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

Solvent-free, under air selective synthesis of α-glycosides adopting glycosyl chlorides as the donors

Serena Traboni,* Giulia Vessella, Emiliano Bedini, and Alfonso Iadonisi*

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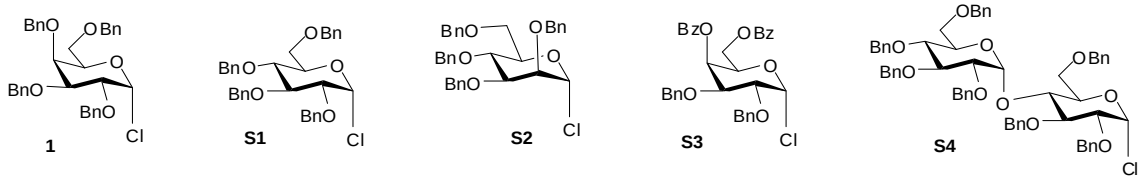
Structure and synthesis of glycosyl chlorides used in glycosylation experiments



Glycosyl chlorides **1**, **S1** and **S2** were synthesized according to literature.[1]

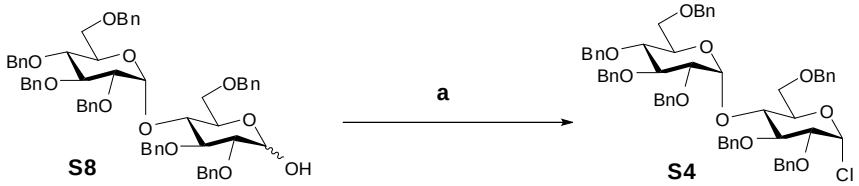
Synthesis of chloride S3

Scheme S1. Synthesis of chloride **S3**. Reagents and conditions: a) BzCl, pyridine, rt, 2.5 h, quantitative; b) $PdCl_2$, MeOH/DCM, rt, overnight, 94%; c) PPh_3, hexachloroacetone, solvent-free, 70°C, 1h, 90%.

Compound S7: To a suspension of **S5**[2] (122 mg, 0.305 mmol) in pyridine (123 μL,1.52 mmol) was added benzoyl chloride (89 μL, 0.76 mmol). The reaction was stirred at room temperature for 2.5 h and then quenched by addition of MeOH. The mixture was then diluted with DCM and washed with water. The organic phase was dried over anhydrous Na_2SO_4 and concentrated under vacuum yielding crude product **S6** in quantitative yield (established by NMR analysis), which was submitted to the following reaction step without any chromatographic purification. To this aim, $PdCl_2$ (5.5 mg, 0.0305 mmol) was added to a solution of crude compound **S6** in MeOH / CH_2Cl_2 (4:1 v/v, 2.5 mL) and the reaction was kept under stirring overnight at room temperature. The crude mixture was concentrated under vacuum and then submitted to silica-gel chromatography to afford pure compound **S7 (**163 mg, 94%, α/β 1.7:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 – 7.27 (aromatic H), 5.95 (1H, bd, J = 2.5 Hz, H-4 α), 5.89 (1H, bd, J = 2.2 Hz, H-4 β), 5.41 (1H, d, J = 3.5 Hz, H-1α), 4.97 – 4.53 (m, overlapped, 2xAB = 2x -CH_2Ph α, 2xAB = 2x -CH_2Ph β, H-1 β, H-5 α, H-5 β, H-6a α, H-6a β), 4.42 (1H, dd, J = 6.0 Hz and 11.4 Hz, H-6b β), 4.37 (1H, dd, J = 5.8 Hz and 11.0 Hz, H-6b α), 4.17 (1H, dd, J = 3.1 Hz and 9.8 Hz, H-3α), 3.98 (1H, dd, J = 3.5 Hz and 9.8 Hz, H-2α), 3.78 – 3.74 (2H, m, overlapped, H-2β and H-3β). ^{13}C NMR (100 MHz, $CDCl_3$): δ= 166.2, 165.8, 137.9, 133.2, 129.8 – 127.6, 97.4 (C-1β), 92.1 (C-1α), 79.8, 79.2, 75.8, 75.3, 73.6, 72.0, 71.8, 71.1, 68.4, 67.4, 66.9, 62.9. MALDI HRMS *m/z* [M+Na]$^+$ Calcd for ([$C_{34}H_{32}O_8$+Na]$^+$) 591.2097; found 591.2099; Anal. Calcd for $C_{34}H_{32}O_8$: C, 71.82; H, 5.67. Found C, 71.80; H, 5.64.

Compound S3: according to the above cited chlorination procedure,[1] hemiacetal **S7** (148 mg, 0.26 mmol) was weighted in a round-bottom flask and then PPh_3(102 mg, 0.39 mmol) and hexachloroacetone (59 μL, 0.39 mmol) were sequentially added. The flask was placed in a oil bath at 70°C and kept under stirring until completion of the reaction (1h, estimated by TLC analysis). The mixture was then cooled to room temperature and then directly submitted to silica-gel chromatography to isolate pure chloride **S3** (138 mg, 90%).^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06 – 7.26 (aromatic H), 6.22 (1H, d, J = 3.5 Hz, H-1), 5.97 (1H, bd, J = 2.9 Hz, H-4), 4.89 – 4.65 (4H, 2xAB = 2x -CH_2Ph), 4.69 (1H, bt, J = 6.5 Hz, H-5), 4.53 (1H, dd, J = 7.0 Hz and 11.7 Hz, H-6a), 4.39 (1H, dd, J = 5.7 Hz and 11.7 Hz, H-6b), 4.19 (1H, dd, J = 2.9 Hz and 9.9 Hz, H-3), 4.14 (1H, dd, J = 3.6 Hz and 9.9 Hz, H-2). ^{13}C NMR (100 MHz, $CDCl_3$): δ= 165.9 and 165.4 (C=O), 137.6 and 137.5 (2xaromatic C = 2x*Ph*CH_2), 133.3 and 133.2 (2x aromatic C = 2x *Ph*-C=O), 129.8 – 127.6 (aromatic CH), 93.9 (C-1), 75.6, 74.7, 73.3, 72.2, 70.1, 67.7, 62.3. MALDI HRMS *m/z* [M+Na]$^+$ Calcd for ([$C_{34}H_{31}ClO_7$+Na]$^+$) 609.1758; found 609.1755; Anal. Calcd for $C_{34}H_{31}ClO_7$: C, 69.56; H, 5.32. Found C, 69.52; H, 5.33.

Synthesis of chloride S4

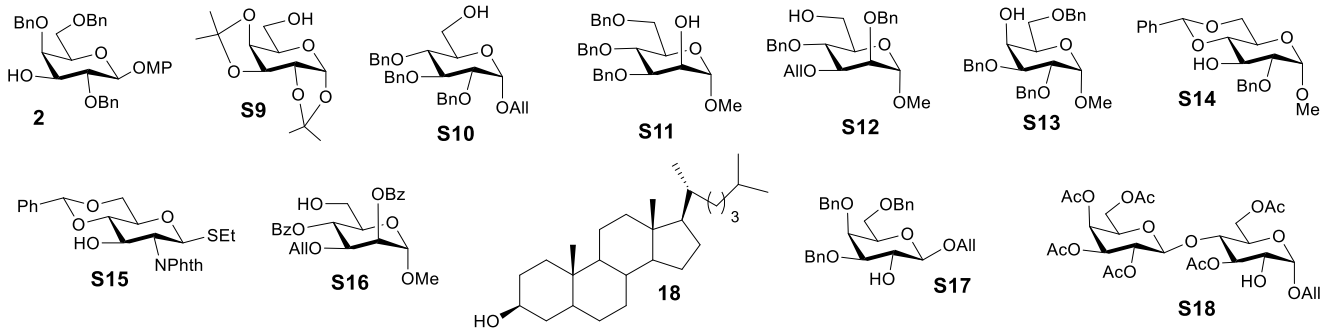


Scheme S2. Synthesis of chloride **S4**. Reagents and conditions: a) PPh_3, hexachloroacetone, solvent-free, 70°C, 45 min, 77%.

Compound S4: according to the above cited chlorination procedure,[1] hemiacetal **S8**[3] (150 mg, 0.154 mmol) was weighted in a round-bottom flask and then PPh_3 (60.7 mg, 0.23 mmol) and hexachloroacetone (35.1 μL, 0.23 mmol) were sequentially added.

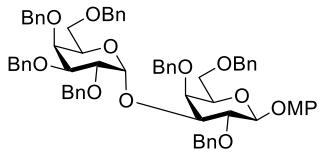
The flask was placed in a oil bath at 70°C and kept under stirring until completion of the reaction (45 min, estimated by TLC analysis). The mixture was then cooled to room temperature and then directly submitted to silica-gel chromatography to isolate pure chloride **S4** (118 mg, 77%).^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36 – 7.17 (aromatic H), 6.15 (1H, d, J = 3.8 Hz, H-1), 5.74 (1H, d, J = 3.8 Hz, H-1'), 5.09 – 4.35 (14H, 7xAB = 7x -CH_2Ph), 4.24 – 4.19 (3H, m, overlapped signals), 4.01 (1H, t, 9.6 Hz), 3.99 (1H, dd, J = 2.7 Hz and 11.4 Hz), 3.85 – 3.82 (2H, m, overlapped signals), 3.77 – 3.70 (2H, m, overlapped signals), 3.62 – 3.58 (2H, m, overlapped signals), 3.48 (1H, bd, J = 10.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ= 138.6 – 137.2 (aromatic C), 128.5 – 126.7 (aromatic CH), 96.9, 93.2 (C-1 and C-1'), 81.9, 81.2, 80.0, 79.4, 77.6, 75.5, 74.9, 74.6, 73.4, 73.3, 73.2, 73.1, 72.9, 71.6, 71.1, 68.1 (x2). MALDI HRMS *m/z* [M+Na]$^+$ Calcd for ([$C_{61}H_{63}ClO_{10}$+Na]$^+$) 1013.4110; found 1013.4114; Anal. Calcd for $C_{61}H_{63}ClO_{10}$: C, 73.89; H, 6.40. Found C, 73.86; H, 6.43.

Structure and synthesis of glycosyl acceptors used in glycosylation experiments

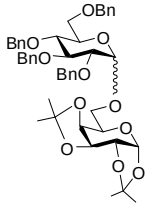


Glycosyl acceptors **2**,[4] **S9** ,[5] **S10,**[6] **S11,**[7] **S12,**[8] **S13,**[9] **S14,**[10] **S15,**[11] **S16,**[12] **S17,**[13] **S18,**[14] were synthesized according to literature (see pertinent references below). Cholestanol **18** is commercially available.

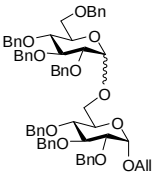
Spectral data of the obtained glycosides



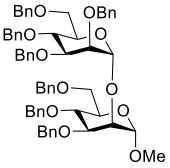
Compound 3[15] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42-7.24 (benzyl aromatic protons), 7.00 (2H, J = 9.0 Hz, aryl aromatic H), 6.80 (2H, J = 9.0 Hz, aryl aromatic protons), 5.26 (1H, d, J = 3.2 Hz, H-1´), 5.11-4.29 (14H, 7 x AB, 7 x –CH_2Ph),4.81 (1H, d, J = 7.6 Hz, H-1), 4.33 (1H, bt, J = 6.0 Hz, H-5´), 4.18 (1H, dd, J = 2.8 and 9.6 Hz, H-2´), 4.09 (1H, dd, J = 7.6 and 9.6 Hz, H-2), 4.01 (1H, bd, J = 9.9 Hz, H-3´), 3.96 (1H, bs, H-4 or H-4´), 3.87 (1H, bd, J = 9.9 Hz, H-3), 3.78 (3H, s, -OCH_3), 3.74 (1H, bs, H-4 or H-4´), 3.63-3.30 (5H, overlapped, H-5, H_2-6 and H_2-6´). ^{13}C NMR (100 MHz, $CDCl_3$): δ= 155.0 and 151.6 (methoxyphenyl C-ipso), 138.6-138.3 (benzyl aromatic C), 128.1-127.4 (benzyl aromatic CH), 118.2, 114.3 (methoxyphenyl aromatic CH), 103.2 (C-1), 95.6 (C-1´), 79.0, 78.0, 76.3, 75.2, 74.9, 74.6, 74.3, 73.6, 73.3, 72.7, 72.4, 69.0, 55.5. MALDI HRMS *m/z* [M+Na]$^+$ Calcd for ([$C_{68}H_{70}O_{12}$+Na]$^+$) 1101.4867; found 1101.4869; Anal. Calcd for $C_{68}H_{70}O_{12}$: C, 75.67; H, 6.54. Found C, 75.69; H, 6.51.



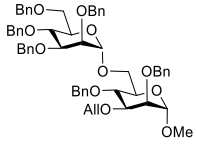
Compound 6[15] Yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39-7.14 (aromatic H), 5.52 (1H, d, J = 5.0 Hz, H-1), 5.01-4.46 (8H, 4xAB, 4xCH_2Ph), 5.01 (1H, d, J = 3.5 Hz, H-1'), 4.60 (1H, m, H-3), 4.37 (1H, dd, J = 8.0 Hz and 1.8 Hz, H-4), 4.32 (1H, dd, J = 5.0 Hz and 2.4 Hz, H-2), 4.06 (1H, t, H-5), 4.00 (1H, t, J = 9.2 Hz, H-3'), 3.86-3.65 (6H), 3.60 (1H, dd, J = 9.5 Hz and 3.6 Hz, H-2'), 1.55, 1.47, 1.34 and 1.33 (12H, 4xs, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ= 138.8, 138.2(x2) and 137.8 (aromatic C), 128.2 – 127.8 (aromatic CH), 109.1 and 108.5 (-*C*(CH_3)$_2$), 96.9 and 96.2 (C-1 and C-1'), 81.9, 79.7, 75.5, 74.9, 73.4, 72.2, 70.5(x4), 70.1, 68.2, 66.1, 65.6, 25.9,(x2), 24.8 and 24.5 (-C(*C*H_3)$_2$). MALDI HRMS *m/z* [M+Na]$^+$ Calcd for ([$C_{46}H_{54}O_{11}$+Na]$^+$) 805.3666; found 805.3669; Anal. Calcd for $C_{46}H_{54}O_{11}$: C, 70.57; H, 6.95. Found C, 70.55; H, 6.91.



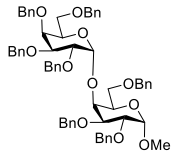
Compound 7[16] Colorless oil;^{1}H NMR (400 MHz, $CDCl_3$): δ = . 7.34 – 7.12 (aromatic H), 5.92 (1H, m, -C*H*=CH_2), 5.32 (1H, bd, J = 17.2 Hz, -CH=$CH_{cis}H_{trans}$), 5.18 (1H, bd, J = 10.2 Hz, -CH=C$H_{cis}H_{trans}$), 5.00 – 4.41 (14H, 7xAB, 7xCH_2Ph), 4.97 (1H, d, J = 3.3 Hz, H-1'), 4.76 (1H, d, J = 3.4 Hz, H-1), 4.18 (1H, m, CH_2=CH-CH_aH_b), 4.05 – 3.95 (3H, overlapped signals, CH_2=CH-CH_aH_b, H-3 and H-3'), 3.88 – 3.63 (7H, overlapped signals, H-5, H-5', H-6a, H-6a', H-6b, H-6b'and H-4'), 3.58 – 3.53 (2H, overlapped signals, H-2 and H-4), 3.46 (1H, dd, J = 9.6 Hz and 3.5 Hz, H-2'). ^{13}C NMR (100 MHz, $CDCl_3$): δ= 138.7 – 137.9 (aromatic C), 133.6 (CH_2=*C*H-CH_2-), 128.2 – 127.5 (aromatic CH), 118.3 (*C*H_2=CH-CH_2-), 97.1 (C-1'), 95.1 (C-1), 82.0, 81.6, 80.0, 79.8, 77.8, 75.6, 75.4, 74.8 (x3), 73.3, 73.1, 72.3, 70.4, 70.1, 68.3, 67.9 and 65.9 (CH_2=CH-*C*H_2-, C-6 and C-6'). MALDI HRMS *m/z* [M+Na]$^+$ Calcd for ([$C_{61}H_{63}O_{10}$+Na]$^+$) 1035.4762; found 1035.4766; Anal. Calcd for $C_{61}H_{63}O_{10}$: C, 76.63; H, 6.64. Found C, 76.68; H, 6.61.



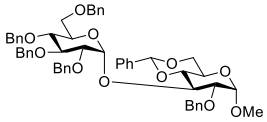
Compound 8[17] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 – 7.18 (aromatic H), 5.20 (1H, d, J = 1.6 Hz, H-1'), 4.89 – 4.84 (2H, 1xAB, CH_2Ph), 4.80 (1H, d, J = 1.5 Hz, H-1), 4.70 – 4.48 (12 H, 6xAB, 6x CH_2Ph), 4.08 (1H, bs, H-2 or H-2'), 3.94-3.89 (4H, m, overlapped signals), 3.83 (1H, bs, H-2 or H-2'), 3.79 – 3.70 (6H,m, overlapped signals), 3.26 (3H, s, -OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ= 138.5 - 138.3 (aromatic C), 128.1-127.3 (aromatic CH), 99.8 and 99.4 (C-1 and C-1'), 79.9, 79.6, 74.9(x5), 74.1, 73.2(x2), 72.3, 72.1(x3), 71.6, 69.4 and 69.3(C-6 and C-6'), 54.6 (-OCH_3). MALDI HRMS *m/z* [M+Na]$^+$ Calcd for ([$C_{62}H_{66}O_{11}$+Na]$^+$) 1009.4605; found 1009.4610; Anal. Calcd for $C_{62}H_{66}O_{11}$: C, 75.43; H, 6.74. Found C, 75.49; H, 6.76.



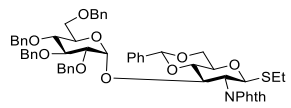
Compound 9 Yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 – 7.17 (aromatic H), 5.96 (1H, m, -C*H*=CH_2), 5.35 (1H, bd, J = 17.2 Hz, -CH=$CH_{cis}H_{trans}$), 5.20 (1H, bd, J = 10.4 Hz, -CH=C$H_{cis}H_{trans}$), 5.14 (1H, bs, H-1'), 4.93 – 4.48 (13 H, 6xAB = 6x CH_2Ph and H-1), 4.11 (2H, m, CH_2=CH-CH_aH_b and CH_2=CH-CH_aH_b), 4.04 (1H, t, J = 10.0 Hz, H-4 or H-4'), 3.95 – 3.72 (9 H, m, overlapped signals, H-2, H-2', H-3, H-3', H-4 or H-4', H-6a, H-6a', H-6b, H-6b'), 3.68 – 3.63 (2H, m, overlapped signals, H-5 and H-5'), 3.26 (3H, s, -OCH_3).^{13}C NMR (100 MHz, $CDCl_3$): δ= 138.6 – 138.3 (aromatic C), 134.8 (CH_2=*C*H-CH_2-), 128.2 – 127.3 (aromatic CH), 116.5 (*C*H_2=CH-CH_2-), 98.9 and 97.9 (C-1 and C-1'), 79.9, 79.3, 74.9(x5), 74.4, 73.1, 72.7, 72.3, 71.7, 71.4, 71.3, 70.9, 69.1, 65.9, 54.5 (-OCH_3). MALDI HRMS *m/z* [M+Na]$^+$ Calcd for ([$C_{58}H_{64}O_{11}$+Na]$^+$) 959.4449; found 959.4451; Anal. Calcd for $C_{58}H_{64}O_{11}$: C, 74.34; H, 6.88. Found C, 74.29; H, 6.90.



