Cation Clock Permits Distinction Between the Mechanisms of α- and β-*O*- and β-*C*-Glycosylation in the Mannopyranose Series; Evidence for the Existence of a Mannopyranosyl Oxocarbenium Ion.

Min Huang[†], Pascal Retailleau[†], Luis Bohé[†], and David Crich*[,†,‡]

† Centre de Recherche de Gif, Institut de Chimie des Substances Naturelles, CNRS, Avenue de la Terrasse, 91190 Gif-sur-Yvette, France, and ‡ Department of Chemistry, Wayne State University, 5101 Cass Avenue Detroit, MI 48202, USA

Supporting Information

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General Methods:

Melting points were recorded with a Büchi Melting Point B-450 apparatus and are uncorrected. The reactions were monitored by TLC and high resolution LC/MS or UHPLC. Visualization was accomplished with UV light (at 254 nm) and exposure to sulfuric acid in ethanol (10:90, v/v), followed by heating. Purifications were performed on pre-packed silica gel columns (50 μm). Proton nuclear magnetic resonance (^{1}H) spectra were recorded with a Bruker Avance 500 (at 500 MHz) spectrometer; multiplicities are given as singlet (s), broad singlet (br s), doublet (d), doublet of doublets (dd), triplet of doublets (td), septuplet (sept), triplet (t), apparent triplet (at), septuplet (sept) or multiplet (m). Carbon nuclear magnetic resonance (^{13}C) spectra were recorded with Bruker Avance 500 (at 125 MHz). Residual solvent signals were used as an internal reference ($CDCl_3$: δ 7.26 ppm ^{1}H NMR, 77.16 ppm ^{13}C NMR) Specific optical rotations were measured on an Anton Paar MCP 300/500 polarimeter with a path length of 100 mm or 2 mm; concentrations are given in g/100 mL. High-resolution (HRMS) electrospray (ESI-TOF) mass spectra were recorded using a Micromass LCT (Waters) instrument. UHPLC analysis was performed on a waters Acquity instrument with a C18 HSS 1.8 μm column (2.1×150 mm) using H_2O/CH_3CN as eluent (Flow rate: 0.4 mL/min; Initial: H_2O 60/CH_3CN 40; 0.5 min: H_2O 60/CH_3CN 40; 12 min: H_2O 24/CH_3CN 76; 25 min: H_2O 0/CH_3CN 100), the apparatus was equipped with a TQ detector (a mass spectrometer detector), a PDA detector (UV) and an ELS detector (Evaporative Light Scattering Detector). Supercritical Fluid Chromatography (SFC) purification on a silica gel (grafted ethyl-pyridine, 60 Å) PRINCETON 5 μm column (10×250 mm, 40 °C) was carried out on a Waters Thar SFC investigator II instrument, which was equipped with a 2998 PDA detector. The pressure at the exit of the column was 150 Bar.

Phenyl 3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside 2 was prepared according to the literature protocols and gave spectra data consistent with the literature[1].

[1] (1) Oshitari, T.; Shibasaki, M.; Yoshizawa, T.; Tomita, M.; Takao, K.-i.; Kobayashi, S. *Tetrahedron* **1997**, *53*, 10993-11006.

Preparation of the glycosyl donnor Phenyl 2-*O*-allyl-[(2-trimethylsilyl)methyl]-3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-α-D-mannopyranosyl sulfoxide 4:

Phenyl 2-*O*-allyl-[(2-trimethylsilyl)methyl]-3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside 3:

To a stirred solution of phenyl 3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside **2** (0.80 g, 1.8 mmol) in anhydrous tetrahydrofuran (1.8 mL), 0.21 g of NaH (60 %) was added portion-wise at room temperature under argon. Twelve min later; 2-chloromethyl-3-trimethyl-silyl-1-propene (0.6 mL, 3.33 mmol) was added into the reaction mixture, which was stirred at 50 °C for 7 days. The mixture was diluted with *tert*-butylmethyl ether (TBME), washed with water, then with brine, and dried over Na_2SO_4. The organic layer was evaporated under reduced pressure. The crude product (1.21 g, dark yellow oil) was purified by flash chromatography on pre-packed silica columns (80 g, 50 μm) with a gradient (AcOEt/Heptane: 0/100 (+1% Et_3N) to AcOEt/Heptane: 50/50 (+0% Et_3N)), to give compound **3** as a pale yellow oil (0.49 g, 47%); $[\alpha]_D^{25}$ +107.8 (*c* = 1, $CHCl_3$); R_f = 0.6 (AcOEt/Heptane, 20/80); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29-7.54 (m, 15 H), 5.66 (s, 1H), 5.56 (d, *J* = 1 Hz, 1H), 4.96 (br s, 1H), 4.89 and 4.75 (AB, *J* = 12.1 Hz, 2H), 4.74 (s, 1H), 4.28-4.33 (m, 2H), 4.22-4.25 (m, 1H), 4.07-3.97 (m, 4H), 3.88-3.92 (m, 1H), 1.58 (s, 2H), 0.02 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.6, 138.6, 137.8, 134.0, 131.8, 129.3, 129.0, 128.5, 128.3, 127.83, 127.76, 127.73,126.2; 110.6, 101.6, 87.2, 79.3, 78.1, 76.3, 75.4, 73.3, 68.7, 65.6, 23.1, –1.3; HRMS (ESI): $[M+NH_4]^+$ calcd for $C_{33}H_{44}NO_5SiS$: 594.2709; found: 594.2726.

Phenyl 2-*O*-allyl-[(2-trimethylsilyl)methyl]-3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-α-D-mannopyranosyl sulfoxide 4:

To a stirred solution of phenyl 2-*O*-allyl-[(2-trimethylsilyl)methyl]-3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside **3** (0.48 g, 0.84 mmol) in anhydrous dichloromethane (21 mL), *m*-CPBA (0.18 g, 0.80 mmol, 77%) was added portion-wise at −78 °C under argon. After 3 h the reaction mixture was neutralized with saturated aqueous $NaHCO_3$ (2 mL) and then warmed up to room temperature. The mixture was extracted twice with dichloromethane; all combined organic phases were washed with brine, dried over Na_2SO_4, filtered, the organic layer was evaporated under reduced pressure. The crude product (0.52 g, pale yellow oil) was purified by flash chromatography on pre-packed silica columns (40 g, 50 μm) with a gradient (AcOEt/Heptane: 0/100 (+1% Et_3N) to AcOEt/Heptane: 15/85 (+1% Et_3N), to give the compound **4** as a pale yellow oil (0.40 g, 81%); $[\alpha]_D^{25}$ −46.3 (*c* = 1,

$CHCl_3$); R_f = 0.3 (AcOEt/Heptane, 20/80); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29-7.60 (m, 15 H), 5.65 (s, 1H), 4.91 and 4.77 (AB, *J* = 12.0 Hz, 2H), 4.73 (d, *J* = 1.3 Hz, 1H), 4.59 (s, 1H), 4.53 (s, 1H), 4.31-4.33 (m, 3H), 4.25 (dd, *J* = 4.9 Hz, 10.3 Hz, 1H), 4.16-4.11 (m, 1H), 3.94 (d, *J* = 12.7 Hz, 1H), 3.77 and 3.87 (AB, *J* = 12.7 Hz, 2H), 1.44 (s, 2H), −0.03 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.1, 141.9, 138.5, 137.4, 131.7, 129.5, 129.1, 128.4, 128.3, 128.0, 127.7, 126.2, 124.5, 110.8, 101.7, 98.0, 78.3, 76.5, 76.0, 73.5, 72.7, 70.2, 68.4, 23.1, –1.3; HRMS (ESI): $[M+H]^+$ calcd for $C_{33}H_{41}O_6SiS$: 593.2393; found: 593.2402.

Preparation of compounds 5 and 6:

Phenyl 2-*O*-allyl-[(2-trimethylsilyl)-methyl]-3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-α-D-mannopyranosyl sulfoxide **4** (0.062 g, 0.11 mmol) and anhydrous TTBP (0.11 g, 0.42 mmol) were dissolved in freshly distilled dichloromethane (5 mL) in a Schlenk tube under argon. Freshly activated molecular sieves (*ca.* 0.15 g, 4 Å, powdered) were added. The mixture was vigorously stirred and then cooled to –72 °C before freshly distilled triflic anhydride (27 µL, 0.16 mmol) was added in one portion. The reaction mixture was stirred for a further 2.5 h at that temperature, and then a saturated aqueous $NaHCO_3$ (1 mL) was added to quench the reaction at –72 °C. The mixture was stirred again for a further 1 h at –72 °C, then warmed to room temperature. It was diluted with dichloromethane, and washed with saturated aqueous $NaHCO_3$ and brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude mixture (0.22 g, white solid) was purified by flash chromatography on pre-packed silica column (12 g, 50 µm) with a gradient (AcOEt/Heptane: 1/99 to AcOEt/Heptane: 25/75, to give the compound **5** as white solid (0.019 g, 45%) and the compound **6** as colorless needles (0.010 g, 25%).

