Enantioselective synthesis of an ophiobolin sesterterpene via a programmed radical cascade

Supplementary Materials

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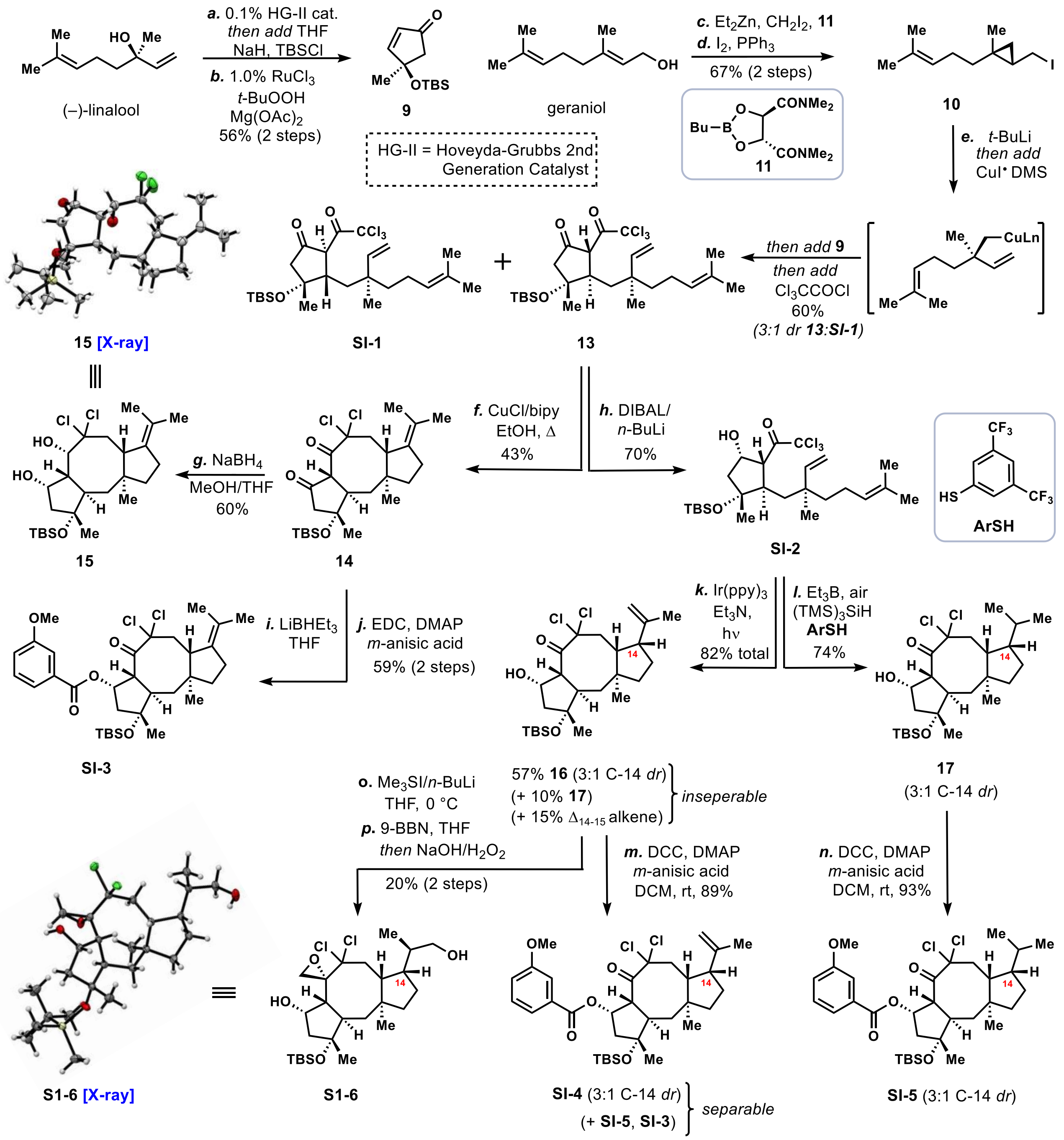
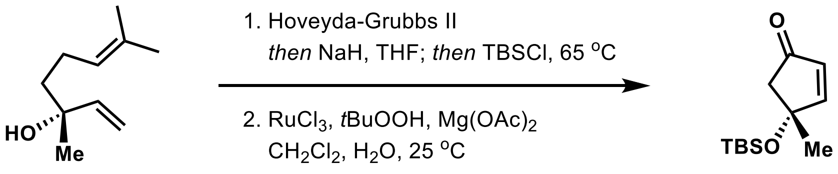
General Procedures

Unless stated otherwise, all reactions were performed in flame-dried glassware under an atmosphere of dry nitrogen or argon. Dry tetrahydrofuran (THF), dichloromethane, diethyl ether (Et_2O), and toluene were obtained either by passing these previously-degassed solvents through activated alumina columns or from Sigma Aldrich SureSeal™ bottles. Dimethoxy ethane, pentane, (L)-linalool, triethylamine (Et_3N), trichloroacetyl chloride, and oxalyl chloride were distilled over calcium hydride prior to use. Geraniol and *trans, trans*-farnesol were purified by column chromatography (7% Et_2O in hexanes → 50% Et_2O in hexanes) prior to use. Chiral boronic ester **11**,[42] acetonide **SI-12**,[43] TADDOL **SI-11**,[44] 2-bromodibenzothiophene (**SI-13**),[45] thiols **25**,[46] **26**,[47] and **27**,[48] and lithium naphthalenide[49] were prepared according to literature procedures. All other reagents were used as received from commercial sources, unless stated otherwise. When indicated, solvents or reagents were degassed by sparging with Argon for 10 minutes in an ultrasound bath at 25 °C. Reactions were monitored by thin layer chromatography (TLC) on Silicycle Siliaplate™ glass-backed TLC plates (250 μm thickness, 60 Å porosity, F-254 indicator) and visualized by UV irradiation or development with an anisaldehyde or phosphomolybdic/cerium sulfate stain. Volatile solvents were removed under reduced pressure with a rotary evaporator. All flash column chromatography was performed using Silicycle SiliaFlash® F60, 230-400 mesh silica gel (40-63 μm). ^1H NMR and ^{13}C NMR spectra were recorded with Bruker AV, AVQ, and DRX spectrometers operating at 300, 400, 500, or 600 MHz for ^1H (75, 100, 125, and 150 MHz for ^{13}C) in $CDCl_3$, benzene-d_6, or acetone-d_6. Except when noted otherwise, chemical shifts are reported relative to the residual solvent signal (^1H NMR: $\delta = 7.26$ ($CDCl_3$); δ 7.16 (benzene-d_6); δ 2.05; ^{13}C NMR: $\delta = 77.16$ ($CDCl_3$); 128.06 (benzene-d_6)). NMR data are reported as follows: chemical shift (multiplicity, coupling constants where applicable, number of hydrogens). Splitting is reported with the following symbols: s = singlet, bs = broad singlet, d = doublet, t = triplet, app t = apparent triplet, dd = doublet of doublets, ddd = doublet of doublet of doublets, dddd = doublet of doublet of doublet of doublets, m = multiplet. IR spectra were recorded on a Nicolet 380 spectrometer using NaCl plates and are reported in frequency of absorption (cm^{-1}). Only selected resonances are reported. High-resolution mass spectra (HRMS) were obtained by the mass spectral facility at the University of California, Berkeley using a Finnigan LTQFT mass spectrometer (Thermo Electron Corporation).

Figure S1: Synthesis scheme for manuscipt Figure 3.



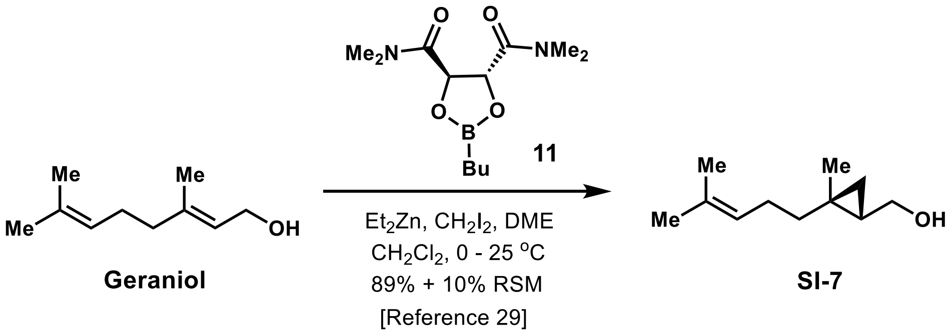
Ester derivatives SI-3, SI-4, and SI-5 were synthesized to reveal the relative components/diastereomeric ratio (*dr*) of cyclization reactions. Derivative SI-6 was synthesized to confirm C-14 selectivity by X-ray crystallographic analysis.



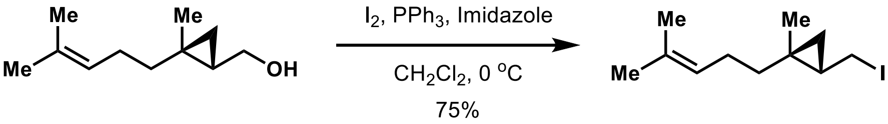
(L)-Linalool **9**

Enone 9: (L)-Linalool (5.8 mL, 32.4 mmol, 1.0 equiv) was transferred to a dry reaction vial equipped with a stir bar and Hoveyda-Grubbs Second Generation Catalyst (20 mg, 0.0319 mmol, 0.0010 equiv). Under a positive nitrogen flow, the reaction was stirred at 25 °C for 45 minutes, during which time significant bubbling was observed (loss of isobutylene). Upon completion of the reaction as determined by TLC, the positive nitrogen flow was ceased and the reaction exposed to air for 15 minutes while stirring at 25 °C. The vial was then quickly backfilled with nitrogen, and THF (6 mL) added. The contents of the vial were transferred to a dry, 500-mL round-bottom flask equipped with a stir bar and an additional 110 mL of THF. The reaction mixture was then cooled to 0 °C, and NaH (60% in mineral oil, 3.89 g, 97.2 mmol, 3.0 equiv) was added. The resulting white suspension was stirred at 0 °C for 5 minutes, at which point TBSCl (7.33 g, 48.6 mmol, 1.5 equiv) was added. The reaction mixture was then heated to 65 °C and stirred at this temperature for 2 hours. After cooling to 0 °C, the reaction was slowly quenched with a saturated aqueous solution of $NaHCO_3$ (40 mL), extracted with Et_2O (3 x 60 mL), washed with brine (75 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The resulting brown oil was then rapidly purified by column chromatography (silica gel pretreated with 2% triethylamine in hexanes, 2% triethylamine in hexanes → 2% trimethylamine, 6% Et_2O in hexanes) to yield 6.75 g of an intermediate cyclopentene (31.8 mmol, 98%). *tert*-Butyl hydrogen peroxide (TBHP, 70% in H_2O, 66.4 mL, 476 mmol, 15 equiv) was added dropwise via syringe pump over a period of 6 hours to the intermediate alkene (6.75 g, 31.8 mmol, 1.0 equiv), $RuCl_3{\cdot}H_2O$ (66 mg, 0.318 mmol, 0.01 equiv), and $Mg(OAc)_2{\cdot}4H_2O$ (13.6 g, 63.5 mmol, 2.0 equiv) in CH_2Cl_2 (71 mL) and H_2O (7 mL) at 25 °C. After the addition was complete, the reaction mixture was stirred for an additional 15 hours at 25 °C, then quenched with saturated aqueous $Na_2S_2O_3$ (60 mL), extracted with Et_2O (3 x 80 mL), washed with a mixture of brine (75 mL) and saturated aqueous $Na_2S_2O_3$ (30 mL), dried over $MgSO_4$, and concentrated *in vacuo* to afford a brown oil. The resulting crude material was purified by column chromatography (3% Et_2O in hexanes → 18% Et_2O in hexanes) to yield 4.09 g of enone **9** (18.1 mmol, 57%) as a colorless oil. **9**: $[\alpha]_D^{25}$ = +27.69° (c = 0.0055 g/mL, $CHCl_3$);

R_f = 0.22 (10% Et_2O in hexanes); ^1H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, *J* = 5.6 Hz, 1 H), 6.04 (d, *J* = 5.6 Hz, 1 H), 2.53 (d, *J* = 18.2 Hz, 1 H), 2.46 (d, *J* = 18.2 Hz, 1 H), 1.48 (s, 3 H), 0.84 (s, 9 H), 0.08 (s, 3 H), 0.07 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 207.2, 167.8, 132.0, 78.4, 51.6, 29.1, 25.7, 18.0, -2.28, -2.34; IR ν_{max} (cm^{-1}) 2956, 2930, 2858, 1722, 1254, 1202; HRMS (EI+) calcd for $C_{12}H_{22}O_2Si$ [M] *m/z* 226.1389, found 226.1393.

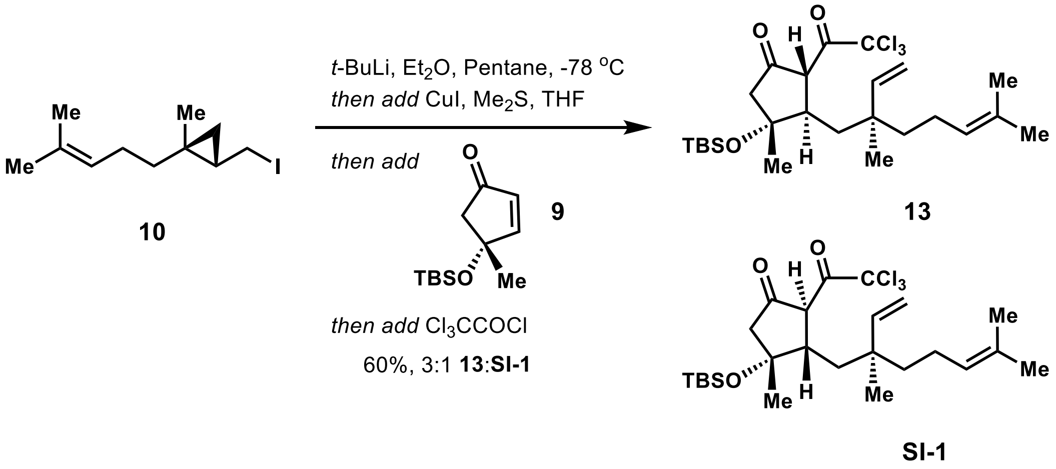


Cyclopropanated Alcohol SI-7:[29] 1,2-Dimethoxyethane (2 mL) and CH_2Cl_2 (24 mL) were added sequentially to a stirring solution of Et_2Zn (1 M in Hexanes, 18 mL, 18.0 mmol, 2.0 equiv) at 25 °C. The reaction mixture was cooled to 0 °C, and CH_2I_2 (2.87 mL, 36.0 mmol, 4.0 equiv) was added dropwise via syringe pump. The resulting solution was stirred for an additional 25 minutes at 0 °C, and then was transferred via canula (over a period of 10 minutes) to a separate round-bottom flask containing geraniol (1.6 mL, 9.00 mmol, 1.0 equiv) and chiral boronic ester (*R*,*R*)-**11** (3.67 g, 13.5 mmol, 1.5 equiv) in CH_2Cl_2 (18 mL). After the transfer was complete, the reaction mixture was stirred for 15 minutes at 0 °C, warmed to 25 °C, and stirred at 25 °C for 5 hours. The reaction mixture was quenched with saturated aqueous NH_4Cl (100 mL), extracted with EtOAc (3 x 100 mL), washed with 3 M HCl (75 mL), 3 M NaOH (2 x 50 mL) and brine (50 mL), dried over $MgSO_4$, and concentrated *in vacuo* to provide a light yellow oil. The crude material was purified by column chromatography (Et_2O in hexanes, 7% → 50%) to yield 1.5 g of a 9:1 inseparable mixture of cyclopropyl alcohol **SI-7** and recovered geraniol (8.04 mmol, 89 + 10% recovered starting material) as a colorless oil. Spectroscopic data was in agreement with that previously reported by Charette and coworkers.[29]



SI-7 **10**

Iodide 10:[30] Iodine (1.24 g, 4.88 mmol, 1.1 equiv) was added to a solution of PPh_3 (1.28 g, 4.89 mmol, 1.1 equiv) and imidazole (542 mg, 7.97 mmol, 1.8 equiv) in CH_2Cl_2 (8 mL) at 25 °C. The resulting yellow/brown-colored suspension was stirred for 5 minutes at 25 °C, then cooled to 0 °C and stirred for another 5 minutes. A solution of cyclopropyl alcohol **SI-7** (745 mg, 4.43 mmol, 1.0 equiv) in CH_2Cl_2 (1 mL) was then added, using an additional 1 mL of CH_2Cl_2 to ensure a quantitative transfer. The reaction mixture was then stirred for 1 hour at 0 °C. Methanol (0.2 mL) was then added and stirring continued until the reaction mixture became homogeneous. H_2O (10 mL) was then added and the reaction mixture was extracted with CH_2Cl_2 (3 x 10 mL), washed with saturated aqueous $NaHSO_3$ (5 mL), and dried over $MgSO_4$. Et_3N (0.1 mL) was added to stabilize cyclopropyl iodide **10** against acid-mediated decomposition. After drying, the combined organic layers were concentrated *in vacuo* at 15 °C in the absence of light to yield a light yellow solid. The crude solid was purified immediately and rapidly by column chromatography (silica gel pretreated with 4% triethylamine in hexanes, eluting with 4% triethylamine in hexanes) to yield 925 mg of cyclopropyl iodide **10** (3.33 mmol, 75%) as a colorless liquid. The isolated iodide generally contains around 10% inseparable alkene decomposition products. (**Note:** The column must be performed in less than 1 minute; otherwise the amount of decomposed material is substantially higher). The iodide **10** obtained was immediately used in the subsequent reaction, as extensive decomposition upon storage has been observed. **10**: $[\alpha]_D^{25}$ = -18.00° (c = 0.001 g/mL, $CHCl_3$); R_f = 0.71 (25% Et_2O in hexanes); ^1H NMR (600 MHz, benzene-d_6) δ 5.04 (app t, J = 7.1 Hz, 1 H), 3.14 (dd, J = 9.9, 6.9 Hz, 1 H), 2.78 (app t, J = 9.8 Hz, 1 H), 2.04-1.94 (m, 2 H), 1.61 (s, 3 H), 1.52 (s, 3 H), 1.29-1.17 (m, 1 H), 1.02-0.92 (m, 2 H), 0.92 (s, 3 H), 0.44 (dd, J = 8.5, 4.7 Hz, 1 H), -0.11 (app t, J = 5.1 Hz, 1 H); ^{13}C NMR (150 MHz, benzene-d_6) δ 131.0, 125.0, 41.6, 28.2, 26.0, 25.9, 25.0, 24.0, 17.9, 15.8, 9.1.



Diketones 13 and SI-1: (NOTE: In our hands, the specific reaction setup and conditions utilized in this procedure were necessary for the success of this reaction; deviation of seemingly trivial factors such as flask shape proved detrimental. However, when the precise setup described in the procedure and shown in the images below was employed, the reaction outcome was highly reproducible. This reaction has been repeated over 10 times with consistent results.)

A fresh sample of cyclopropyl iodide **10** (825 mg, 2.96 mmol, 1.3 equiv) was azeotropically dried by adding benzene and removing the benzene *in vacuo* at 15 °C. The material obtained was then transferred, using Et_2O (11 mL), to a dry 100-mL sealed tube equipped with a stir bar, Pentane (15 mL), a rubber septum secured with Parafilm, and a nitrogen inlet (see Image A on page S10 for setup of reaction flask). This solution was then cooled to -78 °C using a dry ice and acetone bath that allowed for placement of the reaction flask as close to the magnetic stir plate as possible (see Image C). The reaction flask was also excluded from light for the duration of the ensuing procedural steps. *tert*-Butyllithium (1.7 M in pentane, 3.6 mL, 6.14 mmol, 2.7 equiv) was added dropwise over a period of 10 minutes down the walls of the reaction tube. The resulting white suspension was stirred at -78 °C for 2.5 hours. In a separate reaction vial, Me_2S (0.36 mL, 4.86 mmol, 2.1 equiv) was added to a suspension of CuI (230 mg, 1.21 mmol, 0.53 equiv) in THF (2.9 mL) and the mixture was stirred until a colorless solution formed. This solution was then added dropwise to the solution containing the lithiate of **10**. The resulting light yellow suspension was stirred for 15 minutes at -78 °C. (NOTE: during this part of the reaction, the magnetic stirring can terminate due to the formation of solids; this should be prevented, if possible, by increasing the rate of stirring.) A solution of enone **9** (516 mg, 2.28 mmol, 1.0 equiv) in Et_2O (1.6 mL) was then added dropwise. The resulting orange suspension was stirred for 4 hours, slowly warming from -78 °C to -40 °C. Upon reaching -40 °C, the reaction mixture was cooled back to -78 °C, and Cl_3CCOCl (0.84 mL, 7.52 mmol, 3.3 equiv) was added dropwise. The resulting gray suspension was stirred for 2 hours, slowly warming from -78 °C to -40 °C. Upon reaching -40 °C, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ (12 mL), stirred at room temperature for 30 minutes, then poured into water (20 mL). NH_4OH (0.5 mL) was added, and the mixture was extracted with Et_2O (3 x 30 mL), washed with brine (20 mL), dried over $MgSO_4$, and concentrated *in vacuo* to provide a brown oil. The crude product was purified by column chromatography (2% CH_2Cl_2 in hexanes → 28% CH_2Cl_2 in hexanes) to yield 538 mg of diketone **13** (1.03 mmol, 45%) and 178 mg of diketone **SI-1** (0.340 mmol, 15%) as light yellow oils. **13**: $[\alpha]_D^{25}$ = -25.82° (c = 0.0055 g/mL, $CHCl_3$); R_f = 0.55 (50% CH_2Cl_2 in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 5.59 (d, *J* = 17.5, 10.7 Hz, 1 H), 5.05 (app t, *J* = 7.5 Hz, 1 H), 5.01 (d, *J* = 10.5 Hz, 1 H), 4.90 (d, *J* = 17.4, 1 H), 4.01 (d, *J* = 10.8 Hz, 1 H), 2.89-2.82 (m, 1 H), 2.69 (d, *J* = 16.6 Hz, 1 H), 2.55 (d, *J* = 16.6 Hz, 1 H), 1.91-1.76 (m, 3 H), 1.66 (s, 3 H), 1.56 (s, 3 H), 1.47 (dd, *J* = 14.5, 7.0 H, 1 H), 1.38-1.28 (m, 1 H), 1.28-1.28 (m, 1 H), 1.25 (s, 3 H), 1.00 (s, 3 H), 0.90 (s, 9 H), 0.13 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.2, 185.6, 145.4, 131.4, 124.8, 114.5, 96.3, 76.9, 62.2, 55.1, 49.3, 43.0, 41.5, 39.6, 26.0, 25.8, 23.9, 23.0, 21.1, 18.1, 17.7, -2.1, -2.2; IR ν_{max} (cm^{-1}) 2956, 2930, 2858, 1763, 1733, 1471, 1463, 1383, 1260; HRMS (ESI) calcd for $C_{25}H_{40}O_3Cl_3Si$ [M – H^+] *m/z* 521.1818, found 521.1824. **SI-1**: $[\alpha]_D^{25}$ = +24.00° (c = 0.003 g/mL, $CHCl_3$); R_f = 0.51 (50% CH_2Cl_2 in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 5.60 (d, *J* = 17.5, 10.7 Hz, 1 H), 5.09-5.04 (m, 2 H), 4.93 (d, *J* = 17.5, 1 H), 4.34 (d, *J* = 11.3 Hz, 1 H), 2.56 (d, *J* = 17.9 Hz, 1 H), 2.47 (d, *J* = 17.9 Hz, 1 H), 2.39 (ddd, *J* = 11.3, 3.6, 3.6 Hz, 1 H), 1.96 (dd, *J* = 15.5, 2.9 Hz, 1 H), 1.92-1.79 (m, 1 H), 1.67 (s, 3 H), 1.57 (s, 3 H), 1.57-1.52 (m, 1 H), 1.40 (s, 3 H), 1.34-1.21 (m, 3 H), 0.84 (s, 9 H), 0.83 (s, 3 H), 0.14 (s, 3 H), 0.08 (s 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.8, 186.5, 146.3, 131.5, 124.7, 113.7, 96.6, 79.2, 62.6, 54.5, 49.9, 42.9, 40.0, 39.4, 25.83, 25.79, 25.5, 23.1, 20.7, 18.4, 17.7, -2.2, -2.6; IR ν_{max} (cm^{-1}) 2955, 2929, 2857, 1766, 1734, 1462, 1383, 1275; HRMS (ESI) calcd for $C_{25}H_{40}O_3Cl_3Si$ [M – H^+] *m/z* 521.1818, found 521.1827.

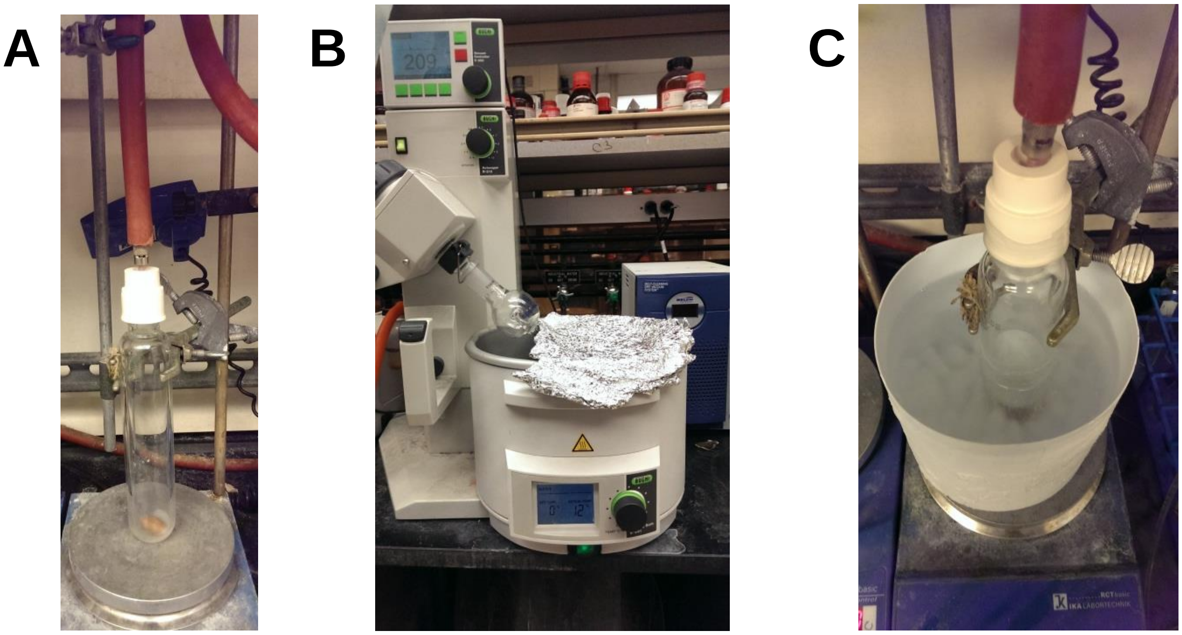


Image A: Reaction tube set up for flame drying. **Image B**: Concentration of iodide **10**, excluded from light and at cold temperature, to prevent decomposition. **Image C**: Reaction right before adding *t*-BuLi. The "cooling bath" allows placement of the magnetic stir bar closer to the stir plate which is essential for maximal stirring.

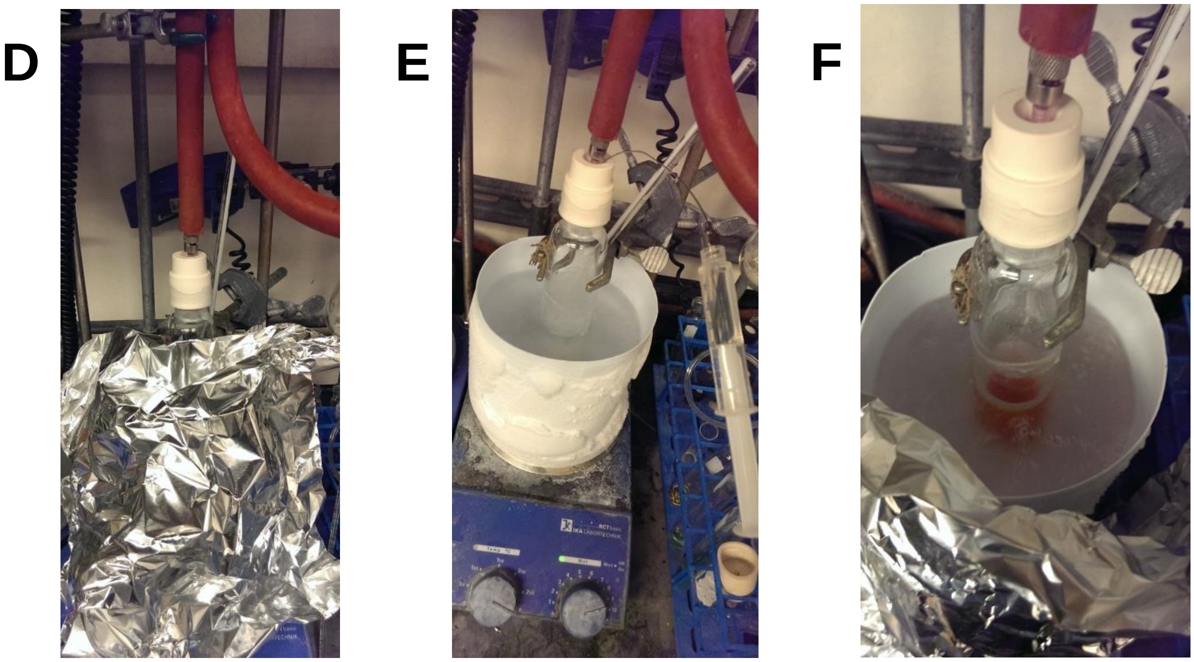


Image D: Reaction following *t*-BuLi addition. In the early stages of the reaction, light should be excluded to prevent decomposition of **10**. **Image E**: Immediately prior to addition of CuI, the reaction appears as a white suspension. The copper iodide-dimethyl sulfide solution in THF is in the syringe on the right. The stirring rate (bottom right) has been increased to a high setting during the addition of copper (returned to normal setting after addition of enone **9**). **Image F**: After addition of enone **9**, the reaction assumes a dark orange color.

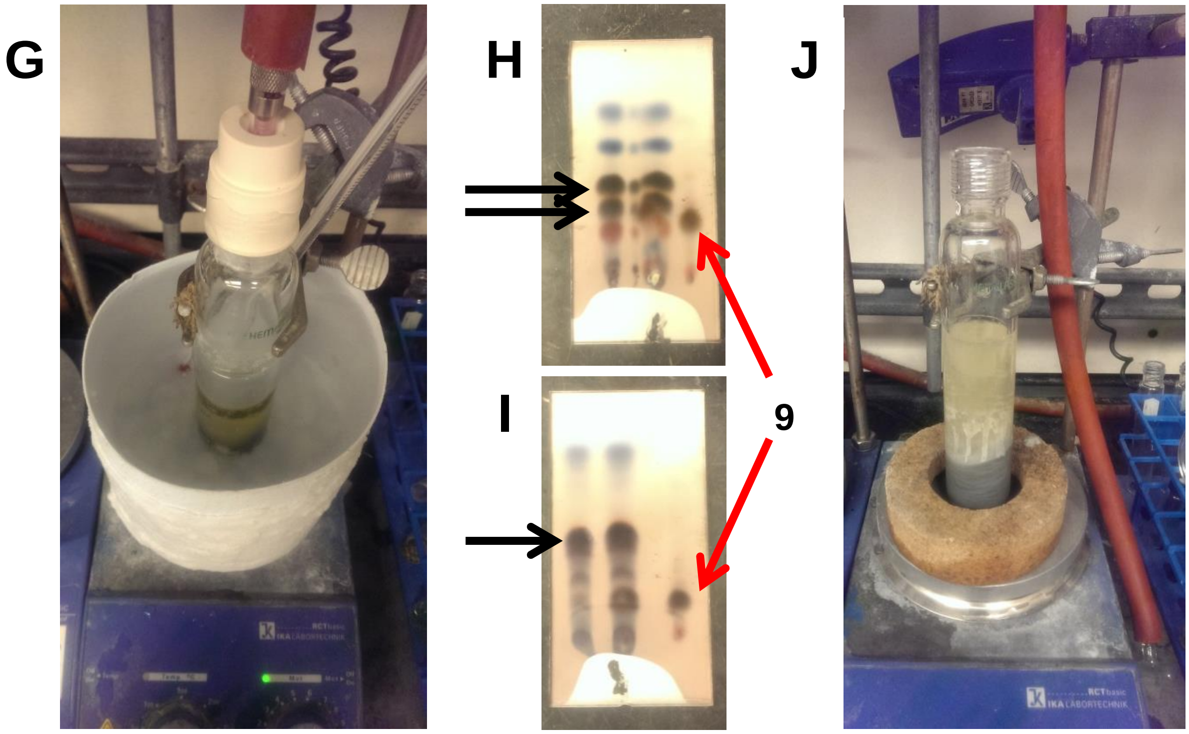
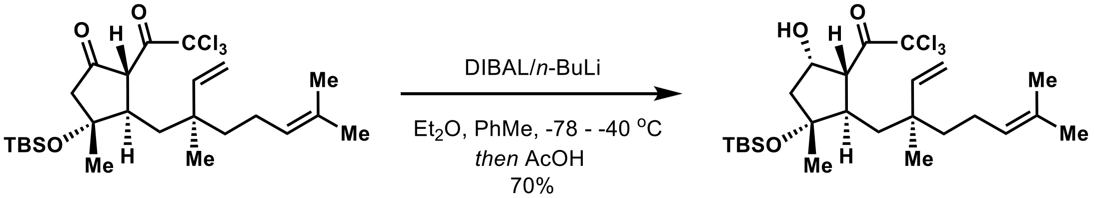


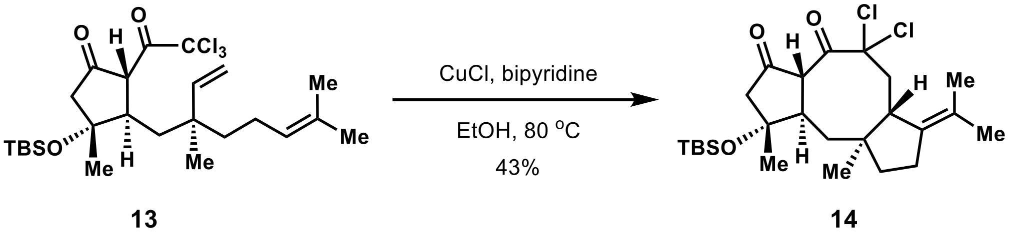
Image G: After adding Cl_3CCOCl, the reaction turns yellow-grey. **Image H**: TLC (17% Et_2O in hexanes) before Cl_3CCOCl addition. Enone **9** is indicated by the red arrow, and the black arrows indicate the two diastereomers of intermediate 1,4-addition product. **Image I**: TLC (17% Et_2O in hexanes) after Cl_3CCOCl addition. Enone **9** is indicated by the red arrow, and the mixture of **13** and **SI-2** by the black arrow. TLCs are visualized by anisaldehyde



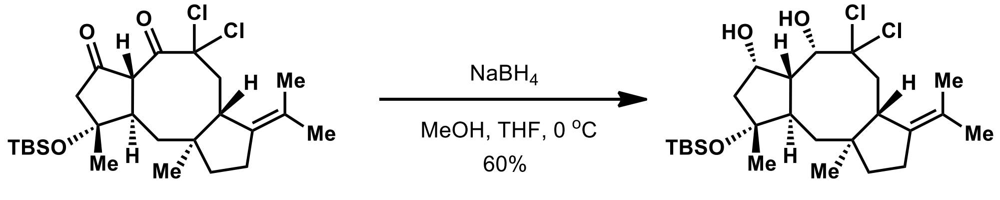
13

SI-2

Keto-alcohol SI-2: *n*-Butyllithium (2.5 M in hexanes, 0.17 mL, 0.422 mmol, 1.0 equiv) was added dropwise to a solution of DIBAL (0.075 mL, 0.422 mmol, 1.0 equiv) in Et_2O (4.2 mL) at -15 °C. The resulting solution was stirred at -15 °C for 1 hour, then slowly transferred to a solution of **13** (221 mg, 0.422 mmol, 1.0 equiv) in toluene (23 mL) at -78 °C. The reaction mixture was stirred for 1 hour, then slowly warmed to -40 °C. The reaction mixture was then cooled back to -78 °C and AcOH (6.0 equiv) added dropwise. The resulting solution was then stirred at -78 °C for 5 minutes, warmed to 0 °C over the course of 1 hour, quenched with saturated aqueous $NaHCO_3$ (8 mL), extracted with Et_2O (3 x 25 mL), washed with brine (20 mL), dried over $MgSO_4$, and concentrated *in vacuo* to yield a light yellow oil. The crude residue was purified by column chromatography (2% Et_2O in hexanes → 12% Et_2O in hexanes) to provide 155 mg of keto-alcohol **SI-2** (0.295 mmol, 70%) as a colorless oil. **SI-2**: $[\alpha]_D^{25}$ = +26.25° (c = 0.008 g/mL, $CHCl_3$); R_f = 0.25 (15% Et_2O in hexanes); ^1H NMR (500 MHz, benzene-d_6) δ 5.67 (dd, *J* = 17.5, 10.8 Hz, 1 H), 5.22 (dddd, *J* = 8.7, 5.7, 2.8, 1.3 Hz, 1 H), 5.09 (dd, *J* = 10.8, 1.3 Hz, 1 H), 4.95 (dd, *J* = 17.7, 1.4 Hz, 1 H), 4.32-4.25 (m, 1 H), 3.41 (dd, *J* = 8.4, 7.4 Hz, 1 H), 2.88 (ddd, *J* = 7.7, 7.6, 3.9 Hz, 1 H), 2.80 (d, *J* = 9.7 Hz, 1 H), 2.02-1.93 (m, 2 H), 1.81 (dd, *J* = 12.9, 4.6 Hz, 1 H), 1.69 (s, 3 H), 1.61 (dd, *J* = 12.9, 5.9 Hz, 1 H), 1.57 (s, 3 H), 1.53 (dd, *J* = 14.4, 4.1 Hz, 1 H), 1.41-1.31 (m, 2 H), 1.04 (s, 3 H), 1.04-0.97 (m, 1 H), 0.97 (s, 3 H), 0.95 (s, 9 H), 0.16 (s, 3 H), 0.08 (s, 3 H); ^{13}C NMR (100 MHz, benzene-d_6) δ 188.6, 146.3, 131.0, 125.5, 113.8, 97.3, 83.5, 73.6, 59.6, 51.2, 48.8, 44.4, 42.8, 39.9, 26.3, 25.9, 24.9, 23.5, 21.6, 18.3, 17.7, -1.8, -1.9; IR ν_{max} (cm^{-1}) 2957, 2929, 2857, 1735, 1449, 1383; HRMS (ESI) calcd for $C_{25}H_{42}O_3Cl_3Si$ $[M - H^+]$ *m/z* 523.1974, found 523.1986.



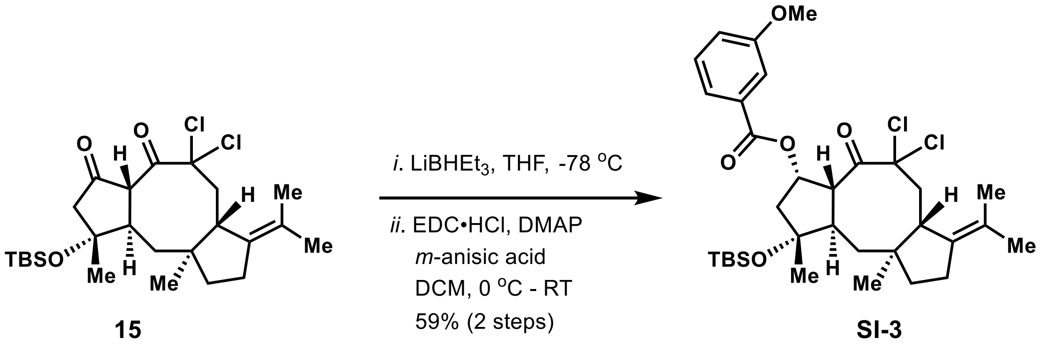
Cyclization Product 14: A solution of **13** (150 mg, 0.286 mmol, 1.0 equiv) in degassed EtOH (4.6 mL) was added to CuCl (20.0 mg, 0.200 mmol, 0.7 equiv) and bipyridine (40.0 mg, 0.275 mmol, 0.9 equiv). The resulting blue suspension was heated at 80 °C for 90 minutes, then cooled and quenched with H_2O (8 mL), extracted with Et_2O (3 x 10 mL), washed with brine (10 mL) dried over $MgSO_4$, and concentrated *in vacuo* to yield a yellow oil. The crude material was purified by column chromatography (3% CH_2Cl_2 in hexanes → 42% CH_2Cl_2 in hexanes) to provide 60 mg of cyclization product **14** (0.123 mmol, 43% yield) as a colorless oil. **14**: $[\alpha]_D^{25}$ = -42.2° (c = 0.005 g/mL, $CHCl_3$); R_f = 0.39 (50% CH_2Cl_2 in hexanes); ^1H NMR (600 MHz, benzene-d_6) δ 4.17 (d, *J* = 11.6 Hz, 1 H), 2.80 (d, *J* = 16.1 Hz, 1 H), 2.72 (ddd, *J* = 12.2, 12.2, 3.0 Hz, 1 H), 2.66-2.60 (m, 2 H), 2.50 (dd, *J* = 16.1, 10.4 Hz, 1 H), 2.24 (d, *J* = 16.4 Hz, 1 H), 2.04 (dd, *J* = 14.2, 6.2 Hz, 1 H), 1.86 (dd, *J* = 13.4, 3.0 Hz, 1 H), 1.76 (s, 3 H), 1.53 (s, 3 H), 1.23-1.11 (m, 3 H), 1.04 (app t, *J* = 13.1 Hz, 1 H), 0.87 (s, 9 H), 0.73 (s , 3 H), 0.60 (s, 3 H), -0.08 (s, 3 H), -0.10 (s, 3 H); ^{13}C NMR (150 MHz, benzene-d_6) δ 206.0, 199.8, 141.3, 123.2, 93.4, 76.7, 66.2, 56.0, 53.9, 51.5, 46.3, 44.7, 43.3, 43.2, 28.4, 25.8, 23.5, 22.3, 21.6, 20.9, 18.1, -2.5, -2.7; IR ν_{max} (cm^{-1}) 2954, 2930, 2857, 1761, 1718, 1472, 1469, 1383, 1259; HRMS (ESI) calcd for $C_{25}H_{39}O_3Cl_2Si$ [M – H$^+$] *m/z* 485.2051, found 485.2050.



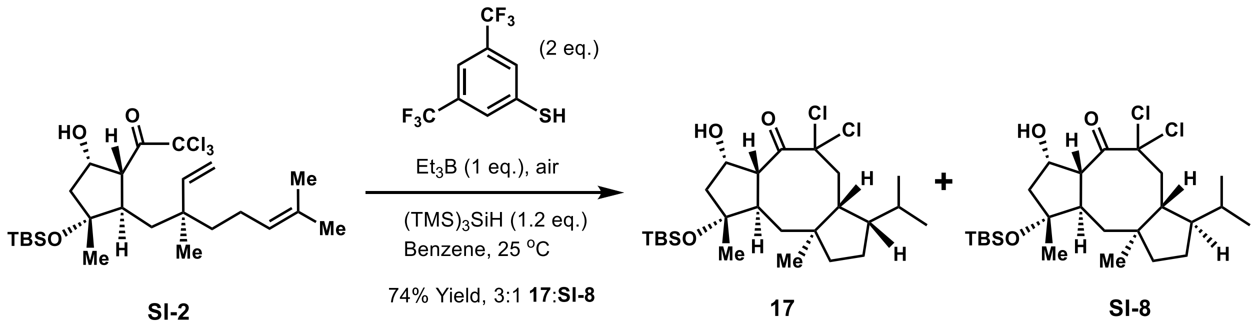
14 **15 [x-ray]**

Diol 15: Sodium borohydride (2 mg, 0.0529 mmol, 5.1 equiv) was added to **14** (5 mg, 0.0102 mmol, 1.0 equiv) in MeOH (0.4 mL) and THF (0.1 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 30 minutes, quenched with H_2O (2 mL), extracted with Et_2O (3 x 3 mL), washed with brine (2 mL), dried over $MgSO_4$, and concentrated *in vacuo* to yield a colorless oil. The crude residue was purified by column chromatography (4% Et_2O in hexanes → 30% Et_2O in hexanes) to provide 3 mg of diol **15** (0.00610 mmol, 60%) as a white solid. Vapor diffusion of an Et_2O solution of **15** with pentane yielded X-ray quality crystals. **15**: $[\alpha]_D^{25}$ = +20.63° (c = 0.0053 g/mL, $CHCl_3$); R_f = 0.26 (18% Et_2O in hexanes); mp 150-151 °C; ^{1}H NMR (600 MHz, benzene-d_6) δ 4.73 (d, *J* = 4.4 Hz, 1 H), 3.97-3.92 (m, 1 H), 2.93 (d, *J* = 9.3 Hz, 1 H), 2.83-2.81 (m, 2 H), 2.80 (d, *J* = 4.5 Hz, 1 H), 2.63 (dd, *J* = 11.4, 9.0 Hz, 1 H), 2.53-2.49 (m, 1 H), 2.20 (dd, *J* = 8.4, 6.0 Hz, 1 H), 2.18-2.07 (m, 2 H), 1.97 (s 3 H), 1.86 (dd, *J* = 13.0, 3.5 Hz, 1 H), 1.75 (dd, *J* = 13.4, 2.2 Hz, 1 H), 1.60 (s, 3 H), 1.42 (dd, *J* = 12.6, 5.4 Hz, 1 H), 1.38-1.34 (m, 1 H), 1.25 (ddd, *J* = 12.4, 12.2, 7.7 Hz, 1 H), 1.06 (s, 3 H), 0.98 (s, 3 H), 0.97 (s, 9 H), 0.62 (app t, *J* = 13.1 Hz, 1 H), 0.14 (s, 3 H), 0.11 (s, 3 H); ^{13}C NMR (150 MHz, benzene-d_6) δ 141.5, 123.5, 102.3, 85.2, 77.8, 76.0, 49.9, 49.5, 46.9, 46.6, 44.7, 44.0, 43.7, 43.5, 29.0, 26.2, 25.3, 23.1, 21.4, 21.3, 18.2, -1.9, -2.0; IR ν_{max} (cm^{-1}) 3365, 2927, 2856, 1469, 1430, 1377, 1256; HRMS (ESI) calcd for $C_{25}H_{44}O_3Cl_2NaSi$ [M + Na$^+$] *m/z* 513.2329, found 513.2332.

Synthesis of Pure Ester Derivative SI-3: The independent synthesis of **SI-3** allows for its identification among a mixture of products obtained in the photoredox cyclization of keto-alcohol **14** (see page S18-S19).



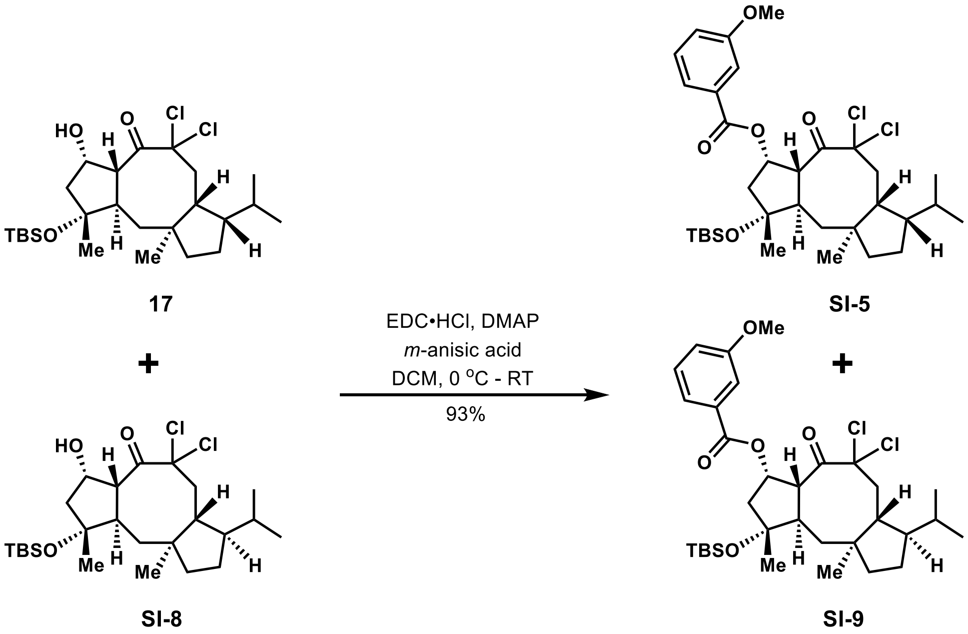
i. Lithium triethylborohydride (1 M in THF, 0.12 mL, 0.120 mmol, 0.98 equiv) was added to **15** (60 mg, 0.122 mmol, 1.0 equiv) in THF (3 mL) at -78 °C, and the resulting solution stirred at -78 °C for 30 minutes. The reaction mixture was then quenched with saturated aqueous NH_4Cl (2 mL), extracted with Et_2O (3 x 6 mL), washed with brine (8 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The crude residue was purified by column chromatography (2% Et_2O in hexanes → 12% Et_2O in hexanes) to provide 39 mg of a keto-alcohol intermediate (0.0797 mmol, 65%) as a colorless oil. *ii*. DMAP (3.6 mg, 0.0295 mmol, 0.40 equiv), *meta*-anisic acid (17 mg, 0.112 mmol, 1.5 equiv) and CH_2Cl_2 (5 mL) were added to the keto-alcohol (36 mg, 0.0735 mmol, 1.0 equiv), and the resulting solution was cooled to 0 °C. EDC·HCl (21 mg, 0.110 mmol, 1.5 equiv) was then added, and the solution stirred for 1 hour, slowly warmed 25 °C, and stirred for 10 hours. The reaction mixture was then quenched with 1 M HCl (4 mL), extracted with CH_2Cl_2 (3 x 10 mL), washed with brine (10 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The resulting crude material was then purified by column chromatography (2 % Et_2O in hexanes → 8% Et_2O in hexanes) to provide 42 mg of ester **SI-3** (0.0672 mmol, 91%) as a colorless oil. **SI-3**: $[\alpha]_D^{25}$ = +56.53° (c = 0.0056 g/mL, $CHCl_3$); R_f = 0.23 (6% Et_2O in hexanes); ^{1}H NMR (600 MHz, benzene-d_6) δ 8.00 (dd, *J* = 7.6, 1.4 Hz, 1 H), 7.91 (dd, *J* = 2.8, 1.4 Hz, 1 H), 7.01 (app t, *J* = 7.9 Hz, 1 H), 6.88 (dd, *J* = 8.3, 2.7 Hz, 1 H), 5.60 (ddd, *J* = 10.1, 10.1, 6.6 Hz, 1 H), 4.00 (app t, *J* = 9.8 Hz, 1 H), 3.39 (s, 3 H), 2.83 (d, *J* = 16.0 Hz, 1 H), 2.77-2.68 (m, 2 H), 2.55 (dd, *J* = 16.0, 10.4 Hz, 1 H), 2.48 (app t, *J* = 11.0 Hz, 1 H), 2.38 (dd, *J* = 11.3, 6.6 Hz, 1 H), 2.04 (dd, *J* = 14.2, 6.0 Hz, 1 H), 1.85-1.77 (m, 1 H), 1.78 (s 3 H), 1.75 (dd, *J* = 13.7, 2.7 Hz, 1 H), 1.53 (s, 3 H), 1.24-1.14 (m, 2 H), 0.95 (app t, *J* = 12.6 Hz, 1 H), 0.93 (s, 9 H), 0.85 (s, 3 H), 0.65 (s, 3 H), 0.05 (s, 3 H), 0.02 (s, 3 H); ^{13}C NMR (150 MHz, benzene-d_6) δ 200.3, 165.9, 160.3, 141.3, 131.8, 129.9, 123.0, 122.7, 120.8, 114.0, 93.6, 79.0, 72.1, 55.3, 55.0, 51.7, 50.4, 47.4, 46.0, 44.8, 43.9, 43.6, 28.3, 25.9, 23.8, 22.3, 21.6, 20.9, 18.2, -2.3, -2.4; IR ν_{max} (cm^{-1}) 2954, 2931, 2856, 1724, 1600, 1490, 1464, 1276; HRMS (ESI) calcd for $C_{33}H_{48}O_5Cl_2NaSi$ [M + Na$^+$] *m/z* 645.2540, found 645.2544.