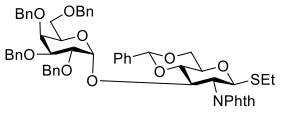
Compound 10[9] Yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 – 7.16 (aromatic H), 5.00 (1H, d, J = 3.4 Hz, H-1'), 4.73 (1H, d, J = 3.2 Hz, H-1), 4.91 – 4.53 (14H, 7xAB = 7x CH_2Ph), 4.41 (1H, bdd, J = 4.1 Hz and 9.7 Hz), 4.23 (1H, bs), 4.11 (2H, bs), 4.07 (1H, bd, J = 9.0 Hz), 3.94 – 3.81 (4H, m), 3.57 – 3.48 (2H, m), 3.36 (3H, s, -OCH_3), 3.22 (1H, dd, J = 4.6 Hz and 8.2 Hz).^{13}C NMR (100 MHz, $CDCl_3$): δ= 138.8 – 138.0 (aromatic C), 128.1 – 127.4 (aromatic CH), 100.2 and 98.7 (C-1 and C-1'), 79.4, 77.9, 76.2, 74.9, 74.8, 74.5, 74.0, 73.2(x2), 73.1, 72.8, 72.5, 72.1, 69.4, 69.1, 68.0, 67.7, 55.2. MALDI HRMS *m/z* [M+Na]$^+$ Calcd for ([$C_{62}H_{66}O_{11}$+Na]$^+$) 1009.4605; found 1009.4608; Anal. Calcd for $C_{62}H_{66}O_{11}$: C, 75.43; H, 6.74. Found C, 75.46; H, 6.68.



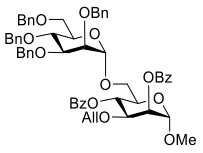
Compound 11[18] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42-6.94 (aromatic H), 5.61 (1H, d, J = 3.6 Hz, H-1'), 5.48 (1H, s, benzylidene -CHPh), 5.03 – 4.33 (11H, 5xAB = 5xCH_2Ph and H-1), 4.28 – 4.21 (2H, m, overlapped signals, H-6eq and H-5'), 4.00 (1H, t, J = 9.3 Hz, H-3), 3.89 (1H, m, H-5), 3.80 (1H, bt, J = 9.3 Hz, H-6ax), 3.73 (1H, t, J = 10.0 Hz, H-3'), 3.70 – 3.65 (2H, m, overlapped signals, H-2 and H-4'), 3.50 – 3.47 (4H, overlapped signals, H_2-6', H-4 and H-2'), 3.43 (3H, s, -OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ= 138.8(x2), 137.9, 137.7, 137.3 and 136.9 (aromatic C), 129.3-126.3 (aromatic CH), 102.0, 98.4 and 96.0 (acetal CH), 82.8, 81.6, 78.7, 77.9, 75.4, 74.7, 73.3 (x3), 72.6, 71.0, 69.7, 69.1, 68.0, 61.7, 55.2. MALDI HRMS *m/z* [M+Na]$^+$ Calcd for ([$C_{55}H_{58}O_{11}$+Na]$^+$) 917.3979; found 917.3982; Anal. Calcd for $C_{55}H_{58}O_{11}$: C, 73.81; H, 6.53. Found C, 73.83; H, 6.51.



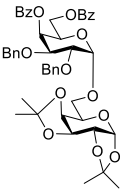
Compound 12 Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 – 6.81 (aromatic H), 5.59 (1H, d, J = 3.5 Hz, H-1'), 5.48 (1H, d, J = 10.5 Hz, H-1), 5.44 (1H, s, benzylidene -C*H*Ph), 4.92 – 4.11 (11H, overlapped signals), 3.94 (1H, m), 3.81 – 3.78 (2H, m, overlapped signals), 3.70 (1H, t, J = 9.5 Hz), 3.41 (1H, t, J = 9.9 Hz), 3.34 (1H, dd, J = 3.3 Hz and 9.5 Hz, H-2'), 3.01 – 2.93 (2H, m), 2.75 – 2.63 (3H, m), 1.21 (3H, t, J = 7.4 Hz, -SCH_2CH_3).^{13}C NMR (100 MHz, $CDCl_3$): δ= 167.9 and 167.6 (C=O), 138.8 – 122.8 (aromatic signals), 101.8 (PhCH), 96.3 (C-1'), 83.0 (C-1), 81.6, 80.8, 78.4, 75.4, 73.9, 73.3(x2), 72.6, 71.2, 70.6, 70.0, 68.7, 67.1, 53.9(C-2), 23.8 (-SCH_2CH_3), 14.7 (-SCH_2CH_3). MALDI HRMS *m/z* [M+Na]$^+$ Calcd for ([$C_{57}H_{57}NO_{11}S$+Na]$^+$) 986.3652; found 986.3656; Anal. Calcd for $C_{57}H_{57}NO_{11}S$: C, 71.01; H, 5.96. Found C, 71.04; H, 5.91.



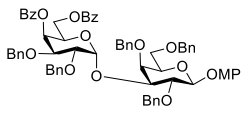
Compound 13[19] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 – 6.99 (aromatic H), 5.59 (1H, d, J = 3.7 Hz, H-1'), 5.43 (1H, d, J = 10.7 Hz, H-1), 5.40 (1H, s, benzylidene -C*H*Ph), 4.92 (1H, t, J = 9.7 Hz), 4.86 – 4.25 (8H, 4xAB = 4xCH_2Ph), 3.93 – 3.88 (4H, m, overlapped signals), 3.80 – 3.76 (3H, m, overlapped signals), 3.66 (1H, bs, H-4'), 4.41 (1H, m), 3.29 (1H, t, J = 9.0 Hz), 2.87 (1H, m), 2.76 – 2.64 (2H, m, -SC*H*$_2$CH$_3$), 1.19 (3H, t, J = 7.4 Hz, -SCH$_2$C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ= 167.9 and 167.6 (C=O), 138.9 – 122.9 (aromatic signals), 101.6 (Ph*C*H), 97.3 (C-1'), 82.9 (C-1), 81.6, 77.9, 75.3, 74.7(x2), 73.2(x2), 72.7, 71.6, 70.0, 69.3, 68.9, 67.7, 54.1(C-2), 23.9 (-S*C*H$_2$CH$_3$), 14.8(-SCH$_2$*C*H$_3$). MALDI HRMS *m/z* [M+Na]$^+$ Calcd for ([$C_{57}H_{57}NO_{11}S$+Na]$^+$) 986.3652; found 986.3655; Anal. Calcd for $C_{57}H_{57}NO_{11}S$: C, 71.01; H, 5.96. Found C, 71.02; H, 5.90.



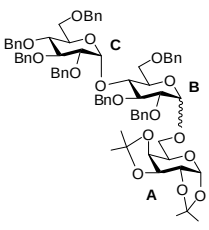
Compound 14 Yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10 – 7.14 (aromatic H), 5.71 – 5.61 (2H, m, overlapped signals, -C*H*=CH$_2$ and H-4), 5.52 (1H, dd, J = 1.8 and 3.2 Hz, H-2), 5.15 (1H, bd, J = 17.2 Hz, -CH=CH$_{cis}$*H*$_{trans}$), 5.03 (1H, bd, J = 10.4 Hz, -CH=C*H*$_{cis}$H$_{trans}$), 4.94 (1H, bs, H-1'), 4.86 (1H, bs, H-1), 4.85 – 4.30 (8H, 4xAB = 4x -CH_2Ph), 4.11 – 4.06 (3H, m, overlapped signals, CH$_2$=CH-C*H*$_a$*H*$_b$ and H-3), 4.03 – 3.89 (5H, m , overlapped signals, H2', H-4', H-5, H-6a and H-6b), 3.84 (1H, dd, J = 3.2 Hz and 9.7 Hz, H-3'), 3.75 – 3.68 (4H, m, overlapped signals, H-5', H-6a' and H-6b'), 3.38 (3H, s, -OCH$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ= 165.7 and 165.2 (2xC=O), 138.5, 138.4, 138.3 and 138.2 (4xaromatic C = 4x*Ph*CH$_2$), 134.2 (CH$_2$=*C*H-CH$_2$-), 133.2 and 133.0 (2x aromatic C = 2x *Ph*-C=O), 129.9 – 127.2 (aromatic CH), 117.3 (*C*H$_2$=CH-CH$_2$-), 98.7 and 97.8 (C-1 and C-1'), 80.1, 74.9, 74.6(x2), 74.3, 73.1, 72.3, 71.8, 71.7, 70.7, 69.5, 69.3, 68.9(x2), 66.9, 55.1 (-OCH$_3$). MALDI HRMS *m/z* [M+Na]$^+$ Calcd for ([$C_{58}H_{60}O_{13}$+Na]$^+$) 987.4034; found 987.4039; Anal. Calcd for $C_{58}H_{60}O_{13}$: C, 72.18; H, 6.27. Found C, 72.13; H, 6.21.



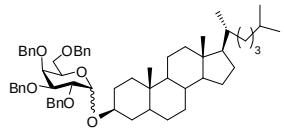
Compound 15 Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 – 7.24 (aromatic H), 5.93 (1H, d, J = 3.2 Hz, H-4'), 5.51 (1H, d, J = 5.0 Hz, H-1), 5.07 (1H, d, J = 3.5 Hz, H-1'), 4.87 – 4.61 (4H, 2xAB = 2x -CH_2Ph), 4.58 (1H, dd, J = 2.3 Hz and 8.0 Hz, H-3), 4.54 – 4.48 (2H, m, overlapped signals, H-6a' and H-6b'), 4.35 – 4.28 (3H, m, overlapped signals, H-2, H-4 and H-5'), 4.16 (1H, dd, J = 3.2 Hz and 9.9 Hz, H-3'), 4.05 (1H, m, H-5), 3.96 (1H, dd, J = 3.5 Hz and 9.9 Hz, H-2'), 3.88 – 3.81 (2H, m, overlapped signals, H-6a and H-6b), 1.51, 1.40, 1.32 and 1.29 (12H, 4xs, -CH$_3$).^{13}C NMR (100 MHz, $CDCl_3$): δ=166.0 and 165.7 (2xC=O), 138.2 and 138.0 (2xaromatic C = 2x*Ph*CH$_2$), 133.0 and 132.9 (2x aromatic C = 2x *Ph*-C=O), 129.6 – 127.3 (aromatic CH), 109.1 and 108.4 (-*C*(CH$_3$)$_2$), 97.9 and 96.2 (C-1 and C-1'), 76.0, 75.1, 73.1, 71.9, 70.9, 70.6, 70.4, 68.6, 67.2, 66.9, 66.5, 63.0, 25.9(x2), 24.8, 24.4 (-C(*C*H$_3$)$_2$). MALDI HRMS *m/z* [M+Na]$^+$ Calcd for ([$C_{46}H_{50}O_{13}$+Na]$^+$) 833.3251; found 833.3256; Anal. Calcd for $C_{46}H_{50}O_{13}$: C, 68.13; H, 6.22. Found C, 68.08; H, 6.21.



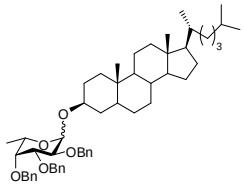
Compound 16 Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 – 6.80 (aromatic H), 5.36 (1H, bs, H-4'), 5.23 (1H, bs, H-1'), 5.14 – 4.24 (14H, overlapped signals, 5x AB = 5x -CH_2Ph, H-1, H-5' and H$_2$-6'), 4.11 (1H, dd, J = 7.6 Hz and 10.0 Hz, H-2), 4.02 (2H, bs), 3.92 – 3.89 (2H, m, overlapped signals), 3.85 (1H, dd, J = 2.4 Hz and 9.9 Hz, H-3), 3.80 (3H, s, -OCH$_3$), 3.61 – 3.55 (2H, m, overlapped signals, H$_2$-6a and H$_2$-6b), 3.50 (1H, bt, J = 6.2 Hz, H-5). ^{13}C NMR (100 MHz, $CDCl_3$): δ= 165.7 and 165.6 (C=O), 155.0 and 151.6 (methoxyphenyl C-ipso), 138.7-137.9 (benzyl aromatic C), 133.0 and 132.8 (benzoyl aromatic C), 129.8 – 127.3 (aromatic CH), 118.2 and 114.4 (methoxyphenyl aromatic CH), 103.6 (C-1), 94.7 (C-1'), 77.9, 75.4, 74.6, 74.4(x4), 73.6, 73.4, 71.7(x2), 71.5, 68.7, 67.2, 63.6, 55.6. MALDI HRMS *m/z* [M+Na]$^+$ Calcd for ([$C_{68}H_{66}O_{14}$+Na]$^+$) 1129.4453; found 1129.4454; Anal. Calcd for $C_{68}H_{66}O_{14}$: C, 73.76; H, 6.01. Found C, 73.70; H, 5.98.



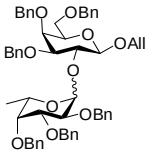
Compound 17 Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 – 7.12 (aromatic H), 5.73 (1H, d, J = 3.4 Hz, H-1 C), 5.55 (1H, d, J = 5.2 Hz, H-1 A), 5.09 – 4.28 (15 H, 7xAB = 7x-CH_2Ph and H-3 A), 5.04 (1H, d, J = 3.4 Hz, H-1 B), 4.40 (1H, dd, J = 1.7 Hz and 8.0 Hz, H-4 A), 4.35 (1H, dd, J = 2.4 Hz and 5.0 Hz, H-2 A), 4.14 – 4.10 (3H, m, overlapped signals), 3.99 – 3.90 (3H, m, overlapped signals), 3.83 – 3.77 (3H, m, overlapped signals), 3.72 – 3.66 (3H, m, overlapped signals), 3.53 (2H, bdd, J = 3.5 Hz and 10.0 Hz, H-2 B and H-2 C), 3.41 (1H, bd, J = 10.6 Hz), 1.60, 1.49, 1.35 and 1.34 (12H, 4xs, CH$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ= 138.9 – 137.9 (aromatic C), 128.2 – 126.7 (aromatic CH), 109.1 and 108.6 (-*C*(CH$_3$)$_2$), 96.5 (x2) and 96.2 (C-1 A, C-1 B and C-1 C), 81.9, 81.7, 79.8, 79.4, 77.6, 75.4, 74.8, 74.1, 73.4, 73.0 (x2), 72.2, 72.1, 70.8 (x2), 70.6 (x2), 69.6, 68.8, 68.1, 66.2, 65.7, 26.1, 26.0, 24.8 and 24.6 (-C(*C*H$_3$)$_2$). MALDI HRMS *m/z* [M+Na]$^+$ Calcd for ([$C_{66}H_{75}O_{15}$+Na]$^+$) 1237.5603; found 1237.5607; Anal. Calcd for $C_{66}H_{75}O_{15}$: C, 71.52; H, 6.82. Found C, 71.56; H, 6.85.



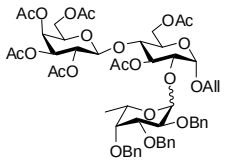
Compound 19[20] Yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 – 7.26 (aromatic H), 5.00 (1H, d, J = 3.7 Hz, H-1), 4.97 – 4.39 (8H, 4xAB = 4x -CH_2Ph), 4.06 (1H, bt, J = 6.5 Hz, cholestanol-H-3), 4.01 (1H, dd, J = 3.6 Hz and 9.6 Hz, H-2), 3.97 – 3.94 (2H, m, overlapped signals, H-4 and H-3), 3.59 – 3.51 (3H, m, overlapped signals, H-5, H-6a and H-6b), 1.99 – 0.56 (m, overlapped signals, cholestanol backbone H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=138.9 – 138.6 (aromatic C), 128.2 – 127.4 (aromatic CH), 95.4 (C-1), 79.1, 76.2, 75.2, 74.6, 73.3, 73.1, 73.0, 69.2, 56.4, 56.2, 54.2, 45.0 – 11.9. MALDI HRMS *m/z* [M+Na]$^+$ Calcd for ([$C_{61}H_{82}O_6$+Na]$^+$) 933.6111; found 933.6117; Anal. Calcd for $C_{61}H_{82}O_6$: C, 80.40; H, 9.07. Found C, 80.37; H, 9.01.



Compound 21[21] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ =7.42 – 7.26 (aromatic H), 5.00 – 4.65 (6H, 3xAB = 3x -CH_2Ph), 4.96 (1H, d, J = 3.7 Hz, H-1), 4.01 (1H, dd, J = 3.7 Hz and 10.0 Hz, H-2), 3.95 (1H, m, H-5), 3.94 (1H, dd, J = 2.8 Hz and 10.0 Hz, H-3), 3.66 (1H, bs, H-4), 3.48 (1H, m, cholestanol-H-3), 1.99 – 0.56 (m, overlapped signals, cholestanol backbone), 1.10, 0.91, 0.88, 0.87 (12H, 4xd, J = 6.50 Hz, 4x -CH_3), 0.81 and 0.66 (6H, 2xs, 2x -CH_3).^{13}C NMR (100 MHz, $CDCl_3$): δ= 139.0 – 138.6 (aromatic C), 128.2 – 127.3 (aromatic CH), 95.3 (C-1), 79.4, 77.8, 76.0, 74.7, 73.2, 72.9, 65.9, 56.4, 56.2, 54.3, 44.7 – 11.9. MALDI HRMS *m/z* [M+Na]$^+$ Calcd for ([$C_{54}H_{76}O_5$+Na]$^+$) 827.5693; found 827.5697; Anal. Calcd for $C_{54}H_{76}O_5$: C, 80.55; H, 9.51. Found C, 80.52; H, 9.49.



Compound 22 Yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 – 7.02 (aromatic H), 5.83 (1H, m, -C*H*=CH_2), 5.67 (1H, d, J = 3.8 Hz, H-1'), 5.21 (1H, bd, J = 17.2 Hz, -CH=CH_{cis}*H*$_{trans}$), 5.09 (1H, bd, J = 10.7 Hz, -CH=C*H*$_{cis}$$H_{trans}$), 4.95 – 4.33 (14 H, m, overlapped signals, 6xAB = 6x -CH_2Ph, H-1 and CH_2=CH-C*H*$_a$$H_b$), 4.24 (1H, dd, J = 7.8 Hz and 9.8 Hz, H-2), 4.03 (1H, dd, J = 3.8 Hz and 10.0 Hz, H-2'), 4.02 (1H, m, -CH_2=CH-CH_a*H*$_b$), 3.95 – 3.92 (2H, m, overlapped signals, H-5' and H-3'), 3.73 (1H, dd, J = 2.4 Hz and 9.9 Hz, H-3), 3.63 – 3.57 (5H, m, overlapped signals, H-4, H-4', H-5, H_2-6), 1.10 (3H, d, J = 6.5 Hz, -CH_3).^{13}C NMR (100 MHz, $CDCl_3$): δ= 138.8 – 137.8 (aromatic C), 134.1 (CH_2=*C*H-CH_2-), 128.2 – 126.2 (aromatic CH), 117.2 (*C*H_2=CH-CH_2-), 101.0 (C-1), 97.1 (C-1'), 84.2, 79.4, 78.0, 75.5, 74.6, 74.2, 73.5, 73.2, 72.8, 72.4, 72.2, 71.8, 71.1, 69.9, 68.7, 66.2, 16.4 (-CH_3). MALDI HRMS *m/z* [M+Na]$^+$ Calcd for ([$C_{57}H_{62}O_{10}$+Na]$^+$) 929.4343; found 929.4345; Anal. Calcd for $C_{57}H_{62}O_{10}$: C, 75.47; H, 6.89. Found C, 75.43; H, 6.91.



