Supporting Information

for

On the Influence of the C2-O2 and C3-O3 Bonds in the 4,6-O-Benzylidene-Directed β-Mannopyranosylation and α-Glucopyranosylation.

David Crich and Olga Vinogradova.*

Department of Chemistry, University of Illinois at Chicago, 845 West Taylor Street, Chicago, Il 60607-7061.

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General. Unless otherwise noted, reactions were conducted under an inert atmosphere of argon or nitrogen.

***S*-Phenyl 3,4,6-tri-*O*-acetyl-2-deoxy-β-D-*arabino*-thiohexopyranoside (17).** Gaseous HCl was bubbled through a solution of triacetylglucal (1.36 g, 5.00 mmol) in toluene (10 mL) at 0 ^{0}C for 20 min. The solution was then stirred for a further 30 min, after which argon was bubbled through for 45 minutes and the solvent was evaporated under reduced

pressure. The residual syrup was redissolved in dry toluene (6 mL), treated with thiophenol (770 μL, 7.5 mmol) at room temperature followed by diisopropylethylamine (1.3 mL, 7.5 mmol) and then left to stir overnight. The reaction mixture was diluted with CH_2Cl_2, washed with H_2O, dried (Na_2SO_4), and concentrated. Purification by flash column chromatography (SiO_2, hexanes to 1:4 ethyl acetate:hexanes) gave **17** (0.896 g 47%) as a white solid. M.p. 61-63 ^{0}C; $[\alpha]^{24}_D$ -60.9 (*c* 0.23, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.48 - 7.53 (m, 2H), 7.28 - 7.33 (m, 3H), 4.99 - 5.06 (m, 1H), 4.96 (t, *J* = 9.6 Hz, 1H), 4.80 (dd, *J* = 11.8, 1.9 Hz, 1H), 4.24 (dd, *J* = 12.2, 5.6 Hz, 1H), 4.13 (dd, *J* = 12.1, 2.4 Hz, 1H), 3.65 (ddd, *J* = 9.7, 5.5, 2.4 Hz, 1H), 2.44 (ddd, *J* = 12.8, 5.3, 1.9 Hz, 1H), 2.07 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 1.80 - 1.89 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 170.7, 170.2, 169.8, 132.8, 132.4, 128.9, 128.0, 82.0, 75.9, 71.7, 68.8, 62.7, 36.2, 20.9, 20.8, 20.7; ESIHRMS Calcd for $C_{18}H_{22}NaO_7S$ $[M+Na]^+$: 405.09842. Found 405.0971.

***S*-Phenyl 4,6-*O*-benzylidene-2-deoxy-β-D-*arabino*-thiohexopyranoside (18).** To a solution of **17** (388 mg, 1.02 mmol) in MeOH (4 mL) was added Na (3 mg, 0.13 mmol). The reaction mixture was stirred for 1.5 h, then opened to the air and quenched by the addition of Amberlyst 15 ion exchange resin until pH 6. Filtration through Celite® and concentration under reduced pressure afforded a yellow oil, which was dissolved in DMF (3.5 mL). Benzaldehyde dimethylacetal (200 μL, 1.33 mmol) and a catalytic amount of p-toluenesulfonic acid hydrate (until pH =4) were added and the reaction mixture was heated for 3 h at 50 ^{0}C on rotovapor. The mixture was cooled to room temperature and neutralized by the addition of triethylamine. Removal of the solvent and a hexanes/ether wash (10:1) afforded **18** (211 mg, 60%) as a white solid. M.p. 160-162 ^{0}C; $[\alpha]^{24}_D$ -49.0

(*c* 0.10, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ: 7.45 - 7.54 (m, 4H), 7.28 - 7.42 (m, 6H), 5.57 (s, 1H), 4.93 (dd, *J* = 12.0, 2.3 Hz, 1H), 4.35 (dd, *J* = 10.5, 4.4 Hz, 1H), 3.94 - 4.01 (m, 1H), 3.79 - 3.85 (m, 1H), 3.44 - 3.52 (m, 2H), 2.49 (br. s., 1H), 2.44 (ddd, *J* = 13.2, 5.3, 2.3 Hz, 1H), 1.88 (ddd, *J* = 13.1, 12.0, 11.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.1, 133.1, 132.0, 129.3, 129.0, 128.4, 127.9, 126.2, 102.0, 82.8, 70.4, 69.4, 68.7, 38.5; ESIHRMS Calcd for $C_{19}H_{20}NaO_4S$ $[M+Na]^+$: 367.0980. Found 367.0975.

***S*-Phenyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-β-D-*arabino*-thiohexopyranoside (19).** To a solution of **18** (211 mg, 0.613 mmol) in THF (5 mL) was added NaH (60% in mineral oil, 49 mg, 1.2 mmol) and benzyl bromide (110 μL, 0.92 mmol). The reaction mixture was refluxed overnight and quenched with saturated aqueous ammonium chloride. Ethyl acetate was added and the organic layer was separated, washed with brine, dried (Na_2SO_4), and concentrated. Purification by flash column chromatography (SiO_2, hexanes to 1:9 ethyl acetate:hexanes) afforded 194 mg (73%) of **19** as white solid. M.p. 117-118^{0}C; $[\alpha]^{24}_D$ -48.4 (*c* 0.13, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ: 7.46 - 7.55 (m, 4H), 7.27 - 7.44 (m, 11H), 5.62 (s, 1H), 4.88 (dd, *J* = 12.1, 2.2 Hz, 1H), 4.83 (d, *J* = 12.1 Hz, 1H), 4.72 (d, *J* = 11.9 Hz, 1H), 4.36 (dd, *J* = 10.5, 5.0 Hz, 1H), 3.85 (t, *J* = 10.3 Hz, 1H), 3.74 - 3.82 (m, 1H), 3.70 (t, *J* = 9.1 Hz, 1H), 3.46 (td, *J* = 9.6, 5.0 Hz, 1H), 2.46 (ddd, *J* = 13.4, 5.1, 2.2 Hz, 1H), 1.90 (ddd, *J* = 13.2, 12.2, 10.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 138.3, 137.5, 133.1, 132.0, 129.0, 128.5, 128.3, 127.8, 127.8, 126.1, 101.4, 83.0, 82.8, 75.6 72.7, 70.9, 68.8, 37.7; ESIHRMS Calcd for $C_{26}H_{26}NaO_4S$ $[M+Na]^+$: 457.1450. Found 457.1451.

1,2,4,6-tetra-*O*-acetyl-3-deoxy-β-D-*ribo*-hexopyranose (21). A mixture of 3-deoxy-3-iodo-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose[1,2] (3.27 g, 8.82 mmol), Amberlite IR-

120 (H^+) ion-exchange resin (3.78 g) and H_2O (21 mL) was heated for 3 hours at 80 ^{0}C, then filtered through a pad of Celite®. The solvent was evaporated and the residual syrup was dissolved in pyridine (20 mL). Acetic anhydride was added (8.3 mL), followed by DMAP (22 mg, 0.18 mmol) and the reaction mixture was allowed to stir overnight. After concentration in *vacuo* the residue was diluted with water and extracted with CH_2Cl_2. The organic layer was separated, washed with brine and dried (Na_2SO_4). Purification by flash column chromatography (SiO_2, 1:4 ethyl acetate:hexanes) afforded 3.43 g (85%) of the crude 1,2,4,6-tetra-*O*-acetyl-3-deoxy-3-iodo-α-D-allofuranose which was used without further purification. To a solution of 1,2,4,6-tetra-*O*-acetyl-3-deoxy-3-iodo-α-D-allopyranose (4.92 g, 10.7 mmol) in toluene (100 mL), AIBN (1.08 g, 6.56 mmol) and Bu_3SnH (3.5 mL, 13.1 mmol) were added and the reaction mixture was refluxed for 1.5 hours. The solvent was evaporated and the residual syrup was dissolved in acetonitrile, washed twice with petroleum ether, and concentrated. Purification by flash column chromatography (SiO_2, 1:4 ethyl acetate:hexanes to 3:7 ethyl acetate:hexanes) gave crude **21**, which was further recrystallized from ether to give 2.80 g (78%) of pure **21**. Spectral data matched that reported in literature[3].

***S*-Phenyl 2,4,6-tri-*O*-acetyl-3-deoxy-β-D-*ribo*-thiohexopyranoside (22) and *S*-Phenyl 2,4,6-tri-*O*-acetyl-3-deoxy-α-D-*ribo*-thiohexopyranoside (23).** To a stirred solution of **21** (1.26 g, 3.80 mmol) in CH_2Cl_2 (19 mL) at 0 ^{0}C was added PhSH (1.2 mL, 11.7 mmol) and $BF_3 \cdot Et_2O$ (1.22 mL, 9.71 mmol). The ice bath was removed and reaction mixture was monitored by TLC analysis. After 30 minutes the starting material was consumed. The reaction was diluted with CH_2Cl_2, washed with saturated aqueous $NaHCO_3$, brine, and dried (Na_2SO_4). The solvent was evaporated and the mixture was

filtered through a pad of SiO_2 (ethyl acetate as eluent) and purified by means of radial chromatography. Combined yield 1.41 g (97%, 1:4 α/β). **23.** White solid. M.p. 63-67 ^{0}C; $[\alpha]^{22}_D$ +235.2 (*c* 0.53, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.44 - 7.49 (m, 2H), 7.23 - 7.33 (m, 3H), 5.81 (d, *J* = 5.1 Hz, 1H), 5.09 (dt, *J* = 12.4, 4.9 Hz, 1H), 4.85 (td, *J* = 10.6, 5.0 Hz, 1H), 4.46 (ddd, *J* = 10.1, 5.6, 2.2 Hz, 1H), 4.24 (dd, *J* = 12.1, 5.7 Hz, 1H), 4.11 (dd, *J* = 12.1, 2.2 Hz, 1H), 2.35 - 2.41 (m, 1H), 2.10 (s, 3H), 2.08 (s, 3H), 2.02 (s, 3H), 1.88 - 1.97 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 170.7, 169.8, 169.7, 133.0, 131.9, 129.1, 127.5, 85.9, 68.6, 67.9, 66.0, 62.5, 30.9, 21.0, 20.8; EIHRMS Calcd for $C_{18}H_{22}O_7S$ $[M]^+$: 382.1086. Found 382.1108 **22.** White solid. M.p. 81-82 ^{0}C; $[\alpha]^{22}_D$ - 12.1 (*c* 1.02, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.44 - 7.50 (m, 2H), 7.25 - 7.31 (m, 3H), 4.74 - 4.82 (m, 2H), 4.65 (d, *J* = 9.9 Hz, 1H), 4.21 (dd, *J* = 12.1, 2.6 Hz, 1H), 4.15 (dd, *J* = 12.1, 5.9 Hz, 1H), 3.66 (ddd, *J* = 9.9, 5.9, 2.6 Hz, 1H), 2.60 (ddd, *J* = 11.9, 5.1, 5.0 Hz, 1H), 2.07 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H), 1.61 (ddd, $J_1 = J_2 = J_3$ = 11.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 170.7, 169.4, 169.3, 132.5, 128.8, 128.0, 87.3, 78.0, 67.2, 65.8, 62.9, 35.2, 21.0, 20.9, 20.8; FABHRMS Calcd for $C_{18}H_{22}NaO_7S$ $[M+Na]^+$: 405.0984. Found 405.1008.

***S*-Phenyl 4,6-*O*-benzylidene-3-deoxy-β-D-*ribo*-thiohexopyranoside (24).** To a solution of **22** (2.04 g, 5.33 mmol) in MeOH (13 mL) was added Na (35 mg, 1.52 mmol). The reaction mixture was stirred for 1 hour, then opened to the air and quenched by the addition of Amberlyst 15 ion exchange resin until pH 6. Filtration through Celite® and concentration under reduced pressure afforded a yellow foam, which was dissolved in DMF (18.5 mL). Benzaldehyde dimethylacetal (1.04 mL, 6.93 mmol) and a catalytic amount of p-toluenesulfonic acid hydrate (5 mg, 0.03 mmol) were added and the reaction

mixture was heated for 1 hour at 50 ^{0}C on rotovapor. The mixture was cooled to room temperature and neutralized by the addition of triethylamine. Removal of the solvent and purification by flash column chromatography (SiO_2, 3:17 to 1:1 ethyl acetate: haxanes) gave **24** (1.76 g, 96%) as a white solid. M.p. 157-159 ^{0}C; $[\alpha]^{22}_D$ -45.9 (*c* 0.90, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.43 - 7.60 (m, 4H), 7.30 - 7.43 (m, 6H), 5.54 (s, 1H), 4.57 (d, *J* = 9.5 Hz, 1H), 4.38 (dd, *J* = 10.4, 4.9 Hz, 1H), 3.78 (t, *J* = 10.4 Hz, 1H), 3.55 - 3.64 (m, 2H), 3.45 - 3.53 (m, 1H), 2.59 (dt, *J* = 11.8, 4.4 Hz, 1H), 2.45 (br. s., 1H), 1.78 (ddd, $J_1 = J_2 = J_3$ = 11.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 137.2, 132.8, 131.8, 129.23, 129.18, 128.42, 128.35, 126.2, 101.8, 91.6, 76.0, 74.0, 69.1, 67.5, 36.7; FABHRMS Calcd for $C_{19}H_{20}NaO_4S$ $[M+Na]^+$: 367.0980. Found 367.0979.

***S*-Phenyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-deoxy-β-D- *ribo*-thiohexopyranoside (25).** To a solution of **24** (589 mg, 1.71 mmol) in of THF (14 mL) was added NaH (60% in mineral oil, 137 mg, 3.42 mmol) and benzyl bromide (311 μL, 2.57 mmol). The reaction mixture was refluxed overnight and quenched with saturated aqueous ammonium chloride. Ethyl acetate was added and the organic layer was separated, washed with water, dried (Na_2SO_4), and concentrated. Purification by flash column chromatography (SiO_2, hexanes to 1:9 ethyl acetate:hexanes) afforded 693 mg (93%) of **25** as white solid. M.p. 139-140 ^{0}C; $[\alpha]^{22}_D$ -46.4 (*c* 0.36, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.46 - 7.62 (m, 4H), 7.29 - 7.44 (m, 11H), 5.53 (s, 1H), 4.79 (d, *J* = 9.5 Hz, 1H), 4.72 (d, *J* = 11.6 Hz, 1H), 4.68 (d, *J* = 11.6 Hz, 1H), 4.37 (dd, *J* = 10.6, 4.8 Hz, 1H), 3.77 (t, *J* = 10.3 Hz, 1H), 3.44 - 3.59 (m, 3H), 2.62 (dt, *J* = 11.7, 4.5 Hz, 1H), 1.81 (ddd, $J_1 = J_2 = J_3$ = 11.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 137.8, 137.3, 133.4, 132.3, 129.3, 129.0, 128.6, 128.5, 128.13, 128.05, 127.7, 126.2, 101.8, 89.3, 75.8, 74.6, 73.6,

72.3,69.2, 36.2; FABHRMS Calcd for $C_{26}H_{26}NaO_4S$ $[M+Na]^+$: 457.1450. Found 457.1435.

***S*-Phenyl 4,6-*O*-benzylidene-3-deoxy-β-D-*arabino*-thiohexopyranoside (26).** To a stirred solution of **24** (200 mg, 0.581 mmol) in CH_2Cl_2 (8 mL) was added Dess-Martin periodinane solution (1.81 mL of 15 wt%, 0.870 mmol) at room temperature and the reaction mixture was allowed to stir overnight. The reaction mixture was diluted with CH_2Cl_2 (80 mL) and washed with water (20 mL) and saturated aqueous $NaHCO_3$ (20 mL), dried (Na_2SO_4), and concentrated. The residue was dissolved in diethyl ether (80 mL), washed sequentially with water (20 mL) and saturated aqueous $NaHCO_3$ (3 × 20 mL) and dried (Na_2SO_4). Evaporation of the solvent afforded a white solid, which was dissolved in THF (5 mL) and cooled to -78 ^{0}C. A solution of L-selectride® (1M in THF, 754 μL, 0.754 mmol) was added and the reaction mixture stirred for 15 minutes. The reaction mixture was quenched by the addition of water, allowed to warm up to room temperature, diluted with CH_2Cl_2, washed sequentially with 5% HCl and saturated aqueous $NaHCO_3$, and dried (Na_2SO_4). Evaporation of the solvents, filtration through a pad of SiO_2 ($CHCl_3$ was used as an eluent), and purification by means of radial chromatography (3:17 hexanes:chloroform) afforded **26** (162 mg, 81%) as a white solid. M.p. 213-215 ^{0}C; $[\alpha]^{22}_D$ -56.5 (*c* 0.168, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.43 - 7.57 (m, 4H), 7.28 - 7.41 (m, 6H), 5.59 (s, 1H), 4.98 (d, *J* = 1.1 Hz, 1H), 4.32 (dd, *J* = 10.5, 5.0 Hz, 1H), 4.23 - 4.28 (m, 1H), 4.07 (ddd, *J* = 12.0, 9.1, 4.4 Hz, 1H), 3.87 (t, *J* = 10.4 Hz, 1H), 3.52 (td, *J* = 9.6, 5.0 Hz, 1H), 2.43 (ddd, *J* = 13.5, 3.8, 3.5 Hz, 1H), 2.36 (d, *J* = 5.3 Hz, 1H), 1.88 (td, *J* = 12.6, 2.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 137.4,

133.2, 131.8, 129.22, 129.17,128.4, 127.9, 126.2, 102.1, 89.7 ($^1J_{CH}$ = 155.4), 74.6, 73.3, 69.6, 68.9, 36.4; EIHRMS Calcd for $C_{19}H_{20}O_4S$ $[M]^+$: 344.1082. Found 344.1056.

***S*-Phenyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-deoxy-β-D-*arabino*-thiohexopyranoside (27).** To a solution of **26** (160 mg, 0.465 mmol) in THF (7.5 mL) was added NaH (60% in mineral oil, 37 mg, 0.925 mmol) and benzyl bromide (83 μL, 0.694 mmol). The reaction mixture was refluxed overnight and quenched with saturated aqueous ammonium chloride. Ethyl acetate was added and the organic layer was separated, washed with water, dried over Na_2SO_4, and concentrated. Filtration through SiO_2 ($CHCl_3$ as an eluent) and purification by radial chromatography (SiO_2, hexanes to 2:3 $CHCl_3$:hexanes) afforded 189 mg (94%) of **27** as white solid. M.p. 175-178 ^{0}C; $[\alpha]^{22}_D$ -31.6 (*c* 0.266, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.45 - 7.58 (m, 6H), 7.24 - 7.43 (m, 9H), 5.59 (s, 1H), 4.97 (d, *J* = 1.7 Hz, 1H), 4.81 (d, *J* = 11.7 Hz, 1H), 4.66 (d, *J* = 11.9 Hz, 1H), 4.31 (dd, *J* = 10.6, 5.0 Hz, 1H), 4.10 (ddd, *J* = 11.9, 9.0, 4.2 Hz, 1H), 4.02 - 4.07 (m, 1H), 3.92 (t, *J* = 10.4 Hz, 1H), 3.52 (td, *J* = 9.6, 5.0 Hz, 1H), 2.52 (dt, *J* = 13.3, 3.6 Hz, 1H), 1.72 - 1.81 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 137.5, 137.4, 135.3, 131.0, 129.1, 129.0, 128.5, 128.4, 128.2, 128.0, 127.3, 126.2, 102.0, 89.6 ($^1J_{CH}$ = 153.5), 76.4, 74.2, 73.5, 72.2, 69.0, 32.9; EIHRMS Calcd for $C_{26}H_{26}O_4S$ $[M]^+$: 434.1552. Found 434.1570.

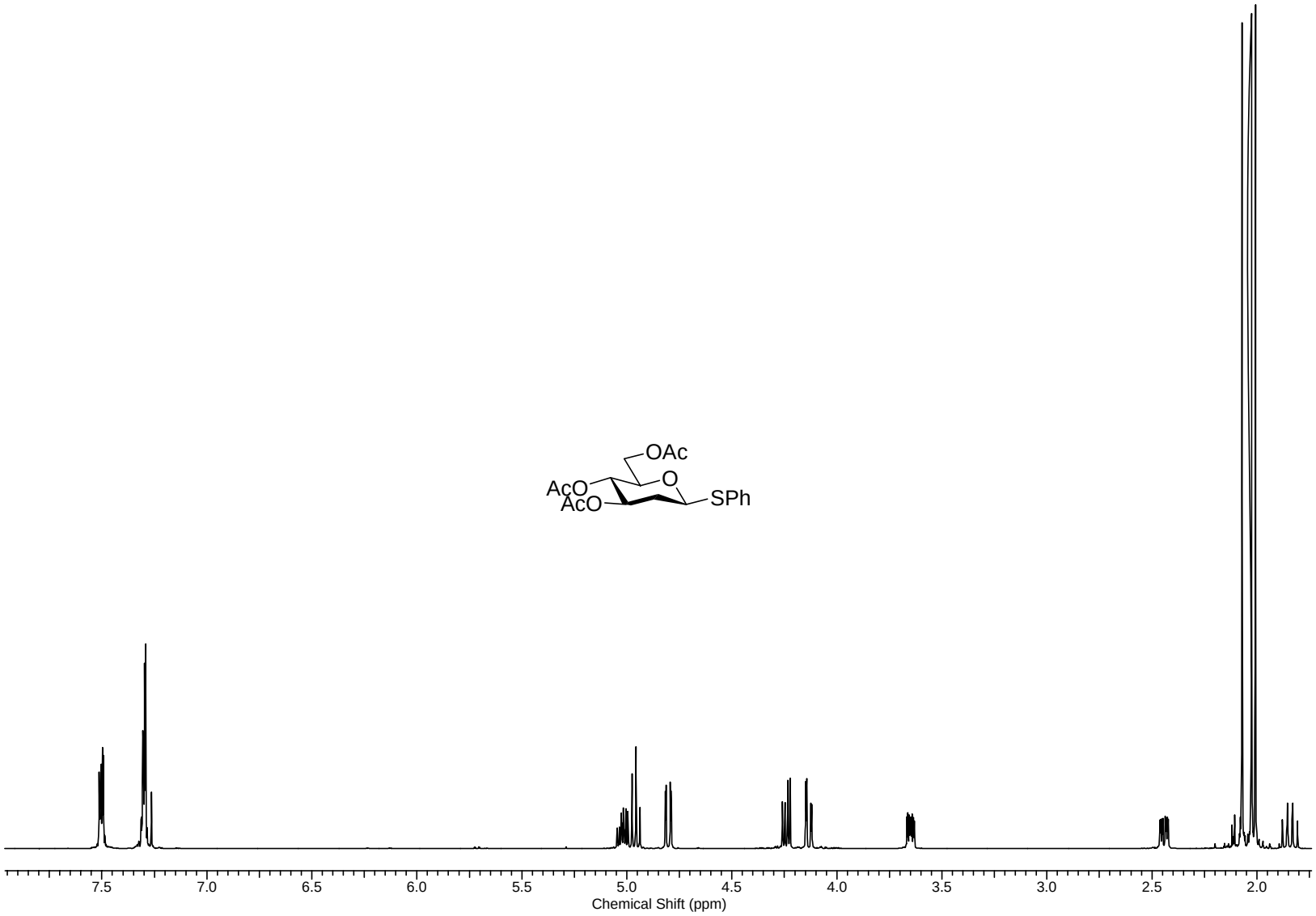
General procedure for VT ^{1}H NMR experiment. A solution of **19, 25**, **27** or **30** (20 mg, 0.046 mmol) in CD_2Cl_2 (1 g) containing BSP (9.6 mg, 0.046 mmol) or Ph_2SO (18.6 mg, 0.092 mmol) and TTBP (22.9 mg, 0.092 mmol) was placed into an NMR tube and cooled to -60 ^{0}C in the NMR probe. The first ^{1}H spectrum was obtained, then the sample was quickly removed from the probe and kept cool in a -60 ^{0}C acetone/dry ice bath

during the addition of Tf_2O (8.5 μL, 0.051 mmol). The sample was returned to the NMR probe and ^1H spectrum was recorded again. The temperature was increased by 10 ^0C increments every 10 minutes and ^1H NMR spectra were acquired at each temperature.

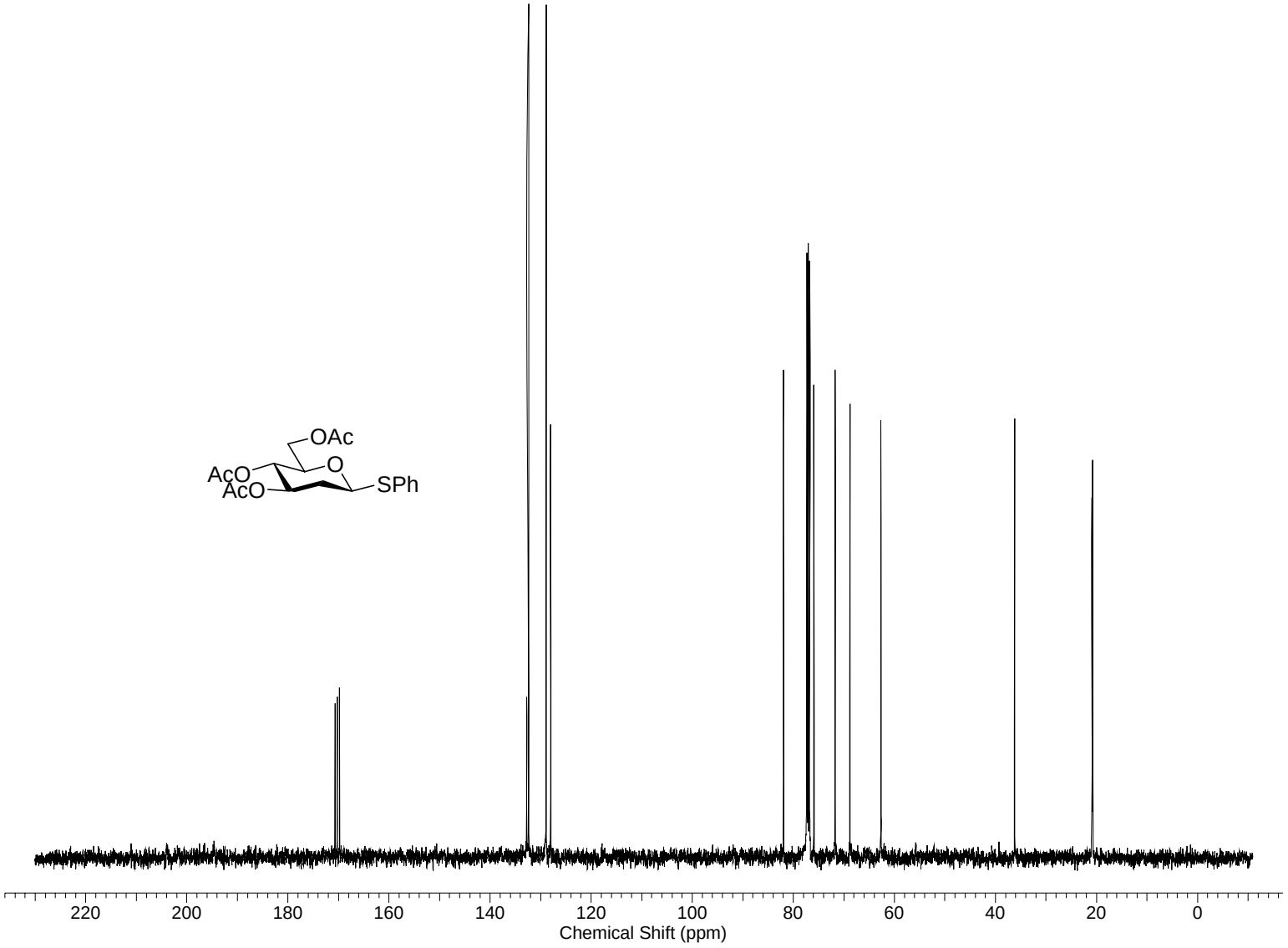
References.

1. Russell, R. N.; Weigel, T. M.; Han, O.; Liu, H.-w. *Carbohydr. Res.* **1990**, *201*, 95-114.
2. Classon, B.; Liu, Z.; Samuelsson, B. *J. Org. Chem.* **1988**, *53*, 6126-6130.
3. Withers, S. G.; Percival, M. D.; Street, I. P. *Carbohydr. Res.* **1989**, *187*, 43-66.

