Electronic Supplementary Material (ESI) for ChemComm.

Enantioselective synthesis of the C_{24}–C_{40} fragment of (−)-pulvomycin

Electronic Supplementary Information

Sandra Börding and Thorsten Bach*

Lehrstuhl für Organische Chemie I, Technische Universität München, Lichtenbergstraße 4,
85747 Garching, Germany

1. Synthetic procedures and analytical data of new compounds

General information

All reactions sensitive to air or moisture were carried out in flame-dried glassware under a positive pressure of argon using standard *Schlenk* techniques. Dry tetrahydrofuran (THF), dichloromethane (CH_2Cl_2) and diethyl ether (Et_2O) were obtained from a *MBRAUN* MB-SPS 800 solvent purification system. Other dry solvents were obtained from *Acros* in the highest purity available and used without further purification. Technical solvents used for aqueous workup and for column chromatography [*n*-pentane (pentane), ethyl acetate (EtOAc), diethyl ether (Et_2O), dichloromethane (CH_2Cl_2), methanol (MeOH)] were distilled prior to use.

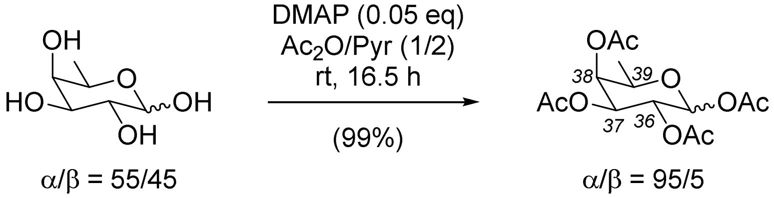
Flash Chromatography was performed on silica gel 60 (Merck, 230-240 mesh) with the eluent mixtures given for the corresponding procedures. Thin-layer Chromatography (TLC) was performed on silica-coated glass plates (silica gel 60 F 254). Compounds were detected by UV ($\lambda = 254$ nm, 366 nm) and CAM solution (cerium ammonium molybdate). All solvents for chromatography were distilled prior to use.

Analytical HPLC was performed using a chiral stationary phase (*Daicel*ChiralCell, Chemical Industries, flow rate: 1.0 mL/min, type and eluent is given for the corresponding compounds) and UV detection ($\lambda = 210$ nm or 254 nm) at 20 °C.

IR spectra were recorded on a *JASCO* IR-4100 (ATR), MS and HRMS measurements were performed on a *Finnigan* MAT 8200 (EI), *Finnigan* MSD 5973 (HR-EI), *Finnigan* LCQ classic (ESI), *ThermoFinnigan* LTQ FT (HRMS-ESI) or a*Thermo Sientific* LTQ Orbitrap XL (HRMS-ESI). ^1H and ^{13}C NMR spectra were recorded at 300 K either on a *Bruker* AV-360 or a *Bruker* AV-500 spectrometer. Chemical shifts are reported in parts per million (ppm) relative to residual $CDCl_3$ ($\delta_H = 7.26$ ppm and $\delta_C = 77.16$ ppm). All coupling constants (*J*) are reported in Hertz (Hz). Apparent multiplets that occur as a result of accidental equality of coupling constants those of magnetically non-equivalent protons are marked as virtual (*virt.*). The relative configuration of chiral products and the multiplicity of the ^{13}C-NMR signals were determined by two-dimensional NMR experiments (COSY, NOESY, HSQC, HMBC). For the assignment the pulvomycin numbering was used.

Specific rotations were measured using a *Perkin-Elmer* 241 MC Polarimeter, UV-Vis Spectra on a*Perkin Elmer* Lambda 35.

Peracetylated fucose S1



$C_{14}H_{20}O_9$
MW = 332.31

To a solution of 5.00 g D-(+)-fucose (30.5 mmol, 1.0 eq) in 67 ml dry pyridine were added 33 ml acetic anhydride and 0.19 g 4-dimethylaminopyridine (0.02 mmol, 0.05 eq). After the mixture was stirred overnight, it was diluted with dichloromethane (100 ml) and1 M HCl (100 ml). The aqueous layer was extracted with dichloromethane (3 × 100 ml), the combined organic layers dried over $MgSO_4$ and the solvent evaporated under reduced pressure. The crude product was subjected to flash column chromatography (pentane/diethyl ether = 5/1) to afford 10.0 g of the title compound (30.3 mmol, 99%) as a mixture of α/β-anomers (95/5).

α-anomer

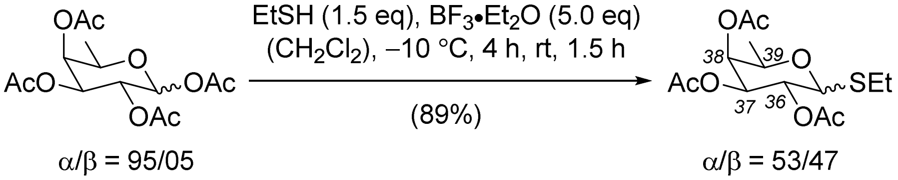
TLC: $R_f = 0.44$ (P:Et_2O = 1/2, [CAM]).

^{1}H-NMR (500 MHz, $CDCl_3$, 300 K): δ [ppm] = 1.15 (d, $^3J = 6.5$ Hz, 3 H; H_3-40), 2.00 [s, 3 H; $C(O)CH_3$], 2.01 (s, 3 H; $C(O)CH_3$), 2.14 [s, 3 H; $C(O)CH_3$], 2.17 [s, 3 H; $C(O)CH_3$], 4.26 (q, $^3J = 6.5$ Hz, 1 H; H-39), 5.29–5.38 (m, 3 H; H-36, H-37, H-38), 6.33 (d, $^3J = 2.9$ Hz, 1 H; H-35).

^{13}C-NMR (91 MHz, $CDCl_3$, 300 K): δ[ppm] = 15.9 (q, CH_3-40), 20.5 [q, $C(O)\mathit{C}H_3$], 20.6 [q, $C(O)\mathit{C}H_3$], 20.7 [q, $C(O)\mathit{C}H_3$], 20.9 [q, $C(O)\mathit{C}H_3$], 66.5 (d, CH-37), 67.3 (d, CH-39), 67.8 (d, CH-36), 70.6 (d, CH-38), 89.9 (d, CH-35), 169.1 [s, $\mathit{C}(O)CH_3$], 169.9 [s, $\mathit{C}(O)CH_3$], 170.2 [s, $\mathit{C}(O)CH_3$], 170.5 [s, $\mathit{C}(O)CH_3$].

The obtained data matched those reported in literature.[1]

Thioglycoside 3



$C_{14}H_{22}O_7S$
MW = 334.38

A solution of 10.0 g peracetylated fucose **S1** (30.3 mmol, 1.0 eq) in 76 ml dry dichloromethane was cooled to −10 °C, 3.37 ml ethanethiol (45.6 mmol, 1.5 eq) and 18.9 ml boron trifluoride diethyl etherate (150 mmol, 5.0 eq) were added. After stirring the reaction mixture for four hours at −10 °C it was allowed to warm to room temperatue and stirred another 1.5 hours. The mixture was diluted with dichloromethane (50 ml) and successively washed with ice-cold water (100 ml), saturated aqueous $NaHCO_3$ solution (100 ml) and saturated aqueous NaClsolution (100 ml). The organic layer was dried over $MgSO_4$ and the solvent evaporated under reduced pressure. Purification by flash column chromatography on silica (pentane/diethyl ether = 5/1) gave the title compound as a mixture of α/β-anomers (57/43) in 9.00 g (27.0 mmol, 89%) yield.

α-anomer

TLC: $R_f = 0.53$ (P:Et_2O = 1/1 [CAM]).

^{1}H-NMR (500 MHz, $CDCl_3$, 300 K): δ [ppm] = 1.14 (d, $^3J = 6.5$ Hz, 3 H; CH_3-40), 1.24 (t, $^3J = 7.4$ Hz, 3 H; CH_3), 1.97 [s, 3 H; C(O)CH_3], 2.05 [s, 3 H; C(O)CH_3], 2.15 [s, 3 H; C(O)CH_3], 2.46–2.62 (m, 2 H; CH_2), 4.47 (q, $^3J = 6.5$ Hz, 1 H; H-39), 5.18–5.29 (m, 3 H; H-37, H-36, H-38), 5.68 (d, $^3J = 5.4$ Hz, 1 H; H-35).

^{13}C-NMR (91 MHz, $CDCl_3$, 300 K): δ [ppm] = 14.8 (q, CH_3), 15.9 (q, CH_3-40), 20.6 [q, C(O)*C*H_3], 20.6 [q, C(O)*C*H_3], 20.8 [q, C(O)*C*H_3], 24.1 (t, CH_2), 64.6 (d, CH-39), 68.0 (s d, CH-36*), 68.6 (d, CH-37*), 71.0 (d, CH-38*), 81.9 (d, CH-35), 169.9 [s, *C*(O)CH_3], 170.2 [s, *C*(O)CH_3], 170.5 [s, *C*(O)CH_3].

*commutable signals.

β-anomer

TLC: $R_f = 0.36$ (P:Et_2O = 1/1 [CAM]).

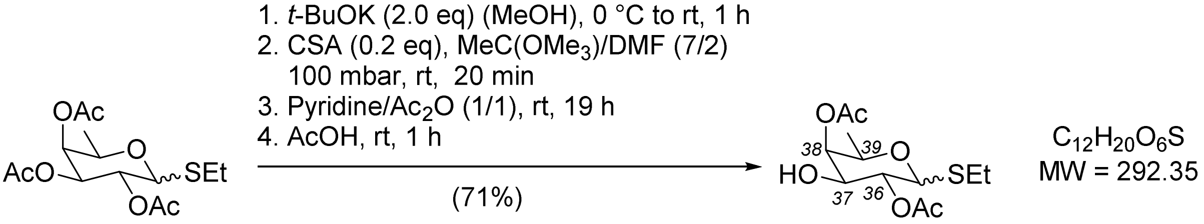
^{1}H-NMR (500 MHz, $CDCl_3$, 300 K): δ [ppm] = 1.20 (d, $^3J = 6.4$ Hz, 3 H; CH_3-40), 1.26 (t, $^3J = 7.5$ Hz, 3 H; CH_3), 1.97 [s, 3 H; C(O)CH_3], 2.05 [s, 3 H; C(O)CH_3], 2.16 [s, 3 H;

$C(O)CH_3$], 2.63–2.80 (m, 2 H; CH_2), 3.81 (qd, $^3J = 6.4, 0.6$ Hz, 1 H; H-39), 4.44 (d, $^3J = 10.0$ Hz, 1 H; H-35), 5.03 (dd, $^3J = 10.0, 3.4$ Hz, 1 H; H-37), 5.21 (t, $^3J = 10.0$ Hz, 1 H; H-36), 5.26 (dd, $^3J = 3.4, 0.6$ Hz, 1 H; H-38).

^{13}C-NMR (91 MHz, $CDCl_3$, 300 K): δ [ppm] = 14.9 (q, CH_3), 16.6 (q, CH_3-40), 20.7 [q, $C(O)\mathit{C}H_3$], 20.8 [q, $C(O)\mathit{C}H_3$], 21.0 [q, $C(O)\mathit{C}H_3$], 24.3 (t, CH_2), 67.5 (d, CH-39), 70.6 (d, CH-36), 72.5 (d, CH-37), 73.3 (d, CH-38), 83.5 (d, CH-35), 169.8 [s, $\mathit{C}(O)CH_3$], 170.3 [s, $\mathit{C}(O)CH_3$], 170.8 [s, $\mathit{C}(O)CH_3$].

The obtained data matched those reported in literature.[1]

Alcohol 4



$C_{12}H_{20}O_6S$
MW = 292.35

To a solution of 8.10 g thioether **3** (24.2 mmol, 1.0 eq) in 121 ml MeOH was added 5.43 g potassium *tert*-butoxide (48.4 mmol, 2.0 eq). The reaction was stirred for one hour before Amberlyst-15 was added. After filtration the solvent was evaporated under reduced pressure. The residue was diluted with 125 ml of a mixture of dimethylformamide and trimethyl orthoacetate (7/2) and stirred at 100 mbar for 30 minutes. 97 ml pyridine, 97 ml acetic anhydride and 0.15 g 4-dimethylaminopyridine (1.21 mmol, 0.05 eq) were added and the mixture stirred at room temperature overnight. After coevaporation with toluene (4 × 140 ml) acetic acid (145 ml, 80% in H_2O) was added and the mixture stirred for another hour. The mixture was again coevaporated with toluene (3 × 70 ml) and the crude product subjected to flash column chromatography on silica (pentane/diethyl ether = 5/1 to 1/5) to afford 4.37 g (14.7 mmol, 71%) of **4** as a mixture of anomers.

α-anomer

TLC: $R_f = 0.56$ (P:Et_2O = 1/10, [CAM]).

IR (ATR): $\tilde{\nu}(cm^{-1}) = 3397$ (m, OH), 2979 (w, C–H), 2934 (w, C–H), 2855 (w, C–H), 1722 (s, C=O), 1377 (m), 1262 (m), 1229 (s), 1060 (s).

^{1}H-NMR (500 MHz, $CDCl_3$, 300 K): δ [ppm] = 1.16 (d, ^3J = 6.5 Hz, 3 H; CH_3-40), 1.26 (t, ^3J = 7.4 Hz, 3 H; CH_3), 2.12 [s, 3 H; $C(O)CH_3$], 2.19 [s, 3 H; $C(O)CH_3$], 2.47–2.62 (m, 2 H; CH_2), 4.09 (dd, ^3J = 10.4, 2.9 Hz, 1 H; H-37), 4.43 (q, ^3J = 6.5 Hz, 1 H; H-39), 5.10 (dd, ^3J = 10.4, 5.6 Hz, 1 H; H-36), 5.24 (d, ^3J = 2.9 Hz, 1 H; H-38), 5.65 (d, ^3J = 5.6 Hz, 1 H; H-35).

^{13}C-NMR (91 MHz, $CDCl_3$, 300 K): δ [ppm] = 15.0 (q, CH_3), 16.3 (q, CH_3-40), 20.9 [q, $C(O)\mathit{C}H_3$], 21.1 [q, $C(O)\mathit{C}H_3$], 24.5 (t, CH_2), 65.1 (d, CH-39), 68.0 (d, CH-37), 71.5 (d, CH-36), 73.5 (d, CH-38), 82.1 (d, CH-35), 170.9 [s, $\mathit{C}(O)CH_3$], 171.5 [s, $\mathit{C}(O)CH_3$].

β-anomer

TLC: R_f = 0.38 (P:Et_2O = 1/10, [CAM]).

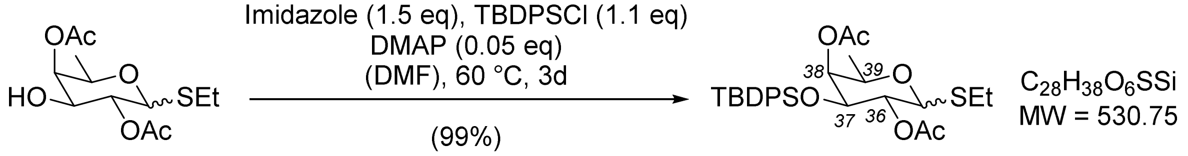
^{1}H-NMR (500 MHz, $CDCl_3$, 300 K): δ [ppm] = 1.22 (d, ^3J = 6.4 Hz, 3 H; CH_3-40), 1.28 (t, ^3J = 7.4 Hz, 3 H; CH_3), 2.14 [s, 3 H; $C(O)CH_3$], 2.20 [s, 3 H; $C(O)CH_3$], 2.65-2.79 (m, 2 H; CH_2), 3.75 (q, ^3J = 6.4 Hz, 1 H; H-39), 3.85 (ddd, ^3J = 9.8, 6.3, 3.5 Hz, 1 H; H-37), 4.42 (d, ^3J = 9.8 Hz, 1 H; H-35), 5.01 (t, ^3J = 9.8 Hz, 1 H; H-36), 5.22 (d, ^3J = 3.5 Hz, 1 H; H-38).

^{13}C-NMR (91 MHz, $CDCl_3$, 300 K): δ [ppm] = 14.9 (q, CH_3), 16.8 (q, CH_3-40), 21.0 [q, $C(O)\mathit{C}H_3$], 21.2 [q, $C(O)\mathit{C}H_3$], 24.3 (t, CH_2), 71.1 (d, CH-36), 72.6 (d, CH-37), 73.2 (d, CH-38), 73.6 (d, CH-39), 83.3 (d, CH-35), 171.1 [s, $\mathit{C}(O)CH_3$], 171.5 [s, $\mathit{C}(O)CH_3$].

HRMS (ESI)	$C_{16}H_{24}O_3Si$	calcd.: [$(M+Na)^+$]	315.0873
		found: [$(M+Na)^+$]	315.0874.

The obtained data for the β-anomer matched those reported in literature.[2]

Protected sugar 5



A solution of 1.46 g alcohol **4** (4.99 mmol, 1.0 eq) in 5 ml dimethylformamide was treated with 1.02 g imidazole (15.0 mmol, 3.0 eq), 2.85 ml *tert*-butyldiphenylchlorosilane (11.0 mmol, 2.2 eq) and 0.06 g 4-dimethylaminopyridine (0.50 mmol, 0.1 eq). The reaction mixture was heated to 60 °C an stirred for three days. After addition of saturated aqueous NH_4Cl solution (10 ml) the aqueous layer was extracted with dichloromethane (3 × 15 ml). The combined organic layers were dried over $MgSO_4$, the solvent evaporated under reduced pressure and the crude product subjected to flash column chromatography on silica (pentane/diethyl ether= 20/1 to 2/1). Sugar **5** was obtained in 2.62 g (4.94 mmol, 99%).

α-anomer

TLC: $R_f = 0.52$ (P:Et_2O = 2/1, [UV, CAM]).

^{1}H-NMR (500 MHz, $CDCl_3$, 300 K): δ [ppm] = 1.01 [s, 9 H; $C(CH_3)_3$], 1.08 (d, $^3J = 6.4$ Hz, 3 H; CH_3-40), 1.16 (t, $^3J = 7.4$ Hz, 3 H; CH_3), 1.38 [s, 3 H; $C(O)CH_3$-36], 2.21 [s, 3 H; $C(O)CH_3$-38], 2.32–2.49 (m, 2 H; CH_2), 4.12 (dd, $^3J = 10.2$, 3.5 Hz, 1 H; H-37), 4.20 (q, $^3J = 6.4$ Hz, 1 H; H-39), 5.14 (dd, $^3J = 3.5$, 0.8 Hz, 1 H; H-38), 5.19 (dd, $^3J = 10.2$, 5.7 Hz, 1 H; H-36), 5.60 (d, $^3J = 5.7$ Hz, 2 H; H-35), 7.32–7.50 (m, 6 H; H_{arom}), 7.53–7.58 (m, 2 H; H_{arom}), 7.69–7.76 (m, 2 H; H_{arom}).

^{13}C-NMR (91 MHz, $CDCl_3$, 300 K): δ [ppm] = 14.9 (q, CH_3), 16.3 (q, CH_3-40), 19.4 [s, $\mathit{C}(CH_3)_3$], 20.4 [q, $C(O)\mathit{C}H_3$-36*], 21.0 [q, $C(O)\mathit{C}H_3$-38*], 24.2 (t, CH_2), 26.6 [q, $C(\mathit{C}H_3)_3$], 65.3 (d, CH-39), 69.0 (d, CH-37), 71.7 (d, CH-36), 73.9 (d, CH-38), 82.0 (d, CH-35), 127. 6, 127.8, 127.9 (d, CH_{arom}), 129.6, 129.7, 130.2 (s, C_{arom}), 132.2 (s, C_{arom}) 134.7, 134.9, 135.4, 135.64, 136.3 (d, CH_{arom}), 170.6 [s, $\mathit{C}(O)CH_3$-36*], 170.7 [s, $\mathit{C}(O)CH_3$-38*].

*commutable signals.

β-anomer

TLC: $R_f = 0.42$ (P:Et_2O = 2/1, [UV, CAM]).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3071 (w, C–H), 3048 (w, C–H), 3016 (w, C–H), 2958 (m, C–H), 2931 (m, C–H), 2892 (w, C–H), 2858 (w, C–H), 1745 (s, C=O), 1228 (s), 1065 (s).

^{1}H-NMR (500 MHz, $CDCl_3$, 300 K): δ [ppm] = 1.01 [s, 9 H; $C(CH_3)_3$], 1.09 (d, $^3J = 6.4$ Hz, 3 H; CH_3-40), 1.21 (t, $^3J = 7.5$ Hz, 3 H; CH_3), 1.54 [s, 3 H; $C(O)CH_3$-36], 2.20 [s, 3 H; $C(O)CH_3$-38], 2.61–2.72 (m, 2 H; CH_2), 3.49 (qd, $^3J = 6.4$, 0.7 Hz; H-39), 3.90 (dd, $^3J = 9.7$, 3.3 Hz; H-37), 4.14 (d, $^3J = 9.7$ Hz; H-35), 5.02 (dd, $^3J = 3.3$, 0.7 Hz; H-38), 5.26 (t, $^3J = 9.7$ Hz; H-36), 7.34–7.49 (m, 6 H; H_{arom}), 7.56–7.60 (m, 2 H; H_{arom}), 7.66–7.71 (m, 2 H; H_{arom}).

^{13}C-NMR (91 MHz, $CDCl_3$, 300 K): δ [ppm] = 14.7 (q, CH_3), 16.9 (q, CH_3-40), 19.3 [s, $C(CH_3)_3$], 20.9 [q, $C(O)CH_3$-36*], 21.1 [q, $C(O)CH_3$-38*], 24.0 (t, CH_2), 26.7 [q, $C(CH_3)_3$], 70.3 (d, CH-36), 73.3 (d, CH-37), 73.6 (d, CH-38), 73.6 (d, CH-39), 83.8 (d, CH-35), 127.6, 127.9 (d, CH_{arom}), 129.8, 130.1 (d, CH_{arom}), 132.1, 133.1 (s, C_{arom}), 135.9, 136.3 (d, CH_{arom}), 170.1 [s, $C(O)CH_3$-36], 170.7 [s, $C(O)CH_3$-38].

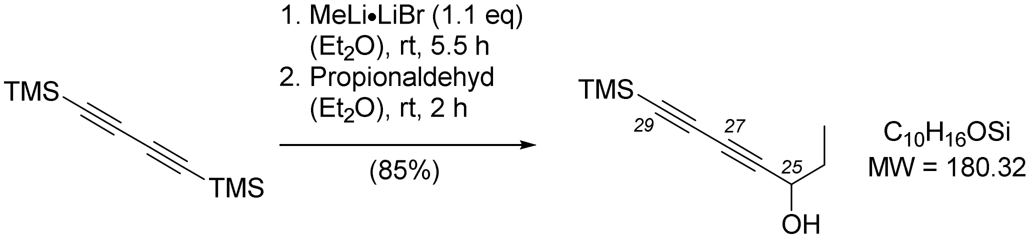
*commutable signals.

MS (ESI): *m/z* (%) = 553 [$(M+Na)^+$] (3), 531 [$(M+H)^+$](1), 469 [$(M-SC_2H_6)^+$] (100).

HRMS (ESI) $C_{16}H_{24}O_3Si$ calcd.: [$(M+Na)^+$] 553.2051

found: [$(M+Na)^+$] 553.2060.

Diynol S2



To a solution of 0.50 g 1,4-bis(trimethylsilyl)buta-1,3-diyne (2.57 mmol, 1.0 eq) in 5 ml diethyl ether was added 1.29 ml methyllithium lithium bromide complex (2.83 mmol, 2.2 M in diethyl ether, 1.1 eq). After stirring for 5.5 hours at room temperature the mixture was cooled to 0 °C and 0.21 ml of propionic aldehyde (2.83 mmol, 1.1 eq) were added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for two hours at this temperature before it was quenched by the addition of saturated aqueous NH_4Cl solution (5 ml). The aqueous layer was extracted with diethyl ether (3 × 5 ml), the combined organic layers dried over $MgSO_4$ and the solvent evaporated under reduced pressure. Flash column chromatography on silica (pentane/diethyl ether = 10/1) afforded 0.39 g of **S2** (2.19 mmol, 85%).

TLC: R_f = 0.47 (P:Et_2O = 2/1, [UV, CAM]).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3310 (w, OH), 2965 (m, C–H), 2938 (m, C–H), 2899 (w, C–H), 2878 (w, C–H), 2107 (m, C–C_{alkyne}), 1251 (m, C–O), 840 (s).

^{1}H-NMR (500 MHz, $CDCl_3$, 300 K): δ [ppm] = 0.20 [s, 9 H; $Si(CH_3)_3$], 1.01 (t, $^3J = 7.4$ Hz, 3 H; CH_3), 1.70–1.79 (m, 3 H; CH_2-24, OH), 4.37 (t, $^3J = 6.5$ Hz, 1 H; H-25).

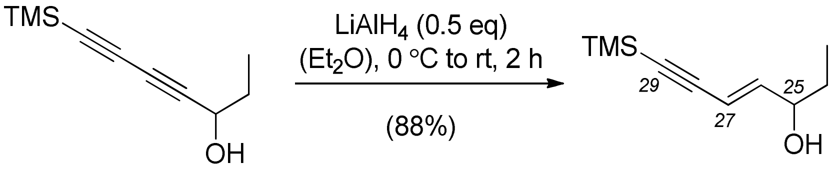
^{13}C-NMR (91 MHz, $CDCl_3$, 300 K): δ [ppm] = –0.3 [q, $Si(CH_3)_3$], 9.5 (q, CH_3), 30.8 (t, CH_2-24), 64.2 (d, CH-25), 70.0 (s, C-27), 78.6 (s, C-26), 87.3 (s, C-28), 87.8 (s, C-29).

MS (EI): *m/z* (*%*) = 179 [$(M–H)^+$] (2), 165 [$(M–CH_3)^+$](93), 123 (58), 75 (54).

HRMS (EI)	$C_{16}H_{24}O_3Si$	calcd.: [$(M–H)^+$]	179.0887
		found: [$(M–H)^+$]	179.0882.

The obtained data matched those reported in literature.[3]

TMS-enynol S3



$C_{10}H_{18}OSi$
MW = 182.34

A solution of 0.30 g **S2** (1.66 mmol, 1.0 eq) in 4 ml diethyl ether was cooled to 0 °C and 0.03 g lithium aluminium hydride (0.83 mmol, 0.5 eq) were cautiously added. After the reaction mixture was stirred for two hours ice-cold water (5 ml) was added and the aqueous layer extracted with diethyl ether (3 x 5 ml). The combined organic layers were dried over $MgSO_4$ and the solvent evaporated. The crude product was subjected to flash column chromatography on silica (pentane/diethyl ether = 10/1) to afford 0.27 g of **S3** (1.46 mmol, 88%).

TLC: $R_f = 0.40$ (P:Et_2O = 2/1, [UV, CAM]).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3316 (w, OH), 2962 (m, C–H), 2933 (w, C–H), 2899 (w, C–H), 2877 (w, C–H), 2154 (w, C=C), 2132 (w, C–C_{alkyne}), 1250 (m, C–O), 839 (s).

^{1}H-NMR (500 MHz, $CDCl_3$, 300 K): δ [ppm] = 0.19 [s, 9 H; $Si(CH_3)_3$], 0.94 (t, $^3J = 7.5$ Hz, 3 H; CH_3), 1.53–1.60 (m, 3 H; CH_2-24, OH), 4.08 (dd, $^3J = 6.2$, $^4J = 1.4$ Hz, 1 H; H-25), 5.73 (dd, $^3J = 16.0$ Hz, $^4J = 1.4$ Hz, 1 H; H-27), 6.20 (dd, $^3J = 16.0$, 6.2 Hz, 1 H; H-26).

^{13}C-NMR (91 MHz, $CDCl_3$, 300 K): δ [ppm] = 0.1 [q, $Si(CH_3)_3$], 9.7 (q, CH_3), 29.9 (t, CH_2-24), 73.7 (d, CH-25), 95.3 (s, C-29), 103.2 (s, C-28), 110.1 (d, CH-27), 146.7 (d, CH-26).

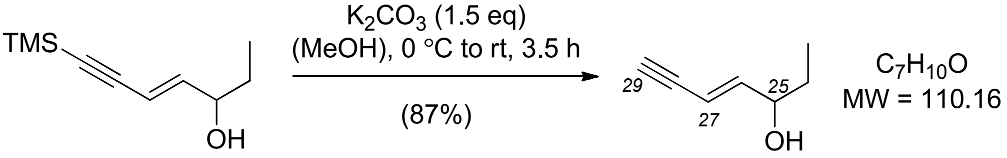
MS (EI): *m/z* (%) = 181 [$(M{-}H)^+$] (2), 167 [$(M{-}CH_3)^+$](96), 153 (65), 75 (93), 73 (100).

HRMS (EI) $C_{16}H_{24}O_3Si$ calcd.: [$(M{-}H)^+$] 181.1043

found: [$(M{-}H)^+$] 181.1042.

The obtained data matched those reported in literature.[3]

Enynol S4



A solution of 0.25 g **S3** (1.37 mmol, 1.0 eq) in 6 ml methanol and 3 ml tetrahydrofuran was treated with 0.28 g powdered potassium carbonate (2.05 mmol, 1.5 eq) and stirred for 3.5 hours. The reaction was quenched by the addition of saturated aqueous NH_4Cl solution (10 ml), the aqueous layer extracted with diethyl ether (3 × 10 ml), the combined organic layers dried over $MgSO_4$ and the solvents evaporated under reduced pressure. The crude product was subjected to flash column chromatography on silica (pentane/diethyl ether = 10/1) to yield 0.13 g of the desired compound **S4** (1.19 mmol, 87%).

TLC: $R_f = 0.37$ (P:Et_2O = 2/1, [UV, CAM]).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3335 (w, OH), 2955 (m, C–H), 2921 (s, C–H), 2861 (m, C–H), 1563 (w, C=C), 997 (s).

^{1}H-NMR (500 MHz, $CDCl_3$, 300 K): δ [ppm] = 0.94 (t, ^3J = 7.5 Hz, 3 H; CH_3), 1.58 (m, 2 H; CH_2-24), 1.62 (br. s, 1 H; OH), 2.88 (d, ^4J = 2.0 Hz, 1 H; H-29), 4.11 (qd, ^3J = 6.1, ^4J = 2.0 Hz, 1 H; CH-25), 5.70 (dt, ^3J = 16.0 Hz, ^4J = 2.0 Hz, 1 H; H-27), 6.24 (dd, ^3J = 16.0, 6.1 Hz, 1 H; H-26).