Compound 23 Yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 – 7.26 (aromatic H), 5.88 (1H, m, -C*H*=CH_2), 5.49 (1H, t, J = 9.8 Hz, H-3 Glc), 5.33 (1H, d, J = 3.0 Hz, H-4 Gal), 5.29 (1H, bd, J = 17.0 Hz, -CH=CH_{cis}*H*$_{trans}$), 5.17 (1H, bd, J = 10.7 Hz, -CH=C*H*$_{cis}$$H_{trans}$), 5.12 (1H, dd, J = 8.0 Hz and 10.0 Hz, H-2 Gal), 4.99 – 4.93 (3H, m, overlapped signals, H-1 Fuc, H-1 Glc and H-3 Gal), 4.85 – 4.59 (6H, 3xAB = 3x -CH_2Ph), 4.53 (1H, d, J = 7.8 Hz, H-1 Gal), 4.37 (1H, bd, J = 11.6 Hz, H-6a Glc), 4.16 – 4.03 (6H, m, overlapped signals, CH_2=CH-C*H*$_a$*H*$_b$, H-6b Glc, H_2-6 Gal and H-2 Glc), 3.96 – 3.83 (4H, m, overlapped signals, H-5 Gal, H-5 Glc, H-2 Fuc and H-5 Fuc), 3.72 (1H, t, J = 9.5 Hz, H-4 Glc), 3.59 (1H, bs, H-4 Fuc), 3.46 (1H, dd, J = 3.1 Hz and 10.0 Hz, H-3 Fuc), 2.14, 2.12, 2.04, 2.03, 1.96 and 1.78 (18H, 6xs, 6x -$COCH_3$), 1.03 (3H, d, J = 6.5 Hz, -CH_3 Fuc). ^{13}C NMR (100 MHz, $CDCl_3$): δ= 170.4, 171.1 (x3), 169.5 and 168.9 (C=O), 138.8, 138.6 and 138.5 (aromatic C), 133.3 (CH_2=*C*H-CH_2-), 128.2 – 127.4 (aromatic CH), 117.5 (*C*H_2=CH-CH_2-), 100.7 (x2) and 97.2 (C-1 Gal, C-1 Glc and C-1 Fuc), 79.7, 78.9, 77.8, 76.3, 74.7, 73.3, 73.1, 71.0, 70.3, 70.1, 69.0, 68.9, 67.9, 67.1, 66.4, 62.2, 60.5(x2), 20.5(x6 *C*H_3C=O), 16.6 (-CH_3). MALDI HRMS *m/z* [M+Na]$^+$ Calcd for ([$C_{54}H_{66}O_{21}$+Na]$^+$) 1073.4097; found 1073.4100; Anal. Calcd for $C_{54}H_{66}O_{21}$: C, 61.71; H, 6.33. Found C, 61.74; H, 6.29.

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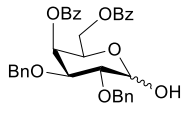
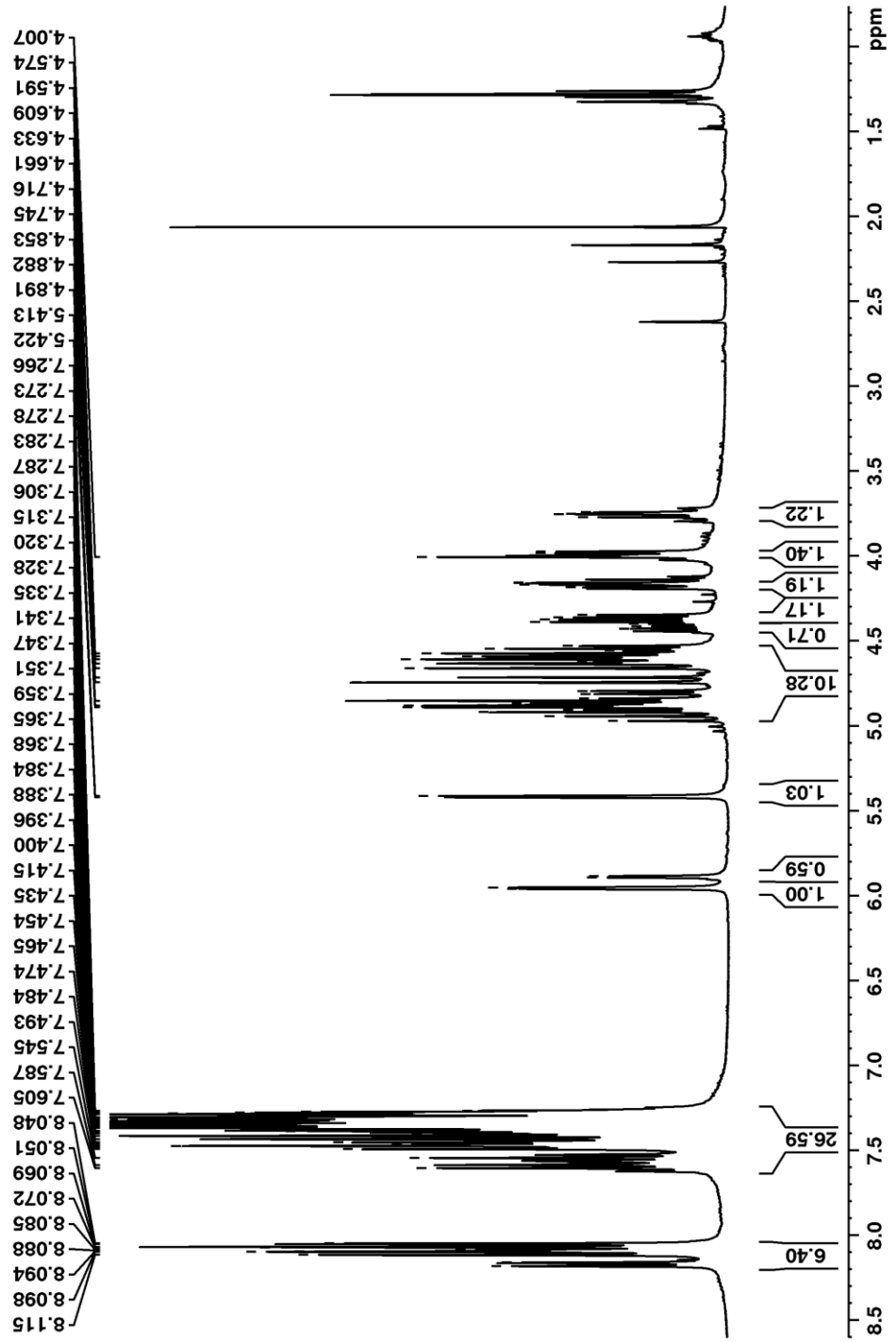
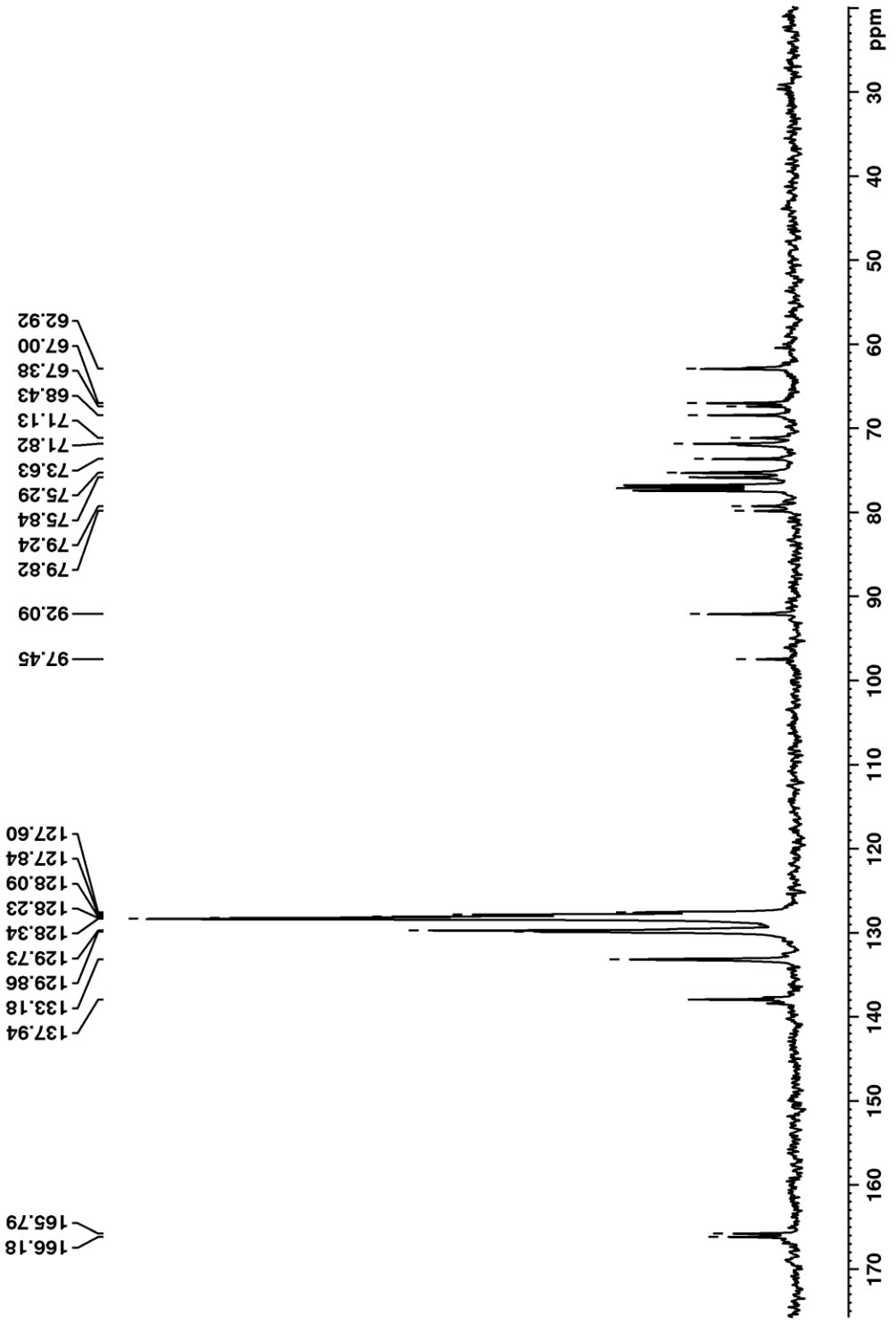
Copies of ^{1}H and ^{13}C NMR spectra



S7

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128.23
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127.84
127.60
97.45
92.09
79.82
79.24
75.84
75.29
73.63
71.82
71.13
68.43
67.38
67.00
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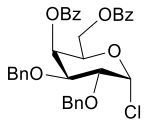
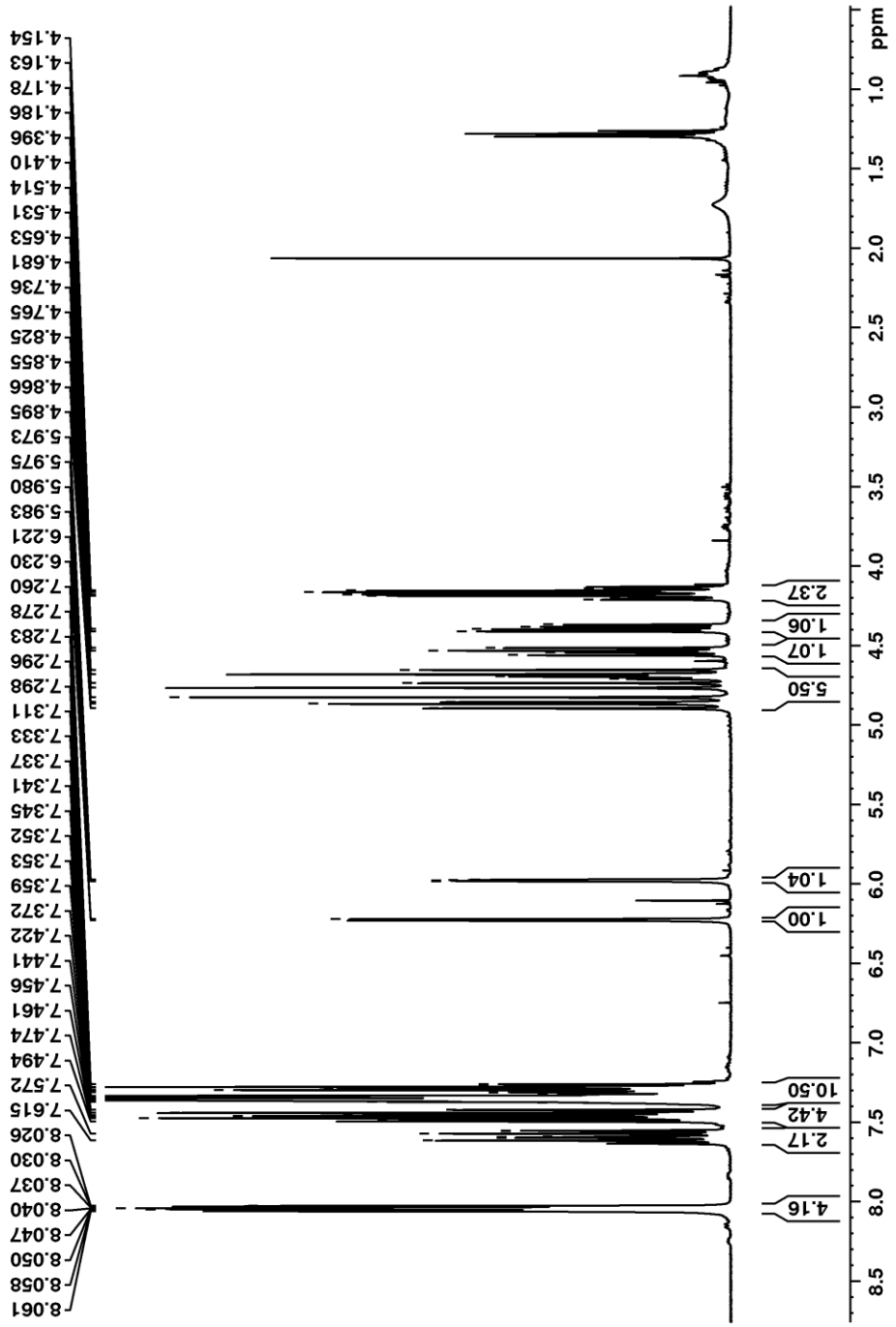
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm


OBz
OBz
O
BnO
BnO
Cl

S3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7.461
7.456
7.441
7.422
7.372
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7.353
7.352
7.345
7.341
7.337
7.333
7.311
7.298
7.296
7.283
7.278
7.260
6.230
6.221
5.983
5.980
5.975
5.973
4.895
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4.855
4.825
4.765
4.736
4.681
4.653
4.531
4.514
4.410
4.396
4.186
4.178
4.163
4.154
4.16
2.17
4.42
10.50
1.04
1.00
5.50
1.07
1.06
2.37
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

165.94
165.44
137.50
133.31
133.16
129.83
129.69
129.36
128.23
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127.59
93.93
75.56
74.75
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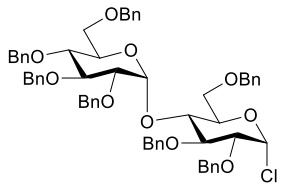
72.20
70.13
67.73
62.27
ppm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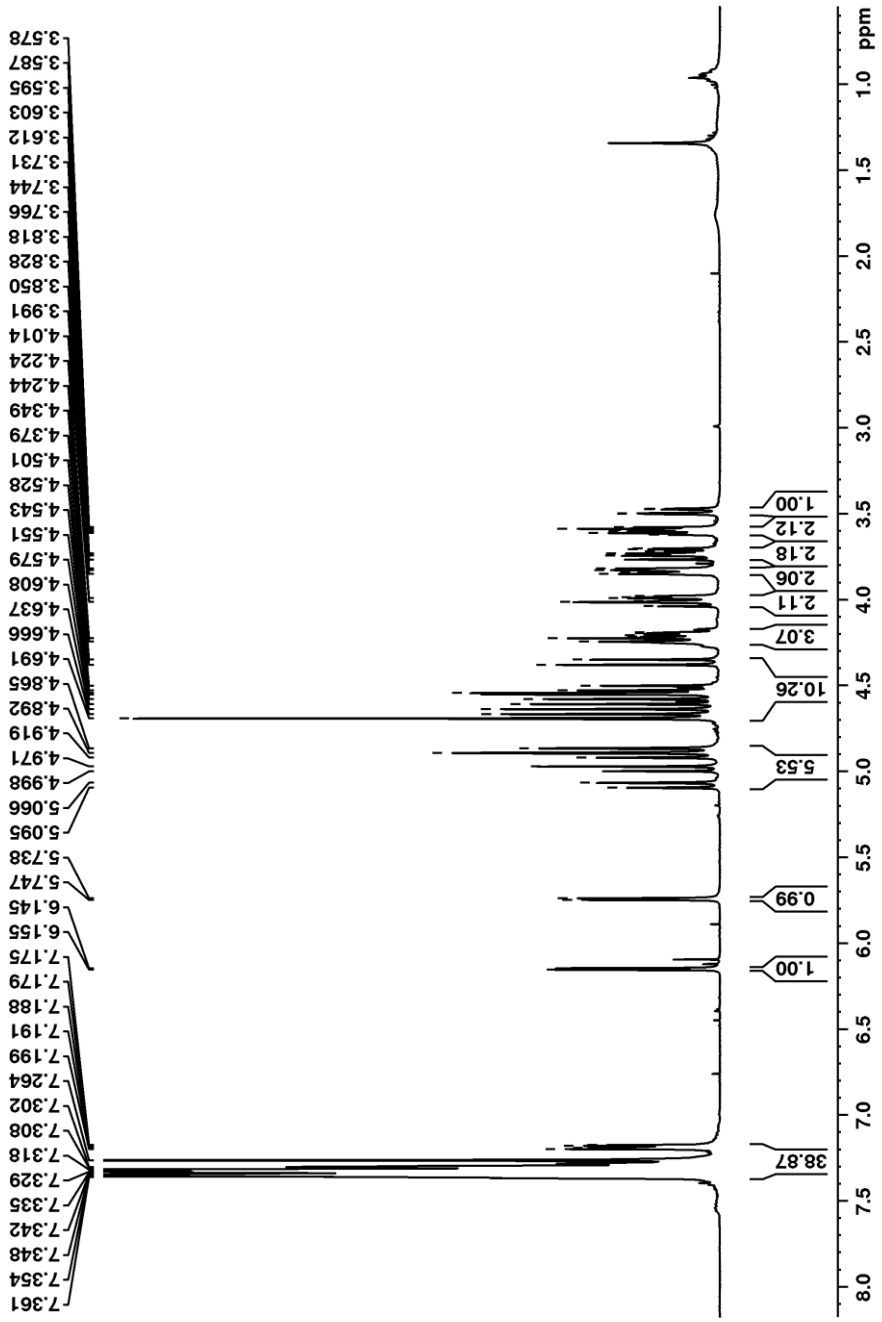
OBn
O
BnO
BnO
Cl

