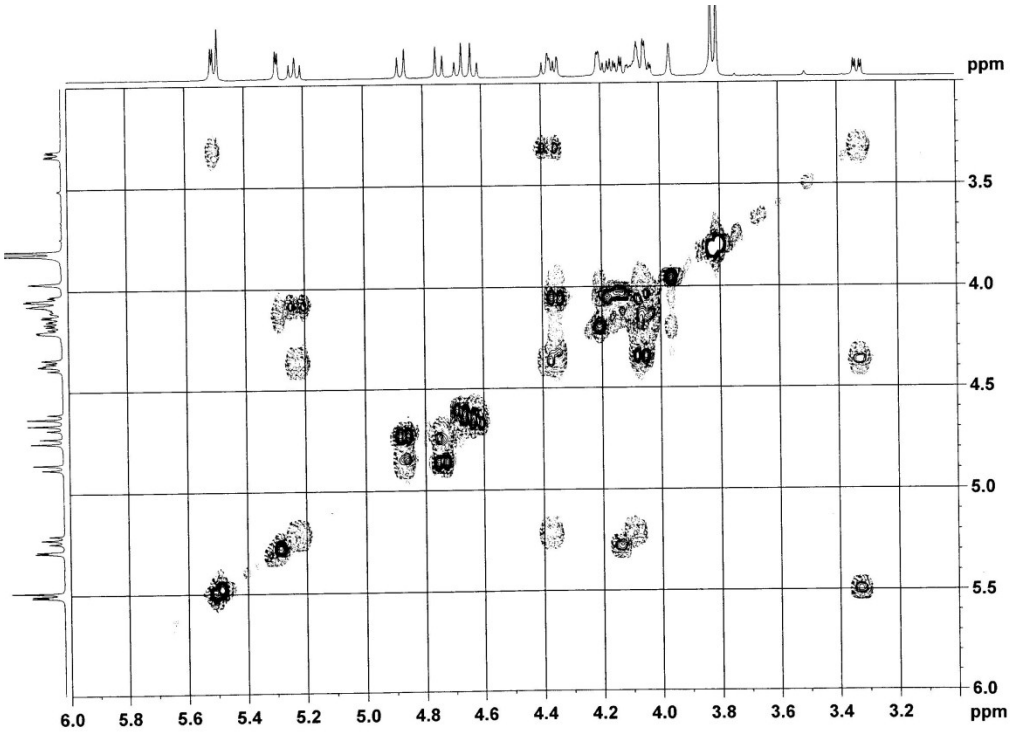
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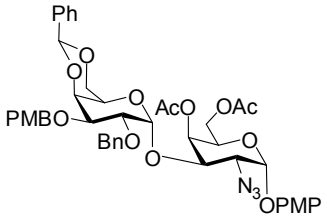
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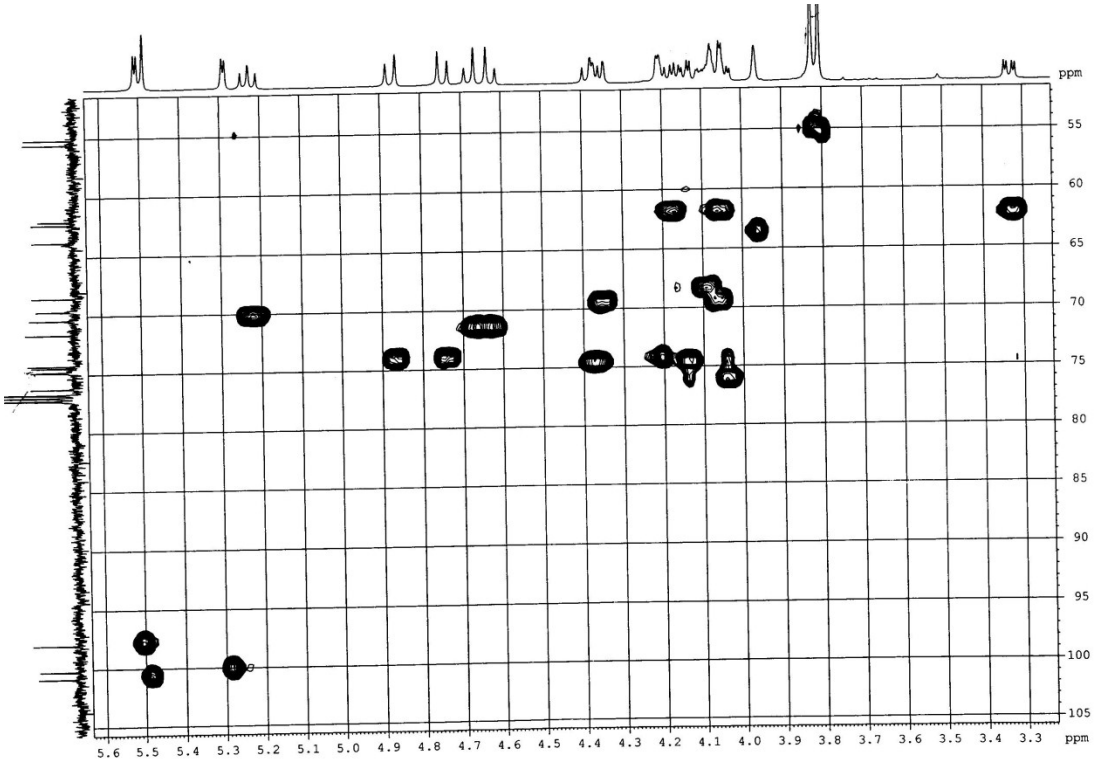
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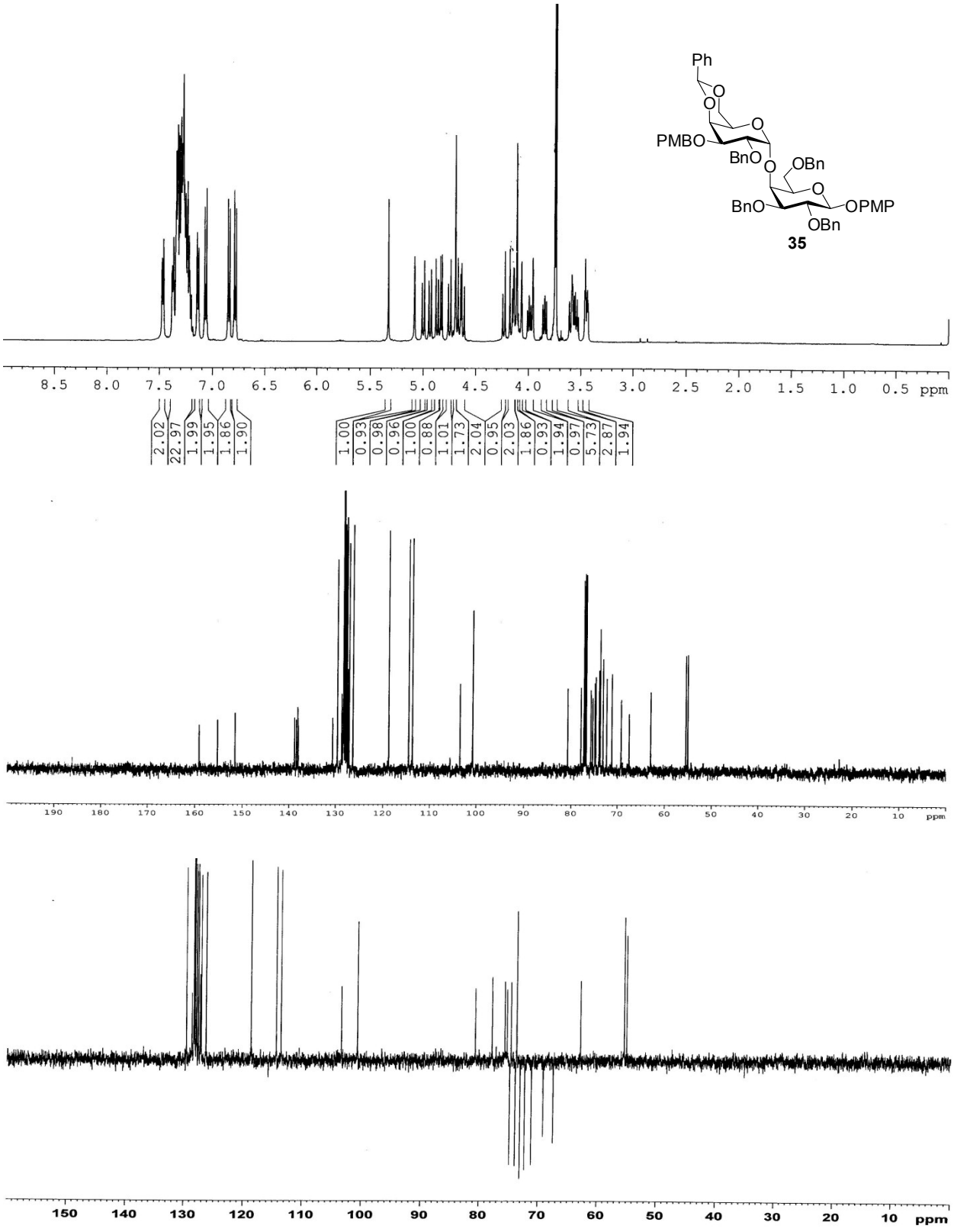
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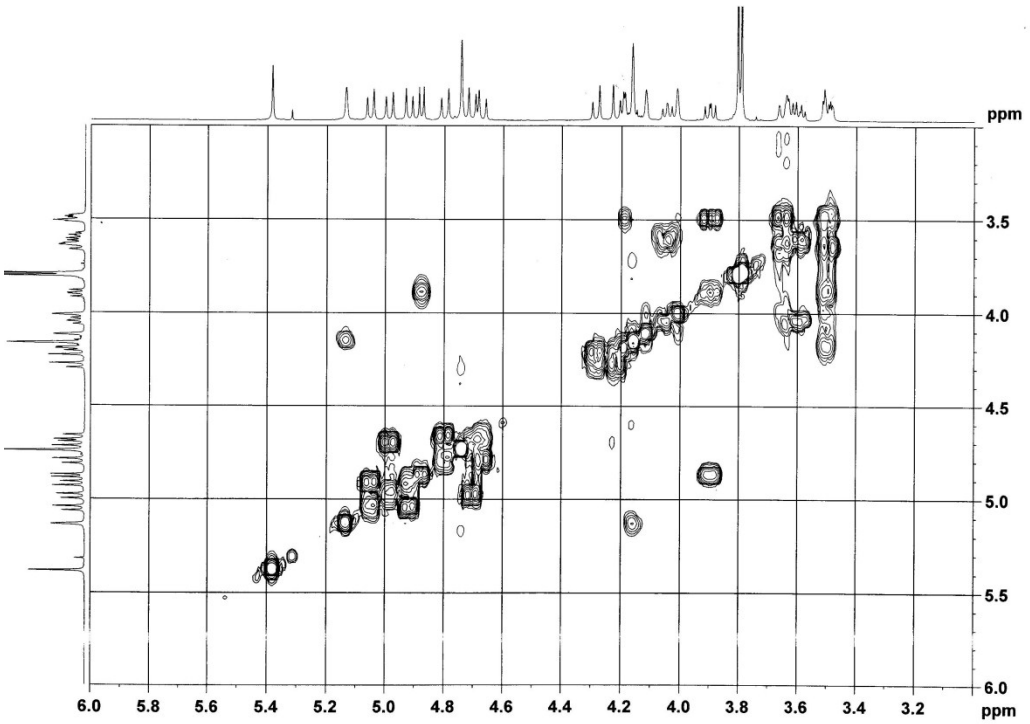
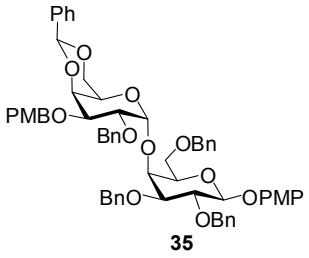
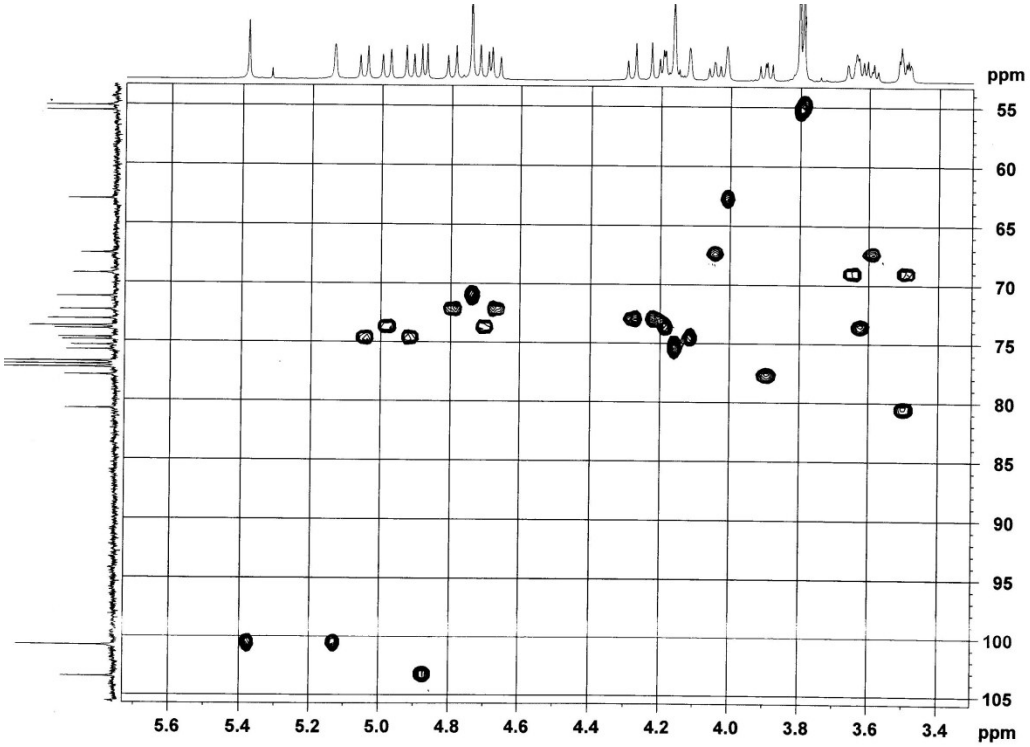
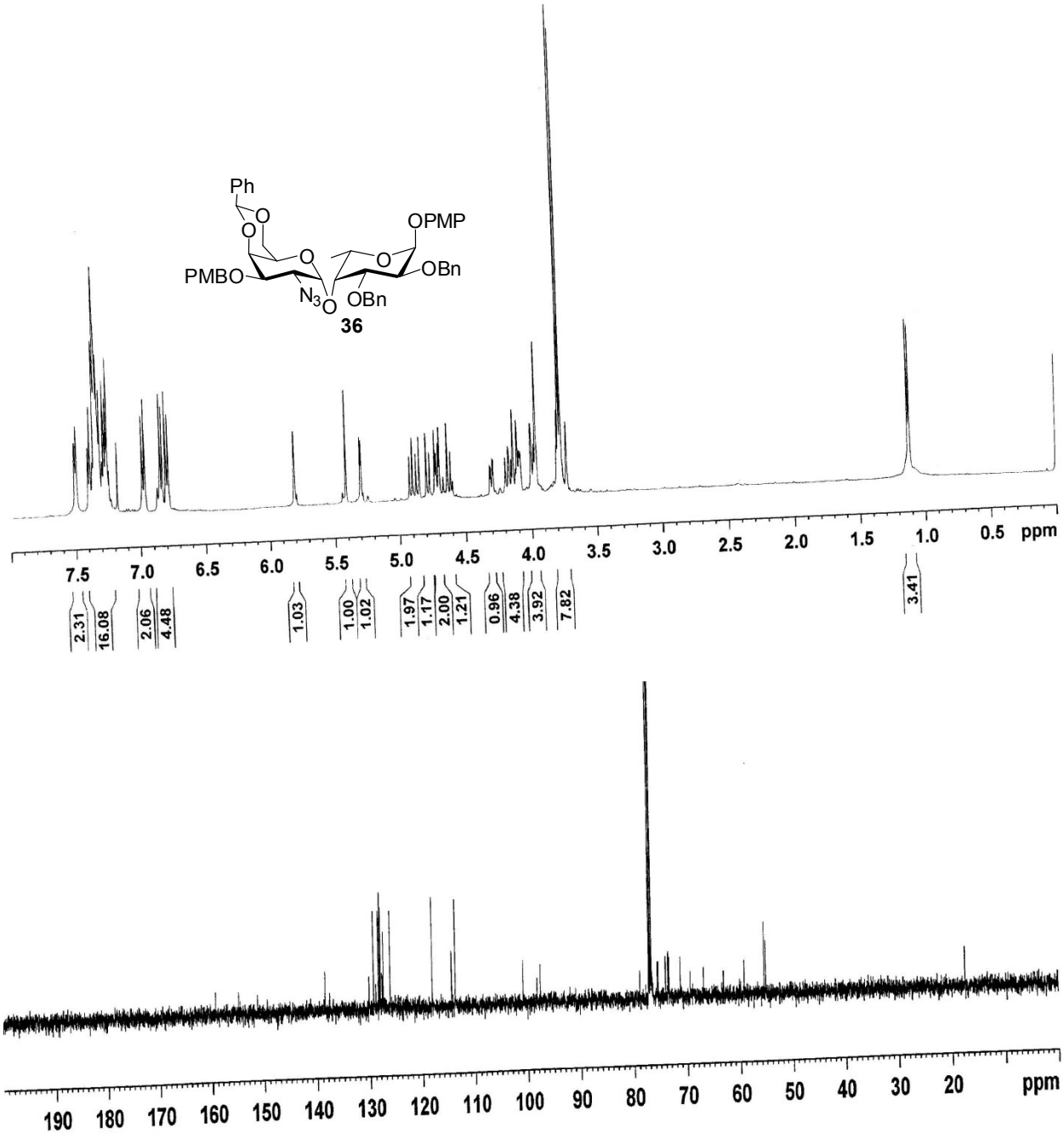
2.02 22.97 1.99 1.95 1.86 1.90
1.00 0.93 0.98 0.96 1.00 0.88 1.01 1.73 2.04 0.95 2.03 1.86 0.93 1.94 0.97 5.73 2.87 1.94
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

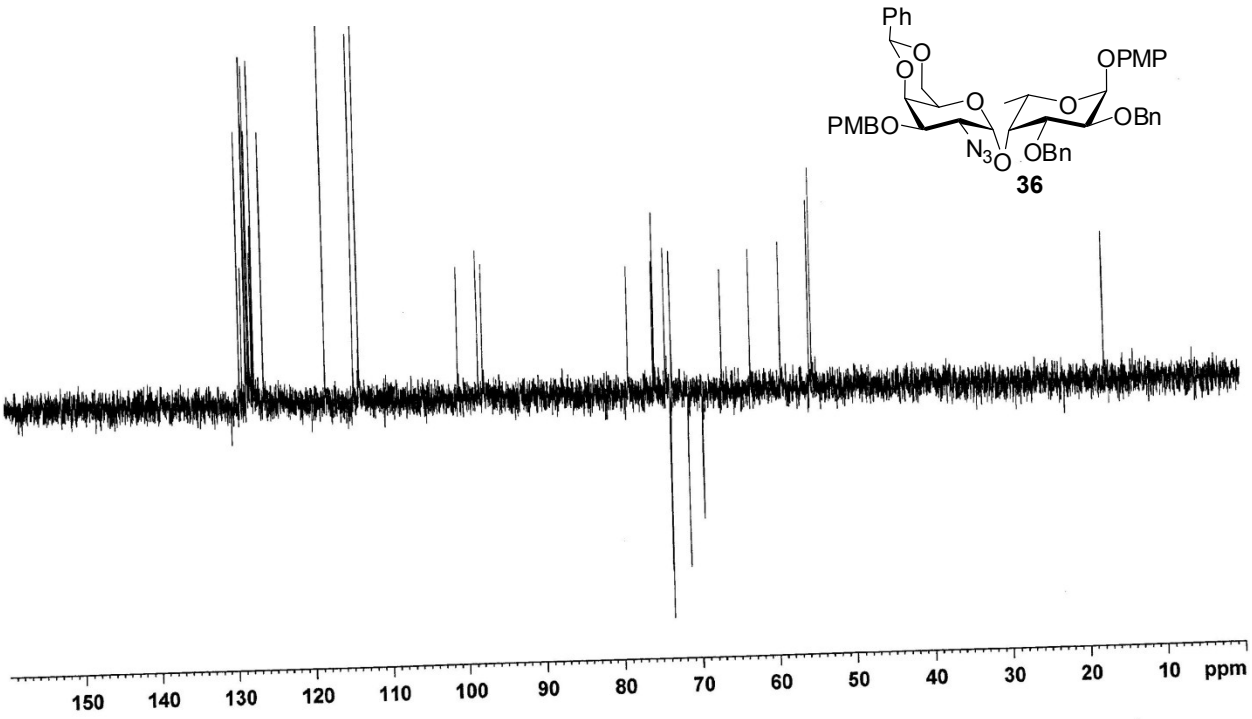

ppm
3.5
4.0
4.5
5.0
5.5
6.0
6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2
ppm

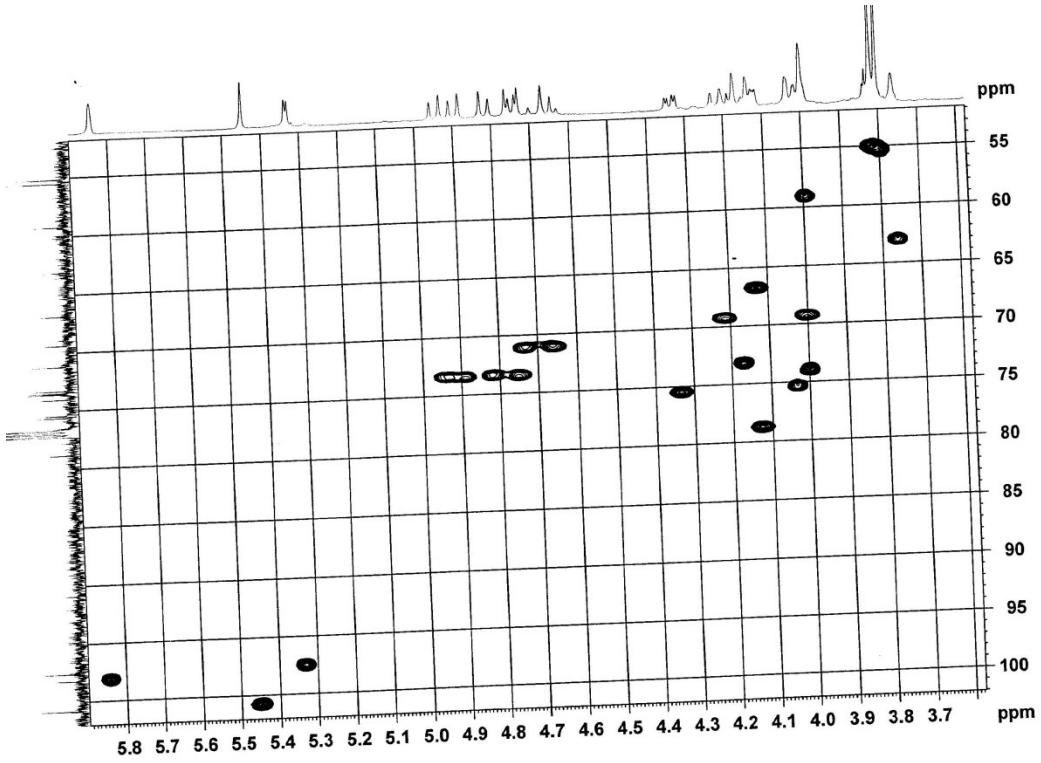

Ph
O
O
O
PMBO
BnO
O
OBn
O
BnO
OPMP
OBn

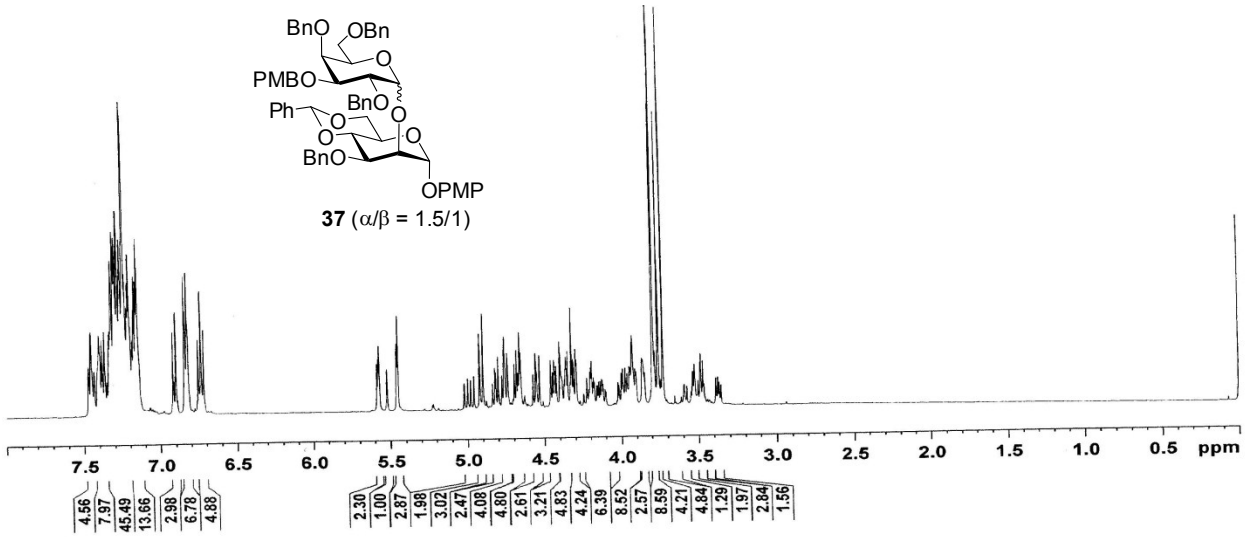
35


ppm
55
60
65
70
75
80
85
90
95
100
105
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

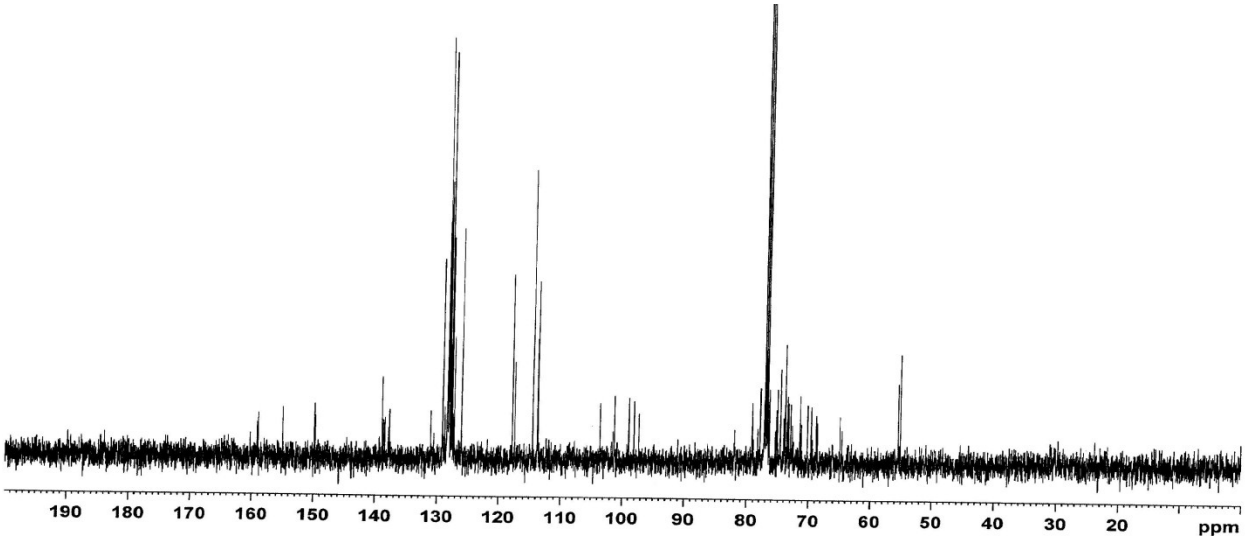

Ph
O
O
OPMP
O
O
PMBO
OBn
N3
O
OBn
36
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.31
16.08
2.06
4.48
1.03
1.00
1.02
1.97
1.17
2.00
1.21
0.96
4.38
3.92
7.82
3.41
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

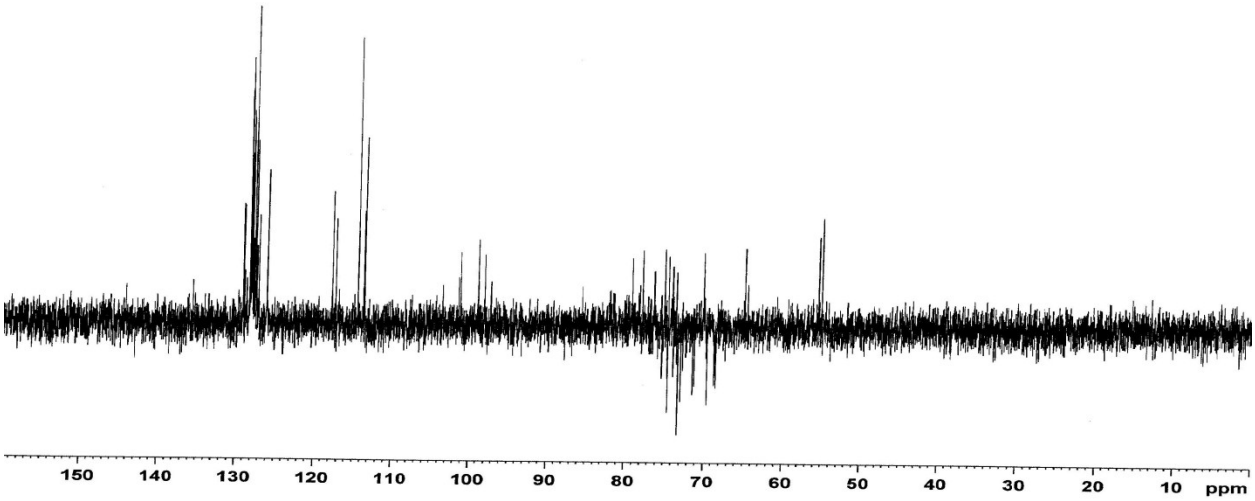

Ph
O
O
OPMP
O
O
PMBO
OBn
N3
O
OBn
36
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

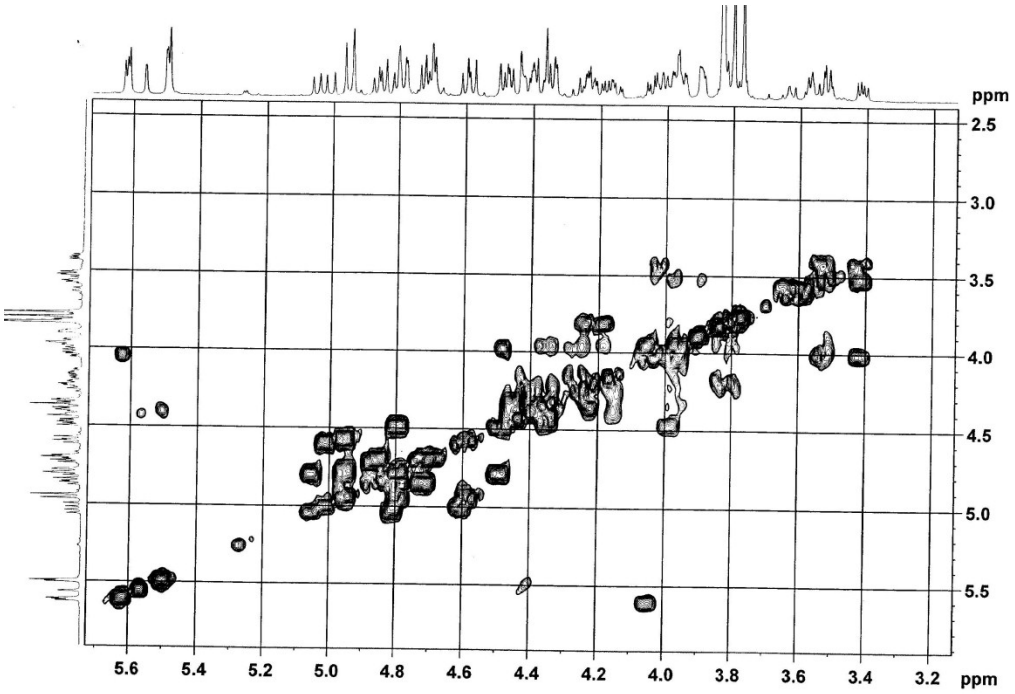

ppm
55
60
65
70
75
80
85
90
95
100
ppm
5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7

