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Direct Chemical Synthesis of the β-Mannans: the β-(1→2)- and β-(1→4)-Series

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Ethyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-*O*-*p*-methoxybenzyl-1-thio-α-D-mannopyranoside (2). To a stirred mixture of ethyl 4,6-*O*-benzylidene-3-*O*-benzyl-1-thio-α-D-mannopyranoside **1**[1] (9.29 g, 20.6 mmol) and Bu_4NI (1.52 g , 4.12 mmol) in DMF (250 mL), NaH was added at 0 °C. After 20 minutes, PMBCl (3.63 mL, 26.8 mmol) was slowly added to the above mixture, which was then warmed to room temperature and stirred overnight. The reaction mixture was quenched with MeOH (2 mL) followed by removal of DMF by rotary evaporation under reduced pressure. The residue was taken up in EtOAc (150 mL), washed with saturated aq. Na_2CO_3, and brine, and dried over anhydrous Na_2SO_4. Concentration and purification by column chromatography over silica gel (eluent: hexane/ethyl acetate = 10:1) afforded compound **2** (8.11 g, 15.5 mmol) as a syrup in 75% yield. $[\alpha]_D$ +63.1 (*c*, 3.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$), δ: 7.52-7.59 (m, 2H), 7.26-7.38 (m,10H), 6.86 (d, *J* = 8.7 Hz, 2H), 5.63 (s, 1H), 5.26 (s, 1H), 4.78 (d, *J* =12.0 Hz, 1H), 4.67 (s, 2H), 4.60 (d, *J* =12.0 Hz, 1H), 4.18-4.26 (m, 3H), 3.88-3.92 (m, 3H),

3.81 (s, 3H), 2.26-2.53 (m, 2H), 1.24 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$), δ: 138.62, 137.81, 130.31, 129.91, 128.98, 128.45, 128.34, 127.74, 127.69, 126.63, 113.90, 101.60, 93.74, 79.41, 77.74, 76.57, 73.14, 72.84, 68.77, 64.76, 55.44, 25.49, 15.10. Anal. Calcd. For $C_{30}H_{34}O_6S$: C, 68.94, H, 6.56. Found: C, 68.79; H, 6.60.

Ethyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-*O*-*p*-methoxybenzyl-1-thio-α-D-mannopyranoside *S*-oxide (3). To a stirred solution of **2** (8.11 g, 15.5 mmol) in CH_2Cl_2 (150 mL) was added 90% *m*-CPBA (2.97 g, 15.5 mmol) at -78 °C. The reaction mixture was stirred at -78 °C for 4 h, warmed to -20 °C, and quenched with saturated aq. Na_2CO_3. The solution was washed with saturated aq. Na_2CO_3, brine, and dried over anhydrous Na_2SO_4. Removal of solvent and recrytallization from ethyl acetate and hexane gave **3** (7.00 g, 13.0 mmol) as a crystalline solid in 84% yield. M.p.: 106 ±1°C; $[\alpha]_D$ +15.0 (*c*, 2.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$), δ: 7.49-7.52 (m, 2H), 7.26-7.40 (m, 10H), 6.87 (d, J = 8.1 Hz, 2H), 5.62 (s, 1H), 4.64-4.82 (m, 4H), 4.59 (s, 1H), 4.51 (d, J = 3.0 Hz, 1H), 4.33 (t, J = 9.6, 1H), 4.20 (dd, J = 4.5 Hz, 9.9 Hz, 1H), 4.11 (dd, J = 3.6 Hz, 9.9 Hz, 1H), 3.80 (s, 3H), 3.70-3.86 (m, 2H), 2.61-2.95 (m, 2H), 1.35 (t, J = 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$), δ: 159.64, 138.26, 137.33, 130.25, 129.75, 129.17, 128.49, 128.39, 127.81, 127.77, 126.17, 114.01, 101.72, 92.84, 78.02, 76.26, 73.72, 73.23, 72.60, 70.21, 68.31, 55.43, 44.15, 6.04. Anal. Calcd. for $C_{30}H_{34}O_7S$: C, 66.89; H, 6.36. Found: C, 68.68; H, 6.43.

General procedure for the sulfoxide glycosylation. A mixture of sulfoxide (1.0 equiv, 0.03 M.), **TTBP** (2.0 equiv), and molecular sieves (1.0 weight equiv.) in CH_2Cl_2 was stirred for 30 min at -78 °C and Tf_2O (1.1 equiv) was added at this temperature. After 10

min, acceptor (1.0 M, for specific amounts, see the products below) in CH_2Cl_2, was added. The solution was further stirred for 4 h at -78 °C, slowly warmed to -30 °C, quenched with MeOH and filtered. The filtrate was washed with saturated aq. Na_2CO_3 and brine and dried over anhydrous Na_2SO_4. Concentration and purification by column chromatography over silica gel afforded the corresponding mannopyranosides.

General procedure for removal of the PMB group with DDQ. To a solution of the 2-*O*-PMB protected-D-mannopyranosides (0.03 M) in a mixture of CH_2Cl_2/H_2O (17/1) was added DDQ (2.3 equiv) at 0 °C. After 30 min, the reaction mixture was warmed to room temperature and further stirred for 1 h before it was quenched with saturated aq. Na_2CO_3. The organic phase was washed with saturated aq. Na_2CO_3 and brine, and dried over anhydrous Na_2SO_4. Concentration and purification by column chromatography over silica gel provided the corresponding alcohol.

Cyclohexyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-*O*-*p*-methoxybenzyl-β-D-mannopyranoside (4). Coupling of sulfoxide **3** (1.50 g, 2.78 mmol) and cyclohexanol (0.59 mL, 5.56 mmol) by the standard coupling protocol gave β-D-mannopyranoside **4** (1.20g, 2.14 mmol) as a syrup in 77% yield without a detectable amount of α-anomer. $[\alpha]_D$ -57.1 (*c*, 4.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$), δ: 7.50-7.51 (m, 2H), 7.28-7,38 (m, 10 H), 6.86 (d, *J* = 9.0 Hz, 2H), 5.62 (s, 1H), 4.96 (d, *J* = 12.3 Hz, 1H), 4.87(d, *J* = 12.3 Hz, 1H), 4.66 (d, *J* = 12.9 Hz, 1H), 4.61 (d, *J* = 12.9 Hz, 1H), 4.58 (s, 1H), 4.31 (dd, *J* = 4.7, 10.2 Hz, 1H), 4.22 (t, *J* = 9.6 Hz, 1H), 3.95 (t, *J* = 10.2 Hz, 1 H), 3.88 (d, *J* = 3.0 Hz 1H), 3.81 (s, 3H),

3.70-3.75 (m, 1H), 3.57 (dd, *J* = 3.6 Hz, 9.9 Hz, 1H), 3.28-3.36 (m, 1H), 1.20-2.00 (m, 10H); ^{13}C NMR ($CDCl_3$), δ: 159.30, 138.61, 137.82, 130.54, 128.41, 128.32, 127.63, 126.20, 113.62, 101.49, 78.77, 78.25, 74.22, 72.38, 68.85, 67.68, 55.42, 33.53, 31.60, 22.58, 22.90, 23.76; ESIHRMS Calcd. for $C_{34}H_{40}O_7Na$ ($[M+Na]^+$) 583.2627; found, 583.2687.

Cyclohexyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-*O*-*p*-methoxybenzyl-β-D-mannopyranoside (5). Removal of the PMB group from compound **4** (1.08 g, 1.91 mmol) with by the general procedure afforded alcohol **5** (0.71 g, 1.62 mmol) in 85% yield. $[\alpha]_D$ -20.0 (*c*, 3.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$), δ: 7.28-7.53 (m, 10H), 5.60 (s, 1H). 4.86 (d, *J* = 12.0 Hz, 1H), 4.79 (d, *J* = 12.0 Hz, 1H), 4.63 (s, 1H), 4.32 (dd, *J* = 4.9 Hz, 10.5 Hz, 1H), 4.16 (t, *J* = 9.5 Hz, 1H), 4.08 (d, *J* = 2.4 Hz, 1H), 3.69-3.74 (m, 1H), 3.65 (dd, *J* = 3.2 Hz, 9.6 Hz, 1H), 3.29-3.38 (m, 1H), 2.62 (bs, 1H), 1.18-2.04 (m, 10H); ^{13}C NMR ($CDCl_3$), δ: 138.34, 137.72, 129.13, 128.60, 128.39, 128.04, 126.28, 101.63, 98.24, 78.61, 77.18, 77.14, 72.53, 68.81, 67.04, 33.62, 31.76, 25.73, 24.30, 24.23; ESIHRMS: Calcd. for $C_{26}H_{32}O_6Na$ ($[M+Na]^+$): 463.2121; found: 463.2100.

Cyclohexyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-*O*-*p*-methoxybenzyl-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranoside (6). Coupling of sulfoxide **3** (1.52 g, 2.82 mmol) and acceptor **97** (0.62 g, 1.41 mmol) by the standard coupling protocol gave the β-D-mannopyranoside **6** (1.29 g, 1.34 mmol) as a syrup in 94% yield without any detectable α-anomer. $[\alpha]_D$ -97.2 (*c*, 0.95, $CHCl_3$); ^{1}H NMR

($CDCl_3$), δ: 7.22–7.55 (m, 22H), 6.87 (d, *J* = 8.6 Hz, 2H), 5.65 (s, 1H), 5.51 (s, 1H), 5.02 (dd, *J* =11.9 Hz, 30.7 Hz, 2H), 4.88 (s, 1H), 4.83 (s, 2H), 4.64 (s, 1H), 4.53 (s, 2H), 4.33-4.37 (m, 2H), 4.25(t, *J* = 9.6 Hz, 1H), 4.24 (d, *J* = 3.3 Hz, 1H), 4.17 (t, *J* = 9.6 Hz, 1H), 4.00 (t, *J* = 10.6 Hz, 1H)), 3.80 (t, *J* = 10.1 Hz, 1H), 3.80 (s, 3H), 3.72-3.78 (m, 1H), 3.66 (dd, *J* = 3.2 Hz, 9.9 Hz, 1H), 3.53 (dd, *J* = 3.2Hz, 9.9 Hz, 1H), 3.34-3.38 (m, 2H), 1.18-2.04 (m, 10H); ^{13}C NMR ($CDCl_3$), δ: 159.50, 139.20, 138.85, 137.91, 131.45, 131.03, 129.30, 129.19, 128.63, 128.58, 128.00, 127.84, 127.78, 126.47, 113.87, 104.51, 101.96, 101.74, 99.40, 78.86, 78.42, 77.55, 76.54, 76.50, 74.76, 74.27, 71.62, 69.27, 69.19, 68.13, 67.87, 33.72, 31.69, 25.94, 24.11, 23.86; ESIHRMS: Calcd. for $C_{54}H_{60}O_{12}Na$ ($[M+Na]^+$) 923.3982; found, 923.3972.

Cyclohexyl 3-*O*-Benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranoside (7). Removal of the PMB group from disaccharide **6** (1.75 g, 1.95 mmol) by the general procedure afforded the alcohol **7** (1.42 g, 1.89 mmol) in 97% yield. $[\alpha]_D$ -48.4 (*c*, 0.19, $CHCl_3$); ^{1}H NMR ($CDCl_3$), δ: 7.31-7.51 (m, 20H), 5.60 (s, 1H), 5.58 (s, 1H), 4.96 (s, 1H), 4.89 (d, *J* = 12.5 Hz 1H), 4.85 (d, *J* = 12.5 Hz, 1H), 4.77 (s, 2H), 4.62 (s, 1H), 4.24-4.36 (m, 5H), 4.12 (t, *J* = 9.5 Hz, 1H), 3.90 (t, *J* = 10.2 Hz, 1H), 3.89 (t, *J* = 10.3 Hz, 1H), 3.70-3.72 (m, 1H), 3.62-3.67 (m, 2H), 3.32-3.39 (m, 2H), 1.18-2.04 (m, 10H); ^{13}C NMR ($CDCl_3$), δ: 138.76, 138.72, 138.00, 137.85, 129.29, 128.72, 128.61, 128.21, 127.95, 126.46, 101.89, 101.83, 101.34, 99.27, 78.75, 78.51, 77.05, 76.84, 74.83, 72.48, 72.24, 69.53, 69.14, 68.96, 67.78, 67.72, 33.63, 31.78, 25.89, 24.69, 23.93; ESIHRMS, Calcd. for $C_{46}H_{52}O_{11}Na$ ($[M+Na]^+$): 803.3407; found, 803.3466.

Cyclohexyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-*O*-*p*-methoxybenzyl-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranoside (8) and Cyclohexyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-*O*-*p*-methoxybenzyl-α-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranoside (9). Sulfoxide **3** (2.62 g, 4.87 mmol) coupled with dimeric alcohol **7** (1.90 g, 2.43 mmol) by the standard coupling protocol to give β-D-mannopyranoside **8** (2.51 g, 2.16 mmol) as a foam in 89% yield along with its α-anomer **9** (0.25 g, 0.22 mmol) in 9% yield. **8**: $[\alpha]_D$ -98.3 (*c*, 0.47, $CHCl_3$); ^{1}H NMR ($CDCl_3$), δ: 7.13-7.48 (m, 32H), 6.74 (d, *J* = 8.6 Hz, 2H), 5.63 (s, 1H), 5.48 (s, 1H), 5.21 (s, 1H), 5.17 (s, 1H), 4.95 (d, *J* = 12.0 Hz, 1H), 4.60-4.89 (m, 7H), 4.59 (s, 1H), 4.46 (d, *J* = 12.4Hz, 1H), 4.61 (d, *J* = 3.2 Hz, 1H), 4.39 (d, *J* = 3.2 Hz 1H), 4.35 (dd, *J* = 4.7 Hz, 10.4 Hz, 1H), 4.31 (dd, *J* = 4.7, 10.4 Hz, 1H), 4.26 (t, *J* =9.6 Hz, 1H), 4.22 (dd, *J* = 4.7 Hz, 10.4 Hz, 1H), 4.20 (d, *J* = 3.5 Hz, 1H), 4.12 (t, *J* = 9.6 Hz, 1H), 3.97 (t, *J* = 10.3Hz, 1H), 3.84 (t, *J* = 10.2 Hz, 1H), 3.79 (t, *J* = 9.6 Hz, 1H), 3.70-3.72 (m, 1H), 3.63 (dd, *J* = 3.1 Hz, 9.6 Hz, 2H), 3.57 (dd, *J* = 3.2 Hz, 9.6 Hz, 1H), 3.54 (t, *J* = 10.4 Hz, 1H), 3.51 (s, 3H), 3.27-3.43 (m, 3H), 1.20-1.90 (m, 10H); ^{13}C NMR ($CDCl_3$), δ: 158.83, 138.75, 138.38, 137.63, 137.51, 137.09, 130.92, 130.52, 128.91, 128.75, 128.25, 128.22, 128.18, 128.15, 128.05, 127.59, 127.29, 127.18, 127.03, 126.11, 126.06, 125.97, 113.45, 103.65, 103.49, 101.61, 101.56, 101.21, 98.85, 78.70, 78.51, 78.46, 78.19, 77.91, 76.38, 76.06, 75.85, 74.45, 73,93, 72.09, 71.57, 70.76, 68.86, 68.82, 68.67, 67.69, 67.59, 67.35, 54.90, 33.39, 31.28, 25.46, 23.77, 23.46. ESI-HRMS, Calcd. for $C_{74}H_{84}O_{17}N$ ($[M+NH_4]^+$): 1258.5739; found: 1258.5753. **9**: $[\alpha]_D$ -44.4

(*c*,6.7, $CHCl_3$), ^1H NMR ($CDCl_3$), δ: 7.14-7.60 (m, 32H), 6.80 (d, *J* = 8.6Hz, 2H), 5.70 (s, 1H), 5.69 (s, 1H), 5.64 (s, 1H), 5.24 (s, 1H), 4.75-4.89 (m, 6H), 4.53-4.59 (m, 5H), 4.49 (dd, *J* = 4.9 Hz, 9.8 Hz, 1H), 4.37-4.43 (m, 1H), 4.36 (dd, *J* = 5.0 Hz, 10.4 Hz, 1H), 4.23-4.29 (m, 2H), 4.17 (d, *J* = 3.50 Hz, 1H), 4.03-4.15 (m, 2H), 3.95 (t, *J* = 10.3 Hz 1H), 3.88 (t, *J* = 10.3 Hz, 1H), 3.77 (s, 3H), 3.73-3.77 (m, 1H), 3.71 (dd, *J* =2.6 Hz, 9.8 Hz, 1H), 3.60 (dd, *J* = 3.7 Hz, 10.1 Hz 1H), 3.39-3.44 (m, 1H), 3.21-3.24 (m, 1H), 1.20-1.90 (m, 10H); ^{13}C NMR ($CDCl_3$), δ: 159.20, 130.68, 129.71, 129.16, 128.65, 128.46, 128.28, 128.25, 128.16, 128.09, 127.97, 127.72, 127.46, 127.29, 126.25, 126.15, 113.69, 103.26, 101.68, 101.52, 100.70, 99.35, 99.32, 79.80, 79.33, 78.77, 77.29, 76.79, 76.50, 76.10, 73.57, 73.36, 72.71, 72.61, 71.16, 68.83, 68.80, 68.02, 67.98, 64.25, 55.40, 33.56, 31.665, 25.78, 23.83, 23.65; ESIHRMS, Calcd. for $C_{74}H_{80}O_{17}Na$ ($[M+NH_4]^+$): 1258.5293; found: 1258.5306.

Cyclohexyl 3-*O*-Benzyl-4,6-*O*-benzylidene-β-D-mannopyran-osyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranoside (10). Removal of the PMB group from trisaccharide **8** (0.313 g, 0.252 mmol) by the general procedure afforded alcohol **10** (0.258 g, 0.227 mmol) as a foam in 91% yield $[\alpha]_D$ -58.9 (*c*, 6.4, $CHCl_3$), ^1H NMR ($CDCl_3$), δ: 7.19-7.51 (m, 30H), 5.63 (s, 2H), 5.31 (s, 1H), 5.17 (s, 1H), 4.84 (s, 1H), 4.68-4.83 (m, 6H), 4.67 (d, *J* = 3.2 Hz, 1H), 4.57 (s, 1H), 4.42 (d, *J* = 2.9 Hz, 1H), 4.28-4.36 (m, 3H), 4.24 (dd, *J* = 4.7 Hz, 10.4 Hz, 1H), 4.17 (t, *J* = 9.6 Hz, 1H), 4.12 (d, *J* = 2.8 Hz, 1H), 3.97 (t, *J* = 10.2 Hz, 1H), 3.92 (t, *J* = 10.5 Hz, 1H), 3.87 (t, *J* = 9.6 Hz, 1H), 3.66-3.75 (m, 1H), 3.58-3.66 (m, 3H), 3.53 (t, *J* = 10.3 Hz, 1H), 3.35-3.40 (m, 2H), 3.24-3.30 (m, 1H), 1.20-1.90 (m, 10H); ^{13}C

NMR ($CDCl_3$), δ: 138.36, 138.10, 137.53, 137.28, 128.87, 128.25, 127.66, 127.57, 126.09, 126.03, 103.30, 101.45, 101.39, 100.76, 98.77, 78.55, 78.41, 77.67, 76.20, 76.06, 73.23, 71.91, 71.12, 69.12, 68.67, 68.59, 67.65, 67.35, 67.06, 33.37, 31.26, 25.47, 23.77, 23.44; ESIHRMS, Calcd. for $C_{66}H_{76}O_{16}N$ ($[M+NH_4]^+$): 1138.5164; found: 1138.5177.

Cyclohexyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-*O*-*p*-methoxybenzyl-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene -β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene β-D-mannopyranoside (11) and Cyclohexyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-*O*-*p*-methoxybenzyl-α-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene β-D-mannopyranoside (12). Sulfoxide **3** (1.73 g, 3.21 mmol) coupled with trisaccharide **10** (1.65 g, 1.47 mmol) by the standard coupling protocol to give β-D-mannopyranoside **11** (1.80 g, 1.13 mmol) as a foam in 77% yield along with its α-anomer **12** (0.458 g, 0.294 mmol) in 20% yield. **11**: $[\alpha]_D$ -94.8 (*c*, 3.0, $CHCl_3$); ^1H NMR ($CDCl_3$), δ: 7.10-7.52 (m, 42H), 6.76 (d, *J* = 8.6 Hz, 2H), 5.62 (s, 1H), 5.50 (s, 1H), 5.49 (s, 1H), 5.32 (s, 1H), 5.29 (s, 1H), 5.25 (s, 1H), 4.99 (d, *J* = 12.0 Hz, 1H), 4.73-4.85 (m, 8H), 4.67 (d, *J* =3.0 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 4.60 (s, 1H), 4.52-4.54 (m, 2H), 4.44 (d, *J* = 12.0 Hz, 1H), 4.35-4.37 (m, 2H), 4.29-4.33 (m, 2H), 4.14-4.26 (m, 2H), 4.10 (d, *J* = 3.2 Hz, 1H), 3.96 (t, *J* = 10.0 Hz, 1H), 3.94 (t, *J* = 9.2 Hz, 1H), 3.86 (t, *J* = 10.0 Hz, 2H), 3.73-3.78 (m, 1H), 3.69 (t, *J* = 9.6 Hz, 1H), 3.69 (t, *J* = 9.4 Hz, 2H), 3.61 (s, 3H), 3.61 (dd, *J* = 3.2 Hz, 9.6 Hz, 2H), 3.56 (t, *J* = 10.2 Hz, 1H), 3.40-3.48 (m, 3H), 3.30-3.33 (m, 1H), 1.20-1.90 (m, 10H); ^{13}C NMR ($CDCl_3$), δ: 159.15, 138.98,

138.89, 138.74, 138.21, 137.92, 137.58, 137.50, 131.96, 130.27, 129.35, 129.05, 128.73, 128.69, 128.64, 128.61, 128.53, 128.50, 128.39, 128.14, 127.97, 127.80, 127.75, 127.64, 127.54, 127.48, 126.54, 126.52, 126.48, 126.46, 113.81, 104.63, 103.67, 102.42, 102.24, 102.05, 101.86, 101.61, 99.03, 79.83, 79.72, 79.00, 78.73, 78.70, 76.96, 76.90, 76.74, 75.99, 74.74, 74.17, 72.59, 72.56, 71.36, 71.11, 69.64, 69.23, 69.18, 69.08, 68.14, 68.06, 67.98, 67.84, 55.41, 33.85, 31.63, 25.88, 24.22, 23.88, 16.64; ESIHRMS, Calcd. for $C_{94}H_{103}O_{23}$ ($[M+H_3O]^+$): 1599.6890; found: 1599.6943. **12**: $[\alpha]_D$ -74.0 (*c*, 1.3, $CHCl_3$); ^1H NMR ($CDCl_3$), δ: 7.14-7.58 (m, 42H), 6.75 (d, *J* = 8.6 Hz, 2H), 5.69 (s, 1H), 5.67(s, 1H), 5.59 (s, 1H), 5.50 (s, 1H), 5.31 (s, 1H), 5.25 (s, 1H), 4.94 (s, 1H), 4.75-4.87 (m, 7H), 4.59-4.64 (m, 5H), 4.64-4.53 (m, 4H), 4.35 (dd, *J* = 5.0 Hz, 10.4 Hz, 2H), 4.24-4.28 (m, 3H), 4.08-4.20 (m, 3H), 3.91-4.01 (m, 3H), 3.82-3.86 (m, 2H), 3.71-3.78 (m, 5H), 3.68 (dd, *J* = 3.5 Hz, 10.0 Hz, 1H), 3.62 (dd, *J* = 3.5 Hz, 10.0 Hz, 1H), 3.42-3.47 (m, 1H); 3.21-3.38 (m, 2H), 1.20-1.90 (m, 10H); ^{13}C NMR ($CDCl_3$), δ: 159.39, 139.73, 139.49, 138.78, 138.36, 138.27, 138.05, 137.96, 137.64, 130.95, 129.86, 129.35, 128.80, 128.76, 128.71, 128.68, 128.65, 1128.61, 128.56, 128.51, 128.49, 128.46, 128.36, 128.17, 128.05, 128.00, 127.88, 127.64, 127.49, 113.89, 103.61, 102.47, 102.21, 101.83, 100.96, 99.76, 99.52, 80.53, 80.03, 79.68, 78.94, 77.66, 77.25, 77.11, 76.75, 76.53, 76.45, 76.20, 73.93, 73.73, 72.96, 72.81, 71.52, 70.90, 69.16, 69.09, 68.71, 68.35, 68.15, 67.84, 64.56, 55.62, 33.85, 31.75, 25.87, 24.17, 24.86; ESIHRMS, Calcd. for $C_{94}H_{103}O_{23}$ ($[M+H_3O]^+$): 1599.6890; found: 1599.6901.

Cyclohexyl 3-*O*-Benzyl-4,6-*O*-benzylidene-β-D-mannopyran-osyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-

mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene β-D-mannopyranoside (13). Removal of the PMB group from tetrasaccharide **11** (1.56 g, 0.987 mmol) by the general procedure afforded alcohol **13** (1.22 g, 0.84 mmol) in 85 %. M. p. 9ethyl acetate/hexane) 112 ±1° $[\alpha]_D$ -83.6 (*c*, 1.12, $CHCl_3$); ^1H NMR ($CDCl_3$), δ: 7.10-7.50 (m, 40H), 5.63 (s, 1H), 5.56 (s, 1H), 5.52 (s, 1H), 5.33 (s, 1H), 5.29 (s, 1H), 4.94 (s, 1H), 4.87 (s, 1H), 4.57 (s, 1H), 4.61-4.81 (m, 9H), 4.54 (d, *J* = 3.1 Hz, 1H), 4.38 (d, *J*= 3.1 Hz, 1H), 4.21-4.35 (m, 3H), 4.16 (d, *J* = 3.1 Hz, 1H), 3.93-4.01 (m, 2H), 3.80-3.85 (m, 3H), 3.65-3.75 (m, 1H), 3.59-3.64 (m, 4H), 3.51 (dd, *J* = 3.2 Hz, 9.6 Hz 1H), 3.27-3.43 (m, 4H), 1.20-1.90 (m, 10H); ^{13}C NMR ($CDCl_3$), δ: 138.29, 138.27, 137.64, 137.27, 137.07, 128.37, 128.25, 128.20, 128.15, 127.82, 127.71, 127.46, 127.26, 127.00, 126.11, 126.05, 103.56, 101.69, 101.60, 101.55, 101.44, 101.31, 101.25, 98.82, 78.55, 78.46, 78.41, 78.11, 77.81, 76.45, 75.61, 74.75, 73.59, 72.36, 71.92, 71.53, 70.82, 69.01, 68.67, 67.80, 67.65, 67.33, 67.04, 33.34, 31.29, 29.26, 25.42, 23.42. Anal. Calcd. for $C_{86}H_{92}O_{21}$•EtOAc: C, 69.75; H, 6.50; Found: C, 69.67; H, 6.34.

Cyclohexyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-*O*-*p*-methoxybenzyl-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranoside (14) and Cyclohexyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-*O*-*p*-methoxybenzyl-α-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benz-

ylidene-2-*O*-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-manno-pyranoside (15). Coupling of sulfoxide **3** (0.295 g, 0.547 mmol) and acceptor **13** (0.400 g, 0.274 mmol) by the standard coupling protocol gave β-D-mannopyranoside **14** (0.364 g, 0.19 mmol) as a foam in 69% yield with its α-anomer **15** (81.9mg, 0.044 mmol) in 16% yield. **14**: $[\alpha]_D$ -104 (*c*, 1.3, $CHCl_3$); ^{1}H NMR ($CDCl_3$), δ: 7.51-7.10 (m, 52H), 6.74 (d, *J* = 9.0 Hz), 5.57 (s, 1H), 5.56 (s, 1H), 5.44 (s, 1H), 5.40 (s, 1H), 5.24 (s, 1H), 5.23 (s, 1H), 5.21 (s, 1H), 5.02 (s, 1H), 4.99 (d, *J* = 12.0Hz, 1H), 4.95 (d, *J* = 12.0Hz, 1H), 4.95 (s, 1H), 4.57-4.79 (m, 12H), 4.42 (d, *J* = 3.5 Hz, 1H), 4.31-4.38 (m, 3H), 4.11-4.25 (m, 6H), 3.97 (t, *J* = 9.5 Hz, 2H), 3.82-3.90 (m, 4H), 3.56-3.76 (m, 9H), 3.49-3.51 (m, 1H), 3.45 (s, 3H), 3.33-3.41 (m, 3H), 3.12-3.16 (m, 1H), 1.20-1.90 (m, 10H); ^{13}C NMR ($CDCl_3$), δ: 159.85, 139.27, 139.05, 138.64, 138.57, 138.55, 138.33, 138.06, 137.56, 137.53, 131.00, 129.43, 129.35, 129.28, 129.16, 128.98, 128.88, 128.84, 128.74, 128.68, 128.61, 128.56, 128.50, 128.43, 128.39, 128.32, 128.22, 128.08, 127.99, 127.95, 127.88, 127.78, 127.73, 127.68, 127.62, 127.49, 127.43, 127.34, 127.28, 126.54, 126.44, 113.86, 104.43, 103.59, 103.54, 102.75, 102.12, 101.99, 101.89, 101.55, 99.35, 79.23, 79.13, 78.99, 78.93, 78.76, 78.46, 78.20, 78.12, 78.00, 77.02, 76.65, 75.66, 74.96, 73.96, 72.77, 72.49, 71.75, 71.56, 71.39, 69.27, 69.19, 69.11, 68.17, 67.77, 67.66, 67.41, 55.22, 33.77, 31.64, 30.13, 25.82, 24.14, 23.86; ESIHRMS, Calcd. for $C_{114}H_{123}O_{28}$ ($[M+H_3O]^+$): 1939.8210; found: 1939.8190. **15**: $[\alpha]_D$ -65.0 (*c*, 2.3, $CHCl_3$), ^{1}H NMR ($CDCl_3$), δ: 7.02-7.53 (m, 52H), 6.73 (d, *J* = 8.5Hz, 2H), 5.67 (s, 1H), 5.64 (s, 1H), 5.59 (s, 1H), 5.57 (s, 1H), 5.38 (s, 1H), 5.35 (s, 1H), 5.32 (s, 1H), 5.27 (s, 1H), 4.92 (d, *J* = 12.5 Hz 1H), 4.61-4.88 (m, 13H), 4.56 (s, 1H), 4.45-4.53 (m, 3H), 4.36-4.41 (m, 4H), 4.11-4.30 (m, 6H), 4.09 (t, *J* = 9.5 Hz, 1H), 4.01-4.05 (m, 2H), 3.98 (s, 1H), 3.85-3.91 (m, 4H), 3.74 (s, 3H),

3.65-3.72 (m, 4H), 3.60 (dd, *J* = 3.0 Hz, 10 Hz, 1H), 3.52-3.56 (m, 1H), 3.36-3.43 (m, 2H), 3.27-3.31 (m, 1H), 1.20-1.90 (m, 10H); ^{13}C NMR ($CDCl_3$), δ: 159.36, 139.71, 139.29, 138.86, 138.79, 138.53, 138.26, 138.17, 138.06, 137.67, 137.62, 130.95, 129.82, 129.33, 129.26, 129.18, 128.77, 128.60, 128.56, 128.44, 128.37, 128.24, 128.05, 128.01, 127.96, 127.89, 127.56, 127.48, 126.54, 126.52, 126.45, 113.84, 104.99, 102.69, 102.38, 102.20, 101.88, 101.84, 101.78, 101.12, 99.45, 98.85, 80.92, 80.33, 80.05, 79.62, 78.96, 78.74, 77.55, 76.87, 76.79, 76.50, 76.41, 76.13, 74.20, 73.99, 73.71, 73.24, 72.74, 72.57, 70.92, 70.65, 69.23, 69.10, 69.08, 69.05, 68.75, 68.47, 68.12, 67.87, 64.48, 55.61, 33.89, 32.37, 31.60, 30.15, 25.86, 24.24, 23.92; ESIHRMS, Calcd. for $C_{114}H_{120}O_{27}$ ($[M+Cs]^+$): 2053.7071; found: 2053.6990.

Cyclohexyl 3-*O*-Benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranoside (16). Removal of the PMB group from pentasaccharide **14** (312 mg, 0.162 mmol) by the general procedure afforded alcohol **16** (234 mg, 0.130 mmol) as a foam in 80 % $[\alpha]_D$ -85.7 (*c*, 1.3, $CHCl_3$); ^{1}H NMR ($CDCl_3$), δ: 7.00-7.49 (m, 50H), 5.56 (s, 1H), 5.54 (s, 1H), 5.53 (s, 1H), 5.52 (s, 1H), 5.27 (s, 1H), 5.24 (s, 1H), 5.22 (s, 1H), 4.87 (s, 1H), 4.84 (s, 1H), 4.55-4.76 (m, 15H), 4.21-4.34 (m, 7H), 4.17 (t, *J* = 9.6 Hz, 1H), 4.08 (d, *J* = 4.0Hz, 1H), 4.07 (t, *J* = 9.6Hz, 1H), 3.76-3.91 (m, 6H), 3.68-3.75 (m, H), 3.52-3.66 (m, 4H), 3.47 (dd, *J* = 3.2Hz, 9.2Hz, 1H), 3.34-3.43 (m, 2H), 3.42-3.32 (m, 3H), 1.20-1.90 (m, 10H); ^{13}C NMR ($CDCl_3$), δ: 138.69, 138.56, 138.40, 138.29, 138.21, 137.85, 137.71, 137.49, 137.19,

137.15, 129.18, 129.08, 128.95, 128.87, 128.55, 128.52, 128.41, 128.35, 128.29, 128.64, 128.22, 127.96, 127.90, 127.80, 127.59, 127.54, 127.48, 127.43, 127.35, 126.99, 126.28, 126.25, 126.23, 126.20, 126.14, 104.06, 102.13, 101.96, 101.87, 101.80, 101.69, 101.45, 101.42, 98.76, 79.04, 78.69, 78.66, 78.56, 78.35, 77.97, 77.33, 76.59, 76.34, 76.30, 75.60, 75.19, 73.76, 72.65, 72.36, 72.04, 71.22, 71.03, 69.31, 68.95, 68.89, 68.79, 68.70, 67.95, 67.79, 67.67, 67.50, 66.99, 33.52, 31.29, 25.57, 23.90, 23.54; ESIHRMS, Calcd. for $C_{106}H_{115}O_{27}$ ($[M+H_3O]^+$) 1819.7620; found: 1819.7710.

Cyclohexyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-*O*-*p*-methoxybenzyl-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranoside (17). Coupling of sulfoxide **3** (299 mg, 0.56 mmol) and acceptor **16** (500 mg, 0.28 mmol) by the standard coupling protocol gave 60% of β-D-mannopyranoside **17** (374 mg, 0.166 mmol) as a foam and 23% of a mixture of isomers (145mg, 0.064 mmol) which contained 8% β-anomer (**17**) and 15% α-anomer (**18**) according to the ^{1}H NMR spectrum. **17**: $[\alpha]_D$ -100 (*c*, 2.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$), δ: 6.94-7.50 (m, 62H), 6.17 (d, *J* = 8.8 Hz, 2H), 5.57 (s, 1H), 5.52 (s, 2H), 5.40 (s, 1H), 5.32 (s, 1H), 5.24 (s, 1H), 5,21 (s, 1H), 5.06 (s, 1H), 5.04 (s, 1H), 4.95 (s, 1H), 4.57-4.84 (m, 17H), 4.49 (d, *J* = 11.2 Hz, 1H), 4.24-4.40 (m, 5H), 4.07-4.20 (m, 8H), 3.98 (t, *J* = 9.6 Hz, 1H), 3.92 (t, *J* = 9.6 Hz, 1H), 3.88 ((t, *J* = 9.6 Hz, 1H), 3.64-3.83 (m, 7H), 3.53-3.62 (m, 5H), 3.48 (t, *J* = 10.2 Hz, 1H), 3.39-3.45 (m, 3H), 3.37 (s, 3H), 3.24-3.30 (m, 1H), 3.16-3.22 (m, 1H), 2.96-3.02 (m, 1H), 1.20-1.90 (m, 10H);

^{13}C NMR ($CDCl_3$), δ: 158.73, 138.84, 138.70, 138.36, 138.24, 138.17, 137.96, 137.90, 137.74, 137.32, 136.97, 136.90, 136.82, 130.86, 130.74, 129.06, 128.98, 128.95, 128.76, 128.73, 128.53, 128.47, 128.38, 128.29, 128.23, 128.20, 128.15, 128.10, 128.05, 128.01, 127.96, 127.85, 127.46, 127.28, 127.18, 127.09, 127.05, 126.99, 126.88, 126.78, 126.18, 126.13, 126.05, 125.96, 113.44, 104.04, 104.00, 103.84, 102.74, 101.90, 101.64, 101.51, 101.47, 101.42, 101.32, 101.15, 98.55, 79.03, 78.99, 78.94, 78.75, 78.57, 78.54, 78.38, 78.16, 77.97, 77.23, 77.11, 76.90, 76.57, 76.52, 76.19, 74.22, 73.52, 73.24, 72.48, 72.32, 71.44, 71.33, 71.25, 71.18, 68.84, 68.79, 68.62, 67.54, 67.34, 66.84, 66.76, 60.41, 33.36, 31.61, 31.10, 25.41, 23.73, 23.36, 21.09, 14.21; ESIHRMS, Calcd. for $C_{134}H_{144}O_{32}N$ ($[M+ NH_4]^+$): 2278.9671; found: 2278.9717. A pure sample of the α-anomer **18** was not isolated and as such no data is given here for this byproduct.

