Supporting Information: Experimental Part

Determination of the Influence of Side Chain Conformation on Glycosylation Selectivity Using Conformationally Restricted Donors

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General Experimental Section:

^{1}H NMR spectra were recorded in $CDCl_3$ solution unless otherwise stated at 400, 500, or 600 MHz. ^{13}C NMR spectra were recorded in $CDCl_3$ solution unless otherwise stated at 100, 125, or 150 MHz. Mass spectra were recorded in the +ve ion mode using electrospray ionization (ESI-TOF). Specific rotations were recorded in dichloromethane solution at room temperature unless otherwise stated. Molecular sieves used in glycosylation reactions were of the commercial. All reaction solvents were dried by standing over molecular sieves.

Phenyl 4,6-*O*-*p*-methoxybenzylidene-2,3-di-*O*-methyl-1-thio-α-D-*manno*pyranoside (4)

To a stirred solution of diol **2** (0.5 g, 1.28 mmol) and NaH (60%, 0.15 g, 3.84 mmol) in dry DMF (5 ml) was added MeI (0.24 ml, 3.84 mmol) dropwise at about 0 °C (ice-water bath). The reaction mixture was stirred at 0 °C for 0.5 h before TLC (20 % ethyl acetate in hexane) showed reaction completion. The reaction mixture was quenched with water (5 ml), extracted with EtOAc (3 × 20 ml), and washed with brine solution (1 × 15 ml). The combined extracts were dried over Na_2SO_4 and concentrated under high vacuum. Column chromatography on silica gel (eluent: 10% ethyl acetate in hexane) afforded **4** (0.41 g, 76%) as a colorless oil. R_f= 0.70 (hexane/EtOAc 4:1); $[\alpha]_D^{22}$= +196.4 (*c* 0.85, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.40 (m, 4H, Ar-*H*), 7.35 – 7.26 (m, 3H, Ar-*H*), 6.90 – 6.88 (m, 2H, Ar-*H*), 5.63 (d, *J* = 1.1 Hz, 1H, H-1), 5.56 (s, 1H, Benzylidene-*H*), 4.31 (td, *J* = 9.8, 4.8 Hz, 1H, H-5), 4.20 (dd, *J* = 10.3, 4.8 Hz, 1H, H-6), 4.13 (t, *J* = 9.7 Hz, 1H, H-4), 3.92 (dd, *J* = 3.2, 1.4 Hz, 1H, H-2), 3.89 – 3.81 (m, 1H, H-6′), 3.80 (s, 3H, OC*H*$_3$), 3.72 (dd, *J* = 9.9, 3.2 Hz, 1H, H-3), 3.58 (s, 3H, OC*H*$_3$), 3.53 (s, 3H, OC*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 133.9, 131.3, 129.9, 129.1, 127.6, 127.4, 113.5, 101.1, 85.9, 80.3, 79.0, 76.8, 68.4, 65.0, 59.0, 58.9, 55.2; HRMS (ESI) m/z calcd for $C_{25}H_{26}O_6Na$ $[M+Na]^+$, 441.1348; found, 441.1350.

Phenyl 4-*O*-benzyl-2, 3-di-*O*-methyl-1-thio-α-D-*manno*pyranoside (5)

To a solution of thioglycoside **3** (1.0 g, 2.57 mmol) and BH_3.THF (5.1 ml, 5.15 mmol) in CH_2Cl_2 (20 ml) was added $Yb(OTf)_3$ (0.16 g, 0.25 mmol) at room temperature. The reaction mixture was stirred for 2 h at room temperature before TLC (50% ethyl acetate in hexane) showed reaction completion. The reaction mixture was quenched with Et_3N (0.36 ml), MeOH (5 ml), and solvents were concentrated under high vacuum. The crude residue was purified through silica gel column chromatography (eluent: 50% ethyl acetate in hexane) to give **5** (0.74 g, 74%) as a colorless oil.

R_f= 0.60 (hexane/EtOAc 1:1); $[\alpha]_D^{22}$ = +174.0 (*c* 1.15, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 – 7.47 (m, 2H, Ar-*H*), 7.37 – 7.26 (m, 8H, Ar-*H*), δ 5.63 (d, *J* = 1.0 Hz, 1H, H-1), 4.91 (d, *J* = 11.0 Hz, 1H, -OCH_aH$_b$Ph), 4.64 (d, *J* = 11.0 Hz, 1H, OCH$_a$$H_b$Ph), 4.13 (ddd, *J* = 9.5, 4.2, 2.9 Hz, 1H, H-5), 3.89 – 3.87 (m, 1H, H-2), 3.86 (t, *J* = 9.6 Hz, 1H, H-4), 3.80 (dd, *J* = 11.7, 2.5 Hz, 1H, H-6), 3.77 (dd, *J* = 11.7, 4.4 Hz, 1H, H-6′), 3.62 (dd, *J* = 9.1, 3.3 Hz, 1H, H-3), 3.54 (s, 3H, OCH_3), 3.49 (s, 3H, OCH_3), 1.89 (s, 1H, O*H*); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.3, 134.0, 131.6, 129.1, 128.4, 128.0, 127.7, 127.6, 84.9, 81.9, 78.7, 75.2, 74.7, 72.9, 62.1, 58.3, 57.8; HRMS (ESI) m/z calcd for $C_{21}H_{26}O_5SNa$ $[M+Na]^+$, 413.1399; found, 413.1392.

Phenyl 4-*O*-*p*-methoxybenzyl-2,3-di-*O*-methyl-1-thio-α-D-*manno*pyranoside (6)

Compound **6** was prepared analogously as **5** from the mannopyranoside **4**, as a colorless oil (68%, 2.7 g). R_f= 0.30 (hexane/EtOAc 4:6); $[\alpha]_D^{22}$ = +150.0 (*c* 0.70, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.53 – 7.40 (m, 2H, Ar-*H*), 7.35 – 7.20 (m, 5H, Ar-*H*), 6.87 (m, 2H, Ar-*H*), 5.62 (d, *J* = 1.5 Hz, 1H, H-1), 4.84 (d, *J* = 10.6 Hz, 1H, OCH_aH$_b$Ph), 4.56 (d, *J* = 10.6 Hz, 1H, OCH$_a$$H_b$Ph), 4.15 – 4.05 (m, 1H, H-5), 3.88 (dd, *J* = 2.9, 1.6 Hz, 1H, H-2), 3.84 (t, *J* = 9.6 Hz, 1H, H-4), 3.80 (s, 3H, OCH_3), 3.79 – 3.72 (m, 2H, H-6, H-6′), 3.61 (dd, *J* = 9.7, 2.9 Hz, 1H, H-3), 3.56 (s, 3H, OCH_3), 3.50 (s, 3H, OCH_3), 1.77 (t, *J* = 6.5 Hz, 1H, O-*H*); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 159.3, 134.0, 131.6, 130.5, 129.6, 129.1, 127.6, 113.8, 84.9, 81.9, 78.7, 74.8, 74.5, 72.8, 62.2, 58.3, 57.8, 55.2; HRMS (ESI) m/z calcd for $C_{22}H_{28}O_6SNa$ $[M+Na]^+$, 443.1504; found, 443.1517.

(6*R*) Phenyl 6-*C*-Allyl-4-*O*-benzyl-2,3-di-*O*-methyl-1-thio-α-D-*manno*pyranoside (7) and (6*S*) Phenyl 6-*C*-Allyl-4-*O*-benzyl-2,3-di-*O*-methyl-1-thio-α-D-*manno*pyranoside (9)

To a stirred solution of primary alcohol **5** (1.3 g, 3.33 mmol) and $NaHCO_3$ (1.4 g, 16.66 mmol) in CH_2Cl_2 (20 ml) was added Dess-Martin periodinane (2.8 g, 6.66 mmol) at room temperature. This reaction mixture was allowed to react for 8 h at room temperature before Et_2O (50 ml) and a saturated aqueous solution of $NaHCO_3$/$Na_2S_2O_3$ (120 ml) were added. After stirring additional 2 h, the organic phase was extracted with Et_2O (3 × 20 ml), dried over Na_2SO_4, and evaporated under high vacuum to give an oil which was used for further reaction without purification. The crude product was dissolved in dry THF (10 ml), after which allylmagnesium chloride (16.7 ml, 16.7 mmol) was added at 0 ^{o}C. The reaction mixture was stirred for 15 min at 0 °C before TLC (30% ethyl acetate in hexane) showed reaction completion. The reaction mixture was quenched

with sat. NH_4Cl solution (10 ml), extracted with ethyl acetate, and dried over Na_2SO_4. The ethyl acetate layer was dried and concentrated. Silica gel column chromatography purification (eluent: 30% ethyl acetate in hexane) afforded **7** (0.50 g, 35%) and **9** (0.57 g, 40%) as a colorless oils.

7: R_f= 0.45 (hexane/EtOAc 7:3); $[\alpha]_D^{22}$= +179.0 (*c* 1.05, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.27 (m, 10H, Ar-*H*), 5.85 – 5R_f= 0.30 (hexane/EtOAc 4:6); $[\alpha]_D^{20}$ =3 (m, 1H, CH_2CH=CH_aH_b), 5.63 (d, *J* = 1.7 Hz, 1H, H-1), 5.05 – 5.02 (m, 2H, CH_2CH=CH_aH_b), 4.99 (d, *J* = 11.0 Hz, 1H, OCH_aH_bPh), 4.66 (d, *J* = 11.0 Hz, 1H, OCH_aH_bPh), 4.09 (dd, *J* = 9.5, 4.8 Hz, 1H, H-5), 3.94 – 3.92 (m, 1H, H-6), 3.90 (t, *J* = 9.3 Hz, 1H, H-4), 3.89 – 3.87 (m, 1H, H-2), 3.65 (dd, *J* = 8.9, 3.0 Hz, 1H, H-3), 3.53 (s, 3H, OCH_3), 3.50 (s, 3H, OCH_3), 2.63 (d, *J* = 4.4 Hz, 1H, O-*H*), 2.36 – 2.28 (m, 1H, H-7), 2.22 – 2.13 (m, 1H, H-7′); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 135.1, 133.9, 131.5, 129.14 128.5, 128.0, 127.8, 127.6, 117.1, 84.7, 82.2, 78.3, 76.7, 74.9, 73.6, 71.9, 58.3, 57.5, 36.7; HRMS (ESI) m/z calcd for $C_{24}H_{30}O_5SNa$ $[M+Na]^+$, 453.1712; found, 453.1710.

9: R_f= 0.40 (hexane/EtOAc 7:3); $[\alpha]_D^{22}$= +154.0 (*c* 0.45, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.27 (m, 10H, Ar-*H*), 5.78 – 5.71 (m, 1H, CH_2CH=CH_aH_b), 5.72 (d, *J* = 1.5 Hz, 1H, H-1), 5.02 (dd, *J* = 10.2, 1.0 Hz, 1H, CH_2CH=CH_aH_b), 4.98 (dd, *J* = 17.2, 1.0 Hz, 1H, CH_2CH=CH_aH_b), 4.92 (d, *J* = 10.8 Hz, 1H, OCH_aH_bPh), 4.69 (d, *J* = 10.8 Hz, 1H, OCH_aH_bPh), 4.04 (t, *J* = 9.9 Hz, 1H, H-4), 3.93 – 3.91 (m, 2H, H-5, H-6), 3.87 (dd, *J* = 2.9, 1.5 Hz, 1H, H-2), 3.60 (dd, *J* = 9.3, 2.9 Hz, 1H, H-3), 3.55 (s, 3H, OCH_3), 3.51 (s, 3H, OCH_3), 2.28 (dt, *J* = 15.1, 7.8 Hz, 1H, H-7), 2.15 (dt, *J* = 14.1, 5.8 Hz, 1H, H-7′), 1.83 (s, 1H, O-*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 138.5, 134.7, 130.6, 129.0, 128.4, 127.9, 127.6, 127.2, 117.5, 84.7, 82.0, 78.7, 75.3, 74.6, 73.7, 68.6, 58.4, 57.9, 38.6; HRMS (ESI) m/z calcd for $C_{24}H_{30}O_5SNa$ $[M+Na]^+$, 453.1712; found, 453.1714.

(6*R*) Phenyl 6-*C*-Allyl-4-*O*-*p*-methoxybenzyl-2,3-di-*O*-methyl-1-thio-α-D-*manno*pyranoside (8)

Compound **8** (35%, 0.50 g) was synthesized analogously as **7** from mannopyranoside **6**, as a colorless oil. R_f= 0.35 (hexane/EtOAc 6:4); $[\alpha]_D^{22}$ = +168.8 (*c* 0.85, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.47 (m, 2H, Ar-*H*), 7.34 – 7.24 (m, 5H, Ar-*H*), 6.89 – 6.87 (m, 2H, Ar-*H*), 5.85 – 5.75 (m, 1H, CH_2CH=CH_aH_b), 5.64 (d, *J* = 1.4 Hz, 1H, H-1), 5.05 – 5.01 (m, 2H, CH_2CH=CH_aH_b), 4.91 (d, *J* = 10.6 Hz, 1H, OCH_aH_bPh), 4.60 (d, *J* = 10.6 Hz, 1H, OCH_aH_bPh),

4.05 (dd, J = 9.5, 4.9 Hz, 1H, H-5), 3.94 – 3.84 (m, 3H, H-2, H-3, H-6), 3.79 (s, 3H, OCH_3), 3.63 (dd, J = 9.2, 2.9 Hz, 1H, H-3), 3.54 (s, 3H, OCH_3), 3.50 (s, 3H, OCH_3), 2.68 (d, J = 4.3 Hz, 1H, O-H), 2.33 – 2.23 (m, 1H, H-7), 2.22 – 2.11 (m, 1H, H-7′); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 135.1, 134.0, 131.5, 130.0, 129.8, 129.2, 127.5, 117.0, 114.0, 84.8, 82.2, 78.4, 76.6, 74.6, 73.6, 72.0, 58.3, 57.5, 55.2, 36.8; HRMS (ESI) m/z calcd for $C_{25}H_{32}O_6SNa$ $[M+Na]^+$, 483.1817; found, 483.1800.

(6*S*) Phenyl 6-*C*-Allyl-4-*O*-*p*-methoxybenzyl-2,3-di-*O*-methyl-1-thio-α-D-*manno*pyranoside (10)

Compound **10** (32%, 0.45 g) was synthesized analogously as **9** from mannopyranoside **6**, as a colorless oil. R_f= 0.30 (hexane/EtOAc 6:4); $[\alpha]_D^{22}$ = +180.0 (c 0.30, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.44 (m, 2H, Ar-H), 7.33 – 7.27 (m, 5H, Ar-H), 6.89 – 6.87 (m, 2H, Ar-H), 5.80 – 5.69 (m, 1H, CH_2CH=CH_aH_b), 5.72 (d, J = 1.5 Hz, 1H, H-1), 5.02 (dd, J = 10.7, 1.9 Hz, 1H, CH_2CH=CH_aH_b), 4.97 (dd, J = 17.7, 1.9 Hz, 1H, CH_2CH=CH_aH_b), 4.84 (d, J = 10.2 Hz, 1H, OCH_aH_bPh), 4.62 (d, J = 10.2 Hz, 1H, OCH_aH_bPh), 4.02 (t, J = 9.3 Hz, 1H, H-4), 3.93 – 3.89 (m, 2H, H-5, H-6), 3.87 (dd, J = 3.4, 1.9 Hz, 1H, H-2), 3.80 (s, 3H, OCH_3), 3.58 (dd, J = 9.3, 3.4 Hz, 1H, H-3), 3.56 (s, 3H, OCH_3), 3.50 (s, 3H, OCH_3), 2.28 (dt, J = 15.2, 7.8 Hz, 1H, H-7), 2.18 – 2.09 (m, 1H, H-7′), 1.84 (d, J = 8.3 Hz, 1H, O-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 134.8, 130.7, 130.6, 129.7, 129.1, 127.2, 117.5, 113.9, 84.8, 82.0, 78.8, 75.0, 74.4, 73.8, 68.6, 58.4, 57.9, 55.2, 38.6; HRMS (ESI) m/z calcd for $C_{25}H_{32}O_6SNa$ $[M+Na]^+$, 483.1817; found, 483.1812.

(6*R*) Phenyl 6-*C*-Allyl-4-*O*-benzyl-2,3,6-tri-*O*-methyl-1-thio-α-D-*manno*pyranoside (11)

Compound **11** was synthesized from **7** in 72% (0.38 g) yield following procedure as used for **4**, as a colorless oil. R_f= 0.60 (hexane/EtOAc 7:3); $[\alpha]_D^{22}$ = +128.0 (c 0.15, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 – 7.48 (m, 2H, Ar-H), 7.38 – 7.25 (m, 8H, Ar-H), 5.87 – 5.81 (m, 1H, CH_2CH=CH_aH_b), 5.63 (d, J = 1.7 Hz, 1H, H-1), 5.06 (dd, J = 17.1, 1.5 Hz, 1H, CH_2CH=CH_aH_b), 5.03 (dd, J = 10.3, 1.4 Hz, 1H, CH_2CH=CH_aH_b), 4.91 (d, J = 11.0 Hz, 1H, OCH_aH_bPh), 4.65 (d, J = 11.0 Hz, 1H, OCH_aH_bPh), 4.36 (d, J = 10.1 Hz, 1H, H-5), 3.87 (dd, J = 2.8, 1.8 Hz, 1H, H-2), 3.83 (t, J = 9.3 Hz, 1H, H-4), 3.62 (dd, J = 8.9, 3.0 Hz, 1H, H-3), 3.54 (s, 3H), 3.53 – 3.50 (m, 1H, H-6), 3.48 (s, 3H, OCH_3), 3.38 (s, 3H, OCH_3), 2.44 (ddd, J = 15.5, 8.2, 7.4 Hz, 1H, H-7), 2.34 – 2.28 (m, 1H, H-7′); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.5, 136.0, 134.8, 131.5, 129.0,

128.4, 128.0, 127.7, 127.4, 116.4, 85.0, 82.3, 80.5, 78.4, 75.1, 74.8, 71.9, 57.8, 57.7, 57.6, 34.9; HRMS (ESI) m/z calcd for $C_{25}H_{32}O_5SNa$ $[M+Na]^+$, 467.1868; found, 467.1875.

(6*R*) Phenyl 6-*C*-Allyl-4-*O*-*p*-methoxybenzyl-2,3,6-tri-*O*-methyl-1-thio-α-D-*manno*pyranoside (12)

Compound **12** (82%, 1.68 g) was synthesized analogously as **11** from compound **8**, as a colorless oil. R_f= 0.60 (hexane/EtOAc 7:3); $[\alpha]_D^{22}$ = +171.8 (*c* 1.35, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.49 (m, 2H, Ar-*H*), 7.34 – 7.24 (m, 5H, Ar-*H*), 6.94 – 6.83 (m, 2H, Ar-*H*), 5.83 (ddt, *J* = 17.0, 10.2, 6.8 Hz, 1H, CH_2CH=CH_aH_b), 5.62 (d, *J* = 1.9 Hz, 1H, H-1), 5.08 (dd, *J* = 17.4, 1.4 Hz, 1H, CH_2CH=CH_aH_b), 5.03 (dd, *J* = 8.3, 1.4 Hz, 1H, CH_2CH=CH_aH_b), 4.82 (d, *J* = 10.6 Hz, 1H, OCH_aH_bPh), 4.57 (d, *J* = 10.6 Hz, 1H, OCH_aH_bPh), 4.32 (dd, *J* = 9.8, 1.2 Hz, 1H, H-5), 3.86 (dd, *J* = 2.9, 1.9 Hz, 1H, H-2), 3.82 (t, *J* = 9.7 Hz, 1H, H-4), 3.81 (s, 3H, OCH_3), 3.60 (dd, *J* = 8.9, 3.1 Hz, 1H, H-3), 3.55 (s, 3H, OCH_3), 3.52 – 3.49 (m, 1H, H-6), 3.47 (s, 3H, OCH_3), 3.37 (s, 3H, OCH_3), 2.47 – 2.38 (m, 1H, H-7), 2.32 – 2.24 (m, 1H, H-7′); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 136.1, 134.8, 131.4, 130.6, 129.7, 129.0, 127.4, 116.3, 113.8, 85.0, 82.3, 80.3, 78.4, 74.7, 74.5, 71.9, 57.8, 57.7, 57.4, 55.3, 34.8; HRMS (ESI) m/z calcd for $C_{26}H_{34}O_6SNa$ $[M+Na]^+$, 497.1974; found, 497.1978.

(6*S*) Phenyl 6-*C*-Allyl-4-*O*-benzyl-2,3,6-tri-*O*-methyl-1-thio-α-D-*manno*pyranoside (13)

Compound **13** (78%, 0.41 g) was synthesized analogously as **11** from Compound **9**, as a colorless oil. R_f= 0.70 (hexane/EtOAc 7:3); $[\alpha]_D^{22}$ = +163.5 (*c* 1.10, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 – 7.44 (m, 2H, Ar-*H*), 7.35 – 7.33 (m, 4H, Ar-*H*), 7.33 – 7.27 (m, 3H, Ar-*H*), 7.21 (t, *J* = 7.3 Hz, 1H, Ar-*H*), 5.82 (s, 1H, H-1), 5.66 – 5.59 (m, 1H, CH_2CH=CH_aH_b), 4.96 (d, *J* = 11.0 Hz, 1H, OCH_aH_bPh), 4.90 (dd, *J* = 10.3, 0.7 Hz, 1H, CH_2CH=CH_aH_b), 4.86 (dd, *J* = 18.3, 1.4 Hz, 1H CH_2CH=CH_aH_b), 4.60 (d, *J* = 11.0 Hz, 1H, OCH_aH_bPh), 4.05 (t, *J* = 9.5 Hz, 1H, H-4), 3.95 (d, *J* = 9.5 Hz, 1H, H-5), 3.85 (dd, *J* = 3.3, 1.4 Hz, 1H, H-2), 3.61 – 3.59 (m, 1H, H-6), 3.56 (dd, *J* = 9.2, 3.3 Hz, 1H, H-3), 3.52 (s, 3H, OCH_3), 3.49 (s, 3H, OCH_3), 3.36 (s, 3H, OCH_3), 2.48 – 2.41 (m, 1H, H-7), 2.27 – 2.20 (m, 1H, H-8); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.7, 135.2, 134.3, 129.4, 129.0, 128.4, 127.7, 127.6, 126.7, 117.5, 84.3, 82.3, 78.9, 76.8, 75.0, 74.4, 72.3, 58.5, 57.7, 57.6, 33.4; HRMS (ESI) m/z calcd for $C_{25}H_{32}O_5SNa$ $[M+Na]^+$, 467.1868; found, 467.1869.

(6*S*) Phenyl 6-*C*-Allyl-4-*O*-*p*-methoxybenzyl-2,3,6-tri-*O*-methyl-1-thio-α-D-*manno*pyranoside (14)

Compound **14** (90%, 1.85) was synthesized analogously as **11** from compound **10**, as a colorless oil. R_f= 0.60 (hexane/EtOAc 1:1); $[\alpha]_D^{22}$ = +158.2 (*c* 0.35, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.42 (m, 2H, Ar-*H*), 7.31 – 7.18 (m, 5H, Ar-*H*), 6.90 – 6.87 (m, 2H, Ar-*H*), 5.82 (d, *J* = 1.4 Hz, 1H, H-1), 5.63 (ddt, *J* = 17.2, 10.3, 7.2 Hz, 1H, CH_2CH=CH_aH_b), 4.91 – 4.89 (m, 1H, CH_2CH=CH_aH_b), 4.88 (d, *J* = 10.6 Hz, 1H, OCH_aH_bPh), 4.84 (dd, *J* = 17.2, 1.6 Hz, 1H, CH_2CH=CH_aH_b), 4.54 (d, *J* = 10.6 Hz, 1H, OCH_aH_bPh), 4.04 (t, *J* = 9.5 Hz, 1H, H-4), 3.93 (dd, *J* = 9.7, 1.3 Hz, 1H, H-5), 3.85 (dd, *J* = 3.2, 1.6 Hz, 1H, H-2), 3.80 (s, 3H, OCH_3), 3.64 – 3.57 (m, 1H, H-6), 3.56 (dd, *J* = 9.7, 3.4 Hz, 1H, H-3), 3.54 (s, 3H, OCH_3), 3.49 (s, 3H, OCH_3), 3.39 (s, 3H, OCH_3), 2.49 – 2.41 (m, 1H, H-7), 2.28 – 2.18 (m, 1H, H-7′); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 135.3, 134.3, 130.9, 129.4, 129.3, 129.0, 126.7, 117.2, 113.8, 84.3, 82.3, 78.9, 77.4, 74.8, 74.1, 72.9, 58.5, 57.7, 57.6, 55.3, 33.4; HRMS (ESI) m/z calcd for $C_{26}H_{34}O_6SNa$ $[M+Na]^+$, 497.1974; found, 497.1972.

Phenyl 4-*O*-benzyl-7-deoxy-2,3,6-tri-*O*-methyl-D-*glycero*-α-D-thio-*manno*octopyranoside (15)

Compound **15** (85%, 0.22 g) was synthesized analogously as **16** from compound **11**, as a colorless oil. R_f= 0.30 (hexane/EtOAc 4:6); $[\alpha]_D^{22}$ = +182.0 (*c* 1.45, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 – 7.46 (m, 2H, Ar-*H*), 7.37 – 7.22 (m, 8H, Ar-*H*), 5.62 (d, *J* = 1.6 Hz, 1H, H-1), 4.89 (d, *J* = 11.0 Hz, 1H, OCH_aH_bPh), 4.63 (d, *J* = 11.0 Hz, 1H, OCH_aH_bPh), 4.35 (dd, *J* = 9.9, 1.2 Hz, 1H, H-5), 3.86 (dd, *J* = 2.9, 1.9 Hz, 1H, H-2), 3.75 (t, *J* = 9.1 Hz, 1H, H-4), 3.71 – 3.63 (m, 3H, H-6, H-8, H-8′), 3.59 (dd, *J* = 3.0, 9.1 Hz, 1H, H-3), 3.53 (s, 3H, OCH_3), 3.45 (s, 3H, OCH_3), 3.36 (s, 3H, OCH_3), 2.46 (br s, 1H, O-*H*), 1.95 (ddt, *J* = 15.6, 9.9, 5.8 Hz, 1H, H-7), 1.64 – 1.55 (m, 1H, H-7′); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.3, 134.8, 131.1, 129.0, 128.5, 128.3, 127.8, 127.4, 84.9, 82.3, 79.7, 78.4, 74.8, 74.7, 71.4, 60.9, 57.8, 57.6, 57.0, 32.2; HRMS (ESI) m/z calcd for $C_{24}H_{32}O_6SNa$ $[M+Na]^+$, 471.1817; found, 471.1806.

Phenyl 4-*O*-*p*-methoxybenzyl-7-deoxy-2,3,6-tri-*O*-methyl-D-*glycero*-α-D-thio-*manno*octopyranoside (16)

Ozone gas was bubbled through a solution of olefin **12** (1.6 g, 3.37 mmol) in CH_2Cl_2/MeOH (200 ml/100 ml) at -78 ^oC until the solution turned to faint blue color. Ar gas was bubbled through solution for 5 min to remove excess ozone. To this mixture was added $NaBH_4$ (0.79 g, 33.6 mmol) at −78 ^oC and the reaction mixture slowly brought to room temperature, stirred for 3 h before solvents were evaporated under reduced pressure. The crude reaction mixture was extracted with EtOAc (3 x 30 ml), washed with hydrochloric acid (1 M), brine, dried over Na_2SO_4, and concentrated. Silica gel column chromatography (eluent: hexane/ethyl acetate = 50:50) afforded **16** (1.3 g, 81%)) as a colorless oil. R_f= 0.20 (hexane/EtOAc 4:6); $[\alpha]_D^{22}$ = +181.1 (*c* 1.80, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.49 (m, 2H, Ar-*H*), 7.32 – 7.23 (m, 5H, Ar-*H*), 6.89 – 6.87 (m, 2H, Ar-*H*), 5.62 (d, *J* = 0.9 Hz, 1H, H-1), 4.82 (d, *J* = 10.7 Hz, 1H, OC*H*$_a$H$_b$Ph), 4.57 (d, *J* = 10.7 Hz, 1H, OC*H*$_a$H$_b$Ph), 4.34 (d, *J* = 9.7 Hz, 1H, H-5), 3.86 (t, *J* = 2.4 Hz, 1H, H-2), 3.80 (s, 3H, OC*H*$_3$), 3.73 (t, *J* = 9.7 Hz, 1H, H-4), 3.70 – 3.67 (m, 3H, H-6, H-8, H-8′), 3.59 (dd, *J* = 8.8, 2.9 Hz, 1H, H-3), 3.55 (s, 3H, OC*H*$_3$), 3.46 (s, 3H, OC*H*$_3$), 3.36 (s, 3H, OC*H*$_3$), 2.55 (br s, 1H, O-*H*), 2.00 – 1.91 (m, 1H, H-7), 1.63 – 1.56 (m, 1H, H-7′); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 134.8, 131.1, 130.4, 129.9, 129.0, 127.4, 113.9, 84.9, 82.5, 79.9, 78.4, 74.5, 74.3, 71.3, 61.1, 57.8, 57.7, 57.0, 55.3, 32.1; HRMS (ESI) m/z calcd for $C_{25}H_{34}O_7SNa$ $[M+Na]^+$, 501.1923; found, 501.1900.

Phenyl 4-*O*-benzyl-7-deoxy-2,3,6-tri-*O*-methyl-L-*glycero*-*a*-D-thio-*manno*octopyranoside (17)

Compound **17** (70%, 0.14 g) was synthesized analogously as **16** from compound **13**, as a colorless oil. R_f= 0.30 (hexane/EtOAc 4:6); $[\alpha]_D^{22}$ = +145.1 (*c* 2.00, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 – 7.40 (m, 2H, Ar-*H*), 7.38 – 7.31 (m, 4H, Ar-*H*), 7.30 – 7.25 (m, 3H, Ar-*H*), 7.22 (t, *J* = 7.4 Hz, 1H, Ar-*H*), 5.81 (d, *J* = 1.4 Hz, 1H, H-1), 4.98 (d, *J* = 11.0 Hz, 1H, OC*H*$_a$H$_b$Ph), 4.63 (d, *J* = 11.0 Hz, 1H, OCH$_a$*H*$_b$Ph), 4.04 (t, *J* = 9.5 Hz, 1H, H-4), 3.92 (dd, *J* = 9.5, 1.1 Hz, 1H, H-5), 3.85 (dd, *J* = 3.0, 1.4 Hz, 1H, H-2), 3.81 – 3.78 (m, 1H, H-6), 3.59 (dd, *J* = 9.2, 3.2 Hz, 1H, H-3), 3.54 – 3.53 (m, 2H, H-8, H-8′), 3.52 (s, 3H, OC*H*$_3$), 3.49 (s, 3H, OC*H*$_3$), 3.37 (s, 3H, OC*H*$_3$), 1.90 (dq, *J* = 13.3, 6.5 Hz, 1H, H-7), 1.65 (dq, *J* = 13.2, 6.2 Hz, 1H, H-7′), 1.52 (s, 1H, O-*H*); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.6, 134.6, 129.9, 129.0, 128.4, 127.8, 127.6, 126.9, 84.3, 82.4, 78.6, 75.3, 75.0, 74.5, 73.4, 59.5, 58.3, 57.9, 57.5, 32.1; HRMS (ESI) m/z calcd for $C_{24}H_{32}O_6SNa$ $[M+Na]^+$, 471.1817; found, 471.1823.

Phenyl 4-*O*-*p*-methoxybenzyl-7-deoxy-2,3,6-tri-*O*-methyl-L-*glycero*-α-D-thio-*manno*octopyranoside (18)

Compound **18** (88%, 2.0 g) was synthesized analogously as **16** from compound **14**, as a colorless oil. $[\alpha]_D^{22}$ = +154.7 (*c* 0.70, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.42 (m, 2H, Ar-*H*), 7.32 – 7.21 (m, 5H, Ar-*H*), 6.89 – 6.87 (m, 2H, Ar-*H*), 5.82 (d, *J* = 1.4 Hz, 1H, H-1), 4.90 (d, *J* = 10.7 Hz, 1H, OC*H*$_a$H$_b$Ph), 4.57 (d, *J* = 10.7 Hz, 1H, OCH$_a$*H*$_b$Ph), 4.03(t, *J* = 9.2 Hz, 1H, H-4), 3.91 (dd, *J* = 9.7, 1.4 Hz, 1H, H-5), 3.85 (dd, *J* = 1.4, 3.4 Hz, 1H, H-2), 3.82 – 3.78 (m, 1H, H-6), 3.80 (s, 3H, OC*H*$_3$), 3.89 (dd, *J* = 9.2, 3.4 Hz, 1H), 3.57 – 3.56 (m, 2H, H-8, H-8′), 3.54 (s, 3H, OC*H*$_3$), 3.50 (s, 3H, OC*H*$_3$), 3.41 (s, 3H, OC*H*$_3$), 1.91 (dq, *J* = 13.1, 6.5 Hz, 1H, H-7), 1.71 – 1.60 (m, 1H, H-7′), 1.46 (br s, 1H, O-*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 134.6, 130.8, 129.9, 129.5, 129.1, 126.9, 113.7, 84.3, 82.4, 78.6, 75.5, 74.7, 74.3, 73.5, 59.7, 58.5, 57.9, 57.6, 55.3, 32.2; HRMS (ESI) m/z calcd for $C_{25}H_{34}O_7SNa$ $[M+Na]^+$, 501.1923; found, 501.1916.

Phenyl 7-deoxy-2,3,6-tri-*O*-methyl-D-*glycero*-α-D-thio-*manno*octofuranoside (19)

To a stirred solution of mannopyranoside **15** (50 mg, 0.11 mmol) in CH_2Cl_2 (1.0 ml) was added BCl_3 (0.13 ml, 1M solution in CH_2Cl_2) at −78 °C. The reaction mixture was stirred additional 3h at −78 °C before it was quenched with $NaHCO_3$ solution. After extraction of aqueous phase with CH_2Cl_2 (2 x 10 ml), the combined organic extracts were washed with water (10 ml), dried over Na_2SO_4, and concentrated. Silica gel column purification (eluent: 100% ethyl acetate) afforded **19** (25 mg, 64 %) as a colorless oil. R_f= 0.30 (EtOAc/MeOH 9:1); $[\alpha]_D^{22}$ = −185.1 (*c* 0.35, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.44 (m, 2H, Ar-*H*), 7.42 – 7.15 (m, 3H, Ar-*H*), 5.65 (d, *J* = 5.8 Hz, 1H, H-1), 4.46 (dd, *J* = 2.9, 8.3 Hz, 1H, H-5), 4.10 – 4.02 (m, 3H, H-2, H-3, H-4), 3.81 (ddd, *J* = 11.7, 8.3, 3.9 Hz, 1H, H-6), 3.74 – 3.72 (m, 1H, H-8), 3.71 – 3.66 (m, 1H, H-8′), 3.64 (s, 3H, OC*H*$_3$), 3.57 (s, 3H, OC*H*$_3$), 3.42 (s, 3H, OC*H*$_3$), 2.83 (br s, 2H, O-*H*), 1.95 – 1.91 (m, 1H, H-7), 1.85 – 1.74 (m, 1H, H-7′); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.7, 130.6, 128.9, 126.7, 89.8, 82.6, 81.1, 79.9, 79.0, 68.6, 60.5, 60.4, 59.5, 57.3, 30.7; HRMS (ESI) m/z calcd for $C_{17}H_{26}O_6SNa$ $[M+Na]^+$, 381.1348; found, 381.1340.

Phenyl 5,8-anhydro-7-deoxy-2,3,6-tri-*O*-methyl-D-*glycero*-α-D-thio-*manno*octofuranoside (20)

To a stirred solution of mannopyranoside **15** (50 mg, 0.11 mmol) in CH_2Cl_2 (1 ml) was added BCl_3 (0.13 ml, 1M solution in CH_2Cl_2) at −78 ^oC. The reaction mixture was stirred for further 3 h before it was quenched with $NaHCO_3$ solution. After extraction of aqueous phase with CH_2Cl_2 (2 x 10 ml), the combined organic extracts were washed with water (10 ml), dried over Na_2SO_4, and concentrated. The crude residue was dissolved in pyridine (1.0 ml), to which then was added TsCl (29.2 mg, 0.15 mmol) and DMAP (1.7 mg) at room temperature. This reaction mixture was stirred for additional 8 h before solvents were evaporated under high vacuum. The crude residue was purified through silica gel column chromatography (eluent: 40% ethyl acetate in hexane) to give **20** (66% over 2 steps, 25 mg,) as a white solid. R_f= 0.50 (hexane/EtOAc 1:1); $[\alpha]_D^{22}$ =Mp = 88 – 90 ^oC; $[\alpha]_D^{22}$ = −201.4 (*c* 0.55, CH_2Cl_2); ^1H NMR (600 MHz, $CDCl_3$) δ 7.54 – 7.44 (m, 2H, Ar-*H*), 7.26 – 7.23 (m, 2H, Ar-*H*), 7.22 – 7.11 (m, 1H, Ar-*H*), 5.65 (d, *J* = 6.6 Hz, 1H, H-1), 4.34 (d, *J* = 7.3 Hz, 1H, H-5), 4.19 – 4.18 (m, H-6), 4.08 (dd, *J* = 4.0, 6.6 Hz, 1H, H-2), 3.93 – 3.91 (m, 1H, H-3), 3.92 – 3.91 (m, 1H, H-8), 3.86 – 3.82 (m, 1H, H-8′), 3.77 (dd, *J* = 7.7, 4.0 Hz, 1H, H-4), 3.62 (s, 3H, OC*H*$_3$), 3.52 (s, 3H, OC*H*$_3$), 3.31 (s, 3H, OC*H*$_3$), 1.99 – 1.84 (m, 2H, H-7, H-7′); ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.5, 130.5, 128.7, 126.4, 89.7, 83.0, 83.0, 81.6, 81.1, 78.9, 67.4, 60.7, 58.8, 56.7, 32.6; HRMS (ESI) m/z calcd for $C_{17}H_{24}O_5SNa$ $[M+Na]^+$, 363.1242; found, 363.1249.

Phenyl 7-deoxy-2,3,6-tri-*O*-methyl-L-*glycero*-α-D-thio-*manno*octofuranoside (21)

Compound **21** (66%, 26mg) was synthesized analogously as **19** from **17**, as a colorless oil. R_f= 0.30 (EtOAc/MeOH 9:1); $[\alpha]_D^{22}$ = −142.0 (*c* 1.15, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.48 (m, 2H), 7.30 – 7.19 (m, 3H), 5.65 (d, *J* = 6.4 Hz, 1H), 4.16 – 4.05 (m, 4H), 3.82 – 3.67 (m, 3H), 3.62 (s, 3H), 3.56 (s, 3H), 2.42 (s, 3H), 2.90 (br s , 2H), 2.01 – 1.86 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 130.5, 128.8, 126.6, 89.7, 82.6, 79.9, 79.0, 76.7, 71.4, 60.4, 59.4, 58.8, 58.4, 33.1; HRMS (ESI) m/z calcd for $C_{17}H_{26}O_6SNa$ $[M+Na]^+$, 381.1348; found, 381.1343.

Phenyl 5,8-anhydro-7-deoxy-2,3,6-tri-*O*-methyl-L-*glycero*-α-D-thio-*manno*octofuranoside (22)

Compound **22** (54%, 20 mg) was synthesized analogously as **20** from **17**, as a colorless oil. R_f= 0.50 (hexane/EtOAc 1:1); $[\alpha]_D^{22}$ = −151.6 (*c* 0.50, CH_2Cl_2); ^1H NMR (600 MHz, $CDCl_3$) δ 7.51 – 7.50 (m, 2H, Ar-*H*), 7.26 – 7.24 (m 2H, Ar-*H*), 7.18 (t, *J* = 7.4 Hz, 1H, Ar-*H*), 5.69 (d, *J* = 6.6

Hz, 1H, H-1), 4.23 (dd, *J* = 9.6, 4.0 Hz, 1H, H-4), 4.15 (dd, *J* = 4.0, 6.2 Hz, 1H, H-2), 4.12 (dd, *J* = 9.5, 3.3 Hz, 1H, H-5), 4.00 – 3.94 (m, 3H, H-3, H-6, H-8), 3.92 – 3.86 (m, 1H, H-8′), 3.62 (s, 3H, OCH_3), 3.52 (s, 3H, OCH_3), 3.37 (s, 3H, OCH_3), 2.11 (ddd, *J* = 13.3, 6.8, 2.9 Hz, 1H, H-7), 1.98 – 1.89 (m, 1H, H-7′); ^{13}C NMR (150 MHz, $CDCl_3$) δ 137.7, 130.3, 128.6, 126.3, 89.4, 82.9, 81.1, 79.4, 79.3, 78.2, 66.8, 60.7, 58.8, 57.1, 30.9; HRMS (ESI) m/z calcd for $C_{17}H_{24}O_5SNa$ $[M+Na]^+$, 363.1242; found, 363.1245.

Phenyl 7-deoxy-2,3,6-tri-*O*-methyl-D-*glycero*-α-D-thio-*manno*octopyranoside (23)

To a stirred solution of compound **16** (1.3 g, 2.71 mmol) in CH_2Cl_2/H_2O (36:4; v/v) was added DDQ (1.2 g, 5.43 mmol) at room temperature. The reaction was stirred at room temperature for 0.5 h before TLC (5% methanol in ethyl acetate) showed reaction completion. The reaction mixture was quenched with sat. $NaHCO_3$ solution, extracted with CH_2Cl_2 (3 x 30 ml), dried over Na_2SO_4, and concentrated. Column chromatography on silica gel (eluent: methanol/ethyl acetate =1:9) afforded **23** (0.8 g, 82%) as a colorless oil. R_f= 0.40 (EtOAc/MeOH 9.5:0.5); $[\alpha]_D^{22}$ = +132.4 (*c* 2.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.47 (m, 2H, Ar-*H*), 7.34 – 7.23 (m, 3H, Ar-*H*), 5.65 (d, *J* = 1.6 Hz, 1H, H-1), 4.24 (dd, *J* = 9.6, 4.0 Hz, 1H, H-5), 3.92 (t, *J* = 9.3 Hz, 1H, H-4), 3.87 (dd, *J* = 3.0, 1.7 Hz, 1H, H-2), 3.76 – 3.69 (m, 3H, H-6, H-8, H-8′), 3.51 (s, 3H, OCH_3), 3.45 (s, 3H, OCH_3), 3.43 (dd, *J* = 9.7, 3.1 Hz, 1H, H-3), 3.41 (s, 3H, OCH_3), 3.27 (br s, 1H, O-*H*), 2.41 (br s, 1H, O-*H*), 1.97 – 1.79 (m, 2H, H-7, H-7′); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.6, 130.9, 129.1, 127.4, 85.1, 81.3, 80.4, 76.7, 71.6, 68.3, 60.1, 58.1, 57.5, 57.3, 32.0; HRMS (ESI) m/z calcd for $C_{17}H_{26}O_6SNa$ $[M+Na]^+$, 381.1348; found, 381.1341.

Phenyl 7-deoxy-2,3,6-tri-*O*-methyl-L-*glycero*-α-D-thio-*manno*octopyranoside (25)

Compound **25** (89%, 0.87 g) was synthesized analogously as **23** from compound **18**, as a colorless oil. R_f= 0.50 (EtOAc/MeOH 9.5:0.5); $[\alpha]_D^{22}$ = +106.2 (*c* 0.35, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.44 (m, 2H, Ar-*H*), 7.33 – 7.23 (m, 3H, Ar-*H*), 5.79 (br s 1H, H-1), 4.14 (t, *J* = 9.7 Hz, 1H, H-4), 3.99 (d, *J* = 9.3 Hz, 1H, H-5), 3.88 (br s, 1H, H-2), 3.79 (t, *J* = 6.0 Hz, 1H, H-6), 3.68 – 3.65 (m, 2H, H-8, H-8′), 3.51 (s, 3H, OCH_3), 3.50 (s, 3H, OCH_3), 3.47 (s, 3H, OCH_3), 3.44 – 3.43 (m, 1H, H-3), 2.67 (br s, 1H, O-*H*), 1.91 (dd, *J* = 13.6, 7.4 Hz, 1H, H-7), 1.79 (br s, 1H, O-*H*), 1.64 (dd, *J* = 14.0, 5.9 Hz, 1H, H-7′); ^{13}C NMR (150 MHz, $CDCl_3$) δ 134.4,

130.3, 129.1, 127.1, 84.7, 81.4, 76.8, 73.3, 66.5, 60.2, 59.4, 58.4, 57.1, 33.0; HRMS (ESI) m/z calcd for $C_{17}H_{26}O_6SNa$ $[M+Na]^+$, 381.1348; found, 381.1331.

Phenyl 7-deoxy-2,3-di-*O*-methyl4-*O*-(*p*-methoxybenzyl)-D-*glycero*-α-D-thio-*manno*heptopyranoside (27)

Compound **27** (12%, 50 mg) was synthesized analogously as **7** from compound **6**, as a colorless oil (MeMgI was used as a Grignard reagent). R_f= 0.45 (hexane/EtOAc 6:4); $[\alpha]_D^{22}$ = +167.5 (*c* 0.20, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.47 (m, 2H, Ar-*H*), 7.38 – 7.21 (m, 5H, Ar-*H*), 6.89 – 6.87 (m, 2H, Ar-*H*), 5.63 (d, *J* = 1.5 Hz, 1H, H-1), 4.91 (d, *J* = 10.6 Hz, 1H, OC$H_a$$H_b$Ph), 4.58 (d, *J* = 10.5 Hz, 1H, OC$H_a$$H_b$Ph), 4.03 – 3.94 (m, 2H, H-5, H-6), 3.87 (dd, *J* = 2.9, 1.5 Hz, 1H, H-2), 3.84 – 3.75 (m, 1H, H-4), 3.80 (s, 3H, OCH_3), 3.64 (dd, *J* = 9.0, 3.0 Hz, 1H), 3.54 (s, 3H, OCH_3), 3.52 (s, 3H, OCH_3), 2.69 (d, *J* = 4.5 Hz, 1H, O-*H*), 1.10 (d, *J* = 6.0 Hz, 3H, H-7); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 133.8, 131.7, 130.1, 129.8, 129.1, 127.6, 113.9, 84.7, 82.3, 78.4, 74.7, 74.4, 68.7, 58.3, 57.5, 55.3, 18.2; HRMS (ESI) m/z calcd for $C_{23}H_{30}O_6SNa$ $[M+Na]^+$, 357.1661; found, 357.1683.

Phenyl 7-deoxy-2,3-di-*O*-methyl-4-*O*-(*p*-methoxybenzyl)-L-*glycero*-α-D-thio-*manno*heptopyranoside (28)

Compound **28** (61%, 0.31 g) was synthesized analogously as **7** from compound **6**, as a colorless oil (MeMgI was used as a Grignard reagent). R_f= 0.40 (hexane/EtOAc 6:4); $[\alpha]_D^{22}$ = +173.3 (*c* 0.15, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.44 (m, 2H, Ar-*H*), 7.33 – 7.26 (m, 5H, Ar-*H*), 6.89 – 6.87 (m, 2H, Ar-*H*), 5.68 (d, *J* = 1.6 Hz, 1H, H-1), 4.85 (d, *J* = 10.5 Hz, 1H, OC$H_a$$H_b$Ph), 4.61 (d, *J* = 10.5 Hz, 1H, OC$H_a$$H_b$Ph), 4.10 – 4.05 (m, 1H, H-6), 3.97 (t, *J* = 9.7 Hz, 1H, H-4), 3.86 (dd, *J* = 2.8, 1.6 Hz, 1H, H-2), 3.83 – 3.82 (m, 1H, H-5), 3.80 (s, 3H, OCH_3), 3.60 (dd, *J* = 9.3, 2.8 Hz, 1H, H-3), 3.57 (s, 3H, OCH_3), 3.50 (s, 3H, OCH_3), 1.78 (d, *J* = 8.1 Hz, 1H, O-*H*), 1.14 (d, *J* = 6.5 Hz, 3H, H-7); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 134.2, 131.3, 130.6, 129.8, 129.1, 127.5, 113.9, 84.9, 82.1, 78.7, 75.1, 75.0, 74.6, 65.4, 58.4, 57.9, 55.3, 20.2; HRMS (ESI) m/z calcd for $C_{23}H_{30}O_6SNa$ $[M+Na]^+$, 357.1661; found, 357.1658.

Phenyl 2,3-di-*O*-methyl-4-*O*-(*p*-methoxybenzyl)-6-*O*-(*p*-nitrobenzoyl)-D-glycero-α-D-thio-*manno*heptopyranoside (29)

A solution of **28** (0.5 g, 1.15 mmol), PPh_3 (0.60 g, 2.30 mmol) and *p*-nitrobenzoic acid (0.38 g, 2.30 mmol) in THF (15 ml) was treated with DIAD (0.45 ml, 2.30 mmol) at room temperature and stirred for 3 h. The reaction mixture was then concentrated and chromatographic purification on silica gel (20% ethyl acetate in hexane) afforded **29** (0.7 g, 89%) as a colorless oil. R_f= 0.7 (hexane/EtOAc 7:3); $[\alpha]_D^{22}$ = +51.7 (*c* 1.30, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 – 8.11 (m, 2H, Ar-*H*), 8.07 – 7.97 (m, 2H, Ar-*H*), 7.47 – 7.45 (m, 2H, Ar-*H*), 7.36 – 7.20 (m, 5H, Ar-*H*), 6.93 – 6.86 (m, 2H, Ar-*H*), 5.77 (d, *J* = 1.3 Hz, 1H, H-1), 5.48 (dq, *J* = 6.5, 1.9 Hz, 1H, H-6), 4.89 (d, *J* = 10.8 Hz, 1H, OC*H*$_a$H$_b$Ph), 4.57 (d, *J* = 10.7 Hz, 1H, OCH$_a$*H*$_b$Ph), 4.35 (dd, *J* = 9.9, 1.9 Hz, 1H, H-5), 3.89 (dd, *J* = 2.9, 1.5 Hz, 1H, H-2), 3.80 (s, 3H, OC*H*$_3$), 3.74 (t, *J* = 9.0 Hz, 1H, H-4), 3.63 (dd, *J* = 9.3, 3.0 Hz, 1H, H-3), 3.56 (s, 3H, OC*H*$_3$), 3.51 (s, 3H, OC*H*$_3$), 1.28 (d, *J* = 6.5 Hz, 3H, H-7); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 159.4, 150.3, 135.9, 134.4, 130.7, 130.5, 130.1, 129.8, 129.0, 127.1, 123.3, 113.9, 84.0, 82.3, 78.2, 74.4, 74.1, 73.3, 71.3, 58.0, 57.7, 55.3, 13.6; HRMS (ESI) m/z calcd for $C_{30}H_{33}NO_9SNa$ $[M+Na]^+$, 606.1774; found, 606.1771; The compound **29** (0.6 g, 1.02 mmol) was treated with K_2CO_3 (0.17g, 1.23 mmol) in MeOH/CH_2Cl_2 (15ml:1ml) at room temperature. After 6h, solvents were evaporated under high vacuum to give crude residue which was purified through silica gel column (eluent: 30% ethyl acetate in hexane) to give **27** (0.35 g., 78%) as a colorless oil.

Phenyl 7-deoxy-2,3-di-*O*-methyl-4,6-*O*-(*p*-methoxybenzylidene)-D-*glycero*-α-D-thio-*mannohepto*pyranoside (30) and Phenyl 7-deoxy-2,3-di-*O*-methyl-D-*glycero*-α-D-thio-*manno*heptopyranoside (32)

A solution of **27** (0.35 g, 0.80 mmol) in CH_3CN:H_2O (8:2, 10 ml) was treated with DDQ (0.36 g, 1.60 mmol) at room temperature and stirred for 3h. The reaction mixture was then diluted with EtOAc and washed with a saturated solution of NaHCO3, water, and brine. The organic layer was dried over Na_2SO_4 and concentrated under high vacuum. Column chromatography on silica gel afforded benzylidene acetal **30** (11%, 40 mg) and diol **32** (61%, 0.15g) as a colorless oils.

30: R_f= 0.80 (hexane/EtOAc 6:4); $[\alpha]_D^{22}$ = +208.0 (*c* 0.25, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.49 (m, 2H, Ar-*H*), 7.45 – 7.43 (m, 2H, Ar-*H*), 7.36 – 7.25 (m, 3H, Ar-*H*), 6.90 – 6.86 (m, 2H, Ar-*H*), 5.67 (d, *J* = 1.0 Hz, 1H, H-1), 5.63 (s, 1H, Benzylidene-*H*), 4.13 (t, *J* = 9.8 Hz, 1H, H-4), 3.99 – 3.92 (m, 1H, H-6), 3.90 (dd, *J* = 3.4, 1.4 Hz, 1H, H-2), 3.87 (t, *J* = 9.3 Hz, 1H, H-5), 3.79 (s, 3H, OC*H*$_3$), 3.72 (dd, *J* = 9.9, 3.4 Hz, 1H, H-3), 3.58 (s, 3H, OC*H*$_3$), 3.54 (s, 3H,

OCH_3), 1.23 (d, J = 6.0 Hz, 3H, H-7); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9, 133.8, 131.5, 130.2, 129.1, 127.6, 127.5, 113.6, 101.1, 85.7, 80.2, 78.3, 76.7, 75.0, 70.8, 59.1, 59.0, 55.3, 17.8; HRMS (ESI) m/z calcd for $C_{23}H_{28}O_6SNa$ $[M+Na]^+$, 455.1504; found, 455.1511.

32: R_f= 0.10 (hexane/EtOAc 6:4); $[\alpha]_D^{22}$ = +128.2 (*c* 0.70, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.47 (m, 2H, Ar-*H*), 7.35 – 7.25 (m, 3H, Ar-*H*), 5.65 (d, J = 1.3 Hz, 1H, H-1), 4.07 – 4.00 (m, 1H, H-6), 3.97 (t, J = 9.3 Hz, 1H, H-4), 3.92 – 3.86 (m, 2H, H-2, H-5), 3.50 (s, 3H, OCH_3), 3.48 (s, 3H, OCH_3), 3.46 (dd, J = 9.3, 3.1 Hz, 1H, H-3), 2.54 (br s, 2H, O-*H*), 1.17 (t, J = 6.4 Hz, 3H, H-7); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.8, 131.5, 129.1, 127.6, 84.9, 81.1, 77.3, 74.5, 70.6, 70.0, 58.3, 57.1, 19.1. HRMS (ESI) m/z calcd for $C_{15}H_{22}O_5SNa$ $[M+Na]^+$, 337.1086; found, 337.1093.

Phenyl 7-deoxy-2,3-di-*O*-methyl-4,6-*O*-(*p*-methoxybenzylidene)-L-*glycero*-α-D-thio-*manno*heptopyranoside (31)

Compound **31** (5%, 17 mg) was synthesized analogously as **30** from **28**, as a colorless oil. R_f= 0.70 (hexane/EtOAc 6:4); $[\alpha]_D^{22}$ = +178.8 (*c* 1.40, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 4H, Ar-*H*), 7.36 – 7.28 (m, 3H, Ar-*H*), 6.89 – 6.87 (m, 2H, Ar-*H*), 5.85 (s, 1H, Benzylidene-*H*), 5.63 (d, J = 1.4 Hz, 1H, H-1), 4.51 (dd, J = 10.0, 5.7 Hz, 1H, H-5), 4.44 – 4.39 (m, 1H, H-6), 4.36 (t, J = 9.8 Hz, 1H, H-4), 3.89 (dd, J = 3.1, 1.4 Hz, 1H, H-2), 3.80 (s, 3H, OCH_3), 3.68 (dd, J = 9.6, 3.2 Hz, 1H, H-3), 3.56 (s, 3H, OCH_3), 3.51 (s, 3H, OCH_3), 1.47 (d, J = 6.8 Hz, 3H, H-7); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 134.1, 131.5, 130.4, 129.1, 127.6, 127.5, 113.6, 94.2, 85.9, 80.1, 78.5, 72.6, 70.4, 67.3, 59.0, 58.8, 55.3, 11.8; HRMS (ESI) m/z calcd for $C_{23}H_{28}O_6SNa$ $[M+Na]^+$, 455.1504; found, 455.1514.

Phenyl 7-deoxy-2,3-di-*O*-methyl-L-*glycero*-α-D-thio-*manno*heptopyranoside (33)

Compound **33** (70%, 0.18g) was synthesized analogously as **32** from **28**, as a colorless oil. R_f= 0.15 (hexane/EtOAc 6:4); $[\alpha]_D^{22}$ = +165.7 (*c* 1.05, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.44 (m, 2H, Ar-*H*), 7.30 – 7.22 (m, 3H, Ar-*H*), 5.69 (d, J = 1.4 Hz, 1H, H-1), 4.15 – 4.10 (m, 1H, H-6), 4.07 (t, J = 9.1 Hz, 1H, H-4), 3.86 (dd, J = 1.4, 3.2 Hz, 1H, H-2), 3.84 – 3.81 (m, 1H, H-5), 3.48 (s, 3H, OCH_3), 3.44 (s, 3H, OCH_3), 3.46 (dd, J = 9.8, 3.23 Hz, 1H, H-3), 3.07 (br s, 2H, O-*H*), 1.15 (t, J = 6.4 Hz, 3H, H-7); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.2, 131.4, 129.1, 129.0, 127.4, 85.1, 81.5, 77.8, 76.8, 75.4, 66.4, 65.5, 58.4, 57.4, 19.7; HRMS (ESI) m/z calcd for $C_{15}H_{22}O_5SNa$ $[M+Na]^+$, 337.1086; found, 337.1075.

Methyl 4,8-anhydro-7-deoxy-2,3,6-tri-*O*-methyl-D-*glycero*-β-D-*manno*octopyranosyl-(1→6)-2',3',4'-tri-*O*-benzyl-α-D-*gluco*pyranoside (39β) and Methyl 4,8-anhydro-7-deoxy-2,3,6-tri-*O*-methyl-D-*glycero*-α-D-*manno*octopyranosyl-(1→6)-2',3',4'-tri-*O*-benzyl-α-D-*gluco*pyranoside (39α)

Coupling of **24** with **36** following the general procedure afforded **39β** and **α** in 86% yield in 4.2:1 ratio (Repetition: Yield = 83%; 4.6:1=β:α). **39β:** R_f= 0.30 (hexane/EtOAc 2:8); $[\alpha]_D^{22}$ = +18.0 (*c* 0.60, CH_2Cl_2);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 15H, Ar-*H*), 4.98 (d, *J* = 10.8 Hz, 1H, OC*H*$_2$Ph), 4.89 (d, *J* = 11.3 Hz, 1H, OC*H*$_2$Ph), 4.81 (d, *J* = 10.8 Hz, 1H, OC*H*$_2$Ph), 4.79 (d, *J* = 12.2 Hz, 1H, OC*H*$_2$Ph), 4.66 (d, *J* = 12.2 Hz, 1H, OC*H*$_2$Ph), 4.58 (d, *J* = 3.9 Hz, 1H, H-1′), 4.56 (d, *J* = 11.2 Hz, 1H, OC*H*$_2$Ph), 4.23 (s, 1H, H-1), 4.17 (dd, *J* = 10.6, 1.7 Hz, 1H, H-6a′), 4.01 (t, *J* = 9.2 Hz, 1H, H-4′), 3.93 (t, *J* = 9.7 Hz, 1H, H-4), 3.89 – 3.82 (m, 1H, H-5′), 3.76 – 3.68 (m, 3H, H-6, H-8a, H-8b), 3.60 (d, *J* = 3.1 Hz, 1H, H-2), 3.56 (s, 3H, OC*H*$_3$), 3.51 – 3.48 (m, 2H, H-2′, H-6b′), 3.47 (s, 3H, OC*H*$_3$), 3.43 (s, 3H, OC*H*$_3$), 3.37 (s, 3H, OC*H*$_3$), 3.39 – 3.33 (m, 1H, H-3′), 3.10 (dd, *J* = 9.8, 3.1 Hz, 1H, H-3), 3.02 (dd, *J* = 9.7, 2.4 Hz, 1H, H-5), 1.91 – 1.84 (m, 1H, H-7a), 1.73 – 1.61 (m, 1H, H-7b); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 138.3, 138.1, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 127.7, 102.5 (J_{C-H} = 151.5 Hz, C-1), 97.7 (J_{C-H} = 162.1 Hz, C-1′), 82.1, 81.5, 79.9, 78.2, 77.2, 75.9, 75.1, 74.8, 73.9, 73.4, 71.5, 69.9, 69.0, 62.5, 61.7, 58.0, 57.3, 55.0, 30.1; HRMS (ESI) m/z calcd for $C_{39}H_{50}O_{11}Na$ $[M+Na]^+$, 717.3251; found, 717.3254.

39α: R_f= 0.35 (hexane/EtOAc 2:8); $[\alpha]_D^{22}$ = +26.0 (*c* 0.25, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 15H), 4.99 (d, *J* = 10.3 Hz, 1H), 4.98 (s, 1H), 4.96 (d, *J* = 10.3 Hz, 1H), 4.80 (d, *J* = 11.7 Hz, 1H), 4.77 (d, *J* = 9.2 Hz, 1H), 4.68 (d, *J* = 12.1 Hz, 1H), 4.60 (d, *J* = 9.2, 1H), 4.58 (d, *J* = 3.7 Hz, 1H), 4.00 (d, *J* = 9.5 Hz, 1H), 3.93 (d, *J* = 9.9 Hz, 1H), 3.90 (dd, *J* = 3.6, 10.6 Hz, 1H), 3.78 – 3.75 (m ,1H), 3.66 – 3.61 (m, 3H), 3.53 (t, *J* = 9.9 Hz, 1H), 3.53 (dd, *J* = 9.5, 3.6 Hz, 1H), 3.52 – 3.49 (m, 2H), 3.49 – 3.46 (m, 2H), 3.45 (s, 3H), 3.43 (s, 3H), 3.37 (s, 3H), 3.36 (s, 3H), 1.78 – 1.75 (m, 1H), 1.33 – 1.27 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 138.3, 138.1, 128.5, 128.4, 128.4, 128.1, 127.8, 127.7, 127.6, 127.2, 98.5 (J_{C-H} = 168.0 Hz, C-1), 98.0 (J_{C-H} = 167.2 Hz, C-1′), 82.1, 79.9, 79.1, 77.6, 75.9, 74.7, 74.0, 73.4, 71.8, 71.1, 69.6, 66.2, 62.2, 60.0, 59.3, 57.6, 57.0, 55.2, 28.8; HRMS (ESI) m/z calcd for $C_{39}H_{50}O_{11}Na$ $[M+Na]^+$, 717.3251; found, 717.3248.

Methyl 4,8-anhydro-7-deoxy-2,3,6-tri-*O*-methyl-D-*glycero*-β-D-*manno*octopyranosyl-(1→4)-2',3',6'-tri-*O*-benzyl-α-D-*gluco*pyranoside (40β) and Methyl 4,8-anhydro-7-deoxy-2,3,6-tri-*O*-methyl-D-*glycero*-α-D-*manno*octopyranosyl-(1→4)-2',3',6'-tri-*O*-benzyl-α-D-*gluco*pyranoside (40α)

Coupling of **24** with **37** following the general procedure afforded **40β** and **α** in 71% yield in 4.0:1 ratio (Repetition: Yield = 78%; 3.9:1=β:α) **40β:** R_f= 0.40 (hexane/EtOAc 2:8); $[\alpha]_D^{22}$ = +18.0 (*c* 0.95, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.22 (m, 15H, Ar-*H*), 5.07 (d, *J* = 12.0 Hz, 1H, OC*H*$_2$Ph), 4.98 (d, *J* = 12.0 Hz, 1H, OC*H*$_2$Ph), 4.73 (d, *J* = 12.4 Hz, 1H, OC*H*$_2$Ph), 4.70 (d, *J* = 12.4 Hz, 1H, OC*H*$_2$Ph), 4.62 (d, *J* = 3.4 Hz, 1H, H-1′), 4.61 (d, *J* = 12.2 Hz, 1H, OC*H*$_2$Ph), 4.49 (d, *J* = 12.2 Hz, 1H, OC*H*$_2$Ph), 4.48 (br s, 1H, H-1), 3.98 (t, *J* = 9.0 Hz, 1H, H-3′), 3.90 (t, *J* = 9.3 Hz, 1H, H-4), 3.85 – 3.77 (m, 3H, H-4′, H-5′, H-6a′), 3.68 – 3.63 (m, 3H, H-6b′, H-8a, H-8b), 3.55 (dd, *J* = 9.3, 3.6 Hz, 1H, H-2′), 3.47 (s, 3H, OC*H*$_3$), 3.42 (d, *J* = 2.7 Hz, 1H, H-2), 3.38 (s, 3H, OC*H*$_3$), 3.37 (s, 3H, OC*H*$_3$), 3.29 – 3.28 (m, 1H, H-6), 3.26 (s, 3H, OC*H*$_3$), 2.92 (dd, *J* = 9.7, 2.9 Hz, 1H, H-3), 2.74 (dd, *J* = 9.8, 2.3 Hz, 1H, H-5), 1.66 (dd, *J* = 8.7, 7.2 Hz, 1H, H-7a), 1.41 – 1.29 (m, 1H, H-7b); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.8, 138.1, 137.9, 128.5, 128.4, 128.1, 127.9, 127.8, 127.7, 126.8, 126.6, 102.1 (J_{C-H} = 155.7 Hz, C-1), 98.1 (J_{C-H} = 166.6 Hz, C-1′), 81.9, 80.3, 79.7, 77.4, 77.2, 76.7, 75.1, 74.5, 73.6, 73.5, 73.3, 71.3, 69.4, 68.8, 62.5, 61.4, 58.2, 57.4, 55.2, 30.3; HRMS (ESI) m/z calcd for $C_{39}H_{50}O_{11}Na$ $[M+Na]^+$, 717.3251; found, 717.3246

40α: R_f= 0.45 (hexane/EtOAc 2:8); $[\alpha]_D^{22}$ = +35.0 (*c* 0.20, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.23 (m, 15H), 5.31 (d, *J* = 1.4 Hz, 1H), 5.16 (d, *J* = 11.6 Hz, 1H), 4.69 (d, *J* = 12.1 Hz, 1H), 4.67 (d, *J* = 11.7 Hz, 1H), 4.61 (d, *J* = 3.7 Hz, 1H), 4.59 (d, *J* = 12.1 Hz, 1H), 4.58 (d, *J* = 11.7 Hz, 1H), 4.53 (d, *J* = 12.1 Hz, 1H), 3.93 (t, *J* = 9.9 Hz, 1H), 3.90 (t, *J* = 9.1 Hz, 1H), 3.74 – 3.64 (m, 5H), 3.55 (dd, *J* = 9.5, 3.7 Hz, 1H), 3.50 (dd, *J* = 10.2, 2.6 Hz, 1H), 3.48 (dd, *J* = 1.5, 2.9 Hz, 1H), 3.45 (d, *J* = 2.9 Hz, 1H), 3.41 (dd, *J* = 9.9, 2.9 Hz, 1H), 3.41 – 3.40 (m, 1H), 3.40 (s, 3H), 3.37 (s, 3H), 3.30 (s, 3H), 3.04 (s, 3H), 1.81 – 1.78 (m, 1H), 1.53 – 1.47 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.6, 138.1, 137.8, 128.5, 128.4, 128.3, 128.1, 127.9, 127.5, 127.4, 127.3, 126.7, 100.4 (J_{C-H} = 171.6 Hz, C-1), 97.7 (J_{C-H} = 168.1 Hz, C-1′), 81.6, 80.0, 78.9, 77.0, 76.8, 75.1, 73.9, 73.5, 73.1, 72.0, 71.8, 69.7, 69.4, 62.3, 60.0, 58.8, 57.4, 57.3, 55.3, 29.8; HRMS (ESI) m/z calcd for $C_{39}H_{50}O_{11}Na$ $[M+Na]^+$, 717.3251; found, 717.3231.