(1S)-1,5-Anhydro-3-*O*-benzyl-4,6-*O*-benzylidene-1-*C*,2-*O*-(3-methylenetetrahydro-2H-pyran)-D-mannitol 5:

mp 150-152 °C (from MeOH/TBME); $[\alpha]_D^{25}$ –25 (*c* = 1, $CHCl_3$); R_f = 0.15 (AcOEt/Heptane, 20/80); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28-7.51 (m, 10 H), 5.61 (s, 1H), 4.94 (s, 1H), 4.89 and 4.81 (AB, *J* = 12.8 Hz, 2H), 4.87 (s,1H), 4.38 and 4.00 (AB, *J* = 12.5 Hz, 2H), 4.27 (dd, *J* = 4.9 Hz, 10.4 Hz, 1H), 4.17 (t, *J* = 9.5 Hz, 1H), 3.86 (t, *J* = 10.4 Hz, 1H), 3.77 (d, *J* = 3.3 Hz, 1H), 3.68 (dd, *J* = 3.3 Hz, *J* = 9.7 Hz, 1H), 3.63-3.62 (m, 1H), 3.39 (td, *J* = 4.9 Hz, 9.8 Hz, 1H), 2.56 (dt, *J* = 14.9 Hz, 1H), 2.41 (dd, *J* = 14.9 Hz, 2.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.1, 138.6, 137.9, 129.0, 128.5, 128.4, 128.1, 127.8, 126.2, 112.1, 101.5, 78.9,

75.8, 74.2, 72.7, 72.3, 71.9, 68.8, 36.6; HRMS (ESI): $[M+NH_4]^+$ calcd for $C_{24}H_{30}NO_5$: 412.2124; found: 412.2105.

(1R)-1,5-Anhydro-3-*O*-benzyl-4,6-*O*-benzylidene-1-*C*,2-*O*-(3-methylenetetrahydro-2H-pyran)-D-mannitol 6:

mp 130-132 °C (from MeOH/TBME); $[\alpha]_D^{25}$ –35 (*c* = 0.5, $CHCl_3$); R_f = 0.31 (AcOEt/Heptane, 20/80); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27-7.46 (m, 10 H), 5.47 (s, 1H), 4.94 and 4.74 (AB, *J* = 12.4 Hz, 2H), 4.93 (br s, 1H), 4.91 (br s, 1H), 4.30 (dd, *J* = 4.8 Hz, 10.5 Hz), 4.28 (d, *J* = 12.4 Hz, 1H), 4.11 (at, *J* = 5.4 Hz, 1H), 4.07 (dd, *J* = 5.1 Hz, 10.7 Hz, 1H), 3.93-3.98 (m, 2H), 3.85 (d, *J* = 5.83 Hz, 10.5 Hz, 1H), 3.79 (td, *J* = 4.9 Hz, 10.1 Hz, 1H), 3.59 (at, *J* = 10.0 Hz, 1H), 2.78 (dd, *J* = 5.0 Hz, 13.1 Hz, 1H), 2.22 (at, *J* = 11.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.3, 138.8, 137.4, 129.1, 128.4, 127.9, 127.6, 126.2, 112.6, 101.3, 83.1, 76.4, 75.5, 73.6, 72.2, 70.7, 68.5, 63.6, 39.6; HRMS (ESI): $[M+NH_4]^+$ calcd for $C_{24}H_{30}NO_5$: 412.2124; found: 412.2119.

General procedure for cyclization and *O*-glycosylation competition reactions (Table 1):

Freshly activated molecular sieves (*ca.* 0.15 g, 4 Å, powdered) and distilled 1-octene (10 equiv) were added to the phenyl 2-*O*-allyl-[(2-trimethylsilyl)-methyl]-3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-α-D-mannopyranosyl sulfoxide **4** (0.017 M) and anhydrous TTBP (4 equiv) in freshly distilled dichloromethane under argon. The mixture was vigorously stirred and then cooled to –72 °C before freshly distilled triflic anhydride (1.2 equiv) was added in one portion. After 5 min, freshly distilled isopropanol (0.8-10 equiv) was added. The reaction mixture was stirred for a further 2.5 h at that temperature, and then a small sample (5-10 μL) was withdrawn (with a micro-syringe) and then dissolved in acetonitrile for UHPLC analysis before saturated aqueous $NaHCO_3$ (1 mL) was added to quench the reaction at –72 °C. The mixture was stirred again for a further 1 h at this temperature, and then warmed to room temperature. It was diluted with dichloromethane, and washed with saturated aqueous $NaHCO_3$ and with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on pre-packed silica columns.

Isolation of compounds 9 and 10: example of entry 3 in Table 1

According to general procedure described above, sulfoxide **4** (0.088 g, 0.15 mmol), TTBP (0.15 g, 0.60 mmol), 1-octene (0.25 mL, 1.59 mmol), triflic anhydride (30 μL, 0.18 mmol)

and isopropanol (17.5 μL, 0.23 mmol) gave, after purification by flash chromatography on pre-packed silica column (25 g, 50 μm) with a gradient (AcOEt/Heptane: 0/100 (+1% Et_3N) to AcOEt/Heptane: 50/50 (+0% Et_3N), the two diastereoisomers **9** and **10** as a colorless oils (0.033 g, 42%). A portion of this mixture was separated to obtain samples of the pure anomers by Supercritical Fluid Chromatography (SFC) using isopropanol (5%) as co-solvent, to give the analytical samples.

Isopropyl 2-*O*-allyl-[(2-trimethylsilyl)methyl]-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranoside 9:

$[\alpha]_D^{28}$ –40 (*c* = 1, $CHCl_3$); R_f = 0.45 (AcOEt/Heptane, 20/80); colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27-7.50 (m, 10 H), 5.61 (s, 1H), 5.05 (br s, 1H), 4.80 and 4.74 (AB, *J* = 12.4 Hz, 2H), 4.73 (br s, 1H), 4.53 (s, 1H), 4.16-4.30 (m, 4H), 3.98 (sept, *J* = 6.2 Hz, 1H), 3.94 (at, *J* = 10.3 Hz, 1H), 3.86 (d, *J* = 2.8 Hz, 1H), 3.60 (dd, *J* = 3.1 Hz, 10.0 Hz, 1H), 3.31 (td, *J* = 4.8 Hz, 9.8 Hz, 1H), 1.68 and 1.63 (AB, *J* = 13.7 Hz, 2H), 1.24 (d, *J* = 6.2 Hz, 1H), 1.16 (d, *J* = 6.2 Hz, 1H), 0.01 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.4, 138.7, 137.9, 128.9, 128.4, 128.3, 127.8, 127.6, 126.2, 110.7, 101.5, 100.3, 78.8, 78.4, 77.1, 76.4, 72.6, 71.4, 68.9, 67.8, 23.7, 23.2, 21.8, –1.2; HRMS (ESI): $[M+NH_4]^+$ calcd for $C_{30}H_{46}NO_6Si$: 544.3094; found: 544.3109.

Isopropyl 2-*O*-allyl-[(2-trimethylsilyl)methyl]-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside 10:

$[\alpha]_D^{28}$ +60 (*c* = 1, $CHCl_3$); R_f = 0.52 (AcOEt/Heptane, 20/80); colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29-7.50 (m, 10 H), 5.64 (s, 1H), 4.95 (br s, 1H), 4.93 (d, *J* = 1.2 Hz, 1H), 4.86 and 4.71 (AB, *J* = 12.1 Hz, 2H), 4.73 (br s, 1H), 4.18-4.24 (m, 2H), 4.03-4.12 (AB, *J* = 13.0 Hz, 2H), 3.97 (dd, *J* = 3.2 Hz, 10.0 Hz, 1H), 3.90 (sept, 6.2 Hz, 1H), 3.87-3.85 (m, 1H), 3.75 (dd, *J* = 3.0 Hz, 1.6 Hz, 2H), 1.56 (br s, 1H), 1.20 (d, *J* = 6.2 Hz, 1H), 1.13 (d, *J* = 6.2 Hz, 1H), 0.01 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.1, 139.1, 137.9, 128.9, 128.4, 128.3, 127.6, 127.5, 126.2, 110.3, 101.5, 97.6, 79.6, 77.1, 76.7, 76.0, 73.4, 69.4, 69.1, 64.4, 23.4, 23.1, 21.4, –1.2; HRMS (ESI): $[M+Na]^+$ calcd for $C_{30}H_{42}O_6NaSi$: 549.2648; found: 549.2656.

General procedure for cyclization and *C*-glycosylation competition reactions (Table 2):

Freshly activated molecular sieves (*ca.* 0.15 g, 4 Å, powdered), anhydrous methallyltrimethylsilane (2-30 equiv) and anhydrous triphenylmethane (0.1-0.3 equiv) were

added.to the phenyl 2-*O*-allyl-[(2-trimethylsilyl)-methyl]-3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-α-D-mannopyranosyl sulfoxide **4** (0.017 M) and anhydrous TTBP (4 equiv) in freshly distilled dichloromethane under argon. The mixture was vigorously stirred and then cooled to –72 °C before freshly distilled triflic anhydride (1.2 equiv) was added in one portion. The reaction mixture was stirred for a further 2.5 h at that temperature, and then a small sample (5-10 μL) was withdrawn (with a micro-syringe) and then dissolved in acetonitrile for UHPLC analysis before saturated aqueous $NaHCO_3$ (1 mL) was added to quench the reaction at –72 °C. The mixture was stirred again for a further 1 h at this temperature, and then warmed to room temperature. It was diluted with dichloromethane, and washed with saturated aqueous $NaHCO_3$ and with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude mixture was purified to flash chromatography on pre-packed silica columns.