S4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4.014
4.224
4.244
4.349
4.379
4.501
4.528
4.543
4.551
4.579
4.608
4.637
4.666
4.691
4.865
4.892
4.919
4.971
4.998
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5.095
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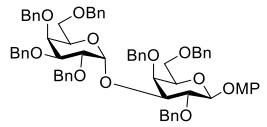
5.747
6.145
6.155
7.175
7.179
7.188
7.191
7.199
7.264
7.302
7.308
7.318
7.329
7.335
7.342
7.348
7.354
7.361
1.00
2.12
2.18
2.06
2.11
3.07
10.26
5.53
0.99
1.00
38.87
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

138.65
138.37
137.87
137.19
128.49
128.08
127.77
127.61
127.50
127.36
127.18
126.76
96.98
93.21
81.89
81.23
80.01
79.38
77.59
75.52
74.95
74.58
73.43
73.19
73.07
72.90
71.59
71.07
68.15
ppm


BnO
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BnO
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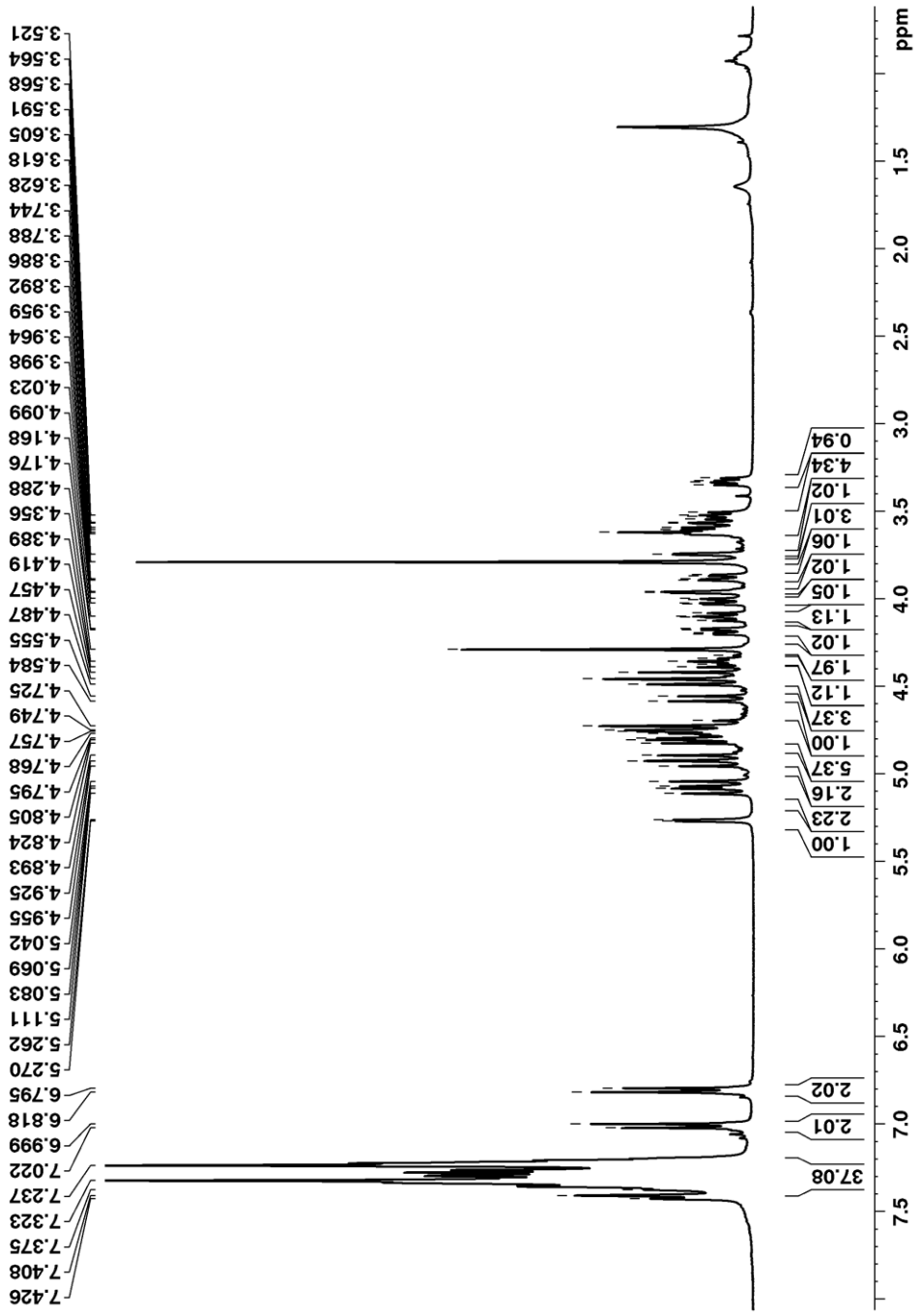
BnO
O
BnO
OBn
O
OMP
BnO

3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3.886
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3.959
3.964
3.998
4.023
4.099
4.168
4.176
4.288
4.356
4.389
4.419
4.457
4.487
4.555
4.584
4.725
4.749
4.757
4.768
4.795
4.805
4.824
4.893
4.925
4.955
5.042
5.069
5.083
5.111
5.262
5.270
6.795
6.818
6.999
7.022
7.237
7.323
7.375
7.408
7.426
0.94
4.34
1.02
3.01
1.06
1.02
1.05
1.13
1.02
1.97
1.12
3.37
1.00
5.37
2.16
2.23
1.00
2.02
2.01
37.08
ppm
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5

155.00
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138.57
138.24
128.12
127.48
127.34
118.24
114.34
103.19
95.63
79.05
78.04
77.28
76.97
76.65
76.34
75.18
74.98
74.66
74.34
73.60
73.36
72.67
72.44
69.03
55.55
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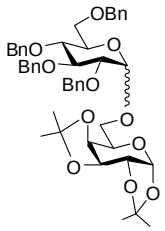
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180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BnO
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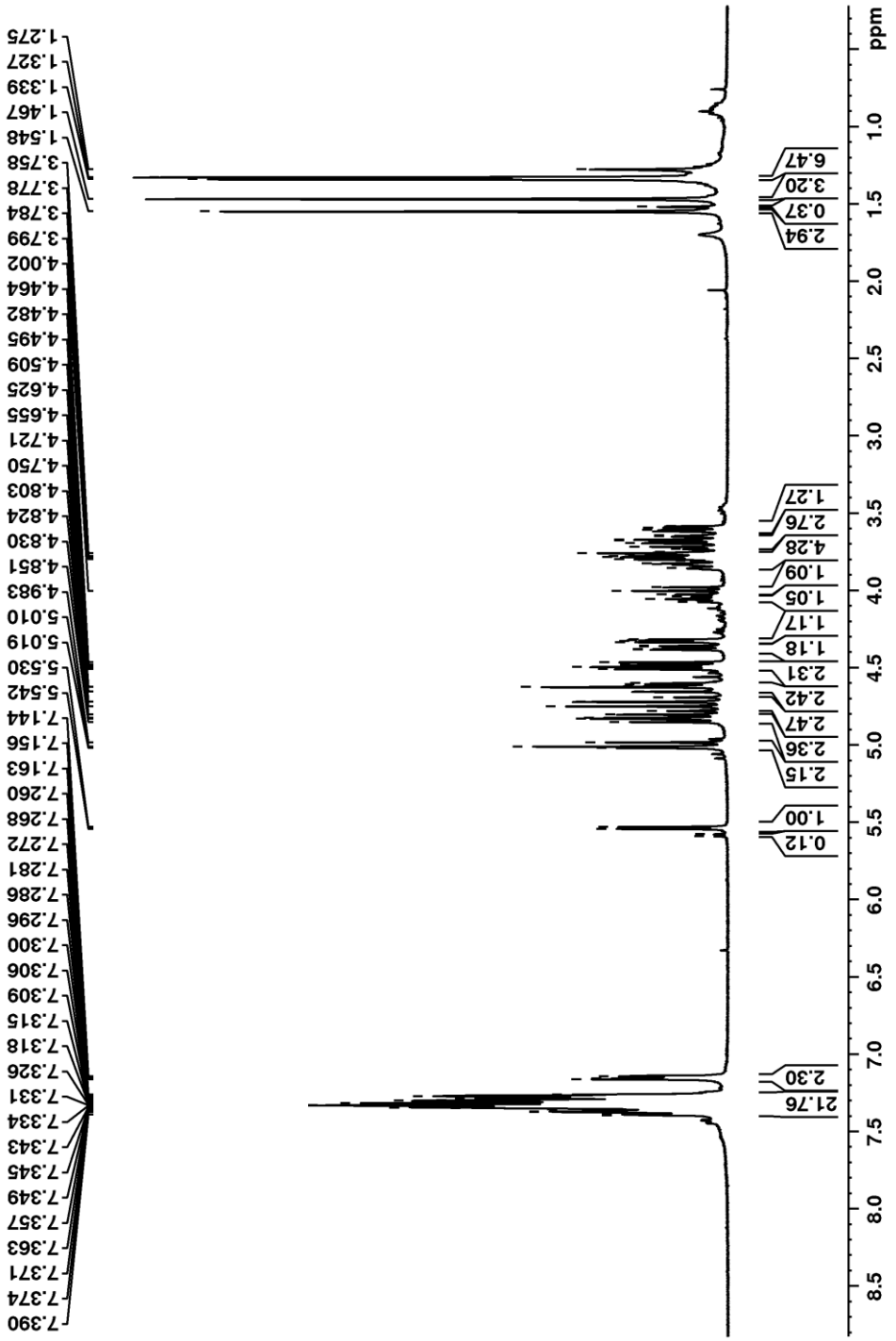
O
O

6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5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
6.47
3.20
0.37
2.94
1.27
2.76
4.28
1.09
1.05
1.17
1.18
2.31
2.42
2.47
2.36
2.15
1.00
0.12
2.30
21.76
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7.374
7.371
7.363
7.357
7.349
7.345
7.343
7.334
7.331
7.326
7.318
7.315
7.309
7.306
7.300
7.296
7.286
7.281
7.272
7.268
7.260
7.163
7.156
7.144
5.542
5.530
5.019
5.010
4.983
4.851
4.830
4.824
4.803
4.750
4.721
4.655
4.625
4.509
4.495
4.482
4.464
4.002
3.799
3.784
3.778
3.758
1.548
1.467
1.339
1.327
1.275

24.55
24.83
25.98
65.59
66.10
68.25
70.12
70.55
72.24
73.36
74.89
75.52
76.62
76.94
77.25
79.70
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96.21
96.94
108.48
109.10
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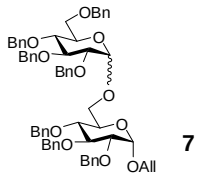
128.24
137.87
138.25
138.83
ppm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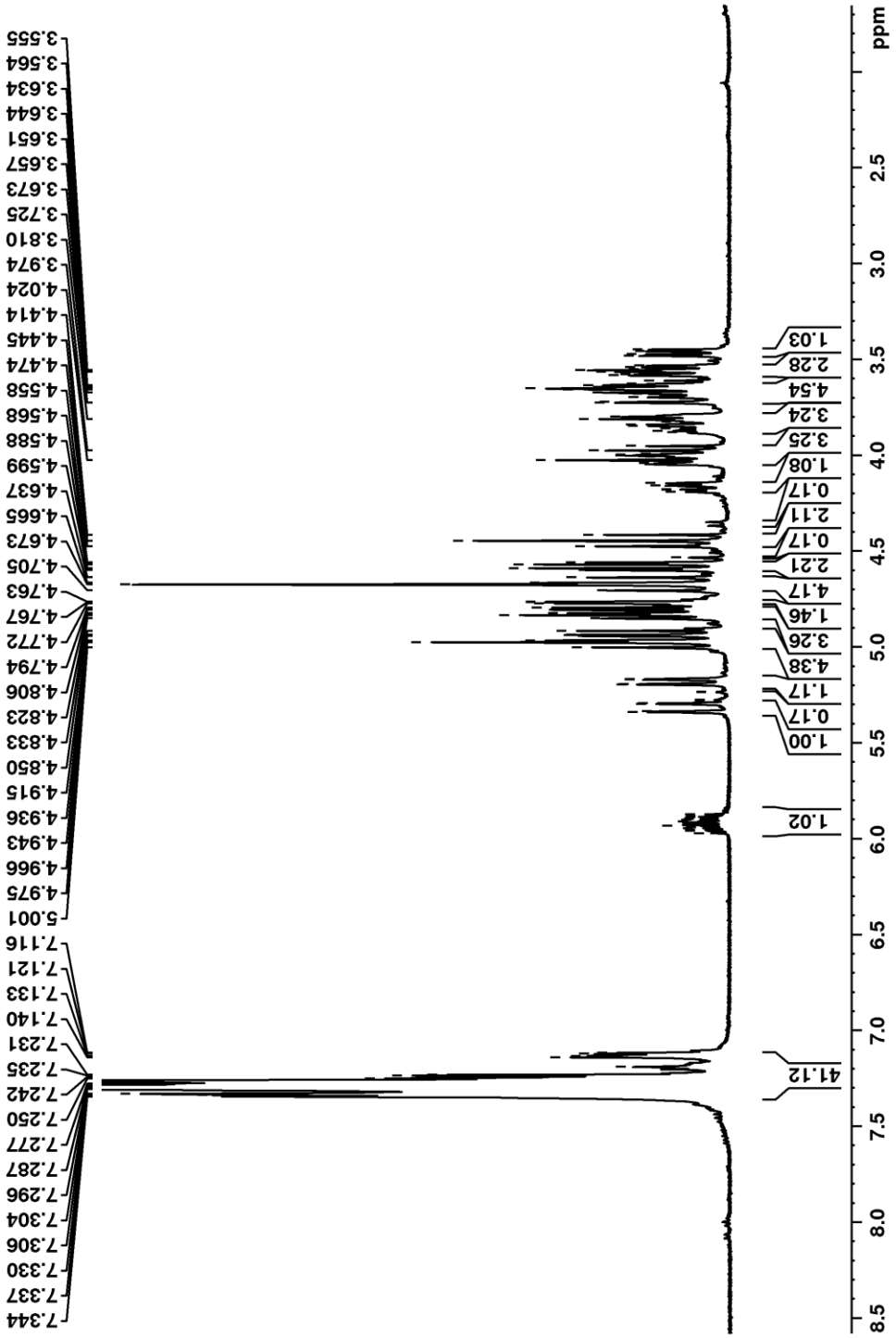
O
BnO
BnO
BnO
O
OAll

7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7.231
7.140
7.133
7.121
7.116
5.001
4.975
4.966
4.943
4.936
4.915
4.850
4.833
4.823
4.806
4.794
4.772
4.767
4.763
4.705
4.673
4.665
4.637
4.599
4.588
4.568
4.558
4.474
4.445
4.414
4.024
3.974
3.810
3.725
3.673
3.657
3.651
3.644
3.634
3.564
3.555
41.12
1.02
1.00
0.17
1.17
4.38
3.26
1.46
4.17
2.21
0.17
2.11
0.17
1.08
3.25
3.24
4.54
2.28
1.03
ppm

65.96
67.96
68.36
70.09
70.45
72.28
73.06
73.28
74.82
75.44
75.58
77.78
79.89
80.04
81.65
82.01
95.07
97.13
118.35
127.52
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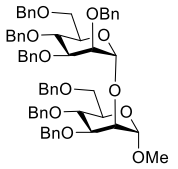
128.24
133.61
137.87
138.11
138.71
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 ppm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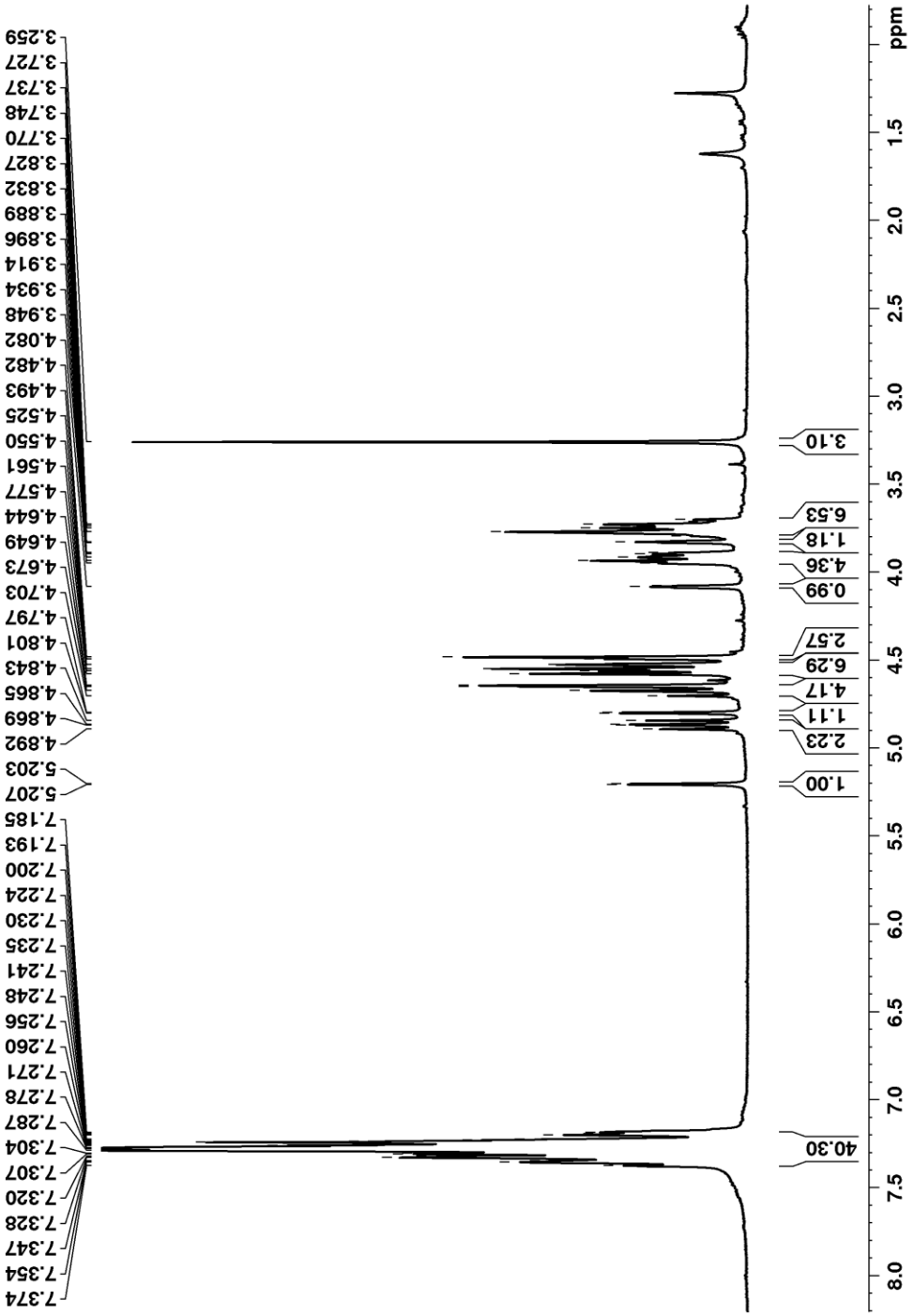
OBn
BnO
O
BnO
BnO
O
BnO
O
BnO
OMe

