Supporting information
for

Mannopyranosylation through the Use of Sterically Minimal Propargyl Ether Protecting Groups

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Phenyl 4,6-*O*-benzylidene-2-*O*-allyl-3-*O*-*p*-methoxybenzyl-1-thio-α-D-mannopyranoside (8).

To a stirred solution of phenyl 4,6-*O*-benzylidene-3-*O*-*p*-methoxybenzyl-1-thio-α-D–mannopyranoside (1.68 g, 3.5 mmol) in dry dimethylformamide (10 mL), was added NaH 60% in oil (0.23 g, 7.5 mmol) followed by allyl bromide (0.46 mL, 5.2 mmol) at 0 ^{o}C.The stirring was continued overnight before the rection mixture was quenched with methanol, diluted with CH_2Cl_2 (25 mL) and washed with sat. $NaHCO_3$. The organic layer was separated and dried over anhydrous Na_2SO_4 and concentrated under vaccum. The crude product was purified by flash column cromatography on silica gel (hexane:ethyl acetate 5:1) to give **8** (1.75 g, 96%); $[\alpha]^{25}_{D}$ + 148 (*c*, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.82 (s, 3H), 3.89 (t, *J* = 9.96 Hz, 1H), 3.94-3.97 (m, 2H), 4.18-4.31 (m, 5H), 3.88 (d, *J* = 11.8 Hz, 1H), 4.81 (d, *J* = 11.8 Hz, 1H), 5.21 (ddd, *J* = 1.5, 2.5, 10.0 Hz, 1H), 5.31 (ddd, *J* = 1.5, 3.0, 17.0 Hz, 1H), 5.54 (s, 1H), 5.65 (s, 1H), 5.89-5.96 (m, 1H), 6.9 (d, *J* = 8.6 Hz, 1H), 7.3-7.45 (m, 10H), 7.5-7.56 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 55.3, 65.4, 68.5, 72.5, 72.8, 75.7, 78.1, 79.0, 87.3, 101.5, 113.8, 117.9, 126.1, 127.6, 128.2, 128.8, 129.1, 129.4, 130.4, 131.5, 133.8, 134.5, 137.6, 159.2. Anal. Calcd for $C_{30}H_{32}O_6S$: C, 69.21; H, 6.20. Found: C, 68.98; H, 6.22.

Phenyl 4,6-*O*-benzylidene-2-*O*-allyl-1-thio-α-D-mannopyranoside (9).

To stirred solution of **8** (1.75 g, 3.36 mmol) in CH_2Cl_2 (10 mL) and water (0.5 mL) was added DDQ (1.53 g, 6.72 mmol) at room temp. After 3 h, sat. $NaHCO_3$ was added, and the mixture was extracted with CH_2Cl_2. The extract was washed several times with sat $NaHCO_3$, and dried over Na_2SO_4. Evaporation of the solvent in vacuo gave an oil, which

was chromatographed on a flash silica gel column (hexane:ethyl acetate, 4:1) to give colorless oil of **9** (1.25 g, 93%).$[\alpha]^{27}_{D}$ +155 (*c*, 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ : 2.5 (bs, 1H), 3.85 (t, *J* = 10.2 Hz, 1H), 3.9 (t, *J* = 9.6 Hz, 1H), 4.02 (dd, *J* = 1.1, 3.6 Hz, 1H), 4.1-4.15 (m, 2H), 4.21-4.25 (m, 2H), 4.29-4.34 (m, 1H), 5.25 (ddd, *J* = 1.3, 2.5 10.0 Hz, 1H), 5.33 (ddd, *J* = 1.5, 3.0, 17.0 Hz, 1H), 5.59 (s, 1H), 5.62 (s, 1H), 5.9-5.98 (m, 1H), 7.33-7.53 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 64.6, 68.5, 68.9, 72.1, 79.6, 79.7, 86.2, 102.2, 118.5, 126.3, 127.4, 128.3, 129.2, 131.6, 133.7, 133.8, 137.2. ESIHRMS Calcd for $C_{22}H_{324}O_5S[M+Na]^+$: 423.1242. Found 423.1237.

Phenyl 4,6-*O*-benzylidene-2-*O*-allyl-3-*O*-*tert*-butyldimethylsilyl-1-thio-α-D-mannopyranoside (10).

To a stirred solution of **9** (0.8 g, 1.9 mmol) and imidazole (0.28 g, 3.9 mmol) in dry dimethylformamide (10 mL) was added *tert*-buyldimethylsilyl chloride (0.46 g, 2.9 mmol) at room temperature and the mixture was stirred for 12 h. The solvent was evaporated off and the residue was dissolved in CH_2Cl_2 (15 mL) and washed with sat. $NaHCO_3$. The organic layer was separated and dried over anhydrous Na_2SO_4 and then concentrated under reduced pressure, and the resulting residue was purified by flash column chromatgraphy on silica gel (hexane:ethyl acetate; 8:1) to yield **10** as a colorless oil (0.93 g, 92%) $[\alpha]^{25}_{D}$ + 118.5 (*c*, 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ : 0.114 and 0.116 (2s, 6H), 0.94 (s, 9H), 3.89-3.91 (m, 2H), 4.09 (t, *J* = 9.5 Hz, 1H), 4.19 (dd, *J* = 3.2, 9.8 Hz, 1H), 4.2-4.25 (m, 2H), 4.28-4.33 (m, 2H), 5.23 (dd, *J* = 1.4, 9.4 Hz,1H), 4.1-4.15 (m, 2H), 4.21-4.25 (m, 2H), 4.29-4.34 (m, 1H), 5.23 (ddd, *J* = 1.0, 2.5, 10.0 Hz, 1H), 5.33 (ddd, *J* = 1.5, 3.5, 17.5 Hz, 1H), 5.57 (s, 1H), 5.61 (s, 1H), 5.9-5.98 (m, 1H), 7.33-

7.53 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$) δ:-4.7, -4.3, 18.4, 25.9, 65.5, 68.5, 70.6, 73.1, 79.1, 80.7, 87.6, 101.9, 117.9, 126.2, 127.5, 128.0, 128.8, 129.1, 131.3, 134.2, 134.7, 137.6. Anal. Calcd for $C_{28}H_{38}O_5SSi$: C, 65.33; H, 7.44. Found: C, 65.13; H, 7.37.

Phenyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-*p*-methoxybenzyl-1-thio-α-D-mannopyranoside (11).

To a stirred solution of phenyl 4,6-*O*-benzylidene-3-*O*-*p*-methoxybenzyl-1-thio-α-D-mannopyranoside (2.5 g, 5.5 mmol) in dry dimethylformamide (15 mL) at 0 ^{o}C was added NaH 60% in oil (0.33 g, 8.3 mmol) and stirred for 15 min. Propargyl bromide (0.93 mL, 8.3 mmol) was added drop wise to the above reaction mixture and continued stirring for 3 h. The rection mixture was quenched by addition of methanol, diluted with CH_2Cl_2 (25 mL) and washed with sat. $NaHCO_3$. The organic layer was separated and dried over anhydrous Na_2SO_4 and concentrated under vaccum. The crude product was purified by flash column cromatography on silica gel (hexane:ethyl acetate; 8:1) to give **11** (2.46 g, 85%), $[\alpha]^{24.5}_{D}$ + 155.8 (*c*, 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.4 (t, *J* = 2.4 Hz, 1H), 3.82 (s, 3H), 3.87 (t, *J* = 11.0 Hz, 1H), 3.98 (dd, *J* = 3.0, 10.0 Hz, 1H), 4.19-4.24 (m, 3H), 4.26-4.31 (m, 1H), 4.4 (dd, *J* = 0.5, 2.0 Hz, 2H), 4.70 (d, *J* = 12.0 Hz, 1H), 4.81 (d, *J* = 12.0 Hz, 1H), 5.61 (d, *J* = 1.5 Hz, 1H), 5.63 (s, 1H), 6.9 (d, *J* = 8.6 Hz, 2H), 7.3-7.45 (m, 10H), 7.5-7.56 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 55.3, 58.8, 65.4, 68.5, 72.9, 75.2, 75.7, 77.6, 79.0, 79.4, 87.4, 101.5, 113.8, 126.1, 127.6, 128.2, 128.8, 129.1, 129.2, 129.4, 130.2, 131.6, 133.7, 134.5, 137.5, 159.3 ESIHRMS Calcd for $C_{30}H_{30}O_6S$ $[M+Na]^+$: 541.1661. Found 541.1658.

Phenyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl) -1-thio-α-D-mannopyranoside (12).

To stirred solution of **11** (0.47 g, 0.91 mmol) in CH_2Cl_2 (8 mL) and water (0.4 mL) was added DDQ (0.3 g, 1.3 mmol) at room temp. After 3 h, sat. $NaHCO_3$ was added, and the mixture was extracted with CH_2Cl_2. The extract was washed several times with sat $NaHCO_3$, and dried over Na_2SO_4. Evaporation of the solvent in vacuo gave an oil, which was chromatographed on a flash silica gel column (hexane:ethyl acetate; 4:1) to give **12** (0.34 g, 93%) as a white solid MP 128 ^oC $[\alpha]^{27}_D$ + 119 (*c*, 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 2.49 (t, *J* = 2.4 Hz, 1H), 2.5 (bs, 1H), 3.84 (t, *J* = 10.2 Hz, 1H), 3.9 (t, *J* = 9.6 Hz, 1H), 4.16 (dd, *J* = 3.6, 10.0 Hz, 1H), 4.21-4.24 (m, 2H), 4.27-4.32 (m, 1H), 4.34 (dd, *J* = 2.4, 16.1 Hz, 1H), 4.42 (dd, *J* = 2.4, 16.1 Hz, 1H), 5.59 (s, 1H), 5.68 (s, 1H), 7.32-7.53 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 58.6, 64.7, 68.4, 68.9, 75.7, 78.9, 79.3, 79.4, 86.4, 102.2, 126.3, 127.7, 128.3, 129.2, 131.7, 133.8, 137.2. ESIHRMS Calcd for $C_{22}H_{22}O_5S$ $[M+Na]^+$: 421.1086. Found 421.1095.

Phenyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-*tert*-butyldimethylsilyl-1-thio-α-D-mannopyranoside (13).

To a stirred solution of **12** (0.68 g, 1.7 mmol) and imidazole (0.23 g, 3.4 mmol) in dry dimethylformamide (10 mL) was added *tert*-buyldimethylsilyl chloride (0.39 g, 2.5 mmol) at room temperature and mixture was stirred for 12 h. The solvent was evaporated off and the residue was disolved in CH_2Cl_2 (15 mL) and washed with sat. $NaHCO_3$. The organic layer was separated and dried over anhydrous Na_2SO_4 and then concentrated under reduced pressure,and the resulting residue was purified by flash column chromatgraphy on silica gel (hexane:ethyl acetate; 9:1) to yield **13** as a colorless oil (0.79

g, 92%) $[\alpha]^{24}_{D}$ + 143 (*c*, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ : 0.10 and 0.16 (2s, 6H), 0.92 (s, 9H), 2.4 (t, *J* = 2.3 Hz, 1H), 3.86 (t, *J* = 10.2 Hz, 1H), 4.0 (t, *J* = 9.5 Hz, 1H), 4.16 (dd, *J* = 1.4, 3.1 Hz, 1H), 4.18-4.23 (m, 2H), 4.26-4.31 (m, 1H), 4.48 (d, *J* = 2.4, 2H), 5.59 (s, 1H), 5.63 (s, 1H), 7.31-7.38 (m, 6H), 7.48-7.52 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ:-4.8, -4.5 18.4, 25.8, 59.2, 65.5, 68.5, 70.8, 75.2, 79.2, 79.8, 87.7, 101.9, 117.9, 126.2, 127.6, 128.0, 128.9, 129.2, 131.4, 133.9, 137.5. ESIHRMS Calcd for $C_{28}H_{36}O_5SSi$ $[M+Na]^+$: 535.1951. Found 535.1947.

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-[4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-*tert*-butyldimethylsilyl-β-D-mannopyranosyl] (1→4)-α-D-glucopyranoside (15β).

$[\alpha]^{24}_{D}$ - 15.6 (*c*, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ : 0.01 and 0.06 (2s, 6H), 0.8 (s, 9H), 2.3 (t, *J* = 2.5 Hz, 1H), 3.0-3.04 (m, 1H), 3.39 (s, 3H), 3.53 (dd, *J* = 3.5, 9.0 Hz, 1H), 3.56 (d, *J* = 10.0 Hz, 1H), 3.66 (dd, *J* = 3.0, 10.0 Hz, 1H), 3.68 (dd, *J* = 1.3, 10.5 Hz, 1H), 3.7-3.82 (m, 4H), 3.9 (t, *J* = 9.4 Hz, 1H), 3.95 (t, *J* = 9.4 Hz, 1H), 4.0 (dd, *J* = 5.0, 11.0 Hz, 1H), 4.47 (d, *J* = 12.5 Hz, 1H), 4.50 (dd, *J* = 3.0, 15.5 Hz, 1H), 4.54 (s, 1H), 4.55 (dd, *J* = 2.5, 15.5 Hz, 1H), 4.61 (d, *J* = 3.5 Hz, 1H), 4.65 (d, *J* = 12.0 Hz, 1H), 4.72 (d, *J* = 12.0 Hz, 1H), 4.81 (d, *J* = 12.0 Hz, 1H), 4.82 (d, *J* = 10.5 Hz, 1H), 5.05 (d, *J* = 10.5 Hz, 1H), 5.4 (s, 1H), 7.26-7.38 (m, 18H), 7.41-7.46 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ:-4.8, -4.4, 18.3, 25.8, 55.3, 60.0, 67.3, 68.5, 68.7, 69.7, 72.7, 73.5, 73.6, 74.7, 75.2, 77.4, 78.48, 78.5, 79.2, 80.3, 98.3, 101.3, 101.8, 126.2, 127.3, 127.7, 127.8, 128.0, 128.1, 128.4, 128.5, 128.8, 137.5, 137.8, 138. 3, 139.4. ESIHRMS Calcd for $C_{50}H_{62}O_{11}Si$ $[M+Na]^+$: 889.3959. Found 889.395

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-[4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-*tert*-butyldimethylsilyl-α-D-mannopyranosyl](1→4)-α-D-glucopyranoside (15α).

$[\alpha]^{24}_{D}$ + 32.7 (*c*, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ : 0.013 and 0.07 (2s, 6H), 0.8 (s, 9H), 2.19 (t, *J* = 2.4 Hz, 1H), 3.4 (s, 3H), 3.57 (dd, *J* = 3.6, 9.4 Hz, 1H), 3.72 (d, *J* = 3.0 Hz, 2H), 3.76-3.78 (m, 4H), 3.87 (t, *J* = 9.4 Hz, 1H), 3.94 (m, 2H), 4.05 (dd, *J* = 2.5, 15.5 Hz, 1H), 4.07 (t, *J* = 3.5 Hz, 1H), 4.12 (dd, *J* = 3.0, 10.0 Hz, 1H), 4.23 (dd, *J* = 2.5, 15.5 Hz, 1H), 4.53 (d, *J* = 11.9 Hz, 1H), 4.56 (d, *J* = 12.0 Hz, 1H), 4.63 (d, *J* = 11.8 Hz, 1H), 4.68 (d, *J* = 12.0 Hz, 1H), 4.77 (d, *J* = 11.4 Hz, 1H), 5.12 (d, *J* = 11.4 Hz, 1H), 5.33 (d, *J* = 1.7 Hz, 1H), 5.5 (s, 1H), 7.26-7.36 (m, 18H), 7.45-7.47 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ:-4.9, -4.4, 18.3, 25.8, 55.4, 59.2, 65.2, 68.6, 68.9, 69.5, 70.5, 73.2, 73.6, 74.7, 75.1, 76.9, 78.9, 80.0, 81.7, 97.5, 101.7, 101.8, 126.2, 126.9, 127.4, 127.5, 127.6, 127.9, 128.0, 128.1, 128.3, 128.4, 128.5, 128.8, 137.6, 137.8, 137.9, 138.7. ESIHRMS Calcd for $C_{50}H_{62}O_{11}Si$ $[M+Na]^+$: 889.3959. Found 889.3979.

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(4,6-*O*-benzylidene-2-*O*-allyl-3-*O*-*tert*-butyldimethylsilyl-β-D-mannopyranosyl) (1→4)-α-D-glucopyranoside (16β).

$[\alpha]^{24}_{D}$ - 22.2 (*c*, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ : 0.005 and 0.05 (2s, 6H), 0.8 (s, 9H), 3.0-3.04 (m, 1H), 3.4 (s, 3H), 3.49 (dd, *J* = 2.5 Hz, 1H), 3.42-3.55 (m, 3H), 3.66 (dd, *J* = 1.5, 10.5 Hz, 1H), 3.7-3.76 (m, 2H), 3.82 (t, *J* = 9.5 Hz, 1H), 3.89 (t, *J* = 9.0 Hz, 1H), 3.97 (t, *J* = 9.5 Hz, 1H), 4.05 (dd, *J* = 5.0, 10.0 Hz, 1H), 4.27 (d, *J* = 6.0 Hz, 2H), 4.45 (d, *J* = 12.5 Hz, 1H), 4.49 (s, 1H), 4.62 (d, *J* = 3.5 Hz, 1H), 4.65 (d, *J* = 12.5 Hz, 1H), 4.71 (d, *J* = 12.0 Hz, 1H), 4.77 (d, *J* = 10.5 Hz, 1H), 4.82 (d, *J* = 12.5 Hz, 1H), 5.08-5.12 (m, 2H), 5.25 (ddd, *J* = 1.5, 3.5, 17.5 Hz, 1H), 5.46 (s, 1H), 5.92-5.97 (m, 1H), 7.26-7.36 (m, 20H) ^{13}C NMR (125 MHz, $CDCl_3$) δ:-4.8, -4.4, 18.3, 25.8, 55.4, 67.3, 68.6,

68.63, 69.7, 72.7, 73.6, 73.7, 74.9, 75.3, 76.9, 78.7, 79.0, 79.8, 80.3, 98.4, 101.1, 101.7, 116.6, 126.2, 127.3, 127.8, 127.9, 128.0, 128.1, 128.3, 128.5, 128.8, 135.6, 137.6, 137.7, 138.4, 139.4. ESIHRMS Calcd for $C_{50}H_{64}O_{11}Si$ $[M+Na]^+$: 891.4116. Found 891.4123.

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(4,6-*O*-benzylidene-2-*O*-allyl-3-*O*-*tert*-butyldimethylsilyl-β-D-mannopyranosyl) (1→4)-α-D-glucopyranoside (16α).

$[\alpha]^{24}_D$ + 32.8 (*c*, 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ : 0.03 and 0.07 (2s, 6H), 0.8 (s, 9H), 3.4 (s, 3H), 3.52-3.54 (m, 1H), 3.58 (dd, *J* = 3.0, 9.5 Hz, 1H), 3.66 (ddt, *J* = 1.5, 6.0, 12.5 Hz, 1H), 3.7-3.8 (m, 5H), 3.83 (t, *J* = 9.3 Hz, 1H), 3.92 (dd, *J* = 9.0, 10.0 Hz, 1H), 3.94-3.98 (m, 2H), 4.09 (dd, *J* = 3.0, 9.7 Hz, 2H), 4.53 (d, *J* = 12.5 Hz, 1H), 4.58 (d, *J* = 12.0 Hz, 1H), 4.63 (d, *J* = 9.5 Hz, 1H), 4.64 (s, 1H), 4.68 (d, *J* = 12.0 Hz, 1H), 4.70 (d, *J* = 11.5 Hz, 1H), 5.0 (ddd, *J* = 2.0, 3.5, 12.06 Hz, 1H), 5.05 (ddd, *J* = 2.0, 3.5, 17.0 Hz, 1H), 5.17 (d, *J* = 12.0 Hz, 1H), 5.24 (d, *J* = 1.5 Hz, 1H), 5.5 (s, 1H), 5.65-5.72 (m, 1H), 7.19-7.47 (m, 20H) ^{13}C NMR (125 MHz, $CDCl_3$) δ:-4.8, -4.4, 18.3, 25.8, 55.4, 65.2, 68.6, 69.0, 69.6, 70.3, 73.1, 73.3, 73.7, 75.0, 79.0, 80.0, 80.2, 81.7, 97.7, 101.7, 102.1, 116.6, 126.2, 126.7, 127.4, 127.5, 127.6, 127.9, 128.0, 128.1, 128.3, 128.4, 128.5, 128.7, 135.0, 137.7, 137.8, 137.9, 138.7. ESIHRMS Calcd for $C_{50}H_{64}O_{11}Si$ $[M+Na]^+$: 891.4116. Found 891.4106.

3β-Cholestanyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-*tert*-butyldimethylsilyl-β-D-mannopyranoside (24β).

$[\alpha]^{24}_D$ - 28.8 (*c*, 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ: 0.05 and 0.1 (2s, 6H), 0.51-0.61 (m, 1H), 0.65 (s, 3H), 0.8 (s, 3H), 0.86-1.7 (m, 36H), 1.78-1.8 (m, 1H), 1.86-1.9 (m, 1H), 1.93-1.98 (m, 1H), 2.39 (t, *J* = 2.5 Hz, 1H), 3.28-3.32 (m, 1H), 3.62-3.68 (m, 1H) 3.48-3.58 (m, 1H), 3.8-3.9 (m, 4H), 4.28 (dd, *J* = 4.8, 10.4 Hz, 1H), 4.55 (dd, *J* = 2.35,

16.1 Hz, 1H) 4.6 (dd, *J* = 2.3, 16.1 Hz, 1H), 4.68 (s, 1H), 5.52 (s, 1H) 7.32-7.37 (m, 3H), 7.45-7.48 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: -4.9, -4.4, 12.0, 12.3, 18.5, 18.7, 21.2, 22.5, 22.8, 23.8, 24.2, 25.9, 28.0, 28.3, 28.9, 29.2, 32.1, 34.2, 35.5, 35.6, 35.8, 36.2, 36.9, 39.5, 40.0, 42.6, 44.6, 54.3, 56.2, 56.5, 60.0, 67.6, 68.6, 72.7, 74.5, 76.7, 78.0, 78.6, 78.7, 99.3, 101.8, 126.1, 128.0, 128.8, 137.5. ESIHRMS Calcd for $C_{49}H_{78}O_6Si$ $[M+Na]^+$: 813.5466. Found 813.5478.

3β-Cholestanyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-*tert*-butyldimethylsilyl-α-D-mannopyranoside (24α). $[\alpha]^{24}_D$ + 75.1 (*c*, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.04 and 0.1 (2s, 6H), 0.51-0.61 (m, 1H), 0.65 (s, 3H), 0.8 (s, 3H), 0.84-1.59 (m, 39H), 1.64-1.67 (m, 1H), 1.70-1.74 (m, 1H), 1.78-1.86 (m, 2H), 1.94-1.98 (m, 1H), 2.4 (t, *J* = 2.4 Hz, 1H), 3.48-3.58 (m, 1H), 3.79-3.86 (m, 3H), 3.9 (t, *J* = 9.0 Hz, 1H), 4.17 (dd, *J* = 3.5, 10.0 Hz, 1H), 4.2 (dd, *J* = 3, 8.5 Hz, 1H), 4.45 (dd, *J* = 2.5, 16.5 Hz, 1H) 4.48 (dd, *J* = 2.5, 16.5 Hz, 1H), 5.0 (d, *J* = 1.5 Hz, 1H), 5.5 (s, 1H) 7.33-7.37 (m, 3H), 7.47-7.49 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: -4.9, -4.4, 12.0, 12.33, 14.1, 18.3, 18.7, 21.2, 22.5, 22.8, 23.8, 24.2, 25.8, 27.5, 28.0, 28.2, 28.7, 31.6, 32.0, 35.5, 35.6, 35.8, 35.9, 36.1, 36.8, 39.5, 40.0, 42.6, 44.9, 54.3, 56.3, 56.4, 56.5, 59.5, 64.0, 68.8, 70.5, 74.5, 76.5, 77.3, 78.9, 79.5, 80.0, 98.0, 101.8, 125.0, 126.1, 128.0, 128.7, 128.9, 137.6. ESIHRMS Calcd for $C_{49}H_{78}O_6Si$ $[M+Na]^+$: 813.5466. Found 813.5469.

Methyl 4-*O*-[4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-*tert*-butyldimethylsilyl-β-D-mannopyranosyl]-(1→4)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (25β).

$[\alpha]^{24}_D$ - 60 (*c*, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ : 0.05 and 0.1 (2s, 6H), 0.8 (s, 9H), 1.32 (d, *J* = 5.9 Hz, 3H), 1.36 (s, 3H), 1.52 (s, 3H), 2.39 (t, *J* = 2.4 Hz, 1H), 3.27-3.32 (m, 1H), 3.37 (s, 1H), 3.62-3.70 (m, 2H), 3.87-3.95 (m, 4H), 4.1 (d, *J* = 5.6 Hz, 1H),

4.2-4.26 (m, 2H), 4.5 (d, *J* = 2.4 Hz, 2H), 4.87 (s, 1H), 5.0 (s, 1H), 5.53 (s, 1H), 7.26-7.36 (m, 3H), 7.45-7.48 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ:-4.8, -4.4, 14.1, 17.6, 18.4, 25.8, 26.5, 27.8, 31.6, 54.8, 60.0, 64.1, 67.6, 68.6, 72.7, 74.5, 76.1, 77.5, 78.3, 78.4, 78.9, 80.2, 97.8, 99.4, 101.8, 109.3, 126.1, 128.0, 128.8, 137.5. Anal. Calcd for $C_{32}H_{48}O_{10}Si$: C, 61.91; H, 7.79. Found: C, 61.64; H, 7.56.

Methyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-*p*-methoxybenzyl-β-D-mannopyranoside (26).

To a stirred solution of donor **11** (277 mg, 0.53 mmol), BSP (134 mg 0.64 mmol), TTBP (199 mg, 0.8 mmol), and 4 Å molecular sieves in CH_2Cl_2 (6 mL), at -60 ^{o}C under an Ar atmosphere, was added Tf_2O (117.3 µL 0.69 mmol). After 30 min. of stirring at -60 ^{o}C, dry methanol (64 µL 1.59 mmol) was added. The reaction mixture was stirred for further 2 h. at -60 ^{o}C, and allowed to reach room temperature. The reaction mixture was diluted with CH_2Cl_2 (10 mL) and molecular sieves were filtered off and washed with saturated $NaHCO_3$. The organic layer was separated, dried and concentrated. The crude was purified by flash column chromatography on silica gel (hexane:ethyl acetate; 8:1) to give **26** (186 mg, 79%) as colorlrss oil. $[\alpha]^{24.5}_{D}$ - 38.5 (*c*, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ : 2.4 (t, *J* = 2.4 Hz, 1H), 3.0-3.3 (m, 1H), 3.53 (s, 3H), 3.6 (dd, *J* = 3.2, 10.0 Hz, 1H), 3.8 (s, 3H), 3.9 (t, *J* = 10.3 Hz, 1H), 4.1 (t, *J* = 9.6 Hz, 1H), 4.3 (dd, *J* = 4.9, 10.5, 1H), 4.4 (s, 1H), 4.5 (dd, *J* = 2.4, 16.1 1H), 4.6 (dd, *J* = 2.4, 16.1 1H), 4.73 (d, *J* = 12.0 1H), 4.76 (d, *J* = 12.0 1H), 5.6 (s, 1H), 6.84-6.87 (m, 2H), 7.26-7.4 (m, 5H), 7.48-7.5 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 57.4, 59.9, 67.5, 68.6, 72.1, 74.8, 75.1, 78.4, 80.2,

101.4, 102.9, 113.7, 126.0, 128.2, 128.8, 129.5, 130.2, 137.5, 159.2. ESIHRMS Calcd for $C_{25}H_{28}O_7$ $[M+Na]^+$: 463.1733. Found 463.1729.

Methyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-β-D-mannopyranoside (27). To stirred solution of **26** (108 mg, 0.25 mmol) in CH_2Cl_2 (5 mL) and water (0.2 mL) was added DDQ (167 mg, 0.74 mmol) at room temp. After 3 h, sat. $NaHCO_3$ was added, and the mixture was extracted with CH_2Cl_2. The extract was washed several times with sat $NaHCO_3$, and dried over Na_2SO_4 and concentrated on a rotary evaporator. The crude was purified by flash column chromatography on silica gel (hexane:ethyl acetate; 4:1) to give **27** (93 mg, 95%) as white solid MP 126 ^oC; $[\alpha]^{27}_D$ - 119.9 (*c*, 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ : 2.5 (t, *J* = 2.4 Hz, 1H), 3.31-3.36 (m, 1H), 3.5 (s, 3H), 3.76-3.83 (m, 2H), 3.87 (t, *J* = 10.3 Hz, 1H), 4.0 (dd, *J* = 0.5, 3.2 Hz, 1H), 4.3 (dd, *J* = 4.9, 10.5 Hz, 1H), 4.46 (dd, *J* = 2.4, 16.1 1H), 4.48 (s, 1H), 4.6 (dd, *J* = 2.4, 16.1 1H), 5.5 (s, 1H), 7.26-7.38 (m, 3H), 7.48-7.5 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 57.5, 60.6, 67.0, 68.4, 70.3, 75.5, 77.2, 79.1, 79.7, 102.0, 103.0, 126.3, 128.2, 129.1, 137.2. ESIHRMS Calcd for $C_{17}H_{20}O_6$ $[M+H]^+$: 321.1338. Found 321.1347.

Phenyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl)-1-thio-α-D-mannopyranoside 29β and the α-anomer 29α.

To a stirred solution of donor **28** (480 mg, 0.88 mmol), BSP (223 mg 1.06 mmol), TTBP (331 mg, 1.33 mmol), and 4 Å molecular sieves in CH_2Cl_2 (5 mL), at -60 ^oC under an Ar atmosphere, was added Tf_2O (195 µL 1.15 mmol). After 30 min. the temperature was brought down to -78 ^oC, and then acceptor **12** (424 mg 1.06 mmol) in CH_2Cl_2 (3 mL),

was slowly added. The reaction mixture was stirred for 2h. at -78 ^{o}C, and quenched by the addition of triethylphosphite (435 µL, 2.7 mmol), and continued stirring for 1 h at -78 ^{o}C and allowed to reached room temperature. The reaction mixture was diluted with CH_2Cl_2 (10 mL) and molecular sieves were filtered off and washed with saturated $NaHCO_3$. The organic layer was separated, dried and concentrated. The crude was purified by radial chromatography (hexane:ethyl acetate; 8:1) to give **29β** and **29α** in 83% and 5% yield respectively. **29β:** $[\alpha]^{24}_{D}$ + 26.3 (*c*, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ : 2.23 (t, *J* = 2.4 Hz, 1H), 3.29-3.34 (m, 1H), 3.6 (dd, *J* = 3.2, 9.7 Hz, 1H), 3.86 (t, *J* = 10.3 Hz, 1H), 3.93 (t, *J* = 10.3 Hz, 1H), 4.0 (d, *J* = 3.0 Hz, 1H), 4.13 (t, *J* = 9.7 Hz, 1H), 4.25-4.40 (m, 8H), 4.65 (d, *J* = 12.5, Hz, 1H), 4.76 (d, *J* = 12.5 Hz, 1H), 4.84 (s, 1H), 4.86 (d, *J* = 11.9 Hz, 1H), 4.98 (d, *J* = 11.8 Hz, 1H), 5.58 (s, 1H), 5.62 (s, 1H), 5.64 (s, 1H), 7.24-7.49 (m, 25H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 57.5, 65.3, 67.8, 68.5, 68.6, 72.3, 73.4, 74.8, 75.6, 75.7, 76.5, 77.5, 77.6, 78.6, 79.0, 86.0, 98.9, 101.3, 101.9, 126.0, 126.2, 127.4, 127.6, 127.7, 127.8, 128.0, 128.1, 128.2, 128.3, 128.4, 128.8, 129.0, 129.2, 131.6, 133.6, 137.3, 137.6, 138.4, 138.7. ESIHRMS Calcd for $C_{49}H_{48}O_{10}S$ $[M+Na]^{+}$: 851.2866. Found 851.2875. **29α:** $[\alpha]^{24}_{D}$ + 76.4 (*c*, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ : 2.4 (t, *J* = 2.4 Hz, 1H), 3.8 (t, *J* = 10.5 Hz, 1H), 3.92-3.96 (m, 2H), 3.99-4.04 (m, 2H), 4.15 (t, *J* = 9.5 Hz, 1H), 4.2 (dd, *J* = 2.5, 16.1 Hz, 1H), 4.25-4.38 (m, 7H), 4.5 (d, *J* = 12.4 Hz, 1H), 4.62 (d, *J* = 12.4 Hz, 1H), 4.63 (d, *J* = 12.2 Hz, 1H), 4.7 (d, *J* = 12.2 Hz, 1H), 5.4 (d, *J* = 1.2 Hz, 1H), 5.57 (s, 1H), 5.59 (s, 1H), 5.67 (s, 1H), 7.15-7.52 (m, 25H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 58.3, 64.7, 65.1, 68.5, 68.8, 72.1, 72.7, 72.8, 75.3, 75.7, 78.5, 79.0, 79.2, 86.9, 99.6, 101.4, 101.9, 125.9, 126.1, 127.5, 127.6, 127.7, 127.8,

128.2, 128.4, 128.8, 129.2, 129.3, 131.6, 133.5, 137.3, 137.7, 137.8, 138.5. ESIHRMS Calcd for $C_{49}H_{48}O_{10}S$ $[M+Na]^+$: 851.2866. Found 851.2874.

Methyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→3)-4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-β-D-mannopyranosyl-(1→3)-4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-β-D-mannopyranoside 30β and the α-anomer 30α. To a stirred solution of donor **29β** (146 mg, 0.17 mmol), BSP (44 mg 0.21 mmol), TTBP (66 mg, 0.26 mmol), and 4 Å molecular sieves in CH_2Cl_2 (4 mL), at -60 ^oC under an Ar atmosphere, was added Tf_2O (39 μL 0.23 mmol). After 30 min. of stirring at -60 ^oC, acceptor **27** (67 mg, 0.21 mmol) in CH_2Cl_2 (3 mL), was added slowly. The reaction mixture was stirred for further 2 h. at -60 ^oC, and allowed to reach room temperature. The reaction mixture was diluted with CH_2Cl_2 (10 mL) and molecular sieves were filtered off and washed with saturated $NaHCO_3$. The organic layer was separated, dried and concentrated. The crude was purified by radial chromatography on silica gel (Hexane: Chloroform; 4:1) to give **30β** and **30α** in 67% and 13% yield, respectively. **30β:** $[\alpha]^{24}_D$ - 151.3 (*c*, 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ : 1.9 (t, *J* = 2.3 Hz, 1H), 2.49 (t, *J* = 2.3 Hz, 1H), 3.36-3.40 (m, 3H), 3.54 (m, 1H), 3.56 (s, 3H), 3.87-4.12 (m, 9H), 4.21 (t, *J* = 9.5 Hz, 1H), 4.26-4.93 (m, 3H), 4.36 (dd, *J* = 4.8, 10.4 Hz, 1H), 4.47 (dd, *J* = 2.4, 16.5 Hz, 1H), 4.5 (s, 1H), 4.55 (dd, *J* = 2.3, 16.3 Hz, 1H), 4.65 (d, *J* = 12.7 Hz, 2H), 4.7 (d, *J* = 12.7 Hz, 2H), 4.8 (d, *J* = 11.9 Hz, 1H), 4.98 (s, 1H), 5.03 (d, *J* = 11.9 Hz, 1H) 5.07 (s, 1H), 5.55 (s, 1H), 5.60 (s, 1H), 7.26-7.46 (m, 25H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 57.7, 59.3, 59.5, 67.5, 67.8, 67.9, 68.5, 71.9, 72.1, 72.3, 73.2, 73.7, 74.7, 74.8, 75.2, 76.2, 76.7, 78.5, 80.6, 97.4, 97.7, 101.3, 101.5, 101.7, 103.5, 125.9, 126.0, 126.2, 127.3, 127.6, 127.7, 128.0, 128.2,

128.3, 128.4, 128.8, 128.9, 129.0, 137.2, 137.5, 138.3, 138.8. ESIHRMS Calcd for $C_{60}H_{62}O_{16}$ $[M+Na]^+$: 1061.3936. Found 1061.3939. **30α:** $[\alpha]^{24}_D$ - 58.3 (*c*, 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ : 1.6 (t, *J* = 2.3 Hz, 1H), 2.66 (t, *J* = 2.2 Hz, 1H), 3.27-3.32 (m, 1H), 3.36-3.41 (m, 1H), 3.56 (s, 3H), 3.57 (m, 1H), 3.8-3.93 (m, 4H), 3.96-4.09 (m, 4H), 4.14-4.20 (m, 5H), 4.28 (dd, *J* = 4.6, 10.2 Hz, 1H), 4.35 (dd, *J* = 4.9, 10.6 Hz, 1H), 4.45-4.58 (m, 4H), 4.63 (d, *J* = 12.6 Hz, 1H), 4.62 (d, *J* = 12.5 Hz, 1H), 4.73 (s, 1H), 4.84 (d, *J* = 11.9 Hz, 1H), 4.93 (d, *J* = 11.9 Hz, 1H), 5.3 (d, *J* = 1.4 Hz, 1H), 5.54 (s, 1H), 5.56 (s, 1H), 7.22-7.36 (m, 25H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 57.7, 58.1, 60.0, 67.1, 67.6, 68.5, 68.8, 72.2, 73.1, 73.7, 74.1, 74.7, 75.0, 76.1, 76.3, 77.4, 77.7, 78.5, 78.6, 79.0, 80.4, 99.2, 99.7, 101.3, 101.7, 101.8, 103.3, 126.0, 126.1, 126.3, 127.3, 127.5, 127.6, 128.0, 128.1, 128.2, 128.3, 128.33, 128.8, 128.9, 129.2, 137.2, 137.5, 137.6, 138.4, 138.7. ESIHRMS Calcd for $C_{60}H_{62}O_{16}$ $[M+Na]^+$: 1061.3936. Found 1061.3917.

Phenyl 4,6-*O*-benzylidene-3-*O*-benzyl-2-*O*-(prop-2-ynyl)-1-thio-α-D-mannopyranoside (33)

To a stirred solution of phenyl 4,6-*O*-benzylidene-3-*O*-benzyl-1-thio-α-D-mannopyranoside **32** (1.8 g, 4.0 mmol) at 0 °C was added NaH 60% in mineral oil (0.256 g, 6.4 mmol). After 15 min. propargyl bromide [80% wt. in PhMe, (668 µL, 6.0 mmol)] was added dropwise to the reaction mixture and continued stirring for 3 h. The reaction mixture was quenched by addition of methanol, diluted with CH_2Cl_2 (25 mL) and washed with sat. $NaHCO_3$. The organic layer was separated and dried over anhydrous Na_2SO_4 and concentrated under vaccum. The crude product was purified by flash column cromatography on silica gel (hexane:ethyl acetate; 5:1) to give **33** (1.89 g, 95%). $[\alpha]^{26}_D$ + 167.5 (*c*, 2.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ : 2.47 (t, *J* = 2.4 Hz, 1H), 3.9 (t, *J* =

10.0 Hz, 1H), 4.03 (dd, *J* = 3.1, 9.7 Hz, 1H), 4.24-4.37 (m, 4H), 4.44 (dd, *J* = 2.4, 16.1 Hz, 1H), 4.47 (dd, *J* = 2.4, 16.1 Hz, 1H), 4.78 (d, *J* = 12.0 Hz, 1H), 4.91 (d, *J* = 12.0 Hz, 1H), 5.65 (s, 1H), 5.66 (s, 1H), 7.32-7.53 (m, 15H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 58.8, 65.3, 68.5, 73.3, 75.3, 76.1, 77.7, 79.1, 79.4, 87.4, 101.6, 126.1, 127.6, 127.7, 127.8, 128.2, 128.4, 128.9, 129.2, 131.6, 133.7, 137.5, 138.2. ESIHRMS Calcd for $C_{29}H_{28}O_5S[M+Na]^+$: 511.1555. Found 511.1569.

Phenyl 4,6-*O*-benzylidene-2-*O*-benzyl-3-*O*-(prop-2-ynyl)-1-thio-α-D-mannopyranoside (35). To a stirred solution of phenyl 4,6-*O*-benzylidene-2-*O*-benzyl-1-thio-α-D-mannopyranoside **34** (0.23 g, 0.63 mmol) at 0 °C was added NaH 60% in mineral oil (0.088 g, 2.2 mmol). After 15 min. propargyl bromide [80% wt.in PhMe, (212 μL, 1.9 mmol)] was added dropwise to the reaction mixture and continued stirring for 3 h. The reaction mixture was quenched by addition of methanol, diluted with CH_2Cl_2 (25 mL) and washed with sat. $NaHCO_3$. The organic layer was separated and dried over anhydrous Na_2SO_4 and concentrated under vaccum. The crude product was purified by flash column cromatography on silica gel (hexane:ethyl acetate; 5:1) to give **35** (0.382 g, 95%).$[\alpha]^{24}_D$ + 158.7 (*c*, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ : 2.50 (t, *J* = 2.4 Hz, 1H), 3.9 (t, *J* = 10.1 Hz, 1H), 4.13 (dd, *J* = 3.2, 9.6 Hz, 1H), 4.18 (dd, *J* = 3.2 Hz, 1H), 4.24 (dd, *J* = 4.7, 10.4 Hz, 1H), 4.28 (t, *J* = 9.6 Hz, 1H), 4.32-4.37 (m, 1H), 4.37 (dd, *J* = 2.3, 15.9 Hz, 1H), 4.43 (dd, *J* = 2.3, 15.9 Hz, 1H), 4.75 (d, *J* = 12.0 Hz, 1H), 4.81 (d, *J* = 12.0 Hz, 1H), 5.52 (s, 1H), 5.62 (s, 1H), 7.26-7.42 (m, 13H), 7.50-7.52 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 58.7, 65.3, 68.5, 73.3, 74.8, 75.5, 78.6, 79.1, 79.9, 87.2,

101.6, 126.1, 127.7, 127.9, 128.0, 128.2, 128.4, 128.9, 129.2, 131.6, 133.7, 137.4, 137.7. ESIHRMS Calcd for $C_{29}H_{28}O_5S[M+Na]^+$: 511.1555. Found 511.1573.

Phenyl 4,6-*O*-benzylidene-2,3-di-*O*-(prop-2-ynyl)-1-thio-α-D-mannopyranoside (36)

To a stirred solution of phenyl 4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside **31** (0.23 g, 0.63 mmol) at 0 °C was added NaH 60% in mineral oil (0.088 g, 2.2 mmol). After 15 min. propargyl bromide [80% wt. in PhMe, (212 μL, 1.9 mmol)] was added dropwise to the reaction mixture and continued stirring for 3 h. The reaction mixture was quenched by addition of methanol, diluted with CH_2Cl_2 (25 mL) and washed with sat. $NaHCO_3$. The organic layer was separated and dried over anhydrous Na_2SO_4 and concentrated under vaccum. The crude product was purified by flash column cromatography on silica gel (hexane:ethyl acetate; 5:1) to give **36** (0.246 g, 89%). $[\alpha]^{24}_D$ + 193.6 (*c*, 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ : 2.43 (t, *J* = 2.4 Hz, 1H), 2.52 (t, *J* = 2.4 Hz, 1H), 3.87 (t, *J* = 10.3 Hz, 1H), 4.13-4.25 (m, 3H), 4.32 - 4.35 (m, 2H), 4.43 (dd, *J* = 2.4, 16.1 Hz, 1H), 4.44-4.47 (m, 2H), 4.50 (dd, *J* = 2.4, 16.1 Hz, 1H), 5.60 (s, 1H), 5.67 (d, *J* = 1.3 Hz, 1H), 7.31-7.38 (m, 6H), 7.48 - 7.50 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 58.9, 65.1, 68.5, 74.9, 75.2, 75.3, 78.2, 79.1, 79.3, 79.7, 87.3, 101.6, 126.1, 127.6, 127.7, 128.9, 129.2, 131.6, 133.6, 137.3. ESIHRMS Calcd for $C_{25}H_{24}O_5S[M+Na]^+$: 459.1242. Found 459.1258.

General procedure for the coupling of mannosyl donors with acceptors using BSP/TTBP/Tf_2O system.

To a stirred solution of donor (0.12g, 1 eq) BSP (1.1 eq), TTBP (1.5 eq), and 4 Å molecular sieves in CH_2Cl_2 (0.05 M in substrate), at -60 ^oC under an Ar atmosphere, was added Tf_2O (1.2 eq). After 30 min. of stirring at -60 ^oC, a solution of the glycosyl

acceptor (1.5 eq) in CH_2Cl_2 (0.02 M in acceptor) was added slowly. The reaction mixture was stirred for further 2h. at -60 ^oC, and allowed to reach room temperature. The reaction mixture was diluted with dichloromethane (10 mL) and molecular sieves were filtered off and washed with saturated $NaHCO_3$. The organic layer was separated and dried and concentrated. Purification by flash column chromatography on silica gel (hexane /ethyl acetate) afforded the corresponding alpha/beta mannopyranosides.

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl)-(1→4)-α-D-glucopyranoside (37β); Characterization data were in agreement with literature values[1]

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranosyl)-(1→4)-α-D-glucopyranoside (37α); Characterization data were in agreement with literature values[1]

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-[4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-benzyl-β-D-mannopyranosyl]-(1→4)-α-D-glucopyranoside (38β).

$[\alpha]^{24}_D$ - 9.6 (*c*, 2.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ : 2.44 (t, *J* = 2.5 Hz, 1H), 3.02-3.05 (m, 1H), 3.35 (dd, *J* = 3.0, 10.0 Hz, 1H), 3.40 (s, 3H), 3.51-3.56 (m, 2H), 3.65 (dd, *J* = 3.0, 9.9 Hz, 1H), 3.75 (d, *J* = 9.2 Hz, 2H), 3.86-3.96 (m, 3H), 3.99-4.03 (m, 2H), 4.39 (d, *J* = 12.0 Hz, 1H), 4.43 (s, 1H), 4.50 (dd, *J* = 2.3, 15.8 Hz, 1H), 4.62 (dd, *J* = 2.3, 15.8 Hz, 1H), 4.62 (d, *J* = 3.6 Hz, 1H), 4.66 (d, *J* = 12.2 Hz, 1H), 4.69 (d, *J* = 12.2 Hz, 1H), 4.73 (s, 1H), 4.79 (d, *J* = 12.6 Hz, 1H), 4.82 (d, *J* = 12.2 Hz, 1H), 4.83 (d, *J* = 10.7 Hz, 1H), 5.03 (d, *J* = 10.7 Hz, 1H), 5.51 (s, 1H), 7.20-7.43 (m, 25H); ^{13}C NMR (125

MHz, $CDCl_3$) δ: 55.4, 59.9, 67.2, 68.5, 69.6, 72.4, 73.6, 73.62, 74.7, 75.2, 75.9, 77.5, 78.4, 79.1, 80.2, 80.3, 98.4, 101.3, 101.5, 126.0, 127.3, 127.6, 127.7, 127.8, 128.0, 128.06, 128.1, 128.2, 128.3, 128.4, 128.6, 128.8, 137.6, 137.64, 138.3, 138.4, 139.3. ESIHRMS Calcd for $C_{51}H_{54}O_{11}[M+Na]^+$: 865.3564 Found 865.3549.

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-[4,6-*O*-benzylidene-2-*O*-benzyl-3-*O*-(prop-2-ynyl)-β-D-mannopyranosyl]-(1→4)-α-D-glucopyranoside (39β)

$[\alpha]^{25}_D$ - 9.1 (*c*, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ : 2.42 (t, *J* = 2.3 Hz, 1H), 3.06-3.10 (m, 1H), 3.41 (s, 3H), 3.48-3.55 (m, 5H), 3.59 (dt, *J* = 2.3, 9.4 Hz, 1H), 3.73 (d, *J* = 2.9 Hz, 1H), 3.87 (t, *J* = 8.9 Hz, 1H), 3.91 (t, *J* = 8.9 Hz, 1H), 4.00-4.05 (m, 2H), 4.26 (dd, *J* = 2.4, 15.9 Hz, 1H), 4.36 (dd, *J* = 2.4, 15.9 Hz, 1H), 4.38 (d, *J* = 12.0 Hz, 1H), 4.46 (s, 1H), 4.60 (d, *J* = 3.7 Hz, 1H), 4.65 (d, *J* = 12.0 Hz, 1H), 4.67 (d, *J* = 11.7 Hz, 1H), 4.76-4.83 (m, 4H), 5.05 (d, *J* = 10.7 Hz, 1H), 5.48 (s, 1H), 7.26-7.46 (m, 25H); ^{13}C NMR (125 MHz, $CDCl_3$) δ : 55.4, 58.5, 67.1, 68.4, 68.6, 69.6, 73.6, 74.4, 75.1, 75.3, 77.4, 77.8, 77.9, 78.6, 79.0, 80.3, 98.4, 101.4, 101.6, 126.1, 127.2, 127.5, 127.6, 127.8, 128.0, 128.1, 128.2, 128.3, 128.4, 128.6, 128.9, 137.5, 137.6, 138.3, 138.6, 139.4; ESIHRMS Calcd for $C_{51}H_{54}O_{11}[M+Na]^+$: 865.3564. Found 865.3557.

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-[4,6-*O*-benzylidene-2-*O*-benzyl-3-*O*-(prop-2-ynyl)-α-D-mannopyranosyl]-(1→4)-α-D-glucopyranoside (39α).

$[\alpha]^{26}_D$ + 36.0 (*c*, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ : 2.43 (t, *J* = 2.2 Hz, 1H), 3.41 (s, 3H), 3.58 (dd, *J* = 3.5, 9.5 Hz, 1H), 3.73-3.93 (m, 8H), 4.07-4.10 (m, 2H), 4.16-4.19 (m, 2H), 4.32 (dd, *J* = 2.2, 16.8 Hz, 1H), 4.39 (dd, *J* = 2.2, 16.8 Hz, 1H), 4.40 (d, *J* =

11.7 Hz, 1H), 4.53 (d, *J* = 12.5 Hz, 1H), 4.61 (d, *J* = 12.1 Hz, 1H), 4.62 (d, *J* = 12.5 Hz, 1H), 4.65 (d, *J* = 3.5 Hz, 1H), 4.70 (d, *J* = 11.5 Hz, 1H), 4.71 (d, *J* = 12.1 Hz, 1H), 5.15 (d, *J* = 11.5 Hz, 1H), 5.27 (s, 1H), 5.60 (s, 1H), 7.16-7.49 (m, 25H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 55.4, 58.5, 65.0, 68.7, 69.0, 69.6, 73.2, 73.3, 73.6, 74.4, 75.2, 78.1, 79.1, 80.0, 80.3, 81.5, 97.8, 101.4, 101.5, 126.1, 127.0, 127.3, 127.4, 127.5, 127.6, 127.7, 128.0, 128.1, 128.2, 128.3, 128.5, 128.9, 137.6, 137.8, 138.0, 138.3, 138.7; ESIHRMS Calcd for $C_{51}H_{54}O_{11}[M+Na]^+$: 865.3564. Found 865.3569.

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-[4,6-*O*-benzylidene-2,3-di-*O*-(prop-2-ynyl)-β-D-mannopyranosyl]-(1→4)-α-D-glucopyranoside (40β).

$[\alpha]^{24}_D$ - 0.7 (*c*, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ : 2.41-2.43 (m, 2H), 3.05-3.10 (m, 1H), 3.40 (s, 3H), 3.51-3.60 (m, 3H), 3.69 (dd, *J* = 1.4, 10.5 Hz, 1H), 3.74-3.80 (m, 2H), 3.89 (dd, *J* = 6.3, 9.0 Hz, 1H), 3.96 (t, *J* = 9.5 Hz, 1H), 4.0 (dd, *J* = 4.8, 10.4 Hz, 1H), 4.35 (dd, *J* = 2.4, 15.9 Hz, 1H), 4.42 (dd, *J* = 2.4, 15.9 Hz, 1H), 4.45 (dd, *J* = 2.5, 15.8 Hz, 1H), 4.46 (d, *J* = 12.0 Hz, 1H), 4.51 (dd, *J* = 2.5, 15.8 Hz, 1H), 4.54 (s, 1H), 4.62 (d, *J* = 3.7 Hz, 1H), 4.66 (d, *J* = 12.2 Hz, 1H), 4.74 (d, *J* = 12.0 Hz, 1H), 4.82 (d, *J* = 12.2 Hz, 1H), 4.85 (d, *J* = 10.7 Hz, 1H), 5.03 (d, *J* = 10.7 Hz, 1H), 5.46 (s, 1H), 7.26-7.45 (m, 20H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 55.4, 58.3, 60.0, 60.4, 67.0, 68.5, 68.6, 69.6, 73.6, 73.7, 74.6, 74.8, 75.2, 76.4, 76.8, 77.7, 78.4, 79.2, 80.0, 80.04, 80.2, 98.4, 101.4, 101.5, 126.0, 127.3, 127.7, 127.8, 128.0, 128.1, 128.16, 128.2, 128.4, 128.7, 128.9, 137.4, 137.7, 138.3, 139.4. ESIHRMS Calcd for $C_{47}H_{50}O_{11}[M+Na]^+$: 813.3251 Found 813.3229.

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-[4,6-*O*-benzylidene-2,3-di-*O*-(prop-2-ynyl)-α-D-mannopyranosyl]-(1→4)-α-D-glucopyranoside (40α).

$[\alpha]^{22}_{D}$ + 33.4 (*c*, 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.25 (t, *J* = 2.5 Hz, 1H), 2.40 (t, *J* = 2.5 Hz, 1H), 3.40 (s, 3H), 3.58 (dd, *J* = 3.5, 9.5 Hz, 1H), 3.70-3.80 (m, 4H), 3.84-3.88 (m, 2H), 3.91-3.98 (m, 3H), 4.0-4.07 (m, 4H), 4.32 (dd, *J* = 2.5, 16.0 Hz, 1H), 4.39 (dd, *J* = 2.5, 16.0 Hz, 1H), 4.53 (d, *J* = 12.0 Hz, 1H), 4.59 (d, *J* = 12.0 Hz, 1H), 4.62 (d, *J* = 12.0 Hz, 1H), 4.63 (d, *J* = 3.5 Hz, 1H), 4.70 (d, *J* = 12.5 Hz, 1H), 4.77 (d, *J* = 11.5 Hz, 1H), 5.12 (d, *J* = 11.0 Hz, 1H), 5.30 (d, *J* = 1.5 Hz, 1H), 5.55 (s, 1H), 7.25-7.39 (m, 18H), 7.45-7.47 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 55.4, 58.8, 58.9, 64.9, 68.7, 68.9, 69.6, 73.3, 73.6, 74.6, 74.7, 74.9, 75.3, 77.1, 77.2, 79.0, 79.6, 80.0, 80.1, 81.5, 97.8, 101.3, 101.6, 126.1, 127.2, 127.5, 127.6, 127.7, 128.0, 128.19, 128.2, 128.4, 128.5, 128.9, 137.5, 137.8, 137.9, 138.6. ESIHRMS Calcd for $C_{47}H_{50}O_{11}[M+Na]^+$: 813.3251 Found 813.3235.

