Allylative Approaches to the Synthesis of Complex Guaianolide Sesquiterpenes from *Apiaceae* and *Asteraceae*

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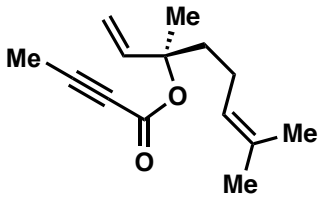
General Procedures:

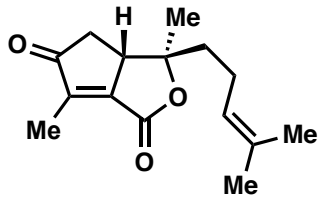
Unless otherwise stated, all reactions were performed in oven-dried or flame-dried glass round-bottom flask with a rubber septum, or Fisherbrand® borosilicate glass reaction tubes with a black phenolic screw cap, under an atmosphere of dry nitrogen or argon. Dry tetrahydrofuran (THF), dichloromethane (DCM), diethyl ether, *N,N*-dimethylformamide (DMF), toluene, and acetonitrile were obtained by passing these previously degassed solvents through activated alumina columns. Anhydrous *N*-methylformamide (NMF) and acetone were purchased from Fisher Chemical and used directly without further purification. Amine and alcohol reagents and solvents were distilled from calcium hydride prior to use. L-Carvone, R-carvone, L-linalool, and 2,2-dimethoxyacetaldehyde (60% in H_2O) were purchased from Sigma-Aldrich and used directly without further purification. Methyl acrylate, 2-butynoic acid, and 3,3-dimethylacrylic acid were purchased from Fisher Chemical and used directly without further purification. Reactions were monitored by thin layer chromatography (TLC) on TLC silica gel 60 F_{254} glass plates (EMD Millipore) and visualized by UV irradiation and staining with *p*-anisaldehyde, phosphomolybdic acid, or potassium permanganate. Volatile solvents were removed under reduced pressure using a rotary evaporator. Flash column chromatography was performed using Silicycle F60 silica gel (60Å, 230-400 mesh, 40-63 μm). Ethyl acetate and hexanes were purchased from Fisher Chemical and used for chromatography without further purification. Proton nuclear magnetic resonance (^{1}H NMR) and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on Bruker spectrometers operating at 400, 500, 600, 700, and 900 MHz for ^{1}H NMR and 100, 125, 150, 175, and 225 MHz for ^{13}C NMR. For the 900 MHz ^{13}C spectra of **23**, 32 points were back linear predicted, prior to zero filling, apodization, and Fourier transformation. Chemical shifts are reported in parts per million (ppm) with respect to the residual solvent signal $CDCl_3$ (^{1}H NMR: $\delta = 7.26$; ^{13}C NMR: $\delta = 77.16$), CD_2Cl_2 (^{1}H NMR: $\delta = 5.32$; ^{13}C NMR: $\delta = 53.84$), DMSO-d_6 (^{1}H NMR: $\delta = 2.50$; ^{13}C NMR: $\delta = 39.52$), C_6D_6 (^{1}H NMR: $\delta = 7.16$;^{13}C NMR: $\delta = 128.06$), and CD_3OD (^{1}H NMR: $\delta = 3.31$; ^{13}C NMR: $\delta = 49.00$). Peak multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, dd = doublet of doublets, td = triplet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, ddt = doublet of doublet of triplets, ddq = doublet of doublet of quartets, dddd = doublet of doublet of doublet of doublets, m = multiplet, br = broad, app = apparent. Melting points were determined using MEl-TEMP™ apparatus and are uncorrected. IR spectra were recorded on a Nicolet 380 FT-IR spectrometer. High-resolution mass spectra (HRMS) were obtained by the QB3/chemistry mass spectrometry facility at the University of California, Berkeley using a Thermo LTQ-FT mass spectrometer; and at the Lawrence–Berkeley National Laboratory Catalysis Center using a Perkin Elmer AxION 2 TOF mass spectrometer. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. X-ray crystallographic analyses were performed at the UC-Berkeley College of Chemistry X-ray crystallography facility (MicroSTAR-H APEX II, ChexSTAR: RUA #1091).



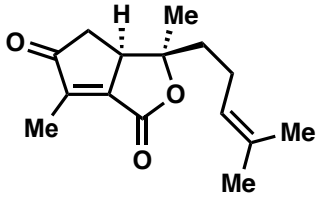
Alkyne 32: A 250 mL round-bottom flask was charged with a stir bar, 2-butynoic acid (1.80 g, 21.4 mmol, 3 equiv), and THF (72 mL). The mixture was cooled to 0 °C, and NaH (856 mg, 60% w/w, 3 equiv, washed with hexane) was added in three portions. The resulting mixture was stirred at 0 °C for 15 minutes, and then freshly distilled pivaloyl chloride (2.18 mL, 17.7 mmol, 2.5 equiv) was slowly added. The mixture was stirred for 1 hour at 0 °C, 15 minutes at room temperature, and then re-cooled to –45 ºC. In a separate 100 mL round-bottom flask, L-linalool (1.42 mL, 7.90 mmol, 1 equiv) was dissolved in THF (20 mL) and NaHMDS (15.8 mL, 2 equiv, 1 M) added in one portion. The mixture was stirred at room temperature for 1 hour, and then slowly added to the 250 mL flask containing the mixed anhydride via a syringe pump over 3 hours at –45 ºC. The reaction mixture was gradually warmed to room temperature, and stirred for 8 hours. After full consumption of the starting material as judged by TLC (EtOAc/hexane, 1:10), the reaction mixture was diluted with EtOAc (100 mL) and quenched by addition of *sat.* $NaHCO_3$ (100 mL). The aqueous phase was extracted by Et_2O (100 mL × 2) and the combined organic phase was washed with washed with brine (200 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude mixture was purified by column chromatography (Et_2O/hexanes, 1:100 to 1:20), affording ester **32** (1.13 g, 65%) as a colorless oil: $[\alpha]_D^{20} = -20.3°$ (c 0.007 g/mL, $CHCl_3$); ^{1}H NMR (700 MHz, $CDCl_3$) δ 5.98 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.20 (dd, *J* = 17.5, 0.8 Hz, 1H), 5.16 (dd, *J* = 11.0, 0.8 Hz, 1H), 5.11 – 5.05 (m, 1H), 2.03 – 1.96 (m, 2H), 1.96 (s, 3H), 1.91 – 1.84 (m, 1H), 1.85 – 1.78 (m, 1H), 1.67 (d, *J* = 1.3 Hz, 3H), 1.59 (brs, 3H), 1.57 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.5, 141.0, 132.2, 123.7, 114.1, 85.5, 83.5, 73.6, 39.7, 25.8, 23.7, 22.5, 17.8, 3.9; IR (thin film, cm^{-1}) 2969, 2924, 2856, 2242, 1700, 1449, 1376; HRMS (ESI) *calcd.* for $[C_{14}H_{20}O_2Na]^+$ $(M+Na)^+$: m/z 243.1361, found 243.1364. [Note: This compound is not stable in chloroform at room temperature.]

Lactone 33 and *epi*-33: A 250 mL round-bottom flask was charged with a stir bar, ester **32** (0.67 g, 3.0 mmol, 1 equiv), $Co_2(CO)_8$ (1.15 g, 3.36 mmol, 1.1 equiv) and DCM (120 mL). The resulting solution was stirred at room temperature for 1 hour and then cooled to 0 ºC. 4-Methylmorpholine *N*-oxide (3.35 g, 28.6 mmol, 9.5 equiv) was added in 5 portions over 1 hour at 0 ºC. After complete consumption of the starting material as judged by TLC (EtOAc/hexane, 1:10), the reaction was quenched by addition of saturated *aq.* $Na_2S_2O_3$ (100 mL). The aqueous phase was extracted with DCM (100 mL × 2) and the combined organic phases were washed with saturated *aq*. $Na_2S_2O_3$ (100 mL) and brine (100 mL), dried over Na_2SO_4, and concentrated *in vacuo* to a *ca.* 40 mL solution. The solution was filtered through a short silica gel column and washed with Et_2O. The filtrate was concentrated *in vacuo* and purified by

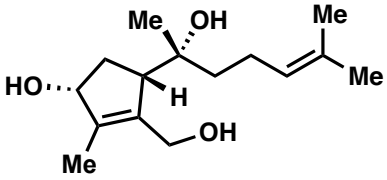
column chromatography (EtOAc/hexane, 1:10 to 1:5), affording enones **33** and ***epi*-33** (0.56 g, 65%, 5:2 *dr*) as white foams.



Compound 33 (major): $[\alpha]_D^{20}$ = +153.3° (c 0.010 g/mL, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 5.00 (app. tt, *J* = 7.1, 1.6 Hz, 1H), 3.33 (ddq, *J* = 6.5, 3.5, 3.1 Hz, 1H), 2.72 (dd, *J* = 18.3, 6.5 Hz, 1H), 2.37 (dd, *J* = 18.3, 3.5 Hz, 1H), 2.16 – 2.04 (m, 2H), 2.02 (d, *J* = 3.1 Hz, 3H), 1.65 (d, *J* = 1.5 Hz, 3H), 1.58 (s, 3H), 1.57 (s, 3H), 1.41 (ddd, *J* = 14.0, 10.8, 5.9 Hz, 1H), 1.38 – 1.32 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 208.2, 165.4, 157.5, 143.7, 133.1, 122.8, 88.5, 51.2, 38.6, 35.6, 25.7, 25.5, 21.8, 17.8, 9.0; IR (thin film, cm^{-1}) 2977, 2932, 2860, 1750, 1722, 1681, 1456, 1438; HRMS (ESI) *calcd.* for $[C_{15}H_{20}O_3Na]^+$ $(M+Na)^+$: m/z 271.1310, found 271.1312.

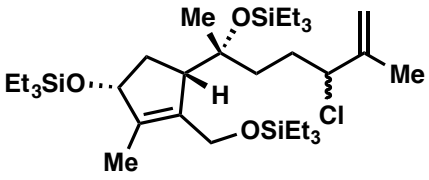


Compound *epi*-33 (minor): $[\alpha]_D^{20}$ = –41.9° (c 0.010 g/mL, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 5.07 (app. t, *J* = 7.2 Hz, 1H), 3.32 (dt, *J* = 6.5, 3.3 Hz, 1H), 2.69 (dd, *J* = 18.4, 6.5 Hz, 1H), 2.28 (dd, *J* = 18.4, 3.4 Hz, 1H), 2.15 – 2.04 (m, 2H), 2.02 (d, *J* = 3.0 Hz, 3H), 1.94 – 1.79 (m, 2H), 1.68 (s, 3H), 1.60 (s, 3H), 1.18 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 208.2, 165.2, 157.5, 143.9, 133.0, 122.7, 89.5, 48.9, 41.1, 39.2, 25.8, 22.7, 20.0, 17.8, 8.9; IR (thin film, cm^{-1}) 2972, 2927, 2859, 1764, 1722, 1682, 1439, 1408; HRMS (ESI) *calcd.* for $[C_{15}H_{20}O_3Na]^+$ $(M+Na)^+$: m/z 271.1310, found 271.1305.

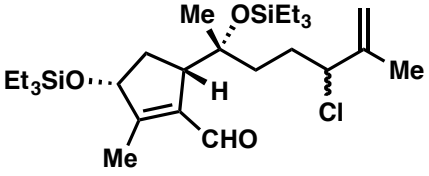


Triol 34: A 25 mL round-bottom flask was charged with a stir bar, enone **33** (112 mg, 0.451 mmol, 1 equiv), and DCM (5 mL). The resulting mixture was cooled to –78 ºC and DIBAL (1.2 mL, 1.5 M in toluene, 4 equiv) was slowly added over 1 hour via syringe pump. The reaction mixture was warmed to room temperature and stirred for an additional 16 hours. The reaction was quenched by the addition of *aq.* Rochelle's salt solution (15 mL, 10% w/w). The biphasic mixture was rapidly stirred at room temperature for 30 minutes, and was then extracted with DCM (20 mL × 3). The organic phase was washed with *sat.* $NaHCO_3$ (30 mL), H_2O (30 mL), brine (30 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude mixture was purified by column chromatography (EtOAc/hexane, 1:1), affording triol **34** (93 mg, 81%) as a white foam: $[\alpha]_D^{20}$ = +28.5º (c 0.010 g/ml CH_2Cl_2); ^1H NMR (600 MHz, CD_3OD) δ 5.13 (app. tt, *J* = 7.3, 1.6 Hz, 1H), 4.38 (dd, *J* = 7.9, 5.2 Hz, 1H), 4.31 (d, *J* = 12.7 Hz, 1H), 4.10 (d, *J* = 12.7 Hz, 1H), 2.80 – 2.73 (m, 1H), 2.34 (dt, *J* =

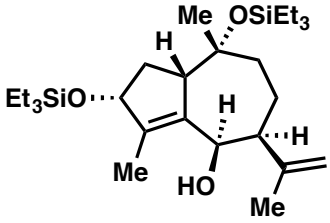
13.7, 8.3 Hz, 1H), 2.14 (tt, *J* = 12.5, 5.7 Hz, 1H), 2.01 (tt, *J* = 13.0, 6.2 Hz, 1H), 1.73 (brs, 3H), 1.66 (s, 3H), 1.61 (s, 3H), 1.51 (ddd, *J* = 14.0, 11.9, 5.3 Hz, 1H), 1.43 (ddd, *J* = 14.1, 12.0, 4.9 Hz, 1H), 1.37 (ddd, *J* = 13.7, 6.5, 5.0 Hz, 1H), 1.19 (s, 3H); ^{13}C NMR (150 MHz, CD_3OD) δ 141.5, 138.7, 131.9, 126.1, 79.0, 75.1, 59.4, 57.8, 37.7, 36.5, 26.0, 25.9, 23.2, 17.6, 11.6; IR (thin film, cm^{-1}) 3296, 2968, 2916, 2859, 1692, 1650, 1439, 1377; HRMS (ESI) *calcd.* for $[C_{15}H_{26}O_3Na]^+$ $(M+Na)^+$: m/z 277.1780, found 277.1770.



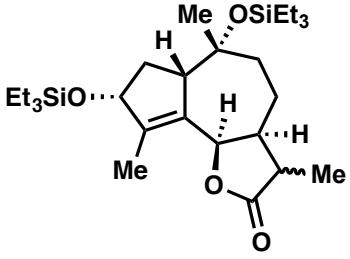
Allylic Chloride 36: A reaction tube was charged with a stir bar, triol **34** (23 mg, 0.09 mmol, 1 equiv), and DCM (2 mL). The mixture was cooled to –78 ºC and 2,4,6-Collidine (0.13 mL, 0.99 mmol, 10 equiv) and TESOTf (0.1 mL, 0.44 mmol, 5 equiv) were added dropwise and sequentially to the reaction mixture. The reaction mixture was gradually warmed to room temperature and stirred until starting material was consumed as judged by TLC (EtOAc/hexane, 1:5). The reaction mixture was then re-cooled to –78 ºC, and SO_2Cl_2 (9 μL, 1.2 equiv) was added in one portion. The resulting mixture was then gradually warmed to room temperature, and after the chlorination was deemed complete as judged by TLC (EtOAc/hexane, 1:10), the reaction was quenched by the addition of saturated *aq.* $Na_2S_2O_3$ solution (5 mL) and saturated *aq.* $NaHCO_3$ solution (5 mL). The aqueous phase was extracted by EtOAc (15 mL × 2) and the combined organic phase was washed with washed with H_2O (20 mL) and brine (20 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude mixture was purified by flash column chromatography (Et_2O/hexane, 1:100 to 1:20), affording allylic chloride **36** (42 mg, 74%) as a mixture of two diastereomers. Both diastereomers were subjected to the next step without further purification.



Aldehyde 37: A 25 mL round-bottom flask was charged with a stir bar, allylic chloride **36** (431 mg, 0.682 mmol, 1 equiv), and DCM (6.8 mL). The mixture was cooled to 0 ºC over an ice bath, and CrO_3•2py (530 mg, 2.05 mmol, 3 equiv) was added in one portion. The reaction mixture was stirred in a cold room (0 – 4 ºC) until the consumption of the starting material was near completion as judged by TLC (EtOAc/hexane, 1:10). The mixture was then filtered through a short column of silica gel (washed with Et_3N/DCM, 1:10). The filtrate was concentrated *in vacuo*, and The crude mixture was purified by column chromatography (EtOAc/hexane, 1:20), affording recovered **36** (42 mg, 10%), as well as aldehyde **37** (186 mg, 54%) as a mixture of two diastereomers. Both diastereomers were subjected to the next step without further purification.



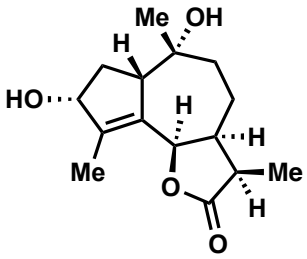
Bicycle 38: A 50 mL round-bottom flask was charged with a stir bar, anhydrous $CrCl_2$ (222 mg, 1.81mmol, 5 equiv), anhydrous $NiCl_2$ (4 mg, 0.03 mmol, 0.1 equiv), and dry DMF (12 mL). The resulting mixture was heated at 60 ºC, while a solution of aldehyde **37** (186 mg, 0.361 mmol, 1 equiv) in DMF (6 mL) was slowly added over 30 minutes via syringe pump. After the addition was complete, the reaction mixture was further stirred at 60 ºC for 1 hour. After the starting material was consumed as judged by TLC (EtOAc/hexane, 1:5), the reaction mixture was cooled to room temperature, and quenched by addition of Et_2O (20 mL) and *aq.* $(NH_2CH_2)_2$ (10 mL, 10% w/w). The mixture was stirred at room temperature for 10 minutes, and was then extracted with Et_2O (30 mL × 3). The organic phase was washed with H_2O (50 mL × 2) and brine (50 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude mixture was purified by column chromatography (EtOAc/hexane, 1:10 to 1:5) to give bicycle **38** (98 mg, 57%, 9:1 *dr*) as a colorless oil: $[\alpha]_D^{20} = -51^o$ (c 0.0001 g/ml $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.86 – 4.80 (m, 2H), 4.70 (s, 1H), 4.42 (app. t, J = 7.4 Hz, 1H), 2.66 – 2.58 (m, 1H), 2.49 (dd, J = 11.1, 5.6 Hz, 1H), 2.22 (app. dt, J = 12.3, 7.4 Hz, 1H), 1.90 – 1.76 (m, 6H), 1.69 – 1.62 (m, 5H), 1.33 (s, 3H), 1.00 – 0.90 (m, 18H), 0.65 – 0.55 (m, 12H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.6, 139.5, 138.8, 110.0, 77.8, 76.6, 70.1, 54.9, 48.5, 39.5, 36.7, 30.6, 24.5, 22.8, 11.6, 7.4, 7.1, 7.0, 5.1. IR (thin film, cm^{-1}) 2954, 2911, 2876, 1728,1709, 1669, 1457, 1413, 1376, 1264; HRMS (ESI) calcd. for $[C_{27}H_{53}O_3Si_2]^+$ $(M+H)^+$: m/z 481.3528, found 481.3526.



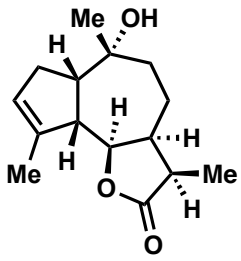
Lactone 39: *i.* A reaction tube was charged with a stir bar, bicycle **38** (9.0 mg, 0.019 mmol, 1 equiv), and THF (0.2 mL). The mixture was cooled to 0 ºC and BH_3•THF (34 μL, 1 M in THF, 1.8 equiv) was added in one portion. The reaction mixture was stirred in a cold room (0 – 4 ºC) for *ca.* 16 hours. After the consumption of the starting material was complete as judged by TLC (EtOAc/hexane, 1:8), *aq.* NaOH (25 μL) and *aq.* H_2O_2 (4 μL, 30% w/w) were added sequentially to the reaction. The reaction mixture was stirred at room temperature until the consumption of the borane adducts was complete as judged by TLC (EtOAc/hexane, 1:8), and was then diluted with saturated *aq.* $Na_2S_2O_3$ (5 mL) and EtOAc (5 mL). The resulting mixture was extracted with EtOAc (10 mL × 3), and the combined organic phases were washed with brine (30 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude mixture was purified by column chromatography (EtOAc/hexane, 1:5 to 1:1), affording the corresponding primary alcohol (7.5

mg, 80%) as a mixture of two diastereomers (5:4 *dr*). Both diastereomers were subjected to the next step without further purification.

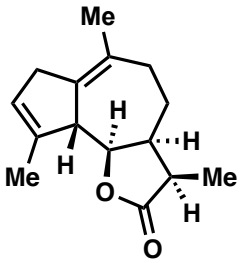
ii. The aforementioned primary alcohol (7.5 mg, 0.015 mmol, 1 equiv) was dissolved in DCM (0.1 mL) and a solution of TEMPO (2.3 mg, 0.015 mmol, 1 equiv) and PIDA (48 mg, 0.15 mmol, 10 equiv) in DCM (0.1 mL) was added to the reaction in one portion. The resulting mixture was stirred at room temperature for 8 hours. After complete consumption of the starting material, as judged by TLC (EtOAc/hexane, 1:4), the reaction was quenched by addition of saturated *aq*. $Na_2S_2O_3$ (5 mL), and diluted with EtOAc (5 mL). The resulting mixture was extracted with EtOAc (10 mL × 3), and the combined organic phases were washed with brine (30 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude mixture was purified by column chromatography (EtOAc/hexane, 1:5 to 1:1), affording lactone **39** (5.8 mg, 78%) as a mixture of two diastereomers (5:4 *dr*). Both diastereomers were subjected to the next step without further purification.



Diol 40: A reaction tube was charged with a stir bar, lactone **39** (8.0 mg, 0.016 mmol, 1 equiv) as a mixture of two diastereomers (5:4 *dr*), and dry THF (0.3 mL). The mixture was cooled to – 78 ºC and a solution of freshly prepared lithium diisopropylamide (64 μL, 0.5 M in THF) was added dropwise. The reaction mixture was stirred at –78 ºC for 30 minutes and was allowed to warm to –40 ºC over 1 hour. The reaction mixture was then cooled back to –78 ºC, followed by the addition of acetic acid (5 μL, 5 equiv) and TBAF (0.1 mL, 1M in THF, 6 equiv). The mixture was further stirred at room temperature for 8 hours until the consumption of the silyl ether intermediates was complete as judged by TLC (EtOAc/hexane, 1:1). The reaction was then quenched by addition of *sat.* NH_4Cl (5 mL). The resulting mixture was extracted with EtOAc (10 mL × 3), and the combined organic phase was washed with brine (30 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude mixture was purified by column chromatography (EtOAc/hexane, 1:5 to 1:1), affording diol **40** (4.2 mg, 98%) as a white solid: $[\alpha]_D^{20}$ = +17.4º (c 0.0016 g/ml $CHCl_3$); ^{1}H NMR (700 MHz, $CDCl_3$) δ 5.36 (d, *J* = 6.6 Hz, 1H), 4.30 (d, *J* = 6.9 Hz, 1H), 2.92 – 2.85 (m, 2H), 2.69 (dddd, *J* = 9.0, 5.7, 5.7, 3.2 Hz, 1H), 2.15 (ddd, *J* = 15.0, 8.6, 6.9 Hz, 1H), 1.92 (ddd, *J* = 16.1, 10.8, 5.5 Hz, 1H), 1.88 (d, *J* = 14.2 Hz, 1H), 1.80 (s, 3H), 1.56 (dd, *J* = 15.0, 8.7 Hz, 1H), 1.50 (dd, *J* = 15.0, 10.8 Hz, 1H), 1.45 (ddd, *J* = 15.7, 8.9, 3.2 Hz, 1H), 1.27 (s, 3H), 1.22 (d, *J* = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.0, 142.9, 134.4, 79.4, 79.2, 71.4, 52.2, 41.6, 38.2, 37.2, 34.9, 31.4, 19.1, 12.1, 10.3; IR (thin film, cm^{-1}) 3352, 3273, 2966, 2929, 2873, 2858, 1766, 1559, 1457, 1379; HRMS (ESI) *calcd.* for $[C_{15}H_{22}O_4Na]^+$ $(M+Na)^+$: m/z 289.1416, found 289.1437.



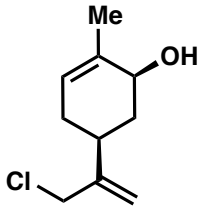
Alkene 41: A reaction tube was charged with a stir bar, diol **40** (2.0 mg, 7.5 μmol, 1 equiv), PPh_3 (6.0 mg, 23 μmol, 3 equiv), and *N*-isopropylidene-*N'*-2-nitrobenzenesulfonyl hydrazine (IPNBSH) (5.8 mg, 23 μmol, 3 equiv). The mixture was azeotropically dried with toluene (2 mL × 3), and then dissolved in dry THF (0.15 mL). The reaction mixture was then cooled to 0 ºC and a solution of diisopropyl azodicarboxylate (DIAD) (4.5 μL, 3 equiv) in THF (50 μL) was added dropwise. The resulting mixture was stirred at 0 ºC for 1 hour, and then at room temperature for an additional 4 hours. After the starting material was consumed, as judged by TLC (EtOAc/hexane, 1:1), the reaction was cooled to 4 ºC (cold room) and a solution of TFE in H_2O (0.2 mL, 1:1 ratio) was added. The resulting solution was stirred for 14 hours at the same temperature, then diluted with DCM (2 mL) and filtered through a short column of silica gel (washed with EtOAc). The filtrate was concentrated *in vacuo*, and purified by preparative TLC (EtOAc/hexane, 1:1), affording recovered diol **40**, as well as alkene **41** (1.2 mg, 64%) as a white solid, $[\alpha]_D^{20}$ = –54º (c 0.0005 g/ml $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.46 (dd, *J* = 3.2, 1.6 Hz, 1H), 4.88 (dd, *J* = 10.6, 7.8 Hz, 1H), 3.37 – 3.29 (m, 1H), 2.83 – 2.74 (m, 1H), 2.58 (app. q, *J* = 9.4 Hz, 1H), 2.48 – 2.41 (m, 1H), 2.36 – 2.30 (m, 1H), 1.90 (app. dt, *J* = 13.1, 7.1 Hz, 1H), 1.86 – 1.84 (m, 3H), 1.83 – 1.71 (m, 2H), 1.65 – 1.59 (m, 1H), 1.20 (s, 3H), 1.18 (s, 1H), 1.16 (d, *J* = 7.6 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 180.3, 143.4, 125.3, 85.2, 73.4, 52.1, 50.2, 40.0, 37.7, 37.7, 33.5, 32.5, 21.0, 18.2, 11.7; IR (thin film, cm^{-1}) 3488, 2920, 2852, 1746, 1669, 1594, 1565, 1455, 1378, 1348; HRMS (ESI) *calcd.* for $[C_{15}H_{22}O_3Na]^+$ $(M+Na)^+$: m/z 273.1467, found 1273.1467.



Sinodielide A (12): A flame-dried 6 mL reaction tube was charged with a stir bar and alkene **41** (4.1 mg, 0.016 mmol, 1.0 equiv), which was azeotropically dried with toluene (1.5 mL) three times. The reaction tube was cooled in an acetonitrile–dry ice bath, and a solution of pyridine (13.3 μL, 0.164 mmol, 10.0 equiv) in THF (0.2 mL) was added. After the compound was fully dissolved, a solution of $SOCl_2$ (10 μL, 0.131 mmol, 8 equiv) in THF (0.2 mL) was added. The resulting mixture was slowly warmed to rt over 1.5 hours, and then quenched by addition of saturated *aq.* $NaHCO_3$ (1.5 mL). The mixture was extracted with EtOAc (3 mL × 3), and the combined organic phases were washed with brine (2 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The crude mixture was purified by column chromatography (EtOAc/hexane, 1:3), affording sinodielide (**12**) (3.6 mg, 95%) as a white foam. $[\alpha]_D^{20}$ = –20º (c 0.00011 g/ml $CHCl_3$); ^{1}H NMR (900 MHz, Chloroform-d) δ 5.44 (s, 1H), 4.37

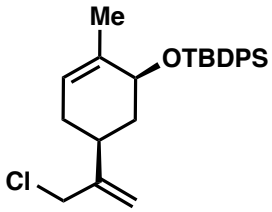
(dd, J = 10.0, 5.9 Hz, 1H), 3.56 (d, J = 10.1 Hz, 1H), 2.95 (d, J = 10.8 Hz, 2H), 2.84 – 2.71 (m, 1H), 2.56 (td, J = 15.0, 13.7, 8.2 Hz, 2H), 2.07 (d, J = 10.6 Hz, 1H), 1.94 – 1.79 (m, 3H), 1.79 (qd, J = 12.8, 5.4 Hz, 1H), 1.56 (s, 4H), 1.19 (d, J = 7.3 Hz, 3H); ^{13}C NMR (226 MHz, Chloroform-d) δ 179.7, 142.3, 131.2, 127.8, 124.4, 86.4, 51.0, 42.4, 38.8, 38.3, 36.6, 21.6, 19.2, 17.0, 10.5; IR (thin film, cm^{-1}) 2918, 2850, 1756, 1458, 1434, 1374, 1351; HRMS (EI) *calcd.* for $[C_{15}H_{20}O_2]^+$ $(M)^+$: m/z 232.1463, found 232.1463.

Chloro-carveol 45: An oven-dried 3 L three-necked flask equipped with a large stir bar was charged with D-carvone (30.0 g, 0.200 mol), sodium carbonate (63.6 g, 0.600 mol), and DCM (1 L). The resulting



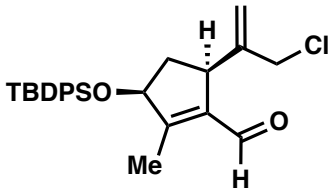
mixture was stirred vigorously at room temperature for 30 minutes, followed by slow addition of SO_2Cl_2 (20.0 mL, 0.247 mol) over 2 hours via a syringe pump. The reaction was monitored by TLC (EtOAc:hexane 1:4) and additional SO_2Cl_2 was added if necessary. After complete consumption of the starting material, methanol (1 L) and $CeCl_3 \cdot 7H_2O$ (82.0 g, 0.220 mol) were added and the resulting mixture was stirred at room temperature for 30 minutes. The reaction was then cooled to 0 °C and $NaBH_4$ (22.8 g, 0.600 mol) was added in 4 portions over 1 hour. After the ketone intermediate was completely consumed as indicated by TLC, the reaction was quenched by addition of 1*N* aqueous HCl (300 mL) and H_2O (500 mL) sequentially. The aqueous layer was extracted with ethyl acetate (700 mL × 3). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The resulting crude material was purified by column chromatography (EtOAc:hexane = 1:10 to 1:5), affording chloro-carveol **45** (29.2 g, 0.156 mol, 78%) as a light yellow oil: $[\alpha]_D^{20} = +37.4°$ (c 0.01 g/mL, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.53 – 5.49 (m, 1H), 5.19 (s, 1H), 5.03 (s, 1H), 4.27 – 4.21 (m, 1H), 4.11 (s, 2H), 2.55 (ddd, *J* = 15.5, 8.0, 3.5 Hz, 1H), 2.24 (ddt, *J* = 12.2, 5.6, 2.3 Hz, 1H), 2.19 (dddd, *J* = 13.9, 6.9, 3.4, 1.6 Hz, 1H), 1.95 (ddq, *J* = 16.6, 10.8, 2.7 Hz, 1H), 1.77 (dd, *J* = 2.8, 1.5 Hz, 3H), 1.53 (td, *J* = 12.2, 9.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.6, 136.4, 123.6, 113.9, 70.9, 47.6, 38.1, 36.9, 31.5, 19.0; IR (thin film, cm^{-1}) 3324, 2969, 2942, 2916, 2884, 2838, 1716, 1642, 1451, 1434, 1407, 1258; HRMS (EI+) *calcd.* for [$C_{10}H_{15}ClO$]: m/z 186.0811, found 186.0810.

[Note: This compound is somewhat volatile and should not be placed under high vacuum for extended periods. On a 1-mmol scale, an 85% yield of product was obtained.]

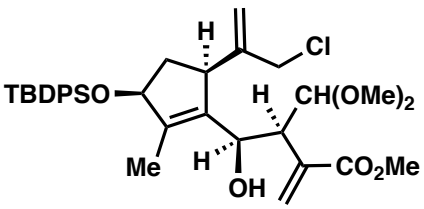


Allylic Chloride 46: An oven-dried 1 L round-bottom flask was charged with a stir bar, chloro-carveol **45** (18.6 g, 0.100 mol), imidazole (20.4 g, 0.300 mol), and 4-dimethylaminopyridine (0.6 g, 0.005 mol). The flask was placed under vacuum and back-filled with N_2, followed by addition of dry DMF (500 mL). The resulting mixture was cooled to 0 °C, and TBDPSCl (32.8 g, 0.120 mol) was added slowly. The reaction was warmed to room temperature and stirred overnight. After the reaction was complete as indicated by TLC, the reaction mixture was poured into a separatory funnel charged with aqueous LiCl (10% w/w, 1 L). The aqueous layer was extracted with diethyl ether (500 mL × 3) and the combined organic phase was washed with H_2O (500 mL × 2), brine (500 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The crude material was purified by flash

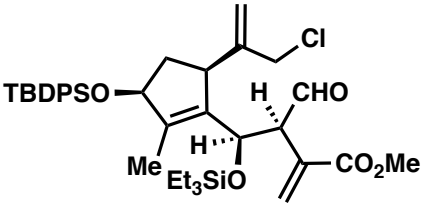
column chromatography (EtOAc:hexane = 1:100 to 1:30), affording allylic chloride **46** (38.5 g, 0.0906 mol, 91%) as a colorless oil: $[\alpha]_D^{20}$ = +58.0° (c 0.01 g/mL, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.75 – 7.69 (m, 4H), 7.45 – 7.40 (m, 2H), 7.40 – 7.35 (m, 4H), 5.43 (dq, *J* = 5.4, 1.7 Hz, 1H), 5.04 (s, 1H), 4.80 (s, 1H), 4.33 (br s, 1H), 3.92 (dd, *J* = 11.8, 1.0 Hz, 1H), 3.85 (dd, *J* = 11.8, 1.0 Hz, 1H), 2.29 – 2.20 (m, 1H), 2.06 (dddt, *J* = 16.9, 5.1, 3.0, 1.7 Hz, 1H), 1.88 (dddd, *J* = 14.4, 11.7, 5.4, 3.0 Hz, 1H), 1.83 (ddt, *J* = 12.5, 5.8, 2.3 Hz, 1H), 1.74 (dt, *J* = 2.6, 1.3 Hz, 3H), 1.48 (td, *J* = 12.5, 10.0 Hz, 1H), 1.08 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.6, 137.7, 136.2, 136.2, 135.0, 134.0, 129.8, 129.7, 127.7, 127.5, 122.9, 113.4, 72.8, 47.3, 38.3, 36.2, 31.3, 27.3, 20.2, 19.7; IR (thin film, cm^{-1}) 3072, 3049, 2999, 2963, 2930, 2889, 2857, 1472, 1449, 1428; HRMS (EI+) *calcd*. for [$C_{26}H_{33}ClOSi$]: m/z 424.1989, found 424.1990.



Aldehyde 47: An oven-dried 1 L round-bottom flask equipped with a large stir bar was charged with allylic chloride **46** (21.3 g, 50.1 mmol), pyridine (1.18 mL, 15.0 mmol), and DCM (500 mL). The reaction flask was connected to a Welsbach ozone generator through plastic tubing and a glass bubbler, and cooled to -78 °C. The system was purged with O_2 for 5 min, and ozone generation was initiated (5~6 psi, 1.6~1.8 L/min, 90 V). The reaction was monitored carefully by TLC (EtOAc:hexane 1:30), and disconnected from the ozone generator immediately after complete consumption of the starting material (20~40 min). Nitrogen was then bubbled through the reaction mixture for 10 minutes, followed by the addition of dimethyl sulfide (7.35 mL, 100 mmol). The reaction mixture was slowly warmed to room temperature and stirred for 8 hours. Piperidine (0.74 mL, 7.6 mmol) and acetic acid (0.58 mL, 10 mmol) were then added, and the mixture heated at reflux for 16 hours. After complete conversion of the intermediates, the reaction mixture was filtered through a short column of silica gel (washed with DCM), concentrated *in vacuo*, and purified by flash column chromatography (EtOAc:hexane 1:30) to afford aldehyde **47** (9.16 g, 20.9 mmol, 42%) as a colorless oil: $[\alpha]_D^{20}$ = –12.3° (c 0.01 g/mL, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 9.92 (s, 1H), 7.73 – 7.63 (m, 4H), 7.48 – 7.43 (m, 2H), 7.43 – 7.37 (m, 4H), 5.22 (s, 1H), 5.06 (s, 1H), 4.67 (ddt, *J* = 7.8, 5.5, 1.0 Hz, 1H), 4.23 (dd, *J* = 11.8, 1.2 Hz, 1H), 4.09 (dd, *J* = 11.8, 0.9 Hz, 1H), 3.36 (ddd, *J* = 8.4, 6.0, 2.1 Hz, 1H), 2.36 (ddd, *J* = 13.6, 8.4, 7.8 Hz, 1H), 2.03 (dd, *J* = 2.1, 1.0 Hz, 3H), 1.69 (ddd, *J* = 13.6, 6.0, 5.5 Hz, 1H), 1.10 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 189.1, 161.7, 148.2, 139.1, 136.2, 136.1, 133.7, 133.6, 130.1, 130.0, 127.9, 127.8, 115.3, 80.5, 48.4, 44.9, 41.2, 27.1, 19.4, 12.3; IR (thin film, cm^{-1}) 3072, 3050, 2960, 2931, 2892, 2857, 1725, 1674, 1472, 1428; HRMS (EI+) *calcd*. for [$C_{26}H_{31}ClO_2Si$]: m/z 438.1782, found 438.1779.

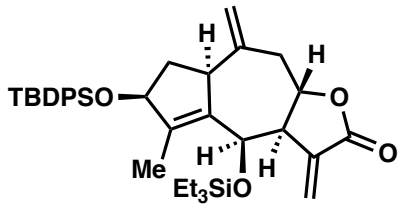


Acetal 49: A flame-dried 500 mL round-bottom flask equipped with a stir bar was charged with aldehyde **47** (14.0 g, 31.9 mmol), allyl bromide **48** (6.73 g, 26.6 mmol),[1] and indium shot (4.58 g, 39.9 mmol). The flask was placed under vacuum and back-filled twice with N_2, followed by the addition of DMF (80 mL) and H_2O (0.48 mL, 26.6 mmol). The reaction was stirred vigorously at room temperature while bubbling with N_2 for 1 hour. The resulting mixture was stirred overnight and filtered through a pad of Celite®. The filtrate was diluted with H_2O (800 mL) and the aqueous layer was extracted with ethyl acetate (3 × 500 mL). The combined organic phase was washed with H_2O (500 mL × 2) and brine (500 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude material was purified by flash column chromatography (EtOAc:hexane 1:20 to 1:10), affording acetal **49** as a mixture of diastereomers (11.0 g, 17.9 mmol, 67%, 2:1 *dr*).

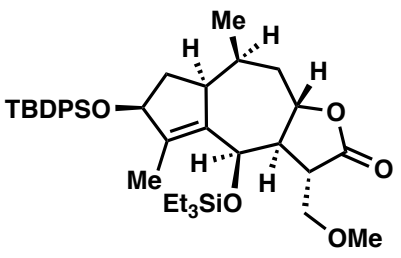


Aldehyde 50: A flame-dried 500 mL round-bottom flask equipped with a stir bar was charged with acetal **49** (12.3 g, 20.1 mmol, *dr* 2:1), 2,4,6-collidine (14.5 g, 120 mmol) and DCM (300 mL). The reaction was cooled to –78 °C and TESOTf (21.1 g, 80.0 mmol) was added dropwise. The reaction was allowed to warm gradually and stirred at approximately 0 °C for 24 hours. After the complete consumption of dimethyl acetal as indicated by TLC, the reaction was quenched by the addition of H_2O (50 mL) and stirred at room temperature for 30 min until the disappearance of polar collidine adducts on TLC (EtOAc:hexane 1:5). The resulting mixture was diluted with H_2O (200 mL) and the aqueous layer was extracted with DCM (200 mL × 3). The combined organic phase was washed with brine (300 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The crude product was purified by flash column chromatography (EtOAc:hexane 1:30), affording triethyl silyl aldehyde **50** (7.05 g, 10.4 mmol, 78% from **49**) as a light yellow oil: $[\alpha]_D^{20}$ = +25.0˚ (c 0.01 g/mL, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.86 (d, *J* = 2.1 Hz, 1H), 7.68 – 7.62 (m, 4H), 7.45 – 7.41 (m, 2H), 7.39 – 7.35 (m, 4H), 6.17 (s, 1H), 5.58 (s, 1H), 5.36 (s, 1H), 5.27 (s, 1H), 5.18 (d, *J* = 9.9 Hz, 1H), 4.43 (dd, *J* = 7.6, 3.1 Hz, 1H), 4.31 (d, *J* = 12.5 Hz, 1H), 4.14 (d, *J* = 12.5 Hz, 1H), 3.64 (dd, *J* = 9.9, 2.1 Hz, 1H), 3.63 (s, 3H), 3.19 (ddd, *J* = 8.7, 4.3, 1.8 Hz, 1H), 2.09 (ddd, *J* = 14.0, 8.7, 7.6 Hz, 1H), 1.71 (ddd, *J* = 14.0, 4.3, 3.1 Hz, 1H), 1.46 (d, *J* = 1.8 Hz, 3H), 1.07 (s, 9H), 0.95 (t, *J* = 7.9 Hz, 9H), 0.66 – 0.56 (m, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.8, 166.1, 148.2, 141.1, 138.1, 136.2, 136.2, 134.7, 134.3, 134.2, 129.9, 129.8, 129.8, 127.7, 127.7, 116.3, 80.0, 68.2, 60.3, 52.3, 47.8, 47.6,

40.1, 27.1, 19.4, 12.7, 7.0, 4.9; IR (thin film, cm^{-1}) 3072, 2956, 2932, 2877, 2857, 1718, 1627, 1590, 1470, 1428; HRMS (ESI) *calcd.* for $[C_{38}H_{53}ClNaO_5Si_2]^+$ $(M+Na)^+$: m/z 703.3018, found 703.3025

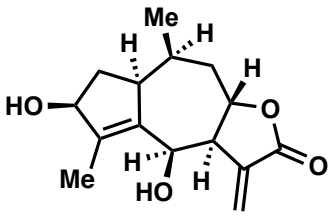


Lactone 51: A flame-dried 500 mL round-bottom flask was charged with a stir bar, NaI (14.9 g, 99.3 mmol) and anhydrous $SnCl_2$ (9.40 g, 49.6 mmol). The flask was placed under vacuum and back-filled twice with nitrogen, followed by the addition of dry, degassed DMF (250 mL). The resulting mixture was covered by aluminum foil to avoid exposure to light and stirred at room temperature for 30 minutes. Aldehyde **50** (7.60 g, 11.1 mmol) in dry DMF (50 mL) was degassed by bubbling with argon, and then transferred to the reaction flask via syringe in one portion. The reaction mixture was stirred in the dark at 60 °C for 12 hours. After complete consumption of the starting material as indicated by TLC (EtOAc:hexane 1:10, developed twice), the reaction was cooled to room temperature, diluted with ethyl acetate (100 mL), and quenched by addition of *aq.* NH_4F (10% w/w, 100 mL). The resulting mixture was diluted with H_2O (500 mL) and extracted with ethyl acetate (300 mL × 3). The combined organic phase was washed with H_2O (500 mL), brine (500 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude material was purified by flash column chromatography (EtOAc:hexane = 1:20), affording unsaturated lactone **51** (6.18 g, 10.0 mmol, 90%) as a colorless oil: $[\alpha]_D^{20}$ = +57.9° (c 0.007 g/mL, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 – 7.67 (m, 4H), 7.47 – 7.41 (m, 2H), 7.42 – 7.35 (m, 4H), 6.28 (d, *J* = 3.4 Hz, 1H), 5.52 (d, *J* = 3.1 Hz, 1H), 5.04 (s, 1H), 4.95 (s, 1H), 4.91 (s, 1H), 4.70 (ddd, *J* = 11.8, 9.8, 4.3 Hz, 1H), 4.57 (br t, *J* = 7.1 Hz, 1H), 3.06 (dd, *J* = 11.8, 4.3 Hz, 1H), 2.84 – 2.77 (m, 1H), 2.68 (ddd, *J* = 9.8, 3.4, 3.1 Hz, 1H), 2.22 (dd, *J* = 11.8, 11.8 Hz, 1H), 1.96 (ddd, *J* = 11.9, 6.1, 6.1 Hz, 1H), 1.85 (ddd, *J* = 11.9, 11.3, 8.2 Hz, 1H), 1.71 (dd, *J* = 2.5, 1.2 Hz, 3H), 1.11 (s, 9H), 0.89 (t, *J* = 7.9 Hz, 9H), 0.62 – 0.48 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.0, 142.4, 140.1, 139.5, 137.6, 136.1, 134.5, 134.2, 129.8, 127.7, 127.7, 119.5, 113.8, 78.6, 77.7, 63.6, 51.8, 48.8, 44.8, 39.3, 27.1, 19.5, 13.1, 7.1, 5.3; IR (thin film, cm^{-1}) 3072, 2963, 2930, 2889, 2857, 1472, 1449, 1428, 1343; HRMS (ESI) *calcd.* for $[C_{37}H_{50}NaO_4Si_2]^+$ $(M+Na)^+$: m/z 637.3140, found 637.3133.



Lactone 52: A flame-dried 250 mL round-bottom flask was charged with a stir bar and unsaturated lactone **51** (6.18 g, 10.0 mmol). The flask was placed under vacuum and back-filled twice with nitrogen, followed by the addition of methanol (100 mL) and DCM (35 mL). NaOMe (54 mg, 1.0 mmol) was then added

in one portion and the resulting mixture was stirred at room temperature for 16 hours. The reaction was monitored periodically by ^{1}H NMR with an aliquot (0.1 mL) concentrated *in vacuo*. After complete consumption of the starting material, acetic acid (60 mL, 1.0 mmol) and PtO_2 (227 mg, 1.00 mmol) were added sequentially to the reaction. The reaction mixture was bubbled with H_2 until a black suspension formed, and was stirred under an atmosphere of H_2 (1 atm) for 6 hours. After the reaction was complete as indicated by ^{1}H NMR, the reaction mixture was filtered through a pad of Celite® and concentrated *in vacuo*. The crude was purified by flash column chromatography (EtOAc:hexane 1:20), affording mono-reduction product **52** (6.23 g, 9.60 mmol, 96%) as a colorless oil: $[\alpha]_D^{20}$ = +48.8˚ (c 0.01 g/mL, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 – 7.65 (m, 4H), 7.45 – 7.41 (m, 2H), 7.40 – 7.35 (m, 4H), 4.81 (ddd, *J* = 12.1, 10.2, 3.9 Hz, 1H), 4.64 (s, 1H), 4.52 (br t, *J* = 7.4 Hz, 1H), 3.65 (dd, *J* = 9.8, 4.8 Hz, 1H), 3.59 (dd, *J* = 9.8, 3.5 Hz, 1H), 3.30 (s, 3H), 2.81 (ddd, *J* = 12.0, 4.8, 3.5 Hz, 1H), 2.58 – 2.50 (m, 1H), 2.28 (ddd, *J* = 12.7, 3.9, 3.9 Hz, 1H), 2.14 (dd, *J* = 12.0, 10.2 Hz, 1H), 1.93 (ddd, *J* = 12.3, 7.4, 7.1 Hz, 1H), 1.89 – 1.81 (m, 1H), 1.65 – 1.63 (m, 3H), 1.61 (ddd, *J* = 12.7, 12.1, 3.9 Hz, 1H), 1.51 (ddd, *J* = 12.3, 9.9, 7.4 Hz, 1H), 1.08 (s, 9H), 1.03 (d, *J* = 7.3 Hz, 3H), 0.97 (t, *J* = 7.9 Hz, 9H), 0.72 – 0.57 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.2, 143.1, 139.0, 136.1, 136.1, 134.6, 134.4, 129.7, 129.7, 127.6, 127.6, 79.4, 76.5, 68.9, 63.8, 59.4, 50.2, 50.0, 44.1, 40.9, 39.3, 31.5, 27.1, 19.4, 13.9, 13.0, 7.2, 5.7; IR (thin film, cm^{-1}) 3071, 2958, 2932, 2876, 2857, 1781, 1472, 1428, 1389; HRMS (EI) *calcd*. for [$C_{38}H_{56}O_5Si_2$]: m/z 648.3666, found 648.3660.



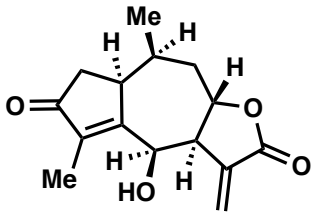
Diol SI-1: [Condition 1] A reaction tube (Fisher Scientific, 13 × 100 mm) was charged with a stir bar and compound **52** (100 mg, 0.154 mmol) in THF (1 mL). The reaction mixture was cooled to 0 °C and TBAF (0.46 mL, 0.46 mmol, 1M in THF) was added dropwise. The resulting mixture was warmed to room temperature and stirred overnight. After the reaction was judged complete, as indicated by TLC (pure EtOAc), acetic acid (54 μL) was added to quench the reaction. The reaction mixture was concentrated *in vacuo*, and the crude mixture purified by flash column chromatography (EtOAc/hexane, 3:1), affording a mixture of **SI-1** and **SI-1 methanol adduct** (33.9 mg, 0.128 mmol, 83%, 5:2 ratio). The mixture could be separated by preparative TLC (acetone:toluene 1:4, developed 3 times).

[Condition 2] A 250 mL round-bottom flask was charged with a stir bar and compound **52** (3.90 g, 6.00 mmol) in THF (100 mL). TBAF (24 mL, 24 mmol, 1 M in THF) was added at 0 °C and the resulting mixture was stirred for 24 hours at room temperature. Acetic acid (0.5 mL) was then added to the reaction. The reaction mixture was concentrated *in vacuo* and then re-dissolved in DCM (20 mL) and

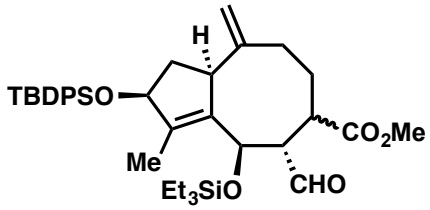
toluene (120 ml). DBU (1.0 mL, 6.6 mmol) was added to the reaction and the flask was equipped with a reflux condenser and heated at 120 °C for 24 hours. After removing the solvent *in vacuo,* the crude material was purified by flash column chromatography (pure EtOAc), affording diol **SI-1** (1.09 g, 4.12 mmol, 69%) which contained up to 3% **SI-1 methanol adduct**.

Diol **SI-1**, colorless oil: $[\alpha]_D^{20}$ = +96.8° (c 0.005 g/mL, MeOH); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.37 (d, *J* = 3.4 Hz, 1H), 5.64 (d, *J* = 3.1 Hz, 1H), 4.91 (s, 1H), 4.80 (ddd, *J* = 12.6, 9.6, 3.7 Hz, 1H), 4.52 (dd, *J* = 8.0, 5.1 Hz, 1H), 2.87 – 2.82 (m, 1H), 2.80 (dddd, *J* = 9.6, 3.4, 3.1, 1.6 Hz, 1H), 2.53 (ddd, *J* = 14.0, 8.4, 8.0 Hz, 1H), 2.39 (ddd, *J* = 12.6, 3.7, 3.7 Hz, 1H), 2.06 – 1.99 (m, 1H), 1.90 (d, *J* = 2.2 Hz, 3H), 1.80 (ddd, *J* = 12.6, 12.6, 3.7 Hz, 1H), 1.41 (ddd, *J* = 14.0, 6.1, 5.1 Hz, 1H), 0.98 (d, *J* = 7.3 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.8, 145.1, 139.4, 137.1, 120.4, 79.0, 75.6, 63.5, 51.2, 50.4, 40.9, 38.8, 32.8, 13.5, 12.6; IR (thin film, cm^{-1}) 3448, 2960, 2924, 2877, 2855, 1748, 1662, 1463, 1404, 1384; HRMS (EI) *calcd.* for [$C_{15}H_{20}O_4$]: m/z 264.1362, found 264.1355. [Note: Diol **SI-1** is not stable in chloroform at room temperature.]

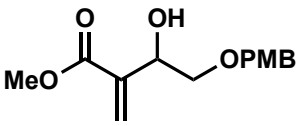
Mikanokryptin 8: An oven-dried 100 mL round bottom flask was charged with a stir bar, diol **SI-1**



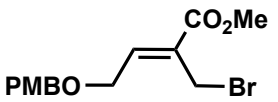
(1.088 g, 4.116 mmol), and DCM (50 mL). Activated MnO_2 (10.7 g, 123 mmol) was added in one portion. The resulting mixture was stirred vigorously at room temperature for 16 hours. The reaction was monitored by TLC (pure EtOAc), and filtered through a pad of Celite® when complete conversion was achieved. The filtrate was concentrated *in vacuo*, affording spectroscopically pure mikanokryptin **(8)** (1.051 g, 4.007 mmol, 97%) as a light-yellow to white solid: mp 230.5 – 232.4 °C; $[\alpha]_D^{20}$ = +235.0˚ (lit. +264˚, c 0.00098 g/mL, MeOH); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.46 (d, *J* = 3.5 Hz, 1H), 5.70 (d, *J* = 3.1 Hz, 1H), 5.17 (br s, 1H), 4.80 (ddd, *J* = 12.6, 9.6, 3.5 Hz, 1H), 3.15 – 3.10 (m, 1H), 3.06 (dddd, *J* = 9.6, 3.5, 3.1, 1.9 Hz, 1H), 2.67 (ddd, *J* = 19.1, 6.9, 1.1 Hz, 1H), 2.45 (ddd, *J* = 12.8, 3.5, 3.5 Hz, 1H), 2.34 – 2.27 (m, 1H), 2.19 (dd, *J* = 19.1, 1.9 Hz, 1H), 1.94 (ddd, *J* = 12.8, 12.6, 4.1 Hz, 1H), 1.92 (dd, *J* = 2.1, 0.9 Hz, 3H), 0.85 (d, *J* = 7.3 Hz, 3H); ^{1}H NMR (600 MHz, DMSO-d_6) δ 6.20 (d, *J* = 3.4 Hz, 1H), 5.80 (d, *J* = 3.1 Hz, 1H), 5.74 (d, *J* = 6.5 Hz, 1H), 5.09 (d, *J* = 6.5 Hz, 1H), 4.64 (ddd, *J* = 12.5, 9.4, 3.4 Hz, 1H), 3.24 – 3.14 (m, 2H), 2.55 (dd, *J* = 19.0, 6.7 Hz, 1H), 2.21 (ddd, *J* = 12.0, 3.4, 3.4 Hz, 1H), 2.19 – 2.15 (m, 1H), 2.05 (dd, *J* = 19.0, 1.9 Hz, 1H), 1.94 (ddd, *J* = 12.5, 12.0, 4.0 Hz, 1H), 1.76 (d, *J* = 1.0 Hz, 3H), 0.73 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 207.2, 172.5, 169.5, 141.5, 136.5, 120.8, 75.0, 62.7, 49.5, 44.2, 40.9, 39.4, 32.4, 12.5, 8.6; IR (thin film, cm^{-1}) 3434, 2961, 2924, 2882, 1762, 1679, 1633, 1450, 1407, 1385, 1325; HRMS (EI) *calcd.* for [$C_{15}H_{18}O_4$]: m/z 262.1205, found 262.1207.



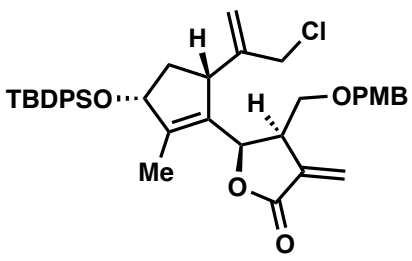
Cyclooctane 53: A flame-dried reaction tube was charged with a stir bar, compound **50** (34.0 mg, 0.0499 mmol), and NaI (75.0 mg, 0.500 mmol). The tube was placed under vacuum and back-filled twice with N_2, followed by addition of dry acetone (6 mL). The resulting mixture was stirred at 40 °C overnight protected from light by aluminum foil. The reaction mixture was concentrated *in vacuo*, re-dissolved in dry diethyl ether, and filtered through a pad of Celite®. The filtrate was collected in another reaction tube wrapped by alumina foil and concentrated *in vacuo*. Activated zinc powder (32.0 mg, 0.496 mmol) and THF (2 mL) was added to the reaction followed by the addition of degassed saturated aq. NH_4Cl (1 mL). The reaction mixture was vigorously stirred for 20 min and the aqueous layer was extracted with ethyl acetate (5 mL × 3). The combined organic phase was washed with H_2O (10 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Flash column chromatography (EtOAc/hexane, 1:20) afforded recovered **50** (11.5 mg, 0.0169 mmol, 34%) and cyclooctane **53** (16.5 mg, 0.0240 mmol, 51%, 5:2 *dr*) as an inseparable mixture of two diastereomers: colorless oil; Major diastereomer: ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.93 (d, *J* = 2.1 Hz, 1H), 7.72 – 7.65 (m, 4H), 7.46 – 7.34 (m, 6H), 4.85 (app. t, *J* = 1.7 Hz, 1H), 4.83 (br s, 1H), 4.63 – 4.57 (m, 1H), 4.21 (d, *J* = 10.4 Hz, 1H), 3.65 (s, 3H), 3.29 – 3.23 (m, 1H), 3.10 – 3.05 (m, 1H), 2.66 – 2.63 (m, 1H), 2.54 (d, *J* = 10.4 Hz, 1H), 2.12 (d, *J* = 9.2 Hz, 1H), 2.00 (app. dt, *J* = 13.3, 7.5 Hz, 1H), 1.87 (dd, *J* = 2.6, 1.1 Hz, 3H), 1.69 – 1.65 (m, 1H), 1.62 (ddd, *J* = 13.2, 7.9, 6.5 Hz, 1H), 1.59 – 1.54 (m, 1H), 1.09 (s, 9H), 0.81 (t, *J* = 8.0 Hz, 9H), 0.40 (q, *J* = 8.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.1, 176.5, 146.9, 140.6, 139.3, 136.2, 136.1, 134.7, 134.2, 129.8, 129.7, 127.7, 127.6, 117.3, 80.5, 71.5, 58.4, 53.3, 52.2, 41.4, 37.6, 34.1, 27.2, 19.4, 12.7, 6.8, 4.6.; IR (thin film, cm^{-1}) 3072, 2957, 2932, 2877, 2857, 1735, 1635, 1471, 1429; HRMS (EI) calcd. for [$C_{38}H_{54}O_5Si_2$]: m/z 646.3510, found 646.3503;



Allyl alcohol SI-2: A 250 mL round-bottom flask equipped with a stir bar was charged with 2-((4-methoxybenzyl)oxy)acetaldehyde (3.66 g, 0.02 mol), methyl acrylate (5.4 mL,0.06 mol), and DABCO (1.12g, 0.01 mol). The resulting mixture was stirred at room temperature for 2 days and concentrated *in vacuo*. The resulting oil was diluted with diethyl ether (50 mL) and washed with 1N HCl (30 mL), H_2O (30 mL), and brine (30 mL) sequentially. The organic phase was dried over Na_2SO_4 and concentrated *in vacuo*. The crude mixture was purified by flash column chromatography, affording allylic alcohol **SI-2** (3.4 g, 0.012 mol, 60%) as a colorless oil. ^{1}H NMR (500 MHz, Benzene-d_6) δ 7.11 (d, J = 8.6 Hz, 2H), 6.77 (d, J = 8.6 Hz, 2H), 6.30 (dd, J = 1.7, 1.1 Hz, 1H), 5.99 (t, J = 1.6 Hz, 1H), 4.89 (ddd, J = 7.5, 3.0, 1.4 Hz, 1H), 4.47 – 4.13 (m, 2H), 3.72 (dd, J = 9.5, 3.6 Hz, 1H), 3.49 – 3.30 (m, 1H), 3.29 (s, 3H), 3.28 (s, 3H); ^{13}C NMR (151 MHz, C_6D_6) δ 165.91, 159.46, 139.72, 130.17, 129.21, 125.71, 113.75, 73.55, 72.59, 69.5, 54.4, 50.9; IR (thin film, cm^{-1}) 3460, 2950, 2905, 2859, 2837, 1716, 1611, 1585, 1513, 1438. HRMS (EI+) *calcd.* for $[C_{14}H_{18}O_5]^+$ $(M)^+$: m/z 266.1152, found 266.1154.



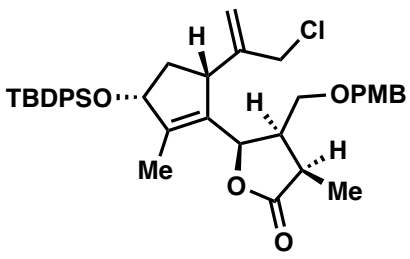
Allylic bromide 54: A flame-dried 500 mL round-bottom flask was charged with a stir bar, *N*-bromosuccinimide (6.8 g, 36 mmol) and DCM (80 mL). The reaction mixture was cooled to 0 ºC, followed by the addition of dimethyl sulfide (2.86 mL, 39 mmol) in DCM (70 mL). The resulting mixture was stirred at 0 ºC for 20 minutes, and allylic alcohol **SI-2** (7.95 g, 30 mmol) in DCM (75 mL) was added slowly. The reaction mixture was warmed to room temperature gradually and stirred overnight. After full consumption of the starting material, as indicated by TLC (EtOAc/hexane, 1:5), the reaction was quenched by the addition of saturated *aq*. $NaHCO_3$ (60 mL). The aqueous phase was extracted with diethyl ether (200 mL × 2). The combined organic phases were washed with H_2O (60 mL) and brine (100 mL) sequentially, dried over Na_2SO_4, and concentrated *in vacuo*. The crude material was purified by flash column chromatography, affording allylic bromide **54** (5.9 g, 18 mmol, 60%) as a colorless oil: ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.28 (d, J = 8.6 Hz, 2H), 7.04 (t, J = 5.7 Hz, 1H), 6.90 (d, J = 8.6 Hz, 2H), 4.51 (s, 2H), 4.28 (d, J = 5.7 Hz, 2H), 4.19 (s, 2H), 3.81 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.66, 159.55, 143.89, 130.23, 129.66, 129.51, 114.04, 72.93, 66.09, 55.43, 52.55, 23.96.; IR (thin film, cm^{-1}) 3000, 2951, 2907, 2836, 1719, 1646, 1612, 1585, 1512, 1437.



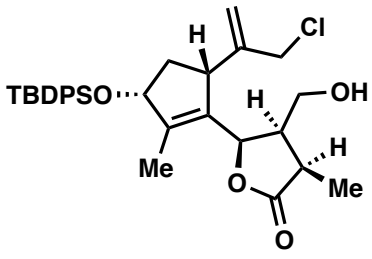
Lactone 55: A 500 mL round bottom flask was charged with a stir bar, anhydrous $ZnCl_2$ (200 mg, 1.47 mmol, 0.06 equiv), activated zinc powder (2.43 g, 37.2 mmol, 1.5 equiv), and dry NMF (100 mL). The mixture was degassed by bubbling of argon for 30 minutes. A solution of aldehyde *ent*-**47** (10.9 g, 24.8 mmol, 1 equiv) and allylic bromide **54** (12.3 g, 37.2 mmol, 1.5 equiv) in degassed NMF (50 mL) were then added to the reaction flask. The reaction mixture was stirred at room temperature until the consumption of aldehyde *ent*-**47** was complete as judged by TLC (EtOAc/hexane, 1:4). The mixture was then diluted with DCM (200 mL) and filtered through Celite®. The filtrate was combined with H_2O (200 mL) and further stirred at room temperature for 30 minutes. The aqueous phase was extracted with DCM (100 mL × 2), and the combined organic phase was washed with saturated *aq.* NH_4Cl (200 mL), H_2O (200 mL), and brine (200 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude mixture was purified by flash column chromatography (EtOAc/hexane, 1:20 to 1:5), affording lactones **55** and 6,7-*epi*-**55** (10.65 g, 65%, 2:1 *dr*) as a colorless oil. Compound **55** (major): $[\alpha]_D^{20}$ = –46.8° (c 0.005 g/mL, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 – 7.61 (m, 4H), 7.46 – 7.36 (m, 6H), 7.09 (d, *J* = 8.3 Hz, 2H), 6.80 (d, *J* = 8.3 Hz, 2H), 6.30 (d, *J* = 2.0 Hz, 1H), 5.70 (d, *J* = 2.0 Hz, 1H), 5.32 (s, 1H), 5.22 (s, 1H), 5.05 (d, *J* = 7.6 Hz, 1H), 4.50 (dd, *J* = 7.4, 2.8 Hz, 1H), 4.26 (d, *J* = 11.3 Hz, 1H), 4.23 (d, *J* = 11.3 Hz, 1H), 4.09 – 4.03 (m, 2H), 3.77 (s, 3H), 3.41 – 3.35 (m, 1H), 3.29 (dd, *J* = 9.2, 7.2 Hz, 1H), 3.23 (dd, *J* = 9.2, 6.7 Hz, 1H), 3.15 (brd, *J* = 8.6 Hz, 1H), 2.07 (app. dt, *J* = 13.9, 8.1 Hz, 1H), 1.66 (brs, 3H), 1.58 (app. dt, *J* = 13.9, 3.4 Hz, 1H), 1.06 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.0, 159.5, 147.2, 142.0, 136.8, 136.2, 136.2, 134.4, 134.1, 132.6, 129.9, 129.80, 129.6, 129.4, 127.8, 127.7, 124.0, 117.0, 113.9, 81.7, 77.6, 73.2, 69.9, 55.4, 49.8, 47.2, 43.1, 39.8, 27.1, 19.4, 13.5; IR (thin film, cm^{-1}) 3072, 2932, 2896, 2858, 1769, 1665, 1612, 1587, 1514, 1428; HRMS (ESI+) *calcd.* for $[C_{39}H_{45}ClO_5SiNa]^+$ $(M+Na)^+$: m/z 679.2623, found 679.2624.

Compound 6,7-*epi*-**55** (minor): $[\alpha]_D^{20}$ = –31.6° (c 0.010 g/mL, $CHCl_3$); ^{1}H NMR (600 MHz, C_6D_6) δ 7.81 – 7.74 (m, 4H), 7.27 – 7.20 (m, 6H), 7.00 (d, *J* = 8.3 Hz, 2H), 6.74 (d, *J* = 8.3 Hz, 2H), 6.14 (d, *J* = 2.6 Hz, 1H), 5.33 (s, 1H), 5.20 (s, 1H), 5.09 (d, *J* = 2.6 Hz, 1H), 4.95 (d, *J* = 8.1 Hz, 1H), 4.50 (dd, *J* = 7.6, 2.6 Hz, 1H), 4.30 (d, *J* = 12.5 Hz, 1H), 4.19 (d, *J* = 12.5 Hz, 1H), 4.00 (d, *J* = 11.4 Hz, 1H), 3.89 (d, *J* = 11.4 Hz, 1H), 3.29 (s, 3H), 3.04 (d, *J* = 8.3 Hz, 1H), 2.99 (dd, *J* = 9.1, 5.7 Hz, 1H), 2.88 (dd, *J* = 9.1, 6.4 Hz, 1H), 2.82 (app. ddt, *J* = 11.8, 6.1, 3.0 Hz, 1H), 2.06 (app. dt, *J* = 14.0, 8.0 Hz, 1H), 1.90 (app. dt, *J* = 14.0, 3.2 Hz, 1H), 1.43 (s, 3H), 1.19 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.8, 159.5, 147.4, 142.9, 136.8, 136.2, 136.2, 136.2, 134.9, 134.1, 129.9, 129.9, 129.5, 129.4, 127.8, 127.7, 122.0,

115.8, 113.9, 80.0, 76.8, 73.4, 68.6, 55.4, 50.0, 46.4, 43.7, 40.1, 27.1, 19.4, 12.6; IR (thin film, cm^{-1}) 3071, 2932, 2894, 2857, 1770, 1664, 1612, 1587, 1514, 1428; HRMS (ESI+) *calcd.* for $[C_{39}H_{45}ClO_5SiNa]^+$ $(M+Na)^+$: m/z 679.2623, found 679.2623.