8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4.493
4.525
4.550
4.561
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4.649
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4.843
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4.869
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7.230
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7.328
7.347
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7.374
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6.29
4.17
1.11
2.23
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40.30
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7.0
6.5
6.0
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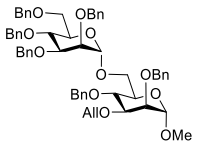
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5

138.47
138.32
128.16
127.66
127.34
99.78
99.42
79.91
79.62
74.94
74.16
73.23
72.29
72.07
71.63
69.43
69.26
54.56
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55
ppm


BnO
OBn
BnO
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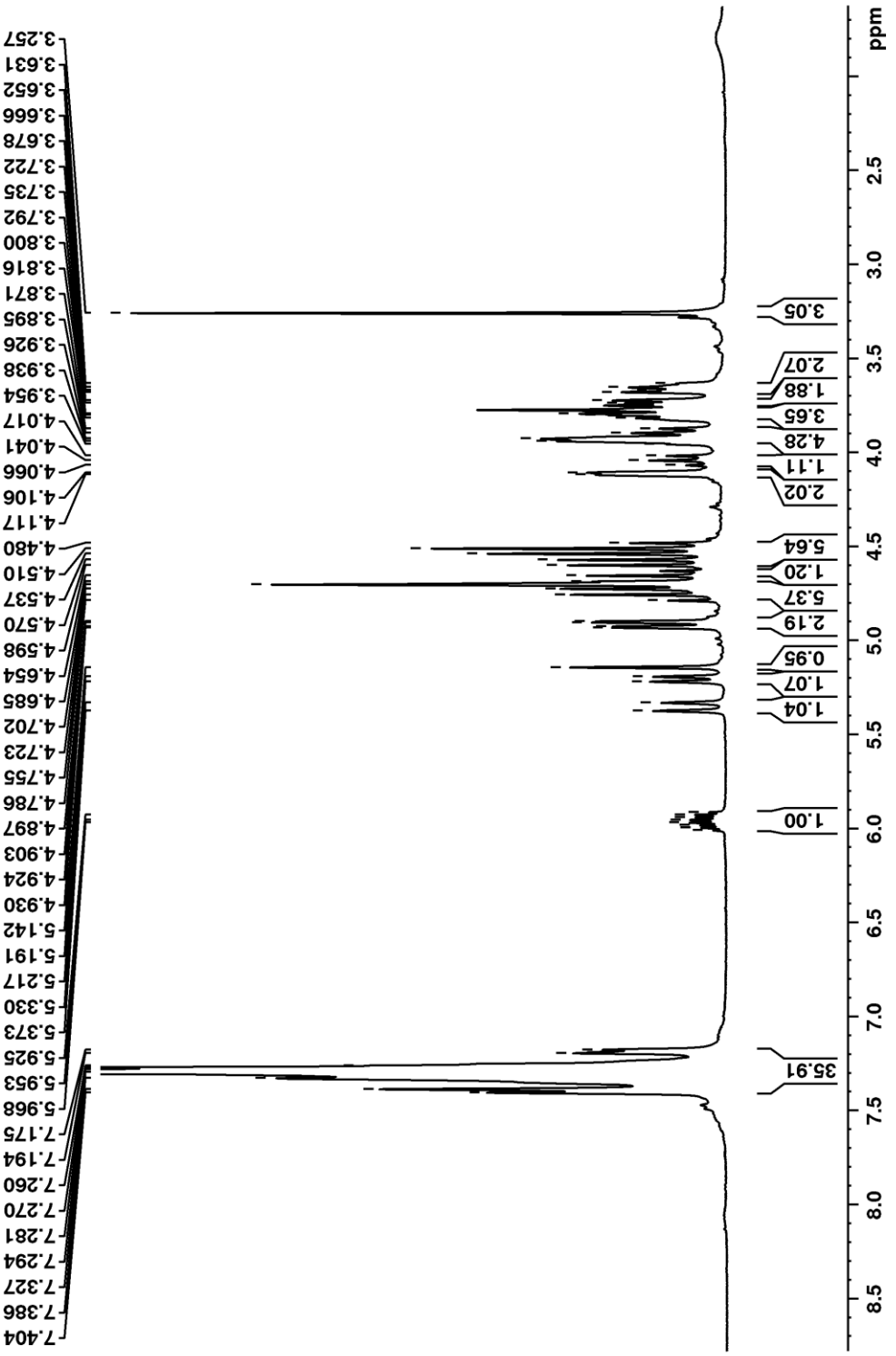
BnO
O
OBn
BnO
O
AllO
OMe

9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4.117
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4.510
4.537
4.570
4.598
4.654
4.685
4.702
4.723
4.755
4.786
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1.20
5.37
2.19
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1.07
1.04
1.00
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ppm
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7.0
6.5
6.0
5.5
5.0
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3.5
3.0
2.5

138.61
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127.50
127.28
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79.31
74.88
74.44
73.17
72.74
72.30
71.74
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50
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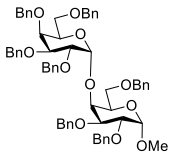
ppm


BnO
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OBn
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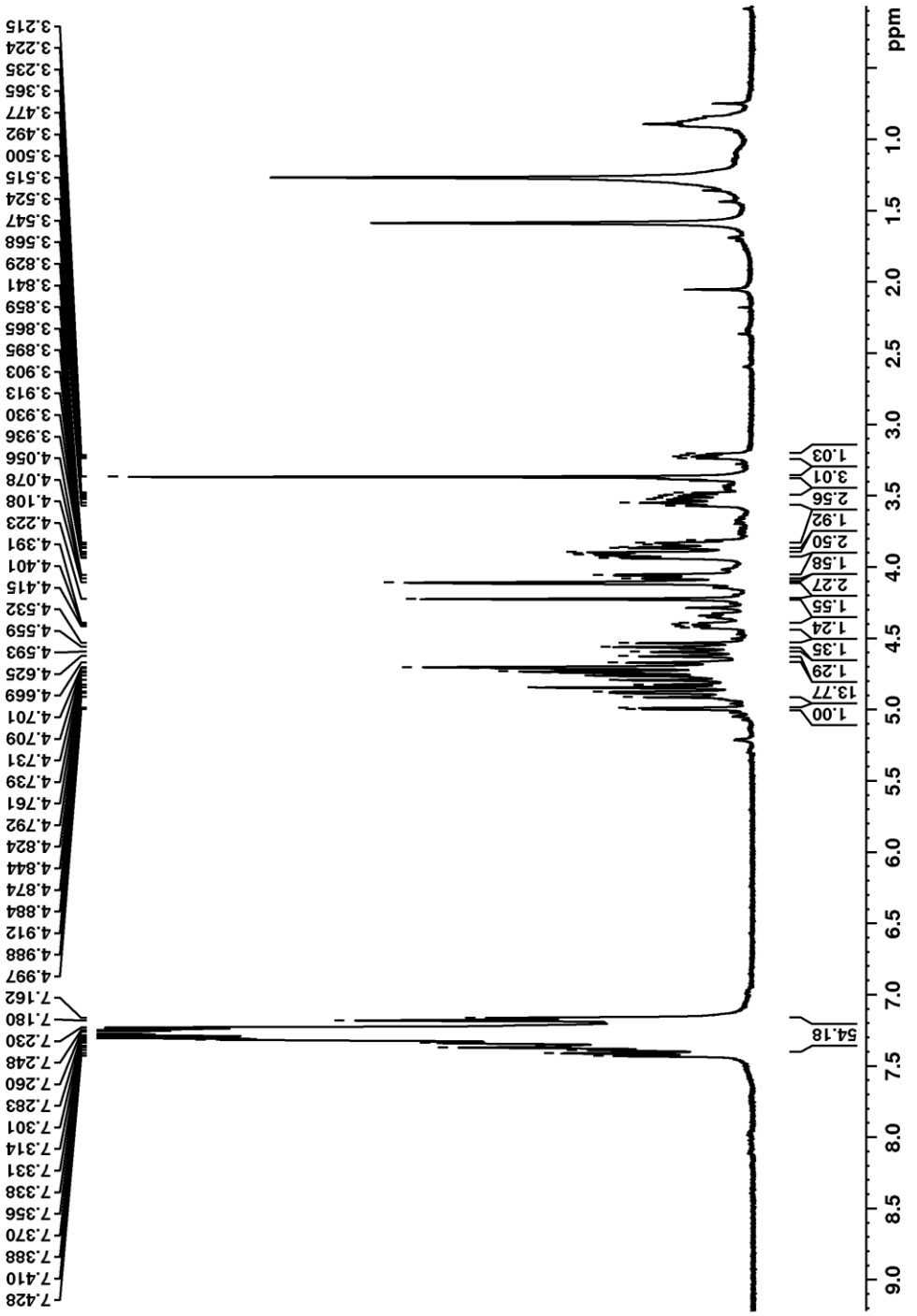
BnO
BnO
OMe

10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2.5
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1.5
1.0
1.00
13.77
1.29
1.35
1.24
1.55
2.27
1.58
2.50
1.92
2.56
3.01
1.03
54.18

138.86
138.58
138.01
128.16
127.99
127.69
127.36
100.22
98.66
79.37
77.22
76.90
76.58
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72.53
72.14
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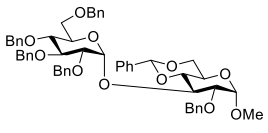
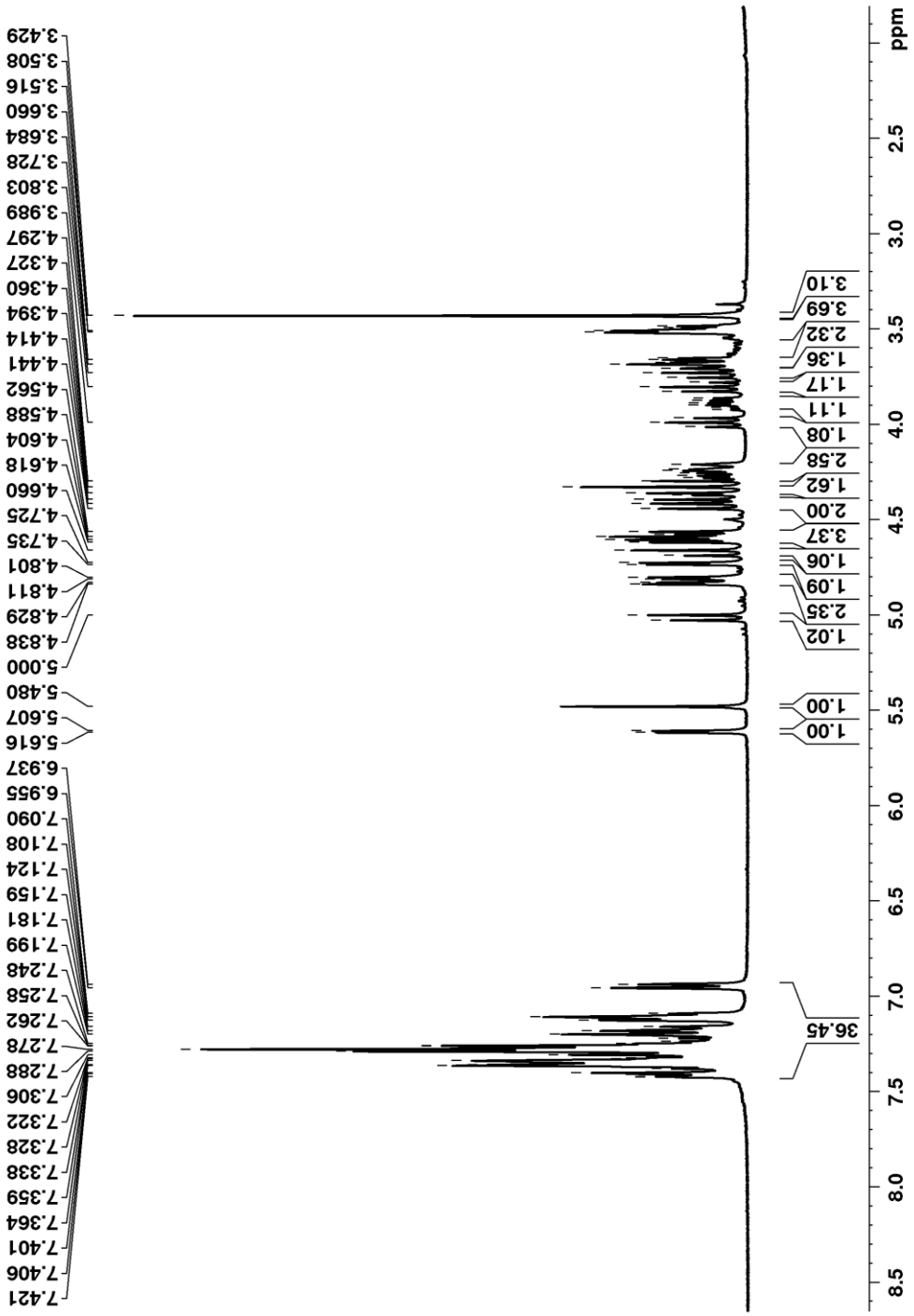
69.16
68.05
67.68
55.18
ppm


OBn
BnO
BnO
BnO
O
Ph
O
O
O
O
BnO
OMe

11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4.562
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4.811
4.829
4.838
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5.607
5.616
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1.11
1.08
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1.62
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1.06
1.09
2.35
1.02
1.00
1.00
36.45
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4.5
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3.5
3.0
2.5

138.79
137.96
137.71
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128.03
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127.50
127.30
126.31
102.00
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96.03
82.82
81.56
78.66
77.91
77.25
76.94
76.62
75.44
74.68
73.31
72.63
71.01
69.70
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150
140
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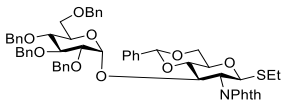
ppm


OBn
BnO
BnO
BnO
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Ph
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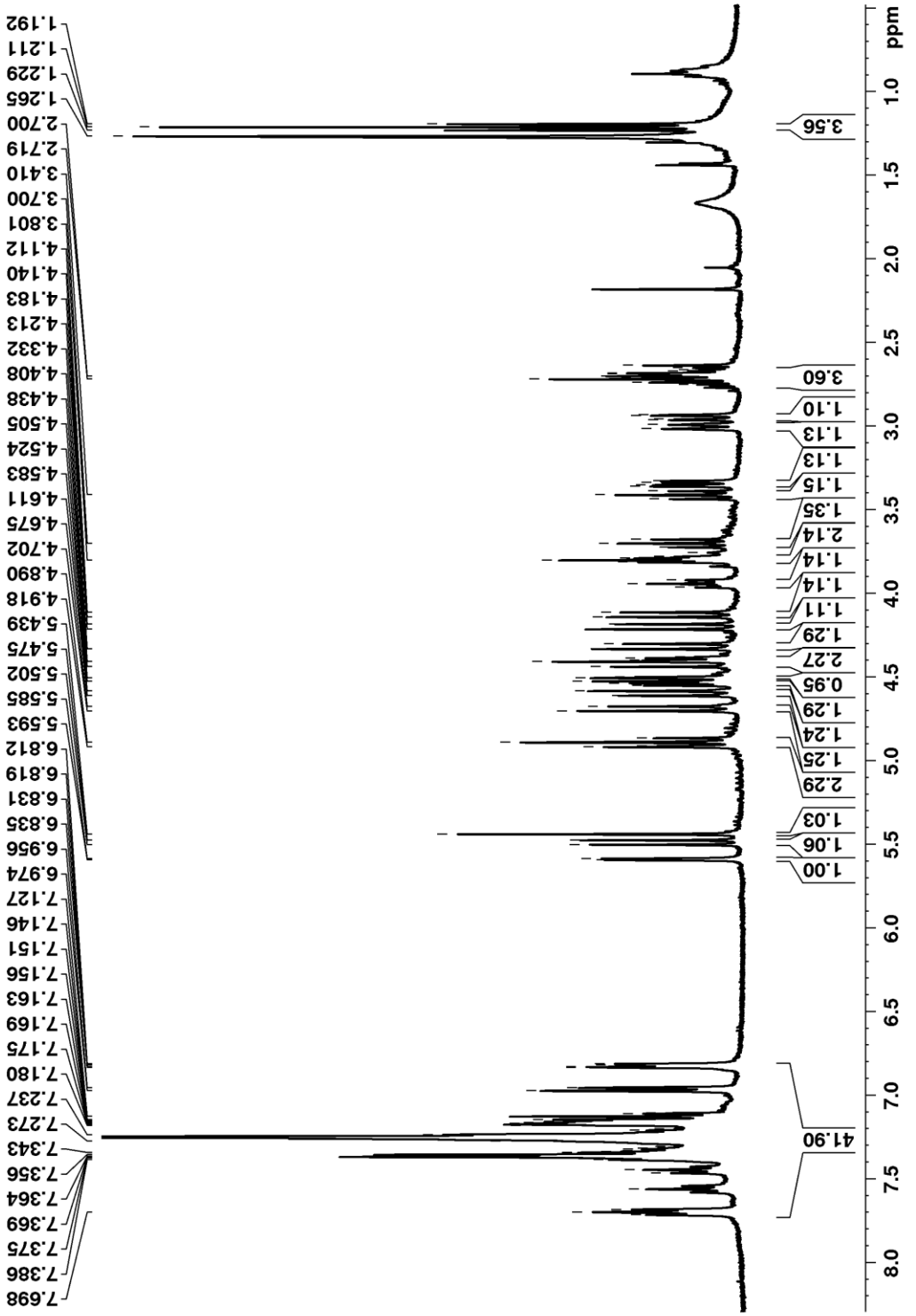
O
O
SEt
NPhth

12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4.408
4.438
4.505
4.524
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4.675
4.702
4.890
4.918
5.439
5.475
5.502
5.585
5.593
6.812
6.819
6.831
6.835
6.956
6.974
7.127
7.146
7.151
7.156
7.163
7.169
7.175
7.180
7.237
7.273
7.343
7.356
7.364
7.369
7.375
7.386
7.698
3.56
3.60
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1.13
1.13
1.15
1.35
2.14
1.14
1.14
1.11
1.29
2.27
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1.29
1.24
1.25
2.29
1.03
1.06
1.00
41.90
ppm
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1.5
2.0
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3.5
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6.0
6.5
7.0
7.5
8.0