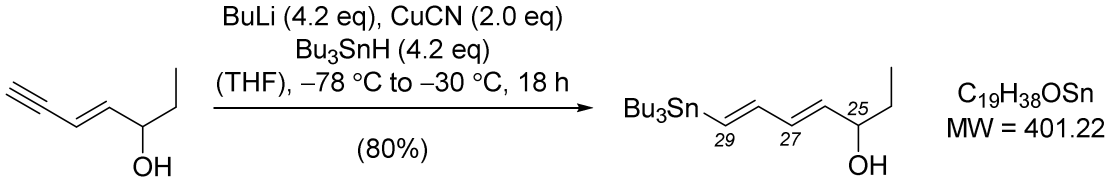
^{13}C-NMR (91 MHz, $CDCl_3$, 300 K): δ [ppm] = 9.6 (q, CH_3), 29.9 (t, CH_2-24), 73.5 (d, CH-25), 77.9 (d, CH-29), 81.8 (s, C-28), 109.0 (d, CH-27) 147.5 (d, CH-26).

MS (EI): *m/z* (%) = 109 [$(M{-}H)^+$] (9), 95 [$(M{-}CH_3)^+$] (10), 81 [$(M{-}C_2C_5)^+$] (100), 57 (52), 53 (82).

HRMS (EI)	$C_{16}H_{24}O_3Si$	calcd.: [$(M{-}H)^+$]	109.0648
		found: [$(M{-}H)^+$]	109.0645.

The obtained data matched those reported in literature.[3]

Tributylstannane 16



A suspension of 81.3 mg copper cyanide (0.91 mmol, 2.0 eq) in 3.6 ml tetrahydrofuran was cooled to –78 °C and 0.80 ml *n*-butyllithium (1.91 mmol, 2.4 M in hexane, 4.2 eq) were added dropwise. The reaction mixture was stirred at –40 °C for ten minutes and recooled to –78 °C. At this temperature 0.51 ml tributyltin hydride (1.91 mmol, 4.2 eq) were added dropwise and the reaction mixture again stirred at –40 °C for ten minutes. At –78 °C a solution of 50.0 mg **S4** (0.45 mmol, 1.0 eq) in 0.5 ml tetrahydrofuran was added and the reaction mixture slowly allowed to warm to –30 °C. After stirring at –30 °C overnight, a solution of ammonia and saturated aqueous NH_4Cl solution (6 ml, 5/1) was added. The aqueous layer was extracted with diethyl ether (3 × 10 ml), the combined organic layers dried over $MgSO_4$ and the solvent evaporated under reduced pressure. After flash column chromatography (pentane/diethyl ether = 10/1) 146 mg stannane **16** (0.36 mmol, 80%) were obtained.

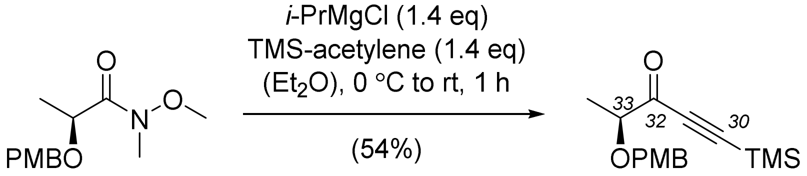
TLC: R_f = 0.36 (P:Et_2O = 2/1, [UV, CAM]).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3293 (m, OH), 2968 (w, C–H), 2930 (w, C–H), 2873 (w, C–H), 2101 (w, $C{-}C_{alkyne}$), 1631 (w, C=C), 957 (s).

^{1}H-NMR (500 MHz, $CDCl_3$, 300 K): δ [ppm] = 0.83–0.99 (m, 15 H; 3×CH_2, 3×CH_3, CH_3), 1.31 (sxt, ^3J = 7.3 Hz, 6 H; 3×CH_2), 1.43–1.64 (m, 8 H; 3×CH_2, CH_2-24), 4.04–4.11 (m, 1 H; H-25), 5.65 (dd, ^3J = 15.3, 6.8 Hz, 1 H; H-26), 6.16–6.23 (m, 1 H; H-27), 6.25 (d, ^3J = 18.8 Hz, 1 H; H-29), 6.52 (dd, ^3J = 18.8, 9.9 Hz, 1 H; H-28).

^{13}C-NMR (91 MHz, $CDCl_3$, 300 K): δ [ppm] = 9.7 (q, CH_3), 9.9 (q, CH_2CH_3), 13.8 (t, CH_2), 27.4 (q, CH_3), 29.3 (t, CH_2), 30.3 (t, CH_2-24), 74.1 (d, CH-25) 134.0 (d, CH-27), 134.8 (d, CH-26), 134.9 (d, CH-29), 146.2 (d, CH-28).

Alkynyl ketone S5



$C_{16}H_{22}O_3Si$
MW = 290.43

To a solution of 0.28 ml *iso*-propylmagnesiumchloride (0.55 mmol, 2 M in THF, 1.4 eq) in 1 ml diethyl ether were added 0.08 ml trimethylsilylacetylene (0.55 mmol, 1.4 eq). The solution was stirred for 1.5 hours before it was cooled to 0 °C and 0.10 g (*S*)-N-methoxy-2-[(4-methoxybenzyl)oxy]-*N*-methylpropanamide (0.39 mmol, 1.0 eq) in 1 ml diethyl ether were added dropwise. After one hour water (5 ml) was added and the aqueous layer was extracted with ethyl acetate (3 × 5 ml), the organic layer was dried over $MgSO_4$. The solvent was evaporated under reduced pressure and the crude product subjected to flash column chromatography (pentane/diethyl ether = 5/1) to afford 0.06 g of alkynyl ketone **S5** (0.21 mmol, 54%).

TLC: $R_f = 0.40$ (P:Et_2O = 5/1, [UV, CAM]).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2959 (w, C–H) , 2902 (w, C–H), 2871 (w, C–H), 2844 (w, C–H), 2150 (w, C–C_{alkyne}), 1679 (m), 1513 (m), 1247 (s, C–O), 1082 (m), 1034 (m), 845 (s).

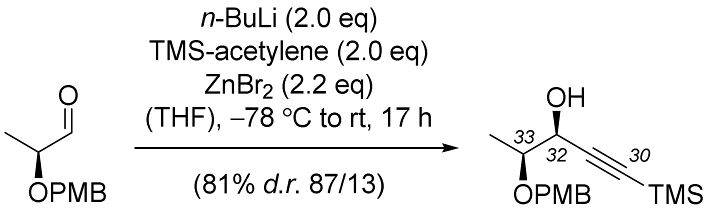
^{1}H-NMR (500 MHz, $CDCl_3$, 300 K): δ [ppm] = 0.26 [s, 9 H; $Si(CH_3)_3$], 1.41 (d, ^3J = 6.9 Hz, 3 H; CH_3-34), 3.81 (s, 3 H; OCH_3), 4.02 (q, ^3J = 6.9 Hz, 1 H; H-33); 4.40 (d, ^2J = 11.2 Hz, 1 H; CH*H*O), 4.64 (d, ^2J = 11.2 Hz, 1 H; C*H*HO), 6.86–6.90 (m, 2 H; H_{arom}), 7.29–7.33 (m, 2 H; H_{arom}).

^{13}C-NMR (91 MHz, $CDCl_3$, 300 K): δ [ppm] = –0.7 [q, $Si(CH_3)_3$], 17.9 (q, CH_3-34), 55.4 (q, OCH_3), 72.0 (t, CH_2), 80.5 (d, CH-33), 100.4 (s, C-30), 101.8 (s, C-31), 114.0 (d, CH_{arom}), 129.7 (s, C_{arom}), 129.8 (d, CH_{arom}), 159.6 (s, $C_{arom\text{-}OMe}$), 189.7 (s, C=O).

Reduction of alkynyl ketone S5

reagent	Yield (after purification)	dr (*syn*/*anti*) (obtained from crude NMR)
sodium borohydride	n.d.	≅ 44/55 TMS cleaved
lithium borohydride	65%	≅ 48/52 TMS cleaved
lithium tri-*sec*-butylborohydride (L-selectride)	65%	≅ 80/20 TMS partially cleaved
potassium tri-*sec*-butylborohydride (K-selectride)	31%	≅ 80/20 TMS partially cleaved
(*S*)-(−)-2-Methyl-CBS-oxazaborolidine, BH_3•Me_2S	73%	≅ 58/42
(*R*)-(+)-2-Methyl-CBS-oxazaborolidine, BH_3•Me_2S	82%	≅ 47/53

Alcohol 7



$C_{16}H_{24}O_3Si$
MW = 292.45

1.52 ml trimethylsilylacetylene (10.8 mmol, 2.0 eq) were dissolved in 22 ml diethyl ether. At 0 °C 4.5 ml *n*-butyllithium (10.8 mmol, 2.4 M in hexane, 2.0 eq) were added dropwise and the solution stirred for 30 minutes. The reaction mixture was transferred into a *Schlenk* flask with 2.67 g dry zinc bromide (11.9 mmol, 2.2 eq) and stirred at 0 °C for another 20 minutes before it was cooled to −78 °C and 1.05 g aldehyde (5.41 mmol, 1.0 eq) in 6 ml diethyl ether were added dropwise. The reaction mixture was stirred at −78 °C and allowed to warm to room temperature overnight. After addition of saturated aqueous NH_4Cl solution (30 ml), the aqueous layer was extracted with dichloromethane (3 × 25 ml). The combinedorganic layers were washed with saturated aqueous NaCl solution, dried over $MgSO_4$ and the solvent evaporated under reduced pressure. Flash column chromatography (pentane/diethyl ether = 10/1) afforded 1.03 g of clean *syn*-alcohol **7** (3.50 mmol, 65%) and 0.25 g of a mixture of *syn*- and *anti*-alcohol **7** (16%, *syn*/*anti* = 33/67).

syn-diastereoisomer **7**

TLC: R_f = 0.36 (P:Et_2O = 2/1, [UV, CAM]).

Specific rotation: $[\alpha]_D^{20}$ = +45.6 (c = 1.0, $CHCl_3$).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3419 (w, OH), 2958 (m, C–H), 2899 (m, C–H), 2836 (w, C–H), 2172 (w, C–C_{alkyne}), 1512 (m) 1247 (s, C–O), 840 (s), 759 (s).

^{1}H-NMR (500 MHz, $CDCl_3$, 300 K): δ [ppm] = 0.18 [s, 9 H; $Si(CH_3)_3$], 1.27 (d, ^3J = 6.3 Hz, 3 H; CH_3-34), 2.67 (d, ^3J = 4.3 Hz, 1 H; OH), 3.61 (dq, ^3J = 6.7, 6.3 Hz, 1 H; H-33), 3.81 (s, 3 H; OCH_3), 4.20 (dd, ^3J = 6.7, 4.3 Hz, 1 H; H-32), 4.50 (d, ^2J = 11.2 Hz, 1 H; CH*H*O), 4.63 (d, ^2J = 11.2 Hz, 1 H; C*H*HO), 6.85–6.93 (m, 2 H; H_{arom}), 7.23–7.30 (m, 2 H; H_{arom}).

^{13}C-NMR (91 MHz, $CDCl_3$, 300 K): δ [ppm] = –0.1 [q, $Si(CH_3)_3$], 16.3 (q, CH_3-34), 55.4 (q, OCH_3), 67.0 (d, CH-32), 71.5 (t, CH_2), 78.0 (d, CH-33), 90.9 (s, C-30), 104.0 (s, C-31), 114.1 (d, CH_{arom}), 129.6 (d, CH_{arom}), 130.3 (s, C_{arom}), 159.5 (s, $C_{arom\text{-}OMe}$).

anti-diastereoisomer *epi*-**7**

TLC: R_f = 0.32 (P:Et_2O = 2/1, [UV, CAM]).

Specific rotation: $[\alpha]_D^{20}$ = +8.4 (c = 1.0, $CHCl_3$).

^{1}H-NMR (500 MHz, $CDCl_3$, 300 K): δ [ppm] = 0.17 [s, 9 H; $Si(CH_3)_3$], 1.27 (d, ^3J = 6.3 Hz, 3 H; H_3-34), 2.32 (br. s, 1 H; OH), 3.65 (qd, ^3J = 6.3, 3.8 Hz, 1 H; H-33), 3.81 (s, 3 H; OCH_3), 4.45 (br. s, 1 H; H-32), 4.49 (d, ^2J = 11.6 Hz, 1 H; CH*H*O), 4.58 (d, ^2J = 11.6 Hz, 1 H; C*H*HO), 6.88–6.90 (m, 2 H; H_{arom}), 7.25–7.29 (m, 2 H; H_{arom}).

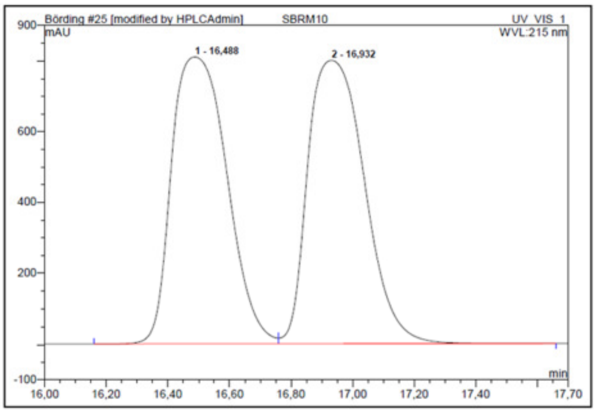
^{13}C-NMR (91 MHz, $CDCl_3$, 300 K): δ [ppm] = 0.0 (s, $Si(CH_3)_3$, 14.7 (q, CH_3-34), 55.4 (q, OCH_3), 65.5 (d, CH-32), 70.8 (t, CH_2), 76.6 (d, CH-33), 91.1 (s, C-30), 103.7 (s, C-31), 114.0 (d, $CH_{arom\text{-}PMB}$), 129.4 (d, $CH_{arom\text{-}PMB}$), 130.4 (s, C_{arom}), 159.4 (s, $C_{arom\text{-}OMe}$).

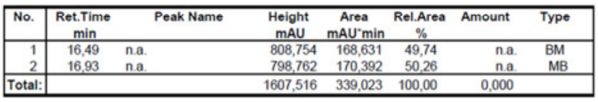
MS (ESI): *m/z* (%) = 310 (18) [$(M+NH_4)^+$], 315 (98) [$(M+Na)^+$], 275 (100), 241 (41).

HRMS (ESI) $C_{16}H_{24}O_3Si$ calcd.: [$(M+Na)^+$] 315.1387
found: [$(M+Na)^+$] 315.1385.

Chiral HPLC: t_R [racemate] = t_R [racemate] = 16.4 min, 16.9 min; t_R [**7**] = 16.4 min, t_R [*ent*-**7**] = 16.9 min; (OJ-RH, 150 × 4.6 mm, acetonitrile/H_2O = 20/80 to 100/0, 1 mL/min, λ = 210 nm).

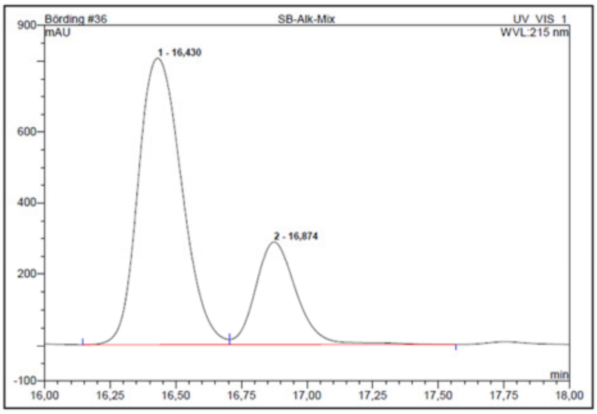
- racemic mixture of **7**

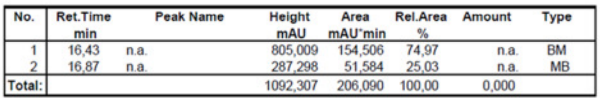




No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16,49	n.a.	808,754	168,631	49,74	n.a.	BM
2	16,93	n.a.	798,762	170,392	50,26	n.a.	MB
Total:			1607,516	339,023	100,00	0,000	

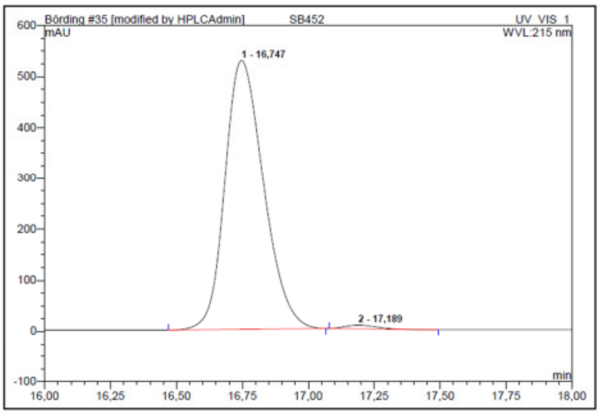
- enantioenriched mixture of **7**

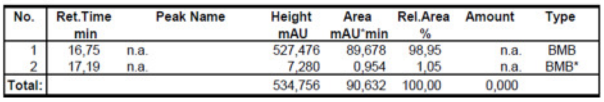




No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16,43	n.a.	805,009	154,506	74,97	n.a.	BM
2	16,87	n.a.	287,298	51,584	25,03	n.a.	MB
Total:			1092,307	206,090	100,00	0,000	

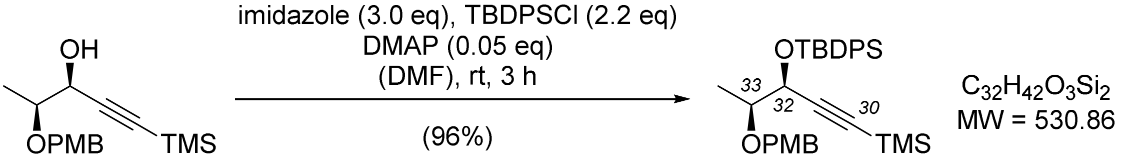
- enantiopure compound **7** (98% *ee*)





No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16,75	n.a.	527,476	89,678	98,95	n.a.	BMB
2	17,19	n.a.	7,280	0,954	1,05	n.a.	BMB*
Total:			534,756	90,632	100,00	0,000	

Protected diol S6



To a solution of 0.54 g alcohol **7** (1.84 mmol, 1.0 eq) in 2 ml dimethylformamide were added 1.06 ml *tert*-butyldiphenylchlorosilane (4.06 mmol, 2.2 eq), 0.35 g imidazole (5.57 mmol, 3.0 eq) and 0.01 g 4-dimethylaminopyridine (0.09 mmol, 0.05 eq). The reaction mixture was stirred for three hours before saturated aqueous $NaHCO_3$ solution (5 ml) was added. The aqueous layer was extracted with dichloromethane (3 × 5 ml), the combined organic layers dried over $MgSO_4$ and the solvents evaporated under reduced pressure. The crude product was subjected to flash column chromatography on silica (pentane/diethyl ether = 20/1) to give 0.94 g of protected alcohol **S6** (1.78 mmol, 96%).

TLC: $R_f = 0.42$ (P:Et_2O = 10/1, [UV, CAM]).

Specific rotation: $[\alpha]_D^{20} = +31.8$ (c = 1.0, $CHCl_3$).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2957 (m, C–H), 2932 (m, C–H), 2895 (m, C–H), 2858 (m, C–H), 2174 (w, $C–C_{alkyne}$), 1552 (m), 1247 (s, C-O), 1092 (s), 841 (s), 700 (s).

^{1}H-NMR (500 MHz, $CDCl_3$, 300 K): δ [ppm] = 0.07 [s, 9 H; $Si(CH_3)_3$], 1.08 [s, 9 H; $C(CH_3)_3$], 1.28 (d, ^3J = 6.3 Hz, 3 H; CH_3-34), 3.53 (qd, ^3J = 6.3, 5.8 Hz, 2 H; H-33), 3.80 (s, 3 H; OCH_3), 4.35 (d, ^2J = 11.6 Hz, 1 H; C*H*HO), 4.42 (d, ^2J = 11.6 Hz, 1 H; CH*H*O), 4.44 (d, ^3J = 5.8 Hz, 1H; H-32), 6.80–6.83 (m, 2 H; $H_{arom\text{-}PMB}$), 7.13–7.17 (m, 2 H; $H_{arom\text{-}PMB}$), 7.30–7.39 (m, 4 H; H_{TBDPS}), 7.39–7.45 (m, 2 H; H_{TBDPS}), 7.67–7.79 (m, 2 H; H_{TBDPS}), 7.75–7.79 (m, 2 H; H_{TBDPS}).

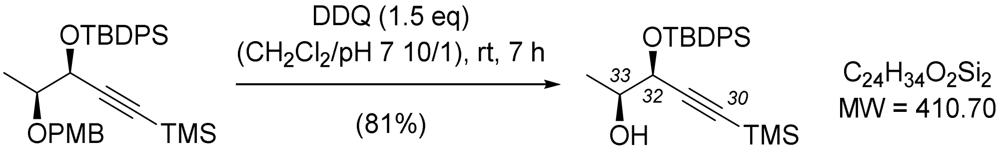
^{13}C-NMR (91 MHz, $CDCl_3$, 300 K): δ [ppm] = –0.1 [q, $Si(CH_3)_3$], 15.8 (q, CH_3-34), 19.5 [s, *C*$(CH_3)_3$], 27.1 [q, C(*C*$H_3)_3$], 55.4 (q, OCH_3), 67.4 (d, CH-32), 71.2 (t, CH_2), 77.3 (d, CH-33), 91.2 (s, C-30), 104.6 (s, C-31), 113.8 (d, $CH_{arom\text{-}PMB}$), 127.5, 127.7 (d, $CH_{arom\text{-}TBDPS}$), 129.3 (d, $CH_{arom\text{-}PMB}$), 129.7 (d, $CH_{arom\text{-}TBDPS}$), 129.8 (s, $C_{arom\text{-}TBDPS}$), 130.9 (s, $C_{arom\text{-}PMB}$), 133.7 (s, $C_{arom\text{-}TBDPS}$), 136.1, 136.3 (d, $CH_{arom\text{-}TBDPS}$), 159.2 (s, $C_{arom\text{-}PMB\text{-}OMe}$).

MS (ESI): *m/z* (%) = 553 [$(M+Na)^+$] (100), 548 [$(M+NH_4)^+$] (98), 532 [$(M+H)^+$] (14), 423 (28), 395 (41), 275 (64).

HRMS (ESI) $C_{32}H_{42}O_3Si_2$ calcd.: $[(M+Na)^+]$ 553.2565

found: $[(M+Na)^+]$ 553.2566.

Alcohol 8



To a solution of 0.68 g protected alcohol **S6** (1.28 mmol, 1.0 eq) in 8 ml of a mixture of dichloromethane and pH 7 buffer (10/1) was added 0.44 g 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (1.90 mmol, 1.5 eq). After stirring the reaction mixture for seven hours, the reaction was quenched by the addition of saturated aqueous NH_4Cl solution (10 ml) and the aqueous layer extracted with dichloromethane (3 × 10 ml). The combined organic layers were dried over $MgSO_4$ and the solvent evaporated under reduced pressure. Flash column chromatography on silica (pentane/diethyl ether = 20/1) afforded 0.43 g of deprotected alcohol **8** (1.04 mmol, 81%).

TLC: $R_f = 0.36$ ($P:Et_2O = 5/1$, [UV, CAM]).

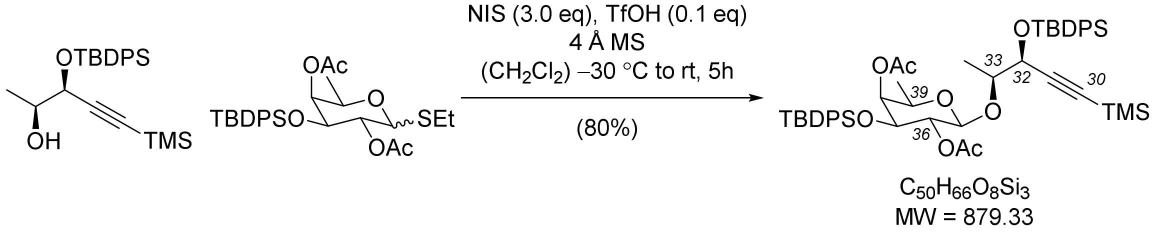
Specific rotation: $[\alpha]_D^{20} = +89.6$ (c = 1.0, $CHCl_3$).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3581 (w, OH), 2959 (m, C–H), 2931 (m, C–H), 2894 (m, C–H), 2856 (m, C–H), 2173 (w, $C–C_{alkyne}$), 1250 (s, C–O), 1105 (m), 1083 (m), 840 (s), 699 (s).

^{1}H-NMR (500 MHz, $CDCl_3$, 300 K): δ [ppm] = 0.02 [s, 9 H; $Si(CH_3)_3$], 1.11 [s, 9 H; $C(CH_3)_3$], 1.25 (d, $^3J = 6.3$ Hz, 3 H; CH_3-34), 2.47 (d, $^3J = 4.0$ Hz, 1 H; OH), 3.80–3.88 (m, 1 H; H-33), 4.16 (d, $^3J = 7.0$ Hz, 1 H; H-32), 7.36–7.47 (m, 6 H; H_{arom}), 7.70–7.78 (m, 4 H; H_{arom}).

^{13}C-NMR (91 MHz, $CDCl_3$, 300 K): δ [ppm] = –0.3 [q, $Si(CH_3)_3$], 18.0 (q, CH_3-34), 19.5, 19.5 [s, $C(CH_3)_3$], 27.1 [q, $C(CH_3)_3$], 69.8 (d, CH-32), 71.3 (d, CH-33), 92.3 (s, C-30), 103.7 (s, C-31), 127.5, 127.8 (d, CH_{arom}), 129.8, 130.0 (d, CH_{arom}), 133.1, 133.4 (s, C_{arom}), 136.0, 136.2 (d, CH_{arom}).

Glycoside 9



A solution of 1.06 g sugar **5** (1.99 mmol, 1.0 eq) and 0.98 g alcohol **8** (2.39 mmol, 1.2 eq) in 20 ml dichloromethane sieves was stirred for two hours with powdered 4Å molecular at room temperature before it was cooled to −30 °C. In the dark 1.34 g *N*-iodosuccinimide (5.97 mmol, 3.0 eq) was added and 0.02 ml trifluoromethanesulfonic acid (0.20 mmol, 0.1 eq) was added dropwise. The reaction mixture was allowed to slowly warm to room temperature over five hours. After filtration through a pad of Celite, saturated aqueous $Na_2S_2O_3$ solution (30 ml) was added and the aqueous layer was extracted with dichloromethane (3 × 40 ml). The combined organic layers were washed with saturated aqueous NaCl solution (40 ml) and dried over $MgSO_4$. The solvent was evaporated under reduced pressure and the crude product subjected to flash column chromatography (pentane/diethyl ether = 5/1) to afford 1.40 g of the desired product **9** (1.59 mmol, 80%).

TLC: $R_f = 0.16$ (P:Et_2O = 5/1, [UV, CAM]).

Specific rotation: $[\alpha]_D^{20} = +24.4$ (c = 1.0, $CHCl_3$).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3071 (w, C–H), 2957 (m, C–H), 2933 (m, C–H), 2893 (m, C–H), 2859 (m, C–H), 2360 (w, C–C$_{alkyne}$), 2174 (w, C–C$_{alkyne}$), 1748 (m, C=O), 1221 (s, C–O), 1066 (s), 842 (m).

^{1}H-NMR (500 MHz, $CDCl_3$, 300 K): δ [ppm] = 0.09 [s, 9 H; Si(CH_3)$_3$], 0.97 [s, 9 H; C(CH_3)$_3$], 0.96–0.99 (m, 3 H; CH_3-40), 1.05 [s, 9 H; C(CH_3)$_3$], 1.30 (d, ^3J = 6.3 Hz, 3 H; CH_3-34), 1.46 [s, 3 H; C(O)CH_3-36], 2.12 [s, 3 H; C(O)CH_3-38], 3.05 (q, ^3J = 6.4 Hz, 1 H; H-39), 3.44 (d, ^3J = 8.1 Hz, 1 H; H-35), 3.41 (qd, ^3J = 6.3, 3.9 Hz, 1 H; H-33), 3.60 (dd, ^3J = 9.8, 3.3 Hz, 1 H; H-37), 4.19 (d, ^3J = 3.9 Hz, 1 H; H-32), 4.79 (d, ^3J = 3.3 Hz, 1 H; H-38), 5.06 (dd, ^3J = 9.8, 8.1 Hz, 1 H; H-36), 7.23–7.27 (m, 4 H; H$_{arom}$), 7.30–7.48 (m, 10 H; H$_{arom}$), 7.55–7.58 (m, 2 H; H$_{arom}$), 7.60–7.65 (m, 4 H; H$_{arom}$), 7.69–7.73 (m, 2 H; H$_{arom}$).

^{13}C-NMR (91 MHz, $CDCl_3$, 300 K): δ [ppm] = −0.1 [q, Si(CH_3)$_3$], 15.8 (q, CH_3-34), 16.5 (s, CH_3-40), 19.3 [s, *C*(CH_3)$_3$], 21.0 [q, C(O)*C*H_3-38*], 21.1 [q, C(O)*C*H_3-36*], 26.7 [q,

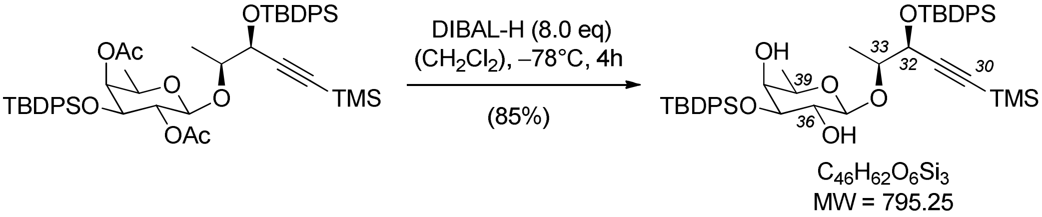
$C(CH_3)_3$], 27.0 [q, $C(CH_3)_3$], 66.4 (d, CH-32), 69.2 (d, CH-39), 71.3 (d, CH-36), 72.2 (d, CH-37), 73.3 (d, CH-38), 77.3 (d, CH-33), 91.3 (s, C-30), 100.8 (d, CH-35), 103.4 (s, C-31), 127.6, 127.6, 127.8, 127.8, 129.8, 129.8, 129.9, 130.2 (d, CH_{arom}), 132.8, 133.3, 133.5 (s, C_{arom}), 136.0, 136.1, 136.2, 136.3 (d, CH_{arom}), 169.1 (s, CO-36), 170.8 (s, CO-38).

*commutable signals.

MS (ESI): *m/z* (%) = 901 [$(M+Na)^+$] (42), 896 [$(M+NH_4)^+$] (34), 469 (100).

HRMS (ESI)	$C_{50}H_{66}O_8Si_3$	calcd.: [$(M+Na)^+$]	901.3958
		found: [$(M+Na)^+$]	901.3964.