Cyclohexyl 3-*O*-Benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranoside (19). Removal of the PMB group from hexasaccharide **17** (362 mg, 0.160 mmol) by the general procedure afforded the alcohol **19** (291.5 mg, 0.136 mmol) as a foam in 85% yield. $[\alpha]_D$ -91.7 (*c*, 2.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$), δ: 7.02-7.45 (m, 60H), 5.56 (s, 1H), 5.54 (s, 1H), 5.52 (s, 2H), 5.43 (s, 1H), 5.32 (s, 2H), 5.14 (s, 1H), 5.10 (s, 1H), 5.09 (s, 1H), 4.90 (s, 1H), 4.55-4.81 (m, 17H), 4.29-4.40 (m, 5H), 4.11-4.26 (m, 5H), 3.92-4.03 (m, 3H), 3.73-3.84 (m, 6H), 3.60-3.69 (m, 6H), 3.51-3.56 (m, 2H), 3.36-3.48 (m, 3H), 3.26-3.34 (m, 2H), 3.17-3.23 (m, 1H), 1.20-1.90 (m,

10H); ^{13}C NMR ($CDCl_3$), δ: 138.65, 138.37, 138.31, 138.21, 138.17, 137.95, 137.79, 137.69, 137.48, 136.97, 136.90, 129.02, 128.74, 128.65, 128.43, 128.28, 128.20, 128.13, 128.10, 128.07, 127.90, 127.86, 127.80, 127.68, 127.47, 127.43, 127.36, 127.31, 127.25, 126.86, 126.83, 126.15, 126.06, 126.01, 103.67, 102.63, 102.60, 101.94, 101.88, 101.60, 101.38, 101.32, 101.27, 98.75, 78.89, 77.32, 77.28, 77.23, 77.01, 76.92, 76.82, 76.58, 76.43, 76.04, 75.16, 74.42, 72.25, 72.21, 71.82, 71.53, 71.38, 71.29, 69.23, 68.94, 68.73, 68.68, 68.61, 67.70, 67.53, 67.34, 67.07, 66.73, 33.38, 31.19, 29.73, 25.43, 23.76, 23.42. ESIHRMS, Calcd. for $C_{126}H_{136}O_{31}N$ ($[M+ NH_4]^+$): 2158.9096; found: 2158.9038.

Cyclohexyl 3-*O*-Benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranoside (22) and Cyclohexyl 3-*O*-Benzyl-4,6-*O*-benzylidene-α-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranoside (23). Coupling of sulfoxide **3** (66.9 mg, 0.124 mmol) and acceptor **19** (133 mg, 0.0621 mmol) by the standard coupling protocol gave an inseparable mixture of anomeric isomers **20** and **21** (124 mg, 0.048 mmol) in 77% yield. The mixture was treated with DDQ by the general procedure to give 67% of the β-

anomeric alcohol **22** (78.4 mg, 0.032 mmol) as a foam and the 14% of the α-anomeric alcohol **23** (16.0 mg) as a foam. **22**: $[\alpha]_D$ -75.6 (*c*, 0.90, $CHCl_3$); ^1H NMR ($CDCl_3$), δ: 7.02-7.55 (m, 70H), 5.59 (s, 1H), 5.58 (s, 1H), 5.56 (s, 1H), 5.55 (s, 1H), 5.45 (s, 1H), 5.44 (s, 1H), 5.36 (s, 1H), 5.31 (s, 1H), 5.30 (s, 1H), 5.19 (s, 1H), 5.11 (s, 1H), 5.01 (s, 1H), 4.90(s, 1H), 4.58-4.84 (m, 30H), 4.23-4.43 (m, 8H), 4.20 (t, *J* = 10.5 Hz, 1H), 4.12-4.17 (m, 2H), 3.93-4.06 (m, 4H), 3.81-4.91 (m, 5H), 3.64-3.79 (m, 7H), 3.55-3.60 (m, 3H), 3.52 (dd, *J* = 3.0 Hz, 9.5 Hz, 1H), 3.38-3.49 (m, 4H), 3.28-3.36 (m, 2H), 3.16-3.21 (m, 1H), 1.20-1.90 (m, 10H); ^{13}C NMR ($CDCl_3$), δ: 139.15, 138.90, 138.80, 138.67, 138.62, 138.57, 138.35, 138.22, 138.01, 137.62, 137.43, 137.35, 137.30, 129.50, 129.45, 129.28, 129.12, 129.08, 128.91, 128.81, 128.76, 128.58, 128.48, 128.36, 128.32, 128.12, 128.02, 127.80, 127.73, 127.70, 127.62, 127.57, 127.52, 127.29, 127.21, 126.62, 126.59, 126.56, 126.48, 126.43, 104.34, 103.71, 103.01, 102.72, 102.33, 102.25, 102.20, 102.08, 101.99, 101.86, 101.76, 101.66, 101.54, 99.08, 79.40, 79.29, 79.06, 79.01, 78.98, 78.94, 78.90, 78.25, 77.83, 77.71, 77.62, 77.20, 77.17, 76.99, 76.82, 76.77, 75.24, 74.45, 72.69, 72.57, 72.20, 71.97, 71.86, 69.51, 69.34, 69.20, 69.16, 69.08, 69.03, 68.10, 68.06, 67.96, 67.81, 67.55, 67.47, 67.28, 33.83, 31.60, 30.16, 25.86, 24.18, 23,85; ESIHRMS, Calcd. for $C_{146}H_{152}O_{36}Na$ ($[M+ Na]^+$): 2503.9961; found: 2504.0034. **23:** $[\alpha]_D$ -77.2 (*c*, 2.40, $CHCl_3$); ^1H NMR ($CDCl_3$), δ: 6.90-7.45 (m, 70H), 5.71 (s, 1H), 5.63 (s, 1H), 5.61 (s, 1H), 5.58 (s, 1H), 5.54 (s, 1H), 5.48 (s, 1H), 5.35 (s, 1H), 5.29 (s, 1H), 5.10 (s, 1H), 5.06 (s, 1H), 5.02 (s, 1H), 4.55-4.93 (m, 21H), 4.42-4.78 (m, 3H), 4.22-4.38 (m, 3H), 4.24 (dd, *J* = 4.0 Hz, 10.4 Hz, 1H), 3.96-4.20 (m, 9H), 3.65-3.93 (m, 16H), 3.50 (dd, *J* = 4.7 Hz, 10.4 Hz, 1H), 3.35-3.40 (m, 3H), 3.14-3.40 (m, 2H), 2.46-2.52 (m, 1H), 1.20-1.90 (m, 10H); ^{13}C NMR ($CDCl_3$), δ: 139.10, 138.56, 138.51, 138.27, 138.24, 138.18, 138.11,

138.02, 137.89, 137.52, 137.08, 136.88, 136.81, 129.06, 129.01, 128.94, 128.68, 128.57, 128.49, 128.37, 128.30, 128.26, 128.23, 128.16, 128.12, 128.08, 128.06, 127.97,. 127.94, 127.91, 127.82, 127.76, 127.44, 127.36, 127.17, 126.75, 126.65, 126.59, 126.56, 126.16, 126.12, 126.07, 126.03, 125.98, 125.95, 104.46, 103.51, 103.22, 102.86, 101.88, 101.60, 101.35, 101.30, 101.20, 101.10, 101.07, 100.42, 100.06, 98.33, 80.05, 79.73, 79.68, 79.41, 79.28, 79.19, 78.51, 78.31, 78.12, 77.92, 77.58, 77.43, 77.24, 76.81, 76.58, 76.52, 76.44, 76.33, 76.06, 73.40, 73.23, 72.92, 72.67, 72.40, 71.59, 71.44, 70.99, 70.66, 70.19, 68.95, 68.65, 68.59, 68.74, 67.76, 67.67, 67.38, 67.34, 66.93, 66.75, 63.35, 60.42, 33.35, 31.03, 29.70, 25.43, 23.72, 23.34, 22.70; ESIHRMS, Calcd. for $C_{146}H_{152}O_{36}Na$ ([M+ Na]$^+$): 2503.9961; found: 2504.0016.

Cyclohexyl 3-*O*-Benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranoside (26) and Cyclohexyl 3-*O*-Benzyl-4,6-*O*-benzylidene-α-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranoside (27). Coupling of

sulfoxide **3** (31.2 mg, 0.058 mmol) and acceptor **22** (66.7 mg, 0.027 mmol) by the standard coupling protocol gave an inseparable mixture of anomeric isomers **24** and **25** (61.3 mg, 0.021 mmol) in 78% yield. The mixture was treated with DDQ by the general procedure to give 58% of the β-anomeric alcohol **26** (33.1 mg, 0.012 mmol) and 13% of the α-anomeric alcohol **27** (7.4 mg, 0.003 mmol). **26**: $[\alpha]_D$ -94.8 (*c*, 0.9, $CHCl_3$); ^1H NMR ($CDCl_3$), δ: 7.00-7.41 (m, 80H), 5.56 (s, 1H), 5.54 (s, 1H), 5.532 (s, 1H), 5.525 (s, 1H), 5.45 (s, 1H), 5.54 (s, 1H), 5.39 (s, 1H), 5.30 (s, 3H), 5.18(s, 1H), 5.12 (s, 1H), 5.07 (s, 1H), 5.03 (s, 1H), 4.89 (s, 1H), 4.51-4.81 (m, 23H), 4.29-4.40 (m, 6H), 4.19-4.26(m, 3H), 4.13-4.17 (m, 3H), 3.90-4.02 (m, 5H), 3.74-3.86 (m, 5H), 3.72-3.73 (m, 1H), 3.53-3.70 (m, 11H), 3.46 (dd, *J* = 3.0 Hz, 9.5 Hz, 1H), 3.35-3.43 (m, 4H), 3.29-3.43 (m, 2H), 3.19-(3.26 (m, 2H), 1.20-1.90 (m, 10H); ^{13}C NMR ($CDCl_3$), δ: 139.05, 138.88, 138.80, 138.77, 138.61, 138.54, 138.30, 138.17, 138.02, 137.71, 137.56, 137.37, 137.27, 129.47, 129.42, 129.22, 129.03, 129.00, 128.87, 128.83, 128.73, 128.68, 128.62, 128.56, 128.53, 128.49, 128.44, 128.39, 128.31, 128.08, 128.02, 127.83, 127.75, 127.67, 127.62, 127.57, 127.52, 127.48, 127.31, 127.25, 127.17, 127.06, 126.65, 126.62, 126.59, 126.50, 126.45, 126.40, 104.16, 103.58, 103.24, 103.03, 102.38, 102.26, 102.15, 101.99, 101.94, 101.89, 101.71, 101.65, 101.58, 99.14, 79.32, 79.22, 79.07, 78.99, 78.96, 78.88, 78.80, 78.02, 77,66, 77.55, 77.01, 76.90, 76.82, 76.64, 76.03, 75.08, 74.93, 72.61, 72.55, 72.34, 72.24, 71.96, 71.65, 69.49, 69.28, 69.17, 69.14, 69.07, 68.97, 68.09, 67.99, 67.83, 67.80, 67.69, 67.62, 67.40, 67.22, 33.81, 31.60, 30.13, 25.84, 24.17, 23.83; ESIHRMS, Calcd. for $C_{166}H_{172}O_{41}Na$ ($[M+ Na]^+$): 2844.1272; found: 2844.1272. **27**: $[\alpha]_D$ -77.9 (*c*, 0.7, $CHCl_3$); ^1H NMR ($CDCl_3$), δ: 7.09-7.41 (m, 80H), 5.65 (s, 1H), 5.60 (s, 1H), 5.57 (s, 1H), 5.56 (s, 1H), 5.51 (s, 1H), 5.46 (s, 1H), 5.38 (s, 1H), 5.30 (s, 2H), 5.23 (s, 1H), 5.21

(s, 1H), 5.07 (s, 1H), 4.99 (s, 1H),4.55-4.88 (m, 24H), 4.44-4.47 (m, 2H), 4.38 (d, *J* = 12.5 Hz, 1H), 4.22-4.34 (m, 6H), 4.05-4.20 (m, 6H), 3.95-4.03 (m, 4H), 3.79-3.88 (m, 6H), 3.53-3.76 (m, 14H), 3.41-3.48 (m, 2H), 3.28-3.35 (m, 3H), 2.48-.60 (m, 1H), 1.20-1.90 (m, 10H); ^{13}C NMR ($CDCl_3$), δ: 139.57, 139.00, 138.88, 138.85, 138.58, 138.55, 138.46, 138.28, 137.61, 137.40, 137.36, 137.24, 137.05, 129.39, 128.81, 128.77, 128.70, 128.65, 128.62, 128.59, 128.54, 128.48, 128.43, 128.39, 128.36, 128.32, 128.25, 128.22, 128.14, 128.11, 127.98, 127.72, 127.56, 127.49, 127.46, 127.39, 127.12, 127.07, 127.03, 126.93, 126.83, 126.61, 126.58, 126.55, 126.48, 126.42, 126.37, 104.45, 103.57, 102.86, 102.35, 102.21, 102.03, 101.81, 101.75, 101.69, 101.67, 101.55, 100.86, 100.56, 100.04, 99.12, 96.50, 79.63, 79.53, 79.39, 78.95, 78.88, 78.80, 78.67, 78.62, 78.45, 78.43, 78.31, 77.89, 77.18, 76.90, 76..84, 76.37, 75.82, 75.46, 73.60, 73.19, 72.43, 72.11, 72.03, 71.56, 71.00, 69.27, 69.05, 68.94, 68.20, 68.07, 67.93, 67.82, 67.77, 67.50, 67.32, 34.82, 30.13, 25.80, 24.17, 23.83, 14.64; ESIHRMS, Calcd. for $C_{166}H_{172}O_{41}Na$ ($[M+Na]^+$): 2844.1272; found: 2844.1280.

Cyclohexyl β-D-Mannopyranosyl-β-D-mannopyranosyl-(1→2)-β-D-mannopyranosyl-β-D-mannopyranosyl-(1→2)-β-D-mannopyranosyl-(1→2)-β-D-mannopyranosyl-(1→2)-β-D-mannopyranosyl-β-D-mannopyranoside (28). A mixture of octasaccharide **26** (33.9 mg, 0.0120 mmol) and 10% Pd/C (100 mg) in MeOH (2 mL) was shaken under 50 psi of H_2 for 3 days. The reaction mixture was filtered through Celite followed by removal of solvent to give the target compound **26** (15.0 mg, 0.011 mmol) as a foam in 89% yield. $[\alpha]_D$ -30.9 (*c*, 0.43, MeOH); ^{1}H NMR (CD_3OD), δ: 5.05 (s, 1H), 5.032 (s, 1H), 5.026 (s, 1H), 5.01 (s, 1H), 4.95 (s, 1H), 4.91 (s, 1H), 4.85 (s, 1H), 4.39 (d, *J* = 3.0

Hz, 1H), 4.34-4.38 (m, 5H), 4.17 (d, *J* = 3.0 Hz, 1H), 4.14 (d, *J* = 3.0Hz, 1H), 3.86-3.92 (m, 8H), 3.77-3.82 (m, 1H), 3.59-3.75 (m, 17H), 3.52-3.57(m, 2H), 3.44-3.51 (m, 5H), 3.32-3.42 (m, 8H), 1.19-1.90 (m, 10H); ^{13}C NMR (CD_3OD), δ: 101.80, 101.69, 101.65, 101.48, 101.31, 98.08, 80.40, 79.68, 79.60, 79.49, 82.09, 78.83, 77.73, 76.55, 76.49, 76.45, 76.32, 76.27, 73.28, 72.62, 72.44, 72.35, 72.31, 72.27, 72.24, 70.78, 67.95, 67.61, 67.54, 67.50, 67.39, 67.13, 61.53, 61.22, 61.15, 61.05, 60.99, 60.95, 60.91, 33.08, 31.48, 25.44, 23.80, 23.59; ESIHRMS, Calcd. for $C_{54}H_{92}O_{41}Na$ ($[M+Na]^+$): 1419.5011; found: 1419.4993.

Methyl 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranoside (30) and Methyl 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (31). A stirred solution of thioglycoside **29**[2] (2.140 g, 4.45 mmol), **BSP**[3] (1.024 g, 4.89 mmol), **TTBP**[4] (2.210 g, 8.89 mmol) and activated 3Å powdered sieves in dichloromethane (75 mL) under a nitrogen atmosphere was kept at -60 ^{0}C for 30 mins. Then was added Tf_2O (898 μL, 5.34 mmol) and after 5 mins. MeOH (540 μL, 13.34 mmol) was added slowly and reaction mixture was cooled down to -78 ^{0}C and stirred for additional 1.5 h before molecular sieves were filtered off, and the organic layer was washed with saturated aqueous $NaHCO_3$ solution, brine and dried (Na_2SO_4). The organic layer was concentrated under reduced pressure. Purification by silica gel column chromatography (12% ethyl acetate in hexane) afforded the corresponding α (**31**) and β mannosides (**30**) (1.850 g, 90%) with a ratio of 1:10. **30:** $[\alpha]^{26}_D$ -21.6 (*c*, 0.32, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 7.50 (d, *J* = 1.4 Hz, 2H), 7.47 (d, *J* = 6.9 Hz, 2H), 7.38-7.26 (m, 11H), 5.63 (s, 1H), 4.97 (d, *J* = 12.3 Hz, 1H), 4.85 (d, *J* = 12.3 Hz, 1H), 4.68 (d, *J* = 12.5 Hz, 1H), 4.58 (d, *J* = 12.5 Hz, 1H), 4.38 (s,

1H), 4.35-4.31 (dd, J = 5.3, 12.0 Hz, 1H), 4.21 (t, J = 10.0 Hz, 1H), 3.93 (m, 2H), 3.60-3.56 (dd, J = 3.5,10.0 Hz,1H), 3.54 (s, 3H), 3.36-3.31 (m, 1H); ^{13}C NMR ($CDCl_3$) δ: 57.4, 67.6, 68.6, 72.3, 74.8, 75.8, 77.8, 78.7, 101.4 ($^1J_{CH}$ = 162.1 Hz), 103.4 ($^1J_{CH}$ = 156.6 Hz), 126.03, 126.04, 127.5, 127.53, 127.54, 128.1, 128.2, 128.3, 128.5, 128.9, 137.6, 138.3, 138.5; ESIHRMS Calcd for $C_{28}H_{30}O_6Na$ $[M + Na]^+$: 485.1940, found, 485.1941. **31:** $[\alpha]^{26}_D$ +30.6 (*c*, 1.02, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 7.53-7.50 (m, 2H), 7.44-7.26 (m, 13H), 5.66 (d, J = 2.0 Hz, 1H), 4.85-4.80 (m, 2H), 4.77-4.75 (dd, J = 1.8, 12.5 Hz, 1H), 4.70 (s, 1H), 4.69-4.66 (dd, J = 1.8, 7.0 Hz, 1H), 4.29-4.24 (m, 2H), 3.97-3.94 (m, 1H), 3.93-3.90 (m, 1H), 3.85-3.84 (m, 1H), 3.79-3.78 (m, 1H), 3.33 (d, J = 1.9 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ: 54.8, 64.0, 68.9, 73.1, 73.6, 76.2, 76.4, 77.3, 77.4, 79.1, 100.5 ($^1J_{CH}$ = 168.4 Hz), 101.5 ($^1J_{CH}$ = 161.0 Hz), 126.1, 127.5, 127.8, 128.1, 128.2, 128.3, 128.4, 128.8, 137.7, 138.1, 138.7; ESI-HRMS Calcd for $C_{28}H_{30}O_6Na$ $[M + Na]^+$: 485.1940, found 485.1961.

Methyl 2,3,6-Tri-*O*-benzyl-β-D-mannopyranoside (32). To a solution of compound **30** (1.415 g, 3.09 mmol) in THF (40 mL) was added sodium cyanaborohydride (2.90 g, 46.3 mmol) and a pinch of methyl orange. After stirring at 0 ^{0}C for 15 mins, a 2.0 M solution of hydrochloric acid in diethylether (20 mL) was added slowly until the color of the solution became permanently pink. The reaction mixture was stirred at room temperature for 12 h then diluted with ethyl acetate, washed with saturated aqueous $NaHCO_3$ solution, water and brine. The organic layer was separated, dried (Na_2SO_4) and concentrated under reduced pressure. Purification by silica gel column chromatography (20% ethyl acetate in hexane) afforded **32** (1.032 g, 72%). M.p. 110-112 ^{0}C; $[\alpha]^{26}_D$ -28.8 (*c*, 0.20, $CHCl_3$); ^{1}H

NMR ($CDCl_3$) δ: 7.48-7.20 (m, 15H), 4.98 (d, *J* = 12.5 Hz, 1H), 4.76 (d, *J* = 12.5 Hz, 1H), 4.62 (s, 2H), 4.50 (d, *J* = 12.0 Hz, 1H), 4.37 (s, 1H), 4.34 (s, 1H), 3.98 (t, *J* = 9.4 Hz, 1H), 3.94-3.84 (m, 2H), 3.80 (dd, *J* = 6.3, 10.5 Hz, 1H), 3.56 (s, 3H), 3.54-3.40 (m, 1H), 3.32 (dd, *J* = 2.8, 9.8 Hz, 1H), 2.68 (bs, 1H); ^{13}C NMR ($CDCl_3$) δ: 57.3, 68.5, 71.0, 71.4, 73.6, 73.8, 74.2, 75.4, 81.7, 100.1, 127.5, 127.7, 127.8, 127.9, 128.0, 128.2, 128.3, 128.4, 128.5, 128.6, 135.7, 138.0, 138.3, 138.3, 138.9; HRMS Calcd. for $C_{28}H_{32}O_6Na$ ($[M+Na]^+$), 487.2097; found 487.2104.

Methyl 2,3,6-Tri-*O*-benzyl-4-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl)-β-D-mannopyranoside (33) and Methyl 2,3,6-Tri-*O*-benzyl-4-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranosyl)-β-D-mannopyranoside (34). A stirred solution of thioglycoside **29** (1.619 g, 2.99 mmol), **BSP** (0.690 g, 3.30 mmol), **TTBP** (1.500 g, 5.99 mmol) and activated 3Å powdered sieves in dichloromethane (60 mL) under nitrogen atmosphere was kept at -60 ^{0}C for 30 mins. Then was added Tf_2O (605 μL, 3.60 mmol) and after 5 mins. acceptor **32** (1.217 g, 2.62 mmol) in dichloromethane (10 mL) was added by cannula and reaction mixture was cooled down to -78 ^{0}C and stirred for additional 6 h before molecular sieves were filtered off, and the organic layer was washed with saturated aqueous $NaHCO_3$ solution, brine and dried (Na_2SO_4). The organic layer was concentrated under reduced pressure. Purification by silica gel column chromatography (18% ethyl acetate in hexane) afforded the corresponding α and β mannosides (2.035 g, 80%) with a ratio of 1:10. **33:** $[\alpha]^{24}_D$ -40.3 (*c*, 0.58, $CHCl_3$); ^1H NMR ($CDCl_3$) δ: 7.55-7.53 (dd, *J* = 3.5, 6.0 Hz, 2H), 7.42-7.34 (m, 4H), 7.33-7.21 (m, 24H), 5.52 (s, 1H), 4.90-4.88 (d, *J* = 11.5 Hz, 1H), 4.83-4.81 (d, *J* =

12.0 Hz, 1H), 4.77-4.74 (d, *J* = 13.0 Hz, 1H), 4.71-4.66 (m, 2H), 4.64-4.62 (d, *J* = 12.0 Hz, 1H), 4.58 (s, 1H), 4.57-4.55 (d, *J* = 12.0 Hz, 1H), 4.53-4.51 (d, *J* = 12.0 Hz, 1H), 4.47- 4.44 (d, *J* = 12.5 Hz, 1H), 4.34 (s, 1H), 4.26-4.19 (m, 2H), 4.17-4.14 (t, *J* = 9.0 Hz, 1H), 4.09-4.06 (t, *J* = 8.5 Hz, 1H), 4.02-3.99 (dd, *J* = 5.0, 10.5 Hz, 1H), 3.87 (d, *J* = 3.5 Hz, 1H), 3.76-3.75 (dd, *J* = 3.0, 6.5 Hz, 1H), 3.71-3.68 (dd, *J* = 5.0, 11.5 Hz, 1H), 3.66-3.62 (t, *J* = 10.5 Hz, 1H), 3.54 (d, *J* = 6.0 Hz, 1H), 3.53 (s, 3H), 3.49-3.48 (m, 1H), 3.45-3.43 (dd, *J* = 3.0, 10.0 Hz, 1H), 3.08-3.07 (m, 1H); ^{13}C NMR ($CDCl_3$) δ: 57.2, 67.3, 68.2, 68.6, 69.5, 71.9, 72.5, 73.5, 73.8, 74.5, 74.9, 75.3, 75.9, 78.4, 78.6, 79.8, 101.3, 101.9, 102.3, 126.1, 127.2, 127.3, 127.36, 127.4, 127.5, 127.7, 127.9, 128.0, 128.1, 128.12, 128.15, 128.2, 128.3, 128.4, 128.8, 130.9, 132.4, 137.6, 138.3, 138.7, 138.8; ESIHRMS Calcd for $C_{55}H_{58}O_{11}Na$ $[M + Na]^+$: 917.3877, found: 917.3845. **34:** $[\alpha]^{24}_D$ -26.6 (*c*, 0.97, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 7.51-7.49 (dd, *J* = 2.0, 8.5 Hz, 2H), 7.42-7.35 (m, 4H), 7.33-7.17 (m, 24H), 5.61 (s, 1H), 5.29 (d, *J* = 2.0 Hz, 1H), 4.97-4.94 (d, *J* = 12.0 Hz, 1H), 4.81-4.79(d, *J* = 12.0 Hz, 1H), 4.74-4.71 (d, *J* = 12.5 Hz, 1H), 4.63-4.62 (d, *J* = 12.5 Hz, 1H), 4.59-4.57 (d, *J* = 12.5 Hz, 1H), 4.41-4.39 (d, *J* = 12.0 Hz, 1H), 4.37-4.35 (d, *J* = 12.0 Hz, 1H), 4.33 (s, 1H), 4.27-4.19 (m, 5H), 4.11-4.09 (dd, *J* = 4.0, 9.5 Hz, 1H), 4.03 (t, *J* = 9.5 Hz, 1H), 3.90 (d, *J* = 3.0 Hz, 1H), 3.89-3.86 (m, 2H), 3.85-3.82 (dd, *J* = 4.5, 9.5 Hz, 1H), 3.81-3.76 (m, 2H), 3.56 (s, 3H), 3.48-3.44 (m, 1H), 3.42-3.39 (dd, *J* = 3.0, 9.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ: 57.3, 65.1, 68.2, 68.7, 70.3, 70.7, 72.9, 73.0, 73.7, 73.9, 74.7, 75.4, 76.3, 77.4, 78.9, 82.1, 101.1, 101.3, 102.5, 126.1, 127.3, 127.39, 127.4, 127.5, 127.6, 127.7, 127.8, 128.0, 128.06, 128.09, 128.1, 128.12, 128.2, 128.3, 128.5, 128.7, 128.8, 130.9, 137.6, 137.7, 138.4, 138.6, 138.9; ESIHRMS Calcd for $C_{55}H_{58}O_{11}Na$ $[M + Na]^+$: 917.3877, found 917.3851.

Methyl 2,3-Di-*O*-benzyl-β-D-mannopyranoside (35). A solution of **30** (1.688 g, 3.65 mmol), CSA (0.212 g, 0.91 mmol) and *neo*-pentylglycol (1.14 g, 10.95 mmol) in dichloromethane (25 mL) under a nitrogen atmosphere was stirred at room temperature for 12 h. The reaction mixture was concentrated under reduced pressure, dissolved in ethyl acetate, washed with saturated aqueous $NaHCO_3$ solution, water and brine. The organic layer was separated, dried (Na_2SO_4) and concentrated under reduced pressure. Purification by silica gel column chromatography (60% ethyl acetate in hexane) afforded **35** (1.215 g, 89%). $[\alpha]^{26}_D$ -89.9 (*c*, 0.34, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 7.43 (d, *J* = 1.5 Hz, 1H), 7.30-7.23 (m, 9H), 4.95 (d, *J* = 13.0 Hz, 1H), 4.74 (d, *J* = 13.0 Hz, 1H), 4.46 (d, *J* = 12.0 Hz, 1H), 4.39 (s,1H), 4.26 (d, *J* = 11.5 Hz, 1H), 3.99-3.93 (m, 3H), 3.86-3.82 (m,1H), 3.57 (s, 3H), 3.35-3.30 (m, 2H), 2.40 and 2.22 (2br. s, 2H); ^{13}C NMR ($CDCl_3$) δ: 57.4, 63.1, 67.5, 70.9, 73.1, 74.2, 75.8, 76.7, 81.5, 103.0, 127.6, 127.9, 128.2, 128.3, 128.6, 137.5, 138.5; ESI-HRMS Calcd for $C_{21}H_{26}O_6Na$ $[M + Na]^+$: 397.1627, found 397.1637.

Methyl 2,3-Di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranoside (36). To a stirred solution of **35** (1.215 g, 3.25 mmol) and DMAP (0.099 g, 0.81 mmol) in dichloromethane (30 mL) was added Et_3N (905 μL, 6.49 mmol) followed by pivaloyl chloride (419 μL, 3.42 mmol) at room temperature under a nitrogen atmosphere. The reaction mixture was stirred for 4 h and washed with saturated aqueous $NaHCO_3$ solution and brine. The organic layer was dried (Na_2SO_4) and concentrated under reduced pressure. Purification by silica gel column chromatography (24% ethyl acetate in hexane) afforded **36** (1.417 g,

98%). $[\alpha]^{26}_{D}$ -74.0 (*c*, 0.25, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 7.42 (d, *J* = 7.0 Hz, 1H), 7.34-7.24 (m, 9H), 4.94 (d, *J* = 12.5 Hz, 1H), 4.73 (d, *J* = 12.0 Hz, 1H), 4.48 (d, *J* = 11.5 Hz, 1H), 4.45 (d, *J* = 2.0 Hz, 1H), 4.33-4.28 (m, 3H), 3.91 (d, *J* = 5.0 Hz, 1H), 3.87 (t, *J* = 9.5 Hz, 1H), 3.53 (s, 3H), 3.46-3.42 (m, 1H), 3.30-3.28 (dd, *J* = 3.0, 10.0 Hz, 1H), 2.46 (bs, 1H), 1.19 (s,9H); ^{13}C NMR ($CDCl_3$) δ: 27.2, 57.1, 63.8, 66.9, 71.1, 73.1, 74.0, 74.4, 81.2, 102.9, 127.5, 127.8, 127.9, 128.1, 128.2, 128.5, 137.6, 138.6, 178.7; ESI-HRMS Calcd for $C_{26}H_{34}O_7Na$ $[M + Na]^+$: 481.2202, found 481.2202.

Methyl 2,3-Di-*O*-benzyl-6-*O*-pivaloyl-4-*O*-(2,3-di-*O*-benzyl-4,6-benzylidene-β-D-mannopyranosyl)-β-D-mannopyranoside (37) and Methyl 2,3-Di-*O*-benzyl-6-*O*-pivaloyl-4-*O*-(2,3-di-*O*-benzyl-4,6-benzylidene-α-D-mannopyranosyl)-β-D-mannopyranoside (38). A stirred solution of thioglycoside **29** (0.574 g, 1.06 mmol), **BSP** (0.245 g, 1.17 mmol), **TTBP** (0.528 g, 2.12 mmol) and activated 3Å powdered sieves in dichloromethane (45 mL) under nitrogen atmosphere was kept at -60 ^{0}C for 30 mins. Then was added Tf_2O (214 μL, 1.27 mmol) and after 5 mins. acceptor **36** (0.381 g, 0.83 mmol) in dichloromethane (5 mL) was added by cannula and reaction mixture was cooled down to -78 ^{0}C and stirred for additional 6 h before molecular sieves were filtered off, and the organic layer was washed with saturated aqueous $NaHCO_3$ solution, brine and dried (Na_2SO_4). The organic layer was concentrated under reduced pressure. Purification by silica gel column chromatography (16% ethyl acetate in hexane) afforded the corresponding mannosides (0.846 g, 89%) with a ratio of 1:9. **37:** $[\alpha]^{26}_{D}$ -23.7 (*c*, 0.14, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 7.48-7.37 (m, 8H), 7.33-7.25 (m, 17H), 5.54 (s, 1H), 4.91 (d, *J* = 11.5 Hz, 1H), 4.86 (d, *J* = 5.5 Hz, 1H), 4.83 (d, *J* = 5.5 Hz, 1H), 4.76 (d, *J* =

3.5 Hz, 1H), 4.73 (d, *J* = 3.5 Hz, 1H), 4.66 (d, *J* = 5.5 Hz, 1H), 4.63 (d, *J* = 6.0 Hz, 1H), 4.60 (s, 1H), 4.55 (d, *J* = 12.0 Hz, 1H), 4.43-4.39 (dd, *J* = 2.3, 11.5 Hz, 1H), 4.36 (s, 1H), 4.26-4.23 (dd, *J* = 6.3, 12.0 Hz, 1H), 4.13 (t, *J* = 9.5 Hz, 1H), 4.05-4.01 (m, 2H), 3.94 (d, *J* = 5.0 Hz, 1H), 3.87 (d, *J* = 3.5 Hz, 1H), 3.68 (t, *J* = 10.5 Hz, 1H), 3.60-3.55 (m, 3H), 3.52 (s, 3H), 3.12-3.11 (m, 1H), 1.19 (s, 9H); ^{13}C NMR ($CDCl_3$) δ: 27.2, 57.1, 63.4, 67.4, 68.5, 71.9, 72.5, 73.5, 73.8, 74.3, 75.2, 75.7, 78.2, 78.5, 101.4 ($^1J_{CH}$ = 155.1 Hz), 101.7 ($^1J_{CH}$ = 162.1 Hz), 102.1 ($^1J_{CH}$ = 153.6 Hz), 126.1, 127.2, 127.3, 127.4, 127.5, 128.8, 137.6, 138.3, 138.4, 138.6, 178.1; ESIHRMS Calcd for $C_{53}H_{60}O_{12}Na$ $[M + Na]^+$: 911.3982, found 911.3975. **38:** $[\alpha]^{24}_D$ -11.6 (*c*, 0.90, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 7.52 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 7.0 Hz, 2H), 7.32-7.20 (m, 21H), 5.62 (s, 1H), 5.18 (d, *J* = 1.5 Hz, 1H), 4.93 (d, *J* = 12.5 Hz, 1H), 4.84 (d, *J* = 12.5 Hz, 1H), 4.71 (d, *J* = 12.5 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 4.48-4.45 (dd *J* = 2.0, 12.5 Hz, 1H), 4.42 (d, *J* = 4.0 Hz, 1H), 4.40 (d, *J* = 5.0 Hz, 1H), 4.30-4.18 (m, 6H), 4.00 (t, *J* = 10.0 Hz, 1H), 3.92-3.89 (dd, *J* = 2.5, 3.5 Hz, 2H), 3.85-3.80 (m, 3H), 3.52 (s, 3H), 3.48 (m, 1H), 3.39-3.37 (dd, *J* = 3.3, 9.0 Hz, 1H), 1.20 (s, 9H); ^{13}C NMR ($CDCl_3$) δ: 27.2, 57.1, 63.5, 65.2, 68.4, 70.8, 72.9, 73.1, 73.8, 75.9, 76.3, 77.5, 78.9, 81.6, 101.2 ($^1J_{CH}$ = 165.6 Hz), 101.9 ($^1J_{CH}$ = 170.9 Hz), 102.6 ($^1J_{CH}$ = 154.9 Hz), 126.1, 127.37, 127.4, 127.5, 127.7, 127.9, 128.0, 128.1, 128.14, 128.3, 128.5, 128.7, 137.5, 137.7, 138.4, 138.9, 178.1; ESI-HRMS Calcd for $C_{53}H_{60}O_{12}Na$ $[M + Na]^+$: 911.3982, found 911.4017.