Methyl 2,3,6-tri-*O*-benzyl-6-*O*-[4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-benzyl-β-D-mannopyranosyl]-(1→6)-α-D-glucopyranoside (45β).

$[\alpha]^{27}_{D}$ + 10.4 (*c*, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ : 2.48 (t, *J* = 2.3 Hz, 1H), 3.20-3.25 (m, 1H), 3.37 (s, 3H), 3.47-3.52 (m, 3H), 3.55 (dd, *J* = 3.0, 9.9 Hz, 1H), 3.77 (dd, *J* = 4.3, 10.0 Hz, 1H), 3.89 (t, *J* = 10.3 Hz, 1H), 4.0-4.13 (m, 4H), 4.15 (s, 1H), 4.28 (dd, *J* = 4.8, 10.5 Hz, 1H), 4.47 (dd, *J* = 2.3, 15.9 Hz, 1H), 4.55 (dd, *J* = 2.3, 15.9 Hz, 1H), 4.57 (d, *J* = 3.3 Hz, 1H), 4.61 (d, *J* = 11.5 Hz, 1H), 4.67 (d, *J* = 12.0 Hz, 1H), 4.76-4.87 (m, 4H), 4.90 (d, *J* = 11.5 Hz, 1H), 5.01 (d, *J* = 10.8 Hz, 1H), 5.58 (s, 1H), 7.28-7.44 (m, 25H; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 55.1, 59.8, 67.4, 68.4, 69.6, 72.4, 73.4, 74.8,

75.0, 75.8, 76.8, 77.4, 78.4, 79.8, 80.3, 82.2, 97.8, 101.4, 101.7, 126.0, 127.7, 127.9, 128.0, 128.2, 128.3, 128.4, 128.5, 128.9, 137.5, 138.0, 138.2, 138.4, 138.7. ESIHRMS Calcd for $C_{51}H_{54}O_{11}[M+Na]^+$: 865.3564 Found 865.3549.

Methyl 4-*O*-[4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-benzyl-β-D-mannopyranosyl]-(1→4)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (46β).

$[\alpha]^{27}_D$ - 55.0 (*c*, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ : 1.32 (d, *J* = 5.8 Hz, 3H), 1.34 and 1.50 (2s, 6H), 2.47 (t, *J* = 2.3 Hz, 1H), 3.28-3.33 (m, 1H), 3.38 (s, 3H), 3.63-3.67 (m, 3H), 3.94 (t, *J* = 10.3 Hz, 1H), 4.09 (d, *J* = 5.5 Hz, 1H), 4.12 (t, *J* = 9.6 Hz, 1H), 4.16-4.19 (m, 2H), 4.26 (dd, *J* = 4.9, 10.4 Hz, 1H), 4.52 (dd, *J* = 2.3, 15.9 Hz, 1H), 4.56 (dd, *J* = 2.3, 15.9 Hz, 1H), 4.82 (s, 1H), 4.86 (s, 1H), 5.02 (s, 1H), 5.59 (s, 1H), 7.26 - 7.42 (m, 8H), 7.49-7.50 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 17.6, 26.4, 27.8, 54.9, 59.9, 64.0, 67.5, 68.5, 72.2, 74.7, 75.6, 76.1, 77.7, 78.2, 78.5, 80.2, 97.8, 99.7, 101.4, 109.4, 125.9, 127.5, 127.6, 128.2, 128.3, 128.8, 137.5, 138.3. ESIHRMS Calcd for $C_{33}H_{40}O_{10}[M+Na]^+$: 619.2519 Found 619.2487.

1,6-Anhydro-4-*O*-[4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-benzyl-β-D-mannopyranosyl]-(1→4)-2,3-*O*-isopropylidene-β-D-mannopyranose (47β).

$[\alpha]^{28}_D$ - 59.0 (*c*, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ : 1.32, 1.54 (2s, 6H), 2.50 (t, *J* = 2.4 Hz, 1H), 3.32-3.37(m, 1H), 3.65 (dd, *J* = 3.0, 10.5 Hz, 1H), 3.77 (t, *J* = 6.0 Hz, 1H), 3.92 (t, *J* = 10.0 Hz, 1H), 3.98 (dd, *J* = 1.2, 7.3 Hz, 1H), 4.06-4.07 (m, 2H), 4.15 (t, *J* = 9.6 Hz, 1H), 4.20 (d, *J* = 3.0 Hz, 1H), 4.31 (dd, *J* = 4.9, 10.5 Hz, 1H), 4.37 (d, *J* = 6.4 Hz, 1H), 4.56 (dd, *J* = 2.4, 16.1 Hz, 1H), 4.58-4.59 (m, 1H), 4.62 (dd, *J* = 2.4, 16.1 Hz,

1H), 4.73 (s, 1H), 4.82 (d, *J* = 12.6 Hz, 1H), 4.85 (d, *J* = 12.6 Hz, 1H), 5.36 (d, *J* = 2.8 Hz, 1H), 5.60 (s, 1H), 7.32-7.42 (m, 8H), 7.48-7.50 (m, 2H);^{13}C NMR (125 MHz, $CDCl_3$) δ : 25.8, 25.9, 60.4, 64.3, 67.7, 68.4, 72.1, 72.5, 72.6, 74.8, 75.0, 75.3, 75.7, 76.9, 78.2, 80.0, 99.4, 99.9, 101.5, 109.9, 126.0, 127.7, 128.2, 128.4, 129.0, 137.3, 138.1. ESIHRMS Calcd for $C_{32}H_{36}O_{10}[M+Na]^+$: 603.2206. Found 603.21951.

3-*O*-[4,6-*O*-Benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-benzyl-β-D-mannopyranosyl]-(1→3)-1,2:5,6-di-*O*-isopropylidene-*α*-D-glucofuranose (48β).

$[\alpha]^{27}_D$ - 19.7 (*c*, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ : 1.32 ,1.37, 1.44, 1.50 (4s, 12H), 2.49 (t, *J* = 2.5 Hz, 1H), 3.32 (dt, *J* = 4.5, 9.5 Hz, 1H), 3.65 (dd, *J* = 3.0, 9.5 Hz, 1H), 3.90 (t, *J* = 10.0 Hz, 1H), 4.05 (dd, *J* = 5.5, 8.0 Hz, 1H), 4.09 (d, *J* = 2.5 Hz, 1H), 4.14 (t, *J* = 10.0 Hz, 1H), 4.16-4.19 (m, 1H), 4.28-4.31 (m, 2H), 4.36-4.39 (m, 2H), 4.48 (dd, *J* = 2.5, 16.0 Hz, 1H), 4.54 (d, *J* = 4.0 Hz, 1H), 4.57 (dd, *J* = 2.5, 16.0 Hz, 1H), 4.59 (s, 1H), 4.77 (d, *J* = 2.5 Hz, 1H), 4.85 (d, *J* = 12.5 Hz, 1H), 5.60 (s, 1H), 5.92 (d, *J* = 6.0 Hz, 1H), 7.26-7.40 (m, 8H), 7.45-7.50 (m, 2H);^{13}C NMR (125 MHz, $CDCl_3$) δ : 25.5, 26.3, 26.6, 26.8, 59.9, 66.1, 67.7, 68.4, 72.8, 73.5, 75.1, 75.2, 77.7, 78.5, 79.9, 80.4, 80.6, 82.7, 99.6, 101.4, 105.1, 108.5, 112.0, 126.0, 127.7, 127.8, 128.3, 128.4, 129.0, 137.4, 138.2. ESIHRMS Calcd for $C_{35}H_{42}O_{11}[M+Na]^+$: 661.2625. Found 661.26099.

6-*O*-[4,6-*O*-Benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-benzyl-β-D-mannopyranosyl]-(1→6)-1,2:3,4-di-*O*-isopropylidene-*α*-D-galactopyranose (49β).

$[\alpha]^{29}_D$ - 71.8 (*c*, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ : 1.35, 1.37, 1.45, 1.55 (4s, 12H), 2.50 (t, *J* = 2.5 Hz, 1H), 3.28-3.33 (m, 1H), 3.61 (dd, *J* = 3.0, 10.0 Hz, 1H), 3.64 (dd, *J* = 8.0, 11.0 Hz, 1H), 3.89 (t, *J* = 10.0 Hz, 1H), 4.0 (d, *J* = 8.0 Hz, 1H), 4.11 (t, *J* =

9.5 Hz, 1H), 4.13 (dd, *J* = 2.5, 10.5 Hz, 1H), 4.19 (dd, *J* = 1.5, 8.0 Hz, 1H), 4.21 (d, *J* = 3.0 Hz, 1H), 4.29 (dd, *J* = 5.0, 11.0 Hz, 1H), 4.32 (dd, *J* = 2.5, 5.0 Hz, 1H), 4.53 (dd, *J* = 2.5, 16.0 Hz, 1H), 4.57 (dd, *J* = 2.5, 16.0 Hz, 1H), 4.58 (s, 1H), 4.60 (dd, *J* = 2.5, 8.0 Hz, 1H), 5.54 (d, *J* = 5.0 Hz, 1H), 5.58 (s, 1H), 7.26-7.36 (m, 8H), 7.49-7.50 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 24.4, 25.0, 25.9, 26.0, 60.3, 67.4, 68.0, 68.5, 70.0, 70.5, 70.7, 71.6, 72.5, 74.9, 75.6, 76.9, 78.4, 80.2, 96.3, 101.4, 102.2, 108.8, 109.5, 126.0, 127.6, 127.7, 128.4, 128.8, 137.6, 138.2. ESIHRMS Calcd for $C_{35}H_{42}O_{11}[M+Na]^+$: 661.2625. Found 661.2614.

General procedure for deprotection of propargyl ethers

To a stirred solution of propargyl ether (1 mmol) in dry THF (5 mL) was added KO^{t}Bu (1.1 mmol), stirring was continued at room temperature for 3-12 h untill TLC indicated completion. The reaction mixture was diluted with CH_2Cl_2 (10 mL). The organic phase was separated, washed with water, dried (Na_2SO_4) and concentrated on a rotary evaporator to give the allenyl ethers in quantitative yields. A homogeneous solution of allenyl ethers (1 mmol) in acetone: water (4:1, 5 mL) was treated with OsO_4 (0.1 mmol) and *N*-methyl morpholine *N*-oxide (2 mmol) and the mixture was stirred for 3 h at room temperature. After completion of the reaction, acetone was removed under vaccum and the residue was dissolved in CH_2Cl_2 (10 mL) and washed with sat. $NaHSO_3$. The organic phase was separated, dried (Na_2SO_4), and concentrated on a rotary evaporator. The residues were purified by flash or radial chromatography on silica gel to yield deprotected di and tri saccharides in 80-91%.

3β-Cholestanyl 4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl-β-D-mannopyranoside (50).

Following the general procedure compound **24β** was isomerized to corresponding allene after stirring 3 h at room temperature.$[\alpha]^{27}_{D}$ – 18.9 (*c*, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.07 and 0.1 (2s, 6H), 0.51-0.61 (m, 1H), 0.65 (s, 3H), 0.8 (s, 3H), 0.86-1.7 (m, 36H), 1.78-1.8 (m, 1H), 1.86-1.9 (m, 1H), 1.93-1.98 (m, 1H), 3.32-3.35 (m, 1H), 3.68-3.74 (m, 1H), 3.82-3.88 (m, 3H), 3.92 (d, *J* = 1.4 Hz, 1H), 4.32 (dd, *J* = 5.0, 10.5 Hz, 1H), 4.7 (s, 1H), 5.53 (s, 1H) 7.33-7.38 (m, 3H), 7.46-7.48 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: -5.07, -4.3, 12.1, 12.2, 18.1, 18.7, 21.2, 22.6, 22.8, 23.8, 24.2, 25.7, 25.8, 28.0, 28.2, 28.9, 29.1, 32.1, 34.1, 35.4, 35.6, 35.8, 36.2, 37.0, 39.5, 40.0, 42.6, 44.7, 54.4, 56.2, 56.5, 66.7, 68.6, 72.2, 72.6, 77.8, 78.6, 97.9, 101.7, 126.0, 128.1, 128.8, 137.4. EIHRMS Calcd for $C_{46}H_{76}O_6Si$ $[M]^+$: 751.5333. Found 751.5311.

Methyl 4-*O*-(4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl-β-D-mannopyranosyl)-(1→4)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (51).

Following the general procedure compound **25β** was isomerized to corresponding allene after stirring 3 h at room temperature $[\alpha]^{24}_{D}$ - 68.8 (*c*, 10, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ : 0.07 and 0.1 (2s, 6H), 0.9 (s, 9H), 1.32 (d, *J* = 5.7 Hz, 3H), 1.36 (s, 3H), 1.54 (s, 3H), 2.6 (br.s, 1H), 3.31-3.35 (m, 1H), 3.37 (s, 1H), 3.69-3.71 (m, 2H), 3.84-3.91 (m, 3H), 4.0 (d, *J* = 3.1 Hz, 1H), 4.1 (d, *J* = 5.5 Hz, 1H), 4.22-4.25 (m, 1H), 4.29 (dd, *J* = 4.9, 10.4 Hz,1H), 4.86 (s, 1H), 5.1 (s, 1H), 5.5 (s, 1H), 7.34-7.38 (m, 3H), 7.48-7.49 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ:-5.0, -4.3, 17.5, 18.1, 25.7, 26.4, 27.8, 54.8, 63.9, 66.8,

68.6, 71.9, 72.0, 76.2, 77.9, 78.4, 78.9, 97.8, 98.7, 101.7, 109.4, 126.0, 128.1, 128.8, 137.4. ESIHRMS Calcd for $C_{29}H_{46}O_{10}Si[M+Na]^+$: 605.2758. Found 605.2759.

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl-β-D-mannopyranosyl) (1→4)-α-D-glucopyranoside (52).

Following the general procedure compound **15β** was isomerized to corresponding allene after stirring 12 h at room temperature $[\alpha]^{25}_D$ - 10.6 (*c*, 0.5, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ : 0.03 and 0.05 (2s, 6H), 0.8 (s, 9H), 2.6 (br.s, 1H), 3.04-3.09 (m, 1H), 3.37, (s, 3H), 3.35 (dd, *J* = 3.7, 9.5 Hz, 1H), 3.57 (t, *J* = 10.3 Hz, 1H), 3.59 (dd, *J* = 3.4, 9.3 Hz, 1H), 3.64 (dd, *J* = 1.98, 10.9, Hz, 1H), 3.74 (t, *J* = 9.3 Hz, 1H), 3.76-3.79 (m, 3H), 3.97 (m, 2H), 4.09 (dd, *J* = 4.9, 10.4 Hz, 1H), 4.45 (d, *J* = 12.1 Hz, 1H), 4.59 (d, *J* = 0.96 Hz, 1H), 4.60 (d, *J* = 11.8 Hz, 1H), 4.65 (d, *J* = 12.3 Hz, 1H), 4.7 (d, *J* = 12.1 Hz, 1H), 4.80 (d, *J* = 12.2 Hz, 1H), 4.85 (d, *J* = 10.6 Hz, 1H), 5.0 (d, *J* = 10.6 Hz, 1H), 5.4 (s, 1H), 7.26-7.40 (m, 20H), ^{13}C NMR (125 MHz, $CDCl_3$) δ:-5.0, -4.3, 18.1, 25.7, 55.2, 66.6, 68.3, 68.6, 69.6, 71.7, 71.9, 73.6, 75.4, 78.5, 79.2, 80.4, 98.3, 100.5, 101.7, 126.1, 127.4, 127.7, 127.8, 127.9, 128.1, 128.2, 128.4, 128.5, 128.9, 137.4, 137.7, 138.3, 139.3 ESIHRMS Calcd for $C_{47}H_{60}O_{11}Si$ $[M+Na]^+$: 851.3803. Found 851.3799.

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

$[\alpha]^{24}_D$ - 106.7 (*c*, 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ : 2.6 (br.s, 1H), 3.17-3.20 (m, 1H), 3.21 (br.s, 1H), 3.40-3.44 (m, 2H), 3.55 (dd, *J* = 3.0, 9.7 Hz, 1H), 3.6 (s, 3H), 3.81 (t, *J* = 10.3 Hz, 1H), 3.86 (t, *J* = 10.4 Hz, 1H), 3.88 (t, *J* = 10.3 Hz, 1H), 3.97 (d, *J* =

3.1 Hz, 1H), 4.07-4.13 (m, 3H), 4.16-4.28 (m, 6H), 4.36 (dd, *J* = 4.9, 10.6 Hz, 1H), 4.51 (s, 1H), 4.62 (d, *J* = 12.6 Hz, 1H), 4.68 (d, *J* = 13.2 Hz, 2H), 4.8 (d, *J* = 12.05 Hz, 1H), 4.88 (s, 1H), 5.0 (d, *J* = 12.05 Hz, 1H), 5.47 (s, 1H), 5.53 (s, 1H), 5.57 (s, 1H), 7.20-7.49 (m, 25H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 57.3, 66.9, 67.2, 67.7, 67.9, 68.5, 68.57, 68.6, 69.1, 72.0, 74.0, 74.3, 74.7, 75.8, 76.7, 77.5, 78.4, 96.8, 98.4, 101.0, 101.4, 101.6, 101.9, 126.0, 126.1, 127.4, 127.5, 127.6, 128.1, 128.2, 128.3, 128.8, 128.9, 129.3, 136.9, 137.2, 137.6, 138.4, 138.7. ESIHRMS Calcd for $C_{60}H_{62}O_{16}$ $[M+Na]^+$: 985.3623. Found 985.3618.

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(4,6-*O*-benzylidene-3-*O*-benzyl-β-D-mannopyranosyl)-(1→4)-α-D-glucopyranoside (54).

$[\alpha]^{27}_D$ + 5.15 (*c*, 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ : 3.20-3.25 (m, 1H), 3.36 (dd, *J* = 3.2, 9.6 Hz, 1H), 3.38 (s, 3H), 3.53 (dd, *J* = 3.4, 8.9 Hz, 1H), 3.57-3.63 (m, 2H), 3.71 - 3.77 (m, 2H), 3.88 (dd, *J* = 3.2 Hz, 1H), 3.93 (qt, *J* = 8.6 Hz, 1H), 4.01 (t, *J* = 9.5 Hz, 1H), 4.08 (dd, *J* = 4.8, 10.4 Hz, 1H), 4.38 (d, *J* = 12.0 Hz, 1H), 4.52 (s, 1H), 4.60 (d, *J* = 3.6 Hz, 1H), 4.65 (d, *J* = 12.4 Hz, 1H), 4.66 (d, *J* = 12.2 Hz, 1H), 4.68 (d, *J* = 12.4 Hz, 1H), 4.76 (d, *J* = 12.3 Hz, 1H), 4.80 (d, *J* = 12.2 Hz, 1H), 4.88 (d, *J* = 10.7 Hz, 1H), 4.93 (d, *J* = 10.7 Hz, 1H), 5.52 (s, 1H), 7.26-7.49 (m, 25H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 55.3, 66.8, 68.4, 68.6, 69.4, 69.7, 72.3, 73.5, 73.6, 75.5, 78.2, 79.3, 80.4, 98.3, 100.6, 101.4, 126.0, 127.5, 127.6, 127.7, 127.8, 127.9, 128.0, 128.04, 128.1, 128.2, 128.4, 128.5, 128.9, 137.5, 137.6, 138.1, 138.2, 139.0.ESIHRMS Calcd for $C_{48}H_{52}O_{11}[M+Na]^+$: 827.3408. Found 827.3388.

Methyl 2,3,6-tri-*O*-benzyl-6-*O*-(4,6-*O*-benzylidene-3-*O*-benzyl-β-D-mannopyranosyl)-(1→6)-α-D-glucopyranoside (55).

$[\alpha]^{28}_{D}$ + 25.5 (*c*, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ : 3.20-3.26 (m, 1H), 3.35 (s, 3H), 3.45 (t, *J* = 9.5 Hz, 1H), 3.51-3.59 (m, 2H), 3.77 (ddd, *J* = 1.8, 5.0, 10.0 Hz, 1H), 3.85 (t, *J* = 10.3 Hz, 1H), 3.93 (d, *J* = 3.5 Hz, 1H), 4.00 (t, *J* = 9.3 Hz, 1H), 4.05 (dd, *J* = 1.8, 10.5 Hz, 1H), 4.12 (t, *J* = 9.5 Hz, 1H), 4.16 (s, 1H), 4.28 (dd, *J* = 5.6, 10.5 Hz, 1H), 4.56 (d, *J* = 3.5 Hz, 1H), 4.57 (d, *J* = 11.2 Hz, 1H), 4.66 (d, *J* = 12.4 Hz, 1H), 4.78 (d, *J* = 11.8 Hz, 1H), 4.80 (d, *J* = 11.2 Hz, 1H), 4.82 (d, *J* = 10.6 Hz, 1H), 4.86 (d, *J* = 12.4 Hz, 1H), 4.88 (d, *J* = 11.8 Hz, 1H), 5.01 (d, *J* = 10.6 Hz, 1H), 5.59 (s, 1H), 7.21-7.52 (m, 25);^{13}C NMR (125 MHz, $CDCl_3$) δ : 55.2, 66.9, 68.2, 68.6, 69.7, 70.0, 72.5, 73.4, 74.7, 75.8, 76.3, 77.4, 78.4, 79.8, 82.2, 97.9, 100.5, 101.5, 126.0, 127.6, 127.7, 127.8, 127.9, 128.0, 128.2, 128.3, 128.4, 128.5, 129.0, 137.4, 138.0, 138.1, 138.3, 138.7;

ESIHRMS Calcd for $C_{48}H_{52}O_{11}[M+H]^+$: 805.3588. Found 805.35791.

Methyl 4-*O*-(4,6-*O*-benzylidene-3-*O*-benzyl-β-D-mannopyranosyl)-(1→4)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (56).

$[\alpha]^{28}_{D}$ - 39.4 (*c*, 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ : 1.31 (d, *J* = 5.5 Hz, 3H), 1.34 (s, 3H), 1.51 (s, 3H), 2.50 (br.s, 1H), 3.34 (dt, *J* = 4.5, 5.5 Hz, 1H), 3.37 (s, 3H), 3.66-3.69 (m, 3H), 3.90 (t, *J* = 10.5 Hz, 1H), 4.09 (d, *J* = 5.5 Hz, 1H), 4.14 (t, *J* = 10.0 Hz, 1H), 4.16-4.20 (m, 2H), 4.29 (dd, *J* = 10.5, 4.5 Hz, 1H), 4.79 (d, *J* = 12.5 Hz, 1H), 4.85 (d, *J* =1.5 Hz, 1H), 4.86 (s, 1H), 5.02 (s, 1H), 5.61 (s, 1H), 7.26-7.50 (m, 8H), 7.51 (d, *J* = 1.5 Hz, 2H);^{13}C NMR (125 MHz, $CDCl_3$) δ : 17.6, 26.4, 27.9, 54.9, 63.9, 67.0,

68.6, 70.0, 72.4, 76.2, 78.2, 78.6, 97.8, 98.8, 101.6, 109.4, 126.1, 127.9, 128.3, 128.5, 129.0, 137.5, 138.0. ESIHRMS Calcd for $C_{30}H_{38}O_{10}[M+H]^+$: 559.2543. Found 559.2536.

1,6-Anhydro-4-*O*-(4,6-*O*-benzylidene-3-*O*-benzyl-β-D-mannopyranosyl)-(1→4)-2,3-*O*-isopropylidene-β-D-mannopyranose (57).

$[\alpha]^{27}_D$ - 36.85 (*c*, 2.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ : 1.31 and 1.53 (2s, 6H), 3.34-3.39 (m, 1H), 3.67 (dd, *J* = 3.0, 9.5 Hz, 1H), 3.77 (t, *J* = 7.0 Hz, 1H), 3.90 (t, *J* = 10.0 Hz, 1H), 3.98 (dd, *J* = 3.0, 6.5 1H), 4.11 (s, 1H), 4.14-4.19 (m, 2H), 4.32 (dd, *J* = 5.0, 10.5 Hz, 1H), 4.37 (d, *J* = 6.5 Hz, 1H), 4.58 (dd, *J* = 1.0, 6.5 Hz, 1H), 4.72 (s, 1H), 4.79 (d, *J* = 12.5 Hz, 1H), 4.86 (d, *J* = 12.5 Hz, 1H), 5.36 (d, *J* = 3.0 Hz, 1H), 5.61 (s, 1H), 7.26-7.38 (m, 8H), 7.49-7.52 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 25.8, 25.9, 64.4, 67.3, 68.5, 70.0, 72.0, 72.4, 72.6, 74.8, 75.2, 76.5, 78.2, 98.7, 99.4, 101.6, 109.9, 126.0, 127.9, 128.0, 128.3, 128.5, 129.0, 137.3, 137.8. ESIHRMS Calcd for $C_{29}H_{34}O_{10}[M+Na]^+$: 565.2050. Found 565.2037.

3-*O*-(4,6-*O*-Benzylidene-3-*O*-benzyl-β-D-mannopyranosyl)-(1→3)-1,2:5,6-di-*O*-isopropylidene-*α*-D-glucofuranose (58).

$[\alpha]^{26}_D$ - 25.4 (*c*, 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ : 1.31, 1.38, 1.45, 1.50 (4s, 12H), 2.39 (br.s, 1H), 3.38-3.42 (m, 1H), 3.68 (dd, *J* = 3.5, 9.0 Hz, 1H), 3.88 (t, *J* = 10.0, Hz, 1H), 4.03 (dd, *J* = 5.5, 8.5 Hz, 1H), 4.07 (d, *J* = 3.0 Hz, 1H), 4.15 (dd, *J* = 6.5, 8.5 Hz, 1H), 4.21 (t, *J* = 9.5 Hz, 1H), 4.27 (dd, *J* = 3.5, 6.5 Hz, 1H), 4.32 (dd, *J* = 5.0, 10.5 Hz, 1H), 4.37 (dd, *J* = 6.0, 12.0 Hz, 1H), 4.50 (d, *J* = 3.0 Hz, 1H), 4.54 (d, *J* = 4.0 Hz, 1H), 4.69 (s, 1H), 4.77 (d, *J* = 12.0 Hz, 1H), 4.86 (d, *J* = 12.0 Hz, 1H), 5.60 (s, 1H), 5.90

(d, *J* = 3.5 Hz, 1H), 7.26-7.39 (m, 8H), 7.49-7.51 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 25.5, 26.3, 26.7, 26.8, 66.7, 67.0, 69.8, 72.7, 73.1, 76.3, 78.5, 78.8, 80.6, 82.8, 98.0, 101.5, 105.1, 108.9, 112.0, 126.0, 127.8, 128.3, 128.5, 129.0, 137.4, 137.9. ESIHRMS Calcd for $C_{32}H_{40}O_{11}[M+H]^+$: 601.2649. Found 601.26340.

6-*O*-(4,6-*O*-Benzylidene-3-*O*-benzyl-β-D-mannopyranosyl)-(1→6)-1,2:3,4-di-*O*-isopropylidene-*α*-D-galactopyranose (59).

$[\alpha]^{27}_D$ - 58.8 (*c*, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ : 1.32, 1.34, 1.45, 1.53 (4s, 12H), 3.32-3.37 (m, 1H), 3.65 (dd, *J* = 3.2, 9.6 Hz, 1H), 3.76 (dd, *J* = 8.0, 11.3 Hz, 1H), 3.88 (t, *J* = 10.3 Hz, 1H), 4.02 (dt, *J* = 2.2, 7.9 Hz, 1H), 4.09 (dd, *J* = 2.8, 11.3 Hz, 1H), 4.14 (t, *J* = 9.5 Hz, 1H), 4.20 (dd, *J* = 1.9, 7.9 Hz, 1H), 4.23 (d, *J* = 3.1 Hz, 1H), 4.30-4.34 (m, 2H), 4.60 (dd, *J* = 2.4, 7.9 Hz, 1H), 4.62 (s, 1H), 4.78 (d, *J* = 12.3 Hz, 1H), 4.83 (d, *J* = 12.3 Hz, 1H), 5.55 (d, *J* = 5.0 Hz, 1H), 5.60 (s, 1H), 7.26-7.39 (m, 8H), 7.49-7.51 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 24.3, 24.9, 25.9, 26.0, 66.9, 67.9, 68.6, 69.4, 69.6, 70.3, 70.6, 71.4, 72.3, 76.5, 78.3, 96.3, 100.9, 101.5, 108.7, 109.4, 126.0, 127.8, 127.9, 128.2, 128.4, 128.9, 137.5, 137.9. ESIHRMS Calcd for $C_{32}H_{40}O_{11}[M+H]^+$: 601.2649. Found 601.26351.

Phenyl 3,4-*O*-(2,3-dimethoxybutane-2,3-diyl)-2-*O*-(prop-2-ynyl)-1-thio-β-L-rhamnopyranose (62).

To a stirred solution at 0 °C phenyl 3,4-*O*-(2,3-dimethoxybutane-2,3-diyl)-1-thio-β-L-rhamnopyranoside **61** (4.28 g, 12.4 mmol) in DMF (150 mL) was added NaH [60 % in oil] (595 mg, 24.8 mmol). After 10 min, propargyl bromide [80% wt. in PhMe, (2.06 mL, 18.6 mmol)] was added and the solution stirred for 16 h. The solution was concentrated *in vacuo*, followed by addition of saturated aqueous $NaHCO_3$ (100 mL) and EtOAc (100

mL). The aqueous portion was extracted with EtOAc (3 x 100 mL), and the combined organic extracts were dried (Na_2SO_4) and concentrated *in vacuo* to give the crude product. Purification by flash chromatography (eluting with 20 % EtOAc in Hexanes) gave phenyl 3,4-*O*-(2,3-dimethoxybutane-2,3-diyl)-2-*O*-(prop-2-ynyl)-1-thio-β-L-rhamnopyranoside **62** (4.67 g, 12.2 mmol, 98 %) as an orange oil: $[\alpha]^{25}_{D}$ - 99.57 (*c*, 2.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ : 1.26 (s, 3H), 1.28 (s, 3H), 1.33 (d, *J* = 6.5 Hz, 3H), 2.45 (t, *J* = 2.5 Hz, 1H), 3.22 (s, 3H), 3.24 (s, 3H), 3.46 (dq, *J* = 10.0, 6.5 Hz, 1H), 3.75 (dd, *J* = 3.0, 10.0 Hz, 1H), 3.83 (t, *J* = 10.0 Hz, 1H), 4.20 (t, *J* = 10.0 Hz, 1H), 4.54 (dd, *J* = 2.5, 16.0 Hz, 1H), 4.61 (dd, *J* = 2.5, 16.0 Hz, 1H), 4.84 (d, *J* = 1.0 Hz, 1H), 7.23-7.49 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ : 16.9, 17.7, 17.8, 47.7, 48.0, 59.3, 68.3, 72.7, 74.9, 75.0, 76.0, 80.0, 87.2 ($^1J_{C\text{-}H}$ = 152.5 Hz), 99.6, 99.8, 127.1, 128.8, 131.1, 135.5; ESIHRMS Calcd. for $C_{21}H_{28}O_6S$ $[M+Na]^+$: 431.1505. Found 431.1526.

Phenyl 2-*O*-(prop-2-ynyl)-1-thio-β-L-rhamnopyranoside (63).

To a stirred solution of phenyl 3,4-*O*-(2,3-dimethoxybutane-2,3-diyl)-2-*O*-(prop-2-ynyl)-1-thio-β-L-rhamnopyranoside **62** (4.00 g, 10.4 mmol) in CH_2Cl_2 (120 mL) was added a solution of trifluoroacetic acid (100 mL) in H_2O (15 mL). The solution was stirred for 20 min before neutralization with saturated aqueous $NaHCO_3$ (300 mL). The aqueous portion was extracted with CH_2Cl_2 (3 x 250 mL), and the combined organic extracts were dried (Na_2SO_4) and concentrated *in vacuo* to give the crude product. Recrystallisation (from hot Hexanes:EtOH, 5:1) gave phenyl 2-*O*-(prop-2-ynyl)-1-thio-β-L-rhamnopyranoside **63** (2.05 g, 7.0 mmol, 67 %) as a white solid: mp 178 - 179 °C; $[\alpha]^{25}_{D}$ + 133.60 (*c*, 0.25, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ : 1.39 (d, *J* = 6.0 Hz, 3H), 2.45

(br. s, 2H), 2.59 (t, *J* = 2.0 Hz, 1H), 3.31 (dq, *J* = 9.5, 6.0 Hz, 1H), 3.45 (t, *J* = 9.5 Hz, 1H), 3.53 (dd, *J* = 3.5, 9.5 Hz, 1H), 4.16 (dd, *J* = 1.0, 3.5 Hz, 1H), 4.46 (dd, *J* = 2.0, 16.0 Hz, 1H), 4.68 (dd, *J* = 2.0, 16.0 Hz, 1H), 4.82 (d, *J* = 1.0 Hz, 1H), 7.26-7.33 (m, 3H), 7.49 (d, *J* = 2.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ : 17.8, 61.1, 73.5, 75.0, 76.2, 76.3, 79.8, 80.1, 87.1 ($^1J_{C\text{-}H}$ = 152.3 Hz), 127.6, 129.0, 131.3, 134.5; ESIHRMS Calcd. for $C_{15}H_{18}O_4S$ $[M+Na]^+$: 317.0824. Found 317.0821.

Phenyl 3,4-*O*-carbonyl-2-*O*-(prop-2-ynyl)-1-thio-β-L-rhamnopyranoside (64).

To a stirred solution at 0 °C of phenyl 2-*O*-(prop-2-ynyl)-1-thio-β-L-rhamnopyranoside **63** (500 mg, 1.70 mmol) in CH_2Cl_2 (40 mL) was added DMAP (623 mg, 5.10 mmol), followed by phosgene [20% in PhMe] (990 μL, 1.87 mmol), with the resultant solution stirred for 1 h. The reaction was quenched by addition of saturated aqueous $NaHCO_3$ (20 mL), and aqueous portion was extracted with CH_2Cl_2 (3 x 30 mL). The combined organic extracts were then washed with saturated aqueous $CuSO_4$ (2 x 30 mL) then H_2O (30 mL) before being dried (Na_2SO_4) and concentrated *in vacuo* to give phenyl 3,4-*O*-carbonyl-2-*O*-(prop-2-ynyl)-1-thio-β-L-rhamnopyranoside **64** (471 mg, 1.47 mmol, 87 %) as a white solid: mp 157 - 158 °C; $[\alpha]^{25}_D$ + 64.2 (*c*, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ : 1.45 (d, *J* = 6.0 Hz, 3H), 2.58 (t, *J* = 2.5 Hz, 1H), 3.80 (dq, *J* = 9.5, 6.0 Hz, 1H), 4.27 (dd, *J* = 2.5, 11.5 Hz, 1H), 4.43 (dd, *J* = 2.5, 16.0 Hz, 1H), 4.46 (dd, *J* = 9.5, 11.5 Hz, 1H), 4.52 (dd, *J* = 2.5, 16.0 Hz, 1H), 4.64 (t, *J* = 1.5 Hz, 1H), 4.90 (d, *J* = 1.5 Hz, 1H), 7.30-7.34 (m, 3H), 7.50 (d, , *J* = 2.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ : 18.1, 59.6, 74.8, 75.1, 76.4, 77.9, 78.1, 82.3, 87.1 ($^1J_{C\text{-}H}$ = 156.1 Hz), 128.1, 129.1, 131.9, 133.4, 153.2; ESIHRMS Calcd. for $C_{16}H_{16}O_5S$ $[M+Na]^+$: 343.6016. Found 343.0622.

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2-*O*-(prop-2-ynyl-3,4-*O*-carbonyl-β-L-rhamnopyranosyl-(1→4)-α-D-glucopyranoside (65β).

$[\alpha]^{24}_{D}$ + 33.6 (*c*, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ : 1.23 (d, *J* = 6.0 Hz, 3H), 2.50 (t, *J* = 2.5 Hz, 1H), 3.40 (s, 3H), 3.49 (dd, *J* = 3.5, 9.5 Hz, 1H), 3.50-3.3.58 (m, 2H), 3.61 (dd, *J* = 4.0, 10.5 Hz, 1H), 3.70-3.80 (m, 2H), 3.95 (t, *J* = 9.0 Hz, 1H), 4.18 (dd, *J* = 9.5, 11.5 Hz, 1H), 4.28 (dd, *J* = 2.5, 15.9 Hz, 1H), 4.32 (dd, *J* = 2.5, 15.9 Hz, 1H), 4.50 (d, *J* = 12.0 Hz, 1H), 4.60 (d, *J* = 12.0 Hz, 1H), 4.65 (d, *J* = 11.0 Hz, 1H), 4.67 (d, *J* = 3.0 Hz, 1H), 4.68 (d, *J* = 12.0 Hz, 1H), 4.75 (s, 1H), 4.77 (d, *J* = 11.5 Hz, 1H), 5.10 (d, *J* = 11.5 Hz, 1H), 7.26-7.39 (m, 15H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 17.6, 55.4, 59.3, 70.6, 72.9, 73.1, 73.4, 75.5, 75.8, 76.3, 77.6, 79.1, 80.1, 80.9, 82.1, 97.7, 101.5 ($^1J_{C\text{-}H}$ = 162.4 Hz), 127.4, 127.5, 128.0, 128.1, 128.2, 128.3, 128.6, 128.8, 137.8, 138.4, 138.7, 153.8. ESIHRMS Calcd for $C_{38}H_{42}O_{11}[M+Na]^+$: 697.2625 Found 697.2612.

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2-*O*-(prop-2-ynyl-3,4-*O*-carbonyl-α-L-rhamnopyranosyl-(1→4)-α-D-glucopyranoside (65α).

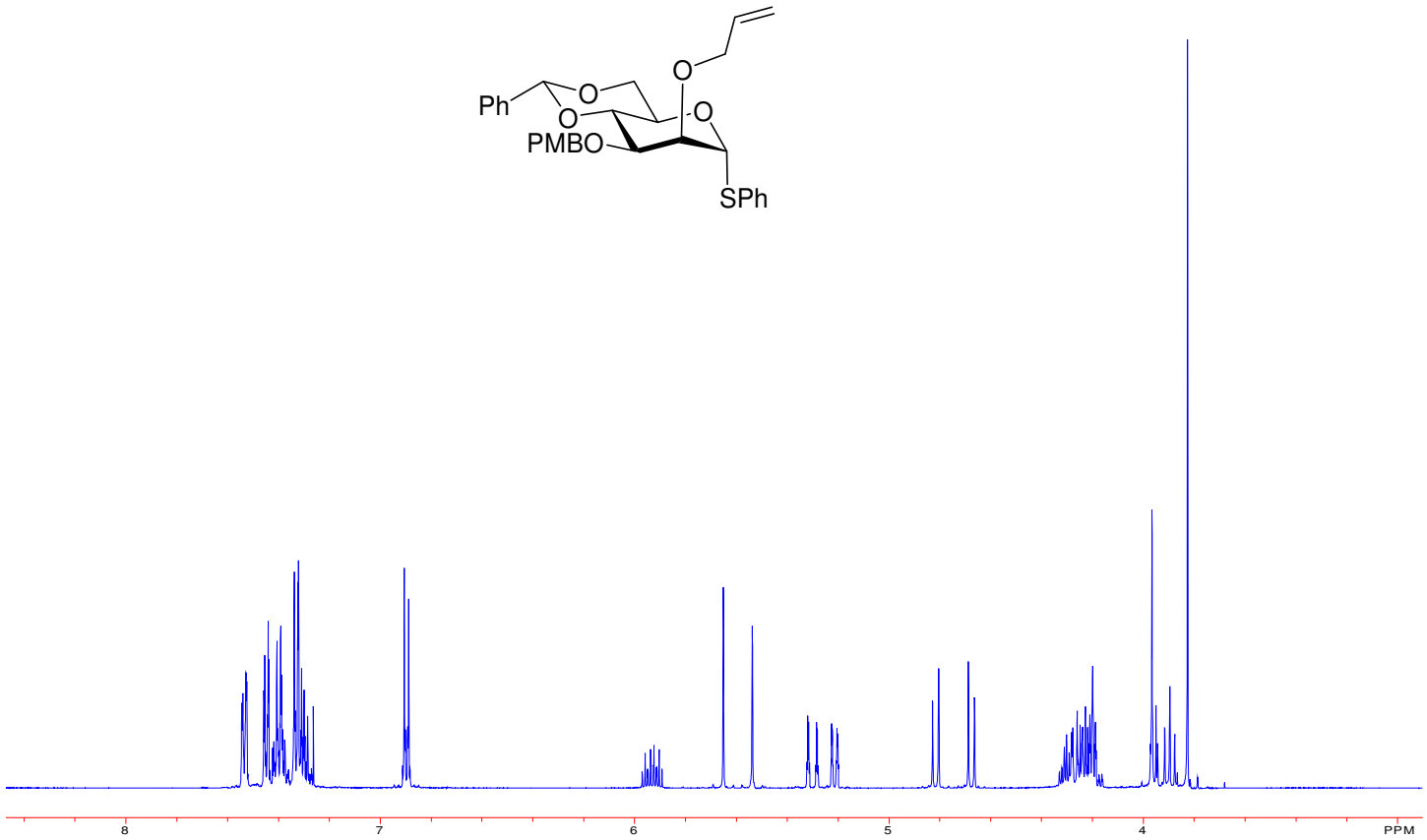
$[\alpha]^{24}_{D}$ -17.2 (*c*, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ : 0.94 (d, *J* = 6.0 Hz, 3H), 2.40 (t, *J* = 2.5 Hz, 1H), 3.37 (s, 3H), 3.60 (dd, *J* = 3.5, 9.0 Hz, 1H), 3.62-3.70 (m, 3H), 3.80-3.82 (m, 2H), 3.96-4.26 (m, 6H), 4.54 (d, *J* = 12.0 Hz, 1H), 4.58 (d, *J* = 12.0 Hz, 1H), 4.60 (d, *J* = 3.5 Hz, 1H), 4.65 (d, *J* = 11.0 Hz, 1H), 4.75 (d, *J* = 12.0 Hz, 1H), 5.03 (s, 1H), 5.10 (d, *J* = 11.0 Hz, 1H), 7.26-7.32 (m, 15H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 17.3, 55.4, 58.2, 68.7, 68.9, 69.8, 73.3, 73.7, 73.8, 73.9, 75.7, 75.8, 77.8, 78.7, 79.6, 79.8, 80.6, 97.9, 98.4 ($^1J_{C\text{-}H}$ = 174.9 Hz), 127.8, 127.89, 127.9, 128.0, 128.1, 128.3, 128.5,

128.6, 137.4, 137.8 138.3, 153.7;ESIHRMS Calcd for $C_{38}H_{42}O_{11}[M+Na]^+$: 697.2625 Found 697.2596.

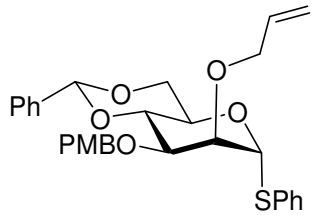
References

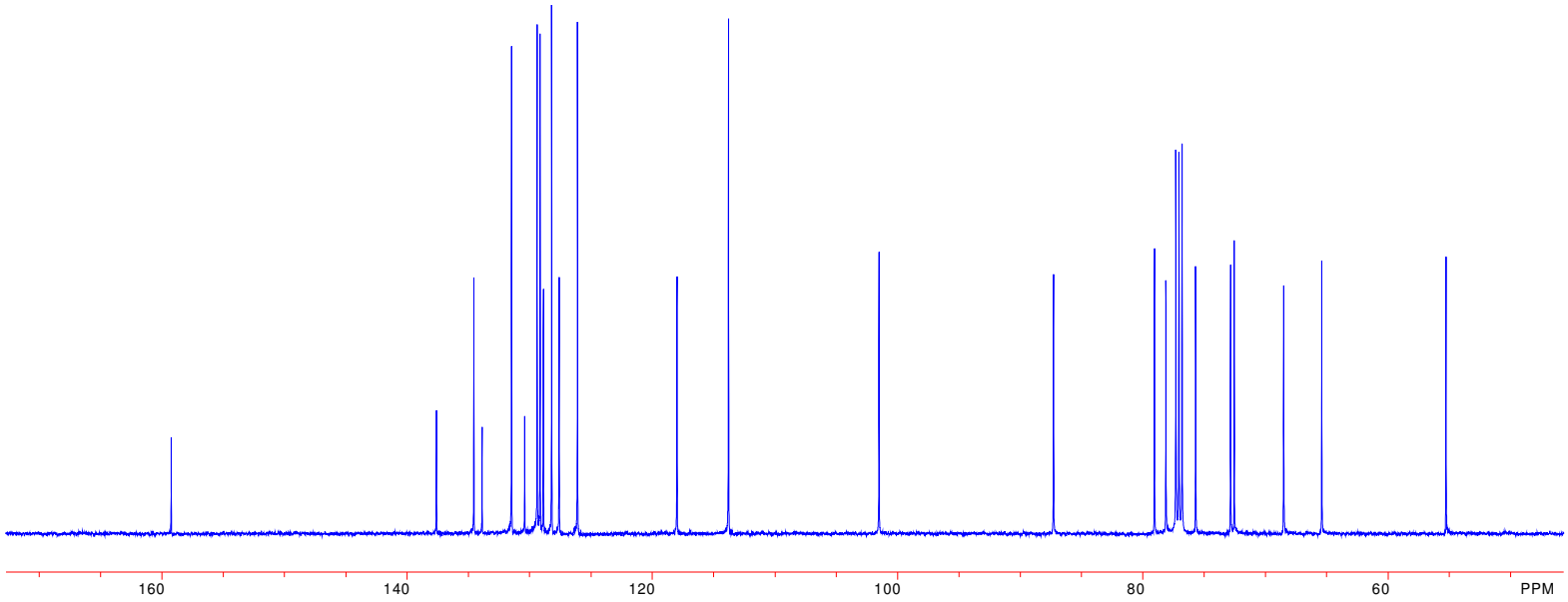
[1] Nagai, H.; Sasaki, K.; Matsumara, S.; Toshima, K. *Carbohydr. Res.* **2005**, *340*, 337.

Phenyl 4,6-*O*-benzylidene-2-*O*-allyl-3-*O*-*p*-methoxybenzyl-1-thio-α-D-mannopyranoside (8).

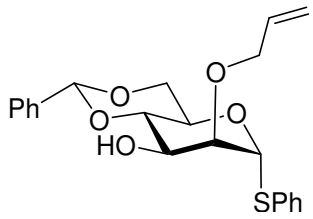


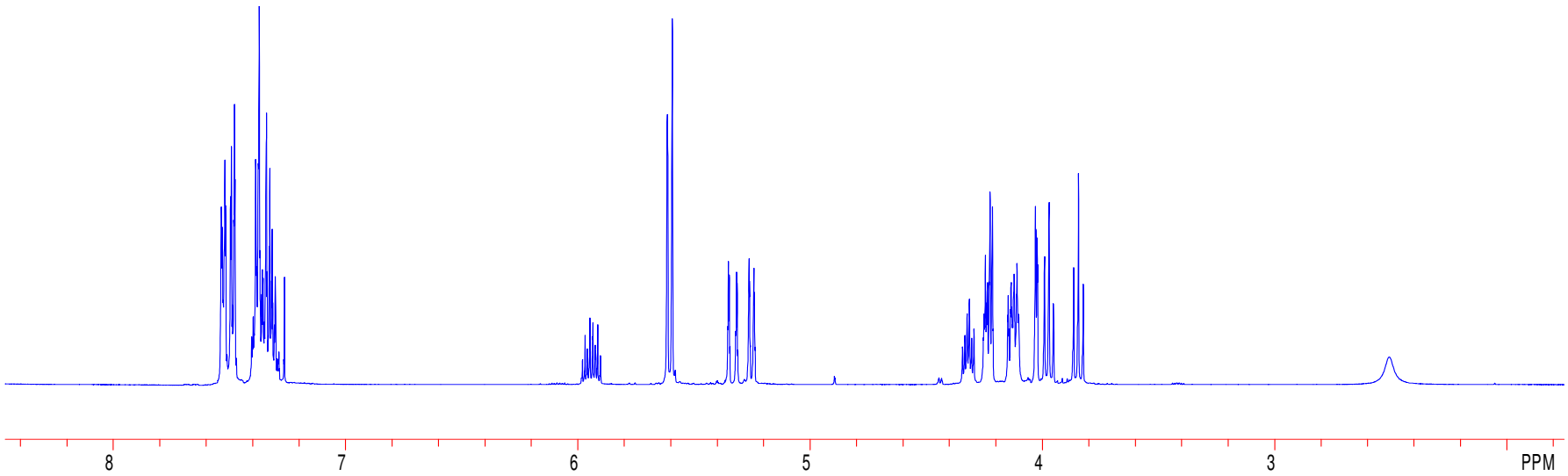
Phenyl 4,6-*O*-benzylidene-2-*O*-allyl-3-*O*-*p*-methoxybenzyl-1-thio-α-D-mannopyranoside (8).



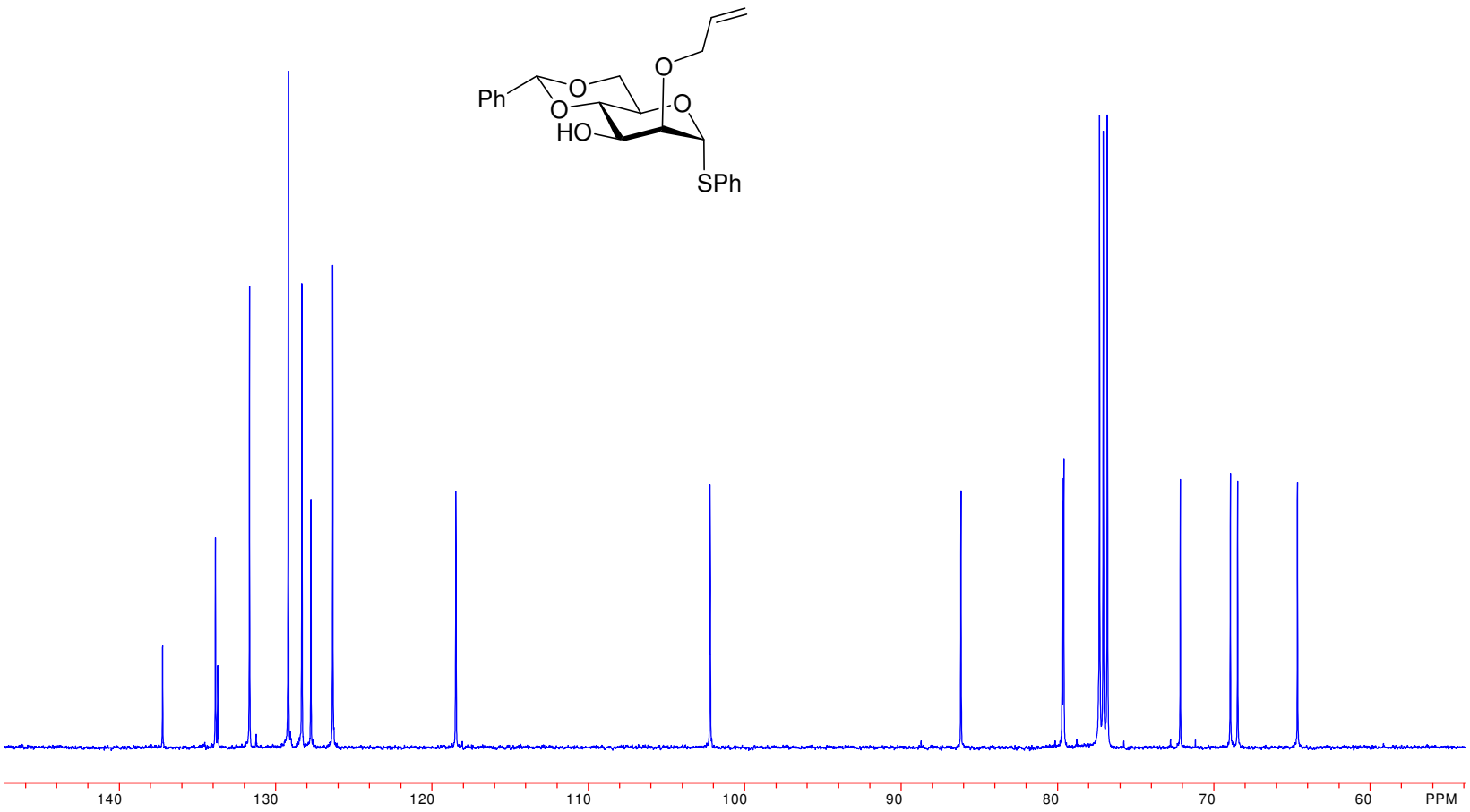


Phenyl 4,6-*O*-benzylidene-2-*O*-allyl-1-thio-α-D-mannopyranoside (9).