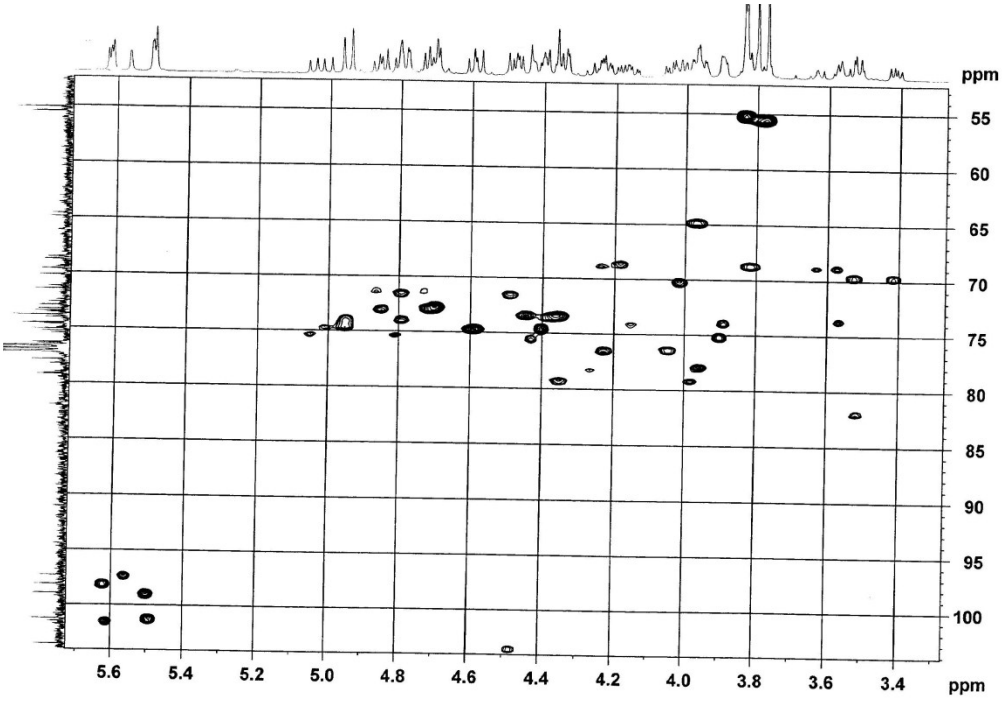


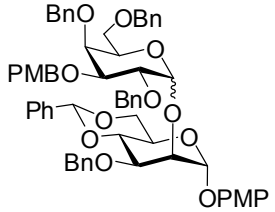
37 (α/β = 1.5/1)



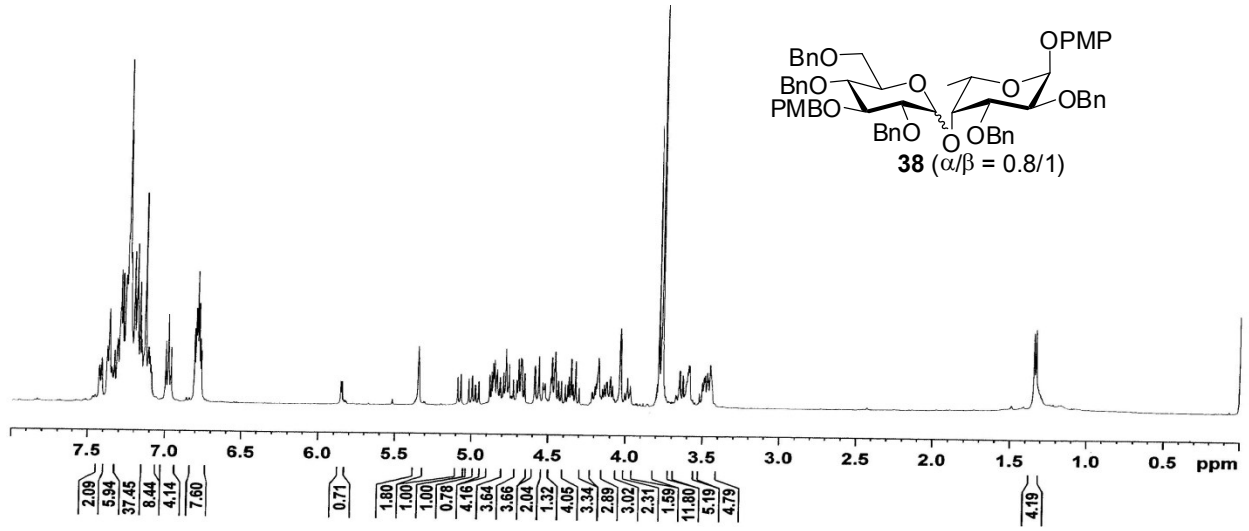




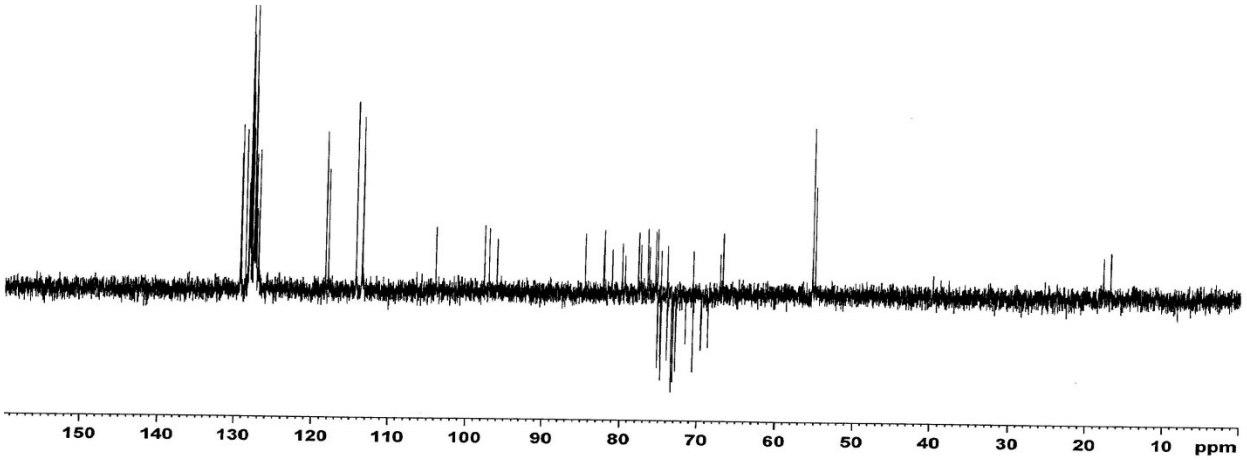


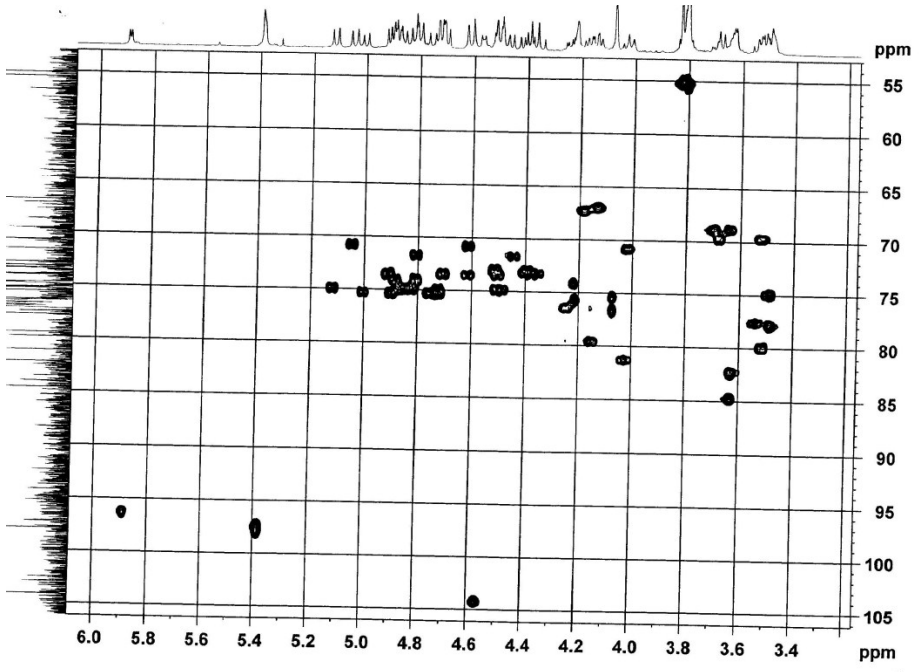


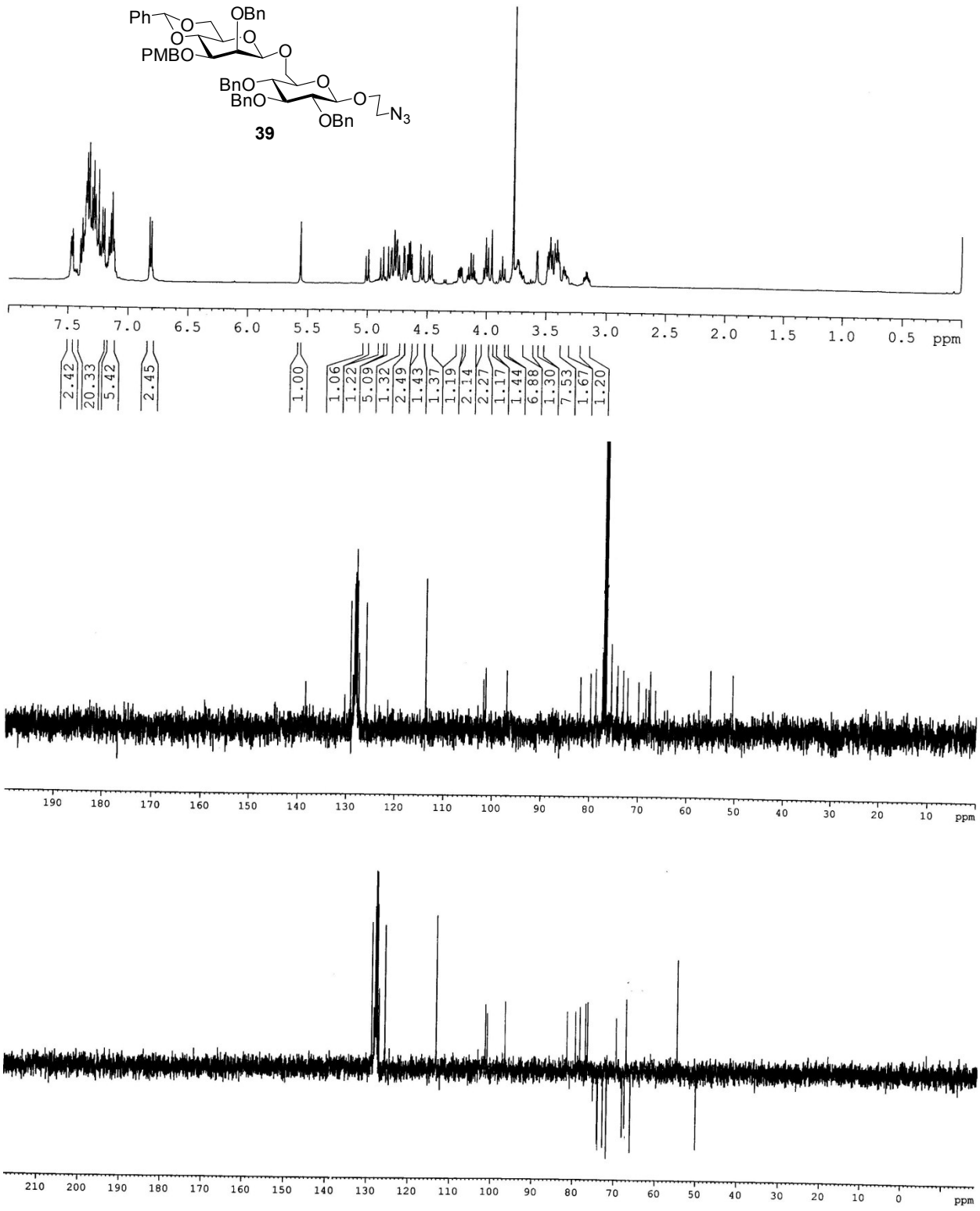
37 (α/β = 1.5/1)

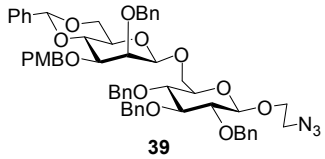


38 (α/β = 0.8/1)

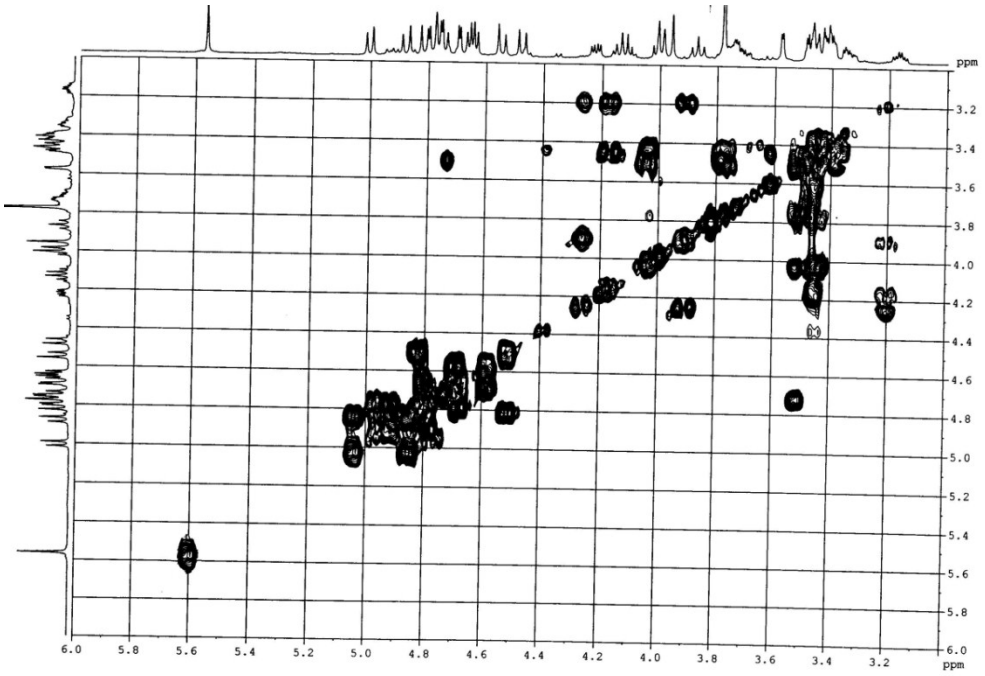


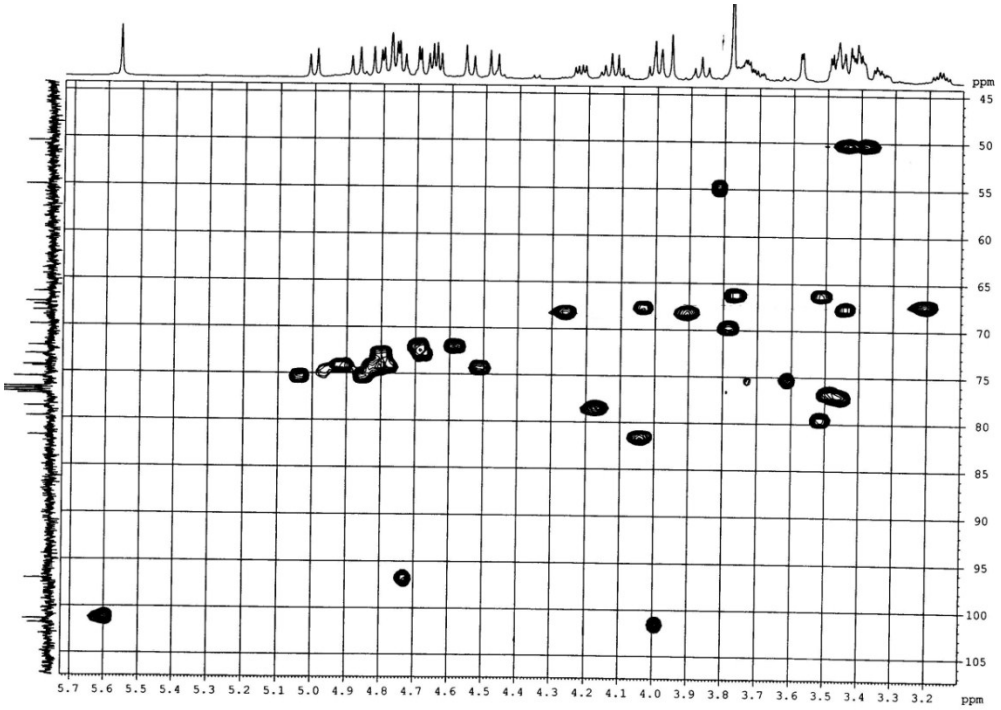


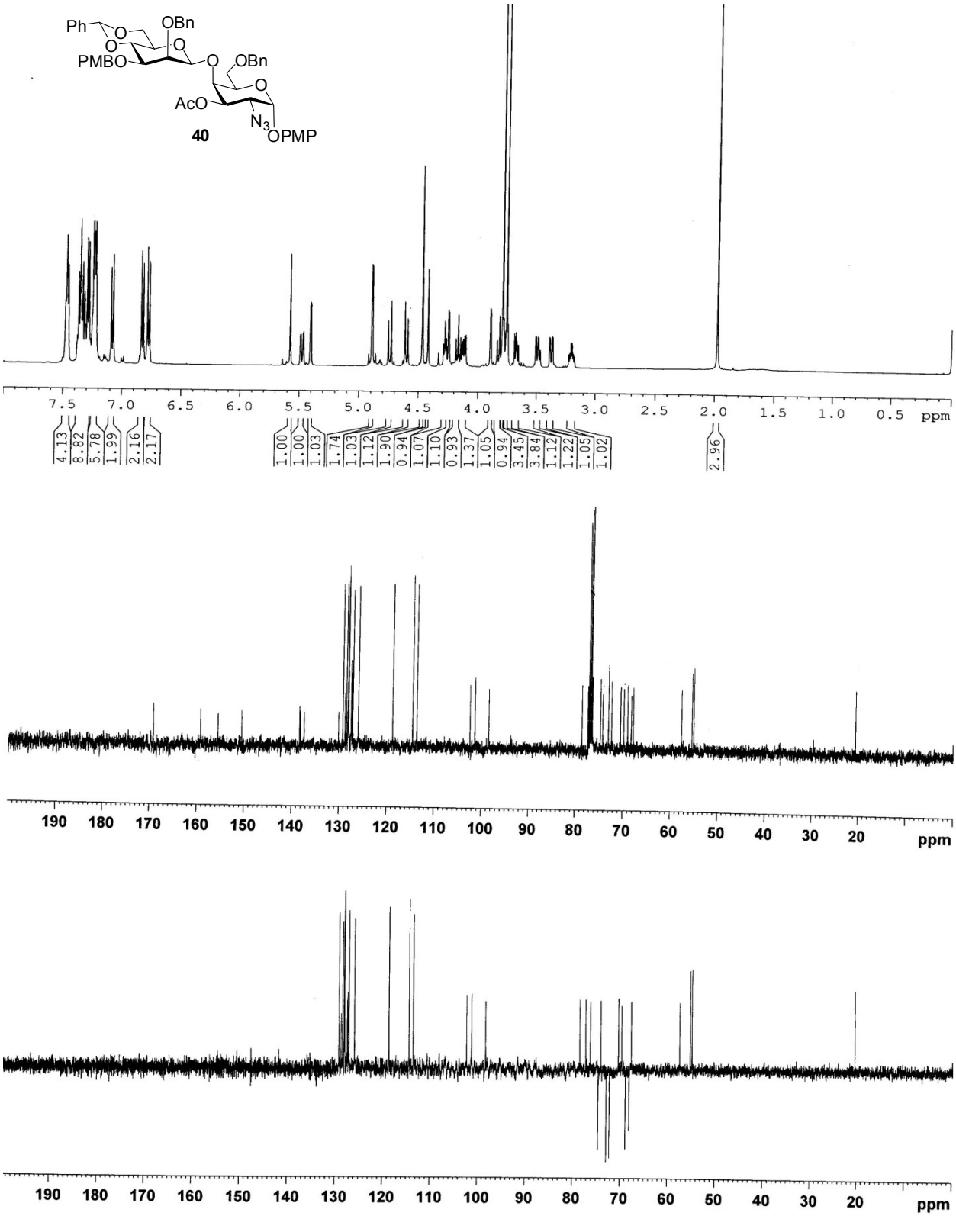

Ph
OBn
PMBO
BnO
BnO
OBn
N3
39
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.42 20.33 5.42 2.45 1.00 1.06 1.22 5.09 1.32 2.49 1.43 1.37 1.19 2.14 2.27 1.17 1.44 6.88 1.30 7.53 1.67 1.20
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

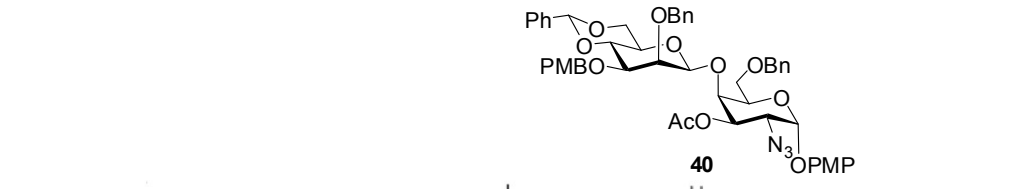

Ph
OBn
O
O
O
PMBO
O
BnO
O
BnO
O
N3
OBn

39

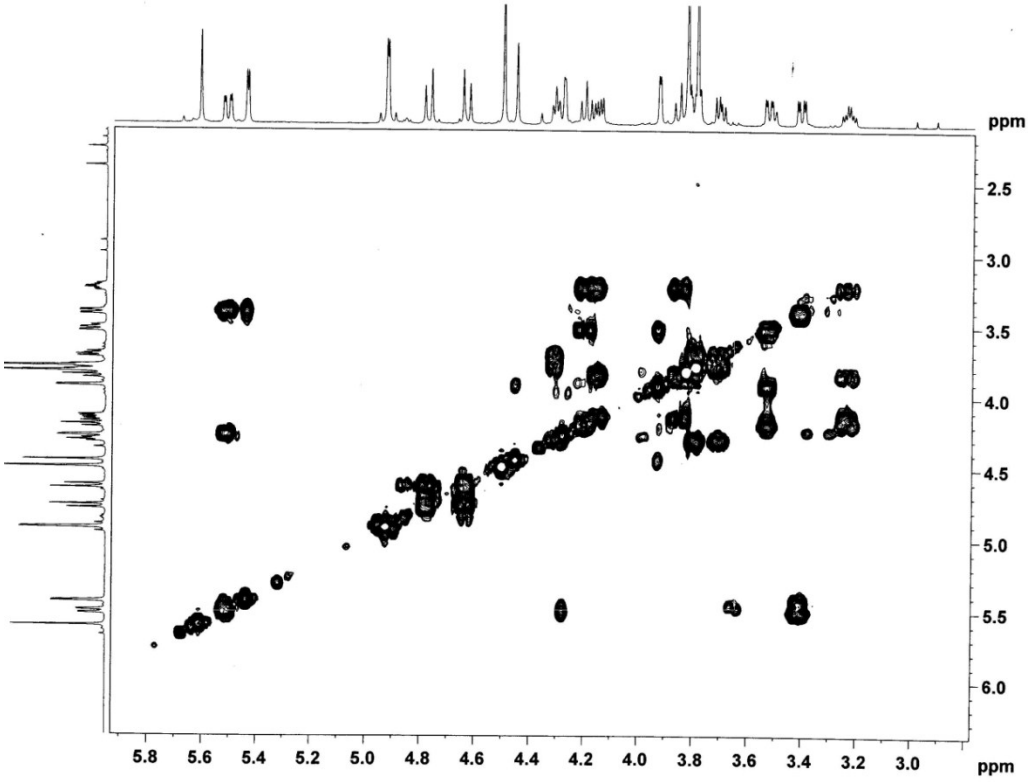

ppm
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2
ppm

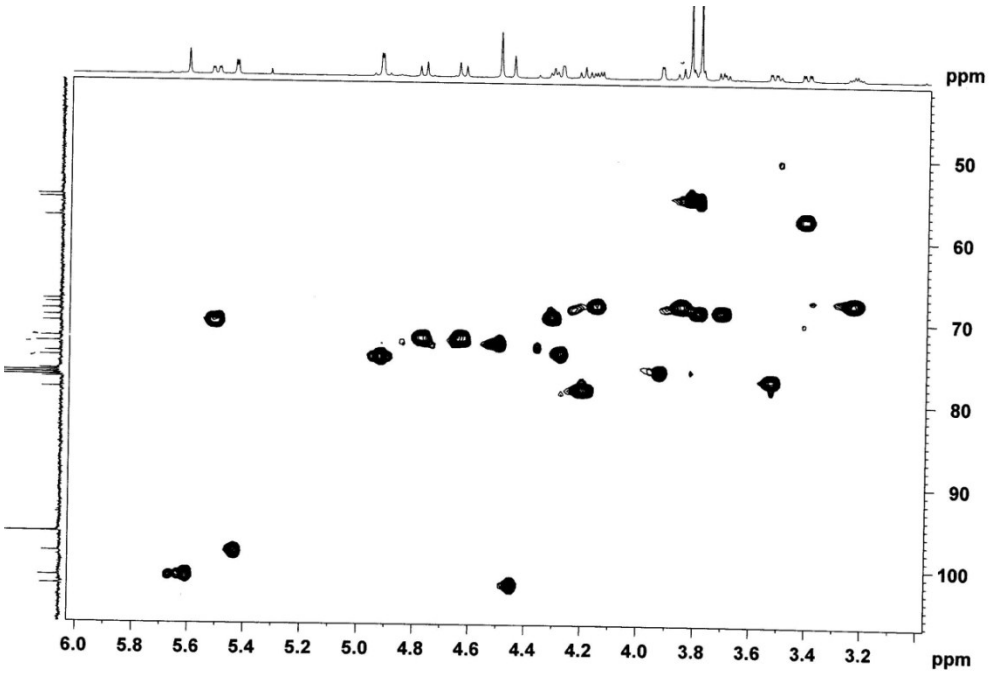

ppm
45
50
55
60
65
70
75
80
85
90
95
100
105
5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2
ppm

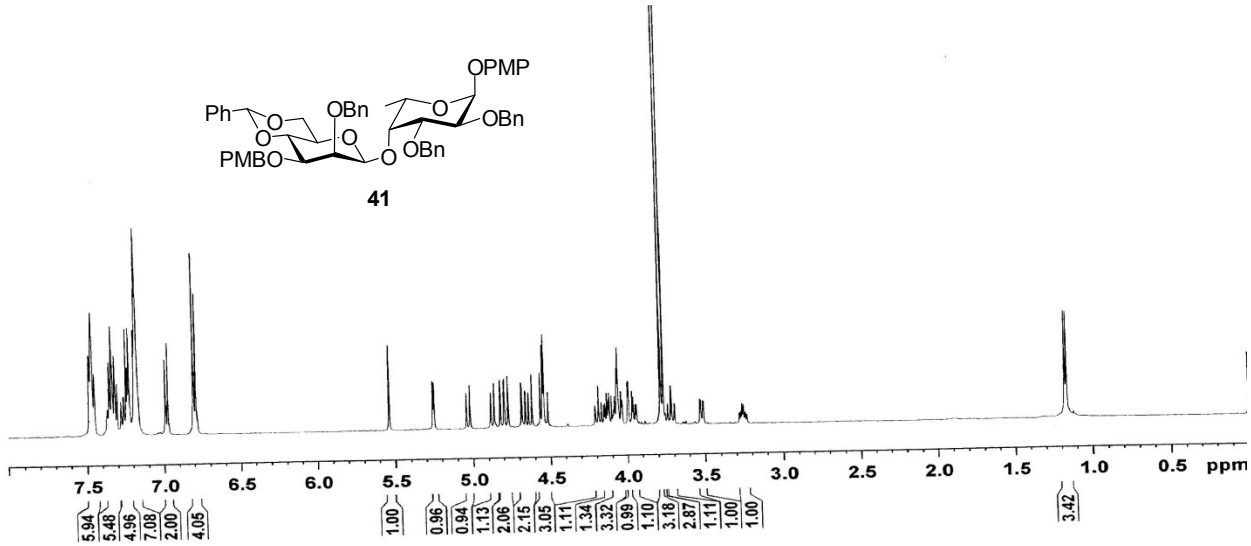

Ph
OBn
O
O
O
PMBO
O
OBn
O
AcO
N3
OPMP
40
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.13
8.82
5.78
1.99
2.16
2.17
1.00
1.00
1.03
1.74
1.03
1.12
1.90
0.94
1.07
1.10
0.93
1.37
1.05
0.94
3.45
3.84
1.12
1.22
1.05
1.02
2.96
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

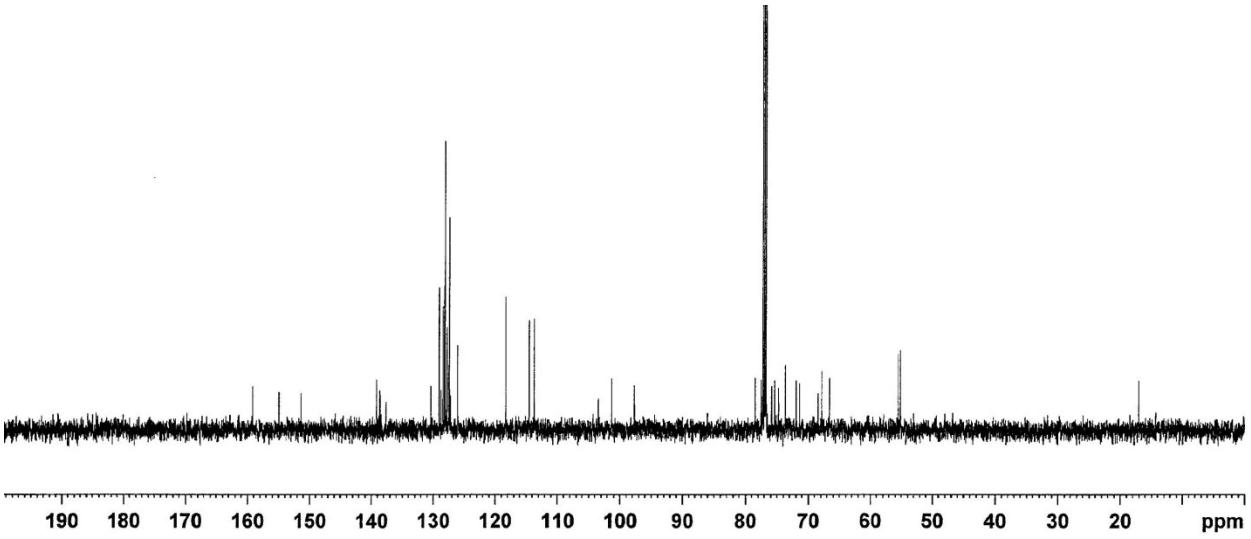

Ph
O
OBn
O
PMBO
O
OBn
O
AcO
N3
OPMP

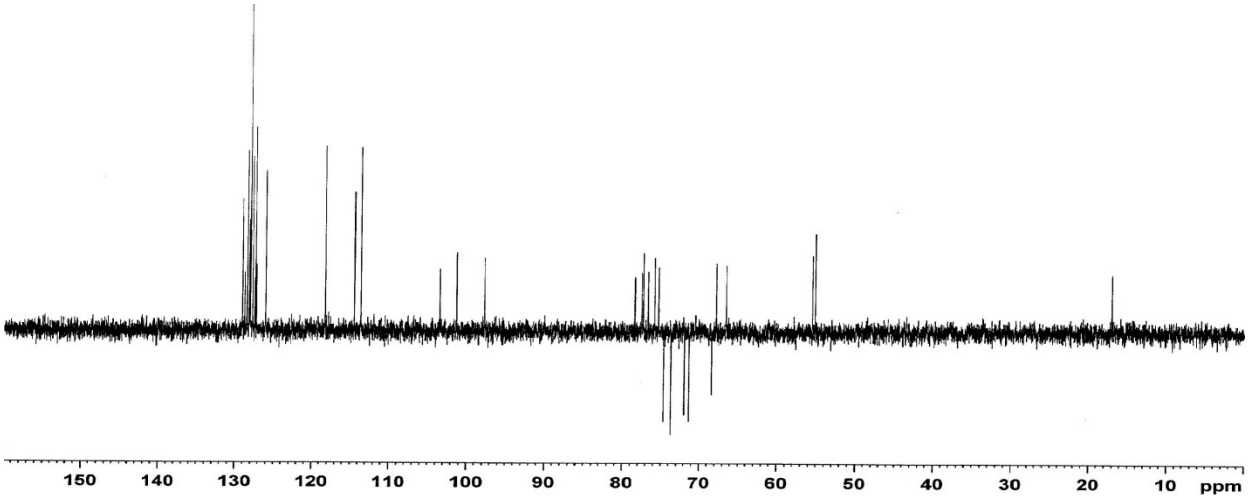
40

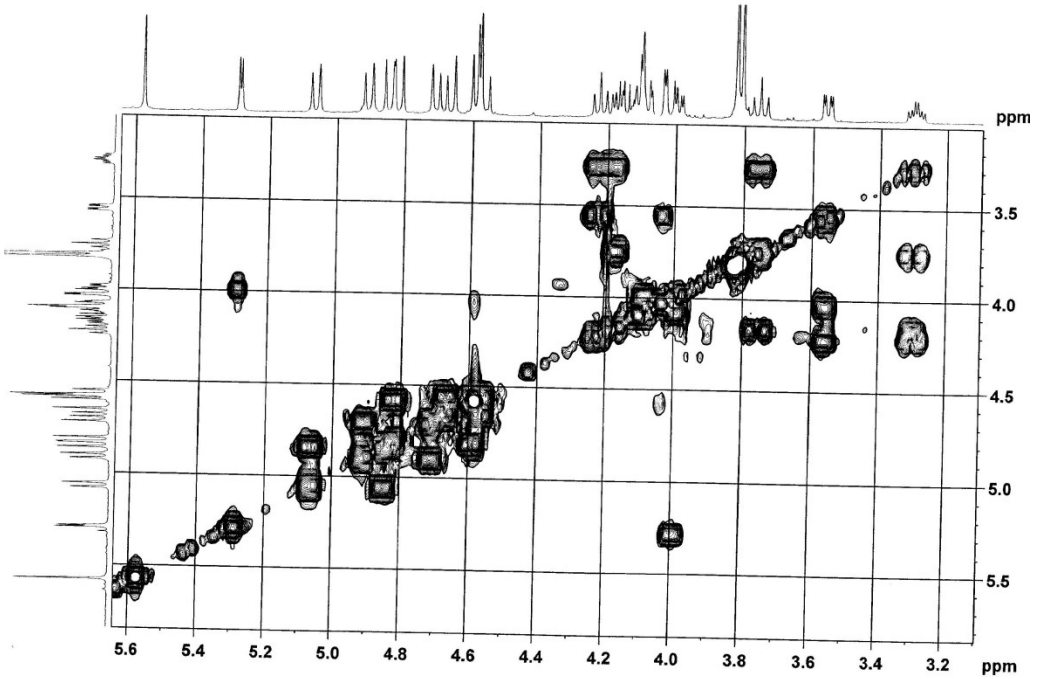

ppm
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0
ppm

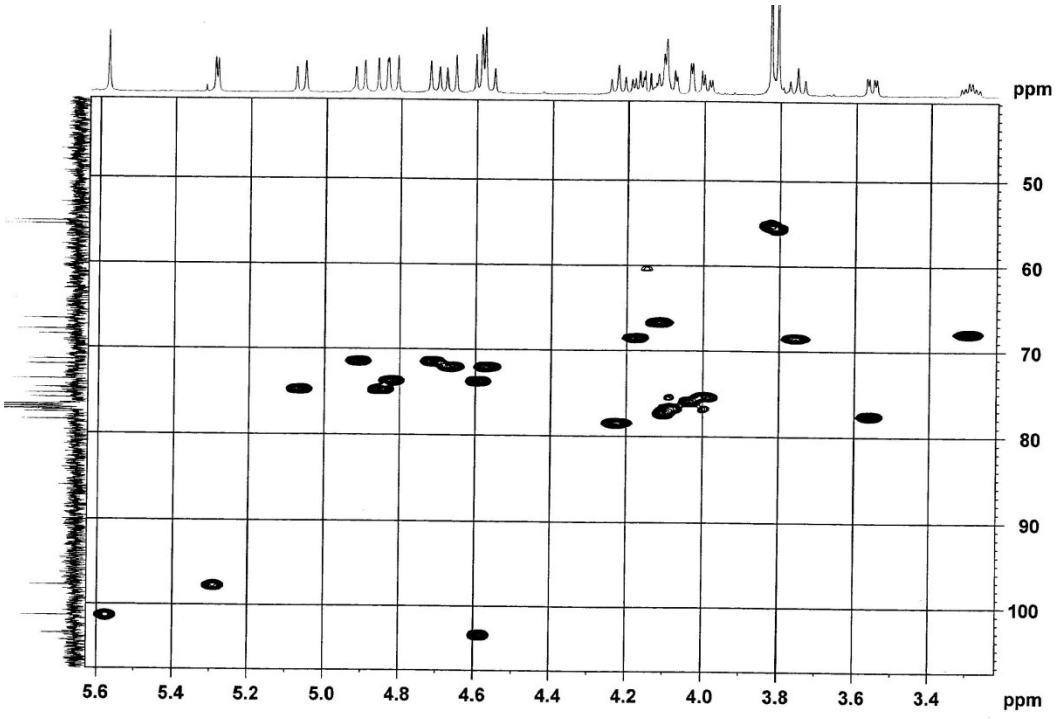

ppm
50
60
70
80
90
100
6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2
ppm