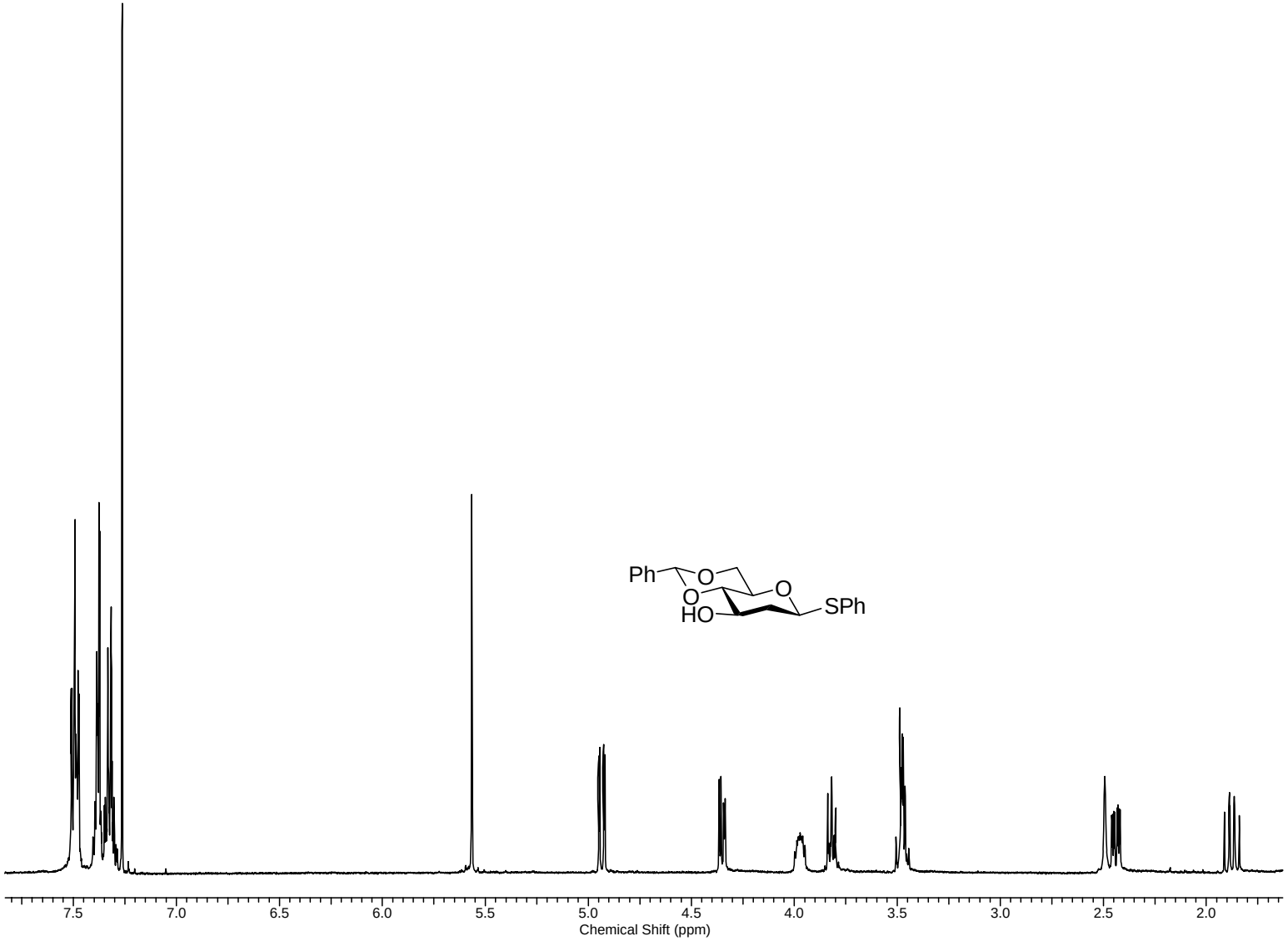
^{1}H spectrum of *S*-Phenyl 3,4,6-tri-*O*-acetyl-2-deoxy-β-D-*arabino*-thiohexopyranoside (17):



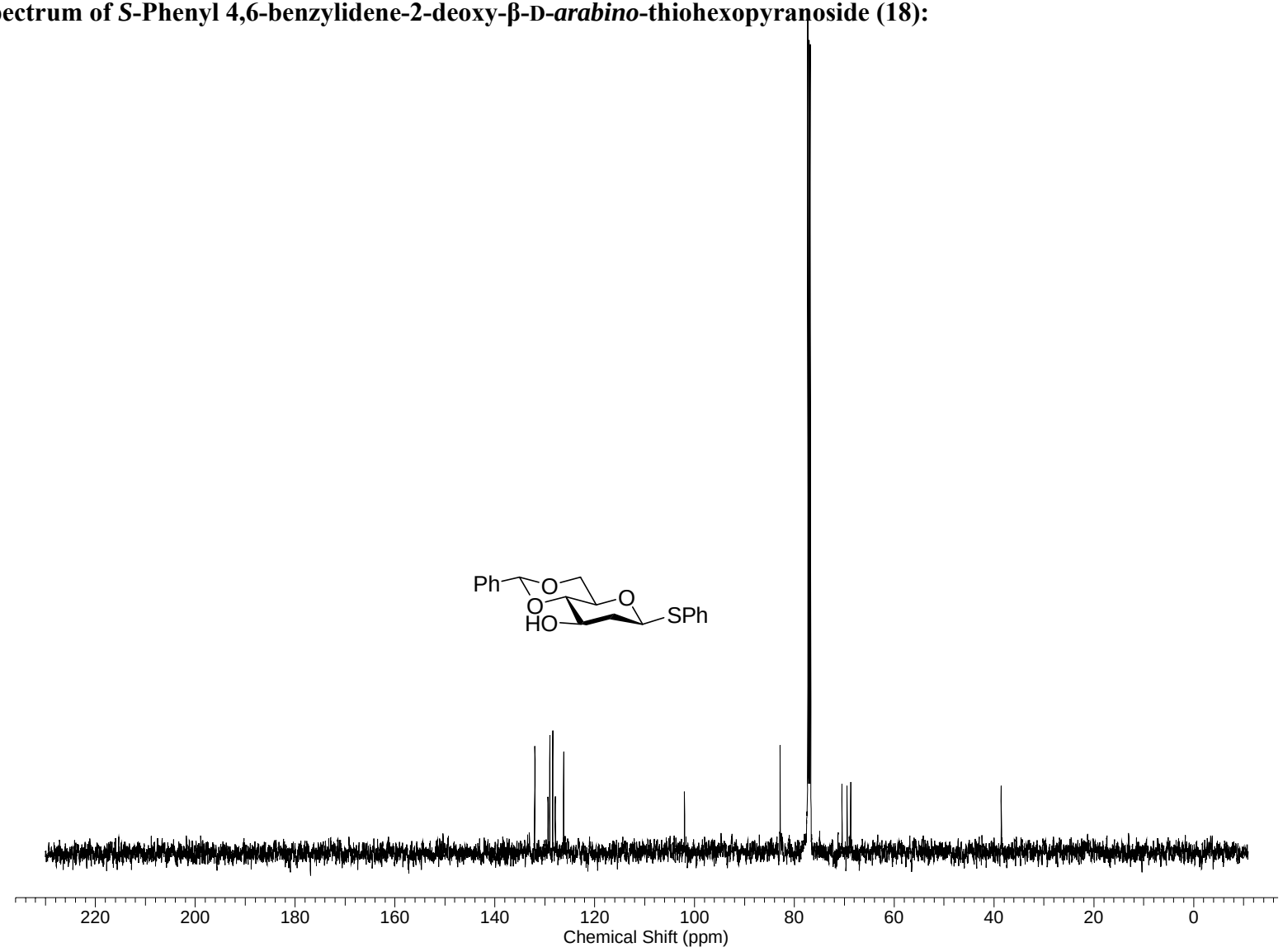
^{13}C spectrum of *S*-Phenyl 3,4,6-tri-*O*-acetyl-2-deoxy-β-D-*arabino*-thiohexopyranoside (17):



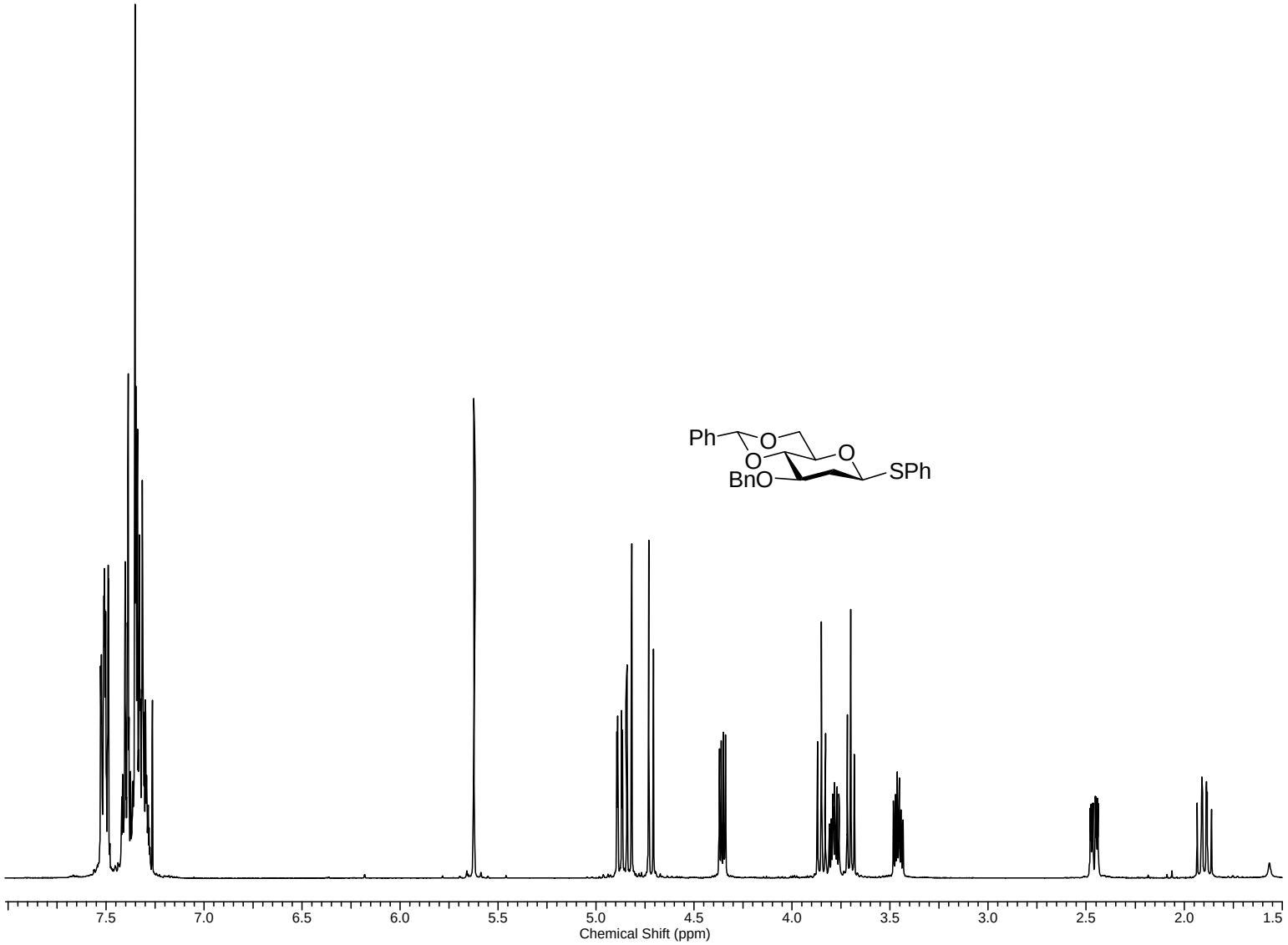
^{1}H spectrum of *S*-Phenyl 4,6-benzylidene-2-deoxy-β-D-*arabino*-thiohexopyranoside (18):



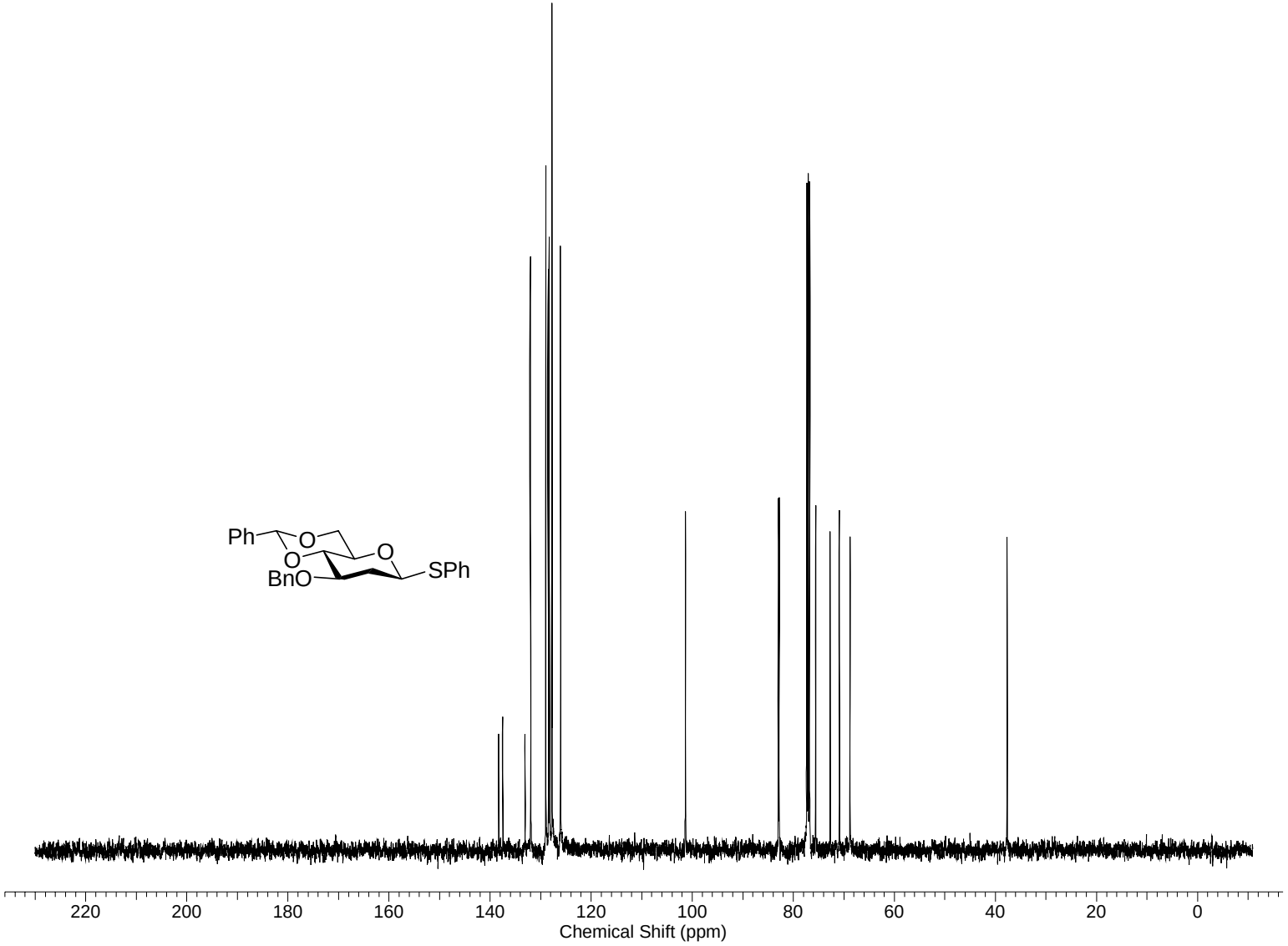
^{13}C spectrum of *S*-Phenyl 4,6-benzylidene-2-deoxy-β-D-*arabino*-thiohexopyranoside (18):



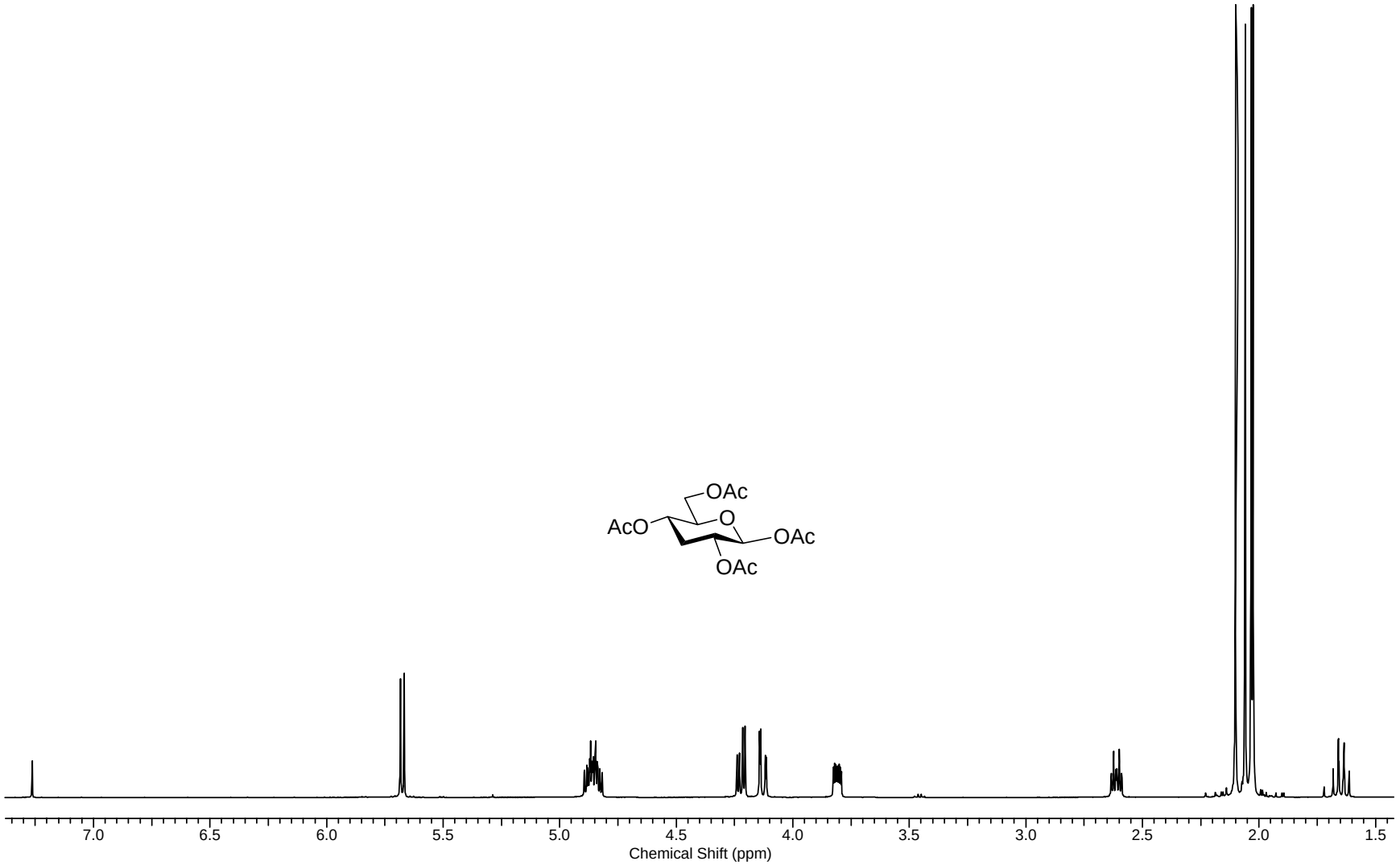
^{1}H spectrum of *S*-Phenyl 3-*O*-benzyl-4,6-benzylidene-2-deoxy-β-D-*arabino*-thiohexopyranoside (19):



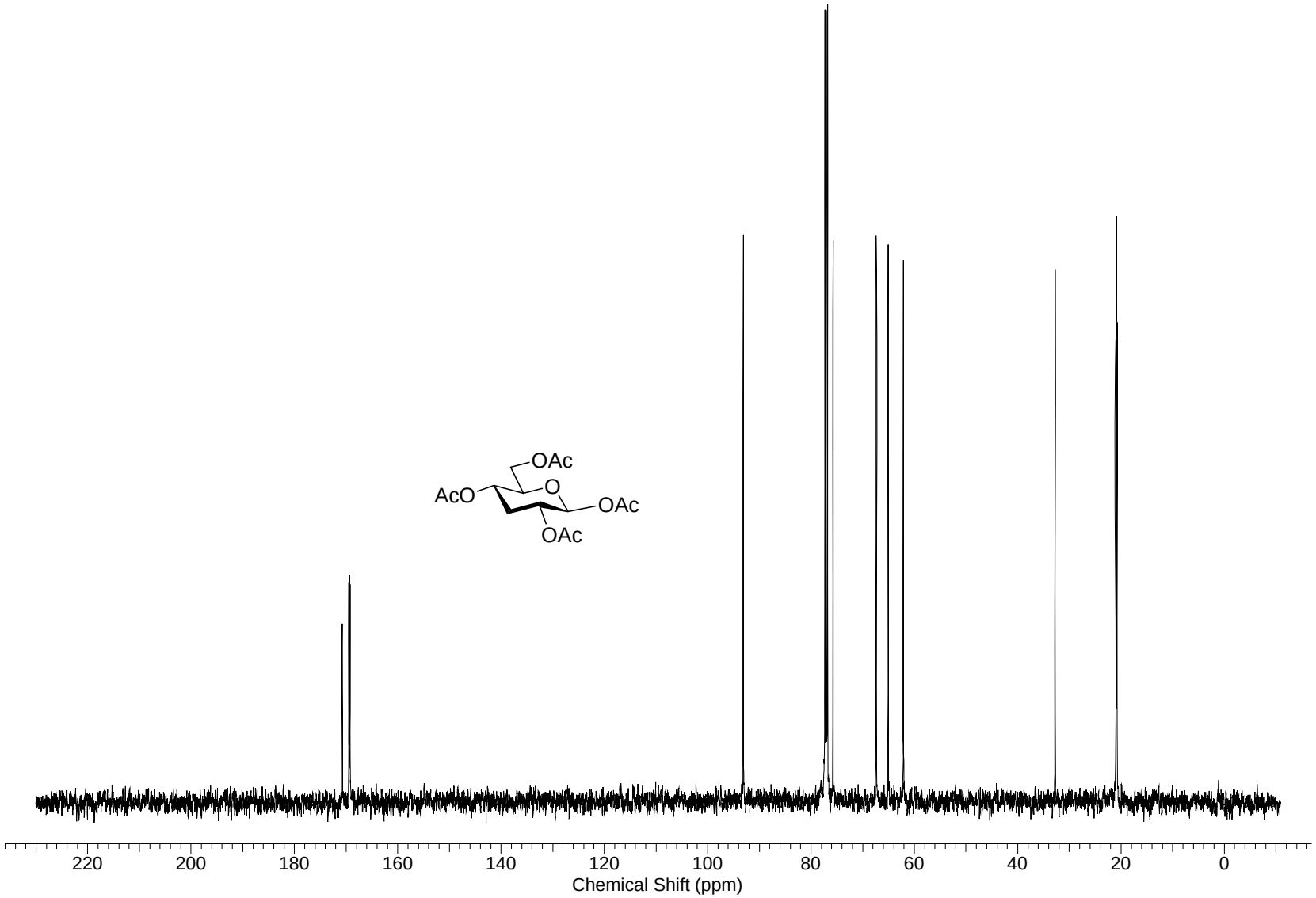
^{13}C spectrum of *S*-Phenyl 3-*O*-benzyl-4,6-benzylidene-2-deoxy-β-D-*arabino*-thiohexopyranoside (19):



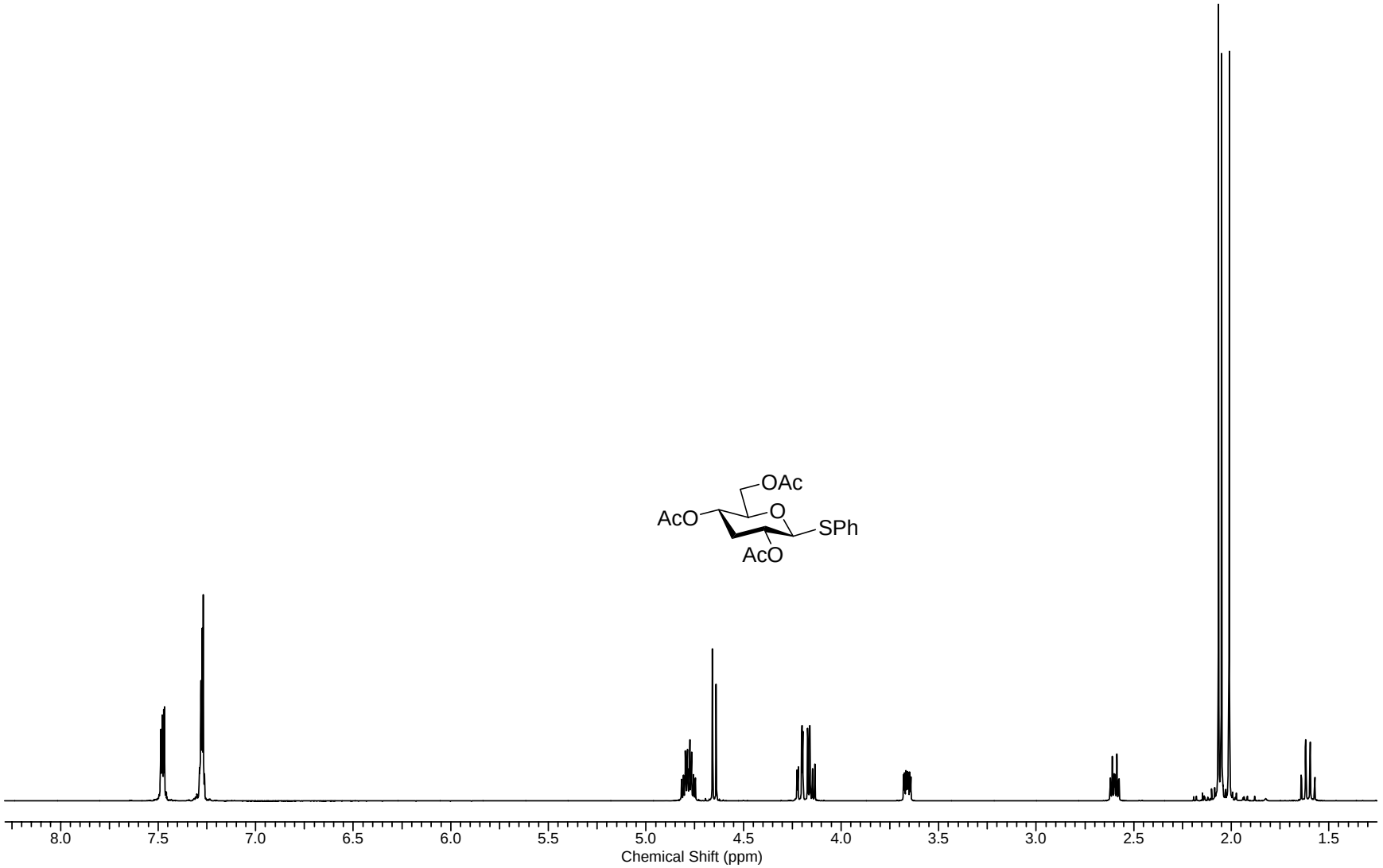
^{1}H spectrum of 1,2,4,6-tetra-*O*-acetyl-3-deoxy-β-D-*ribo*-thiohexopyranose (21):



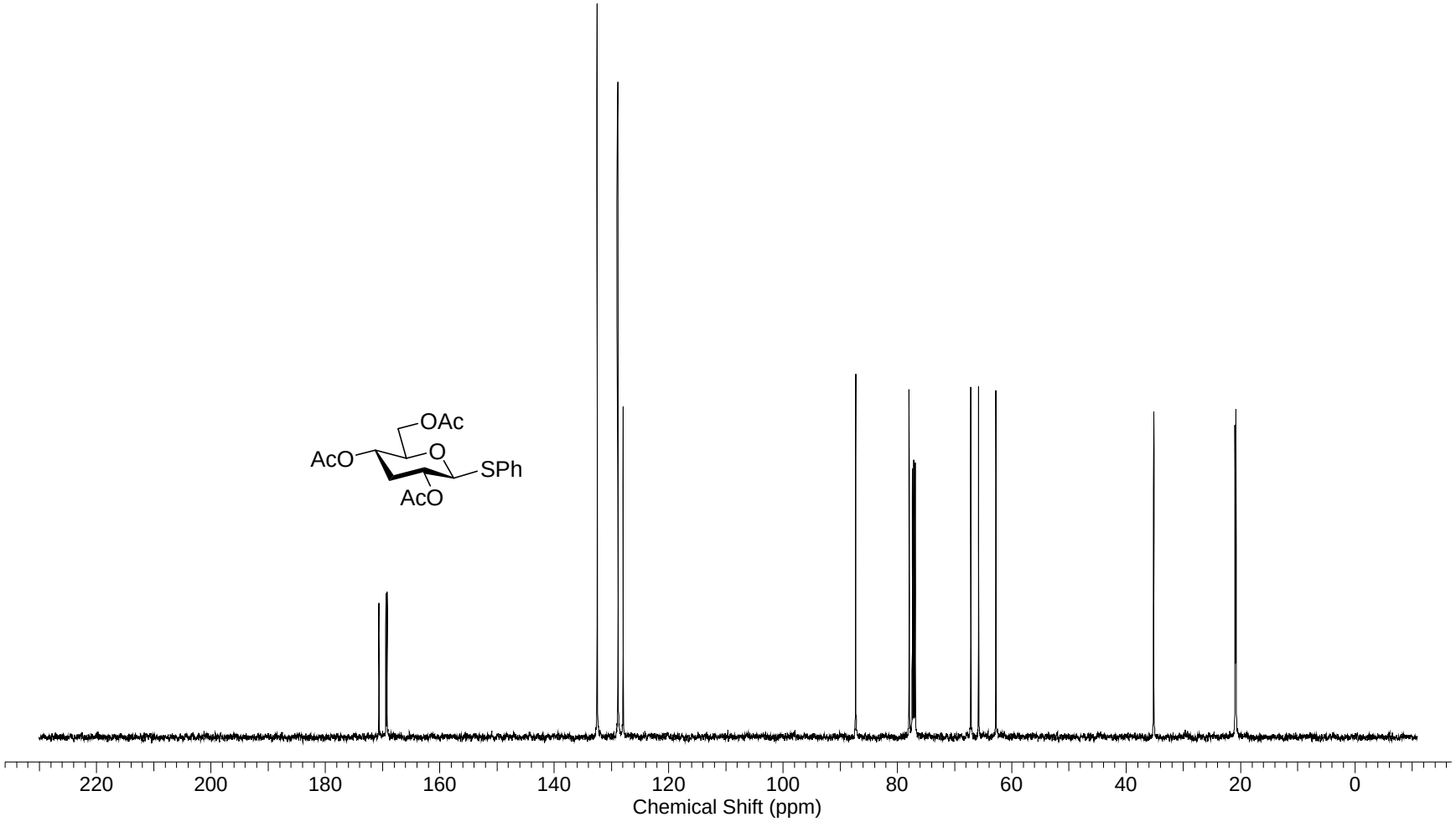
^{13}C spectrum of 1,2,4,6-tetra-*O*-acetyl-3-deoxy-β-D-*ribo*-thiohexopyranose (21):



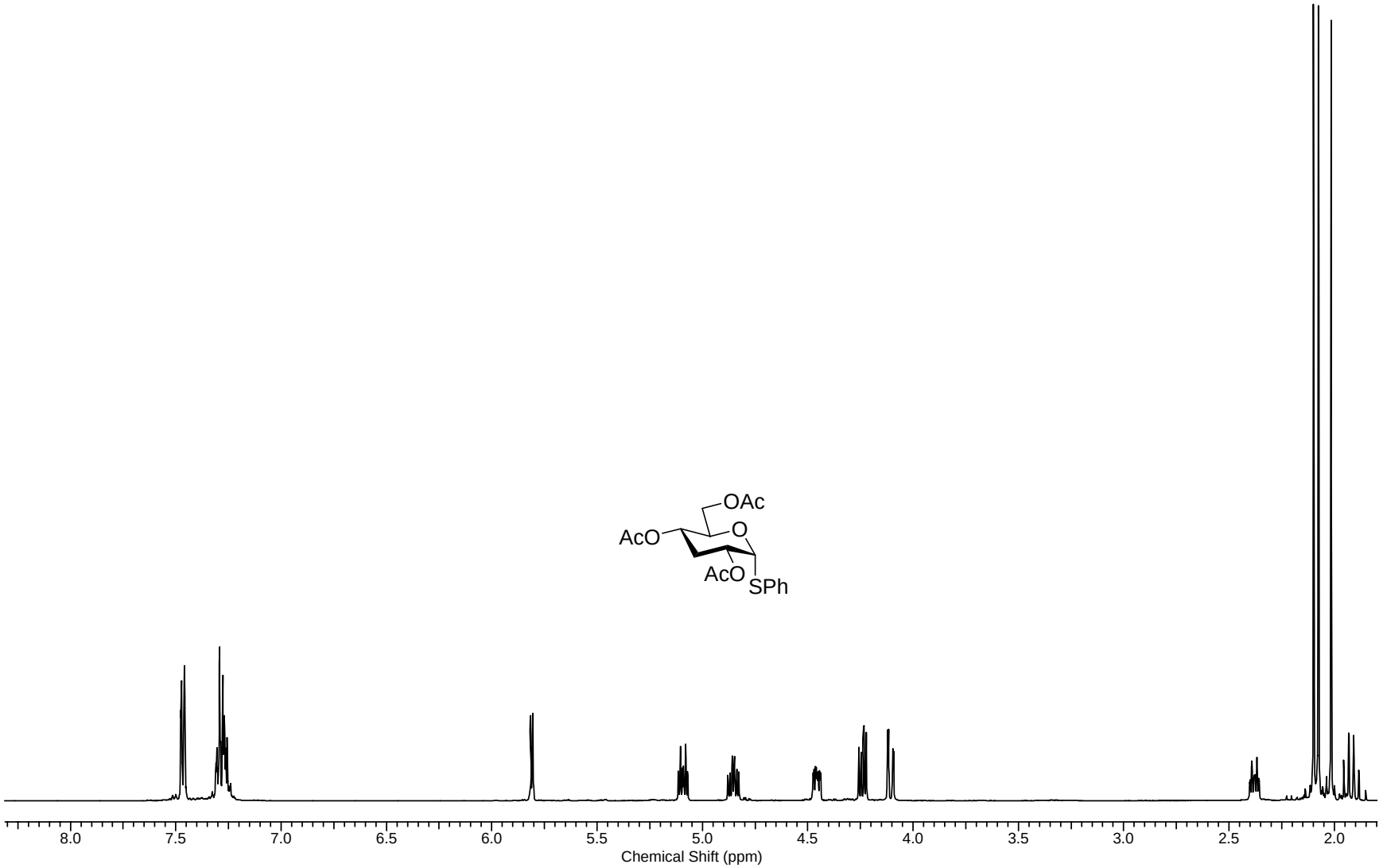
^{1}H spectrum of *S*-Phenyl 2,4,6-tri-*O*-acetyl-3-deoxy-β-D-*ribo*-thiohexopyranoside (22):



