Supporting Information for

Electrochemistry of Chalcogenoglycosides. Rational Design of Iterative Glycosylation Based on Reactivity Control of Glycosyl Donors and Acceptors by Oxidation Potentials

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Contents.

1. Preparation of Selenoglycosides.

Typical procedures. Preparation of 1-Phenylseleno-2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (5a). To a solution of diphenyl diselenide (0.57 g, 1.8 mmol) and 2,3,4,6-tetra-*O*-benzoyl-α-D-bromoglucopyranoside (1.98 g, 3.0 mmol) in a 20 mL of 1:1 mixture of CH_3Cl and EtOH was added $NaBH_4$ (0.14 g, 3.6 mmol) at room temperature under nitrogen. Gas evolved, and the resulting solution was stirred for 2.5 h at room temperature. The volatile materials were removed under reduced pressure, and to this mixture was added water and ethyl acetate. The organic phase was separated and was washed with water, saturated aqueous sodium bicarbonate, 5% aqueous sodium hydroxide, and water, succsessively, and was dried over sodium suflate. Solvent was removed under reduced pressure, and recrystallization of the crude mixture from EtOAc/hexane afforded the titled compound in 94% yield (2.06 g). ^{1}H NMR (300 MHz, $CDCl_3$) 4.18 (ddd, *J* = 9.9, 5.2, 2.7 Hz, 1 H), 4.47 (dd, *J* = 12.0, 5.7 Hz, 1 H), 4.68 (dd, *J* = 12.3, 3.0 Hz, 1 H), 5.25 (d, *J* = 10.2 Hz, 1 H), 5.53 (t, *J* = 9.6 Hz, 1 H), 5.62 (t, *J* = 9.9 Hz, 1 H), 5.89 (t, *J* = 9.6 Hz, 1 H), 7.08-7.16 (m, 2 H), 7.20-7.64 (m, 15 H), 7.76-7.84 (m, 2 H), 7.86-7.93 (m, 2 H), 7.94-8.00 (m, 2 H), 8.00-8.08 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) 62.99 (CH_2), 69.15 (CH), 71.16 (CH), 73.92 (CH), 77.26 (CH), 81.28 (CH), 127.70 (C), 128.27 (CH), 128.42 (CH), 128.65 (C), 128.71 (C), 128.98 (CH), 129.14 (C), 129.58 (C), 129.71 (CH), 129.82 (CH), 129.86 (CH), 133.22 (CH), 133.25 (CH), 133.37 (CH), 133.51(CH), 135.21(CH), 165.18 (C=O), 165.24 (C=O), 165.84 (C=O), 166.12 (C=O) ; Anal. Calcd for $C_{40}H_{32}O_9Se$: C, 65.31; H, 4.38. Found: C, 65.18; H, 4.26.

1-*p*-Methylphenylseleno-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (4b). IR (KBr) 1744, 1256, 1227, 1046; ^{1}H NMR (300 MHz, $CDCl_3$) 1.98 (s, 3 H), 2.01 (s, 3 H), 2.08 (s, 6 H), 2.36 (s, 3 H), 3.68 (ddd, *J* = 9.9, 3.9, 3.0 Hz, 1 H), 4.15-4.24 (m, 2 H), 4.83 (d, *J* = 10.2 Hz, 1 H), 4.97 (dd, *J* = 10.2, 9.3 Hz, 1 H), 5.01 (dd, *J* = 9.9, 9.6 Hz, 1 H), 5.18 (dd, *J* = 9.3 Hz, 1 H), 7.10-7.12 (m, 2 H), 7.48-7.51 (m, 2 H) ; ^{13}C NMR (75 MHz, CDC_3) 20.34 (CH_3), 20.55 (CH_3), 20.74 (CH_3), 20.98 (CH_3), 21.15 (CH_3), 61.99 (CH_2), 67.98 (CH), 70.65 (CH), 73.86 (CH), 76.83 (CH), 80.69 (CH),

122.90 (C), 129.77 (CH), 129.92 (CH), 135.69 (CH), 135.80 (CH), 138.84 (C), 139.38 (C=O), 169.49 (C=O), 170.29 (C=O), 170.67 (C=O) ; Anal. Calcd for $C_{21}H_{26}O_9Se$: C, 50.31; H, 5.23. Found: C, 50.19; H, 5.19.

1-*p*-Methoxyphenylseleno-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (4c). IR (KBr) 2940, 1746 (br), 1227 (br), 1042 (br); ^{1}H NMR (300 MHz, $CDCl_3$) 1.98 (s, 3 H), 2.01 (s, 3 H), 2.07 (s, 3 H), 2.09 (s, 3 H), 3.66 (dt, *J* = 10.2, 3.6 Hz, 1 H), 4.18 (d, *J* = 3.6 Hz, 2 H), 4.77 (d, *J* = 9.3 H, 1 H), 4.94 (dd, *J* = 9.9, 9.0 Hz, 1 H), 4.99 (d, *J* = 9.6 Hz, 1 H), 5.17 (t, *J* = 9.3 Hz, 1 H), 6.82-6.87 (m, 2 H), 7.50-7.56 (m, 2 H); ^{13}C NMR (75MHz, $CDCl_3$) 20.39 (CH_3, 2C), 20.62 (CH_3, 2C), 55.12 (CH_3), 61.94 (CH_2), 68.06 (CH), 70.62 (CH), 73.81 (CH), 76.67 (CH), 80.39 (CH), 114.59 (CH, 2C), 116.20 (C), 137.97 (CH, 2C), 160.47 (C), 169.34 (C=O), 169.46 (C=O), 170.25 (C=O), 170.61 (C=O); Anal. Calcd for $C_{21}H_{26}O_{10}Se$: C, 48.75; H, 5.06. Found: C, 48.50; H, 4.87.

1-*p*-Methylphenylseleno-2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (5b). IR (KBr) 1727, 1267, 1111, 1088, 1069, 1026, 710; ^{1}H NMR (300 MHz, $CDCl_3$) 2.27 (s, 3 H), 4.15 (m, 1 H), 4.46 (dd, *J* = 12.0, 5.1 Hz, 1 H), 4.68 (dd, *J* = 12.0, 1.8 Hz, 1 H), 5.18 (d, *J* = 9.9 Hz, 1 H), 5.49 (t, *J* = 9.6 Hz, 1 H), 5.60 (t, *J* = 9.9 Hz, 1 H), 5.87 (t, *J* = 9.3 Hz, 1 H), 6.85 -6.95 (m, 2 H), 7.20-7.65 (m, 14 H), 7.75-7.85 (m, 2 H), 7.85-7.93 (m, 2 H), 7.93-8.00 (m, 2 H), 8.00-8.10 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) 21.11, 62.91, 69.14, 71.19, 73.99, 77.17, 80.99, 122.81, 128.17, 128.30, 128.59, 128.65, 129.11, 129.55, 129.61, 129.70, 129.76, 133.06, 133.12, 133.22, 133.38, 135.64, 138.52, 164.99, 165.06, 165.70, 165.94; Anal. Calcd for $C_{41}H_{34}O_9Se$: C, 65.69; H, 4.57. Found: C, 65.61; H, 4.39.

1-*p*-Methoxylphenylseleno-2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (5c). IR (KBr) 1717 (br), 1267 (br), 1111, 1086, 1068, 1026, 710; ^{1}H NMR (300 MHz, $CDCl_3$) 3.72 (s, 3 H), 4.14 (ddd, *J* = 12.6, 5.1, 2.7 Hz, 1 H), 4.45 (dd, *J* = 12.0, 2.4 Hz, 1 H), 4.69 (dd, *J* = 12.3, 2.7 Hz, 1 H), 5.13 (d, *J* = 10.2 Hz, 1 H), 5.46 (t, *J* = 9.6 Hz, 1 H), 5.58 (t, *J* = 9.6 Hz, 1 H), 5.87 (t, *J* = 9.6 Hz, 1 H), 6.64 (d, *J* = 10.2 Hz, 2 H), 7.22-7.62 (m, 14 H), 7.77-8.06 (m, 8 H); Anal. Calcd for $C_{41}H_{34}$O10Se: C, 64.32; H, 4.48. Found: C, 64.09; H, 4.56.

1-*p*-Dimethylaminophenylseleno-2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (5d). IR (KBr) 3065, 1717 (br), 1267 (br), 1111, 1086, 1068, 1026, 710; ^{1}H NMR (300 MHz, $CDCl^{3}$) 2.88 (s, 6 H), 4.12 (ddd, *J* = 9.9, 7.2, 2.7 Hz, 1 H), 4.45 (dd, *J* = 12.3, 5.7 Hz, 1 H), 4.69 (dd, *J* = 12.3, 3.0 Hz, 1 H), 5.09 (d, *J* = 10.2 Hz, 1 H), 5.47 (t, *J* = 10.2 Hz, 1 H), 5.60 (t, *J* = 9.9 Hz, 1 H), 5.86 (t, *J* = 9.6 Hz, 1 H), 6.42 (d, *J* = 9.0 Hz, 2 H), 7.20-7.60 (m, 14 H), 7.76-7.84 (m, 2 H), 7.86-7.92 (m, 2 H), 7.95-8.02 (m, 2 H), 8.03-8.08 (m, 2 H); ^{13}C NMR (75MHz, $CDCl_3$) d 39.93 (CH_3, 2C), 62.91 (CH_2), 69.23 (CH), 71.19 (CH), 74.15 (CH), 77.05 (CH), 81.04 (CH), 110.73 (C), 112.45 (CH), 128.19 (CH), 128.35 (CH), 128.74 (C), 128.83 (C), 129.39 (C), 129.67 (CH), 129.71 (C), 129.76 (CH), 129.82 (CH), 129.85 (CH), 133..02 (CH), 133.13 (CH), 133.20 (CH), 133.38 (CH), 137.62 (CH), 150.69 (C), 165.09 (C=O), 165.21 (C=O), 165.84 (C=O), 166.07 (C=O); Anal. Calcd for $C_{42}H_{37}O_9NSe$: C, 64.78; H, 4.79; N, 1.80. Found: C, 64.64; H,4.83; N, 1.80.

1-*p*-Methylphenylseleno-2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside (6b). IR (KBr) 1118, 1089, 1046, 1055, 1029, 743, 695; ^{1}H NMR (300 MHz, $CDCl_3$) 2.29 (s, 3 H), 3.45-3.80 (m, 6 H), 4.50-4.90 (m, 9 H), 6.97-6.99 (m, 2 H), 7.18-7.41 (m, 20 H), 7.56-7.59 (m, 2 H); Anal. Calcd for $C_{41}H_{42}O_5Se$: C, 70.87; H, 6.10. Found: C, 71.15; H, 6.13.

2. Preparation of Telluroglycosides.

Typical procedures. Preparation of 1-phenyltelluro-2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (8a). To a solution of diphenyl ditelluride (1.63 g, 4.0 mmol) and 2,3,4,6-*tetra-O*-benzoyl-α-D-bromoglucopyranoside (4.36 g, 6.6 mmol) in a 20 mL of 1:1 mixture of CH_3Cl and EtOH was added $NaBH_4$ (0.35 g, 9.2 mmol) at room temperature under nitrogen. Gas evolved, and the resulting solution was stirred for 2.5 h at room temperature. Solvent was removed under reduced pressure, and $CHCl_3$ (10 mL), water (3 mL), and triethanolamine (0.5 mL) were added to the crude mixture. The resulting mixture was stirred for 0.5 h, and the organic phase was separated. Water layer was extracted with $CHCl_3$, and the combined organic extracts were dried over magnesium sulfate and were concentrated under reduced pressure.

Recrystallization of the crude mixture from EtOAc/hexane afforded the titled compound in 80% yield (4.14 g, 5.3 mmol). Mp 166.2-167.8 ºC; IR (KBr) 3063, 1736 (br), 1725 (br), 1718 (br), 1271 (br), 1263 (br), 111, 1091, 1066, 1026, 708; ^{1}H NMR (300 MHz, $CDCl_3$) 4.10 (ddd, *J* = 9.9, 5.7, 2.7 Hz, 1 H), 4.45 (dd, *J* = 12.3, 5.4 Hz, 1 H), 4.65 (dd, *J* = 12.0 Hz, 2.7 Hz, 1 H), 5.53 (d, *J* = 10.2 Hz, 1 H), 5.57 (t, *J* = 9.0 Hz, 1 H), 5.63 (t, *J* = 9.3 Hz, 1 H), 5.86 (t, *J* = 9.3 Hz, 1 H), 7.02-7.10 (m, 2 H), 7.22-7.62 (m, 13 H), 7.76-7.86 (m, 4 H), 7.86-7.98 (m, 4 H), 7.98-8.06 (m, 2 H); 13C NMR (75 MHz, CDCl3) 63.20 (CH_2), 66.80 (CH), 69.39 (CH), 72.93 (CH), 73.78 (CH), 78.96 (CH), 111.72 (C), 128.34 (CH, 2 C), 128.48 (CH, 6 C), 128.71 (CH), 128.83 (C), 128.91 (C), 129.24 (CH, 2 C), 129.73 (C), 129.29 (CH, 2 C), 129.91 (CH, 4 C), 129.99 (CH, 2 C), 133.22 (CH), 133.28 (CH), 133.47 (CH), 133.52 (CH), 140.07 (CH, 2 C), 165.31 (C=O), 165.47 (C=O), 165.97 (C=O), 166.24 (C=O), one sp^2 quarternaly carbon signal could not be located owing to overlapping with other signals, Anal. Calcd for $C_{40}H_{32}O_9Te$: C, 61.50; H, 4.03. Found: C, 61.26; H, 4.11.

1-Phenyltelluro-2,3,4,6-tetra-*O* -acetyl-β-D-glucopyranoside (7a). IR (KBr) 1745 (br), 1229, 1078, 733, 692. ^{1}H NMR (300 MHz, $CDCl_3$) 1.98 (s, 3 H), 2.01 (s, 3 H), 2.04 (s, 3 H), 2.07 (s, 3 H), 3.63 (ddd, *J* = 9.9, 4.5, 3.0 Hz, 1 H), 4.12-4.22 (m, 2 H), 5.01-5.20 (m, 4 H), 7.23-7.40(m, 3 H), 7.82-7.85 (m, 2 H); 13C NMR (75 MHz, CDC_3) 20.37 (CH_3), 20.40 (CH_3), 20.52 (CH_3), 20.66 (CH_3), 62.00 (CH_2), 66.36 (CH), 68.10 (CH), 72.19 (CH), 73.42 (CH), 78.26 (CH), 111.34 (C), 128.74 (CH), 129.18 (CH, 2C), 140.02 (CH, 2C), 169.44 (C=O), 169.49 (C=O), 170.23 (C=O), 170.61 (C=O); Anal. Calcd for $C_{20}H_{24}O_9Te$: C, 44.61; H, 4.50. Found: C, 44.54; H, 4.47.

1-*p*-Methylphenyltelluro-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (7b). IR (KBr) 1745 (br), 1379, 1254, 1229 (br), 1042, 914, 804; ^{1}H NMR (300 MHz, $CDCl_3$) 1.98 (s, 3 H), 2.01 (s, 3 H), 2.05 (s, 3 H), 2.07 (s, 3 H), 2.37 (s, 3 H), 3.62 (ddd, *J* = 9.9, 4.5, 3.3 Hz, 1 H), 4.15-4.23 (m, 2 H), 4.98-5.20 (m, 4 H), 7.07 (d, *J* = 7.8 Hz, 2 H), 7.72 (d, *J* = 7.8 Hz, 2 H); ^{13}C NMR (75 MHz, CDC_3) 20.46 (CH_3), 20.49 (CH_3), 20.60 (CH_3), 20.77 (CH_3), 21.21 ($CH_3$3), 62.12 (CH_2), 66.32 (CH), 68.24 (CH), 72.29 (CH), 73.57 (CH), 78.32 (CH), 107.23 (C), 130.21 (CH, 2 C), 139.06 (C), 140.49 (CH, 2 C), 169.56 (C=O, 2 C), 170.35 (C=O), 170.72 (C=O); HRMS (FAB) *m/z*: Calcd for $C_{21}H_{26}O_9Te$

(M - H)$^+$, 551.0561; Found 551.0564; Anal. Calcd for $C_{21}H_{26}O_9Te$: C, 45.65; H, 4.75. Found: C, 45.95; H, 4.75.

