BEILSTEIN JOURNAL OF ORGANIC CHEMISTRY

Supporting Information

for

Synthesis of the tetrasaccharide repeating unit of the *O*-specific polysaccharide of *Azospirillum doebereinerae* type strain GSF71^T using linear and one-pot iterative glycosylations

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Analytical data and NMR spectra of compounds 1, 5, 6 and 7

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1D (^{1}H and ^{13}C NMR) and 2D NMR (COSY and HSQC) spectra of compounds **1**, **5**, **6** and **7** S5–S12

Analytical data of the synthesized products

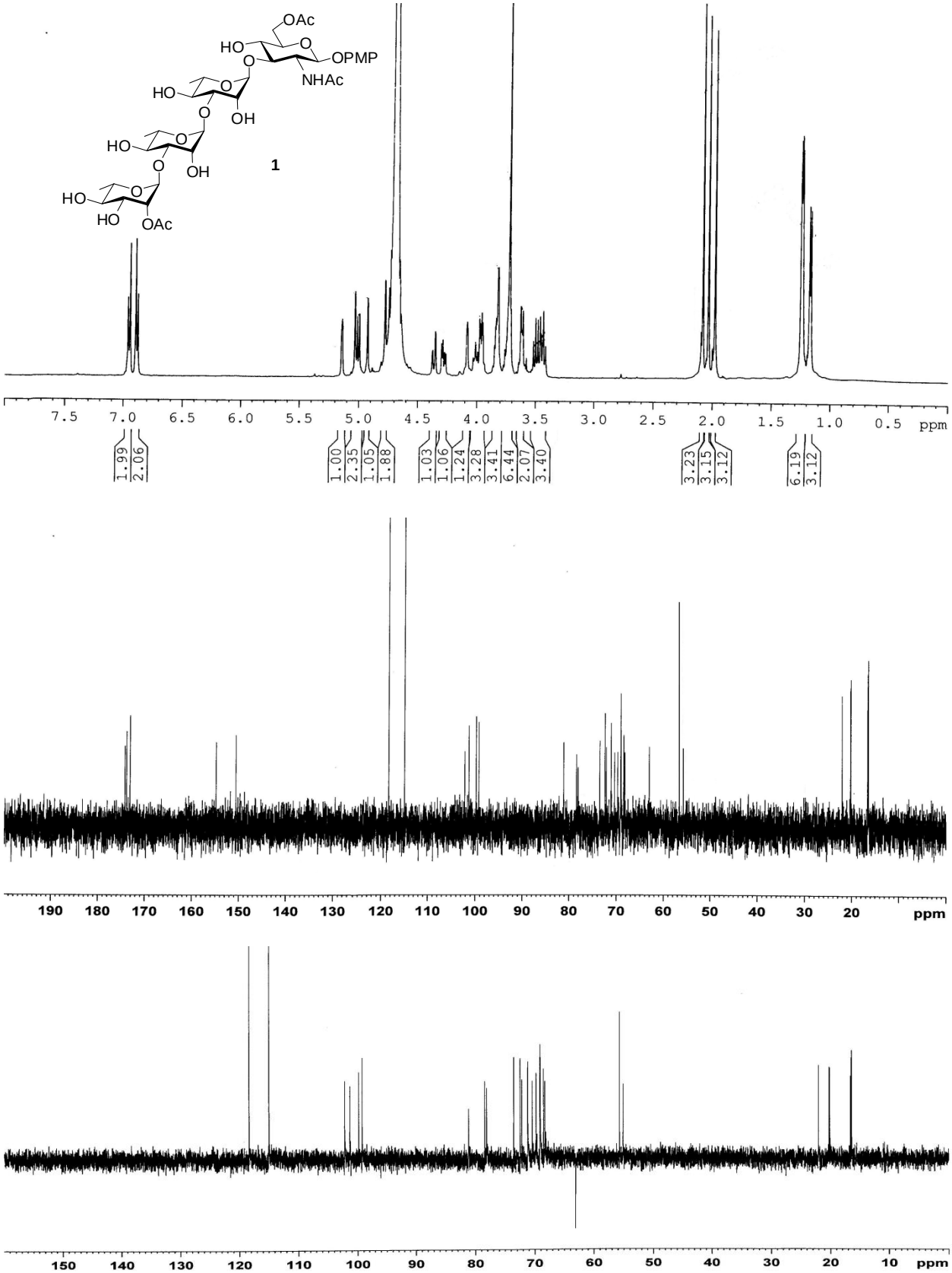
***p*-Methoxyphenyl (2,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (5):** Colorless syrup; $[\alpha]_D$ –11 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.42-6.80 (m, 19 H, Ar-*H*), 5.47 (s, 1 H, PhC*H*), 5.13 (br s, 1 H, H-1_B), 4.81 (d, *J* = 7.5 Hz, 1 H, H-1_A), 4.80 (d, *J* = 11.0 Hz, 1 H, PhC*H*), 4.74 (d, *J* = 11.0Hz, 1 H, PhC*H*), 4.62 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 4.55 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 4.35 (dd, *J* = 12.0 Hz, 5.5 Hz, 1 H, H-6_{aA}), 3.89-3.79 (m, 2 H, H-3_B, H-5_B), 3.77-3.74 (m, 5 H, H-2_B, H-6_{bA}, OCH_3), 3.66 (t, *J* = 9.5 Hz, 1 H, H-3_A), 3.60 (t, *J* = 8.0 Hz, 1 H, H-2_A), 3.55 (t, *J* = 9.0 Hz, 1 H, H-4_A), 3.49-3.46 (m, 1 H, H-5_A), 3.23 (t, *J* = 9.5 Hz, 1 H, H-4_B), 2.20-2.18 (m, 1 H, O*H*), 0.81 (d, *J* = 6.0 Hz, 1 H, CCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.9-114.6 (Ar-*C*), 102.1 (C-1_A), 102.0 (Ph*C*H), 97.8 (C-1_B), 82.2 (C-4_B), 79.1 (C-4_A), 77.9 (C-2_B), 75.8 (C-3_A), 74.6 (Ph*C*H_2), 72.8 (Ph*C*H_2), 71.2 (C-3_B), 68.4 (C-6_A), 67.4 (C-5_B), 67.0 (C-2_A), 66.8 (C-5_A), 55.4 (O*C*H_3), 17.3 (C*C*H_3); HRMS (ESI) calcd. for $C_{40}H_{43}N_3O_{10}$ (725.2948): $[M+H]^+$ 726.3026; found: 726.3034.