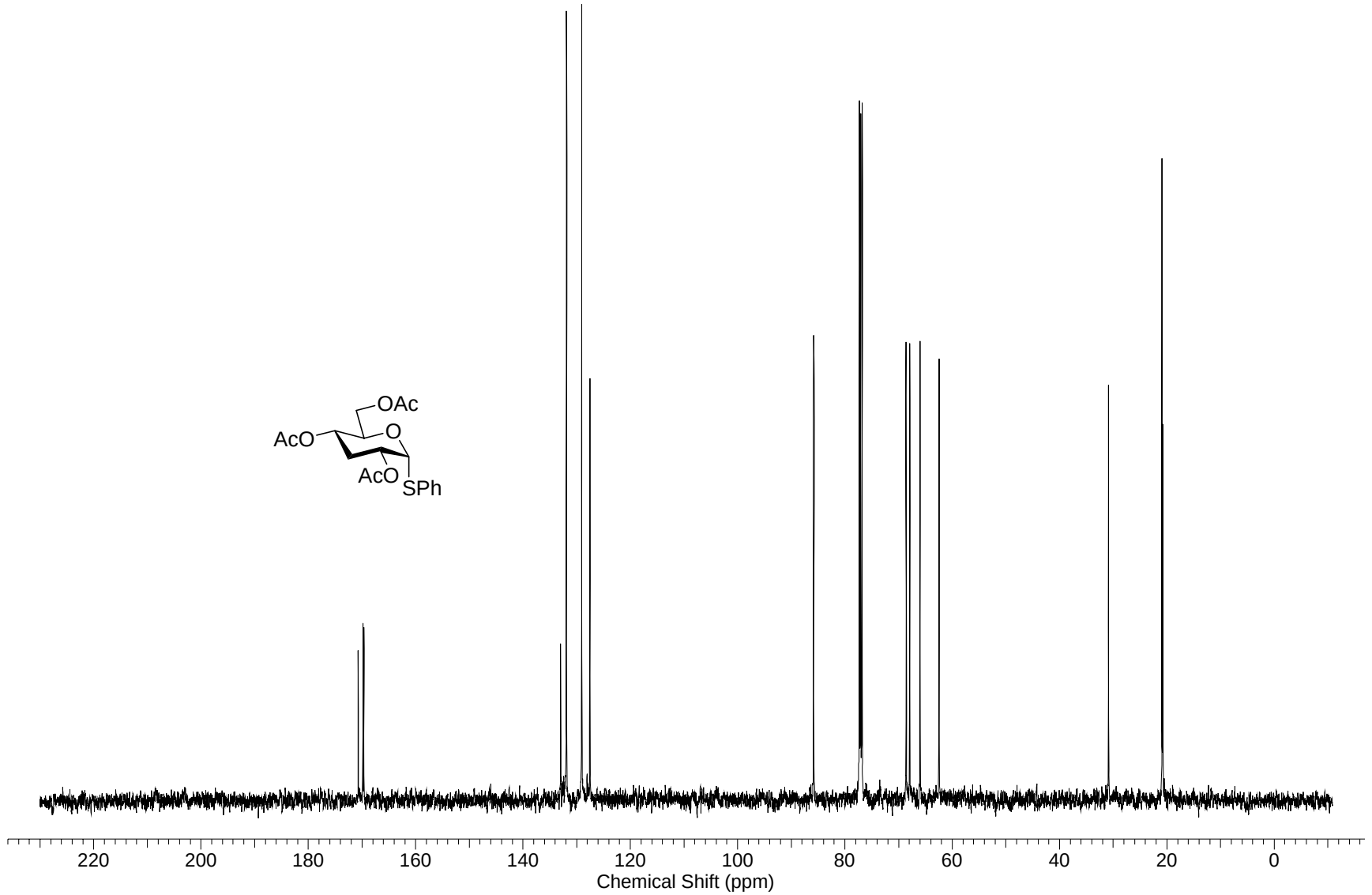
^{13}C spectrum of *S*-Phenyl 2,4,6-tri-*O*-acetyl-3-deoxy-β-D-*ribo*-thiohexopyranoside (22):



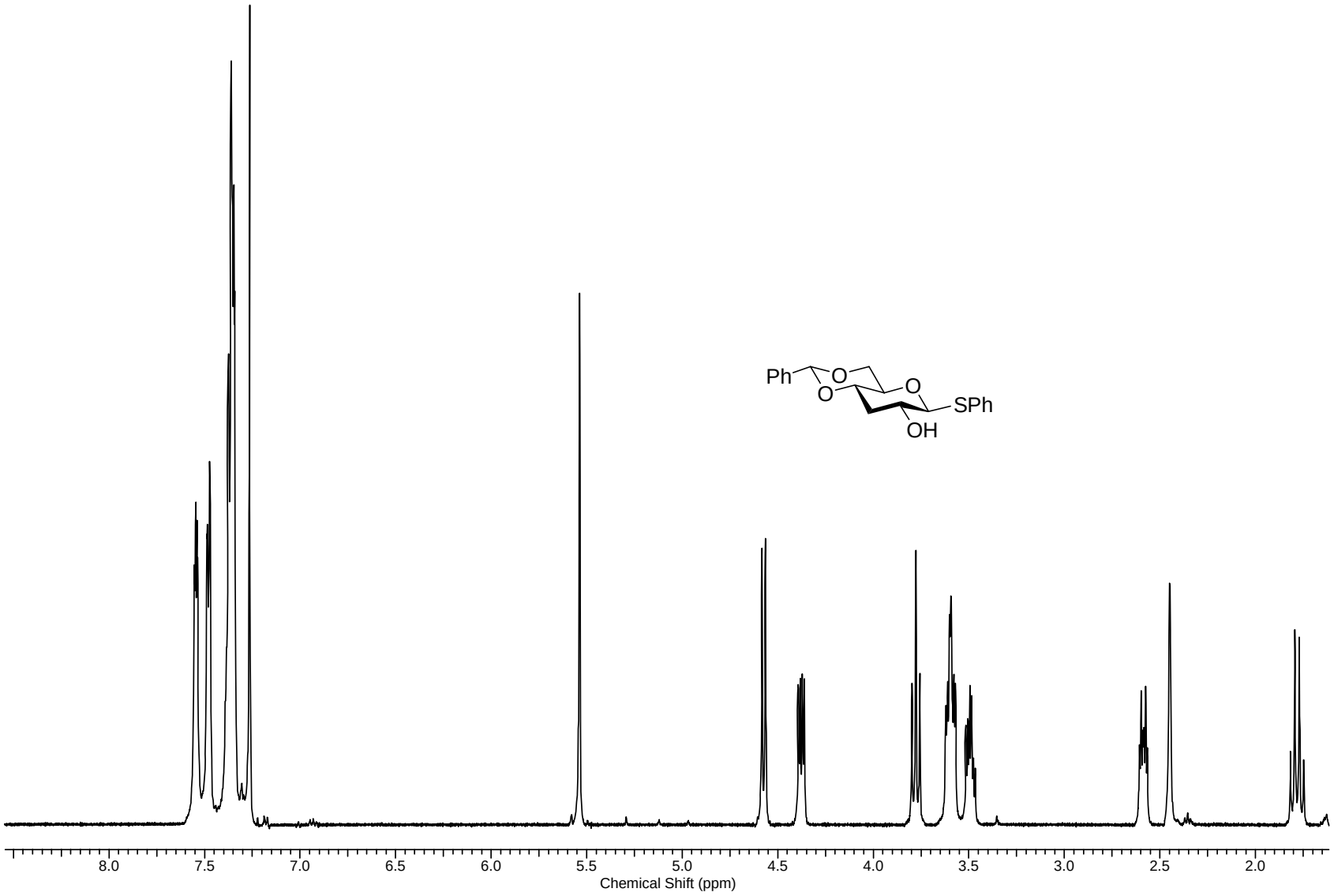
^{1}H spectrum of *S*-Phenyl 2,4,6-tri-*O*-acetyl-3-deoxy-α-D-*ribo*-thiohexopyranoside (23):



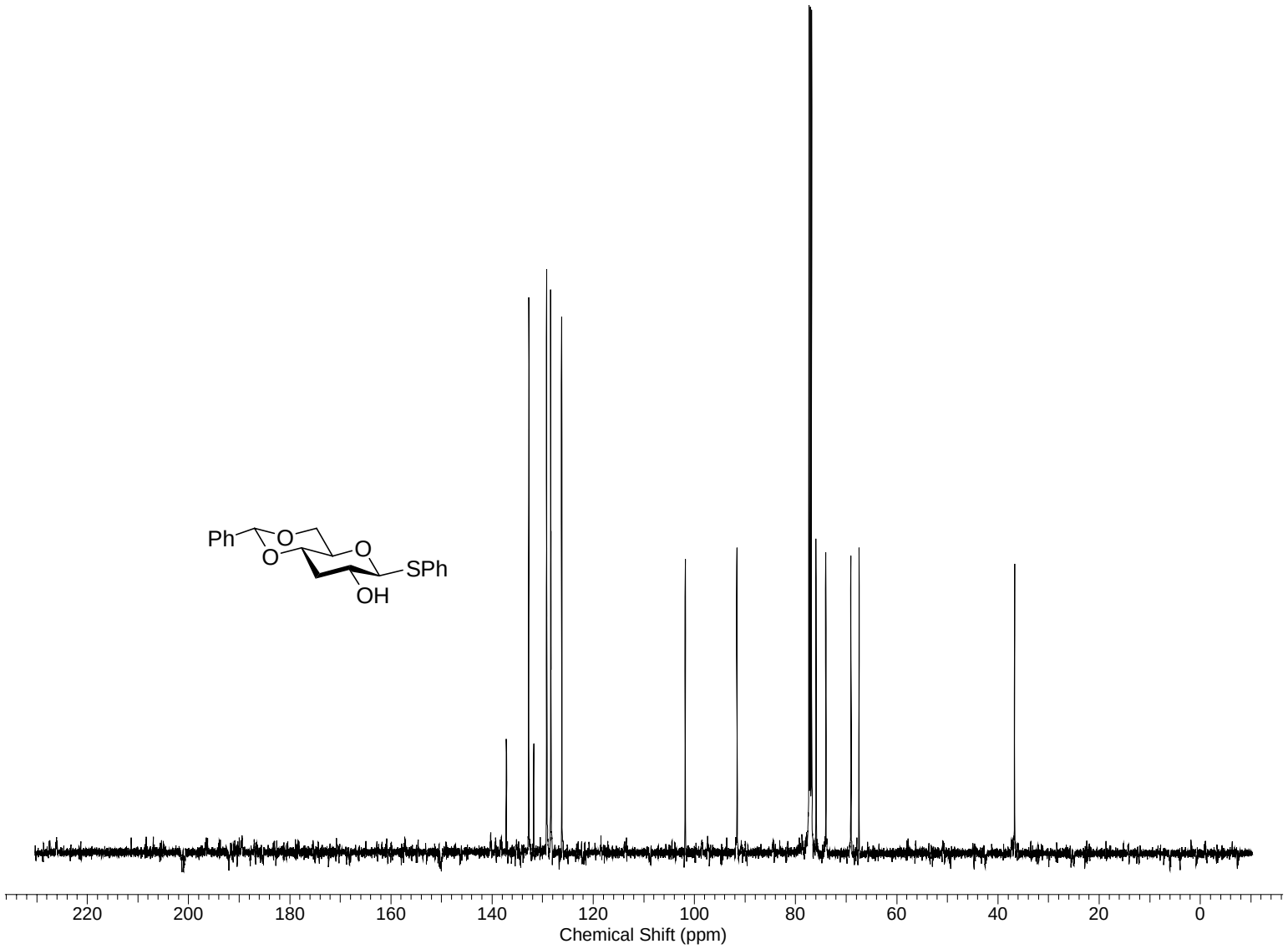
^{13}C spectrum of *S*-Phenyl 2,4,6-tri-*O*-acetyl-3-deoxy-*α*-D-*ribo*-thiohexopyranoside (23):



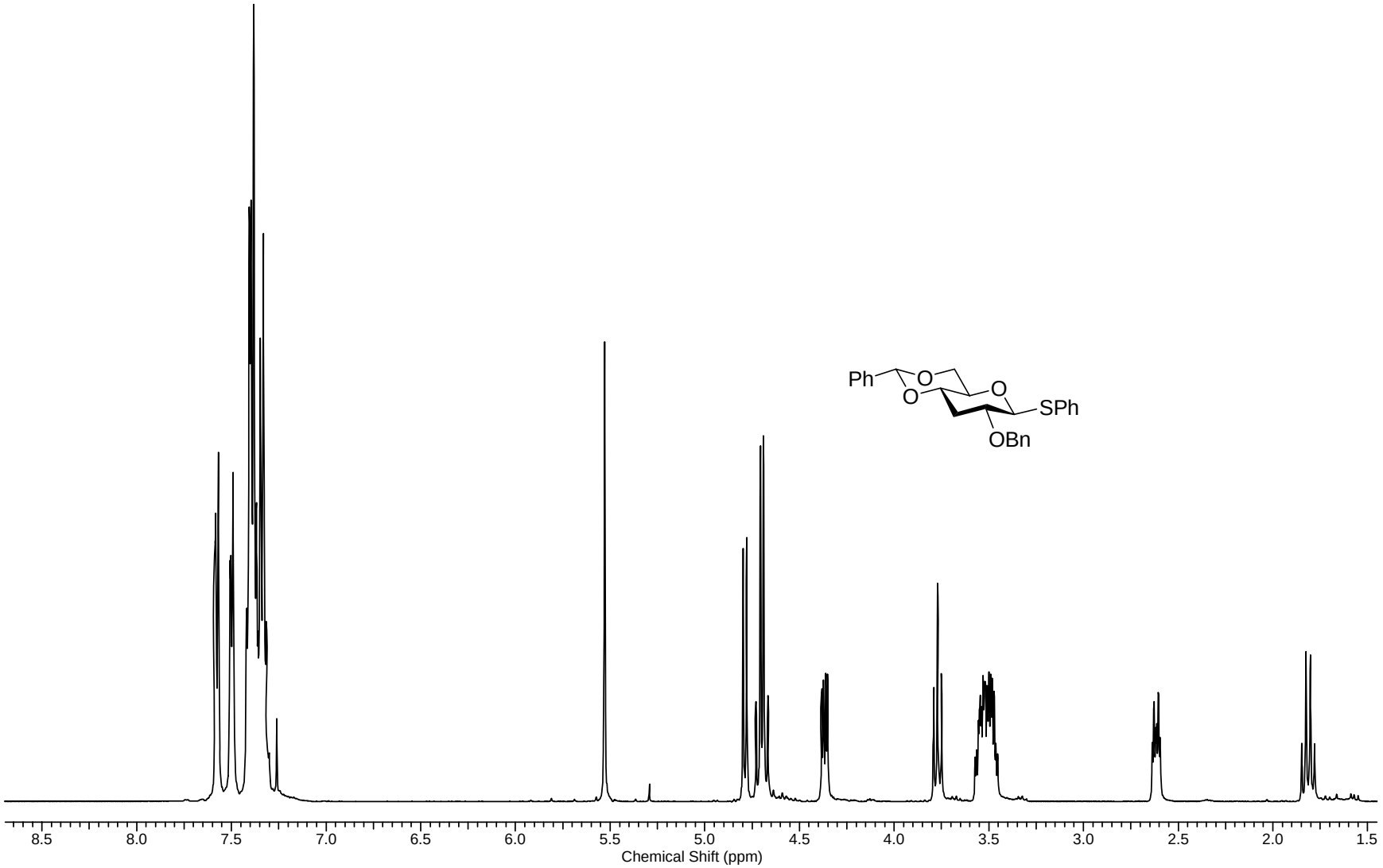
^{1}H spectrum of *S*-Phenyl 4,6-benzylidene-3-deoxy-β-D-*ribo*-thiohexopyranoside (24):



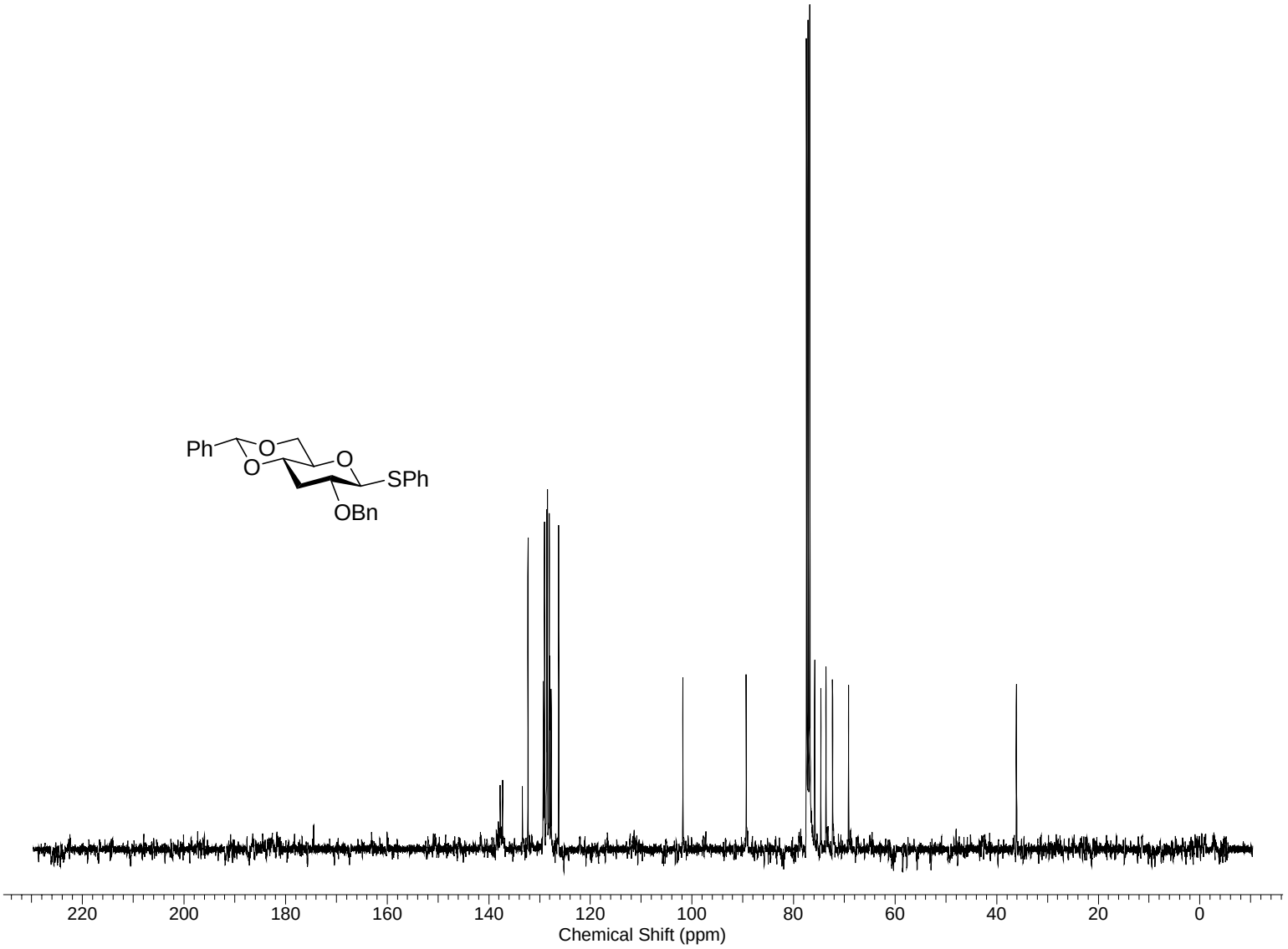
^{13}C spectrum of *S*-Phenyl 4,6-benzylidene-3-deoxy-β-D-*ribo*-thiohexopyranoside (24):



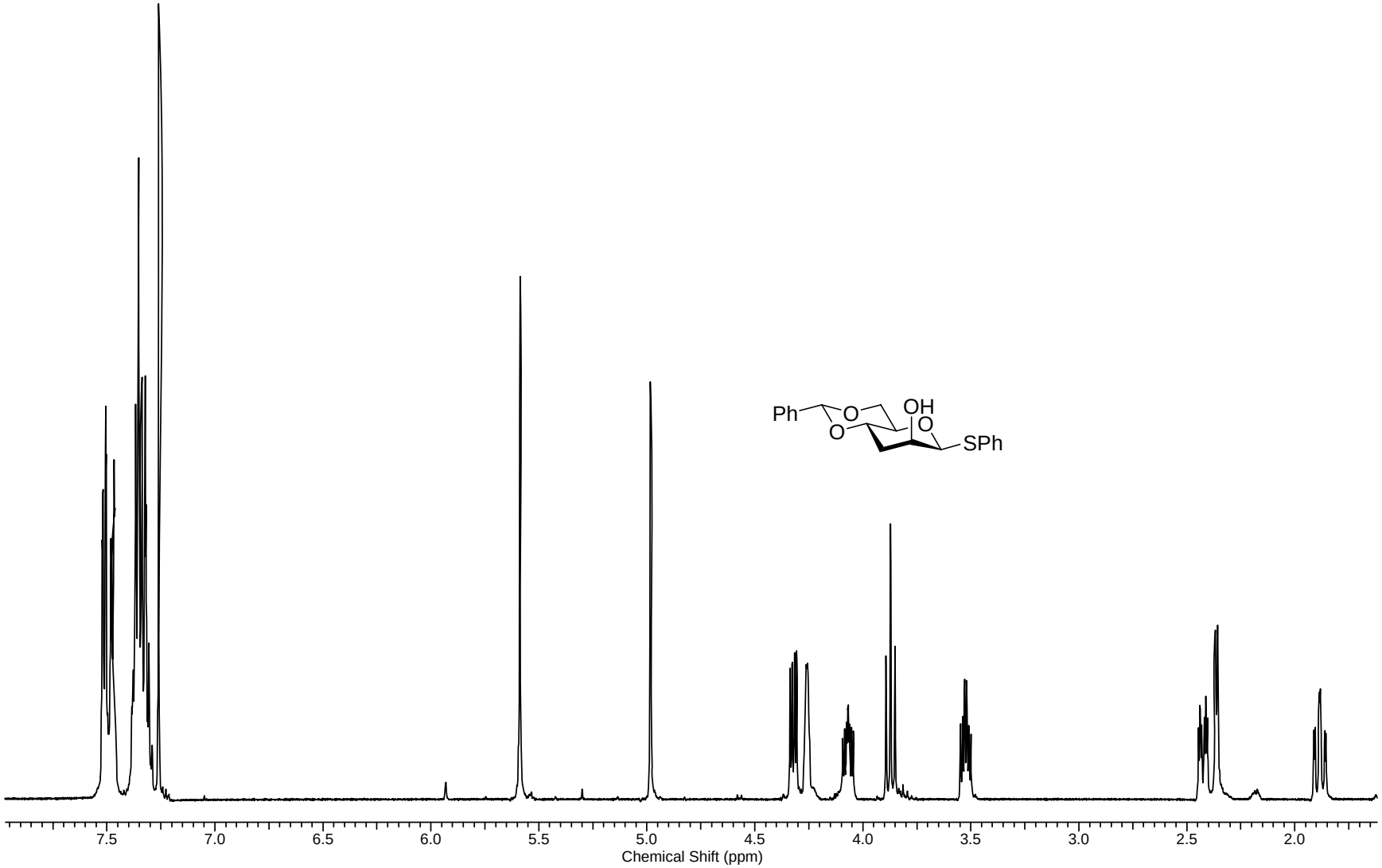
^{1}H spectrum of *S*-Phenyl 2-*O*-benzyl-4,6-benzylidene-3-deoxy-β-D- *ribo*-thiohexopyranoside (25):



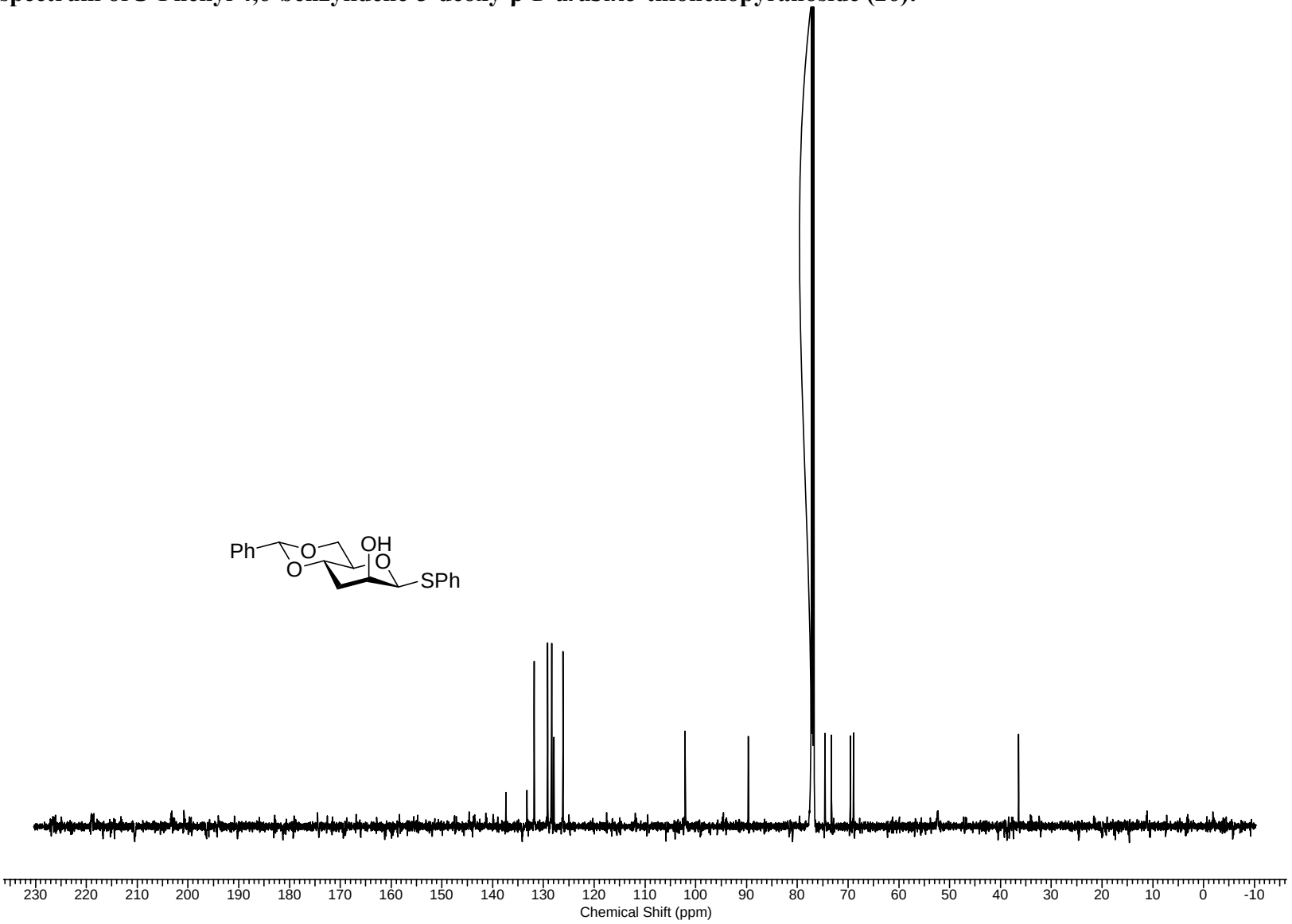
^{13}C spectrum of *S*-Phenyl 2-*O*-benzyl-4,6-benzylidene-3-deoxy-β-D- *ribo*-thiohexopyranoside (25):



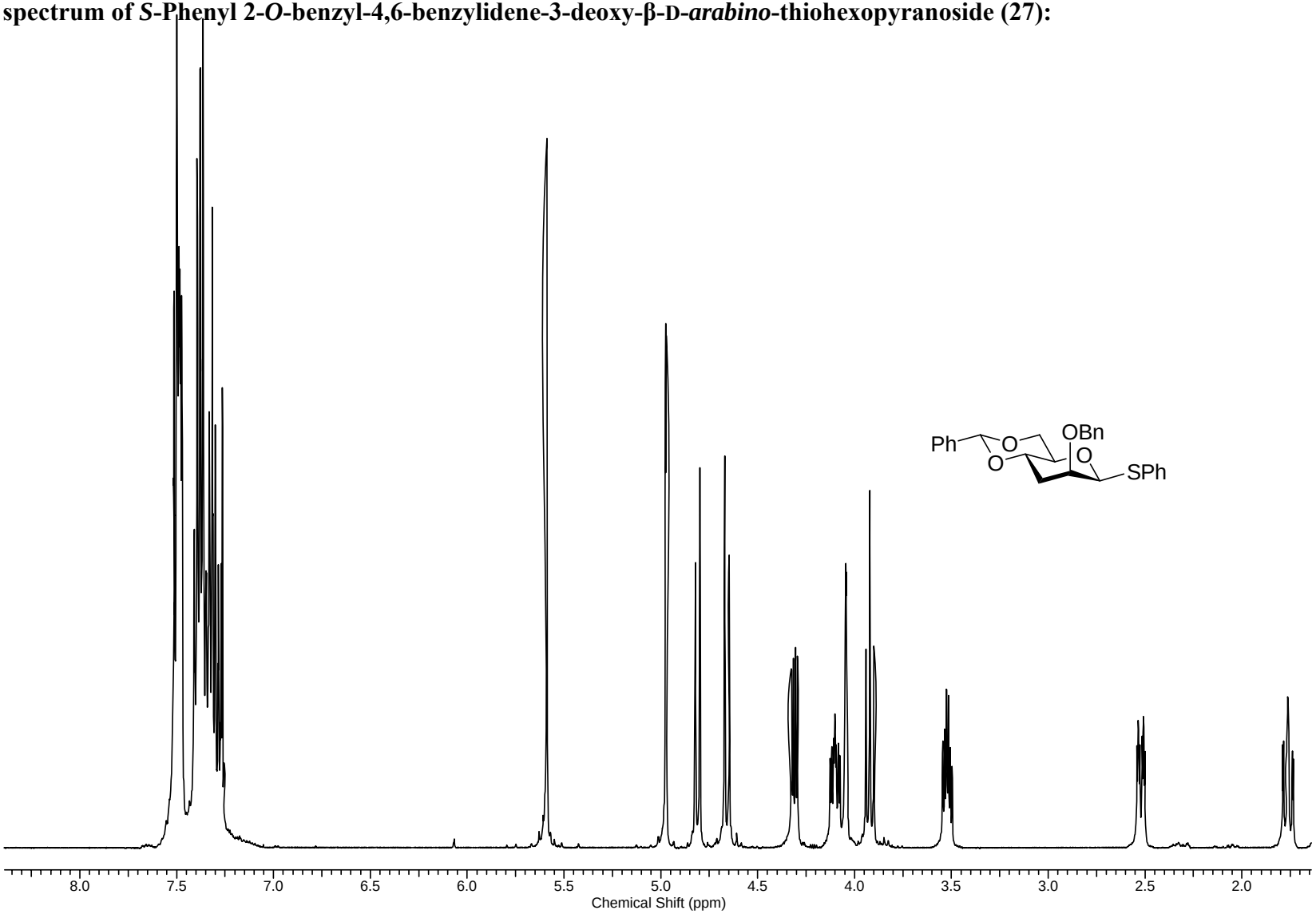
^{1}H spectrum of *S*-Phenyl 4,6-benzylidene-3-deoxy-β-D-*arabino*-thiohexopyranoside (26):



