SUPPORTING INFORMATION

Synthesis of the mycolactone core by ring-closing metathesis

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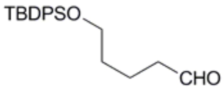
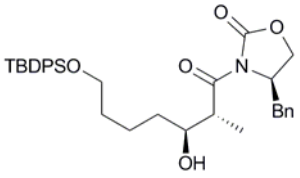
General Experimental Information: Unless otherwise noted, all reagents and chemical compounds were purchased from commercial sources and used without further purification. High purity anhydrous solvents (tetrahydrofuran, dichloromethane, *N*,*N*-dimethylformamide, diethyl ether, and toluene) were obtained by passing through a solvent column composed of activated A-1 alumina.[1] Triethylamine (Et_3N) and ethyl-*N*,*N*-diisopropylamine (*i*-Pr_2NEt) were dried over sodium and freshly distilled. MeOH was distilled from magnesium. Dioxane was distilled from sodium-benzophenone ketyl. All air or moisture sensitive reactions were performed under a positive pressure of dry argon in oven-dried glassware sealed with a septa. Reactions were magnetically stirred with a Teflon-coated stir bar. Flash chromatography was performed on Silica Gel 60 (230-400 mesh) according to the method of Still.[2] Analytical TLC was performed on Silica Gel 60 F254 glass plates that were precoated with a 250 μm layer of silica. Visualization was achieved with UV light and/or an appropriate stain (I_2 on SiO_2, $KMnO_4$, bromocresol green, dinitrophenylhydrazine, ninhydrin, and ceric ammonium molybdate). Yields and characterization data correspond to isolated, homogeneous materials. NMR data were collected at the UCSD Department of Chemistry and Biochemistry NMR facility (http://nmr.ucsd.edu/chemnmrfacility.html). ^{1}H-NMR spectra were recorded on a Varian Mercury Plus spectrometer at 400 MHz or on a Varian Unity spectrometer at 500 MHz. ^{13}C-NMR spectra were recorded at 100 MHz on the Mercury Plus instrument or at 75 MHz on a Varian Mercury spectrometer. FID files were processed using MestRe-C software version 4.9.9.6. Chemical shifts for ^{1}H-NMR and ^{13}C-NMR analyses were reported using the standard of Gottlieb, Kotlyar, and Nudelman[3] and were calibrated using the signal from residual $CHCl_3$ (7.26 ppm, ^{1}H-NMR) or the $CDCl_3$ signal (77.16 ppm, ^{13}C-NMR). Mass spectra were obtained by Dr. Yongxuan Su the UCSD Department of Chemistry and Biochemistry Mass Spectrometry Facility (http://chem-tech.ucsd.edu/Recharges/MassSpec/). Electrospray (ESI) and atmospheric pressure chemical ionization (APCI) analysis was performed using a Finnigan LCQDECA mass spectrometer, and fast atom bombardment (FAB) analysis was carried out using a ThermoFinnigan MAT900XL mass spectrometer.



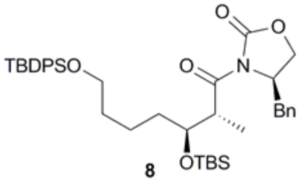
7

5-(*tert*-butyldiphenylsilyloxy)pentanal (7). The known mono-TBDPS 1,5-pentanediol and corresponding aldehyde were prepared according to the literature procedure and had physical properties identical to those reported.[4]



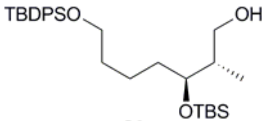
S1

(*R*)-4-benzyl-3-((2*R*,3*S*)-7-(*tert*-butyldiphenylsilyloxy)-3-hydroxy-2-methylheptanoyl)oxazolidin-2-one (S1). A solution of (*R*)-3-(1-oxopropyl)-4-(phenylmethyl)-2-oxazolidinone[5] (1.0 g, 4.29 mmol) in dry CH_2Cl_2 (45 mL) under argon was cooled to -78 °C before Et_3N (710 µL, 5.14 mmol) and Bu_2BOTf (4.71 mL, 4.71 mmol, 1 M in CH_2Cl_2) were added. The solution was stirred for 1 h at -78 °C and 15 min at 0 °C before returning to -78 °C and adding aldehyde **7** (1.60 g, 4.70 mmol) as a solution in CH_2Cl_2 (5 mL). The reaction was stirred for 30 min at -78 °C, 15 min while warm from -78 °C to 0 °C, and 30 min at 0 °C. A 1 M solution of NaOAc in 9:1 MeOH-H_2O (40 mL) and 30% H_2O_2 (4 mL) were added and the solution stirred at 0 °C for 15 min, during which time a white precipitate formed. Hexanes (125 mL) and water (200 mL) were added, the biphasic mixture was transferred to a separatory funnel, and the layers were separated. The aqueous phase was extracted with hexanes (2 x 50 mL) and the combined organic layers were washed with sat. $NaHCO_3$ (100 mL) and brine (100 mL) and dried over Na_2SO_4. Purification by flash chromatography (9:1 to 4:1 hexanes-EtOAc) yielded aldol adduct **S1** (2.34 g, 95%) as a colorless oil: ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 7.67 (m, 4H), 7.35 (m, 9H), 7.20 (m, 2H), 4.70 (m, 1H), 4.20 (m, 2H), 3.94 (m, 1H), 3.75 (dq, *J* = 7.0, 2.7 Hz, 1H), 3.68 (t, *J* = 6.2 Hz, 2H), 3.25 (dd, *J* = 13.4, 3.3 Hz, 1H), 2.82 (br s, 1H), 2.80 (dd, *J* = 13.4, 9.4 Hz, 1H), 1.58 (m, 4H), 1.41 (m, 2H), 1.26 (d, *J* = 7.0 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm 177.7, 153.1, 135.7, 135.2, 134.2, 129.6, 129.6, 129.1, 127.7, 127.6, 71.5, 66.3, 63.9, 55.2, 42.3, 37.9, 33.7, 32.6, 27.0, 22.4, 19.4, 10.6; MS (FAB) *m/z* 574.5 ($[M+H]^+$, 100%); HRMS (FAB) *m/z* calcd for $C_{34}H_{44}NO_5Si$ $(M+H)^+$ 574.2983, found 574.2994.



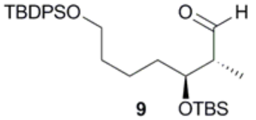
8

(*R*)-4-benzyl-3-((2*R*,3*S*)-3-(*tert*-butyldimethylsilyloxy)-7-(*tert*-butyldiphenylsilyloxy)-2-methylheptanoyl)oxazolidin-2-one (8). The aldol product **S1** (1.92 g, 3.35 mmol) was dissolved in dry CH_2Cl_2 (33 mL) and cooled to 0 °C before *i*-Pr_2NEt (1.5 mL, 8.37 mmol) and TBSOTf (1.0 mL, 4.35 mmol) were added and the reaction stirred overnight at rt. After 8 h of reaction, the starting material was no longer detectable by TLC (2:1 hexanes-EtOAc) and the product had formed (**S1**, R_f 0.22; **8**, R_f 0.57). Water (20 mL) was added and the reaction was stirred for 20 min. The layers were separated, the aqueous phase was extracted with CH_2Cl_2 (2 x 20 mL), and the combined organic layers were washed with sat. $NaHCO_3$ (20 mL) and brine (20 mL) and dried over Na_2SO_4. Purification by flash chromatography (2:1 hexanes-EtOAc) yielded TBS ether **8** (2.26 g, 98%) as a colorless oil: ^{1}H-NMR (400 MHz, $CDCl_3$) 7.69 (m, 4H), 7.32 (m, 11H), 4.60 (m, 1H), 4.14 (m, 2H), 4.03 (q, *J* = 5.7 Hz, 1H), 3.88 (m, 1H), 3.68 (t, *J* = 6.4 Hz, 2H), 3.31 (dd, *J* = 13.3, 3.1 Hz, 1H), 2.78 (dd, *J* = 13.3, 9.7 Hz, 1H), 1.58 (m, 4H), 1.45 (m, 2 H), 1.23 (d, *J* = 6.9 Hz, 3H), 1.07 (s, 9H), 0.91 (s, 9H), 0.06 (s, 3H), 0.02 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm 175.36, 153.12, 135.67, 135.53, 134.18, 129.60, 129.58, 129.05, 127.71, 127.44, 72.99, 66.05, 63.96, 55.90, 42.98, 37.72, 35.55, 33.05, 26.99, 25.97, 21.60, 19.31, 18.16, 11.71, -3.94, -4.68; MS (ESI) *m/z* 710.41 ($[M+Na]^+$, 100%); HRMS (FAB) *m/z* calcd for $C_{40}H_{58}NO_5Si_2$ $(M+H)^+$ 688.3848, found 688.3860.



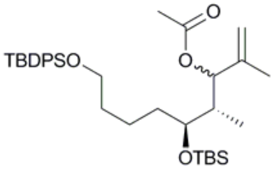
S2

(2*S*,3*S*)-3-(*tert*-butyldimethylsilyloxy)-7-(*tert*-butyldiphenylsilyloxy)-2-methylheptan-1-ol (S2). Oxazolidinone **8** (1.95 g, 2.83 mmol) was dissolved in dry THF (12 mL) under argon and cooled to 0 °C. MeOH (230 μL, 5.67 mmol) and $LiBH_4$ (2 M in THF, 2.84 mL, 5.67 mmol) were added and the reaction stirred for 30 min at 0 °C and 3 h at rt. The reaction was cooled to 0 °C and quenched by the slow addition of sat. NH_4Cl (60 mL). The reaction mixture was extracted with CH_2Cl_2 (3 x 20 mL) and the combined organic layers were dried over Na_2SO_4. Purification by flash chromatography (5:1 hexanes-EtOAc) provided alcohol **S2** (1.08 g, 74 %) as a light yellow oil: ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 7.67 (m, 4H), 7.40 (m, 6H), 3.74 (m, 1H), 3.69 (m, 1H), 3.66 (t, *J* = 6.2 Hz, 2 H), 3.51 (dd, *J* = 10.2, 5.0 Hz, 1H), 2.60 (br s, 1H), 1.96 (m, 1H), 1.55 (m, 2H), 1.47 (m, 3H), 1.28 (m, 1H), 1.04 (s, 9), 0.88 (s, 9H), 0.79 (d, *J* = 6.8 Hz, 3H), 0.092 (s, 3H), 0.061 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm 135.6, 134.1, 129.6, 127.7, 76.0, 66.1, 63.9, 39.7, 32.9, 32.2, 27.0, 26.0, 22.8, 19.3, 18.1, 12.1, -4.2, -4.3; MS (ESI) *m/z* 537.24 ($[M+Na]^+$, 100%), 515.06 ($[M+H]^+$, 71%); HRMS (FAB) *m/z* calcd for $C_{40}H_{51}O_3Si_2$ $(M+H)^+$ 515.3371, found 515.3376.



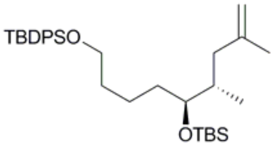
9

(2*R*,3*S*)-3-(*tert*-butyldimethylsilyloxy)-7-(*tert*-butyldiphenylsilyloxy)-2-methylheptanal (9). A dry flask was purged with argon before oxalyl chloride (355 μL, 4.02 mmol) and CH_2Cl_2 (5 mL) were added and the flask was cooled to -78 °C. A solution of DMSO (623 μL, 8.78 mmol) in CH_2Cl_2 (5 mL) was added dropwise over 5 min and the reaction was stirred for 10 min at -78 °C. A solution of alcohol **S2** (1.89 g, 3.66 mmol) in CH_2Cl_2 (9 mL) was added dropwise to the cooled solution over 5 min, during which time a white precipitate formed. The reaction was stirred for 15 min at -78 °C before Et_3N (2.6 mL, 18.4 mmol) was added and the bath was removed. After stirring for 30 min and warming to rt, water (20 mL) was added the biphasic solution was stirred for 10 min. The layers were separated, the aqueous phase was extracted with CH_2Cl_2 (2 x 20 mL), and the combined organic layers were washed with 1% HCl (20 mL), water (20 mL), sat. $NaHCO_3$ (20 mL) and brine (20 mL) and dried over Na_2SO_4. The volatile reaction components were removed at reduced pressure on the rotary evaporator to yield aldehyde **9** (1.79 g, 95%) as a colorless oil that required no further purification: ^{1}H-NMR (500 MHz, $CDCl_3$) δ ppm 9.76 (s, 1H), 7.66 (m, 4H), 7.40 (m, 6H), 4.08 (dt, *J* = 3.6, 6.3 Hz, 1H), 3.65 (t, *J* = 6.3 Hz, 2H), 2.43 (dq, *J* = 3.6, 6.8 Hz, 1H), 1.47 (m, 5H), 1.32 (m, 1H), 1.04 (m, 12H), 0.86 (s, 9H), 0.05 (s, 3H), 0.03 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm 205.5, 135.6, 134.1, 129.6, 127.7, 72.2, 63.7, 51.3, 34.5, 32.7, 27.0, 25.9, 22.3, 19.3, 18.1, 7.8, -4.0, -4.4.



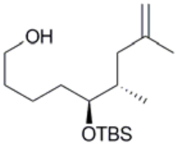
10

(4*S*,5*S*)-5-(*tert*-butyldimethylsilyloxy)-9-(*tert*-butyldiphenylsilyloxy)-2,4-dimethylnon-1-en-3-yl acetate (10). A dry flask backfilled with argon before magnesium turnings (372 mg, 14.7 mmol), a crystal of I_2 (~ 10 mg), and THF (5mL) were added. A solution of vinyl bromide (2.7 mL, 30.2 mmol) in THF (10 mL) was added slowly via cannula. The mixture was stirred vigorously and after 20 min the entirety of magnesium had dissolved. The solution was stirred for 1 h at rt before it was cooled to 0 °C and a solution of aldehyde **10** (1.79 g, 3.49 mmol) in THF (10 mL) was added via cannula. The reaction mixture was stirred for 1 h at rt, quenched with sat. NH_4Cl (20 mL), and extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were washed with sat. $NaHCO_3$ (25 mL), water (50 mL), and brine (50 mL), dried over Na_2SO_4 and concentrated via rotary evaporation. The resulting oil was dissolved in pyridine (50 mL) and acetic anhydride (5 mL) was added. After stirring for 1 h, the flask was placed on the rotary evaporator at low pressure and the volume was reduced to about 5 mL. The crude oil was diluted with 1:1 hexanes-EtOAc (100 mL) and washed with Cu_2SO_4 (100 mL), H_2O (100 mL), $NaHCO_3$ (100 mL), H_2O (100 mL), and brine (100 mL). The organic layer was dried over Na_2SO_4, concentrated to an oil, and purified by flash plug chromatography (1:1 hexanes-$CHCl_3$) to yield a diastereomeric mixture of allyl acetates **10** as a colorless oil (1.76 g, 89%): ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 7.69 (m, 4H), 7.41 (m, 6H), 5.28 (d, *J* = 6.4 Hz, 0.4H), 5.03-4.93 (m, 2.6H), 3.84 (m, 0.4H), 3.69 (m, 2.2H), 3.59 (m, 0.4H), 2.04 (2s, 3H), 1.93-1.84 (m, 0.4H), 1.84-1.73 (m, 0.4H), 1.69 (2s, 3H) 1.65-1.47 (m, 4.2H), 1.47-1.31 (m, 2H), 1.07 (2 s, 9H), 1.00-0.82 (3s, 10.8H), 0.74 (d, *J* = 6.8 Hz, 1.2H), 0.04 (4s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm 177.5, 170.2(2), 160.3, 142.5, 142.3, 135.7, 134.2, 129.7(2), 127.7, 115.7, 113.6, 112.3, 79.8, 77.8, 77.5, 73.0, 70.4, 64.3, 64.0, 63.9, 38.6, 38.2, 35.4, 34.3, 33.0, 32.8, 27.0, 26.1, 22.3, 22.0, 21.4, 21.3, 19.4(2), 18.9, 18.3(2), 17.6, 9.5, 8.6, -3.5, -3.6, -4.2, -4.9; MS (ESI) *m/z* 619.26 ($[M+Na]^+$, 100%); HRMS (FAB) *m/z* calcd for $C_{35}H_{57}O_4Si_2$ $(M+H)^+$ 597.3790, found 597.3788.



11

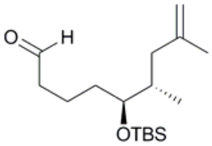
(*S*)-2,2,3,3,12,12-hexamethyl-5-((*S*)-4-methylpent-4-en-2-yl)-11,11-diphenyl-4,10-dioxa-3,11-disilatridecane (11). Dioxane (2.5mL) was added to a mixture of ammonium formate (2.77 g, 0.44) and $Pd(PPh_3)_4$ (167 mg, 0.15 mmol) in a dry flask under argon. PBu_3 (360 μL, 1.44 mmol) was added and the mixture heated at reflux. The evolution of gas was observed prior to reaching reflux temperature. A solution of allyl acetates **11** (1.73 g, 2.89 mmol) in dioxane (3.5 mL) was added via cannula to the heated reaction mixture. The reaction was stirred at reflux for 3 hours, cooled to rt, diluted with hexanes (150mL), washed with H_2O, sat. $NaHCO_3$, brine, and dried over Na_2SO_4. Purification by flash chromatography (20:1 to 1:1 hexanes-$CHCl_3$) yielded terminal olefin **11** (1.38 g, 88%) as a colorless oil. No internal olefin could be detected by NMR spectroscopy: ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 7.67 (m, 4H), 7.40 (m, 6H), 4.73 (s, 1H), 4.66 (s, 1H), 3.65 (t, *J* = 6.3 Hz, 2H), 3.52 (m, 1H), 2.19 (m, 1H), 1.76 (m, 2H), 1.68 (s, 3H), 1.55 (m, 2H), 1.36 (m, 4H), 1.04 (s, 9H), 0.89 (s, 9H), 0.76 (d, *J* = 6.4, 3H), 0.03 (2 s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm 145.1, 135.7, 134.3, 129.6, 127.7, 111.4, 75.9, 64.1, 40.9, 35.6, 33.3, 33.1, 27.0, 26.1, 26.1, 22.6, 22.4, 19.4, 18.3, 14.1, -4.0, -4.2; MS (ESI) *m/z* 407.07 ($[M\text{-}OTBS]^+$, 100%), 561.23 ($[M+Na]^+$, 15%), 538.78 ($[M+H]^+$, 10%); HRMS (FAB) *m/z* calcd for $C_{33}H_{54}O_2Si_2$ $(M)^+$ 538.3662, found 538.3665.



S3

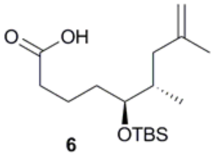
(5*S*,6*S*)-5-(*tert*-butyldimethylsilyloxy)-6,8-dimethylnon-8-en-1-ol (S3). Olefin **11** (1.25 g, 2.32 mmol) was placed in a round bottom flask fitted with a magnetic stir bar and reflux condenser. A solution of NaOH in MeOH (20 mL, 5 M) was added and the reaction stirred at reflux temperature for 10 h. At this point, TLC analysis (3:1 hexanes-EtOAc) indicated that starting material **11** (R_f 0.57) had been consumed and product **S3** (R_f 0.28) and silanol (R_f 0.46) had formed. After cooling to rt, CH_2Cl_2 was added and the resulting solution was washed with water, sat. $NaHCO_3$, and brine, and dried over Na_2SO_4. Purification by flash chromatography provided alcohol **S3** (669 mg, 96 %) as a colorless oil: ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 4.73 (s, 1H), 4.66 (s, 1H), 3.65 (t, *J* = 6.6 Hz, 2H), 3.54 (m, 1H), 2.18 (m, 1H), 1.76 (m, 2H), 1.68 (s, 3H), 1.57 (m, 2H), 1.49-1.21 (m, 6H), 0.89 (s, 9H), 0.77 (d, *J* = 6.4 Hz, 3H), 0.04 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ

ppm 144.9, 111.4, 75.7, 63.1, 40.9, 35.6, 33.2, 33.1, 26.0, 22.4, 22.3, 18.3, 14.0, -4.0, -4.2; MS (ESI) *m/z* 323.21 ($[M+Na]^+$, 100%); HRMS (FAB) *m/z* calcd for $C_{17}H_{37}O_2Si$ $(M+H)^+$ 301.2557, found 301.2561.



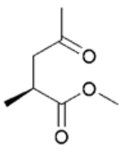
S4

(5*S*,6*S*)-5-(*tert*-butyldimethylsilyloxy)-6,8-dimethylnon-8-enal (S4). A dry flask was purged with argon before oxalyl chloride (51 μL, 0.59 mmol) and CH_2Cl_2 (1 mL) were added and the flask was cooled to -78 °C. A solution of DMSO (90 μL, 1.27 mmol) in CH_2Cl_2 (1 mL) was added dropwise over 5 min and the reaction was stirred for 10 min at -78 °C. A solution of alcohol **S3** (275 mg, 0.53 mmol) in CH_2Cl_2 (2 mL) was added dropwise to the cooled solution over 5 min, during which time a white precipitate formed. The reaction was stirred for 15 min at -78 °C before Et_3N (367 μL, 2.65 mmol) was added and the bath was removed. After stirring for 30 min and warming to rt, water (10 mL) was added the biphasic solution was stirred for 10 min. The layers were separated, the aqueous phase was extracted with CH_2Cl_2, and the combined organic layers were washed with 1% HCl, water, sat. $NaHCO_3$ and brine, and dried over Na_2SO_4. The volatile reaction components were removed at reduced pressure on the rotary evaporator to yield aldehyde **S4** (265 mg, 97%) as a colorless oil that was carried on to the next step without further purification: ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 9.77 (t, *J = 1*.6 Hz, 1H), 4.74 (s, 1H), 4.65 (s, 1H), 3.56 (m, 1H), 2.43 (td, *J = 7.3, 1.8* Hz, 2H), 2.20 (m, 1H), 1.76 (m, 2H), 1.68 (s, 3H), 1.58 (m, 2H), 1.43 (m, 2H), 0.90 (s, 9H), 0.78 (d, *J = 6.4* Hz, 3H), (0.05 (2s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm 202.6, 144.7, 111.5, 75.6, 44.2, 40.6, 35.7, 32.8, 29.8, 26.0, 22.4, 18.8, 14.2, -4.0, -4.1.



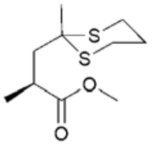
6

(5*S*,6*S*)-5-(*tert*-butyldimethylsilyloxy)-6,8-dimethylnon-8-enoic acid (6). A buffered oxidant solution was made by combining $NaClO_2$ (86 mg) and NaH_2PO_4 (57 mg) in water (2 mL) before adding *t*-BuOH (5 mL) and 2-methyl-2-butene (2 mL, 2 M in THF) and stirring vigorously for 10 min. The oxidant solution was transferred to a flask containing aldehyde **S3** (265 mg, 0.88 mmol) and the reaction was stirred vigorously for 1 h. Water (5 mL) was added and the resulting solution was extracted with EtOAc (3 x 15 mL). The combined organic layers were washed with brine, dried (Na_2SO_4), concentrated and purified by flash chromatography (4:1 hexanes-EtOAc; R_f 0.28) to give acid **6** (244 mg, 88 %) as a colorless oil: ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 4.74 (s, 1H), 4.66 (s, 1H), 3.55 (m, 1H), 2.36 (t, *J = 7.4* Hz, 2H), 2.20 (m, 1H), 1.77 (m, 2H), 1.68 (s, 3H), 1.60 (m, 2H), 1.46 (m, 2H), 0.89 (s, 9H), 0.78 (d, *J = 6.3* Hz, 3H), 0.04 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm 180.0, 144.8, 111.5, 75.5, 40.7, 35.7, 34.3, 32.7, 26.1, 22.4, 21.4, 18.3, 14.2, -4.1, -4.2; MS (ESI^-) *m/z* 313.11 ($[M-H]^-$, 100%), 676.06 ($[M_2-H]^-$, 15%; HRMS (FAB) *m/z* calcd for $C_{17}H_{35}O_3Si$ $(M+H)^+$ 315.2350, found 315.2360.

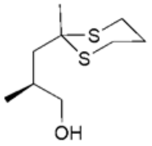


12

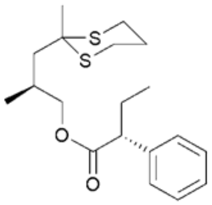
(*S*)-methyl 2-methyl-4-oxopentanoate (12). The γ-keto ester **12**, was prepared as described and all physical data was in agreement with that reported.[6] The stereochemical fidelity of this process was evaluated by making a derivative of alcohol **14** (see below).


13

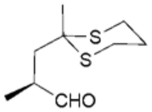
(*S*)-methyl 2-methyl-3-(2-methyl-1,3-dithian-2-yl)propanoate (13). A solution of ketone **12** (850 mg, 5.89 mmol) in CH_2Cl_2 (15 mL) and cooled to -10 °C, and 1,3-propanedithiol (710 μL, 7.07 mmol) and $BF_3 \cdot Et_2O$ (1.1 mL, 8.84 mmol) were added sequentially. The reaction was monitored by TLC (4:1 hexanes-Et_2O) and after stirring 3.5 h at -10 °C, ketone **12** (R_f 0.13) was no longer detectable and dithiane **13** (R_f 0.30) had formed. The reaction was quenched with $NaHCO_3$, the layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated to provide crude dithiane as a yellow oil, which contained a strong stench from the contaminating 1,3-propanedithiol. Purification by flash chromatography provided dithiane **13** (1.32 g, 96%) as an odor-free, colorless oil: ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 3.66 (s, 3H), 2.94 (m, 2H), 2.82 (dd, *J* = 14.5, 9.1 Hz, 1H), 2.69 (m, 3H), 2.00 (m, 1H), 1.86 (m, 1H), 1.78 (dd, *J* = 14.5, 2.5 Hz, 1H), 1.53 (s, 1H), 1.21 (d, *J* = 7.1 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm 177.5, 52.0, 48.3, 44.8, 36.6, 27.9, 27.0, 26.7, 24.9, 20.0; MS (ESI) *m/z* 202.97 ($[M\text{-}OMe]^+$, 100%), 256.98 ($[M+Na]^+$, 30%); HRMS (FAB) *m/z* calcd for $C_{10}H_{18}O_2S_2$ $(M)^+$ 234.0748, found 234.0746.