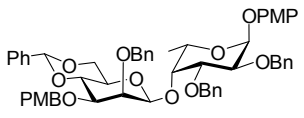

OPMP
Ph
OBn
O
O
O
O
OBn
PMBO
O
OBn
41
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
5.94
5.48
4.96
7.08
2.00
4.05
1.00
0.96
0.94
1.13
2.06
2.15
3.05
1.11
1.34
3.32
0.99
1.10
3.18
2.87
1.11
1.00
1.00
3.42


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

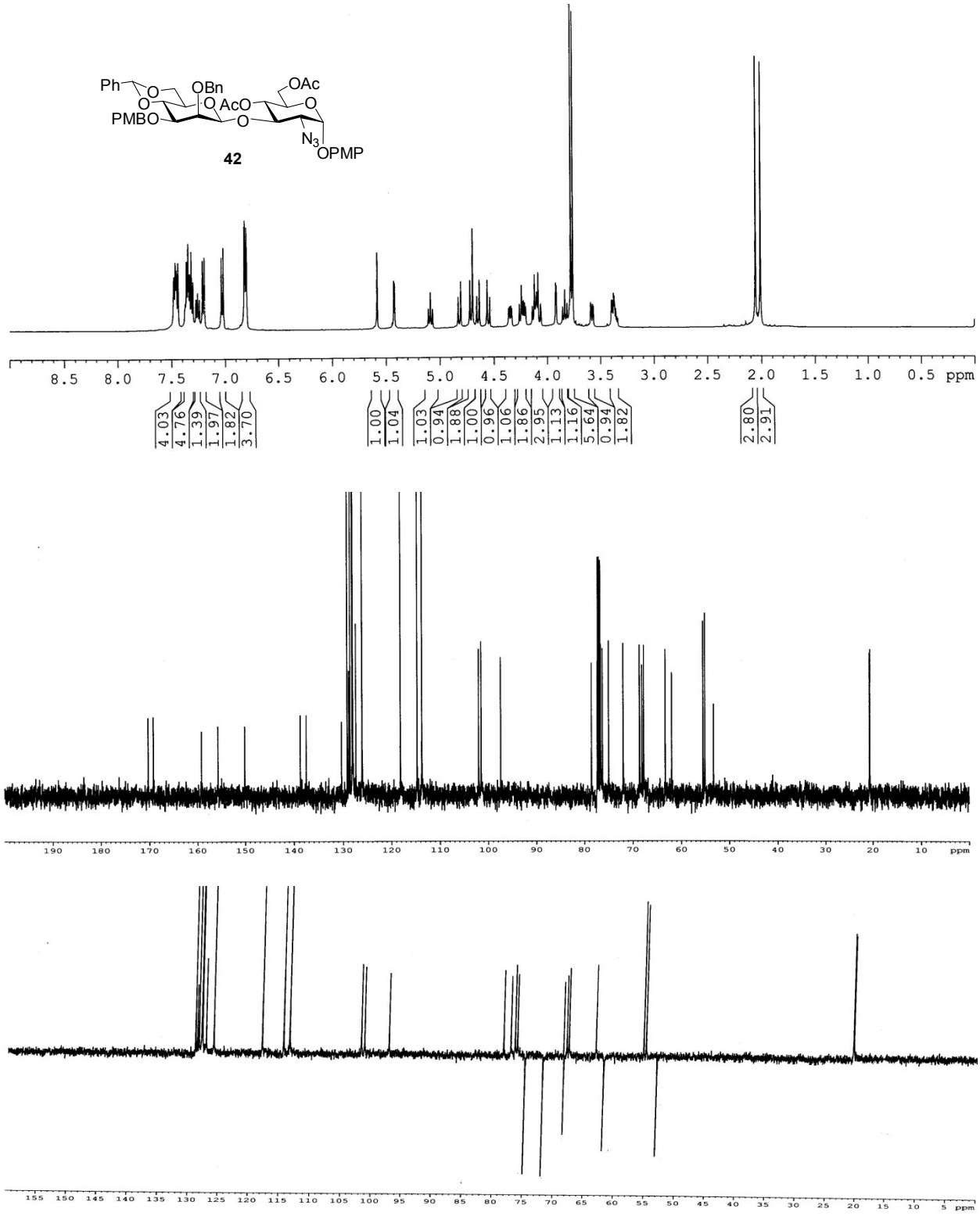

150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

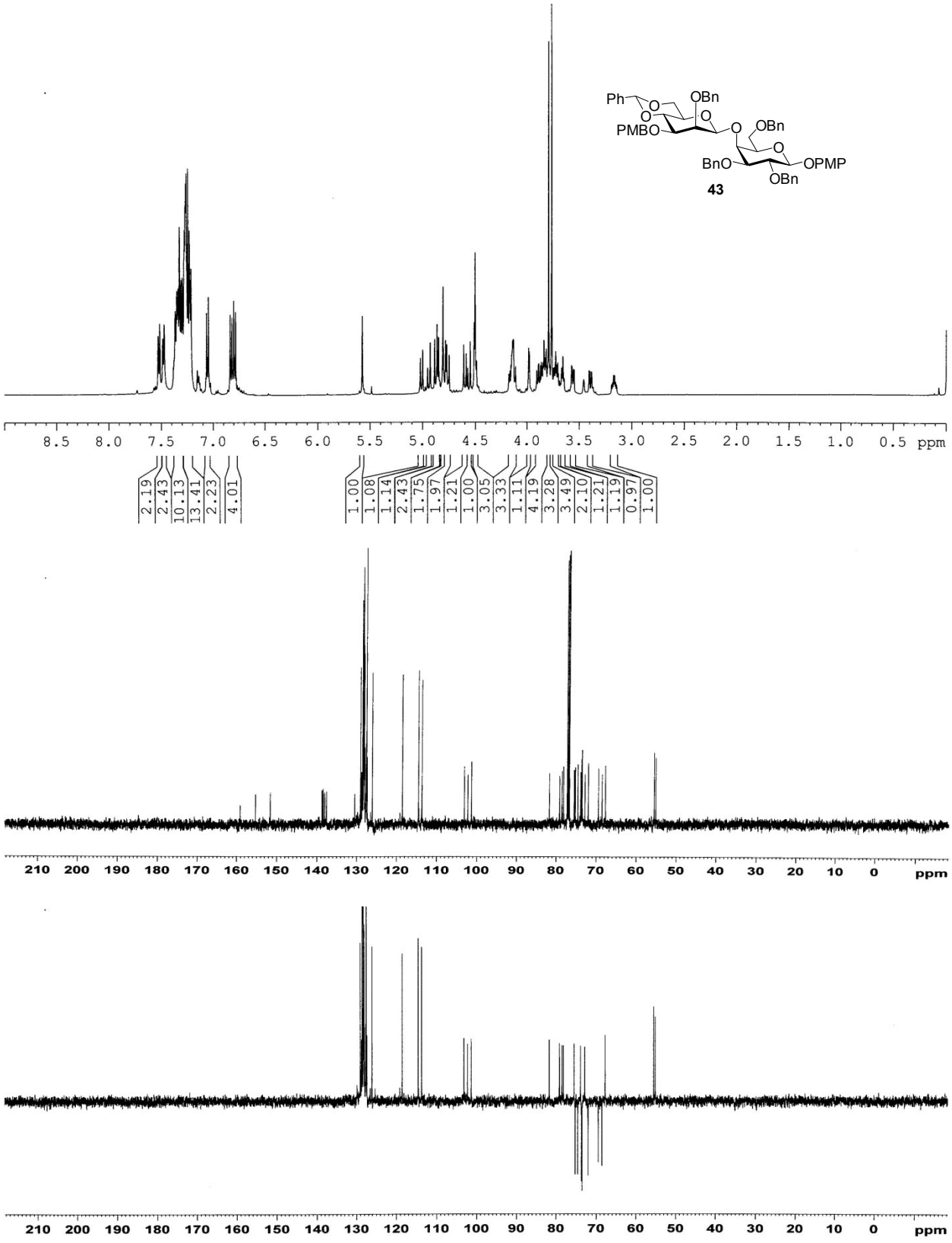

ppm
3.5
4.0
4.5
5.0
5.5
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
ppm

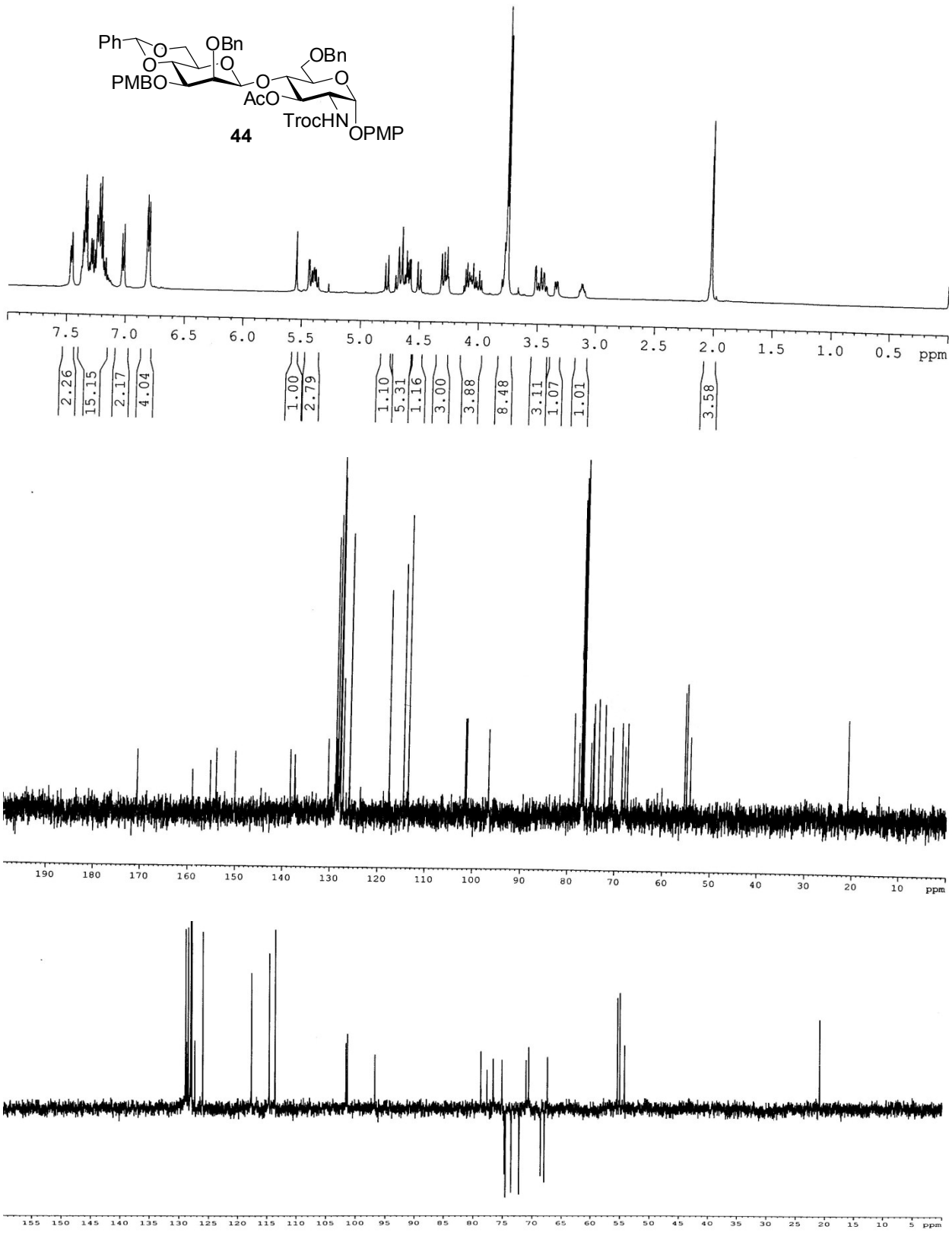

ppm
50
60
70
80
90
100
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
ppm

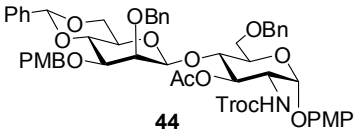

OPMP
Ph
OBn
OBn
PMBO
OBn

41

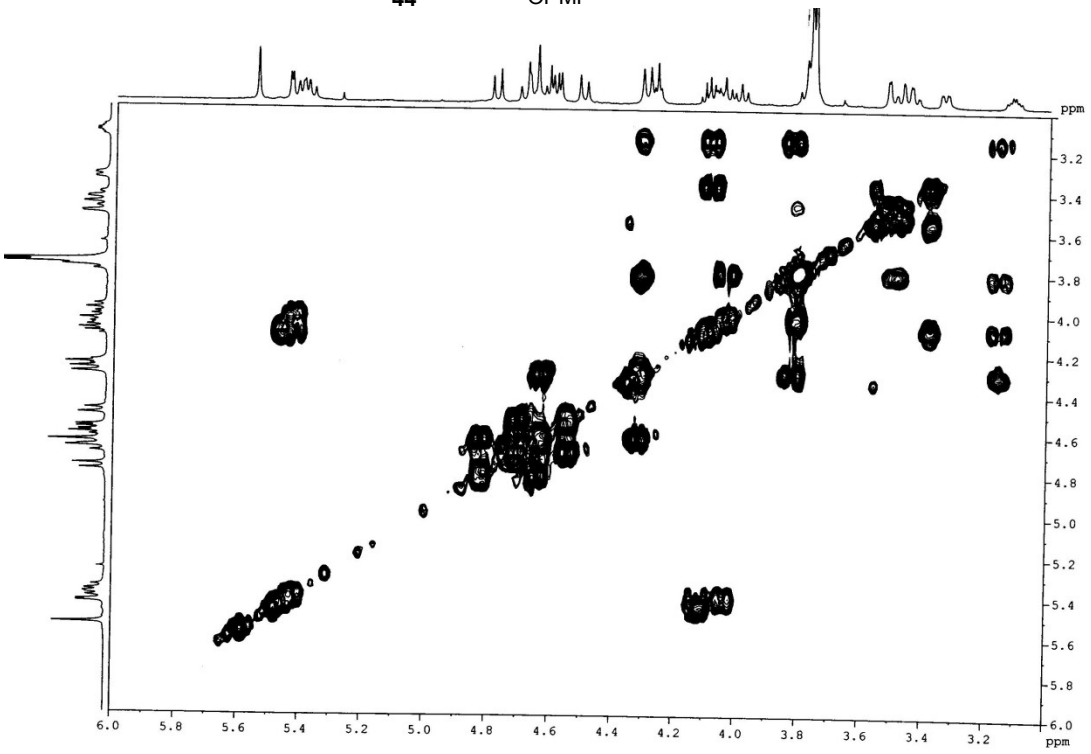

Ph
O
OBn
OAc
O
O
AcO
O
PMBO
O
N3
OPMP
42
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
4.03 4.76 1.39 1.97 1.82 3.70
1.00 1.04
1.03 0.94 1.88 1.00 0.96 1.06 1.86 2.95 1.13 1.16 5.64 0.94 1.82
2.80 2.91
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 ppm

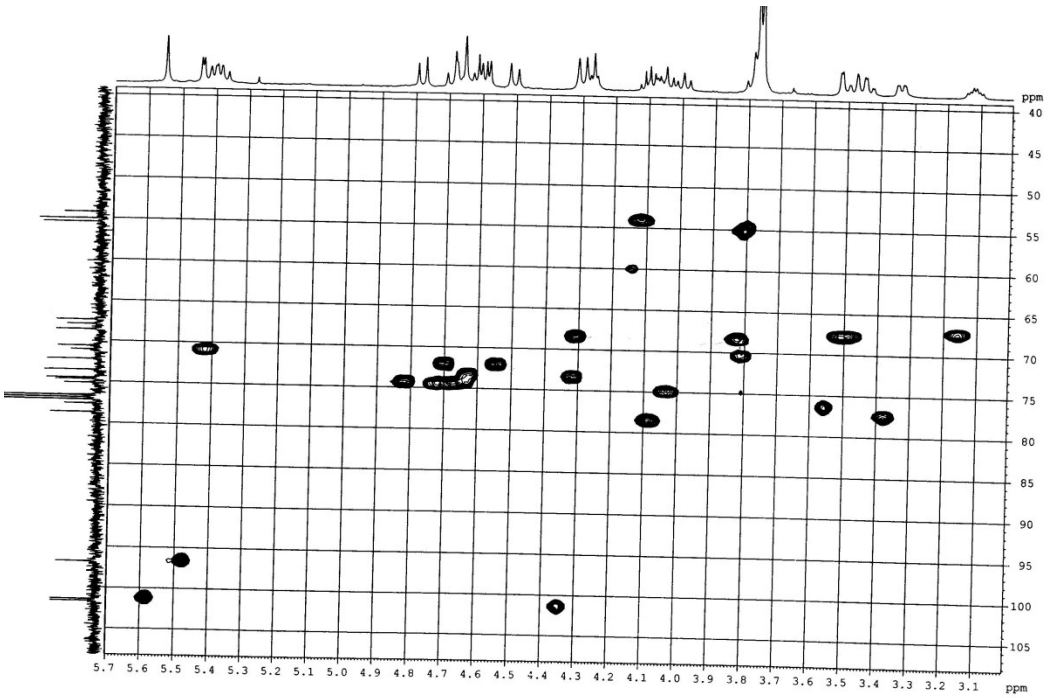

Ph
OBn
PMBO
OBn
BnO
OPMP
OBn
43
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.19 2.43 10.13 13.41 2.23 4.01
1.00 1.08 1.14 2.43 1.75 1.97 1.21 1.00 3.05 3.33 1.11 4.19 3.28 3.49 2.10 1.21 1.19 0.97 1.00
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

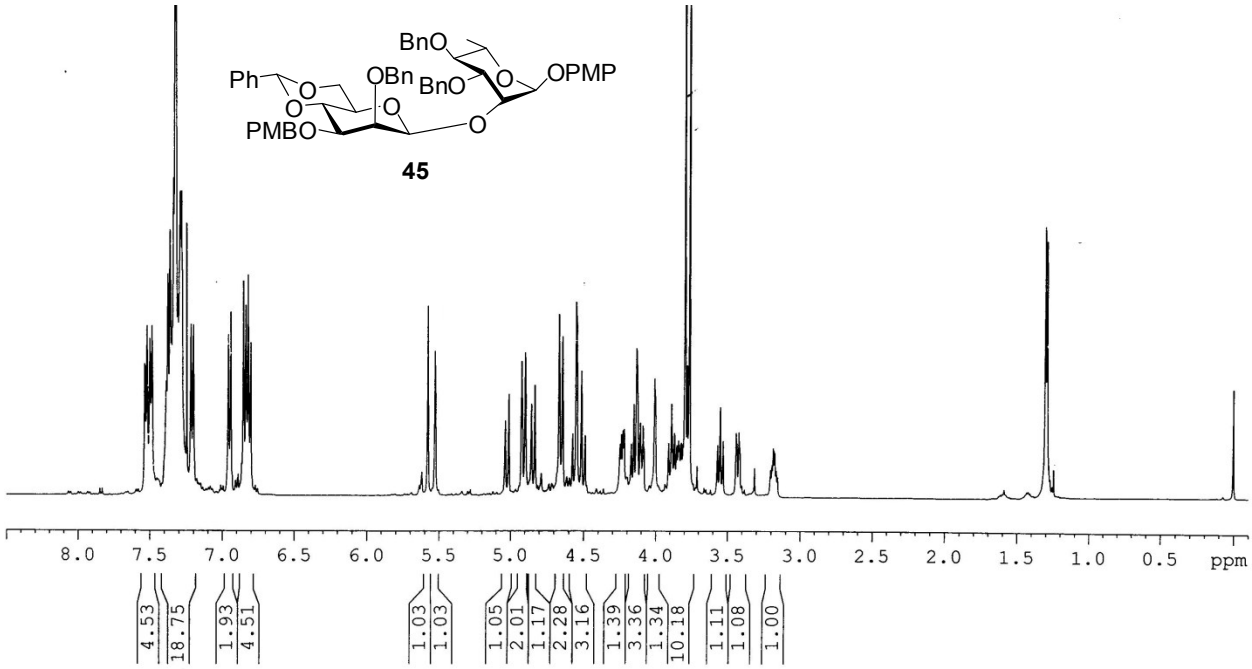

Ph
O
OBn
O
O
PMBO
O
OBn
O
AcO
TrocHN
OPMP
44
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.26
15.15
2.17
4.04
1.00
2.79
1.10
5.31
1.16
3.00
3.88
8.48
3.11
1.07
1.01
3.58
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 ppm

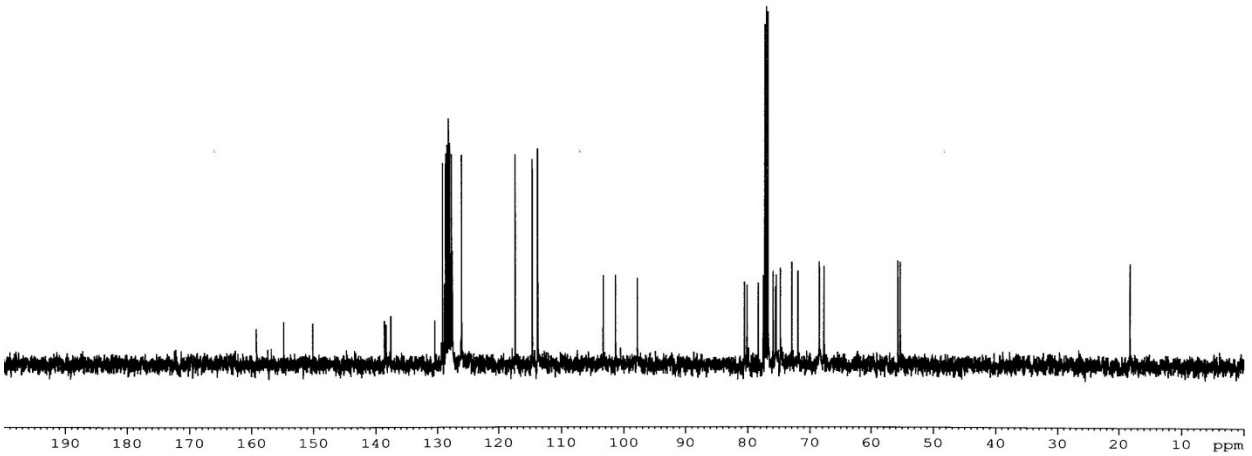

Ph
OBn
OBn
PMBO
AcO
TrocHN
OPMP

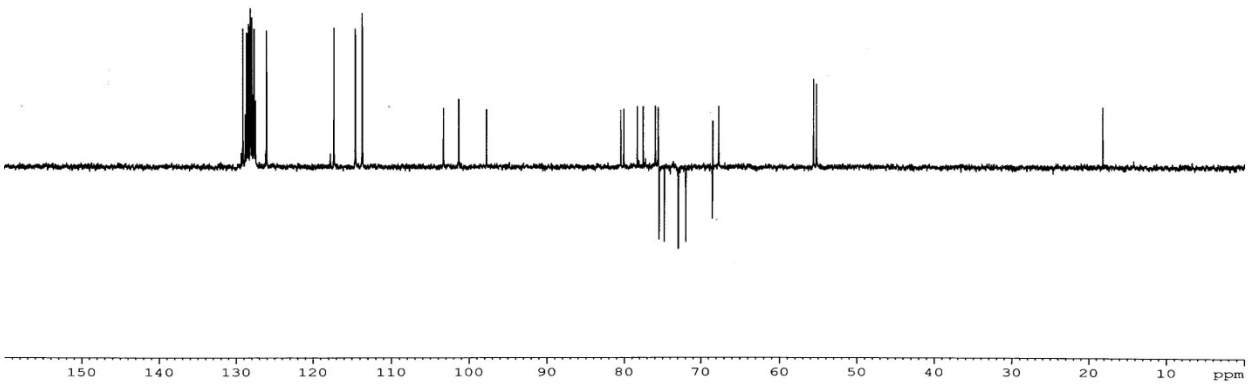
44

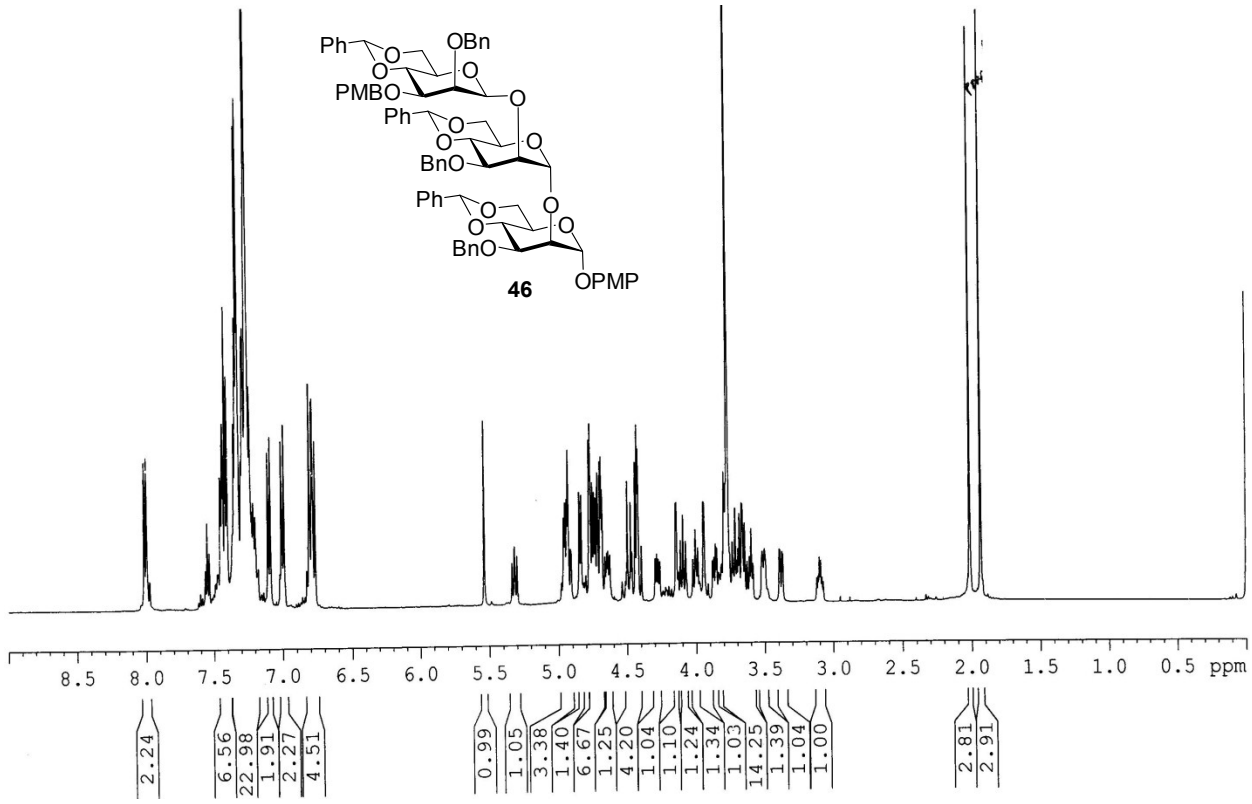

ppm
6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2
ppm

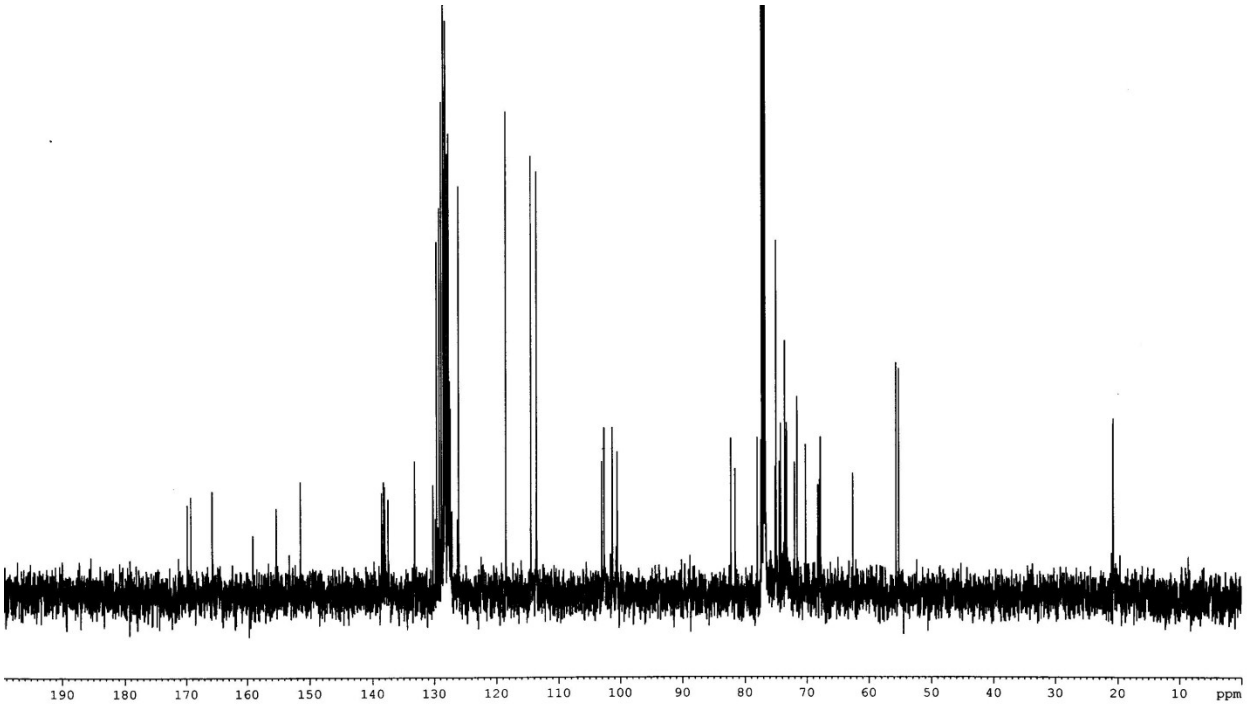

ppm
40 45 50 55 60 65 70 75 80 85 90 95 100 105
5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1
ppm