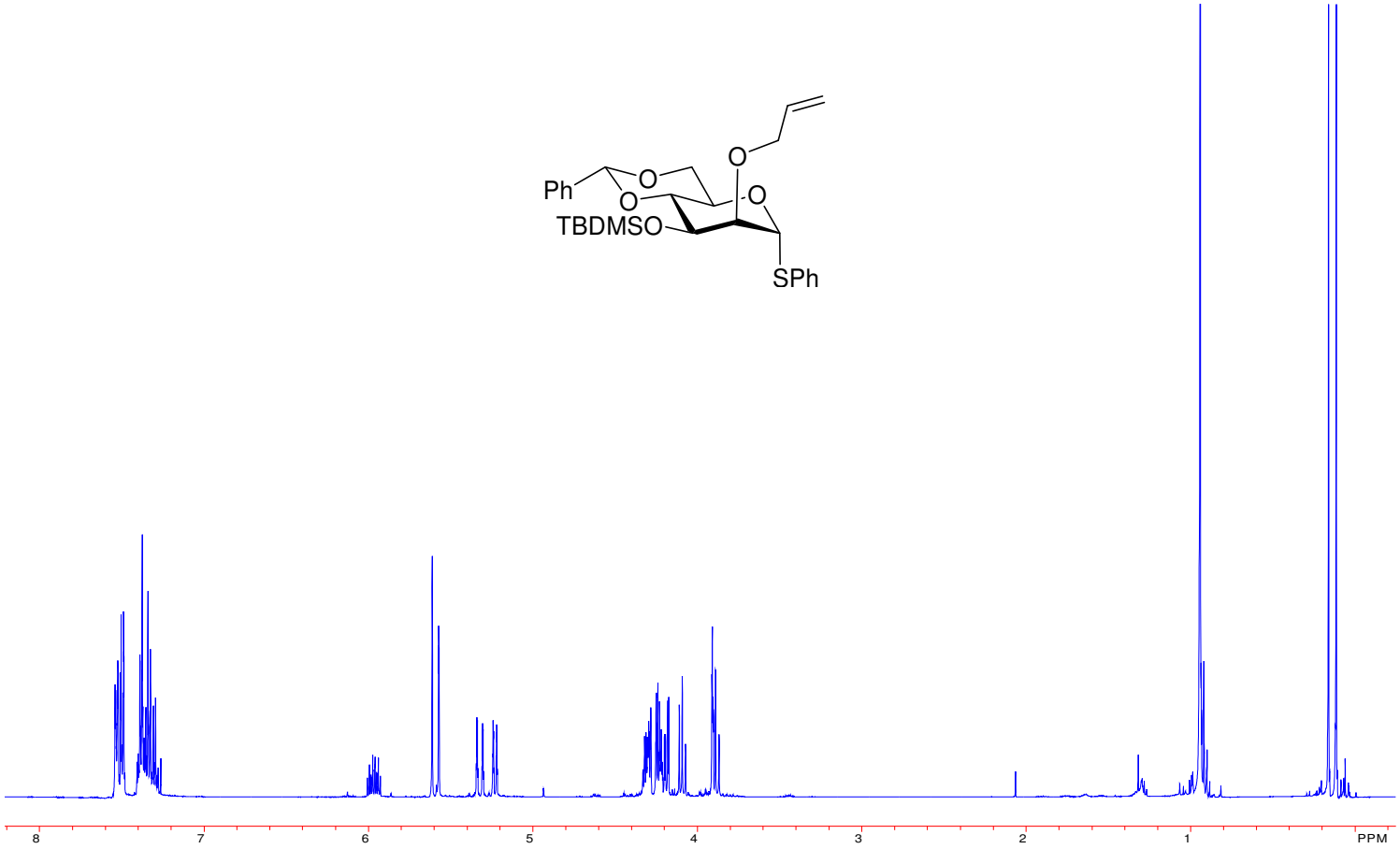




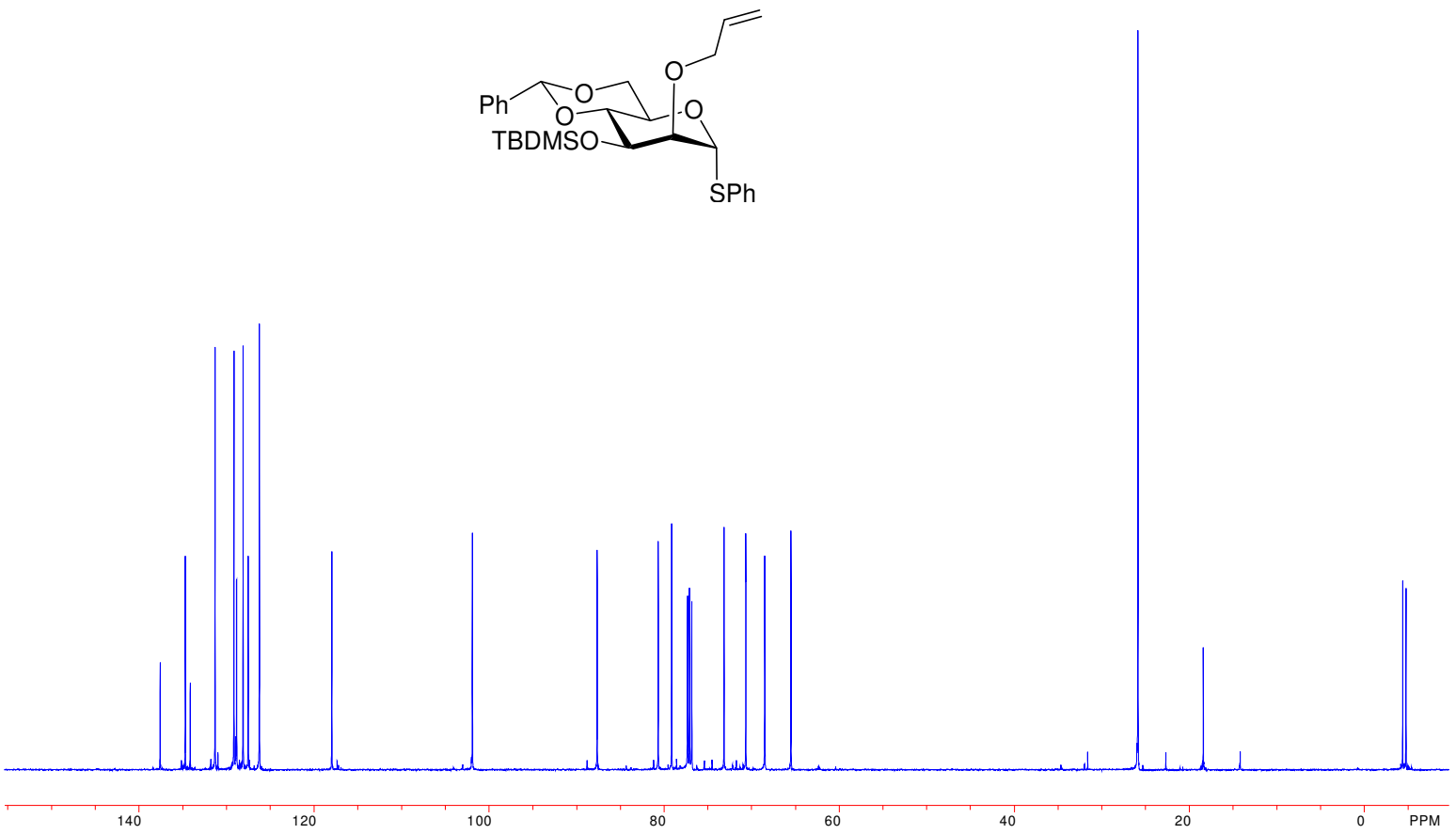
Phenyl 4,6-*O*-benzylidene-2-*O*-allyl-1-thio-α-D-mannopyranoside (9).



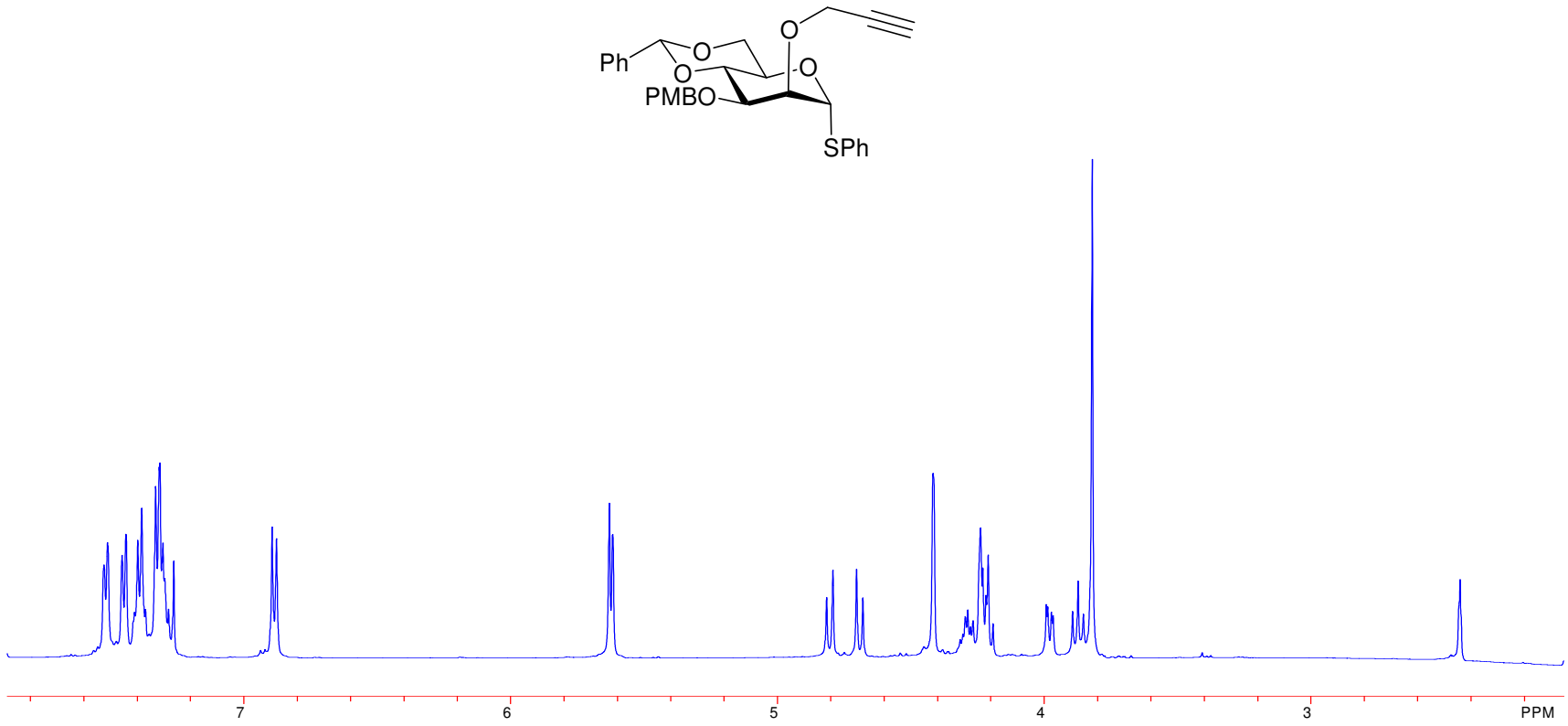
Phenyl 4,6-*O*-benzylidene-2-*O*-allyl-3-*O*-*tert*-butyldimethylsilyl-1-thio-α-D-mannopyranoside (10).



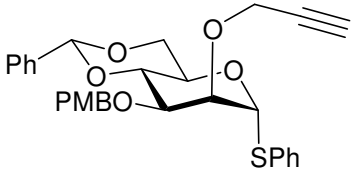
Phenyl 4,6-*O*-benzylidene-2-*O*-allyl-3-*O*-*tert*-butyldimethylsilyl-1-thio-α-D-mannopyranoside (10).



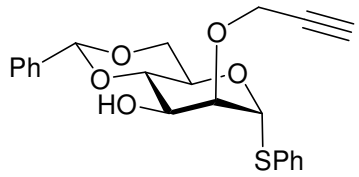
Phenyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-*p*-methoxybenzyl-1-thio-α-D-mannopyranoside (11).

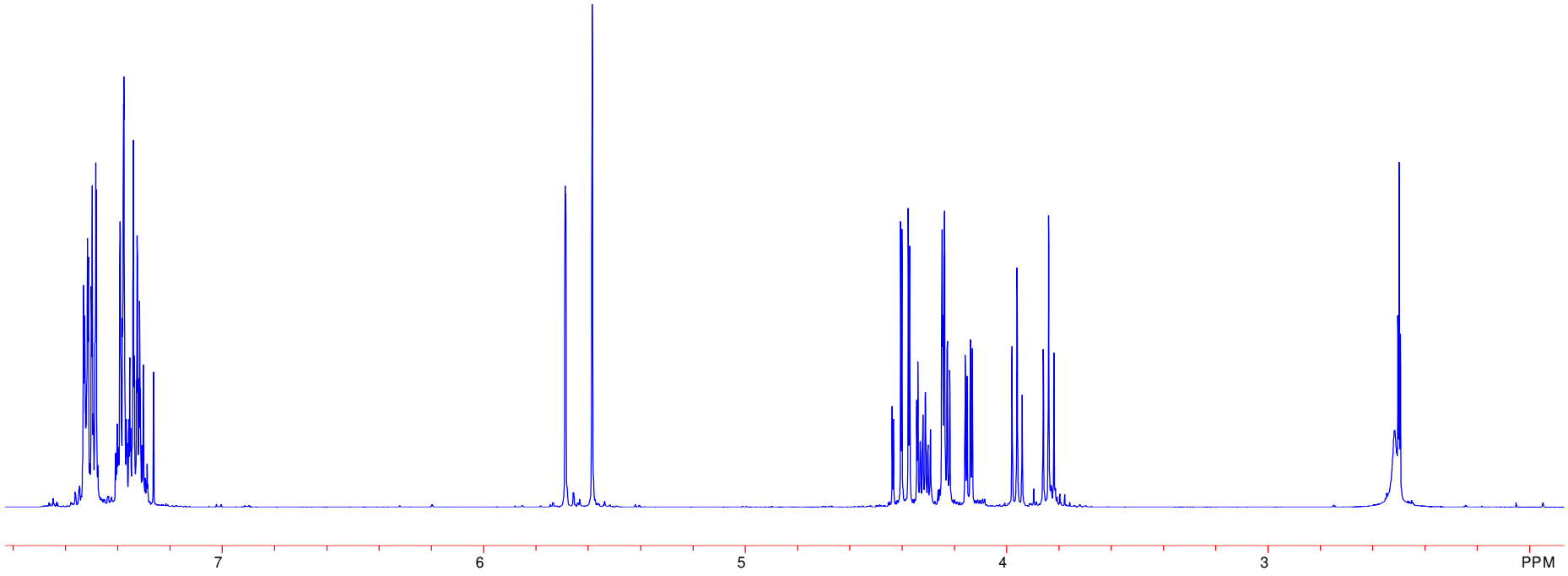


Phenyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-*p*-methoxybenzyl-1-thio-α-D-mannopyranoside (11).

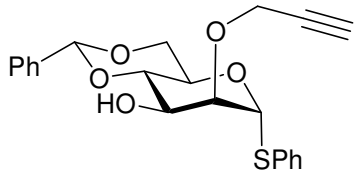


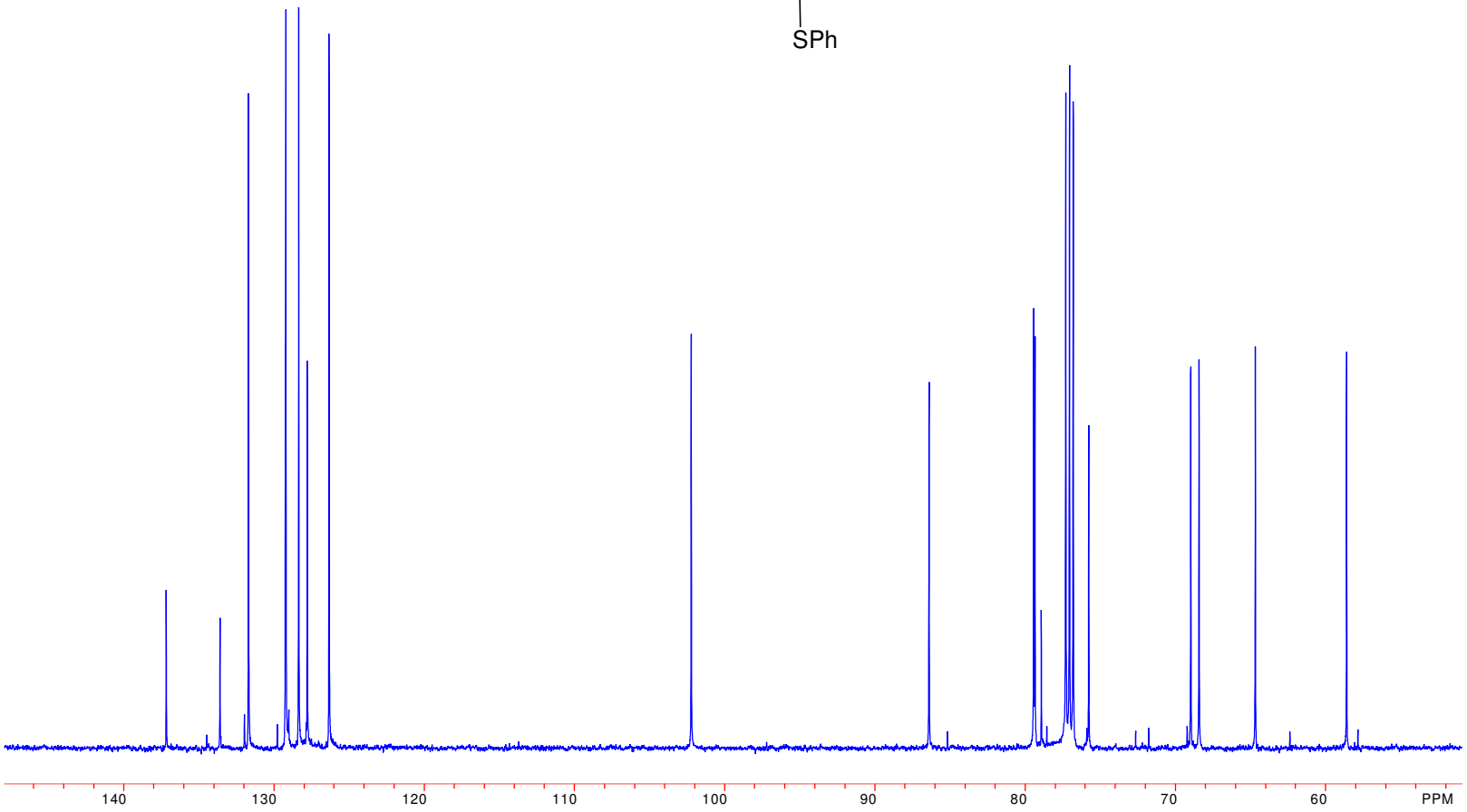
Phenyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-1-thio-α-D-mannopyranoside (12)



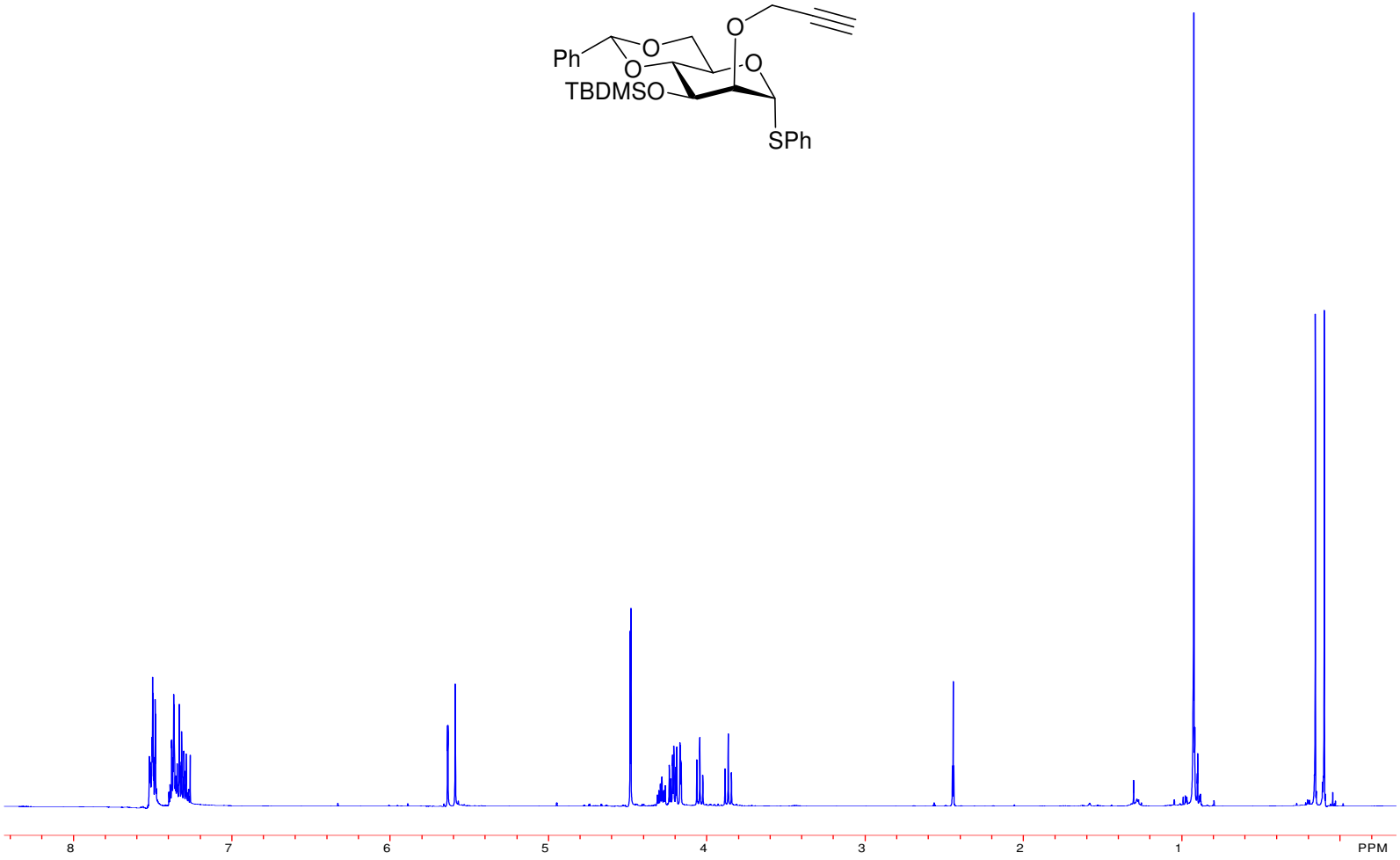


Phenyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-1-thio-α-D-mannopyranoside (12)

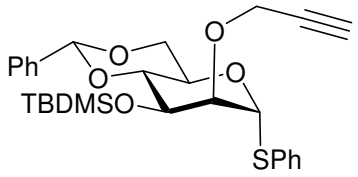




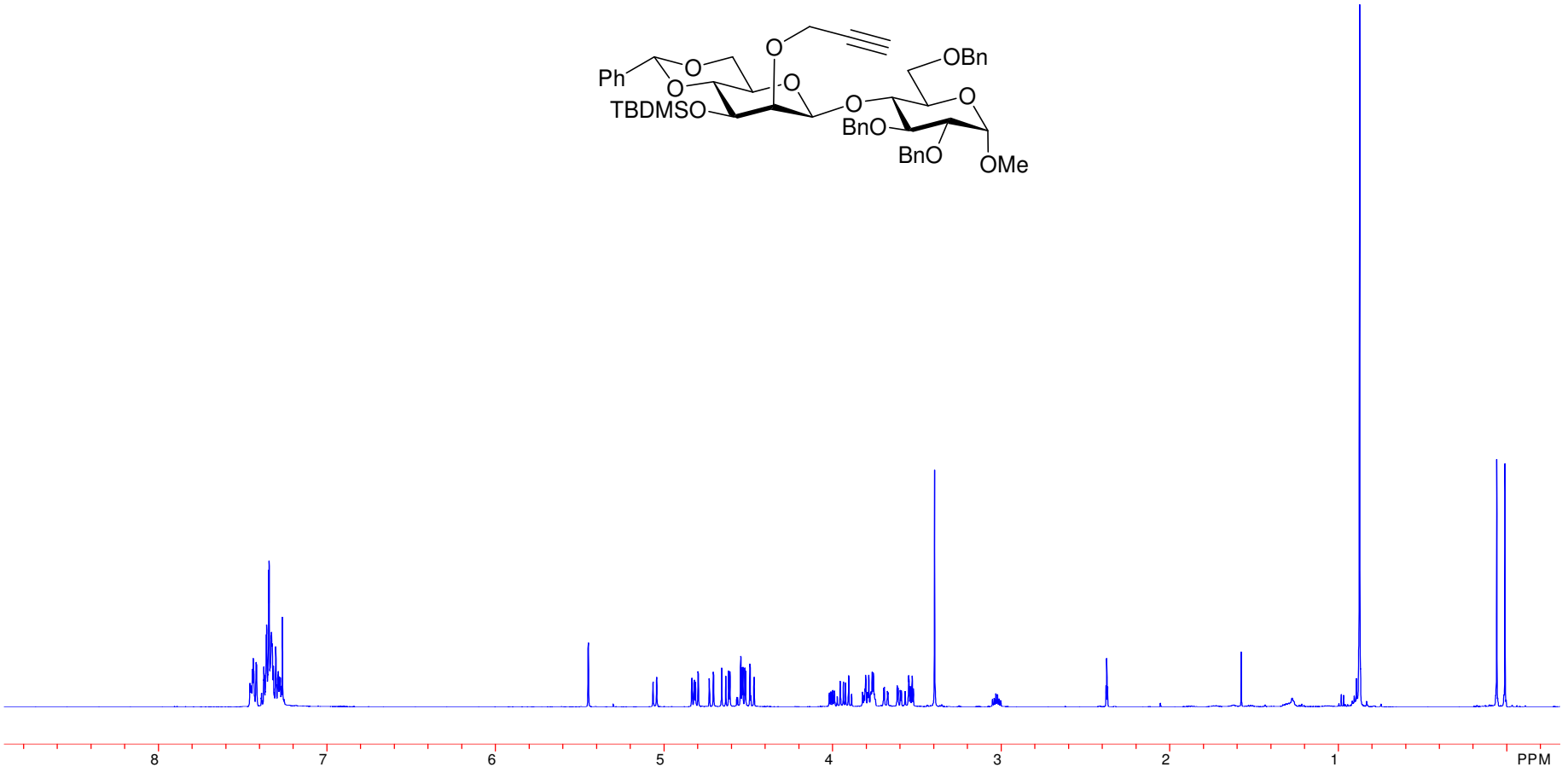
Phenyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-*tert*-butyldimethylsilyl-1-thio-α-D-mannopyranoside (13).



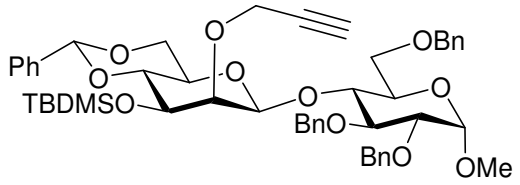
Phenyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-*tert*-butyldimethylsilyl-1-thio-α-D-mannopyranoside (13).

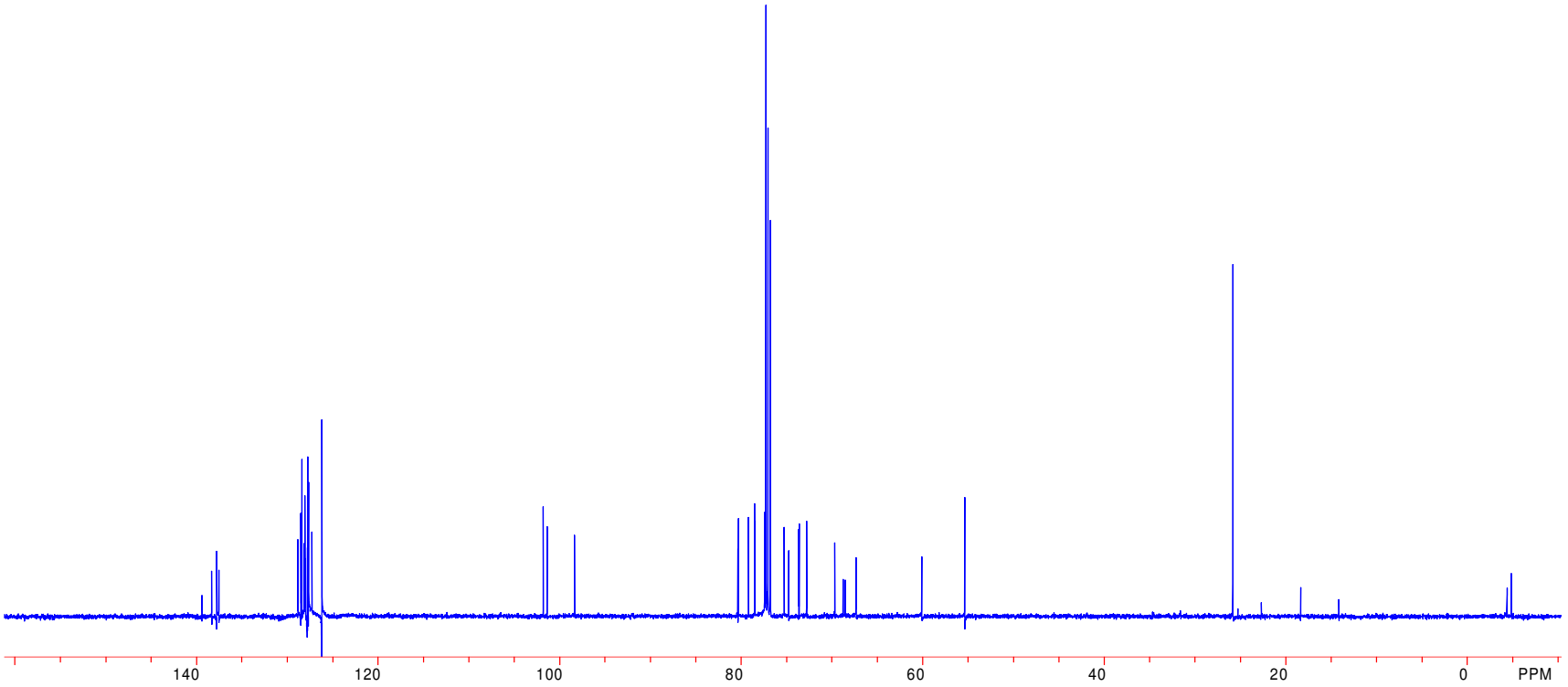


Methyl 2,3,6-tri-*O*-benzyl-4-*O*-[4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-*tert*-butyldimethylsilyl-β-D-mannopyranosyl]-(1→4)-α-D-glucopyranoside (15β).

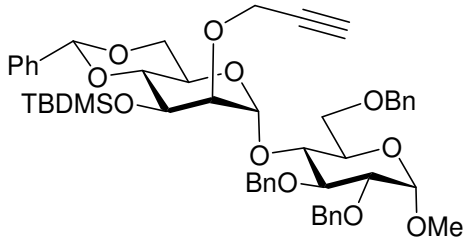


Methyl 2,3,6-tri-*O*-benzyl-4-*O*-[4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-*tert*-butyldimethylsilyl-β-D-mannopyranosyl]-(1→4)-α-D-glucopyranoside (15β).

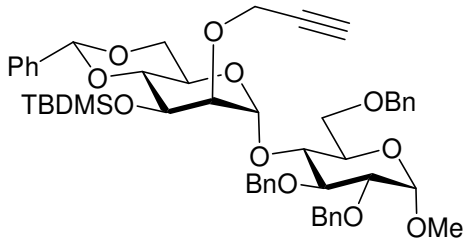


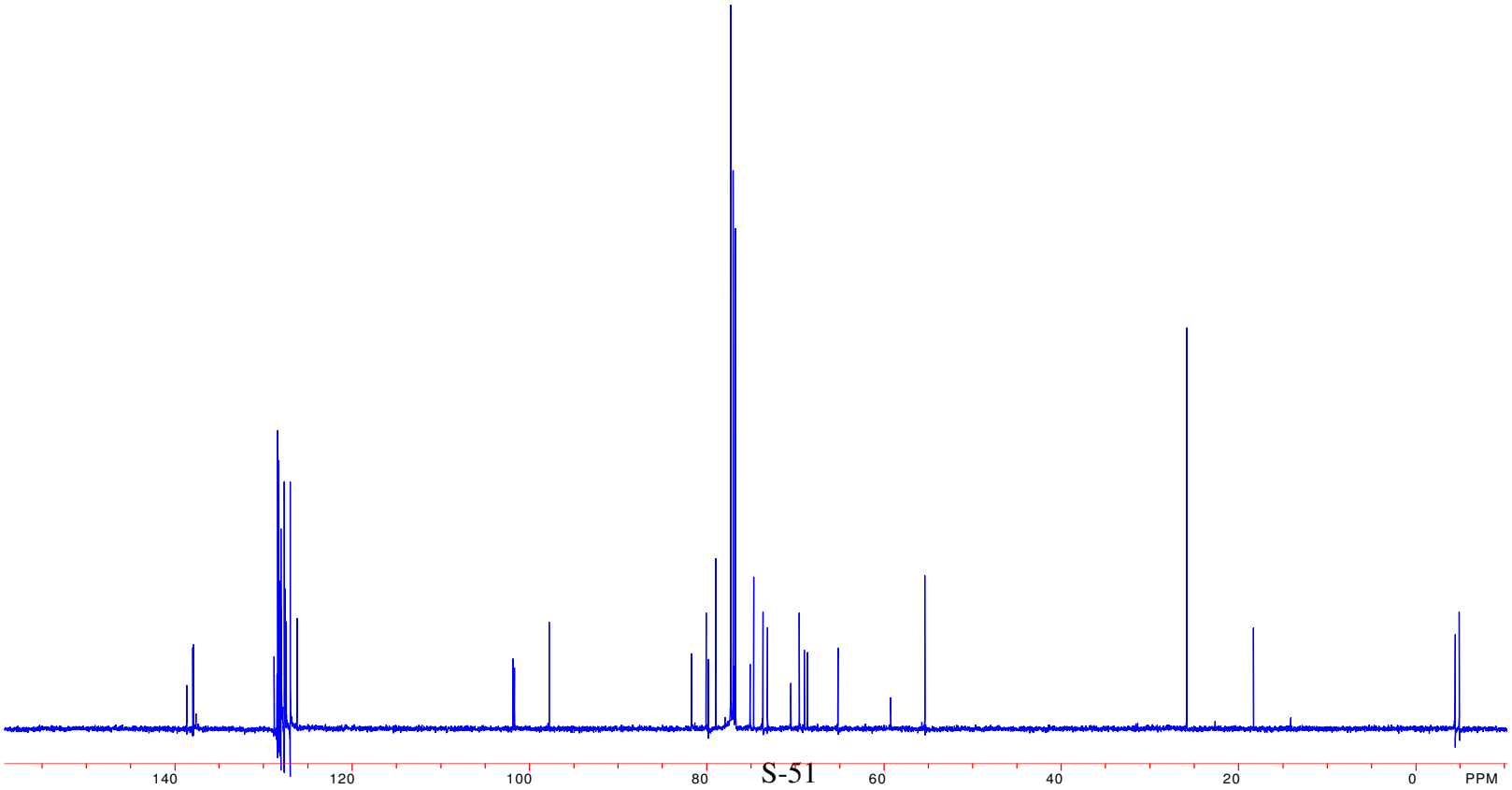


Methyl 2,3,6-tri-*O*-benzyl-4-*O*-[4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-*tert*-butyldimethylsilyl-α-D-mannopyranosyl](1→4)-α-D-glucopyranoside (15α).

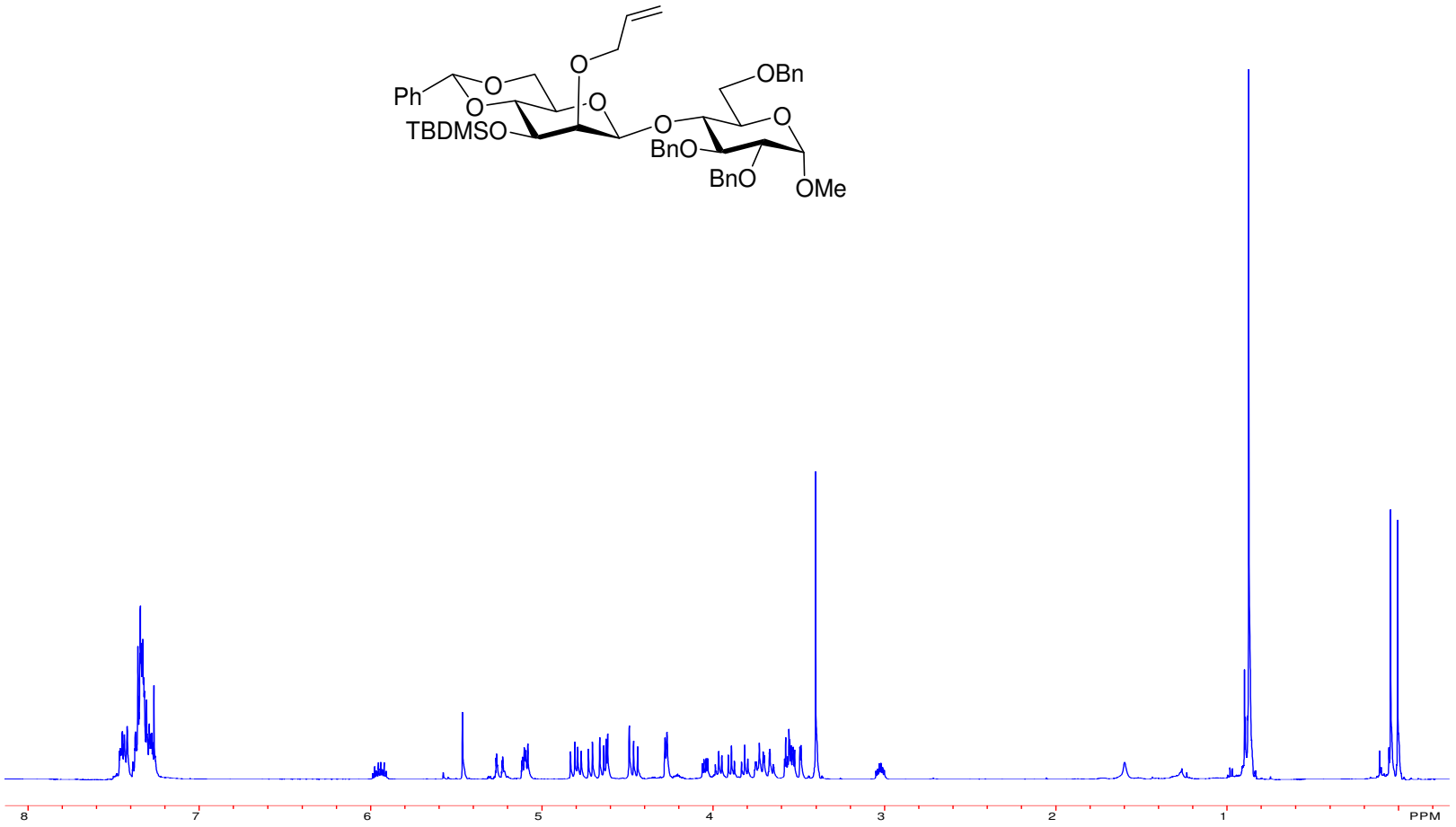


Methyl 2,3,6-tri-*O*-benzyl-4-*O*-[4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-*tert*-butyldimethylsilyl-α-D-mannopyranosyl]-(1→4)-α-D-glucopyranoside (15α).

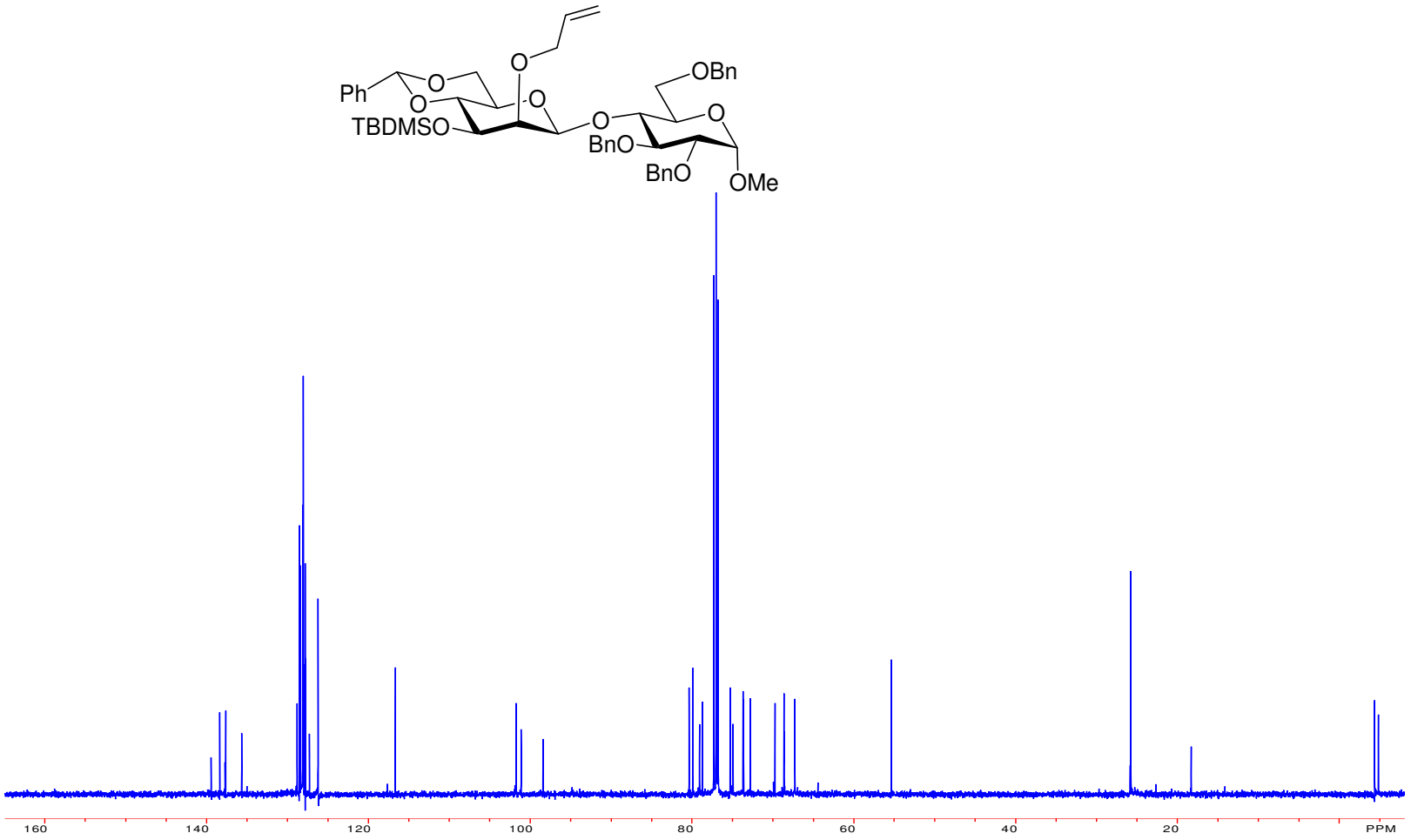




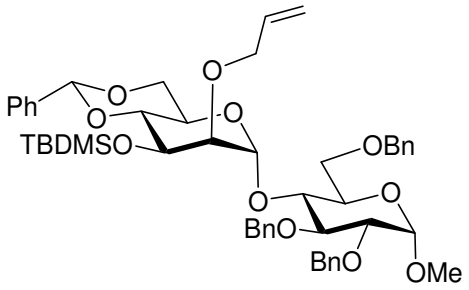
Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(4,6-*O*-benzylidene-2-*O*-allyl-3-*O*-*tert*-butyldimethylsilyl-β-D-mannopyranosyl)-(1→4)-α-D-glucopyranoside (16β).



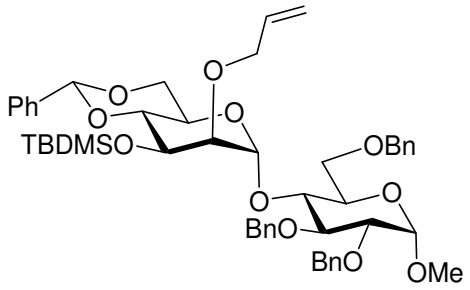
Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(4,6-*O*-benzylidene-2-*O*-allyl-3-*O*-*tert*-butyldimethylsilyl-β-D-mannopyranosyl)-(1→4)-α-D-glucopyranoside (16β).

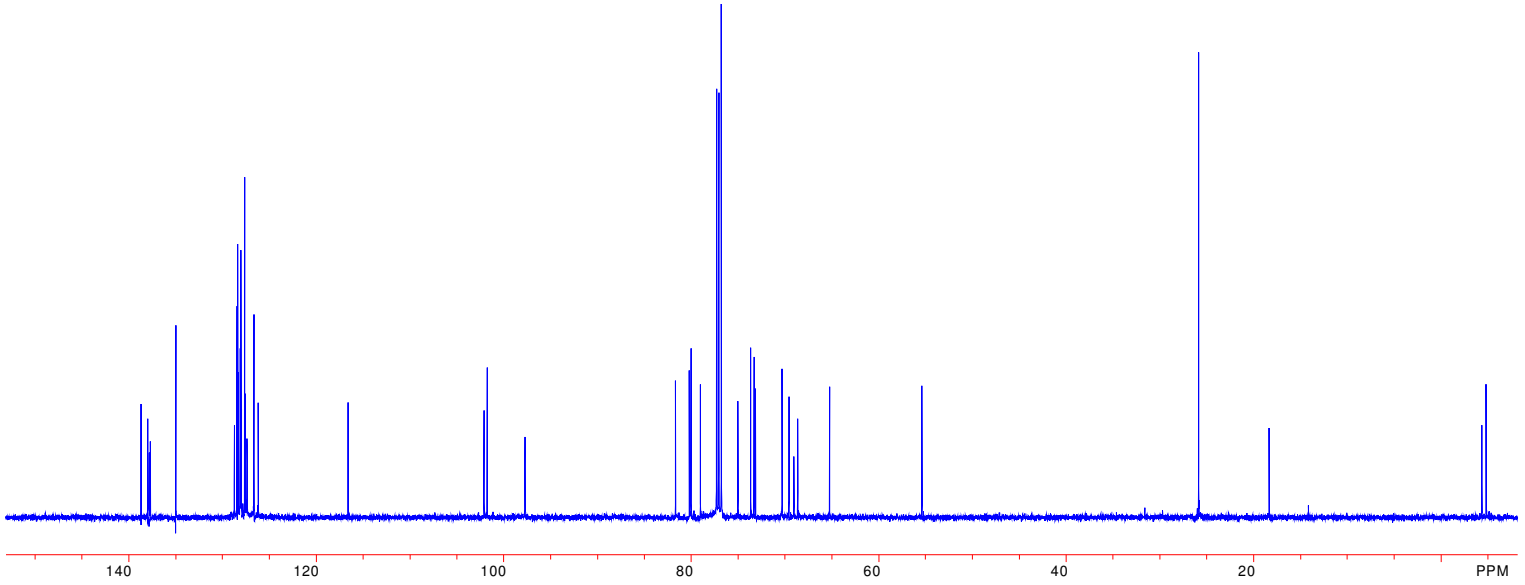


Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(4,6-*O*-benzylidene-2-*O*-allyl-3-*O*-*tert*-butyldimethylsilyl-α-D-mannopyranosyl)-(1→4)-α-D-glucopyranoside (16α).

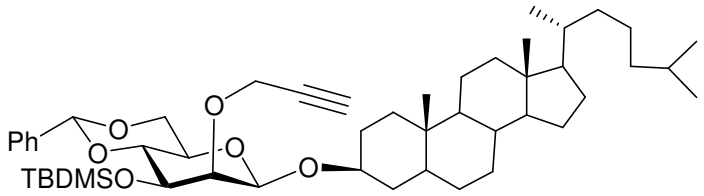


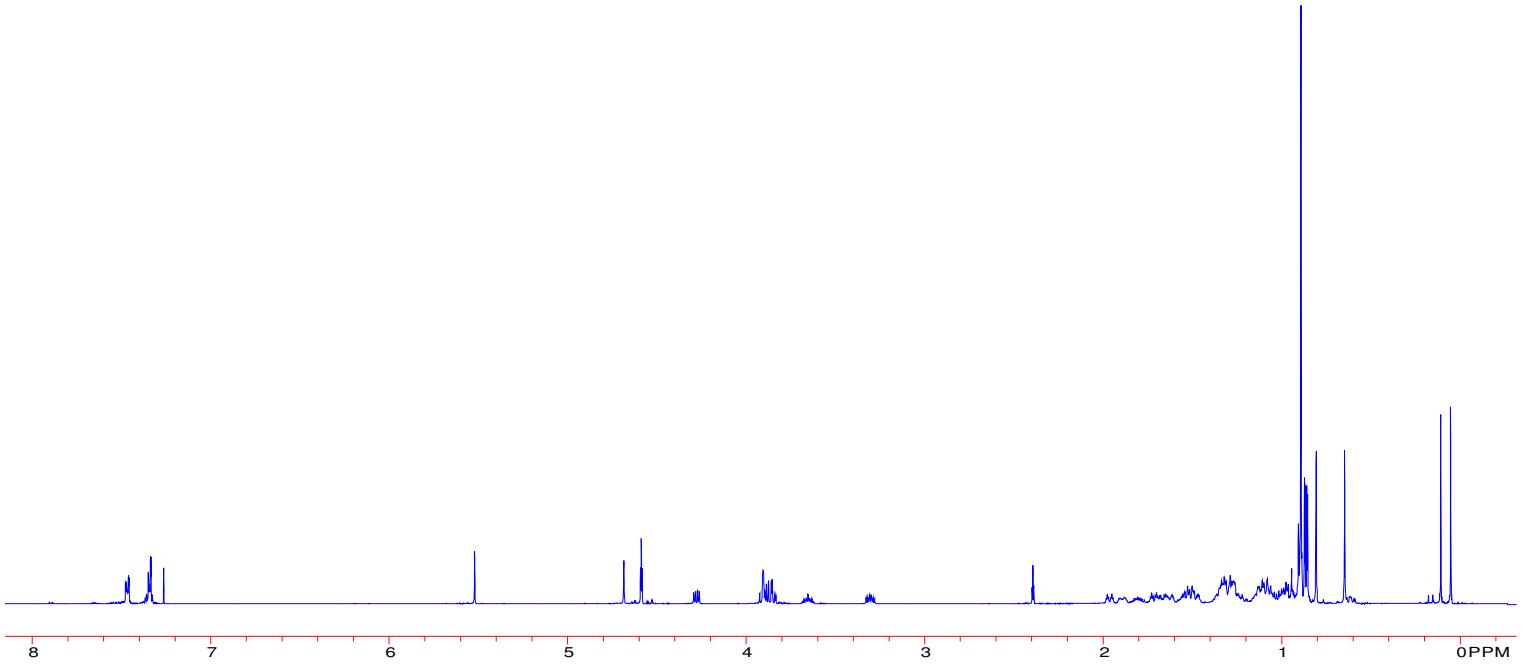
Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(4,6-*O*-benzylidene-2-*O*-allyl-3-*O*-*tert*-butyldimethylsilyl-α-D–mannopyranosyl)-(1→4)-α-D-glucopyranoside (16α).



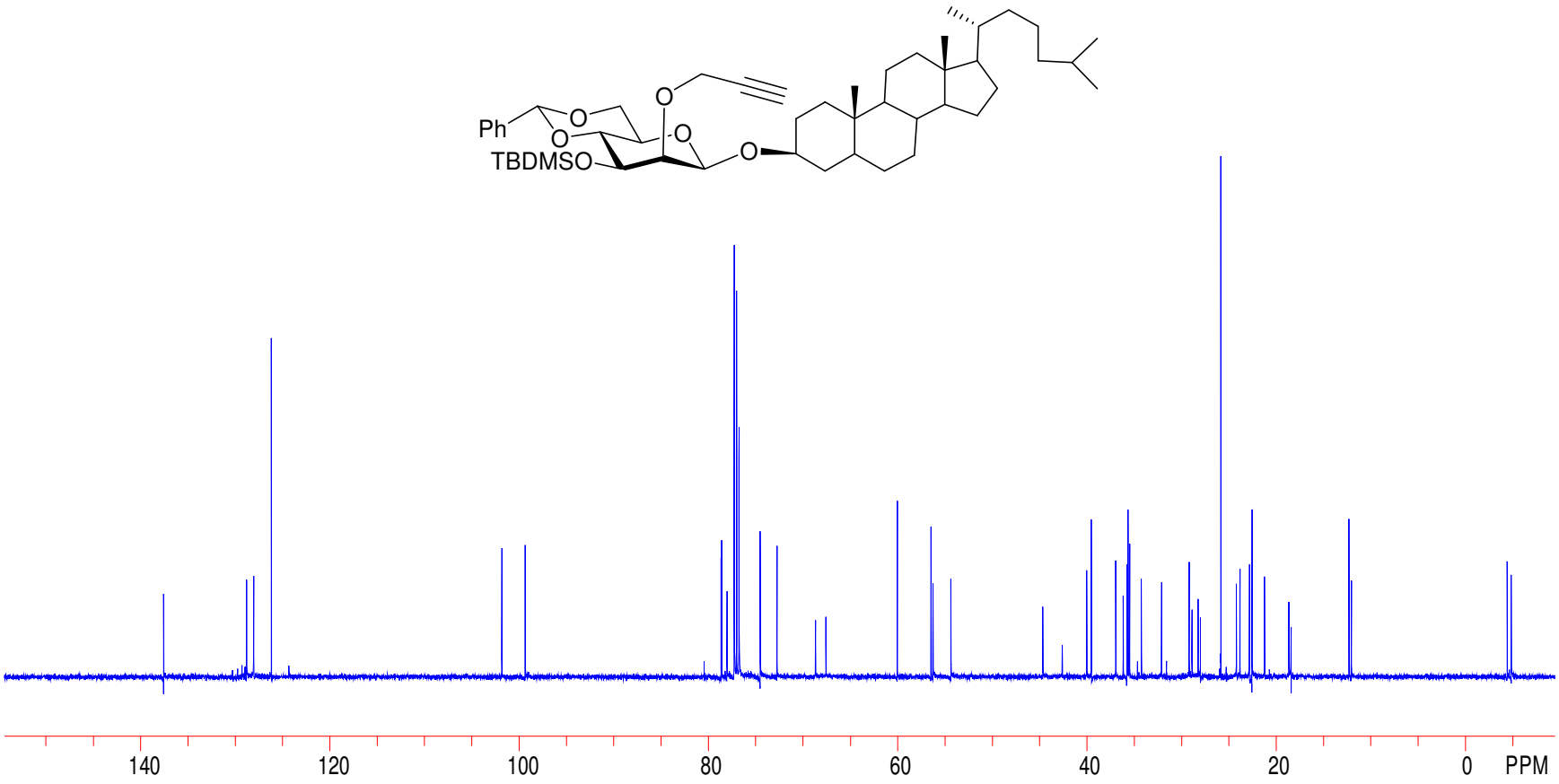


3β-Cholestanyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-*tert*-butyldimethylsilyl-β-D-mannopyranoside (24β).