***p*-Methoxyphenyl (2,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-(2,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (6):** Colorless syrup; $[\alpha]_D$ –7 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.47-6.82 (m, 29 H, Ar-*H*), 5.54 (s, 1 H, PhC*H*), 5.17 (br s, 1 H, H-1_C), 5.11 (br s, 1 H, H-1_B), 4.93 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 4.82 (d, *J* = 8.0 Hz, 1 H, H-1_A), 4.74-4.72 (m, 3 H, 3 PhC*H*), 4.65 (m, 3 H, 3 PhC*H*), 4.38 (dd, *J* = 10.5 Hz, 4.5 Hz, 1 H, H-6_{aA}), 4.07 (dd, *J* = 10.0 Hz, 3.0 Hz, 1 H, H-3_B), 4.04 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 3.98-3.94 (m, 2 H, H-5_B, H-6_{bA}), 3.81 (t, *J* = 9.0 Hz, 1 H, H-3_C), 3.77 (s, 3 H, OCH_3), 3.73-3.71 (m, 2 H, H-2_B, H-5_C), 3.69-3.62 (m, 2 H, H-2_C, H-3_A), 3.60 (t, *J* = 9.0 Hz, 1 H, H-2_A), 3.56 (t, *J* = 9.5 Hz, 1 H, H-4_A), 3.54 (t, *J* = 9.5 Hz, 1 H, H-4_C), 3.50-3.45 (m, 1 H, H-5_A), 3.28 (t, *J* = 9.5 Hz, 1 H, H-4_B), 1.27 (d, *J* = 6.0 Hz, 3 H, CCH_3), 0.82 (d, *J* = 6.0 Hz, 3 H, CCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 129.0-114.6 (Ar-*C*), 102.1 (C-1_A), 102.0 (Ph*C*H), 98.7 (C-1_C), 98.4 (C-1_B), 82.2 (C-4_B), 80.9 (C-4_C), 79.2 (C-2_C), 79.0 (C-4_A), 77.4 (C-3_B), 76.9 (C-2_B), 75.8 (C-3_A), 74.9 (Ph*C*H_2), 74.4 (Ph*C*H_2), 72.5 (Ph*C*H_2), 72.3 (Ph*C*H_2), 71.6 (C-5_B), 68.5 (C-6_A), 68.4 (C-3_C), 67.7 (C-2_A), 67.0 (C-5_C), 66.8 (C-5_A), 55.5 (O*C*H_3), 18.0 (C*C*H_3), 17.2 (C*C*H_3); HRMS (ESI) calcd. for $C_{60}H_{65}N_3O_{14}$ (1051.4467): $[M+H]^+$ 1052.4545; found: 1052.4552.

***p*-Methoxyphenyl (2-*O*-acetyl-3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-(2,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-(2,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (7):** Colorless syrup; $[\alpha]_D$ − 12 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44-6.80 (m, 39 H, Ar-*H*), 5.51 (s, 1 H, PhC*H*), 5.46 (s, 1 H, H-2_D), 5.12 (br s, 1 H, H-1_D), 5.08 (br s, 1 H, H-1_C), 5.07 (br s, 1 H, H-1_B), 4.90 (d, *J* = 11.0 Hz, 1 H, PhC*H*), 4.80 (d, *J* = 8.0 Hz, 1 H, H-1_A), 4.79 (d, *J* = 11.0 Hz, 1 H, PhC*H*), 4.71 (s, 1 H, PhC*H*), 4.69 (br s, 1 H, PhC*H*), 4.64-4.53 (m, 5 H, 5 PhC*H*), 4.40 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 4.36 (dd, *J* = 11.5 Hz, 5.5 Hz, 1 H, H-6_{aA}), 4.22 (d, *J* = 11.0 Hz, 1 H, PhC*H*), 4.20 (d, *J* = 11.0 Hz, 1 H, PhC*H*), 4.13 (dd, *J* = 9.5 Hz, 3.0 Hz, 1 H, H-3_B), 4.03 (dd, *J* = 10.0 Hz, 3.0 Hz, 1 H, H-3_C), 3.91-3.89 (m, 1 H, H-5_B), 3.89 (dd, *J* = 9.5 Hz, 3.0 Hz, 1 H, H-3_D), 3.83-3.77 (m, 2 H, H-5_C, H-5_D), 3.76 (s, 3 H, O*C*H$_3$), 3.67-3.65 (m, 3 H, H-2_B, H-2_C, H-6_{bA}), 3.67 (t, *J* = 9.0 Hz, 1 H, H-3_A), 3.60- 3.55 (m, H-2_A, H-4_A, H-4_C), 3.50 (t, *J* = 10.0 Hz, 1 H, H-4_D), 3.46-3.41 (m, 1 H, H-5_A), 3.37 (t, *J* = 9.0 Hz, 1 H, H-4_B), 2.08 (s, 3 H, COC*H*$_3$), 1.25 (d, *J* = 6.5 Hz, 3 H, CC*H*$_3$), 1.21 (d, *J* = 6.5 Hz, 3 H, CC*H*$_3$), 0.78 (d, *J* = 6.5 Hz, 3 H, CC*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.7 (*C*OCH$_3$), 155.9-114.6 (Ar-*C*), 102.1 (C-1_A), 101.9 (Ph*C*H), 99.3 (2 C, C-1_B, C-1_C), 98.4 (C-1_D), 80.9 (C-4_C), 80.8 (C-4_D), 79.9 (C-4_B), 79.0 (C-4_A), 78.5 (C-2_B), 77.8 (C-3_D), 77.7 (C-3_C), 77.4 (C-3_B), 77.1 (C-2_C), 75.9 (C-3_A), 75.1 (2 C, 2 Ph*C*H$_2$), 74.5 (Ph*C*H$_2$), 72.5 (Ph*C*H$_2$), 72.1 (Ph*C*H$_2$), 71.7 (Ph*C*H$_2$), 68.9 (C-2_D), 68.7 (C-6_A), 68.6 (C-5_B), 68.5 (C-5_C), 68.4 (C-5_D), 68.3 (C-2_A), 66.8 (C-5_A), 55.5 (O*C*H$_3$), 20.9 (CO*C*H$_3$), 18.2 (C*C*H$_3$), 18.0 (C*C*H$_3$), 17.2 (C*C*H$_3$); HRMS (ESI) calcd. for $C_{82}H_{89}N_3O_{19}$ (1419.6090): $[M+H]^+$ 1420.6168; found: 1420.6160.