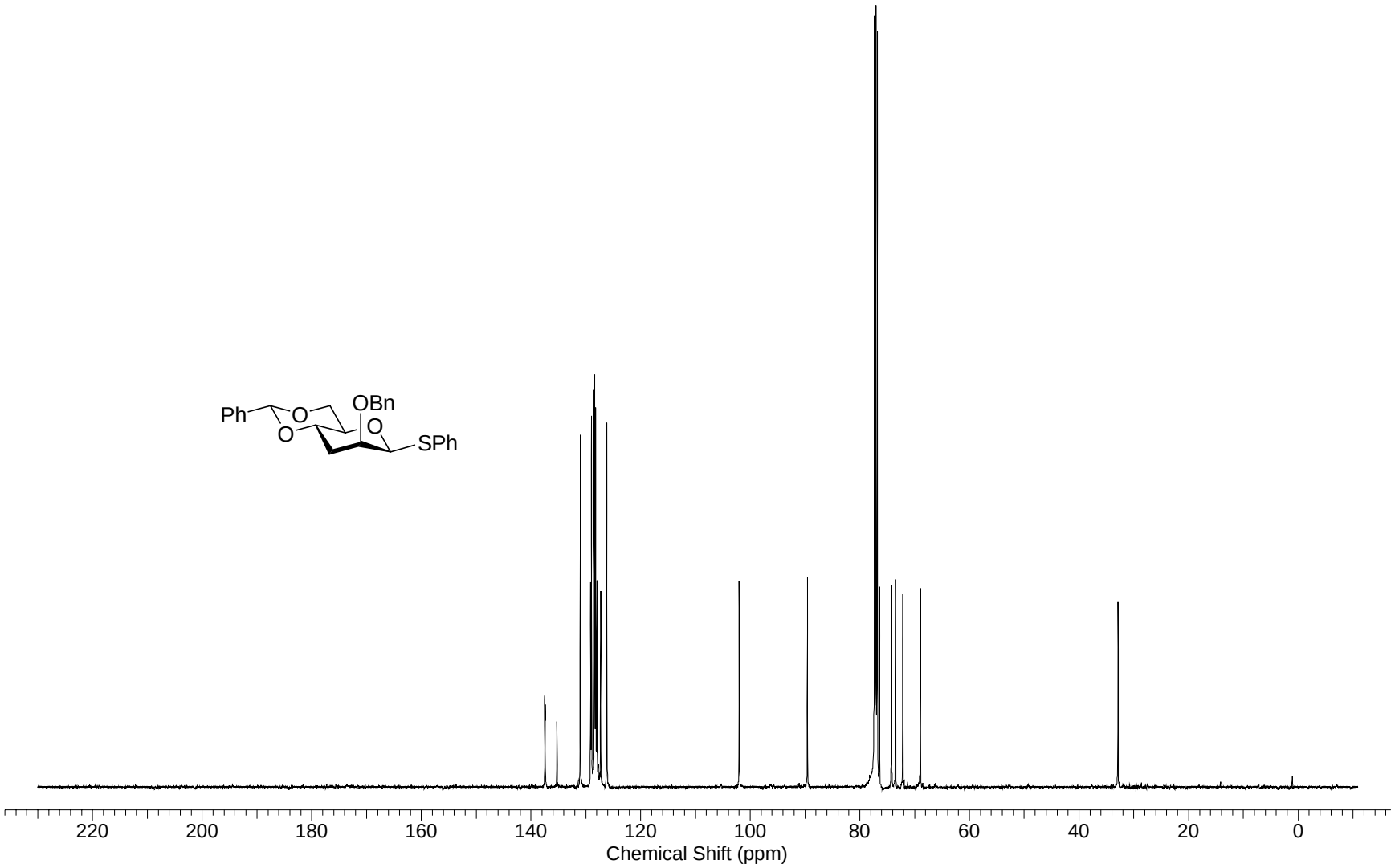
^{13}C spectrum of *S*-Phenyl 4,6-benzylidene-3-deoxy-β-D-*arabino*-thiohexopyranoside (26):



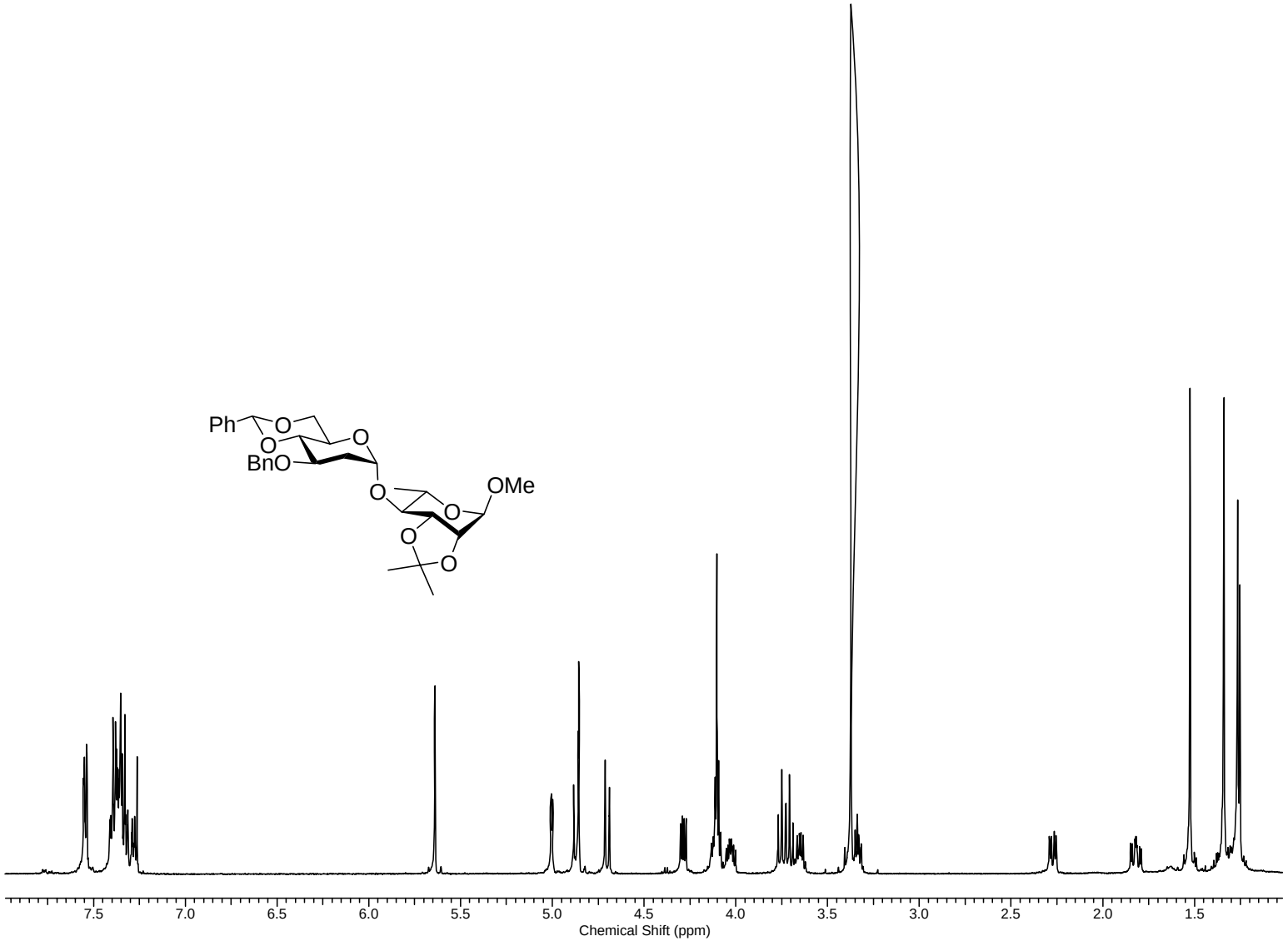
^{1}H spectrum of *S*-Phenyl 2-*O*-benzyl-4,6-benzylidene-3-deoxy-β-D-*arabino*-thiohexopyranoside (27):



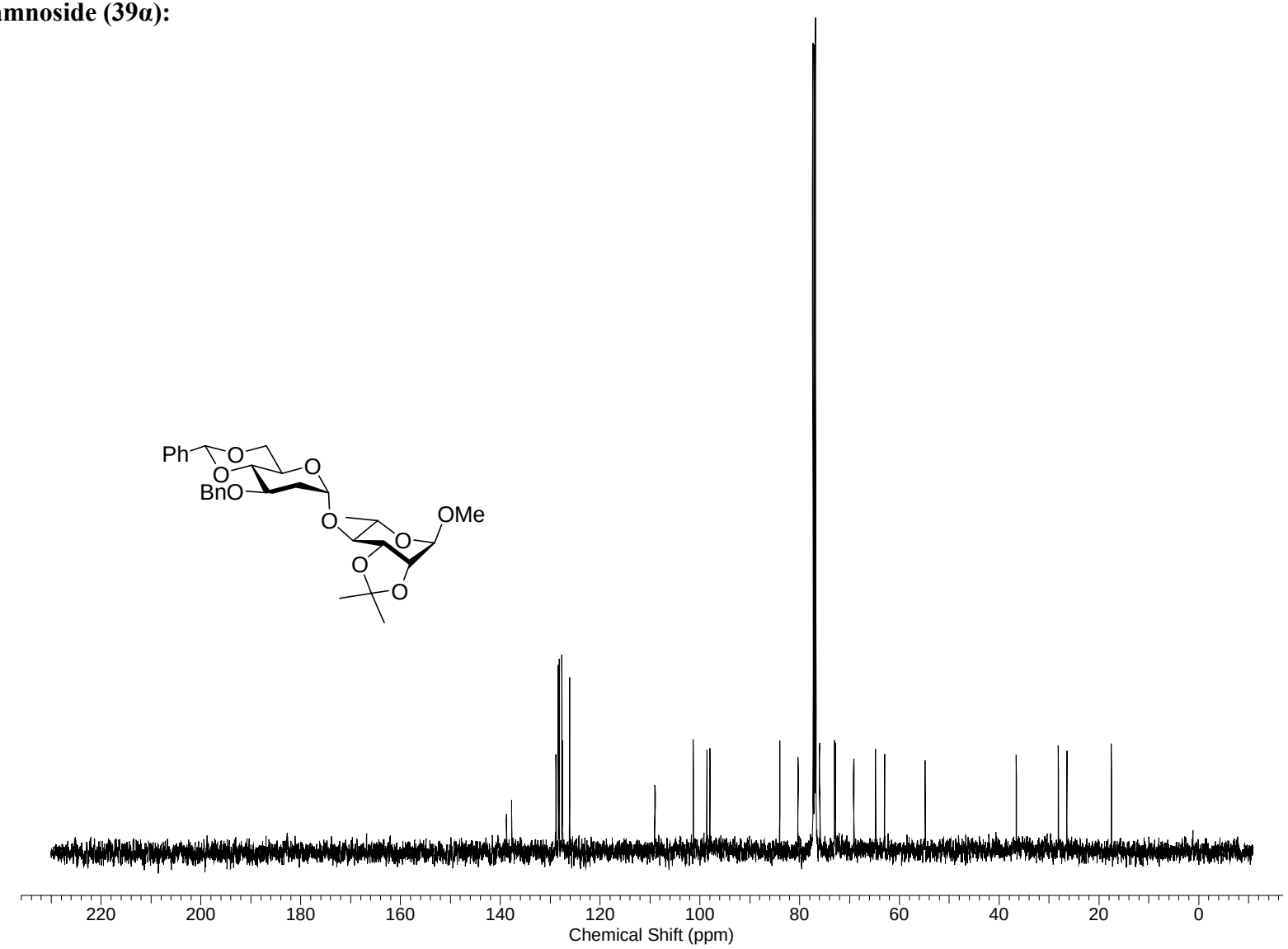
^{13}C spectrum of *S*-Phenyl 2-*O*-benzyl-4,6-benzylidene-3-deoxy-β-D-*arabino*-thiohexopyranoside (27):



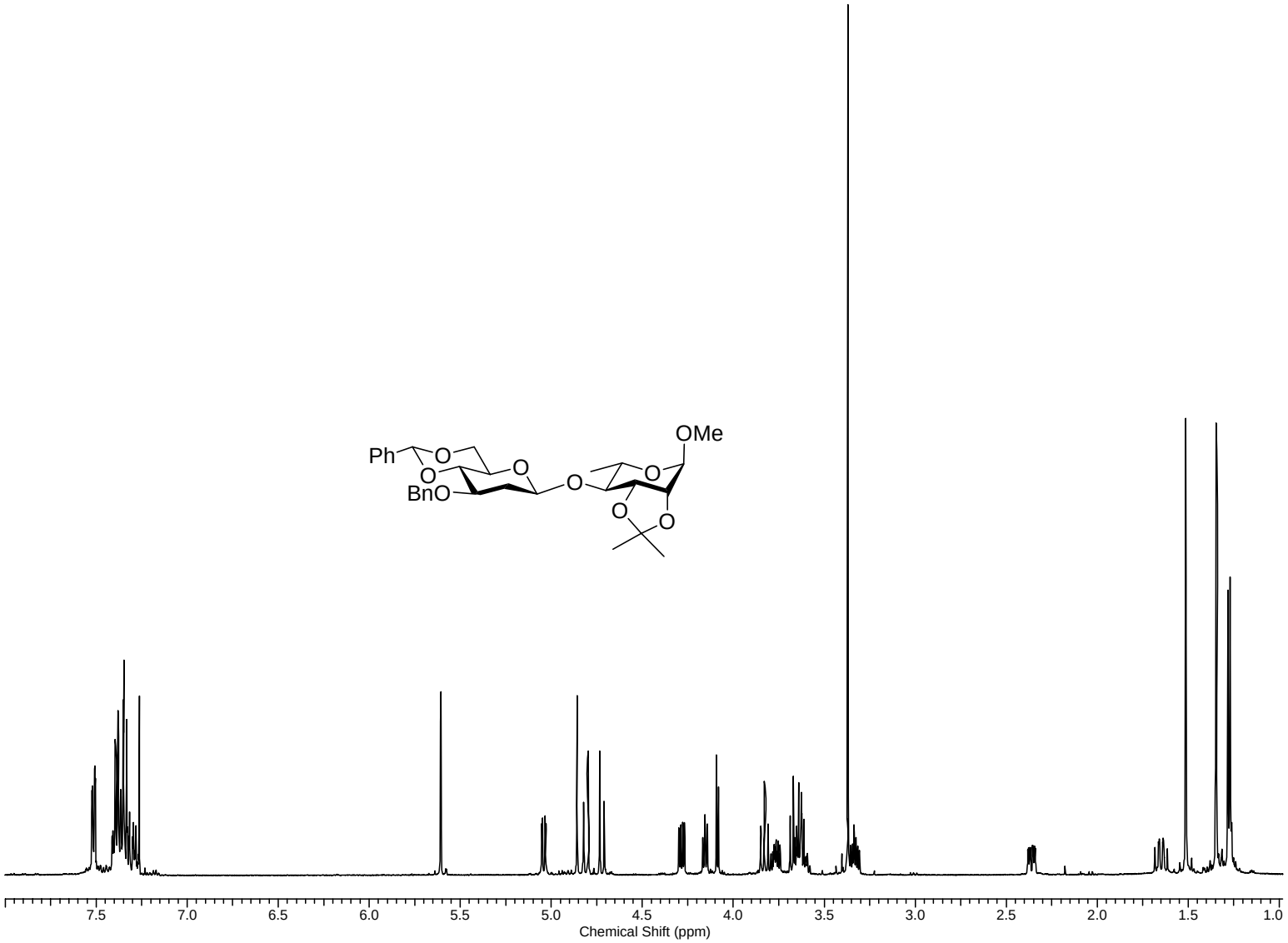
^{1}H spectrum of Methyl 4-*O*-(3'-*O*-benzyl-4',6'-benzylidene-2'-deoxy-α-D-*arabino*-thiohexopyranosyl)-2,3-*O*-isopropylidene-α-L-rhamnoside (39α):



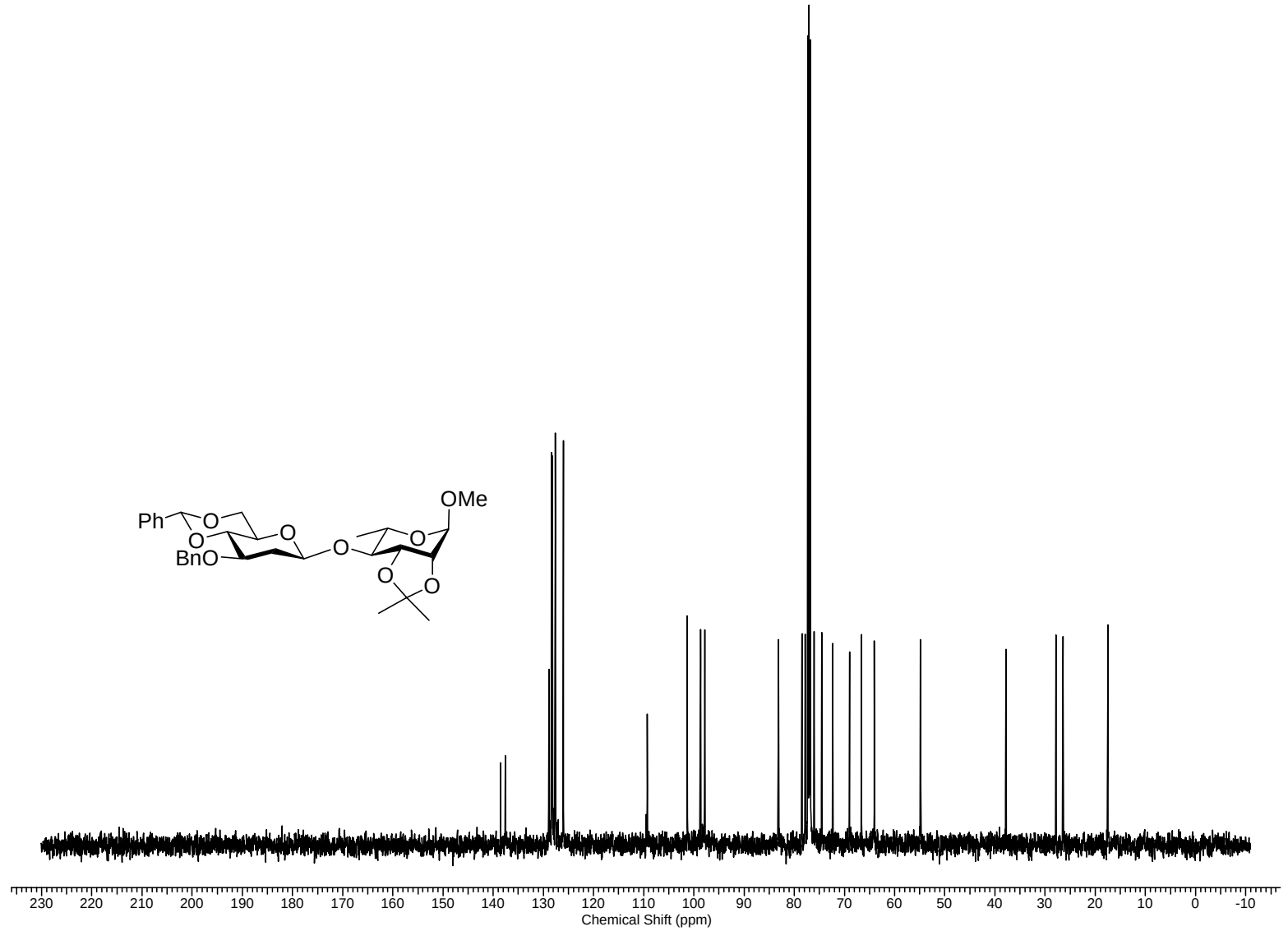
^{13}C spectrum of Methyl 4-*O*-(3'-*O*-benzyl-4',6'-benzylidene-2'-deoxy-α-D-*arabino*-thiohexopyranosyl)-2,3-*O*-isopropylidene-α-L-rhamnoside (39α):



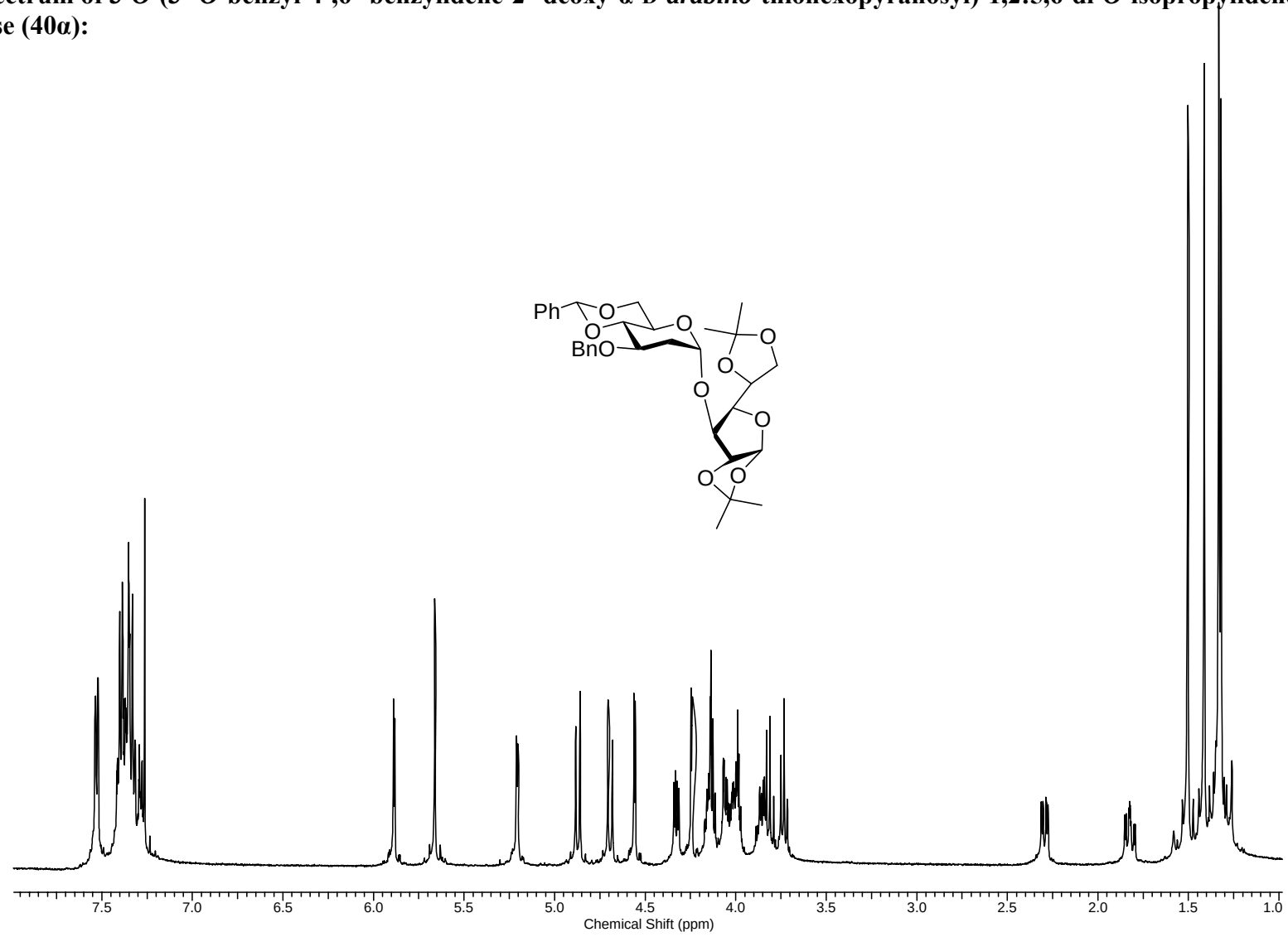
^{1}H spectrum of Methyl 4-*O*-(3'-*O*-benzyl-4',6'-benzylidene-2'-deoxy-β-D-*arabino*-thiohexopyranosyl)-2,3-*O*-isopropylidene-α-L-rhamnoside (39β):



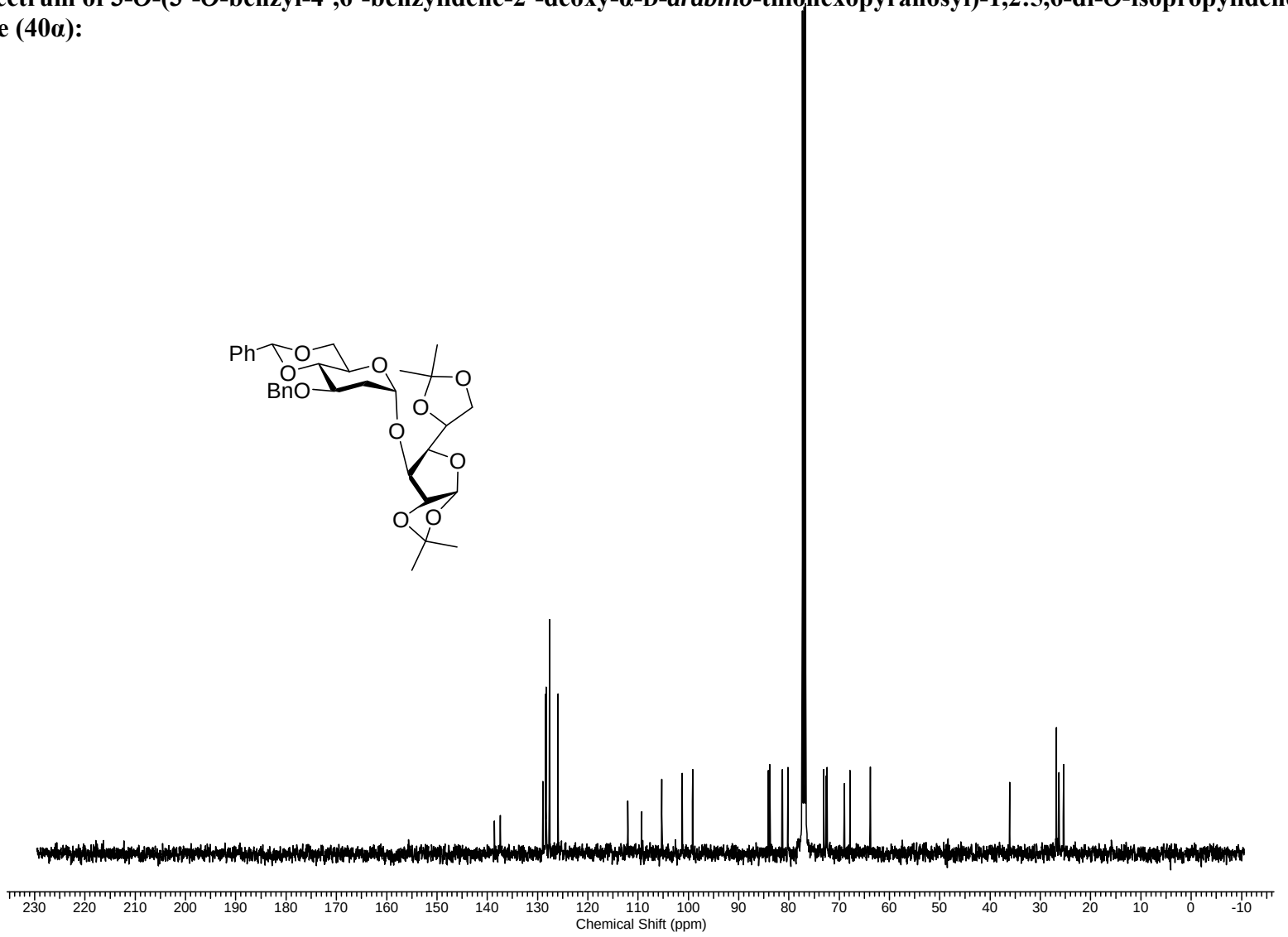
^{13}C spectrum of Methyl 4-*O*-(3'-*O*-benzyl-4',6'-benzylidene-2'-deoxy-β-D-*arabino*-thiohexopyranosyl)-2,3-*O*-isopropylidene-α-L-rhamnoside (39β):



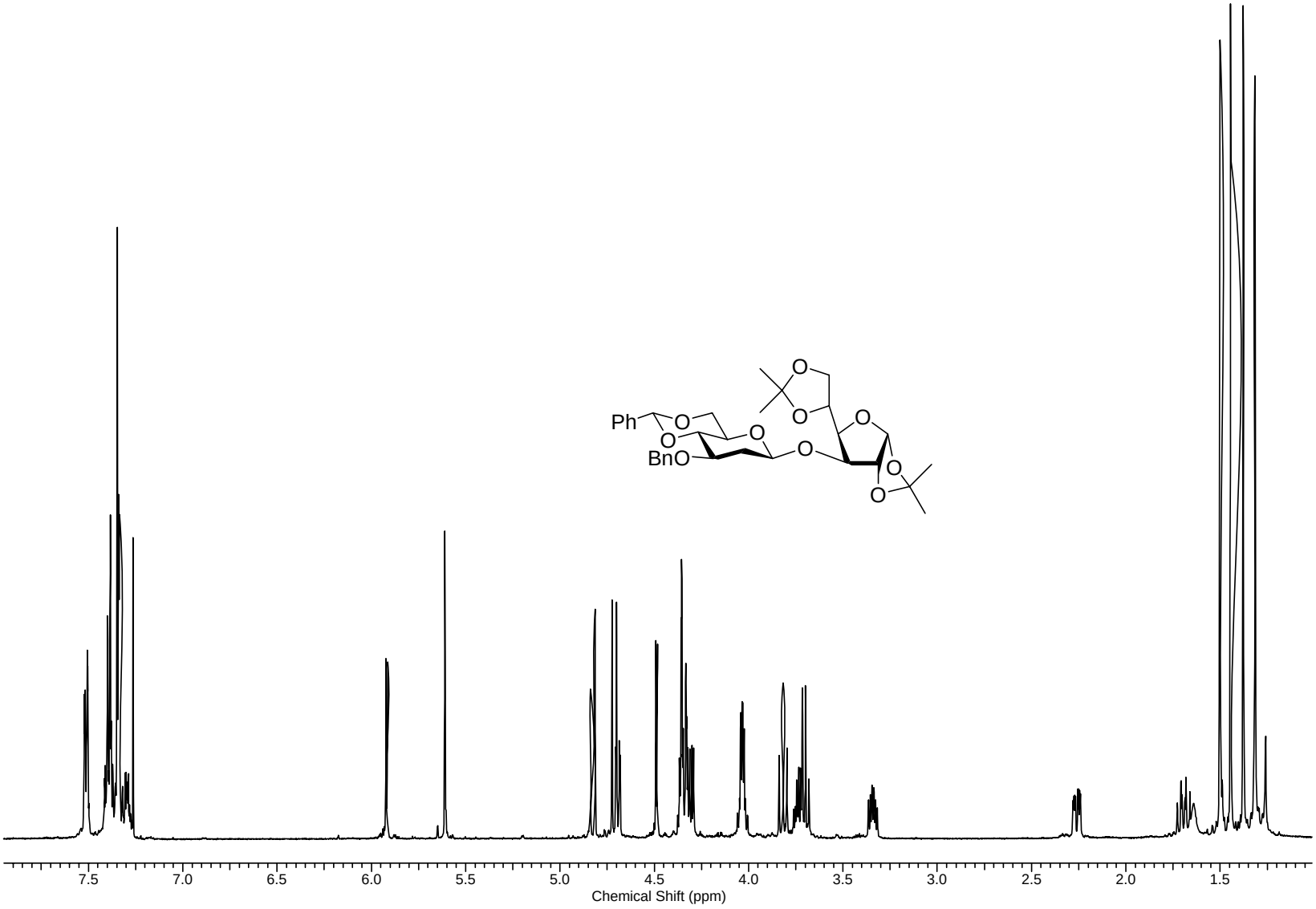
^{1}H spectrum of 3-*O*-(3'-*O*-benzyl-4',6'-benzylidene-2'-deoxy-α-D-*arabino*-thiohexopyranosyl)-1,2:5,6-di-*O*-isopropylidene-α-D-glucose (40*α*):