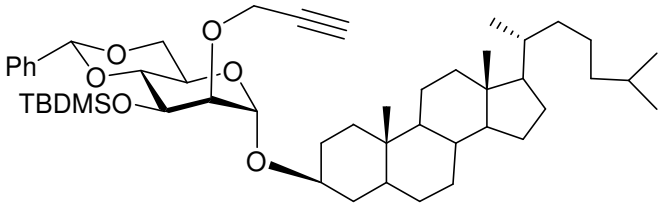


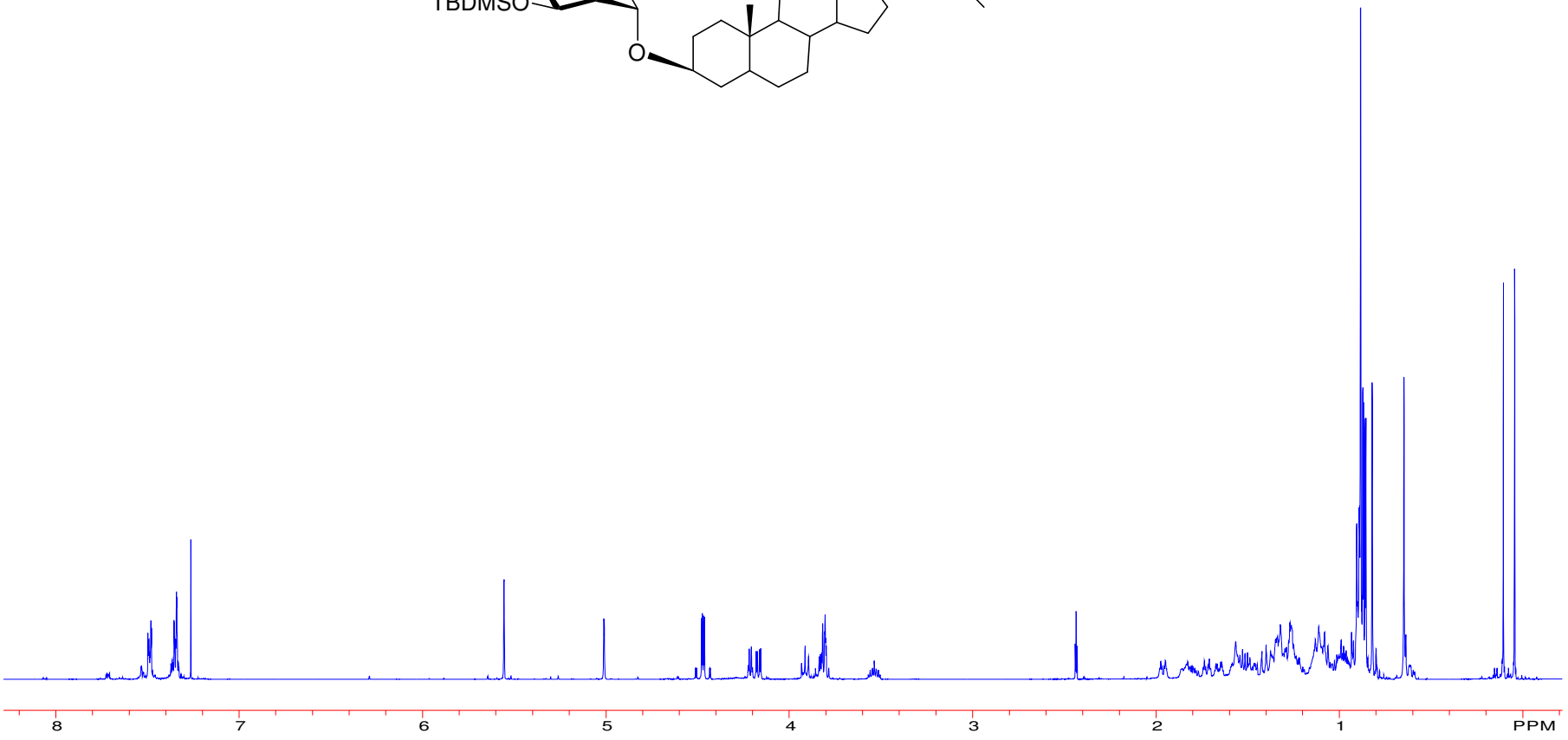


3β-Cholestanyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-*tert*-butyldimethylsilyl-β-D-mannopyranoside (24β).

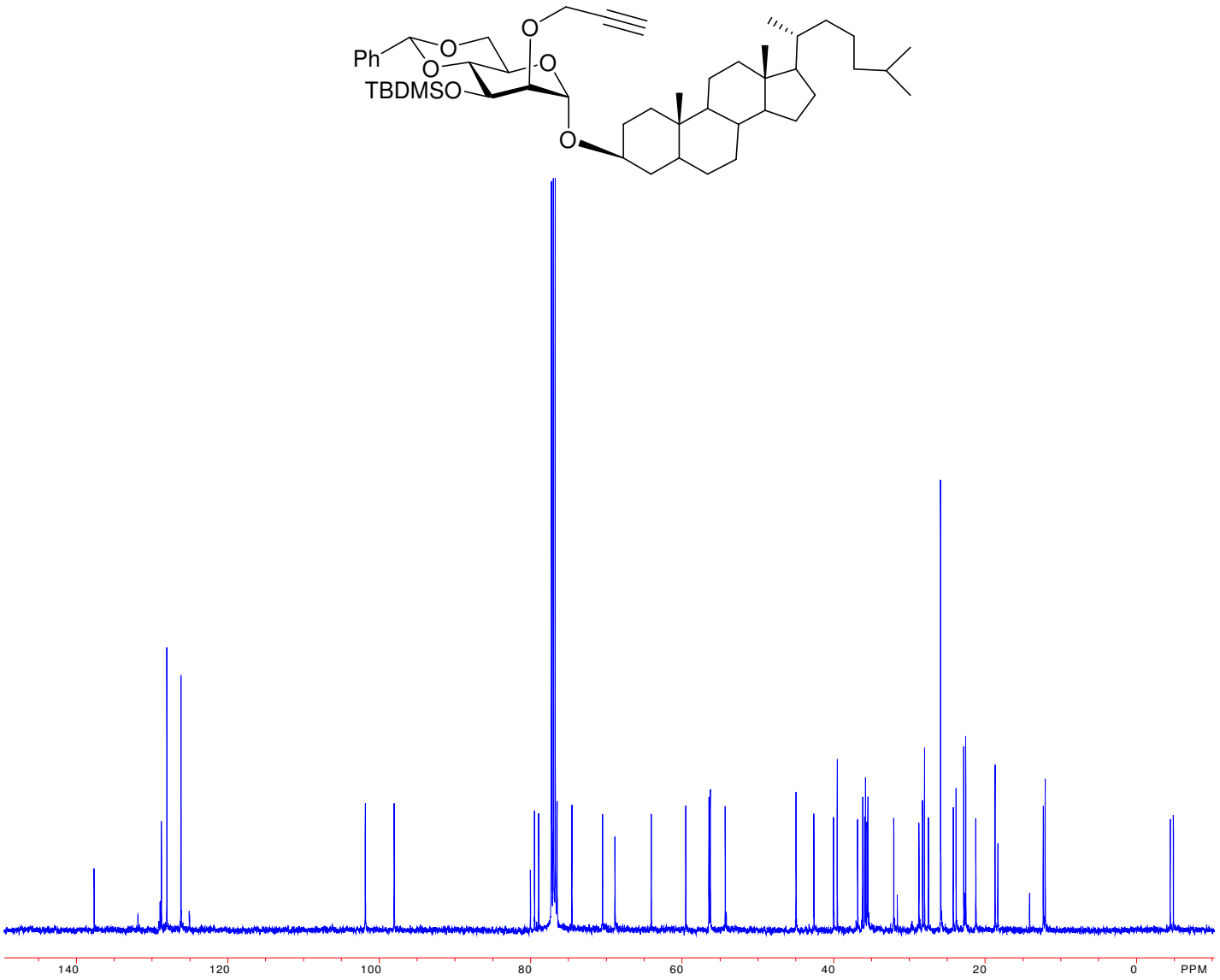


3β-Cholestanyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-*tert*-butyldimethylsilyl-α-D-mannopyranoside (24*α*).

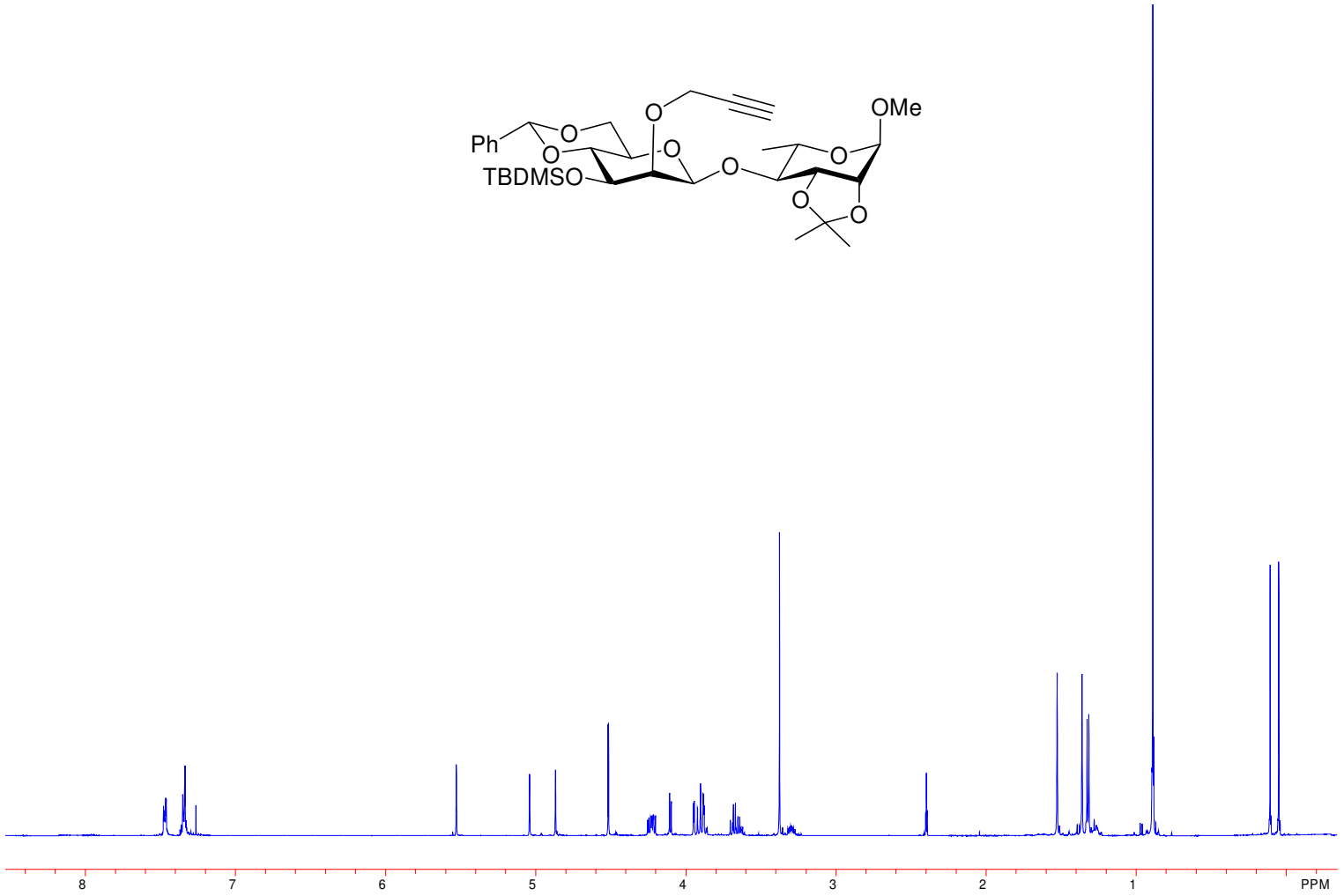




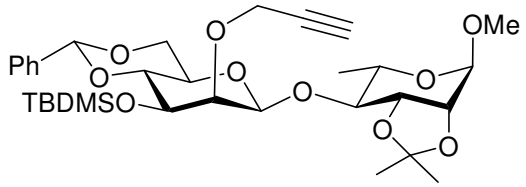
3β-Cholestanyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-*tert*-butyldimethylsilyl-α-D-mannopyranoside (24*α*).

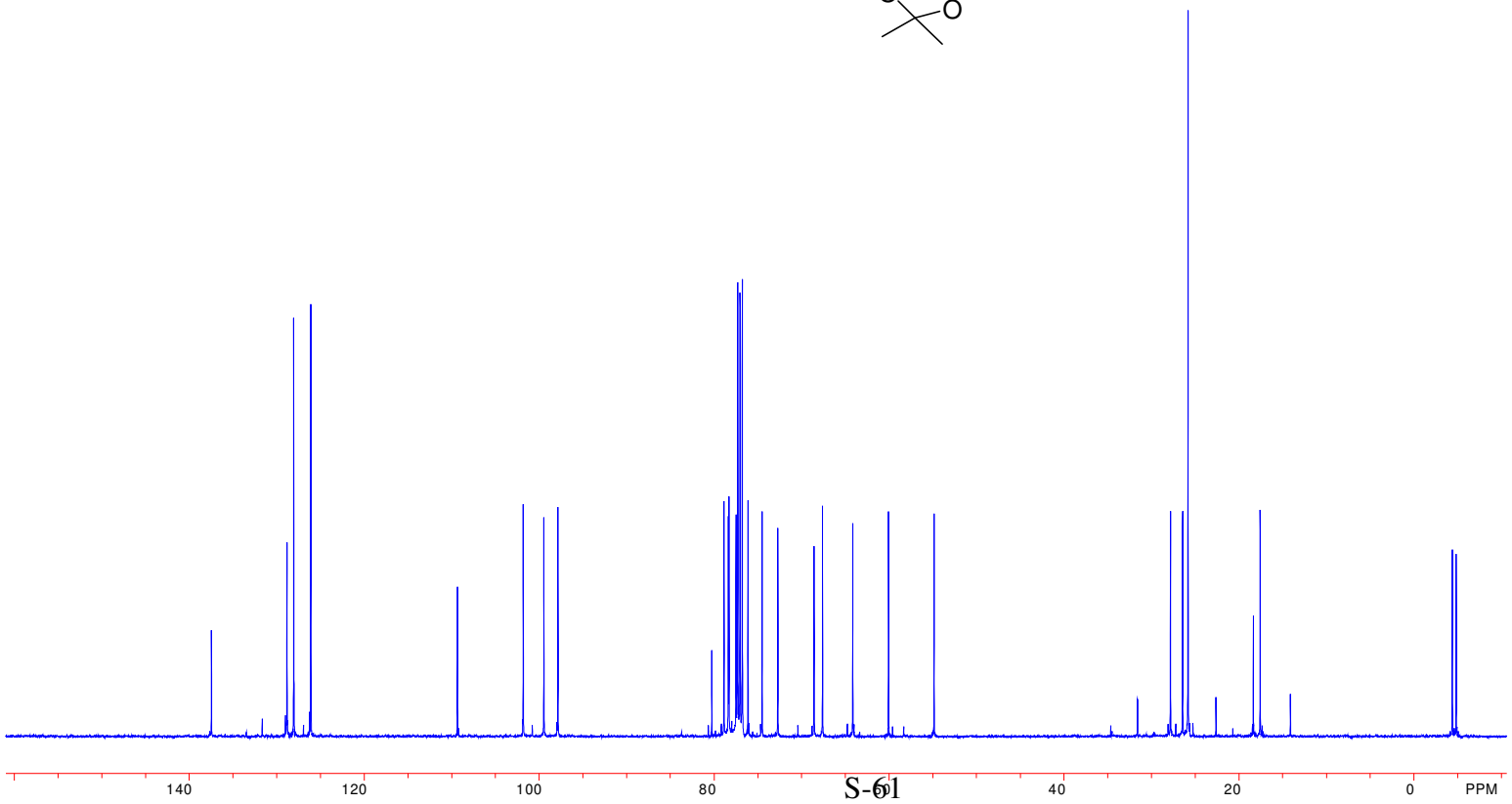


Methyl 4-*O*-(4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-*tert*-butyldimethylsilyl-β-D-mannopyranosyl)-(1→4)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (25β).

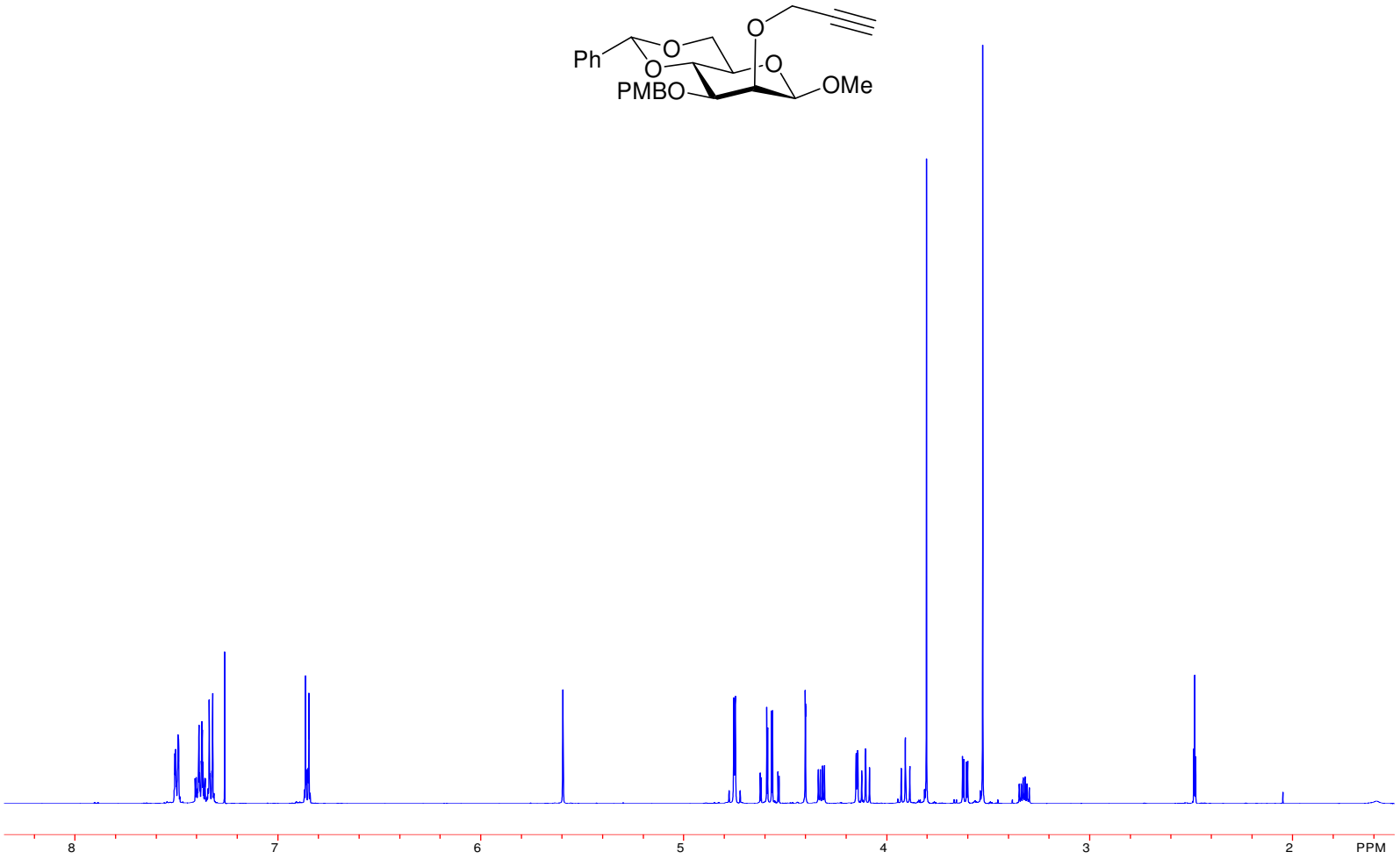


Methyl 4-*O*-(4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-*tert*-butyldimethylsilyl-β-D-mannopyranosyl)-(1→4)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (25β).

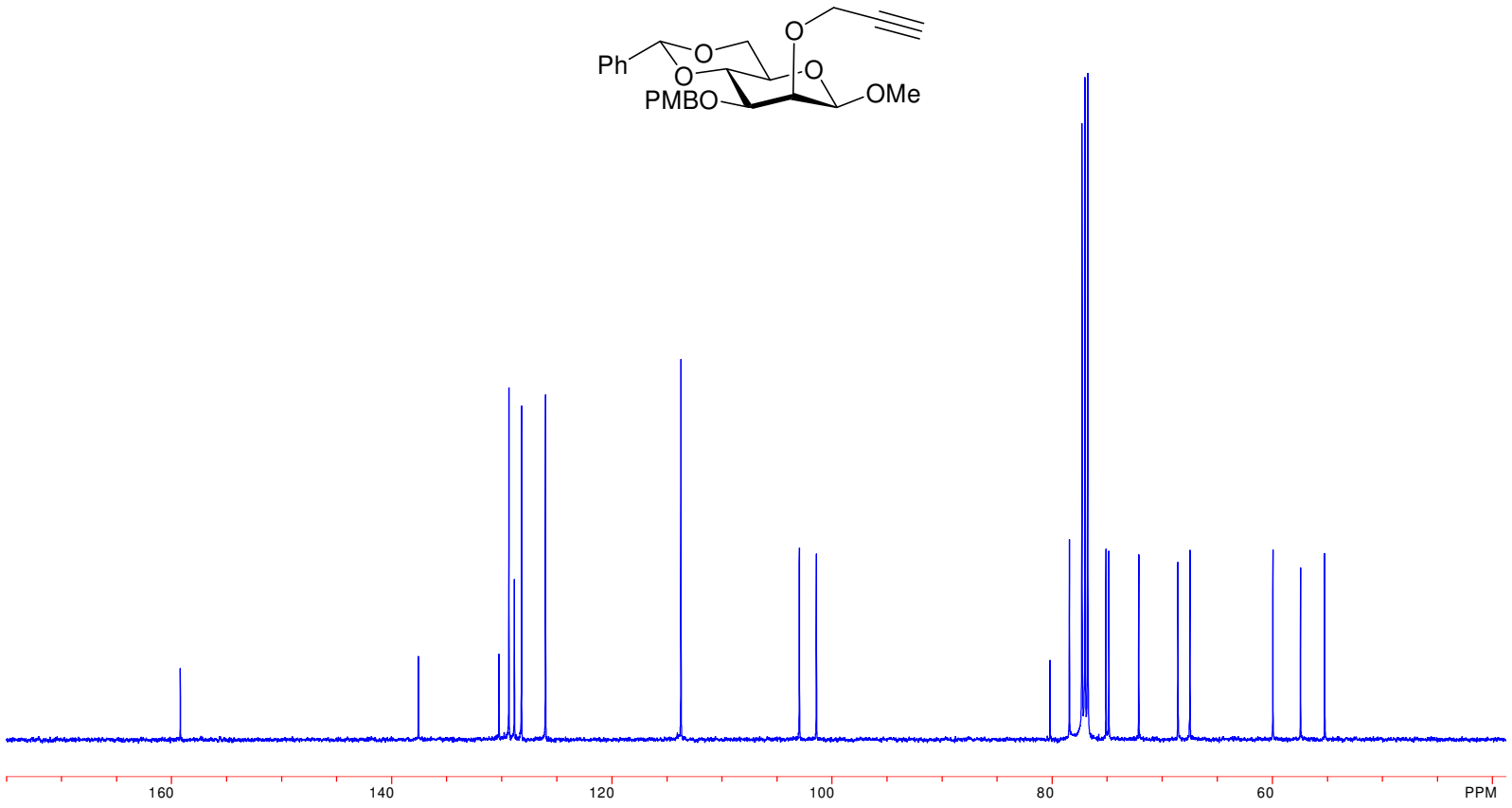




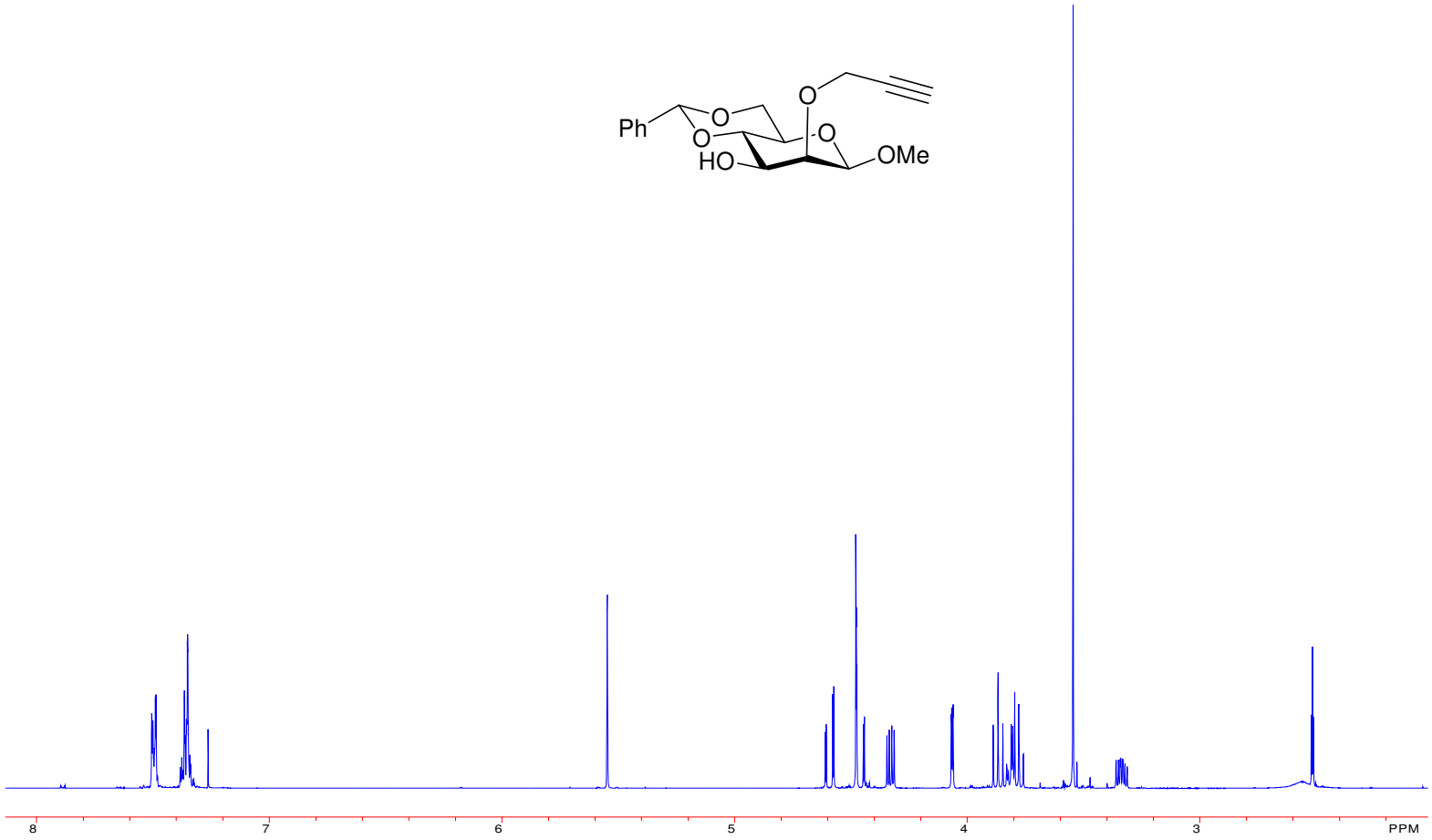
Methyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-*p*-methoxybenzyl-β-D-mannopyranoside (26).



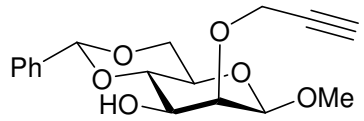
Methyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-*p*-methoxybenzyl-β-D-mannopyranoside (26).

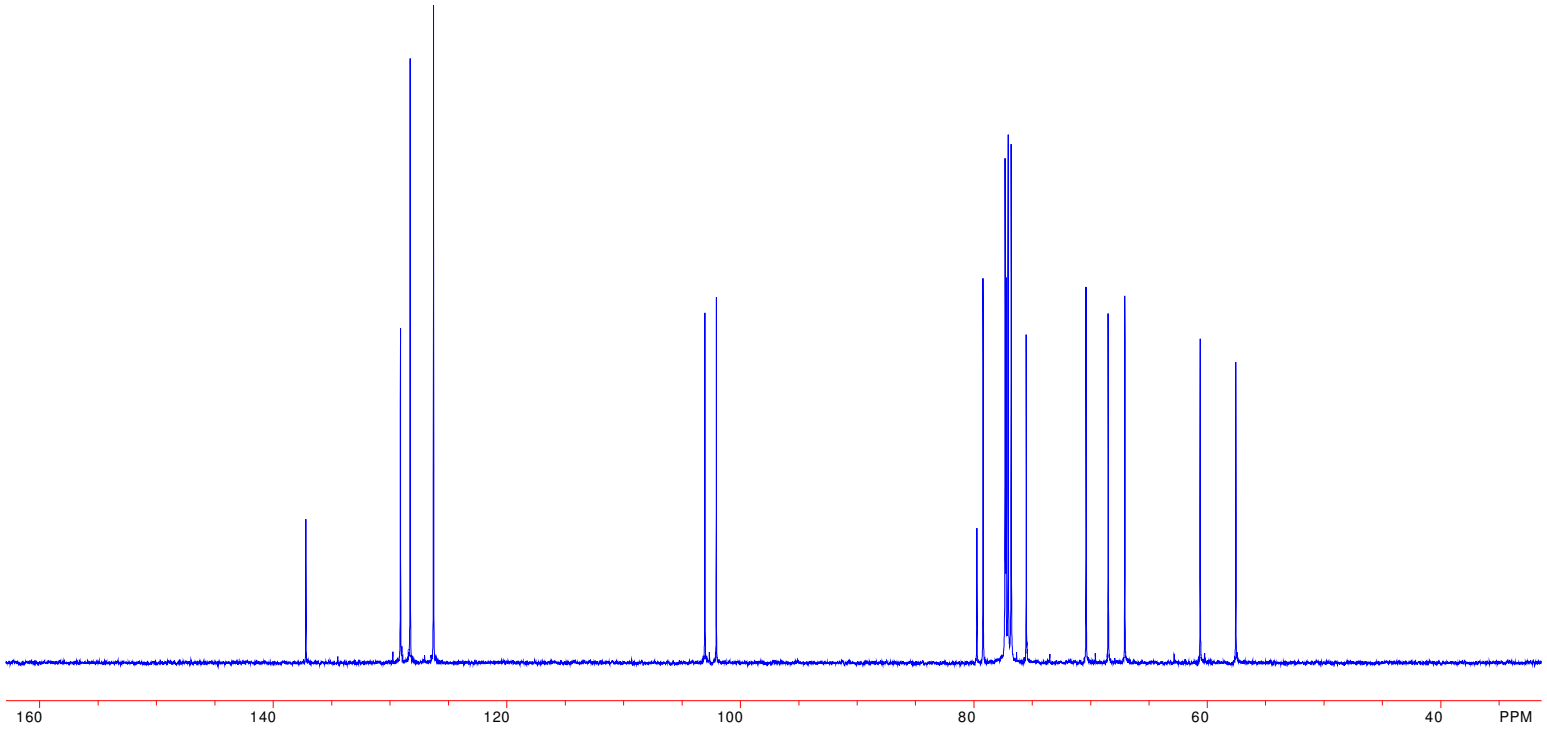


Methyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-β-D-mannopyranoside (27).

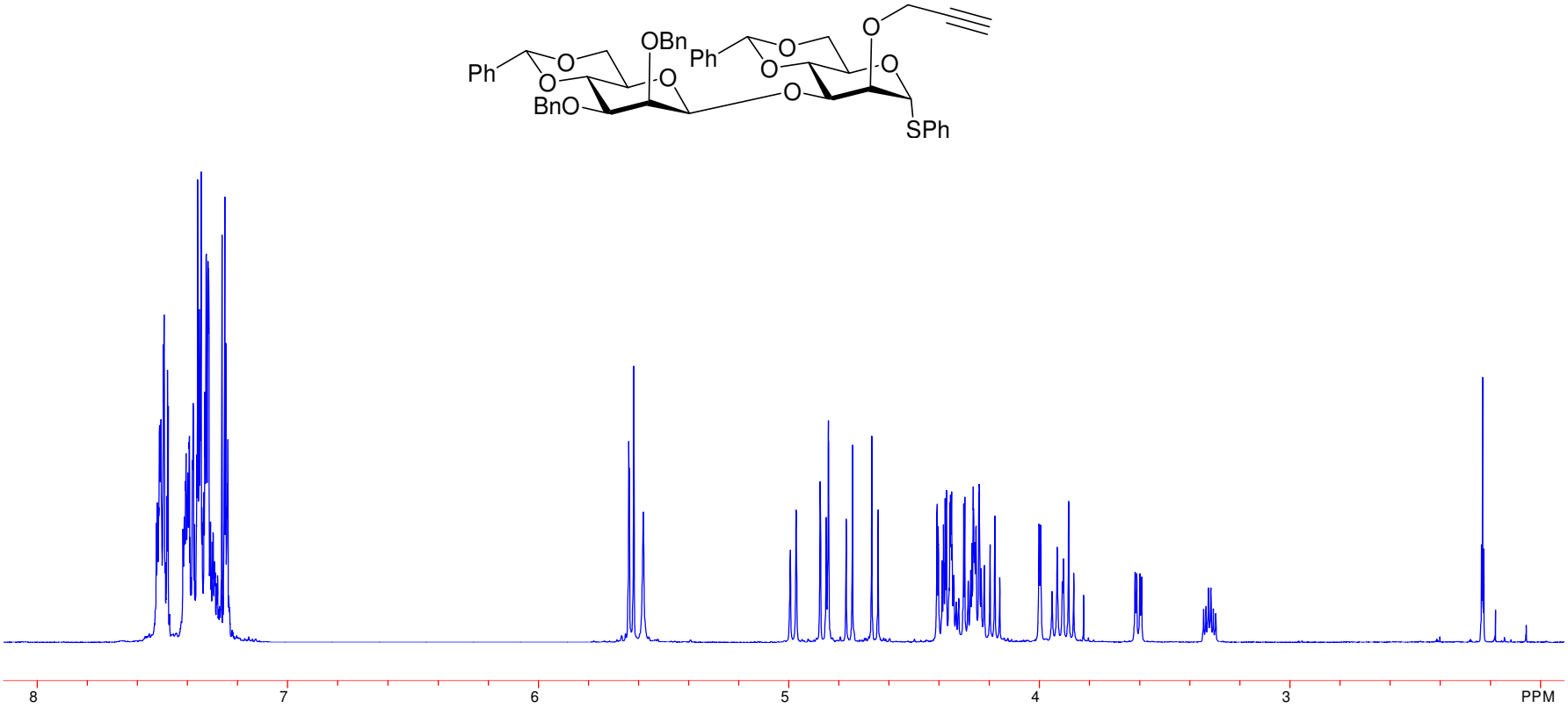


Methyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-β-D-mannopyranoside (27).

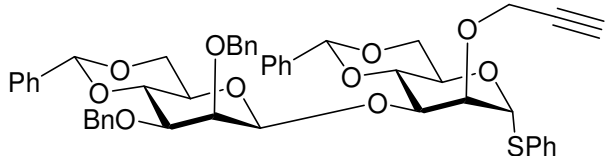


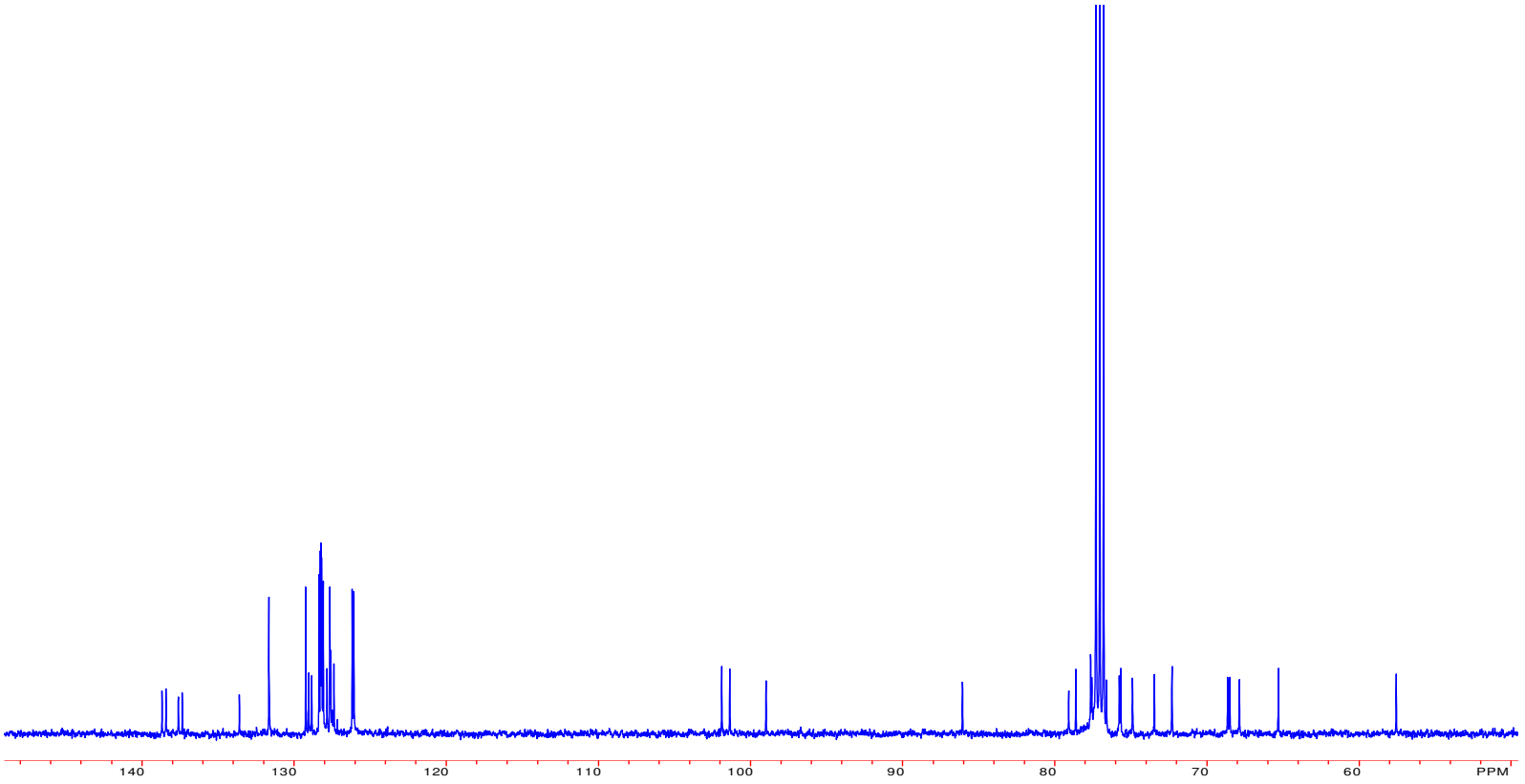


Phenyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl)-1-thio-α-D-mannopyranoside (29β).

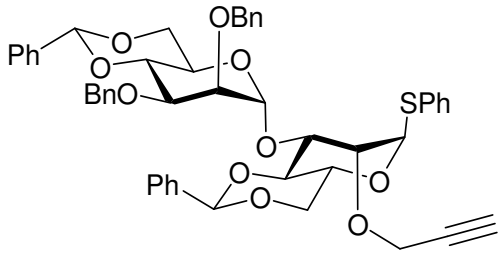


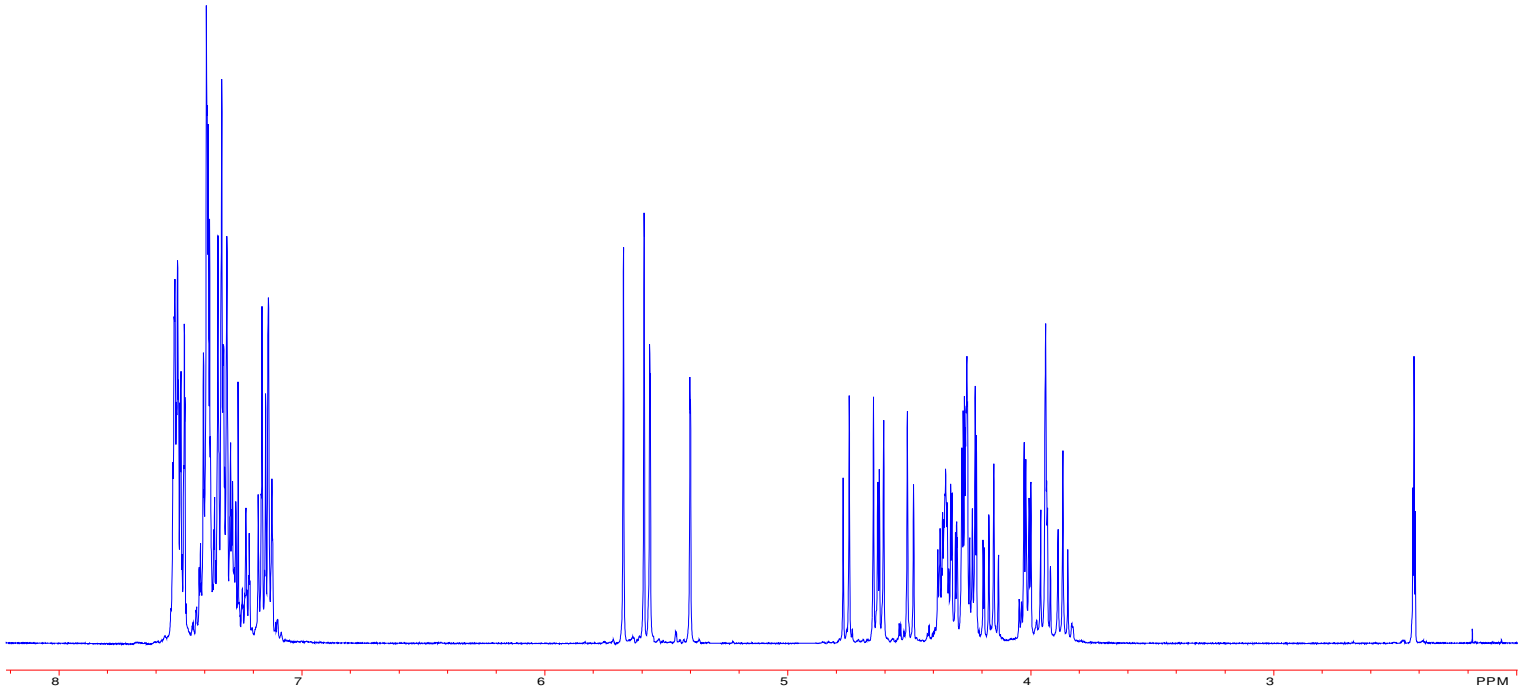
Phenyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl)-1-thio-α-D-mannopyranoside (29β).



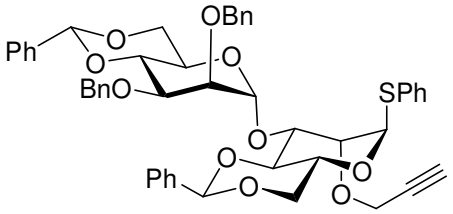


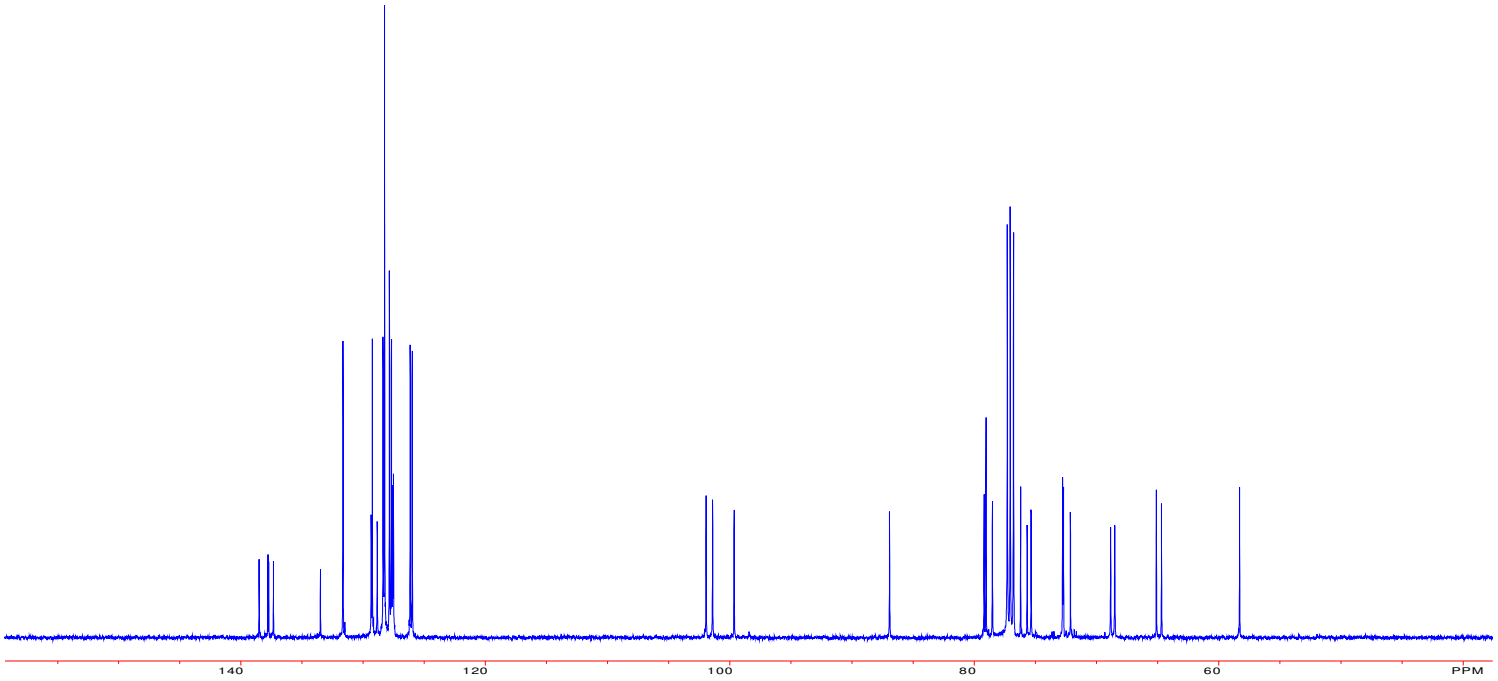
Phenyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranosyl)-1-thio-α-D-mannopyranoside (29α).



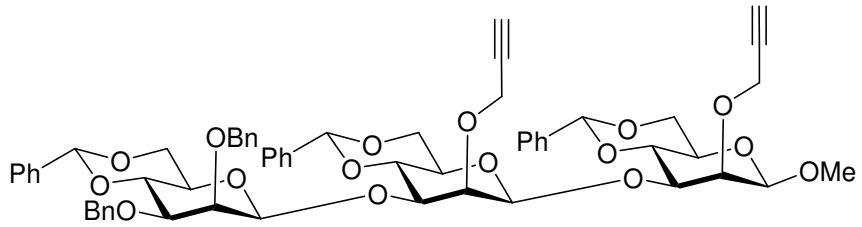


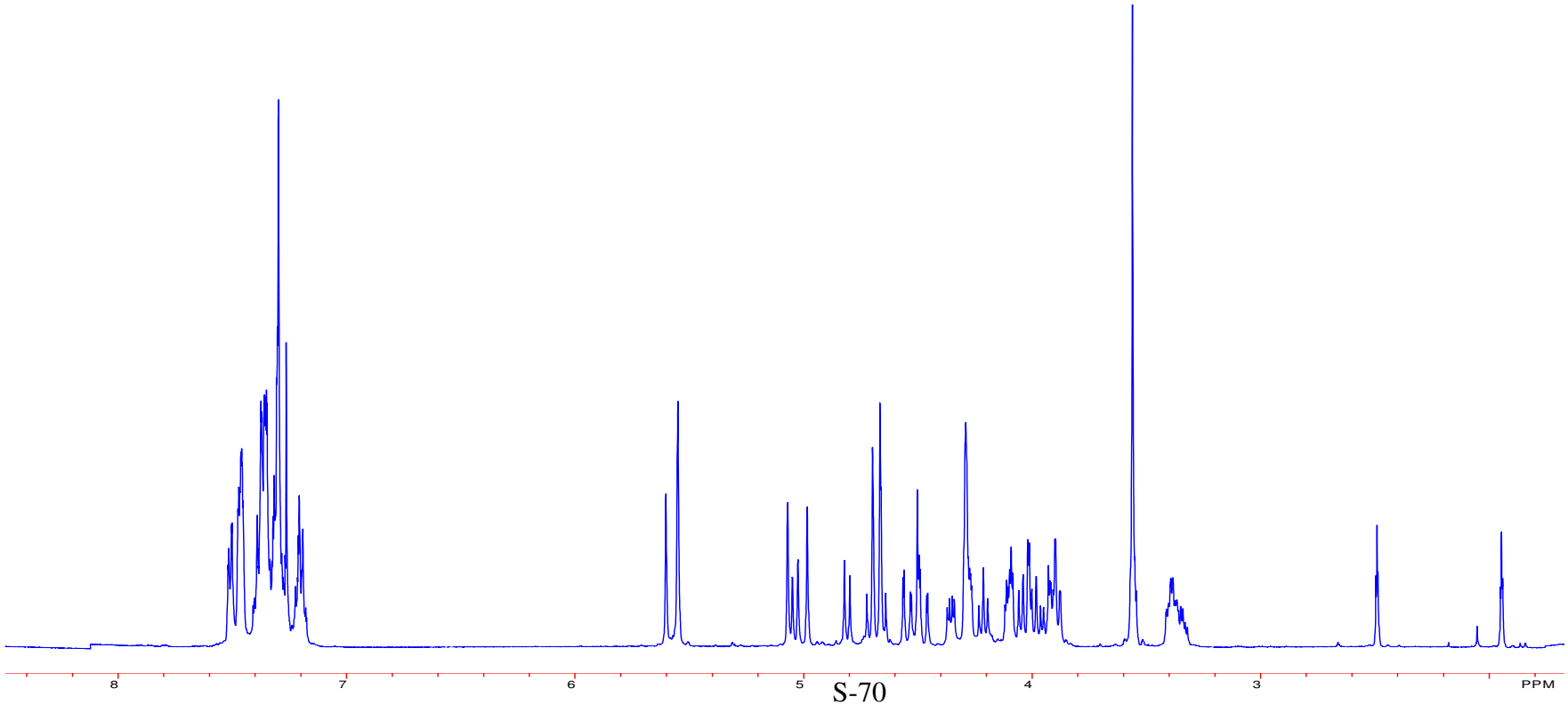
Phenyl 4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranosyl)-1-thio-α-D-mannopyranoside (29α).



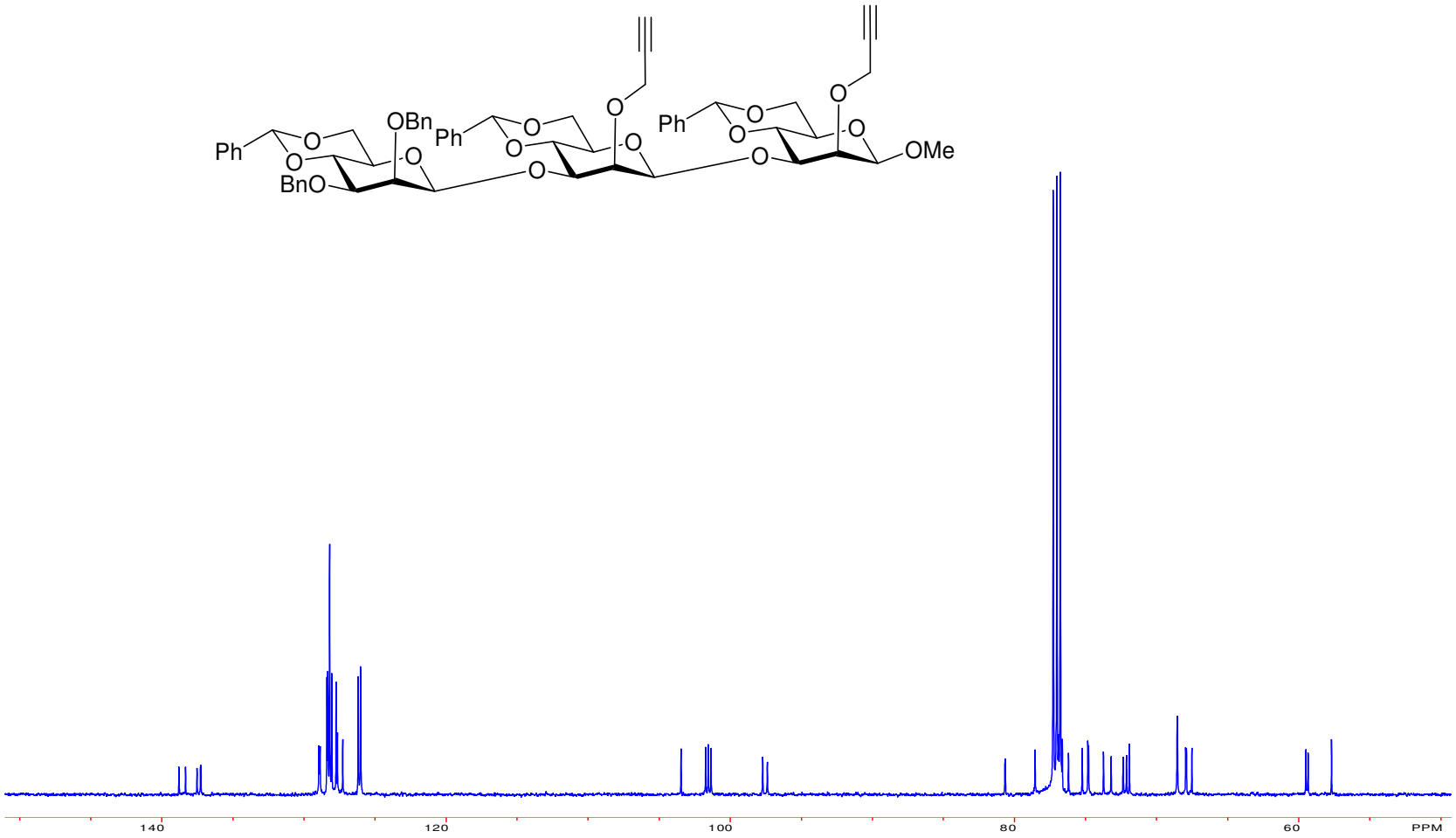


Methyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→3)-4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-β-D-mannopyranosyl-(1→3)-4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-β-D-mannopyranoside (30β).