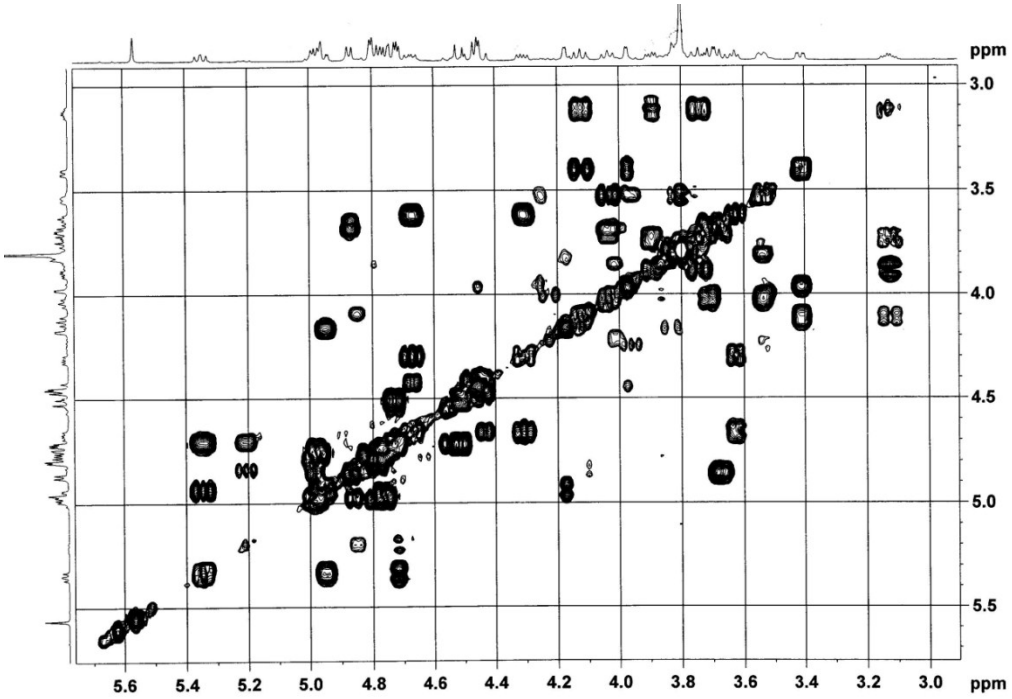

BnO
Ph
OBn
BnO
OPMP
PMBO
45
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
4.53 18.75 1.93 4.51 1.03 1.03 1.05 2.01 1.17 2.28 3.16 1.39 3.36 1.34 10.18 1.11 1.08 1.00

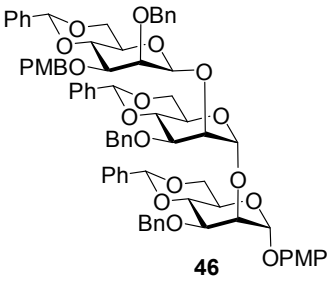

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

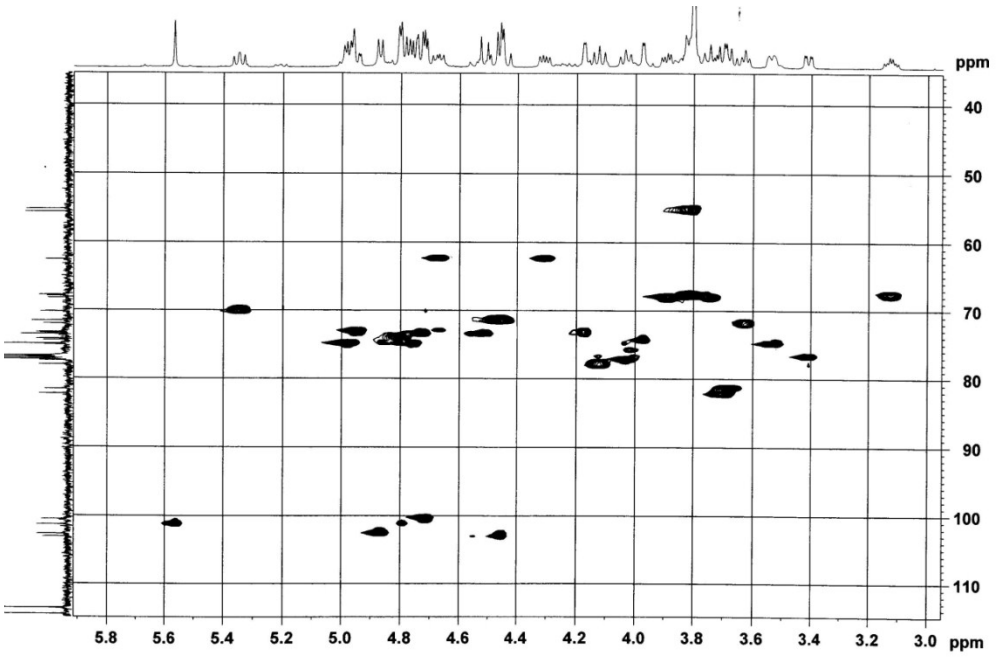

Ph
OBn
PMBO
Ph
BnO
Ph
BnO
OPMP
46
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.24
6.56
22.98
1.91
2.27
4.51
0.99
1.05
3.38
1.40
6.67
1.25
4.20
1.04
1.10
1.24
1.34
1.03
14.25
1.39
1.04
1.00
2.81
2.91

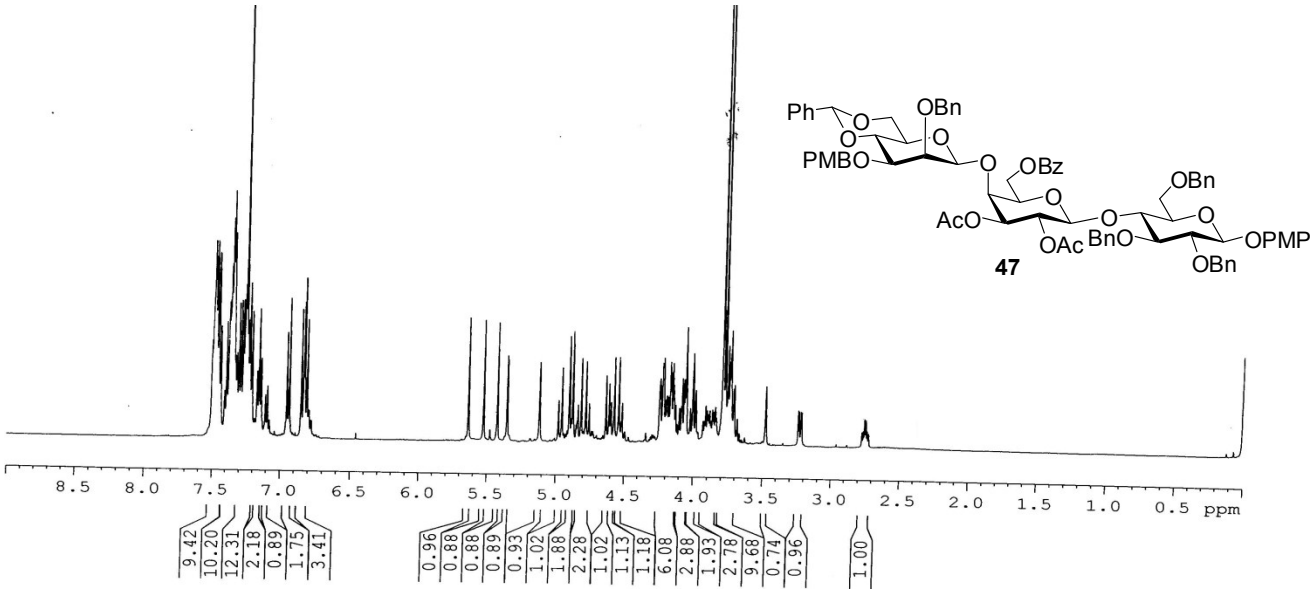

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

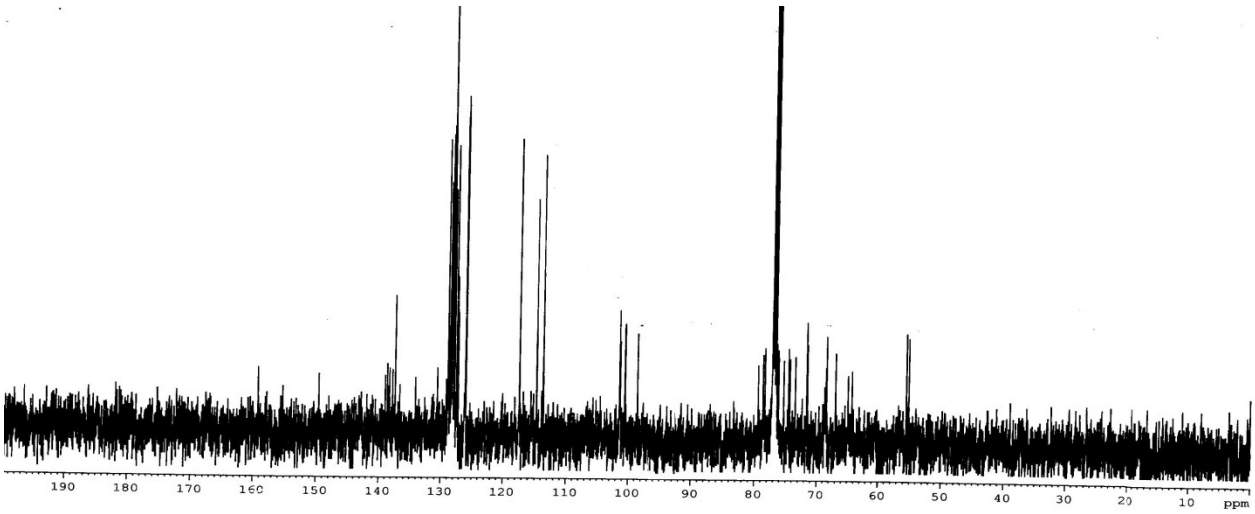

ppm
3.0
3.5
4.0
4.5
5.0
5.5
5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0
ppm

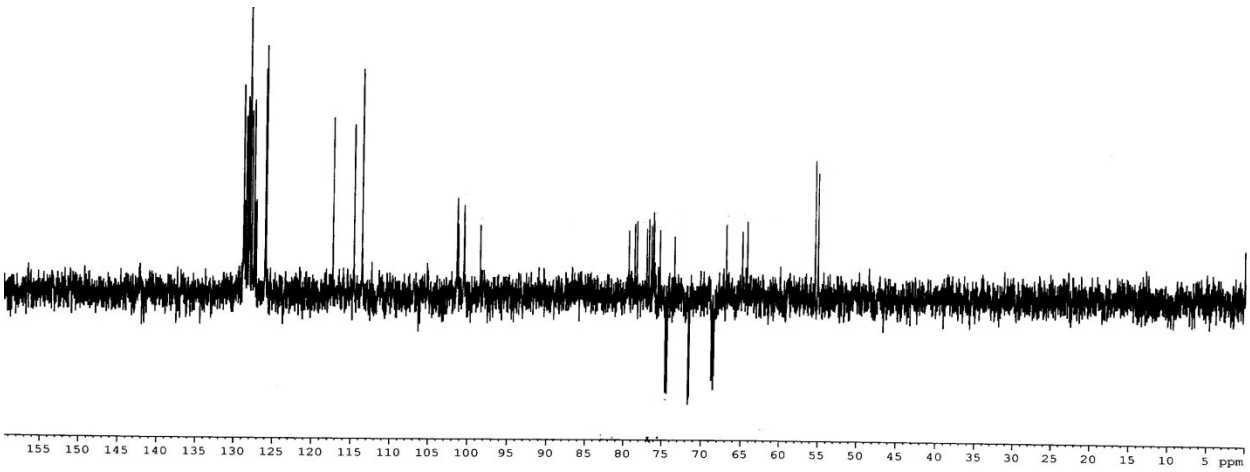

Ph
OBn
PMBO
Ph
BnO
Ph
BnO
OPMP

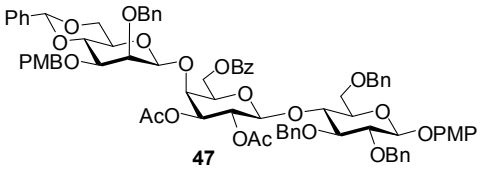
46


ppm
40
50
60
70
80
90
100
110
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 3.0
ppm

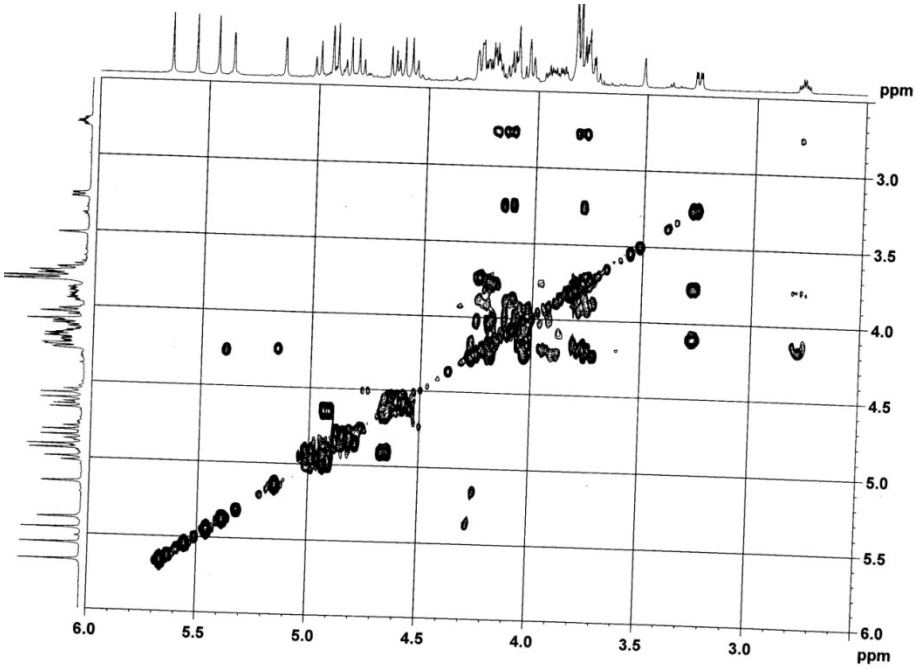

Ph
OBn
PMBO
OBz
AcO
OAc
BnO
OPMP
OBn
OBn
47
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
9.42 10.20 12.31 2.18 0.89 1.75 3.41
0.96 0.88 0.88 0.89 0.93 1.02 1.88 2.28 1.02 1.13 1.18 6.08 2.88 1.93 2.78 9.68 0.74 0.96
1.00

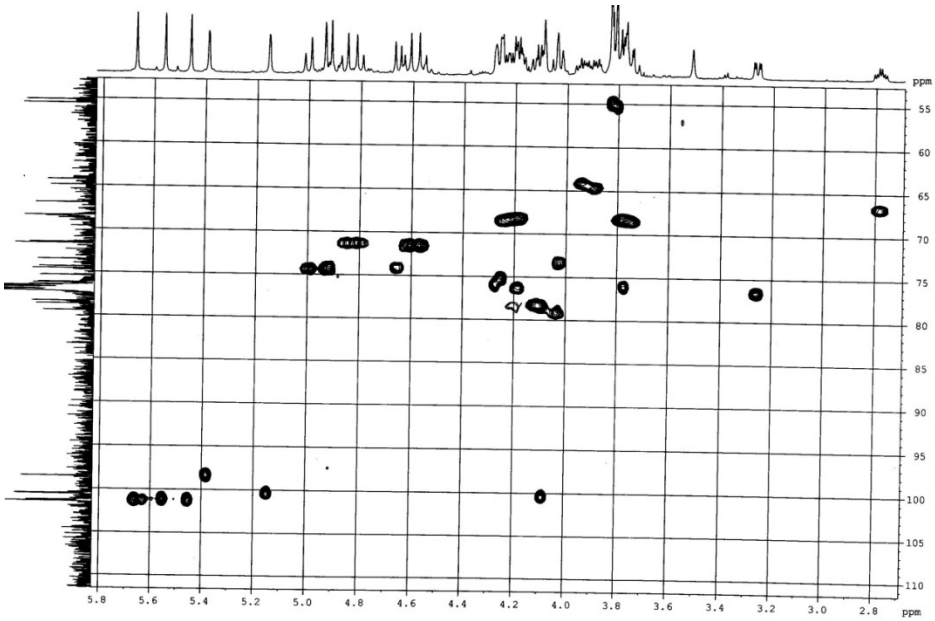

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

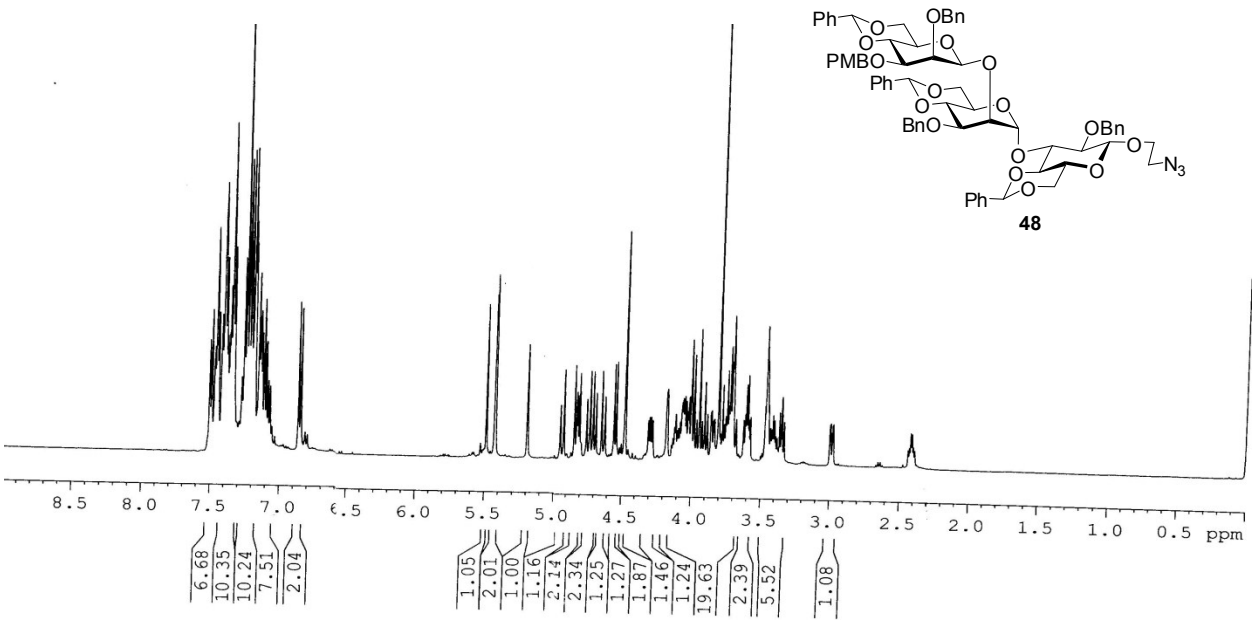

155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 ppm

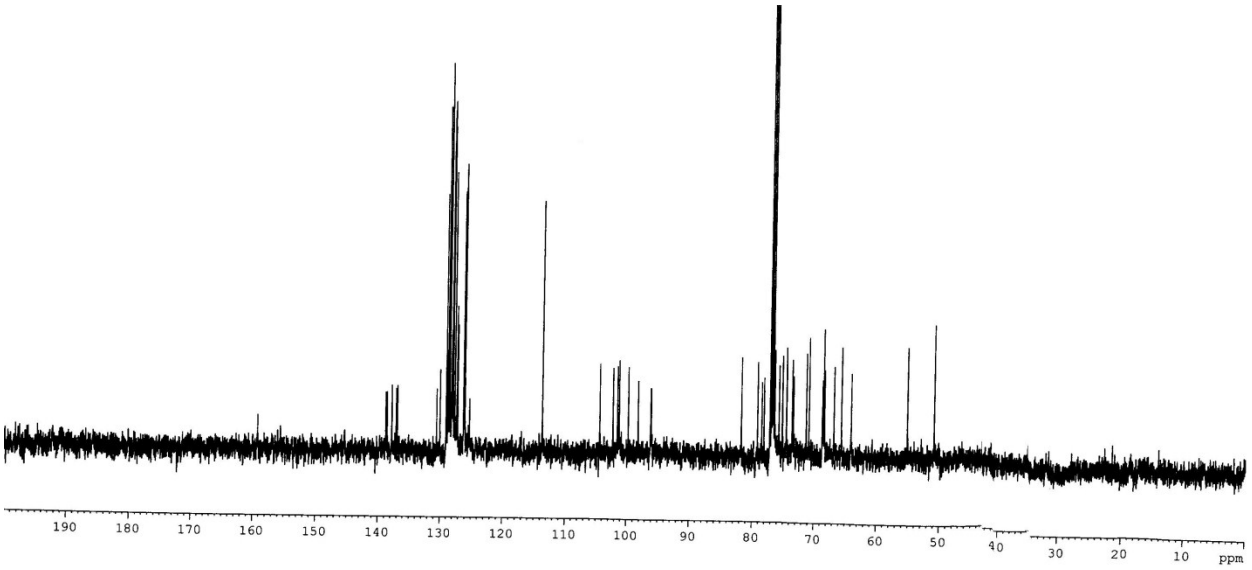

Ph
OBn
O
O
PMBO
O
OBz
O
AcO
O
OAc
BnO
OBn
O
OPMP
OBn

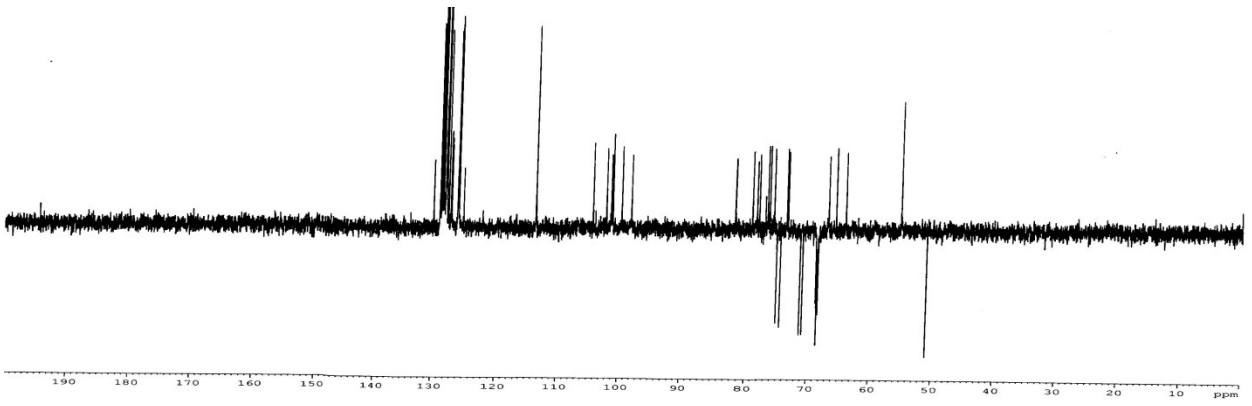
47

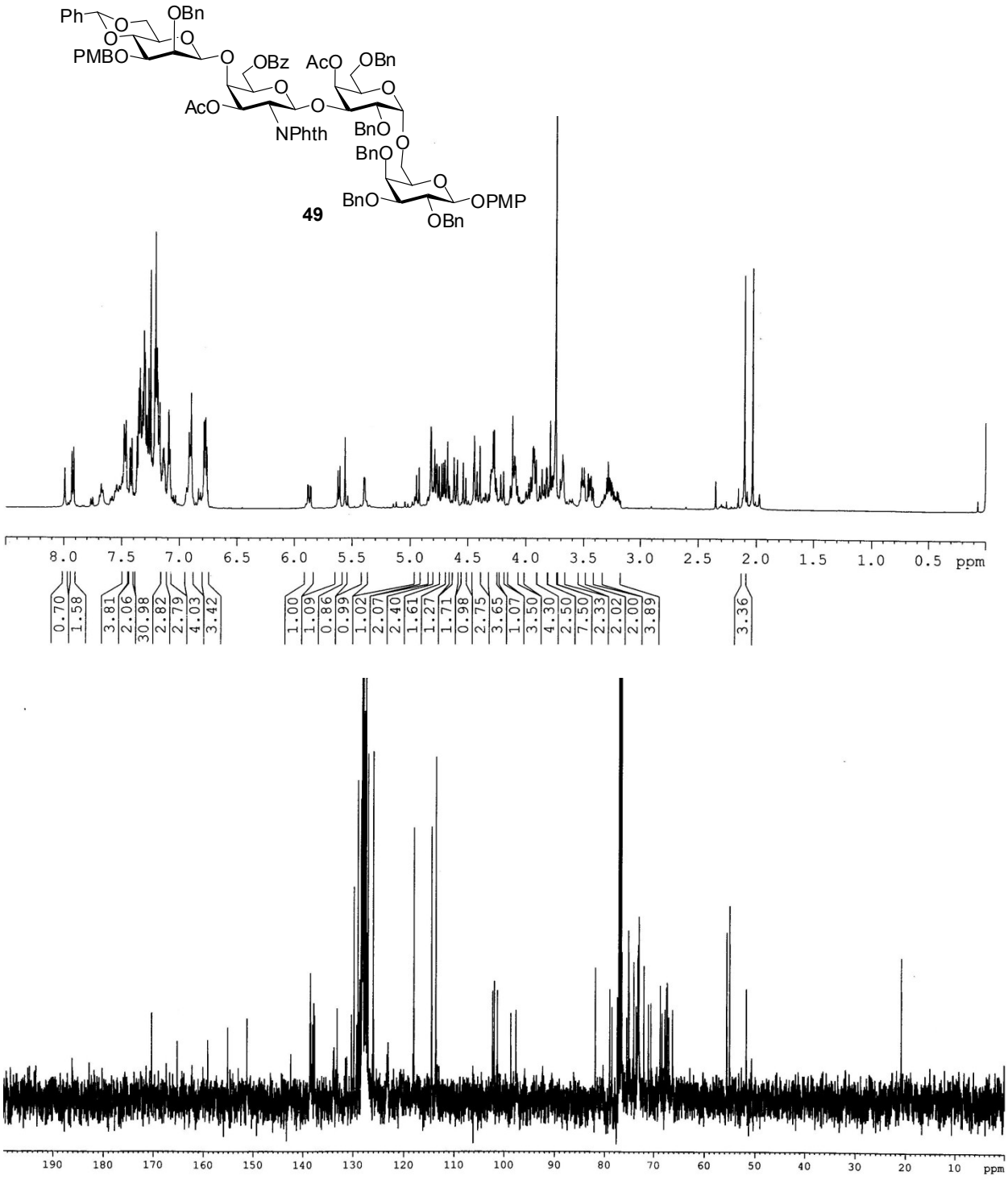

ppm
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm

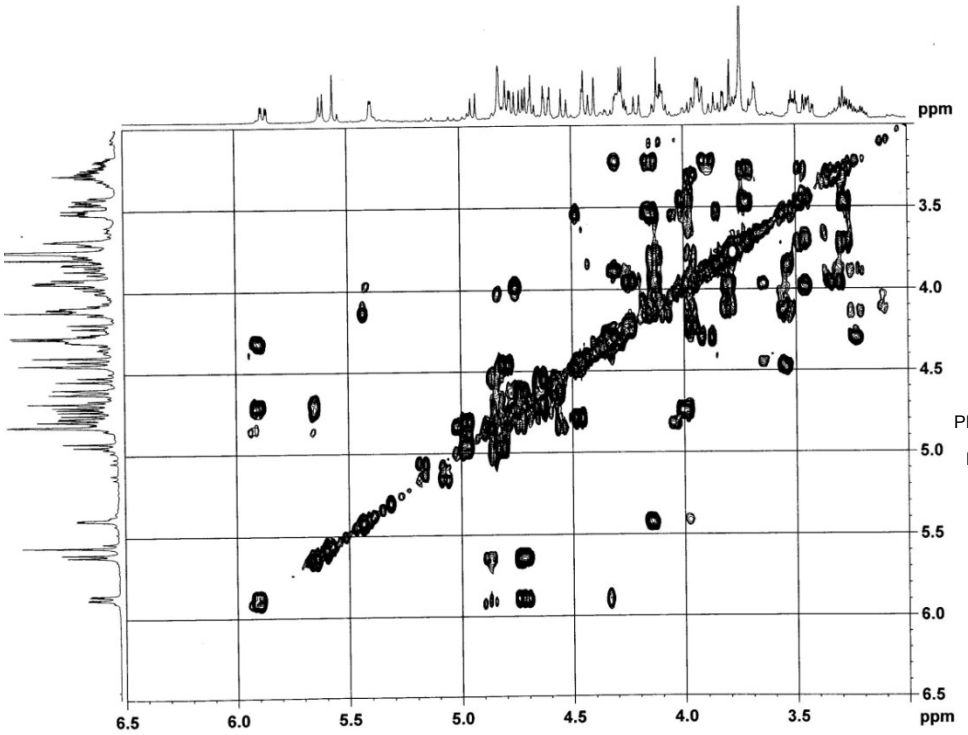

ppm
55
60
65
70
75
80
85
90
95
100
105
110
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
ppm

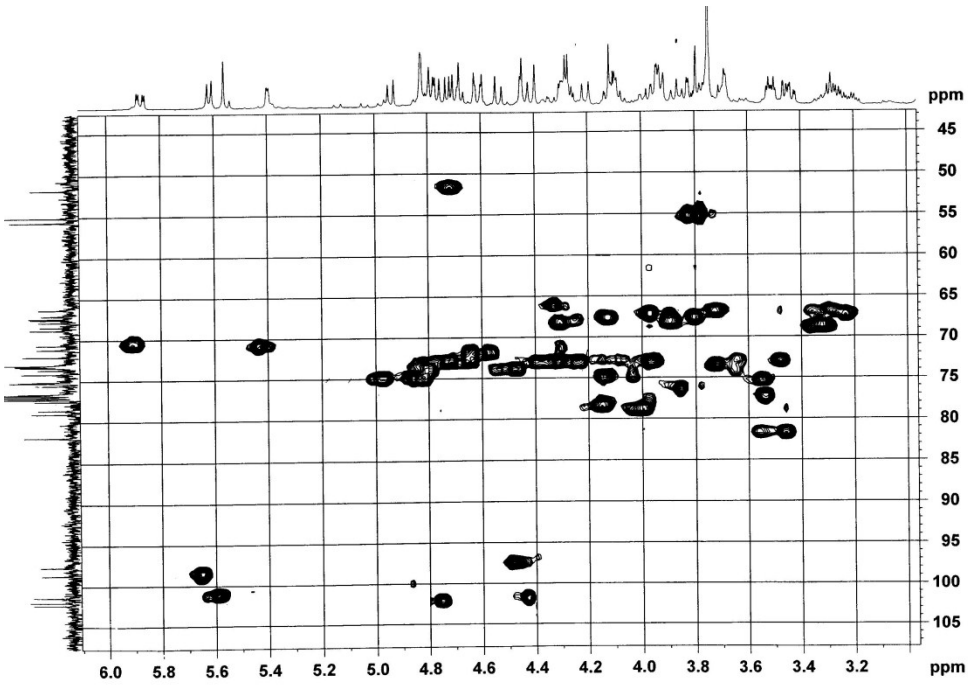

Ph
OBn
PMBO
Ph
BnO
OBn
N3
Ph
48
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
6.68
10.35
10.24
7.51
2.04
1.05
2.01
1.00
1.16
2.14
2.34
1.25
1.27
1.87
1.46
1.24
19.63
2.39
5.52
1.08