(1-Adamantanyl) 4,8-anhydro-7-deoxy-2,3,6-tri-*O*-methyl-D-*glycero*-β-D-*manno*octopyranoside (41β) and (1-Adamantanyl) 4,8-anhydro-7-deoxy-2,3,6-tri-*O*-methyl-D-*glycero*-α-D-*manno*octopyranoside (41α)

Coupling of **24** with **38** following the general procedure afforded **41β** and **α** in 68% yield in 4.4:1 ratio (Repetition: Yield = 86%; 4.2:1= β:α). **41β:** R_f= 0.50 (hexane/EtOAc 1:1); $[\alpha]_D^{22}$ = −59.8 (*c* 1.00, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.64 (s, 1H, H-1), 3.93 (t, *J* = 9.8 Hz, 1H, H-4), 3.74 – 3.67 (m, 3H, H-8a, H8b, H-6, 3.63 (s, 3H, OCH_3), 3.53 (d, *J* = 2.9 Hz, 1H, H-2), 3.47 (s, 3H, OCH_3), 3.43 (s, 3H, OCH_3), 3.17 (dd, *J* = 2.9, 9.8 Hz, 1H, H-3), 3.04 (dd, *J* = 2.0, 9.3 Hz, 1H, H-5), 2.14 (br s, 3H, Ada-*H*), 1.89 – 1.76 (m, 7H, H-7a, Ada-*H*), 1.73 – 1.66 (m, 1H, H-7b), 1.65 – 1.58 (m, 6H, Ada-*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 94.8 (J_{C-H} = 150.9 Hz, C-1), 82.0, 78.8, 74.6, 74.2, 71.5, 62.4, 61.9, 57.9, 57.3, 42.4, 36.3, 30.6, 30.1; HRMS (ESI) m/z calcd for $C_{21}H_{34}O_6Na$ $[M+Na]^+$, 405.2253; found, 405.2261.

41α: R_f= 0.55 (hexane/EtOAc 1:1); $[\alpha]_D^{22}$ = +25.3 (*c* 0.15, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.37 (d, *J* = 1.5 Hz, 1H, H-1), 3.98 (t, *J* = 9.8 Hz, 1H, H-4), 3.77 – 3.74 (m, 2H, H-8a, H-8b), 3.72 (dd, *J* = 10.2, 2.4 Hz, 1H, H-5), 3.63 (dd, *J* = 5.6, 2.6 Hz, 1H, H-6), 3.57 (dd, *J* = 10.2, 3.4 Hz, 1H, H-3), 3.48 (s, 6H, OCH_3), 3.43 (dd, *J* = 2.9, 1.9 Hz, 1H, H-2), 3.41 (s, 3H, OCH_3), 2.14 (br s, 3H, Ada-*H*), 2.00 – 1.93 (m, 1H, H-7a), 1.83 – 1.77 (m, 6H, Ada-*H*), 1.75 – 1.71 (m, 1H, H-7b), 1.70 – 1.61 (m, 6H, Ada-*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 90.9 (J_{C-H} = 165.5Hz, C-1), 79.0, 78.6, 74.4, 74.2, 72.3, 70.6, 62.2, 59.1, 57.4, 57.0, 42.3, 36.3, 30.6, 29.1; HRMS (ESI) m/z calcd for $C_{21}H_{34}O_6Na$ $[M+Na]^+$, 405.2253; found, 405.2265.

Methyl 4,8-anhydro-7-deoxy-2,3,6-tri-*O*-methyl-L-*glycero*-β-D-*manno*octopyranosyl-(1→6)-2',3',4'-tri-*O*-benzyl-α-D-*gluco*pyranoside (42β) and Methyl 4,8-anhydro-7-deoxy-2,3,6-tri-*O*-methyl-L-*glycero*-α-D-*manno*octopyranosyl-(1→6)-2',3',4'-tri-*O*-benzyl-α-D-*gluco*pyranoside (42β)

Coupling of **26** with **36** following the general procedure afforded **42β** and **α** in 88% yield in 8.7:1 ratio (Repetition: Yield = 82%; 8.2:1=β:α). **42β:** R_f= 0.40 (hexane/EtOAc 4:6); $[\alpha]_D^{22}$ = +21.8 (*c* 1.50, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 – 7.25 (m, 15H, Ar-*H*), 4.97 (d, *J* = 10.7 Hz, 1H, OCH_2Ph), 4.88 (d, *J* = 11.2 Hz, 1H, OCH_2Ph), 4.80 (d, *J* = 12.2 Hz, 1H, OCH_2Ph), 4.78 (d, *J* = 11.0 Hz, 1H, OCH_2Ph), 4.64 (d, *J* = 12.1 Hz, 1H, OCH_2Ph), 4.58 (d, *J* = 11.4 Hz, 1H,

OCH_2Ph), 4.55 (d, J = 3.5 Hz, 1H, H-1′), 4.23 (s, 1H, H-1), 4.17 (dd, J = 10.2, 1.8 Hz, 1H, H-6a′), 4.00 (t, J = 9.2 Hz, 1H, H-4′), 3.97 (dd, J = 12.6, 3.4 Hz, 1H, H-8a), 3.81 (ddd, J = 9.9, 5.7, 1.6 Hz, 1H, H-5′), 3.56 (s, 3H, OCH_3), 3.55 – 3.52 (m, 2H, H-2, H-6b′), 3.48 (dd, J = 9.5, 3.6 Hz, 1H, H-2′), 3.46 (s, 3H, OCH_3), 3.43 (s, 3H, OCH_3), 3.42 – 3.40 (m, 3H, H-6, H-3′, H-8b), 3.37 (t, J = 10.0 Hz, 1H, H-4), 3.34 (s, 3H, OCH_3), 3.15 (dd, J = 9.8, 3.2 Hz, 1H, H-3), 2.92 (t, J = 9.1 Hz, 1H, H-5), 1.98 (dd, J = 13.3, 5.1 Hz, 1H, H-7a), 1.54 (ddd, J = 24.4, 13.1, 5.3 Hz, 1H, H-7b); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 138.3, 138.1, 128.4, 128.4, 128.3, 128.1, 128.1, 127.9, 127.8, 127.7, 101.6 ($J_{C–H}$ = 156.1 Hz, C-1), 97.7 ($J_{C–H}$ = 168.7 Hz, C-1′), 82.1, 80.7, 79.91, 78.1, 77.9, 77.8, 77.2, 75.8, 75.9, 74.8, 73.4, 69.6, 68.6, 66.1, 62.0, 58.9, 57.6, 55.0, 31.8; HRMS (ESI) m/z calcd for $C_{39}H_{50}O_{11}Na$ $[M+Na]^+$, 717.3251; found, 717.3238

42α: R_f= 0.45 (hexane/EtOAc 4:6); $[\alpha]_D^{22}$ = +28.6 (*c* 0.15, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 – 7.16 (m, 15H), 4.98 (d, J = 10.6 Hz, 1H), 4.97 (d, J = 1.8 Hz, 1H), 4.91 (d, J = 10.8 Hz, 1H), 4.81 (d, J = 10.6 Hz, 1H), 4.79 (d, J = 12.1 Hz, 1H), 4.67 (d, J = 12.6 Hz, 1H), 4.65 (d, J = 11.0 Hz, 1H), 4.59 (d, J = 3.4 Hz, 1H), 4.00 (t, J = 9.3 Hz, 1H), 3.98 – 3.92 (m, 2H), 3.77 – 3.74 (m, 1H), 3.68 (dd, J = 11.4, 1.8 Hz, 1H), 3.63 (dd, J = 2.9, 1.5 Hz, 1H), 3.54 – 3.51 (m, 3H), 3.46 (s, 6H), 3.44 – 3.39 (m, 4H), 3.39 (s, 3H), 3.36 (s, 3H), 1.98 (d, J = 13.1 Hz, 1H), 1.42 – 1.37 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.5, 138.1, 138.0, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 97.9 ($J_{C–H}$ = 170.7 Hz, C-1, C-1′), 82.1, 79.9, 78.5, 78.0, 77.5, 76.8, 76.1, 75.9, 75.0, 73.5, 73.3, 69.7, 66.1, 60.0, 59.4, 57.8, 57.3, 55.1, 31.2; HRMS (ESI) m/z calcd for $C_{39}H_{50}O_{11}Na$ $[M+Na]^+$, 717.3251; found, 717.3235

Methyl 4,8-anhydro-7-deoxy-2,3,6-tri-*O*-methyl-L-*glycero*-β-D-*manno*octopyranosyl-(1→4)-2',3',6'-tri-*O*-benzyl-α-D-*gluco*pyranoside (43β) and Methyl 4,8-anhydro-7-deoxy-2,3,6-tri-*O*-methyl-L-*glycero*-α-D-*manno*octopyranosyl-(1→4)-2',3',6'-tri-*O*-benzyl-α-D-*gluco*pyranoside (43α)

Coupling of **26** with **37** following the general procedure afforded **43β** and **α** in 75% yield in 10.6:1 ratio (Repetition: Yield = 72%; 9.2:1=β:α). **43β:** R_f= 0.50 (hexane/EtOAc 1:1); $[\alpha]_D^{22}$ = +26.1 (*c* 1.05, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.27 (m, 15H, Ar-*H*), 5.08 (d, J = 10.5 Hz, 1H, OCH_2Ph), 4.81 (d, J = 12.2 Hz, 1H, OCH_2Ph), 4.79 (d, J = 10.2 Hz, 1H, OCH_2Ph), 4.72 (d, J = 12.1 Hz, 1H, OCH_2Ph), 4.67 (d, J = 12.2 Hz, 1H, OCH_2Ph), 4.62 (d, J = 3.5 Hz, 1H, H-1′), 4.45 (d, J = 12.1 Hz, 1H, OCH_2Ph), 4.39 (s, 1H, H-1), 3.96 (dd, J = 12.0, 4.0 Hz, 1H, H-

8a), 3.92 – 3.86 (m, 2H, H-4′, H-3′), 3.78 – 3.75 (m, 1H, H-5), 3.73 (dd, J = 10.8, 2.9 Hz, 1H, H-6a′), 3.62 (dd, J = 10.7, 1.4 Hz, 1H, H-6b′), 3.57 (s, 3H, OCH_3), 3.48 – 3.42 (m, 2H, H-2, H-2′), 3.39 (s, 6H, OCH_3), 3.38 – 3.36 (m, 1H, H-8b), 3.31 (t, J = 9.9 Hz, 1H, H-4), 3.26 (s, 3H, OCH_3), 3.12 – 3.06 (m, 1H, H-6), 2.92 (dd, J = 9.8, 2.9 Hz, 1H, H-3), 2.79 (t, J = 9.0 Hz, 1H, H-5), 1.92 – 1.84 (m, 1H, H-7a), 1.54 – 1.43 (m, 1H, H-7b); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.5, 138.3, 137.6, 128.6, 128.6, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.2, 100.4 ($J_{C–H}$ = 157.3 Hz, C-1), 98.5 ($J_{C–H}$ = 168.1 Hz, C-1′), 80.6, 80.4, 78.7, 78.0, 77.9, 75.9, 75.8, 75.2, 73.7, 73.5, 69.7, 68.3, 66.3, 61.5, 59.4, 57.4, 55.3, 32.1; HRMS (ESI) m/z calcd for $C_{39}H_{50}O_{11}Na$ $[M+Na]^+$, 717.3251; found, 717.3260.

43α: R_f= 0.55 (hexane/EtOAc 1:1); $[\alpha]_D^{22}$ = +42.0 (*c* 0.10, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 15H), 5.20 (br s, 1H), 5.17 (d, J = 12.9 Hz, 1H), 4.70 (d, J = 12.2 Hz, 1H), 4.69 (d, J = 11.7 Hz, 1H), 4.68 (d, J = 11.4 Hz, 1H), 4.62 (d, J = 3.2 Hz, 1H), 4.52 (d, J = 12.1 Hz, 1H), 4.54 (d, J = 11.7 Hz, 1H), 4.01 – 3.97 (m, 1H), 3.91 – 3.85 (m, 2H), 3.81 – 3.75 (m, 1H), 3.69 (t, J = 9.3 Hz, 1H), 3.55 (dd, J = 9.3, 3.3 Hz, 1H), 3.53 – 3.49 (m, 3H), 3.46 – 3.42 (m, 4H), 3.40 (s, 3H), 3.39 (s, 3H), 3.36 (s, 3H), 3.07 (s, 3H), 2.08 – 2.02 (m, 1H), 1.52 – 1.46 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.7, 138.5, 137.8, 129.9, 128.4, 128.3, 128.2, 128.1, 127.9, 127.6, 127.4, 127.3, 126.6, 100.7 ($J_{C–H}$ = 169.9 Hz, C-1), 97.6 ($J_{C–H}$ = 166.7 Hz, C-1′), 81.4, 80.0, 78.6, 78.5, 78.3, 77.1, 76.2, 75.1, 74.1, 73.1, 73.0, 69.8, 69.5, 66.1, 60.0, 58.9, 57.6, 57.3, 55.2, 31.4; HRMS (ESI) m/z calcd for $C_{39}H_{50}O_{11}Na$ $[M+Na]^+$, 717.3251; found, 717.3251.

(1-Adamantanyl) 4,8-anhydro-7-deoxy-2,3,6-tri-*O*-methyl-L-*glycero*-β-D-*manno*octopyranoside (44β) and (1-Adamantanyl) 4,8-anhydro-7-deoxy-2,3,6-tri-*O*-methyl-L-*glycero*-α-D-*manno*octopyranoside (44α)

Coupling of **26** with **38** following the general procedure afforded **44β** and **α** in 72% yield in 2.8:1 ratio (Repetition: Yield = 78%; 3.0:1= β:α). **44β:** R_f= 0.20 (hexane/EtOAc 6:4); $[\alpha]_D^{22}$ = −49.0 (*c* 0.80, CH_2Cl_2);^{1}H NMR (400 MHz, $CDCl_3$) δ 4.72 (br s, 1H, H-1), 3.99 (dd, J = 11.9, 4.4 Hz, 1H, H-8a), 3.66 (s, 3H, OCH_3), 3.55 – 3.54 (m, 1H, H-2), 3.53 (s, 3H, OCH_3), 3.49 (s, 3H, OCH_3), 3.46 – 3.41 (m, 2H, H-6, H-8b), 3.39 (t, J = 9.3 Hz, 1H, H-4), 3.25 (dd, J = 9.7, 3.2 Hz, 1H, H-3), 2.95 (t, J = 9.1 Hz, 1H, H-5), 2.16 (br s, 3H, Ada-*H*), 2.00 (dd, J = 13.2, 5.2 Hz, 1H, H-7a), 1.90 – 1.80 (m, 6H, Ada-*H*), 1.66 – 1.51 (m, 7H, Ada-*H*, H-7b); ^{13}C NMR (100 MHz, $CDCl_3$) δ

94.3 ($J_{C–H}$ = 152.8 Hz, C-1), 81.1, 79.2, 78.3, 77.5, 75.9, 74.9, 66.1, 62.3, 59.0, 57.6, 42.3, 36.2, 31.9, 30.6. HRMS (ESI) m/z calcd for $C_{21}H_{34}O_6Na$ $[M+Na]^+$, 405.2253; found, 405.2252.

44α: R_f= 0.25 (hexane/EtOAc 6:4); $[\alpha]_D^{22}$ = +35.7 (*c* 0.35, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.31 (d, *J* = 1.6 Hz, 1H, H-1), 4.01 (dd, *J* = 11.9, 4.2 Hz, 1H, H-8a), 3.66 (t, *J* = 9.3 Hz, 1H, H-5), 3.63 – 3.61 (m, 1H, H-3), 3.52 (s, 3H, OC*H*$_3$), 3.49 (s, 6H, OC*H*$_3$), 3.46 (dd, *J* = 3.1, 1.5 Hz, 1H, H-2), 3.46 – 3.39 (m, 1H, H-8b), 3.43 (t, *J* = 9.7 Hz, 1H, H-4), 3.40 – 3.24 (m, 1H, H-6), 2.15 (br s, 3H, Ada-*H*), 2.00 (dd, *J* = 13.2, 5.1 Hz, 1H, H-7a), 1.89 – 1.80 (m, 6H, Ada-*H*), 1.68 – 1.55 (m, 7H, Ada-*H*, H-7b); ^{13}C NMR (100 MHz, $CDCl_3$) δ 90.7 ($J_{C–H}$ = 165.8 Hz, C-1), 78.9, 78.7, 78.4, 76.8, 74.8, 73.7, 66.2, 59.3, 58.5, 57.7, 42.3, 36.2, 31.9, 30.6; HRMS (ESI) m/z calcd for $C_{21}H_{34}O_6Na$ $[M+Na]^+$, 405.2253; found, 405.2258.

Phenyl 4,6-*O*-benzylidene-7-deoxy-2,3-di-*O*-methyl-L-*glycero*-β-D-*manno*hetpopyranosyl-(1→6)-2',3',4'-tri-*O*-benzyl-α-D-glucopyranoside (45β) and Phenyl 4,6-*O*-benzylidene-7-deoxy-2,3-di-*O*-methyl-L-*glycero*-α-D-*manno*hetpopyranosyl-(1→6)-2',3',4'-tri-*O*-benzyl-α-D-glucopyranoside (45α)

Coupling of **35** with **36** following the general procedure afforded **45β** and **α** in 87% yield in 7.1:1 ratio (Repetition: Yield = 79%; 7.3:1= β:α). **45β:** R_f= 0.50 (hexane/EtOAc 1:1); $[\alpha]_D^{22}$ = +5.3 (*c* 0.90, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.28 (m, 20H, Ar-H), 5.84 (s, 1H, Benzylidene-*H*), 5.00 (d, *J* = 10.7 Hz, 1H, OC*H*$_2$Ph), 4.92 (d, *J* = 11.3 Hz, 1H, OC*H*$_2$Ph), 4.83 (d, *J* = 10.7 Hz, 1H, OC*H*$_2$Ph), 4.80 (d, *J* = 11.7 Hz, 1H, OC*H*$_2$Ph), 4.67 (d, *J* = 11.8 Hz, 1H, OC*H*$_2$Ph), 4.59 (d, *J* = 10.7 Hz, 1H, OC*H*$_2$Ph), 4.58 (d, *J* = 2.9 Hz, 1H, H-1′), 4.53 – 4.46 (m, 1H, H-6), 4.29 (s, 1H, H-1), 4.20 (t, *J* = 9.8 Hz, 1H, H-4), 4.15 (dd, *J* = 10.3, 1.9 Hz, 1H, H-6a′), 4.01 (t, *J* = 9.3 Hz, 1H, H-4′), 3.86 – 3.82 (m, 1H, H-5), 3.59 (s, 3H, OC*H*$_3$), 3.55 (d, *J* = 2.9 Hz, 1H, H-2), 3.53 (s, 3H, OC*H*$_3$), 3.51 (dd, *J* = 9.3, 3.4 Hz, 1H, H-3), 3.49 – 3.48 (m, 1H, H-6b′), 3.46 (dd, *J* = 10.6, 5.8 Hz, 1H, H-2′), 3.39 (t, *J* = 9.3 Hz, 1H, H-3′), 3.38 (s, 3H, OC*H*$_3$), 3.29 (dd, *J* = 9.3, 2.9 Hz, 1H, H-5), 1.49 (d, *J* = 6.8 Hz, 3H, H-7); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 138.3, 138.1, 137.9, 128.7, 128.5, 128.4, 128.2, 128.1, 127.9, 127.9, 127.8, 127.7, 126.1, 102.3 ($J_{C–H}$ = 156.5 Hz, C-1), 97.8 ($J_{C–H}$ = 166.6 Hz, C-1′), 94.0, 82.2, 80.8, 79.9, 78.6, 77.9, 77.3, 77.2, 77.0, 76.9, 75.9, 74.8, 73.4, 72.2, 70.7, 69.8, 69.7, 69.0, 62.0, 58.9, 55.0, 11.9; HRMS (ESI) m/z calcd for $C_{44}H_{52}O_{11}Na$ $[M+Na]^+$, 779.3407; found, 779.3406

45α: R_f= 0.50 (hexane/EtOAc 1:1); $[\alpha]_D^{22}$ = +80.0 (*c* 0.05, CH_2Cl_2); 1H NMR (400 MHz, CDCL3) δ 7.43 – 7.29 (m, 20H), 5.84 (s, 1H), 5.01 (d, *J* = 10.8 Hz, 1H), 4.96 (d, *J* = 10.8 Hz, 1H), 4.93 (s, 1H), 4.82 (d, *J* = 10.8 Hz, 1H), 4.81 (d, *J* = 11.7 Hz, 1H), 4.68 (d, *J* = 11.7 Hz, 1H), 4.63 (d, *J* = 10.8 Hz, 1H), 4.60 (d, *J* = 3.4 Hz, 1H), 4.38 – 4.31 (m, 1H), 4.27 (t, *J* = 9.3 Hz, 1H), 4.04 – 4.00 (m, 2H), 3.85 (dd, *J* = 11.3, 4.4 Hz, 1H), 3.77 (dq, *J* = 4.8, 1.5 Hz, 1H), 3.67 – 3.62 (m, 3H), 3.58 – 3.50 (m, 2H), 3.52 (s, 3H), 3.48 (s, 3H), 3.39 (s, 3H), 1.46 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCL_3$) δ 138.0, 128.7, 128.5, 128.1, 127.9, 127.8, 127.7, 126.2, 98.5 ($J_{C–H}$ = 168.9 Hz, C-1), 97.9 ($J_{C–H}$ = 169.6 Hz, C-1′), 94.2, 82.1, 79.9, 78.3, 77.3, 75.9, 75.0, 73.3, 72.5, 70.5, 69.7, 66.3, 59.6, 59.0, 55.2, 11.6; HRMS (ESI) m/z calcd for $C_{44}H_{52}O_{11}Na$ $[M+Na]^+$, 779.3407; found, 779.3403

Phenyl 4,6-*O*-benzylidene-7-deoxy-2,3-di-*O*-methyl-L-*glycero*-β-D-*manno*hetpopyranosyl-(1→4)-2',3',6'-tri-*O*-benzyl-α-D-*gluco*pyranoside (46β)

Coupling of **35** with **37** following the general procedure afforded **46β** in 82% yield (Repetition: Yield = 76%; β only). R_f= 0.30 (hexane/EtOAc 6:4); $[\alpha]_D^{22}$ = +4.8 (*c* 1.25, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.24 (m, 20H, Ar-*H*), 5.76 (s, 1H, Benzylidene-H), 5.05 (d, *J* = 11.7 Hz, 1H, OCH_2Ph), 4.88 (d, *J* = 11.7 Hz, 1H, OCH_2Ph), 4.77 (d, *J* = 12.2 Hz, 1H, OCH_2Ph), 4.74 (d, *J* = 11.7 Hz, 1H, OCH_2Ph), 4.63 (d, *J* = 11.7 Hz, 1H, OCH_2Ph), 4.61 (d, *J* = 3.4 Hz, 1H, H-1′), 4.51 (s, 1H, H-1), 4.46 (d, *J* = 12.2 Hz, 1H, OCH_2Ph), 4.22 – 4.17 (m, 1H, H-6), 4.13 (t, *J* = 9.8 Hz, 1H, H-4), 3.93 – 3.88 (m, 2H, H-3′, H-5′), 3.77 – 3.73 (m, 2H, H-4′, H-6a′), 3.65 (dd, *J* = 10.2, 1.4 Hz, 1H, H-6b′), 3.57 – 3.55 (m, 1H, H-2′), 3.53 (s, 3H, OCH_3), 3.47 (s, 3H, OCH_3), 3.39 (s, 4H, OCH_3, H-2), 3.28 (dd, *J* = 9.9, 5.8 Hz, 1H, H-3), 3.07 (dd, *J* = 9.6, 3.0 Hz, 1H, H-5), 1.26 (d, *J* = 6.9 Hz, 3H, H-7); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.5, 138.2, 138.0, 137.7, 128.7, 128.6, 128.3, 128.1, 128.0, 128.0, 127.8, 127.1, 127.0, 126.2, 101.8 ($J_{C–H}$ = 154.8 Hz, C-1), 98.3 ($J_{C–H}$ = 164.0 Hz, C-1′), 94.0, 80.8, 80.3, 79.4, 78.9, 77.2, 74.9, 73.7, 73.5, 72.1, 70.5, 69.6, 69.5, 68.5, 61.7, 58.8, 55.3, 11.5; HRMS (ESI) m/z calcd for $C_{44}H_{52}O_{11}Na$ $[M+Na]^+$, 779.3407; found, 779.3402.

(1-Adamantanyl) 4,6-*O*-benzylidene-7-deoxy-2,3-di-*O*-methyl-L-*glycero*-β-D-*manno*hetpopyranoside (47β) and (1-Adamantanyl) 4,6-*O*-benzylidene-7-deoxy-2,3-di-*O*-methyl-L-*glycero*-α-D-*manno*hetpopyranoside (47α)

Coupling of **35** with **38** following the general procedure afforded **47β** and **α** in 82% yield in 3.6:1 ratio (Repetition: Yield = 92%; 3.5:1= β:α). **47β:** R_f= 0.40 (hexane/EtOAc 8:2); $[\alpha]_D^{22}$ = −65.0 (*c* 0.60, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.45 (m, 2H, Ar-*H*), 7.36 – 7.31 (m, 3H, Ar-*H*), 5.84 (s, 1H, Benzylidene-*H*), 4.78 (s, 1H, H-1), 4.51 – 4.43 (m, 1H, H-6), 4.21 (t, *J* = 9.7 Hz, 1H, H-4), 3.66 (s, 3H, OCH_3), 3.55 (s, 3H, OCH_3), 3.54 – 3.53 (m ,1H, H-2), 3.52 (dd, *J* = 9.7, 3.9 Hz, 1H, H-3), 3.38 (dd, *J* = 9.5, 3.2 Hz, 1H, H-5), 2.16 (br s, 3H, Ada-*H*), 1.88 – 1.86 (m, 6H, Ada-*H*), 1.69 – 1.57 (m, 6H, Ada-*H*), 1.50 (d, *J* = 6.9 Hz, 3H, H-7); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1, 128.7, 128.2, 126.2, 94.6 ($J_{C–H}$ = 152.0 Hz, C-1), 94.0, 81.3, 80.5, 75.1, 72.2, 70.9, 69.5, 62.3, 58.8, 42.3, 36.2, 30.6, 12.0; HRMS (ESI) m/z calcd for $C_{26}H_{36}O_6Na$ $[M+Na]^+$, 467.2410; found, 467.2404.

47α: R_f= 0.45 (hexane/EtOAc 8:2); $[\alpha]_D^{22}$ = +14.6 (*c* 0.15, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.48 (m, 2H, Ar-*H*), 7.40 – 7.28 (m, 3H, Ar-*H*), 5.87 (s, 1H, Benzylidene-*H*), 5.29 (d, *J* = 1.6 Hz, 1H, H-1), 4.31 – 4.24 (m, 1H, H-6), 4.27 (t, *J* = 9.3 Hz, 1H, H-4), 4.22 (dd, *J* = 5.3, 9.7 Hz, 1H, H-5), 3.75 (dd, *J* = 9.3, 3.2 Hz, 1H, H-3), 3.56 (s, 3H, OCH_3), 3.52 (s, 3H, OCH_3), 3.46 (dd, *J* = 3.1, 1.7 Hz, 1H, H-2), 2.15 (br s, 3H, Ada-*H*), 1.85 − 1.77 (m, 6H, Ada-*H*), 1.69 – 1.57 (m, 6H, Ada-*H*), 1.47 (d, *J* = 6.9 Hz, 3H, H-7); ^{13}C NMR (100 MHz, $CDCl_3$) δ 128.6, 128.1, 126.2, 94.0, 91.4 ($J_{C–H}$ = 167.1 Hz, C-1), 80.2, 78.4, 74.7, 73.0, 70.7, 65.8, 59.5, 59.0, 42.4, 36.2, 30.6, 11.7; HRMS (ESI) m/z calcd for $C_{26}H_{36}O_6Na$ $[M+Na]^+$, 467.2410; found, 467.2398.

Phenyl 4,6-*O*-benzylidene-7-deoxy-2,3-di-*O*-methyl-D-*glycero*-β-D-*manno*hetpopyranosyl-(1→6)-2',3',4'-tri-*O*-benzyl-α-D-glucopyranoside (48β) and Phenyl 4,6-*O*-benzylidene-7-deoxy-2,3-di-*O*-methyl-D-*glycero*-α-D-*manno*hetpopyranosyl-(1→6)-2',3',4'-tri-*O*-benzyl-α-D-glucopyranoside (48α)

Coupling of **34** with **36** following the general procedure afforded **48β** and **α** in 82% yield in 7.4:1 ratio (Repetition: Yield = 76%; 7.7:1= β:α). **48β:** R_f= 0.50 (hexane/EtOAc 6:4); $[\alpha]_D^{22}$ = +21.7 (*c* 0.70, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 – 7.45 (m, 2H, Ar-*H*), 7.36 – 7.27 (m, 18H, Ar-*H*), 5.59 (s, 1H, Benzylidene-*H*), 4.99 (d, *J* = 10.7 Hz, 1H, OCH_2Ph), 4.89 (d, *J* = 11.4 Hz, 1H, OCH_2Ph), 4.81 (d, *J* = 11.0, 1H, OCH_2Ph), 4.79 (d, *J* = 12.1 Hz, 1H, OCH_2Ph), 4.65 (d, *J* = 12.1 Hz, 1H, OCH_2Ph), 4.59 (d, *J* = 11.3 Hz, 1H, OCH_2Ph), 4.57 (d, *J* = 3.3 Hz, 1H, H-1′), 4.28 (s, 1H, H-1), 4.14 (dd, *J* = 10.2, 1.6 Hz, 1H, H-6a′), 4.03 – 3.96 (m, 3H, H-4, H-3′, H-6), 3.85 –

3.79 (m, 1H, H-5′), 3.58 (s, 3H, OCH_3), 3.56 (d, J = 3.1 Hz, 1H, H-2), 3.53 (s, 3H, OCH_3), 3.51 (dd, J = 9.4, 3.5 Hz, 1H, H-6b′), 3.48 (dd, J = 9.7, 3.6 Hz, 1H, H-2′), 3.41(t, J = 9.5 Hz, 1H, H-4′), 3.36 (s, 3H, OCH_3), 3.30 (dd, J = 9.9, 3.1 Hz, 1H, H-3), 2.81 (t, J = 9.1 Hz, 1H, H-5), 1.34 (d, J = 6.1 Hz, 3H, H-7); ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.9, 139.6, 139.4, 138.9, 130.1, 129.8, 129.8, 129.7, 129.3, 129.4, 129.4, 129.3, 129.2, 129.1, 129.0, 127.4, 103.4 ($J_{C–H}$ = 155.4 Hz, C-1), 102.3, 99.1 ($J_{C–H}$ = 168.3 Hz, C-1′), 83.5, 81.2, 81.2, 79.9, 79.1, 79.0, 77.2, 76.4, 76.1, 74.7, 74.6, 70.9, 69.9, 63.3, 60.1, 56.3, 19.1; HRMS (ESI) m/z calcd for $C_{44}H_{52}O_{11}Na$ $[M+Na]^+$, 779.3407; found, 779.3421.

48α: R_f= 0.50 (hexane/EtOAc 6:4); $[\alpha]_D^{22}$ = +75.3 (*c* 0.15, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 – 7.43 (m, 2H), 7.38 – 7.23 (m, 18H), 5.62 (s, 1H), 5.00 (d, J = 10.7 Hz, 1H), 4.96 (d, J = 11.0 Hz, 1H), 4.92 (s, 1H), 4.82 (d, J = 10.5 Hz, 1H), 4.79 (d, J = 12.2 Hz, 1H), 4.67 (d, J = 12.1 Hz, 1H), 4.62 (d, J = 11.0 Hz, 1H), 4.60 (d, J = 3.5 Hz, 1H), 4.04 – 4.00 (m, 2H), 3.87 – 3.97 (m, 1H), 3.80 – 3.75 (m, 2H), 3.64 – 3.62 (m, 3H), 3.53 (dd, J = 7.7, 3.6 Hz, 1H), 3.52 (s, 3H), 3.52 – 3.51 (m, 1H), 3.49 (s, 3H), 3.38 (s, 3H), 3.34 (t, J = 9.2 Hz, 1H), 1.26 (d, J = 6.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.5, 138.0, 137.9, 137.8, 128.7, 128.5, 128.4, 128.1, 128.0, 128.0, 127.9, 127.8, 127.7, 127.6, 126.2, 101.1, 98.4 ($J_{C–H}$ = 167.5 Hz, C-1), 97.9 ($J_{C–H}$ = 167.6 Hz, C-1′), 82.1, 80.0, 78.4, 78.2, 77.8, 77.6, 75.9, 75.2, 75.0, 73.3, 69.9, 69.6, 66.0, 59.6, 59.0, 55.1, 17.6: HRMS (ESI) m/z calcd for $C_{44}H_{52}O_{11}Na$ $[M+Na]^+$, 779.3407; found, 779.3407.

Phenyl 4,6-*O*-benzylidene-7-deoxy-2,3-di-*O*-methyl-D-*glycero*-β-D-*manno*hetpopyranosyl-(1→4)-2',3',6'-tri-*O*-benzyl-α-D-*gluco*pyranoside (49β)

Coupling of **34** with **37** following the general procedure afforded **49β** in 80% yield (Repetition: Yield = 78%; β only). R_f= 0.40 (hexane/EtOAc 6:4); $[\alpha]_D^{22}$ = +19.4 (*c* 1.85, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.22 (m, 20H, Ar-*H*), 5.52 (s, 1H, Benzylidene-*H*), 5.04 (d, J = 11.0 Hz, 1H, OCH_2Ph), 4.84 (d, J = 12.2 Hz, 1H, OCH_2Ph), 4.81 (d, J = 11.2 Hz, 1H, OCH_2Ph), 4.73 (d, J = 12.1 Hz, 1H, OCH_2Ph), 4.67 (d, J = 12.2 Hz, 1H, OCH_2Ph), 4.63 (d, J = 3.7 Hz, 1H, H-1′), 4.46 (d, J = 12.1 Hz, 1H, OCH_2Ph), 4.39 (s, 1H, H-1), 3.92 – 3.90 (m, 2H, H-3′, H-4′), 3.87 (d, J = 9.8 Hz, 1H, H-4), 3.80 – 3.77 (m, 1H, H-5′), 3.73 (dd, J = 10.7, 2.9 Hz, 1H, H-6a′), 3.67 (d, J = 10.7, 1.9 Hz, 1H, H-6b′), 3.57 (s, 3H, OCH_3), 3.55 – 3.54 (m, 1H, H-6), 3.53 (dd, J = 9.3, 3.4 Hz, 1H, H-2′), 3.48 (s, 3H, OCH_3), 3.44 (d, J = 3.4 Hz, 1H, H-2), 3.40 (s, 3H, OCH_3), 3.06 (dd, J = 9.9, 3.1 Hz, 1H, H-3), 2.64 (t, J = 9.1 Hz, 1H, H-5), 1.19 (d, J = 6.1 Hz, 3H, H-7); ^{13}C

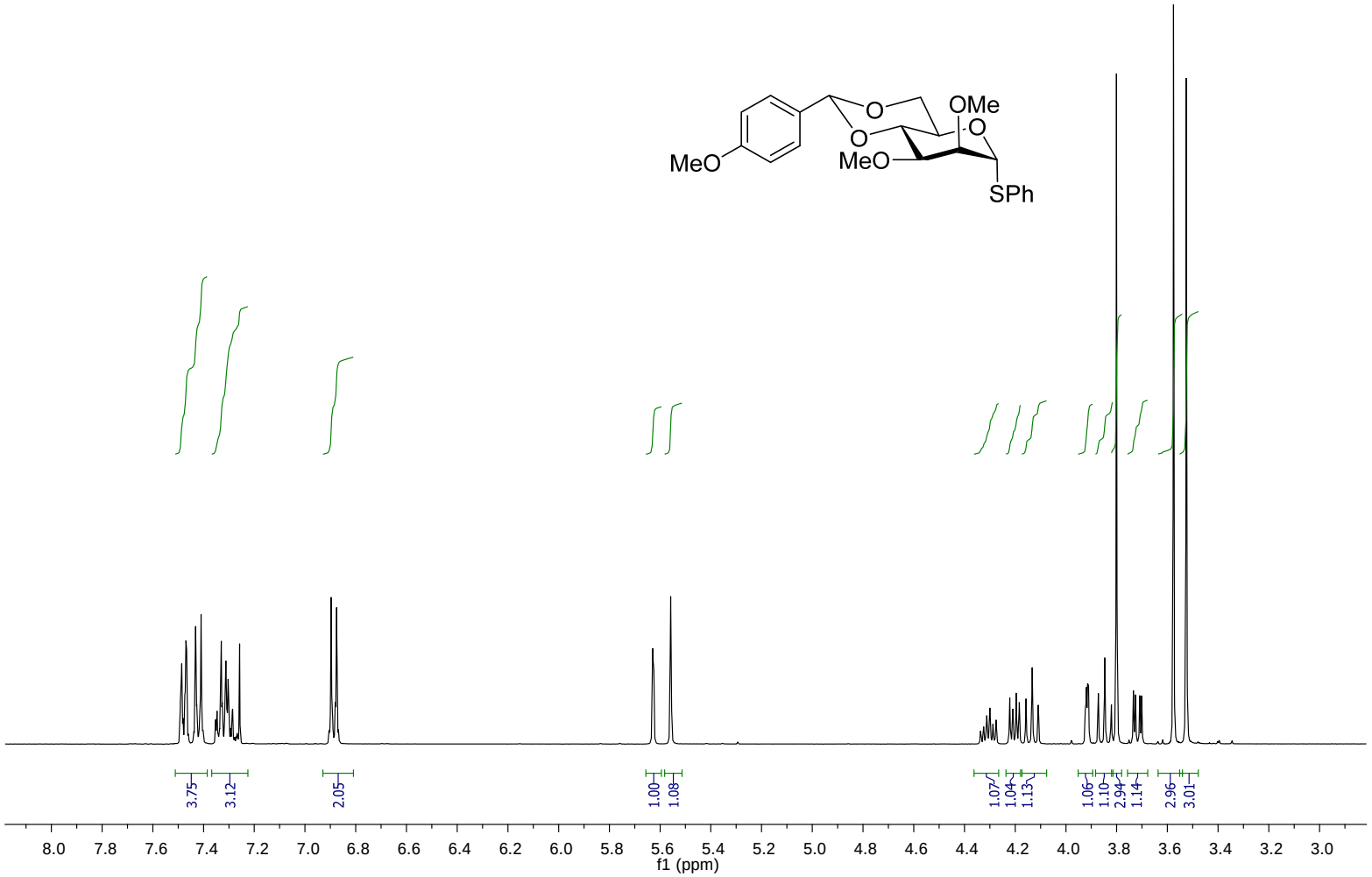
NMR (100 MHz, $CDCl_3$) δ 139.6, 138.3, 137.8, 137.6, 128.7, 128.6, 128.4, 128.1, 128.0, 128.0, 127.8, 127.7, 127.2, 126.2, 101.0, 100.7 (J_{C-H} = 157.2 Hz, C-1), 98.5 (J_{C-H} = 167.8 Hz, C-1′), 79.9, 79.7, 79.1, 78.6, 77.8, 76.3, 75.2, 74.8, 73.7, 73.6, 73.1, 69.6, 68.4, 61.6, 58.6, 55.3, 17.8; HRMS (ESI) m/z calcd for $C_{44}H_{52}O_{11}Na$ $[M+Na]^+$, 779.3407; found, 779.3411.

(1-Adamantanyl) 4,6-*O*-benzylidene-7-deoxy-2,3-di-*O*-methyl-D-*glycero*-β-D-*manno*hetpopyranoside (50β) and (1-Adamantanyl) 4,6-*O*-benzylidene-7-deoxy-2,3-di-*O*-methyl-D-*glycero*-α-D-*manno*hetpopyranoside (50α)

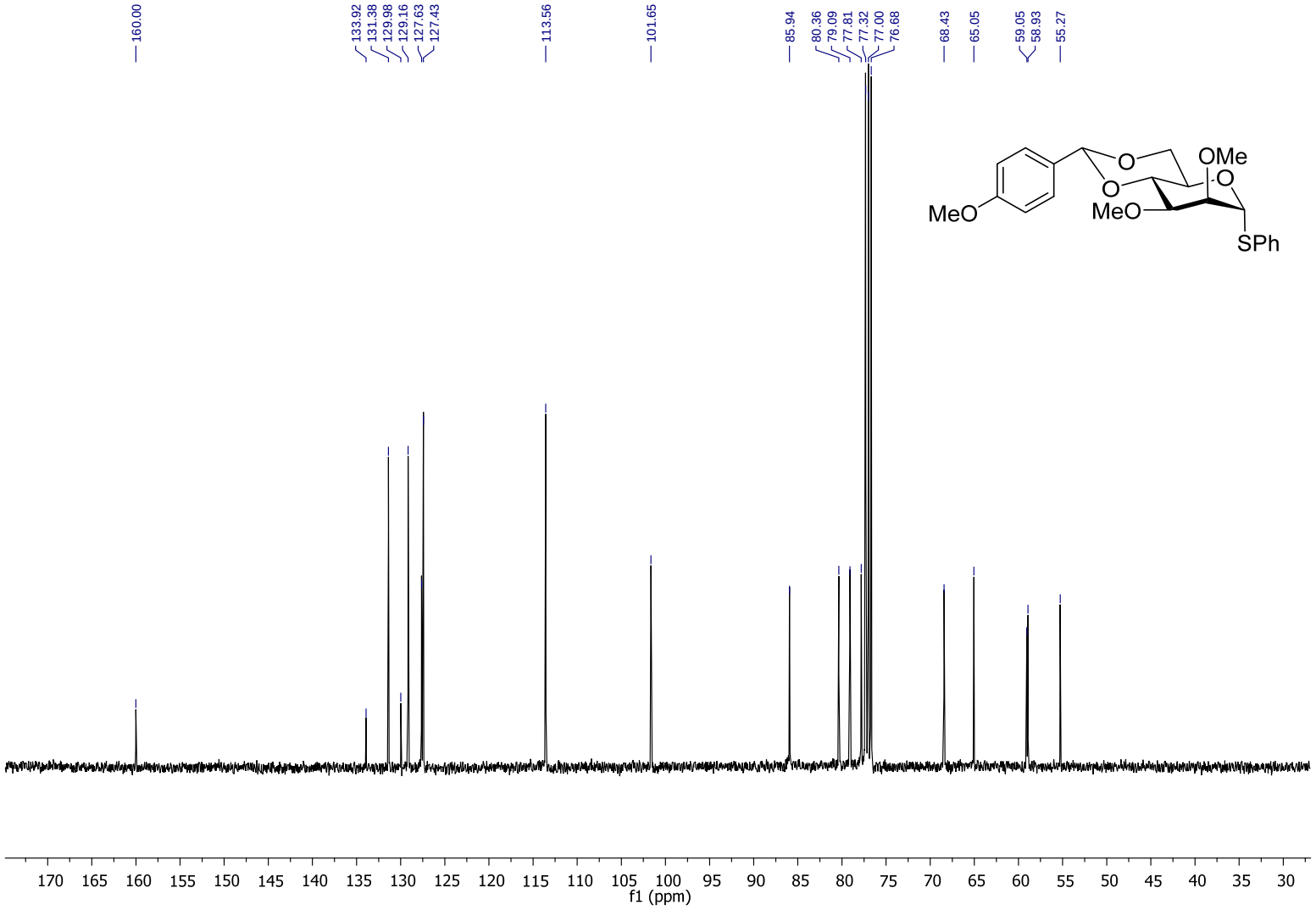
Coupling of **34** with **38** following the general procedure afforded **50β** and **α** in 90% yield in 4.0:1 ratio (Repetition: Yield = 86%; 3.6:1= β:α). **50β:** R_f= 0.80 (hexane/EtOAc 8:2); $[\alpha]_D^{22} = -26.9$ (*c* 1.05, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.45 (m, 2H, Ar-*H*), 7.41 – 7.29 (m, 3H, Ar-*H*), 5.61 (s, 1H, Benzylidene-*H*), 4.76 (s, 1H, H-1), 4.02 (t, *J* = 9.7 Hz, 1H, H-4), 3.99 – 3.95 (m, 1H, H-6), 3.68 (s, 3H, OC*H*$_3$), 3.57 (d, *J* = 3.4 Hz, 1H, H-2), 3.55 (s, 3H, OC*H*$_3$), 3.39 (dd, *J* = 9.7, 2.9 Hz, 1H, H-3), 2.87 (t, *J* = 9.1 Hz, 1H, H-5), 2.17 (br s, 3H, Ada-*H*), 1.81 (m, 6H, Ada-*H*), 1.70 – 1.56 (m, 6H, Ada-*H*), 1.37 (d, *J* = 6.1 Hz, 3H, H-7); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 128.7, 128.1, 126.2, 101.0, 94.9 (J_{C-H} = 153.4 Hz, C-1), 80.5, 80.3, 77.8, 75.1, 75.0, 73.1, 62.3, 58.7, 42.4, 36.2, 30.6, 17.9; HRMS (ESI) m/z calcd for $C_{26}H_{36}O_6Na$ $[M+Na]^+$, 467.2410; found, 467.2414.

50α: R_f= 0.85 (hexane/EtOAc 8:2); $[\alpha]_D^{22}$ = +53.0 (*c* 0.20, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.48 (m, 2H, Ar-*H*), 7.38 – 7.30 (m, 3H Ar-*H*), 5.66 (s, 1H, Benzylidene-*H*), 5.31 (d, *J* = 1.6 Hz, 1H, H-1), 4.03 (t, *J* = 9.7 Hz, 1H, H-4), 3.94 – 3.90 (m, 1H, H-6), 3.76 (dd, *J* = 10.0, 3.2 Hz, 1H, H-3), 3.59 (t, *J* = 9.3 Hz, 1H, H-5), 3.57 (s, 3H, OC*H*$_3$), 3.54 (s, 3H, OC*H*$_3$), 3.47 (dd, *J* = 3.1, 1.7 Hz, 1H, H-2), 2.15 (br s, 3H, Ada-*H*), 1.86 – 1.78 (m, 6H, Ada-*H*), 1.74 – 1.57 (m, 6H, Ada-*H*), 1.34 (d, *J* = 6.2 Hz, 3H, H-7); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 128.6, 128.1, 126.2, 101.0, 91.2 (J_{C-H} = 165.8 Hz, C-1), 80.4, 78.8, 77.5, 75.7, 74.9, 69.6, 59.6, 59.0, 45.3, 42.5, 36.2, 30.6, 18.1; HRMS (ESI) m/z calcd for $C_{26}H_{36}O_6Na$ $[M+Na]^+$, 467.2410; found, 467.2429.

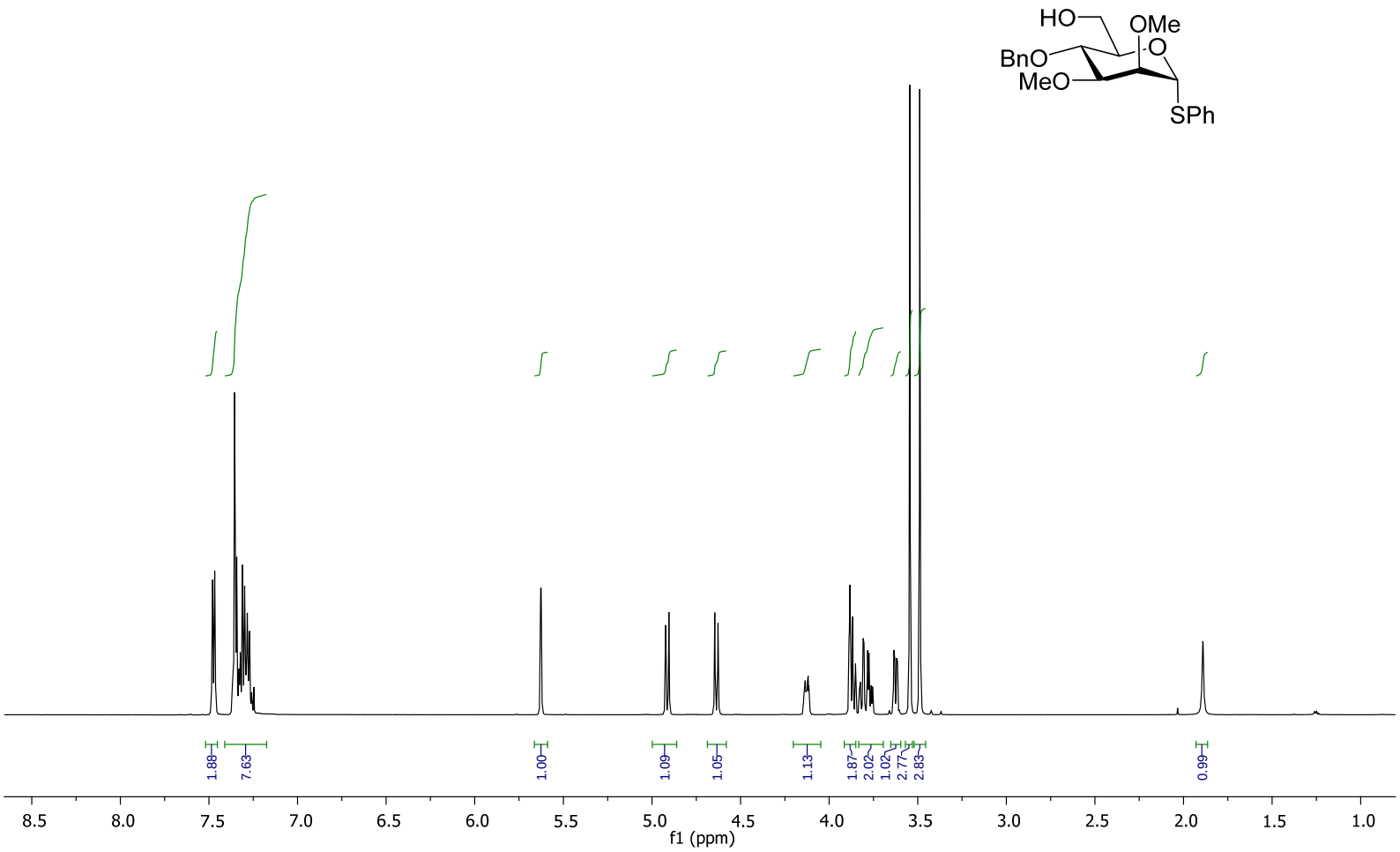
^{1}H NMR (400 MHz, $CDCl_3$) of Phenyl 4,6-*O*-*p*-methoxybenzylidene-2,3-di-*O*-methyl-1-thio-α-D-*manno*pyranoside (4)



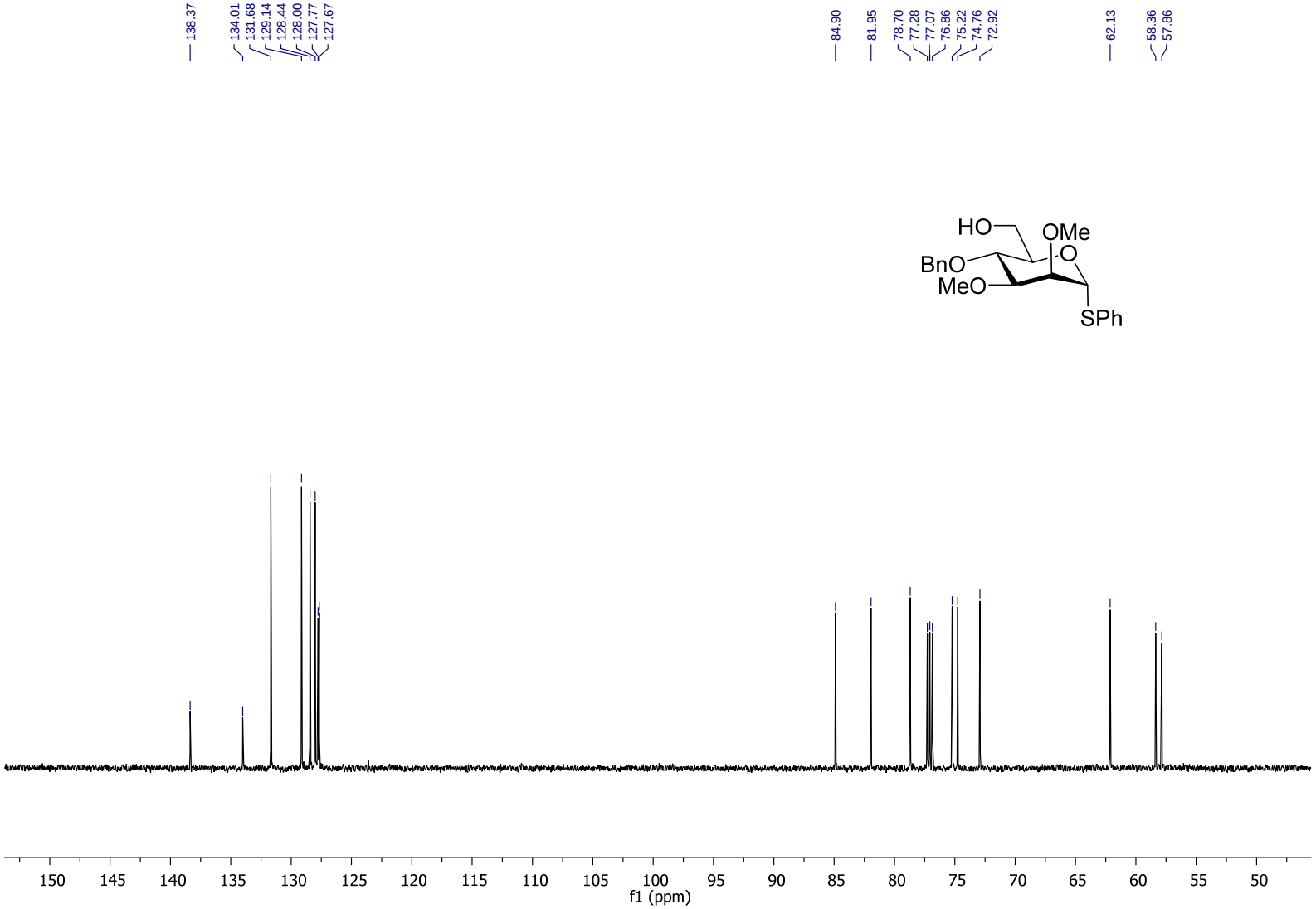
^{13}C NMR (100 MHz, $CDCl_3$) of Phenyl 4,6-*O*-*p*-methoxybenzylidene-2,3-di-*O*-methyl-1-thio-α-D-*manno*pyranoside (4)



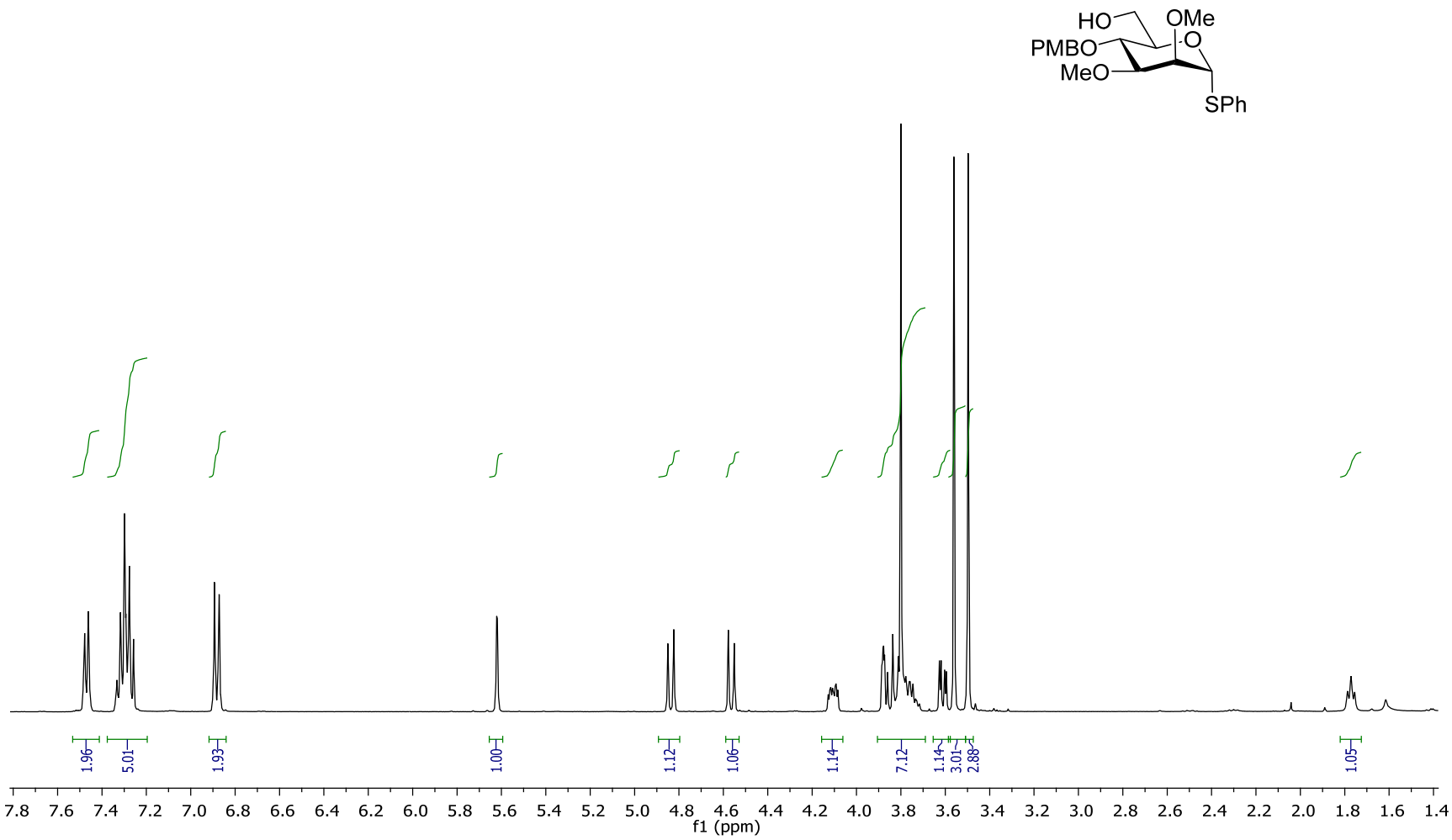
^{1}H NMR (600 MHz, $CDCl_3$) Phenyl 4-*O*-benzyl-2,3-di-*O*-methyl-1-deoxy-1-thio-α-D-*manno*pyranoside (5)



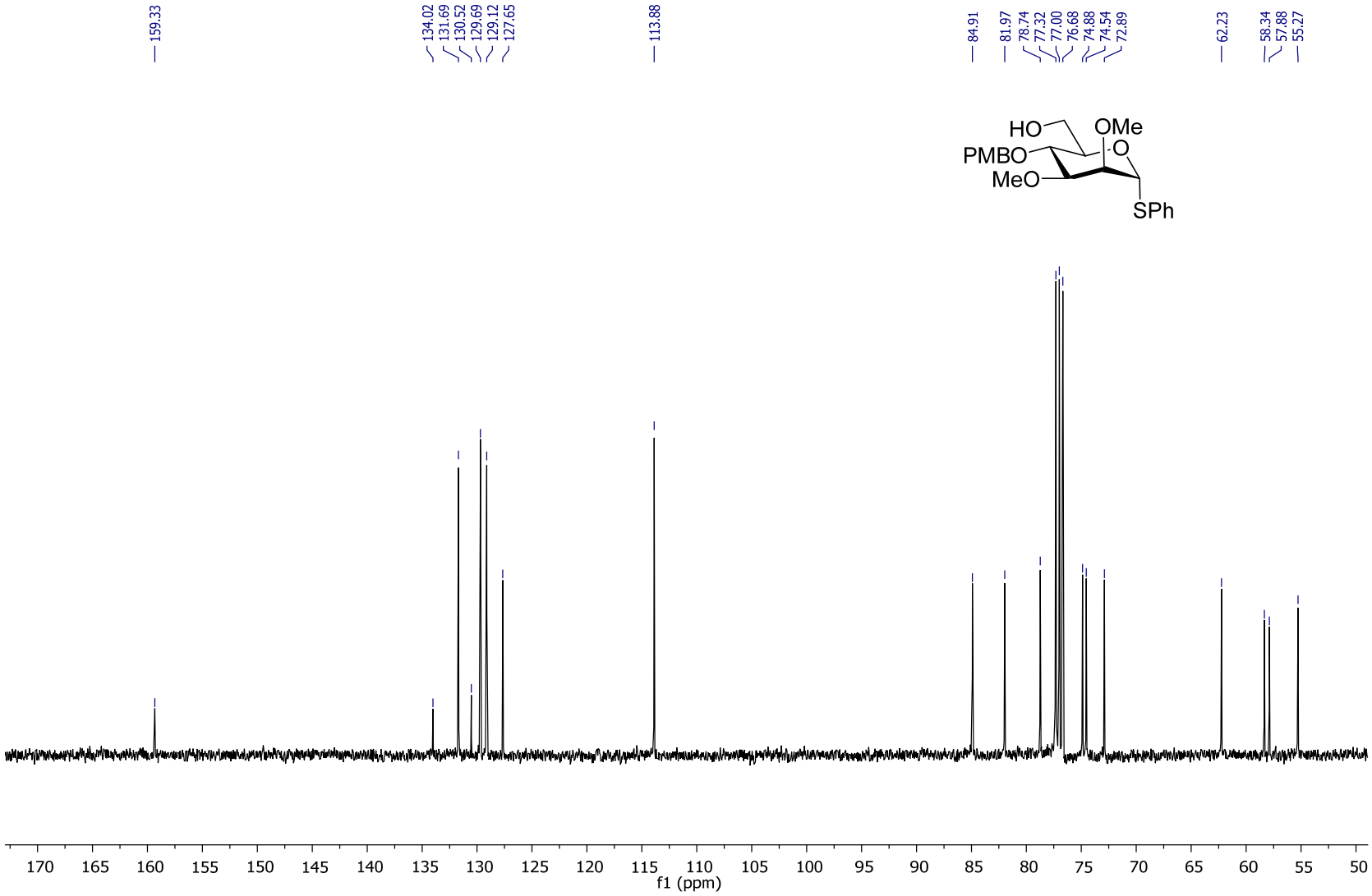
^{13}C NMR (150 MHz, $CDCl_3$) of Phenyl 4-*O*-benzyl-2,3-di-*O*-methyl-1-thio-α-D-*manno*pyranoside (5)



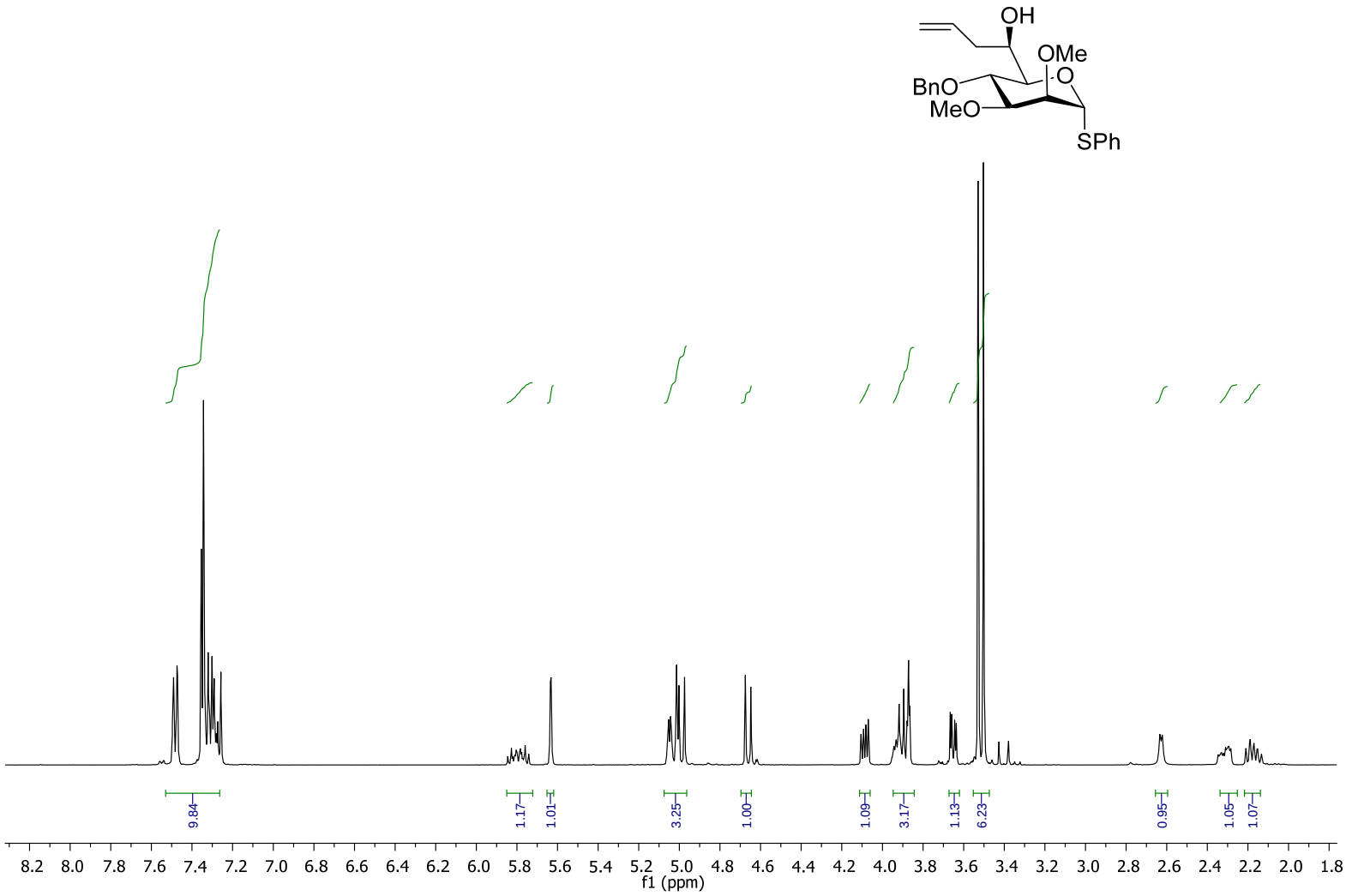
^{1}H NMR (400 MHz, $CDCl_3$) of Phenyl 4-*O*-*p*-methoxybenzyl-2,3-di-*O*-methyl-1-thio-α-D-*manno*pyranoside (6)