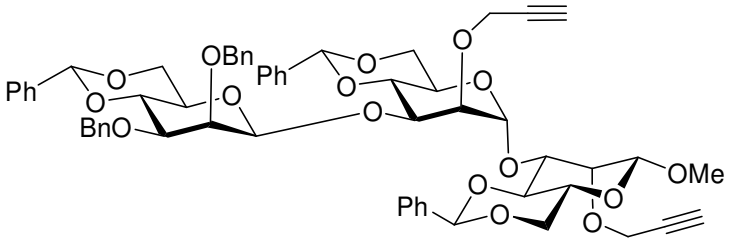


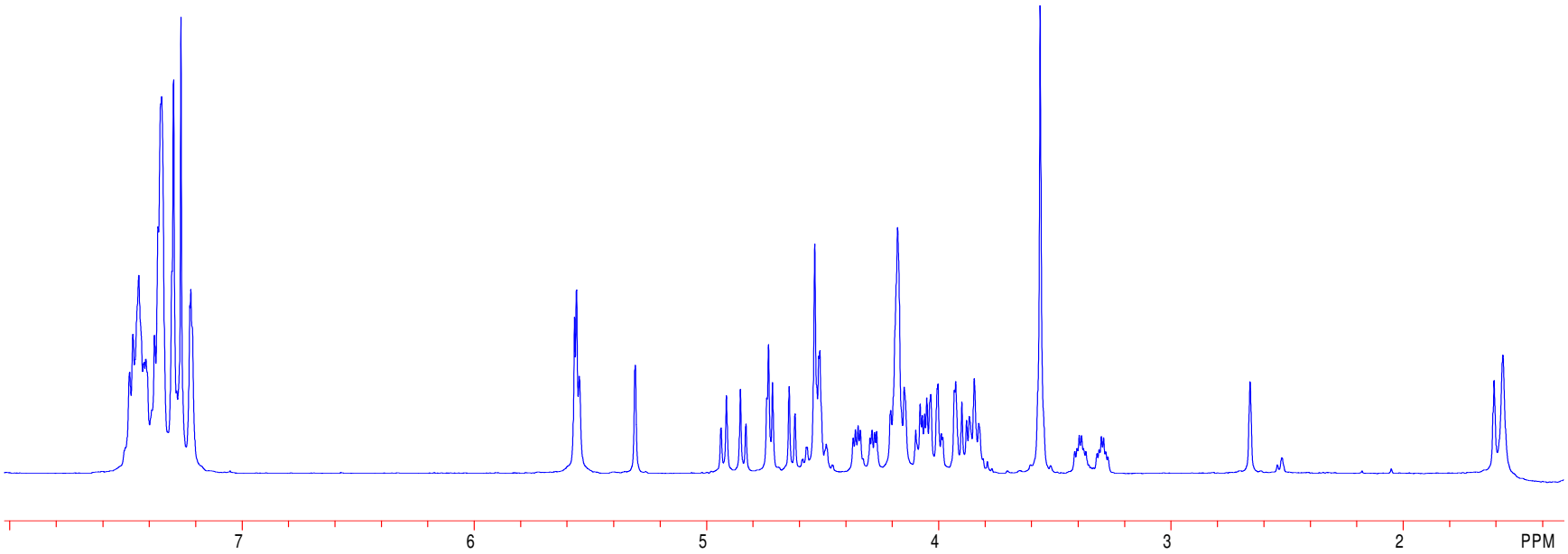


Methyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→3)-4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-β-D-mannopyranosyl-(1→3)-4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-β-D-mannopyranoside (30β).

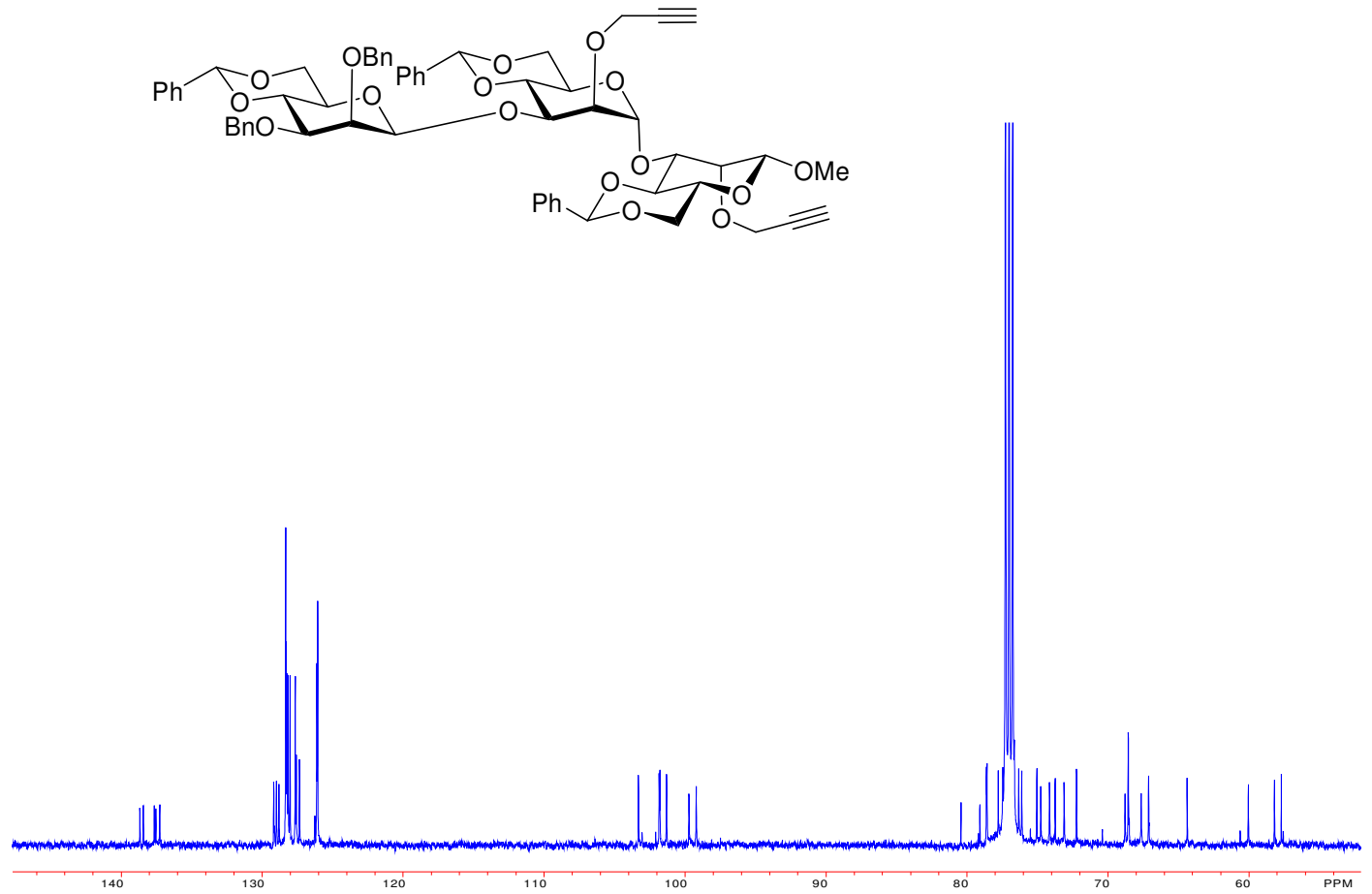


Methyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→3)-4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-β-D-mannopyranosyl-(1→3)-4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-α-D-mannopyranoside (30α).

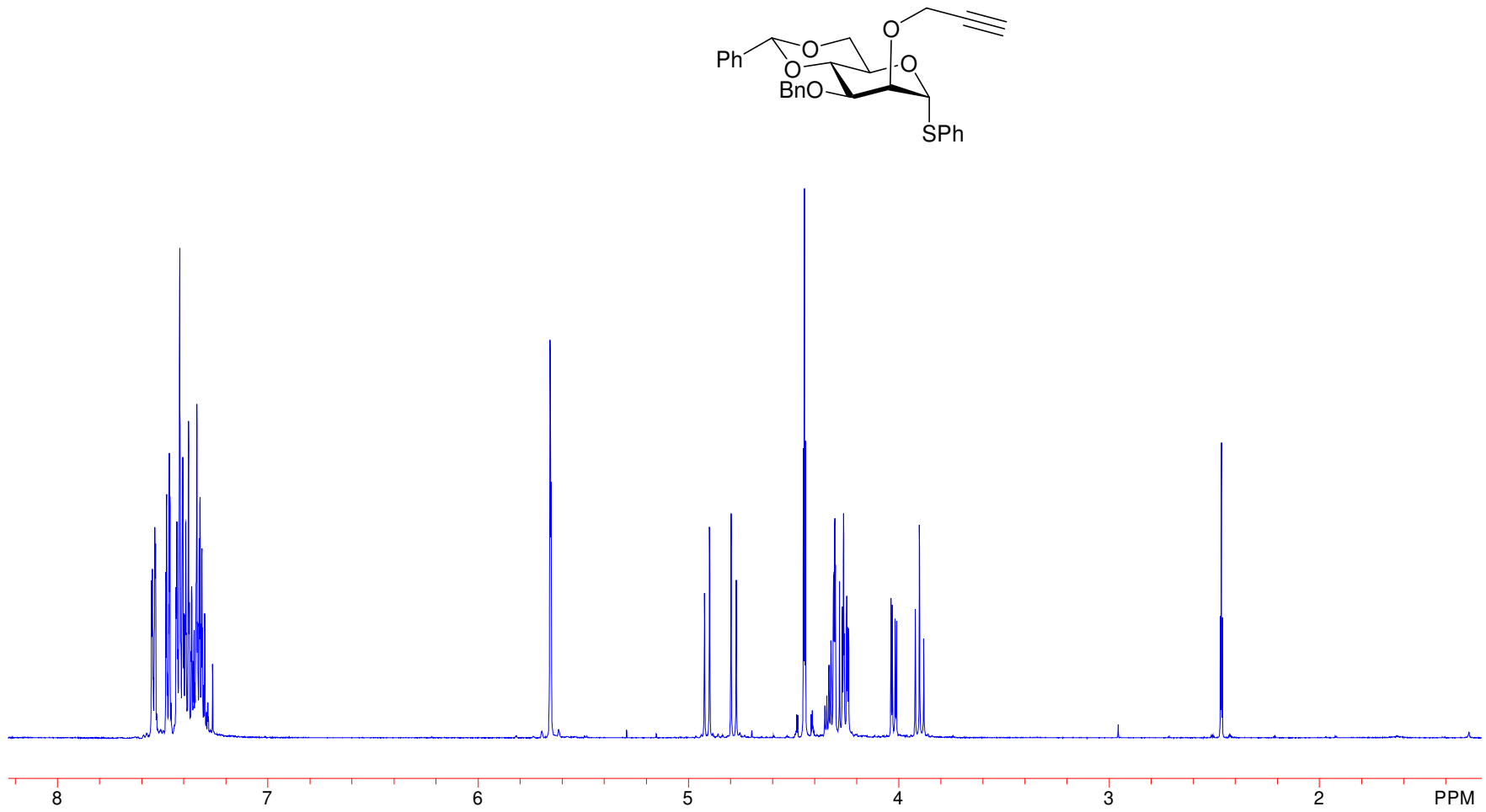




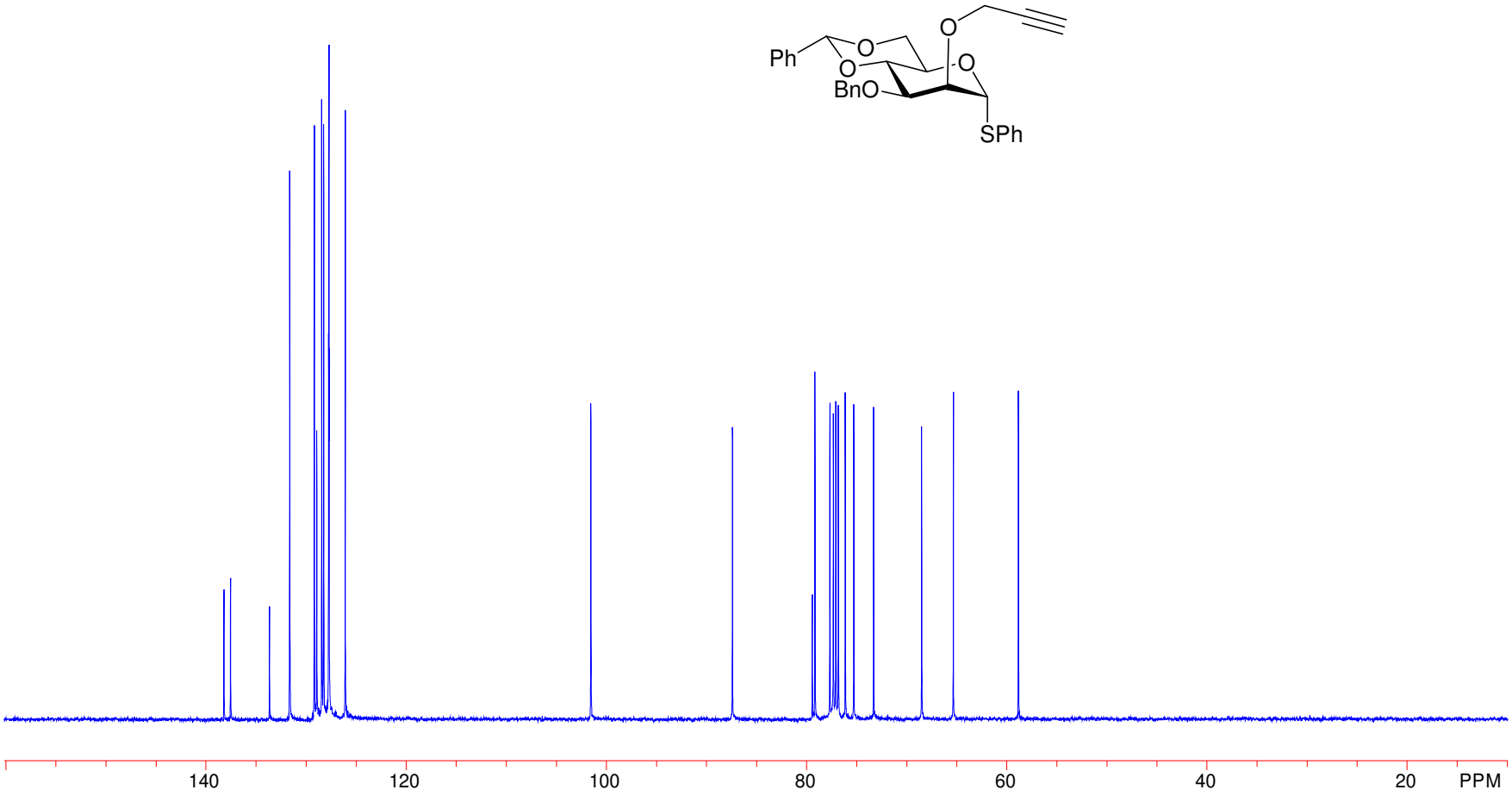
Methyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→3)-4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-β-D-mannopyranosyl-(1→3)-4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-α-D-mannopyranoside (30α).



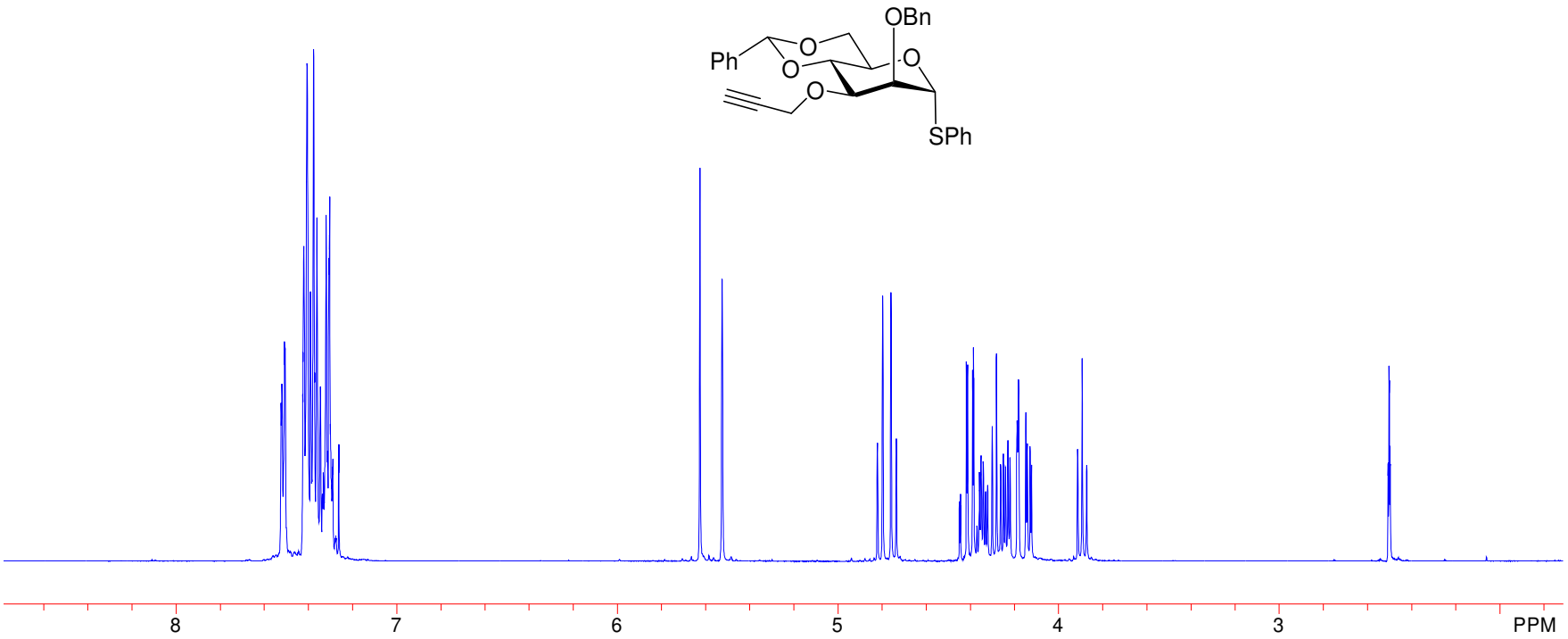
Phenyl 4,6-*O*-benzylidene-3-*O*-benzyl-2-*O*-(prop-2-ynyl)-1-thio-α-D-mannopyranoside (33).



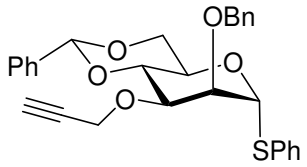
Phenyl 4,6-*O*-benzylidene-3-*O*-benzyl-2-*O*-(prop-2-ynyl)-1-thio-α-D-mannopyranoside (33).

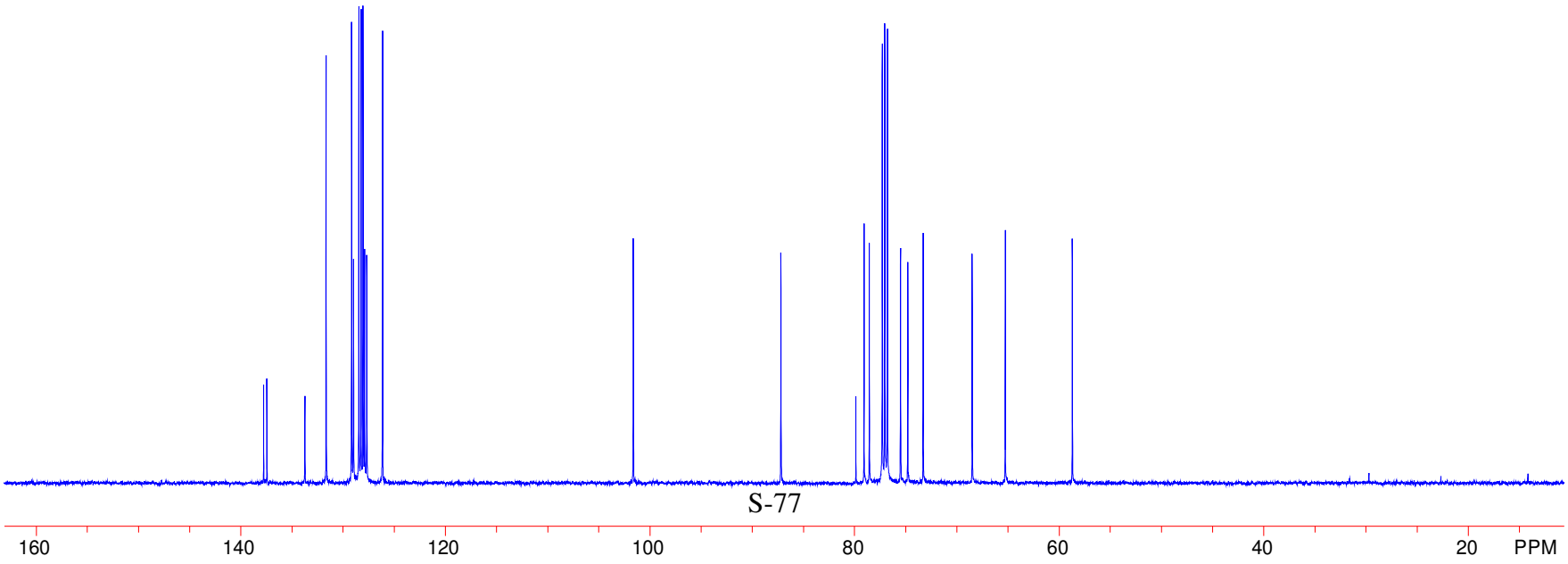


Phenyl 4,6-*O*-benzylidene-2-*O*-benzyl-3-*O*-(prop-2-ynyl)-1-thio-α-D-mannopyranoside (35).

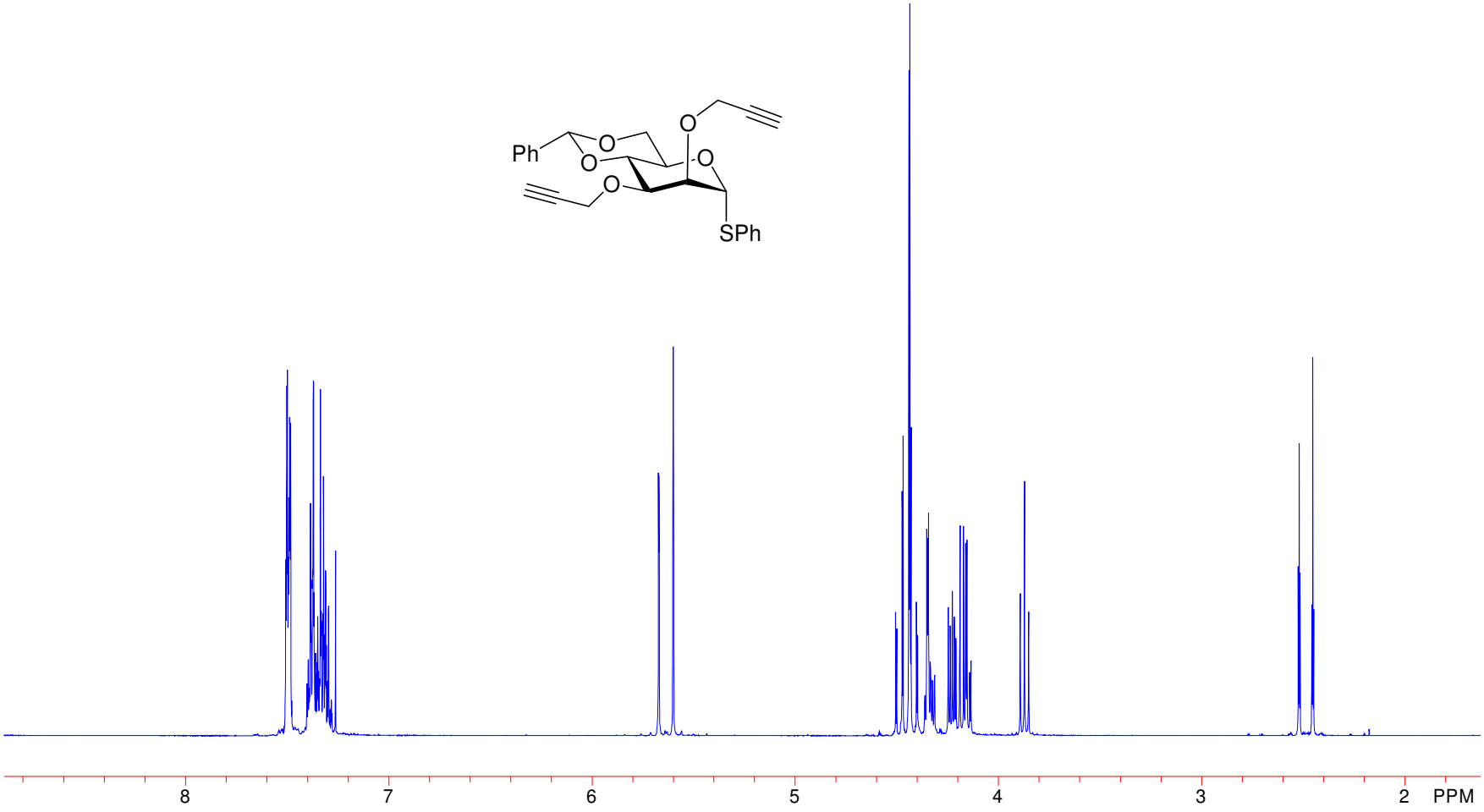


Phenyl 4,6-*O*-benzylidene-2-*O*-benzyl-3-*O*-(prop-2-ynyl)-1-thio-α-D-mannopyranoside (35).

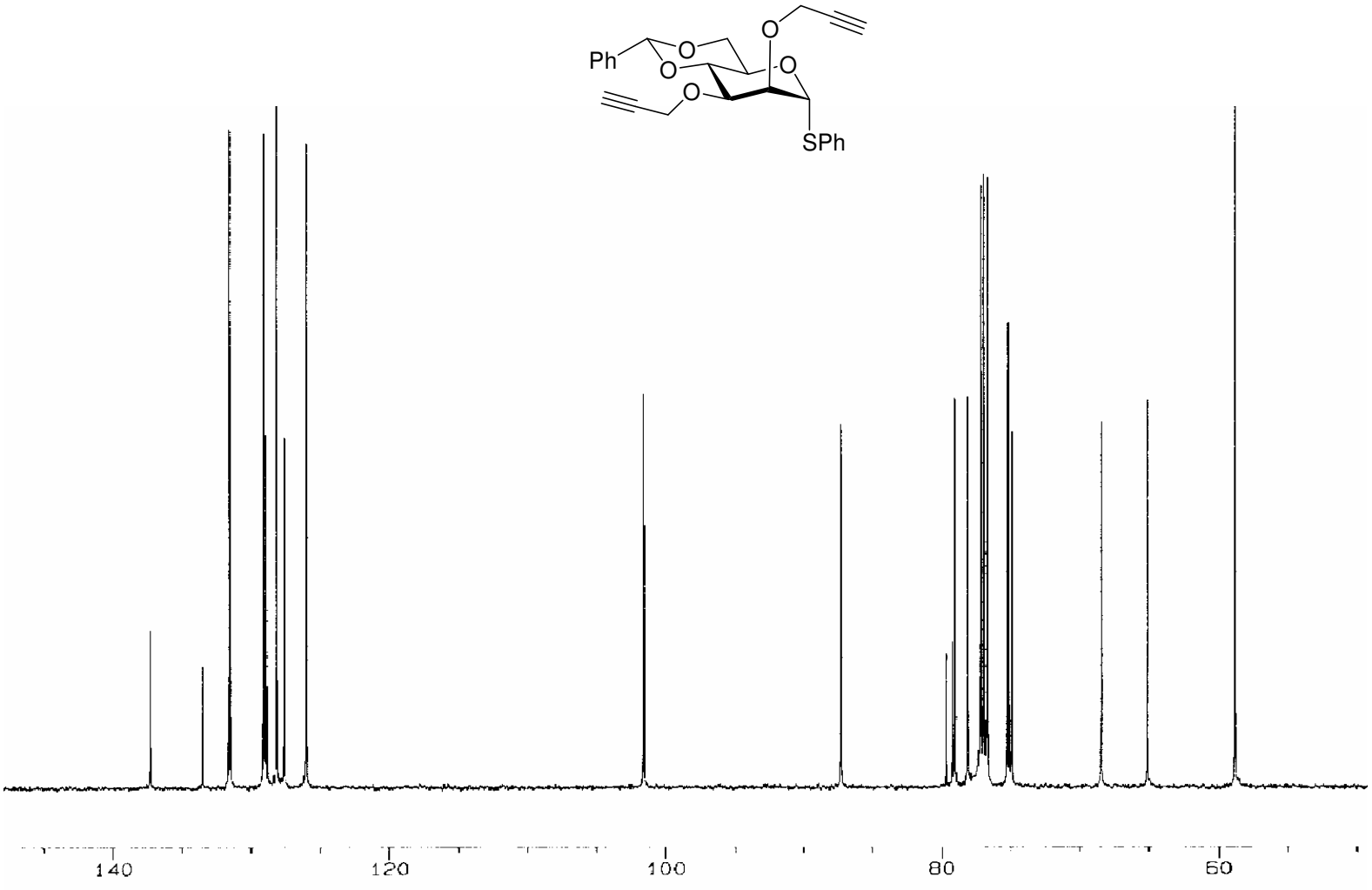




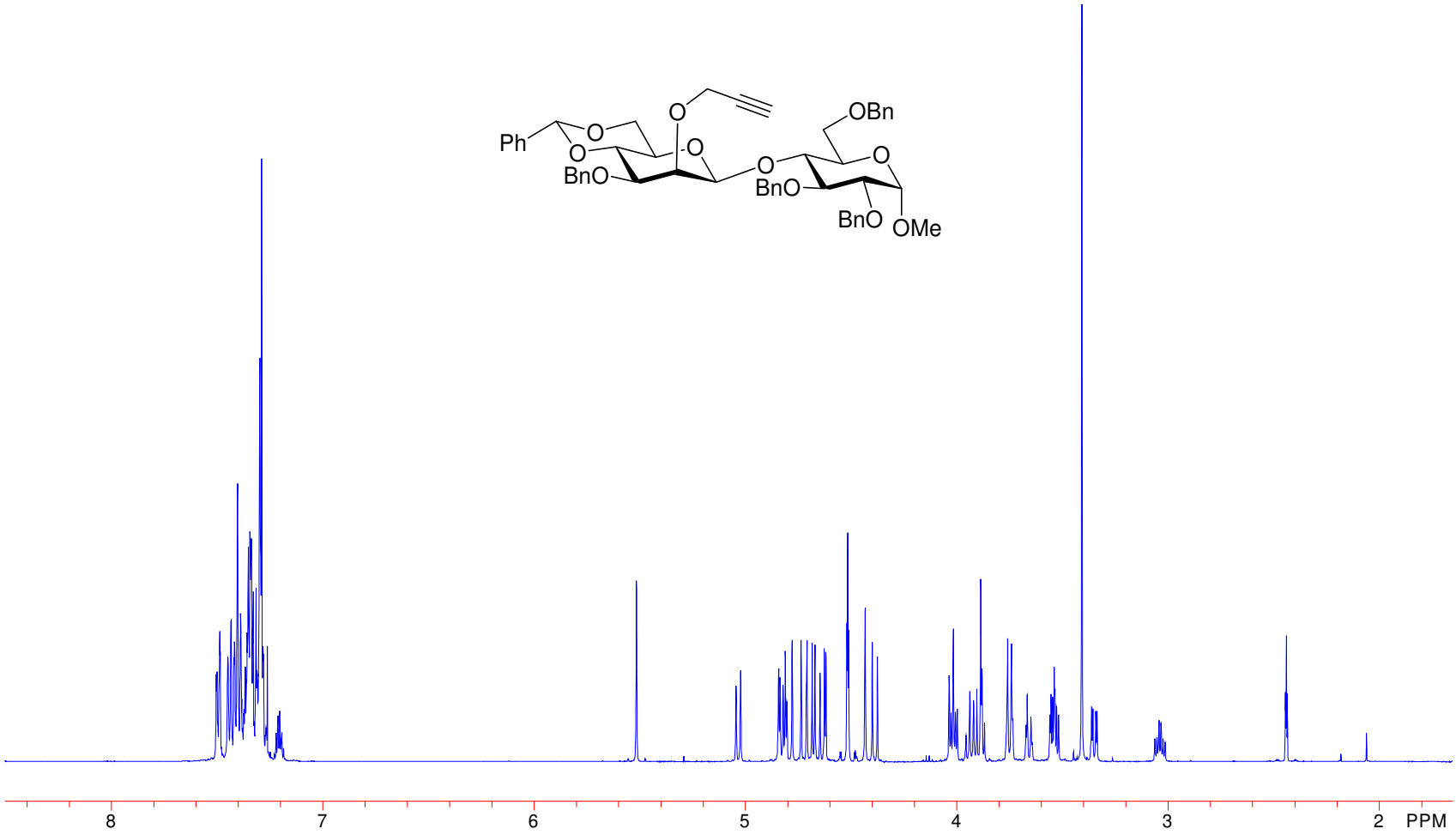
Phenyl 4,6-*O*-benzylidene-2,3-di-*O*-(prop-2-ynyl)-1-thio-α-D-mannopyranoside (36)



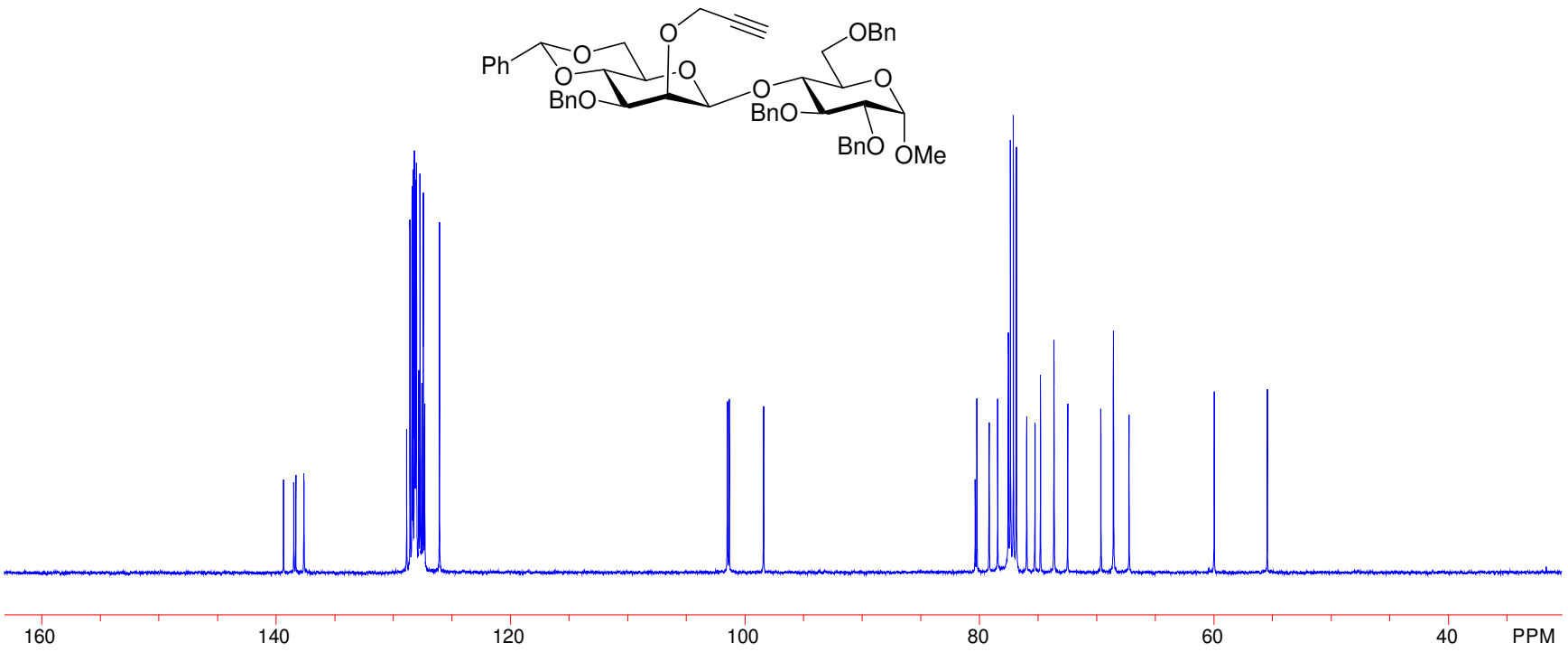
Phenyl 4,6-*O*-benzylidene-2,3-di-*O*-(prop-2-ynyl)-1-thio-α-D-mannopyranoside (36)



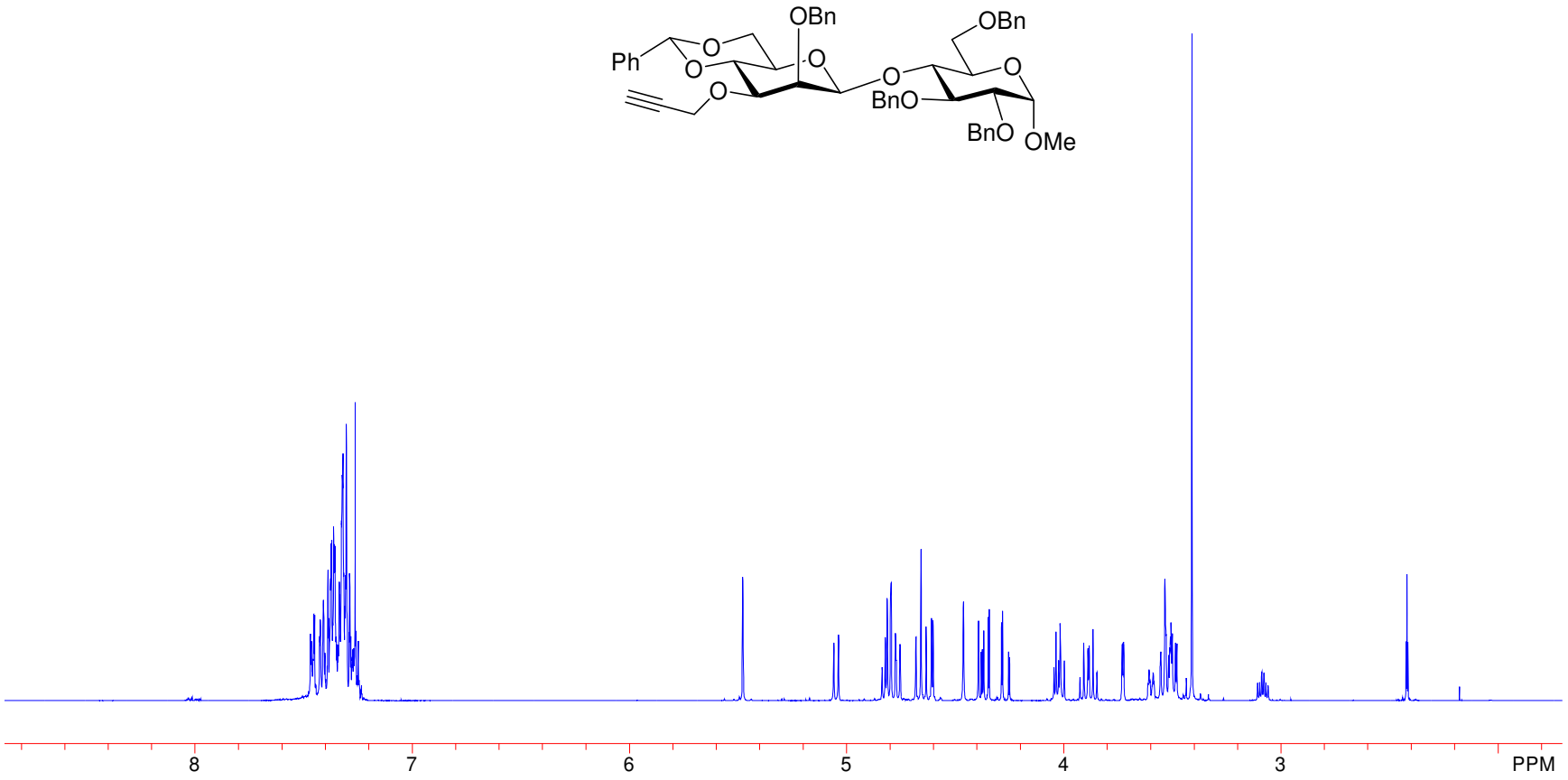
Methyl 2,3,6-tri-*O*-benzyl-4-*O*-[4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-benzyl-β-D-mannopyranosyl]-(1→4)-α-D-glucopyranoside (38β).



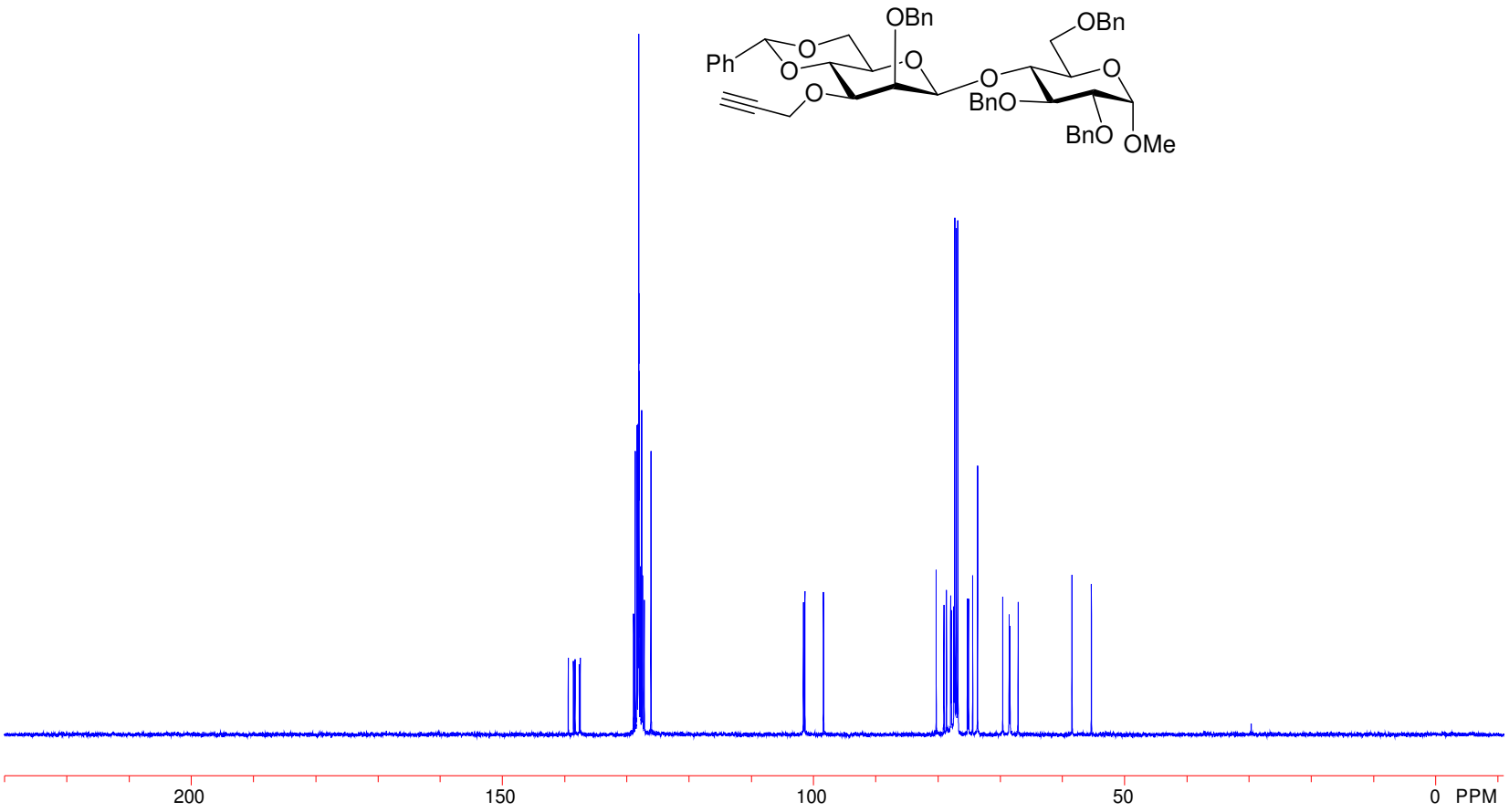
Methyl 2,3,6-tri-*O*-benzyl-4-*O*-[4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-benzyl-β-D-mannopyranosyl]-(1→4)-α-D-glucopyranoside (38β).



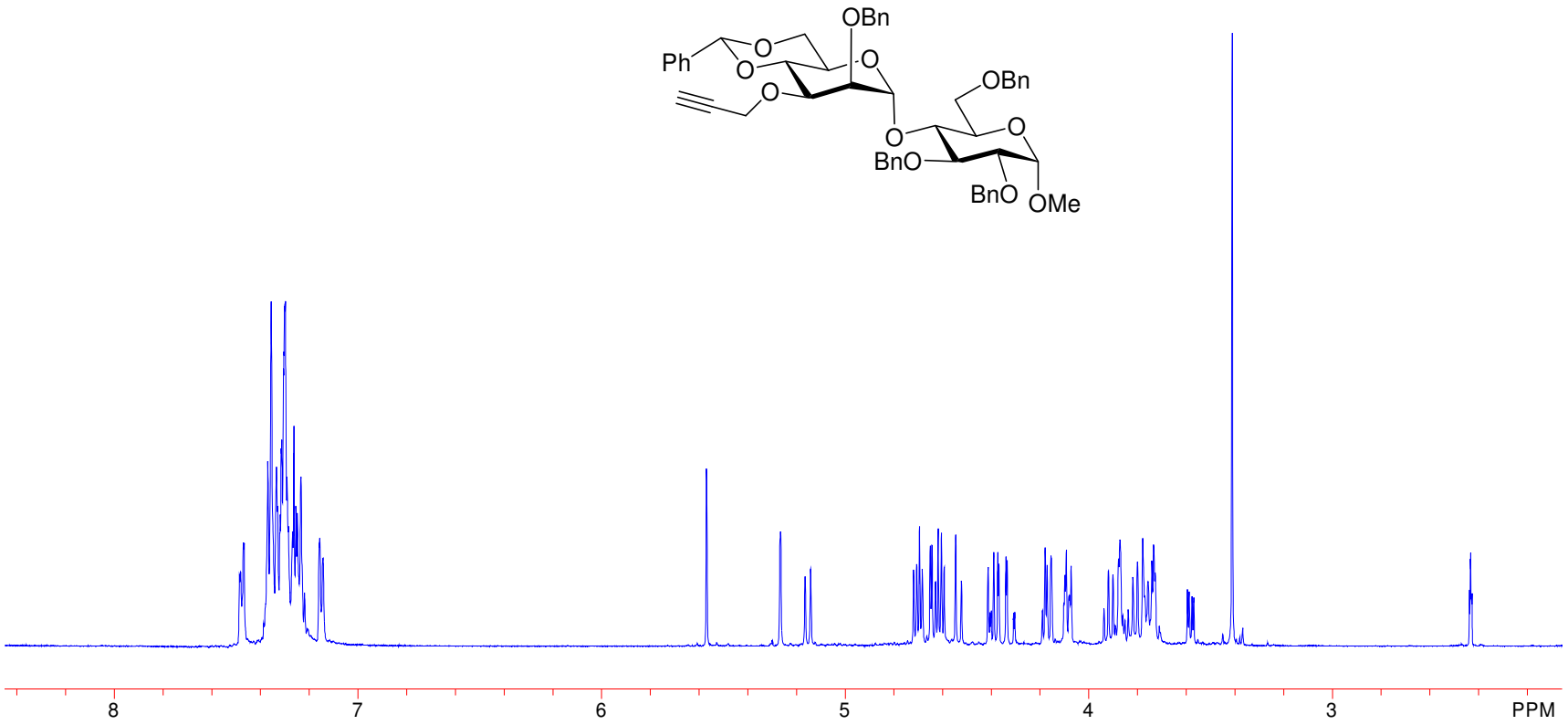
Methyl 2,3,6-tri-*O*-benzyl-4-*O*-[4,6-*O*-benzylidene-2-*O*-benzyl-3-*O*-(prop-2-ynyl)-β-D-mannopyranosyl]-(1→4)-α-D-glucopyranoside (39β)



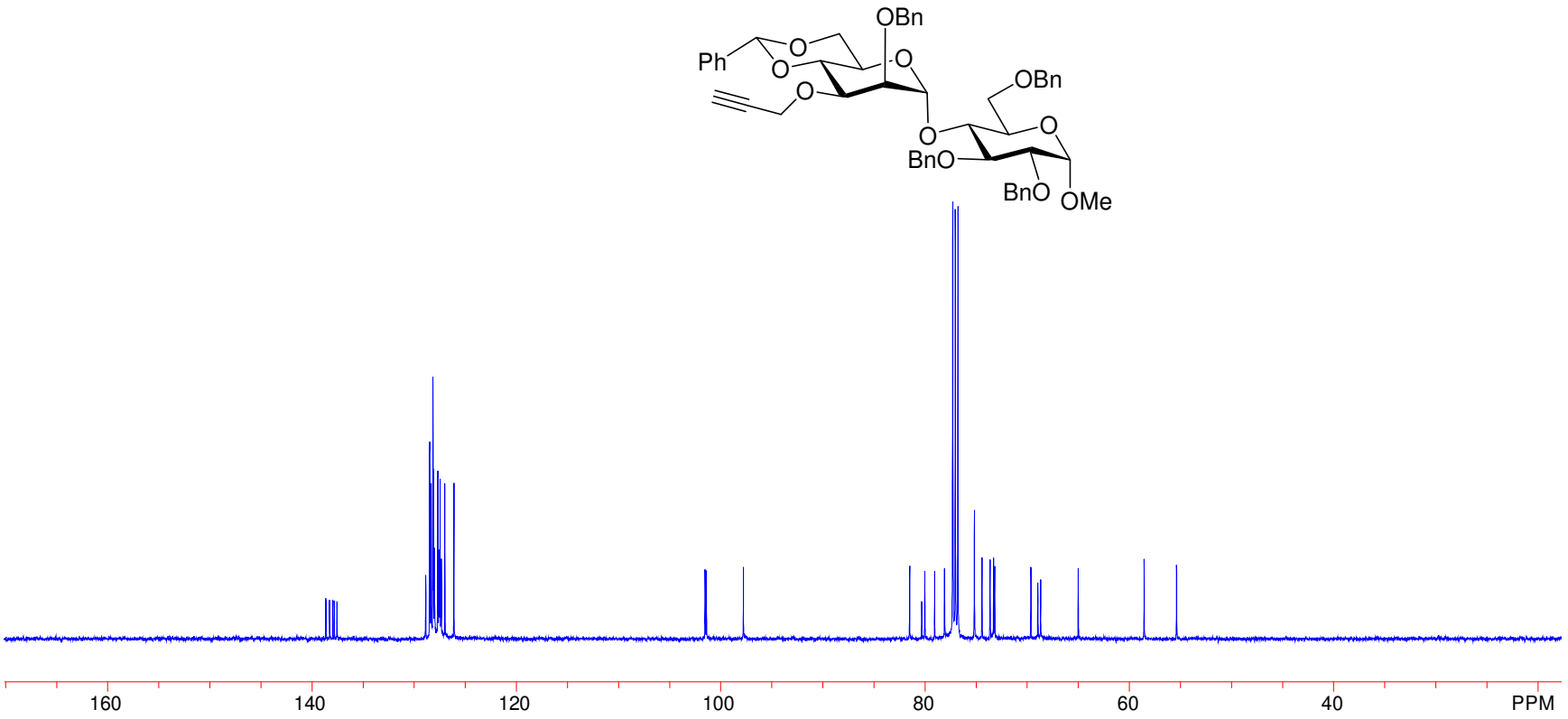
Methyl 2,3,6-tri-*O*-benzyl-4-*O*-[4,6-*O*-benzylidene-2-*O*-benzyl-3-*O*-(prop-2-ynyl)-β-D-mannopyranosyl]-(1→4)-α-D-glucopyranoside (39β).