Methyl 2,3-Di-*O*-benzyl-6-*O*-pivolyl-4-*O*-(2,3-di-*O*-benzyl-β-D-mannopyranosyl)-β-D-mannopyranoside (39). A solution of **37** (0.761 g, 0.86 mmol), CSA (0.040 g, 0.17 mmol) and *neo*-pentyl glycol (0.268 g, 2.57 mmol) in dichloromethane (10 mL) under

nitrogen atmosphere was stirred at room temperature for 16 h. The reaction mixture was concentrated under reduced pressure, dissolved in ethyl acetate, washed with saturated aqueous $NaHCO_3$ solution, water and brine. The organic layer was separated, dried (Na_2SO_4) and concentrated under reduced pressure. Purification by silica gel column chromatography (50% ethyl acetate in hexane) afforded **39** (0.580 g, 85%). $[\alpha]^{26}_D$ -75.5 (*c*, 0.52, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 7.42-7.38 (m, 3H), 7.36-7.21 (m, 17H), 4.91 (d, *J* = 12.0 Hz, 1H), 4.85 (d, *J* = 11.5 Hz, 1H), 4.78-4.75 (dd, *J* = 3.0, 12.5 Hz, 2H), 4.61-4.48 (m, 5H), 4.36 (s, 1H), 4.33 (s, 1H), 4.23-4.19 (dd, *J* = 6.8, 12.0 Hz, 1H), 4.06 (t, *J* = 9.5 Hz, 1H), 3.94 (d, *J* = 3.0 Hz, 1H), 3.90-3.86 (m, 2H), 3.76-3.73 (dd, *J* = 3.0, 11.5 Hz, 1H), 3.59-3.53 (m, 2H), 3.52 (s, 3H), 3.49 (d, *J* = 2.5 Hz, 1H), 3.26-3.23 (dd, *J* = 2.8, 9.5 Hz, 1H), 3.13 (m, 1H), 2.09 (bs, 2H), 1.21 (s, 9H); ^{13}C NMR ($CDCl_3$) δ: 27.2, 57.1, 62.8, 63.5, 67.2, 71.2, 71.9, 73.6, 74.02, 74.06, 74.4, 74.7, 75.5, 75.7, 77.3, 78.8, 81.8, 100.9, 102.3, 127.4, 127.5, 127.6, 127.7, 128.0, 128.1, 128.2, 128.4, 128.6, 137.6, 138.2, 138.5, 178.4; ESI-HRMS Calcd for $C_{46}H_{56}O_{12}Na$ $[M + Na]^+$: 823.3669, found 823.3679.

Methyl 2,3-Di-*O*-benzyl-6-*O*-pivaloyl-4-*O*-(2,3-di-*O*-benzyl-6-*O*-pivaloyl-β-D-manno-pyranosyl)-β-D-mannopyranoside (40). To a stirred solution of **39** (1.570 g, 1.96 mmol) and DMAP (0.060 g, 0.49 mmol) in dichloromethane (25 mL) was added Et_3N (547 μL, 3.92 mmol) followed by pivaloyl chloride (253 μL, 2.06 mmol) at room temperature under nitrogen atmosphere. The reaction mixture was stirred for 4 h and washed with saturated aqueous $NaHCO_3$ solution and brine. The organic layer was dried (Na_2SO_4) and concentrated under reduced pressure. Purification by silica gel column chromatography (24% ethyl acetate in hexane) afforded **40** (1.519 g, 88%). $[\alpha]^{26}_D$ -69.5

(*c*, 0.19, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 7.41-7.40 (d, *J* = 2.0 Hz, 2H), 7.39-7.22 (m, 18H), 4.88-4.82 (m, 4H), 4.62-4.56 (m, 3H), 4.48 (s, 1H), 4.44 (s, 1H), 4.42 (s, 1H), 4.33 (s, 1H), 4.32-4.26 (m, 2H), 4.24-4.20 (dd, *J* = 4.8, 12.5 Hz, 1H), 4.13-4.08 (m, 1H), 3.90-3.88 (dd, *J* = 2.5, 8.0 Hz, 2H), 3.84 (t, *J* = 9.5 Hz, 1H), 3.63-3.59 (m, 1H), 3.58-3.56 (dd, *J* = 3.5, 8.5 Hz, 1H), 3.51 (s, 3H), 3.23-3.20 (dd, *J* = 2.5, 9.5 Hz, 1H), 3.13-3.11 (m, 1H), 2.05 (s, 1H), 1.21 and 1.13 (2s, 18H); ^{13}C NMR ($CDCl_3$) δ: 27.6, 27.7, 57.5, 63.7, 63.8, 66.7, 71.8, 72.1, 74.0, 74.1, 74.6, 74.7, 74.8, 74.9, 75.5, 78.5, 81.6, 101.1, 102.6, 127.7, 127.8, 128.0, 128.1, 128.2, 128.3, 128.4, 128.5, 128.8, 129.0, 138.1, 138.7, 139.0, 139.1, 178.6, 179.3; ESI-HRMS Calcd for $C_{51}H_{64}O_{13}Na$ $[M + Na]^+$: 907.4245, found 907.4218.

Methyl 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranoside (41) and Methyl 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranoside (42). A stirred solution of thioglycoside **29** (1.010 g, 1.87 mmol), **BSP** (0.431 g, 2.06 mmol), **TTBP** (0.929 g, 3.74 mmol) and activated 3Å powdered sieves in dichloromethane (60 mL) under a nitrogen atmosphere was kept at -60 ^{0}C for 30 mins. Then was added Tf_2O (378 μL, 2.24 mmol) and after 5 mins. acceptor **40** (1.513 g, 1.71 mmol) in dichloromethane (5 mL) was added by cannula and reaction mixture was cooled down to -78 ^{0}C and stirred for additional 6 h before molecular sieves were filtered off, and the organic layer was washed with saturated aqueous $NaHCO_3$ solution, brine and dried (Na_2SO_4). The organic layer was concentrated under reduced pressure. Purification by silica gel column chromatography

(18% ethyl acetate in hexane) afforded the corresponding α and β mannosides (1.910 g, 85%) with a ratio of 1:9. **41:** $[\alpha]^{26}_{D}$ -49.2 (*c*, 0.37, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 7.47-7.45 (m, 2H), 7.42-7.33 (m, 9H), 7.32-7.21 (m, 24H), 5.52 (s, 1H), 4.89-4.72 (m, 9H), 4.64-4.53 (m, 5H), 4..45-4.42 (dd, *J* = 2.0, 11.5 Hz, 1H), 4.30 (s, 1H), 4.29-4.22 (m, 2H), 4.12-4.02 (m, 4H), 3.99-3.96 (dd, *J* = 4.8, 10.0 Hz, 1H), 3.91 (d, *J* = 3.0 Hz, 1H), 3.84 (m, 2H), 3.60 (t, *J* = 10.5 Hz, 1H), 3.55-3.52 (m, 3H), 3.49 (s, 3H), 3.48-3.45 (dd, *J* = 2.8, 9.0 Hz, 1H), 3.28-3.26 (m, 1H), 3.09-3.08 (m, 1H), 1.20 and 1.10 (2s,18H); ^{13}C NMR ($CDCl_3$) δ: 27.1, 27.2, 57.1, 62.7, 63.4, 67.4, 68.5, 71.8, 72.2, 72.5, 73.5, 73.6, 73.7, 74.3, 75.1, 75.2, 75.4, 75.6, 77.1, 77.2, 78.3, 78.5, 78.7, 100.7 ($^1J_{CH}$ = 154.2 Hz), 101.3 ($^1J_{CH}$ = 157.5 Hz), 101.9 ($^1J_{CH}$ = 152.5 Hz), 102.3 ($^1J_{CH}$ = 153.8 Hz), 126.1, 127.1, 127.2, 127.3, 127.4, 127.5, 127.6, 127.7, 127.9, 128.0, 128.1, 128.2, 128.3, 128.4, 128.8, 137.6, 138.3, 138.4, 138.5, 138.6, 138.7, 178.1; MALDI-HRMS Calcd for $C_{78}H_{90}O_{18}Na$ $[M + Na]^+$: 1337.6019, found, 1337.6067. **42:** $[\alpha]^{24}_{D}$ -30.1 (*c*, 1.48, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 7.53-7.51 (m, 2H), 7.41-7.33 (m, 9H), 7.31-7.20 (m, 24H), 5.62 (s, 1H), 5.11 (d, *J* = 1.0 Hz, 1H), 4.87-4.81 (m, 4H), 4.76-4.65 (m, 4H), 4.55 (s, 2H), 4.49 (d, *J* = 12.0 Hz, 1H), 4.43-4.39 (m, 3H), 4.32-4.21 (m, 6H), 4.08-3.98 (m, 4H), 3.89-3.87 (m, 2H), 3.78-3.76 (m, 2H), 3.59 (m, 1H), 3.55-3.53 (dd, *J* = 2.8, 8.5 Hz, 1H), 3.51 (s, 3H), 3.26-3.23 (dd, *J* = 2.5, 9.0 Hz, 1H), 3.08-3.06 (m, 1H), 1.21 and 1.14 (2s, 18H); ^{13}C NMR ($CDCl_3$) δ: 27.2, 27.24, 57.1, 63.1, 63.4, 65.2, 68.4, 70.9, 71.5, 72.9, 73.0, 73.1, 73.6, 73.7, 73.9, 74.1, 75.1, 75.2, 76.1, 76.8, 77.1, 77.2, 77.3, 78.9, 81.6, 100.3 ($^1J_{CH}$ = 157.3 Hz), 101.2 ($^1J_{CH}$ = 156.6 Hz), 101.9 ($^1J_{CH}$ = 152.8 Hz), 102.2 ($^1J_{CH}$ = 170.8 Hz), 126.1, 127.3, 127.4, 127.49, 127.5, 127.6, 127.7, 127.8, 127.9, 128.0, 128.1, 128.13, 128.3, 128.4, 128.6,

128.7, 137.5, 138.2, 138.4, 138.6, 138.7, 138.8, 178.1, 178.2; MALDI-HRMS Calcd for $C_{78}H_{90}O_{18}Na$ $[M + Na]^+$: 1337.6019, found 1337.5968.

Methyl 2,3-Di-*O*-benzyl-β-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranoside (43). A solution of **41** (1.723 g, 1.31 mmol), CSA (0.076 g, 0.33 mmol) and *neo*-pentyl glycol (0.409 g, 3.93 mmol) in dichloromethane (10 mL) under a nitrogen atmosphere was stirred under reflux at 45 ^{0}C for 18 h. The reaction mixture was concentrated under reduced pressure, dissolved in ethyl acetate, washed with saturated aqueous $NaHCO_3$ solution, water and brine. The organic layer was separated, dried (Na_2SO_4) and concentrated under reduced pressure. Purification by silica gel column chromatography (44% ethyl acetate in hexane) afforded **43** (1.404 g, 87%). $[\alpha]^{26}_D$ -54.5 (*c*, 1.37, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 7.41-7.38 (m, 4H), 7.36-7.21 (m, 26H), 4.88-4.74 (m, 7H), 4.63-4.50 (m, 4H), 4.50 (s, 1H), 4.44 (s, 1H), 4.42 (d, *J* = 1.5 Hz, 1H), 4.36-4.31 (m, 3H), 4.28-4.24 (dd, *J* = 6.8, 11.5 Hz, 1H), 4.10-4.04 (m, 3H), 3.93 (d, *J* = 2.5 Hz, 1H), 3.89 (d, *J* = 3.0 Hz, 1H), 3.85 (m, 2H), 3.72-3.67 (dd, *J* = 3.3, 12.0 Hz, 1H), 3.57 (m, 1H), 3.54-3.52 (dd, *J* = 2.8, 8.5 Hz, 1H), 3.50 (s, 3H), 3.47-3.44 (dd, *J* = 6.3, 11.5 Hz, 1H), 3.41-3.39 (dd, *J* = 2.5, 9.5 Hz, 1H), 3.25-3.22 (m, 2H), 3.11 (m, 1H), 2.12 (br. s, 2H), 1.21 and 1.11 (2s, 18H); ^{13}C NMR ($CDCl_3$) δ: 27.6, 27.7, 57.5, 63.0, 63.1, 63.8, 67.6, 71.6, 72.2, 72.8, 74.0, 74.1, 74.2, 74.3, 74.7, 74.8, 74.9, 75.3, 75.8, 76.2, 76.6, 78.9, 80.1, 82.3, 101.0, 101.7, 102.7, 127.7, 127.8, 127.9, 128.0, 128.2, 128.3, 128.4, 128.47, 128.5, 128.52, 128.6, 128.7, 128.8, 129.0, 138.0, 138.8, 138.9, 139.0, 139.2, 178.6, 178.6; MALDI-HRMS Calcd for $C_{71}H_{86}O_{18}Na$ $[M + Na]^+$: 1249.5706, found 1249.5672.

Methyl 2,3-Di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-β-D-manno-pyranoside (44). To a stirred solution of **43** (1.193 g, 0.97 mmol) and DMAP (0.030 g, 0.25 mmol) in dichloromethane (15 mL) was added Et_3N (271 μL, 1.94 mmol) followed by pivaloyl chloride (126 μL, 1.02 mmol) at room temperature under nitrogen atmosphere. The reaction mixture was stirred for 4 h and washed with saturated aqueous $NaHCO_3$ solution and brine. Organic layer was dried (Na_2SO_4) and concentrated under reduced pressure. Purification by silica gel column chromatography (24% ethyl acetate in hexane) afforded **44** (1.138 g, 89%). $[\alpha]^{26}_D$ -73.1 (*c*, 0.15, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 7.39-7.29 (m, 10H), 7.23-7.19 (m, 20H), 4.85-4.71 (m, 7H), 4.62-4.54 (m, 4H), 4.50 (s, 1H), 4.46 (s, 1H), 4.43 (s, 1H), 4.43-4.40 (dd, *J* = 2.5, 12.5 Hz, 1H), 4.33-4.30 (m, 2H), 4.24-4.20 (m, 3H), 4.12-4.01 (m, 2H), 3.87 (d, *J* = 2.5 Hz, 1H), 3.84-3.81 (m, 3H), 3.57-3.53 (m, 3H), 3.49 (s, 3H), 3.46-3.43 (dd, *J* = 3.0, 9.0 Hz, 1H), 3.30-3.28 (m, 1H), 3.22-3.20 (dd, *J* = 3.0, 3.0 Hz, 1H), 3.11-3.10 (m, 1H), 1.18, 1.13 and 1.08 (3s, 27H); ^{13}C NMR ($CDCl_3$) δ: 27.1, 27.2, 56.9, 62.6, 63.0, 63.5, 66.2, 71.4, 71.7, 72.1, 73.6, 73.7, 74.1, 74.2, 74.3, 74.5, 74.6, 74.8, 75.3, 75.7, 77.3, 78.3, 78.9, 81.3, 100.5, 101.2, 102.2, 127.2, 127.3, 127.5, 127.6, 127.7, 127.74, 127.8, 127.95, 127.97, 128.0, 128.1, 128.2, 128.3, 128.34, 128.6, 137.7, 138.4, 138.5, 138.6, 138.7, 138.8, 178.1, 178.9; MALDI-HRMS Calcd for $C_{76}H_{94}O_{19}Na$ $[M + Na]^+$: 1333.6282, found 1333.6273.

Methyl 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranoside (45)

and Methyl 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranoside (46). A stirred solution of thioglycoside **29** (1.156 g, 2.14 mmol), **BSP** (0.493 g, 2.36 mmol), **TTBP** (1.026 g, 4.28 mmol) and activated 3Å powdered sieves in dichloromethane (80 mL) under nitrogen atmosphere was kept at -60 ^{0}C for 30 mins. Then was added Tf_2O (432 μL, 2.57 mmol) and after 5 mins. acceptor **44** (2.171 g, 1.66 mmol) in dichloromethane (5 mL) was added by cannula and reaction mixture was cooled down to -78 ^{0}C and stirred for additional 6 h before molecular sieves were filtered off, and the organic layer was washed with saturated aqueous $NaHCO_3$ solution, brine and dried (Na_2SO_4). The organic layer was concentrated under reduced pressure. Purification by silica gel column chromatography (6% ethyl acetate in benzene) afforded the corresponding α and β mannosides (2.297 g, 79%) with a ratio of 1:9. **45:** $[\alpha]^{26}_D$ -52.4 (*c*, 1.37, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 7.47-7.45 (dd, *J* = 2.0, 8.5 Hz, 2H), 7.42-7.21 (m, 43H), 5.52 (s, 1H), 4.89-4.70 (m, 12H), 4.64-4.58 (m, 4H), 4.53 (s, 1H), 4.48 (d, *J* = 7.0 Hz, 2H), 4.42-4.39 (dd, *J* = 1.8, 10.5 Hz, 1H), 4.33 (d, *J* = 11 Hz, 1H), 4.31 (s, 1H), 4.24-4.22 (m, 2H), 4.12-4.02 (m, 6H), 3.98-3.95 (dd, *J* = 4.5, 10.5 Hz, 1H), 3.91 (d, *J* = 3.0 Hz, 1H), 3.84 (d, *J* = 2.5 Hz, 1H), 3.82 (d, *J* = 2.5 Hz, 2H), 3.61 (t, *J* = 10.5 Hz, 1H), 3.56-3.51 (m, 3H), 3.49 (s, 3H), 3.45-3.43 (dd, *J* = 3.0, 8.5 Hz, 1H), 3.42-3.39 (dd, *J* = 2.3, 8.5 Hz, 1H), 3.24 (m, 2H), 3.08 (m, 1H), 1.19, 1.14, 1.07 (3s, 27H); ^{13}C NMR ($CDCl_3$) δ: 27.1, 27.2, 27.3, 56.9, 62.5, 62.6, 63.5, 67.4, 68.5, 71.6, 72.1, 73.5, 73.6, 73.7, 74.1, 74.2, 74.3, 74.9, 75.0, 75.2, 75.7, 75.8, 76.8, 77.2, 78.1, 78.3, 78.5, 79.3, 80.1, 100.4 ($^1J_{CH}$ = 159.6 Hz), 101.1 ($^1J_{CH}$ = 152.8 Hz), 101.3 ($^1J_{CH}$ = 162.0 Hz), 101.9 ($^1J_{CH}$ = 154.3

Hz), 102.2 ($^1J_{CH}$ = 152.5 Hz), 126.1, 127.15, 127.2, 127.3, 127.4, 127.5, 127.6, 127.64, 127.7, 127.9, 128.0, 128.1, 128.11, 128.2, 128.3, 128.33, 128.8, 137.6, 138.3, 138.4, 138.5, 138.6, 138.7, 138.9, 178.02, 178.04; MALDI-HRMS Calcd for $C_{103}H_{120}O_{24}Na$ [M + Na]$^+$: 1763.8062, found 1763.7927. **46:** $[\alpha]^{25}_D$ -32.4 (*c*, 0.87, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 7.51 (d, *J* = 6.0 Hz, 2H), 7.39-7.32 (m, 10H), 7.29-7.18 (m, 33H), 5.61(s, 1H), 5.11 (s, 1H), 4.85-4.72 (m, 7H), 4.69-4.61 (m, 2H), 4.59-4.53 (m, 3H), 4.51-4.48 (m, 2H), 4.43-4.38 (m, 3H), 4.30-4.19 (m, 9H), 4.11-3.97 (m, 5H), 3.87 (d, *J* = 3.5 Hz, 1H), 3.84 (s, 2H), 3.76 (d, *J* = 2.0 Hz, 2H), 3.74 (s, 1H), 3.59-3.54 (m, 2H), 3.49 (s, 3H), 3.43-3.41 (dd, *J* = 3.0, 9.0 Hz, 1H), 3.29-3.27 (m, 1H), 3.24-3.22 (dd, *J* = 2.5, 9.0 Hz, 1H), 3.04-3.03 (m, 1H), 1.19, 1.13 and 1.11 (3s, 27H); ^{13}C NMR ($CDCl_3$) δ: 27.1, 27.2, 56.9, 62.8, 63.5, 65.2, 70.9, 71.6, 71.8, 72.8, 73.0, 73.1, 73.6, 73.7, 74.0, 74.1, 74.2, 74.23, 74.7, 75.0, 75.2, 75.5, 76.0, 76.6, 76.9, 77.2, 77.6, 78.1, 78.9, 81.8, 100.3 ($^1J_{CH}$ = 155.1 Hz), 100.7 ($^1J_{CH}$ = 158.8 Hz), 101.2 ($^1J_{CH}$ = 160.5 Hz), 101.9 ($^1J_{CH}$ = 165.4 Hz), 102.2 ($^1J_{CH}$ = 158.9 Hz), 126.0, 127.2, 127.3, 127.36, 127.4, 127.49, 127.5, 127.58, 127.6, 127.7, 127.8, 128.0, 128.04, 128.1, 128.3, 128.4, 128.6, 128.7, 137.6, 137.7, 138.4, 138.5, 138.6, 138.7, 138.8, 178.05, 178.09; MALDI-HRMS Calcd for $C_{103}H_{120}O_{24}Na$ [M + Na]$^+$: 1763.8062, found 1763.8127.

Methyl 2,3-Di-*O*-benzyl-β-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranoside (47). A solution of **45** (1.794 g, 1.03 mmol), CSA (0.060 g, 0.26 mmol) and *neo*-pentyl glycol (0.322 g, 3.09 mmol) in dichloromethane (15 mL) under nitrogen atmosphere was stirred under reflux at

45 ^{0}C for 18 h. The reaction mixture was concentrated under reduced pressure, dissolved in ethyl acetate, washed with saturated aqueous $NaHCO_3$ solution, water and brine. The organic layer was separated, dried (Na_2SO_4) and concentrated under reduced pressure. Purification by silica gel column chromatography (44% ethyl acetate in hexane) afforded **47** (1.482 g, 87%). $[\alpha]^{25}_D$ -54.2 (*c*, 0.82, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 7.40-7.33 (m, 10H), 7.31- 7.23 (m, 30H), 4.86-4.70 (m, 10H), 4.63-4.56 (m, 4H), 4.54 (s, 1H), 4.48 (d, *J* = 9.5 Hz, 2H), 4.44 (s, 1H), 4.43-4.40 (dd, *J* = 2.5, 12.0 Hz, 1H), 4.37-4.29 (m, 3H), 4.27-4.22 (m, 2H), 4.10-4.03 (m, 5H), 3.92 (d, *J* = 2.0 Hz, 1H), 3.88-3.84 (m, 4H), 3.71-3.68 (dd, *J* = 3.3, 11.5 Hz, 1H), 3.57-3.54 (m, 2H), 3.49 (s, 3H), 3.47-3.44 (m, 2H), 3.40-3.38 (dd, *J* = 2.5, 9.5 Hz, 1H), 3.24-3.22 (m, 3H), 3.10 (m, 1H), 2.13 (br. s, 2H), 1.19, 1.14 and 1.08 (3s, 27H); ^{13}C NMR ($CDCl_3$) δ: 27.1, 27.2, 57.0, 62.6, 62.7, 63.5, 67.2, 71.2, 71.7, 72.0, 72.4, 73.5, 73.6, 73.7, 73.9, 74.1, 74.2, 74.3, 74.5, 74.8, 74.9, 75.2, 75.7, 77.3, 78.2, 79.2, 79.8, 81.9, 100.4, 101.0, 101.3, 102.2, 127.2, 127.3, 127.34, 127.37, 127.4, 127.6, 127.7, 127.8, 127.87, 127.9, 128.0, 128.1, 128.2, 128.3, 128.4, 128.6, 137.6, 138.4, 138.5, 138.6, 138.7, 138.8, 178.05, 178.09, 178.2; MALDI-HRMS Calcd for $C_{96}H_{116}O_{24}Na$ $[M + Na]^+$: 1675.7749, found 1675.7890.

Methyl 2,3-Di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranoside (48). To a stirred solution of **47** (1.452 g, 0.88 mmol) and DMAP (0.027 g, 0.22 mmol) in dichloromethane (12 mL) was added Et_3N (245 μL, 1.76 mmol) followed by Pivolyl Chloride (113 μL, 0.92 mmol) at room temperature under nitrogen atmosphere. The

reaction mixture was stirred for 4 h and washed with saturated aqueous $NaHCO_3$ solution and brine. Organic layer was dried (Na_2SO_4) and concentrated under reduced pressure. Purification by silica gel column chromatography (24% ethyl acetate in hexane) afforded **48** (1.364 g, 89%). $[\alpha]^{25}_{D}$ -48.5 (*c*, 1.14, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 7.38-7.32 (m, 10H), 7.28-7.22 (m, 30H), 4.85-4.69 (m, 10H), 4.62-4.53 (m, 5H), 4.47 (s, 2H), 4.44 (s, 2H), 4.41 (d, *J* = 10.5 Hz, 1H), 4.34-4.28 (m, 3H), 4.26-4.19 (m, 3H), 4.11-4.09 (m, 2H), 4.05-4.01 (m, 3H), 3.87 (d, *J* = 2.5 Hz, 1H), 3.85-3.81 (m, 4H), 3.56-3.53 (m, 2H), 3.49 (s, 3H), 3.42-3.41 (m, 2H), 3.25-3.20 (m, 3H), 3.13-3.11 (m, 1H), 2.53 (bs, 1H), 1.18, 1.12, 1.09 and 1.07 (4s, 36H); ^{13}C NMR ($CDCl_3$) δ: 27.09, 27.14, 27.19, 27.24, 56.9, 62.5, 62.7, 63.1, 66.2, 71.5, 71.7, 71.9, 72.2, 73.5, 73.6, 73.62, 73.7, 74.2, 74.5, 74.6, 74.9, 75.2, 75.6, 75.9, 78.2, 79.1, 79.4, 81.3, 100.4, 100.9, 101.4, 102.2, 127.2, 127.3, 127.4, 127.5, 127.56, 127.6, 127.67, 127.7, 127.8, 127.94, 127.99, 128.0, 128.1, 128.3, 128.32, 128.6, 137.7, 138.4, 138.6, 138.7, 138.8, 138.9, 177.9, 178.1, 178.9; MALDI-HRMS Calcd for $C_{96}H_{116}O_{24}Na$ $[M + K]^+$:1775.8069, found 1775.8063.

Methyl 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranoside (49) and Methyl 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranoside (50). A stirred solution of thioglycoside **29** (0.515 g, 0.95

mmol), **BSP** (0.219 g, 1.05 mmol), **TTBP** (0.473 g, 1.91 mmol) and activated 3Å powdered sieves in dichloromethane (50 mL) under nitrogen atmosphere was kept at -60 ^{0}C for 30 mins. Then was added Tf_2O (192 μL, 1.14 mmol) and after 5 mins. acceptor **48** (1.132 g, 0.76 mmol) in dichloromethane (5 mL) was added by cannula and reaction mixture was cooled down to -78 ^{0}C and stirred for additional 6 h before molecular sieves were filtered off, and the organic layer was washed with saturated aqueous $NaHCO_3$ solution, brine and dried (Na_2SO_4). The organic layer was concentrated under reduced pressure. Purification by silica gel column chromatography (8% ethyl acetate in toluene) afforded the corresponding α and β mannosides (1.299 g, 79%) with a ratio of 1:9. **49:** $[\alpha]^{25}_D$ -53.4 (*c*, 0.40, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 7.48-7.46 (dd, *J* = 1.8, 8.0 Hz, 2H), 7.43-7.20 (m, 53H), 5.53 (s, 1H), 4.90-4.73 (m, 14H), 4.71 (d, *J* = 2.5 Hz, 1H), 4.69 (s, 1H), 4.65 (s, 1H), 4.62-4.59 (m, 4H), 4.57 (d, *J* = 2.0 Hz, 1H), 4.54 (d, *J* = 2.0 Hz, 1H), 4.49 (d, *J* = 5.5 Hz, 2H), 4.45 (s, 1H), 4.44-4.41 (dd, *J* = 2.0, 11.5 Hz, 1H), 4.35-4.26 (m, 3H), 4.24-4.21 (m, 2H), 4.11 (t, *J* = 9.5 Hz, 1H), 4.08-4.02 (m, 5H), 3.98-3.95 (dd, *J* = 5.0, 6.0 Hz, 1H), 3.91 (d, *J* = 3.0 Hz, 1H), 3.85 (d, *J* = 2.5 Hz, 1H), 3.83 (t, *J* = 7.0 Hz, 2H), 3.80 (d, *J* = 2.5 Hz, 1H), 3.63-3.52 (m, 4H), 3.49 (s, 3H), 3.47-3.39 (m, 3H), 3.27-3.25 (m, 2H), 3.21-3.19 (m, 1H), 3.09-3.08 (m, 1H), 1.19, 1.12, 1.11 and 1.07 (4s, 36H); ^{13}C NMR ($CDCl_3$) δ: 27.16, 27.2, 57.0, 63.5, 67.5, 68.5, 71.7, 71.9, 72.1, 72.2, 73.5, 73.6, 73.7, 74.18, 74.2, 74.25, 74.3, 74.8, 74.9, 75.1, 75.2, 75.22, 75.6, 75.7, 75.8, 78.1, 78.2, 78.5, 100.3 ($^1J_{CH}$ = 155.3 Hz), 100.9 ($^1J_{CH}$ = 156.9 Hz), 101.2 ($^1J_{CH}$ = 151.4 Hz), 101.3 ($^1J_{CH}$ = 167.3 Hz), 101.9 ($^1J_{CH}$ = 155.5 Hz), 102.2 ($^1J_{CH}$ = 151.0 Hz), 126.1, 127.15, 127.2, 127.3, 127.4, 127.5, 127.52, 127.56, 127.6, 127.7, 128.0, 128.04, 128.1, 128.2, 128.3, 128.31, 128.34, 128.8, 137.6, 138.3, 138.4, 138.5, 138.6, 138.7, 138.8, 138.9,

177.7, 178.01, 178.1; ESIMS Calcd for $C_{96}H_{116}O_{24}Na$ $[M + Na]^+$:2190.01, found 2190.10. **50:** $[\alpha]^{25}_D$ -33.3 (*c*, 0.90, $CHCl_3$); ^1H NMR ($CDCl_3$) δ: 7.52-7.50 (m, 2H), 7.39-7.33 (m, 15H), 7.32-7.18 (m, 38H), 5.61 (s, 1H), 5.10 (d, *J* = 1.5 Hz, 1H), 4.85- 4.66 (m, 13H), 4.63-4.56 (m, 5H), 4.45-4.43 (m, 4H), 4.42 (d, *J* = 3.0 Hz, 1H), 4.41-4.38 (m, 2H), 4.34-4.30 (m, 2H), 4.28-4.19 (m, 7H), 4.10-4.07 (dd, *J* = 3.3, 12.0 Hz, 1H), 4.06-3.98 (m, 6H), 3.87 (d, *J* = 3 Hz, 1H), 3.85-3.81 (m, 3H), 3.75-3.70 (m, 2H), 3.57-3.52 (m, 2H), 3.49 (s, 3H), 3.44-3.39 (m, 2H), 3.25-3.23 (dd, *J* = 2.0, 2.5 Hz, 2H), 3.09 (m, 1H), 1.18, 1.11, 1.09 and 1.06 (4s, 36H); ^{13}C NMR ($CDCl_3$) δ: 27.1, 27.2, 27.3, 27.4, 56.9, 62.5, 62.7, 62.9, 63.5, 65.2, 68.4, 70.9, 71.7, 71.94, 71.98, 72.9, 73.0, 73.2, 73.6, 73.7, 74.0, 74.1, 74.2, 74.8, 74.9, 75.2, 75.7, 75.8, 76.1, 77.2, 77.6, 78.2, 78.9, 79.0, 81.8, 100.4 ($^1J_{CH}$ = 156.1 Hz), 100.9 ($^1J_{CH}$ = 155.0 Hz), 101.2 ($^1J_{CH}$ = 158.5 Hz), 101.9 ($^1J_{CH}$ = 173.5 Hz), 102.2 ($^1J_{CH}$ = 152.3 Hz), 126.1, 127.1, 127.15, 127.17, 127.2, 127.3, 127.4, 127.49, 127.53, 127.64, 127.66, 127.7, 127.9, 128.0, 128.1, 128.19, 128.2, 128.27, 128.3, 128.4, 128.5, 128.6, 128.7, 137.6, 137.7, 138.4, 138.5, 138.6, 138.7, 138.9, 178.9, 178.0, 178.07; ESIMS Calcd for $C_{96}H_{116}O_{24}Na$ $[M + Na]^+$: 2190.01, found: 2190.08.

Methyl 2,3-Di-*O*-benzyl-β-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranoside (51). A solution of **49** (1.150 g, 0.53 mmol), CSA (0.031 g, 0.13 mmol) and *neo*-pentyl glycol (0.166 g, 1.59 mmol) in dichloromethane (15 mL) under a nitrogen atmosphere was stirred under reflux at 45 ^{0}C for 18 h. The reaction mixture was concentrated under reduced pressure, dissolved in ethyl acetate, washed with

saturated aqueous $NaHCO_3$ solution, water and brine. The organic layer was separated, dried (Na_2SO_4) and concentrated under reduced pressure. Purification by silica gel column chromatography (44% ethyl acetate in hexane) afforded **51** (0.972 g, 88%). $[\alpha]^{25}_D$ -43.9 (*c*, 1.17, $CHCl_3$); ^1H NMR ($CDCl_3$) δ: 7.39-7.34 (m, 10H), 7.33-7.19 (m, 40H), 4.85-4.71 (m, 12H), 4.68 (s, 1H), 4.62-4.53 (m, 6H), 4.47-4.39 (m, 4H), 4.35-4.30 (m, 4H), 4.27-4.22 (m, 3H), 4.08-4.02 (m, 7H), 3.91 (d, *J* = 3.0 Hz, 1H), 3.87-3.83 (m, 3H), 3.82-3.79 (dd, *J* = 2.5, 7.5 Hz, 2H), 3.69-3.67 (dd, *J* = 3.0, 11.5 Hz, 1H), 3.56-3.52 (m, 2H), 3.48 (s, 3H), 3.44-3.37 (m, 4H), 3.24-3.20 (m, 4H), 3.10-3.09 (m, 1H), 1.18, 1.11, 1.09 and 1.07 (4s, 36H); ^{13}C NMR ($CDCl_3$) δ: 27.1, 27.14, 27.17, 27.2, 56.9, 62.5, 62.7, 63.5, 67.2, 71.2, 71.6, 71.9, 72.1, 72.4, 73.5, 73.6, 73.7, 73.75, 73.9, 74.17, 74.2, 74.3, 74.4, 74.5, 74.8, 74.9, 75.2, 75.6, 75.7, 75.9, 76.2, 76.7, 76.72, 76.8, 76.85, 76.9, 76.93, 76.96, 77.2, 77.23, 77.3, 77.4, 77.44, 78.2, 78.9, 79.5, 79.9, 81.9, 100.3, 100.9, 101.2, 101.3, 102.2, 127.2, 127.3, 127.32, 127.4, 127.5, 127.55, 127.6, 127.63, 127.68, 127.7, 127.75, 127.8, 127.82, 127.85, 127.9, 128.01, 128.05, 128.1, 128.2, 128.3, 128.4, 128.5, 137.6, 138.3, 138.4, 138.5, 138.56, 138.6, 138.7, 138.9, 177.9, 178.0, 178.1, 178.2; ESIMS Calcd for $C_{96}H_{116}O_{24}Na$ $[M + Na]^+$: 2101.98, found: 2102.05.

Methyl 2,3-Di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranoside (52). To a stirred solution of **51** (0.940 g, 0.45 mmol) and DMAP (0.014 g, 0.11 mmol) in dichloromethane (8 mL) was added Et_3N (126 μL, 0.91 mmol) followed by pivaloyl chloride (58 μL, 0.47 mmol) at room

temperature under nitrogen atmosphere. The reaction mixture was stirred for 4 h and washed with saturated aqueous $NaHCO_3$ solution and brine. The organic layer was dried (Na_2SO_4) and concentrated under reduced pressure. Purification by silica gel column chromatography (24% ethyl acetate in hexane) afforded **52** (0.841 g, 86%). $[\alpha]^{25}_D$ -47.4 (*c*, 0.87, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 7.39-7.37 (m, 2H), 7.35-7.29 (m, 13H), 7.28-7.19 (m, 35 H), 4.87-4.67 (m, 14H), 4.61-4.52 (m, 7H), 4.46 (s, 2H), 4.44-4.39 (m, 3H), 4.33-4.28 (m, 2H), 4.26-4.17 (m, 6H), 4.11-3.98 (m, 6H), 3.86 (d, *J* = 2.5 Hz, 1H), 3.84-3.80 (m, 4H), 3.78 (d, *J* = 2.5 Hz, 1H), 3.55-3.52 (m, 2H), 3.48 (s, 3H), 3.43-3.38 (m, 3H), 3.25-3.18 (m, 4H), 3.13-3.11 (m, 1H), 2.52 (d, *J* = 2.5 Hz, 1H), 1.18, 1.11, 1.08, 1.07 and 1.06 (5s, 45H); ^{13}C NMR ($CDCl_3$) δ: 27.1, 27.12, 27.15, 27.2, 27.25, 56.9, 62.5, 62.7, 63.1, 63.5, 66.2, 71.4, 71.7, 71.9, 72.0, 72.1, 73.5, 73.6, 73.7, 74.1, 74.2, 74.22, 74.3, 74.5, 74.6, 74.8, 74.9, 75.2, 75.6, 75.7, 75.9, 76.7, 76.72, 76.8, 76.83, 76.85, 76.87, 76.9, 76.96, 77.07, 77.1, 77.12, 77.2, 77.3, 77.4, 77.42, 78.1, 78.4, 81.3, 100.3, 100.8, 101.2, 101.4, 102.2, 127.2, 127.3, 127.34, 127.43, 127.44, 127.49, 127.52, 127.57, 127.6, 127.66, 127.7, 127.8, 127.9, 127.98, 128.0, 128.02, 128.04, 128.08, 128.3, 128.6, 137.7, 138.4, 138.5, 138.6, 138.7, 138.9, 177.95, 177.97, 178.06, 178.08, 178.94; MALDI-HRMS Calcd for $C_{96}H_{116}O_{24}Na$ $[M + Na]^+$:2186.0372, found 2186.0366.