Isolation of compound 11: example of entry 5 in Table 2

According to general procedure described above, sulfoxide **4** (0.041 g, 0.07 mmol), TTBP (0.072 g, 0.29 mmol), triphenylmethane (5 mg, 0.02 mmol), methallyltrimethylsilane (182 μL, 1.04 mmol) and triflic anhydride (14 μL, 0.083 mmol) gave, after purification by flash chromatography on pre-packed silica column (12 g, 50 μm) with a gradient (AcOEt/Heptane: 0/100 (+1% Et_3N) to AcOEt/Heptane: 20/80 (+1% Et_3N), compound **11** as colorless oil (0.0102 g, 28%).

1,5-Anhydro-2-*O*-allyl-[(2-trimethylsilyl)methyl]-3-*O*-benzyl-4,6-*O*-benzylidene-1-methallyl-β-D-mannitol 11:

$[\alpha]_D^{25}$ –35 (*c* = 1, $CHCl_3$); R_f = 0.61 (AcOEt/Heptane, 20/80); colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27-7.51 (m, 10 H), 5.63 (s, 1H), 4.98-4.99 (m, 1H), 4.88 and 4.73 (AB, *J* = 12.4 Hz, 2H), 4.81 (m, 1H), 4.76 (m, 1H), 4.70 (m, 1H), 4.38 and 3.95 (AB, *J* = 12.4 Hz, 2H), 4.27 (dd, *J* = 4.9 Hz, 10.4 Hz, 1H), 4.19 (at, *J* = 9.4 Hz, 1H), 3.84 (at, *J* = 10.3 Hz, 1H), 3.70 (m, 1H), 3.68-3.69 (m, 1H), 3.59 (at, *J* = 6.7 Hz, 1H), 3.37 (td, *J* = 4.9 Hz, 9.8 Hz, 1H), 2.44 and 2.33 (ABX, J_{AB} = 14.4 Hz, J_{AX} = 7.3 Hz, J_{BX} = 5.9 Hz, 2H), 1.75 (s, 3H), 1.55-1.61 (AB, *J* = 13.7 Hz, 2H), 0.01 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.2, 142.3, 138.9, 138.0, 128.9, 128.5, 128.3, 127.6, 126.2, 112.9, 109.6, 101.5, 80.8, 79.7, 78.6, 77.6, 77.4, 73.1, 72.1, 69.0, 39.4, 23.7, 23.1, –1.2; HRMS (ESI): $[M+H]^+$ calcd for $C_{31}H_{43}O_5Si$: 523.2880; found: 523.2882. Anal. Calcd for $C_{31}H_{42}O_5Si$: C, 71.23; H, 8.10. Found: C, 71.23; H, 8.19. The stereochemistry at C_1 in **11** is assigned by Noesy, H_1 and H_2 correlation was observed.

Glycoside to cyclized products ratio determination:

Molar ratios in Figure S1 were determined by UHPLC/UV/MS at 205 nm by integration of the peaks of **5** (t_r: 8.13 min), **6** (t_r: 10.50 min), **9** (t_r: 18.31 min), **10** (t_r: 19.38 min) and **11** (t_r: 19.64 min) with triphenylmethane as an internal standard (t_r: 12.39 min). The linear regression was calculated with the three first points of each series.

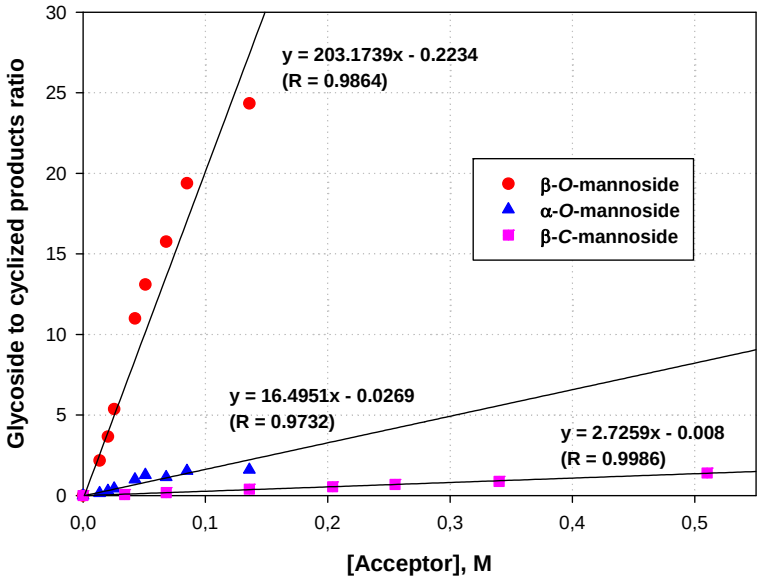
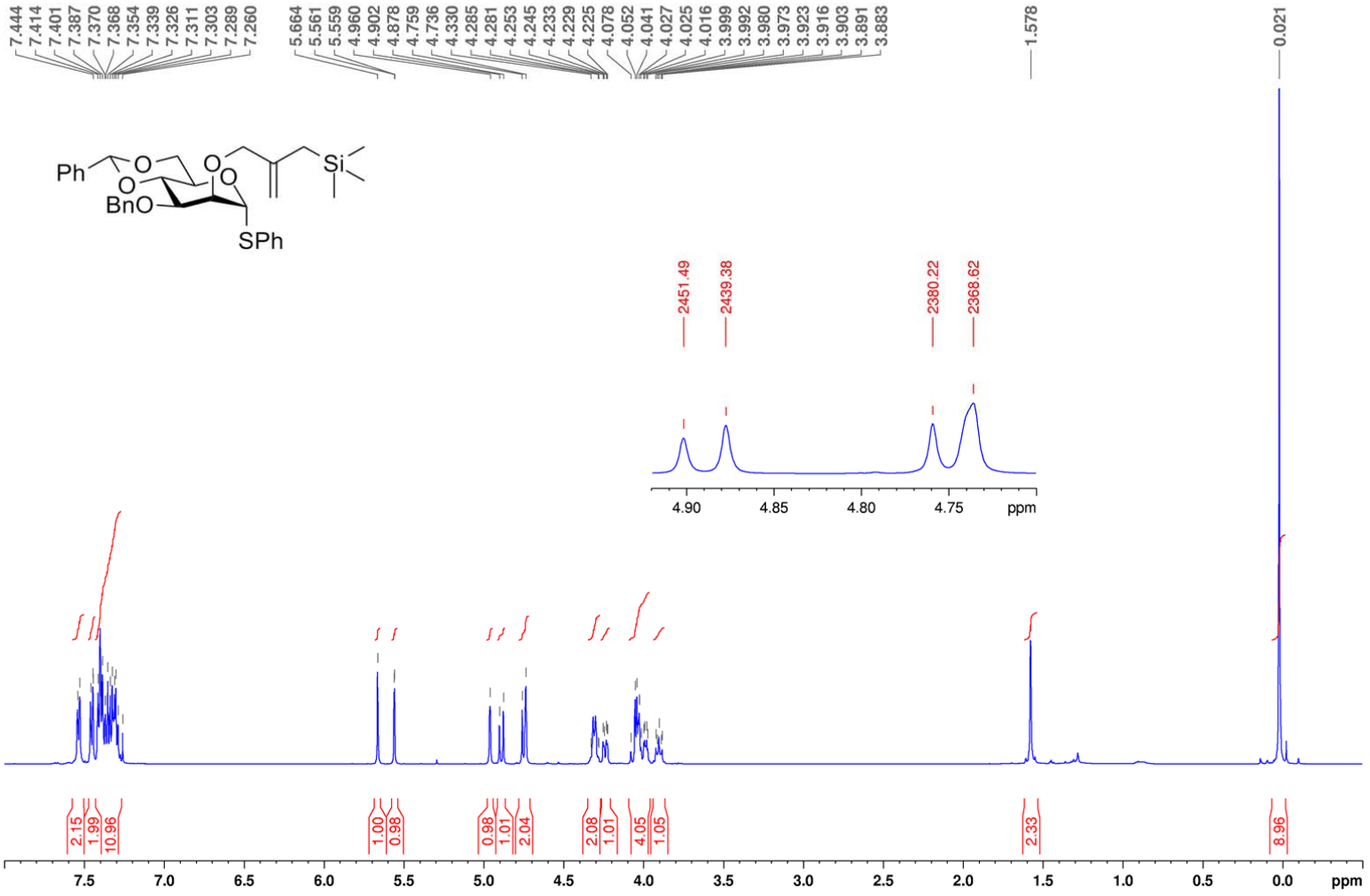
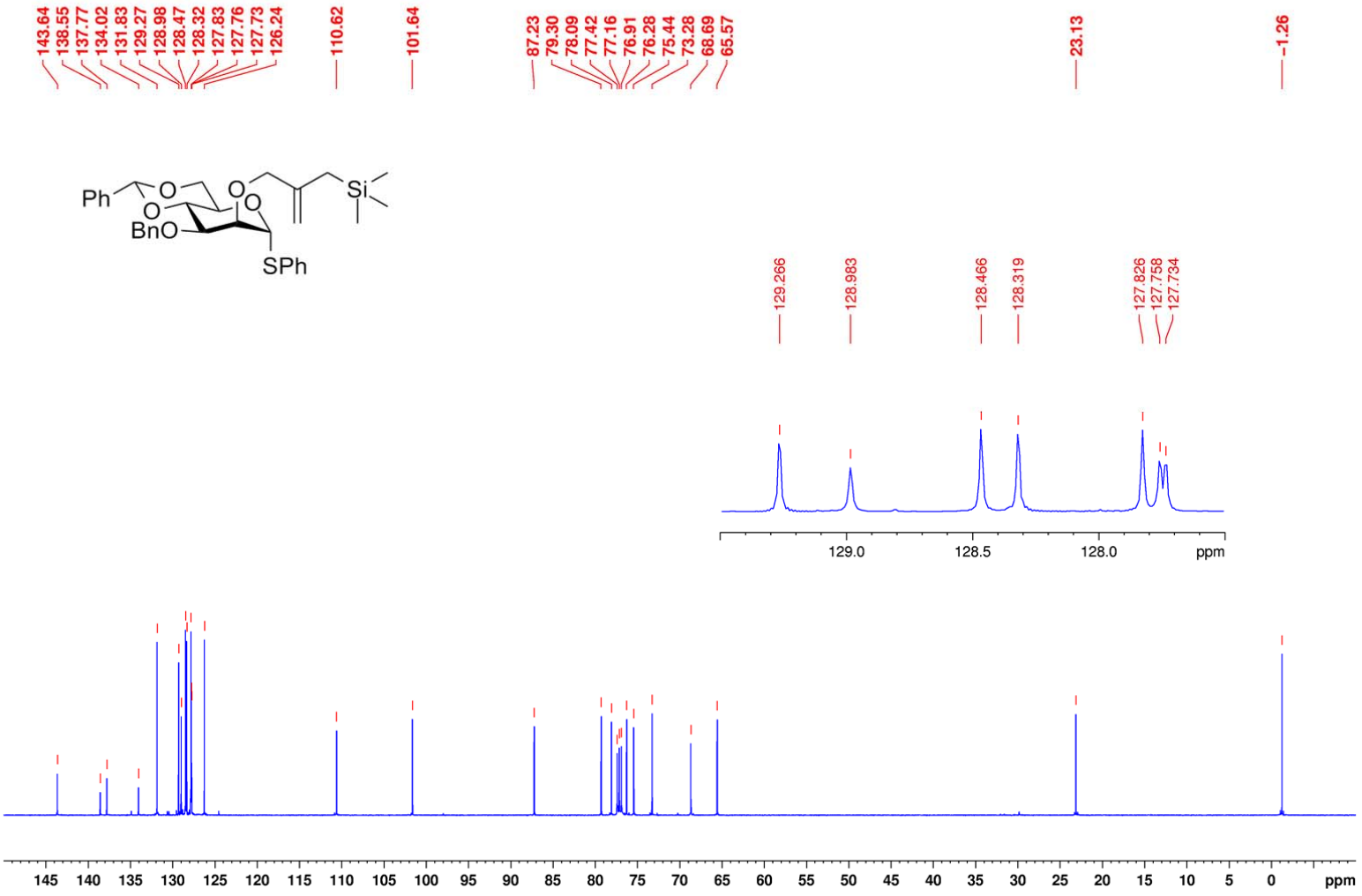