1-*p*-Methylphenyltelluro-2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (8b). mp 160-164 ºC; IR (KBr) 3063, 1725 (br), 1269 (br), 1109, 1092, 1069, 1026, 708; ^{1}H NMR (300 MHz, $CDCl_3$) 2.27 (s, 3 H), 4.07 (ddd, *J* = 9.9, 7.2, 3.0 Hz, 1 H), 4.44 (dd, *J* = 12.3, 5.7 Hz, 1 H), 4.66 (dd, *J* = 12.3, 2.7 Hz, 1 H), 5.46 (d, *J* = 10.5 Hz, 1 H), 5.55 (dd, *J* = 10.5, 8.7 Hz, 1 H), 5.62 (t, *J* = 9.6 Hz, 1 H), 5.84 (t, *J* = 9.3 Hz, 1 H), 6.82-6.90 (m, 2 H), 7.20-7.64 (m, 12 H), 7.66-7.72 (m, 2 H), 7.76-7.82 (m, 2 H), 7.86-7.92 (m, 2 H), 7.92-7.98 (m, 2 H), 8.00-8.06 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) 21.18 (CH_3), 63.19 (CH_2), 66.46 (CH), 69.41 (CH), 72.96 (CH), 73.86 (CH), 78.88 (CH), 107.49 (C), 128.33 (CH, 2 C), 128.47 (CH, C, 6 C), 128.88 (C), 128.95 (C), 129.33 (C), 129.8 (CH, 2 C), 129.91 (CH, 2 C), 129.95 (CH, 2 C), 130.00 (CH, 2 C), 130.19 (CH, 2 C), 133.19 (CH), 133.26 (CH), 133.40 (CH), 133.51 (CH), 138.88 (C), 140.48 (CH, 2 C), 165.33 (C=O), 165.43 (C=O), 166.00 (C=O), 166.25 (C=O), one sp^2 quarternaly carbon signal could not be located owing to overlapping with other signals; HRMS (FAB) *m/z*: Calcd for $C_{41}H_{34}O_9Te$ (M + H)$^+$, 801.1343; Found 801.1360; Anal. Calcd for $C_{41}H_{34}O_9Te$: C, 61.69; H, 4.29. Found: C, 61.40; H, 4.16.

1-*p*-Methoxylphenyltelluro-2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (8c). IR (KBr) 2957, 1726 (br), 1275 (br), 1248, 1111, 1090, 1068, 1026, 710; ^{1}H NMR (300 MHz, $CDCl_3$) 4.08 (ddd, *J* = 9.9, 7.2, 2.7 Hz, 1 H), 4.44 (dd, *J* = 12.0, 5.1 Hz, 1 H), 4.66 (dd, *J* = 9.3, 3.0 Hz, 1 H), 5.42 (d, *J* = 10.5 Hz, 1 H), 5.53 (t, *J* = 9.6 Hz, 1 H), 5.61 (t, *J* = 9.6 Hz, 1 H), 5.84 (t, *J* = 9.0 Hz, 1 H), 6.55-6.64 (m, 2 H), 7.20-7.66 (m, 12 H), 7.70-7.76 (m, 2 H), 7.76-7.84 (m, 2 H), 7.84-7.92 (m, 2 H), 7.92-8.00 (m, 2 H), 8.00-8.10 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) 54.94 (CH_3), 63.02 (CH_2), 66.22 (CH), 69.27 (CH), 72.81 (CH), 73.77 (CH), 78.75 (CH), 100.53 (C), 111.81 (C), 115.09 (CH), 128.28 (CH), 128.42 (CH), 128.77 (C), 128.85 (C), 129.24 (C), 129.73 (CH), 129.83 (CH), 129.86 (CH), 129.92 (CH), 133.17 (CH), 133.22 (CH), 133.37 (CH), 133.48 (CH), 142.37 (CH), 160.42 (C), 165.25 (C=O), 165.36 (C=O), 165.92 (C=O), 166.16 (C=O); Anal. Calcd for $C_{41}H_{34}O_{10}Te$: C, 60.47; H, 4.21. Found: C, 60.25; H, 4.02.

1-*p*-Dimethylaminophenyltelluro-2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (8d). IR (KBr) 3065, 1739 (br), 1722 (br), 1715 (br), 1590, 1270 (br), 1111, 1096, 1069, 1026, 710; ^{1}H NMR (300 MHz, $CDCl_3$) 2.89 (s, 6 H), 4.07 (ddd, *J* = 9.9, 5.4, 2.7 Hz, 1 H), 4.44 (dd, *J* = 12.0, 5.1 Hz, 1 H), 4.66 (dd, *J* = 12.0, 2.7 Hz, 1 H), 5.37 (d, *J* = 10.5 Hz, 1 H), 5.53 (dd, *J* = 10.5, 9.3 Hz, 1 H), 5.61 (t, *J* = 6.9 Hz, 1 H), 5.82 (t, *J* = 9.3 Hz, 1 H), 6.40 (d, *J* = 9.3 Hz, 2 H), 7.21-7.70 (m, 14 H), 7.76-7.84 (m, 2 H), 7.86-7.92 (m, 2 H), 7.92-7.99 (m, 2 H), 8.02-8.08 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) 39.88 (CH_3, 2C), 63.12 (CH_2), 66.33 (CH), 69.38 (CH), 72.80 (CH), 73.86 (CH), 78.64 (CH), 94.72 (C), 113.00 (CH), 128.24 (CH),128.37 (CH), 128.80 (C), 128.89 (C), 129.38 (C), 129.70 (CH), 129.74 (CH), 129.80 (CH), 129.88 (CH), 133.04 (CH), 133.14 (CH), 133.25 (CH), 133.40 (CH), 142.12 (CH), 150.69 (C), 165.25 (C=O), 165.28 (C=O), 165.90 (C=O), 166.15 (C=O); Anal. Calcd for $C_{42}H_{37}O_9NTe$: C, 60.97; H, 4.51; N, 1.69. Found: C, 60.46; H, 4.51; N, 1.64.

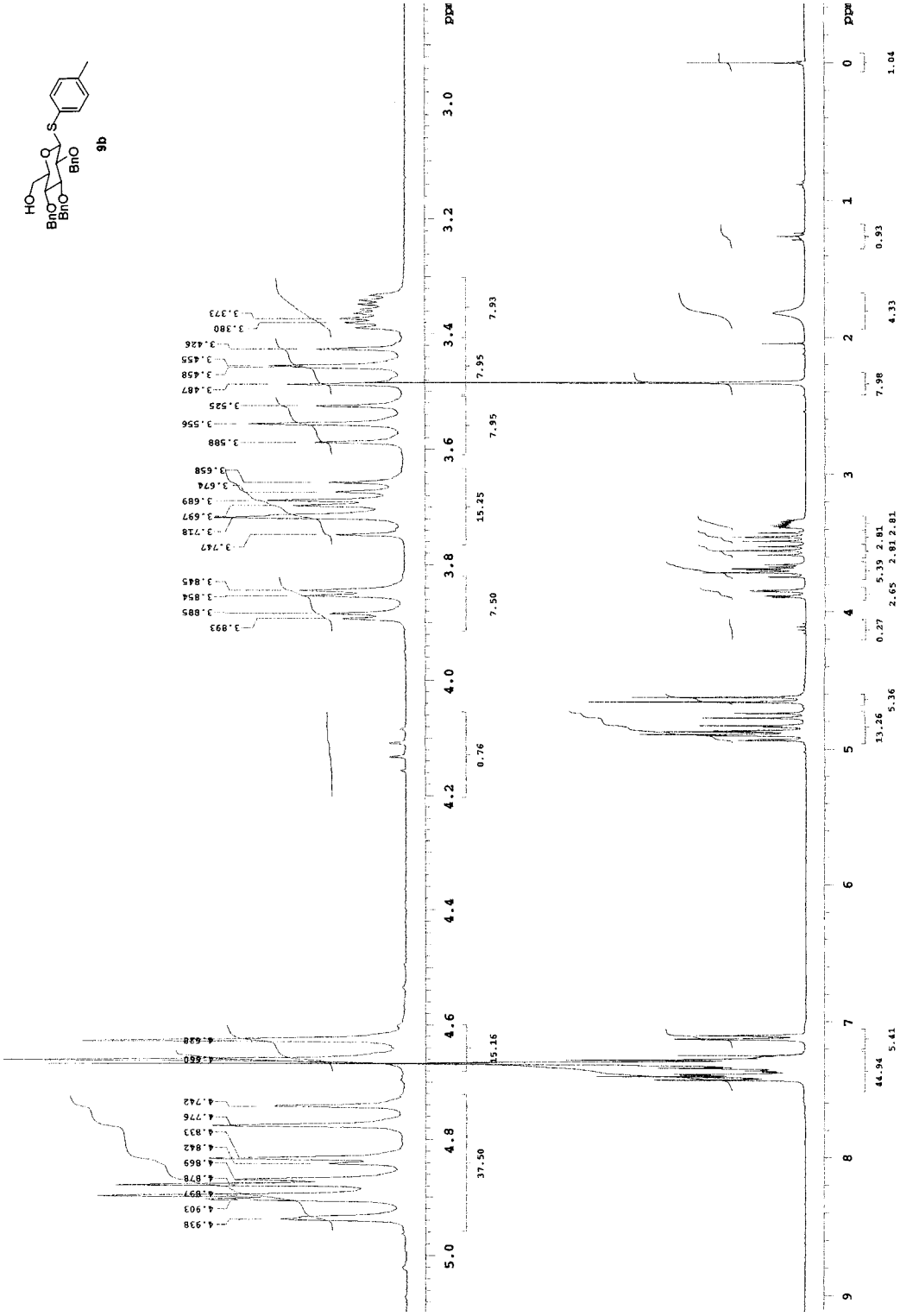
1-*p*-Methylphenylthio-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (9b). IR (KBr) 3503, 1091, 1049, 1032, 735; ^{1}H NMR (300 MHz, $CDCl_3$) 2.34 (s, 3 H), 3.66 (ddd, *J* = 9.5, 4.8, 2.7 Hz, 1 H), 3.46 (dd, *J* = 9.6, 8.7 Hz, 1 H), 3.56 (t, *J* = 9.6 Hz,1 H), 3.64-3.76 (m, 2 H), 3.87 (dd, *J* = 12.0, 2.7 Hz, 1 H), 4.64 (d, *J* = 9.6 Hz, 2 H), 4.76 (d, *J* = 10.2 Hz, 1 H), 4.82-4.95 (m, 4 H), 7.12 (d, *J* = 9.3 Hz, 2 H), 7.24-7.45 (m, 17 H); ^{13}C NMR (75 MHz, $CDCl_3$) 21.13, 62.12, 75.12, 75.50, 75.82, 77.58, 79.20, 81.04, 86.54, 87.78, 127.76, 127.79, 127.91, 127.97, 128.03, 128.21, 128.44, 128.47, 128.52, 129.38, 129.79, 132.65, 137.79, 137.92, 138.05, 138.28; HRMS (FAB) *m/z*: Calcd for $C_{34}H_{36}O_5S$ $(M + H)^+$, 557.2361; Found 557.2369.

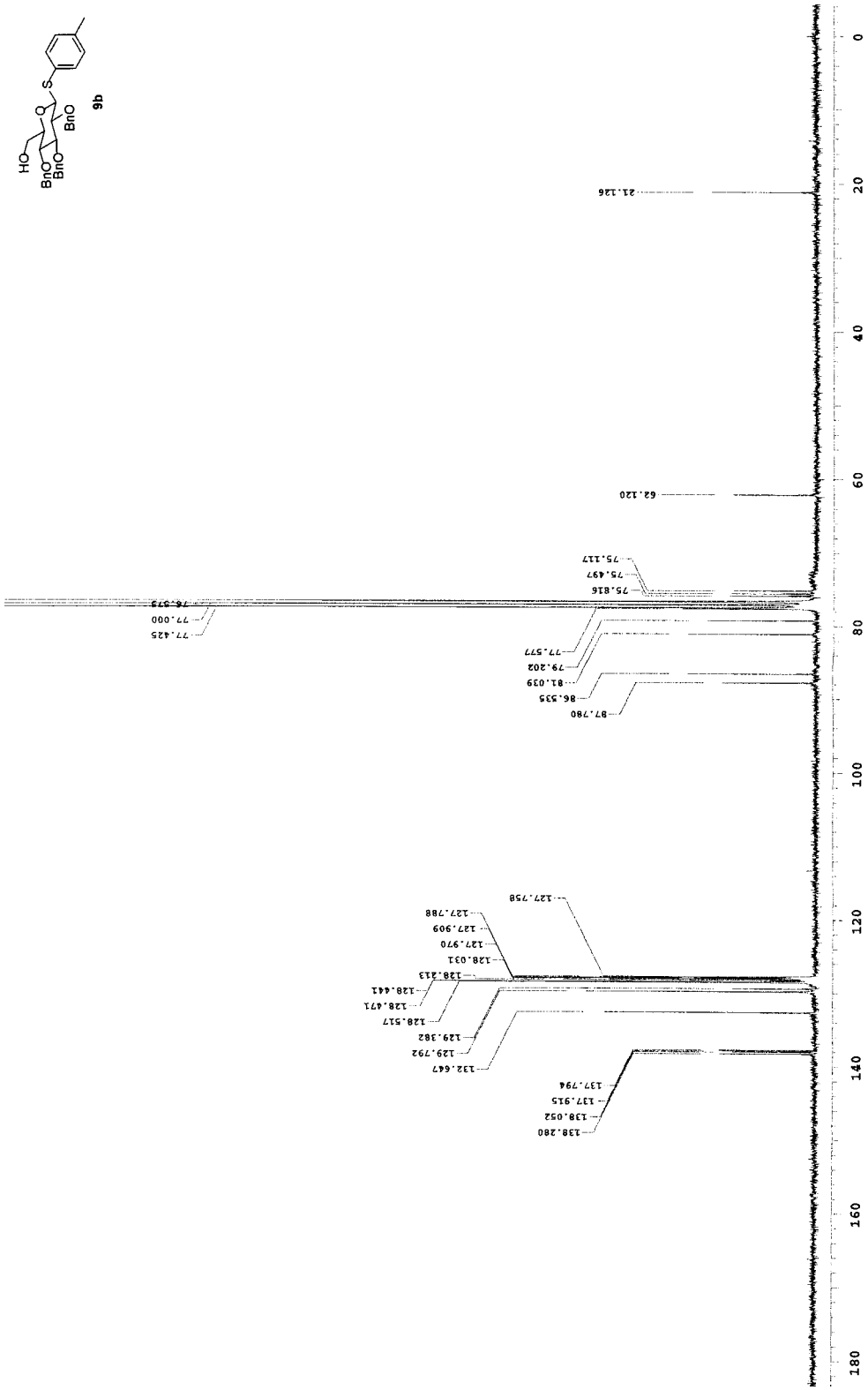
1-*p*-Methylphenylseleno-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (10b). IR (KBr) 3360, 1069, 695; ^{1}H NMR (300 MHz, $CDCl_3$) 1.98 (br t, *J* = 6.3 Hz, 1 H, OH), 2.33 (s, 3 H), 3.34 (ddd, *J* = 9.6, 5.0, 2.6 Hz, 1 H), 3.47 (dd, *J* = 9.6, 9.0 Hz, 1 H), 3.53 (t, *J* = 9.0 Hz, 1 H), 3.62 – 3.72 (m, 1 H), 3.69 (t, *J* = 9.0 Hz, 1 H), 3.86 (br d, *J* = 11.7 Hz, 1 H), 4.63 (d, *J* = 11.1 Hz, 1 H), 4.76 (d, *J* = 10.2 Hz, 1 H), 4.78 – 5.02 (m, 5 H), 7.09 (d, *J* = 7.8 Hz, 2 H), 7.22 – 7.42 (m, 15 H), 7.52 (d, *J* = 7.8 Hz, 2 H); 13C NMR (75 MHz, $CDCl_3$) 21.13, 62.00, 75.07, 75.24, 75.74, 77.53, 80.26, 81.45, 82.68,

86.58, 124.05, 127.76, 127.88, 127.91, 127.96, 128.20, 128.38, 128,44, 129.87; HRMS (FAB) *m/z*: Calcd for $C_{34}H_{36}O_5Se$ $(M + H)^+$, 605.1806; Found 605.1791.