14

(*S*)-2-methyl-3-(2-methyl-1,3-dithian-2-yl)propan-1-ol (14). A solution of methyl ester **13** (1.25 g, 5.33 mmol) in THF (20 mL) was cooled to 0 °C and a partial suspension of $LiAlH_4$ (5.3 mL, 1 M in THF) was added dropwise over 15 min. The reaction was warmed to rt and stirred for 2 h before quenching with water (2 mL) and sat. Rochelle's salt (20 mL). The organic layer was separated and the aqueous was extracted with EtOAc (3 x 10 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated. Purification by flash chromatography (3:1 hexanes-EtOAc; R_f 0.14) provided alcohol **14** (1.08 g, 98%) as a colorless oil: ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 3.51 (m, 2H), 2.87 (m, 4H), 2.20 (dd, *J* = 14.7, 4.3 Hz, 1H), 1.96 (m, 3H), 1.70 (dd, *J* = 14.7, 5.6 Hz, 1H), 1.66 (s, 3H), 1.05 (d, *J* = 6.8 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm 68.6, 49.4, 45.0, 32.9, 28.4, 26.7, 26.6, 25.2, 19.4; MS (APCI) *m/z* 189.03 ($[M\text{-}OH]^+$, 100%); HRMS (FAB) *m/z* calcd for $C_9H_{18}OS_2$ $(M)^+$ 206.0794, found 206.0791.

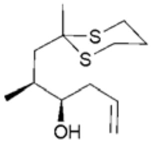

S5

(*R*)-((*S*)-2-methyl-3-(2-methyl-1,3-dithian-2-yl)propyl) 2-phenylbutanoate (S5). To a solution of **14** (40 mg, 0.19 mmol) and *R*-2-phenylbutyric acid (37 mg, 0.23 mmol) in CH_2Cl_2 (1 mL) was added EDC (55 mg, 0.29 mmol) and DMAP (12 mg, 0.10 mmol). The mixture was stirred for 24 h and then flushed through a plug of silica gel with 4:1 hexanes-Et_2O to yield ester **S5** (65 mg, 97 %) as a clear oil. A single diastereomer was confirmed by NMR. **S5**: ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 7.34-7.19 (m, 5H), 3.95 (d, *J* = 6.1 Hz, 2H), 3.46 (t, *J* = 7.7 Hz, 1H), 2.83-2.67 (m, 4H), 2.18-2.03 (m, 2H), 1.99 (dd, *J* = 14.7, 4.0 Hz, 1H), 1.90 (m, 2H), 1.80 (dt, *J* = 13.7, 7.4 Hz, 1H), 1.67 (dd, *J* = 14.7, 5.9 Hz, 1H), 1.57 (s, 3H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.89 (t, *J* = 7.4 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm 174.1, 139.2, 128.6, 128.0, 127.2, 69.8, 53.7, 49.0, 44.5, 29.8, 28.3, 26.7, 26.6, 25.1, 19.4, 12.3.


15

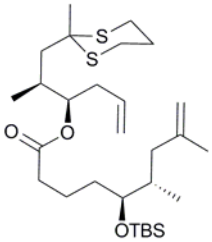
(*S*)-2-methyl-3-(2-methyl-1,3-dithian-2-yl)propanal (15). To a solution of alcohol **14** (200 mg, 0.97 mmol) and *N*-methylmorpholine *N*-oxide (175 mg, 1.5 mmol) in CH_2Cl_2 (2 mL) were added powdered 4 Å molecular sieves (500 mg) and TPAP (17 mg, 0.05 mmol). The reaction was followed closely by TLC (3:1

hexanes-EtOAc; **14**, R_f 0.15; **15**, R_f 0.35) and when complete the mixture was flushed through a plug of silica gel with CH_2Cl_2 to give aldehyde **15** (161 mg, 81%) as a colorless oil: ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 9.73 (d, *J* = 1.9 Hz, 1H), 2.95 (m, 1H), 2.85 (dd, *J* = 14.7, 7.7 Hz, 1H), 2.75 (m, 3H), 2.01 (m, 1H), 1.88 (m, 1H), 1.71 (dd, *J* = 14.7, 3.1 Hz, 1H), 1.57 (s, 3H), 1.16 (d, *J* = 7.3 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm 203.5, 48.5, 43.4, 42.7, 28.5, 26.7, 24.8, 16.4.



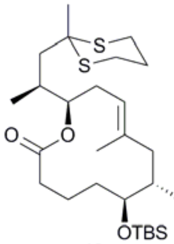
5

(2*S*,3*R*)-2-methyl-1-(2-methyl-1,3-dithian-2-yl)hex-5-en-3-ol (5). Compound **16** was prepared as described by Soderquist[7] by treating the pseudoephedrine salt precursor of the allylborane reagent with allylmagnesiumbromide. A solution of compound **16** (200 mg, 0.8 mmol) in Et_2O (8 mL) containing the magnesium alkoxide salts from pseudoephedrine was cooled to -78 °C and a solution of **15** (150 mg, 0.72 mmol) was added dropwise. The reaction was stirred for 3 h at -78 °C, warmed to rt, and the solvents were removed under vacuum. Dry pentane was added and the mixture was filtered through Celite under an inert atmosphere. The solvent was removed from the filtrate under vacuum and CH_3CN (1.2 mL) and (1*S*,2*S*)-pseudoephedrine (100 mg) were added. The mixture was heated to reflux, at which point all of the material dissolved. After stirring at reflux temperature for 2 h, the reaction was cooled to rt, diluted with pentane, filtered, and concentrated to give the crude homoallylic alcohol product. Purification by flash chromatography gave **5** (156 mg, 88%) as a clear oil: ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 5.85 (dddd, *J* = 16.7, 10.3, 8.1, 6.1 Hz, 1H), 5.16 (m, 2H), 3.46 (ddd, *J* = 8.9, 5.7, 3.0 Hz, 1H), 2.85 (m, 4H), 2.33 (m, 2H), 2.11 (m, 1H), 1.94 (m, 2H), 1.84 (m, 1H), 1.74 (br s, 1H), 1.64 (s, 3H), 1.07 (d, *J* = 6.9 Hz, 3H); 13C-NMR (100 MHz, $CDCl_3$) δ ppm 135.2, 118.3, 75.2, 49.6, 44.4, 38.4, 35.5, 28.5, 26.7, 26.6, 25.2, 18.7; ; MS (APCI$^-$) *m/z* 245.12 ($[M-H]^-$, 100%); HRMS (FAB) *m/z* calcd for $C_{12}H_{22}OS_2$ $(M)^+$ 246.1107, found 246.1110.



17

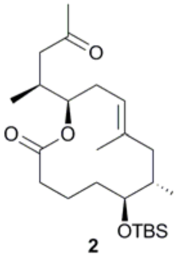
(5*S*,6*S*)-((2*S*,3*R*)-2-methyl-1-(2-methyl-1,3-dithian-2-yl)hex-5-en-3-yl) 5-(*tert*-butyldimethylsilyloxy)-6,8-dimethylnon-8-enoate (17). Alcohol **5** (20 mg, 0.081 mmol) and acid **6** (28 mg, 0.089 mmol) were dissolved in CH_2Cl_2 (0.8 mL) and cooled to 0 °C before DMAP (10 mg), CSA (17 mg), and DCC (27 mg) were added sequentially. The reaction was stirred overnight at rt and checked by TLC after 8 h (3:1 hexanes-EtOAc; **5**, R_f 0.31; **6**, R_f 0.19; **17**, R_f 0.58) to find that **5** had been consumed. The reaction was diluted with hexanes, filtered, and concentrated. Purification by flash chromatography (20:1 hexanes-EtOAc; R_f 0.18) gave **17** (42 mg, 95%) as a colorless oil: ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 5.75 (m, 1H), 5.06 (m, 2H), 4.87 (m, 1H), 4.72 (s, 1H), 4.64 (s, 1H), 3.54 (m, 1H), 2.84 (m, 4H), 2.27 (m, 4H), 2.20 (m, 1H), 1.99 (m, 4H), 1.74 (m, 3H), 1.67 (s, 6H), 1.56 (m, 2H), 1.39 (m, 2H), 1.07 (d, *J* = 6.9 Hz, 3H), 0.88 (s, 9H), 0.76 (d, *J* = 6.2 Hz, 3H), 0.04 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm 173.1, 144.7, 134.2, 117.59, 111.4, 77.2, 75.6, 49.5, 44.5, 40.7, 35.9, 35.6, 35.6, 35.1, 33.4, 33.3, 32.9, 32.8, 29.9, 28.7, 28.6, 27.0, 26.9, 26.2, 25.4, 25.3, 22.5, 22.0, 18.7, 18.4, 14.4, -3.9, -4.0; MS (ESI) *m/z* 565.24 ($[M+Na]^+$, 100%); HRMS (FAB) *m/z* calcd for $C_{29}H_{54}O_3S_2Si$ $(M+H)^+$ 542.3284, found 542.3277.


18

(6*S*,7*S*,12*R*,*E*)-6-(*tert*-butyldimethylsilyloxy)-7,9-dimethyl-12-((S)-1-(2-methyl-1,3-dithian-2-yl)propan-2-yl)oxacyclododec-9-en-2-one (18). The Grubbs 2nd generation catalyst[8] (3 mg, 0.003 mmol) was placed in a dry flask under argon and CH_2Cl_2 (6 mL) was added. The flask was fitted with a condenser and heated at reflux. A solution of diene **17** (35 mg, 0.064 mmol) in CH_2Cl_2 (3 mL) was added through the condenser via syringe. After 24 h of reaction, TLC analysis (100:1 toluene-Et_2O) indicated the starting material had been consumed and the reaction mixture contained benzylidene adduct **S6** (R_f 0.44), desired product **18** (R_f 0.32), and dimer of **17** (**S7**, R_f 0.12). The reaction mixture was flushed through a plug of silica gel with CH_2Cl_2 and concentrated to give a colorless oil that was purified by flash chromatography. Lactone **18** (19 mg, 60%), benzylidene adduct **S6** (3 mg), and dimer **S7** (7 mg) were each obtained as colorless oils (reaction not optimized). **18**: ^{1}H-NMR (500 MHz, $CDCl_3$) δ ppm 5.01 (br d, *J* = 10.7 Hz, 1H), 4.91 (ddd, *J* = 11.7, 5.1, 3.0 Hz, 1H), 3.37 (m, 1H), 2.84 (m, 4H), 2.46 (m, 2H), 2.03 (m, 3H), 1.97 (m, 3H), 1.84 (m, 2H), 1.75 (dd, *J* = 15.3, 7.1 Hz, 1H), 1.68 (s, 3H), 1.67 (s, 3H), 1.66 (m, 3H),1.42 (m, 2H), 1.10 (d, *J* = 6.8 Hz, 3H), 0.96 (d, *J* = 6.8 Hz, 3H), 0.88 (s, 9H), 0.04 (s, 6H); 13C-NMR (75 MHz, *Solvent*) δ ppm 173.8, 137.6, 121.3, 77.5, 76.2, 49.4, 45.4, 44.6, 36.1, 34.3, 33.5, 33.5, 30.3, 28.5, 26.9, 26.7, 26.0, 25.3, 21.8, 18.7, 18.5, 18.2, 15.9, -4.0, -4.5; MS (ESI) *m/z* 515.15 ($[M+H]^+$, 100%), 531.88 ($[M+NH_4]^+$, 93%), 537.17 ($[M+Na]^+$, 48%); HRMS (EI) *m/z* calcd for $C_{27}H_{50}O_3S_2Si$ $(M)^+$ 514.2970, found 514.2958.

S6: ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 7.26 (m, 5H), 6.44 (2 s, 1H), 6.13 (td, *J* = 15.7, 7.2 Hz, 1H), 4.93 (dt, *J* = 8.0, 3.9 Hz, 1H), 4.72 (s, 1H), 4.63 (s, 1H), 3.50 (m, 1H), 2.83 (m, 4H), 2.46 (m, 2H), 2.29 (m, 4H), 2.17 (m, 1H), 2.08 (m, 2H), 1.95 (m, 3H), 1.75 (m, 2H), 1.69 (s, 3H), 1.66 (s, 3H), 1.39 (m, 2H), 1.11 (d, *J* = 6.9 Hz, 3H), 0.88 (s, 9H), 0.73 (d, *J* = 6.2 Hz, 3H), 0.02 (d, *J* = 2.1 Hz, 6H); MS (ESI) *m/z* 641.12 ($[M+Na]^+$, 100%), 635.98 ($[M+NH_4]^+$, 82%); HRMS (EI) *m/z* calcd for $C_{35}H_{58}O_3S_2Si$ $(M)^+$ 618.3597, found 618.3587.

S7: ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 5.43 (m, 2H), 4.77 (m, 2H), 4.73 (s, 2H), 4.64 (s, 2H), 3.55 (m, 2H), 2.84 (m, 8H), 2.27 (m, 10H), 1.95 (m, 8H), 1.74 (m, 6H), 1.67 (s, 6H), 1.66 (s, 6H), 1.57 (m, 4H), 1.40 (m, 4H), 1.05 (d, 6H), 0.89 (s, 18H), 0.76 (d, 6H), 0.04 (s, 12H); MS (ESI) *m/z* 1079.44 ($[M+Na]^+$, 100%), 1074.21 ($[M+NH_4]^+$, 32%).


2

(6*S*,7*S*,12*R*,*E*)-6-(*tert*-butyldimethylsilyloxy)-7,9-dimethyl-12-((S)-4-oxopentan-2-yl)oxacyclododec-9-en-2-one (2). A solution of dithiane **18** (10 mg, 0.019 mmol) in 4:1 CH_3CN-H_2O (650 μL) was added to a stirred solution of $AgNO_3$ (16 mg, 0.095 mmol) and NCS (13 mg, 0.095 mmol) in 4:1 CH_3CN-H_2O (500 μL) which resulted in the formation of white precipitate. The mixture was stirred for 10 min at rt, diluted with Et_2O (5 mL) and pH 7 NaH_2PO_4 buffer (5 mL), and cooled to 0 °C. Sodium bisulfite (18 mg, 0.57 mmol) was added and the reaction stirred for 10 min at 0 °C before filtering through a pad of Celite. The filtrate was extracted with Et_2O and the combined organic layers were washed with water and brine, dried (Na_2SO_4), and concentrated. Purification by flash chromatography (5:1 hexanes-EtOAc, R_f 0.29) afforded ketone **2** (6.5 mg, 81%) as a clear oil that crystallized upon evaporation of hexanes: ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 4.98 (d, *J* = 10.3 Hz, 1H), 4.83 (ddd, *J* = 11.6, 6.5, 3.1 Hz, 1H), 3.35 (m, 1H), 2.49 (m, 2H), 2.36 (td, *J* = 14.0, 11.5 Hz, 1H), 2.27 (m, 2H), 2.14 (s, 3H), 2.09 (m, 1H), 1.95 (td, *J* = 12.2, 3.7, 1H), 1.84 (m, 2H), 1.71 (m, 3H), 1.65 (s, 3H), 1.39 (m, 2H), 0.95 (d, *J* = 6.7 Hz, 3H), 0.94 (d, *J* = 6.2 Hz, 3H), 0.88 (s, 9H), 0.03 (s, 6H); ^{13}C-NMR (100 MHz,

$CDCl_3$) δ ppm 208.0, 173.8, 137.9, 121.0, 77.4, 75.4, 47.1, 45.4, 36.0, 33.9, 33.6, 33.5, 31.6, 30.6, 26.1, 21.8, 18.8, 18.3, 16.7, 15.9, -4.0, -4.6; ; MS (ESI) *m/z* 442.02 ($[M+NH_4]^+$, 100%), 425.02 ($[M+H]^+$, 86%), 425.02 ($[M+Na]^+$, 17%); HRMS (FAB) *m/z* calcd for $C_{24}H_{45}O_4Si$ $(M+H)^+$ 425.3082, found 425.3074.

X-Ray Crystallography

A colorless needle 0.20 × 0.07 × 0.07 mm in size was mounted on a cryoloop with Paratone® oil. Data was collected in a nitrogen gas stream at -173^{o}C. Crystal-to-detector distance was 60 mm and exposure time was 40 seconds per frame using a scan width of 0.5°. Data collection was 99.8% complete to 25^{o} in θ. A total of 4,449 reflections were collected covering the indices, h = -14 to 14, k = -19 to 28, l = -18 to 19. All 4,449 reflections were found to be symmetry independent, with an R_{int} of 0.0523 indicating that the data set was of better than average quality (average = 0.07). Indexing and unit cell refinement indicated a primitive, orthorhombic lattice. The space group was found to be $P2_12_12_1$ (No. 19). The data was integrated using the Bruker SAINT software program and scaled using the Bruker SADABS software program. Solution by direct methods (SIR-2004) produced a complete heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-97). All hydrogen atoms were placed using a riding model and their positions constrained relative to their parent atom using the appropriate HFIX command in SHELXL-97.

Table 1. Crystal data and structure refinement for burk02 (**2**).

Identification code	burk02	
Empirical formula	C24 H44 O4 Si	
Formula weight	424.68	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 7.6150(9) Å	α= 90°.
	b = 13.9000(17) Å	β= 90°.
	c = 23.912(3) Å	γ = 90°.
Volume	2531.0(5) Å^3	
Z	4	
Density (calculated)	1.114 Mg/m^3	
Absorption coefficient	0.117 mm^{-1}	
F(000)	936	
Crystal size	0.20 x 0.07 x 0.07 mm^3	
Theta range for data collection	2.25 to 25.03°.	
Index ranges	-9<=h<=9, 0<=k<=16, 0<=l<=28	
Reflections collected	4449	
Independent reflections	4449 [R(int) = 0.0523]	
Completeness to theta = 25.00°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9918 and 0.9769	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4449 / 0 / 271	
Goodness-of-fit on F^2	1.230	
Final R indices [I>2sigma(I)]	R1 = 0.0604, wR2 = 0.1021	
R indices (all data)	R1 = 0.0658, wR2 = 0.1037	
Absolute structure parameter	0.05(18)	
Largest diff. peak and hole	0.311 and -0.247 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for burk02 (**2**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	5605(4)	10826(2)	7074(1)	16(1)
C(2)	6119(4)	10547(2)	6488(1)	20(1)
C(3)	4725(4)	10888(2)	6067(1)	19(1)
C(4)	2930(4)	10485(2)	6205(1)	17(1)
C(5)	1484(4)	10735(2)	5794(1)	17(1)
C(6)	1022(4)	11803(2)	5752(1)	19(1)
C(7)	501(4)	12227(2)	6326(1)	19(1)
C(8)	1942(4)	12715(2)	6658(1)	15(1)
C(9)	2332(4)	12462(2)	7178(1)	17(1)
C(10)	3728(4)	12894(2)	7540(1)	18(1)
C(11)	5192(4)	12187(2)	7678(1)	15(1)
C(12)	-437(5)	11971(2)	5325(1)	29(1)
C(13)	2825(5)	13531(2)	6354(1)	26(1)
C(14)	6782(4)	12617(2)	7982(1)	16(1)
C(15)	7763(4)	13335(2)	7610(1)	17(1)
C(16)	9248(4)	13887(2)	7871(1)	20(1)
C(17)	10011(5)	14660(2)	7507(2)	29(1)
C(18)	7967(4)	11808(2)	8191(1)	26(1)
C(19)	2159(6)	8330(3)	5408(2)	46(1)
C(20)	-1004(4)	9306(3)	4904(2)	45(1)
C(21)	2542(4)	9333(2)	4275(1)	23(1)
C(22)	4500(5)	9544(3)	4346(2)	36(1)
C(23)	2330(5)	8344(3)	4001(1)	33(1)
C(24)	1735(6)	10099(3)	3892(2)	43(1)
O(1)	5064(3)	10276(2)	7422(1)	28(1)
O(2)	5820(3)	11774(1)	7154(1)	15(1)
O(3)	9793(3)	13752(2)	8336(1)	27(1)
O(4)	1993(3)	10404(1)	5246(1)	18(1)
Si(1)	1433(1)	9359(1)	4973(1)	22(1)

Table 3. Bond lengths [Å] and angles [°] for burk02 (**2**).

C(1)-O(1)	1.204(4)	C(14)-C(18)	1.525(4)
C(1)-O(2)	1.341(3)	C(14)-C(15)	1.533(4)
C(1)-C(2)	1.504(4)	C(14)-H(14)	1.0000
C(2)-C(3)	1.538(4)	C(15)-C(16)	1.503(4)
C(2)-H(2A)	0.9900	C(15)-H(15A)	0.9900
C(2)-H(2B)	0.9900	C(15)-H(15B)	0.9900
C(3)-C(4)	1.513(4)	C(16)-O(3)	1.202(4)
C(3)-H(3A)	0.9900	C(16)-C(17)	1.499(4)
C(3)-H(3B)	0.9900	C(17)-H(17A)	0.9800
C(4)-C(5)	1.516(4)	C(17)-H(17B)	0.9800
C(4)-H(4A)	0.9900	C(17)-H(17C)	0.9800
C(4)-H(4B)	0.9900	C(18)-H(18A)	0.9800
C(5)-O(4)	1.441(3)	C(18)-H(18B)	0.9800
C(5)-C(6)	1.528(4)	C(18)-H(18C)	0.9800
C(5)-H(5)	1.0000	C(19)-Si(1)	1.852(4)
C(6)-C(12)	1.527(4)	C(19)-H(19A)	0.9800
C(6)-C(7)	1.547(4)	C(19)-H(19B)	0.9800
C(6)-H(6)	1.0000	C(19)-H(19C)	0.9800
C(7)-C(8)	1.514(4)	C(20)-Si(1)	1.864(4)
C(7)-H(7A)	0.9900	C(20)-H(20A)	0.9800
C(7)-H(7B)	0.9900	C(20)-H(20B)	0.9800
C(8)-C(9)	1.326(4)	C(20)-H(20C)	0.9800
C(8)-C(13)	1.507(4)	C(21)-C(22)	1.529(5)
C(9)-C(10)	1.496(4)	C(21)-C(23)	1.531(5)
C(9)-H(9)	0.9500	C(21)-C(24)	1.534(5)
C(10)-C(11)	1.522(4)	C(21)-Si(1)	1.871(3)
C(10)-H(10A)	0.9900	C(22)-H(22A)	0.9800
C(10)-H(10B)	0.9900	C(22)-H(22B)	0.9800
C(11)-O(2)	1.459(3)	C(22)-H(22C)	0.9800
C(11)-C(14)	1.534(4)	C(23)-H(23A)	0.9800
C(11)-H(11)	1.0000	C(23)-H(23B)	0.9800
C(12)-H(12A)	0.9800	C(23)-H(23C)	0.9800
C(12)-H(12B)	0.9800	C(24)-H(24A)	0.9800
C(12)-H(12C)	0.9800	C(24)-H(24B)	0.9800
C(13)-H(13A)	0.9800	C(24)-H(24C)	0.9800
C(13)-H(13B)	0.9800	O(4)-Si(1)	1.648(2)
C(13)-H(13C)	0.9800		

O(1)-C(1)-O(2)	124.5(3)	C(3)-C(4)-H(4A)	108.4
O(1)-C(1)-C(2)	124.7(3)	C(5)-C(4)-H(4A)	108.4
O(2)-C(1)-C(2)	110.8(3)	C(3)-C(4)-H(4B)	108.4
C(1)-C(2)-C(3)	110.5(2)	C(5)-C(4)-H(4B)	108.4
C(1)-C(2)-H(2A)	109.6	H(4A)-C(4)-H(4B)	107.5
C(3)-C(2)-H(2A)	109.6	O(4)-C(5)-C(4)	108.6(2)
C(1)-C(2)-H(2B)	109.6	O(4)-C(5)-C(6)	108.3(2)
C(3)-C(2)-H(2B)	109.6	C(4)-C(5)-C(6)	115.6(2)
H(2A)-C(2)-H(2B)	108.1	O(4)-C(5)-H(5)	108.0
C(4)-C(3)-C(2)	111.5(2)	C(4)-C(5)-H(5)	108.0
C(4)-C(3)-H(3A)	109.3	C(6)-C(5)-H(5)	108.0
C(2)-C(3)-H(3A)	109.3	C(12)-C(6)-C(5)	111.1(2)
C(4)-C(3)-H(3B)	109.3	C(12)-C(6)-C(7)	110.4(2)
C(2)-C(3)-H(3B)	109.3	C(5)-C(6)-C(7)	111.8(2)
H(3A)-C(3)-H(3B)	108.0	C(12)-C(6)-H(6)	107.8
C(3)-C(4)-C(5)	115.5(2)	C(5)-C(6)-H(6)	107.8