***p*-Methoxyphenyl (2-*O*-acetyl-α-L-rhamnopyranosyl)-(1→3)-(α-L-rhamnopyranosyl)-(1→3)-(α-L-rhamnopyranosyl)-(1→3)-2-acetamido-6-*O*-acetyl-2-deoxy-β-D-glucopyranoside (1):** White powder; $[\alpha]_D$ −12 (*c* 1.0, H_2O); ^{1}H NMR (500 MHz, D_2O): δ 6.96-6.88 (m, 4 H, Ar-*H*), 5.14 (d, *J* = 1.5 H, 1 H, H-2_D), 5.03 (br s, 1 H, H-1_D), 5.03 (d, *J* = 10.0 Hz, 1 H, H-1_A), 4.92 (br s, 1 H, H-1_C), 4.78 (br s, 1 H, H-1_B), 4.37 (d, *J* = 9.5 Hz, 1 H, H-6_{aA}), 4.30 (dd, *J* = 12.0 Hz, 5.5 Hz, 1 H, H-6_{bA}), 4.08 (s, 1 H, H-3_C), 4.01 (t, *J* = 9.0 Hz, 1 H, H-2_A), 3.99-3.95 (m, 2 H, H-3_B, H-5_C), 3.85-3.82 (m, 3 H, H-2_B, H-3_D, H-5_B), 3.76-3.72 (m, 6 H, H-2_C, H-3_A, H-5_D, OC*H*$_3$), 3.63-3.61 (m, 2 H, H-4_A, H-5_A), 3.52-3.41 (m, 3 H, H-4_B, H-4_C, H-4_D), 2.08 (OCOC*H*$_3$), 2.03 (OCOC*H*$_3$), 1.98 (NHCOC*H*$_3$), 1.26-1.24 (m, 6 H, 2 CC*H*$_3$), 1.23 (d, *J* = 6.0 Hz, 3 H, CC*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.3 (2 C, 2 O*C*OCH$_3$), 173.9 (NH*C*OCH$_3$), 119.1-99.3 (Ar-*C*), 102.2 (C-1_C), 101.3 (C-1_B), 99.8 (C-1_A), 99.3 (C-1_D), 81.2 (C-4_A), 78.4 (C-2_B), 78.1