1-*p*-Methylphenyltelluro-6-*O*-acetyl-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (11). IR (KBr) 1744, 1242, 1130, 1089, 1067, 695; ^{1}H NMR (300 MHz, $CDCl_3$) 2.05 (s, 3H), 2.35 (s, 3H), 3.74-3.54 (m, 3H), 3.68 (t, *J* = 8.7 Hz, 1H), 4.19 (dd, *J* = 11.7, 4.5 Hz, 1H), 4.36 (dd, *J* = 12.0, 1.8 Hz, 1H), 4.56 (d, *J* = 11.1 Hz, 1H), 4.75-4.93 (m, 5H), 5.05 (d, *J* = 10.2 Hz, 1H), 7.01-7.04 (m, 2H), 7.25-7.38 (m, 15H), 7.72-7.75 (m, 2H); ^{13}C NMR (75 MHz, CDC_3) 20.71 (CH_3), 21.13 (CH_3), 63.08 (CH_2), 68.00 (CH), 74.97 (CH_2), 75.06 (CH_2), 75.69 (CH_2), 77.50 (CH), 79.22 (CH), 82.02 (CH), 86.91 (CH), 107.61 (C), 127.84 (CH), 127.99 (CH), 128.06 (CH), 128.18 (CH), 128.36 (CH), 128.48 (CH), 128.56 (CH), 130.05 (CH), 137.64 (C), 137.79 (C), 138.15 (C), 138.41 (C), 140.02 (CH), 170.75 (C=O); HRMS (FAB) *m/z*: Calcd for $C_{36}H_{38}O_6Te$ $(M + H)^+$, 697.1809; Found 697.1810.

3. ^{1}H and ^{13}C NMR spectra of selected compounds.

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BnO
O
BnO
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128.517
128.471
128.441
128.213
128.031
127.970
127.909
127.788
127.758
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81.039
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77.425
77.000
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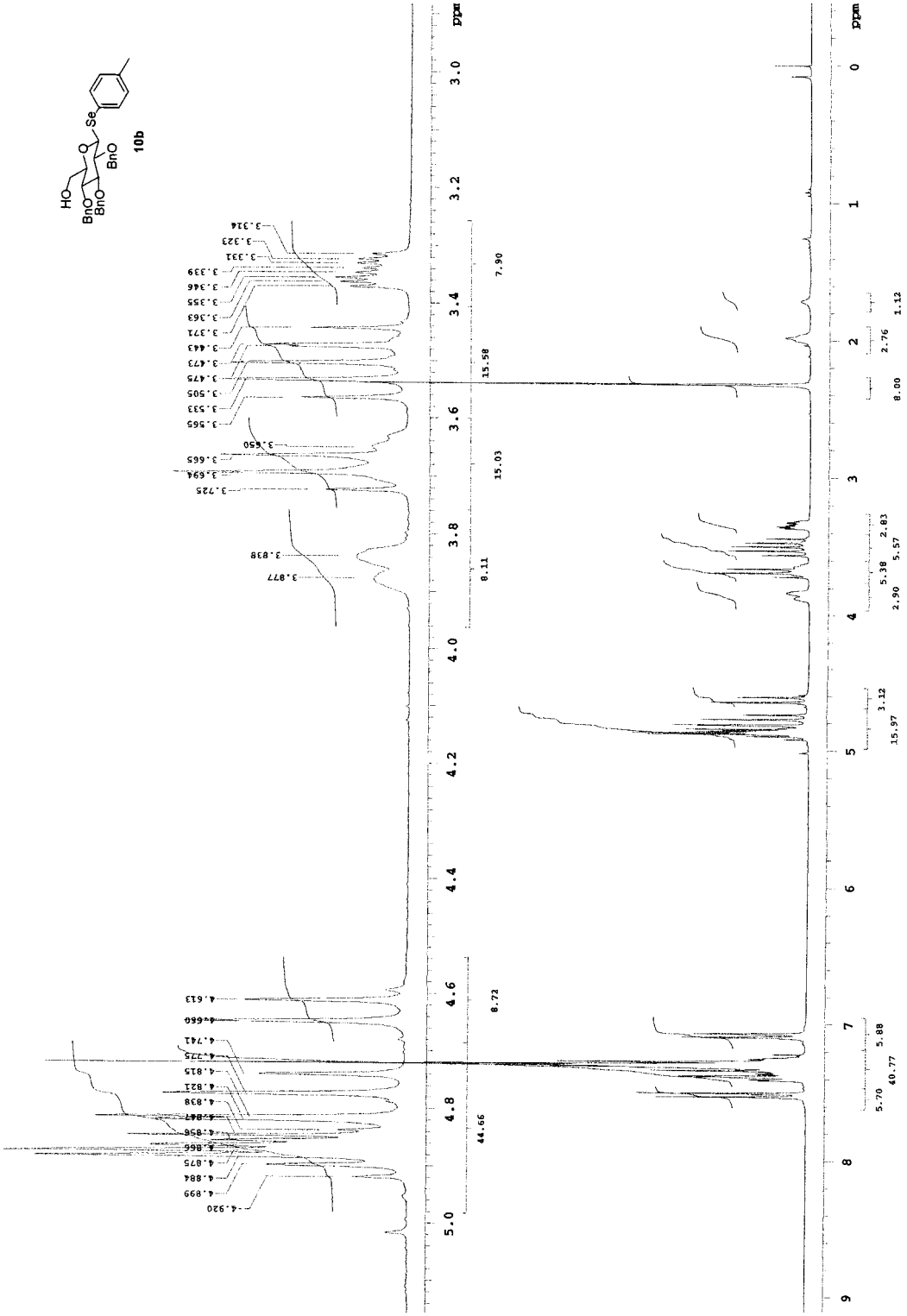
80
100
120
140
160
180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BnO
BnO
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4.775
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3.877
3.838
3.725
3.694
3.665
3.650
3.565
3.533
3.505
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3.473
3.443
3.371
3.363
3.355
3.346
3.339
3.331
3.323
3.314
44.66
8.72
8.11
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7.90
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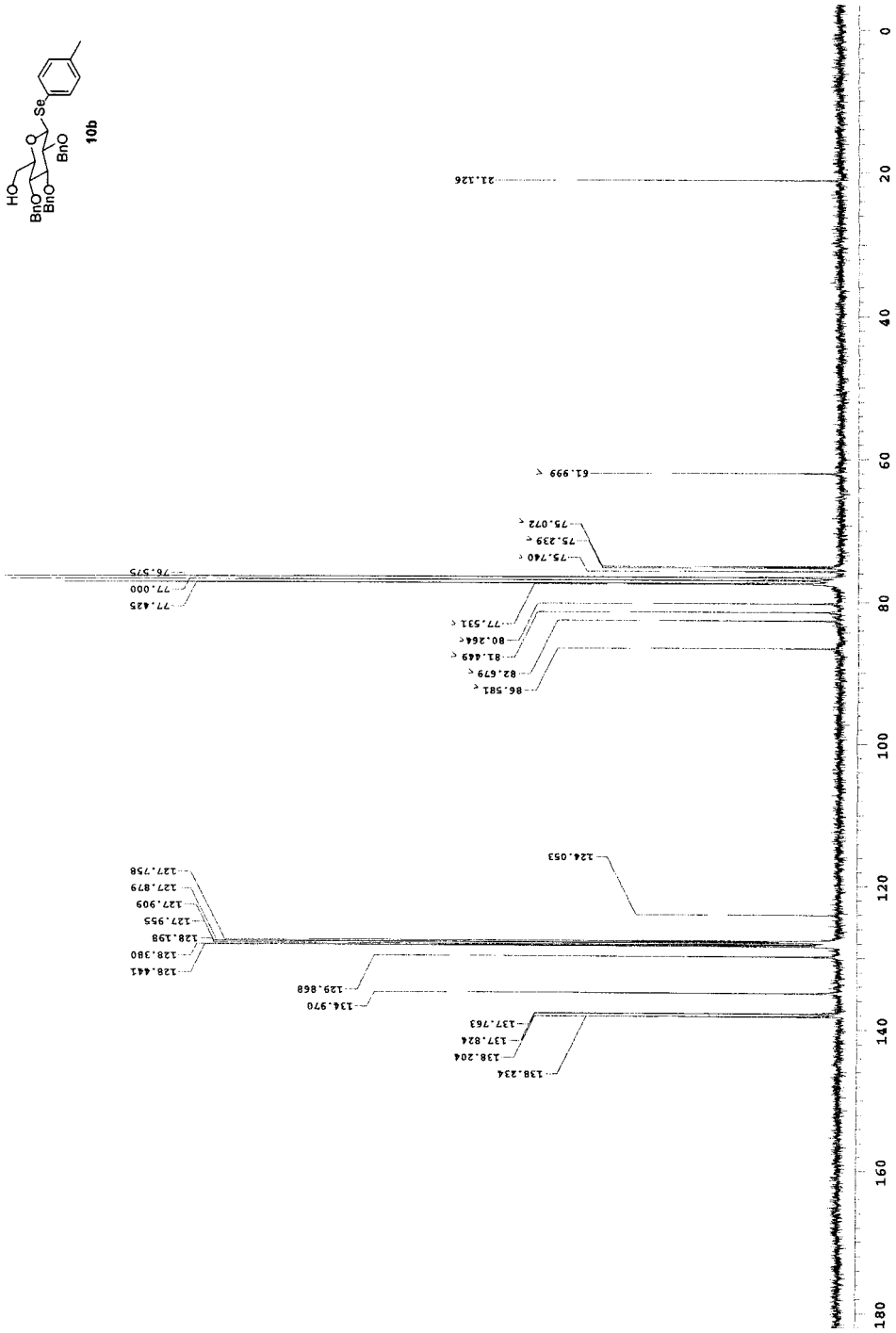
2.76
1.12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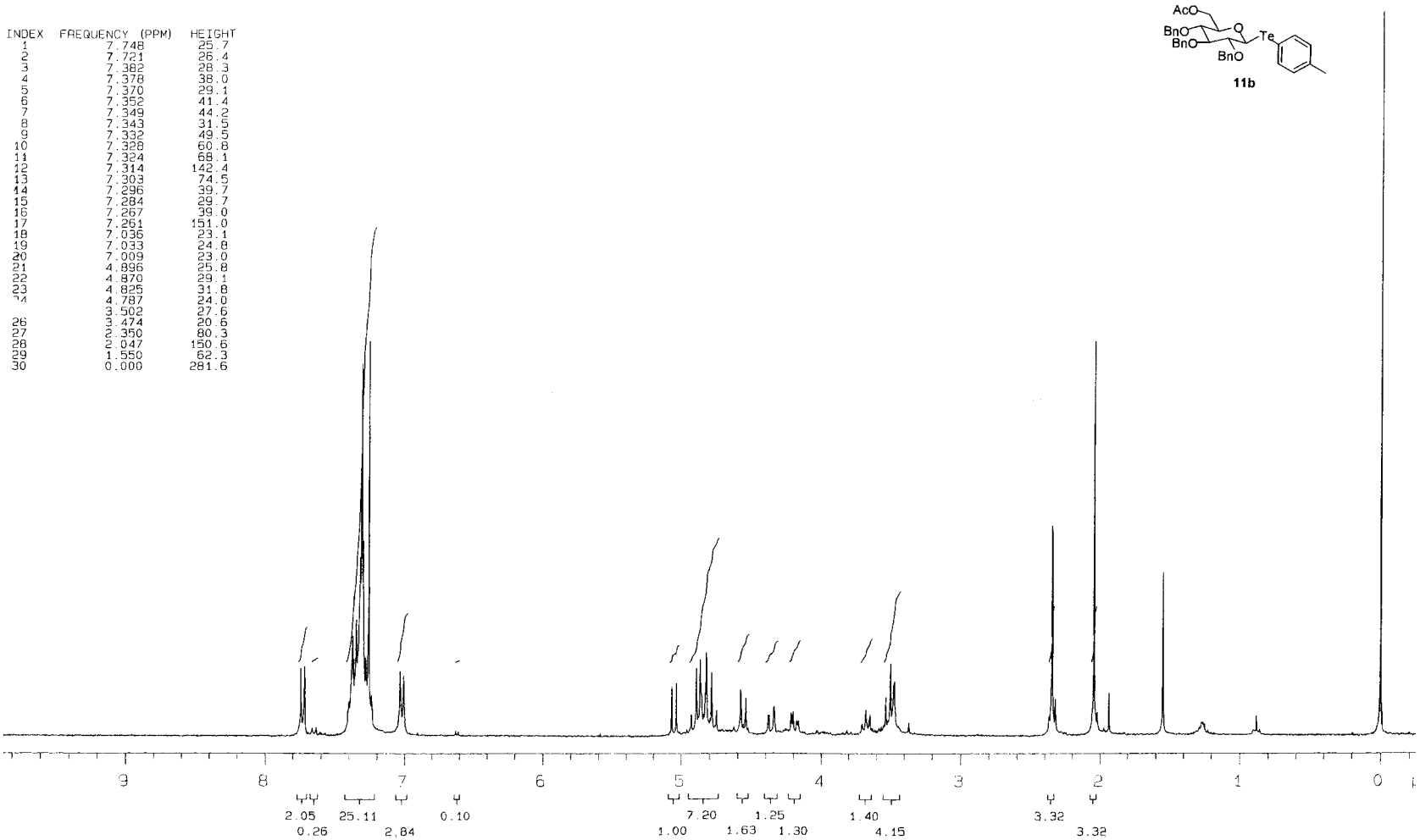

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3	7.382	28.3
4	7.378	38.0
5	7.370	29.1
6	7.352	41.4
7	7.349	44.2
8	7.343	31.5
9	7.332	49.5
10	7.328	60.8
11	7.324	68.1
12	7.314	142.4
13	7.303	74.5
14	7.296	39.7
15	7.284	29.7
16	7.267	39.0
17	7.261	151.0
18	7.036	23.1
19	7.033	24.8
20	7.009	23.0
21	4.896	25.8
22	4.870	29.1
23	4.825	31.8
24	4.787	24.0
	3.502	27.6
26	3.474	20.6
27	2.350	80.3
28	2.047	150.6
29	1.550	62.3
30	0.000	281.6