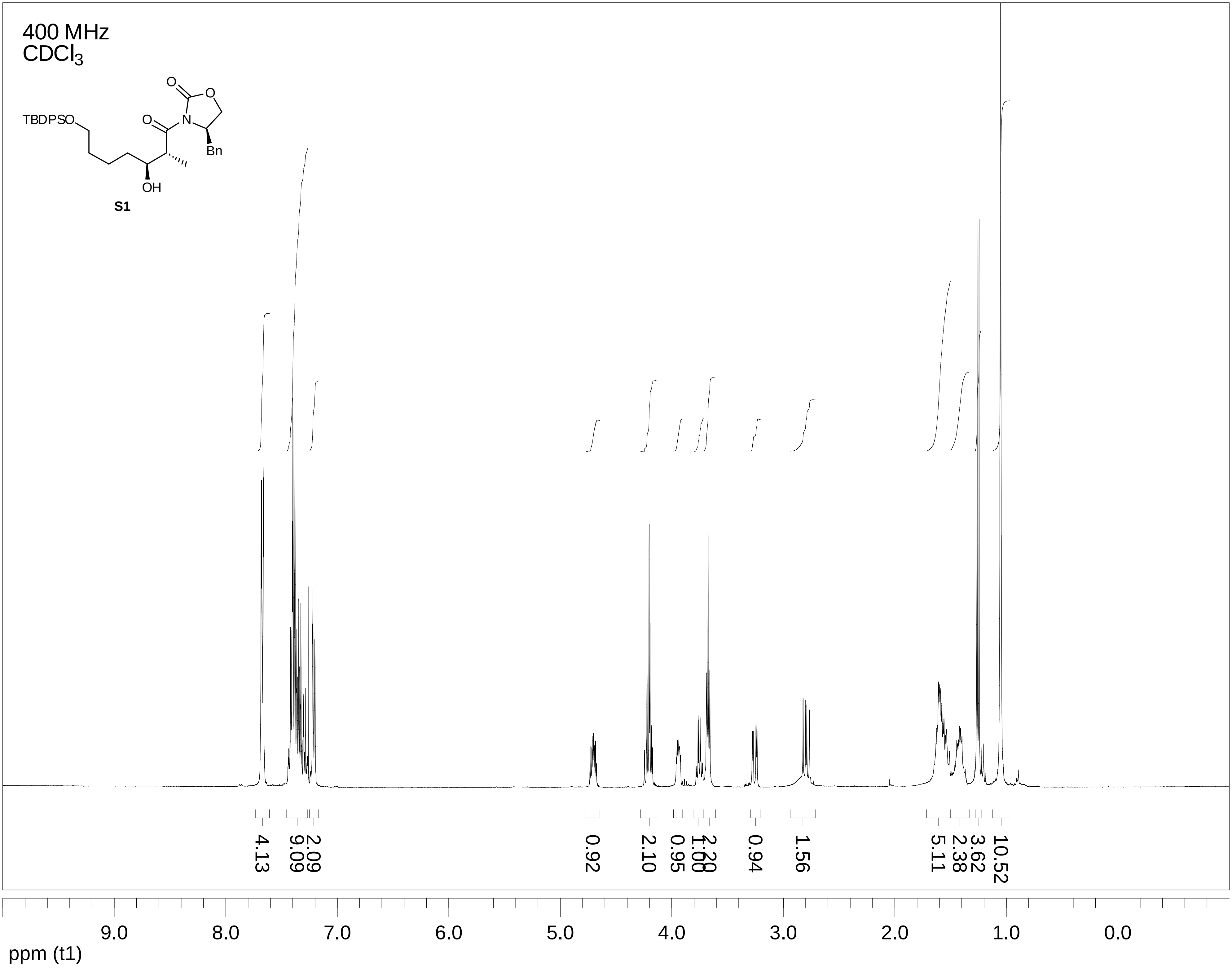
C(7)-C(6)-H(6)	107.8
C(8)-C(7)-C(6)	116.8(3)
C(8)-C(7)-H(7A)	108.1
C(6)-C(7)-H(7A)	108.1
C(8)-C(7)-H(7B)	108.1
C(6)-C(7)-H(7B)	108.1
H(7A)-C(7)-H(7B)	107.3
C(9)-C(8)-C(13)	123.5(3)
C(9)-C(8)-C(7)	122.4(3)
C(13)-C(8)-C(7)	114.1(3)
C(8)-C(9)-C(10)	126.5(3)
C(8)-C(9)-H(9)	116.7
C(10)-C(9)-H(9)	116.7
C(9)-C(10)-C(11)	112.7(2)
C(9)-C(10)-H(10A)	109.1
C(11)-C(10)-H(10A)	109.1
C(9)-C(10)-H(10B)	109.1
C(11)-C(10)-H(10B)	109.1
H(10A)-C(10)-H(10B)	107.8
O(2)-C(11)-C(10)	108.0(2)
O(2)-C(11)-C(14)	107.6(2)
C(10)-C(11)-C(14)	115.4(2)
O(2)-C(11)-H(11)	108.5
C(10)-C(11)-H(11)	108.5
C(14)-C(11)-H(11)	108.5
C(6)-C(12)-H(12A)	109.5
C(6)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(6)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(8)-C(13)-H(13A)	109.5
C(8)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(8)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(18)-C(14)-C(15)	112.4(2)
C(18)-C(14)-C(11)	109.6(2)
C(15)-C(14)-C(11)	111.2(2)
C(18)-C(14)-H(14)	107.8
C(15)-C(14)-H(14)	107.8
C(11)-C(14)-H(14)	107.8
C(16)-C(15)-C(14)	117.2(3)
C(16)-C(15)-H(15A)	108.0
C(14)-C(15)-H(15A)	108.0
C(16)-C(15)-H(15B)	108.0
C(14)-C(15)-H(15B)	108.0
H(15A)-C(15)-H(15B)	107.2
O(3)-C(16)-C(17)	121.0(3)
O(3)-C(16)-C(15)	124.4(3)
C(17)-C(16)-C(15)	114.6(3)
C(16)-C(17)-H(17A)	109.5
C(16)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(16)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(14)-C(18)-H(18A)	109.5
C(14)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(14)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
Si(1)-C(19)-H(19A)	109.5
Si(1)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
Si(1)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
Si(1)-C(20)-H(20A)	109.5
Si(1)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
Si(1)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(22)-C(21)-C(23)	108.8(3)
C(22)-C(21)-C(24)	108.9(3)
C(23)-C(21)-C(24)	109.0(3)
C(22)-C(21)-Si(1)	109.8(2)
C(23)-C(21)-Si(1)	110.6(2)
C(24)-C(21)-Si(1)	109.8(2)
C(21)-C(22)-H(22A)	109.5
C(21)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(21)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
C(21)-C(23)-H(23A)	109.5
C(21)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(21)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(21)-C(24)-H(24A)	109.5
C(21)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(21)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(1)-O(2)-C(11)	118.0(2)
C(5)-O(4)-Si(1)	124.88(19)
O(4)-Si(1)-C(19)	112.41(15)
O(4)-Si(1)-C(20)	109.16(15)
C(19)-Si(1)-C(20)	108.5(2)
O(4)-Si(1)-C(21)	104.68(13)
C(19)-Si(1)-C(21)	110.49(17)
C(20)-Si(1)-C(21)	111.64(17

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3)for burk02 (**2**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	9(2)	12(2)	26(2)	-4(1)	-5(1)	2(1)
C(2)	17(2)	16(2)	27(2)	-7(1)	-2(1)	0(1)
C(3)	16(2)	19(2)	21(2)	-2(1)	0(1)	0(1)
C(4)	19(2)	13(2)	18(2)	1(1)	-3(1)	1(1)
C(5)	16(2)	18(2)	17(2)	-3(1)	0(1)	-1(1)
C(6)	17(2)	18(2)	22(2)	0(1)	-1(1)	0(1)
C(7)	13(2)	20(2)	23(2)	-1(1)	-2(1)	2(1)
C(8)	11(2)	10(2)	25(2)	-3(1)	5(1)	5(1)
C(9)	13(2)	13(2)	25(2)	-3(1)	1(1)	-3(1)
C(10)	16(2)	13(2)	25(2)	-6(1)	0(1)	1(1)
C(11)	18(2)	14(2)	14(1)	-3(1)	0(1)	1(1)
C(12)	35(2)	27(2)	26(2)	-5(2)	-8(2)	8(2)
C(13)	28(2)	21(2)	29(2)	3(2)	-1(2)	1(2)
C(14)	15(2)	16(2)	17(2)	-1(1)	-1(1)	0(1)
C(15)	17(2)	14(2)	21(2)	-1(1)	-3(1)	1(1)
C(16)	18(2)	15(2)	27(2)	-3(1)	2(1)	6(1)
C(17)	24(2)	20(2)	42(2)	2(2)	-1(2)	-4(2)
C(18)	27(2)	19(2)	32(2)	2(2)	-5(2)	4(2)
C(19)	86(3)	26(2)	25(2)	1(2)	-3(2)	1(2)
C(20)	28(2)	46(2)	61(3)	-26(2)	9(2)	-14(2)
C(21)	22(2)	25(2)	24(2)	-5(2)	-2(1)	7(2)
C(22)	33(2)	39(2)	36(2)	-18(2)	12(2)	-5(2)
C(23)	28(2)	42(2)	28(2)	-15(2)	-6(2)	5(2)
C(24)	57(3)	44(2)	27(2)	8(2)	3(2)	17(2)
O(1)	44(2)	14(1)	27(1)	1(1)	2(1)	-2(1)
O(2)	18(1)	10(1)	17(1)	-4(1)	2(1)	-1(1)
O(3)	23(1)	32(1)	26(1)	-3(1)	-4(1)	-5(1)
O(4)	19(1)	20(1)	15(1)	-4(1)	2(1)	0(1)
Si(1)	24(1)	19(1)	22(1)	-5(1)	1(1)	-1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for burk02 (**2**).