SI-2 **17** **SI-8**

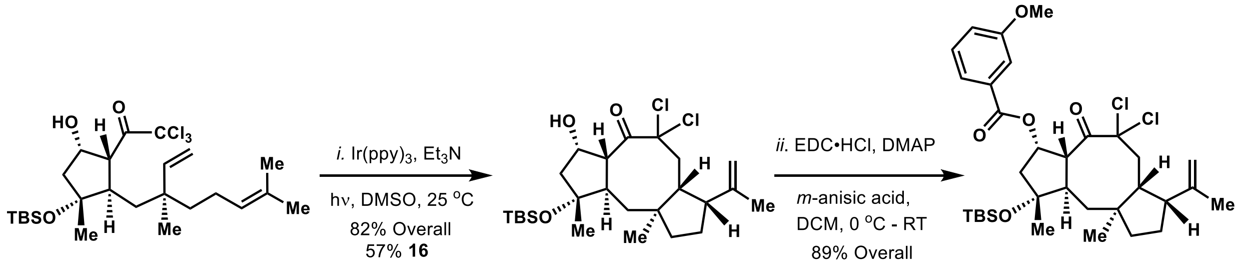
Reductive Cyclization Products 17 and SI-8: (TMS)$_3$SiH (14 µL, 0.0454 mmol, 1.2 equiv) and 3,5-bis(trifluoromethyl)thiophenol (13 µL, 0.0771 mmol, 2.0 equiv) were added to **SI-2** (20 mg, 0.0380 mmol, 1.0 equiv), and the reaction vessel was evacuated and backfilled with N_2. This cycle was repeated two additional times. Degassed benzene (3.5 mL) was added, followed by Et_3B (1M in THF, 38 µL, 0.0380 mmol, 1.0 equiv). Air (0.5 mL) was then injected directly into the stirring solution via a syringe equipped with a long needle. The reaction mixture was stirred at room temperature for 1.5 hours, concentrated *in vacuo*, methanol (3 mL) added, and the resulting solution concentrated again. The crude material was purified by column chromatography (4% CH_2Cl_2 in hexanes → 60% CH_2Cl_2 in hexanes) to yield 14 mg of an inseparable 3:1 mixture of **17** and **SI-8** (0.0283 mmol total, 74%) as a light yellow oil. The diastereomeric ratio (*dr*) of **17** and **SI-8** could be quantitatively determined by derivatization as the ester of *meta*-anisic acid (see below). The major and minor diastereomers have been separately assigned for ^{1}H and ^{13}C NMR through a careful analysis of the spectrum of the mixture and 2D ^{1}H-^{1}H COSY analysis. **17 and SI-8**: R$_f$ = 0.17 (60% CH_2Cl_2 in hexanes); IR ν_{max} (cm^{-1}) 3567, 2956, 2929, 2857, 1728, 1463, 1383, 1256; HRMS (ESI) calcd for $C_{25}H_{44}O_3Cl_2NaSi$ [M + Na$^+$] *m/z* 513.2329, found 513.2331. **17 [Major]:** ^{1}H NMR (500 MHz, benzene-d_6) δ 4.23-4.13 (m, 1 H), 3.76 (dd, *J* = 10.2, 8.7 Hz, 1 H), 2.77 (d, *J* = 15.8 Hz, 1 H), 2.41 (ddd, *J* = 12.9, 10.2, 2.9 Hz, 1 H), 2.34-2.28 (m, 1 H), 2.21 (d, *J* = 12.2 Hz, 1 H), 2.17 (app t, *J* = 10.5 Hz, 1 H), 1.96-1.84 (m, 2 H), 1.74-1.70 (m, 1 H), 1.54 (dddd, *J* = 12.9, 10.5, 9.3, 5.7 Hz, 1 H), 1.35-1.05 (m, 4 H), 1.03-0.95 (m, 1 H), 0.97 (d, *J* = 6.3

Hz, 3 H), 0.95 (s, 9 H), 0.77 (s, 3 H), 0.82-0.72 (m, 1 H), 0.73 (d, *J* = 6.6 Hz, 3 H), 0.58 (s, 3 H), 0.07 (s, 3 H), 0.05 (s, 3 H); ^{13}C NMR (150 MHz, benzene-d_6) 203.2, 94.7, 78.9, 72.0, 55.9, 53.8, 53.1, 52.2, 47.2, 45.4, 44.7, 43.7, 42.5, 27.9, 27.6, 25.98, 25.97, 23.7, 22.7, 21.8, 18.2, -2.2, -2.3. **SI-8 [Minor]:** ^{1}H NMR (500 MHz, benzene-d_6) δ 4.23-4.13 (m, 1 H), 3.80 (dd, *J* = 9.8, 8.5 Hz, 1 H), 2.46-2.43 (m, 2 H), 2.36-2.27 (m, 2 H), 1.96-1.84 (m, 2 H), 1.78-1.70 (m, 2 H), 1.68-1.61 (m, 1 H), 1.35-1.05 (m, 4 H), 0.96-0.91 (m, 1 H), 0.95 (s, 9 H), 0.83 (d, *J* = 7.0 Hz, 3 H), 0.83 (d, *J* = 6.5 Hz, 3 H), 0.79-0.74 (m, 1 H), 0.73 (s, 3 H), 0.60 (s, 3H), 0.07 (s, 3 H), 0.04 (s, 3 H); ^{13}C NMR (150 MHz, benzene-d_6) δ 204.3, 93.2, 79.1, 72.0, 55.6, 54.7, 52.7, 51.7, 50.6, 46.7, 46.2, 44.9, 42.8, 28.0, 25.98, 25.95, 23.7, 22.6, 22.1, 21.4, 16.3, -2.3, -2.4.



Esters SI-5 and SI-9 for *dr* analysis: DMAP (1.5 mg, 0.0122 mmol, 0.40 equiv), *meta*-anisic acid (7 mg, 0.0458 mmol, 1.5 equiv), and CH_2Cl_2 (2.0 mL) were added to a mixture of **17** and **SI-8** (15 mg, 0.0305 mmol, 1.0 equiv) and the resulting solution was cooled to 0 °C. EDC·HCl (9.0 mg, 0.0469 mmol, 1.5 equiv) was then added, and the reaction mixture was stirred for 1 hour, slowly warmed to 25 °C, and stirred for 12 hours at 25 °C. Upon completion of the reaction as determined by TLC, the reaction mixture was quenched 1 M HCl (2 mL), extracted with CH_2Cl_2 (3 x 7 mL), washed with brine (7 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The crude material was purified by column chromatography (2% Et_2O in hexanes → 8% Et_2O in hexanes) affording 18 mg of an inseparable 3:1 mixture of **SI-5** and **SI-9** (0.0285 mmol, 93%). The diastereoselectivity of the reductive cyclization reaction (**SI-2 → 17 and SI-8**) could be determined from the ^{1}H NMR integration ratios of **SI-5** and **SI-9**. The major and minor diastereomers have been separately assigned for ^{1}H and ^{13}C NMR through a careful analysis of the spectrum of the mixture and 2D ^{1}H-^{1}H COSY analysis. **SI-5 and SI-9**: R_f = 0.23 (6% Et$_2$O in hexanes); IR ν_{max} (cm^{-1}) 2955, 2857, 1724, 1600, 1490, 1464, 1276; HRMS (ESI) calcd for C$_{33}$H$_{50}$O$_5$Cl$_2$NaSi [M + Na$^+$] *m/z* 647.2697, found 647.2700. **SI-5 [Major]:** ^{1}H NMR (600 MHz, benzene-*d*$_6$) δ 8.01 (d, *J* = 7.8 Hz, 1 H), 7.94-7.92 (m, 1 H), 7.02 (t, *J* = 7.9 Hz, 1 H), 6.90-6.87 (m, 1 H), 5.58 (ddd, *J* = 10.1, 10.1, 6.7 Hz, 1 H), 3.97 (app t, *J* = 9.8 Hz, 1 H), 3.39 (s, 3 H), 2.74 (d, *J* = 15.7 Hz, 1 H), 2.68 (ddd, *J* = 12.7, 9.9, 2.6 Hz, 1 H), 2.51-2.46 (m, 1 H), 2.36 (dd, *J* = 11.4, 6.6 Hz, 1 H), 2.32 (dd, *J* = 15.6, 10.8 Hz, 1 H), 2.18 (app t, *J* = 10.5 Hz, 1 H), 1.77 (dd, *J* = 13.6, 2.7 Hz, 1 H), 1.60-1.53 (m, 1 H), 1.38-1.10 (m , 4 H), 0.99 (app t, *J* = 13.1 Hz, 1 H), 0.94 (d, *J* = 6.6 Hz, 3 H), 0.93 (s, 9 H), 0.89 (s, 3 H), 0.84-0.74 (m, 1 H), 0.71 (d, *J* = 6.4 Hz, 3 H), 0.62 (s, 3 H), 0.06 (s, 3 H), 0.03 (s, 3 H); ^{13}C NMR (150 MHz, benzene-*d*$_6$) δ 200.4, 166.0, 160.3, 131.8, 129.8, 122.7, 120.8, 114.0, 94.5, 79.0, 72.0, 55.7, 55.0, 53.7, 50.4, 47.34, 47.26, 45.4, 44.4, 43.8, 42.6, 27.9, 27.4, 26.0, 23.8, 23.6, 22.8, 21.7, 18.2, -2.3, -2.4. **SI-9 [Minor]:** ^{1}H NMR (600 MHz, benzene-*d*$_6$) δ 7.99 (d, *J* = 6.6 Hz, 1 H), 7.94-7.92 (m, 1 H), 7.02 (t, *J* = 7.9 Hz, 1 H), 6.90-6.87 (m, 1 H), 5.46 (ddd, *J* = 10.0, 10.0, 6.7 Hz, 1 H), 4.07 (app t, *J* = 9.5 Hz, 1 H), 3.35 (s, 3 H), 2.60-2.42 (m, 4 H), 2.26 (dd, *J* = 11.3, 6.6 Hz, 1 H), 1.80-1.74 (m, 2 H), 1.66-1.59 (m, 1 H), 1.38-1.10 (m, 5 H), 1.07 (app t, *J* = 11.3, 6.6 Hz, 1 H), 0.93 (s, 9 H), 0.84-0.80 (m, 9 H), 0.64 (s, 3 H), 0.06 (s, 3 H), 0.03 (s, 3 H); ^{13}C NMR (150 MHz, benzene-*d*$_6$) δ 201.2, 166.1, 160.3, 131.8, 129.1, 122.7, 120.7, 114.1, 92.8, 79.1, 72.4, 55.3, 55.0, 54.7, 50.9, 50.2, 49.0, 47.0, 46.3, 44.5, 43.0, 30.1, 28.0, 26.0, 23.6, 22.6, 22.1, 21.2, 16.3, -2.3, -2.5.

Photoredox cyclization and product analysis through derivatization as esters SI-4, SI-10, SI-5, SI-9, and SI-3:

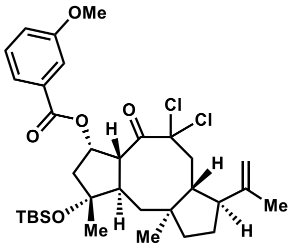


SI-2

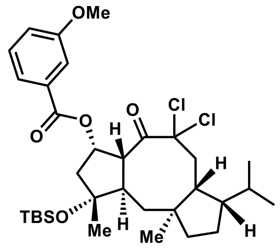
16 (Major)

SI-4 (Major)
53% of Total Material

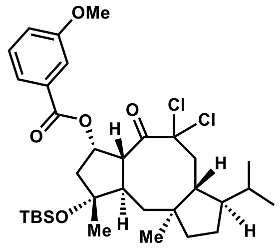
Other Products:



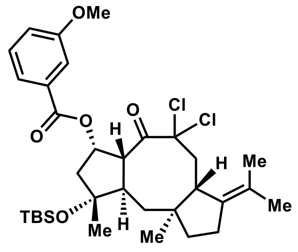
SI-10
17% of Total Material



SI-5
9% of Total Material



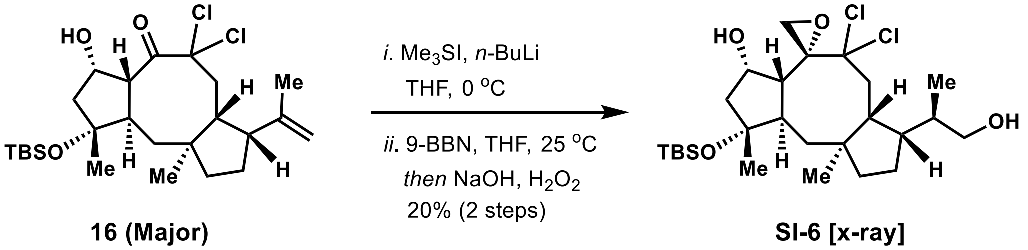
SI-9
3% of Total Material



SI-3
18% of Total Material

i. A degassed solution of Et_3N (21 μL, 0.152 mmol, 0.50 equiv) in DMSO (6 mL) was added to **SI-2** (160 mg, 0.304 mmol, 1.0 equiv) and $Ir(ppy)_3$ (2.0 mg, 0.00305 mmol, 0.010 equiv). The resulting solution was irradiated with light from a Blue LED for 2 hours at 25 °C. The reaction mixture was quenched with H_2O (6 mL), extracted with Et_2O (3 x 20 mL), washed with H_2O (30 mL), brine (30 mL), dried over $MgSO_4$, and concentrated *in vacuo* to yield a yellow oil. The crude residue was purified by column chromatography (5% CH_2Cl_2 in hexanes → 80% CH_2Cl_2 in hexanes) to provide 122 mg of an inseparable mixture of cyclization products (0.249 mmol, 82% overall yield), in which **16** is the major component. The ratio of the cyclization products in this mixture could only be quantitatively determined by derivatization as the ester of *meta*-anisic acid (see below). A ^1H and ^{13}C NMR of this mixture is provided; however, individual structural assignments were not possible at this stage. **16**: $R_f = 0.17$ (60% CH_2Cl_2 in hexanes); IR ν_{max} (cm^{-1}) 3562, 2955, 2930, 2857, 1718, 1472, 1448, 1383, 1276, 1258; HRMS (ESI) calcd for $C_{25}H_{42}O_3Cl_2NaSi$ [M + Na$^+$] *m/z* 511.2173, found 511.2173. *ii*. DMAP (3 mg, 0.0246 mmol, 0.33 equiv), *meta*-anisic acid (17 mg, 0.113 mmol, 1.5 equiv), and CH_2Cl_2 (5 mL) were added to this mixture of cyclization products (37 mg, 0.0756 mmol, 1.0 equiv), and the resulting solution was cooled to 0 °C. EDC·HCl (22 mg, 0.113 mmol, 1.5 equiv) was then added, and the reaction mixture was stirred for 1 hour, slowly warmed to 25 °C, and stirred for 12 hours at 25 °C. The reaction mixture was quenched with 1 M HCl (4 mL), extracted with CH_2Cl_2 (3 x 10 mL), washed with brine (10 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The crude material was purified by column chromatography (2% Et_2O in hexanes → 8% Et_2O in hexanes) to yield 42 mg of a mixture of **SI-4**, **SI-10, SI-5, SI-9,** and **SI-3** (0.0673 mmol, 89%).

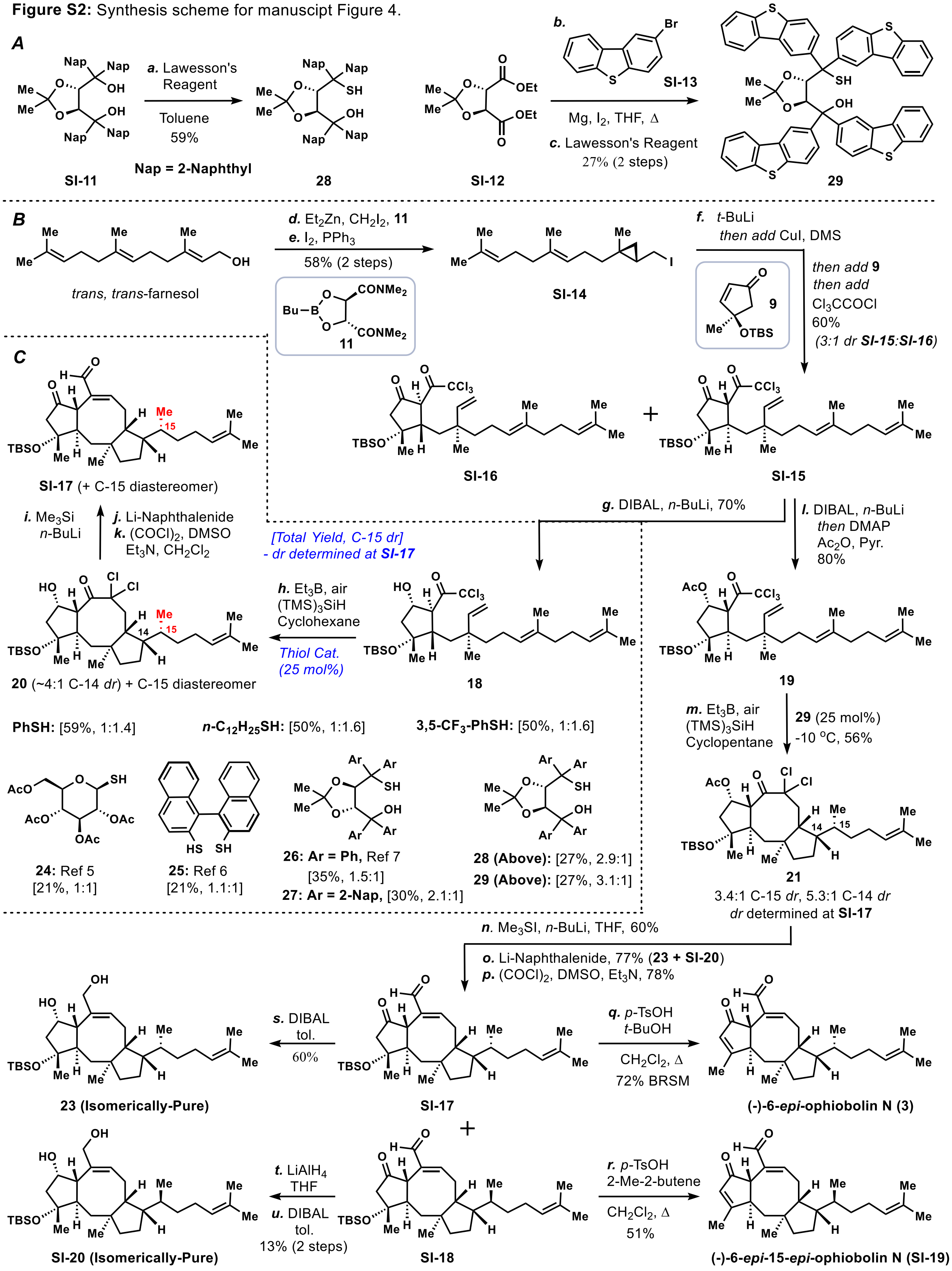
A sample of this mixture was then purified by Preparative TLC (7% Et_2O in hexanes) to produce 25 mg (0.041 mmol) of an inseparable 3:1 mixture of **SI-4** and **SI-10**, and 10.5 mg (0.017 mmol) mg of an inseparable 3.0:1.0:6.4 mixture of **SI-5**, **SI-9**, and **SI-3** (**SI-3** characterized on pages S14-S15). The diastereoselectivity of the photoredox cyclization was determined from the ^{1}H NMR integration ratios of **SI-4** to **SI-10**, and the ratios of **SI-5** to **SI-9** (characterized on page S17). The total ratios of products, calculated from ^{1}H NMR integration and mass of isolated samples, is 18.8 : 6.3 : 3.0 : 1.0 : 6.5 **SI-4** : **SI-10** : **SI-5** : **SI-9** : **SI-3**. Though isolated as an inseparable mixture, **SI-4** and **SI-10** have been independently assigned for ^{1}H and ^{13}C NMR through a careful analysis of the spectrum of the mixture and 2D ^{1}H-^{1}H COSY analysis. **SI-4 and SI-10**: R_f = 0.20 (6% Et_2O in hexanes); IR ν_{max} (cm^{-1}) 2954, 2859, 1724, 1600, 1463, 1383, 1277; HRMS (ESI) calcd for $C_{33}H_{48}O_5Cl_2NaSi$ [M + Na$^+$] *m/z* 645.2540, found 645.2540. **SI-4 [Major]:** ^{1}H NMR (600 MHz, benzene-*d*$_6$) δ 7.98 (d, *J* = 7.2 Hz, 1 H), 7.91-7.90 (m, 1 H), 7.01 (app t, *J* = 8.0 Hz, 1 H), 6.89-6.86 (m, 1 H), 5.57 (ddd, *J* = 10.2, 10.2, 6.7 Hz, 1 H), 4.89 (s, 1 H), 4.70 (s, 1 H), 3.98 (app t, *J* = 9.8 Hz, 1 H), 3.36 (s, 3 H), 2.66-2.61 (m, 2 H), 2.61-2.55 (m, 1 H), 2.51-2.46 (m, 1 H), 2.38-2.31 (m, 2 H), 2.26-2.21 (m, 1 H), 1.77 (dd, *J* = 13.5, 2.9 Hz, 1 H), 1.57 (s, 3 H), 1.45-1.10 (m, 4 H), 0.98 (app t, *J* = 13.0 Hz, 1 H), 0.93 (s, 9 H), 0.90 (s, 3 H), 0.63 (s, 3 H), 0.06 (s, 3 H), 0.04 (s, 3 H); ^{13}C NMR (150 MHz, benzene-*d*$_6$) δ 200.6, 166.0, 160.3, 145.0, 131.8, 129.8, 122.7, 120.7, 114.1, 114.0, 93.9, 79.0, 72.1, 55.4, 55.0, 53.9, 50.3, 48.4, 47.2, 45.0, 44.3, 43.3, 43.1, 27.6, 25.9, 23.8, 23.4, 23.0, 18.2, -2.3, -2.4. **SI-10 [Minor]:** ^{1}H NMR (600 MHz, benzene-*d*$_6$) δ 7.97 (d, *J* = 7.2 Hz, 1 H), 7.91-7.89 (m, 1 H), 7.01 (app t, *J* = 7.8 Hz, 1 H), 6.89-6.86 (m, 1 H), 5.48 (ddd, *J* = 10.1, 10.1, 2.9 Hz, 1 H), 4.83 (s, 1 H), 4.75 (s, 1 H), 4.08 (app t, *J* = 9.6 Hz, 1 H), 3.34 (s, 3 H), 2.68-2.55 (m, 2 H), 2.53-2.46 (m, 1 H), 2.42-2.36 (m, 1 H), 2.30-2.26 (m, 1 H), 1.95-1.86 (m, 2 H), 1.79-1.75 (m, 1 H), 1.65 (s, 3 H), 1.45-0.95 (m, 5 H), 0.93 (s, 9 H), 0.86 (s, 3 H), 0.65 (s, 3 H), 0.06 (s, 3 H), 0.03 (s, 3 H) ; ^{13}C NMR (150 MHz, benzene-*d*$_6$) δ 201.2, 166.1, 160.3, 145.1, 129.8, 122.7, 120.7, 114.1, 113.9, 92.5, 79.1, 72.4, 60.1, 57.1, 55.3, 55.0, 50.0, 49.1, 47.1, 47.0, 45.7, 44.8, 42.1, 28.1, 26.0, 23.6, 22.3, 20.6, 14.2, -2.3, -2.5.



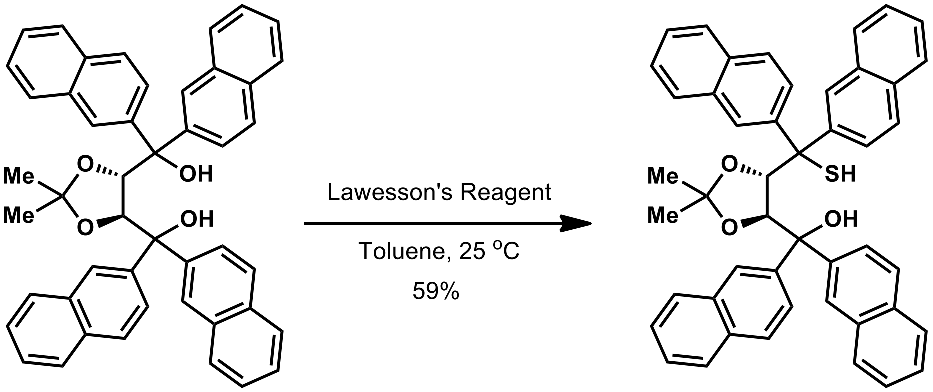
Alcohol SI-6: *i*. A stirring suspension of trimethylsulfonium iodide (301 mg, 1.47 mmol, 24 equiv) in THF (2.2 mL) was cooled to 0 °C, and *n*-butyllithium (2.5 M in hexanes, 0.15 mL, 0.368 mmol, 6.0 equiv) was added dropwise. The resulting suspension was stirred vigorously for 15 minutes, and then a solution of the mixture of isomers wherein alkene **16** is major (30.0 mg, 0.0613 mmol, 1.0 equiv) in THF (0.8 mL) was added dropwise. THF (2 x 0.2 mL) was used to rinse the residual **16** into the reaction. The reaction mixture was then stirred for 10 minutes at 0 °C, quenched with a saturated aqueous solution of NH_4Cl (3 mL), extracted with Et_2O (3 x 10 mL), washed with brine (10 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The resulting crude material was purified by column chromatography (3% Et_2O in hexanes → 10% Et_2O in hexanes) to yield 15 mg of a mixture of intermediate epoxides (0.0297 mmol, 49%). *ii*. 9-BBN (0.5 M in THF, 0.24 mL, 0.119 mmol, 4.0 equiv) was added to the mixture of epoxides (15 mg, 0.0297 mmol, 1.0 equiv) in THF (1 mL) at 0 °C. The resulting colorless solution was stirred for 12 hours, slowly warming to 25 °C. Upon completion of the reaction as judged by TLC, the reaction mixture was cooled to 0 °C, and NaOH (1 M in H_2O, 86 µL, 0.0891 mmol, 3 equiv) added, followed immediately by H_2O_2 (50% in H_2O, 24 µL, 0.356 mmol, 12 equiv). The reaction was then stirred at 0 °C for 30 minutes, warmed to 25 °C, and stirred for an additional 15 minutes. The reaction mixture was quenched with a saturated aqueous solution of $Na_2S_2O_3$ (2 mL), extracted with Et_2O (3 x 8 mL), washed with brine (10 mL), dried, and concentrated *in vacuo*. The crude residue was then purified by column chromatography (5% Et_2O in hexanes → 50% Et_2O in hexanes) to yield 6.2 mg of **SI-6** (0.0119 mmol, 40%) as a white solid. Slow evaporation from a hexane solution of **SI-6** yielded X-ray quality crystals. **SI-6**: $[\alpha]_D^{25}$ = +4.76° (c = 0.0021 g/mL, $CHCl_3$); R_f = 0.19 (45% Et_2O in hexanes); mp 146-148 °C; ^1H NMR (600 MHz, benzene-d_6) δ 4.54 (br s, 1 H), 4.18-4.11 (m, 1 H), 3.75 (d, *J* = 5.2 Hz, 1 H), 3.28 (dd, *J* = 10.3, 3.6 Hz, 1 H), 3.23 (d, *J* = 8.0 Hz, 1 H), 3.18 (dd, *J* = 10.3, 6.1

Hz, 1 H), 2.77 (d, *J* = 15.9 Hz, 1 H), 2.65-2.59 (m, 2 H), 2.57-2.50 (m, 1 H), 2.21 (app t, *J* = 10.1 Hz, 1 H), 1.86-1.77 (m, 1 H), 1.78 (dd, *J* = 12.8, 4.3 Hz, 1 H), 1.74 (dd, *J* = 13.1, 3.1 Hz, 1 H), 1.42 (ddd, *J* = 11.7, 5.8, 5.8 Hz, 1 H), 1.37-1.33 (m, 2 H), 1.26-1.17 (m, 2 H), 1.13 (s, 3 H), 1.12 (d, *J* = 7.2 Hz, 3 H), 1.00 (s, 3 H), 0.99-0.93 (m, 1 H), 0.93 (s, 9 H), 0.71 (app t, *J* = 13.0 Hz, 1 H), 0.14 (s, 3 H), 0.09 (s, 3 H); ^{13}C NMR (150 MHz, benzene-d_6) δ 99.0, 75.2, 66.8, 62.7, 52.1, 49.9, 49.3, 48.6, 47.4, 46.8, 46.1, 43.7, 42.3, 35.7, 27.2, 26.04, 26.03, 25.99, 25.3, 23.7, 18.1, 17.3, -2.0, -2.3; IR ν_{max} (cm^{-1}) 3432. 2956, 2980, 2857, 1462, 1383, 1275, 1260; HRMS (ESI) calcd for $C_{26}H_{46}O_4Cl_2NaSi$ [M + Na$^+$] *m/z* 543.2435, found 543.2440.

Figure S2: Synthesis scheme for manuscipt Figure 4.

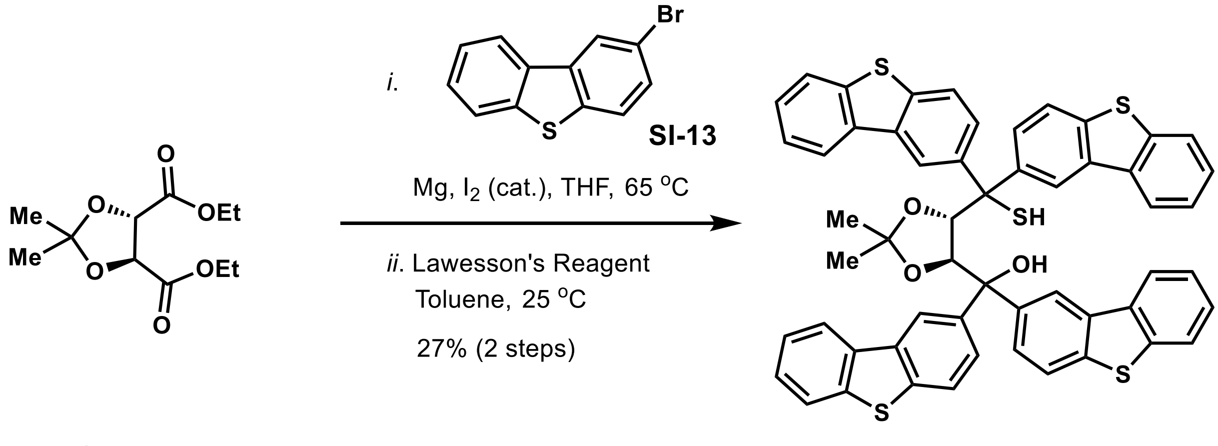


A) Synthesis of new thiol catalysts. **B)** Nine step total synthesis of (-)-6-*epi*-ophiobolin N (**3**) and related compounds. **C)** Thiol screen for C-15 diastereoselectivity. Thiols synthesized by literature procedures are indicated with the associated reference.



SI-11 **28**

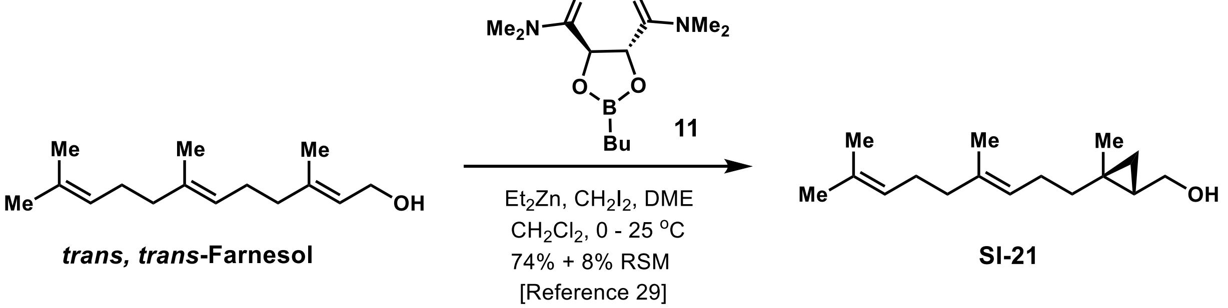
Thiol 28: Toluene (6.5 mL) was added to a mixture of TADDOL **SI-11** (300 mg, 0.450 mmol, 1.0 equiv) and Lawesson's Reagent (364 mg, 0.901 mmol, 2.0 equiv) at 25 °C. The resulting suspension was vigorously stirred for 3 days, then directly purified by column chromatography (4% Et_2O in hexanes → 30% Et_2O in hexanes) to yield 180 mg of monothiol **28** (0.264 mmol, 59%) as a light pink solid. **28**: $[\alpha]_D^{25}$ = -80.00° (c = 0.0045 g/mL, $CHCl_3$); mp 175-177 °C; R_f = 0.19 (40% CH_2Cl_2 in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (br s, 1 H), 8.05 (br s, 1 H), 7.93-7.90 (m, 2 H), 7.88-7.78 (m, 4 H), 7.76 (d, J = 8.8 Hz, 1 H), 7.75-7.71 (m, 2 H), 7.68 (d, J = 8.8 Hz, 1 H), 7.65-7.61 (m, 2 H), 7.60 (dd, J = 8.7, 1.9 Hz, 1 H), 7.52-7.47 (m, 4 H), 7.45-7.38 (m, 5 H), 7.31 (d, J = 8.7 Hz, 2 H), 7.12 (dd, J = 8.9, 1.9 Hz, 1 H), 7.05 (dd, J = 8.8, 1.6 Hz, 1 H), 5.50 (d, J = 6.5 Hz, 1 H), 5.36 (d, J = 6.5 Hz, 1 H), 2.97 (br s, 1 H), 2.51 (s, 1 H), 1.20 (s, 3 H), 1.18 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.8, 142.6, 142.3, 141.8, 132.91, 132.89, 132.72, 132.71 132.66, 132.6, 132.4, 132.3, 129.3, 128.73, 128.68, 128.6, 128.5, 128.0, 127.73, 127.71, 127.68, 127.6, 127.54, 127.52, 127.48, 127.21, 127.17, 127.16, 127.1, 126.47, 126.46, 126.4, 126.30, 126.29, 126.21, 126.16, 126.10, 126.09, 126.0, 125.9, 110.9, 83.7, 82.6, 78.8, 61.4, 28.4, 28.2; IR ν_{max} (cm^{-1}) 3569, 3366, 3056, 2930, 1599, 1505, 1380, 1263; HRMS (ESI) calcd for $C_{47}H_{37}O_3S$ [M – H$^+$] *m/z* 681.2469, found 681.2466.



SI-12 **29**

Thiol 29: *i*. A flame-dried, two-necked 100 mL round-bottom flask equipped with a reflux condenser and a rubber septum was charged with magnesium turnings (1.02 g, 42.4 mmol, 11 equiv), and the magnesium was flame-dried under vacuum two times. After cooling, the flask was placed under an atmosphere of argon, and a crystal of iodine was added. Freshly-distilled THF (15 mL) was added, and then 1 mL of a solution of 2-bromodibenzothiophene **SI-13** (5.56 g, 21.2 mmol, 5.6 equiv) in freshly-distilled THF (10 mL) was introduced slowly. The mixture was heated until initiation of the Grignard reaction was evident, as determined by a color change from brown to colorless. After initiation, the remainder of the **SI-13** solution in THF was added dropwise by syringe pump over 10 minutes. The reaction mixture was stirred for an additional 1 hour, with occasional heating to maintain gentle reflux. The reaction was then cooled to 0 °C, and a solution of acetonide **SI-12** (932 mg, 3.79 mmol, 1.0 equiv) in THF (8 mL) was added dropwise by syringe pump over 10 minutes. The reaction mixture was then heated to 65 °C and stirred for 1 hour. After cooling to 0 °C, the reaction was slowly quenched with saturated aqueous NH_4Cl (50 mL), extracted with EtOAc (3 x 50 mL), washed with brine (40 mL), dried over $MgSO_4$, and concentrated *in vacuo* to yield a yellow foam. The crude material was purified by column chromatography (10% Et_2O in hexanes → 80% Et_2O in hexanes) to yield 2.30 g of the intermediate TADDOL (2.58 mmol, 68%). *ii*. Toluene (42 mL) was then added to a mixture of the intermediate TADDOL (2.30 g, 2.58 mmol, 1.0 equiv) and Lawesson's Reagent (2.08 g, 5.16 mmol, 2.0 equiv) at 25 °C. The resulting pink suspension was vigorously stirred for 36 hours, then directly purified by column chromatography (6% Et_2O in hexanes → 60% Et_2O in hexanes) to yield 930 mg of monothiol **29** (1.03 mmol, 40%) as a yellow solid. **29**: $[\alpha]_D^{25}$ = -93.33° (c = 0.006 g/mL, $CHCl_3$); mp 212-214 °C; R_f = 0.20 (40% CH_2Cl_2 in hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* =

2.0 Hz, 1 H), 8.37 (d, J = 1.8 Hz, 1 H), 8.13 (br s, 2 H), 8.12-8.06 (m, 2 H), 7.92-7.92 (m, 8 H), 7.69 (dd, J = 8.6, 1.8 Hz, 1 H), 7.62 (dd, J = 8.5, 2.0 Hz, 1 H), 7.56-7.50 (m, 2 H), 7.49-7.27 (m, 10 H), 5.54 (d, J = 6.6 Hz, 1 H), 5.31 (d, J = 6.6 Hz, 1 H), 3.05 (br s, 1 H), 2.78 (s, 1 H), 1.25 (s, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.4, 142.2, 141.7, 141.0, 140.1, 139.99, 139.96, 139.9, 138.6, 138.5, 138.44, 138.40, 135.8, 135.7, 135.5, 135.30, 135.28, 135.25, 135.24, 135.1, 129.3, 127.9, 127.4, 127.0, 126.88, 126.86, 126.7, 126.5, 124.6, 124.5, 124.4, 124.3, 123.02, 122.98, 122.9, 122.85, 122.81, 122.5, 122.4, 122.0, 122.0, 121.8, 121.83, 121.75, 121.7, 121.3, 121.2, 120.1, 110.5, 84.1, 82.8, 76.6, 61.2, 28.2, 28.1; IR ν_{max} (cm^{-1}) 3563, 3424, 3067, 2929, 1467, 1431, 1380, 1275; HRMS (ESI) calcd for $C_{55}H_{37}O_3S_5$ [M – H$^+$] m/z 905.1352, found 905.1363.

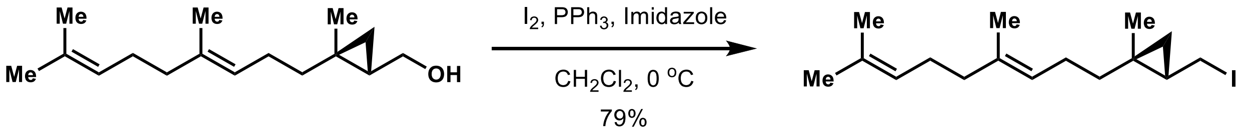


trans, trans-Farnesol

Et_2Zn, CH_2I_2, DME
CH_2Cl_2, 0 - 25 °C
74% + 8% RSM
[Reference 29]

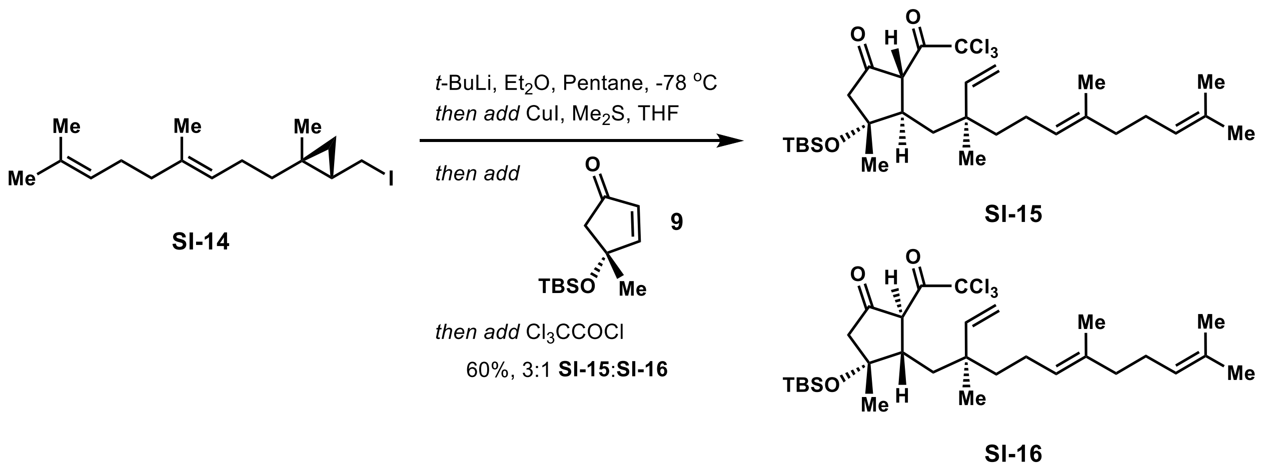
SI-21

Cyclopropanated Alcohol SI-21:[29] 1,2-Dimethoxyethane (DME, 2 mL) and CH_2Cl_2 (24 mL) were added sequentially to a stirring solution of Et_2Zn (1 M in Hexanes, 18.0 mL, 18.0 mmol, 2.0 equiv) at 25 °C. The reaction mixture was cooled to 0 °C, and CH_2I_2 (2.87 mL, 36.0 mmol, 4.0 equiv) was added dropwise via syringe pump over 10 minutes. The resulting solution was stirred for an additional 25 minutes at 0 °C, and then transferred via canula (over a period of 10 minutes) to a separate round-bottom flask containing *trans*, *trans*-farnesol (2.00 g, 9.00 mmol, 1.0 equiv), chiral boronic ester (*R*,*R*)-**11** (3.67 g, 13.5 mmol, 1.5 equiv), and CH_2Cl_2 (18 mL). After the transfer was complete, the reaction mixture was stirred for 15 minutes at 0 °C, warmed to 25 °C, and stirred for 5 hours. The reaction mixture was quenched with saturated aqueous NH_4Cl (100 mL), extracted with EtOAc (3 x 100 mL), washed with 3 M HCl (75 mL), 3 M NaOH (2 x 50 mL) and brine (50 mL), dried over $MgSO_4$, and concentrated *in vacuo* to yield a light yellow oil. The crude material was purified by column chromatography (Et_2O in hexanes, 7% → 50%) to yield 1.75 g of a 9:1 inseparable mixture of cyclopropyl alcohol **SI-21** and recovered farnesol (6.67 mmol, 74% + 8% recovered starting material) as a colorless oil. Spectroscopic data was in agreement with that previously reported by Charette and coworkers.[29]



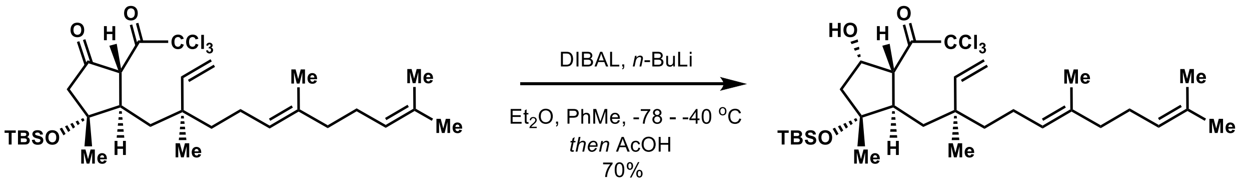
SI-21 **SI-14**

Iodide SI-14: Iodine (1.12 g, 4.43 mmol, 1.1 equiv) was added to a solution of PPh_3 (1.16 g, 4.43 mmol, 1.1 equiv) and imidazole (493 mg, 7.25 mmol, 1.8 equiv) in CH_2Cl_2 (8 mL) at 25 °C. The resulting yellow/brown-colored suspension was stirred for 5 minutes at 25 °C, then cooled to 0 °C and stirred for an additional 5 minutes. A solution of cyclopropyl alcohol **SI-21** (950 mg, 4.03 mmol, 1.0 equiv) in CH_2Cl_2 (1 mL) was then added, using an additional 1 mL of CH_2Cl_2 to rinse the remainder of **SI-21** into the reaction. The reaction mixture was then stirred for 1 hour at 0 °C. After completion of the reaction, methanol (0.2 mL) was added and stirring was continued until the reaction mixture became homogeneous. H_2O was then added and the reaction mixture was extracted with CH_2Cl_2 (3 x 10 mL), washed with saturated aqueous $NaHSO_3$ (5 mL), and dried over $MgSO_4$. Et_3N (0.1 mL) was added to stabilize cyclopropyl iodide **SI-14** against acid-mediated decomposition. After drying, the combined organic layers were concentrated *in vacuo* at 15 °C in the absence of light to yield a light yellow solid. The crude solid was immediately purified by column chromatography (silica gel pretreated with 4% triethylamine in hexanes, eluting with 4% triethylamine in hexanes) to yield 1.10 g of cyclopropyl iodide **SI-14** (3.18 mmol, 79%). The isolated iodide generally contains around 10% alkene decomposition products. **SI-14** proved to be highly unstable, making it necessary to use it immediately in the next reaction. **SI-14**: $[\alpha]_D^{25}$ = -58.67° (c = 0.0075 g/mL, $CHCl_3$); R_f = 0.70 (5% EtOAc in hexanes); ^{1}H NMR (500 MHz, benzene-d_6) δ 5.12-5.04 (m, 2 H), 3.15 (dd, J = 9.9, 6.9 Hz, 1 H), 2.79 (app t, J = 9.9 Hz, 1 H), 2.10-1.92 (m, 6 H), 1.61 (s, 3 H), 1.53 (s, 3 H), 1.52 (s, 3 H), 1.30-1.22 (m, 1 H), 1.02-0.92 (m, 2 H), 0.92 (s, 3 H), 0.45 (dd, J = 8.5, 5.0 Hz, 1 H), -0.10 (app t, J = 5.0 Hz, 1 H); ^{13}C NMR (125 MHz, benzene-d_6) δ 134.8, 131.0, 125.0, 124.8, 41.6, 40.3, 28.1, 27.3, 26.1, 25.8, 25.0, 24.0, 18.1, 16.3, 15.9, 9.2.



Diketones SI-15 and SI-16: (**Note**: See pages S8-S11 for a more detailed procedure for this reaction and accompanying images.)

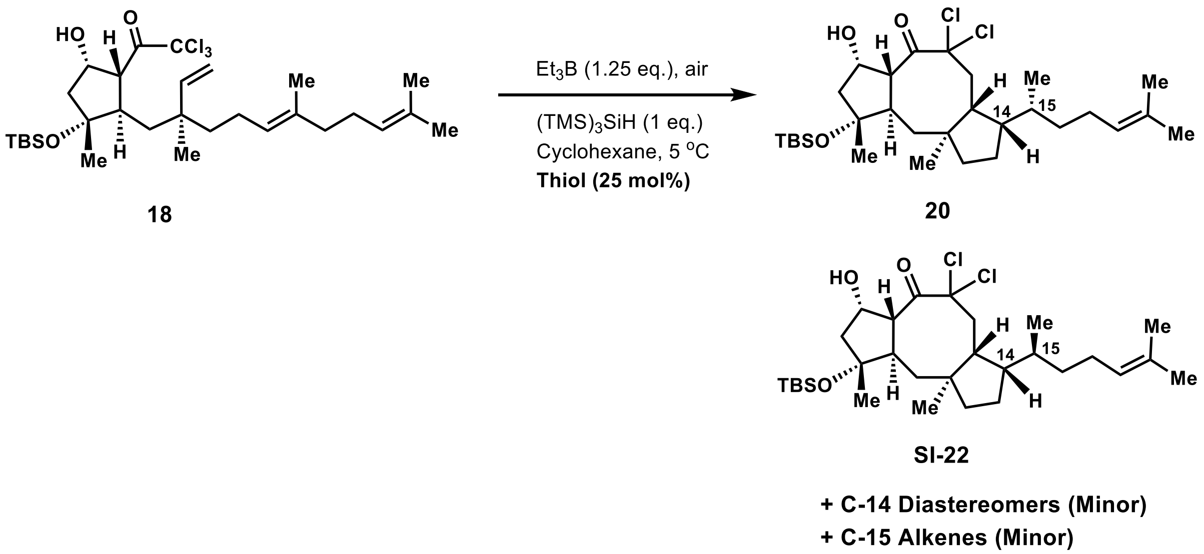
A fresh sample of **SI-14** (900 mg, 2.60 mmol, 1.3 equiv) was azeotropically dried by adding benzene and removing the benzene *in vacuo* at 15 °C. The material thus obtained was then transferred, using Et$_2$O (10 mL), to a dry 100-mL sealed tube equipped with a stir bar, Pentane (14.5 mL), a rubber septum secured with Parafilm, and a nitrogen inlet. This solution was then cooled to -78 °C and excluded from light. *tert*-Butyllithium (1.7 M in pentane, 3.20 mL, 5.44 mmol, 2.7 equiv) was added dropwise over 10 minutes down the walls of the reaction tube. The resulting white suspension was stirred at -78 °C for 2.5 hours. In a separate reaction vial, Me$_2$S (0.310 mL, 4.26 mmol, 2.1 equiv) was added to a suspension of CuI (202 mg, 1.06 mmol, 0.53 equiv) in THF (2.6 mL) and the mixture was stirred until a colorless solution formed. This solution was then added dropwise to the solution containing the lithiate of **SI-14**. The resulting light yellow suspension was stirred for 15 minutes at -78 °C. A solution of enone **9** (453 mg, 2.00 mmol, 1.00 equiv) in Et$_2$O (1.7 mL) was then added dropwise. The resulting orange suspension was stirred for 4 hours, slowly warming from -78 °C to -40 °C. Upon reaching -40 °C, the reaction mixture was cooled back to -78 °C, and Cl$_3$CCOCl (0.74 mL, 6.60 mmol, 3.3 equiv) was added dropwise. The resulting gray suspension was stirred for 2 hours, slowly warming from -78 °C to -40 °C. Upon reaching -40 °C, the reaction mixture was quenched with saturated aqueous NaHCO$_3$ (11 mL). NH$_4$OH (0.5 mL) and H$_2$O (20 mL), were added, and the mixture was extracted with Et$_2$O (3 x 30 mL), washed with brine (20 mL), dried over MgSO$_4$, and concentrated *in vacuo*. The crude product was purified by column chromatography (2% CH_2Cl_2 in hexanes → 28% CH_2Cl_2 in hexanes) to yield 530 mg of diketone **SI-15** (0.900 mmol, 45%) and 179 mg of diketone **SI-16** (0.300 mmol, 15% yield) as light yellow oils. **SI-15**: $[\alpha]_D^{25}$ = -31.23° (c = 0.0065 g/mL, $CHCl_3$); R_f = 0.55 (50% CH_2Cl_2 in hexanes); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.60 (d, *J* = 17.5, 10.8 Hz, 1 H), 5.12-5.04 (m, 2 H), 5.01 (dd, *J* = 10.8, 1.3 Hz, 1 H), 4.90 (d, *J* = 17.5, 1.3 Hz, 1 H), 4.02 (d, *J* = 10.9 Hz, 1 H), 2.86 (ddd, *J* = 10.5, 7.0, 3.0 Hz, 1 H), 2.69 (d, *J* = 16.8 Hz, 1 H), 2.55 (d, *J* = 16.8 Hz, 1 H), 2.07-2.02 (m, 2 H), 1.97-1.93 (m, 2 H), 1.92-1.80 (m, 3 H), 1.68 (s, 3 H), 1.59 (s, 3 H), 1.56 (s, 3 H), 1.47 (dd, *J* = 14.4, 7.0 H, 1 H), 1.37-1.30 (m, 1 H), 1.29-1.23 (m, 1 H), 1.26 (s, 3 H), 1.01 (s, 3 H), 0.90 (s, 9 H), 0.13 (s, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 205.2, 185.6, 145.4, 135.0, 131.4, 124.6, 124.5, 114.4, 96.3, 62.2, 55.1, 49.3, 42.9, 41.5, 39.8, 39.6, 26.9, 26.05, 26.03, 25.8. 23.9, 22.9, 21.2, 18.1, 17.8, 16.1, -2.1, -2.2; IR ν_{max} (cm^{-1}) 2958, 2929, 2857, 1765, 1734, 1472, 1383, 1275, 1260; HRMS (ESI) calcd for $C_{30}H_{48}O_3Cl_3Si$ [M – H$^+$] *m/z* 589.2444, found 589.2446. **SI-16**: $[\alpha]_D^{25}$ = +35.26° (c = 0.0038 g/mL, $CHCl_3$); R_f = 0.51 (50% CH_2Cl_2 in hexanes); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.61 (d, *J* = 17.5, 10.8 Hz, 1 H), 5.10-5.05 (m, 3 H), 4.94 (dd, *J* = 17.5, 1.3 Hz, 1 H), 4.34 (d, *J* = 11.2 Hz, 1 H), 2.55 (d, *J* = 17.8 Hz, 1 H), 2.47 (d, *J* = 17.8 Hz, 1 H), 2.40 (ddd, *J* = 11.3, 4.2, 2.9 Hz, 1 H), 2.08-2.02 (m, 2 H), 1.98-1.93 (m, 3 H), 1.92-1.80 (m, 2 H), 1.68 (s, 3 H), 1.59 (s, 3 H), 1.57-1.53 (m, 1 H), 1.56 (s, 3 H), 1.40 (s, 3H), 1.34-1.22 (m, 2 H), 0.84 (s, 9 H), 0.83 (s, 3 H), 0.14 (s, 3 H), 0.08 (s 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 207.7, 186.5, 146.3, 135.2, 131.5, 124.6, 124.4, 113.7, 96.7, 79.2, 62.7, 54.5, 49.9, 42.9, 40.0, 39.8, 39.4, 26.9, 25.84, 25.81, 25.6, 23.0, 20.8, 18.4, 17.8, 16.1, -2.1, -2.6; IR ν_{max} (cm^{-1}) 2955, 2929, 2857, 1767, 1734, 1471, 1381, 1275, 1259; HRMS (ESI) calcd for $C_{30}H_{48}O_3Cl_3Si$ [M – H$^+$] *m/z* 589.2444, found 589.2447.