(C-2_C), 73.5 (C-3_A), 72.5 (C-2_D), 72.2 (C-4_D), 71.2 (2 C, C-4_B, C-4_C), 70.4 (C-3_D), 69.8 (C-3_B), 69.2 (C-3_C), 69.1 (C-5_D), 69.0 (C-5_C), 68.5 (C-5_B), 68.3 (C-5_A), 63.1 (C-6_A), 55.7 (O*C*H_3), 55.1 (C-2_A), 22.0 (NHCO*C*H_3), 20.3 (OCO*C*H_3), 20.2 (OCO*C*H_3), 16.6 (C*C*H_3), 16.5 (C*C*H_3), 16.4 (C*C*H_3); HRMS (ESI) calcd. for $C_{37}H_{55}NO_{21}$ (849.3267): $[M+H]^+$ 850.3345; found: 850.3354.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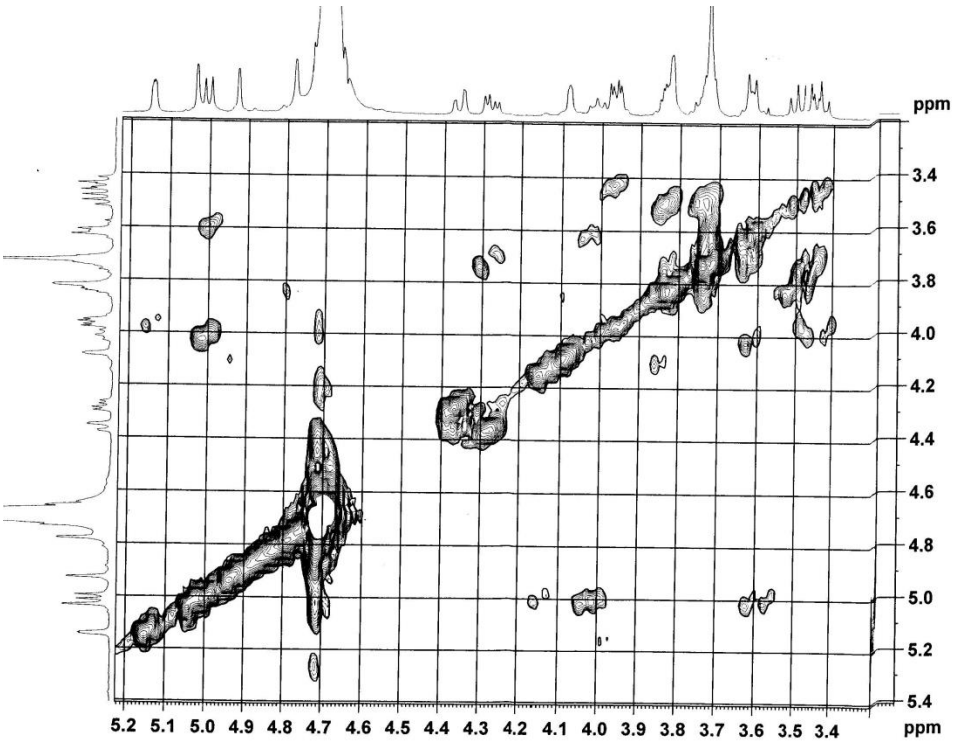
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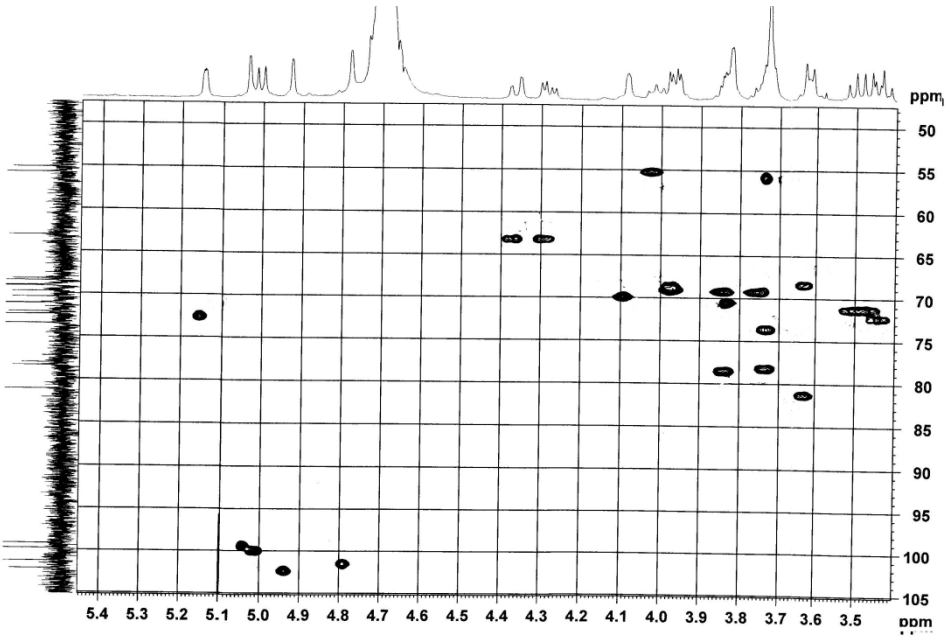