Figure S1: *O*- and *C*-Glycoside to cyclized products ratio as a function of nucleophile concentration

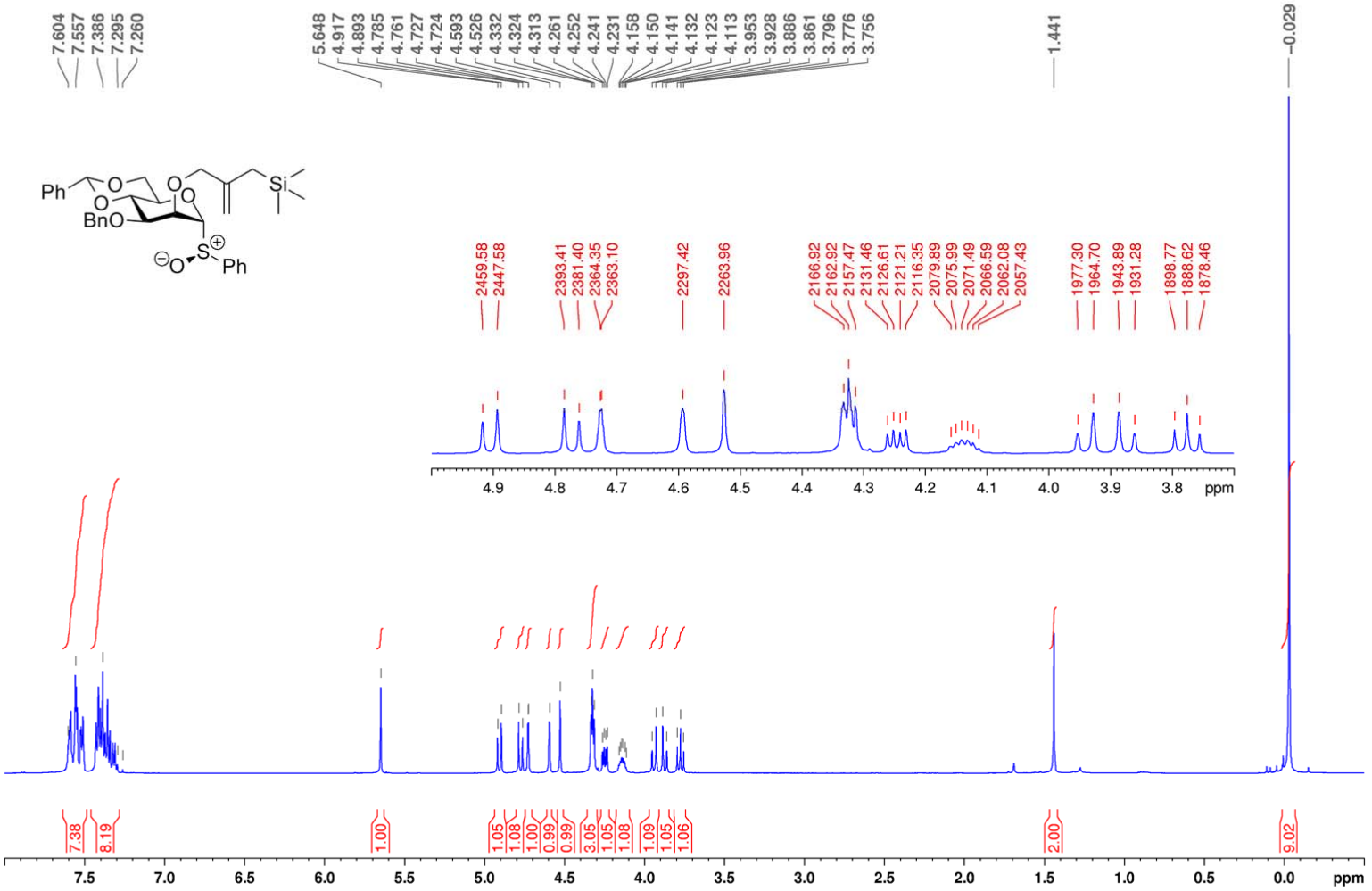
Compound 3, ^{1}H NMR (500 MHz, $CDCl_3$)



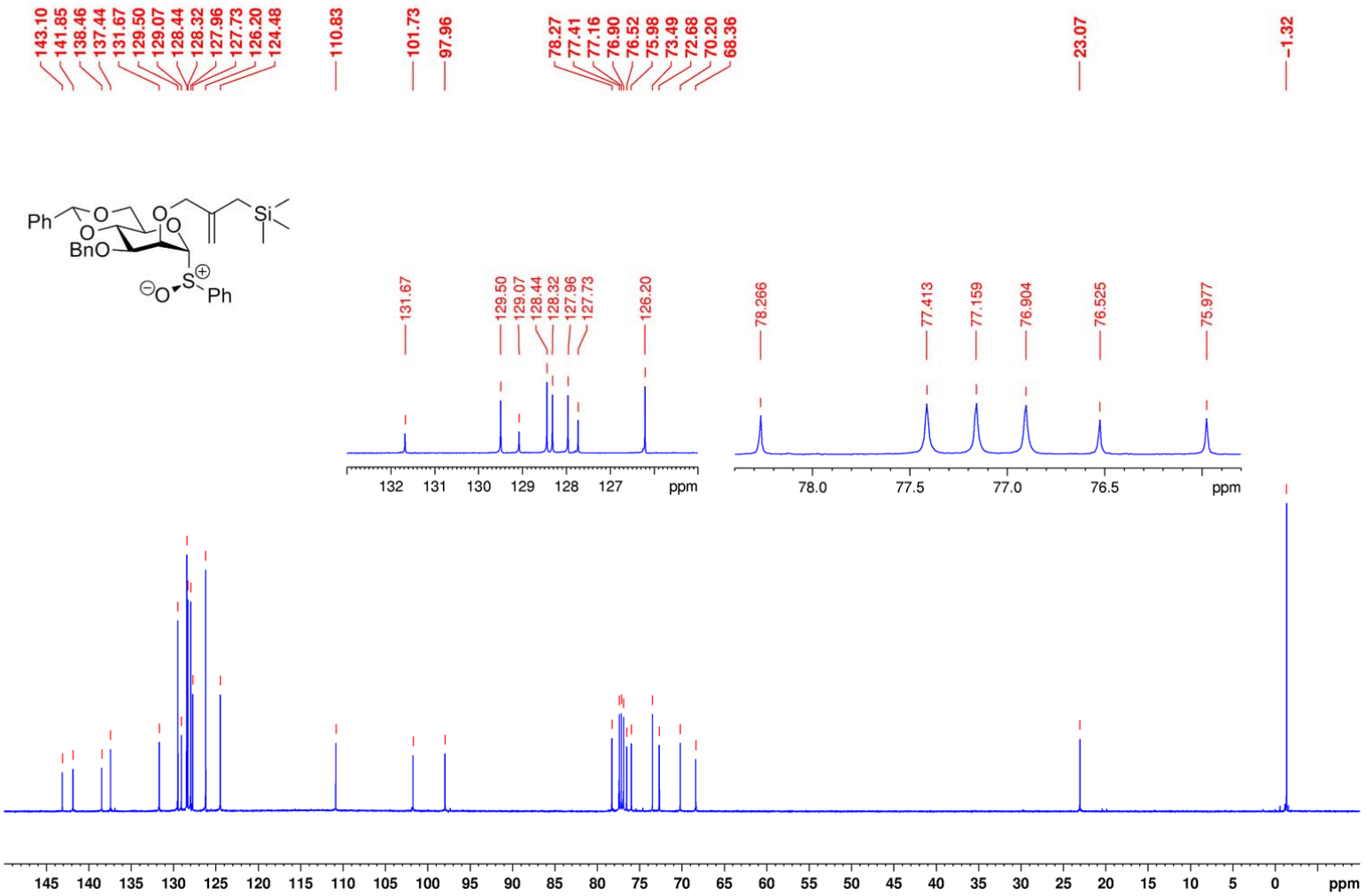
Compound 3, ^{13}C NMR (125 MHz, $CDCl_3$)