	x	y	z	U(eq)
H(2A)	6243	9839	6465	24
H(2B)	7267	10839	6395	24
H(3A)	4671	11600	6071	22
H(3B)	5068	10682	5686	22
H(4A)	2582	10720	6579	20
H(4B)	3024	9775	6227	20
H(5)	401	10378	5907	21
H(6)	2091	12153	5619	23
H(7A)	-452	12701	6266	23
H(7B)	12	11701	6558	23
H(9)	1659	11956	7337	20
H(10A)	3188	13122	7892	22
H(10B)	4236	13459	7347	22
H(11)	4693	11659	7913	18
H(12A)	-105	11680	4967	44
H(12B)	-613	12664	5274	44
H(12C)	-1528	11678	5459	44
H(13A)	3163	14030	6623	39
H(13B)	2012	13804	6078	39
H(13C)	3875	13291	6162	39
H(14)	6337	12975	8316	19
H(15A)	8235	12979	7284	20
H(15B)	6898	13805	7465	20
H(17A)	9201	15207	7492	43
H(17B)	10192	14407	7129	43
H(17C)	11138	14870	7662	43
H(18A)	8415	11442	7871	39
H(18B)	7294	11380	8436	39
H(18C)	8955	12083	8400	39
H(19A)	3440	8346	5447	68
H(19B)	1808	7726	5227	68
H(19C)	1614	8372	5778	68
H(20A)	-1536	9250	5275	67
H(20B)	-1330	8746	4677	67
H(20C)	-1426	9893	4721	67
H(22A)	5033	9051	4585	54
H(22B)	4651	10178	4519	54
H(22C)	5072	9539	3979	54
H(23A)	2856	8355	3627	49
H(23B)	1079	8188	3971	49
H(23C)	2920	7857	4230	49
H(24A)	2317	10080	3526	64
H(24B)	1893	10736	4059	64
H(24C)	479	9970	3844	64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O
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Bn
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2.10
0.95
1.00
2.20
0.94
1.56
5.11
2.38
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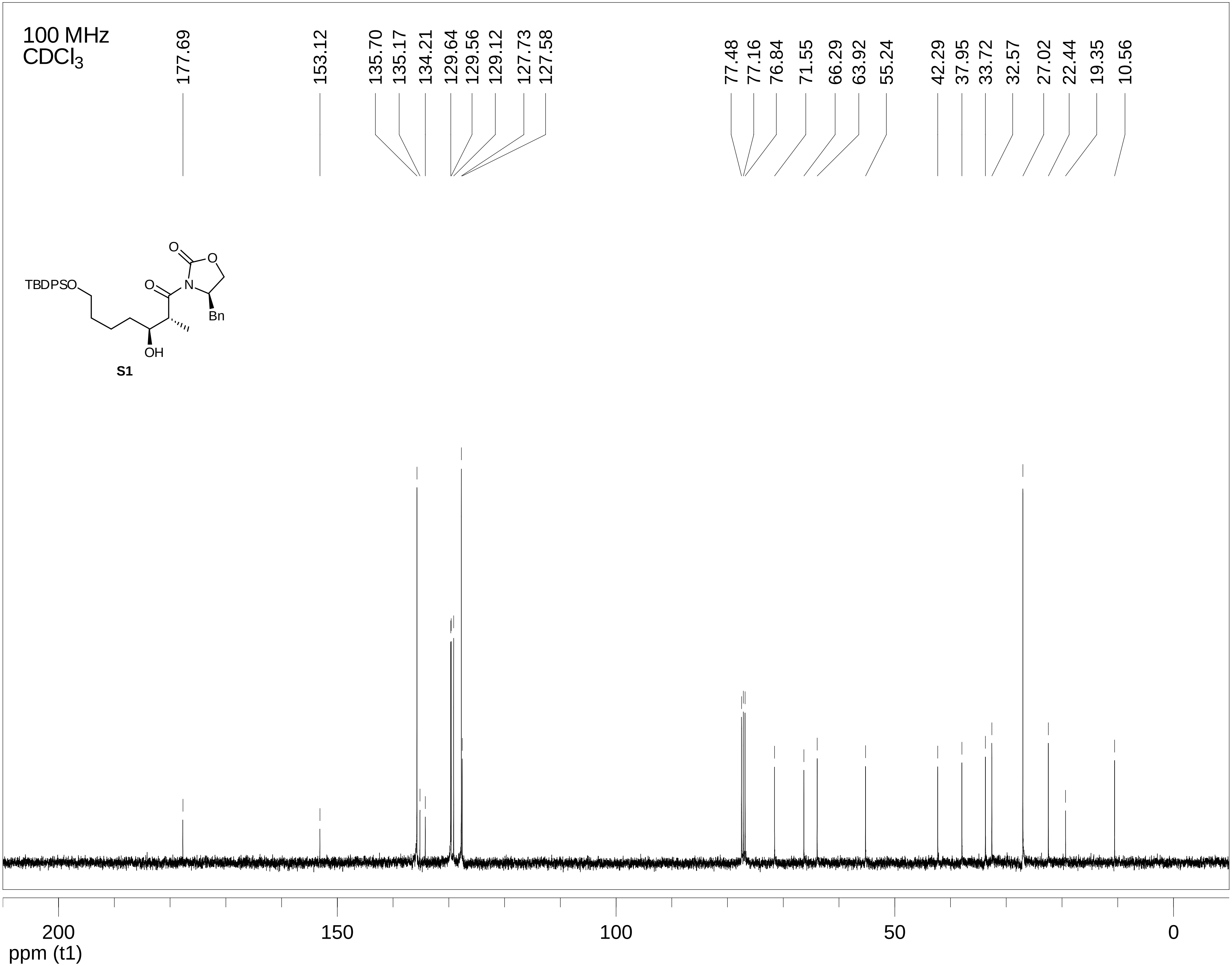
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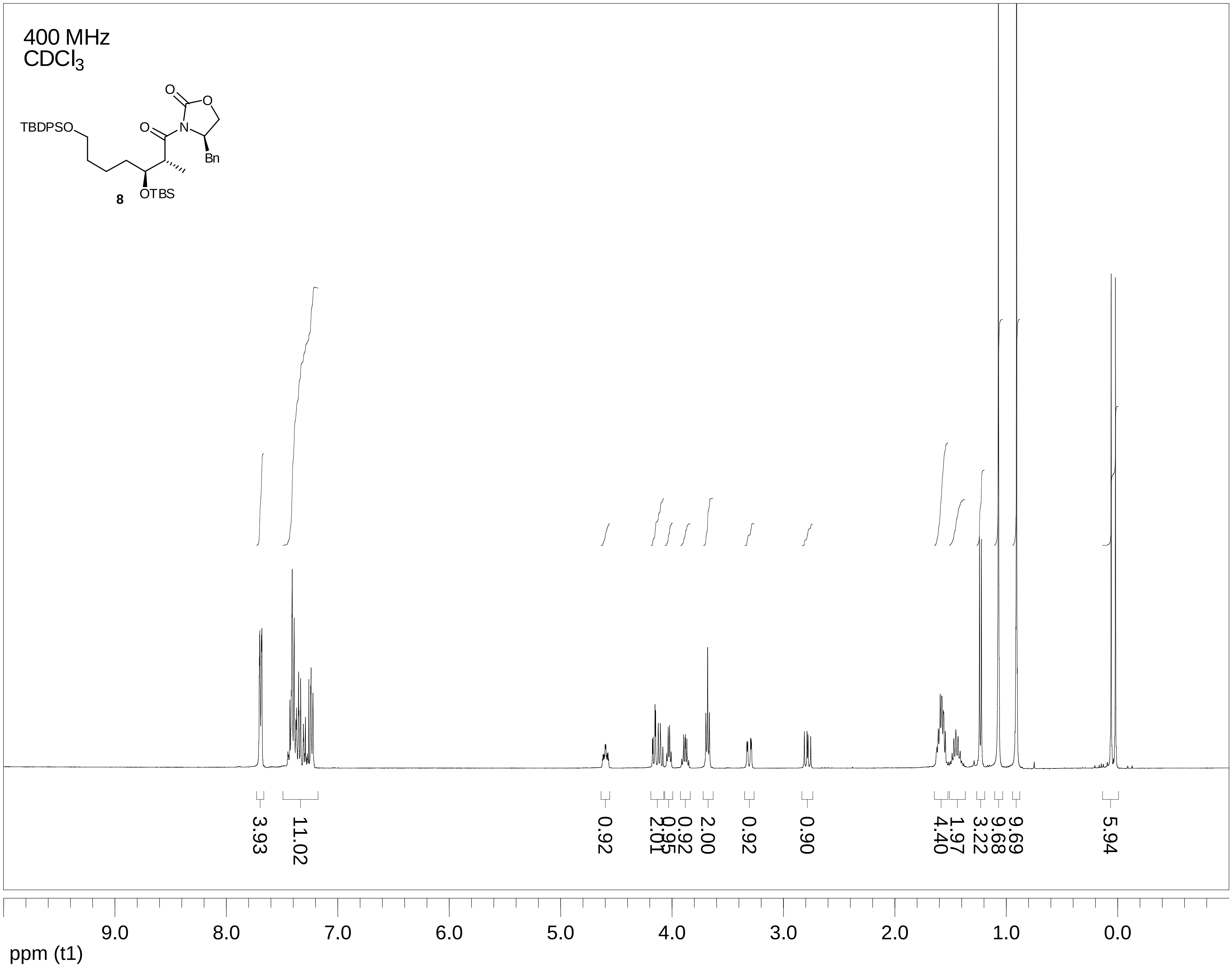
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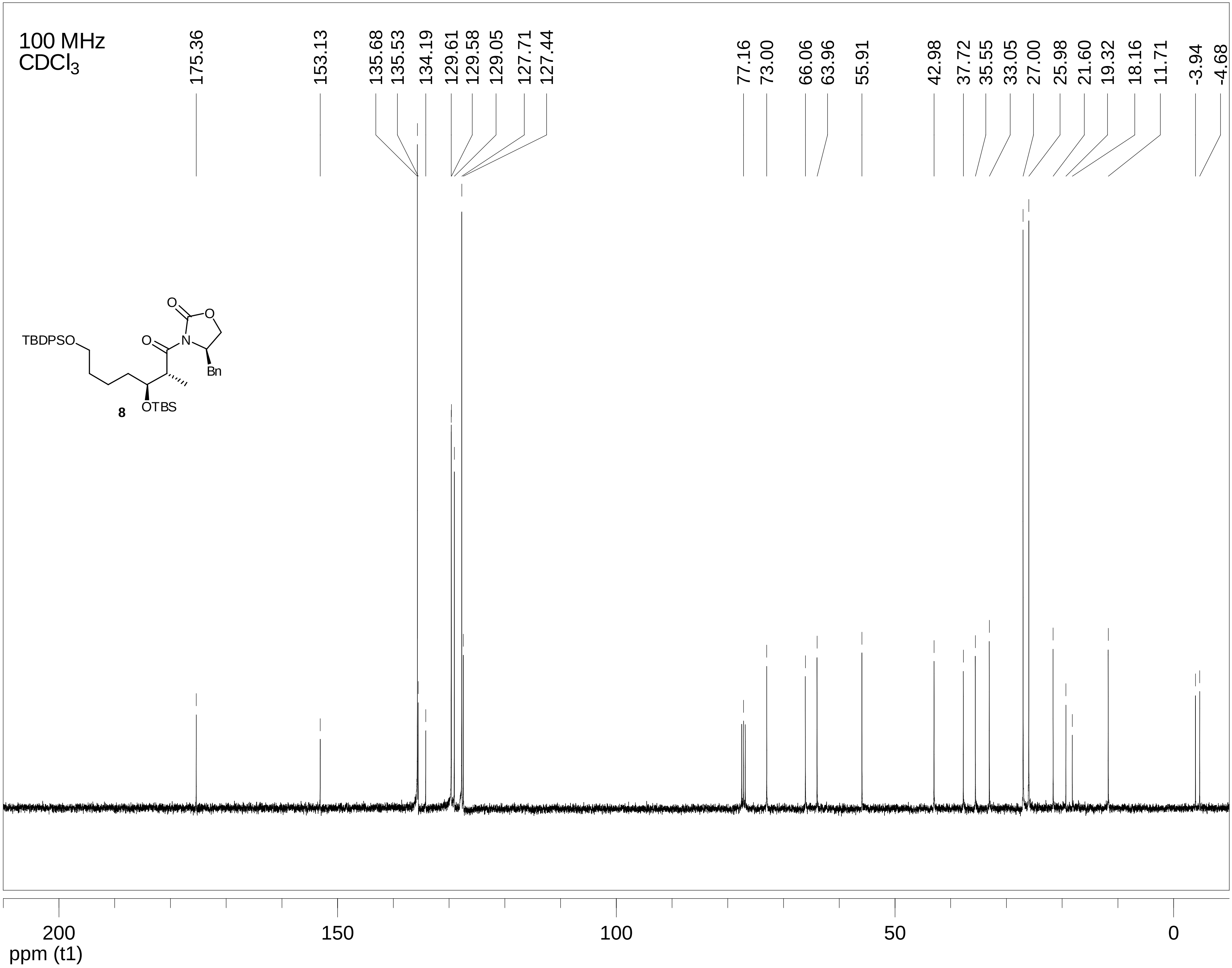
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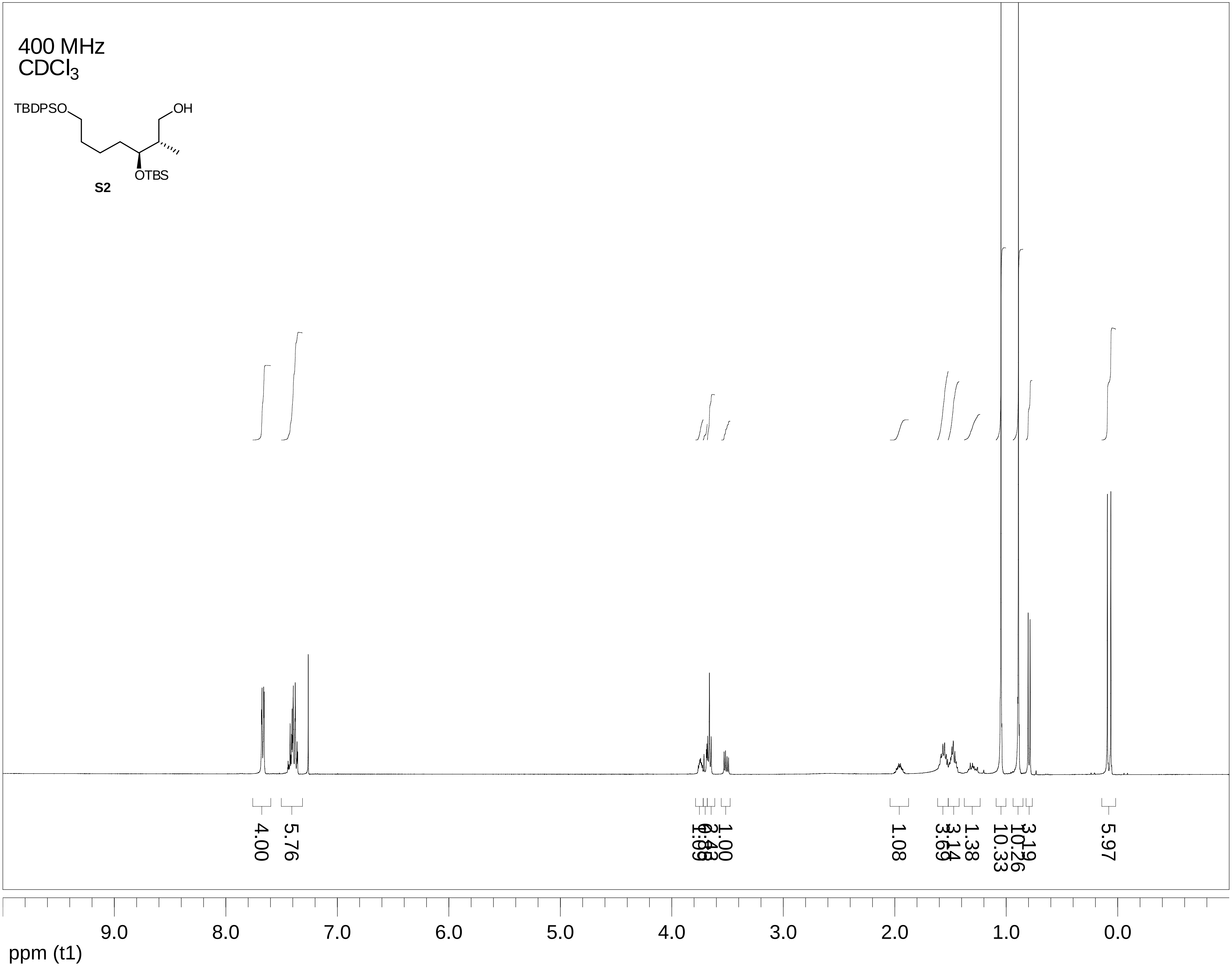
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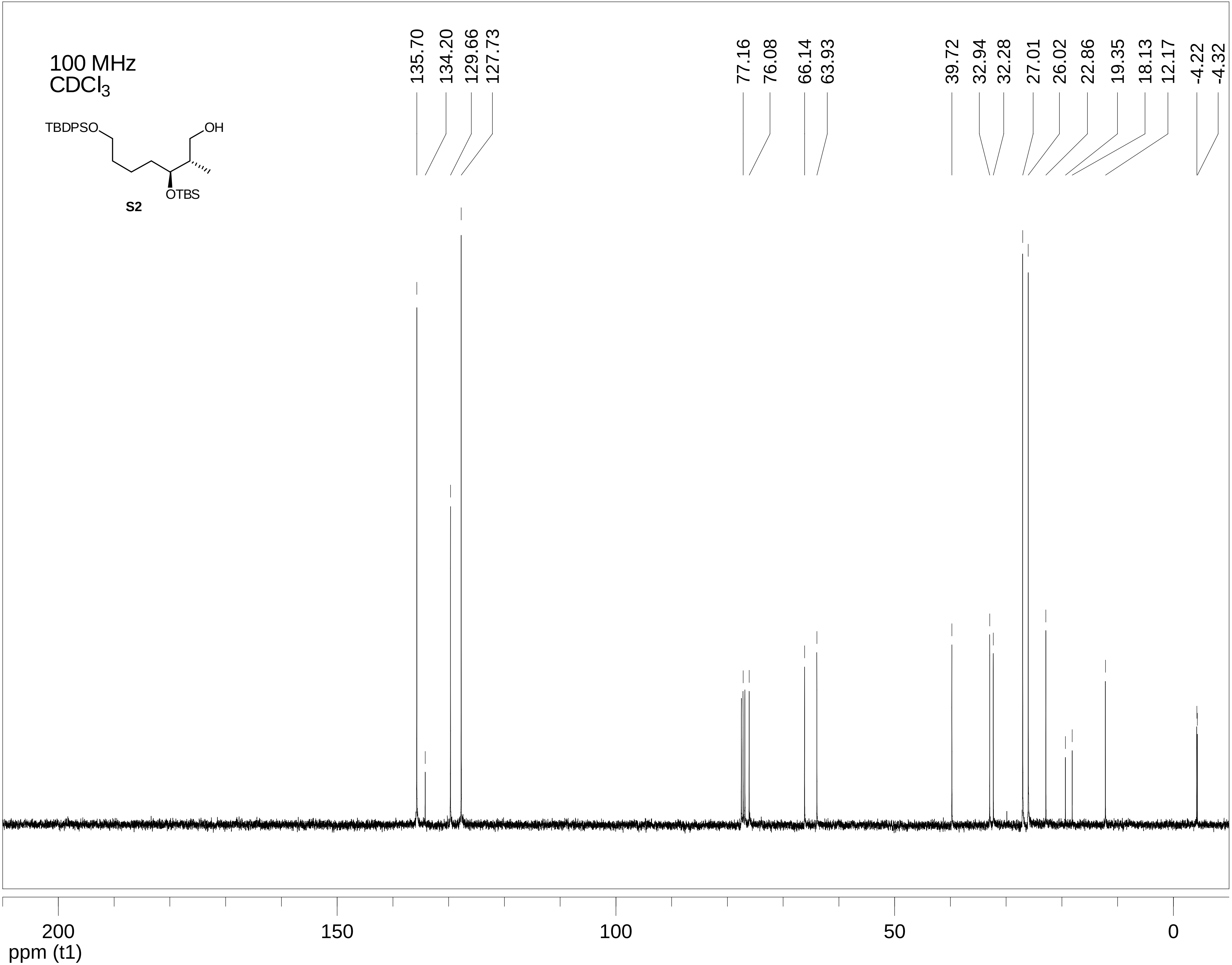
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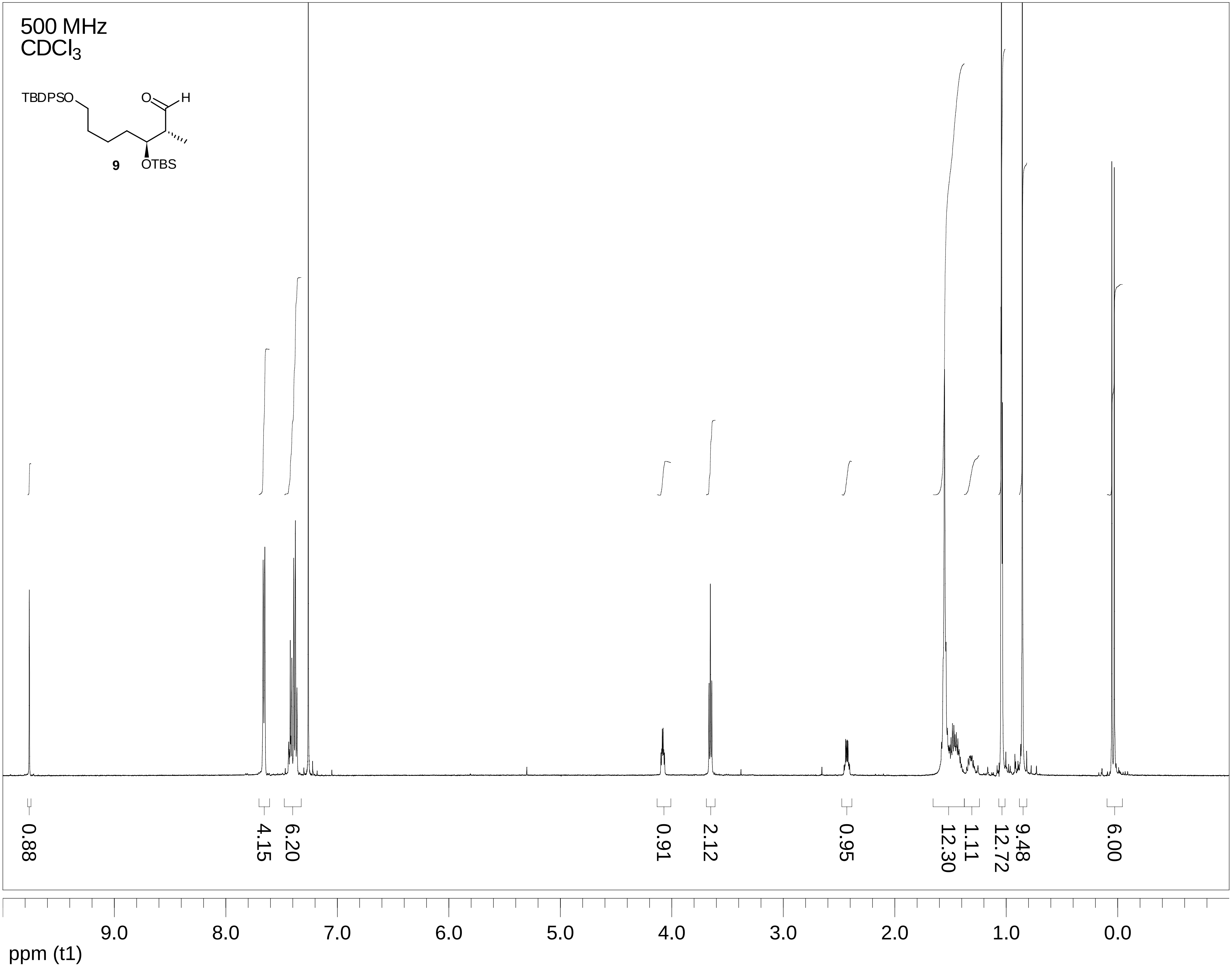
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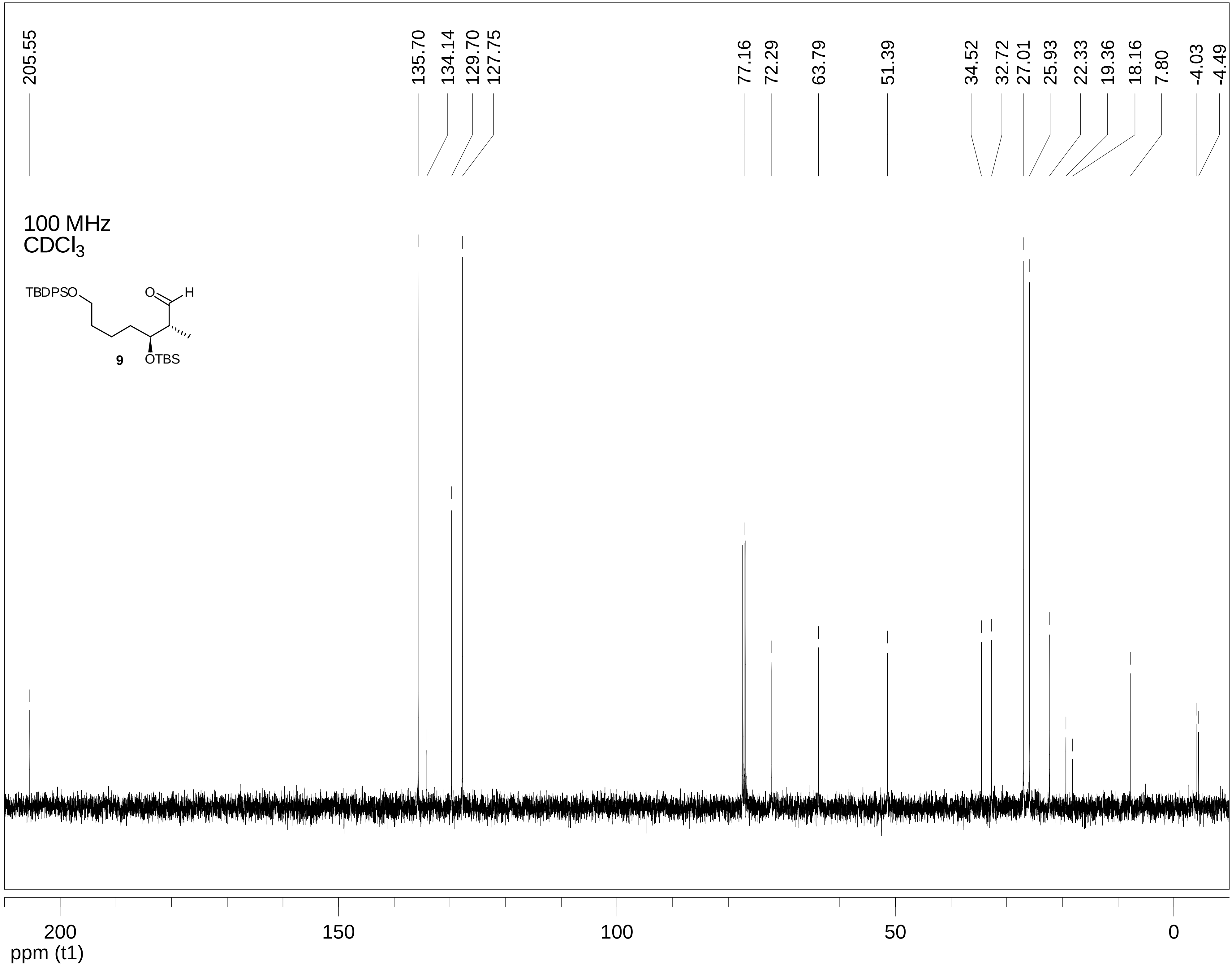
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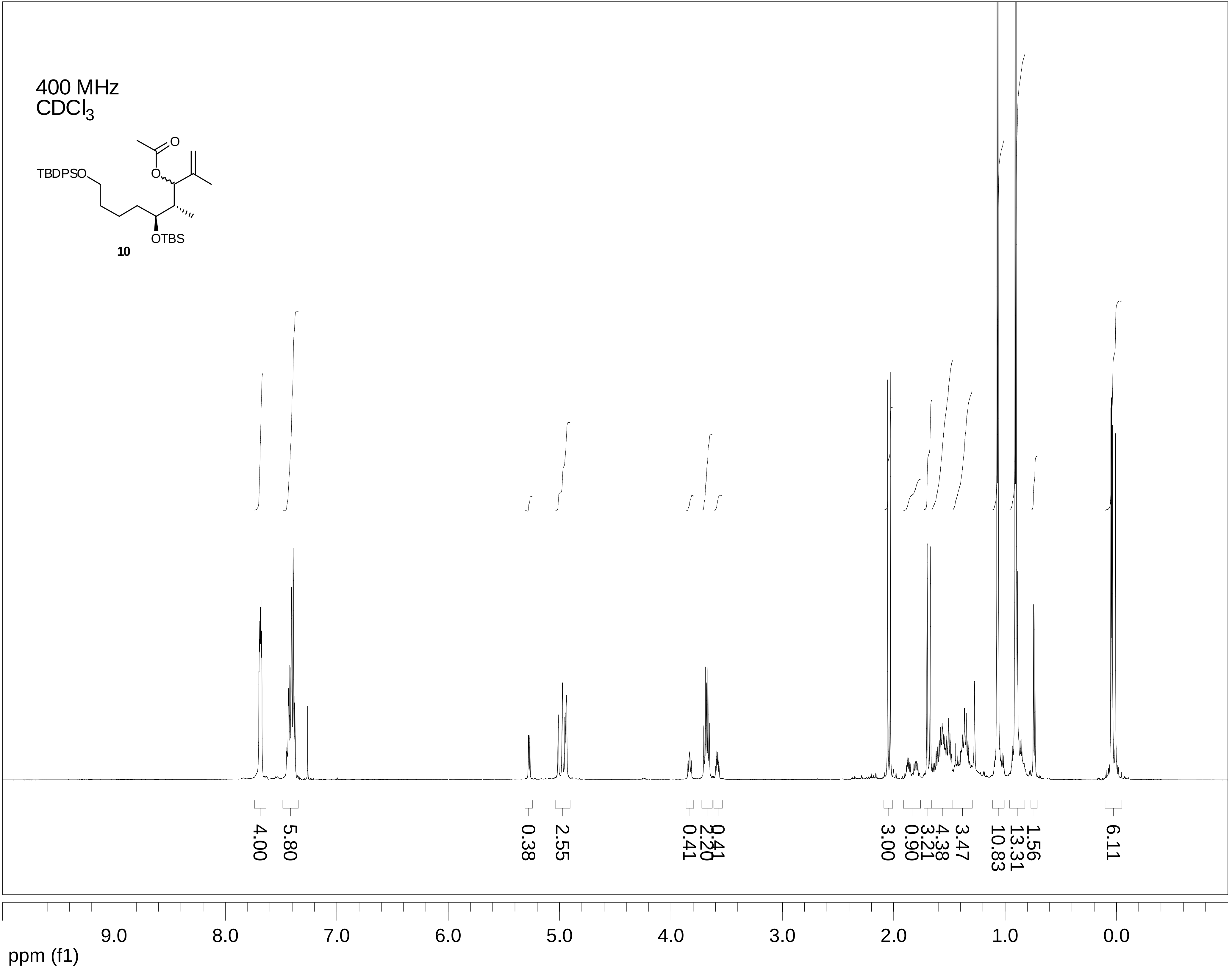
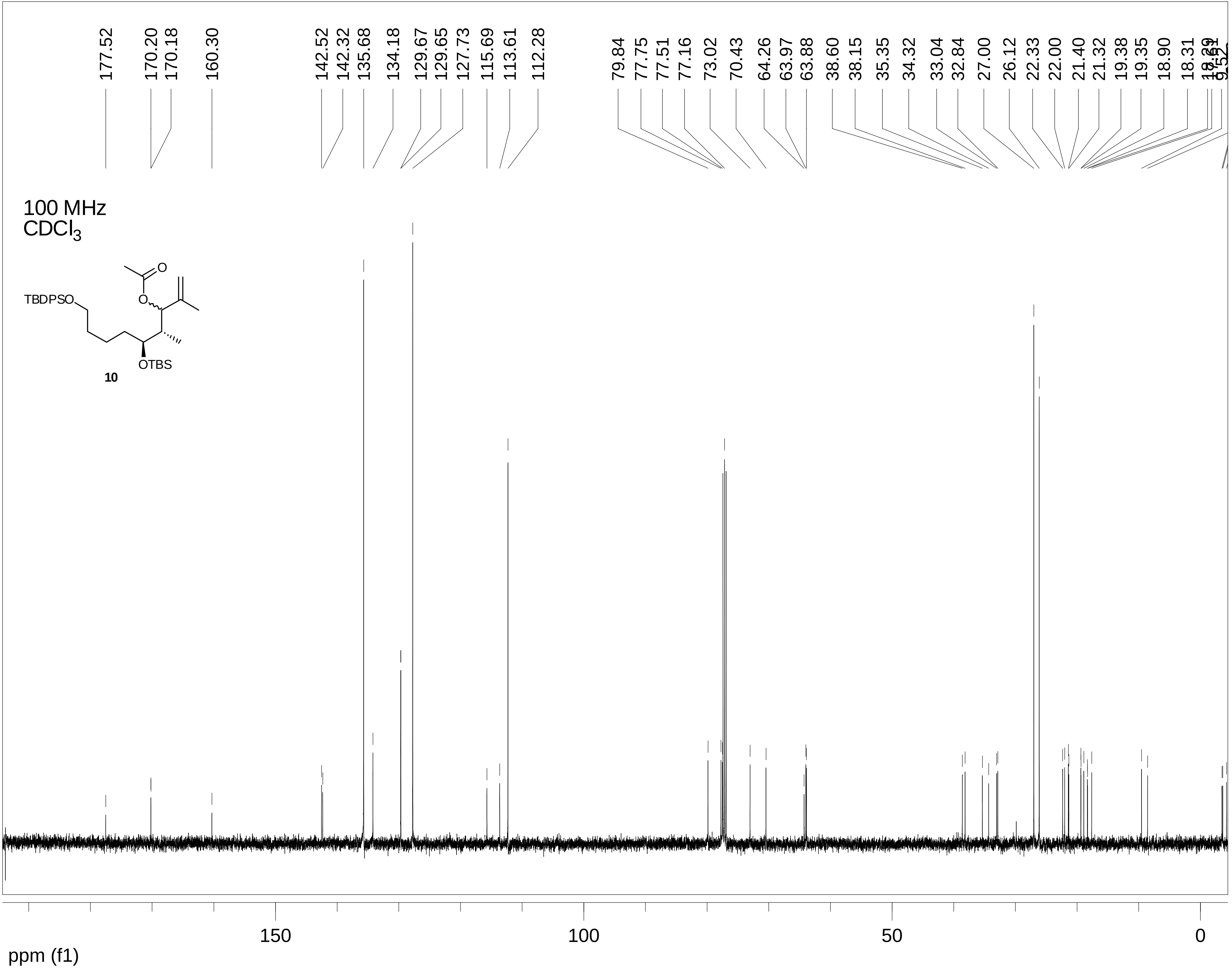
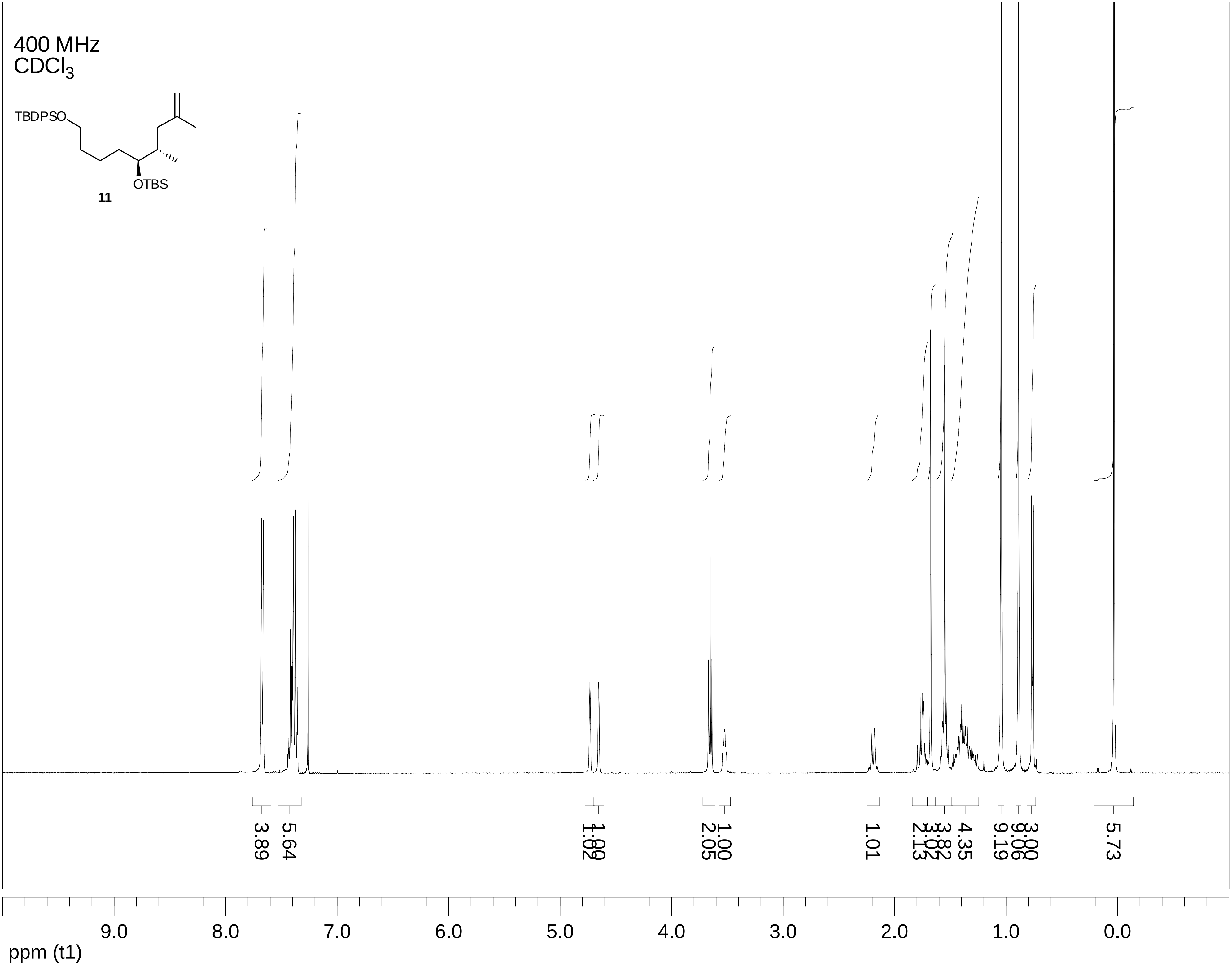
0
ppm (t1)


400 MHz
$CDCl_3$
TBDPSO
O
O
OTBS
10
4.00
5.80
0.38
2.55
0.41
2.20
0.41
3.00
0.90
3.21
4.38
3.47
10.83
13.31
1.56
6.11
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