SI-15

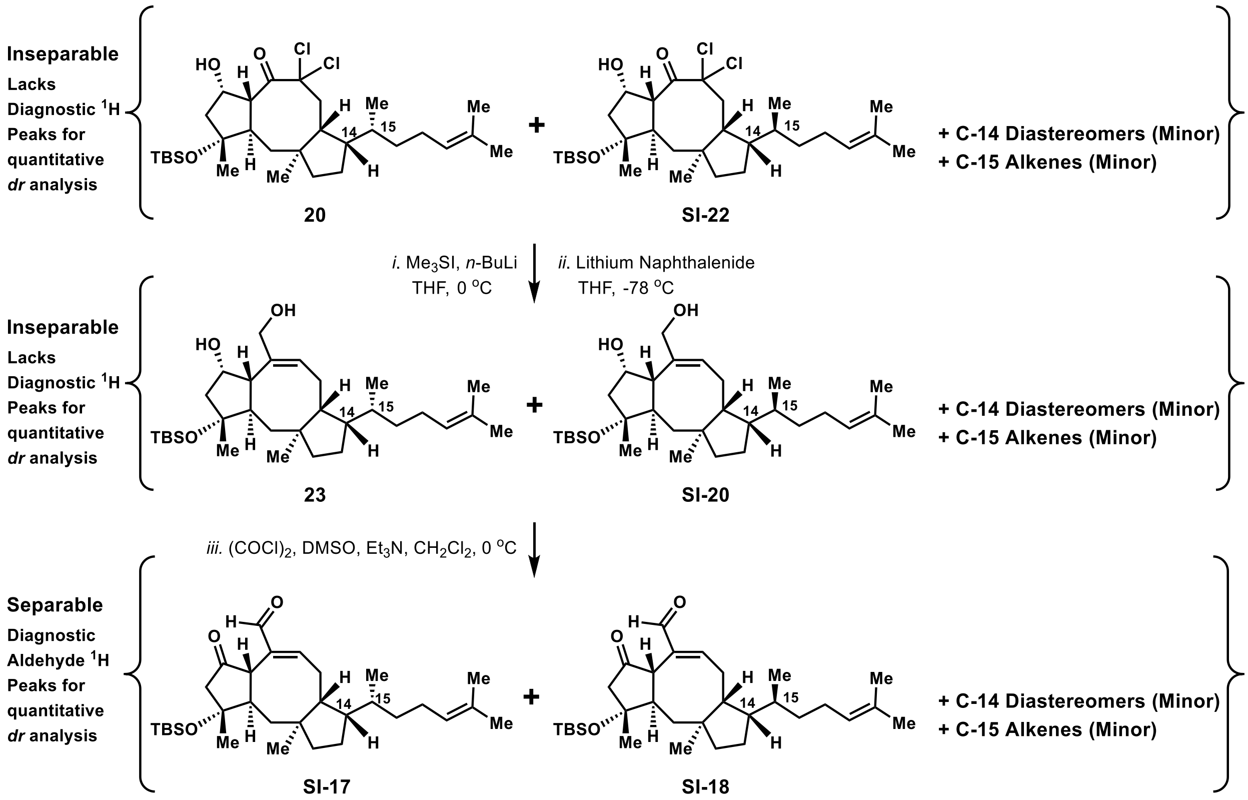
18

Keto-alcohol 18: *n*-Butyllithium (2.5 M in hexanes, 0.680 mL, 1.69 mmol, 1.0 equiv) was added dropwise to a solution of DIBAL (0.300 mL, 1.69 mmol, 1.0 equiv) in Et_2O (16.9 mL) at -15 °C. The resulting solution was stirred at -15 °C for 1 hour, then slowly transferred to a solution of **SI-15** (1.0 g, 1.69 mmol, 1.0 equiv) in toluene (92 mL) at -78 °C. The reaction mixture was stirred for 1 hour, slowly warmed to -40 °C, then recooled to -78 °C. AcOH (6.0 equiv) was added dropwise, and the resulting solution was stirred at -78 °C for 5 min, slowly warmed to 0 °C over the course of 1 hour, quenched with saturated aqueous $NaHCO_3$ (30 mL), extracted with Et_2O (3 x 70 mL), washed with brine (75 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The crude residue was purified by column chromatography (2% Et_2O in hexanes → 12% Et_2O in hexanes) to provide 703 mg of keto-alcohol **18** (1.18 mmol, 70%) as a colorless oil. **18**: $[\alpha]_D^{25}$ = +25.68° (c = 0.0095 g/mL, $CHCl_3$); R_f = 0.25 (15% Et_2O in hexanes); ^1H NMR (500 MHz, benzene-d_6) δ 5.69 (dd, *J* = 17.5, 10.7 Hz, 1 H), 5.29 (app t, *J* = 7.3 Hz, 1 H), 5.26 (app t, *J* = 7.2 Hz, 1 H), 5.11 (dd, *J* = 10.7, 1.4 Hz, 1 H), 4.97 (dd, *J* = 17.5, 1.5 Hz, 1 H), 4.31-4.25 (m, 1 H), 3.42 (app t, *J* = 7.8 Hz, 1 H), 2.92-2.87 (m, 1 H), 2.71 (d, *J* = 9.7 Hz, 1 H), 2.23-2.18 (m, 2 H), 2.13-2.08 (m, 2 H), 2.04-1.98 (m, 2 H), 1.81 (dd, *J* = 13.0, 4.5 Hz, 1 H), 1.69 (s, 3 H), 1.63 (s, 3 H), 1.64-1.59 (m, 1 H), 1.58 (s, 3 H), 1.54 (dd, *J* = 14.4, 4.0 Hz, 1 H), 1.45-1.35 (m, 2 H), 1.06 (s, 3 H), 1.08-0.97 (m, 1 H), 0.96 (s, 3 H), 0.96 (s , 9 H), 0.18 (s, 3 H), 0.08 (s, 3 H); ^{13}C NMR (150 MHz, benzene-d_6) δ 188.6, 146.3, 134.9, 131.2, 125.3, 125.0, 113.8, 97.3, 83.5, 73.6, 59.6, 51.3, 48.8, 44.4, 42.8, 40.3, 39.9, 27.3, 26.3, 25.9, 25.0, 23.4, 21.7, 18.3, 17.8, 16.1, -1.8, -1.9; IR ν_{max} (cm^{-1}) 3480, 2958, 2929, 2857, 1747, 1472, 1381, 1276, 1258; HRMS (ESI) calcd for $C_{30}H_{50}O_3Cl_3Si$ [M – H^+] *m/z* 591.2600, found 591.2618.



General Procedure for the Reductive Cyclization Thiol Screen: The desired thiol catalyst (0.25 equiv) and $(TMS)_3SiH$ (1.0 equiv) were added to keto-alcohol **18** (50 mg, 0.0842 mmol, 1.0 equiv), and the reaction flask was evacuated and backfilled with N_2. This cycle was repeated two additional times. Degassed cyclohexane (9.0 mL) was added, and the resulting solution was cooled to 5 °C (lower temperatures result in freezing). One drop of Et_3B solution (1 M in THF, 1.25 equiv) was added, followed by the addition of air (0.5 mL) directly into the reaction mixture through injection with a syringe equipped with a long needle. The reaction mixture was stirred for 20 minutes at 5 °C, and the process of adding one drop of Et_3B solution and 0.5 mL of air was repeated. This process was continually repeated until 1.25 equivalents of Et_3B had been added to the reaction mixture. Upon completion of the reaction, methanol (3 mL) and water (5 mL) were added, and the reaction mixture was extracted with Et_2O (3 x 8 mL), washed with brine (10 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The resulting crude residue was purified by column chromatography (10% CH_2Cl_2 in hexanes → 70% CH_2Cl_2 in hexanes) to yield an inseparable mixture of reductive cyclization products as a light yellow oil. **20** and **SI-22** were the major products of this mixture. The C-15 selectivity of each cyclization was confirmed by converting this material into aldehydes **SI-17** and **SI-18** (see next section, Page S31) at which point the C-14 *dr* was also determined. A ^1H and ^{13}C NMR of this mixture is provided; however, individual structural assignments were not possible at this stage. **20** and **SI-22**: $R_f = 0.27$ (65% CH_2Cl_2 in hexanes); IR ν_{max} (cm^{-1}) 3567, 2956, 2929, 2857, 1717, 1472, 1383, 1276, 1259; HRMS (ESI) calcd for $C_{30}H_{52}O_3Cl_2NaSi$ [M + Na^+] *m/z* 581.2955, found 581.2956.

General Procedure for Evaluating the Diastereoselectivity of the Cyclization with Different Thiols, by Converting Reductive Cyclization Products 20 and SI-22 to Keto Aldehydes SI-17 and SI-18:



i. A stirring suspension of trimethylsulfonium iodide (24 equiv) in THF (1.2 mL per 20 mg of cyclization products used) was cooled to 0 °C, and *n*-butyllithium (2.5 M in hexanes, 6.0 equiv) was added dropwise. The resulting suspension was stirred vigorously for 15 minutes, and then a solution of cyclization product mixture containing **20** and **SI-22** (1.0 equiv) in THF (0.07 M) was added dropwise. The residual **20** and **SI-22** was rinsed into the reaction with additional THF (2 x 0.2 mL). The reaction mixture was then stirred for 10 minutes at 0 °C, quenched with a saturated aqueous solution of NH_4Cl (3 mL), poured into water (10 mL) extracted with Et_2O (3 x 15 mL), washed with brine (5 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The resulting crude material was purified by column chromatography (3% Et_2O in hexanes → 18% Et_2O in hexanes) to yield a mixture of intermediate epoxides. *ii.* The mixture of epoxides (1.0 equiv) was dissolved in THF (0.05 M), and the solution was added dropwise over 2 minutes to lithium naphthalenide (1 M in THF, 40 equiv) in THF (1.5 mL per 10 mg of epoxides) at -78 °C. THF (2 x 0.2 mL) was then used to rinse the residual epoxides into the reaction flask. The resulting black solution was stirred at -78 °C for 15 minutes, then quenched with Et_2O (4 mL) and a saturated aqueous solution of $NaHCO_3$ (3 mL), poured into water (10 mL), extracted with Et_2O (3 x 15 mL), washed with brine (5 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The resulting crude residue was purified by column chromatography (0% Et_2O in CH_2Cl_2 → 40% Et_2O in CH_2Cl_2) to yield a mixture of diols containing **23** and **SI-20** (24-37% over 2 steps) as a colorless to yellow oil. *iii*. In a separate flask, DMSO (15 equiv) in CH_2Cl_2 (0.5 mL per 10 mg of diols) was added dropwise to oxalyl chloride (10 equiv) in CH_2Cl_2 (1.15 mL per 10 mg of diols) at -78 °C. The resulting solution was stirred at -78 °C for 30 minutes, then a solution of the diols **23** and **SI-20** (1.0 equiv) in CH_2Cl_2 (0.03 M) was added dropwise. CH_2Cl_2 (2 x 0.2 mL) was used to rinse the residual **23** and **2I-20** into the reaction flask. The reaction mixture was stirred at -78 °C for 30 minutes, then Et_3N (20 equiv) was added dropwise. The reaction mixture was stirred for 3 hours, slowly warming to 0 °C, and then quenched with H_2O (10 mL), extracted with CH_2Cl_2 (3 x 15 mL), washed with brine (5 mL), dried over $MgSO_4$, and concentrated *in vacuo*.

The crude ^{1}H NMR spectra of the mixture of **SI-17**, **SI-18**, and minor C-14 diastereomers was analyzed by integrating the aldehyde singlet resonances to quantitatively determine the diastereomeric ratio of the cyclization reaction. To ensure that a dramatic change in the *dr* did not occur during the intermediate steps, diagnostic peaks in the cyclization products **20** and **SI-22** (where a qualitative analysis is possible) are shown in Figure SI-1 below (page S33), in addition to the spectra of **SI-17** and **SI-18** (Figure SI-2, Page S34), and are in general agreement with the values obtained therein.

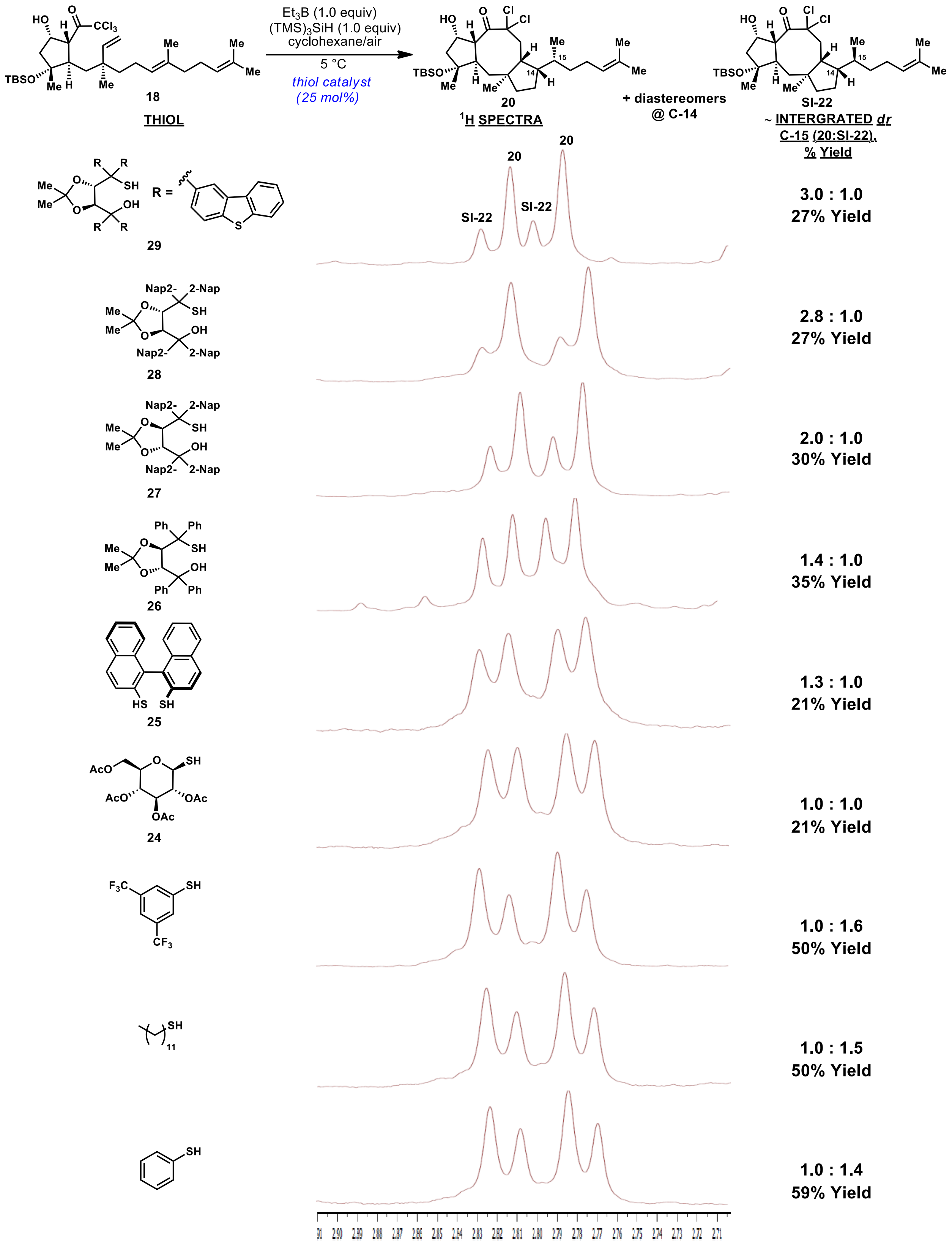


Figure S3: C-15 *dr* comparison for thiol screen at stage of cyclization products **20** and **SI-22**.

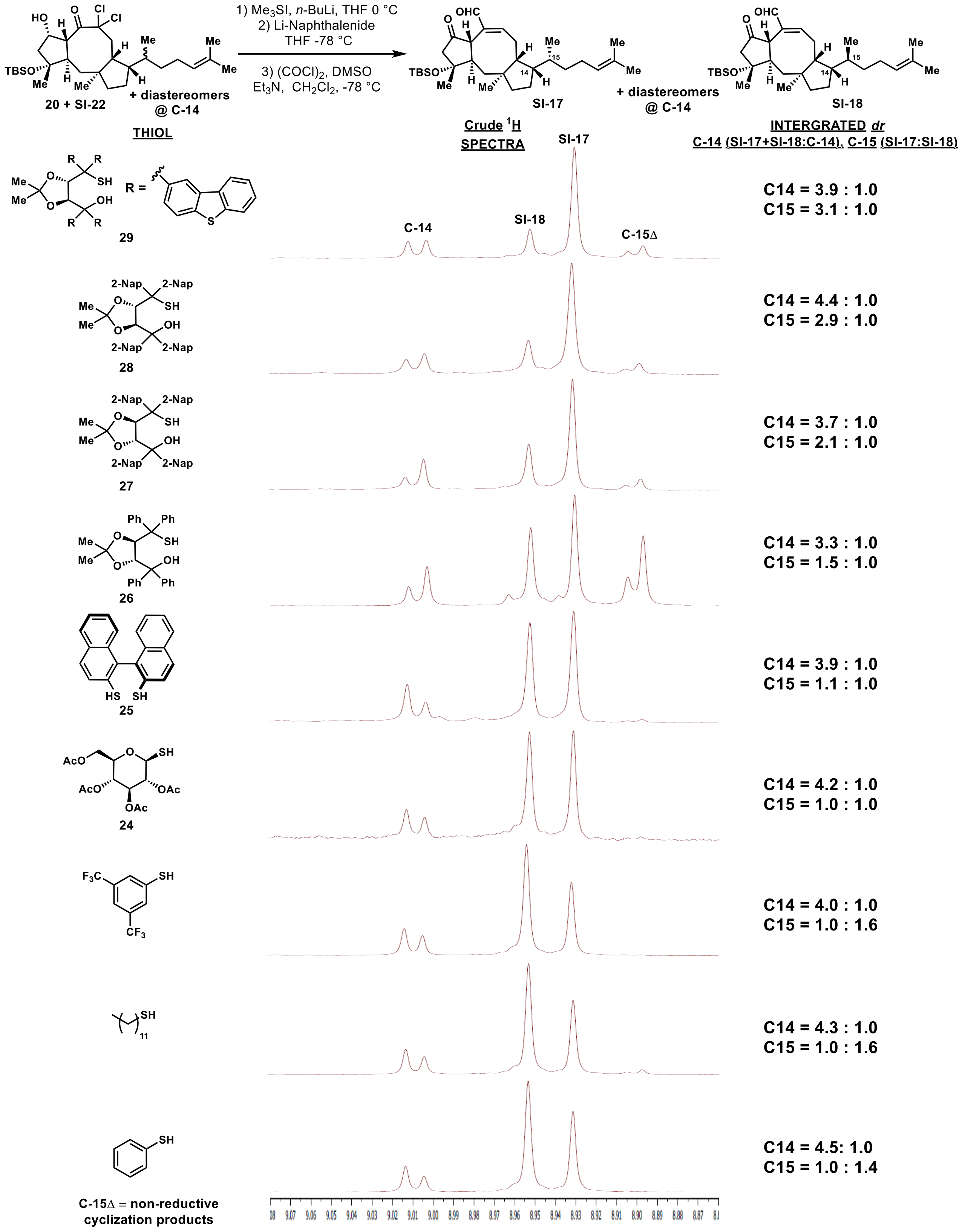
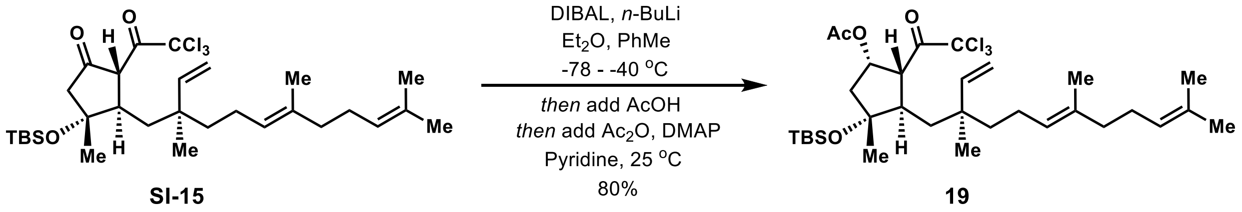
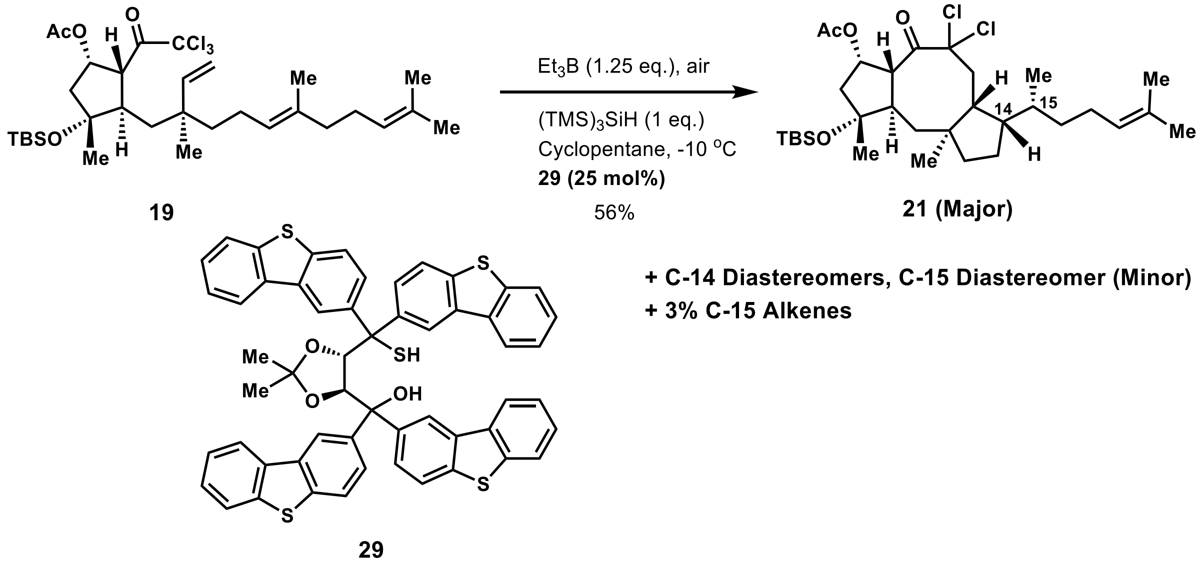


Figure S4: C-15 and C-14 *dr* comparison for thiol screen at stage of aldehydes **SI-17** and **SI-18**.



Acetylated keto-alcohol 19: *n*-Butyllithium (2.5 M in hexanes, 0.47 mL, 1.17 mmol, 1.0 equiv) was added dropwise to a solution of DIBAL (0.21 mL, 1.17 mmol, 1.0 equiv) in Et_2O (11.7 mL) at -15 °C. The resulting solution was stirred at -15 °C for 1 hour, then slowly transferred to a solution of **SI-15** (690 mg, 1.17 mmol, 1.0 equiv) in toluene (63 mL) at -78 °C. The reaction mixture was stirred for 2 hours, slowly warming to -40 °C, then cooled back to -78 °C. AcOH (3 equiv) was added dropwise, and the resulting solution was stirred at -78 °C for 5 min, then warmed to 0 °C over the course of 1 hour. A solution for DMAP (57 mg, 0.467 mmol, 0.40 equiv) in toluene (5 mL) was then added to the reaction mixture followed by the dropwise addition of pyridine (1.9 mL, 23.4 mmol, 20 equiv) and acetic anhydride (2.2 mL, 23.4 mmol, 20 equiv). The solution was then warmed to room temperature over 1 hour, then quenched with saturated aqueous $NaHCO_3$ (30 mL), extracted with Et_2O (3 x 80 mL), washed with brine (70 mL), dried over $MgSO_4$, and concentrated *in vacuo* to yield a light yellow oil. The crude residue was purified by column chromatography (1% Et_2O in hexanes → 5% Et_2O in hexanes) to provide 595 mg of acetylated keto-alcohol **19** (0.936 mmol, 80%) as a colorless oil. **19**: $[\alpha]_D^{25}$ = +42.29° (c = 0.0044 g/mL, $CHCl_3$); R_f = 0.32 (5% Et_2O in hexanes); ^{1}H NMR (500 MHz, benzene-d_6) δ 5.84 (dd, *J* = 17.5, 10.7 Hz, 1 H), 5.37 (ddd, *J* = 8.6, 7.1, 7.1 Hz, 1 H), 5.30 (app t, *J* = 6.5 Hz, 1 H), 5.26 (app t, *J* = 7.0 Hz, 1 H), 5.11 (dd, *J* = 10.9, 1.4 Hz, 1 H), 5.01 (dd, *J* = 17.5, 1.5 Hz, 1 H), 3.36 (dd, *J* = 11.0, 8.7 Hz, 1 H), 3.07 (ddd, *J* = 10.6, 5.9, 4.3 Hz, 1 H), 2.28 (dd, *J* = 12.7, 6.8 Hz, 1 H), 2.23-2.17 (m, 2 H), 2.12-2.08 (m, 2 H), 2.07-1.99 (m, 3 H), 1.69 (s, 3 H), 1.64-1.59 (m, 1 H), 1.62 (s, 3 H), 1.62 (s, 3 H), 1.58 (s, 3 H), 1.55-1.48 (m, 1 H), 1.47-1.41 (m, 1 H), 1.22 (dd, *J* = 14.7, 4.3 Hz, 1 H) 1.14 (s, 3 H), 0.95 (s, 9 H), 0.90 (s, 3 H), 0.06 (s, 3 H), 0.02 (s, 3 H); ^{13}C NMR (150 MHz, benzene-d_6) δ 186.9, 169.4, 146.9, 134.8, 131.2, 125.4, 125.0, 113.0, 97.3, 79.9, 72.6, 53.8, 49.1, 42.43, 42.39, 40.3, 39.80, 27.3, 26.3, 25.9, 24.8, 23.5, 22.1, 20.6, 18.3, 17.8, 16.2, -1.9, -2.1 (one carbon could not be detected); IR ν_{max} (cm^{-1}) 2959, 2929, 2857, 1750, 1463, 1383, 1276, 1260; HRMS (ESI) calcd for $C_{32}H_{53}O_4Cl_3NaSi$ [M + Na$^+$] *m/z* 657.2671, found 657.2675.



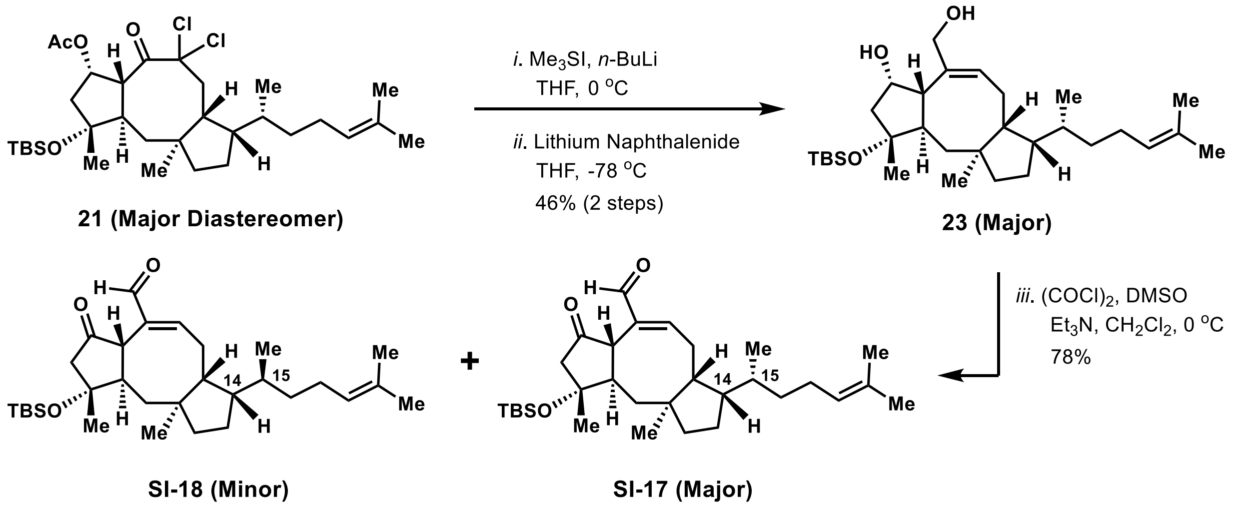
19

21 (Major)

+ C-14 Diastereomers, C-15 Diastereomer (Minor)
+ 3% C-15 Alkenes

29

Reductive Cyclization of Acetate 19: Thiol **29** (72 mg, 0.0790 mmol, 0.25 equiv) and (TMS)$_3$SiH (97 µL, 0.316 mmol, 1.0 equiv) were added to acetylated keto-alcohol **19** (201 mg, 0.316 mmol, 1.0 equiv), and the reaction flask was evacuated and backfilled with N$_2$. This cycle was repeated two additional times. Degassed cyclopentane (34 mL) was added, and the resulting solution was cooled to -10 °C. One drop of Et$_3$B solution (1 M in THF, 400 µL, 0.395 mmol, 1.25 equiv) was added, followed by the addition of air (0.5 mL) directly into the reaction mixture through injection with a syringe and long needle. The reaction mixture was stirred for 20 minutes at -10 °C, and the process of adding one drop of Et$_3$B solution and 0.5 mL of air was repeated. This process was continually repeated until 1.25 equiv of Et$_3$B had been added to the reaction mixture (12 hours). Upon completion of the reaction, methanol (8 mL) and water (20 mL) were added, and the reaction mixture was extracted with Et$_2$O (3 x 35 mL), washed with brine (20 mL), dried over MgSO$_4$, and concentrated *in vacuo*. The resulting crude mixture was purified by column chromatography (1% Et$_2$O in hexanes → 8% Et$_2$O in hexanes) to yield 112 mg of an inseparable mixture of cyclization products (0.177 mmol, 56% reductive, + 3% C-15 alkenes) as a light yellow oil. The major diastereomer was **21**, and the diastereoselectivity at C-15 was determined to be approximately 3.2:1 at this stage (see Figure SI-3, Page S40). It was also possible to measure the *dr* at C-14 at this stage, which was determined to be 5.3:1 (see Figure SI-3). The C-15 and C-14 ratios were confirmed as 3.4:1 and 5.3:1, respectively, by converting this material into keto aldehydes **SI-17** and **SI-18** (see next section, Page S37). A ^{1}H and ^{13}C NMR of this mixture is provided; however, individual structural assignments were not possible at this stage. **21**: R$_f$ = 0.35 (50% CH$_2$Cl$_2$ in hexanes); IR ν_{max} (cm^{-1}) 2956, 2929, 2857, 1745, 1462, 1384, 1276, 1260; HRMS (ESI) calcd for $C_{32}H_{54}O_4Cl_2NaSi$ [M + Na$^+$] *m/z* 623.3061, found 623.3062.



21 (Major Diastereomer)

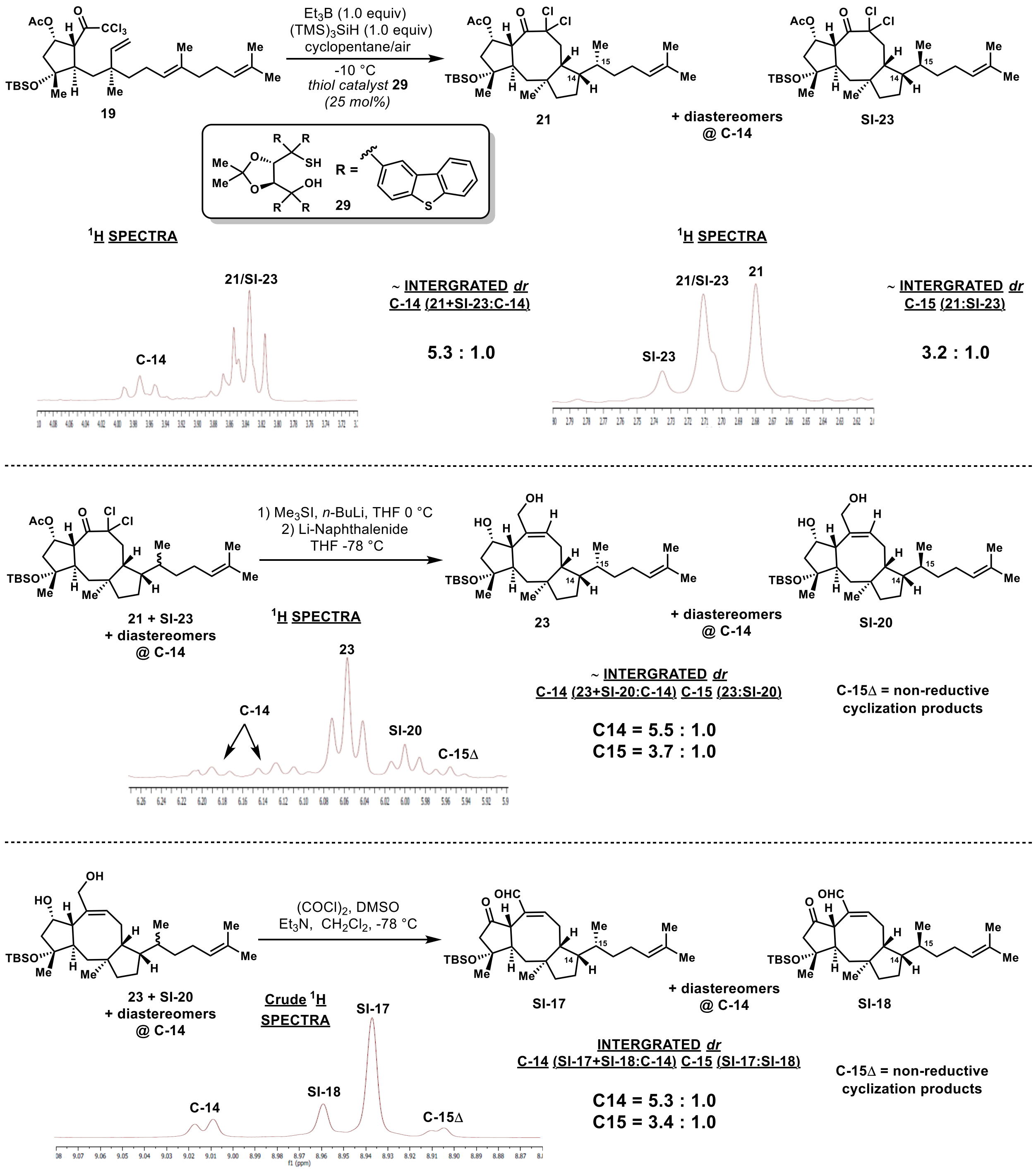
23 (Major)

SI-18 (Minor)

SI-17 (Major)

Keto Aldehydes SI-17 and SI-18: *i*. A stirring suspension of trimethylsulfonium iodide (855 mg, 4.18 mmol, 24 equiv) in THF (7.6 mL) was cooled to 0 °C, and *n*-butyllithium (2.5 M in hexanes, 0.42 mL, 1.04 mmol, 6.0 equiv) was added dropwise. The resulting suspension was stirred vigorously for 15 minutes, and then a solution of cyclization products containing **21** (105 mg, 0.174 mmol, 1.0 equiv) in THF (2 mL) was added dropwise. The residual **21** was rinsed into the reaction with additional THF (2 x 0.2 mL). The reaction mixture was then stirred for 10 minutes at 0 °C, and quenched with a saturated aqueous solution of NH_4Cl (5 mL), poured into water (10 mL) extracted with Et_2O (3 x 20 mL), washed with brine (15 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The crude residue was then purified by column chromatography (3% Et_2O in hexanes → 18% Et_2O in hexanes) to yield 60 mg of intermediate epoxides (0.105 mmol, 60%). *ii*. The aforementioned epoxides (60 mg, 0.105 mmol, 1.0 equiv) were dissolved in THF (2.6 mL), and added dropwise, down the side of the flask, over a period of 5 minutes via syringe pump to lithium naphthalenide (1 M in THF, 4.20 mL, 4.20 mmol, 40 equiv) in THF (9 mL) at -78 °C. THF (2 x 0.7 mL) was then used to rinse the residual starting material into the reaction flask. The resulting black solution was stirred at -78 °C for 20 minutes, then quenched with Et_2O (15 mL) and a saturated aqueous solution of NH_4Cl (15 mL), poured into water (20 mL), extracted with Et_2O (3 x 30 mL), washed with brine (15 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The resulting crude residue was purified by column chromatography (0% Et_2O in CH_2Cl_2 → 40% Et_2O in CH_2Cl_2) to yield 40.6 mg of an inseparable mixture of diols favoring **23** (0.0804 mmol, 77%)

as a colorless oil. Analytically-pure **23** and its C-15 diastereomer **SI-20** could not be isolated at this stage, but they were prepared from samples of aldehydes **SI-17** and **SI-18** in a later reaction (see page S41-S42). *iii*. In a separate flask, DMSO (86 µL, 1.22 mmol, 15 equiv) in CH_2Cl_2 (2.0 mL) was added dropwise to oxalyl chloride (69 µL, 0.802 mmol, 10 equiv) in CH_2Cl_2 (4.7 mL) at -78 °C. The resulting solution was stirred at -78 °C for 30 minutes, then a solution of **23** (40.6 mg, 0.0804 mmol, 1.0 equiv) in CH_2Cl_2 (4 mL) was added dropwise, down the side of the flask, over 5 minutes via syringe pump. CH_2Cl_2 (2 x 1 mL) was used to rinse the residual **23** into the reaction flask. After stirring at -78 °C for 30 minutes, Et_3N (216 µL, 1.61 mmol, 20 equiv) was added dropwise. The reaction mixture was stirred for 3 hours, slowly warming to 0 °C, then quenched with H_2O (25 mL), extracted with CH_2Cl_2 (3 x 30 mL), washed with brine (20 mL), dried over $MgSO_4$, and concentrated *in vacuo*. A crude ^{1}H NMR indicated a 3.4:1 ratio of **SI-17** and **SI-18** (C-15 *dr*), and an overall C-14 *dr* of 5.3:1 (see Figure SI-3, Page S40). The crude material was then purified by column chromatography (2% Et_2O in hexanes → 30% Et_2O in hexanes) to yield 20.5 mg of **SI-17** (0.0409 mmol) containing 6% C-15 alkenes, and 10.9 mg (0.0218 mmol) of a 1.3:1 mixture of **SI-18** and C-14 diastereomers (Total: 31.4 mg, 0.0627 mmol, 78%). Analytically-pure samples of **SI-17** and **SI-18** could be obtained by Preparative TLC (66% CH_2Cl_2 in hexanes, 13% EtOAc in hexanes, respectively). **SI-17**: $[\alpha]_D^{25}$ = -92.75° (c = 0.0029 g/mL, $CHCl_3$); R_f = 0.32 (33% Et_2O in hexanes); ^{1}H NMR (600 MHz, benzene-d_6) δ 8.93 (s, 1 H), 6.03-6.00 (m, 1 H) 5.24 (app t, *J* = 7.2 Hz, 1 H), 3.67 (d, *J* = 15.4 Hz, 1 H), 2.97 (d, *J* = 11.2 Hz, 1 H), 2.52 (d, *J* = 15.4 Hz, 1 H), 2.47 (ddd, *J* = 12.3, 11.8, 4.0 Hz, 1 H), 2.30-2.24 (m, 2 H), 2.19-2.12 (m, 1 H), 2.05-1.95 (m, 2 H), 1.71 (s, 3 H), 1.71-1.63 (m, 1 H), 1.62 (s, 3 H), 1.61-1.53 (m, 1 H), 1.48-1.41 (m, 1 H), 1.40-1.30 (m, 3 H), 1.29-1.21 (m, 2 H), 1.18 (app t, *J* = 12.8 Hz, 1 H), 1.05-0.95 (m, 1 H), 0.97 (s, 3 H), 0.94 (s, 9 H), 0.85 (d, *J* = 6.5 Hz, 3 H) 0.68 (s, 3 H), 0.07 (s, 3 H), 0.04 (s, 3 H); ^{13}C NMR (150 MHz, benzene-d_6) δ 212.0, 193.6, 157.2, 142.4, 131.6, 125.0, 77.8, 56.2, 52.0, 51.5, 50.0, 45.5, 44.5, 43.94, 43.86, 37.5, 32.1, 30.8, 27.2, 26.3, 26.0, 25.9, 24.9, 23.0, 18.7, 18.2, 17.8, -2.4, -2.5; IR ν_{max} (cm^{-1}) 2955, 2928, 2856, 1742, 1689, 1634, 1463, 1378, 1260; HRMS (ESI) calcd for $C_{31}H_{52}O_3NaSi$ [M + Na$^+$] *m/z* 523.3578, found 523.3575. **SI-18**: $[\alpha]_D^{25}$ = -81.90° (c = 0.0014 g/mL, $CHCl_3$); R_f = 0.26 (33% Et_2O in hexanes); ^{1}H NMR (500 MHz, benzene-d_6) δ 8.95 (s, 1 H), 6.00 (dd, *J* = 6.8, 2.4 Hz, 1 H) 5.29 (app t, *J* = 7.0 Hz, 1 H), 3.68 (dd, *J* = 15.5, 1.4 Hz, 1 H), 3.00 (d, *J* = 11.2 Hz, 1 H), 2.53 (dd, *J* = 15.4, 1.5 Hz, 1 H), 2.47 (ddd, *J* = 15.5, 12.5, 4.0 Hz, 1 H), 2.28-2.11 (m, 3 H), 2.04-1.95 (m, 2 H), 1.75 (s, 3 H), 1.65 (s, 3 H), 1.66-1.58 (m, 1 H), 1.56-1.45 (m, 2 H), 1.44-1.18 (m, 4 H), 1.17 (app t, *J* = 13.0 Hz, 1 H), 1.12-1.02 (m, 1 H), 0.99-0.91 (m, 1H), 0.97 (s, 3 H), 0.94 (s, 9 H), 0.81 (d, *J* = 6.3 Hz, 3 H), 0.66 (s, 3 H), 0.07 (s, 3 H), 0.04 (s, 3 H); ^{13}C NMR (150 MHz, benzene-d_6) δ 212.1, 193.6, 157.4, 142.4, 131.3, 125.4, 77.8, 56.2, 52.2, 52.0, 50.1, 45.6, 44.3, 43.8, 43.7, 36.2, 31.8, 30.6, 27.2, 25.97, 25.96, 25.8, 24.9, 23.1, 19.8, 18.2, 17.8, -2.4, -2.5; IR ν_{max} (cm^{-1}) 2927, 2856, 1742, 1689, 1634, 1465, 1416, 1379, 1259; HRMS (ESI) calcd for $C_{31}H_{52}O_3NaSi$ [M + Na$^+$] *m/z* 523.3578, found 523.3575.



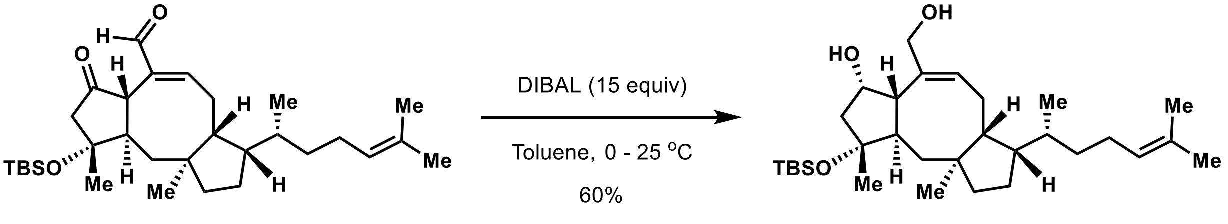
Summary

	@ C-14	@ C-15
dr at stage 21 + SI-23:	5.3 : 1.0	3.2 : 1.0
23 + SI-20:	5.5 : 1.0	3.7 : 1.0
SI-17 + SI-18:	5.3 : 1.0	3.4 : 1.0

dr at stage SI-17 and SI-18 used throughout text

Scheme S5: Determination of C-15 and C-14 *dr* in the conversion of acetylated keto-alcohol **19** to cyclization product **21** and eventually keto aldehydes **SI-17** and **SI-18**.

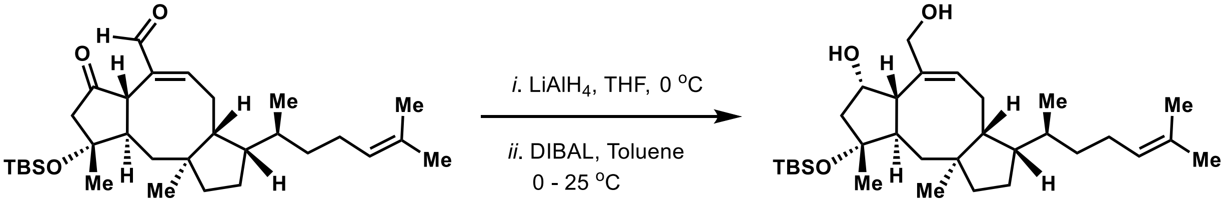
Procedure for preparing pure diol 23 from a pure sample of SI-17:



SI-17 **23 (Isomerically-Pure)**

DIBAL (1 M in hexanes, 0.15 mL, 0.150 mmol, 7.5 equiv) was added dropwise to keto aldehyde **SI-17** (10 mg, 0.0200 mmol, 1.0 equiv) in toluene (1 mL) at 0 °C. The resulting solution was stirred for 30 minutes, then warmed to 25 °C. A second portion of DIBAL (1 M in hexanes, 0.15 mL, 0.150 mmol, 7.5 equiv) was then added dropwise, and the reaction mixture was stirred for an additional 1 hour. Upon completion, the reaction was quenched with Et_2O (1 mL) and 10% aqueous Rochelle's salt solution (1 mL), and stirred at 25 °C for 2 hours. The reaction mixture was then poured into water (10 mL), extracted with Et_2O (3 x 10 mL), washed with brine (5 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The crude material was purified by column chromatography (10% Et_2O in hexanes → 70% Et_2O in hexanes) to provide 6 mg of diol **23** (0.0119 mmol, 60%) as a waxy semi-solid. **23**: $[\alpha]_D^{25}$ = -16.33° (c = 0.00086 g/mL, $CHCl_3$); R_f = 0.47 (25% Et_2O in CH_2Cl_2); ^1H NMR (500 MHz, benzene-d_6) δ 5.98 (app t, *J* = 7.5 Hz, 1 H), 5.28 (app t, *J* = 7.0 Hz, 1 H), 4.21-4.17 (m, 1 H), 4.08 (d, *J* = 11.4, 1 H), 3.82 (d, *J* = 11.4 Hz, 1 H), 3.22 (br s, 1 H), 2.63 (app t, *J* = 10.0 Hz, 1 H), 2.43 (dd, *J* = 11.7, 5.4 Hz, 1 H), 2.18-1.94 (m, 6 H), 1.90 (dd, *J* = 13.2, 2.0 Hz, 1 H), 1.85 (dd, *J* = 13.6, 6.3 Hz, 1 H), 1.71 (s, 3 H), 1.61 (s, 3 H), 1.55-1.44 (m, 4 H), 1.41-1.31 (m, 1 H), 1.29-1.14 (m, 2 H), 1.01 (s, 3 H), 0.99 (s, 9 H), 0.99 (s, 3 H), 0.94-0.90 (m, 1H), 0.88 (dd, *J* = 13.0, 10.0, 1 H), 0.80 (d, *J* = 6.5 Hz, 3 H), 0.13 (s, 3 H), 0.12 (s, 3 H); ^{13}C NMR (150 MHz, benzene-d_6) δ 136.6, 135.8, 131.7, 125.4, 83.3, 71.7, 70.2, 52.8, 52.4, 49.5, 47.5, 44.7, 43.8, 43.5, 38.0, 33.0, 26.7, 26.3, 25.9, 25.4, 24.3, 24.1, 20.9, 18.3, 17.8, 17.3, -1.8, -1.9 (one carbon could not be detected); IR ν_{max} (cm^{-1}) 3348, 2950, 2926, 2855, 1462, 1377, 1256; HRMS (ESI) calcd for $C_{31}H_{56}O_3NaSi$ [M + Na^+] *m/z* 527.3891, found 527.3893.

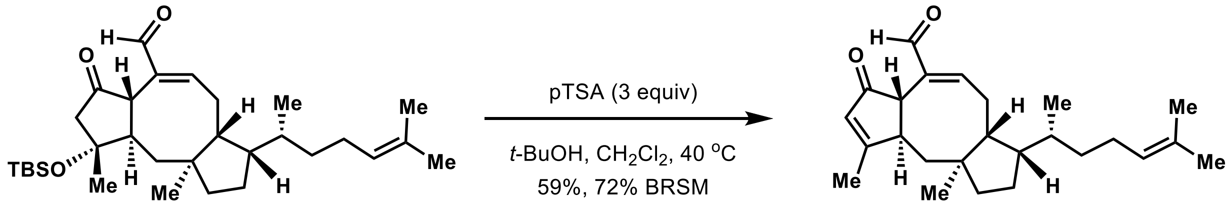
Procedure for preparing pure diol SI-20 from a mixture of SI-18 and C-14 diastereomers:



SI-18
+ C-14 Diastereomers

SI-20 (Isomerically-Pure)

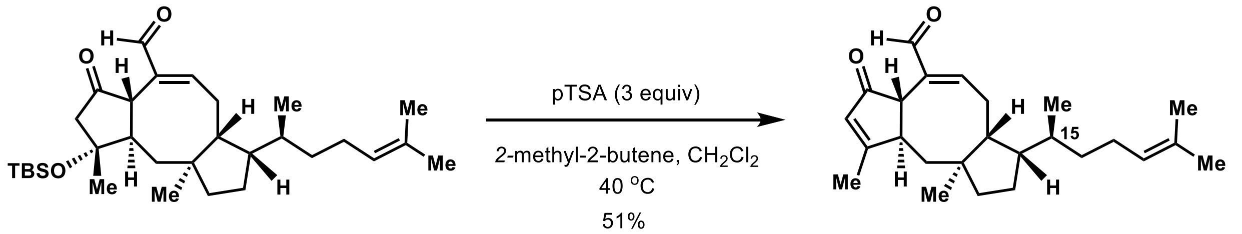
i. Lithium aluminum hydride (2 M in Et_2O, 45 µL, 0.0900 mmol, 3.0 equiv) was added dropwise to a 1.4:1 mixture of **SI-18** and inseparable C-14 diastereomers (15 mg total, 0.0300 mmol, 1.0 equiv) in THF (1.5 mL) at -78 °C. The reaction mixture was then stirred for 2 hours, during which time it was allowed to warm to 0 °C. The reaction was then quenched with 10% aqueous Rochelle's salt solution (1 mL), Et_2O (2 mL) was added, and the resulting biphasic mixture was stirred at 25 °C for 2 hours. The reaction was then poured into water (5 mL), extracted with Et_2O (3 x 10 mL), washed with brine (5 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The crude material was purified by column chromatography (4% Et_2O in hexanes → 40% Et_2O in hexanes) to isolate 4 mg of an isomerically-pure partial reduction intermediate. *ii*. DIBAL (1 M in hexanes, 70 µL, 0.0700 mmol, 8.75 equiv) was added dropwise to this intermediate (4 mg, 0.00800 mmol, 1.0 equiv) in toluene (0.5 mL) at 0 °C. The resulting solution was stirred for 30 minutes and then warmed to 25 °C. A second portion of DIBAL (1 M in hexanes, 70 µL, 0.0700 mmol, 8.75 equiv) was then added dropwise, and the reaction mixture was stirred for an additional 1 hour. Upon completion, the reaction was quenched with Et_2O (1 mL) and 10% aqueous Rochelle's salt solution (1 mL), and stirred at 25 °C for 2 hours. The reaction mixture was then poured into water (10 mL), extracted with Et_2O (3 x 10 mL), washed with brine (5 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The crude material was then purified by Preparative TLC (25% Et_2O in CH_2Cl_2) to provide 2 mg of diol **SI-20** (0.00396 mmol, 13% over 2 steps) as a waxy semi-solid. **SI-20**: $[\alpha]_D^{25}$ = -44.93° (c = 0.0016 g/mL, $CHCl_3$); R_f = 0.47 (25% Et_2O in CH_2Cl_2); ^1H NMR (500 MHz, benzene-d_6) δ 5.93 (app t, *J* = 6.4 Hz, 1 H), 5.28 (app t, *J* = 7.0 Hz, 1 H), 4.21-4.18 (m, 1 H), 4.18 (d, *J* = 11.5, 1 H), 3.88 (d, *J* = 11.5 Hz, 1 H), 2.59-2.50 (m, 2 H), 2.22-1.91 (m, 7 H), 1.86 (dd, *J* = 13.2, 2.0 Hz, 1 H), 1.75 (dd, *J* = 13.6, 6.1 Hz, 1 H), 1.71 (s, 3 H), 1.62 (s, 3 H), 1.60-1.50 (m, 2 H), 1.49-1.40 (m, 2 H), 1.38-1.29 (m, 2H), 1.24 (ddd, *J* = 12.0, 11.8, 6.1 Hz, 1 H), 1.18-1.09 (m, 1 H), 1.01 (s, 3 H), 1.00 (s, 3 H), 0.96 (s, 9 H), 0.95 (d, *J* = 6.5 Hz, 3 H), 0.85 (dd, *J* = 13.2, 9.2, 1 H), 0.10 (s, 3 H), 0.10 (s, 3 H); ^{13}C NMR (150 MHz, benzene-*d*$_6$) δ 136.8, 135.4, 131.1, 125.5, 83.8, 72.3, 70.0, 52.5, 51.1, 49.9, 49.4, 48.3, 45.2, 43.93, 43.88, 34.5, 32.8, 26.4, 26.3, 26.2, 25.9, 24.9, 24.5, 21.3, 20.0, 18.3, 17.8, -1.8, -1.9; IR ν_{max} (cm^{-1}) 3350, 2950, 2930, 2856, 1462, 1372, 1256; HRMS (ESI) calcd for $C_{31}H_{56}O_3NaSi$ [M + Na$^+$] *m/z* 527.3891, found 527.3892.



SI-17

(-)-6-*epi*-ophiobolin N (3)

(-)-6-*epi*-ophiobolin N (3): *tert*-butanol (80 μL) and pTSA (14.8 mg, 0.0773 mmol, 3.0 equiv) were added to a stirring solution of keto-aldehyde **SI-17** (13 mg, 0.0258 mmol, 1.0 equiv) in CH_2Cl_2 (4.2 mL). The mixture was heated to 40 °C and stirred at this temperature for 54 hours. The reaction mixture was then cooled to 25 °C, quenched with saturated aqueous $NaHCO_3$ (3 mL), poured into H_2O (5 mL), extracted with Et_2O (3 x 10 mL), washed with brine (5 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The crude material was purified by column chromatography (10% Et_2O in hexanes → 70% Et_2O in hexanes) to provide 5.6 mg of **(-)-6-*epi*-ophiobolin N** as an oil, along with 2.5 mg of recovered **SI-17** (0.0152 mmol, 59% + 19% recovered starting material). **(-)-6-*epi*-ophiobolin N (3):** $[\alpha]_D^{25}$ = -105.41° (c = 0.0037 g/mL, MeOH), (literature[15] $[\alpha]_D^{23}$ = +88° (c = 0.0034g/mL, MeOH)); R$_f$ = 0.39 (75% Et_2O in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.32 (s, 1 H), 6.84 (dd, *J* = 6.4, 3.3 Hz, 1 H), 6.04 (br s, 1 H), 5.12 (app t, *J* = 7.0 Hz, 1 H), 3.45 (d, *J* = 4.2 Hz, 1 H), 2.75-2.66 (m, 3 H), 2.24 (ddd, *J* = 21.0, 14.7, 6.2 Hz, 1 H), 2.13-2.05 (m, 1 H), 2.07 (s, 3 H), 2.04 (dd, *J* = 13.2, 3.8 Hz, 1 H), 1.92 (dddd, *J* = 15.08, 7.79, 7.79, 7.65 Hz, 1 H), 1.80-1.70 (m, 1 H), 1.70 (s, 3 H), 1.64-1.55 (m, 1 H), 1.61 (s, 3 H), 1.50 (dd, *J* = 11.8, 5.0 Hz, 1 H), 1.46-1.38 (m, 3 H), 1.27-1.18 (m, 1 H), 1.17 (app t, *J* = 13.1 Hz, 1 H), 1.03-0.95 (m, 1 H), 0.90 (d, *J* = 6.5 Hz, 3 H), 0.86 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.4, 193.1, 177.4, 156.9, 140.6, 131.8, 130.4, 124.6, 51.7, 50.2, 49.2, 46.1, 45.2, 44.8, 43.4, 37.4, 32.0, 31.2, 27.2, 25.6, 25.8, 23.2, 18.8, 17.9, 17.3; IR ν_{max} (cm^{-1}) 2958, 2924, 2856, 1709, 1686, 1638, 1621, 1446, 1416, 1377, 1310, 1263, 1226, 1202; HRMS (ESI) calcd for $C_{25}H_{36}O_2Na$ [M + Na$^+$] *m/z* 391.2608, found 391.2602.