Methyl 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranoside (53) and Methyl 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-α-

D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-6-*O*-pivaloyl-β-D-mannopyranoside (54). A stirred solution of thioglycoside **29** (0.301 g, 0.56 mmol), **BSP** (0.128 g, 0.61 mmol), **TTBP** (0.277 g, 1.11 mmol) and activated 3Å powdered sieves in dichloromethane (30 mL) under nitrogen atmosphere was kept at -60 ^{0}C for 30 mins. Then was added Tf_2O (113 μL, 0.67 mmol) and after 5 mins. acceptor **52** (0.805 g, 0.37 mmol) in dichloromethane (5 mL) was added by cannula and reaction mixture was cooled down to -78 ^{0}C and stirred for additional 6 h before molecular sieves were filtered off, and the organic layer was washed with saturated aqueous $NaHCO_3$ solution, brine and dried (Na_2SO_4). The organic layer was concentrated under reduced pressure. Purification by silica gel column chromatography (10% ethyl acetate in toluene) afforded the corresponding α and β mannosides (0.771 g, 80%) with a ratio of 1:10. **53:** $[\alpha]^{25}_D$ -40.6 (*c*, 1.41, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 7.38-7.36 (m, 2H), 7.21-7.34 (m, 63H), 5.51 (s, 1H), 4.69-4.88 (m, 16H), 4.67 (s, 1H), 4.63 (s, 1H), 4.58-4.53 (m, 7H), 4.52 (s, 1H), 4.47 (s, 2H), 4.44-4.40 (m, 3H), 4.33-4.18 (m, 5H), 4.11-4.03 (m, 10H), 3.96-3.93 (dd, *J* = 4.8, 11.0 Hz, 1H), 3.90 (d, *J* = 3 Hz, 1H), 3.84 (d, *J* = 2.5 Hz, 1H), 3.81 (d, *J* = 2.5 Hz, 2H), 3.79 (br. s, 2H), 3.62-3.50 (m, 4H), 3.49 (s, 3H), 3.45-3.38 (m, 4H), 3.24 (d, *J* = 9.5 Hz, 2H), 3.19 (d, *J* = 9.0 Hz, 2H), 3.08-3.07 (m, 1H), 1.18, 1.11, 1.09, 1.08 and 1.05 (5s, 45H); ^{13}C NMR ($CDCl_3$) δ: 27.1, 27.14, 27.18, 27.23, 27.25, 56.9, 62.6, 63.5, 67.4, 68.5, 71.7, 71.9, 72.0, 72.1, 72.4, 73.5, 73.6, 73.7, 74.1, 74.2, 74.3, 74.7, 74.8, 75.0, 75.1, 75.2, 75.22, 75.6, 75.7, 75.8, 75.9, 76.8, 76.9, 77.18, 77.21, 77.24, 77.3, 77.35, 77.4, 78.1, 78.3, 78.5, 80.2,

100.3($^1J_{CH}$ = 155.0 Hz), 100.8 ($^1J_{CH}$ = 154.8 Hz), 101.1 ($^1J_{CH}$ = 156.4 Hz), 101.2 ($^1J_{CH}$ = 157.4 Hz), 101.3 ($^1J_{CH}$ = 157.4 Hz), 101.9 ($^1J_{CH}$ = 155.8 Hz), 102.2 ($^1J_{CH}$ = 152.8 Hz), 126.1, 127.1, 127.2, 127.22, 127.24, 127.3, 127.4, 127.47, 127.55, 127.59, 127.61, 127.64, 127.65, 127.67, 127.9, 128.05, 128.1, 128.12, 128.14, 128.15, 128.26, 128.3, 128.33, 137.6, 138.3, 138.4, 138.57, 138.59, 138.6, 138.64, 138.7, 138.8, 138.9, 177.94, 177.98, 178.1; ESIMS Calcd for $C_{96}H_{116}O_{24}Na$ $[M + Na]^+$: 2616.22, found: 2616.31. **54:** $[\alpha]^{25}_D$ -30.8 (*c*, 1.46, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 7.51 (m, 1H), 7.39-7.30 (m, 16H), 7.29-7.17 (m, 48H), 5.60 (s, 1H), 5.09 (d, *J* = 1.5 Hz, 1H), 4.84 (s, 1H), 4.82 (s, 1H), 4.79 -4.65 (m, 16H), 4.63 (s, 1H), 4.59-4.55 (m, 5H), 4.52-4.51 (m, 1H), 4.49-4.42 (m, 4H), 4.40-4.38 (m, 2H), 4.33-4.19 (m, 9H), 4.11-3.98 (m, 8H), 3.87-3.86 (m, 2H), 3.81-3.76 (m, 3H), 3.75-3.74 (m, 2H), 3.57-3.52 (m, 2H), 3.49 (s, 3H), 3.42-3.39 (m, 3H), 3.25-3.18 (m, 4H), 3.10-3.08 (m, 1H), 1.18, 1.11, 1.08, 1.07 and 1.05 (5s, 45H); ^{13}C NMR ($CDCl_3$) δ: 27.1, 27.15, 27.19, 27.2, 27.3, 56.9, 62.7, 63.5, 65.2, 70.1, 71.7, 71.9, 72.0, 72.9, 73.0, 73.2, 73.5, 73.6, 73.7, 74.0, 74.1, 74.15, 74.2, 74.3, 74.7, 74.8, 74.9, 75.1, 75.2, 75.6, 75.8, 76.1, 76.6, 76.7, 76.72, 76.8, 76.88, 76.9, 77.08, 77.1, 77.2, 77.3, 77.35, 77.4, 77.7, 78.1, 80.2, 100.3 ($^1J_{CH}$ = 155.3 Hz), 100.8 ($^1J_{CH}$ = 160.8 Hz), 100.9 ($^1J_{CH}$ = 154.4 Hz), 101.1 ($^1J_{CH}$ = 171.9 Hz), 101.2 ($^1J_{CH}$ = 165.8 Hz), 102.2 ($^1J_{CH}$ = 152.6 Hz), 126.0, 127.1, 127.2, 127.3, 127.35, 127.4, 127.43, 127.47, 127.5, 127.57, 127.63, 127.7, 127.8, 127.9, 128.0, 128.1, 128.15, 128.2, 128.26, 128.3, 128.38, 128.4, 128.5, 128.6, 128.7, 137.6, 137.7, 138.3, 138.4, 138.5, 138.6, 138.7, 138.8, 138.9, 177.9, 178.1, 178.13; ESIMS Calcd for $C_{96}H_{116}O_{24}Na$ $[M + Na]^+$: 2616.22, found: 2616.19.

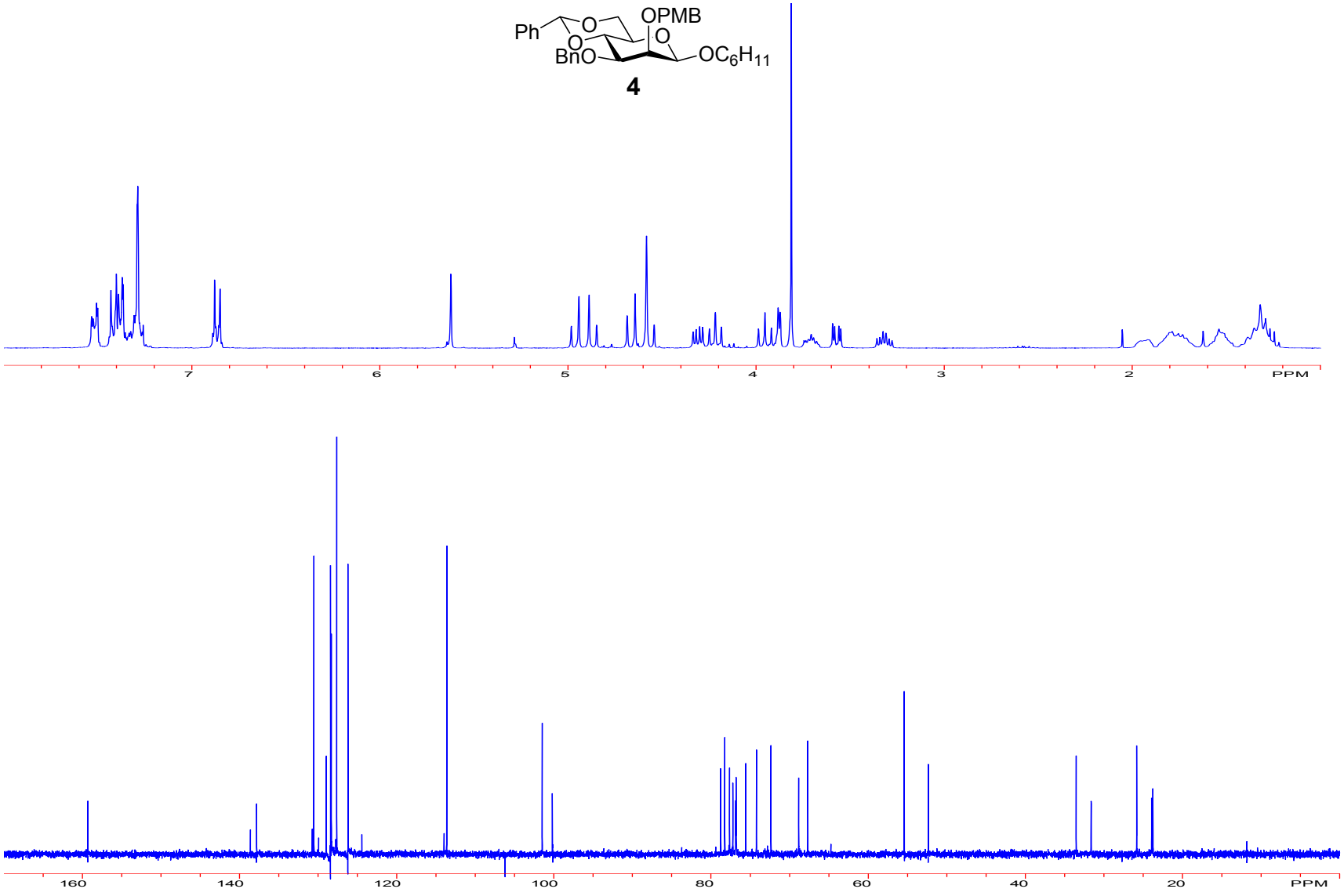
Methyl 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-β-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-β-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-β-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-β-D-mannopyranosyl-(1→4)-2,3-di-*O*-benzyl-β-D-mannopyranoside (55). A stirred solution of **53** (0.529 g, 0.21 mmol) and sodium methoxide (0.044 g, 0.82 mmol) in dry MeOH (6 mL) was refluxed for 27 h at 70 ^{0}C under a nitrogen atmosphere. The reaction mixture was neutralized with Amberlyst 15 ion exchange resin, filtered through Celite and concentrated under reduced pressure. Purification by silica gel column chromatography ($CHCl_3$: MeOH 1:1) afforded **55** (0.415 g, 94%). $[\alpha]^{27}_D$ -55.2 (*c*, 1.47, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 7.46-7.36 (m, 15H), 7.32-7.25 (m, 50H), 5.52 (s, 1H), 4.95-4.80 (m, 16H), 4.78-4.73 (m, 3H), 4.66 (s, 1H), 4.63 (s, 1H), 4.60-4.51 (m, 8H), 4.37 (s, 1H), 4.21 (t, *J* = 9.5 Hz, 1H), 4.13-3.99 (m, 6H), 3.92-3.81 (m, 8H), 3.66-3.57 (m, 6H), 3.55 (s, 3H), 3.51-3.43 (m, 6H), 3.36-3.31 (m, 4H), 3.18-3.15 (m, 5H); ^{13}C NMR ($CDCl_3$) δ: 57.4, 61.8, 61.9, 67.3, 72.1, 72.3, 72.4, 72.5, 72.6 72.7, 74.5, 74.6, 74.67, 74.7, 74.9, 75.0, 75.1, 75.15, 75.2, 75.3, 75.32, 75.4, 75.6, 75.8, 76.4, 76.5, 76.7, 77.2, 77.3, 78.4, 78.6, 79.9, 80.3, 80.5, 100.9, 101.2, 101.3, 102.1, 102.7, 126.1, 126.8, 126.83, 126.9, 127.3, 127.4, 127.5, 127.51, 127.9, 128.0, 128.1, 128.15, 128.2, 128.3, 128.33, 128.35, 128.4, 128.8, 137.7, 138.4, 138.5, 138.7, 138.74, 138.8, 138.83, 138.9; MALDI-HRMS Calcd for $C_{96}H_{116}O_{24}Na$ $[M + Na]^+$:2195.9276, found 2195.9271.

Methyl β-D-Mannopyranosyl-(1→4)-β-D-mannopyranosyl-(1→4)-β-D-mannopyranosyl-(1→4)-β-D-mannopyranosyl-(1→4)-β-D-mannopyranosyl-(1→4)-β-D-mannopyranoside (56). A mixture of hexasaccharide **55** (40 mg, 0.018 mmol) and 10% Pd/C

(60 mg) in MeOH (3 mL) was shaken under 50 psi of H_2 for 48 h. The reaction mixture was filtered through Whatman 1 filter paper, which was washed with water (pH 7) five times. Removal of water under reduced pressure at 50 ^{0}C afforded the target compound **56** (16 mg, 87%). M.p. >300 ^{0}C; $[\alpha]^{24}_D$ -62.0 (*c*, 0.25, H_2O); ^{1}H NMR (D_2O) δ: 4.64 (s, 4H), 4.60 (s, 1H), 4.49 (s, 1H), 4.02 (s, 4H), 3.95 (d, *J* = 4.0 Hz, 1H), 3.94 (d, *J* = 3.0 Hz, 1H), 3.86-3.80 (m, 6H), 3.74-3.69 (m, 10H), 3.68-3.60 (m, 6H), 3.56-3.53 (dd, *J* = 9.0, 3.5 Hz, 1H), 3.48-3.44 (m, 8H), 3.41-3.37 (m, 1H), 3.35-3.31 (m, 1H); ^{13}C NMR (D_2O) δ: 56.8, 60.5, 60.9, 66.6, 69.7, 69.9, 70.4, 71.4, 71.5, 72.7, 74.8, 74.9, 76.4, 76.5, 76.6, 76.7, 100.1 ($^1J_{CH}$ = 160.0 Hz), 100.9 ($^1J_{CH}$ = 161.0 Hz); ESIHRMS Calcd for $C_{37}H_{64}O_{31}Na$ $[M + Na]^+$:1027.3329, found 1027.3303.

References

(1) Crich, D.; Sun, S.; Brunckova, J. *J. Org. Chem.* **1996**, *61*, 605-615.
(2) Crich, D.; Sun, S. *Tetrahedron* **1998**, *54*, 8321-8348.
(3) Crich, D.; Smith, M. *J. Am. Chem. Soc.* **2001**, *123*, 9015-9020.
(4) Crich, D.; Smith, M.; Yao, Q.; Picione, J. *Synthesis* **2001**, 323-326.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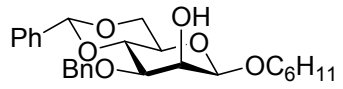

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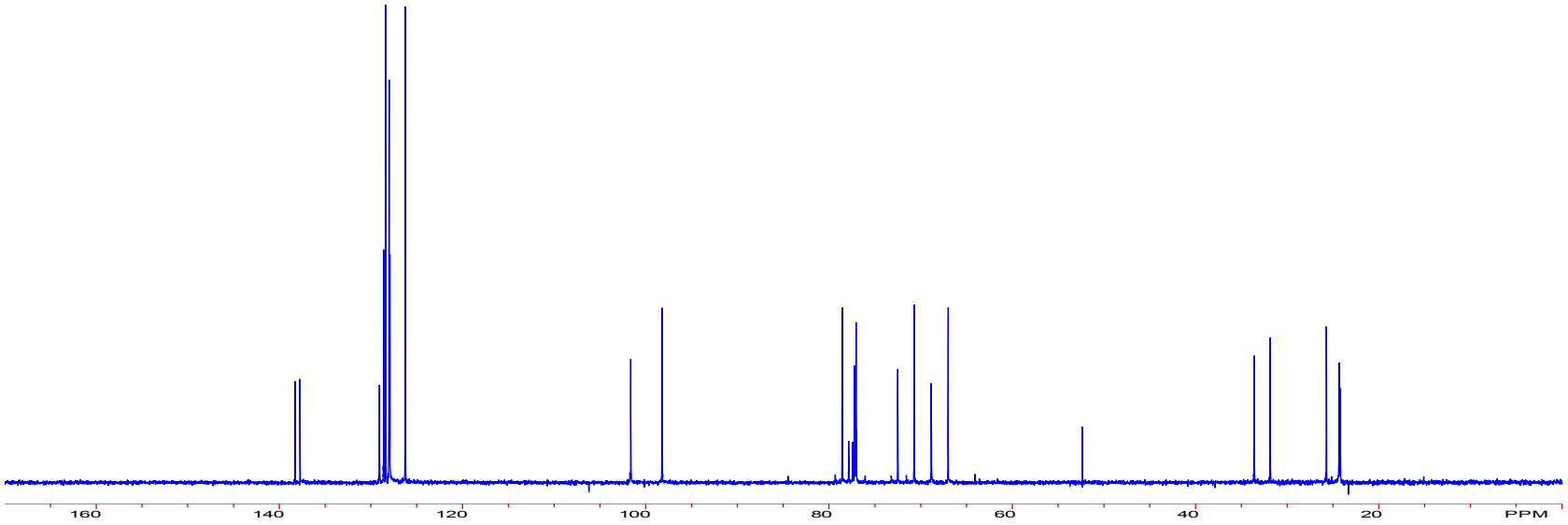