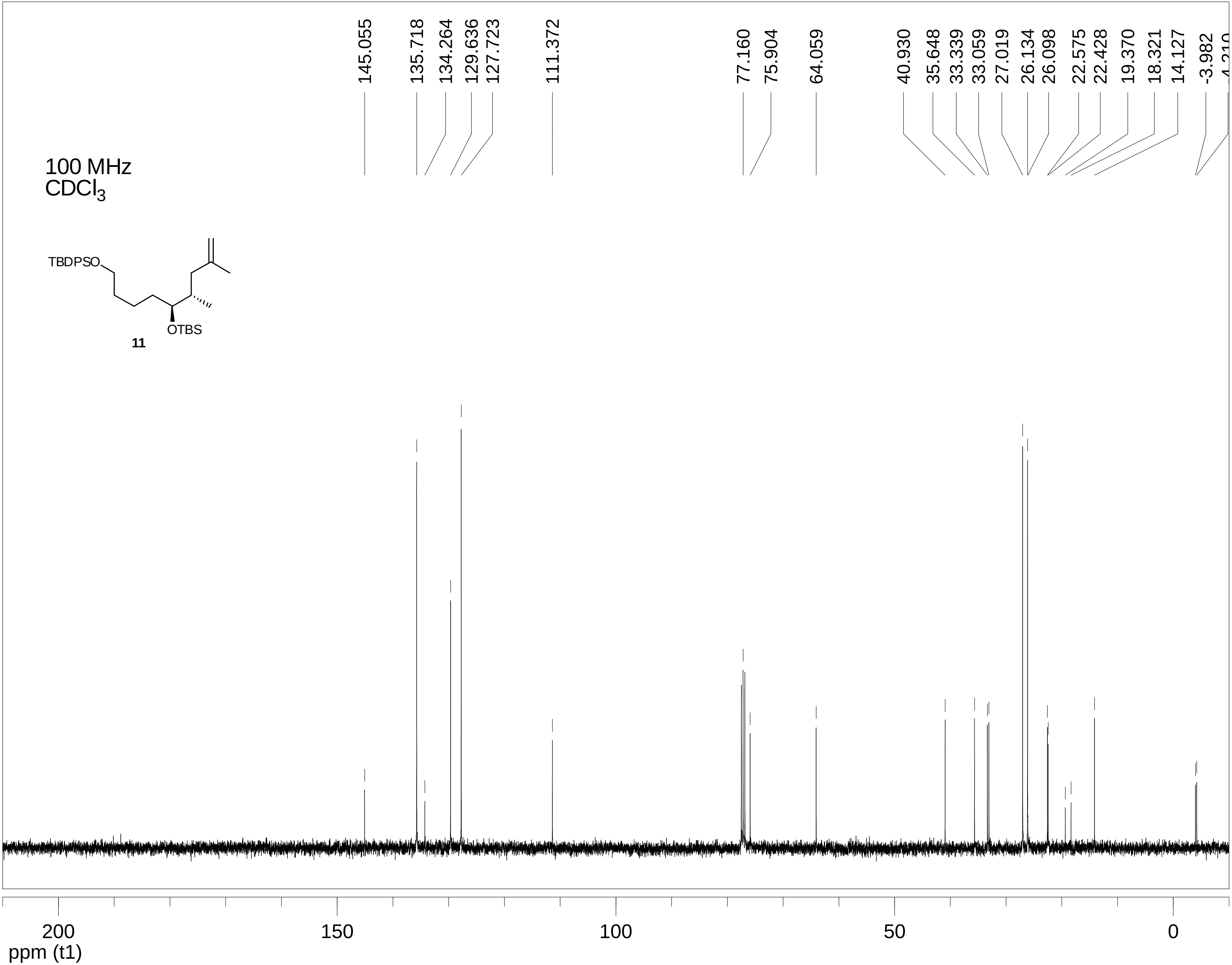


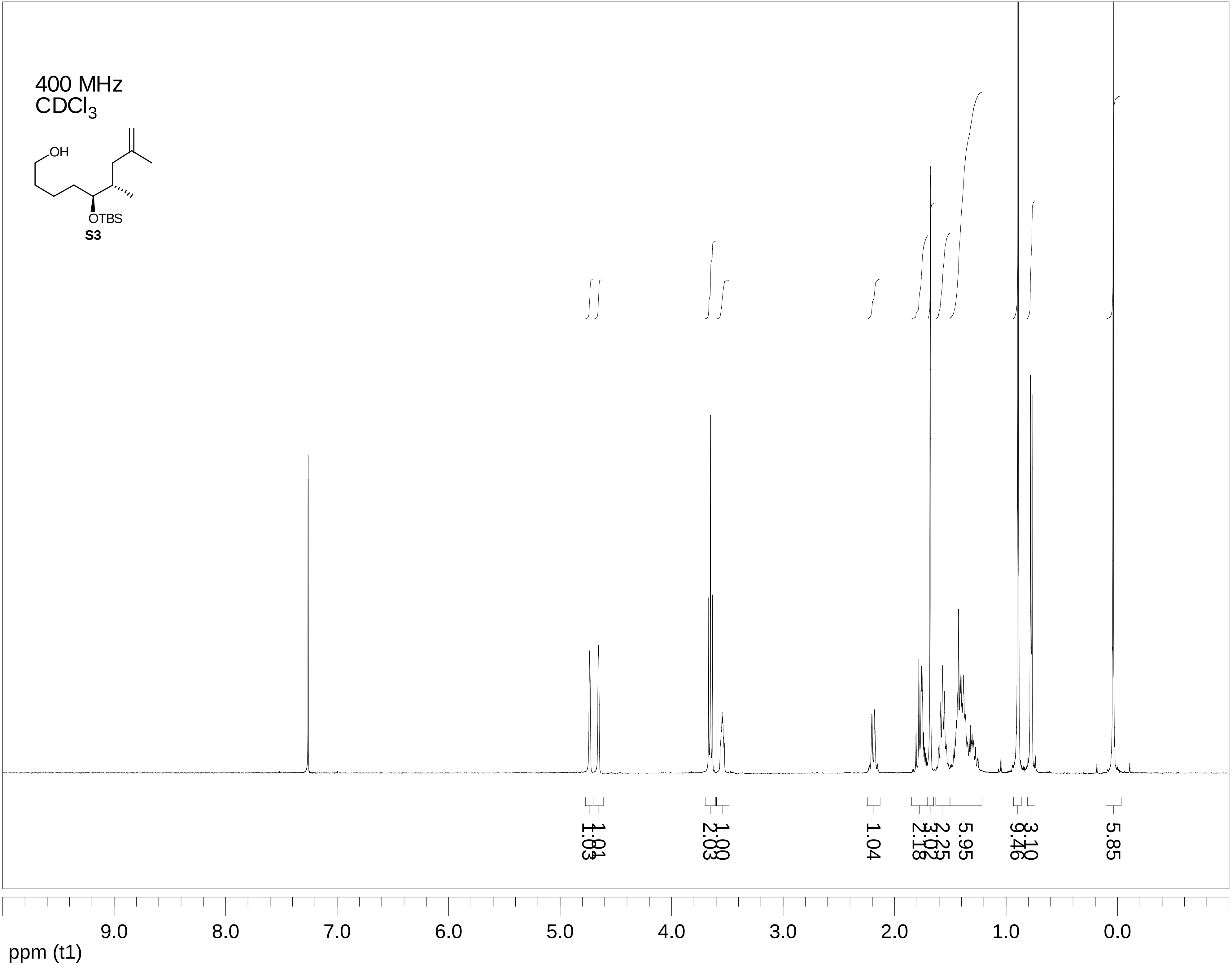
10

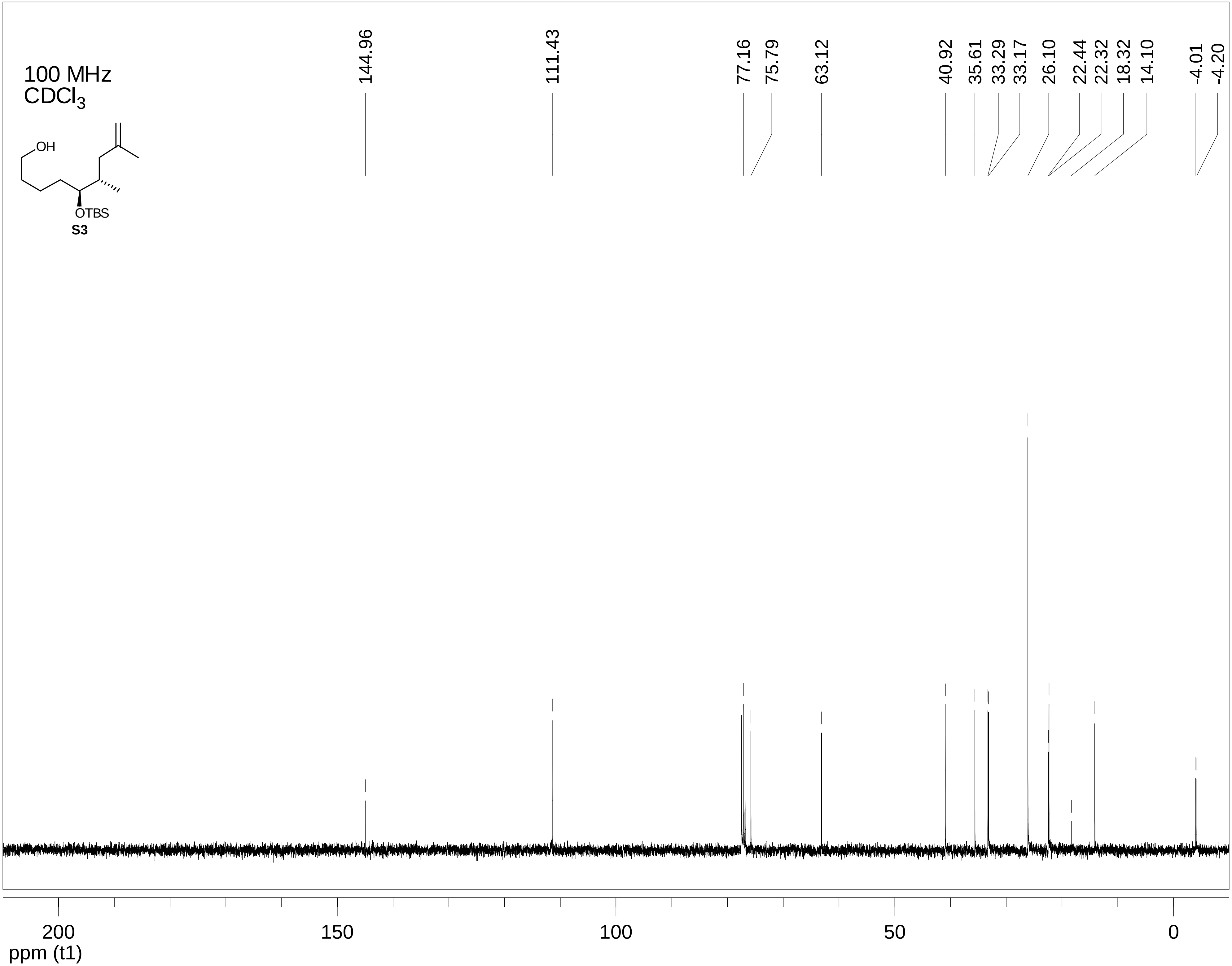
177.52
170.20
170.18
160.30
142.52
142.32
135.68
134.18
129.67
129.65
127.73
115.69
113.61
112.28
79.84
77.75
77.51
77.16
73.02
70.43
64.26
63.97
63.88
38.60
38.15
35.35
34.32
33.04
32.84
27.00
26.12
22.33
22.00
21.40
21.32
19.38
19.35
18.90
18.31
18.29
17.61
9.52
100 MHz
$CDCl_3$
TBDPSO
O
O
OTBS
150
100
50
0
ppm (f1)

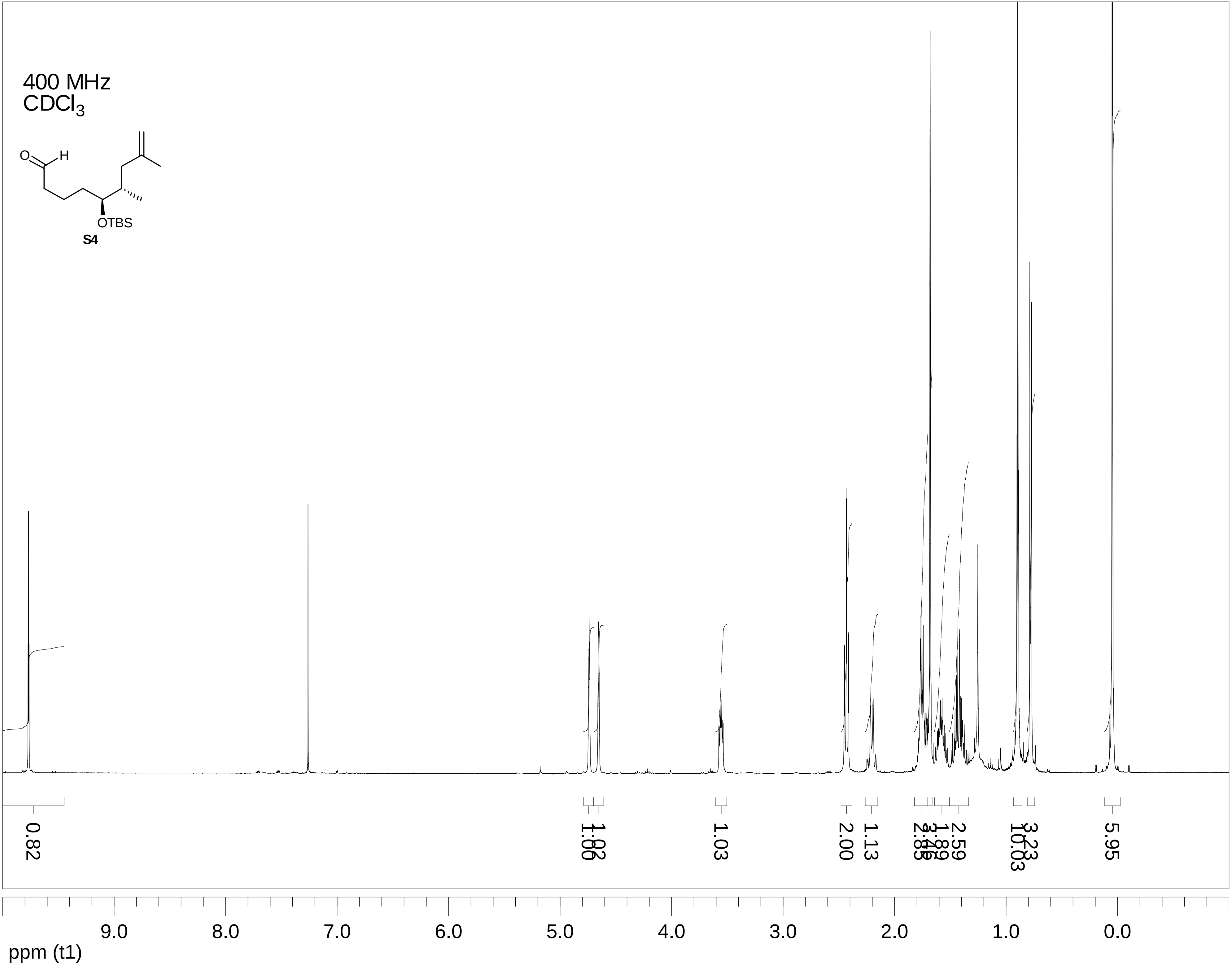


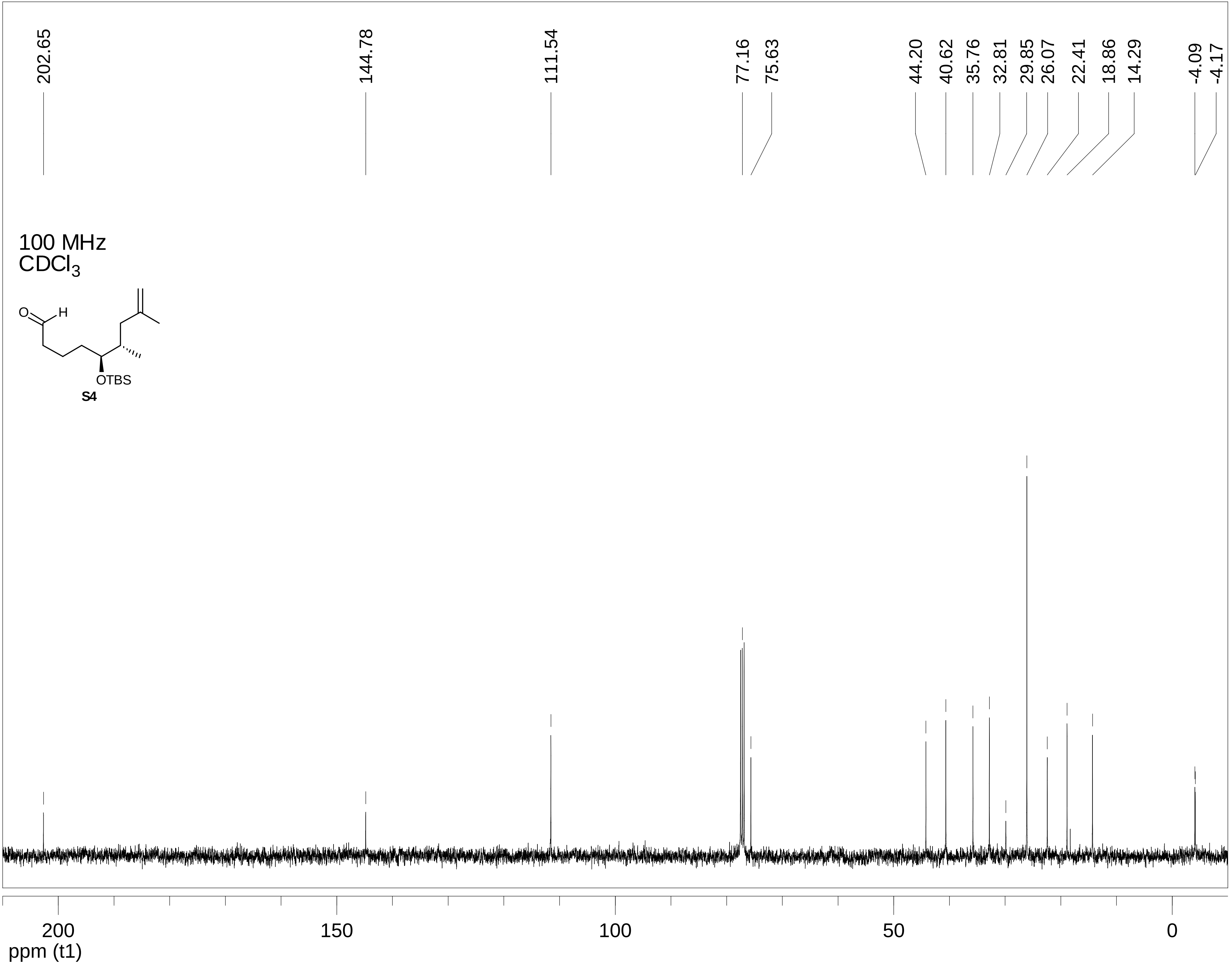
400 MHz
$CDCl_3$
TBDPSO
OTBS
11
3.89
5.64
1.02
1.00
2.05
1.00
1.01
2.13
3.07
3.82
4.35
9.19
9.06
3.00
5.73
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

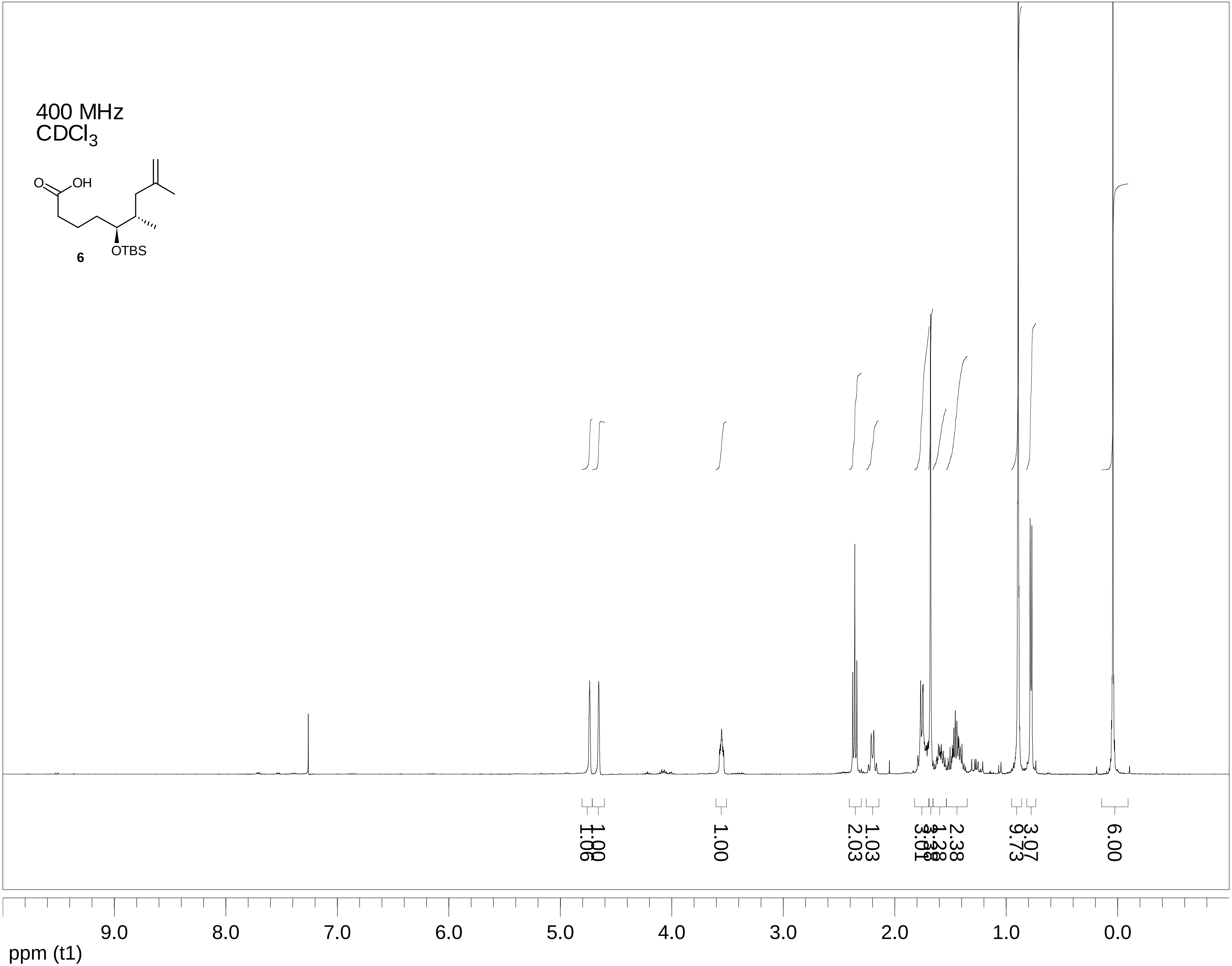

145.055
135.718
134.264
129.636
127.723
111.372
77.160
75.904
64.059
40.930
35.648
33.339
33.059
27.019
26.134
26.098
22.575
22.428
19.370
18.321
14.127
-3.982
100 MHz
CDCl$_3$
TBDPSO
OTBS
11
200
150
100
50
0
ppm (t1)

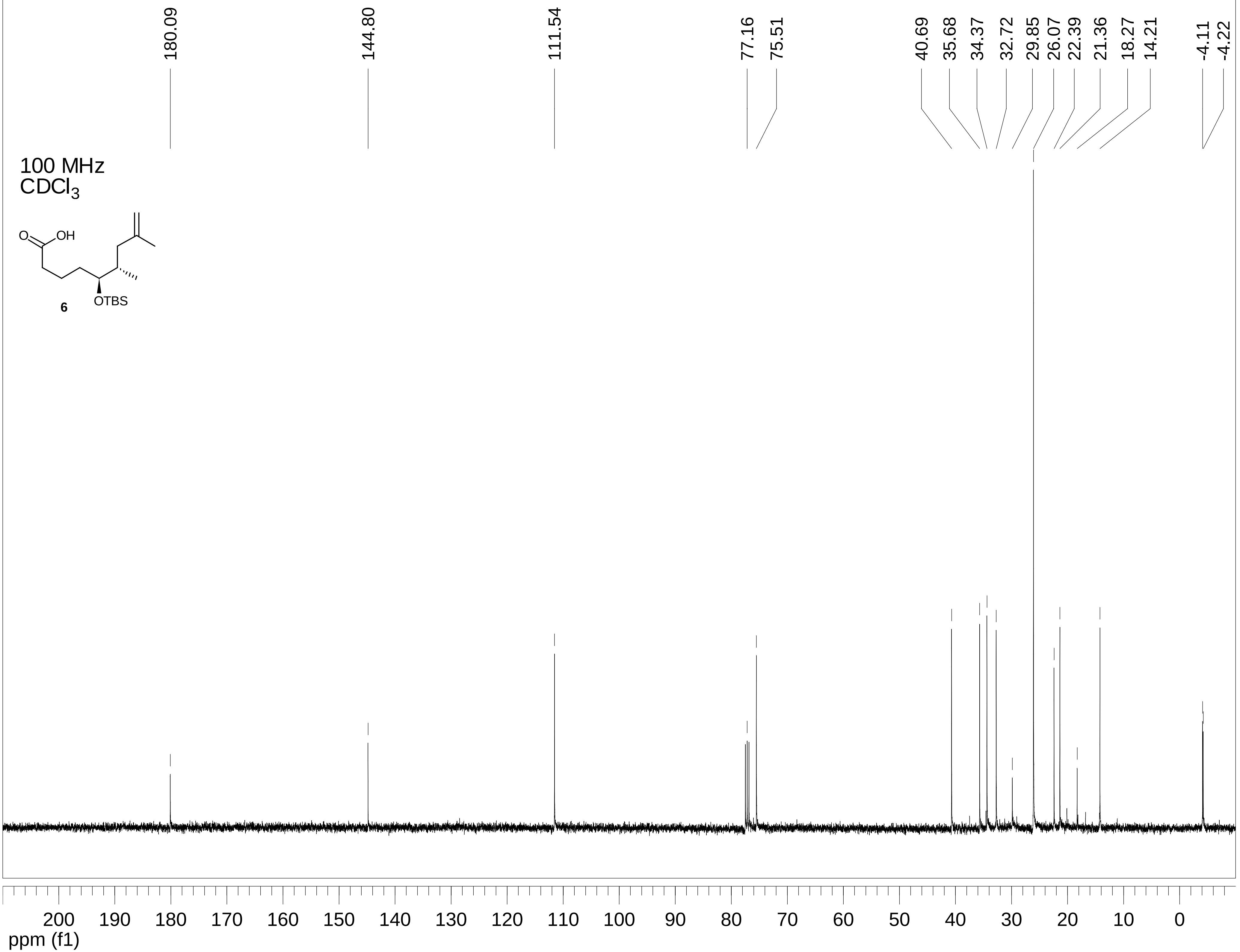

400 MHz
$CDCl_3$
OH
OTBS
S3
1.03
1.01
2.03
1.00
1.04
2.18
3.02
2.25
5.95
9.46
3.10
5.85
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