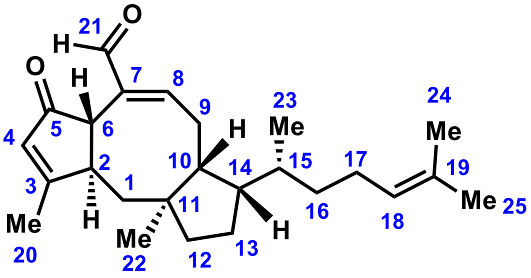


SI-18

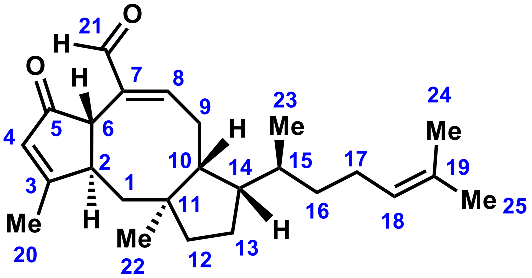
(-)-6-*epi*-15-*epi*-ophiobolin N (SI-19)

(-)-6-*epi*-15-*epi*-ophiobolin N (SI-19): A sample of 4 mg of keto-aldehyde **SI-18** was divided into 2 batches (2 mg, 0.00396 mmol, 1.0 equiv) and dissolved in CH_2Cl_2 (0.5 mL). 2-methyl-2-butene (20 μL) and pTSA (2.3 mg, 0.0119 mmol, 3.0 equiv) were added, and the reaction mixtures were then heated to 40 °C and stirred for 7 hours. After completion, the reaction mixtures were quenched with saturated aqueous $NaHCO_3$ (1 mL), combined and poured into H_2O (4 mL), extracted with Et_2O (3 x 10 mL), washed with brine (5 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The crude material was purified by column chromatography (10% Et_2O in hexanes → 70% Et_2O in hexanes) to provide 1.5 mg of **(-)-6-*epi*-15-*epi*-ophiobolin N** (0.00407 mmol, 51% yield) as an oil. **(-)-6-*epi*-15-*epi*-ophiobolin N (SI-19):** $[\alpha]_D^{25}$ = -47.00° (c = 0.001 g/mL, MeOH); R_f = 0.33 (75% Et_2O in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.32 (s, 1 H), 6.85 (dd, *J* = 6.5, 2.3 Hz, 1 H), 6.04 (br s, 1 H), 5.10 (app t, *J* = 7.1 Hz, 1 H), 3.46 (d, *J* = 4.2 Hz, 1 H), 2.77-2.68 (m, 3 H), 2.25 (ddd, *J* = 21.2, 14.9, 6.2 Hz, 1 H), 2.10-2.02 (m, 1 H), 2.07 (s, 3 H), 2.04 (dd, *J* = 13.0, 3.5 Hz, 1 H), 1.89 (dddd, *J* = 15.0, 7.4, 7.1, 7.1 Hz, 1 H), 1.79-1.69 (m, 1 H), 1.70 (s, 3 H), 1.62 (s, 3 H), 1.62-1.56 (m, 1 H), 1.55-1.37 (m, 4 H), 1.28-1.18 (m, 1 H), 1.18 (app t, *J* = 13.1 Hz, 1 H), 1.12-1.02 (m, 1 H), 0.91 (d, *J* = 6.2 Hz, 3 H), 0.87 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 207.3, 193.1, 177.4, 156.9, 140.6, 131.5, 130.4, 124.9, 52.4, 50.2, 49.1, 46.0, 45.1, 44.9, 43.4, 36.0, 31.7, 31.0, 27.1, 25.9, 25.4, 23.3, 19.9, 17.8, 17.3; IR ν_{max} (cm^{-1}) 2955, 2916, 2850, 1708, 1686, 1638, 1619, 1537, 1439, 1377, 1310, 1262, 1225, 1202; HRMS (ESI) calcd for $C_{25}H_{37}O_2$ [M + H$^+$] *m/z* 369.2788, found 369.2789.

Table S1: ^{1}H NMR Comparison



6-*epi*-ophiobolin N (3)



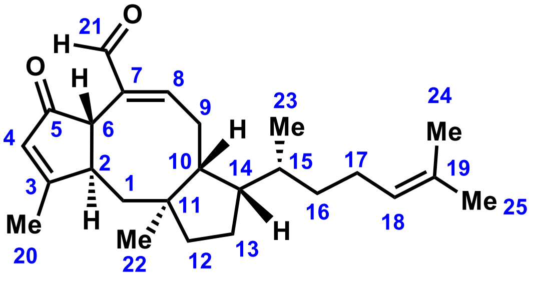
6-*epi*-15-*epi*-ophiobolin N (SI-19)

	6-*epi*-ophiobolin N (3)	6-*epi*-ophiobolin N (3)	6-*epi*-15-*epi*-ophiobolin N (SI-19)
C	600 MHz[15]	500 MHz (This Work)*	500 MHz (This Work)*
1α	1.16 (t, *J* = 13.0 Hz, 1 H)	1.17 (t, *J* = 13.1 Hz, 1 H)	1.18 (t, *J* = 13.1 Hz, 1 H)
1β	2.04 (m, 1 H)	2.04 (m, 1 H)	2.04 (m, 1 H)
2	2.68 (m, 1 H)	2.69 (m, 1 H)	2.70 (m, 1 H)
4	6.04 (s, 1 H)	6.04 (s, 1 H)	6.04 (s, 1 H)
6	3.45 (d, *J* = 4.3 Hz, 1 H)	3.45 (d, *J* = 4.2 Hz, 1 H)	3.46 (d, *J* = 4.2 Hz, 1 H)
8	6.84 (d, *J* = 4.4 Hz, 1 H)	6.84 (d, *J* = 4.0 Hz, 1 H)	6.85 (d, *J* = 4.0 Hz, 1 H)
9α	2.71 (m, 1 H)	2.70 (m, 1 H)	2.74 (m, 1 H)
9β	2.23 (m, 1 H)	2.24 (m, 1 H)	2.25 (m, 1 H)
10	2.71 (m, 1 H)	2.71 (m, 1 H)	2.71 (m, 1 H)
12a	1.43 (m, 1 H)	1.43 (m, 1 H)	1.41 (m, 1 H)
12b	1.51 (m, 1 H)	1.50 (m, 1 H)	1.51 (m, 1 H)
13α	1.25 (m, 1 H)	1.22 (m, 1 H)	1.23 (m, 1 H)
13β	1.61 (m, 1 H)	1.59 (m, 1 H)	1.59 (m, 1 H)
14	1.74 (m, 1 H)	1.75 (m, 1 H)	1.74 (m, 1 H)
15	1.43 (m, 1 H)	1.42 (m, 1 H)	1.48 (m, 1 H)
16a	0.99 (m, 1 H)	0.99 (m, 1 H)	1.08 (m, 1 H)
16b	1.43 (m, 1 H)	1.42 (m, 1 H)	1.48 (m, 1 H)
17a	1.93 (m, 1 H)	1.92 (m, 1 H)	1.89 (m, 1 H)
17b	1.93 (m, 1 H)	2.09 (m, 1 H)**	2.06 (m, 1 H)
18	5.12 (t, *J* = 6.9 Hz, 1 H)	5.12 (t, *J* = 7.0 Hz, 1 H)	5.10 (t, *J* = 7.1 Hz, 1 H)
20	2.07 (s, 3 H)	2.07 (s, 3 H)	2.06 (s, 3 H)
21	9.31 (s, 1 H)	9.32 (s, 1 H)	9.32 (s, 1 H)
22	0.86 (s, 3 H)	0.86 (s, 3 H)	0.87 (s, 3 H)
23	0.90 (d, *J*= 6.6 Hz, 3 H)	0.90 (d, *J* = 6.5 Hz, 3 H)	0.91 (d, *J* = 6.2 Hz, 3 H)
24	1.61 (s, 3 H)	1.61 (s, 3 H)	1.62 (s, 3 H)
25	1.69 (s, 3 H)	1.70 (s, 3 H)	1.70 (s, 3 H)

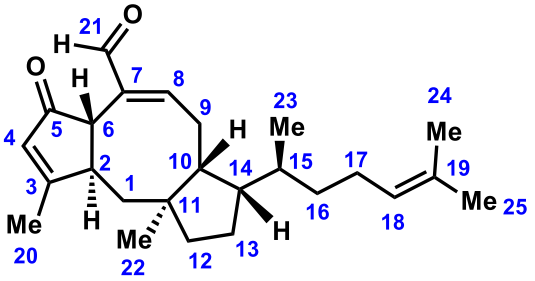
* Although we were able to assign multiplicities and coupling constants to many resonances in the ^{1}H NMR spectrum, reference 15 denotes most resonances as multiplets (m), with the center of the multiplet defining its chemical shift. For direct side-by-side comparison purposes in the table above, we have adopted this designation as well. SI page S43 lists the full assignment using conventional value reporting.

** Reference 15 lists both C-17 protons at δ 1.93, but evidence in 2D ^{1}H COSY suggests diastereotopic resonances at δ 1.92 and 2.09. Other ophiobolins isolated in reference 15 with similar structures also contain a 0.12-0.16 ppm shift between diastereotopic C-17 protons. Thus, we believe this to be a typographical error in reference 15.

Table S2: ^{13}C NMR Comparison



6-*epi*-ophiobolin N (3)



6-*epi*-15-*epi*-ophiobolin N (SI-19)

For this comparison, chemical shifts are reported relative to the residual solvent signal ($CDCl_3$), which is set to δ 77.0 ppm.

	6-*epi*-ophiobolin N (3)	6-*epi*-ophiobolin N (3)	6-*epi*-15-*epi*-ophiobolin N (SI-19)
13C	150 MHz[15]	150 MHz (This Work)	150 MHz (This Work)
1	45.8	45.9	45.9
2	49.0	49.0	49.0
3	177.5	177.3	177.2
4	130.2	130.3	130.3
5	207.4	207.2	207.2
6	50.0	50.0	50.1
7	140.4	140.5	140.5
8	156.9	156.7	156.7
9	31.0	31.0	30.8
10	43.1	43.2	43.2
11	45.0	45.1	44.9
12	44.6	44.6	44.7
13	27.1	27.1	26.9
14	51.5	51.5	52.3
15	31.8	31.9	31.6
16	37.2	37.3	35.8
17	25.7	25.8	25.2
18	124.4	124.4	124.7
19	131.6	131.6	131.3
20	17.2	17.2	17.2
21	193.0	192.9	192.9
22	23.1	23.1	23.2
23	18.6	18.6	19.7
24	17.7	17.7	17.7
25	25.7	25.7	25.7

X-ray Crystallographic Analysis of 15

A colorless blade 0.040 x 0.020 x 0.010 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using phi and omega scans. Crystal-to-detector distance was 60 mm and exposure time was 10 seconds per frame using a scan width of 2.0°. Data collection was 99.8% complete to 67.000° in θ. A total of 27368 reflections were collected covering the indices, -15<=*h*<=15, -8<=*k*<=8, -17<=*l*<=17. 4857 reflections were found to be symmetry independent, with an R_{int} of 0.1273. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be P 21 (No. 4). The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by iterative methods (SHELXT) 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-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014.

Table S3. Crystal data and structure refinement for **15**.

X-ray ID	maimone57	
Sample/notebook ID	ZGBN7P119	
Empirical formula	C25 H44 Cl2 O3 Si	
Formula weight	491.59	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 12.7080(10) Å	α= 90°.
	b = 7.4276(7) Å	β= 103.309(6)°.
	c = 14.6262(11) Å	γ = 90°.
Volume	1343.5(2) Å^3	
Z	2	
Density (calculated)	1.215 Mg/m^3	
Absorption coefficient	2.775 mm^{-1}	
F(000)	532	
Crystal size	0.040 x 0.020 x 0.010 mm^3	
Theta range for data collection	3.105 to 69.221°.	
Index ranges	-15<=h<=15, -8<=k<=8, -17<=l<=17	
Reflections collected	27368	
Independent reflections	4857 [R(int) = 0.1273]	
Completeness to theta = 67.000°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.929 and 0.782	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4857 / 1 / 291	
Goodness-of-fit on F^2	1.139	
Final R indices [I>2sigma(I)]	R1 = 0.1119, wR2 = 0.2594	
R indices (all data)	R1 = 0.1340, wR2 = 0.2828	
Absolute structure parameter	0.127(16)	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.660 and -0.545 e.Å^{-3}	

Table S4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) For **15**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	7480(8)	3555(15)	1996(7)	42(2)
C(2)	7711(7)	3088(13)	3051(6)	36(2)
C(3)	7662(7)	4584(12)	3768(6)	33(2)
C(4)	8503(8)	4288(13)	4701(6)	39(2)
C(5)	7932(8)	4419(17)	5498(7)	45(2)
C(6)	6921(8)	5494(14)	5083(6)	39(2)
C(7)	6560(7)	4814(11)	4063(6)	33(2)
C(8)	5795(7)	6246(11)	3513(5)	31(2)
C(9)	5196(7)	5854(11)	2509(5)	30(2)
C(10)	4256(7)	7227(12)	2106(6)	31(2)
C(11)	4678(8)	8333(12)	1376(7)	36(2)
C(12)	5313(7)	7006(12)	937(6)	33(2)
C(13)	5941(7)	5879(12)	1796(6)	33(2)
C(14)	6331(8)	4098(13)	1470(6)	35(2)
C(15)	9583(8)	4140(13)	4837(7)	39(2)
C(16)	10178(8)	4233(16)	4071(8)	48(2)
C(17)	10312(9)	3914(16)	5796(8)	50(2)
C(18)	5954(8)	3006(15)	4053(8)	44(2)
C(19)	3896(8)	8485(12)	2793(7)	36(2)
C(20)	2892(8)	4122(14)	3137(7)	40(2)
C(21)	1287(7)	6899(13)	2094(7)	40(2)
C(22)	1752(8)	3418(13)	1113(7)	39(2)
C(23)	939(10)	4270(17)	279(8)	51(2)
C(24)	1097(10)	2102(15)	1595(8)	51(2)
C(25)	2648(10)	2365(16)	802(9)	54(3)
O(1)	3335(5)	6216(8)	1577(4)	32(1)
O(2)	4628(5)	5942(9)	236(4)	35(1)
O(3)	5609(6)	2715(9)	1524(4)	38(1)
Si(1)	2357(2)	5222(3)	1986(2)	32(1)
Cl(1)	8384(2)	5321(5)	1780(2)	52(1)
Cl(2)	7825(3)	1565(5)	1418(2)	64(1)

Table S5. Bond lengths [Å] and angles [°] for **15**.

C(1)-C(14)	1.539(13)	C(12)-H(12)	1.0000
C(1)-C(2)	1.544(12)	C(13)-C(14)	1.527(12)
C(1)-Cl(2)	1.806(10)	C(13)-H(13)	1.0000
C(1)-Cl(1)	1.818(12)	C(14)-O(3)	1.392(12)
C(2)-C(3)	1.539(12)	C(14)-H(14)	1.0000
C(2)-H(2A)	0.9900	C(15)-C(16)	1.490(16)
C(2)-H(2B)	0.9900	C(15)-C(17)	1.501(13)
C(3)-C(4)	1.543(12)	C(16)-H(16A)	0.9800
C(3)-C(7)	1.567(12)	C(16)-H(16B)	0.9800
C(3)-H(3)	1.0000	C(16)-H(16C)	0.9800
C(4)-C(15)	1.346(15)	C(17)-H(17A)	0.9800
C(4)-C(5)	1.510(14)	C(17)-H(17B)	0.9800
C(5)-C(6)	1.516(14)	C(17)-H(17C)	0.9800
C(5)-H(5A)	0.9900	C(18)-H(18A)	0.9800
C(5)-H(5B)	0.9900	C(18)-H(18B)	0.9800
C(6)-C(7)	1.541(11)	C(18)-H(18C)	0.9800
C(6)-H(6A)	0.9900	C(19)-H(19A)	0.9800
C(6)-H(6B)	0.9900	C(19)-H(19B)	0.9800
C(7)-C(8)	1.538(11)	C(19)-H(19C)	0.9800
C(7)-C(18)	1.546(13)	C(20)-Si(1)	1.855(9)
C(8)-C(9)	1.518(10)	C(20)-H(20A)	0.9800
C(8)-H(8A)	0.9900	C(20)-H(20B)	0.9800
C(8)-H(8B)	0.9900	C(20)-H(20C)	0.9800
C(9)-C(13)	1.562(12)	C(21)-Si(1)	1.877(9)
C(9)-C(10)	1.578(11)	C(21)-H(21A)	0.9800
C(9)-H(9)	1.0000	C(21)-H(21B)	0.9800
C(10)-O(1)	1.455(11)	C(21)-H(21C)	0.9800
C(10)-C(19)	1.519(11)	C(22)-C(25)	1.534(14)
C(10)-C(11)	1.537(12)	C(22)-C(23)	1.542(13)
C(11)-C(12)	1.508(12)	C(22)-C(24)	1.554(15)
C(11)-H(11A)	0.9900	C(22)-Si(1)	1.887(9)
C(11)-H(11B)	0.9900	C(23)-H(23A)	0.9800
C(12)-O(2)	1.422(11)	C(23)-H(23B)	0.9800
C(12)-C(13)	1.566(11)	C(23)-H(23C)	0.9800

C(24)-H(24A)	0.9800	C(25)-H(25C)	0.9800
C(24)-H(24B)	0.9800	O(1)-Si(1)	1.670(6)
C(24)-H(24C)	0.9800	O(2)-H(2)	0.8400
C(25)-H(25A)	0.9800	O(3)-H(3A)	0.8400
C(25)-H(25B)	0.9800		

C(14)-C(1)-C(2)	119.9(8)	C(5)-C(6)-H(6B)	110.9
C(14)-C(1)-Cl(2)	106.6(7)	C(7)-C(6)-H(6B)	110.9
C(2)-C(1)-Cl(2)	105.8(7)	H(6A)-C(6)-H(6B)	108.9
C(14)-C(1)-Cl(1)	106.8(7)	C(8)-C(7)-C(6)	106.9(7)
C(2)-C(1)-Cl(1)	110.7(7)	C(8)-C(7)-C(18)	110.0(7)
Cl(2)-C(1)-Cl(1)	106.2(5)	C(6)-C(7)-C(18)	109.3(8)
C(3)-C(2)-C(1)	119.4(8)	C(8)-C(7)-C(3)	115.4(7)
C(3)-C(2)-H(2A)	107.5	C(6)-C(7)-C(3)	102.5(7)
C(1)-C(2)-H(2A)	107.5	C(18)-C(7)-C(3)	112.2(8)
C(3)-C(2)-H(2B)	107.5	C(9)-C(8)-C(7)	119.3(7)
C(1)-C(2)-H(2B)	107.5	C(9)-C(8)-H(8A)	107.5
H(2A)-C(2)-H(2B)	107.0	C(7)-C(8)-H(8A)	107.5
C(2)-C(3)-C(4)	111.8(8)	C(9)-C(8)-H(8B)	107.5
C(2)-C(3)-C(7)	116.4(7)	C(7)-C(8)-H(8B)	107.5
C(4)-C(3)-C(7)	104.6(7)	H(8A)-C(8)-H(8B)	107.0
C(2)-C(3)-H(3)	107.9	C(8)-C(9)-C(13)	113.4(7)
C(4)-C(3)-H(3)	107.9	C(8)-C(9)-C(10)	113.9(7)
C(7)-C(3)-H(3)	107.9	C(13)-C(9)-C(10)	105.4(6)
C(15)-C(4)-C(5)	123.1(8)	C(8)-C(9)-H(9)	108.0
C(15)-C(4)-C(3)	128.1(9)	C(13)-C(9)-H(9)	108.0
C(5)-C(4)-C(3)	108.4(8)	C(10)-C(9)-H(9)	108.0
C(4)-C(5)-C(6)	103.8(8)	O(1)-C(10)-C(19)	109.9(7)
C(4)-C(5)-H(5A)	111.0	O(1)-C(10)-C(11)	105.9(7)
C(6)-C(5)-H(5A)	111.0	C(19)-C(10)-C(11)	109.7(7)
C(4)-C(5)-H(5B)	111.0	O(1)-C(10)-C(9)	108.2(6)
C(6)-C(5)-H(5B)	111.0	C(19)-C(10)-C(9)	117.9(7)
H(5A)-C(5)-H(5B)	109.0	C(11)-C(10)-C(9)	104.5(7)
C(5)-C(6)-C(7)	104.5(8)	C(12)-C(11)-C(10)	104.6(7)
C(5)-C(6)-H(6A)	110.9	C(12)-C(11)-H(11A)	110.8
C(7)-C(6)-H(6A)	110.9	C(10)-C(11)-H(11A)	110.8

C(12)-C(11)-H(11B)	110.8
C(10)-C(11)-H(11B)	110.8
H(11A)-C(11)-H(11B)	108.9
O(2)-C(12)-C(11)	111.8(8)
O(2)-C(12)-C(13)	113.3(7)
C(11)-C(12)-C(13)	103.4(7)
O(2)-C(12)-H(12)	109.4
C(11)-C(12)-H(12)	109.4
C(13)-C(12)-H(12)	109.4
C(14)-C(13)-C(9)	119.3(8)
C(14)-C(13)-C(12)	110.8(7)
C(9)-C(13)-C(12)	105.5(7)
C(14)-C(13)-H(13)	106.9
C(9)-C(13)-H(13)	106.9
C(12)-C(13)-H(13)	106.9
O(3)-C(14)-C(13)	110.8(7)
O(3)-C(14)-C(1)	109.9(8)
C(13)-C(14)-C(1)	114.2(7)
O(3)-C(14)-H(14)	107.2
C(13)-C(14)-H(14)	107.2
C(1)-C(14)-H(14)	107.2
C(4)-C(15)-C(16)	124.2(9)
C(4)-C(15)-C(17)	122.4(10)
C(16)-C(15)-C(17)	113.4(9)
C(15)-C(16)-H(16A)	109.5
C(15)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(15)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(15)-C(17)-H(17A)	109.5
C(15)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(15)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(7)-C(18)-H(18A)	109.5
C(7)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(7)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(10)-C(19)-H(19A)	109.5
C(10)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(10)-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
Si(1)-C(21)-H(21A)	109.5
Si(1)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
Si(1)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(25)-C(22)-C(23)	112.5(10)
C(25)-C(22)-C(24)	109.0(9)
C(23)-C(22)-C(24)	106.6(9)
C(25)-C(22)-Si(1)	110.4(7)
C(23)-C(22)-Si(1)	109.8(7)
C(24)-C(22)-Si(1)	108.5(7)
C(22)-C(23)-H(23A)	109.5
C(22)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(22)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5

C(22)-C(24)-H(24A)	109.5	H(25B)-C(25)-H(25C)	109.5
C(22)-C(24)-H(24B)	109.5	C(10)-O(1)-Si(1)	127.8(5)
H(24A)-C(24)-H(24B)	109.5	C(12)-O(2)-H(2)	109.5
C(22)-C(24)-H(24C)	109.5	C(14)-O(3)-H(3A)	109.5
H(24A)-C(24)-H(24C)	109.5	O(1)-Si(1)-C(20)	111.8(4)
H(24B)-C(24)-H(24C)	109.5	O(1)-Si(1)-C(21)	110.5(4)
C(22)-C(25)-H(25A)	109.5	C(20)-Si(1)-C(21)	109.7(5)
C(22)-C(25)-H(25B)	109.5	O(1)-Si(1)-C(22)	107.0(4)
H(25A)-C(25)-H(25B)	109.5	C(20)-Si(1)-C(22)	108.0(5)
C(22)-C(25)-H(25C)	109.5	C(21)-Si(1)-C(22)	109.8(4)
H(25A)-C(25)-H(25C)	109.5		

Symmetry transformations used to generate equivalent atoms.

Table S6. Anisotropic displacement parameters (Å^{2}x 10^3)for **15**. The anisotropic displacement factor exponent takes the form: -2π^2[h^{2}a*^{2}U^{11} + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	39(5)	56(6)	35(4)	-4(4)	19(4)	11(4)
C(2)	33(4)	43(5)	33(4)	-2(3)	7(3)	3(3)
C(3)	31(4)	35(4)	33(4)	1(3)	7(3)	-5(3)
C(4)	40(5)	41(5)	35(4)	2(3)	6(4)	-5(4)
C(5)	38(5)	63(6)	32(4)	0(4)	5(4)	0(4)
C(6)	38(4)	55(5)	26(4)	-2(4)	9(3)	1(4)
C(7)	33(4)	43(5)	24(4)	0(3)	6(3)	-1(3)
C(8)	30(4)	38(4)	24(3)	-2(3)	5(3)	1(3)
C(9)	30(4)	33(4)	28(4)	-3(3)	10(3)	-2(3)
C(10)	33(4)	32(4)	32(4)	-1(3)	14(3)	2(3)
C(11)	38(4)	33(4)	38(4)	3(3)	14(4)	0(3)
C(12)	34(4)	39(4)	30(4)	6(3)	12(3)	-1(3)
C(13)	31(4)	37(4)	29(4)	-6(3)	6(3)	-3(3)
C(14)	37(4)	41(4)	26(4)	-3(3)	4(3)	10(3)
C(15)	40(5)	36(4)	40(4)	0(3)	5(4)	2(3)
C(16)	33(5)	56(6)	55(6)	9(5)	8(4)	-1(4)
C(17)	44(5)	54(6)	46(5)	-1(4)	-1(4)	5(4)
C(18)	36(5)	48(5)	48(5)	15(4)	7(4)	-4(4)
C(19)	35(4)	35(4)	45(5)	-2(3)	20(4)	2(3)
C(20)	33(4)	51(5)	37(4)	11(4)	8(4)	-1(4)
C(21)	30(4)	41(4)	51(5)	-3(4)	13(4)	5(3)
C(22)	38(5)	38(4)	39(5)	-5(4)	4(4)	1(4)
C(23)	47(6)	56(6)	44(5)	2(4)	-4(4)	-2(5)
C(24)	52(6)	43(5)	54(6)	1(4)	7(5)	-9(4)
C(25)	51(6)	47(5)	65(7)	-21(5)	18(5)	-1(4)
O(1)	31(3)	37(3)	27(2)	2(2)	8(2)	1(2)
O(2)	40(3)	40(3)	27(3)	1(2)	11(3)	4(2)
O(3)	45(4)	37(3)	30(3)	-6(2)	6(3)	5(3)
Si(1)	27(1)	36(1)	33(1)	2(1)	7(1)	1(1)
Cl(1)	33(1)	84(2)	42(1)	10(1)	12(1)	0(1)
Cl(2)	57(2)	81(2)	48(1)	-18(1)	2(1)	32(1)

Table S7. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **15**.

	x	y	z	U(eq)
H(2A)	7192	2140	3132	44
H(2B)	8442	2546	3226	44
H(3)	7834	5752	3495	40
H(5A)	8387	5050	6044	54
H(5B)	7746	3210	5697	54
H(6A)	7081	6800	5097	47
H(6B)	6353	5271	5433	47
H(8A)	5247	6522	3876	37
H(8B)	6223	7357	3503	37
H(9)	4871	4625	2495	36
H(11A)	4071	8843	898	43
H(11B)	5147	9330	1682	43
H(12)	5842	7671	652	40
H(13)	6601	6585	2095	39
H(14)	6342	4243	793	42
H(16A)	9659	4273	3461	73
H(16B)	10639	3167	4099	73
H(16C)	10627	5319	4149	73
H(17A)	10770	4983	5952	75
H(17B)	10768	2849	5801	75
H(17C)	9872	3765	6260	75
H(18A)	6477	2044	4282	67
H(18B)	5559	2732	3410	67
H(18C)	5444	3095	4461	67
H(19A)	3296	9232	2456	55
H(19B)	4501	9259	3094	55
H(19C)	3658	7775	3274	55
H(20A)	3248	2990	3042	61
H(20B)	2296	3873	3440	61
H(20C)	3416	4922	3538	61
H(21A)	1442	7380	2735	60

H(21B)	579	6307	1956	60
H(21C)	1282	7885	1648	60
H(23A)	1317	5131	-41	77
H(23B)	373	4897	509	77
H(23C)	612	3325	-163	77
H(24A)	652	1319	1120	76
H(24B)	629	2791	1913	76
H(24C)	1597	1365	2056	76
H(25A)	2329	1349	406	80
H(25B)	3167	1912	1357	80
H(25C)	3020	3160	445	80
H(2)	4433	5019	485	53
H(3A)	5596	1980	1086	56

X-ray Crystallographic Analysis of SI-6

A colorless block 0.060 x 0.040 x 0.030 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using phi and omega scans. Crystal-to-detector distance was 40 mm and exposure time was 10 seconds per frame using a scan width of 1.0°. Data collection was 100.0% complete to 25.000° in θ. A total of 32793 reflections were collected covering the indices, $-26<=h<=26$, $-12<=k<=12$, $-17<=l<=17$. 5158 reflections were found to be symmetry independent, with an R_{int} of 0.0320. Indexing and unit cell refinement indicated a C-centered, monoclinic lattice. The space group was found to be C 2 (No. 5). The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by iterative methods (SHELXT) 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-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014. Absolute stereochemistry was unambiguously determined to be *R* at C4, C5, C8, C9, C12, C13, and C16, and *S* at C1 and C10, respectively.

Table S8. Crystal data and structure refinement for **SI-6**.

X-ray ID	maimone65	
Sample/notebook ID	HG_B-105-4	
Empirical formula	C26 H46 Cl2 O4 Si	
Formula weight	521.62	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2	
Unit cell dimensions	a = 21.8212(6) Å	α= 90°.
	b = 10.4160(3) Å	β= 122.6120(10)°.
	c = 14.5639(4) Å	γ = 90°.
Volume	2788.33(14) Å^3	
Z	4	
Density (calculated)	1.243 Mg/m^3	
Absorption coefficient	0.305 mm^{-1}	
F(000)	1128	
Crystal size	0.060 x 0.040 x 0.030 mm^3	
Theta range for data collection	1.660 to 25.404°.	
Index ranges	-26<=h<=26, -12<=k<=12, -17<=l<=17	
Reflections collected	32793	
Independent reflections	5158 [R(int) = 0.0320]	
Completeness to theta = 25.000°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.928 and 0.889	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5158 / 1 / 308	
Goodness-of-fit on F^2	1.029	
Final R indices [I>2sigma(I)]	R1 = 0.0286, wR2 = 0.0697	
R indices (all data)	R1 = 0.0302, wR2 = 0.0709	
Absolute structure parameter	-0.022(15)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.305 and -0.160 e.Å^{-3}	

Table S9. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **SI-6**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	6437(1)	6362(3)	7136(2)	18(1)
C(2)	5944(2)	7554(3)	6857(2)	25(1)
C(3)	5333(2)	7115(3)	6986(2)	24(1)
C(4)	5744(1)	6403(3)	8074(2)	19(1)
C(5)	6397(1)	5703(2)	8088(2)	17(1)
C(6)	6347(1)	4222(2)	8053(2)	20(1)
C(7)	7053(1)	3430(2)	8681(2)	20(1)
C(8)	7583(1)	3626(3)	8309(2)	19(1)
C(9)	7986(1)	4916(2)	8658(2)	16(1)
C(10)	8837(1)	4834(3)	9317(2)	18(1)
C(11)	9037(1)	5309(3)	8525(2)	20(1)
C(12)	8498(1)	6394(3)	7912(2)	20(1)
C(13)	7772(1)	5820(2)	7684(2)	17(1)
C(14)	7202(1)	6819(3)	7483(2)	19(1)
C(15)	6113(2)	5546(3)	6099(2)	24(1)
C(16)	5267(1)	5593(3)	8333(2)	20(1)
C(17)	5679(2)	5220(3)	9537(2)	27(1)
C(18)	4550(1)	6253(3)	7998(2)	23(1)
C(19)	7861(2)	2527(3)	8005(2)	24(1)
C(20)	8733(2)	7620(3)	8583(3)	30(1)
C(21)	8845(2)	8200(3)	5748(2)	30(1)
C(22)	9802(2)	6036(3)	7186(2)	31(1)
C(23)	8310(2)	5419(3)	5093(2)	27(1)
C(24)	8637(2)	5401(3)	4383(3)	39(1)
C(25)	7516(2)	5849(3)	4393(2)	31(1)
C(26)	8328(2)	4061(3)	5522(3)	37(1)
O(1)	4627(1)	7430(2)	8552(2)	30(1)
O(2)	7238(1)	3237(2)	7183(2)	24(1)
O(3)	9150(1)	3626(2)	9803(2)	26(1)
O(4)	8397(1)	6695(2)	6883(2)	30(1)
Si(1)	8835(1)	6576(1)	6266(1)	21(1)

Cl(1)	7527(1)	3741(1)	10123(1)	25(1)
Cl(2)	6761(1)	1777(1)	8522(1)	32(1)

Table S10. Bond lengths [Å] and angles [°] for **SI-6**.

C(1)-C(15)	1.534(4)	C(12)-C(20)	1.520(4)
C(1)-C(14)	1.537(3)	C(12)-C(13)	1.552(4)
C(1)-C(2)	1.547(4)	C(13)-C(14)	1.525(4)
C(1)-C(5)	1.589(3)	C(13)-H(13)	1.0000
C(2)-C(3)	1.515(4)	C(14)-H(14A)	0.9900
C(2)-H(2A)	0.9900	C(14)-H(14B)	0.9900
C(2)-H(2B)	0.9900	C(15)-H(15A)	0.9800
C(3)-C(4)	1.527(4)	C(15)-H(15B)	0.9800
C(3)-H(3A)	0.9900	C(15)-H(15C)	0.9800
C(3)-H(3B)	0.9900	C(16)-C(17)	1.528(4)
C(4)-C(16)	1.536(4)	C(16)-C(18)	1.529(4)
C(4)-C(5)	1.591(3)	C(16)-H(16)	1.0000
C(4)-H(4)	1.0000	C(17)-H(17A)	0.9800
C(5)-C(6)	1.546(4)	C(17)-H(17B)	0.9800
C(5)-H(5)	1.0000	C(17)-H(17C)	0.9800
C(6)-C(7)	1.539(4)	C(18)-O(1)	1.427(3)
C(6)-H(6A)	0.9900	C(18)-H(18A)	0.9900
C(6)-H(6B)	0.9900	C(18)-H(18B)	0.9900
C(7)-C(8)	1.532(3)	C(19)-O(2)	1.440(3)
C(7)-Cl(1)	1.802(3)	C(19)-H(19A)	0.9900
C(7)-Cl(2)	1.806(3)	C(19)-H(19B)	0.9900
C(8)-O(2)	1.446(3)	C(20)-H(20A)	0.9800
C(8)-C(19)	1.471(4)	C(20)-H(20B)	0.9800
C(8)-C(9)	1.534(4)	C(20)-H(20C)	0.9800
C(9)-C(13)	1.550(3)	C(21)-Si(1)	1.858(3)
C(9)-C(10)	1.568(3)	C(21)-H(21A)	0.9800
C(9)-H(9)	1.0000	C(21)-H(21B)	0.9800
C(10)-O(3)	1.425(3)	C(21)-H(21C)	0.9800
C(10)-C(11)	1.520(4)	C(22)-Si(1)	1.874(3)
C(10)-H(10)	1.0000	C(22)-H(22A)	0.9800
C(11)-C(12)	1.526(4)	C(22)-H(22B)	0.9800
C(11)-H(11A)	0.9900	C(22)-H(22C)	0.9800
C(11)-H(11B)	0.9900	C(23)-C(25)	1.528(4)
C(12)-O(4)	1.427(3)	C(23)-C(26)	1.539(4)

C(23)-C(24)	1.541(4)	C(25)-H(25C)	0.9800
C(23)-Si(1)	1.890(3)	C(26)-H(26A)	0.9800
C(24)-H(24A)	0.9800	C(26)-H(26B)	0.9800
C(24)-H(24B)	0.9800	C(26)-H(26C)	0.9800
C(24)-H(24C)	0.9800	O(1)-H(1)	0.8400
C(25)-H(25A)	0.9800	O(3)-H(3)	0.8400
C(25)-H(25B)	0.9800	O(4)-Si(1)	1.6331(19)

C(15)-C(1)-C(14)	109.7(2)	C(1)-C(5)-H(5)	107.0
C(15)-C(1)-C(2)	107.4(2)	C(4)-C(5)-H(5)	107.0
C(14)-C(1)-C(2)	108.4(2)	C(7)-C(6)-C(5)	119.0(2)
C(15)-C(1)-C(5)	114.0(2)	C(7)-C(6)-H(6A)	107.6
C(14)-C(1)-C(5)	114.0(2)	C(5)-C(6)-H(6A)	107.6
C(2)-C(1)-C(5)	102.68(19)	C(7)-C(6)-H(6B)	107.6
C(3)-C(2)-C(1)	105.0(2)	C(5)-C(6)-H(6B)	107.6
C(3)-C(2)-H(2A)	110.7	H(6A)-C(6)-H(6B)	107.0
C(1)-C(2)-H(2A)	110.7	C(8)-C(7)-C(6)	115.0(2)
C(3)-C(2)-H(2B)	110.7	C(8)-C(7)-Cl(1)	108.62(18)
C(1)-C(2)-H(2B)	110.7	C(6)-C(7)-Cl(1)	110.95(18)
H(2A)-C(2)-H(2B)	108.8	C(8)-C(7)-Cl(2)	111.32(18)
C(2)-C(3)-C(4)	102.1(2)	C(6)-C(7)-Cl(2)	105.31(18)
C(2)-C(3)-H(3A)	111.3	Cl(1)-C(7)-Cl(2)	105.20(14)
C(4)-C(3)-H(3A)	111.3	O(2)-C(8)-C(19)	59.17(17)
C(2)-C(3)-H(3B)	111.3	O(2)-C(8)-C(7)	109.4(2)
C(4)-C(3)-H(3B)	111.3	C(19)-C(8)-C(7)	120.9(2)
H(3A)-C(3)-H(3B)	109.2	O(2)-C(8)-C(9)	118.4(2)
C(3)-C(4)-C(16)	115.1(2)	C(19)-C(8)-C(9)	121.7(2)
C(3)-C(4)-C(5)	104.93(19)	C(7)-C(8)-C(9)	114.0(2)
C(16)-C(4)-C(5)	117.8(2)	C(8)-C(9)-C(13)	113.2(2)
C(3)-C(4)-H(4)	106.1	C(8)-C(9)-C(10)	115.7(2)
C(16)-C(4)-H(4)	106.1	C(13)-C(9)-C(10)	105.41(19)
C(5)-C(4)-H(4)	106.1	C(8)-C(9)-H(9)	107.4
C(6)-C(5)-C(1)	116.0(2)	C(13)-C(9)-H(9)	107.4
C(6)-C(5)-C(4)	114.2(2)	C(10)-C(9)-H(9)	107.4
C(1)-C(5)-C(4)	105.06(19)	O(3)-C(10)-C(11)	114.1(2)
C(6)-C(5)-H(5)	107.0	O(3)-C(10)-C(9)	116.4(2)

C(11)-C(10)-C(9)	104.38(19)
O(3)-C(10)-H(10)	107.2
C(11)-C(10)-H(10)	107.2
C(9)-C(10)-H(10)	107.2
C(10)-C(11)-C(12)	103.8(2)
C(10)-C(11)-H(11A)	111.0
C(12)-C(11)-H(11A)	111.0
C(10)-C(11)-H(11B)	111.0
C(12)-C(11)-H(11B)	111.0
H(11A)-C(11)-H(11B)	109.0
O(4)-C(12)-C(20)	107.4(2)
O(4)-C(12)-C(11)	114.2(2)
C(20)-C(12)-C(11)	111.1(2)
O(4)-C(12)-C(13)	107.3(2)
C(20)-C(12)-C(13)	114.4(2)
C(11)-C(12)-C(13)	102.5(2)
C(14)-C(13)-C(9)	113.7(2)
C(14)-C(13)-C(12)	114.3(2)
C(9)-C(13)-C(12)	105.6(2)
C(14)-C(13)-H(13)	107.6
C(9)-C(13)-H(13)	107.6
C(12)-C(13)-H(13)	107.6
C(13)-C(14)-C(1)	118.8(2)
C(13)-C(14)-H(14A)	107.6
C(1)-C(14)-H(14A)	107.6
C(13)-C(14)-H(14B)	107.6
C(1)-C(14)-H(14B)	107.6
H(14A)-C(14)-H(14B)	107.1
C(1)-C(15)-H(15A)	109.5
C(1)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(1)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(17)-C(16)-C(18)	110.4(2)
C(17)-C(16)-C(4)	111.4(2)
C(18)-C(16)-C(4)	112.8(2)
C(17)-C(16)-H(16)	107.4
C(18)-C(16)-H(16)	107.4
C(4)-C(16)-H(16)	107.4
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
O(1)-C(18)-C(16)	114.7(2)
O(1)-C(18)-H(18A)	108.6
C(16)-C(18)-H(18A)	108.6
O(1)-C(18)-H(18B)	108.6
C(16)-C(18)-H(18B)	108.6
H(18A)-C(18)-H(18B)	107.6
O(2)-C(19)-C(8)	59.55(16)
O(2)-C(19)-H(19A)	117.8
C(8)-C(19)-H(19A)	117.8
O(2)-C(19)-H(19B)	117.8
C(8)-C(19)-H(19B)	117.8
H(19A)-C(19)-H(19B)	115.0
C(12)-C(20)-H(20A)	109.5
C(12)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(12)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
Si(1)-C(21)-H(21A)	109.5
Si(1)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
Si(1)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
Si(1)-C(22)-H(22A)	109.5
Si(1)-C(22)-H(22B)	109.5

H(22A)-C(22)-H(22B)	109.5	H(25A)-C(25)-H(25B)	109.5
Si(1)-C(22)-H(22C)	109.5	C(23)-C(25)-H(25C)	109.5
H(22A)-C(22)-H(22C)	109.5	H(25A)-C(25)-H(25C)	109.5
H(22B)-C(22)-H(22C)	109.5	H(25B)-C(25)-H(25C)	109.5
C(25)-C(23)-C(26)	108.2(3)	C(23)-C(26)-H(26A)	109.5
C(25)-C(23)-C(24)	108.9(2)	C(23)-C(26)-H(26B)	109.5
C(26)-C(23)-C(24)	110.0(3)	H(26A)-C(26)-H(26B)	109.5
C(25)-C(23)-Si(1)	109.5(2)	C(23)-C(26)-H(26C)	109.5
C(26)-C(23)-Si(1)	110.4(2)	H(26A)-C(26)-H(26C)	109.5
C(24)-C(23)-Si(1)	109.8(2)	H(26B)-C(26)-H(26C)	109.5
C(23)-C(24)-H(24A)	109.5	C(18)-O(1)-H(1)	109.5
C(23)-C(24)-H(24B)	109.5	C(19)-O(2)-C(8)	61.28(16)
H(24A)-C(24)-H(24B)	109.5	C(10)-O(3)-H(3)	109.5
C(23)-C(24)-H(24C)	109.5	C(12)-O(4)-Si(1)	139.19(17)
H(24A)-C(24)-H(24C)	109.5	O(4)-Si(1)-C(21)	107.02(13)
H(24B)-C(24)-H(24C)	109.5	O(4)-Si(1)-C(22)	113.36(12)
C(23)-C(25)-H(25A)	109.5	C(21)-Si(1)-C(22)	108.01(15)
C(23)-C(25)-H(25B)	109.5	O(4)-Si(1)-C(23)	107.17(13)
C(22)-Si(1)-C(23)	110.85(14)		
C(21)-Si(1)-C(23)	110.36(14)		

Symmetry transformations used to generate equivalent atoms:

Table S11. Anisotropic displacement parameters ($Å^2$x 10^3)for **SI-6**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

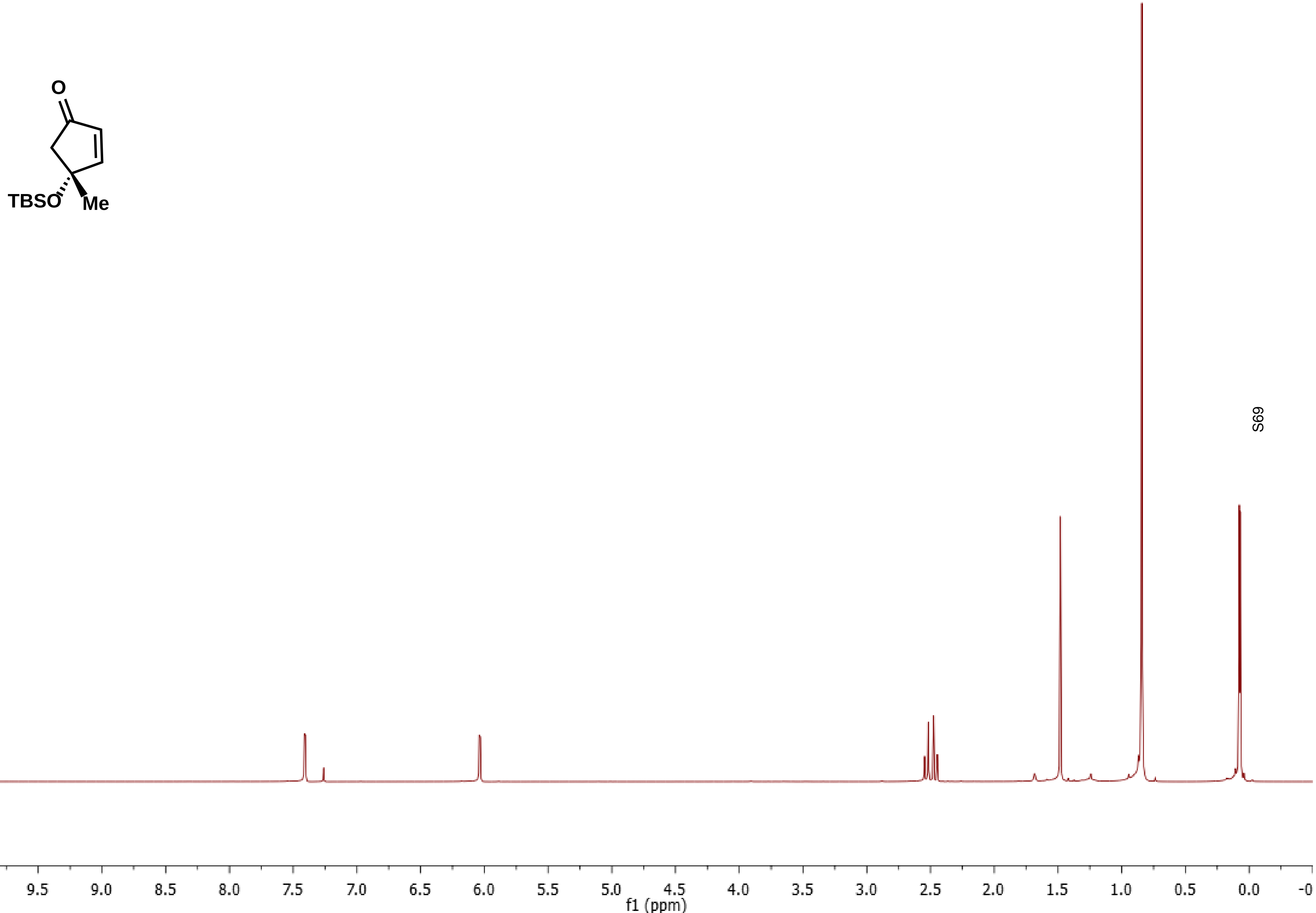
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	16(1)	23(1)	15(1)	4(1)	8(1)	5(1)
C(2)	23(2)	29(2)	24(1)	11(1)	14(1)	12(1)
C(3)	18(1)	30(2)	25(1)	4(1)	12(1)	8(1)
C(4)	15(1)	21(1)	21(1)	1(1)	11(1)	4(1)
C(5)	15(1)	18(1)	18(1)	0(1)	10(1)	1(1)
C(6)	15(1)	20(1)	24(1)	1(1)	11(1)	2(1)
C(7)	20(1)	17(1)	24(1)	1(1)	13(1)	2(1)
C(8)	17(1)	20(1)	19(1)	3(1)	9(1)	3(1)
C(9)	14(1)	20(1)	16(1)	2(1)	9(1)	3(1)
C(10)	14(1)	23(1)	17(1)	2(1)	7(1)	3(1)
C(11)	16(1)	27(1)	19(1)	1(1)	9(1)	1(1)
C(12)	20(1)	27(2)	18(1)	3(1)	13(1)	2(1)
C(13)	18(1)	20(1)	14(1)	1(1)	8(1)	3(1)
C(14)	20(1)	22(1)	18(1)	3(1)	12(1)	1(1)
C(15)	17(1)	34(2)	17(1)	-2(1)	6(1)	5(1)
C(16)	16(1)	22(1)	25(1)	-3(1)	13(1)	1(1)
C(17)	26(2)	30(2)	30(2)	6(1)	19(1)	8(1)
C(18)	18(1)	27(1)	26(1)	-6(1)	13(1)	-1(1)
C(19)	21(1)	22(1)	28(2)	-3(1)	13(1)	3(1)
C(20)	25(2)	24(2)	40(2)	-3(1)	18(1)	-4(1)
C(21)	37(2)	26(2)	28(2)	1(1)	18(1)	-8(1)
C(22)	22(1)	43(2)	30(2)	7(1)	16(1)	2(1)
C(23)	27(2)	22(2)	27(2)	-2(1)	12(1)	1(1)
C(24)	45(2)	39(2)	40(2)	-7(2)	26(2)	6(2)
C(25)	28(2)	28(2)	28(2)	0(1)	9(1)	-1(1)
C(26)	36(2)	21(2)	43(2)	2(1)	14(2)	2(1)
O(1)	24(1)	31(1)	32(1)	-10(1)	13(1)	4(1)
O(2)	20(1)	23(1)	24(1)	-7(1)	9(1)	1(1)
O(3)	21(1)	31(1)	31(1)	13(1)	16(1)	10(1)
O(4)	28(1)	44(1)	27(1)	16(1)	20(1)	11(1)
Si(1)	19(1)	24(1)	22(1)	3(1)	13(1)	-1(1)

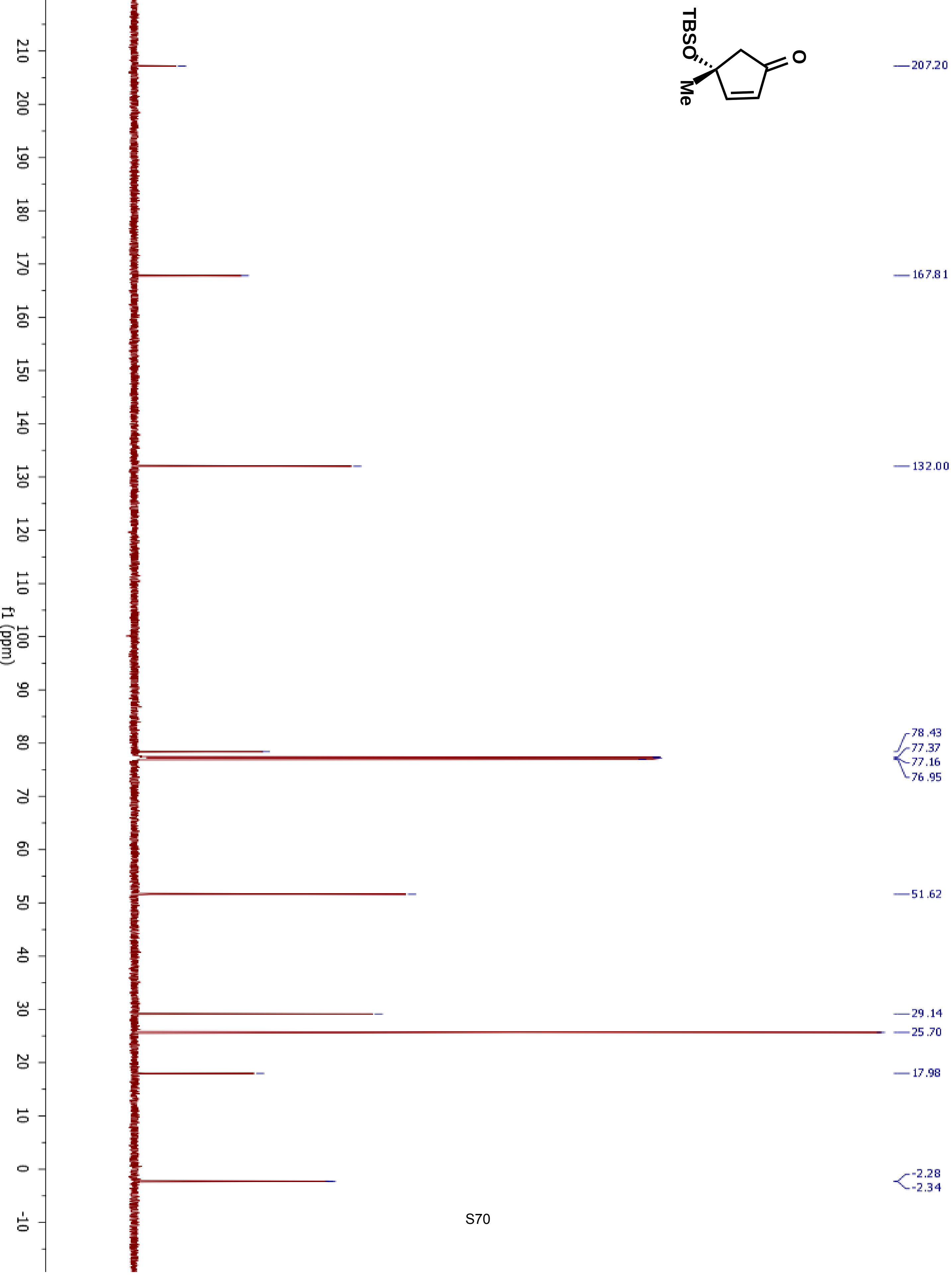
Cl(1)	24(1)	30(1)	24(1)	9(1)	15(1)	5(1)
Cl(2)	27(1)	18(1)	56(1)	2(1)	26(1)	0(1)

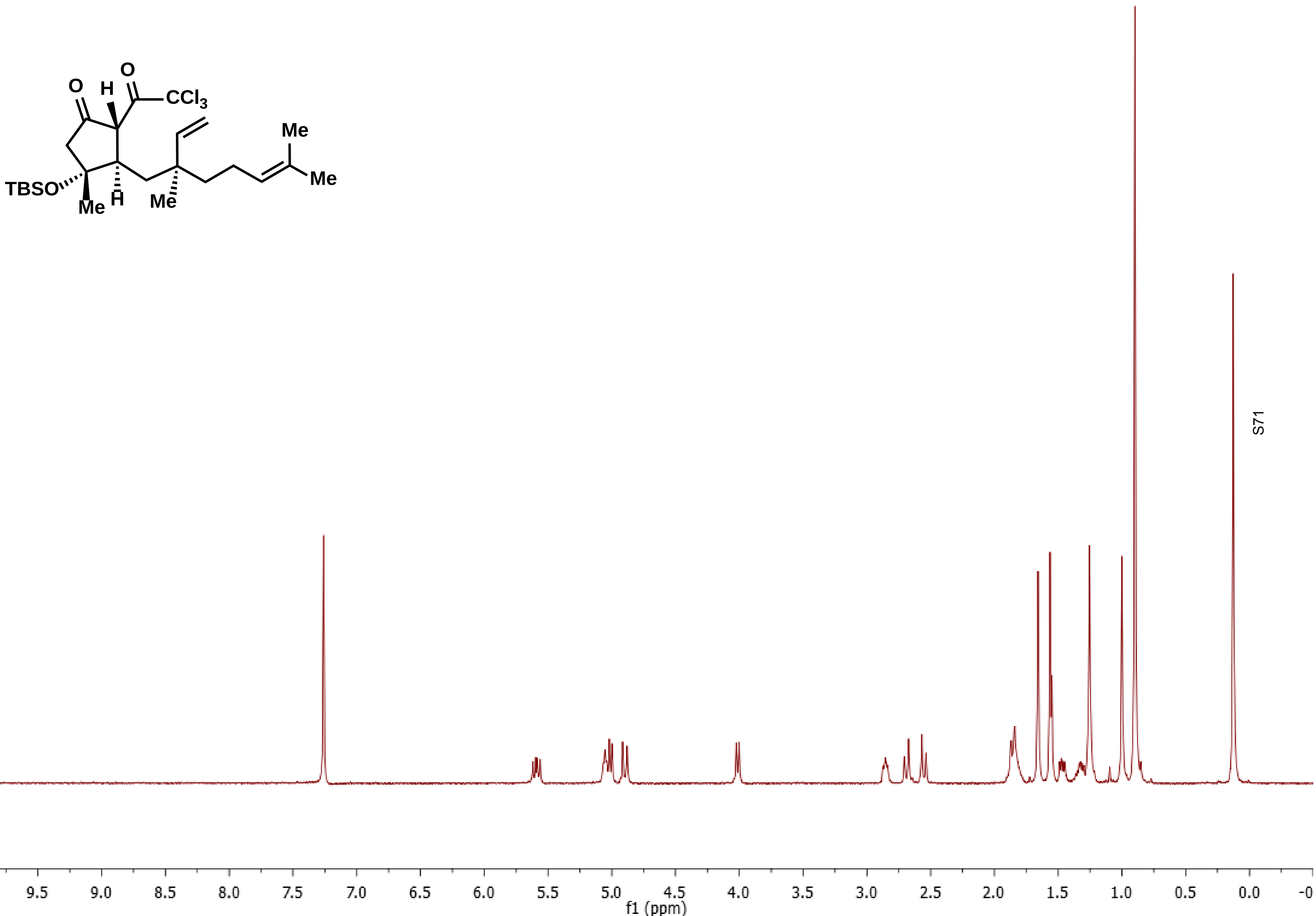
Table S12. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **SI-6**.