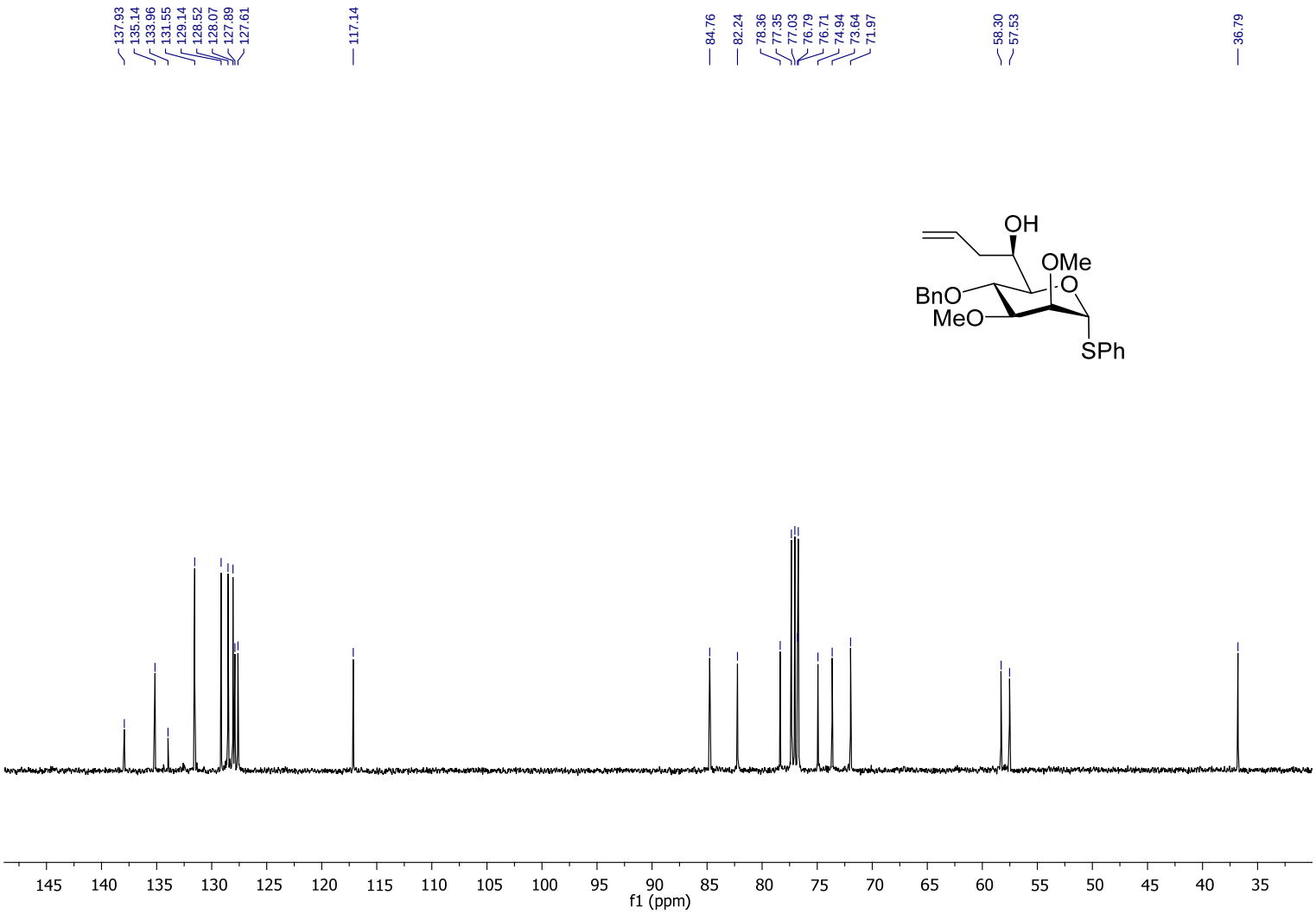
^{13}C NMR (100 MHz, $CDCl_3$) of Phenyl 4-*O*-*p*-methoxybenzyl-2,3-di-*O*-methyl-1-thio-α-D-*manno*pyranoside (6)



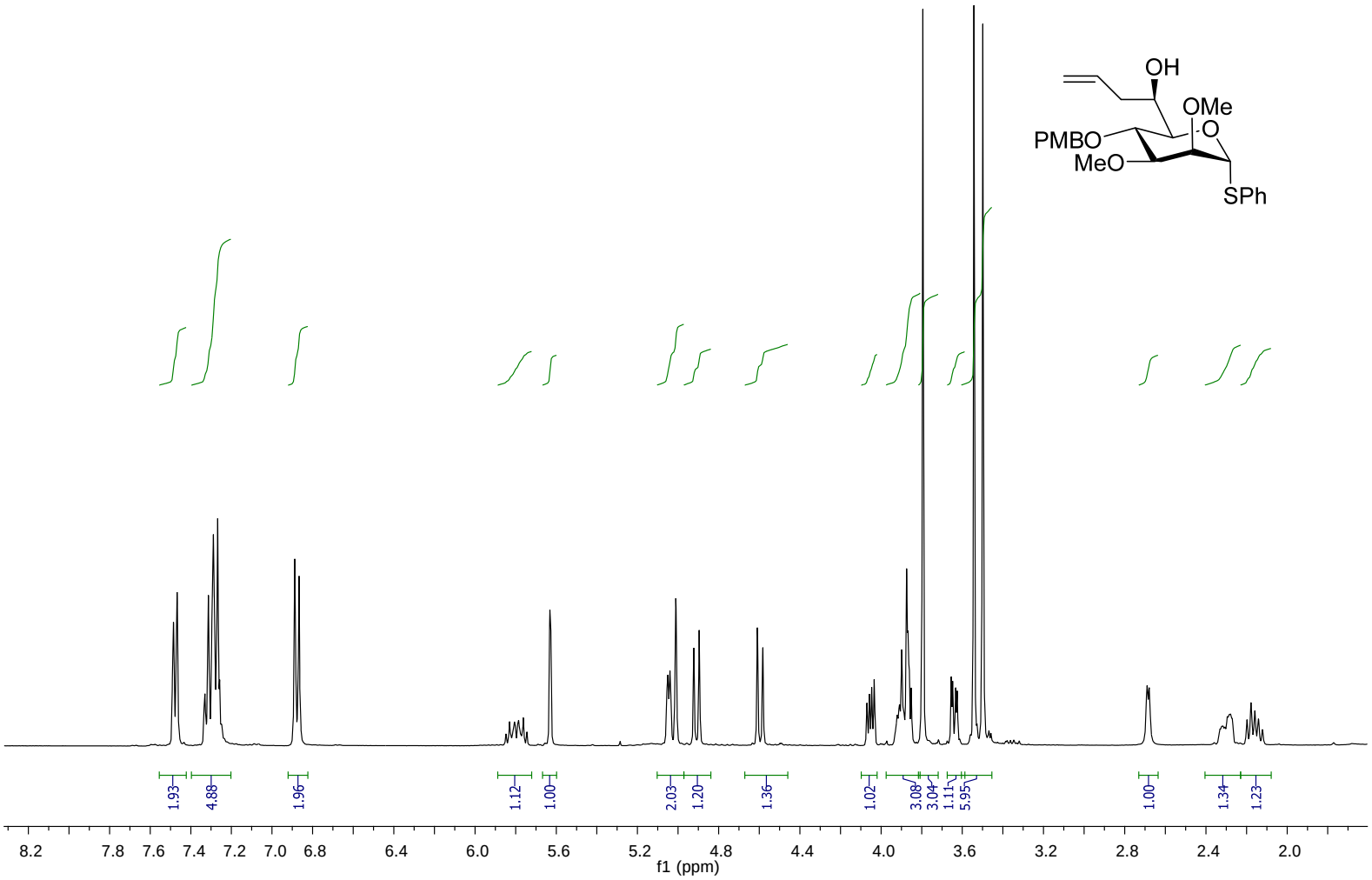
^{1}H NMR (400 MHz, $CDCl_3$) of (6*R*) Phenyl 6-*C*-Allyl-4-*O*-benzyl-2,3-di-*O*-methyl-1-thio-*α*-D-*manno*pyranoside (7)



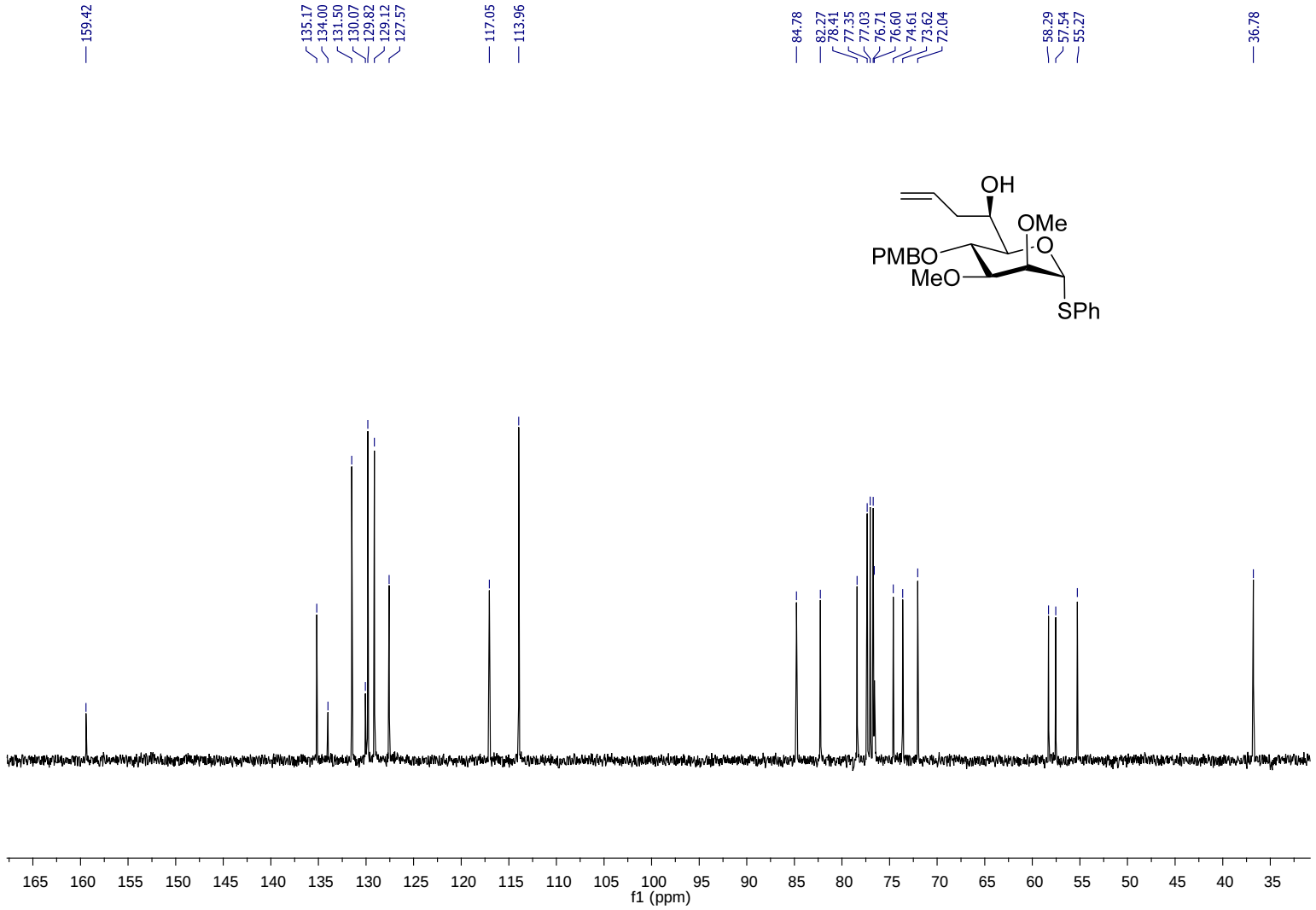
^{13}C NMR (100 MHz, $CDCl_3$) of (6*R*) Phenyl 6-*C*-Allyl-4-*O*-benzyl-2,3-di-*O*-methyl-1-thio-*α*-D-*mann*opyranoside (7)



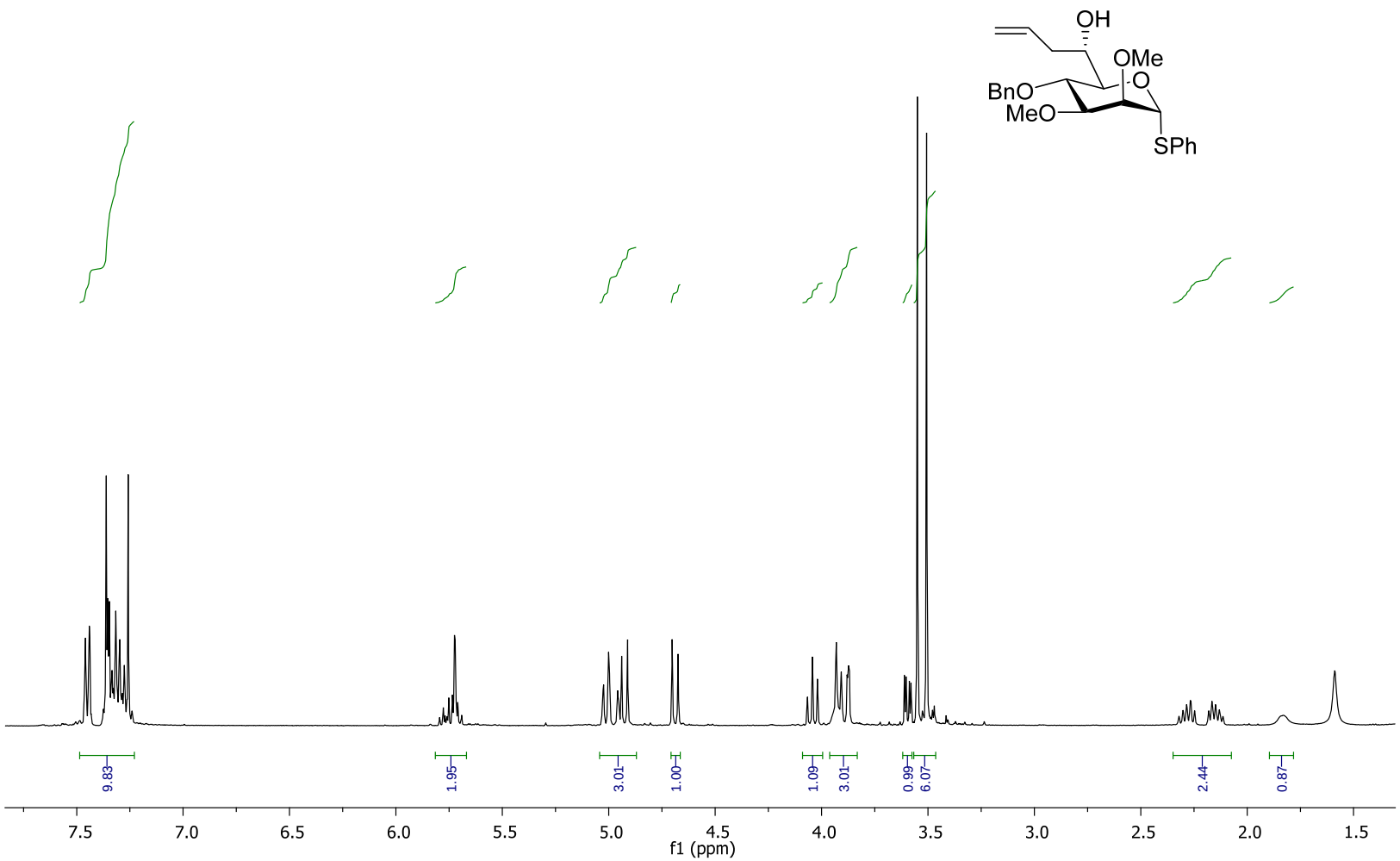
^{1}H NMR (400 MHz, $CDCl_3$) of (6*R*) Phenyl 6-*C*-Allyl-4-*O*-*p*-methoxybenzyl-2,3-di-*O*-methyl-1-thio-α-D-*manno*pyranoside (8)



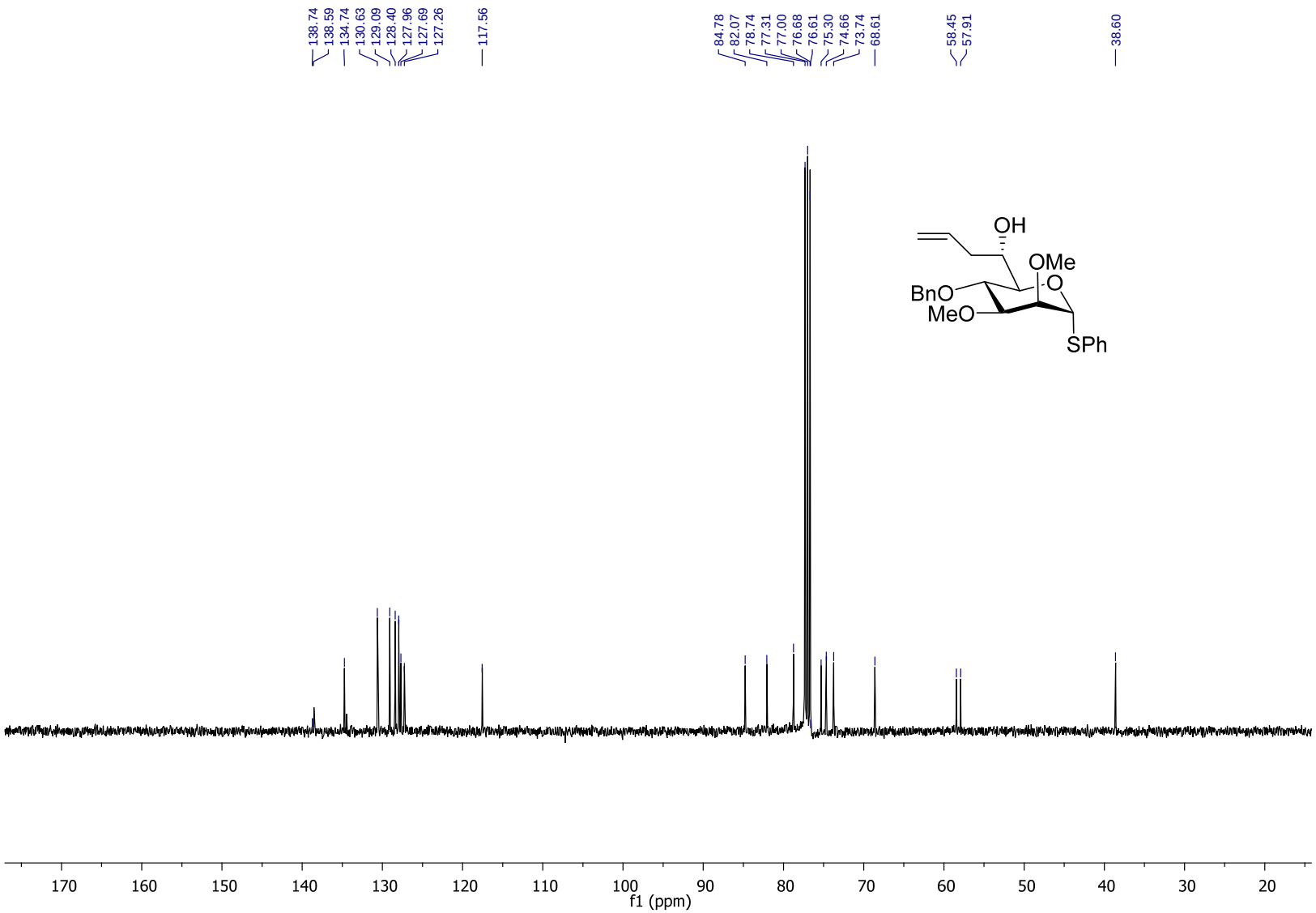
^{13}C NMR (100 MHz, $CDCl_3$) of (6*R*) Phenyl 6-*C*-Allyl-4-*O*-*p*-methoxybenzyl-2,3-di-*O*-methyl-1-thio-α-D-*manno*pyranoside (8)



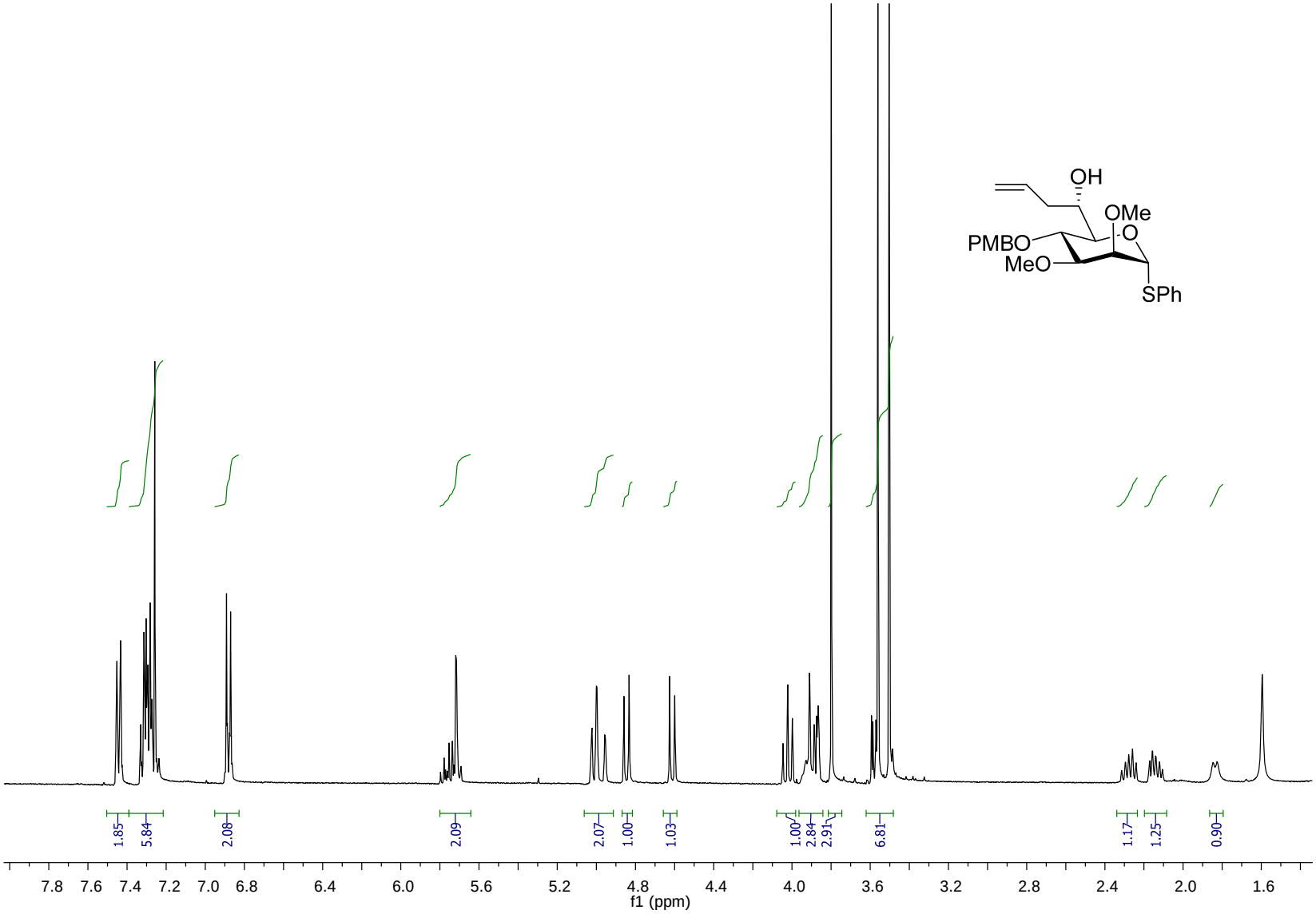
^{1}H NMR (400 MHz, $CDCl_3$) of (6*S*) Phenyl 6-*C*-Allyl-4-*O*-benzyl-2,3-di-*O*-methyl-1-thio-α-D-*manno*pyranoside (9)



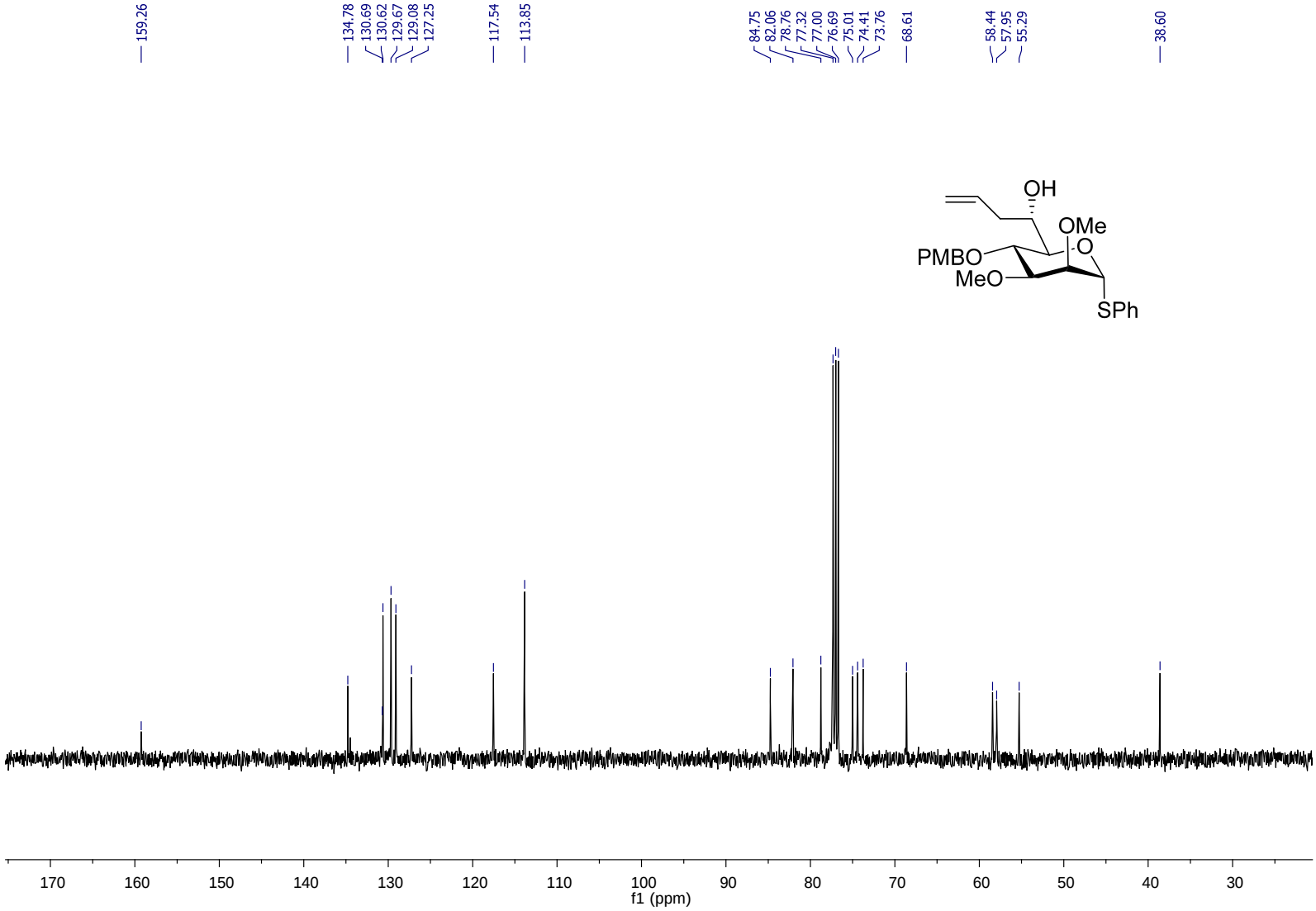
^{13}C NMR (100 MHz, $CDCl_3$) of (6*S*) Phenyl 6-*C*-Allyl-4-*O*-benzyl-2,3-di-*O*-methyl-1-thio-α-D-*manno*pyranoside (9)



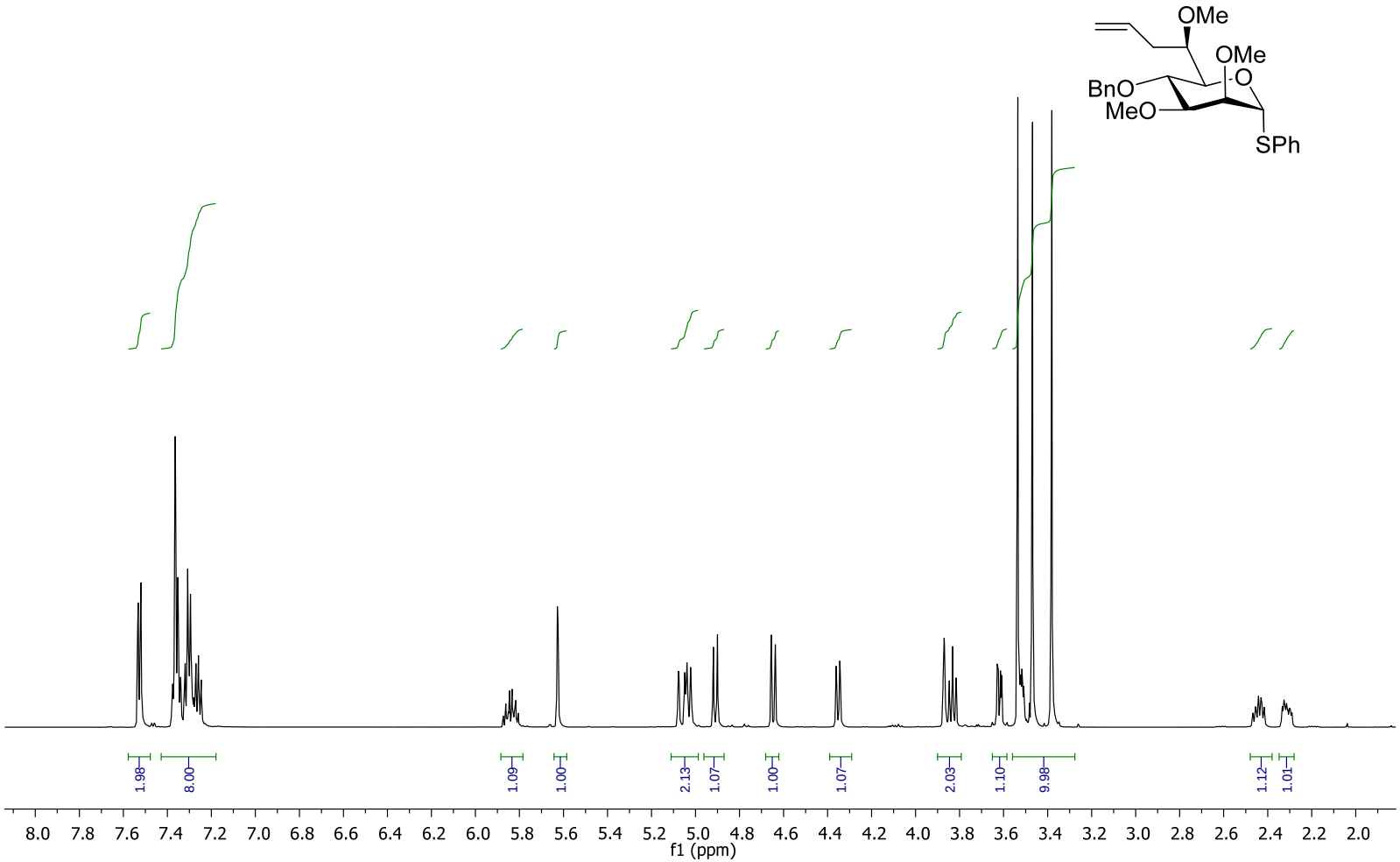
^{1}H NMR (400 MHz, $CDCl_3$) of (6*S*) Phenyl 6-*C*-Allyl-4-*O*-*p*-methoxybenzyl-2,3-di-*O*-methyl-1-thio-α-D-*manno*pyranoside (10)



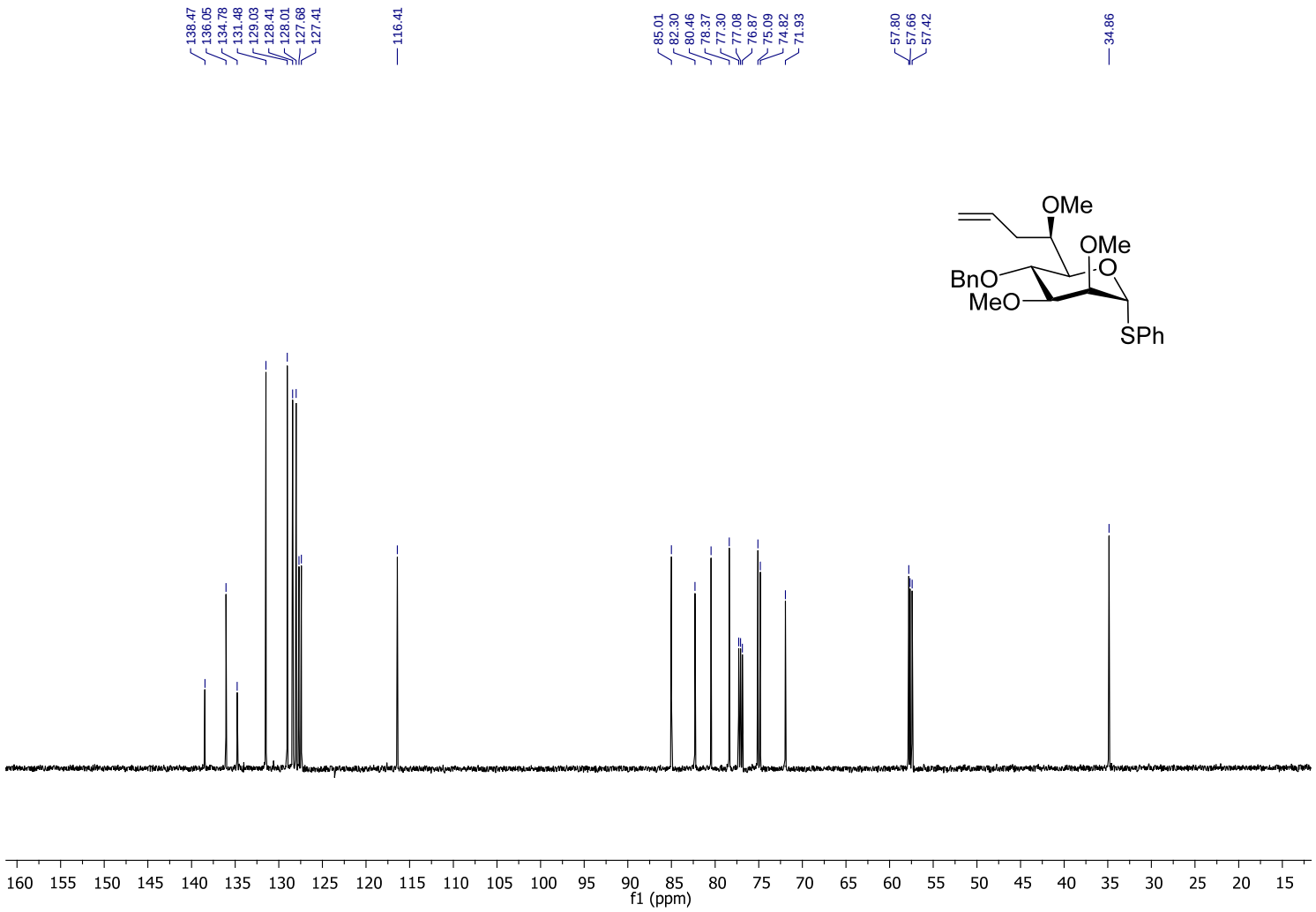
^{13}C NMR (100 MHz, $CDCl_3$) of (6*S*) Phenyl 6-*C*-Allyl-4-*O*-*p*-methoxybenzyl-2,3-di-*O*-methyl-1-thio-α-D-*manno*pyranoside (10)



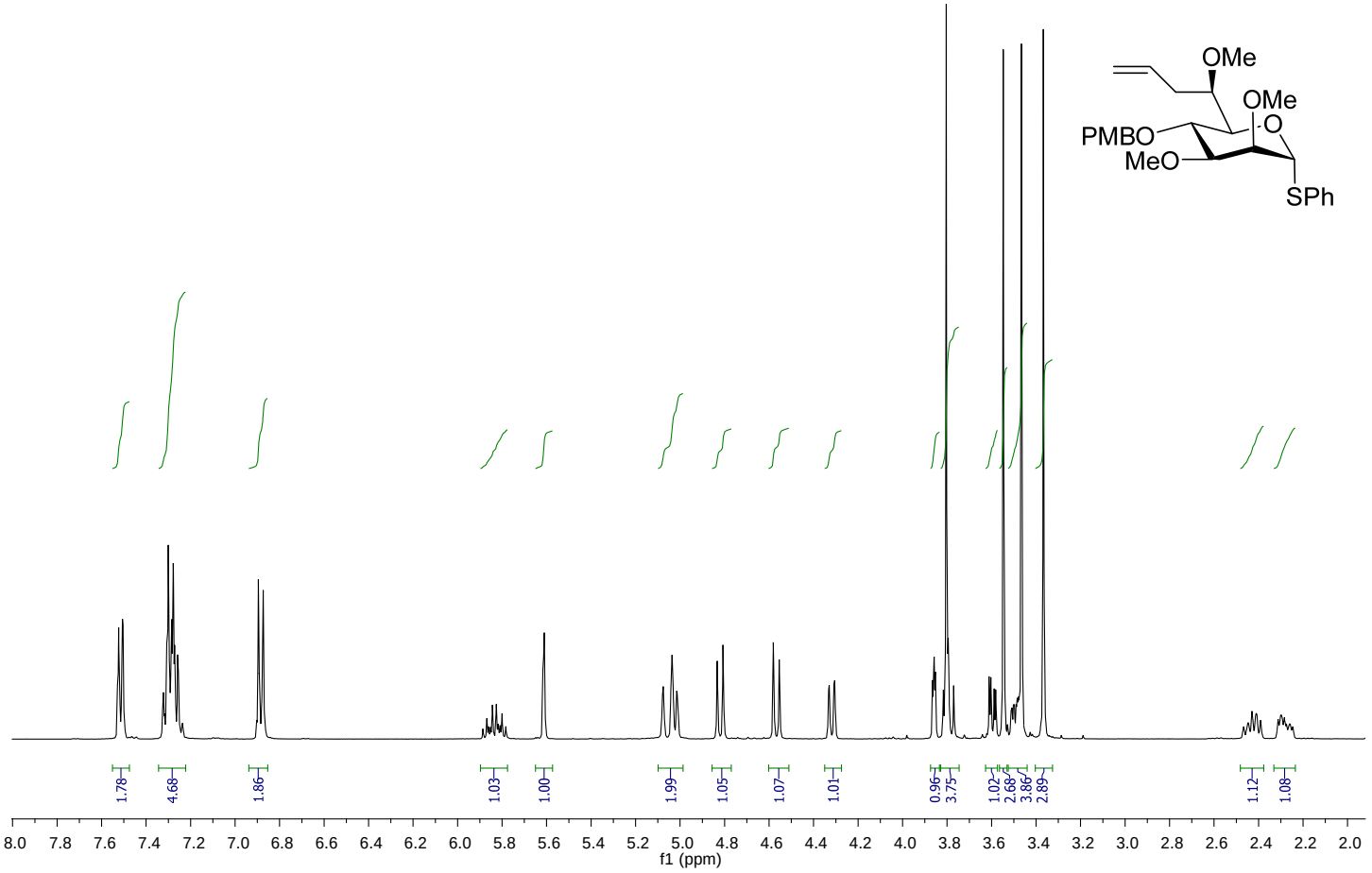
^{1}H NMR (600 MHz, $CDCl_3$) of (6*R*) Phenyl 6-*C*-Allyl-4-*O*-benzyl-2,3,6-tri-*O*-methyl-1-thio-α-D-*manno*pyranoside (11)



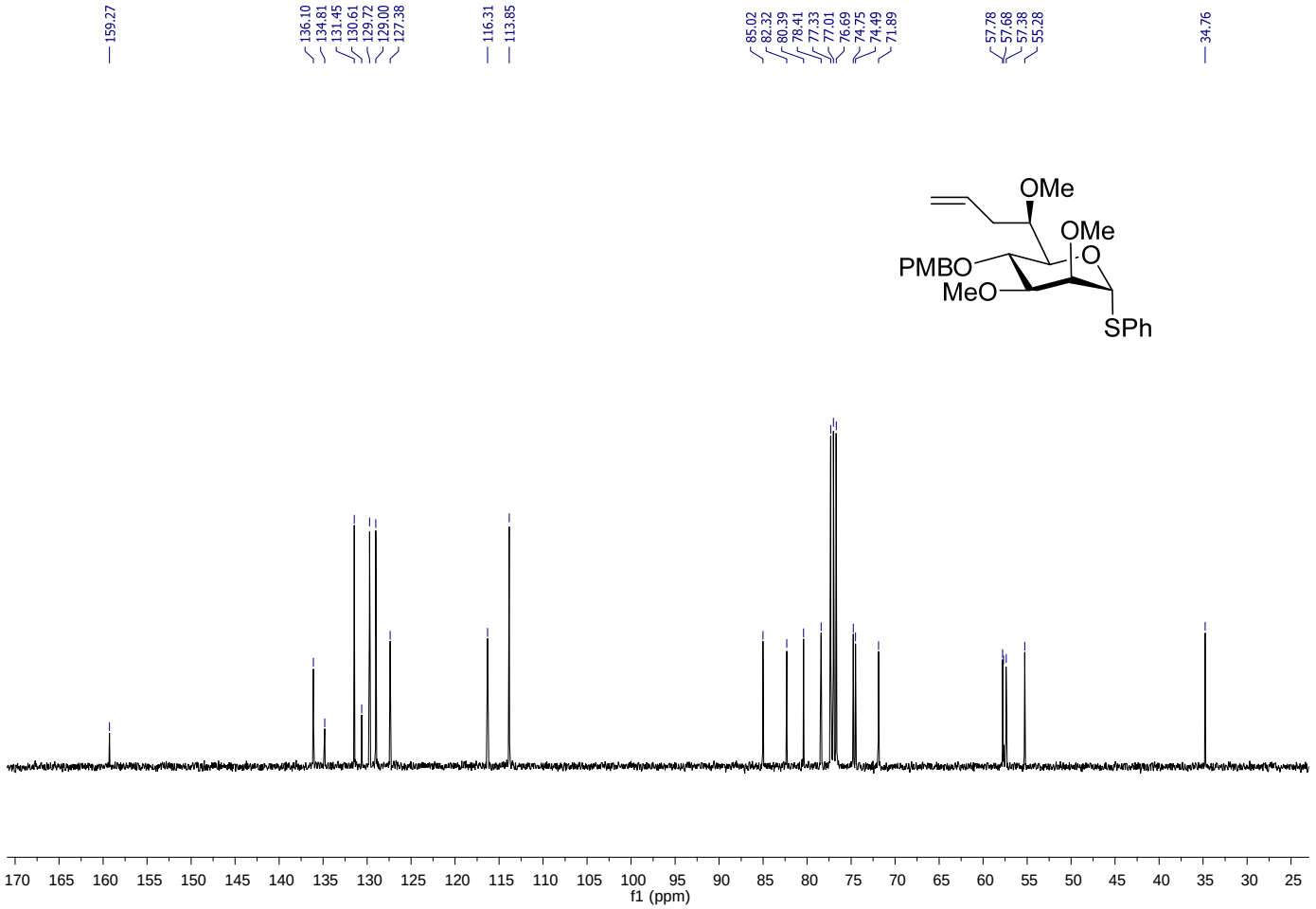
^{13}C NMR (150 MHz, $CDCl_3$) of (6*R*) Phenyl 6-*C*-Allyl-4-*O*-benzyl-2,3,6-tri-*O*-methyl-1-thio-α-D-*manno*pyranoside (11)



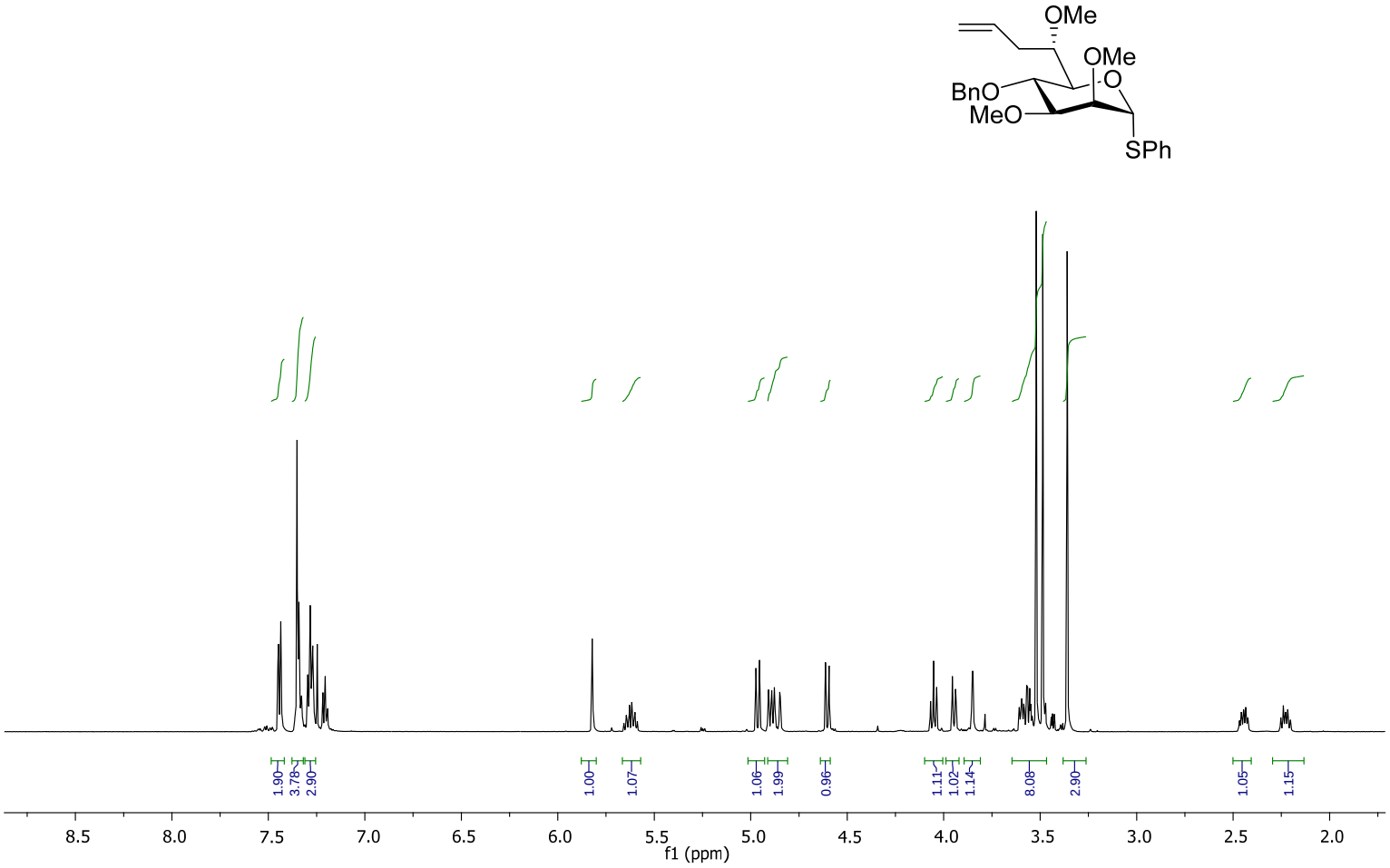
^{1}H NMR (400 MHz, $CDCl_3$) of (6*R*) Phenyl 6-*C*-Allyl-4-*O*-*p*-methoxybenzyl-2,3,6-tri-*O*-methyl--1-thio-α-D-*manno*pyranoside (12)



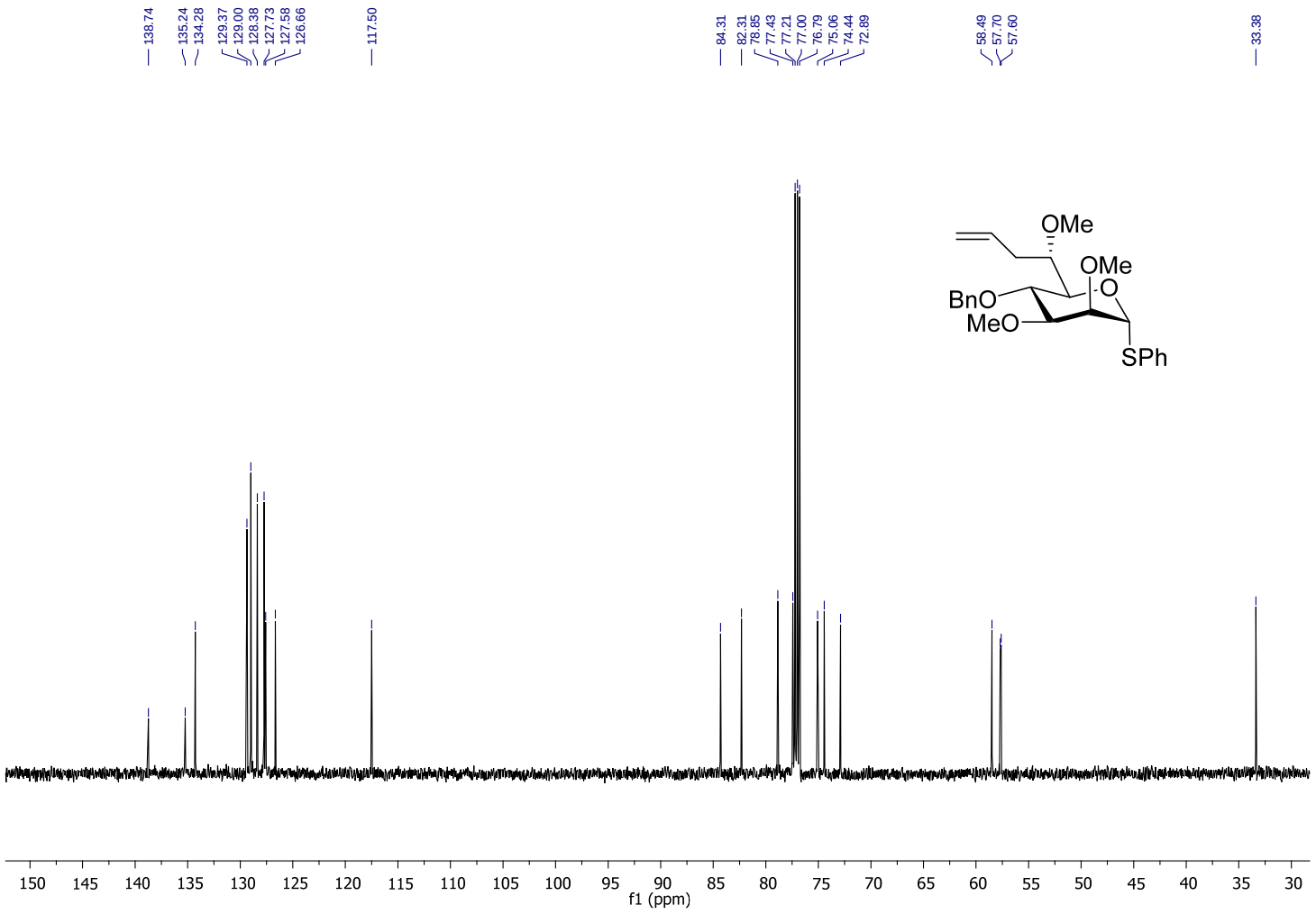
^{13}C NMR (100 MHz, $CDCl_3$) of (6*R*) Phenyl 6-*C*-Allyl-4-*O*-*p*-methoxybenzyl-2,3,6-tri-*O*-methyl--1-thio-α-D-*manno*pyranoside (12)



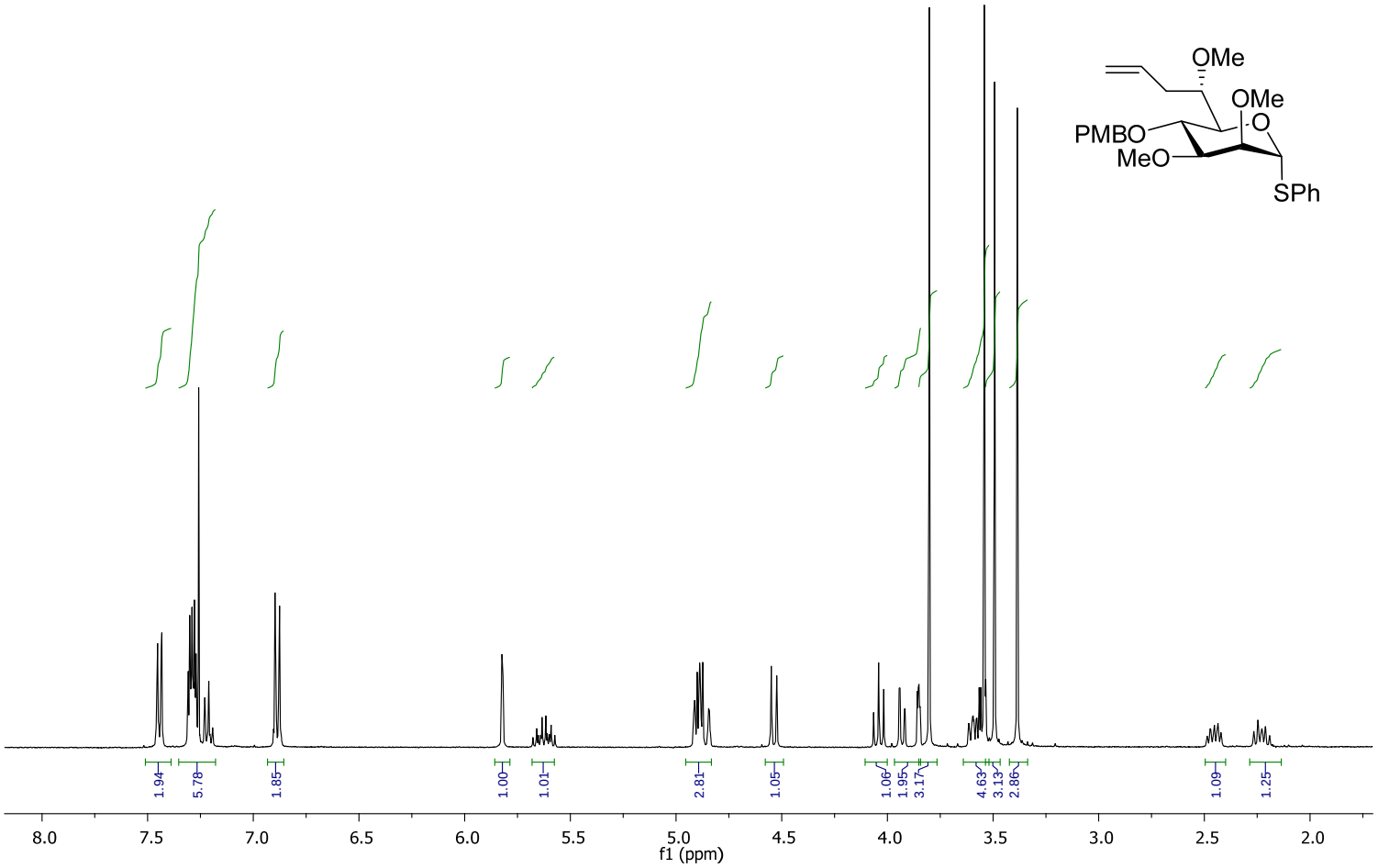
^{1}H NMR (600 MHz, $CDCl_3$) of (6*S*) Phenyl 6-*C*-Allyl-4-*O*-benzyl-2,3,6-tri-*O*-methyl-1-thio-*α*-D-*manno*pyranoside (13)



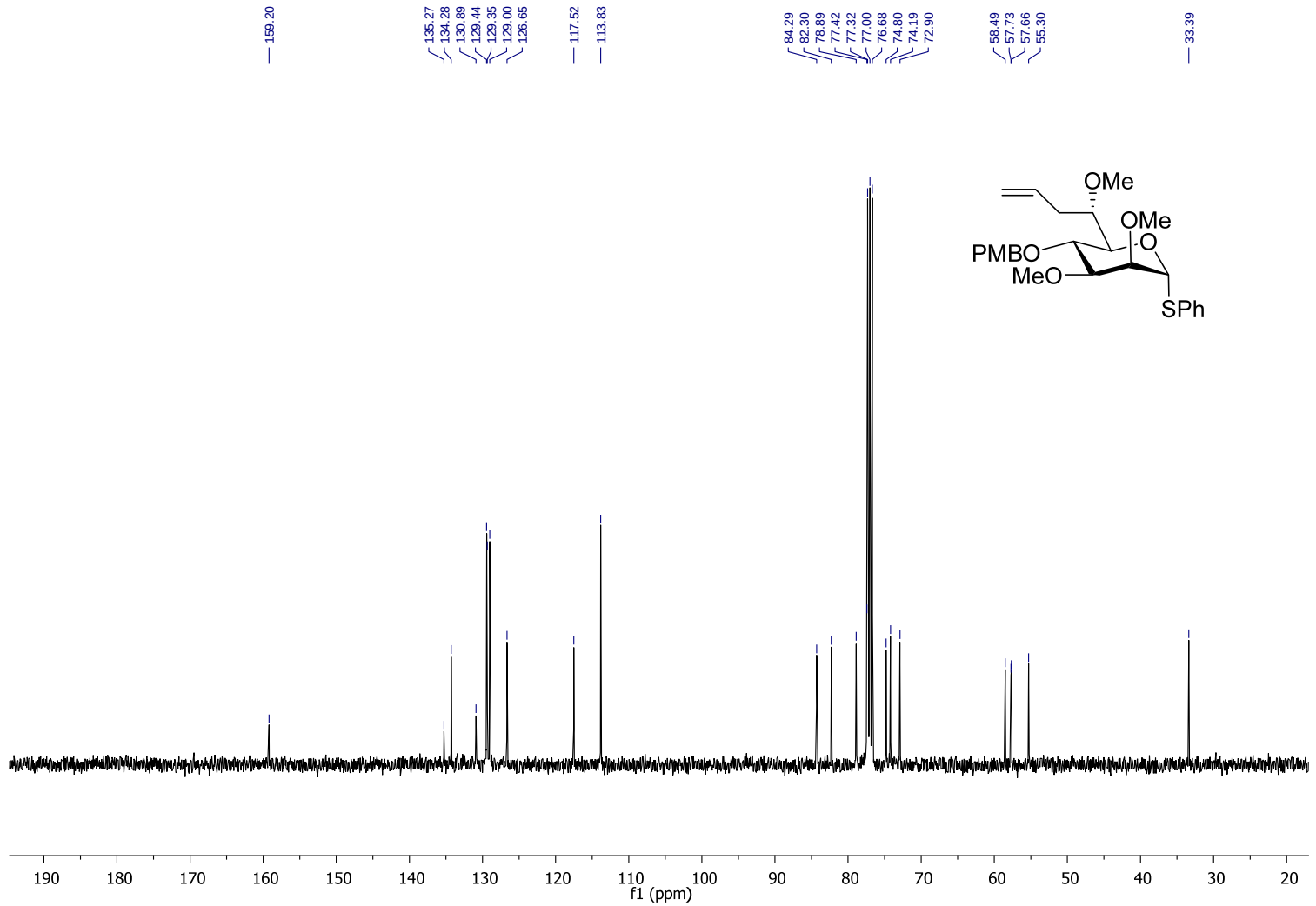
^{13}C NMR (150 MHz, $CDCl_3$) of (6*S*) Phenyl 6-*C*-Allyl-4-*O*-benzyl-2,3,6-tri-*O*-methyl-1-thio-*α*-D-*mann*opyranoside (13)



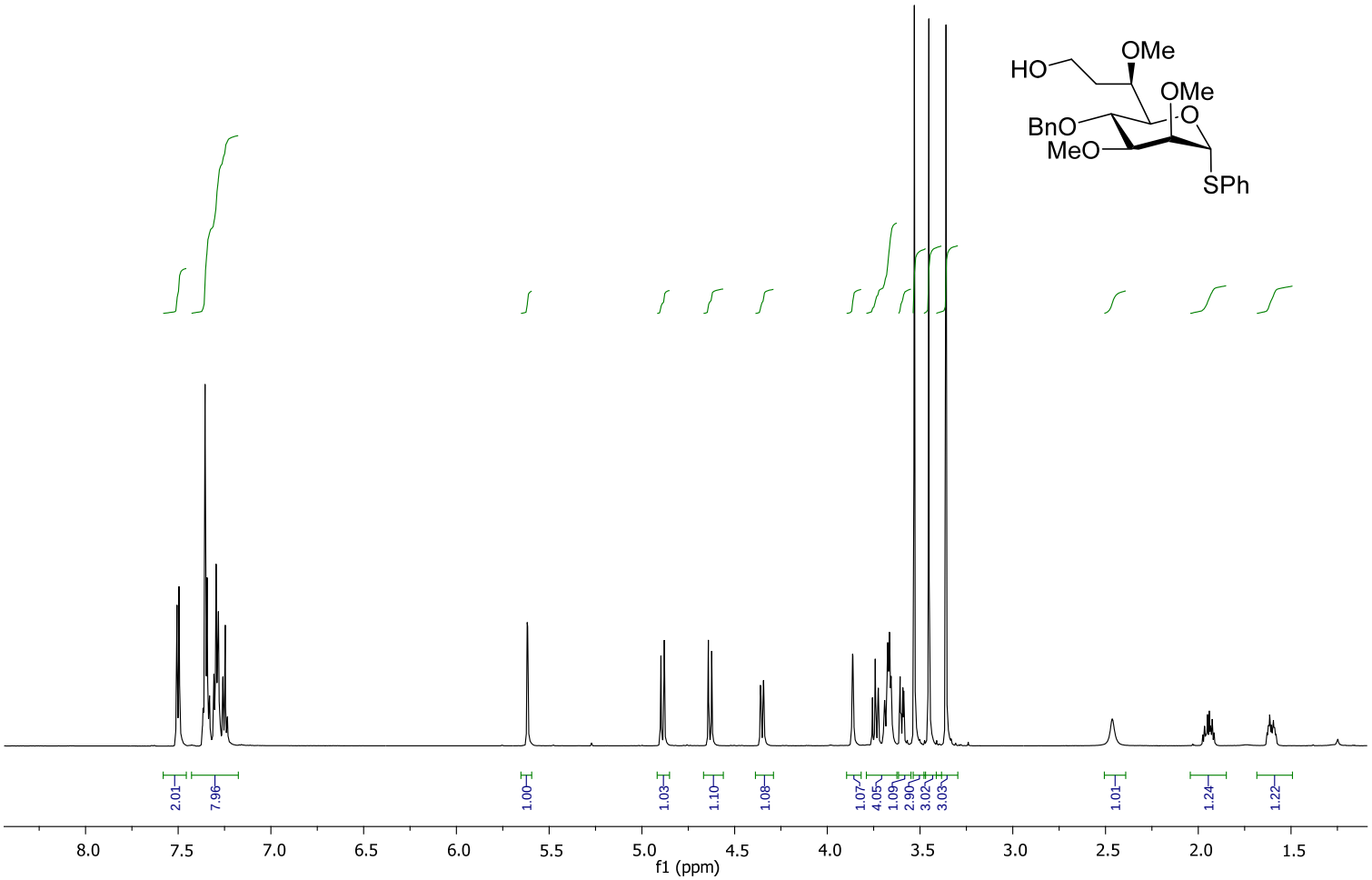
^{1}H NMR (400 MHz, $CDCl_3$) of (6*S*) Phenyl 6-*C*-Allyl-4-*O*-*p*-methoxybenzyl-2,3,6-tri-*O*-methyl-1-thio-α-D-*manno*pyranoside (14)



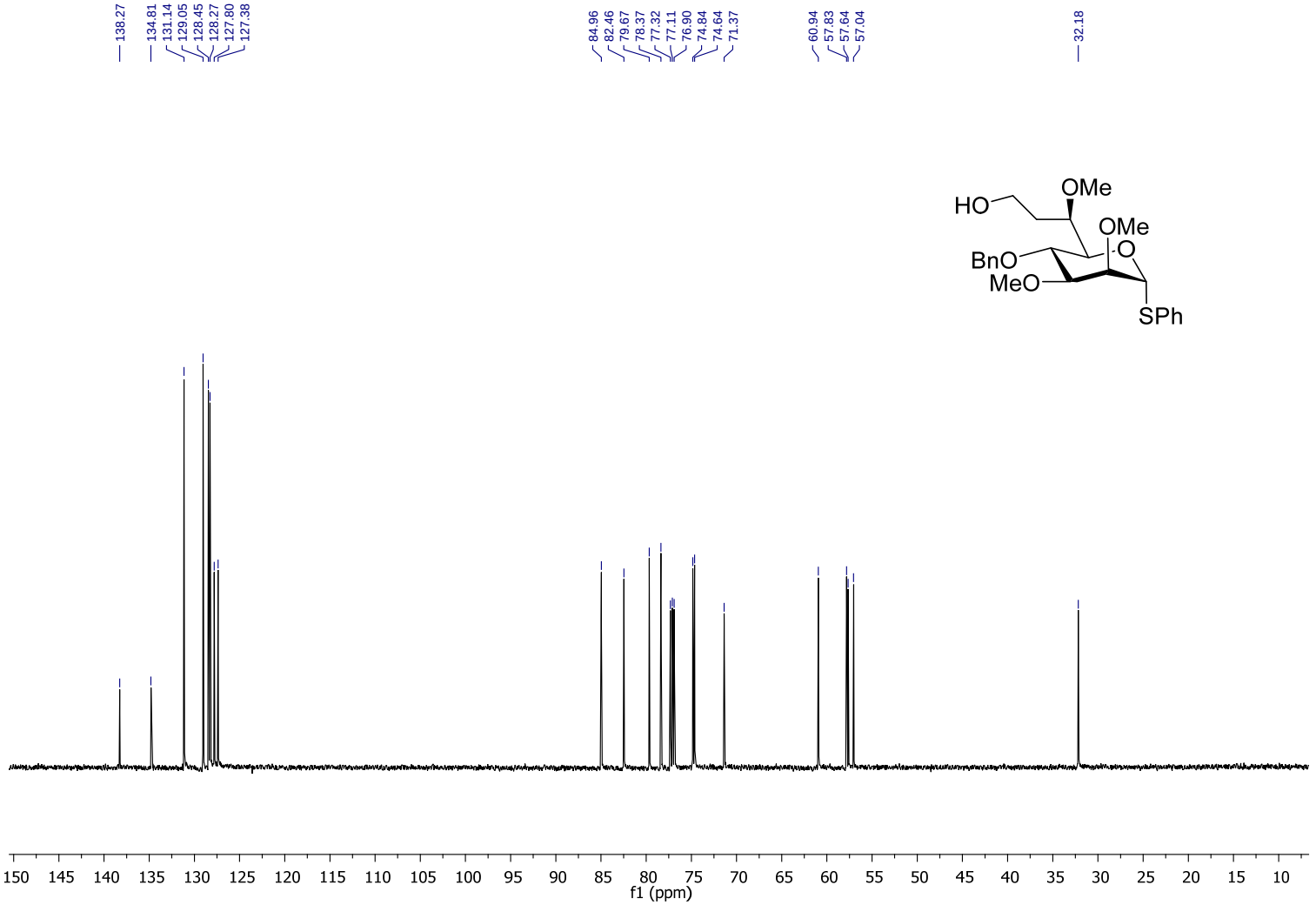
^{13}C NMR (100 MHz, $CDCl_3$) of (6*S*) Phenyl 6-*C*-Allyl-4-*O*-*p*-methoxybenzyl-2,3,6-tri-*O*-methyl-1-thio-α-D-*manno*pyranoside (14)