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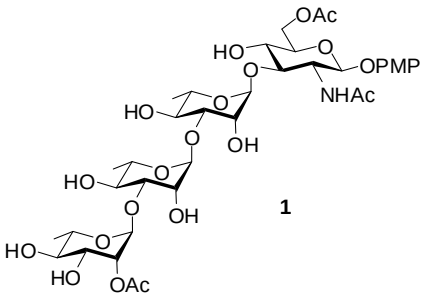
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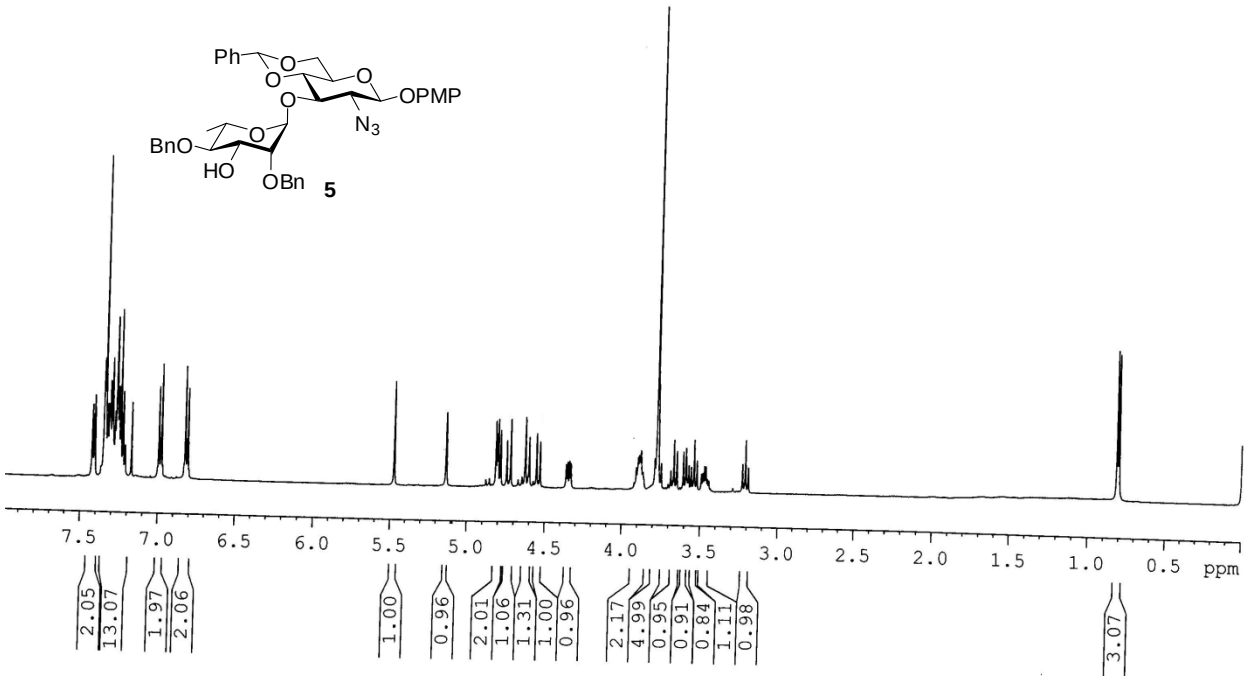
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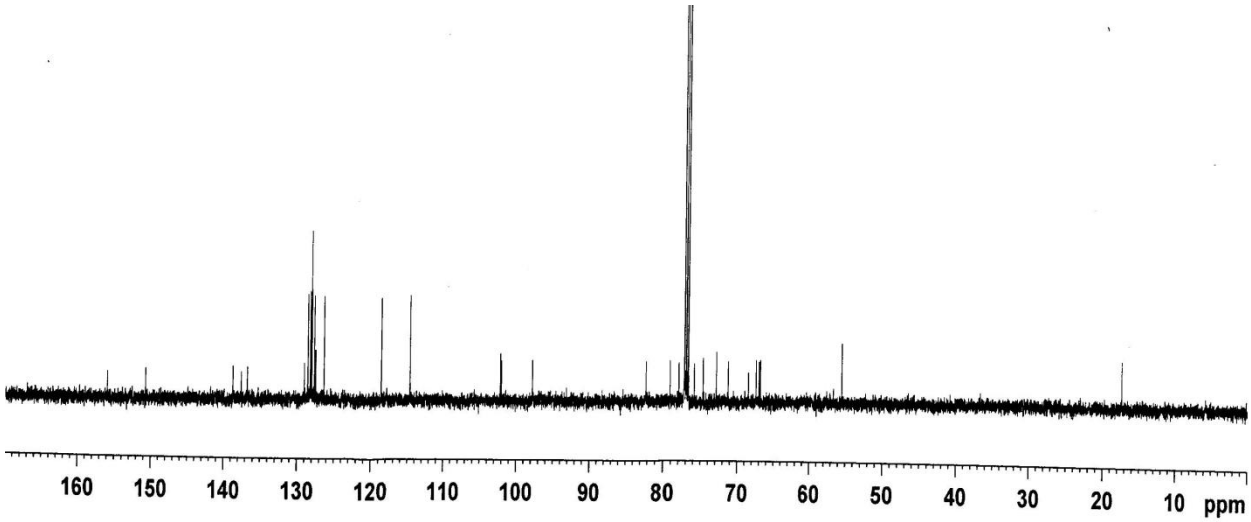
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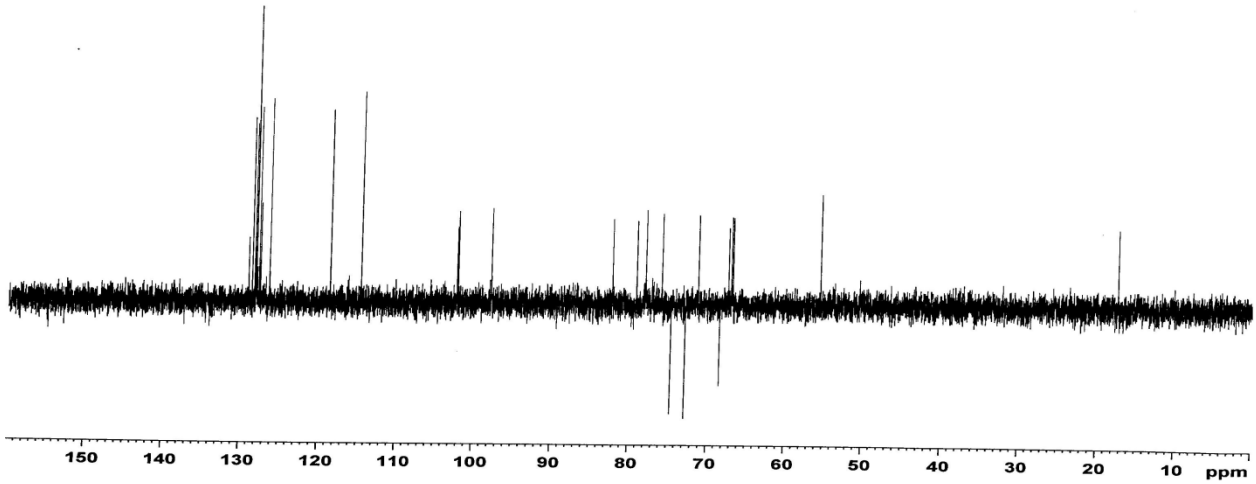
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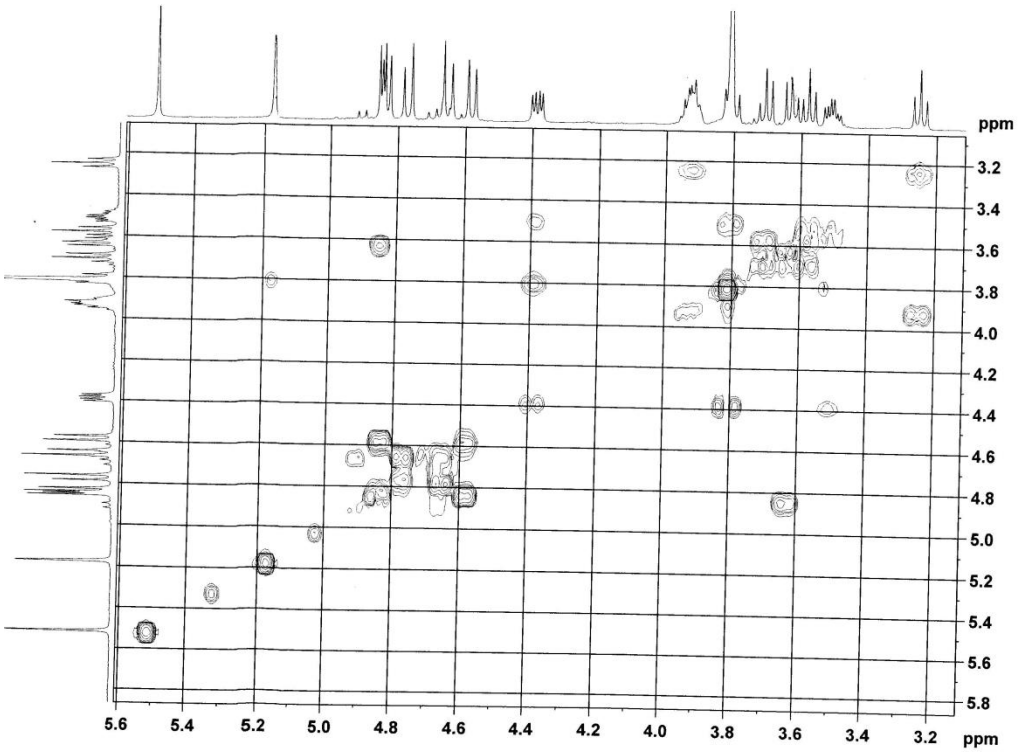