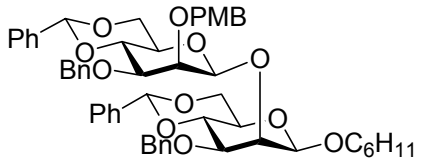
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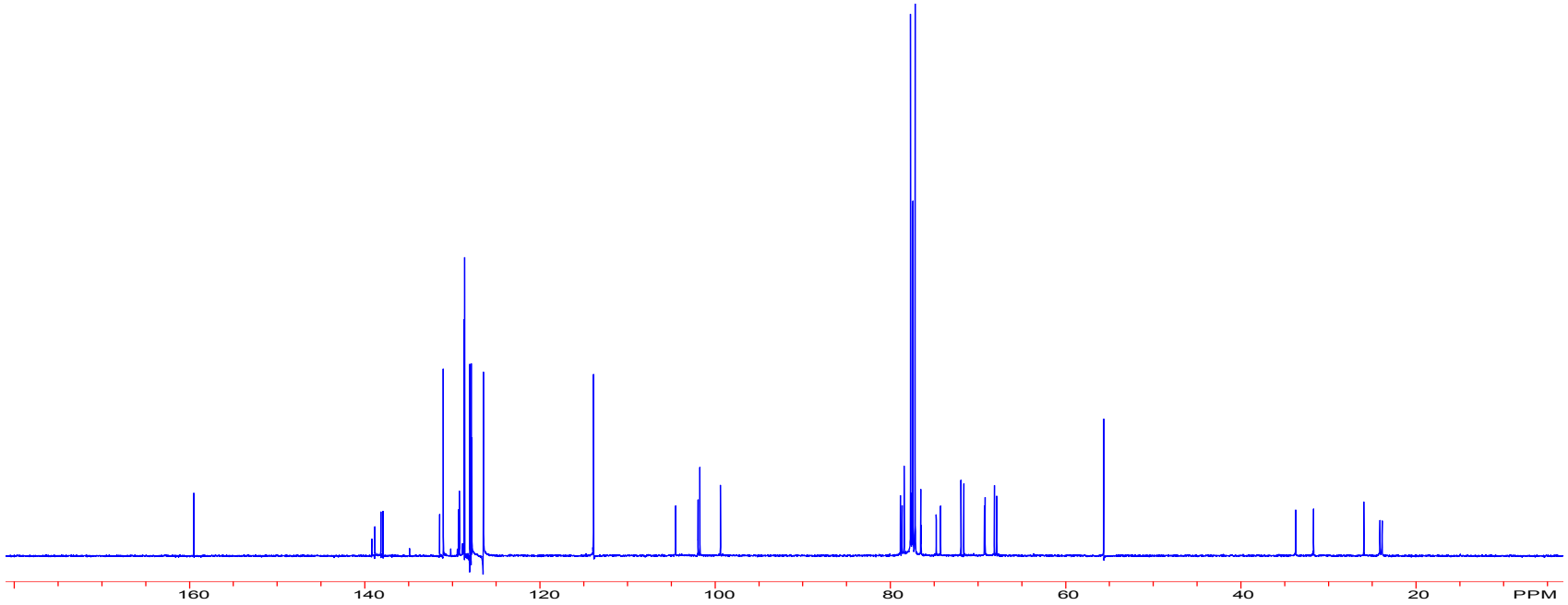
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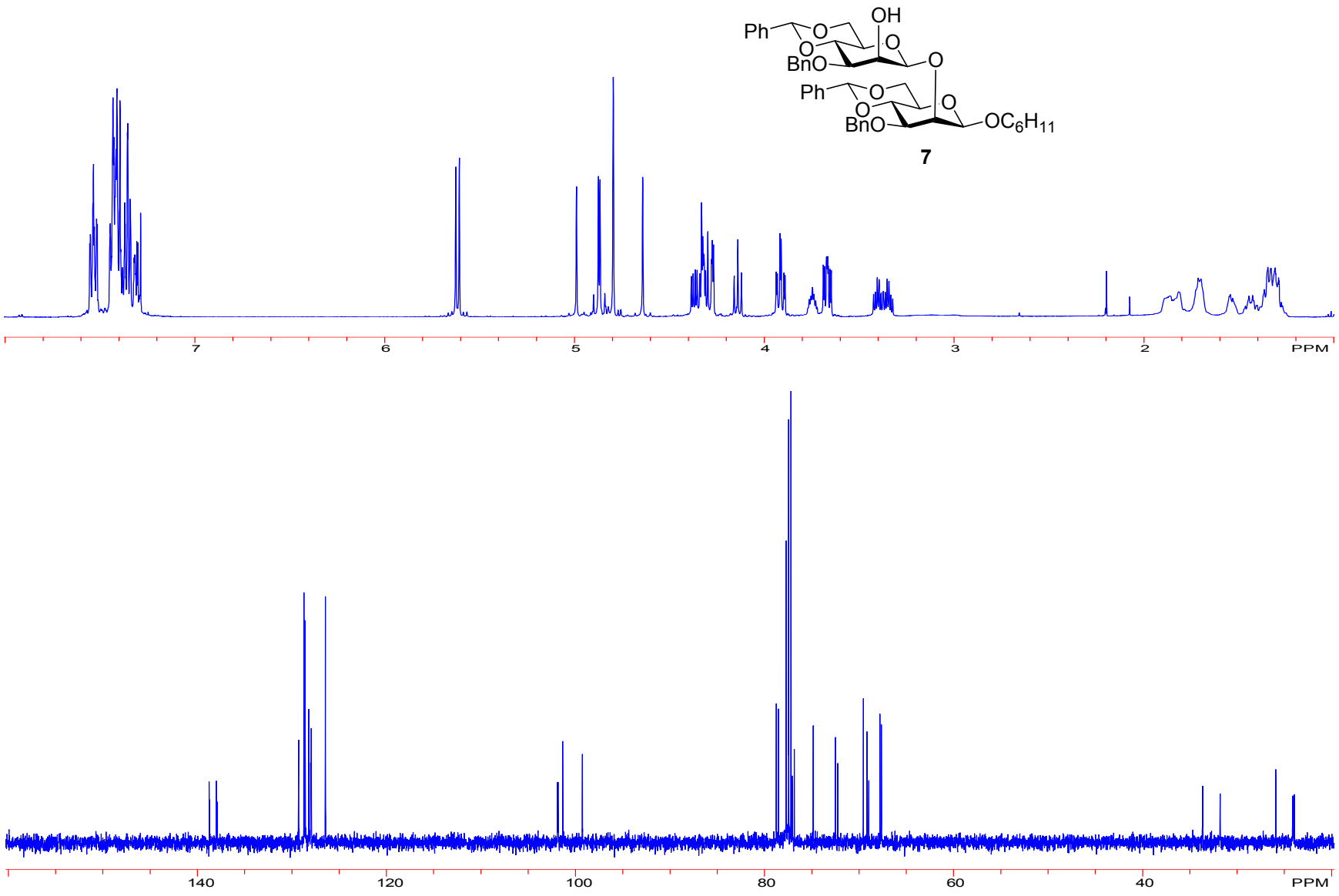
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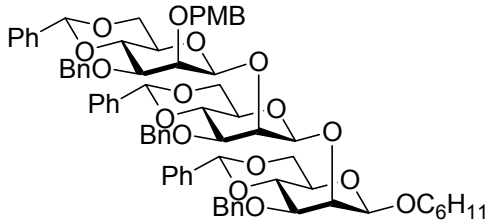
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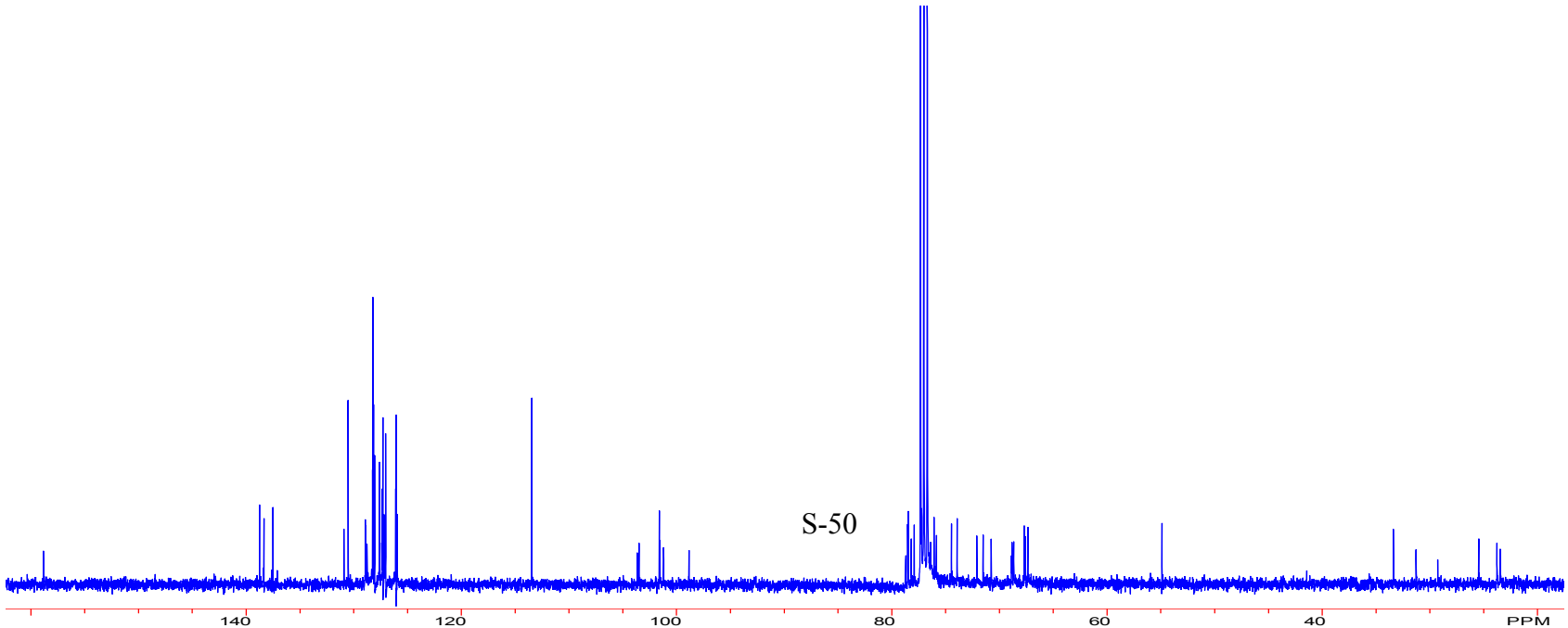
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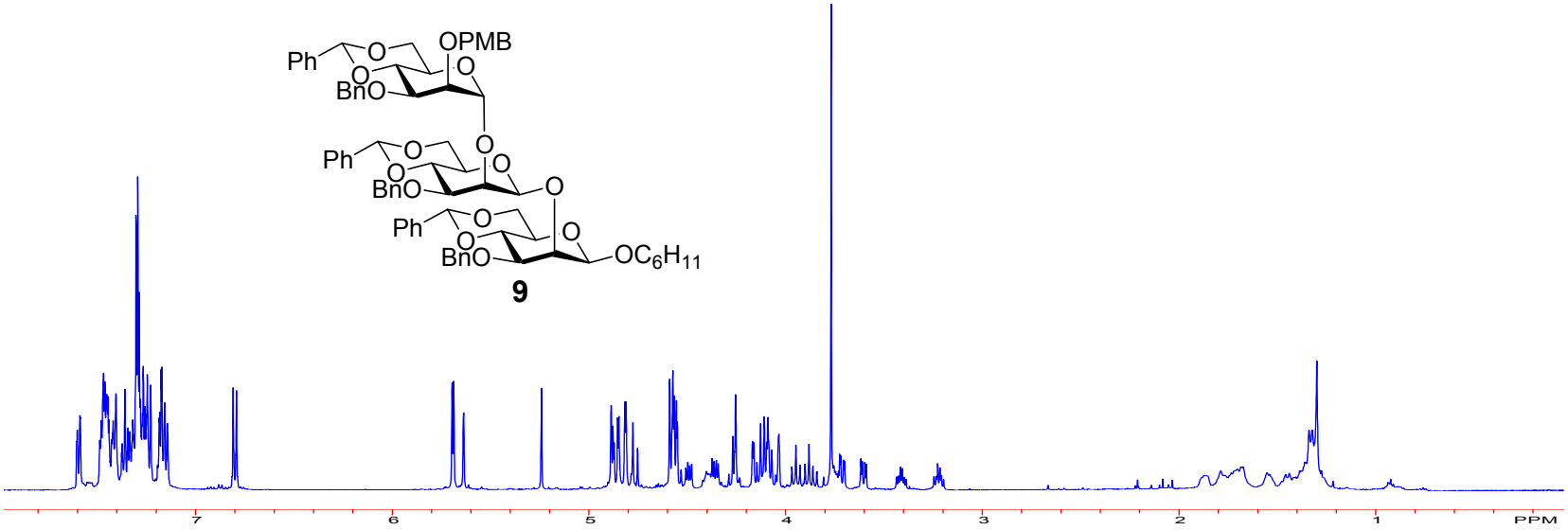
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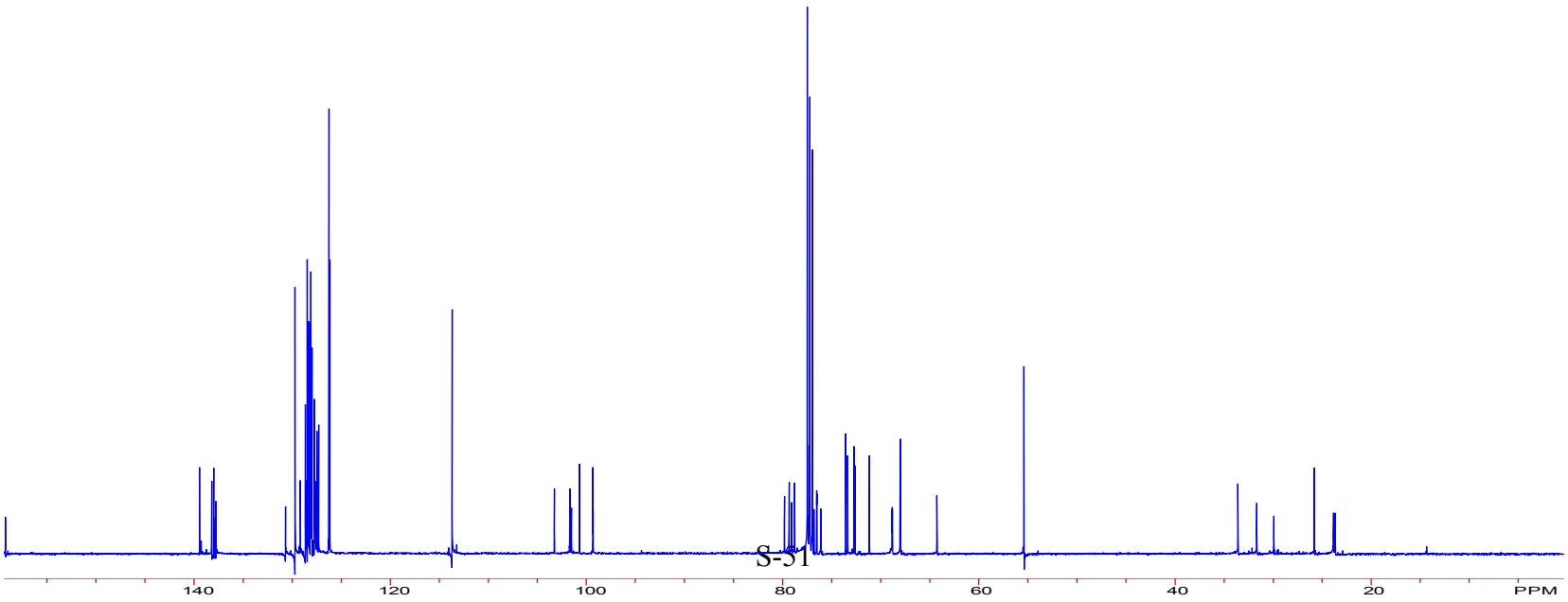
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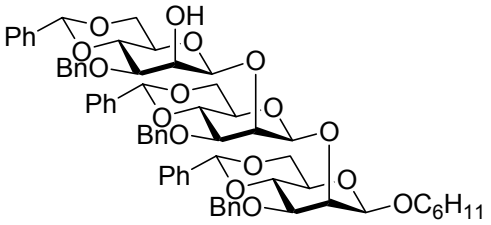
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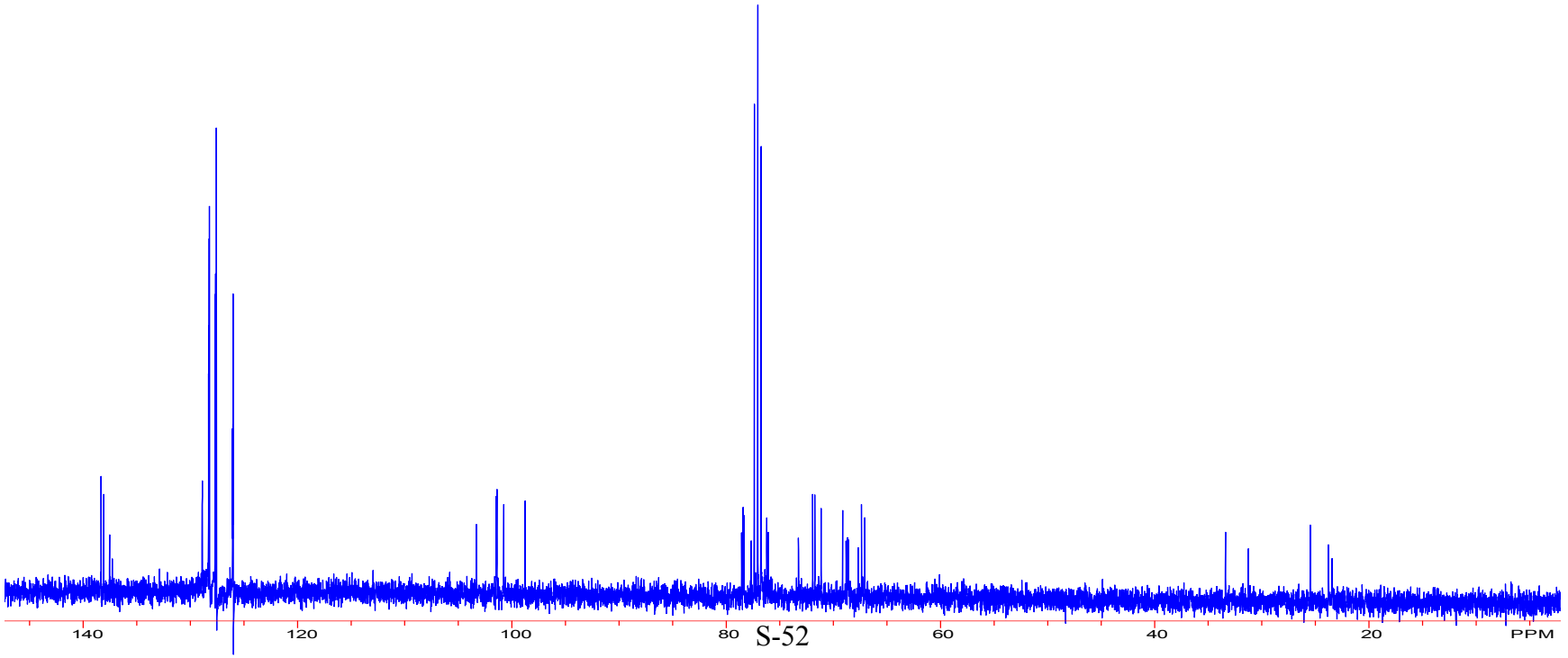
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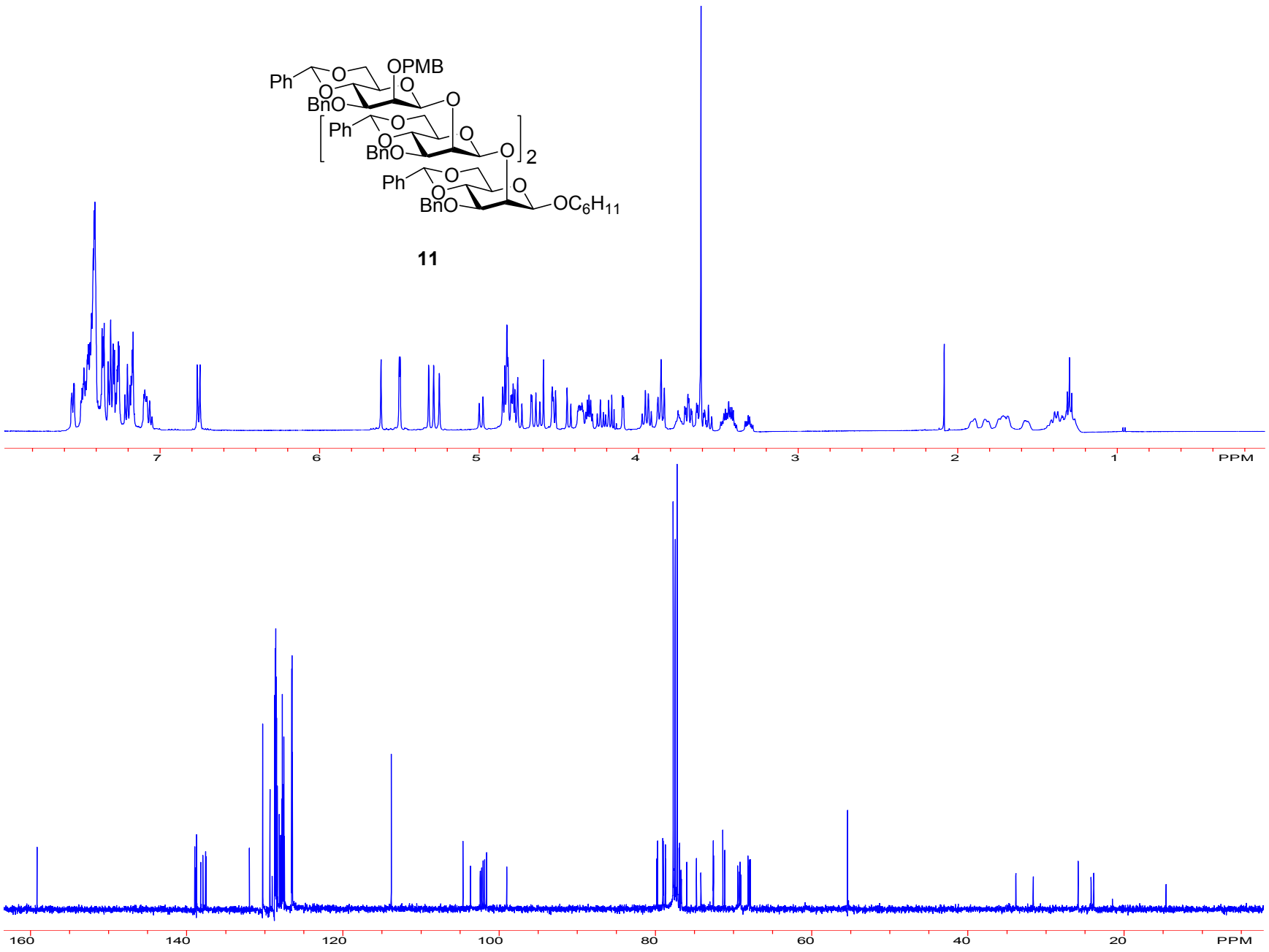
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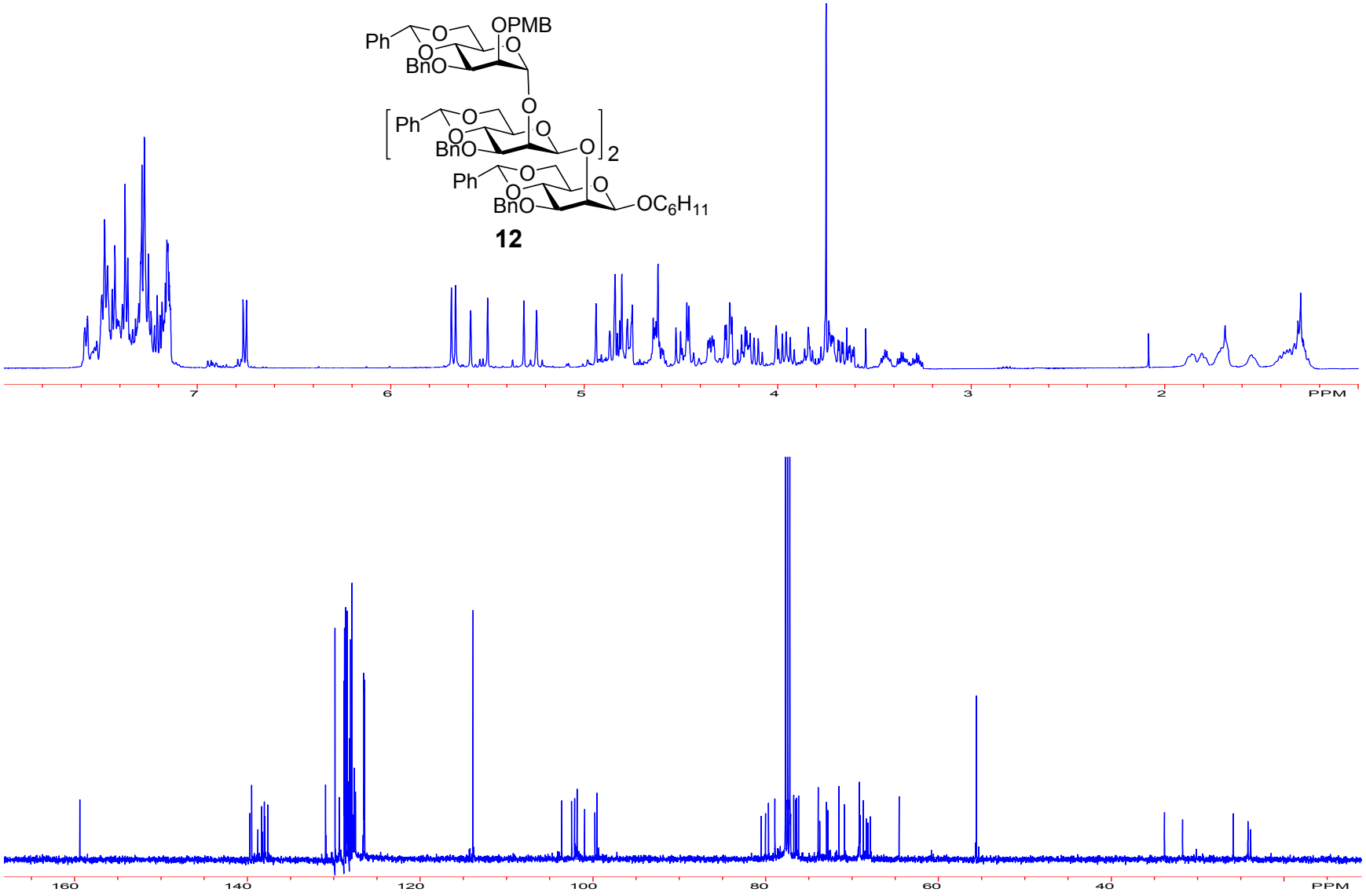
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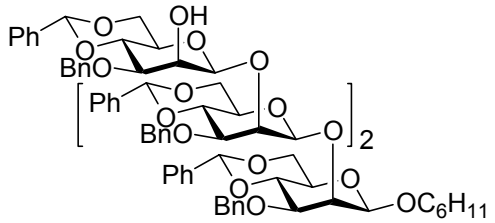
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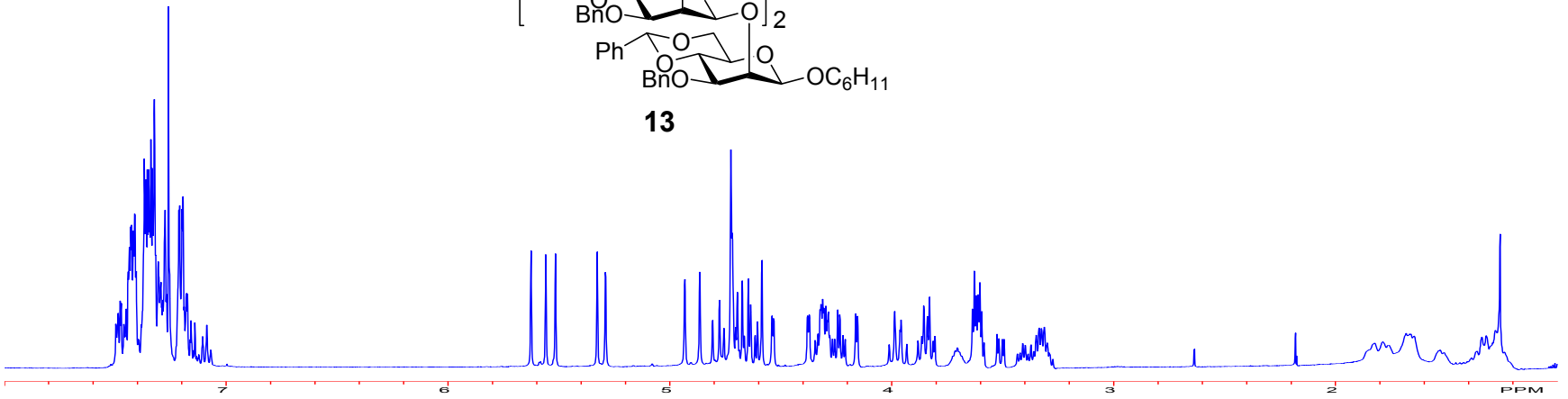
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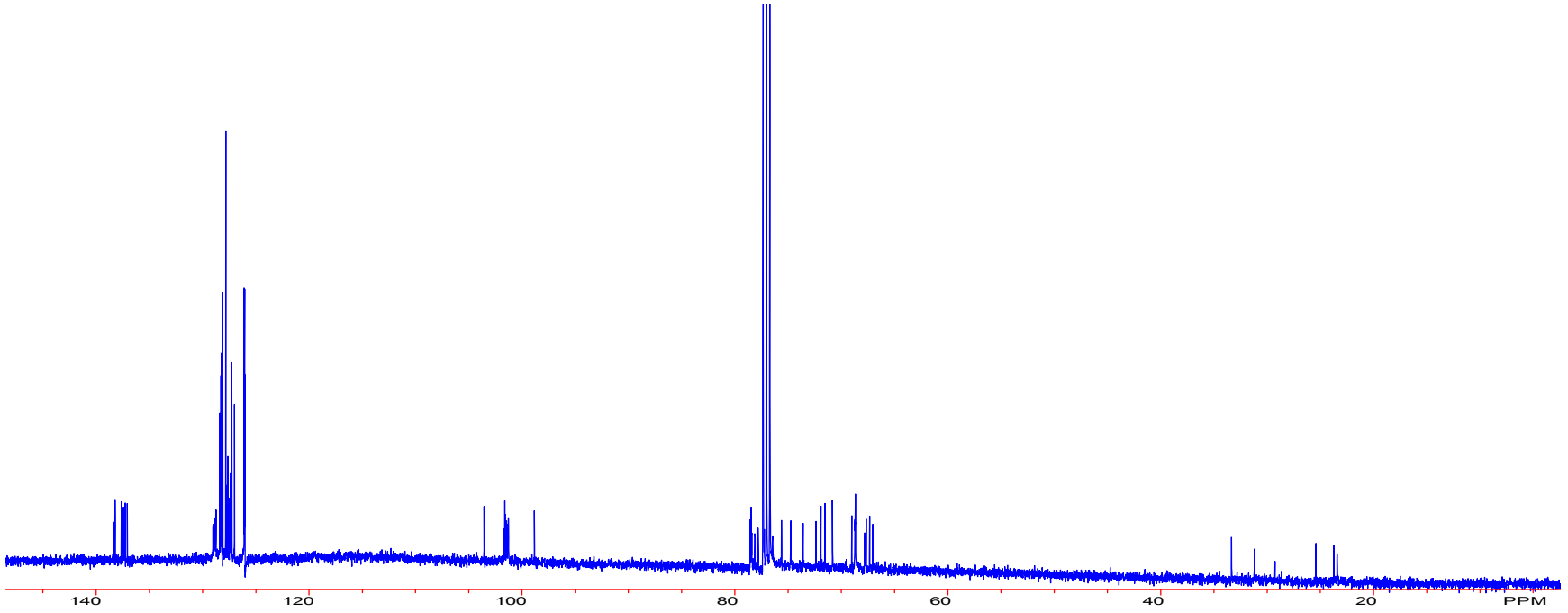
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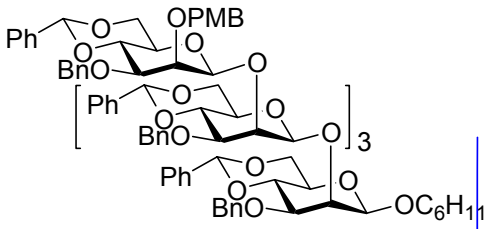
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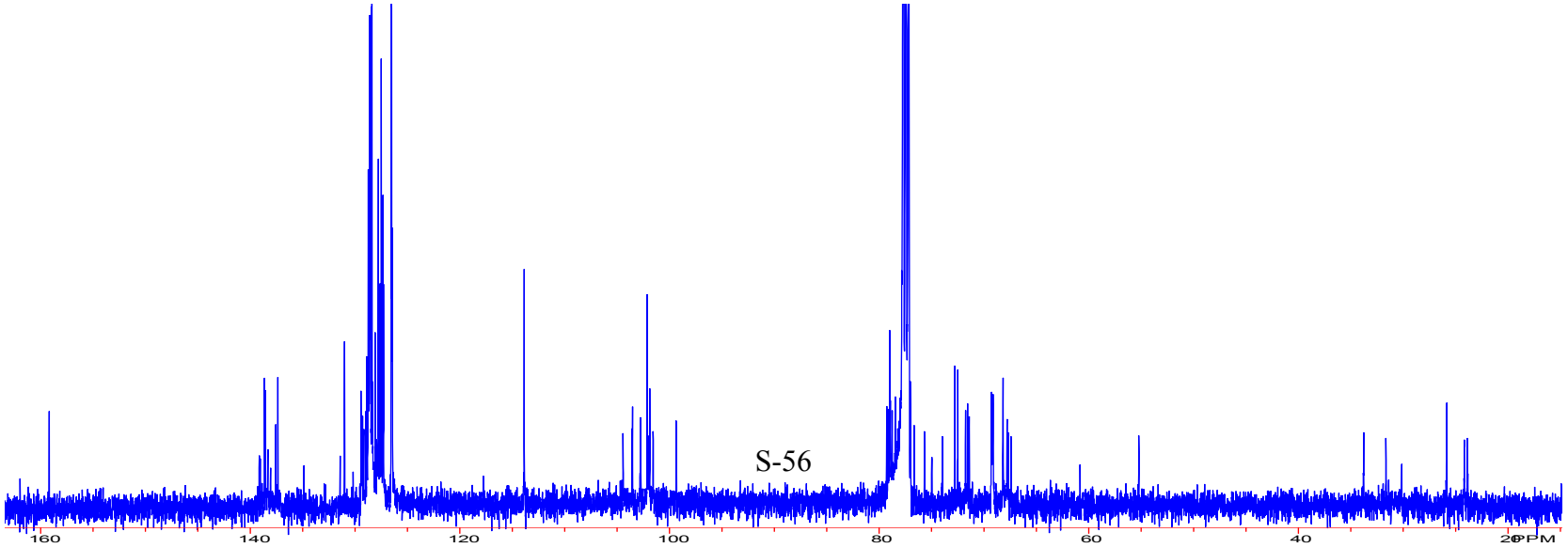
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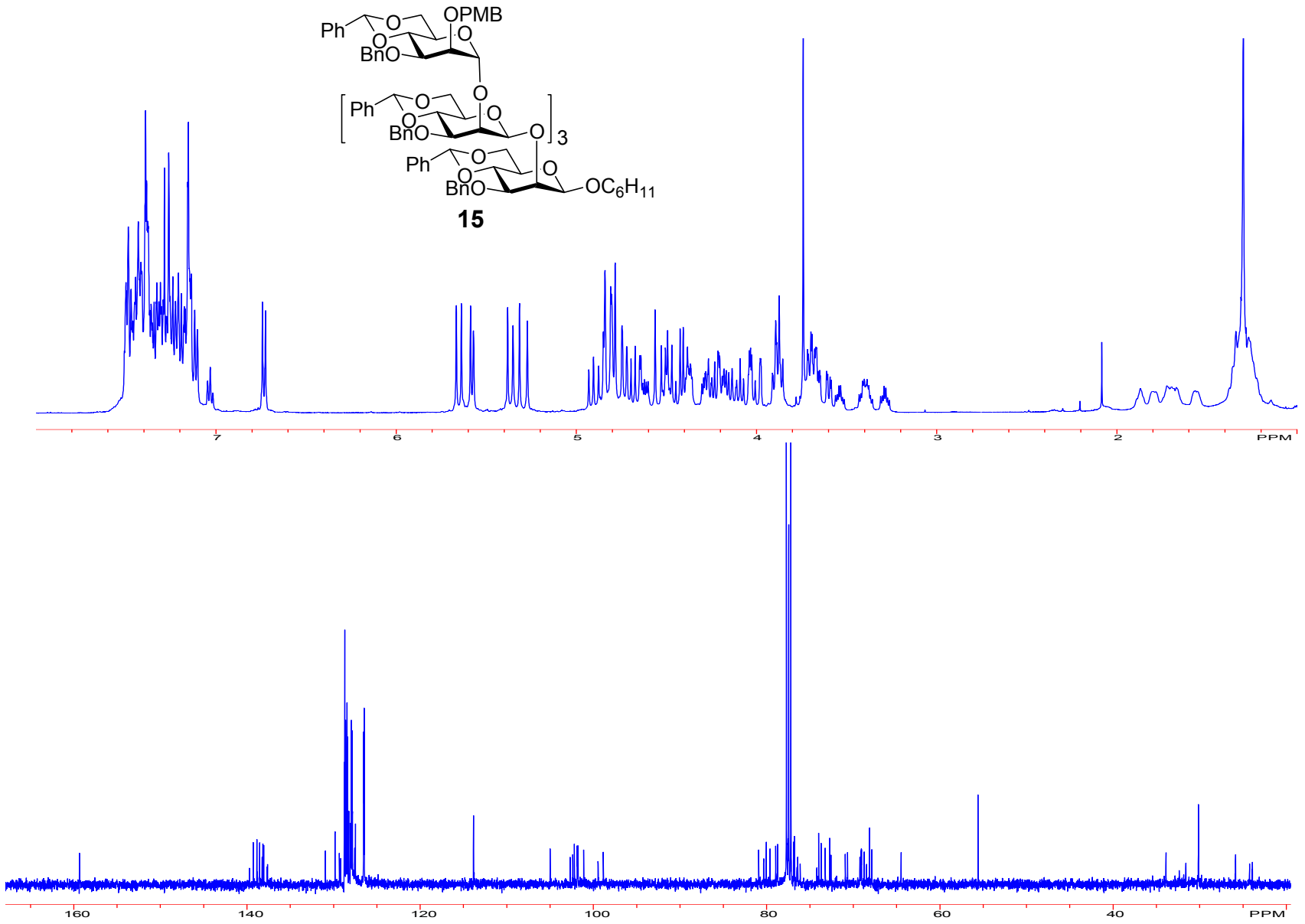
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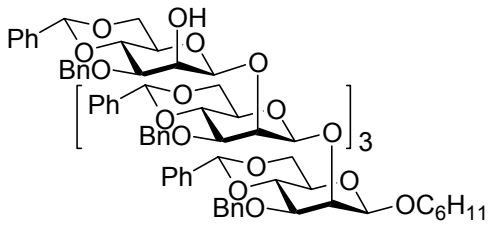
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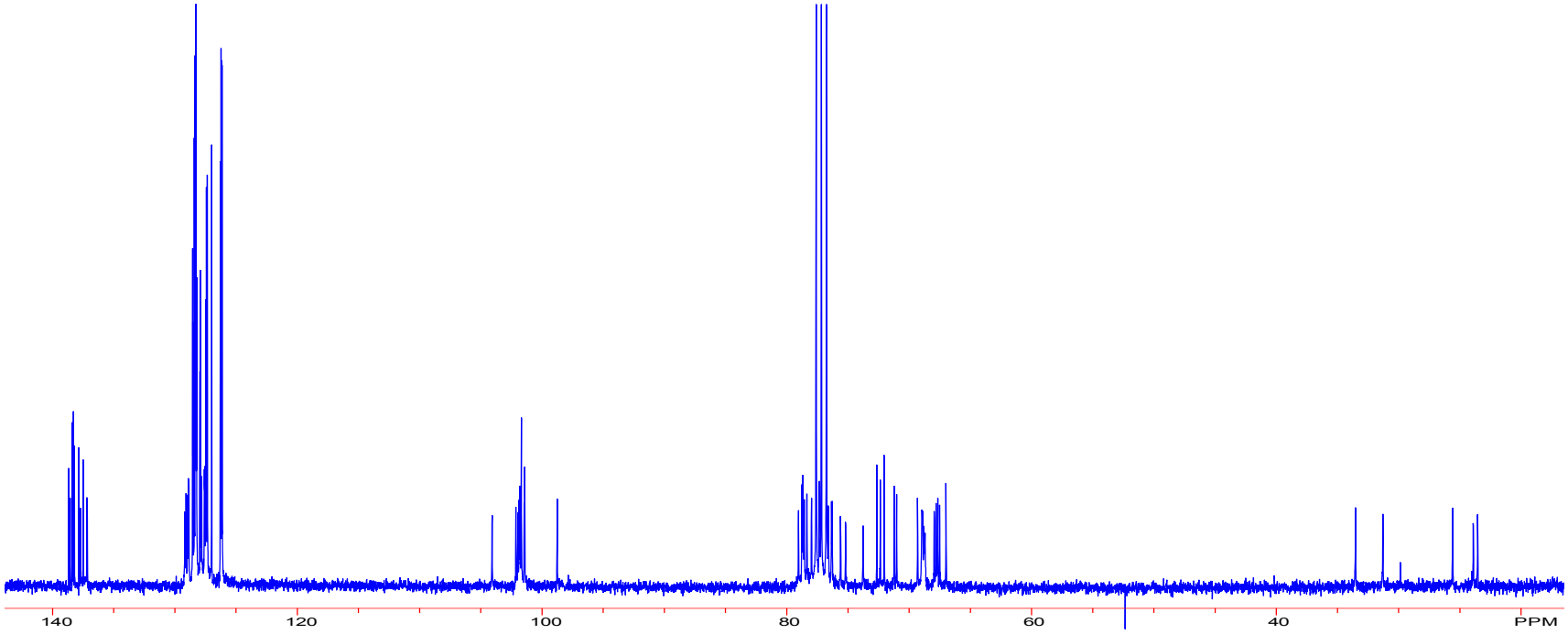
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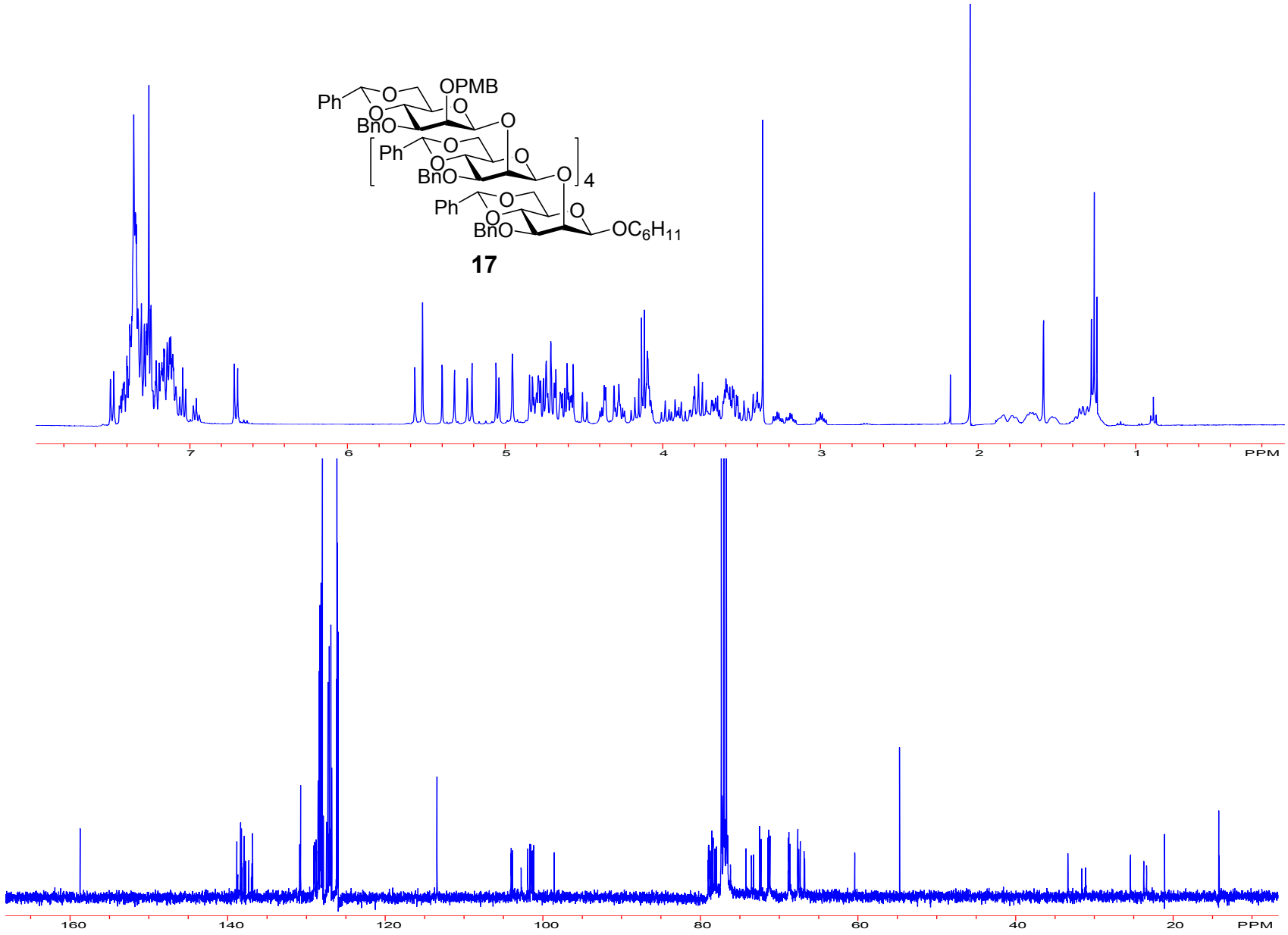
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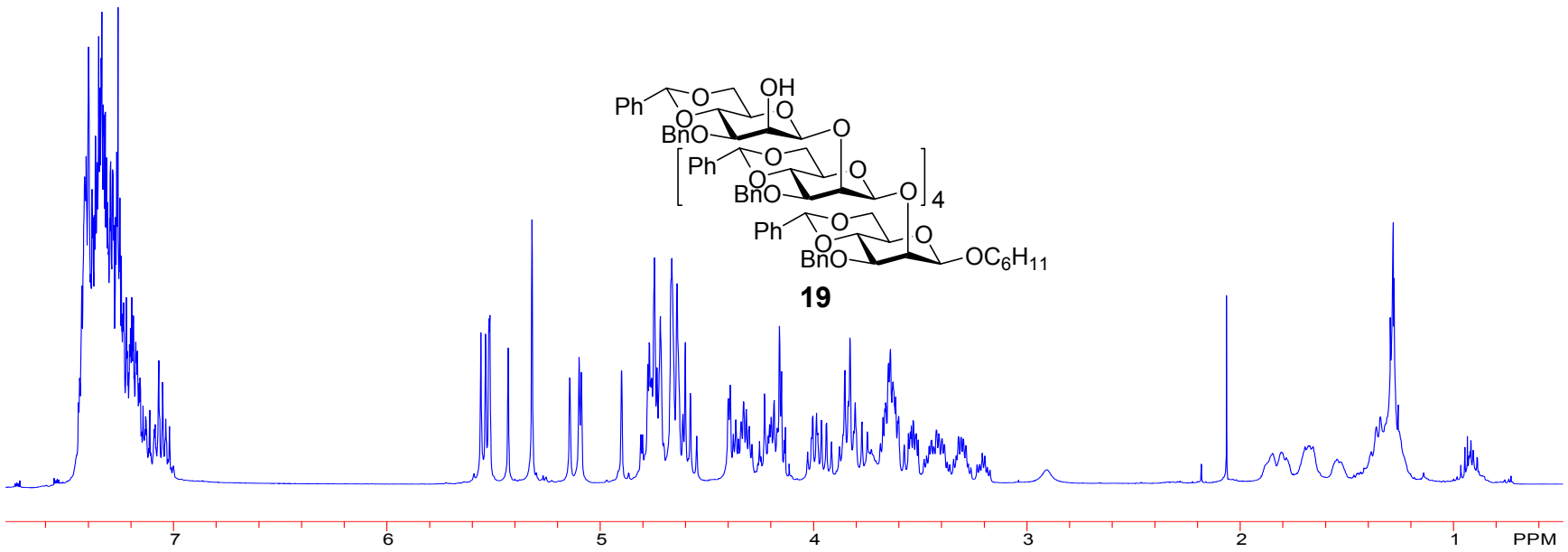
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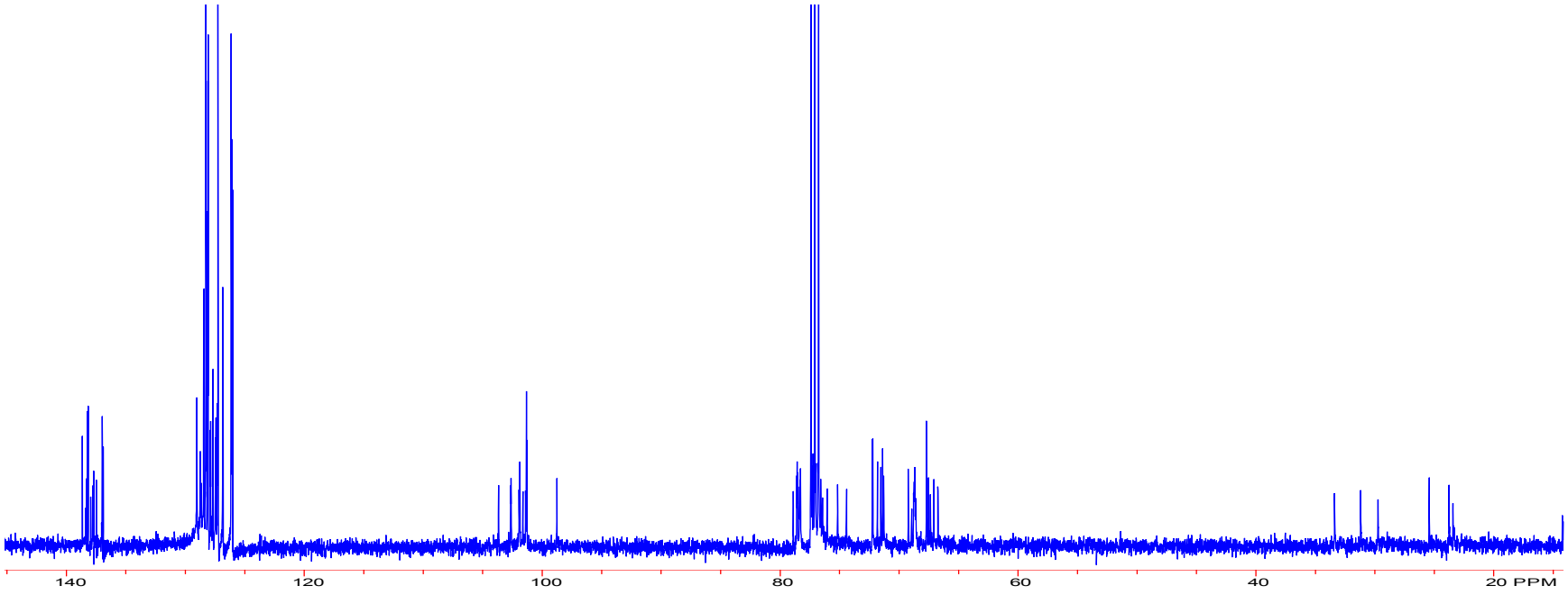
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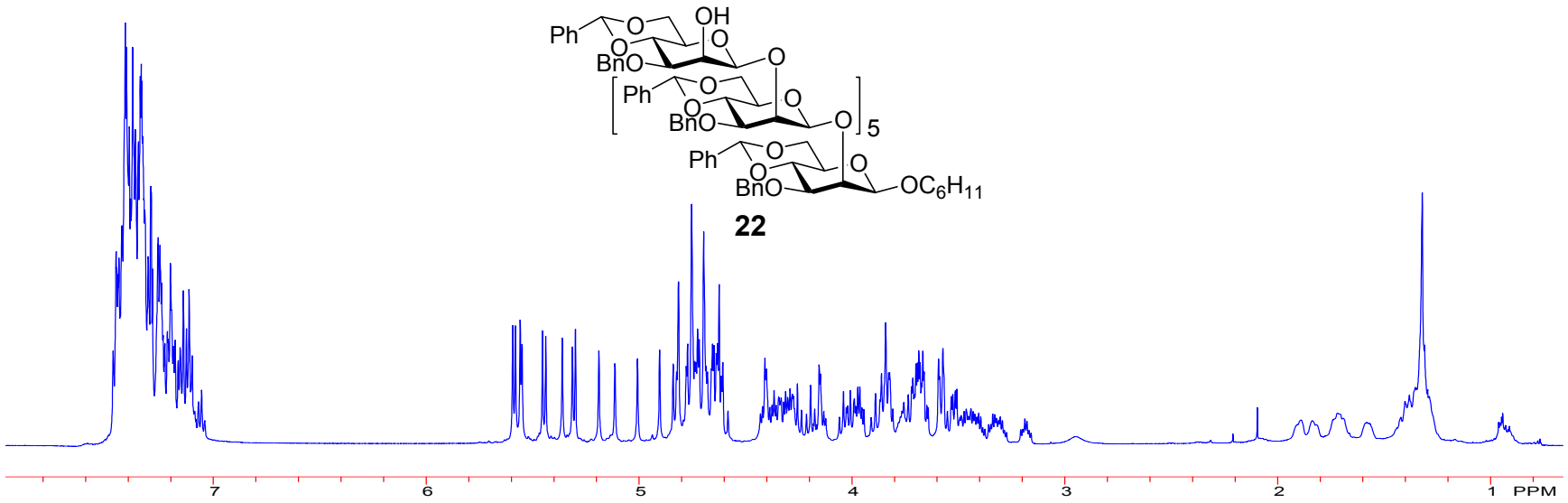
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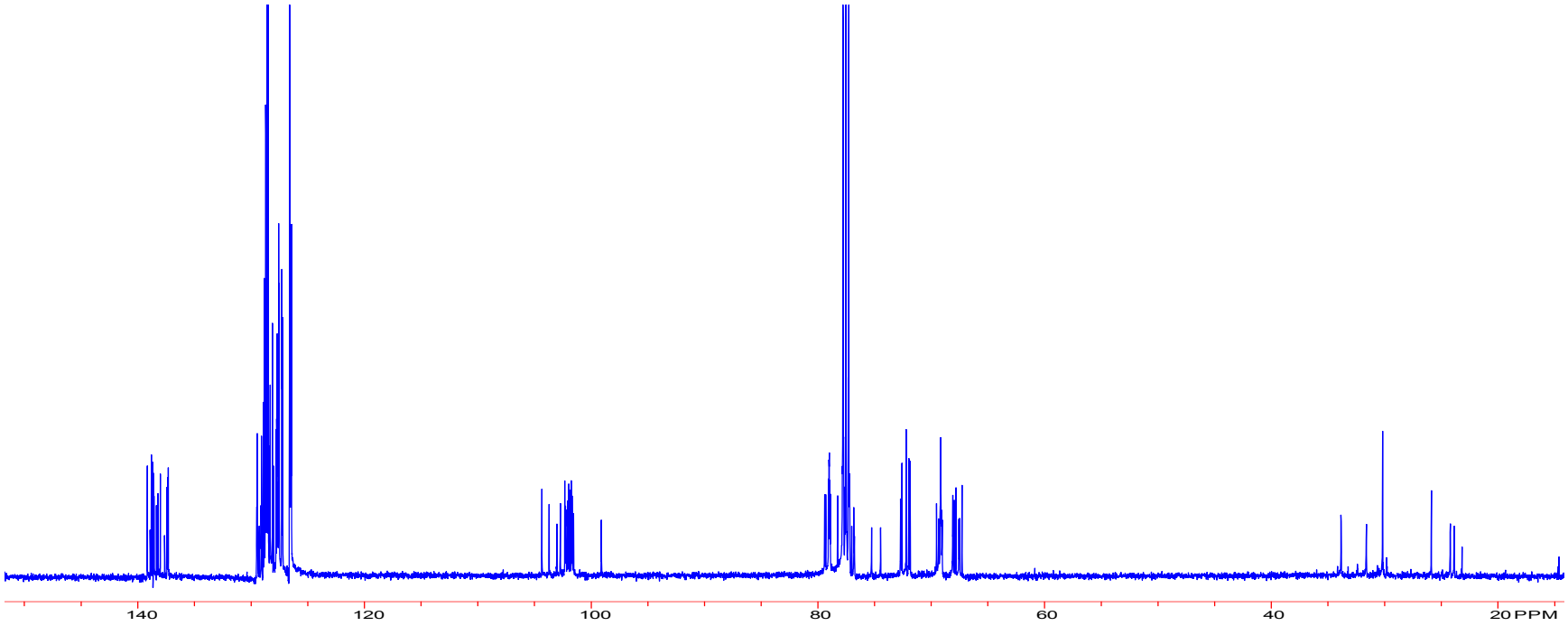
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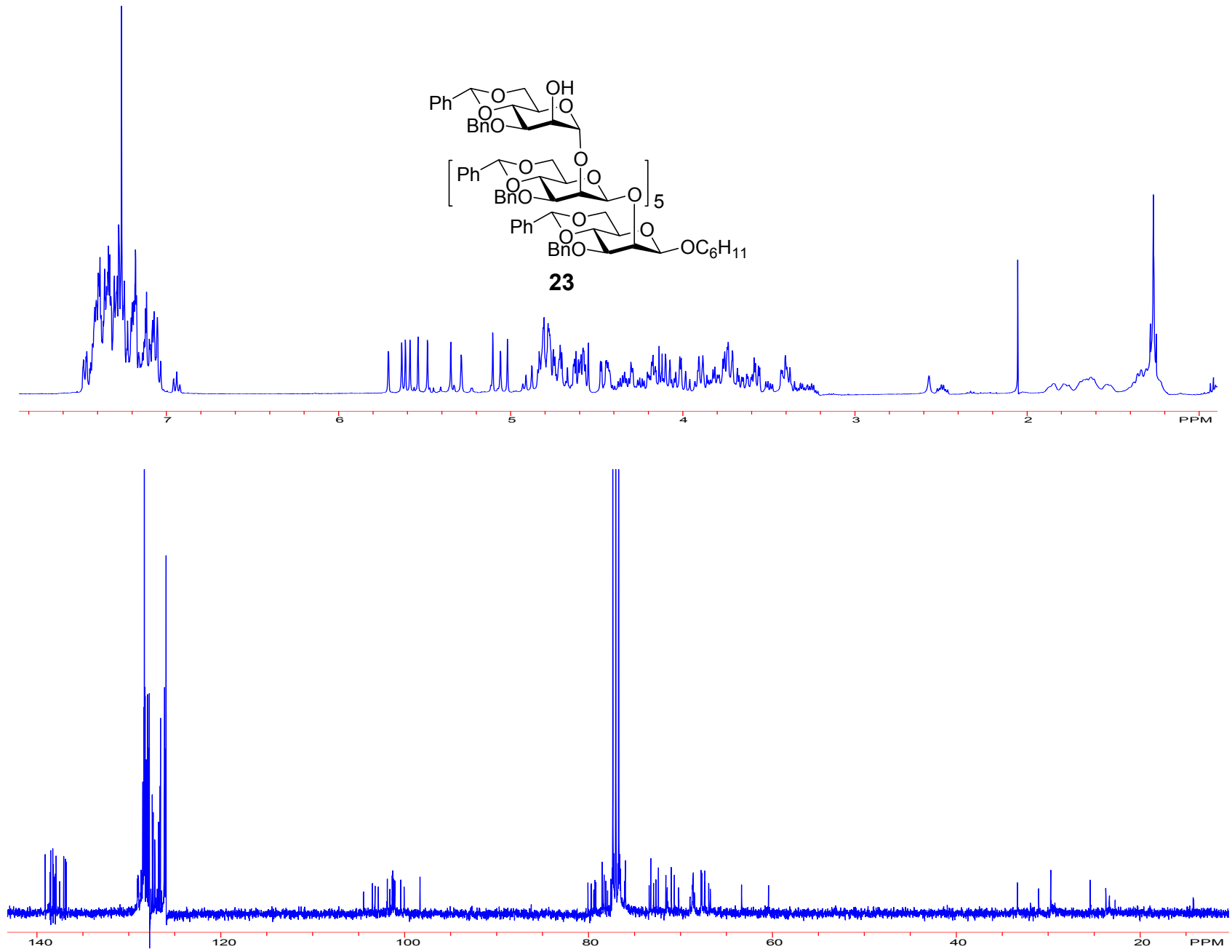
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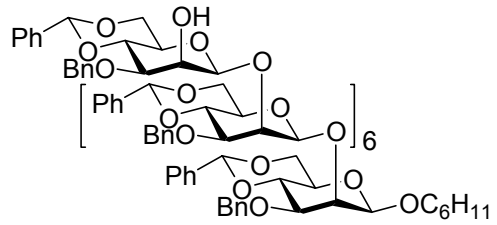
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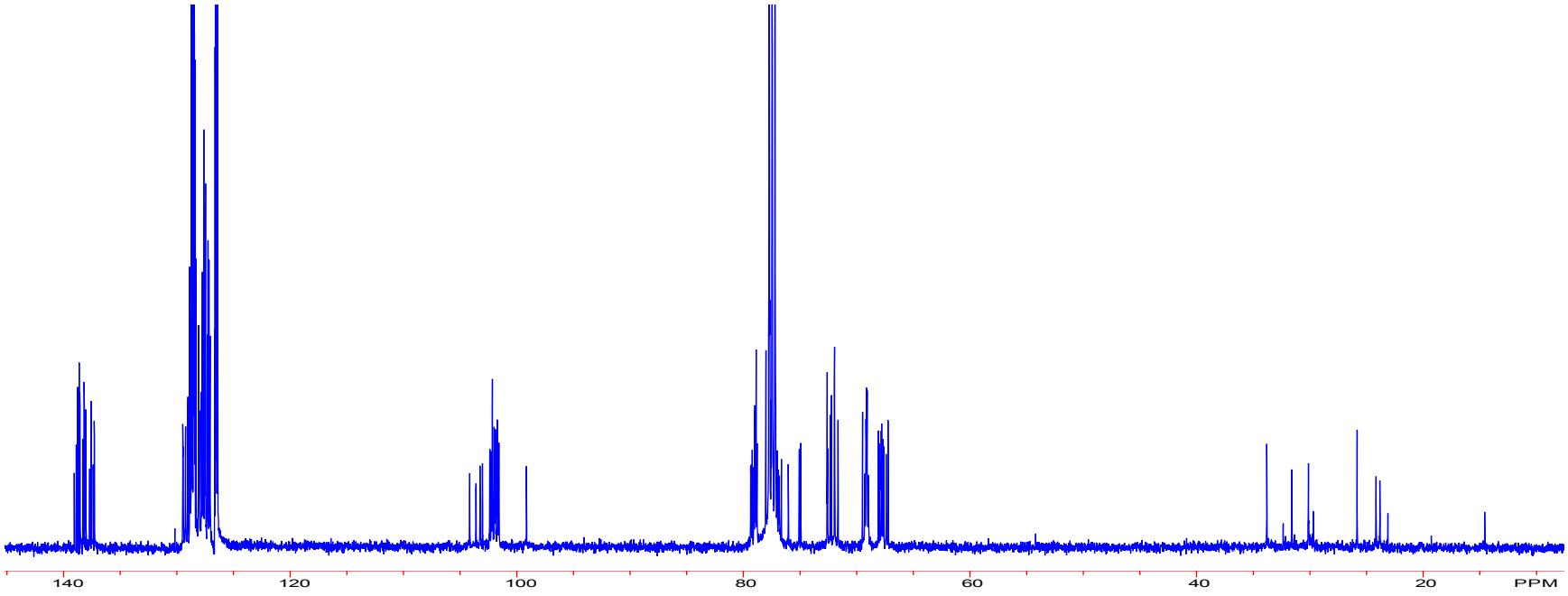
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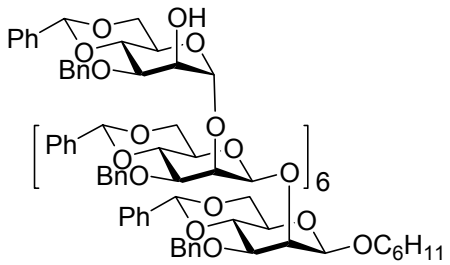
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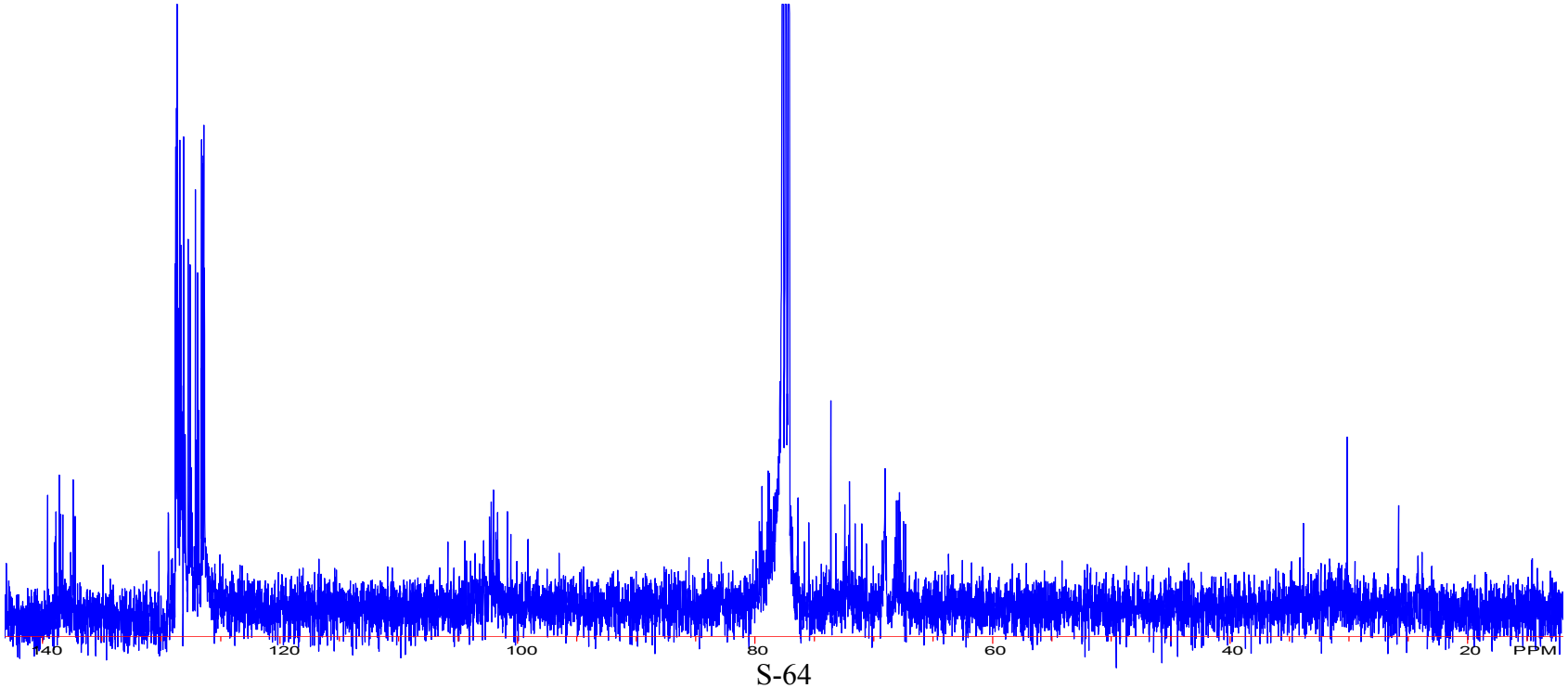
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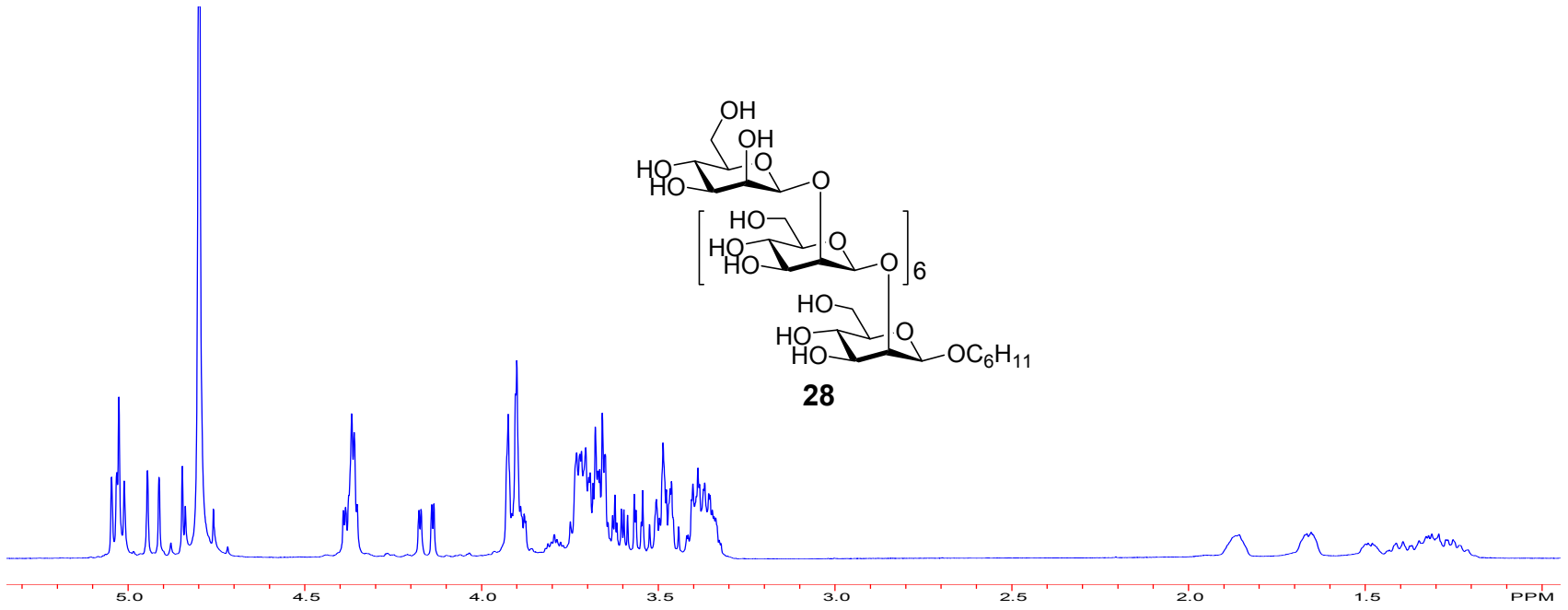
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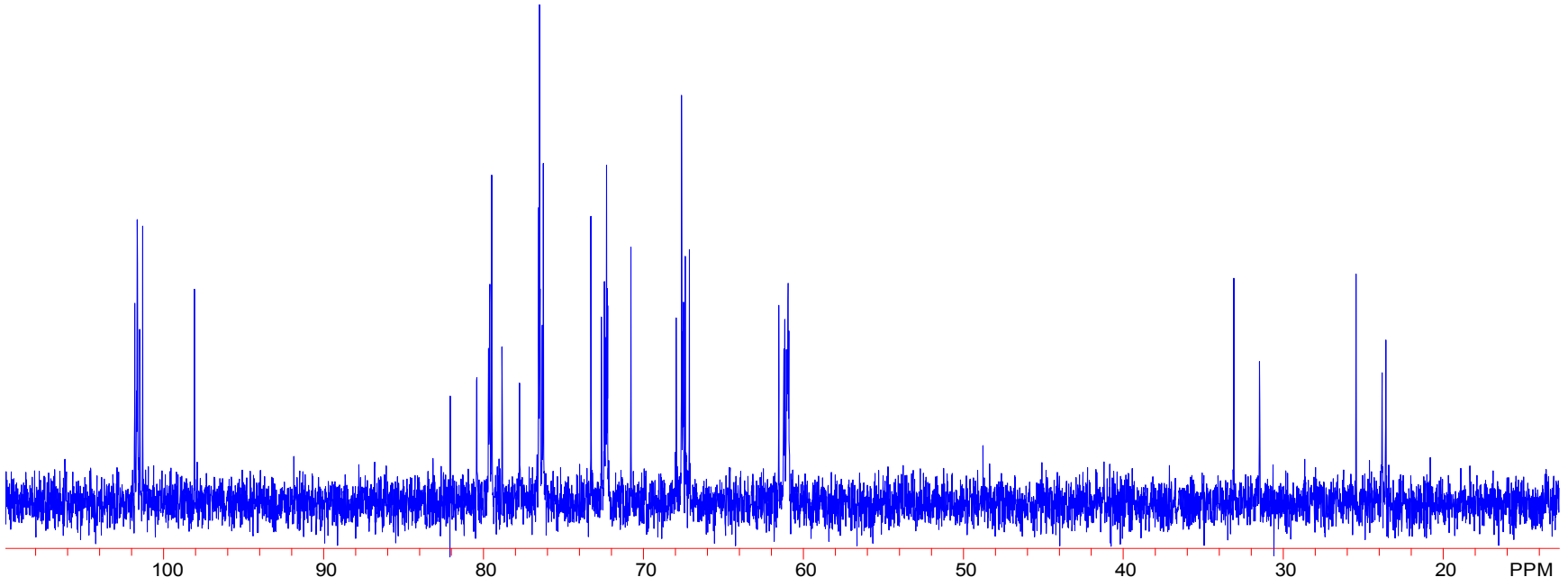
28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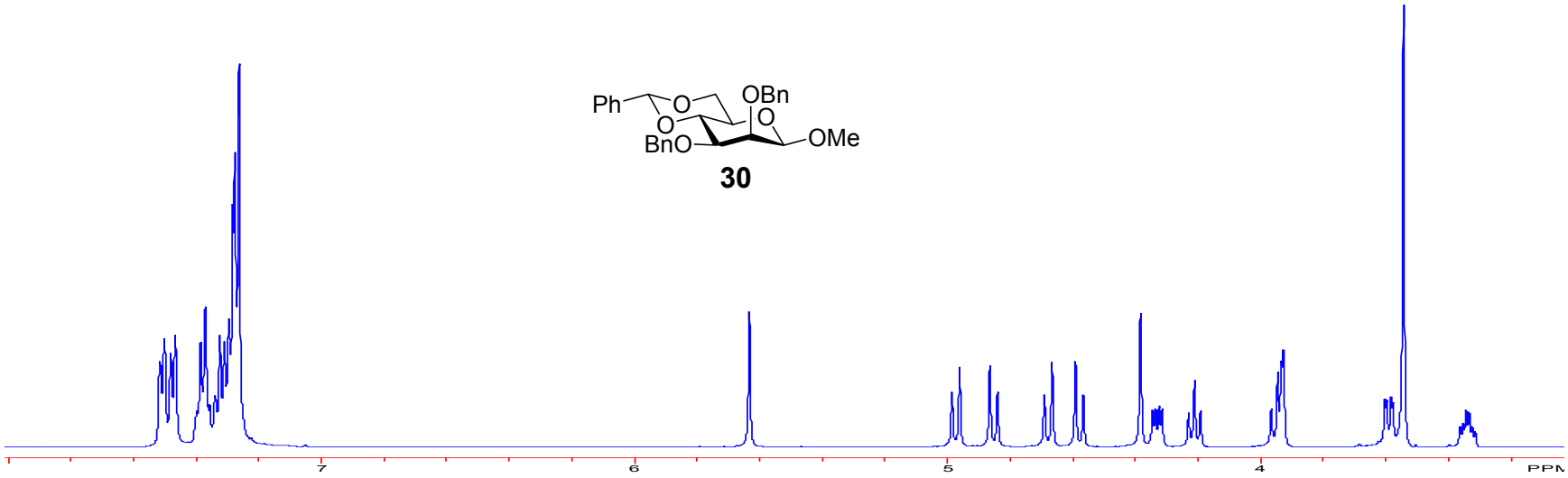