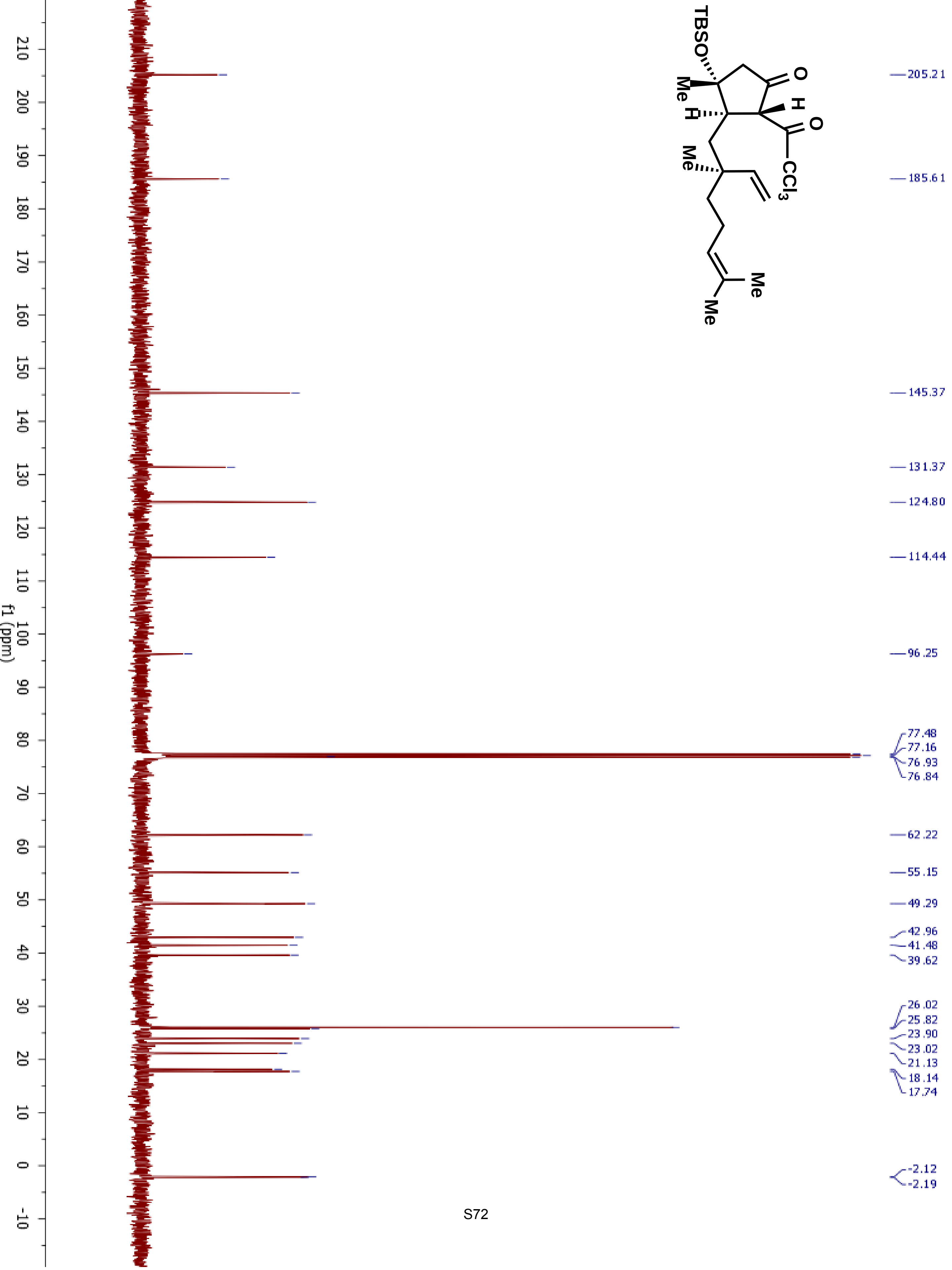
	x	y	z	U(eq)
H(2A)	6217	8270	7362	30
H(2B)	5751	7841	6101	30
H(3A)	4993	6536	6385	29
H(3B)	5058	7854	7015	29
H(4)	5972	7081	8650	22
H(5)	6854	5939	8790	20
H(6A)	6037	3971	8328	23
H(6B)	6088	3958	7279	23
H(9)	7849	5357	9132	19
H(10)	9027	5478	9919	22
H(11A)	8982	4617	8019	25
H(11B)	9544	5629	8919	25
H(13)	7563	5277	7014	20
H(14A)	7149	7413	6913	23
H(14B)	7398	7327	8160	23
H(15A)	6132	6029	5537	37
H(15B)	5606	5337	5834	37
H(15C)	6393	4751	6262	37
H(16)	5145	4781	7902	24
H(17A)	5741	5980	9977	40
H(17B)	6158	4877	9759	40
H(17C)	5403	4566	9649	40
H(18A)	4279	6425	7205	28
H(18B)	4254	5655	8133	28
H(19A)	8325	2637	8045	28
H(19B)	7777	1656	8189	28
H(20A)	9212	7882	8743	44
H(20B)	8760	7468	9268	44
H(20C)	8378	8301	8172	44
H(21A)	8350	8440	5168	45

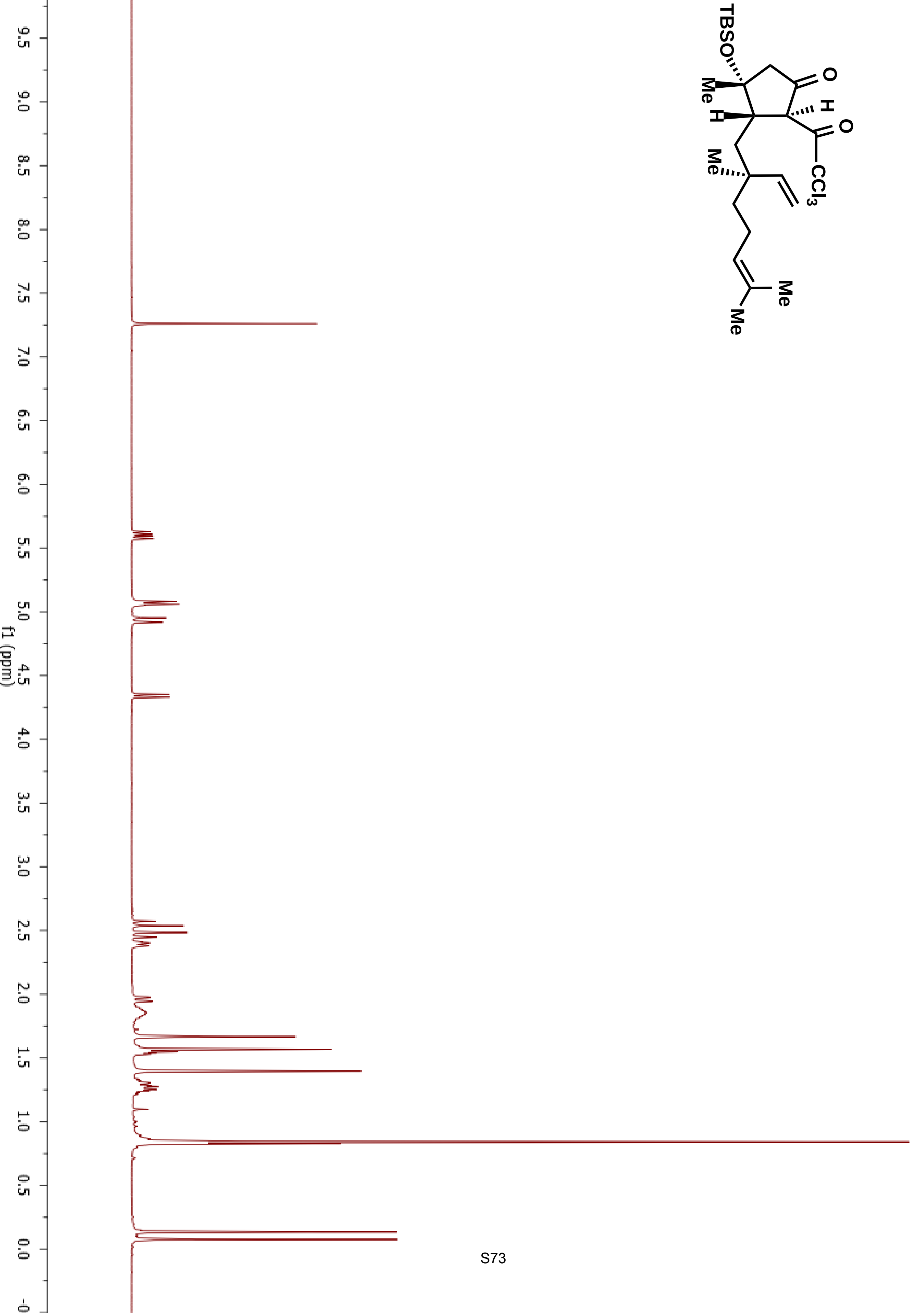
H(21B)	9159	8195	5457	45
H(21C)	9032	8823	6344	45
H(22A)	10056	6620	7810	46
H(22B)	10045	6040	6783	46
H(22C)	9810	5164	7446	46
H(24A)	9140	5092	4818	59
H(24B)	8629	6271	4121	59
H(24C)	8350	4828	3759	59
H(25A)	7239	5230	3802	47
H(25B)	7491	6697	4082	47
H(25C)	7309	5896	4844	47
H(26A)	8124	4082	5979	56
H(26B)	8832	3756	5955	56
H(26C)	8039	3479	4906	56
H(1)	5033	7759	8760	45
H(3)	9237	3210	9392	39

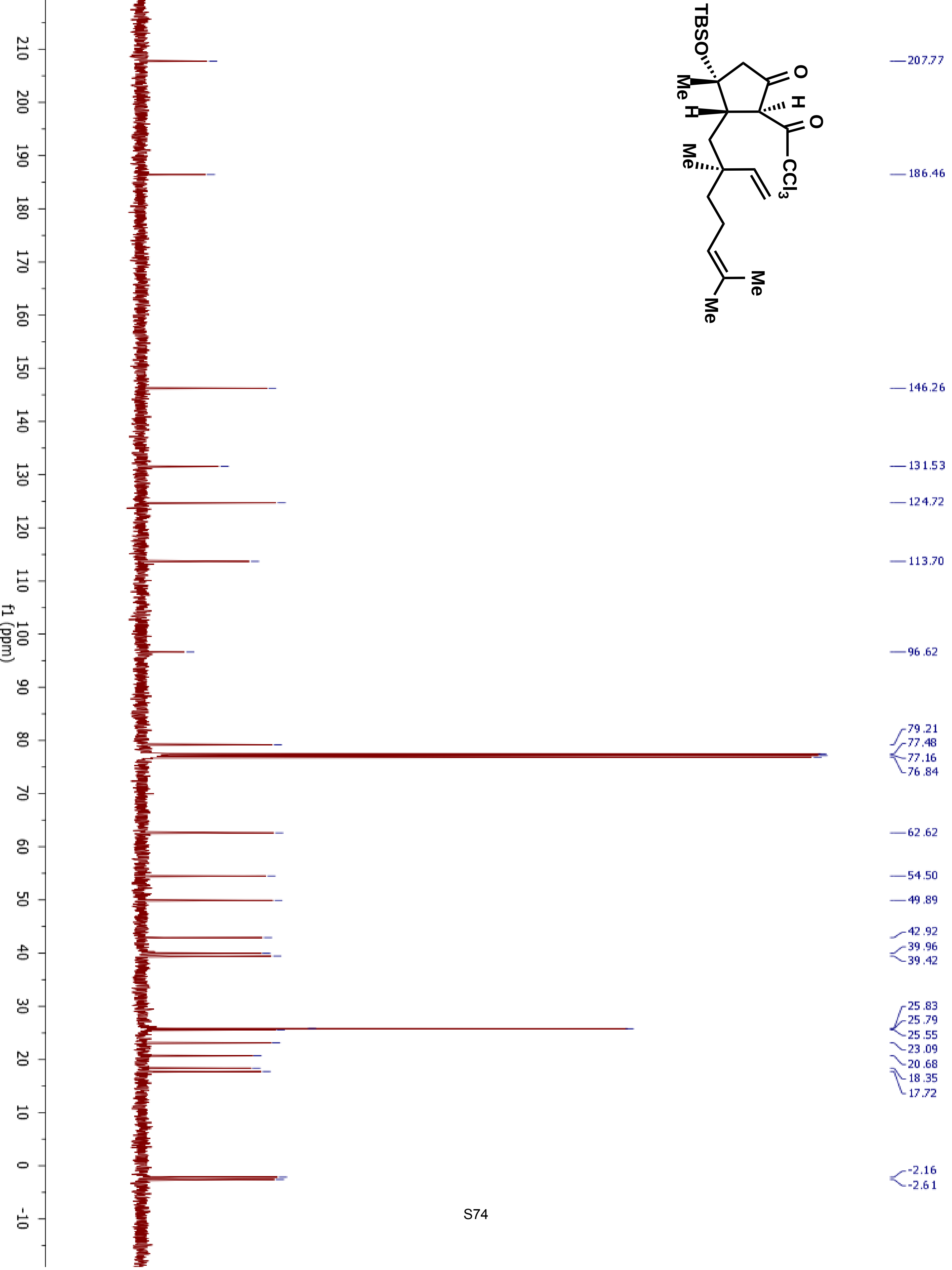

O
TBSO
Me
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

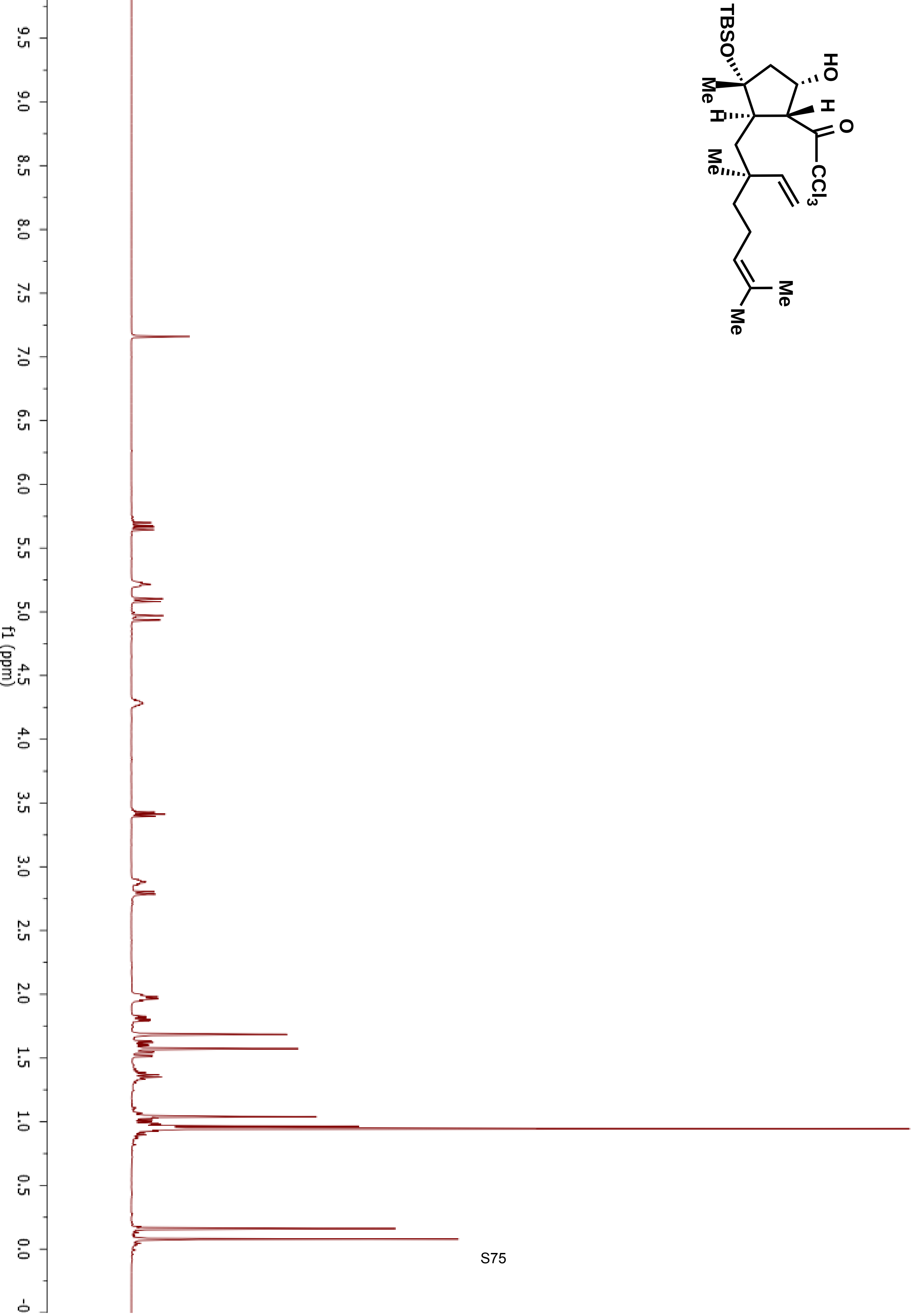

TBSO
Me
O
207.20
167.81
132.00
78.43
77.37
77.16
76.95
51.62
29.14
25.70
17.98
-2.28
-2.34
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
H
O
CCl$_3$
Me
Me
TBSO
Me
H
Me
9.5
9.0
8.5
8.0
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
0.0
-0
f1 (ppm)

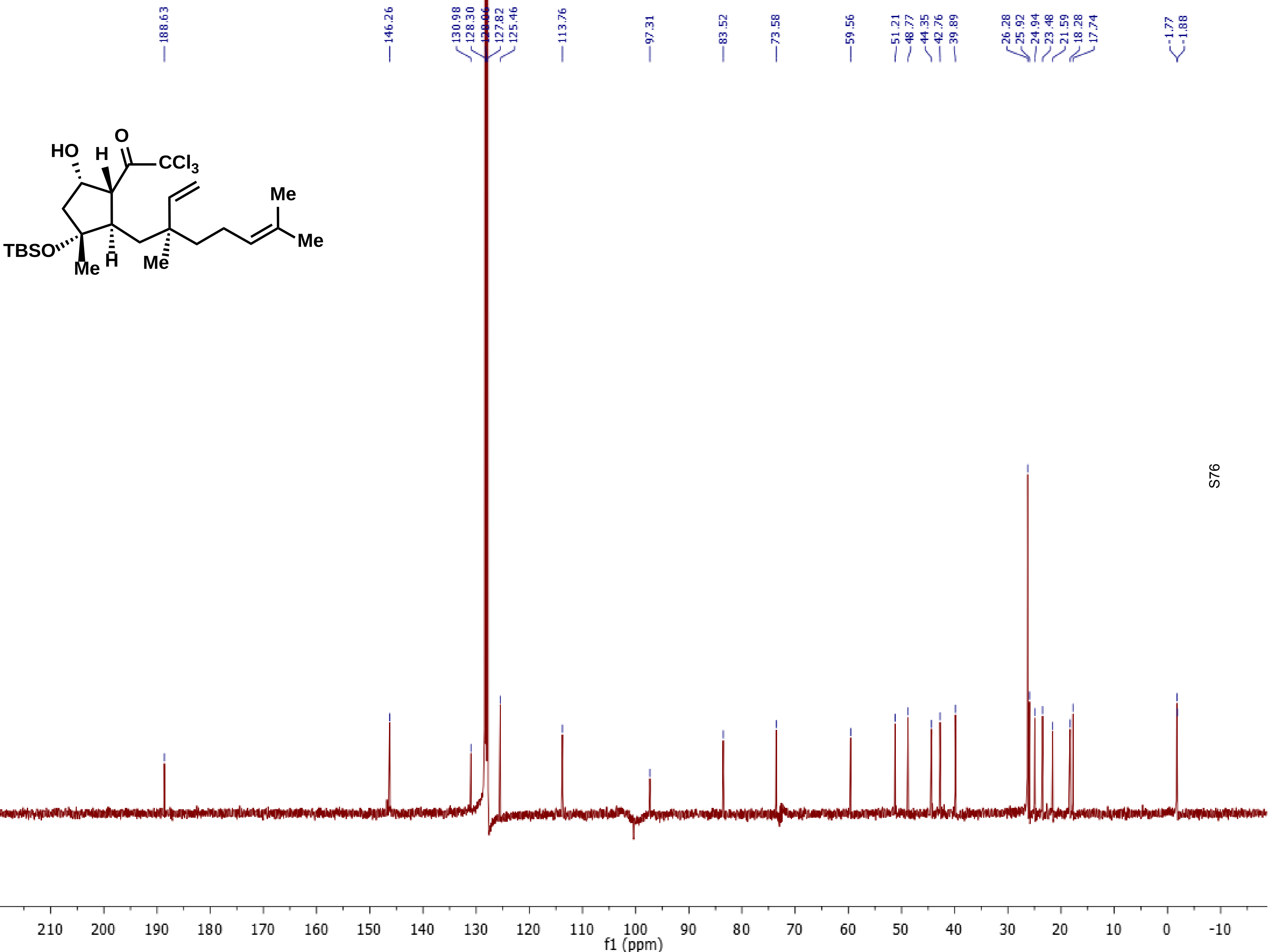

TBSO
Me
H
O
H
O
CCl3
Me
Me
Me
205.21
185.61
145.37
131.37
124.80
114.44
96.25
77.48
77.16
76.93
76.84
62.22
55.15
49.29
42.96
41.48
39.62
26.02
25.82
23.90
23.02
21.13
18.14
17.74
-2.12
-2.19
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

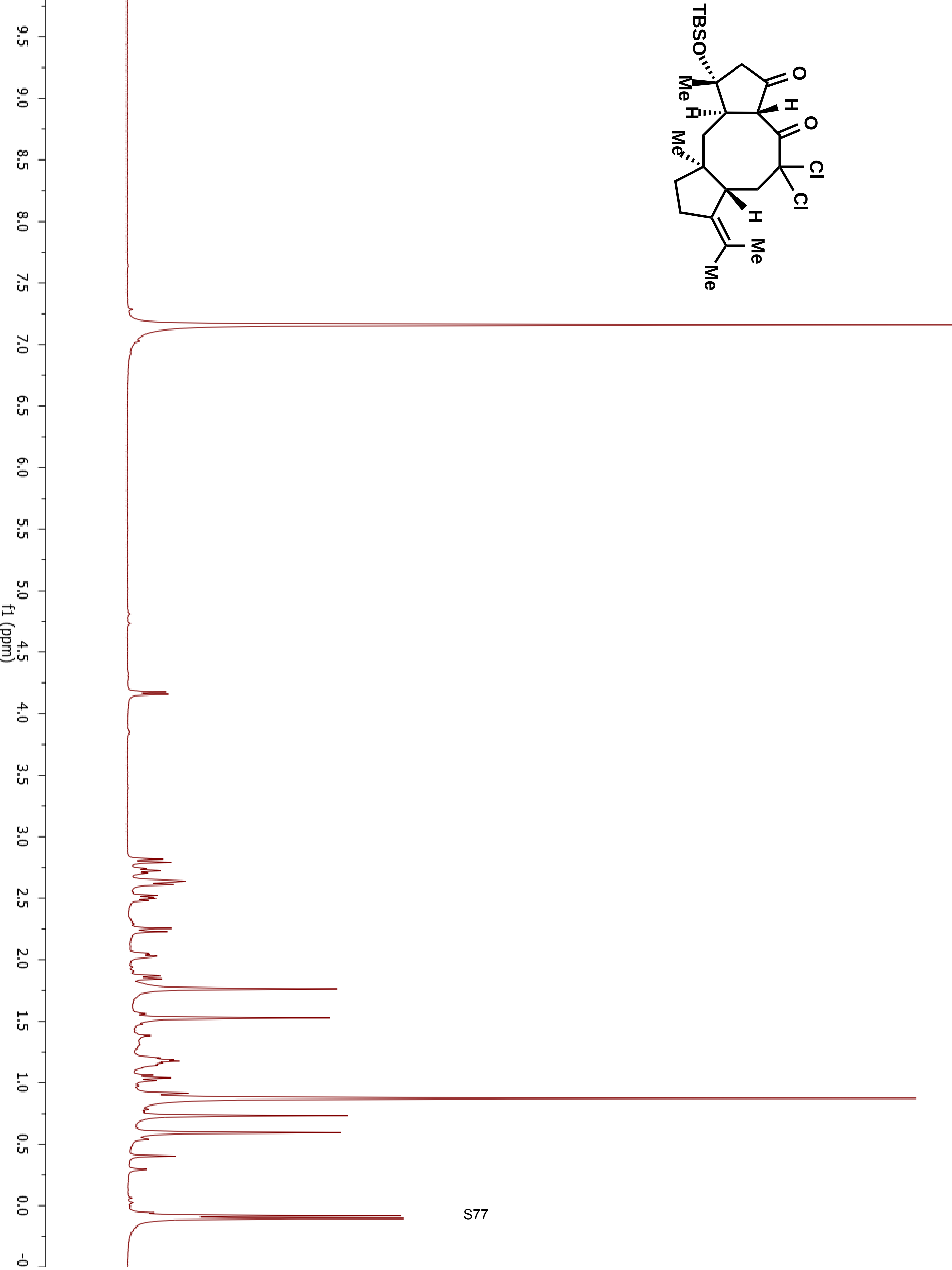

TBSO
Me
H
O
H
O
CCl3
Me
Me
Me
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

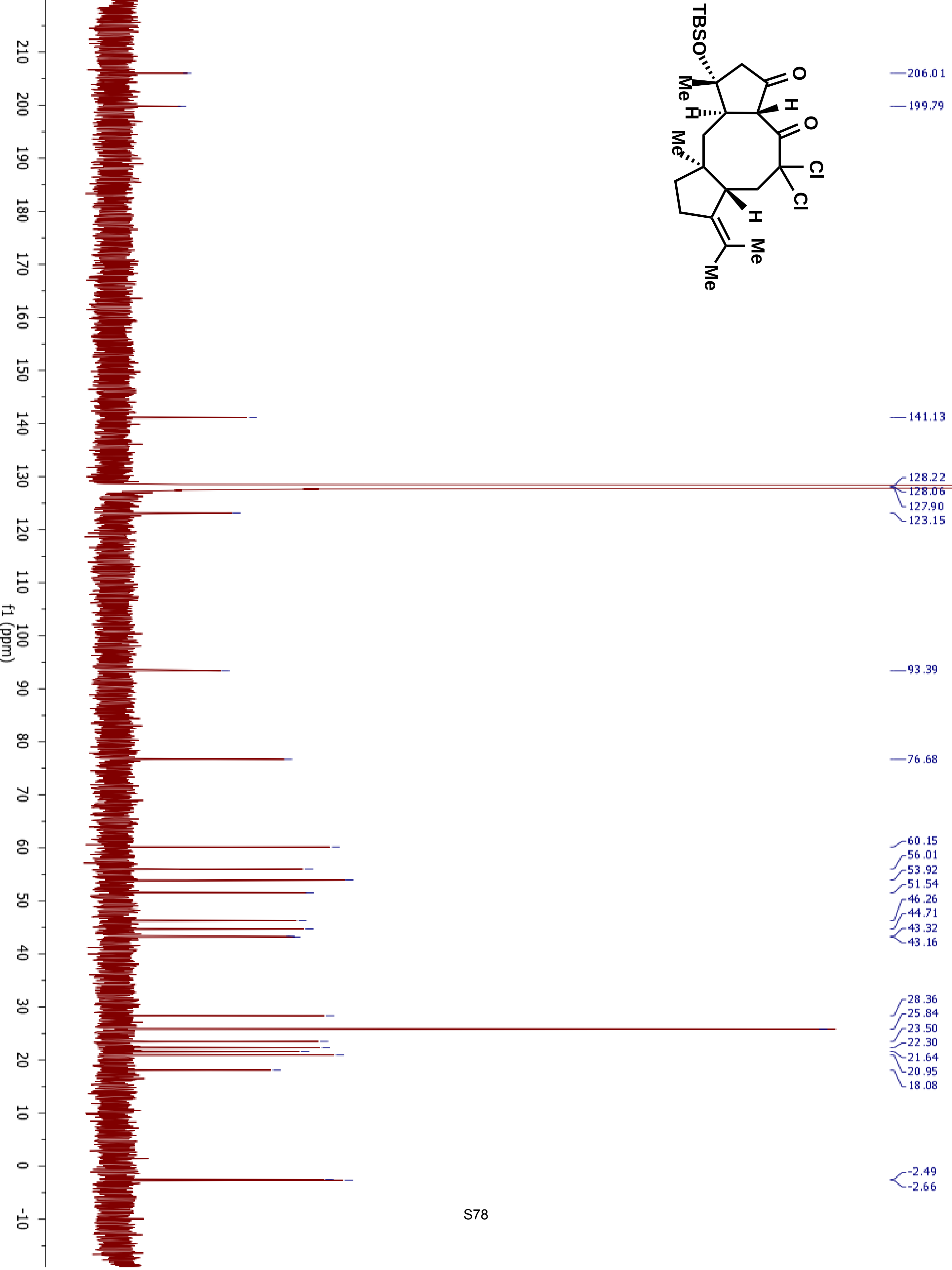

TBSO
O
H
O
Me
H
Me
CCl3
Me
Me
207.77
186.46
146.26
131.53
124.72
113.70
96.62
79.21
77.48
77.16
76.84
62.62
54.50
49.89
42.92
39.96
39.42
25.83
25.79
25.55
23.09
20.68
18.35
17.72
-2.16
-2.61
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

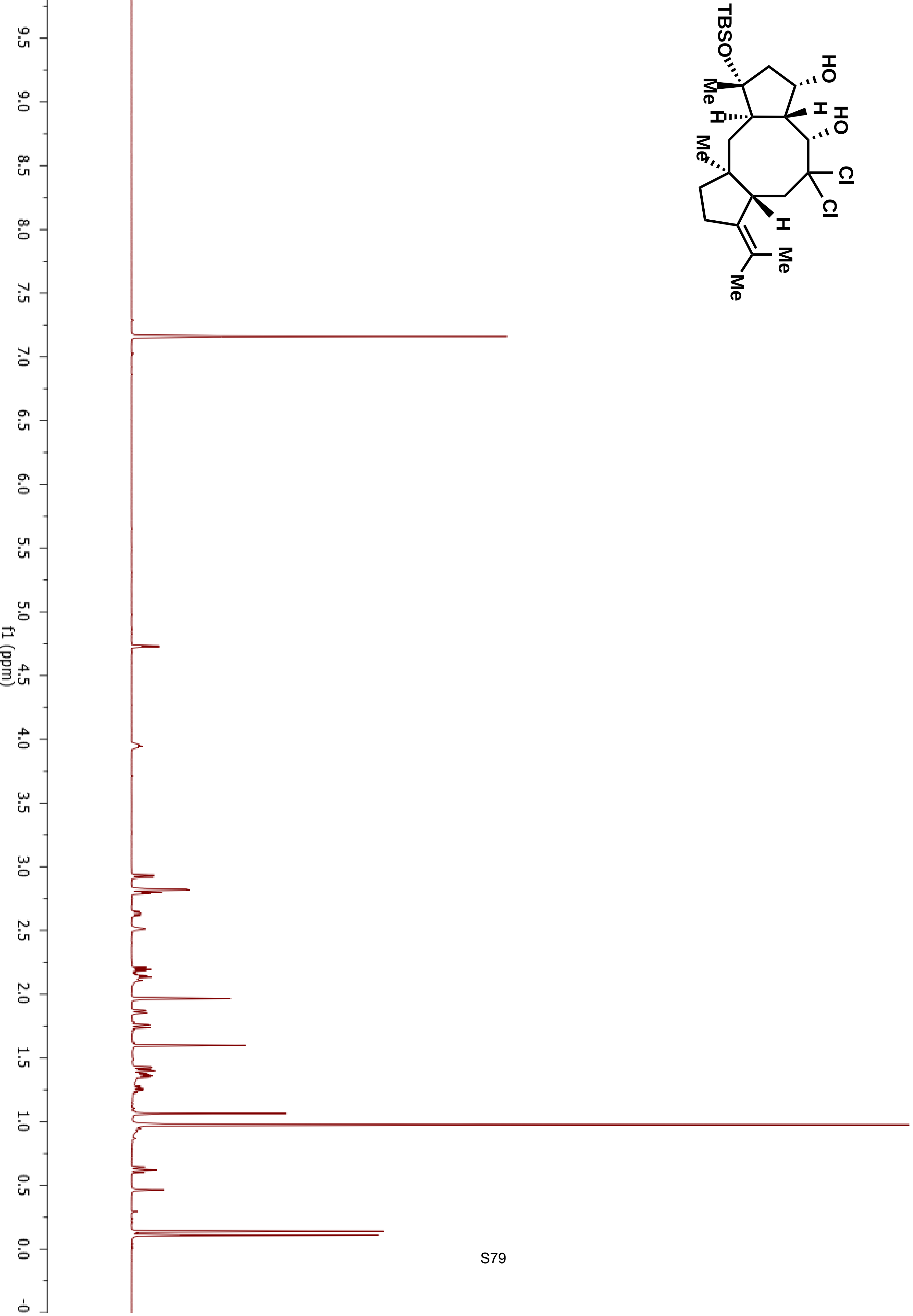


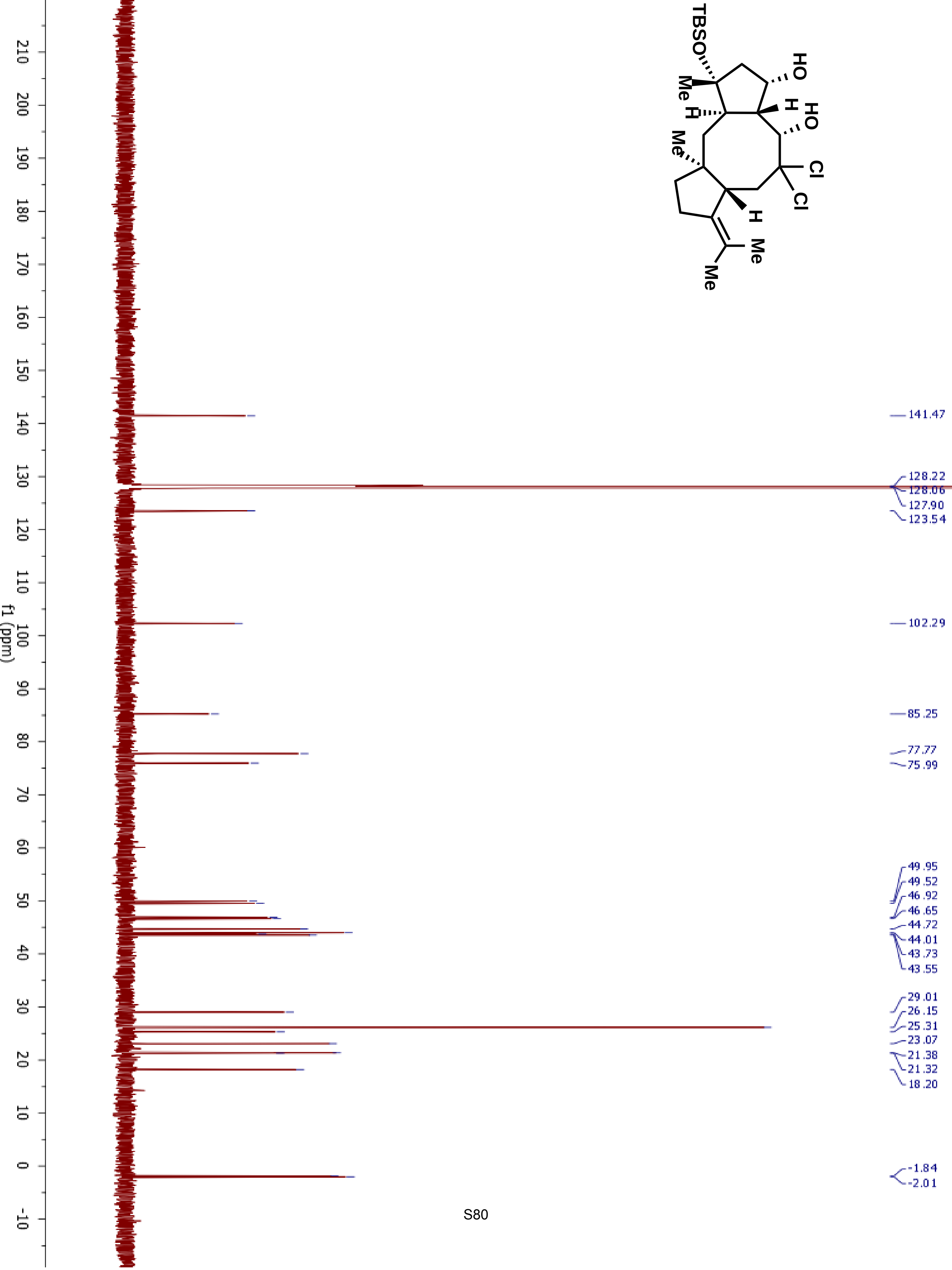
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)
TBSO
HO
H
O
Me
H
Me
CCl_3
Me
Me

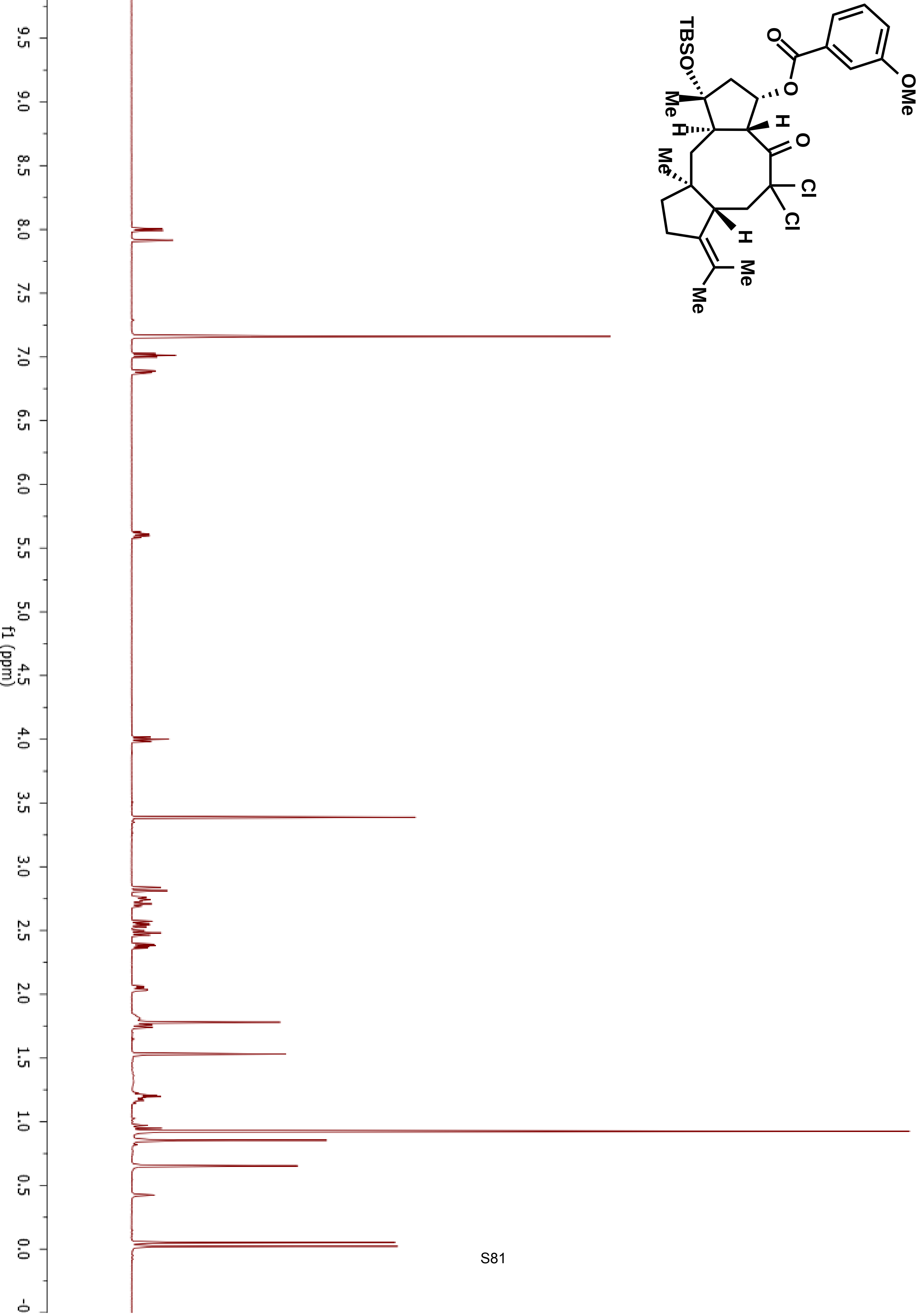

188.63
146.26
130.98
128.30
128.06
127.82
125.46
113.76
97.31
83.52
73.58
59.56
51.21
48.77
44.35
42.76
39.89
26.28
25.92
24.94
23.48
21.59
18.28
17.74
-1.77
-1.88
HO
H
O
CCl3
Me
Me
TBSO
Me
H
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

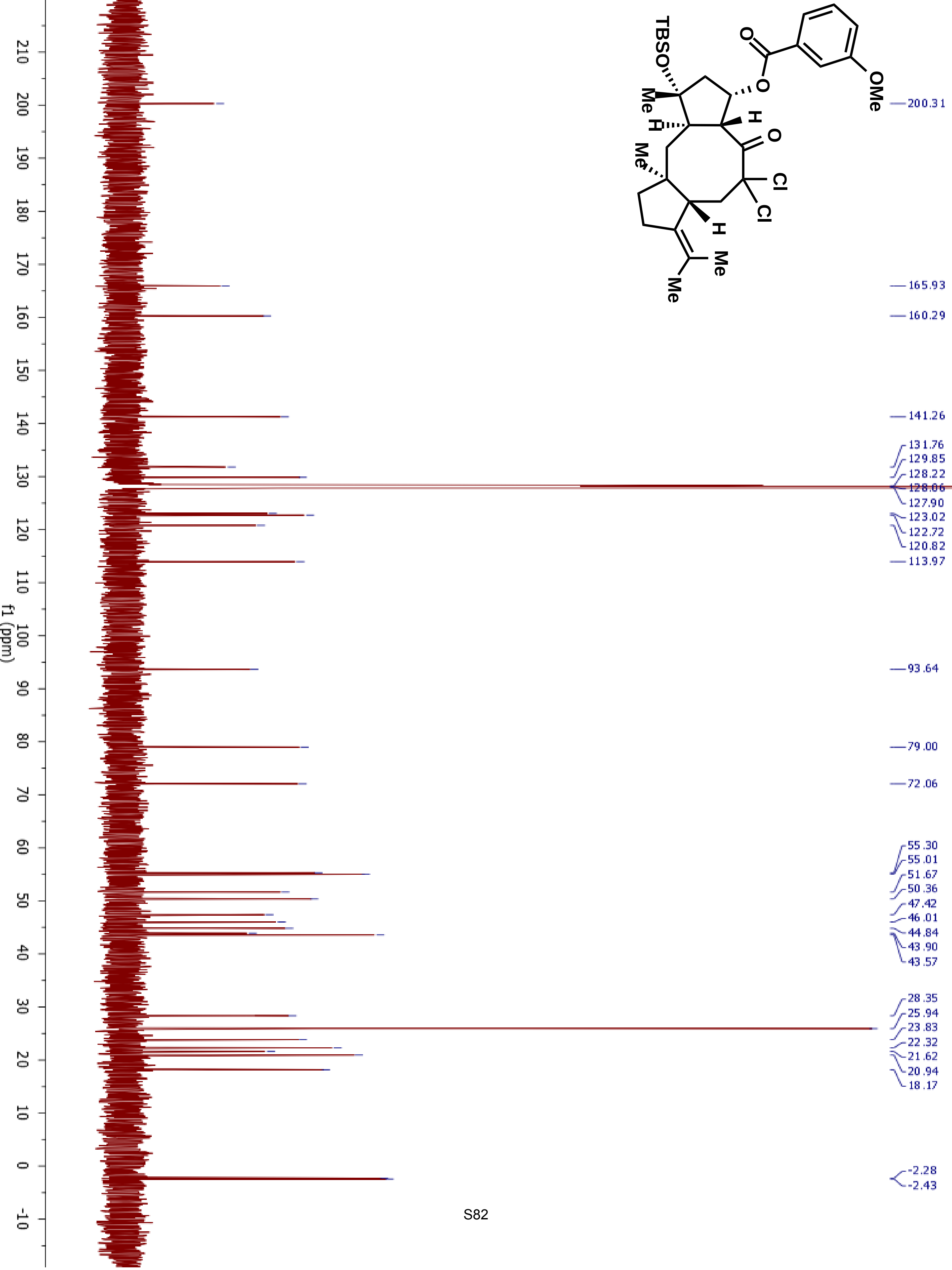

9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)
TBSO
Me
H
O
H
O
Me
Cl
Cl
H
Me
Me

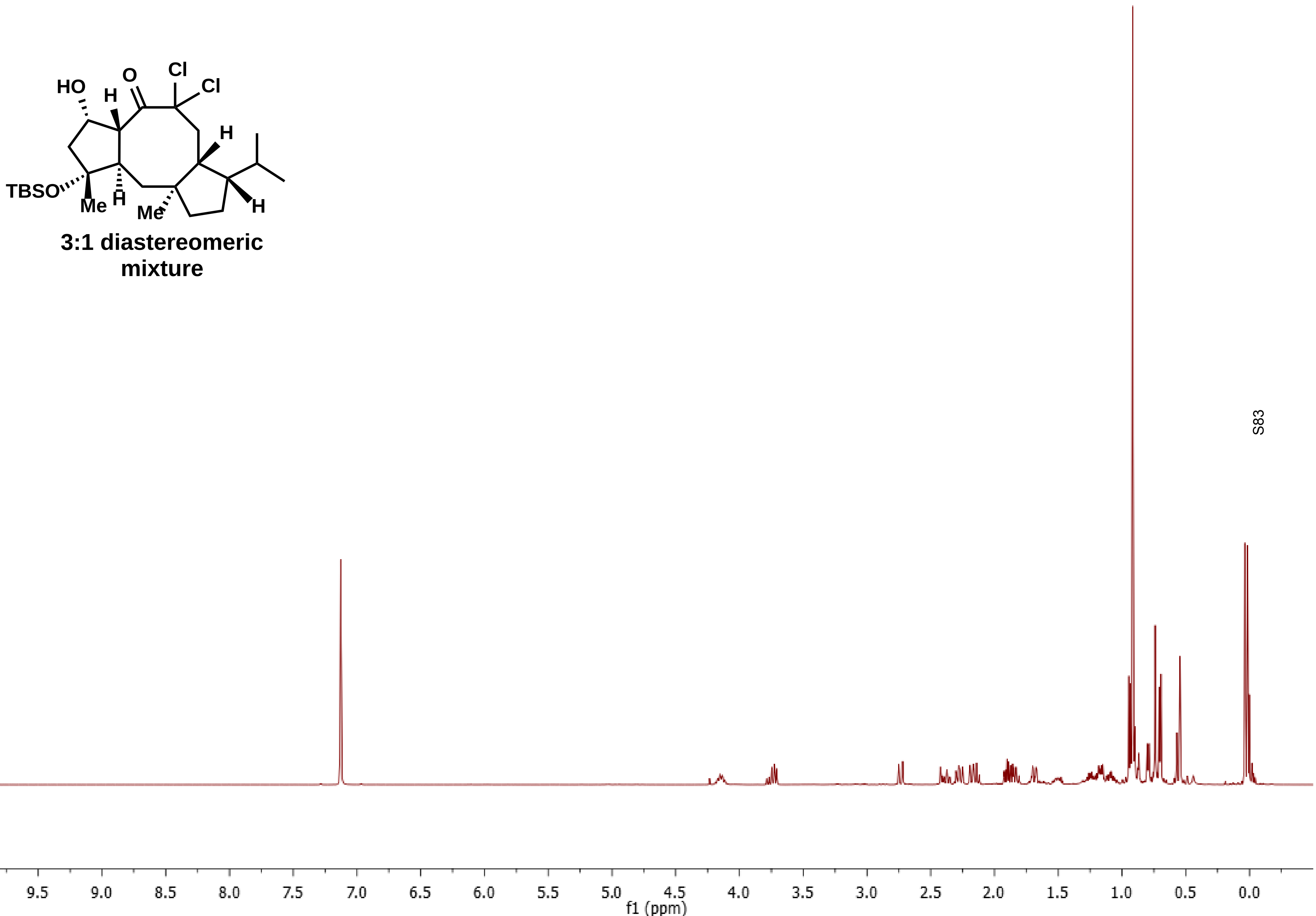

TBSO
Me
H
O
H
O
Me
Cl
Cl
H
Me
Me
206.01
199.79
141.13
128.22
128.06
127.90
123.15
93.39
76.68
60.15
56.01
53.92
51.54
46.26
44.71
43.32
43.16
28.36
25.84
23.50
22.30
21.64
20.95
18.08
-2.49
-2.66
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

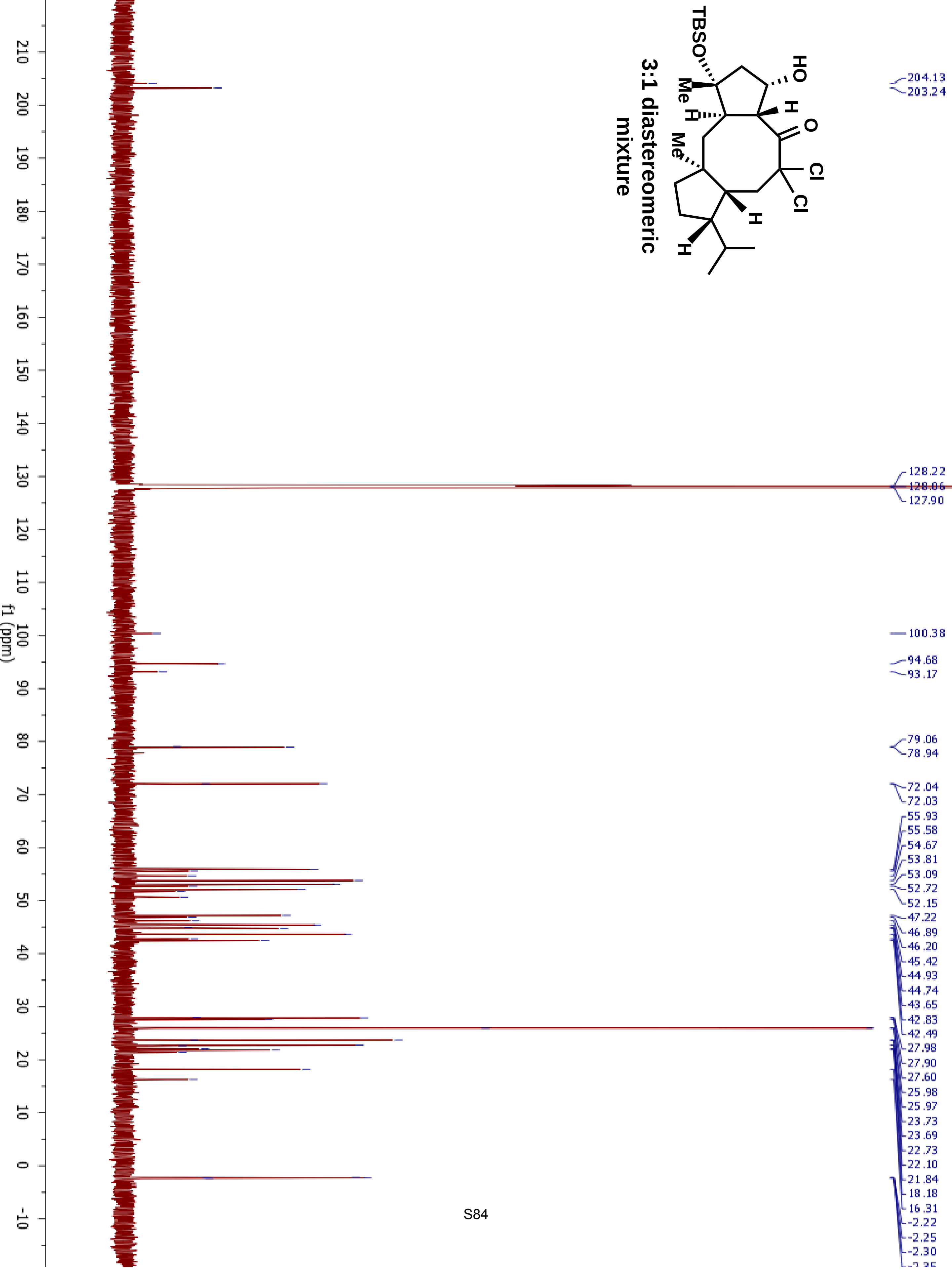

TBSO
HO
HO
H
Me
H
Me
Cl
Cl
H
Me
Me
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