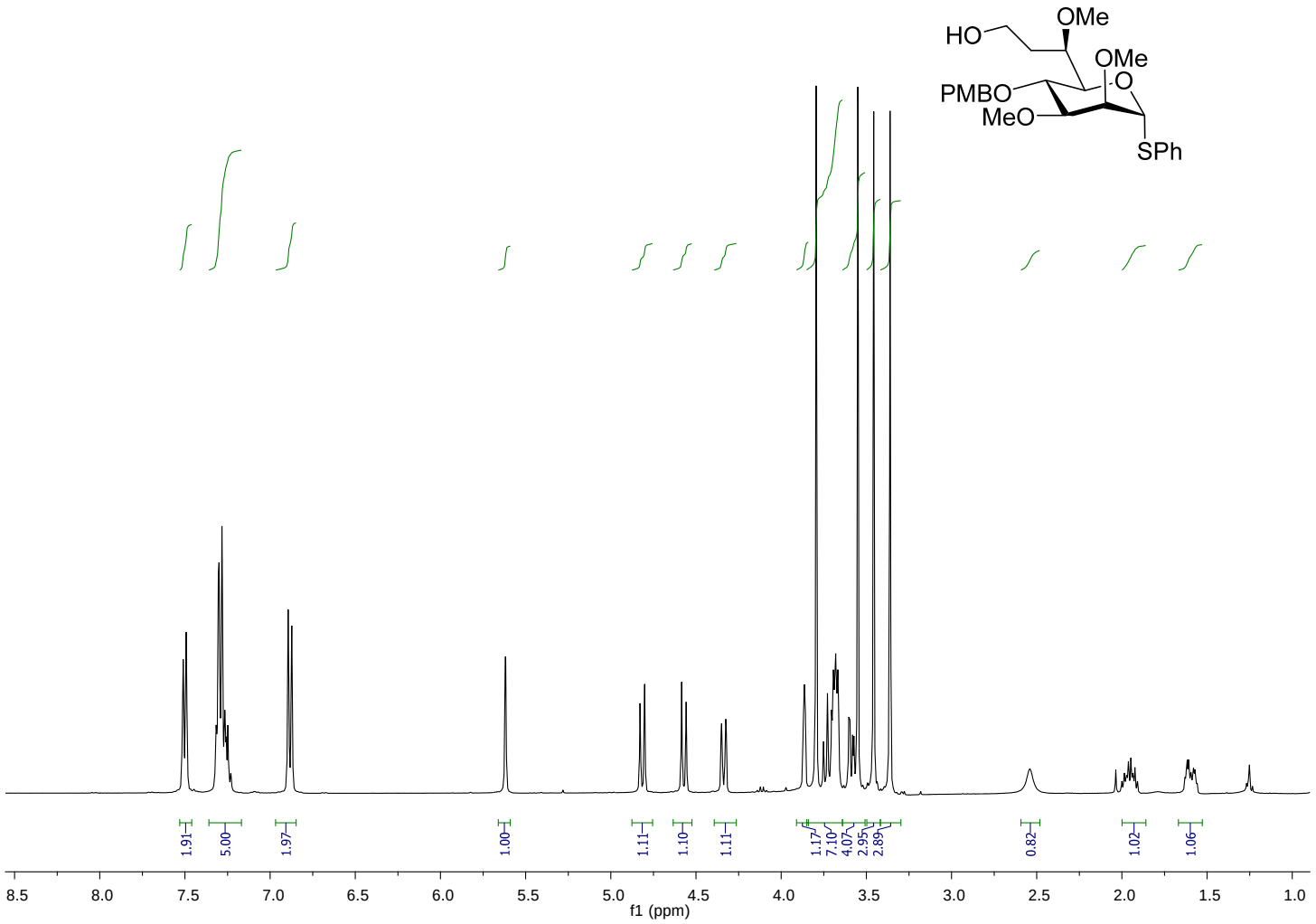
^{1}H NMR (600 MHz, $CDCl_3$) of Phenyl 4-*O*-benzyl-7-deoxy-2,3,6-tri-*O*-methyl-D-*glycero*-α-D- thio-*manno*octopyranoside (15)



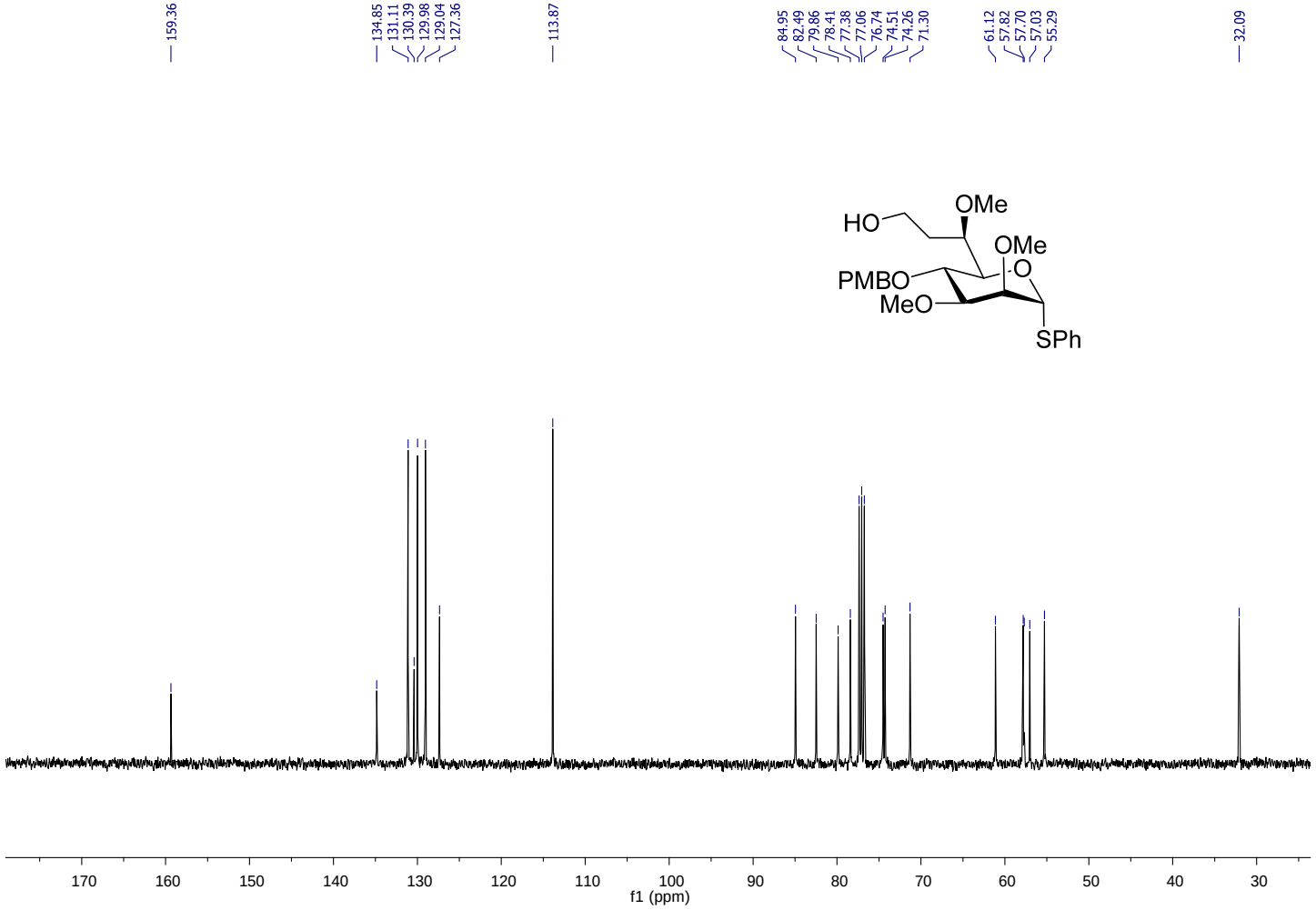
^{13}C NMR (150 MHz, $CDCl_3$) of Phenyl 4-*O*-benzyl-7-deoxy-2,3,6-tri-*O*-methyl-D-*glycero*-α-D- thio-*manno*octopyranoside (15)



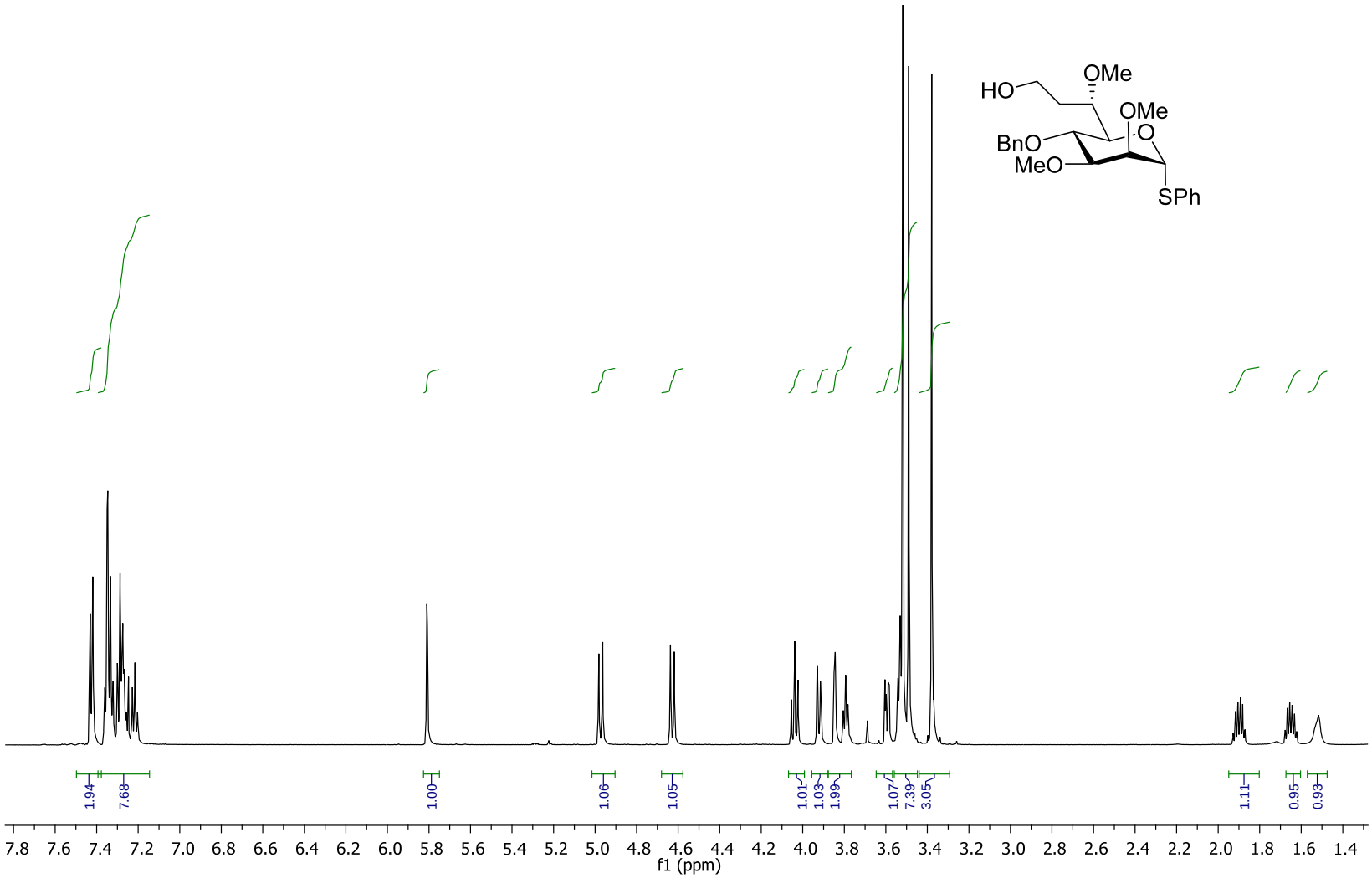
^{1}H NMR (400 MHz, $CDCl_3$) of Phenyl 4-*O*-*p*-methoxybenzyl-7-deoxy-2,3,6-tri-*O*-methyl-D-*glycero*-α-D- thio-*manno*octopyranoside (16)



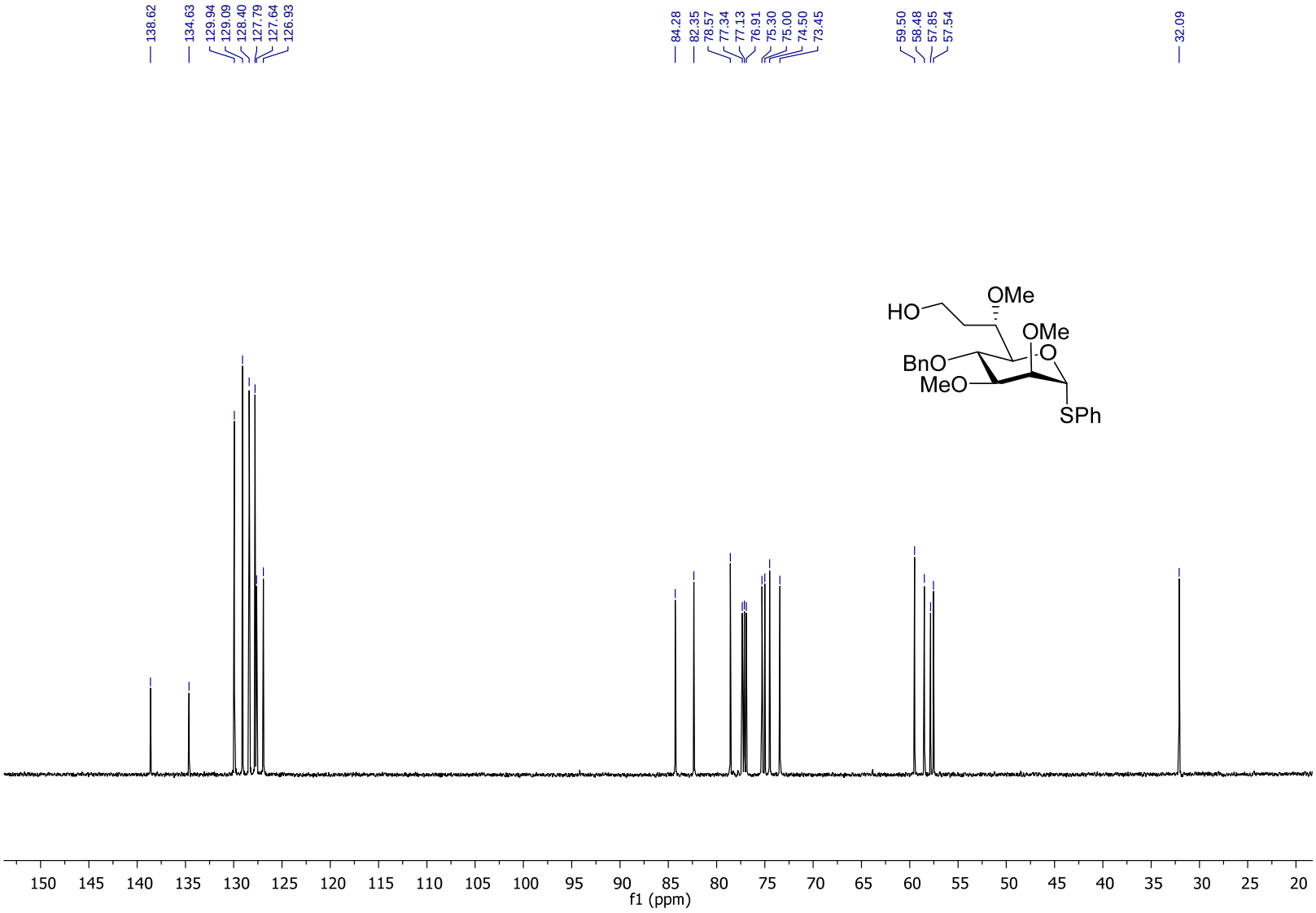
^{13}C NMR (100 MHz, $CDCl_3$) of Phenyl 4-*O*-*p*-methoxybenzyl-7-deoxy-2,3,6-tri-*O*-methyl-D-*glycero*-α-D- thio-*manno*octopyranoside (16)



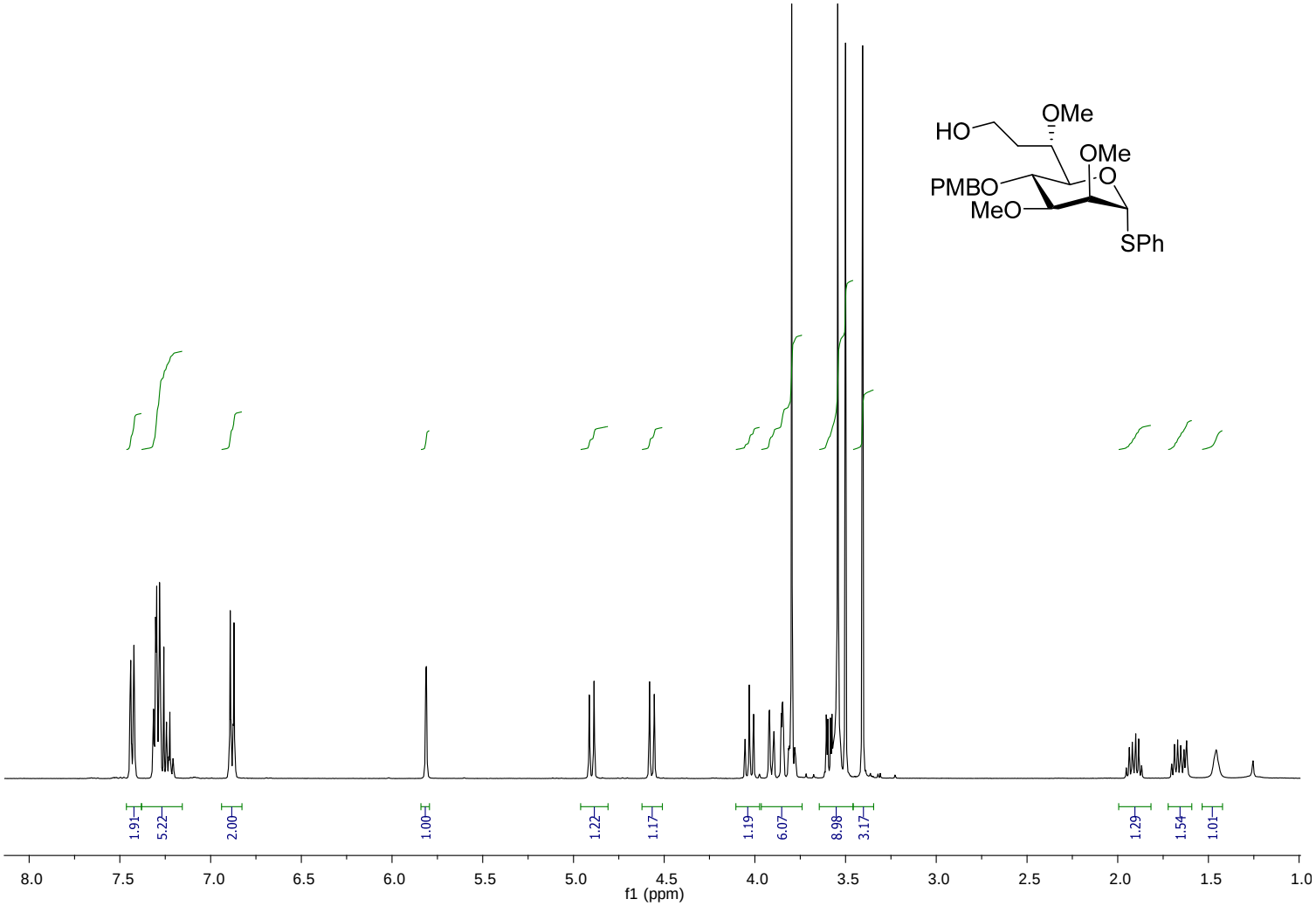
^{1}H NMR (600 MHz, $CDCl_3$) of Phenyl 4-*O*-benzyl-7-deoxy-2,3,6-tri-*O*-methyl-L-*glycero*-α-D-thio-*manno*octopyranoside (17)



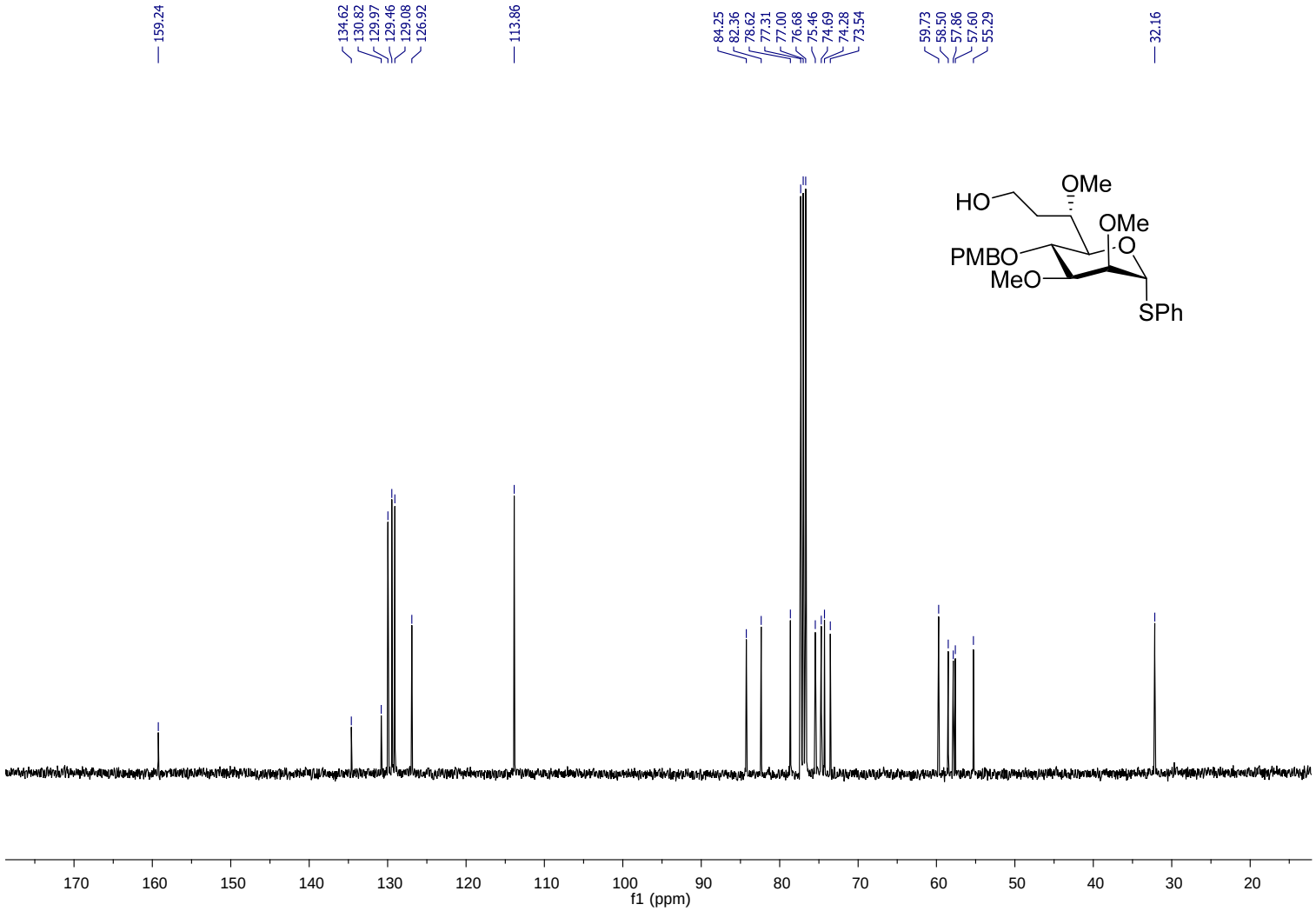
^{13}C NMR (150 MHz, $CDCl_3$) of Phenyl 4-*O*-benzyl-7-deoxy-2,3,6-tri-*O*-methyl-L-*glycero*-α-D-thio-*manno*octopyranoside (17)



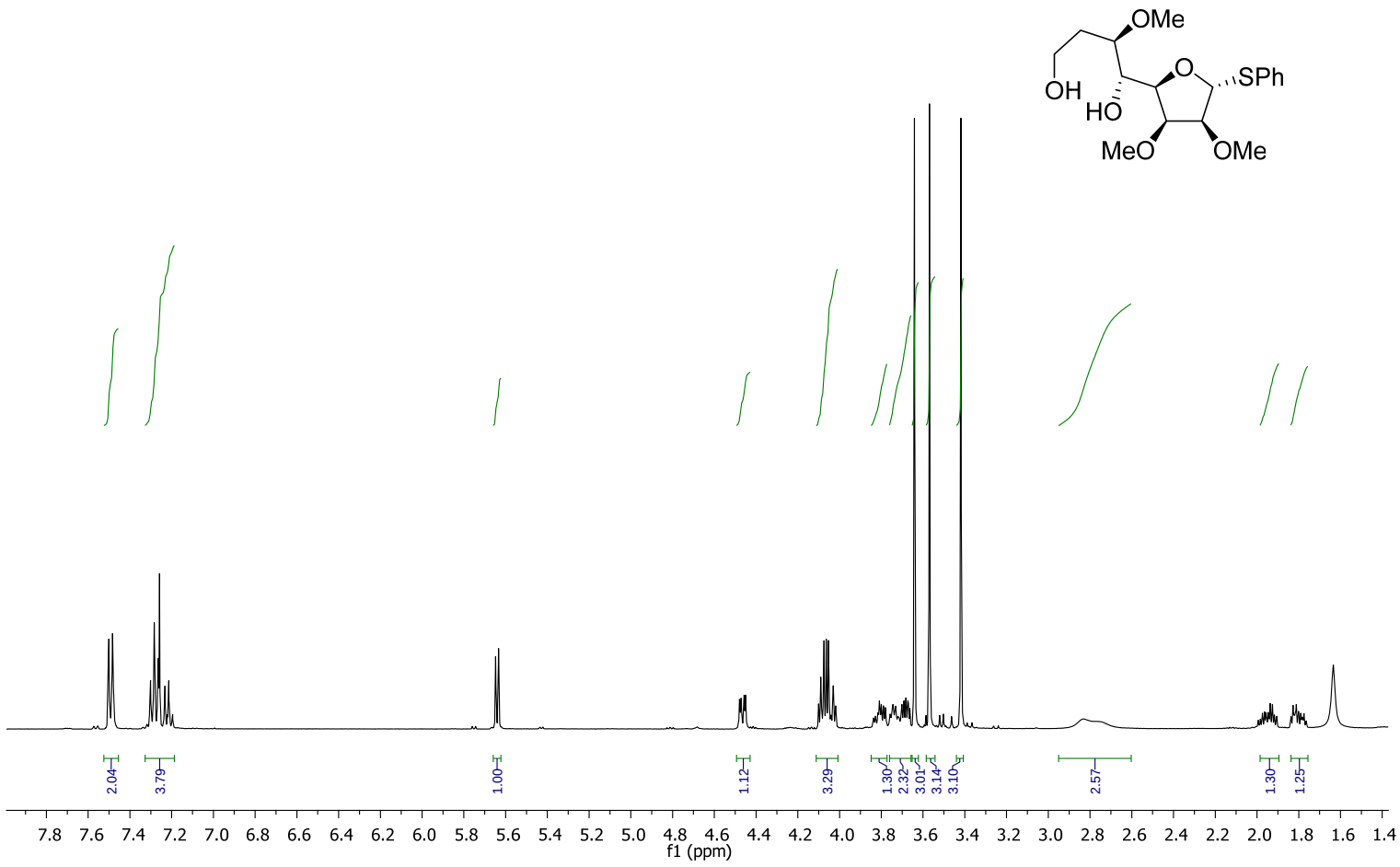
^{1}H NMR (400 MHz, $CDCl_3$) of Phenyl 4-*O*-*p*-methoxybenzyl-7-deoxy-2,3,6-tri-*O*-methyl-L-*glycero*-α-D-thio-*manno*octopyranoside (18)



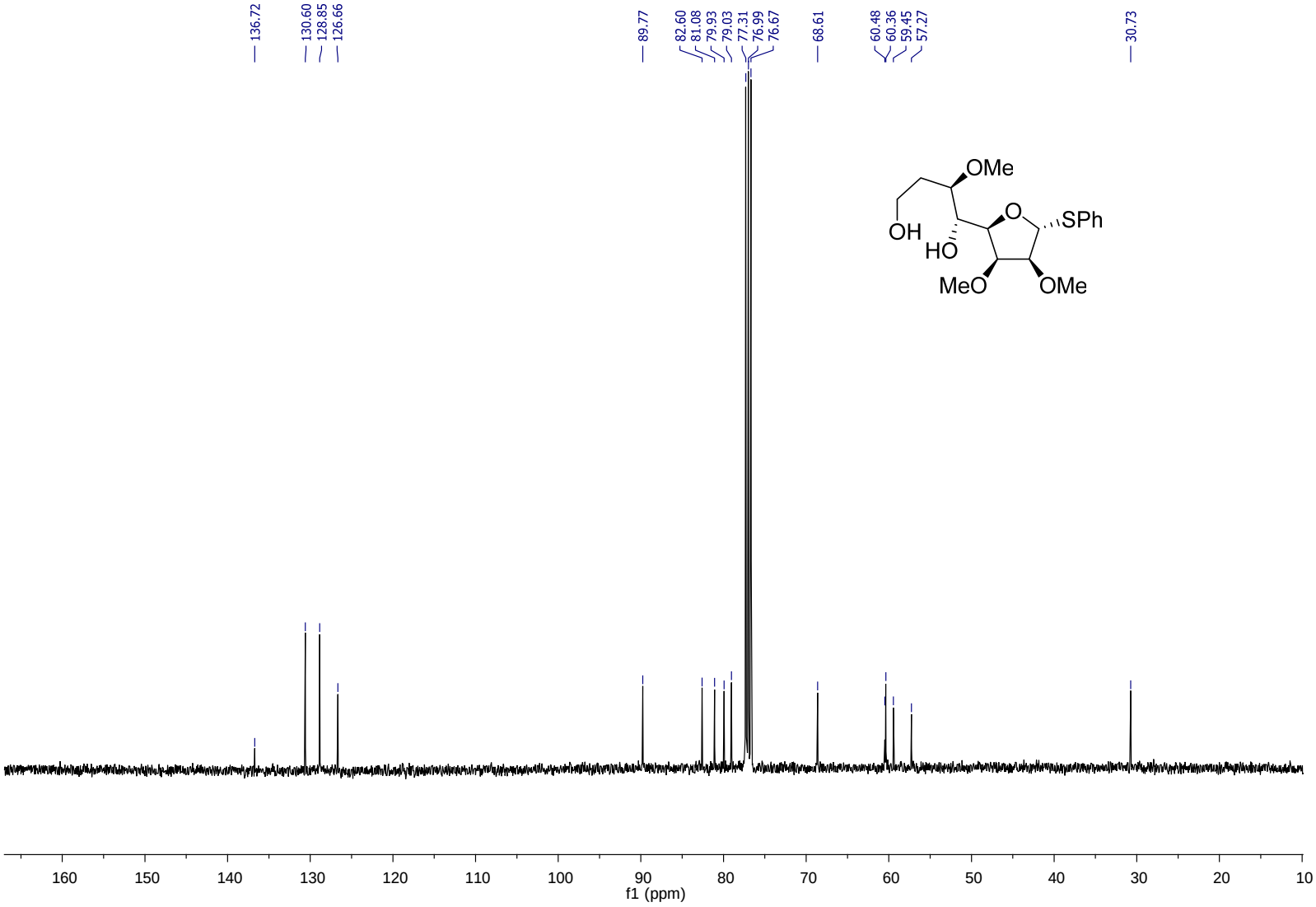
^{13}C NMR (100 MHz, $CDCl_3$) of Phenyl 4-*O*-*p*-methoxybenzyl-7-deoxy-2,3,6-tri-*O*-methyl-L-*glycero*-α-D-thio-*manno*octopyranoside (18)



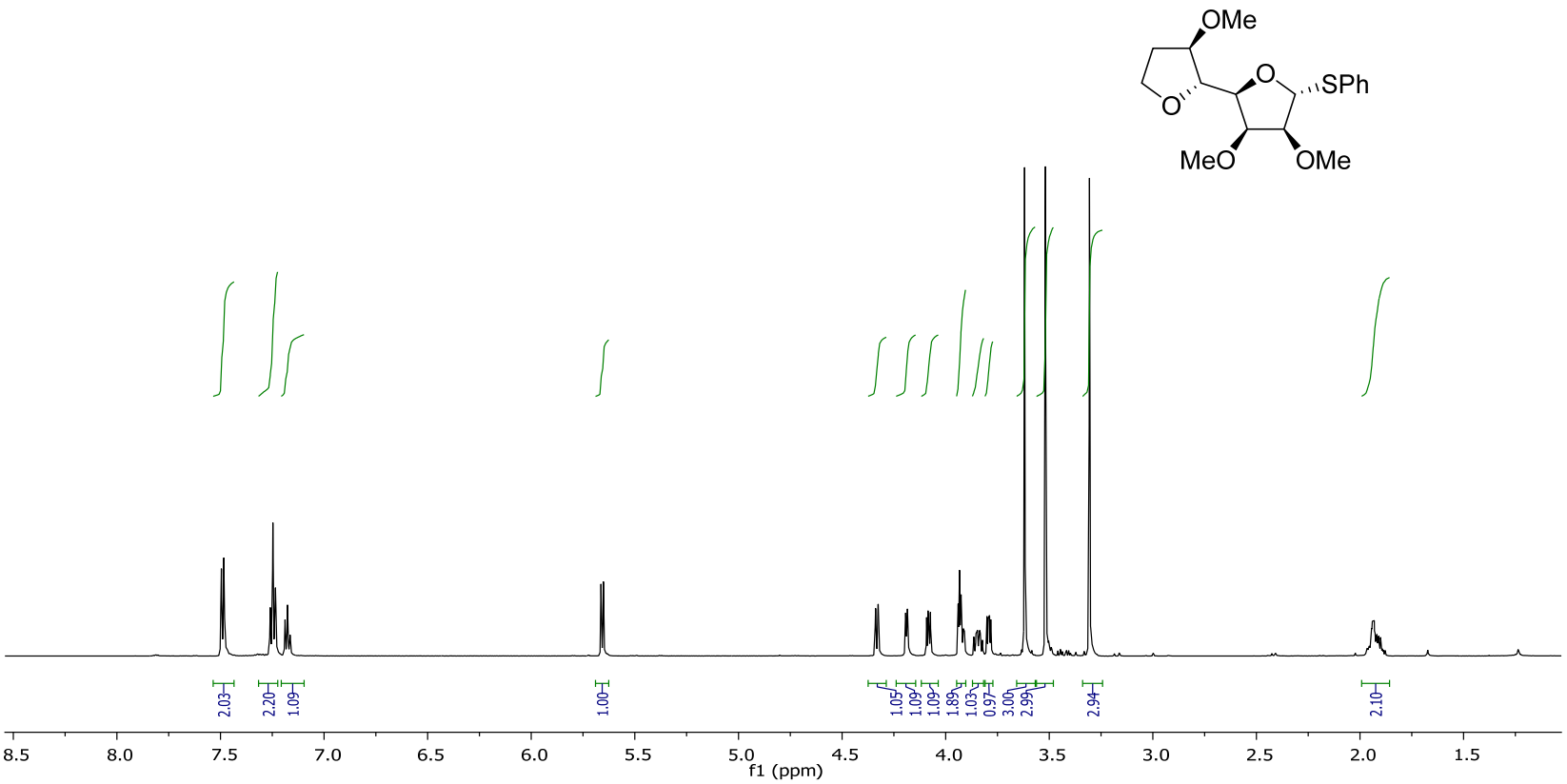
^{1}H NMR (400 MHz, $CDCl_3$) of Phenyl 7-deoxy-2,3,6-tri-*O*-methyl-D-*glycero*-α-D-thio-*manno*octofuranoside (19)



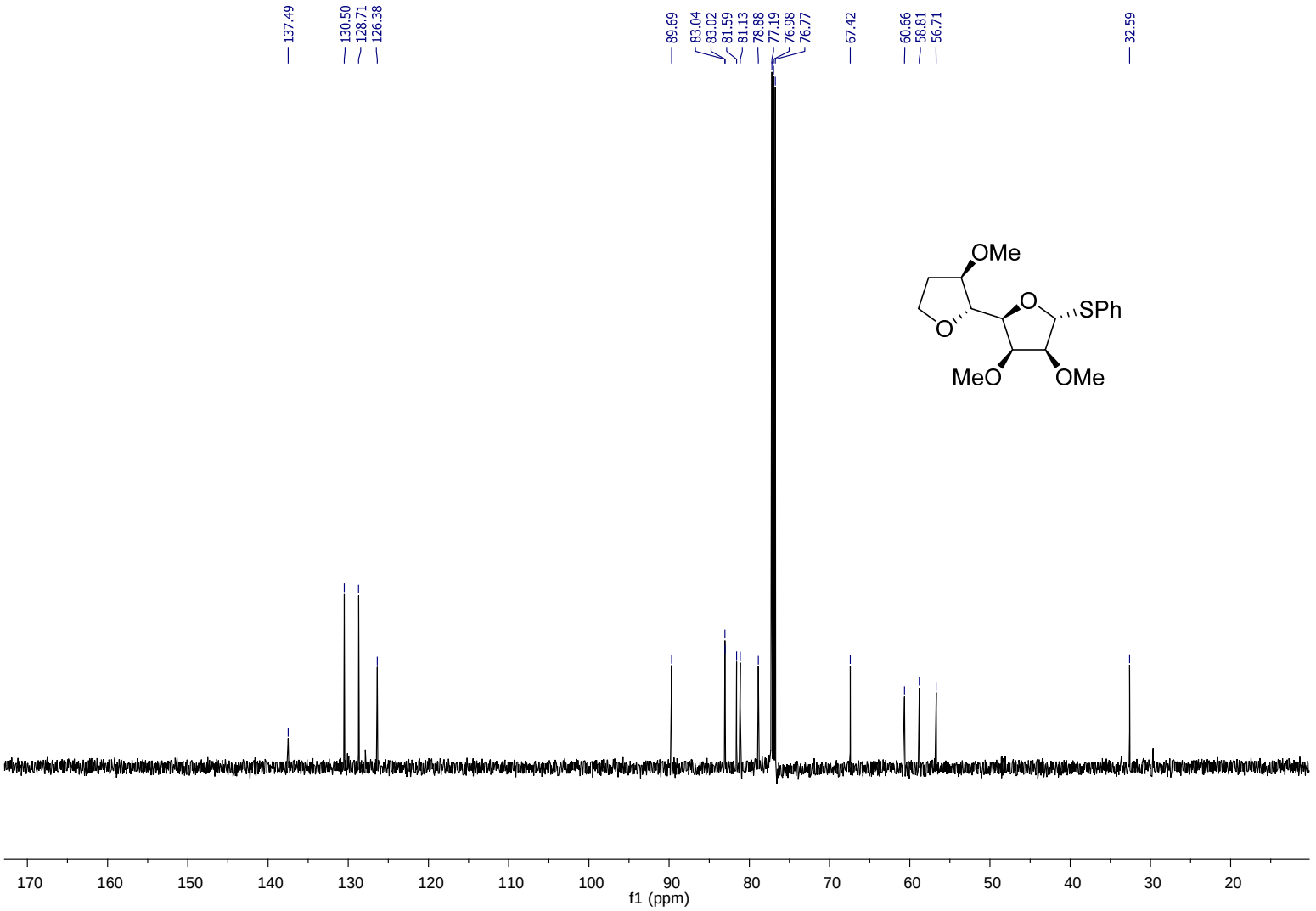
^{13}C NMR (100 MHz, $CDCl_3$) of Phenyl 7-deoxy-2,3,6-tri-*O*-methyl-D-*glycero*-α-D-thio-*manno*octofuranoside (19)



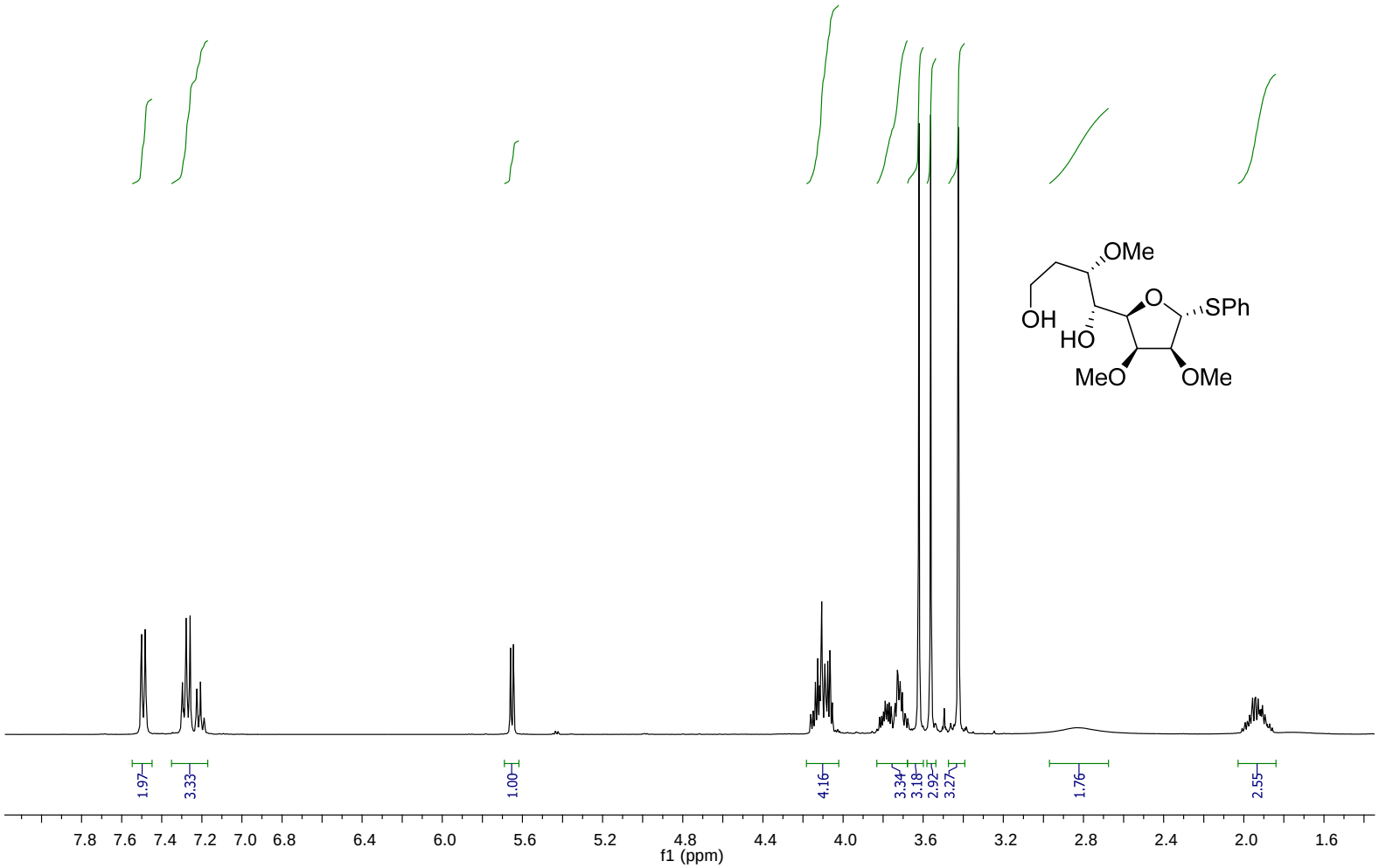
^{1}H NMR (600 MHz, $CDCl_3$) of Phenyl 5,8-anhydro-7-deoxy-2,3,6-tri-*O*-methyl-D-*glycero*-α-D-thio-*manno*octofuranoside (20)



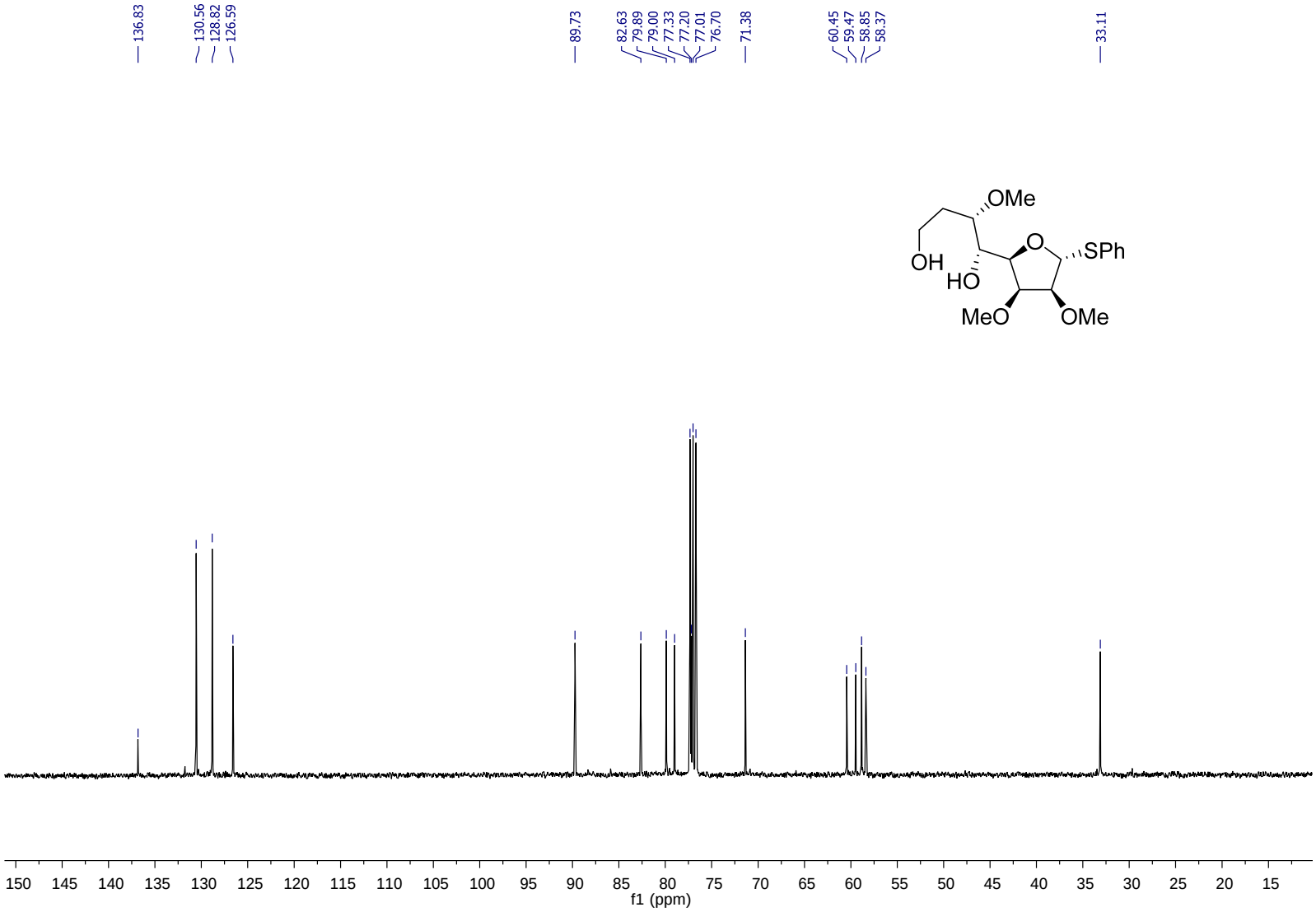
^{13}C NMR (150 MHz, $CDCl_3$) of Phenyl 5,8-anhydro-7-deoxy-2,3,6-tri-*O*-methyl-D-*glycero*-α-D-thio-*mann*ooctofuranoside (20)



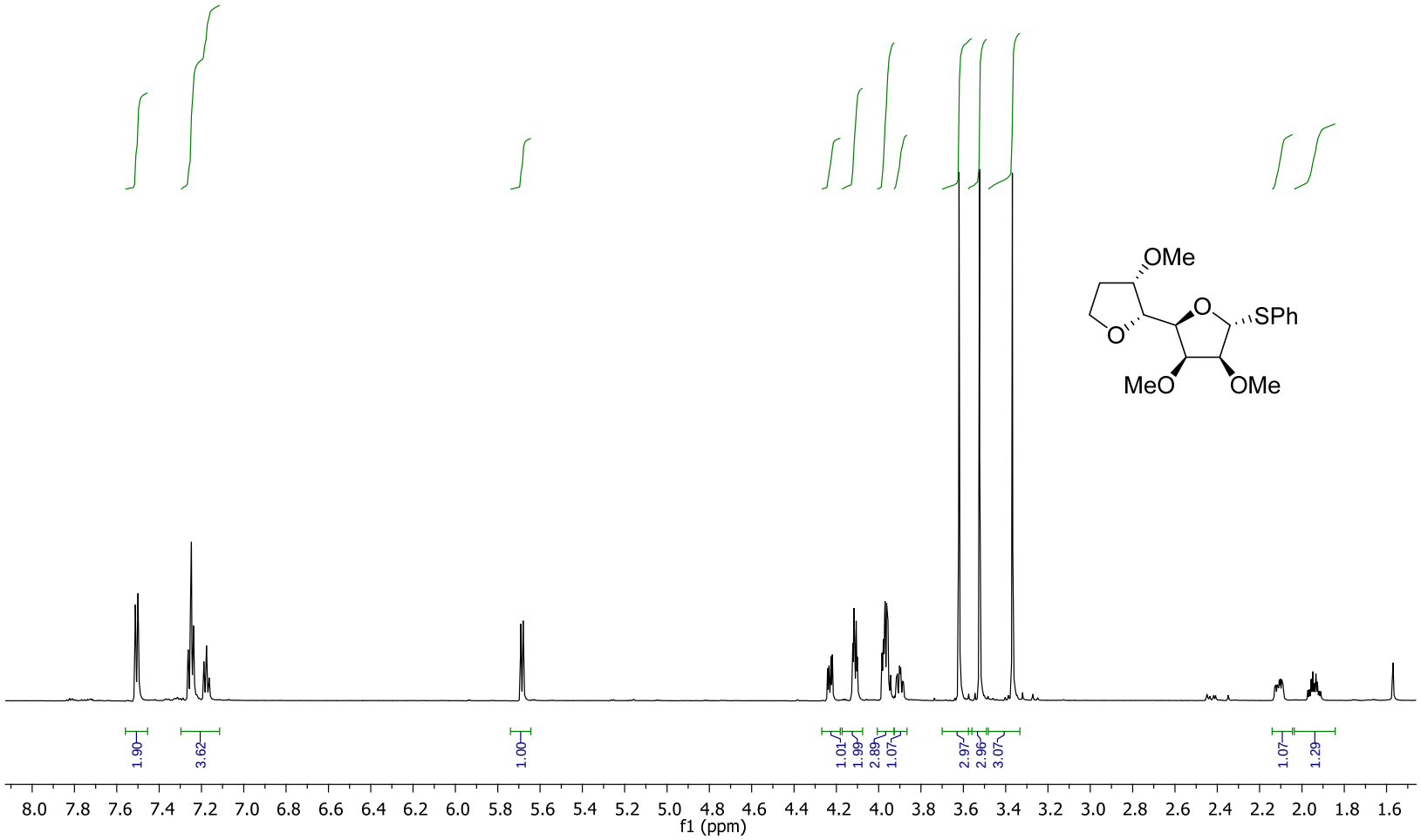
^{1}H NMR (400 MHz, $CDCl_3$) of Phenyl 7-deoxy-2,3,6-tri-*O*-methyl-L-*glycero*-α-D-thio-*manno*octofuranoside (21)



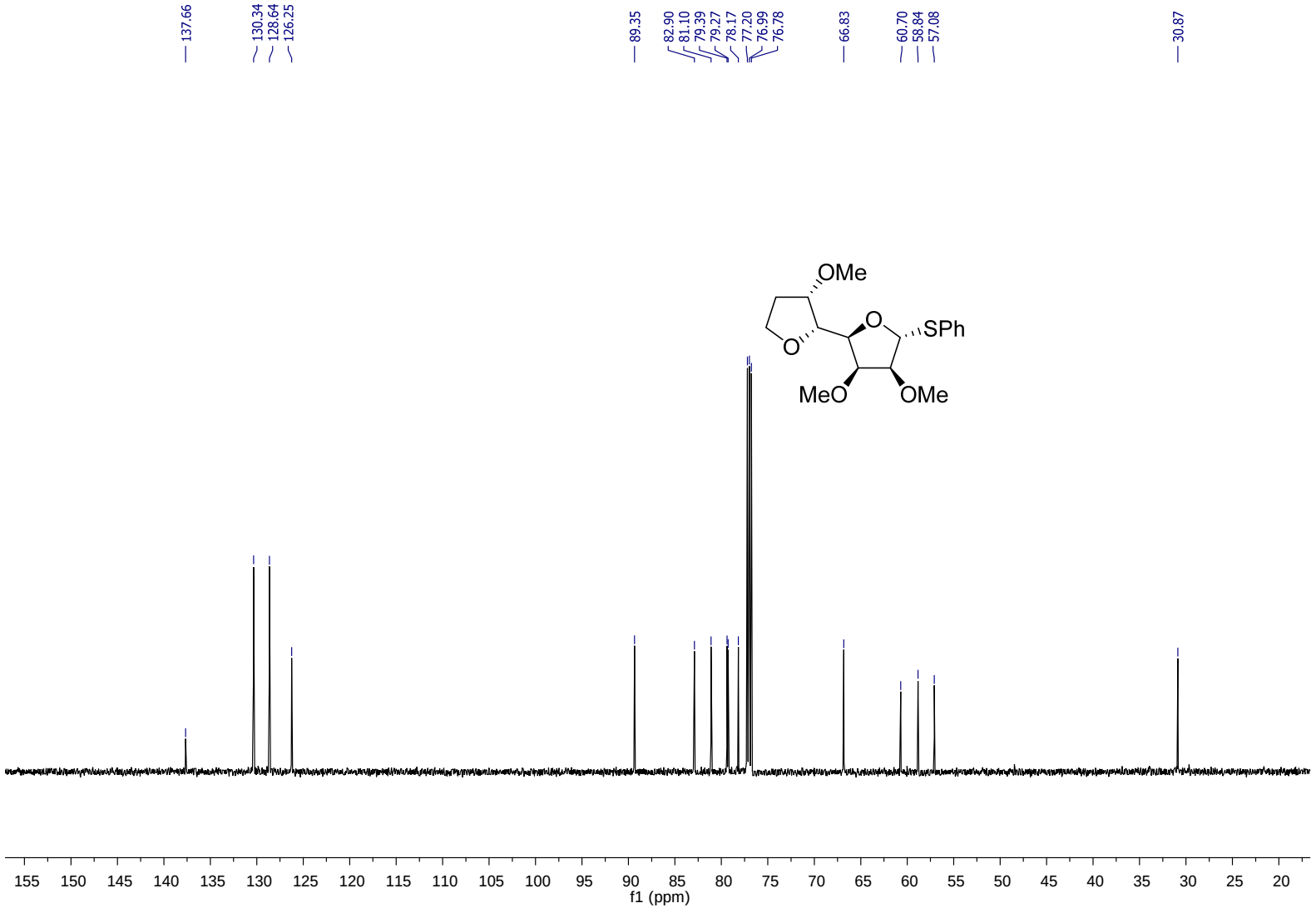
^{13}C NMR (100 MHz, $CDCl_3$) of Phenyl 7-deoxy-2,3,6-tri-*O*-methyl-L-*glycero*-α-D-thio-*manno*octofuranoside (21)



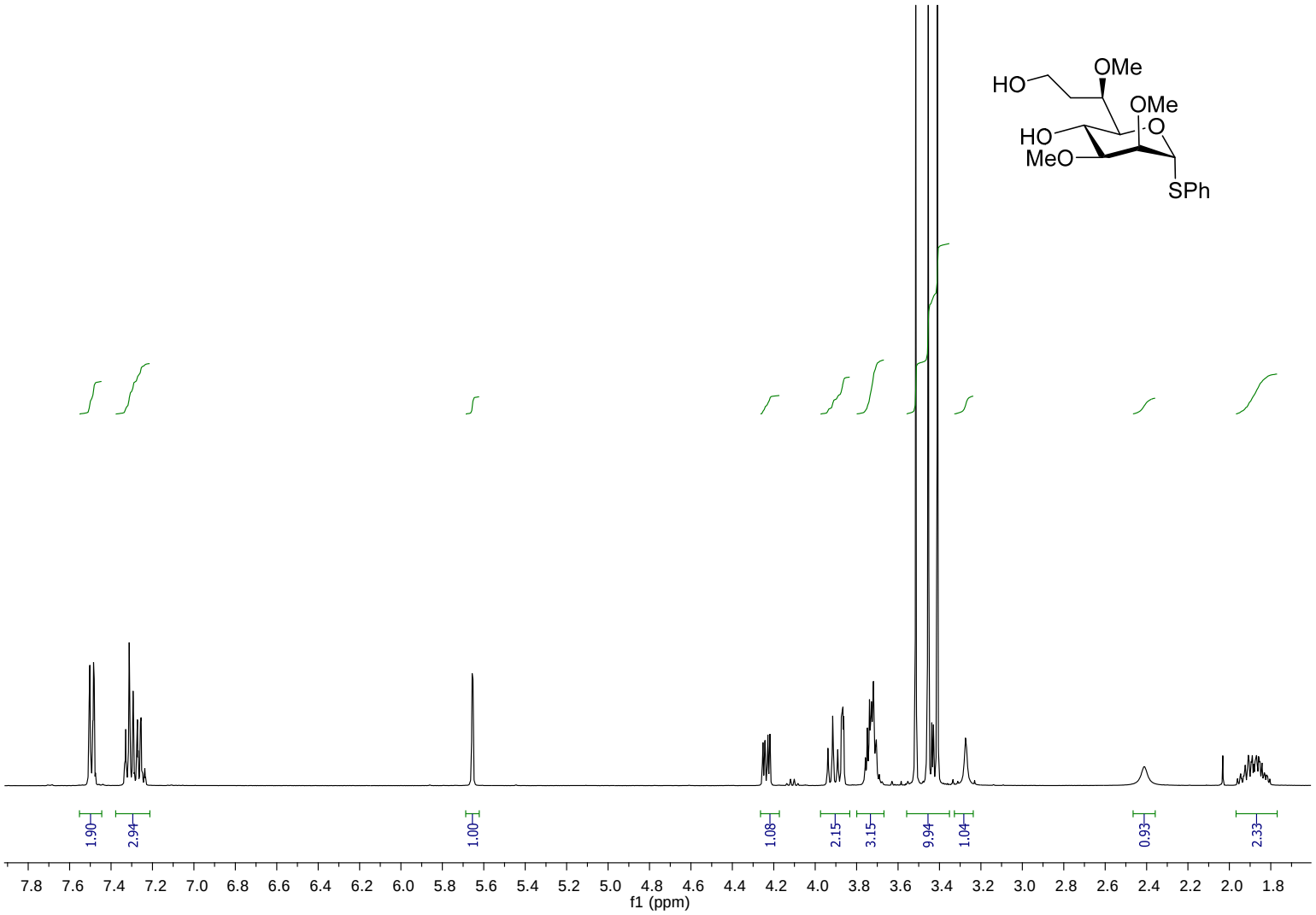
^{1}H NMR (600 MHz, $CDCl_3$) of Phenyl 5,8-anhydro-7-deoxy-2,3,6-tri-*O*-methyl-L-*glycero*-α-D-thio-*manno*octofuranoside (22)



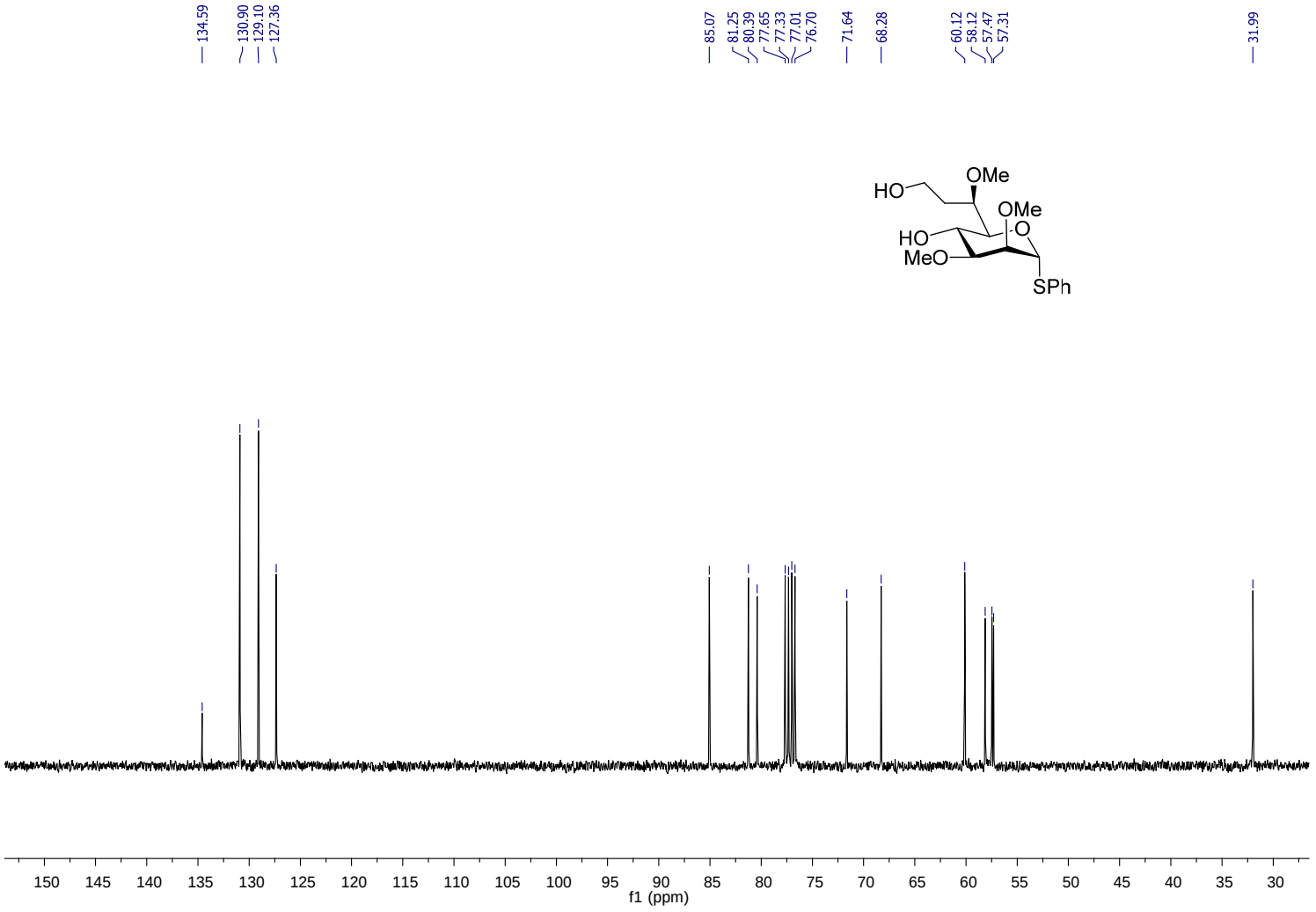
^{13}C NMR (150 MHz, $CDCl_3$) of Phenyl 5,8-anhydro-7-deoxy-2,3,6-tri-*O*-methyl-L-*glycero*-α-D-thio-*manno*octofuranoside (22)



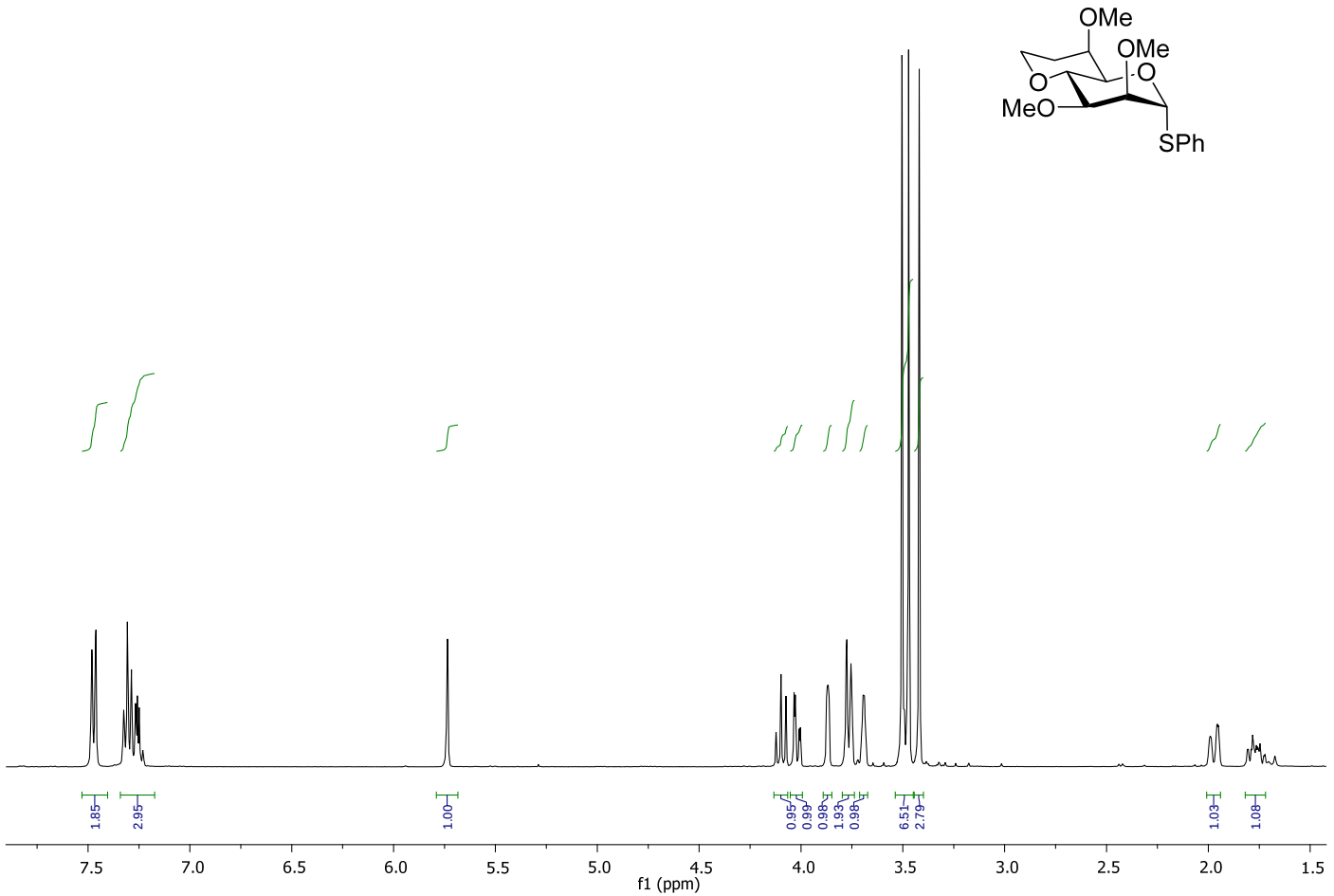
^{1}H NMR (400 MHz, $CDCl_3$) of Phenyl 7-deoxy-2,3,6-tri-*O*-methyl-D-*glycero*-α-D-thio-*manno*octopyranoside (23)