INDEX	FREQUENCY (PPM)	HEIGHT
1	170.748	24.2
2	140.020	79.5
3	139.838	8.7
4	138.411	22.3
5	138.153	18.7
6	137.788	26.0
7	137.636	19.5
8	130.045	91.3
9	128.558	178.0
10	128.482	121.7
11	128.360	99.1
12	128.178	22.2
13	128.057	146.4
14	127.996	74.9
15	127.844	88.7
16	107.607	14.9
17	86.914	41.4
18	82.025	33.6
19	79.217	35.0
20	77.501	39.2
21	77.425	51.9
22	77.000	50.2
23	76.575	48.5
24	75.694	46.9
[illegible]	75.057	50.7
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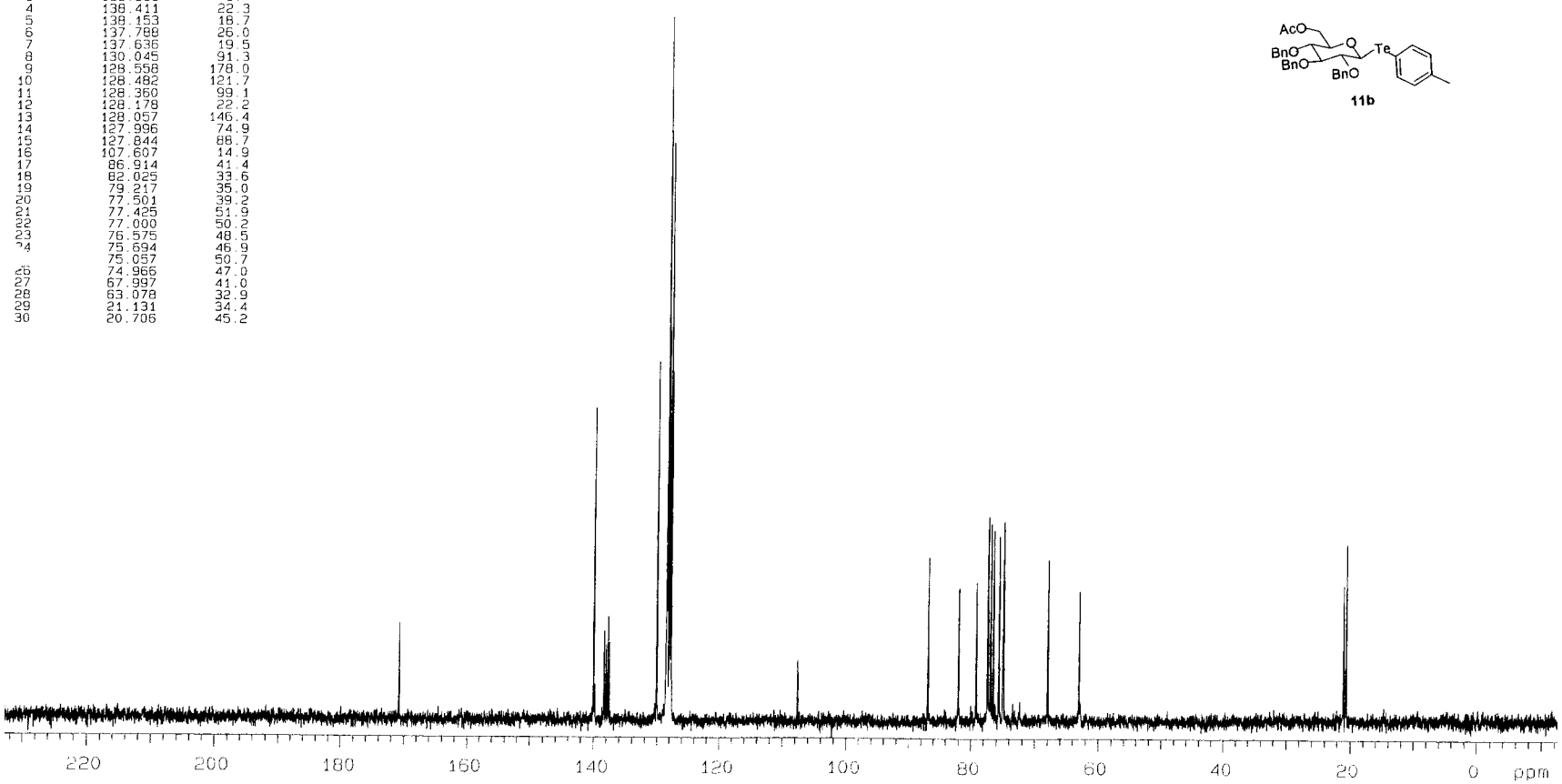
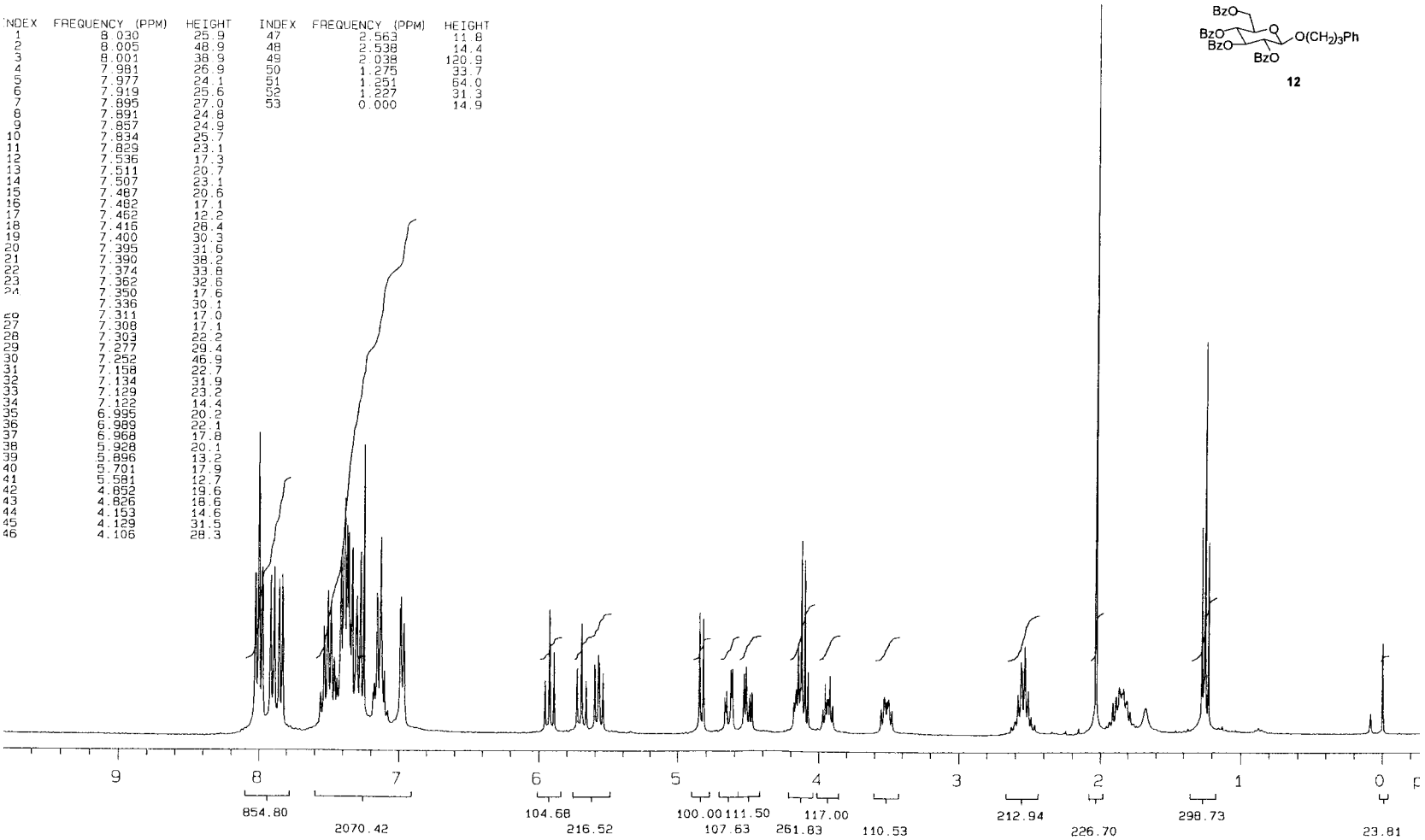
29	21.131	34.4
30	20.706	45.2



11b



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3	8.001	38.9	49	2.038	120.9
4	7.981	25.9	50	1.275	33.7
5	7.977	24.1	51	1.251	64.0
6	7.919	25.6	52	1.227	31.3
7	7.895	27.0	53	0.000	14.9
8	7.891	24.8			
9	7.857	24.9			
10	7.834	25.7			
11	7.829	23.1			
12	7.536	17.3			
13	7.511	20.7			
14	7.507	23.1			
15	7.487	20.6			
16	7.482	17.1			
17	7.462	12.2			
18	7.416	28.4			
19	7.400	30.3			
20	7.395	31.6			
21	7.390	38.2			
22	7.374	33.8			
23	7.362	32.6			
24	7.350	17.6			
	7.336	30.1			
26	7.311	17.0			
27	7.308	17.1			
28	7.303	22.2			
29	7.277	29.4			
30	7.252	46.9			
31	7.158	22.7			
32	7.134	31.9			
33	7.129	23.2			
34	7.122	14.4			
35	6.995	20.2			
36	6.989	22.1			
37	6.968	17.8			
38	5.928	20.1			
39	5.896	13.2			
40	5.701	17.9			
41	5.581	12.7			
42	4.852	19.6			
43	4.826	18.6			
44	4.153	14.6			
45	4.129	31.5			
46	4.106	28.3			

INDEX	FREQUENCY (PPM)	HEIGHT
1	166.269	13.2
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3	165.313	15.3
4	165.207	9.9
5	141.477	11.8
6	133.477	25.7
7	133.294	44.8
8	133.173	24.3
9	129.863	83.2
10	129.833	92.9
11	129.803	86.3
12	129.772	78.3
13	129.636	14.3
14	129.362	11.4
15	128.861	18.5
16	128.451	150.1
17	128.406	83.6
18	128.345	61.6
19	128.254	65.2
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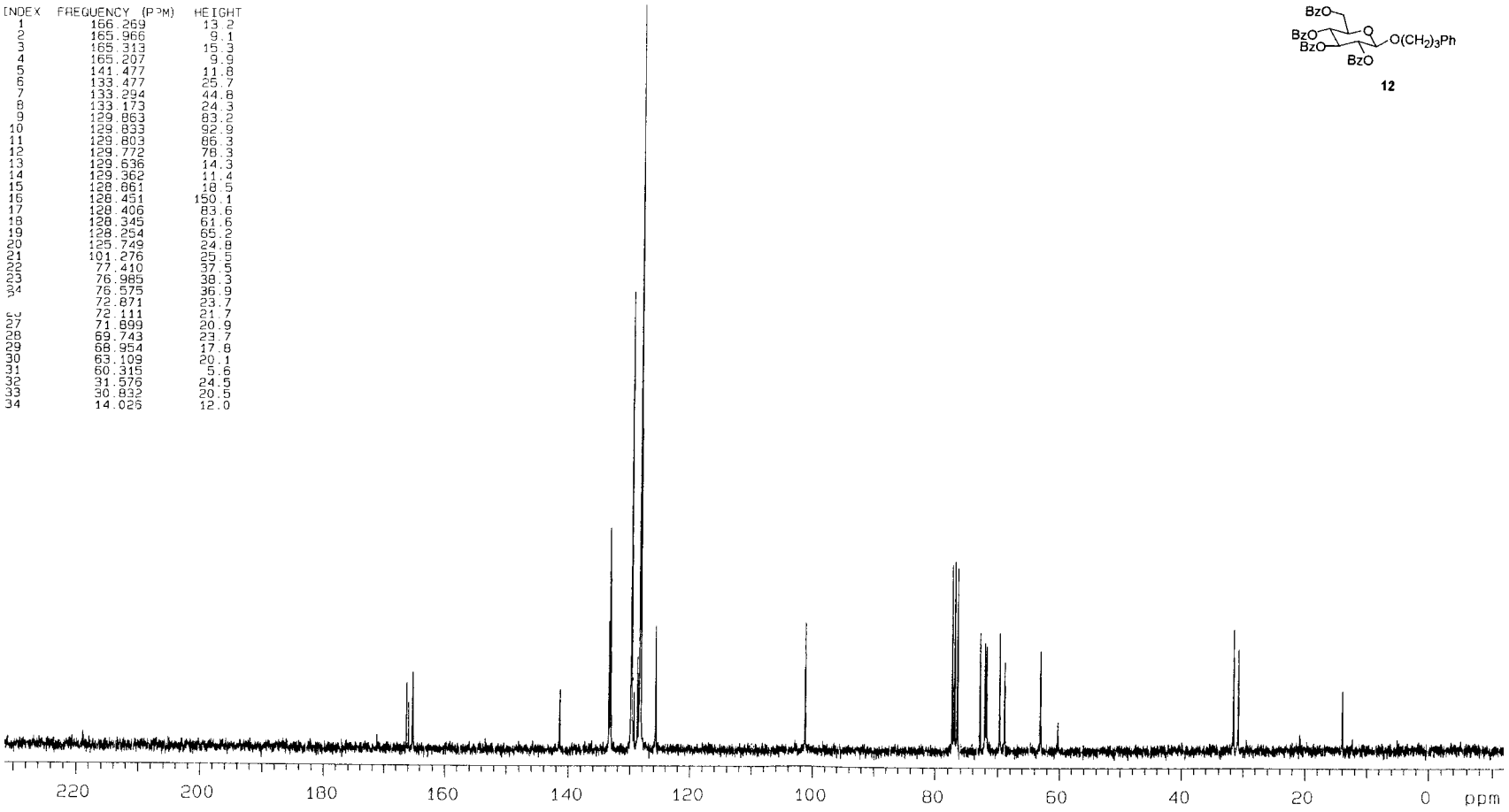
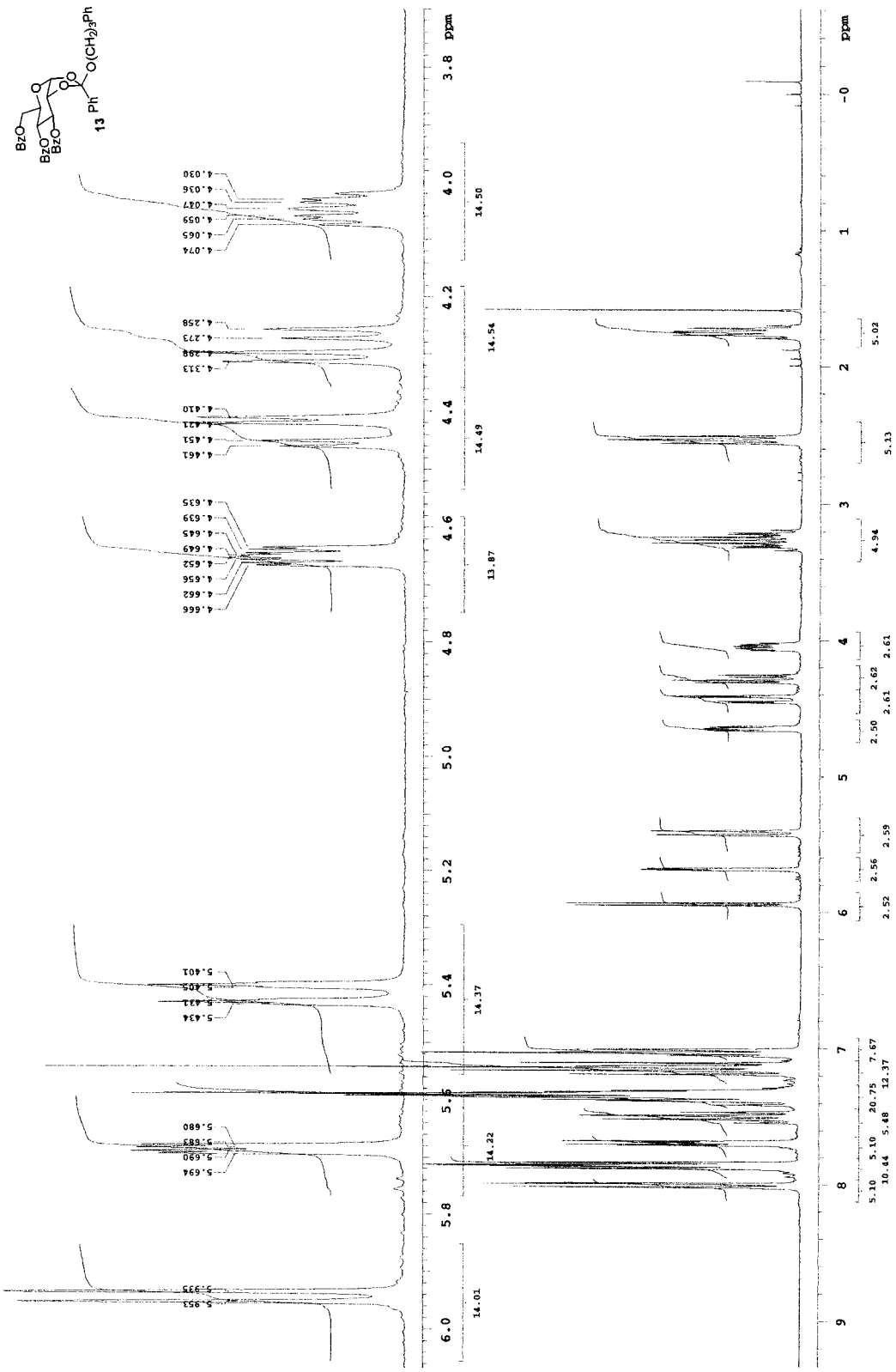
33	30.832	20.5
34	14.026	12.0