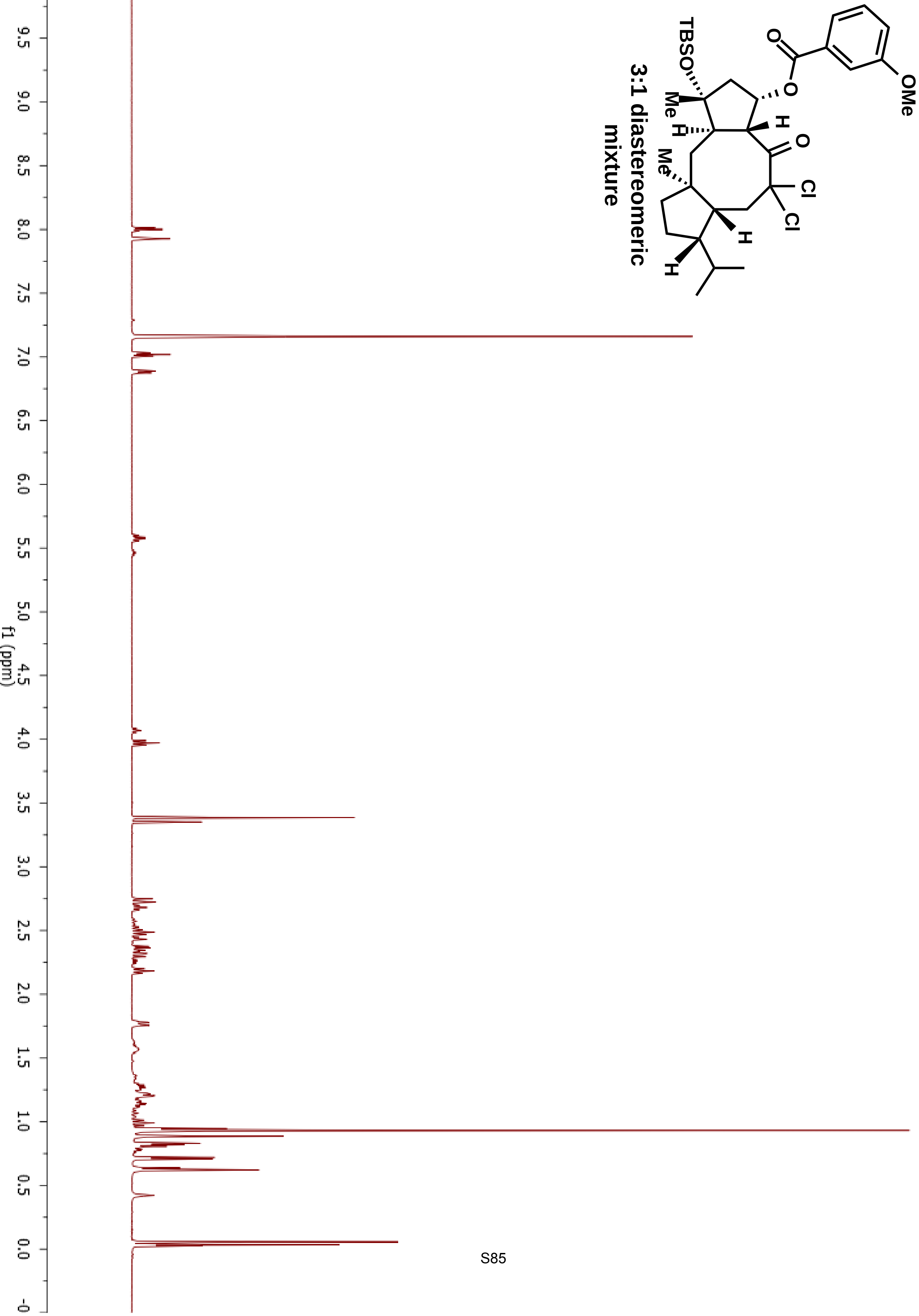

TBSO
HO
HO
H
H
Me
Me
Cl
Cl
H
Me
Me
141.47
128.22
128.06
127.90
123.54
102.29
85.25
77.77
75.99
49.95
49.52
46.92
46.65
44.72
44.01
43.73
43.55
29.01
26.15
25.31
23.07
21.38
21.32
18.20
-1.84
-2.01
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

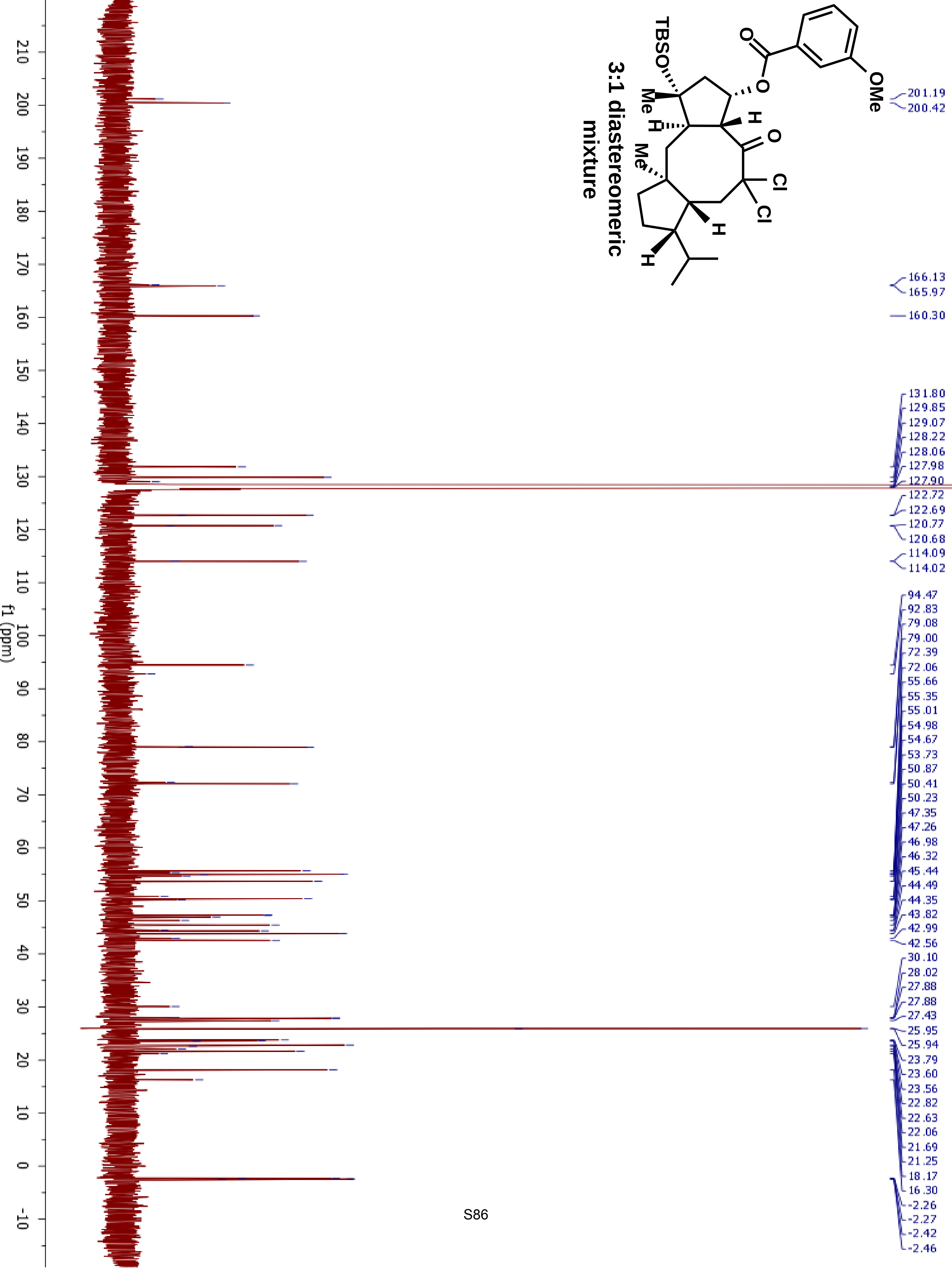

TBSO
Me
H
O
O
OMe
H
O
Cl
Cl
Me
H
Me
Me
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


TBSO
Me
H
Me
H
O
O
O
OMe
Cl
Cl
H
Me
Me
200.31
165.93
160.29
141.26
131.76
129.85
128.22
128.06
127.90
123.02
122.72
120.82
113.97
93.64
79.00
72.06
55.30
55.01
51.67
50.36
47.42
46.01
44.84
43.90
43.57
28.35
25.94
23.83
22.32
21.62
20.94
18.17
-2.28
-2.43
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

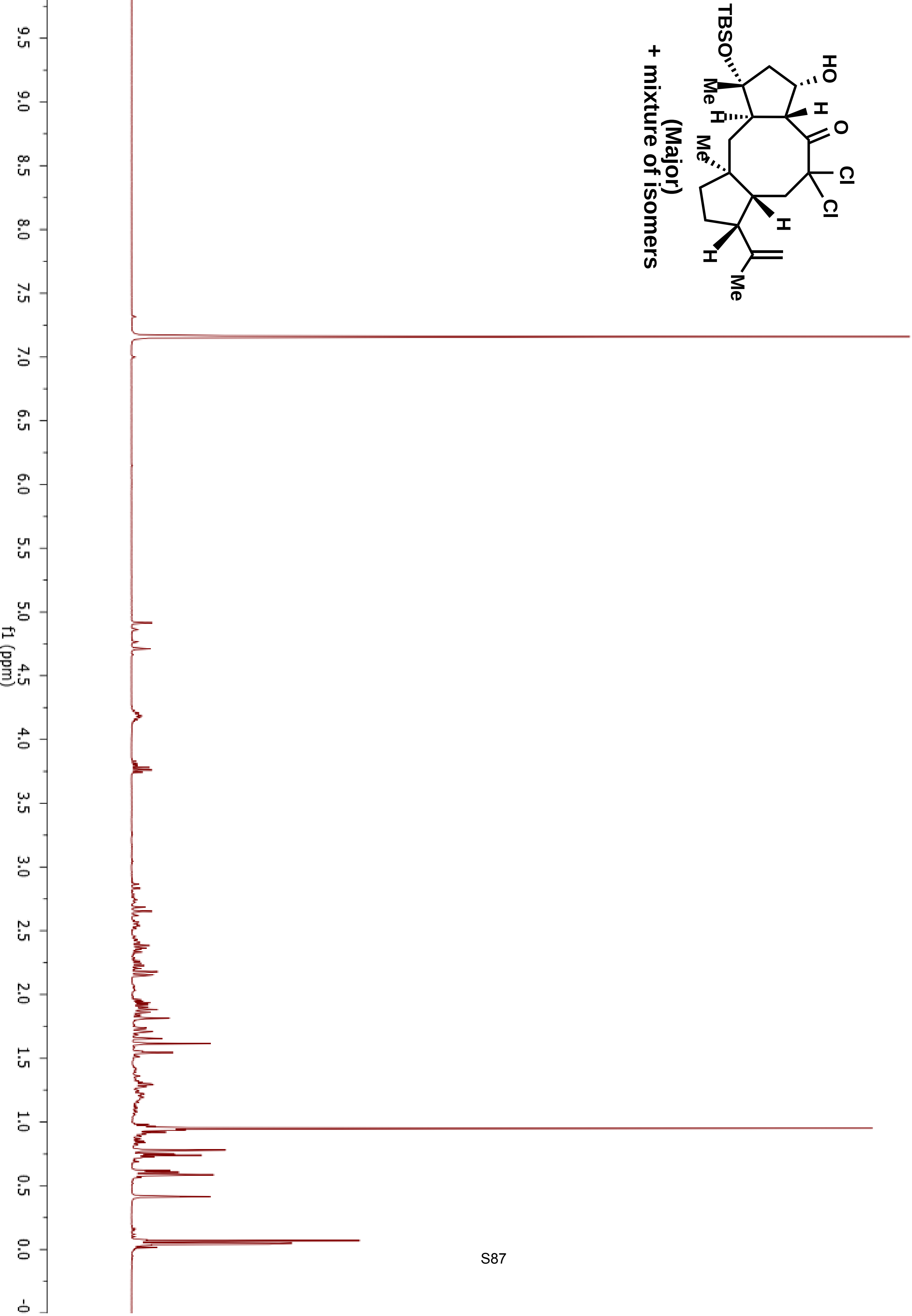

HO
O
Cl
Cl
H
H
TBSO
Me
H
Me
H
3:1 diastereomeric mixture
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


TBSO
HO
H
O
Cl
Cl
Me
H
Me
H
H
3:1 diastereomeric
mixture
204.13
203.24
128.22
128.06
127.90
100.38
94.68
93.17
79.06
78.94
72.04
72.03
55.93
55.58
54.67
53.81
53.09
52.72
52.15
47.22
46.89
46.20
45.42
44.93
44.74
43.65
42.83
42.49
27.98
27.90
27.60
25.98
25.97
23.73
23.69
22.73
22.10
21.84
18.18
16.31
-2.22
-2.25
-2.30
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

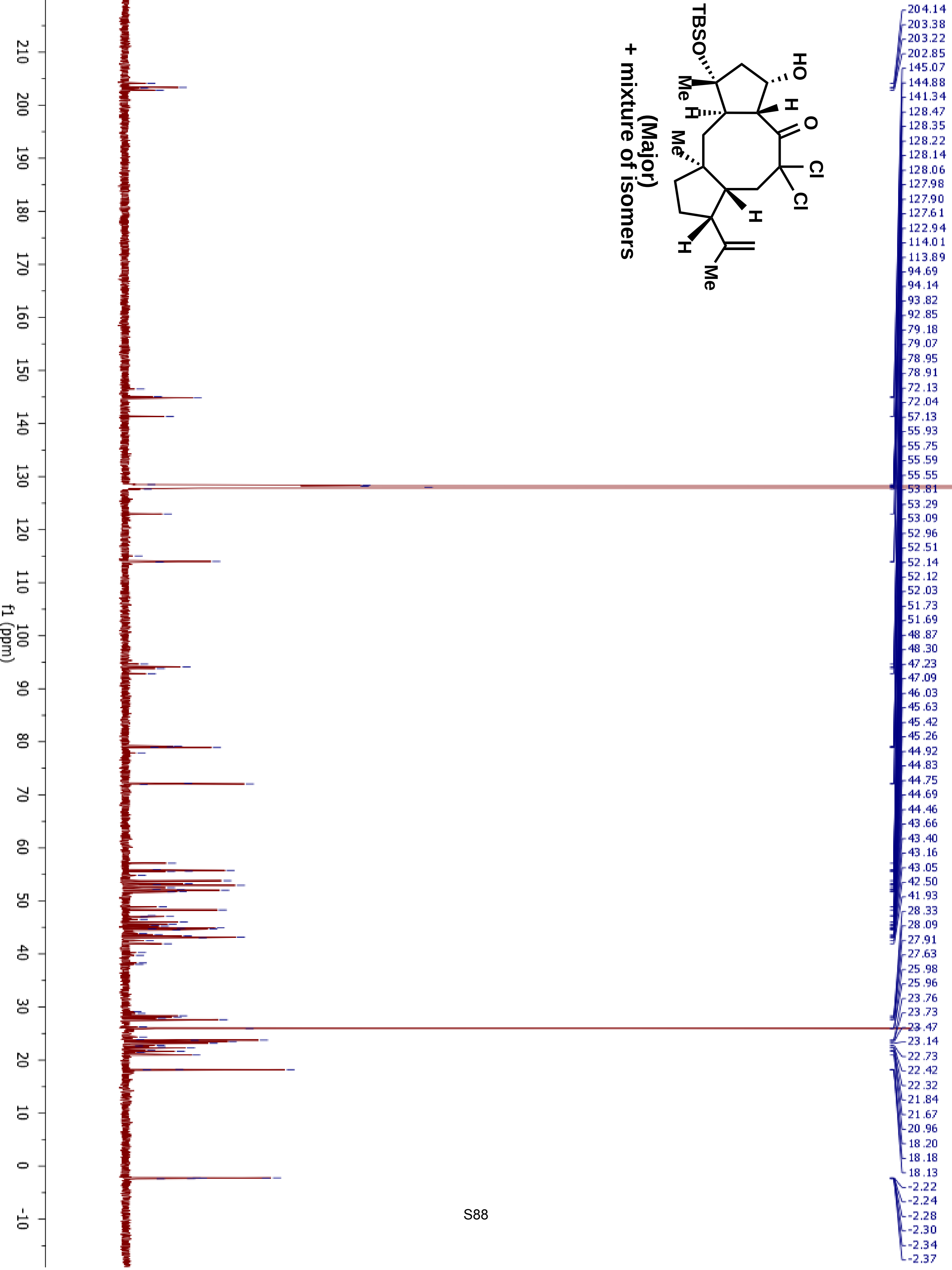

3:1 diastereomeric mixture
TBSO
OMe
O
O
H
O
Cl
Cl
Me
H
Me
H
H
f1 (ppm)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0



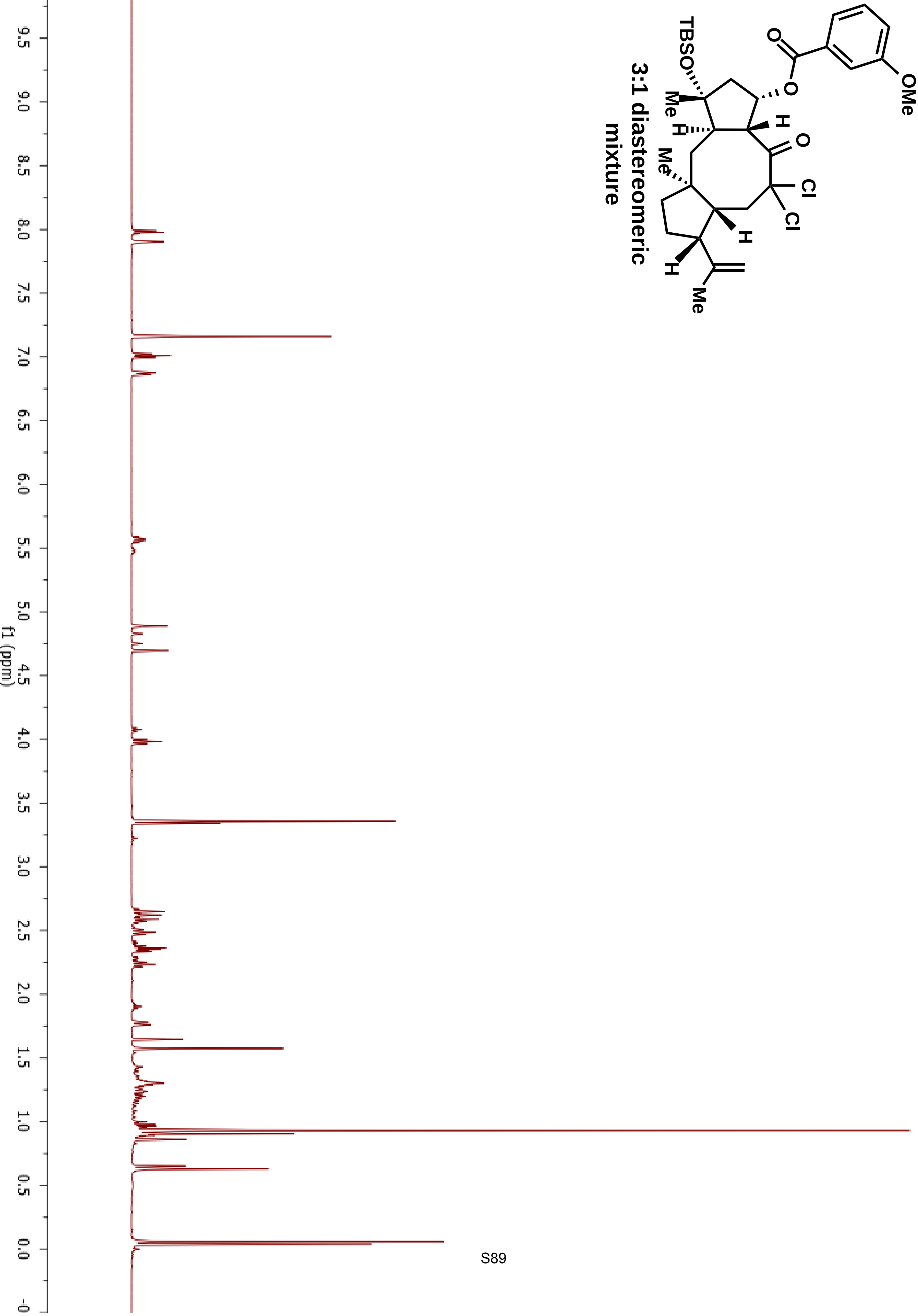
3:1 diastereomeric mixture



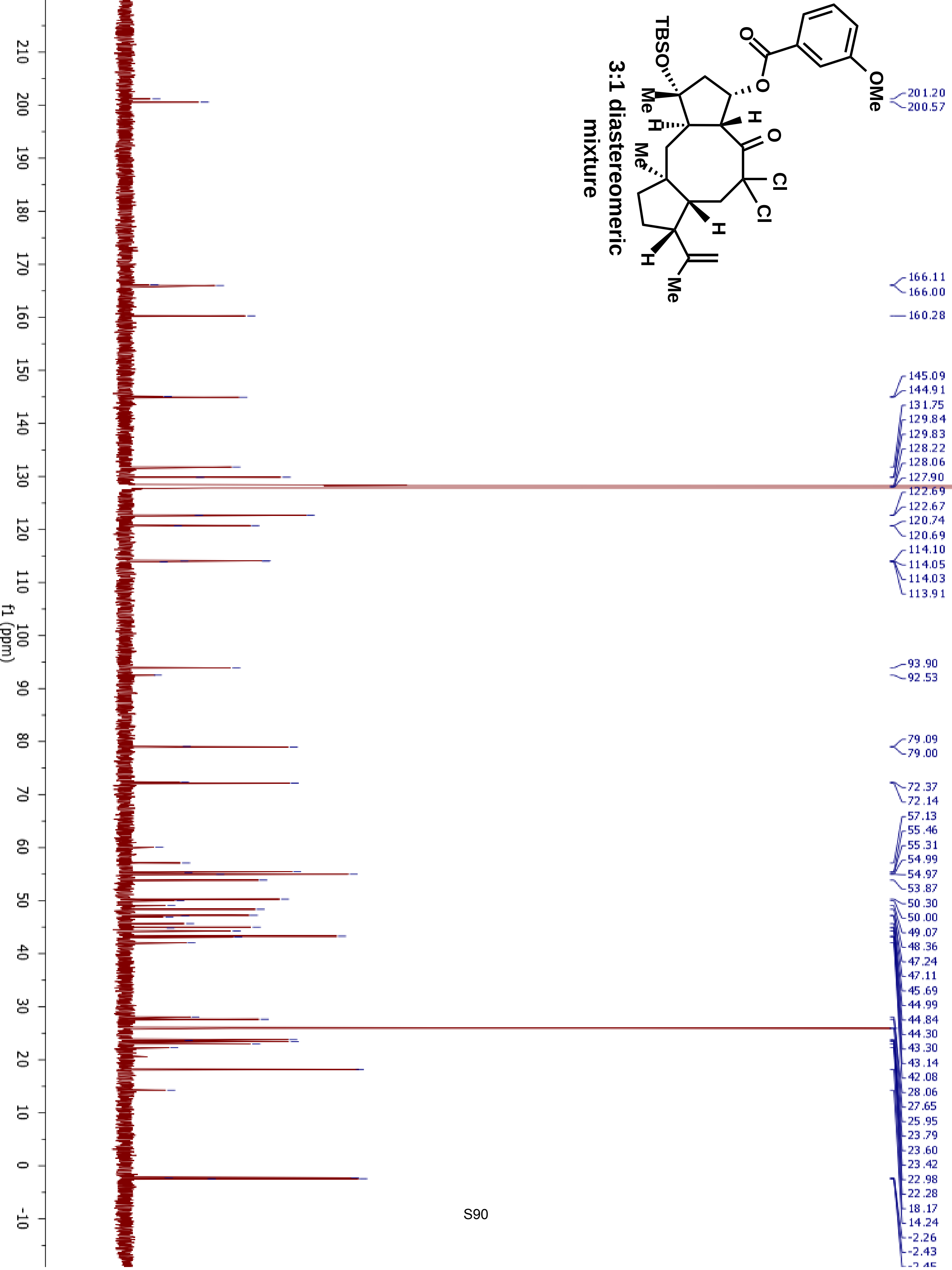
HO
H
O
Cl
Cl
TBSO
Me
H
Me
H
H
Me
(Major)
+ mixture of isomers
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)



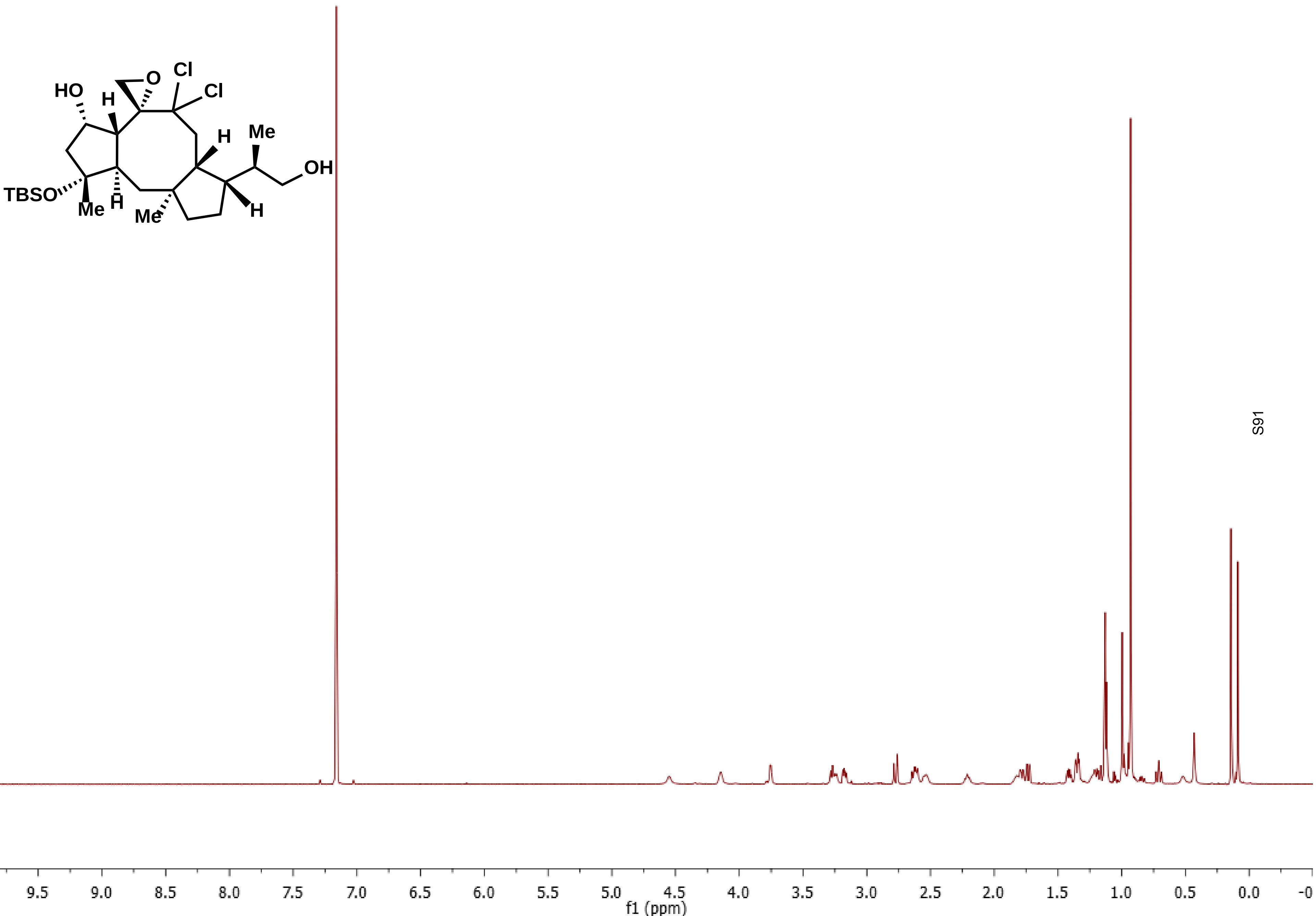
(Major)
+ mixture of isomers

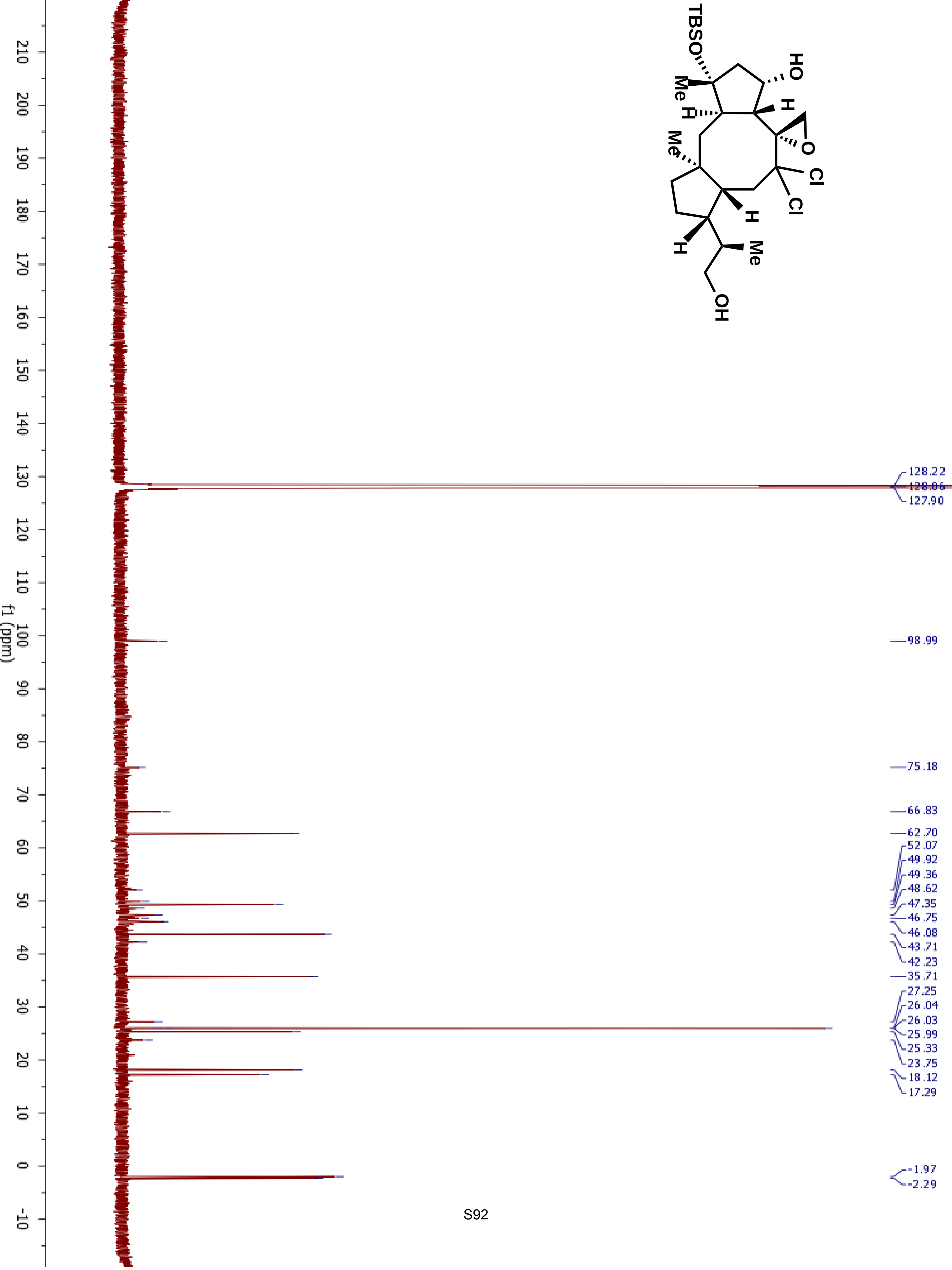


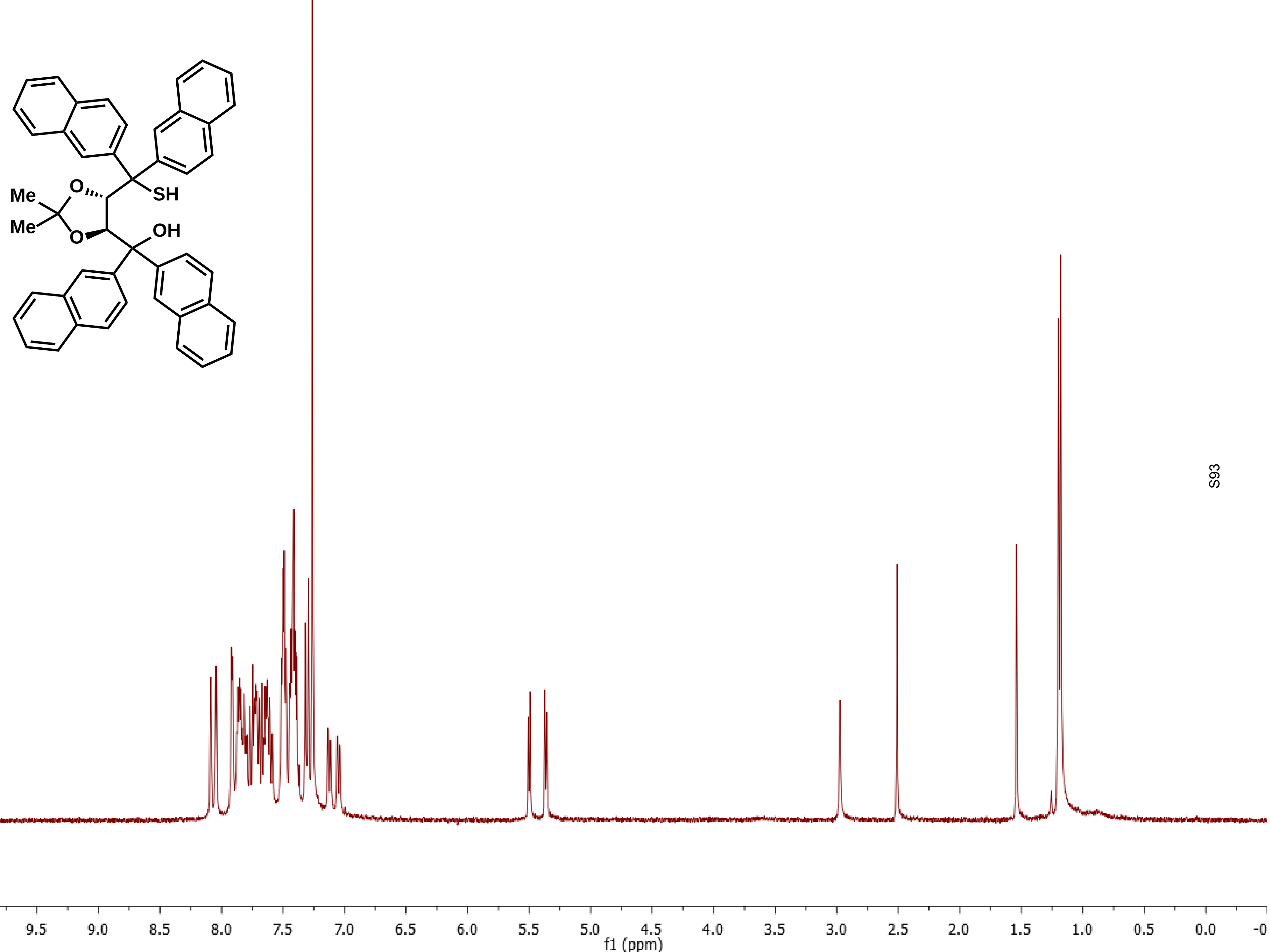
3:1 diastereomeric mixture



3:1 diastereomeric mixture


HO
H
O
Cl
Cl
H
Me
OH
TBSO
Me
H
Me
H
9.5
9.0
8.5
8.0
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
0.0
f1 (ppm)


TBSO
HO
Me
H
H
O
Cl
Cl
Me
H
H
Me
OH
128.22
128.06
127.90
98.99
75.18
66.83
62.70
52.07
49.92
49.36
48.62
47.35
46.75
46.08
43.71
42.23
35.71
27.25
26.04
26.03
25.99
25.33
23.75
18.12
17.29
-1.97
-2.29
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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Me
O
O
SH
OH
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9.0
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7.5
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6.5
6.0
5.5
5.0
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3.5
3.0
2.5
2.0
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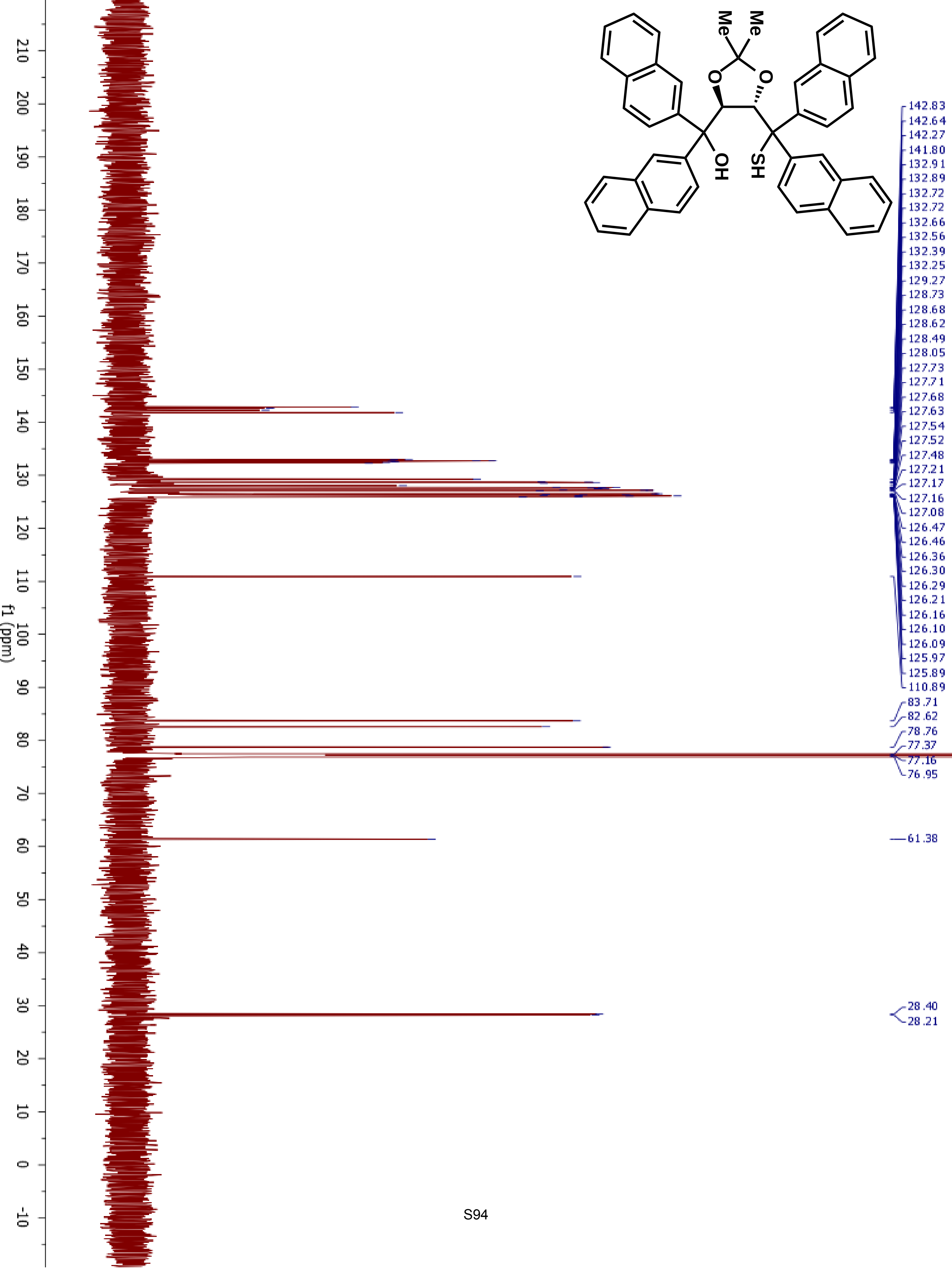
1.0
0.5
0.0
f1 (ppm)


Me
Me
O
O
OH
SH
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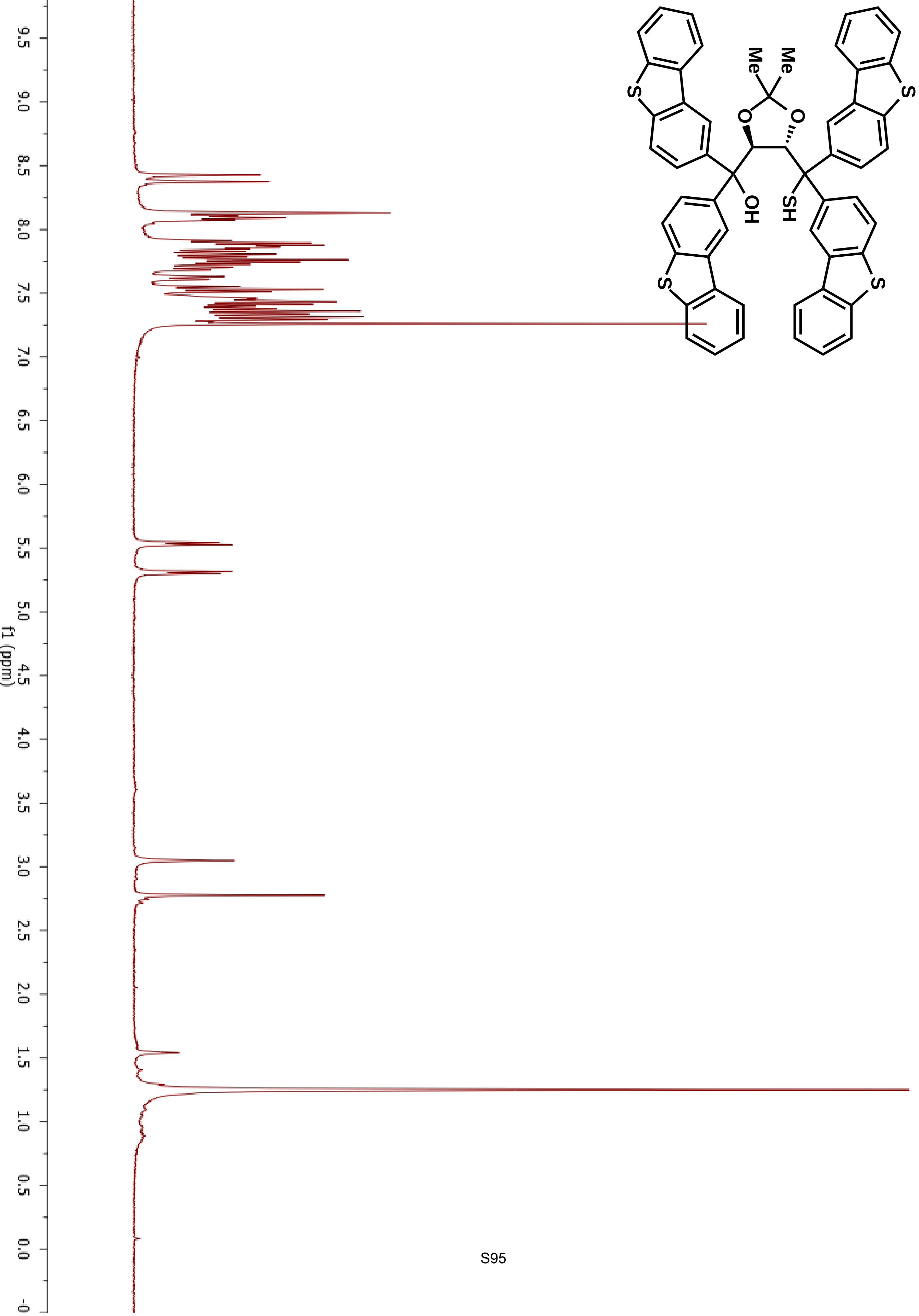
142.64
142.27
141.80
132.91
132.89
132.72
132.72
132.66
132.56
132.39
132.25
129.27
128.73
128.68
128.62
128.49
128.05
127.73
127.71
127.68
127.63
127.54
127.52
127.48
127.21
127.17
127.16
127.08
126.47
126.46
126.36
126.30
126.29
126.21
126.16
126.10
126.09
125.97
125.89
110.89
83.71
82.62
78.76
77.37
77.16
76.95
61.38
28.40
28.21
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


9.5
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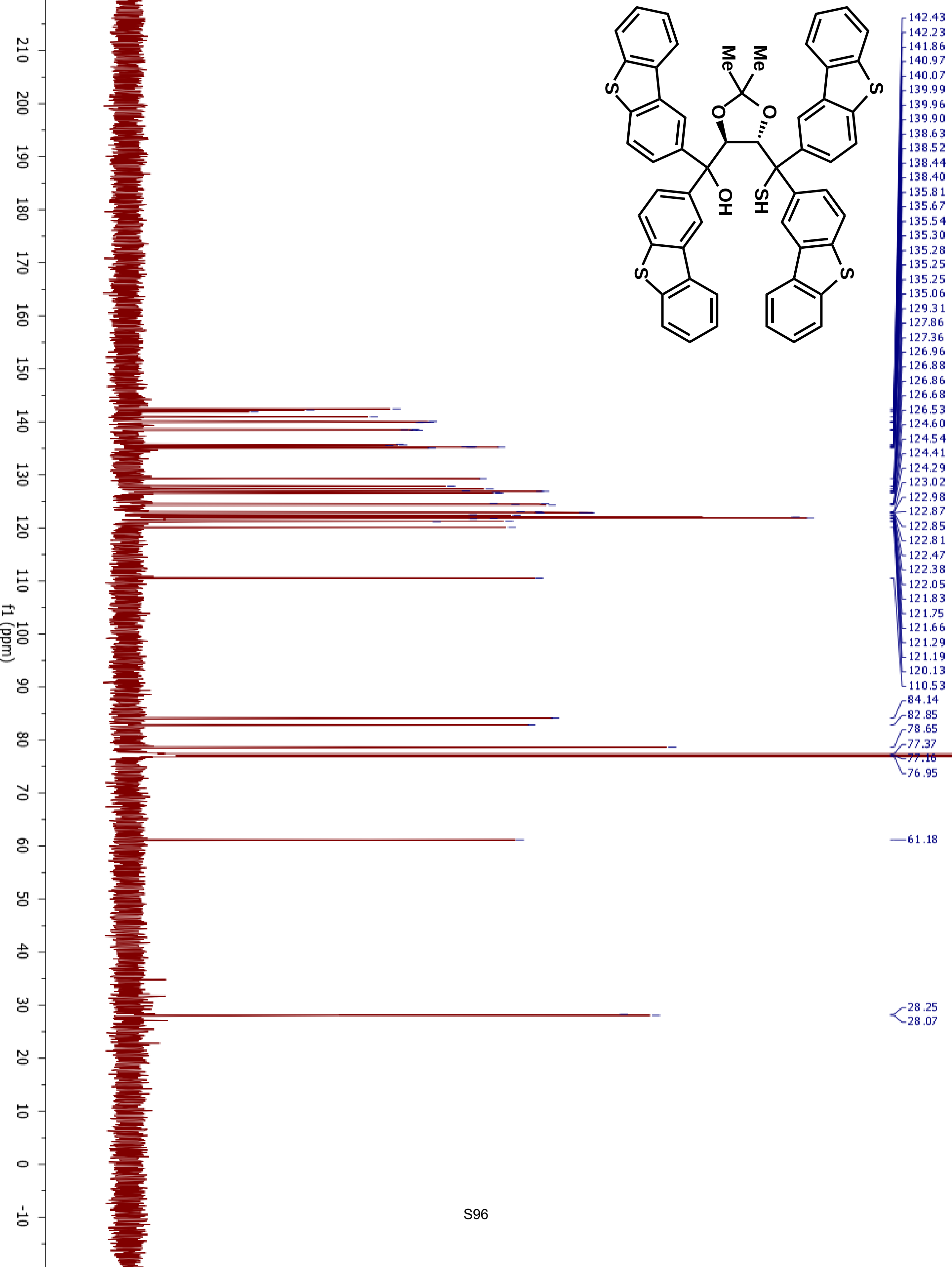
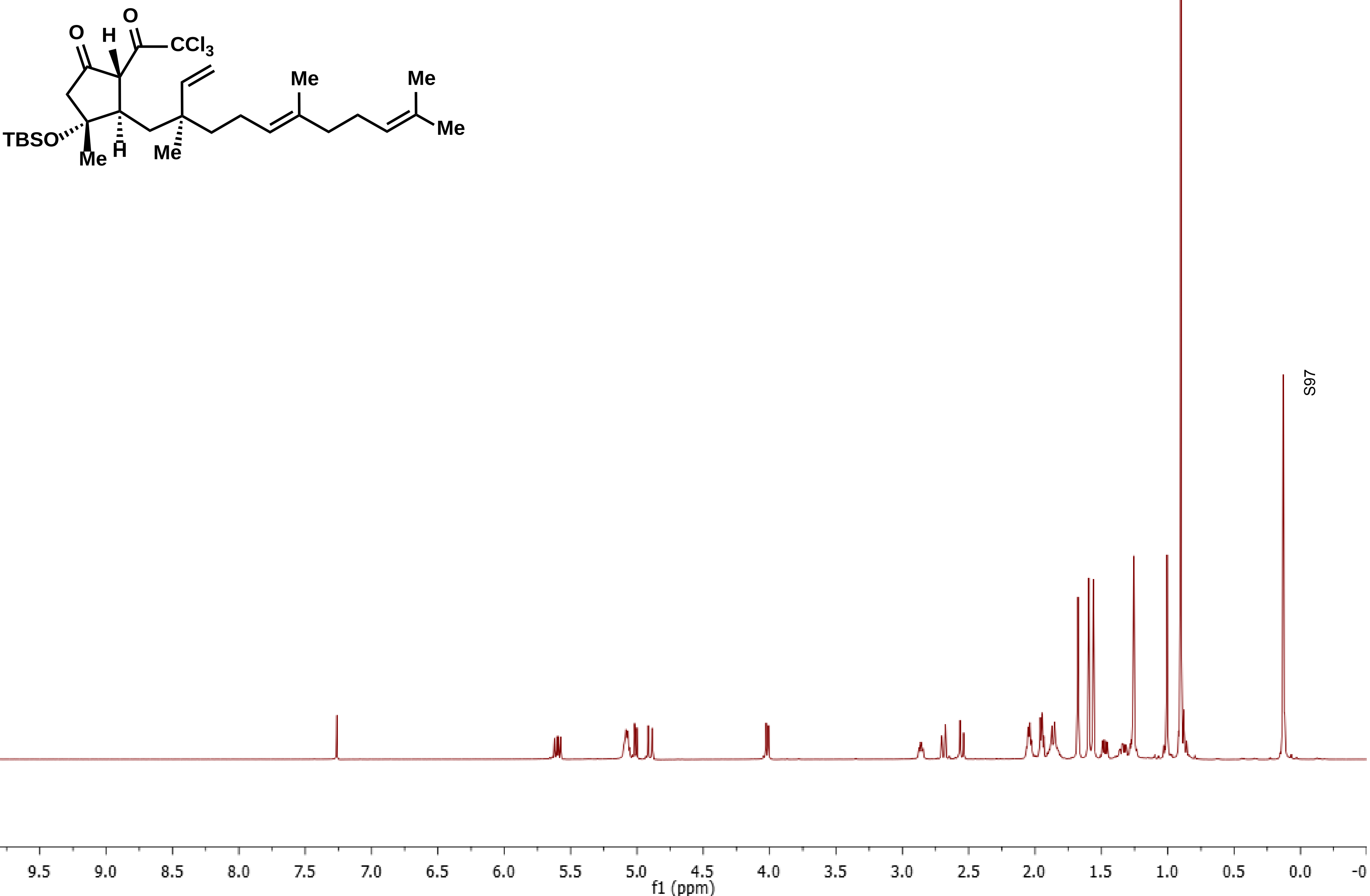
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)
S
S
S
S
Me
Me
O
O
OH
SH