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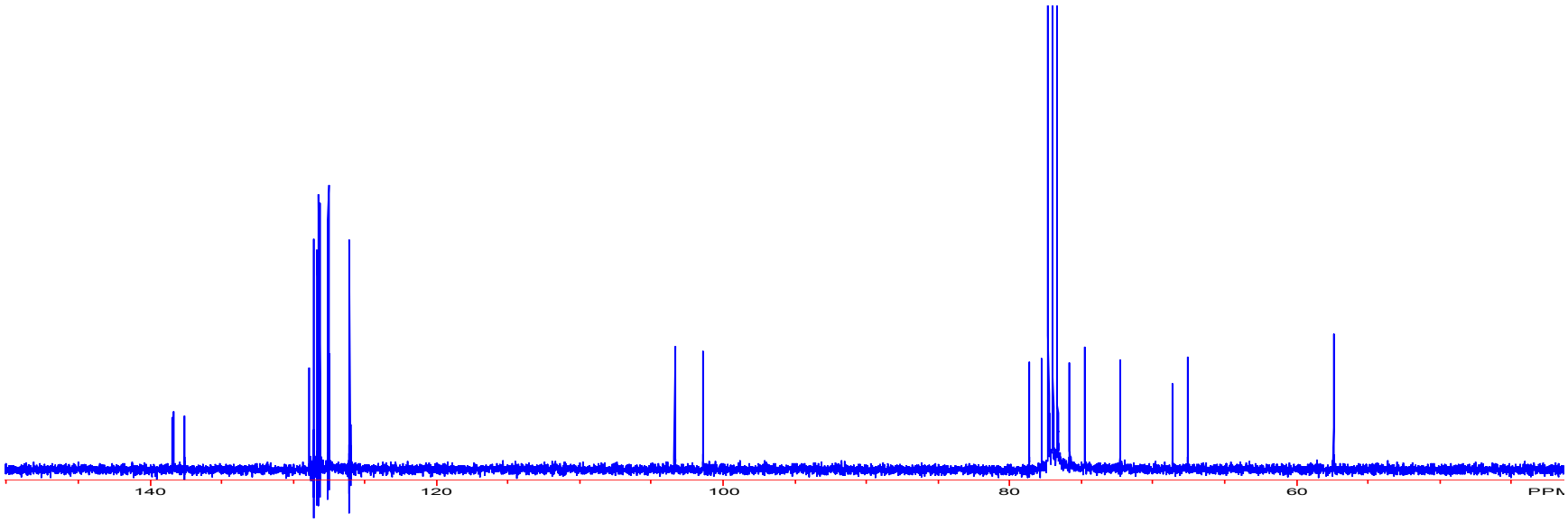

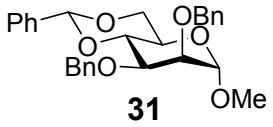

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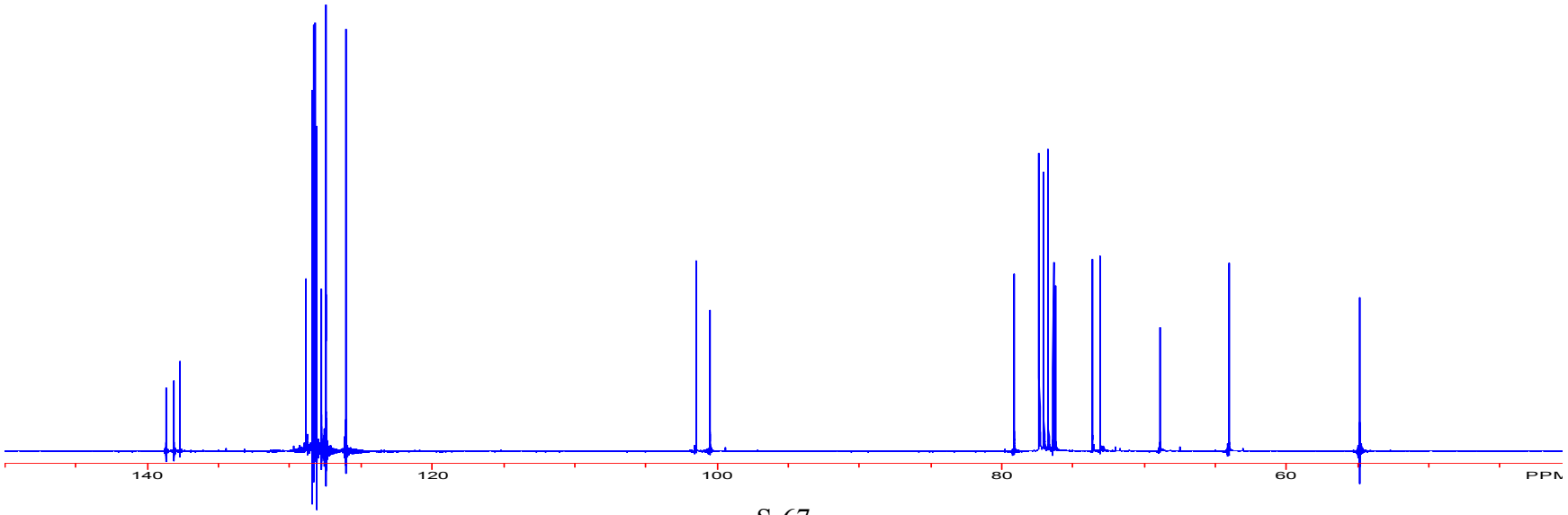

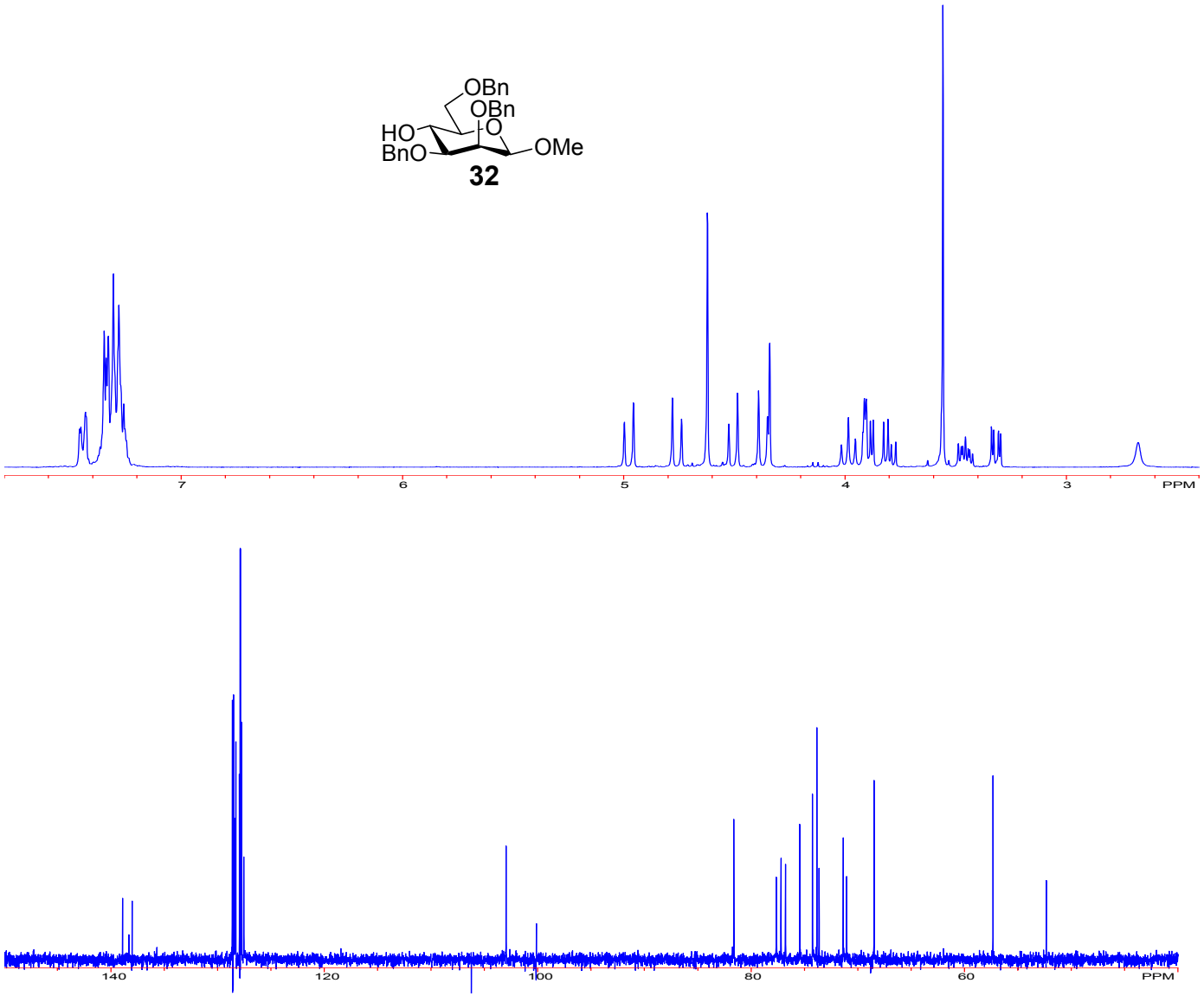
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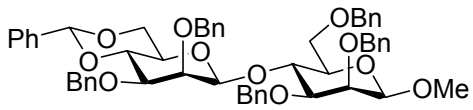

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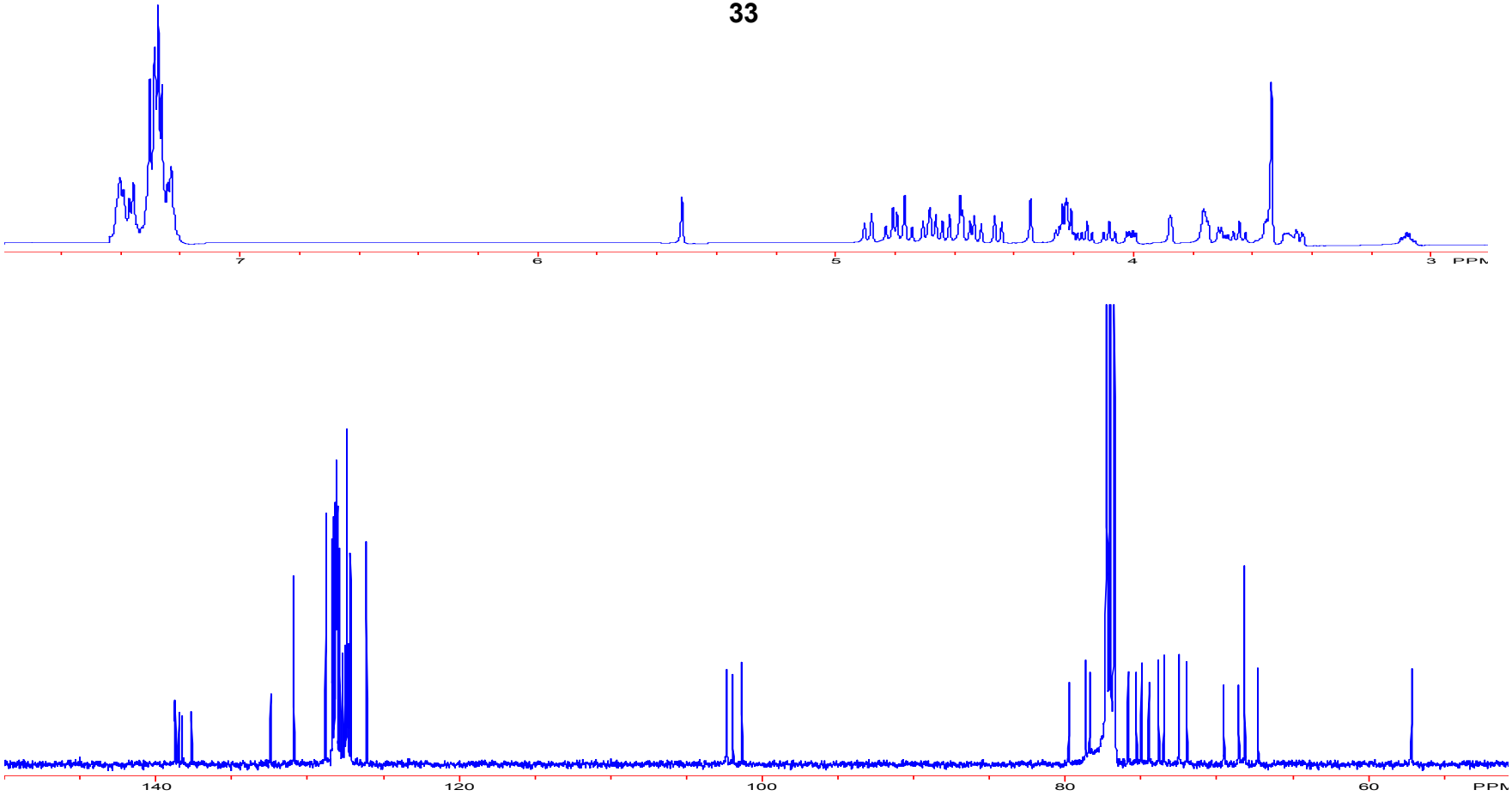