12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BzO
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O
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Ph
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12.37
7.67
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2.56
2.59
2.50
2.62
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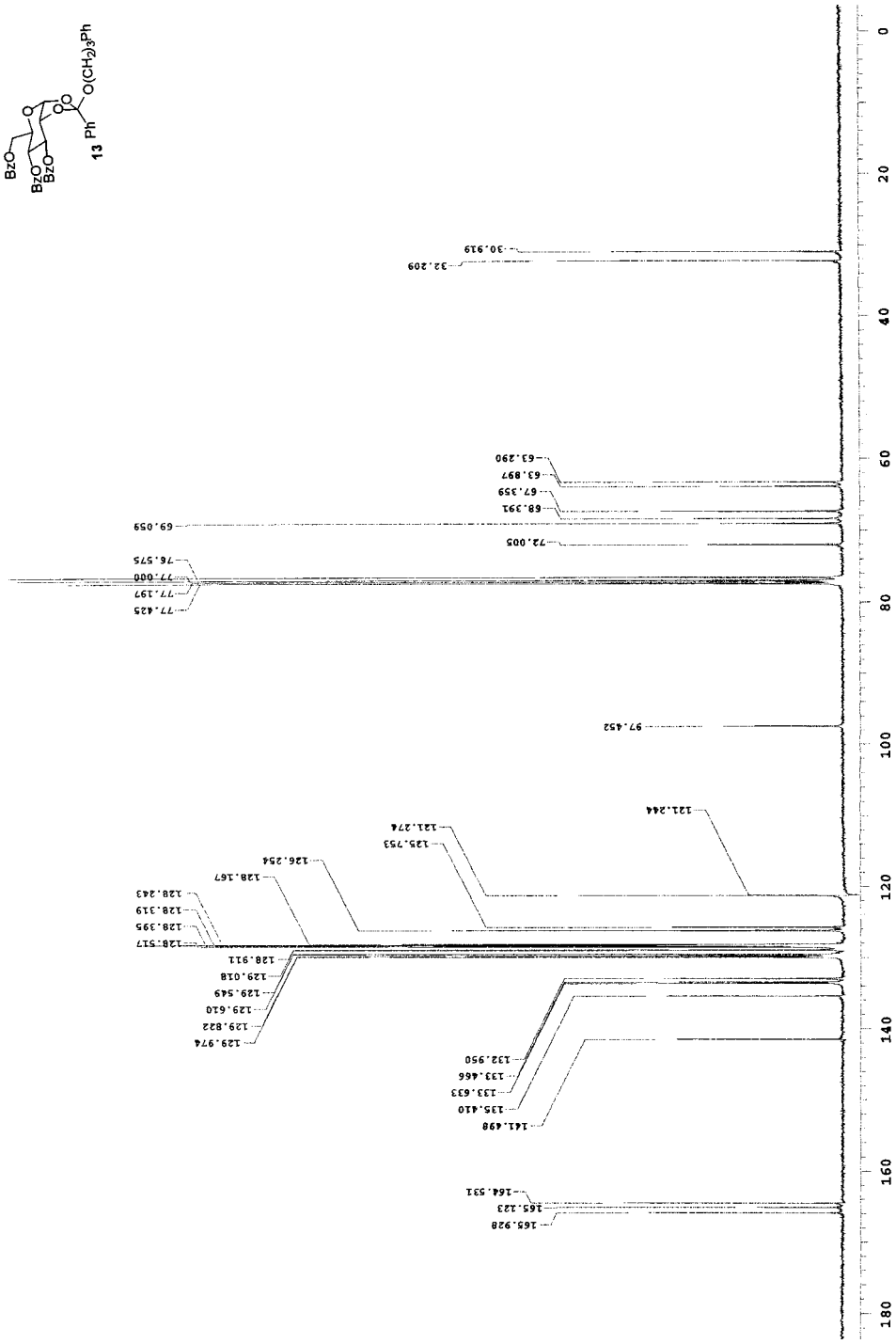
14.54
14.50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BzO
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140
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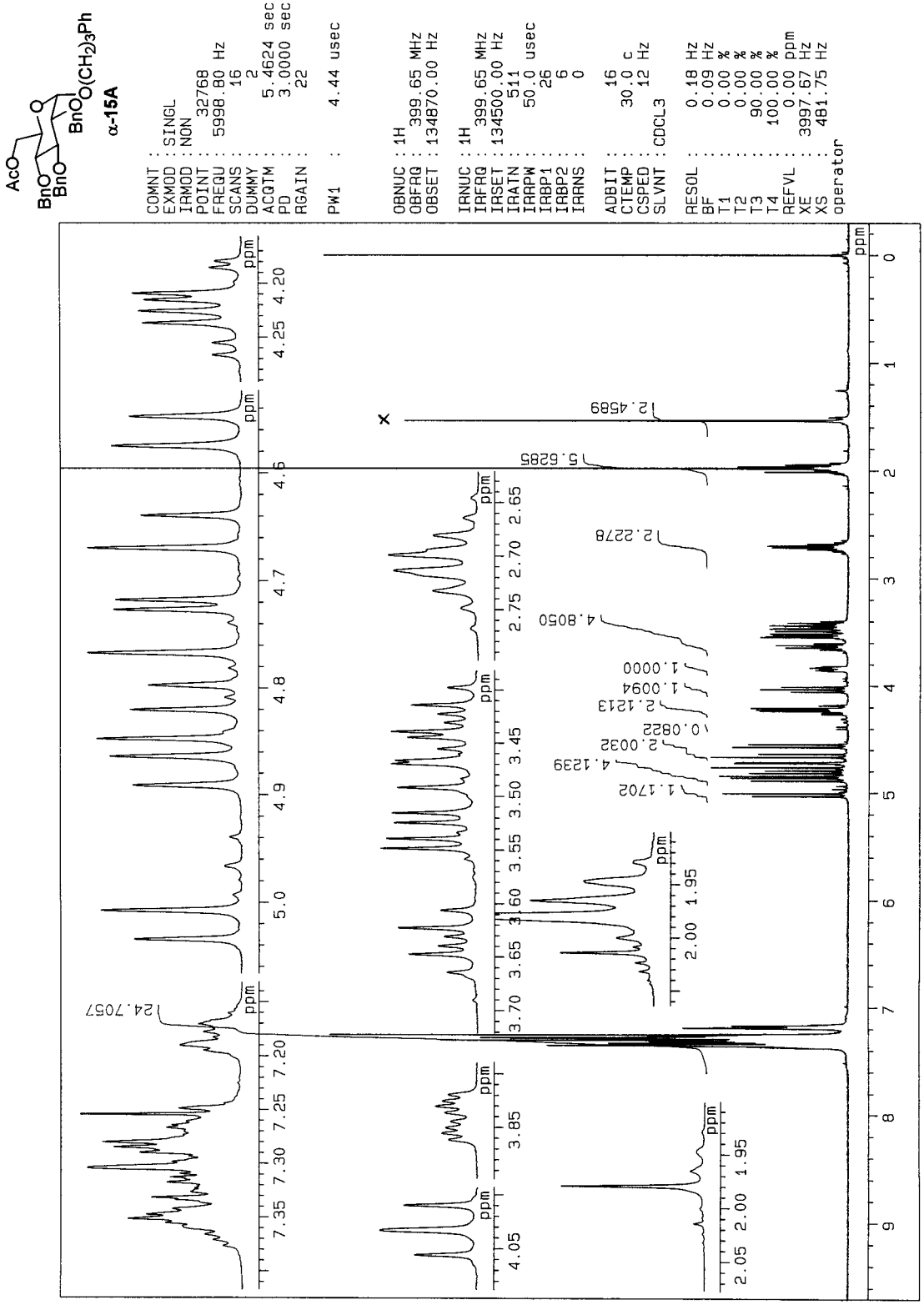
165.123
165.928


α-15A
AcO
BnO
BnO
BnO
O(CH2)3Ph
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IRMOD : 32768
POINT : 5998.80 Hz
FREQU : 16
SCANS : 2
DUMMY : 5.4624 sec
ACQTM : 3.0000 sec
PD : 22
RGAIN :
PW1 : 4.44 usec
OBNUC : 1H
OBFRQ : 399.65 MHz
OBSET : 134870.00 Hz
IRNUC : 1H
IRFRQ : 399.65 MHz
IRSET : 134500.00 Hz
IRATN : 511
IRAPW : 50.0 usec
IRBP1 : 26
IRBP2 : 6
IRANS : 0
ADBIT : 16
CTEMP : 30.0 c
CSPED : 12 Hz
SLVNT : CDCL3
RESOL : 0.18 Hz
BF : 0.09 Hz
T1 : 0.00 %
T2 : 0.00 %
T3 : 90.00 %
T4 : 100.00 %
REFVL : 0.00 ppm
XE : 3997.67 Hz
XS : 481.75 Hz
operator
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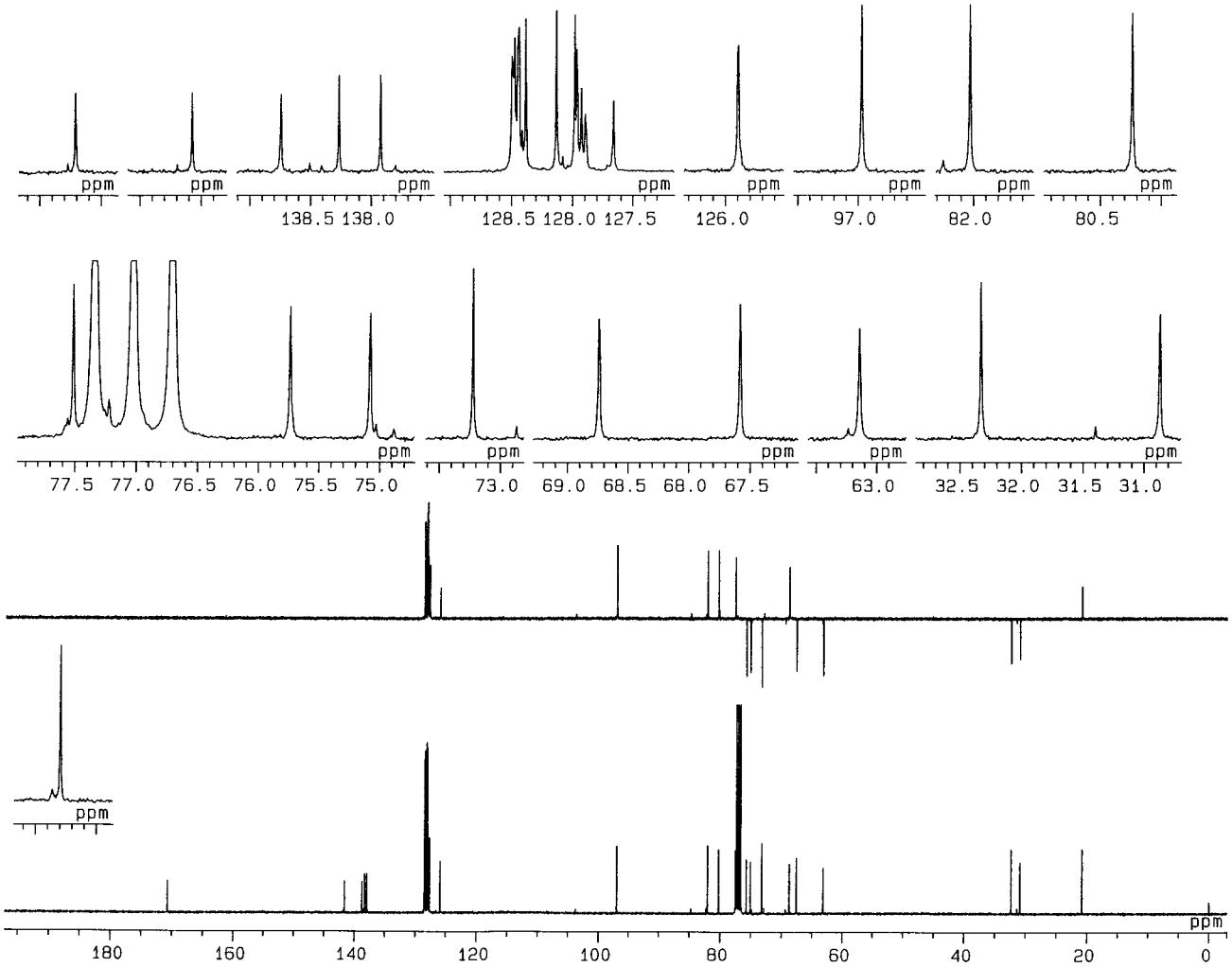

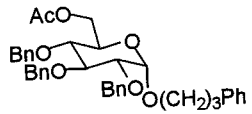

α-15A

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PD    :      1.2000 sec
RGAIN :       27

PW1   :     4.22 usec


OBNUC : 13C
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OBSET : 137395.00 Hz

IRNUC : 1H
IRFRQ :   399.65 MHz
IRSET : 134500.00 Hz
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IRRNS :        0

ADBIT :       16
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CSPED :       12 Hz
SLVNT : CDCL3