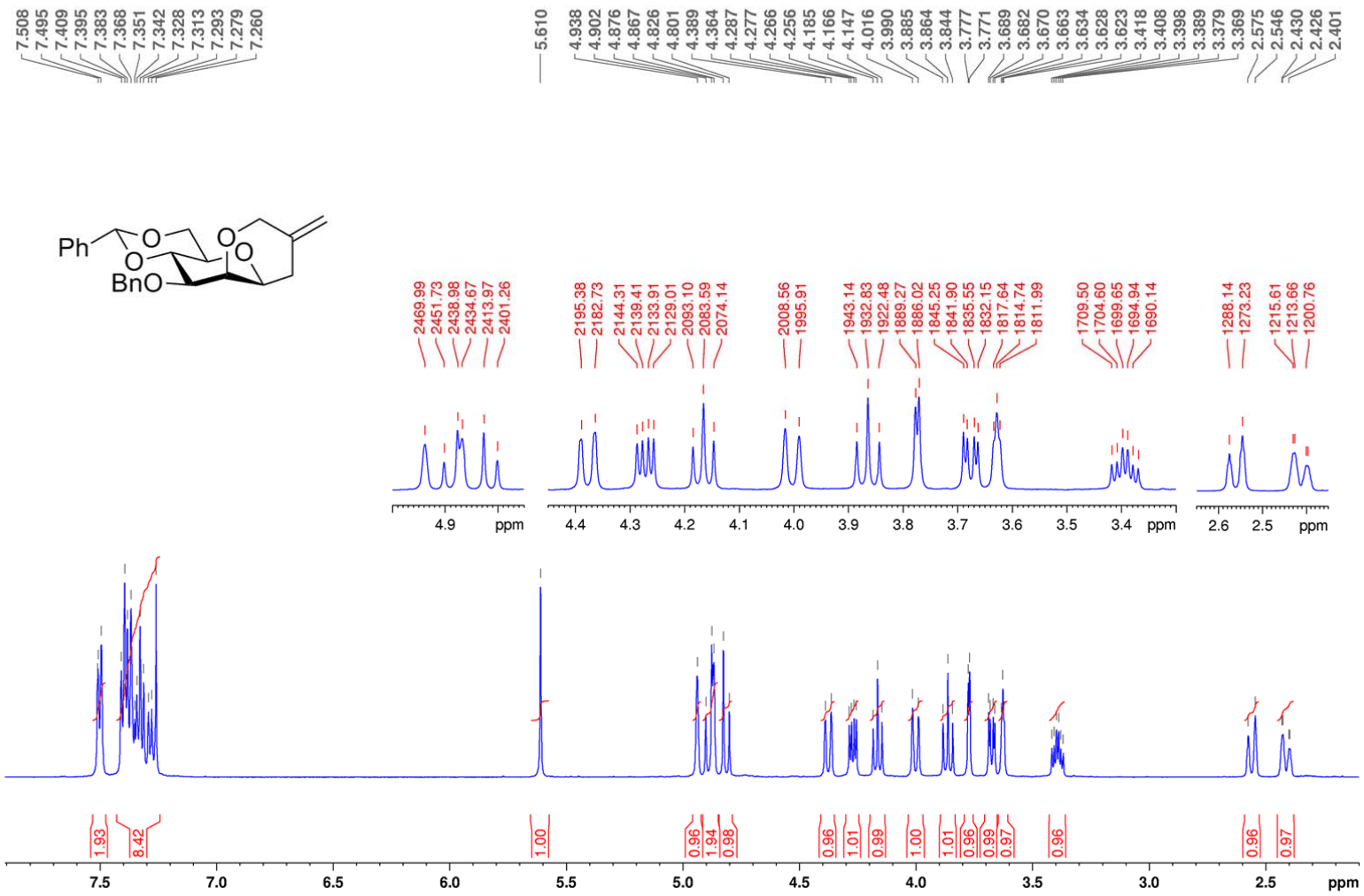
Compound 4, ^{1}H NMR (500 MHz, $CDCl_3$)



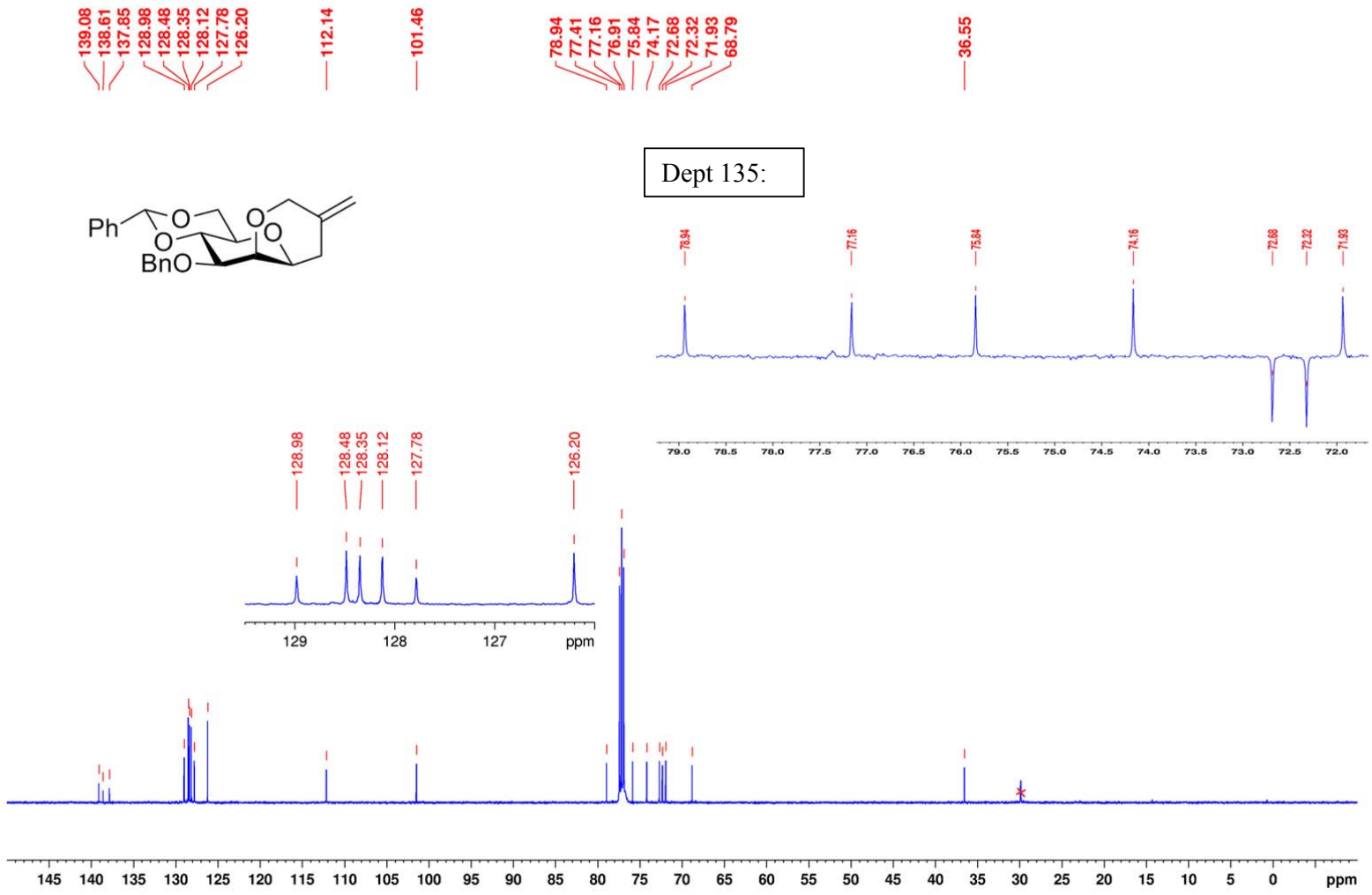
Compound 4, ^{13}C NMR (125 MHz, $CDCl_3$)