14.74
23.83
53.92
67.07
68.69
70.03
70.63
71.20
72.59
73.36
73.97
75.41
78.43
80.80
81.61
83.06
96.32
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124.05
126.26
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137.83
138.74
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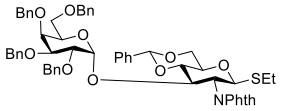
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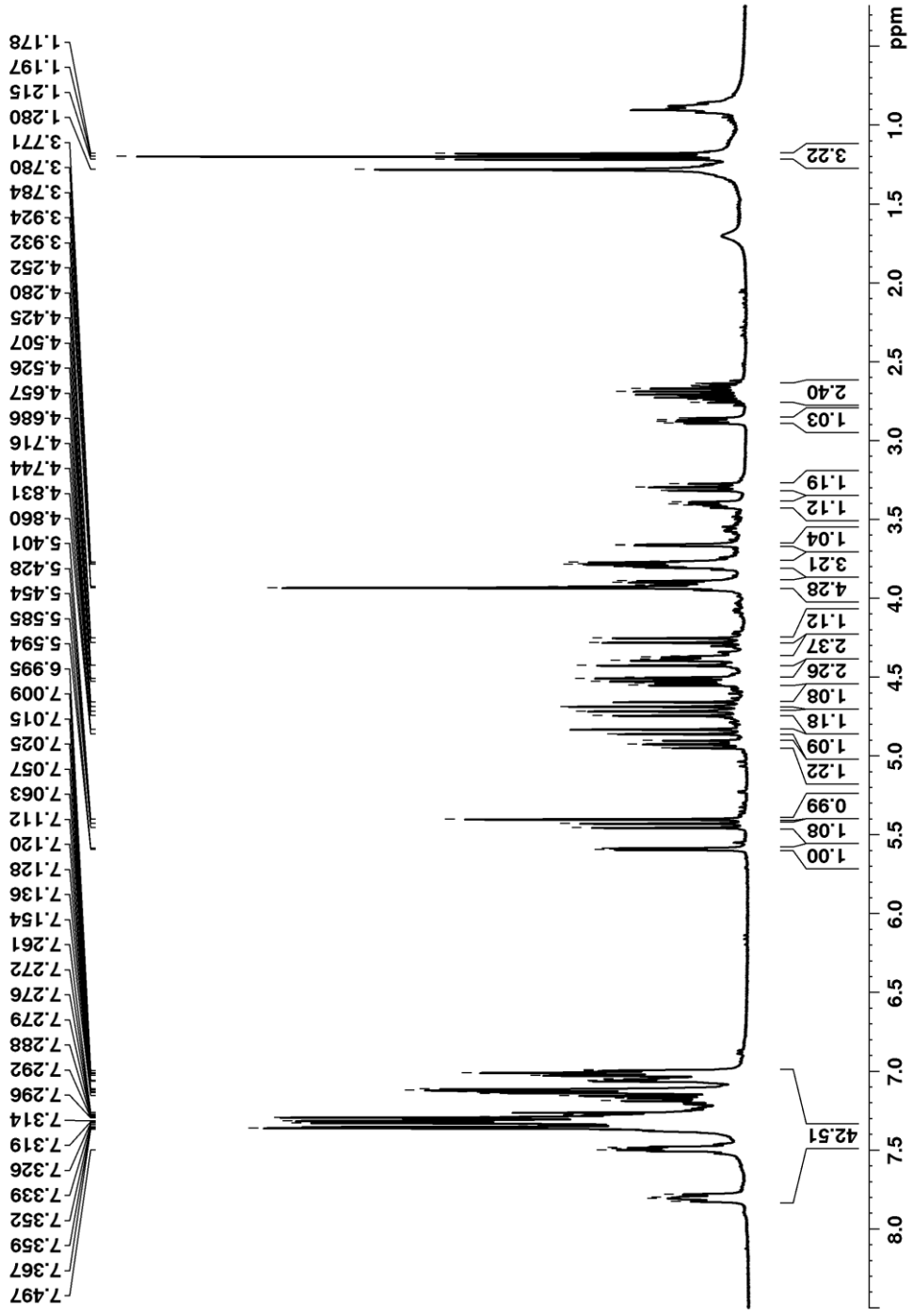
BnO
BnO
O
Ph
O
O
O
SEt
NPhth

13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7.272
7.261
7.154
7.136
7.128
7.120
7.112
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7.057
7.025
7.015
7.009
6.995
5.594
5.585
5.454
5.428
5.401
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4.831
4.744
4.716
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4.526
4.507
4.425
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4.252
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3.924
3.784
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3.771
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1.215
1.197
1.178
3.22
2.40
1.03
1.19
1.12
1.04
3.21
4.28
1.12
2.37
2.26
1.08
1.18
1.09
1.22
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1.08
1.00
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ppm
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4.0
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2.5
2.0
1.5
1.0

14.75
23.89
29.59
54.10
67.67
68.67
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71.68
72.76
73.23
74.70
75.29
76.62
76.94
77.99
81.62
82.93
97.28
101.58
122.99
123.77
126.16
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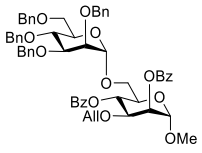
ppm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BnO
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BnO
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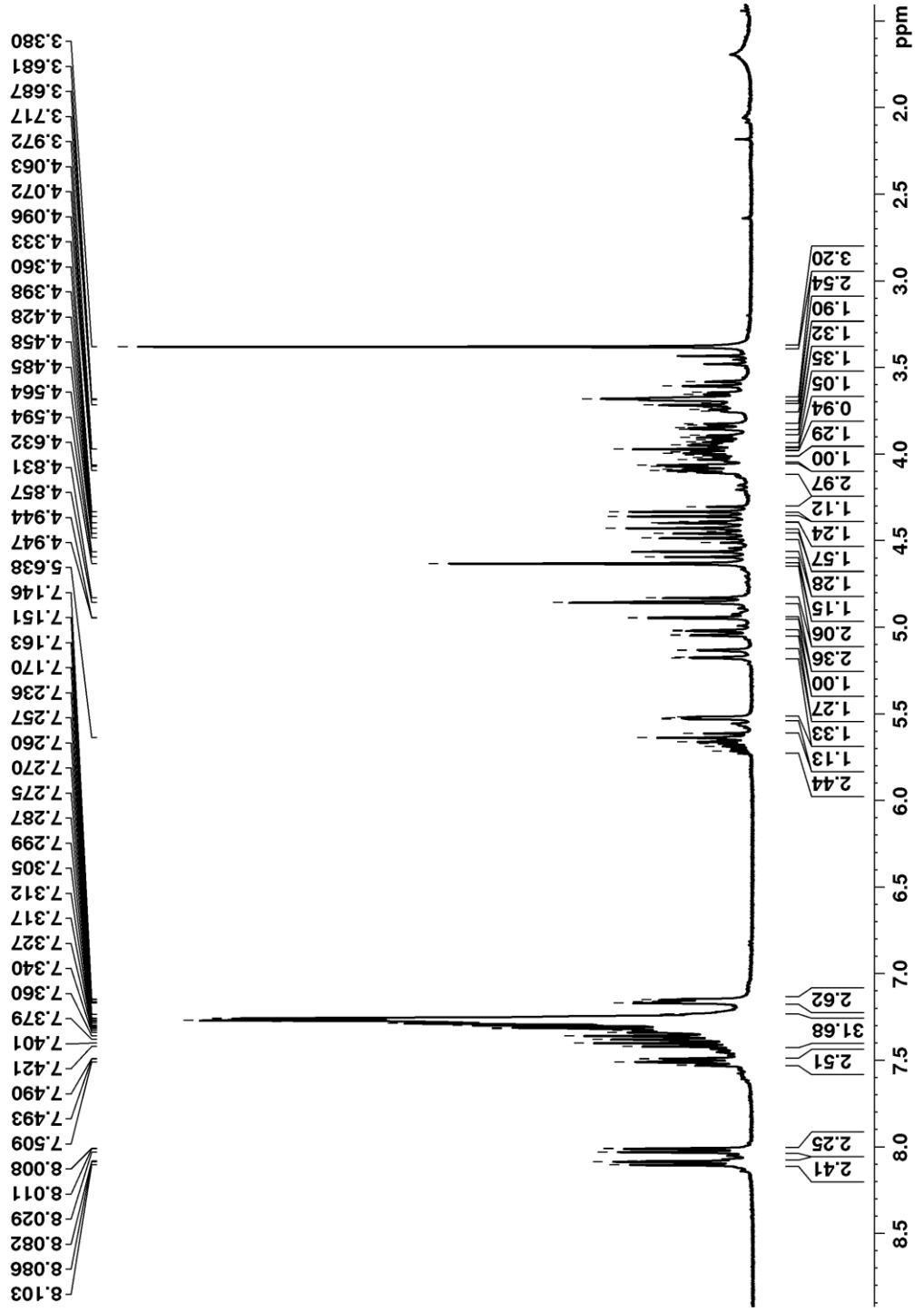
OBz
BzO
O
AllO
OMe

14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4.485
4.564
4.594
4.632
4.831
4.857
4.944
4.947
5.638
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7.151
7.163
7.170
7.236
7.257
7.260
7.270
7.275
7.287
7.299
7.305
7.312
7.317
7.327
7.340
7.360
7.379
7.401
7.421
7.490
7.493
7.509
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8.011
8.029
8.082
8.086
8.103
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1.33
1.27
1.00
2.36
2.06
1.15
1.28
1.57
1.24
1.12
2.97
1.00
1.29
0.94
1.05
1.35
1.32
1.90
2.54
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2.51
2.25
2.41
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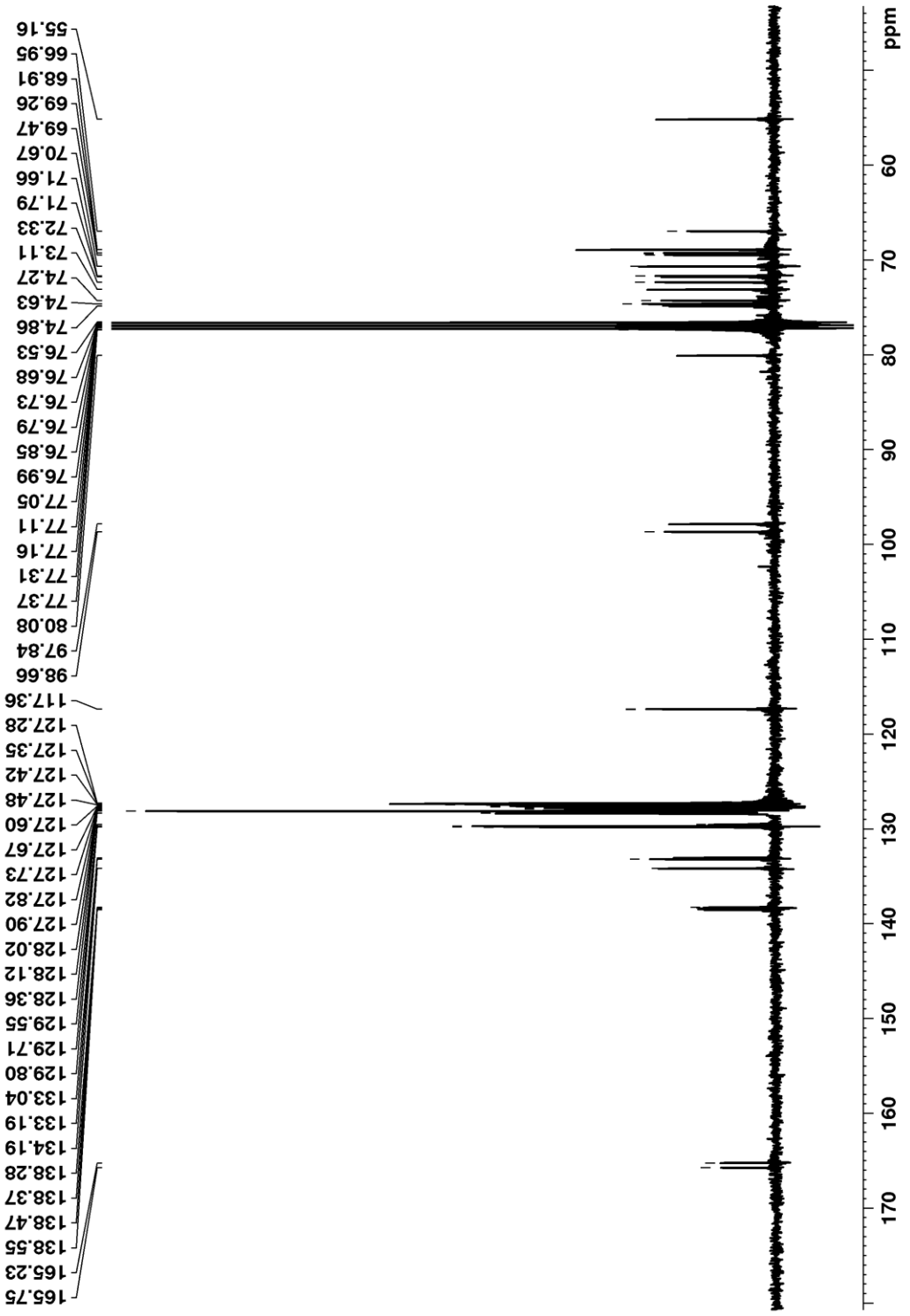
2.5
2.0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71.79
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76.53
76.68
76.73
76.79
76.85
76.99
77.05
77.11
77.16
77.31
77.37
80.08
97.84
98.66
117.36
127.28
127.35
127.42
127.48
127.60
127.67
127.73
127.82
127.90
128.02
128.12
128.36
129.55
129.71
129.80
133.04
133.19
134.19
138.28
138.37
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165.75
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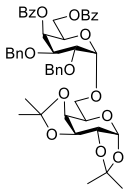
70
60


BzO
OBz
BnO
BnO
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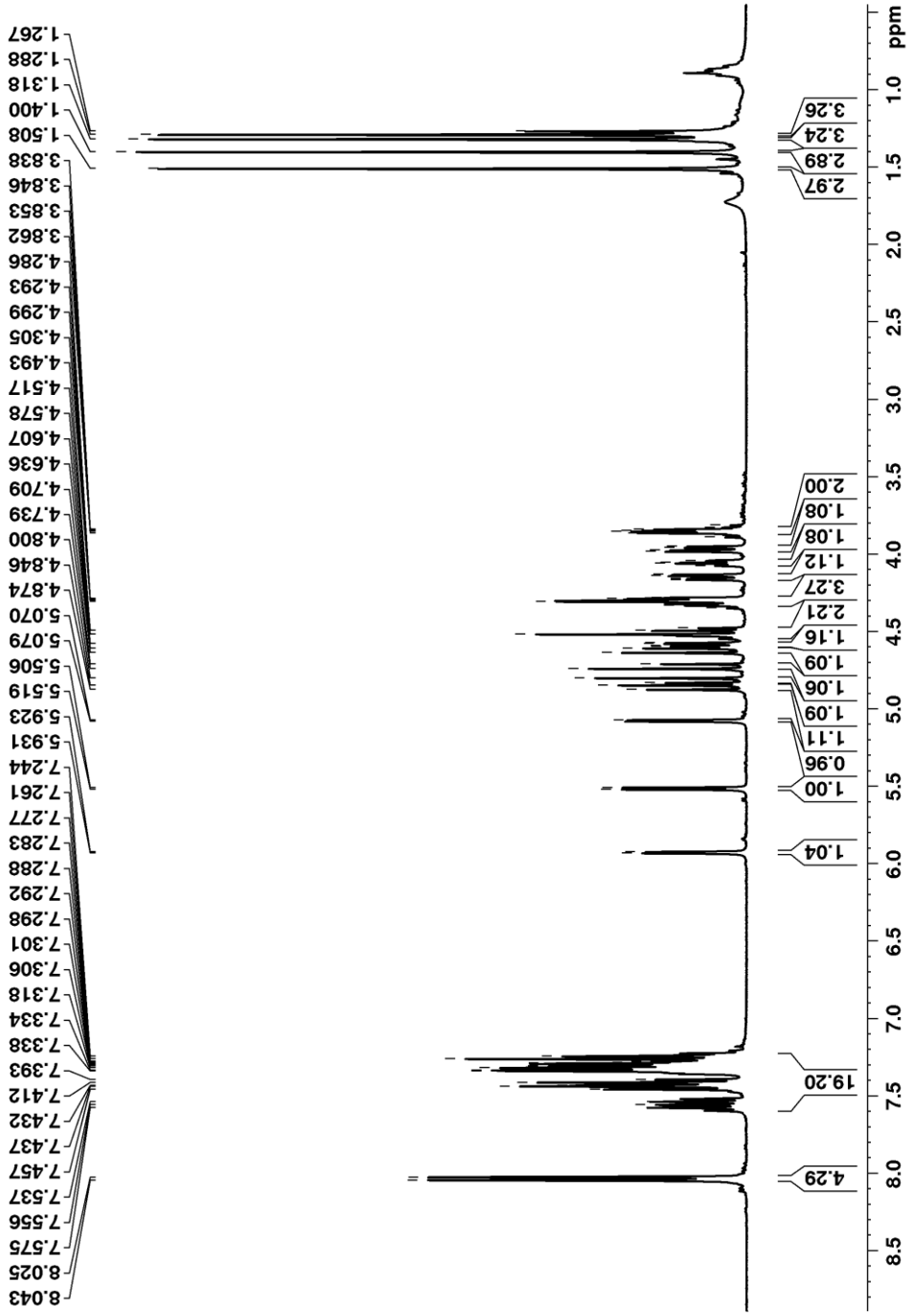
O
O

15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7.334
7.318
7.306
7.301
7.298
7.292
7.288
7.283
7.277
7.261
7.244
5.931
5.923
5.519
5.506
5.079
5.070
4.874
4.846
4.800
4.739
4.709
4.636
4.607
4.578
4.517
4.493
4.305
4.299
4.293
4.286
3.862
3.853
3.846
3.838
1.508
1.400
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1.288
1.267
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3.24
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2.97
2.00
1.08
1.08
1.12
3.27
2.21
1.16
1.09
1.06
1.09
1.11
0.96
1.00
1.04
19.20
4.29
ppm