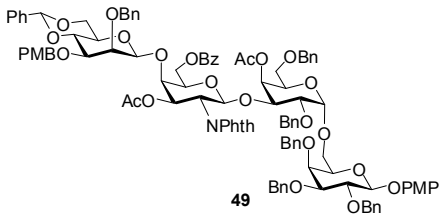

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

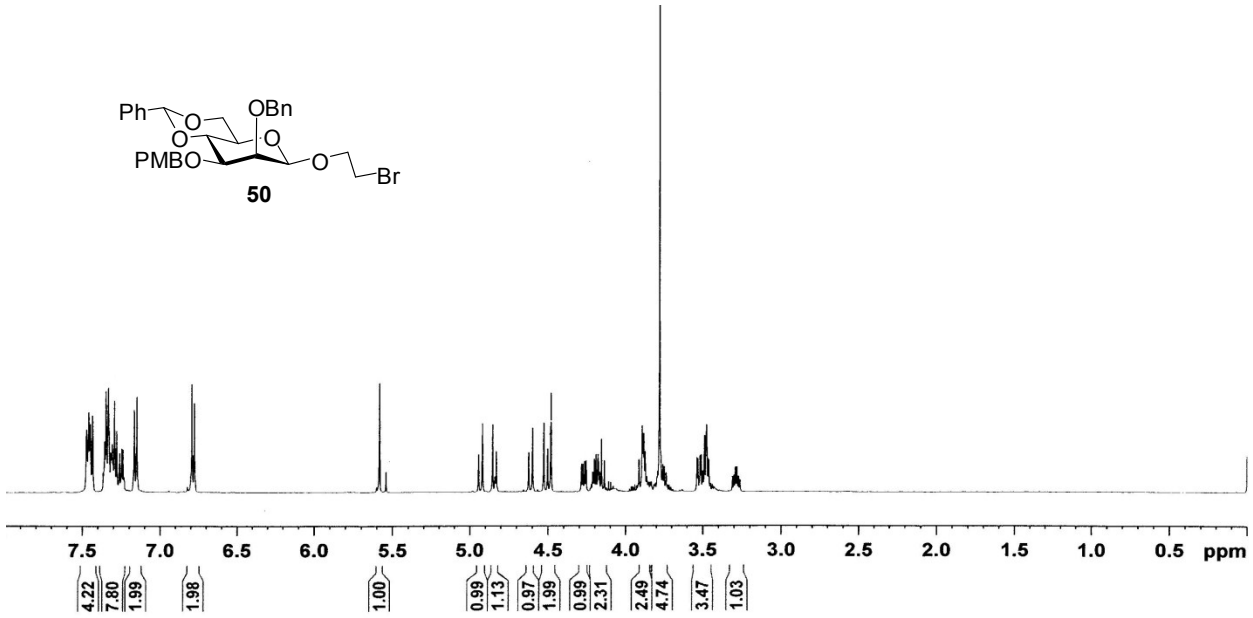

Ph
OBn
PMBO
OBz
AcO
OBn
AcO
NPhth
BnO
BnO
BnO
OPMP
OBn
49
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.70 1.58 3.81 2.06 30.98 2.82 2.79 4.03 3.42 1.00 1.09 0.86 0.99 1.02 2.07 2.40 1.61 1.27 1.71 0.98 2.75 3.65 1.07 3.50 4.30 2.50 7.50 2.33 2.02 2.00 3.89 3.36
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

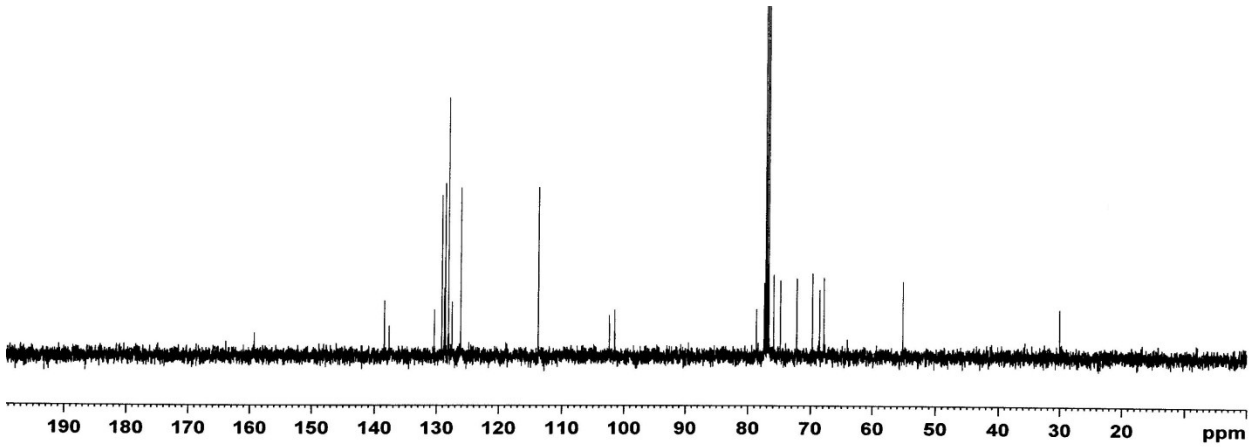

ppm
3.5
4.0
4.5
5.0
5.5
6.0
6.5
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm

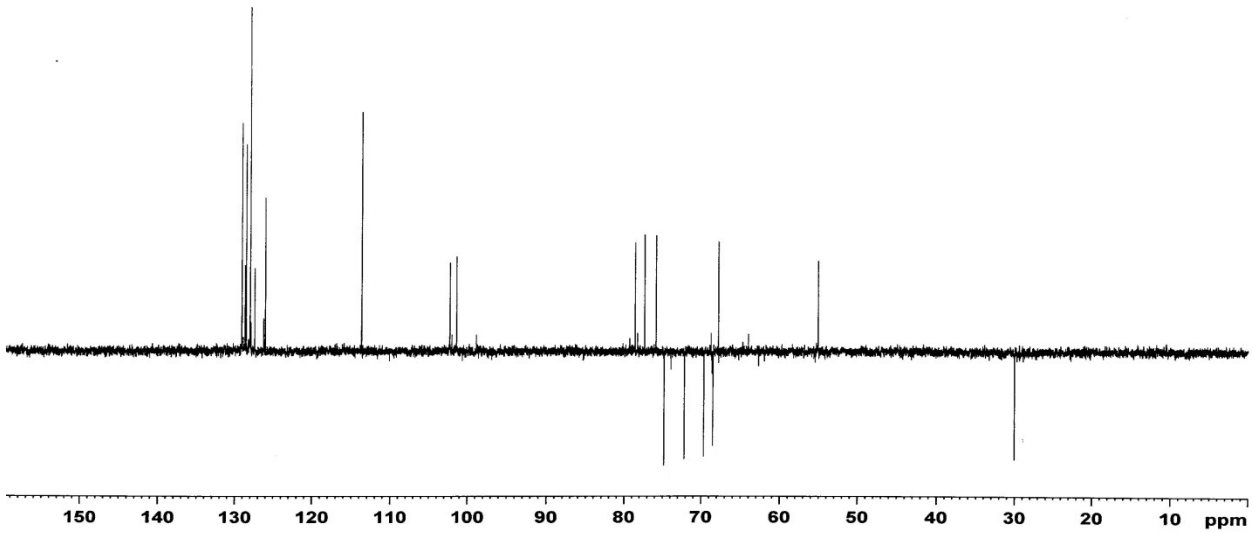

ppm
45
50
55
60
65
70
75
80
85
90
95
100
105
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
ppm

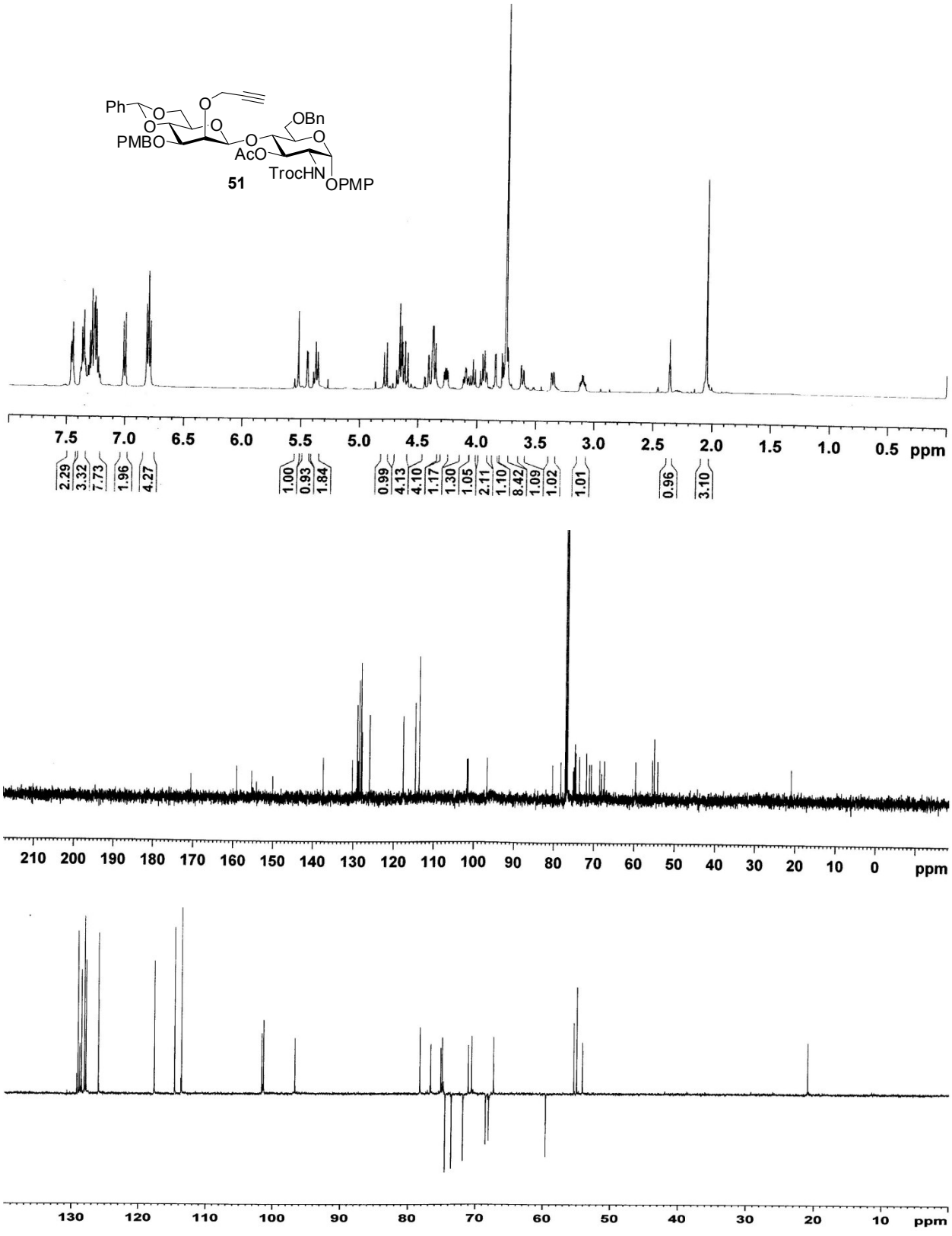

Ph
OBn
PMBO
OBz
AcO
OBn
AcO
NPhth
BnO
BnO
BnO
OPMP
OBn

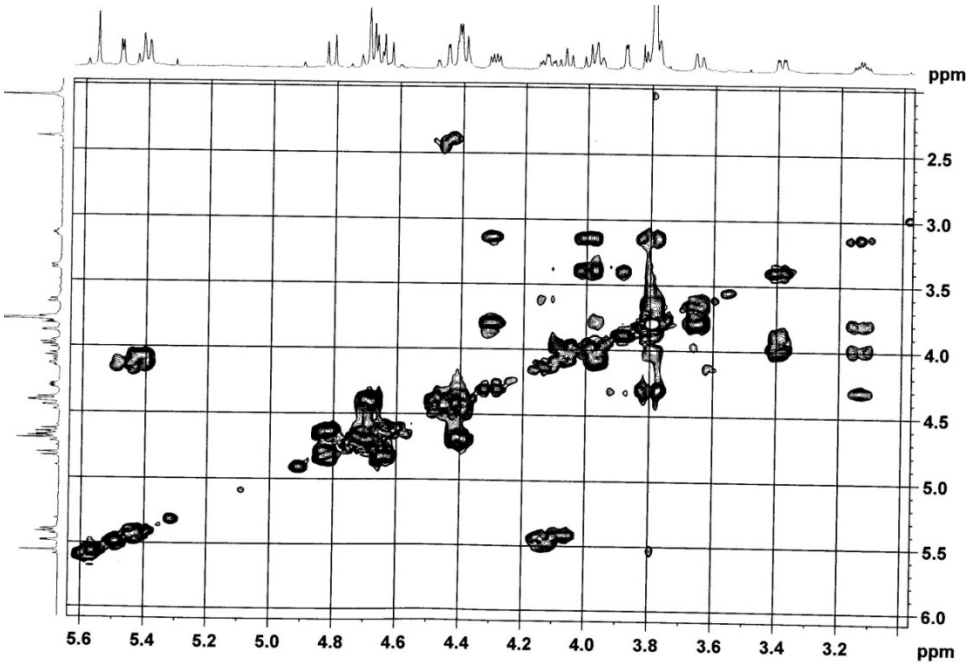
49

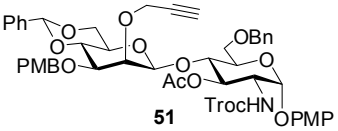

Ph
OBn
O
O
O
PMBO
O
Br
50
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.22
7.80
1.99
1.98
1.00
0.99
1.13
0.97
1.99
0.99
2.31
2.49
4.74
3.47
1.03


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

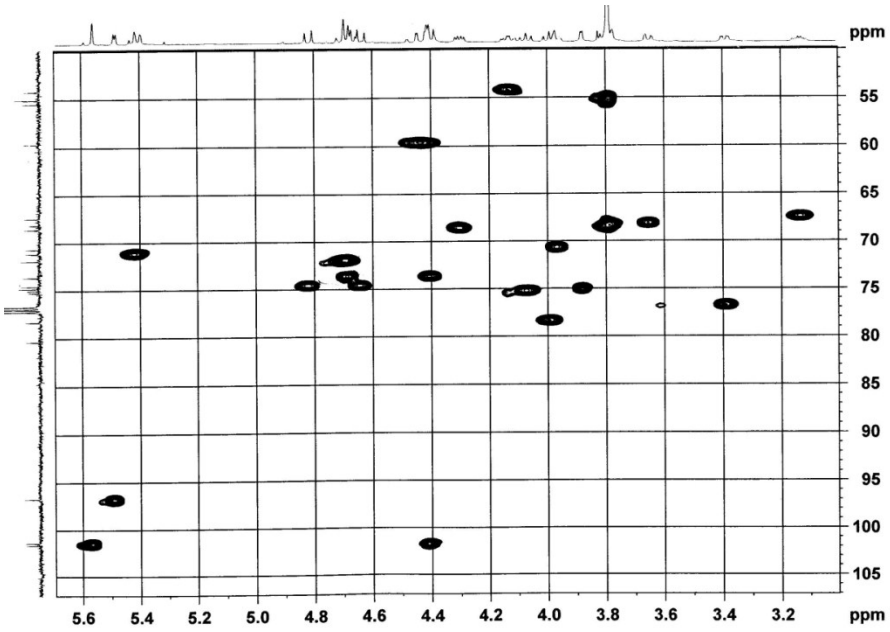

150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

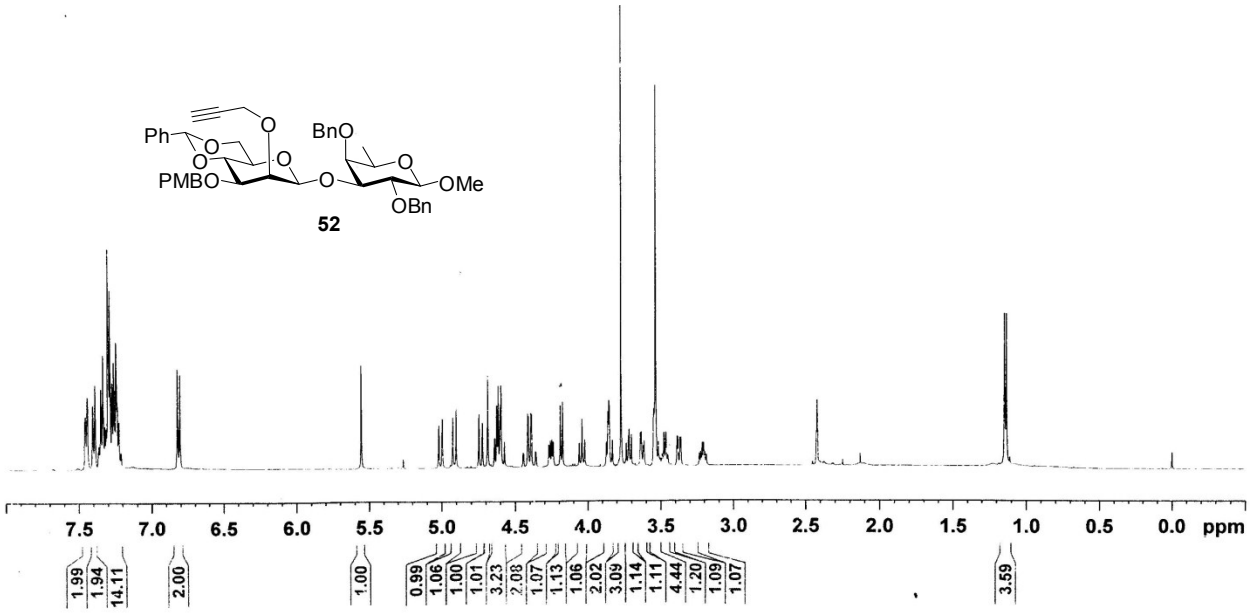

Ph
O
O
O
O
PMBO
O
OBn
O
AcO
TrocHN
OPMP
51
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.29 3.32 7.73 1.96 4.27 1.00 0.93 1.84 0.99 4.13 4.10 1.17 1.30 1.05 2.11 1.10 8.42 1.09 1.02 1.01 0.96 3.10
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

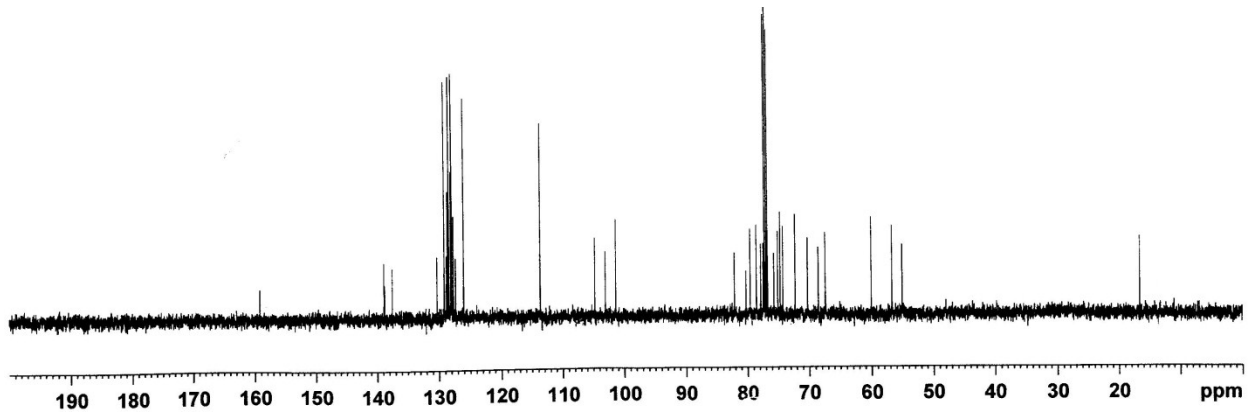

ppm
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
ppm

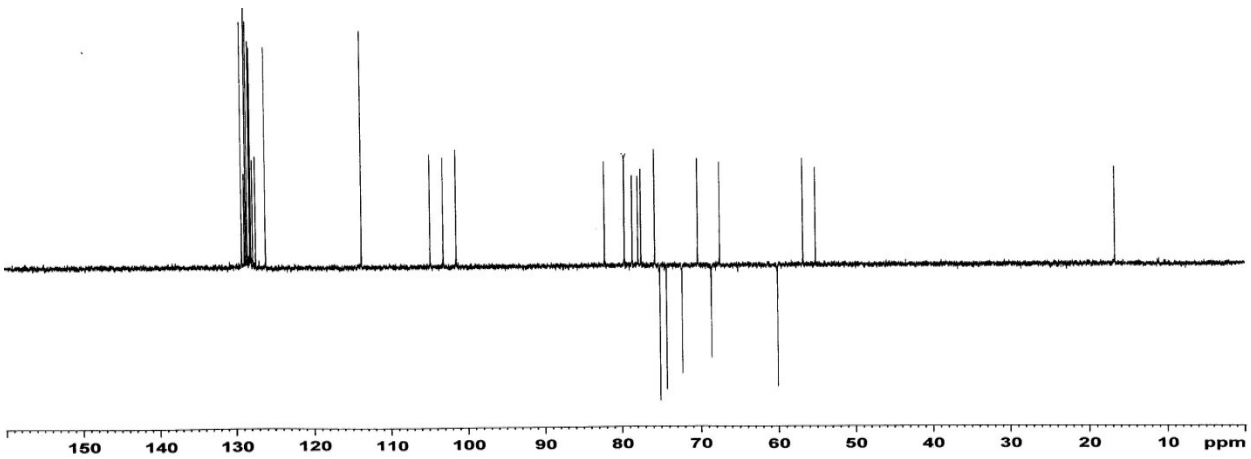

Ph
O
O
O
O
PMBO
O
AcO
OBn
O
TrocHN
OPMP

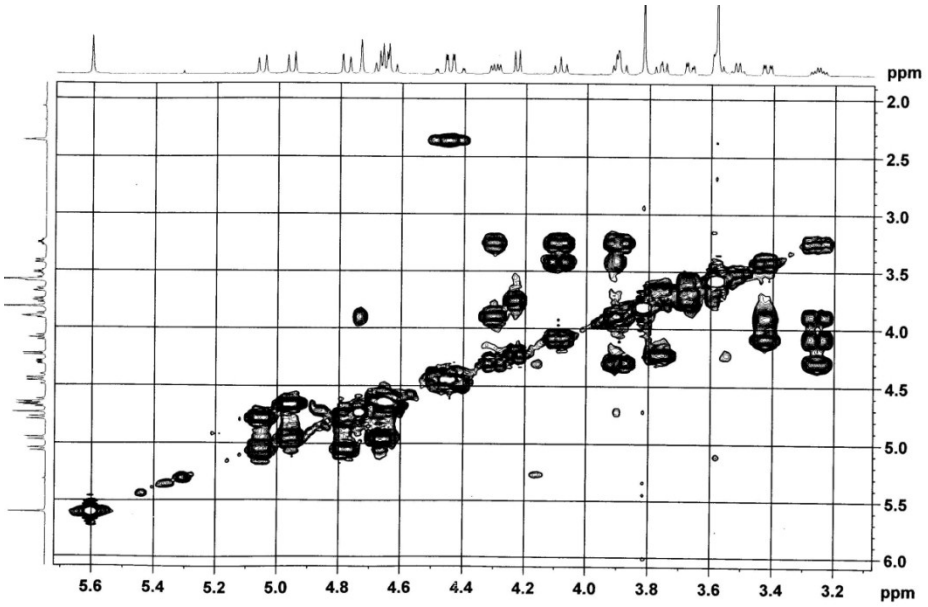
51

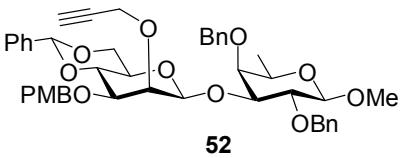

ppm
55
60
65
70
75
80
85
90
95
100
105
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
ppm


Ph
O
O
O
PMBO
O
BnO
O
OMe
OBn
52
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 ppm
1.99 1.94 14.11 2.00 1.00 0.99 1.06 1.00 1.01 3.23 2.08 1.07 1.13 1.06 2.02 3.09 1.14 1.11 4.44 1.20 1.09 1.07 3.59

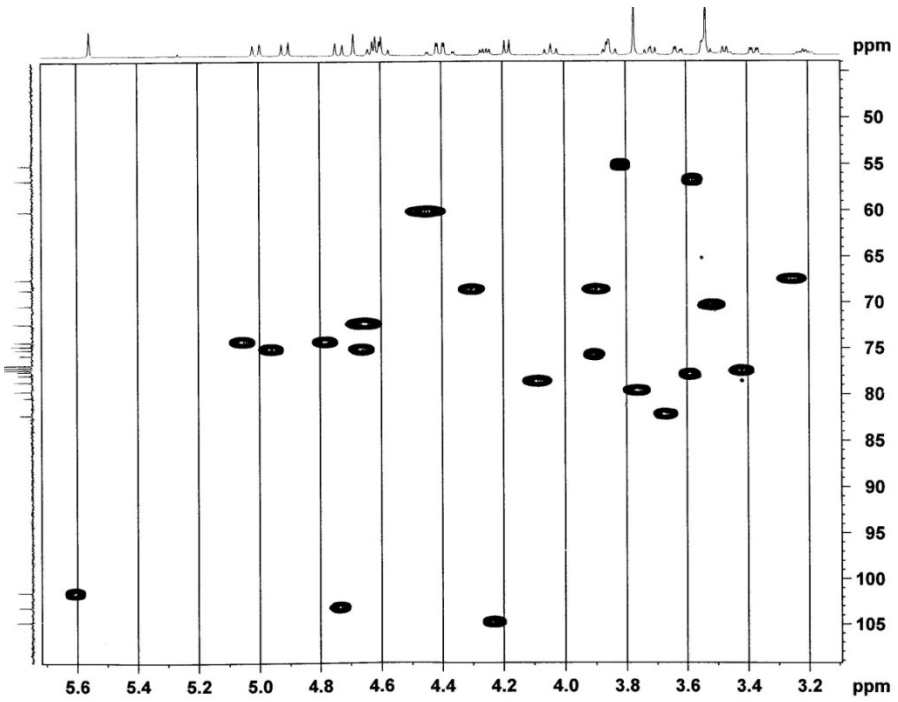

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

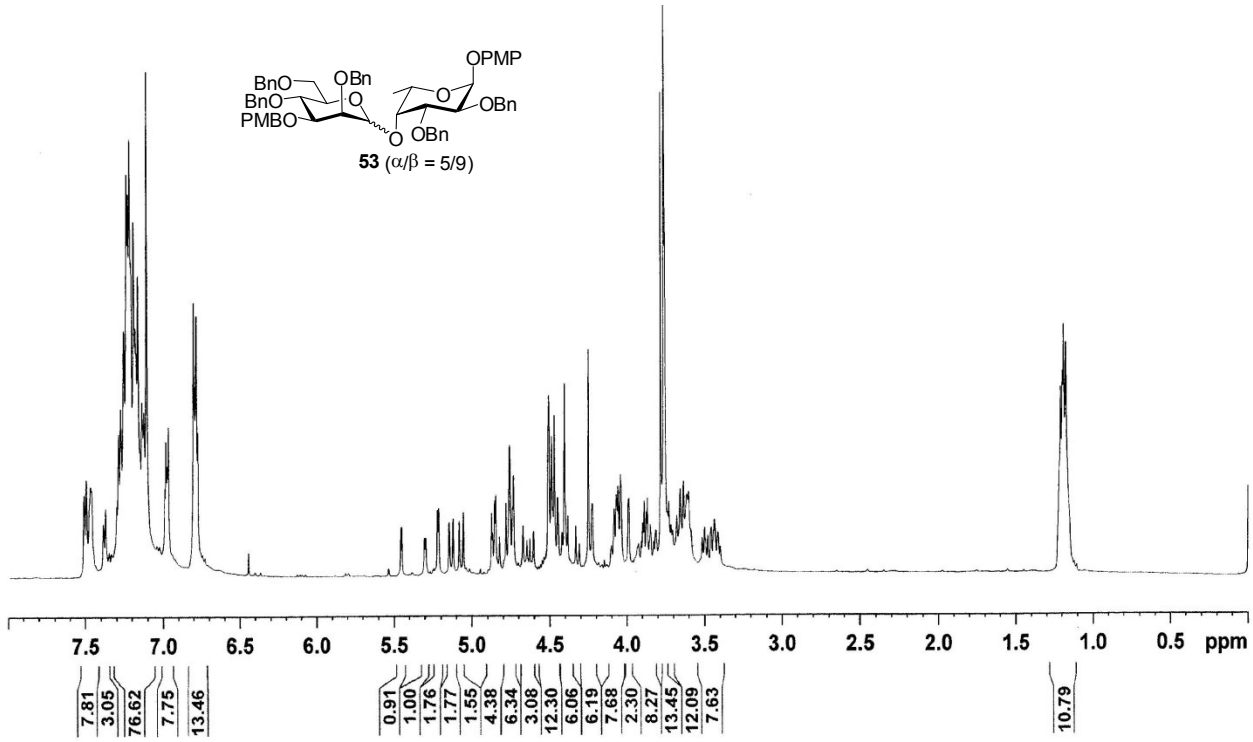

150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


ppm
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
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

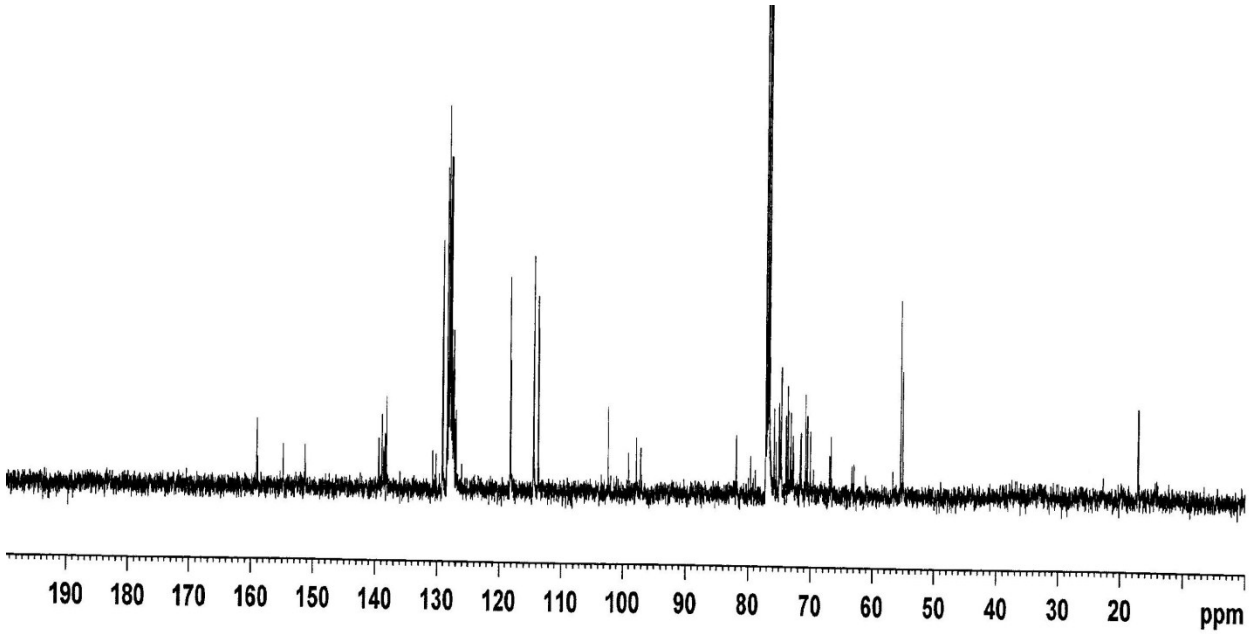

Ph
O
O
O
O
PMBO
O
BnO
O
OMe
OBn

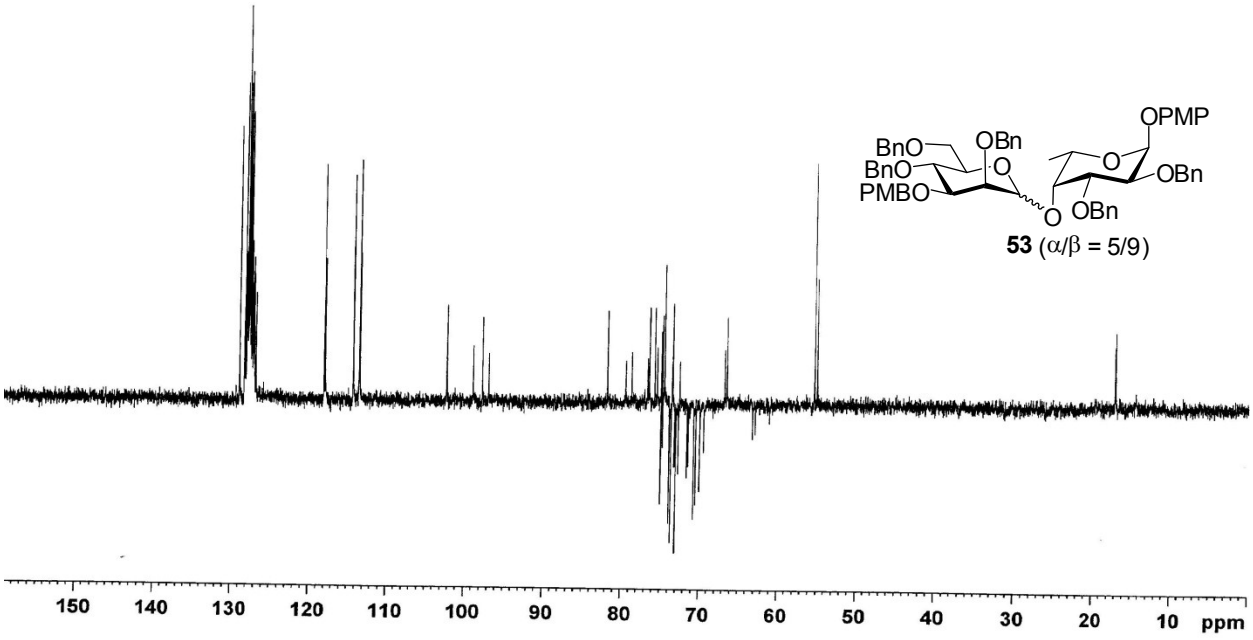
52


ppm
50
55
60
65
70
75
80
85
90
95
100
105
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