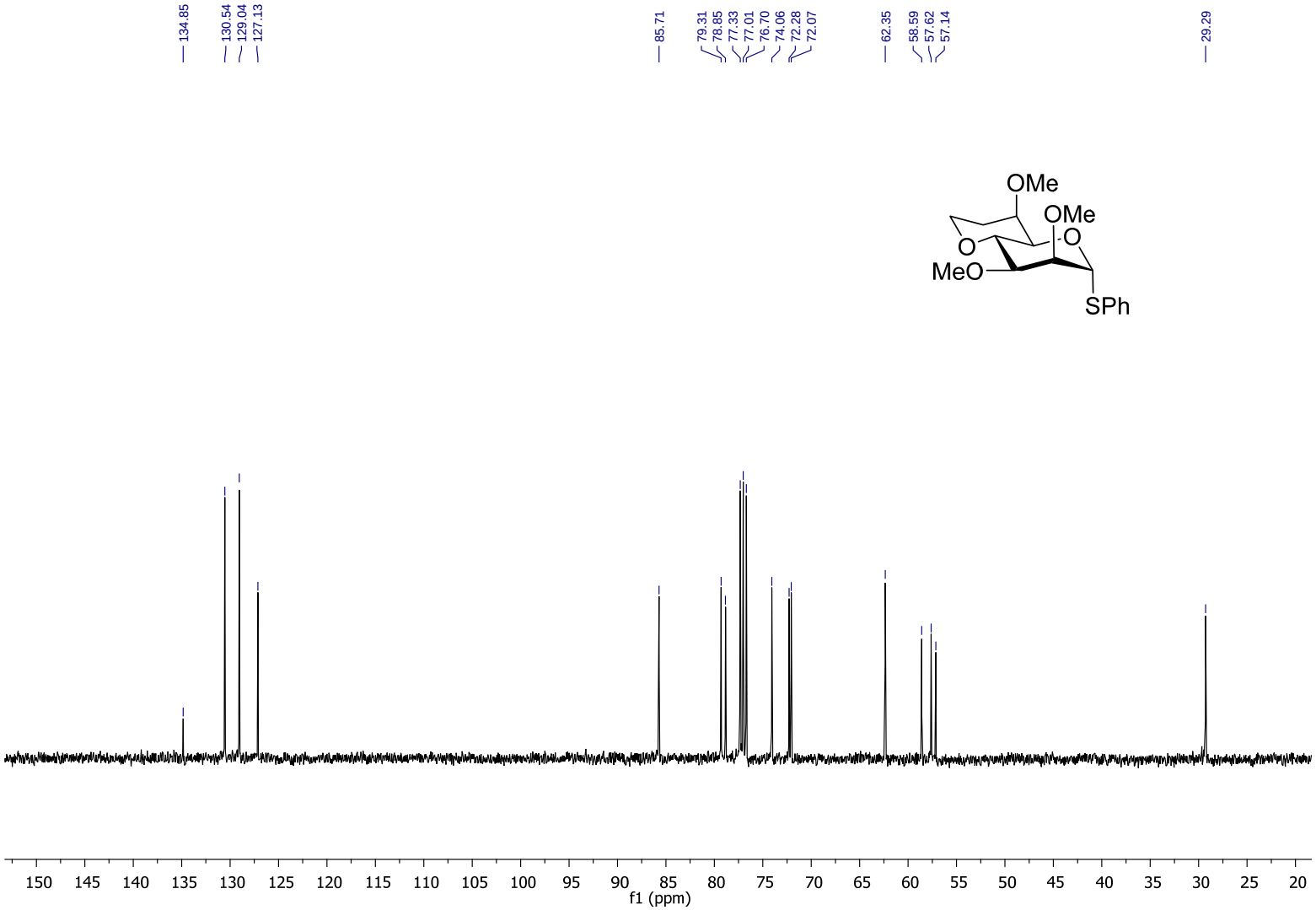
^{13}C NMR (100 MHz, $CDCl_3$) of Phenyl 7-deoxy-2,3,6-tri-*O*-methyl-D-*glycero*-α-D-thio-*manno*octopyranoside (23)



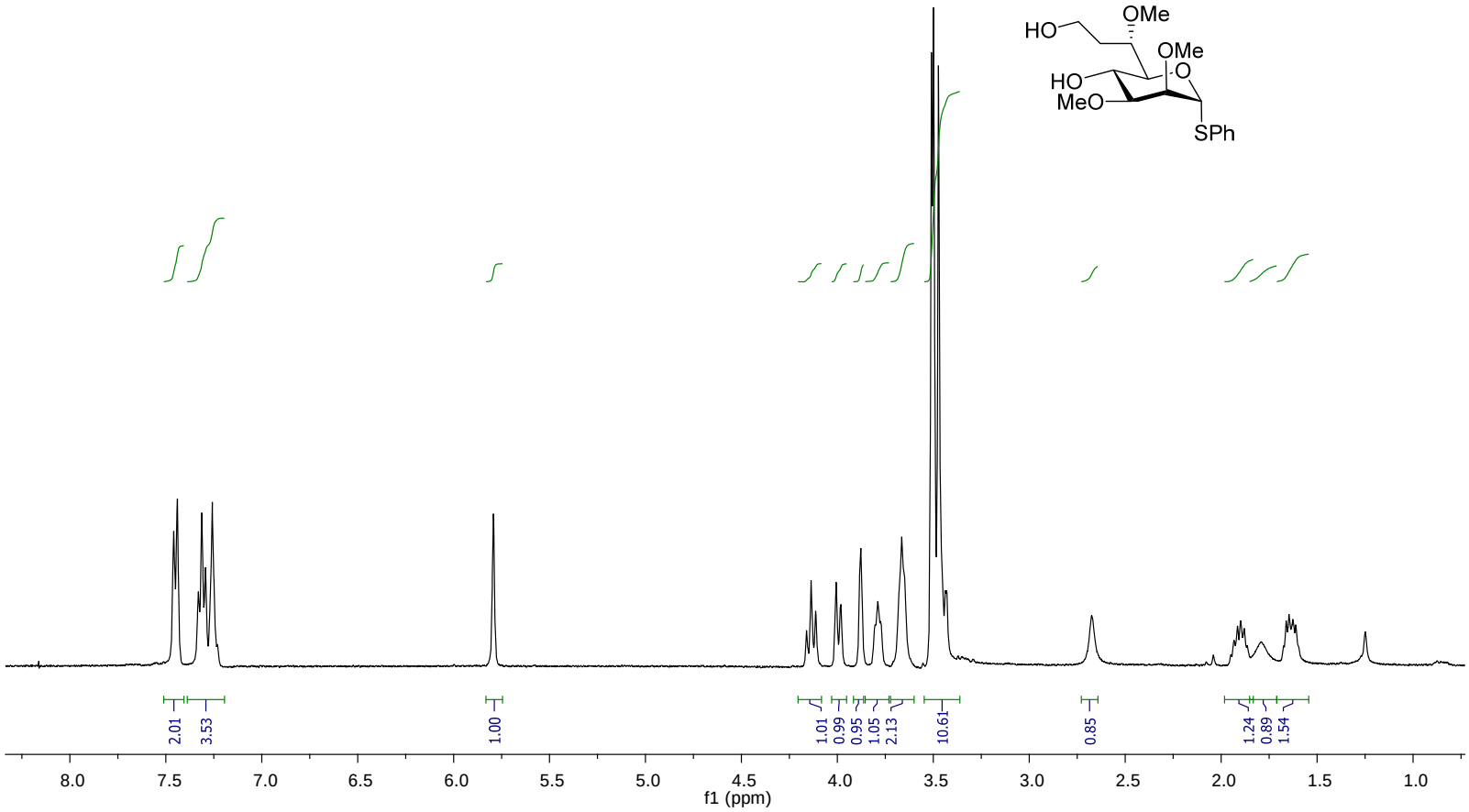
^{1}H NMR (400 MHz, $CDCl_3$) of Phenyl4,8-anhydro-7-deoxy-2,3,6-tri-*O*-methyl-D-*glycero*-α-D-thio-*manno*octopyranoside (24)



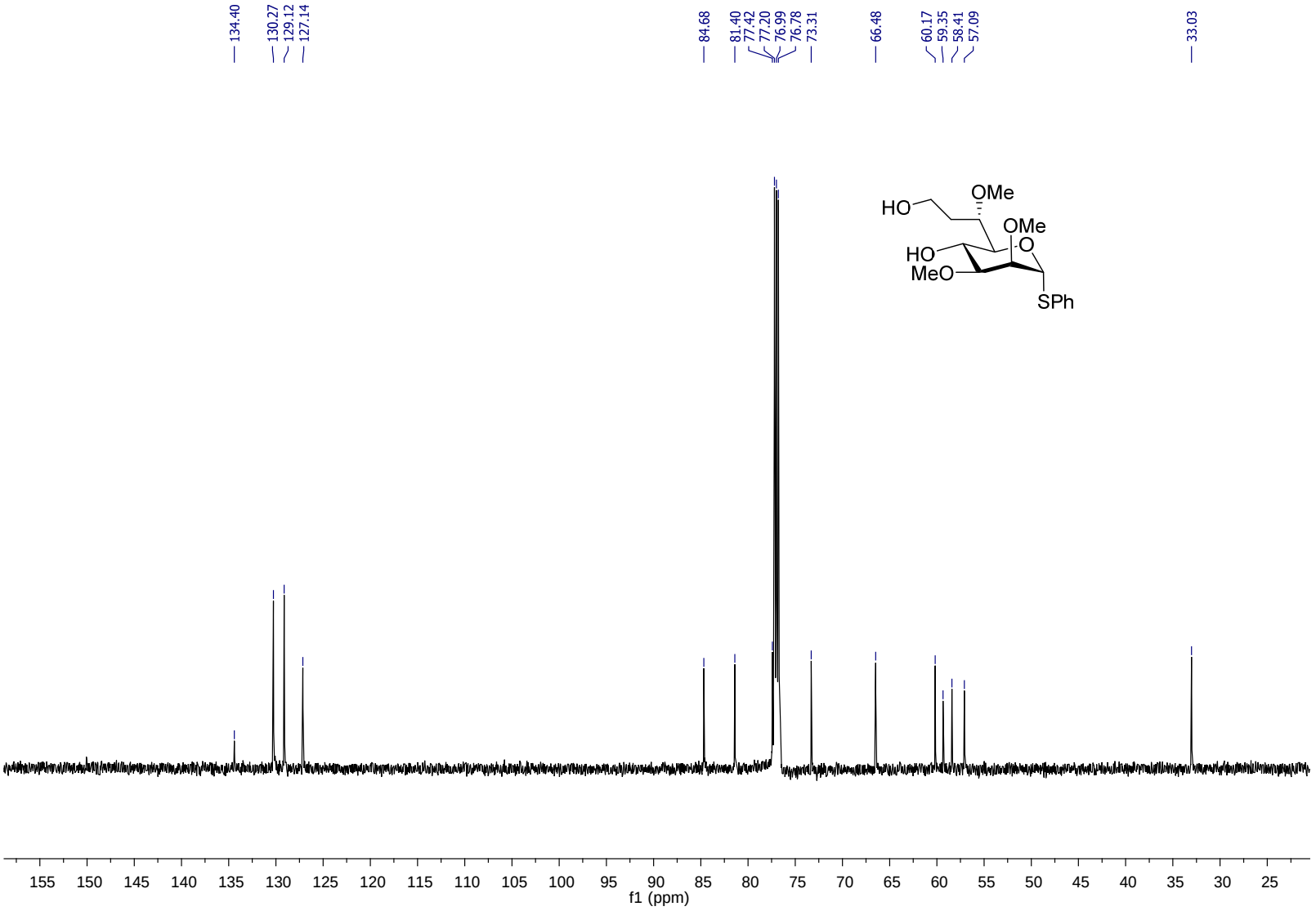
^{13}C NMR (100 MHz, $CDCl_3$) of Phenyl 4,8-anhydro-7-deoxy-2,3,6-tri-*O*-methyl-D-*glycero*-α-D-thio-*manno*octopyranoside (24)



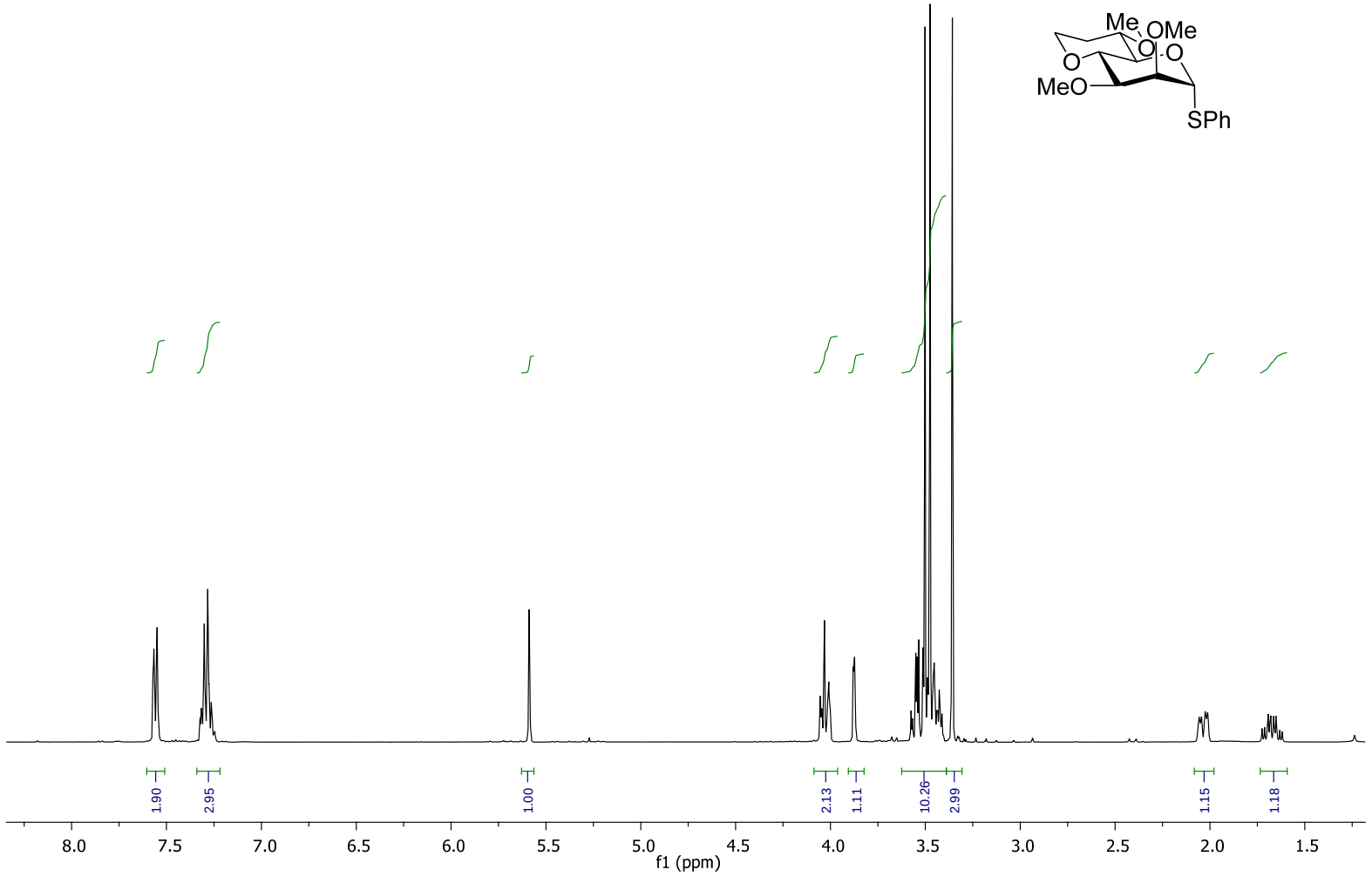
^{1}H NMR (400 MHz, $CDCl_3$) of Phenyl 7-deoxy-2,3,6-tri-*O*-methyl-L-*glycero*–α-D-thio-*manno*octopyranoside (25)



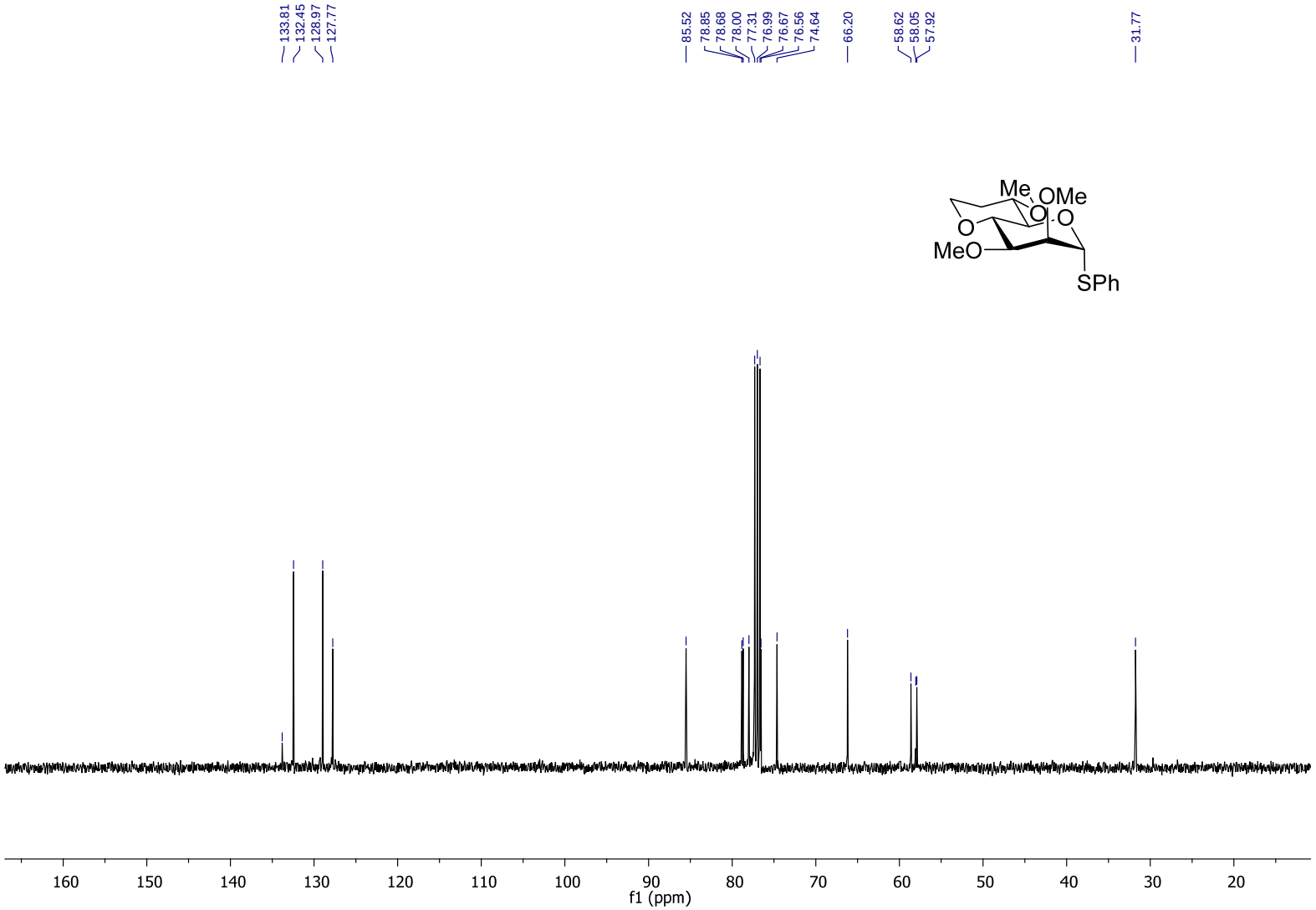
^{13}C NMR (150 MHz, $CDCl_3$) of Phenyl 7-deoxy-2,3,6-tri-*O*-methyl-L-*glycero*–α-D-thio-*manno*octopyranoside (25)



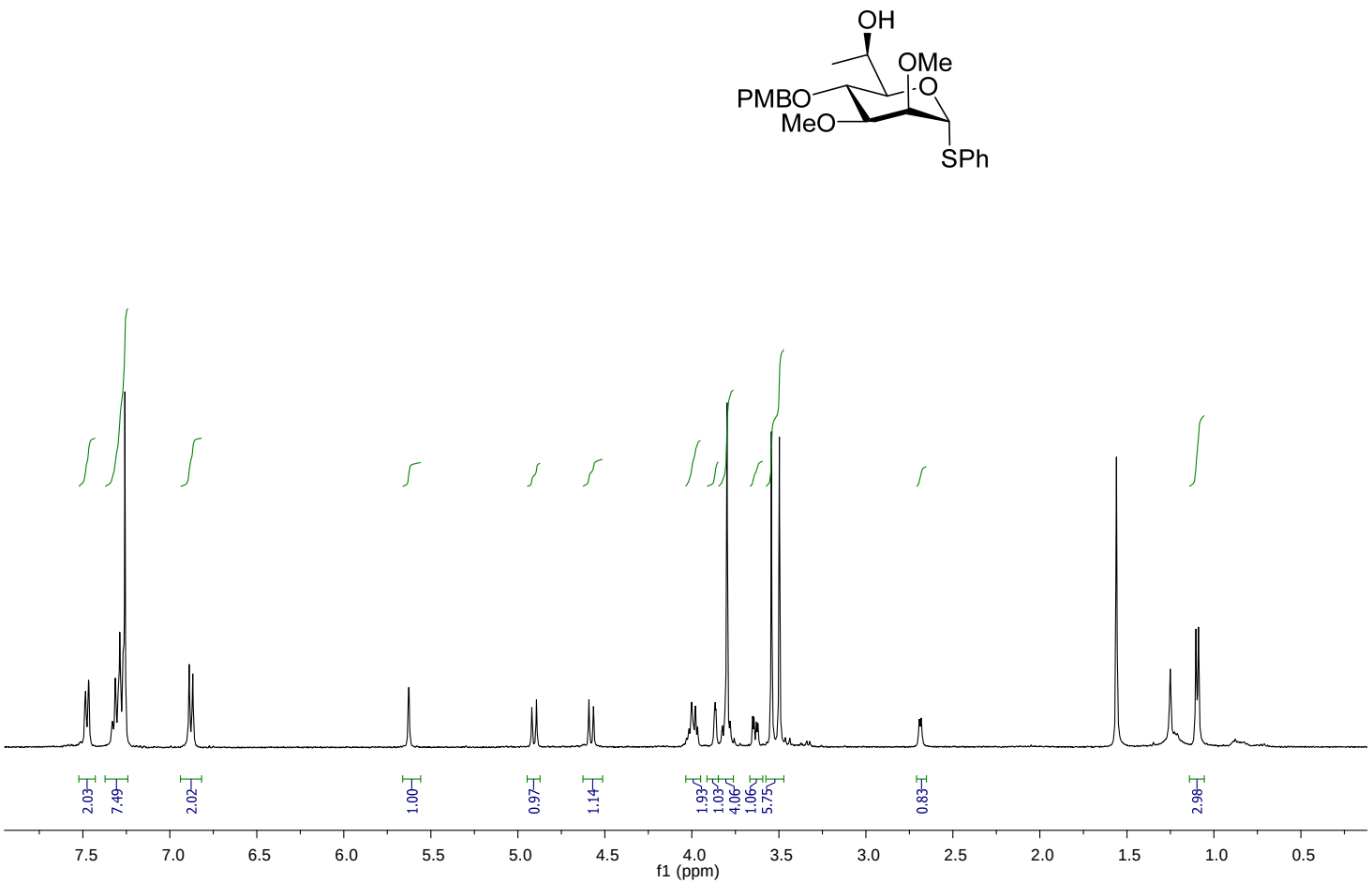
^{1}H NMR (400 MHz, $CDCl_3$) of Phenyl 4,8-anhydro-7-deoxy-2,3,6-tri-*O*-methyl-L-*glycero*–α-D-thio-*manno*octopyranoside (26)



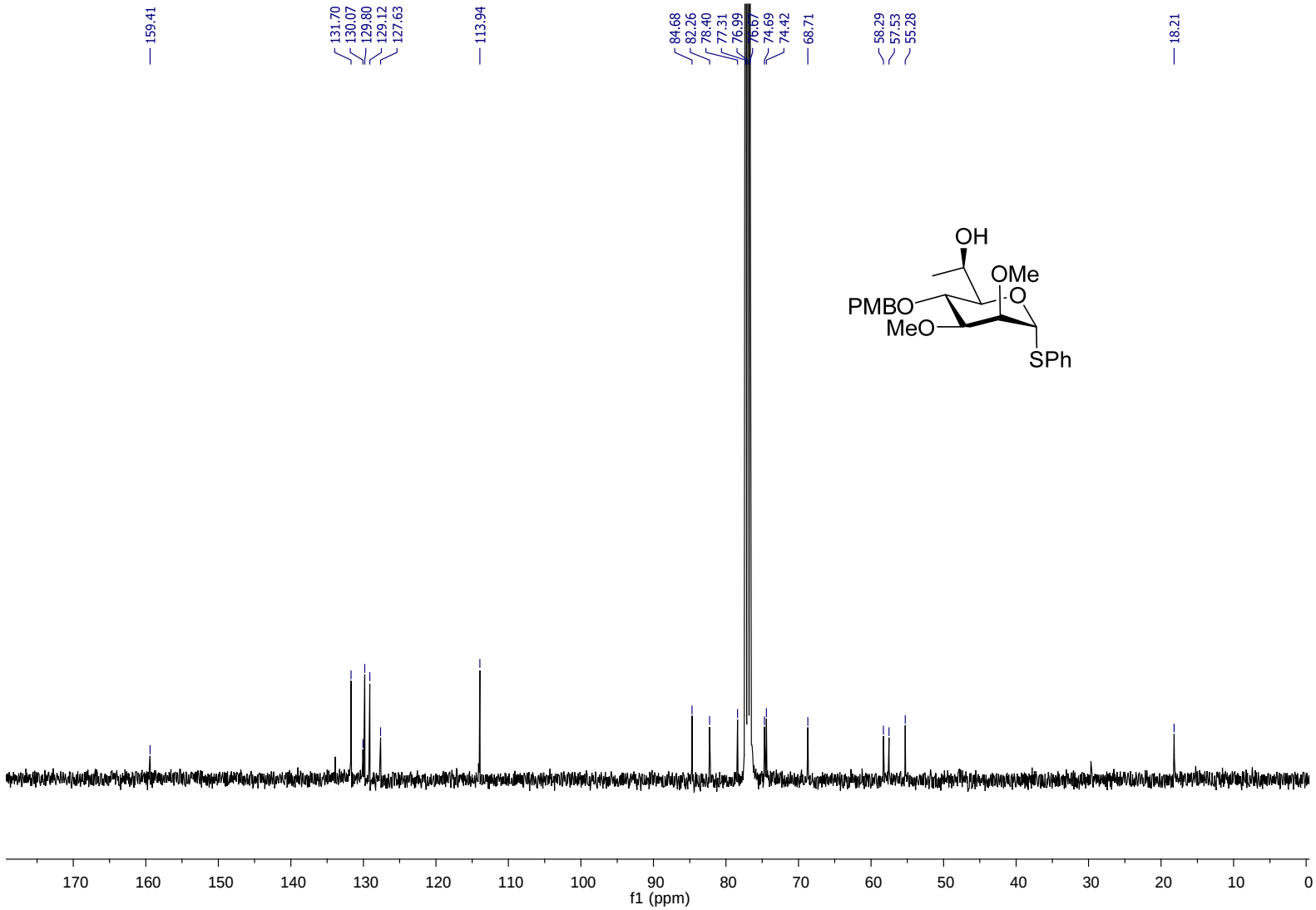
^{13}C NMR (100 MHz, $CDCl_3$) of Phenyl 4,8-anhydro-7-deoxy-2,3,6-tri-*O*-methyl-L-*glycero*–α-D-thio-*manno*octopyranoside (26)



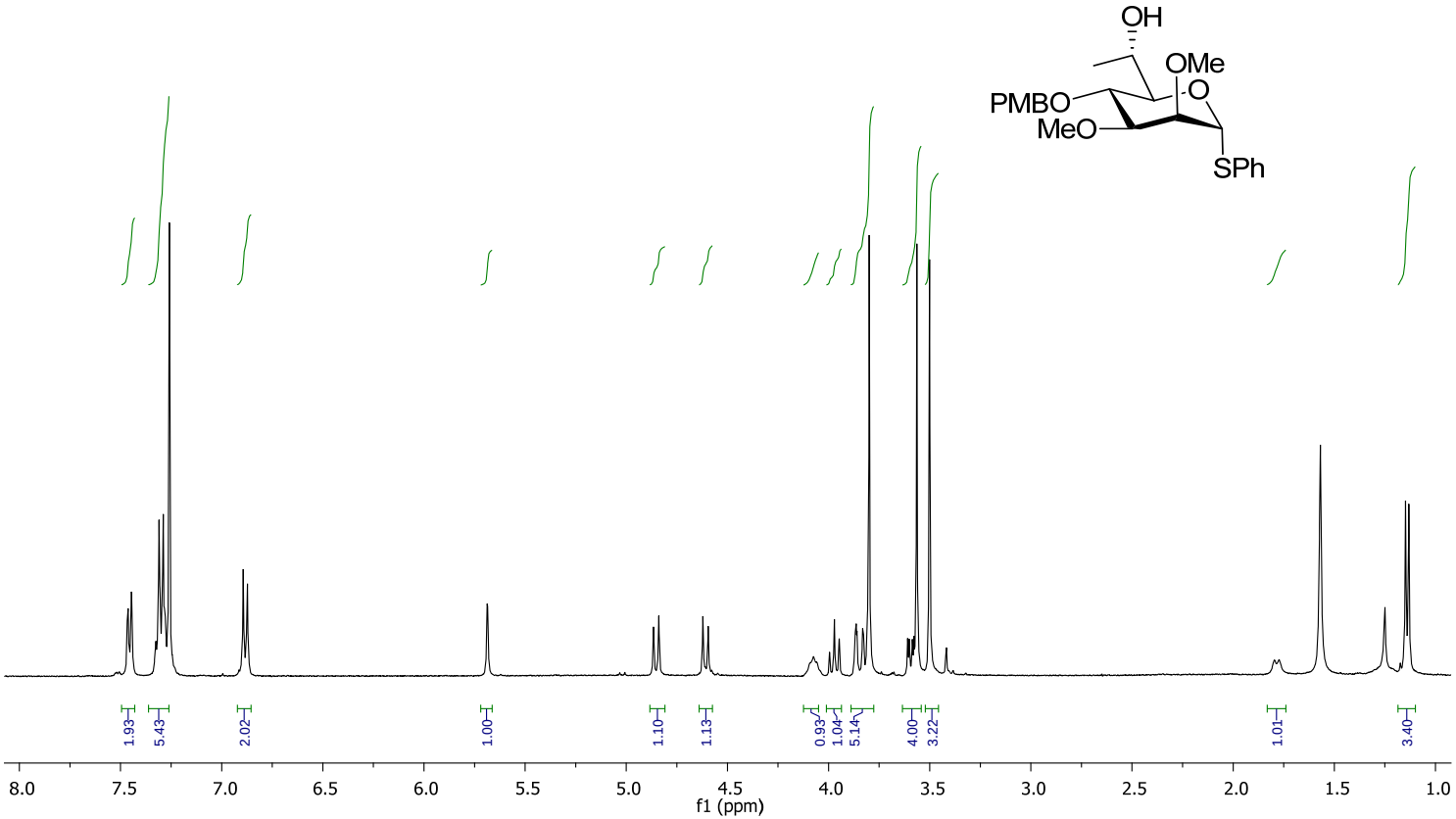
^{1}H NMR (400 MHz, $CDCl_3$) of Phenyl 7-deoxy-2,3-di-*O*-methyl4-*O*-(*p*-methoxybenzyl)-D-*glycero*-α-D-thio-*manno*heptopyranoside (27)



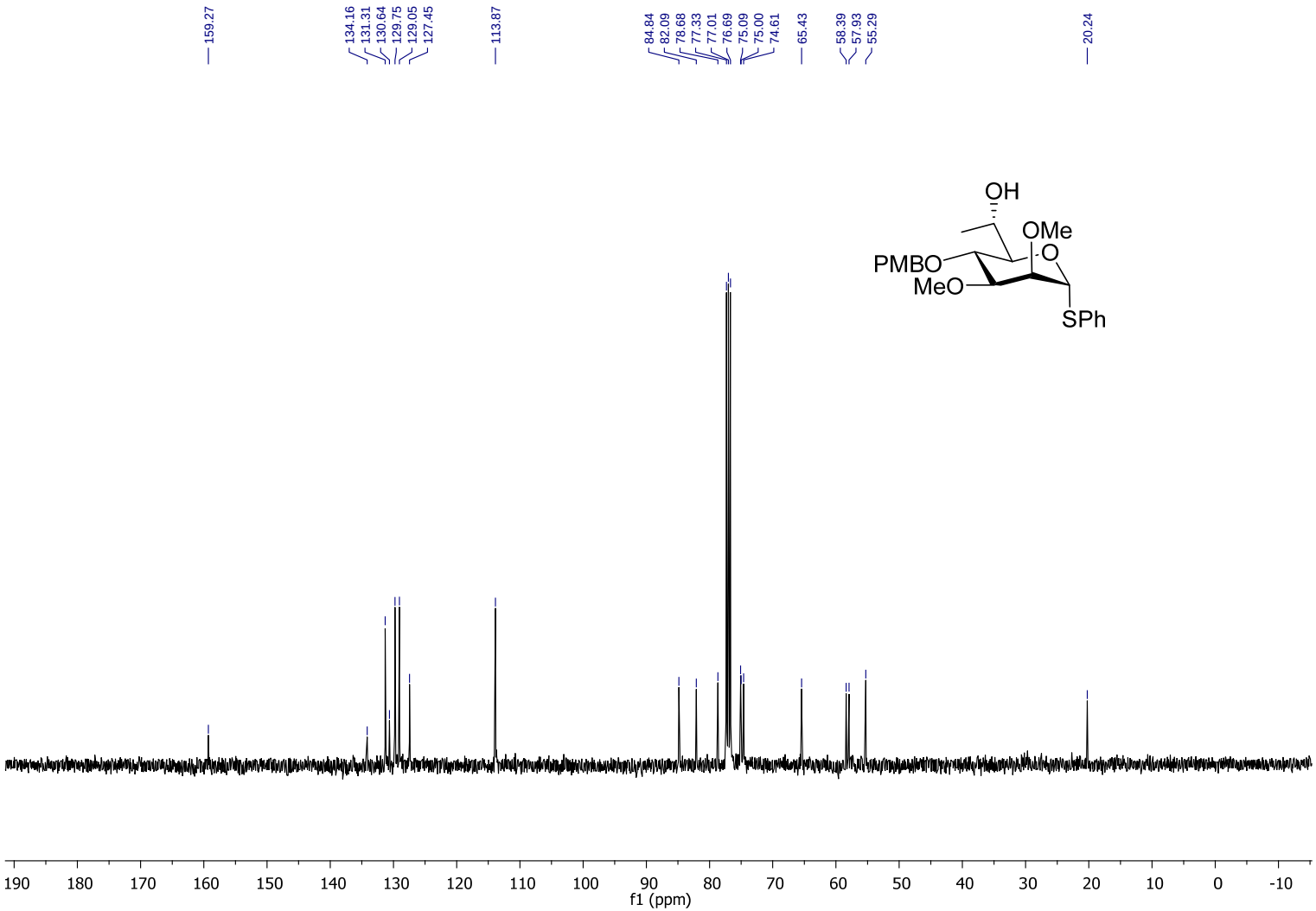
^{13}C NMR (100 MHz, $CDCl_3$) of Phenyl 7-deoxy-2,3-di-*O*-methyl-4-*O*-(*p*-methoxybenzyl)-D-*glycero*-α-D-thio-*manno*heptopyranoside (27)



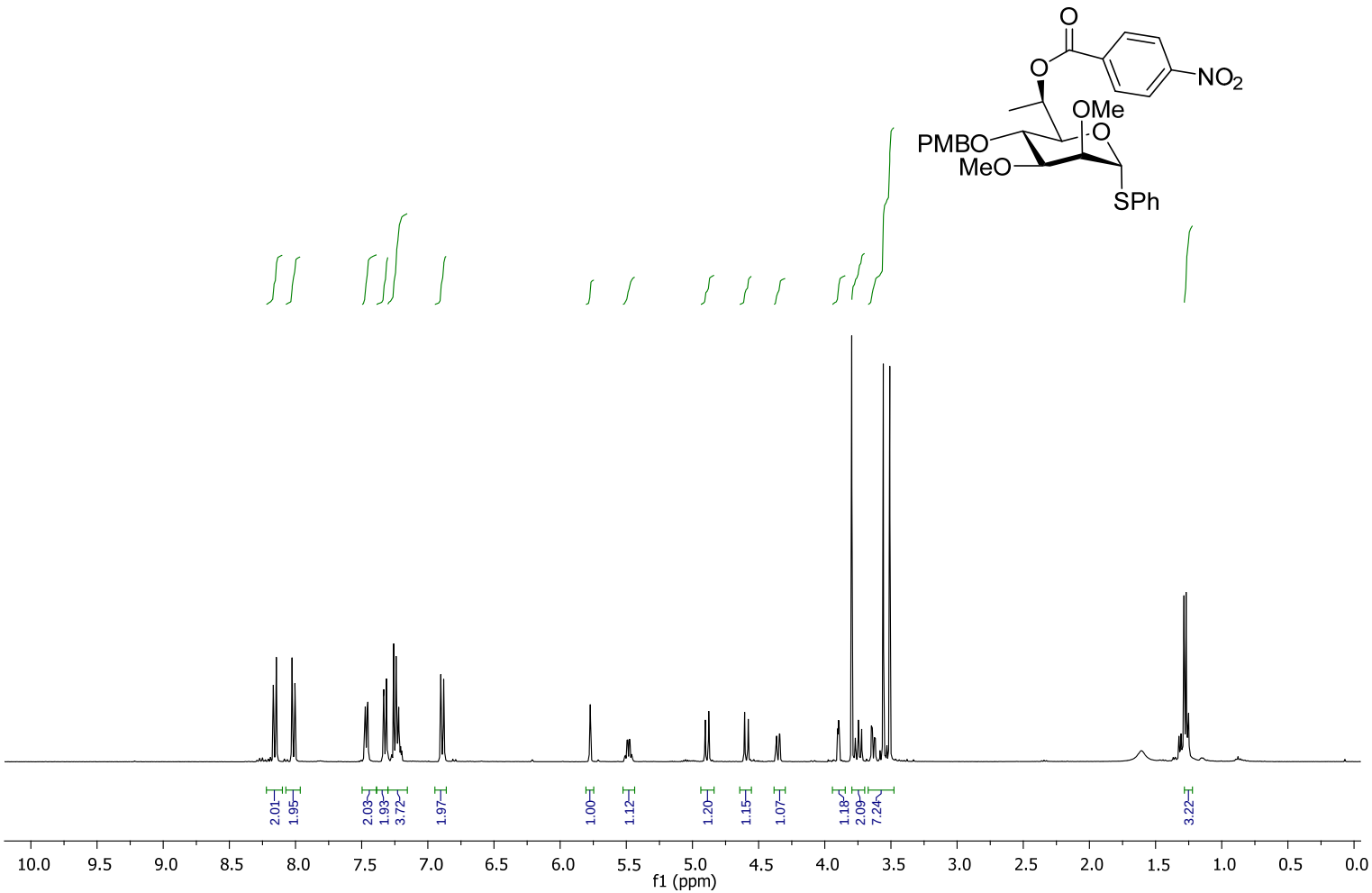
^{1}H NMR (400 MHz, $CDCl_3$) of Phenyl 7-deoxy-2,3-di-*O*-methyl-4-*O*-(*p*-methoxybenzyl)-L-*glycero*-α-D-thio-*manno*heptopyranoside (28)



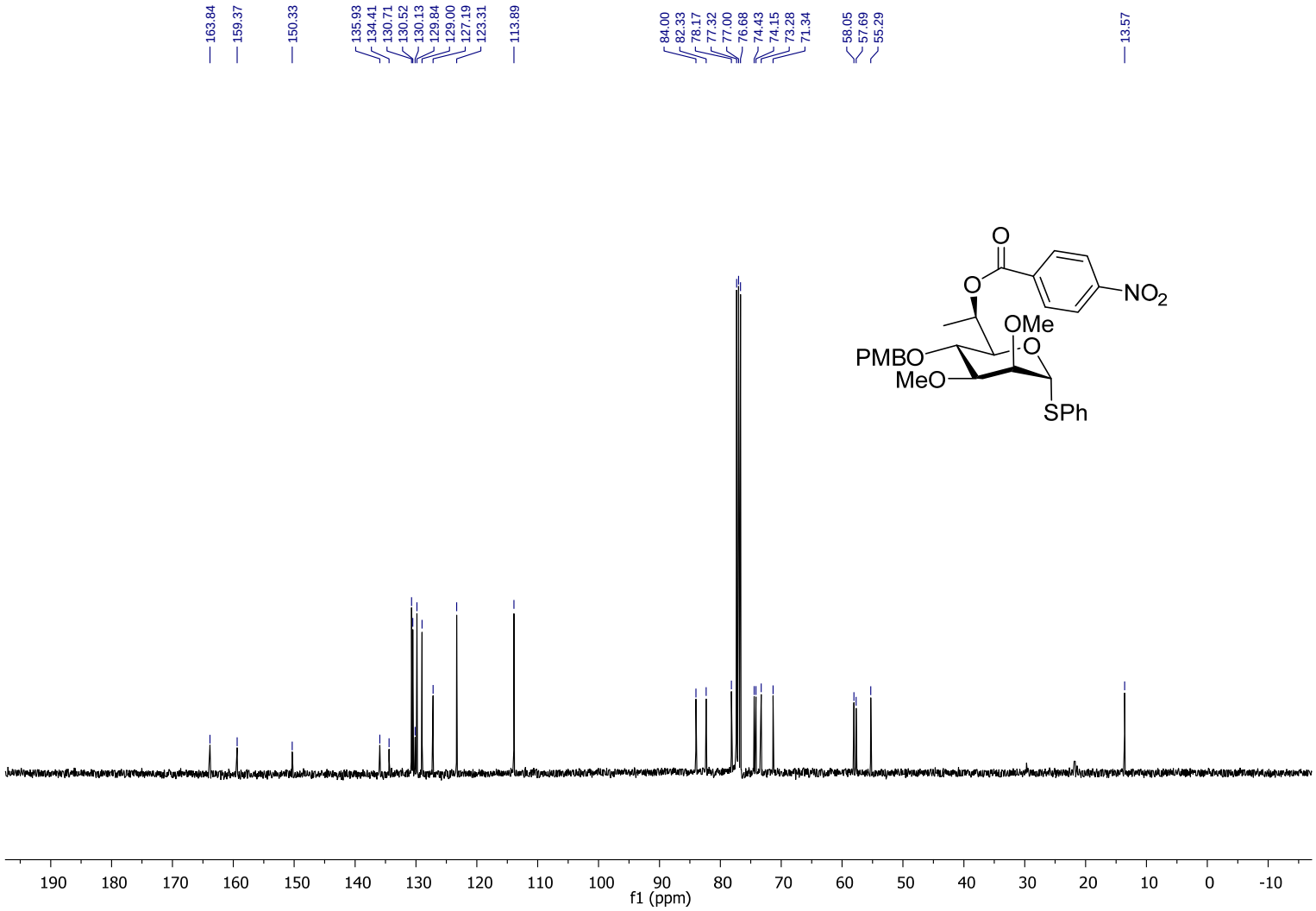
^{1}H NMR (100 MHz, $CDCl_3$) of Phenyl 7-deoxy-2,3-di-*O*-methyl-4-*O*-(*p*-methoxybenzyl)-L-*glycero*-α-D-thio-*manno*heptopyranoside (28)



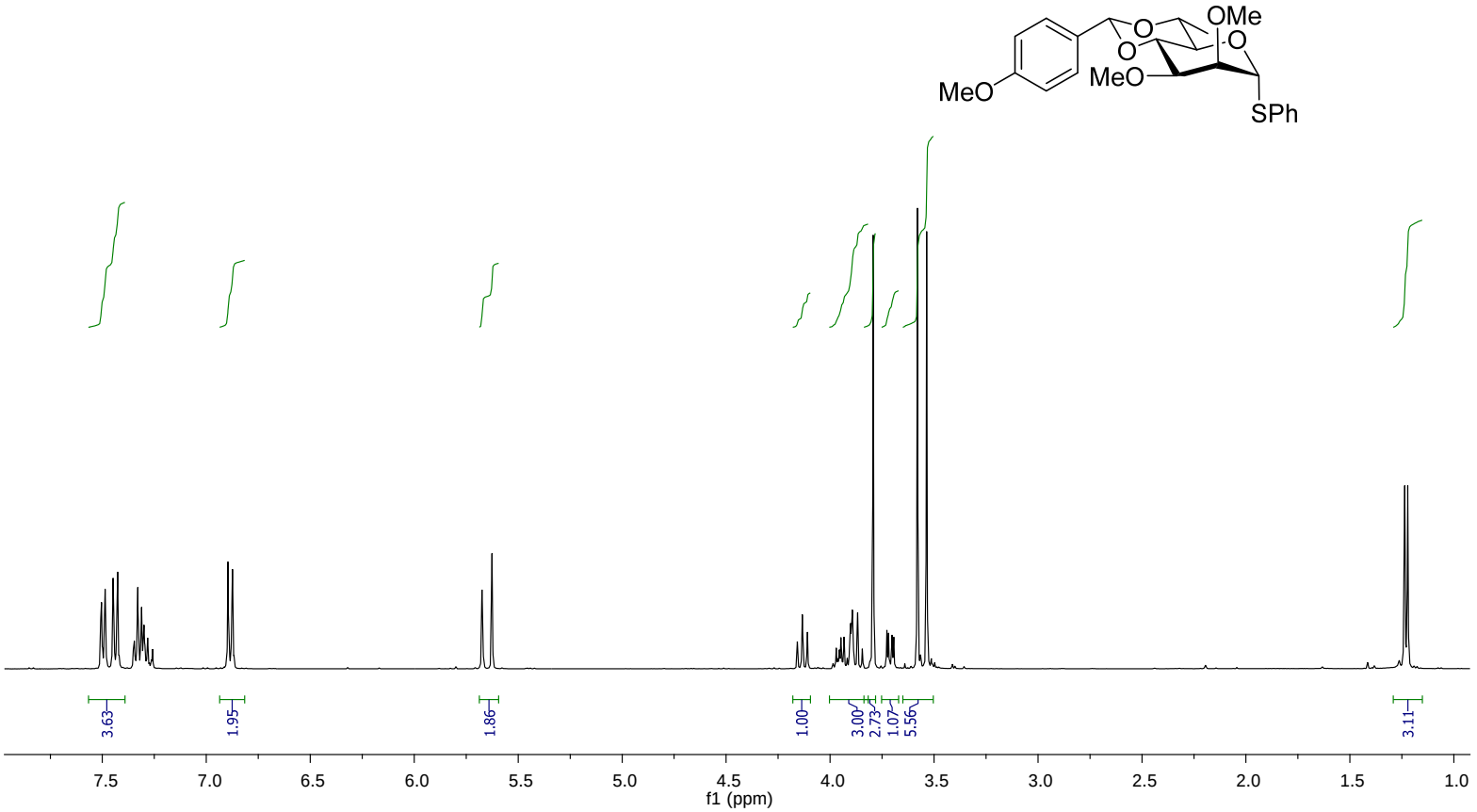
^{1}H NMR (400 MHz, $CDCl_3$) of Phenyl 2,3-di-*O*-methyl-4-*O*-(*p*-methoxybenzyl)-6-*O*-(*p*-nitrobenzoyl)-D-glycero-α-D-thio-*manno*heptopyranoside (29)



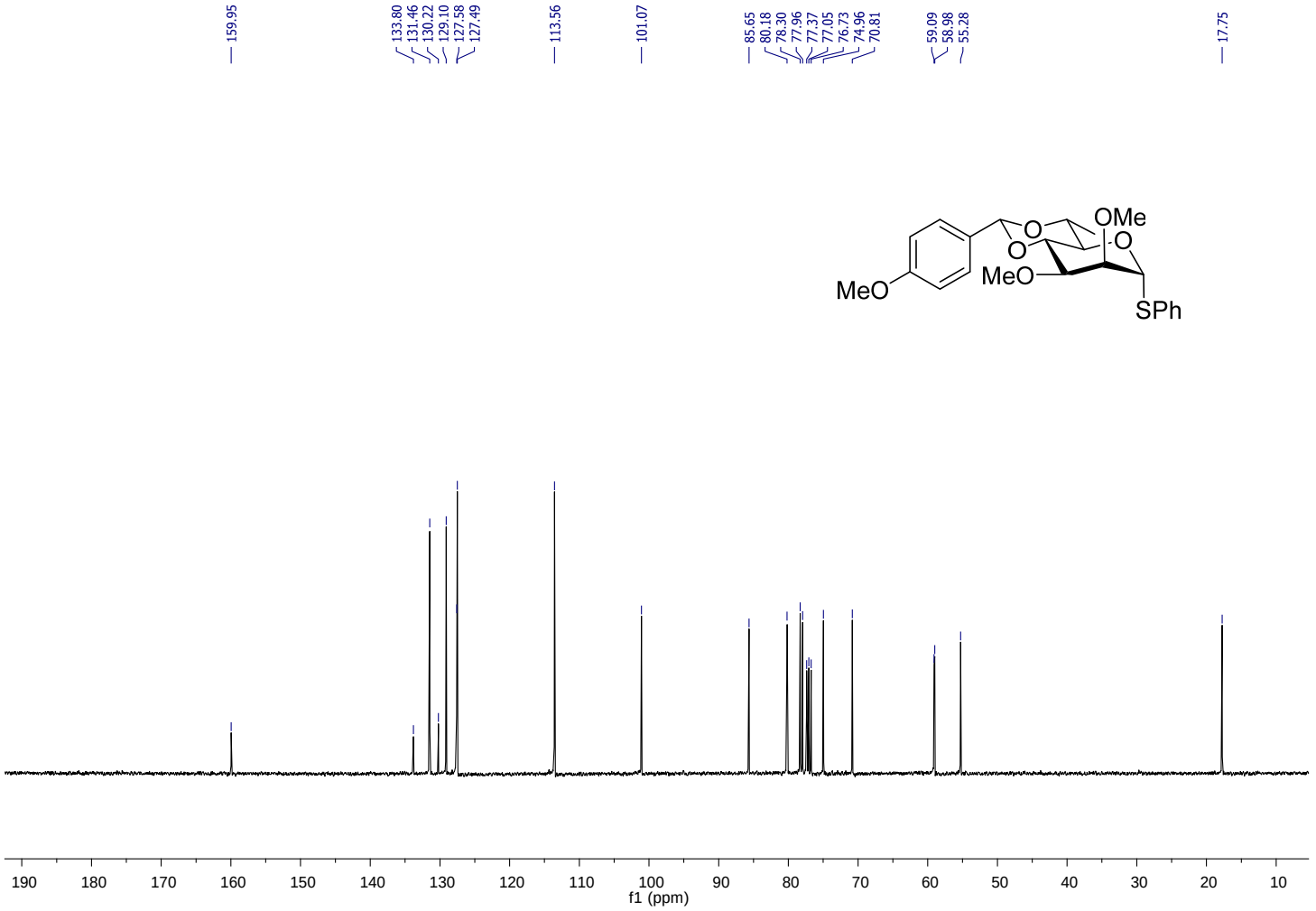
^{13}C NMR (100 MHz, $CDCl_3$) of Phenyl 2,3-di-*O*-methyl-4-*O*-(*p*-methoxybenzyl)-6-*O*-(*p*-nitrobenzoyl)-D-glycero-α-D-thio-*manno*heptopyranoside (29)



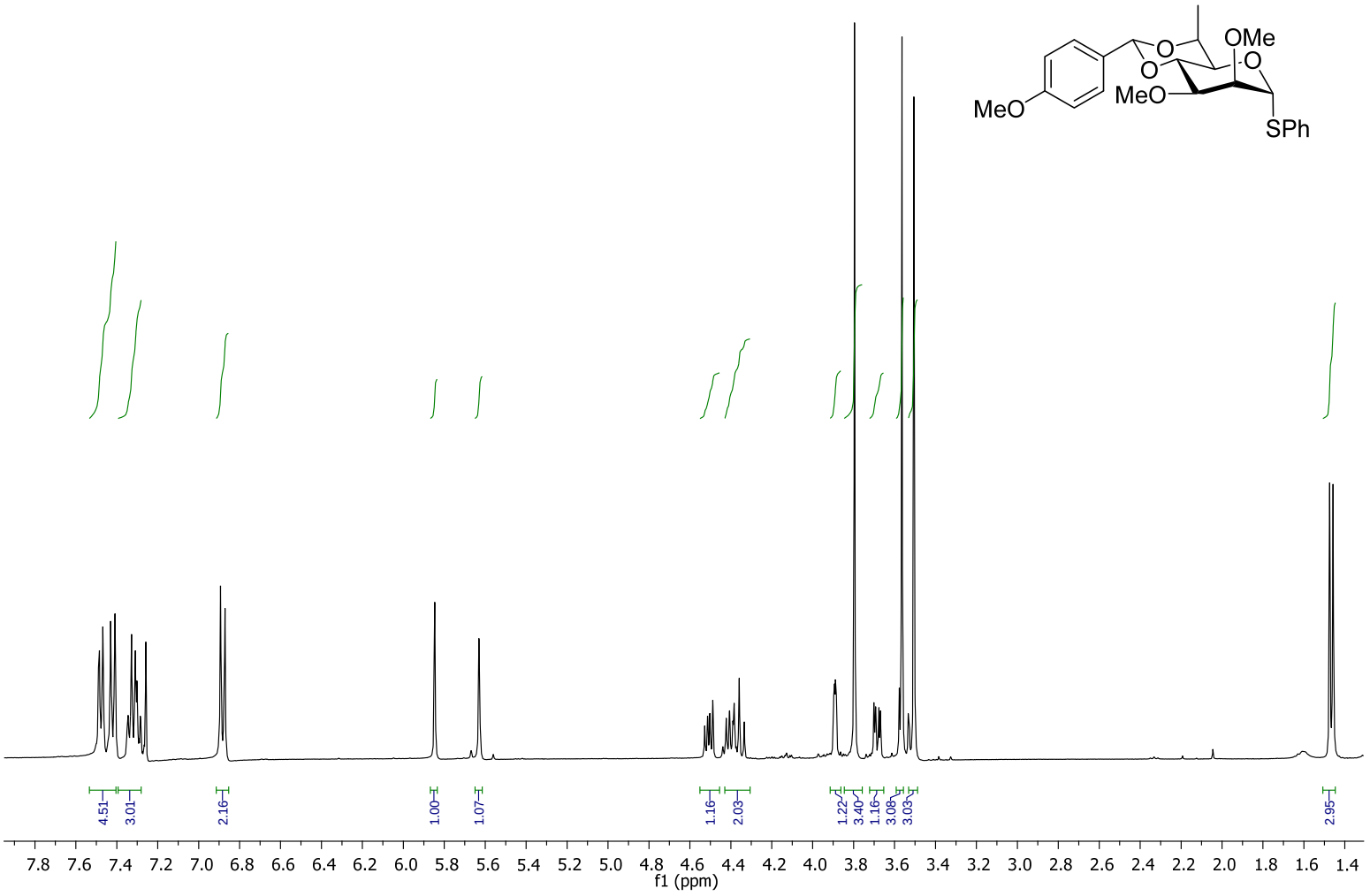
^{1}H NMR (400 MHz, $CDCl_3$) of Phenyl 2,3-di-*O*-methyl-4,6-*O*-(p-methoxybenzylidene)-D-*glycero*-α-D-thio-*manno*heptopyranoside (30)



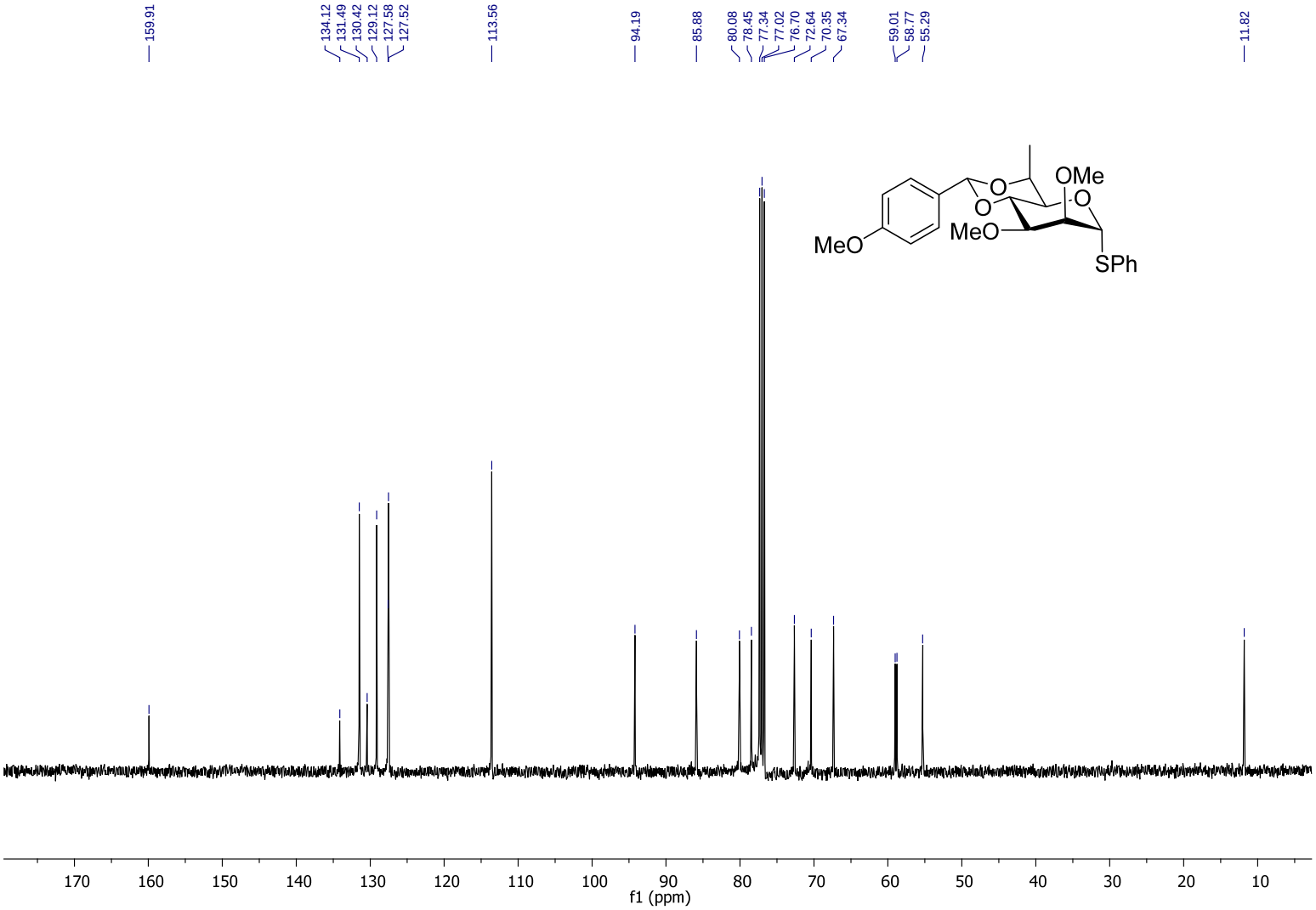
^{13}C NMR (100 MHz, $CDCl_3$) of Phenyl 2,3-di-*O*-methyl-4,6-*O*-(p-methoxybenzylidene)-D-*glycero*-α-D-thio-*manno*heptopyranoside (30)



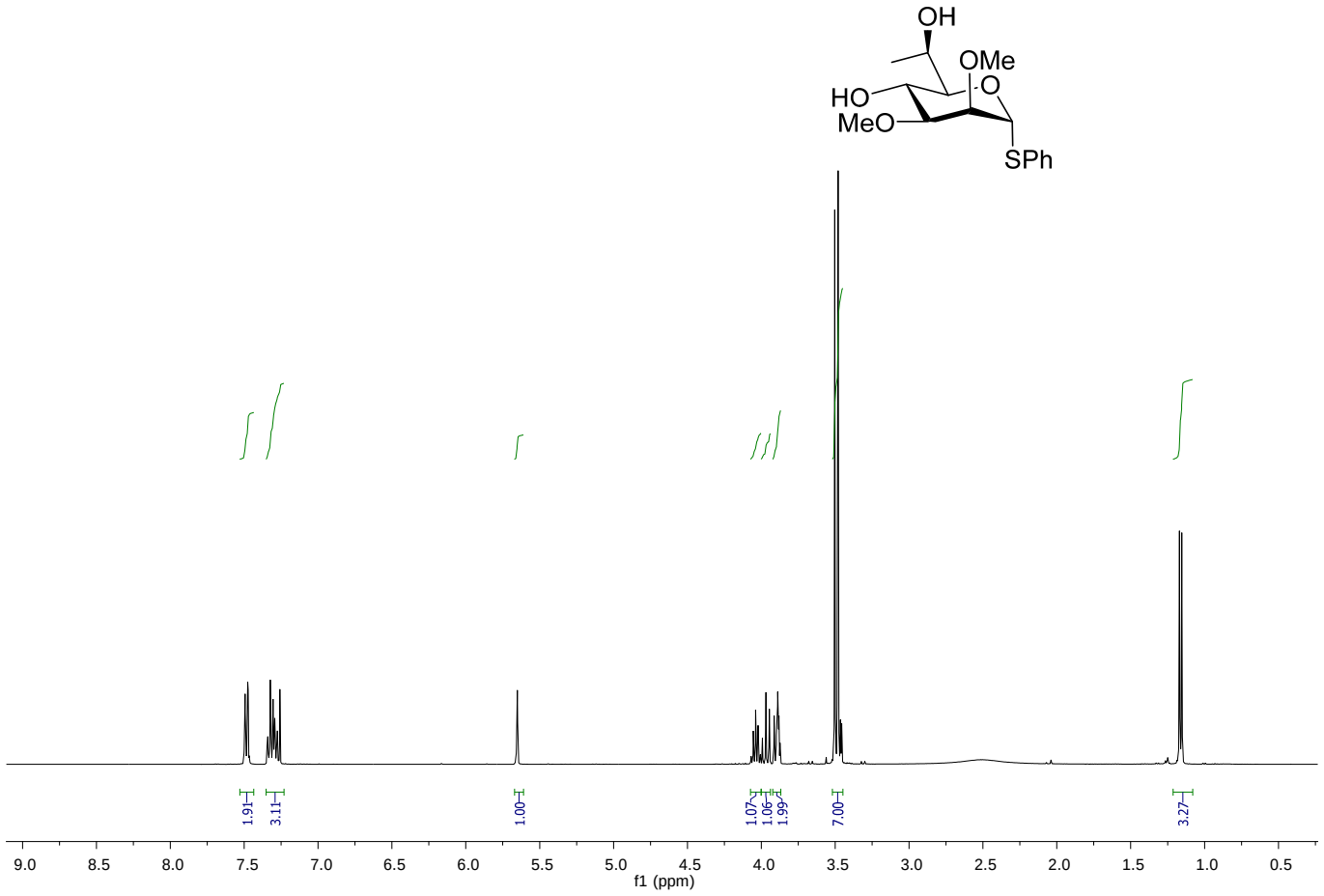
^{1}H NMR (400 MHz, $CDCl_3$) of Phenyl 2,3-di-*O*-methyl-4,6-*O*-(p-methoxybenzylidene)-L-*glycero*-α-D-thio-*manno*heptopyranoside (31)