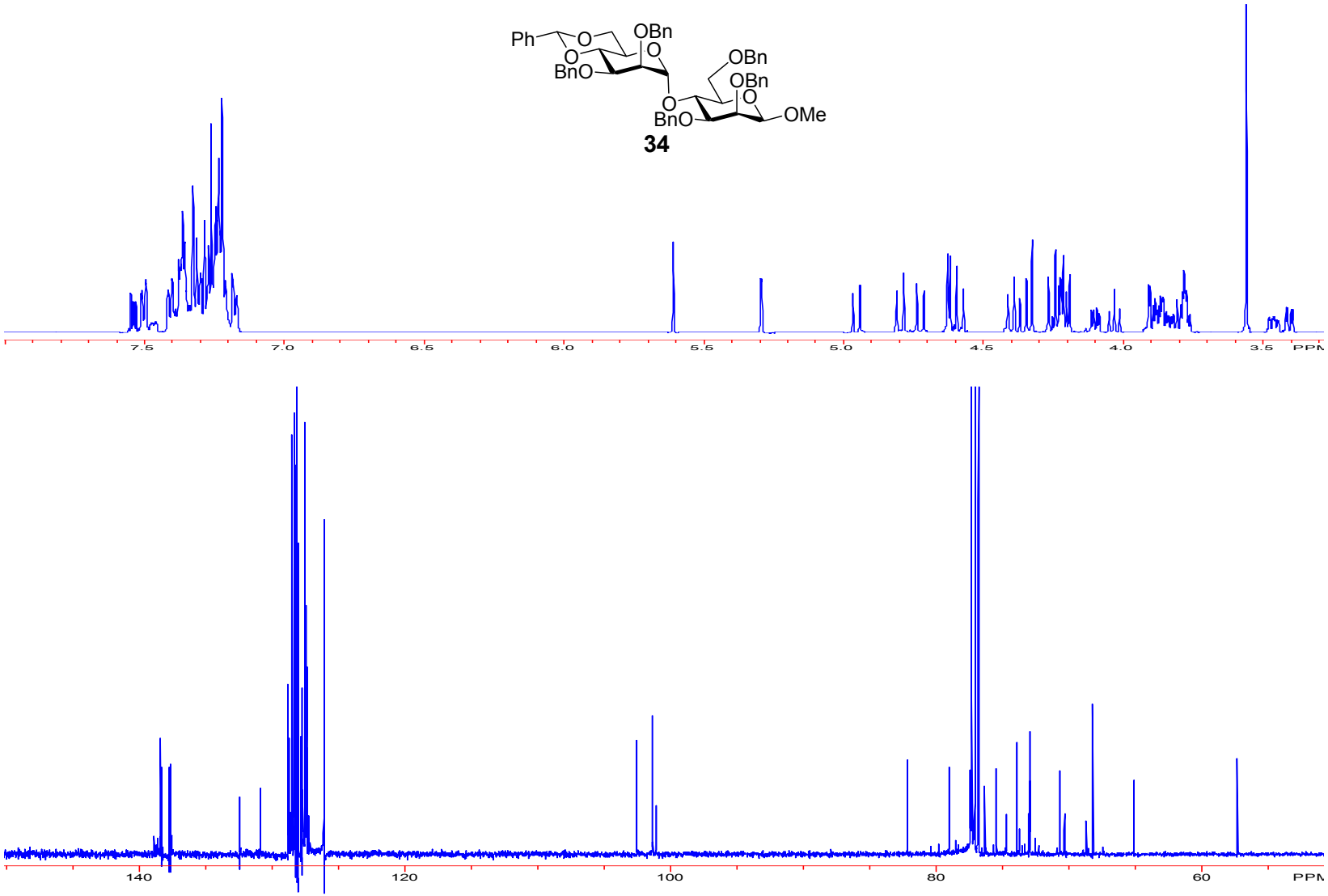
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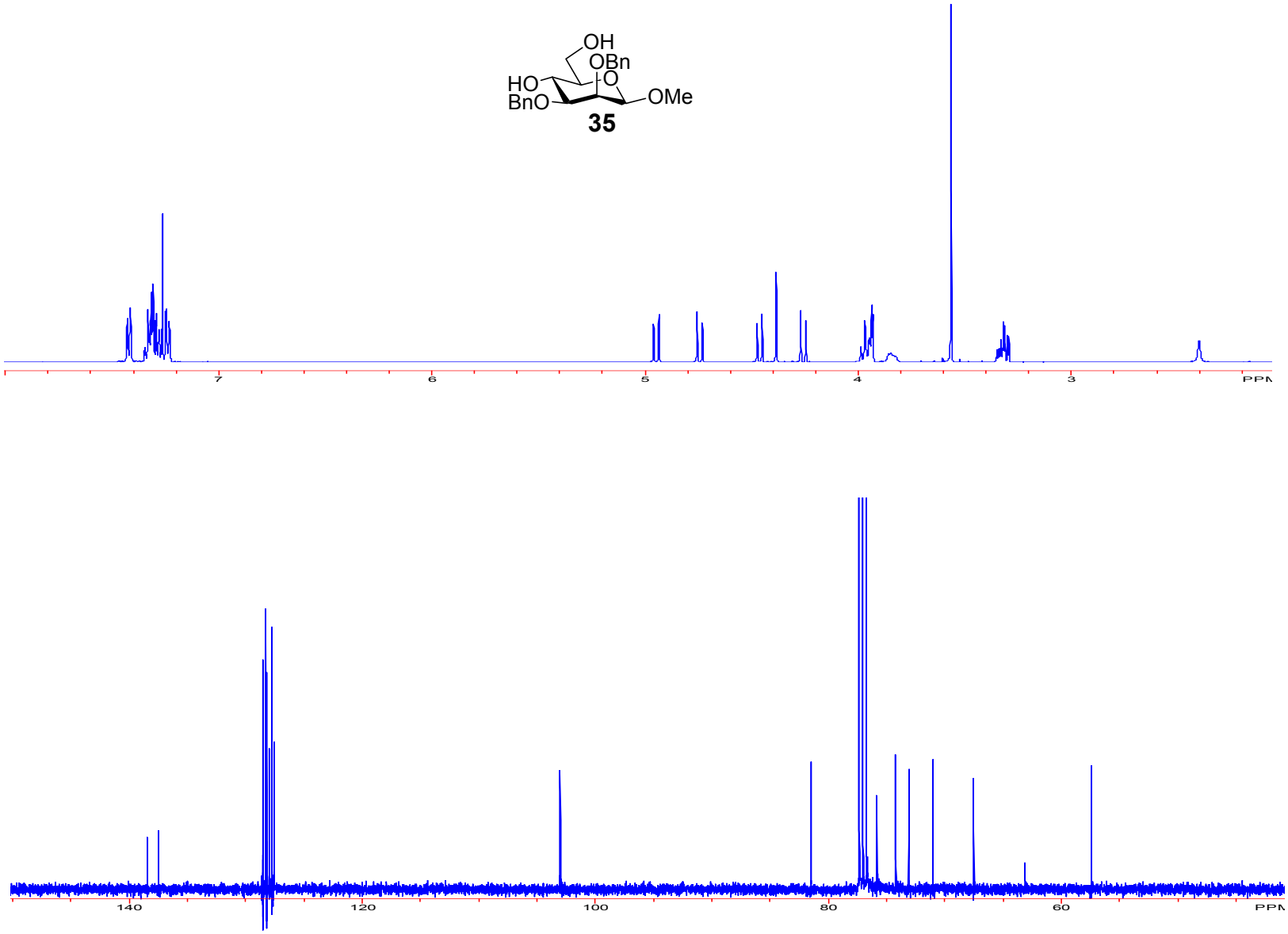
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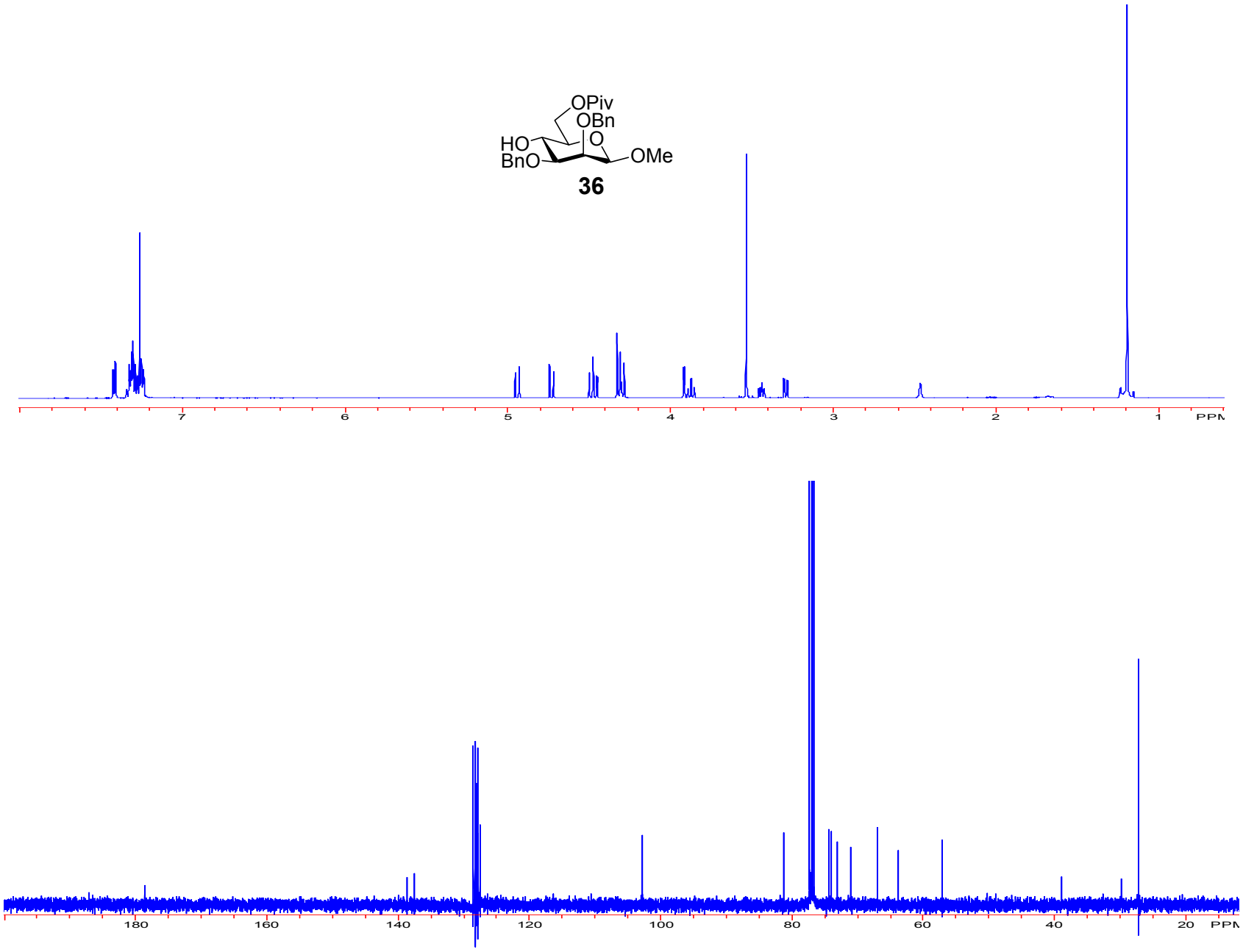
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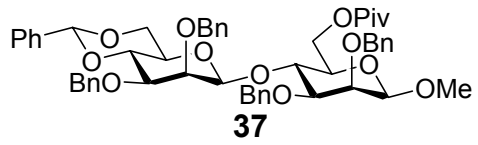
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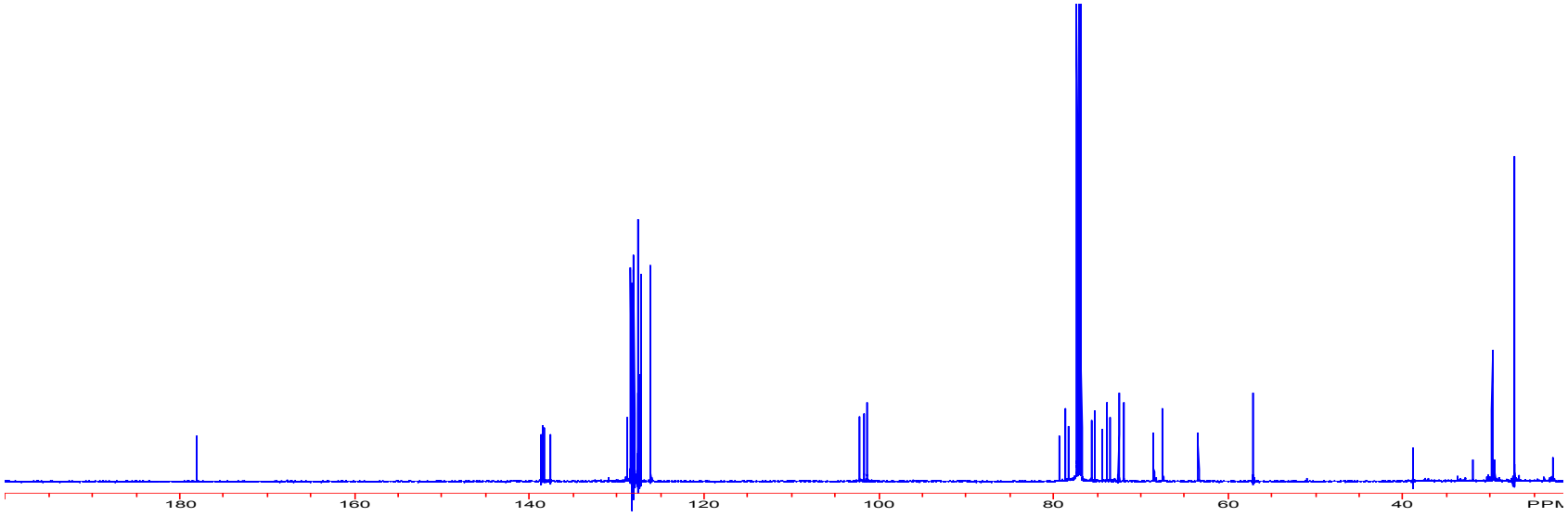
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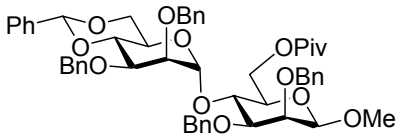
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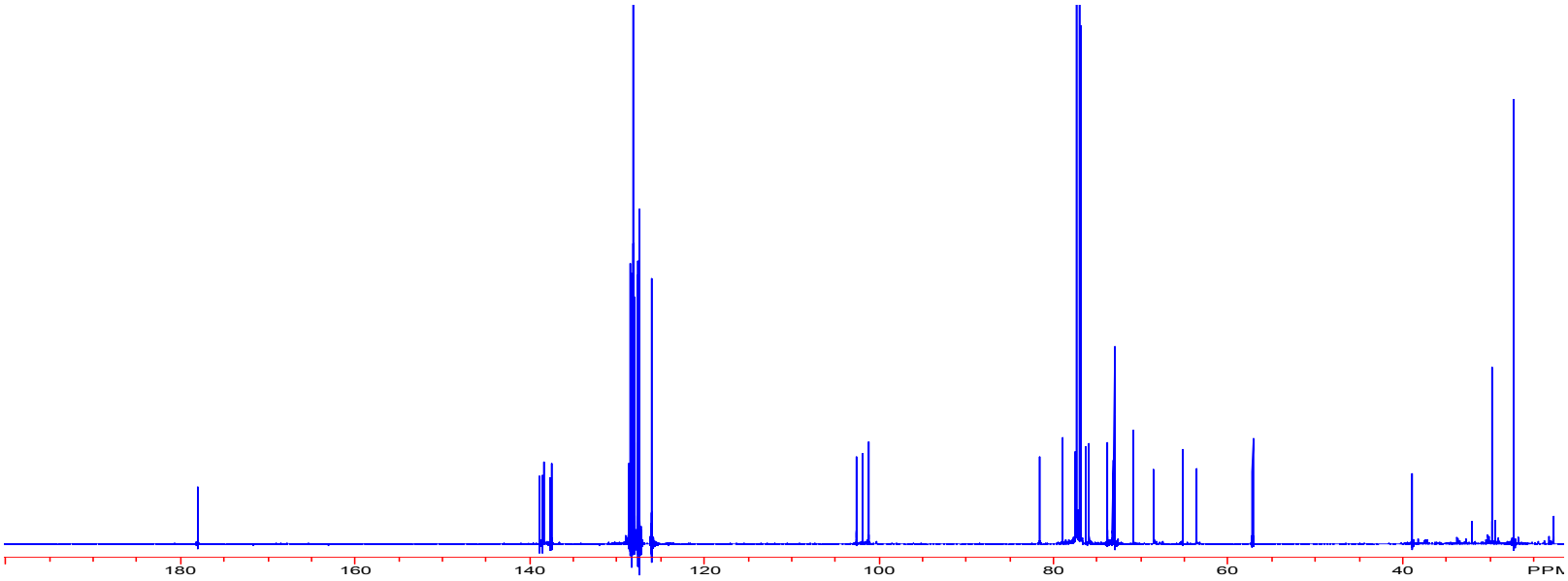
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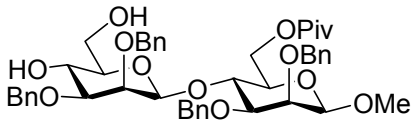
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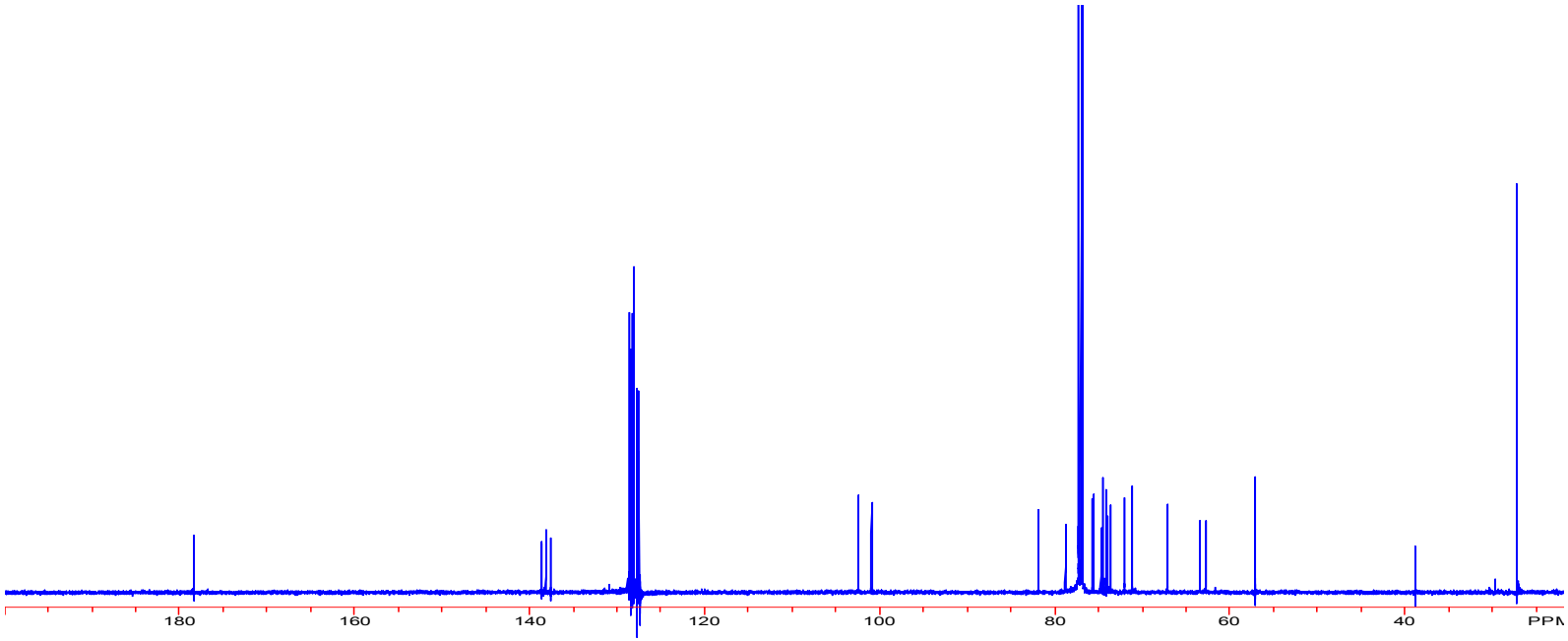
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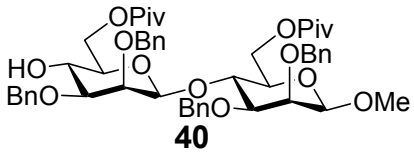
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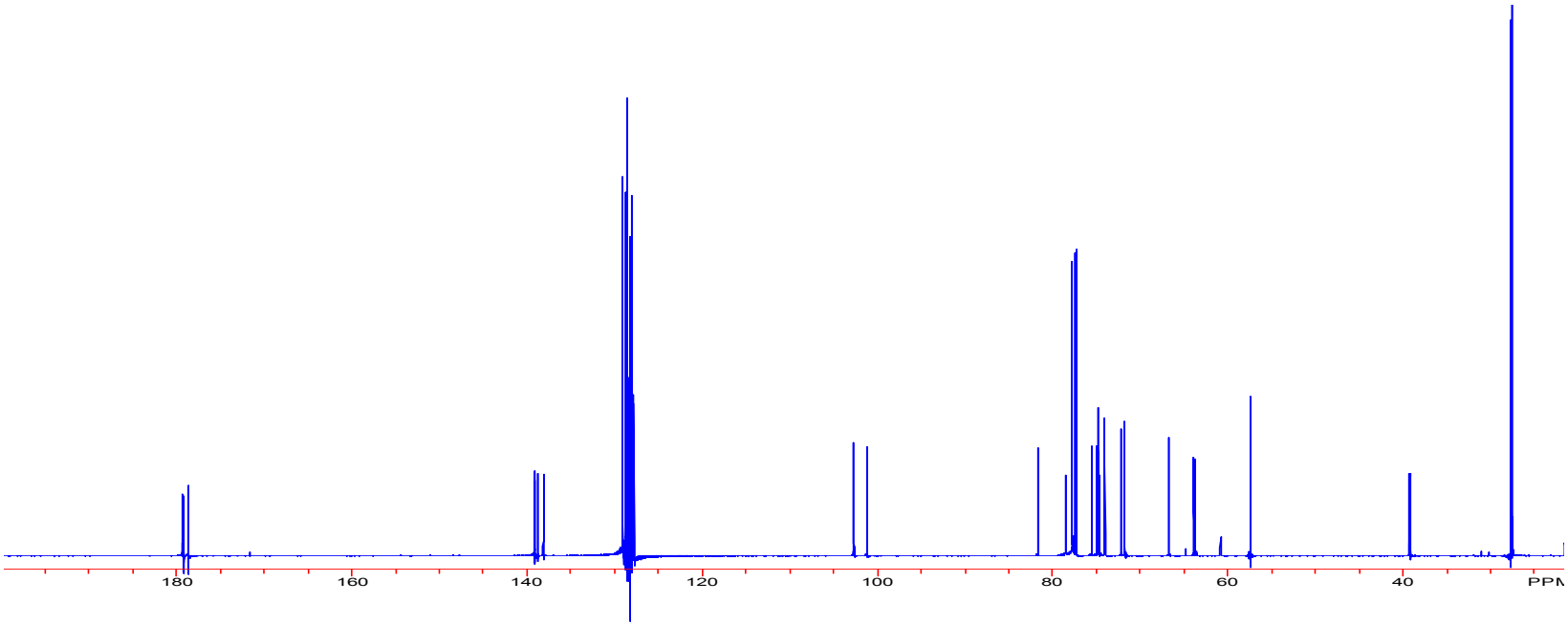
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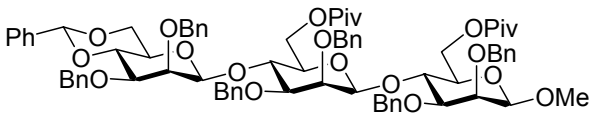
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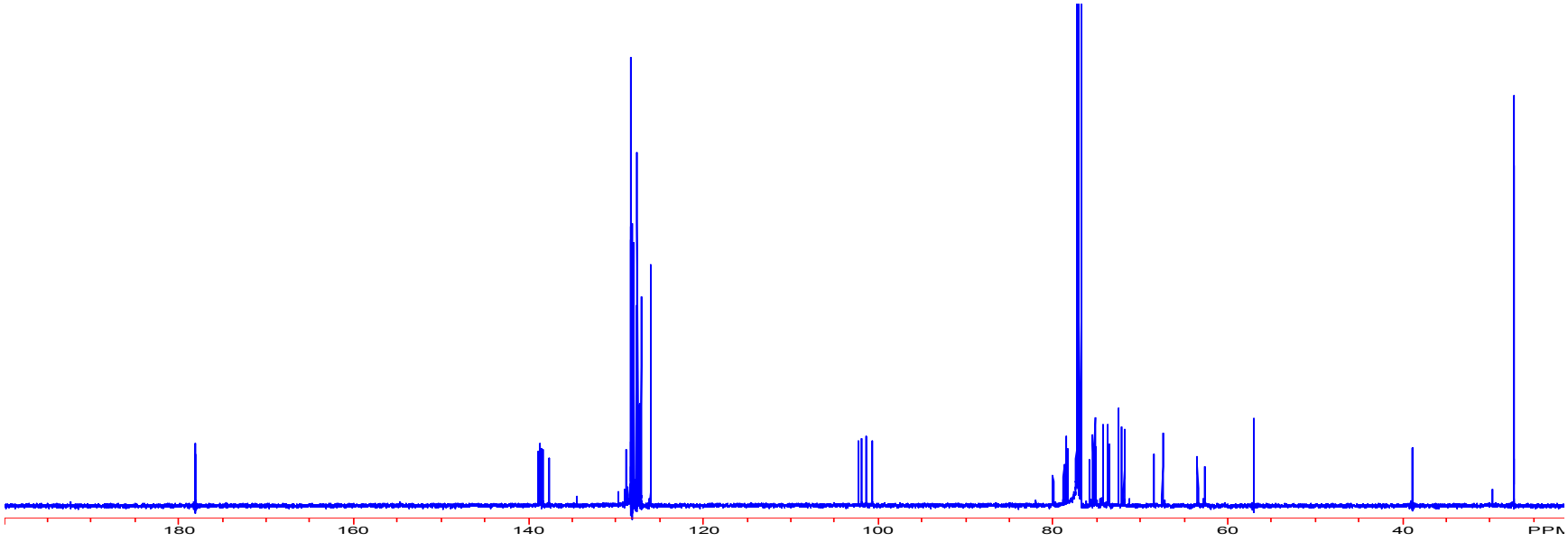
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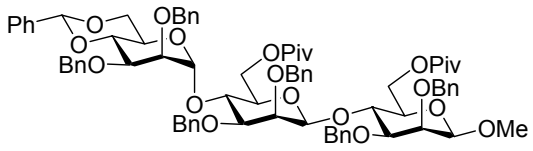
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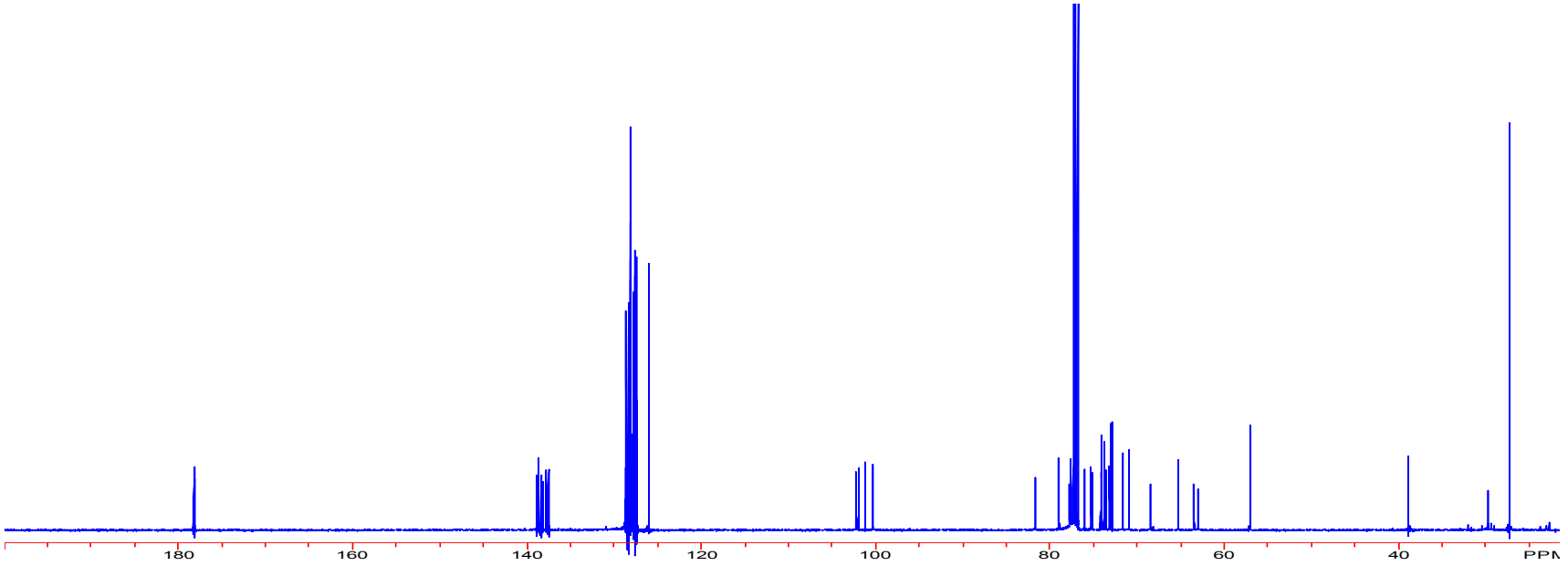
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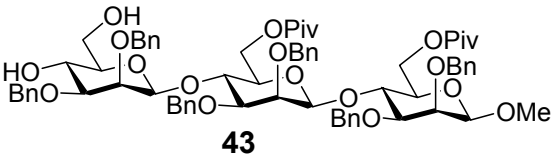
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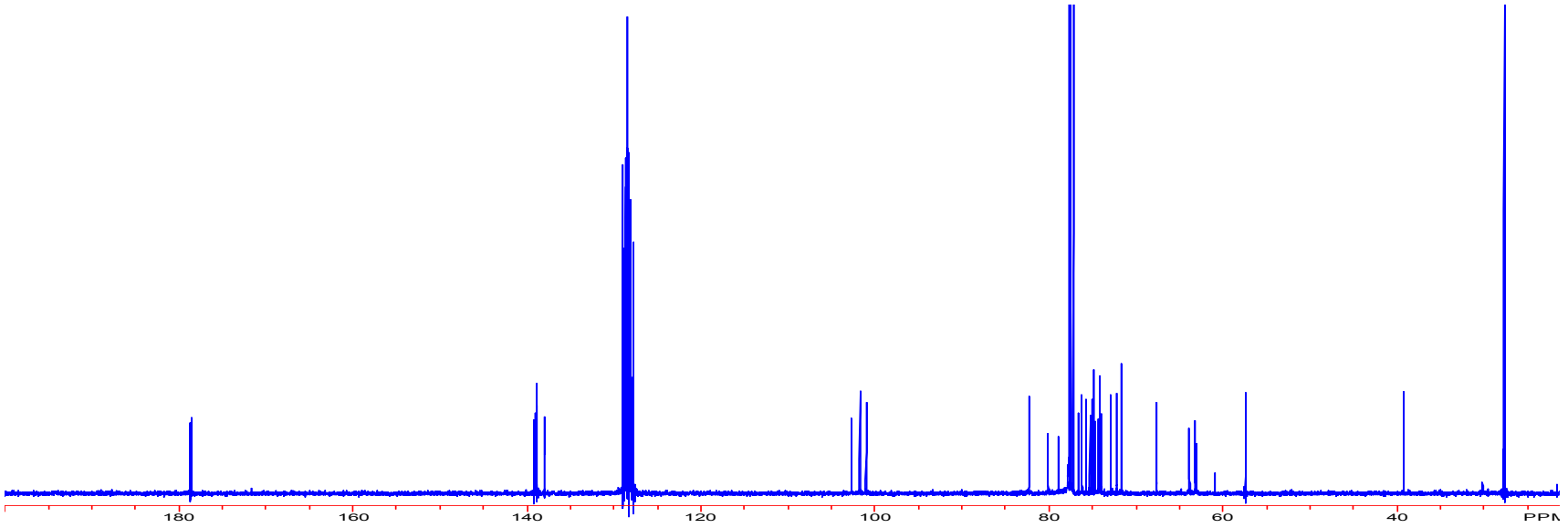
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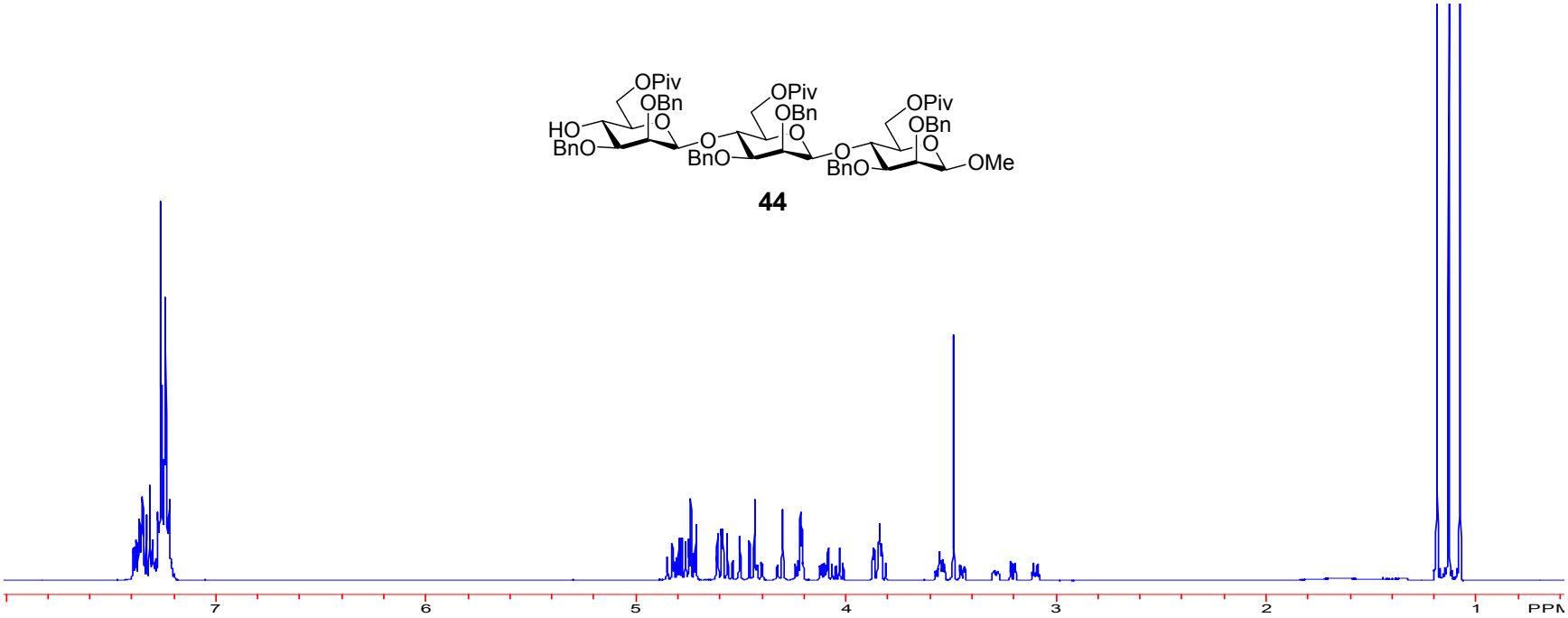
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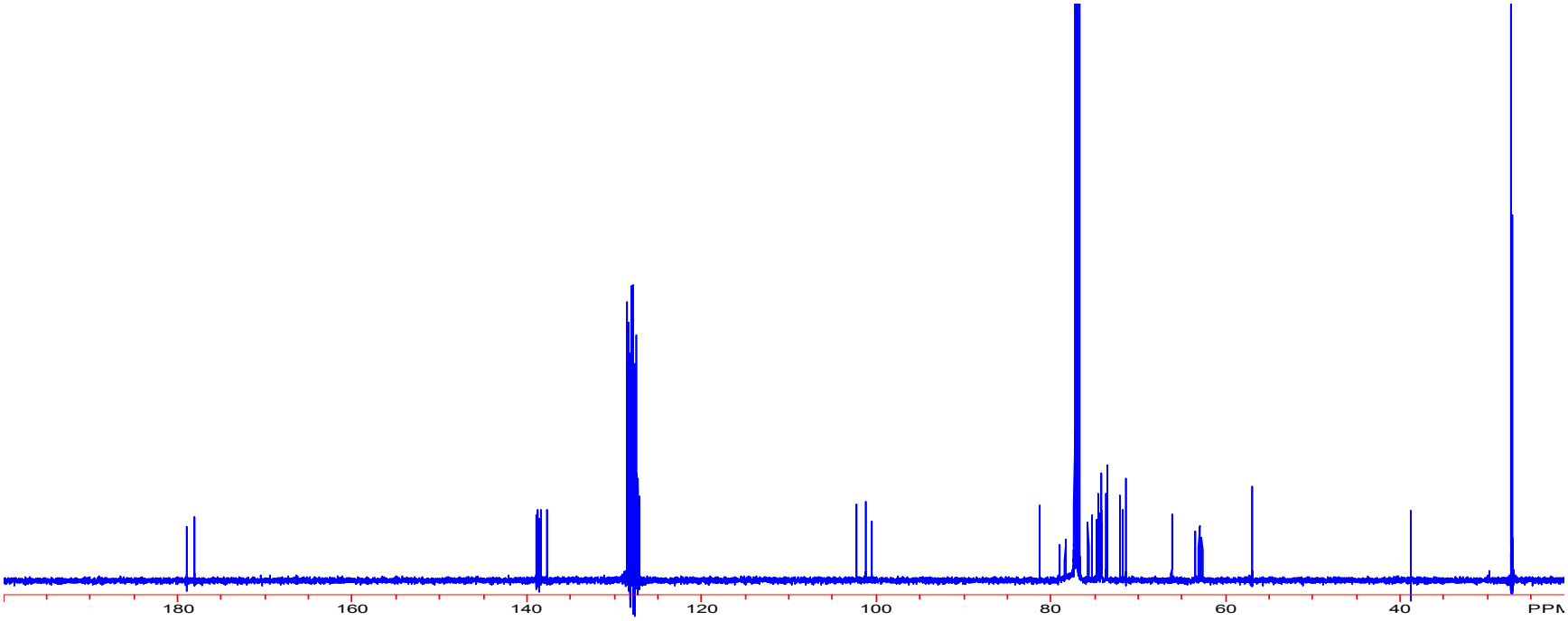
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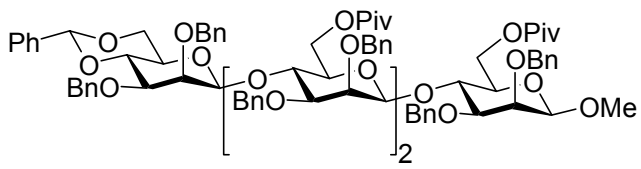
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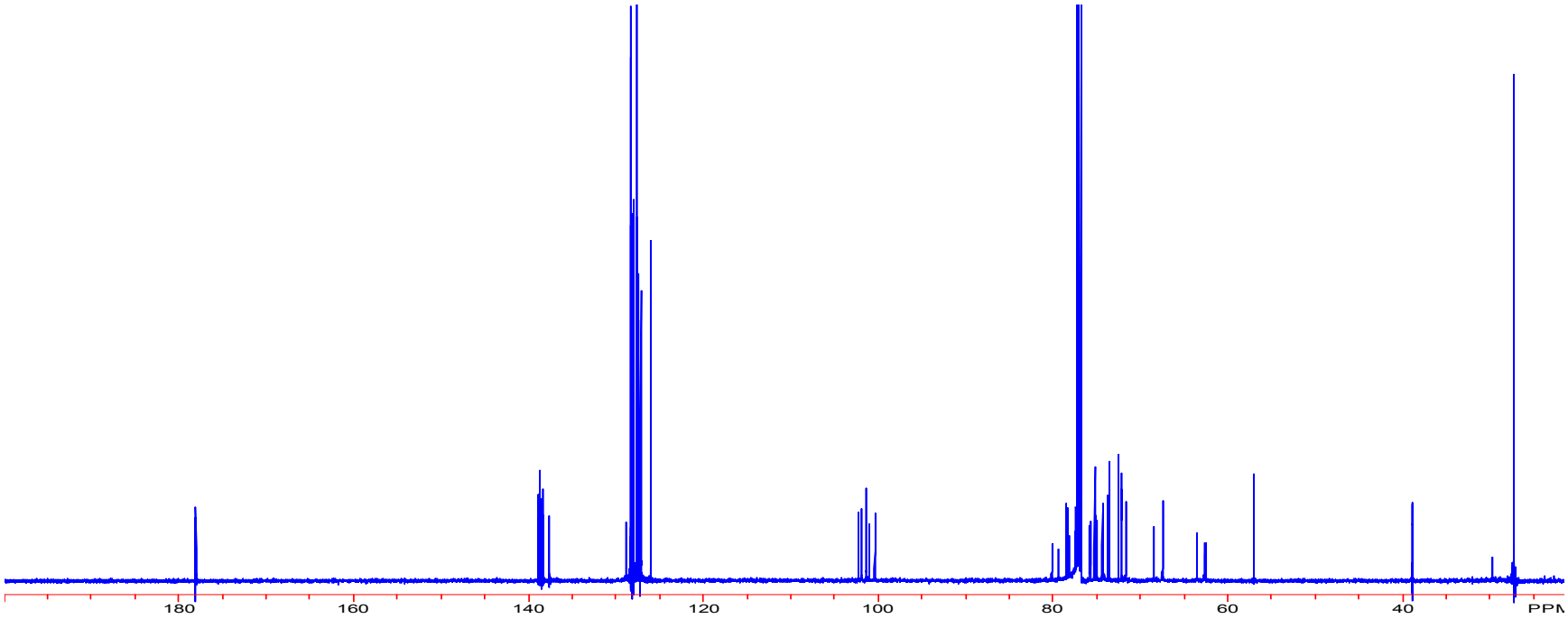
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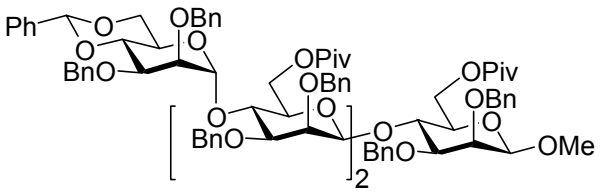
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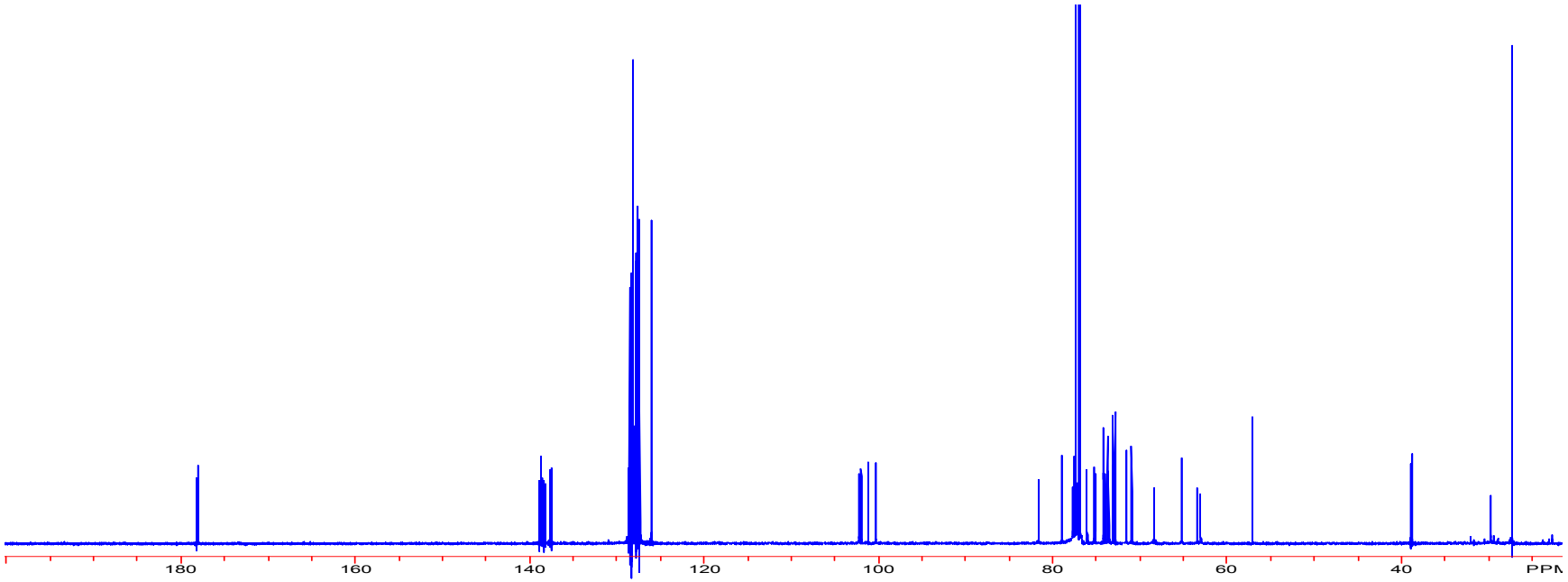
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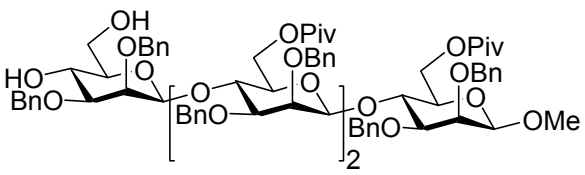
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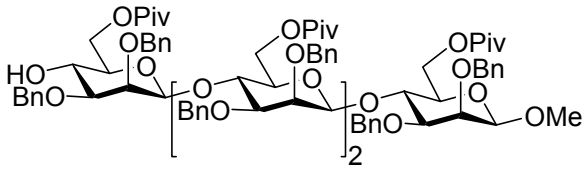
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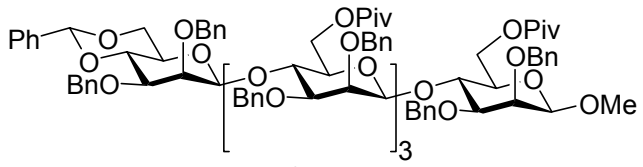
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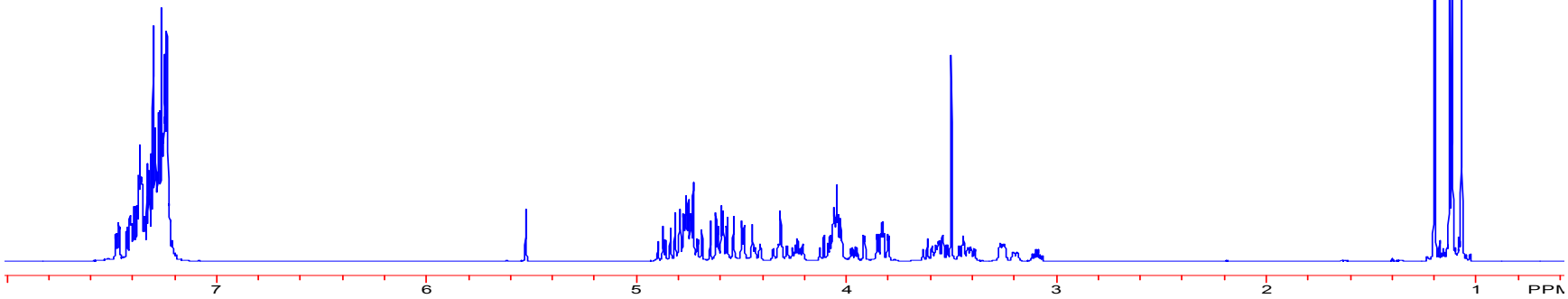
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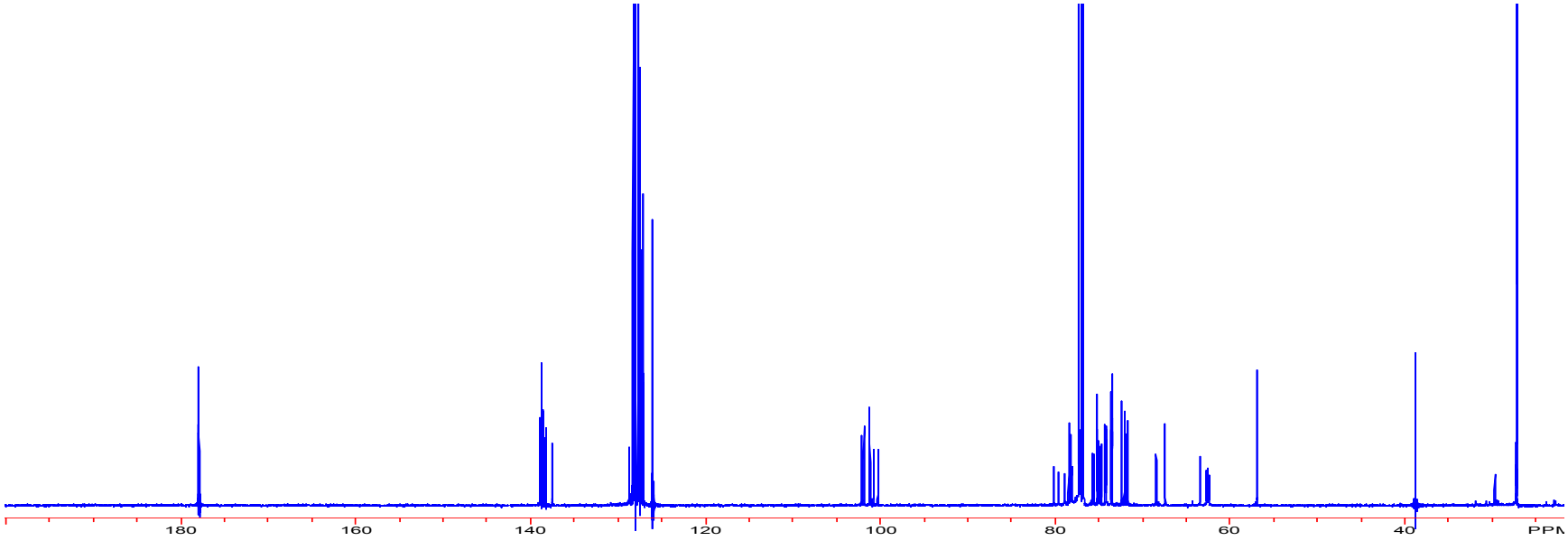
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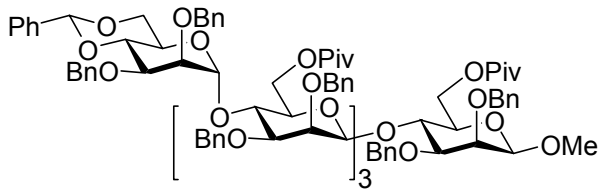
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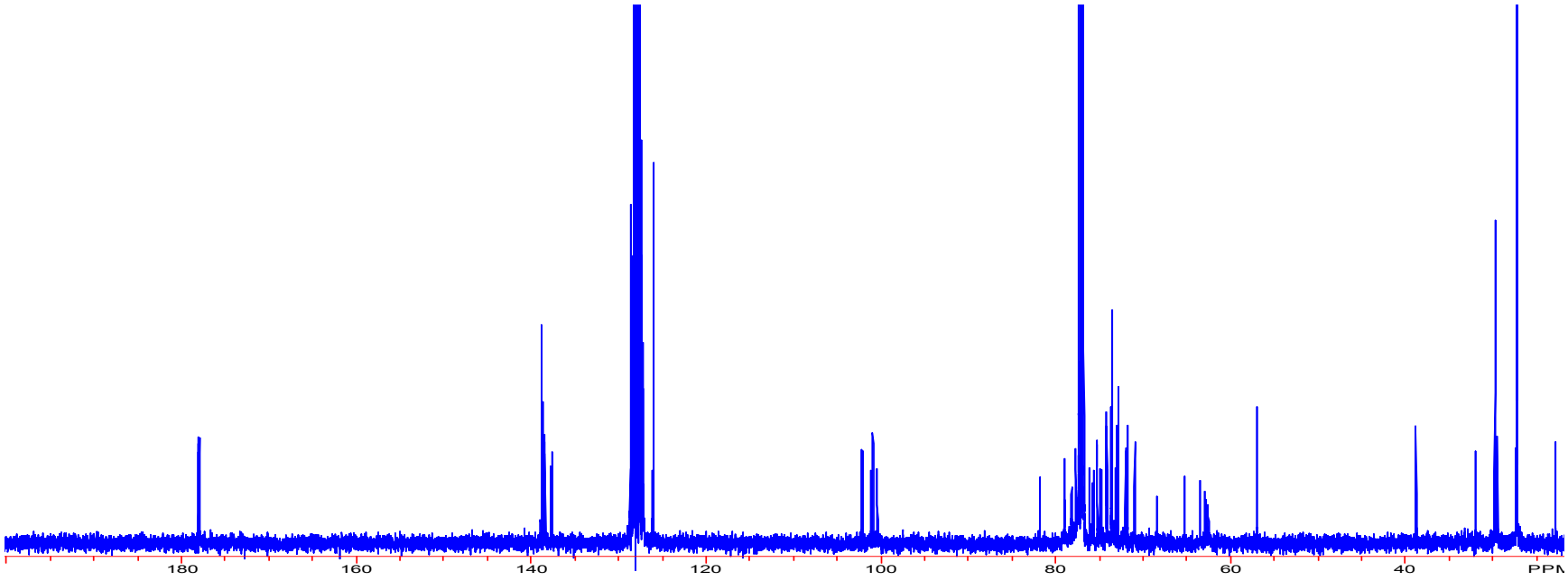
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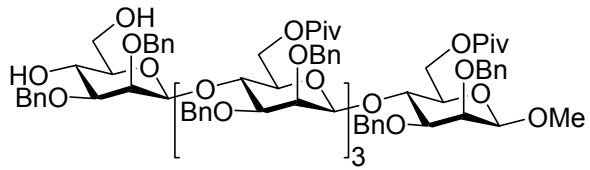
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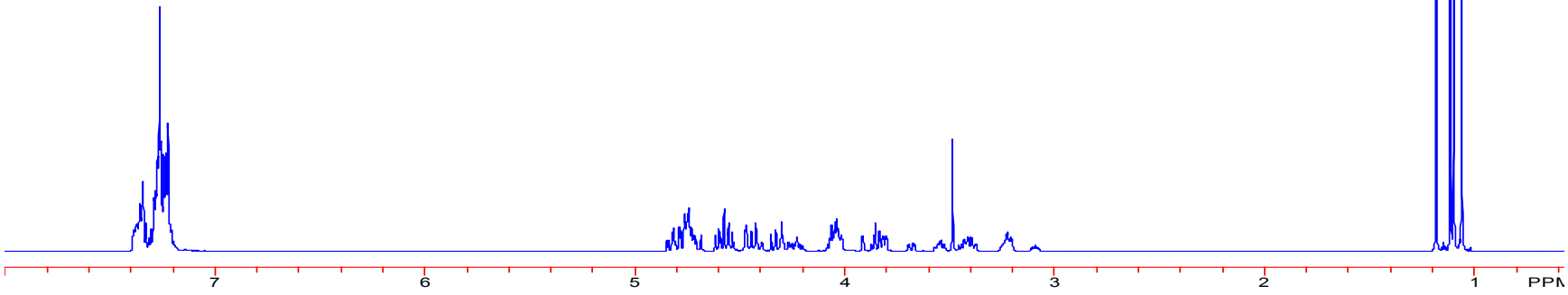
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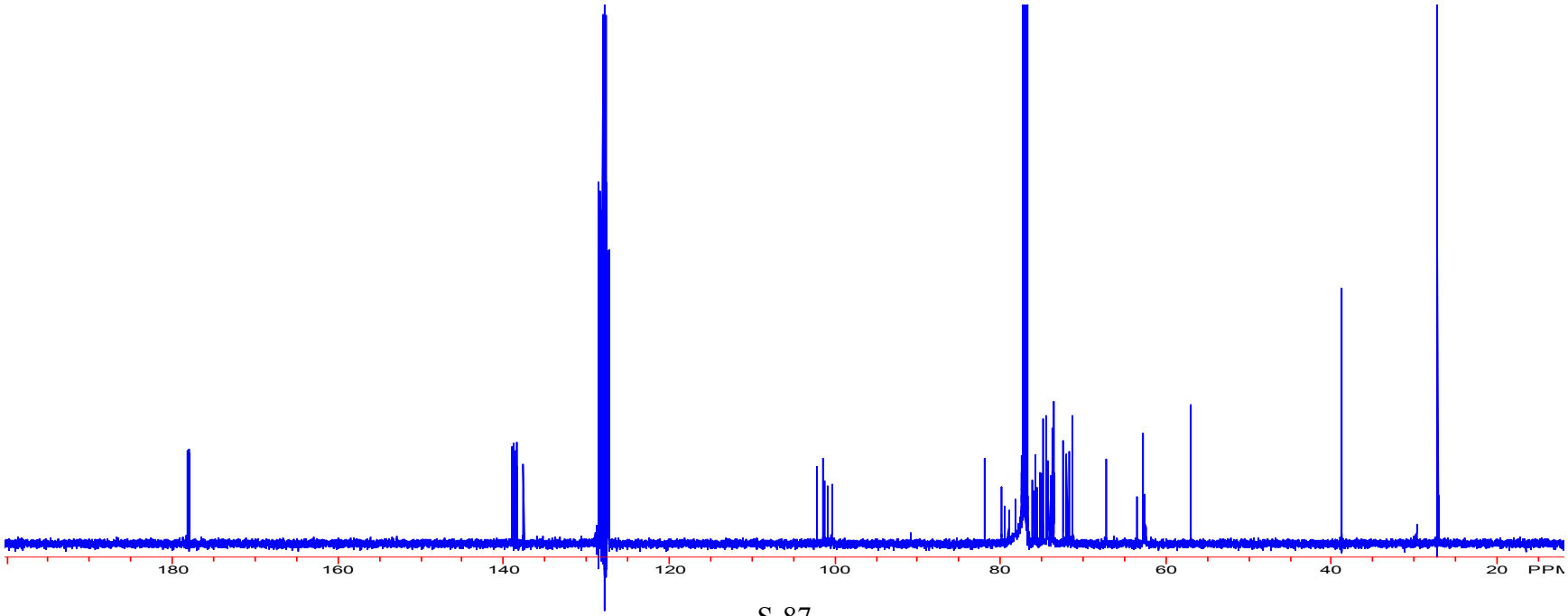
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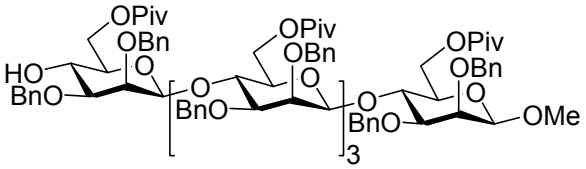
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52