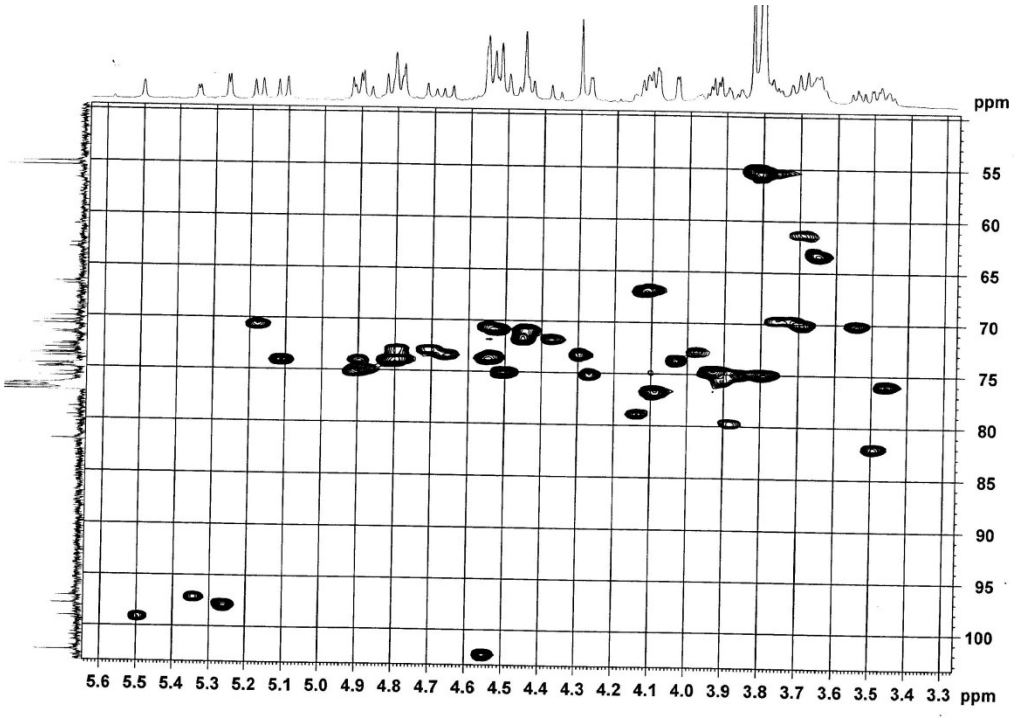


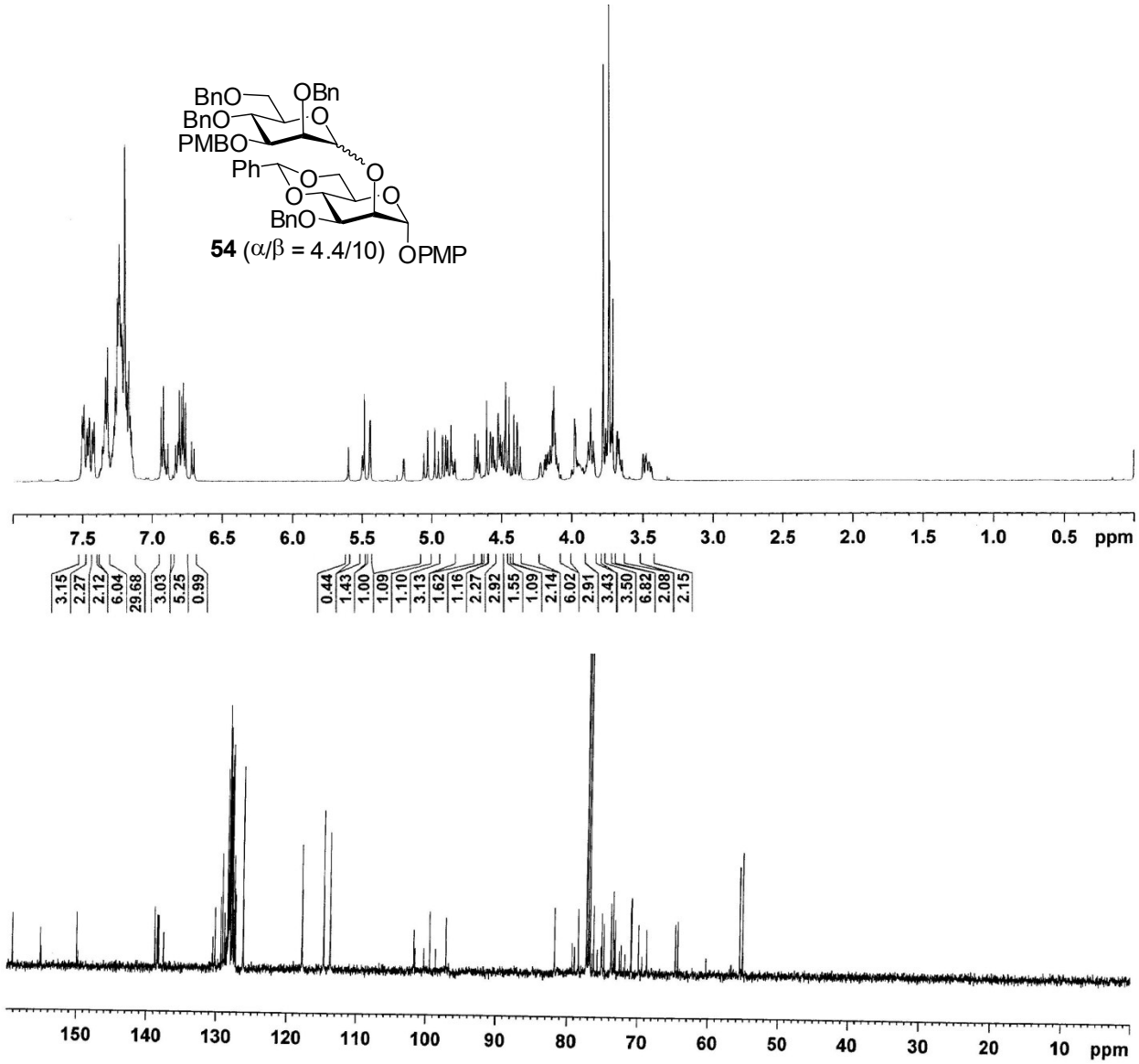
53 (α/β = 5/9)

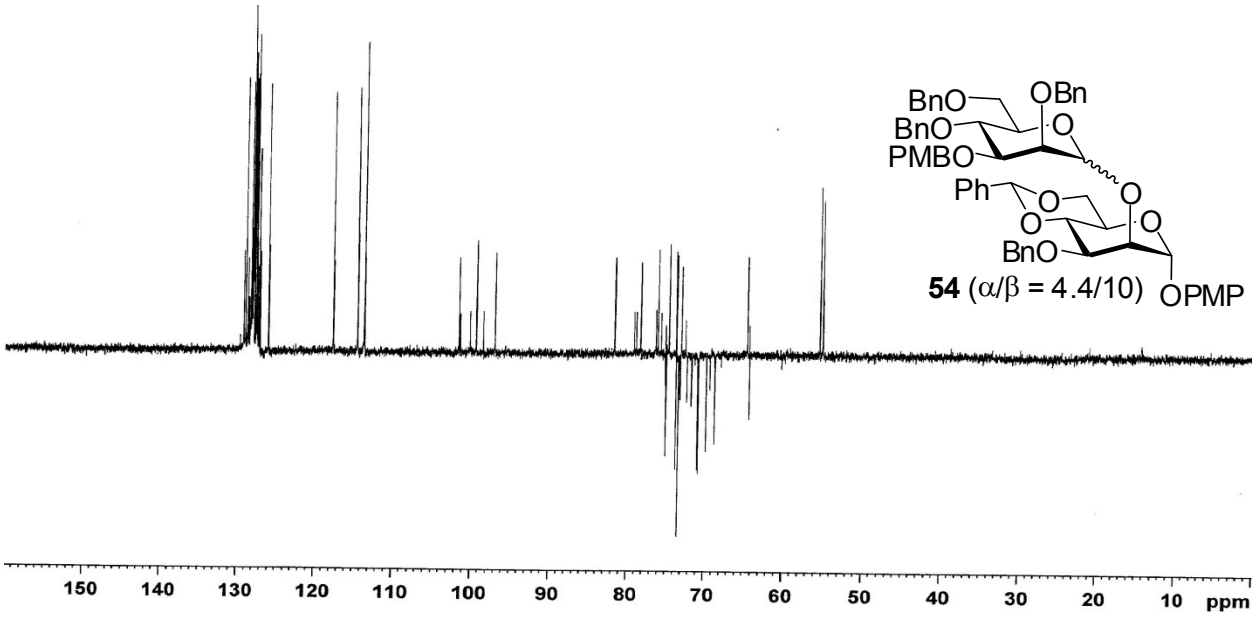




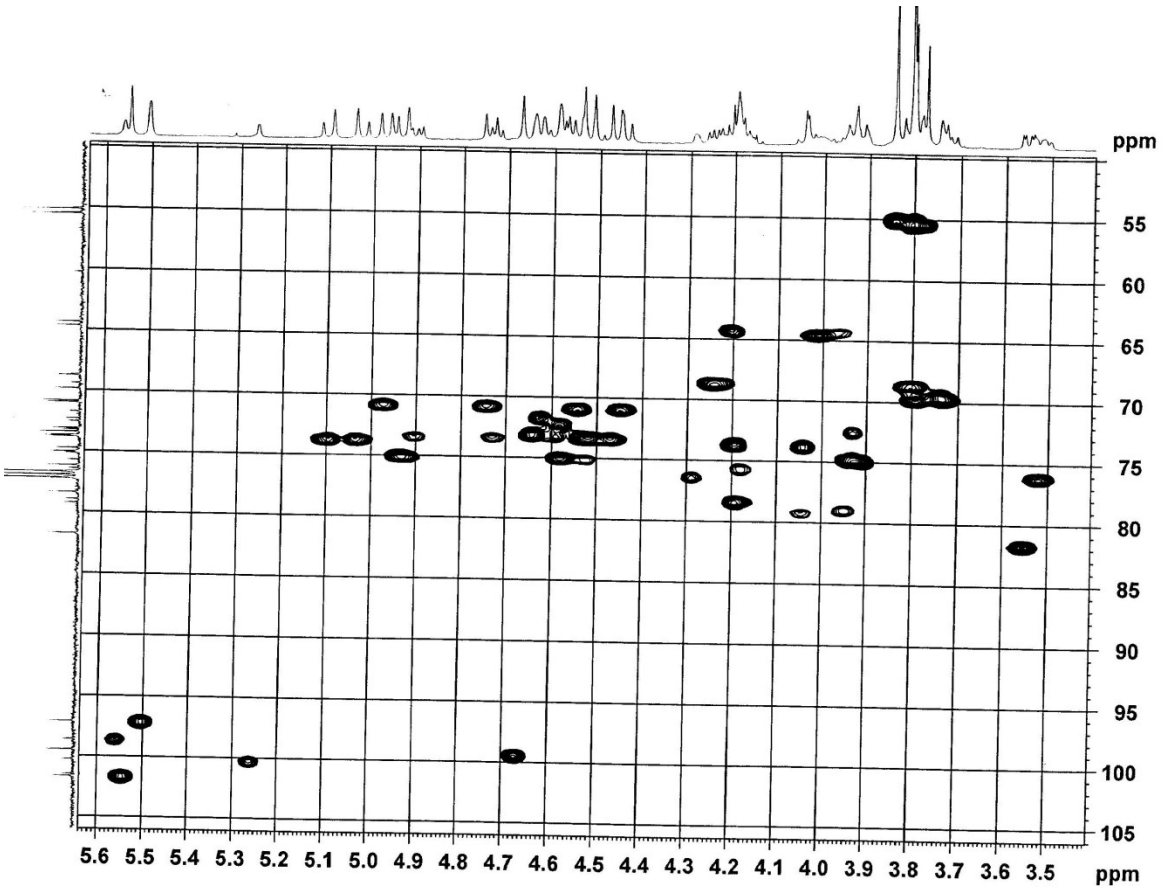
53 (α/β = 5/9)

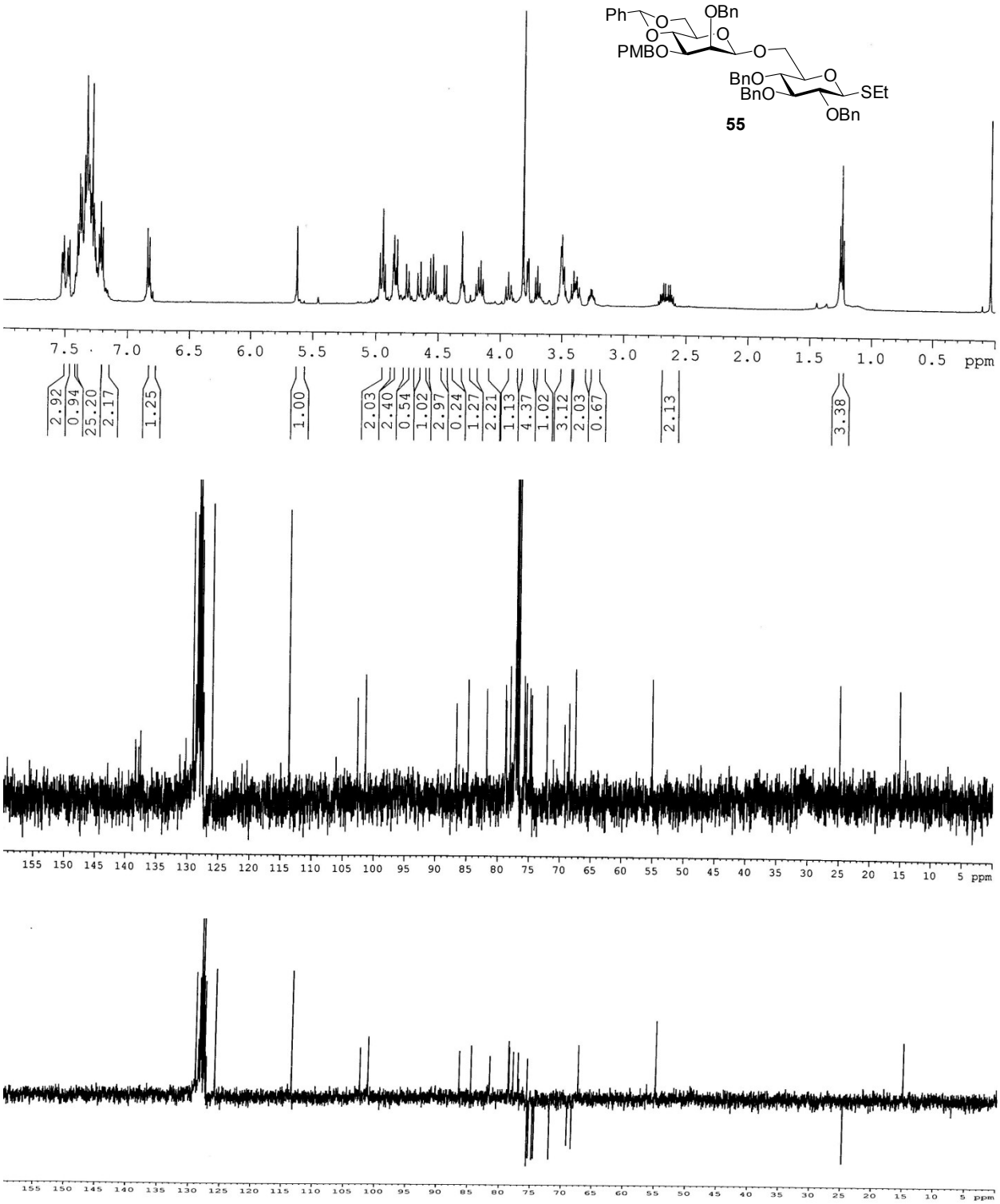


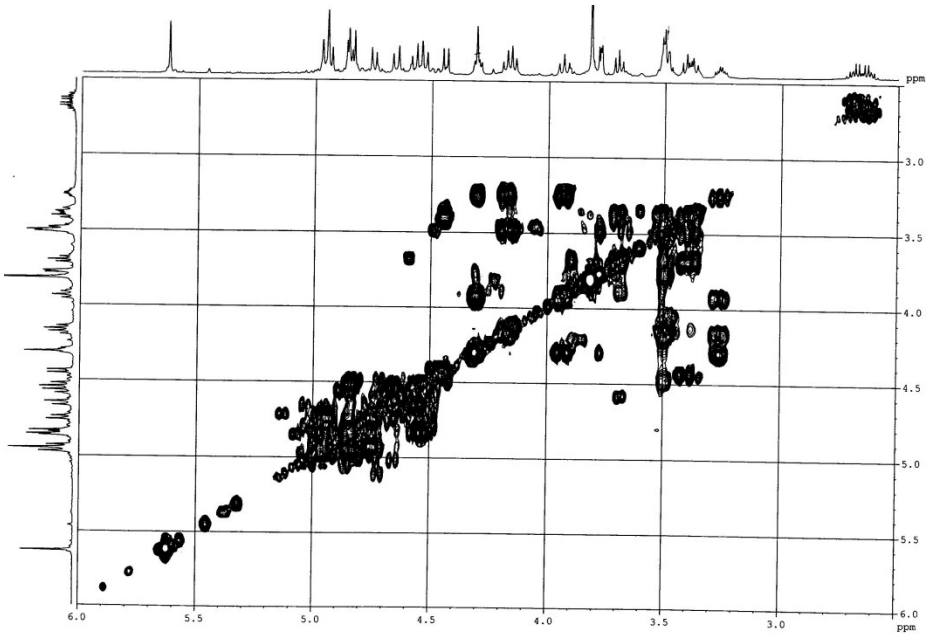

BnO
OBn
BnO
O
PMBO
Ph
O
O
O
O
BnO
OPMP
54 (α/β = 4.4/10)
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
3.15 2.27 2.12 6.04 29.68 3.03 5.25 0.99
0.44 1.43 1.00 1.09 1.10 3.13 1.62 1.16 2.27 2.92 1.55 1.09 2.14 6.02 2.91 3.43 3.50 6.82 2.08 2.15
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

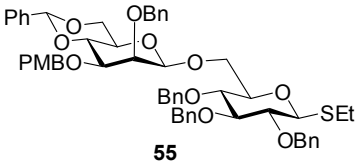


54 (α/β = 4.4/10)

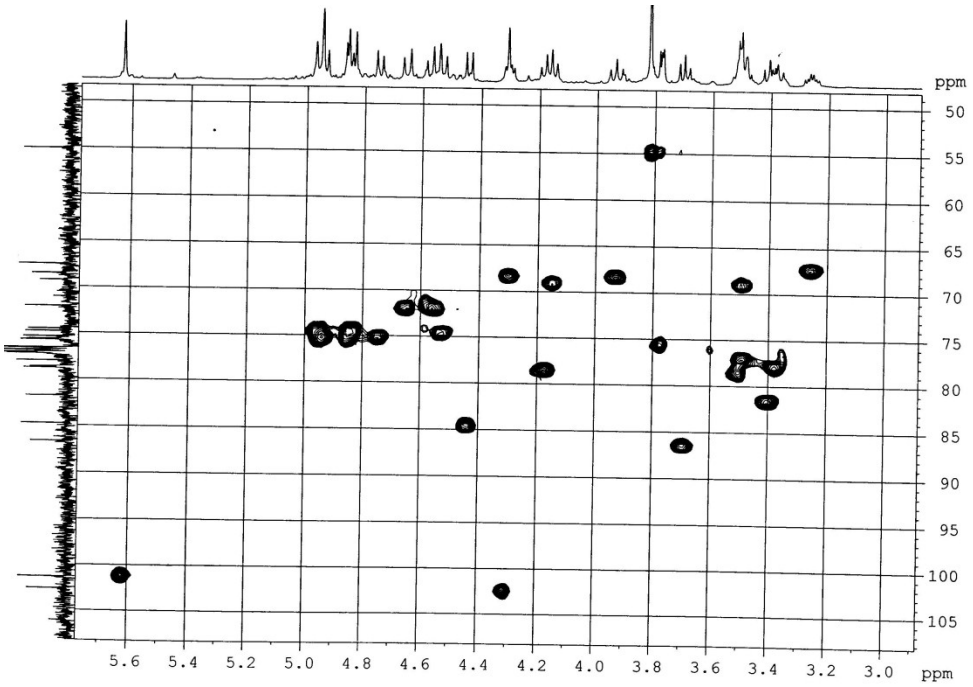


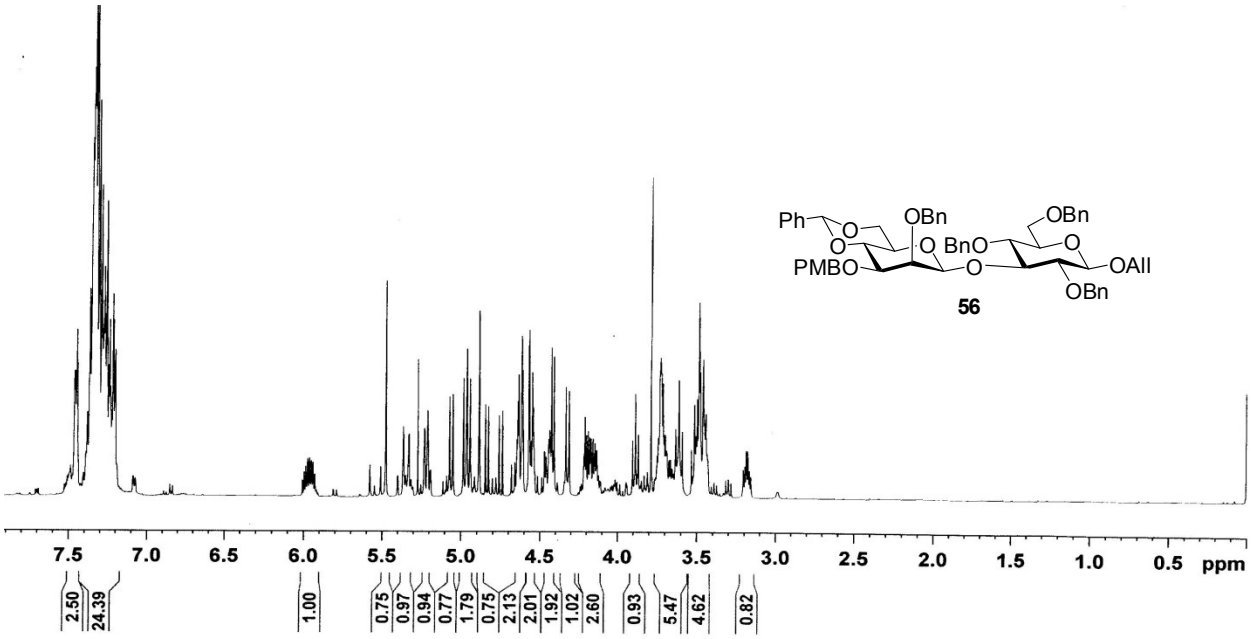

Ph
OBn
O
O
O
PMBO
O
BnO
O
BnO
SEt
OBn
55
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.92 0.94 25.20 2.17 1.25 1.00 2.03 2.40 0.54 1.02 2.97 0.24 1.27 2.21 1.13 4.37 1.02 3.12 2.03 0.67 2.13 3.38
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 ppm
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 ppm

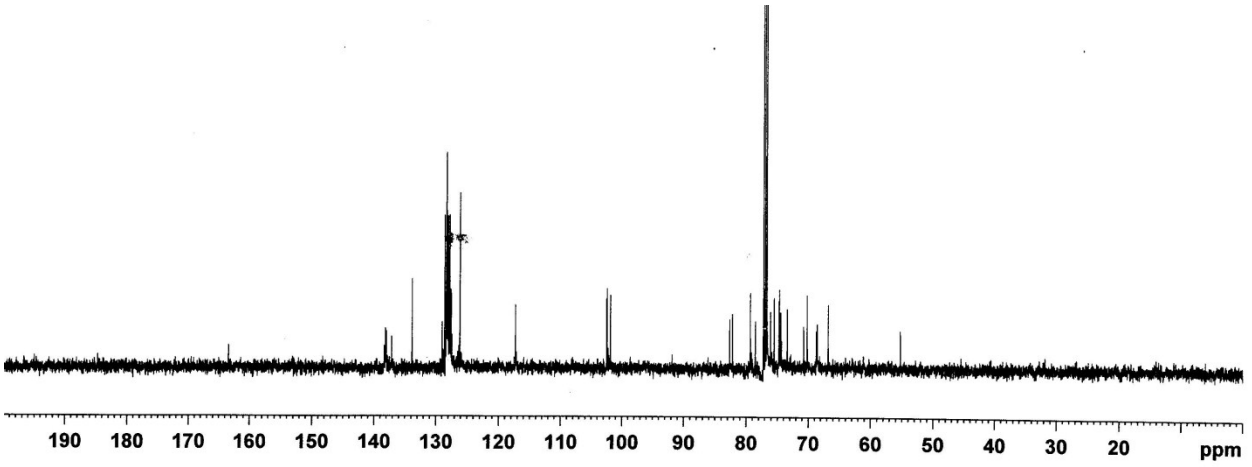

ppm
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm

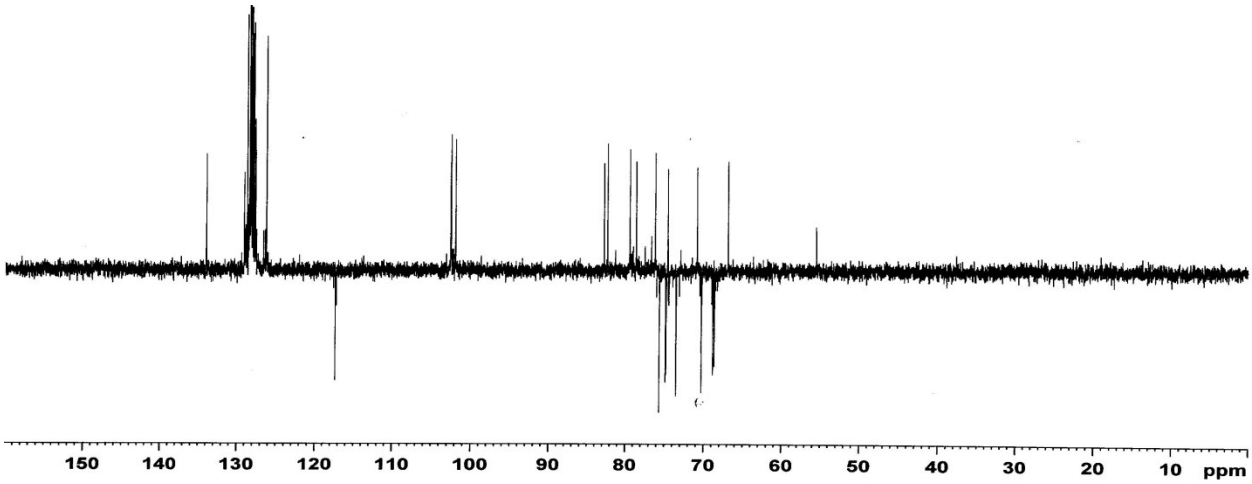

Ph
OBn
O
O
PMBO
O
O
BnO
BnO
O
SEt
OBn

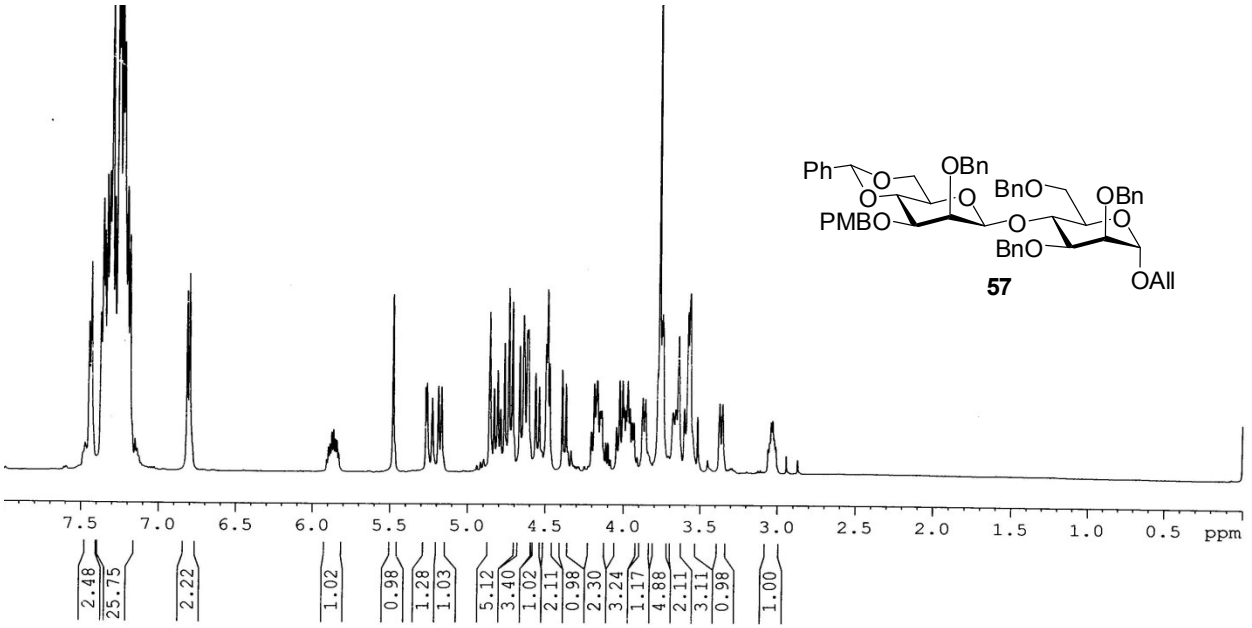
55

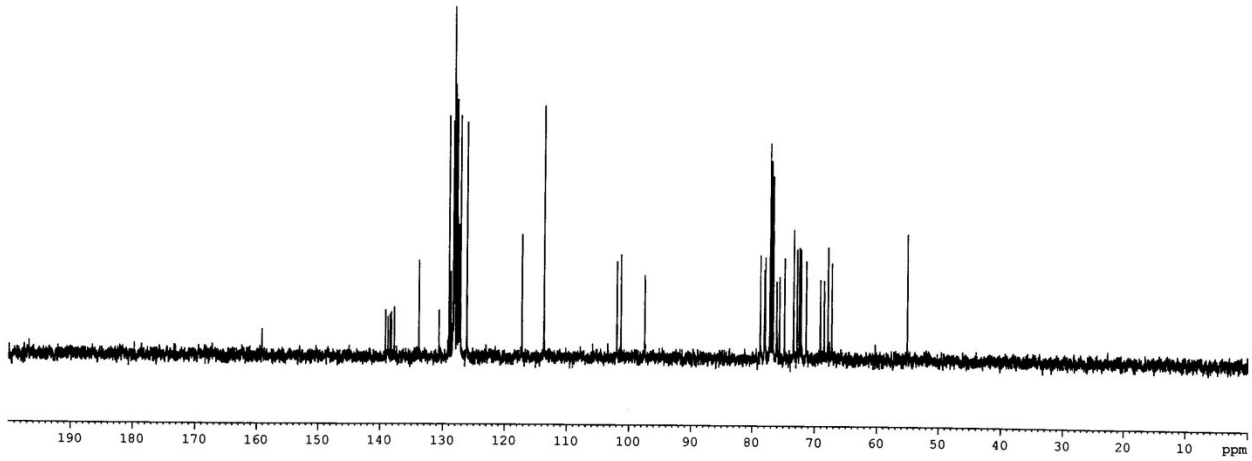

ppm
50
55
60
65
70
75
80
85
90
95
100
105
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
ppm