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operator
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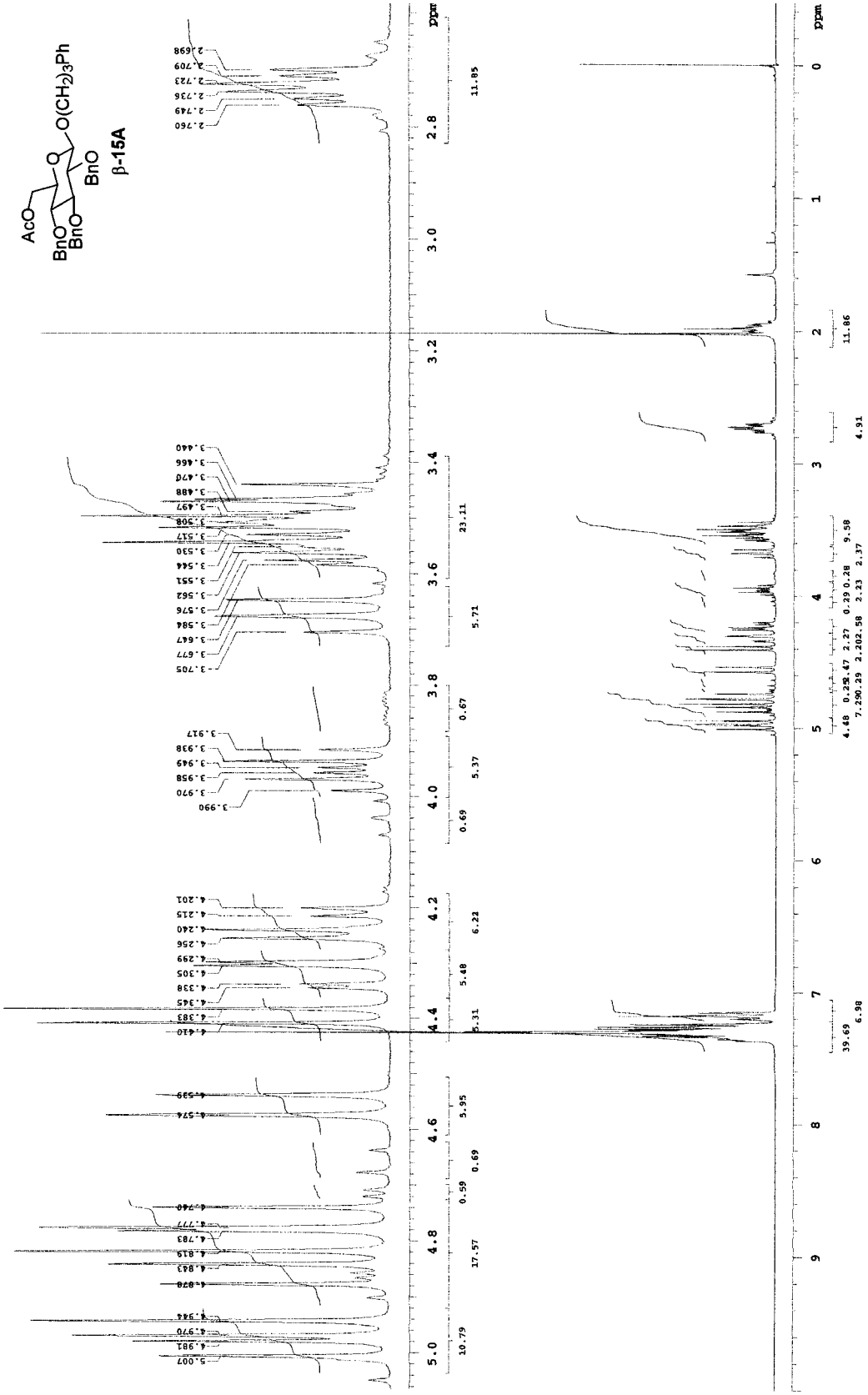
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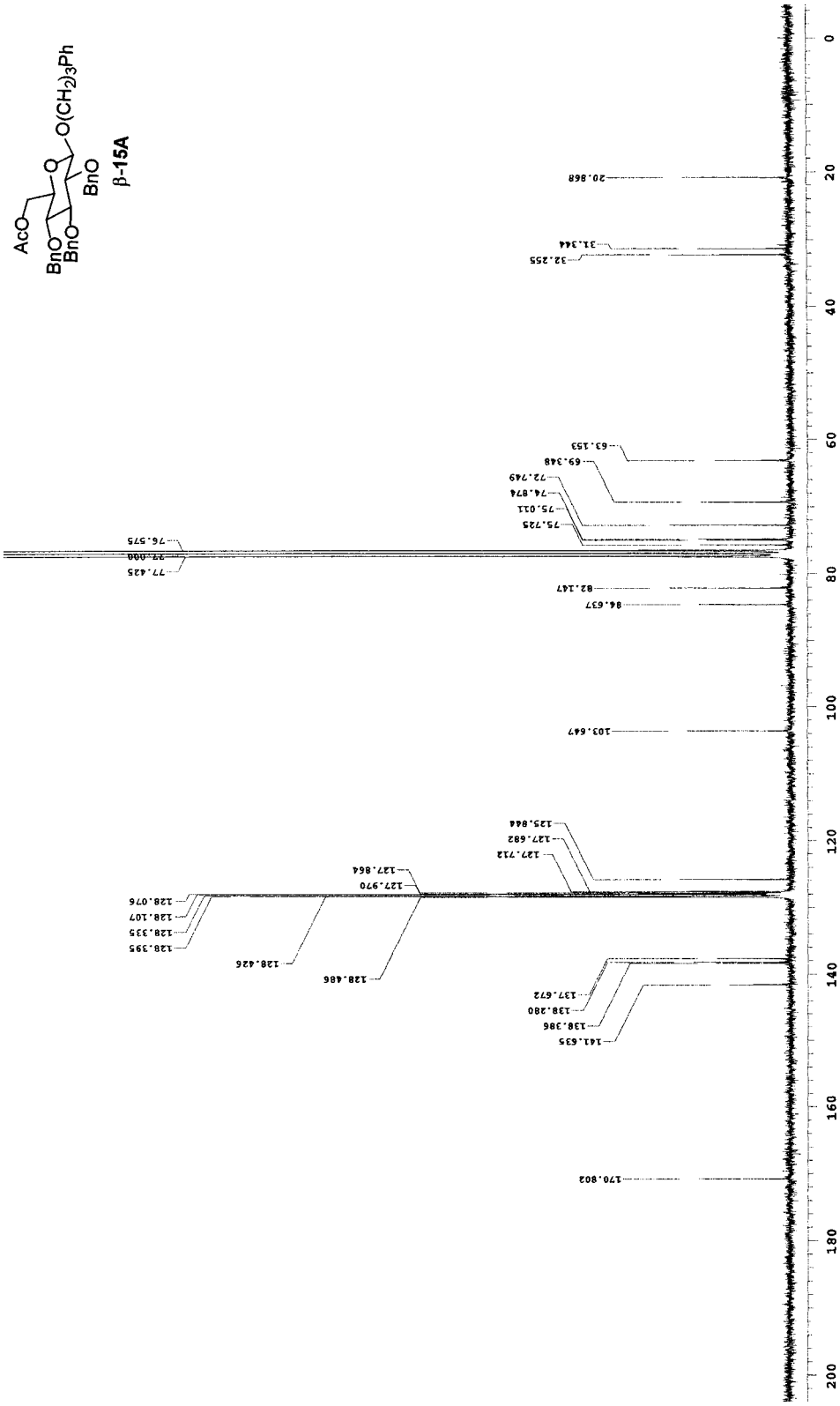
β-15A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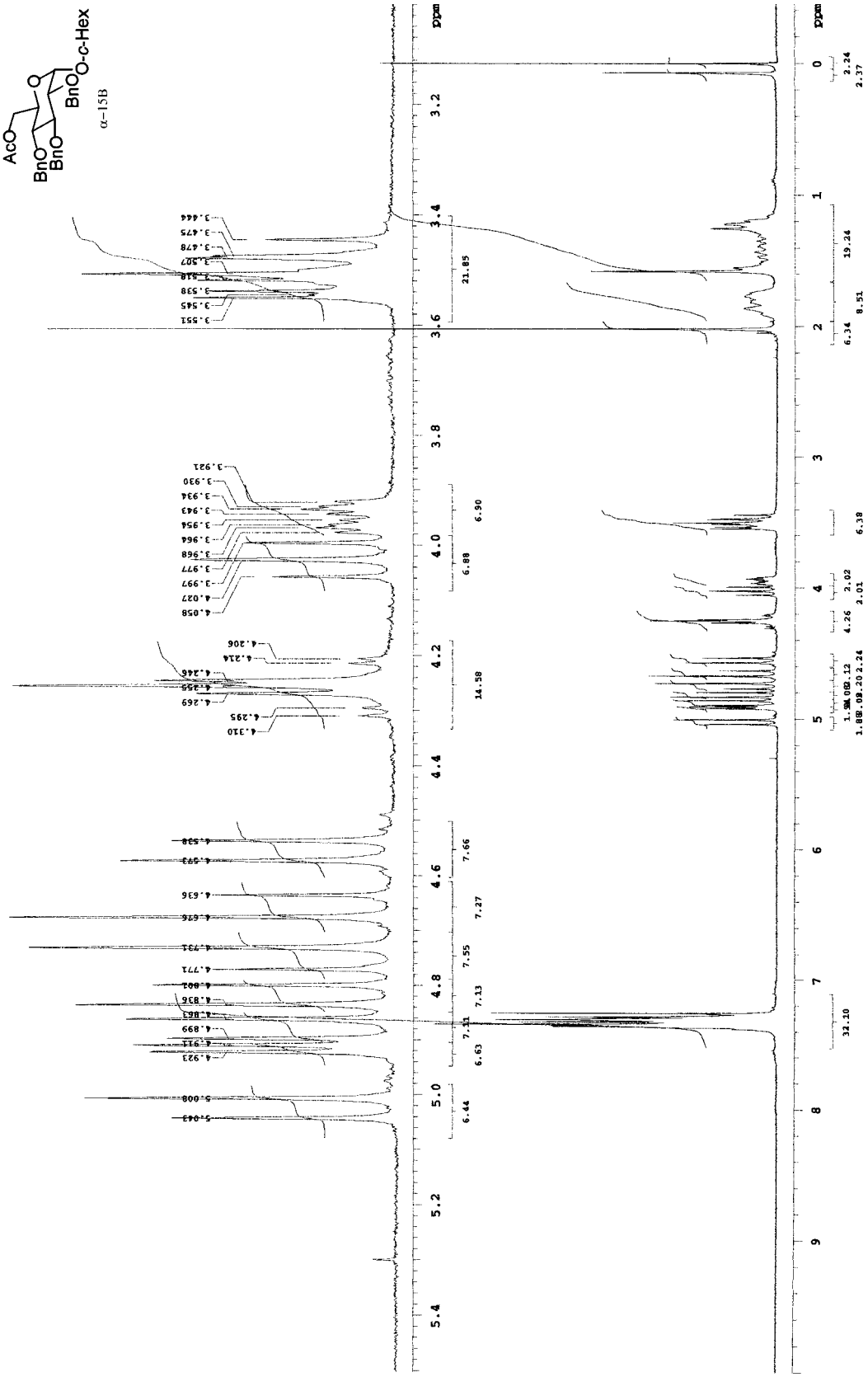
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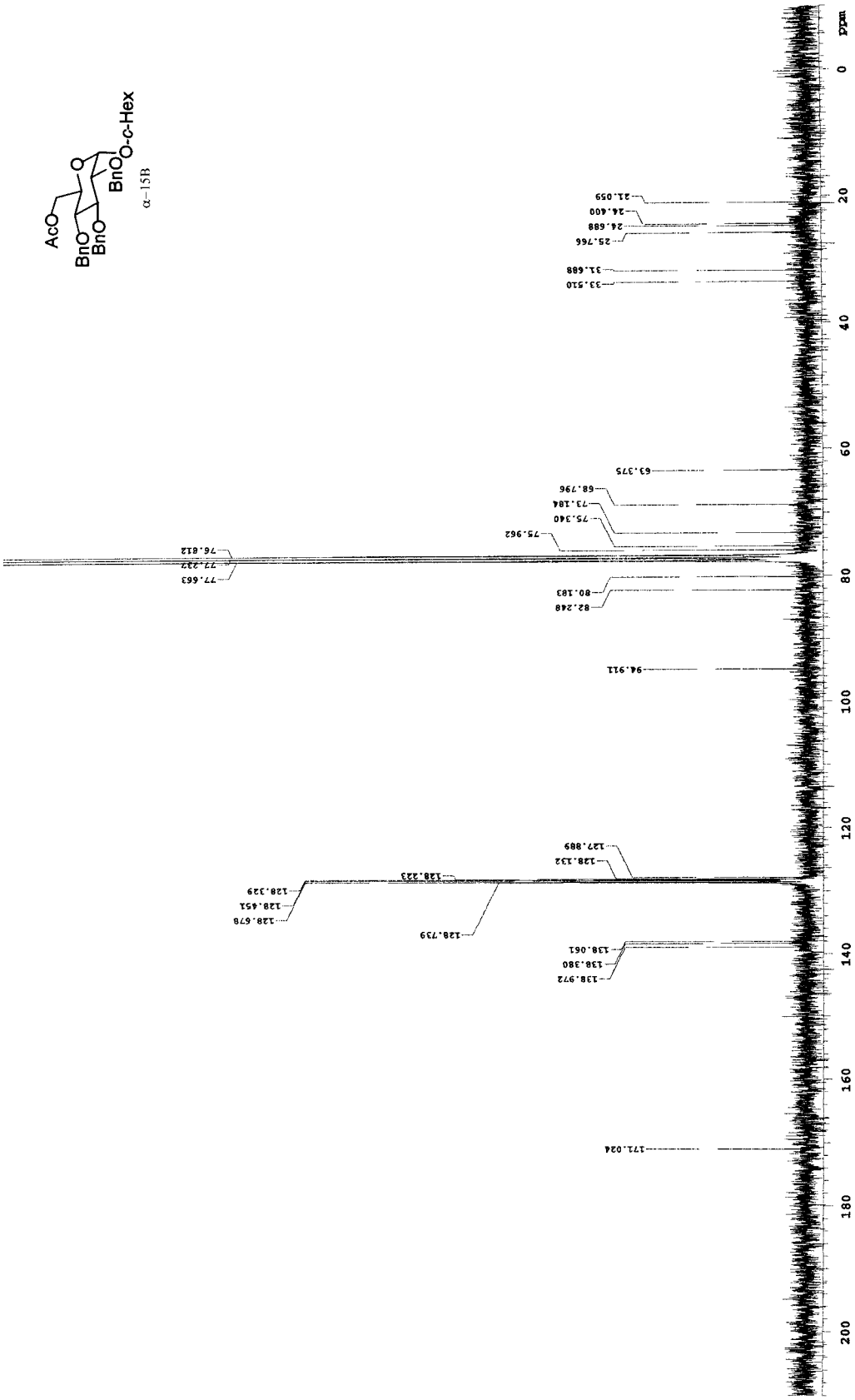
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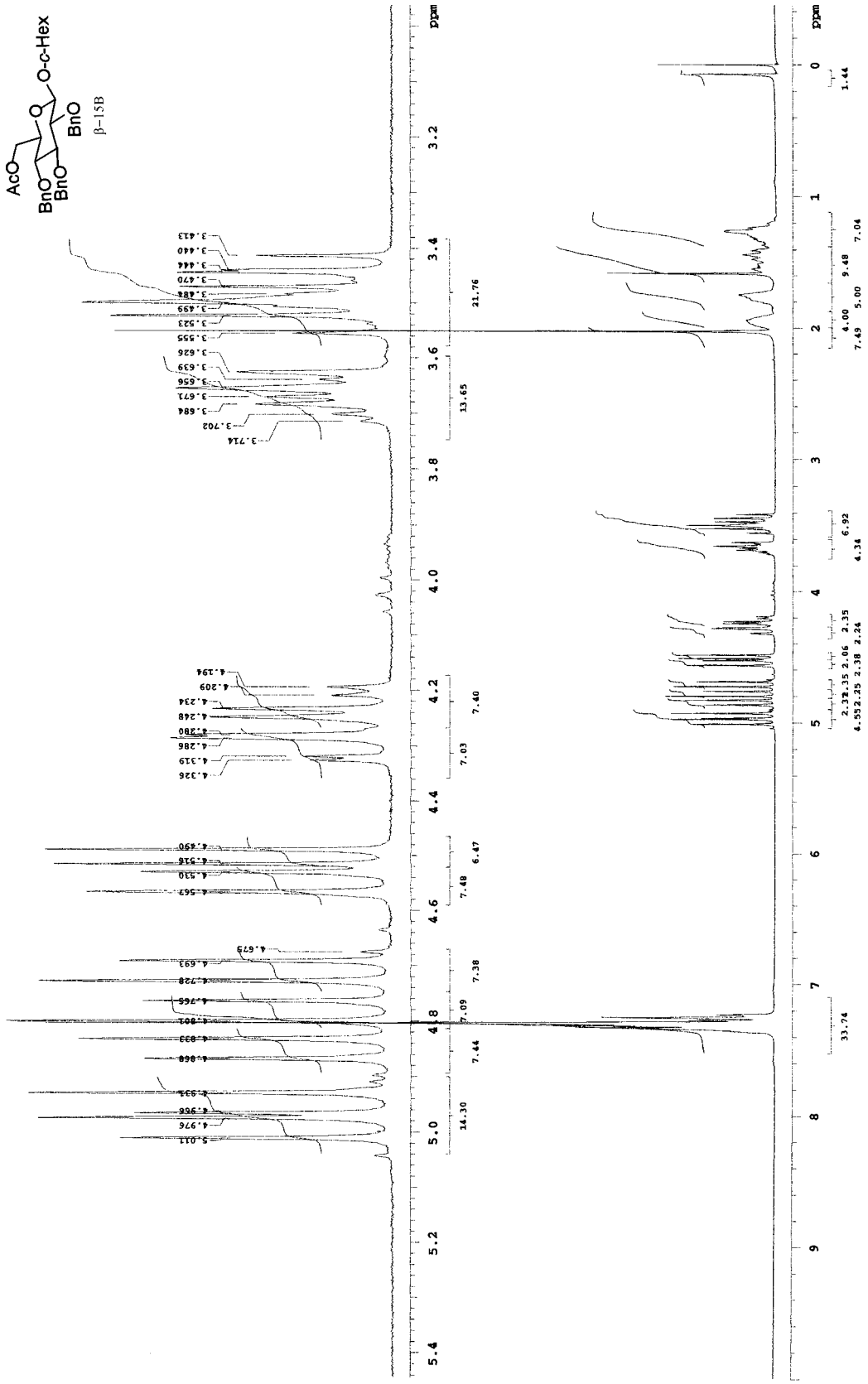
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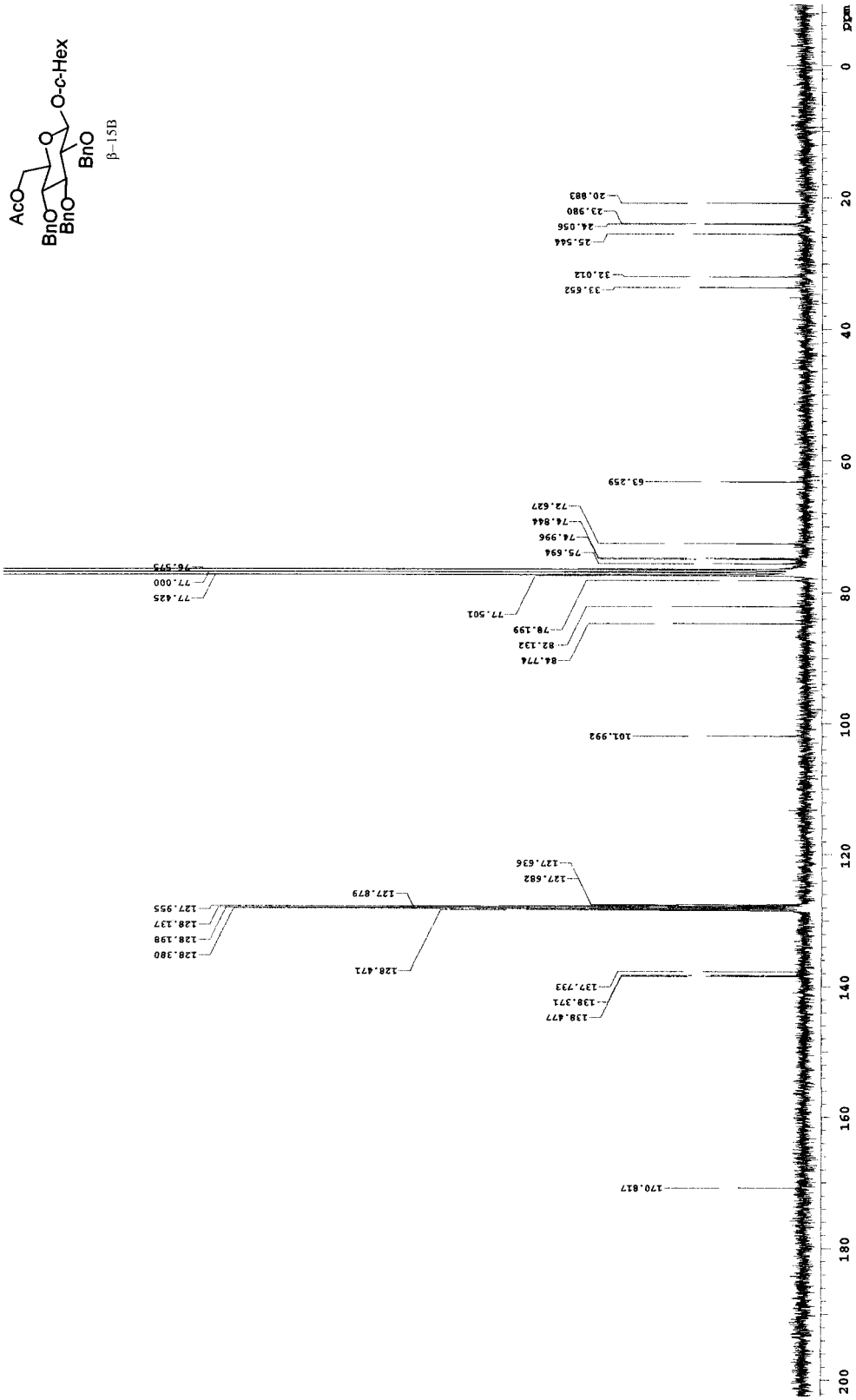