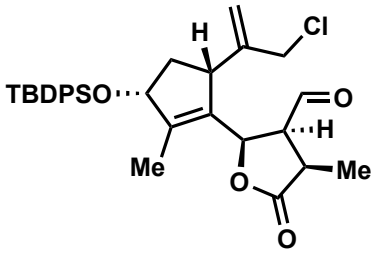
Compound SI-3: A 100 mL round-bottom flask was charged with a stir bar, lactone **55** (7.347 g, 11.2 mmol, 1 equiv), and anhydrous methanol (37 mL). To this solution was added $NaBH_4$ (634.3 mg, 16.8 mmol, 1.5 equiv) in one portion. The reaction mixture was stirred at room temperature until the starting material was consumed as judged by TLC (EtOAc/hexanes, 1:4). The reaction was then quenched by addition of saturated *aq.* NH_4Cl (50 mL), and the resulting mixture was extracted three times with EtOAc. The combined organic phase was washed with H_2O and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The crude mixture was purified by column chromatography (EtOAc/hexanes, 1:8 to 1:4), affording the reduced product **SI-3** (7.384 g, 100%) as a colorless oil. $[\alpha]_D^{20}$ = –27º (c 0.003 g/mL $CHCl_3$); IR (thin film) 2930, 2980, 2856, 1773, 1612, 1513, 1427 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.70 – 7.62 (m, 4H), 7.46 – 7.35 (m, 6H), 7.04 (d, *J* = 8.6 Hz, 2H), 6.75 (d, *J* = 8.6 Hz, 2H), 5.30 (s, 1H), 5.23 (s, 1H), 4.92 (d, *J* = 5.5 Hz, 1H), 4.49 (dd, *J* = 7.4, 2.7 Hz, 1H), 4.19 (d, *J* = 11.6 Hz, 1H), 4.13 (d, *J* = 11.6 Hz, 1H), 4.09 (d, *J* = 12.2 Hz, 1H), 4.05 (d, *J* = 12.2 Hz, 1H), 3.75 (s, 3H), 3.24 (dd, *J* = 9.7, 4.0 Hz, 1H), 3.15 (dd, *J* = 9.7, 3.4 Hz, 1H), 3.01 (brd, *J* = 8.6 Hz, 1H), 2.75 (dq, *J* = 7.7, 7.2 Hz, 1H), 2.60 (dddd, *J* = 7.7, 5.5, 4.0, 3.4 Hz, 1H), 2.07 – 1.99 (m, 1H), 1.77 (s, 3H), 1.57 – 1.51 (m, 1H), 1.23 (d, *J* = 7.2 Hz, 3H), 1.05 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 178.6, 159.3, 147.3, 141.6, 136.2, 136.2, 134.5, 134.1, 131.2, 129.8, 129.8, 129.6, 129.2, 127.7, 127.7, 116.8, 113.8, 82.0, 79.4, 73.2, 65.7, 55.4, 49.3, 47.1, 43.4, 39.7, 38.1, 27.1, 19.4, 10.1; HRMS (ESI) *calcd.* for $[C_{39}H_{47}ClO_5SiNa]^+$ $(M+Na)^+$: m/z 681.2779, found 681.2776.



Lactone 56: A 250 mL round-bottom flask was charged with a stir bar, lactone **SI-3** (4.6 g, 6.98 mmol, 1 equiv), DCM (63 mL) and pH = 7.5 buffer (6.3 mL). To this solution was added DDQ (4.75 g, 20.93 mmol, 3 equiv) in one portion. The reaction mixture was stirred at room temperature until the consumption of the starting material was deemed complete as judged by TLC (30% EtOAc in hexanes). The reaction was then quenched by addition of saturated *aq.* $NaHCO_3$ and saturated *aq.* $Na_2S_2O_3$ solutions. The DCM layer was separated, and the aqueous layer was extracted with minimal DCM. The combined organic phase was

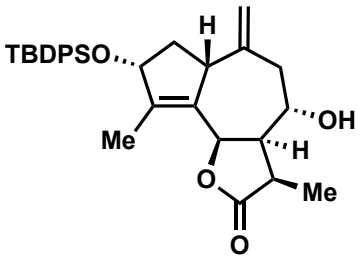
loaded directly onto a column without concentration and purified by column chromatography (EtOAc/hexane, 0% to 34%), affording alcohol **56** (2.83 g, 75%) as a colorless oil. $[\alpha]_D^{23}$ = –27° (c 0.001 g/ml $CHCl_3$); IR (thin film): 3492, 2929, 2890, 2856, 1761, 1472, 1458, 1427, 1350, 1285, 1260, 1175 cm^{-1} ^1H NMR (700 MHz, C_6D_6) δ 7.78 – 7.71 (m, 4H), 7.23 (td, *J* = 5.1, 4.7, 2.0 Hz, 6H), 5.17 (s, 1H), 5.15 (s, 1H), 4.65 (d, *J* = 4.9 Hz, 1H), 4.49 (dd, *J* = 7.3, 2.4 Hz, 1H), 3.90 – 3.82 (m, 2H), 3.05 (dd, *J* = 11.6, 3.6 Hz, 1H), 2.98 (dd, *J* = 11.4, 3.0 Hz, 1H), 2.83 (dt, *J* = 8.7, 2.6 Hz, 1H), 1.94 (s, 3H), 1.93 – 1.86 (m, 3H), 1.63 (dt, *J* = 13.9, 2.9 Hz, 1H), 1.17 (s, 9H), 1.10 (d, *J* = 6.7 Hz, 3H).; ^{13}C NMR (176 MHz, C_6D_6) δ 177.21, 147.97, 140.91, 136.51, 136.48, 134.73, 134.25, 133.02, 130.15, 130.08, 128.35, 128.31, 116.45, 82.25, 78.63, 58.75, 49.45, 47.18, 44.52, 39.94, 37.46, 27.28, 19.54, 13.49, 10.26.; HRMS (ESI) *calcd.* for $[M+Na]^+$ $(C_{31}H_{39}O_4SiClNa)^+$ requires *m/z* 561.2198, found *m/z* 561.2198.

Aldehyde 57: A 250 mL round-bottom flask was charged with a stir bar, Dess-Martin periodinane (3.3

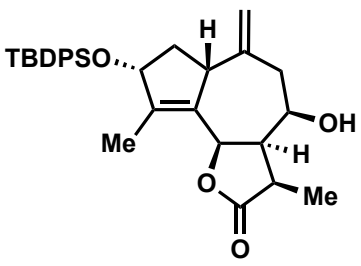


g, 7.79 mmol, 1.5 equiv), $NaHCO_3$ (654 mg, 7.79 mmol, 1.5 equiv), DCM (50 mL) and stirred at room temperature for 5 minutes. To this solution was added alcohol **56** (2.799 g, 5.19 mmol, 1 equiv) in DCM (10 mL) and the reaction was stirred at room temperature for 1 hour. Upon complete consumption of the starting material as judged by TLC (30% EtOAc in hexanes), the reaction was quenched by addition of saturated *aq.*$NaHCO_3$ and saturated *aq.* $Na_2S_2O_3$ solutions. The aqueous phase was extracted with DCM three times and the combined organic phase was washed with brine, dried over Na_2SO_4, and concentrated *in vacuo* to give the crude aldehyde **57** (2.83 g, 75%) as a white foam [Note: this procedure provided the title compound in sufficient purity for subsequent steps. Column chromatography often led to the formation of various side products and]. **57**: $[\alpha]_D^{23}$ = –36° (c 0.001 g/ml $CHCl_3$); IR (thin film): 2929, 2856, 1785, 1725, 1427, 1166 cm^{-1}; ^1H NMR (700 MHz, C_6D_6) δ 9.11 (d, *J* = 5.7 Hz, 1H), 7.69 (ddt, *J* = 22.6, 6.5, 1.8 Hz, 4H), 7.25 – 7.18 (m, 6H), 5.07 (s, 1H), 5.06 (d, *J* = 1.1 Hz, 1H), 4.64 – 4.60 (m, 1H), 4.41 (dd, *J* = 7.4, 3.0 Hz, 1H), 3.79 (dd, *J* = 12.1, 0.9 Hz, 1H), 3.71 (dd, *J* = 12.1, 1.1 Hz, 1H), 2.86 – 2.82 (m, 1H), 2.65 (dt, *J* = 7.9, 5.6 Hz, 1H), 1.87 (s, 3H), 1.86 (m, 1H), 1.77 (p, *J* = 7.5 Hz, 1H), 1.48 (dt, *J* = 13.8, 3.5 Hz, 1H), 1.14 (s, 9H), 0.87 (d, *J* = 7.4 Hz, 3H).; ^{13}C NMR (176 MHz, C_6D_6) δ 198.34, 175.45, 147.50, 142.32, 136.43, 136.40, 134.53, 134.13, 130.76, 130.18, 130.10, 128.35, 128.31, 116.68, 81.73, 76.79, 54.99, 48.76, 46.87, 40.08, 37.04, 27.24, 19.49, 13.27, 10.17.; HRMS (ESI) *calcd.* for $[M+Na]^+$ $(C_{31}H_{37}O_4SiClNa)^+$ requires *m/z* 559.2042, found *m/z* 559.2044.

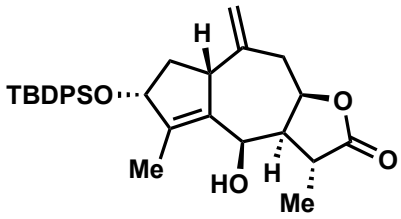
Lactone 58: A 250 mL round-bottom flask was charged with a stir bar, Cp_2TiCl_2 (463.5 mg, 1.86 mmol, 1 equiv), activated zinc powder (973.7 mg, 14.89 mmol, 8 equiv), and anhydrous THF (80 mL). The mixture was stirred at room temperature until the solution turned green (typically 10 minutes). The mixture was heated to 55 °C in an oil bath and then a solution of aldehyde **57** (1.0 g, 1.86 mmol, 1 equiv) in THF (20 mL) was added over 1 hour via a syringe pump. The reaction mixture was stirred further at 55 °C until the starting material was consumed as determined by TLC (20% EtOAc in hexanes). The reaction was then quenched by addition of saturated *aq.* NH_4Cl, and the resulting mixture was extracted three times with EtOAc. The combined organic phase was washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The crude mixture was purified by column chromatography (EtOAc/hexanes, 0% to 20%), affording the title compound (702 mg, 75%, 10:1 *dr*) as a white solid. $[\alpha]_D^{23}$ = –139º (c 0.001 g/ml $CHCl_3$); IR (thin film) 3452, 2930, 2856, 1771, 1716, 1507, 1472, 1456, 1427, 1375, 1362, 1339, 1281, 1203, 1166 cm^{-1}; ^1H NMR (900 MHz, C_6D_6) δ 7.90 – 7.68 (m, 4H), 7.28 – 7.19 (m, 6H), 4.79 (s, 1H), 4.71 (s, 1H), 4.66 (d, *J* = 4.9 Hz, 1H), 4.57 (t, *J* = 6.6 Hz, 1H), 3.30 (dddd, *J* = 10.3, 7.7, 5.5, 2.6 Hz, 1H), 3.26 (d, *J* = 8.0 Hz, 1H), 2.31 (dd, *J* = 12.4, 10.7 Hz, 1H), 2.14 (p, *J* = 7.2 Hz, 1H), 2.09 (dt, *J* = 12.8, 7.3 Hz, 1H), 1.88 (td, *J* = 7.1, 4.8 Hz, 1H), 1.85 (dd, *J* = 12.5, 2.6 Hz, 1H), 1.61 (dt, *J* = 13.3, 6.9 Hz, 1H), 1.56 (d, *J* = 2.2 Hz, 3H), 1.20 (d, *J* = 7.3 Hz, 3H), 1.18 (s, 9H), 0.84 (d, *J* = 5.5 Hz, 1H).; ^{13}C NMR (226 MHz, C_6D_6) δ 177.69, 146.42, 143.63, 136.42, 134.58, 134.43, 133.56, 130.16, 130.13, 128.35, 128.28, 128.02, 113.87, 80.44, 76.34, 71.99, 50.89, 47.86, 41.76, 41.66, 40.99, 27.31, 19.53, 12.09, 10.63.; HRMS (ESI) *calcd.* for $[M+H]^+$ $(C_{31}H_{39}O_4Si)^+$ requires *m/z* 503.2612, found *m/z* 503.2610.



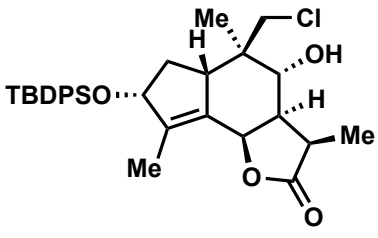
Lactones 64 and **65:** A reaction tube was charged with a stir bar, $SnCl_2$ (9.5 mg, 0.05 mmol, 5 equiv), NaI (7.5 mg, 0.05 mmol, 5 equiv) and DMF (0.3 mL). The resulting mixture was stirred at room temperature for 5 minutes. To this mixture was added aldehyde **57** (5.4 mg, 0.01 mmol, 1 equiv) in DMF (0.1 mL), and the reaction mixture was heated at 60 °C overnight. Upon cooling to room temperature, the reaction was quenched with an aqueous NH_4F solution diluted with EtOAc and the resulting mixture was extracted three times with EtOAc. The combined organic phase was washed twice with a saturated *aq*. LiCl solution, brine, dried over Na_2SO_4, and concentrated *in vacuo*. The crude mixture was purified by preparative TLC (30% EtOAc/hexanes), affording compounds **64** (1.8 mg, 45%) and **65** (1.4 mg, 35%):



Compound 64: IR (thin film, cm^{-1}) 3505, 3071, 2930, 2857, 1769, 1666, 1469, 1428, 1358; ^1H NMR (700 MHz, $CDCl_3$) δ 7.70 – 7.63 (m, 4H), 7.45 (s, 2H), 7.41 – 7.36 (m, 4H), 5.12 (d, *J* = 4.2 Hz, 1H), 5.07 (brs, 1H), 4.94 (s, 1H), 4.57 (app. t, *J* = 6.6 Hz, 1H), 4.11 – 4.06 (m, 1H), 3.44 – 3.38 (m, 1H), 2.81 (qd, *J* = 6.8, 5.8 Hz, 1H), 2.63 (d, *J* = 13.2 Hz, 1H), 2.53 (dd, *J* = 13.2, 7.7 Hz, 1H), 2.31 (ddd, *J* = 6.8, 4.9, 4.2 Hz, 1H), 2.29 – 2.25 (m, 1H), 2.04 (d, *J* = 8.4 Hz, 1H), 1.67 (dd, *J* = 2.2, 1.0 Hz, 3H), 1.59 – 1.52 (m, 1H), 1.46 (d, *J* = 6.8 Hz, 3H), 1.07 (s, 9H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 179.6, 146.3, 136.1, 136.1, 133.9, 131.6, 129.9, 129.9, 127.8, 127.8, 127.7, 117.5, 79.6, 78.4, 64.6, 50.2, 46.9, 43.3, 41.3, 37.8, 27.2, 19.4, 12.3, 10.2; HRMS (ESI) *calcd.* for $[C_{31}H_{38}O_4SiNa]^+$ $(M+Na)^+$: m/z 525.2432, found 525.2442.

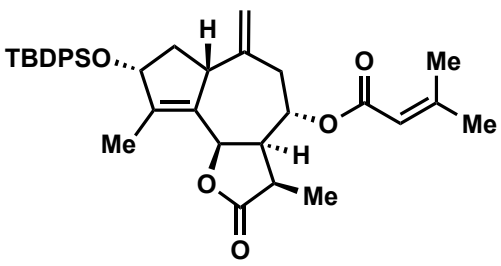


Compound 65: $[\alpha]_D^{23}$ = –5º (c 0.001 g/ml $CHCl_3$); IR (thin film): 3471, 2960, 2930, 2891, 2856, 1760, 1457, 1427, 1352, 1194 cm^{-1}; ^1H NMR (900 MHz, C_6D_6) δ 7.84 – 7.76 (m, 4H), 7.31 – 7.19 (m, 6H), 4.81 (s, 1H), 4.78 (s, 1H), 4.61 (t, *J* = 7.3 Hz, 1H), 4.11 (dd, *J* = 8.6, 3.6 Hz, 1H), 4.02 (td, *J* = 6.6, 3.5 Hz, 1H), 2.93 (d, *J* = 8.6 Hz, 1H), 2.61 (dd, *J* = 13.7, 6.8 Hz, 2H), 2.26 (dd, *J* = 13.5, 3.6 Hz, 1H), 2.04 (dt, *J* = 13.6, 7.1 Hz, 1H), 1.59 (dt, *J* = 13.3, 8.4 Hz, 1H), 1.46 (d, *J* = 2.8 Hz, 3H), 1.35 (dt, *J* = 5.9, 2.7 Hz, 1H), 1.32 – 1.27 (m, 1H), 1.21 (d, *J* = 2.8 Hz, 9H), 0.93 (dd, *J* = 7.7, 2.2 Hz, 3H).; ^{13}C NMR (226 MHz, C_6D_6) δ 178.40, 143.85, 138.13, 137.72, 136.44, 136.42, 134.71, 134.44, 130.20, 130.18, 128.35, 128.28, 115.90, 80.36, 78.25, 70.94, 50.64, 49.24, 40.78, 40.04, 35.03, 27.33, 19.54, 15.58, 11.63.; HRMS (ESI) *calcd.* for $[M+H]^+$ $(C_{31}H_{39}O_4Si)^+$ requires *m/z* 503.2612, found *m/z* 503.2608.



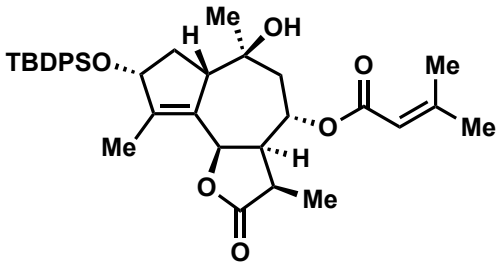
Chloride 66: A reaction tube was charged with a stir bar, SmI_2 (1.0 mL, 0.1M in THF, 10 equiv), and HMPA (69.6 μL, 0.4 mmol, 40 equiv) and cooled to –40 °C. To this solution was added aldehyde **57** (5.4 mg, 0.01 mmol, 1 equiv) in THF (0.1 mL) and the reaction was stirred at –40 °C for 1 hour. Upon complete consumption starting material, as judged by TLC (30% EtOAc in hexanes), the reaction was quenched with a mixture of saturated *aq*. Rochelle's salt solution and saturated *aq*. NH_4Cl, diluted with EtOAc, and the resulting mixture was extracted three times with EtOAc. The combined organic phase was washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The crude mixture was purified by preparative TLC (20% Et_2O/toluene), affording compound **66** (0.7 mg, 12%). $[\alpha]_D^{23}$ = –33º (c 0.001

g/ml $CHCl_3$); IR (thin film): 2931, 2885, 2856, 1769, 1472, 1457, 1427, 1351, 1200 cm^{-1}; ^1H NMR (900 MHz, C_6D_6-d_6) δ 7.79 – 7.71 (m, 4H), 7.24 (ddt, *J* = 12.0, 5.2, 2.1 Hz, 6H), 4.59 – 4.54 (m, 1H), 4.41 (s, 1H), 3.65 (dd, *J* = 10.4, 5.6 Hz, 1H), 3.28 (d, *J* = 11.4 Hz, 1H), 2.79 (d, *J* = 11.4 Hz, 1H), 2.62 – 2.57 (m, 1H), 2.21 (p, *J* = 7.4 Hz, 1H), 1.84 (dt, *J* = 13.3, 8.1 Hz, 1H), 1.73 (ddd, *J* = 10.4, 7.2, 5.0 Hz, 1H), 1.59 (d, *J* = 2.8 Hz, 3H), 1.31 (dt, *J* = 13.3, 6.0 Hz, 1H), 1.19 (s, 3H), 1.18 (s, 9H), 1.03 (d, *J* = 5.6 Hz, 1H), 0.53 (s, 3H).; ^{13}C NMR (226 MHz, C_6D_6) δ 177.67, 144.43, 136.37, 136.32, 134.68, 134.38, 130.21, 130.20, 128.35, 128.28, 127.76, 80.68, 72.25, 69.04, 49.31, 43.73, 43.16, 42.91, 40.67, 33.17, 27.31, 19.58, 12.01, 11.88, 11.67.; HRMS (ESI) *calcd.* for $[M+H]^+$ $(C_{31}H_{40}O_4SiCl)^+$ requires *m/z* 539.2379, found *m/z* 539.2379.



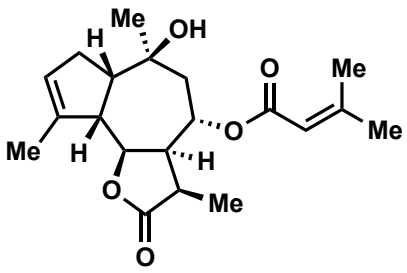
Lactone 59: A 25 mL round-bottom flask was charged with a stir bar, compound **58** (282 mg, 0.56 mmol, 1 equiv), DCC (231.5 mg, 1.12 mmol, 2 equiv), DMAP (137.1 mg, 1.12 mmol, 2 equiv), and dry DCM (5.6 mL). 3,3-Dimethylacrylic acid (112.3 mg, 1.12 mmol, 2 equiv) was added in one portion and the reaction was stirred at room temperature overnight. The reaction was quenched by the addition of saturated *aq*. $NaHCO_3$ solution and diluted with DCM. The aqueous phase was extracted with DCM three times and the combined organic phase was washed with 1M HCl, brine, dried over Na_2SO_4, and concentrated *in vacuo*. The crude mixture was purified by flash column chromatography (DCM, 1% MeOH in DCM), affording compound **59** (275 mg, 84%) as a white foam. $[\alpha]_D^{23}$ = –20º (c 0.001 g/ml $CHCl_3$); IR (thin film): 2929, 2855, 1777, 1716, 1648, 1445, 1427, 1380, 1261 cm^{-1}; ^1H NMR (900 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 39.8, 7.4 Hz, 4H), 7.47 – 7.33 (m, 6H), 5.63 (s, 1H), 5.15 (d, *J* = 4.9 Hz, 1H), 5.00 (s, 1H), 4.87 (s, 1H), 4.69 – 4.61 (m, 2H), 3.30 (s, 1H), 2.90 (p, *J* = 7.3 Hz, 1H), 2.62 (q, *J* = 7.0 Hz, 1H), 2.40 (t, *J* = 11.5 Hz, 1H), 2.37 – 2.32 (m, 1H), 2.23 – 2.19 (m, 1H), 2.19 (s, 3H), 1.90 (s, 3H), 1.70 (s, 3H), 1.46 (dt, *J* = 13.7, 7.7 Hz, 1H), 1.14 (d, *J* = 7.1 Hz, 3H), 1.08 (s, 9H).; ^{13}C NMR (226 MHz, $CDCl_3$) δ 178.31, 165.33, 158.12, 145.31, 145.05, 136.14, 136.13, 134.31, 134.03, 131.52, 129.90, 129.85, 127.78, 127.70, 115.86, 114.89, 79.93, 76.68, 73.38, 48.03, 47.48, 41.99, 41.94, 36.44, 27.66, 27.19, 20.49, 19.43, 12.24, 9.83.; HRMS (ESI) *calcd.* for $[M+H]^+$ $(C_{36}H_{45}O_5Si)^+$ requires *m/z* 585.3031, found *m/z* 585.3026.

Lactone 61: A reaction tube was charged with a stir bar, compound **59** (50 mg, 0.085 mmol, 1 equiv), and Carreira's catalyst **60** (8.0 mg, 0.017 mmol, 20 mol%). The tube was degassed and backfilled with O_2. In a separate tube, O_2 was bubbled through EtOH while sonicating for 10 minutes. This EtOH was used as the reaction solvent. To the reaction vial was added 0.9 mL of the oxygenated EtOH followed by $PhSiH_3$ (26.3 μL, 0.214 mmol, 2.5 equiv), and the reaction was stirred at room temperature for 2 hours. After full consumption of starting material, as judged by TLC (30% EtOAc in hexanes), PPh_3 (44.8 mg, 0.171 mmol, 2 equiv) was added and the solution was stirred for an additional 30 minutes. The solution was then passed through a plug of silica using EtOAc as the eluent and concentrated *in vacuo*. The crude mixture was purified by flash column chromatography (EtOAc/hexanes, 0% to 30%), affording compound **61** (26 mg, 50%, 1.9:1 *dr*) as a colorless oil. $[\alpha]_D^{23}$ = +14º (c 0.001 g/ml $CHCl_3$); IR (thin

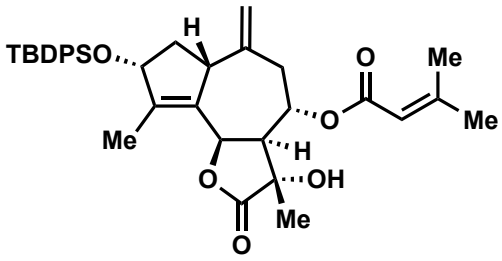


film): 2928, 2855, 1771, 1714, 1650, 1428, 1227 cm^{-1}; ^1H NMR (900 MHz, $CDCl_3$) δ 7.67 (m, 4H), 7.45 – 7.42 (m, 2H), 7.39 – 7.36 (m, 4H), 5.66 – 5.58 (m, 1H), 5.24 (d, *J* = 6.1 Hz, 1H), 5.18 (td, *J* = 9.4, 1.6 Hz, 1H), 4.54 (dd, *J* = 7.7, 3.1 Hz, 1H), 2.91 (p, *J* = 7.5 Hz, 1H), 2.81 – 2.75 (m, 2H), 2.37 (s, 1H), 2.19 (d, *J* = 1.3 Hz, 3H), 2.06 (dt, *J* = 13.9, 7.9 Hz, 1H), 1.94 (dd, *J* = 14.7, 9.6 Hz, 1H), 1.91 (d, *J* = 1.4 Hz, 3H), 1.78 (dq, *J* = 13.9, 3.5, 2.5 Hz, 2H), 1.54 (dd, *J* = 1.9, 0.8 Hz, 3H), 1.23 (s, 3H), 1.22 (d, *J* = 7.4 Hz, 3H), 1.08 (s, 9H).; ^{13}C NMR (226 MHz, $CDCl_3$) δ 178.27, 165.83, 158.99, 146.22, 136.18, 136.17, 134.13, 133.99, 132.95, 129.97, 129.90, 127.79, 127.75, 115.60, 79.54, 75.88, 72.63, 67.01, 53.23, 48.53, 46.25, 40.38, 35.23, 27.71, 27.49, 27.22, 20.53, 19.45, 12.57, 11.17.; HRMS (ESI) *calcd.* for $[C_{36}H_{46}O_6SiNa]^+$ $(M+Na)^+$: m/z 625.2956, found 625.2951.

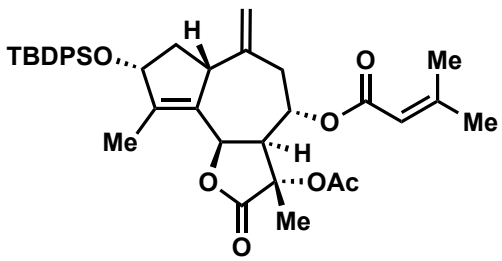
Compound SI-4: A reaction tube was charged with a stir bar, compound **61** (12.3 mg, 0.02 mmol, 1 equiv), THF (0.3 mL) and HOAc (11.6 μL, 0.204 mmol, 10 equiv). TBAF (0.32 mL, 1.0M in THF, 16 equiv) was then added and the reaction stirred at room temperature for 48 hours. After the starting material was consumed as judged by TLC (70% EtOAc in hexanes), the reaction was quenched by the addition of saturated *aq*. NH_4Cl and the mixture was extracted three times with EtOAc. The combined organic phase was washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The crude mixture was purified by column chromatography (EtOAc/hexanes, 0% to 60%), affording the desired product **SI-4** (5.9 mg, 79%) as a colorless oil. $[\alpha]_D^{23}$ = +12° (c 0.001 g/ml $CHCl_3$); IR (thin film): 2924, 2854, 1773, 1741, 1717, 1458, 1427, 1376, 1349, 1228 cm^{-1}; ^1H NMR (900 MHz, C_6D_6) δ 5.62 (s, 1H), 5.47 – 5.38 (m, 1H), 4.79 (d, *J* = 6.0 Hz, 1H), 3.94 (q, *J* = 6.5, 5.8 Hz, 1H), 2.66 (q, *J* = 6.0, 4.4 Hz, 1H), 2.26 – 2.23 (m, 1H), 2.23 – 2.19 (m, 1H), 2.06 (d, *J* = 1.2 Hz, 3H), 2.06 (s, 1H), 1.89 (dt, *J* = 13.7, 7.8 Hz, 1H), 1.77 (dd, *J* = 14.4, 2.1 Hz, 1H), 1.68 (dd, *J* = 14.4, 9.8 Hz, 1H), 1.57 (d, *J* = 1.9 Hz, 3H), 1.43 (d, *J* = 1.3 Hz, 3H), 1.38 (dt, *J* = 13.8, 4.4 Hz, 1H), 1.23 (d, *J* = 7.2 Hz, 3H), 1.04 (s, 3H), 0.85 (d, *J* = 5.8 Hz, 1H).; ^{13}C NMR (226 MHz, C_6D_6) δ 177.22, 165.43, 158.14, 144.93, 134.10, 116.14, 78.16, 75.35, 71.82, 67.44, 53.89, 48.60, 45.49, 40.22, 35.78, 27.46, 27.09, 20.17, 11.92, 11.22.; HRMS (ESI) *calcd.* for $[C_{20}H_{28}O_6Na]^+$ $(M+Na)^+$: m/z 387.1778, found 387.1776.



Slovanolide 18: A reaction tube was charged with a stir bar, compound **SI-4** (2.7 mg, 7.4 μmol, 1 equiv), PPh_3 (5.8 mg, 22.2 μmol, 3 equiv), IPNBSH (5.7 mg, 22.2 μmol, 3 equiv), THF (0.15 mL), and cooled to 0 °C. To this mixture was added a solution of DIAD (4.4 μL, 22.2 μmol, 3 equiv) in THF (0.05 mL) and the reaction was stirred at 0 °C for 1 hour. TLC analysis (50% EtOAc in hexanes) of the reaction mixture showed complete consumption of starting material, at which point 0.1 mL of TFE/H_2O (1:1 mixture) was added, the vial was removed from the ice bath and allowed to stir at room temperature overnight. The reaction was diluted with brine and the resulting mixture was extracted three times with EtOAc. The combined organic phase was washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The crude mixture was purified by preparative TLC (50% EtOAc/hexanes), affording the desired product **18** (1.0 mg, 39%) as a colorless film. $[\alpha]_D^{23}$ = +18º (c 0.001 g/ml $CHCl_3$); IR (thin film): 3480, 2922, 2854, 1770, 1714, 1695, 1646, 1454, 1377, 1349, 1265, 1230 cm^{-1}; ^1H NMR (900 MHz, $CDCl_3$) δ 5.66 (p, *J* = 1.3 Hz, 1H), 5.55 – 5.50 (m, 1H), 5.43 – 5.39 (m, 1H), 4.58 (dd, *J* = 11.5, 9.1 Hz, 1H), 3.08 – 3.01 (m, 1H), 2.89 (s, 1H), 2.75 – 2.68 (m, 1H), 2.62 (dd, *J* = 11.5, 5.6 Hz, 1H), 2.43 (dt, *J* = 12.4, 6.3 Hz, 1H), 2.19 (d, *J* = 1.3 Hz, 3H), 2.09 (t, *J* = 13.7 Hz, 1H), 2.05 (dd, *J* = 14.7, 9.5 Hz, 1H), 1.93 (d, *J* = 1.4 Hz, 3H), 1.89 (dt, *J* = 3.0, 1.5 Hz, 3H), 1.87 – 1.83 (m, 1H), 1.31 (d, *J* = 7.8 Hz, 3H), 1.23 (s, 3H).; ^{13}C NMR (226 MHz, $CDCl_3$) δ 179.60, 167.02, 159.28, 147.28, 125.39, 115.59, 80.92, 71.62, 66.62, 55.84, 50.27, 45.66, 43.44, 36.41, 32.41, 31.30, 27.75, 20.57, 18.90, 13.63.; HRMS (ESI) *calcd.* for $[C_{20}H_{28}O_5Na]^+$ $(M+Na)^+$: m/z 371.1829, found 371.1828.

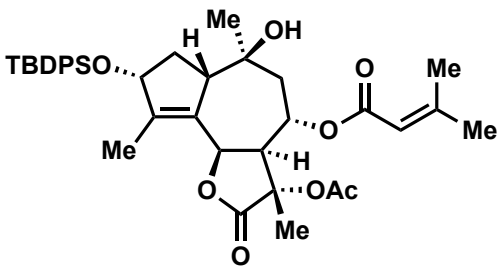


Compound SI-5: A large reaction tube was charged with a stir bar, compound **59** (58.5 mg, 0.1 mmol, 1 equiv), and dry THF (2.0 mL). The solution was cooled to –78 °C and NaHMDS (0.11 mL, 1.0 M in THF, 1.1 equiv) was added dropwise. The mixture was allowed to stir at –78 °C for 30 minutes at which point a solution of Davis oxaziridine (31.4 mg, 0.12 mmol, 1.2 equiv) in THF (0.5 mL) was added dropwise. The reaction was further stirred at –78 °C for 30 minutes until consumption of the starting material was complete as judged by TLC (30% EtOAc in Hexanes), the reaction was quenched with a 1M HOAc solution and warmed to room temperature. The mixture was diluted with EtOAc and 1M aqueous HCl, the aqueous phase was extracted with EtOAc three times, the combined organic phase was washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The crude mixture was purified by flash column chromatography (gradient 100% DCM to 10% Et_2O in DCM), affording compound **SI-5** (55 mg, 92%) as a white foam. $[\alpha]_D^{23} = -39^{o}$ (c 0.001 g/ml $CHCl_3$); IR (thin film): 2931, 2856, 1785, 1717, 1649, 1445, 1427, 1379, 1219 cm^{-1}; ^1H NMR (900 MHz, $CDCl_3$) δ 7.72 – 7.68 (m, 2H), 7.66 – 7.63 (m, 2H), 7.47 – 7.41 (m, 2H), 7.38 (dt, *J* = 19.0, 7.4 Hz, 4H), 5.73 (d, *J* = 5.2 Hz, 1H), 5.66 (p, *J* = 1.4 Hz, 1H), 4.99 (s, 1H), 4.87 (s, 1H), 4.65 – 4.61 (m, 1H), 4.61 – 4.56 (m, 1H), 3.28 (t, *J* = 8.3 Hz, 1H), 2.52 (dd, *J* = 8.6, 5.2 Hz, 1H), 2.42 (dd, *J* = 12.6, 10.5 Hz, 1H), 2.34 (dd, *J* = 12.6, 3.0 Hz, 1H), 2.22 – 2.19 (m, 1H), 2.19 (d, *J* = 1.4 Hz, 3H), 1.91 (d, *J* = 1.4 Hz, 3H), 1.73 (dd, *J* = 2.3, 1.1 Hz, 3H), 1.45 (ddd, *J* = 12.9, 8.3, 7.1 Hz, 1H), 1.39 (s, 3H), 1.08 (s, 9H). ^{13}C NMR (226 MHz, $CDCl_3$) δ 176.34, 165.39, 158.58, 145.98, 145.09, 136.14, 136.13, 134.33, 134.00, 131.00, 129.90, 129.84, 127.78, 127.69, 115.74, 114.85, 79.94, 77.74, 75.96, 72.87, 53.84, 47.31, 41.97, 36.45, 27.69, 27.19, 20.53, 19.71, 19.43, 12.25.; HRMS (ESI) *calcd.* for $[C_{36}H_{44}O_6SiNa]^+$ $(M+Na)^+$: m/z 623.2799, found 623.2800.



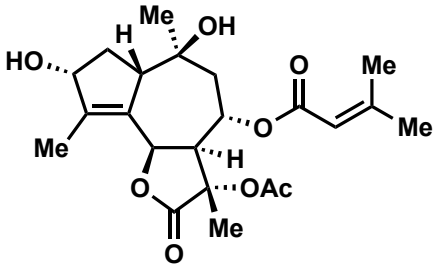
Compound 62: A reaction tube was charged with a stir bar, compound **SI-5** (49.3 mg, 0.082 mmol, 1 equiv), DMAP (1.0 mg, 8.2 μmol, 10 mol%) and DCM (1.0 mL). To the solution was added pyridine (19.8 μL, 0.246 mmol, 3 equiv) then Ac_2O (11.6 μL, 0.123 mmol, 1.5 equiv) and the reaction was stirred at room temperature for 3 hours. Upon full consumption of the starting material as judged by TLC (20% EtOAc in Hexanes), the reaction was quenched with 1M HCl and diluted with EtOAc. The aqueous phase was extracted with EtOAc three times, the combined organic phase was washed with brine, dried over

Na_2SO_4, and concentrated *in vacuo*. The crude mixture was purified by flash column chromatography (gradient 100% hexanes to 20% EtOAc in hexanes), affording compound **62** (52.2 mg, 99%) as a colorless oil. $[\alpha]_D^{23}$ = –46º (c 0.001 g/ml $CHCl_3$); IR (thin film): 2927, 2855, 1793, 1748, 1716, 1649, 1444, 1427, 1377, 1224 cm^{-1}; ^1H NMR (900 MHz, $CDCl_3$) δ 7.71 – 7.67 (m, 2H), 7.66 – 7.63 (m, 2H), 7.46 – 7.41 (m, 2H), 7.37 (dt, *J* = 22.0, 7.4 Hz, 4H), 5.70 – 5.66 (m, 1H), 5.54 (d, *J* = 7.0 Hz, 1H), 4.95 (td, *J* = 7.3, 5.2 Hz, 1H), 4.90 (s, 1H), 4.88 (t, *J* = 1.2 Hz, 1H), 4.65 (t, *J* = 7.0 Hz, 1H), 3.28 (t, *J* = 7.5 Hz, 1H), 3.20 (t, *J* = 7.1 Hz, 1H), 2.55 – 2.46 (m, 2H), 2.19 (d, *J* = 1.3 Hz, 3H), 2.15 – 2.10 (m, 1H), 2.08 (s, 3H), 1.89 (d, *J* = 1.4 Hz, 3H), 1.72 (dd, *J* = 2.3, 1.1 Hz, 3H), 1.54 (s, 3H), 1.53 – 1.50 (m, 1H), 1.08 (s, 4H). ^{13}C NMR (226 MHz, $CDCl_3$) δ 173.46, 169.84, 165.42, 158.70, 144.91, 144.54, 136.15, 136.12, 134.35, 133.92, 131.29, 129.94, 129.86, 127.81, 127.69, 115.71, 115.21, 82.18, 79.87, 75.87, 70.87, 50.81, 47.84, 41.37, 37.19, 27.69, 27.17, 21.50, 20.54, 19.43, 18.10, 12.15.; HRMS (ESI) *calcd.* for $[C_{38}H_{46}O_7SiNa]^+$ $(M+Na)^+$: m/z 665.2905, found 665.2908.

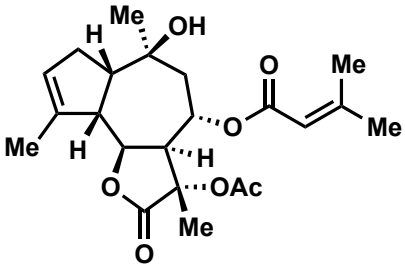


Compound 63: A reaction tube was charged with a stir bar, compound **62** (12.9 mg, 0.02 mmol, 1 equiv), and Carreira's catalyst **60** (1.9 mg, 0.004 mmol, 20 mol%). The tube was degassed and backfilled with O_2. In a separate tube O_2 was bubbled through EtOH while sonicating for 10 minutes. This EtOH was used as the reaction solvent. To the reaction vial was added 0.2 mL of the oxygenated EtOH followed by $PhSiH_3$ (6.2 μL, 0.05 mmol, 2.5 equiv) and the reaction was allowed to stir at room temperature for 2 hours. After the consumption of the starting material was complete as judged by TLC (30% EtOAc in hexanes), PPh_3 (10.5 mg, 0.04 mmol, 2 equiv) was added and the solution was allowed to stir for an additional 30 minutes. The solution was then pushed through a plug of silica using EtOAc as the eluent and concentrated *in vacuo*. The crude mixture was purified by flash column chromatography (EtOAc/hexanes, 0% to 20%), affording compound **63** (6.1 mg, 45%) as a colorless oil. $[\alpha]_D^{23}$ = –72º (c 0.001 g/ml $CHCl_3$); IR (thin film): 3462, 2929, 2856, 1788, 1742, 1717, 1647, 1446, 1427, 1375, 1350, 1229 cm^{-1}; ^1H NMR (700 MHz, C_6D_6) δ 7.76 – 7.70 (m, 4H), 7.25 – 7.19 (m, 6H), 5.65 – 5.53 (m, 2H), 5.19 (d, *J* = 10.2 Hz, 1H), 4.41 (d, *J* = 7.8 Hz, 1H), 3.72 (t, *J* = 9.9 Hz, 1H), 2.65 (d, *J* = 8.0 Hz, 1H), 2.13 (d, *J* = 27.8 Hz, 1H), 2.05 (s, 3H), 1.93 (dt, *J* = 14.4, 2.9 Hz, 1H), 1.87 (ddd, *J* = 13.4, 8.8, 7.3 Hz, 1H), 1.73 (dd, *J* = 15.2, 2.2 Hz, 1H), 1.66 (s, 3H), 1.64 (s, 3H), 1.44 (s, 3H), 1.41 (s, 3H), 1.17 (s, 9H), 1.11 (s, 3H).; ^{13}C NMR (176 MHz, C_6D_6) δ 173.41, 169.58, 165.74, 158.68, 146.67, 136.48, 136.41, 134.52, 134.42, 133.30, 130.16, 130.12, 128.35, 127.99, 115.94, 79.51, 79.25, 73.30, 72.21, 65.66, 54.26,

49.00, 46.91, 33.78, 27.35, 27.08, 25.15, 20.53, 20.27, 20.02, 19.60, 13.12.; HRMS (ESI) *calcd.* for $[M+Na]^+$ $(C_{38}H_{48}O_8SiNa)^+$ requires *m/z* 683.3011, found *m/z* 683.3009.

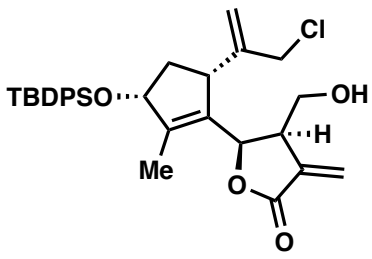


Compound SI-6: A reaction tube was charged with a stir bar, compound **63** (6.3 mg, 9.5 μmol, 1 equiv), and THF (0.2 mL) followed by HOAc (5.4 μL, 0.095 mmol, 10 equiv) then TBAF (0.16 mL, 1.0M in THF, 16 equiv) and the reaction was allowed to stir at room temperature for 48 hours. After the consumption of the starting material was complete as judged by TLC (70% EtOAc in hexanes), the reaction was quenched by addition of *sat.* NH_4Cl, and the resulting mixture was extracted three times with EtOAc. The combined organic phase was washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The crude mixture was purified by column chromatography (EtOAc/hexanes, 0% to 75%), affording the desired product **SI-6** (3.1 mg, 77%) as a colorless oil. $[\alpha]_D^{23}$ = –26° (c 0.001 g/ml $CHCl_3$); IR (thin film): 3432, 3418, 3373, 2918, 2851, 1784, 1742, 1718, 1647, 1447, 1376, 1351 cm^{-1}; ^1H NMR (700 MHz, C_6D_6) δ 5.64 (t, *J* = 10.1 Hz, 1H), 5.61 (p, *J* = 1.4 Hz, 1H), 5.17 – 5.13 (m, 1H), 3.93 (m, 1H), 3.73 (t, *J* = 10.0 Hz, 1H), 2.73 (d, *J* = 8.6 Hz, 1H), 2.10 (d, *J* = 4.2 Hz, 1H), 2.05 (d, *J* = 1.2 Hz, 3H), 1.97 (dt, *J* = 14.6, 8.3 Hz, 1H), 1.73 – 1.69 (m, 4H), 1.68 (dt, *J* = 14.8, 2.9 Hz, 1H), 1.65 (s, 3H), 1.47 (s, 3H), 1.41 (d, *J* = 1.3 Hz, 3H), 1.38 (dd, *J* = 15.2, 10.5 Hz, 1H), 0.95 (s, 1H), 0.91 (s, 3H). ^{13}C NMR (176 MHz, C_6D_6) δ 173.43, 169.59, 165.74, 158.70, 146.53, 133.31, 115.92, 79.18, 77.96, 73.25, 71.87, 65.57, 54.35, 48.98, 46.88, 33.54, 27.07, 24.77, 20.53, 20.26, 19.98, 12.63.; HRMS (ESI) *calcd.* for $[C_{22}H_{30}O_8Na]^+$ $(M+Na)^+$: m/z 445.1833, found 445.1828.

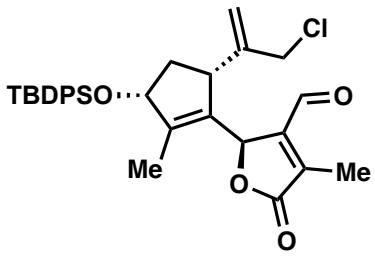


Montanolide (23): A reaction tube was charged with a stir bar, compound **SI-6** (2 mg, 5.2 μmol, 1 equiv), PPh_3 (4 mg, 15.5 μmol, 3 equiv), IPNBSH (3.9 mg, 15.5 μmol, 3 equiv), THF (0.15 mL), and cooled to 0 °C. To this mixture was added a solution of DIAD (3 μL, 15.5 μmol, 3 equiv) in THF (0.05 mL) and the reaction was stirred at 0-4 °C overnight. A solution of *p*TsOH (0.4 mg, 2.6 μmol, 0.5 equiv) in 0.1 mL of H_2O was added and the vial was heated to 55 °C for 1 hour. The reaction was diluted with brine and the resulting mixture was extracted three times with EtOAc. The combined organic phase was washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The crude mixture was purified by preparative TLC (15% Et_2O in DCM), affording **23** (0.8 mg, 51%). $[\alpha]_D^{23}$ = –7° (c 0.001 g/ml $CHCl_3$);

IR (thin film): 3490, 2921, 2851, 2018, 1977, 1788, 1739, 1717, 1649, 1377, 1320 cm^{-1}; ^{1}H NMR (900 MHz, $CDCl_3$) δ 5.61 (p, *J* = 1.4 Hz, 1H), 5.56 (dt, *J* = 3.5, 1.7 Hz, 1H), 5.50 (dd, *J* = 11.4, 9.3 Hz, 1H), 4.70 (dd, *J* = 11.6, 9.9 Hz, 1H), 3.61 (dd, *J* = 11.4, 9.9 Hz, 1H), 2.77 (s, 1H), 2.57 (dd, *J* = 11.6, 5.6 Hz, 1H), 2.41 (dt, *J* = 12.2, 6.3 Hz, 1H), 2.20 (d, *J* = 1.3 Hz, 3H), 2.20 – 2.16 (m, 1), 2.09 (m, 4H), 2.00 (dd, *J* = 14.9, 9.4 Hz, 1H), 1.94 (d, *J* = 1.4 Hz, 3H), 1.88 (dt, *J* = 2.9, 1.5 Hz, 3H), 1.82 (dd, *J* = 14.4, 1.7 Hz, 1H), 1.54 (s, 1H)*, 1.22 (s, 3H).; ^{13}C NMR (226 MHz, $CDCl_3$) δ 174.35, 169.98, 166.78, 159.45, 147.28, 125.89, 115.52, 78.51, 78.42, 71.42, 66.22, 56.07, 49.39, 47.47, 43.71, 32.30, 31.24, 27.83, 21.20, 20.65, 20.22, 18.94.; ^{1}H NMR (900 MHz, C_6D_6) δ 5.67 (dd, *J* = 11.4, 9.5 Hz, 1H), 5.65 (t, *J* = 1.5 Hz, 1H), 5.34 (dt, *J* = 3.5, 1.7 Hz, 1H), 4.35 (dd, *J* = 11.6, 9.7 Hz, 1H), 3.76 (dd, *J* = 11.4, 9.7 Hz, 1H), 2.61 (s, 1H), 2.50 (dd, *J* = 11.6, 5.6 Hz, 1H), 2.34 (dt, *J* = 12.2, 6.4 Hz, 1H), 2.05 (d, *J* = 1.3 Hz, 3H), 1.92 (q, *J* = 1.8 Hz, 3H), 1.81 – 1.74 (m, 1H), 1.70 (s, 3H), 1.61 – 1.54 (m, 2H), 1.47 (s, 3H), 1.47 – 1.44 (m, 1H), 1.43 (d, *J* = 1.3 Hz, 3H), 0.86 (s, 3H). ^{13}C NMR (226 MHz, C_6D_6) δ 173.53, 169.51, 166.69, 158.78, 147.30, 125.89, 116.07, 78.87, 77.69, 70.92, 66.68, 56.16, 49.71, 47.60, 43.87, 32.28, 31.05, 27.14, 20.69, 20.26, 18.86; HRMS (ESI) *calcd*. for $[M+Na]^+$ ($C_{22}H_{30}O_7Na$)$^+$ requires *m/z* 429.1884, found *m/z* 429.1885. *Not visible, shielded by water peak.

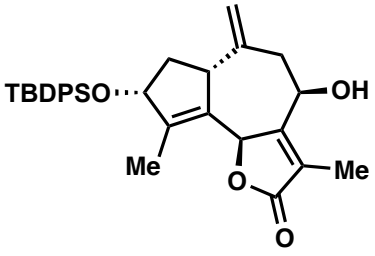


Compound SI-7: A 500 mL round-bottom flask was charged with a stir bar, compound **55** (4.0 g, 5.9 mmol, 1 equiv), phosphate buffer (12 mL, pH = 7.5), and DCM (120 mL). 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (2.7 g, 12 mmol, 2 equiv) was added in one portion, and the resulting mixture was vigorously stirred at room temperature for 8 hours. After consumption of the starting material was deemed complete as judged by TLC, the reaction was quenched by the addition of saturated *aq.* $Na_2S_2O_3$ (80 mL). The aqueous phase was extracted with DCM (120 mL × 2), and the combined organic phase was washed with saturated *aq* $NaHCO_3$ (200 mL), H_2O (200 mL), and brine (200 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude mixture was purified by flash column chromatography (EtOAc/hexane, 1:4 to 2:1), affording **SI-7** (3.1 g, 94%) as a colorless oil: $[\alpha]_D^{20} = -40°$ (c 0.008 g/mL, $CHCl_3$); ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.71 – 7.62 (m, 4H), 7.47 – 7.35 (m, 6H), 6.27 (d, *J* = 1.9 Hz, 1H), 5.73 (d, *J* = 1.9 Hz, 1H), 5.36 (s, 1H), 5.27 (s, 1H), 5.05 (d, *J* = 7.2 Hz, 1H), 4.58 (dd, *J* = 7.4, 2.9 Hz, 1H), 4.17 – 4.08 (m, 2H), 3.52 (app. dt, *J* = 11.0, 6.4 Hz, 1H), 3.39 (ddd, *J* = 11.0, 7.5, 5.2 Hz, 1H), 3.26 (app. q, *J* = 7.1 Hz, 1H), 3.20 (brd, *J* = 8.8 Hz, 1H), 2.22 (ddd, *J* = 14.0, 8.7, 7.4 Hz, 1H), 1.71 (dd, *J* = 2.0, 0.9 Hz, 3H), 1.64 (app. dt, *J* = 14.1, 3.4 Hz, 1H), 1.48 (app. t, *J* = 5.8 Hz, 1H), 1.07 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.7, 147.2, 142.3, 136.7, 136.2, 136.2, 134.3, 133.9, 132.1, 129.9, 129.8, 127.8, 127.7, 124.2, 117.2, 81.6, 77.5, 77.4, 77.2, 76.9, 62.3, 49.6, 47.3, 45.0, 39.9, 27.1, 19.4, 13.5; IR (thin film, cm^{-1}) 3482, 3072, 3049, 2932, 2890, 2858, 1766, 1662, 1472, 1428; HRMS (ESI+) *calcd.* for $[C_{31}H_{37}ClO_4SiNa]^+$ $(M+Na)^+$: m/z 559.2047, found 559.2060.



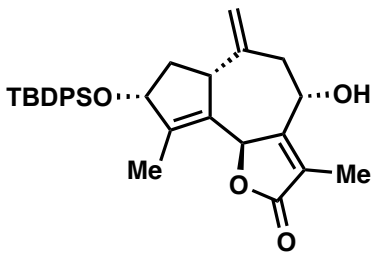
Aldehyde 70: A 100 mL round-bottom flask was charged with a stir bar, compound **SI-7** (1.26 g, 2.34 mmol, 1 equiv), $RuHCl(CO)(PPh_3)_3$ (223 mg, 0.234 mmol, 0.1 equiv), and DCE (24 mL). The mixture was degassed by bubbling of argon for 10 minutes, and then stirred at 60 ºC for 16 hours. After the conversion of the starting material to intermediate was complete as judged by TLC (EtOAc/hexane, 1:1), *aq.* $NaHCO_3/Na_2CO_3$ buffer (24 mL, pH = 8.6), KBr (0.28 g, 2.34 mmol, 1 equiv), *aq.* NaOCl (2.4 mL, 14% available chlorine), and (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) (37 mg, 0.24 mmol, 0.1 equiv) were added sequentially to the reaction flask. The reaction mixture was further stirred at room temperature for 1 hour until the reaction was complete as judged by TLC (EtOAc/hexane, 1:2). The mixture was then mixed with saturated *aq.* $Na_2S_2O_3$ (50 mL). The resulting mixture was extracted with DCM (50 mL × 2), and the combined organic phase was washed with *sat.* $NaHCO_3$ (100 mL), H_2O (100

mL), and brine (100 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude mixture was purified by flash column chromatography (EtOAc:DCM:hexane, 1:1:15 to 1:1:5), affording **70** (1.08 g, 86%) as a colorless oil: $[\alpha]_D^{20}$ = +21.2° (c 0.010 g/mL, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.09 (s, 1H), 7.71 – 7.59 (m, 4H), 7.47 – 7.34 (m, 6H), 5.81 (d, *J* = 2.3 Hz, 1H), 5.20 (s, 1H), 5.06 (s, 1H), 4.58 (dd, *J* = 7.5, 2.7 Hz, 1H), 3.95 (d, *J* = 13.3 Hz, 1H), 3.80 (d, *J* = 13.3 Hz, 1H), 3.35 (d, *J* = 8.7 Hz, 1H), 2.23 – 2.14 (m, 4H), 1.71 (d, *J* = 1.8 Hz, 3H), 1.51 (app. dt, *J* = 14.1, 3.4 Hz, 1H), 1.06 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.0, 173.5, 151.0, 147.2, 146.3, 139.5, 136.2, 136.1, 134.0, 133.9, 130.9, 129.9, 129.9, 127.8, 127.8, 116.5, 80.7, 77.3, 47.8, 45.9, 39.4, 27.1, 19.4, 12.8, 9.5; IR (thin film, cm^{-1}) 3072, 3049, 2932, 2892, 2857, 1766, 1688, 1589, 1472, 1458; HRMS (ESI+) *calcd.* for $[C_{31}H_{35}ClO_4SiNa]^+$ $(M+Na)^+$: m/z 557.1891, found 557.1887.

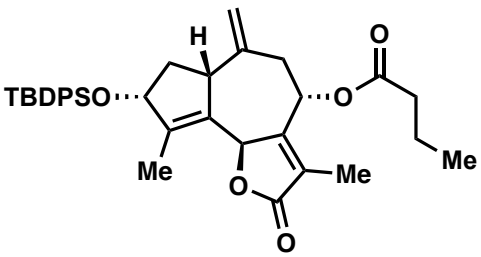


Compound 71: A reaction tube was charged with a stir bar, anhydrous $SnCl_2$ (57 mg, 0.3 mmol, 5 equiv), $PdCl_2(PhCN)_2$ (3.5 mg, 0.0091 mmol, 0.15 equiv), and dry DMF (2 mL). The resulting mixture was stirred at room temperature for 10 minutes and compound **70** (32 mg, 0.06 mmol, 1 equiv) was added in one portion as a solution in dry DMF (1 mL). The reaction mixture was then stirred at 60 ºC for 8 hours. After the reaction was deemed complete as judged by TLC (EtOAc/hexane, 1:2), the reaction mixture was diluted with EtOAc (10 mL) and quenched by addition of *aq.* NH_4F (10 mL, 5% w/w). The aqueous phase was extracted with EtOAc (10 mL × 2) and the combined organic phase was washed with H_2O (20 mL × 2) and brine (20 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude mixture was purified by flash column chromatography (EtOAc/hexane, 1:4), affording **71** (29.0 mg, 95%) as a colorless oil: $[\alpha]_D^{20}$ = –42.6° (c 0.007 g/mL, $CHCl_3$); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.69 – 7.63 (m, 4H), 7.46 – 7.41 (m, 2H), 7.40 – 7.35 (m, 4H), 5.53 (s, 1H), 4.92 – 4.87 (m, 2H), 4.82 – 4.78 (m, 1H), 4.55 (dd, *J* = 7.0, 6.3 Hz, 1H), 3.07 – 3.00 (m, 1H), 2.84 (dd, *J* = 13.5, 5.1 Hz, 1H), 2.31 (dd, *J* = 13.5, 4.0 Hz, 1H), 2.22 (ddd, *J* = 13.2, 8.0, 7.0 Hz, 1H), 2.07 (d, *J* = 8.5 Hz, 1H), 2.02 (app. t, *J* = 1.8 Hz, 3H), 1.76 (dd, *J* = 2.3, 1.0 Hz, 3H), 1.51 (ddd, *J* = 13.2, 7.2, 6.3 Hz, 1H), 1.11 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.5, 159.7, 148.6, 146.8, 136.1, 136.1, 134.2, 133.9, 131.6, 130.0, 129.9, 127.8, 127.7, 126.7, 113.7, 79.0, 76.6, 68.9, 47.5, 42.0, 41.5, 27.2, 19.4, 12.3, 9.9; IR (thin film, cm^{-1}) 3444, 3071, 2956, 2931, 2892, 2857, 1736, 1674, 1472, 1428; HRMS (ESI+) *calcd.* for $[C_{31}H_{37}O_4Si]^+$ $(M+H)^+$: m/z 501.2461, found 501.2453.

[Note: These conditions afforded **71** in 90% yield on a gram scale as well.]



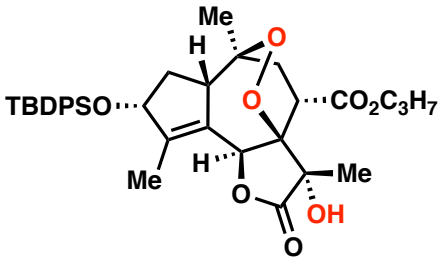
epi-**71:** $[\alpha]_D^{20}$ = –50.2° (c 0.010 g/mL, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.70 – 7.64 (m, 4H), 7.47 – 7.40 (m, 2H), 7.41 – 7.35 (m, 4H), 5.80 (s, 1H), 5.00 (s, 1H), 4.92 – 4.84 (m, 2H), 4.59 (app. t, *J* = 6.4 Hz, 1H), 2.95 – 2.90 (m, 1H), 2.59 (dd, *J* = 12.7, 6.0 Hz, 1H), 2.53 (dd, *J* = 12.7, 7.3 Hz, 1H), 2.14 (app. dt, *J* = 13.3, 7.6 Hz, 1H), 2.09 (d, *J* = 5.0 Hz, 1H), 1.80 (app. t, *J* = 1.5 Hz, 3H), 1.75 (s, 3H), 1.59 (app. dt, *J* = 13.3, 5.7 Hz, 2H), 1.09 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.3, 160.8, 148.0, 145.6, 136.1, 136.1, 134.2, 133.9, 131.7, 129.9, 129.9, 127.8, 127.7, 125.3, 114.5, 79.2, 76.4, 65.7, 48.4, 41.2, 40.7, 27.2, 19.5, 12.4, 8.6; IR (thin film, cm^{-1}) 3434, 3071, 2957, 2931, 2891, 2858, 1758, 1737, 1472, 1428; HRMS (ESI+) *calcd.* for $[C_{31}H_{37}O_4Si]^+$ $(M+H)^+$: m/z 501.2461, found 501.2454.



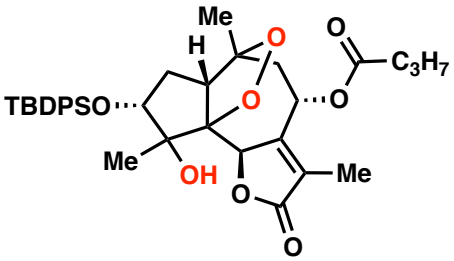
Compound 69: A 100 mL round-bottom flask was charged with a stir bar, compound **71** (711 mg, 1.42 mmol, 1 equiv), and PPh_3 (1.18 g, 4.26 mmol, 3 equiv). The mixture was azeotropically dried with toluene (20 mL × 3), and then dissolved in THF (14.2 mL). The reaction mixture was cooled to 0 ºC over an ice bath, followed by the addition of *n*-butyric acid (0.4 mL, 4.31 mmol, 3 equiv) and diisopropyl azodicarboxylate (DIAD) (0.84 mL, 4.29, 3 equiv). The resulting mixture was allowed to warm up to room temperature and stirred for 8 hours. After the consumption of the starting material was complete as judged by TLC (EtOAc/hexane, 1:2), the reaction was quenched by addition of *sat.* $NaHCO_3$ (50 mL). The aqueous phase was extracted with EtOAc (50 mL × 2), and the combined organic phase was washed with H_2O (20 mL × 2) and brine (20 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude mixture was purified by flash column chromatography (EtOAc/hexane, 1:4), affording **69** (570 mg, 70%) as a colorless oil: $[\alpha]_D^{20}$ = –67.3° (c 0.010 g/mL, $CHCl_3$); ^1H NMR (700 MHz, $CDCl_3$) δ 7.71 – 7.63 (m, 4H), 7.50 – 7.40 (m, 2H), 7.41 – 7.35 (m, 4H), 5.78 (app. t, *J* = 8.2 Hz, 1H), 5.68 (brs, 1H), 4.81 (s, 1H), 4.77 (s, 1H), 4.57 (app. tdt, *J* = 6.9, 2.0, 1.0 Hz, 1H), 3.04 – 2.98 (m, 1H), 2.66 (dd, *J* = 12.6, 7.9 Hz, 1H), 2.51 (dd, *J* = 12.6, 8.5 Hz, 1H), 2.33 (td, *J* = 7.4, 2.6 Hz, 2H), 2.16 (ddd, *J* = 12.9, 7.8, 6.9 Hz, 1H), 1.85 (d, *J* = 2.0 Hz, 3H), 1.81 (dd, *J* = 2.4, 1.1 Hz, 3H), 1.67 (app. h, *J* = 7.4 Hz, 2H), 1.46 (ddd, *J* = 12.9, 7.9, 6.9 Hz, 1H), 1.09 (s, 8H), 0.97 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 173.8, 172.7, 155.5, 149.5, 144.9, 136.1, 134.2, 133.8, 130.9, 130.0, 129.9, 128.6, 127.8, 127.7, 114.2, 78.9, 76.4, 67.3, 47.6, 41.8, 36.2, 35.8, 27.2, 19.4, 18.5, 13.8, 12.2, 8.9; IR (thin film, cm^{-1}) 2961, 2931, 2857, 1762, 1428, 1380, 1359; HRMS (ESI) *calcd.* for $[C_{35}H_{42}O_5SiNa]^+$ $(M+Na)^+$: m/z 593.2699, found 593.2682.

Compounds 74, 75, 77: A reaction tube (Biotage® microwave vial 351521, 2-5 mL) was charged with a stir bar and compound **69** (22.0 mg, 0.0385 mmol, 1 equiv). The tube was sealed, placed under vacuum, and back-filled with O_2. In a separate container, $Co(acac)_2$ (10 mg, 0.039 mmol) was dissolved in anhydrous ethanol (5 mL), and the mixture was degassed by bubbling of O_2 for 10 minutes assisted by sonication. A portion of this catalyst solution (1 mL, 0.0077 mmol of [Co], 0.2 equiv) was then added to the reaction tube. The resulting mixture was vigorously stirred at room temperature under an atmosphere of O_2 (balloon), while a solution of Et_3SiH (31 μL, 0.19 mmol, 5 equiv) in ethanol (0.5 mL) was slowly added over 24 hours via a syringe pump. After the addition of silane was complete, the reaction mixture was stirred at room temperature for an additional 24 hours, and was then diluted with EtOAc (10 mL) and H_2O (10 mL). The aqueous phase was extracted with EtOAc (10 mL × 3), and the combined organic phase was washed with H_2O (20 mL) and brine (20 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude mixture was purified by flash column chromatography (EtOAc/hexane, 1:8 to 1:4), affording **74** (4.0 mg, 16%), **75** (2.5 mg, 10%), and **77** (4.6 mg, 20%).

[Note: Peroxides **74** and **75** are not stable at room temperature and undergo partial decomposition during purification and spectroscopic analysis]

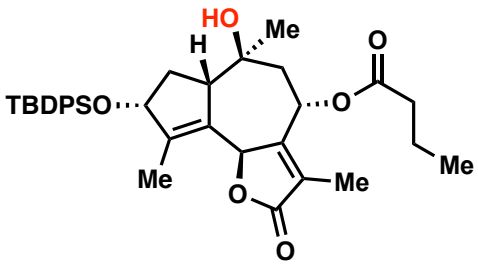


Compound **74** was obtained as a colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 – 7.65 (m, 4H), 7.48 – 7.35 (m, 6H), 5.72 (app. t, J = 8.9 Hz, 1H), 5.65 (s, 1H), 4.63 (app. t, J = 7.6 Hz, 1H), 2.98 (brs, 1H), 2.34 – 2.29 (m, 2H), 2.26 (s, 1H), 2.14 (dd, J = 13.1, 8.7 Hz, 1H), 2.06 (app. dt, J = 12.2, 6.3 Hz, 1H), 1.86 (brs, 3H), 1.74 – 1.63 (m, 4H), 1.53 (s, 3H), 1.11 (s, 9H), 1.03 (s, 3H), 0.98 – 0.95 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.6, 172.7, 152.6, 136.1, 136.1, 134.2, 133.5, 130.1, 130.0, 129.7, 127.9, 127.8, 84.6, 83.4, 77.7, 76.9, 76.8, 62.7, 52.0, 38.6, 36.4, 33.9, 27.2, 27.2, 23.6, 19.5, 18.2, 16.7, 13.8, 12.6. IR (thin film, cm^{-1}) 3419, 2959, 2932, 2857, 1787, 1744, 1461, 1427.HRMS (ESI+) *calcd.* for $[C_{35}H_{44}O_8SiNa]^+$ $(M+Na)^+$: m/z 643.2698, found 643.2700.

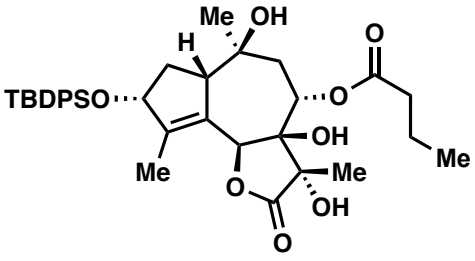


Compound **75** was obtained a colorless oil: (major isomer) ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 – 7.66 (m, 4H), 7.47 – 7.36 (m, 6H), 5.91 (dd, J = 5.5, 2.2 Hz, 1H), 4.76 (d, J = 1.9 Hz, 1H), 3.69 (dd, J = 11.0, 5.4 Hz, 1H), 2.91 (s, 1H), 2.37 – 2.31 (m, 3H), 2.13 (dd, J = 11.2, 7.6 Hz, 1H),

1.96 – 1.88 (m, 4H), 1.68 – 1.61 (m, 3H), 1.38 (s, 3H), 1.12 (s, 3H), 1.09 (s, 9H), 0.94 (t, J = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.3, 172.0, 156.3, 135.9, 135.8, 133.7, 133.0, 129.9, 129.8, 127.8, 127.6, 127.5, 91.5, 85.0, 78.9, 78.3, 78.1, 66.4, 54.9, 44.1, 36.1, 30.6, 26.9, 20.8, 19.3, 18.5, 18.2, 13.6, 8.7. IR (thin film, cm^{-1}) 3419, 2957, 2929, 2856, 1772, 1736, 1460, 1427. .HRMS (ESI+) *calcd.* for $[C_{35}H_{44}O_8SiNa]^+$ $(M+Na)^+$: m/z 643.2698, found 643.2694.

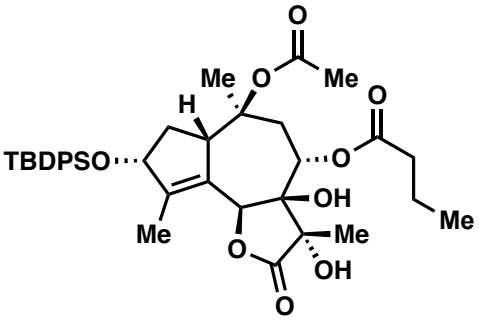


Compound **77** was obtained a colorless oil: $[\alpha]_D^{20}$ = –78° (c 0.002 g/mL, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 – 7.60 (m, 4H), 7.47 – 7.41 (m, 2H), 7.44 – 7.35 (m, 4H), 6.00 (app. t, J = 4.4 Hz, 1H), 5.62 (s, 1H), 4.58 (d, J = 8.3 Hz, 1H), 2.48 (brd, J = 8.7 Hz, 1H), 2.39 (dd, J = 14.8, 5.7 Hz, 1H), 2.37 – 2.29 (m, 2H), 2.07 (app. dt, J = 16.3, 8.7 Hz, 1H), 1.88 (s, 3H), 1.85 – 1.74 (m, 2H), 1.72 – 1.63 (m, 5H), 1.37 – 1.33 (m, 4H), 1.10 (s, 9H), 0.98 (td, J = 7.4, 1.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.7, 172.3, 156.9, 147.8, 136.2, 136.1, 134.1, 134.1, 131.1, 130.0, 129.9, 127.8, 127.8, 125.6, 78.9, 76.9, 74.2, 66.2, 54.8, 46.9, 36.3, 33.9, 27.3, 24.8, 19.5, 18.4, 13.9, 12.9, 8.9; IR (thin film, cm^{-1}) 3466, 2961, 2932, 2857, 1742, 1461, 1428, 1381, 1361; HRMS (ESI) *calcd.* for $[C_{35}H_{44}O_6SiNa]^+$ $(M+Na)^+$: m/z 611.2805, found 611.2807.