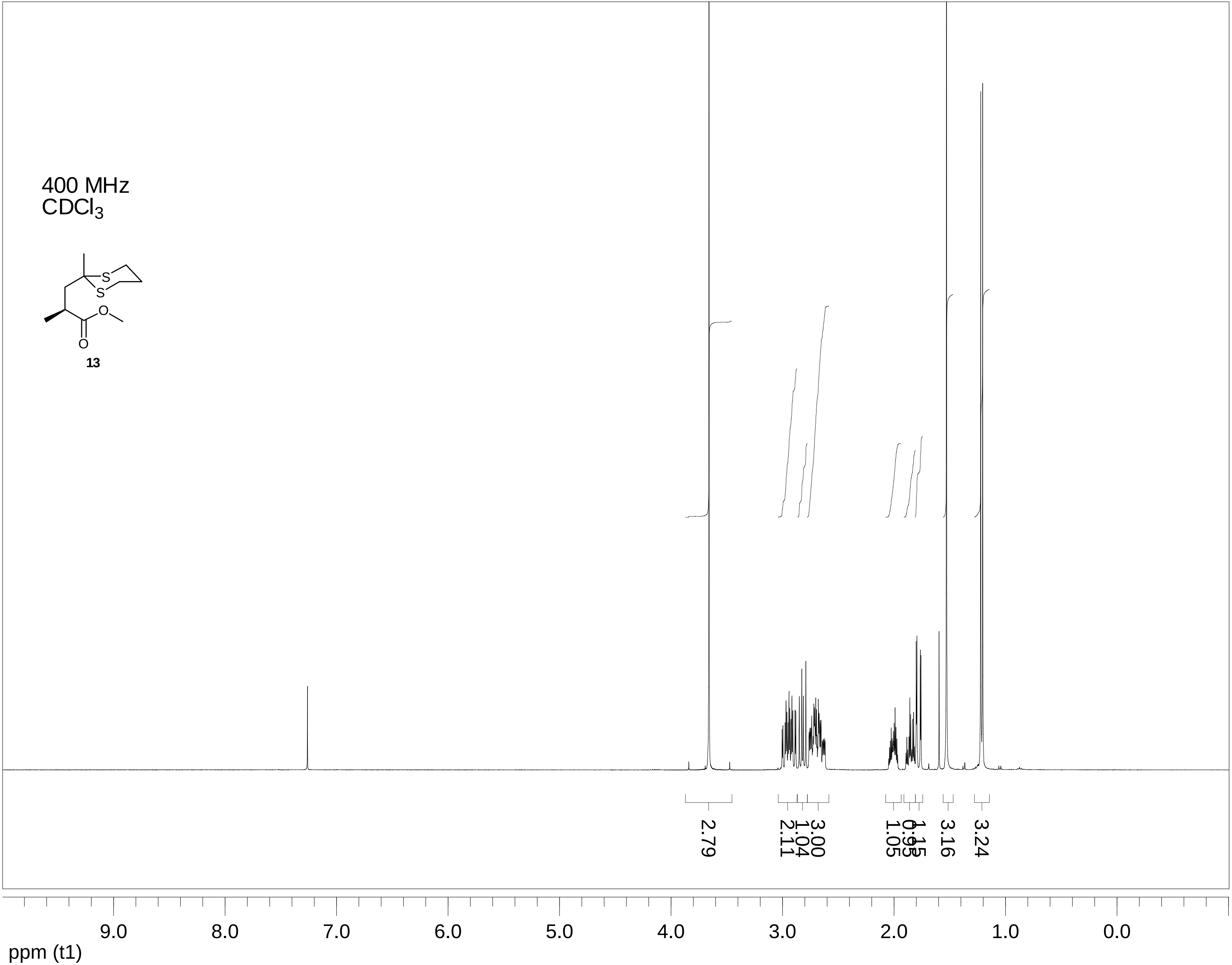

100 MHz
CDCl$_3$
OH
OTBS
S3
144.96
111.43
77.16
75.79
63.12
40.92
35.61
33.29
33.17
26.10
22.44
22.32
18.32
14.10
-4.01
-4.20
200
150
100
50
0
ppm (t1)


400 MHz
CDCl3
O
H
OTBS
S4
0.82
1.00
1.02
1.03
2.00
1.13
2.85
3.46
1.89
2.59
10.03
3.23
5.95
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

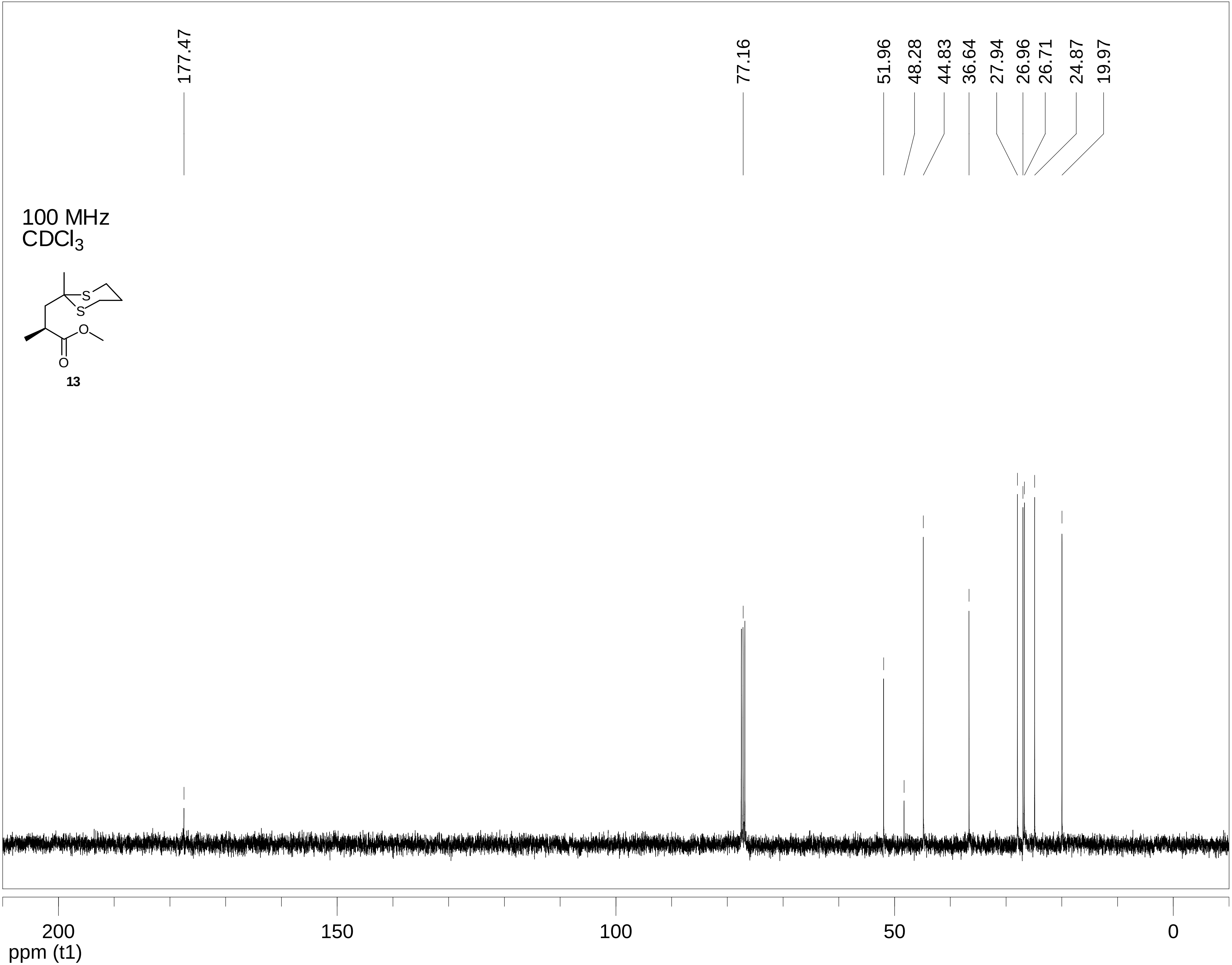

202.65
144.78
111.54
77.16
75.63
44.20
40.62
35.76
32.81
29.85
26.07
22.41
18.86
14.29
-4.09
-4.17
100 MHz
CDCl$_3$
O
H
OTBS
S4
200
150
100
50
0
ppm (t1)

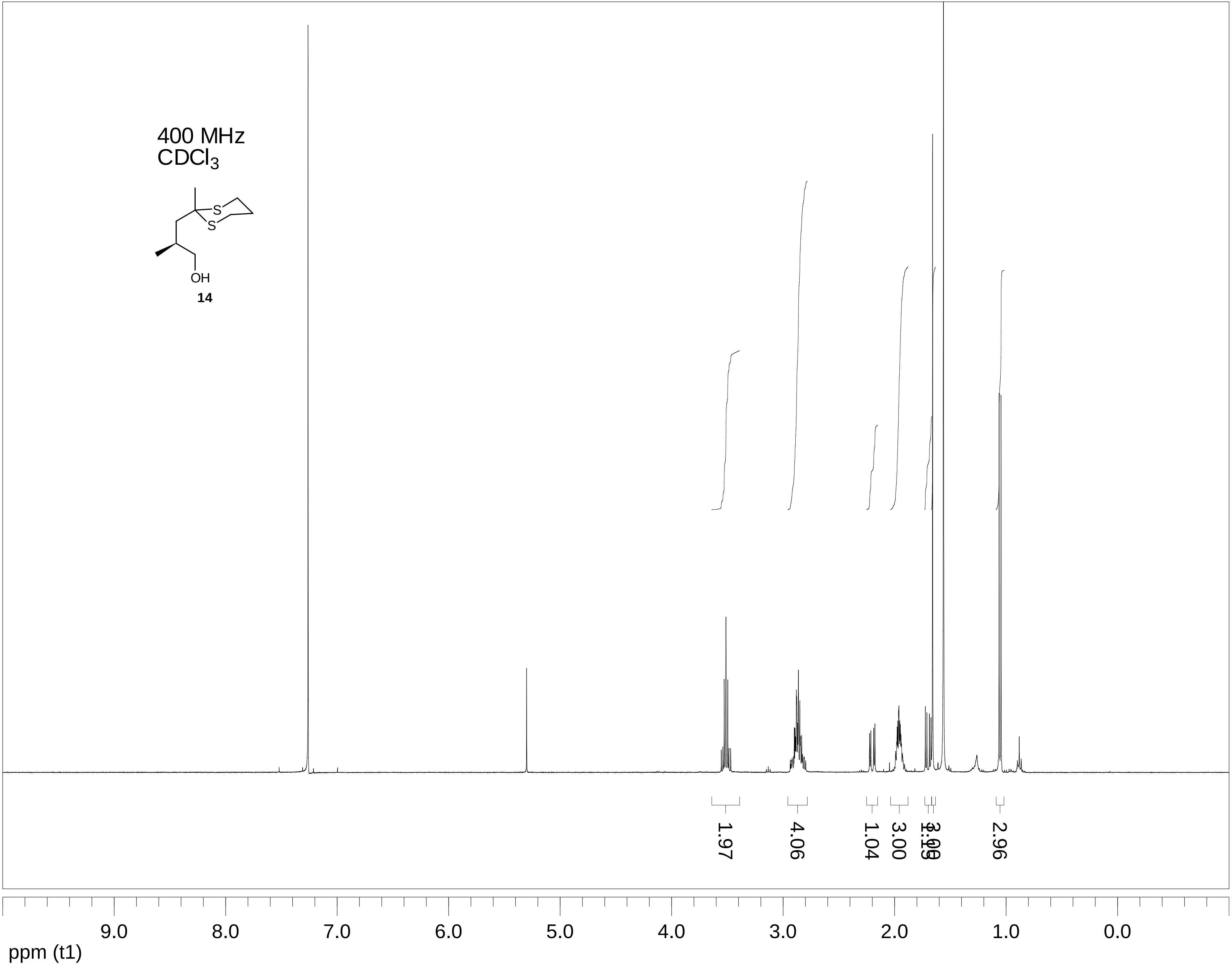

400 MHz
CDCl3
O
OH
OTBS
6
1.06
1.00
1.00
2.03
1.03
3.01
1.28
2.38
9.73
3.07
6.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

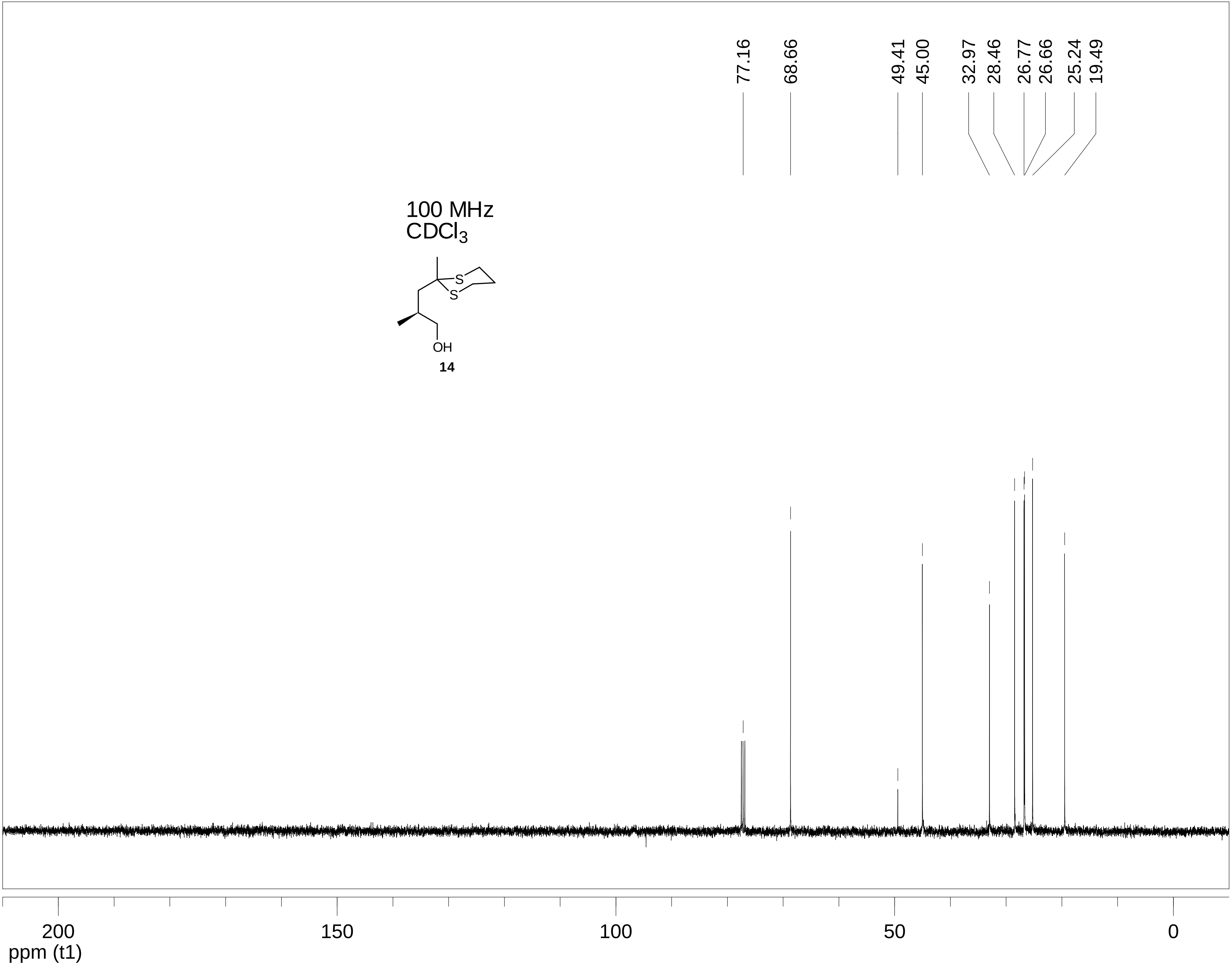

180.09
144.80
111.54
77.16
75.51
40.69
35.68
34.37
32.72
29.85
26.07
22.39
21.36
18.27
14.21
-4.11
-4.22
100 MHz
$CDCl_3$
O
OH
OTBS
6
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (f1)

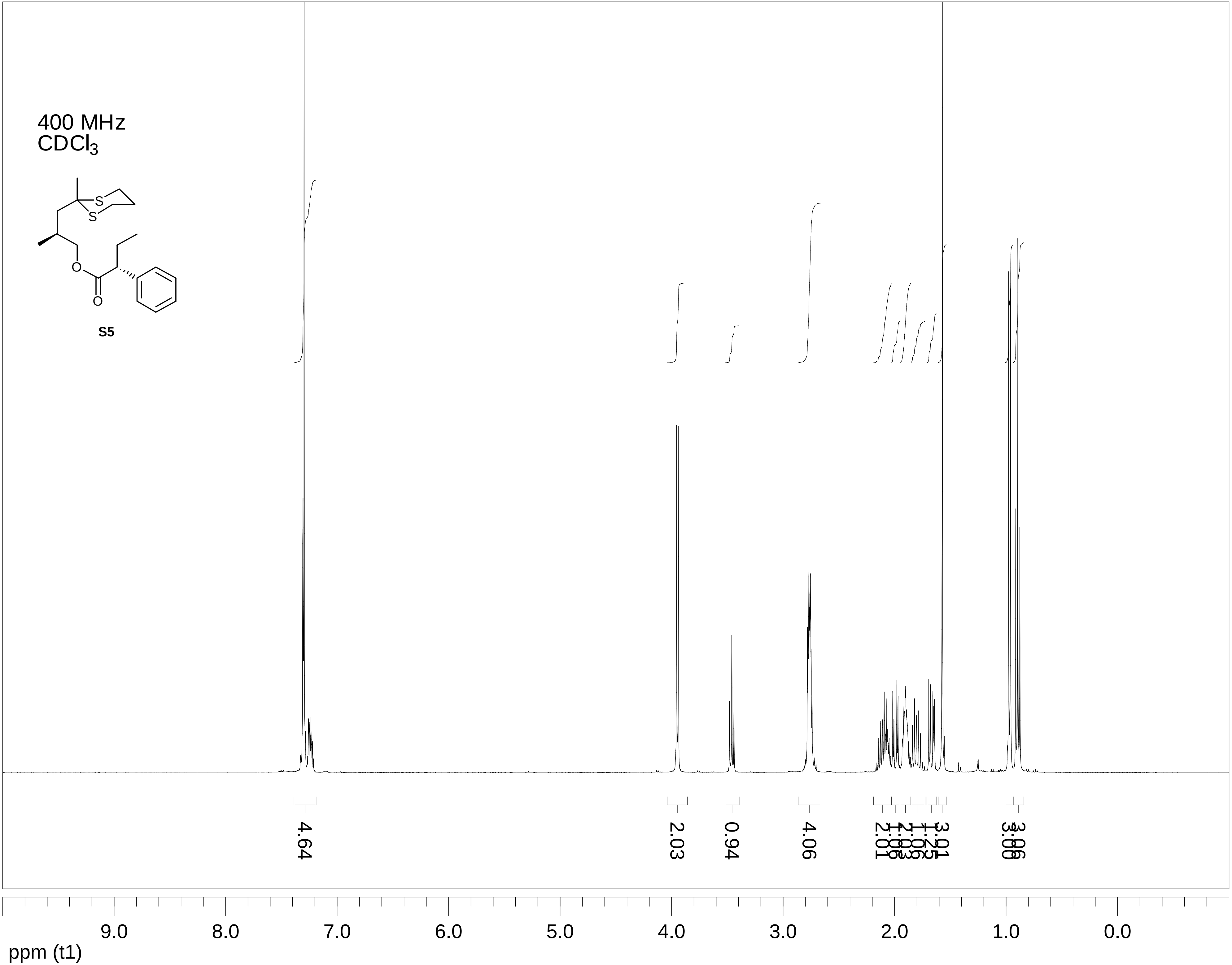


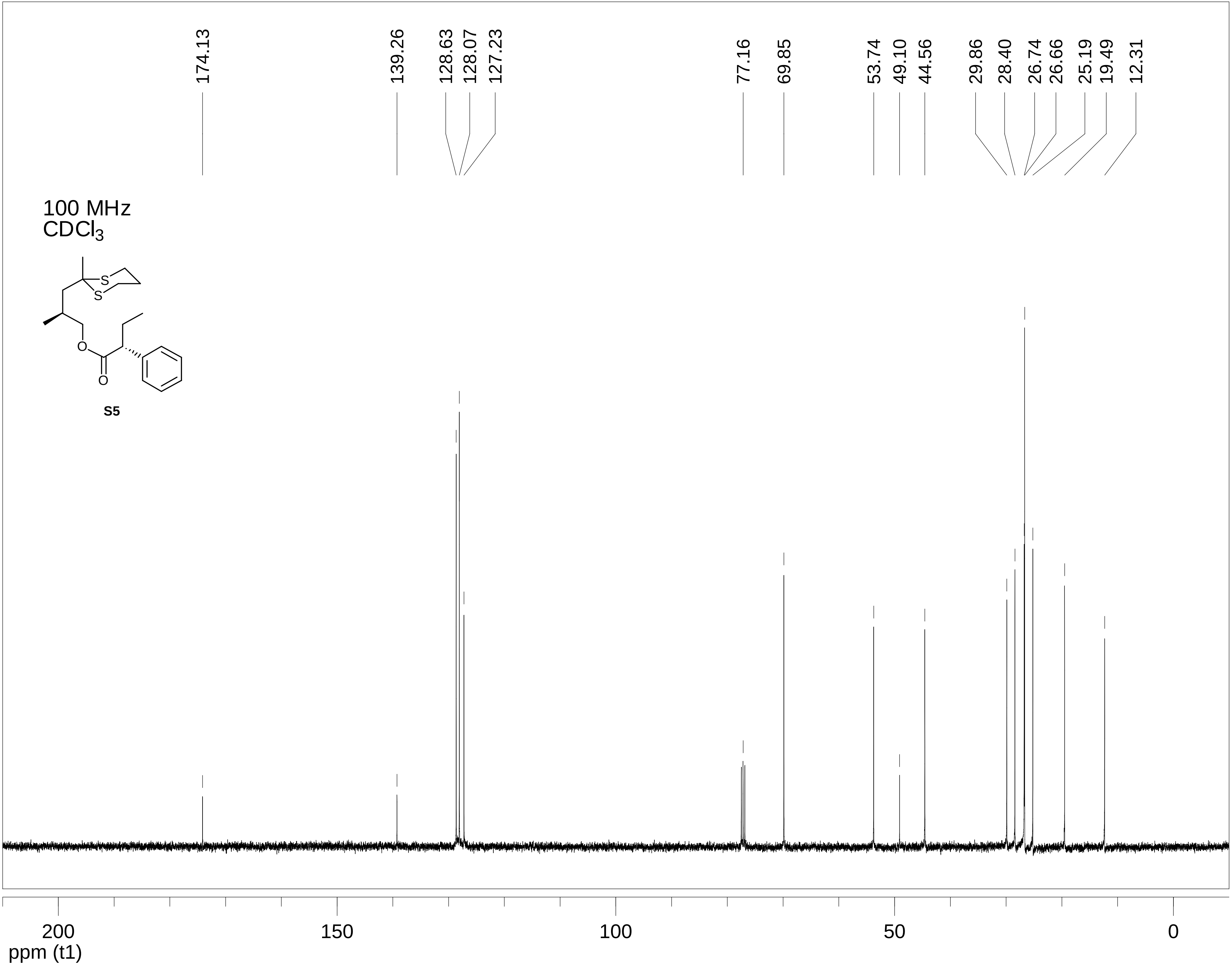
400 MHz
CDCl$_3$
S
S
O
O
13
2.79
2.11
1.04
3.00
1.05
0.95
1.15
3.16
3.24
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


177.47
77.16
51.96
48.28
44.83
36.64
27.94
26.96
26.71
24.87
19.97
100 MHz
$CDCl_3$
S
S
O
O
13
200
150
100
50
0
ppm (t1)