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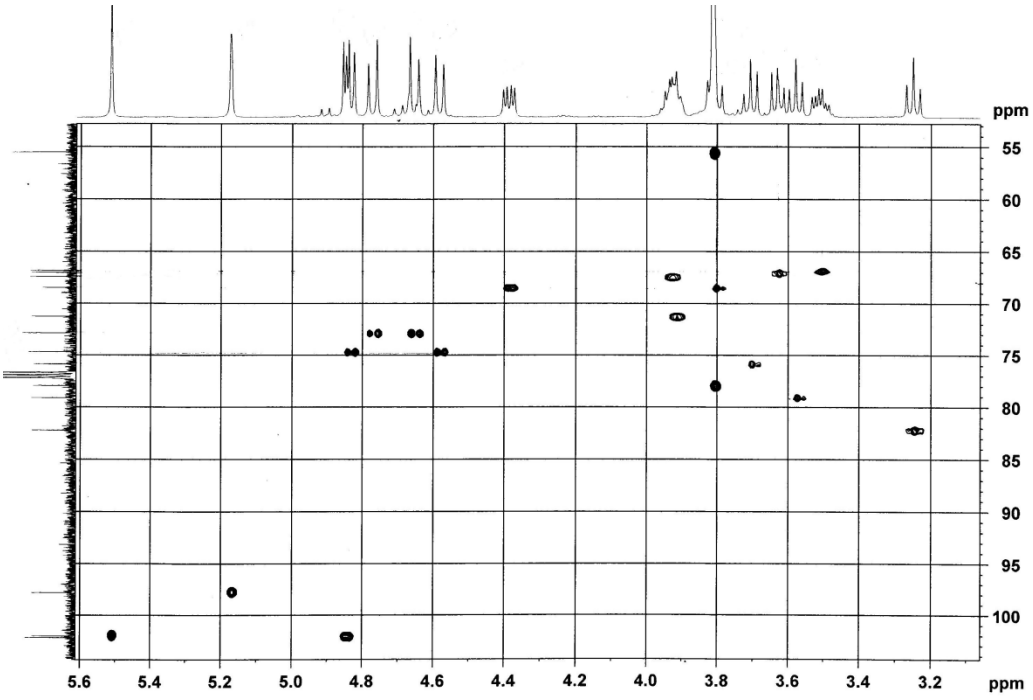
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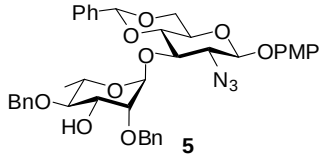
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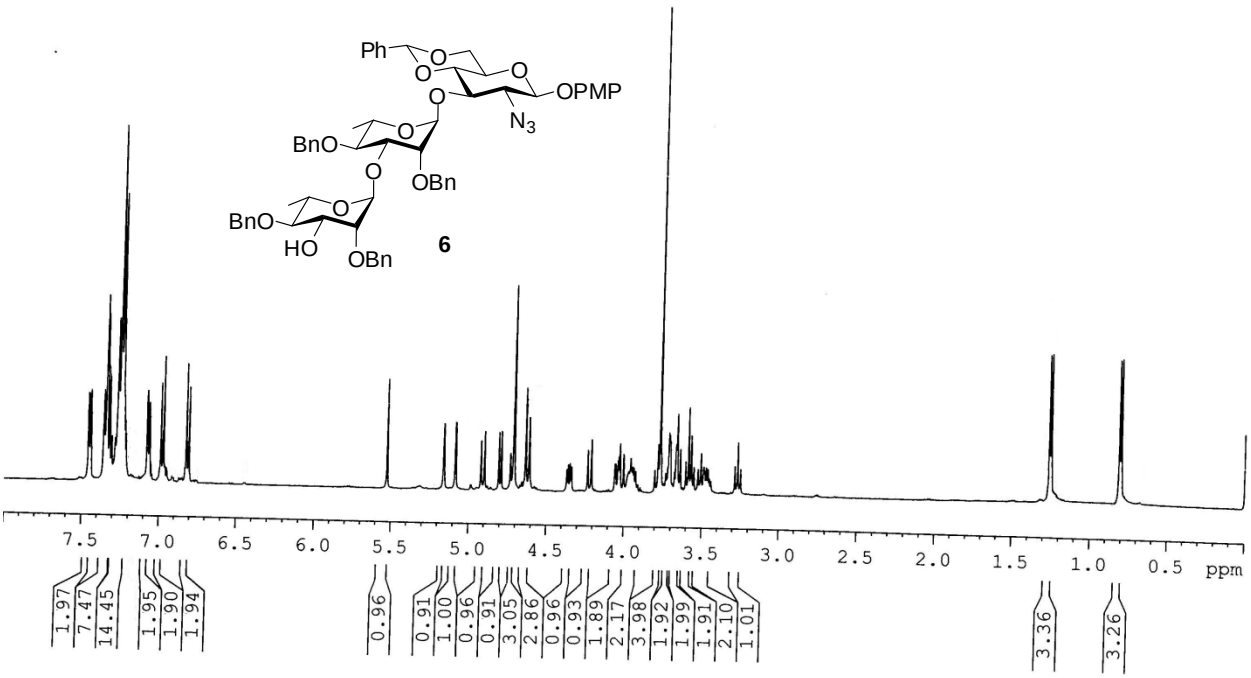
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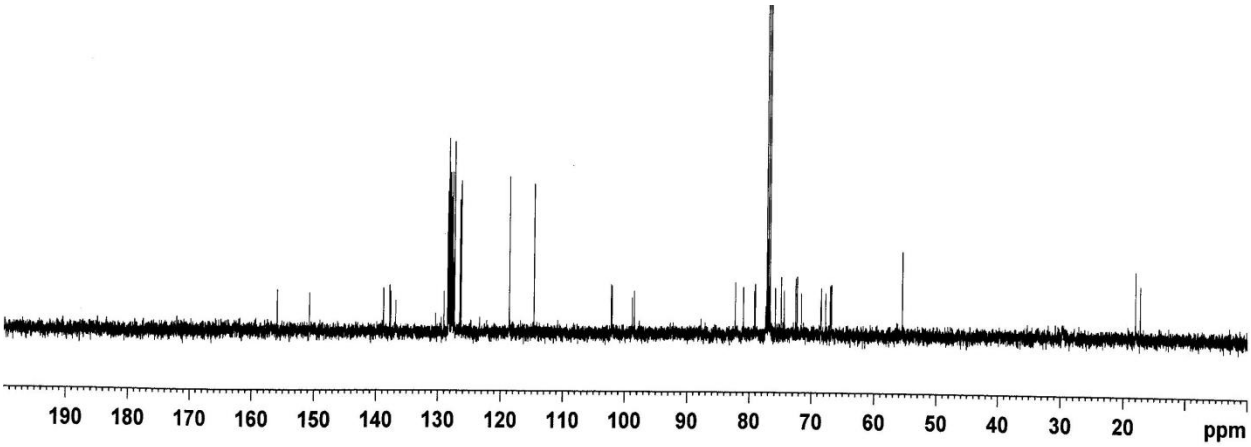
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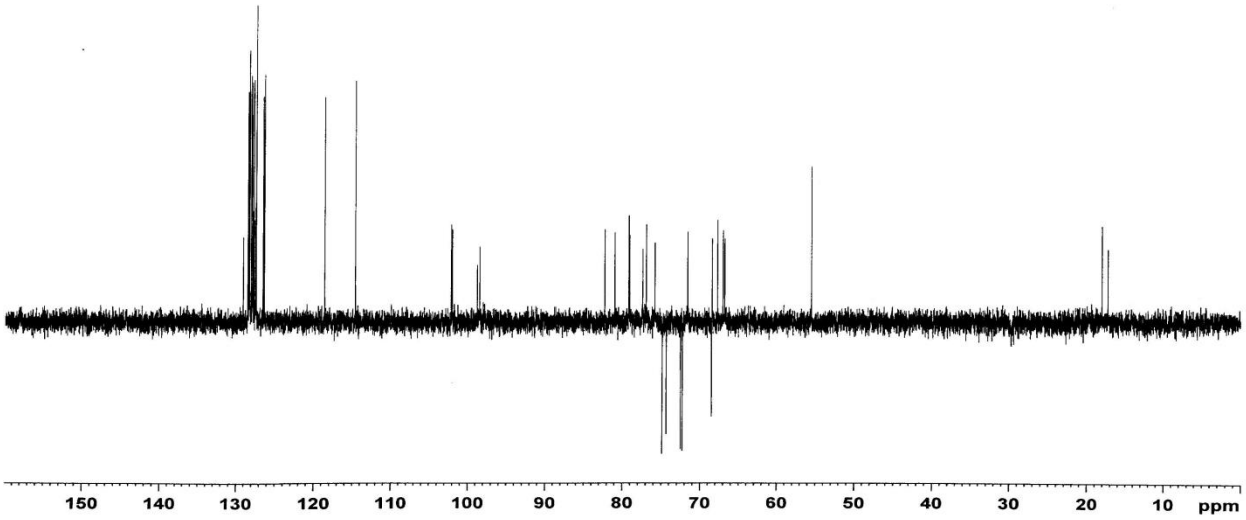
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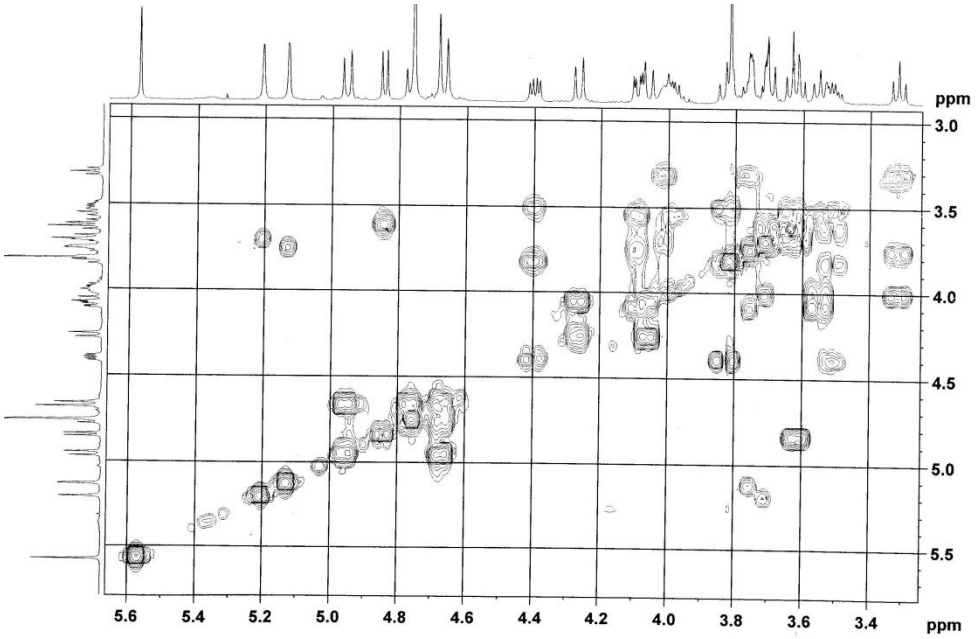