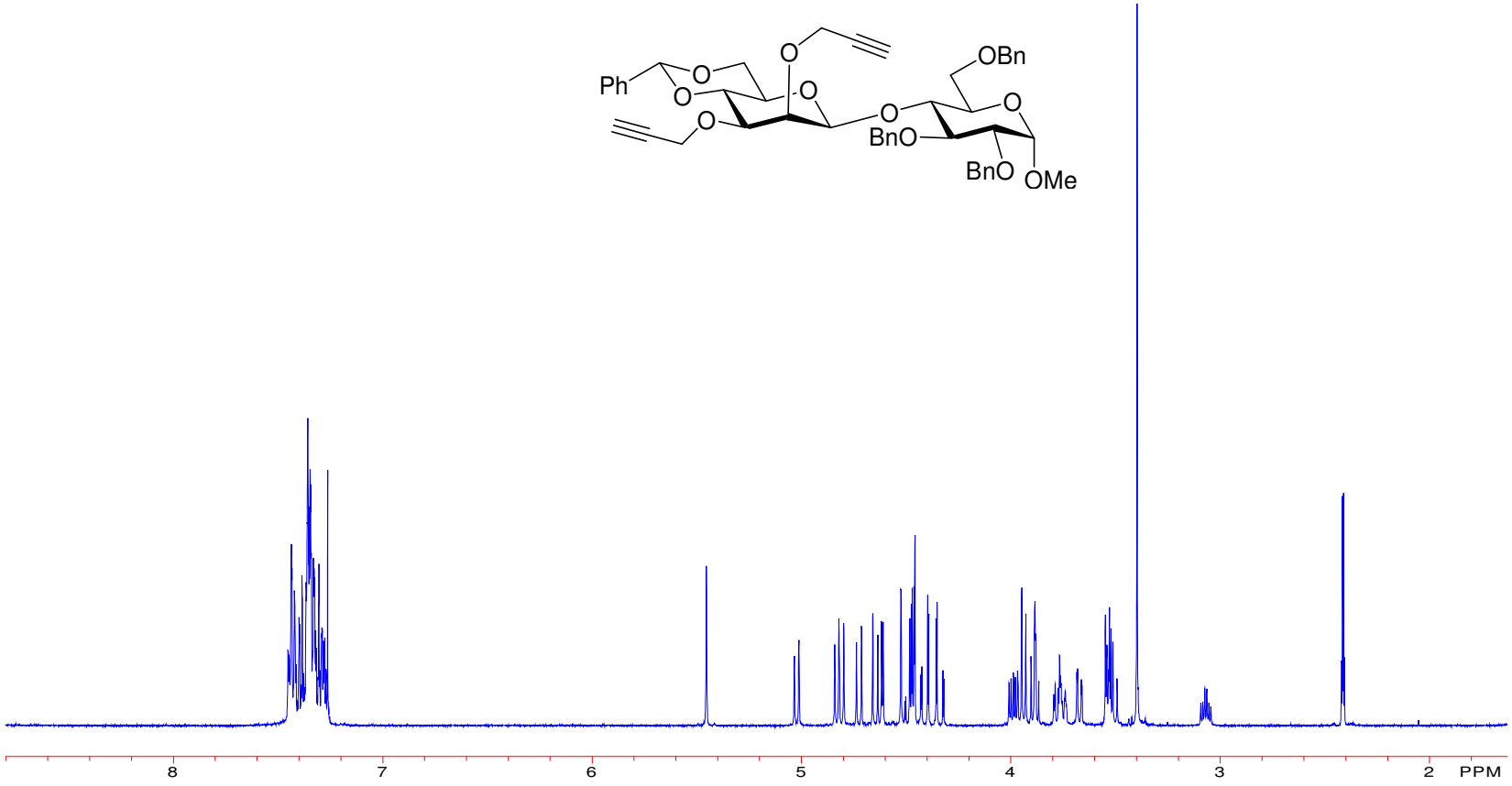
Methyl 2,3,6-tri-*O*-benzyl-4-*O*-[4,6-*O*-benzylidene-2-*O*-benzyl-3-*O*-(prop-2-ynyl)-α-D-mannopyranosyl]-(1→4)-α-D-glucopyranoside (39α).



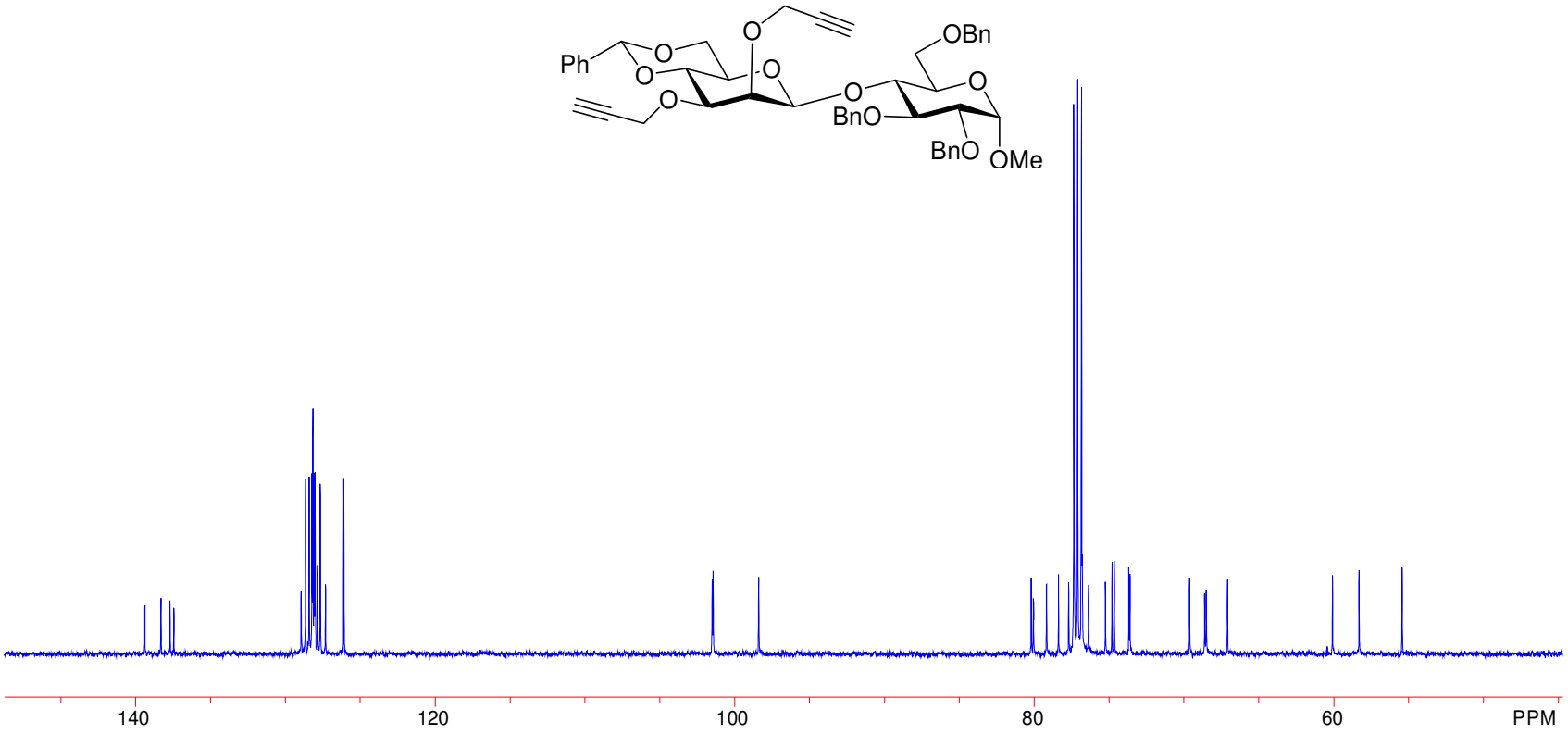
Methyl 2,3,6-tri-*O*-benzyl-4-*O*-[4,6-*O*-benzylidene-2-*O*-benzyl-3-*O*-(prop-2-ynyl)-α-D-mannopyranosyl]-(1→4)-α-D-glucopyranoside (39α).



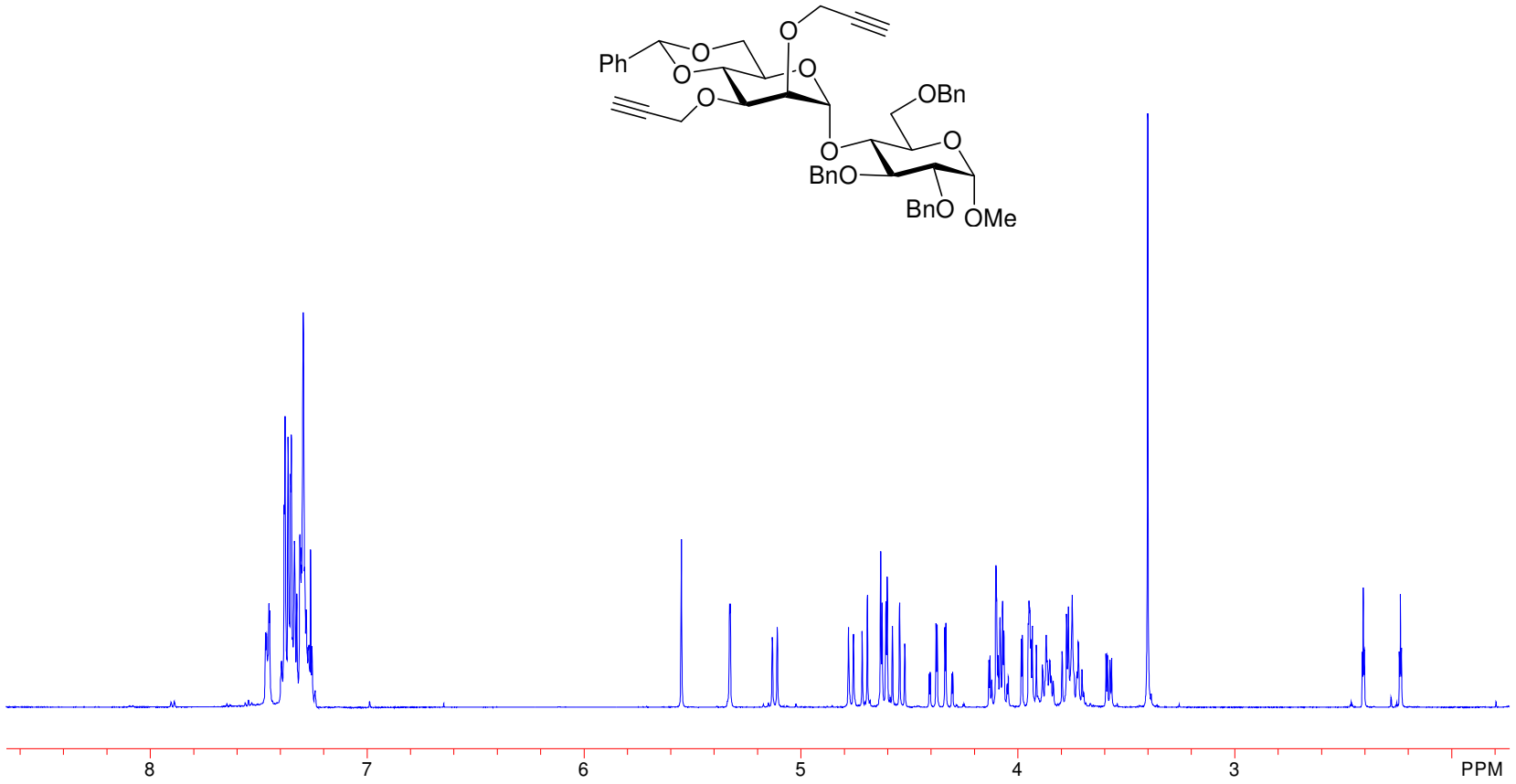
Methyl 2,3,6-tri-*O*-benzyl-4-*O*-[4,6-*O*-benzylidene-2,3-di-*O*-(prop-2-ynyl)-β-D-mannopyranosyl]-(1→4)-α-D-glucopyranoside (40β).



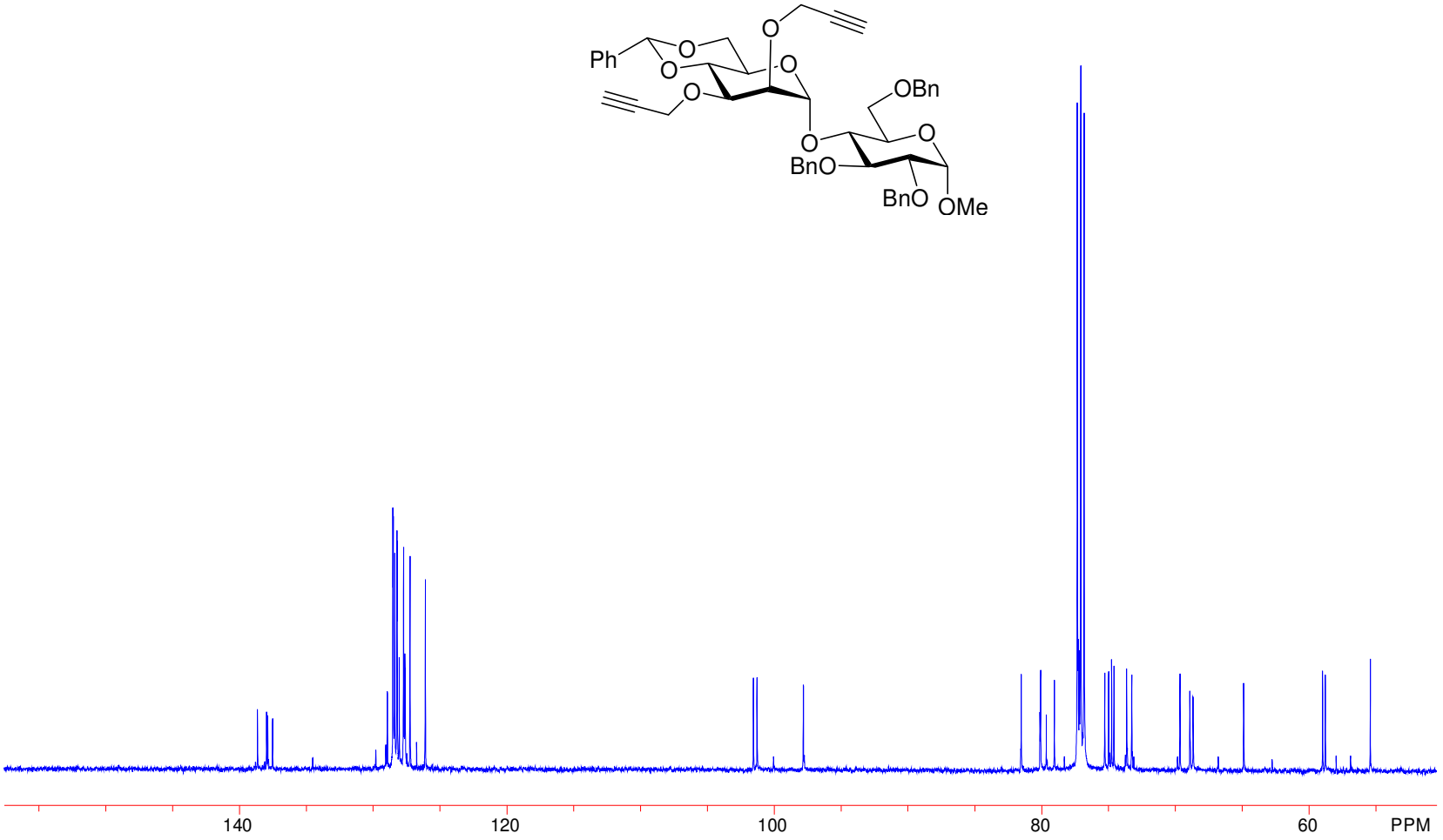
Methyl 2,3,6-tri-*O*-benzyl-4-*O*-[4,6-*O*-benzylidene-2,3-di-*O*-(prop-2-ynyl)-β-D-mannopyranosyl]-(1→4)-α-D-glucopyranoside (40β).



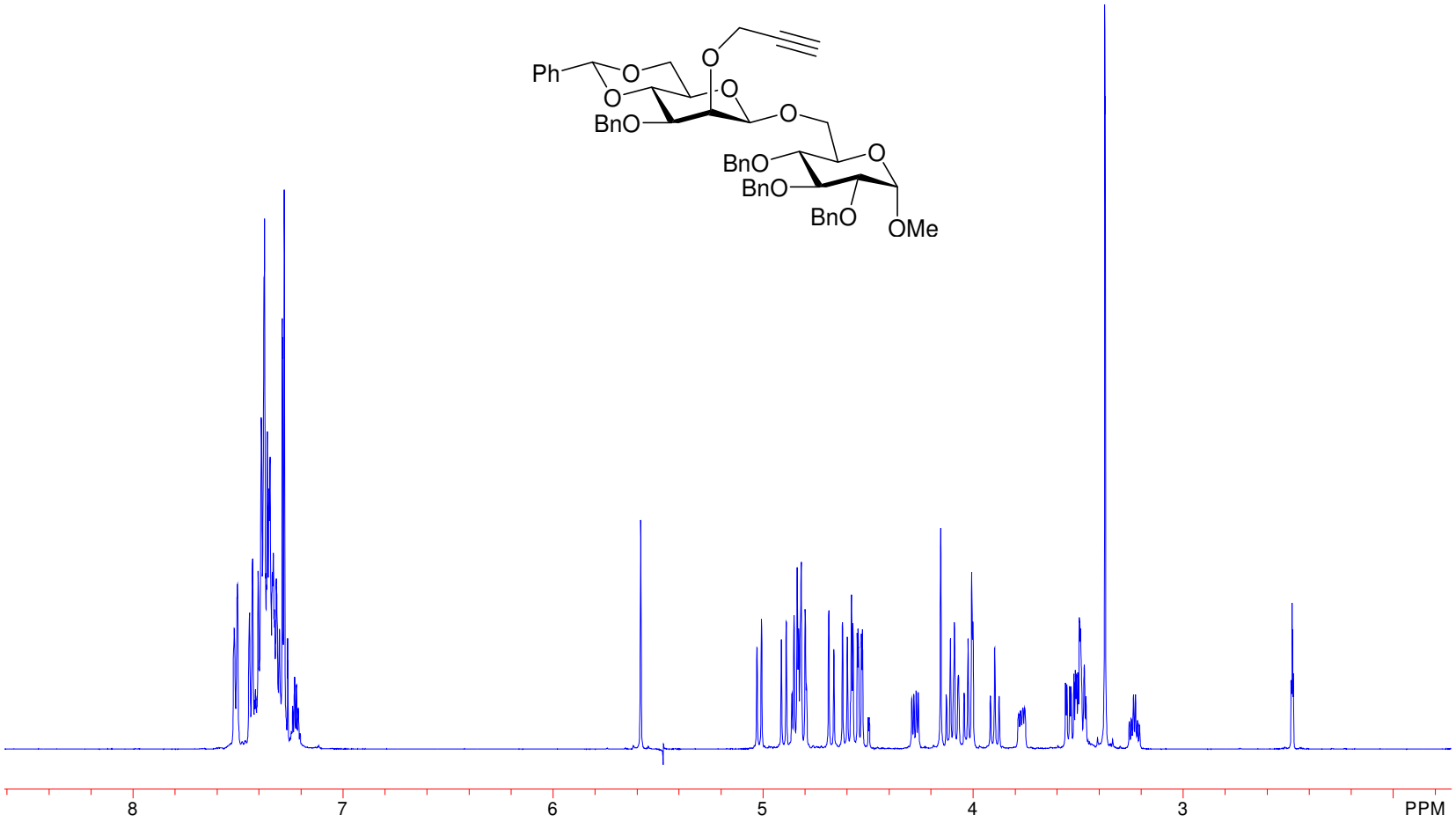
Methyl 2,3,6-tri-*O*-benzyl-4-*O*-[4,6-*O*-benzylidene-2,3-di-*O*-(prop-2-ynyl)-α-D-mannopyranosyl]-(1→4)-α-D-glucopyranoside (40α).



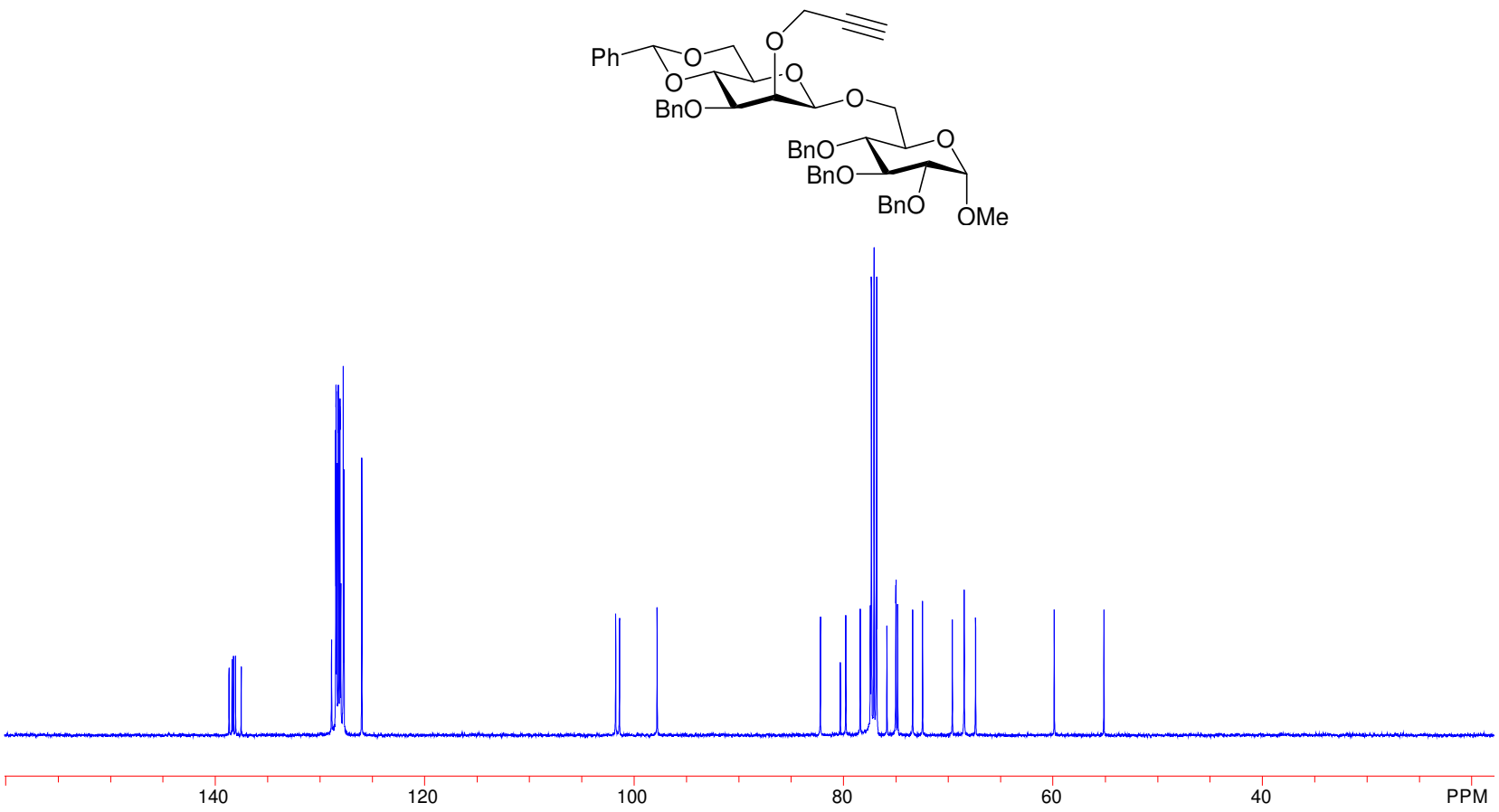
Methyl 2,3,6-tri-*O*-benzyl-4-*O*-[4,6-*O*-benzylidene-2,3-di-*O*-(prop-2-ynyl)-α-D-mannopyranosyl]-(1→4)-α-D-glucopyranoside (40α).



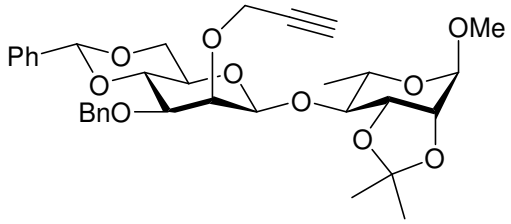
Methyl 2,3,6-tri-*O*-benzyl-6-*O*-[4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-benzyl-β-D-mannopyranosyl]-(1→6)-α-D-glucopyranoside (45β).



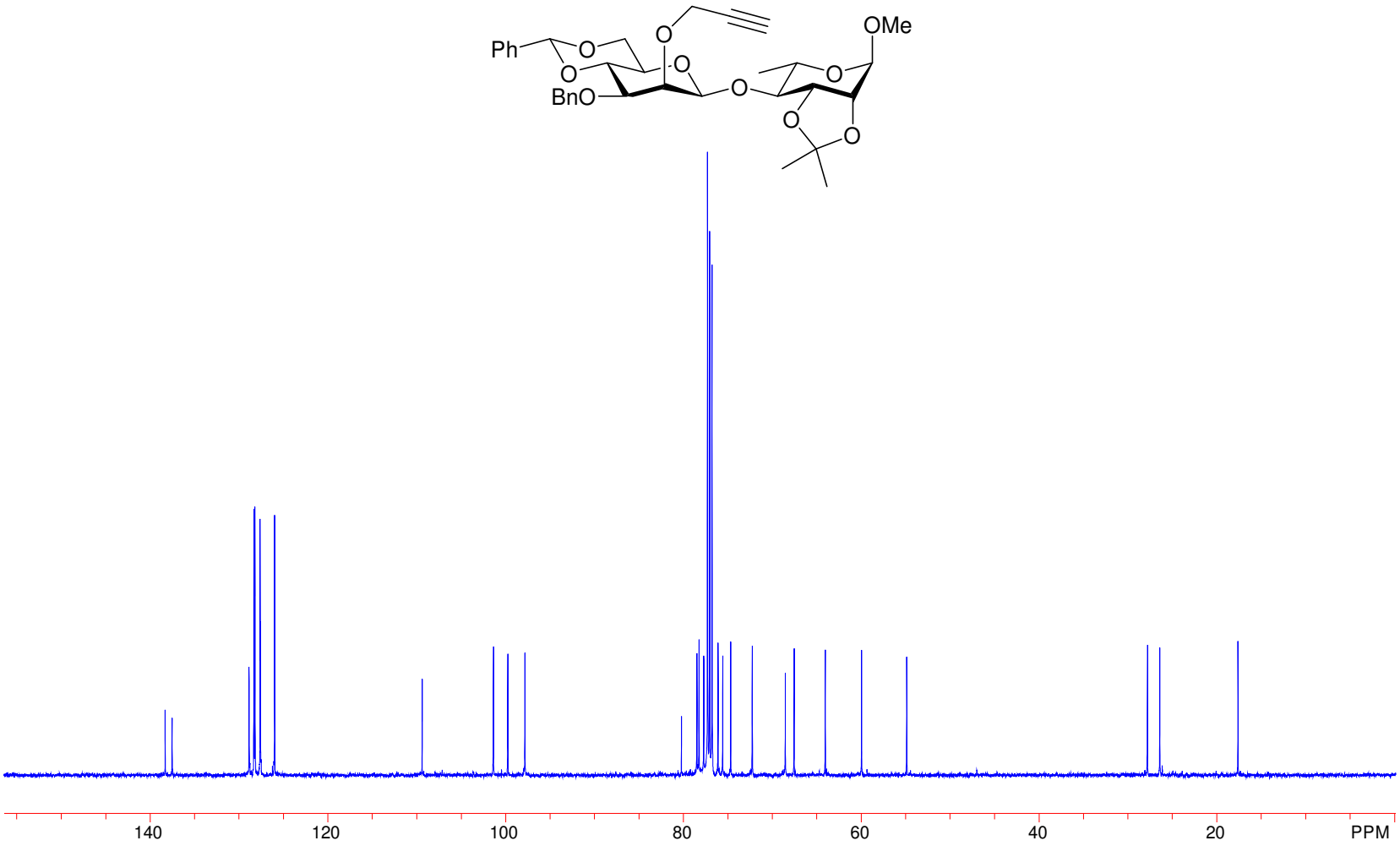
Methyl 2,3,6-tri-*O*-benzyl-6-*O*-[4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-benzyl-β-D-mannopyranosyl]-(1→6)-α-D-glucopyranoside (45β).



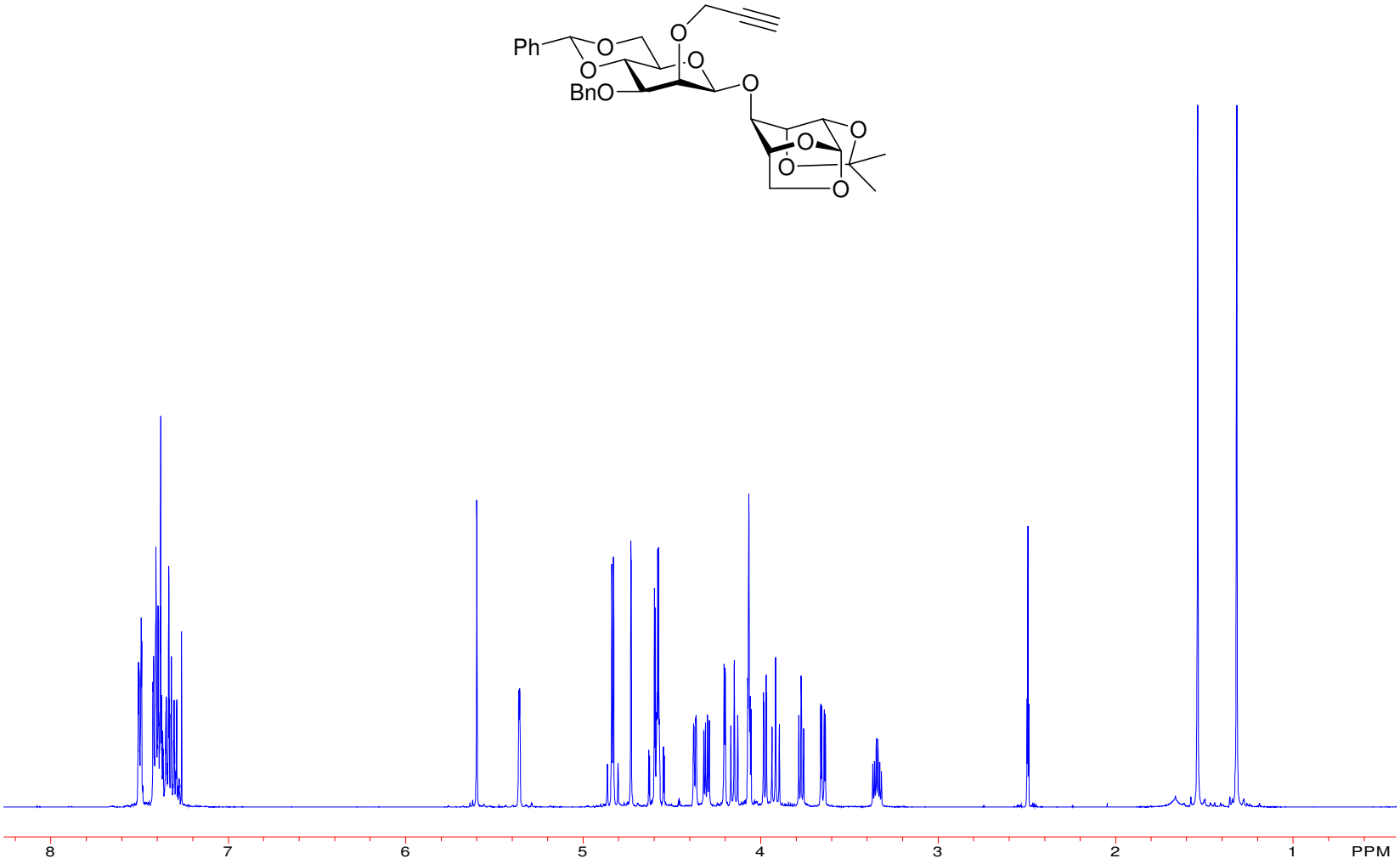
Methyl 4-*O*-[4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-benzyl-β-D-mannopyranosyl]-(1→4)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (46β).



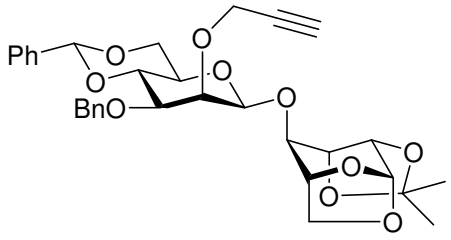
Methyl 4-*O*-[4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-benzyl-β-D-mannopyranosyl]-(1→4)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (46β).

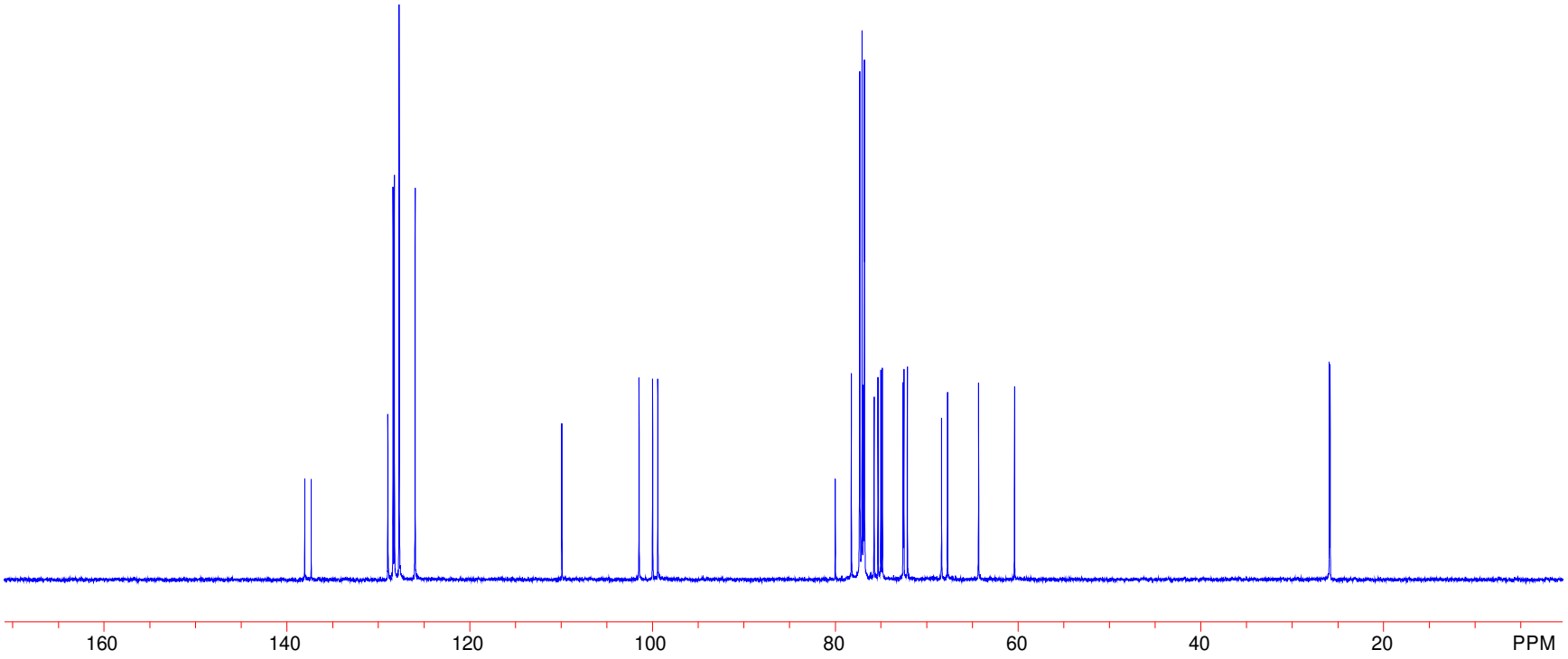


1,6-Anhydro-4-*O*-[4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-benzyl-β-D-mannopyranosyl]-(1→4)-2,3-*O*-isopropylidene-β-D-mannopyranose (47β).

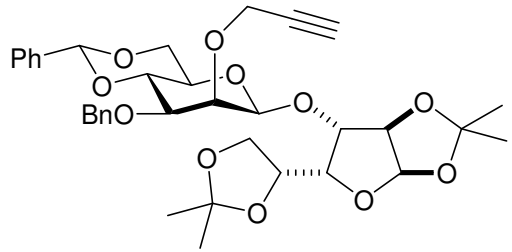


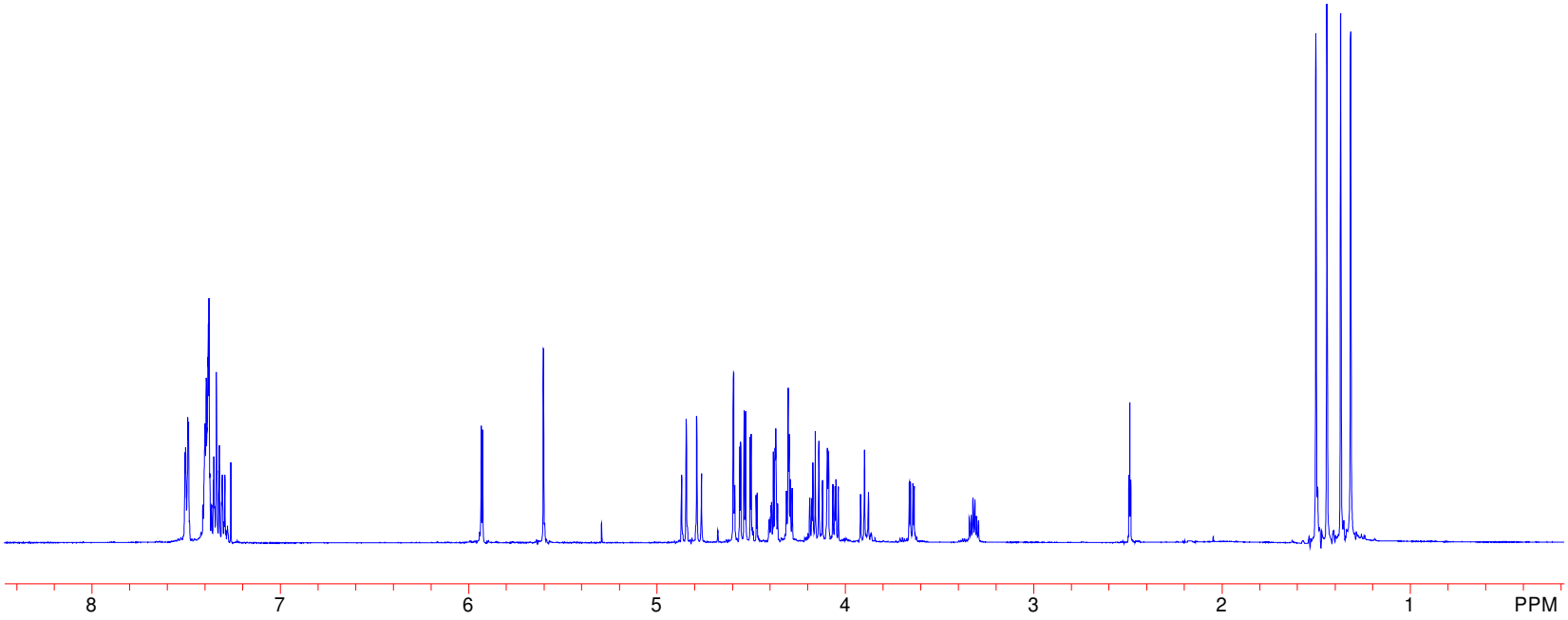
1,6-Anhydro-4-*O*-[4,6-*O*-benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-benzyl-β-D-mannopyranosyl]-(1→4)-2,3-*O*-isopropylidene-β-D-mannopyranose (47β).



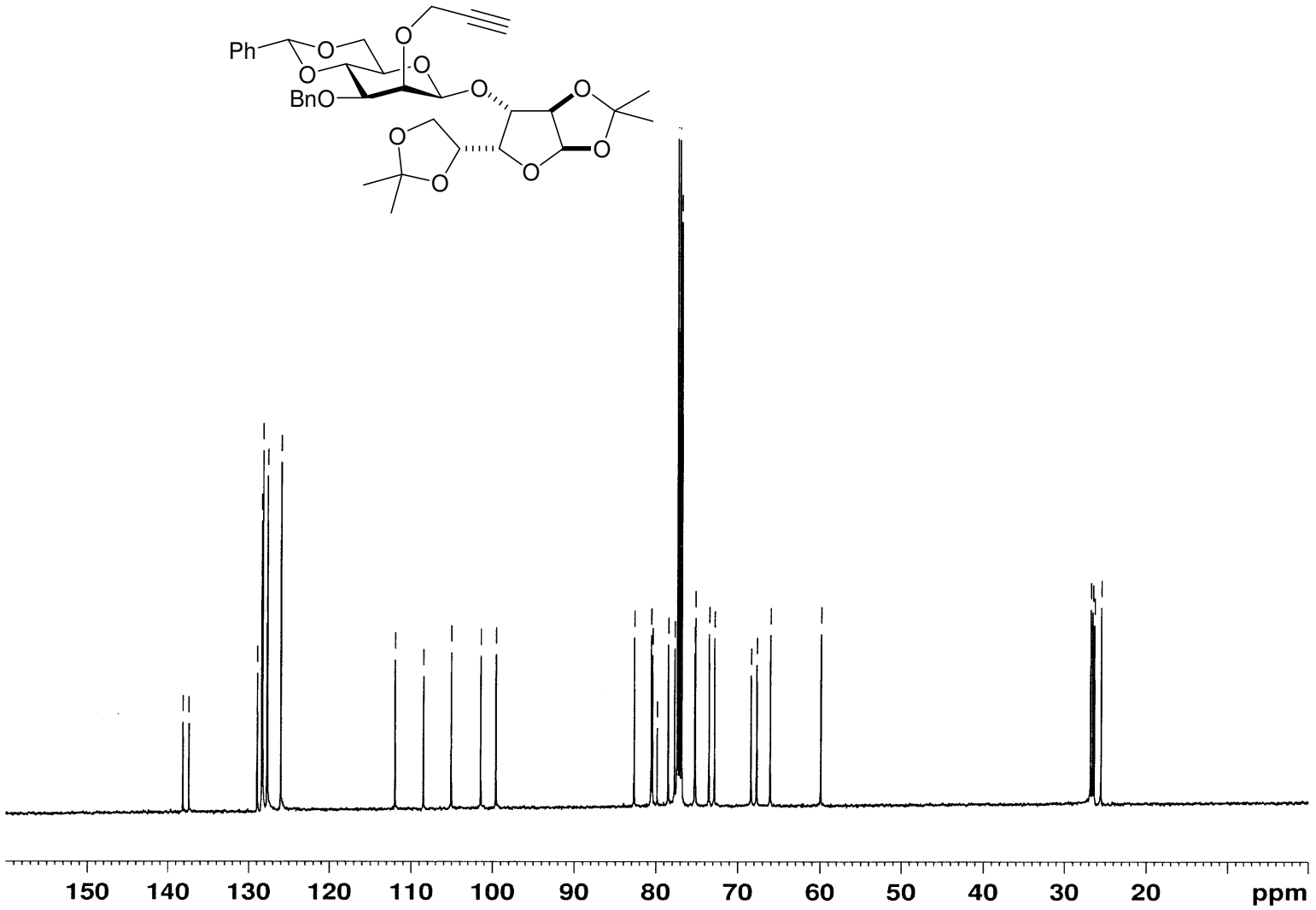


3-*O*-[4,6-*O*-Benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-benzyl-β-D-mannopyranosyl]-(1→3)-1,2:5,6-di-*O*-isopropylidene-*α*-D-glucofuranose (48β).

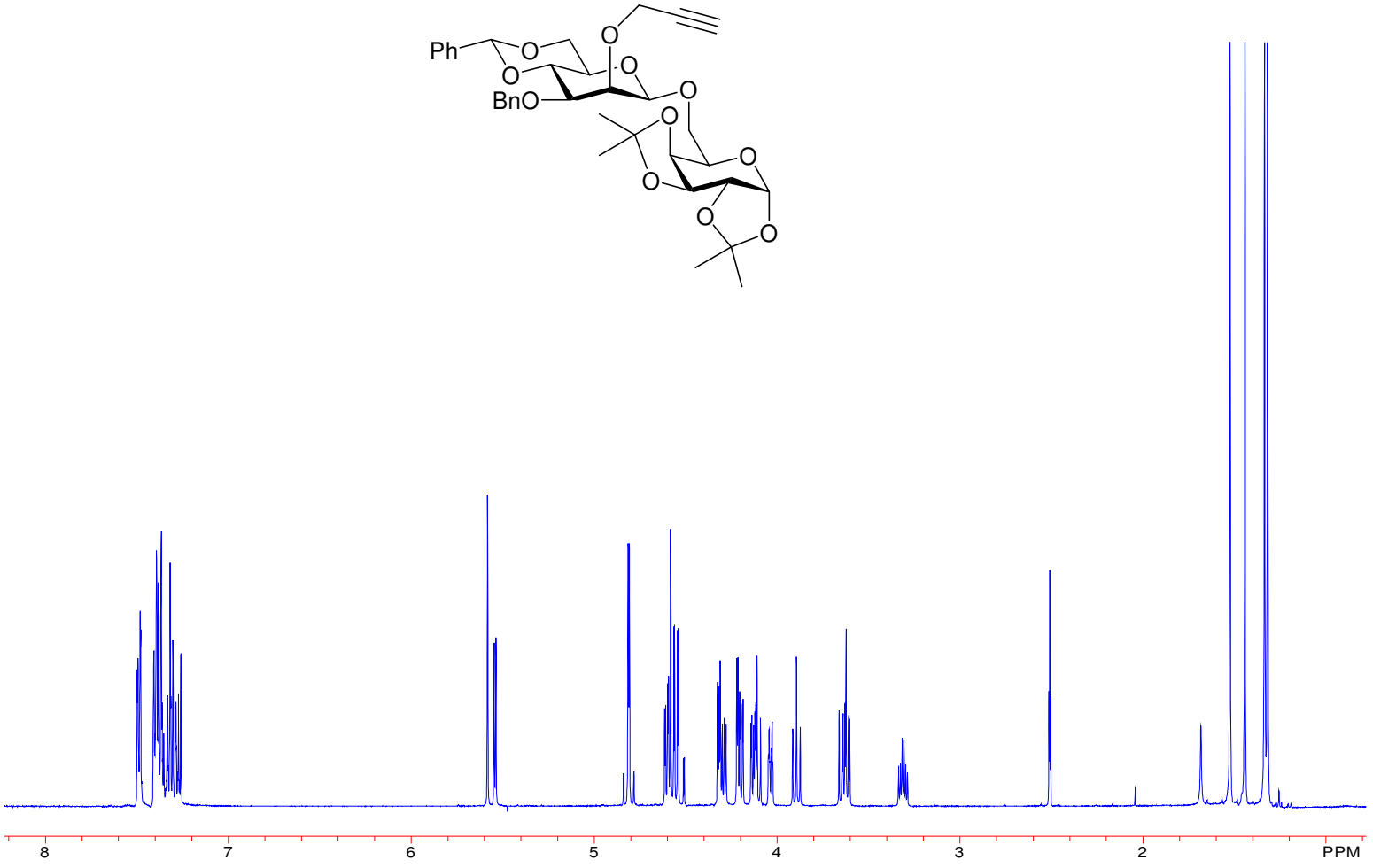




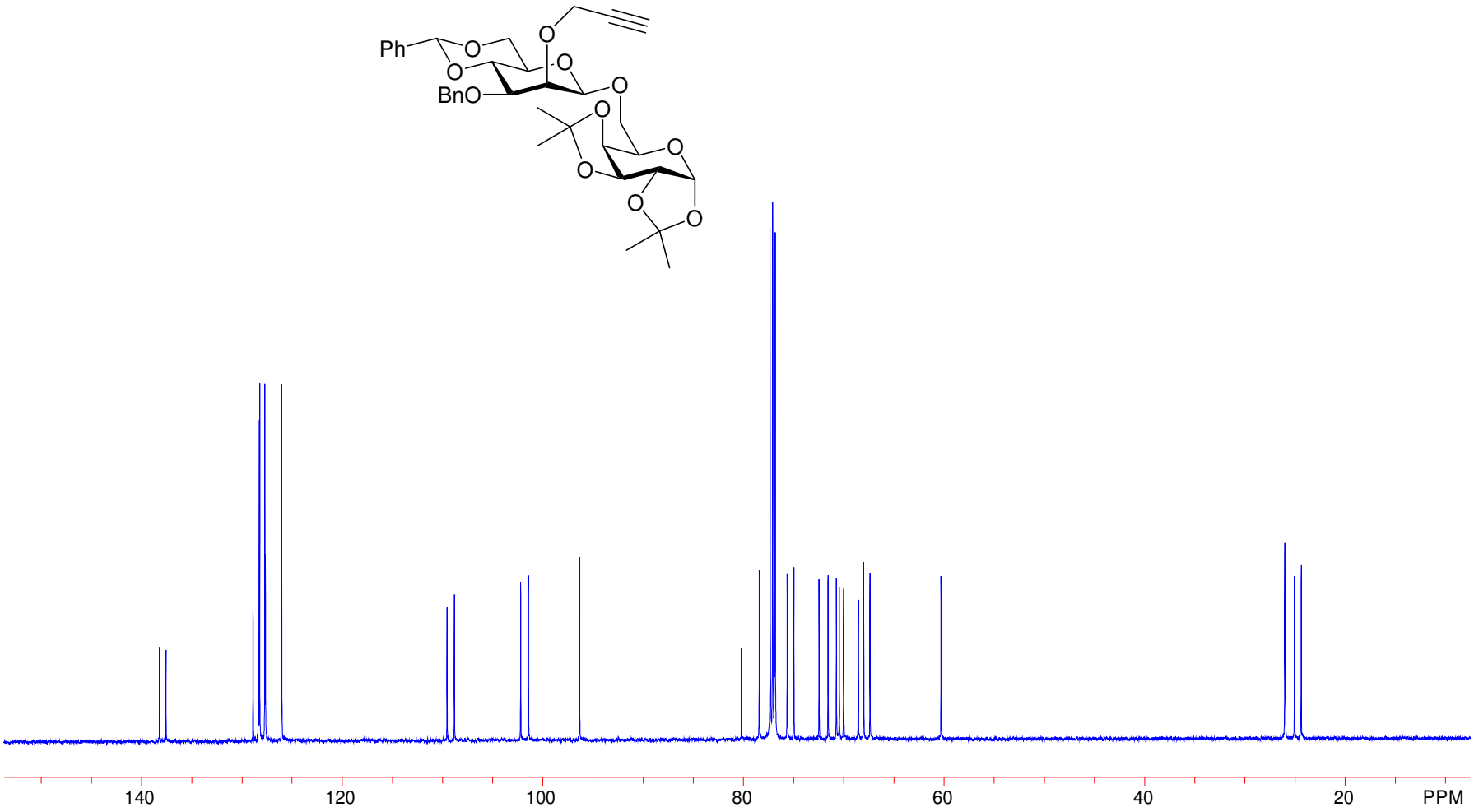
3-*O*-[4,6-*O*-Benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-benzyl-β-D-mannopyranosyl]-(1→3)-1,2:5,6-di-*O*-isopropylidene-*α*-D-glucofuranose (48β).



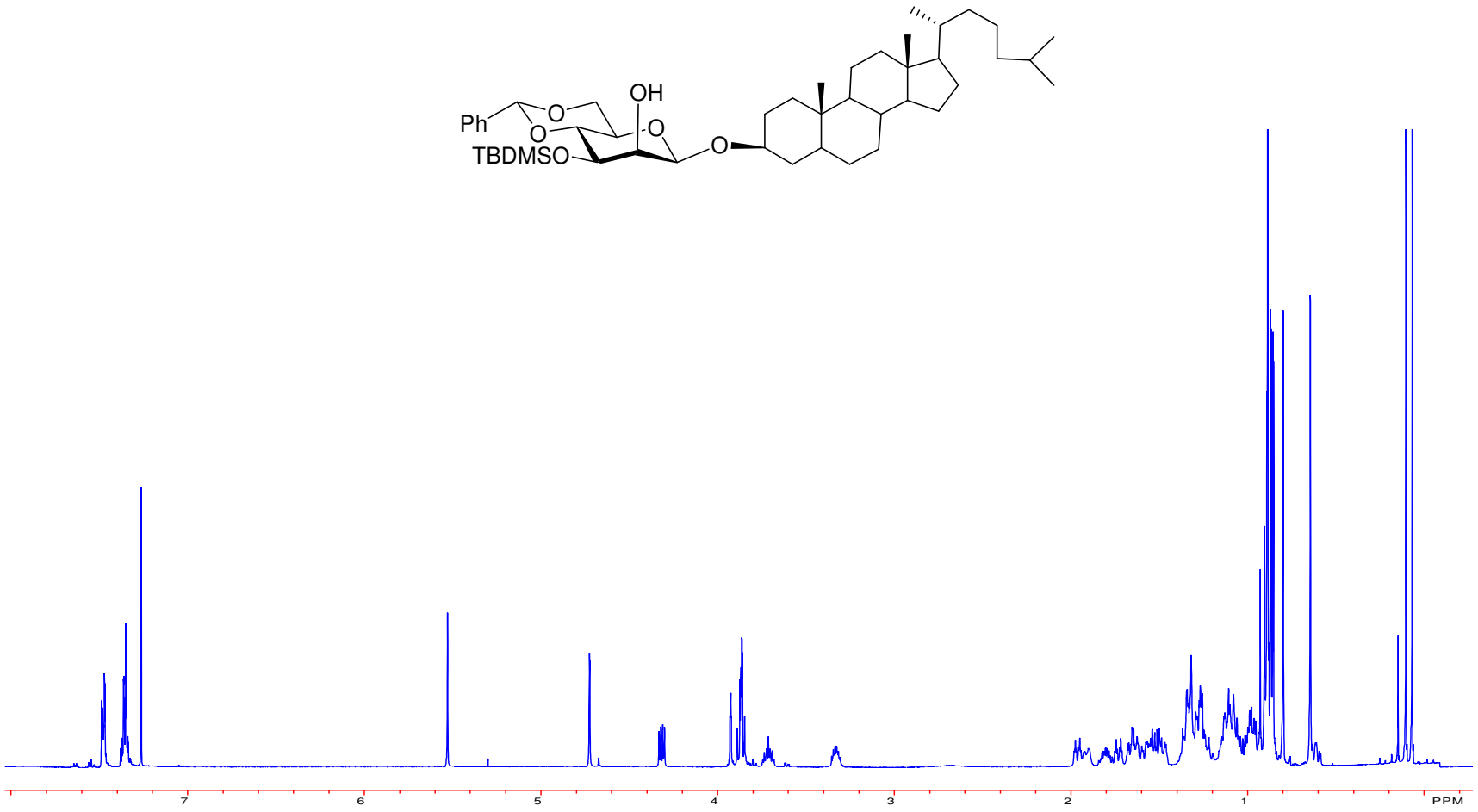
6-*O*-[4,6-*O*-Benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-benzyl-β-D-mannopyranosyl]-(1→6)-1,2:3,4-di-*O*-isopropylidene-*α*-D-galactopyranose (49β).