S
Me
Me
O
O
OH
SH
S
S
S
142.43
142.23
141.86
140.97
140.07
139.99
139.96
139.90
138.63
138.52
138.44
138.40
135.81
135.67
135.54
135.30
135.28
135.25
135.25
135.06
129.31
127.86
127.36
126.96
126.88
126.86
126.68
126.53
124.60
124.54
124.41
124.29
123.02
122.98
122.87
122.85
122.81
122.47
122.38
122.05
121.83
121.75
121.66
121.29
121.19
120.13
110.53
84.14
82.85
78.65
77.37
77.16
76.95
61.18
28.25
28.07
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
H
O
CCl3
Me
Me
Me
TBSO
Me
H
Me
9.5
9.0
8.5
8.0
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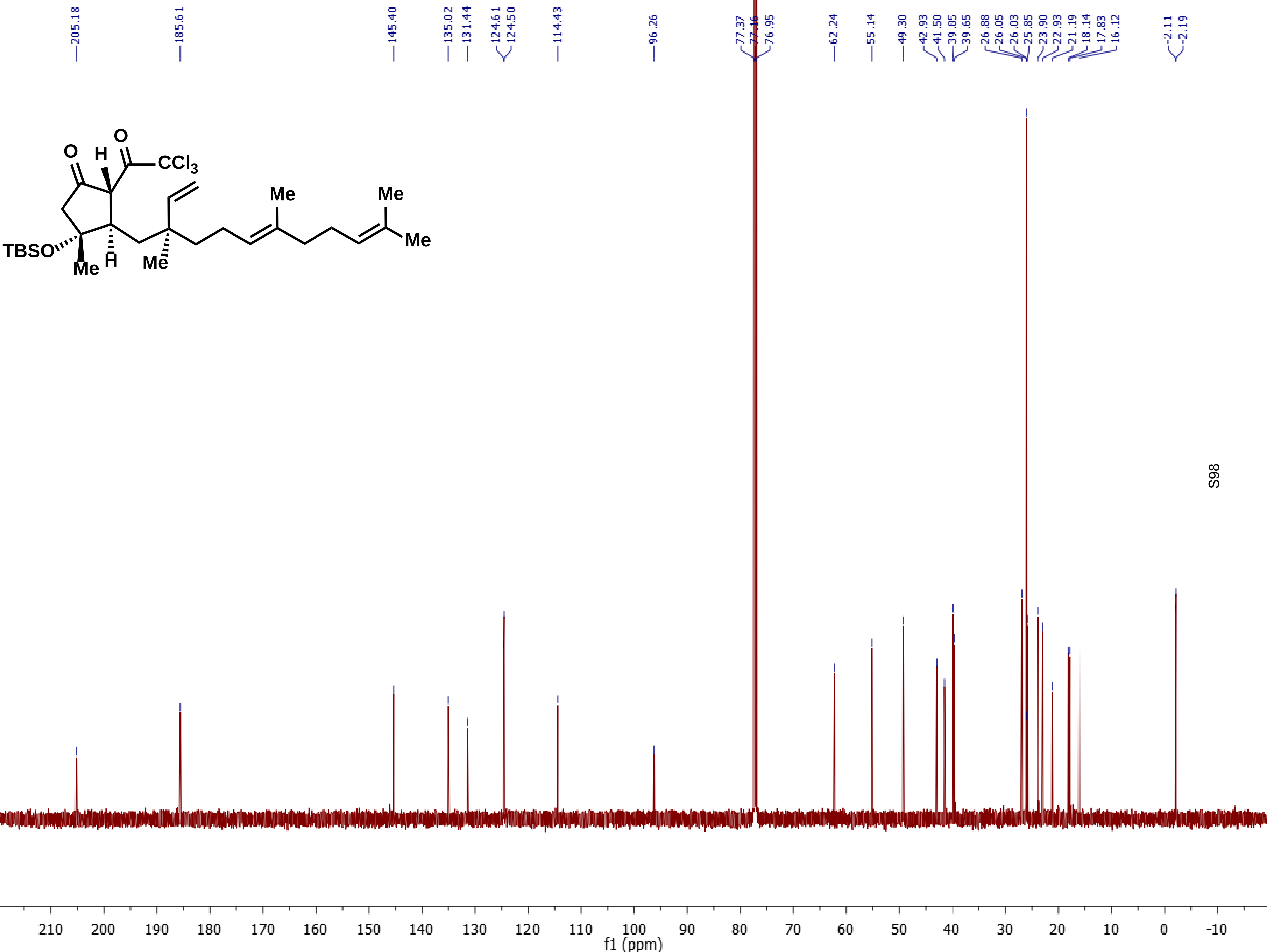
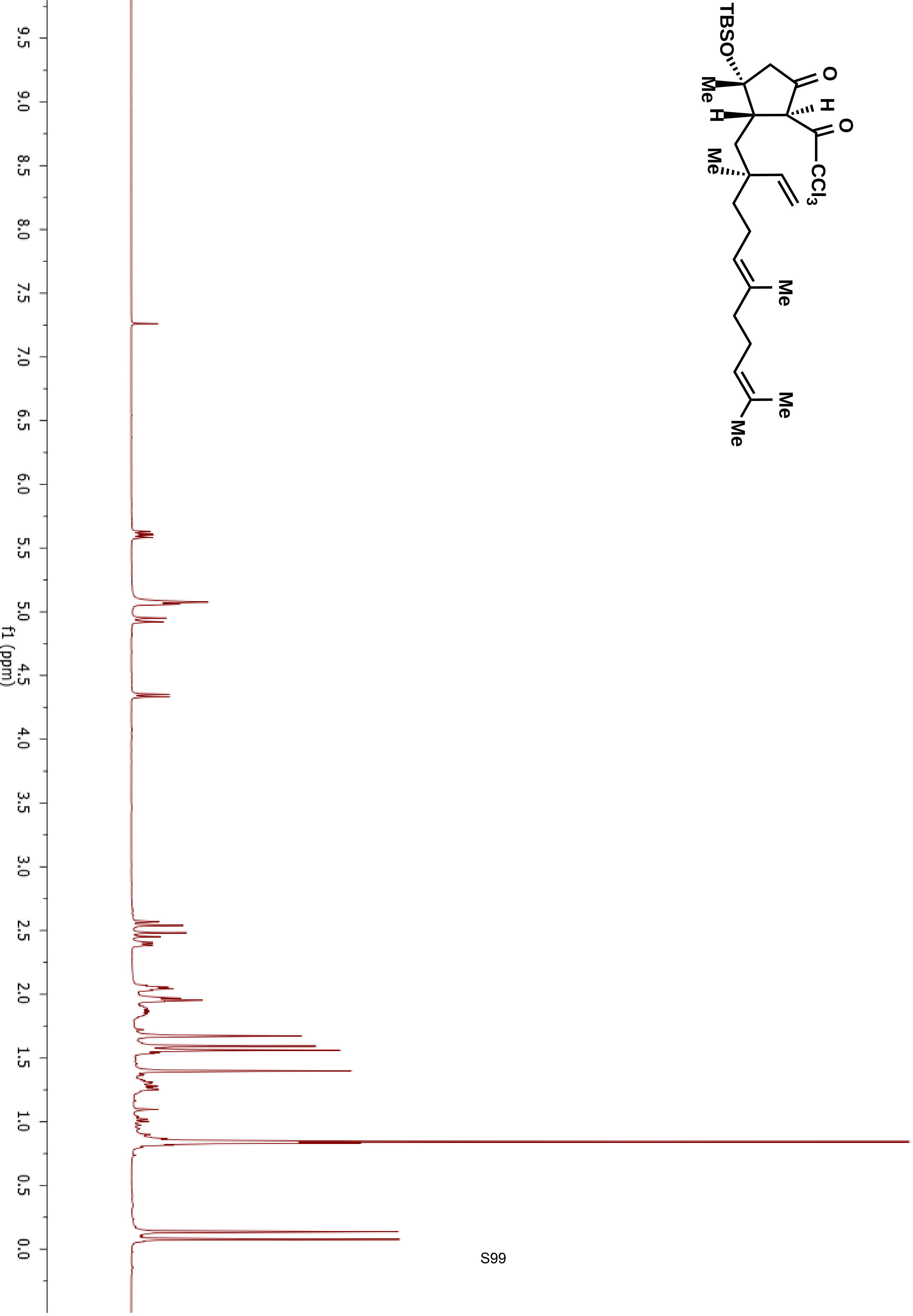
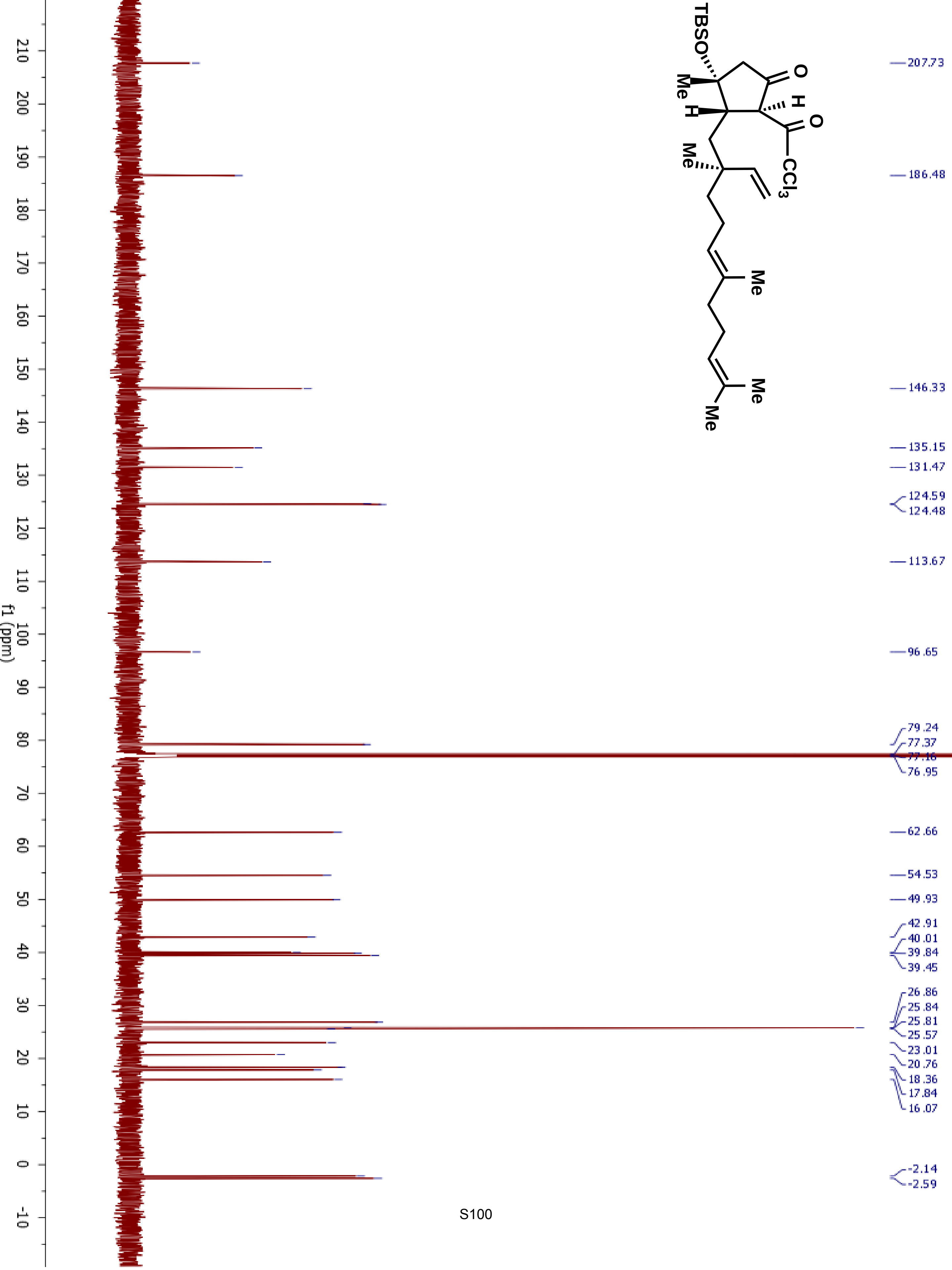
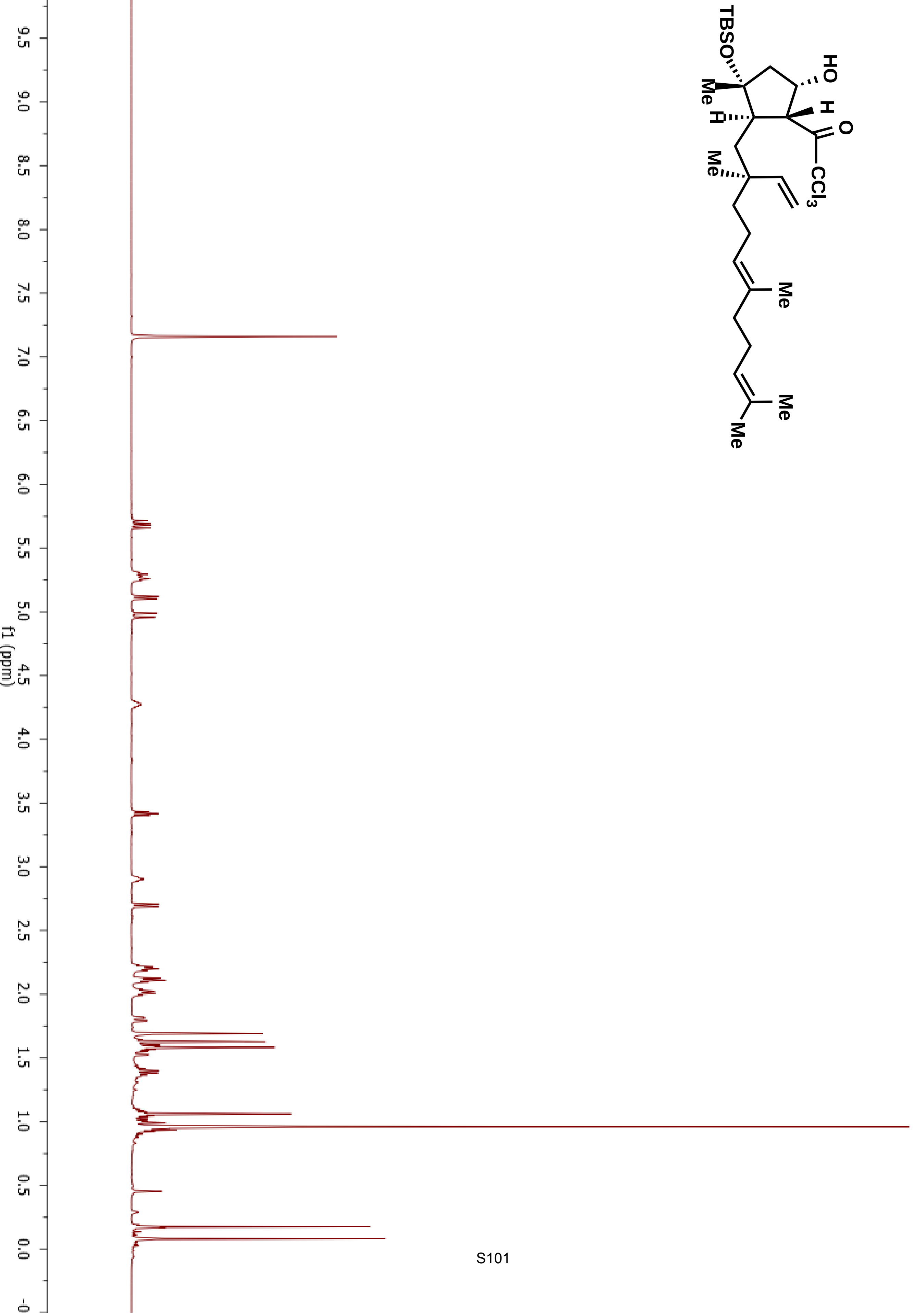
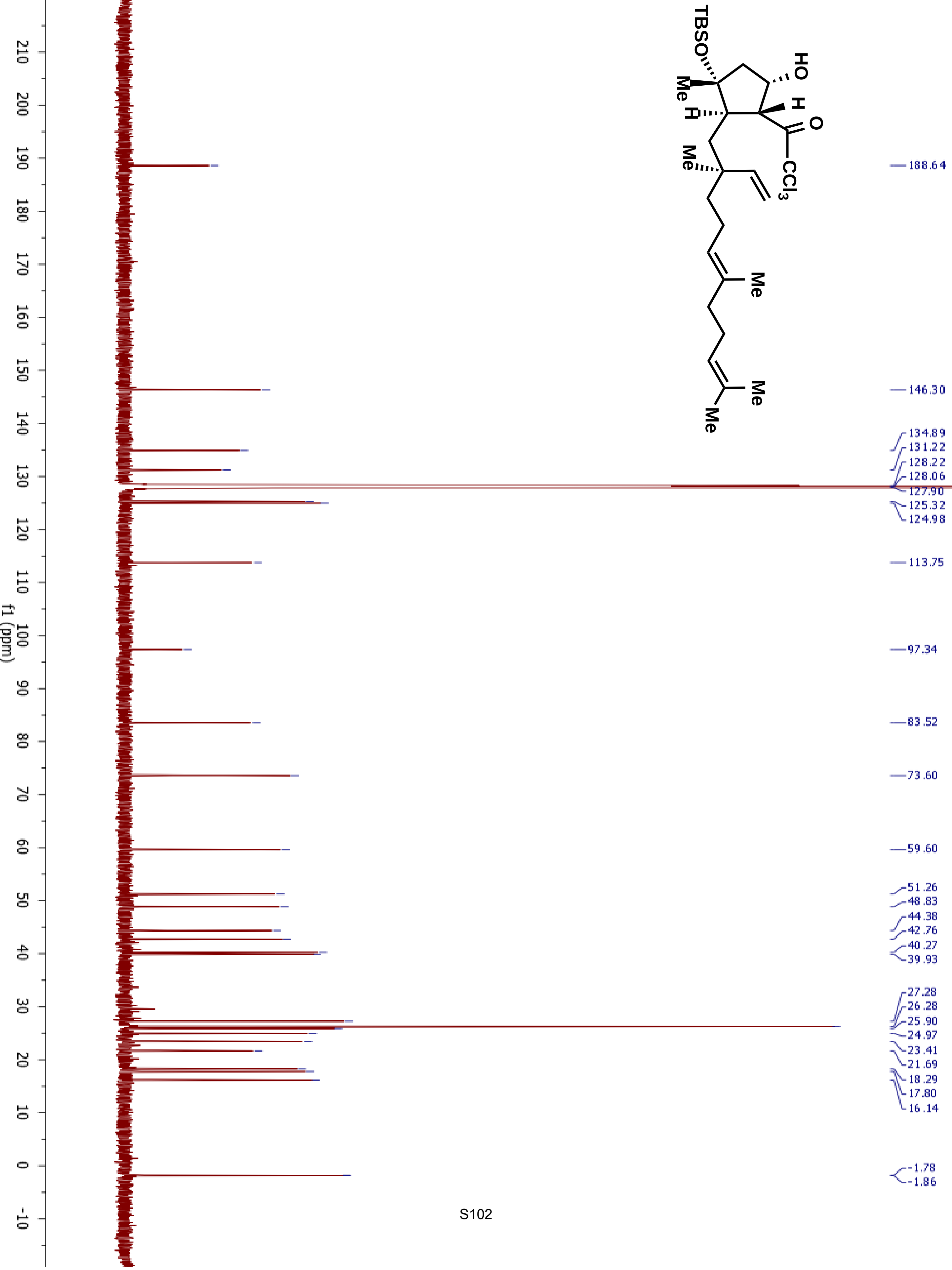
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

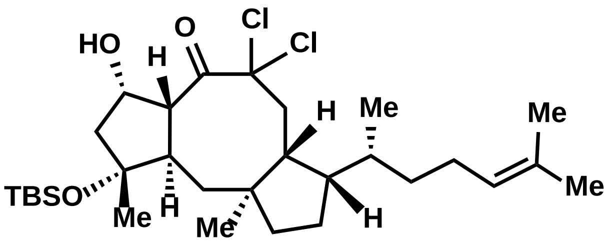

205.18
185.61
145.40
135.02
131.44
124.61
124.50
114.43
96.26
77.37
77.16
76.95
62.24
55.14
49.30
42.93
41.50
39.85
39.65
26.88
26.05
26.03
25.85
23.90
22.93
21.19
18.14
17.83
16.12
-2.11
-2.19
O
H
O
CCl3
TBSO
Me
H
Me
Me
Me
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


TBSO
Me
H
O
H
O
CCl3
Me
Me
Me
Me
9.5
9.0
8.5
8.0
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
0.0
f1 (ppm)

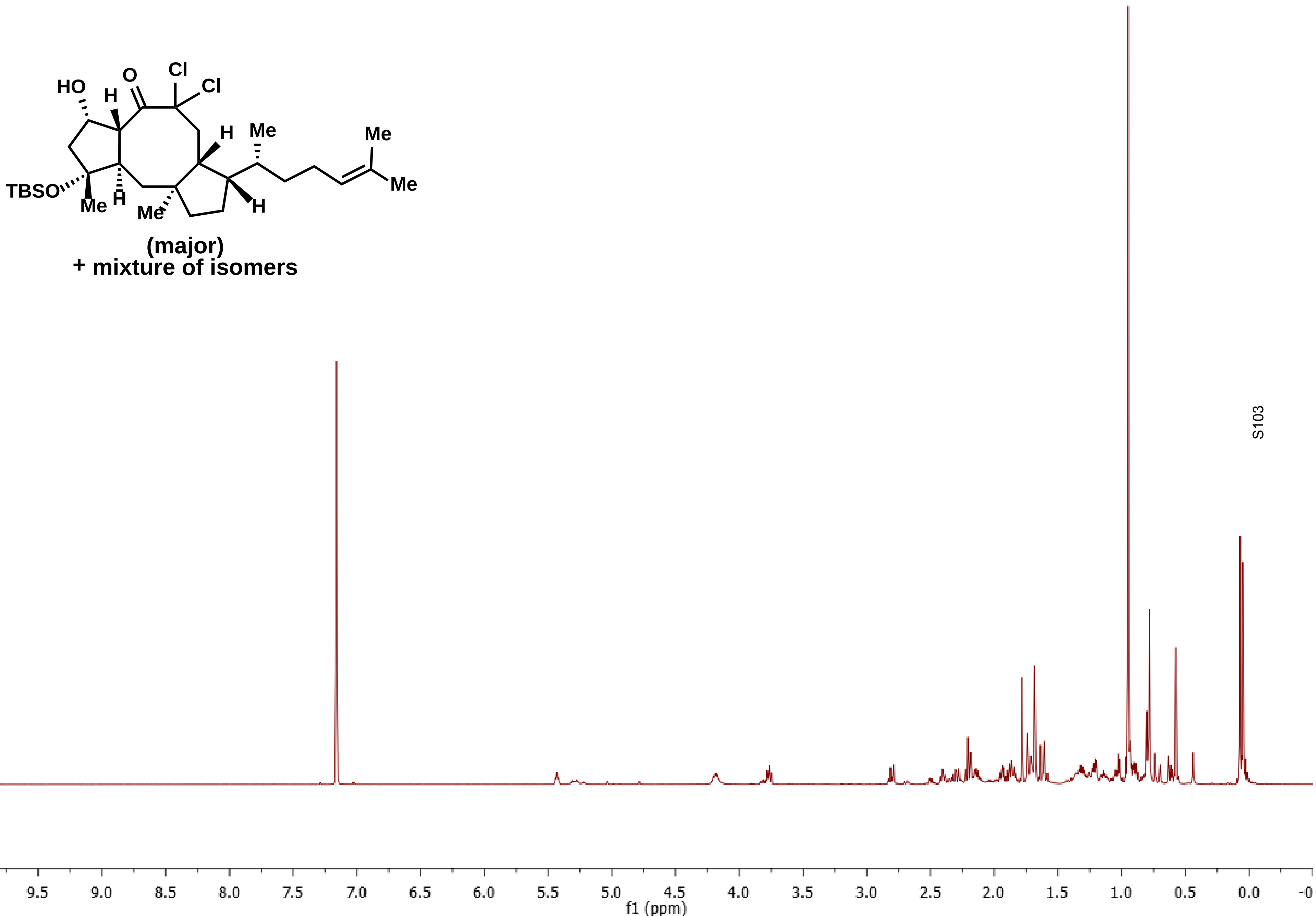

TBSO
Me
H
O
H
O
CCl$_3$
Me
Me
Me
Me
207.73
186.48
146.33
135.15
131.47
124.59
124.48
113.67
96.65
79.24
77.37
77.16
76.95
62.66
54.53
49.93
42.91
40.01
39.84
39.45
26.86
25.84
25.81
25.57
23.01
20.76
18.36
17.84
16.07
-2.14
-2.59
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

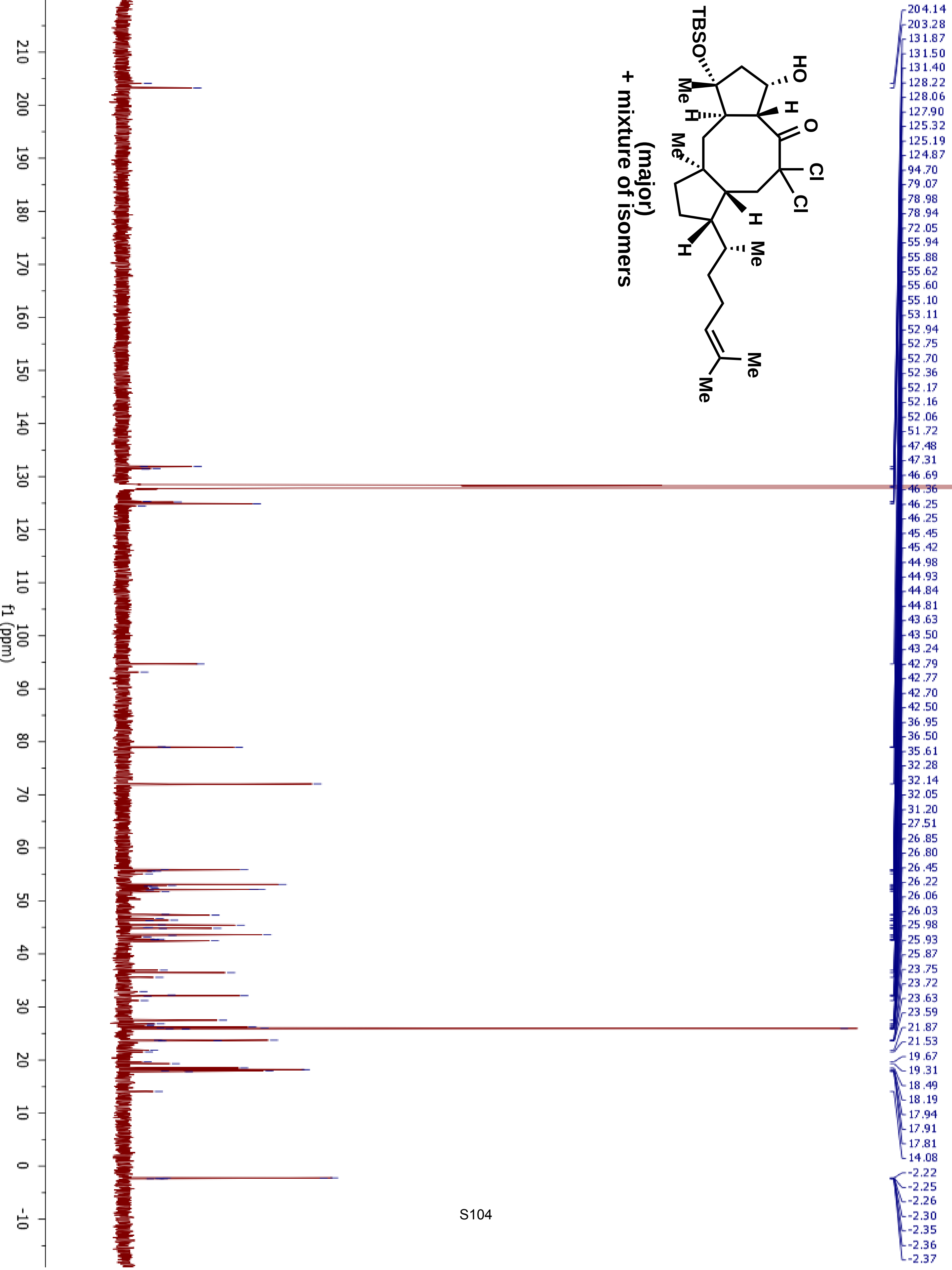

TBSO
HO
H
O
CCl$_3$
Me
H
Me
Me
Me
Me
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

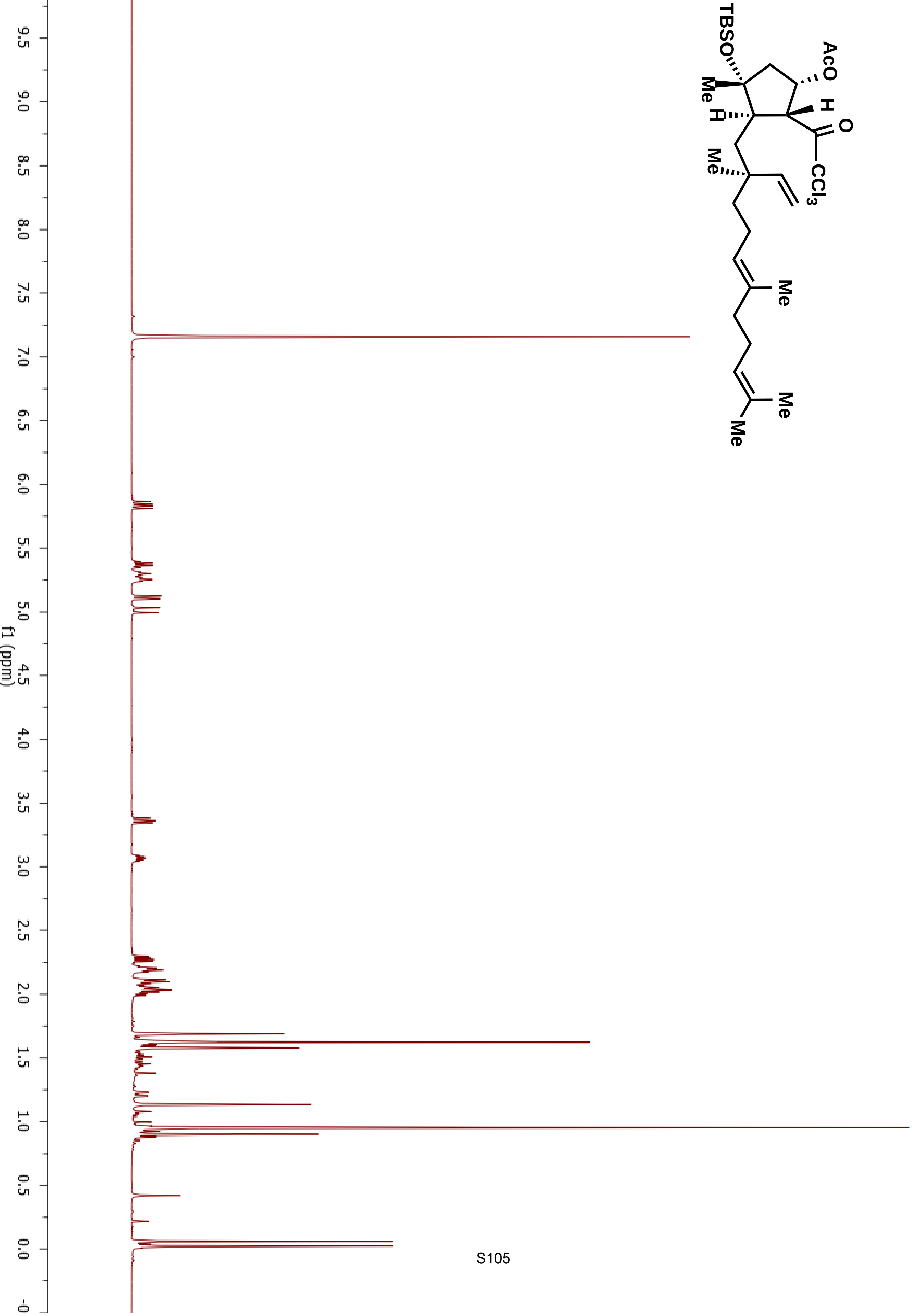

TBSO
HO
H
O
Me
H
CCl3
Me
Me
Me
Me
188.64
146.30
134.89
131.22
128.22
128.06
127.90
125.32
124.98
113.75
97.34
83.52
73.60
59.60
51.26
48.83
44.38
42.76
40.27
39.93
27.28
26.28
25.90
24.97
23.41
21.69
18.29
17.80
16.14
-1.78
-1.86
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

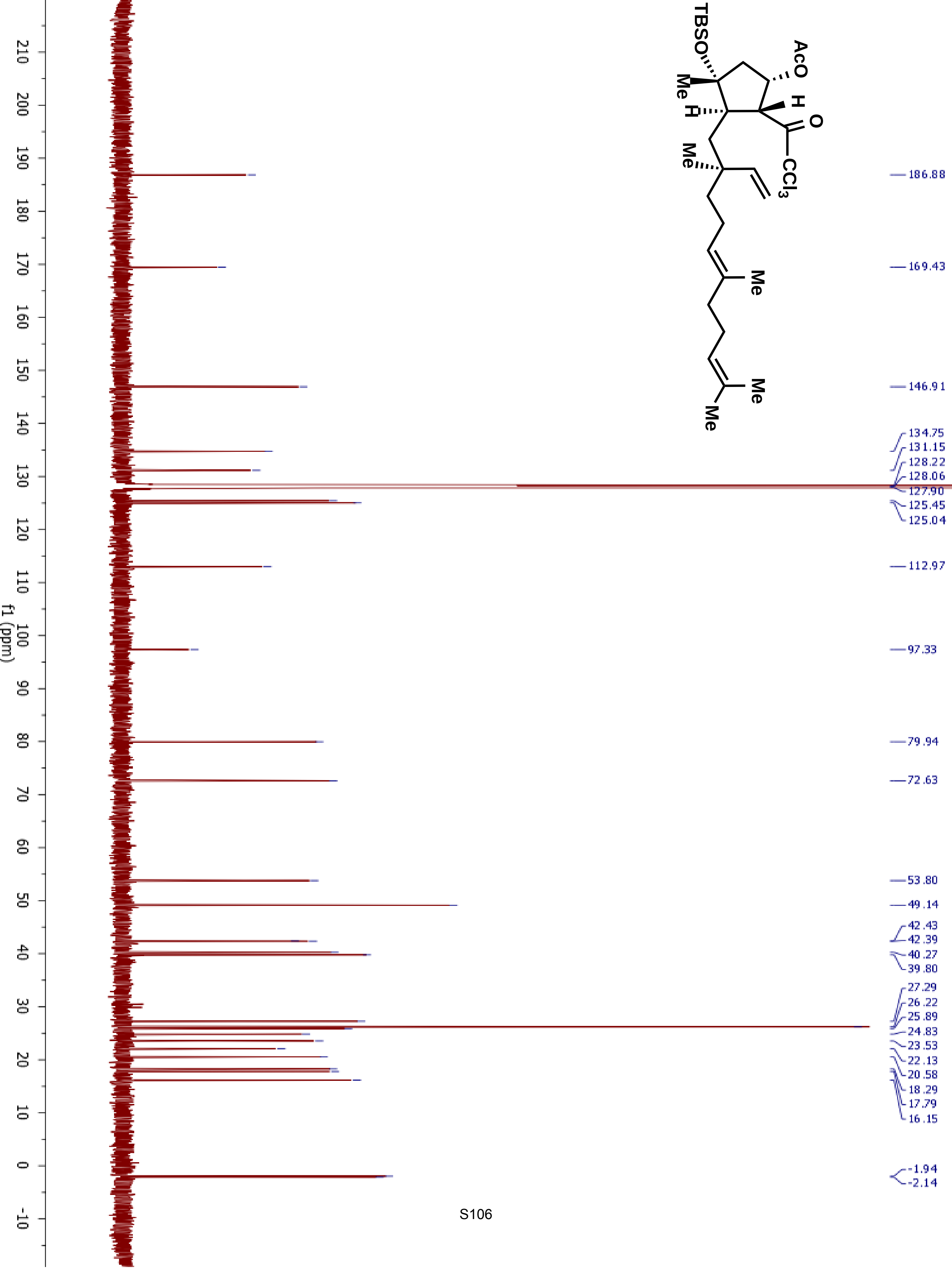


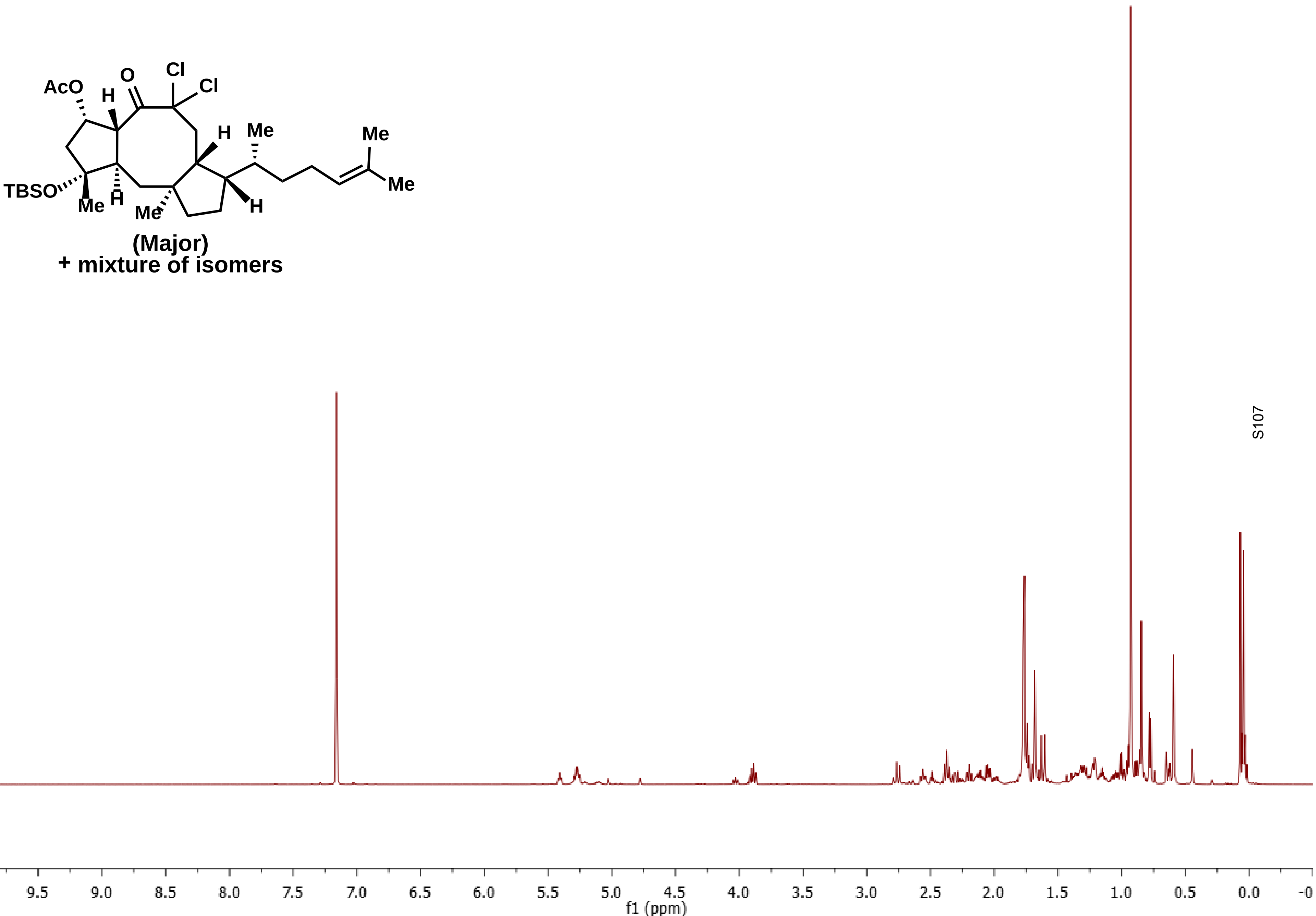
(major)
+ mixture of isomers

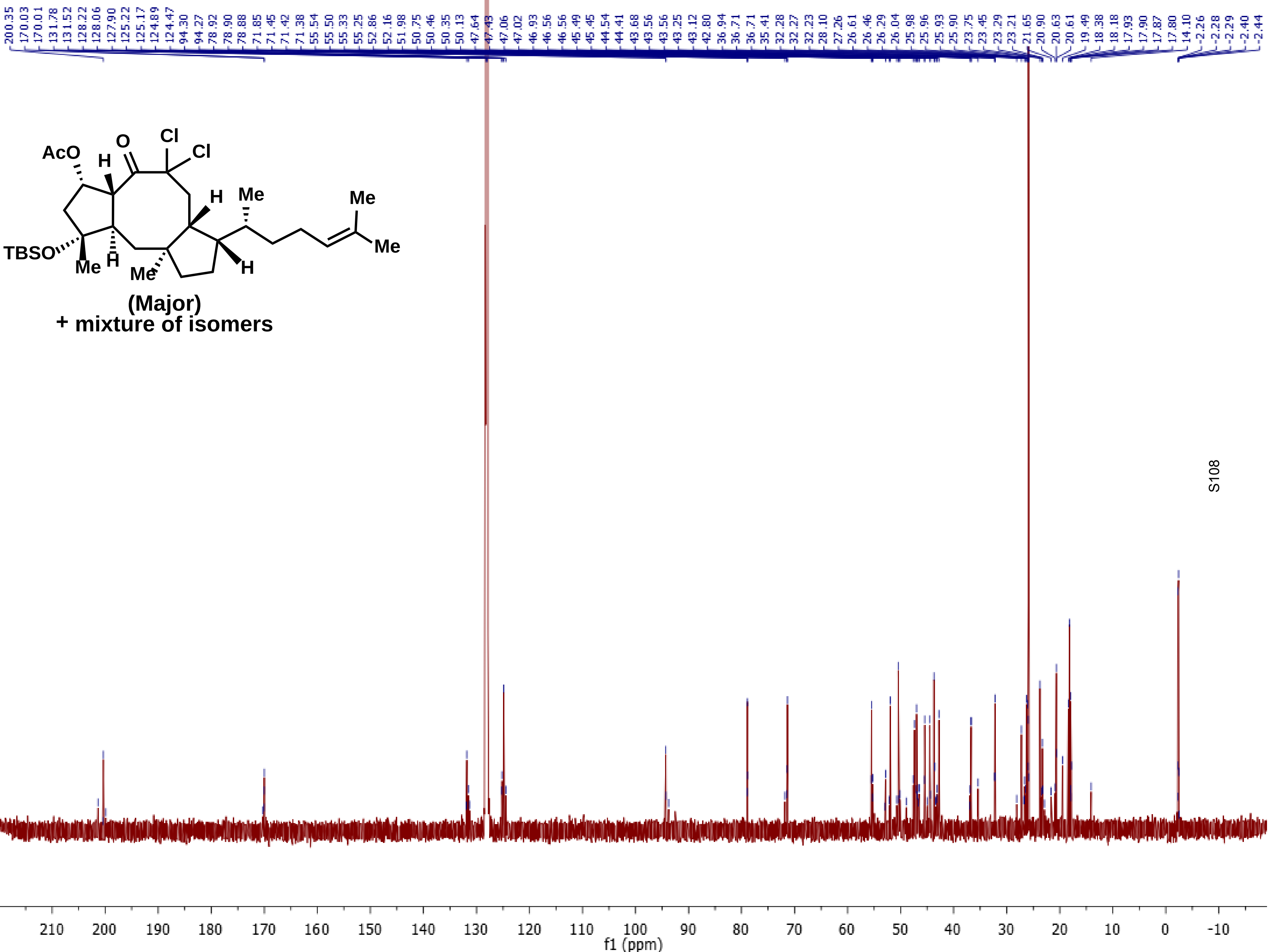


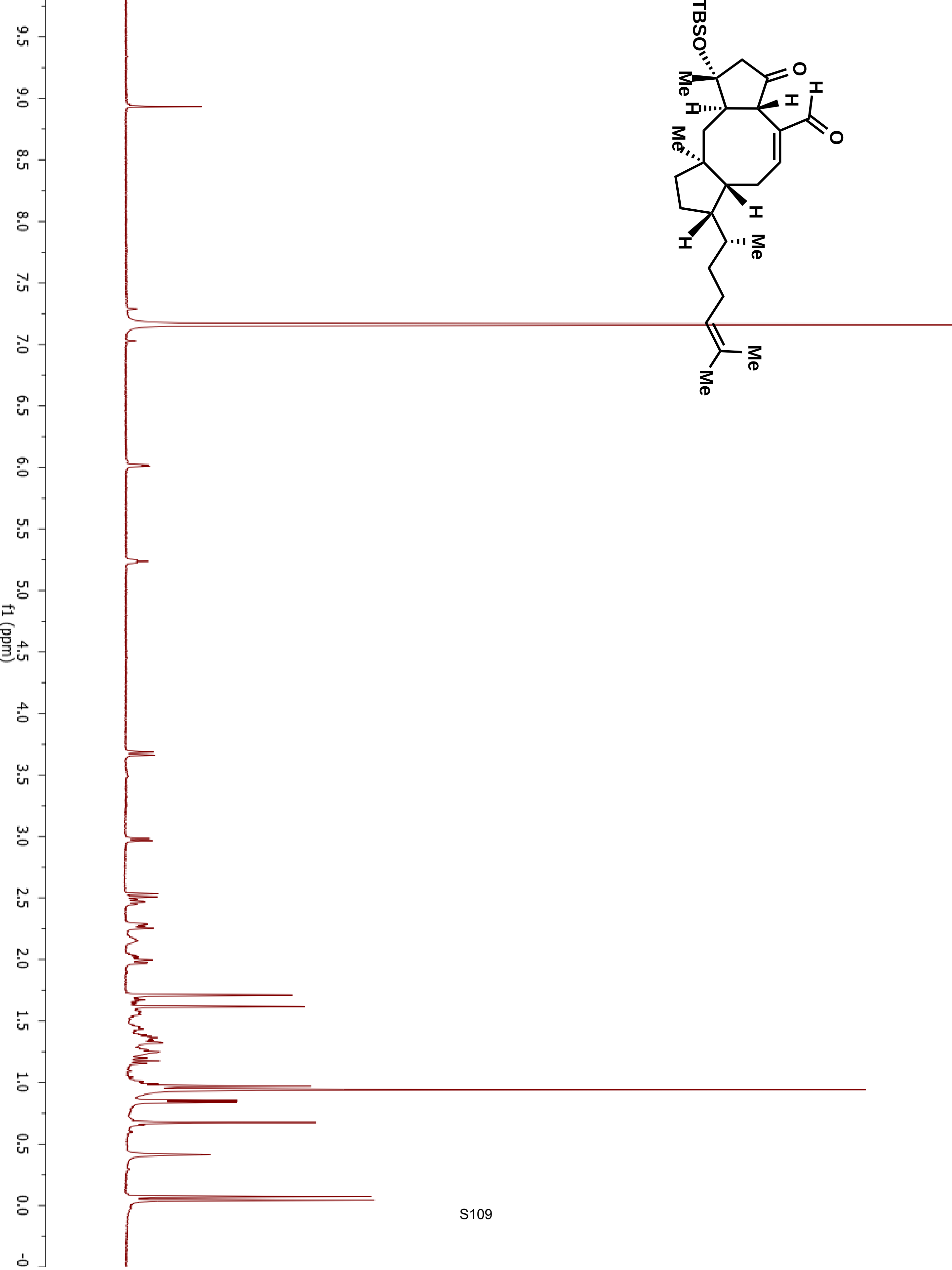

TBSO
HO
H
O
Cl
Cl
Me
H
Me
H
Me
H
Me
Me
(major)
+ mixture of isomers
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
204.14
203.28
131.87
131.50
131.40
128.22
128.06
127.90
125.32
125.19
124.87
94.70
79.07
78.98
78.94
72.05
55.94
55.88
55.62
55.60
55.10
53.11
52.94
52.75
52.70
52.36
52.17
52.16
52.06
51.72
47.48
47.31
46.69
46.36
46.25
46.25
45.45
45.42
44.98
44.93
44.84
44.81
43.63
43.50
43.24
42.79
42.77
42.70
42.50
36.95
36.50
35.61
32.28
32.14
32.05
31.20
27.51
26.85
26.80
26.45
26.22
26.06
26.03
25.98
25.93
25.87
23.75
23.72
23.63
23.59
21.87
21.53
19.67
19.31
18.49
18.19
17.94
17.91
17.81
14.08
-2.22
-2.25
-2.26
-2.30
-2.35
-2.36
-2.37

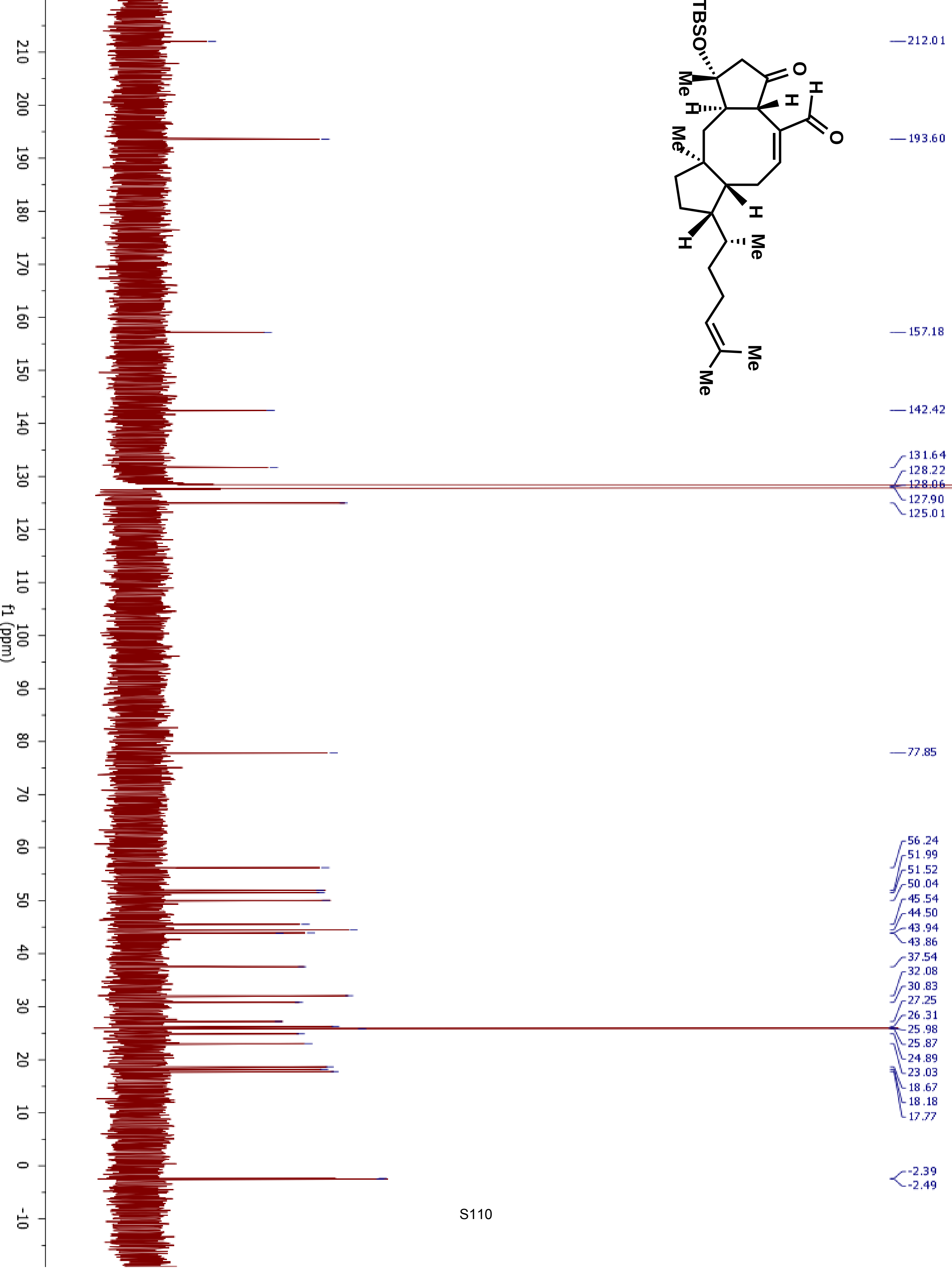

TBSO
Me
H
AcO
H
O
CCl$_3$
Me
Me
Me
Me
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

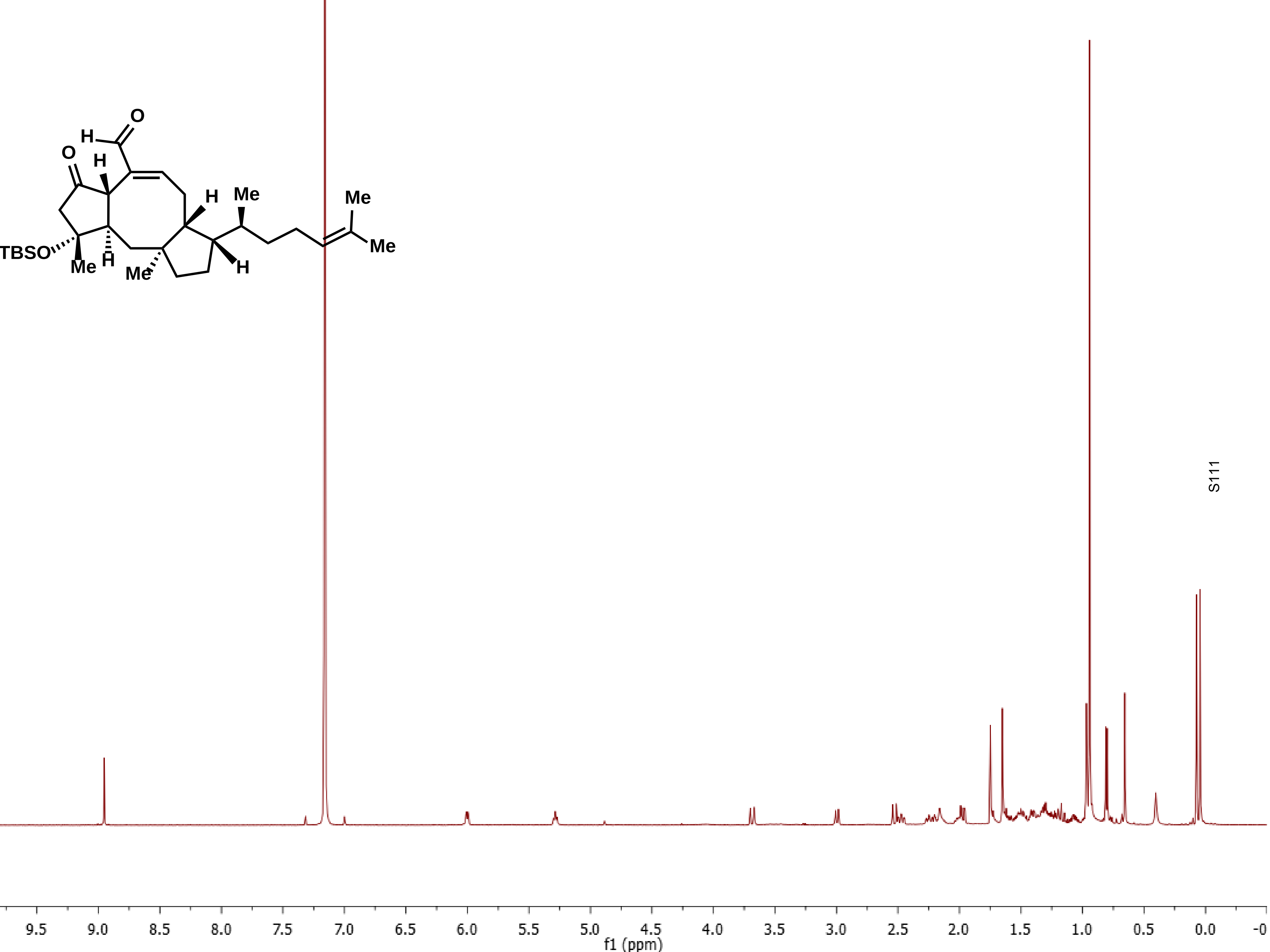

TBSO
AcO
Me
H
H
O
CCl3
Me
Me
Me
Me
186.88
169.43
146.91
134.75
131.15
128.22
128.06
127.90
125.45
125.04
112.97
97.33
79.94
72.63
53.80
49.14
42.43
42.39
40.27
39.80
27.29
26.22
25.89
24.83
23.53
22.13
20.58
18.29
17.79
16.15
-1.94
-2.14
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