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β-15B
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82.132
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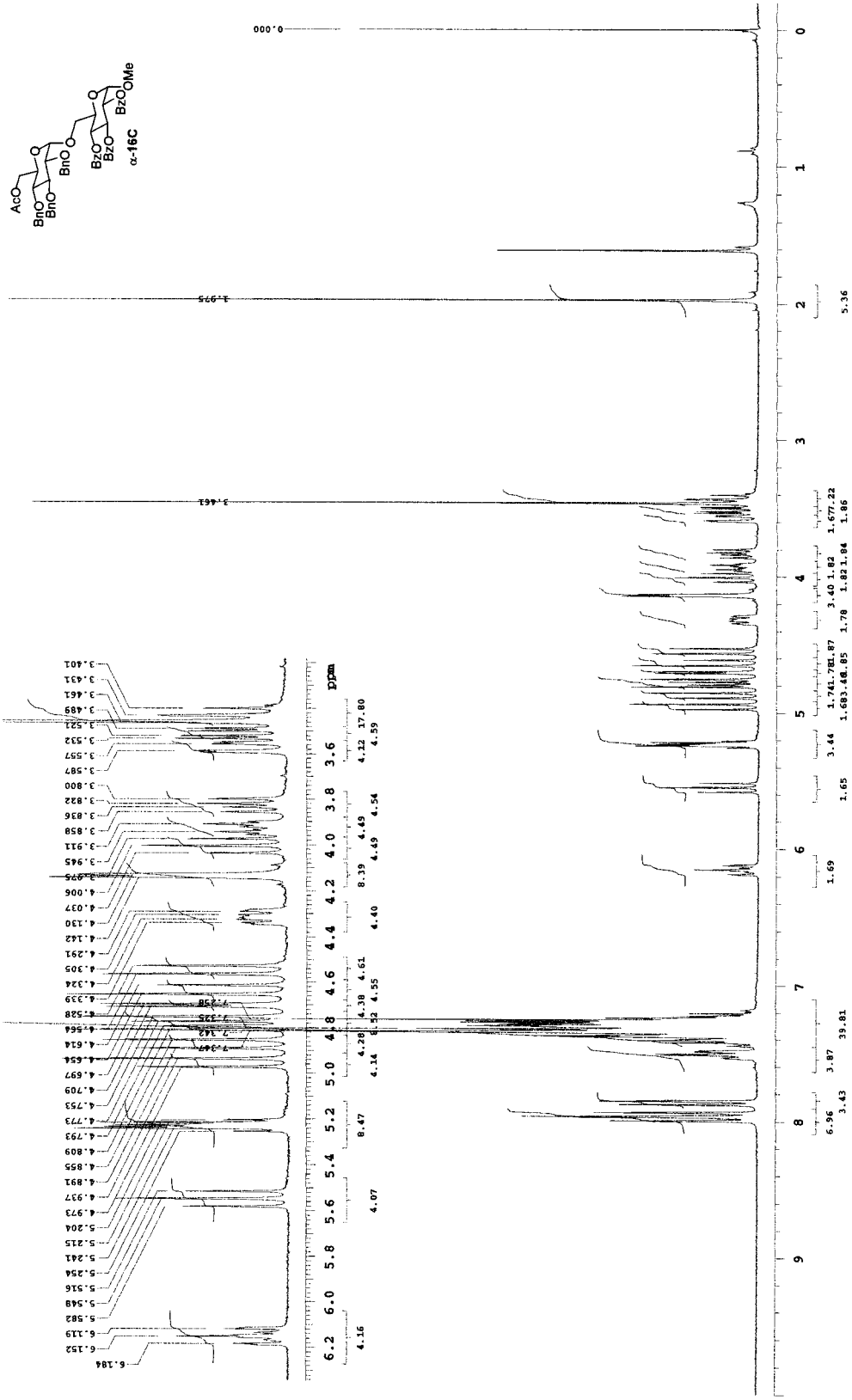
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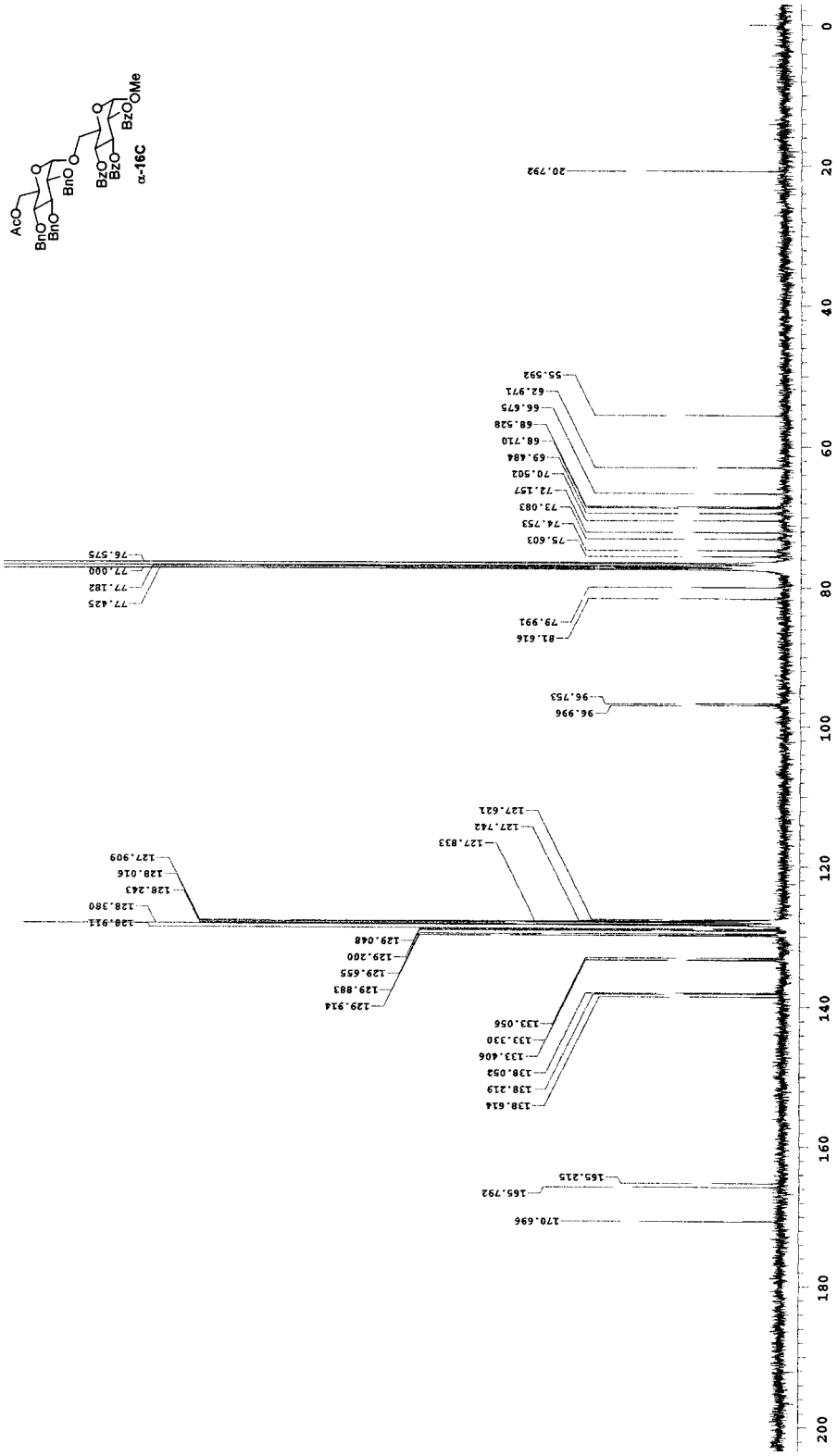
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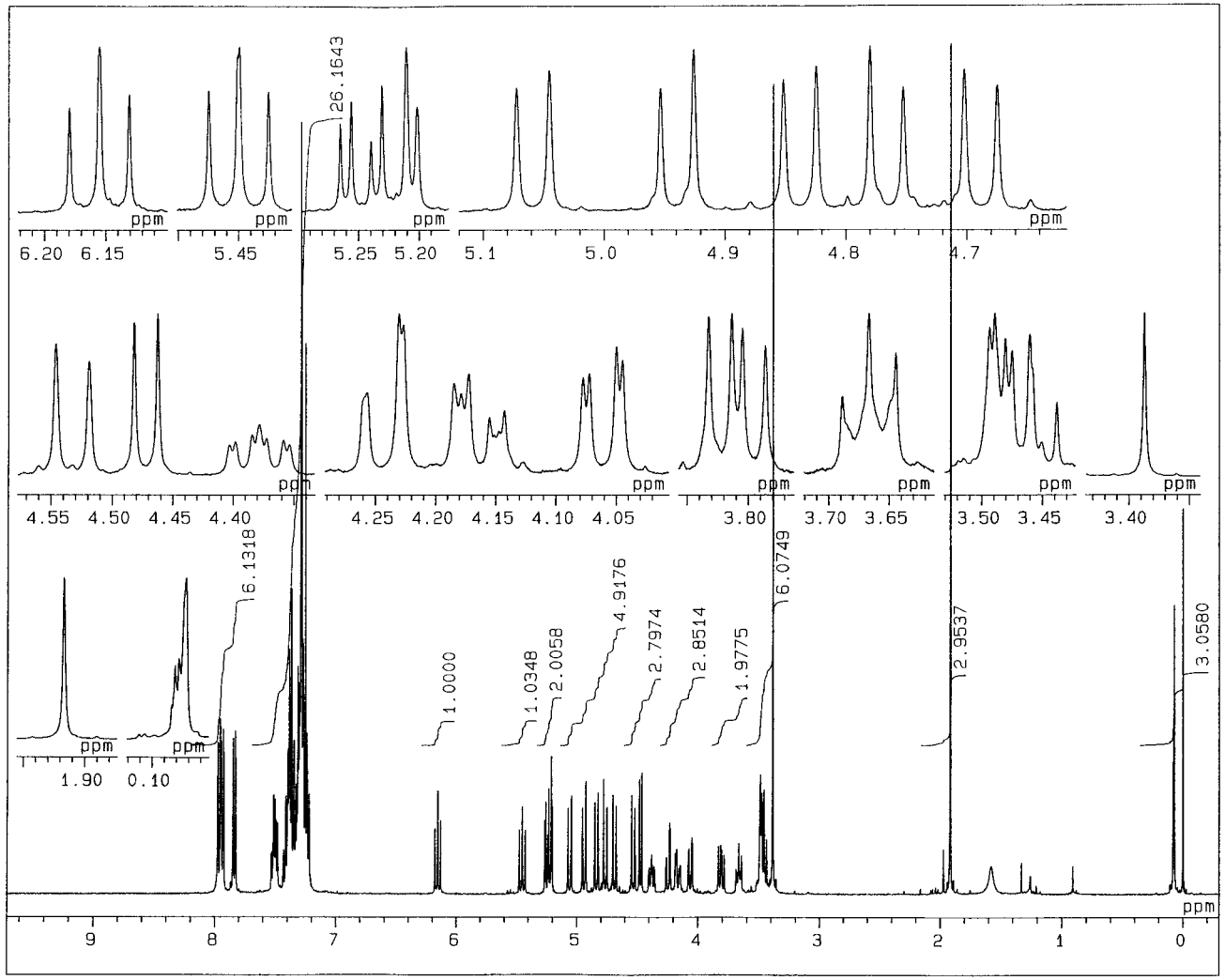
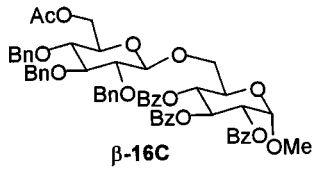
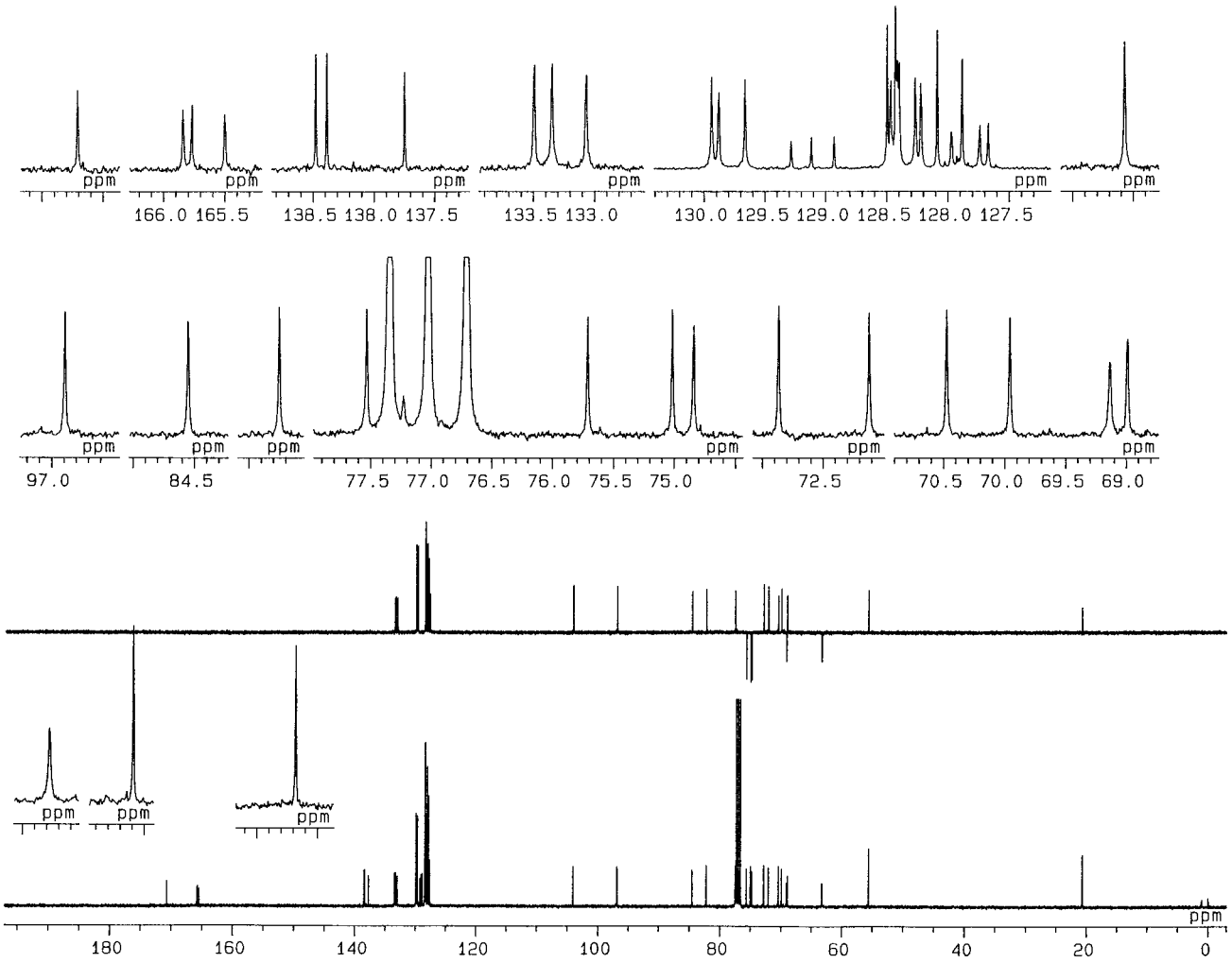
128.380
128.911
129.048
129.200
129.655
129.883
129.914
133.056
133.330
133.406
138.052
138.219
138.614
165.215
165.792
170.696