165.68
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128.27
127.82
108.44
96.21
73.10
71.90
70.61
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25.90
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ppm
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170
160
150
140
130
120
110
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90
80
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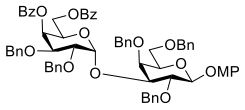
60
50
40
30
20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OBz
BnO
BnO
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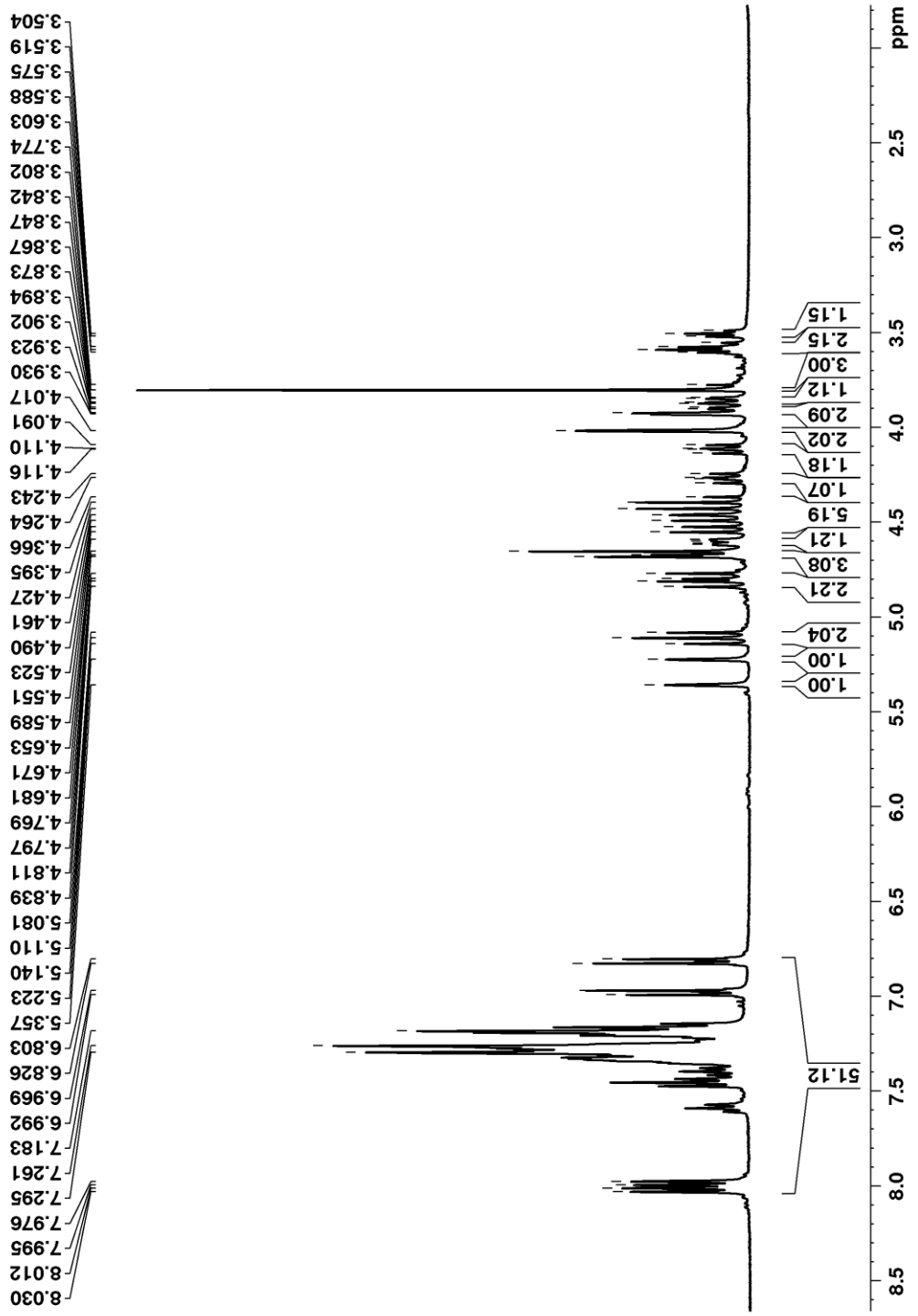
BnO
OBn
O
OMP
BnO

16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3.894
3.902
3.923
3.930
4.017
4.091
4.110
4.116
4.243
4.264
4.366
4.395
4.427
4.461
4.490
4.523
4.551
4.589
4.653
4.671
4.681
4.769
4.797
4.811
4.839
5.081
5.110
5.140
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6.969
6.992
7.183
7.261
7.295
7.976
7.995
8.012
8.030
1.15
2.15
3.00
1.12
2.09
2.02
1.18
1.07
5.19
1.21
3.08
2.21
2.04
1.00
1.00
1.00
51.12
ppm
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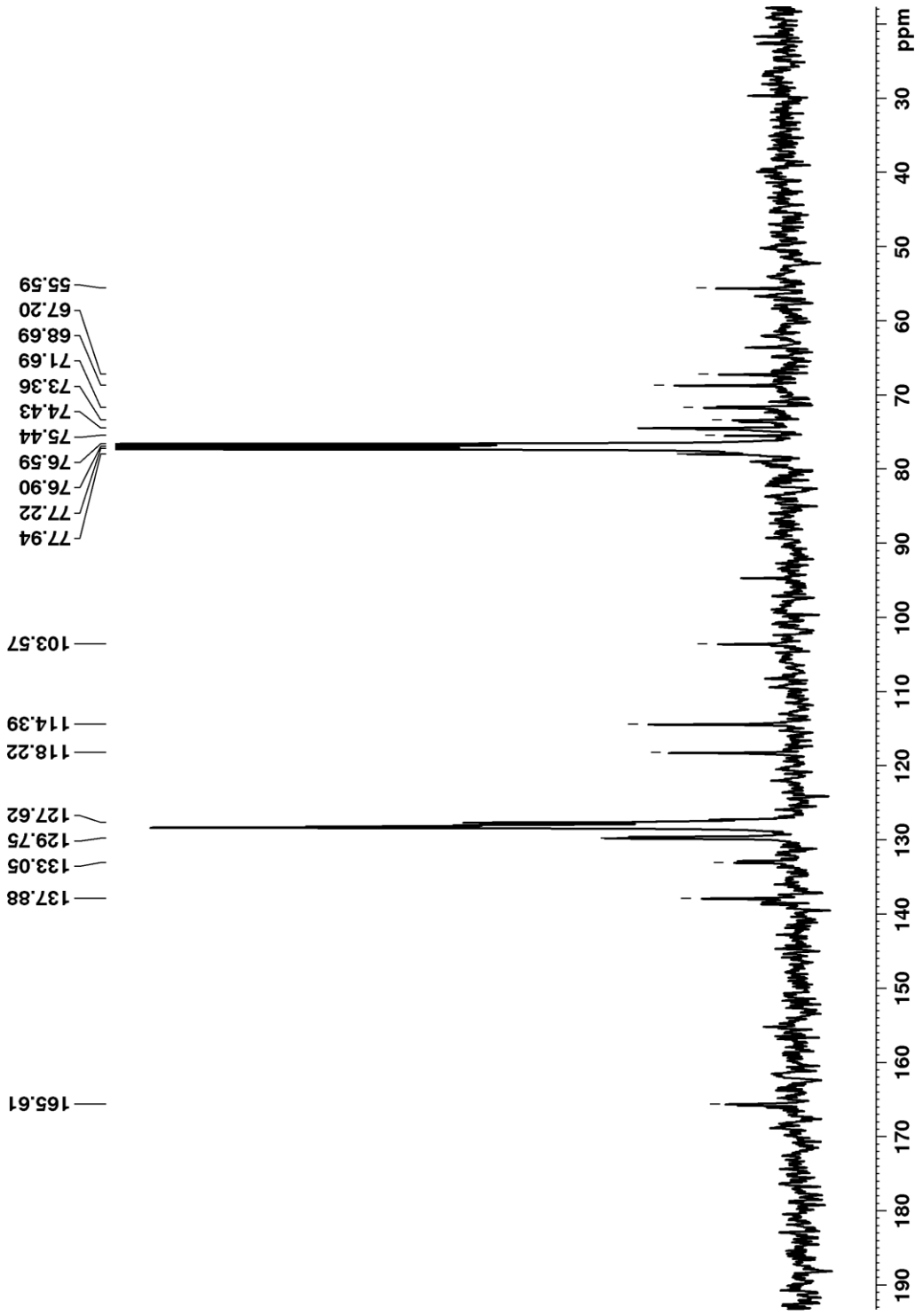
3.5
3.0
2.5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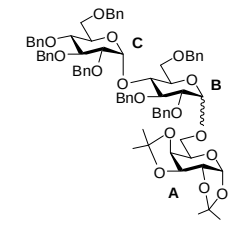
127.62
118.22
114.39
103.57
77.94
77.22
76.90
76.59
75.44
74.43
73.36
71.69
68.69
67.20
55.59
ppm

17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BnO
BnO
BnO
C
OBn
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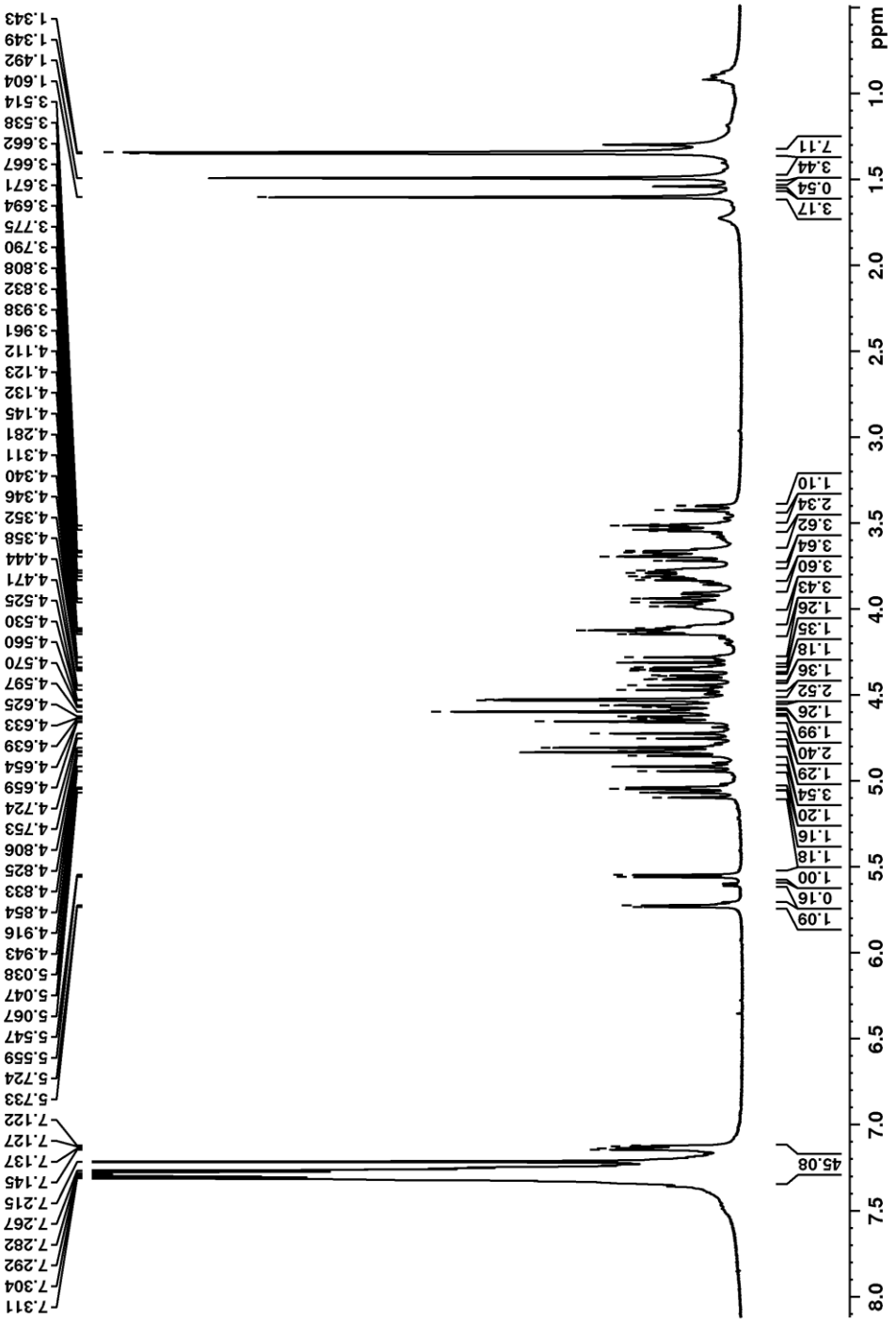
B
BnO
BnO
O
O
O
O
O
O
A
O
O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3.790
3.808
3.832
3.938
3.961
4.112
4.123
4.132
4.145
4.281
4.311
4.340
4.346
4.352
4.358
4.444
4.471
4.525
4.530
4.560
4.570
4.597
4.625
4.633
4.639
4.654
4.659
4.724
4.753
4.806
4.825
4.833
4.854
4.916
4.943
5.038
5.047
5.067
5.547
5.559
5.724
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7.127
7.137
7.145
7.215
7.267
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7.292
7.304
7.311
7.11
3.44
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3.17
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2.34
3.62
3.64
3.60
3.43
1.26
1.35
1.18
1.36
2.52
1.26
1.99
2.40
1.29
3.54
1.20
1.16
1.18
1.00
0.16
1.09
45.08
ppm
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1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0

138.98
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138.44
138.20
137.90
128.19
127.94
127.72
127.46
127.18
126.71
109.15
108.58
96.53
96.23
81.93
81.74
79.85
79.45
77.57
75.45
74.86
74.10
73.37
73.03
72.25
72.14
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68.10
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26.14
26.03
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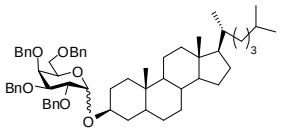
24.62
ppm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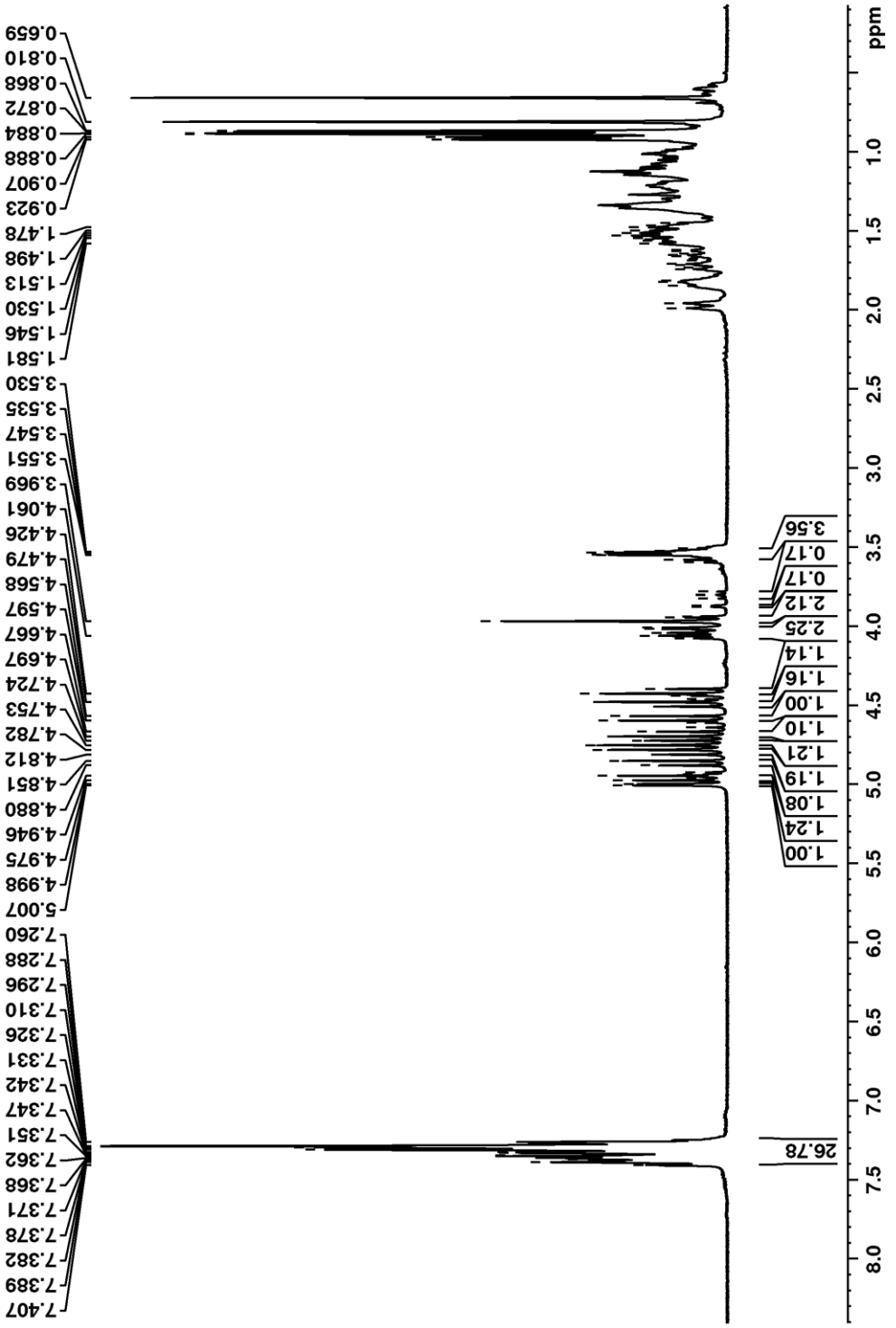
BnO
BnO
O
3