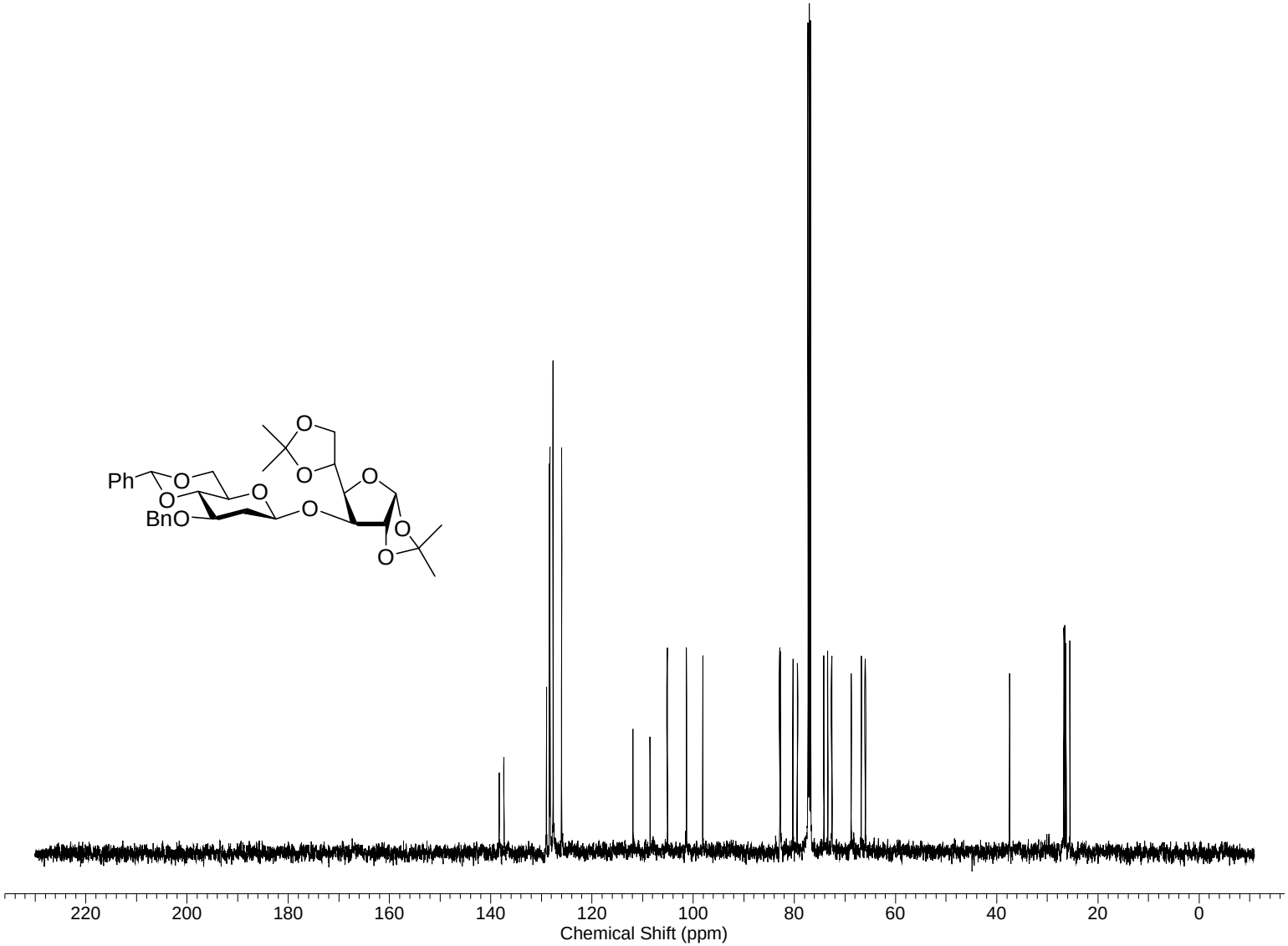
^{13}C spectrum of 3-*O*-(3'-*O*-benzyl-4',6'-benzylidene-2'-deoxy-α-D-*arabino*-thiohexopyranosyl)-1,2:5,6-di-*O*-isopropylidene-α-D-glucose (40*α*):



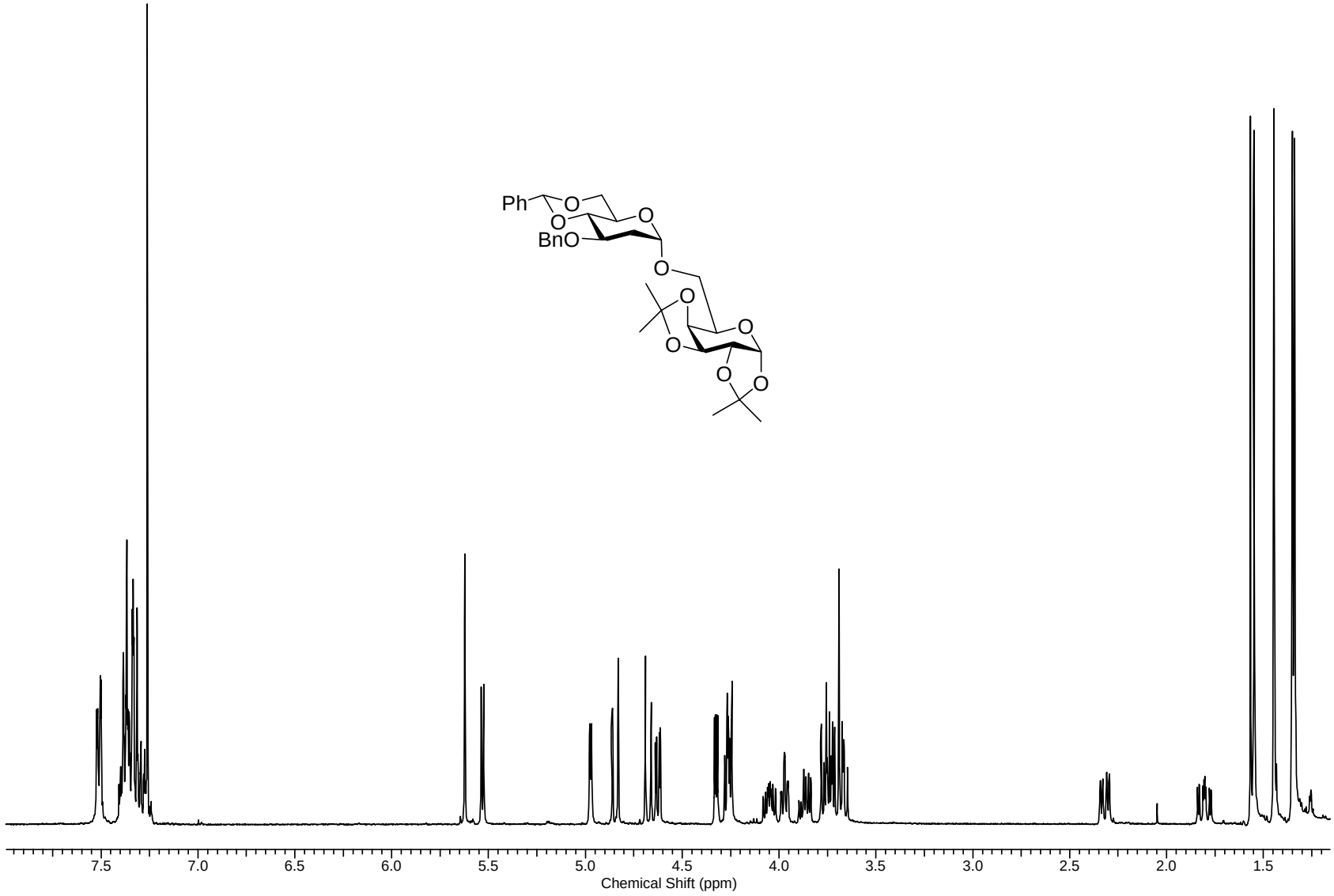
^{1}H spectrum of 3-*O*-(3'-*O*-benzyl-4',6'-benzylidene-2'-deoxy-β-D-*arabino*-thiohexopyranosyl)-1,2:5,6-di-*O*-isopropylidene-α-D-glucose (40β):



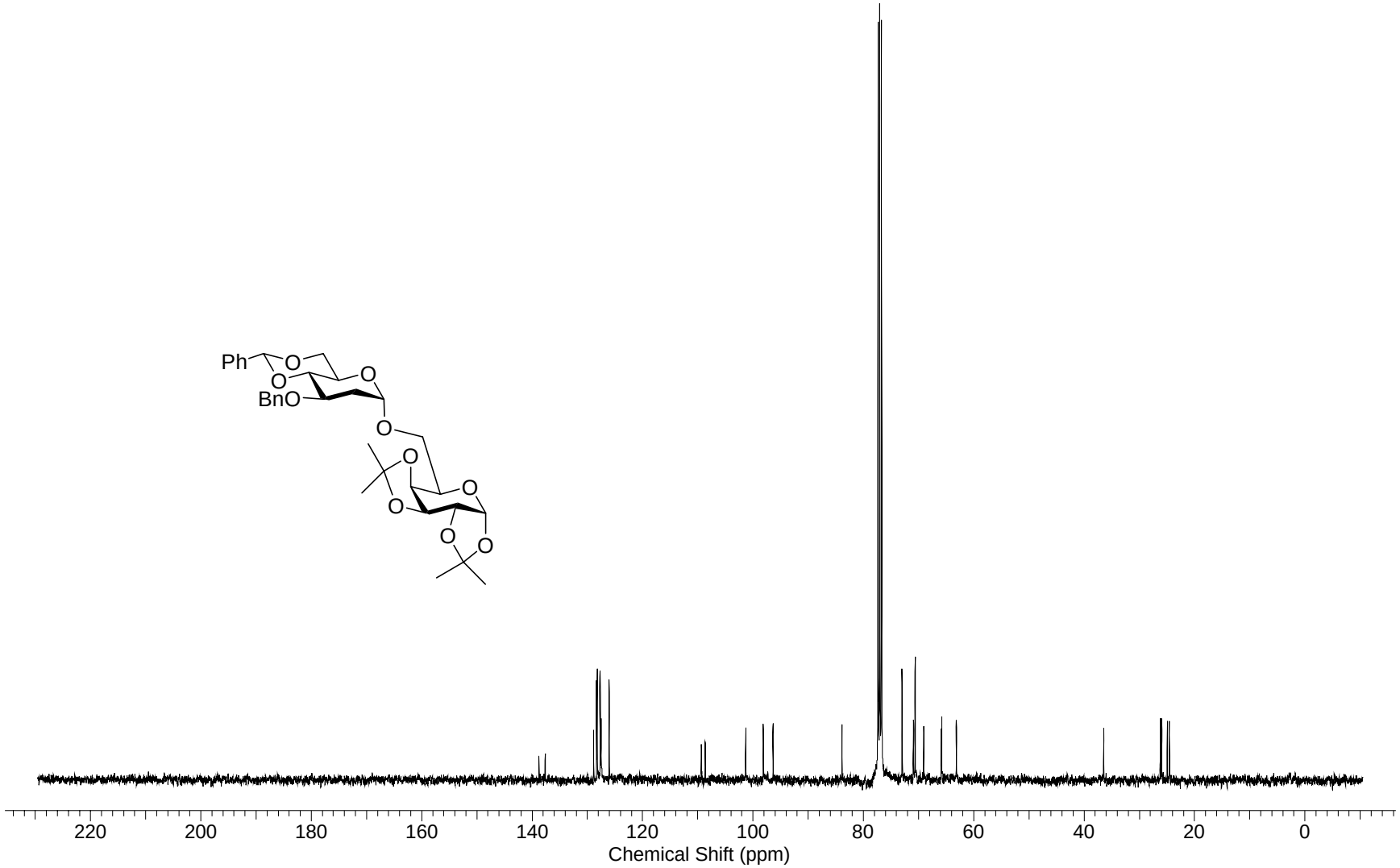
^{13}C spectrum of 3-*O*-(3'-*O*-benzyl-4',6'-benzylidene-2'-deoxy-β-D-*arabino*-thiohexopyranosyl)-1,2:5,6-di-*O*-isopropylidene-α-D-glucose (40β):



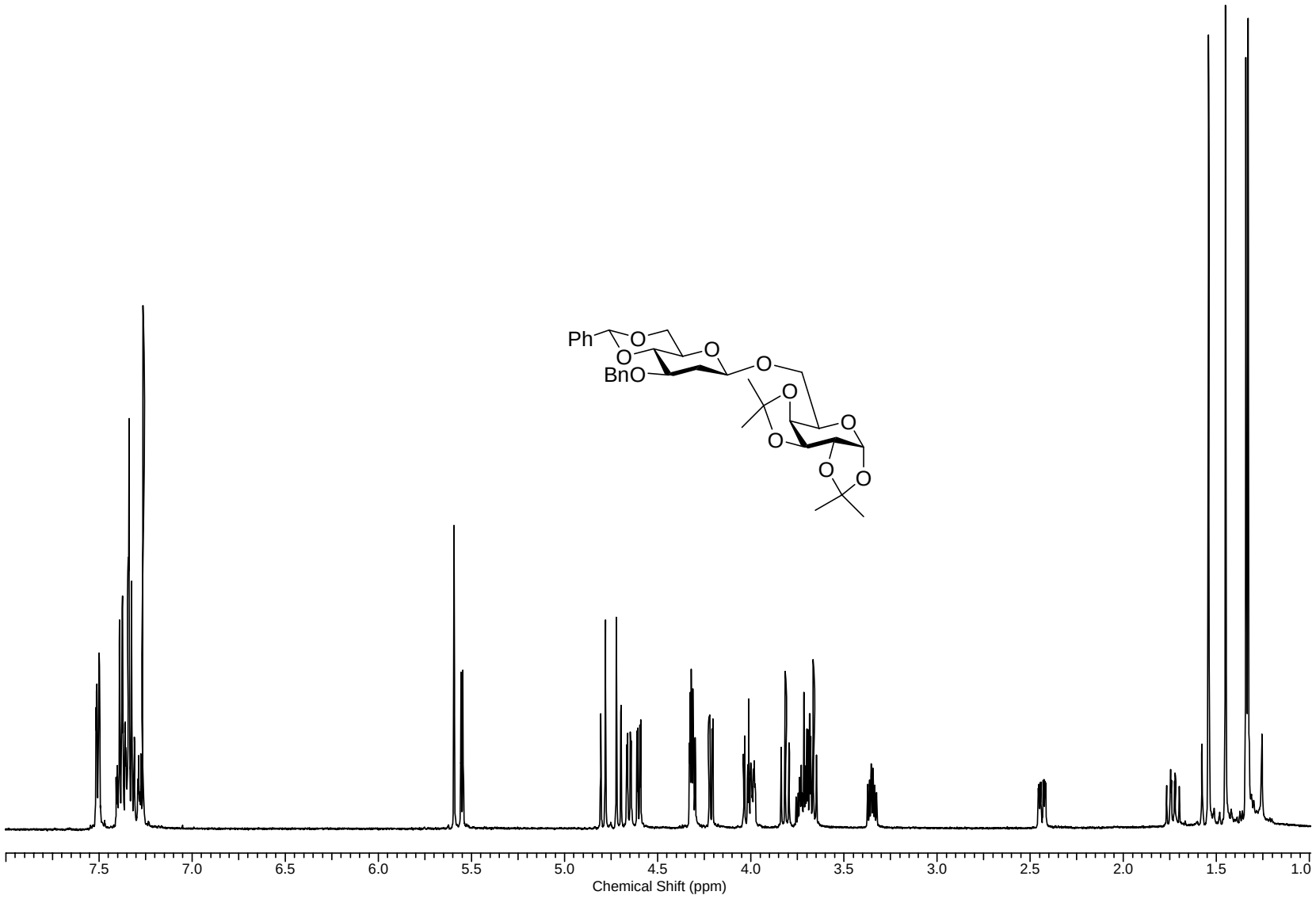
^{1}H spectrum of 6-*O*-(3'-*O*-benzyl-4',6'-benzylidene-2'-deoxy-α-D-*arabino*-thiohexopyranosyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactose (41α):



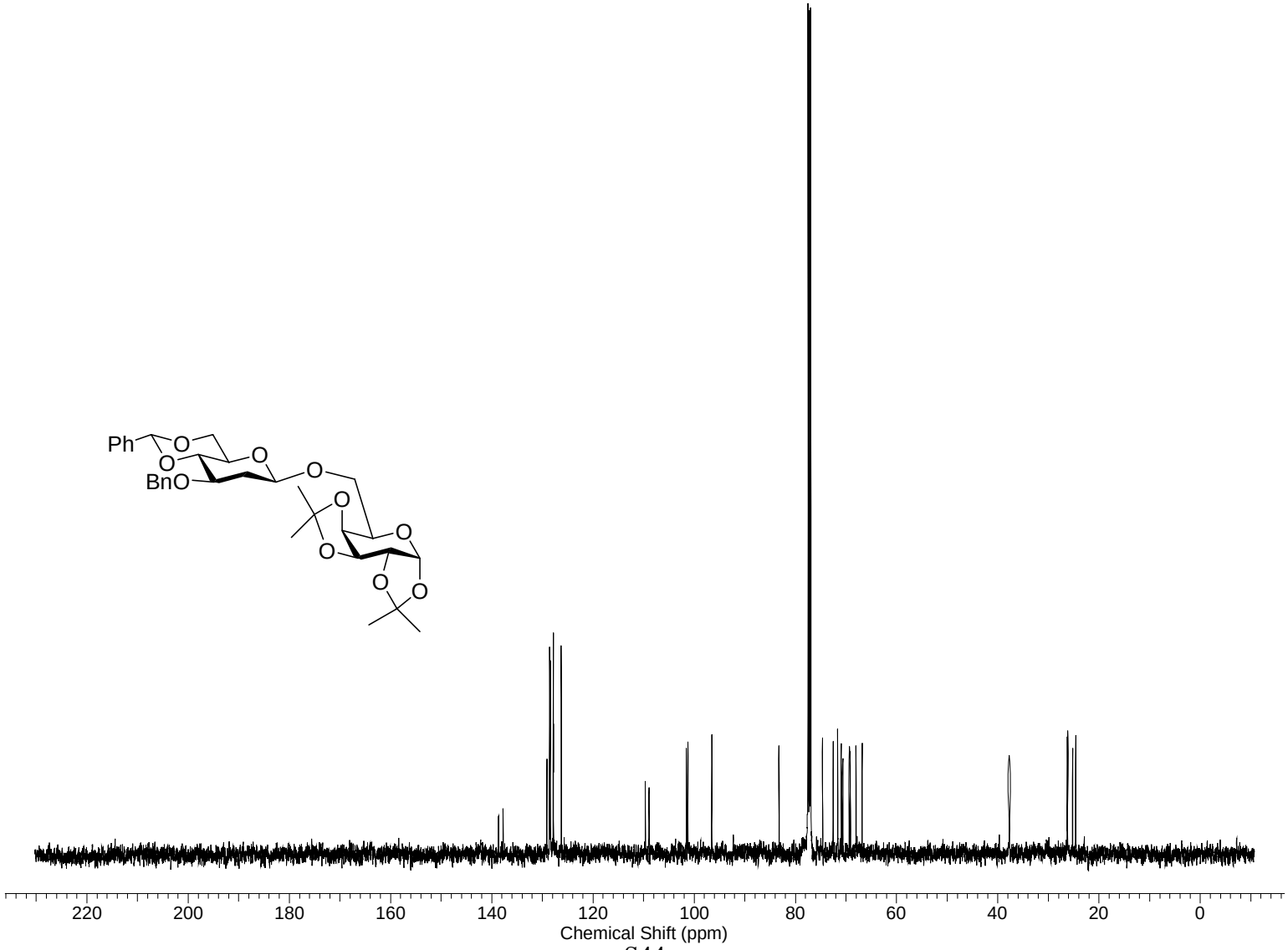
^{13}C spectrum of 6-*O*-(3'-*O*-benzyl-4',6'-benzylidene-2'-deoxy-α-D-*arabino*-thiohexopyranosyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactose (41α):



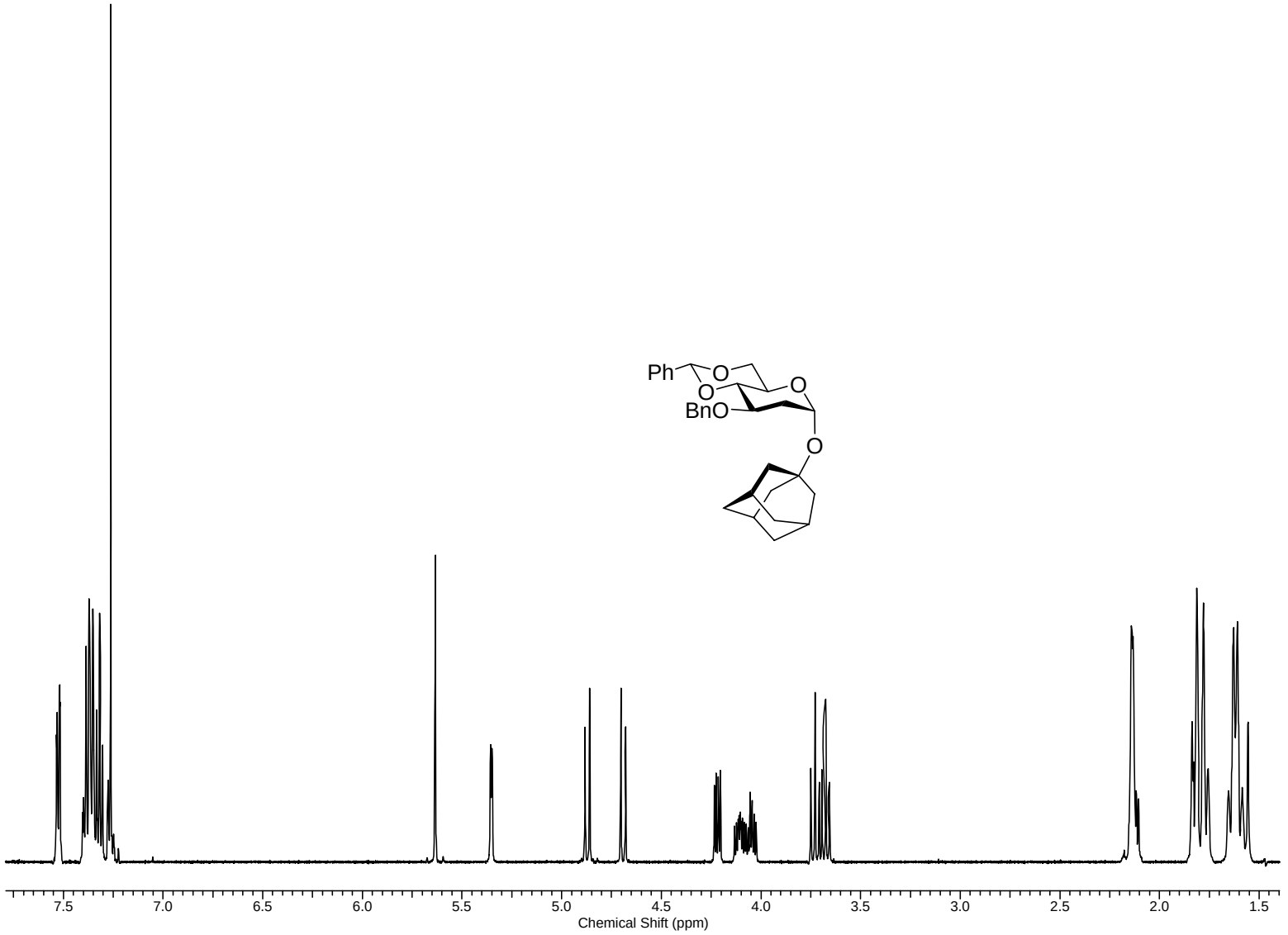
^{1}H spectrum of 6-*O*-(3'-*O*-benzyl-4',6'-benzylidene-2'-deoxy-β-D-*arabino*-thiohexopyranosyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactose (41β):



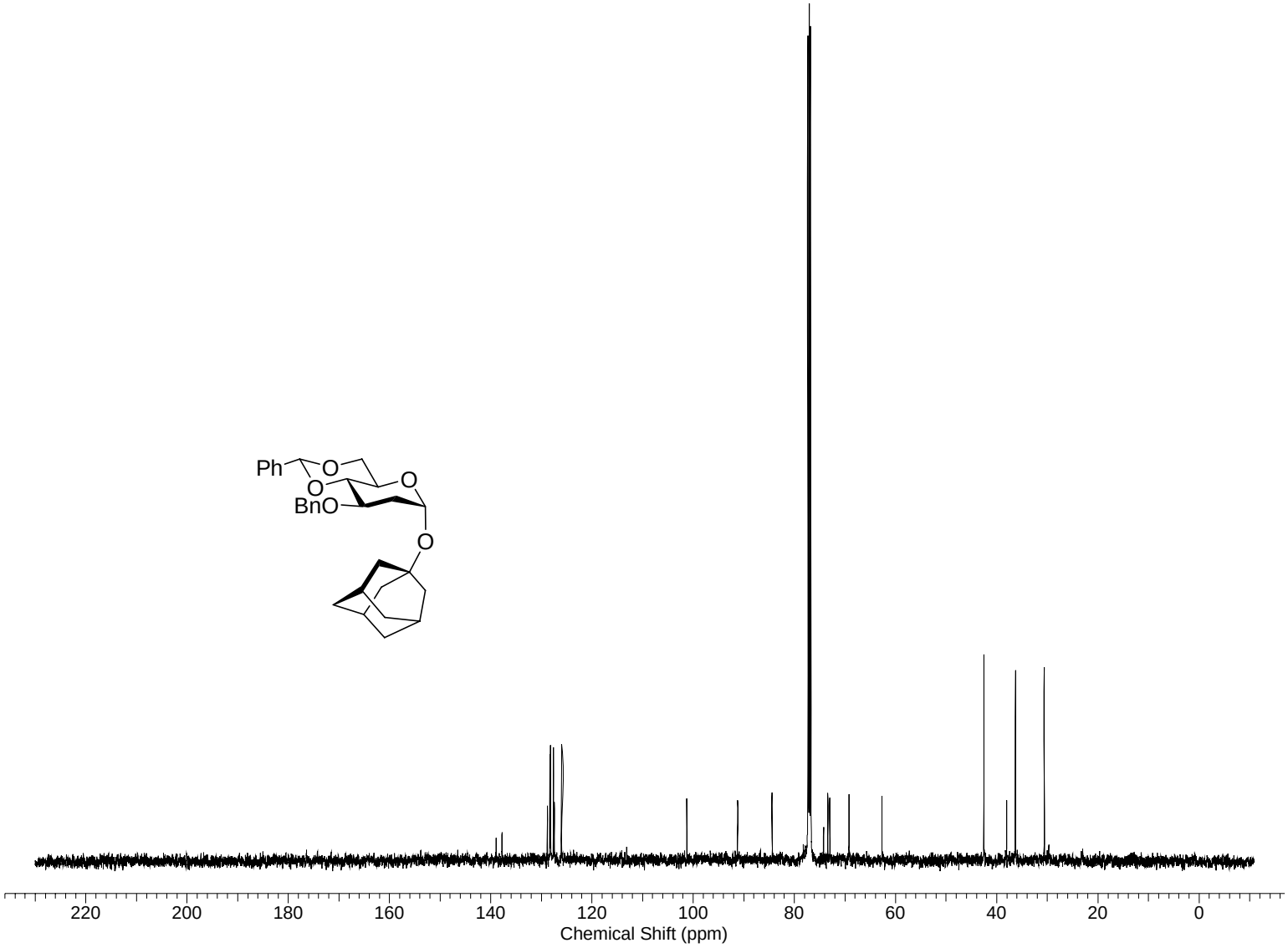
^{13}C spectrum of 6-*O*-(3'-*O*-benzyl-4',6'-benzylidene-2'-deoxy-β-D-*arabino*-thiohexopyranosyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactose (41β):



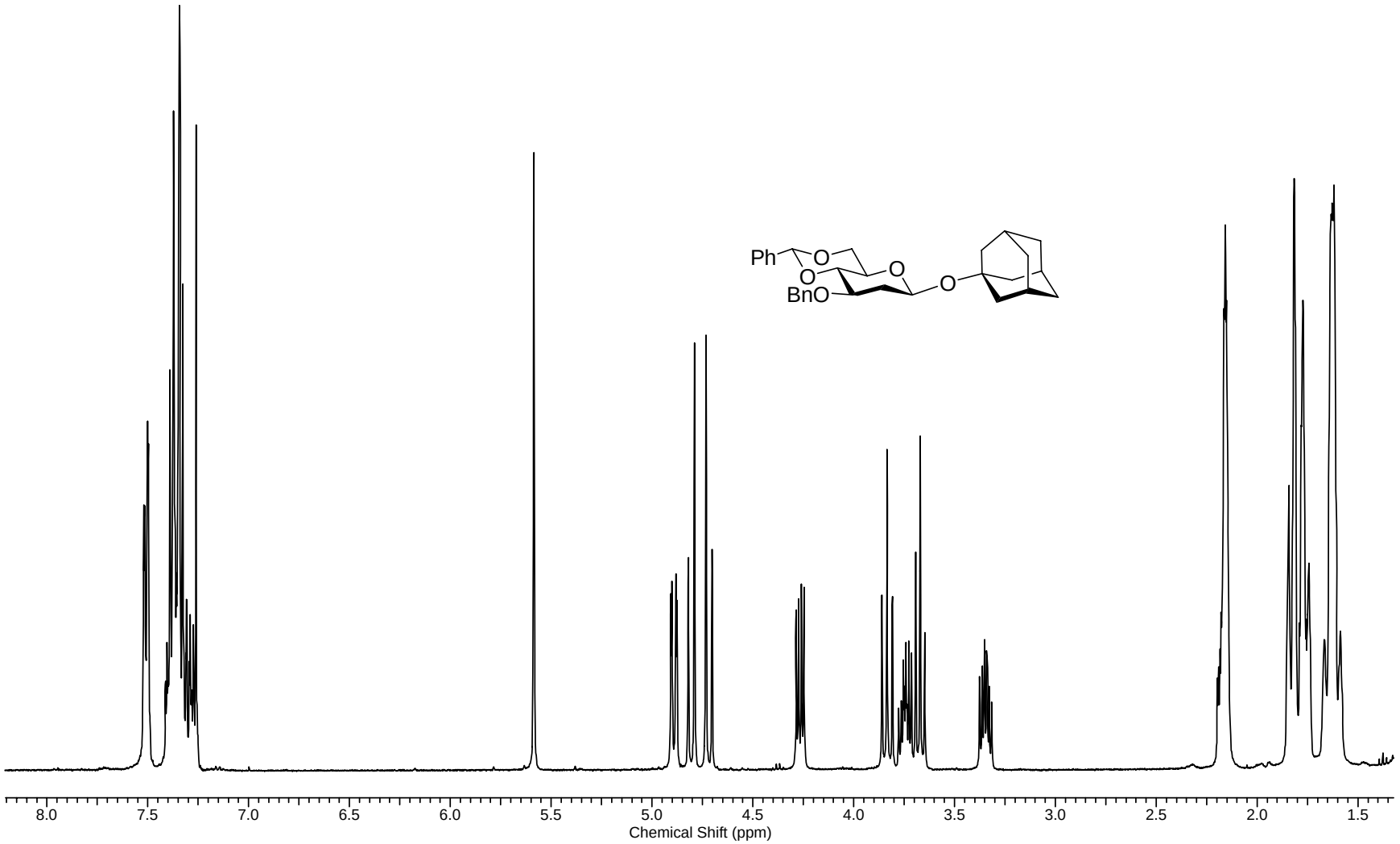
^{1}H spectrum of (1-Adamantyl) 3-*O*-benzyl-4,6-benzylidene-2'-deoxy-α-D-*arabino*-hexopyranoside (42*α*):