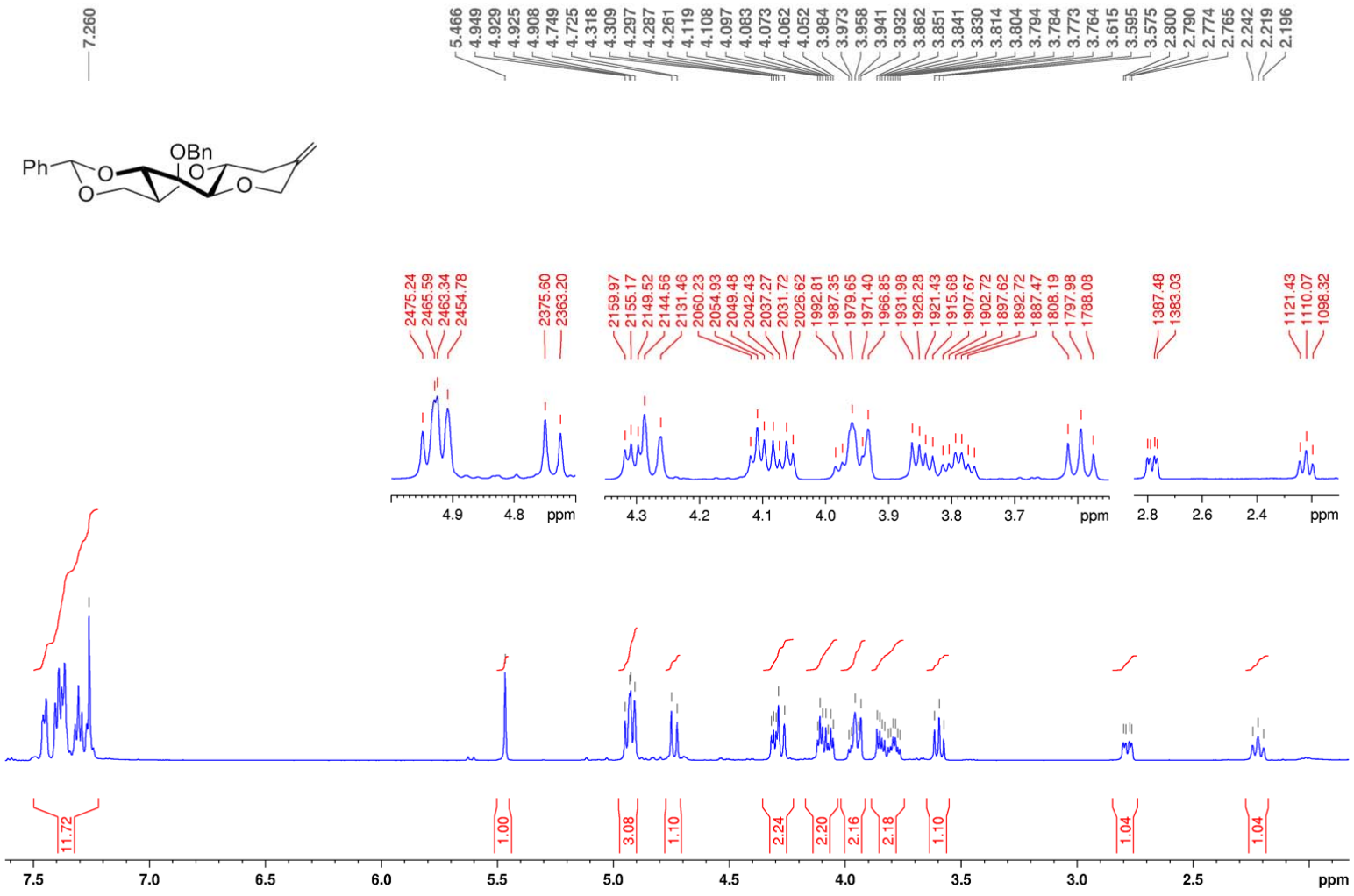
Compound 5, ^{1}H NMR (500 MHz, $CDCl_3$)



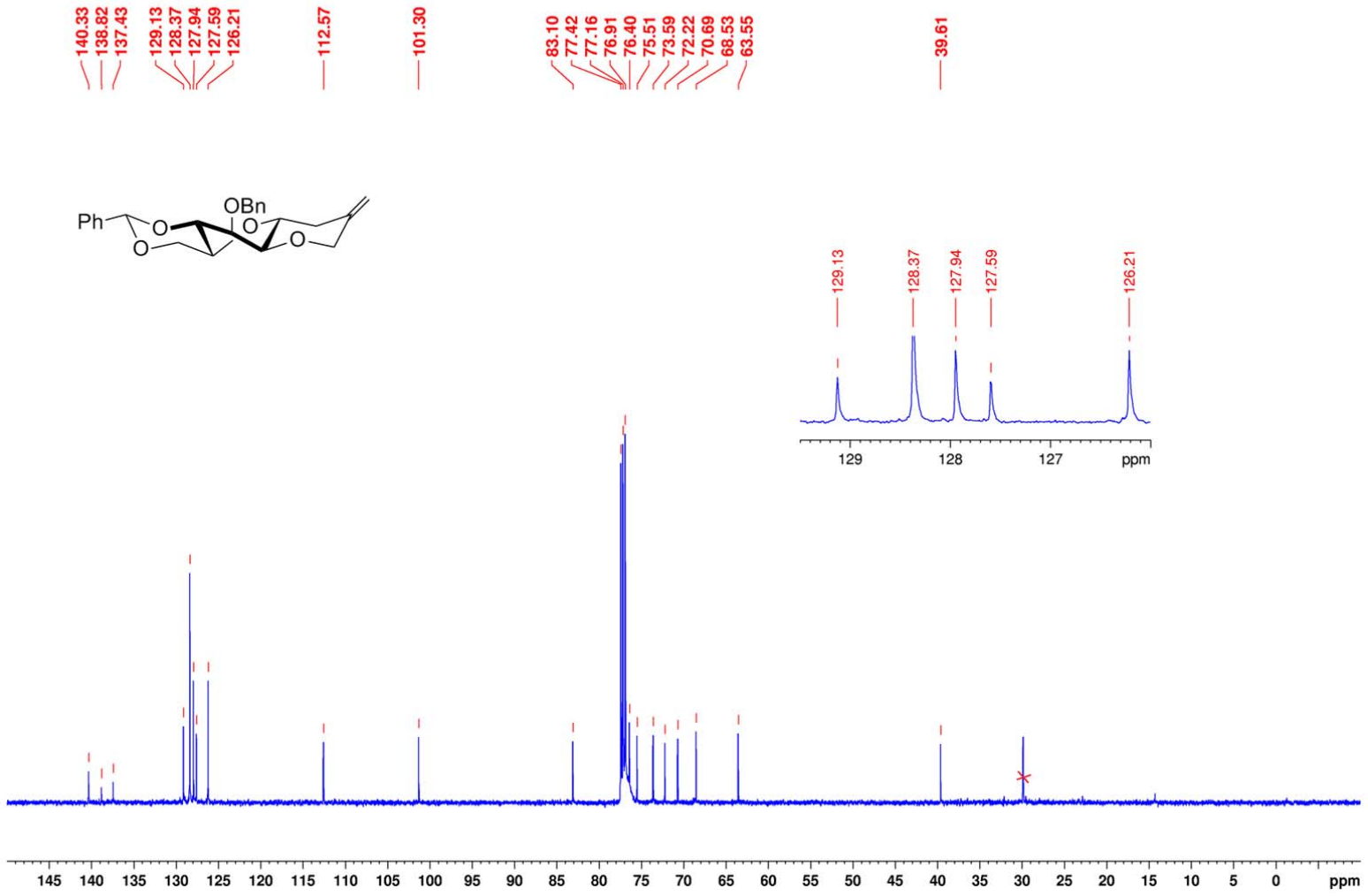
Compound 5, ^{13}C NMR (125 MHz, $CDCl_3$)