Diol 10



To a solution of 1.27 g **9** (1.45 mmol, 1.0 eq) in 11 ml dichloromethane at −78 °C were added 11.6 ml diisobutylaluminium hydride (11.6 mmol, 1 M in dichloromethane, 8.0 eq). The reaction mixture was stirred at that temperature for four hours before saturated aqueous potassium sodium tartrate solution (20 ml) was added at −78 °C. The solution was warmed to room temperature and stirred until a clear solution resulted. The aqueous layer was extracted with ethyl acetate (3 × 30 ml), the combined organic layers dried over $MgSO_4$ and the solvent evaporated under reduced pressure. Flash column chromatography (pentane/diethyl ether = 5/1) afforded 0.98 g diol **10** (1.23 mmol, 85%).

TLC: $R_f = 0.17$ (P:Et_2O = 5/1, [UV, CAM]).

Specific rotation: $[\alpha]_D^{20} = +20.0$ (c = 1.0, $CHCl_3$).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3567 (w, OH), 3071 (w, C–H), 3050 (w, C–H), 2957 (m, C–H), 2931 (m, C–H), 2894 (m, C–H), 2857 (m, C–H), 2361 (w), 2173 (w), 1110 (s, C–O), 845 (m).

^{1}H-NMR (500 MHz, $CDCl_3$, 300 K): δ [ppm] = 0.03 [s, 9 H; $Si(CH_3)_3$], 1.06 [s, 9 H; $C(CH_3)_3$], 1.09 [s, 9 H; $C(CH_3)_3$], 1.22 (d, ^3J = 6.5 Hz, 3 H; CH_3-40), 1.35 (d, ^3J = 6.3 Hz, 3 H; CH_3-34), 2.26 (s, 1 H; OH-36), 2.52 (s, 1 H; OH-38), 3.11 (q, $^3J = 6.5$ Hz, 1 H; H-39), 3.23 (br. s., 1 H; H-38), 3.51 (dd, $^3J = 8.9$, 3.5 Hz, 1 H; H-37), 3.60–3.72 (m, 3 H; H-36, H-33, H-35), 4.37 (d, $^3J = 4.6$ Hz, 1 H; H-32), 7.27–7.45 (m, 12 H; H_{arom}), 7.64–7.71 (m, 4 H; H_{arom}), 7.71–7.75 (m, 4 H; H_{arom}).

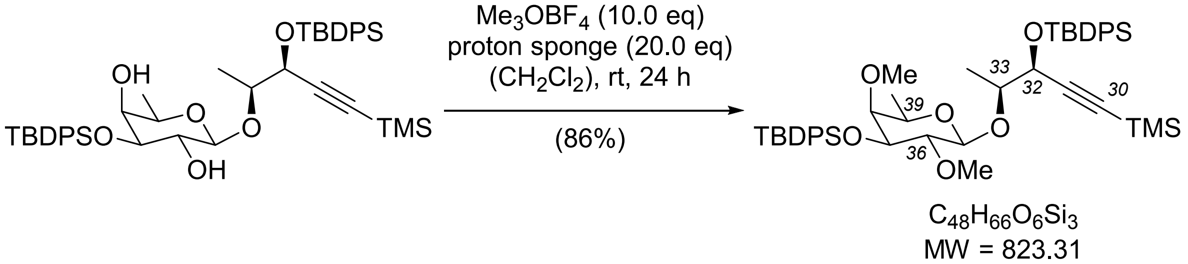
^{13}C-NMR (91 MHz, $CDCl_3$, 300 K): δ [ppm] = –0.3 [q, $Si(CH_3)_3$], 16.5 (s, CH_3-40*), 16.7 (s, CH_3-34*), 19.4 [q, $C(CH_3)_3$], 19.6 [q, $C(CH_3)_3$], 27.1 [q, $C(CH_3)_3$], 27.1 [q, $C(CH_3)_3$], 66.7 (d, CH-32), 70.0 (d, CH-39), 71.9 (d, CH-38*), 71.9 (d, CH-36*), 75.6 (d, CH-37), 77.3 (d, CH-33), 92.0 (s, C-30), 102.7 (d, CH-35), 104.1 (s, C-31), 127.5, 127.6, 127.8, 127.9 (d, CH_{arom}), 129.8, 129.9, 130.0 (d, CH_{arom}), 133.3, 133.4, 133.5, 133.8 (s, C_{arom}) 136.0, 136.1, 136.2, 136.3 (d, CH_{arom}).

*commutable signals.

MS (ESI): *m/z* (%) = 817 [(M+Na)$^+$] (100), 812 [(M+NH$_4$)$^+$] (84).

HRMS (ESI)	$C_{46}H_{62}O_6Si_3$	calcd.: [(M+Na)$^+$]	817.3746
		found: [(M+Na)$^+$]	817.3760 .

Methylated diol 11



A solution of 0.69 g trimethyloxoniumtetrafluoroborate (4.65 mmol, 10.0 eq) and 1.98 g 1,8-bis(dimethylamino)naphthalene (9.29 mmol, 20.0 eq) in 5 ml dichloromethane were stirred with powdered 4Å molecular sieves in the dark for two hours before 0.37 g diol **10** (0.47 mmol, 1.0 eq) in 5 ml dichloromethane were added. After the reaction mixture was stirred for 24 hours, it was diluted with ethyl acetate (10 ml) and filtered through a pad of Celite. Saturated aqueous NH_4Cl solution (50 ml) was added and the aqueous layer extracted with ethyl acetate (3 × 50 ml). The combined organic layers were washed with 0.25 M $NaHSO_4$ solution(2 × 30 ml), $NaHCO_3$ solution (30 ml) and NaCl solution (30 ml), dried over $MgSO_4$ and the solvent evaporated under reduced pressure. After flash column chromatography on silica (pentane/diethyl ether = 10/1) 0.33 g of the desired product **11** (39.9 mmol, 86%) were obtained.

TLC: $R_f = 0.49$ (P:Et_2O = 5/1, [UV, CAM]).

Specific rotation: $[\alpha]_D^{20} = +5.0$ (c = 1.0, $CHCl_3$).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3071 (w, C–H), 3050 (w, C–H), 2957 (m, C–H), 2932 (m, C–H), 2894 (m, C–H), 2858 (m, C–H), 1109 (s, C–O), 1066 (s), 841 (m).

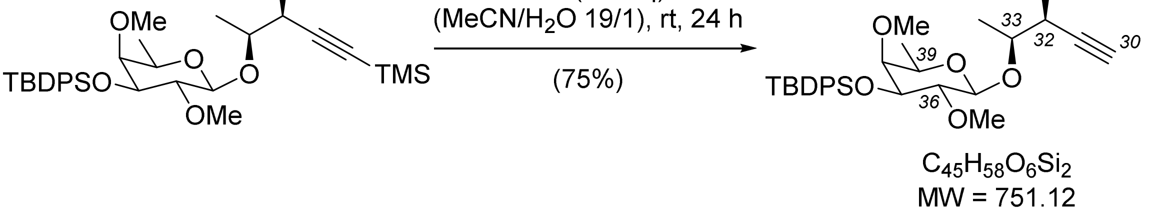
^{1}H-NMR (500 MHz, $CDCl_3$, 300 K): δ [ppm] = 0.05 [s, 9 H; $Si(CH_3)_3$], 1.07–1.14 (m, 21 H; 2×$C(CH_3)_3$, CH_3-40), 1.32 (d, ^3J = 6.3 Hz, 3 H; CH_3-34), 2.70 (d, ^3J = 2.9 Hz, 1 H; H-38), 2.93 (q, ^3J = 6.4 Hz, 1 H; H-39), 3.15 (dd, ^3J = 9.5, 7.6 Hz, 1 H; H-36), 3.22 (s, 3 H; OCH_3-36), 3.41 (s, 3 H; OCH_3-38), 3.50 (dd, ^3J = 9.5, 2.9 Hz, 1 H; H-37), 3.57–3.67 (m, 2 H; H-35, H-33), 4.40 (d, ^3J = 4.2 Hz, 1 H; H-32), 7.28–7.34 (m, 2 H; H_{arom}), 7.34–7.48 (m, 10 H; H_{arom}), 7.66–7.71 (m, 2 H; H_{arom}), 7.73–7.78 (m, 6 H; H_{arom}).

^{13}C-NMR (91 MHz, $CDCl_3$, 300 K): δ [ppm] = –0.2 [q, $Si(CH_3)_3$], 16.3 (q, CH_3-40), 16.7 (q, CH_3-34), 19.4 [s, $\mathit{C}(CH_3)_3$], 19.6 [s, $\mathit{C}(CH_3)_3$], 27.0 [q, $C(\mathit{C}H_3)_3$], 27.2 [q, $C(\mathit{C}H_3)_3$], 60.4 (q, OCH_3-36), 62.2 (q, OCH_3-38), 66.2 (d, CH-32), 69.8 (d, CH-39), 76.2 (d, CH-33), 76.2 (d, CH-37), 80.9 (d, CH-36), 82.1 (d, CH-38), 90.9 (d, CH-35), 102.8 (s, C-31), 104.3 (s, C-31,) 127.4, 127.5, 127.6, 127.7 (d, CH_{arom}), 129.5, 129.7, 129.8 (d, CH_{arom}), 133.6, 133.6, 134.2, 134.5 (s, C_{arom}), 136.1, 136.1, 136.2, 136.3 (d, CH_{arom}).

MS (ESI): *m/z* (%) = 845 [$(M+Na)^+$] (18), 840 [$(M+NH_4)^+$] (100).

HRMS (ESI) $C_{48}H_{66}O_6Si_3$ calcd.: [$(M+ NH_4)^+$] 840.4505
found: [$(M+NH_4)^+$] 840.4513.

Alkyne 12



To a solution of 0.31 g **11** (0.38 mmol, 1.0 eq) in 4 ml acetonitrile/water (19/1) was added 0.07 ml 1,8-diazabicyclo[5.4.0]undec-7-ene (0.45 mmol, 1.2 eq). The reaction mixture was stirred for 24 hours before the solvent was evaporated under reduced pressure. Flash column chromatography on silica (pentane/diethyl ether = 10/1) afforded 0.21 g of alkyne **12** (0.28 mmol, 75%).

TLC: $R_f = 0.35$ (P:Et_2O = 5/1, [UV, CAM]).

Specific rotation: $[\alpha]_D^{20} = -4.5$ (c = 1.0, $CHCl_3$).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3071 (w, C–H), 3049 (w, C–H), 2932 (m, C–H), 2891 (m, C–H), 2857 (m, C–H), 1106 (s, C–O), 1089 (s), 1061 (s).

^{1}H-NMR (500 MHz, $CDCl_3$, 300 K): δ [ppm] = 1.06 (d, $^3J = 6.4$ Hz, 3 H; CH_3-40), 1.08 [s, 18 H; 2×$C(CH_3)_3$], 1.35 (d, $^3J = 6.3$ Hz, 3 H; CH_3-34), 2.29 (d, $^4J = 2.1$ Hz, 1 H; H-30), 2.71 (d, $^3J = 2.8$ Hz, 1 H; H-38), 2.89 (q, $^3J \cong 6.4$ Hz, 1 H; H-39), 3.14 (dd, $^3J = 9.5$, 7.7 Hz, 1 H; H-36), 3.19 (s, 3 H; OCH_3-36), 3.37 (d, $^3J = 7.7$ Hz, 1 H; H-35), 3.43 (s, 3 H; OCH_3-38), 3.44–3.53 (m, 2 H; H-37, H-33), 4.43–4.46 (m, 1 H; H-32), 7.26–7.31 (m, 2 H; H_{arom}), 7.32–7.46 (m, 10 H; H_{arom}), 7.63–7.67 (m, 2 H; H_{arom}), 7.70–7.76 (m, 6 H; H_{arom}).

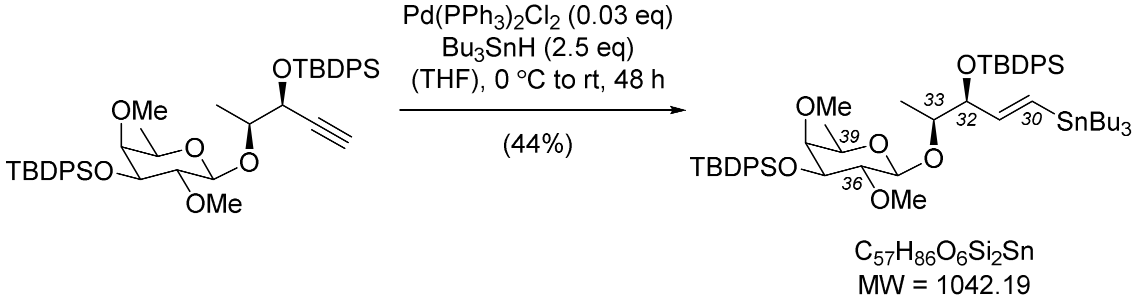
^{13}C-NMR (91 MHz, $CDCl_3$, 300 K): δ [ppm] = 15.9 (q, CH_3-34), 16.7 (q, CH_3-40), 19.3 [s, $C(CH_3)_3$], 19.6 [s, $\mathit{C}(CH_3)_3$], 27.0 [q, $C(\mathit{C}H_3)_3$], 27.2 [q, $C(\mathit{C}H_3)_3$], 60.4 (q, OCH_3-36), 62.1 (q, OCH_3-38), 65.6 (d, CH-32), 69.8 (d, CH-39), 74.2 (d, CH-30), 76.2 (d, CH-37*), 76.3 (d, CH-33*), 80.7 (d, CH-36), 82.1 (d, CH-38), 82.2 (s, C-31), 102.9 (d, CH-35), 127.4, 127.6, 127.6, 127.8 (d, CH_{arom}) 129.5, 129.7, 129.9, 129.9 (d, CH_{arom}), 133.3, 133.5 (s, C_{arom}), 134.2, 134.4 (s, C_{arom}), 136.0, 136.1, 136.2, 136.3 (d, CH_{arom}).

*commutable signals.

MS (ESI): *m/z* (%) = 773 [$(M+Na)^+$] (100), 768 [$(M+NH_4)^+$] (59), 694 (26), 613 (15), 397 (19).

HRMS (ESI) $C_{45}H_{58}O_6Si_2$ calcd.: [$(M+Na)^+$] 773.3664
found: [$(M+Na)^+$] 773.3670.

Vinylstannane 13



A solution of 100 mg alkyne **12** (133 μmol, 1.0 eq) in 0.5 ml tetrahydofuran was cooled to 0 °C and 2.8 mg $PdCl_2(PPh_3)_2$ (3.99 μmol, 0.03 eq) were added. 88.0 μl tributyltin hydride (33.3 μmol, 2.5 eq) were added dropwise and the reaction mixture was allowed to reach room temperature. After 48 hours the solvent was evaporated under reduced pressure and the crude product subjected to flash column chromatography on silica (pentane/diethyl ether = 50/1 to 20/1) to give 61.1 mg of vinyl stannane **13** (58.7 μmol, 44%).

TLC: $R_f = 0.56$ ($P:Et_2O = 5/1$, [UV, CAM]).

Specific rotation: $[\alpha]_D^{20} = -14.8$ (c = 1.0, $CHCl_3$)

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3070 (w, C–H), 3049 (w, C–H), 2955 (m, C–H), 2928 (m, C–H), 2856 (m, C–H), 1645 (w, C=C), 1590 (w, C=C), 1108 (s, C–O), 1089 (s), 1060 (m).

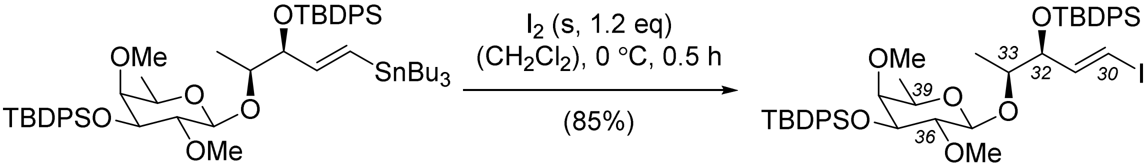
^{1}H-NMR (500 MHz, $CDCl_3$, 300 K): δ [ppm] = 0.82–0.90 (m, 15 H; 3×CH_3, 3×CH_2), 1.00 (d, ^3J = 6.4 Hz, 3 H; CH_3-40), 1.05–1.10 [m, 21 H; $C(CH_3)_3$; CH_3-34], 1.25–1.34 (m, 6 H; 3×CH_2), 1.44–1.52 (m, 6 H; 3×CH_2), 2.65 (d, ^3J = 2.9 Hz, 1 H; H-38), 2.82 (q, ^3J = 6.4 Hz, 1 H; H-39), 3.12 (dd, ^3J = 9.5, 7.9 Hz, 1 H; H-36), 3.21 (s, 3 H; OCH_3-36), 3.36–3.42 (m, 5 H; H-33, H-35, OCH_3-38), 3.49 (dd, ^3J = 9.5, 2.9 Hz, 1 H; H-37), 4.27–4.32 (m, 1 H; H-32), 6.05 (dd, ^3J = 19.2, 4.2 Hz, 1 H; H-31), 6.30 (d, ^3J = 19.2 Hz, 1 H; H-30), 7.24–7.45 (m, 12 H; H_{arom}), 7.60–7.66 (m, 4 H; H_{arom}), 7.71–7.75 (m, 4 H; H_{arom}).

^{13}C-NMR (91 MHz, $CDCl_3$, 300 K): δ [ppm] = 9.6 (t, CH_2), 13.9 (q, CH_3), 15.7 (q, CH_3-34), 16.7 (d, CH_3-40), 19.5 [s, $C(CH_3)_3$], 19.6 [s, $C(CH_3)_3$], 27.2 [q, $C(CH_3)_3$], 27.4 (t, CH_2), 29.3 (t, CH_2), 60.5 (q, OCH_3-36), 62.1 (q, OCH_3-38), 69.7 (d, CH-39), 75.8 (d, CH-32), 76.3 (d, CH-37), 77.4 (d, CH-33), 81.0 (d, CH-36), 82.1 (d, CH-38), 103.0 (d, CH-35), 127.4, 127.5, 127.6 (d, CH_{arom}), 128.8 (d, CH-30), 129.5, 129.6, 129.7, 129.8 (d, CH_{arom}), 134.2, 134.2, 134.5, 134.6 (s, C_{arom}), 136.1, 136.2, 136.3 (d, CH_{arom}), 145.7 (d, CH-31).

MS (ESI): *m/z* (%) = 1065 [$(M+Na)^+$] (44), 1060 [$(M+NH_4)^+$] (40), 1044 [$(M+H)^+$] (4), 332 (100).

HRMS (ESI)	$C_{57}H_{86}O_6Si_2Sn$	calcd.: [$(M+Na)^+$]	1065.4877
		found: [$(M+Na)^+$]	1065.4909.

Vinyliodide 14



$C_{45}H_{59}IO_6Si_2$
MW = 879.04

A solution of 97.0 mg stannane **13** (92.6 µmol, 1.0 eq) in 0.5 ml dichloromethane was cooled to 0 °C and 28.2 mg solid iodine (111 µmol, 1.2 eq) were added. After 20 minutes saturated aqueous $Na_2S_2O_3$ solution (5 ml) was added. The aqueous layer was extracted with dichloromethane (3 × 5 ml), the combined organic layers dried over $MgSO_4$ and the solvent evaporated under reduced pressure. Flash column chromatography on silica (pentane/diethyl ether = 10/1) afforded 69.2 mg of vinyliodide **14** (78.7 µmol, 85%).

TLC: $R_f = 0.42$ (P:Et_2O = 5/1, [UV, CAM]).

Specific rotation: $[\alpha]_D^{20} = -9.1$ (c = 0.88, $CHCl_3$)

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3070 (w, C–H), 3049 (w, C–H), 2931 (m, C–H), 2891 (m, C–H), 2857 (m, C–H), 1607 (w, C=C), 1109 (s, C–O), 1061 (m).

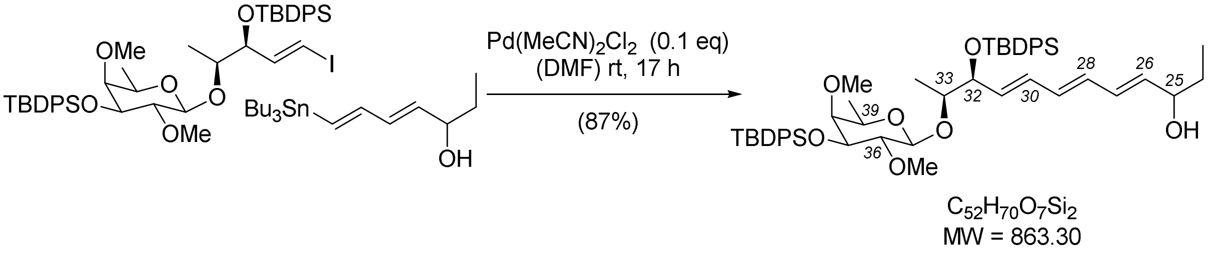
^{1}H-NMR (500 MHz, $CDCl_3$, 300 K): δ [ppm] = 1.01 (d, ^3J = 6.4 Hz, 3 H; CH_3-40), 1.06 [s, 9 H; $SiC(CH_3)_3$], 1.08 [s, 9 H; $SiC(CH_3)_3$], 1.11 (d, ^3J = 6.4 Hz, 3 H; CH_3-34), 2.64 (d, ^3J = 2.8 Hz, 1 H; H-38), 2.85 (q, ^3J = 6.4 Hz, 1 H, H-39), 3.12 (dd, ^3J = 9.5, 7.8 Hz, 1 H; H-36), 3.20 (s, 3 H; OCH_3-36), 3.39 (s, 3 H; OCH_3-38), 3.34–3.41 (m, 2 H; H-33, H-35), 3.49 (dd, ^3J = 9.5, 2.8 Hz, 1 H, H-37), 4.22–4.26 (m, 1 H; H-32), 6.22 (dd, ^3J = 14.4 Hz, ^4J = 1.4 Hz, 1 H; H-30), 6.60 (dd, ^3J = 14.4, 5.1 Hz, 1 H; H-31), 7.27–7.46 (m, 12 H; H_{arom}), 7.55–7.63 (m, 4 H; H_{arom}), 7.70–7.75 (m, 4 H; H_{arom}).

^{13}C-NMR (91 MHz, CDCl$_3$, 300 K): δ [ppm] = 15.5 (q, CH$_3$-34), 16.7 (q, CH$_3$-40), 19.5 [s, *C*(CH$_3$)$_3$], 19.5 [s, *C*(CH$_3$)$_3$], 27.1 [q, C(*C*H$_3$)$_3$], 27.2 [q, C(*C*H$_3$)$_3$], 60.7 (q, OCH$_3$-36), 62.1 (q, OCH$_3$-38), 69.9 (q, CH-39), 75.9 (d, CH-32), 76.3 (d, CH-37), 76.7 (d, CH-33), 77.4 (d, CH-30), 80.9 (d, CH-36), 82.0 (d, CH-38), 102.9 (d, CH-35), 127.5, 127.7, 127.8, 127.8, 127.9 (d, CH$_{\text{arom}}$), 129.6, 129.8, 130.0 (d, CH$_{\text{arom}}$), 133.3, 133.7, 134.1, 134.5, 134.9 (s, C$_{\text{arom}}$), 135.9, 136.0, 136.2, 136.3 (d, CH$_{\text{arom}}$), 144.3 (d, CH-31).

MS (ESI): *m/z* (%) = 901 [(M+Na)$^+$] (81), 896 [(M+NH$_4$)$^+$] (100), 741 (28).

HRMS (ESI)	$C_{45}H_{59}IO_6Si_2$	calcd.: [(m+NH$_4$)$^+$]	896.3233
		found: [(m+NH$_4$)$^+$]	896.3255.

Trienol 17



In the dark 1.3 mg PdCl$_2$(MeCN)$_2$ (5.1 µmol, 0.1 eq) were added to a solution of 44.6 mg vinyliodide **14** (50.7 µmol, 1.0 eq) in 1 ml dimethylformamide. After stirring for ten minutes, 24.4 mg stannane **16** (60.9 µl, 1.2 eq) were added and the reaction mixture stirred for 17 hours. After evaporation of the solvent under reduced pressure flash column chromatography (pentane/diethyl ether = 2/1) afforded 38.1 mg of trienol **17** (44.1 µmol, 87%).

TLC: $R_f = 0.18$ (P:Et$_2$O = 2/1, [UV, CAM]).

^{1}H-NMR (500 MHz, CDCl$_3$, 300 K): δ [ppm] = 0.94 (t, ^3J = 6.8 Hz, 3 H; CH$_2$C*H*$_3$), 1.00 (d, ^3J = 6.4 Hz, 3 H; CH$_3$-40), 1.07 [s, 9 H; SiC(CH$_3$)$_3$], 1.08 [s, 12 H; SiC(CH$_3$)$_3$, CH$_3$-34], 1.52–1.67 (m, 2 H; CH$_2$-24), 2.66 (d, ^3J = 2.8 Hz, 1 H; H-38), 2.85 (q, ^3J = 6.4 Hz, 1 H, H-39), 3.11 (dd, ^3J = 9.5, 7.9 Hz, 1 H; H-36), 3.18 (s, 3 H; OCH$_3$-36), 3.39 (s, 3 H; OCH$_3$-38), 3.37–3.41 (m, 2 H; H-33, H-35), 3.49 (dd, ^3J = 9.5, 2.8 Hz, 1 H, H-37), 4.10 (q, ^3J = 6.7 Hz, 1 H; H-25), 4.36 (t, ^3J = 4.2 Hz, 1 H; H-32), 5.69 (dd, ^3J = 15.1, 6.7 Hz, 1 H; H-26), 5.78 (dd, ^3J = 14.6, 5.2 Hz, 1 H; H-31), 6.09–6.30 (m, 4 H; H-27, H-28, H-29, H-30), 7.26–7.46 (m, 12 H; H$_{\text{arom}}$), 7.57–7.65 (m, 4 H;H$_{\text{arom}}$), 7.70–7.75 (m, 4 H; H$_{\text{arom}}$).

^{13}C-NMR (91 MHz, $CDCl_3$, 300 K): δ [ppm] = 9.9 (q, CH_3), 15.6 (q, CH_3-34), 16.7 (q, CH_3-40), 19.5 [s, $C(CH_3)_3$], 19.6 [s, $C(CH_3)_3$], 27.2 [q, $C(CH_3)_3$], 30.3 (t, CH_2), 60.5 (q, OCH_3-36), 62.1 (q, OCH_3-38), 69.9 (d, CH-39), 74.3 (d, CH-25), 76.3 (d, CH-37), 77.4 (d, CH-33), 80.9 (d, CH-36), 82.1 (d, CH-38), 103.0 (d, CH-35), 127.4, 127.6, 127.6, 127.7 (d, CH_{arom}), 129.6, 129.7, 129.8 (d, CH_{arom}), 131.1 (d, CH-27*), 131.2 (d, CH-28*), 131.2 (d, CH-30*), 132.7 (d, CH-31), 133.1 (d, CH-29*) 133.9, 134.2, 134.2, 134.5 (s, C_{arom}), 135.7 (d, CH-26), 136.0, 136.2, 136.3 (d, CH_{arom}).

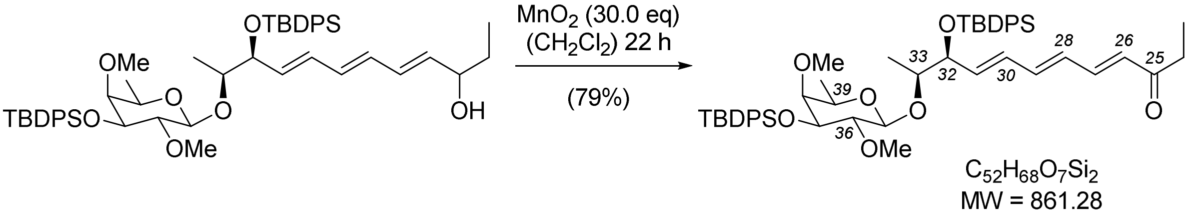
*commutable signals.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3443 (w, OH), 3070 (w, C–H), 3048 (w, C–H), 2958 (m, C–H), 2930 (m, C–H), 2857 (m, C–H), 1111 (s, C–O), 1063 (m), 999 (m).

MS (ESI): *m/z* (%) = 885 [$(M+Na)^+$] (23), 881 [$(M+NH_4)^+$] (19), 863 [$(M+H)^+$] (9), 845 [$(M–OH)^+$] (100), 332 (42).

HRMS (ESI) $C_{52}H_{70}O_7Si_2$ calcd.: [$(M+Na)^+$] 885.4552
found: [$(M+Na)^+$] 885.4577.

Trienone1



To a solution of 13.0 mg alcohol **17** (15.1 µmol, 1.0 eq) in 0.5 ml dichloromethane was added 39.3 mg manganese dioxide (450 µmol, 30.0 eq) and the reaction mixture stirred at room temperature for 22 hours. The solvent was evaporated under reduced pressure and the crude product subjected to flash column chromatography on silica (pentane/diethyl ether = 5/1) to afford 10.2 mg of trienone **1** (11.8 µmol, 79%).

TLC: R_f = 0.45 (P:Et_2O = 2/1, [UV, CAM]).

Specific rotation: $[\alpha]_D^{20} = -16.9$ (c = 0.96, $CHCl_3$).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3070 (w, C–H), 3048 (w, C–H), 2933 (m, C–H), 2892 (m, C–H), 2856 (m, C–H), 1686 (w, C=C), 1664 (w, C=C), 1603 (w, C=C), 1582 (w, C=C), 1111 (s, C–O), 1064 (m).

^{1}H-NMR (500 MHz, CDCl$_3$, 300 K): δ [ppm] = 1.00 (d, ^{3}J = 6.4 Hz, 3 H; CH$_3$-40); 1.08 [s, 21 H; 2×SiC(CH$_3$)$_3$, CH$_3$-34], 1.13 (t, ^{3}J = 7.3 Hz, 3 H; CH$_2$C*H*$_3$), 2.60 (q, ^{3}J = 7.3 Hz, 2 H; CH$_2$-24), 2.66 (d, ^{3}J = 2.7 Hz, 1 H; H-38), 2.86 (q, ^{3}J = 6.4 Hz, 1 H; H-39), 3.12 (dd, ^{3}J = 9.5, 7.9 Hz, 1 H; H-36), 3.19 (s, 3H; OCH$_3$-35), 3.36–3.45 (m, 5 H; H-33, H-35, OCH$_3$-38), 3.50 (dd, ^{3}J = 9.5, 2.7 Hz, 1 H; H-37), 4.39–4.44 (m, 1 H; H-32), 6.00 (dd, ^{3}J = 15.3, 4.8 Hz, 1 H; H-31), 6.17 (d, ^{3}J = 15.5 Hz, 1 H; H-26), 6.23 (dd, ^{3}J = 14.8, 11.2 Hz, 1 H; H-28), 6.38 (dd, ^{3}J = 15.3, 11.1 Hz, 1 H; H-30), 6.57 (dd, ^{3}J = 14.8, 11.1 Hz, 1 H; H-29), 7.19 (dd, ^{3}J = 15. 5, 11.2 Hz, 1 H; H-27), 7.26–7.47 (m, 12 H; H$_{\mathrm{arom}}$), 7.55–7.65 (m, 4 H; H$_{\mathrm{arom}}$), 7.69–7.75 (m, 4 H; H$_{\mathrm{arom}}$).