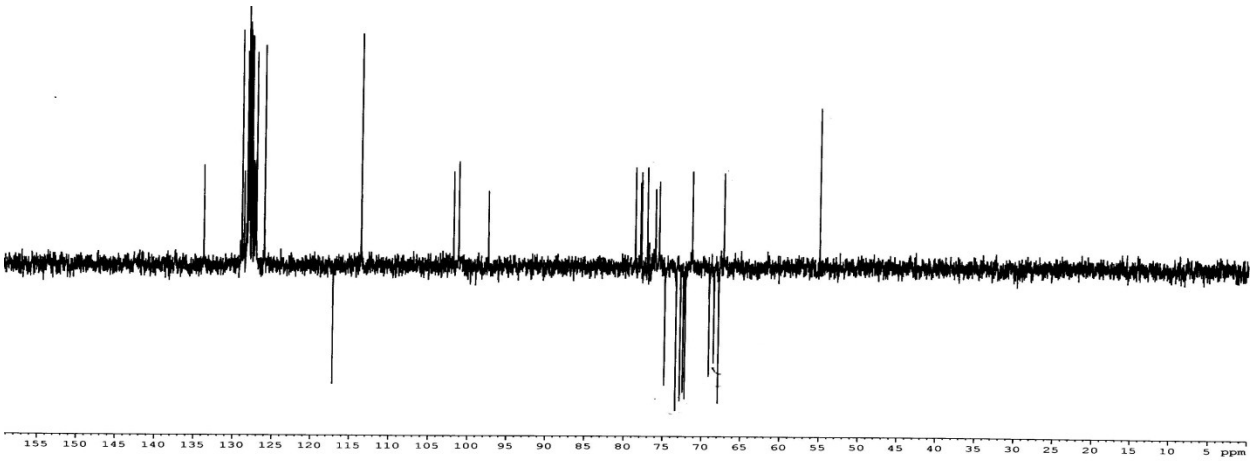

Ph
O
O
OBn
O
BnO
PMBO
O
OBn
O
OAll
OBn
56
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.50
24.39
1.00
0.75
0.97
0.94
0.77
1.79
0.75
2.13
2.01
1.92
1.02
2.60
0.93
5.47
4.62
0.82

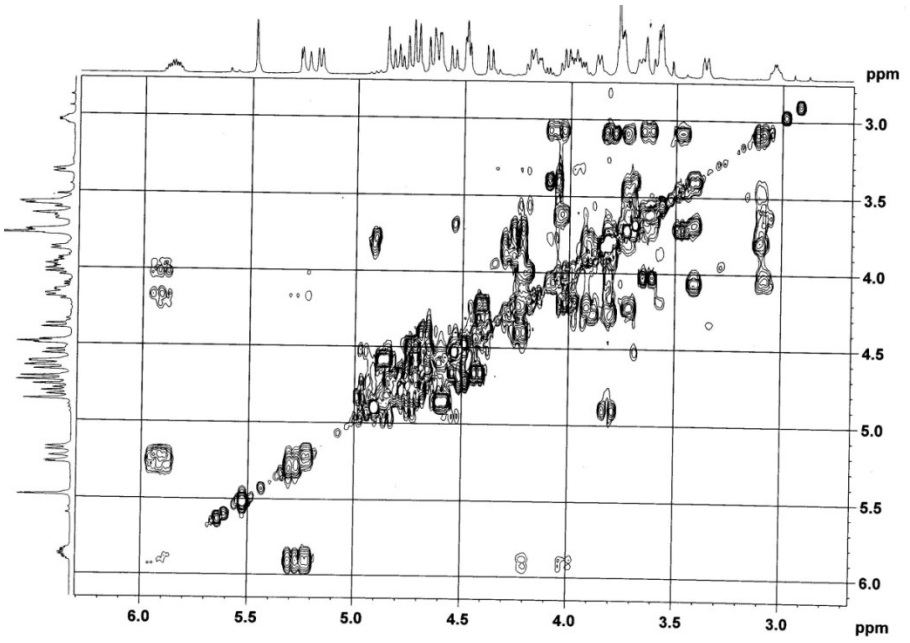

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

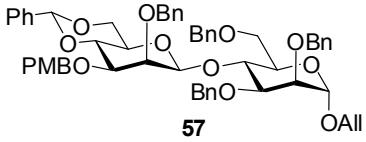

150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Ph
OBn
BnO
OBn
PMBO
BnO
OAll
57
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 ppm
2.48
25.75
2.22
1.02
0.98
1.28
1.03
5.12
3.40
1.02
2.11
0.98
2.30
3.24
1.17
4.88
2.11
3.11
0.98
1.00

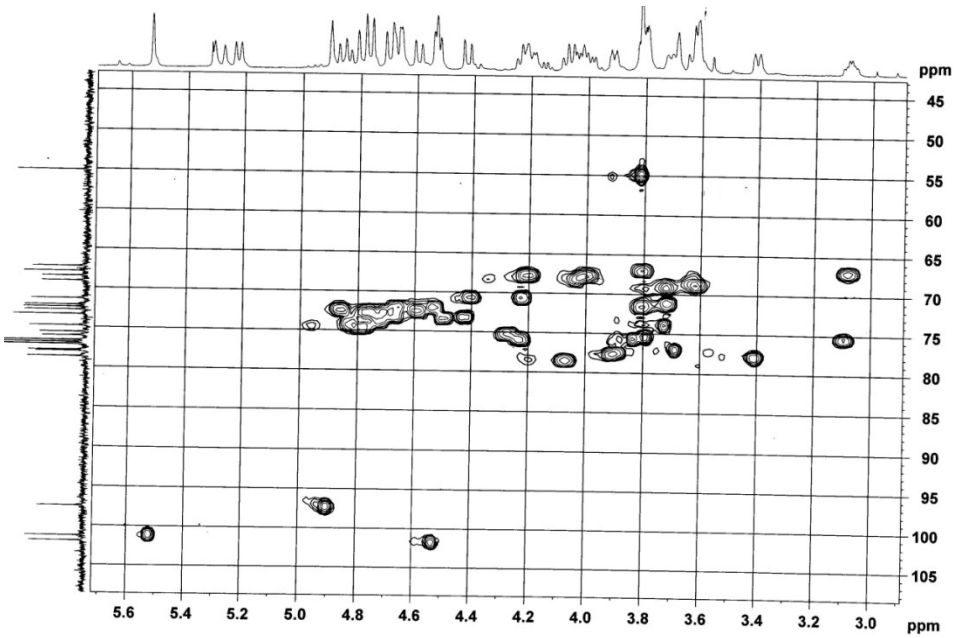

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

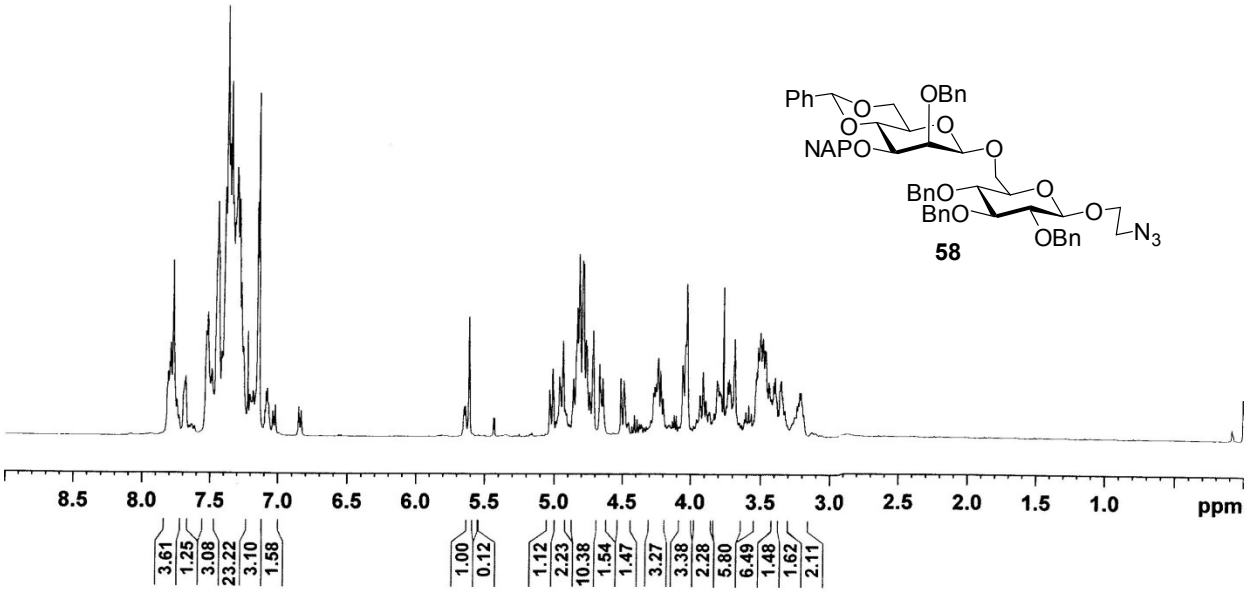

155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 ppm


ppm
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm


Ph
OBn
BnO
OBn
PMBO
BnO
OAll

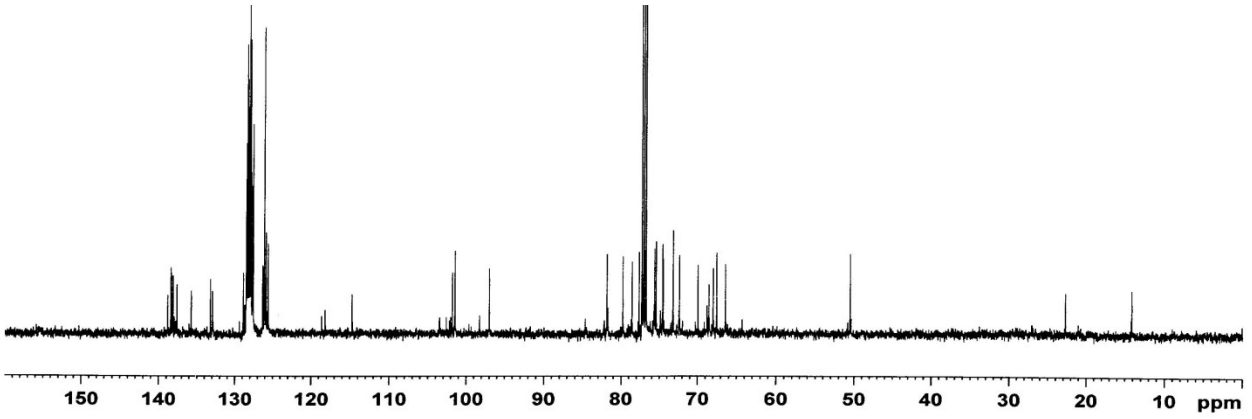
57

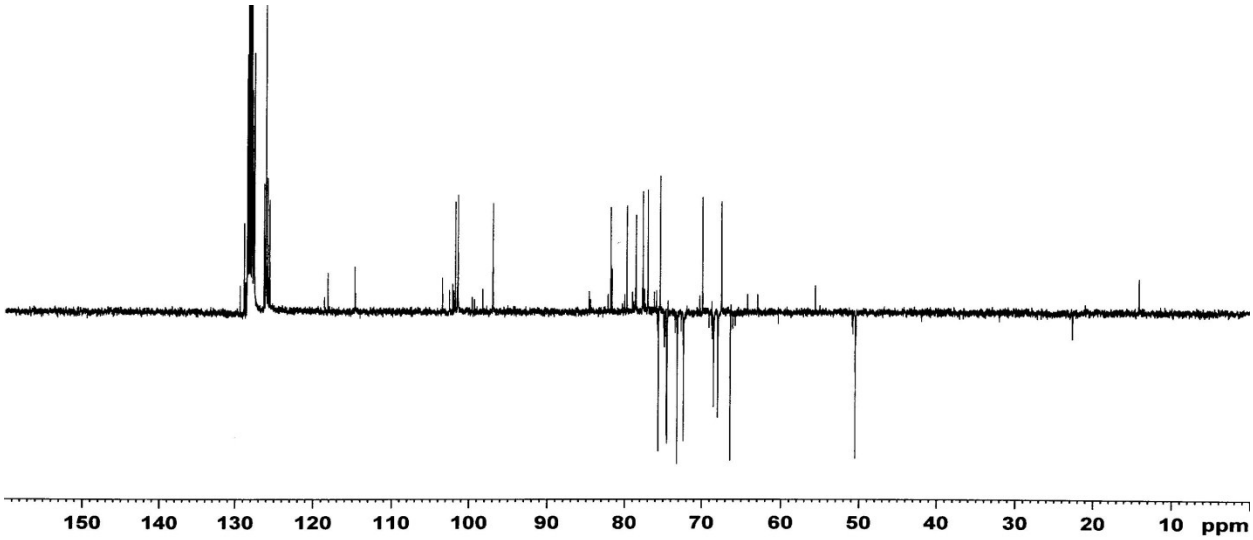

ppm
45
50
55
60
65
70
75
80
85
90
95
100
105
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
ppm

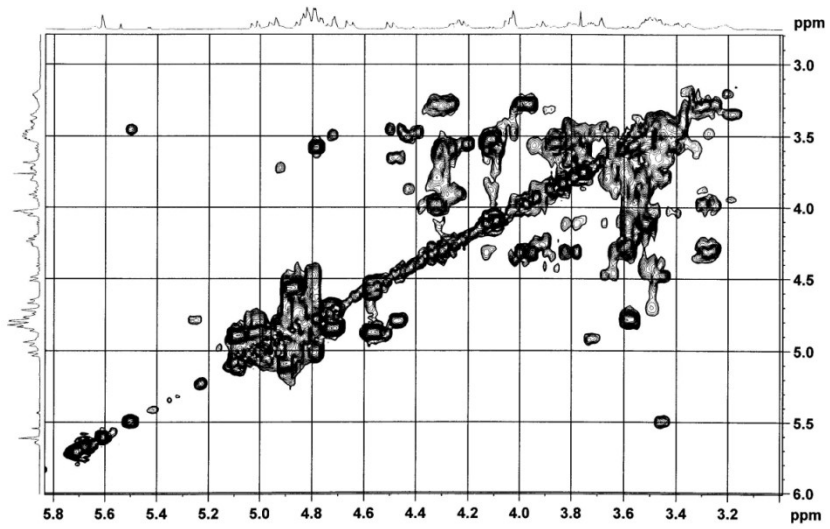

Ph
O
OBn
O
O
NAPO
O
BnO
O
BnO
O
N3
OBn

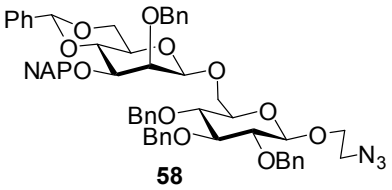
58

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 1.0 ppm
3.61 1.25 3.08 23.22 3.10 1.58 1.00 0.12 1.12 2.23 10.38 1.54 1.47 3.27 3.38 2.28 5.80 6.49 1.48 1.62 2.11

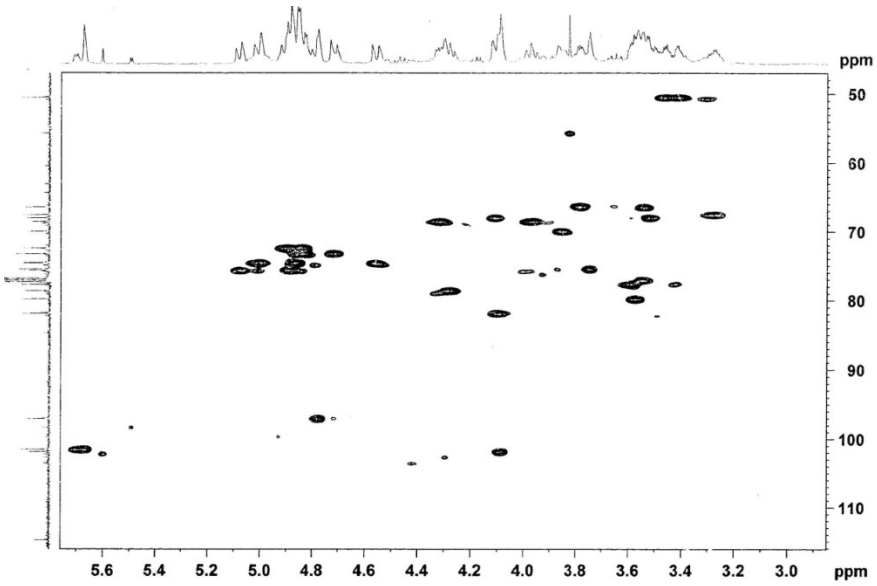

150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

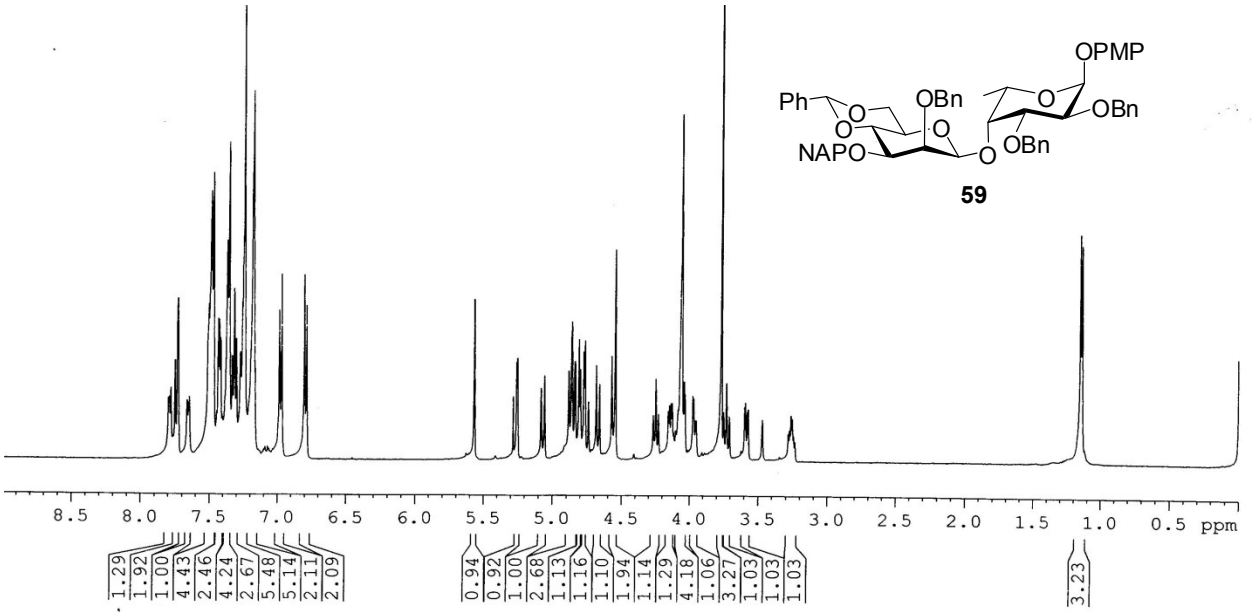

150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

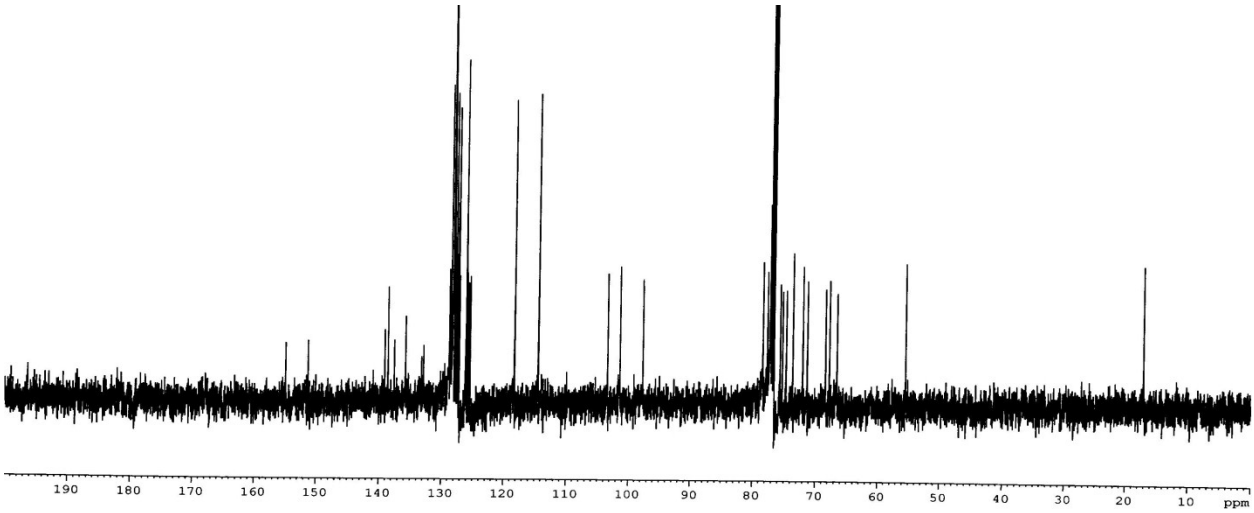

ppm
3.0
3.5
4.0
4.5
5.0
5.5
6.0
5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2
ppm

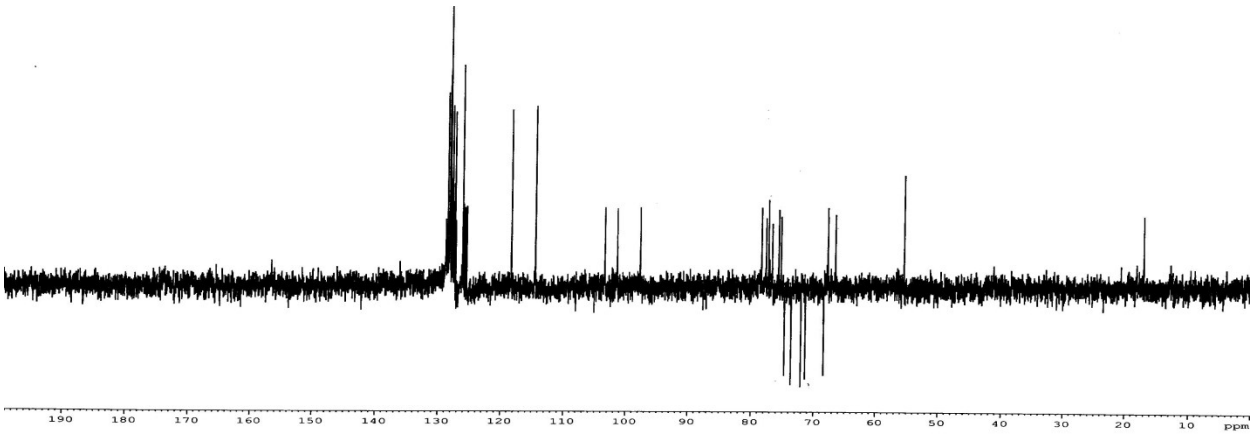

Ph
OBn
O
O
NAPO
O
BnO
BnO
O
O
OBn
N3

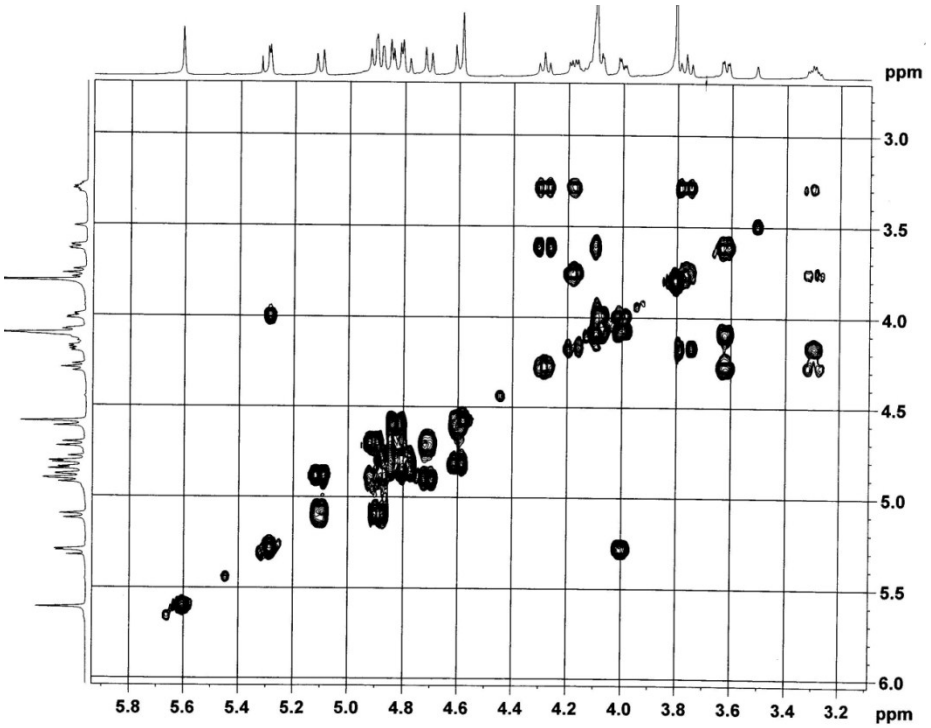
58

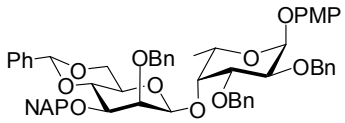

ppm
50
60
70
80
90
100
110
5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0
ppm


OPMP
Ph
OBn
O
O
O
O
OBn
NAPO
O
OBn
59
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 1.0 0.5 ppm
1.29 1.92 1.00 4.43 2.46 4.24 2.67 5.48 5.14 2.11 2.09
0.94 0.92 1.00 2.68 1.13 1.16 1.10 1.94 1.14 1.29 4.18 1.06 3.27 1.03 1.03 1.03
3.23

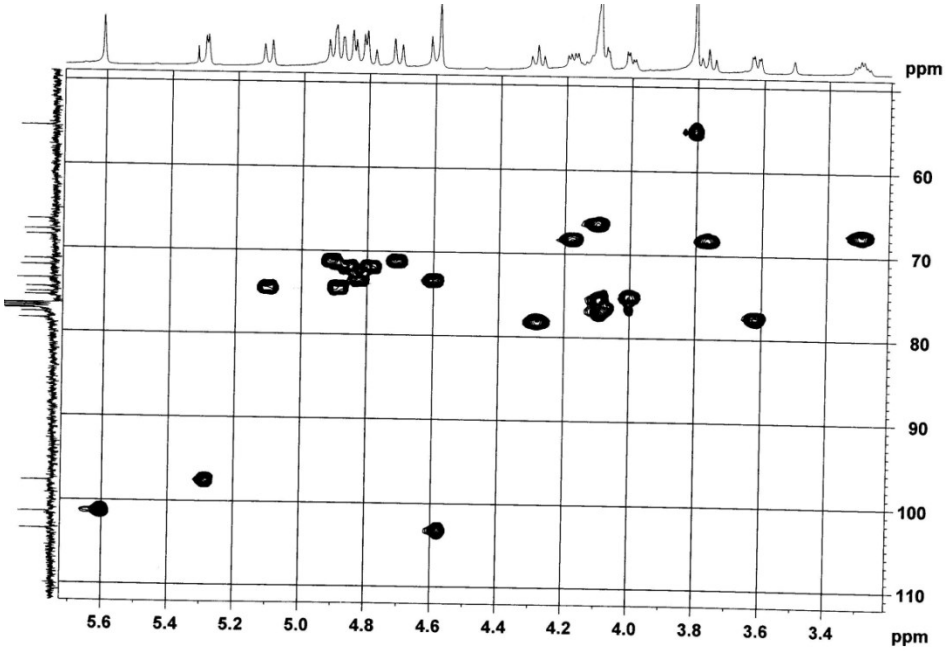

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

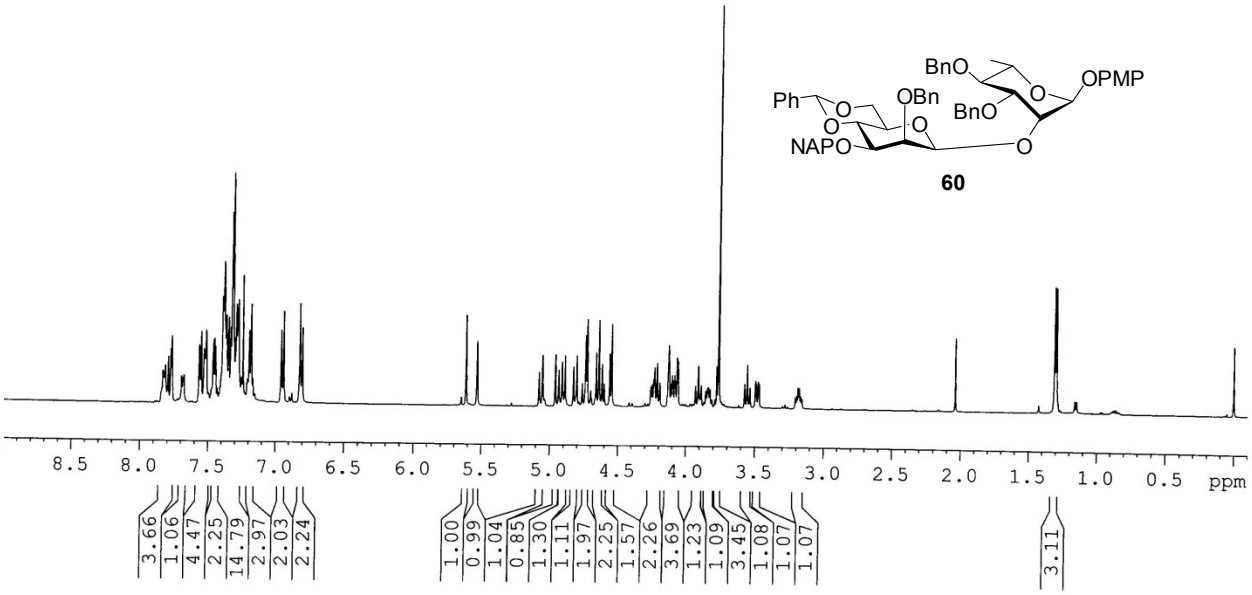

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

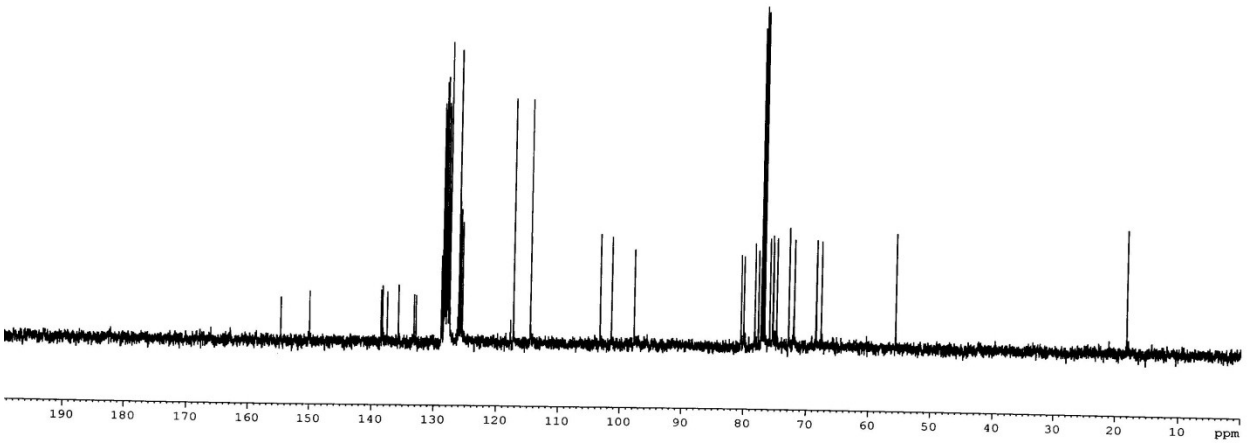

ppm
3.0
3.5
4.0
4.5
5.0
5.5
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
ppm