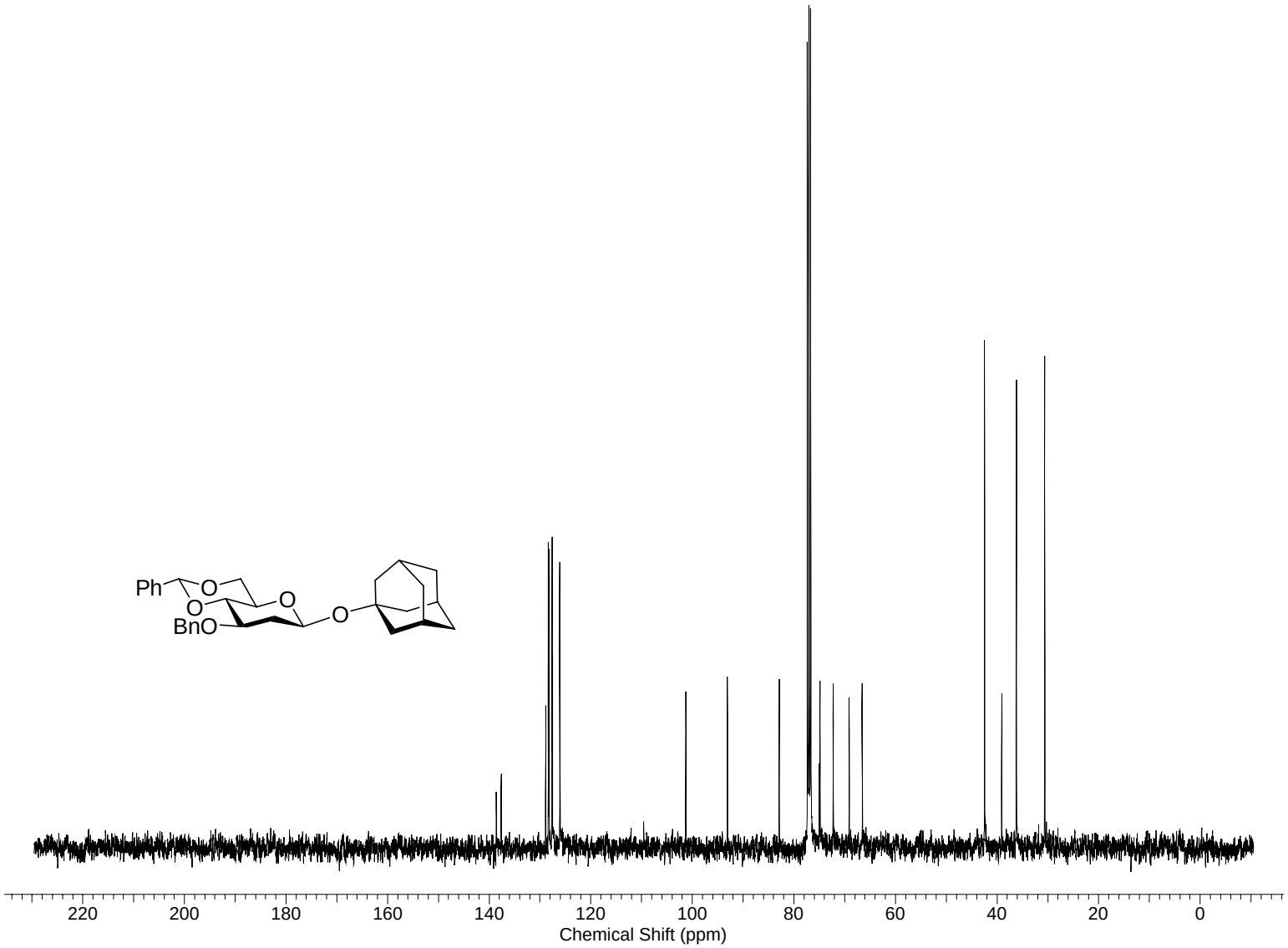
^{13}C spectrum of (1-Adamantyl) 3-*O*-benzyl-4,6-benzylidene-2'-deoxy-α-D-*arabino*-hexopyranoside (42α):



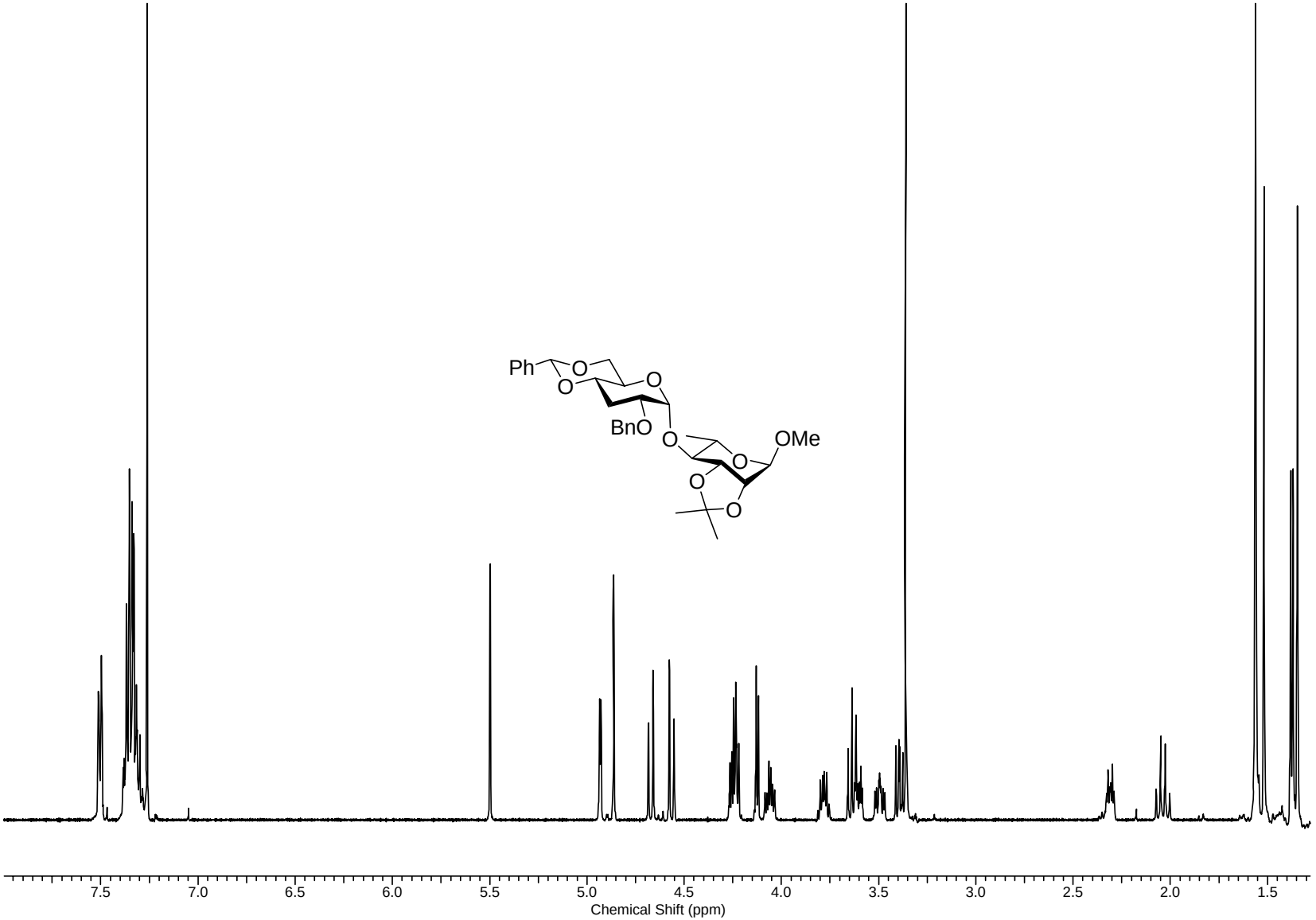
^{1}H spectrum of (1-Adamantyl) 3-*O*-benzyl-4,6-benzylidene-2'-deoxy-β-D-*arabino*-hexopyranoside (42β):



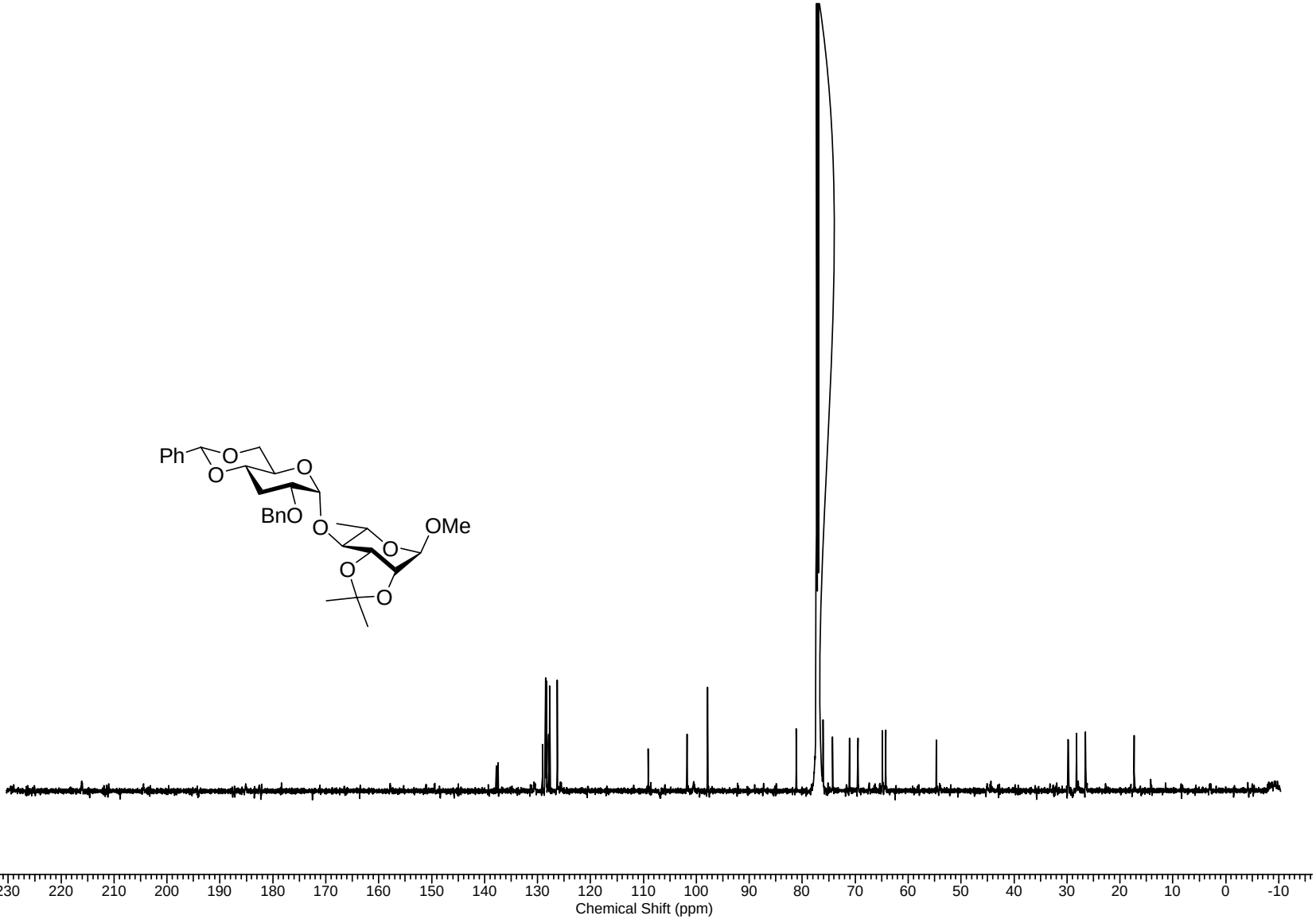
^{13}C spectrum of (1-Adamantyl) 3-*O*-benzyl-4,6-benzylidene-2'-deoxy-β-D-*arabino*-hexopyranoside (42β):



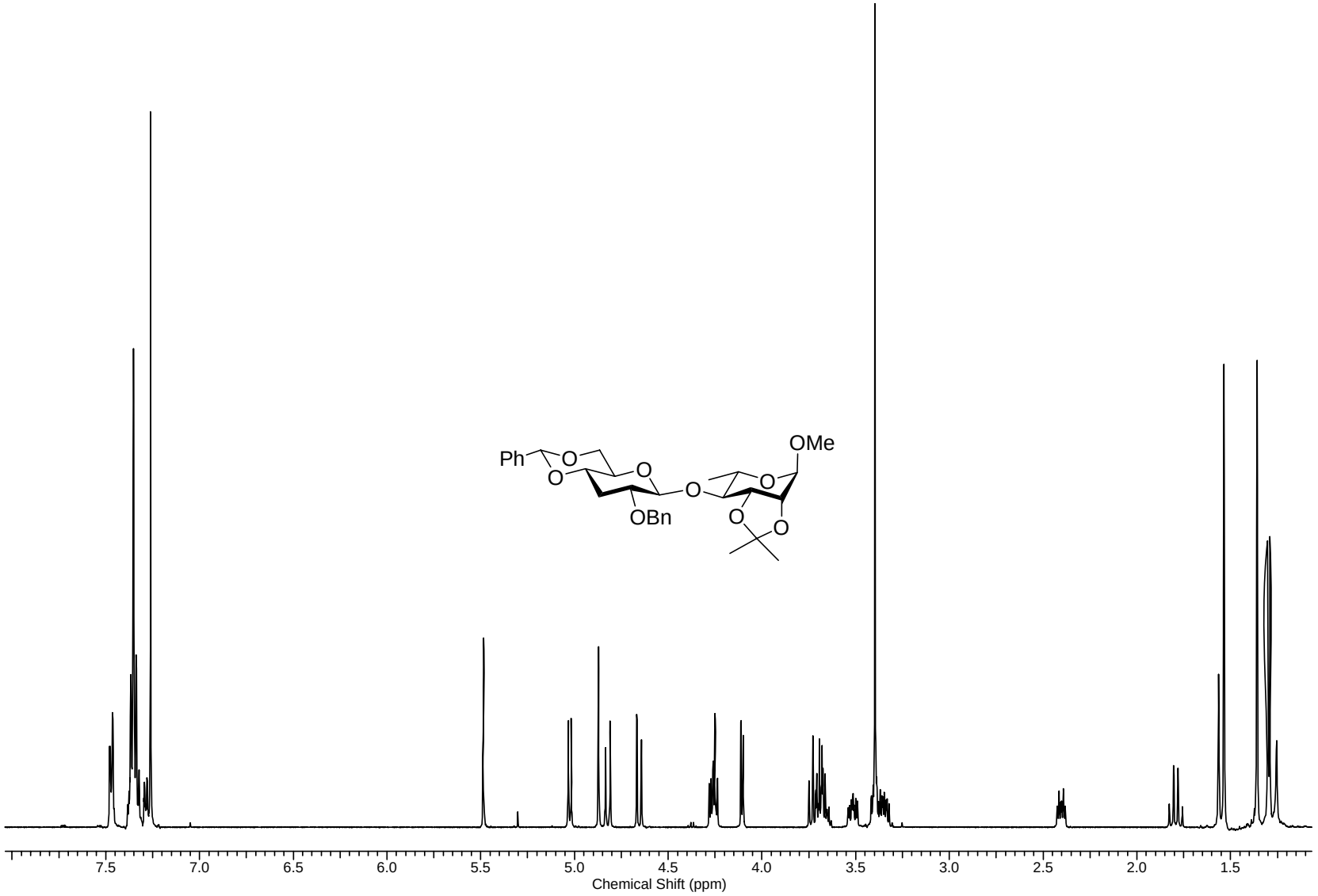
^{1}H spectrum of Methyl 4-*O*-(2'-*O*-benzyl-4',6'-benzylidene-3'-deoxy-α-D-*ribo*-thiohexopyranosyl)-2,3-*O*-isopropylidene-α-L-rhamnoside (43α):



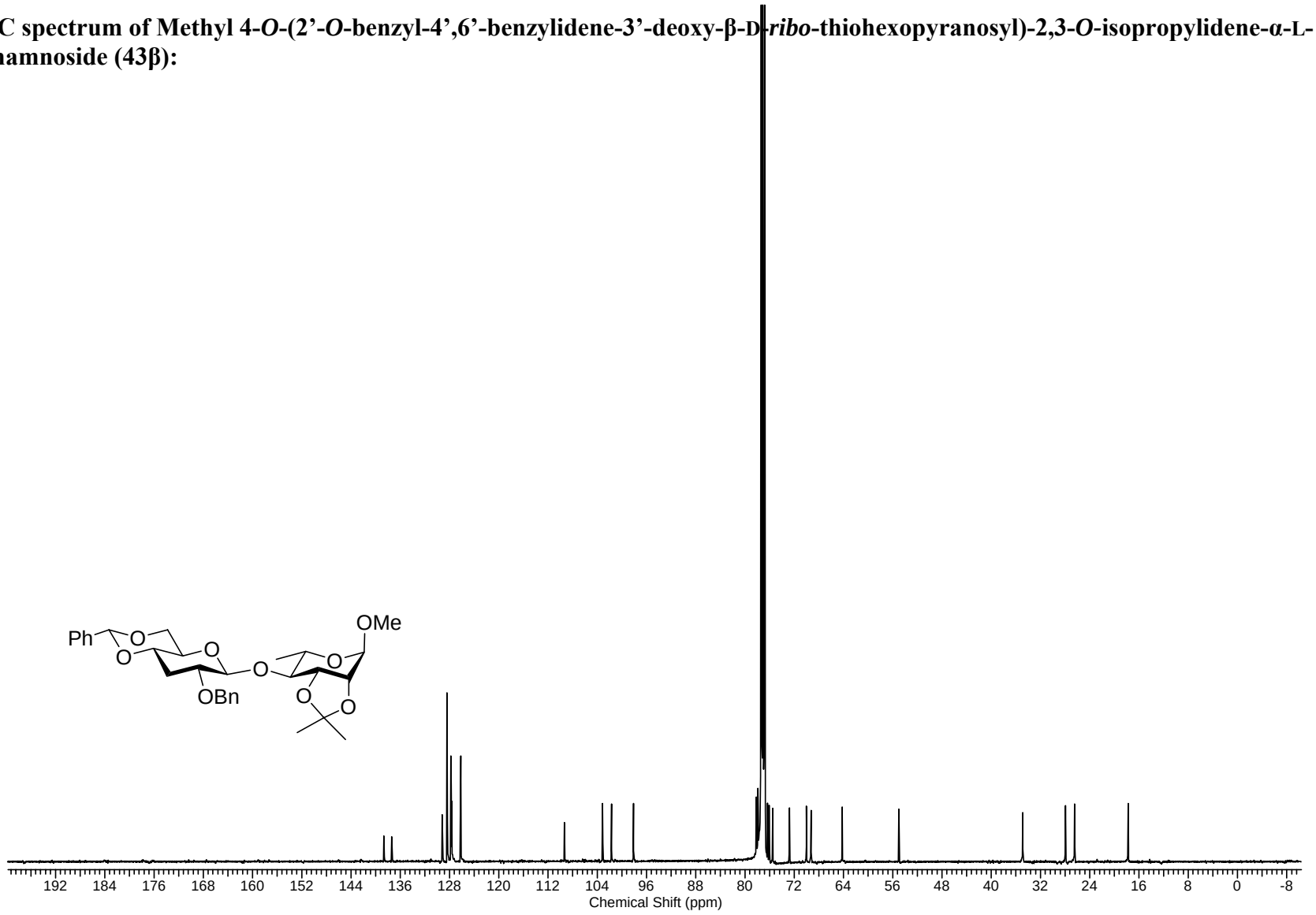
^{13}C spectrum of Methyl 4-*O*-(2'-*O*-benzyl-4',6'-benzylidene-3'-deoxy-α-D-*ribo*-thiohexopyranosyl)-2,3-*O*-isopropylidene-α-L-rhamnoside (43α):



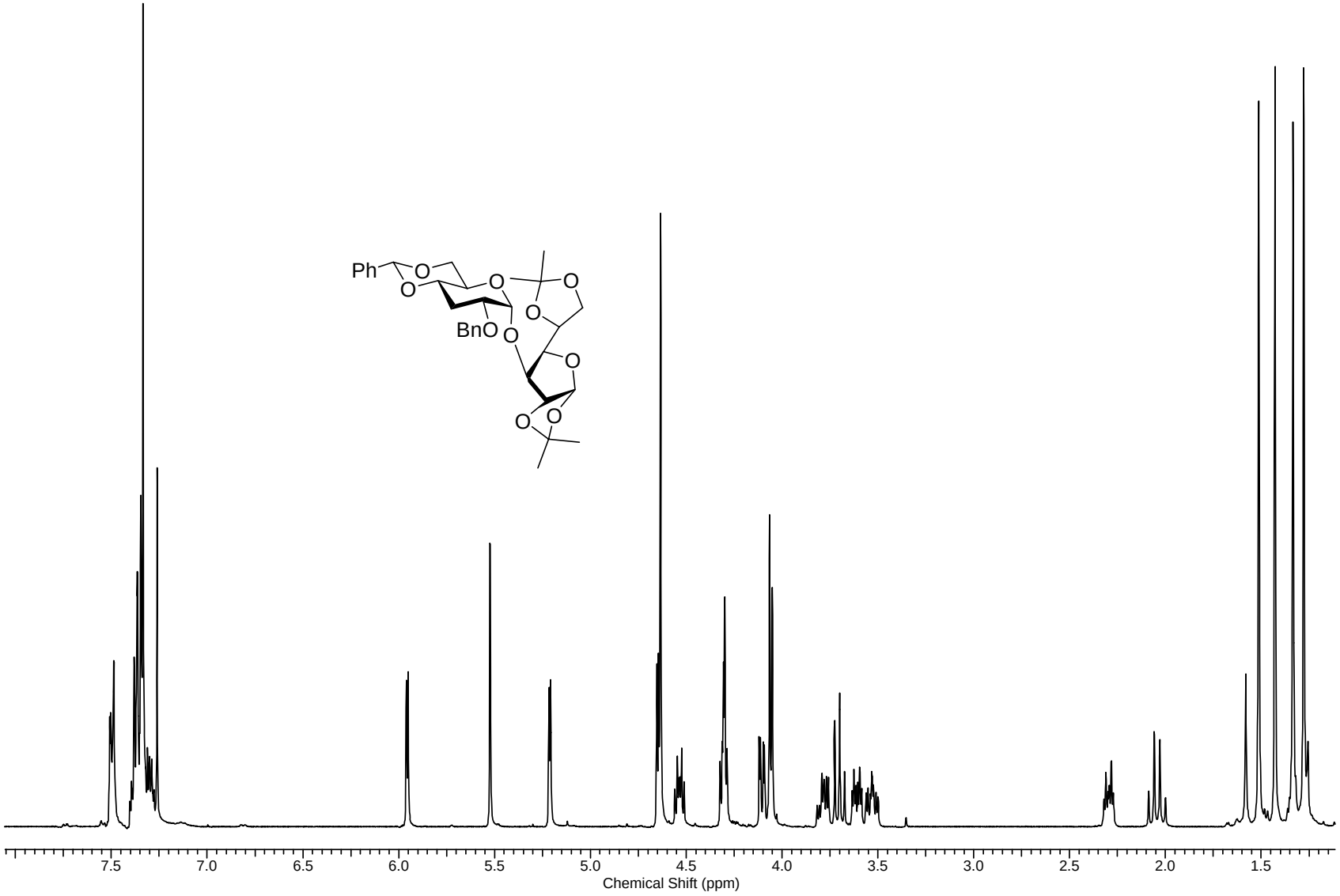
^{1}H spectrum of Methyl 4-*O*-(2'-*O*-benzyl-4',6'-benzylidene-3'-deoxy-β-D-*ribo*-thiohexopyranosyl)-2,3-*O*-isopropylidene-α-L-rhamnoside (43β):



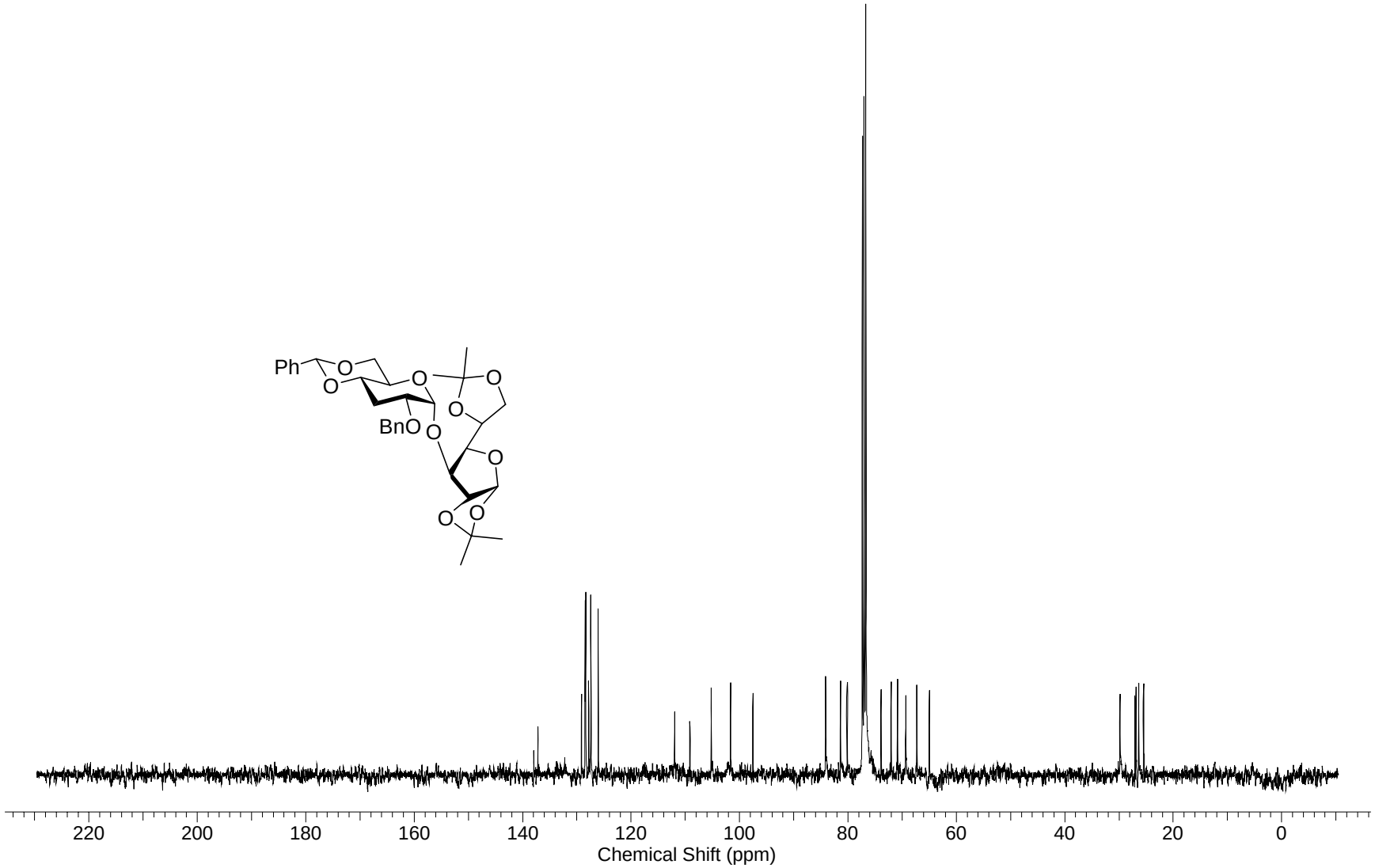
^{13}C spectrum of Methyl 4-*O*-(2'-*O*-benzyl-4',6'-benzylidene-3'-deoxy-β-D-*ribo*-thiohexopyranosyl)-2,3-*O*-isopropylidene-α-L-rhamnoside (43β):



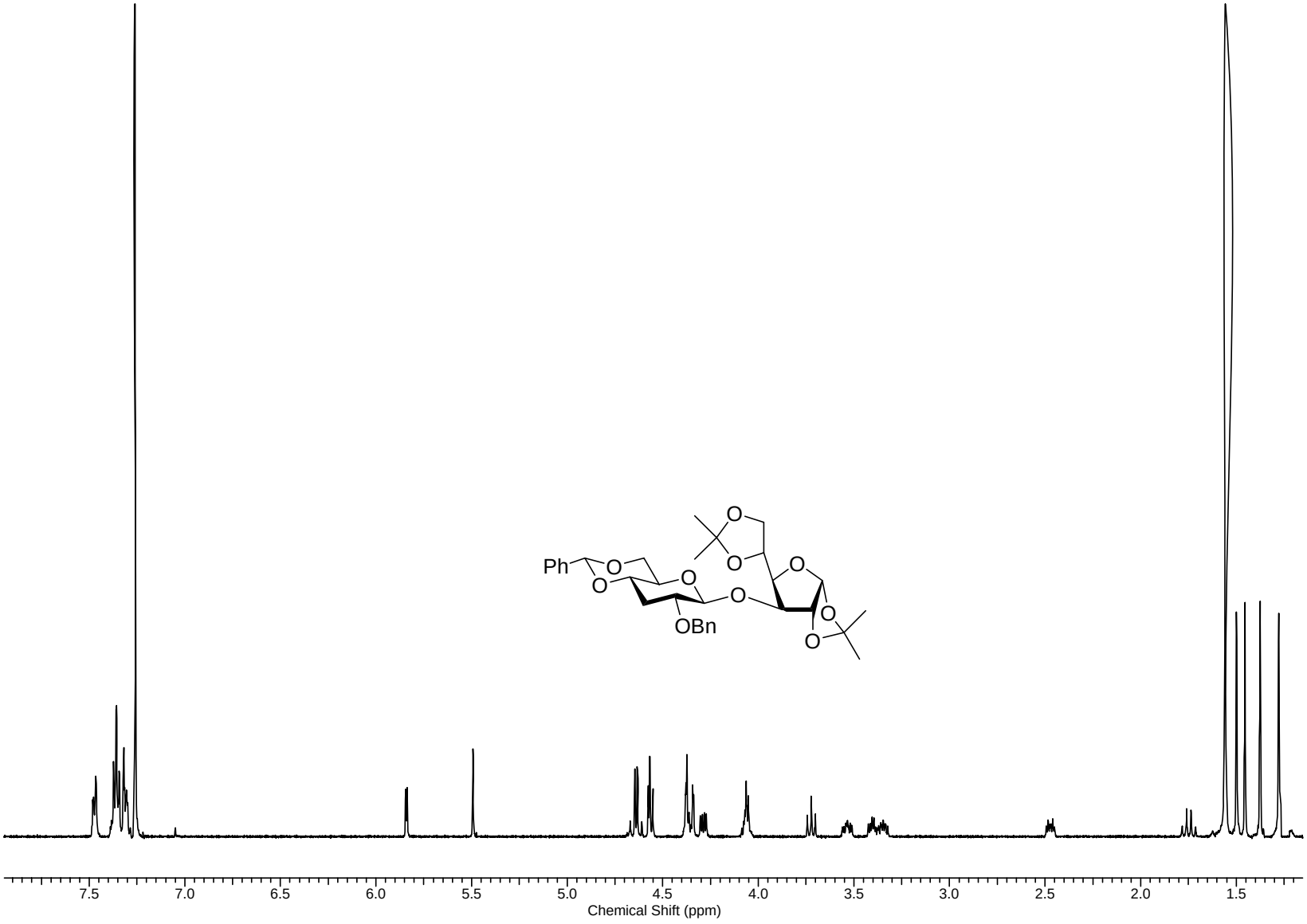
^{1}H spectrum of 3-*O*-(2'-*O*-benzyl-4',6'-benzylidene-3'-deoxy-α-D-*ribo*-thiohexopyranosyl)-1,2:5,6-di-*O*-isopropylidene-α-D-glucose (44*α*):