^{13}C-NMR (91 MHz, CDCl$_3$, 300 K): δ [ppm] = 8.5 (q, CH$_2$*C*H$_3$), 15.6 (q, CH$_3$-34), 16.7 (q, CH$_3$-40), 19.5 [s, *C*(CH$_3$)$_3$], 19.6 [s, *C*(CH$_3$)$_3$], 27.2 [q, C(*C*H$_3$)$_3$], 33.8 (t, CH$_2$), 60.5 (q, OCH$_3$-36), 62.1 (q, OCH$_3$-38), 69.8 (d, CH-39), 73.6 (d, CH-32), 76.3 (d, CH-37), 77.4 (d, CH-33), 80.9 (d, CH-36), 82.0 (d, CH-38), 103.0 (d, CH-35) 127.5, 127.6, 127.7, 127.8 (d, CH$_{\mathrm{arom}}$), 129.0 (d, CH-26), 129.6, 129.8, 129.8, 129.9 (d, CH$_{\mathrm{arom}}$), 129.9 (d, CH-28), 130.6 (d, CH-30), 133.7, 134.0, 134.2, 134.5 (s, C$_{\mathrm{arom}}$), 136.0, 136.0, 136.2, 136.3 (d, CH$_{\mathrm{arom}}$), 137.6 (d, C-31), 141.3 (d, CH-29), 142.5 (d, CH-27), 201.2 (s, C=O).

MS (ESI): *m/z* (%) = 883 [(M+Na)$^+$] (100), 878 [(M+NH$_4$)$^+$] (60), 861 [(M+H)$^+$] (27), 845 [(M–OH)$^+$] (100).

HRMS (ESI)	$C_{52}H_{68}O_7Si_2$	calcd.: [(M+Na)$^+$]	883.4396
		found: [(M+Na)$^+$]	883.4407.

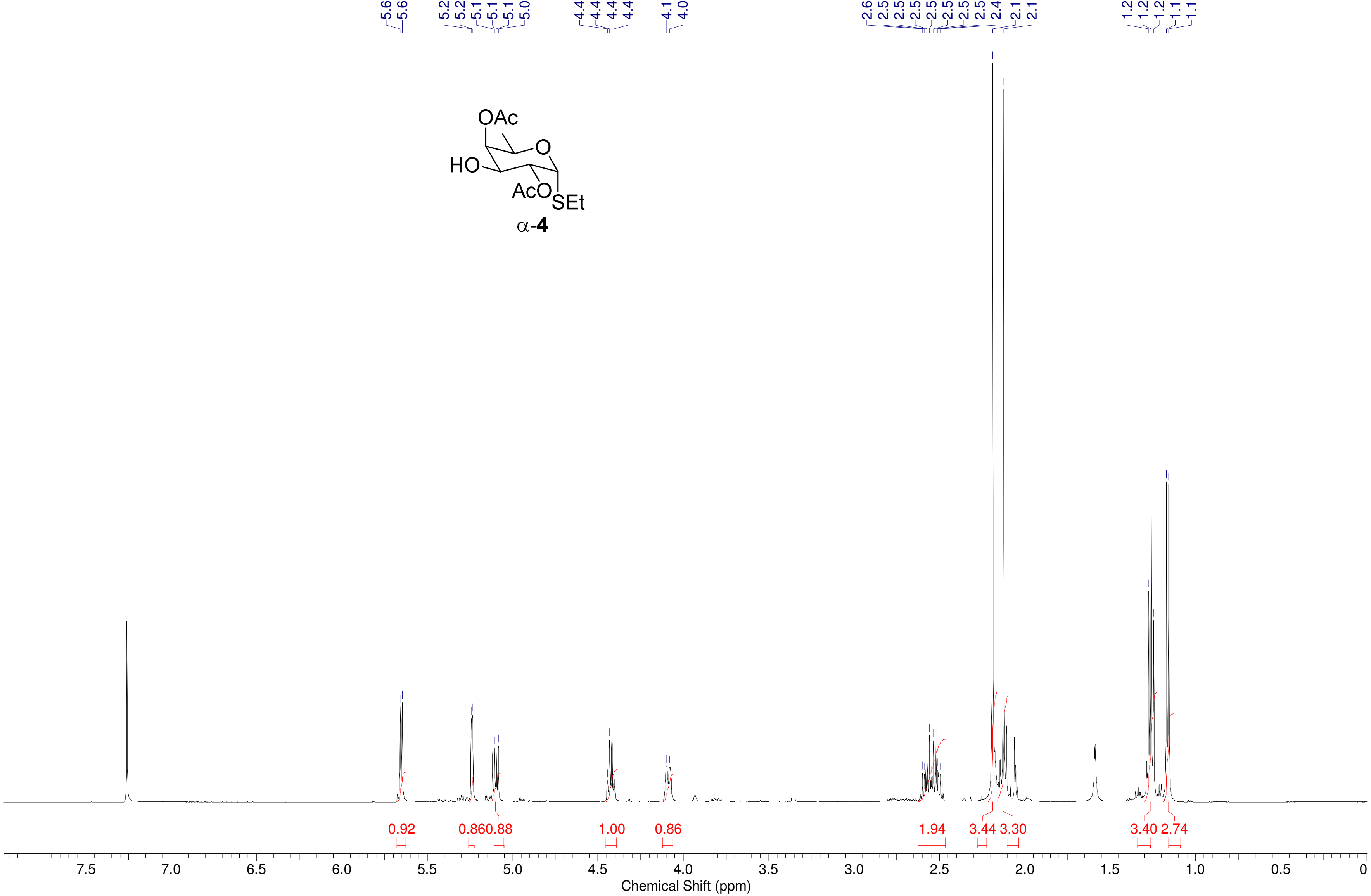
2. References for the Supporting Information

[1] P. Sjölin, S. K. George, K.-E. Bergquist, S. Roy, A. Svensson and J. Kihlberg, *J. Chem. Soc., Perkin Trans. 1*, 1999, 1731-1742.

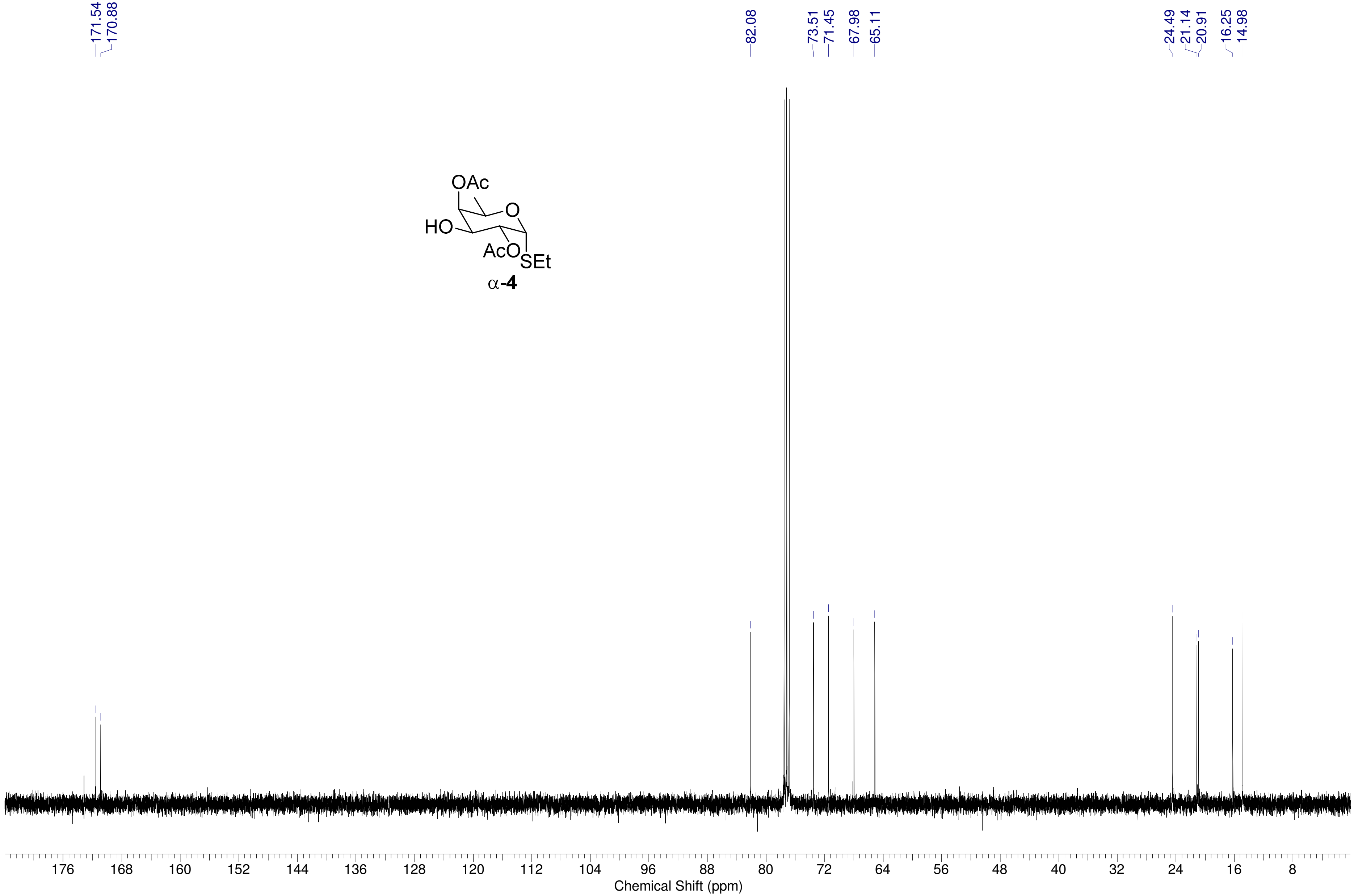
[2] D. Comegna, E. Bedini and M. Parrilli, *Tetrahedron*, 2008, **64**, 3381-3391.

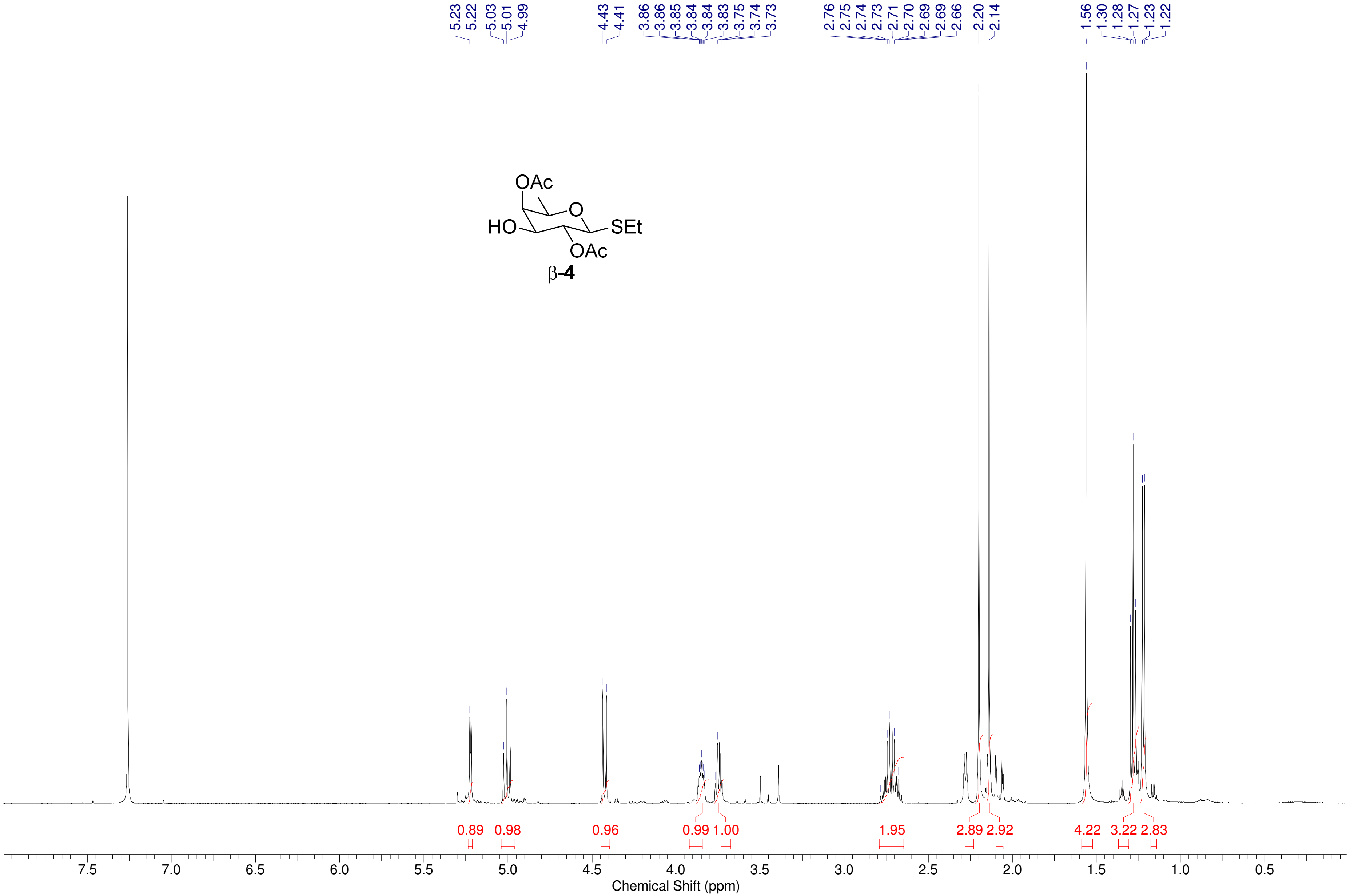
[3] K. Green, J. W. Keeping and V. Thaller, *J. Chem. Res. (S)*, 1985, 103; *J. Chem. Res. (M)*, 1985, 1260-1267.

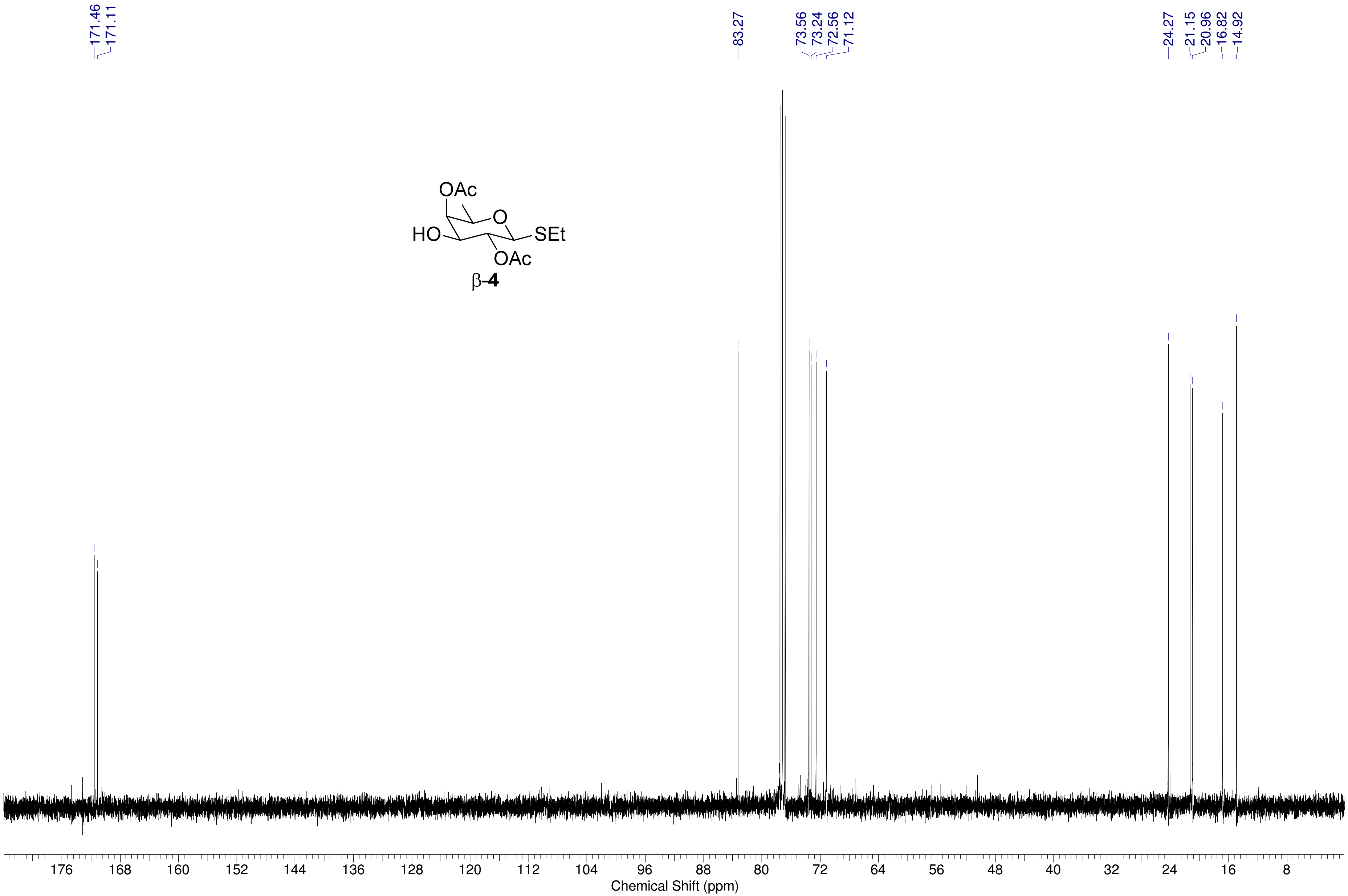
3. NMR spectra of new compounds

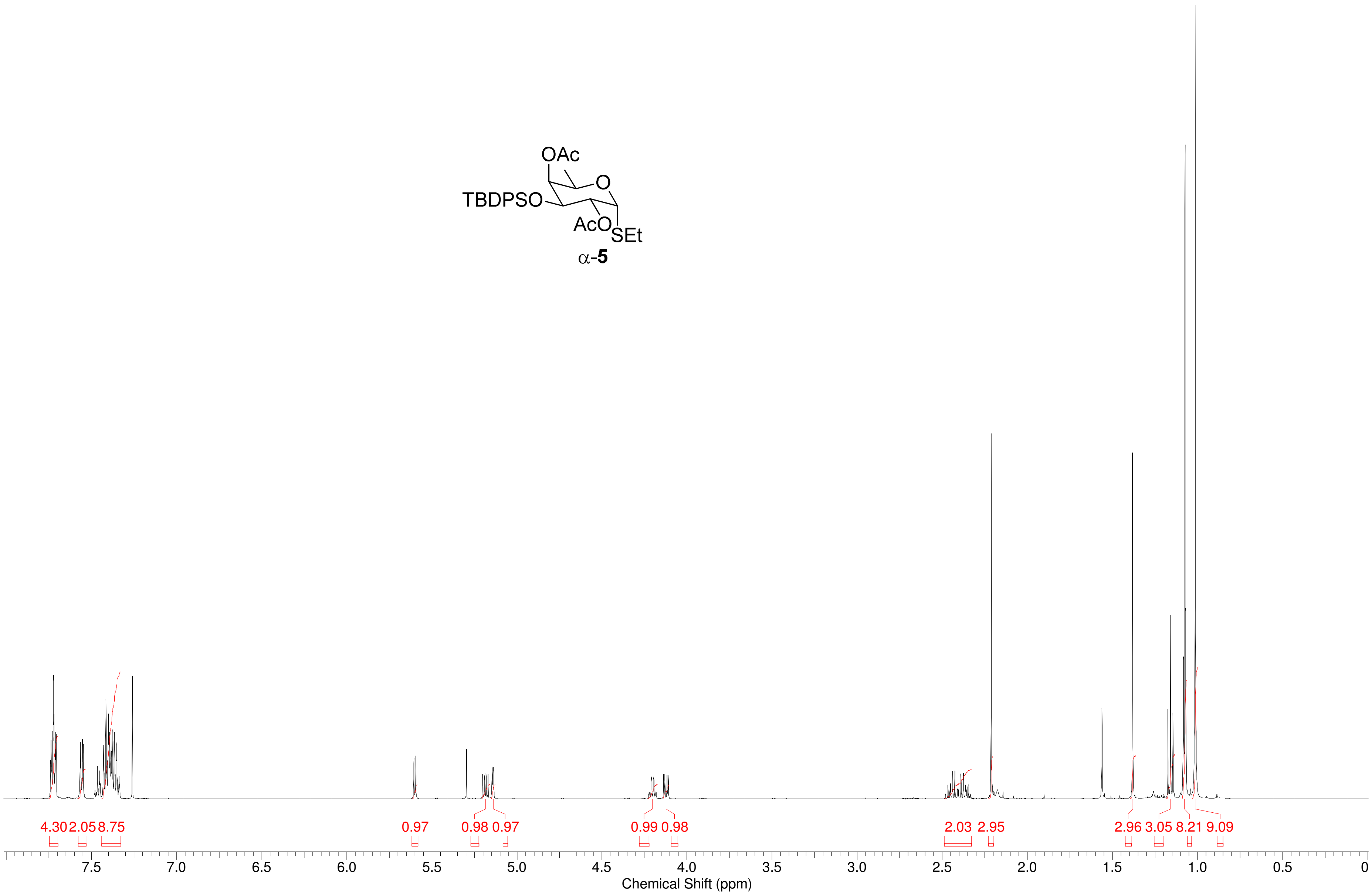


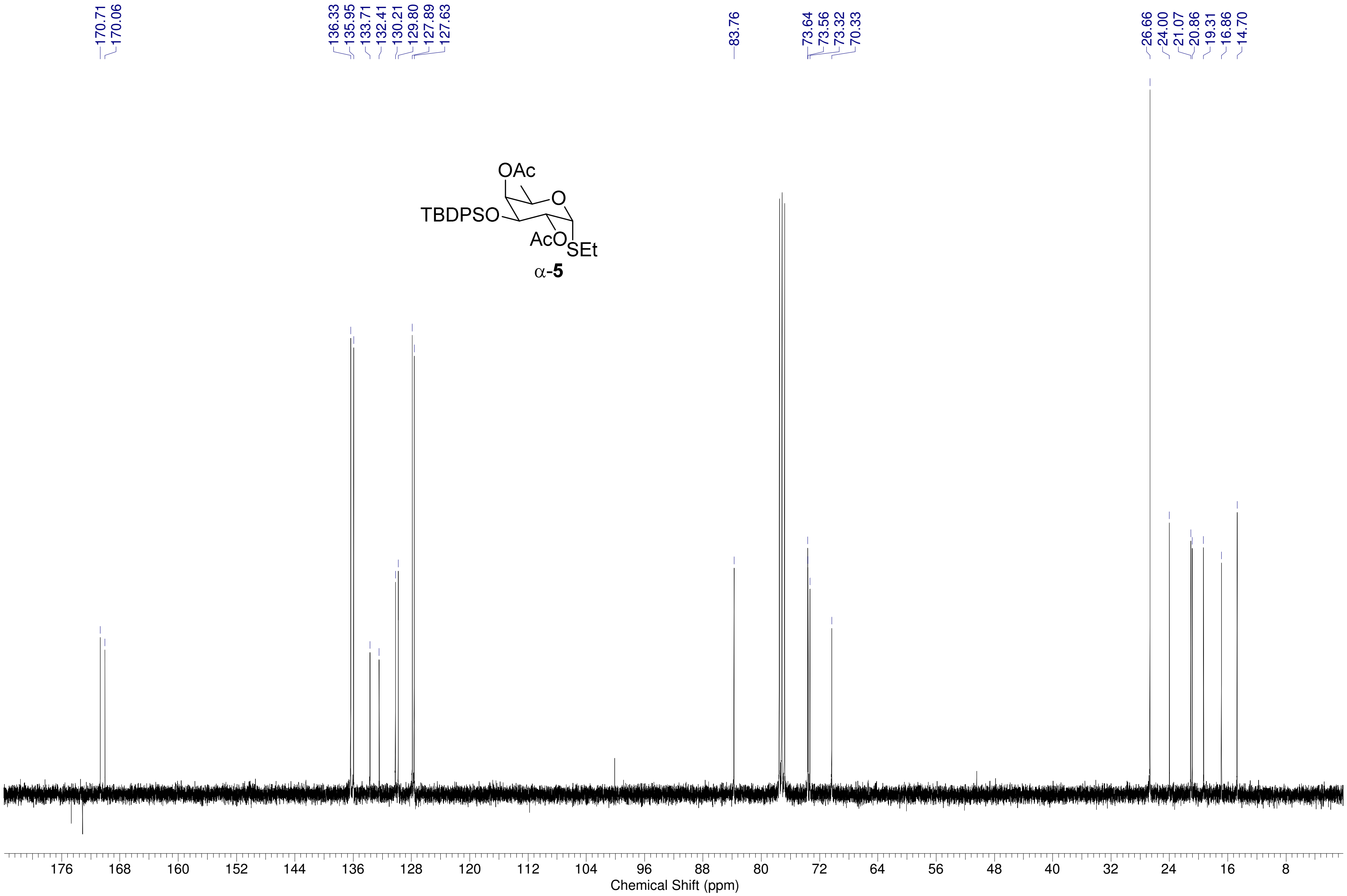
α-**4**

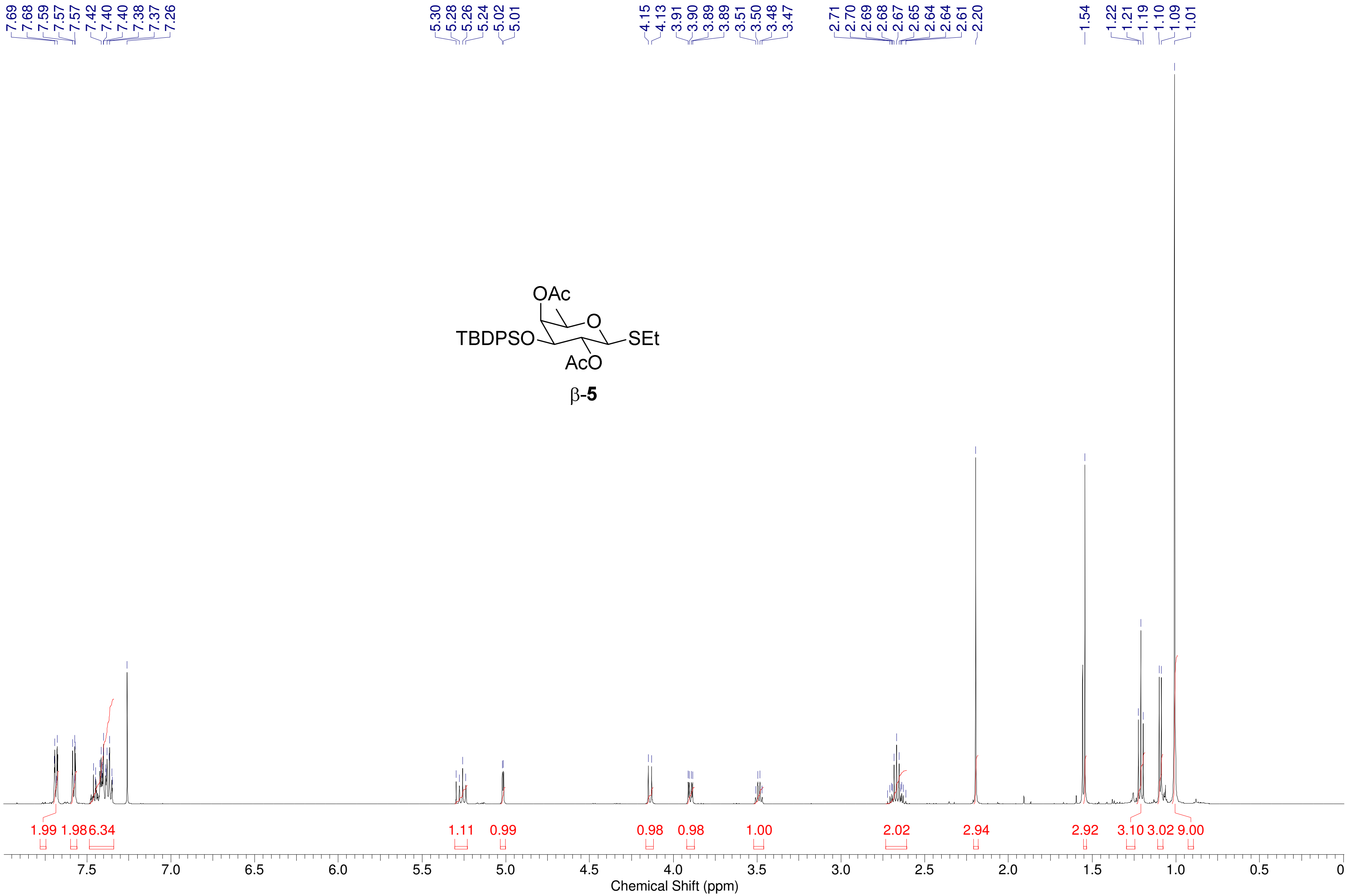

171.54
170.88
82.08
73.51
71.45
67.98
65.11
24.49
21.14
20.91
16.25
14.98
OAc
O
HO
AcO
SEt
α-4
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