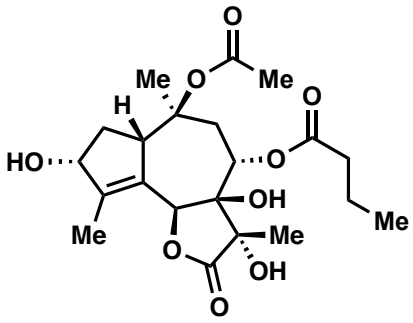


Compound 72: The same conditions used above were employed, but the reaction mixture was alternatively quenched by bubbling with N_2 for 10 minutes, followed by the addition of activated zinc powder (7.5 mg) and an aqueous solution of NH_4Cl (10 mg in 75 μL H_2O). The resulting mixture was vigorously stirred at room temperature until the endoperoxide intermediates were consumed as judged by TLC (EtOAc/hexane, 1:2). The mixture was then filtered through Celite®, and diluted with EtOAc (10 mL) and saturated *aq*. $NaHCO_3$ (10 mL). The aqueous phase was extracted with EtOAc (10 mL × 3), and the combined organic phase was washed with H_2O (20 mL), brine (20 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude mixture was purified by flash column chromatography (EtOAc/hexane, 1:1 to pure EtOAc), affording **72** (3.6 mg, 15%) as a colorless film: $[\alpha]_D^{20}$ = –38.5° (c 0.002 g/mL, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 – 7.66 (m, 4H), 7.45 – 7.41 (m, 2H), 7.40 – 7.35 (m, 4H), 5.74 (s, 1H), 5.53 – 5.49 (m, 1H), 4.62 (app. t, J = 7.3 Hz, 1H), 3.07 (brs, 1H), 2.27 (t, J = 7.5 Hz, 2H), 2.23 (dd, J = 14.9, 3.4 Hz, 1H), 2.13 – 2.06 (m, 2H), 1.94 (dd, J = 14.9, 4.1

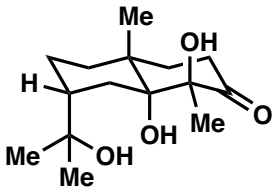
Hz, 1H), 1.85 – 1.80 (m, 4H), 1.68 – 1.60 (m, 3H), 1.45 (s, 3H), 1.20 (s, 3H), 1.11 (s, 9H), 0.95 (t, J = 7.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.1, 172.5, 149.1, 136.2, 134.4, 134.0, 129.9, 129.9, 127.8, 127.7, 127.1, 79.0, 78.8, 78.5, 78.4, 73.9, 66.6, 54.3, 44.8, 36.7, 35.3, 27.3, 23.8, 19.5, 18.2, 16.6, 13.9, 13.5; IR (thin film, cm^{-1}) 3435, 3047, 3378, 2955, 2928, 2856, 1767, 1719, 1458, 1428; HRMS (ESI) *calcd.* for $[C_{35}H_{46}O_8SiNa]^+$ $(M+Na)^+$: m/z 645.2860, found 645.2862.



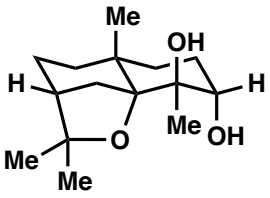
Compound SI-8: A reaction tube was charged with a stir bar and compound **72** (6.0 mg, 9.6 μmol, 1 equiv). In a separate round-bottom flask, TsOH•H_2O (23 mg, 0.12 mmol) was azeotropically dried with toluene 3 times, and then dissolved in isopropenyl acetate (1 mL). A portion of this prepared solution (0.1 mL, 0.012 mmol of TsOH, 1.2 equiv) was added to the reaction tube at 0 ºC. The mixture was warmed to room temperature, and stirred for *ca.* 2 hours. The reaction was carefully monitored by TLC (EtOAc/hexane, 2:1), and after complete consumption of the starting material was observed, the mixture was cooled to 0 ºC, and EtOAc (5 mL) and saturated *aq.* $NaHCO_3$ (5 mL) were added. The aqueous phase was extracted with EtOAc (5 mL × 2), and the combined organic phase was washed with H_2O (20 mL) and brine (20 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude mixture was purified by flash column chromatography (EtOAc/hexane, 1:2 to 1:1), affording **SI-8** (5.1 mg, 80%) as a colorless oil: $[\alpha]_D^{20}$ = –32° (c 0.001 g/mL, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 – 7.66 (m, 4H), 7.46 – 7.40 (m, 2H), 7.40 – 7.35 (m, 4H), 5.70 (s, 1H), 5.55 (dd, J = 4.0, 3.7 Hz, 1H), 4.67 – 4.60 (m, 1H), 3.87 (brs, 1H), 2.97 (dd, J = 14.8, 3.7 Hz, 1H), 2.27 (t, J = 7.6 Hz, 2H), 2.18 (dd, J = 14.8, 4.0 Hz, 1H), 2.07 (s, 1H), 1.99 (s, 1H), 1.89 (s, 3H), 1.86 – 1.79 (m, 4H), 1.65 (app. h, J = 7.4 Hz, 2H), 1.49 (app. dt, J = 13.3, 6.5 Hz, 1H), 1.45 (s, 3H), 1.33 (s, 3H), 1.11 (s, 8H), 0.95 (t, J = 7.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.9, 172.2, 170.2, 148.7, 136.0, 135.9, 134.4, 133.6, 129.7, 129.6, 127.6, 127.5, 126.4, 85.3, 78.8, 78.6, 78.2, 77.9, 66.4, 50.4, 38.6, 36.5, 35.1, 27.1, 22.2, 22.1, 19.3, 18.0, 16.3, 13.7, 13.3; IR (thin film, cm^{-1}) 3425, 2926, 2855, 1787, 1734, 1464, 1368; HRMS (ESI+) *calcd.* for $[C_{37}H_{48}O_9SiNa]^+$ $(M+Na)^+$: m/z 687.2966, found 687.2969.



Compound 73: A plastic tube was charged with a stir bar, compound **SI-8** (1.4 mg, 2.1 μmol), and mixture of *aq.* HF and MeCN (0.2 mL, 1:5 v/v). The resulting mixture was stirred at room temperature for 2 hours. After the consumption of the starting material was complete as judged by TLC (EtOAc/hexane, 1:1), the mixture was diluted with EtOAc (5 mL), and then added dropwise to a solution of saturated *aq.* $NaHCO_3$ (5 mL) in a separate container. The aqueous phase was extracted with EtOAc (5 mL × 3), and the combined organic phase was washed with H_2O (10 mL) and brine (10 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude mixture was purified by preparative TLC (EtOAc/hexane, 1:1), affording **73** (0.5 mg, 56%) as a colorless film. The spectral data of **73** was in full agreement with that previously reported (see Tables S5 and S6).



Triol 79: An oven-dried 25 mL round-bottom flask was charged with enone **78** (250 mg, 1.15 mmol, 1 equiv), $Co(acac)_2$ (58.9 mg, 20 mol%), EtOH (3 mL), and a stir bar. The resulting mixture was bubbled with oxygen for 15 min, and was then vigorously stirred under an O_2 atmosphere (balloon). A solution of Et_3SiH (0.44 ml, 2.4 equiv) in EtOH (1.5 mL) was slowly added over 12h via syringe pump. After the addition was complete and the consumption of the starting material was deemed complete as judged by TLC, the reaction mixture was diluted with EtOH (10 mL), and bubbled with N_2 for 15 minutes. Freshly activated Zn^0 power (150.4 mg, 2 equiv) and saturated *aq.* NH_4Cl solution (3 mL) were then added, and the resulting mixture was stirred at room temperature for 2 hours until the peroxide intermediates were consumed. The mixture was then diluted with EtOAc (5 mL) and water (10 mL). The aqueous layer was extracted with EtOAc (3 × 10 mL), and the combined organic layers were washed with brine (30 mL), dried over Na_2SO_4, filtered through Celite®, and concentrated *in vacuo*. The crude residue was purified via SiO_2 flash chromatography (30 to 40% EtOAc/hexanes) to afford triol **80** (154 mg, 0.57 mmol, 50% yield) as a colorless oil. TLC (50 % EtOAc/Hexanes): R_f = 0.32 (*p*-anisaldehyde). ^{1}H NMR (600 MHz, CD_2Cl_2): δ 5.43 (s, 1H), 2.75 (ddd, *J* = 14.3, 8.6 Hz, 4.8 Hz, 1H), 2.46 (ddd, *J* = 14.3, 7.8, 3.8 Hz, 1H), 2.25 (s, 1H), 2.12 (dd, *J* = 15.4, 7.8 Hz, 1H), 1.98 (m, 2H), 1.87 (m, 2H), 1.90 (m, 1H), 1.73 (m, 1H), 1.37 (s, 3H), 1.34 (s, 3H), 1.28 (s, 3H), 1.20 (s, 3H), 1.05 (m, 1H). ^{13}C NMR (151 MHz, CD_2Cl_2): δ 215.2, 80.1, 77.1, 75.2, 40.3, 37.4, 36.1, 36.0, 33.9, 30.7, 29.7, 26.5, 22.7, 20.6, 20.5. FTIR: 3365, 2979, 2942, 2870, 1710, 1648, 1611, 1465, 1449, 1420, 1370 cm^{-1}.HRMS (ESI+): calculated for $[C_{15}H_{26}O_4Na]^+$ m/z 293.1729, found 293.1728. $[\alpha]_D$ = –65.5º (c = 0.01 g/mL, $CHCl_3$)

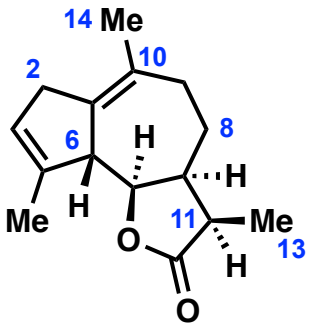


Boariol (80): An oven-dried 50 mL round-bottom flask with a stir bar was charged with triol **79** (154 mg, 0.57 mmol, 1 equiv) and anhydrous Et_2O (11 mL). The reaction mixture was cooled to 0 ºC over an ice bath, followed by addition of $LiAlH_4$ power (32.5 mg, 1.5 equiv) in one portion. The mixture was then stirred at 0 ºC for 45 minutes. After the consumption of the starting material was complete as judged by TLC, the reaction was quenched with careful addition of *aq.* HCl (1 N, 15 mL). The resulting mixture was allowed to warm to room temperature, diluted with Et_2O (10 mL), and further stirred for 30 minutes. The layers were then separated, and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (30 mL), dried over Na_2SO_4, filtered through Celite®, and concentrated *in vacuo*. The crude residue was purified via SiO_2 flash chromatography (30 to 40% EtOAc/hexanes) to afford **80** (106 mg, 73% yield) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.85 (s, 1H), 3.54 – 3.43 (m, 1H), 2.14 (dd, *J* = 12.1, 4.8 Hz, 1H), 2.05 (tdd, *J* = 14.2, 3.8, 2.5 Hz, 1H),

1.90 (dd, J = 5.0, 3.0 Hz, 1H), 1.86 (d, J = 12.0 Hz, 1H), 1.78 (td, J = 14.1, 3.7 Hz, 1H), 1.74 – 1.63 (m, 3H), 1.53 (dq, J = 14.0, 3.3 Hz, 1H), 1.39 (s, 3H), 1.35 (s, 3H), 1.27 (s, 3H), 1.19 (s, 3H), 1.16 – 1.12 (m, 1H), 1.03 (dt, J = 13.6, 3.3 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 89.6, 84.0, 76.6, 74.3, 43.6, 38.8, 38.4, 32.6, 31.5, 30.2, 25.2, 24.9, 24.6, 24.5, 22.8. FTIR: 3429, 3394, 3002, 2991, 2955, 2920, 2862, 1463, 1424, 1386 cm^{-1}. HRMS (ESI+): calculated for $[C_{15}H_{27}O_3]^+$ m/z 255.1960, found 255.1964. $[\alpha]_D$ = –39.6º (c = 0.01 g/mL, $CHCl_3$).

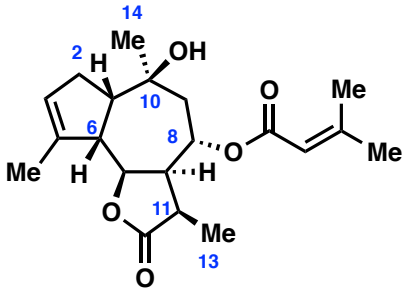
Slow evaporation of an Et_2O solution of **80** afforded X-ray quality crystals. The crystal structure of synthetic **80** matched that of natural **80** previously report by Gonzales and coworkers.[2]

Table S1. ^{1}H and ^{13}C NMR comparison of natural and synthetic sinodielide (**12**).[2]



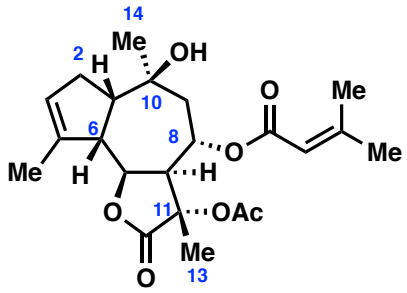
	^{1}H NMR for natural **12**	^{1}H NMR for synthetic **12**	^{13}C NMR for natural **12**	^{13}C NMR for synthetic **12**
C1			131.0	131.2
C2	2.95 (brs, 2H)	3.11-2.89 (brd, 2H)	38.1	38.2
C3	5.44 (tq, *J* = 5.3, 1.6 Hz)	5.44 (d, J=1.9Hz, 1H)	124.2	124.3
C4			142.0	142.2
C5	3.56 (brd, *J* = 9.8 Hz, 1H)	3.56 (d, J=10.1Hz, 1H)	50.7	50.9
C6	4.37 (dd, *J* = 9.8, 5.8 Hz, 1H)	4.37 (dd, J=10.0, 5.8Hz, 1H)	86.1	86.3
C7	2.56 (m, 2H)	2.56 (ddd, J=13.8, 10.7, 6.2Hz, 2H)	42.1	42.3
C8	1.54 (m, 1H)	1.55 (brs, 4H)	18.9	19.1
	1.78 (m, 1H)	1.78 (qd,J= 12.8,5.3 Hz, 1H)		
C9	2.56 (m, 2H)	2.56 (ddd, J=13.8, 10.7, 6.2Hz, 2H)	36.4	36.6
	2.09 (m, 1H)	2.26-2.00 (m, 1H)		
C10			127.6	127.7
C11	2.79 (dq, *J* = 7.3, 7.3 Hz, 1H)	2.78 (ap, J=7.6Hz, 1H)	38.6	38.7
C2			179.5	179.7
C10	1.19 (d, *J* = 7.3 Hz, 3H)	1.18 (d, *J* = 7.3 Hz, 3H)	10.3	10.5
C11	1.56 (brs, 3H)	1.55 (brs, 4H)	21.3	21.5
C2	1.83 (dd, *J* = 1.6, 0.9 Hz, 3H)	1.83 (s, 3H)	16.8	17.0

Table S2. [1]H NMR comparison of natural and synthetic slovanolide **18**.[3]



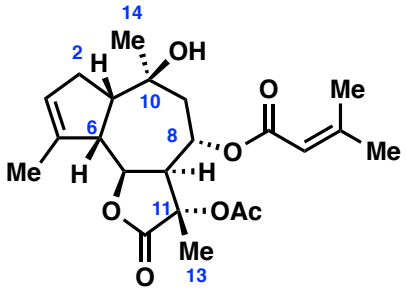
	[1]H NMR for isolated **18**	[1]H NMR for synthetic **18**	[13]C NMR isolated **18**	[13]C NMR synthetic **18**
C1	2.37 (m)	2.43 (dt, J=12.4, 6.3Hz, 1H)	55.5	55.8
C2	2.15 (m)	2.19 (m, 2H)	32.2	32.4
C3	5.46 (m)	5.53 (s, 1H)	125.2	125.4
C4			146.9	147.9
C5	2.54 (dd, J =11.4, 5.6 Hz)	2.62 (dd, J =11.5, 5.6Hz, 1H)	50.0	50.3
C6	4.51 (dd, J =11.5, 9.0 Hz)	4.58 (dd, J=11.5, 9.1 Hz, 1H)	90.7	80.9
C7	2.99 (dt, J = 11.0, 9.2 Hz)	3.05 (aq, J = 9.6 Hz, 1H)	45.5	45.7
C8	5.37 (t, J=11.0Hz)	5.47-5.34 (m,1H)	66.3	66.62
C9	2.05 (dd, J=9.5, 14.6Hz)	2.10 (d, J= 13.3Hz, 1H)	43.2	43.4
	2.37 (m)	1.87-1.82 (m,1H)		
C10			71.3	71.62
C11	2.64 (dq, J=7.9, 9.2Hz)	2.72 (ap, J=8.2Hz)	36.1	36.4
C12			179.4	179.6
C13	1.24 (d, J=7.9Hz)	1.31 (d, J=7.9Hz, 3H	13.4	13.6
C14	1.16 (s)	1.23 (s, 3H)	30.9	31.3
C15	1.85 (d, J=1.4Hz)	1.93 (s, 3H)	18.6	18.9
Sen			168.0	167.0
	5.59 (qq, J=1.2Hz)	5.66 (d, J=1.7Hz, 1H)	115.4	115.6
			158.8	158.2
	2.11 (d, J=1.2Hz)	2.19 (s, 3H)	27.4	27.7
	1.81 (m)	1.87-1.79(m,3H)	20.3	20.6

Table S3. [1]H NMR comparison of natural and synthetic montanolide (**23**)



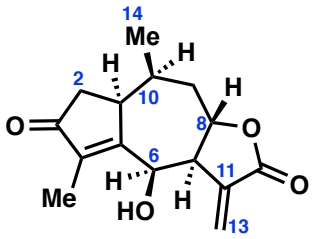
	1H NMR of natural **23**[4]	1H NMR of natural **23**[5]	1H NMR of natural **23**[6]	1H NMR of synthetic **23** (this work)
C1	2.41 (J = 11.5, 6.9, 5.5Hz)	2.40 m		2.41 (1H, J = 12.2, 6.3 Hz)
C2-a	2.09 (1H)	2.04 m		2.09 (1H , m)
C2-b	2.19 (1H, J = 15.1, 6.9, 3.2Hz)	2.12 d (1H, J = 9.6 Hz)		2.18 (1H, m)
C3	5.56 (1H, J = 3.2, 1.6Hz)	5.56 bs	5.54	5.56 (1H, dt, J = 3.5, 1.7 Hz)
C5	2.58 (1H, J = 11.6, 5.5Hz)	2.58 q (1H, J = 5.7 Hz)		2.57 (1H, J = 11.6, 5.6 Hz)
C6	4.71 (1H, J = 11.6, 9.9Hz)	4.71 dd (1H, J = 11.4, 10.2 Hz)	4.71	4.70 (1H, dd, J = 11.6, 9.9 Hz)
C7	3.61 (1H, J = 11.5, 9.9Hz)	3.61 dd (1H, J = 11.1,10.2 Hz)	3.62	3.61 (1H, dd, J = 11.4, 9.9 Hz)
C8	5.51 (1H, J = 11.5, 9.2Hz)	5.52 dd (1H, J = 11.1, 9.6 Hz)	5.54	5.50 (1H, dd, J = 11.4, 9.3 Hz)
C9-α	2.01 (1H, J = 14.8, 9.2Hz)	1.99 d (1H J = 9.6 Hz)		2.00 (1H, dd, J = 14.9, 9.4 Hz)
C9-β	1.81 (1H, J = 14.8, 1.0Hz)	1.82 m		1.82 (1H, dd, J = 14.4, 1.7 Hz)
C13	1.54 (3H)	1.55 s	1.54	1.54 (s, 3H)
C14	1.22 (3H)	1.22 s	1.21	1.22 (s, 3H)
C15	1.88 (3H)	1.88 s	1.88	1.88 (3H, dt, J = 2.9, 1.5 Hz)
Sen	5.62 (1H, J = 1.4, 1.3)	5.62 m		5.61 (1H, p, J = 1.4)
	2.20 (3H)	2.2		2.20 (3H, d, J = 1.4Hz)
	1.94 (3H)	1.94 m		1.94 (3H, d, J = 1.4Hz)
Ac	2.09 (3H)	2.08 s		2.09 (s, 3H)

Table S3. ^{13}C NMR of montanolide (**23**)



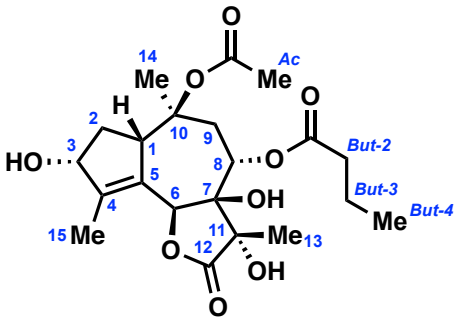
	^{13}C NMR of synthetic **23**
C1	56.1
C2	32.3
C3	126.0
C4	147.3
C5	49.4
C6	78.4
C7	47.5
C8	66.2
C9	43.7
C10	78.5
C11	71.4
C12	174.4
C13	20.2
C14	31.2
C15	18.9
Sen	166.8
	115.5
	159.5
	27.8
	20.7
Ac	170.0
	21.2

Table S4. [1]H NMR comparison of natural and synthetic mikanokryptin (**8**).



	mikanokryptin (**8**)[7]	mikanokryptin (**8**) this work	mikanokryptin (**8**)[8]	mikanokryptin (**8**) this work
C1	3.16 (m, 1H)	3.19 (m, 1H)	3.12 (ddddd, *J* = 6.8, 2.2, 2.0, 2.0, 1.0 Hz, 1H)	3.12 (m, 1H)
C2-α	obscured signal	2.55 (dd, *J* = 19.0, 6.7 Hz, 1H)	2.65 (ddd, *J* = 19.1, 6.8, 1.1 Hz, 1H)	2.67 (ddd, *J* = 19.1, 6.9, 1.1 Hz, 1H)
C2-β	obscured signal	2.05 (dd, *J* = 19.0, 1.9 Hz, 1H)	2.17 (dd, *J* = 19.1, 2.0 Hz, 1H)	2.19 (dd, *J* = 19.1, 1.9 Hz, 1H)
C6	5.10 (br d, *J* = 6.2 Hz, 1H)	5.09 (d, *J* = 6.5 Hz, 1H)	5.13 (ddddd, *J* = 5.6, 3.5, 1.1, 1.0, 0.8 Hz, 1H)	5.17 (br s, 1H)
C7	3.16 (m, 1H)	3.19 (m, 1H)	3.01 (dddd, *J* = 9.6, 3.5, 3.4, 3.0 Hz, 1H)	3.06 (dddd, *J* = 9.6, 3.5, 3.1, 1.9 Hz, 1H)
C8	4.66 (ddd, *J* = 12, 10, 3.7 Hz, 1H)	4.64 (ddd, *J* = 12.5, 9.4, 3.4 Hz, 1H)	4.84 (ddd, *J* = 12.1, 9.6, 3.5 Hz, 1H)	4.80 (ddd, *J* = 12.6, 9.6, 3.5 Hz, 1H)
C9-α	obscured signal	1.94 (ddd, *J* = 12.5, 12.0, 4.0 Hz, 1H)	1.92 (ddd, *J* = 12.6, 12.1, 3.9 Hz, 1H)	1.94 (ddd, *J* = 12.8, 12.6, 4.1 Hz, 1H)
C9-β	obscured signal	2.21 (ddd, *J* = 12.0, 3.4, 3.4 Hz, 1H)	2.42 (ddd, *J* = 12.6, 3.5, 3.5 Hz, 1H)	2.45 (ddd, *J* = 12.8, 3.5, 3.5 Hz, 1H)
C10	obscured signal	2.17 (m, 1H)	2.29 (dddd, *J* = 7.3, 3.9, 3.5, 2.2 Hz, 1H)	2.31 (m, 1H)
$C13_{cis}$	6.24 (d, *J* = 3.5 Hz, 1H)	6.20 (d, *J* = 3.4 Hz, 1H)	6.40 (d, *J* = 3.4 Hz, 1H)	6.46 (d, *J* = 3.5 Hz, 1H)
$C13_{trans}$	5.81 (d, *J* = 3.1 Hz, 1H)	5.80 (d, *J* = 3.1 Hz, 1H)	5.72 (d, *J* = 3.0 Hz, 1H)	5.70 (d, *J* = 3.1 Hz, 1H)
C14	0.69 (d, *J* = 7.2 Hz, 1H)	0.73 (d, *J* = 7.1 Hz, 3H)	1.90 (dd, *J* = 2.0, 0.8 Hz, 3H)	1.92 (dd, *J* = 2.1, 0.9 Hz, 3H)
C15	1.74 (dd, *J* = 1, 0.9 Hz, 1H)	1.76 (d, *J* = 1.0 Hz, 3H)	0.86 (d, *J* = 7.3 Hz, 3H)	0.85 (d, *J* = 7.3 Hz, 3H)
OH	5.60 (d, *J* = 6.2 Hz, 1H)	5.74 (d, *J* = 6.5 Hz, 1H)	4.54 (d, *J* = 5.6 Hz, 1H)	not observed

Table S5. ^{1}H NMR comparison of common intermediate **73**.



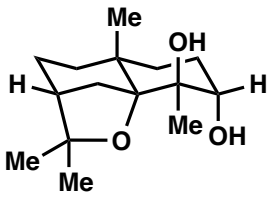
No.	Christensen[9]	Evans[10]	Baran[11]	this work
6	5.69 (1H, s)	5.69 (s, 1H)	5.70 (s, 1H)	5.70 (s, 1H)
8	5.61 (1H, t, J = 3.6 Hz)	5.61 (app. t, J = 3.7 Hz, 1H)	5.60 (t, J = 3.8 Hz, 1H)	5.60 (at, J = 3.8 Hz, 1H)
3	4.59 (1H, t, J = 6.8 Hz)	4.59 (app. q, J = 6.6 Hz, 1H)	4.59 (s, 1H)	4.60 (app. q, J = 6.6, 1H)
1	4.16 (1H, t, J = 7.1 Hz)	4.19 (app. t, J = 6.9 Hz, 1H)	4.13 (s, 1H)	4.11 (brs, 1H)
9a	3.08 (1H, dd, J = 15.0, 3.5 Hz)	3.10 (dd, J = 14.9, 3.3 Hz, 1H)	3.04 (dd, J = 14.8, 3.5 Hz, 1H)	3.03 (dd, J = 14.8, 3.6 Hz)
OH	2.52 (1H, s)	2.66 (s, 1H)		
2a	2.40 (1H, dt, J = 13.5, 8.2 Hz)	2.39 (app. dt, J = 14.0, 8.2 Hz, 1H)	2.41 (dt, J = 14.0, 8.2 Hz, 1H)	2.42 (app. dt, J = 14.0, 8.2, 1H)
But-2 9b OH	2.27 (3H, t, J = 6.8 Hz) 2.22 (1H, dd, J = 14.8, 3.9 Hz)	2.28 (s, 1H) 2.27 (t, J = 7.7 Hz, 2H) 2.19 (dd, 14.7, 4.0 Hz, 1H)	2.30 – 2.22 (m, 4H) 2.22 (s, 1H)	2.29 – 2.25 (m, 3H) 2.11 (s, 1H)
OH			2.17 (s, 1H)	2.05 (s, 1H)
Ac	1.97 (3H, s)	1.97 (s, 3H)	1.98 (s, 3H)	1.98 (s, 3H)
15	1.95 (3H, s)	1.95 (s, 3H)	1.96 (s, 3H)	1.96 (s, 3H)
3-OH	1.79 (1H, s)	1.80 (d, J = 6.3 Hz, 1H)	1.78 (d, J = 6.3 Hz, 1H)	1.77 (d, J = 6.3 Hz, 1H)
2b, But-3	1.69−1.53 (3H, m)	1.66-1.59 (m, 3H)	1.63 (dq, J = 13.5, 7.0, 6.3 Hz, 3H)	1.68-1.59 (m, 3H)
13	1.49 (3H, s)	1.48 (s, 3H)	1.49 (s, 3H)	1.49 (s, 3H)

14	1.34 (3H, s)	1.33 (s, 3H)	1.35 (s, 3H)	1.36 (s, 3H)
But-4	0.95 (3H, t, J = 7.4 Hz)	0.94 (t, J = 7.4 Hz, 3H)	0.95 (t, J = 7.4 Hz, 3H)	0.95 (t, J = 7.4 Hz, 3H)

Table S6. ^{13}C NMR comparison of common intermediate **73**.

Baran (150 MHz, $CDCl_3$)[11]	This Work (225 MHz, $CDCl_3$)
175.1	175.0
172.5	172.5
170.6	170.5
147.6	147.7
128.4	128.2
85.4	85.3
79.0	79.1
78.8	78.8
77.9	77.9
77.7	77.6
66.6	66.5
50.8	50.8
38.8	38.8
36.7	36.7
34.9	34.9
22.5	22.6
22.3	22.2
18.2	18.2
16.5	16.5
13.9	13.9
13.0	13.0

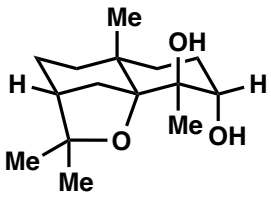
Table S7. ^{1}H NMR Comparison Tables for boariol **(80)***



Gonzalez and coworkers[12] Natural boariol $CDCl_3$	Li and coworkers[13] Synthetic boariol $CDCl_3$	This Work, Synthetic boariol 600 MHz, $CDCl_3$
3.87 (d, 1H, J = 10.4 Hz, interchangeable with D_2O)	3.81 (d, 1H, J = 10.2 Hz, interchangeable with D_2O)	3.85 (brs, 1H)
3.48 (m, 1H)	3.48 (m, 1H)	3.54 – 3.43 (m, 1H)
–	–	2.14 (dd, *J* = 12.1, 4.8 Hz, 1H)
–	–	2.05 (tdd, *J* = 14.2, 3.8, 2.5 Hz, 1H)
–	–	1.90 (dd, *J* = 5.0, 3.0 Hz, 1H)
–	–	1.86 (d, *J* = 12.0 Hz, 1H)
–	–	1.78 (td, *J* = 14.1, 3.7 Hz, 1H)
–	–	1.74 – 1.63 (m, 3H)
–	–	1.53 (dq, *J* = 14.0, 3.3 Hz, 1H)
1.40 (s, 3H)	1.40 (s, 3H)	1.39 (s, 3H)
1.39 (s, 3H)	1.39 (s, 3H)	1.35 (s, 3H)
1.28 (s, 3H)	1.29 (s, 3H)	1.27 (s, 3H)
1.20 (s, 3H)	1.21 (s, 3H)	1.19 (s, 3H)
–	–	1.16 – 1.12 (m, 1H)
–	–	1.03 (dt, *J* = 13.6, 3.3 Hz, 1H)

*Limited ^{1}H NMR data was provided in reference 12 and 13.

Table S8. ^{13}C NMR Comparison Tables for boariol **(80)**



Gonzalez and coworkers[12] Natural boariol ^{13}C NMR, $CDCl_3$ ^{13}C (δ) ppm	This Work, Synthetic boariol ^{13}C NMR, 151 MHz, $CDCl_3$ ^{13}C (δ) ppm
23.49	22.8
25.13	24.5
25.26	24.6
25.51	24.9
25.83	25.2
30.65	30.2
32.19	31.5
33.22	32.6
39.05	38.4
30.49	38.8
44.16	43.6
75.00	74.3
77.22	76.6
84.64	84.0
90.25	89.6

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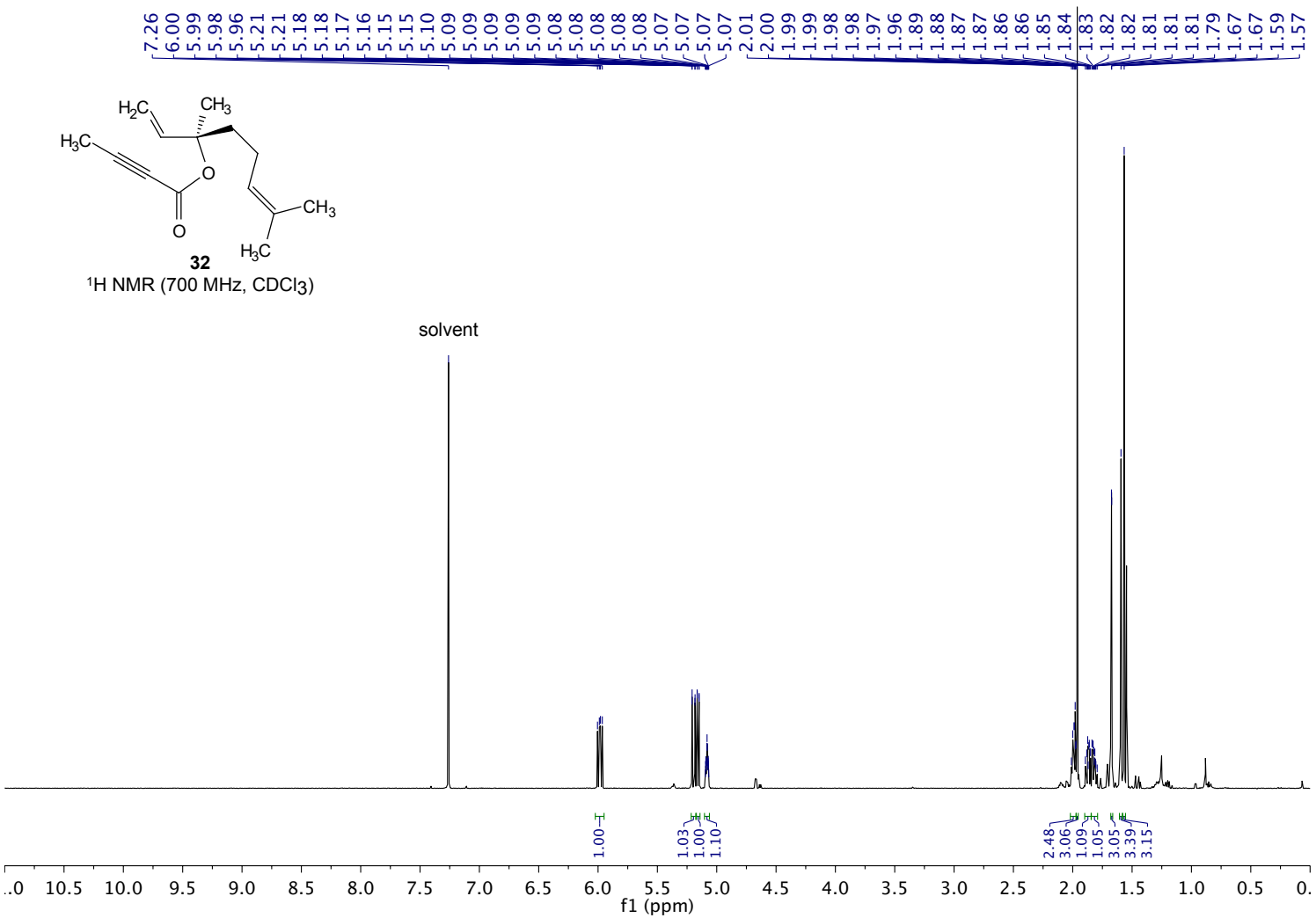
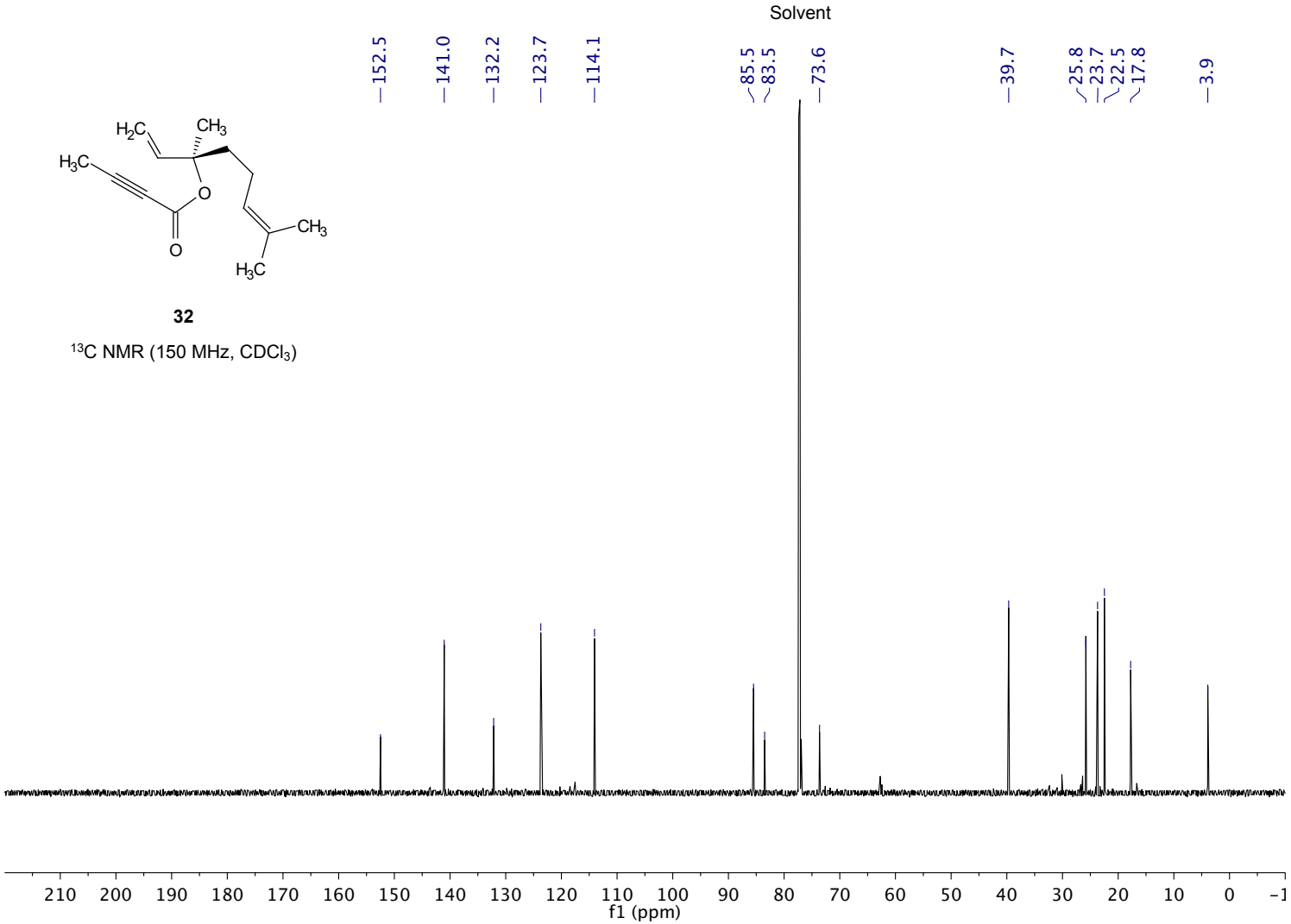
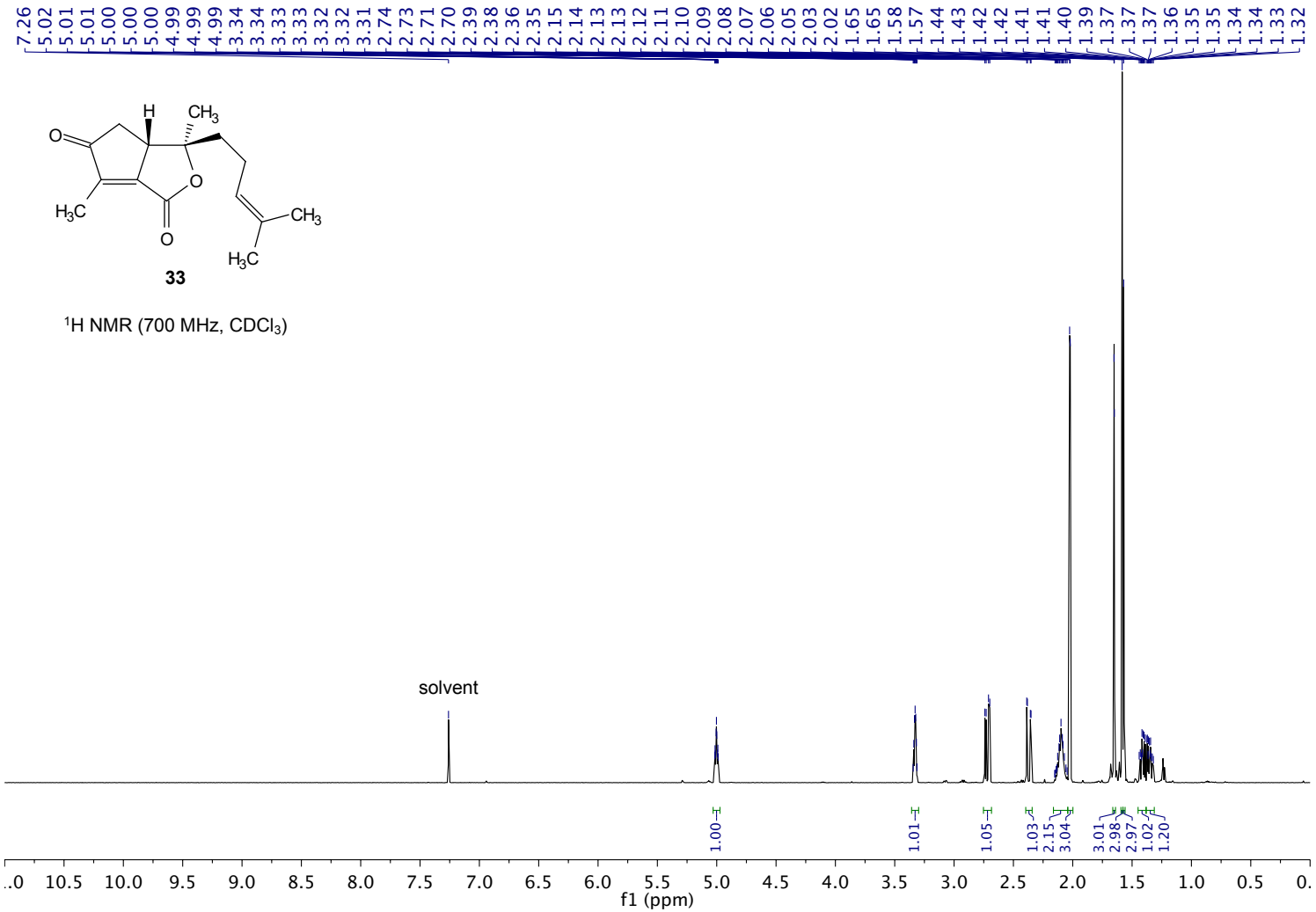
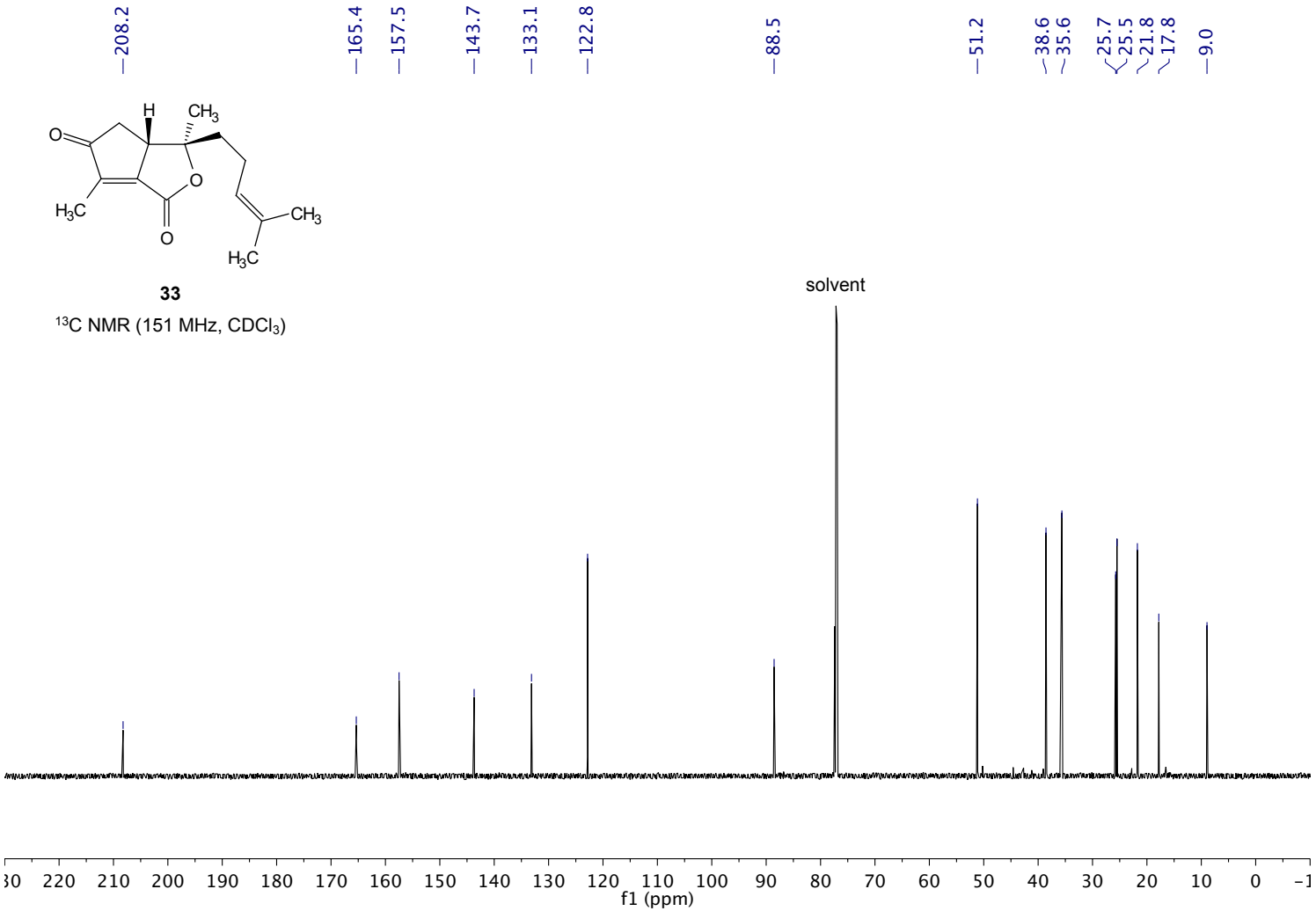

7.26
6.00
5.99
5.98
5.96
5.21
5.21
5.18
5.18
5.17
5.16
5.15
5.15
5.10
5.09
5.09
5.09
5.09
5.08
5.08
5.08
5.08
5.07
5.07
5.07
5.07
2.01
2.00
1.99
1.99
1.98
1.98
1.97
1.96
1.89
1.88
1.87
1.87
1.86
1.86
1.85
1.84
1.83
1.82
1.82
1.81
1.81
1.81
1.79
1.67
1.67
1.59
1.57
H2C
CH3
H3C
O
O
CH3
H3C
32
1H NMR (700 MHz, CDCl3)
solvent
1.00
1.03
1.00
1.10
2.48
3.06
1.09
1.05
3.05
3.39
3.15
10.5
10.0
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
f1 (ppm)



32

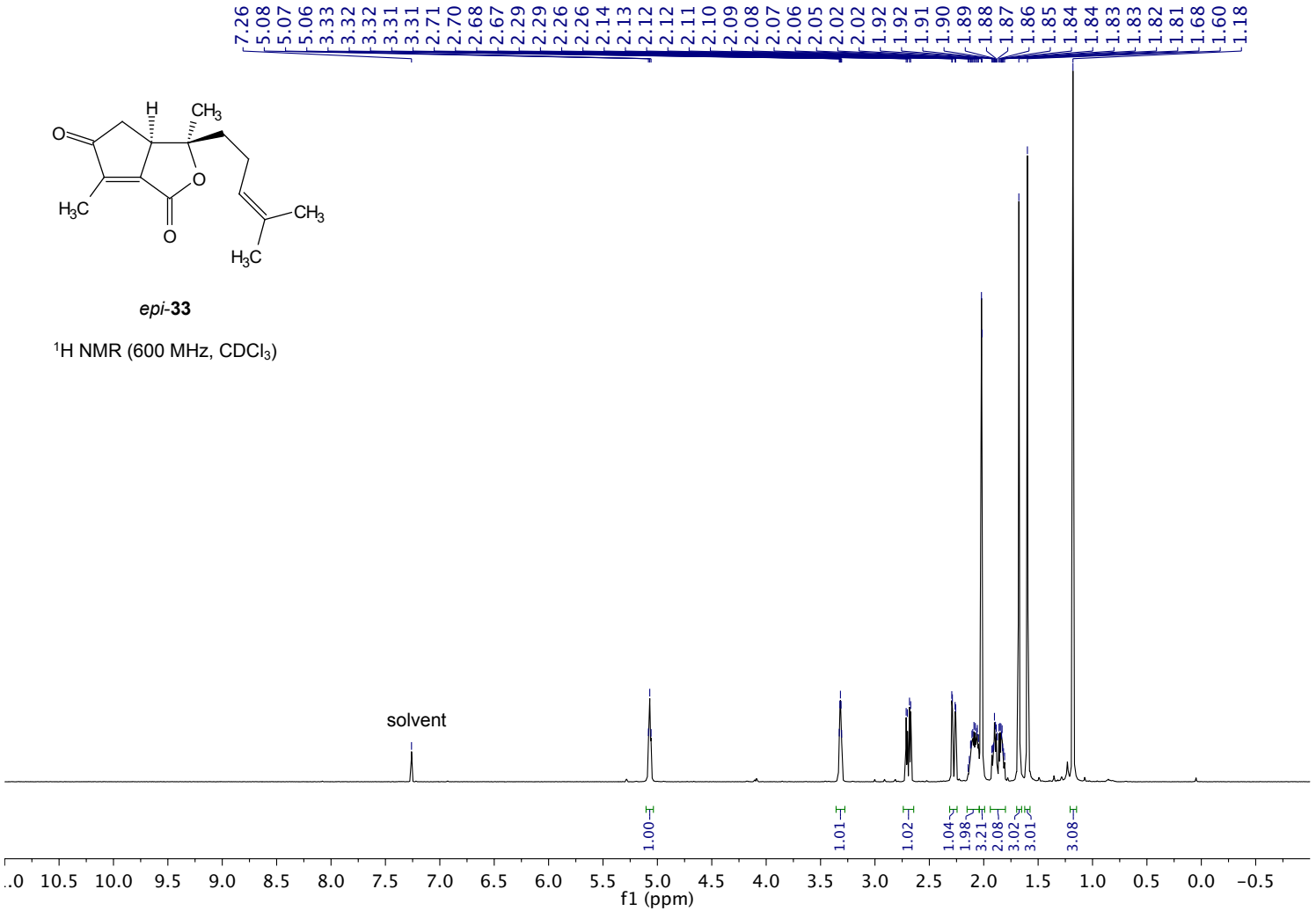
^{13}C NMR (150 MHz, $CDCl_3$)


7.26 5.02 5.01 5.01 5.00 5.00 5.00 4.99 4.99 4.99 3.34 3.34 3.33 3.33 3.32 3.32 3.31 2.74 2.73 2.71 2.70 2.39 2.38 2.36 2.35 2.15 2.14 2.13 2.13 2.12 2.11 2.10 2.09 2.08 2.07 2.06 2.05 2.03 2.02 1.65 1.65 1.58 1.57 1.44 1.43 1.42 1.42 1.41 1.41 1.40 1.39 1.37 1.37 1.37 1.36 1.35 1.35 1.34 1.34 1.33 1.32
H
CH3
O
O
H3C
O
CH3
H3C
33
1H NMR (700 MHz, CDCl3)
solvent
1.00
1.01
1.05
1.03
2.15
3.04
3.01
2.98
2.97
1.02
1.20
10.5 10.0 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
f1 (ppm)



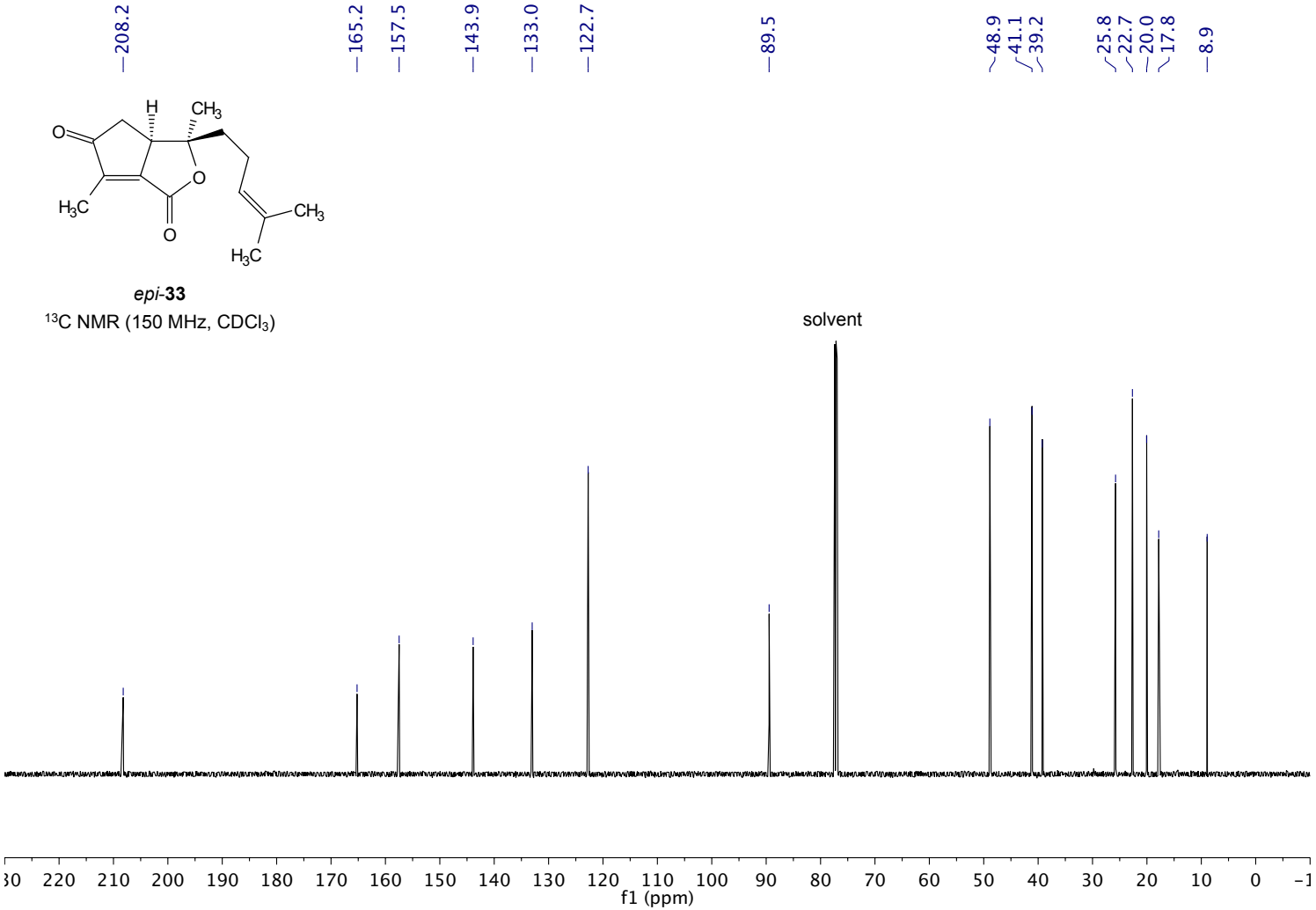
33

^{13}C NMR (151 MHz, $CDCl_3$)



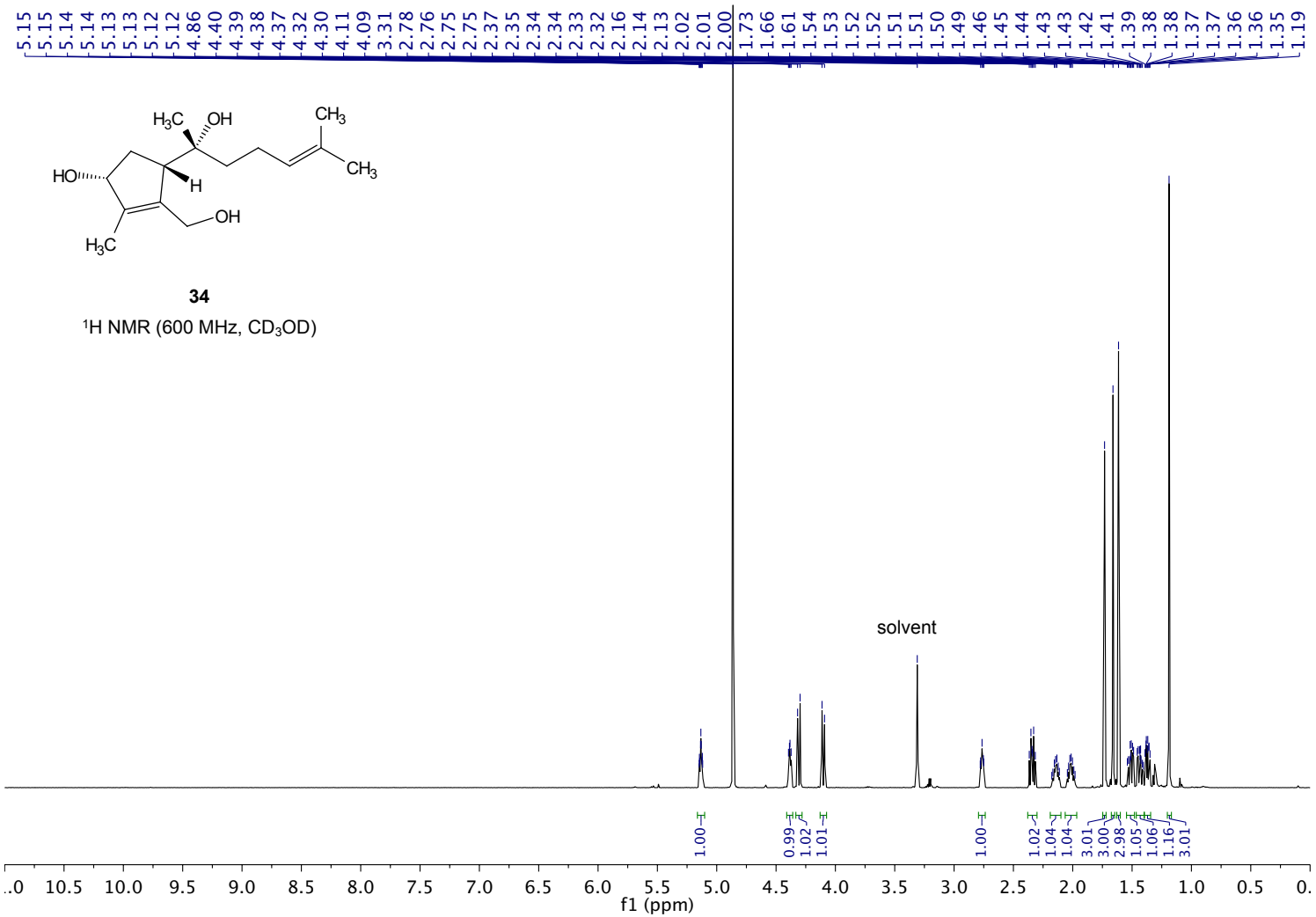
***epi*-33**

^{1}H NMR (600 MHz, $CDCl_3$)



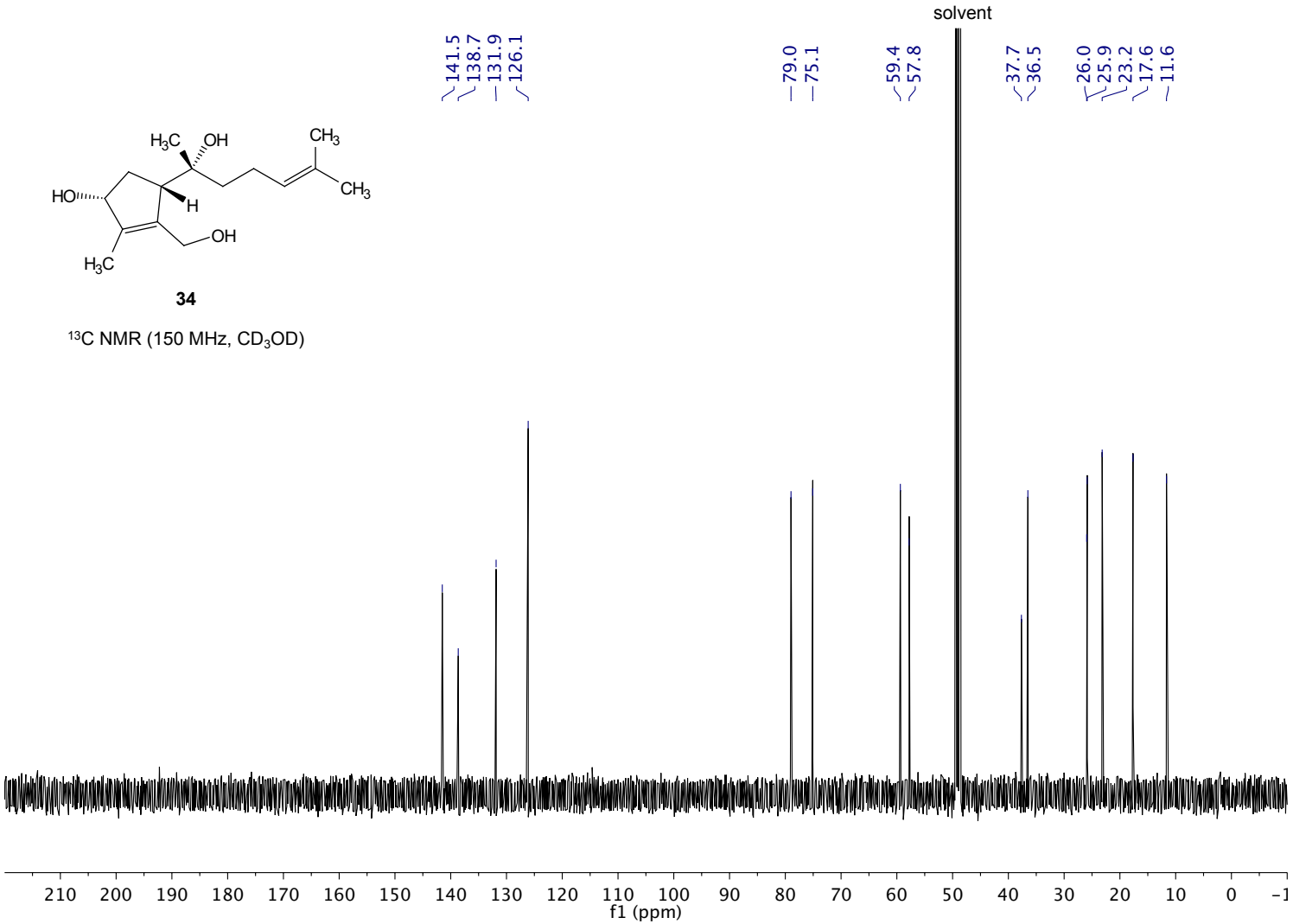
epi-**33**

^{13}C NMR (150 MHz, $CDCl_3$)



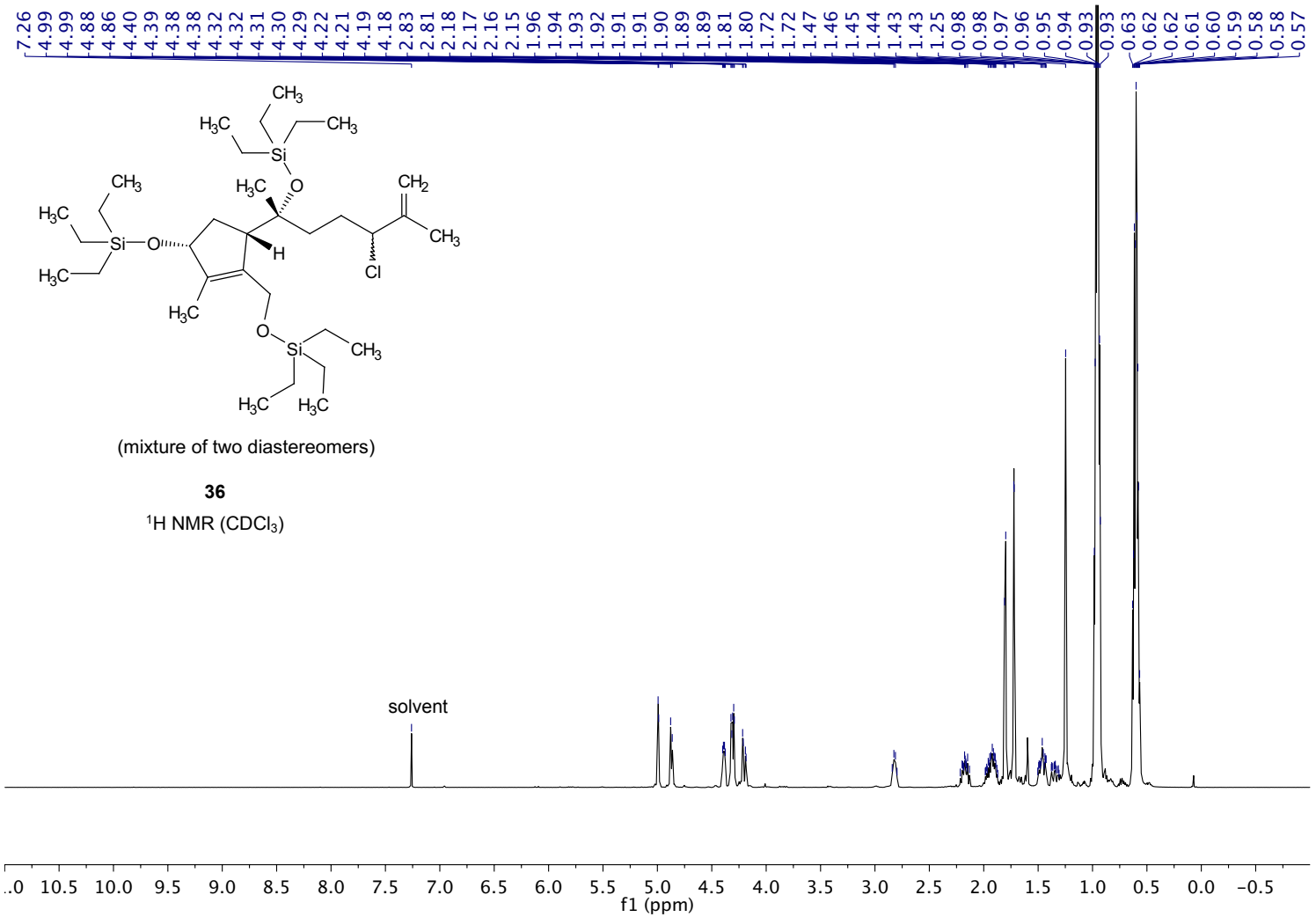
34

^{1}H NMR (600 MHz, CD_3OD)