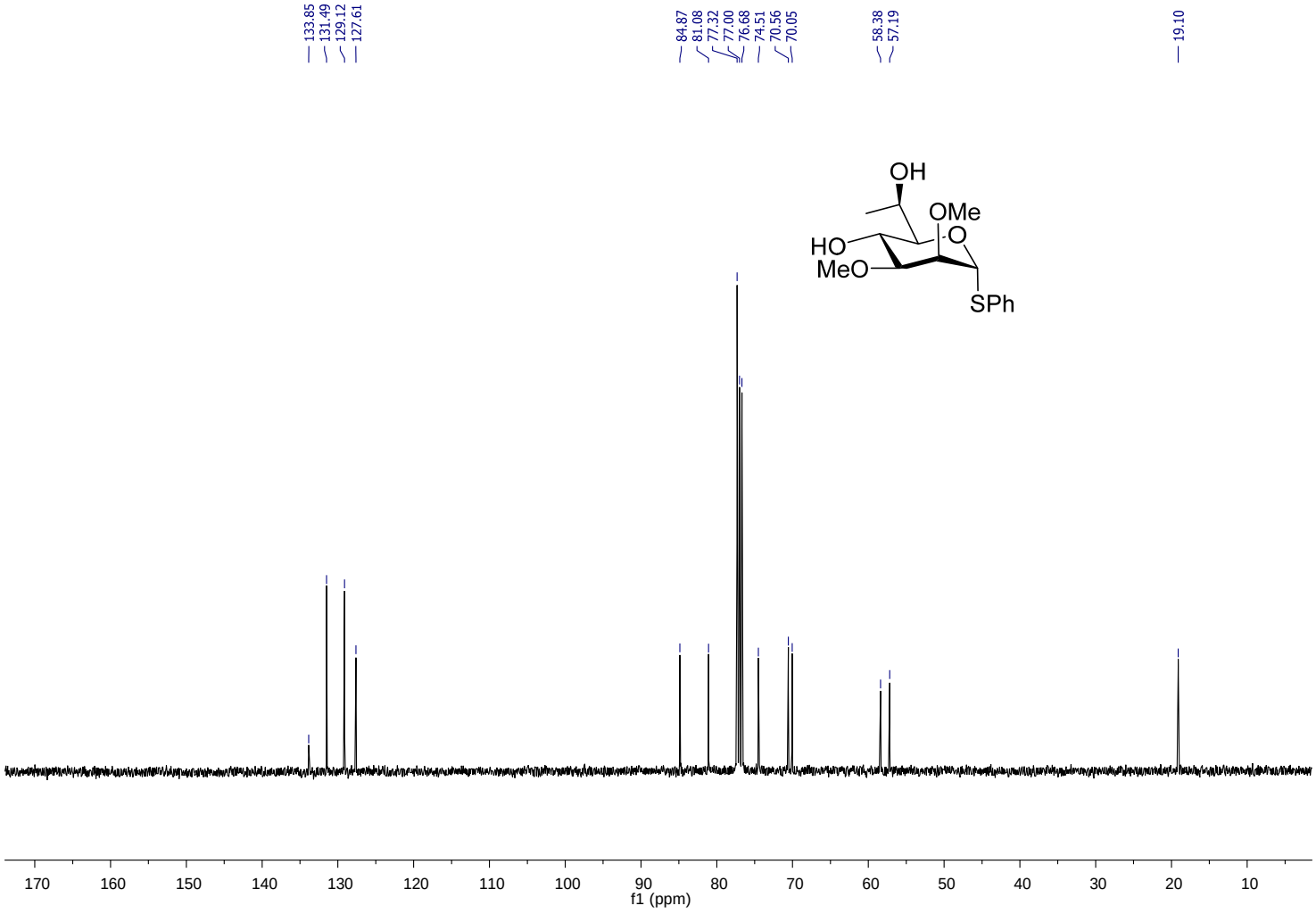
^{13}C NMR (100 MHz, $CDCl_3$) of Phenyl 2,3-di-*O*-methyl-4,6-*O*-(*p*-methoxybenzylidene)-L-*glycero*-α-D-thio-*manno*heptopyranoside (31)



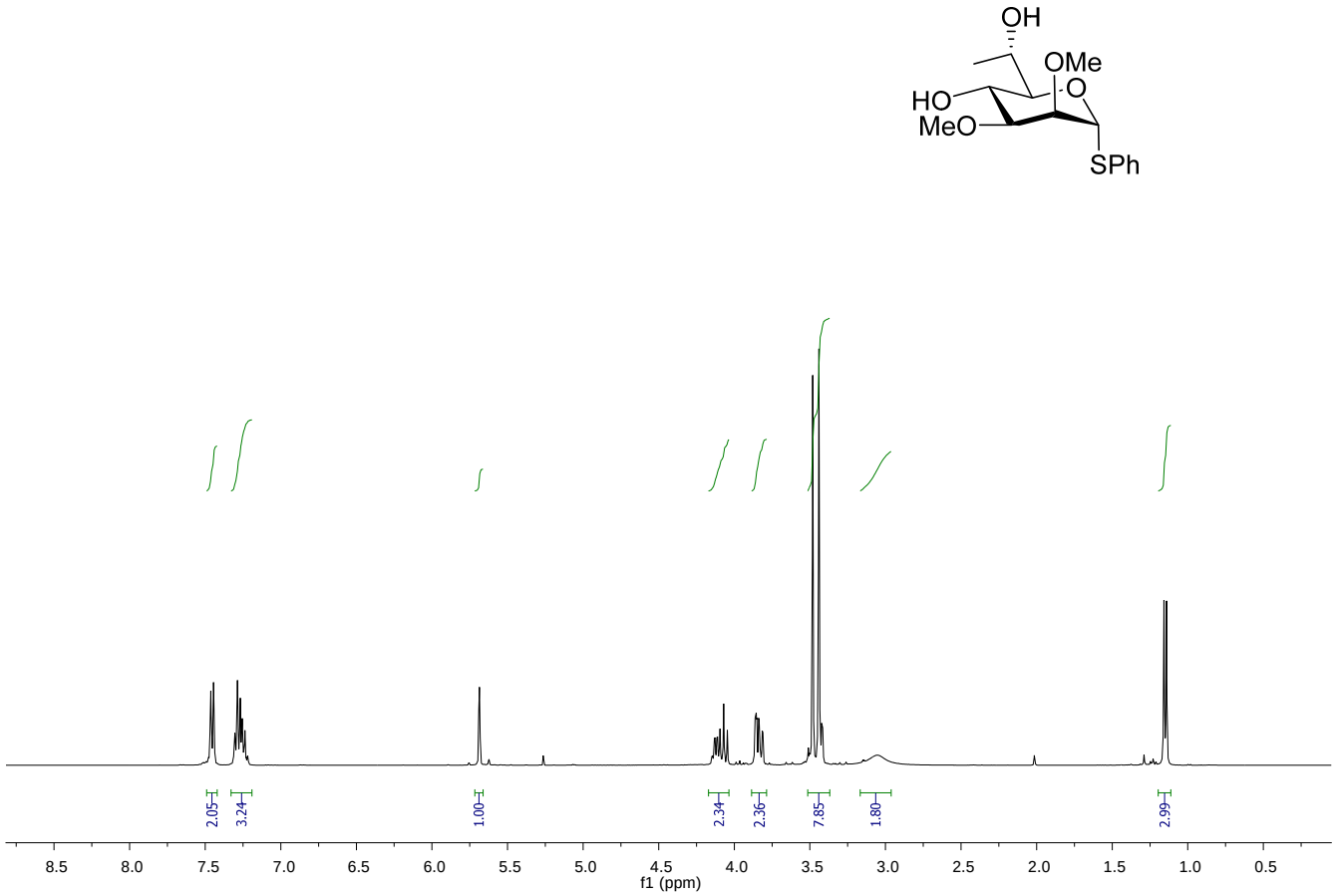
^{1}H NMR (400 MHz, $CDCl_3$) of Phenyl 7-deoxy-2,3-di-*O*-methyl-D-*glycero*-α-D-thio-*manno*heptopyranoside (32)



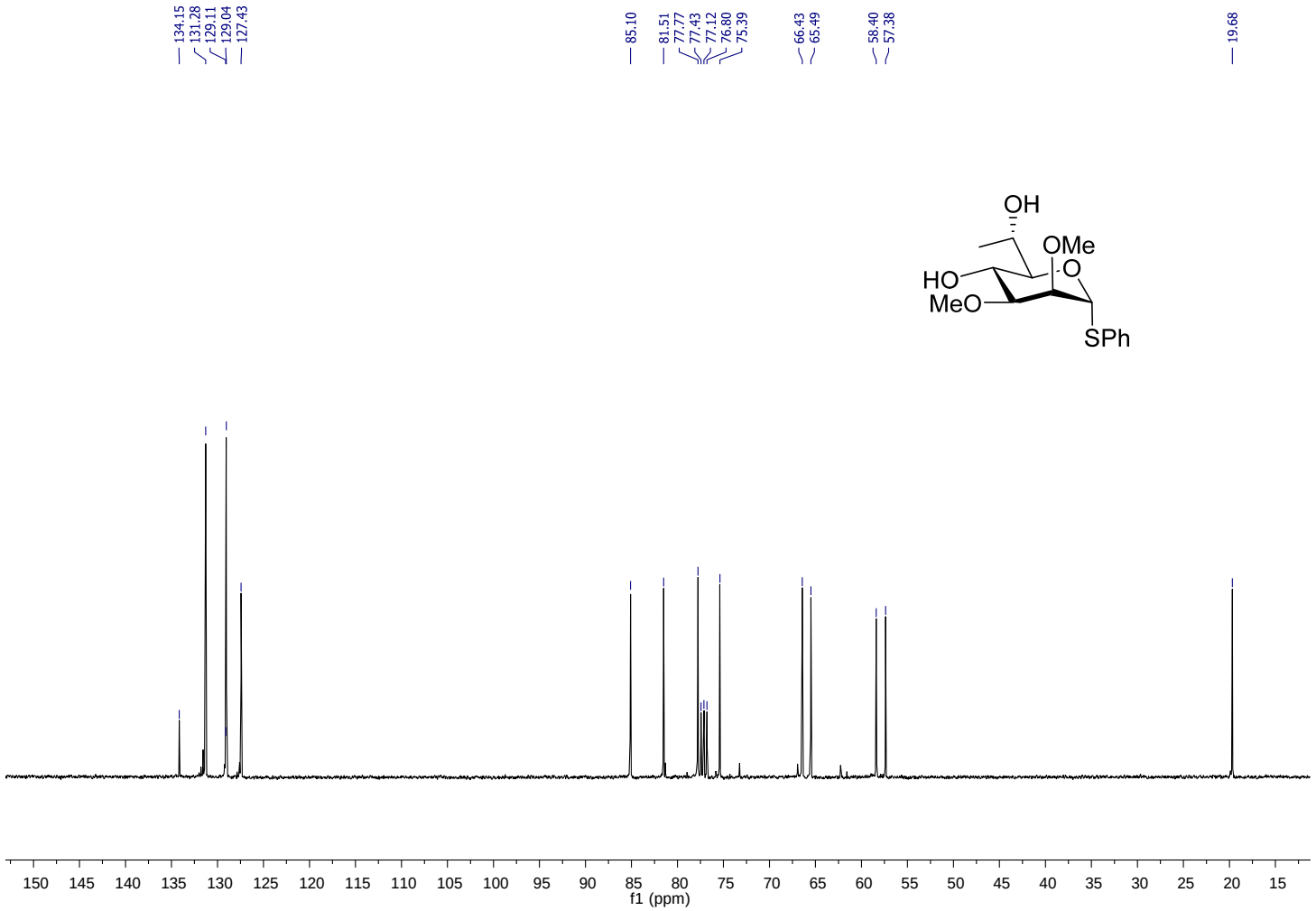
^{13}C NMR (100 MHz, $CDCl_3$) of Phenyl 7-deoxy-2,3-di-*O*-methyl-D-*glycero*-α-D-thio-*manno*heptopyranoside (32)



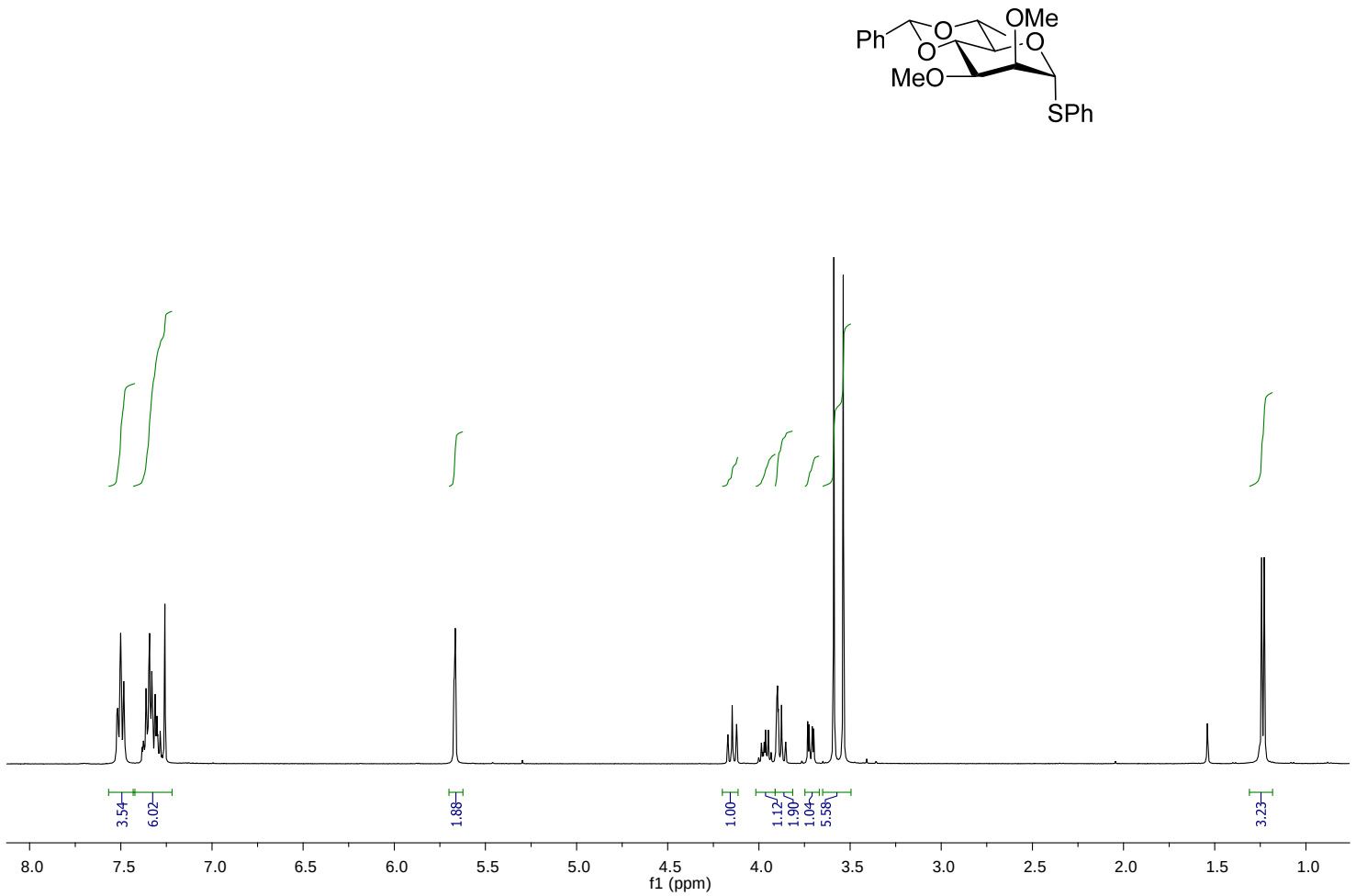
^{1}H NMR (400 MHz, $CDCl_3$) of Phenyl 7-deoxy-2,3-di-*O*-methyl-L-glycero-α-thio-D-*manno*heptopyranoside (33)



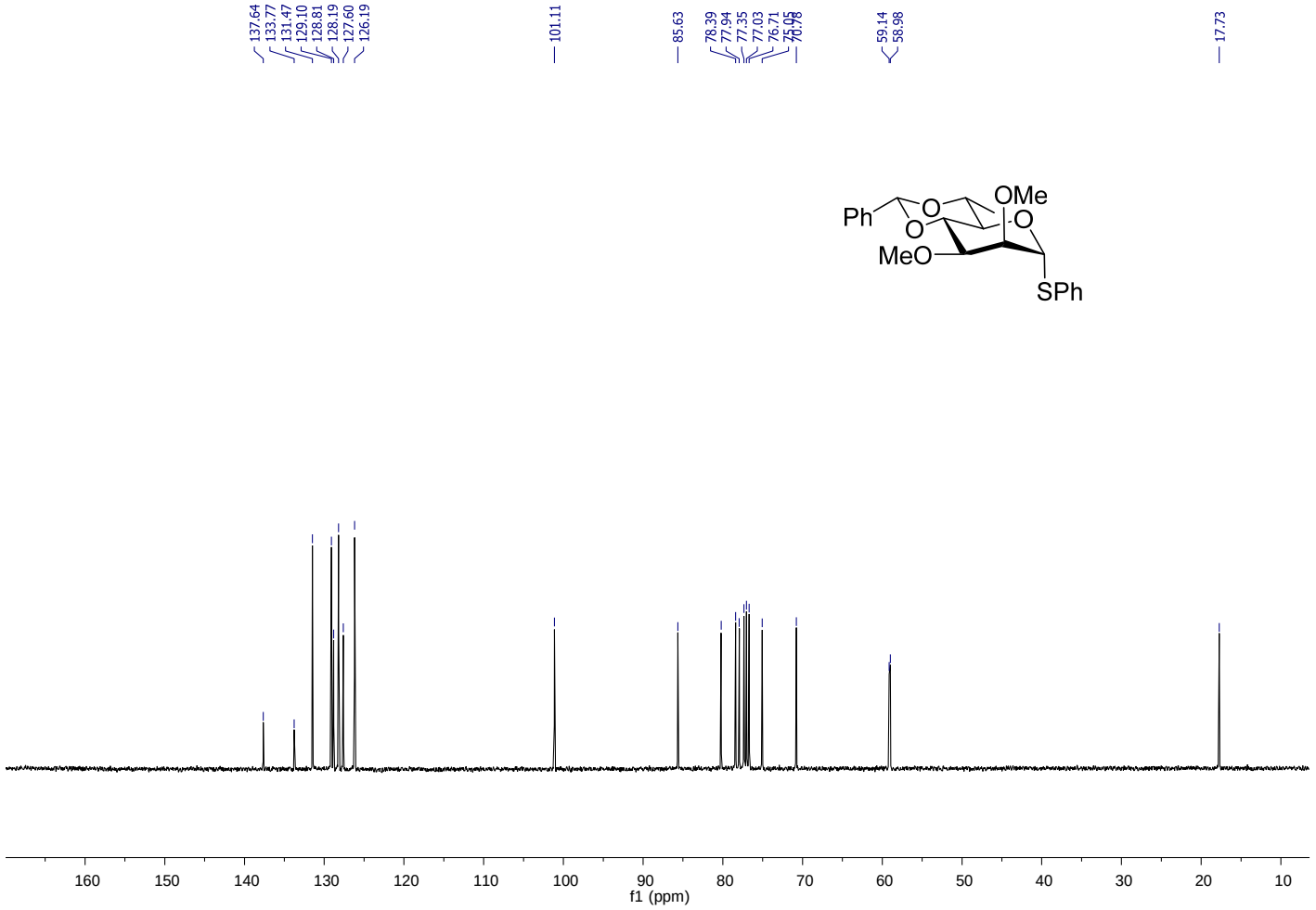
^{13}C NMR (100 MHz, $CDCl_3$) of Phenyl 7-deoxy-2,3-di-*O*-methyl-L-glycero-α-D-thio-*manno*heptopyranoside (33)



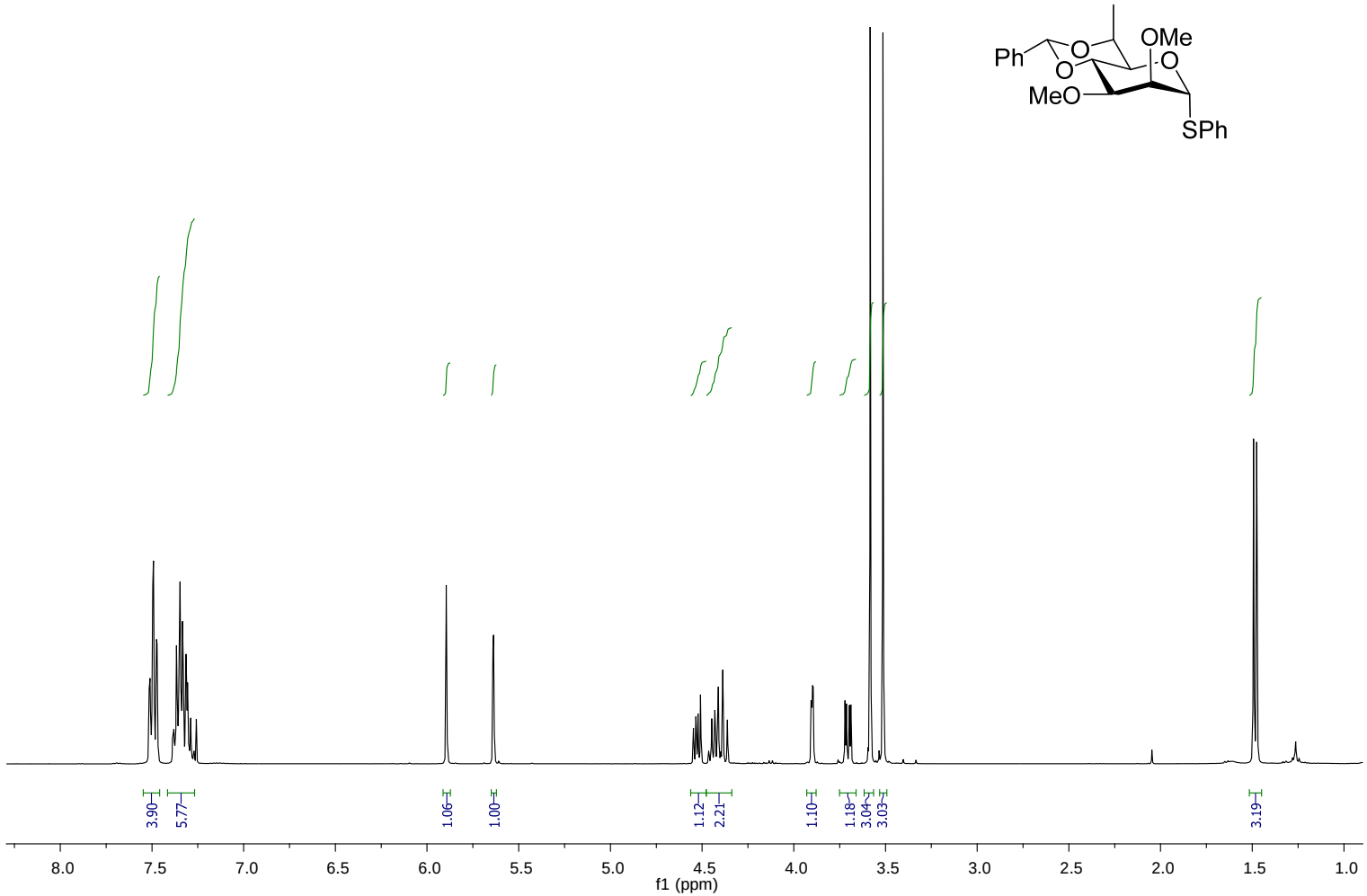
^{1}H NMR (400 MHz, $CDCl_3$) of Phenyl 4,6-*O*-benzylidene-2,3-di-*O*-methyl-7-deoxy-D-*glycero*-α-D-thio-*manno*heptopyranoside (34)



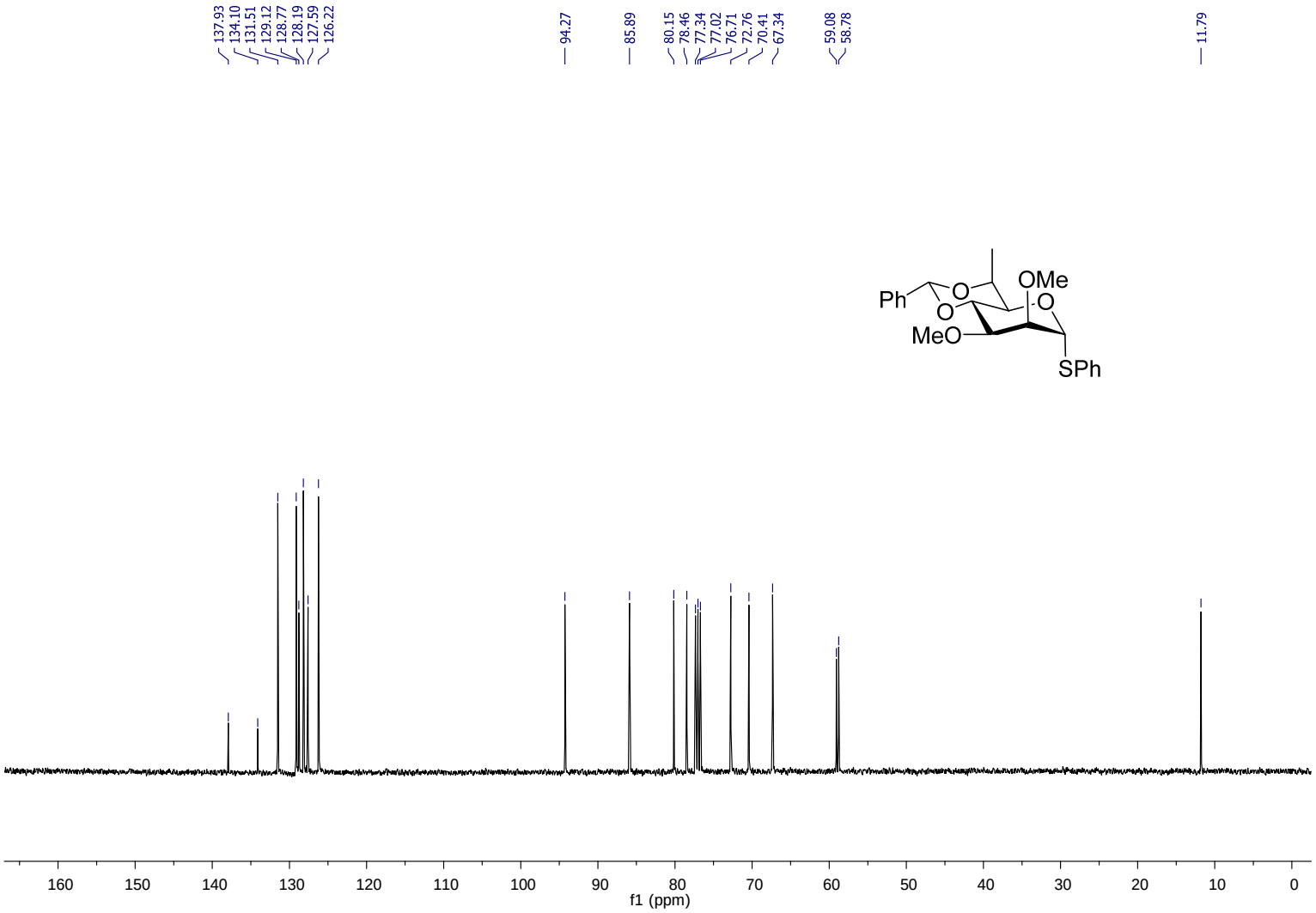
^{13}C NMR (100 MHz, $CDCl_3$) of Phenyl 4,6-*O*-benzylidene-2,3-di-*O*-methyl-7-dexoy-D-*glycero*-α-D-thio-*manno*heptopyranoside (34)



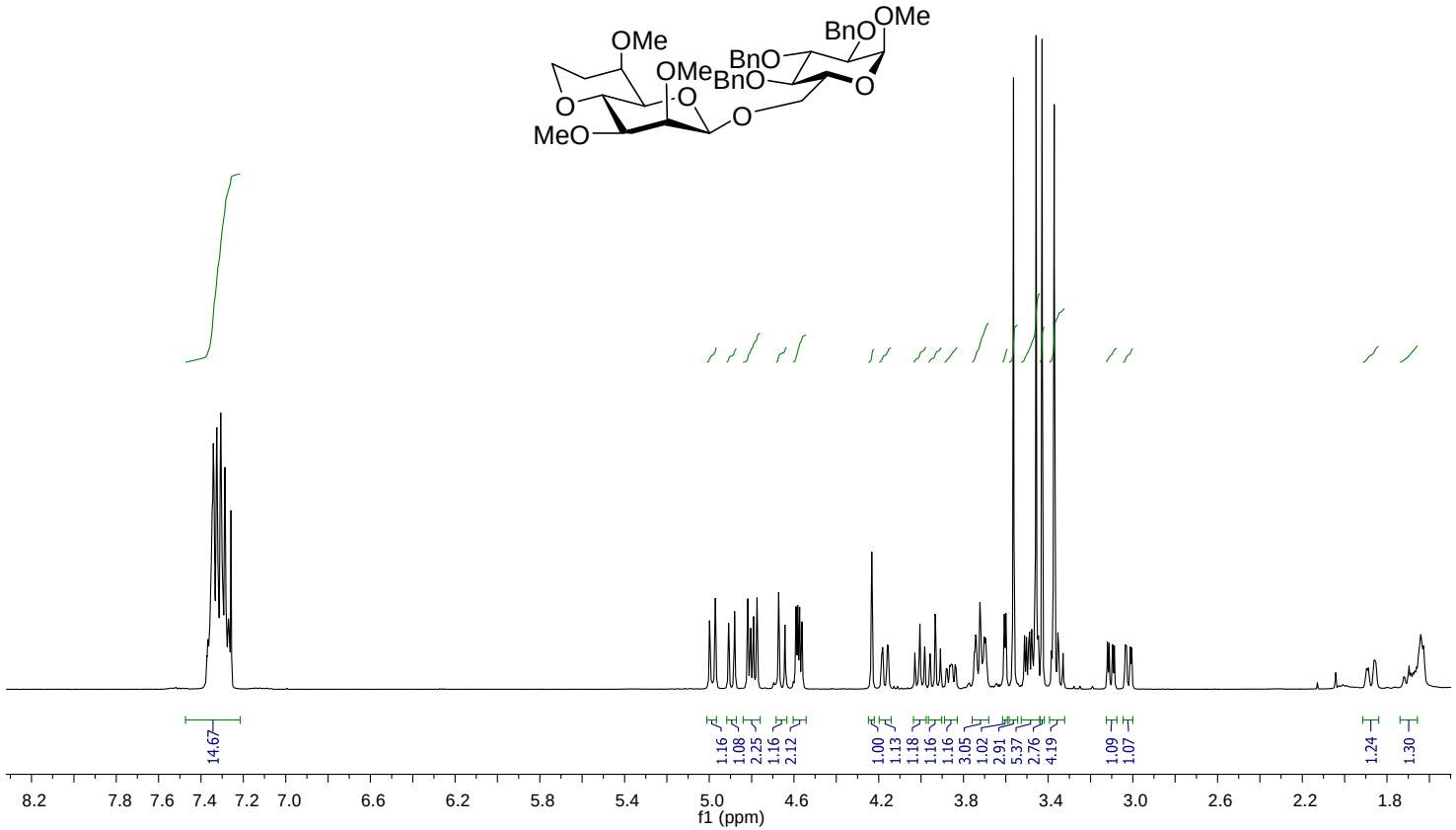
^{1}H NMR (400 MHz, $CDCl_3$) of Phenyl 4,6-*O*-benzylidene-7-dexoy-2,3-di-*O*-methyl-L-*glycero*-α-D-thio-*manno*heptopyranoside (35)



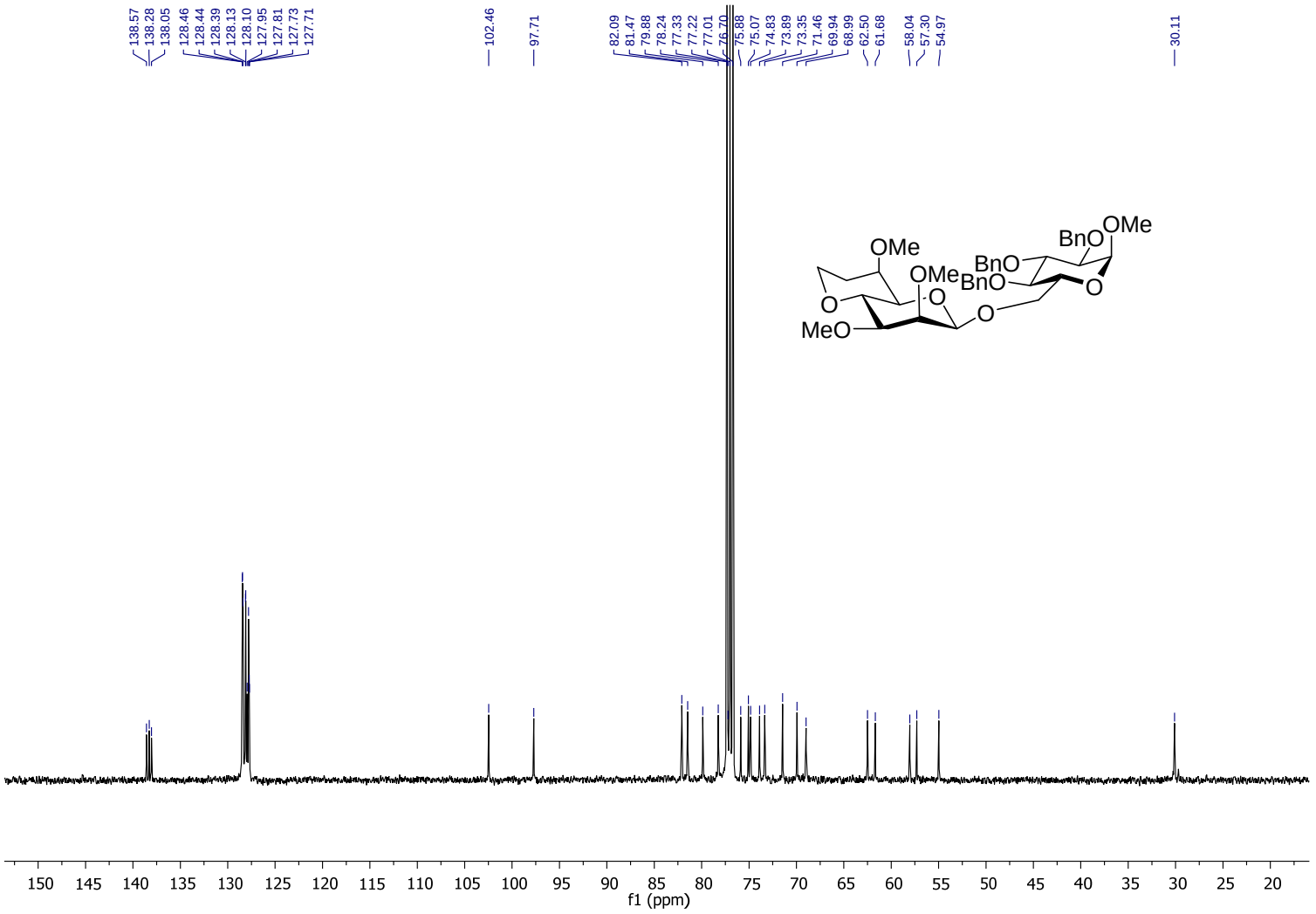
^{13}C NMR (100 MHz, $CDCl_3$) of Phenyl 4,6-*O*-benzylidene-7-deoxy-2,3-di-*O*-methyl-L-*glycero*-α-D-thio-*manno*heptopyranoside (35)



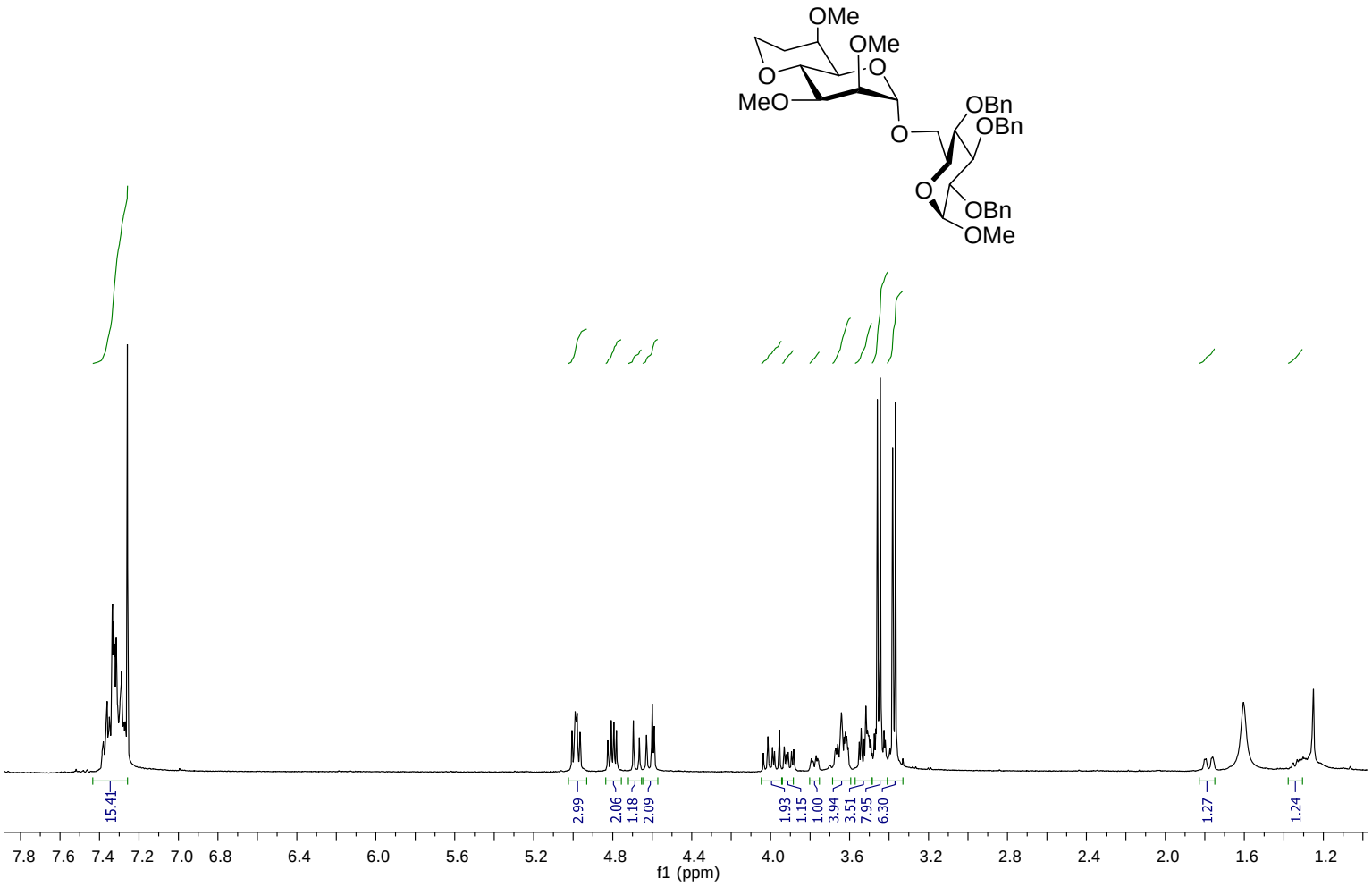
^{1}H NMR (400 MHz, $CDCl_3$) of Methyl 4,8-anhydro-7-deoxy-2,3,6-tri-*O*-methyl-D-*glycero*-β-D-*manno*octopyranosyl-(1→6)-2',3',4'-tri-*O*-benzyl-α-D-*gluco*pyranoside (39β)



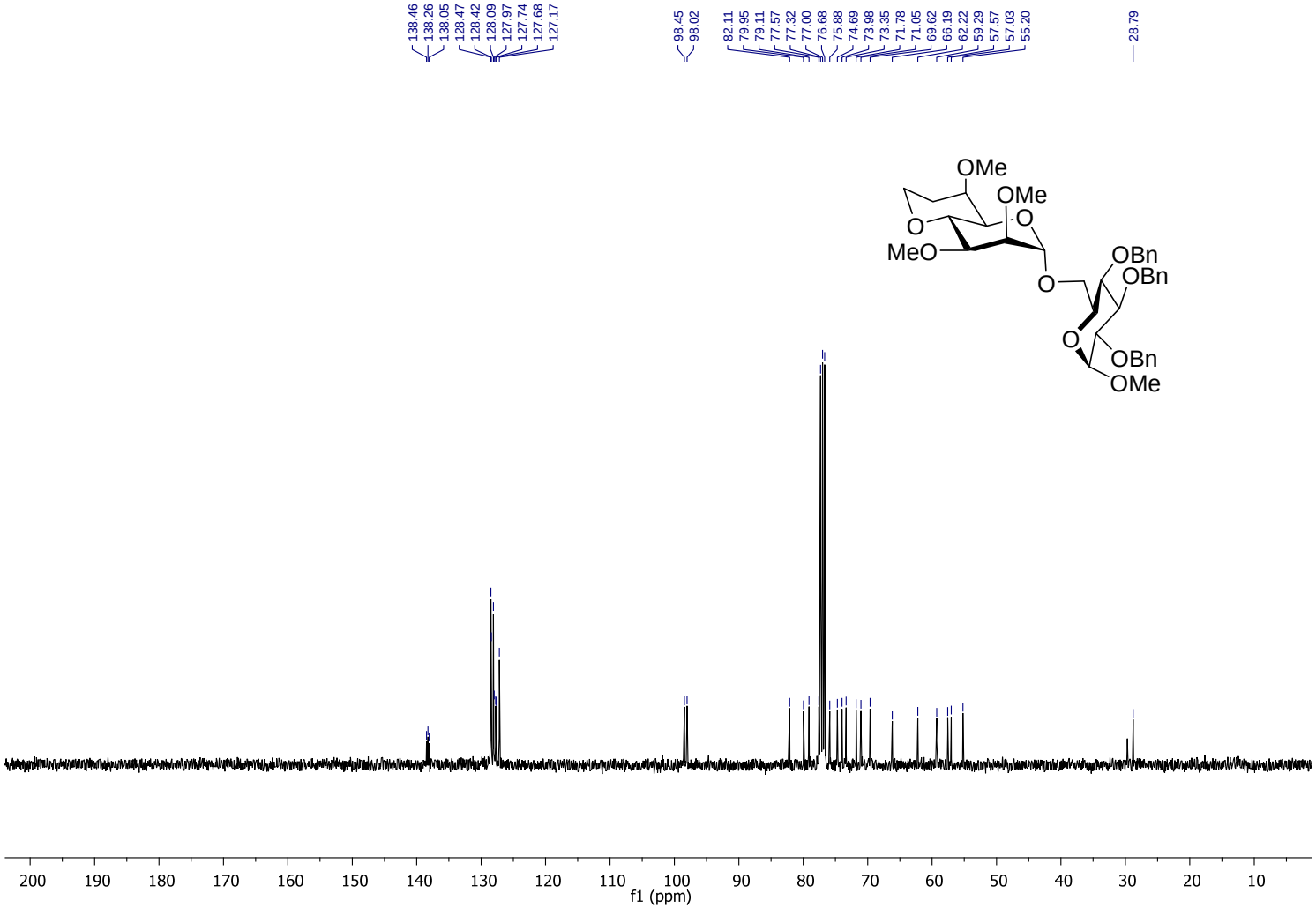
^{13}C NMR (100 MHz, $CDCl_3$) of Methyl 4,8-anhydro-7-deoxy-2,3,6-tri-*O*-methyl-D-*glycero*-β-D-*manno*octopyranosyl-(1→6)-2',3',4'-tri-*O*-benzyl-α-D-*gluco*pyranoside (39β)



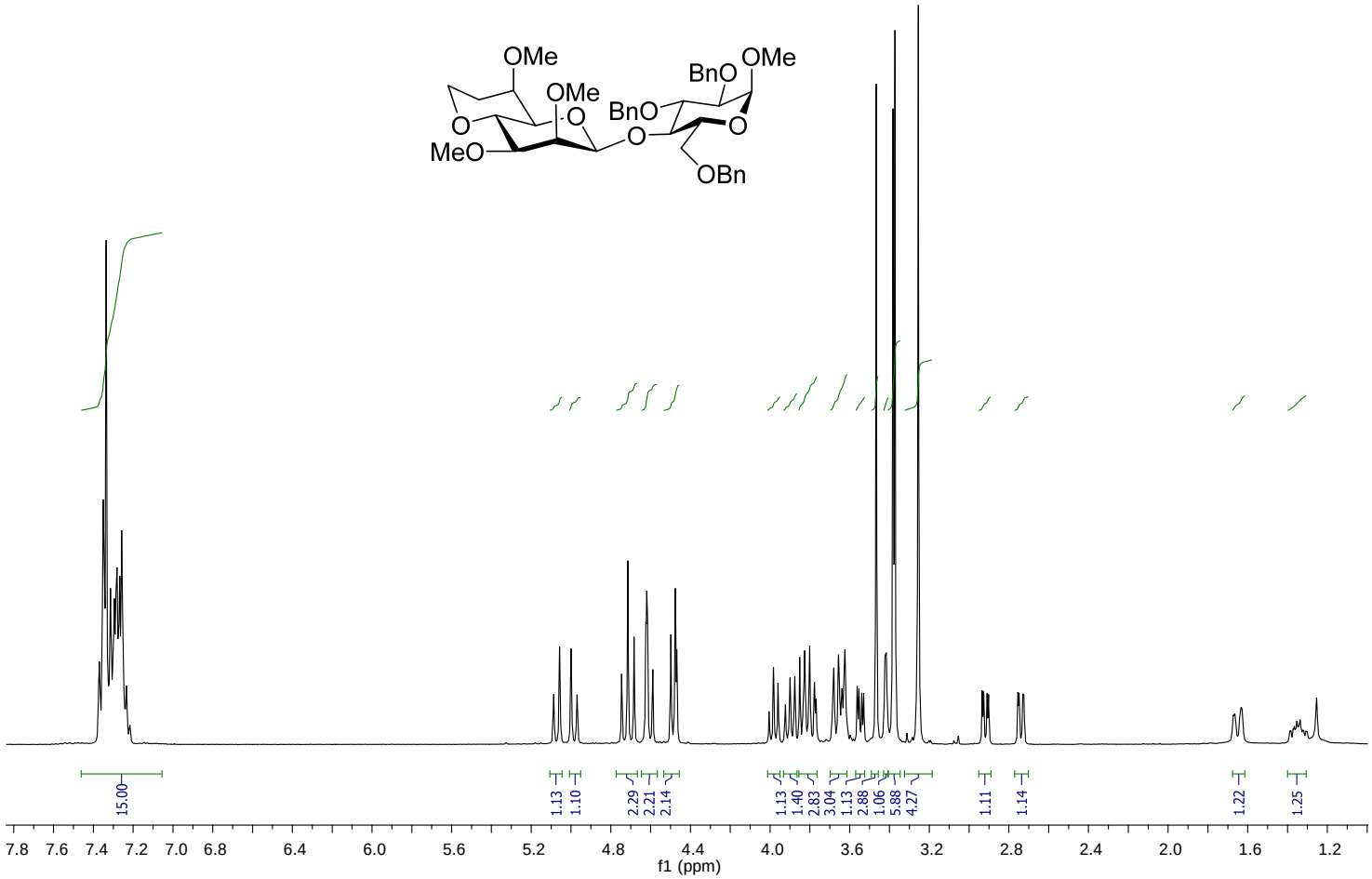
^{1}H NMR (600 MHz, $CDCl_3$) of Methyl 4,8-anhydro-7-deoxy-2,3,6-tri-*O*-methyl-D-*glycero*-α-D-*manno*octopyranosyl-(1→6)-2',3',4'-tri-*O*-benzyl-α-D-*gluco*pyranoside (39α)



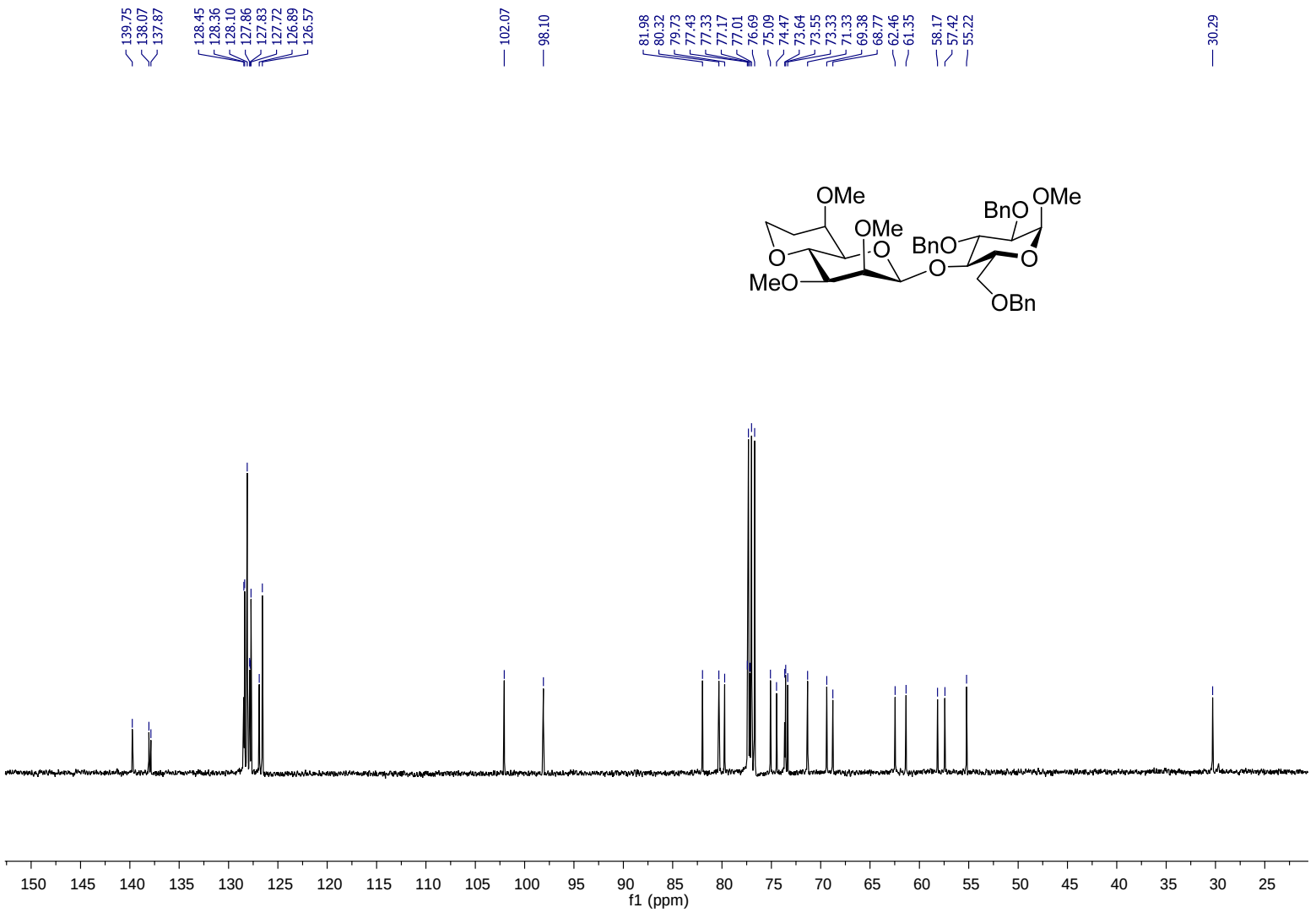
^{13}C NMR (100 MHz, $CDCl_3$) of Methyl 4,8-anhydro-7-deoxy-2,3,6-tri-*O*-methyl-D-*glycero*-α-D-*manno*octopyranosyl-(1→6)-2',3',4'-tri-*O*-benzyl-α-D-*gluco*pyranoside (39α)



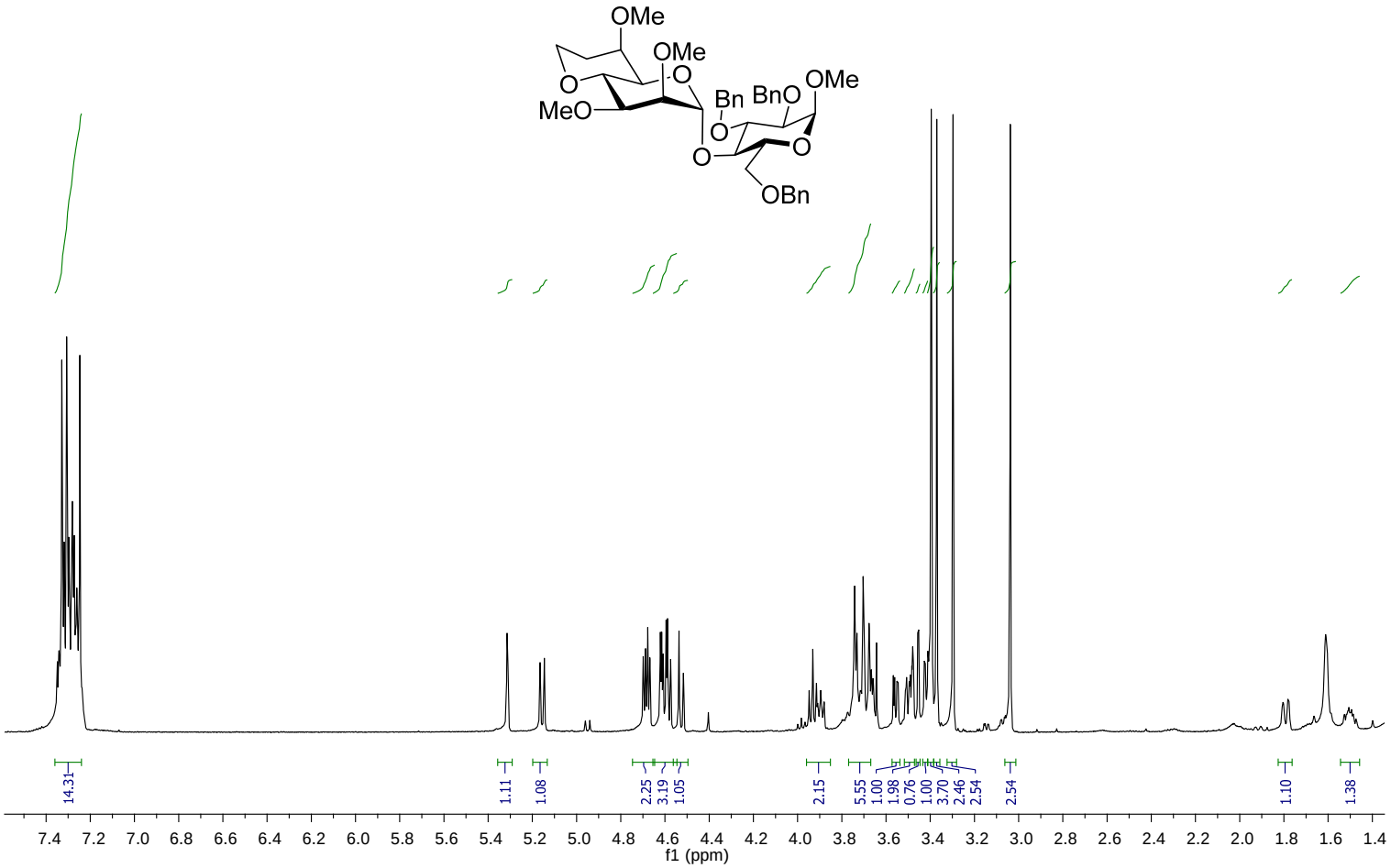
^{1}H NMR (400 MHz, $CDCl_3$) of Methyl 4,8-anhydro-7-deoxy-2,3,6-tri-*O*-methyl-D-*glycero*-β-D-*manno*octopyranosyl-(1→4)-2',3',6'-tri-*O*-benzyl-α-D-*gluco*pyranoside (40β)



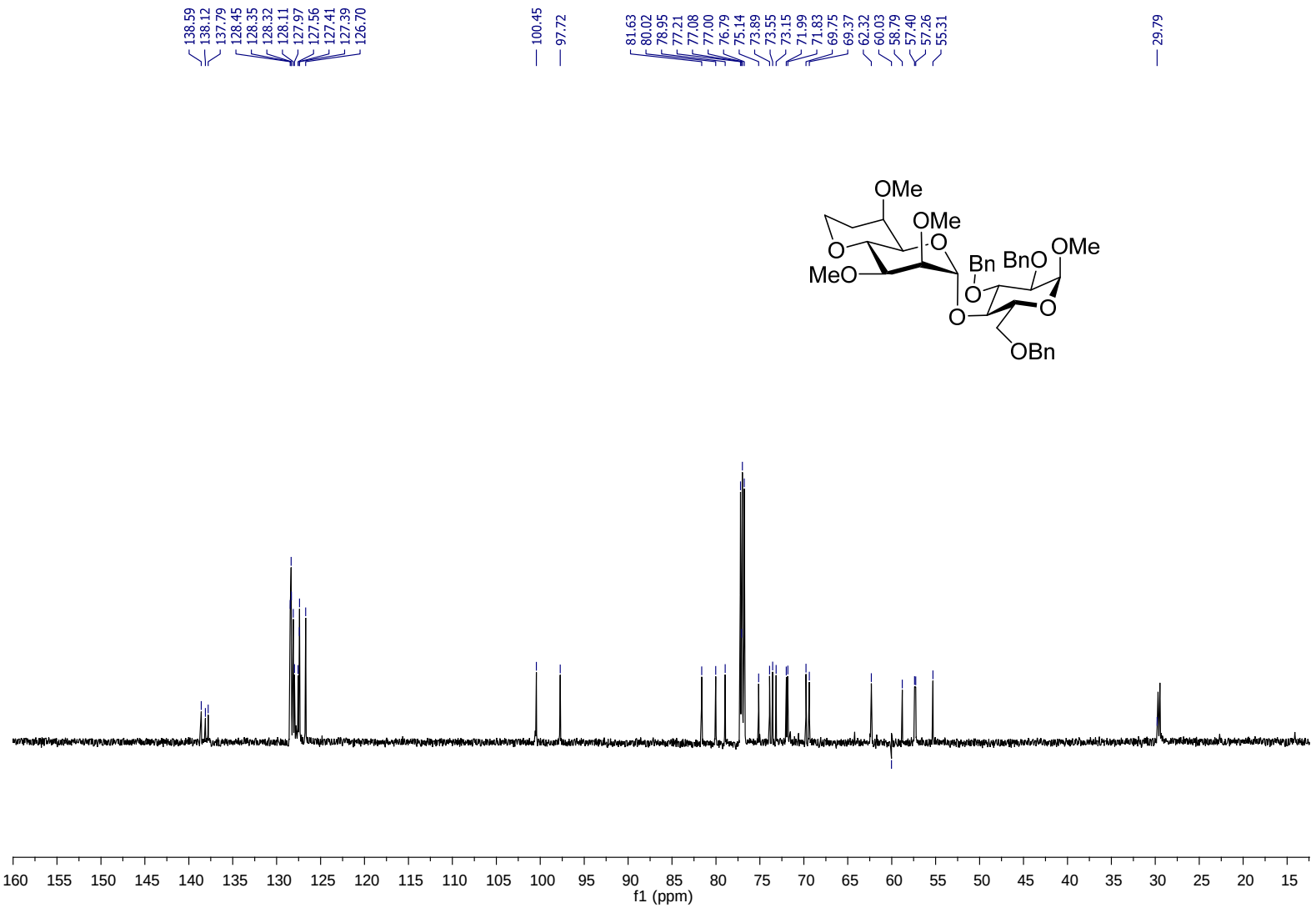
^{13}C NMR (100 MHz, $CDCl_3$) of Methyl 4,8-anhydro-7-deoxy-2,3,6-tri-*O*-methyl-D-*glycero*-β-D-*manno*octopyranosyl-(1→4)-2',3',6'-tri-*O*-benzyl-α-D-*gluco*pyranoside (40β)



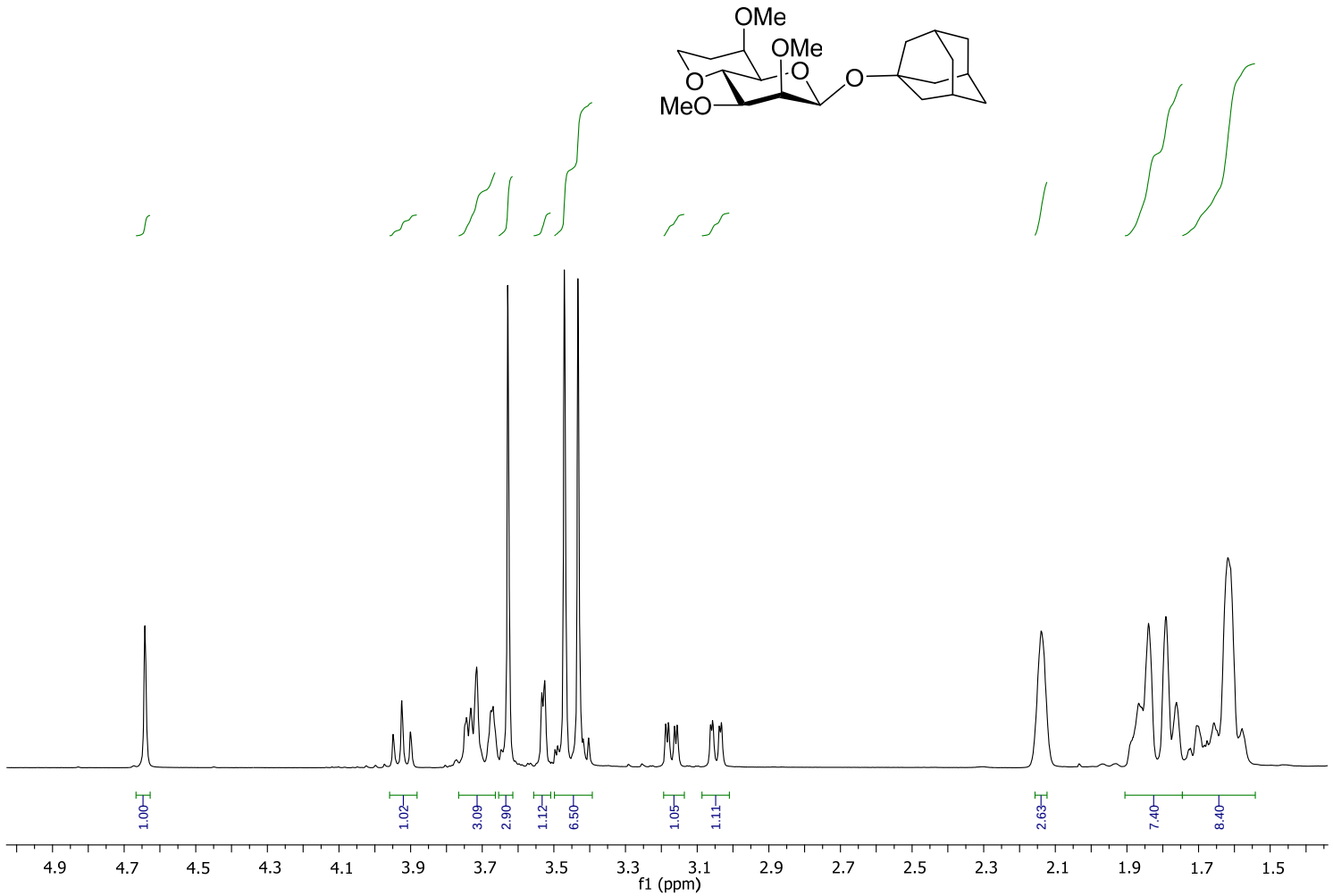
^{1}H NMR (600 MHz, $CDCl_3$) of Methyl 4,8-anhydro-7-deoxy-2,3,6-tri-*O*-methyl-D-*glycero*-α-D-*manno*octopyranosyl-(1→4)-2',3',6'-tri-*O*-benzyl-α-D-*gluco*pyranoside (40α)



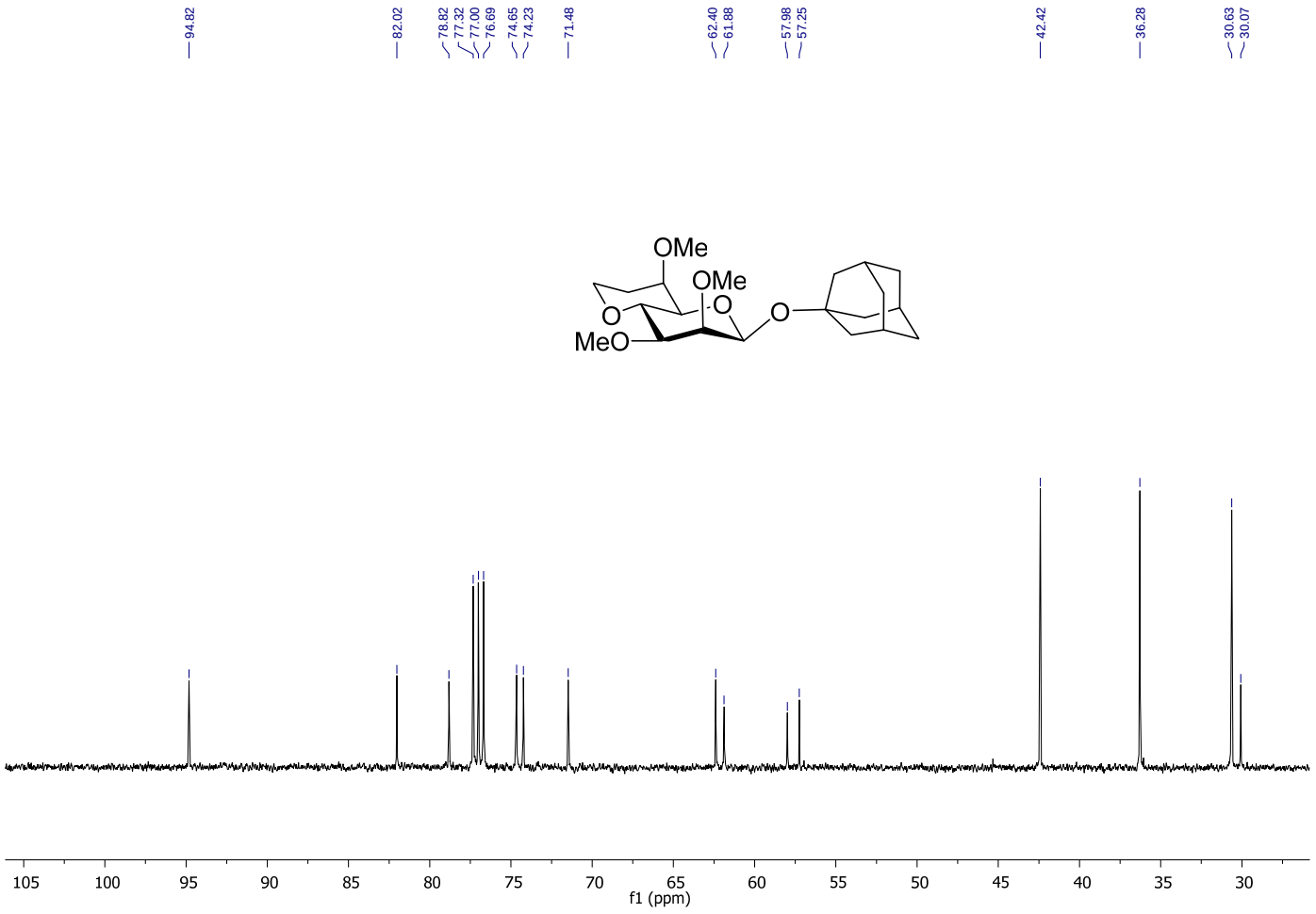
^{13}C NMR (150 MHz, $CDCl_3$) of Methyl 4,8-anhydro-7-deoxy-2,3,6-tri-*O*-methyl-D-*glycero*-α-D-*manno*octopyranosyl-(1→4)-2',3',6'-tri-*O*-benzyl-α-D-*gluco*pyranoside (40α)