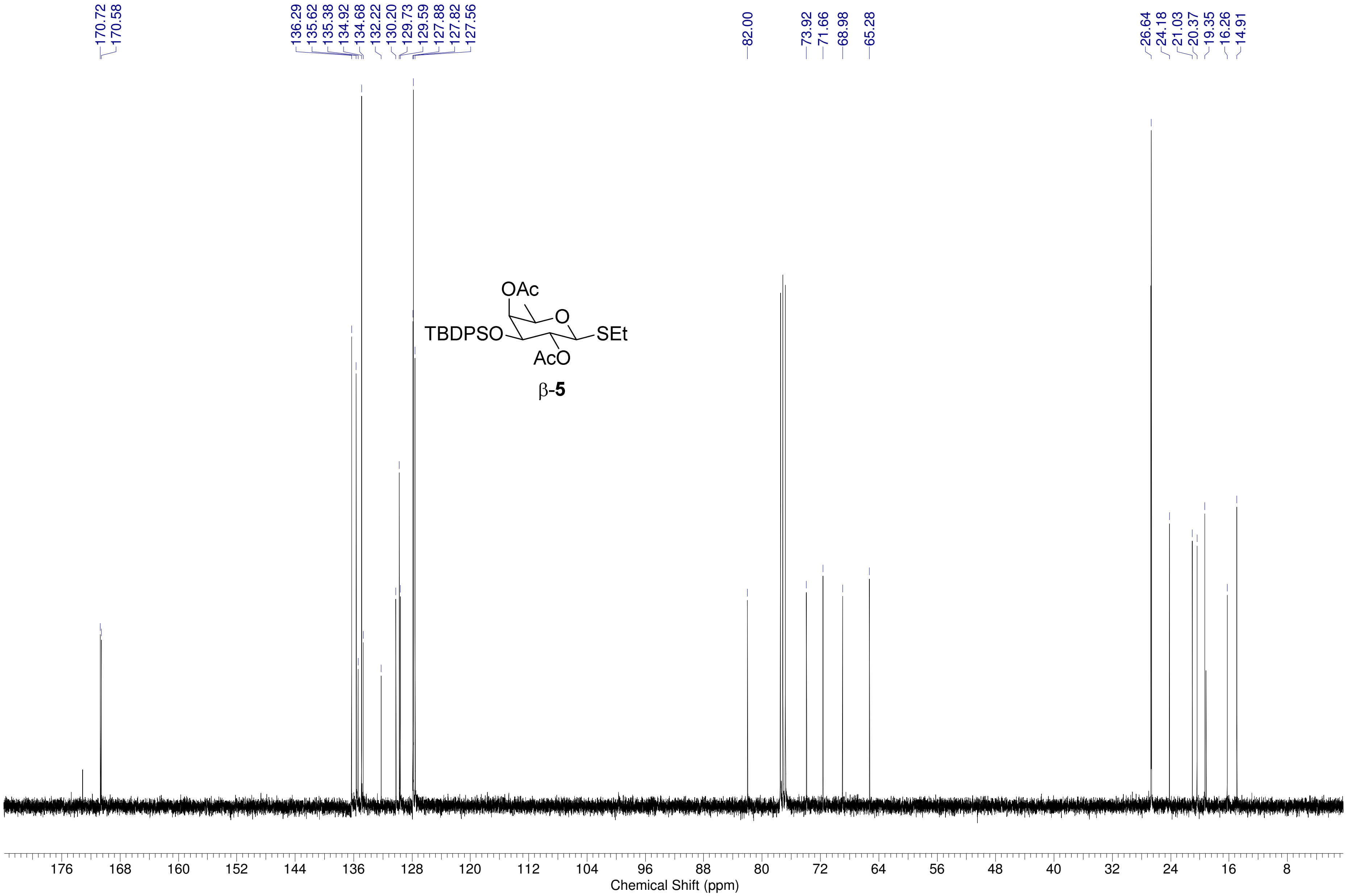

5.23
5.22
5.03
5.01
4.99
4.43
4.41
3.86
3.86
3.85
3.84
3.84
3.83
3.75
3.74
3.73
2.76
2.75
2.74
2.73
2.71
2.70
2.69
2.69
2.66
2.20
2.14
1.56
1.30
1.28
1.27
1.23
1.22
OAc
O
HO
SEt
OAc
β-4
0.89
0.98
0.96
0.99
1.00
1.95
2.89
2.92
4.22
3.22
2.83
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

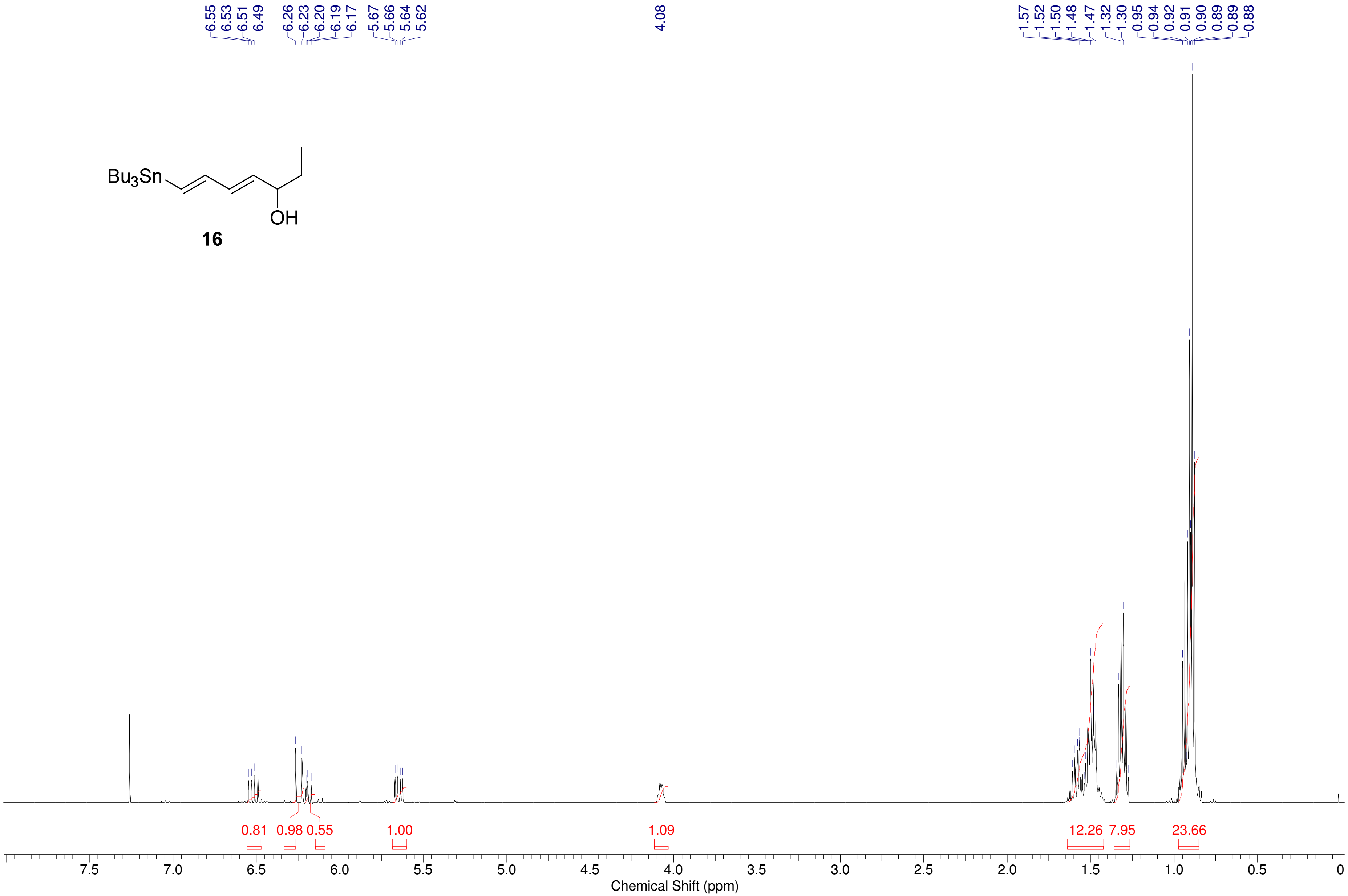

171.46
171.11
83.27
73.56
73.24
72.56
71.12
24.27
21.15
20.96
16.82
14.92
OAc
O
HO
SEt
OAc
β-4
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

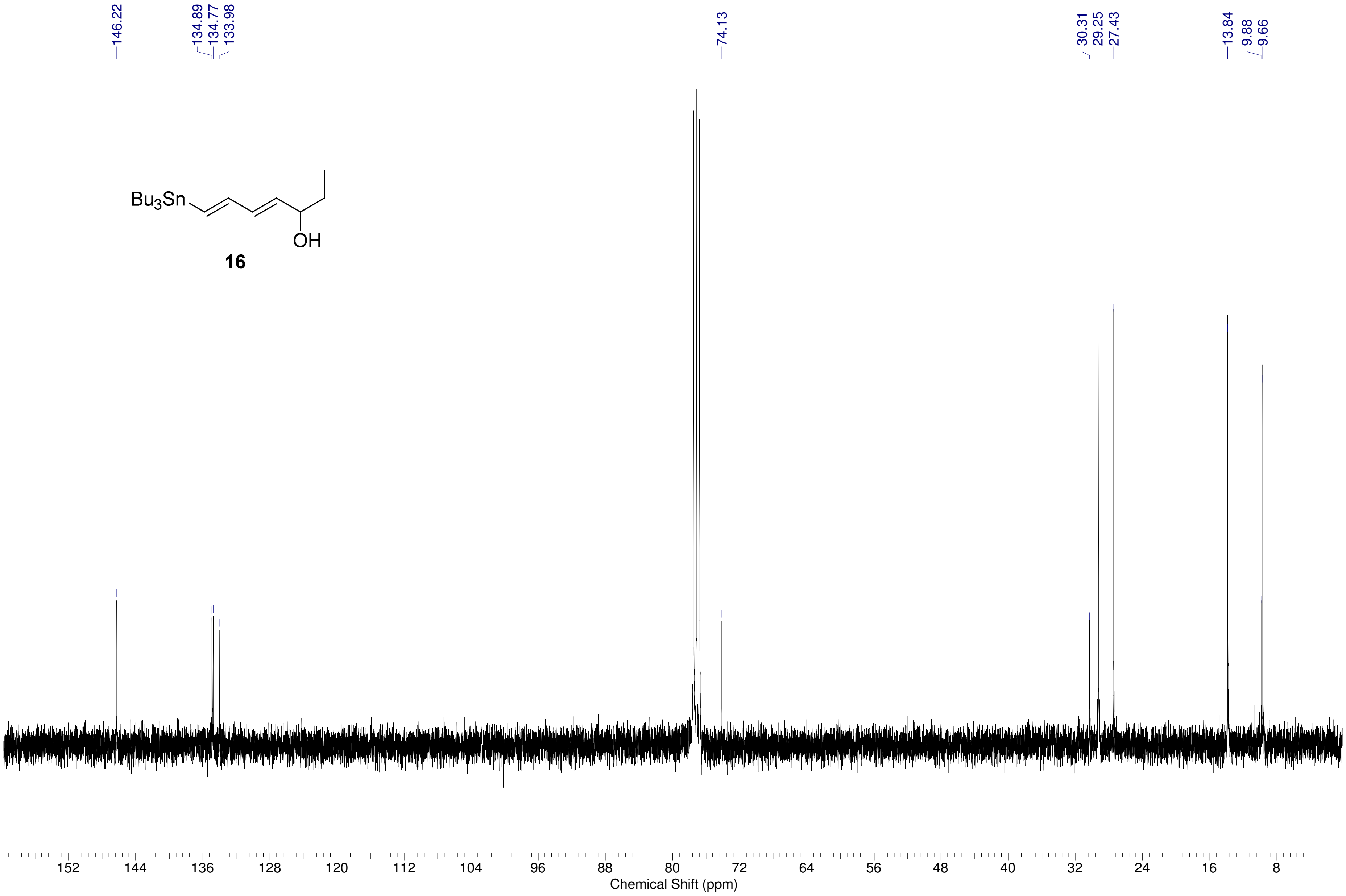

OAc
TBDPSO
O
AcO
SEt
α-5
4.30
2.05
8.75
0.97
0.98
0.97
0.99
0.98
2.03
2.95
2.96
3.05
8.21
9.09
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


170.71
170.06
136.33
135.95
133.71
132.41
130.21
129.80
127.89
127.63
83.76
73.64
73.56
73.32
70.33
26.66
24.00
21.07
20.86
19.31
16.86
14.70
OAc
O
TBDPSO
AcO
SEt
α-5
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

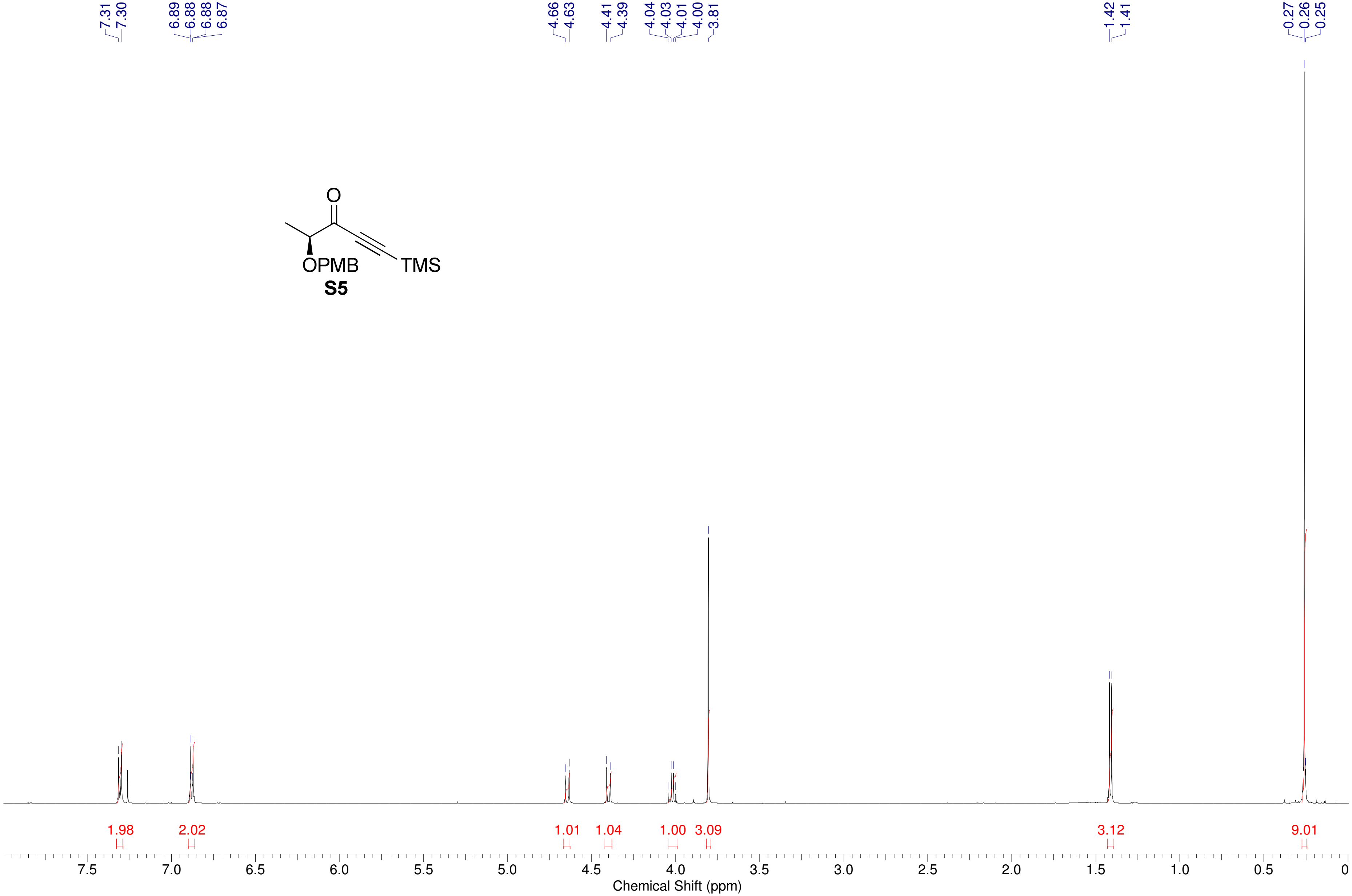

7.69
7.68
7.59
7.57
7.57
7.42
7.40
7.40
7.38
7.37
7.26
5.30
5.28
5.26
5.24
5.02
5.01
4.15
4.13
3.91
3.90
3.89
3.89
3.51
3.50
3.48
3.47
2.71
2.70
2.69
2.68
2.67
2.65
2.64
2.64
2.61
2.20
1.54
1.22
1.21
1.19
1.10
1.09
1.01
OAc
O
TBDPSO
SEt
AcO
β-5
1.99
1.98
6.34
1.11
0.99
0.98
0.98
1.00
2.02
2.94
2.92
3.10
3.02
9.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

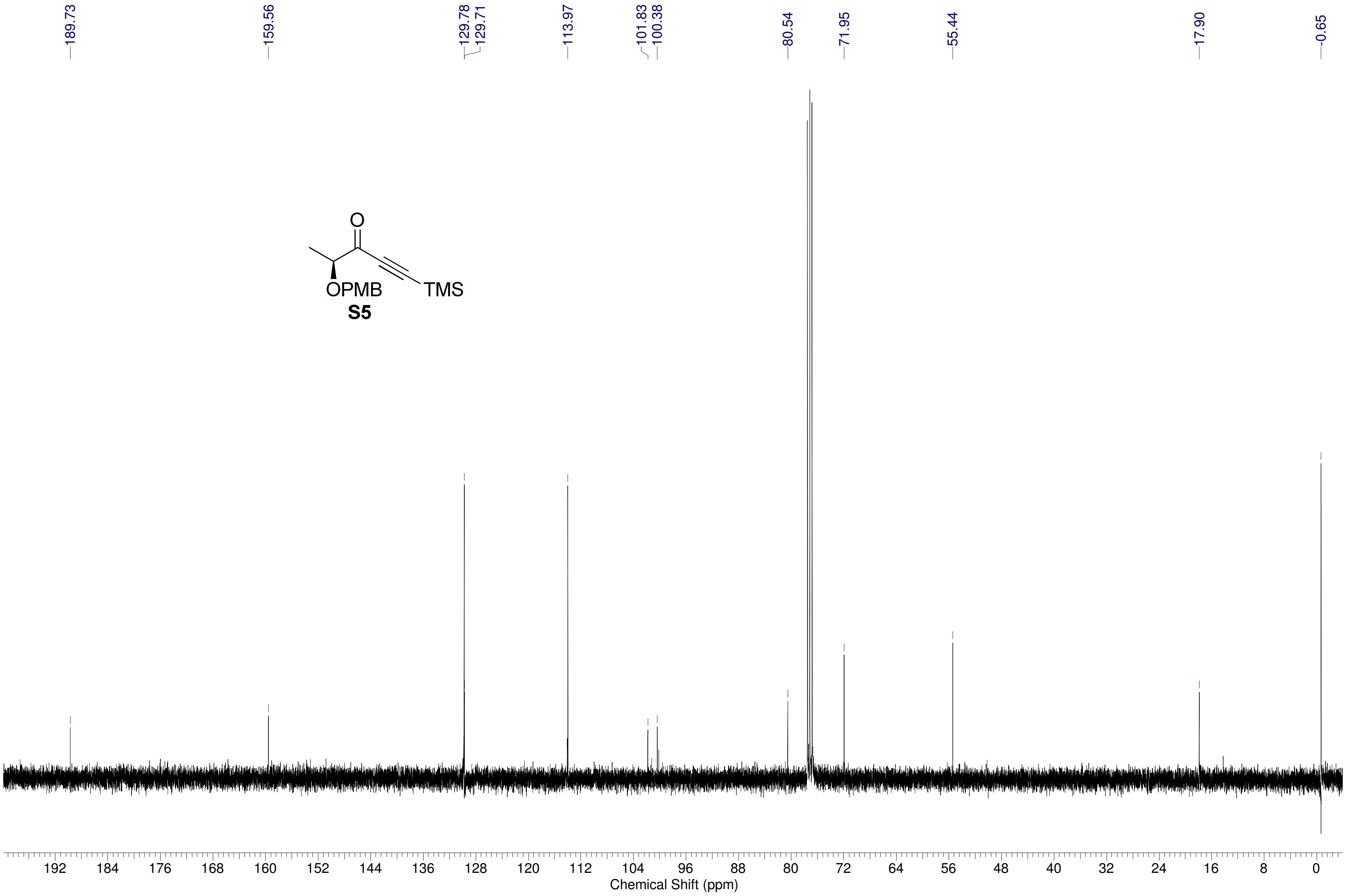

170.72
170.58
136.29
135.62
135.38
134.92
134.68
132.22
130.20
129.73
129.59
127.88
127.82
127.56
82.00
73.92
71.66
68.98
65.28
26.64
24.18
21.03
20.37
19.35
16.26
14.91
OAc
O
TBDPSO
SEt
AcO
β-5
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

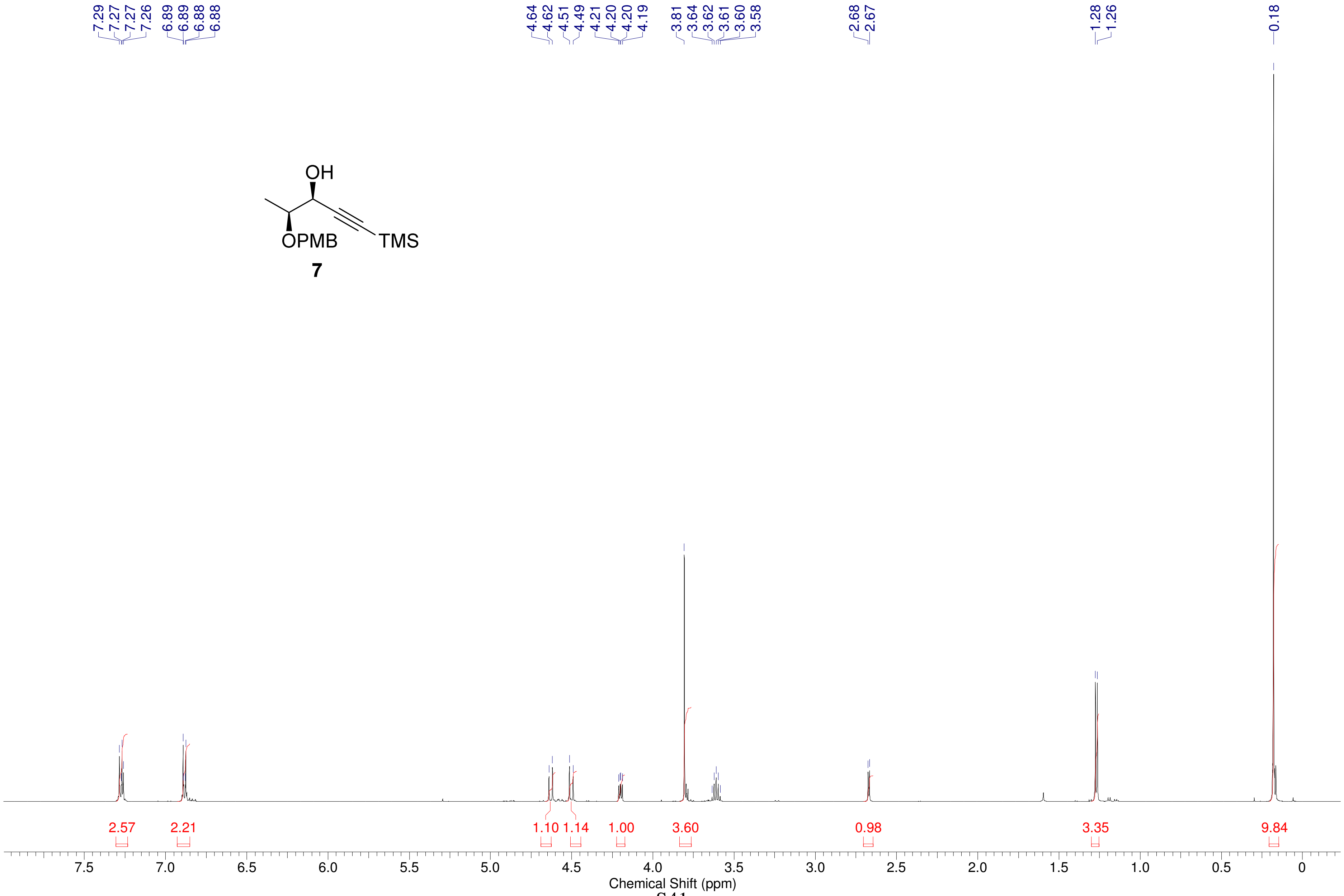

6.55
6.53
6.51
6.49
6.26
6.23
6.20
6.19
6.17
5.67
5.66
5.64
5.62
4.08
1.57
1.52
1.50
1.48
1.47
1.32
1.30
0.95
0.94
0.92
0.91
0.90
0.89
0.88
Bu3Sn
OH
16
0.81
0.98
0.55
1.00
1.09
12.26
7.95
23.66
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

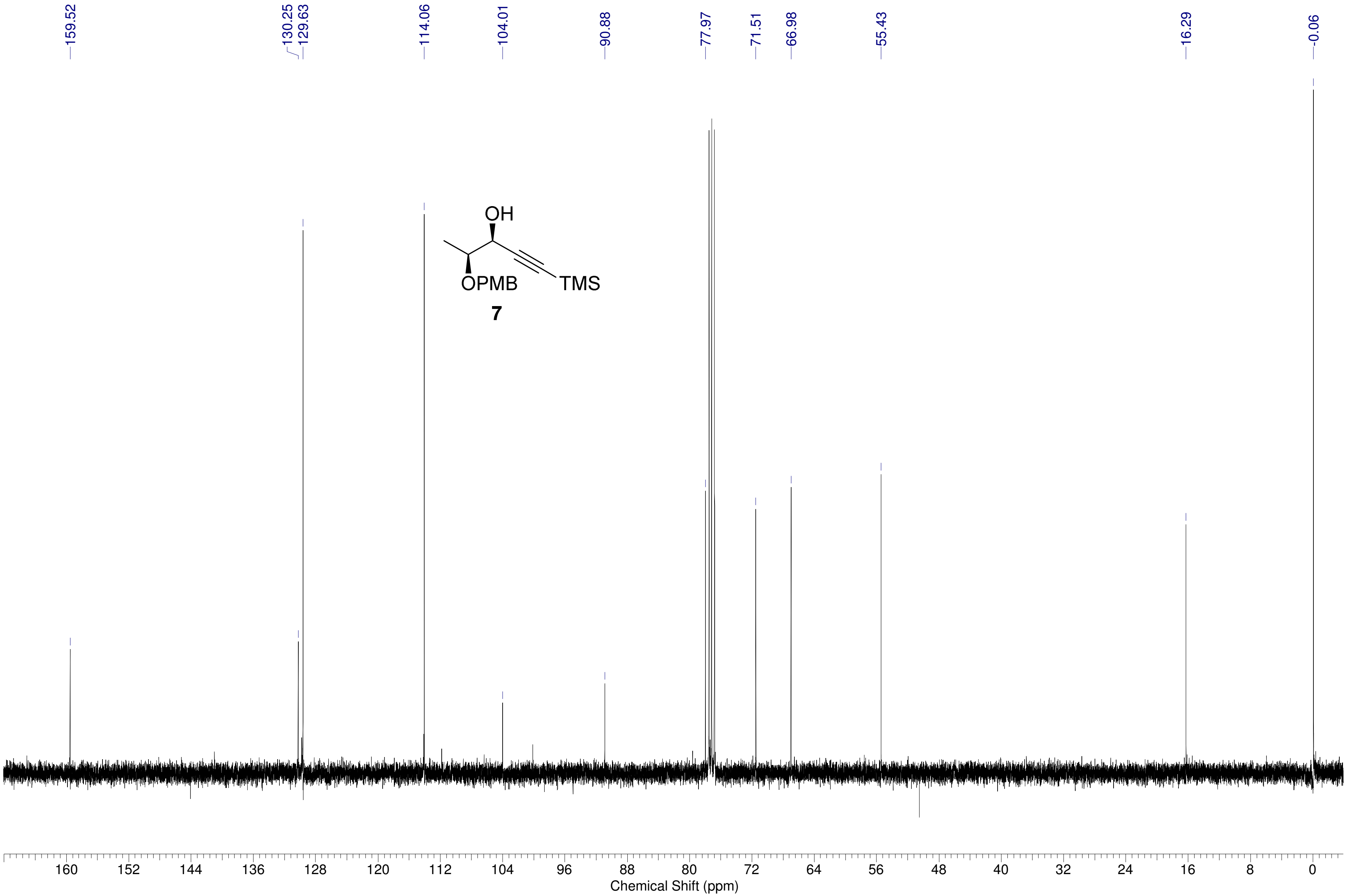

146.22
134.89
134.77
133.98
74.13
30.31
29.25
27.43
13.84
9.88
9.66
Bu_3Sn
OH
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