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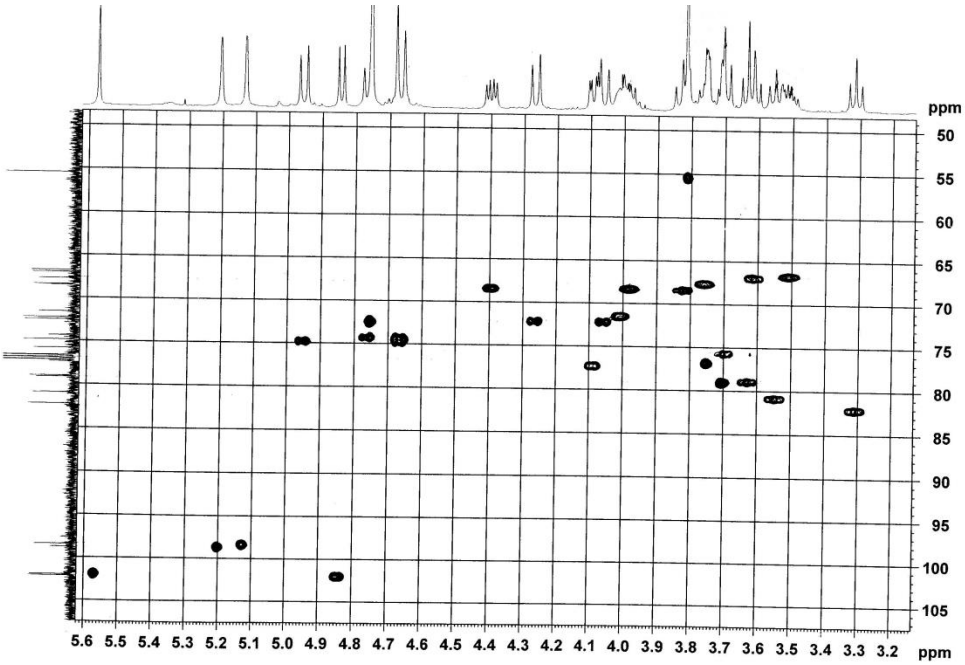
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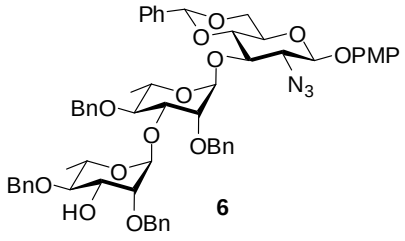
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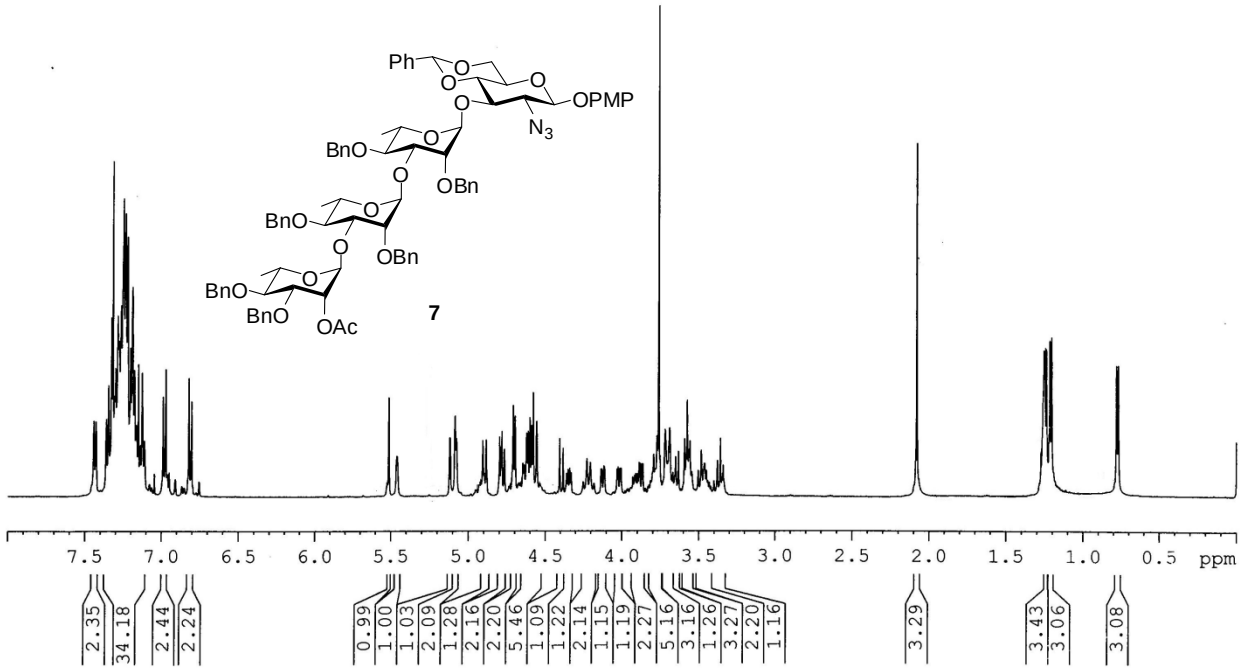
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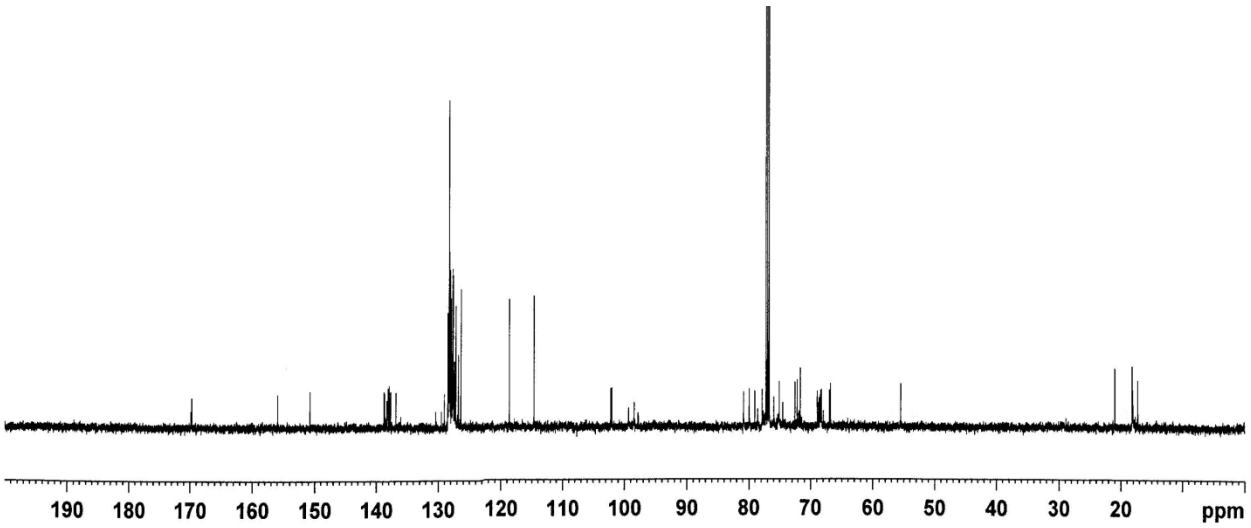
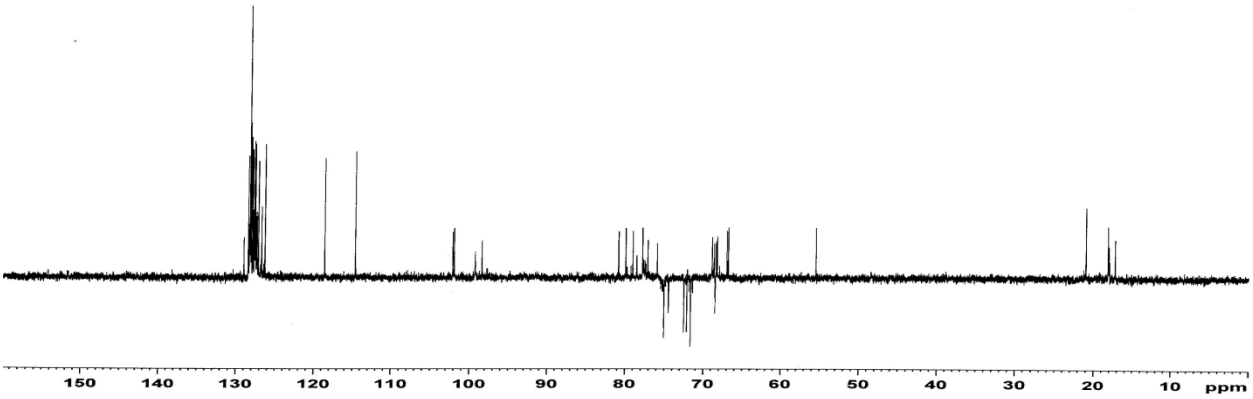
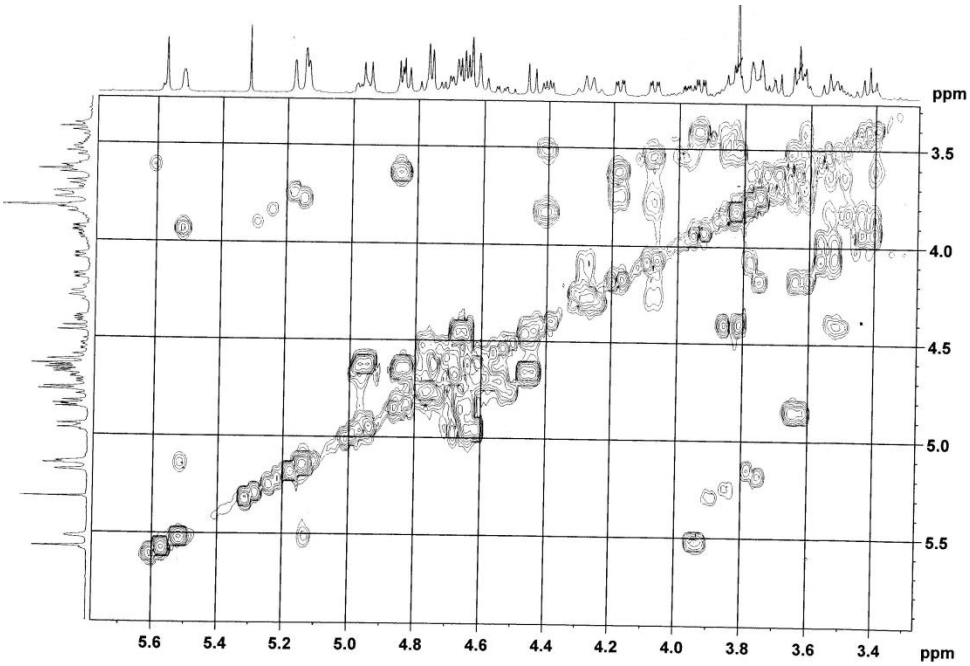
2.35 34.18 2.44 2.24 0.99 1.00 1.03 2.09 1.28 2.16 2.20 5.46 1.09 1.22 2.14 1.15 1.19 2.27 5.16 3.16 1.26 3.27 2.20 1.16 3.29 3.43 3.06 3.08