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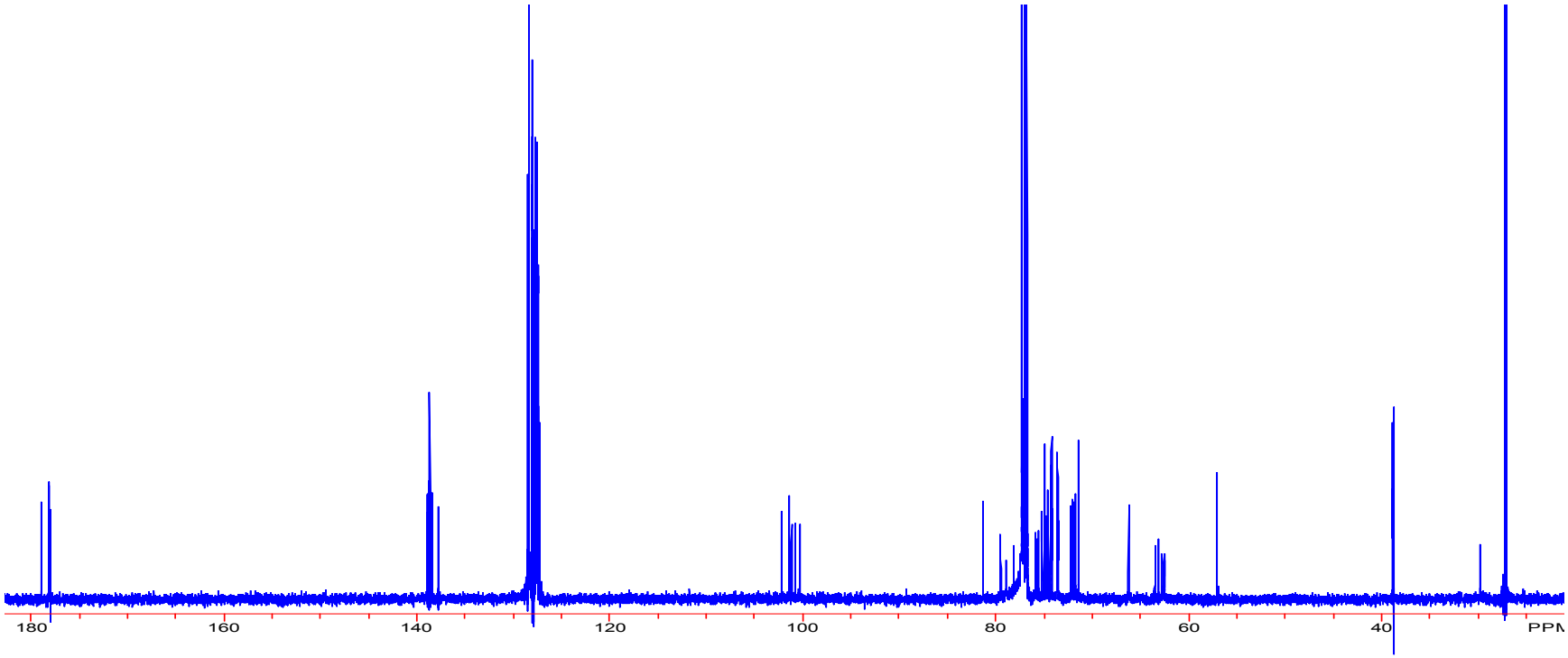
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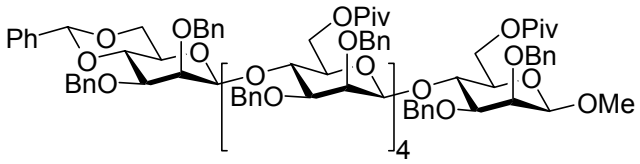
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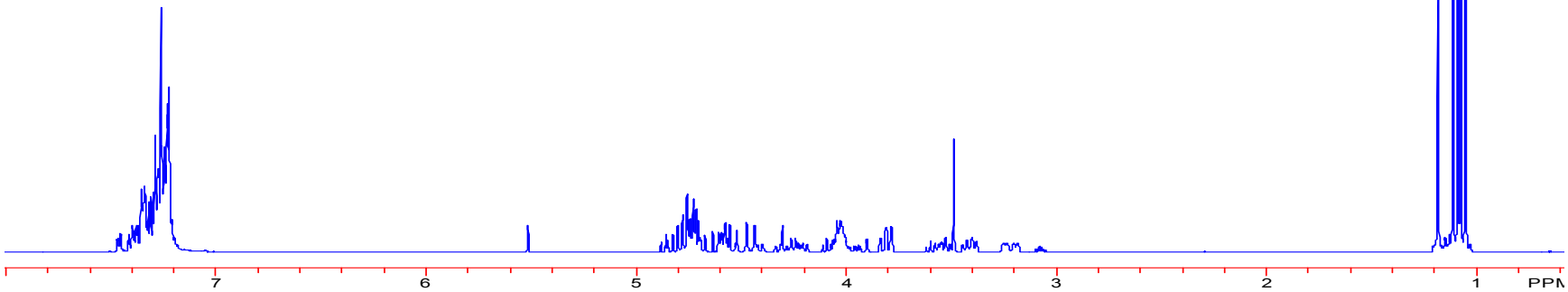
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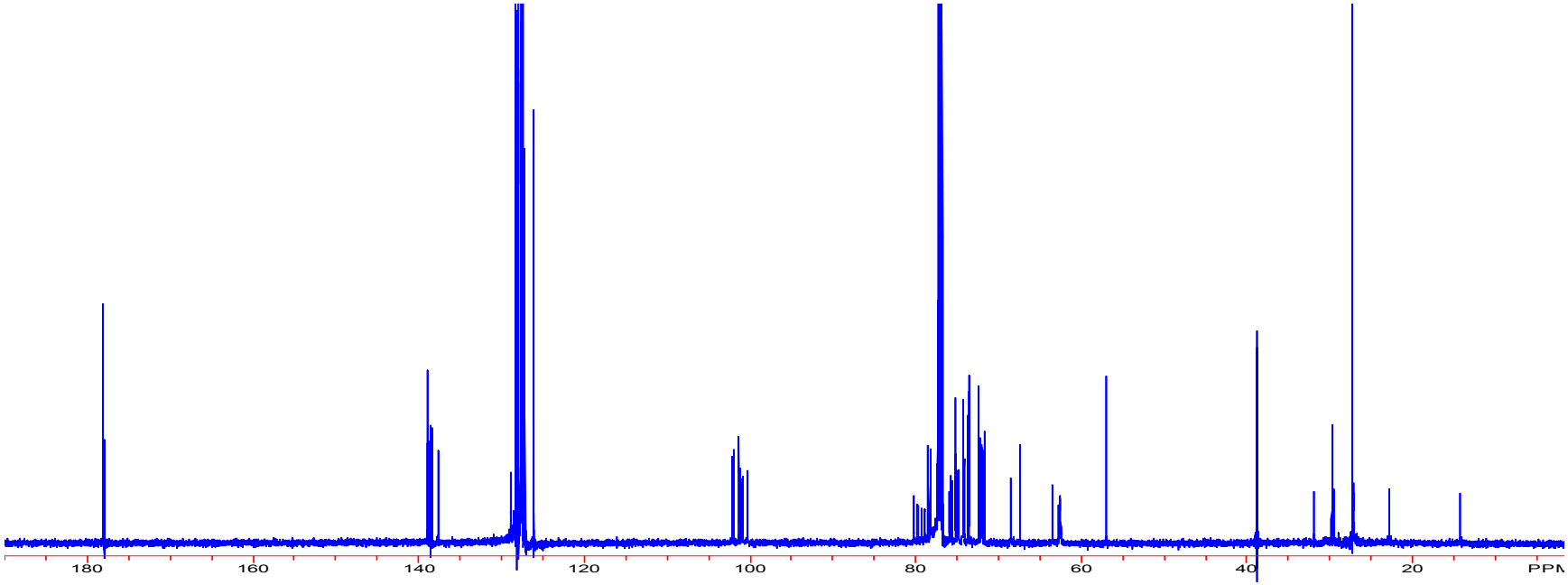
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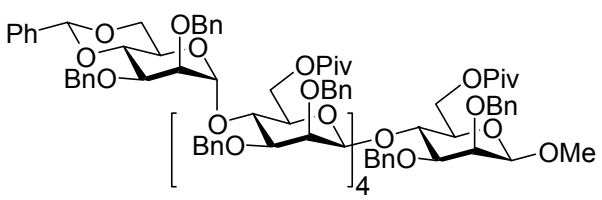
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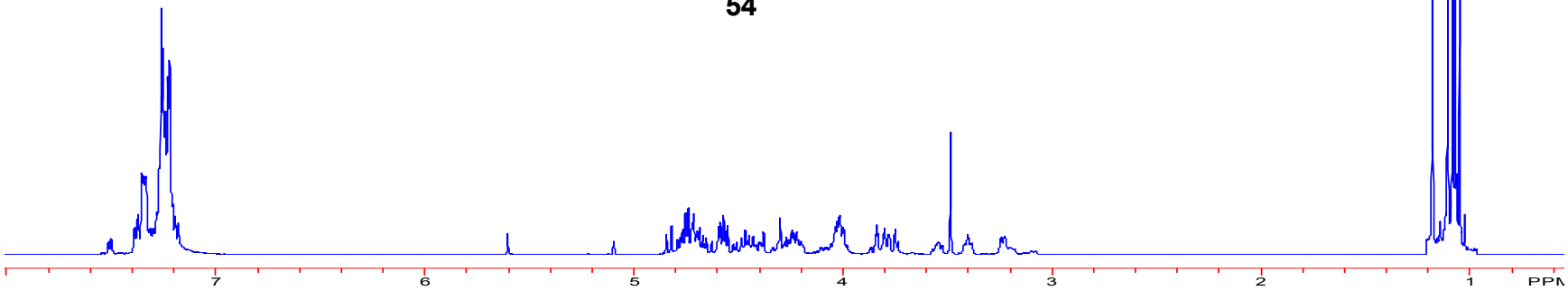
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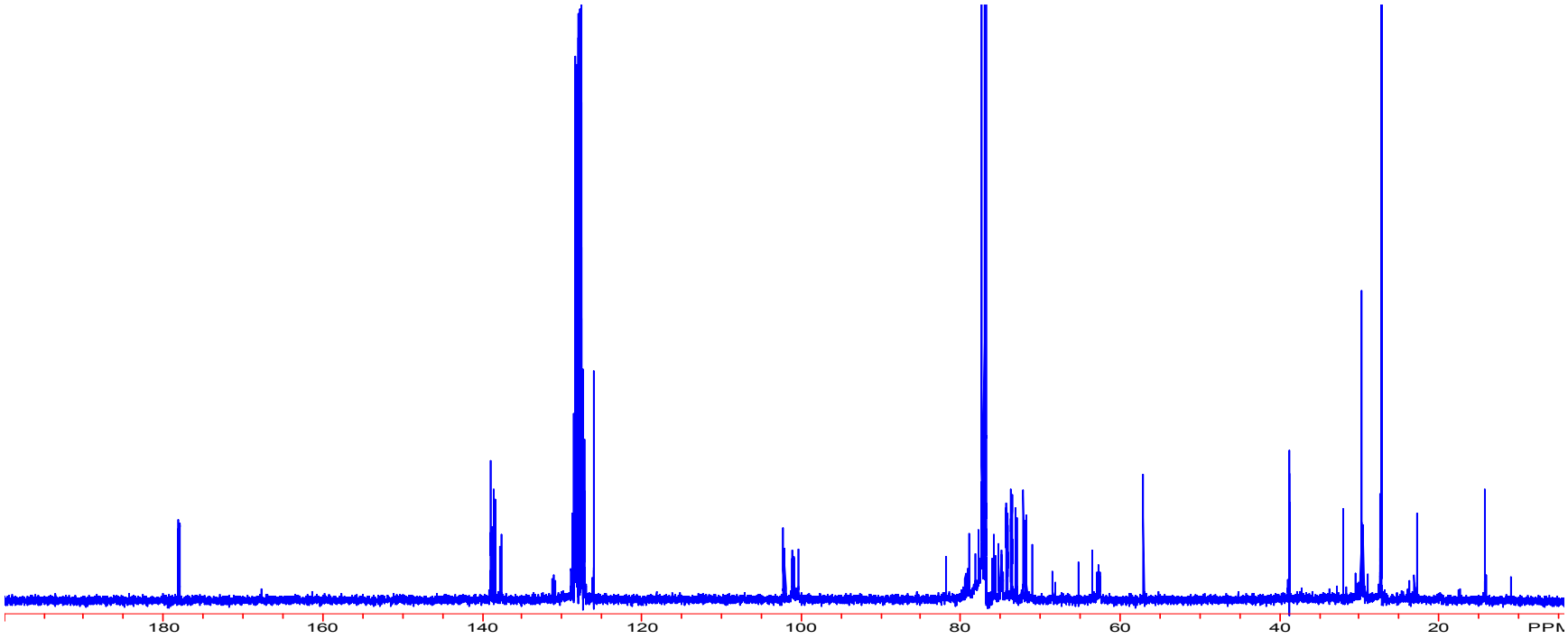
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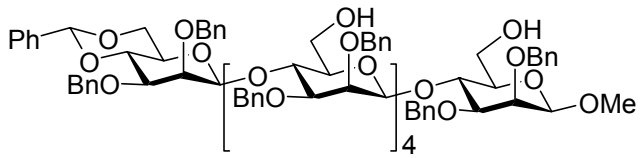
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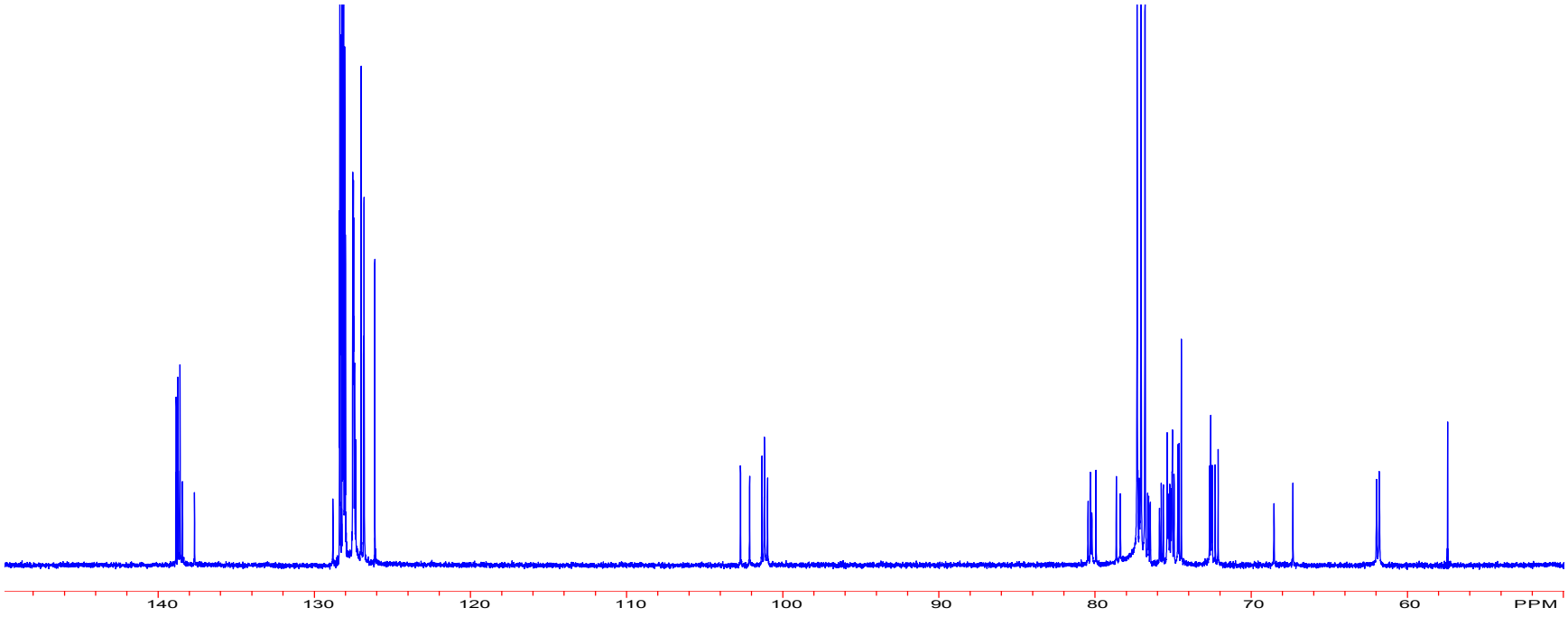
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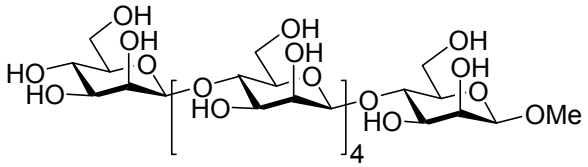
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56

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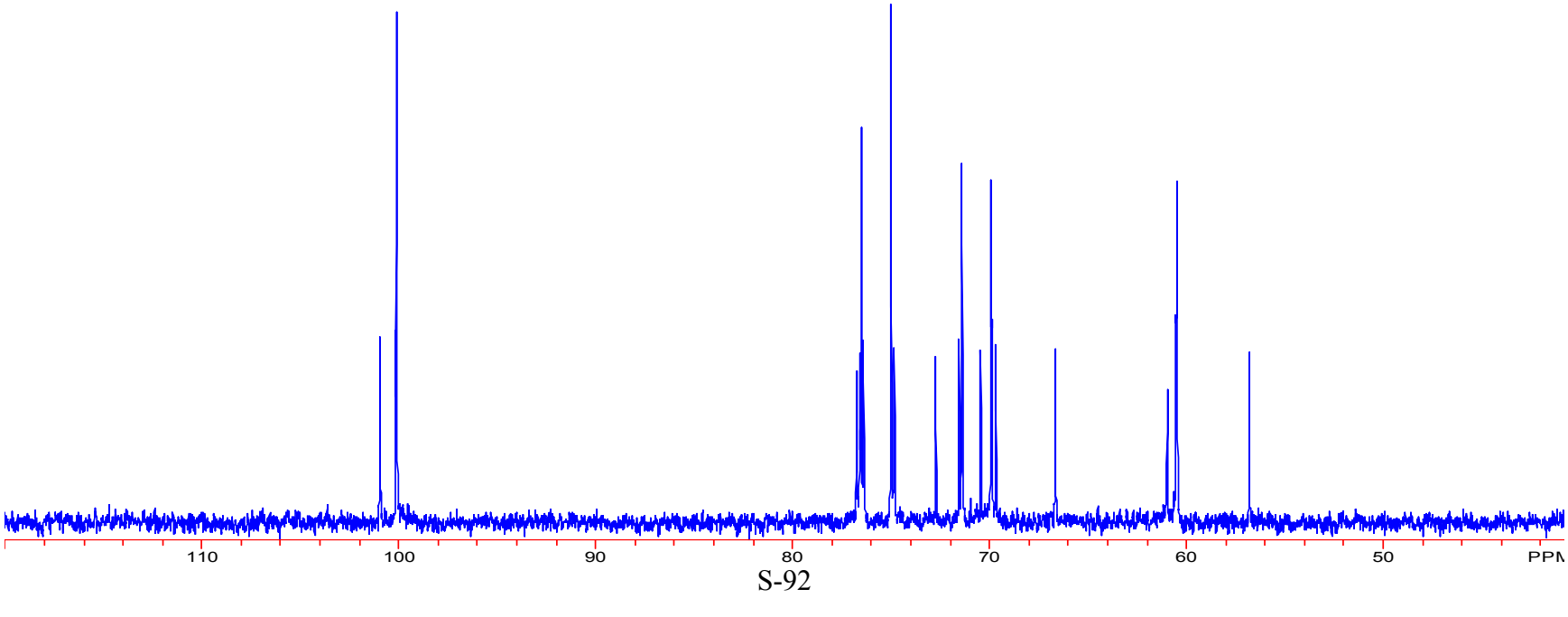
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