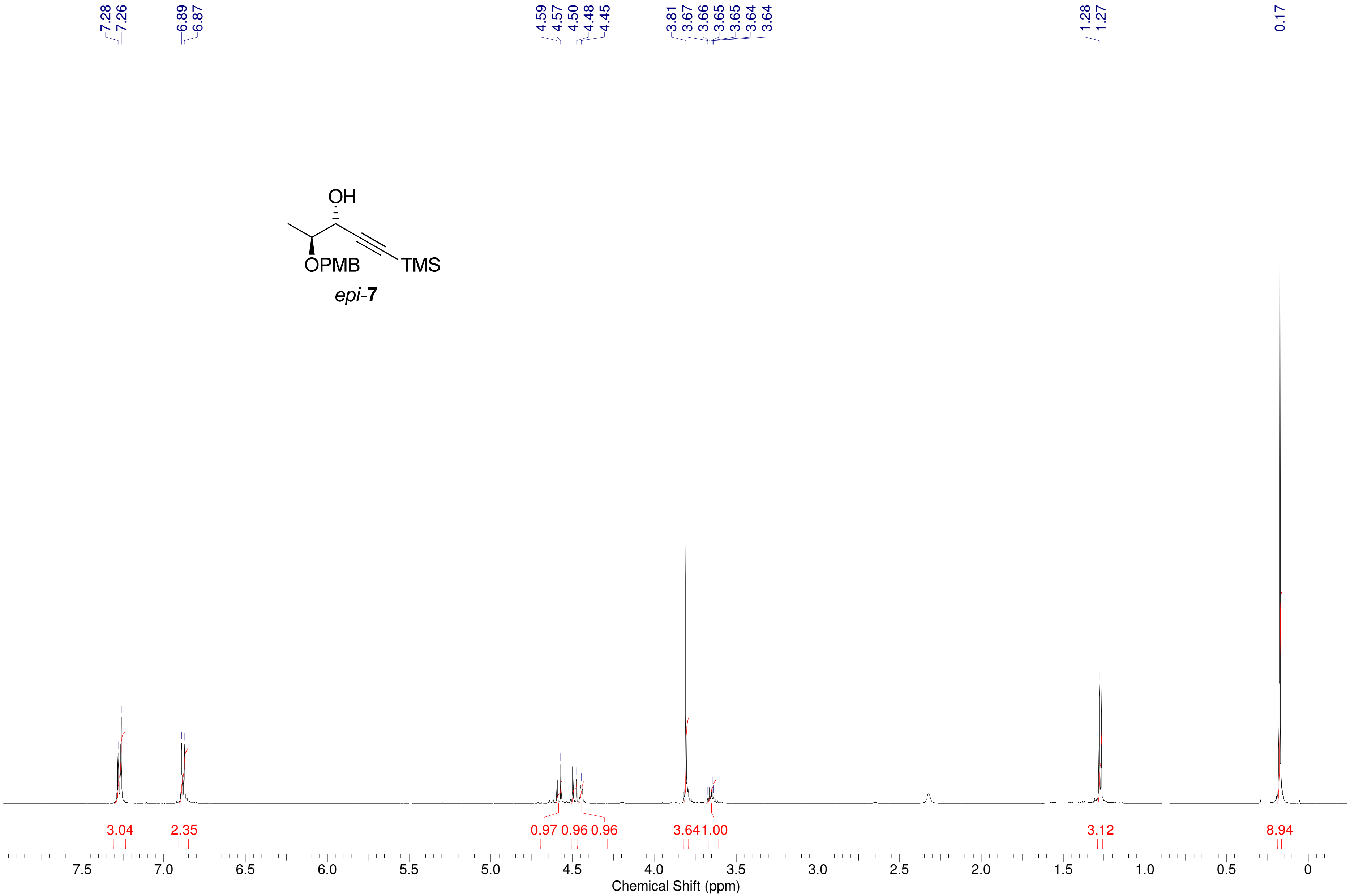
16

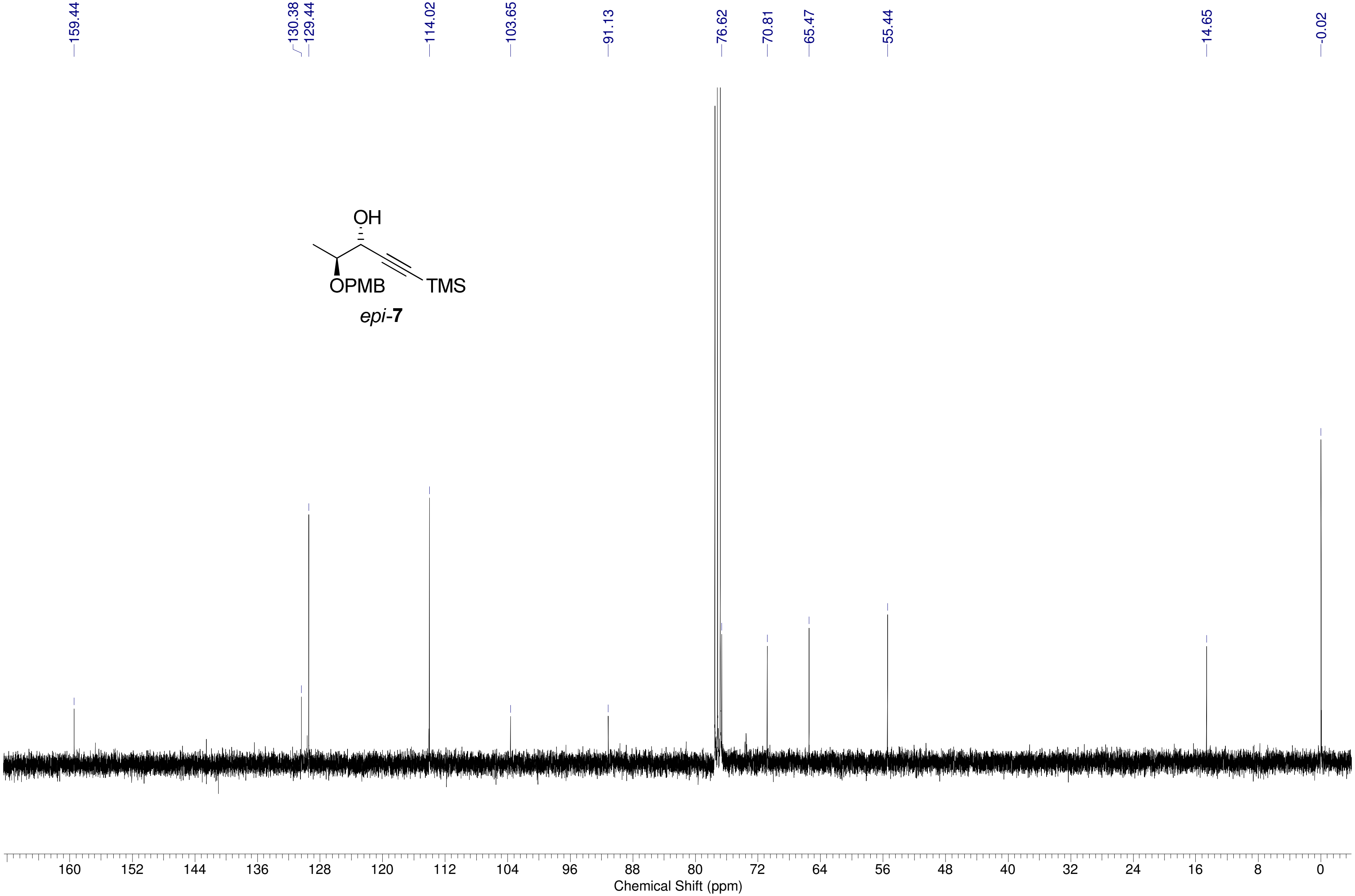

7.31
7.30
6.89
6.88
6.88
6.87
4.66
4.63
4.41
4.39
4.04
4.03
4.01
4.00
3.81
1.42
1.41
0.27
0.26
0.25
O
OPMB
TMS
S5
1.98
2.02
1.01
1.04
1.00
3.09
3.12
9.01
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


189.73
159.56
129.78
129.71
113.97
101.83
100.38
80.54
71.95
55.44
17.90
-0.65
O
OPMB
TMS
S5
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

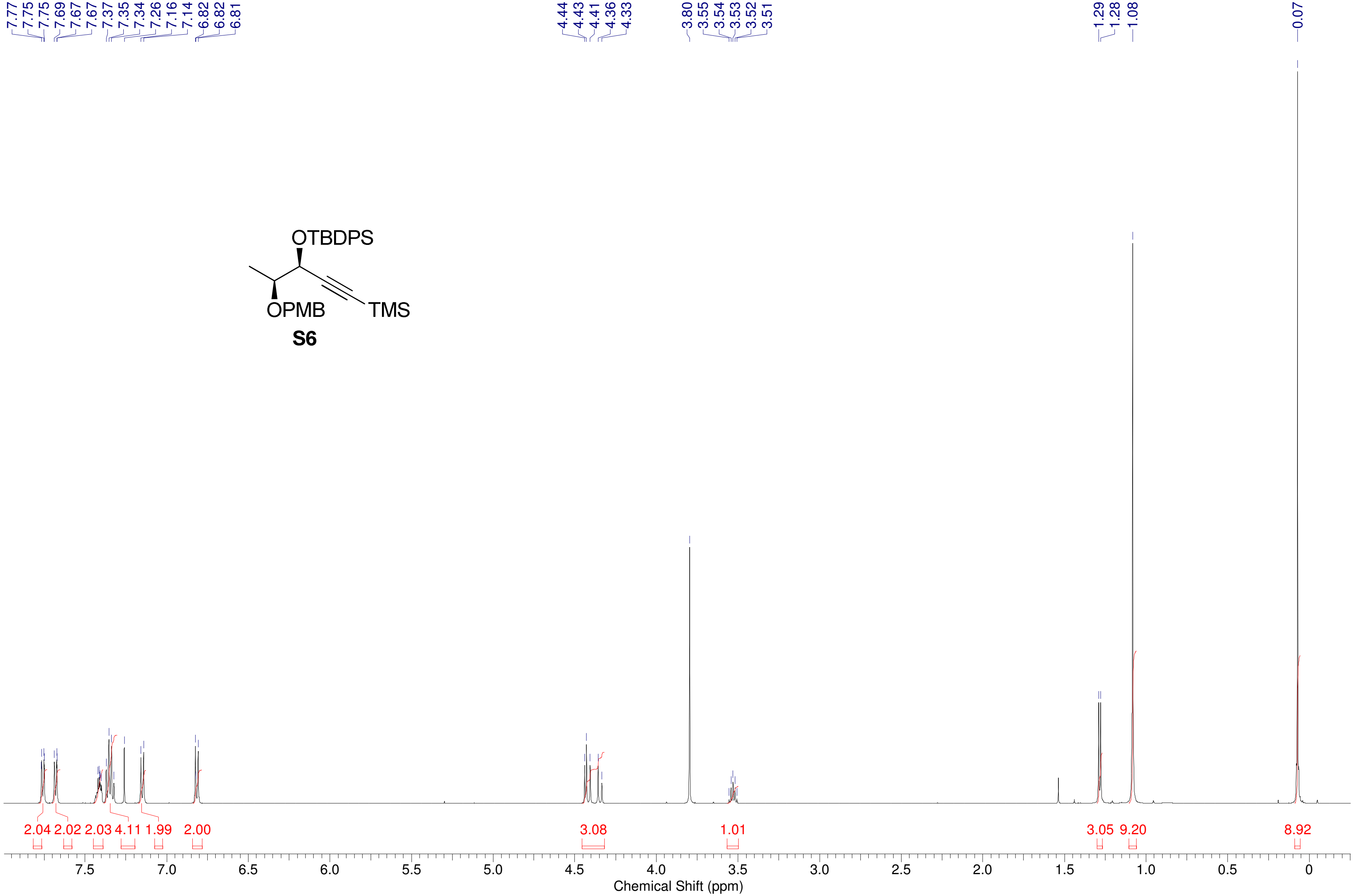

7.29
7.27
7.27
7.26
6.89
6.89
6.88
6.88
4.64
4.62
4.51
4.49
4.21
4.20
4.20
4.19
3.81
3.64
3.62
3.61
3.60
3.58
2.68
2.67
1.28
1.26
0.18
OH
OPMB
TMS
7
2.57
2.21
1.10
1.14
1.00
3.60
0.98
3.35
9.84
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

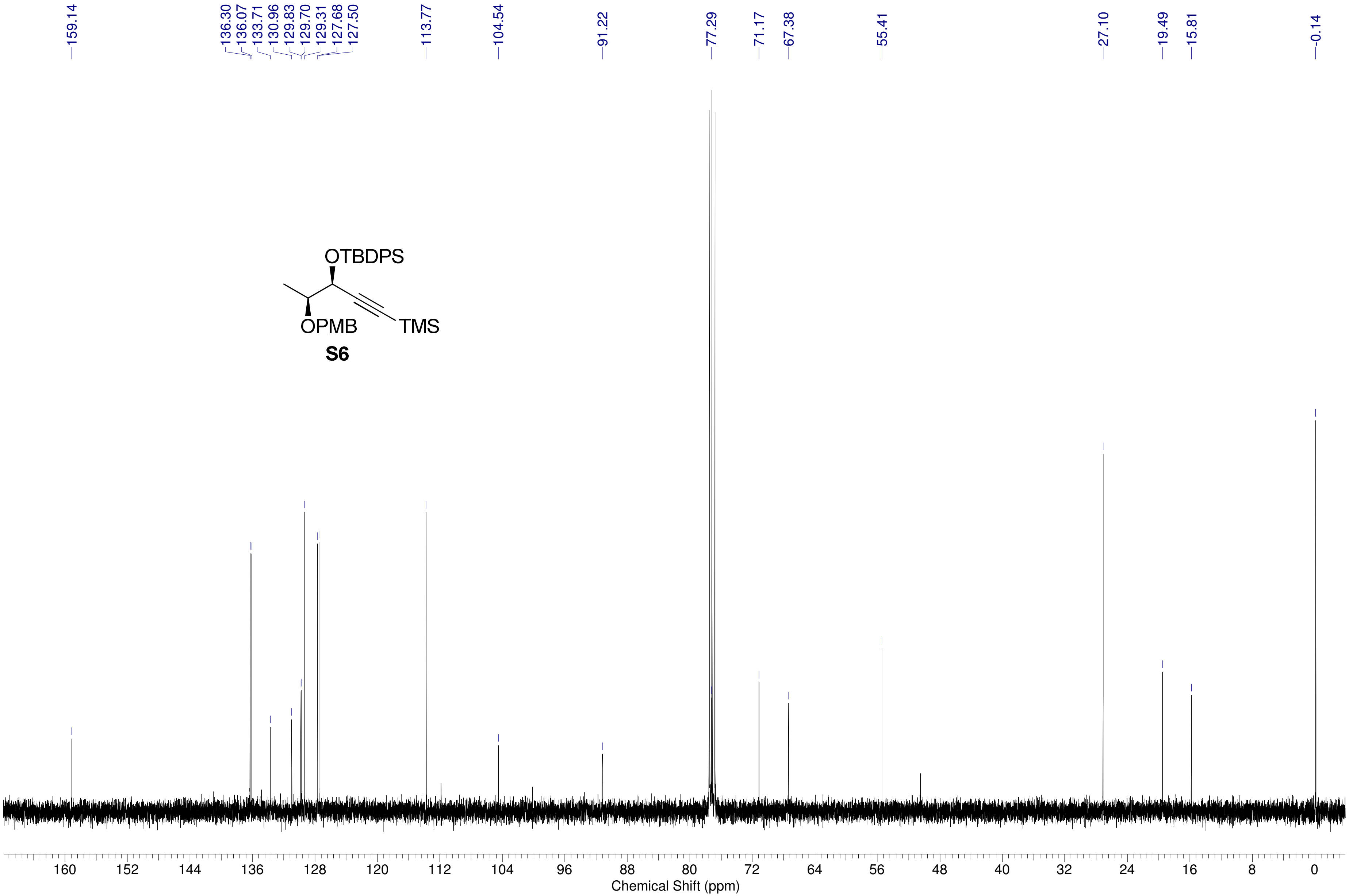

159.52
130.25
129.63
114.06
104.01
90.88
77.97
71.51
66.98
55.43
16.29
-0.06
OH
OPMB
TMS
7
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


7.28
7.26
6.89
6.87
4.59
4.57
4.50
4.48
4.45
3.81
3.67
3.66
3.65
3.65
3.64
3.64
1.28
1.27
0.17
OH
OPMB
TMS
epi-7
3.04
2.35
0.97
0.96
0.96
3.64
1.00
3.12
8.94
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

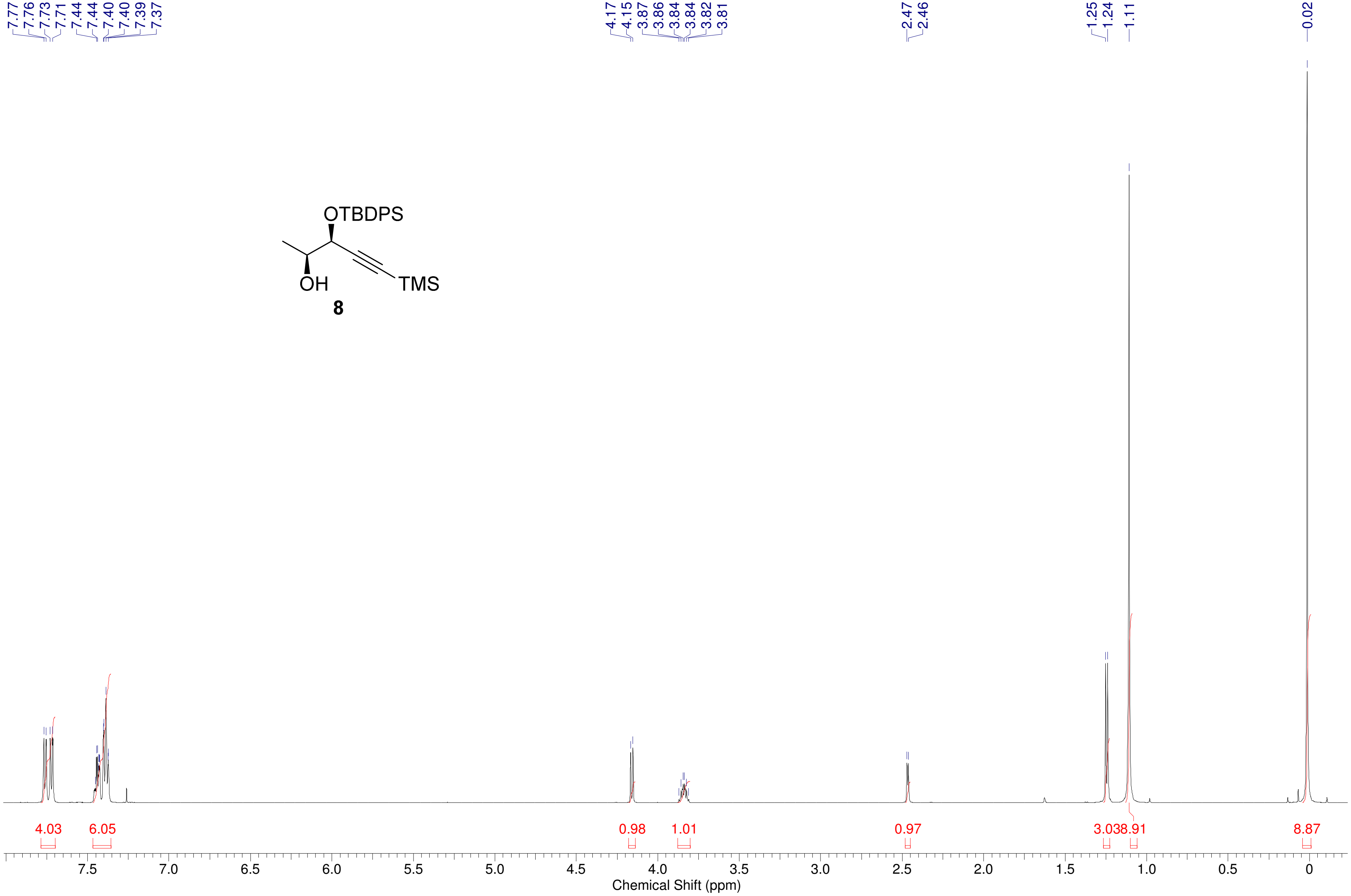

159.44
130.38
129.44
114.02
103.65
91.13
76.62
70.81
65.47
55.44
14.65
-0.02
OH
OPMB
TMS
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

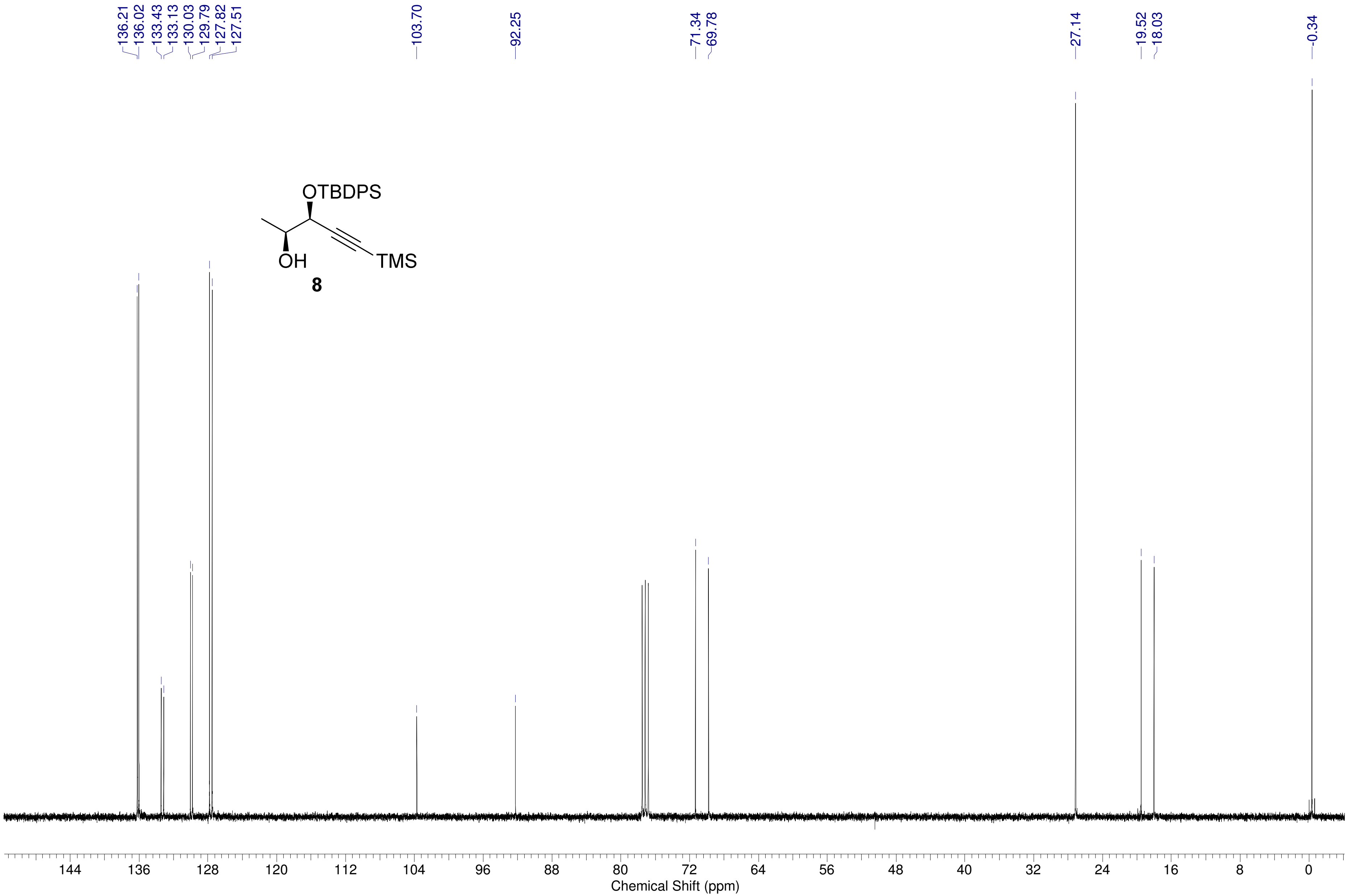
epi-**7**

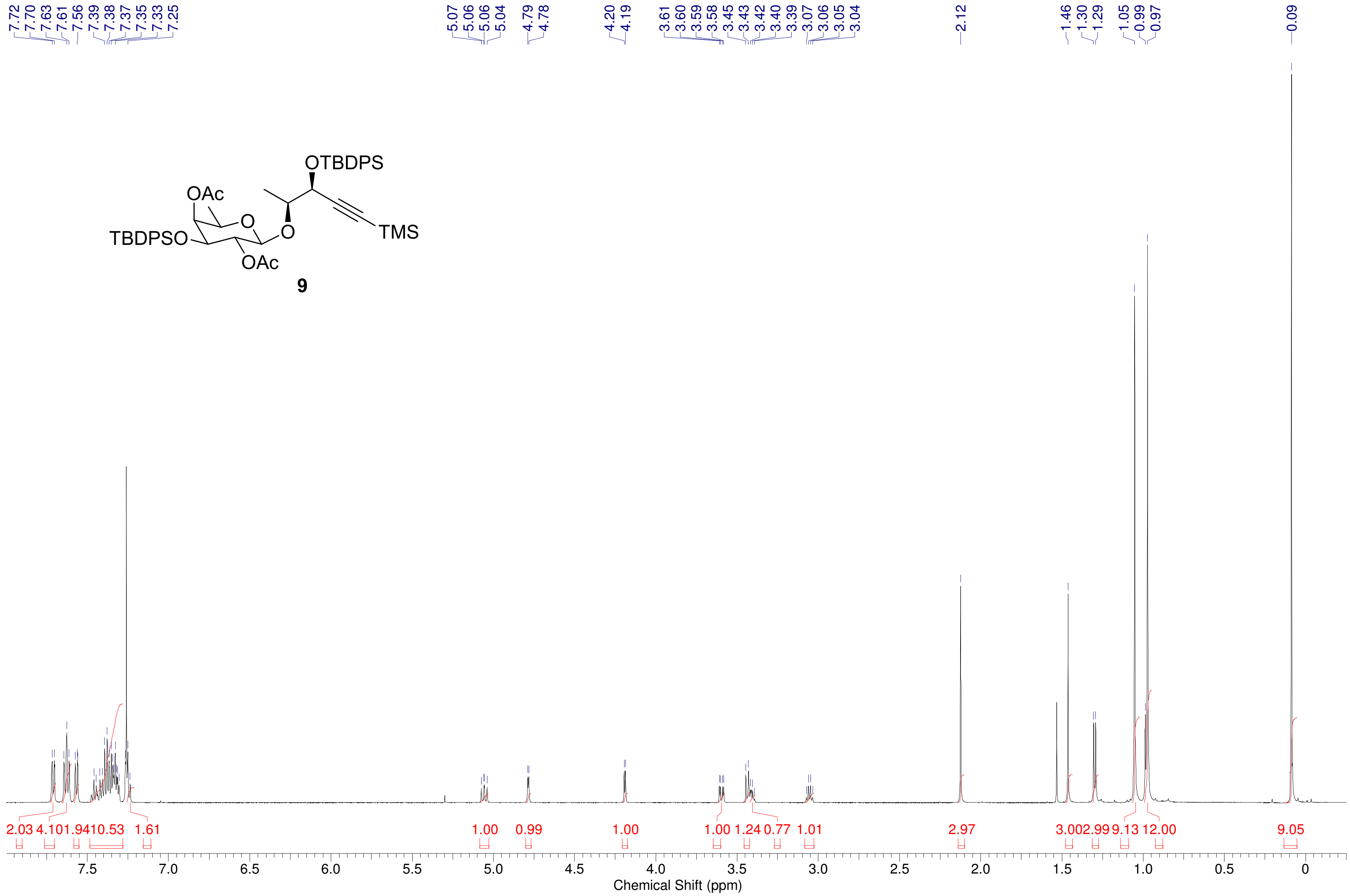

7.77
7.75
7.75
7.69
7.67
7.67
7.37
7.35
7.34
7.26
7.16
7.14
6.82
6.82
6.81
4.44
4.43
4.41
4.36
4.33
3.80
3.55
3.54
3.53
3.52
3.51
1.29
1.28
1.08
0.07
OTBDPS
OPMB
TMS
S6
2.04
2.02
2.03
4.11
1.99
2.00
3.08
1.01
3.05
9.20
8.92
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

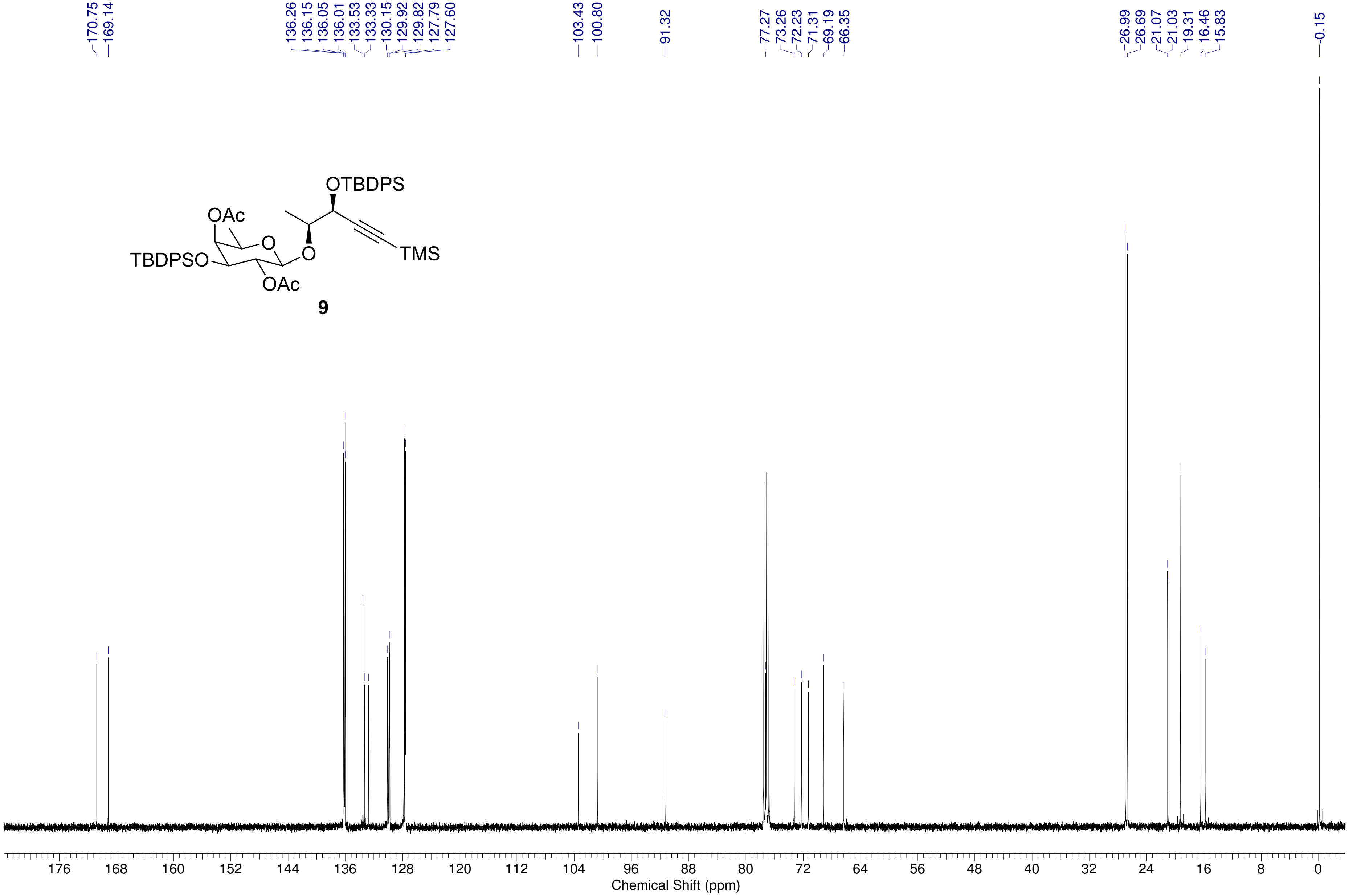

159.14
136.30
136.07
133.71
130.96
129.83
129.70
129.31
127.68
127.50
113.77
104.54
91.22
77.29
71.17
67.38
55.41
27.10
19.49
15.81
-0.14
OTBDPS
OPMB
TMS
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