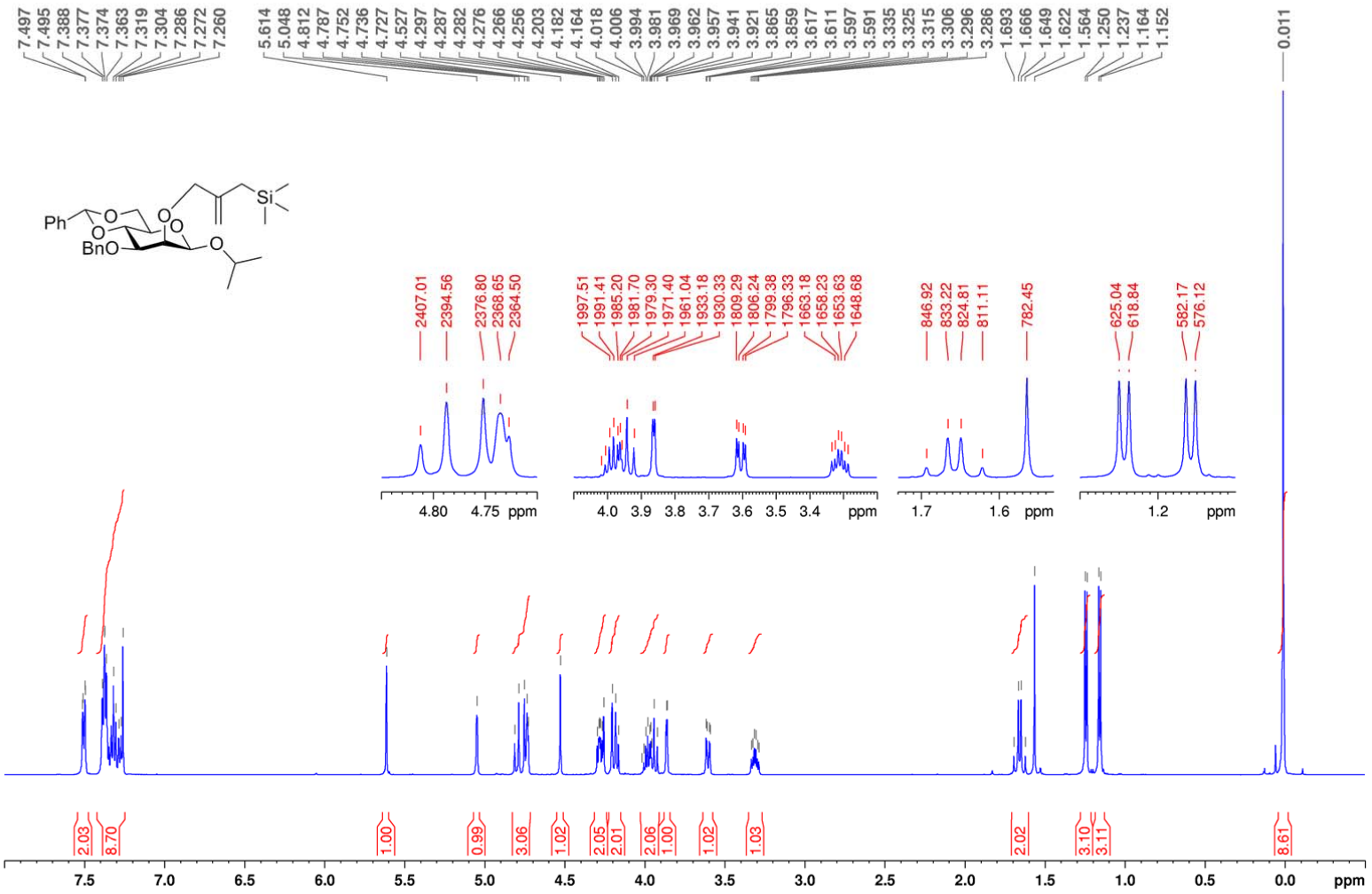
Compound 6, ^{1}H NMR (500 MHz, $CDCl_3$)



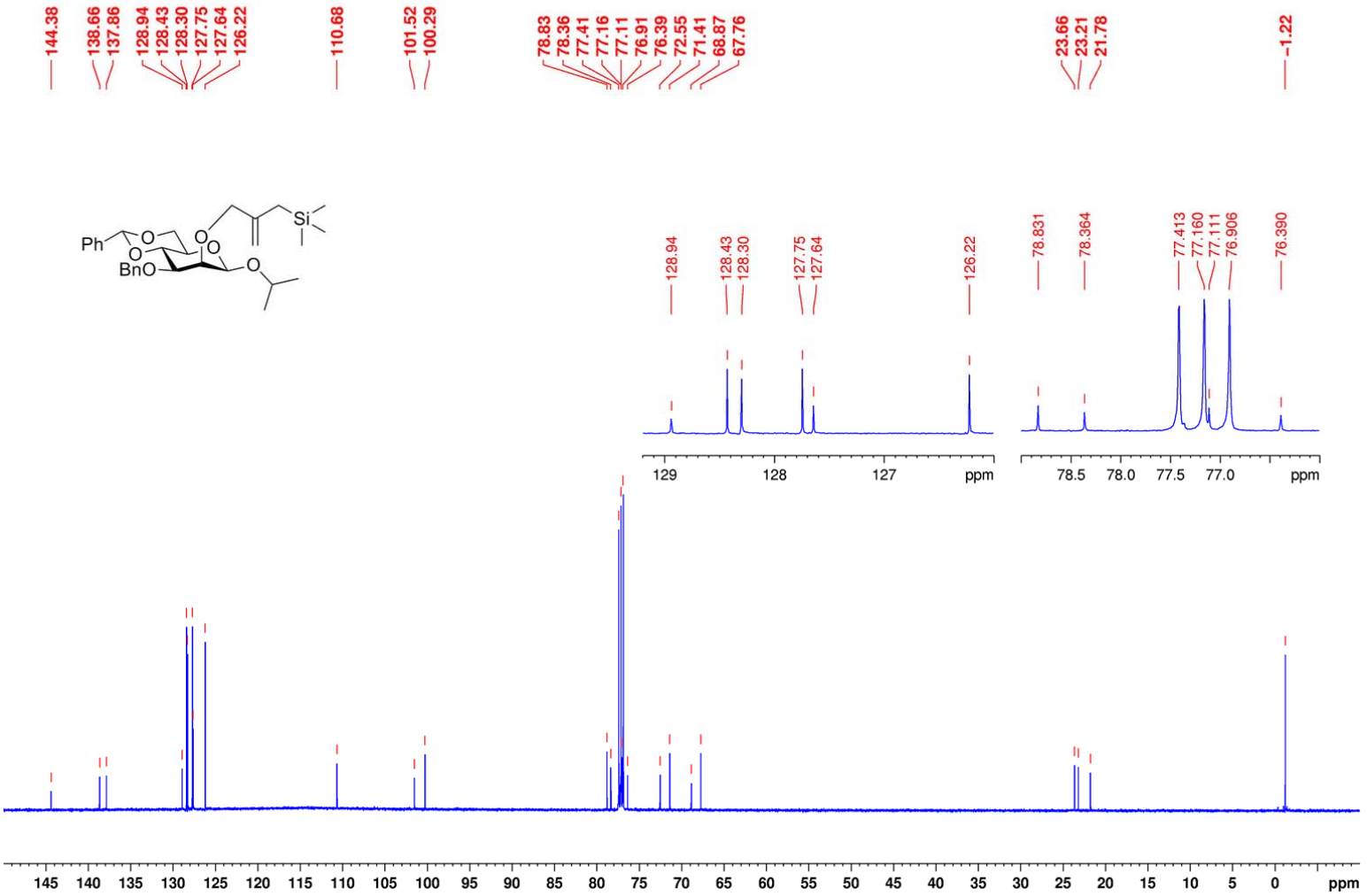
Compound 6, ^{13}C NMR (125 MHz, $CDCl_3$)



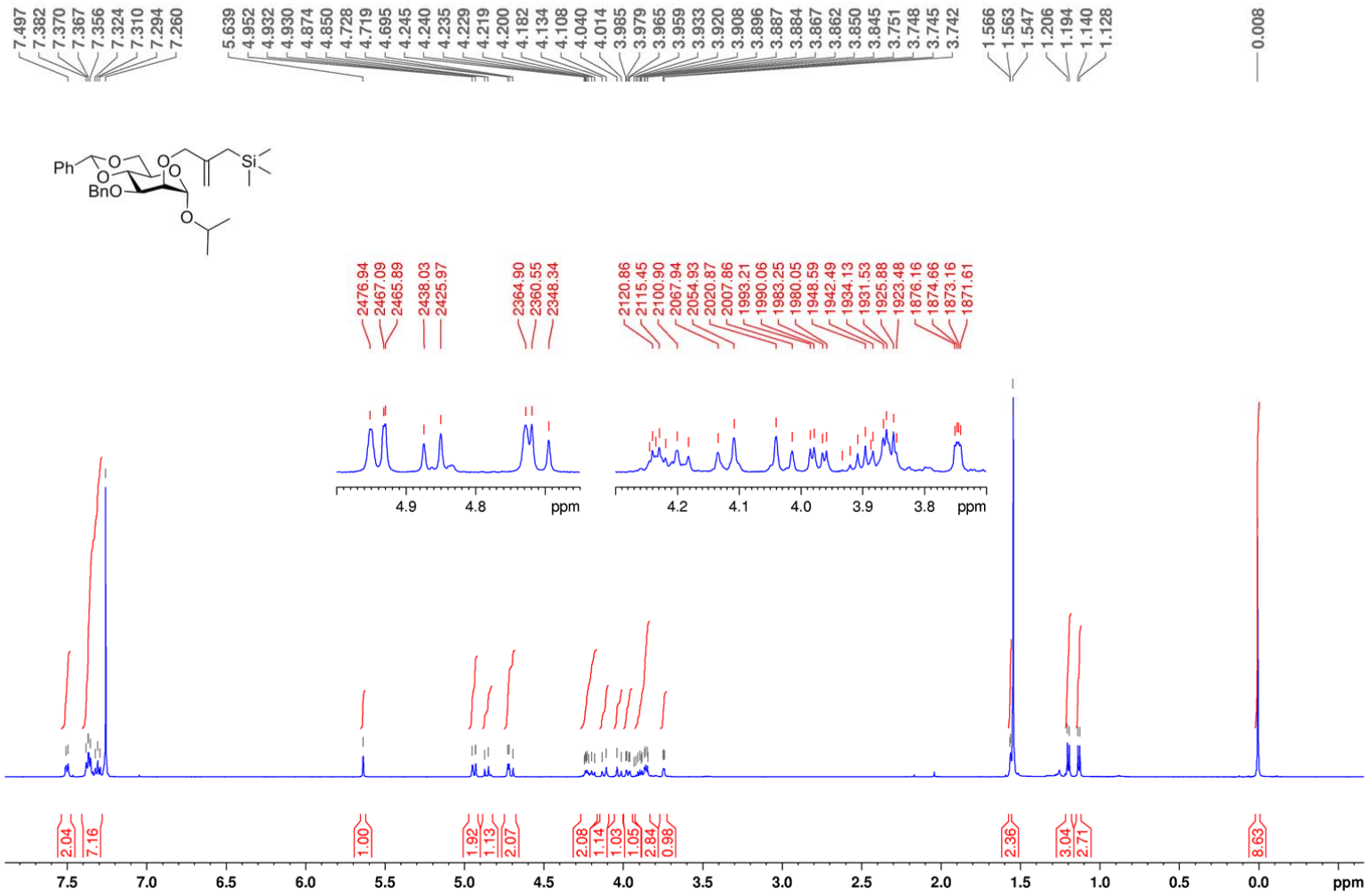
Compound 9, ^{1}H NMR (500 MHz, $CDCl_3$)