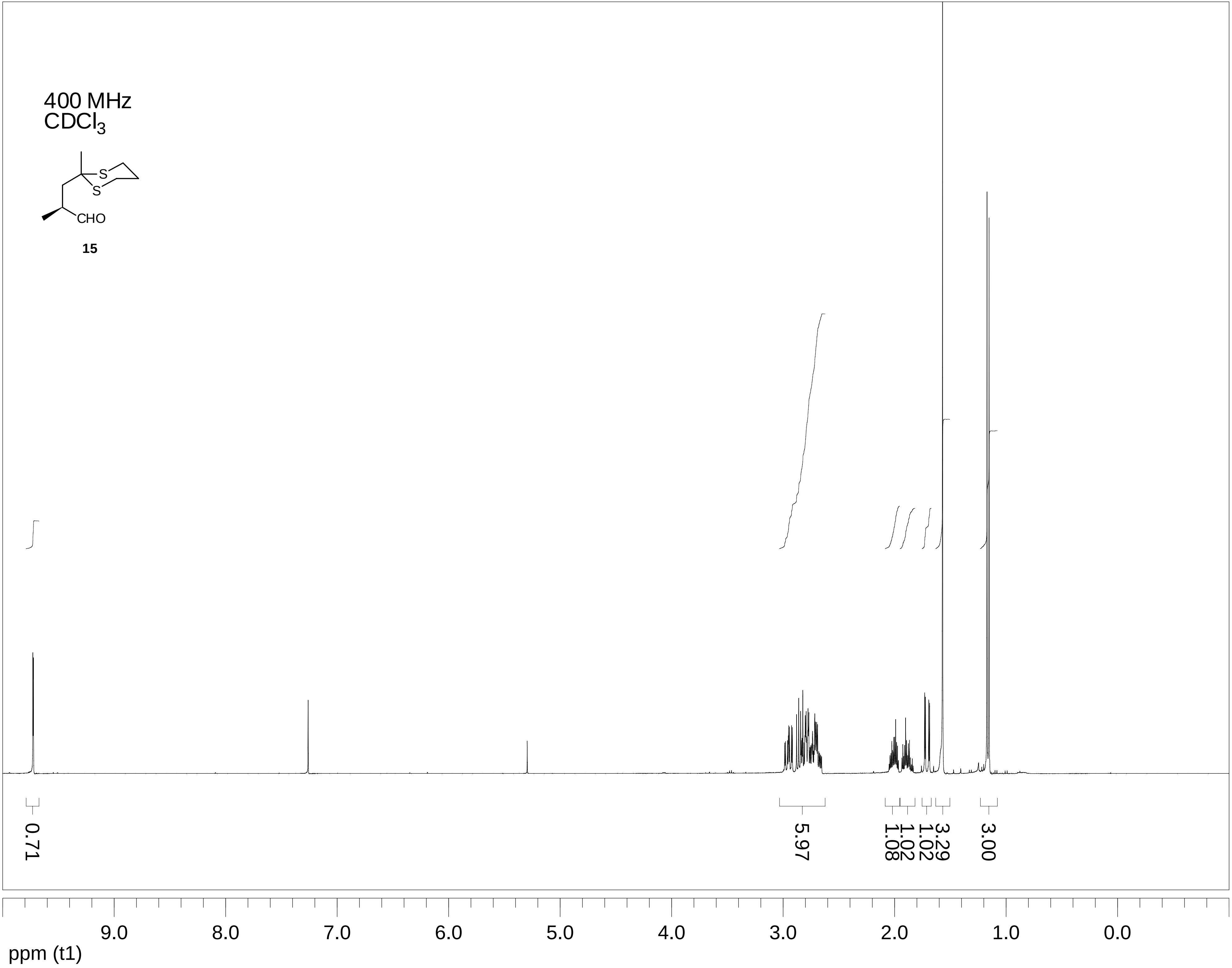

400 MHz
$CDCl_3$
S
S
OH
14
1.97
4.06
1.04
3.00
1.19
3.00
2.96
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

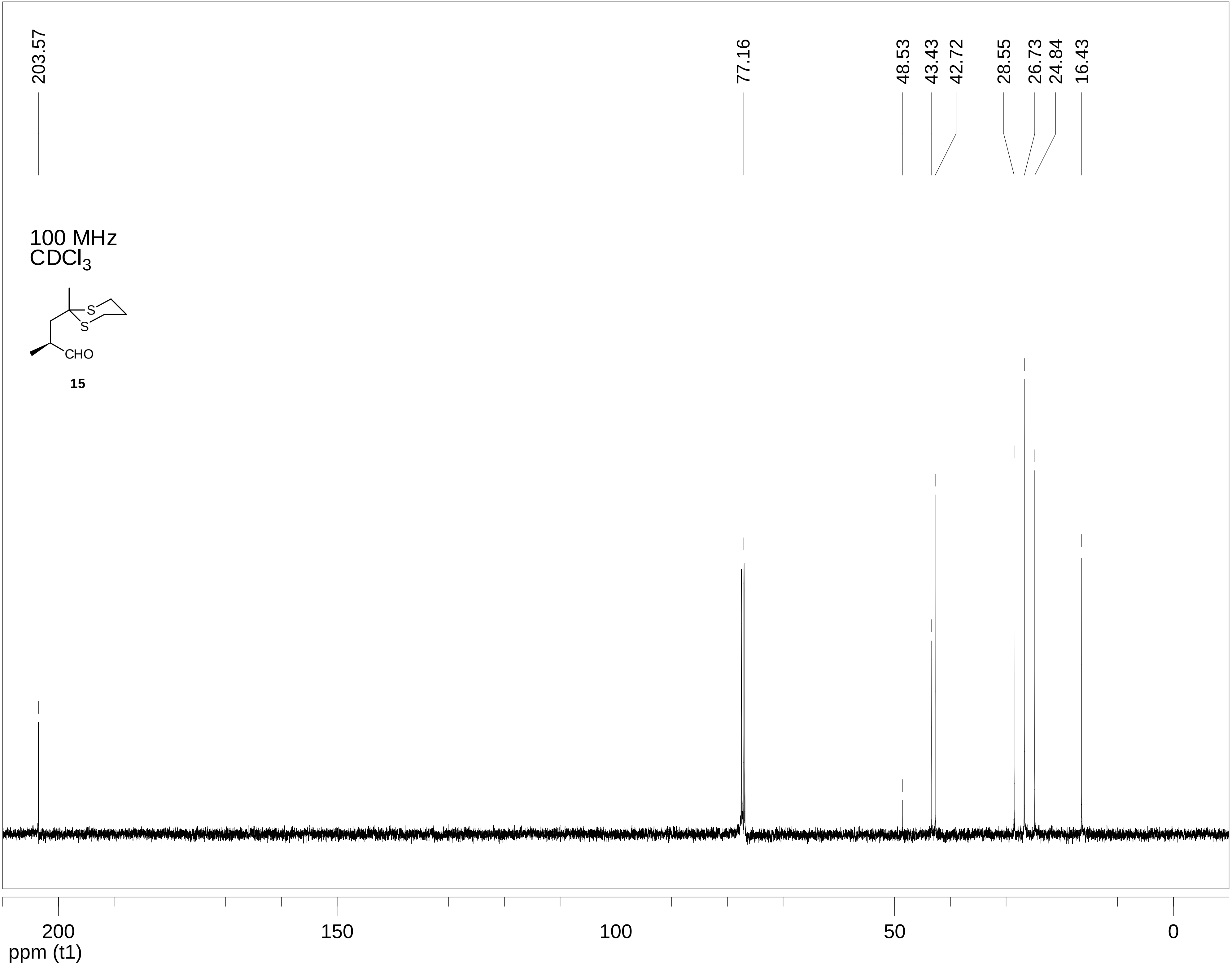

77.16
68.66
49.41
45.00
32.97
28.46
26.77
26.66
25.24
19.49
100 MHz
$CDCl_3$
S
S
OH
14
200
150
100
50
0
ppm (t1)

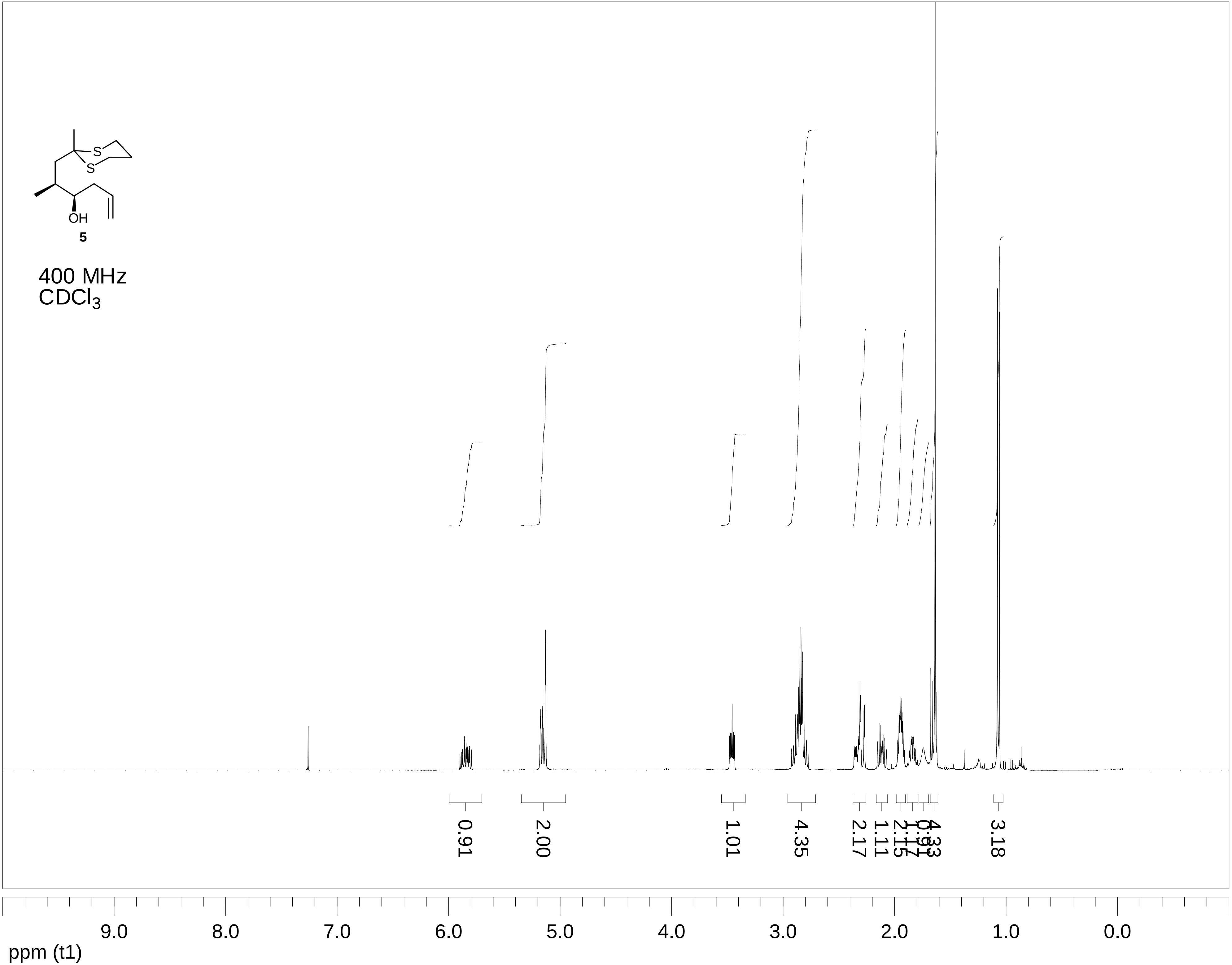

400 MHz
CDCl3
S
S
O
O
S5
4.64
2.03
0.94
4.06
2.01
1.06
2.03
1.08
1.25
3.01
3.00
3.06
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

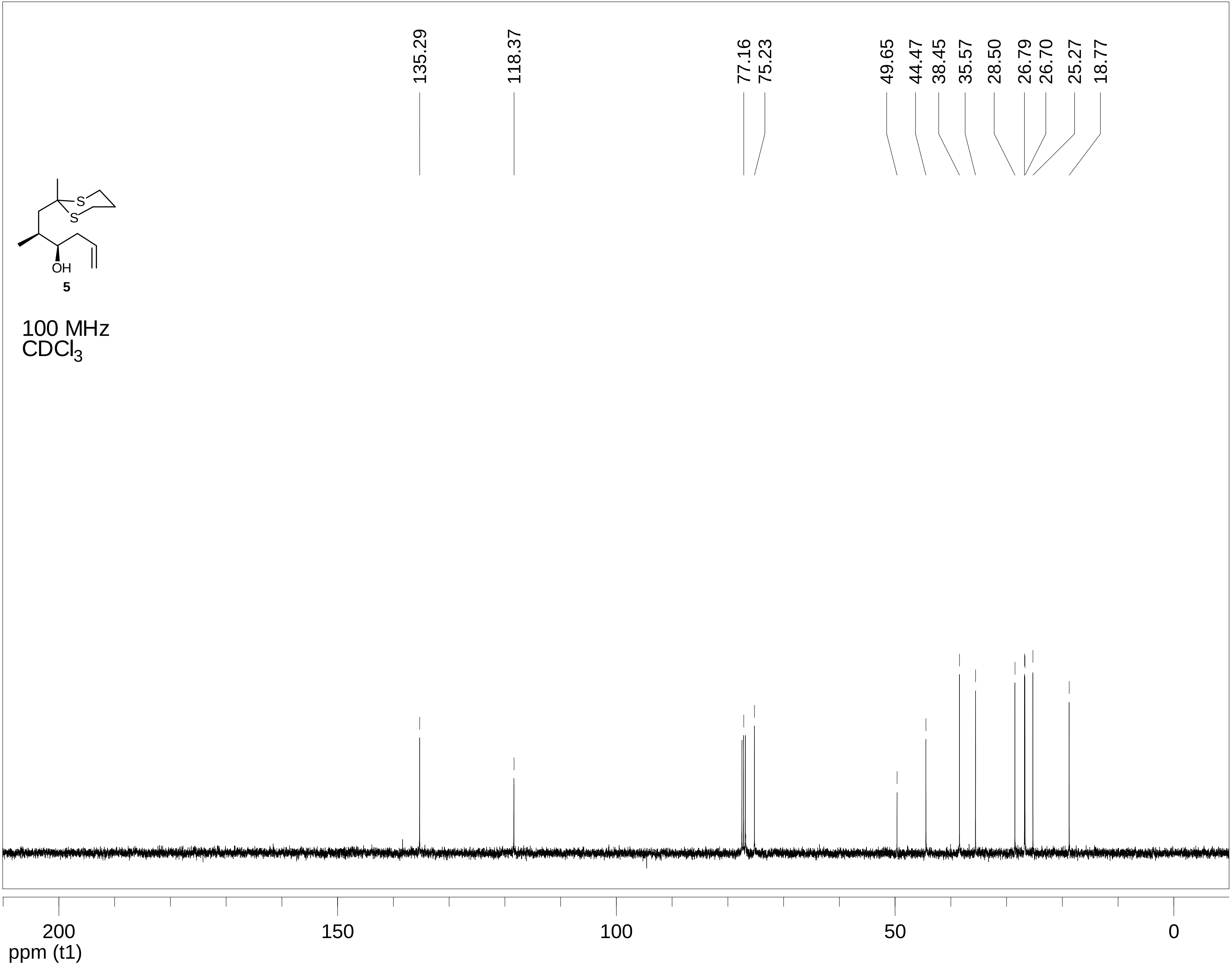

174.13
139.26
128.63
128.07
127.23
77.16
69.85
53.74
49.10
44.56
29.86
28.40
26.74
26.66
25.19
19.49
12.31
100 MHz
$CDCl_3$
S
S
O
O
200
150
100
50
0
ppm (t1)

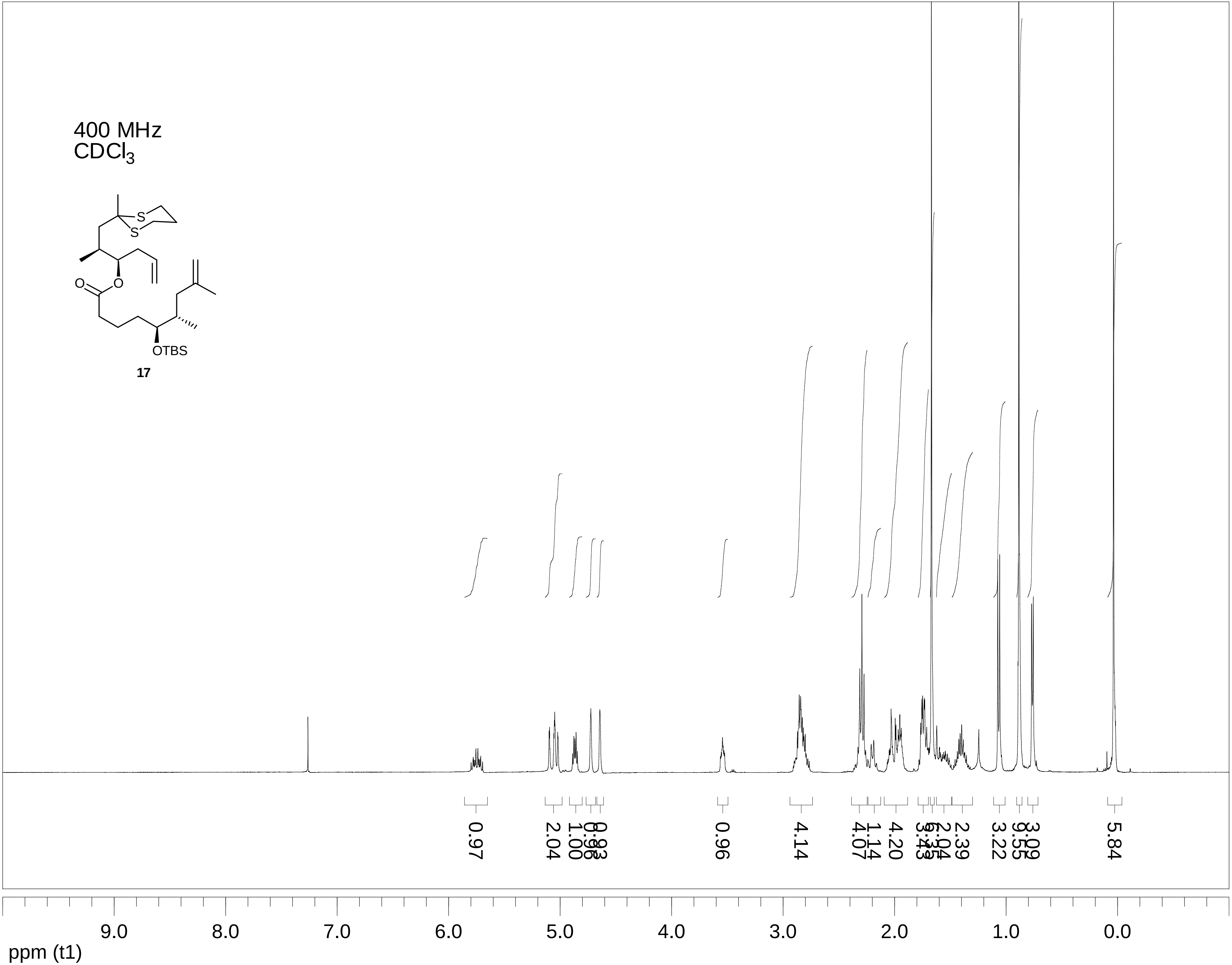
S5

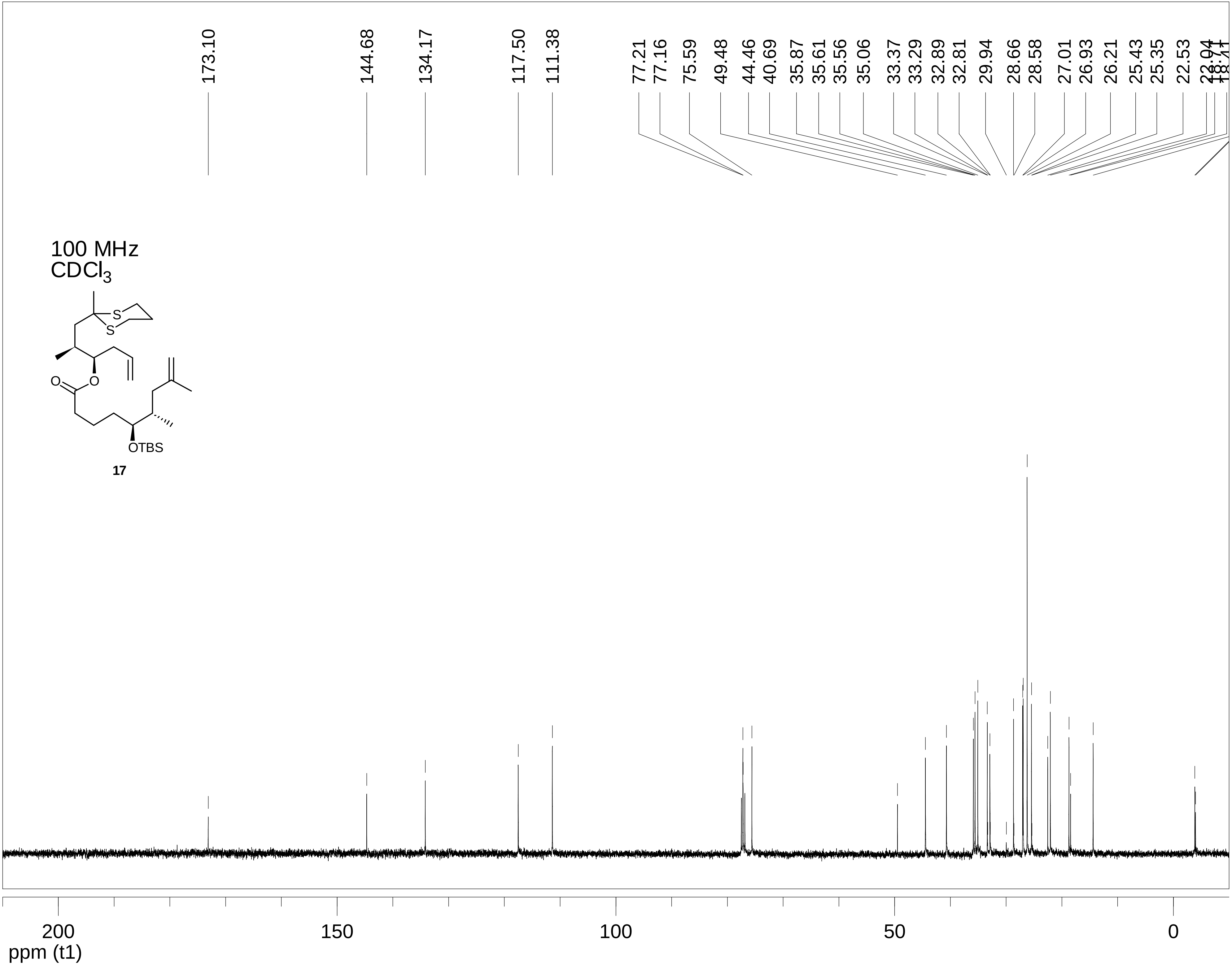

400 MHz
$CDCl_3$
S
S
CHO
15
0.71
5.97
1.08
1.02
1.02
3.29
3.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


203.57
77.16
48.53
43.43
42.72
28.55
26.73
24.84
16.43
100 MHz
CDCl$_3$
S
S
CHO
15
200
150
100
50
0
ppm (t1)


5
400 MHz
CDCl3
0.91
2.00
1.01
4.35
2.17
1.11
2.15
1.17
0.91
4.33
3.18
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

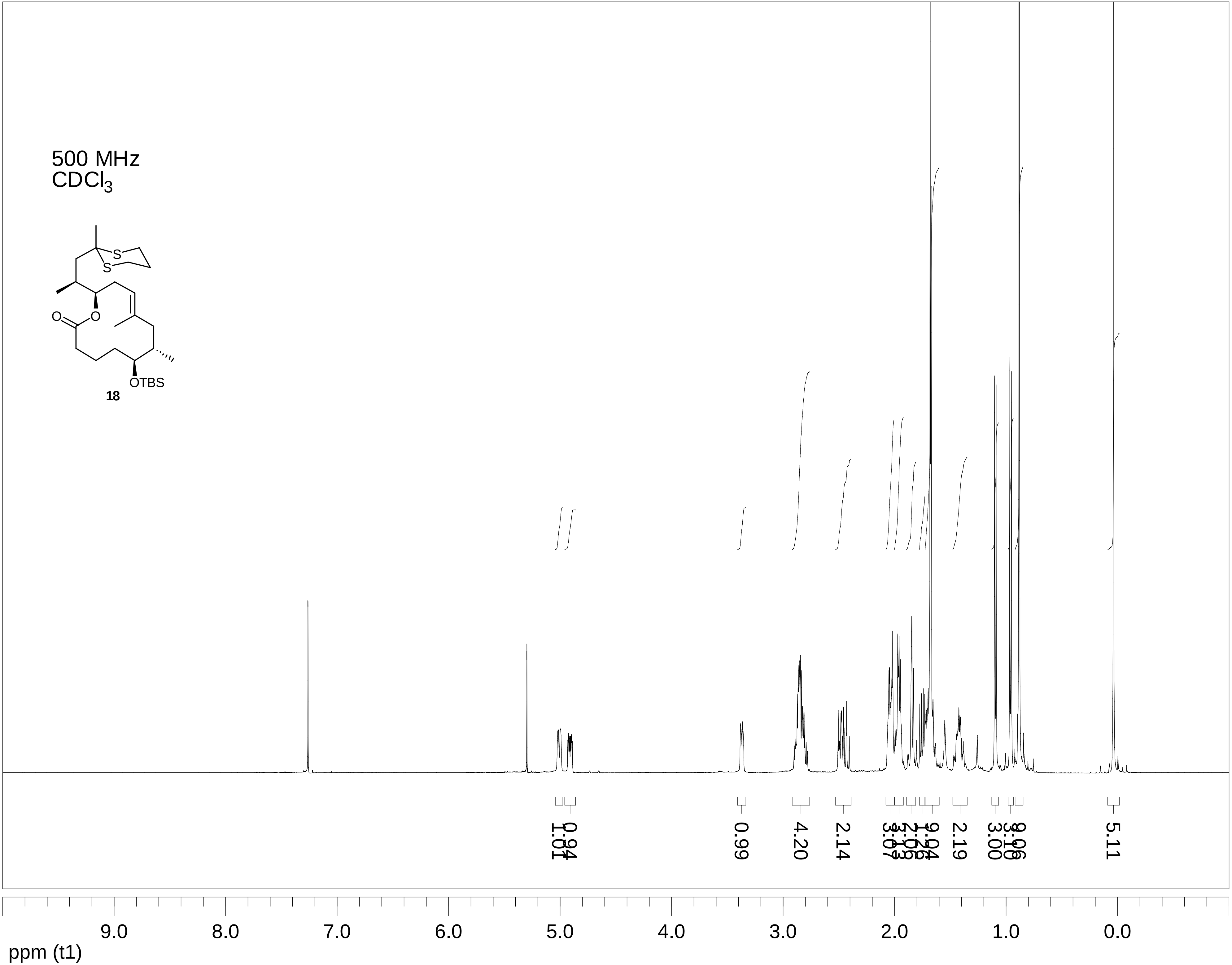

135.29
118.37
77.16
75.23
49.65
44.47
38.45
35.57
28.50
26.79
26.70
25.27
18.77
S
S
OH
5
100 MHz
$CDCl_3$
200
150
100
50
0
ppm (t1)

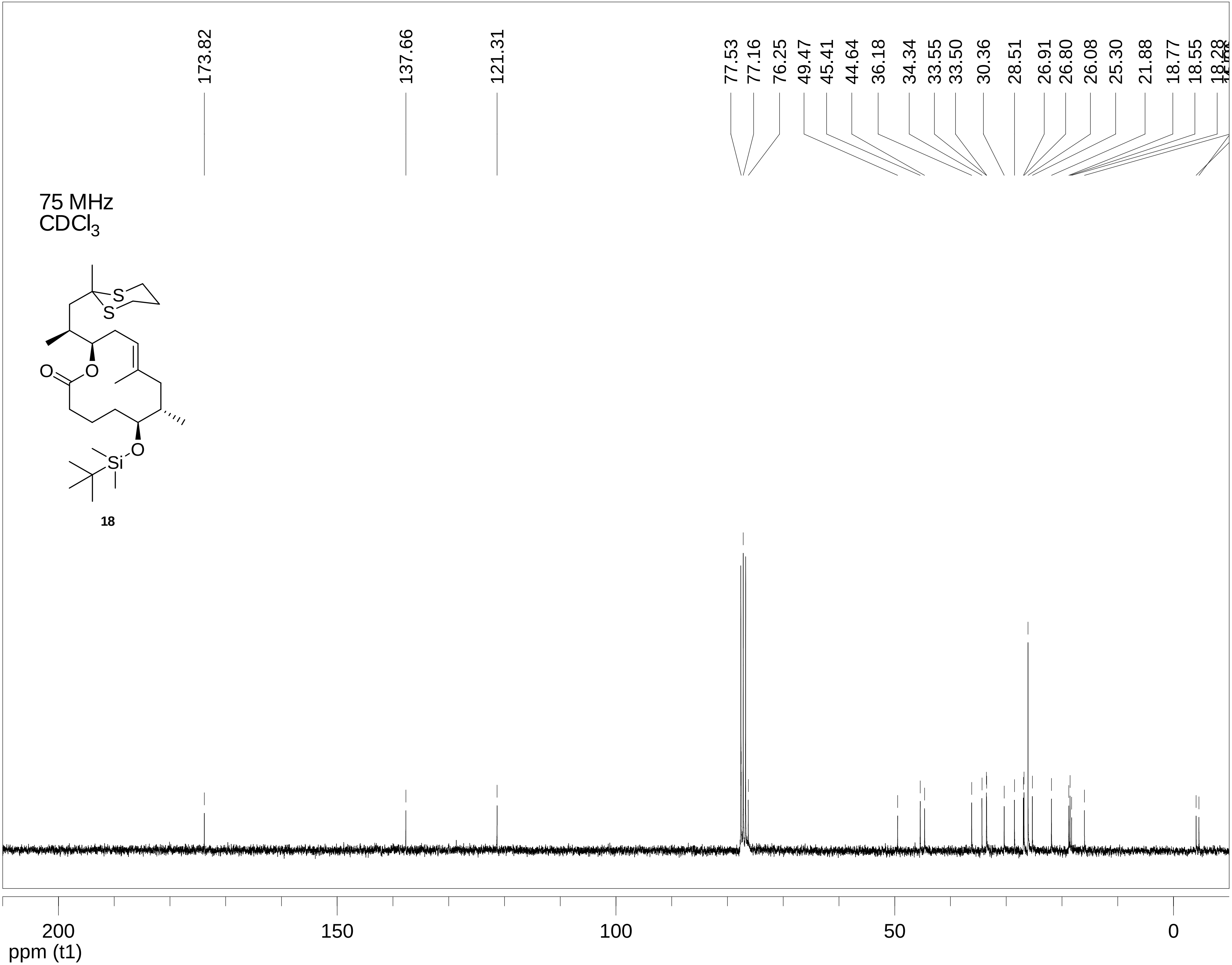

400 MHz
$CDCl_3$
S
S
O
O
OTBS
17
0.97
2.04
1.00
0.96
0.93
0.96
4.14
4.07
1.14
4.20
3.43
6.35
2.04
2.39
3.22
9.55
3.09
5.84
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