34

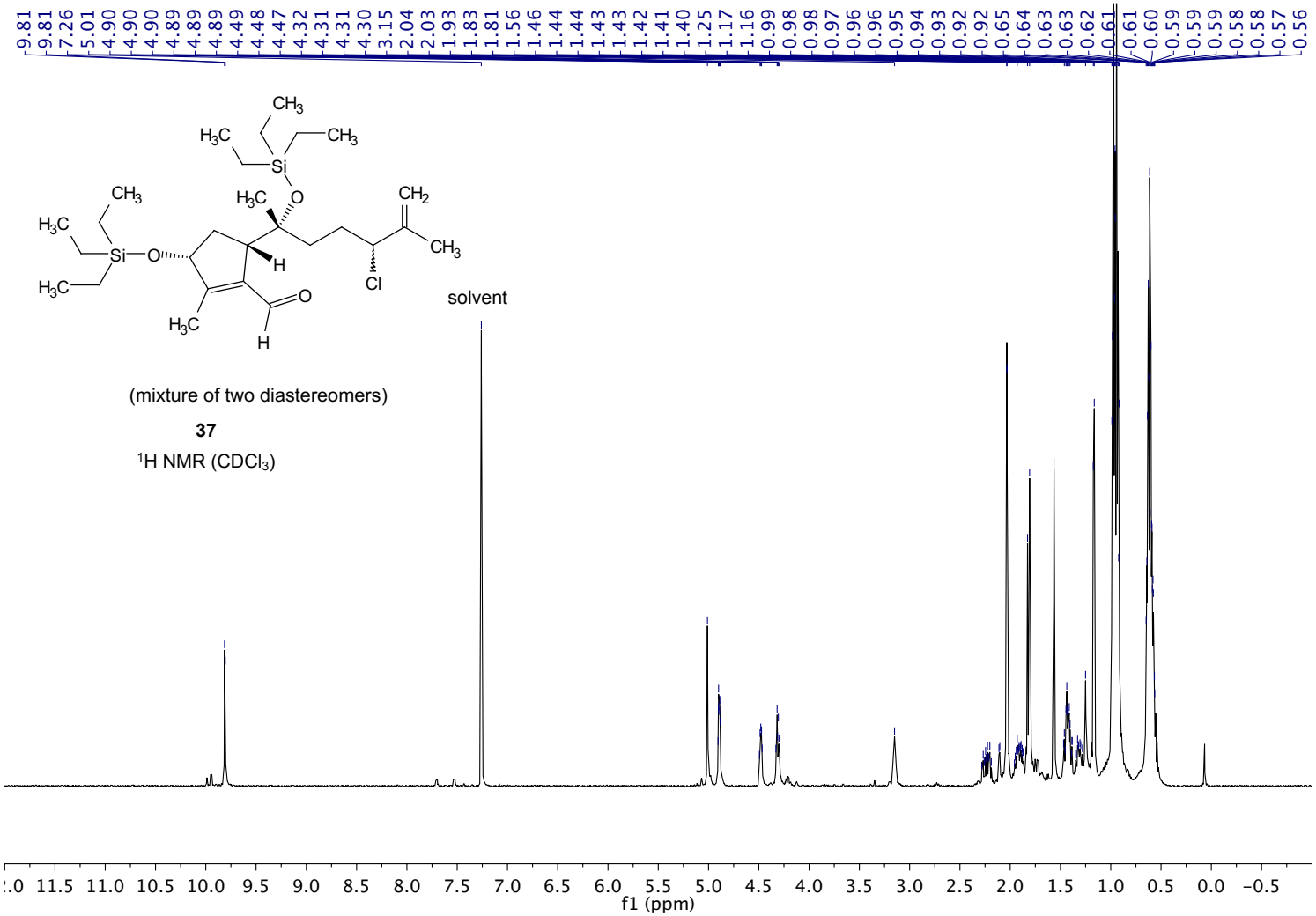
^{13}C NMR (150 MHz, CD_3OD)

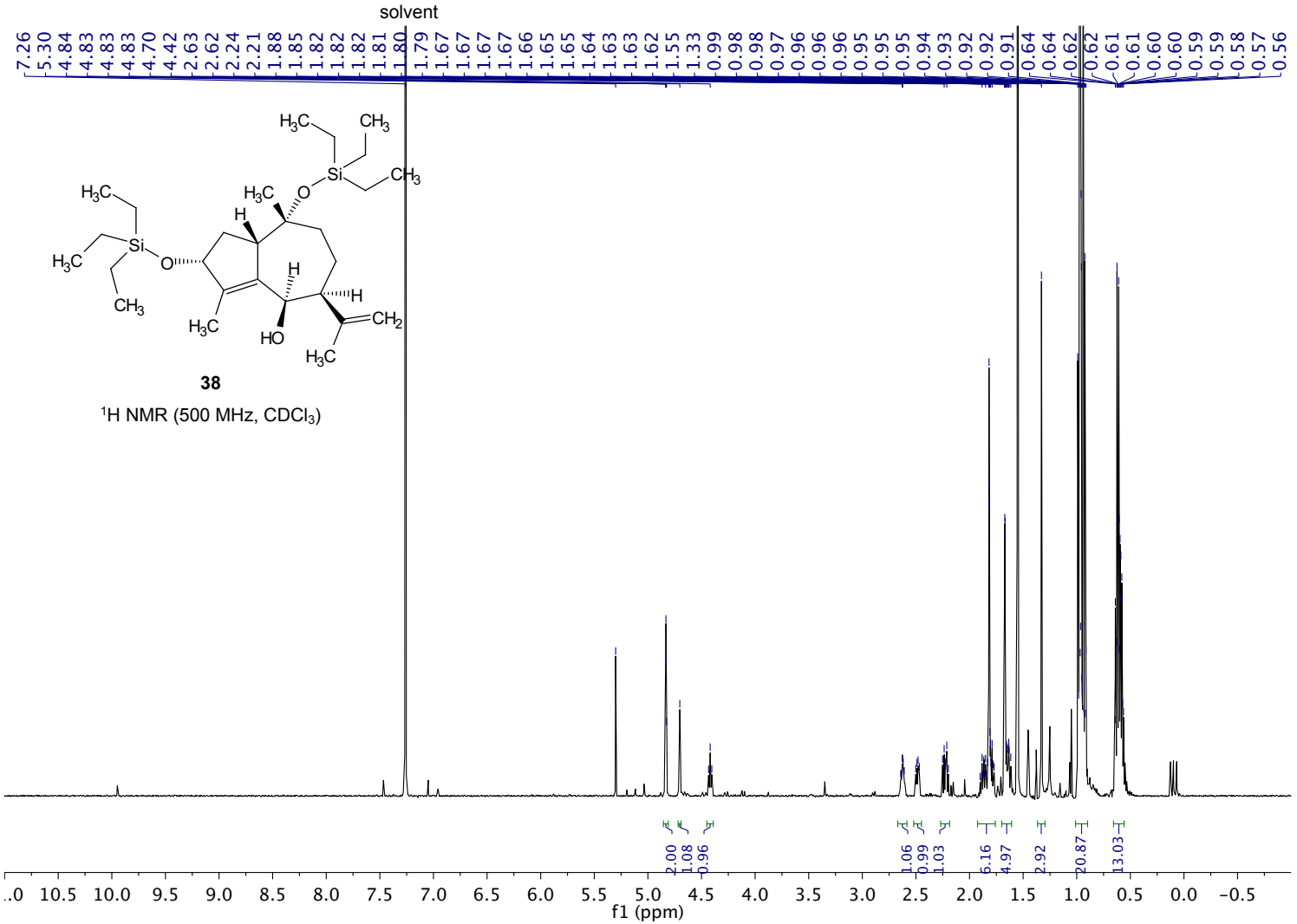


(mixture of two diastereomers)

36

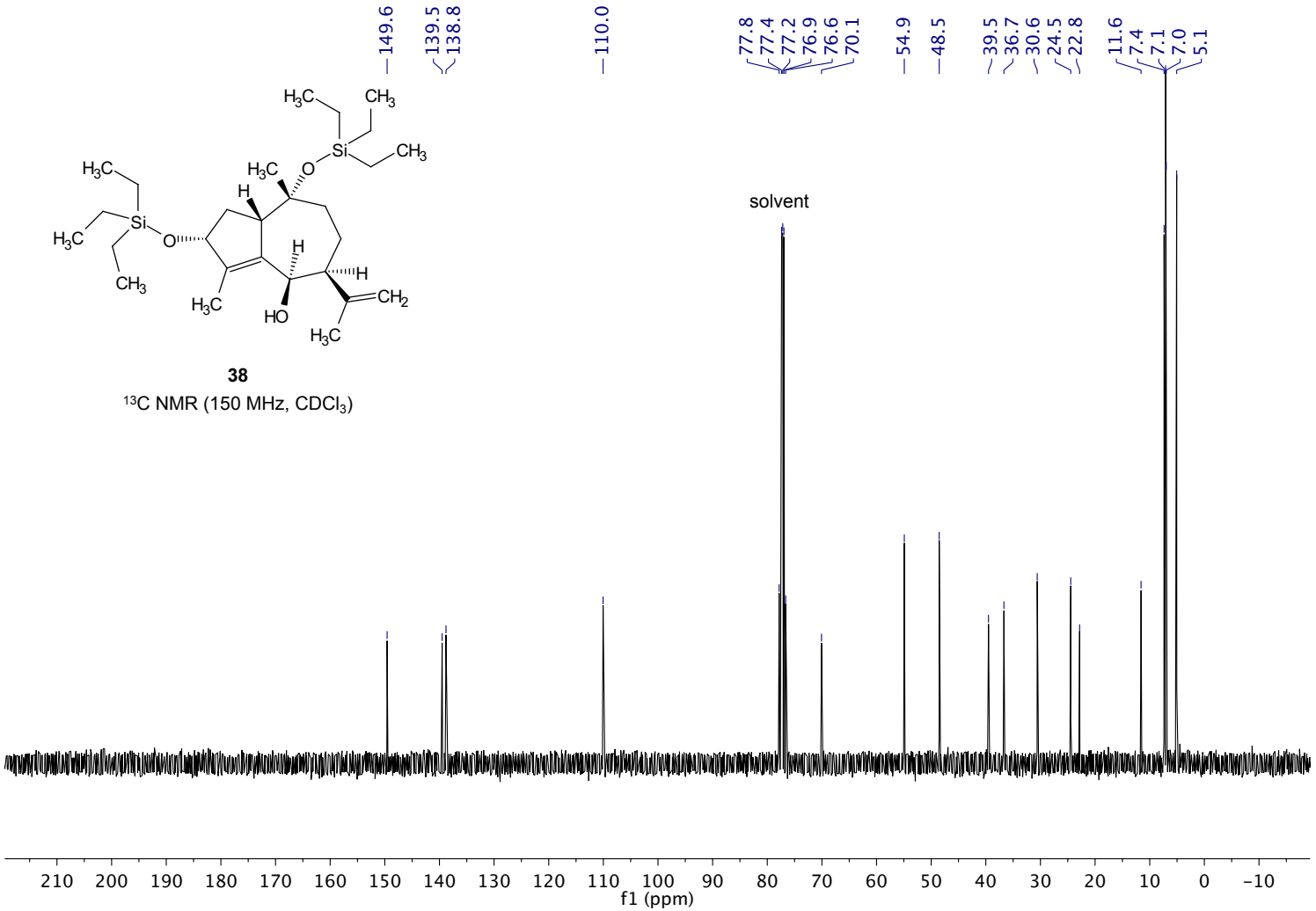
^{1}H NMR ($CDCl_3$)


9.81
9.81
7.26
5.01
4.90
4.90
4.90
4.89
4.89
4.89
4.49
4.48
4.47
4.32
4.31
4.31
4.30
3.15
2.04
2.03
1.93
1.83
1.81
1.56
1.46
1.44
1.44
1.43
1.43
1.42
1.41
1.40
1.25
1.17
1.16
0.99
0.98
0.98
0.97
0.96
0.96
0.95
0.94
0.93
0.92
0.92
0.65
0.64
0.63
0.63
0.62
0.61
0.61
0.60
0.59
0.59
0.59
0.58
0.58
0.57
0.56
solvent
(mixture of two diastereomers)
37
^{1}H NMR ($CDCl_3$)
11.5 11.0 10.5 10.0 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 −0.5
f1 (ppm)



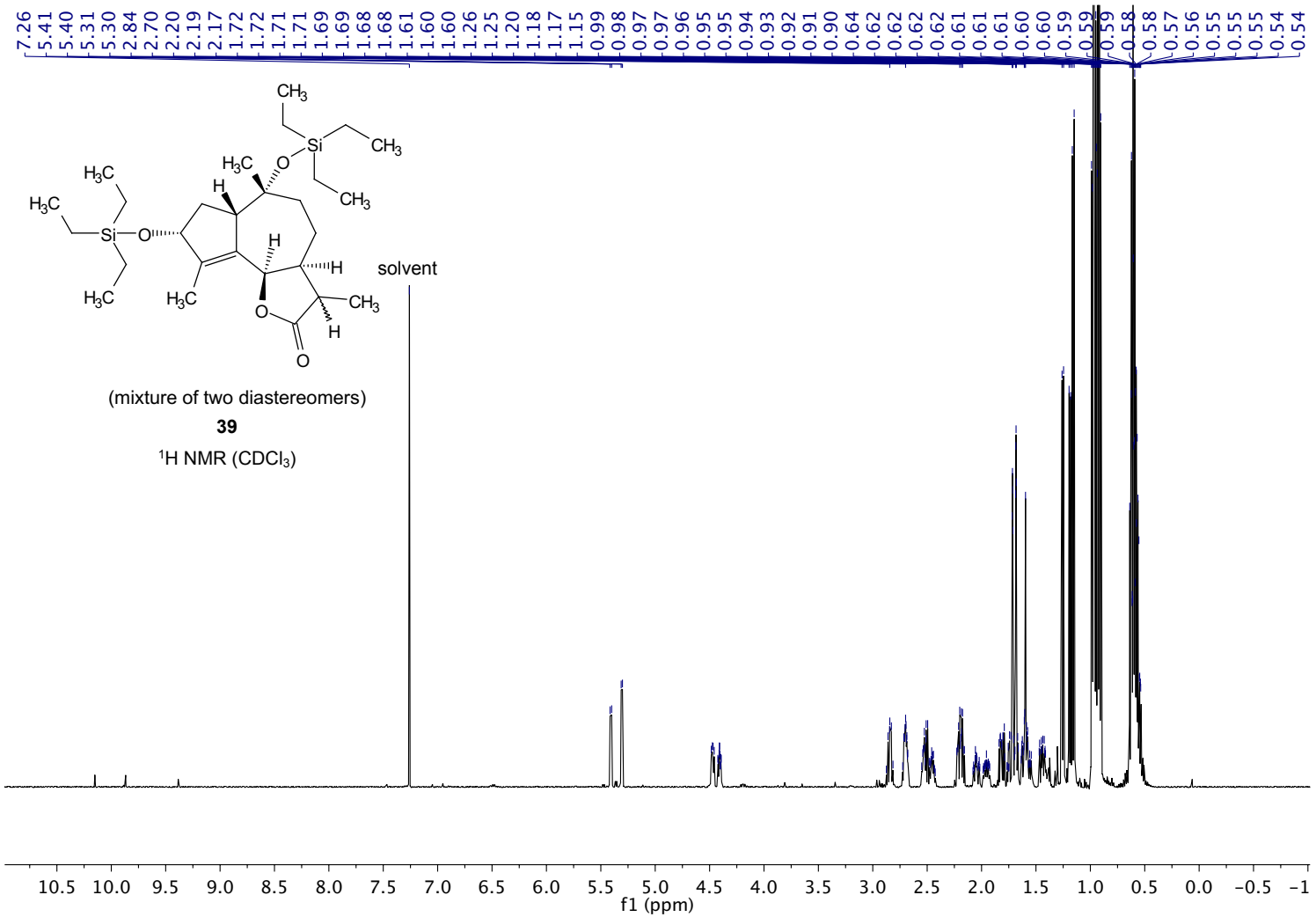
38

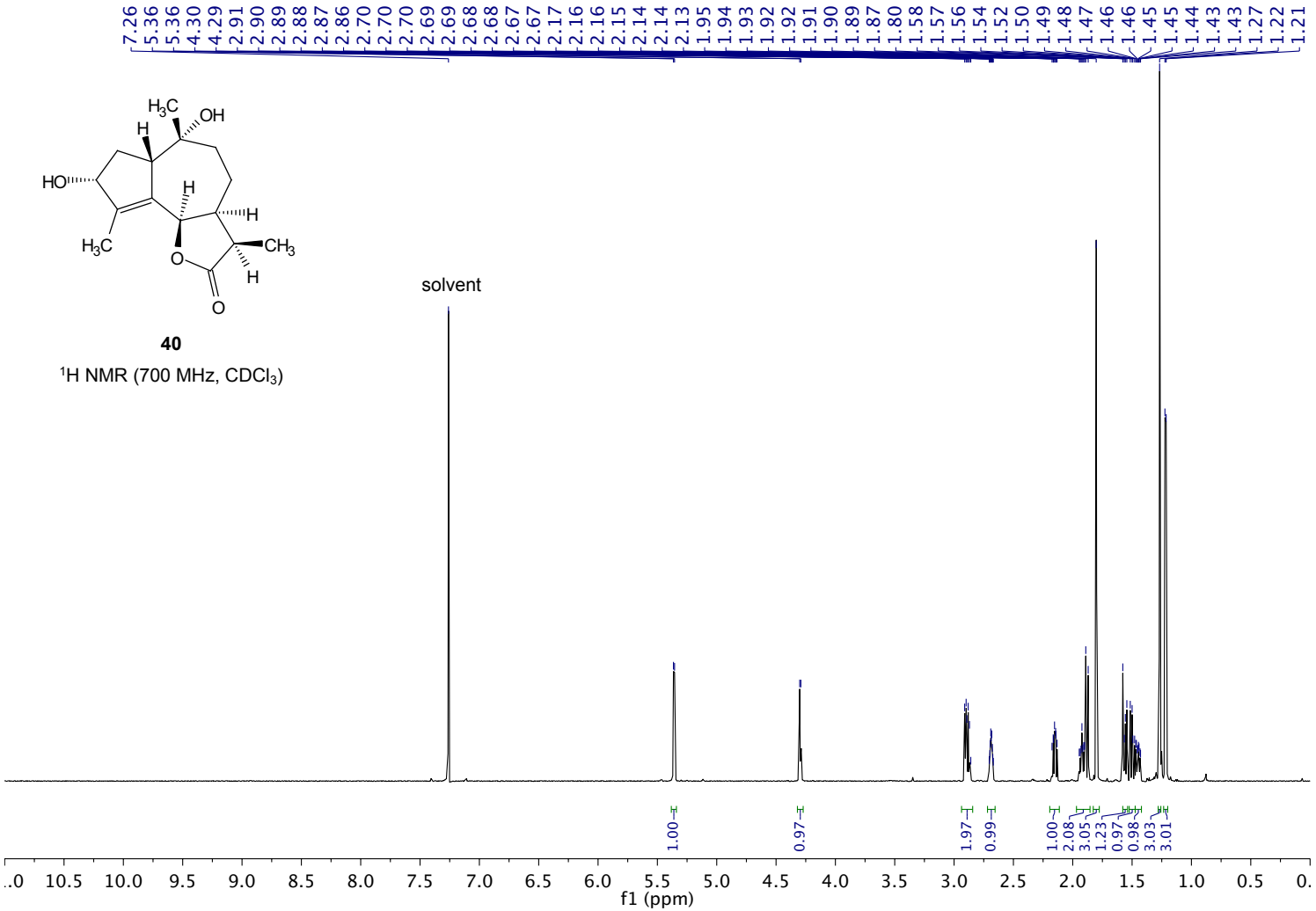
^{1}H NMR (500 MHz, $CDCl_3$)



38

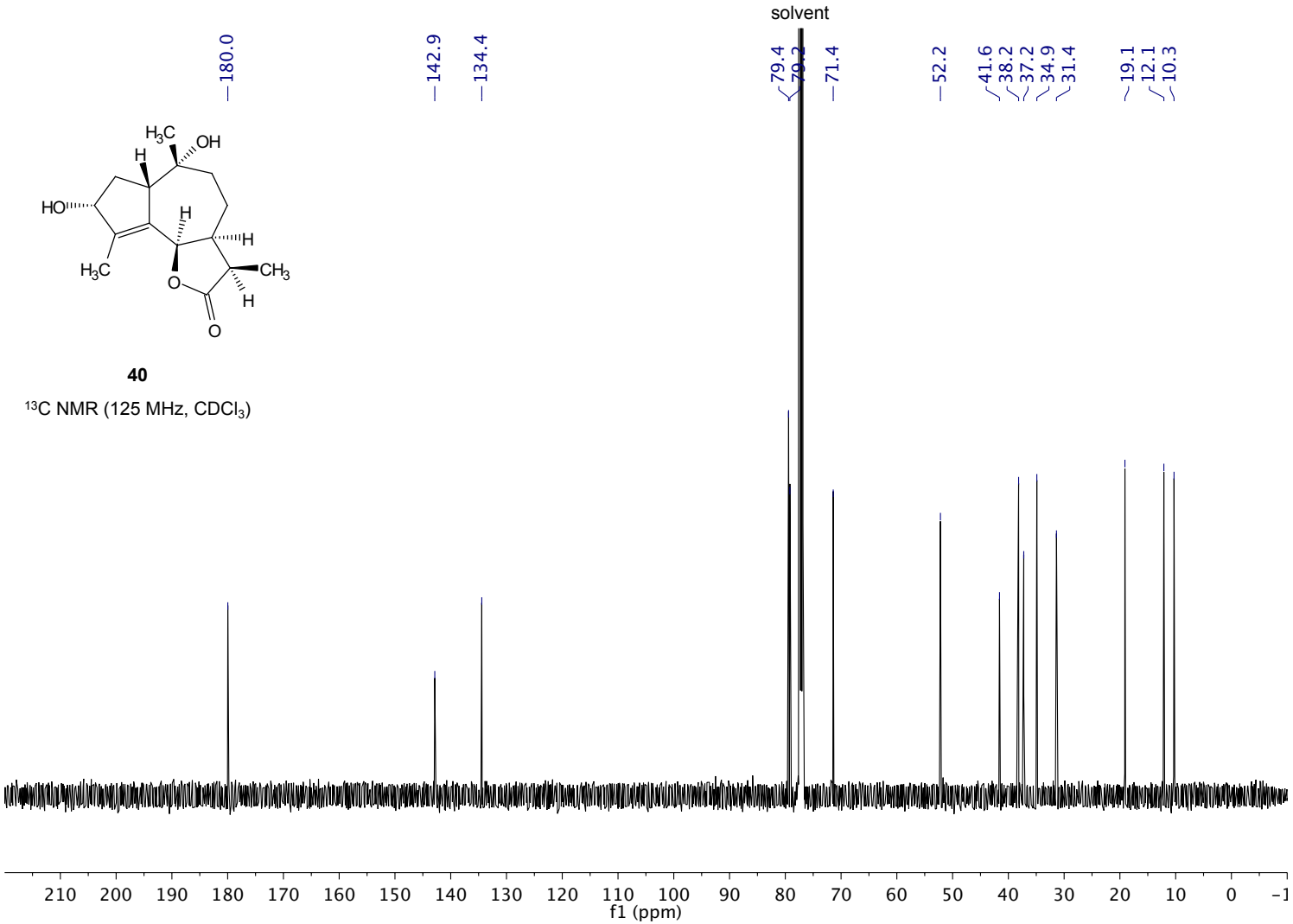
^{13}C NMR (150 MHz, $CDCl_3$)

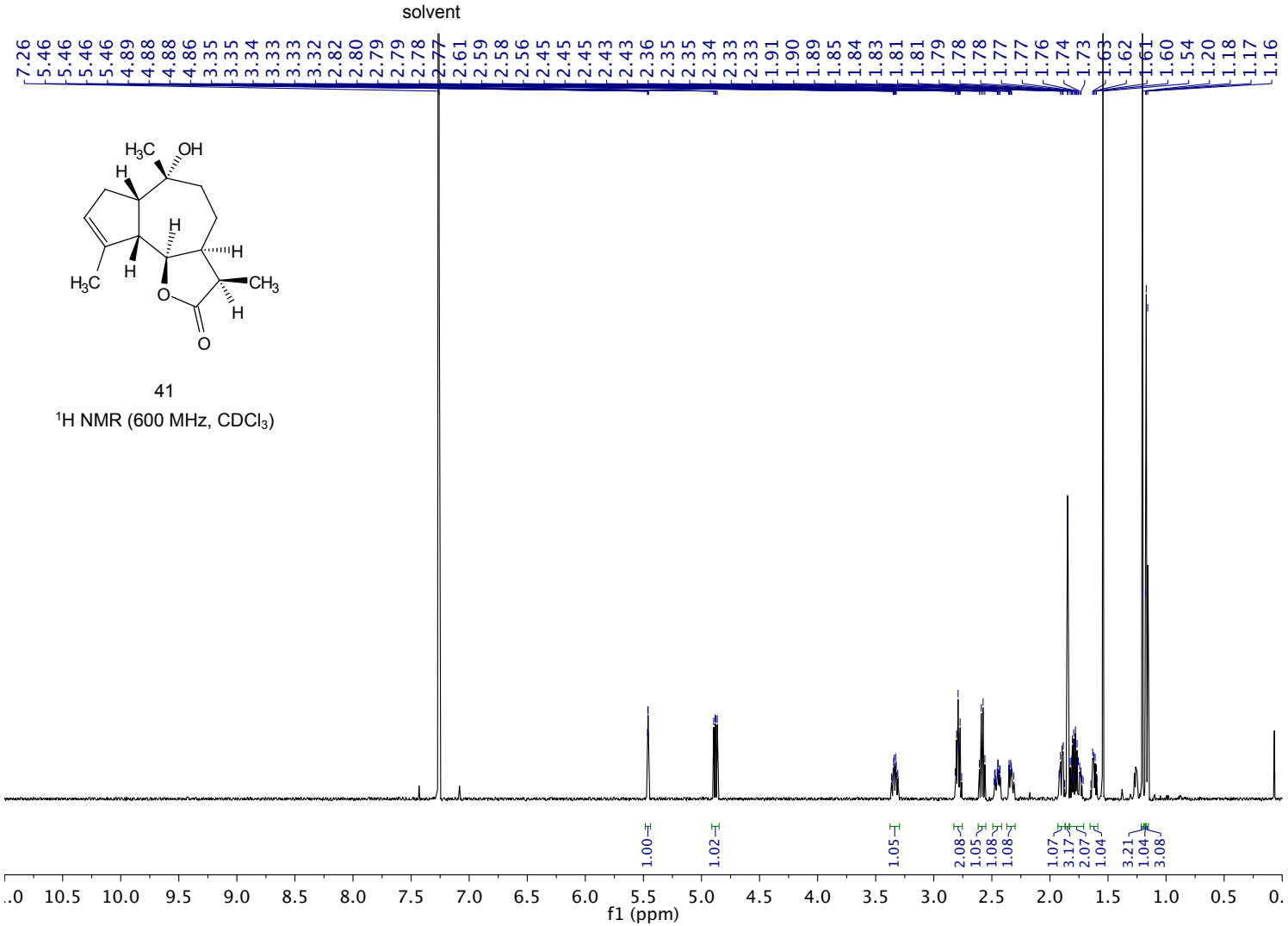

7.26 5.41 5.40 5.31 5.30 2.84 2.70 2.20 2.19 2.17 1.72 1.72 1.71 1.71 1.69 1.69 1.68 1.68 1.61 1.60 1.60 1.26 1.25 1.20 1.18 1.17 1.15 0.99 0.98 0.97 0.97 0.96 0.95 0.95 0.94 0.93 0.92 0.91 0.90 0.64 0.62 0.62 0.62 0.62 0.61 0.61 0.61 0.60 0.60 0.59 0.59 0.59 0.58 0.58 0.57 0.56 0.55 0.55 0.55 0.54 0.54
solvent
(mixture of two diastereomers)
39
^{1}H NMR ($CDCl_3$)
10.5 10.0 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 -0.5 -1
f1 (ppm)



40

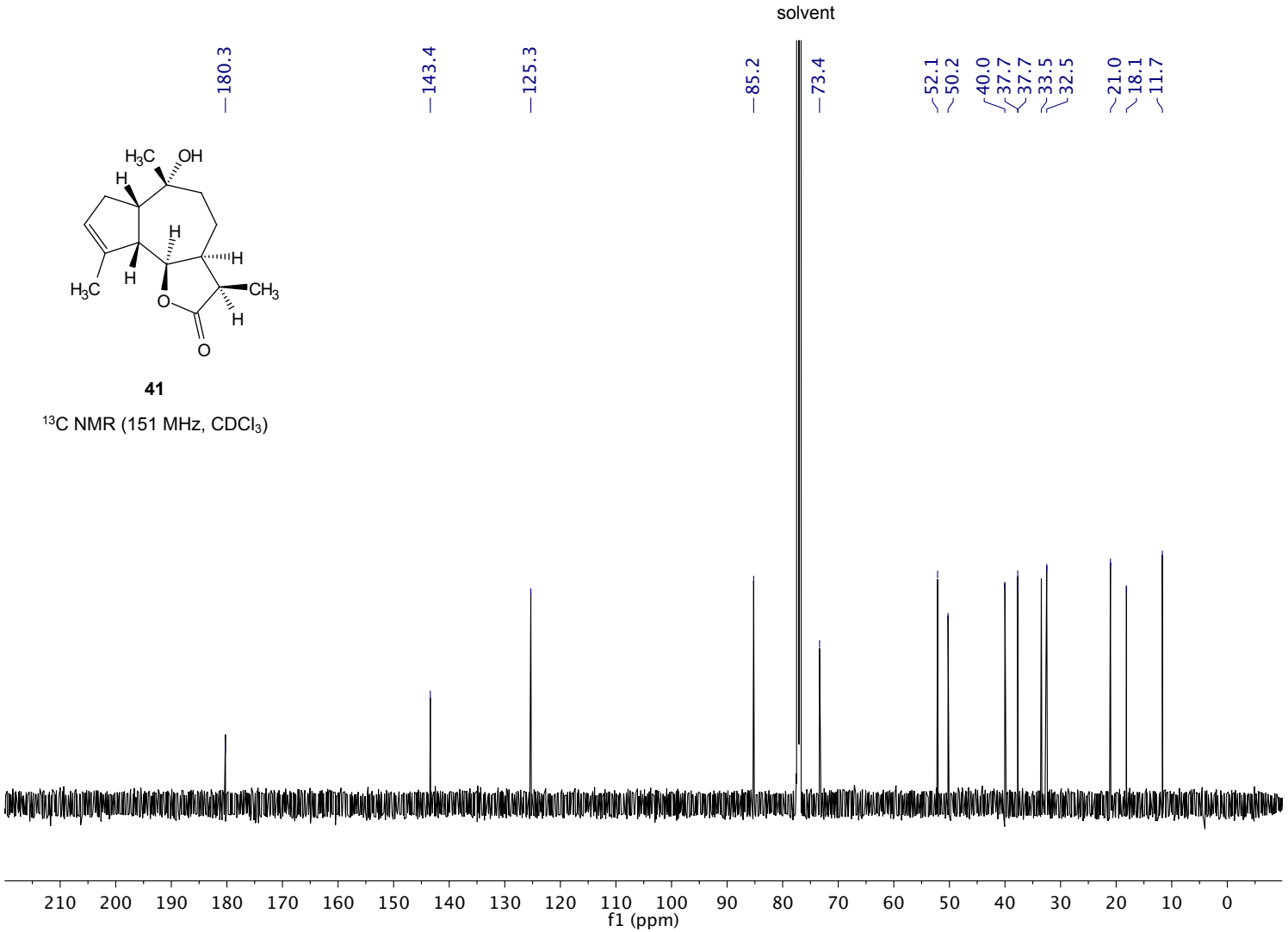
^{1}H NMR (700 MHz, $CDCl_3$)


solvent
180.0
142.9
134.4
79.4
79.2
71.4
52.2
41.6
38.2
37.2
34.9
31.4
19.1
12.1
10.3
H3C
OH
H
HO
H
H
H3C
CH3
O
H
O
40
13C NMR (125 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)



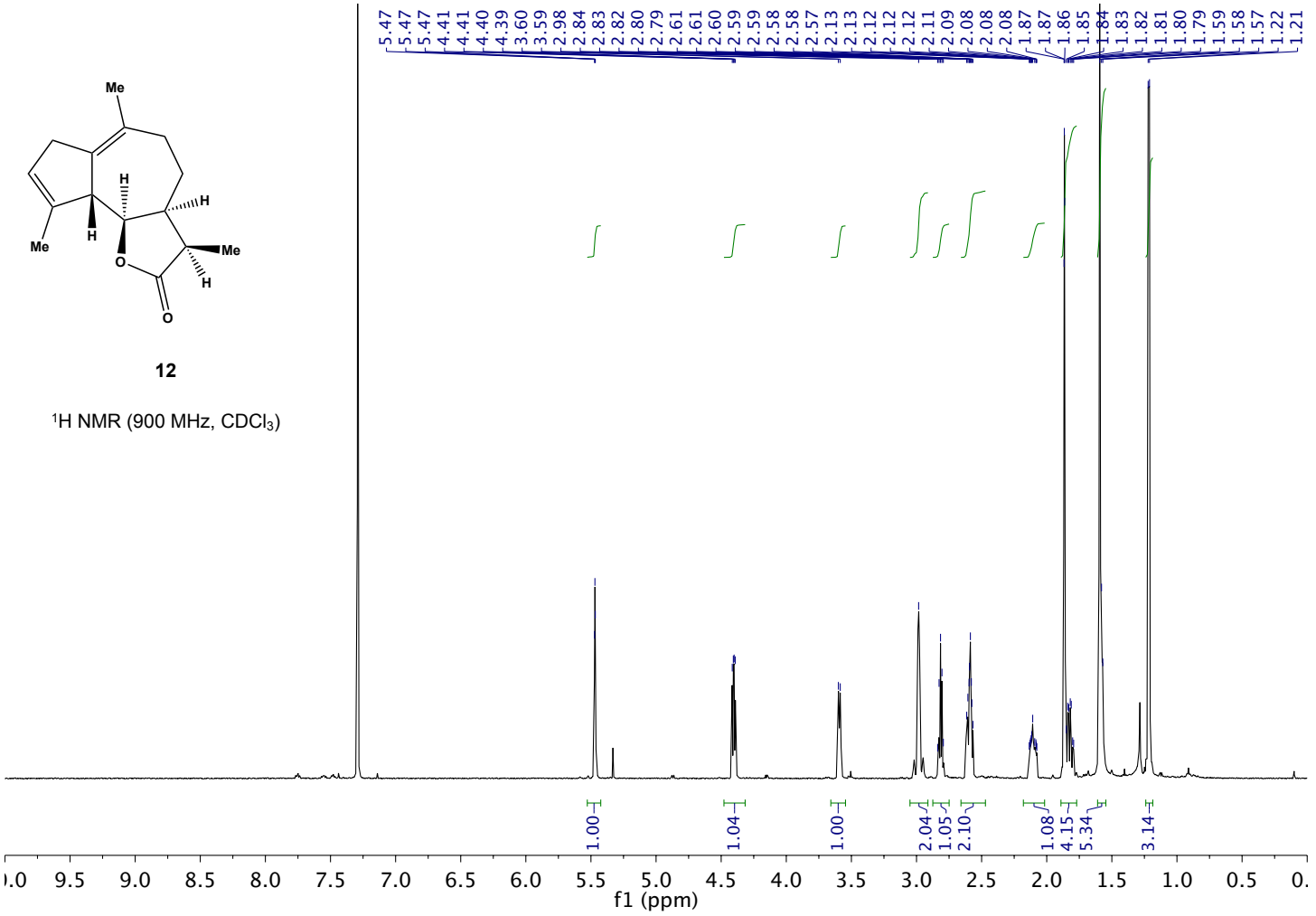
41

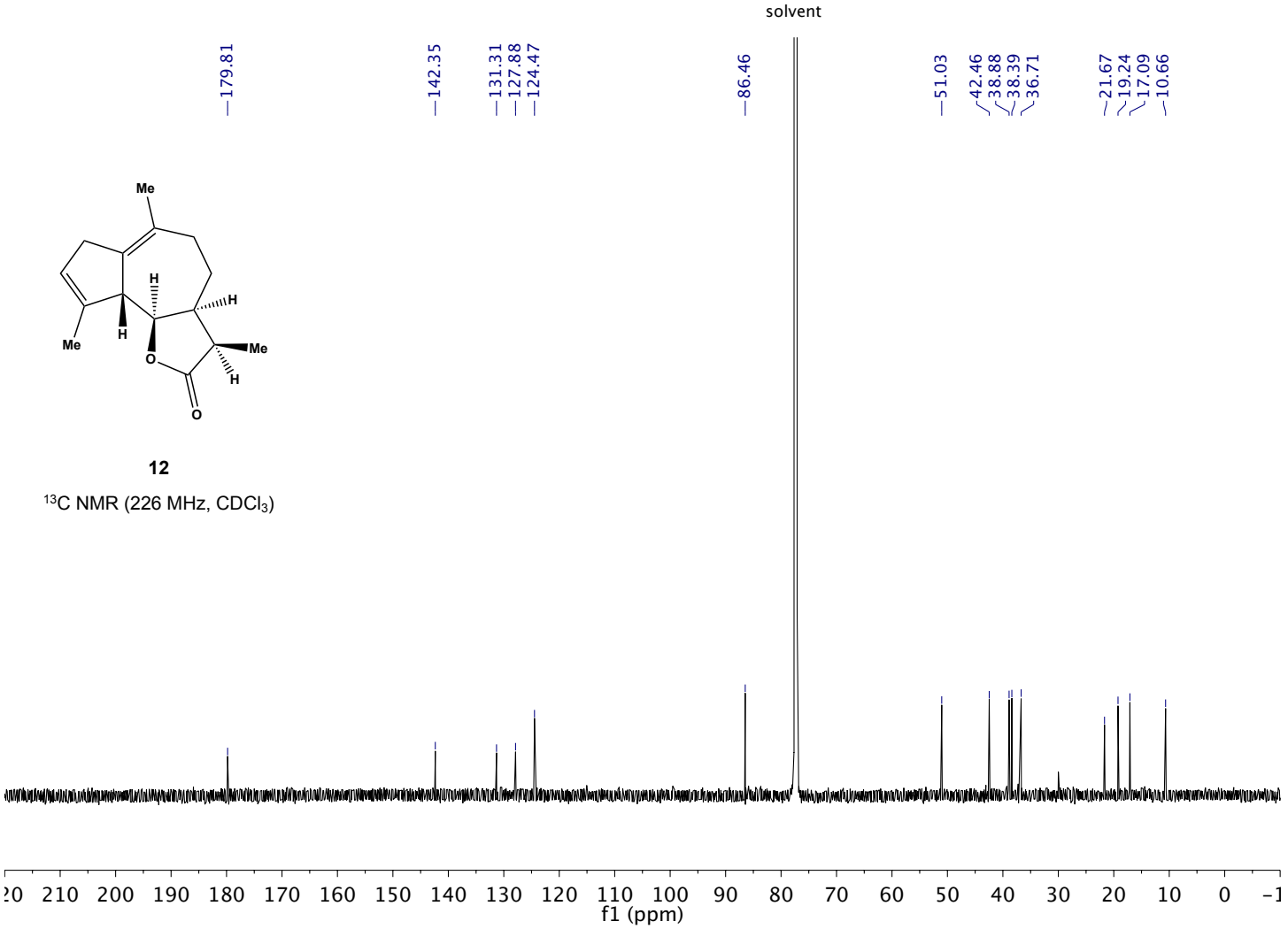
^{1}H NMR (600 MHz, $CDCl_3$)



41

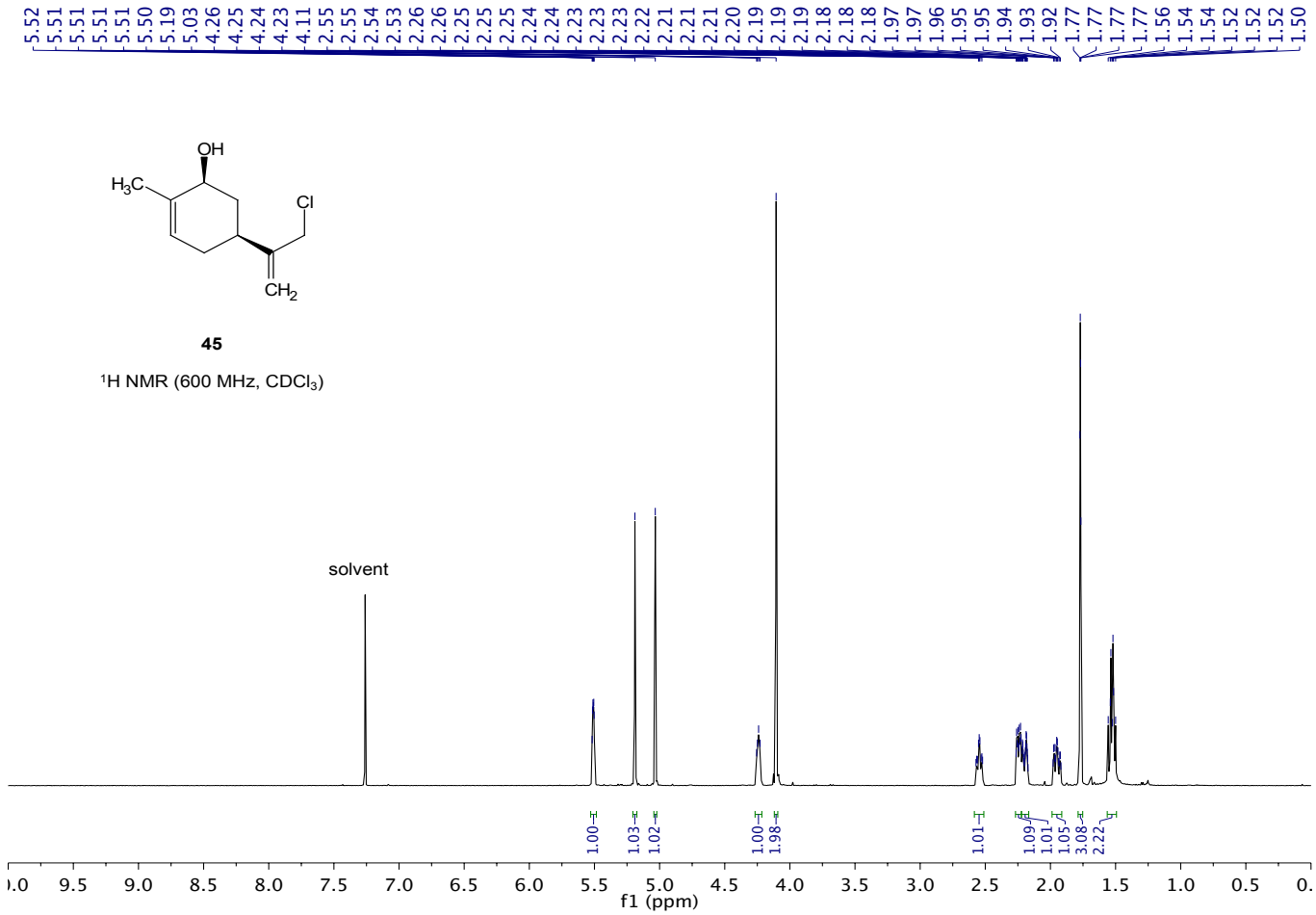
^{13}C NMR (151 MHz, $CDCl_3$)

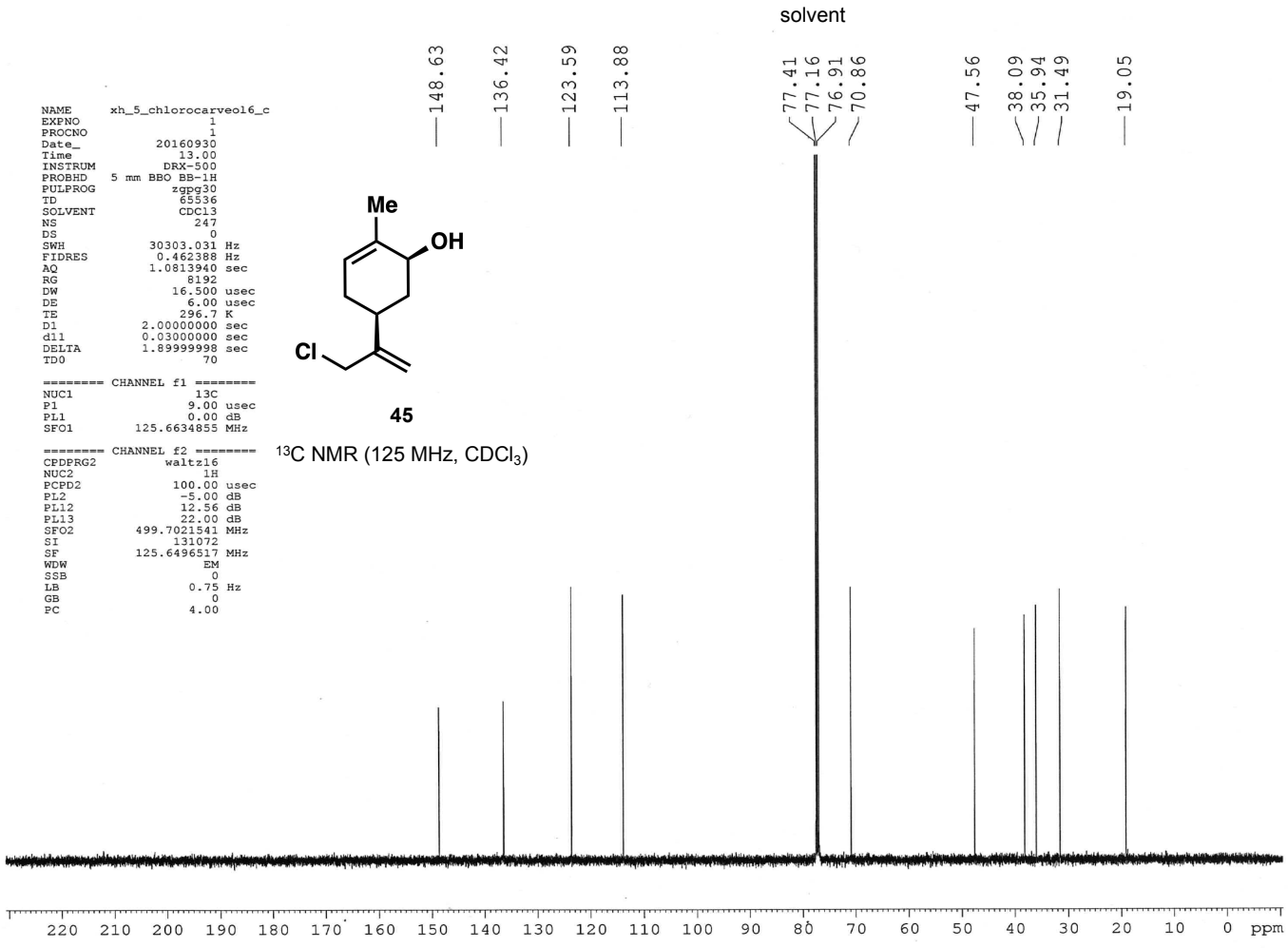

Me
H
H
Me
Me
H
O
H
O
12
^{1}H NMR (900 MHz, $CDCl_3$)
5.47 5.47 5.47 4.41 4.41 4.40 4.39 3.60 3.59 2.98 2.84 2.83 2.82 2.80 2.79 2.61 2.61 2.60 2.59 2.59 2.58 2.58 2.57 2.13 2.12 2.12 2.12 2.11 2.09 2.08 2.08 2.08 1.87 1.87 1.86 1.85 1.84 1.83 1.82 1.81 1.80 1.79 1.59 1.58 1.57 1.22 1.21
1.00 1.04 1.00 2.04 1.05 2.10 1.08 4.15 5.34 3.14
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
f1 (ppm)



12

^{13}C NMR (226 MHz, $CDCl_3$)


5.52 5.51 5.51 5.51 5.51 5.50 5.19 5.03 4.26 4.25 4.24 4.23 4.11 2.55 2.55 2.54 2.53 2.26 2.26 2.25 2.25 2.25 2.24 2.24 2.23 2.23 2.23 2.22 2.21 2.21 2.21 2.20 2.19 2.19 2.19 2.18 2.18 2.18 1.97 1.97 1.96 1.95 1.95 1.94 1.93 1.92 1.77 1.77 1.77 1.77 1.56 1.54 1.54 1.52 1.52 1.52 1.50
OH
H3C
Cl
CH2
45
1H NMR (600 MHz, CDCl3)
solvent
1.00 1.03 1.02 1.00 1.98 1.01 1.09 1.01 1.05 3.08 2.22
f1 (ppm)



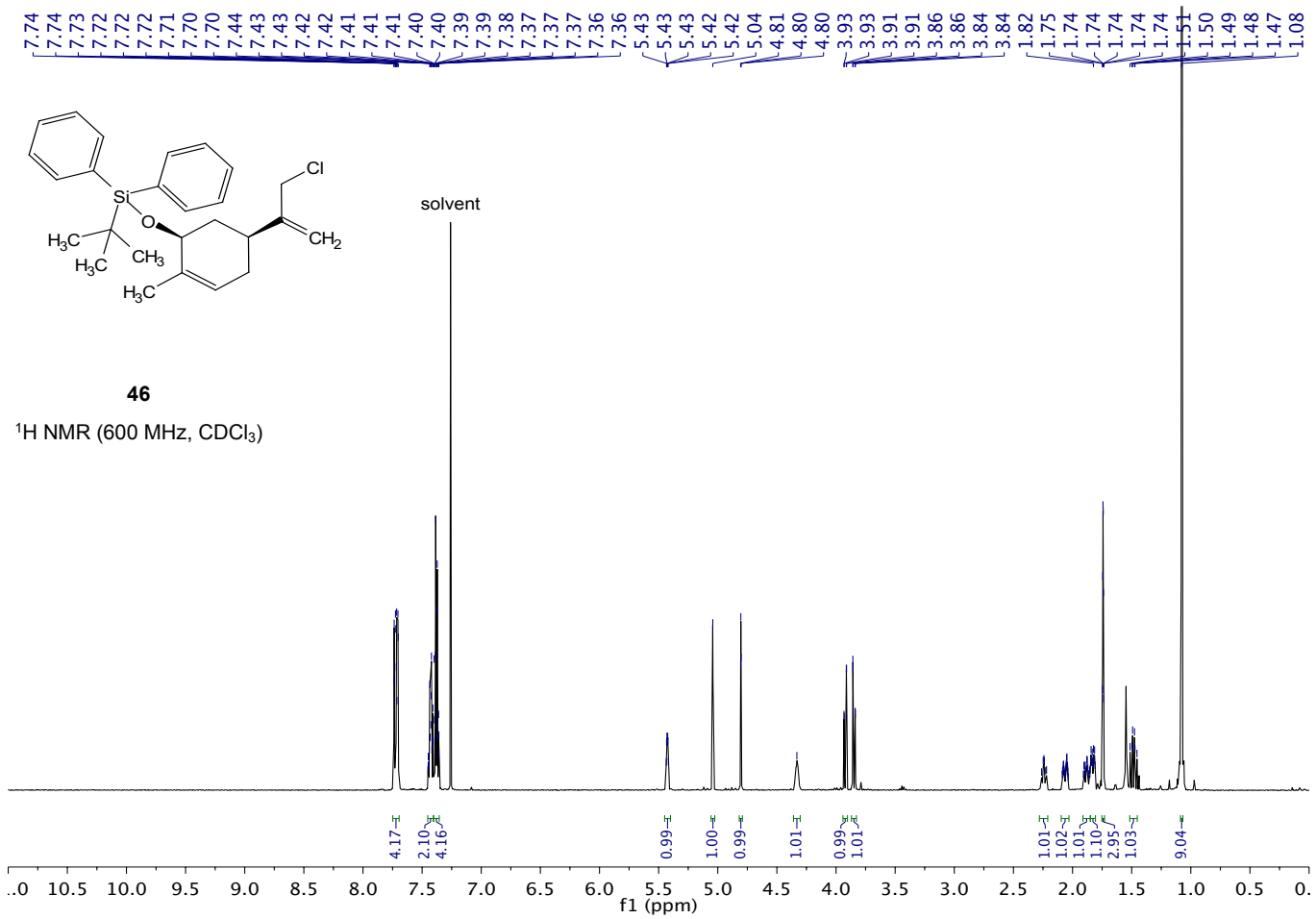

```
NAME        xh_5_chlorocarveol6_c
EXPNO                           1
PROCNO                          1
Date_                    20160930
Time                        13.00
INSTRUM                  DRX-500
PROBHD      5 mm BBO BB-1H
PULPROG                  zgpg30
TD                           65536
SOLVENT                  CDCl3
NS                             247
DS                               0
SWH                  30303.031 Hz
FIDRES                0.462388 Hz
AQ                    1.0813940 sec
RG                            8192
DW                      16.500 usec
DE                       6.00 usec
TE                       296.7 K
D1                    2.00000000 sec
d11                   0.03000000 sec
DELTA                 1.89999998 sec
TD0                             70

======== CHANNEL f1 ========
NUC1                         13C
P1                         9.00 usec
PL1                        0.00 dB
SFO1                125.6634855 MHz

======== CHANNEL f2 ========
CPDPRG2                  waltz16
NUC2                         1H
PCPD2                    100.00 usec
PL2                       -5.00 dB
PL12                      12.56 dB
PL13                      22.00 dB
SFO2                499.7021541 MHz
SI                          131072
SF                  125.6496517 MHz
WDW                           EM
SSB                            0
LB                          0.75 Hz
GB                             0
PC                          4.00
```

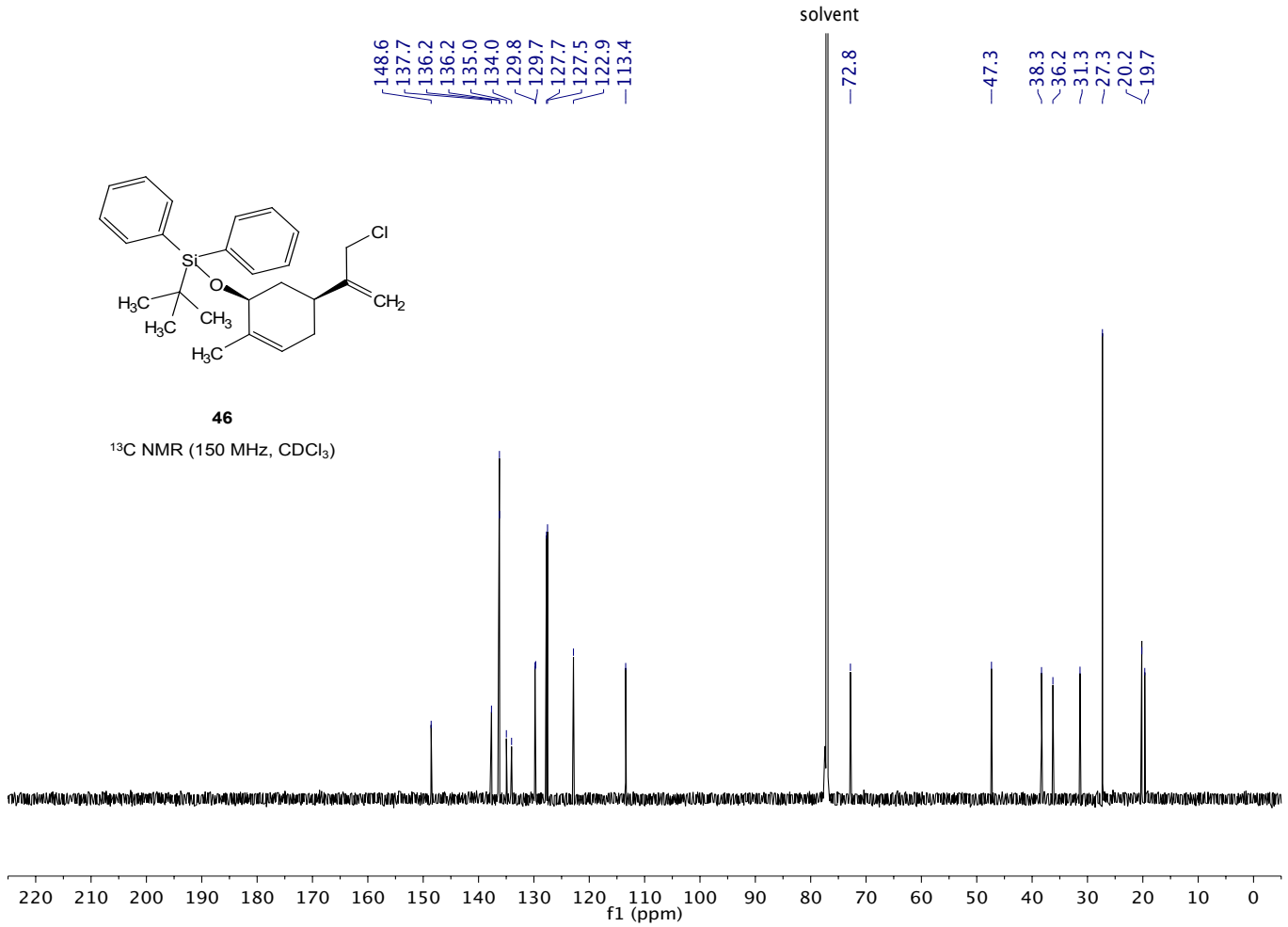
45

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



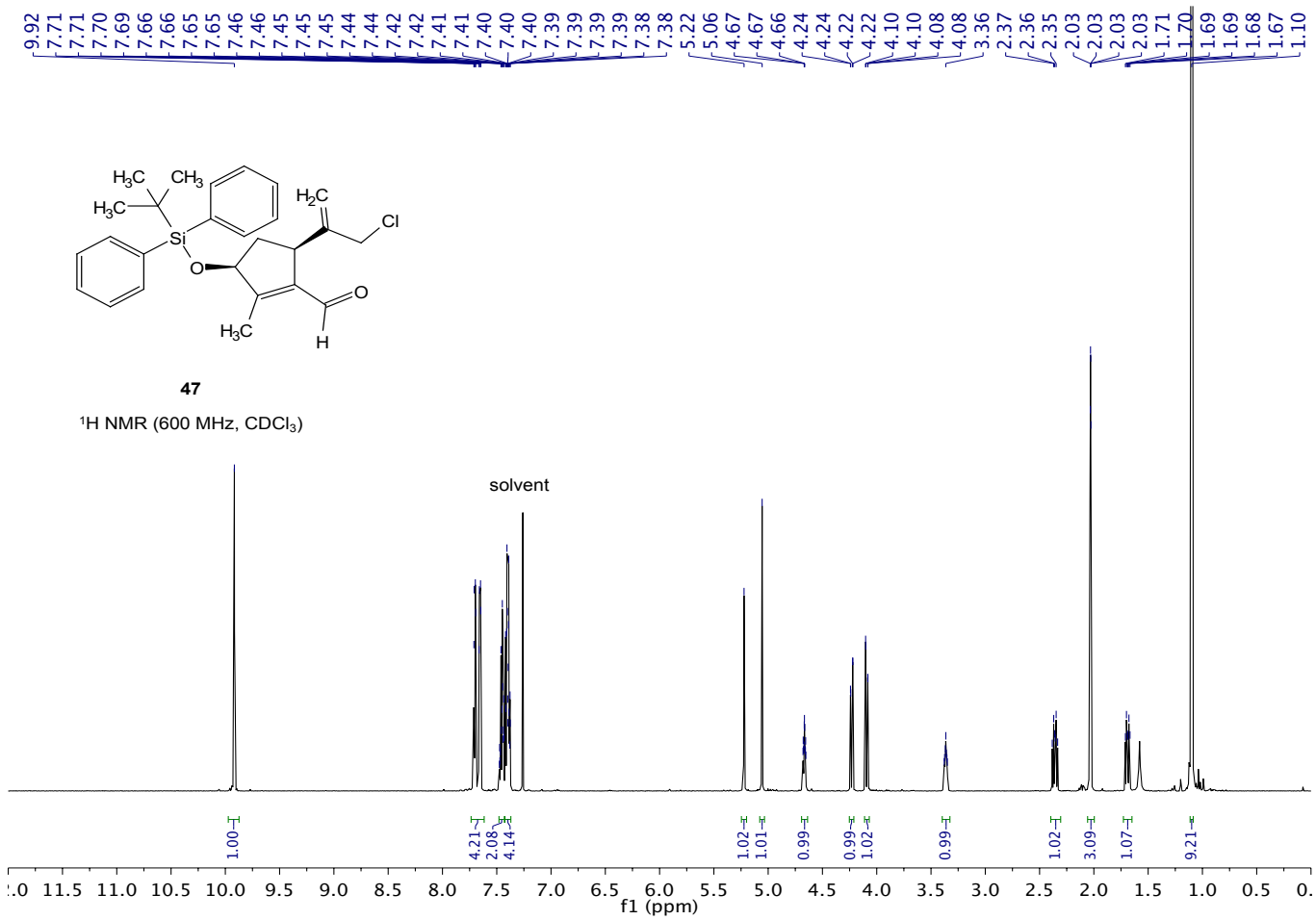
46

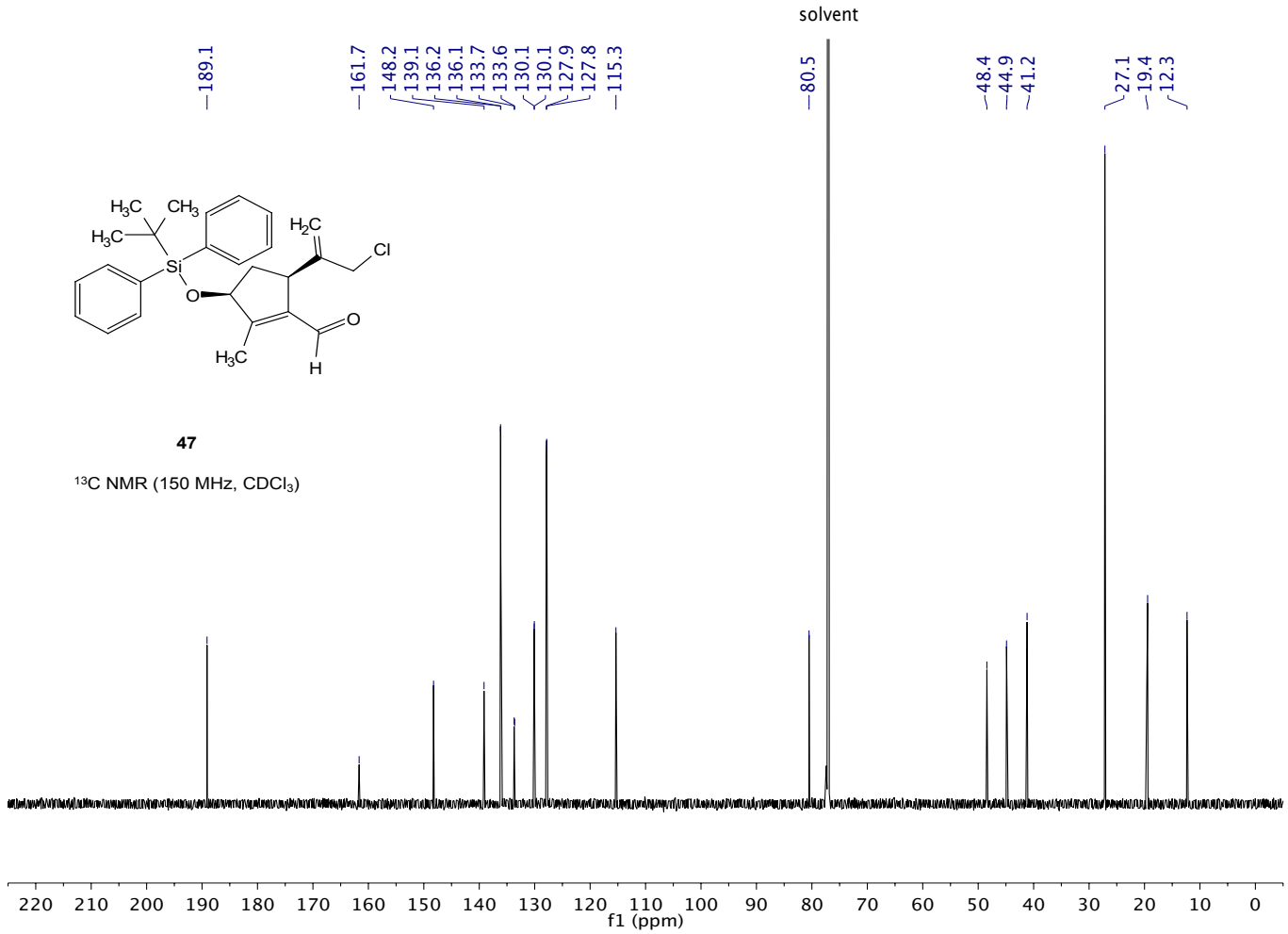
^{1}H NMR (600 MHz, $CDCl_3$)