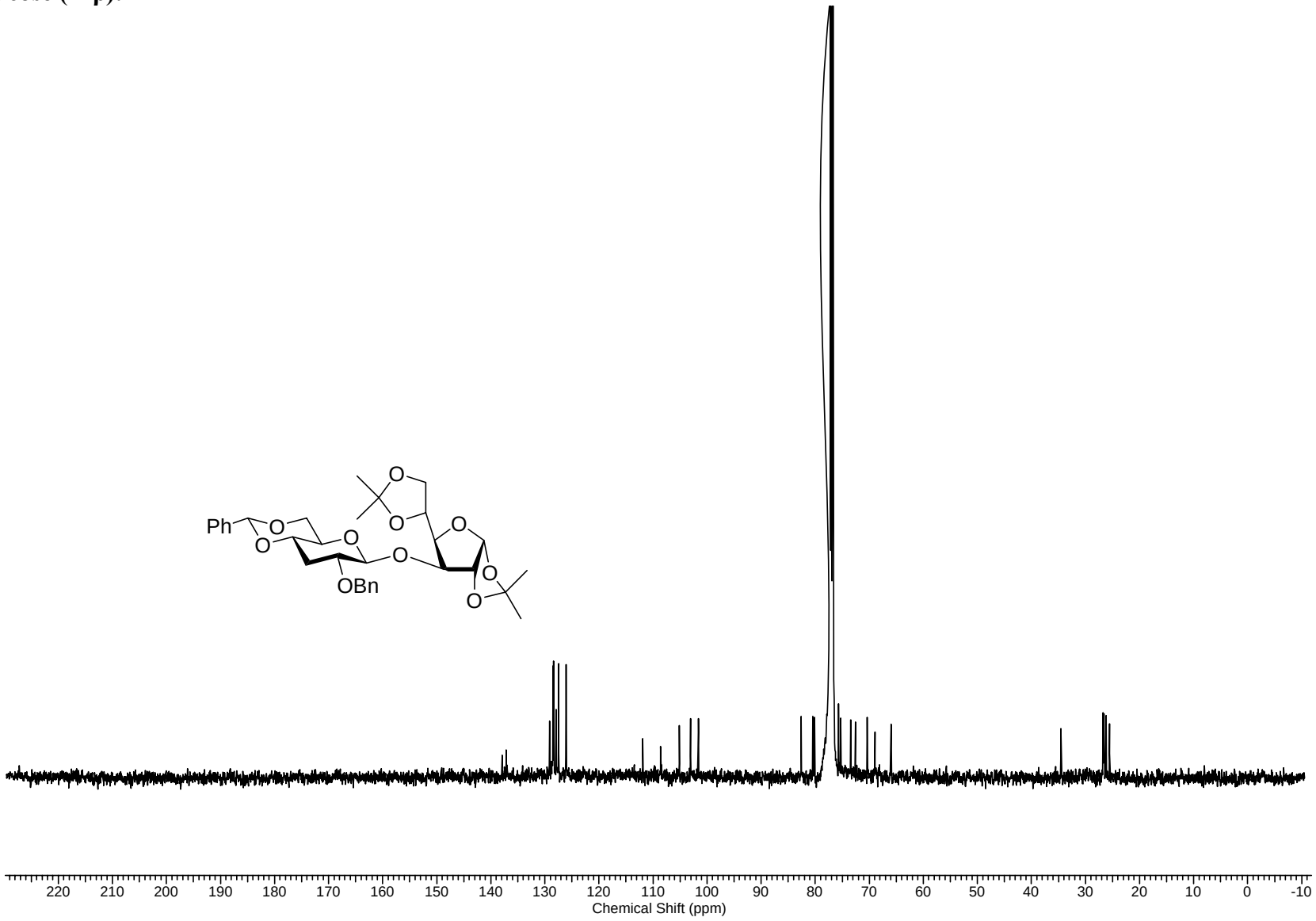
^{13}C spectrum of 3-*O*-(2'-*O*-benzyl-4',6'-benzylidene-3'-deoxy-α-D-*ribo*-thiohexopyranosyl)-1,2:5,6-di-*O*-isopropylidene-α-D-glucose (44*α*):



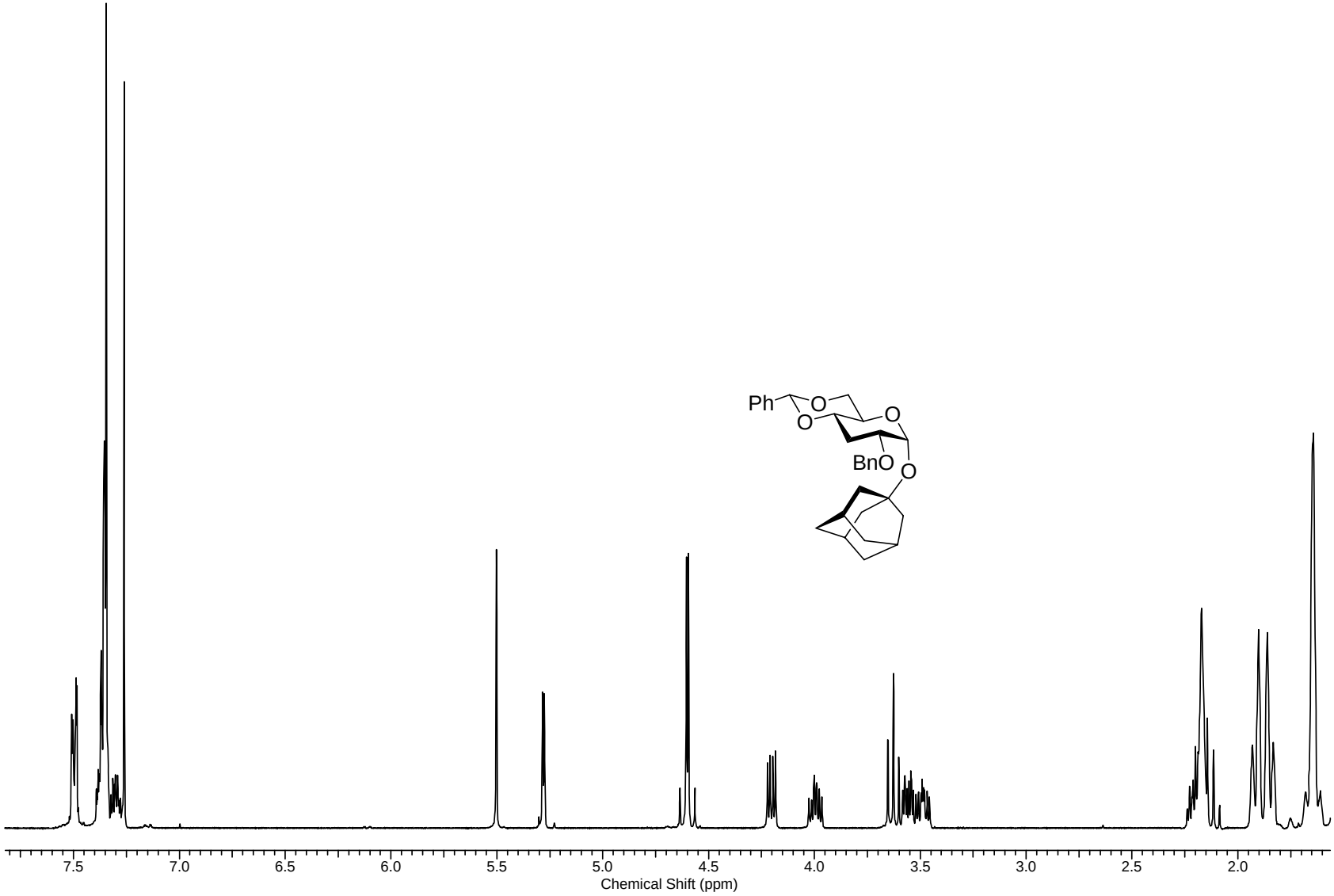
^{1}H spectrum of 3-*O*-(2'-*O*-benzyl-4',6'-benzylidene-3'-deoxy-β-D-*ribo*-thiohexopyranosyl)-1,2:5,6-di-*O*-isopropylidene-α-D-glucose (44β):



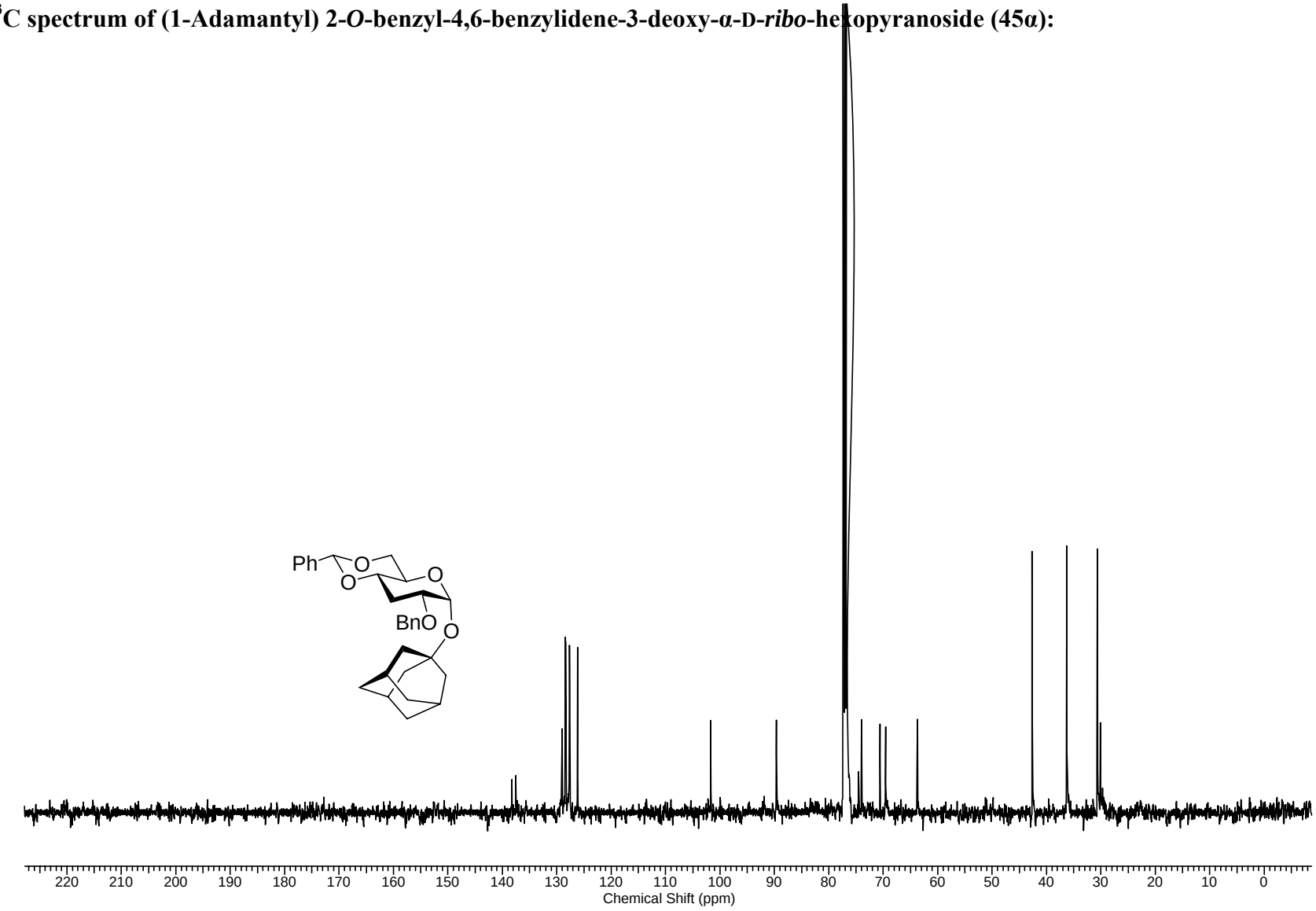
^{13}C spectrum of 3-*O*-(2'-*O*-benzyl-4',6'-benzylidene-3'-deoxy-β-D-*ribo*-thiohexopyranosyl)-1,2:5,6-di-*O*-isopropylidene-α-D-glucose (44β):



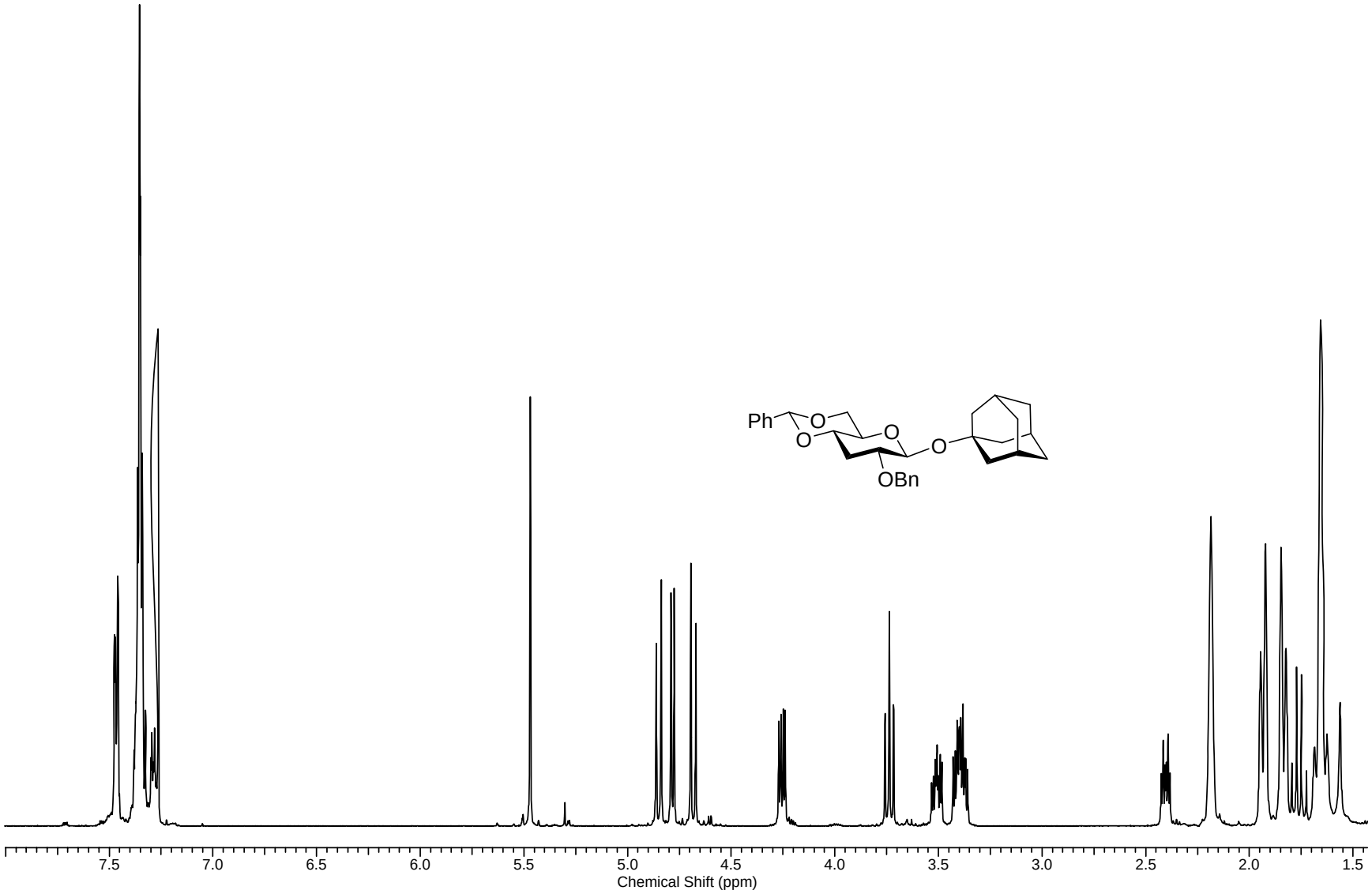
^{1}H spectrum of (1-Adamantyl) 2-*O*-benzyl-4,6-benzylidene-3-deoxy-*α*-D-*ribo*-hexopyranoside (45*α*):



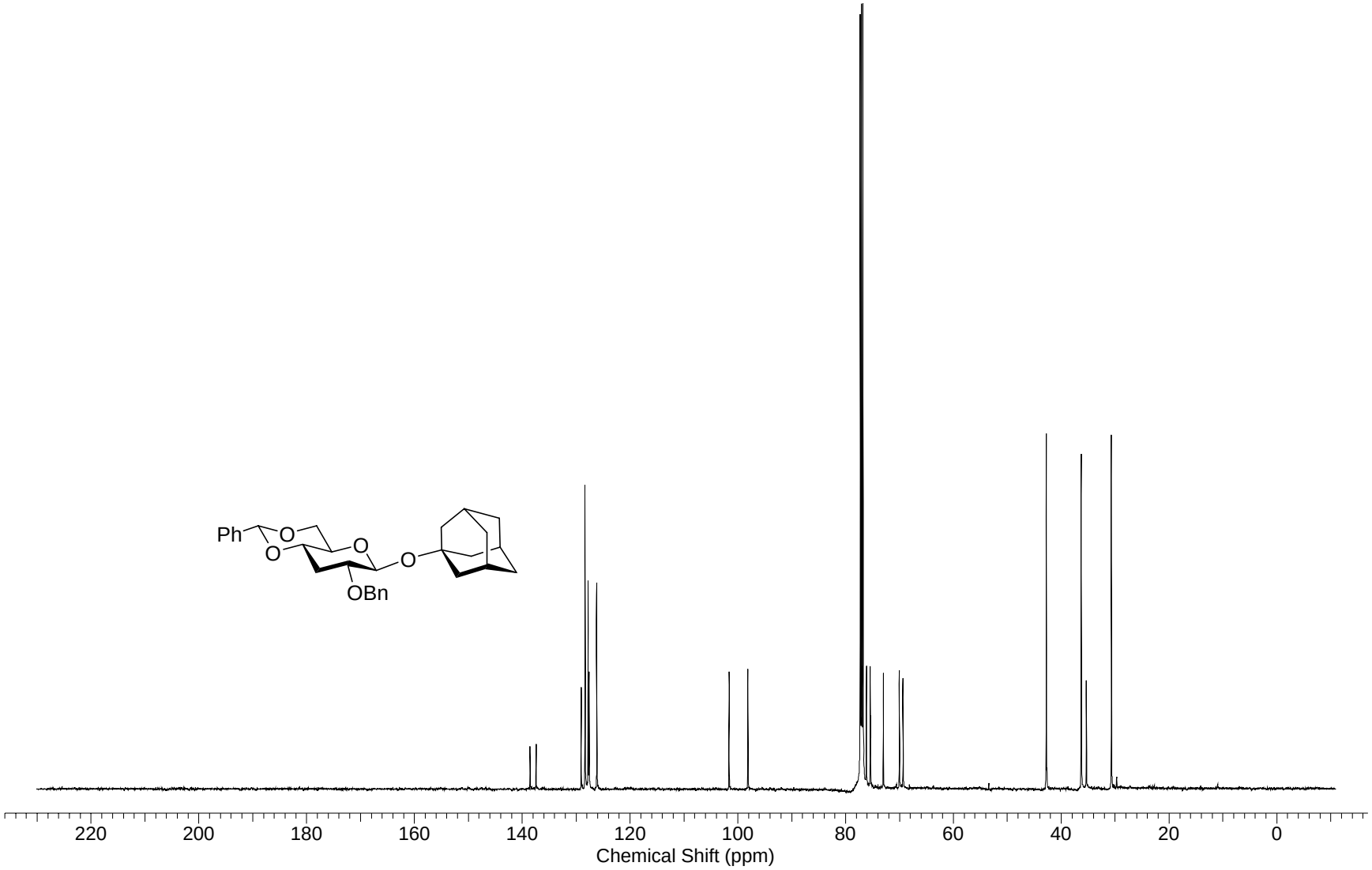
^{13}C spectrum of (1-Adamantyl) 2-*O*-benzyl-4,6-benzylidene-3-deoxy-α-D-*ribo*-hexopyranoside (45α):



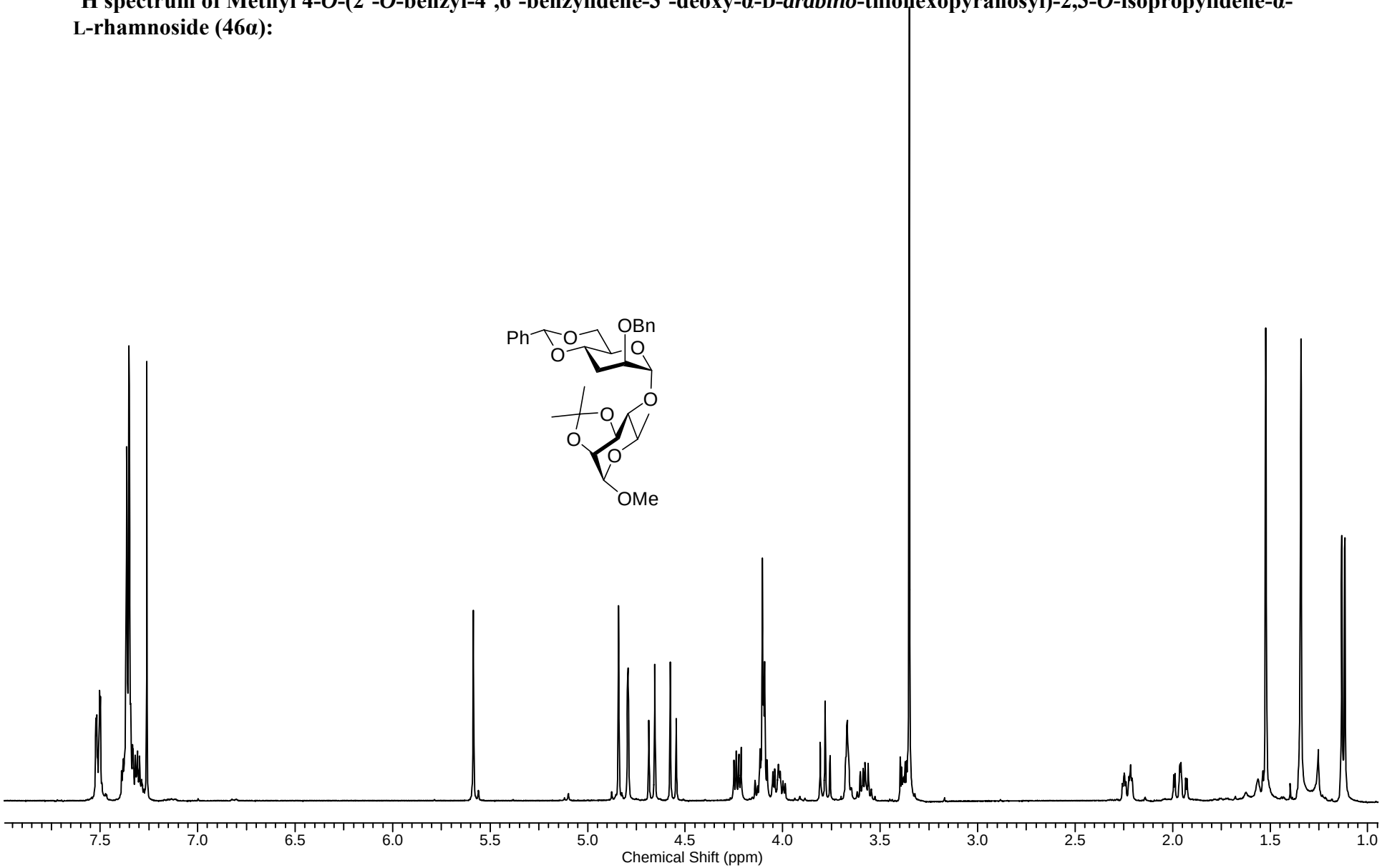
^{1}H spectrum of (1-Adamantyl) 2-*O*-benzyl-4,6-benzylidene-3-deoxy-β-D-*ribo*-hexopyranoside (45β):



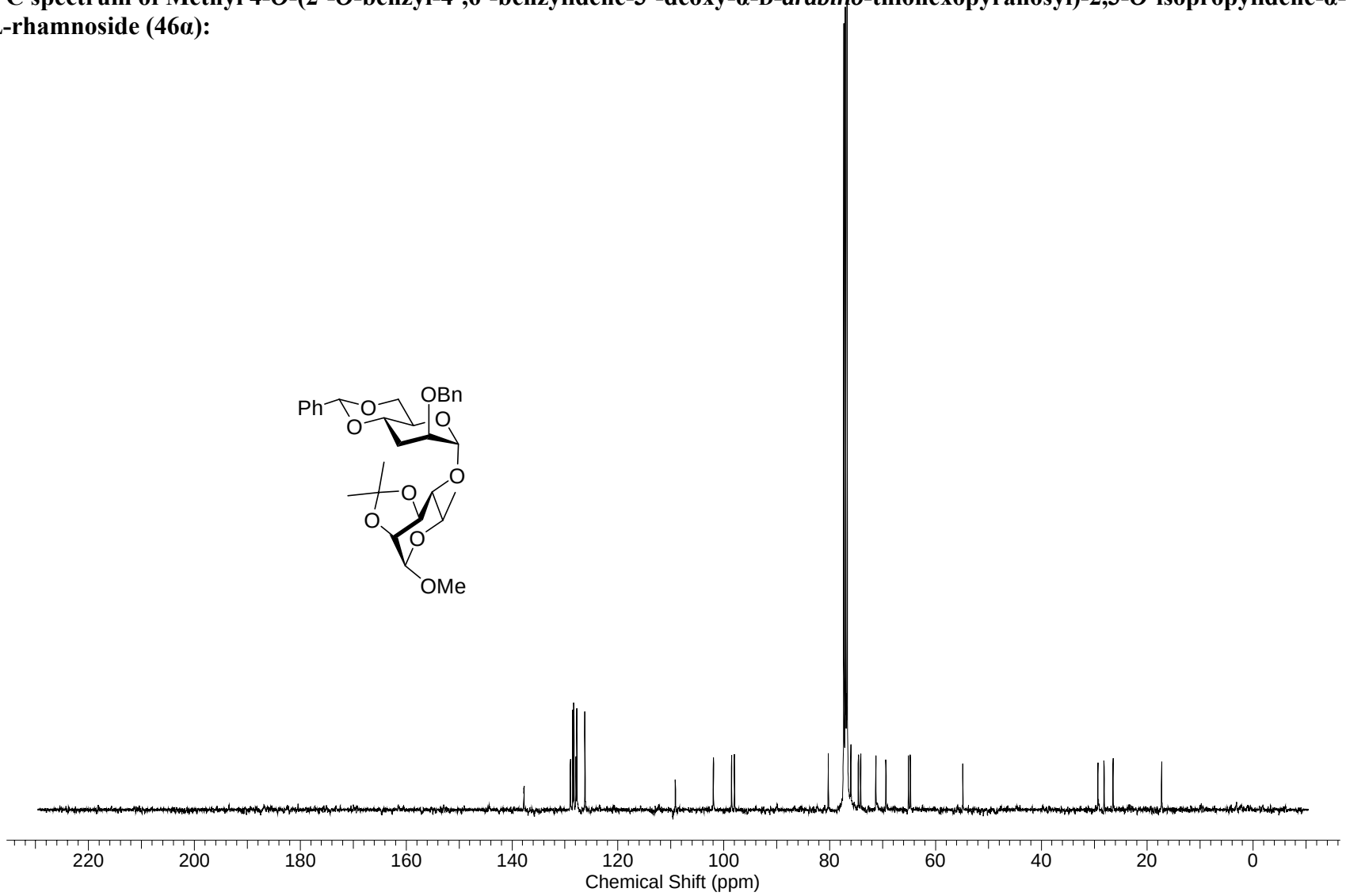
^{13}C spectrum of (1-Adamantyl) 2-*O*-benzyl-4,6-benzylidene-3-deoxy-β-D-*ribo*-hexopyranoside (45β):



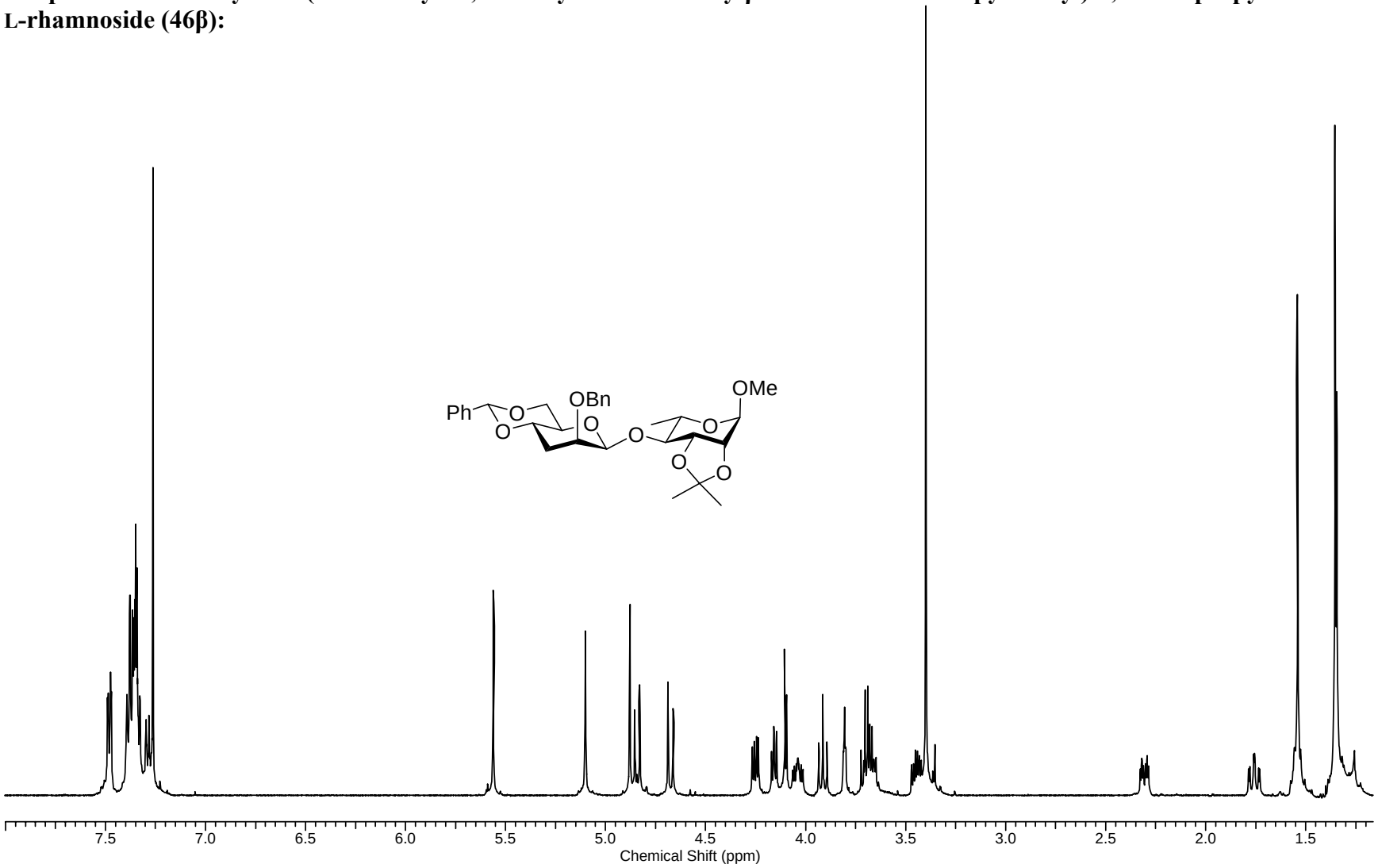
^{1}H spectrum of Methyl 4-*O*-(2'-*O*-benzyl-4',6'-benzylidene-3'-deoxy-α-D-*arabino*-thiohexopyranosyl)-2,3-*O*-isopropylidene-α-L-rhamnoside (46α):