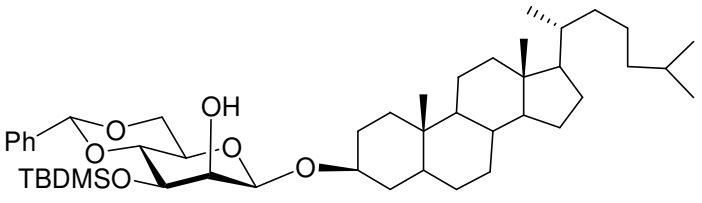
6-*O*-[4,6-*O*-Benzylidene-2-*O*-(prop-2-ynyl)-3-*O*-benzyl-β-D-mannopyranosyl]-(1→6)-1,2:3,4-di-*O*-isopropylidene-*α*-D-galactopyranose (49β).

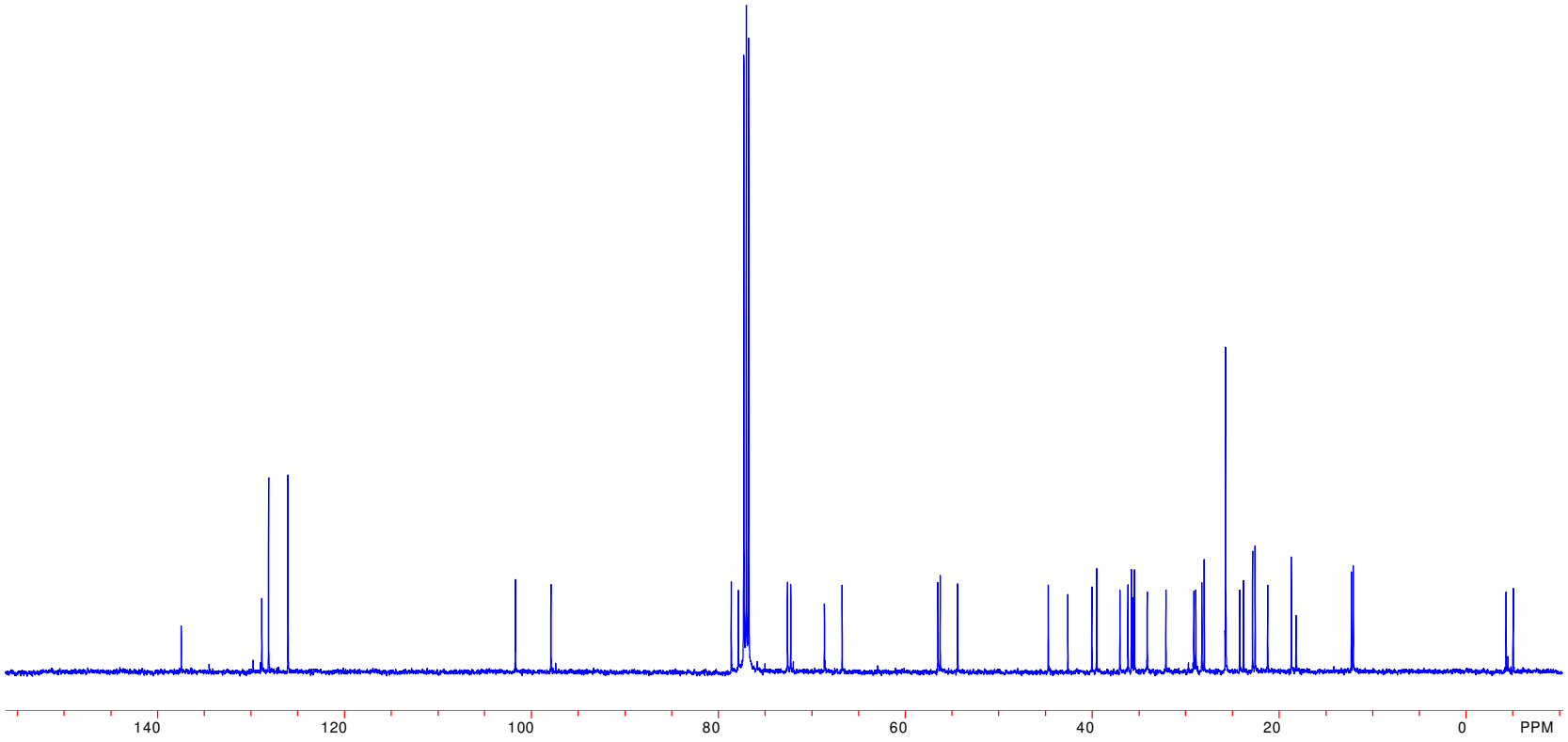


3β-Cholestanyl 4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl-β-D-mannopyranoside (50).

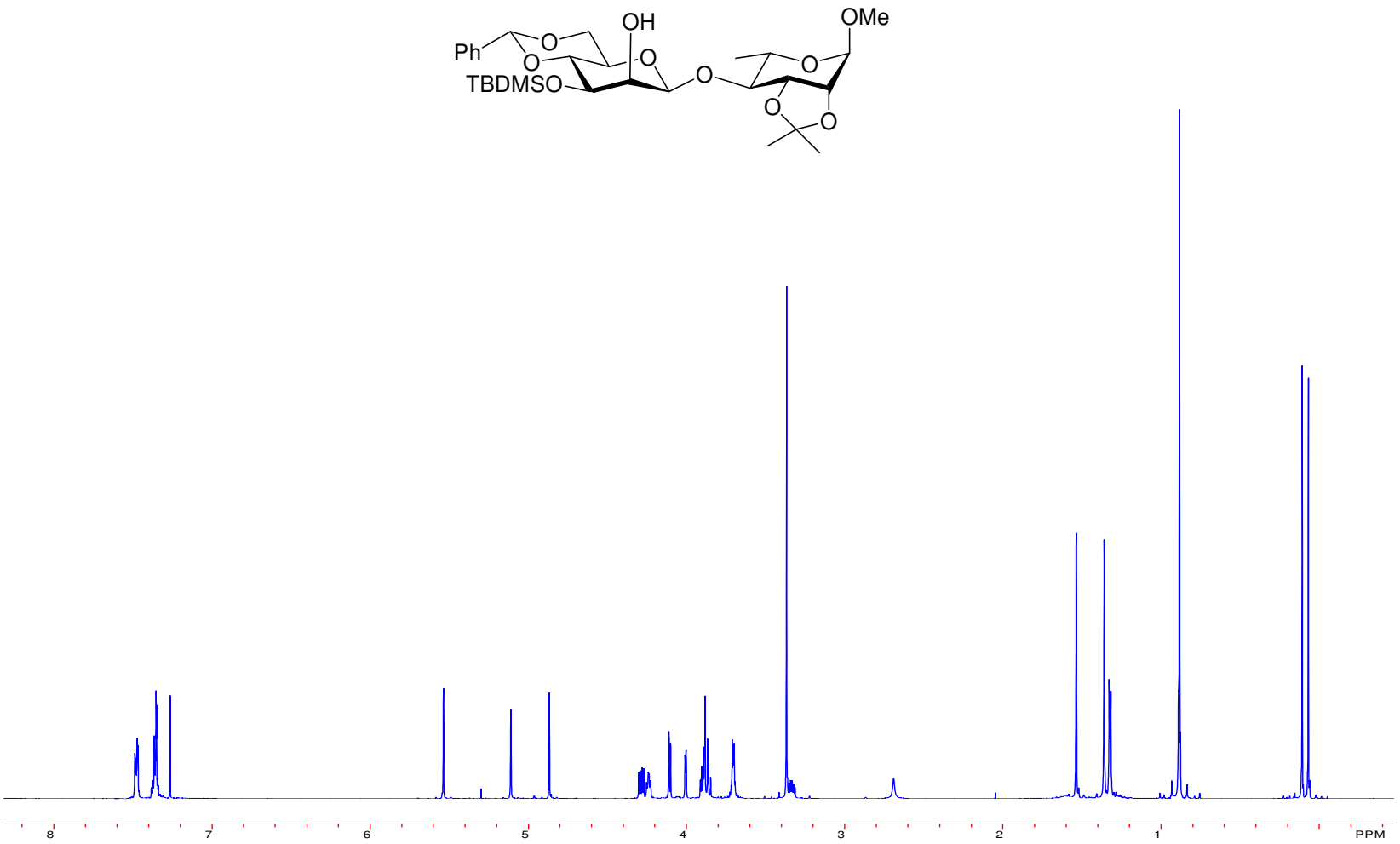


3β-Cholestanyl 4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl-β-D-mannopyranoside (50).

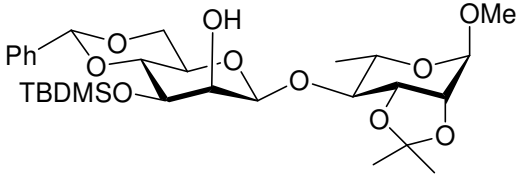


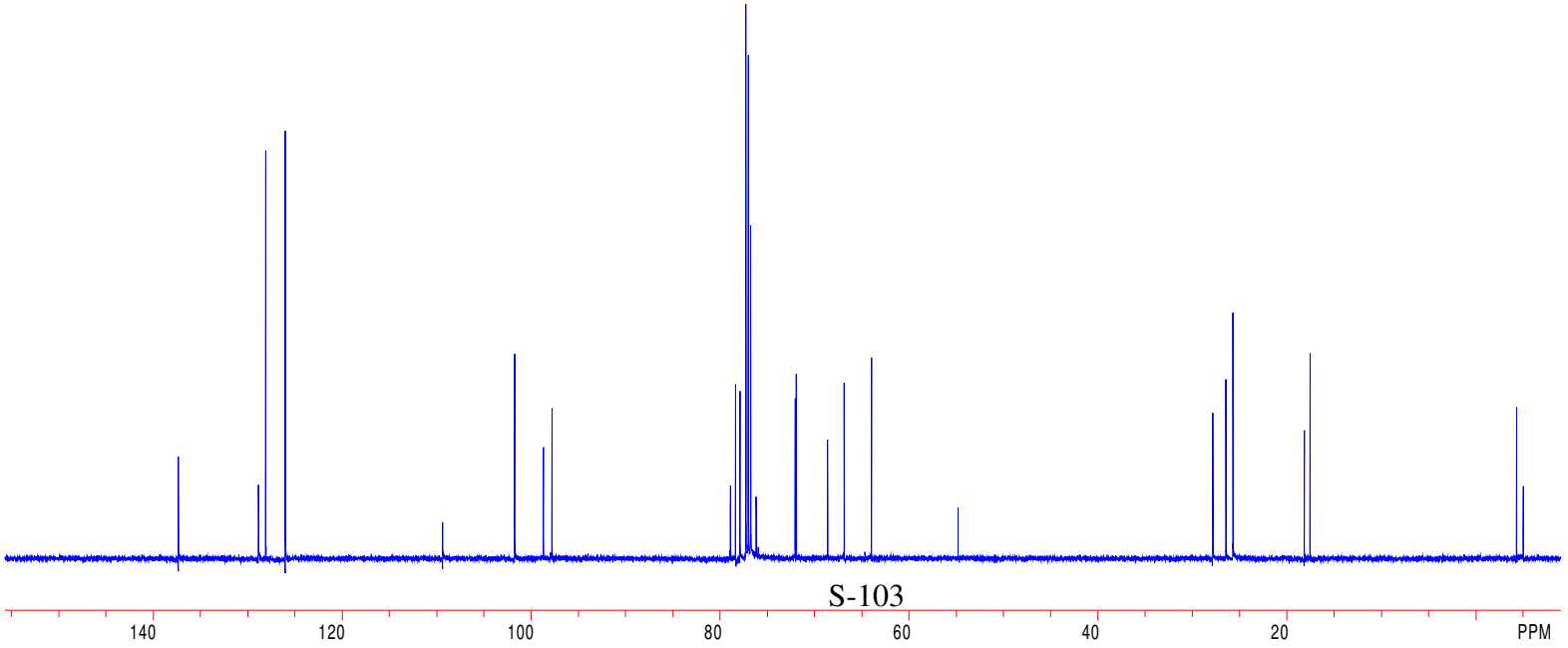


Methyl 4-*O*-(4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl-β-D-mannopyranosyl)-(1→4)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (51).

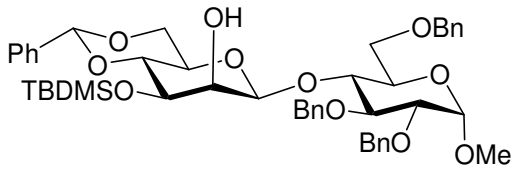


Methyl 4-*O*-(4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl-β-D-mannopyranosyl)-1→4)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (51).

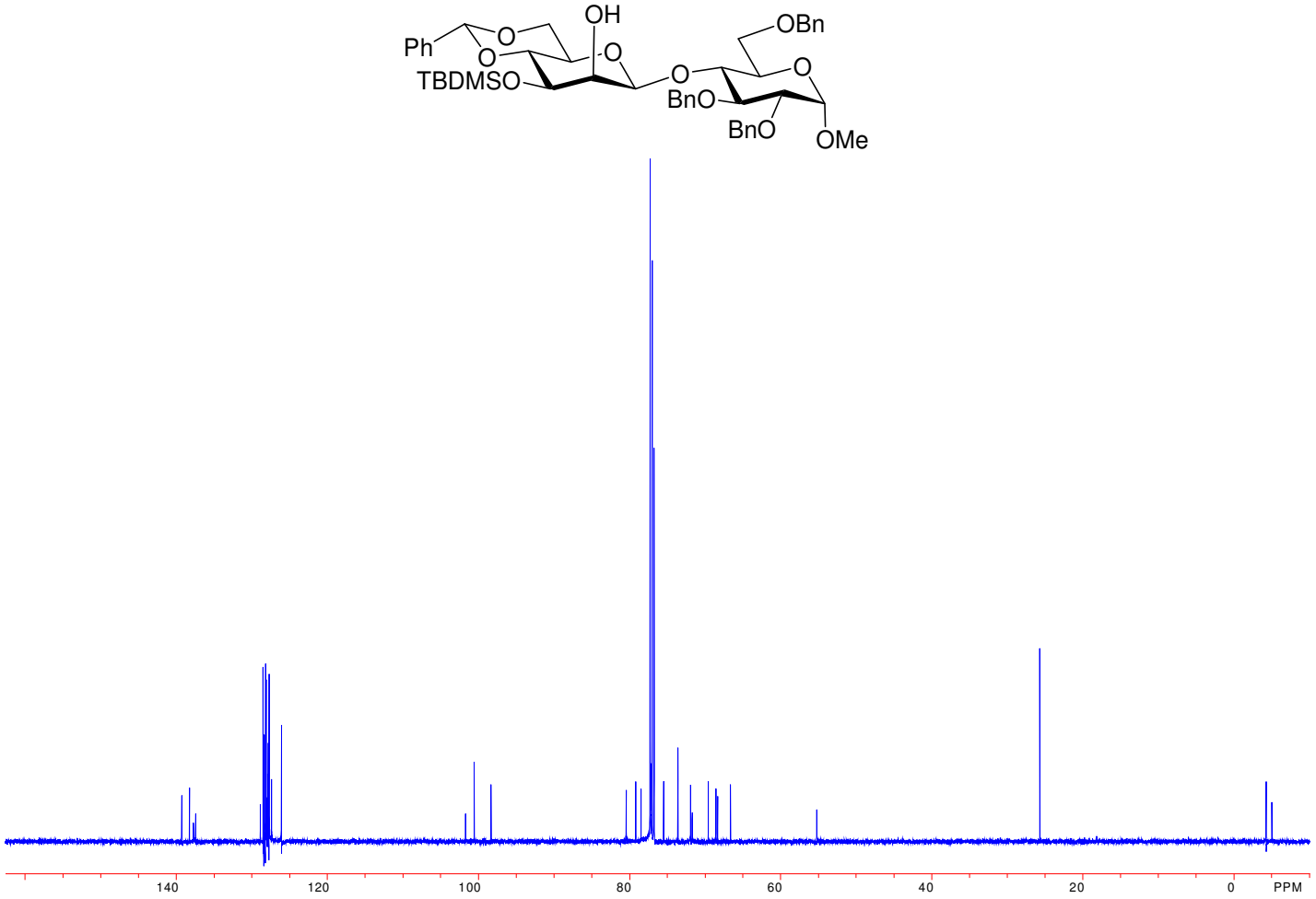




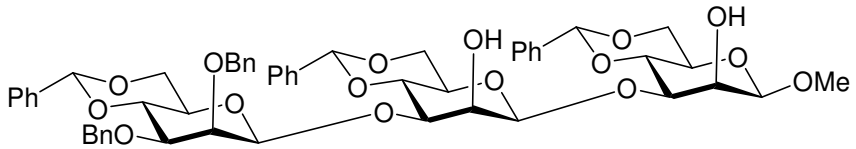
Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl-β-D-mannopyranosyl)-(1→4)-α-D-glucopyranoside (52).

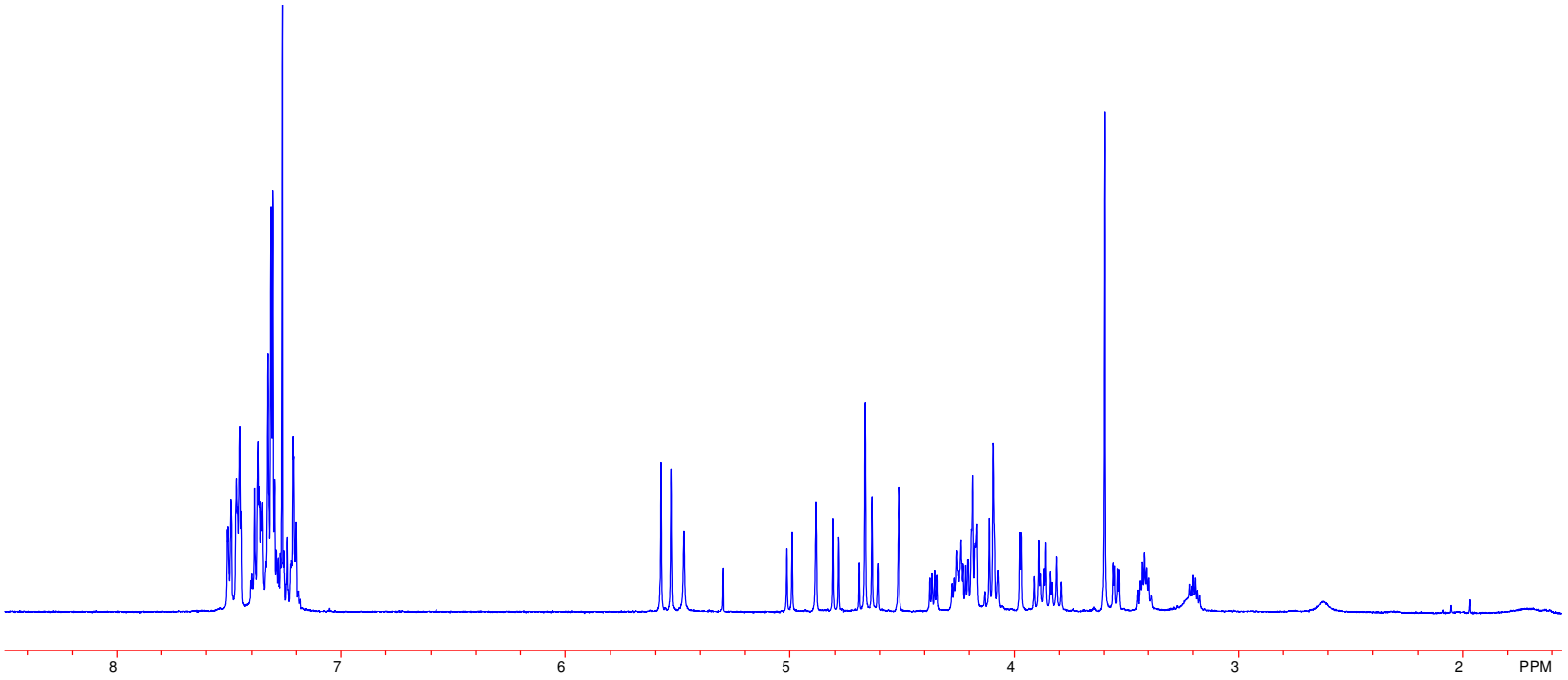


Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl-β-D-mannopyranosyl)-(1→4)-α-D-glucopyranoside (52).

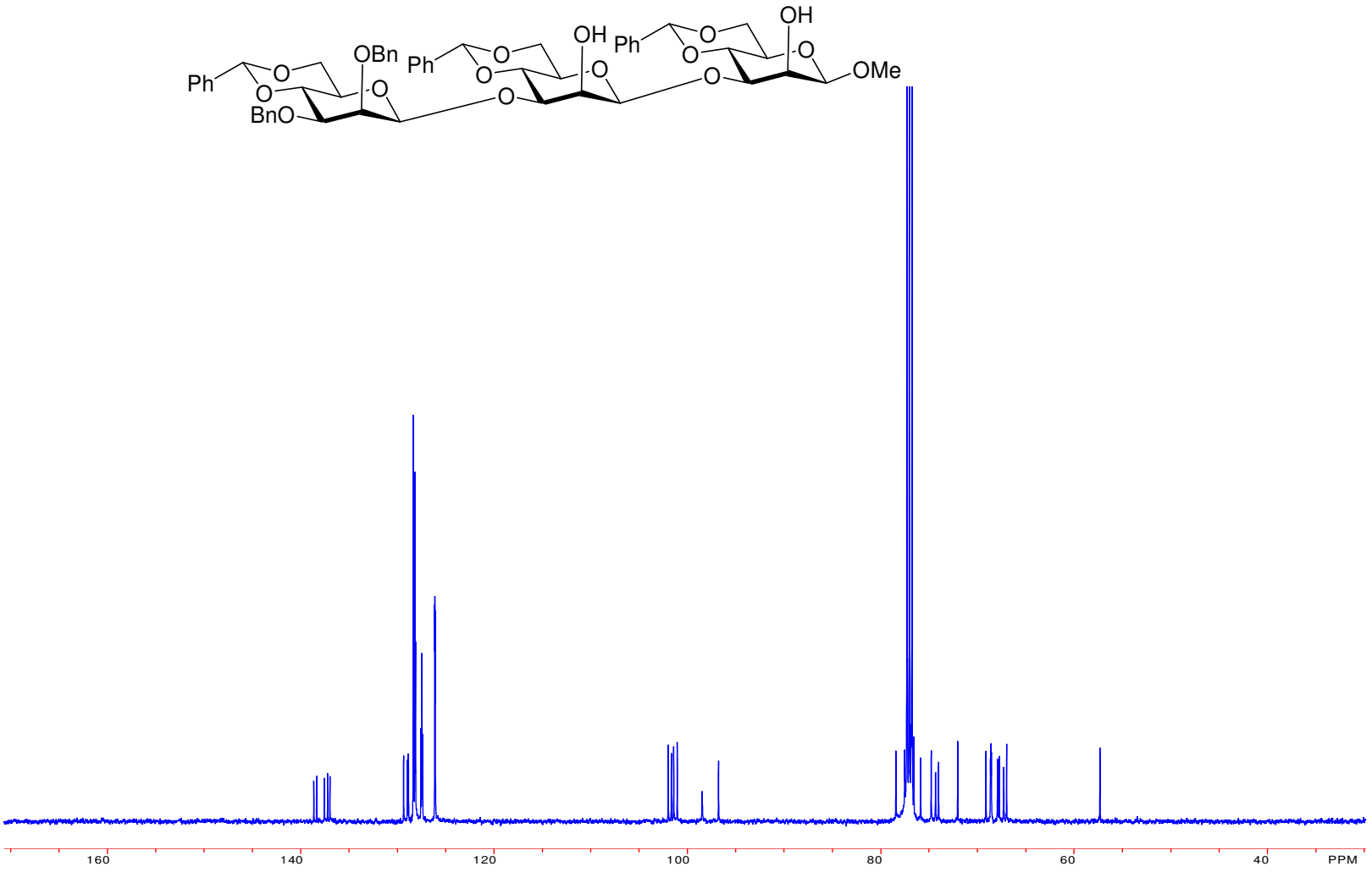


Methyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→3)-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→3)-4,6-*O*-benzylidene-β-D-mannopyranoside (53).

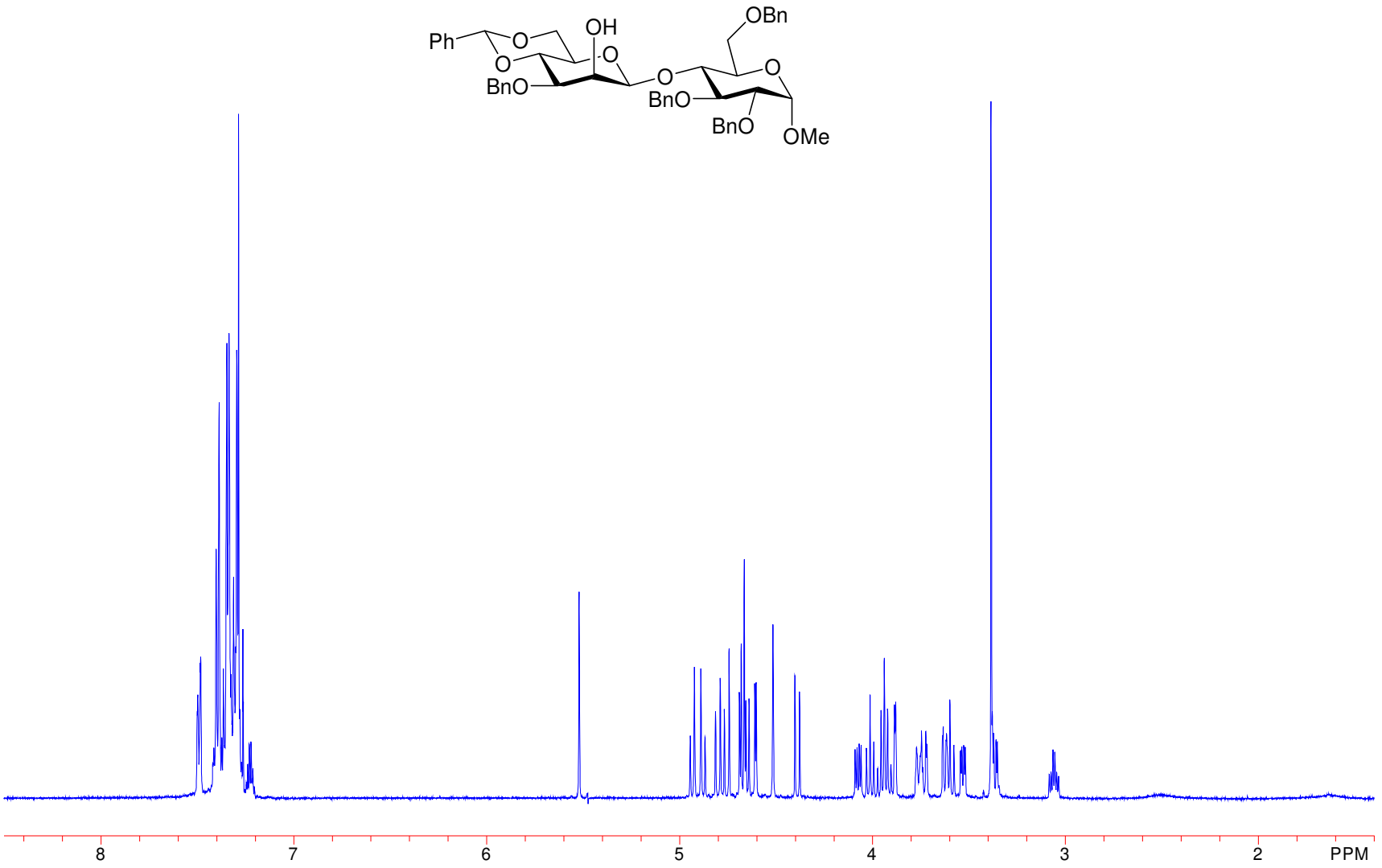




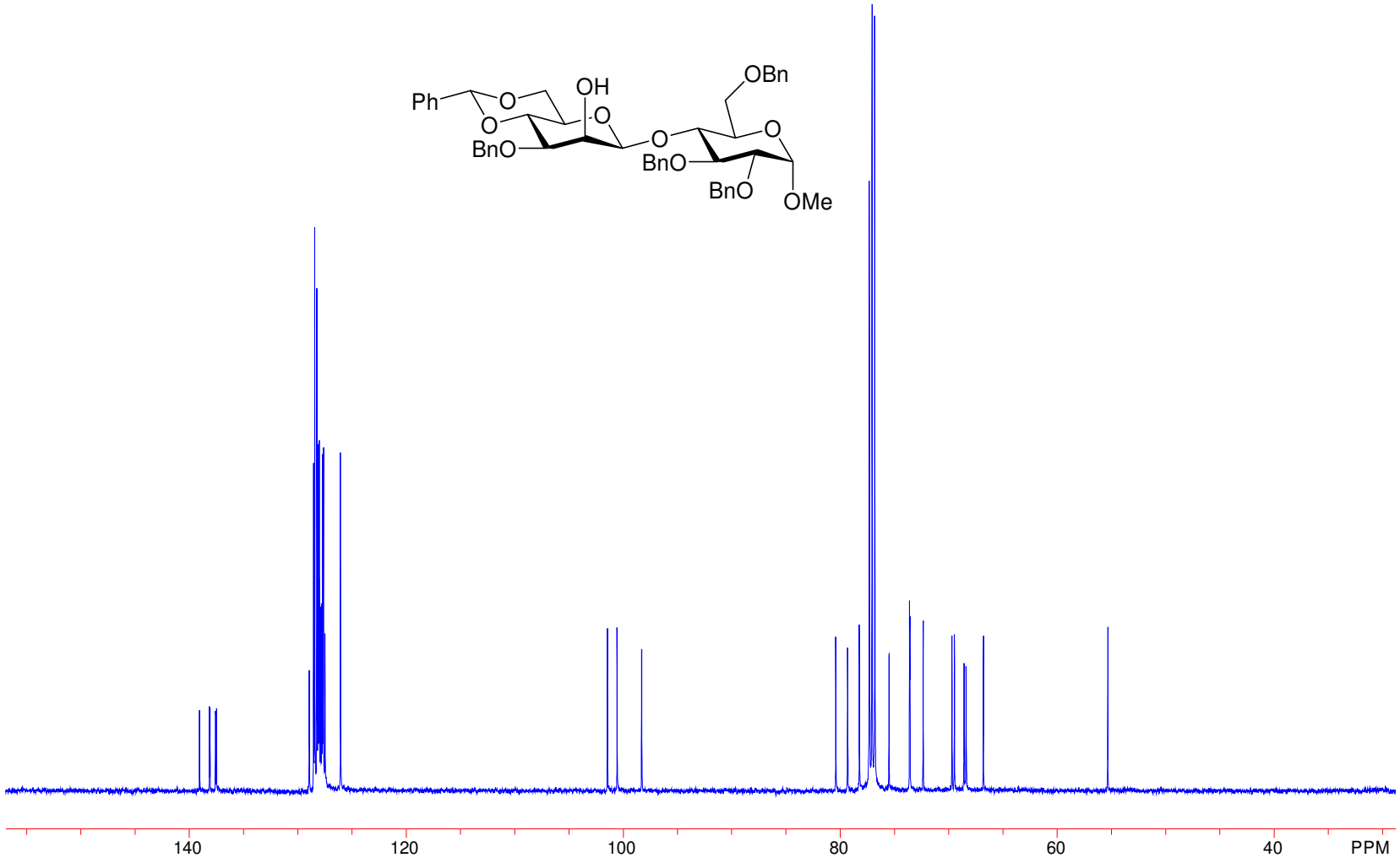
Methyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→3)-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1→3)-4,6-*O*-benzylidene-β-D-mannopyranoside (53).



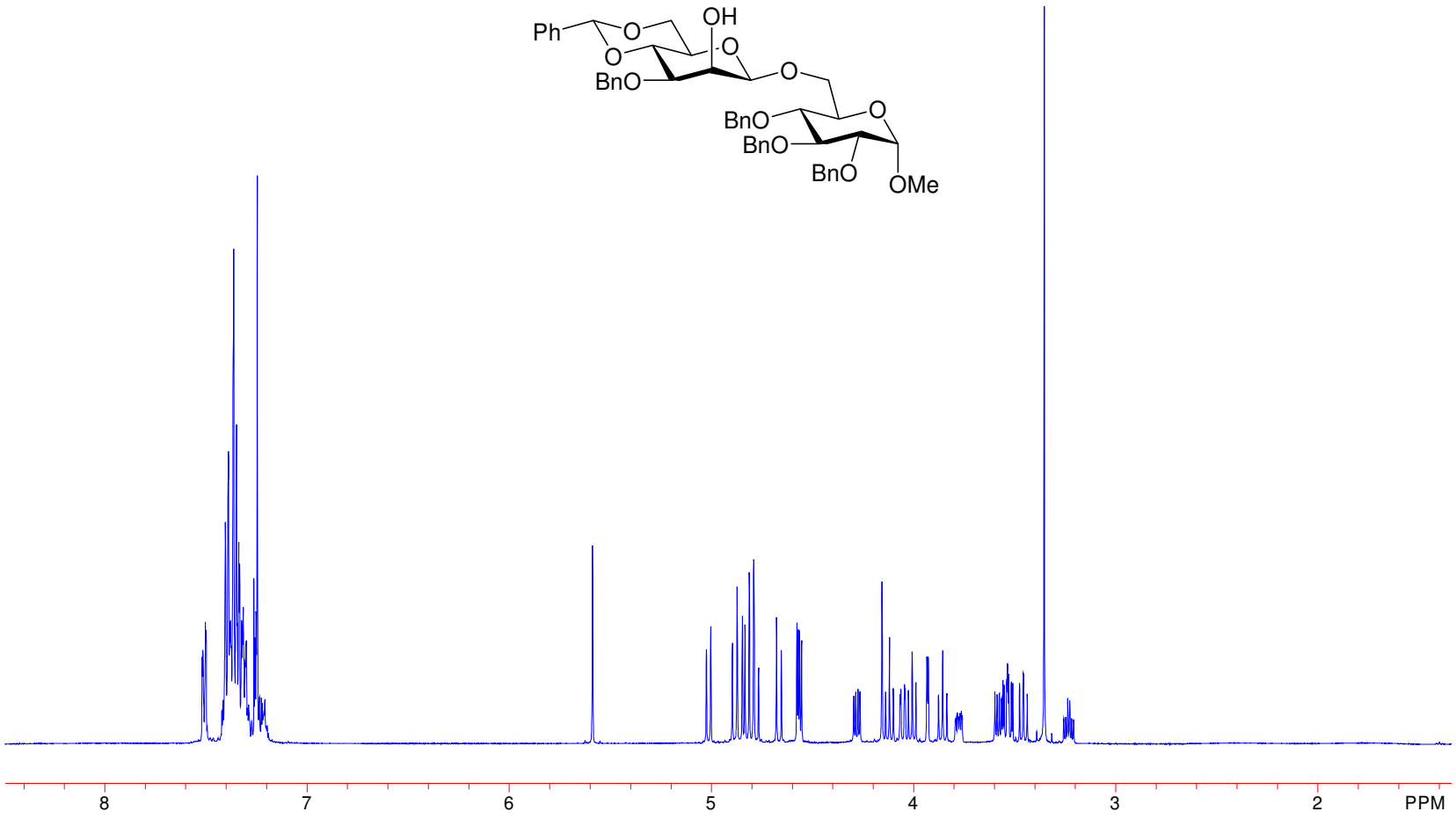
Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(4,6-*O*-benzylidene-3-*O*-benzyl-β-D-mannopyranosyl)-(1→4)-α-D-glucopyranoside (54).



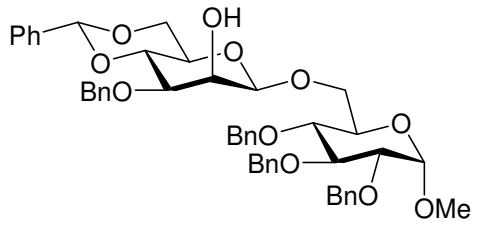
Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(4,6-*O*-benzylidene-3-*O*-benzyl-β-D-mannopyranosyl)-(1→4)-α-D-glucopyranoside (54).

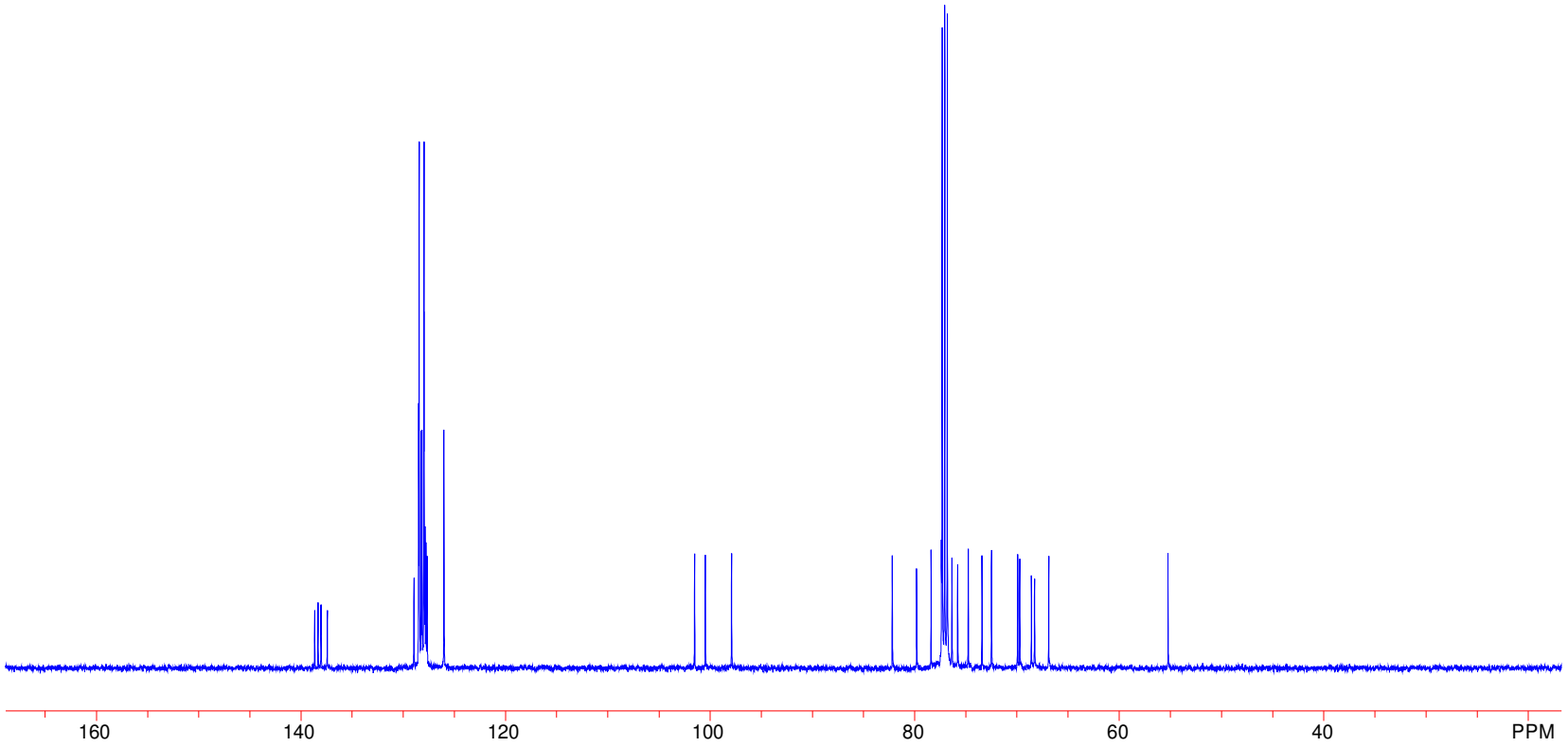


Methyl 2,3,6-tri-*O*-benzyl-6-*O*-(4,6-*O*-benzylidene-3-*O*-benzyl-β-D-mannopyranosyl)-(1→6)-α-D-glucopyranoside (55).

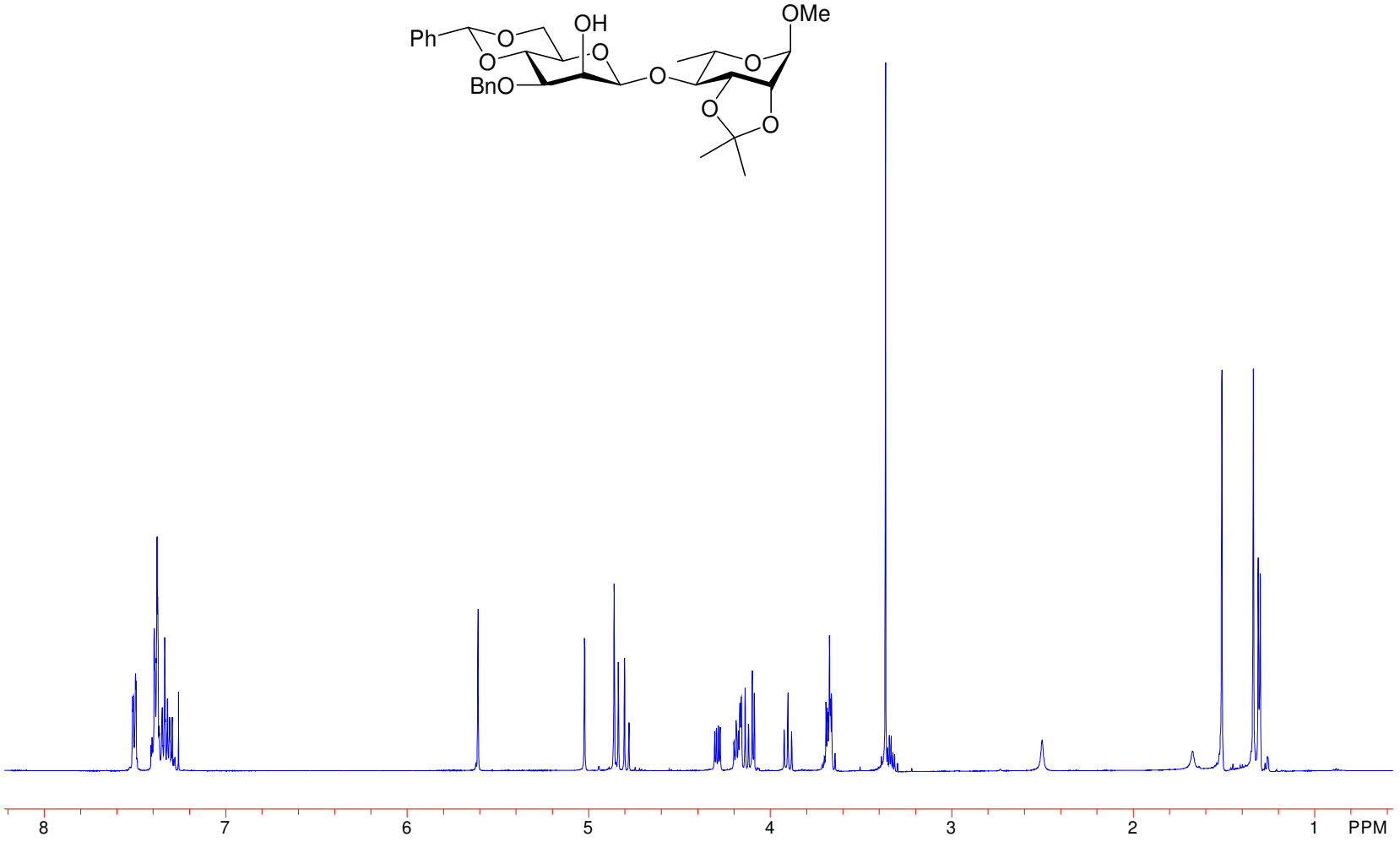


Methyl 2,3,6-tri-*O*-benzyl-6-*O*-(4,6-*O*-benzylidene-3-*O*-benzyl-β-D-mannopyranosyl)-(1→6)-α-D-glucopyranoside (55).

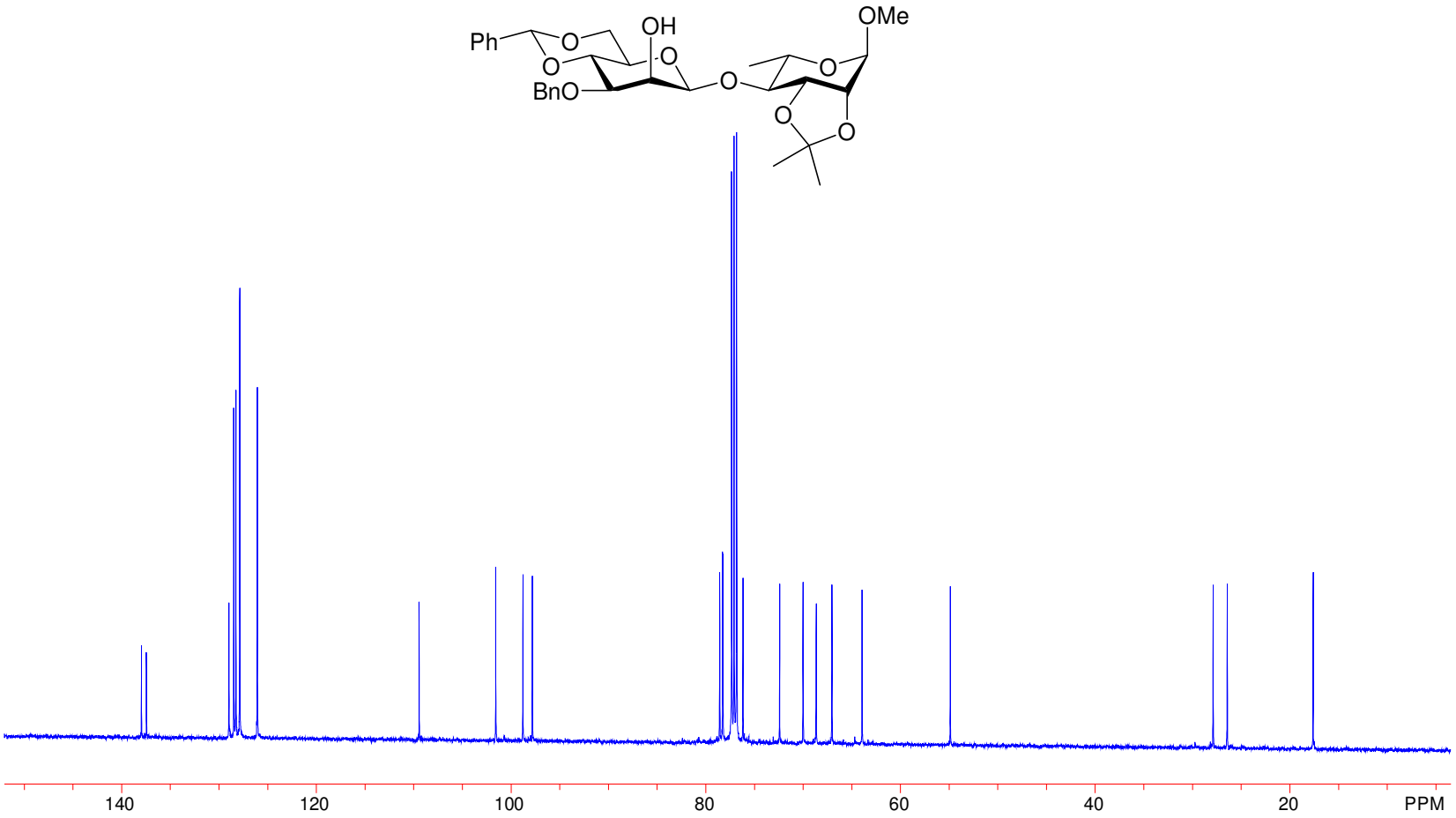




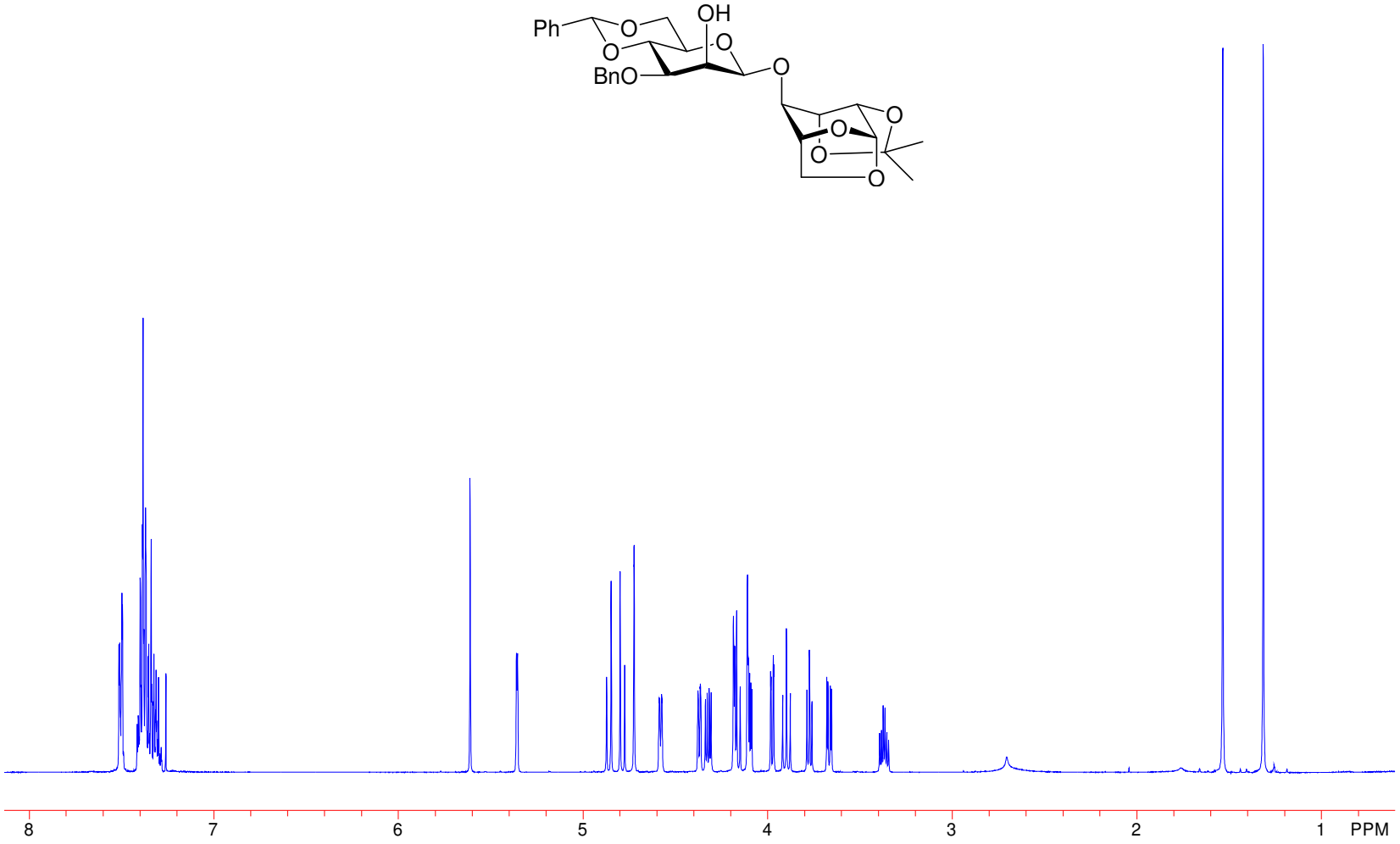
Methyl 4-*O*-[4,6-*O*-benzylidene-3-*O*-benzyl-β-D-mannopyranosyl]-(1→4)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (56).



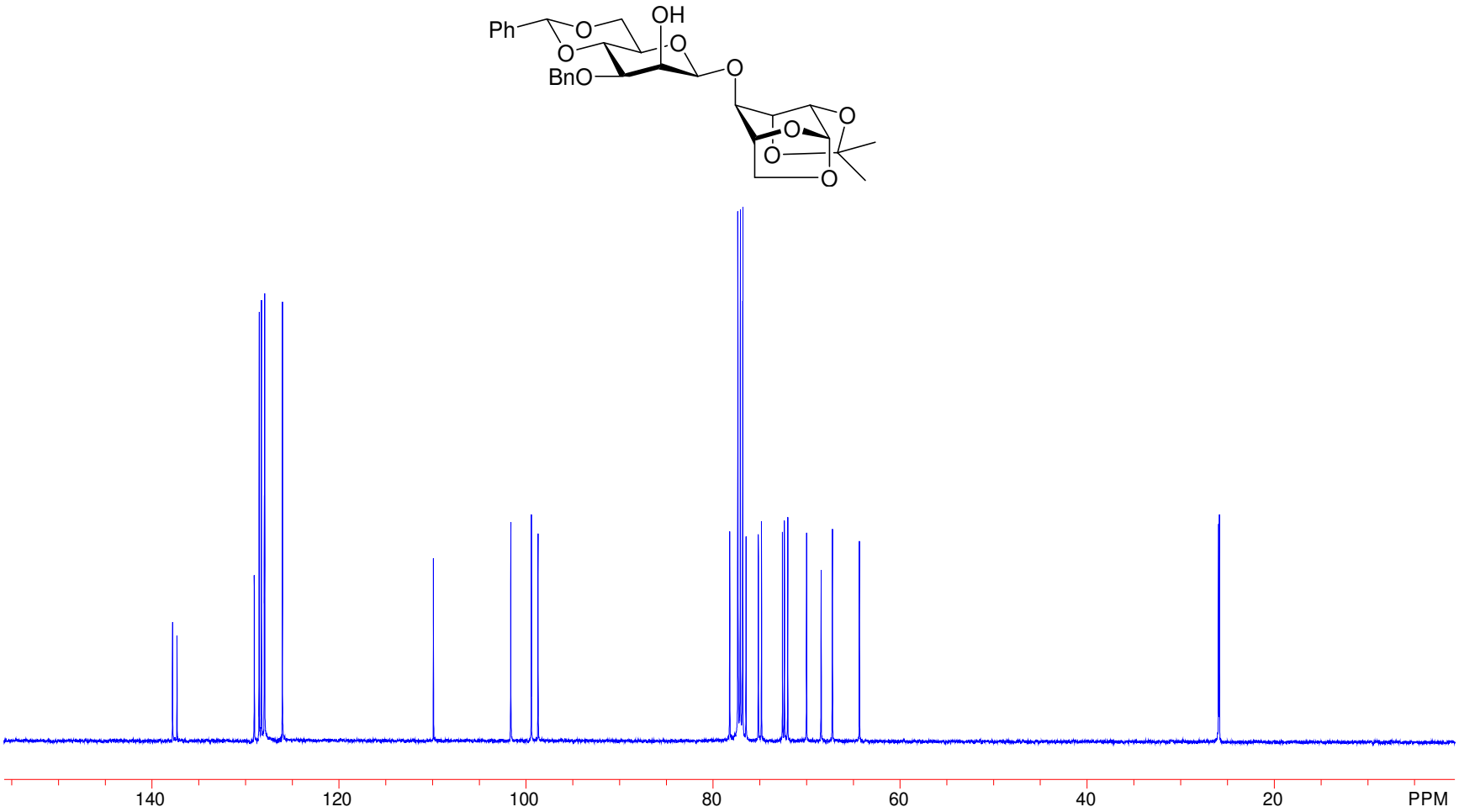
Methyl 4-*O*-[4,6-*O*-benzylidene-3-*O*-benzyl-β-D-mannopyranosyl]-(1→4)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (56).