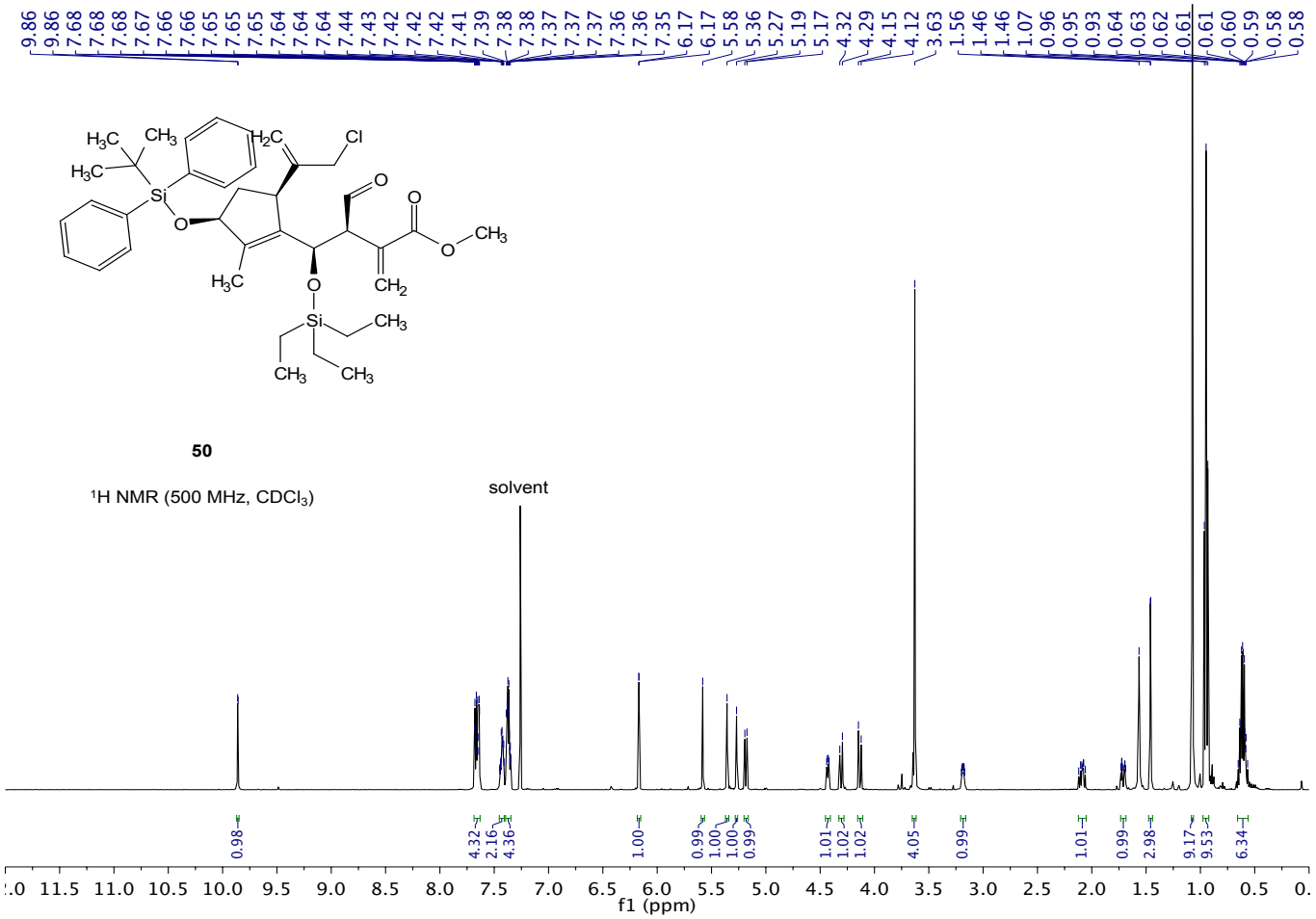


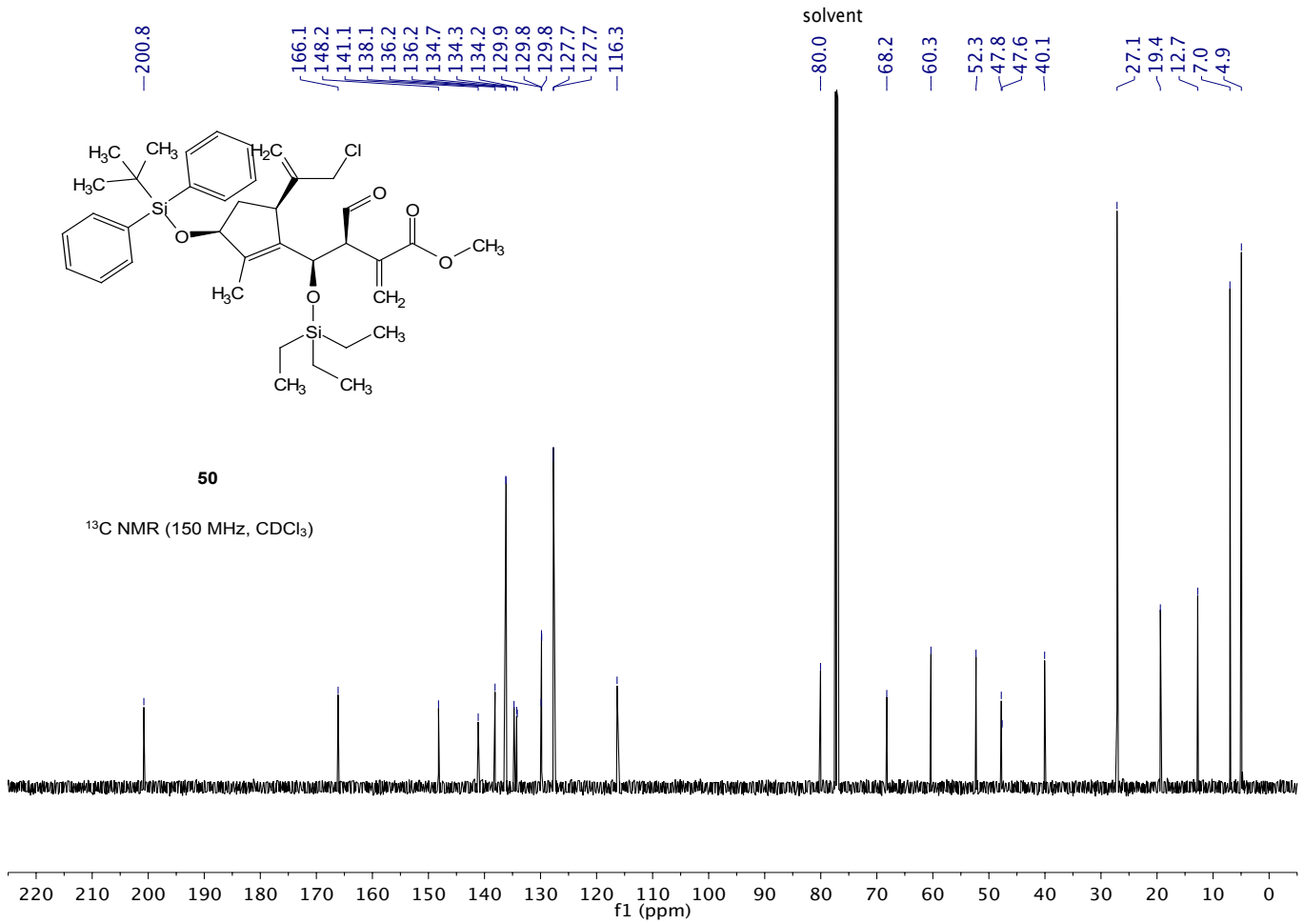
46

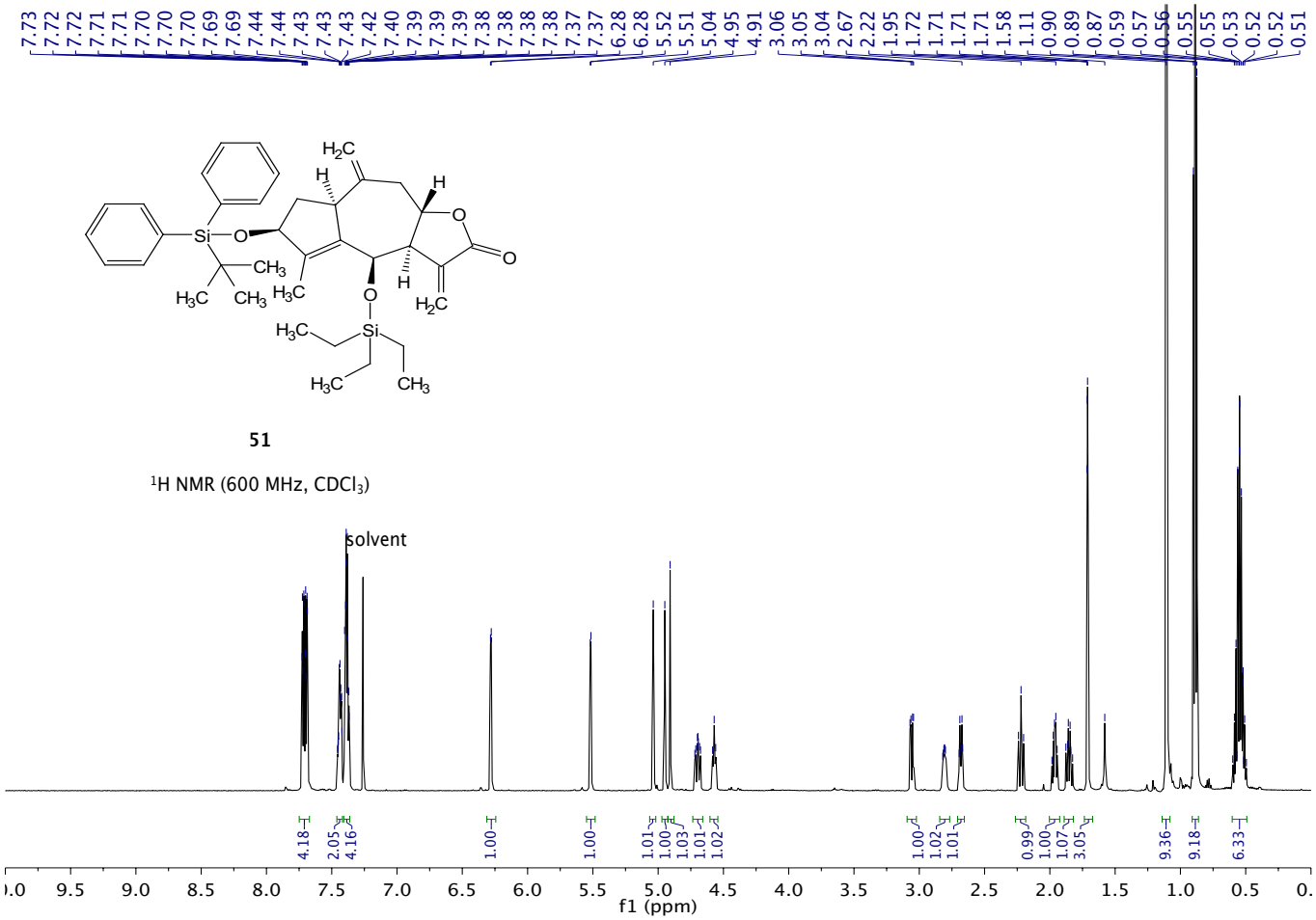
^{13}C NMR (150 MHz, $CDCl_3$)

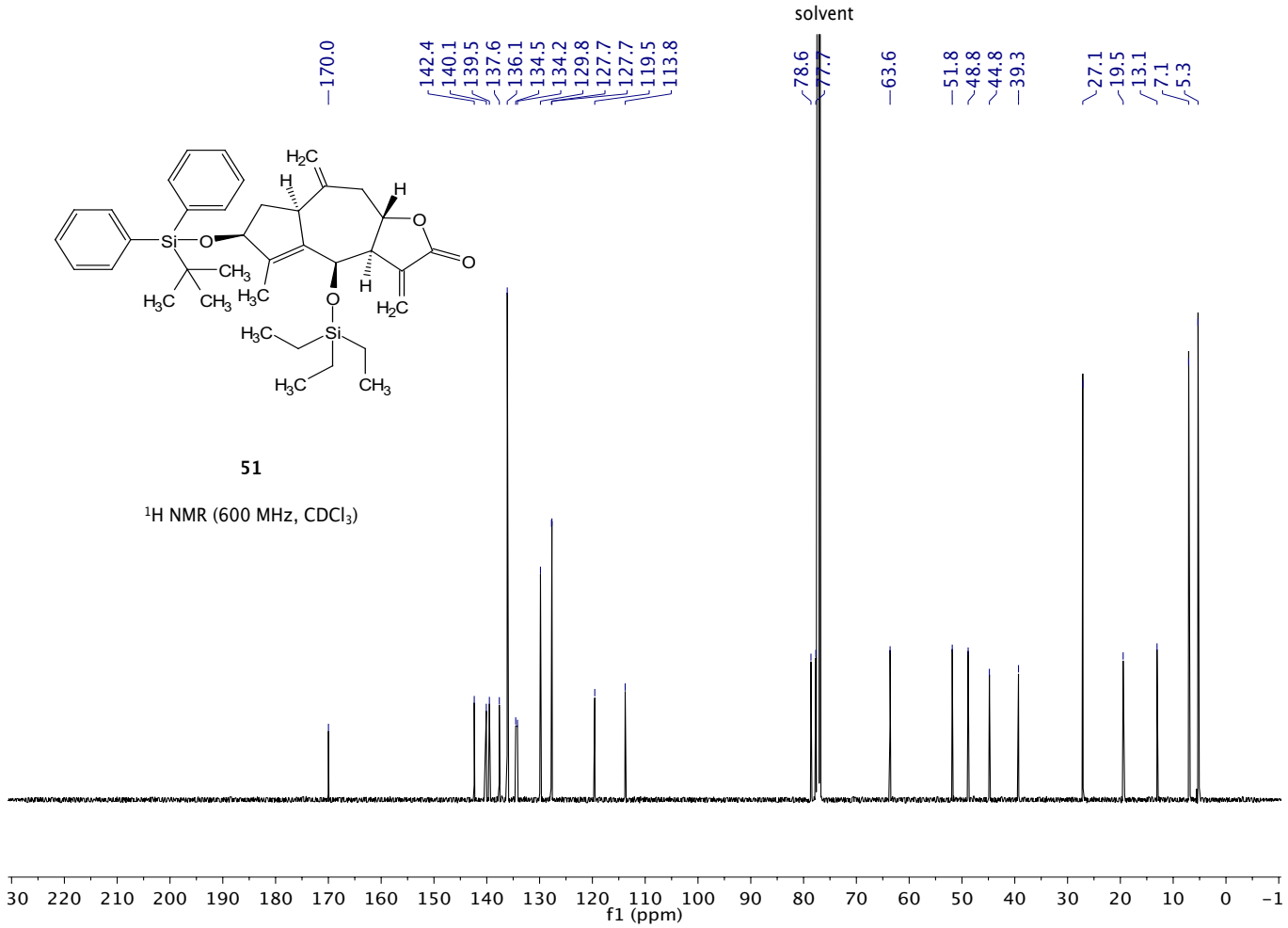

9.92
7.71
7.71
7.70
7.69
7.66
7.66
7.65
7.65
7.46
7.45
7.45
7.45
7.44
7.44
7.42
7.42
7.41
7.41
7.40
7.40
7.40
7.39
7.39
7.39
7.39
7.38
7.38
5.22
5.06
4.67
4.67
4.66
4.24
4.24
4.22
4.22
4.10
4.10
4.08
4.08
3.36
2.37
2.36
2.35
2.03
2.03
2.03
2.03
1.71
1.70
1.69
1.69
1.68
1.67
1.10
H3C
CH3
H3C
Si
O
H2C
Cl
O
H3C
H
47
1H NMR (600 MHz, CDCl3)
solvent
1.00
4.21
2.08
4.14
1.02
1.01
0.99
0.99
1.02
0.99
1.02
3.09
1.07
9.21
f1 (ppm)


solvent
189.1
161.7
148.2
139.1
136.2
136.1
133.7
133.6
130.1
130.1
127.9
127.8
115.3
80.5
48.4
44.9
41.2
27.1
19.4
12.3
H3C
CH3
H3C
Si
O
H2C
Cl
O
H3C
H
47
13C NMR (150 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


9.86 9.86 7.68 7.68 7.68 7.67 7.66 7.66 7.65 7.65 7.65 7.64 7.64 7.64 7.44 7.43 7.42 7.42 7.42 7.41 7.39 7.38 7.38 7.37 7.37 7.37 7.36 7.36 7.35 6.17 6.17 5.58 5.36 5.27 5.19 5.17 4.32 4.29 4.15 4.12 3.63 1.56 1.46 1.46 1.07 0.96 0.95 0.93 0.64 0.63 0.62 0.61 0.61 0.60 0.59 0.58 0.58
H3C CH3 H3C Si O H2C Cl O O O CH3 H3C O CH2 Si CH3 CH3 CH3
50
1H NMR (500 MHz, CDCl3)
solvent
0.98 4.32 2.16 4.36 1.00 0.99 1.00 1.00 0.99 1.01 1.02 1.02 4.05 0.99 1.01 0.99 2.98 9.17 9.53 6.34
f1 (ppm)

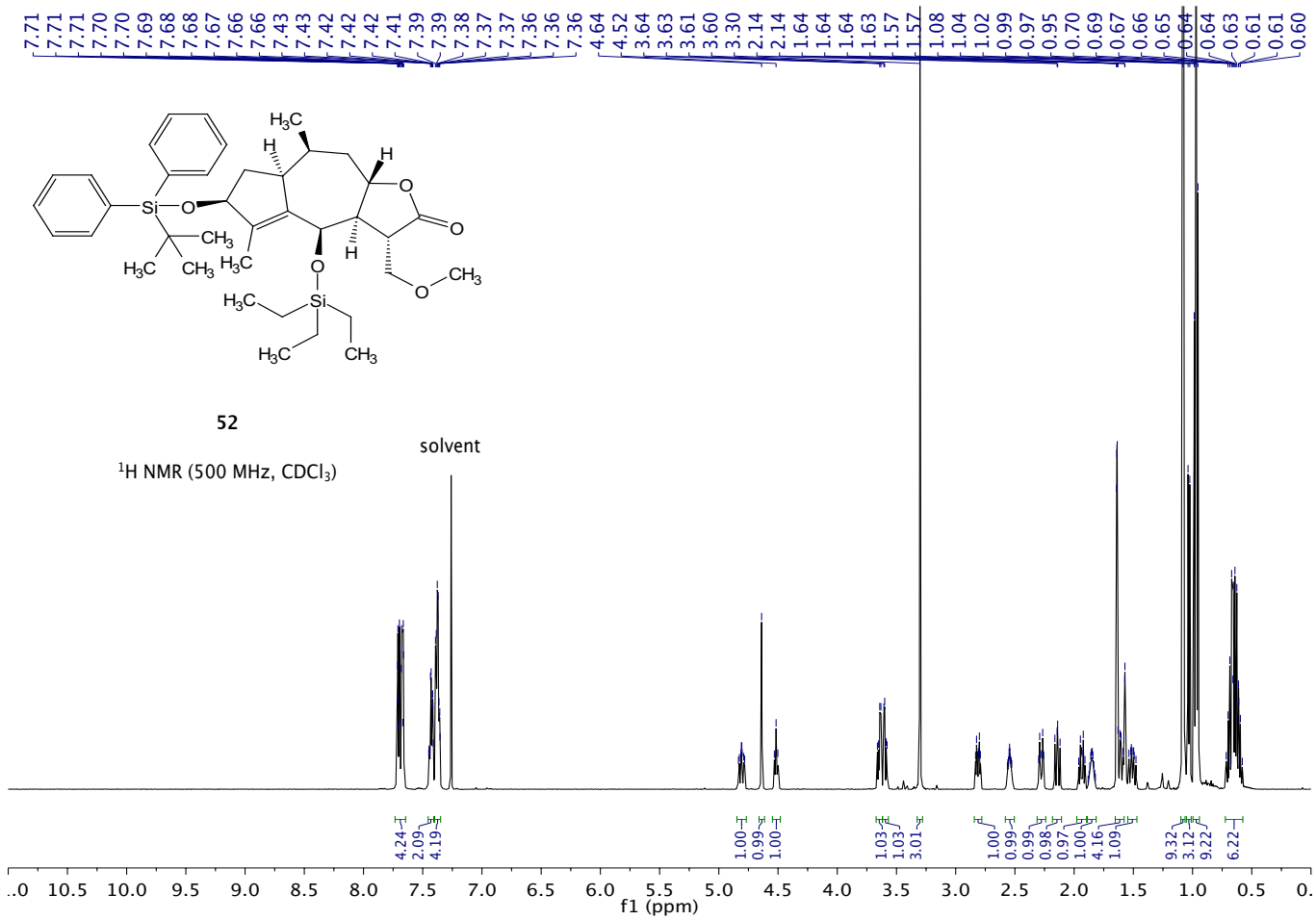

200.8
166.1
148.2
141.1
138.1
136.2
136.2
134.7
134.3
134.2
129.9
129.8
129.8
127.7
127.7
116.3
solvent
80.0
68.2
60.3
52.3
47.8
47.6
40.1
27.1
19.4
12.7
7.0
4.9
50
13C NMR (150 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

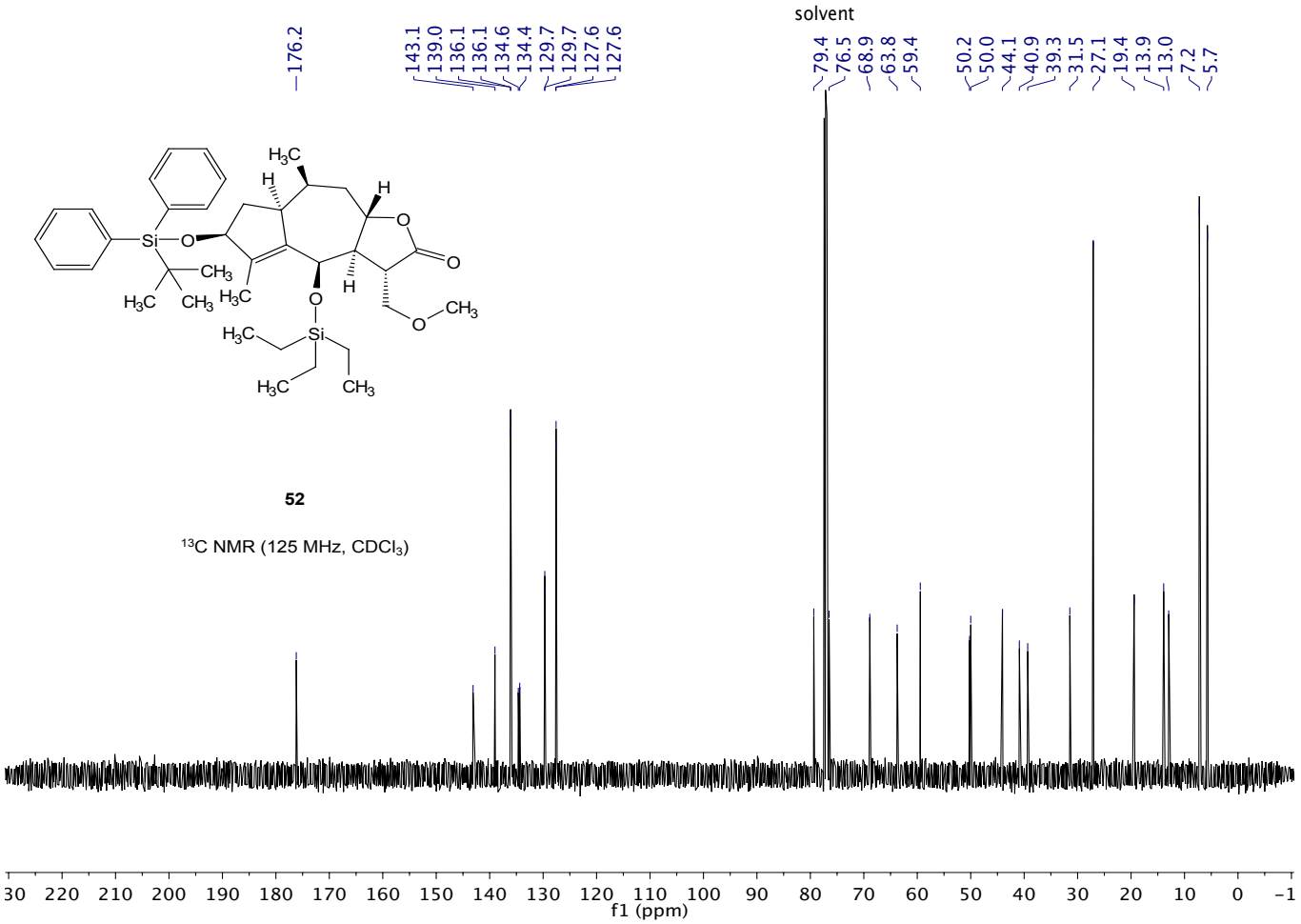

7.73 7.72 7.72 7.71 7.71 7.70 7.70 7.70 7.69 7.69 7.44 7.44 7.43 7.43 7.43 7.42 7.40 7.39 7.39 7.39 7.38 7.38 7.38 7.38 7.37 7.37 6.28 6.28 5.52 5.51 5.04 4.95 4.91 3.06 3.05 3.04 2.67 2.22 1.95 1.72 1.71 1.71 1.71 1.58 1.11 0.90 0.89 0.87 0.59 0.57 0.56 0.55 0.55 0.53 0.52 0.52 0.51
H2C
H
H
O
O
Si
O
CH3
H3C
CH3
H3C
H3C
O
H
H2C
H3C
Si
H3C
CH3
51
1H NMR (600 MHz, CDCl3)
solvent
4.18
2.05
4.16
1.00
1.00
1.01
1.00
1.03
1.01
1.02
1.00
1.02
1.01
0.99
1.00
1.07
3.05
9.36
9.18
6.33
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
f1 (ppm)

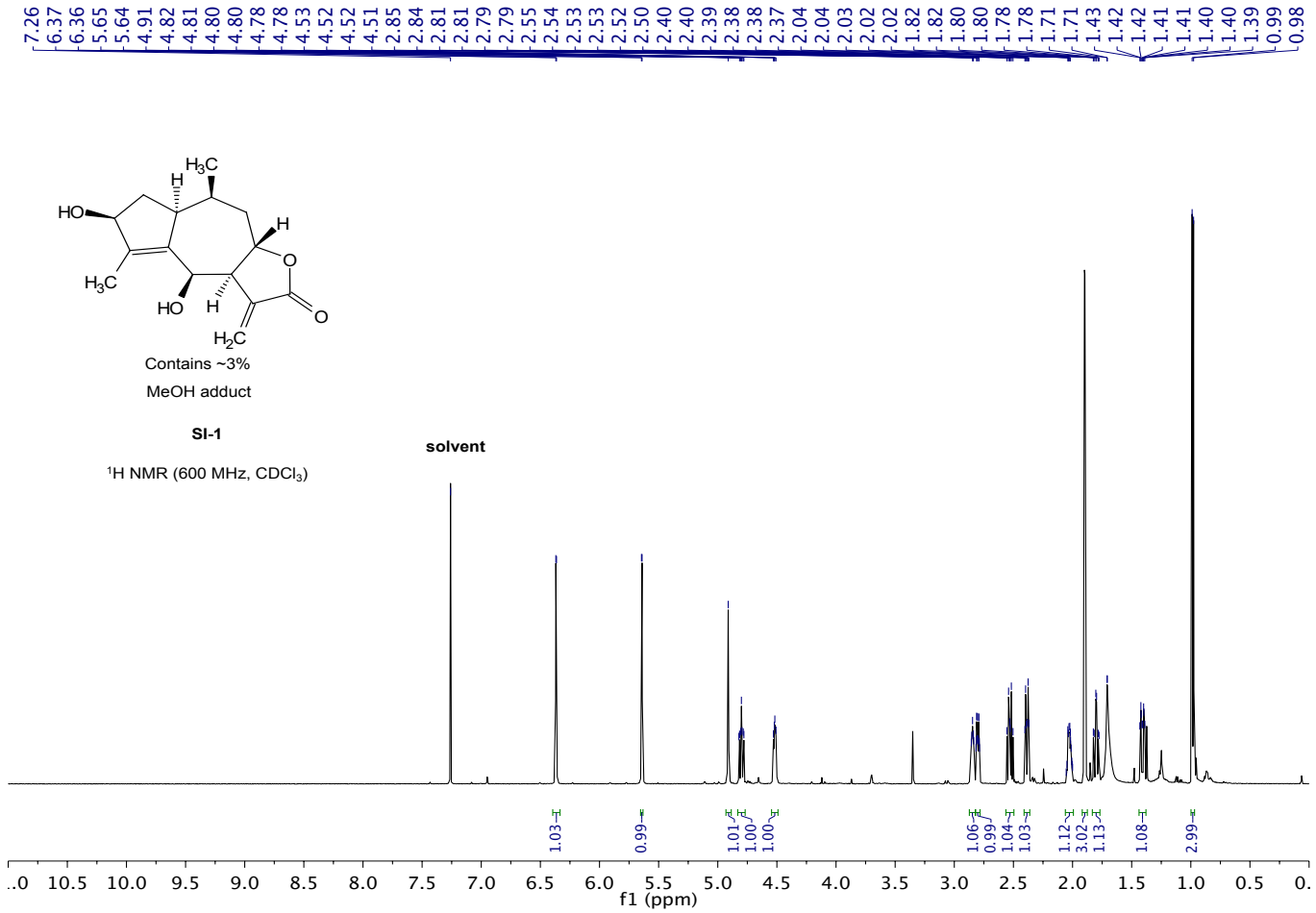


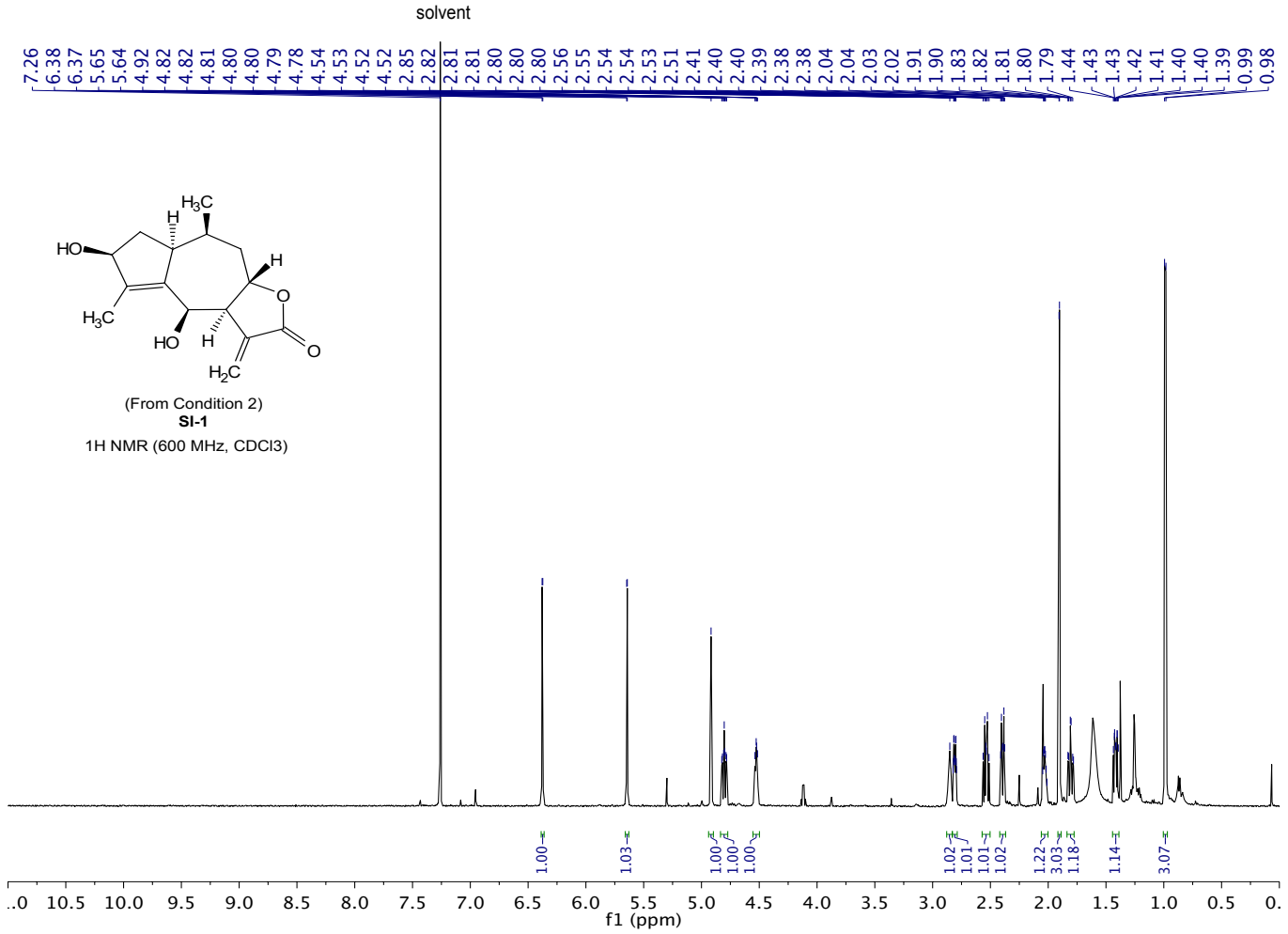
51

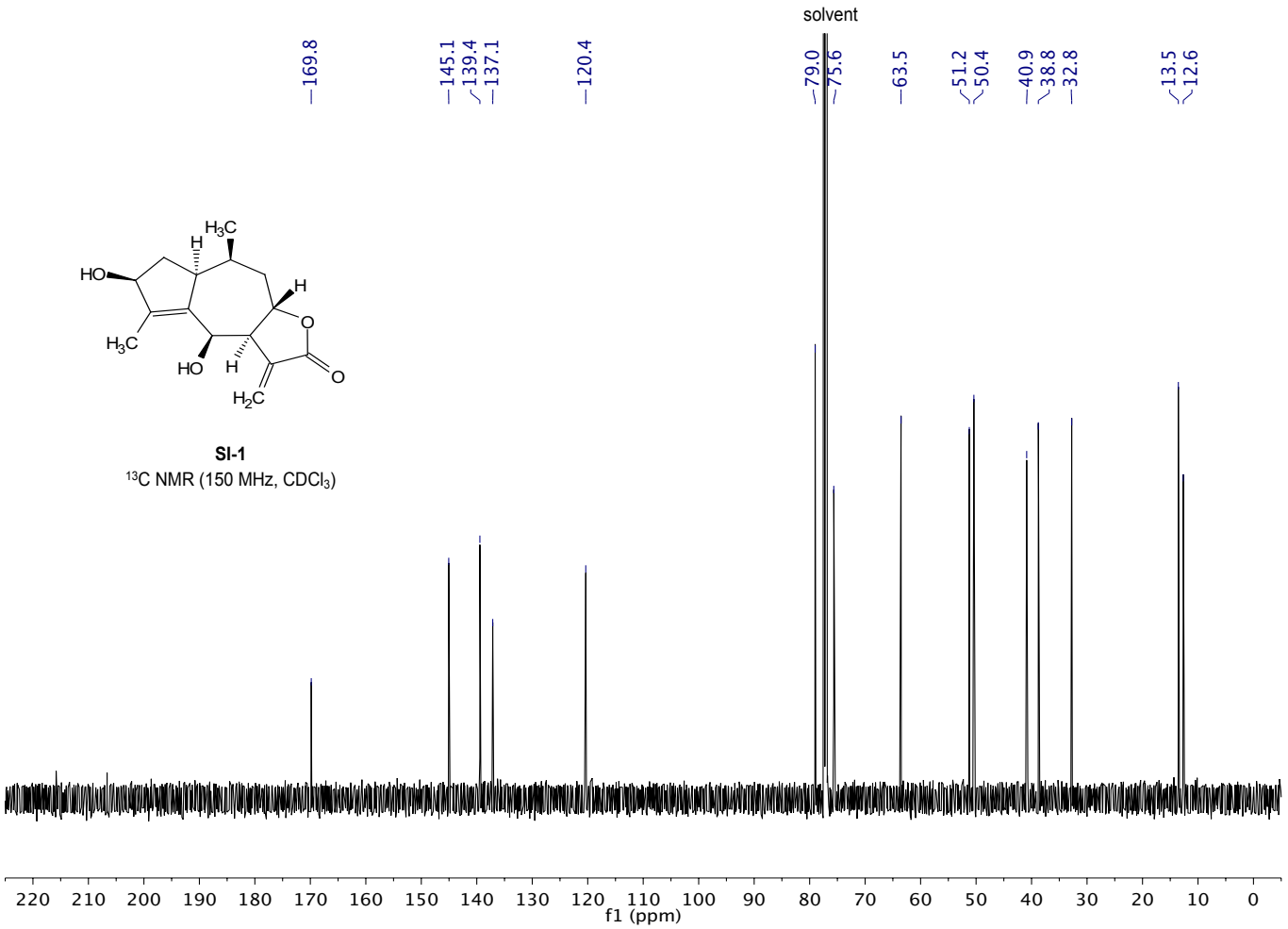
^{1}H NMR (600 MHz, $CDCl_3$)


7.71 7.71 7.71 7.70 7.70 7.69 7.68 7.68 7.67 7.66 7.66 7.43 7.43 7.42 7.42 7.42 7.41 7.39 7.39 7.38 7.37 7.37 7.36 7.36 7.36
4.64 4.52 3.64 3.63 3.61 3.60 3.30 2.14 2.14 1.64 1.64 1.64 1.63 1.57 1.57 1.08 1.04 1.02 0.99 0.97 0.95 0.70 0.69 0.67 0.66 0.65 0.64 0.64 0.63 0.61 0.61 0.60
52
solvent
^{1}H NMR (500 MHz, $CDCl_3$)
4.24 2.09 4.19 1.00 0.99 1.00 1.03 1.03 3.01 1.00 0.99 0.99 0.98 0.97 1.00 4.16 1.09 9.32 3.12 9.22 6.22
f1 (ppm)


solvent
176.2
143.1
139.0
136.1
136.1
134.6
134.4
129.7
129.7
127.6
127.6
79.4
76.5
68.9
63.8
59.4
50.2
50.0
44.1
40.9
39.3
31.5
27.1
19.4
13.9
13.0
7.2
5.7
52
13C NMR (125 MHz, CDCl3)
f1 (ppm)

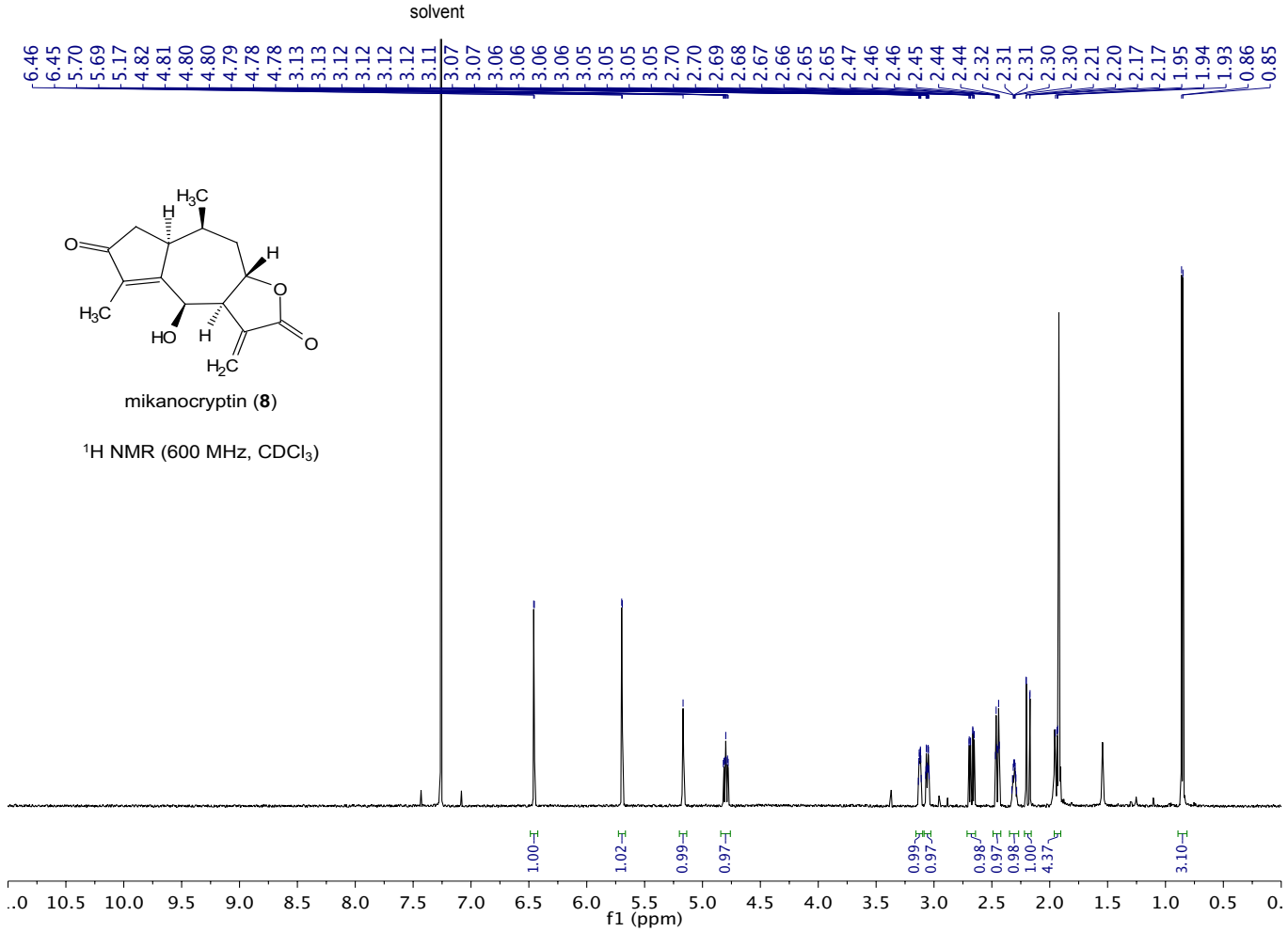

7.26
6.37
6.36
5.65
5.64
4.91
4.82
4.81
4.80
4.80
4.78
4.78
4.53
4.52
4.52
4.51
2.85
2.84
2.81
2.81
2.79
2.79
2.55
2.54
2.53
2.53
2.52
2.50
2.40
2.40
2.39
2.38
2.38
2.37
2.04
2.04
2.03
2.02
2.02
1.82
1.82
1.80
1.80
1.78
1.78
1.71
1.71
1.43
1.42
1.42
1.41
1.41
1.40
1.40
1.39
0.99
0.98
HO
H
H3C
H
O
H3C
HO
H
O
H2C
Contains ~3%
MeOH adduct
SI-1
1H NMR (600 MHz, CDCl3)
solvent
1.03
0.99
1.01
1.00
1.00
1.06
0.99
1.04
1.03
1.12
3.02
1.13
1.08
2.99
f1 (ppm)


solvent
7.26 6.38 6.37 5.65 5.64 4.92 4.82 4.82 4.81 4.80 4.80 4.79 4.78 4.54 4.53 4.52 4.52 2.85 2.82 2.81 2.81 2.80 2.80 2.80 2.56 2.55 2.54 2.54 2.53 2.51 2.41 2.40 2.40 2.39 2.38 2.38 2.04 2.04 2.03 2.02 1.91 1.90 1.83 1.82 1.81 1.80 1.79 1.44 1.43 1.43 1.42 1.41 1.40 1.40 1.39 0.99 0.98
HO
H3C
H
H
O
H3C
HO
H
O
H2C
(From Condition 2)
SI-1
1H NMR (600 MHz, CDCl3)
1.00 1.03 1.00 1.00 1.00 1.02 1.01 1.01 1.02 1.22 3.03 1.18 1.14 3.07
10.5 10.0 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
f1 (ppm)



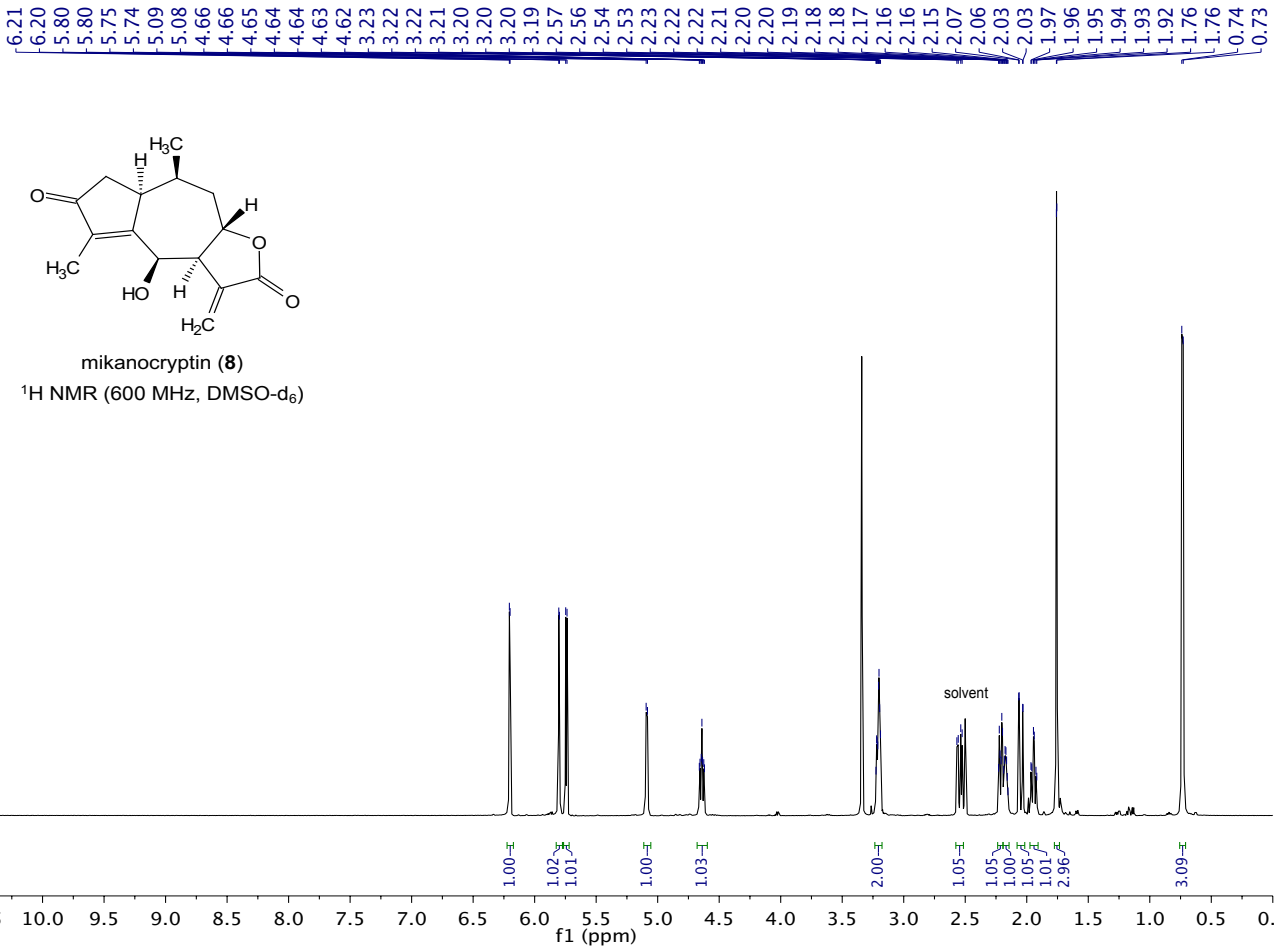
SI-1

^{13}C NMR (150 MHz, $CDCl_3$)



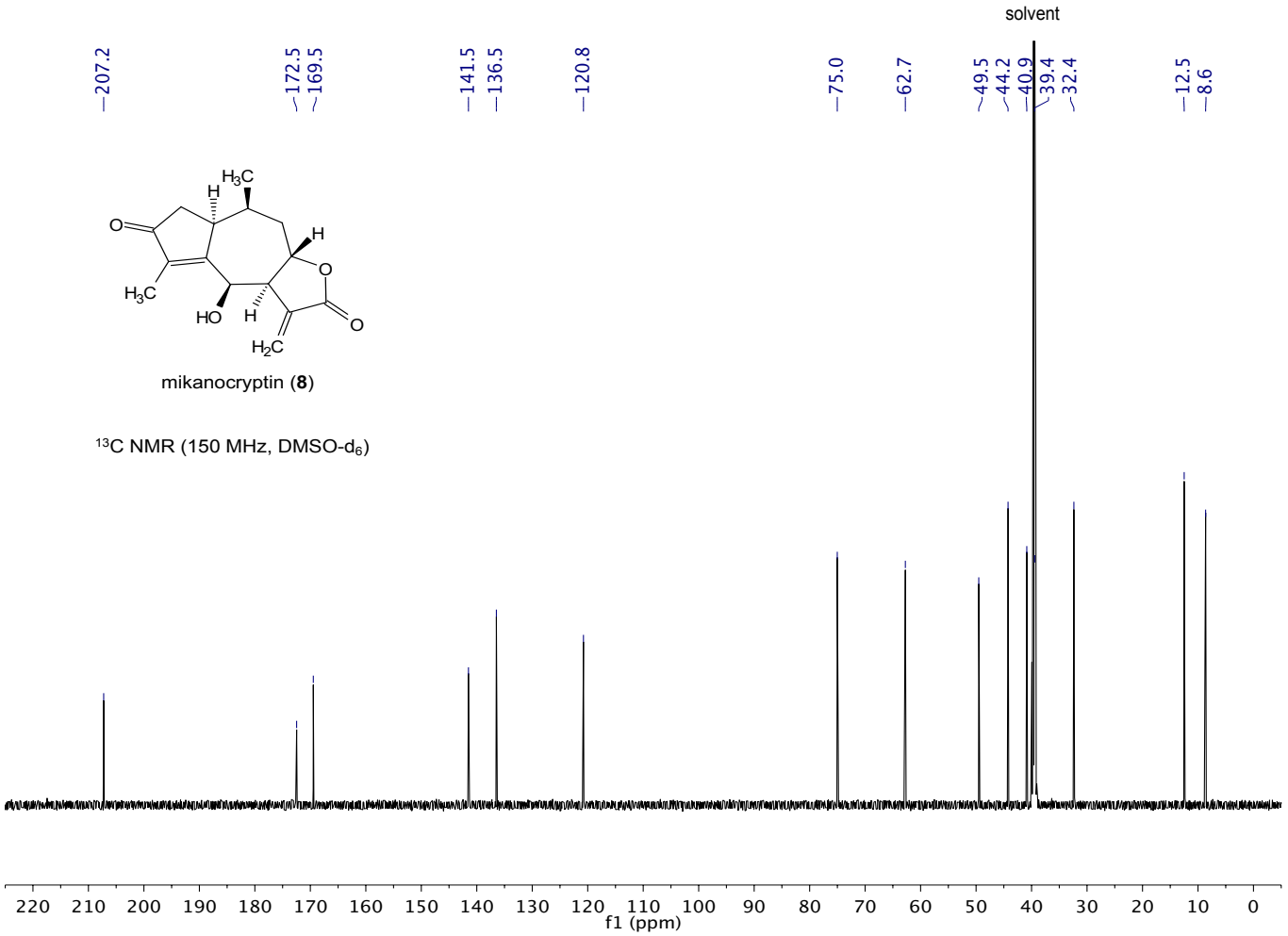
mikanocryptin (**8**)

^{1}H NMR (600 MHz, $CDCl_3$)



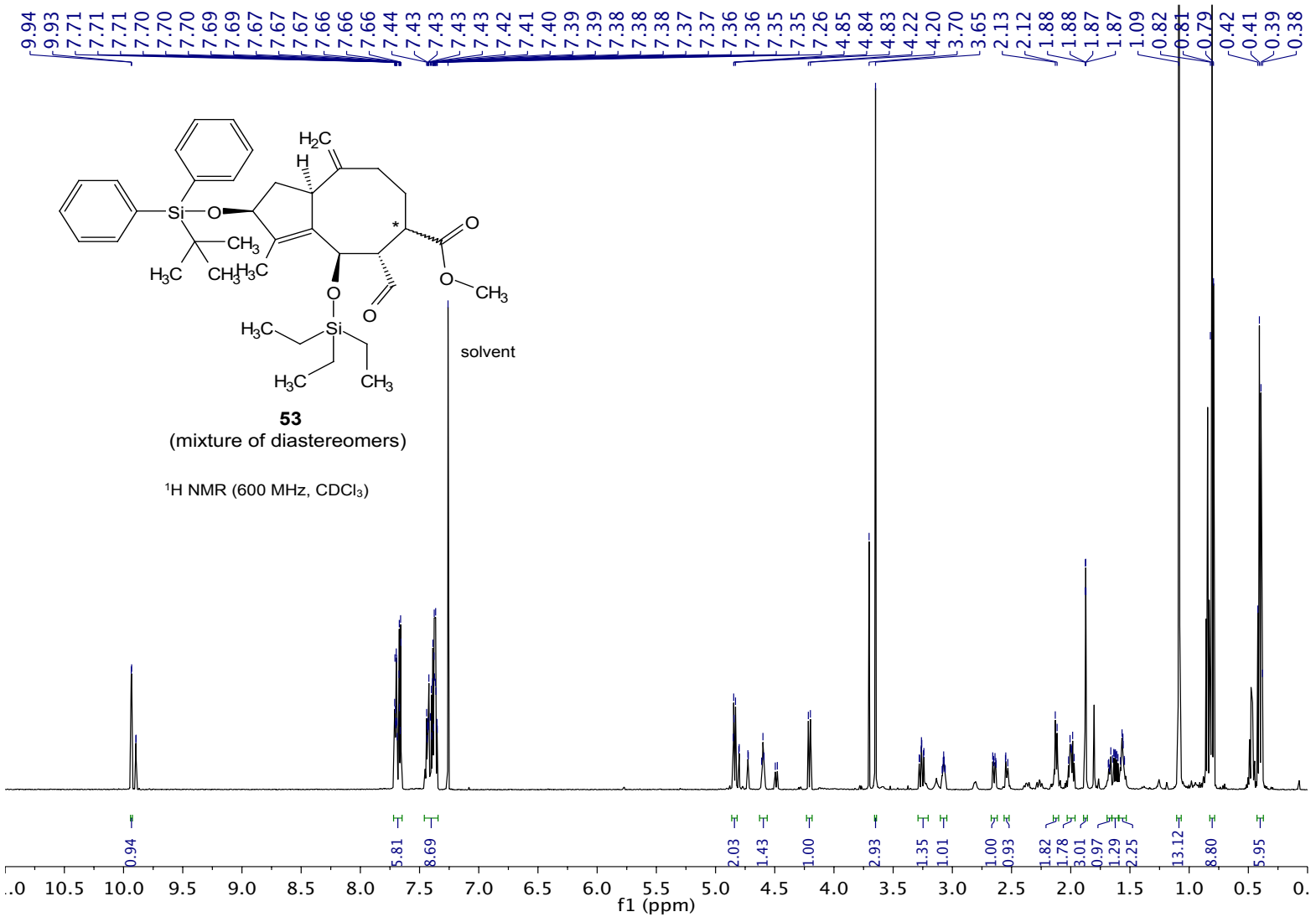
mikanocryptin (**8**)

^{1}H NMR (600 MHz, DMSO-d_6)



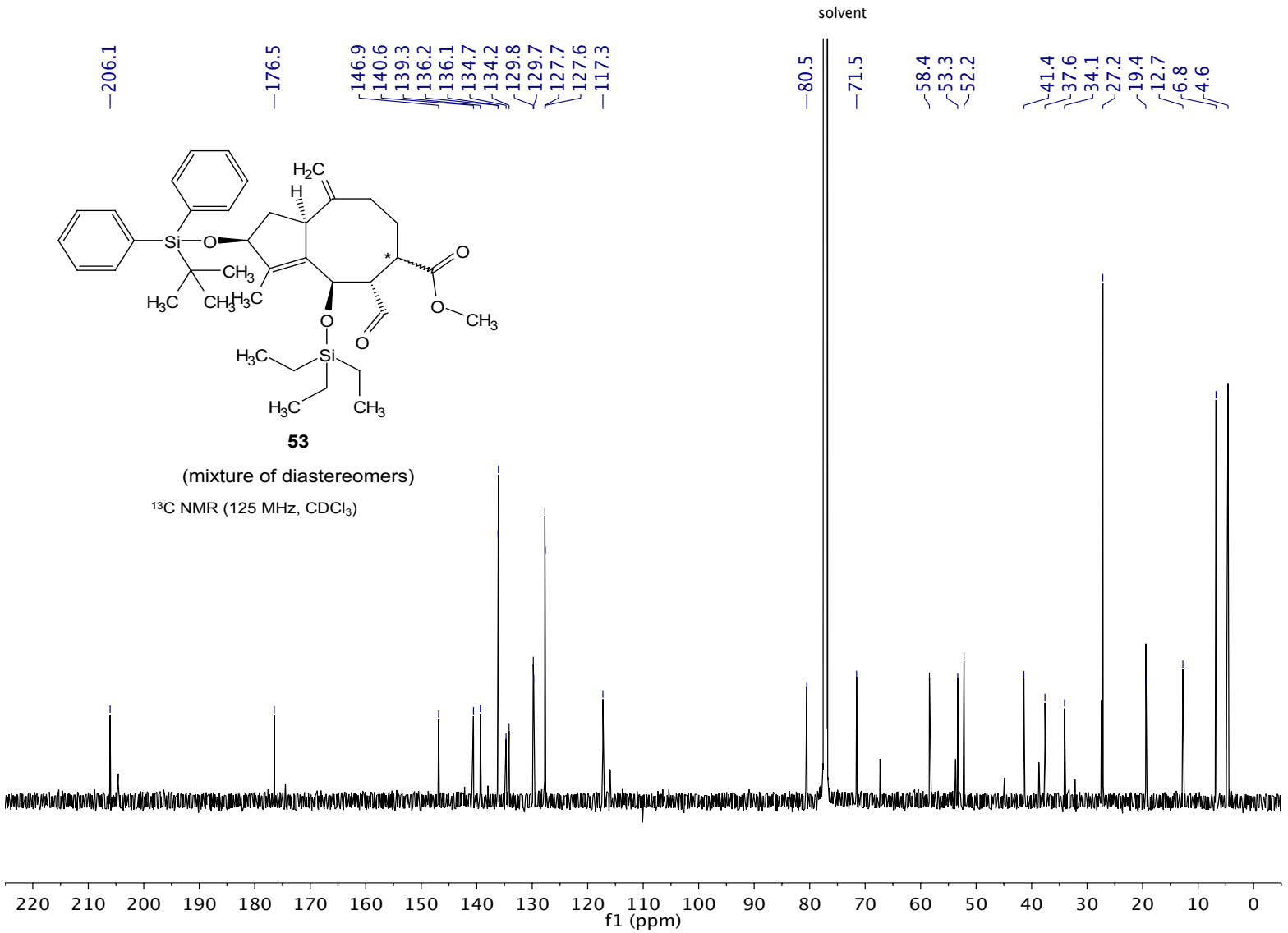
mikanocryptin (**8**)

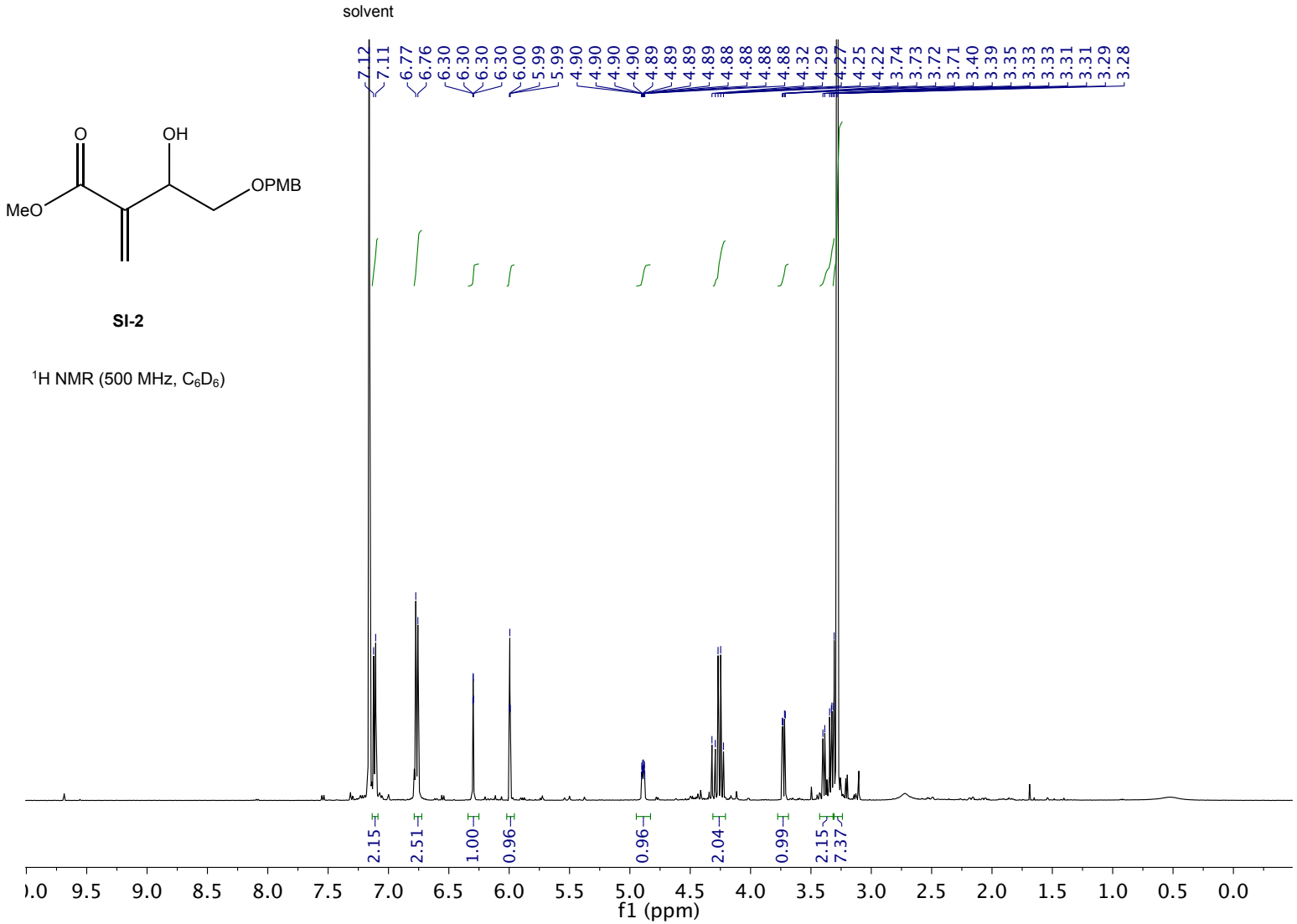
^{13}C NMR (150 MHz, DMSO-d_6)



53
(mixture of diastereomers)

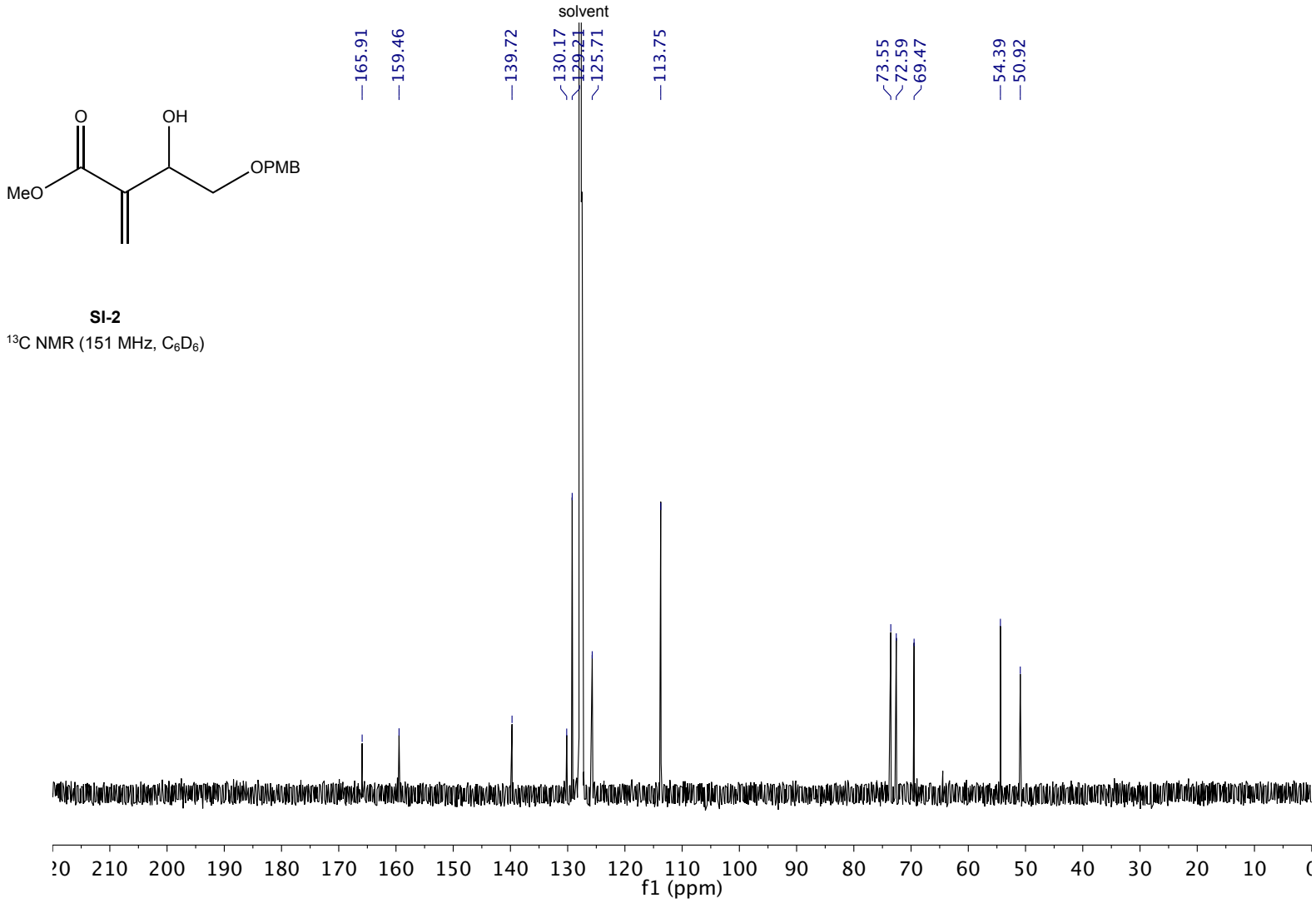
^{1}H NMR (600 MHz, $CDCl_3$)


solvent
206.1
176.5
146.9
140.6
139.3
136.2
136.1
134.7
134.2
129.8
129.7
127.7
127.6
117.3
80.5
71.5
58.4
53.3
52.2
41.4
37.6
34.1
27.2
19.4
12.7
6.8
4.6
53
(mixture of diastereomers)
13C NMR (125 MHz, CDCl3)
f1 (ppm)



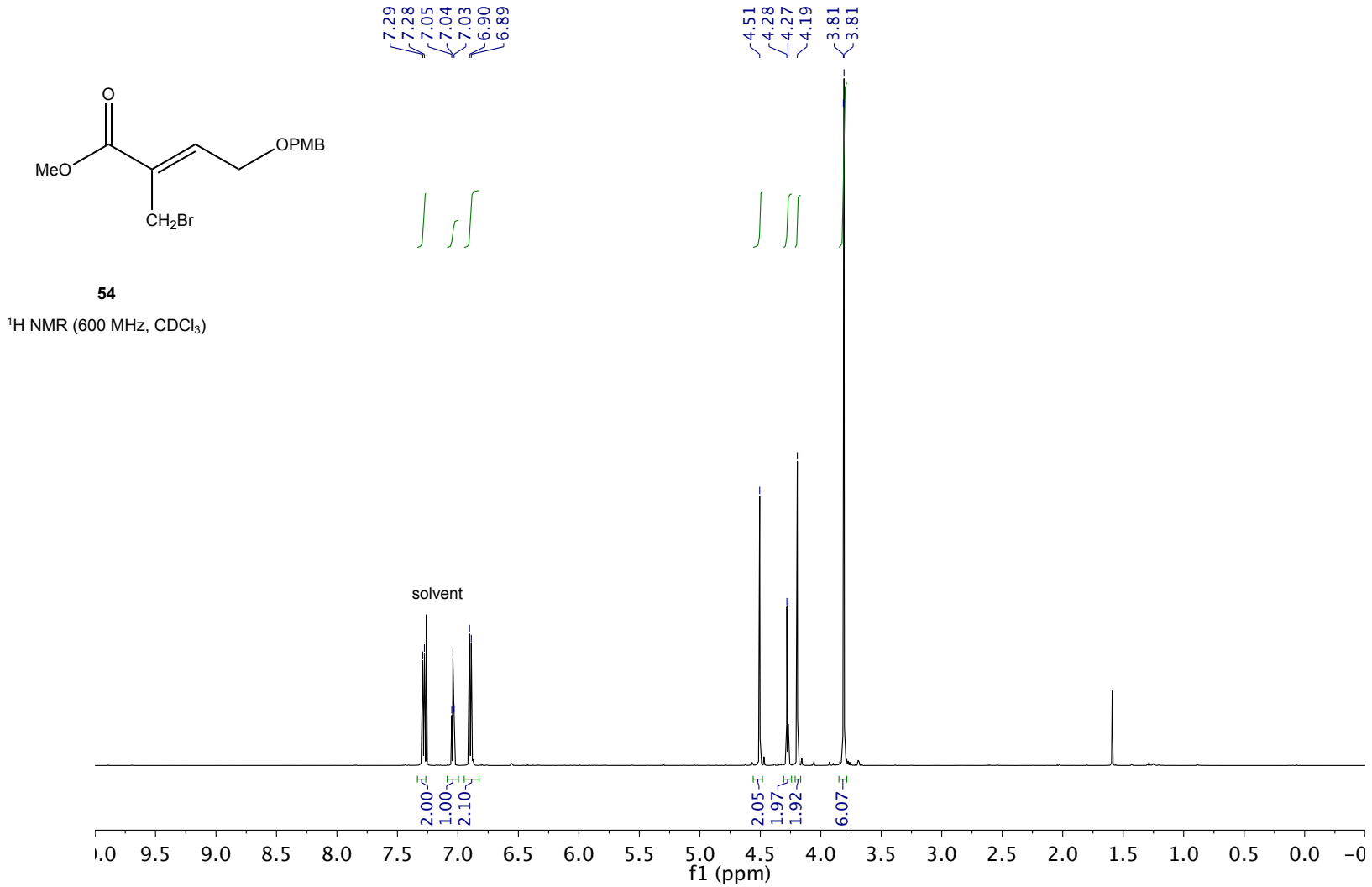
SI-2

^{1}H NMR (500 MHz, C_6D_6)



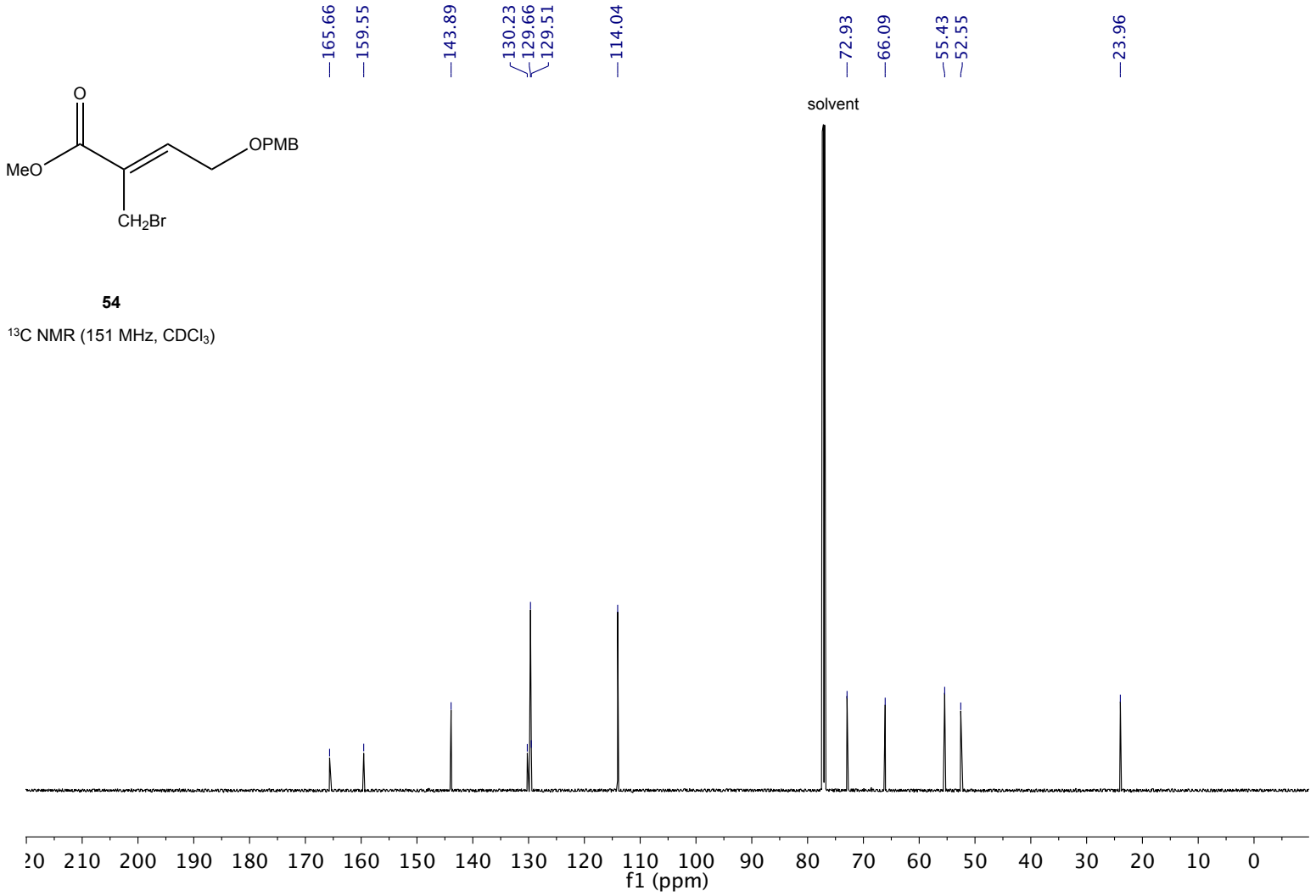
SI-2

^{13}C NMR (151 MHz, C_6D_6)