19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1.546
1.581
3.530
3.535
3.547
3.551
3.969
4.061
4.426
4.479
4.568
4.597
4.667
4.697
4.724
4.753
4.782
4.812
4.851
4.880
4.946
4.975
4.998
5.007
7.260
7.288
7.296
7.310
7.326
7.331
7.342
7.347
7.351
7.362
7.368
7.371
7.378
7.382
7.389
7.407
3.56
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0.17
2.12
2.25
1.14
1.16
1.00
1.10
1.21
1.19
1.08
1.24
1.00
26.78
ppm
1.0
1.5
2.0
2.5
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6.0
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7.0
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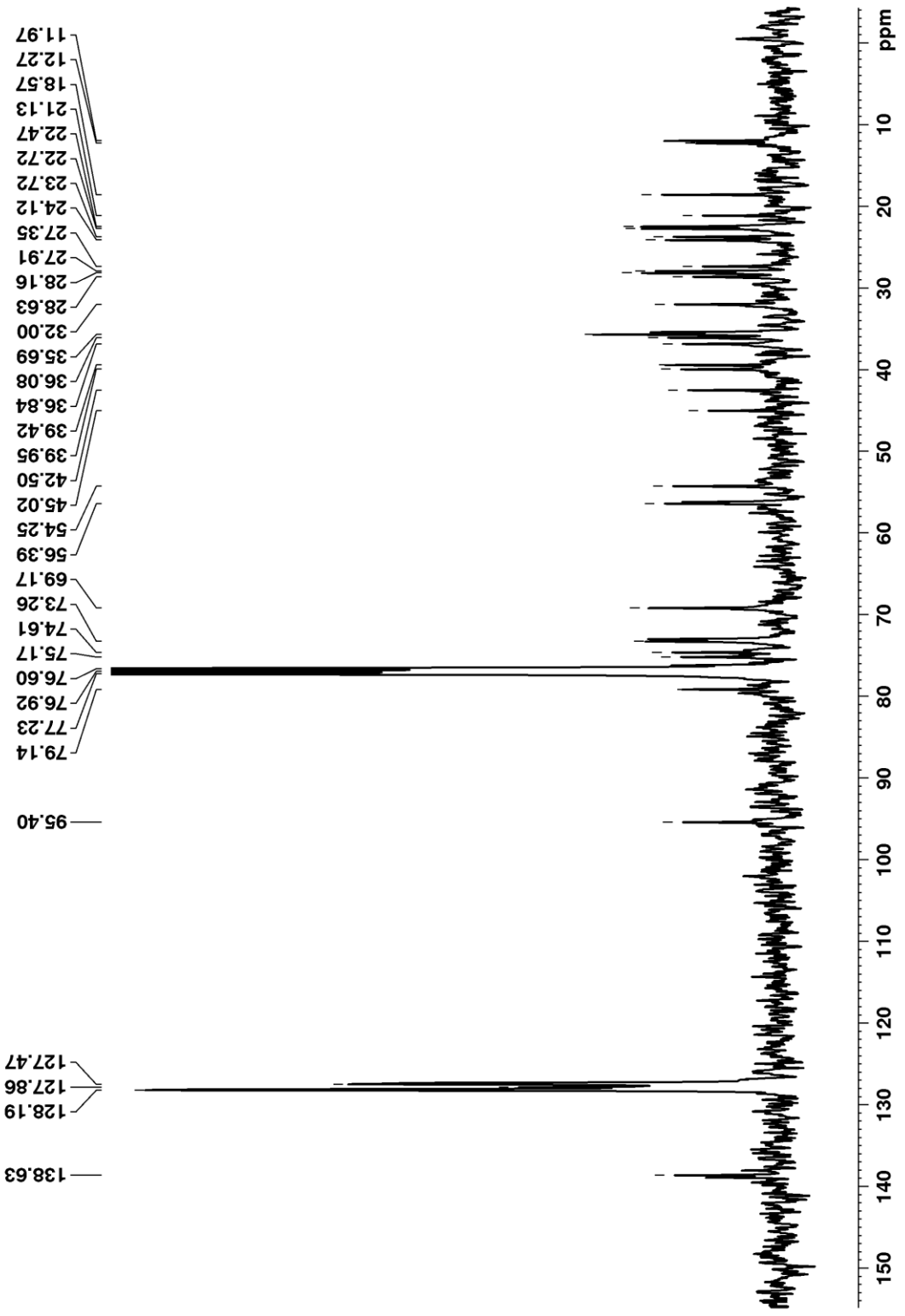
8.0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23.72
24.12
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27.91
28.16
28.63
32.00
35.69
36.08
36.84
39.42
39.95
42.50
45.02
54.25
56.39
69.17
73.26
74.61
75.17
76.60
76.92
77.23
79.14
95.40
127.47
127.86
128.19
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ppm
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20
30
40
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60
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80
90
100
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140
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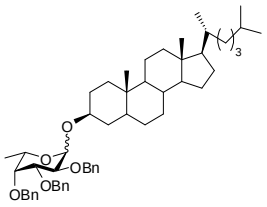
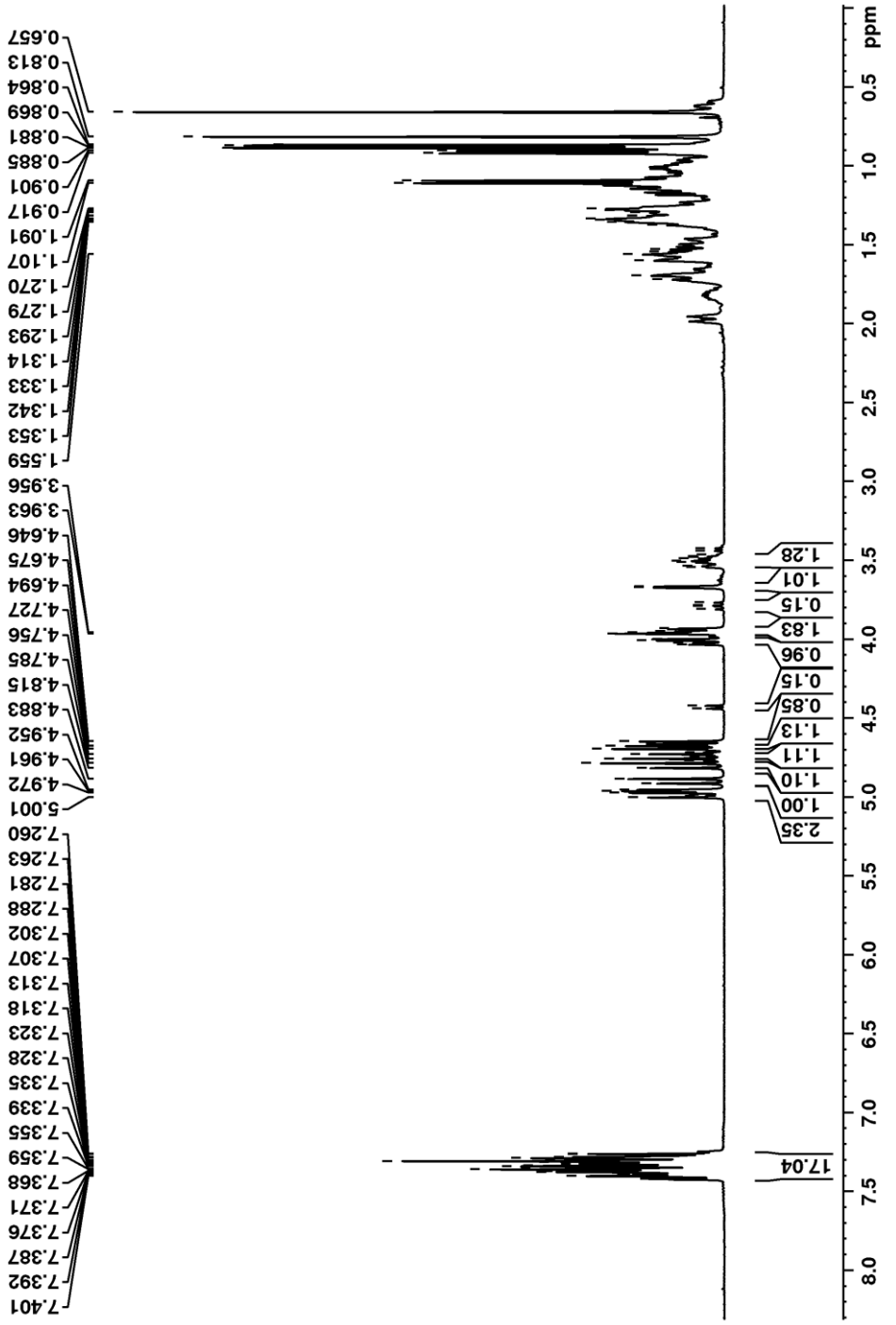

O
OBn
OBn
OBn

21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1.293
1.314
1.333
1.342
1.353
1.559
3.956
3.963
4.646
4.675
4.694
4.727
4.756
4.785
4.815
4.883
4.952
4.961
4.972
5.001
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7.281
7.288
7.302
7.307
7.313
7.318
7.323
7.328
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7.339
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7.359
7.368
7.371
7.376
7.387
7.392
7.401
17.04
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1.00
1.10
1.11
1.13
0.85
0.15
0.96
1.83
0.15
1.01
1.28
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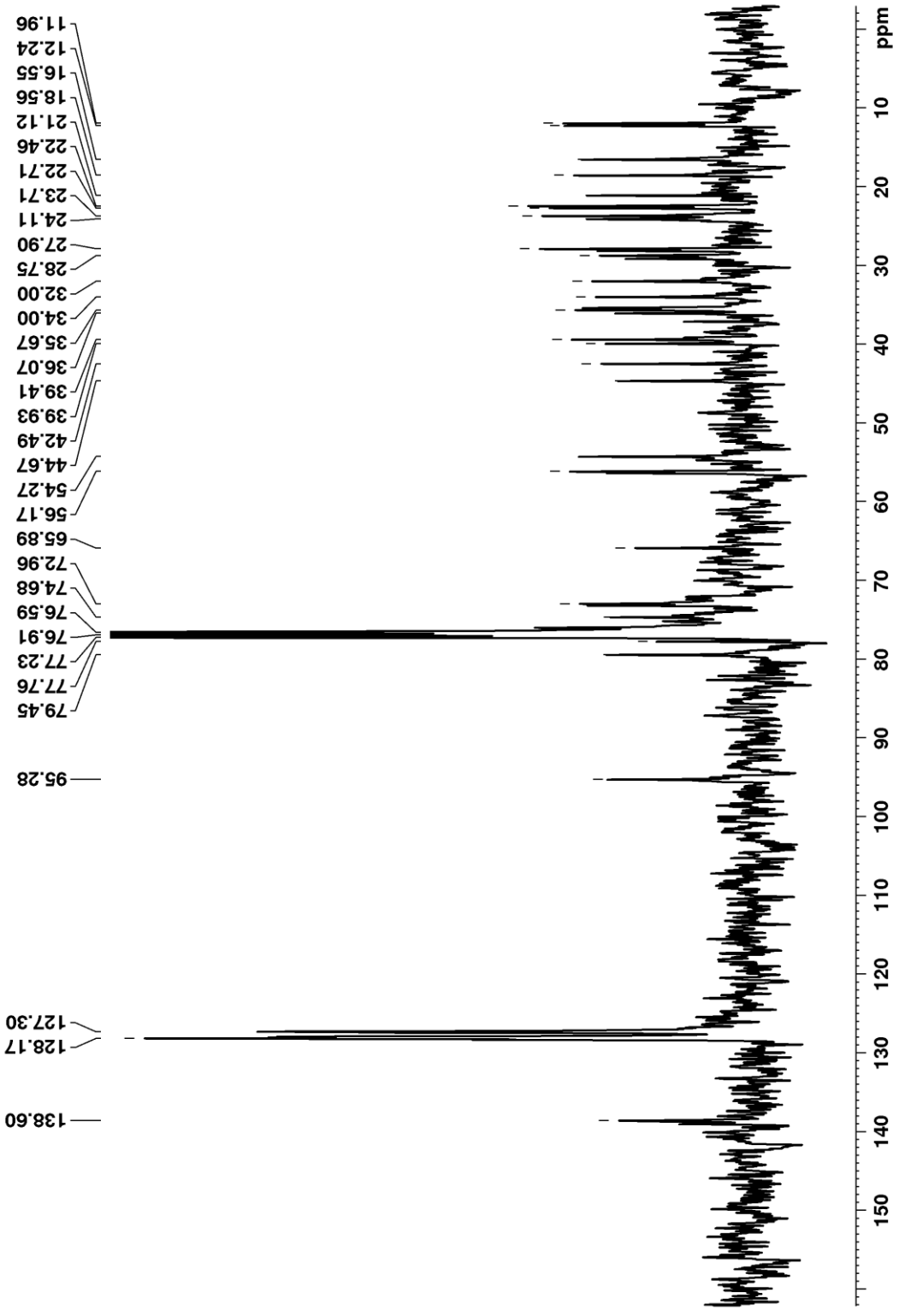
8.0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28.75
32.00
34.00
35.67
36.07
39.41
39.93
42.49
44.67
54.27
56.17
65.89
72.96
74.68
76.59
76.91
77.23
77.76
79.45
95.28
127.30
128.17
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ppm
10
20
30
40
50
60
70
80
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100
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140
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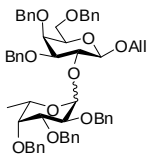
BnO
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BnO
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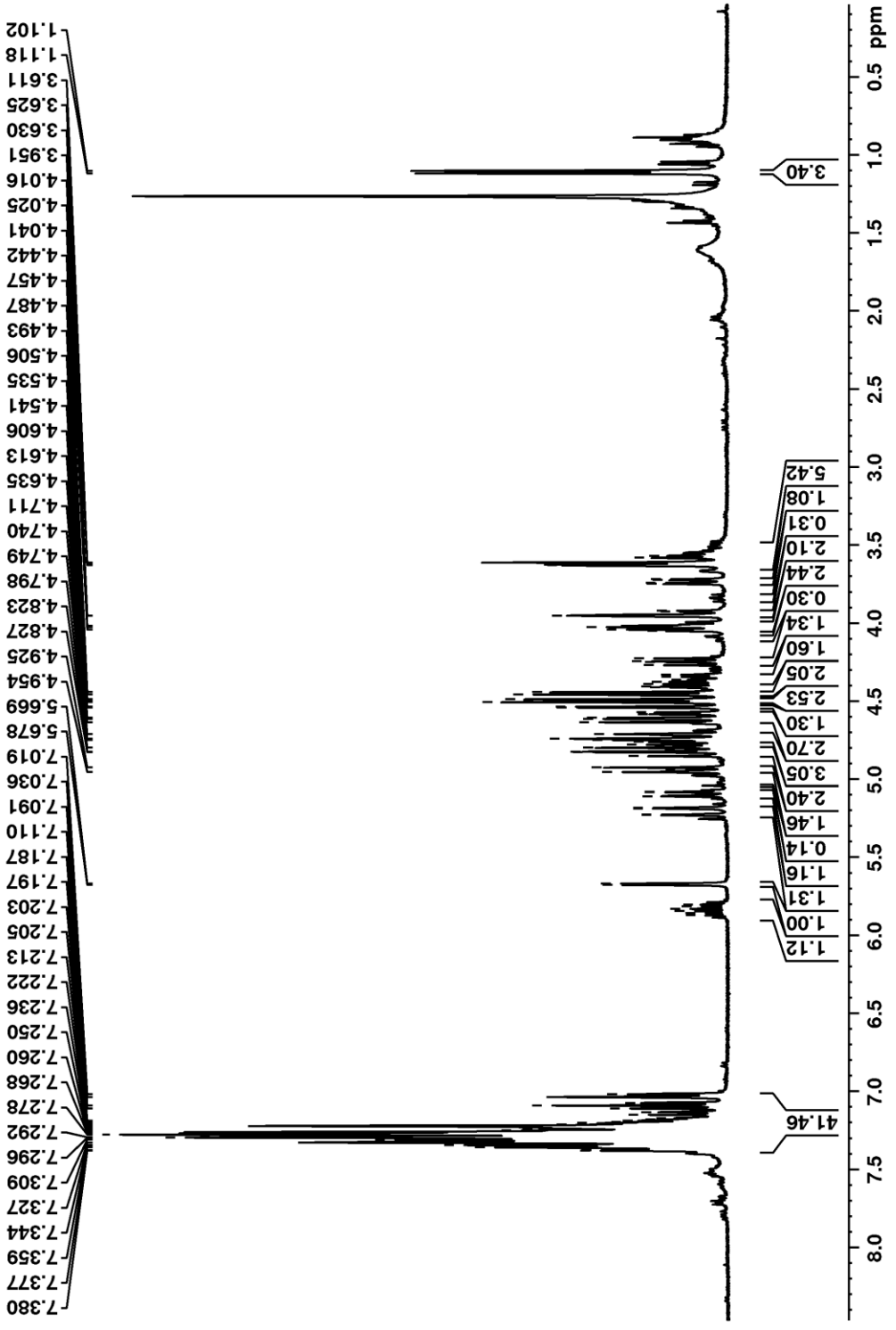
OBn
OBn
OBn

22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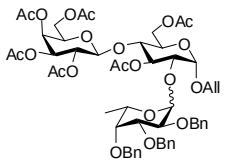
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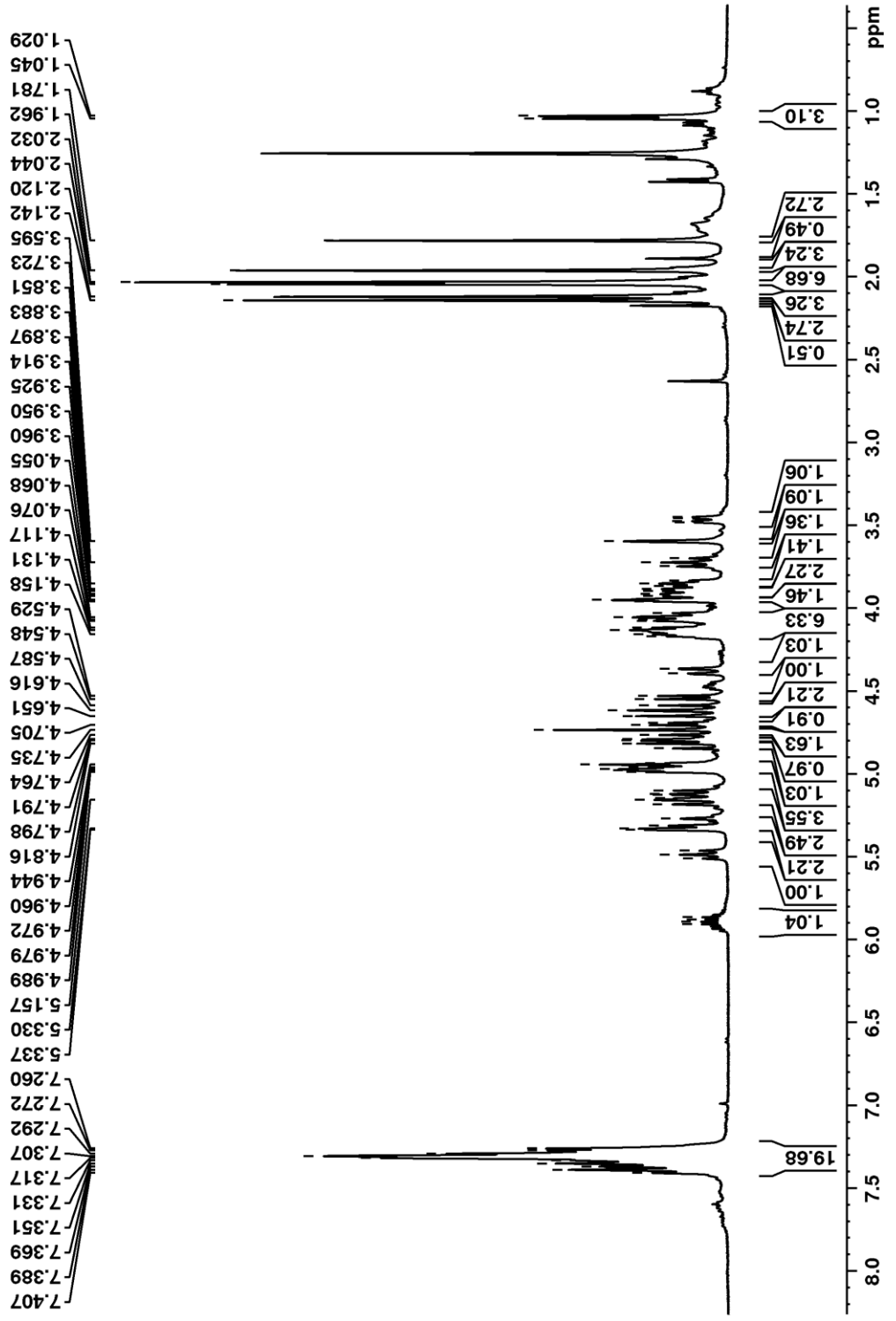
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