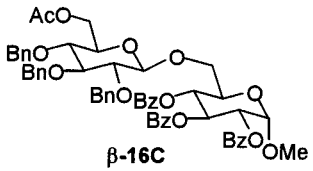




β-16C

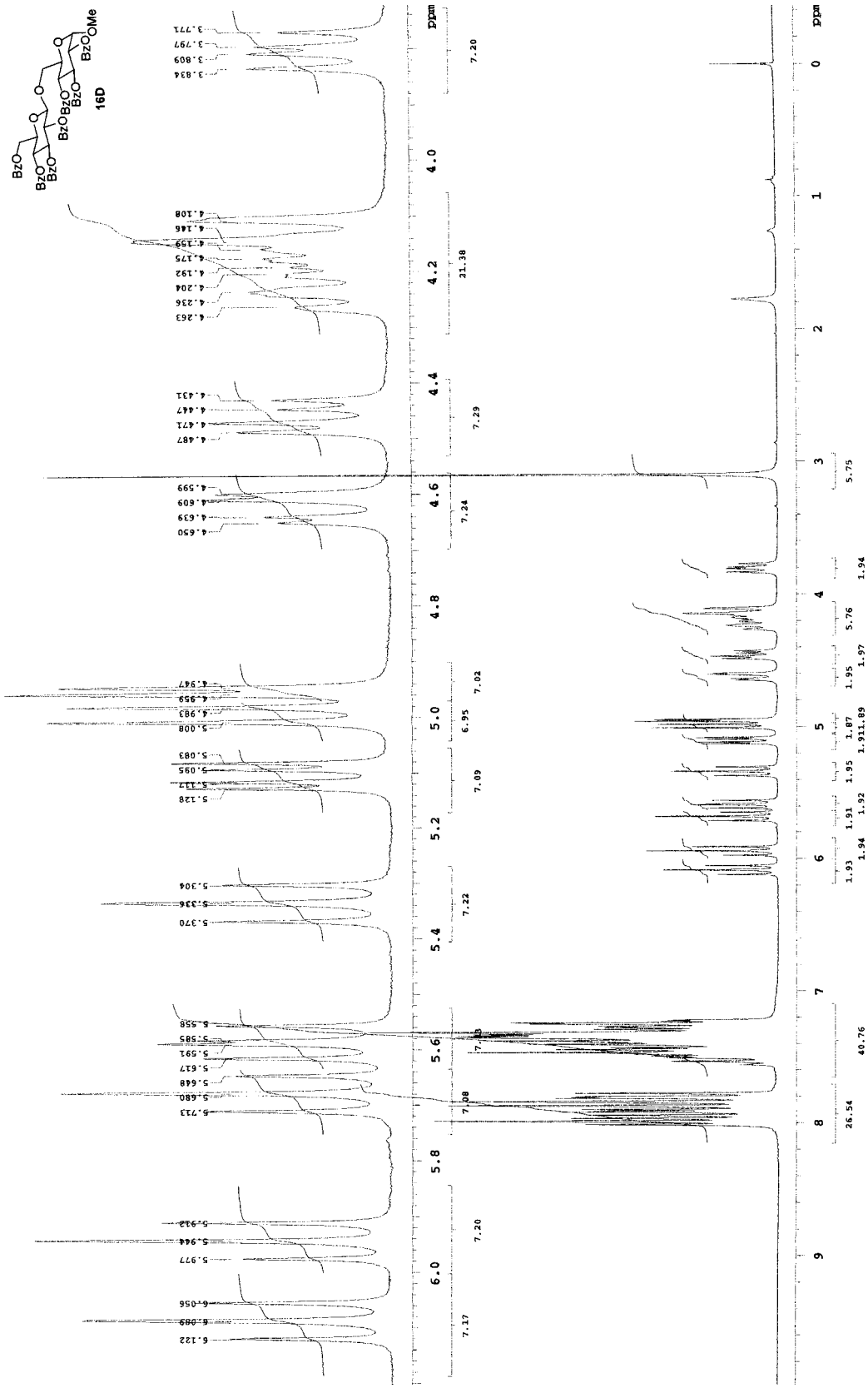
```
COMNT :
EXMOD : SINGL
IRMOD : NON
POINT :    32768
FREQU :  5998.80 Hz
SCANS :       16
DUMMY :        2
ACQTM :      5.4624 sec
PD    :      3.0000 sec
RGAIN :       20

PW1   :     4.44 usec


OBNUC : 1H
OBFRQ :   399.65 MHz
OBSET : 134870.00 Hz

IRNUC : 1H
IRFRQ :   399.65 MHz
IRSET : 134500.00 Hz
IRATN :      511
IRRPW :     50.0 usec
IRBP1 :       26
IRBP2 :        6
IRRNS :        0

ADBIT :       16
CTEMP :     29.9 c
CSPED :       10 Hz
SLVNT : CDCL3

RESOL :     0.18 Hz
BF    :     0.09 Hz
T1    :     0.00 %
T2    :     0.00 %
T3    :    90.00 %
T4    :   100.00 %
REFVL :     0.00 ppm
XE    :  3997.67 Hz
XS    :   481.38 Hz
operator
```

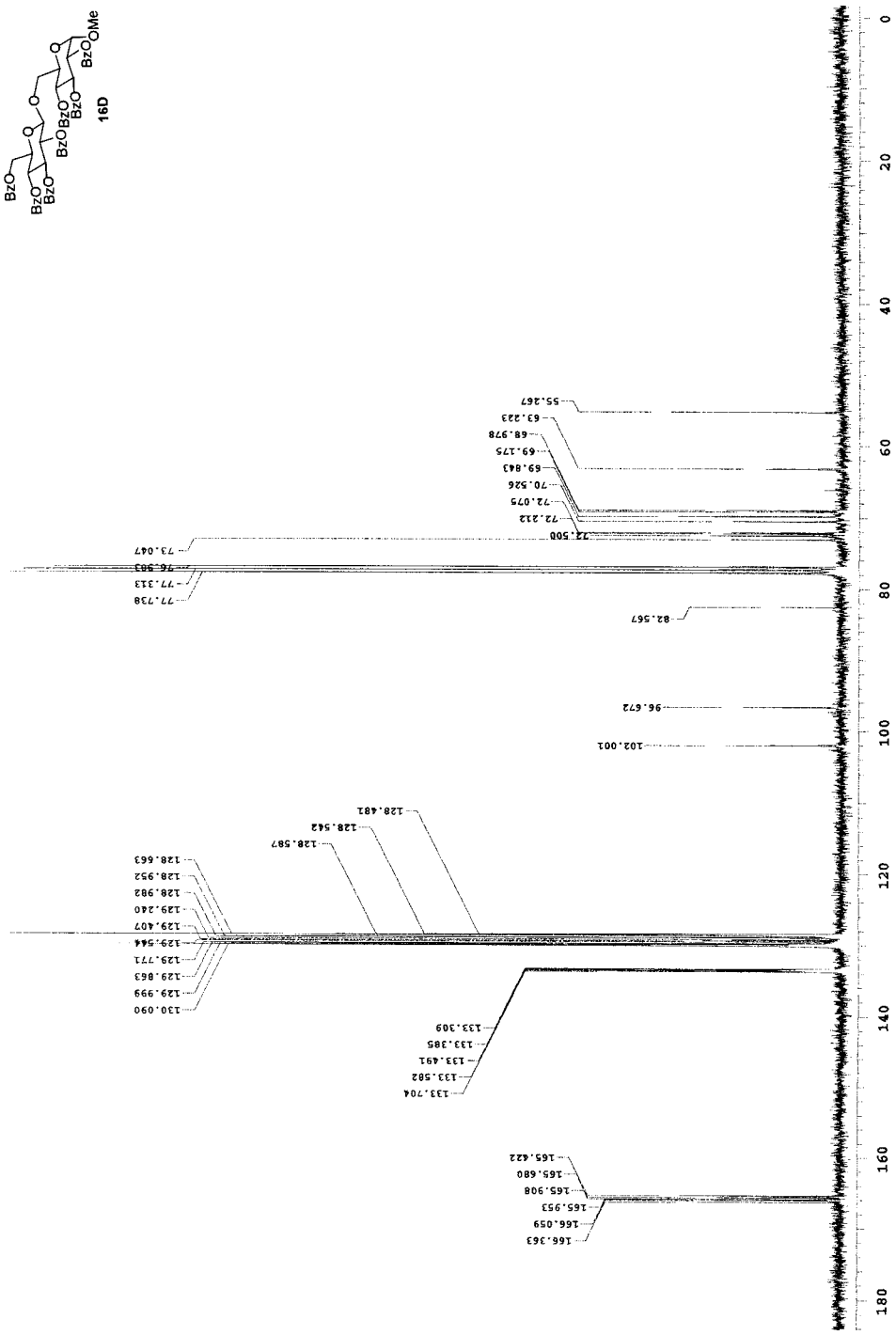




β-16C

```
COMNT :
EXMOD : SINGL
IRMOD : BCM
POINT :    32768
FREQU : 25000.00 Hz
SCANS :    12000
DUMMY :       16
ACQTM :     1.3107 sec
PD    :     1.2000 sec
RGAIN :       27

PW1   :     4.22 usec


OBNUC : 13C
OBFRQ :   100.40 MHz
OBSET : 137395.00 Hz

IRNUC : 1H
IRFRQ :   399.65 MHz
IRSET : 134500.00 Hz
IRATN :      511
IRRPW :     50.0 usec
IRBP1 :       26
IRBP2 :        6
IRRNS :        0

ADBIT :       16
CTEMP :     30.0 c
CSPED :       10 Hz
SLVNT : CDCL3

RESOL :     0.76 Hz
BF    :     0.38 Hz
T1    :     0.00 %
T2    :     0.00 %
T3    :    90.00 %
T4    :   100.00 %
REFVL :     0.00 ppm
XE    : 20104.22 Hz
XS    :  2257.16 Hz
operator
```


BzO
BzO
BzO
BzO
BzO
BzO
BzO
BzO
OMe
16D
ppm
ppm


BzO
BzO
BzO
BzO
BzO
BzO
BzO
BzO
OMe
16D
0
20
40
60
80
100
120
140
160
180
55.367
63.223
68.978
69.175
69.843
70.526
72.075
72.212
72.500
73.047
76.903
77.313
77.738
82.567
96.672
102.001
128.481
128.542
128.587
128.663
128.952
128.982
129.240
129.407
129.544
129.771
129.863
129.999
130.090
133.309
133.385
133.491
133.502
133.704
165.422
165.680
165.908
165.953
166.059
166.363