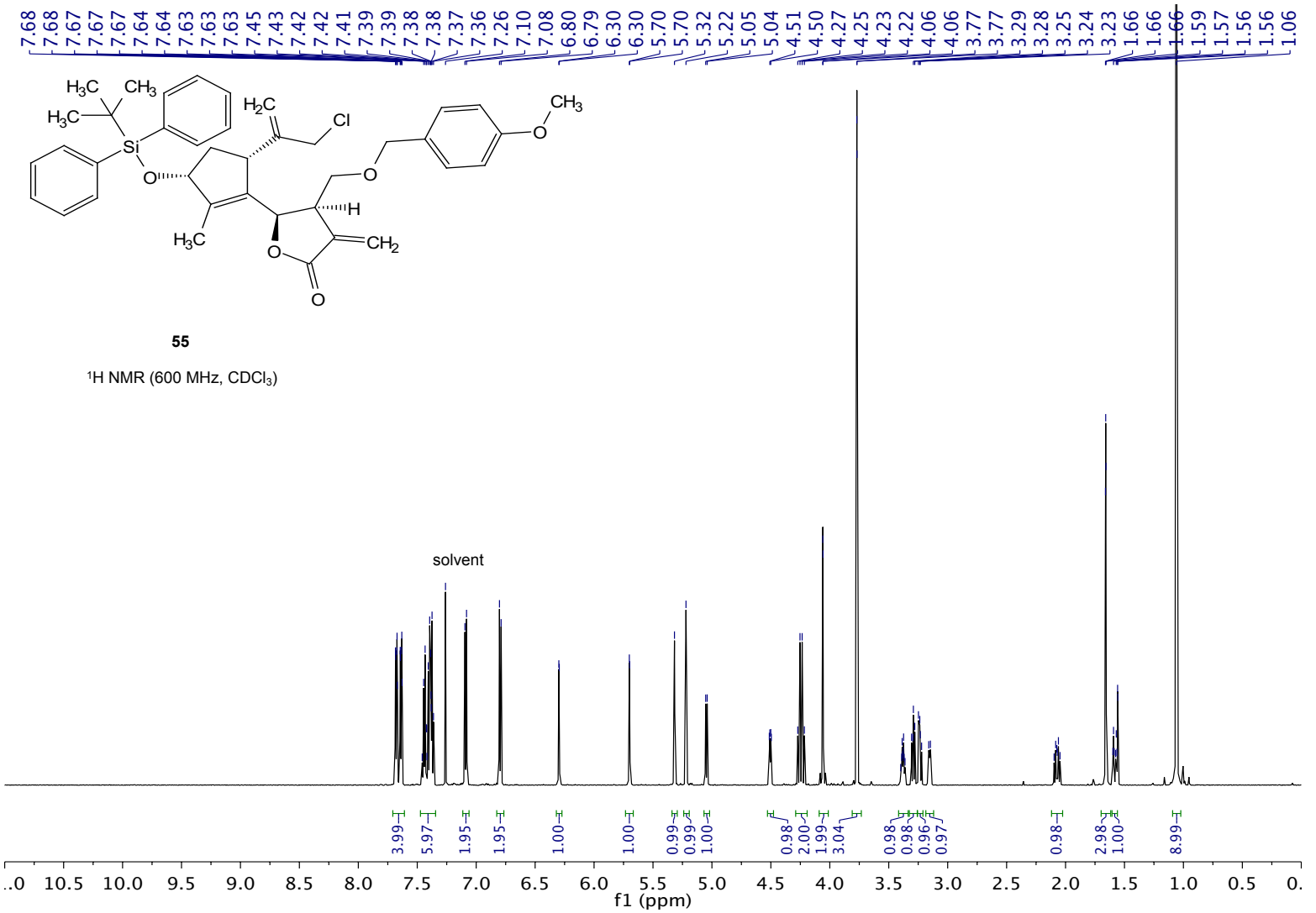
54

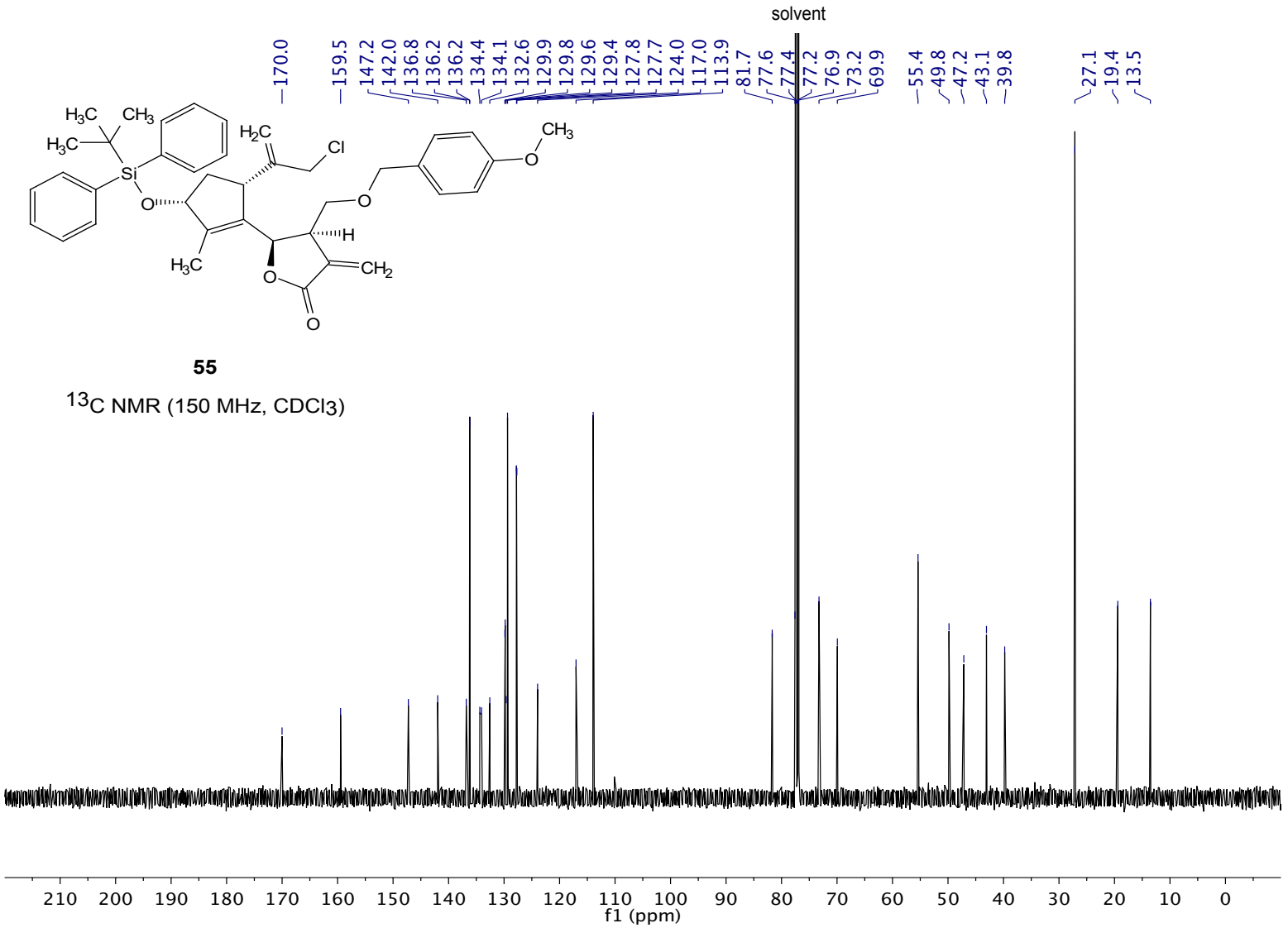
^{1}H NMR (600 MHz, $CDCl_3$)

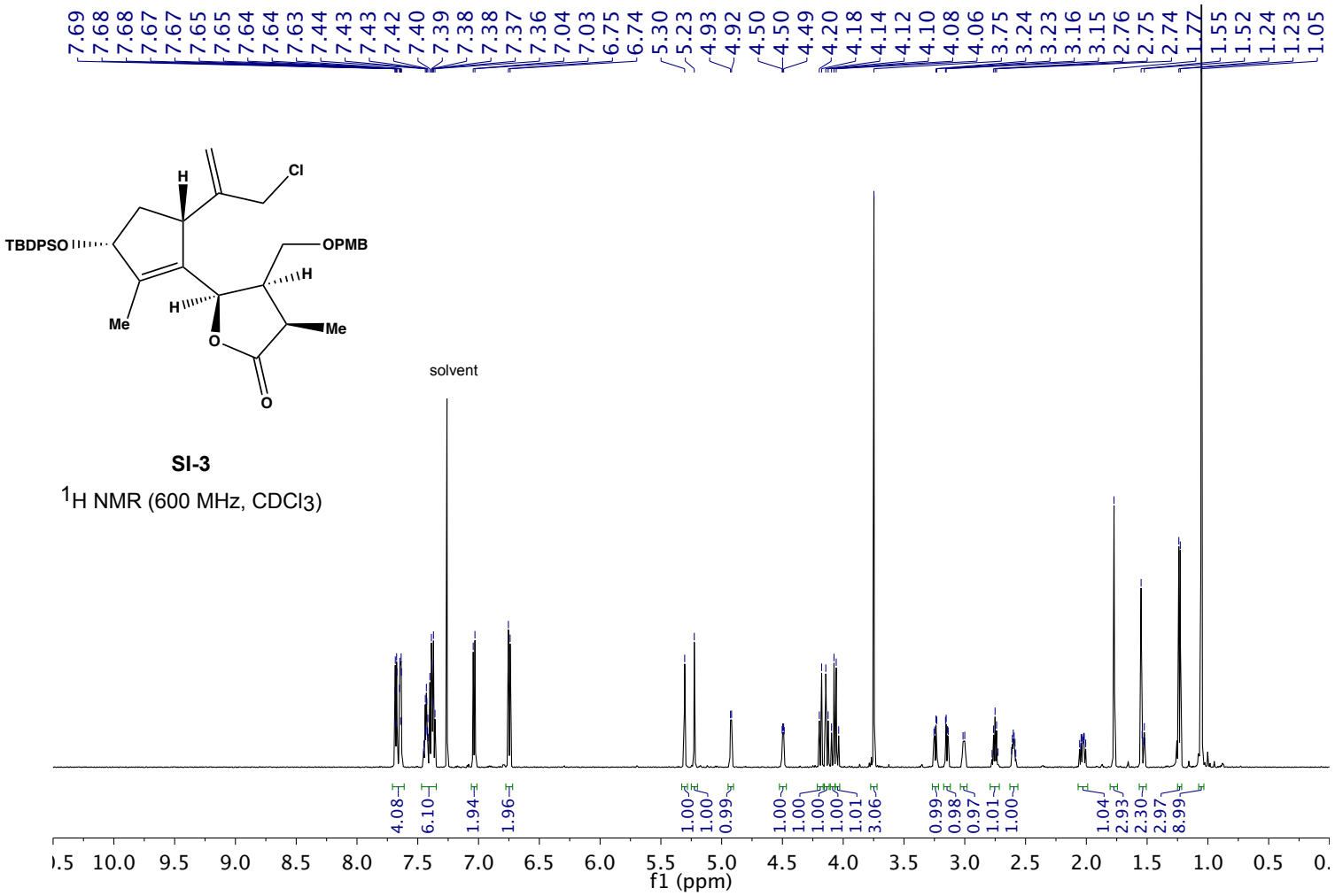


54

^{13}C NMR (151 MHz, $CDCl_3$)

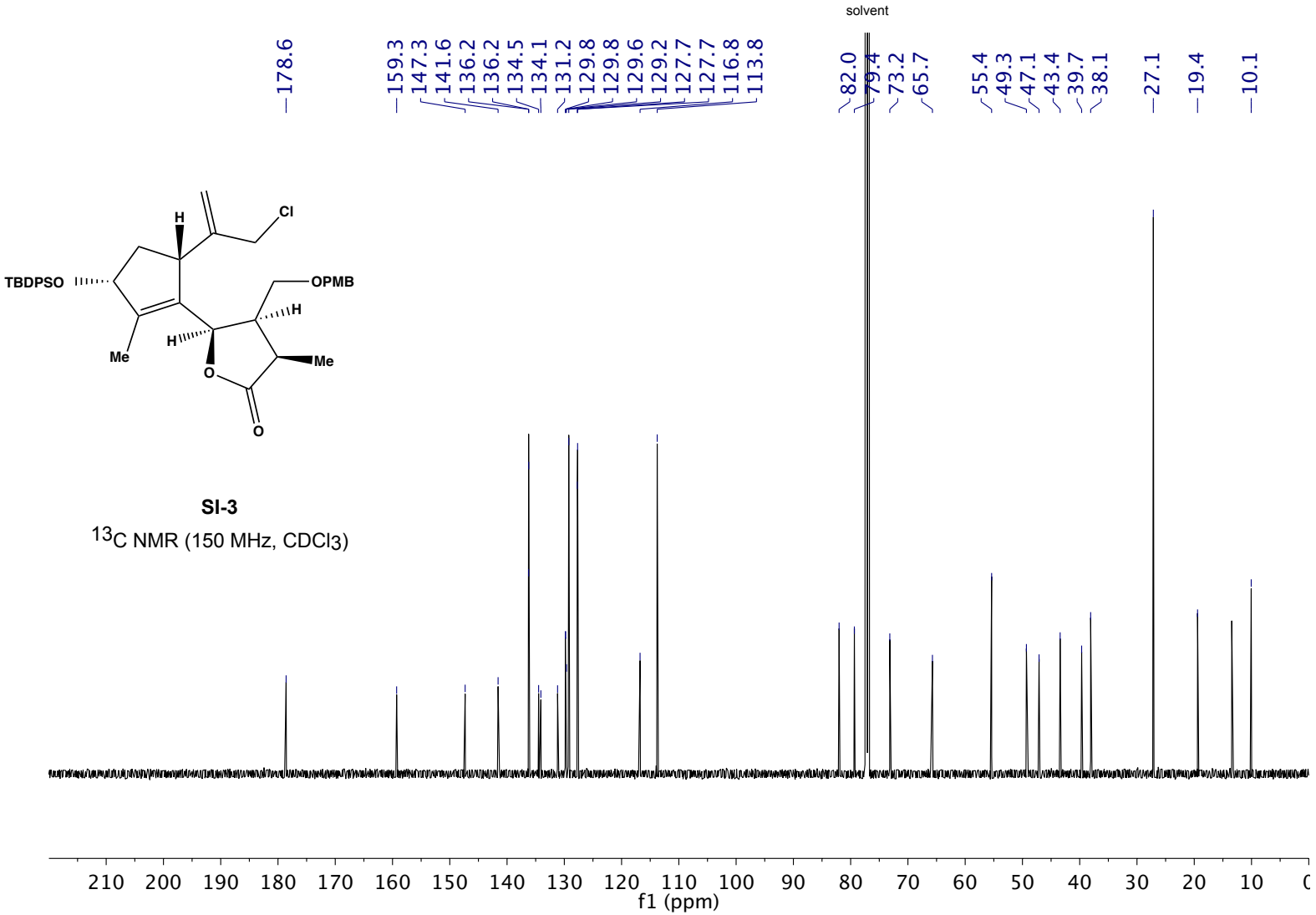

7.68 7.68 7.67 7.67 7.67 7.64 7.64 7.63 7.63 7.63 7.45 7.43 7.42 7.42 7.41 7.39 7.39 7.38 7.38 7.37 7.36 7.26 7.10 7.08 6.80 6.79 6.30 6.30 5.70 5.70 5.32 5.22 5.05 5.04 4.51 4.50 4.27 4.25 4.23 4.22 4.06 4.06 3.77 3.77 3.29 3.28 3.25 3.24 3.23 1.66 1.66 1.66 1.59 1.57 1.56 1.56 1.06
H3C CH3
H3C
Si
O
H2C
Cl
O
CH3
O
H
H3C
O
CH2
O
55
1H NMR (600 MHz, CDCl3)
solvent
3.99 5.97 1.95 1.95 1.00 1.00 0.99 0.99 1.00 0.98 2.00 1.99 3.04 0.98 0.98 0.96 0.97 0.98 2.98 1.00 8.99
f1 (ppm)


solvent
170.0
159.5
147.2
142.0
136.8
136.2
136.2
134.4
134.1
132.6
129.9
129.8
129.6
129.4
127.8
127.7
124.0
117.0
113.9
81.7
77.6
77.4
77.2
76.9
73.2
69.9
55.4
49.8
47.2
43.1
39.8
27.1
19.4
13.5
H3C
CH3
H3C
Si
O
H2C
Cl
O
CH3
O
H
H3C
CH2
O
O
55
13C NMR (150 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



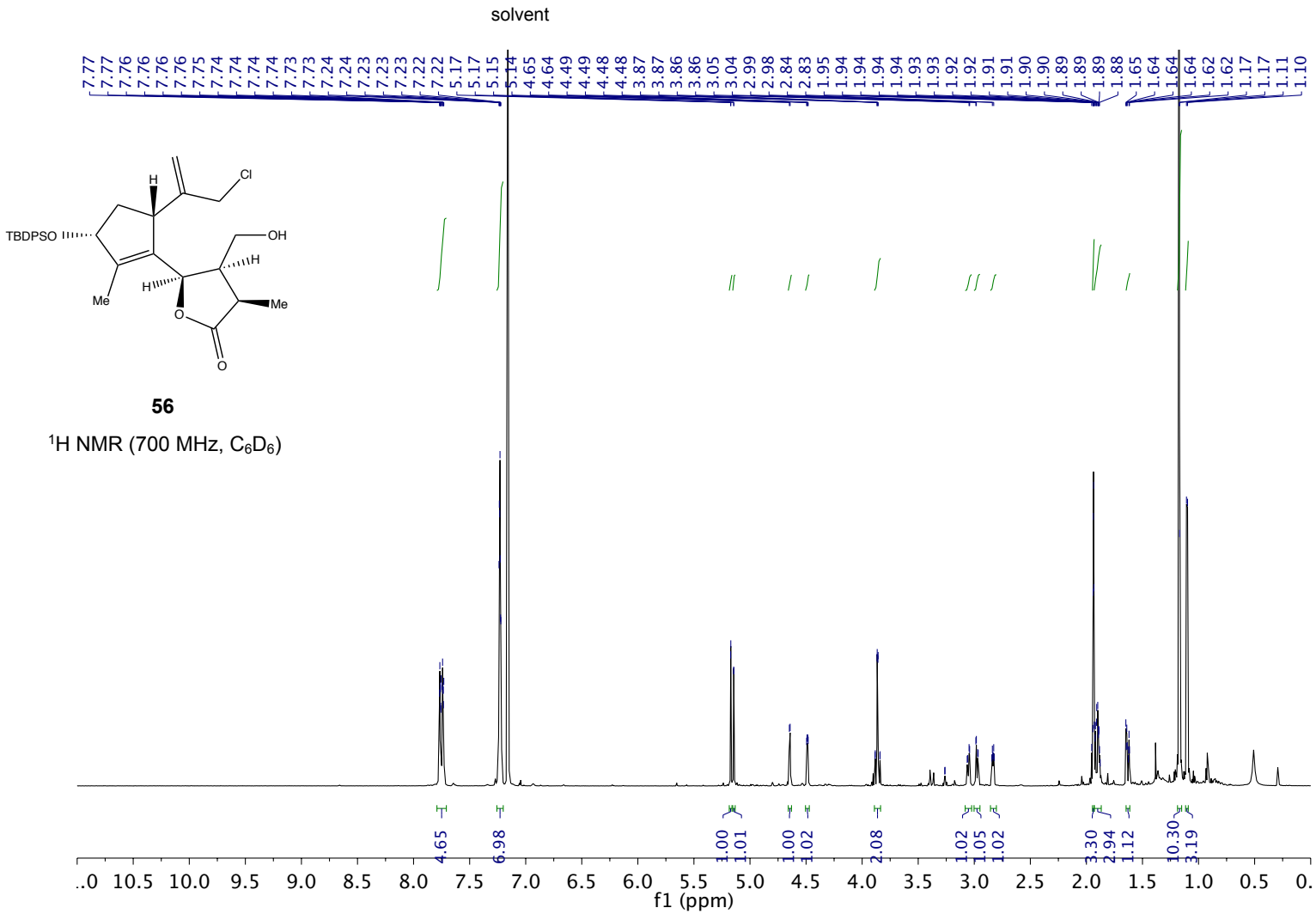
SI-3

^{1}H NMR (600 MHz, $CDCl_3$)



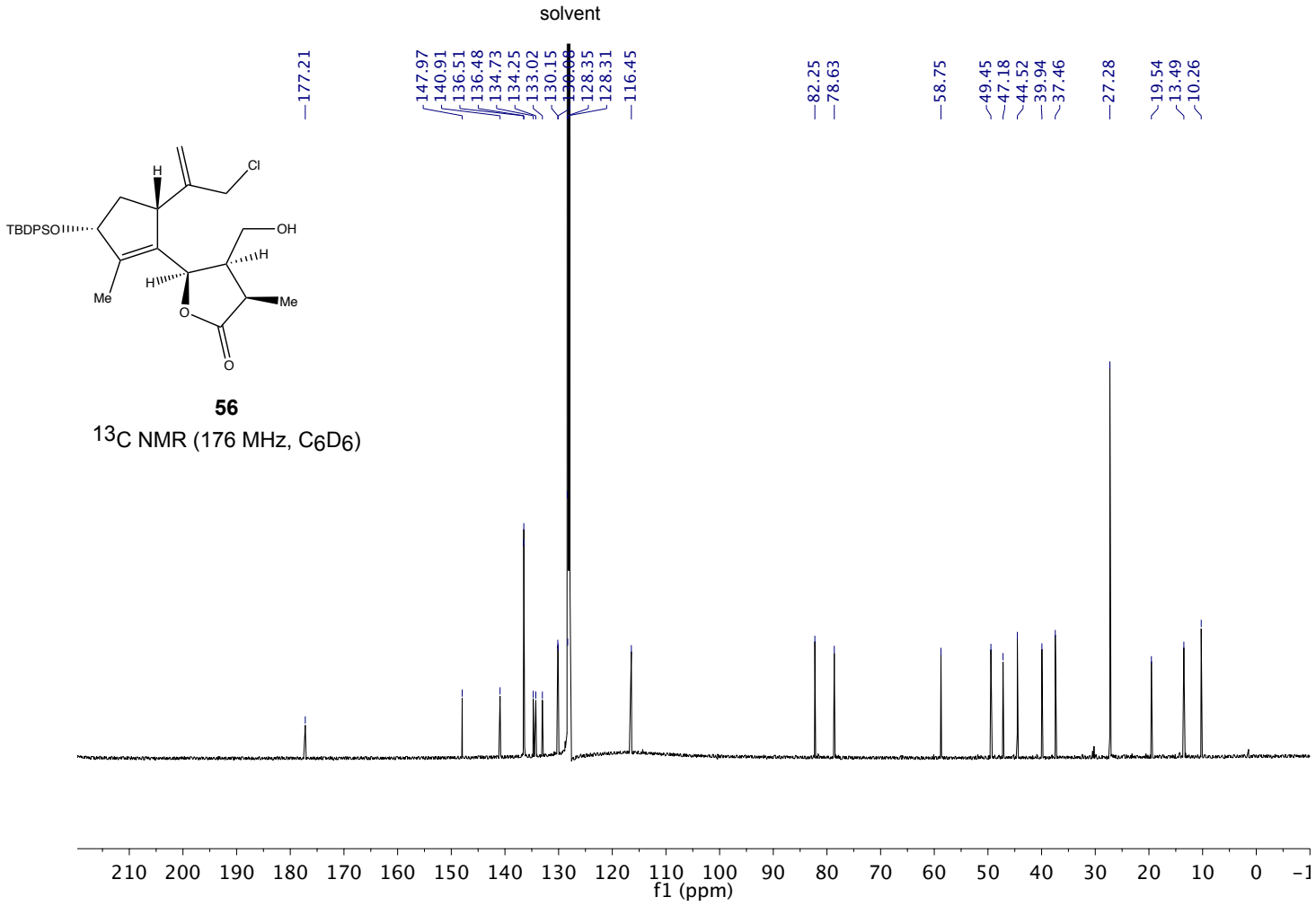
SI-3

^{13}C NMR (150 MHz, $CDCl_3$)



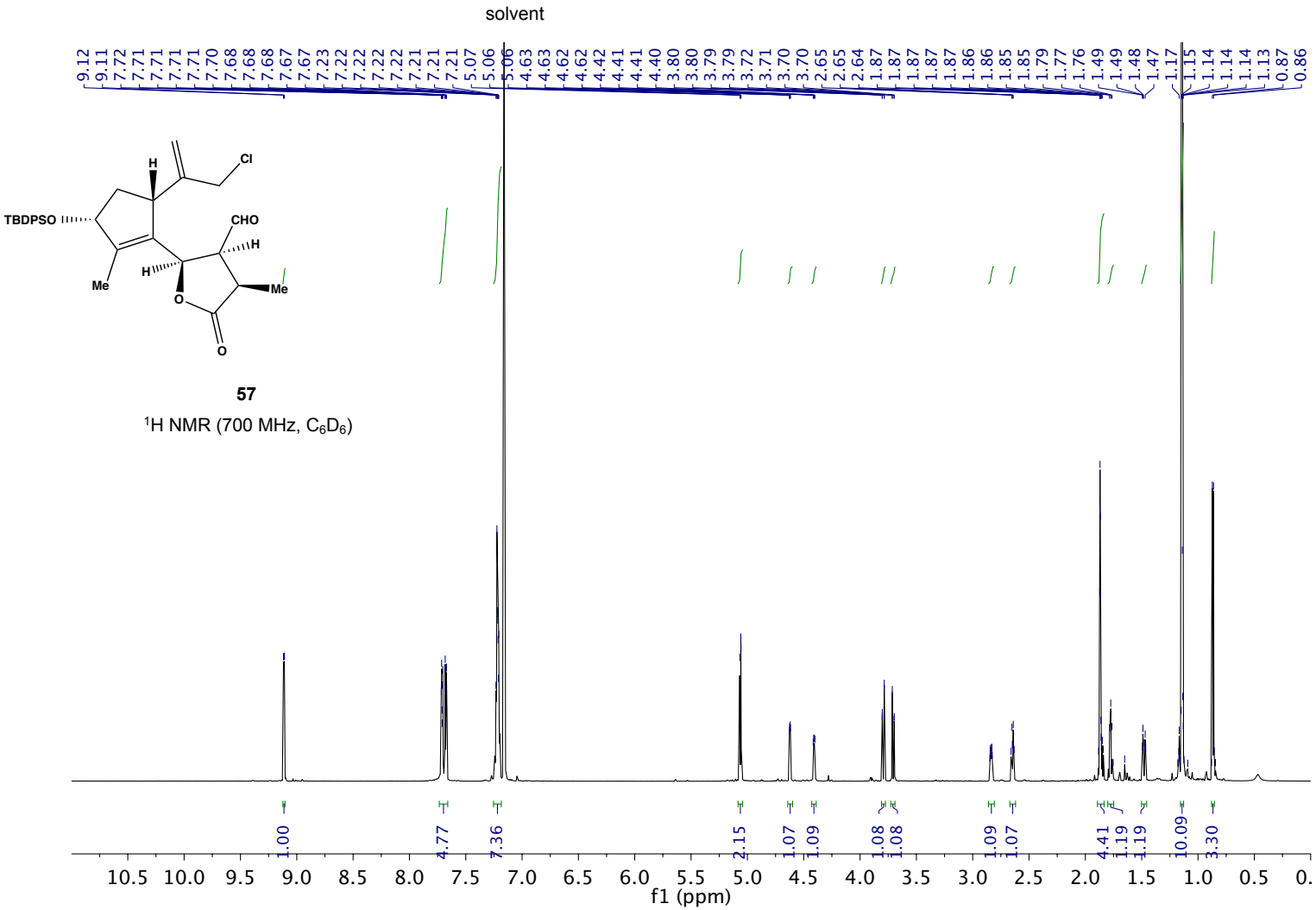
56

^{1}H NMR (700 MHz, C_6D_6)



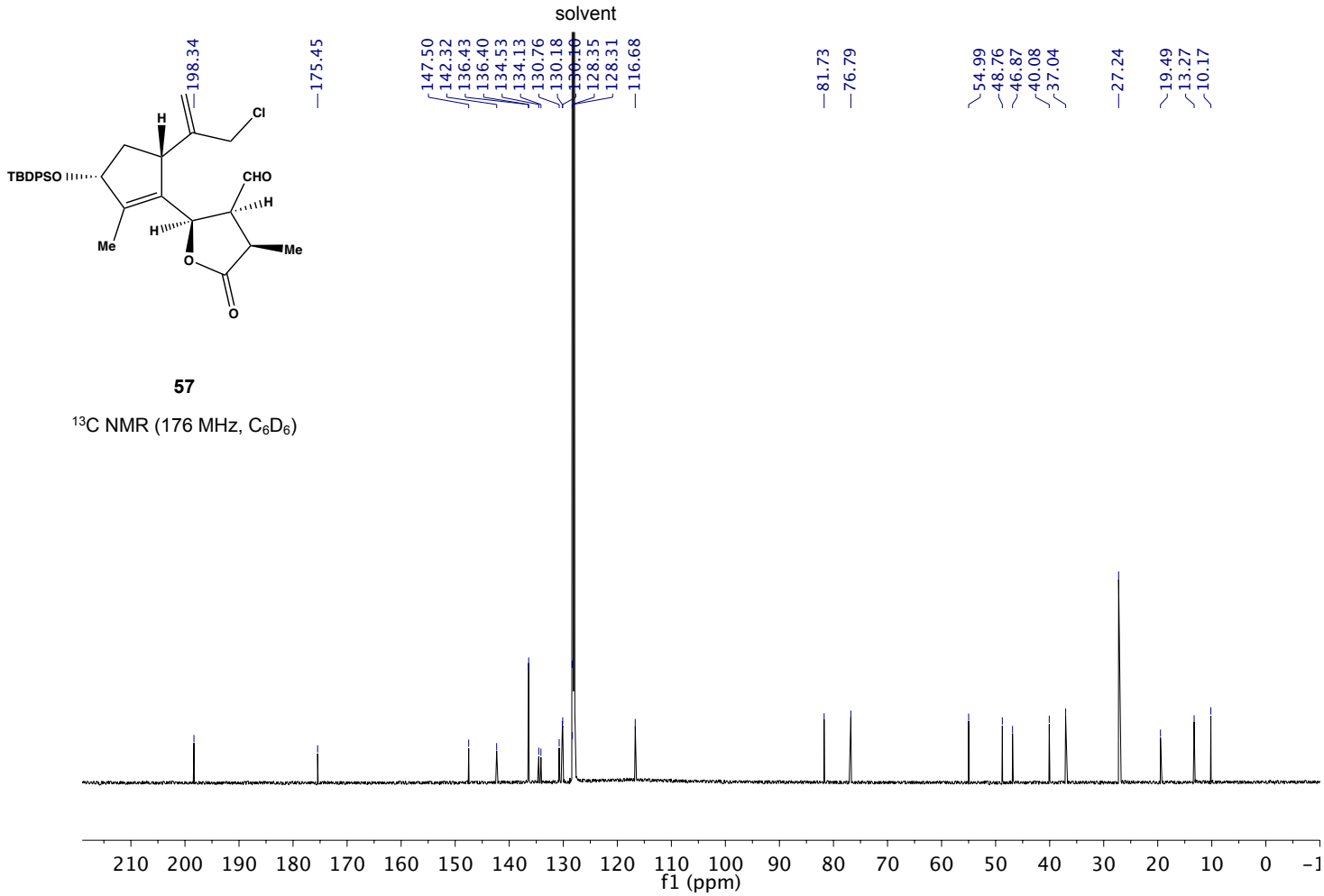
56

^{13}C NMR (176 MHz, C_6D_6)



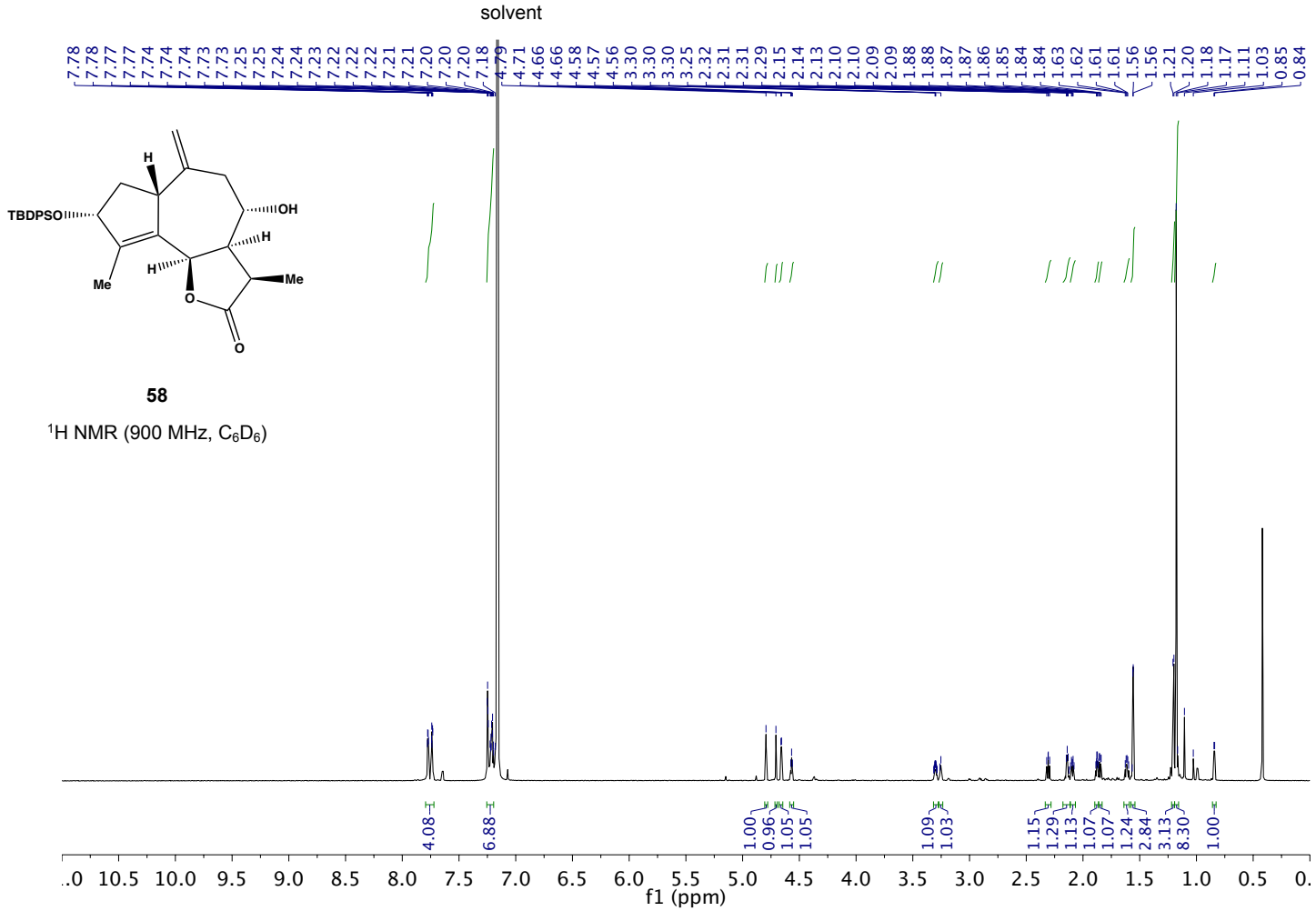
57

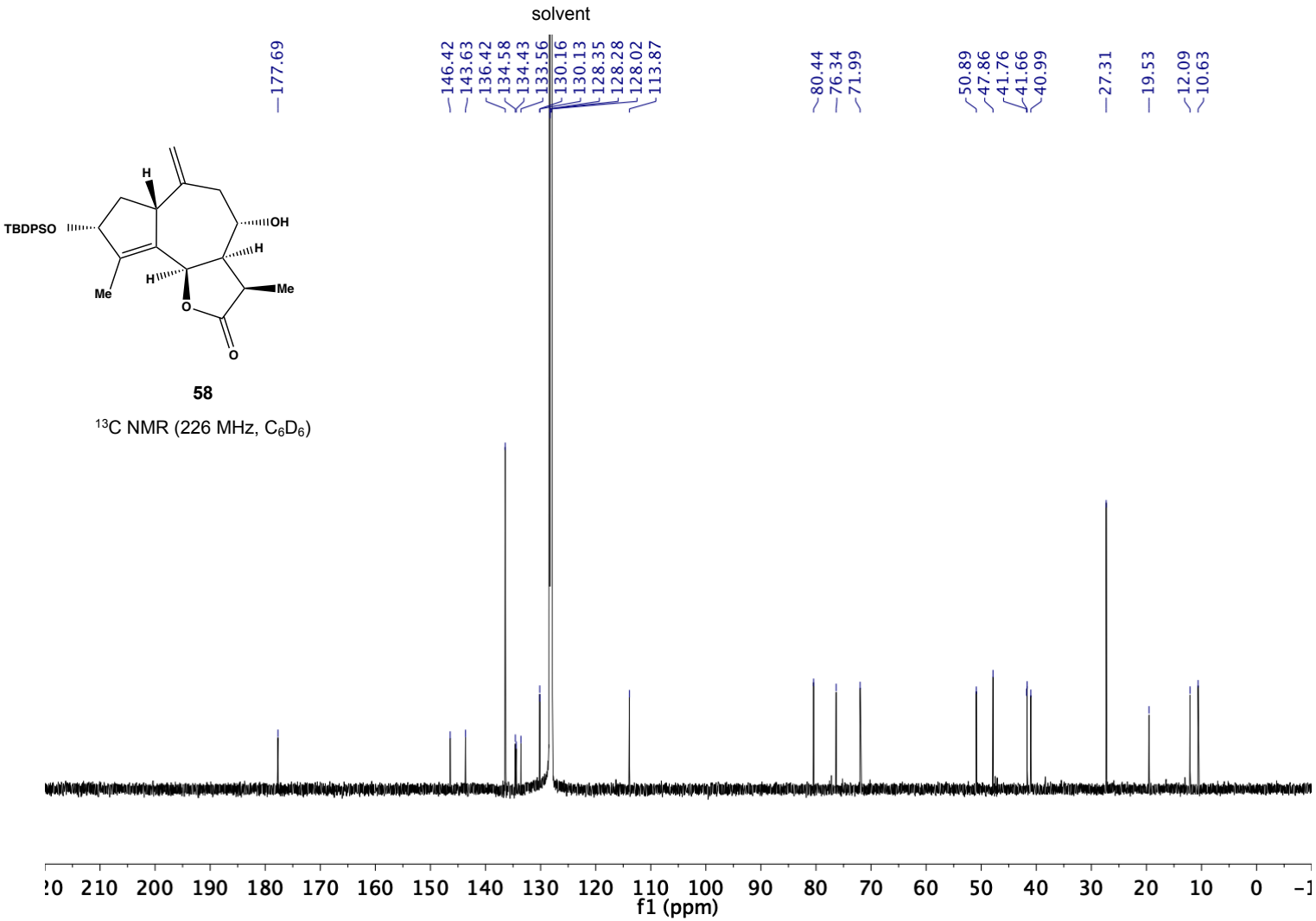
^{1}H NMR (700 MHz, C_6D_6)



57

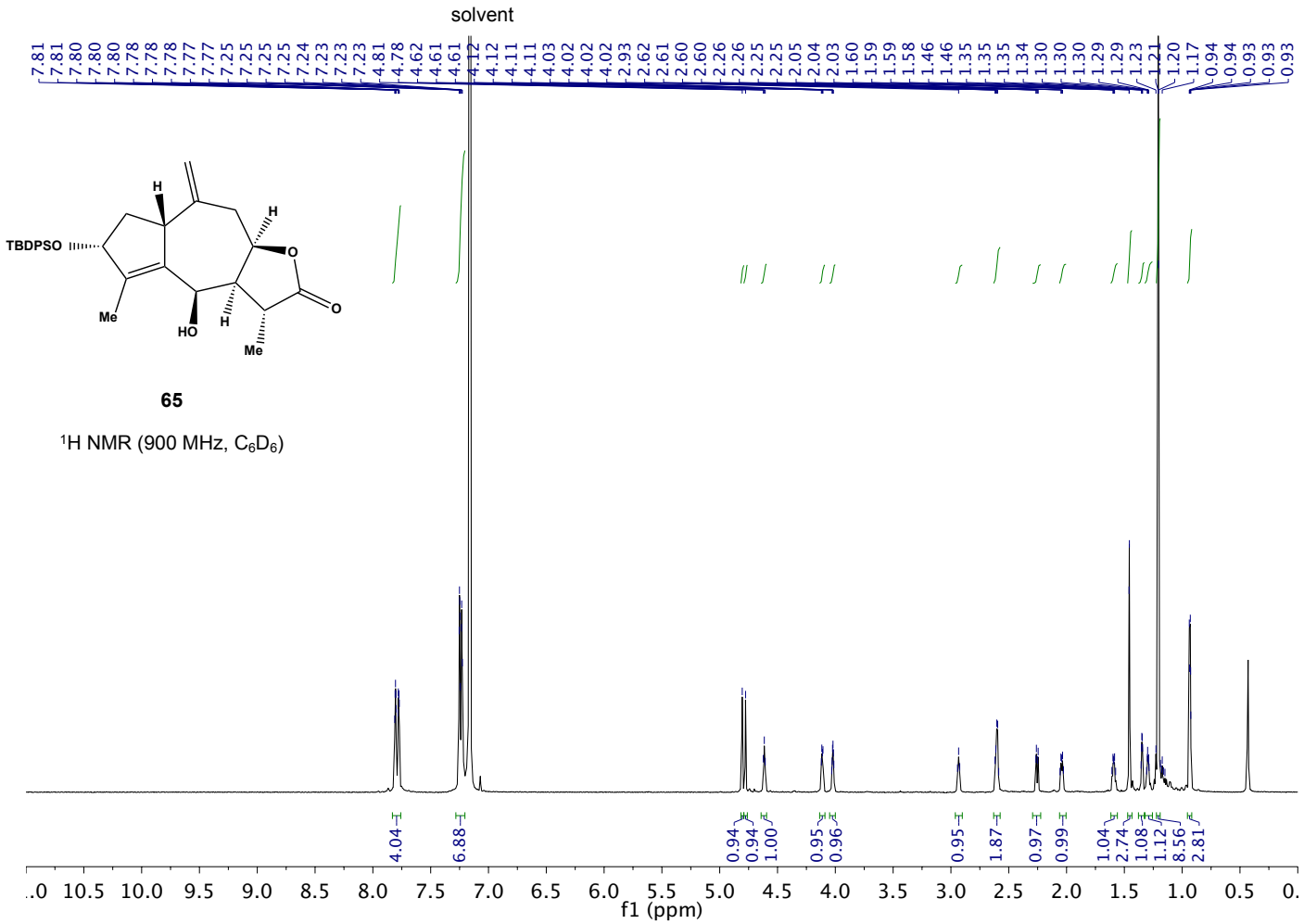
^{13}C NMR (176 MHz, C_6D_6)

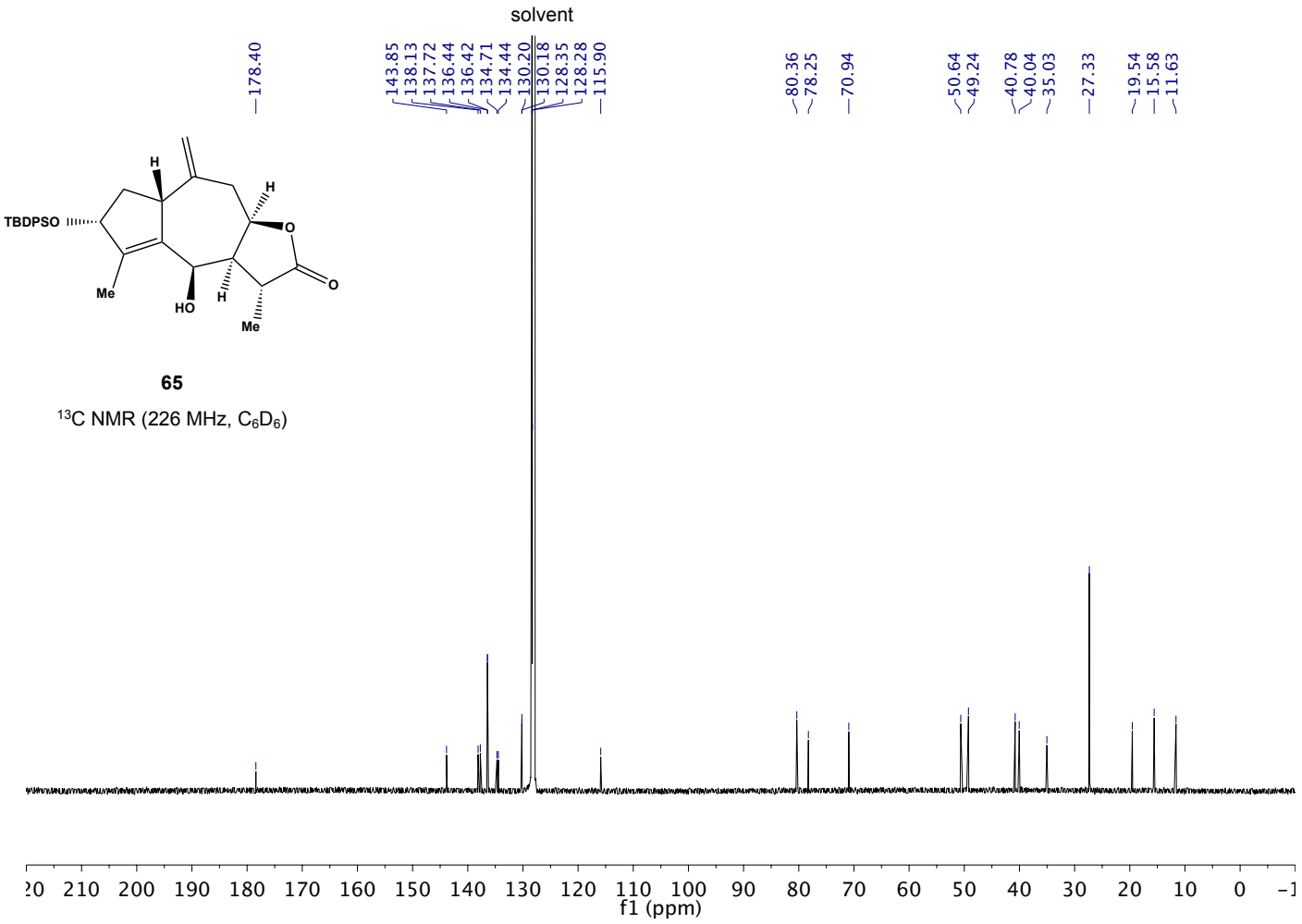

solvent
TBDPSO
OH
H
H
H
Me
Me
O
O
58
1H NMR (900 MHz, C6D6)
f1 (ppm)



58

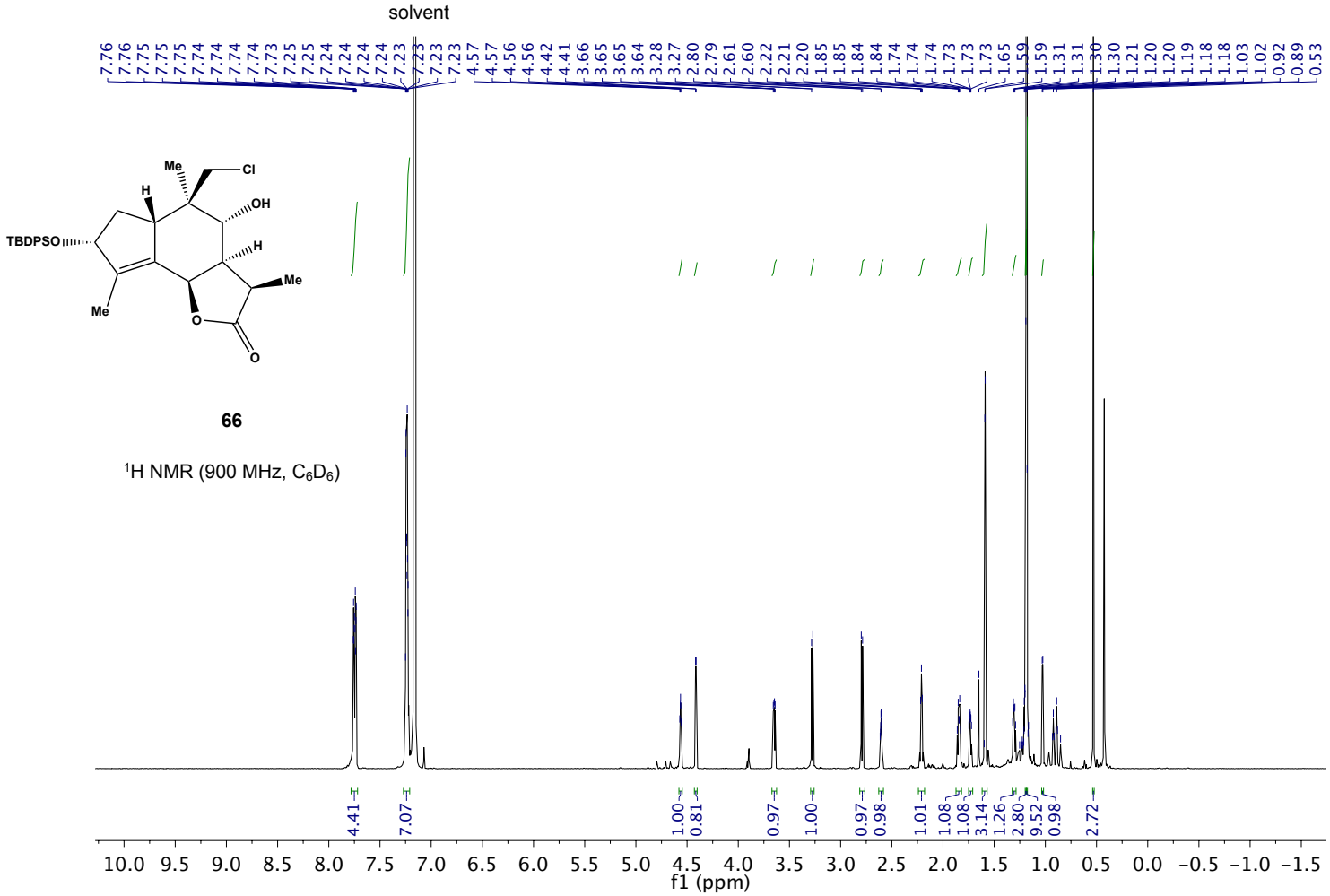
^{13}C NMR (226 MHz, C_6D_6)

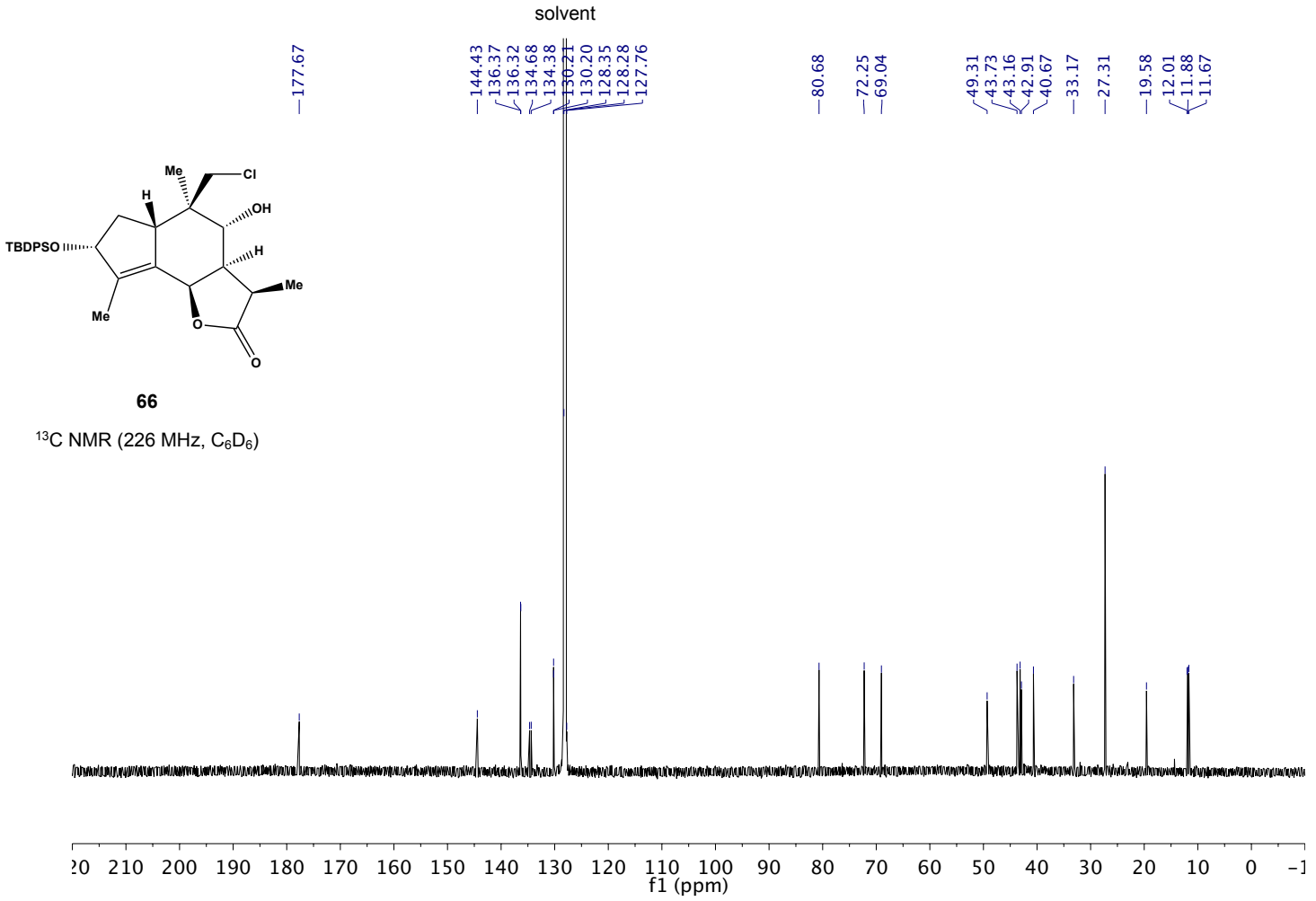

solvent
TBDPSO
H
H
O
O
Me
HO
H
Me
65
^{1}H NMR (900 MHz, C_6D_6)
f1 (ppm)



65

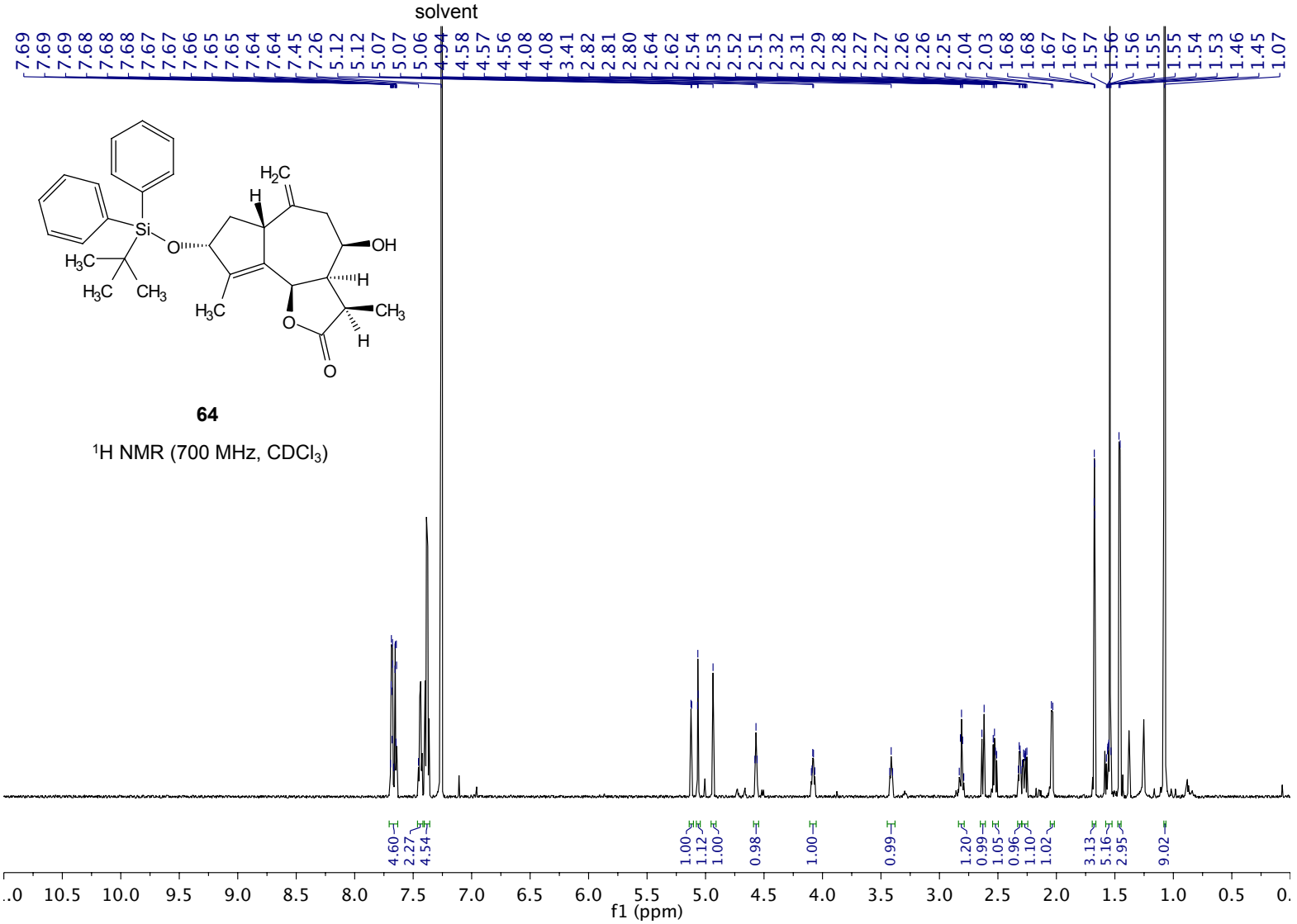
^{13}C NMR (226 MHz, C_6D_6)

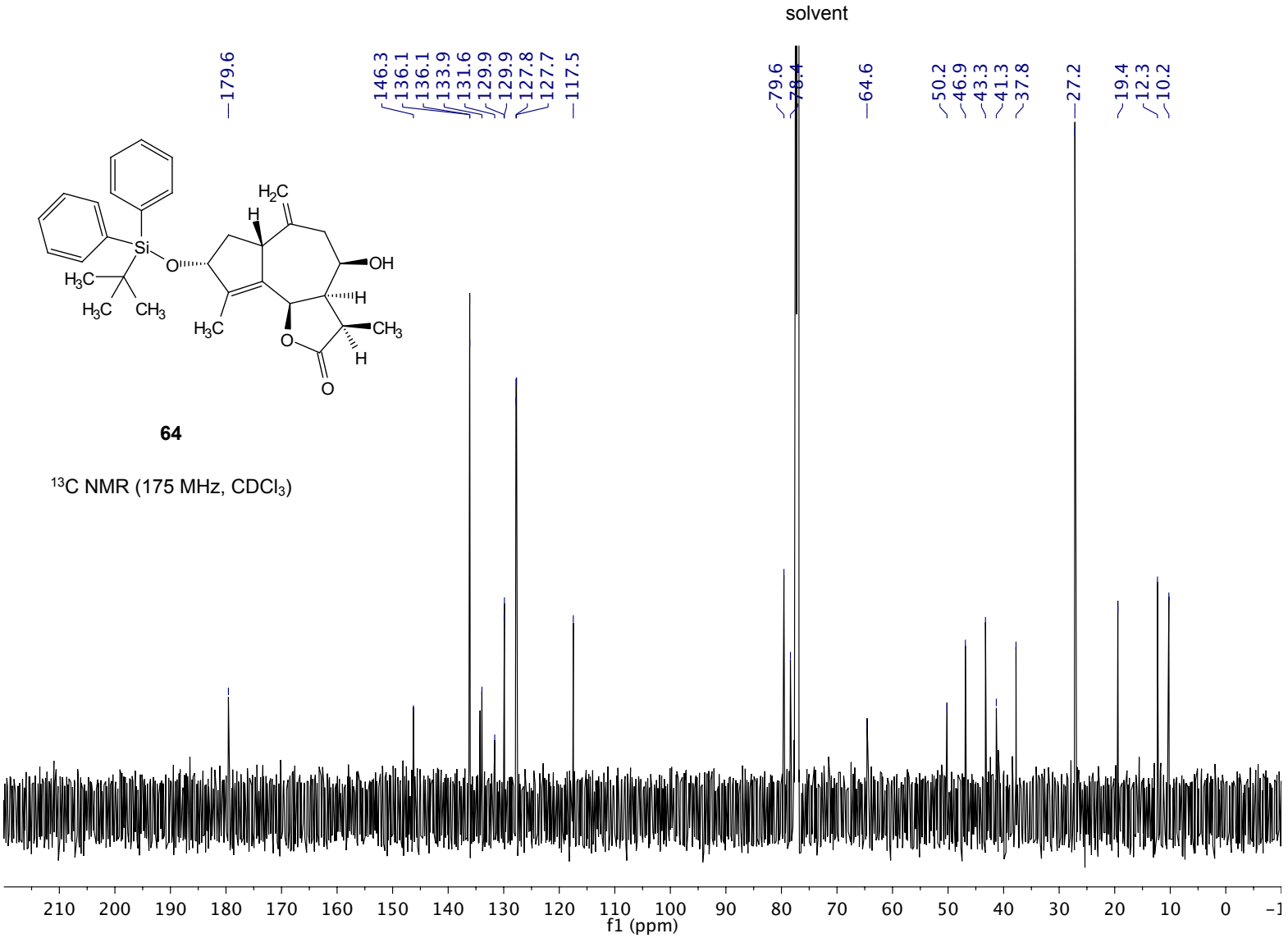

solvent
Me
Cl
H
OH
TBDPSO
H
Me
Me
O
O
66
^{1}H NMR (900 MHz, C_6D_6)
f1 (ppm)



66

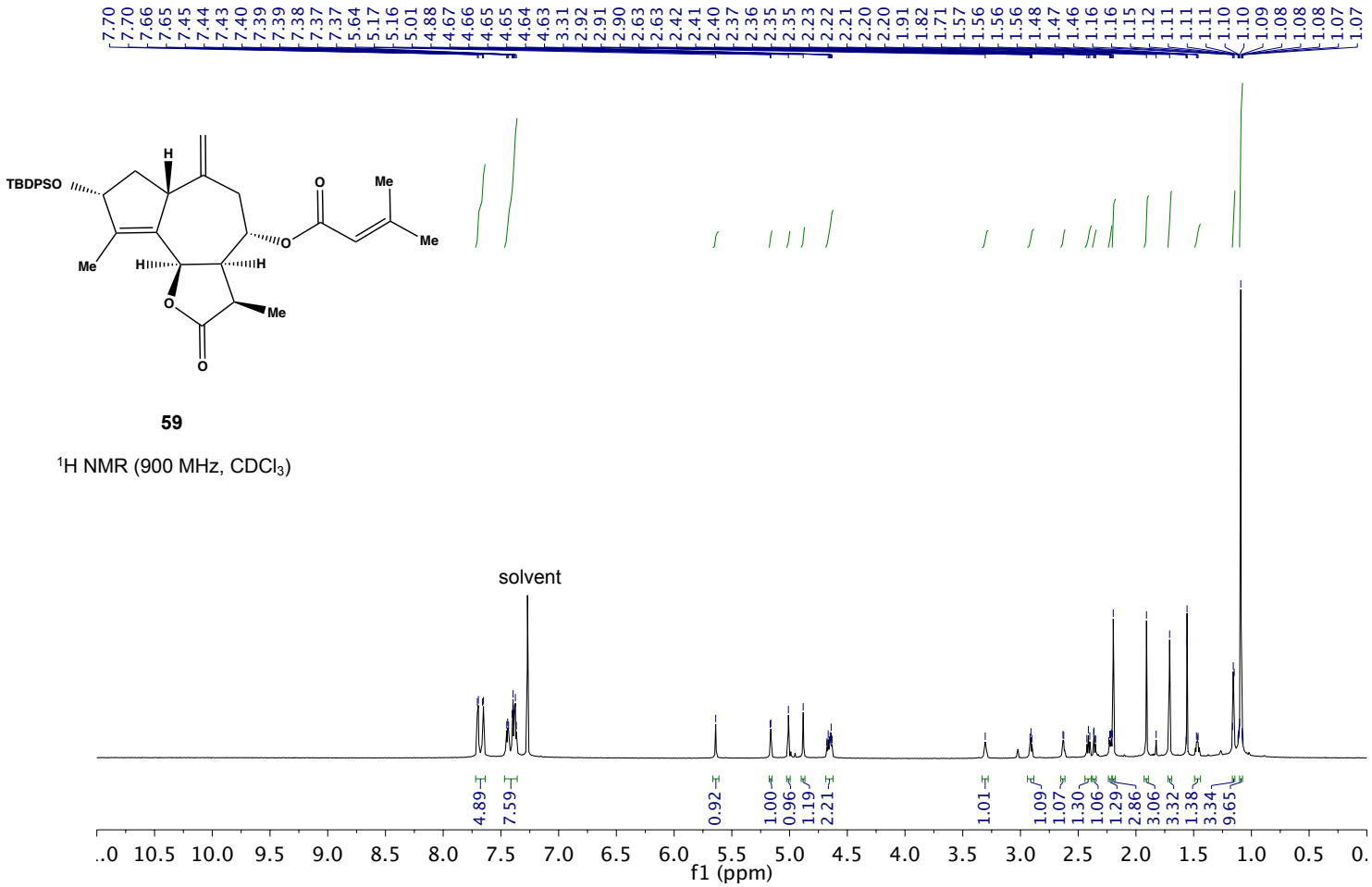
^{13}C NMR (226 MHz, C_6D_6)


solvent
7.69 7.69 7.69 7.68 7.68 7.68 7.67 7.67 7.66 7.65 7.65 7.64 7.64 7.45 7.26 5.12 5.12 5.07 5.07 5.06 4.94 4.58 4.57 4.56 4.08 4.08 3.41 2.82 2.81 2.80 2.64 2.62 2.54 2.53 2.52 2.51 2.32 2.31 2.29 2.28 2.27 2.27 2.26 2.26 2.25 2.04 2.03 1.68 1.68 1.67 1.67 1.57 1.56 1.56 1.55 1.55 1.54 1.53 1.46 1.45 1.07
H2C
H
Si
O
OH
H3C
H3C
CH3
H
H3C
O
CH3
H
O
64
1H NMR (700 MHz, CDCl3)
4.60 2.27 4.54 1.00 1.12 1.00 0.98 1.00 0.99 1.20 0.99 1.05 0.96 1.10 1.02 3.13 5.16 2.95 9.02
10.5 10.0 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
f1 (ppm)