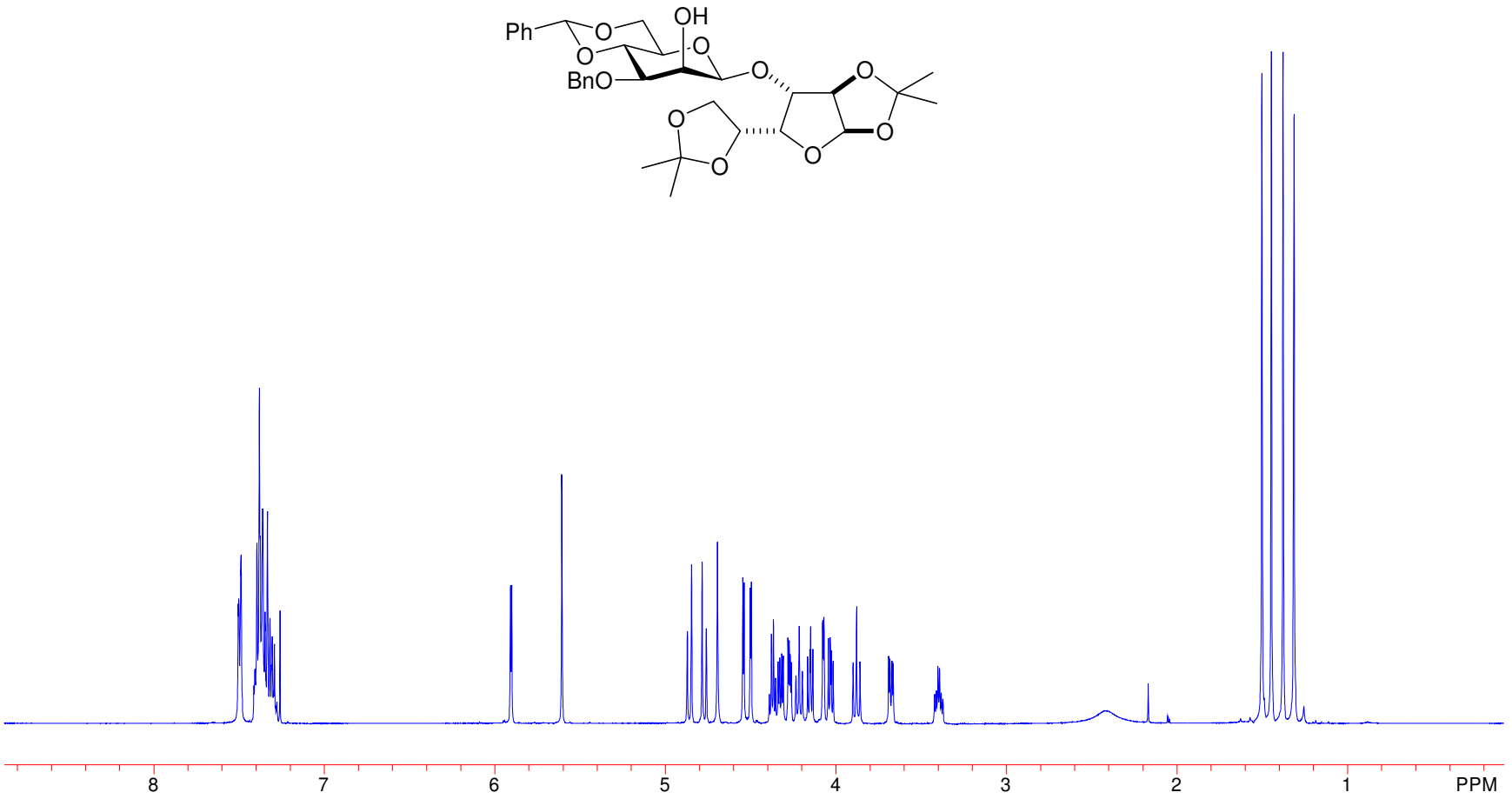
1,6-Anhydro-4-*O*-(4,6-*O*-benzylidene-3-*O*-benzyl-β-D-mannopyranosyl)-(1→4)-2,3-*O*-isopropylidene-β-D-mannopyranose (57).



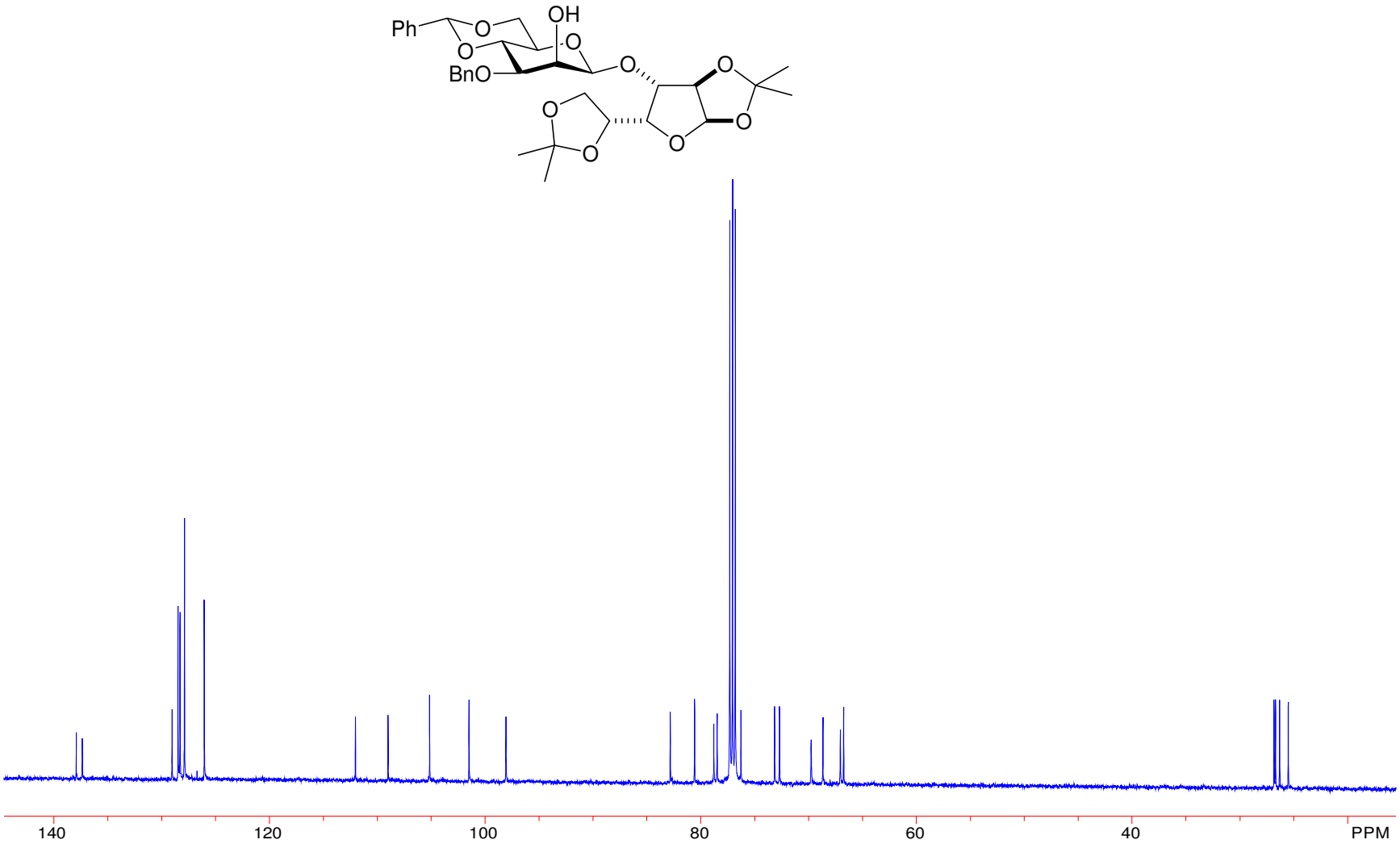
1,6-Anhydro-4-*O*-(4,6-*O*-benzylidene-3-*O*-benzyl-β-D-mannopyranosyl)-(1→4)-2,3-*O*-isopropylidene-β-D-mannopyranose (57).



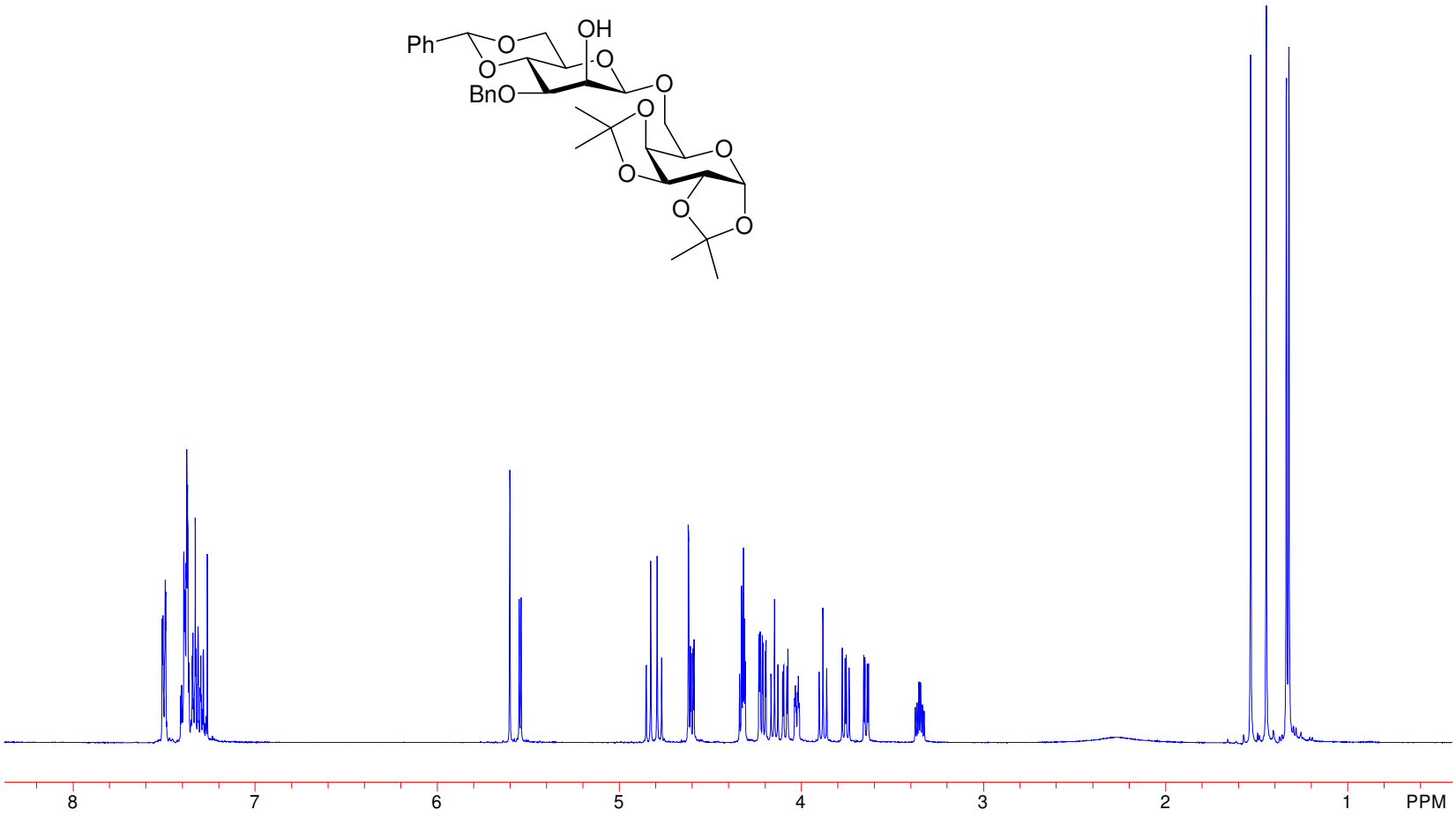
3-*O*-(4,6-*O*-Benzylidene-3-*O*-benzyl-β-D-mannopyranosyl)-(1→3)-1,2:5,6-di-*O*-isopropylidene-*α*-D-glucofuranose (58).



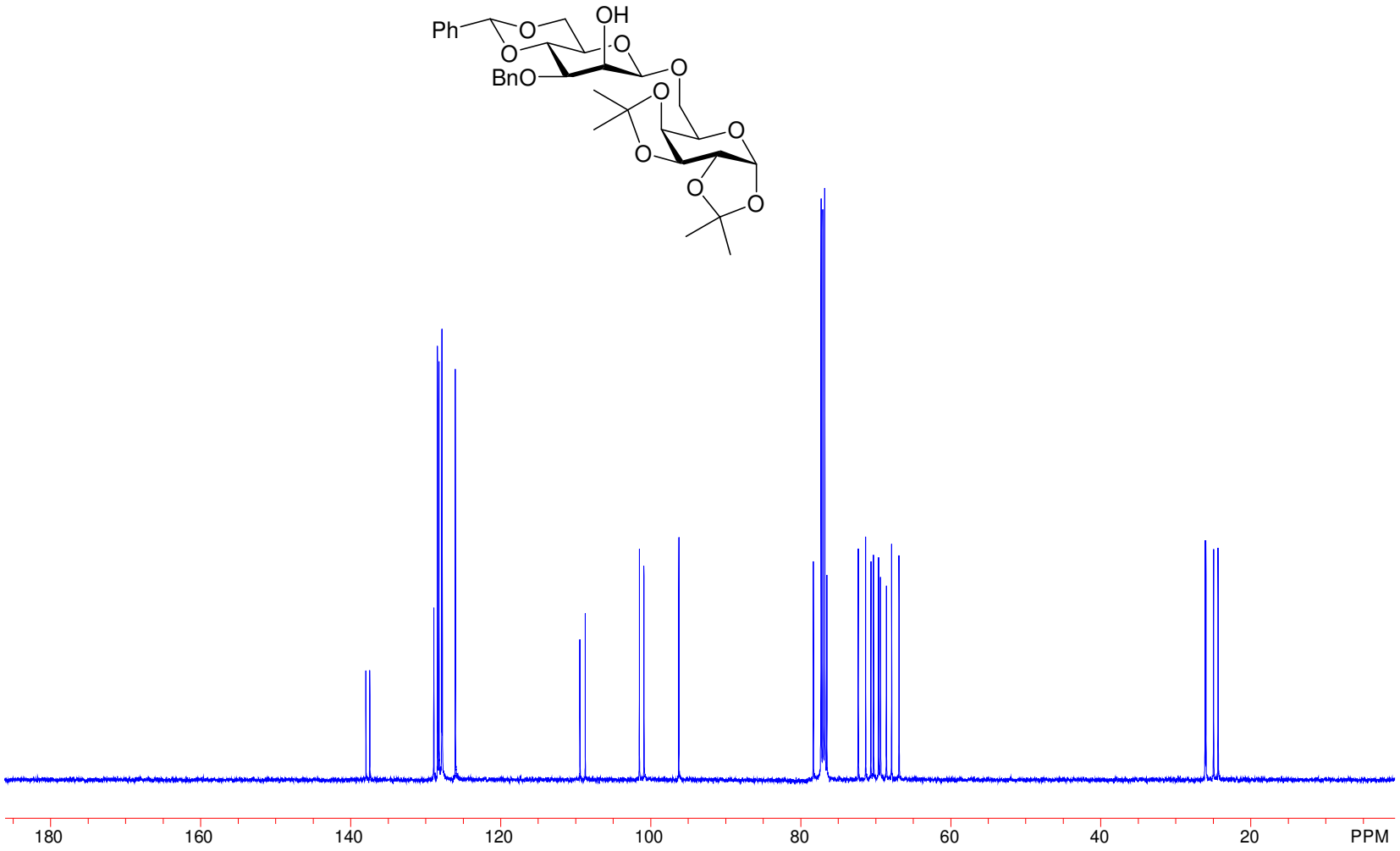
3-*O*-(4,6-*O*-Benzylidene-3-*O*-benzyl-β-D-mannopyranosyl)-(1→3)-1,2:5,6-di-*O*-isopropylidene-*α*-D-glucofuranose (58).



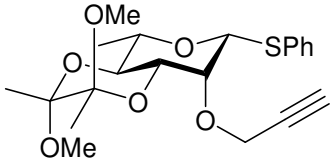
6-*O*-(4,6-*O*-Benzylidene-3-*O*-benzyl-β-D-mannopyranosyl)-(1→6)-1,2:3,4-di-*O*-isopropylidene-*α*-D-galactopyranose (59).

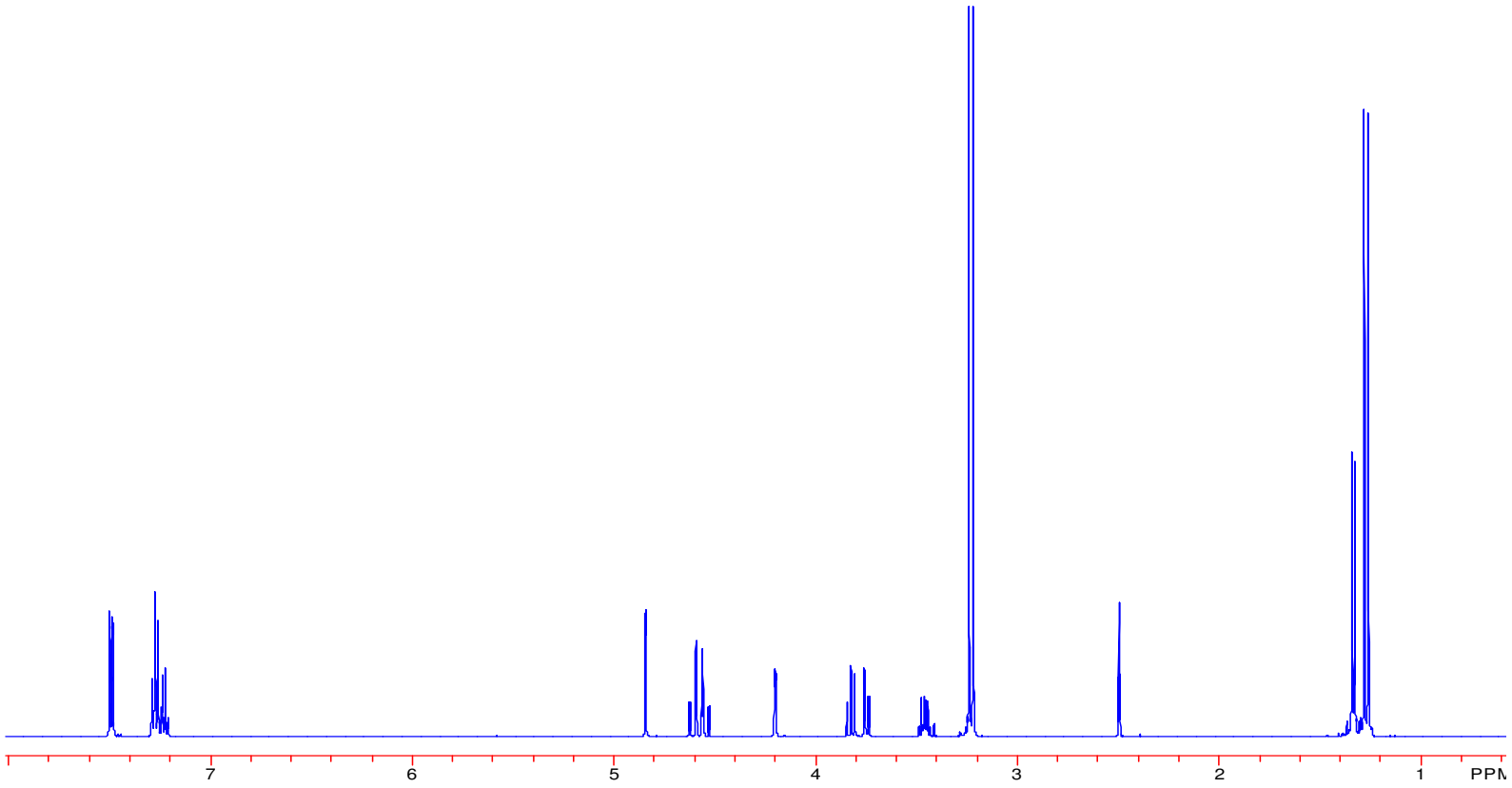


6-*O*-(4,6-*O*-Benzylidene-3-*O*-benzyl-β-D-mannopyranosyl)-(1→6)-1,2:3,4-di-*O*-isopropylidene-*α*-D-galactopyranose (59).

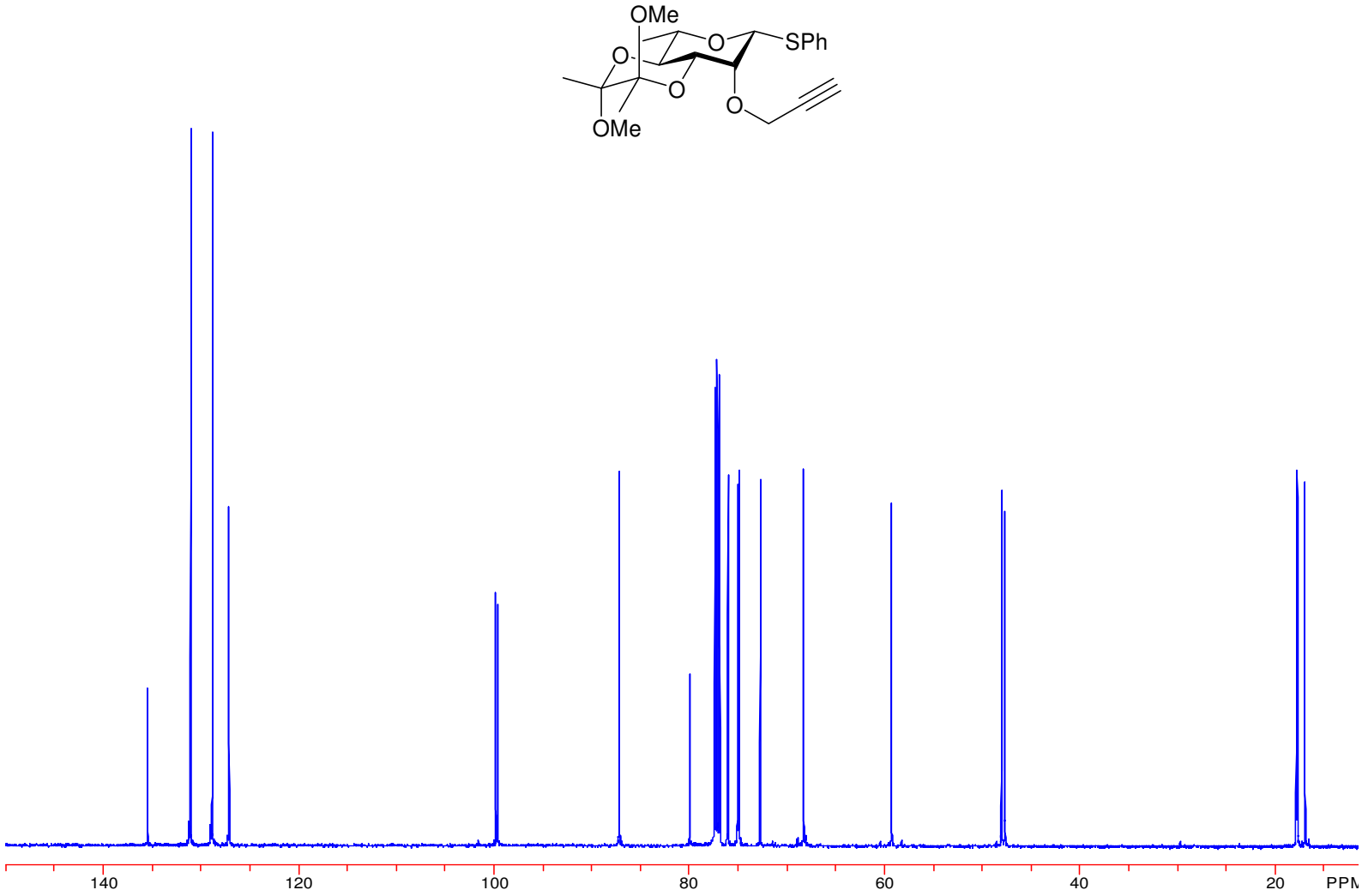


Phenyl 3,4-*O*-(2,3-dimethoxybutane-2,3-diyl)-2-*O*-(prop-2-ynyl)-1-thio-β-L-rhamnopyranoside (62).

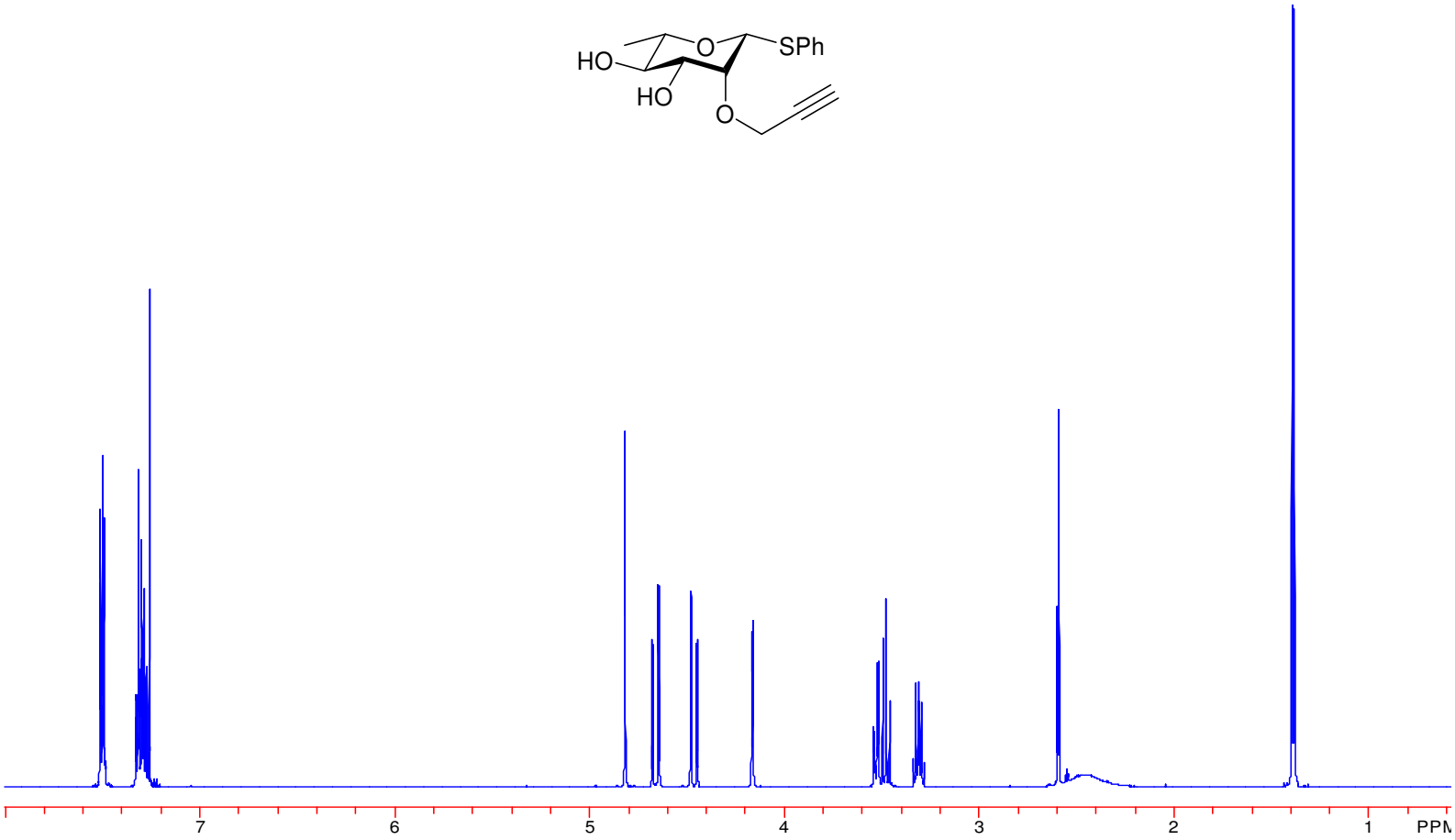




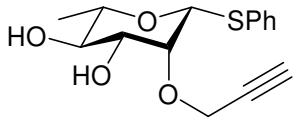
Phenyl 3,4-*O*-(2,3-dimethoxybutane-2,3-diyl)-2-*O*-(prop-2-ynyl)-1-thio-β-L-rhamnopyranoside (62).

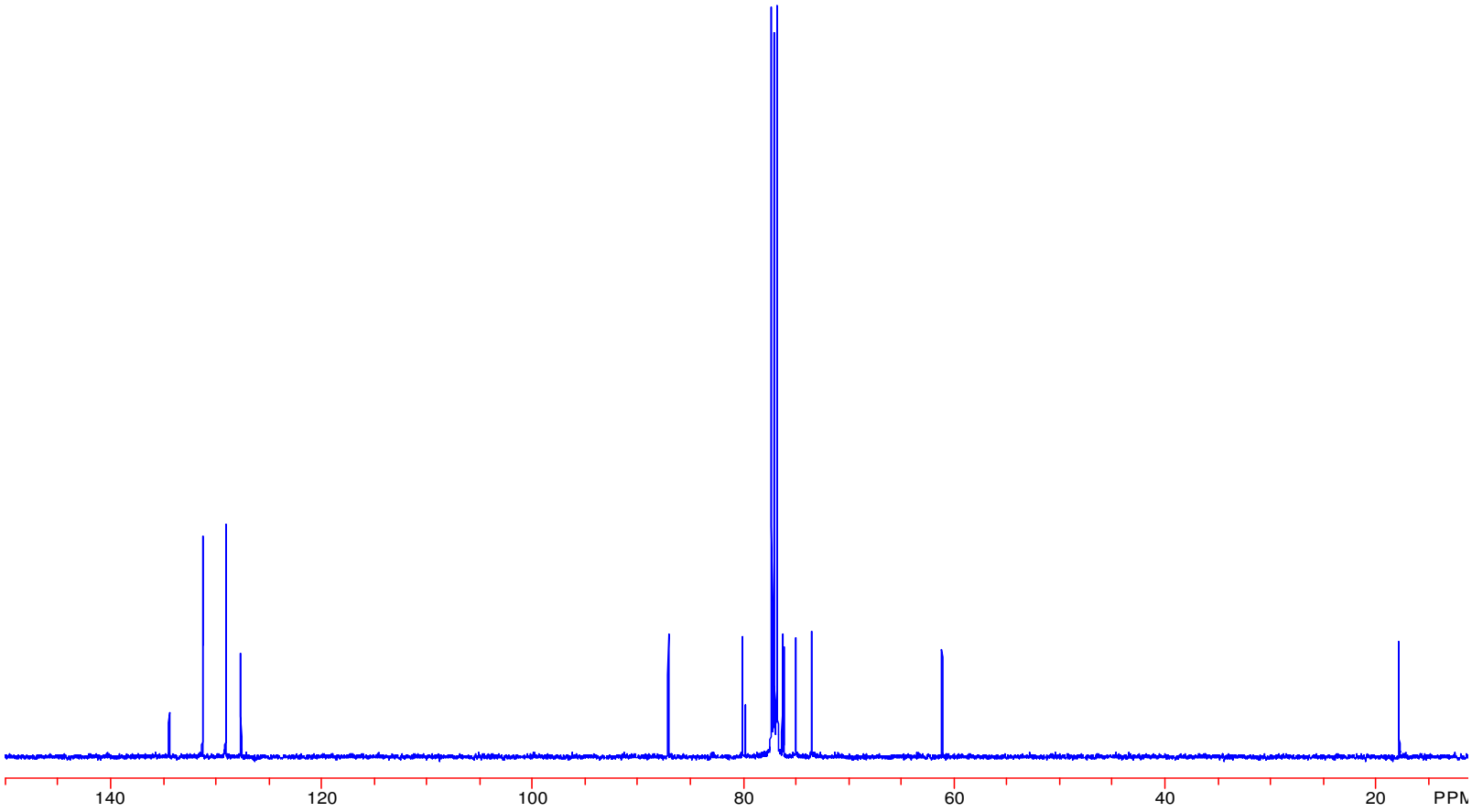


Phenyl 2-*O*-(prop-2-ynyl)-1-thio-β-L-rhamnopyranoside (63).

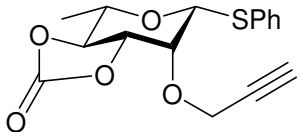


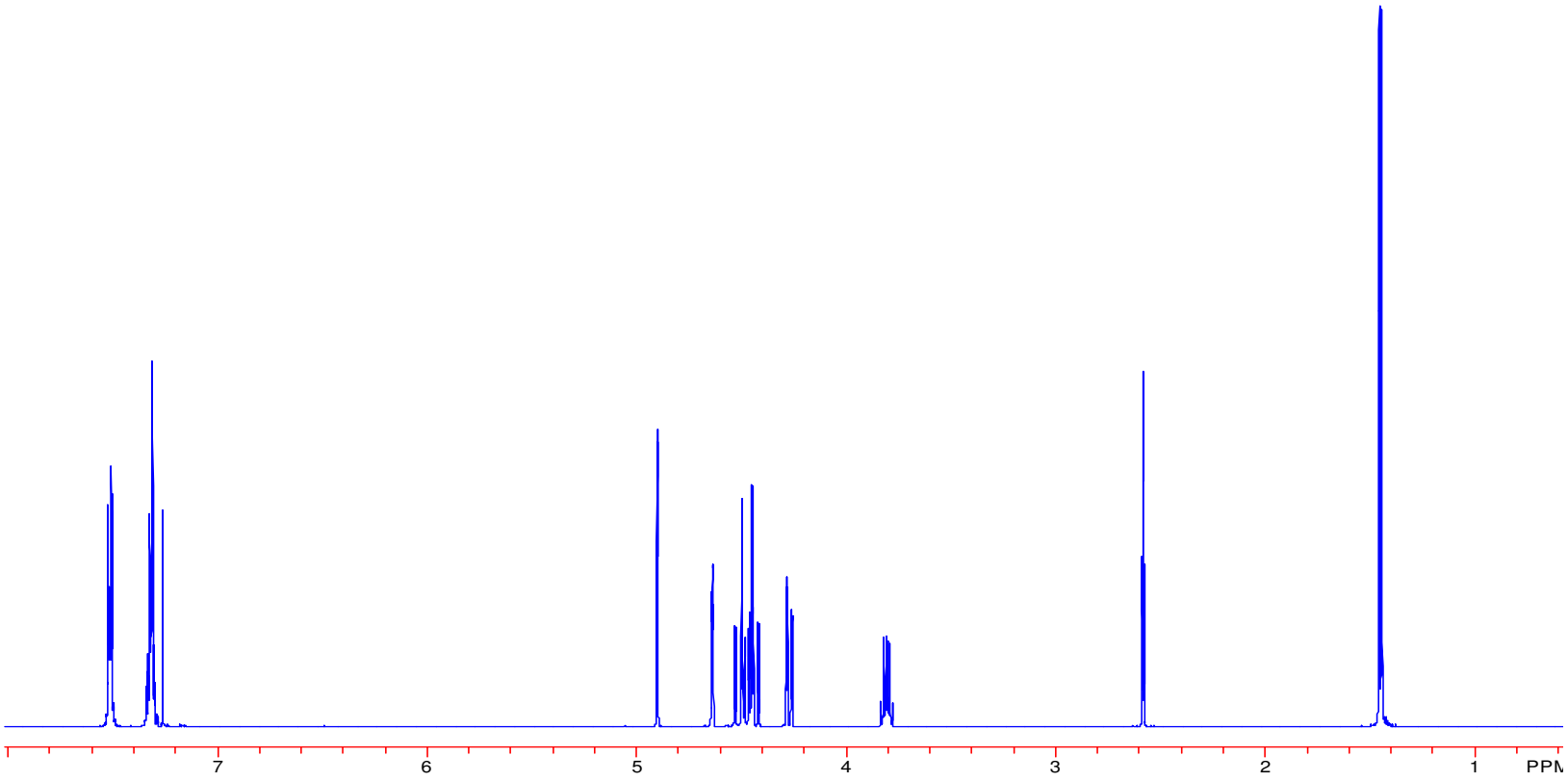
Phenyl 2-*O*-(prop-2-ynyl)-1-thio-β-L-rhamnopyranoside (63).



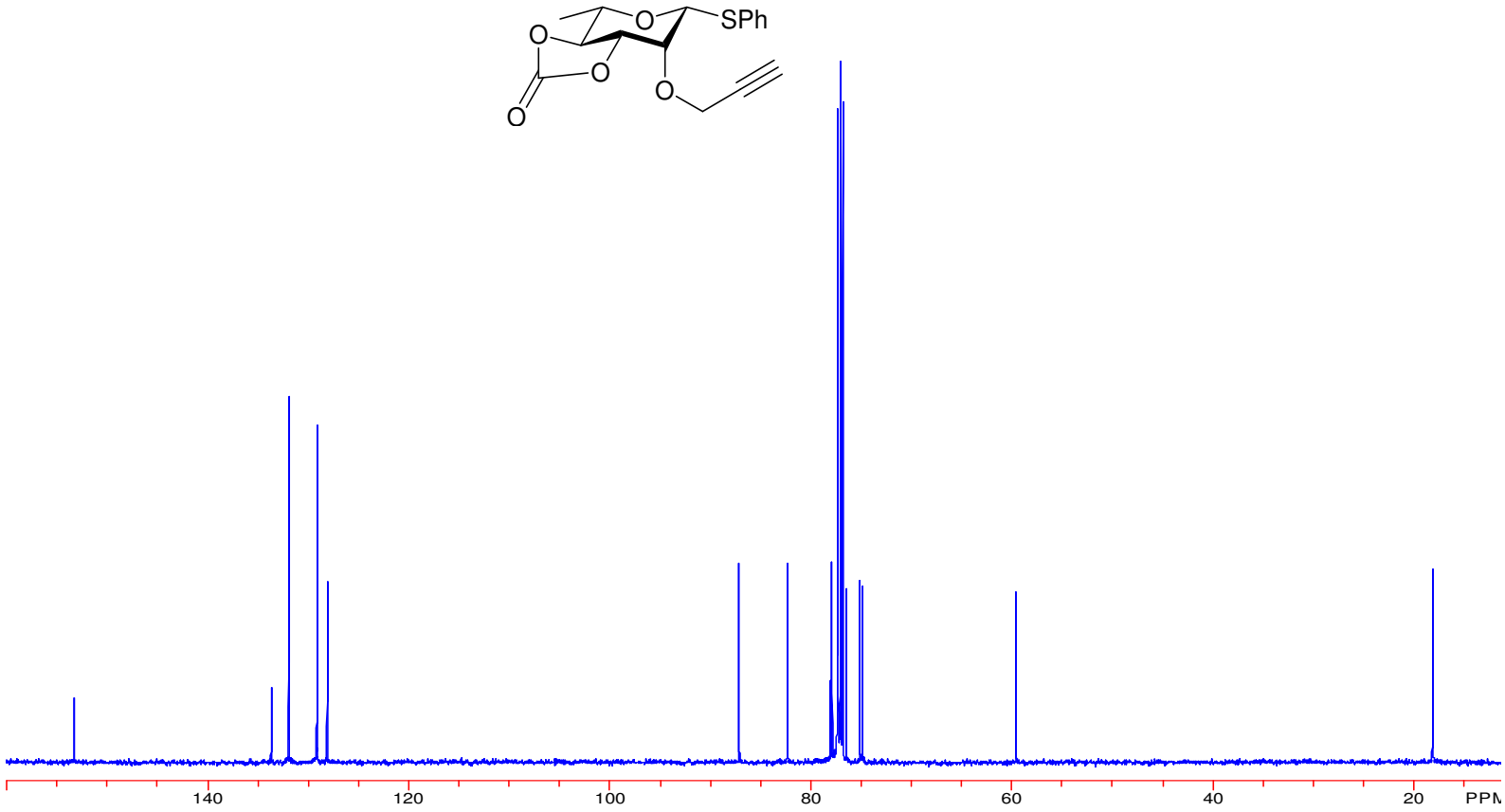


Phenyl 3,4-*O*-carbonyl-2-*O*-(prop-2-ynyl)-1-thio-β-L-rhamnopyranoside (64).

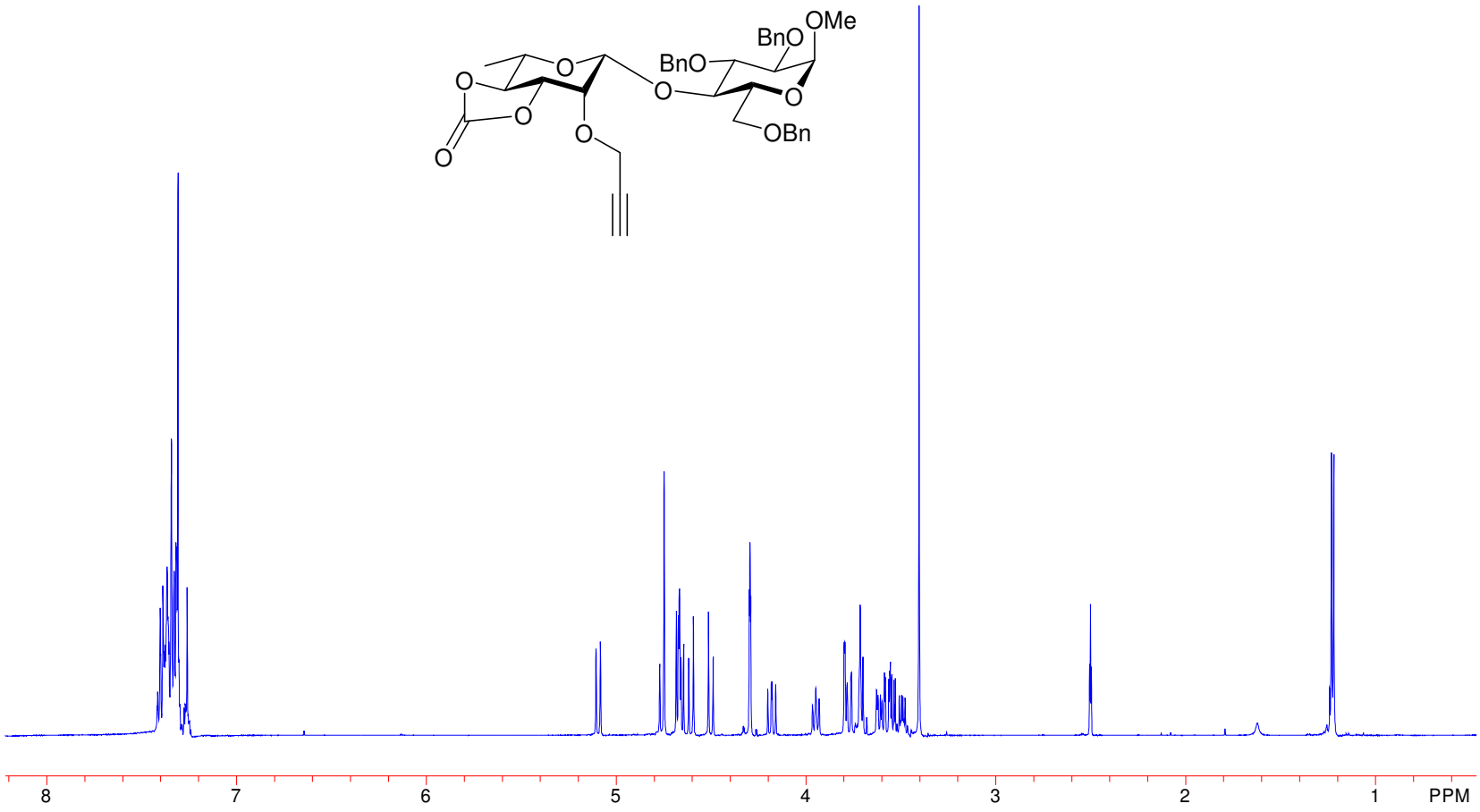




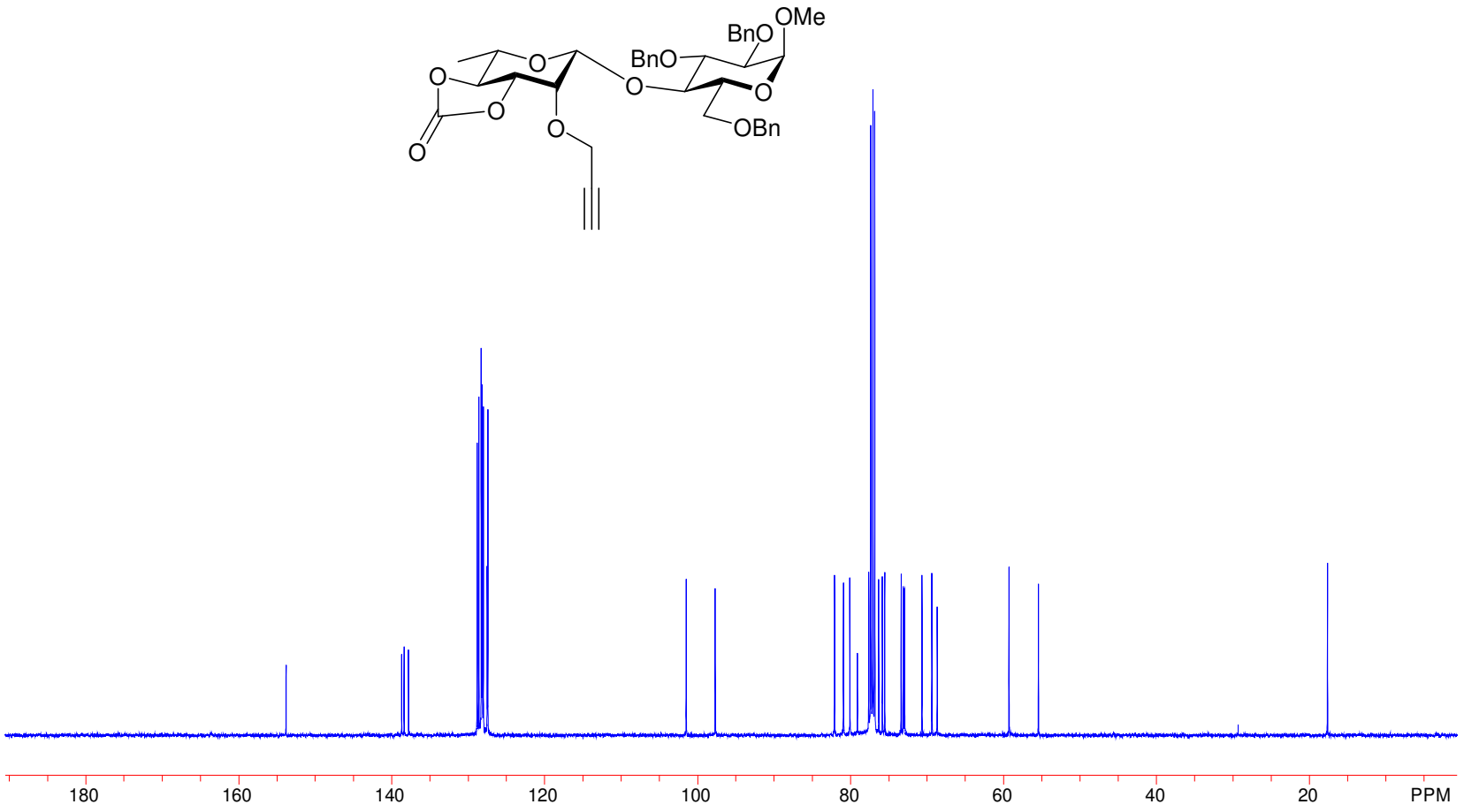
Phenyl 3,4-*O*-carbonyl-2-*O*-(prop-2-ynyl)-1-thio-β-L-rhamnopyranoside (64).



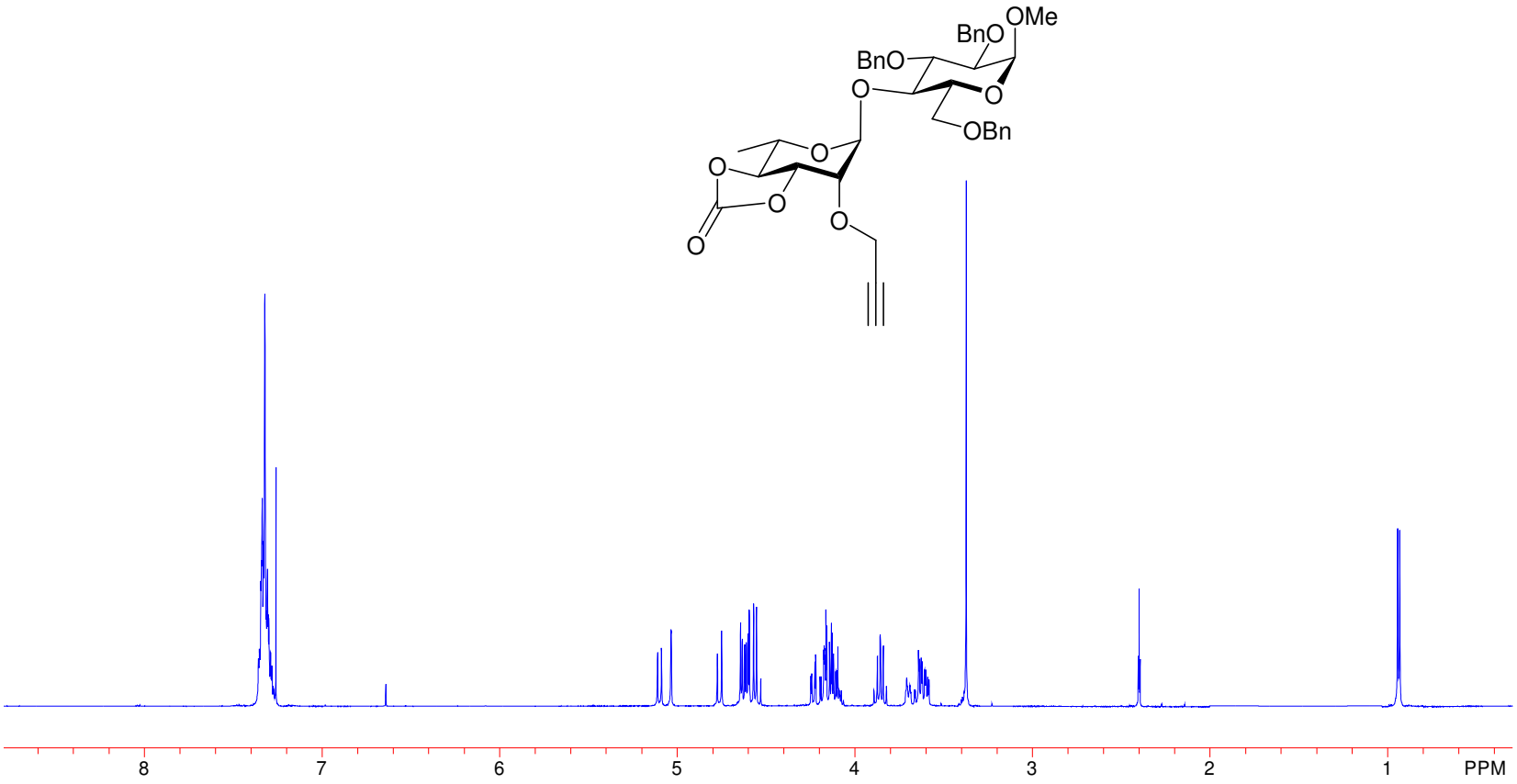
Methyl 2,3,6-tri-*O*-benzyl-4-*O*-[2-*O*-(prop-2-ynyl)-3,4-*O*-carbonyl-β-L-rhamnopyranosyl]-(1→4)-α-D-glucopyranoside (65β) .



Methyl 2,3,6-tri-*O*-benzyl-4-*O*-[2-*O*-(prop-2-ynyl)-3,4-*O*-carbonyl-β-L-rhamnopyranosyl]-(1→4)-α-D-glucopyranoside (65β)



Methyl 2,3,6-tri-*O*-benzyl-4-*O*-[2-*O*-(prop-2-ynyl)-3,4-*O*-carbonyl-α-L-rhamnopyranosyl]-(1→4)-α-D-glucopyranoside (65α).



Methyl 2,3,6-tri-*O*-benzyl-4-*O*-[2-*O*-(prop-2-ynyl)-3,4-*O*-carbonyl-α-L-rhamnopyranosyl]-(1→4)-α-D-glucopyranoside (65α).