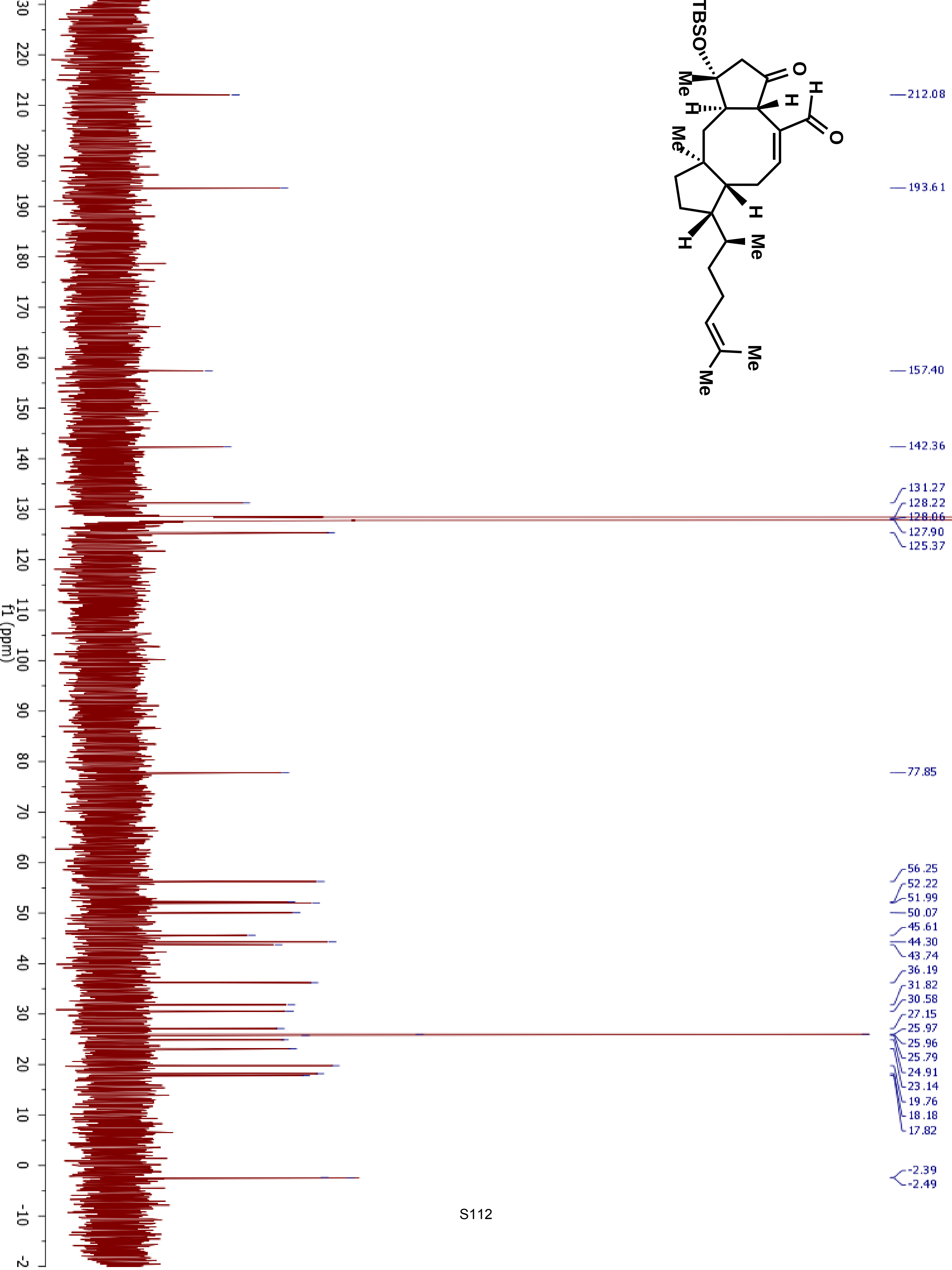

AcO
H
O
Cl
Cl
H
Me
Me
Me
TBSO
Me
H
Me
H
(Major)
+ mixture of isomers
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

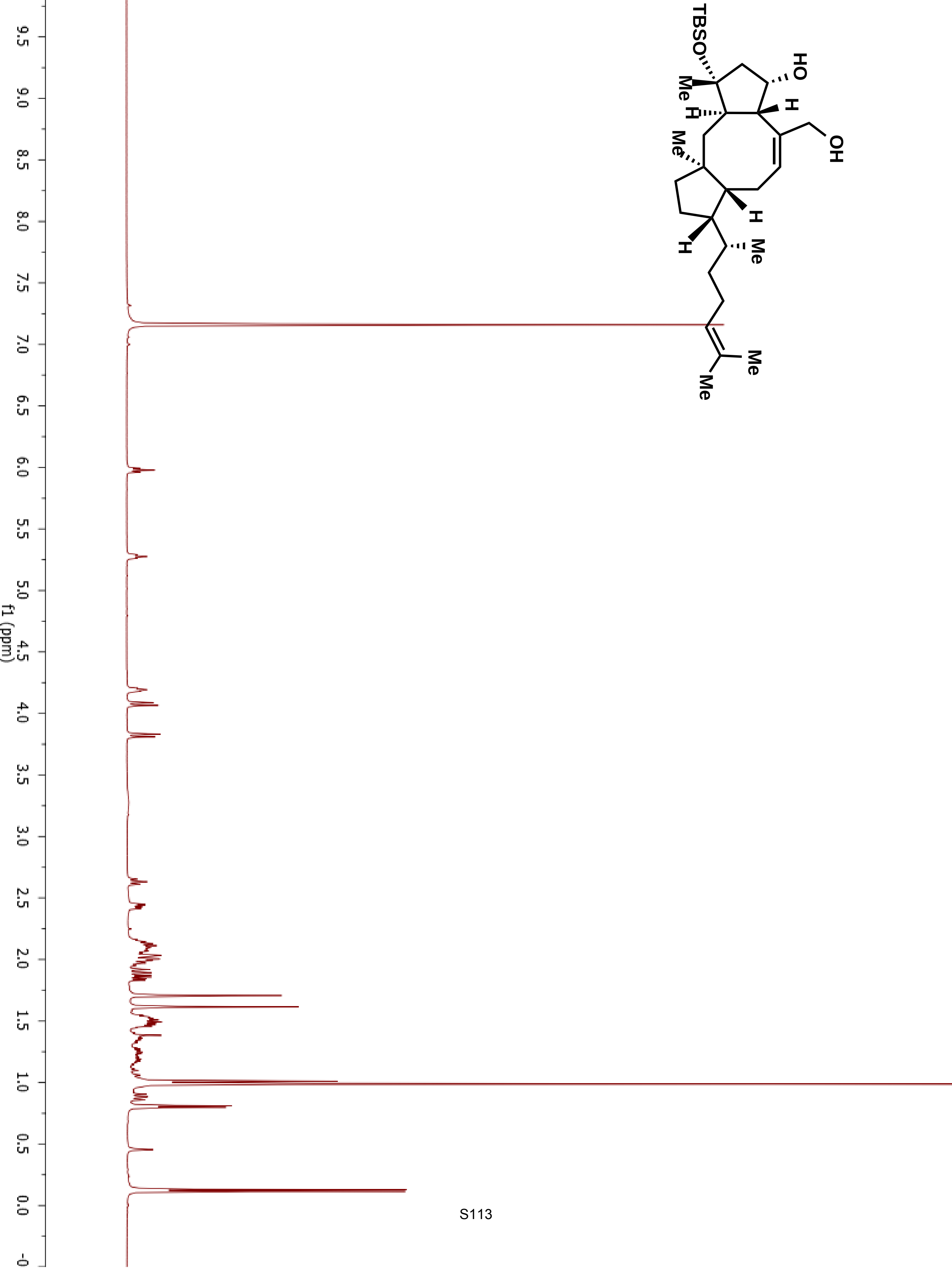

200.35
170.03
170.01
131.78
131.52
128.22
128.06
127.90
125.22
125.17
124.89
124.47
94.30
94.27
78.92
78.90
78.88
71.85
71.45
71.42
71.38
55.54
55.50
55.33
55.25
52.86
52.16
51.98
50.75
50.46
50.35
50.13
47.64
47.43
47.06
47.02
46.93
46.56
46.56
45.49
45.45
44.54
44.41
43.68
43.56
43.56
43.25
43.12
42.80
36.94
36.71
36.71
35.41
32.28
32.27
32.23
28.10
27.26
26.61
26.46
26.29
26.04
25.98
25.96
25.93
25.90
23.75
23.45
23.29
23.21
21.65
20.90
20.63
20.61
19.49
18.38
18.18
17.93
17.90
17.87
17.80
14.10
-2.26
-2.28
-2.29
-2.40
-2.44
AcO
H
O
Cl
Cl
H
Me
Me
Me
TBSO
Me
H
Me
H
(Major)
+ mixture of isomers
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

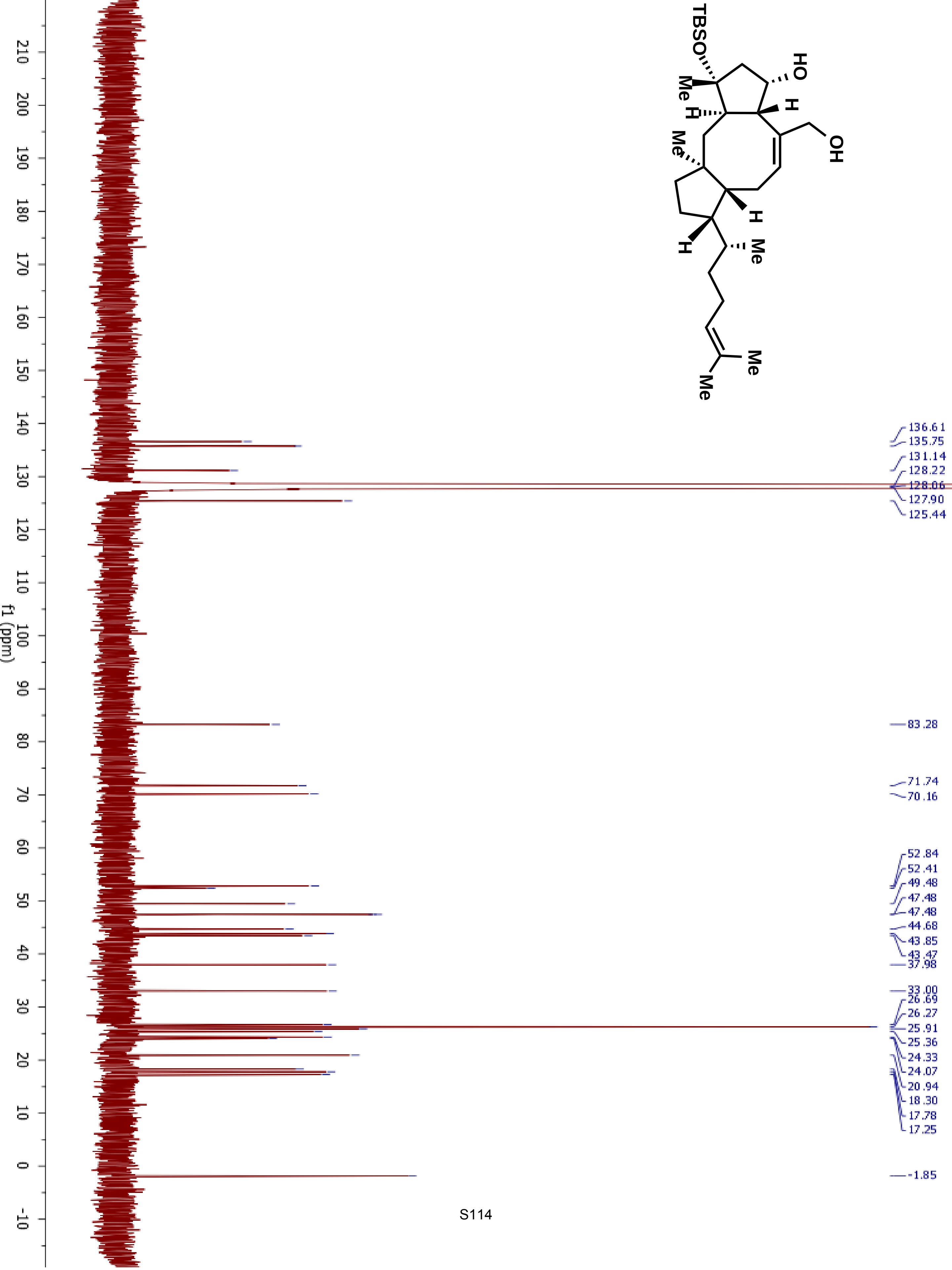

TBSO
O
H
O
Me
H
H
Me
H
H
Me
Me
Me
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

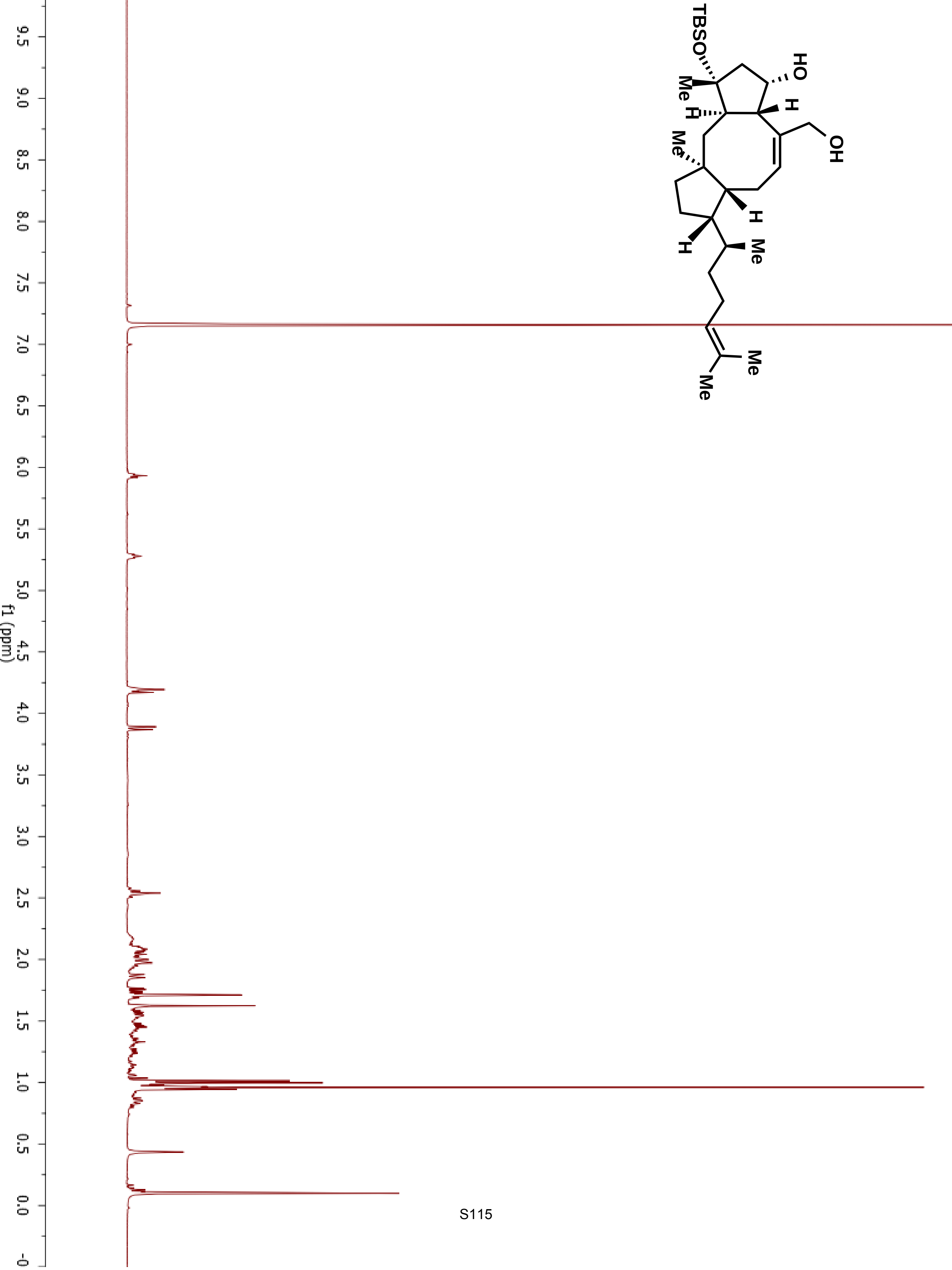

TBSO
Me
H
O
H
O
Me
H
H
Me
Me
Me
212.01
193.60
157.18
142.42
131.64
128.22
128.06
127.90
125.01
77.85
56.24
51.99
51.52
50.04
45.54
44.50
43.94
43.86
37.54
32.08
30.83
27.25
26.31
25.98
25.87
24.89
23.03
18.67
18.18
17.77
-2.39
-2.49
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

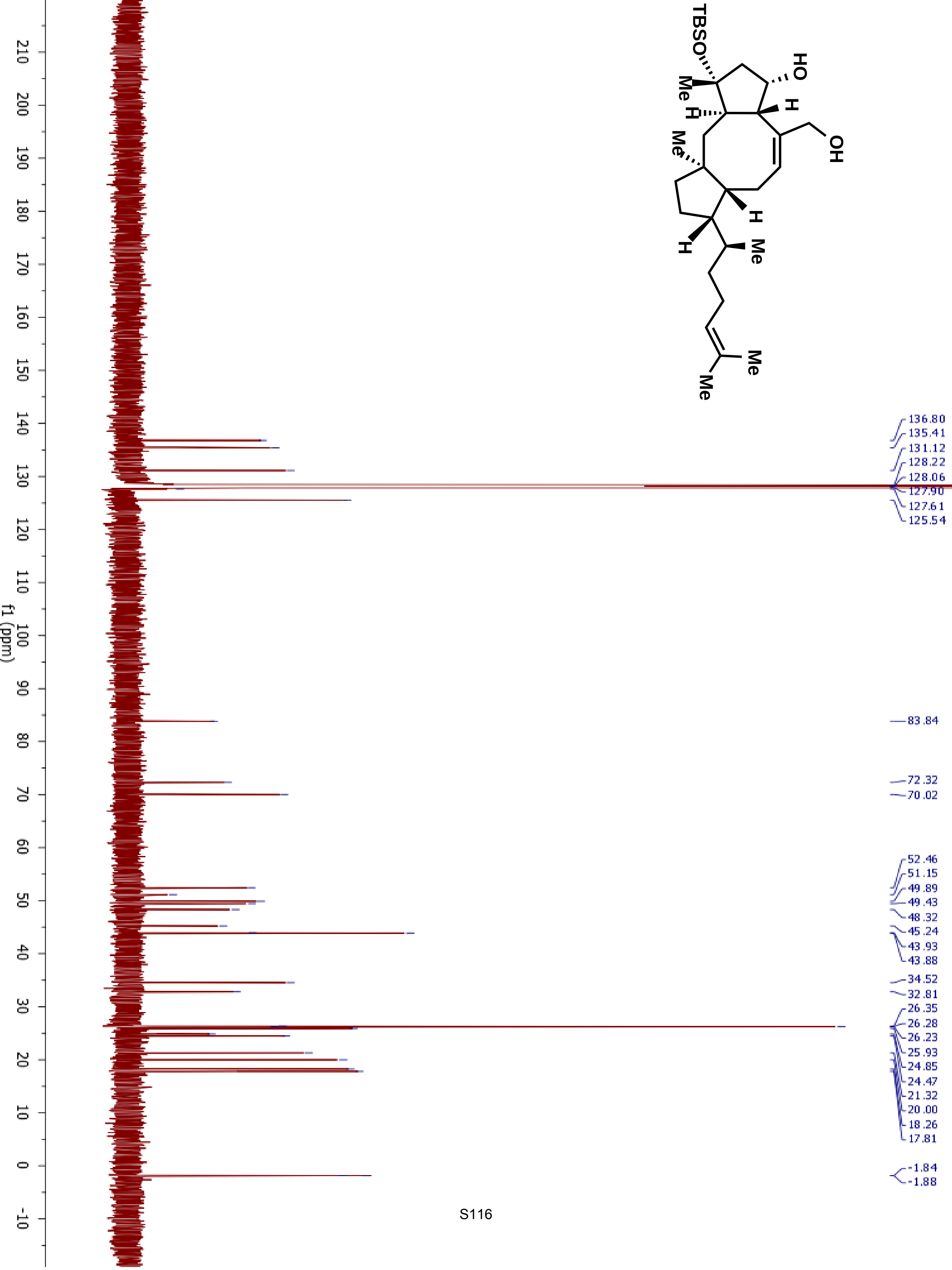

TBSO
Me
H
O
H
H
O
Me
H
Me
H
Me
Me
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

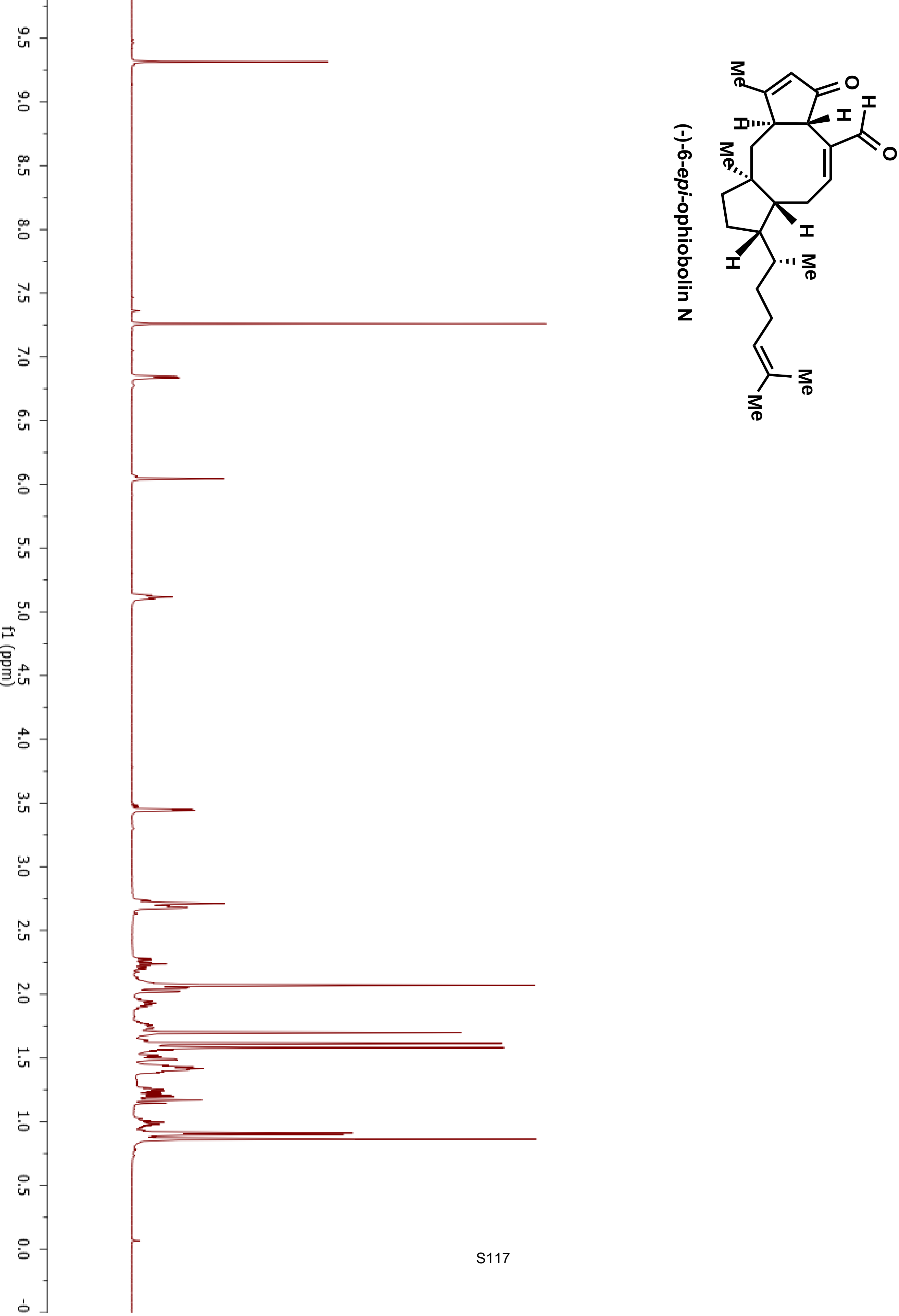

TBSO
Me
H
O
H
H
O
Me
H
H
Me
Me
Me
212.08
193.61
157.40
142.36
131.27
128.22
128.06
127.90
125.37
77.85
56.25
52.22
51.99
50.07
45.61
44.30
43.74
36.19
31.82
30.58
27.15
25.97
25.96
25.79
24.91
23.14
19.76
18.18
17.82
-2.39
-2.49
30
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-2
f1 (ppm)


TBSO
HO
H
OH
Me
H
Me
H
H
Me
Me
Me
9.5
9.0
8.5
8.0
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
0.0
-0
f1 (ppm)

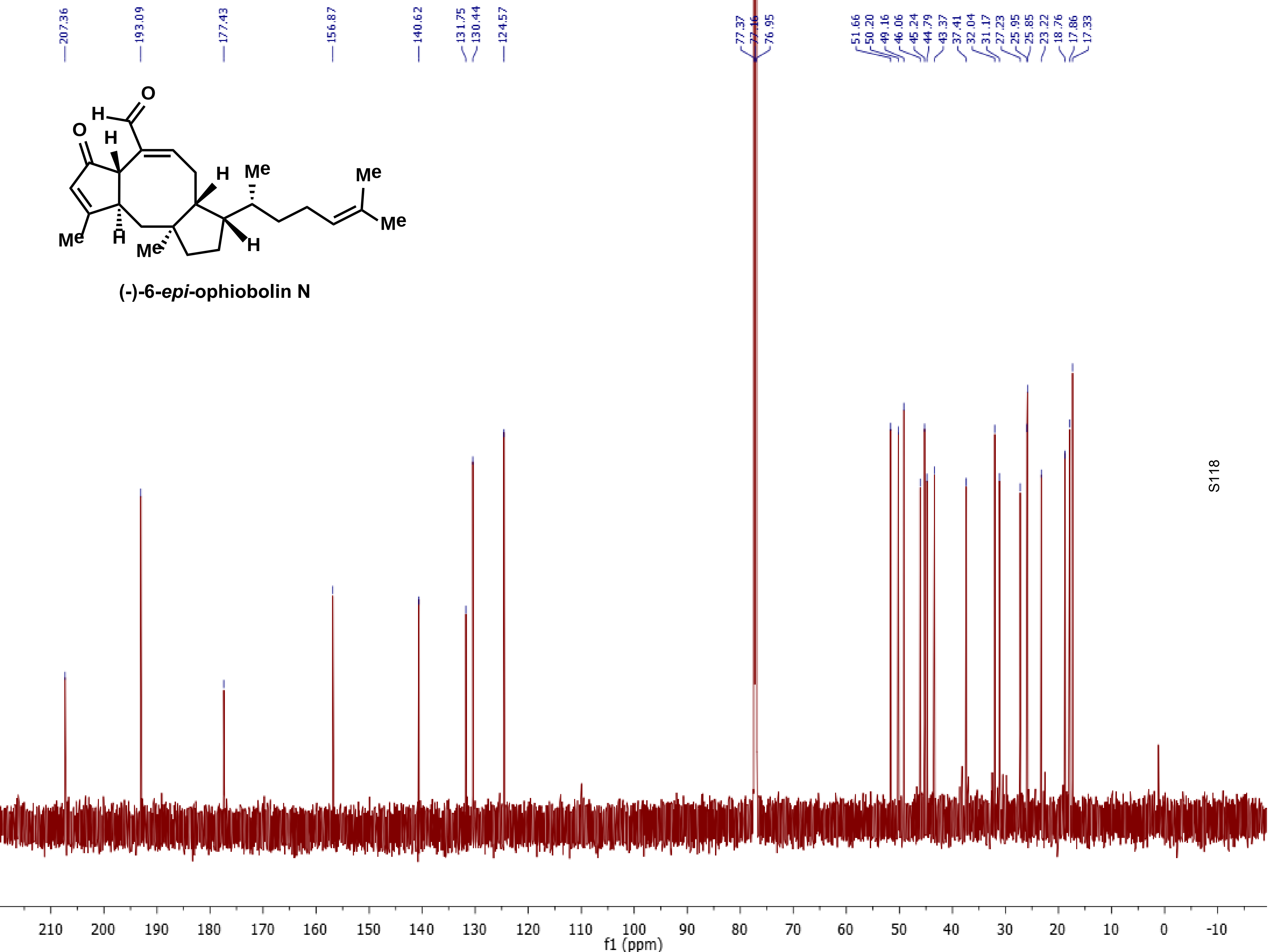

TBSO
HO
Me
H
H
OH
Me
H
H
Me
Me
Me
136.61
135.75
131.14
128.22
128.06
127.90
125.44
83.28
71.74
70.16
52.84
52.41
49.48
47.48
47.48
44.68
43.85
43.47
37.98
33.00
26.69
26.27
25.91
25.36
24.33
24.07
20.94
18.30
17.78
17.25
-1.85
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

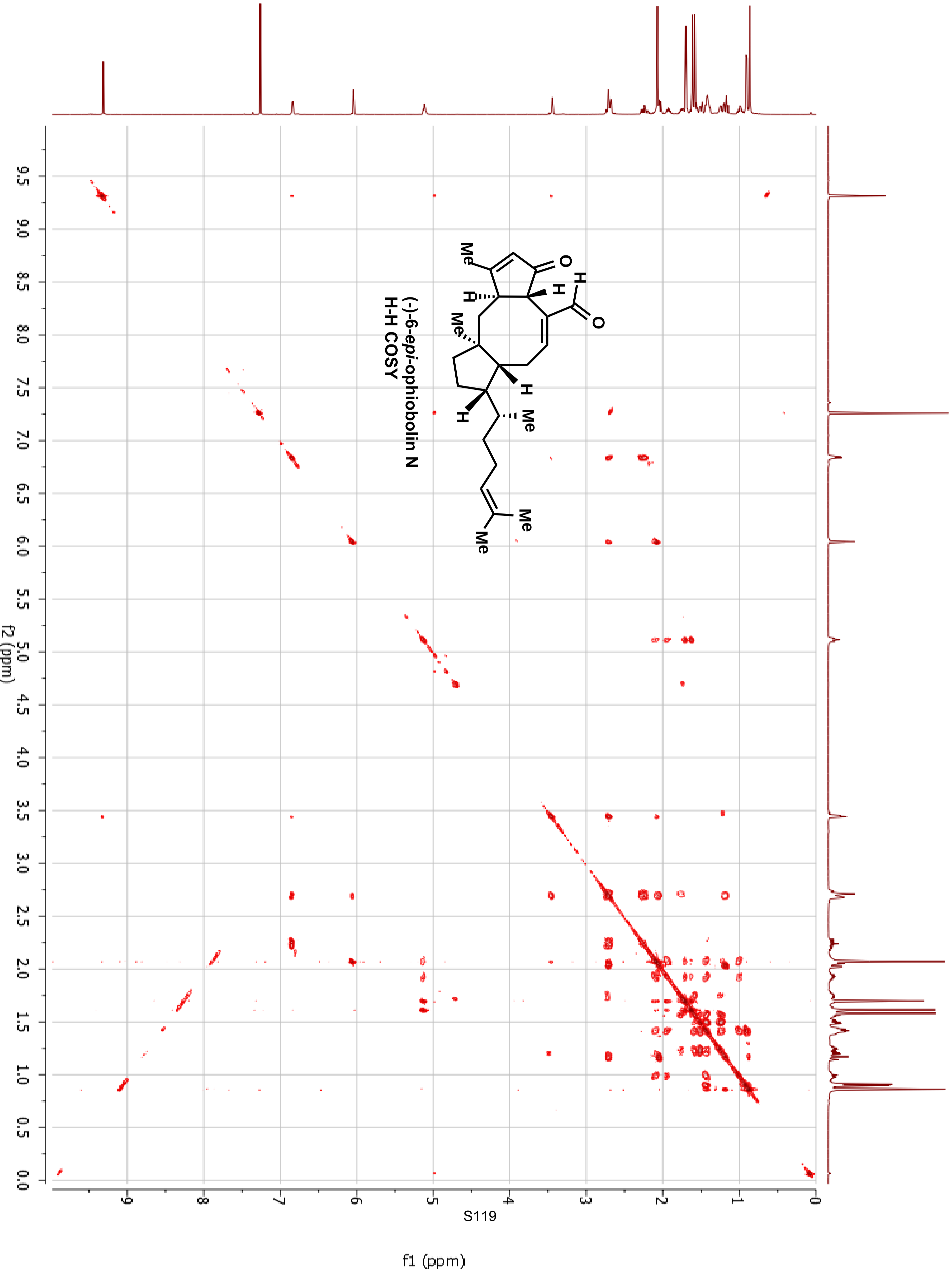

TBSO
HO
Me
H
H
OH
Me
H
H
Me
Me
Me
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

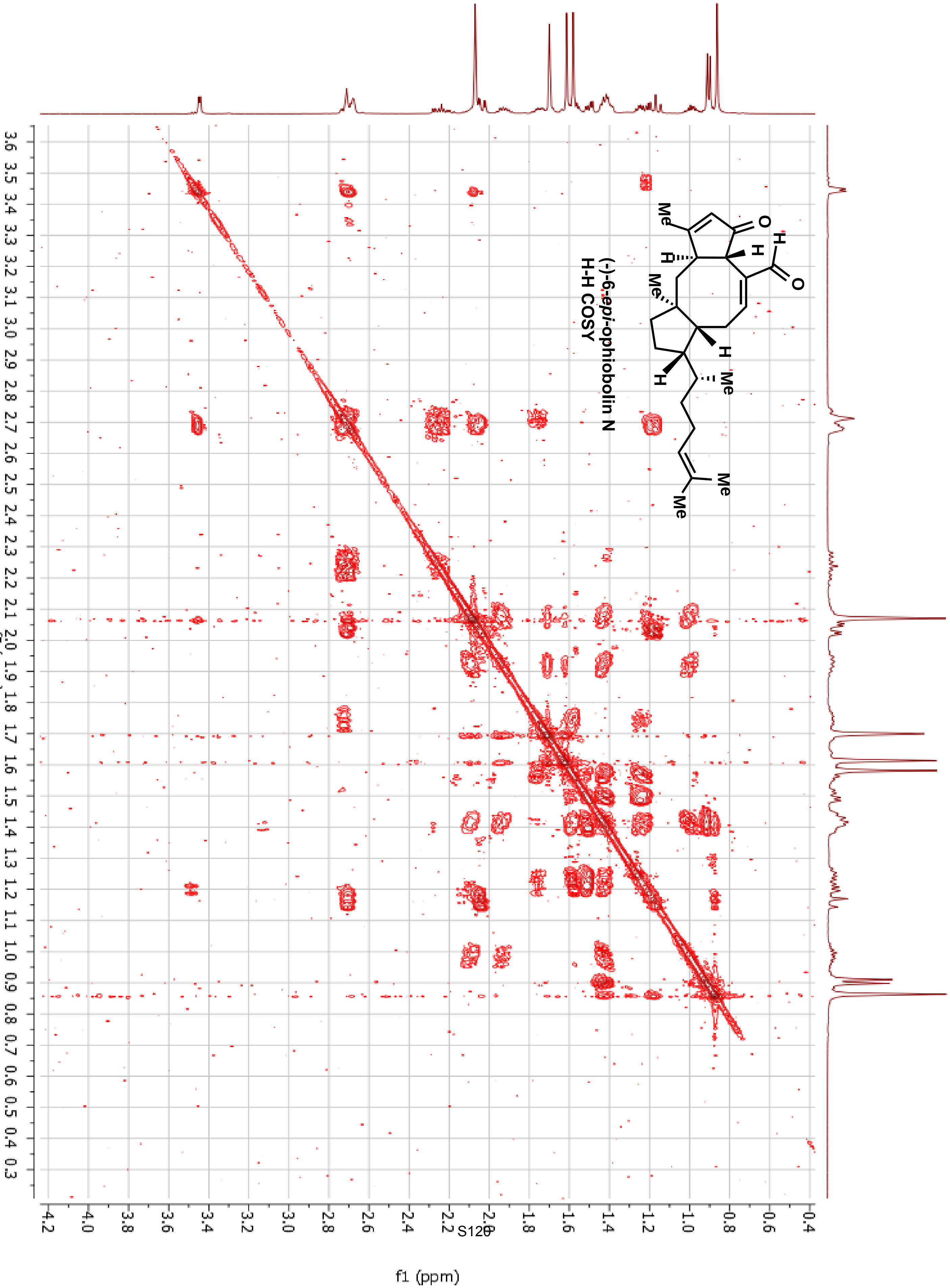

TBSO
HO
Me
H
H
OH
Me
H
H
Me
Me
Me
136.80
135.41
131.12
128.22
128.06
127.90
127.61
125.54
83.84
72.32
70.02
52.46
51.15
49.89
49.43
48.32
45.24
43.93
43.88
34.52
32.81
26.35
26.28
26.23
25.93
24.85
24.47
21.32
20.00
18.26
17.81
-1.84
-1.88
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



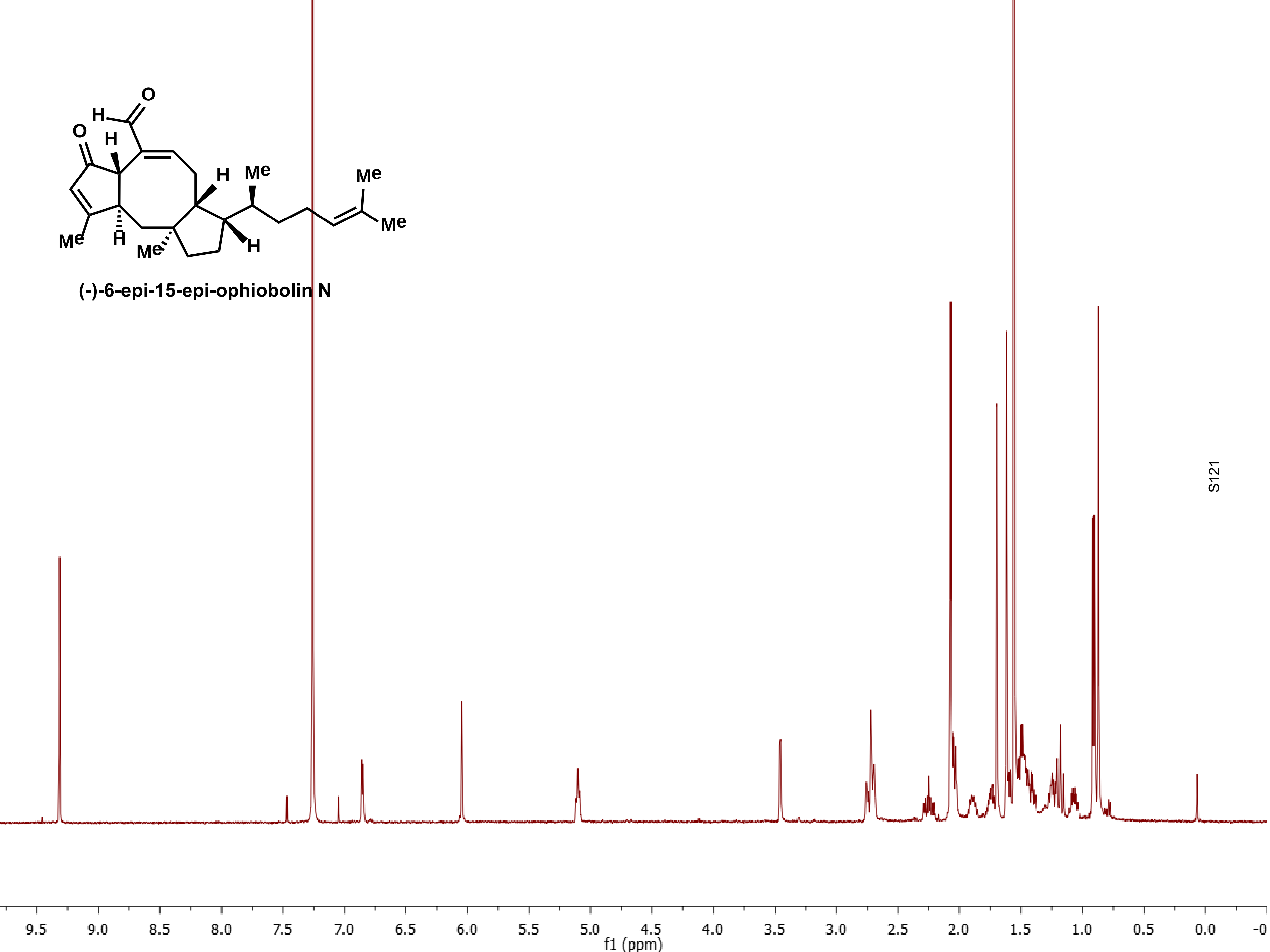
(-)-6-*epi*-ophiobolin N


(-)-6-*epi*-ophiobolin N

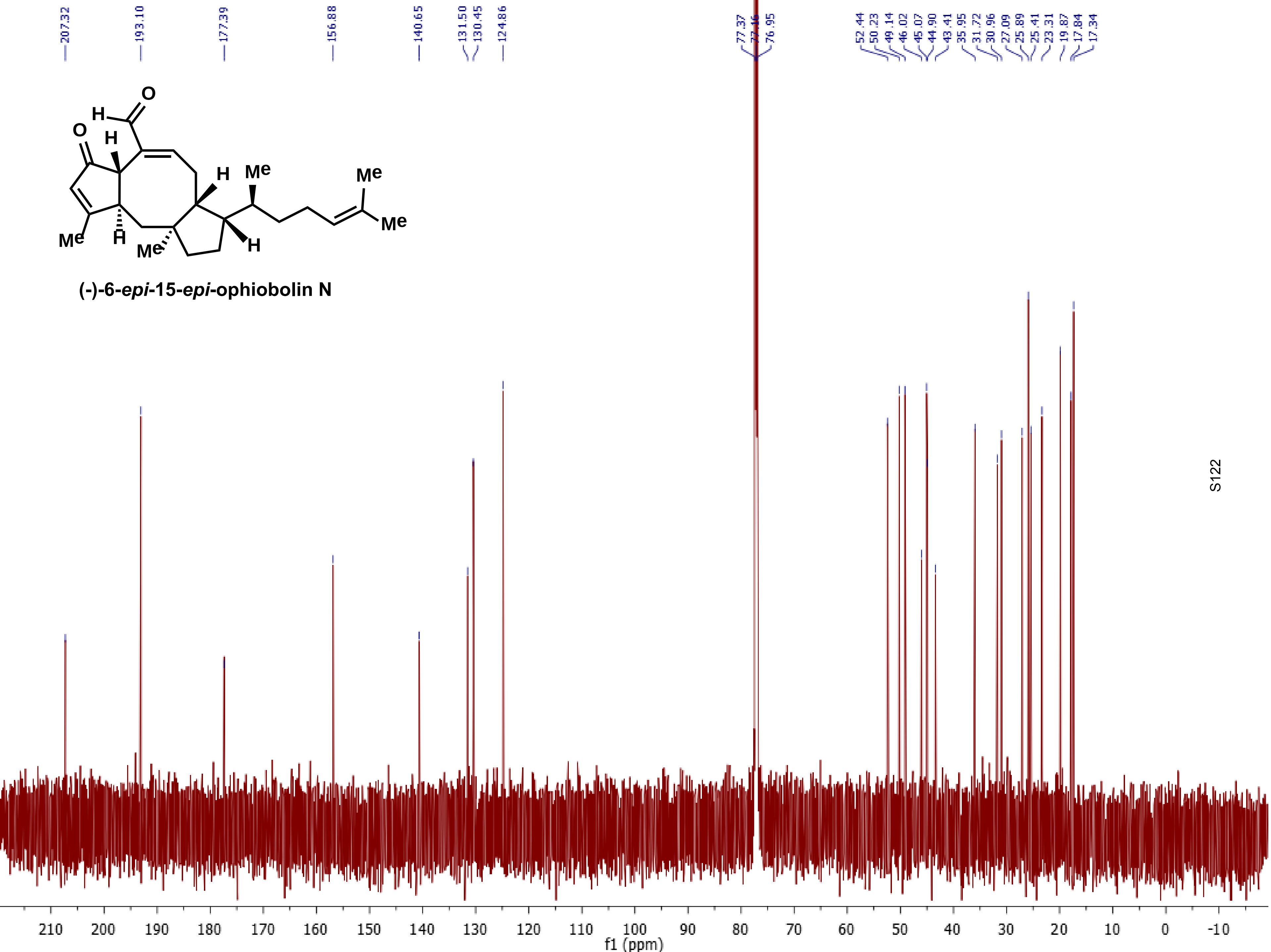

(-)-6-*epi*-ophiobolin N
H-H COSY
Me
O
H
H
O
H
Me
H
H
Me
Me
Me
f2 (ppm)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
9
8
7
6
5
4
3
2
1
0
f1 (ppm)



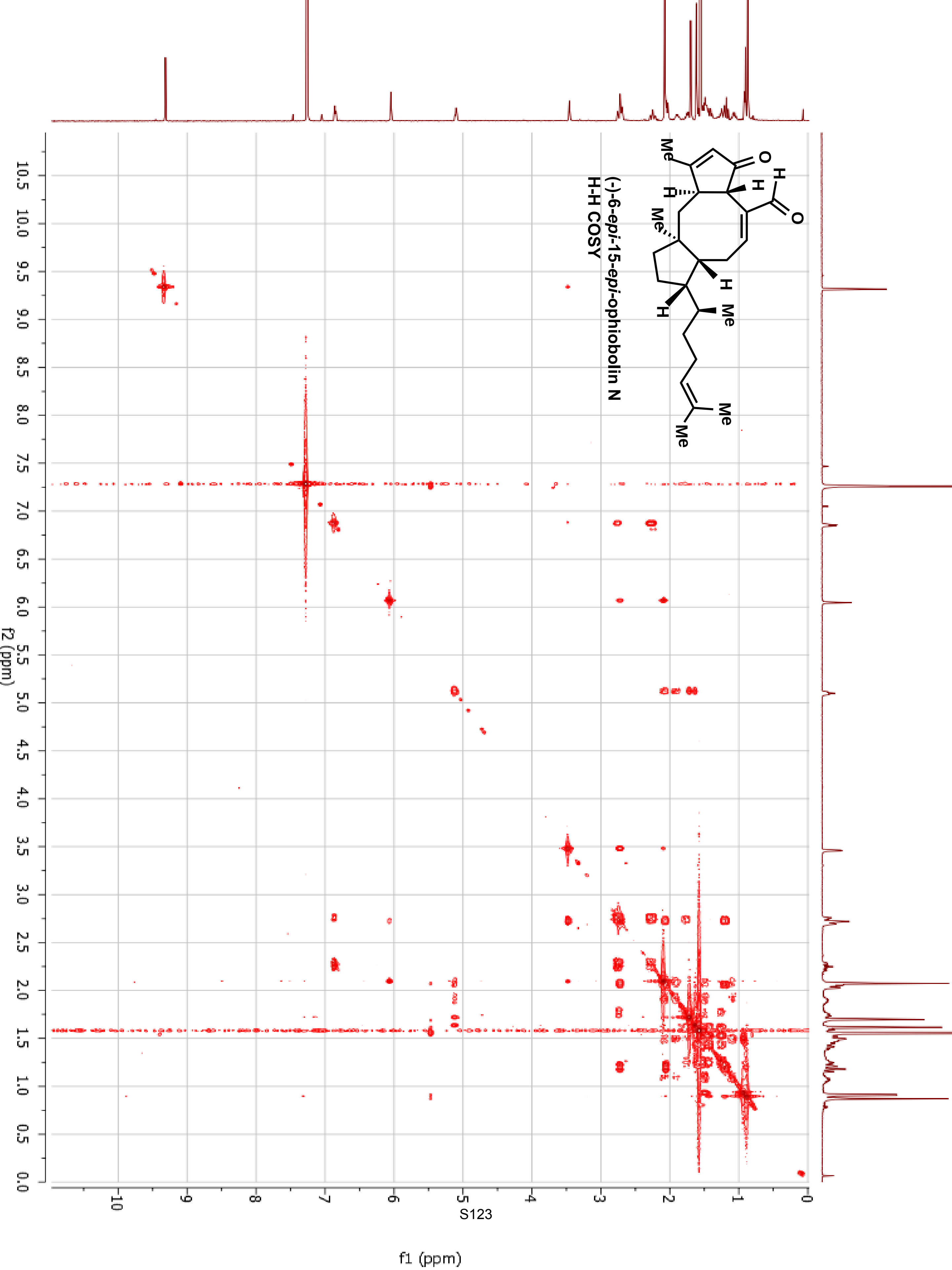
(-)-6-*epi*-ophiobolin N
H-H COSY



(-)-6-epi-15-epi-ophiobolin N



(-)-6-*epi*-15-*epi*-ophiobolin N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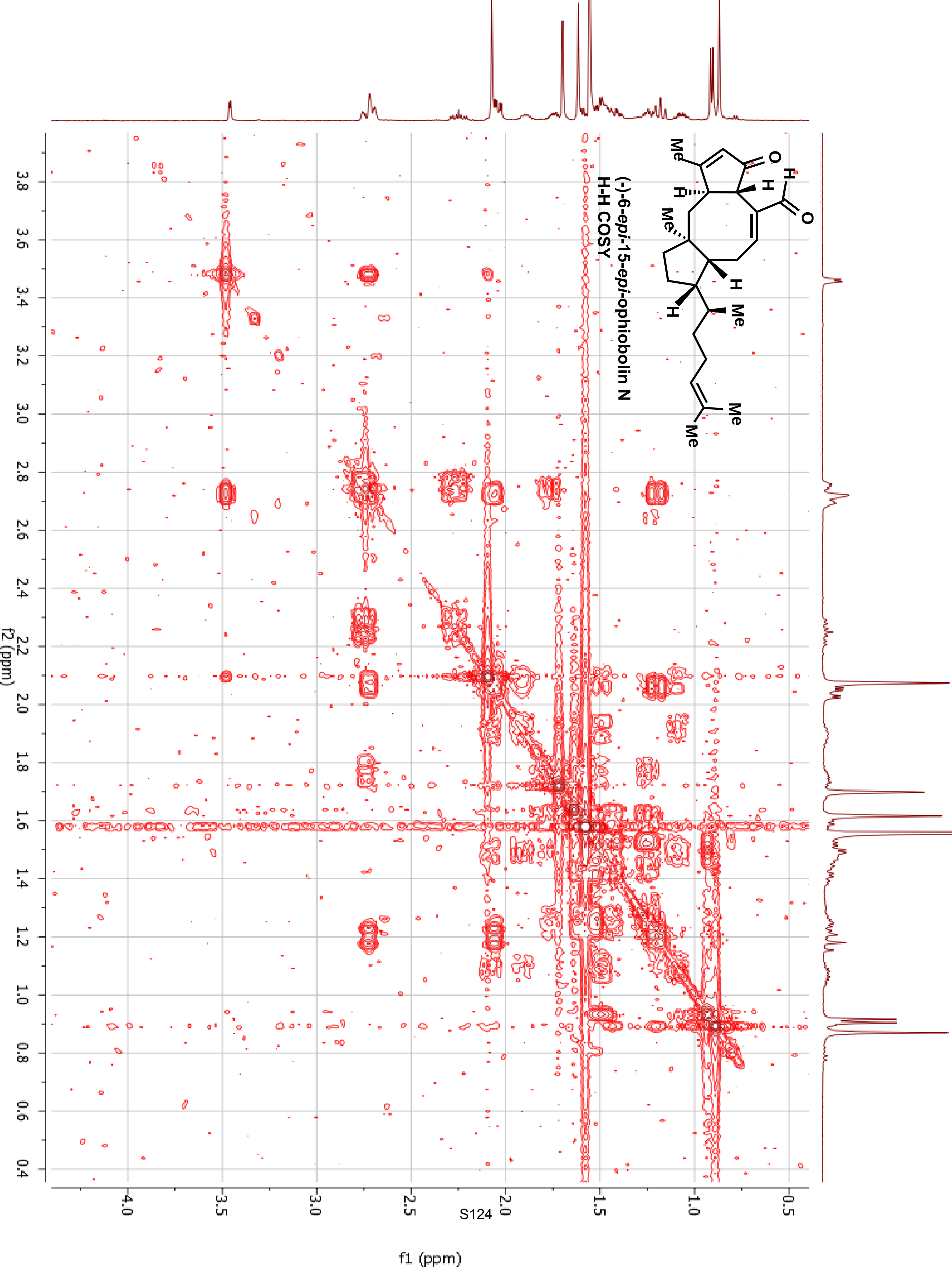
H-H COSY



(-)-6-*epi*-15-*epi*-ophiobolin N
H-H COSY

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