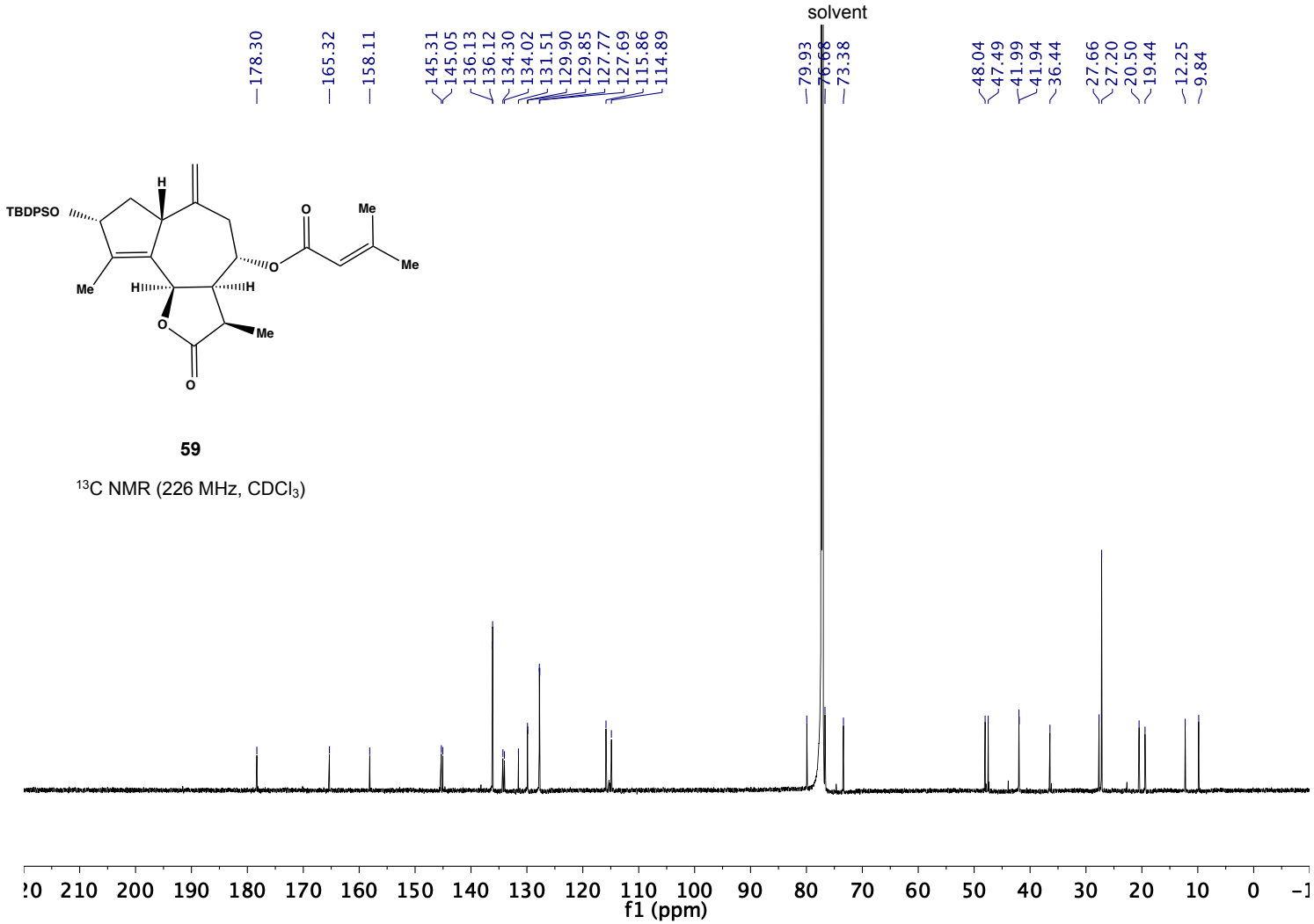
64

^{13}C NMR (175 MHz, $CDCl_3$)



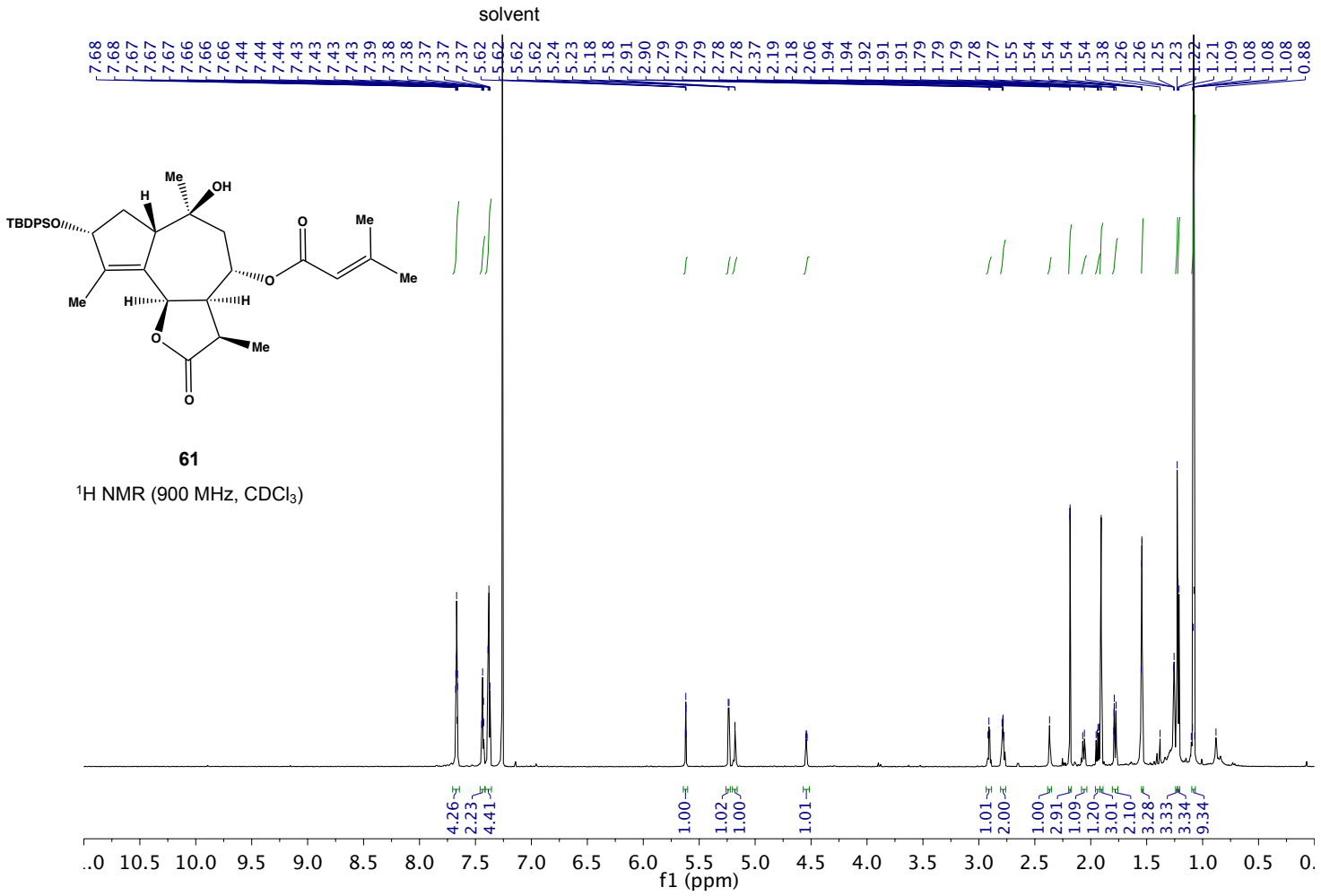
59

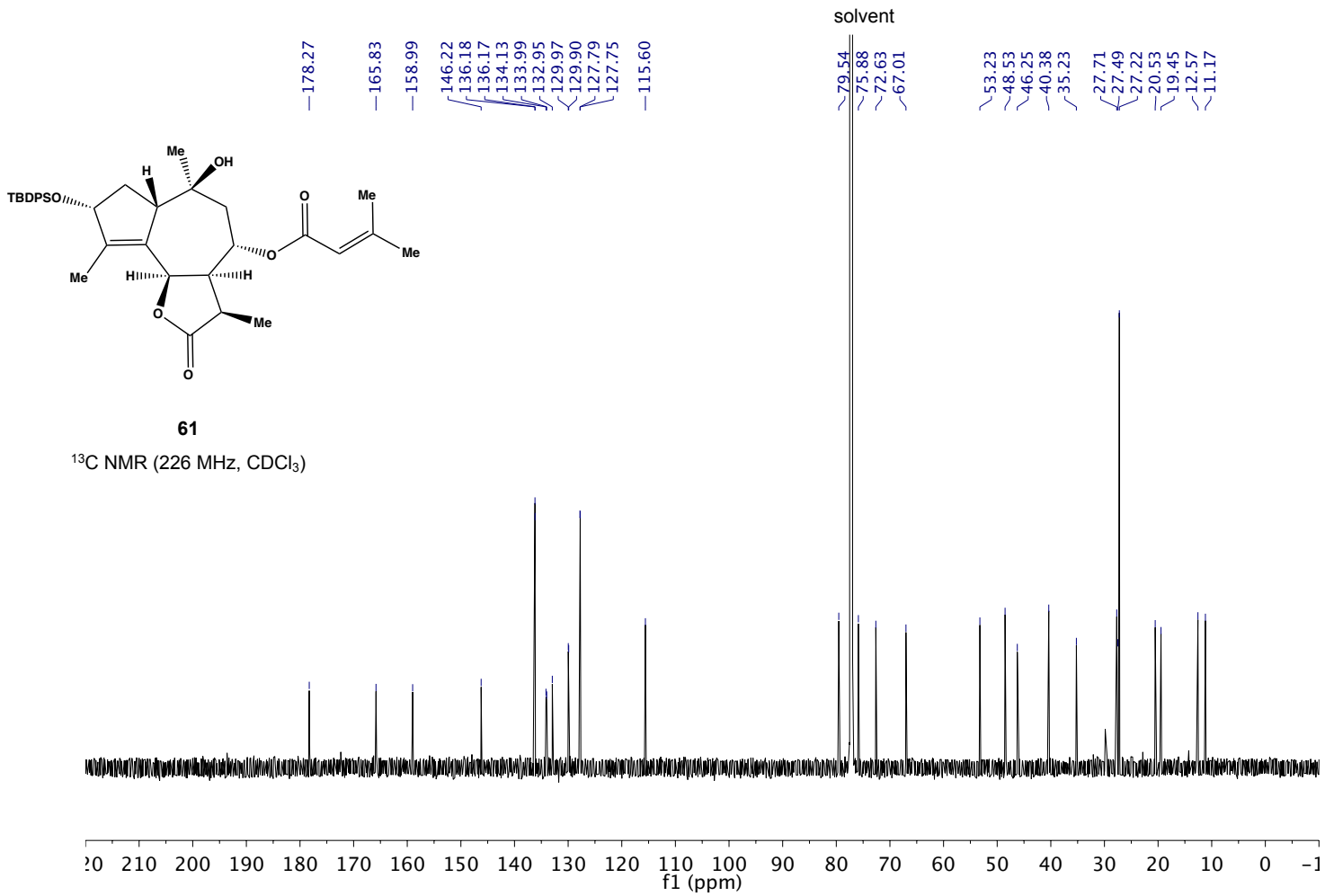
^{1}H NMR (900 MHz, $CDCl_3$)



59

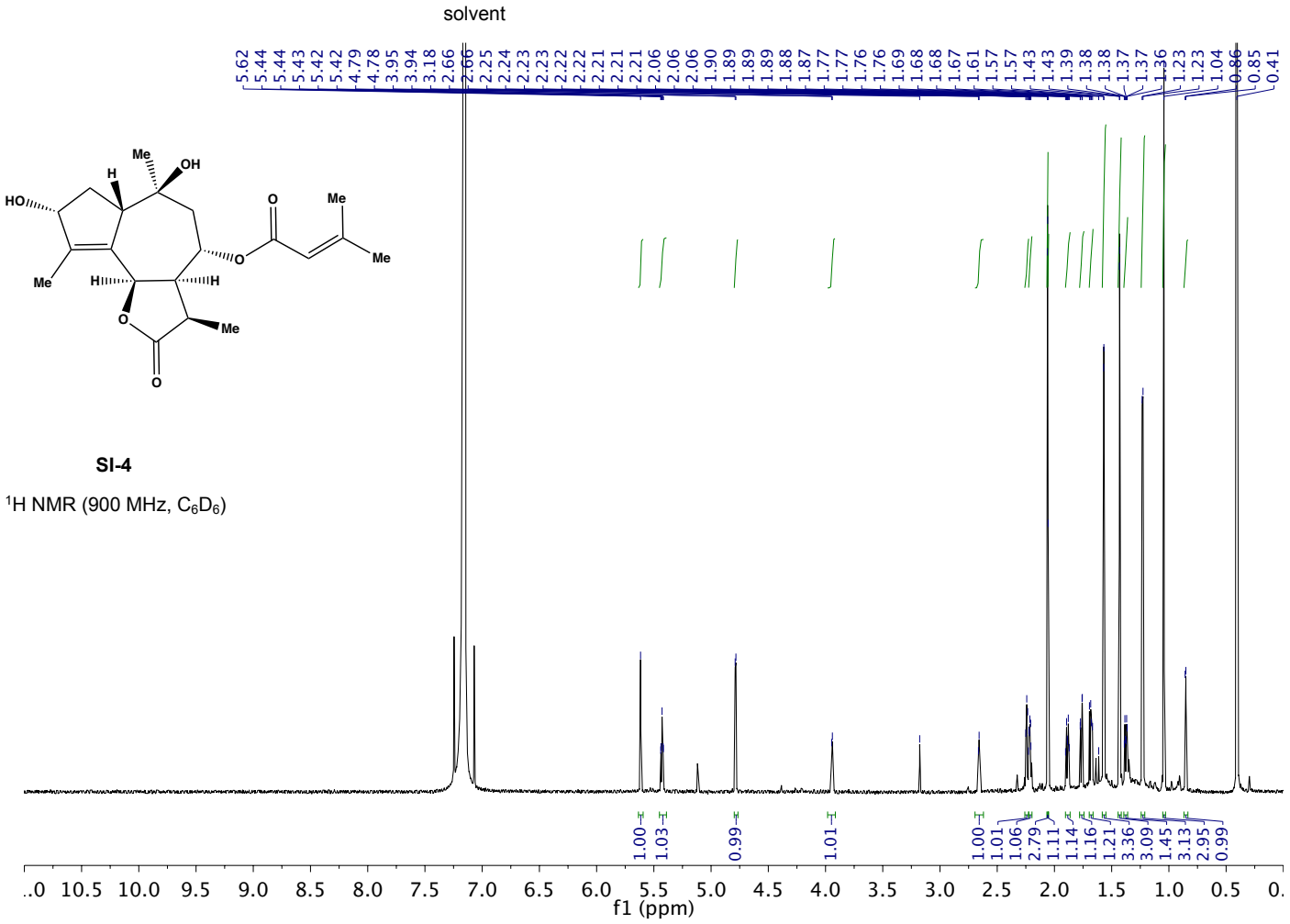
^{13}C NMR (226 MHz, $CDCl_3$)


solvent
TBDPSO
Me
OH
H
O
Me
Me
H
H
O
Me
O
Me
61
1H NMR (900 MHz, CDCl3)
f1 (ppm)



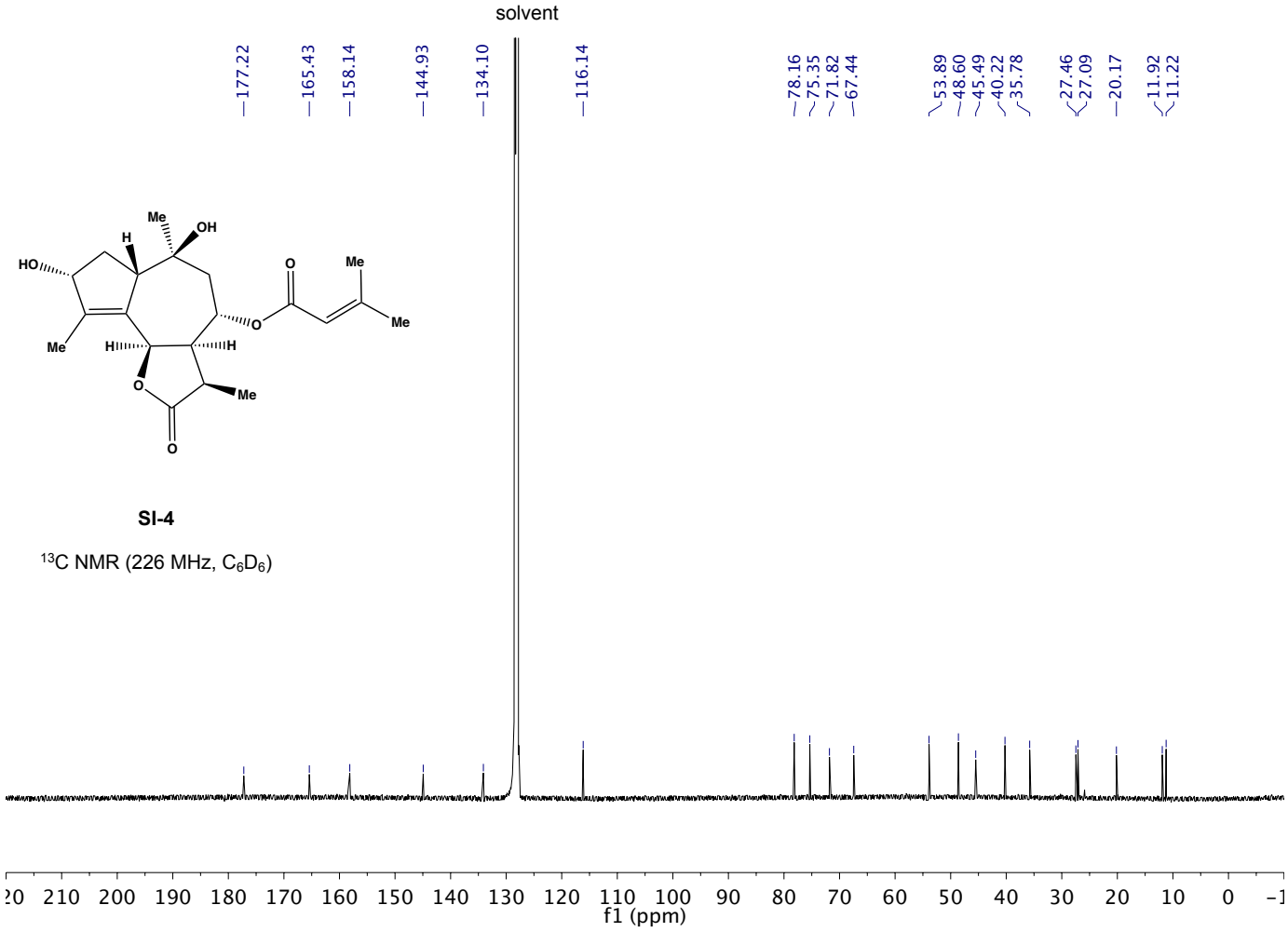
61

^{13}C NMR (226 MHz, $CDCl_3$)



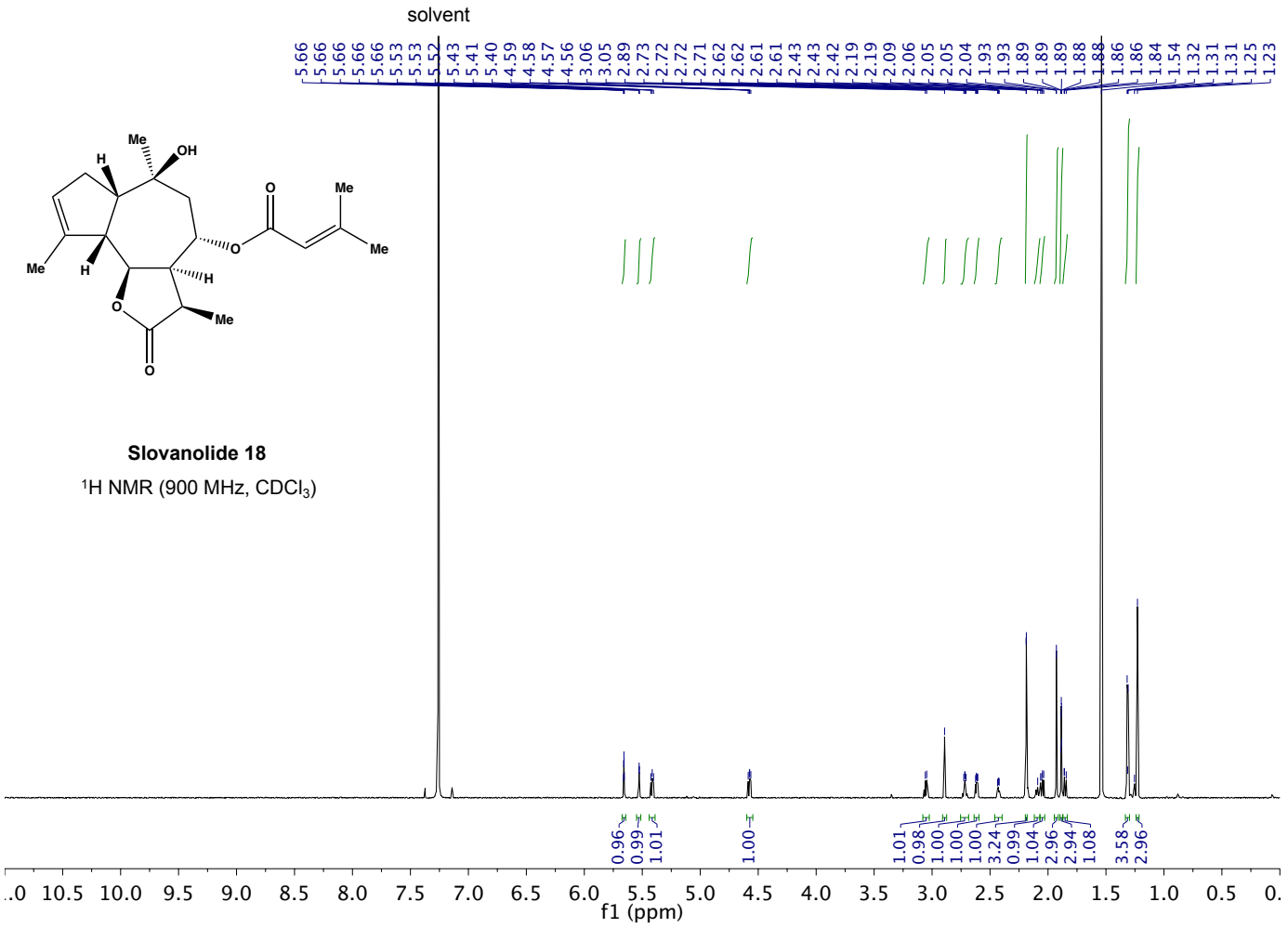
SI-4

^{1}H NMR (900 MHz, C_6D_6)



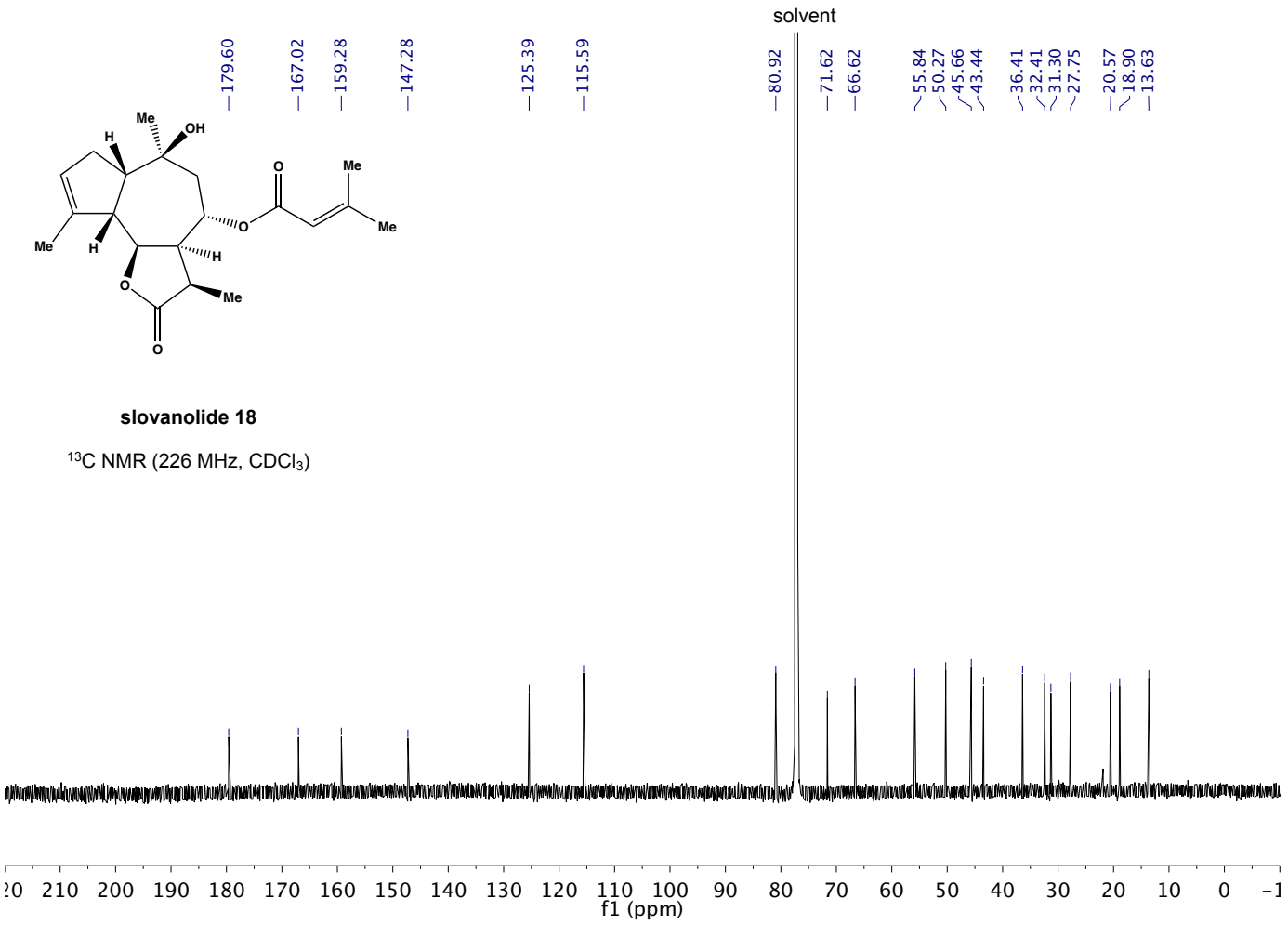
SI-4

^{13}C NMR (226 MHz, C_6D_6)



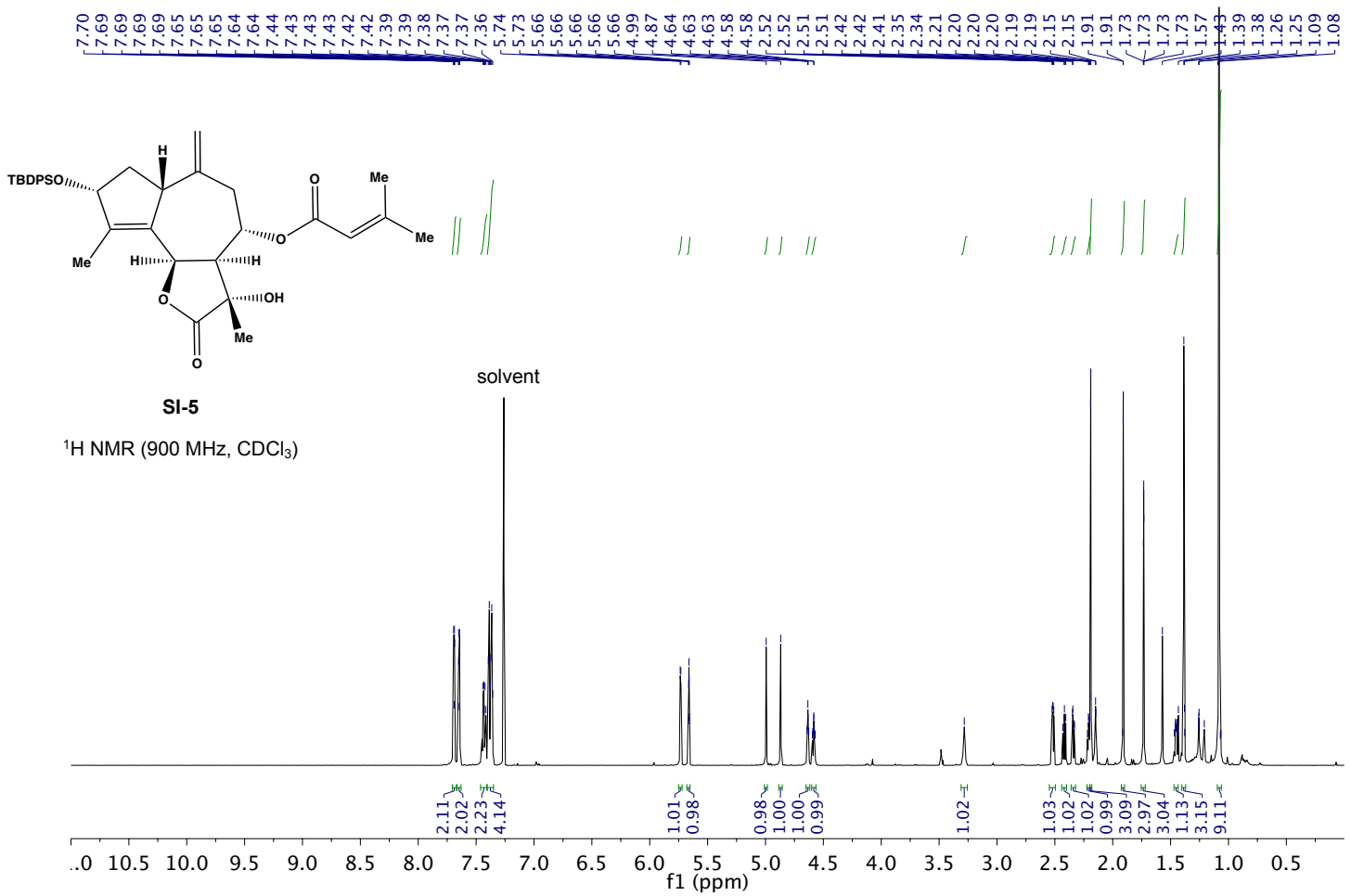
Slovanolide 18

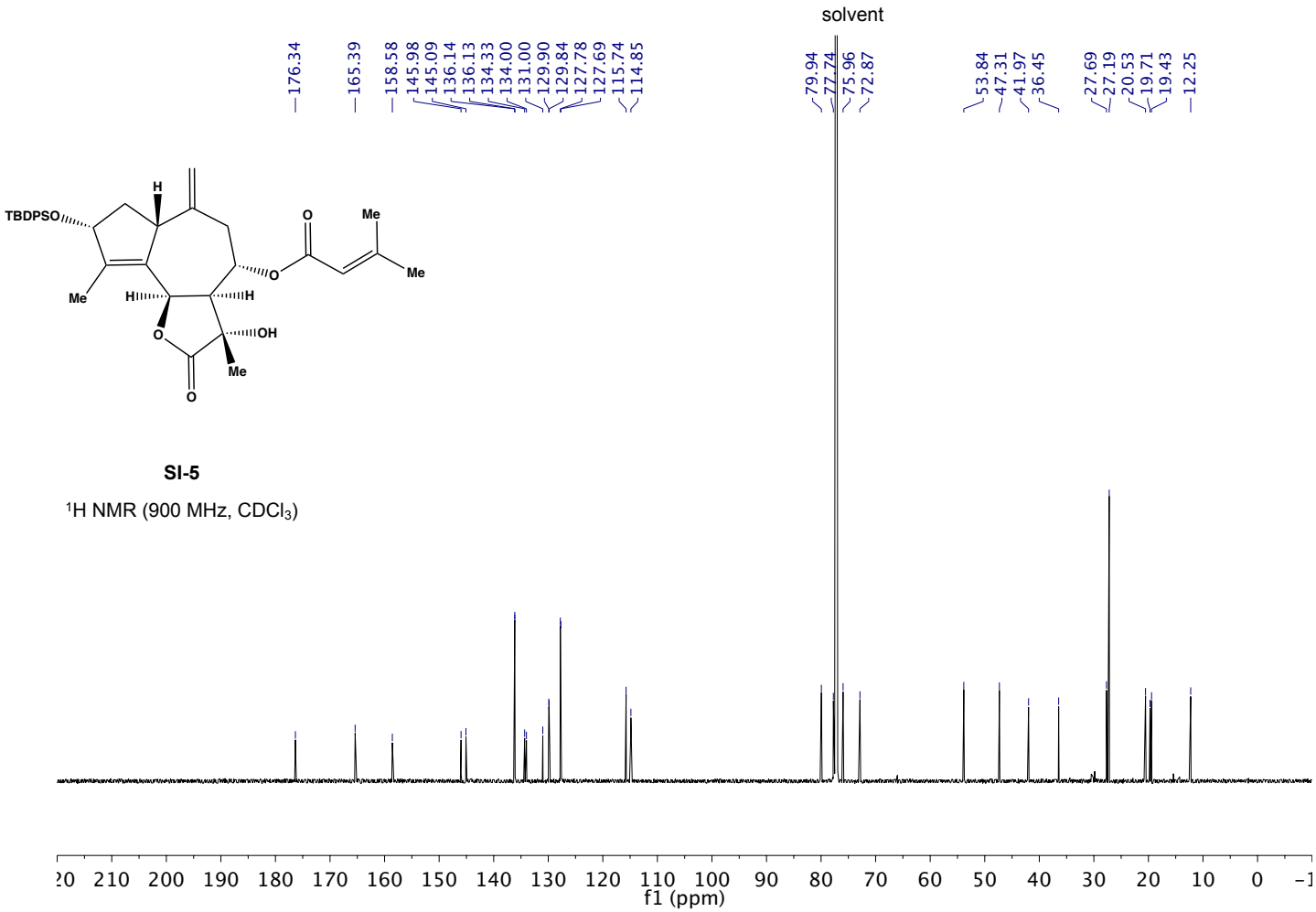
^{1}H NMR (900 MHz, $CDCl_3$)



slovanolide 18

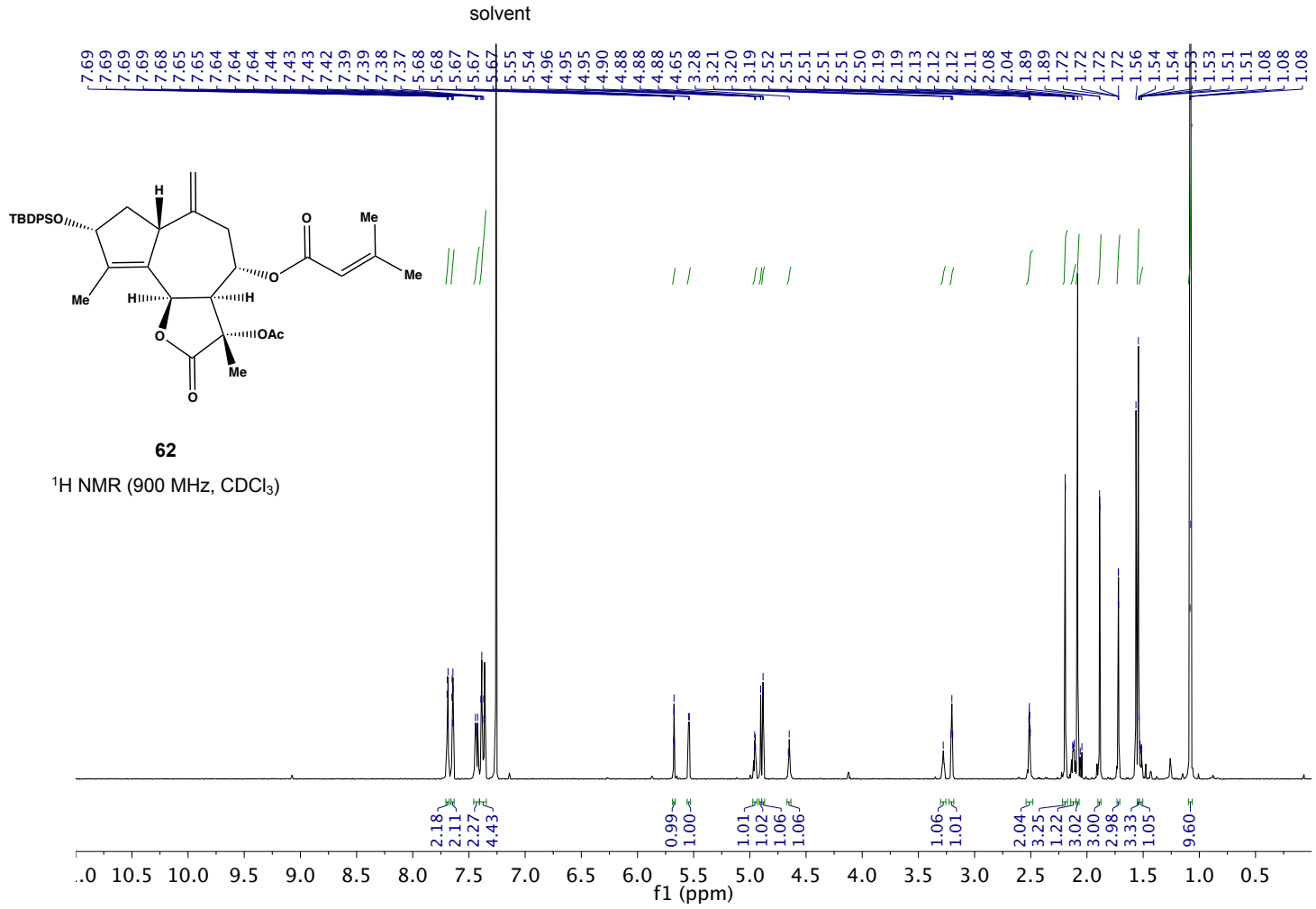
^{13}C NMR (226 MHz, $CDCl_3$)


TBDPSO
H
Me
H
H
O
OH
Me
O
O
Me
Me
SI-5
1H NMR (900 MHz, CDCl3)
solvent
f1 (ppm)



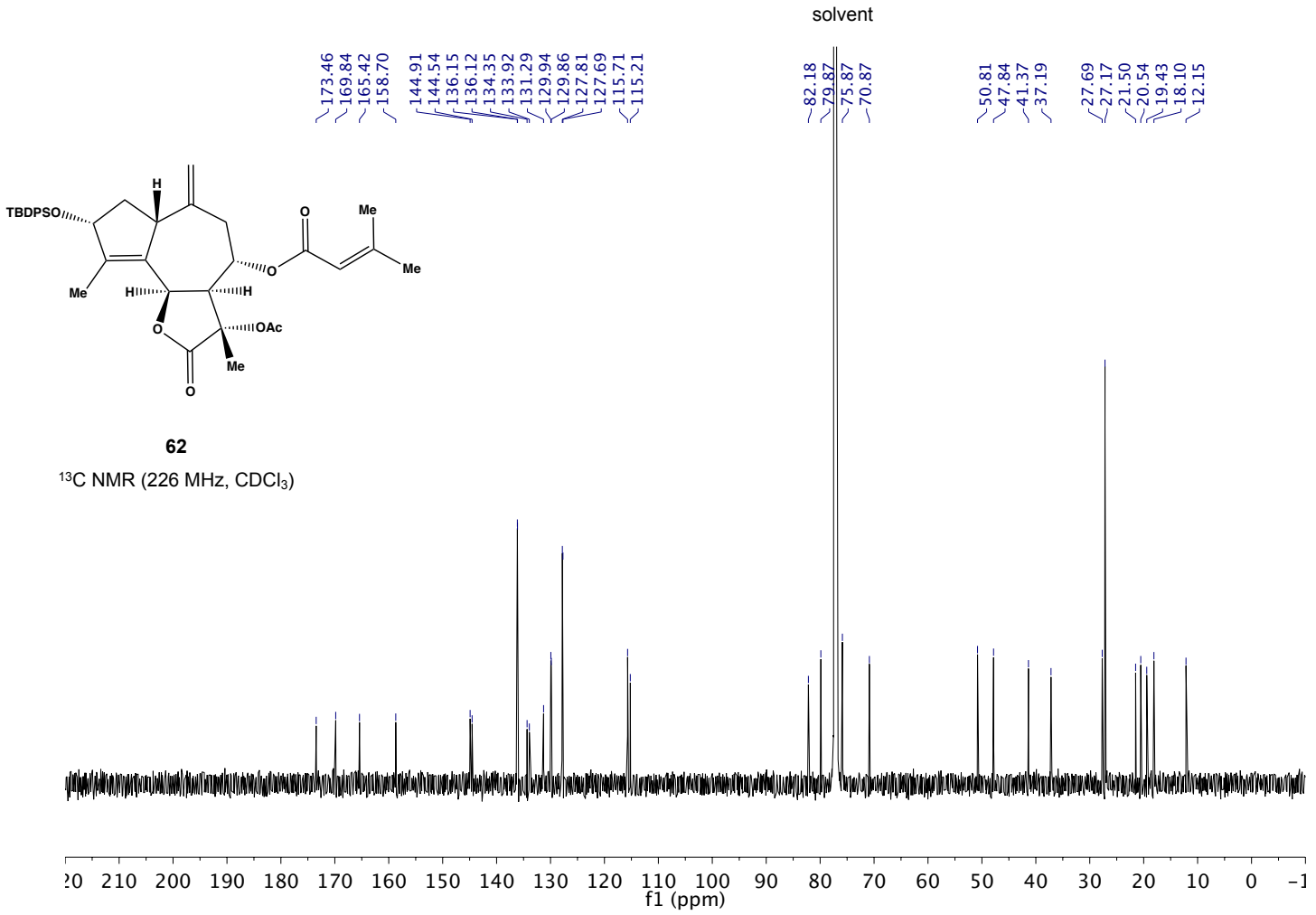
SI-5

^{1}H NMR (900 MHz, $CDCl_3$)



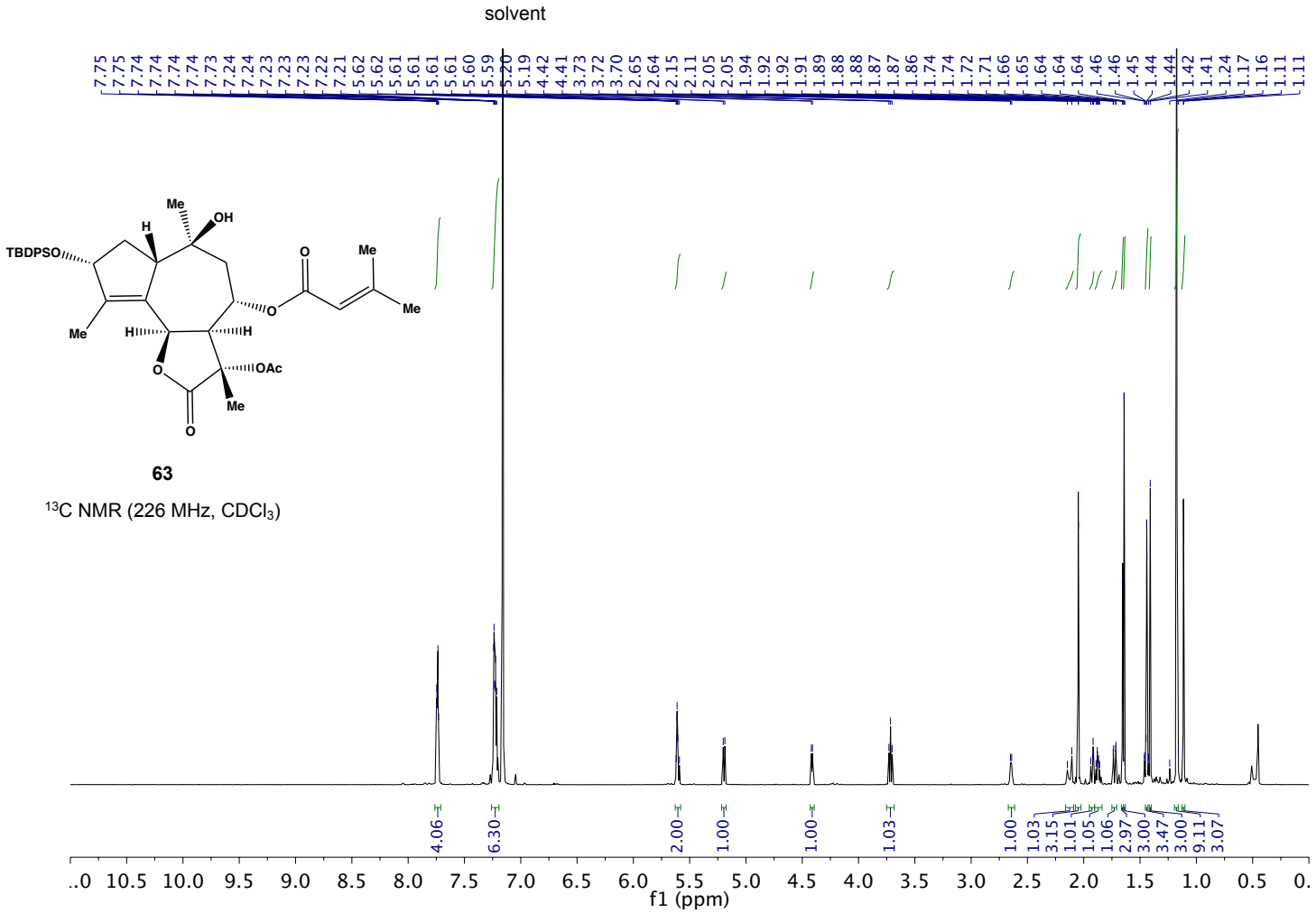
62

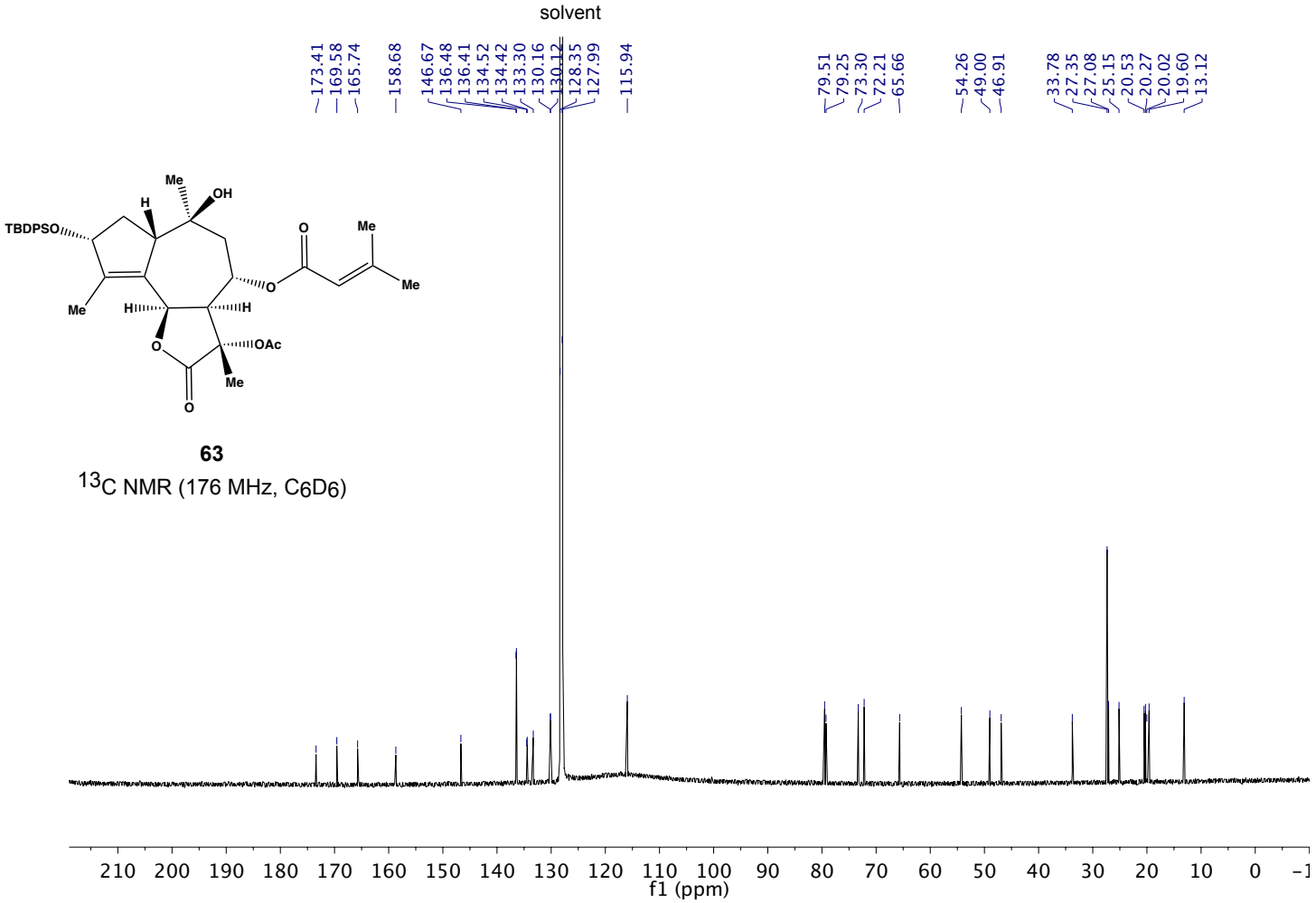
^{1}H NMR (900 MHz, $CDCl_3$)



62

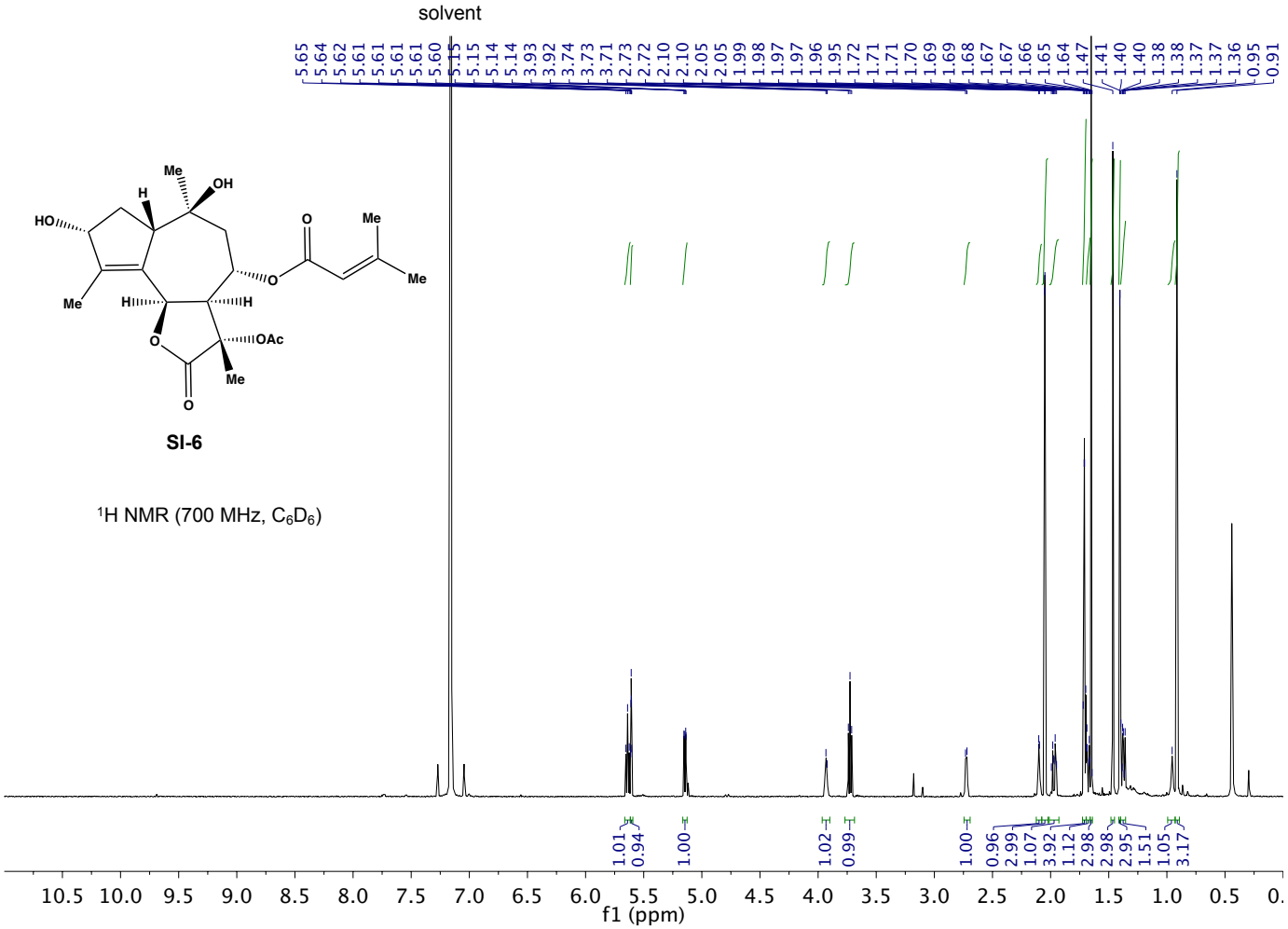
^{13}C NMR (226 MHz, $CDCl_3$)

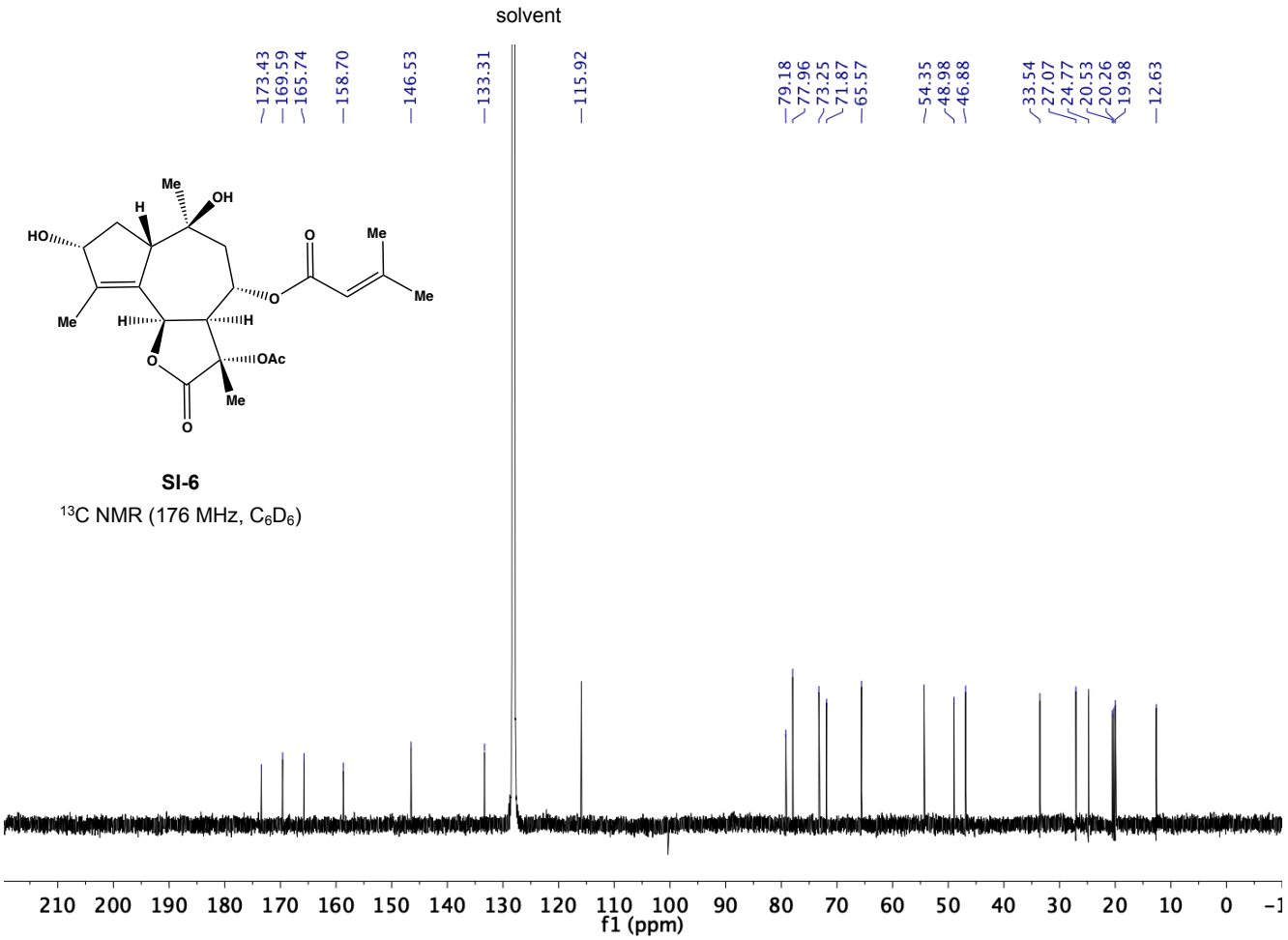

solvent
TBDPSO
Me
OH
H
O
Me
Me
Me
H
H
O
OAc
Me
O
63
^{13}C NMR (226 MHz, $CDCl_3$)
f1 (ppm)



63

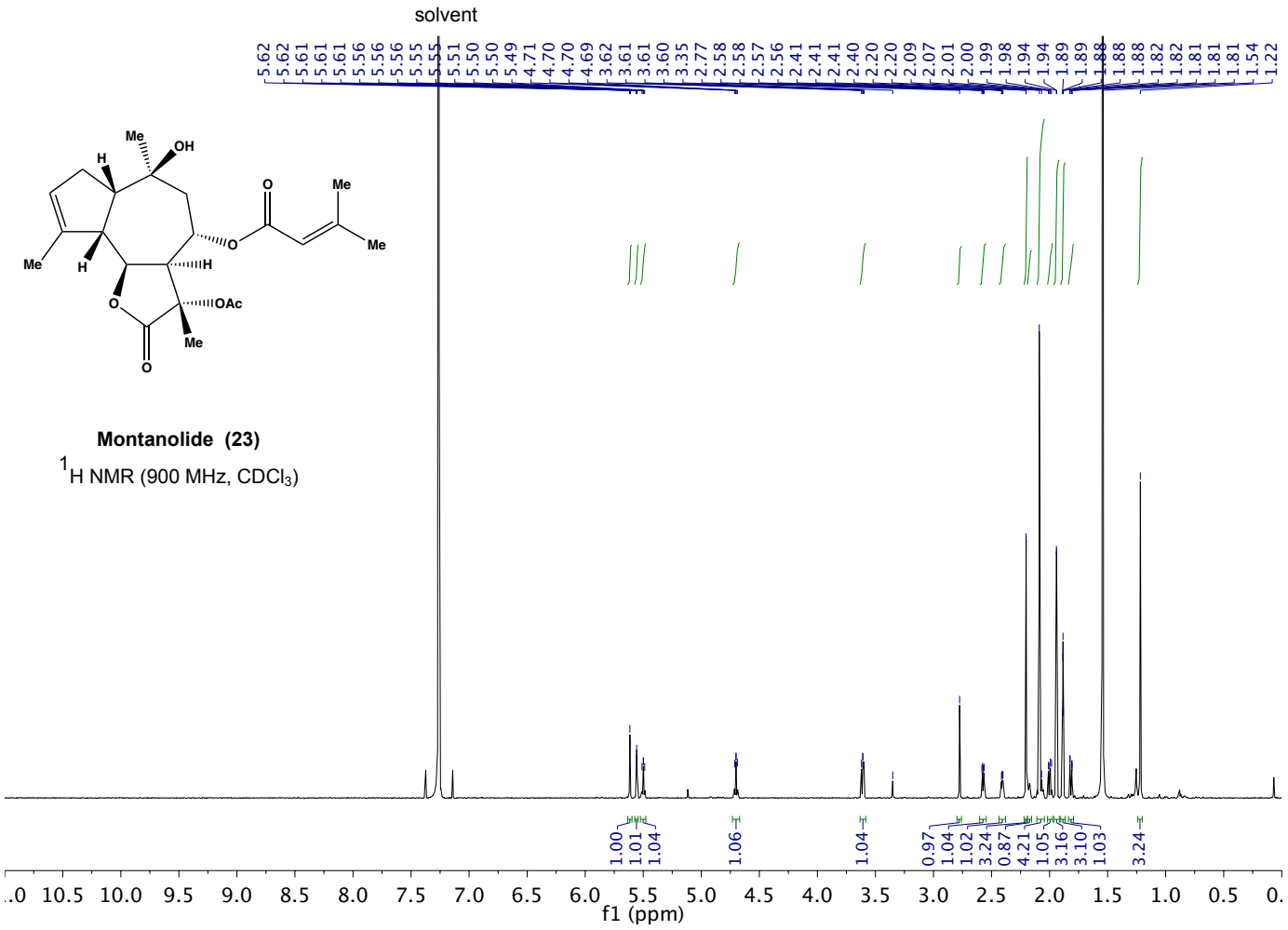
^{13}C NMR (176 MHz, C_6D_6)

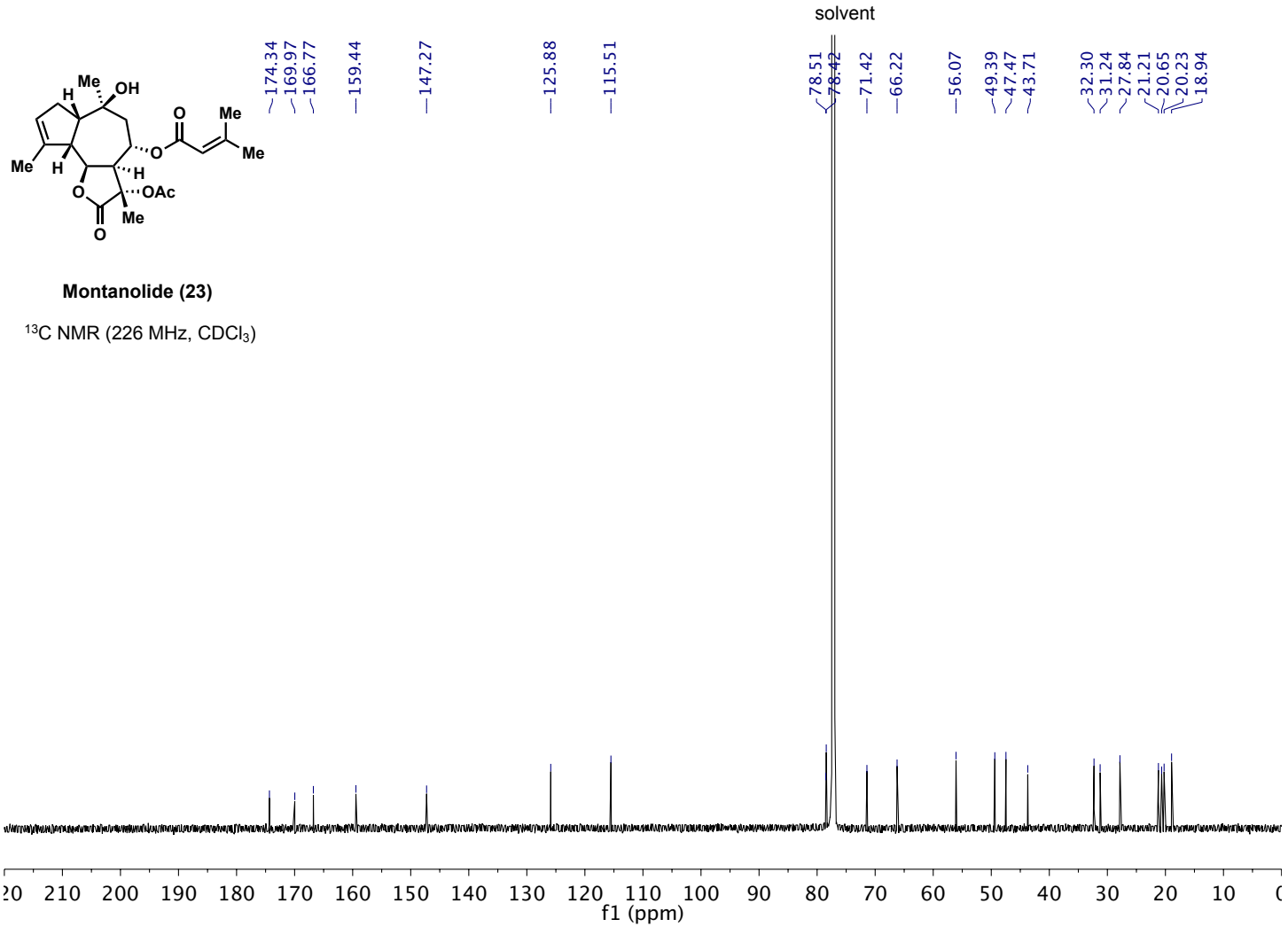

solvent
5.65 5.64 5.62 5.61 5.61 5.61 5.61 5.60 5.15 5.15 5.14 5.14 3.93 3.92 3.74 3.73 3.71 2.73 2.72 2.10 2.05 2.05 1.99 1.98 1.97 1.97 1.96 1.95 1.72 1.71 1.71 1.70 1.69 1.69 1.68 1.67 1.67 1.66 1.65 1.64 1.47 1.41 1.40 1.40 1.38 1.38 1.37 1.37 1.36 0.95 0.91
Me
OH
H
HO
O
Me
Me
H
H
H
O
OAc
Me
O
SI-6
1H NMR (700 MHz, C6D6)
1.01 0.94 1.00 1.02 0.99 1.00 0.96 2.99 1.07 3.92 1.12 2.98 2.98 2.95 1.51 1.05 3.17
10.5 10.0 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.
f1 (ppm)



SI-6

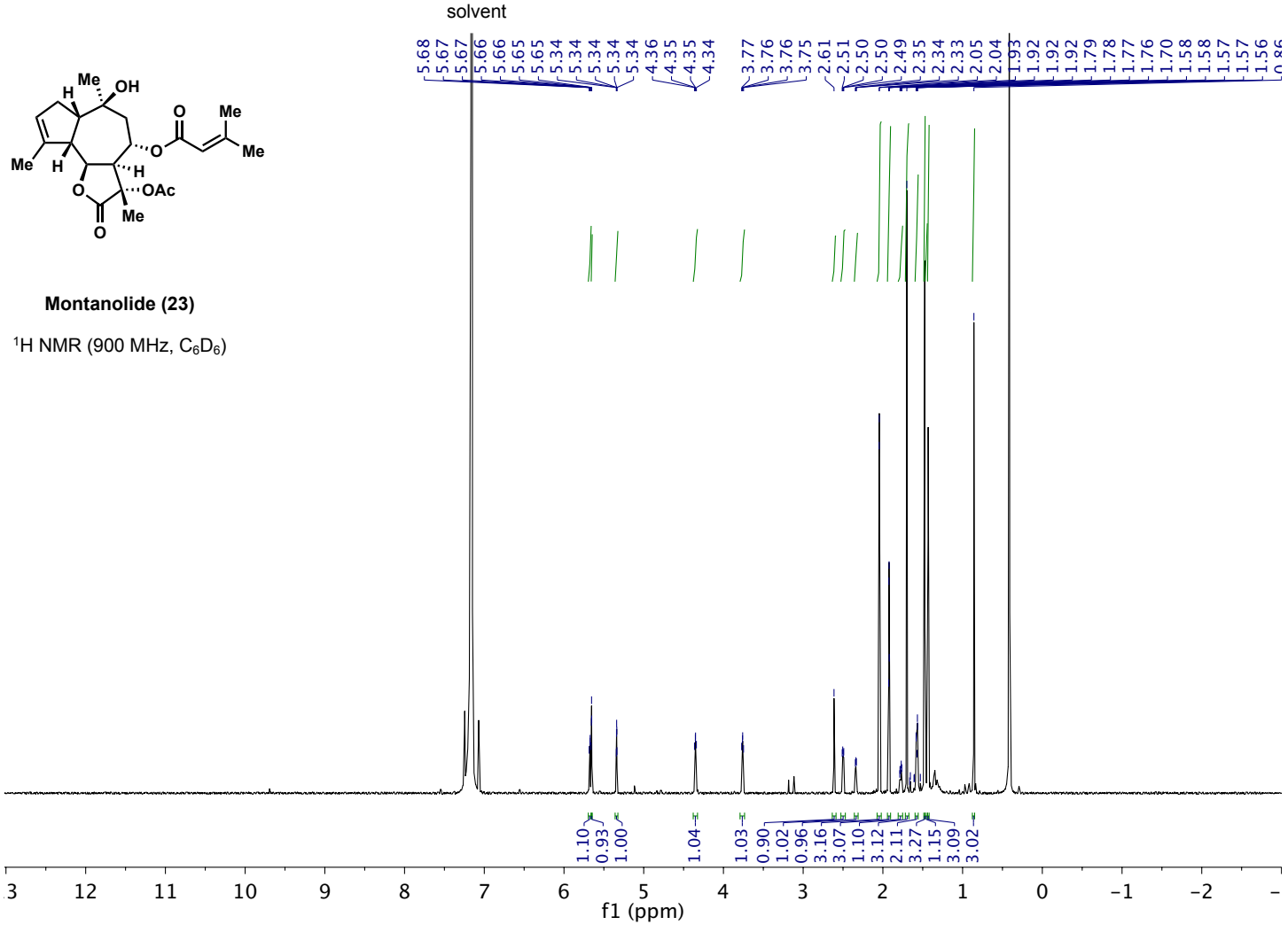
^{13}C NMR (176 MHz, C_6D_6)


solvent
Me
OH
H
O
Me
Me
H
H
O
OAc
Me
O
Montanolide (23)
1H NMR (900 MHz, CDCl3)
f1 (ppm)