S6

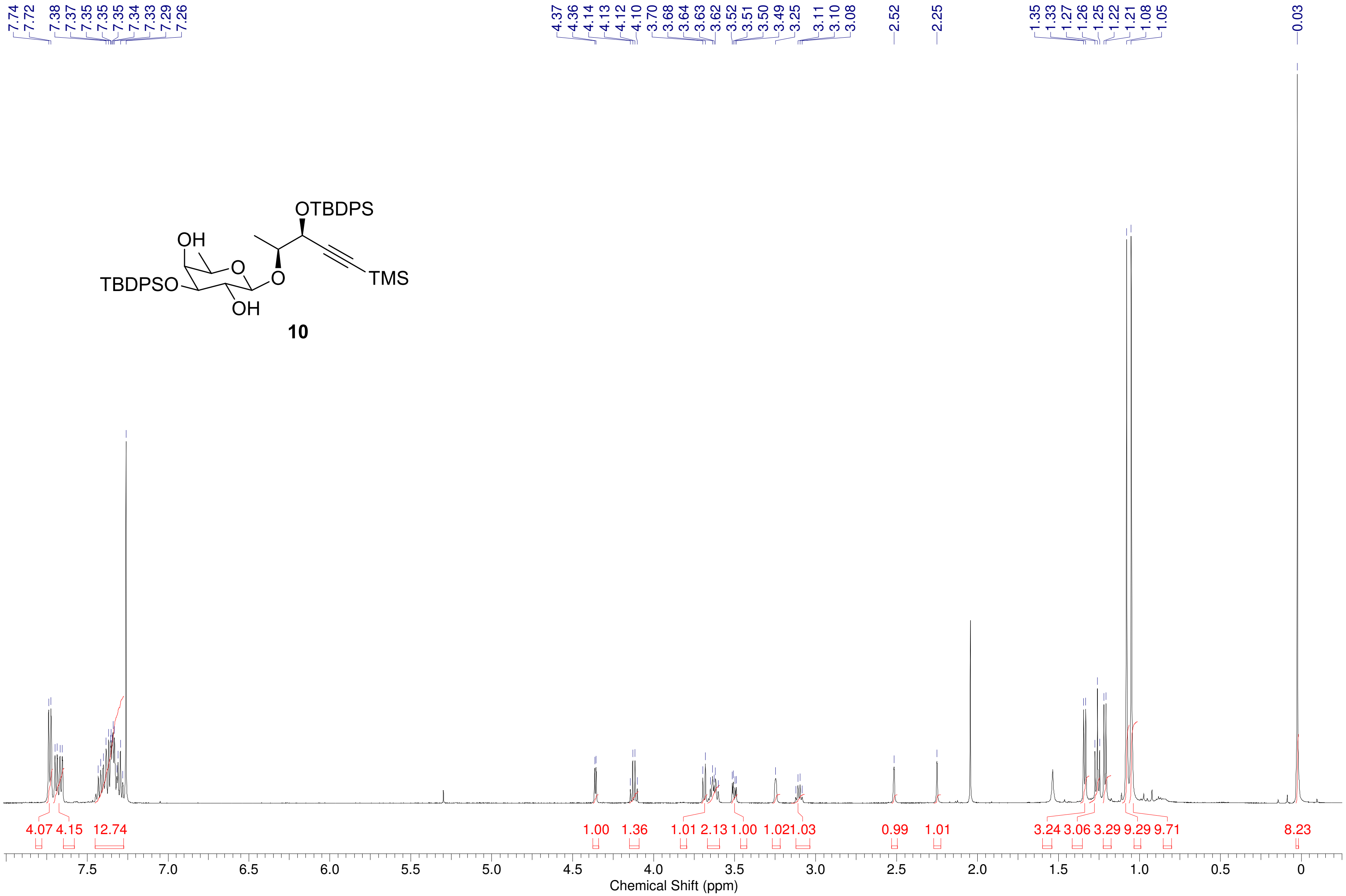

7.77
7.76
7.73
7.71
7.44
7.44
7.40
7.40
7.39
7.37
4.17
4.15
3.87
3.86
3.84
3.84
3.82
3.81
2.47
2.46
1.25
1.24
1.11
0.02
OTBDPS
OH
TMS
8
4.03
6.05
0.98
1.01
0.97
3.03
8.91
8.87
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


136.21
136.02
133.43
133.13
130.03
129.79
127.82
127.51
103.70
92.25
71.34
69.78
27.14
19.52
18.03
-0.34
OTBDPS
OH
TMS
8
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

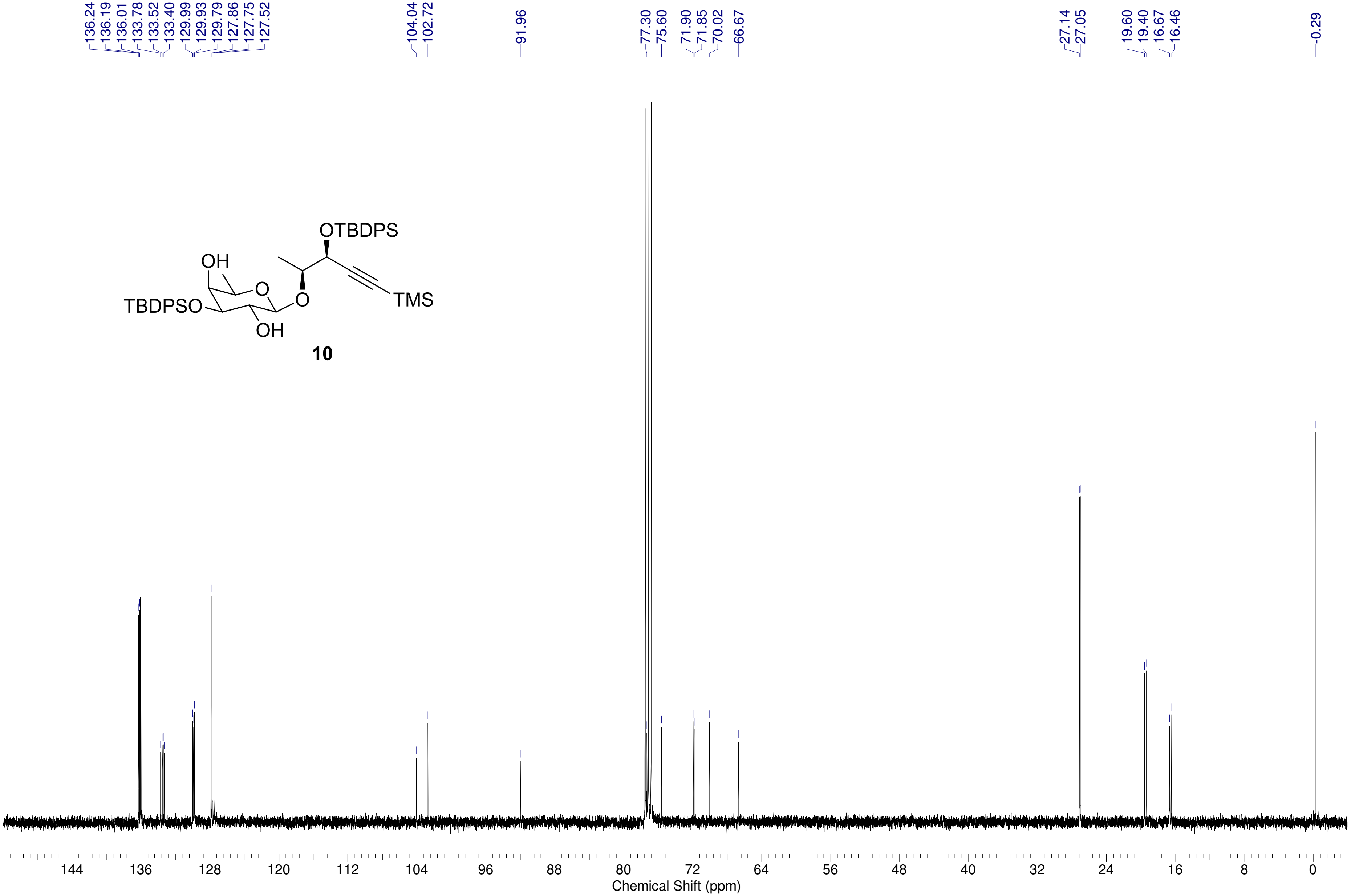

7.72
7.70
7.63
7.61
7.56
7.39
7.38
7.37
7.35
7.33
7.25
5.07
5.06
5.06
5.04
4.79
4.78
4.20
4.19
3.61
3.60
3.59
3.58
3.45
3.43
3.42
3.40
3.39
3.07
3.06
3.05
3.04
2.12
1.46
1.30
1.29
1.05
0.99
0.97
0.09
OTBDPS
OAc
O
TBDPSO
O
TMS
OAc
9
2.03
4.10
1.94
10.53
1.61
1.00
0.99
1.00
1.00
1.24
0.77
1.01
2.97
3.00
2.99
9.13
12.00
9.05
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


170.75
169.14
136.26
136.15
136.05
136.01
133.53
133.33
130.15
129.92
129.82
127.79
127.60
103.43
100.80
91.32
77.27
73.26
72.23
71.31
69.19
66.35
26.99
26.69
21.07
21.03
19.31
16.46
15.83
-0.15
OTBDPS
OAc
TBDPSO
O
O
TMS
OAc
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

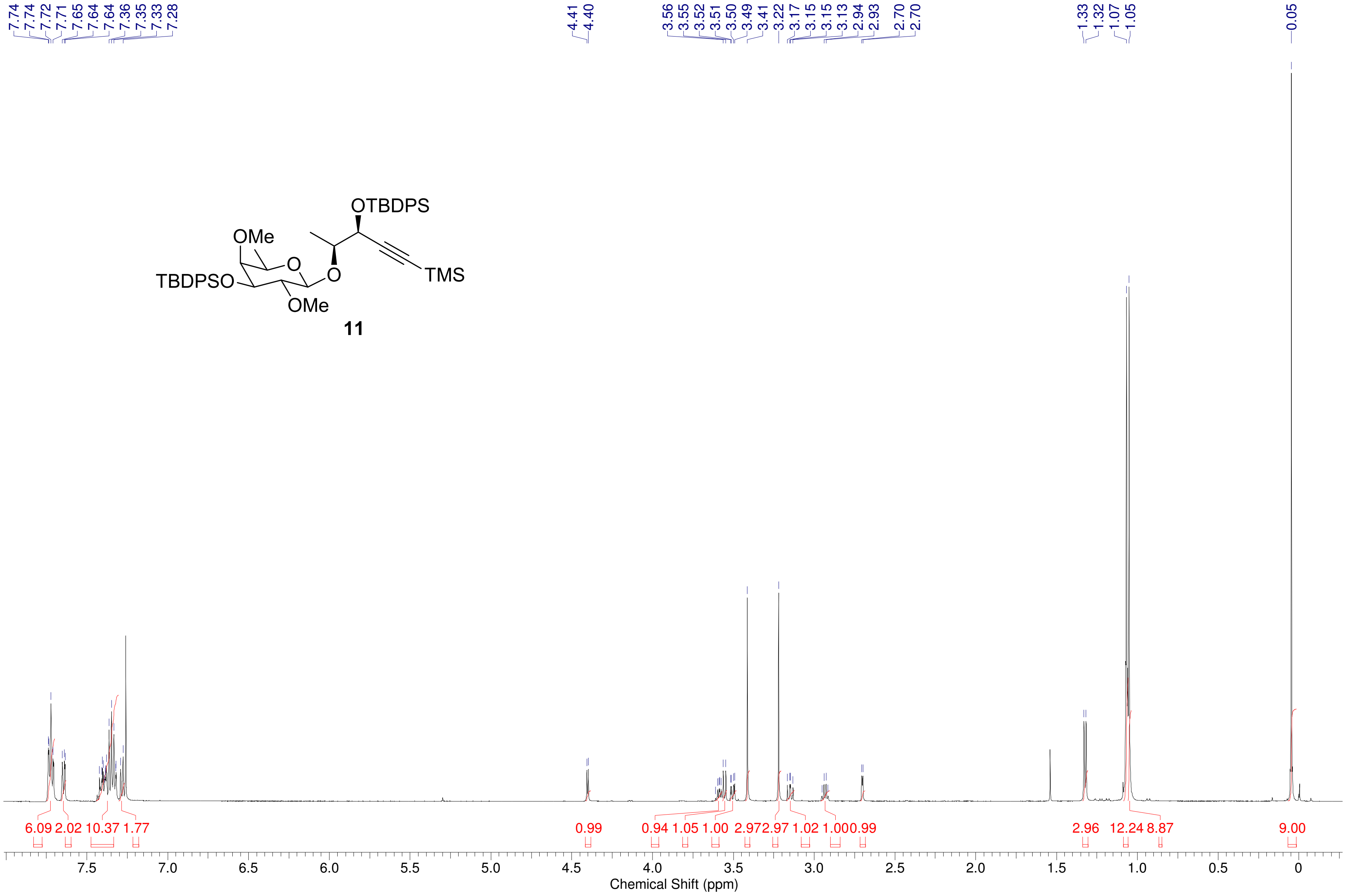
9

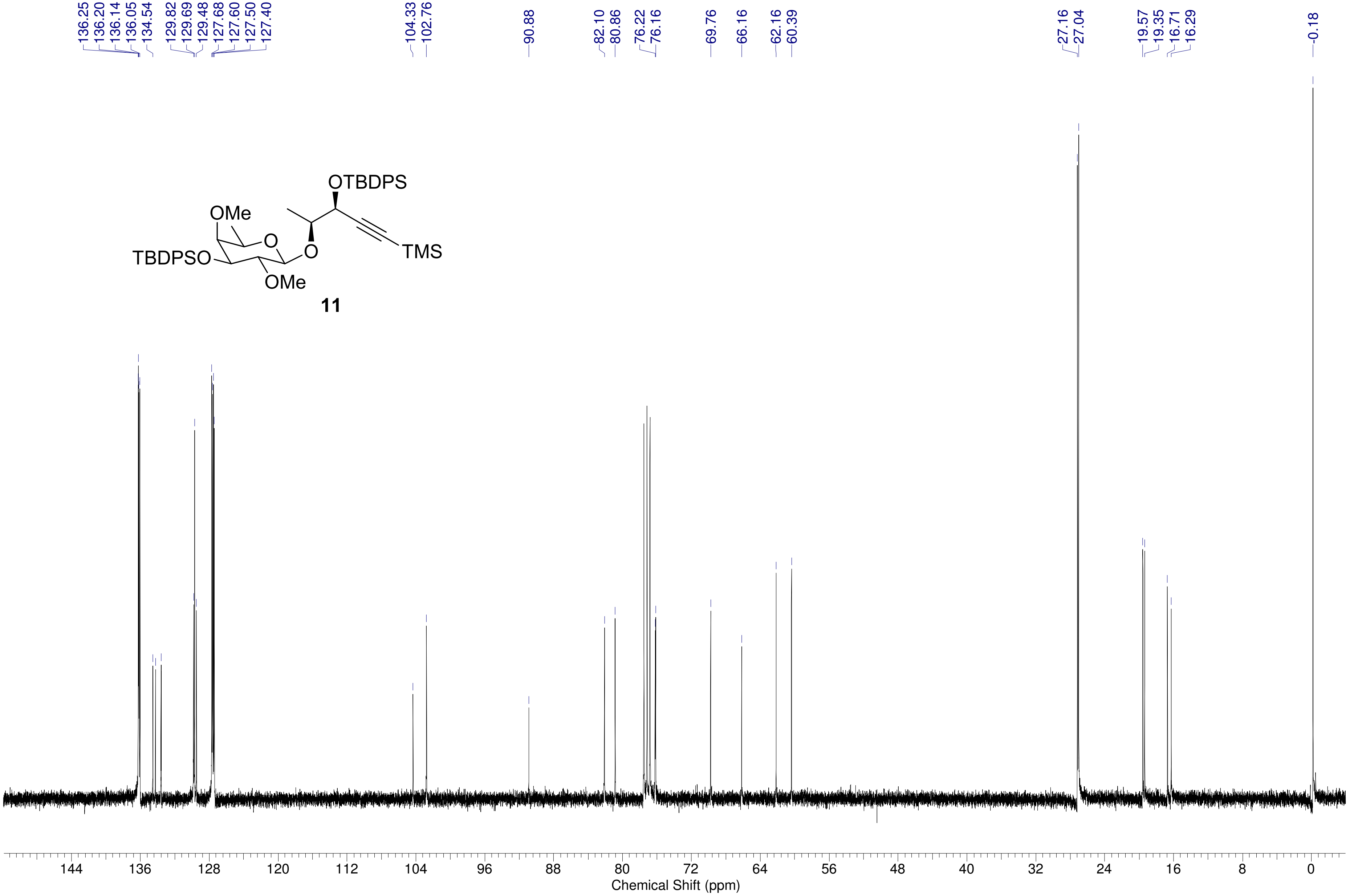

7.74
7.72
7.38
7.37
7.35
7.35
7.35
7.34
7.33
7.29
7.26
4.37
4.36
4.14
4.13
4.12
4.10
3.70
3.68
3.64
3.63
3.62
3.52
3.51
3.50
3.49
3.25
3.11
3.10
3.08
2.52
2.25
1.35
1.33
1.27
1.26
1.25
1.22
1.21
1.08
1.05
0.03
OTBDPS
OH
O
TBDPSO
O
TMS
OH
4.07
4.15
12.74
1.00
1.36
1.01
2.13
1.00
1.02
1.03
0.99
1.01
3.24
3.06
3.29
9.29
9.71
8.23
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

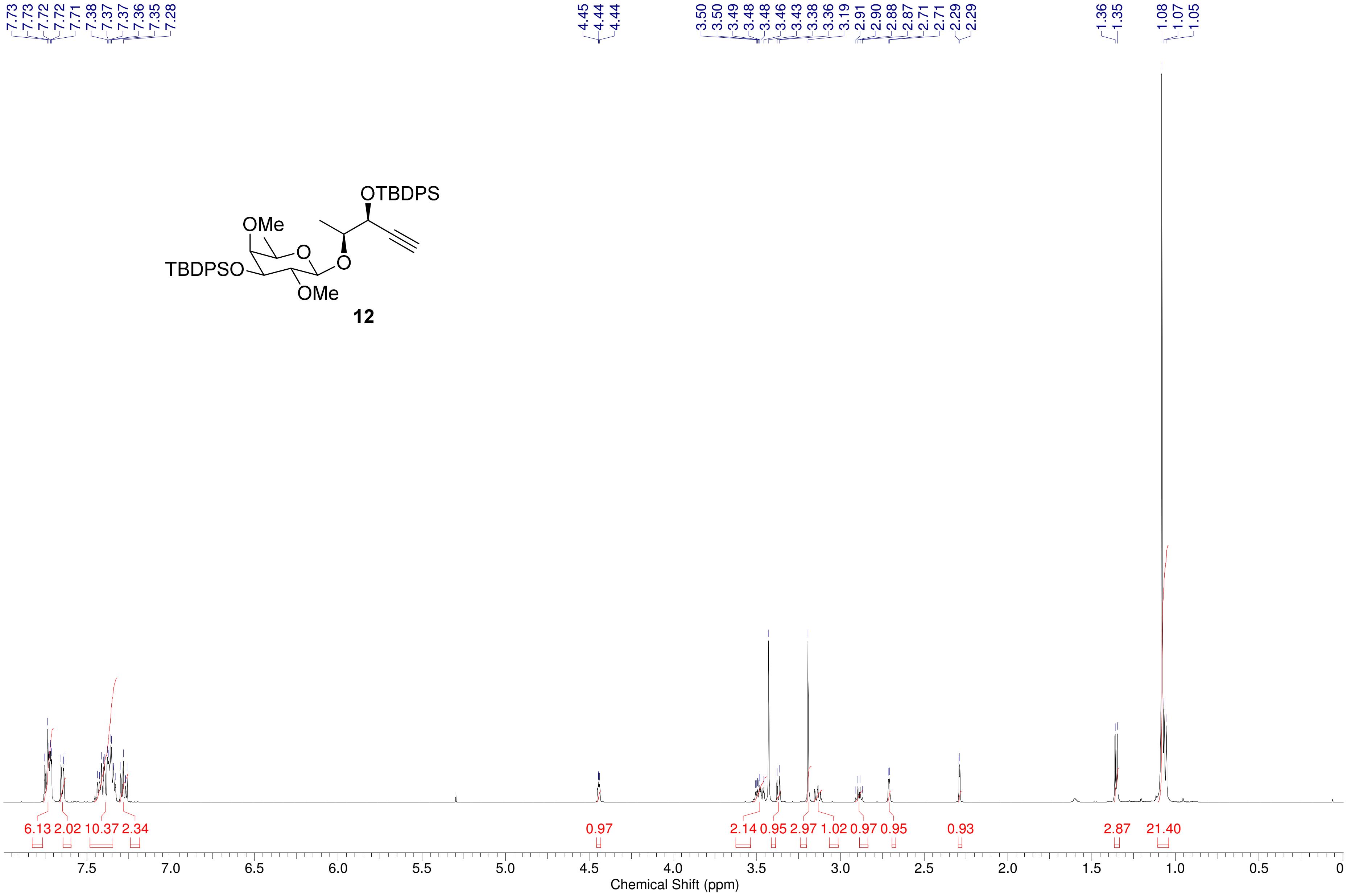
10


136.24
136.19
136.01
133.78
133.52
133.40
129.99
129.93
129.79
127.86
127.75
127.52
104.04
102.72
91.96
77.30
75.60
71.90
71.85
70.02
66.67
27.14
27.05
19.60
19.40
16.67
16.46
-0.29
OTBDPS
OH
O
TBDPSO
O
OH
TMS
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

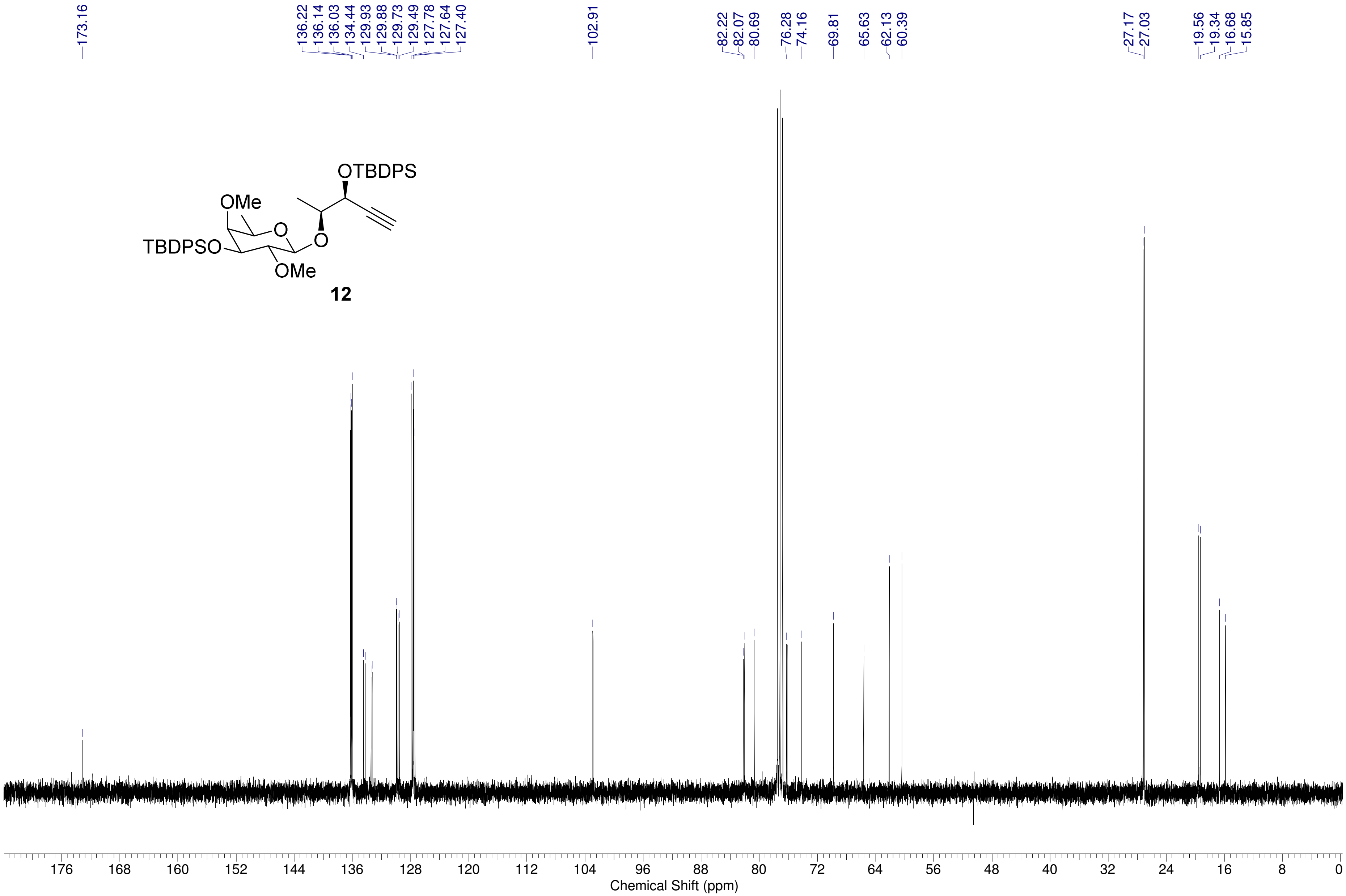
10


7.74
7.74
7.72
7.71
7.65
7.64
7.64
7.36
7.35
7.33
7.28
4.41
4.40
3.56
3.55
3.52
3.51
3.50
3.49
3.41
3.22
3.17
3.15
3.15
3.13
2.94
2.93
2.70
2.70
1.33
1.32
1.07
1.05
0.05
OTBDPS
OMe
O
O
TBDPSO
TMS
OMe
11
6.09
2.02
10.37
1.77
0.99
0.94
1.05
1.00
2.97
2.97
1.02
1.00
0.99
2.96
12.24
8.87
9.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

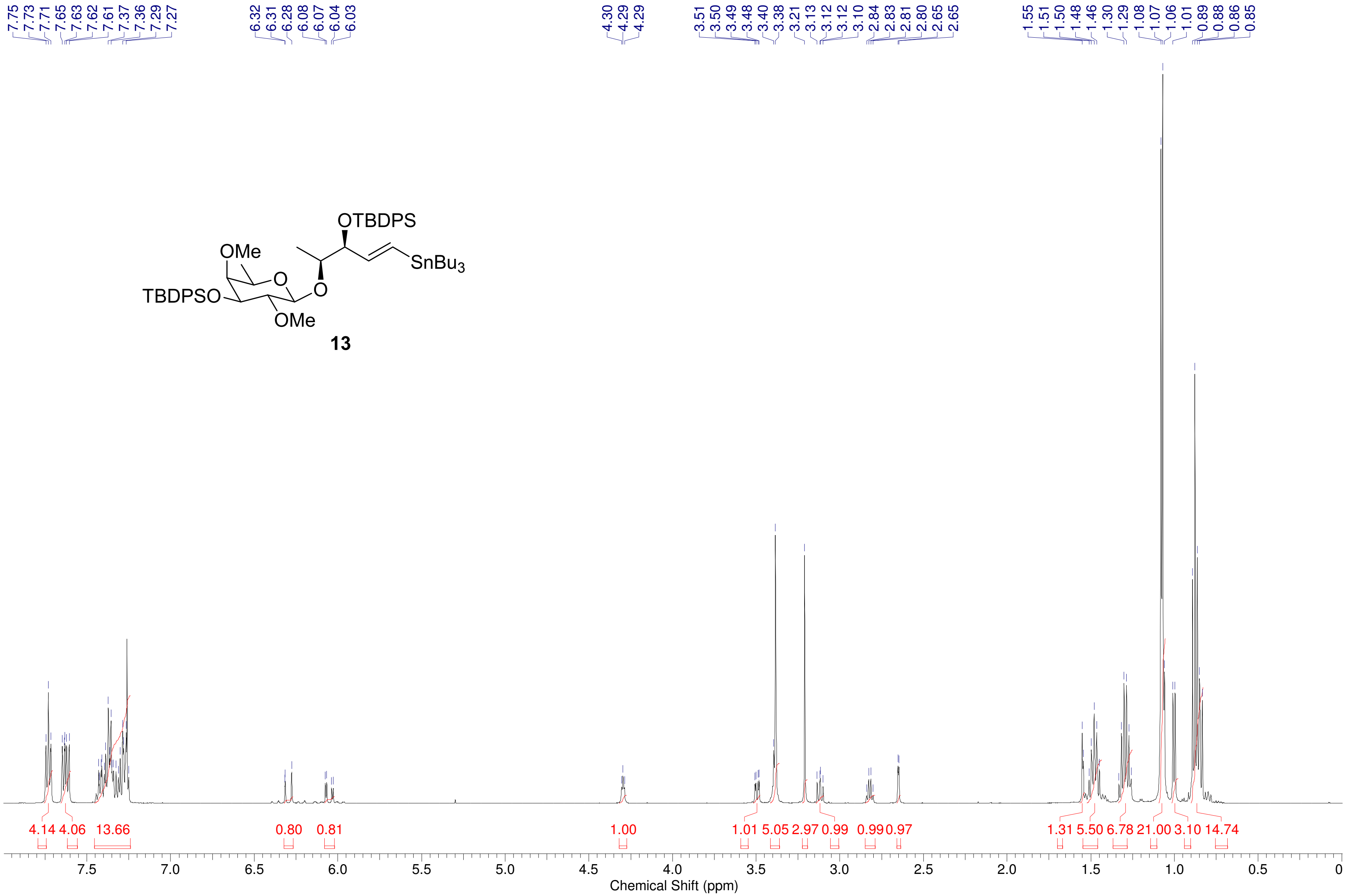

136.25
136.20
136.14
136.05
134.54
129.82
129.69
129.48
127.68
127.60
127.50
127.40
104.33
102.76
90.88
82.10
80.86
76.22
76.16
69.76
66.16
62.16
60.39
27.16
27.04
19.57
19.35
16.71
16.29
-0.18
OTBDPS
OMe
TBDPSO
O
O
OMe
TMS
11
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


7.73
7.73
7.72
7.72
7.71
7.38
7.37
7.37
7.36
7.35
7.28
4.45
4.44
4.44
3.50
3.50
3.49
3.48
3.48
3.46
3.43
3.38
3.36
3.19
2.91
2.90
2.88
2.87
2.71
2.71
2.29
2.29
1.36
1.35
1.08
1.07
1.05
OTBDPS
OMe
O
TBDPSO
O
OMe
6.13
2.02
10.37
2.34
0.97
2.14
0.95
2.97
1.02
0.97
0.95
0.93
2.87
21.40
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