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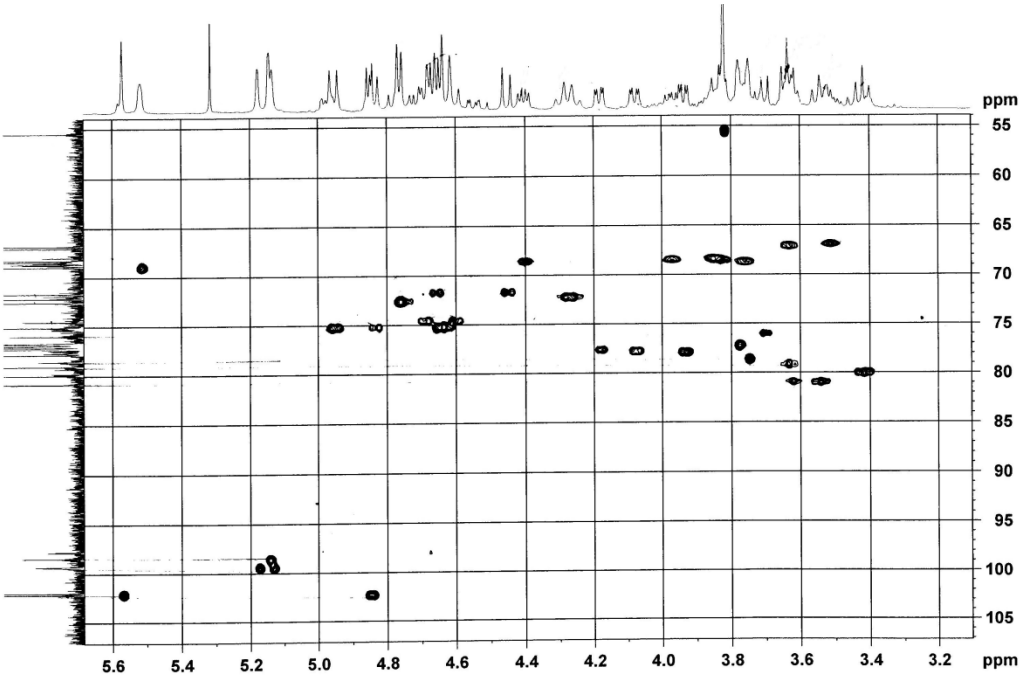
4.0
4.5
5.0
5.5
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
ppm


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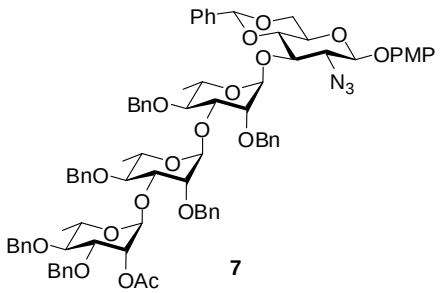
60
65
70
75
80
85
90
95
100
105
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
ppm


Ph
O
O
O
O
OPMP
N3
BnO
O
OBn
BnO
O
OBn
BnO
O
BnO
OAc

7