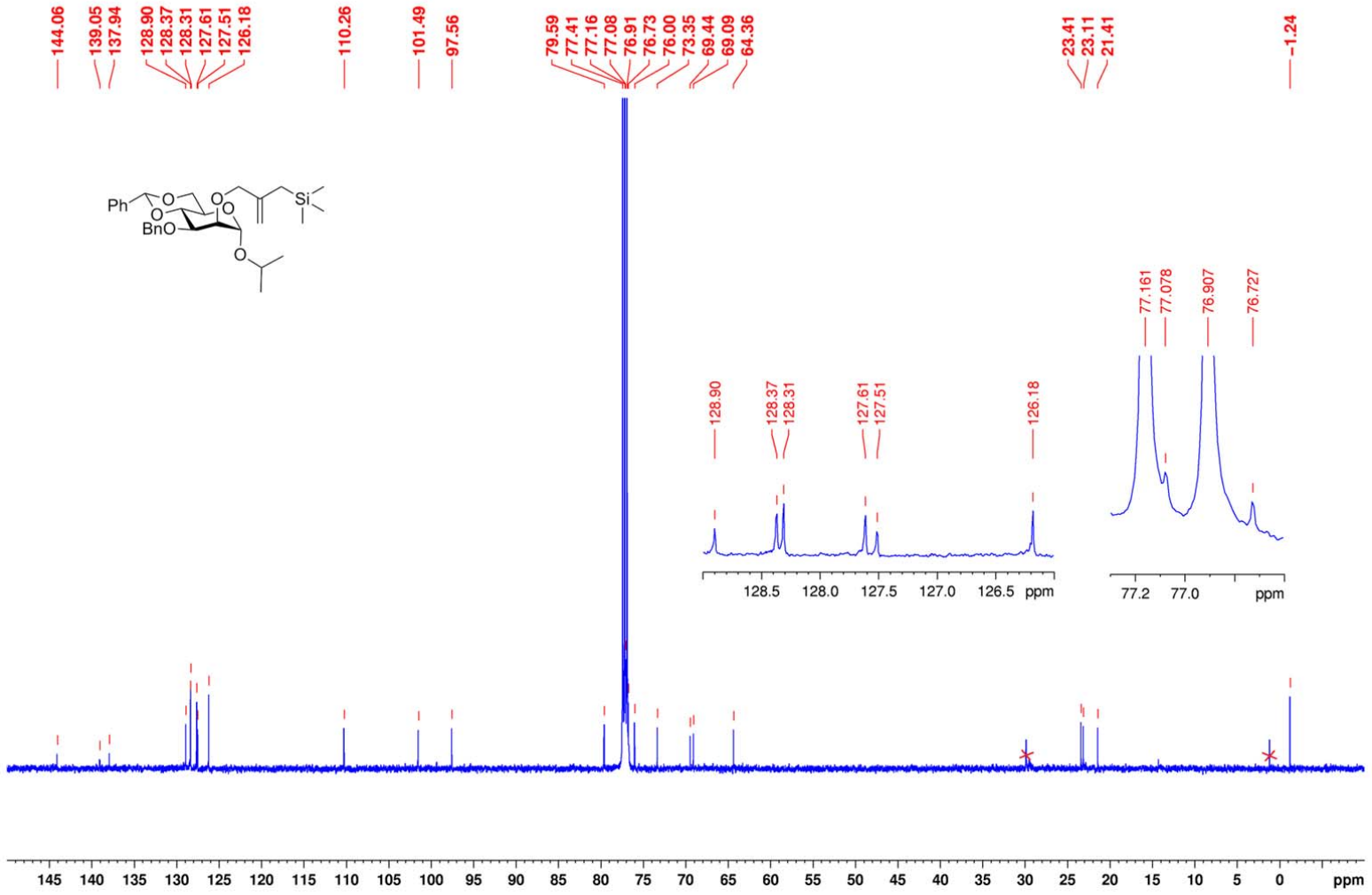
Compound 9, ^{13}C NMR (125 MHz, $CDCl_3$)



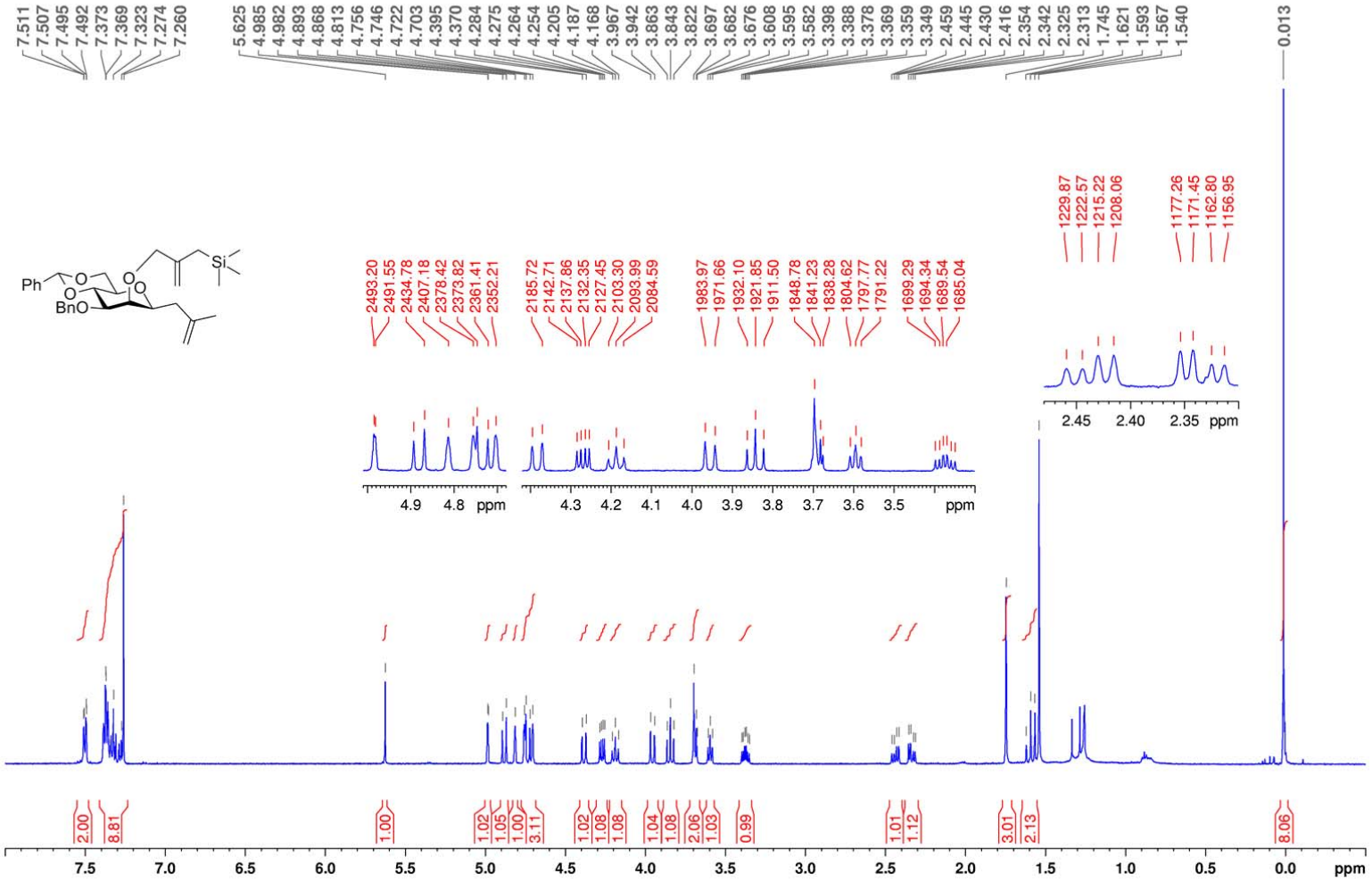
Compound 10, ^{1}H NMR (500 MHz, $CDCl_3$)



Compound 10, ^{13}C NMR (125 MHz, $CDCl_3$)



Compound 11, ^{1}H NMR (500 MHz, $CDCl_3$)



Compound 11, ^{13}C NMR (125 MHz, $CDCl_3$)