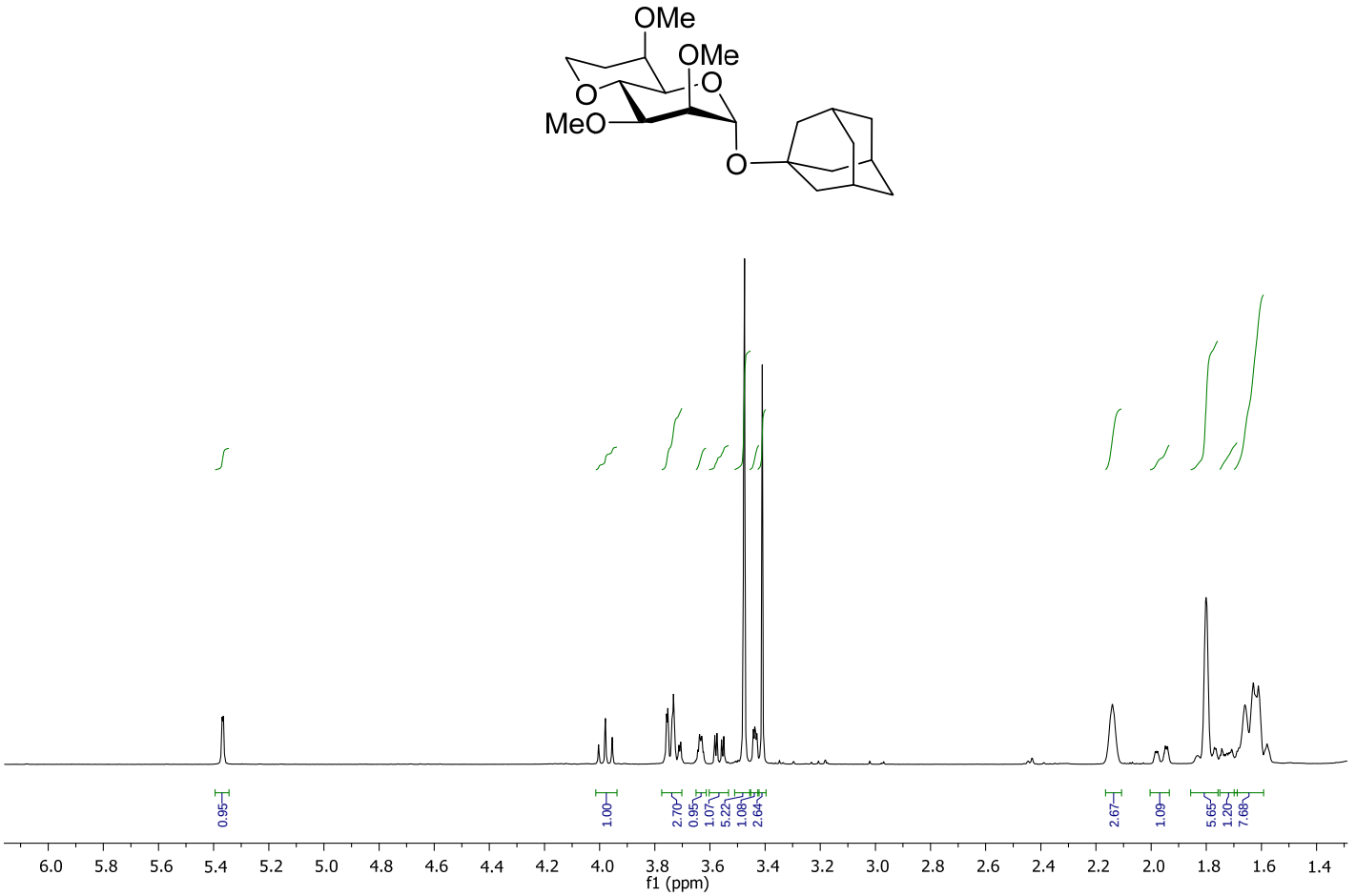
^{1}H NMR (400 MHz, $CDCl_3$) of (1-Adamantanyl) 4,8-anhydro-7-deoxy-2,3,6-tri-*O*-methyl-D-*glycero*-β-D-*manno*octopyranoside (41β)



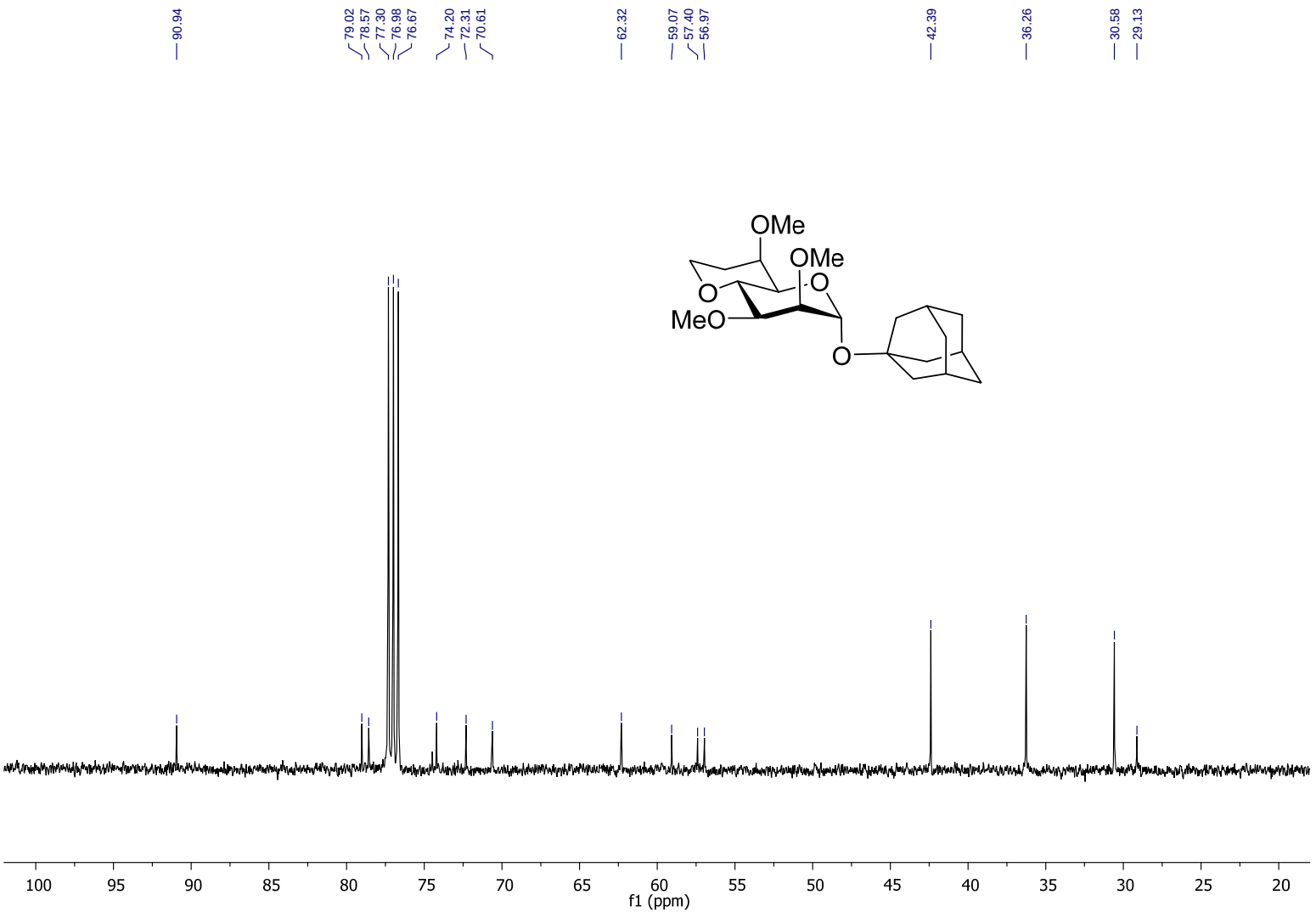
^{13}C NMR (100 MHz, $CDCl_3$) of (1-Adamantanyl) 4,8-anhydro-7-deoxy-2,3,6-tri-*O*-methyl-D-*glycero*-β-D-*manno*octopyranoside (41β)



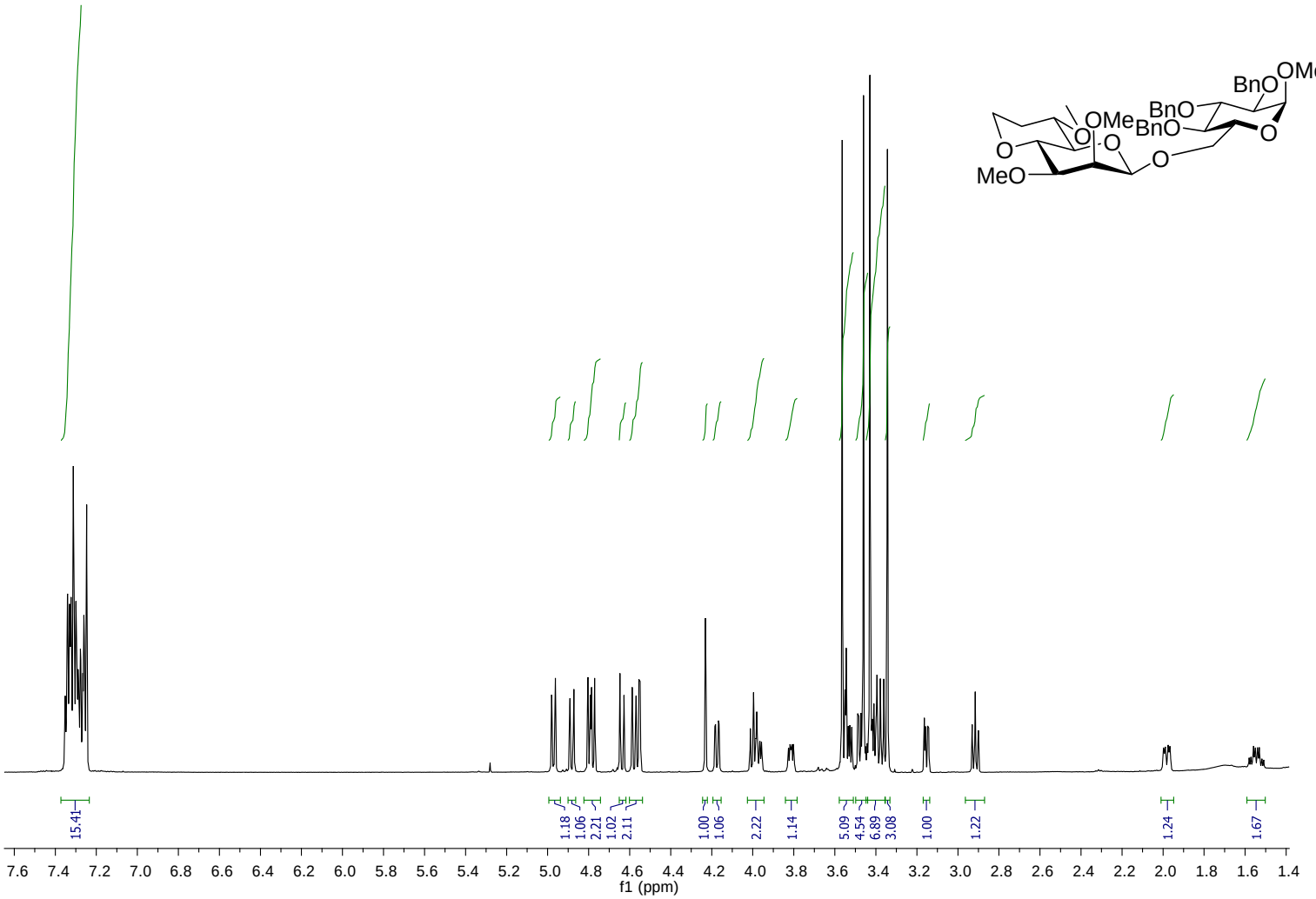
^{1}H NMR (400 MHz, $CDCl_3$) of (1-Adamantanyl) 4,8-anhydro-7-deoxy-2,3,6-tri-*O*-methyl-D-*glycero*-α-D-*manno*octopyranoside (41α)



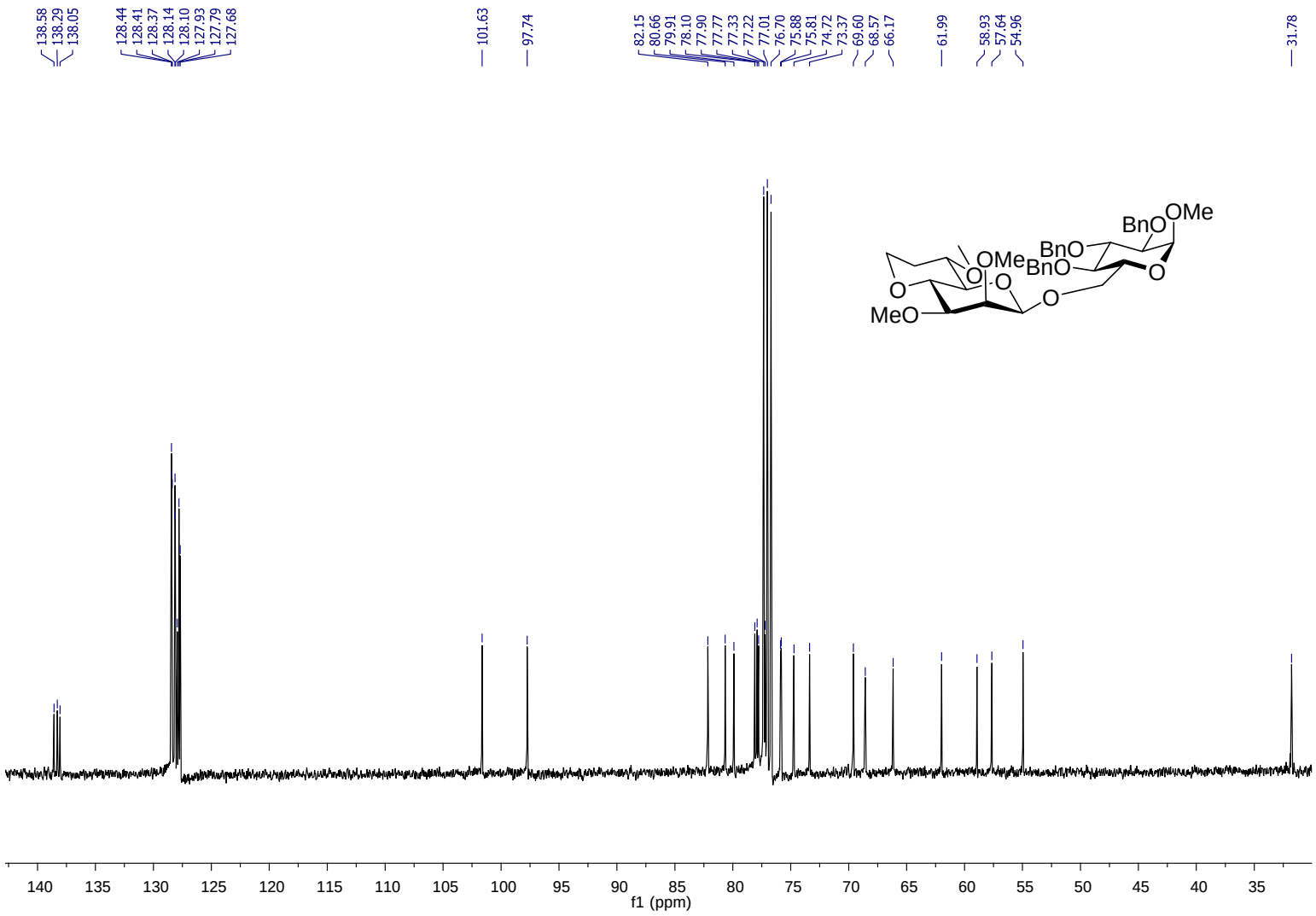
^{13}C NMR (100 MHz, $CDCl_3$) of (1-Adamantanyl) 4,8-anhydro-7-deoxy-2,3,6-tri-*O*-methyl-D-*glycero*-α-D-*manno*octopyranoside (41α)



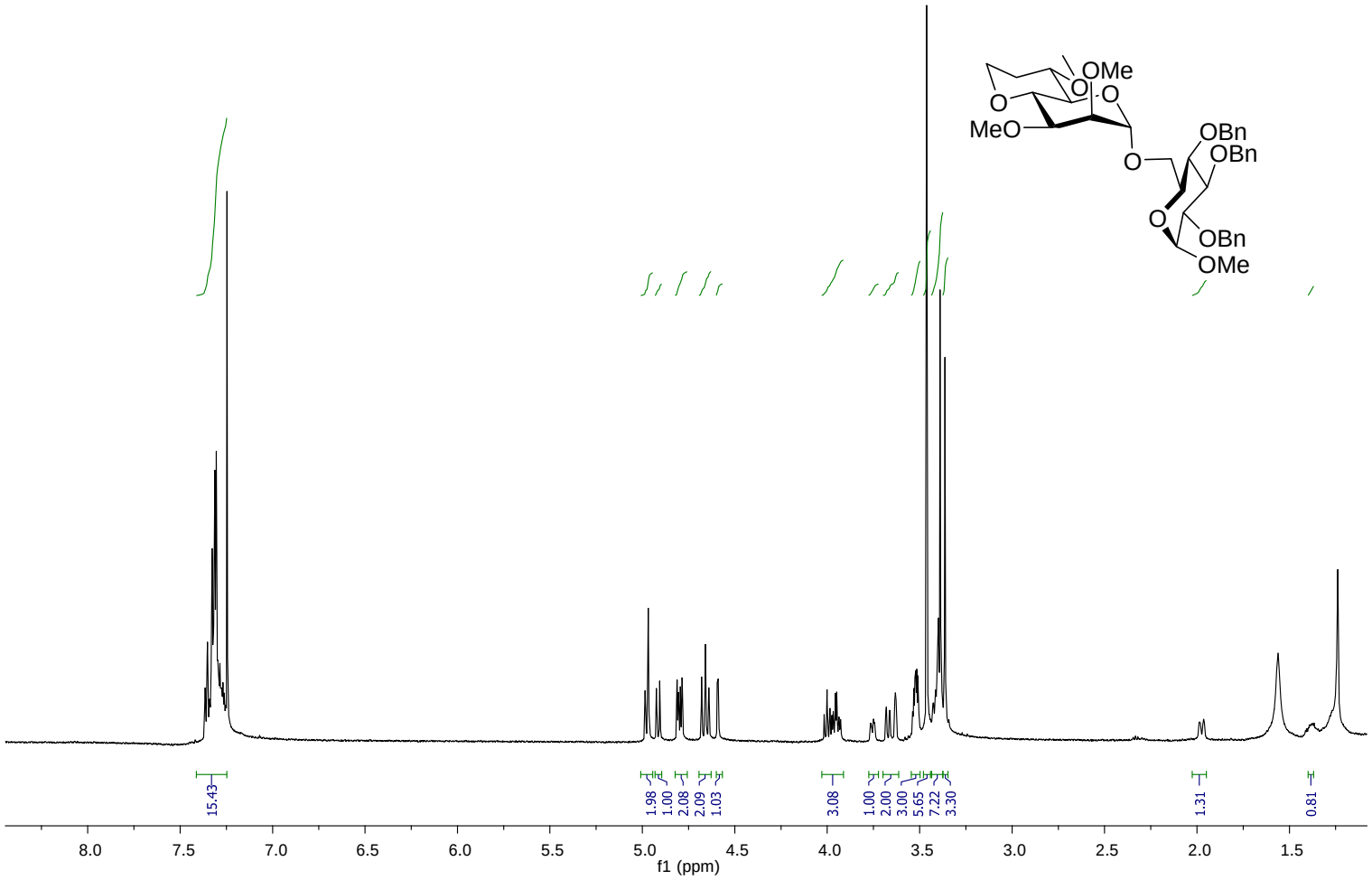
^{1}H NMR (600 MHz, $CDCl_3$) of Methyl 4,8-anhydro-7-deoxy-2,3,6-tri-*O*-methyl-L-*glycero*-β-D-*manno*octopyranosyl-(1→6)-2',3',4'-tri-*O*-benzyl-α-D-*gluco*pyranoside (42β)



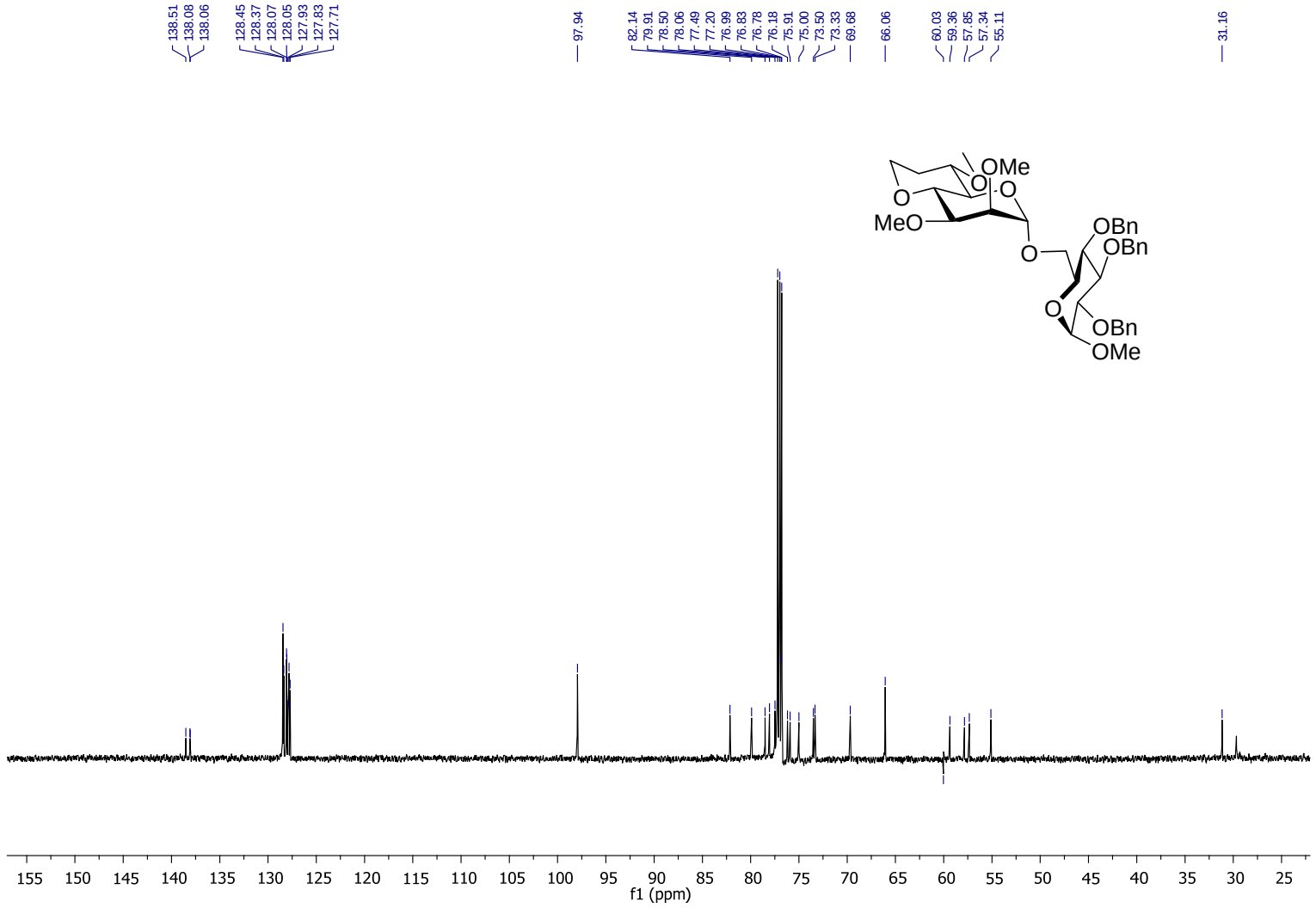
^{13}C NMR (100 MHz, $CDCl_3$) of Methyl 4,8-anhydro-7-deoxy-2,3,6-tri-*O*-methyl-L-*glycero*-β-D-*manno*octopyranosyl-(1→6)-2',3',4'-tri-*O*-benzyl-α-D-*gluco*pyranoside (42β)



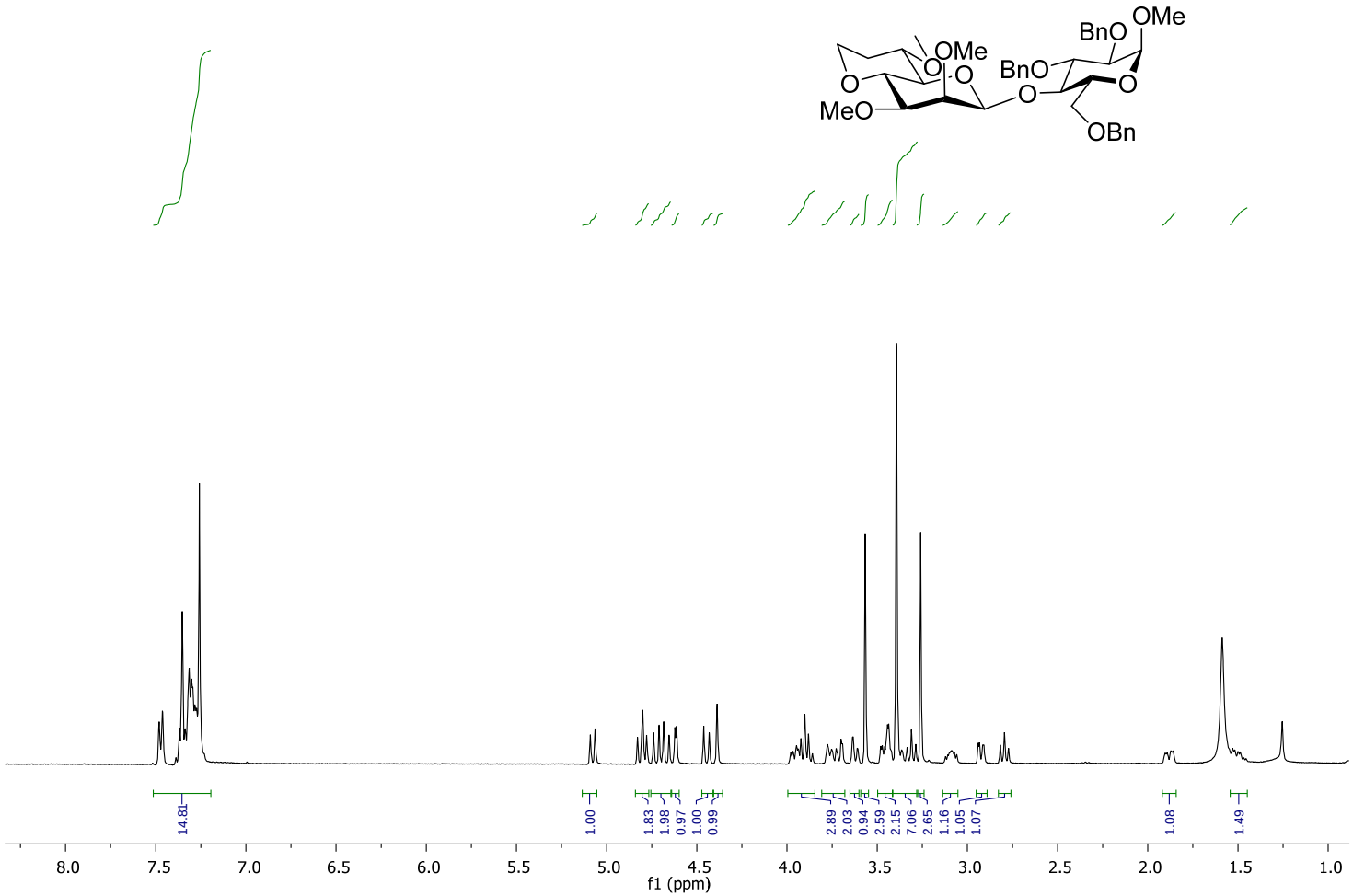
^{1}H NMR (600 MHz, $CDCl_3$) of Methyl 4,8-anhydro-7-deoxy-2,3,6-tri-*O*-methyl-L-*glycero*-α-D-*manno*octopyranosyl-(1→6)-2',3',4'-tri-*O*-benzyl-α-D-*gluco*pyranoside (42α)



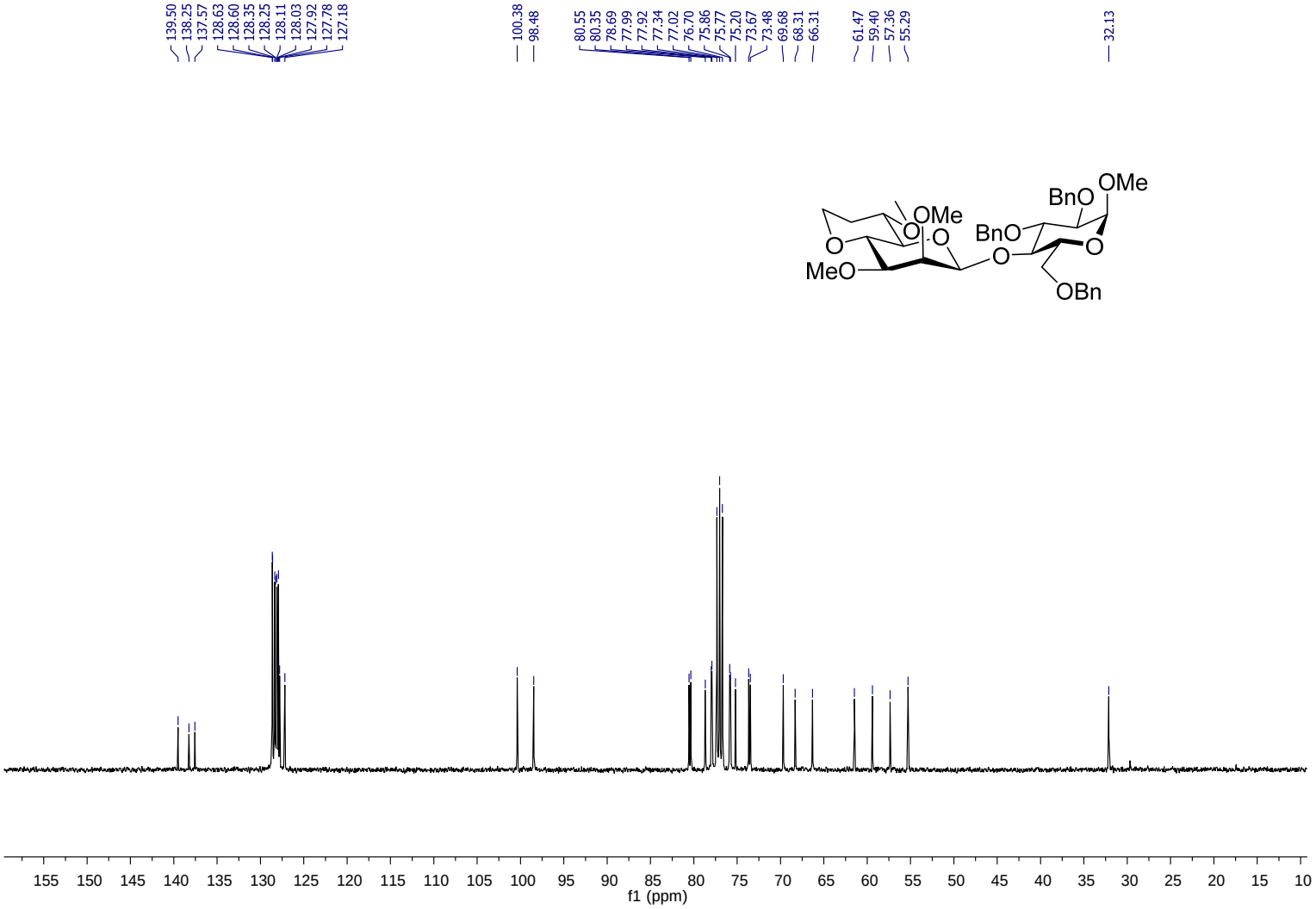
^{13}CNMR (150 MHz, $CDCl_3$) of Methyl 4,8-anhydro-7-deoxy-2,3,6-tri-*O*-methyl-L-*glycero*-α-D-*manno*octopyranosyl-(1→6)-2',3',4'-tri-*O*-benzyl-α-D-*gluco*pyranoside (42α)



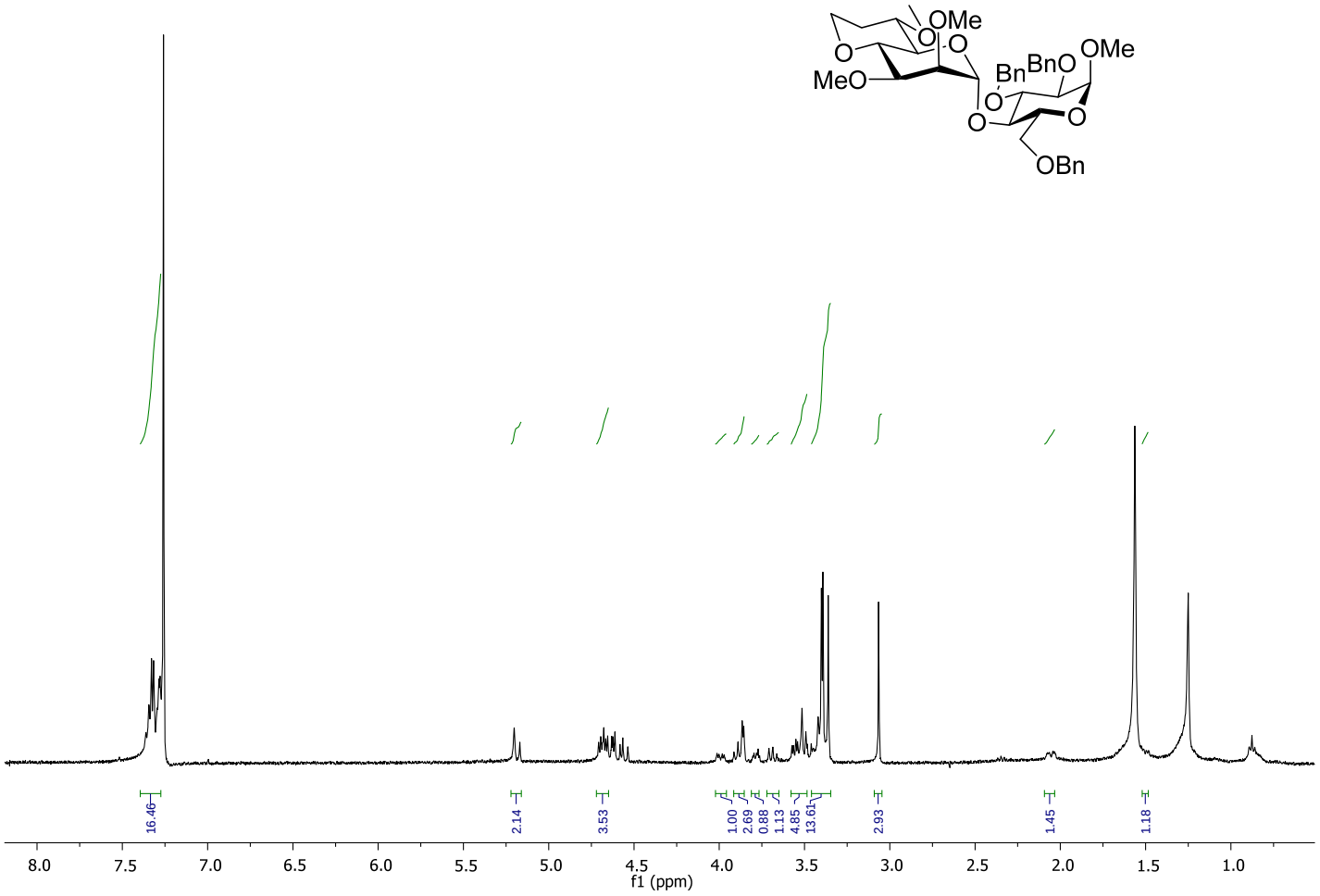
^{1}H NMR (400 MHz, $CDCl_3$) of Methyl 4,8-anhydro-7-deoxy-2,3,6-tri-*O*-methyl-L-*glycero*-β-D-*manno*octopyranosyl-(1→4)-2',3',6'-tri-*O*-benzyl-α-D-*gluco*pyranoside (43β)



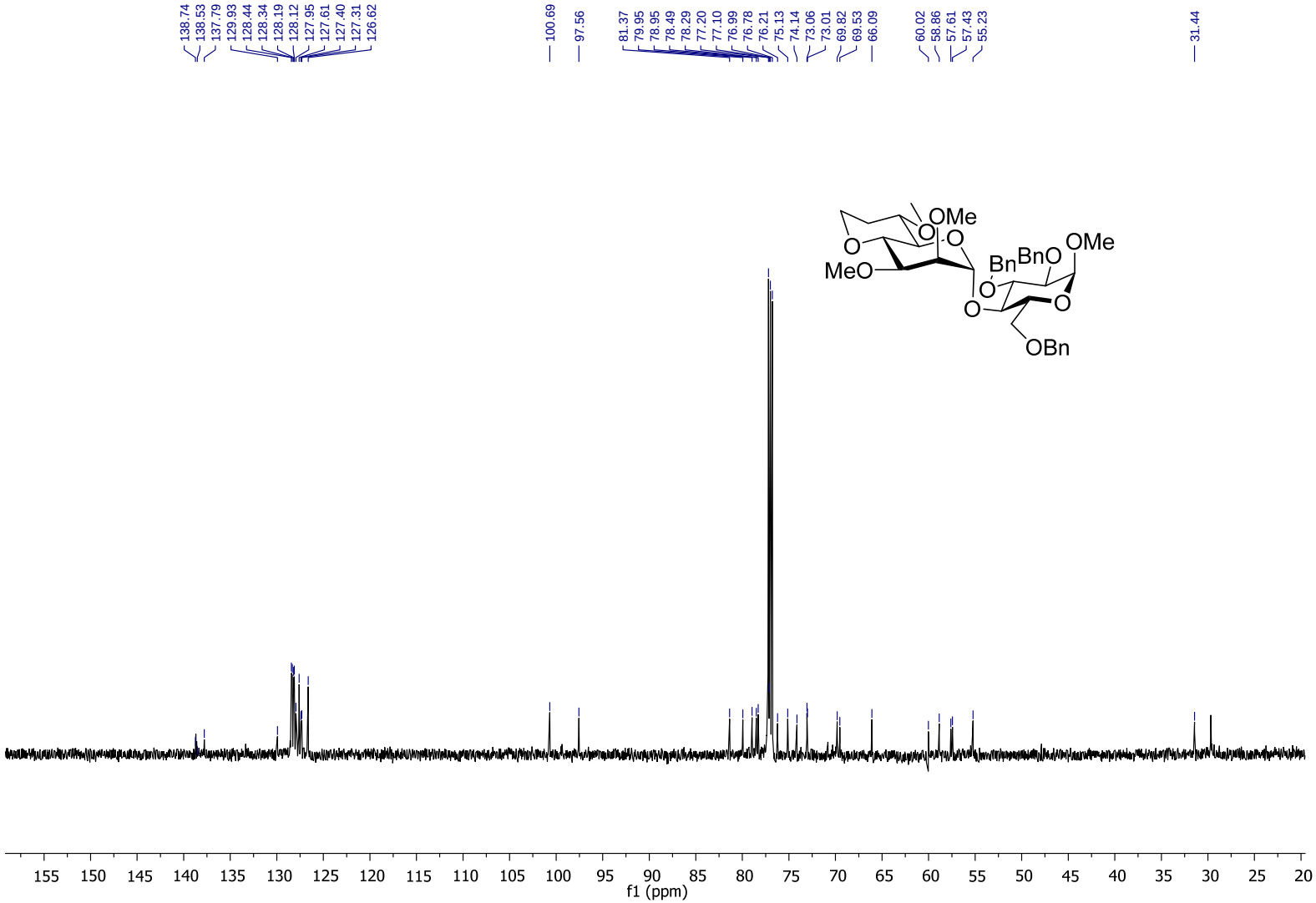
^{13}C NMR (100 MHz, $CDCl_3$) of Methyl 4,8-anhydro-7-deoxy-2,3,6-tri-*O*-methyl-L-*glycero*-β-D-*manno*octopyranosyl-(1→4)-2',3',6'-tri-*O*-benzyl-α-D-*gluco*pyranoside (43β)



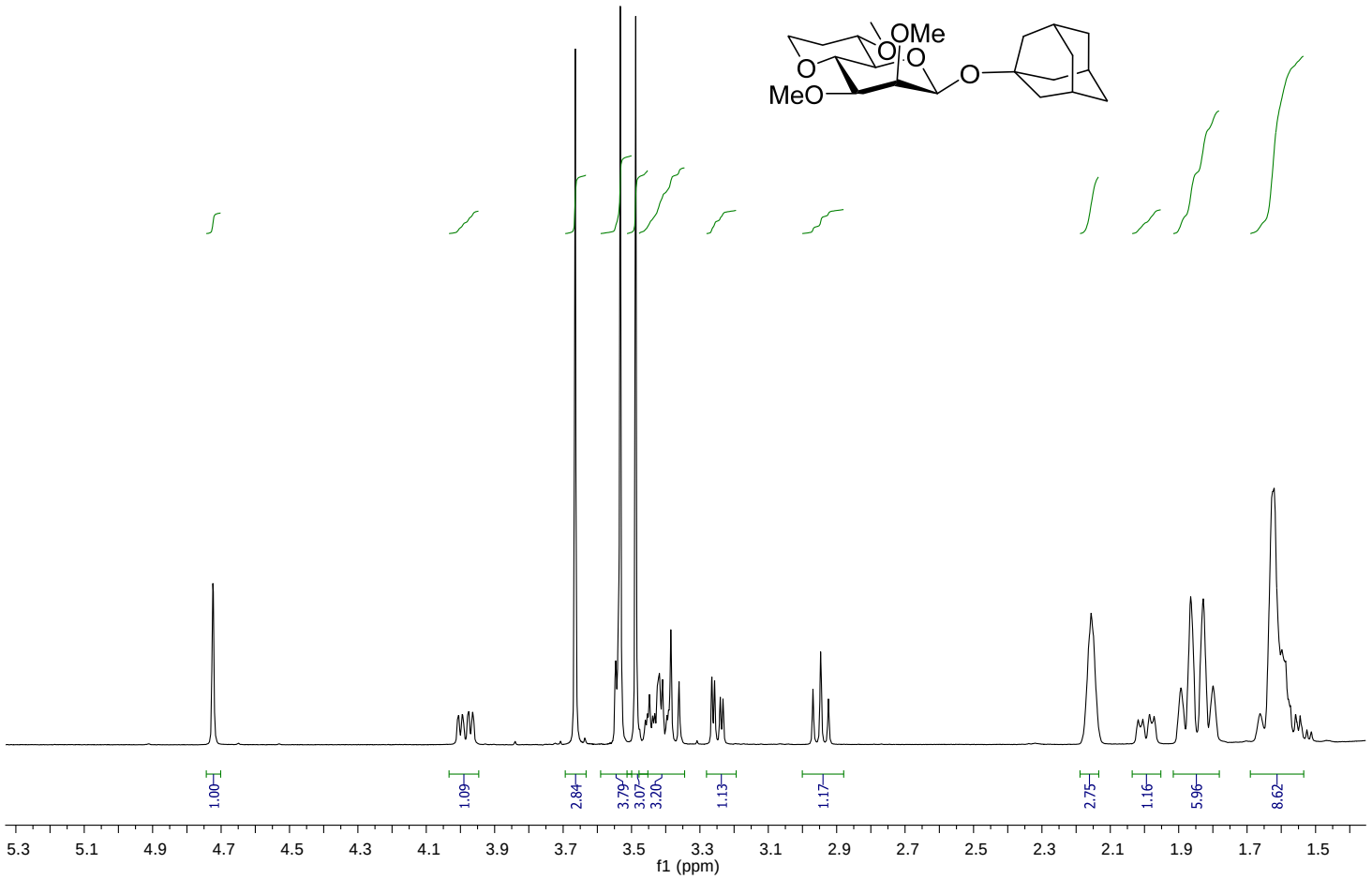
^{1}H NMR (400 MHz, $CDCl_3$) of Methyl 4,8-anhydro-7-deoxy-2,3,6-tri-*O*-methyl-L-*glycero*-α-D-*manno*octopyranosyl-(1→4)-2',3',6'-tri-*O*-benzyl-α-D-*gluco*pyranoside (43α)



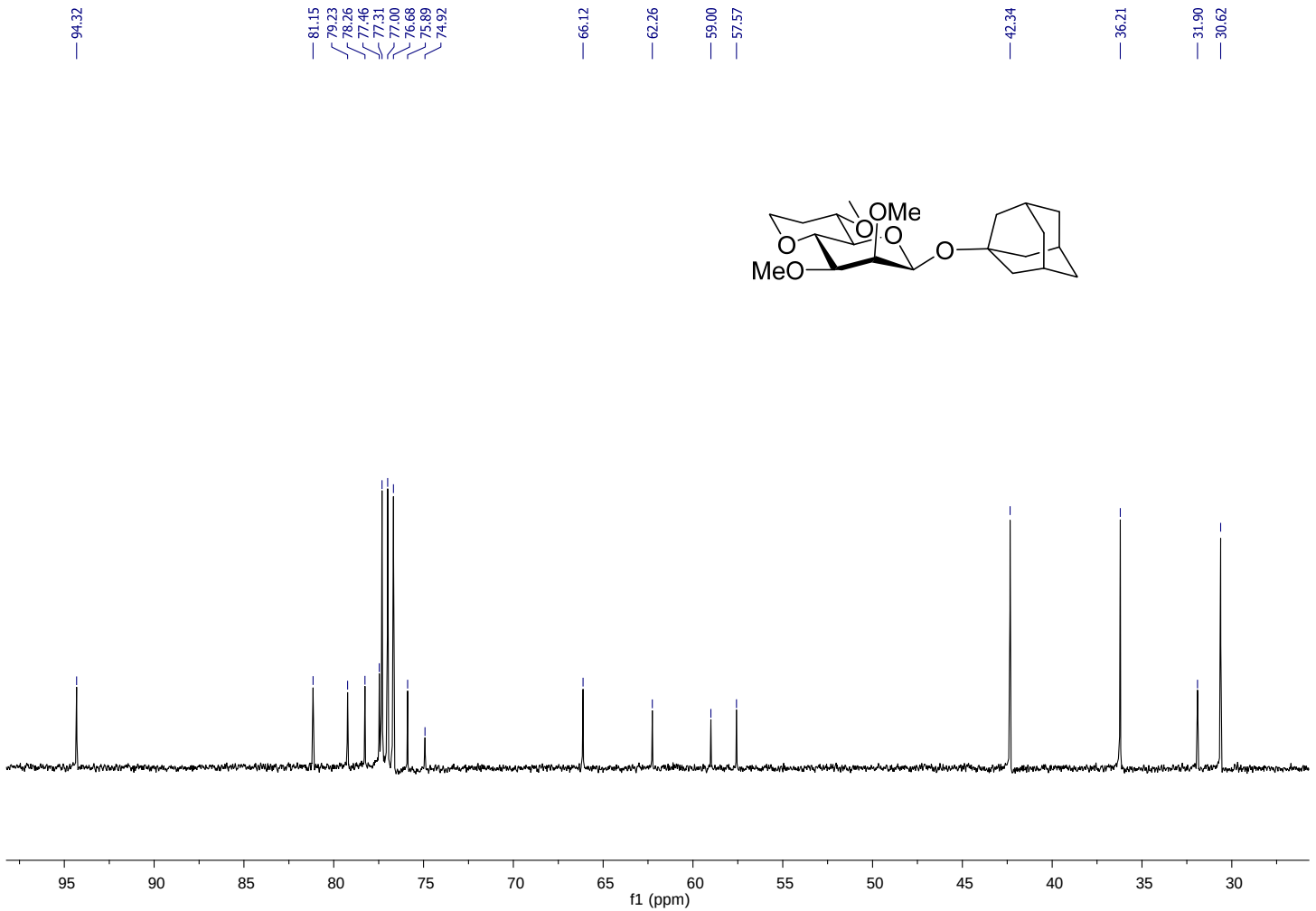
^{13}C NMR (150 MHz, $CDCl_3$) Methyl 4,8-anhydro-7-deoxy-2,3,6-tri-*O*-methyl-L-*glycero*-α-D-*manno*octopyranosyl-(1→4)-2',3',6'-tri-*O*-benzyl-α-D-*gluco*pyranoside (43α)



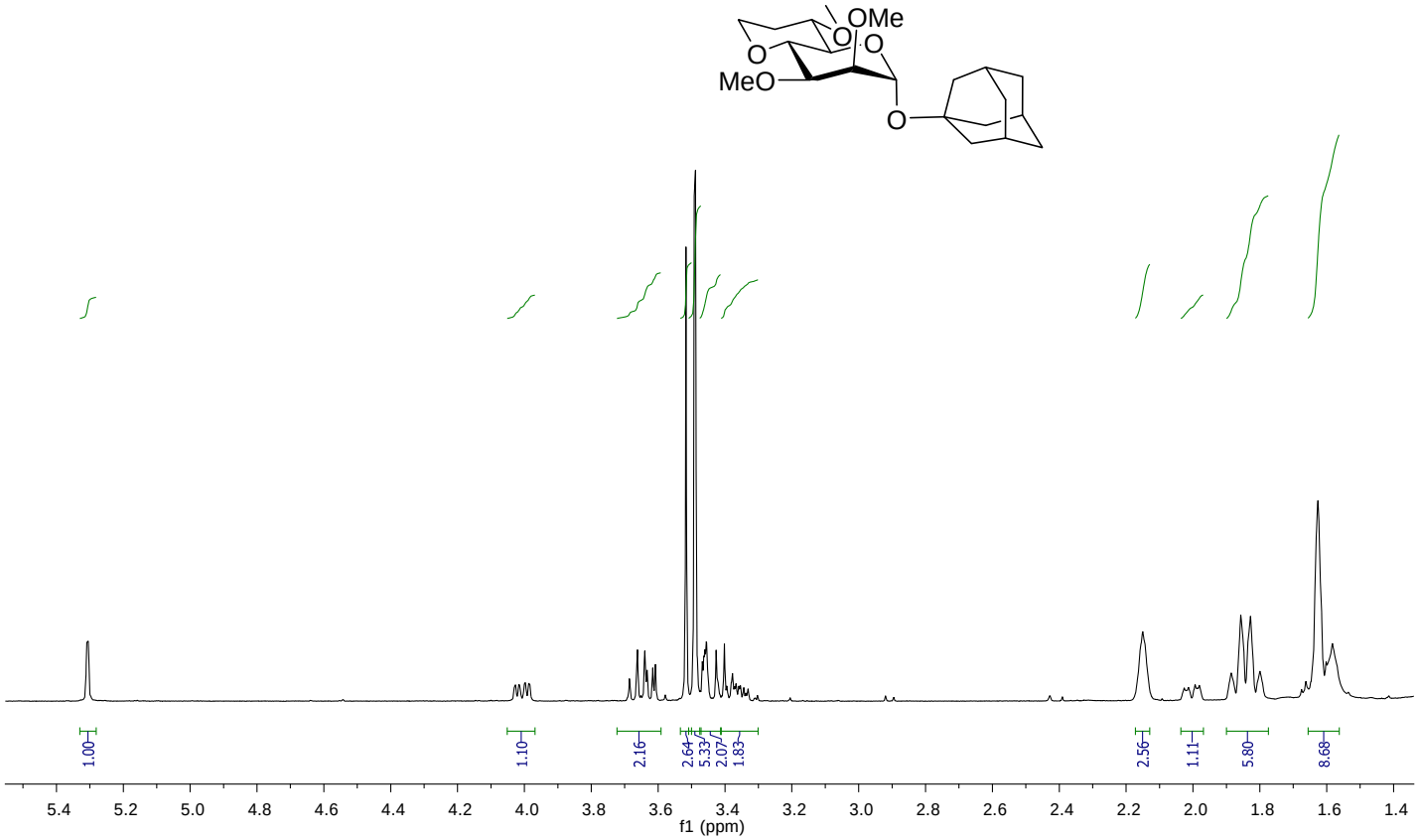
^{1}H NMR (400 MHz, $CDCl_3$) of (1-Adamantanyl) 4,8-anhydro-7-deoxy-2,3,6-tri-*O*-methyl-L-*glycero*-β-D-*manno*octopyranoside (44β)



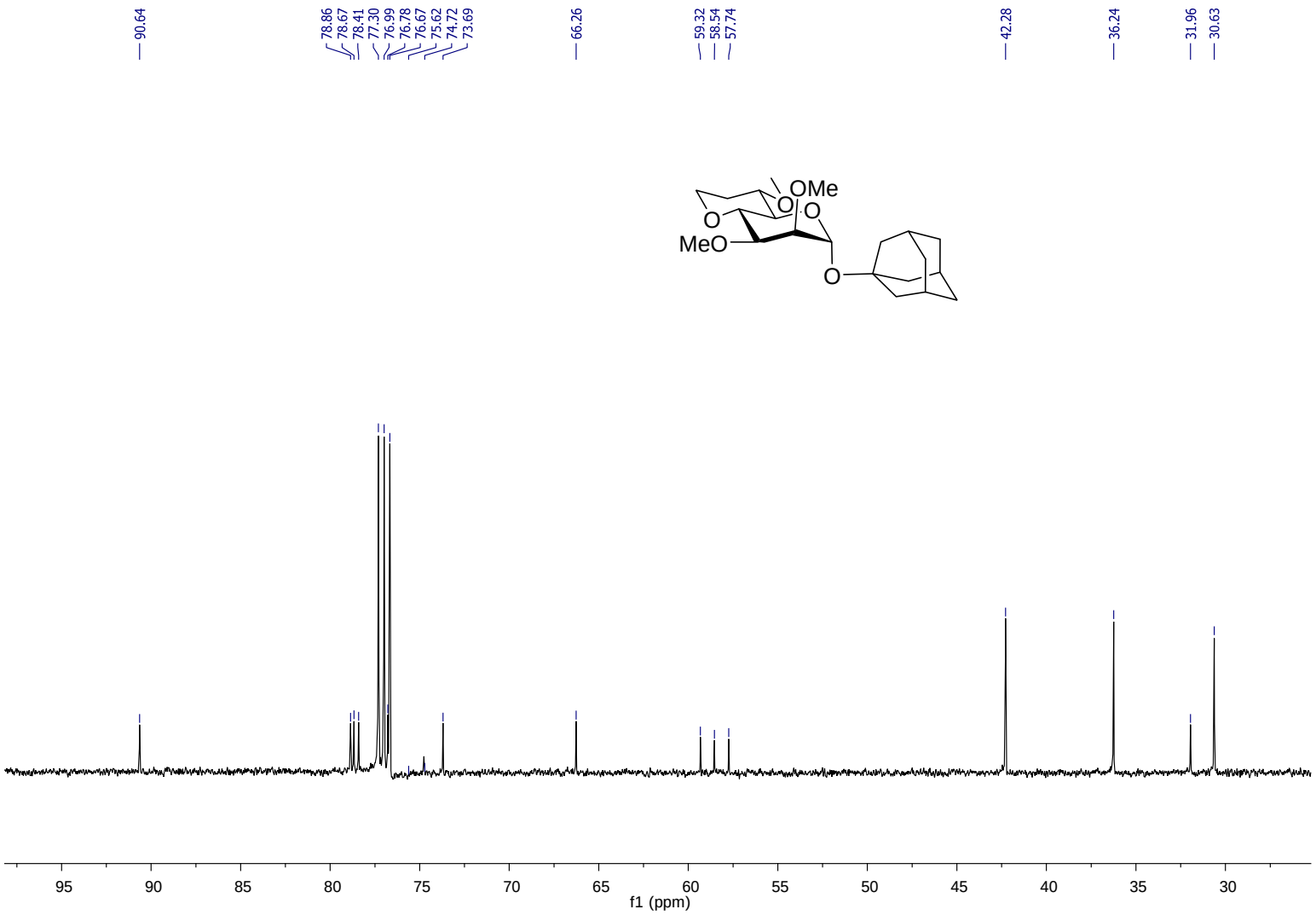
^{13}C NMR (100 MHz, $CDCl_3$) of (1-Adamantanyl) 4,8-anhydro-7-deoxy-2,3,6-tri-*O*-methyl-L-*glycero*-β-D-*manno*octopyranoside (44β)



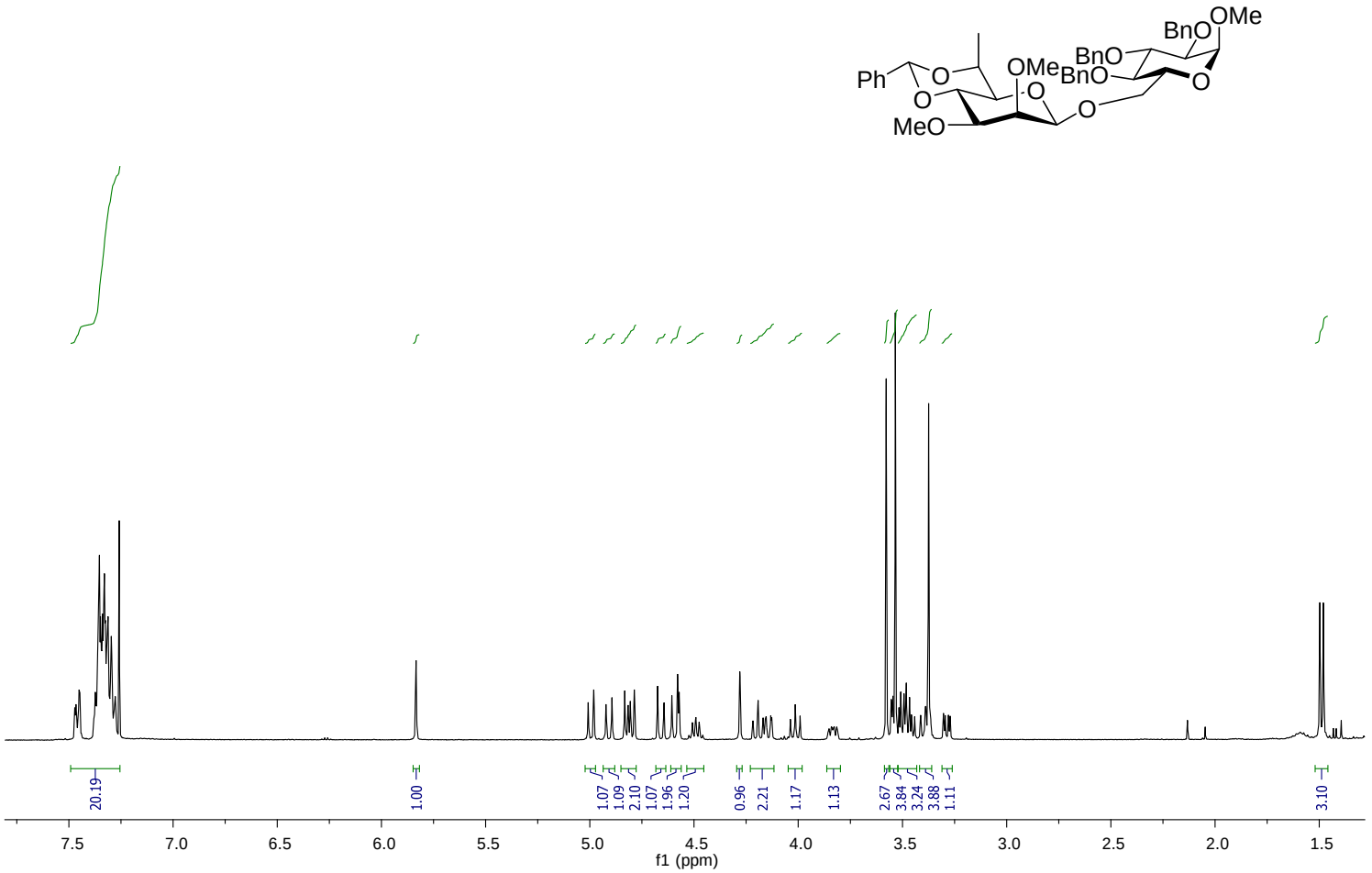
^{1}H NMR (400 MHz, $CDCl_3$) of (1-Adamantanyl) 4,8-anhydro-7-deoxy-2,3,6-tri-*O*-methyl-L-*glycero*-α-D-*manno*octopyranoside (44α)



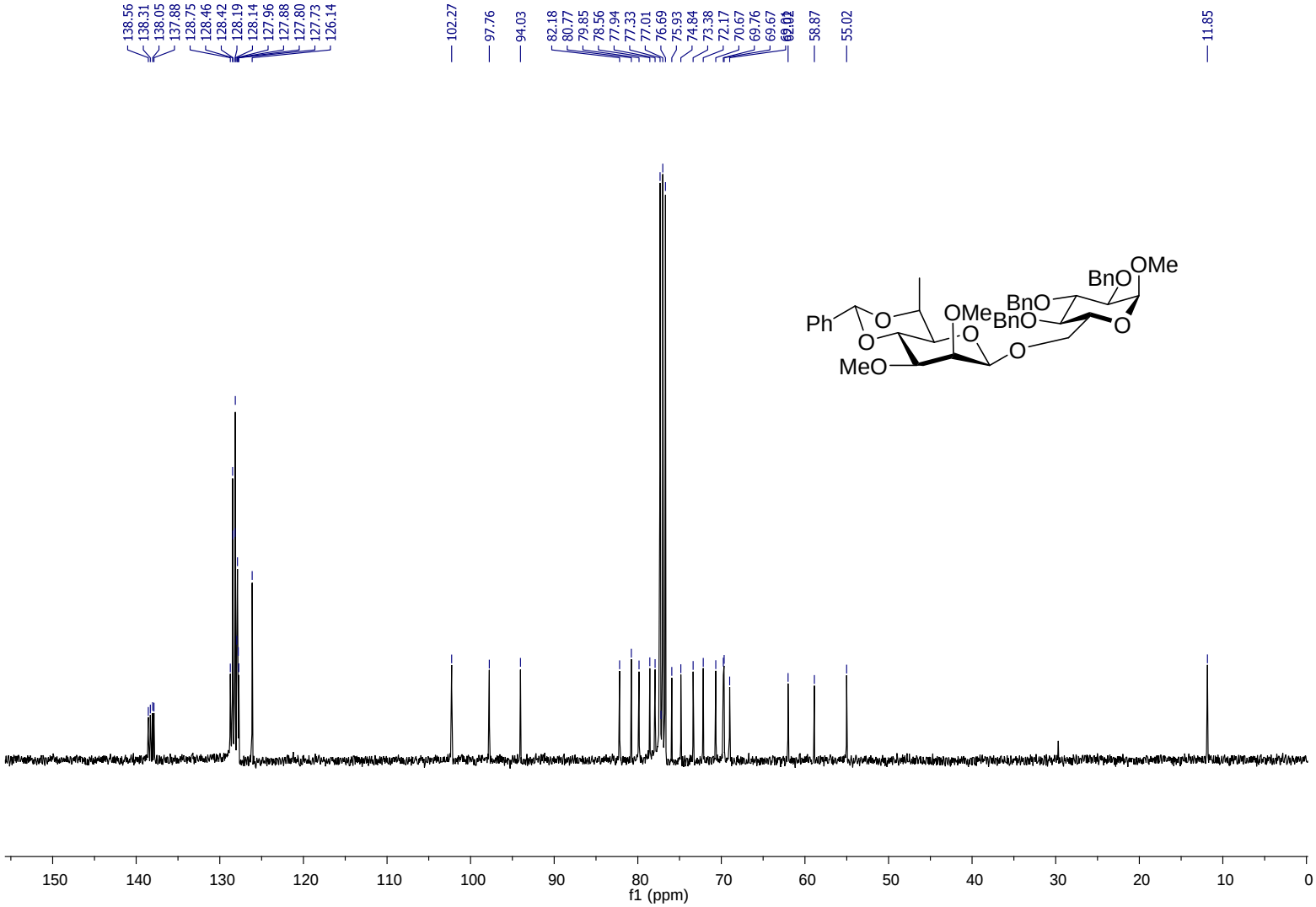
^{13}C NMR (100 MHz, $CDCl_3$) of (1-Adamantanyl) 4,8-anhydro-7-deoxy-2,3,6-tri-*O*-methyl-L-*glycero*-α-D-*manno*octopyranoside (44α)



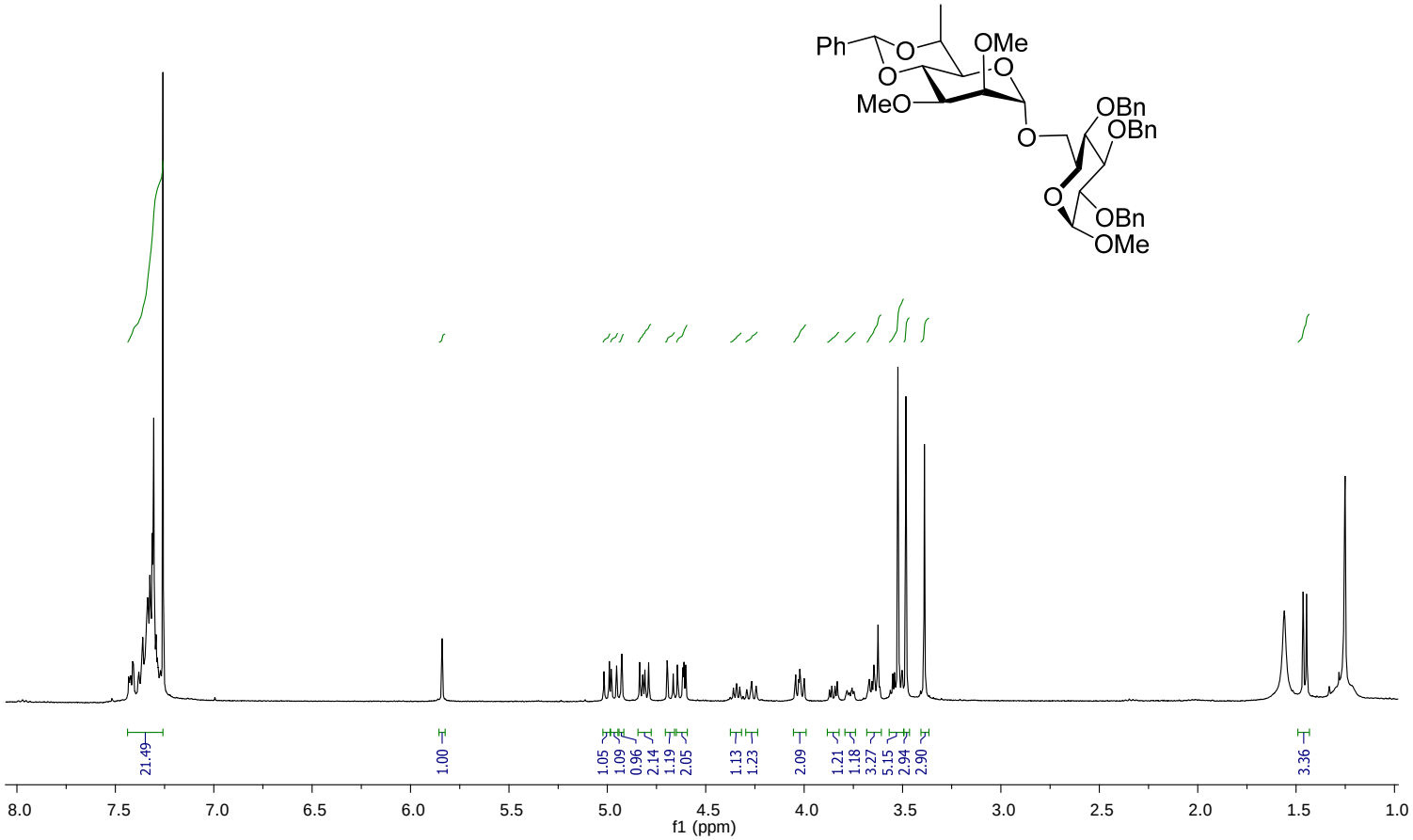
^{1}H NMR (400 MHz, $CDCl_3$) of Methyl 4,6-*O*-benzylidene-7-deoxy-2,3-di-*O*-methyl-L-*glycero*-β-D-*manno*hetpopyranosyl-(1→6)-2',3',4'-tri-*O*-benzyl-α-D-*gluco*pyranoside (45β)