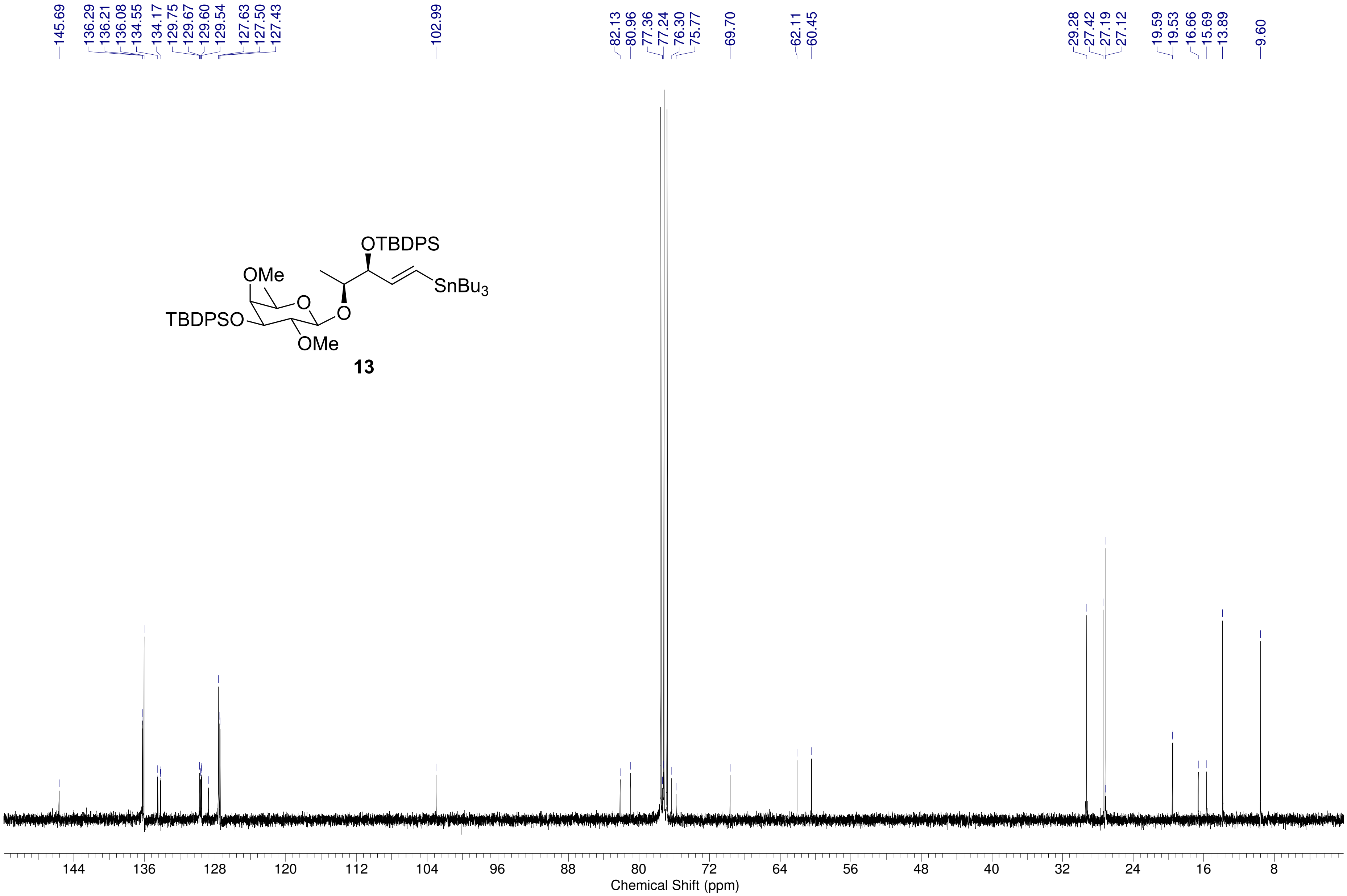
12


173.16
136.22
136.14
136.03
134.44
129.93
129.88
129.73
129.49
127.78
127.64
127.40
102.91
82.22
82.07
80.69
76.28
74.16
69.81
65.63
62.13
60.39
27.17
27.03
19.56
19.34
16.68
15.85
OTBDPS
OMe
O
O
TBDPSO
OMe
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

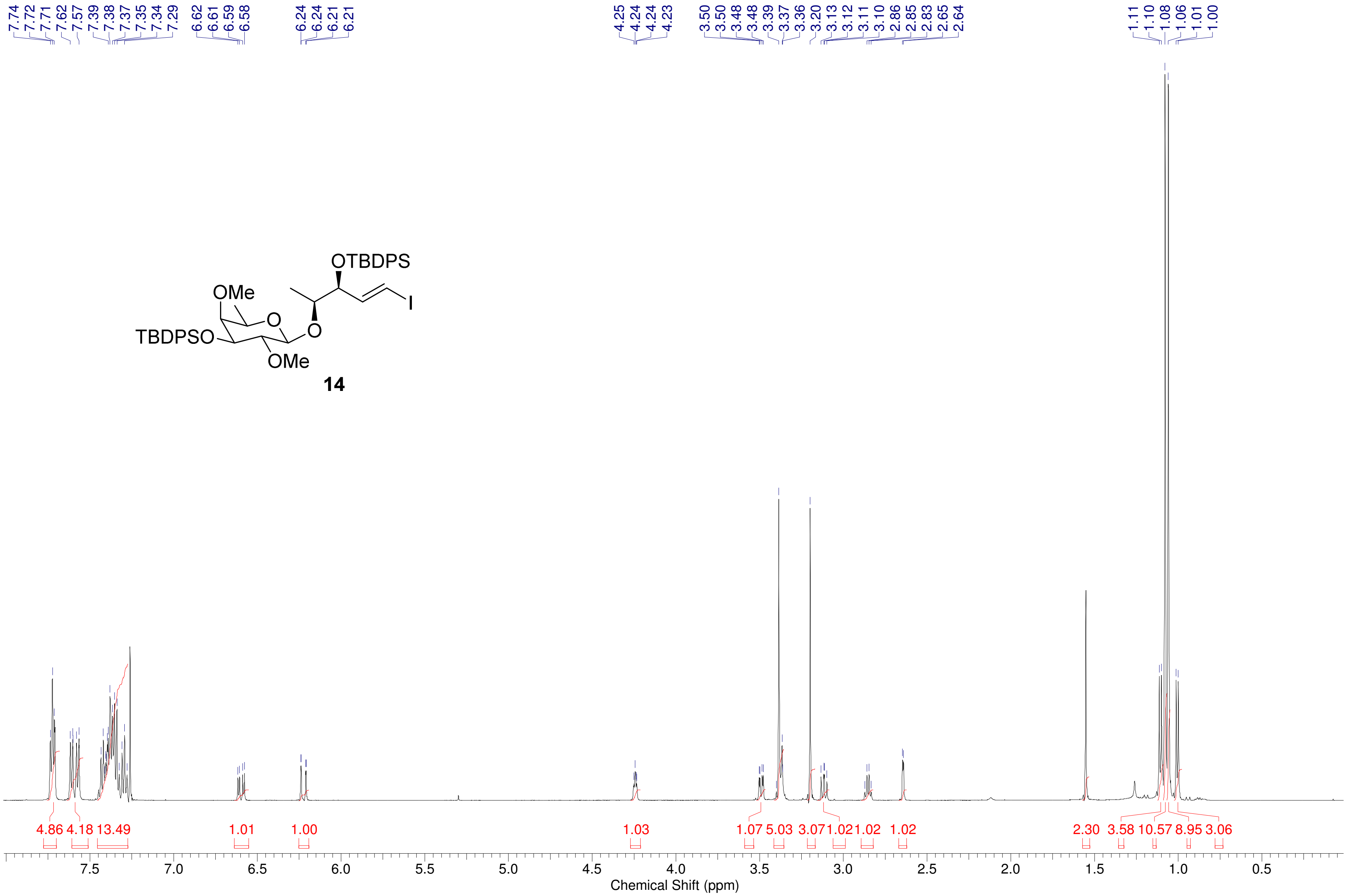
12

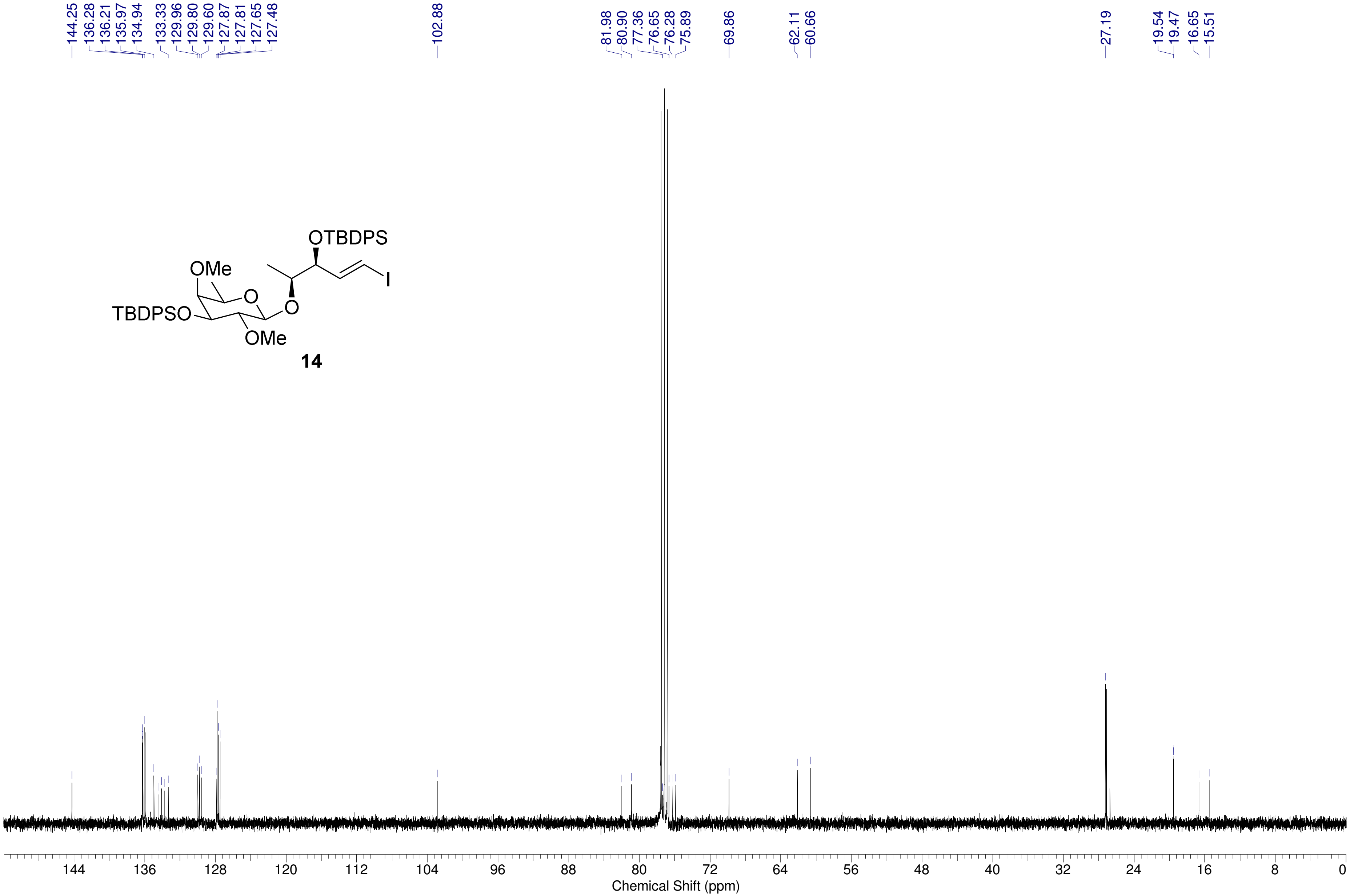

7.75
7.73
7.71
7.65
7.63
7.62
7.61
7.37
7.36
7.29
7.27
6.32
6.31
6.28
6.08
6.07
6.04
6.03
4.30
4.29
4.29
3.51
3.50
3.49
3.48
3.40
3.38
3.21
3.13
3.12
3.12
3.10
2.84
2.83
2.81
2.80
2.65
2.65
1.55
1.51
1.50
1.48
1.46
1.30
1.29
1.08
1.07
1.06
1.01
0.89
0.88
0.86
0.85
OTBDPS
OMe
O
TBDPSO
O
OMe
SnBu3
4.14
4.06
13.66
0.80
0.81
1.00
1.01
5.05
2.97
0.99
0.99
0.97
1.31
5.50
6.78
21.00
3.10
14.74
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

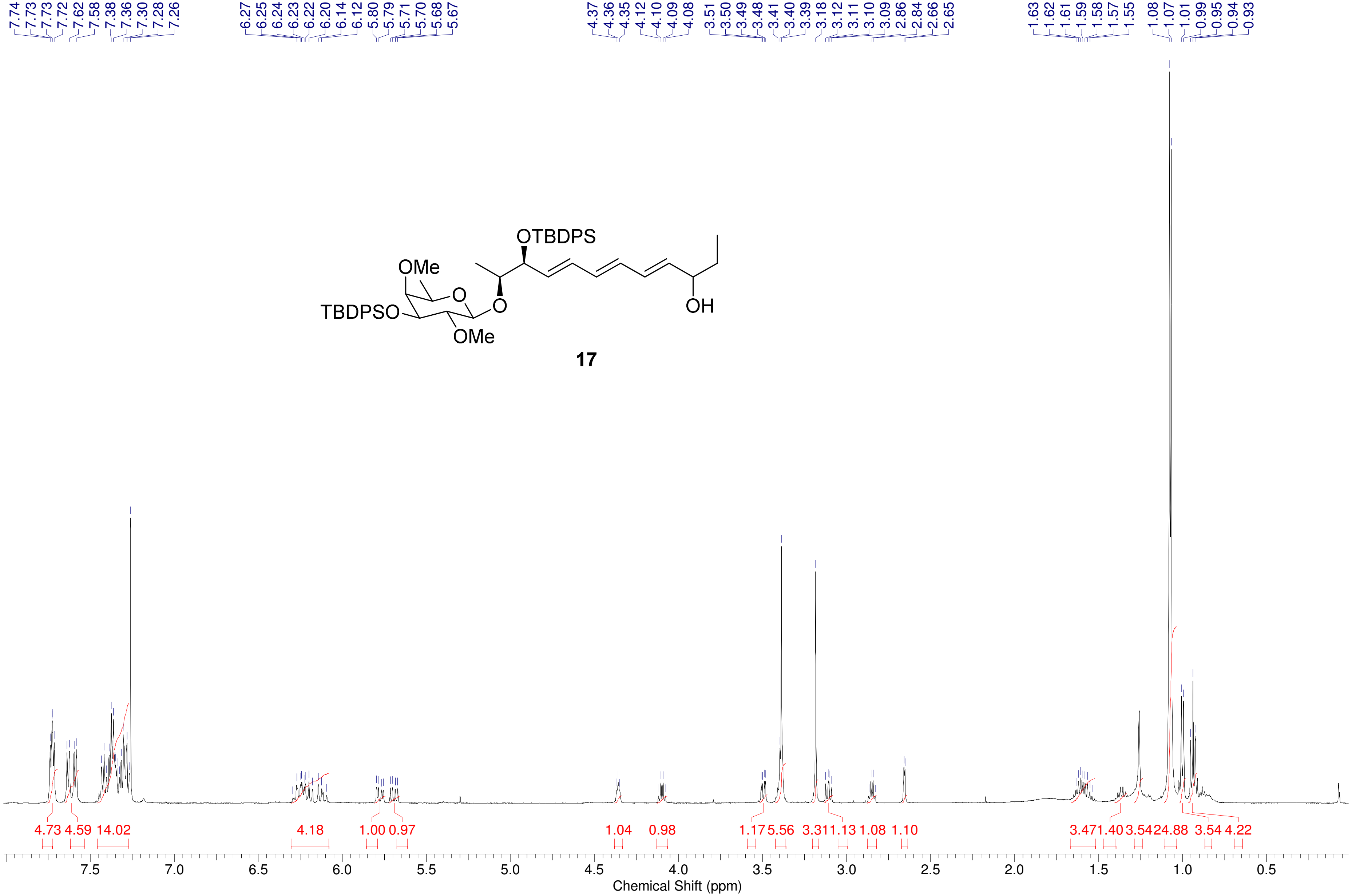
13

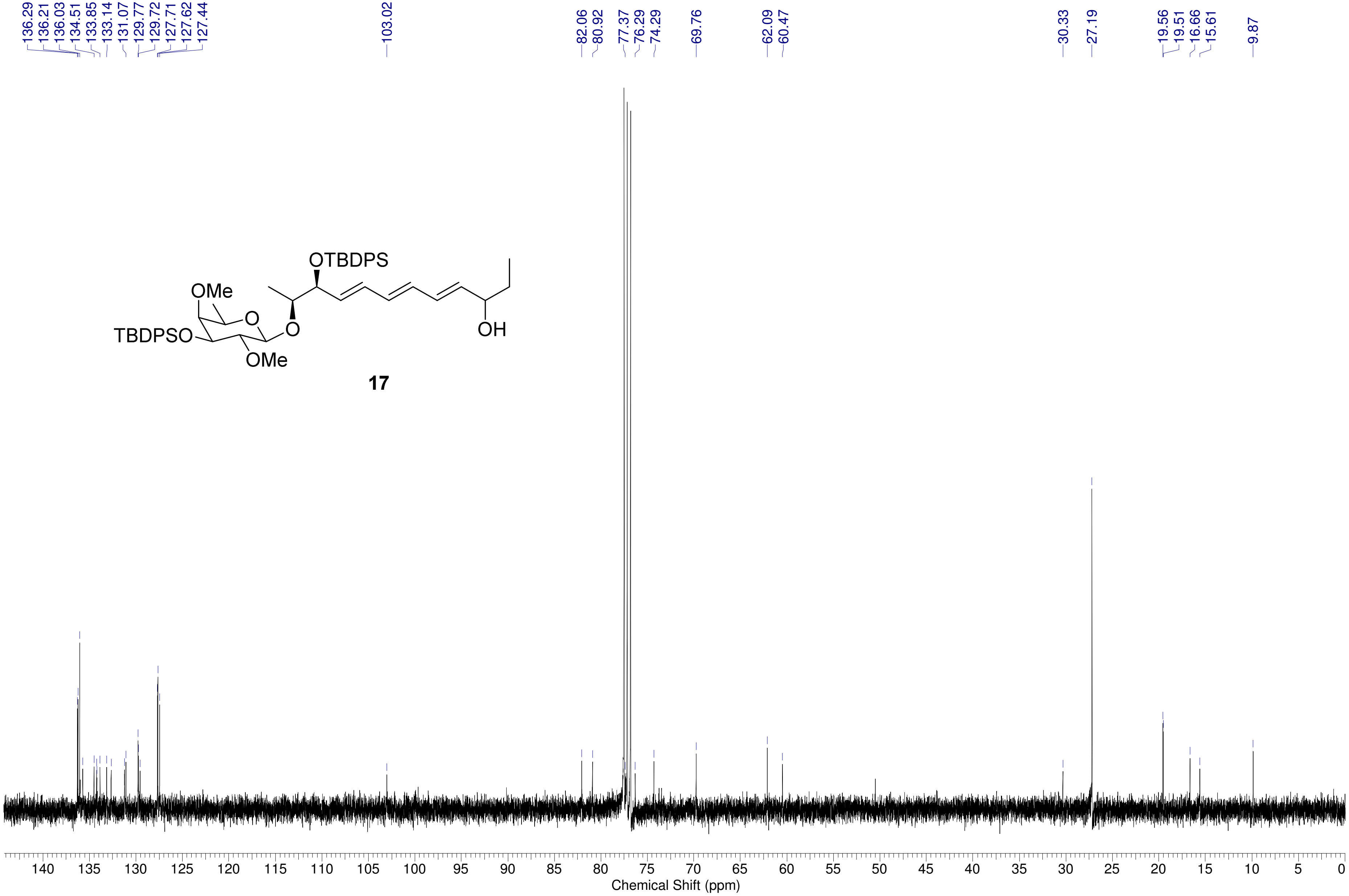

145.69
136.29
136.21
136.08
134.55
134.17
129.75
129.67
129.60
129.54
127.63
127.50
127.43
102.99
82.13
80.96
77.36
77.24
76.30
75.77
69.70
62.11
60.45
29.28
27.42
27.19
27.12
19.59
19.53
16.66
15.69
13.89
9.60
OTBDPS
OMe
SnBu3
TBDPSO
O
O
OMe
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

13

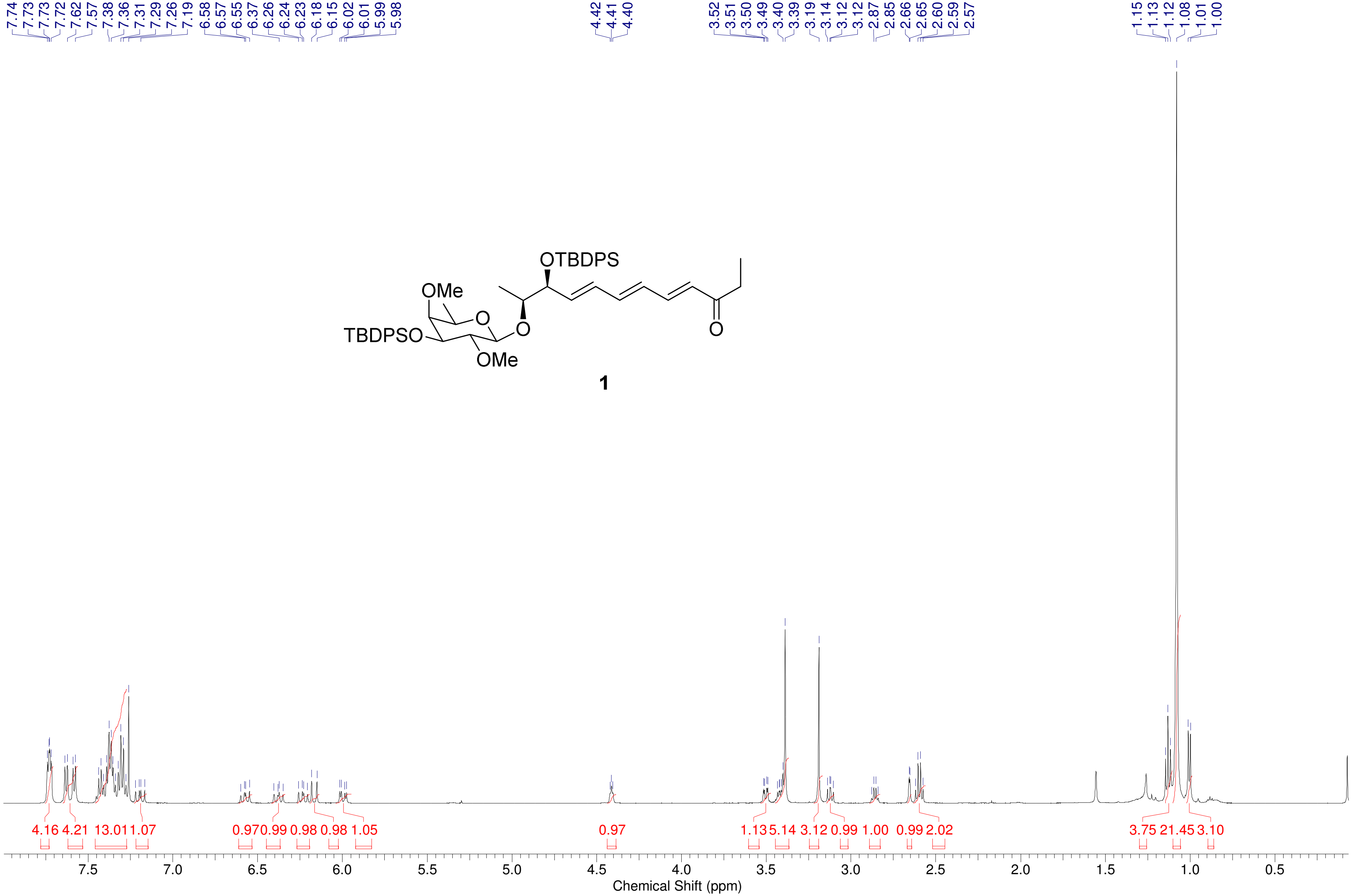

7.74
7.72
7.71
7.62
7.57
7.39
7.38
7.37
7.35
7.34
7.29
6.62
6.61
6.59
6.58
6.24
6.24
6.21
6.21
4.25
4.24
4.24
4.23
3.50
3.50
3.48
3.39
3.37
3.36
3.20
3.13
3.12
3.11
3.10
2.86
2.85
2.83
2.65
2.64
1.11
1.10
1.08
1.06
1.01
1.00
OTBDPS
OMe
O
I
TBDPSO
O
OMe
14
4.86
4.18
13.49
1.01
1.00
1.03
1.07
5.03
3.07
1.02
1.02
1.02
2.30
3.58
10.57
8.95
3.06
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

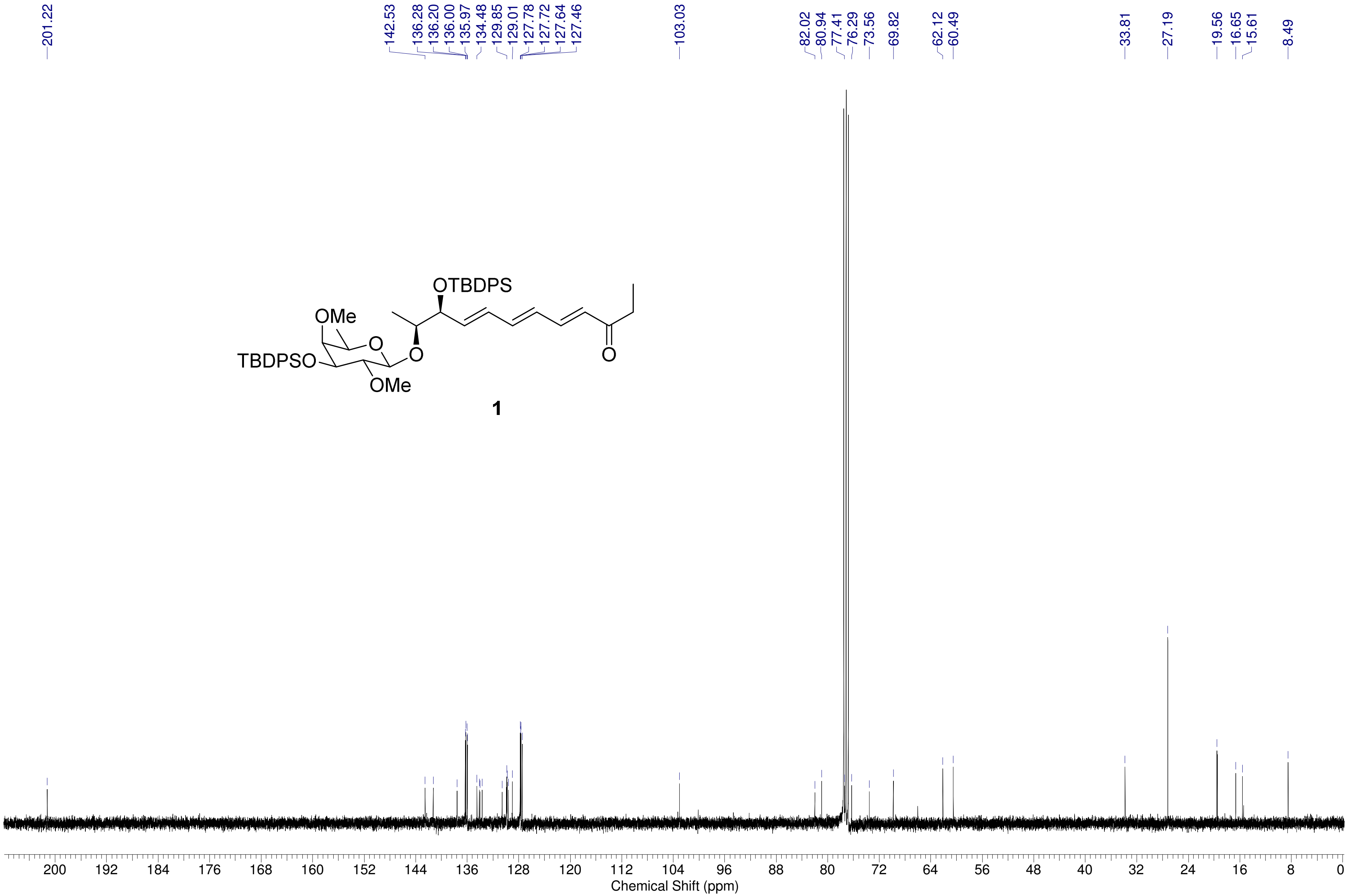

144.25
136.28
136.21
135.97
134.94
133.33
129.96
129.80
129.60
127.87
127.81
127.65
127.48
102.88
81.98
80.90
77.36
76.65
76.28
75.89
69.86
62.11
60.66
27.19
19.54
19.47
16.65
15.51
OTBDPS
OMe
TBDPSO
O
O
I
OMe
14
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


7.74
7.73
7.73
7.72
7.62
7.58
7.38
7.36
7.30
7.28
7.26
6.27
6.25
6.24
6.23
6.22
6.20
6.14
6.12
5.80
5.79
5.71
5.70
5.68
5.67
4.37
4.36
4.35
4.12
4.10
4.09
4.08
3.51
3.50
3.49
3.48
3.41
3.40
3.39
3.18
3.12
3.11
3.10
3.09
2.86
2.84
2.66
2.65
1.63
1.62
1.61
1.59
1.58
1.57
1.55
1.08
1.07
1.01
0.99
0.95
0.94
0.93
OTBDPS
OMe
O
TBDPSO
O
OMe
OH
17
4.73
4.59
14.02
4.18
1.00
0.97
1.04
0.98
1.17
5.56
3.31
1.13
1.08
1.10
3.47
1.40
3.54
24.88
3.54
4.22
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)


136.29
136.21
136.03
134.51
133.85
133.14
131.07
129.77
129.72
127.71
127.62
127.44
103.02
82.06
80.92
77.37
76.29
74.29
69.76
62.09
60.47
30.33
27.19
19.56
19.51
16.66
15.61
9.87
OTBDPS
OMe
O
TBDPSO
O
OMe
OH
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
Chemical Shift (ppm)

17


7.74
7.73
7.73
7.72
7.62
7.57
7.38
7.36
7.31
7.29
7.26
7.19
6.58
6.57
6.55
6.37
6.26
6.24
6.23
6.18
6.15
6.02
6.01
5.99
5.98
4.42
4.41
4.40
3.52
3.51
3.50
3.49
3.40
3.39
3.19
3.14
3.12
3.12
2.87
2.85
2.66
2.65
2.60
2.59
2.57
1.15
1.13
1.12
1.08
1.01
1.00
OTBDPS
OMe
O
TBDPSO
O
OMe
O
1
4.16
4.21
13.01
1.07
0.97
0.99
0.98
0.98
1.05
0.97
1.13
5.14
3.12
0.99
1.00
0.99
2.02
3.75
21.45
3.10
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)


201.22
142.53
136.28
136.20
136.00
135.97
134.48
129.85
129.01
127.78
127.72
127.64
127.46
103.03
82.02
80.94
77.41
76.29
73.56
69.82
62.12
60.49
33.81
27.19
19.56
16.65
15.61
8.49
OTBDPS
OMe
O
TBDPSO
OMe
O
O
1
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)