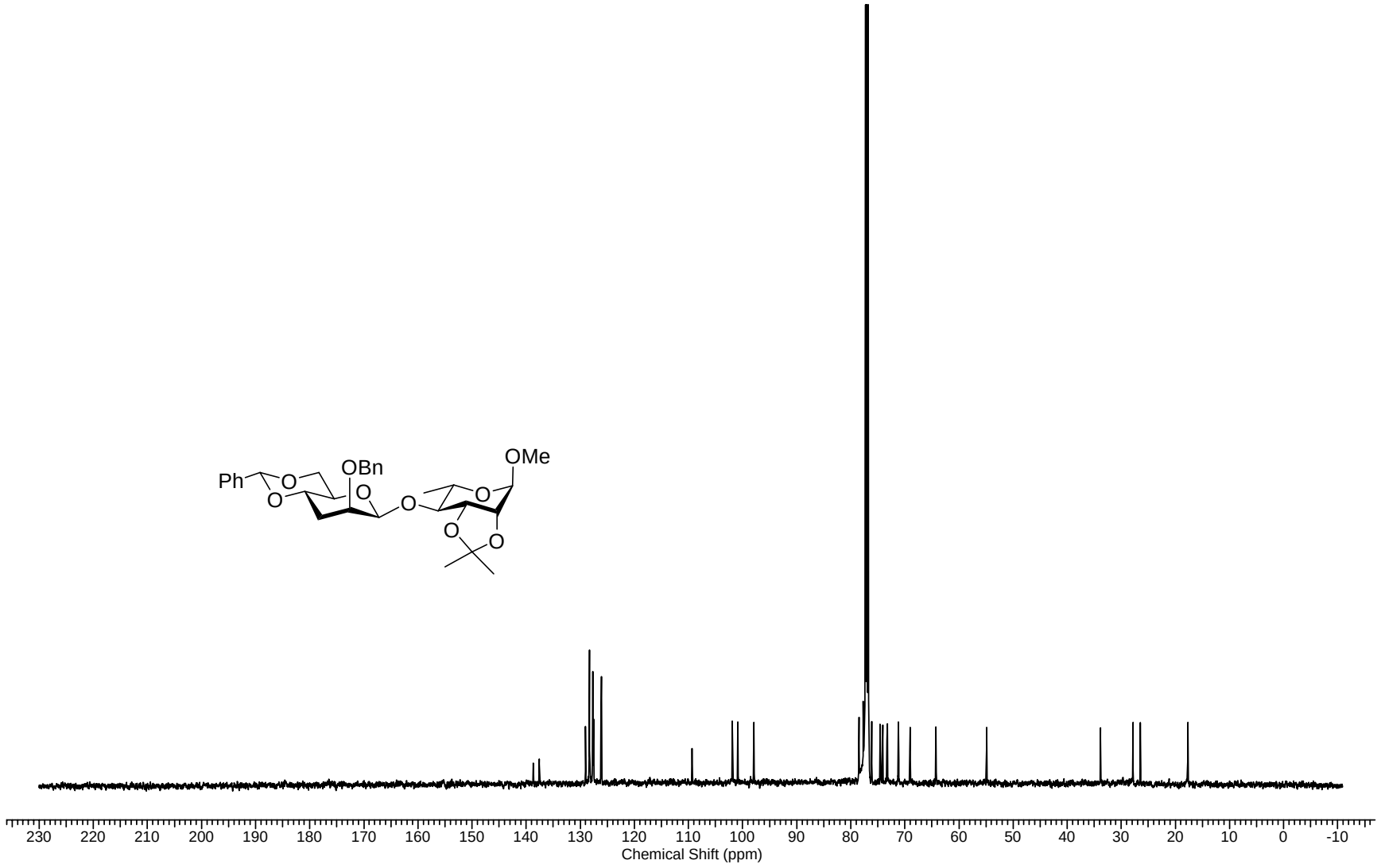
^{13}C spectrum of Methyl 4-*O*-(2'-*O*-benzyl-4',6'-benzylidene-3'-deoxy-α-D-*arabino*-thiohexopyranosyl)-2,3-*O*-isopropylidene-α-L-rhamnoside (46α):



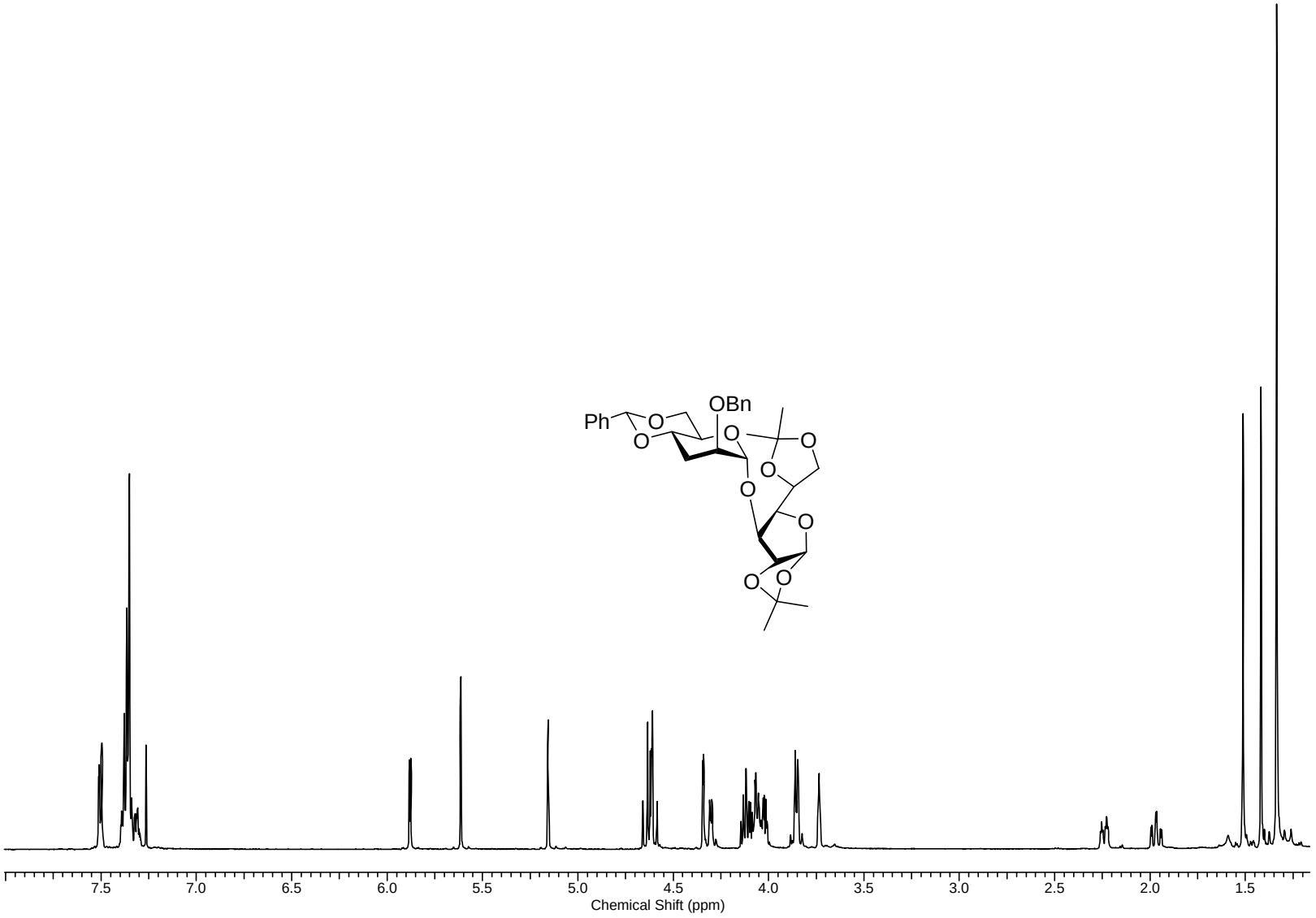
^{1}H spectrum of Methyl 4-*O*-(2'-*O*-benzyl-4',6'-benzylidene-3'-deoxy-β-D-*arabino*-thiohexopyranosyl)-2,3-*O*-isopropylidene-α-L-rhamnoside (46β):



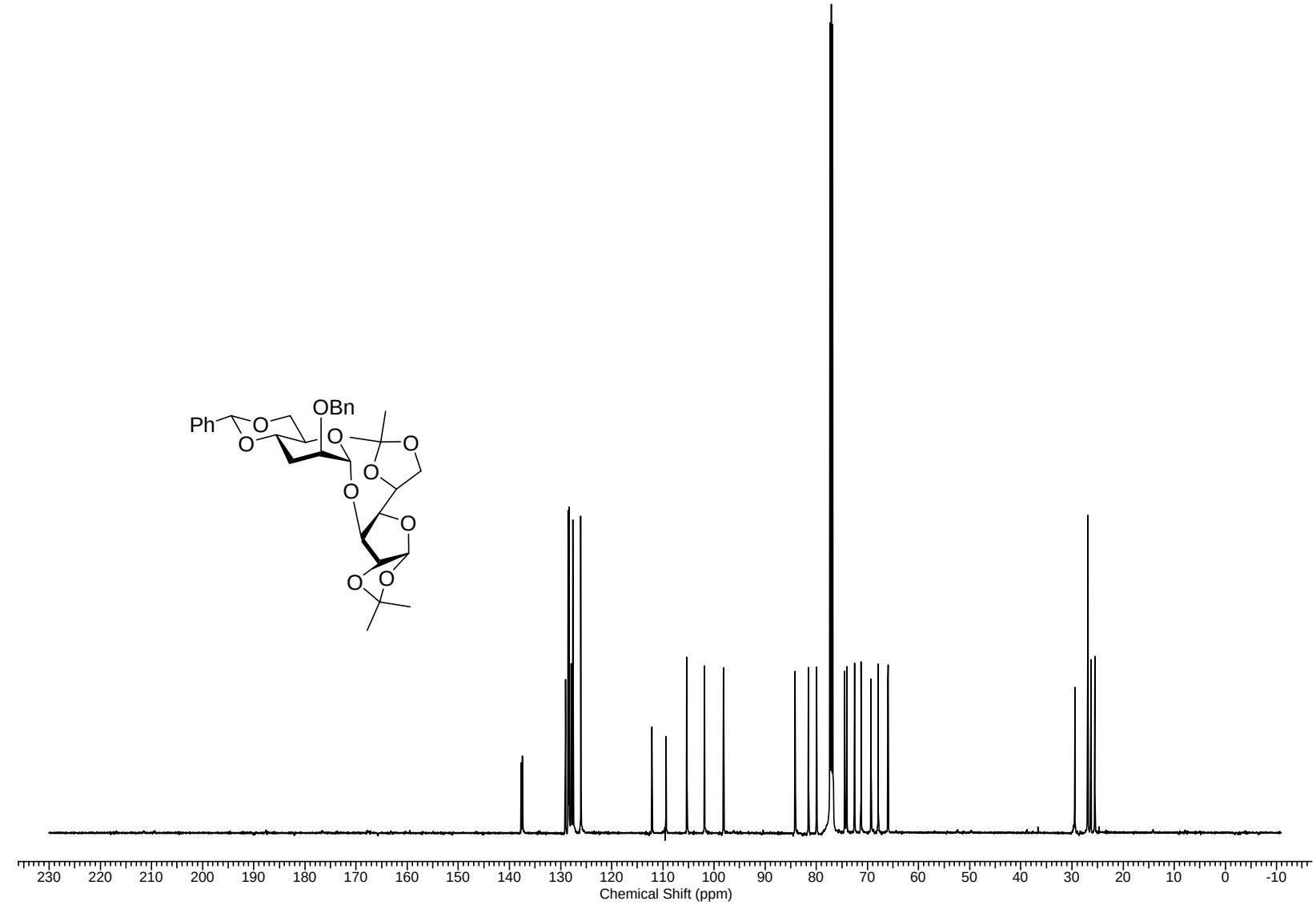
^{13}C spectrum of Methyl 4-*O*-(2'-*O*-benzyl-4',6'-benzylidene-3'-deoxy-β-D-*arabino*-thiohexopyranosyl)-2,3-*O*-isopropylidene-α-L-rhamnoside (46β):



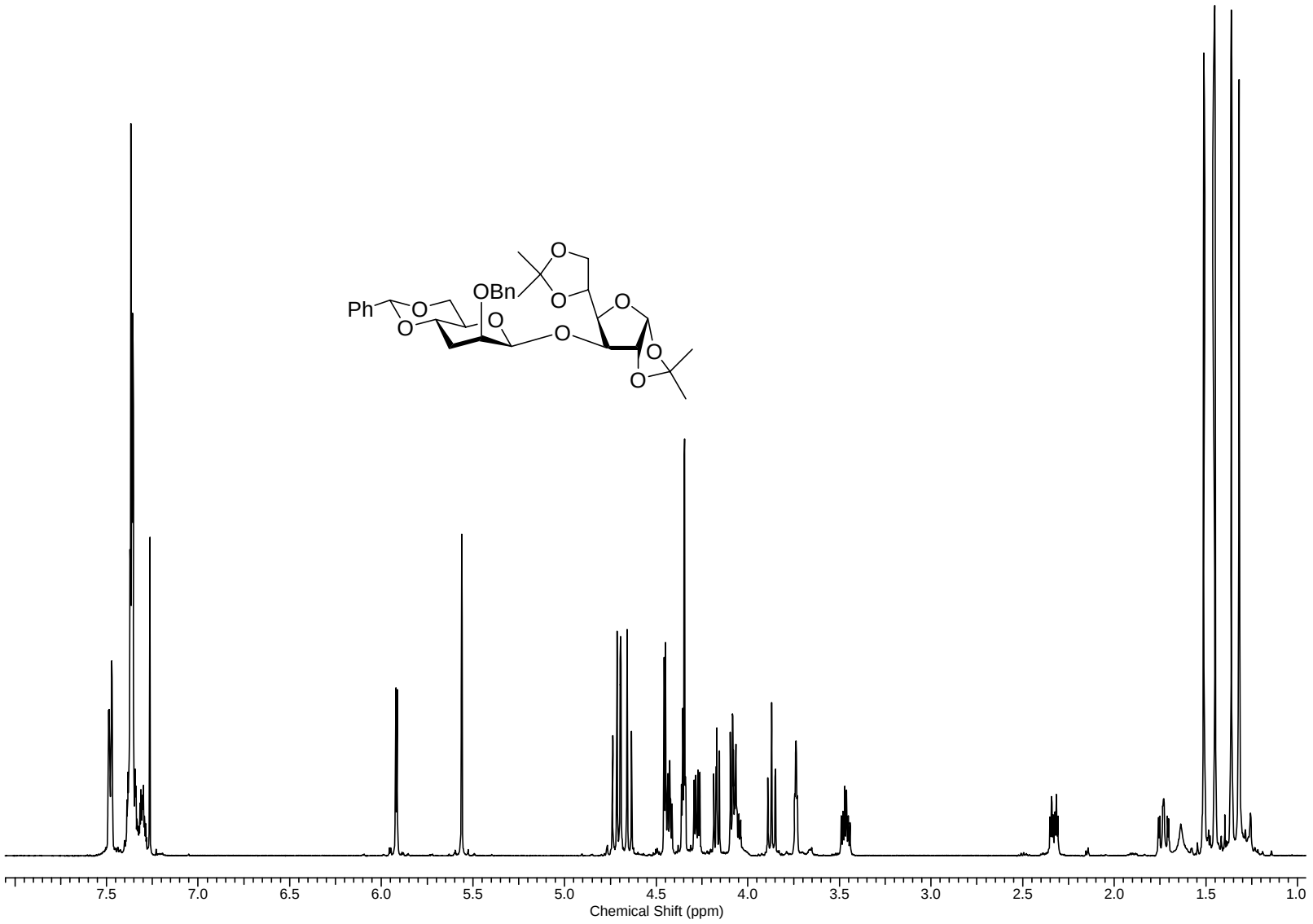
^{1}H spectrum of 3-*O*-(2'-*O*-benzyl-4',6'-benzylidene-3'-deoxy-α-D-*arabino*-thiohexopyranosyl)-1,2:5,6-di-*O*-isopropylidene-α-D-glucose (47α):



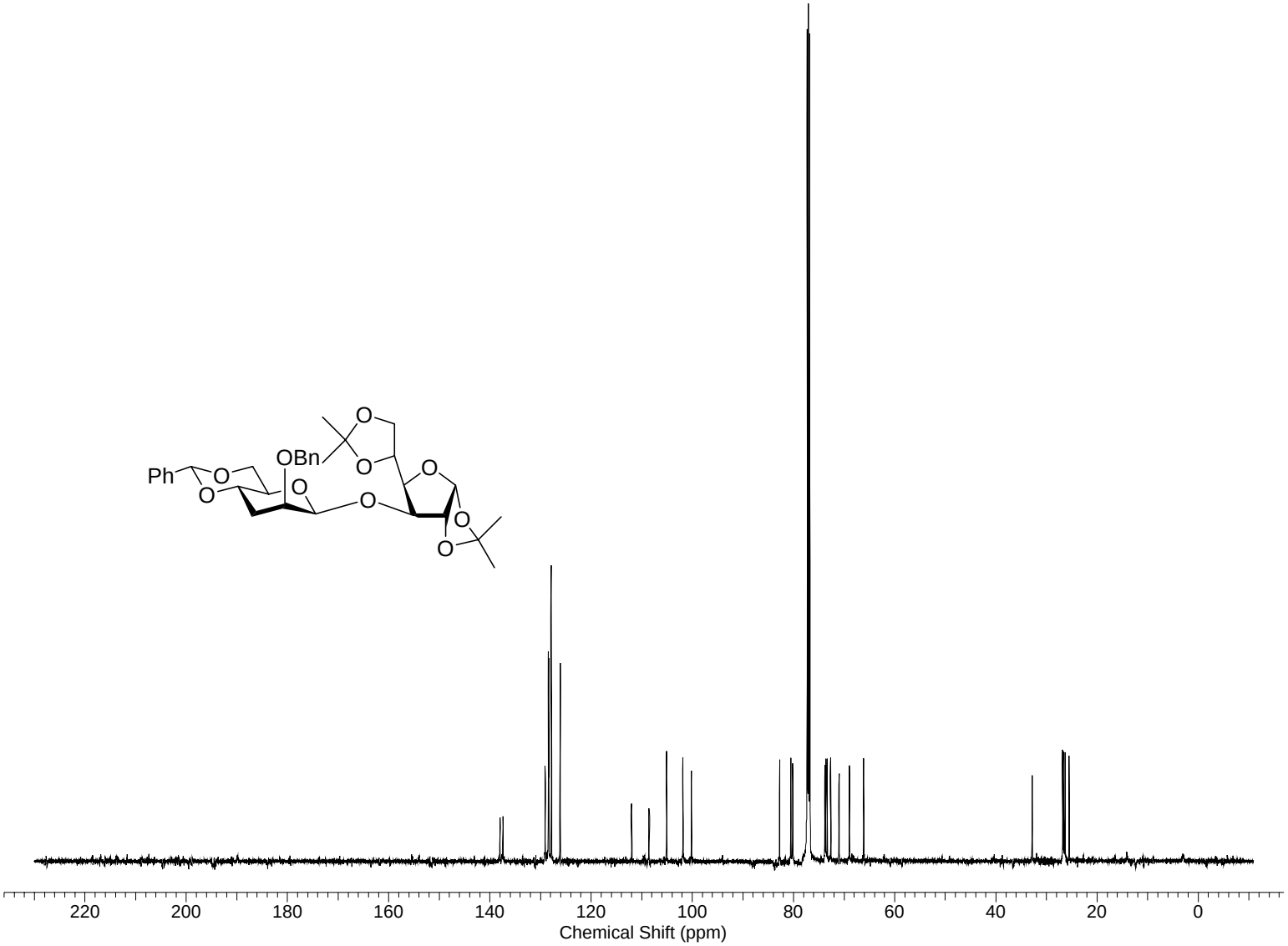
^{13}C spectrum of 3-*O*-(2'-*O*-benzyl-4',6'-benzylidene-3'-deoxy-α-D-*arabino*-thiohexopyranosyl)-1,2:5,6-di-*O*-isopropylidene-α-D-glucose (47α):



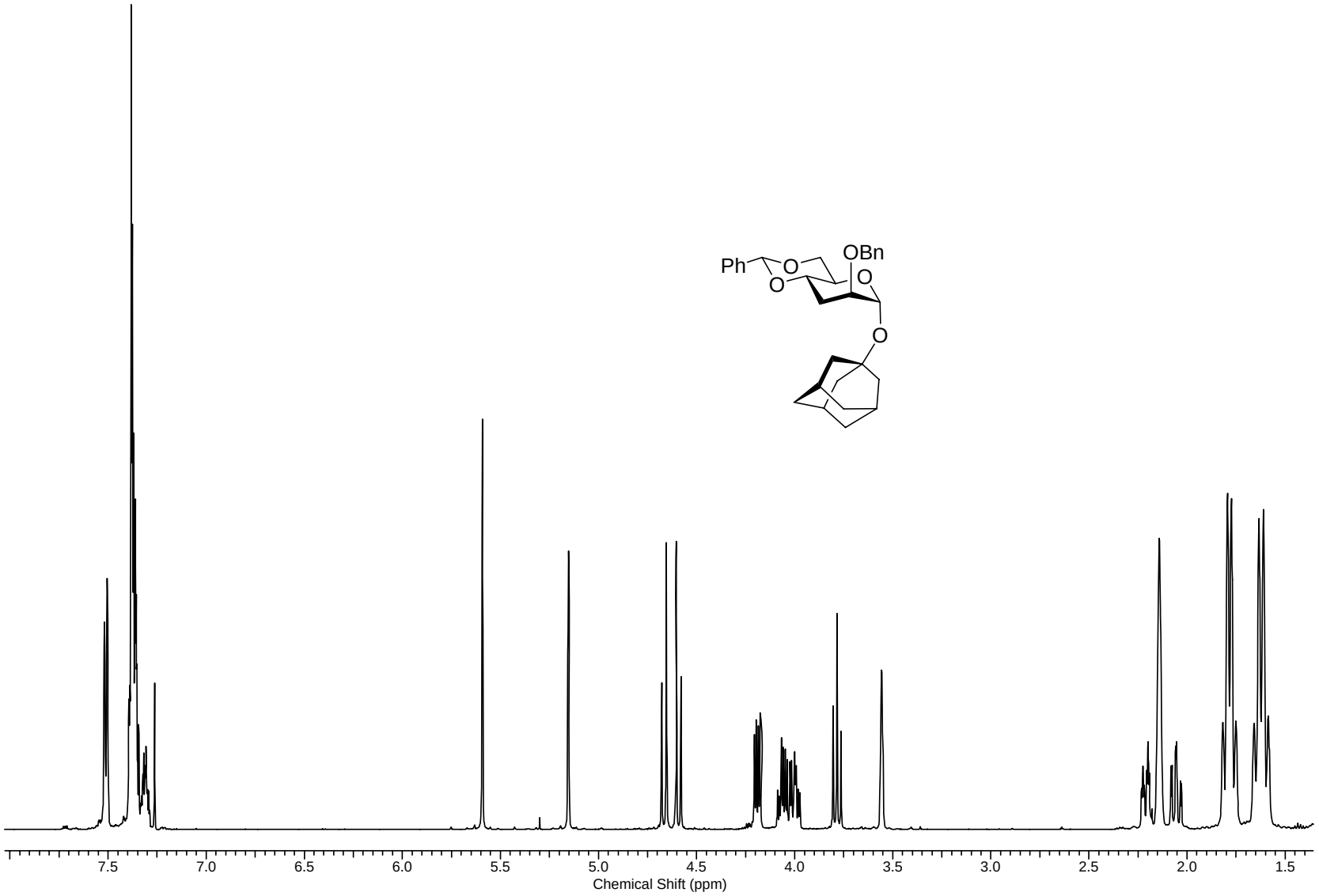
^{1}H spectrum of 3-*O*-(2'-*O*-benzyl-4',6'-benzylidene-3'-deoxy-β-D-*arabino*-thiohexopyranosyl)-1,2:5,6-di-*O*-isopropylidene-α-D-glucose (47β):



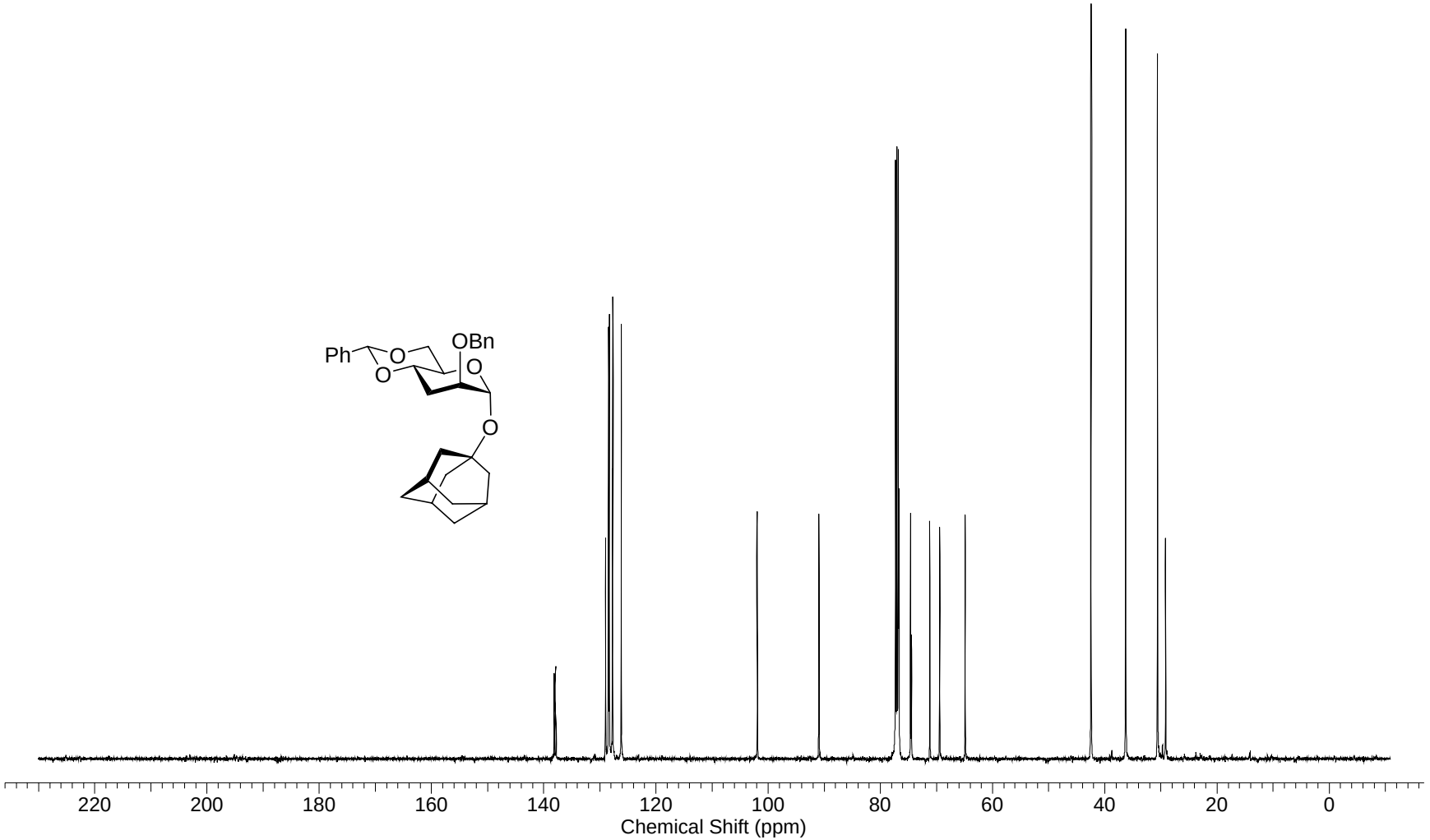
^{13}C spectrum of 3-*O*-(2'-*O*-benzyl-4',6'-benzylidene-3'-deoxy-β-D-*arabino*-thiohexopyranosyl)-1,2:5,6-di-*O*-isopropylidene-α-D-glucose (47β):



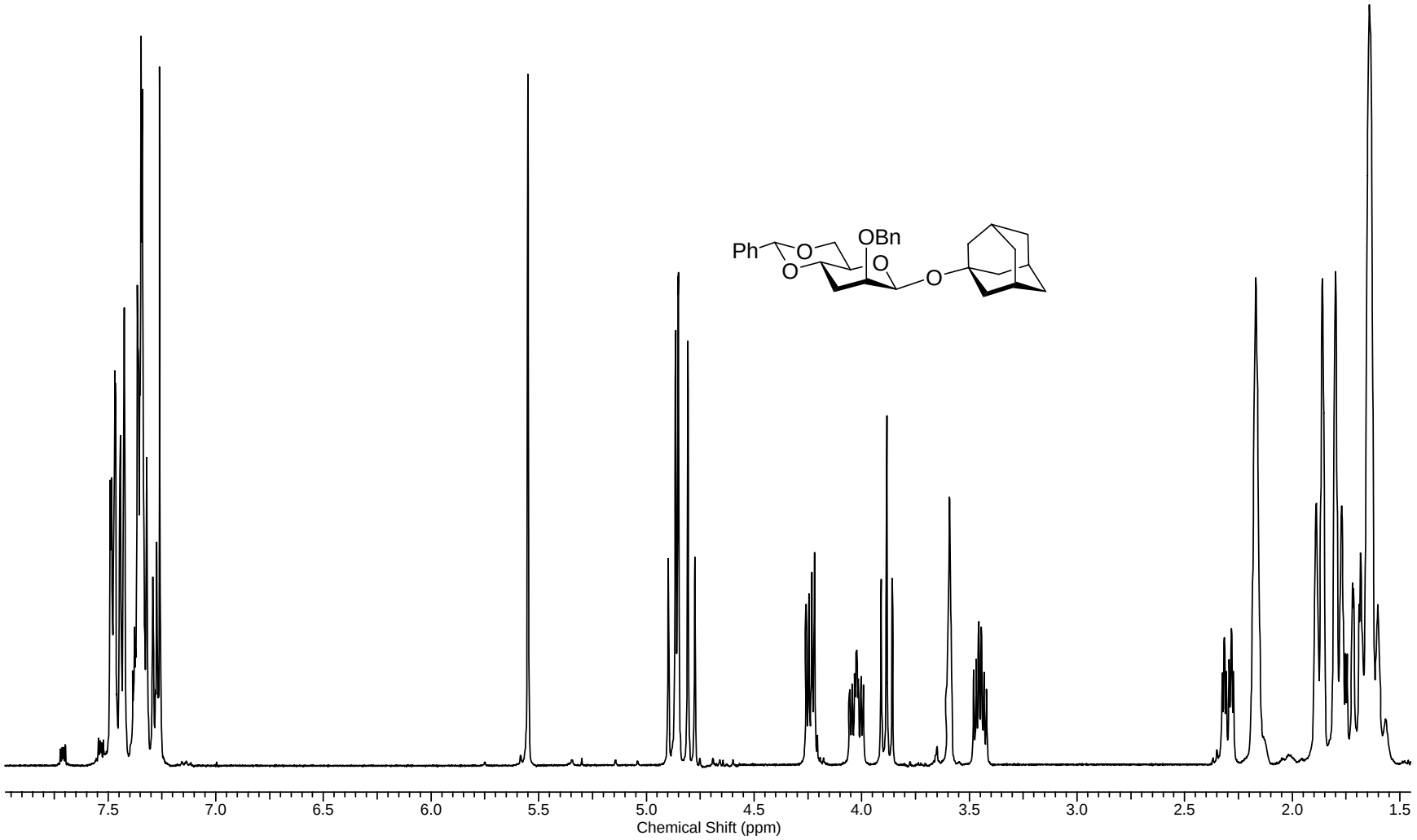
^{1}H spectrum of (1-Adamantyl) 2-*O*-benzyl-4,6-benzylidene-3-deoxy-α-D-*arabino*-hexopyranoside (48α):



^{13}C spectrum of (1-Adamantyl) 2-*O*-benzyl-4,6-benzylidene-3-deoxy-α-D-*arabino*-hexopyranoside (48α):



^{1}H spectrum of (1-Adamantyl) 2-*O*-benzyl-4,6-benzylidene-3-deoxy-β-D-*arabino*-hexopyranoside (48β):



^{13}C spectrum of (1-Adamantyl) 2-*O*-benzyl-4,6-benzylidene-3-deoxy-β-D-*arabino*-hexopyranoside (48β):