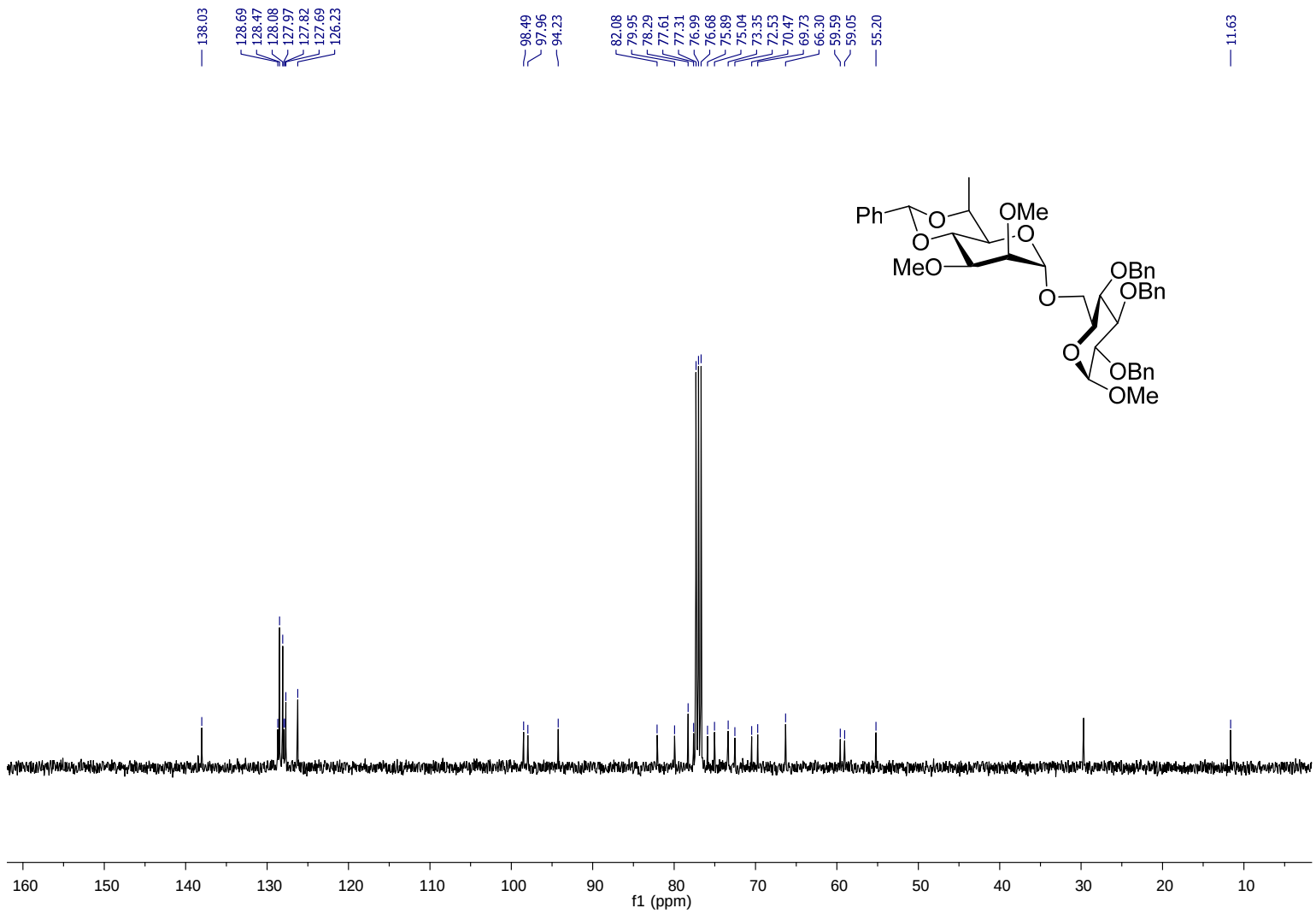
^{13}C NMR (100 MHz, $CDCl_3$) of Methyl 4,6-*O*-benzylidene-7-deoxy-2,3-di-*O*-methyl-L-*glycero*-β-D-*manno*hetpopyranosyl-(1→6)-2',3',4'-tri-*O*-benzyl-α-D-*gluco*pyranoside (45β)



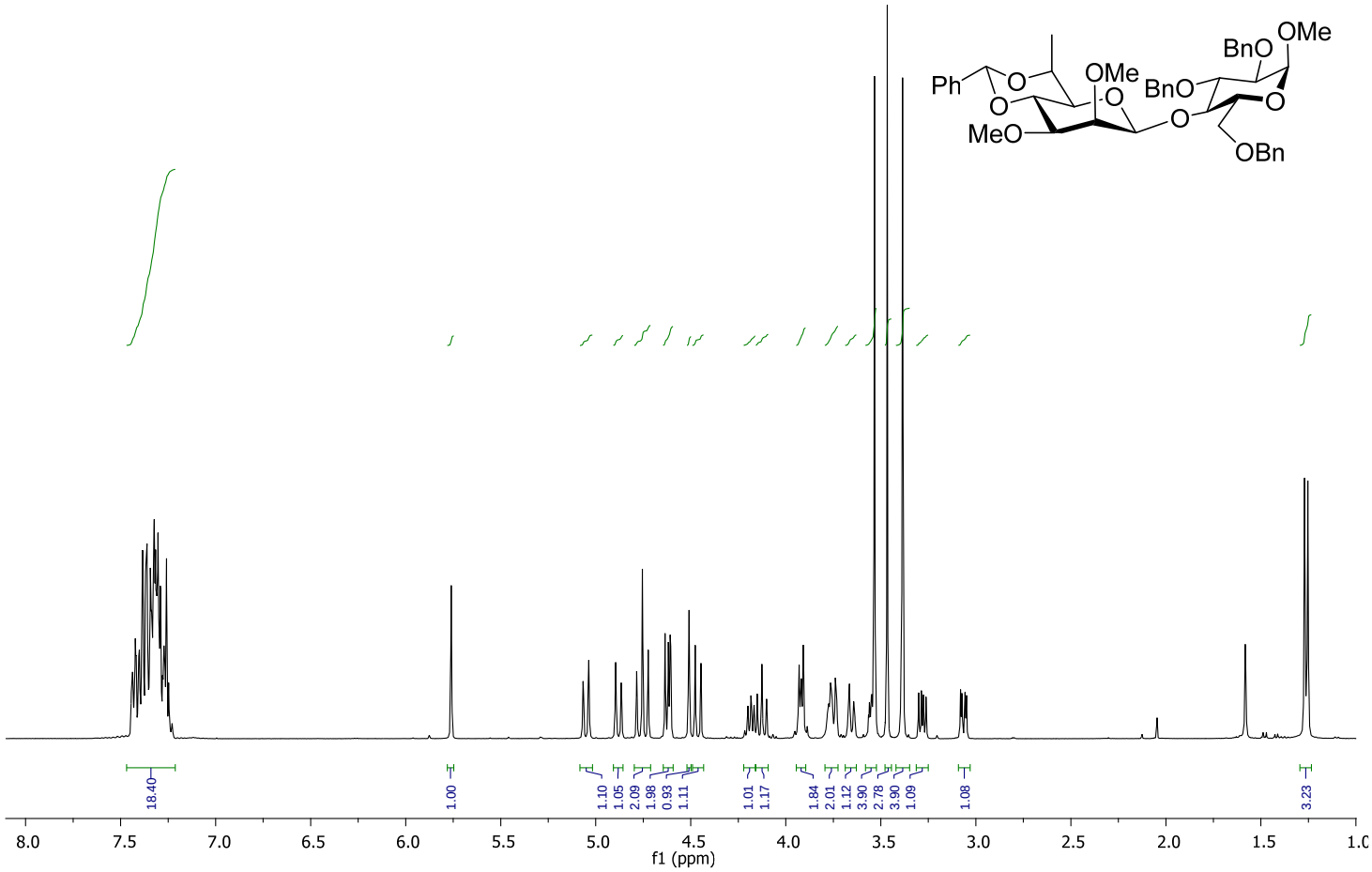
^{1}H NMR (400 MHz, $CDCl_3$) of Methyl 4,6-*O*-benzylidene-7-deoxy-2,3-di-*O*-methyl-L-*glycero*-α-D-*manno*hetpopyranosyl-(1→6)-2',3',4'-tri-*O*-benzyl-α-D-*gluco*pyranoside (45α)



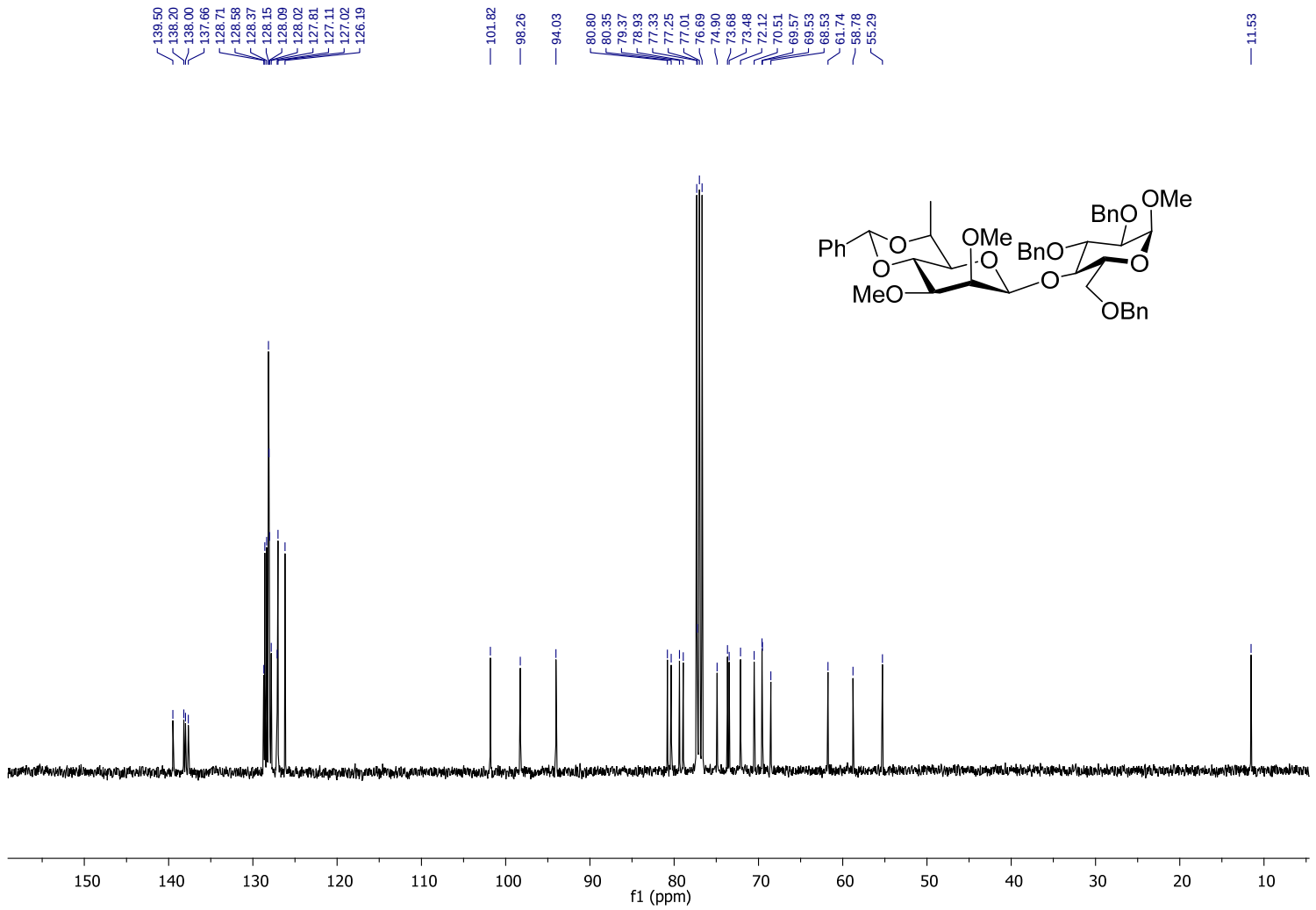
^{13}C NMR (100 MHz, $CDCl_3$) of Methyl 4,6-*O*-benzylidene-7-deoxy-2,3-di-*O*-methyl-L-*glycero*-α-D-*manno*hetpopyranosyl-(1→6)-2',3',4'-tri-*O*-benzyl-α-D-*gluco*pyranoside (45α)



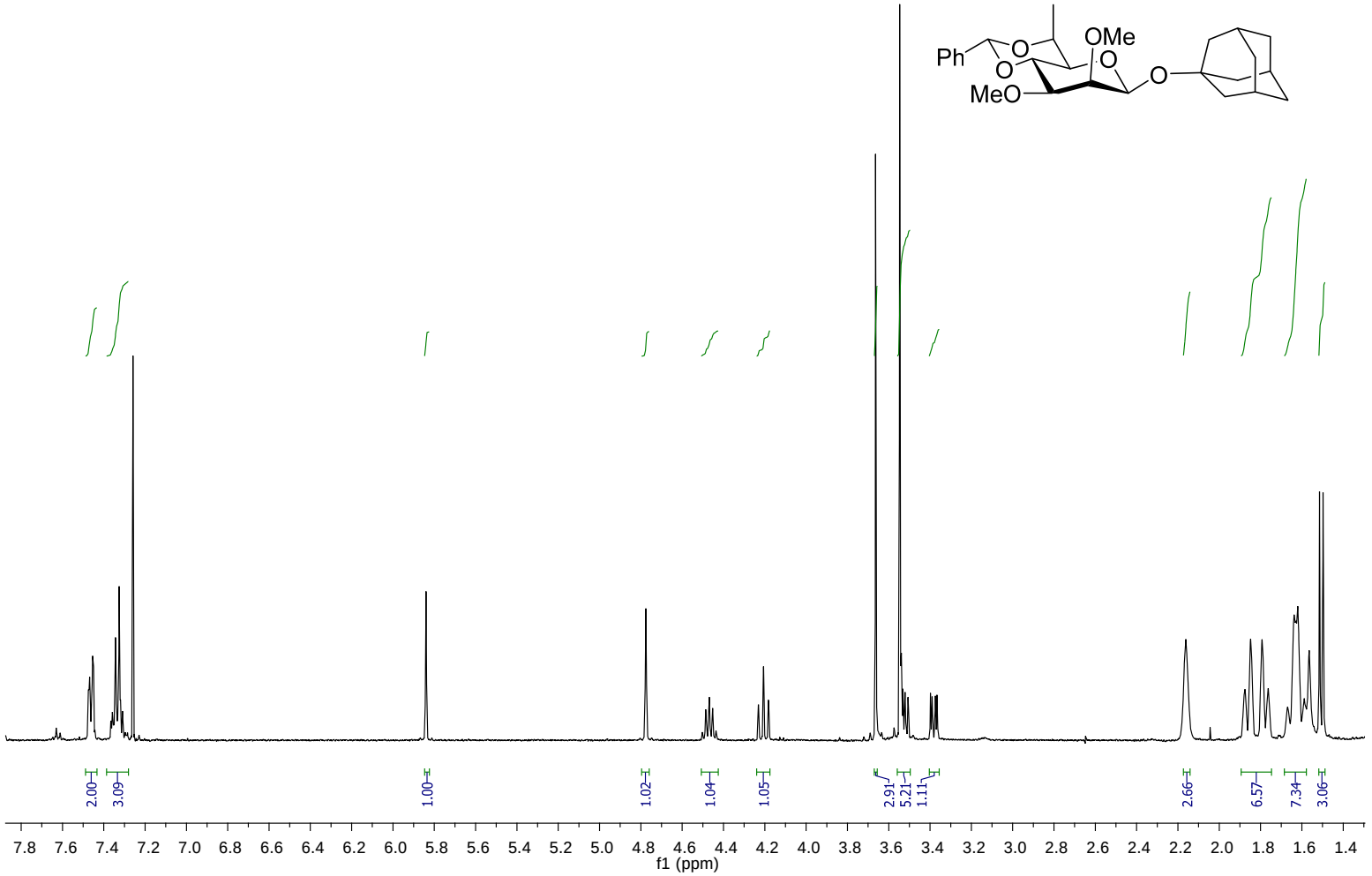
^{1}H NMR (400 MHz, $CDCl_3$) of Methyl 4,6-*O*-benzylidene-7-deoxy-2,3-di-*O*-methyl-L-*glycero*-β-D-*manno*hetpopyranosyl-(1→4)-2',3',6'-tri-*O*-benzyl-α-D-*gluco*pyranoside (46β)



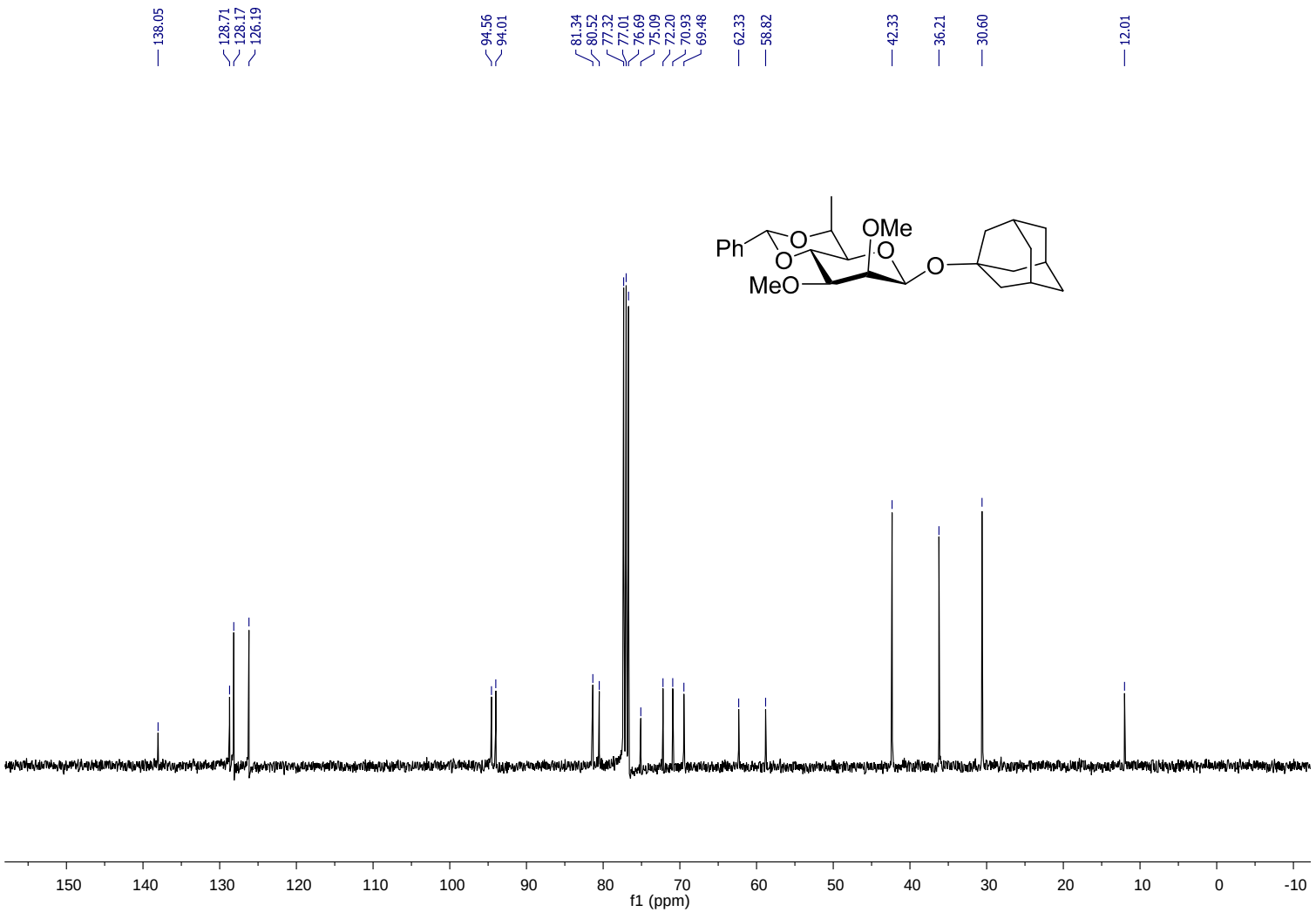
^{13}C NMR (100 MHz, $CDCl_3$) of Methyl 4,6-*O*-benzylidene-7-deoxy-2,3-di-*O*-methyl-L-*glycero*-β-D-*manno*hetpopyranosyl-(1→4)-2',3',6'-tri-*O*-benzyl-α-D-*gluco*pyranoside (46β)



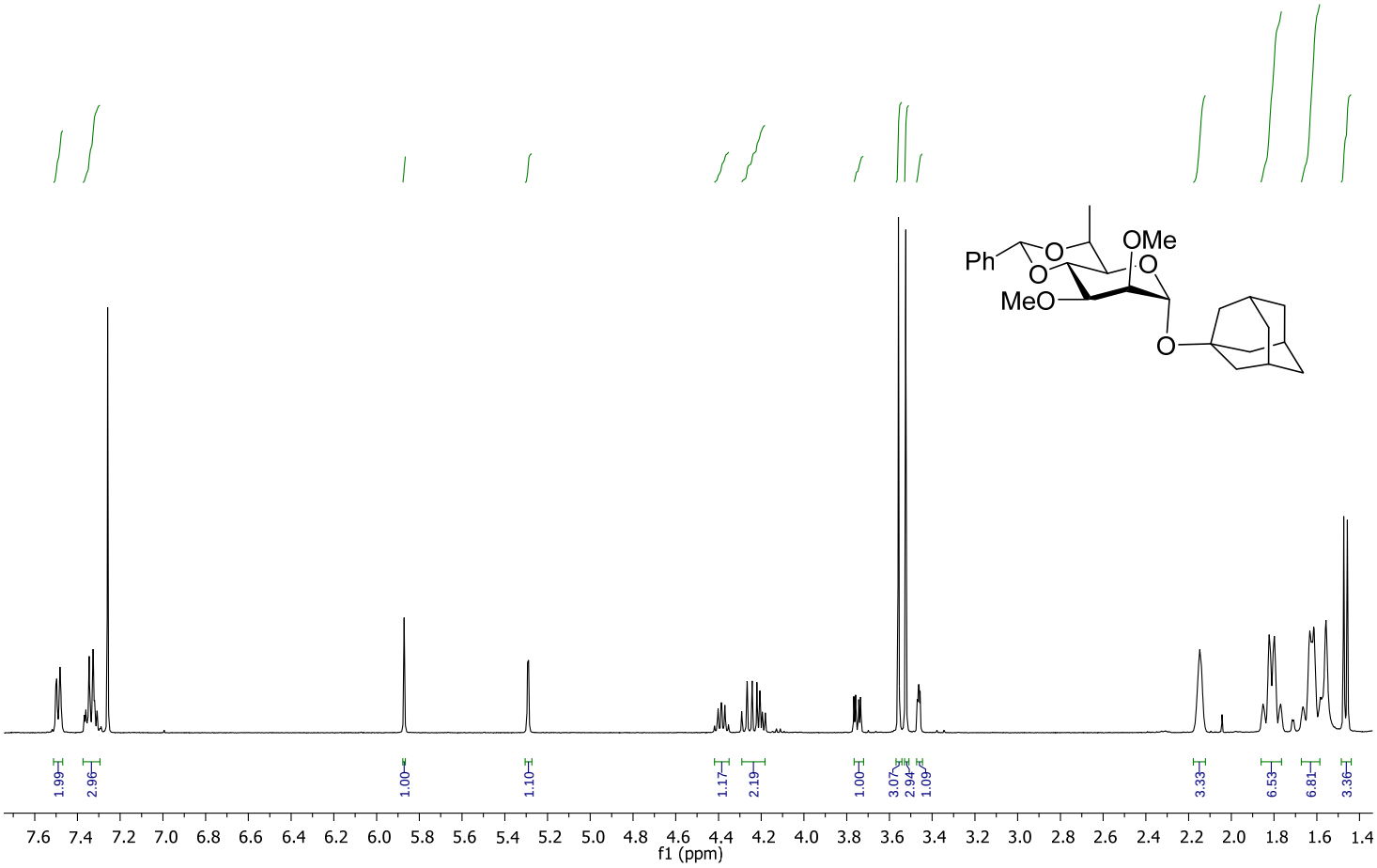
^{1}H NMR (400 MHz, $CDCl_3$) of (1-Adamantanyl) 4,6-*O*-benzylidene-7-deoxy-2,3-di-*O*-methyl-L-*glycero*-β-D-*manno*hetpopyranoside (47β)



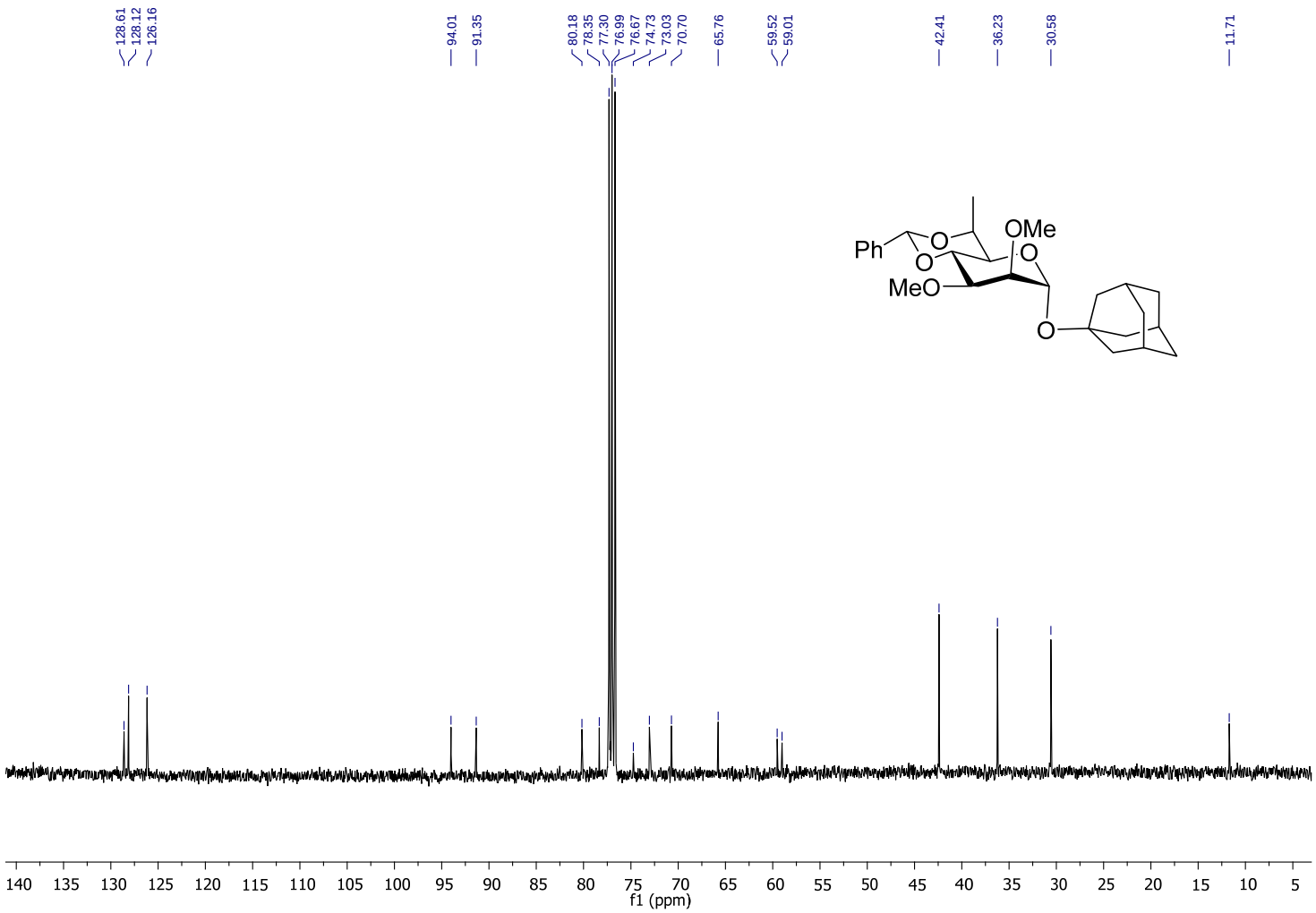
^{13}C NMR (100 MHz, $CDCl_3$) of (1-Adamantanyl) 4,6-*O*-benzylidene-7-deoxy-2,3-di-*O*-methyl-L-*glycero*-β-D-*manno*hetpopyranoside (47β)



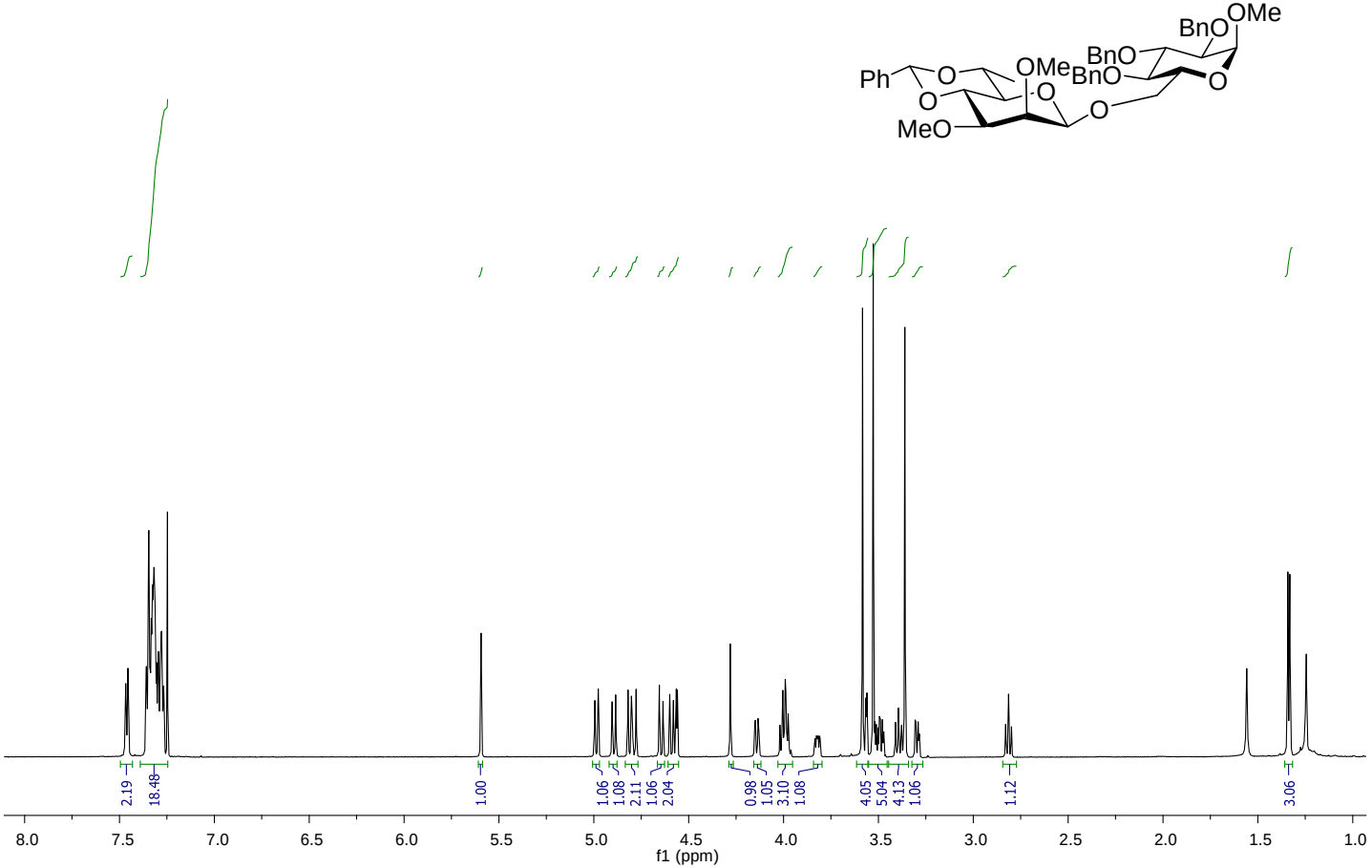
^{1}H NMR (400 MHz, $CDCl_3$) of (1-Adamantanyl) 4,6-*O*-benzylidene-7-deoxy-2,3-di-*O*-methyl-L-*glycero*-α-D-*manno*hetpopyranoside (47α)



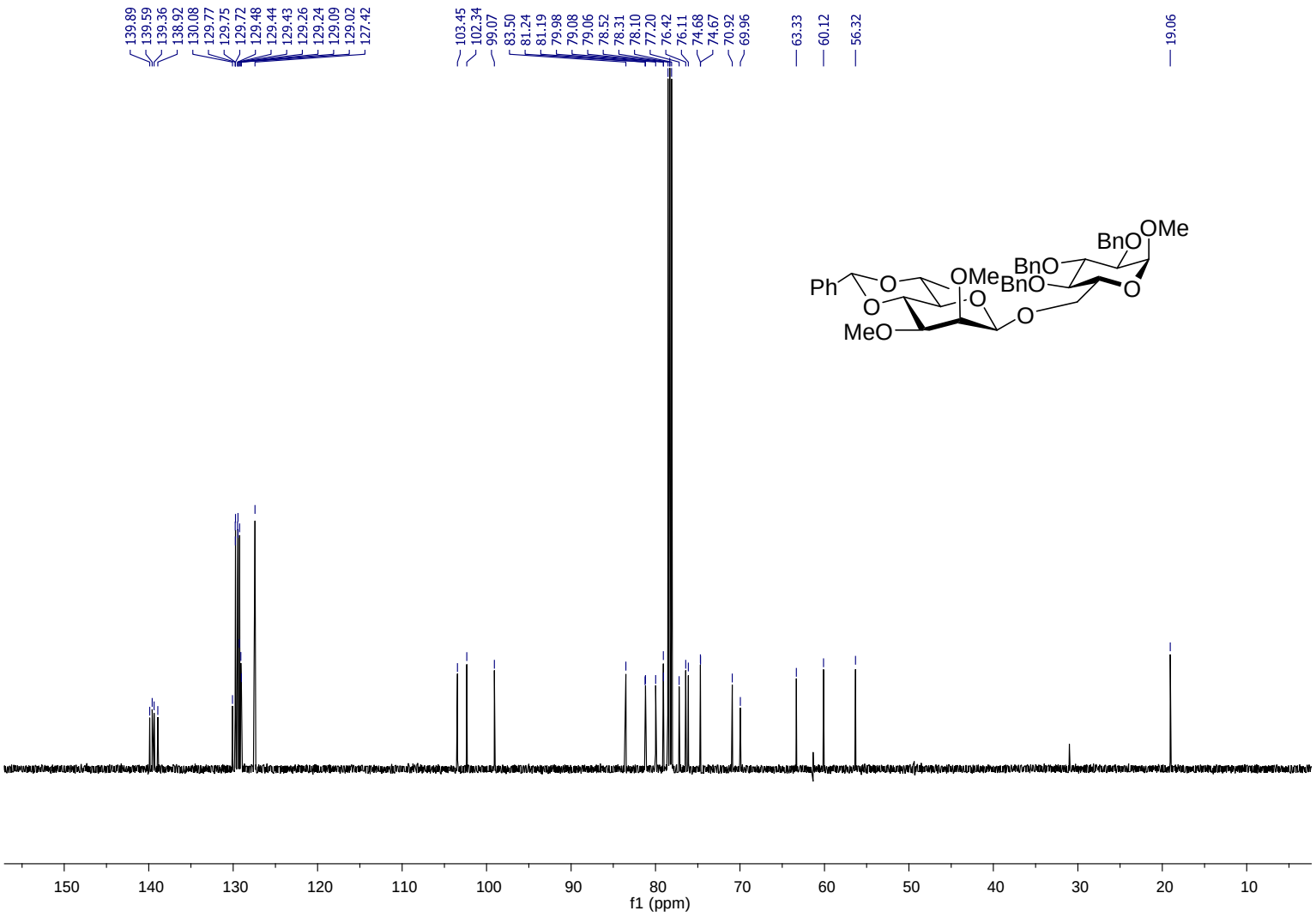
^{13}C NMR (100 MHz, $CDCl_3$) of (1-Adamantanyl) 4,6-*O*-benzylidene-7-deoxy-2,3-di-*O*-methyl-L-*glycero*-α-D-*manno*hetpopyranoside (47α)



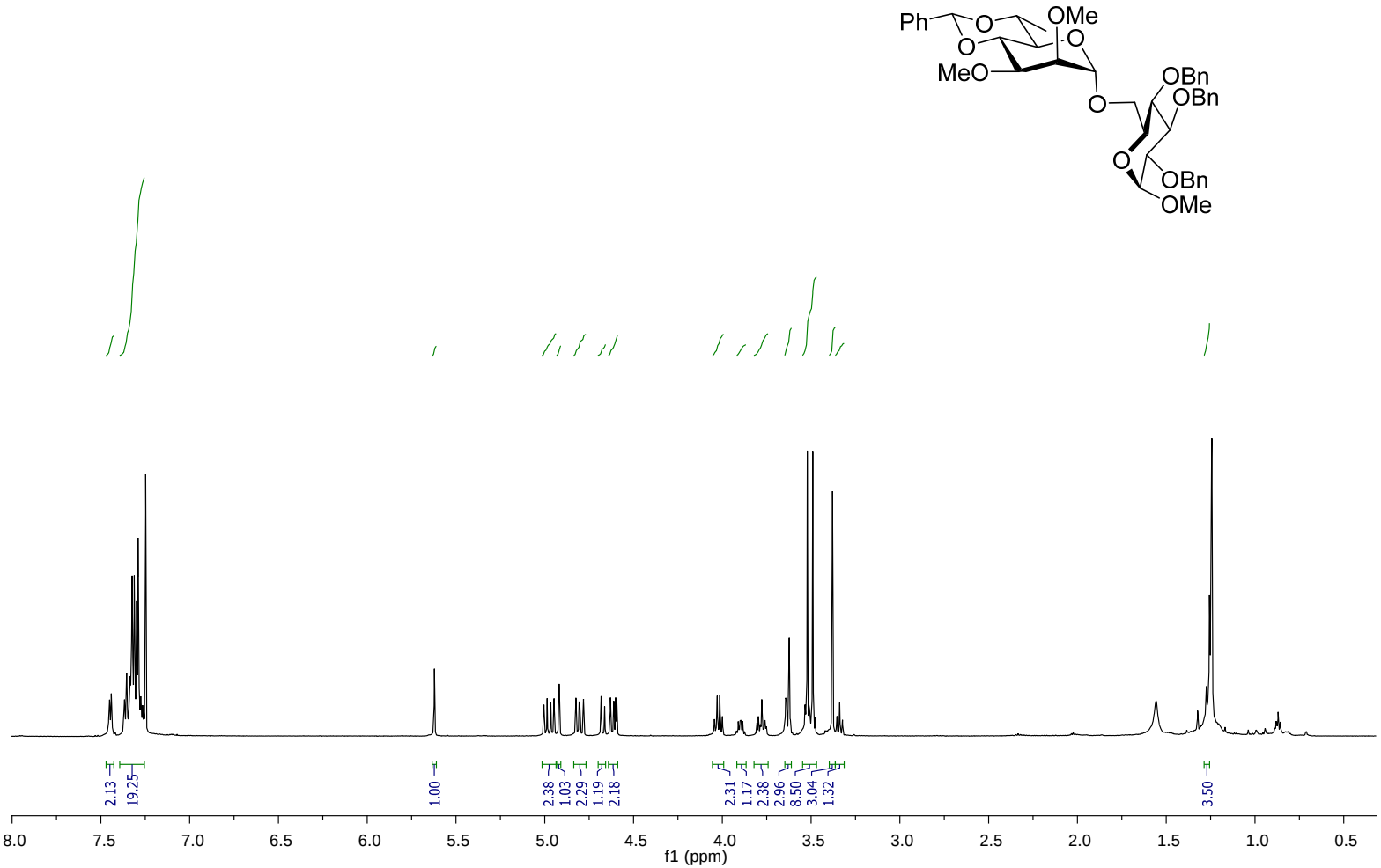
^{1}H NMR (600 MHz, $CDCl_3$) of Methyl 4,6-*O*-benzylidene-7-deoxy-2,3-di-*O*-methyl-D-*glycero*-β-D-*manno*hetpopyranosyl-(1→6)-2',3',4'-tri-*O*-benzyl-α-D-*gluco*pyranoside (48β)



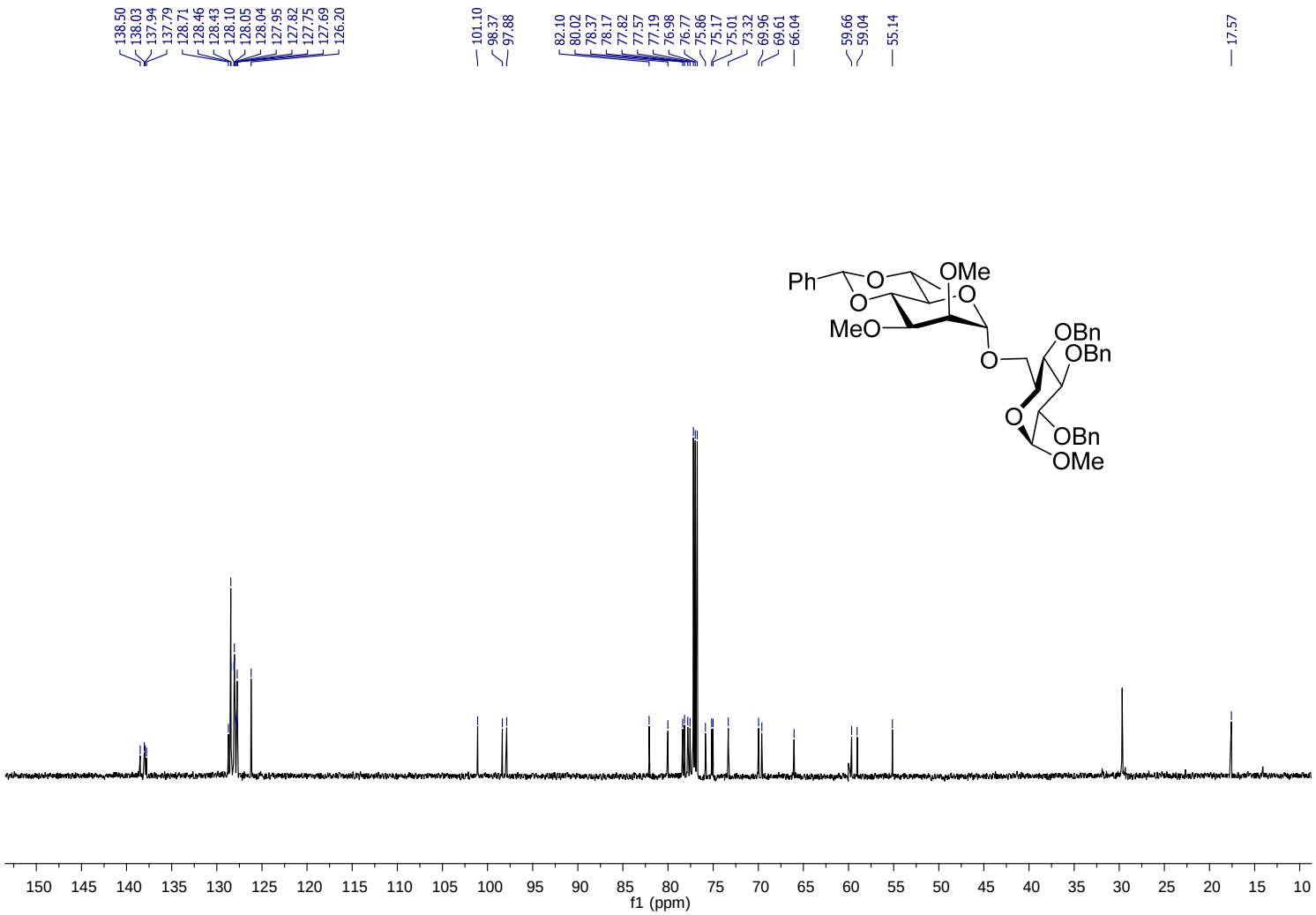
^{13}C NMR (150 MHz, $CDCl_3$) of Methyl 4,6-*O*-benzylidene-7-deoxy-2,3-di-*O*-methyl-D-*glycero*-β-D-*manno*hetpopyranosyl-(1→6)-2',3',4'-tri-*O*-benzyl-α-D-*gluco*pyranoside (48β)



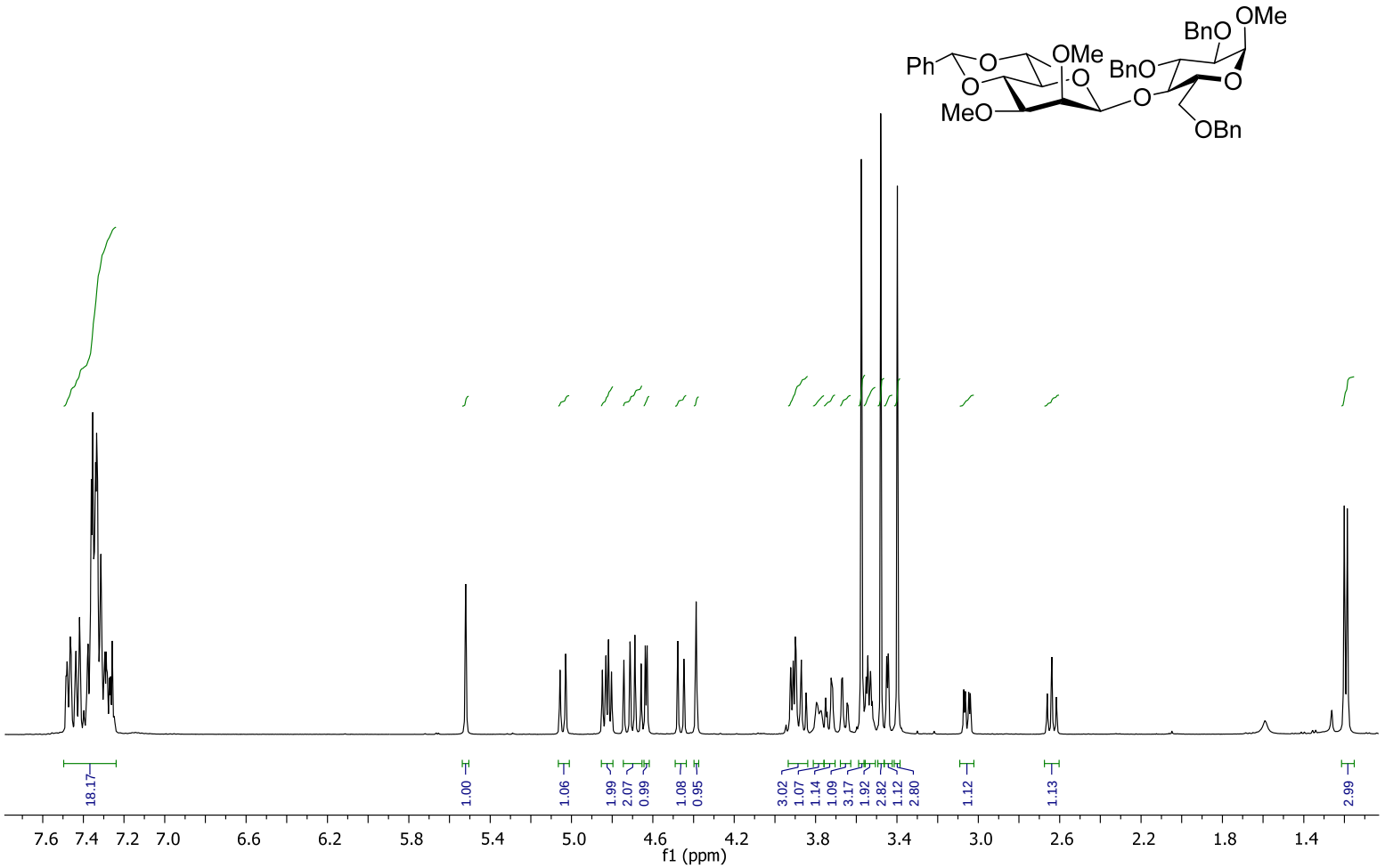
^{1}H NMR (600 MHz, $CDCl_3$) of Methyl 4,6-*O*-benzylidene-7-deoxy-2,3-di-*O*-methyl-D-*glycero*-α-D-*manno*hetpopyranosyl-(1→6)-2',3',4'-tri-*O*-benzyl-α-D-*gluco*pyranoside (48α)



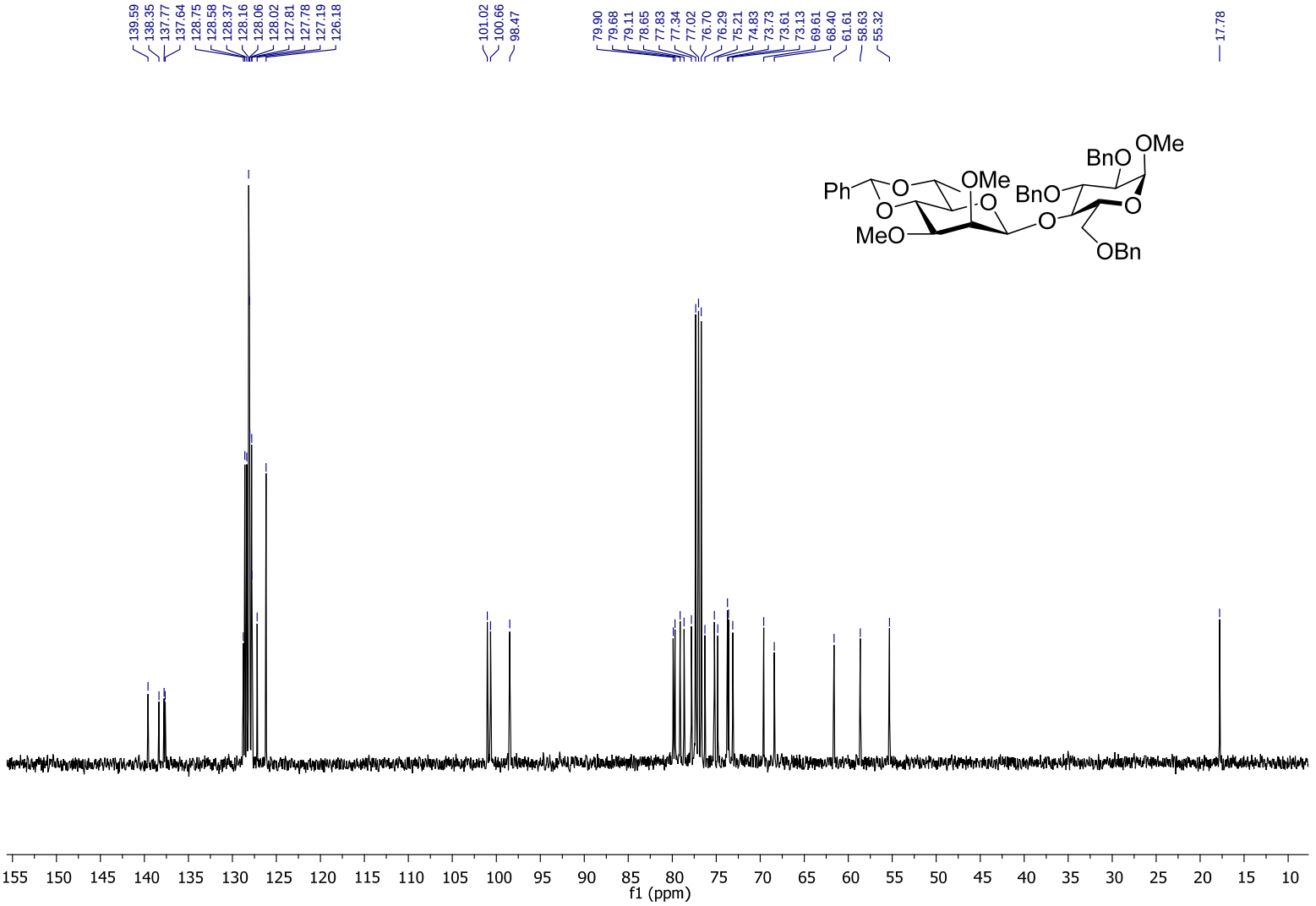
^{13}C NMR (150 MHz, $CDCl_3$) of Methyl 4,6-*O*-benzylidene-7-deoxy-2,3-di-*O*-methyl-D-*glycero*-α-D-*manno*hetpopyranosyl-(1→6)-2',3',4'-tri-*O*-benzyl-α-D-*gluco*pyranoside (48α)



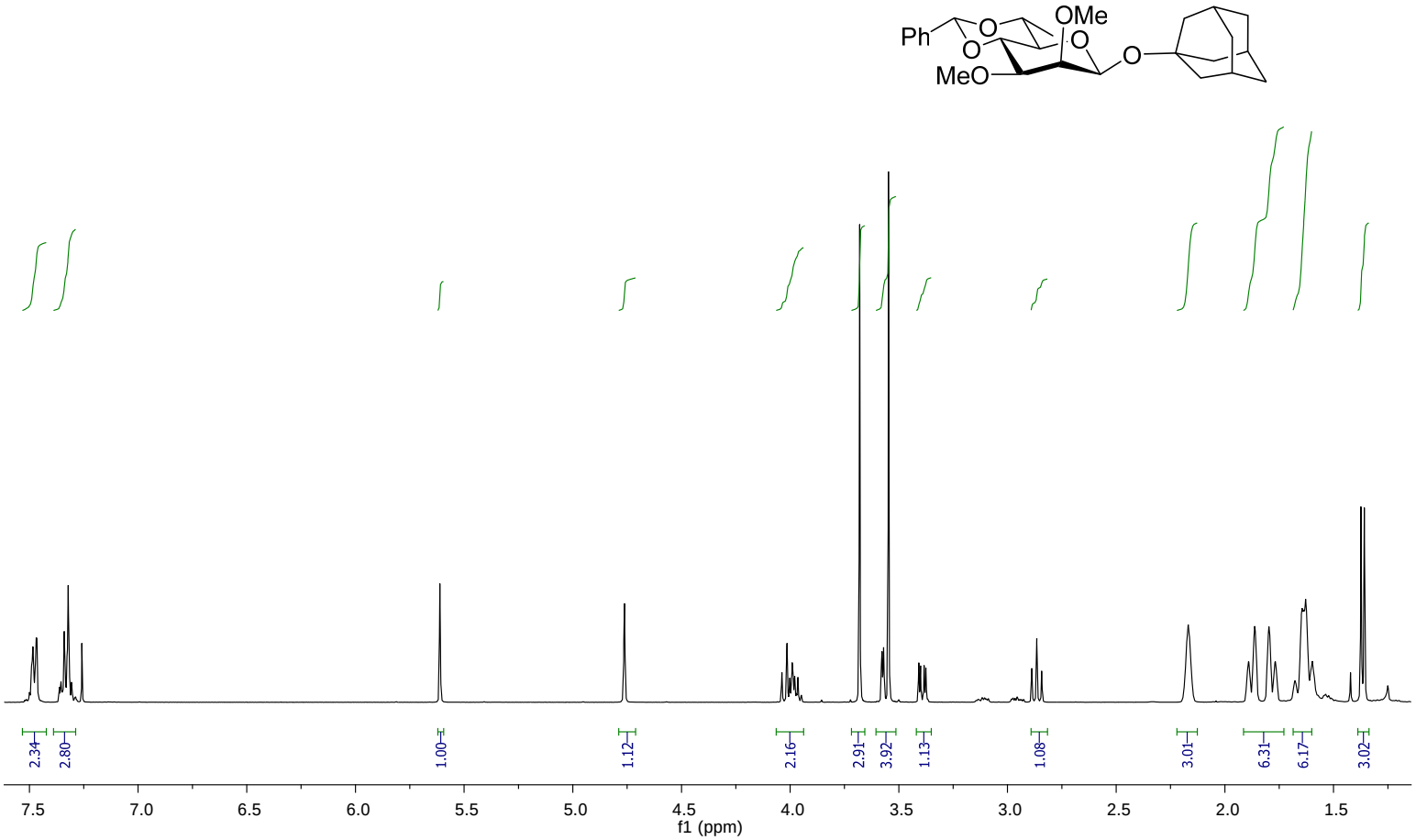
^{1}H NMR (400 MHz, $CDCl_3$) of Methyl 4,6-*O*-benzylidene-7-deoxy-2,3-di-*O*-methyl-D-*glycero*-β-D-*manno*hetpopyranosyl-(1→4)-2',3',6'-tri-*O*-benzyl-α-D-*gluco*pyranoside (49β)



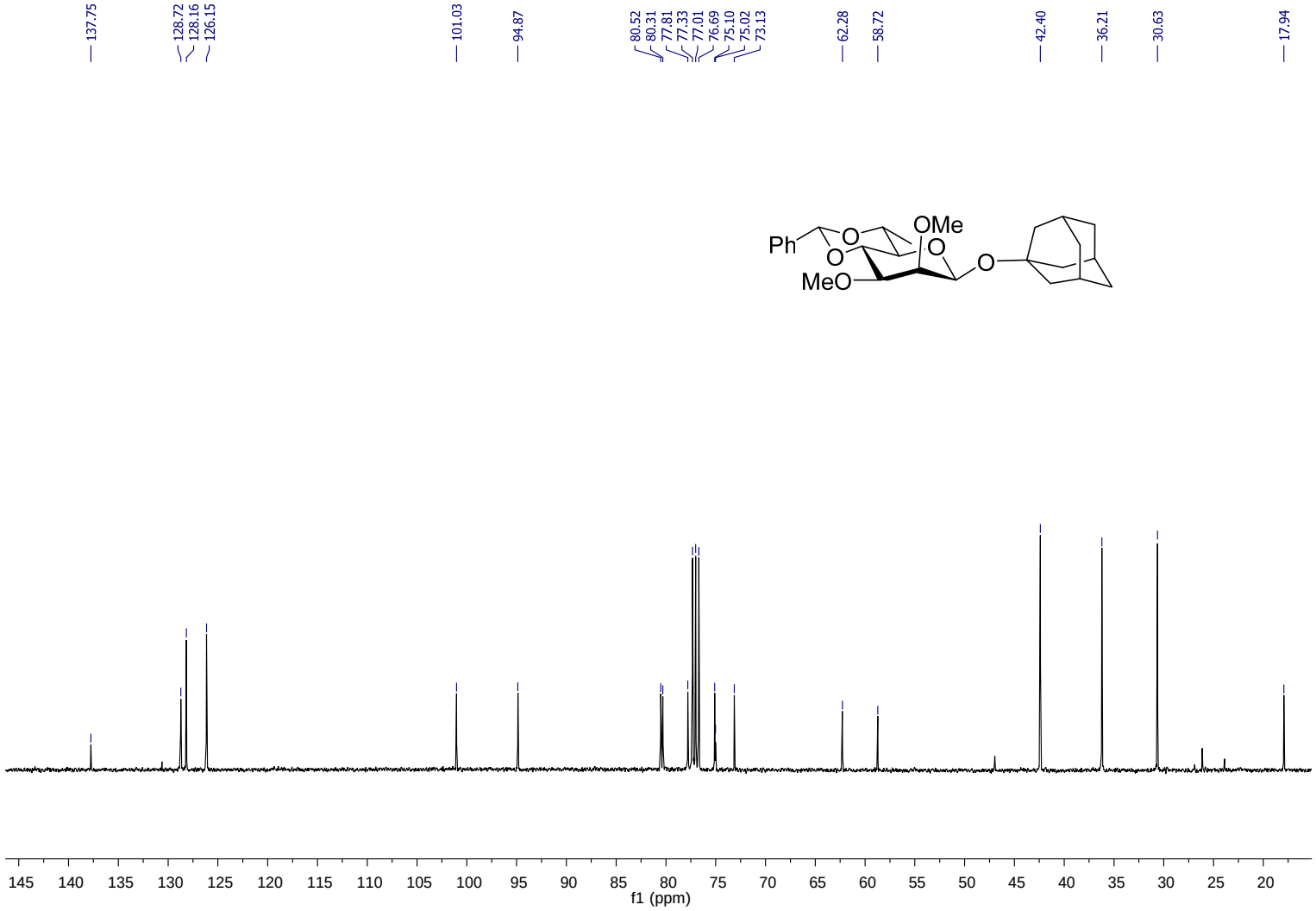
^{13}C NMR (100 MHz, $CDCl_3$) of Methyl 4,6-*O*-benzylidene-7-deoxy-2,3-di-*O*-methyl-D-*glycero*-β-D-*manno*hetpopyranosyl-(1→4)-2',3',6'-tri-*O*-benzyl-α-D-*gluco*pyranoside (49β)



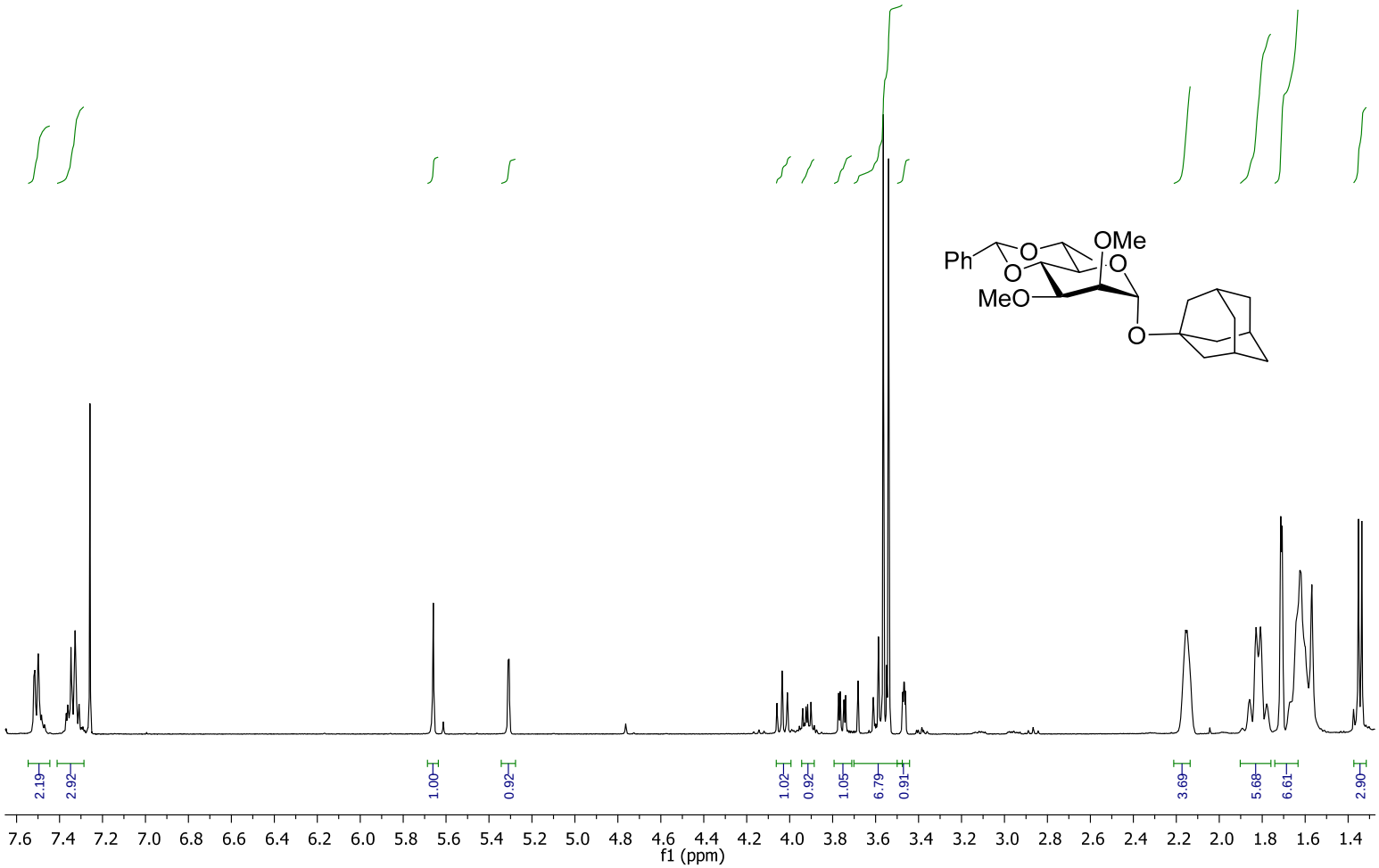
^{1}H NMR (400 MHz, $CDCl_3$) of (1-Adamantanyl) 4,6-*O*-benzylidene-7-deoxy-2,3-di-*O*-methyl-D-*glycero*-β-D-*manno*hetpopyranoside (50β)



^{13}C NMR (100 MHz, $CDCl_3$) of (1-Adamantanyl) 4,6-*O*-benzylidene-7-deoxy-2,3-di-*O*-methyl-D-*glycero*-β-D-*manno*hetpopyranoside (50β)



^{1}H NMR (400 MHz, $CDCl_3$) of (1-Adamantanyl) 4,6-*O*-benzylidene-7-deoxy-2,3-di-*O*-methyl-D-*glycero*-α-D-*manno*hetpopyranoside (50α)



^{13}C NMR (100 MHz, $CDCl_3$) of (1-Adamantanyl) 4,6-*O*-benzylidene-7-deoxy-2,3-di-*O*-methyl-D-*glycero*-α-D-*manno*hetpopyranoside (50α)