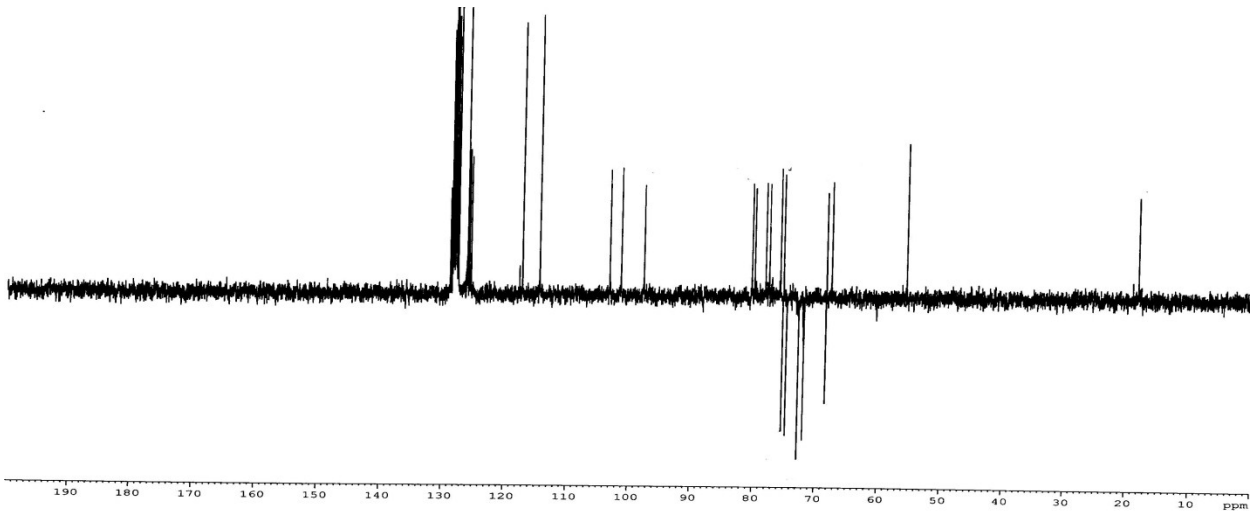

OPMP
Ph
O
OBn
O
O
O
OBn
NAPO
O
OBn

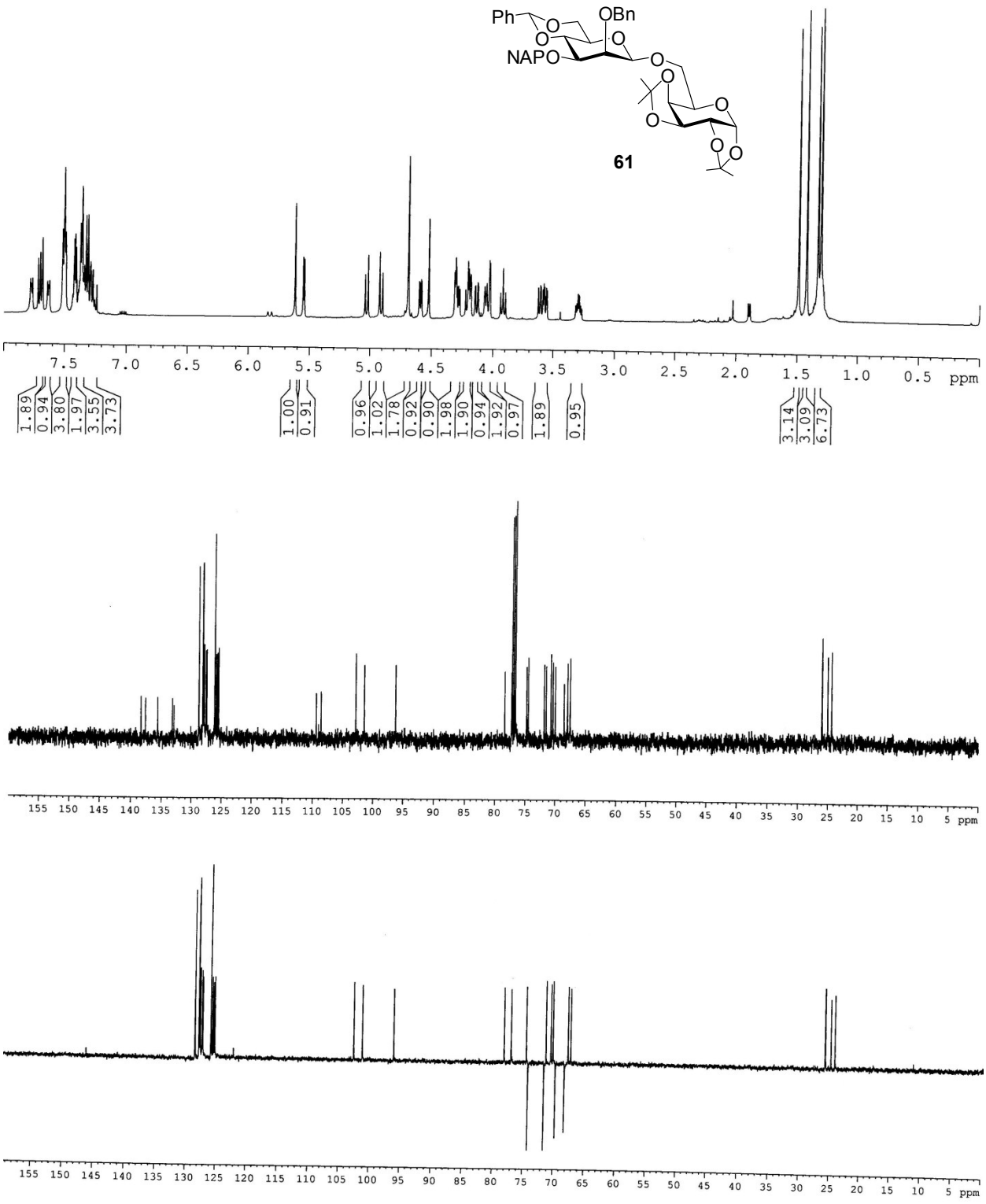
59

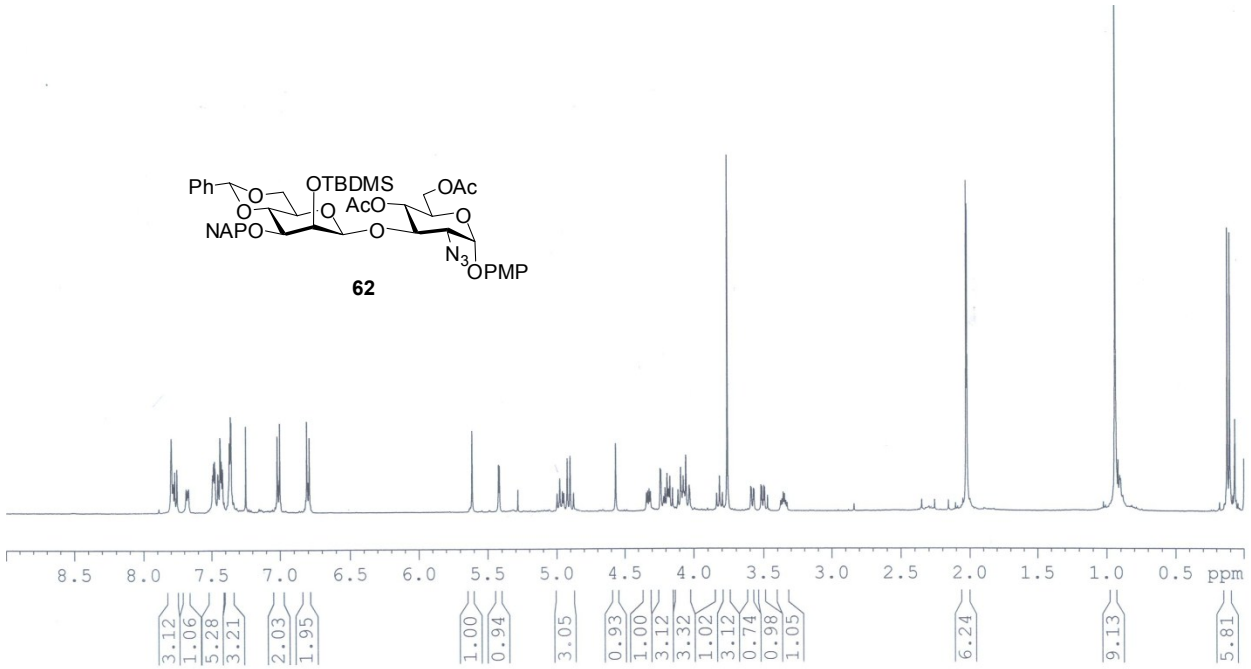

ppm
60
70
80
90
100
110
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
ppm


BnO
OPMP
Ph
OBn
BnO
O
O
O
NAPO
O
60
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 1.0 0.5 ppm
3.66 1.06 4.47 2.25 14.79 2.97 2.03 2.24
1.00 0.99 1.04 0.85 1.30 1.11 1.97 2.25 1.57 2.26 3.69 1.23 1.09 3.45 1.08 1.07 1.07
3.11

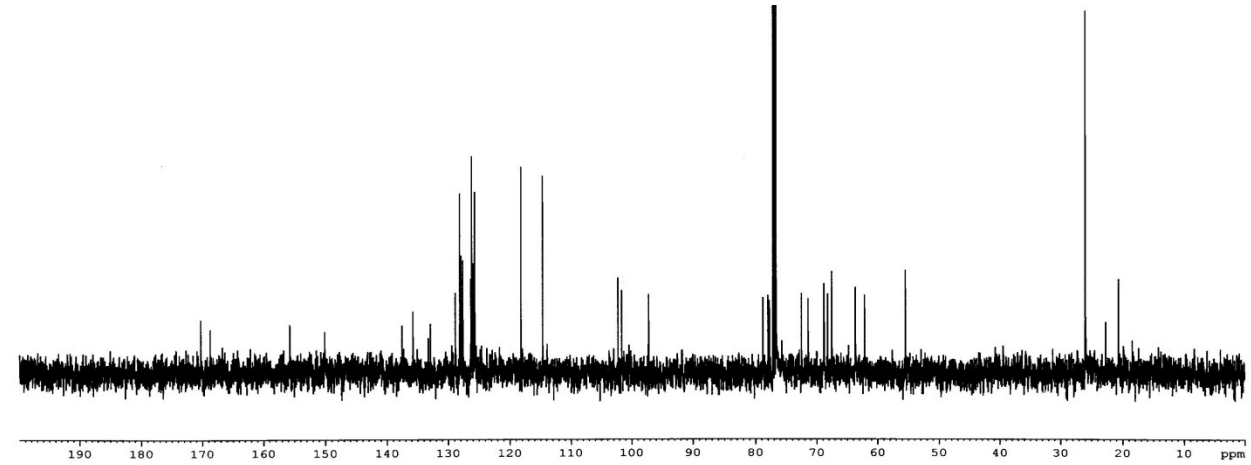

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

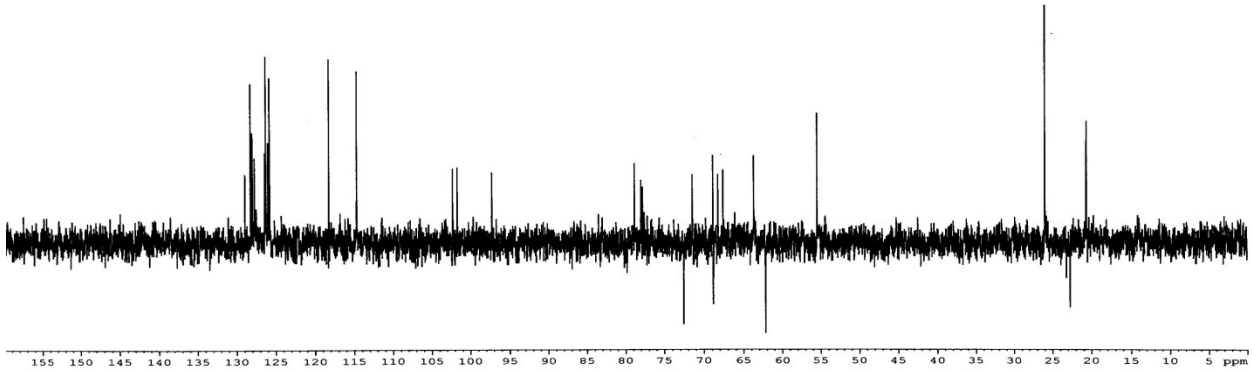

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

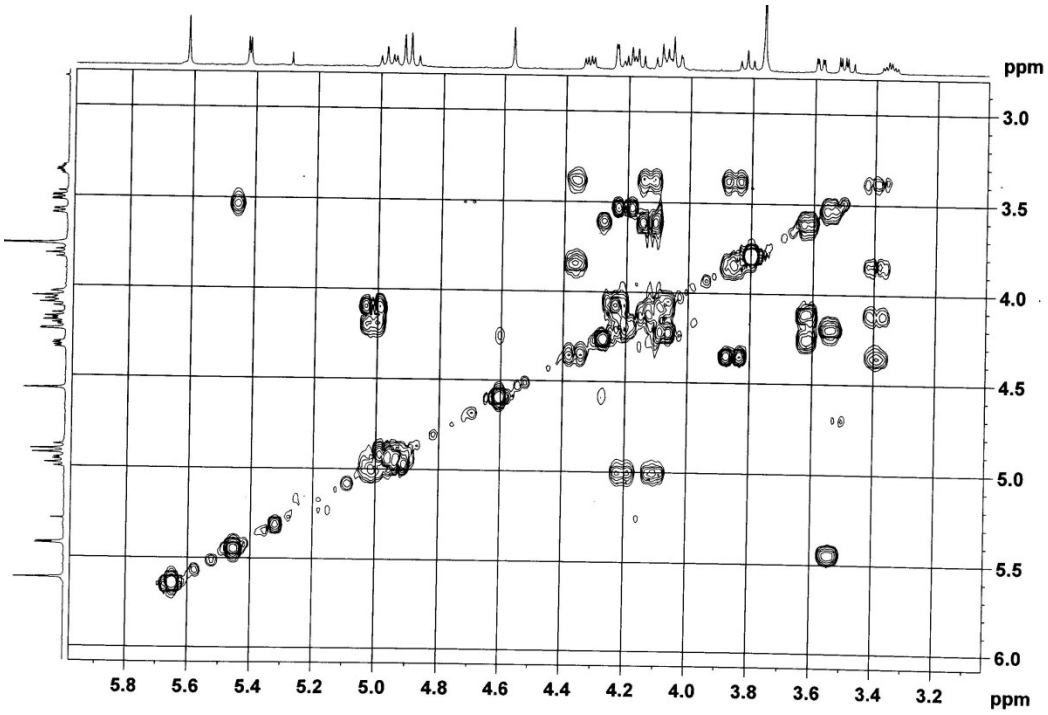

Ph
OBn
NAPO
61
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.89 0.94 3.80 1.97 3.55 3.73
1.00 0.91
0.96 1.02 1.78 0.92 0.90 1.98 1.90 0.94 1.92 0.97
1.89
0.95
3.14 3.09 6.73
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 ppm
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 ppm

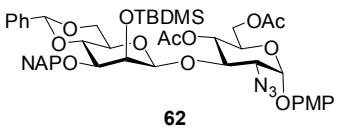

Ph
O
O
NAPO
OTBDMS
O
AcO
OAc
O
O
N3
OPMP
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
3.12 1.06 5.28 3.21 2.03 1.95 1.00 0.94 3.05 0.93 1.00 3.12 3.32 1.02 3.12 0.74 0.98 1.05 6.24 9.13 5.81

62

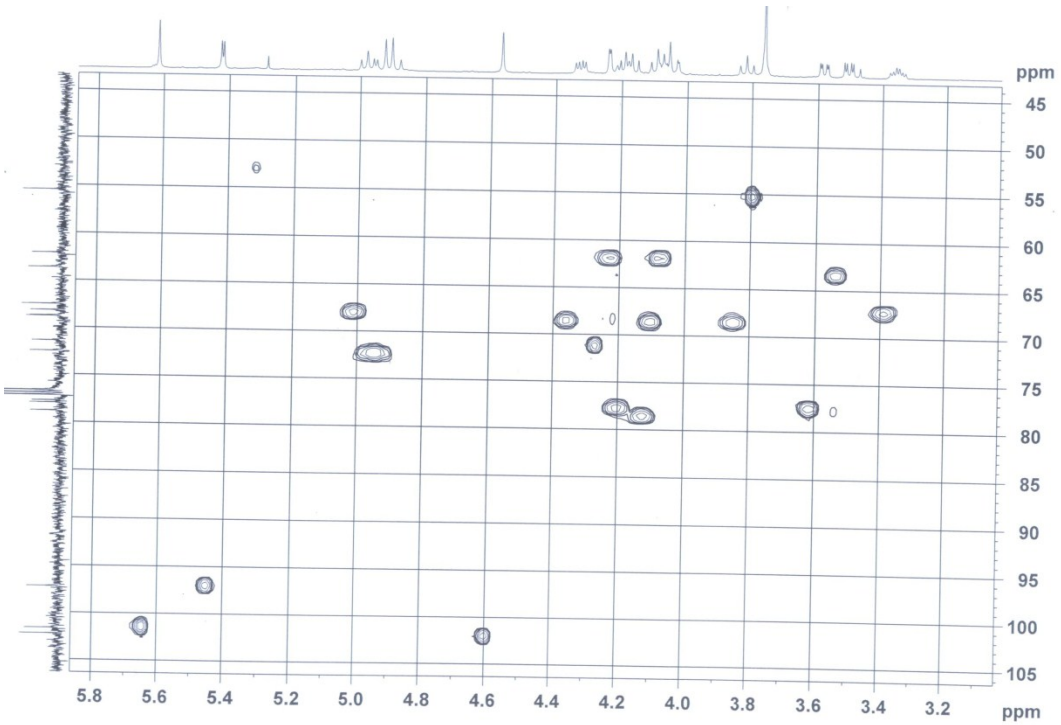

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

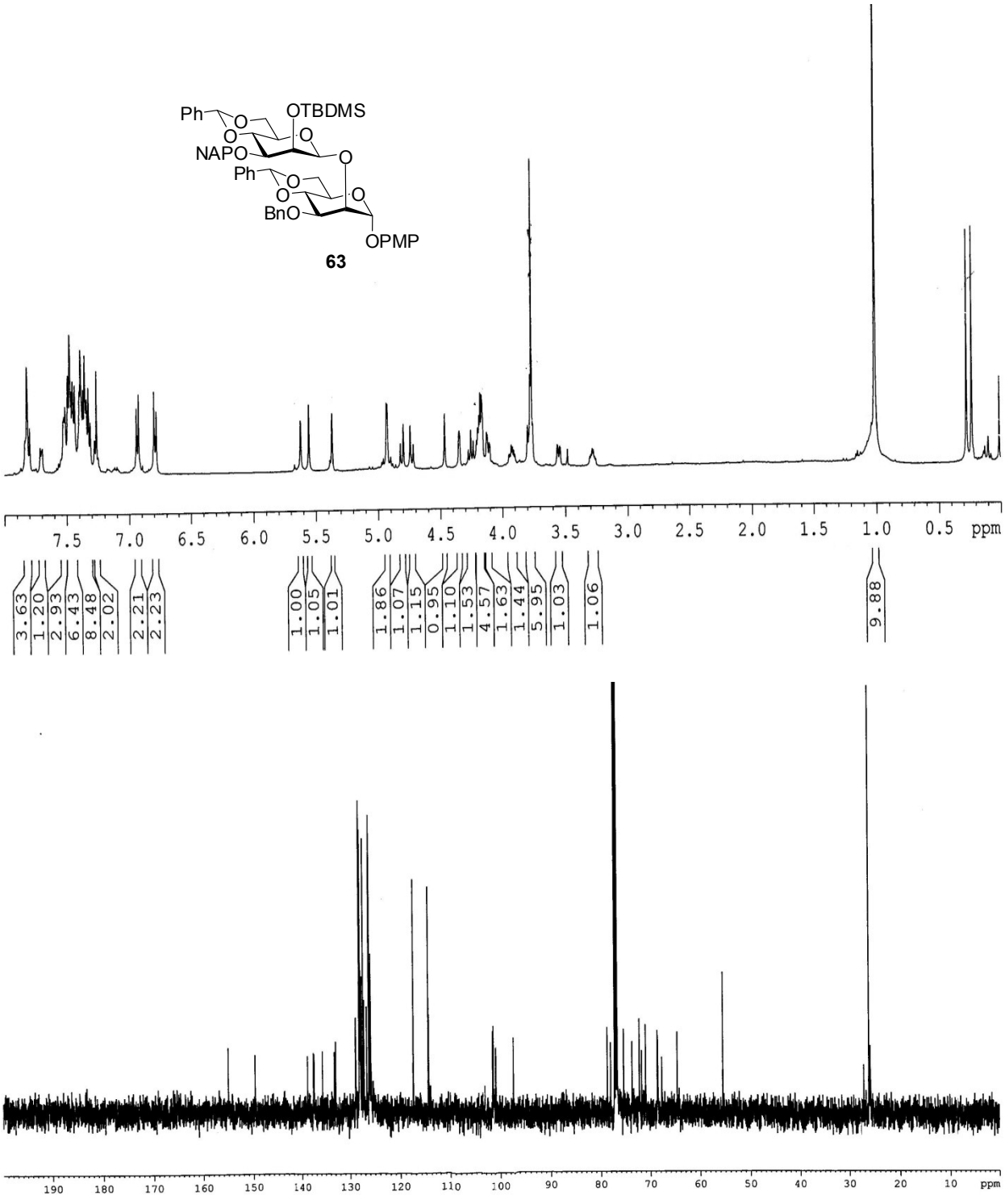

155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 ppm

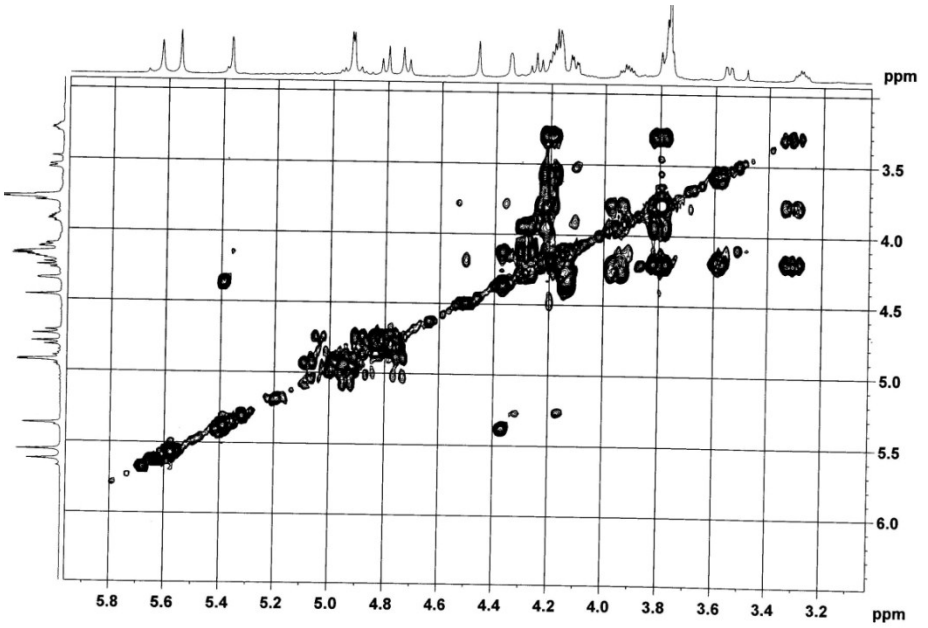

ppm
3.0
3.5
4.0
4.5
5.0
5.5
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
ppm

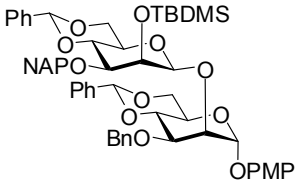

Ph
O
O
NAPO
OTBDMS
O
AcO
O
OAc
O
N3
OPMP

62

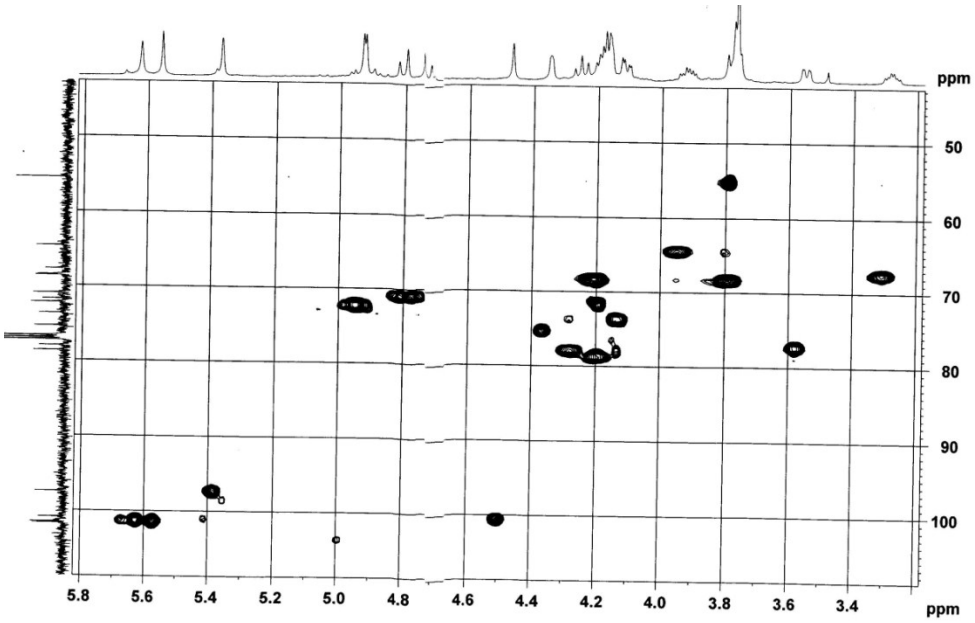

ppm
45
50
55
60
65
70
75
80
85
90
95
100
105
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
ppm

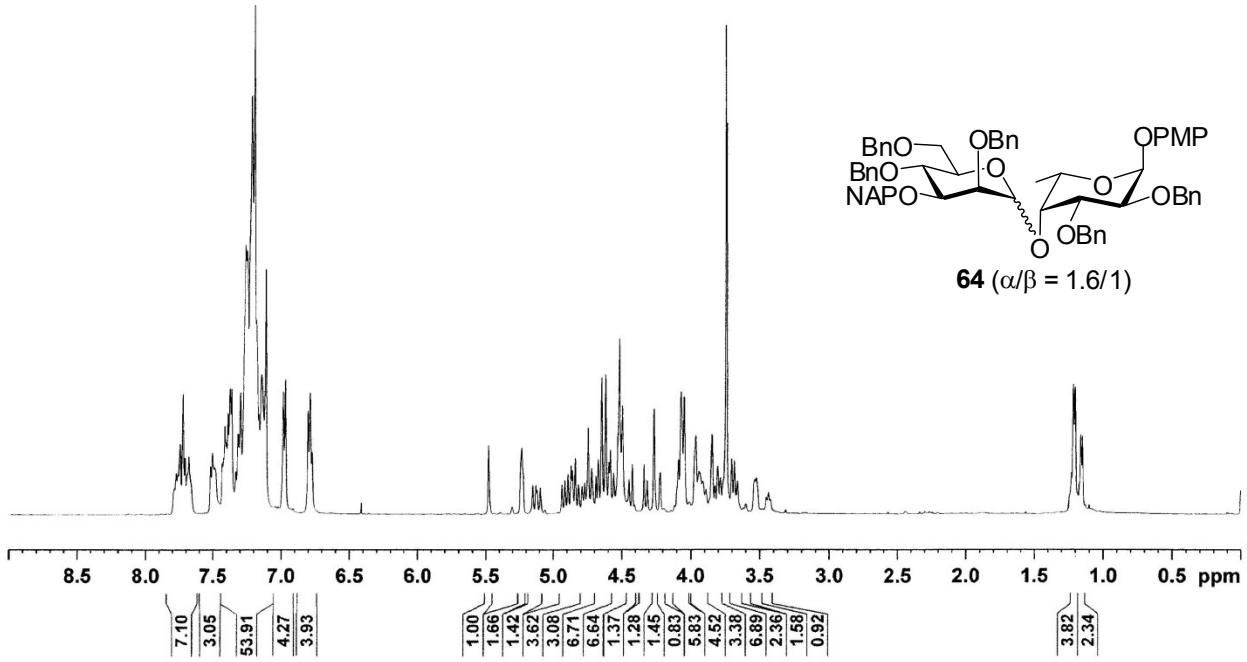

Ph
OTBDMS
O
O
O
NAPO
O
Ph
O
O
O
BnO
OPMP
63
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
3.63
1.20
2.93
6.43
8.48
2.02
2.21
2.23
1.00
1.05
1.01
1.86
1.07
1.15
0.95
1.10
1.53
4.57
1.63
1.44
5.95
1.03
1.06
9.88
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


ppm
3.5
4.0
4.5
5.0
5.5
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

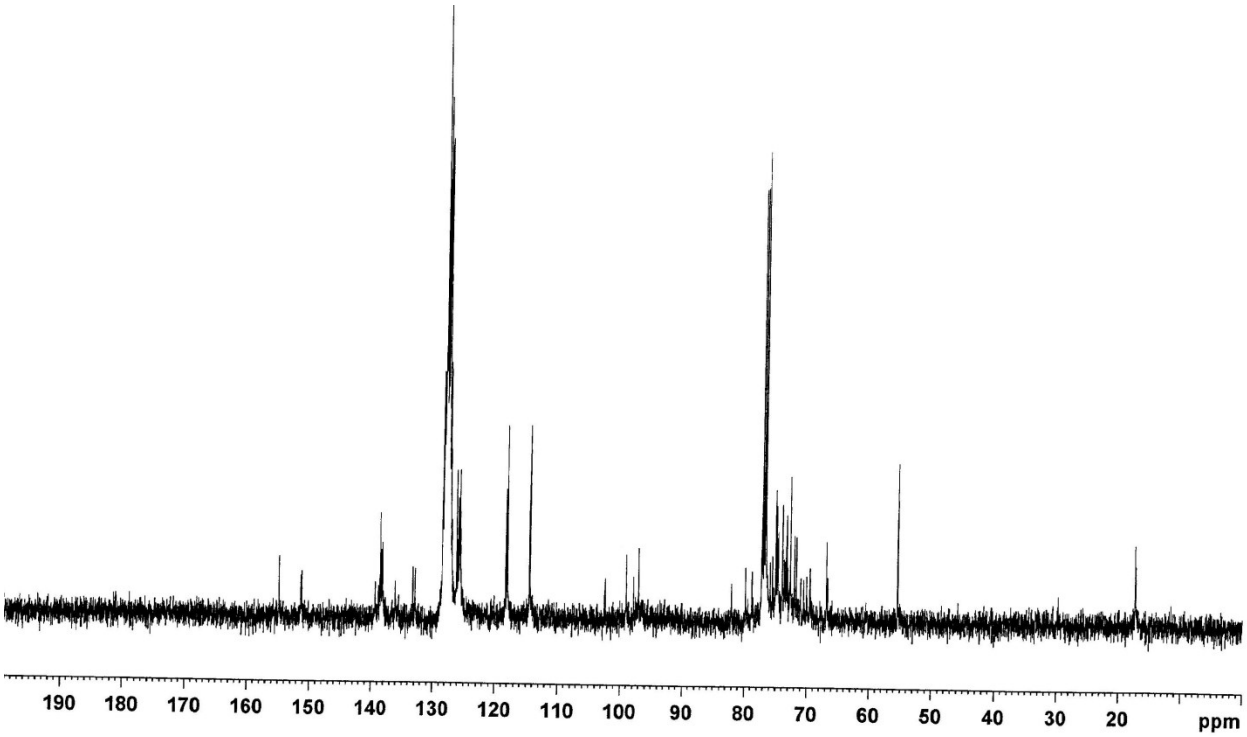

Ph
O
OTBDMS
O
O
NAPO
O
Ph
O
O
O
BnO
OPMP

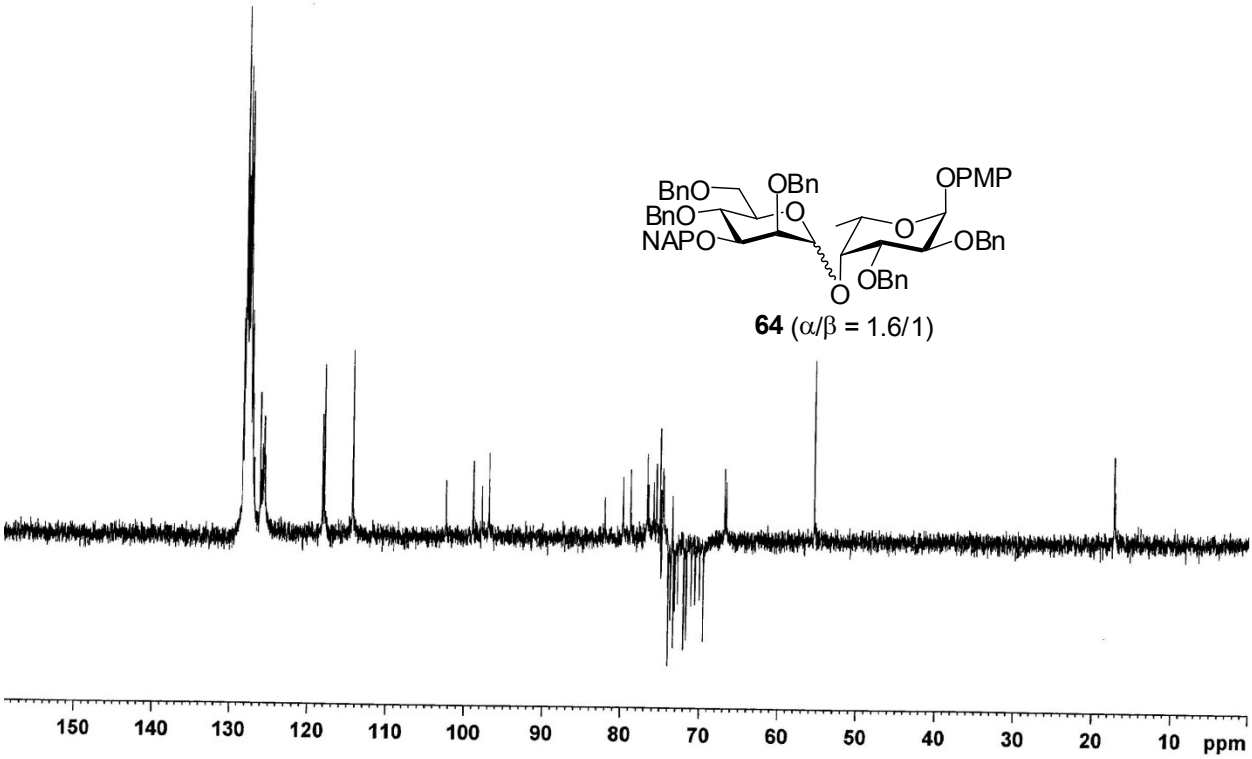
63


ppm
50
60
70
80
90
100
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



64 (α/β = 1.6/1)





64 (α/β = 1.6/1)