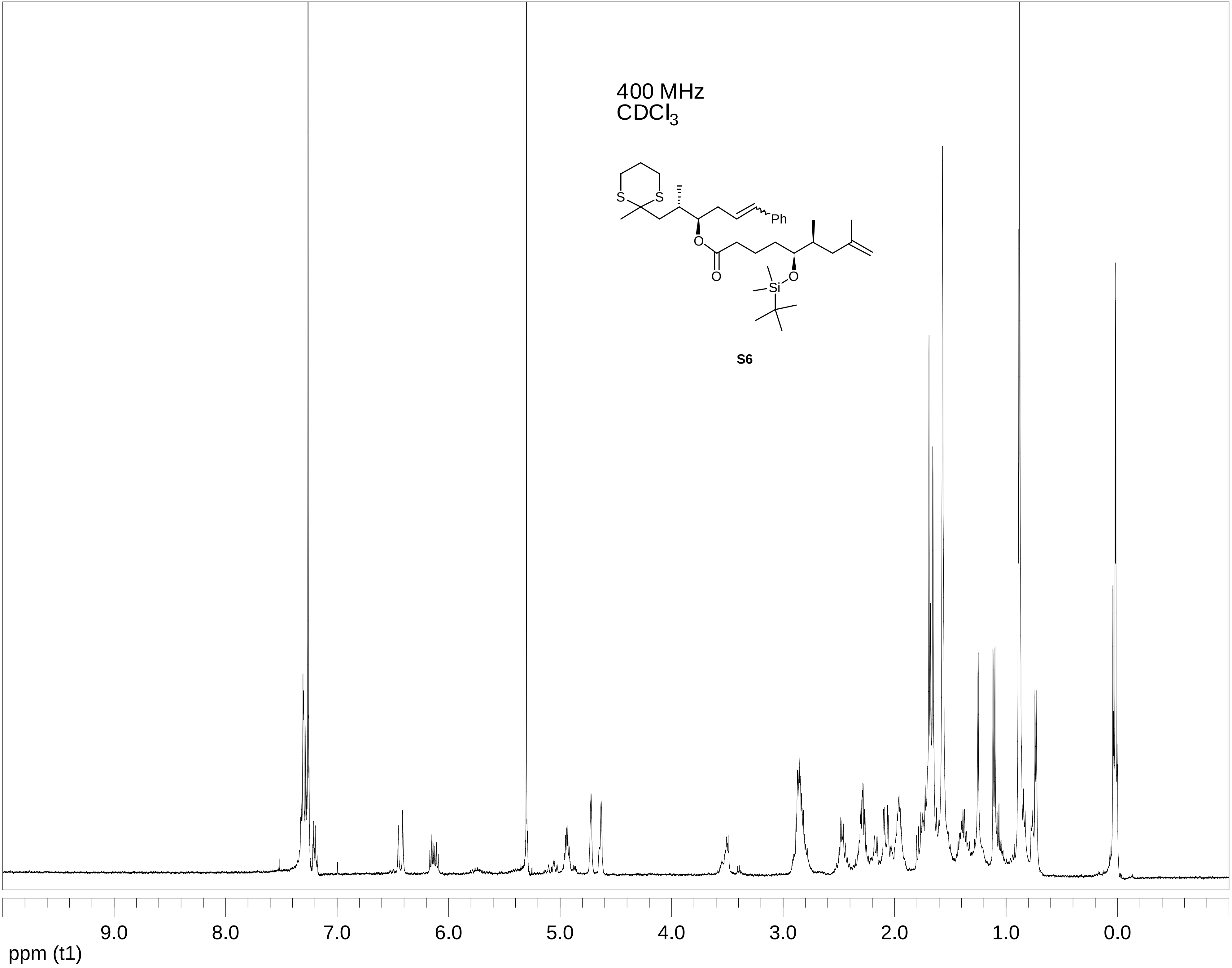


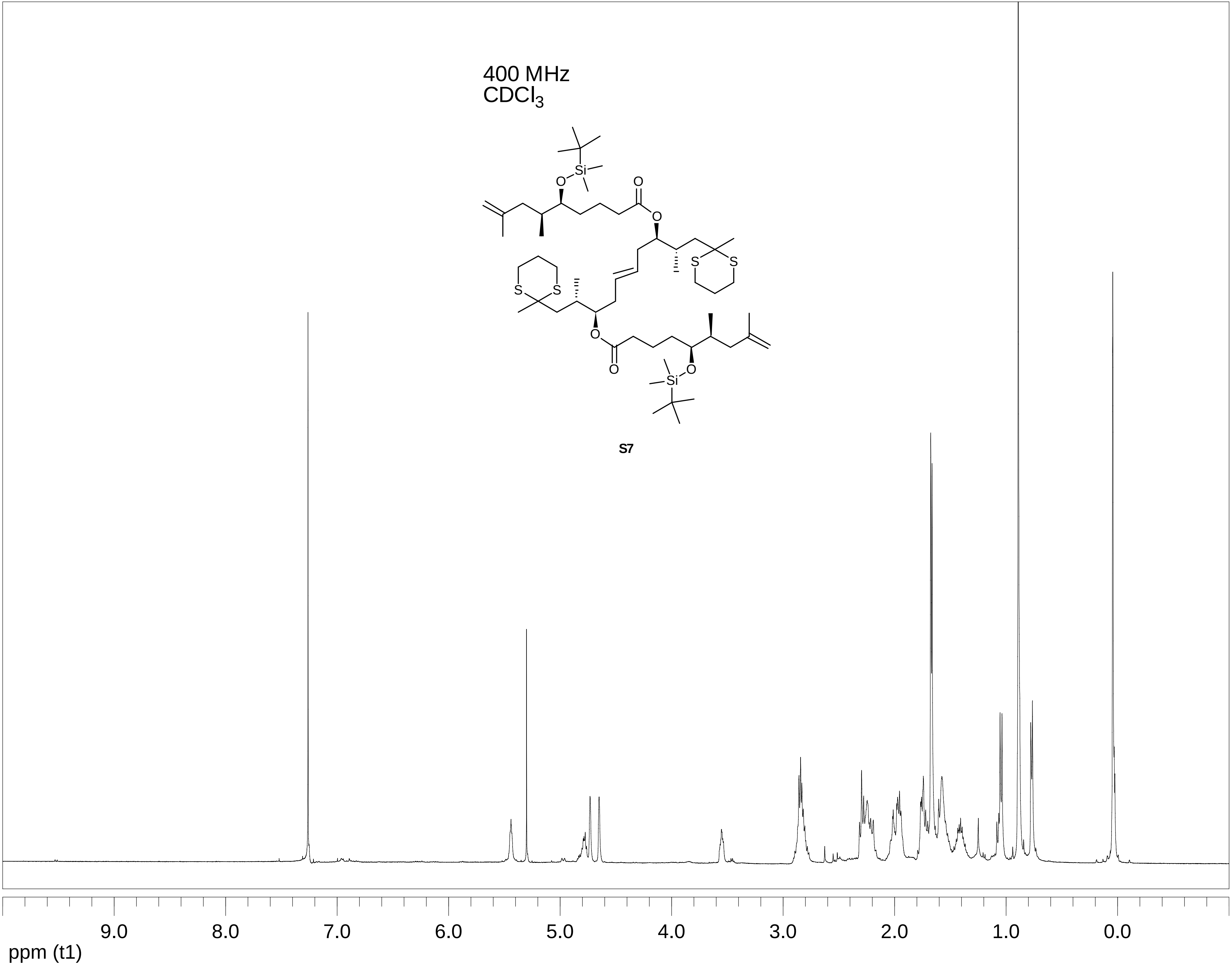
100 MHz
$CDCl_3$

17


500 MHz
$CDCl_3$
S
S
O
O
OTBS
18
1.01
0.94
0.99
4.20
2.14
3.07
2.08
3.13
2.26
9.04
2.19
3.00
3.10
8.06
5.11
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

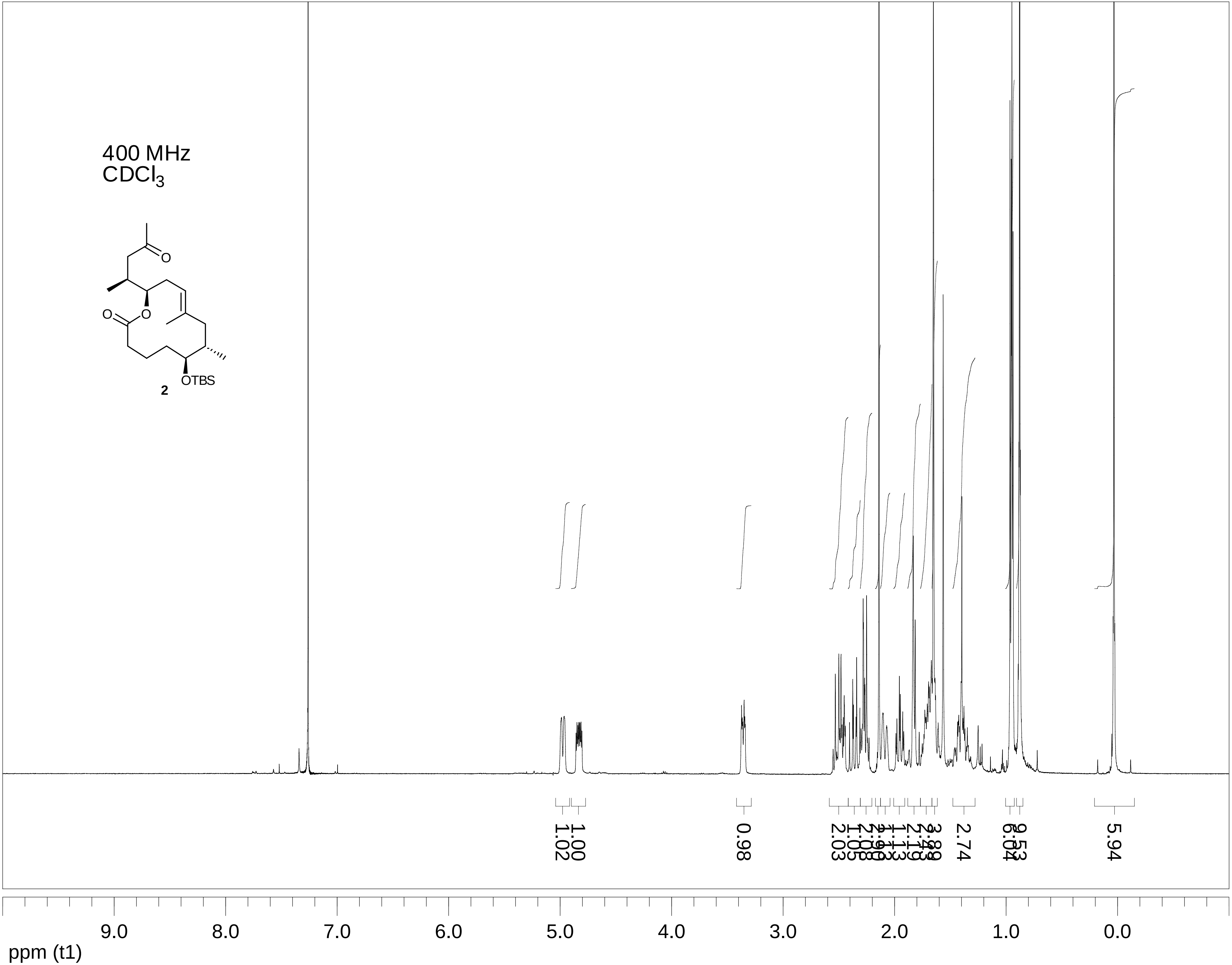

173.82
137.66
121.31
77.53
77.16
76.25
49.47
45.41
44.64
36.18
34.34
33.55
33.50
30.36
28.51
26.91
26.80
26.08
25.30
21.88
18.77
18.55
18.28
75 MHz
CDCl$_3$
S
S
O
O
O
Si
18
200
150
100
50
0
ppm (t1)

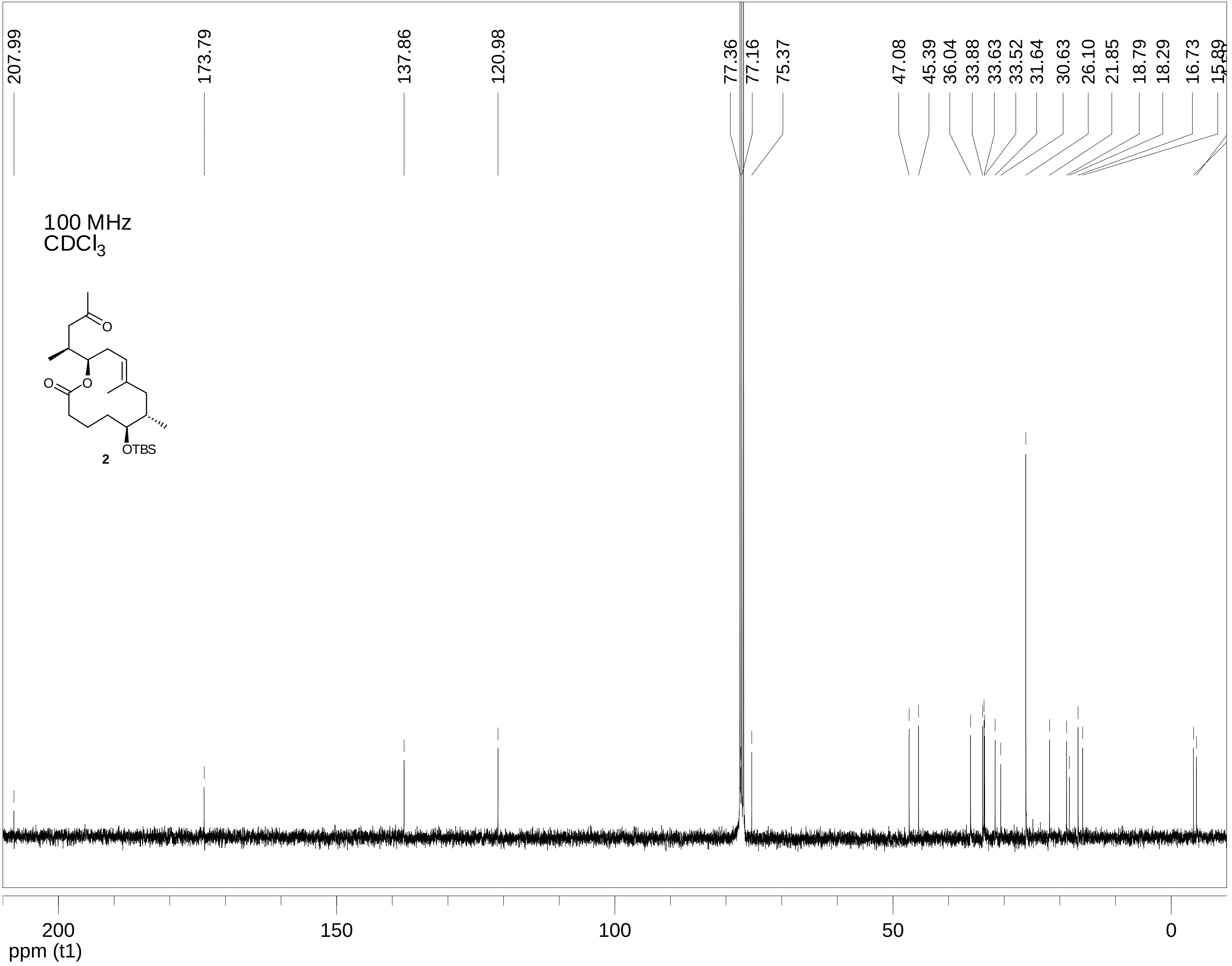

400 MHz
CDCl$_3$
S
S
Ph
O
O
O
Si
S6
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)



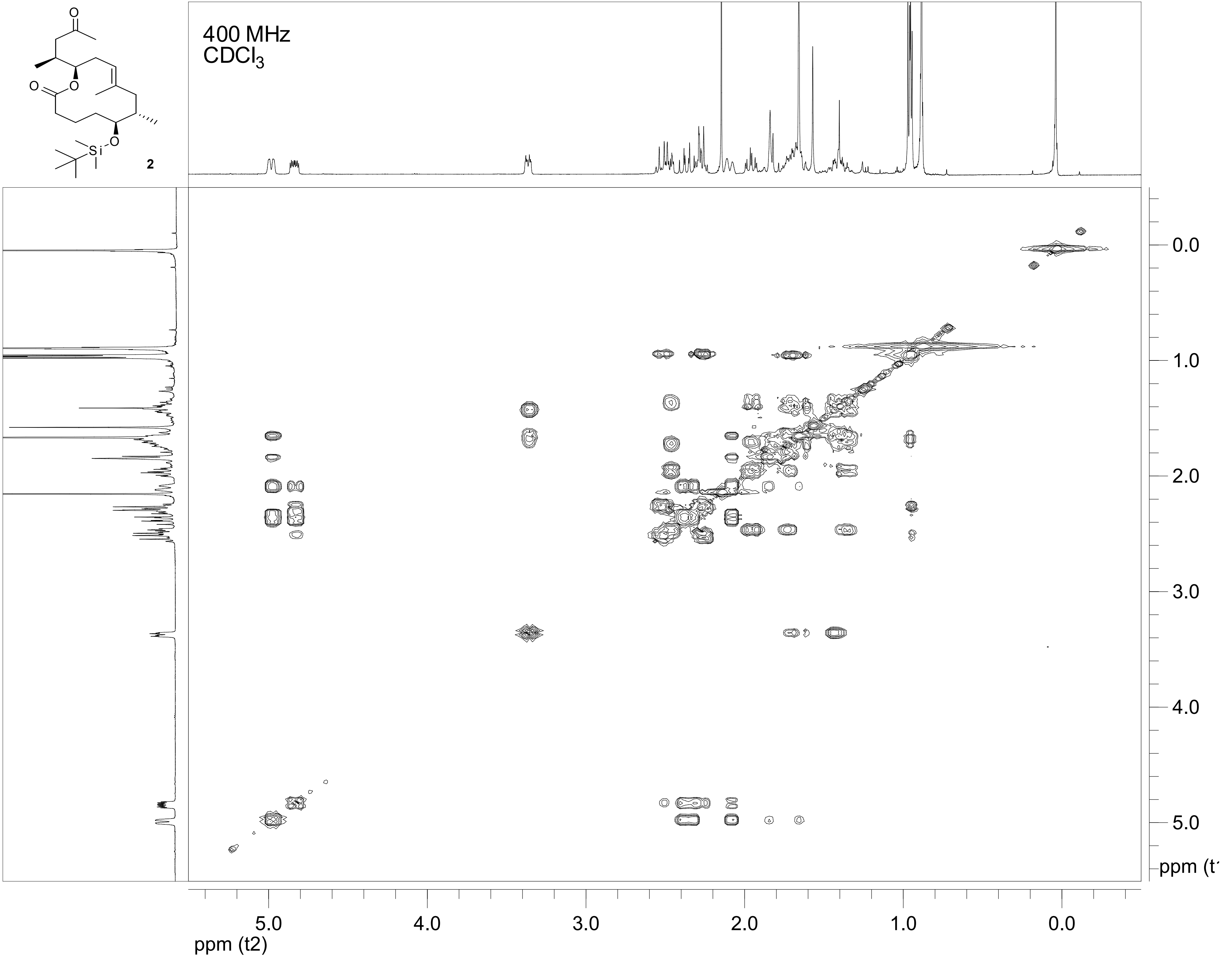
S7

400 MHz
$CDCl_3$
O
Si
O
O
S
S
S
S
O
O
O
Si
O
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

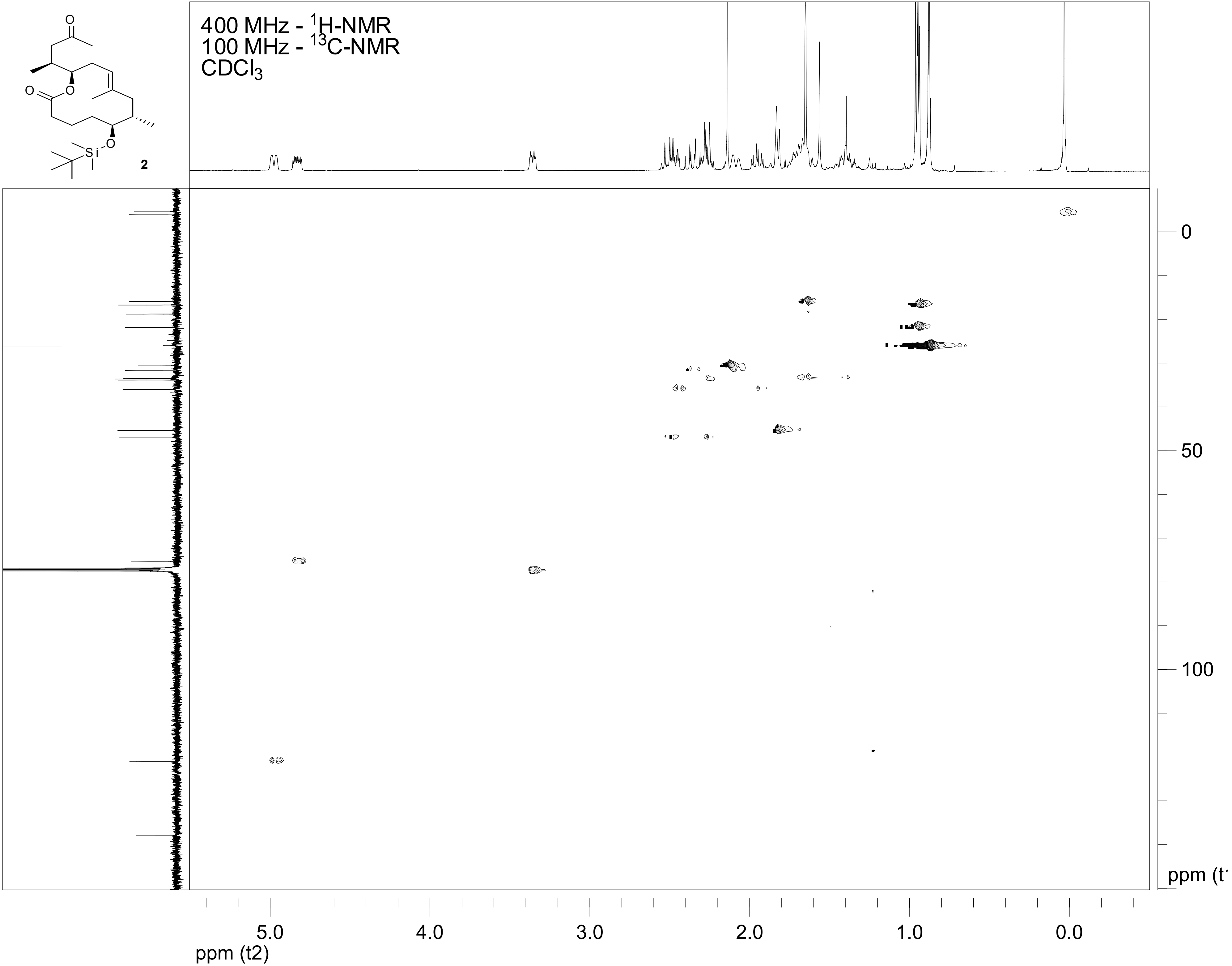

400 MHz
CDCl3
O
O
O
O
OTBS
2
1.02
1.00
0.98
2.03
1.05
2.08
2.00
1.13
1.13
2.19
2.43
3.88
2.74
6.04
9.53
5.94
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)



207.99
173.79
137.86
120.98
77.36
77.16
75.37
47.08
45.39
36.04
33.88
33.63
33.52
31.64
30.63
26.10
21.85
18.79
18.29
16.73
15.89
100 MHz
CDCl$_3$
O
O
O
OTBS
2
200
150
100
50
0
ppm (t1)



2



2
400 MHz - ^{1}H-NMR
100 MHz - ^{13}C-NMR
$CDCl_3$
O
O
O
O
Si
0
50
100
ppm (t
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t2)

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