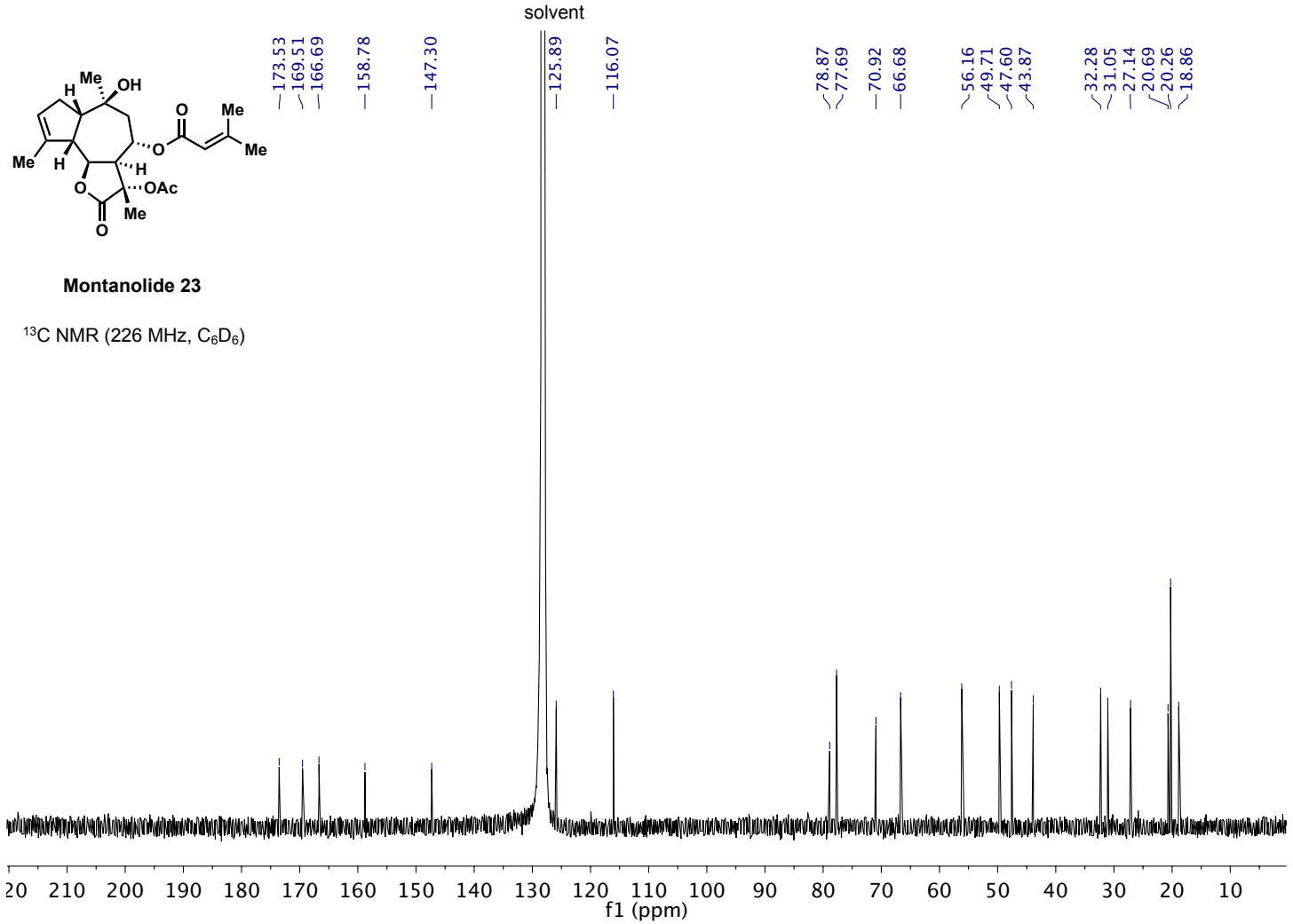
Montanolide (23)

^{13}C NMR (226 MHz, $CDCl_3$)



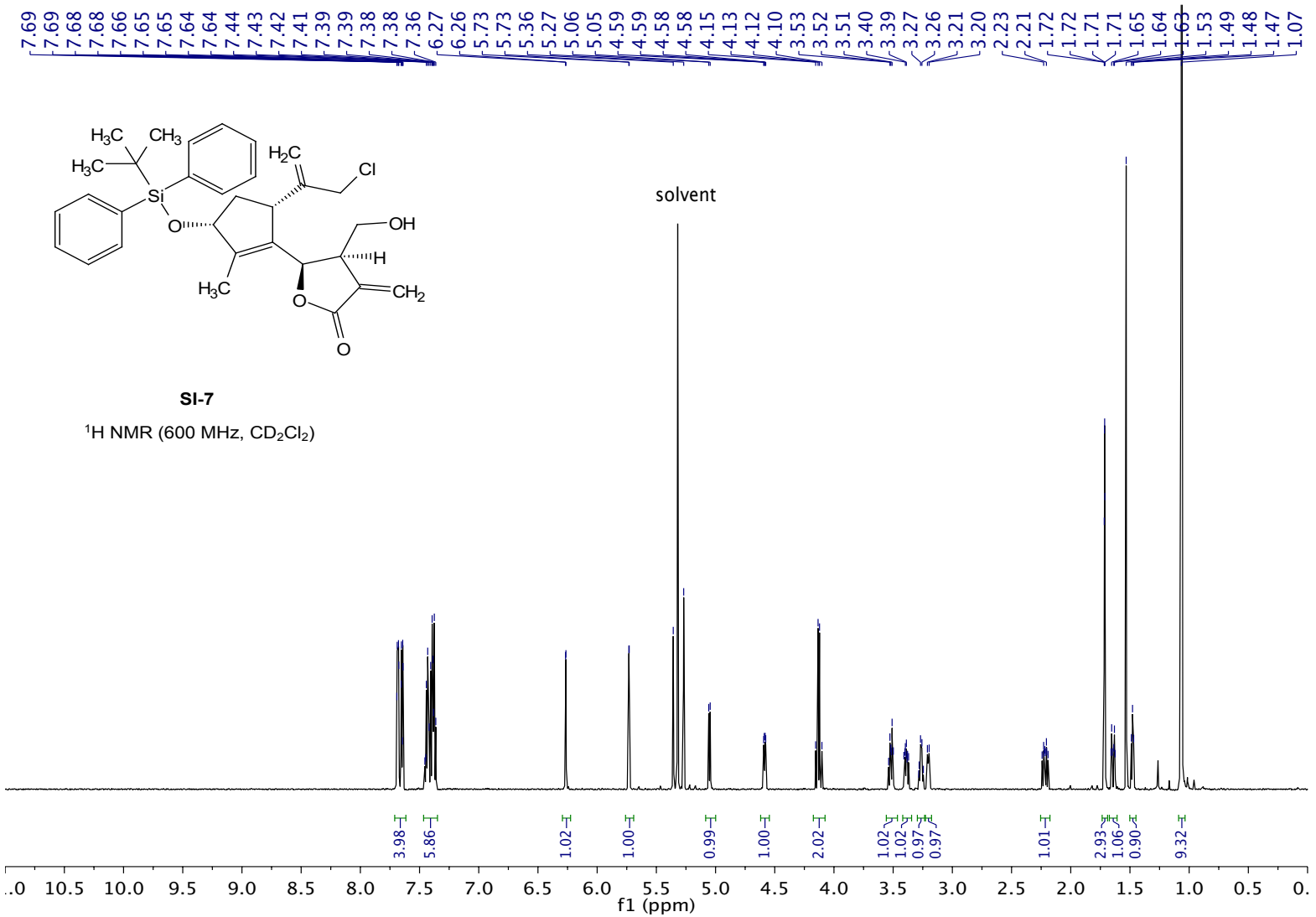
Montanolide (23)

^{1}H NMR (900 MHz, C_6D_6)



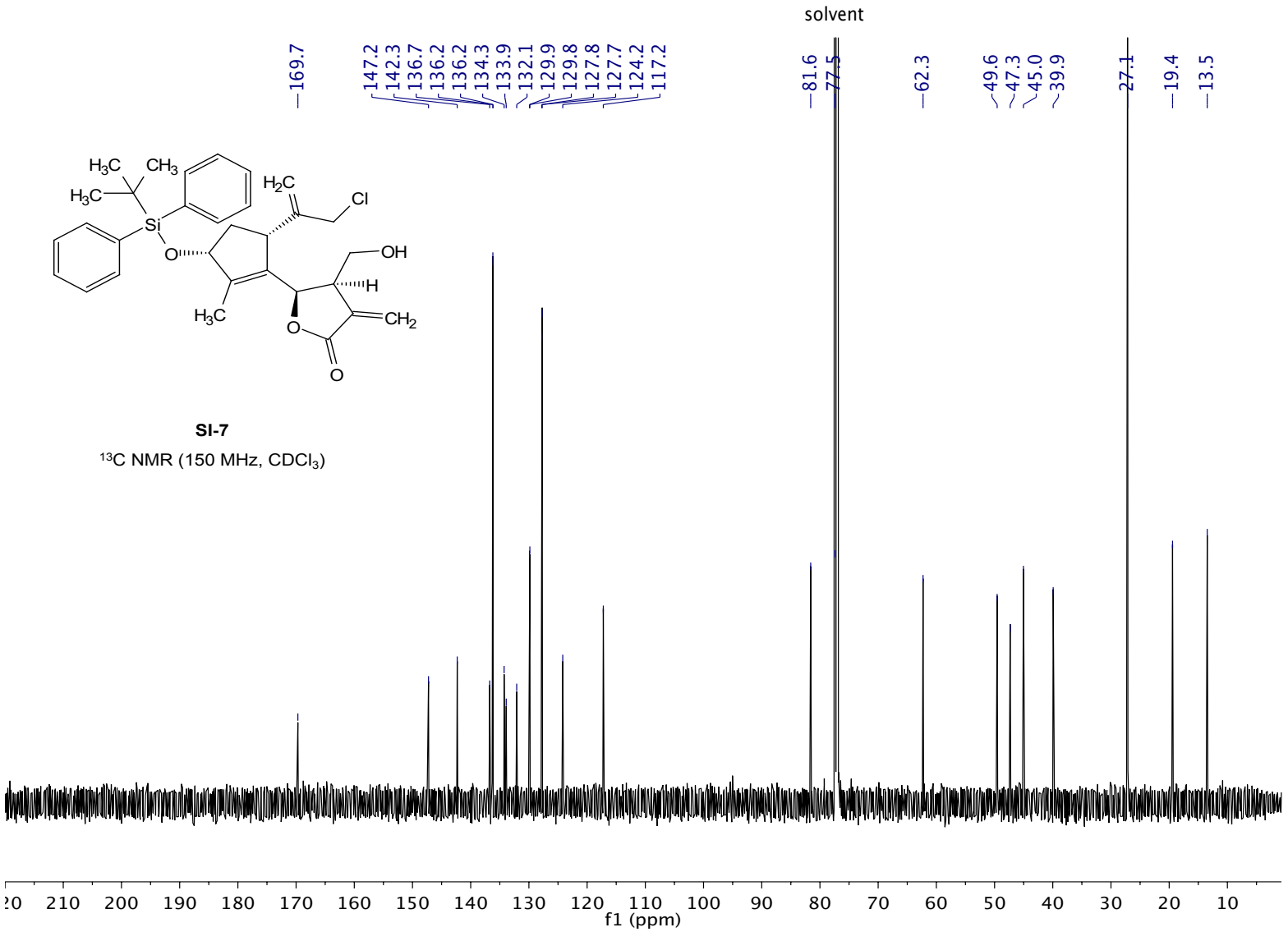
Montanolide 23

^{13}C NMR (226 MHz, C_6D_6)



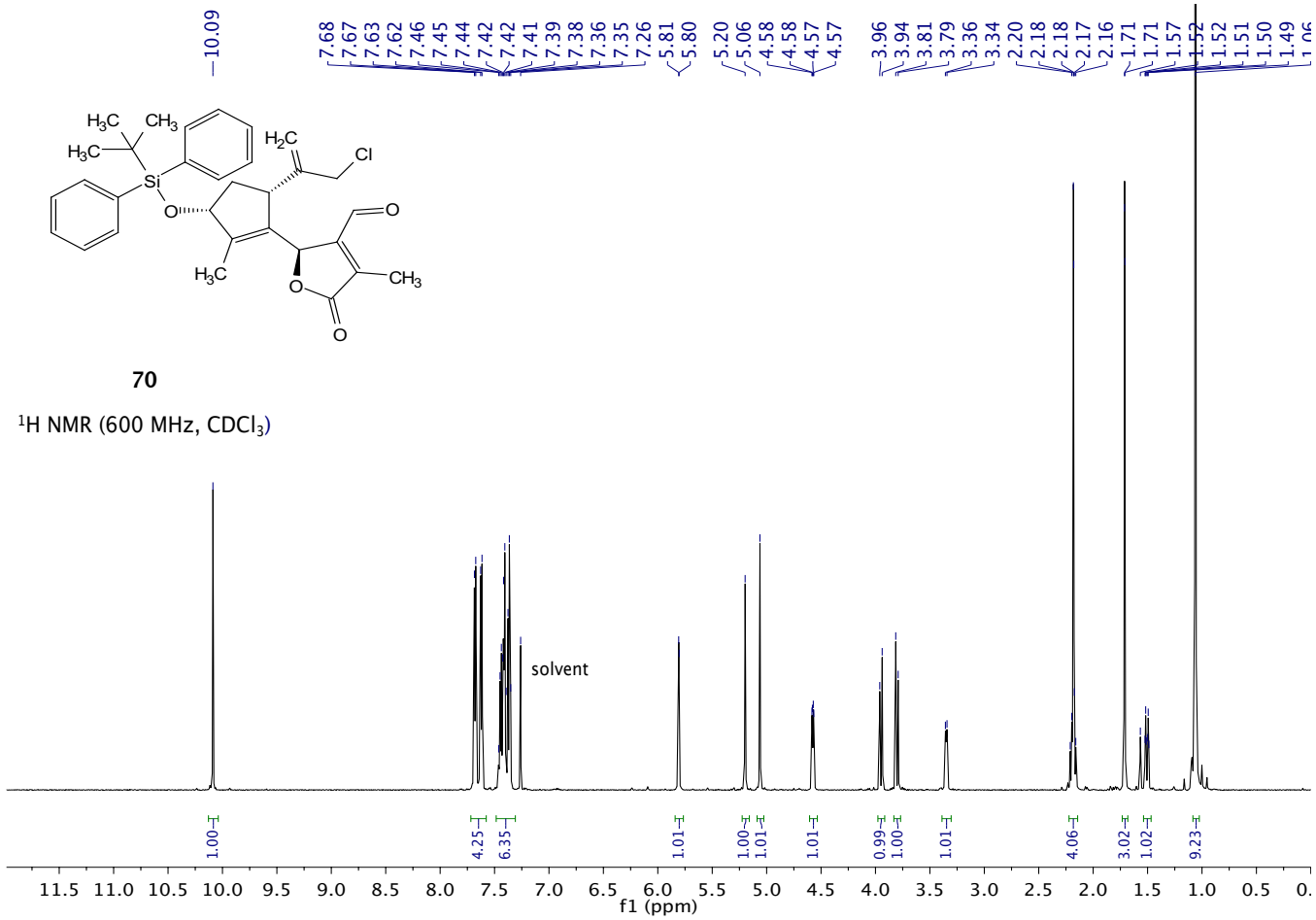
SI-7

^{1}H NMR (600 MHz, CD_2Cl_2)



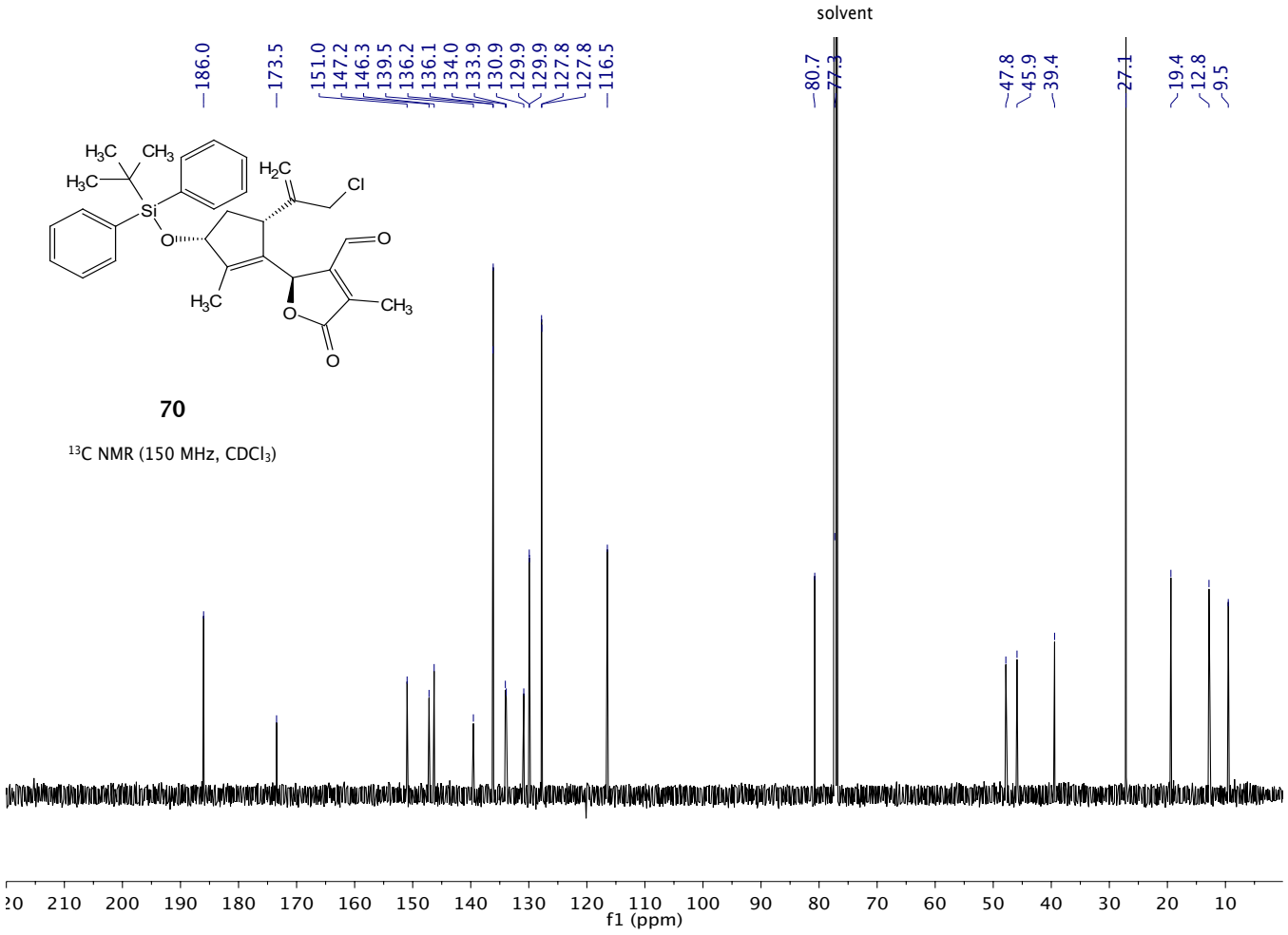
SI-7

^{13}C NMR (150 MHz, $CDCl_3$)



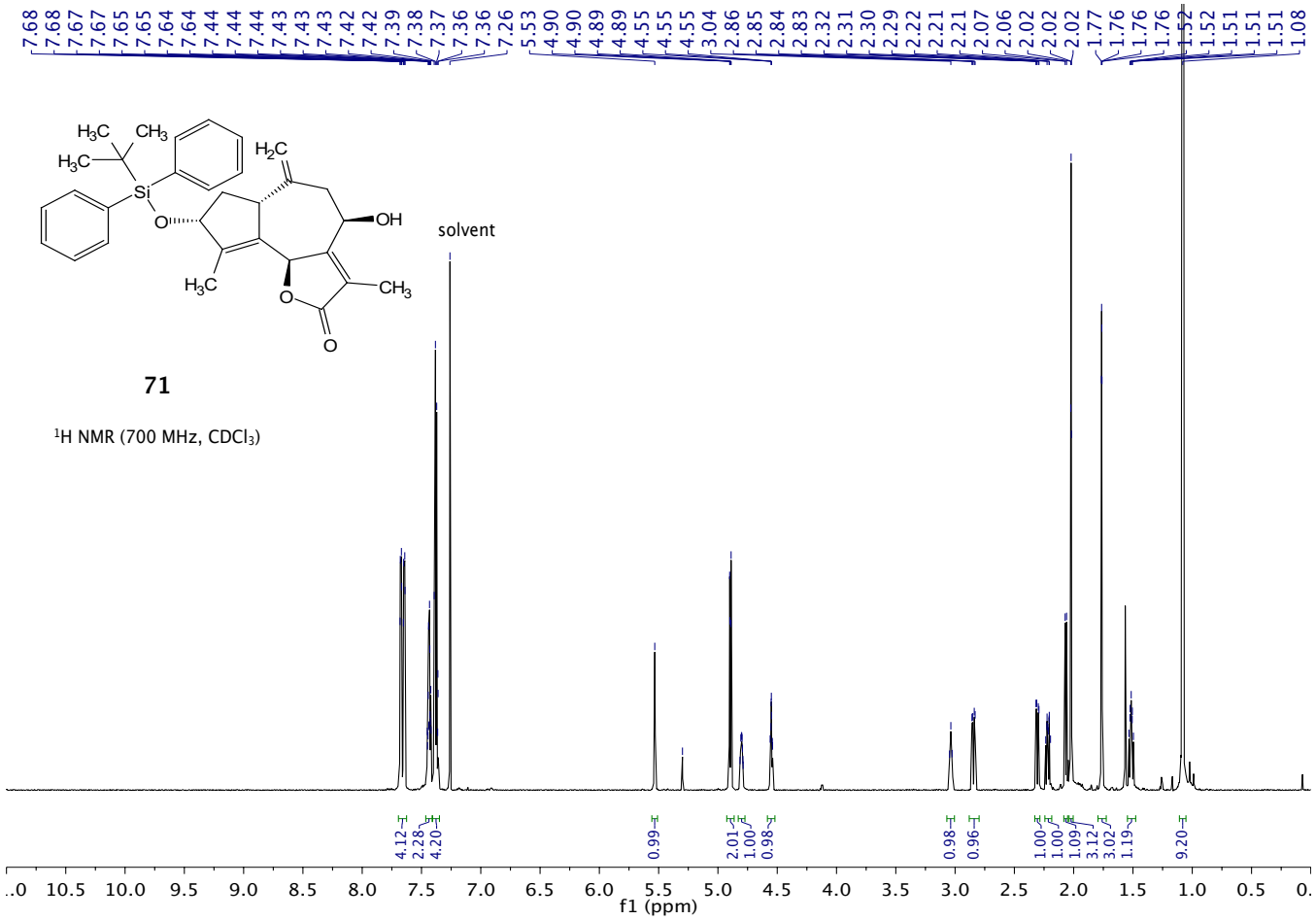
70

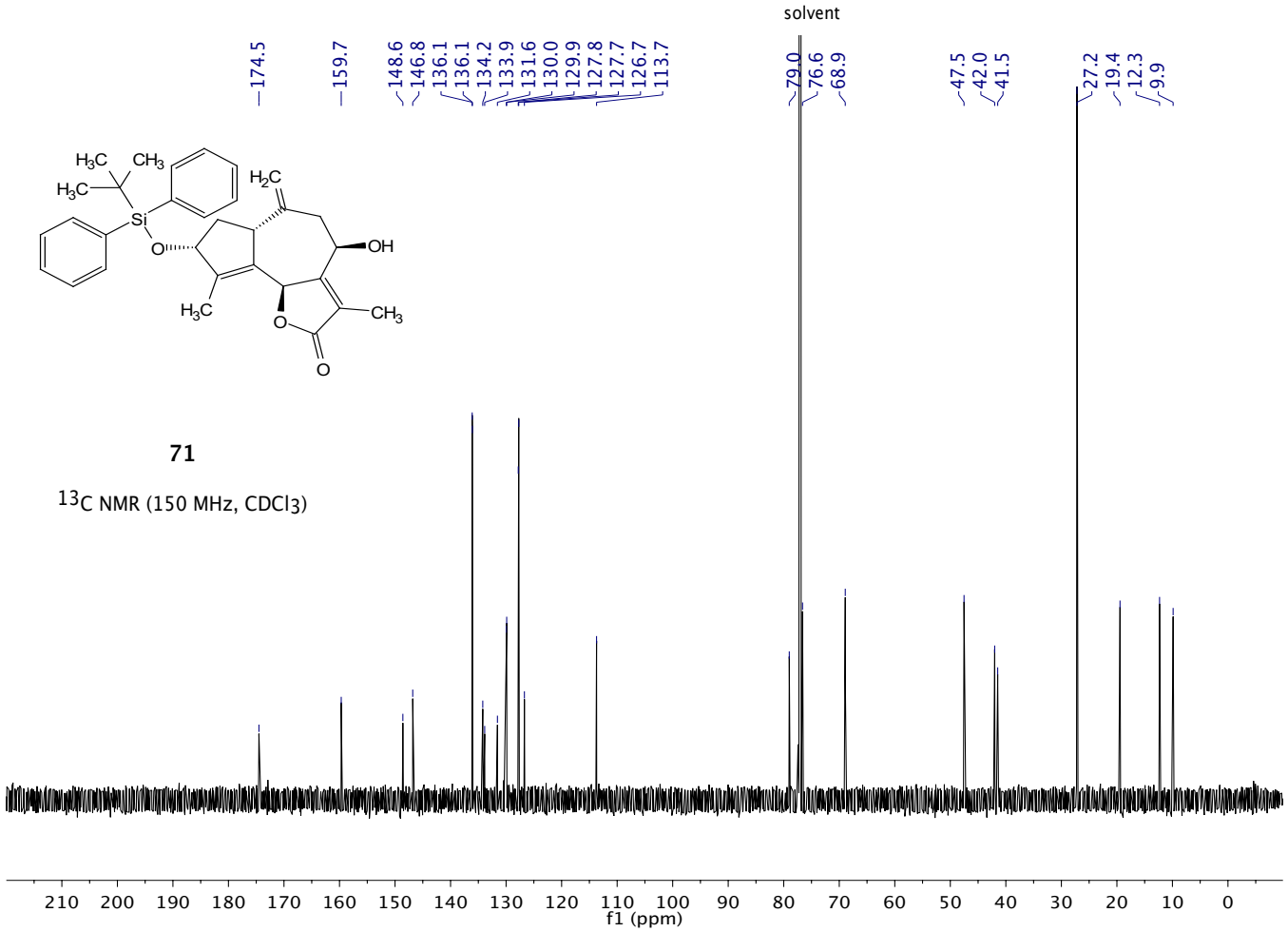
^{1}H NMR (600 MHz, $CDCl_3$)

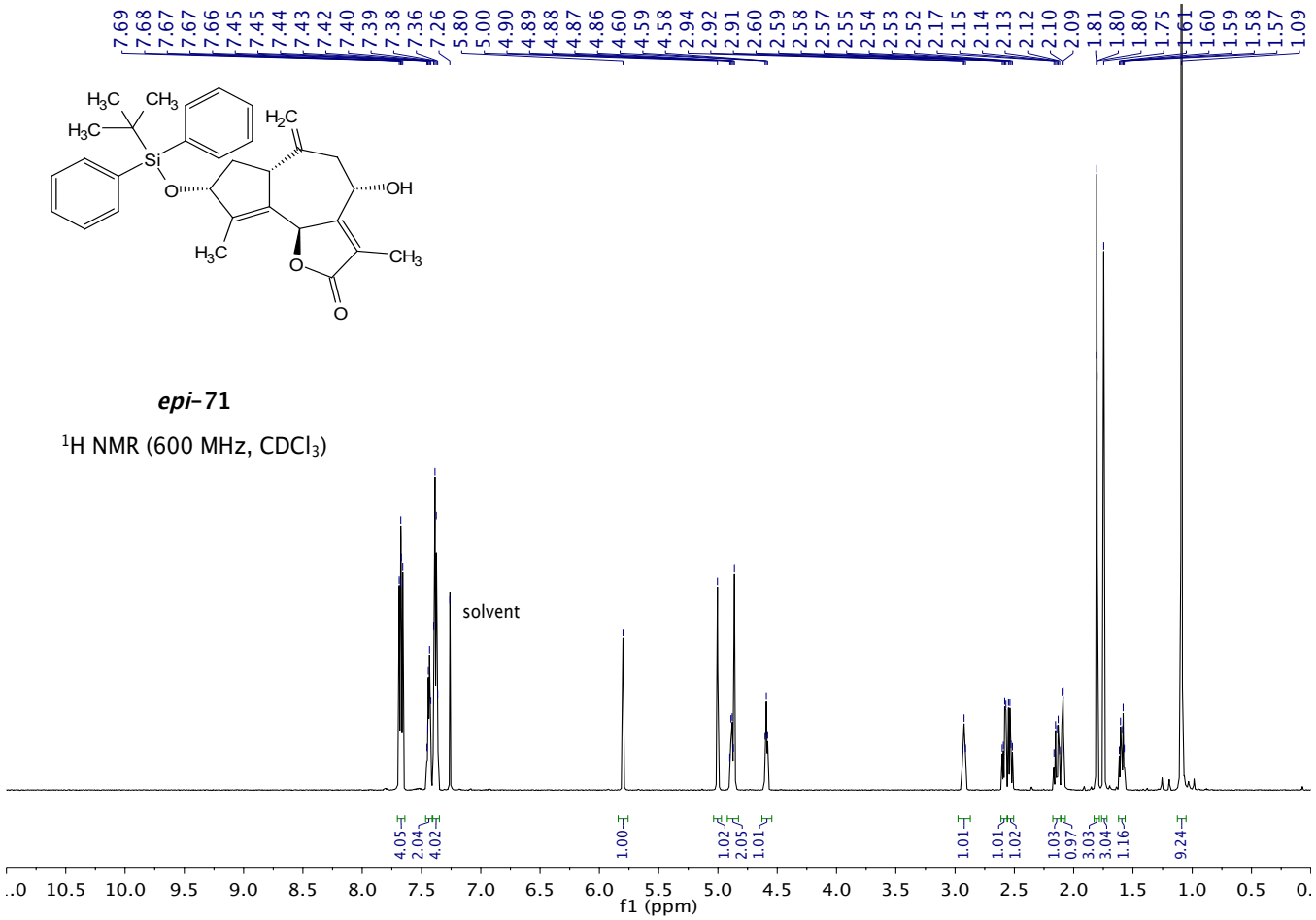


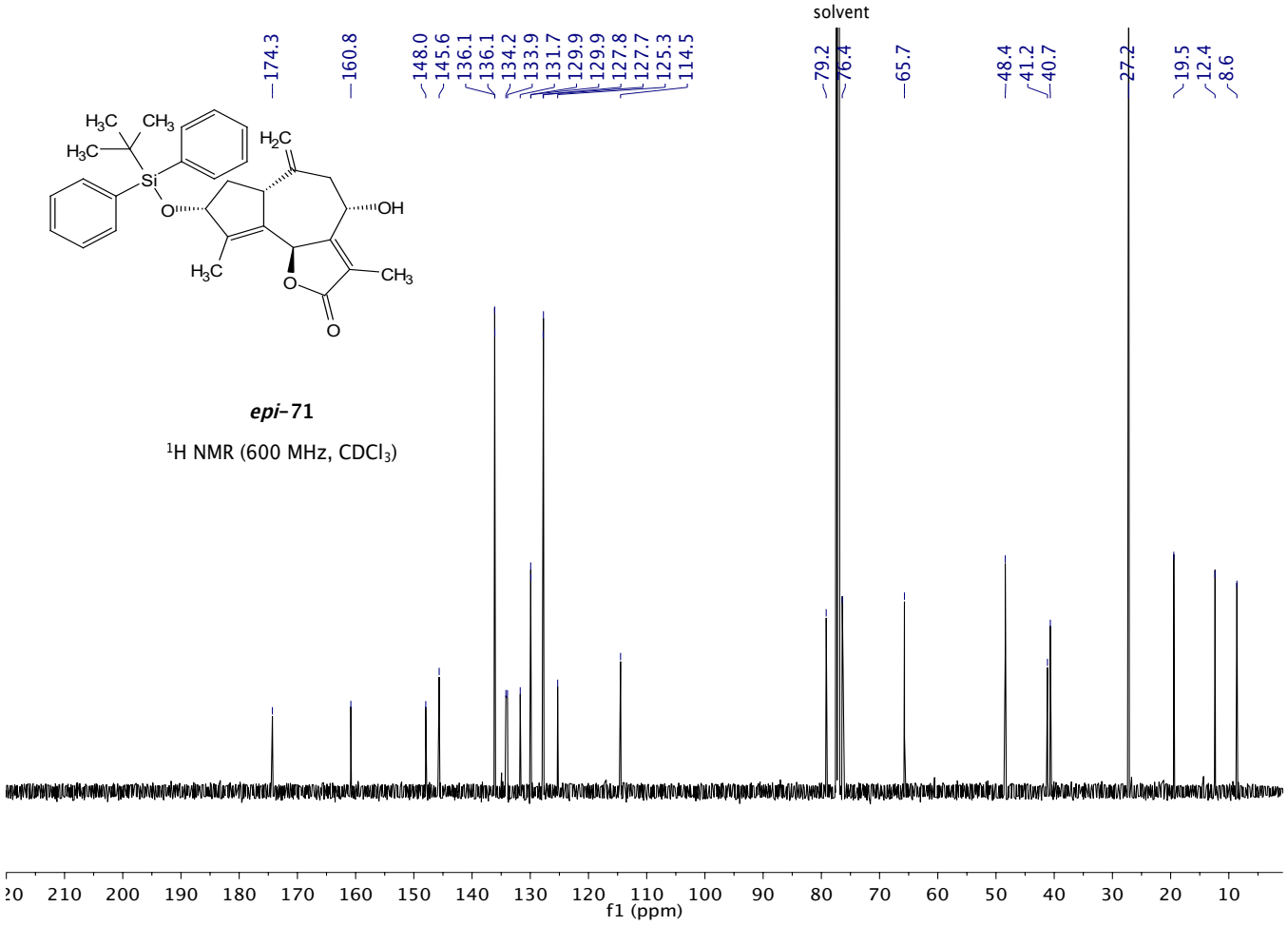
70

^{13}C NMR (150 MHz, $CDCl_3$)


7.68 7.68 7.67 7.67 7.65 7.65 7.64 7.64 7.44 7.44 7.44 7.43 7.43 7.43 7.42 7.42 7.39 7.38 7.37 7.36 7.36 7.26 5.53 4.90 4.90 4.89 4.89 4.55 4.55 4.55 3.04 2.86 2.85 2.84 2.83 2.32 2.31 2.30 2.29 2.22 2.21 2.21 2.07 2.06 2.02 2.02 2.02 1.77 1.76 1.76 1.76 1.52 1.52 1.51 1.51 1.51 1.08
H3C CH3
H3C
Si
O
H2C
OH
H3C
O
CH3
O
O
solvent
71
1H NMR (700 MHz, CDCl3)
4.12 2.28 4.20 0.99 2.01 1.00 0.98 0.98 0.96 1.00 1.00 1.09 3.12 3.02 1.19 9.20
10.5 10.0 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
f1 (ppm)

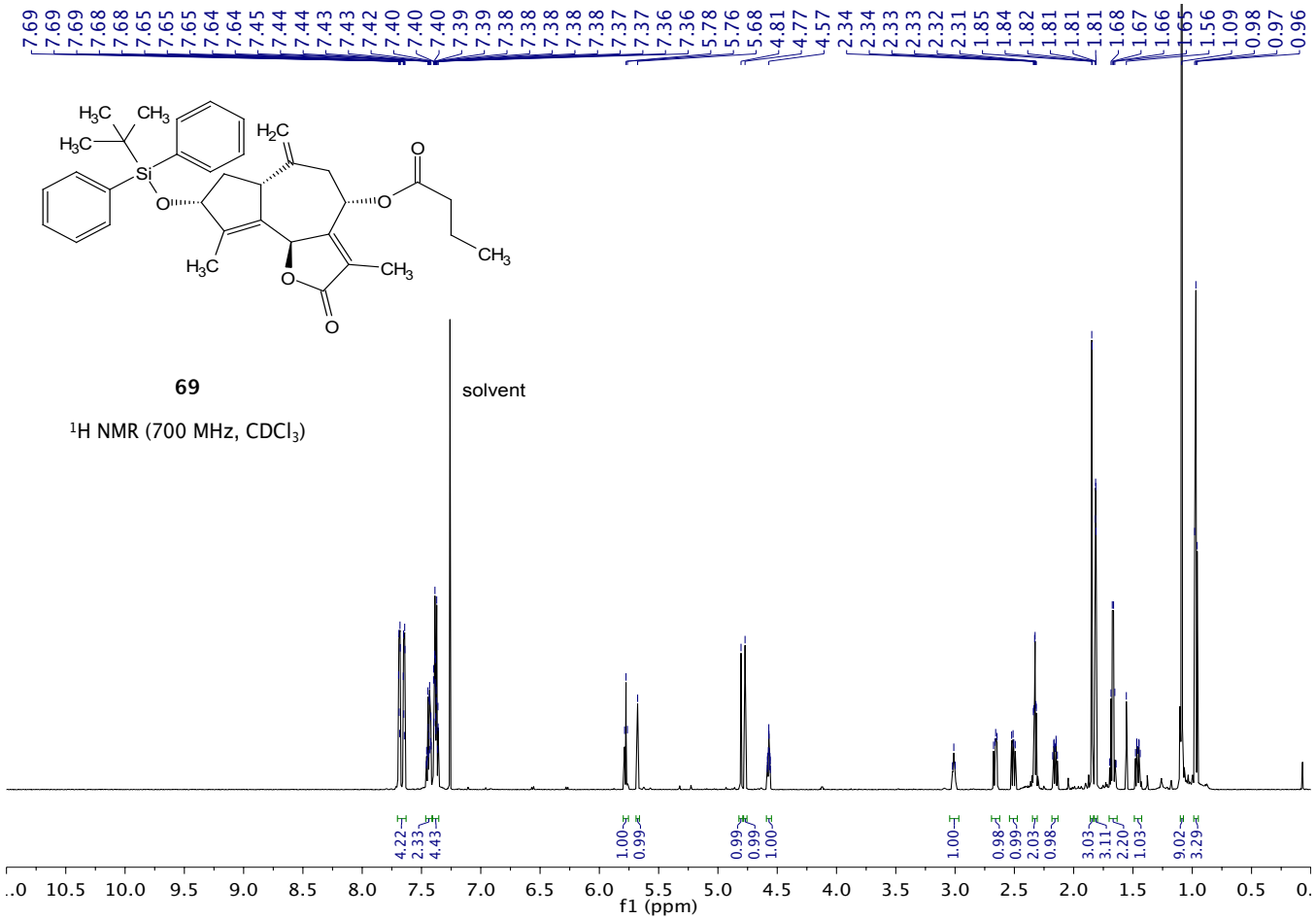

solvent
174.5
159.7
148.6
146.8
136.1
136.1
134.2
133.9
131.6
130.0
129.9
127.8
127.7
126.7
113.7
79.0
76.6
68.9
47.5
42.0
41.5
27.2
19.4
12.3
9.9
H3C
CH3
H3C
Si
O
H2C
OH
H3C
CH3
O
O
71
13C NMR (150 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

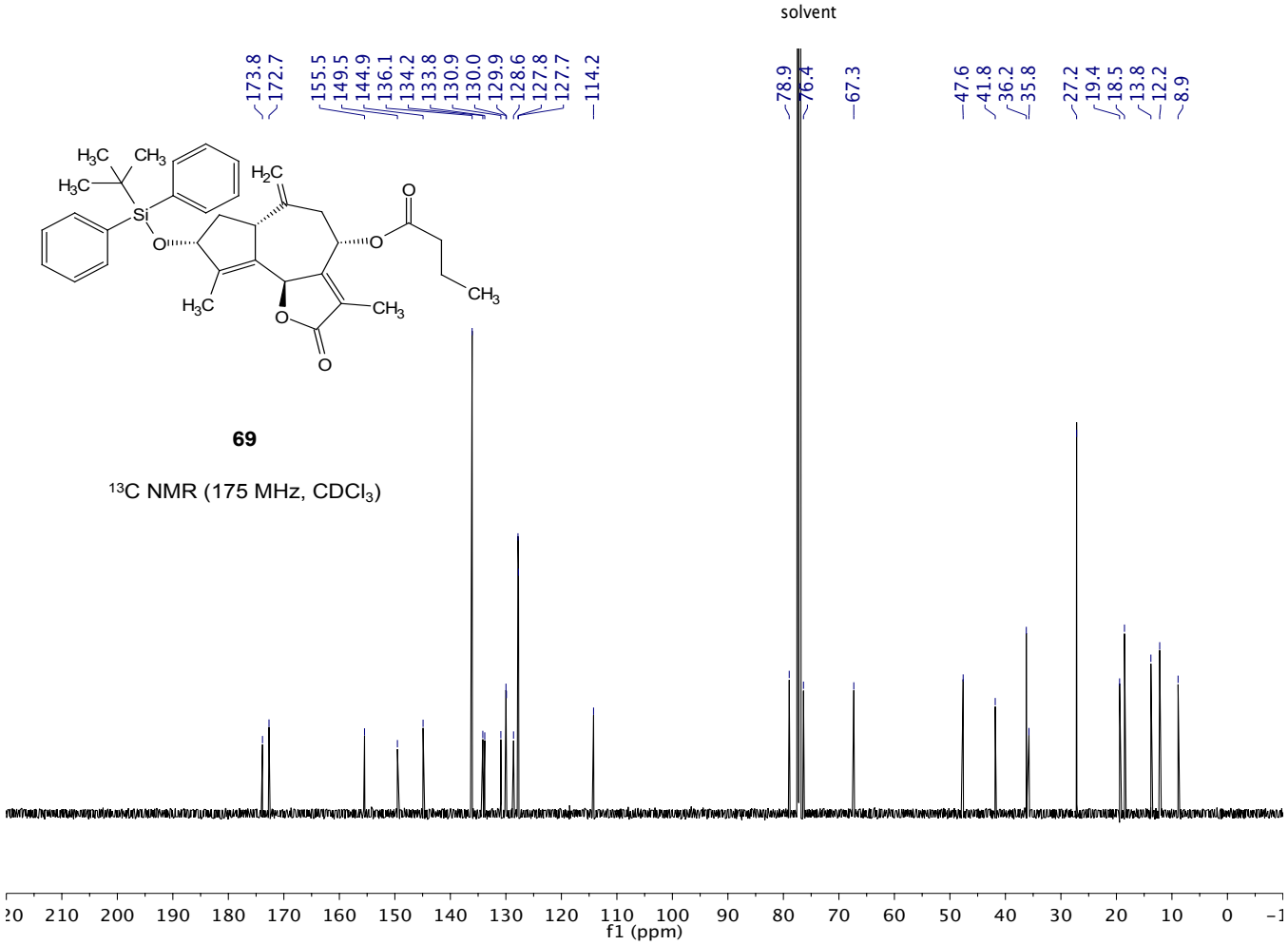

7.69 7.68 7.67 7.67 7.66 7.45 7.45 7.44 7.43 7.42 7.40 7.39 7.38 7.36 7.26 5.80 5.00 4.90 4.89 4.88 4.87 4.86 4.60 4.59 4.58 2.94 2.92 2.91 2.60 2.59 2.58 2.57 2.55 2.54 2.53 2.52 2.17 2.15 2.14 2.13 2.12 2.10 2.09 1.81 1.80 1.80 1.75 1.61 1.60 1.59 1.58 1.57 1.09
H3C CH3 H3C Si O H2C OH H3C CH3 O O
epi-71
1H NMR (600 MHz, CDCl3)
solvent
4.05 2.04 4.02 1.00 1.02 2.05 1.01 1.01 1.01 1.02 1.03 0.97 3.03 3.04 1.16 9.24
10.5 10.0 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
f1 (ppm)



***epi*-71**

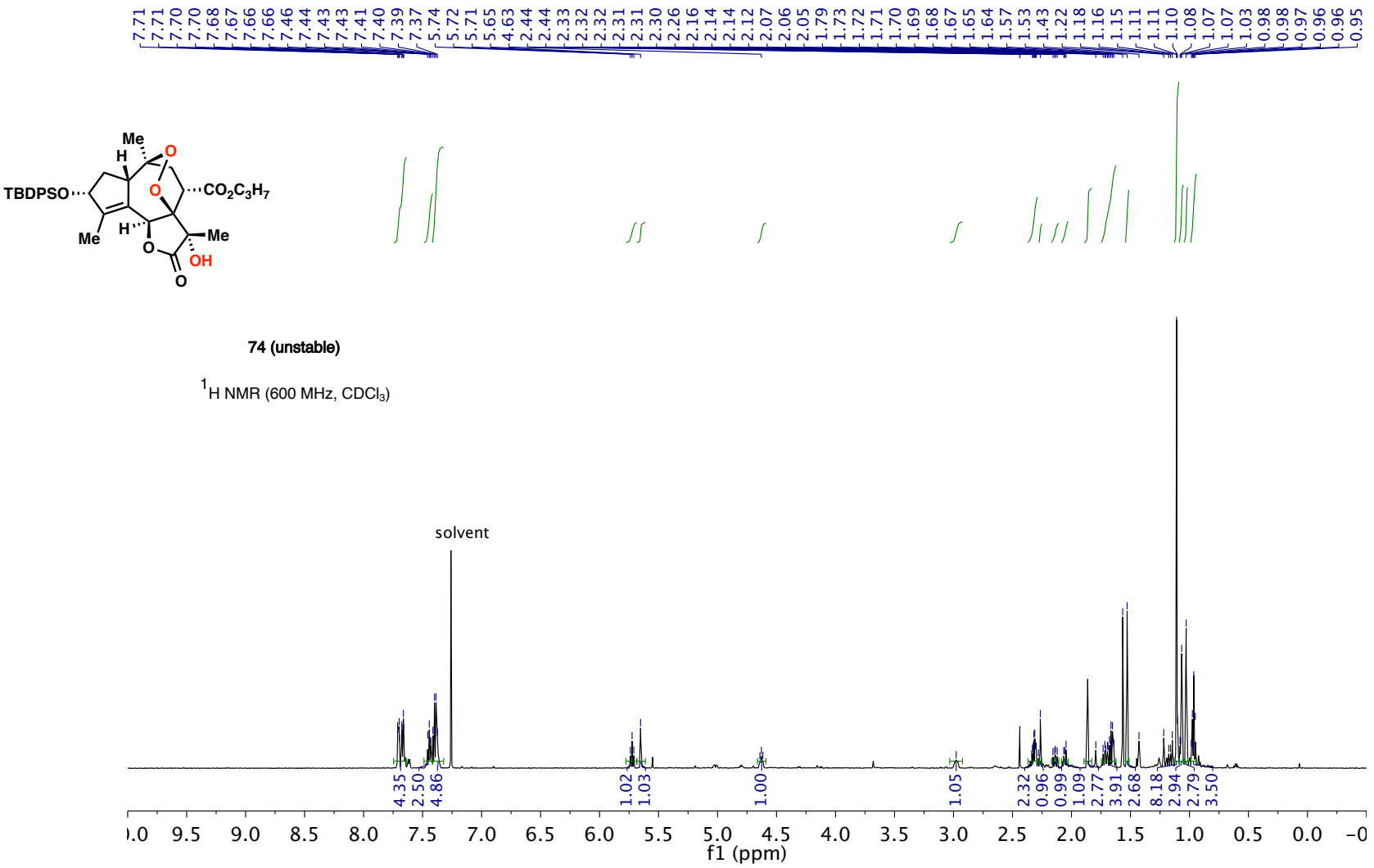
^{1}H NMR (600 MHz, $CDCl_3$)

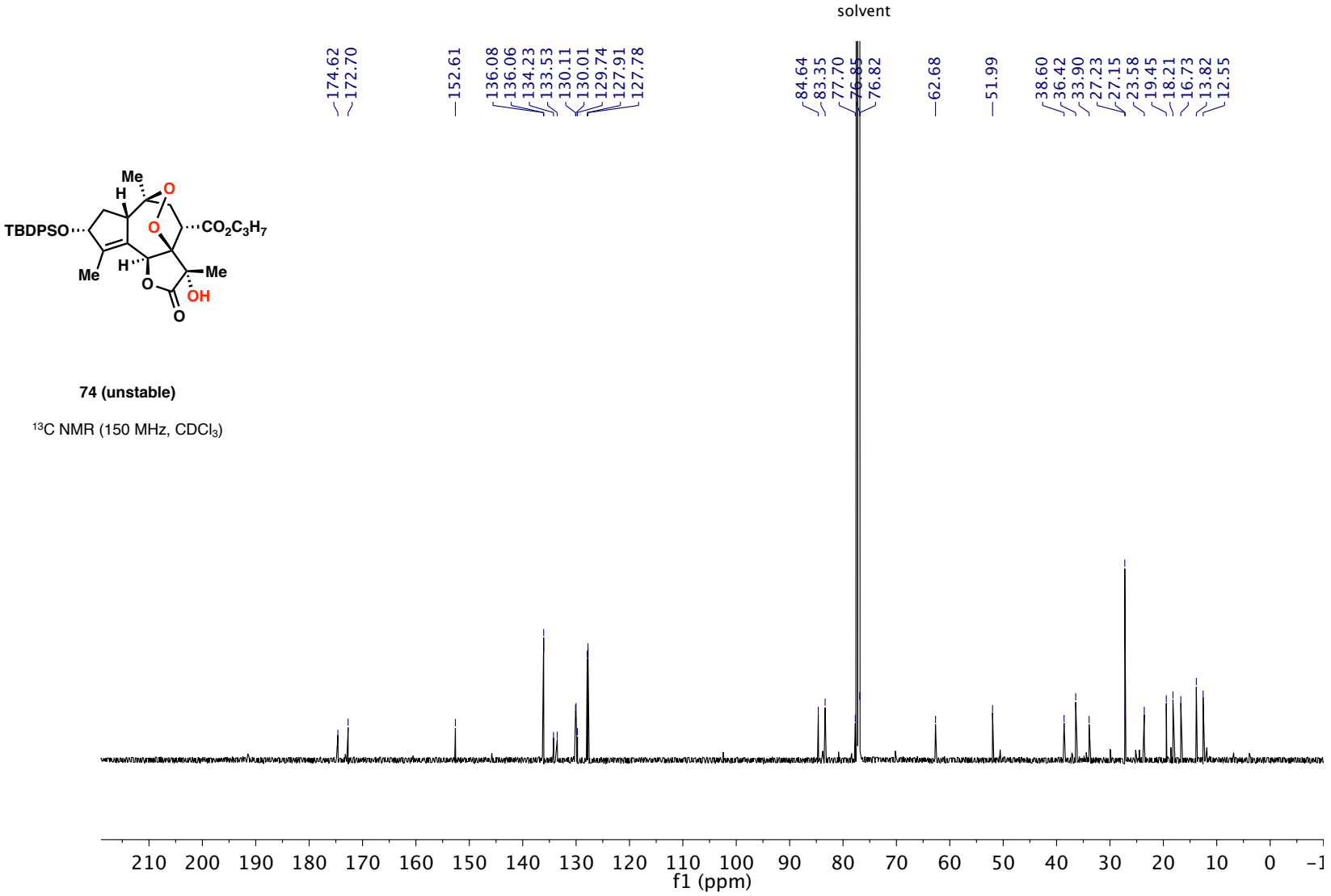

7.69
7.69
7.69
7.68
7.68
7.65
7.65
7.64
7.64
7.45
7.44
7.44
7.43
7.43
7.42
7.40
7.40
7.39
7.39
7.38
7.38
7.38
7.38
7.37
7.37
7.36
7.36
5.78
5.76
5.68
4.81
4.77
4.57
2.34
2.34
2.33
2.33
2.32
2.31
1.85
1.84
1.82
1.81
1.81
1.81
1.68
1.67
1.66
1.65
1.56
1.09
0.98
0.97
0.96
H3C
CH3
H3C
Si
O
H2C
O
O
CH3
H3C
O
CH3
O
69
1H NMR (700 MHz, CDCl3)
solvent
4.22
2.33
4.43
1.00
0.99
0.99
0.99
1.00
1.00
0.98
0.99
2.03
0.98
3.03
3.11
2.20
1.03
9.02
3.29
10.5
10.0
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
f1 (ppm)



69

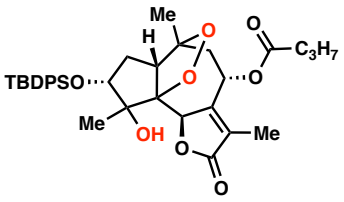
^{13}C NMR (175 MHz, $CDCl_3$)


7.71 7.71 7.70 7.70 7.68 7.67 7.66 7.66 7.46 7.44 7.43 7.43 7.41 7.40 7.39 7.37 5.74 5.72 5.71 5.65 4.63 2.44 2.44 2.33 2.32 2.32 2.31 2.31 2.30 2.26 2.16 2.14 2.14 2.12 2.07 2.06 2.05 1.79 1.73 1.72 1.71 1.70 1.69 1.68 1.67 1.65 1.64 1.57 1.53 1.43 1.22 1.18 1.16 1.15 1.11 1.11 1.10 1.08 1.07 1.07 1.03 0.98 0.98 0.97 0.96 0.96 0.95
Me
H
O
TBDPSO
CO2C3H7
O
Me
H
Me
O
OH
O
74 (unstable)
1H NMR (600 MHz, CDCl3)
solvent
4.35 2.50 4.86 1.02 1.03 1.00 1.05 2.32 0.96 0.99 1.09 2.77 3.91 2.68 8.18 2.94 2.79 3.50
f1 (ppm)



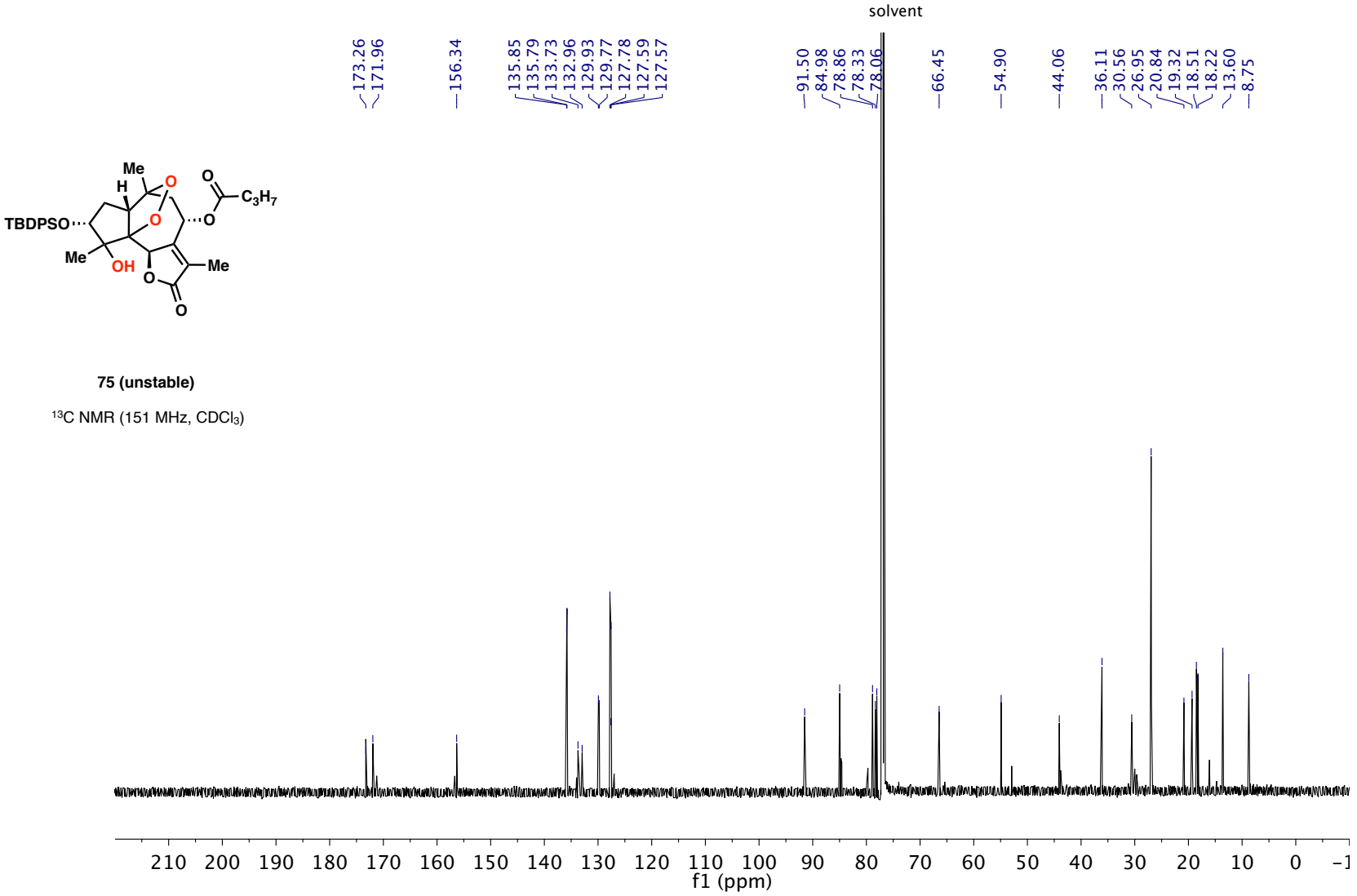
74 (unstable)

^{13}C NMR (150 MHz, $CDCl_3$)



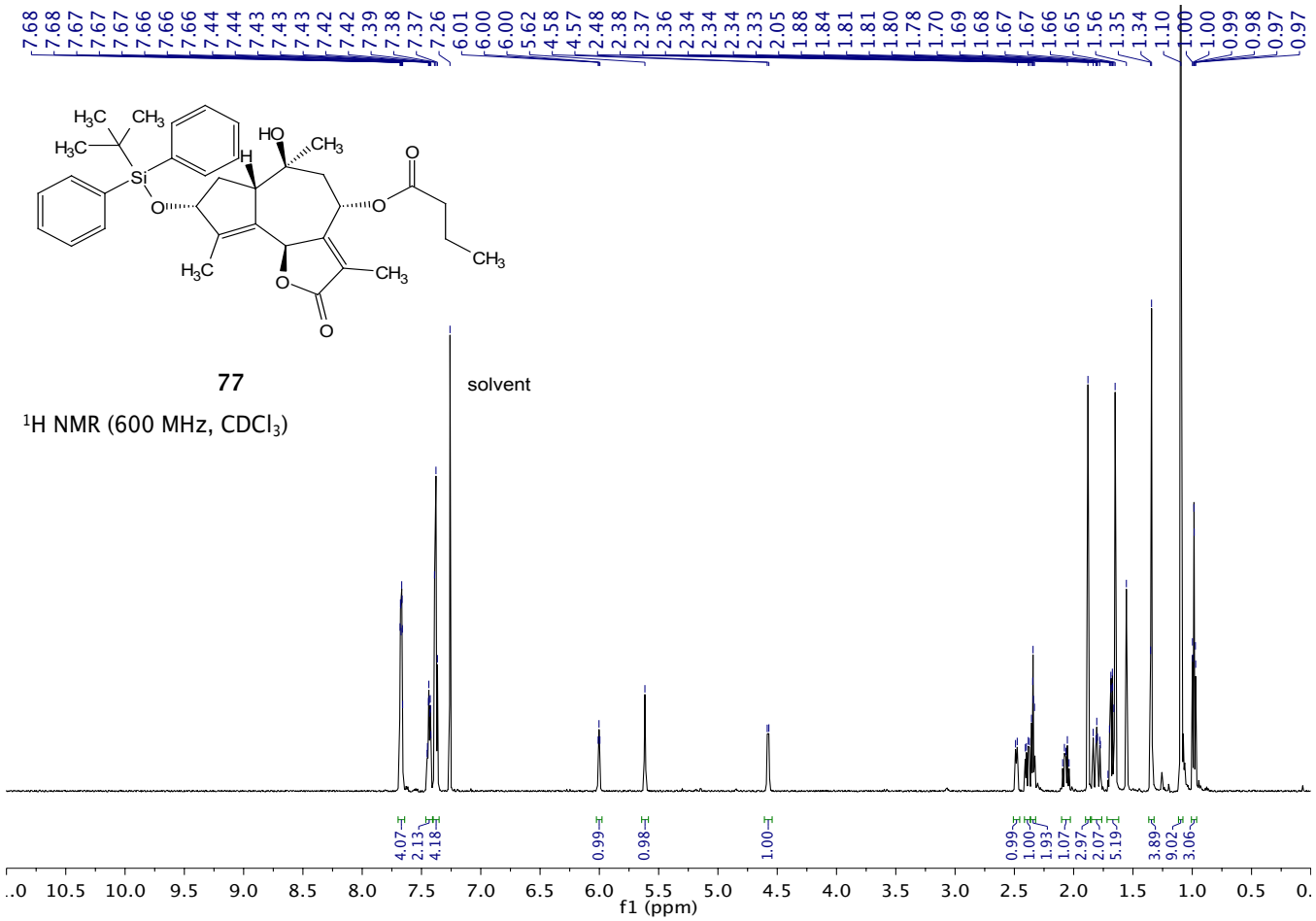
75 (unstable)

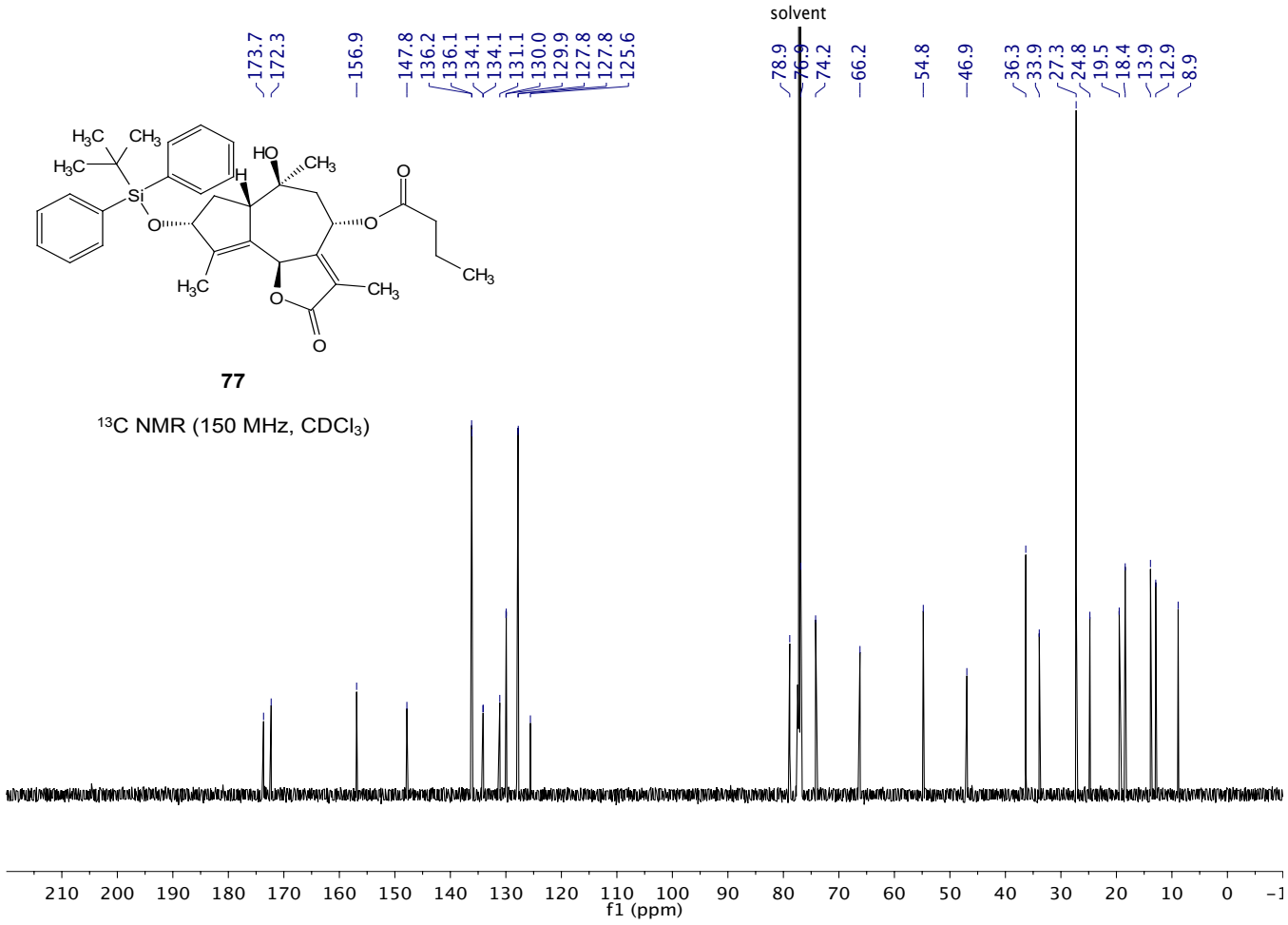
^{13}C NMR (150 MHz, $CDCl_3$)



75 (unstable)

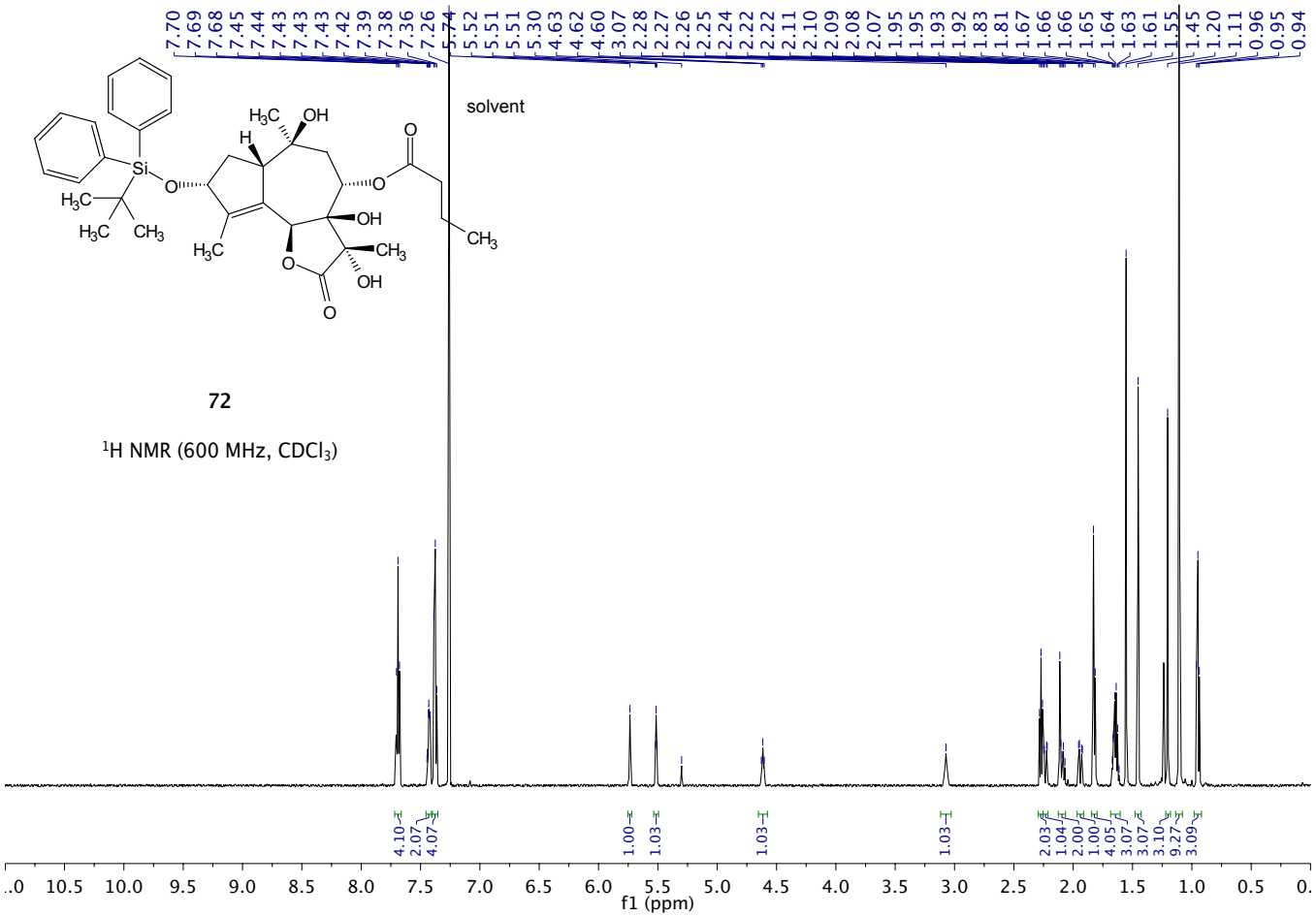
^{13}C NMR (151 MHz, $CDCl_3$)


7.68 7.68 7.67 7.67 7.67 7.66 7.66 7.66 7.44 7.44 7.43 7.43 7.43 7.42 7.42 7.39 7.38 7.37 7.26 6.01 6.00 6.00 5.62 4.58 4.57 2.48 2.38 2.37 2.36 2.34 2.34 2.34 2.33 2.05 1.88 1.84 1.81 1.81 1.80 1.78 1.70 1.69 1.68 1.67 1.67 1.66 1.65 1.56 1.35 1.34 1.10 1.00 1.00 0.99 0.98 0.97 0.97
H3C CH3 H3C Si O HO CH3 H O O O CH3 H3C O CH3 O
77
solvent
1H NMR (600 MHz, CDCl3)
4.07 2.13 4.18 0.99 0.98 1.00 0.99 1.00 1.93 1.07 2.97 2.07 5.19 3.89 9.02 3.06
10.5 10.0 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
f1 (ppm)



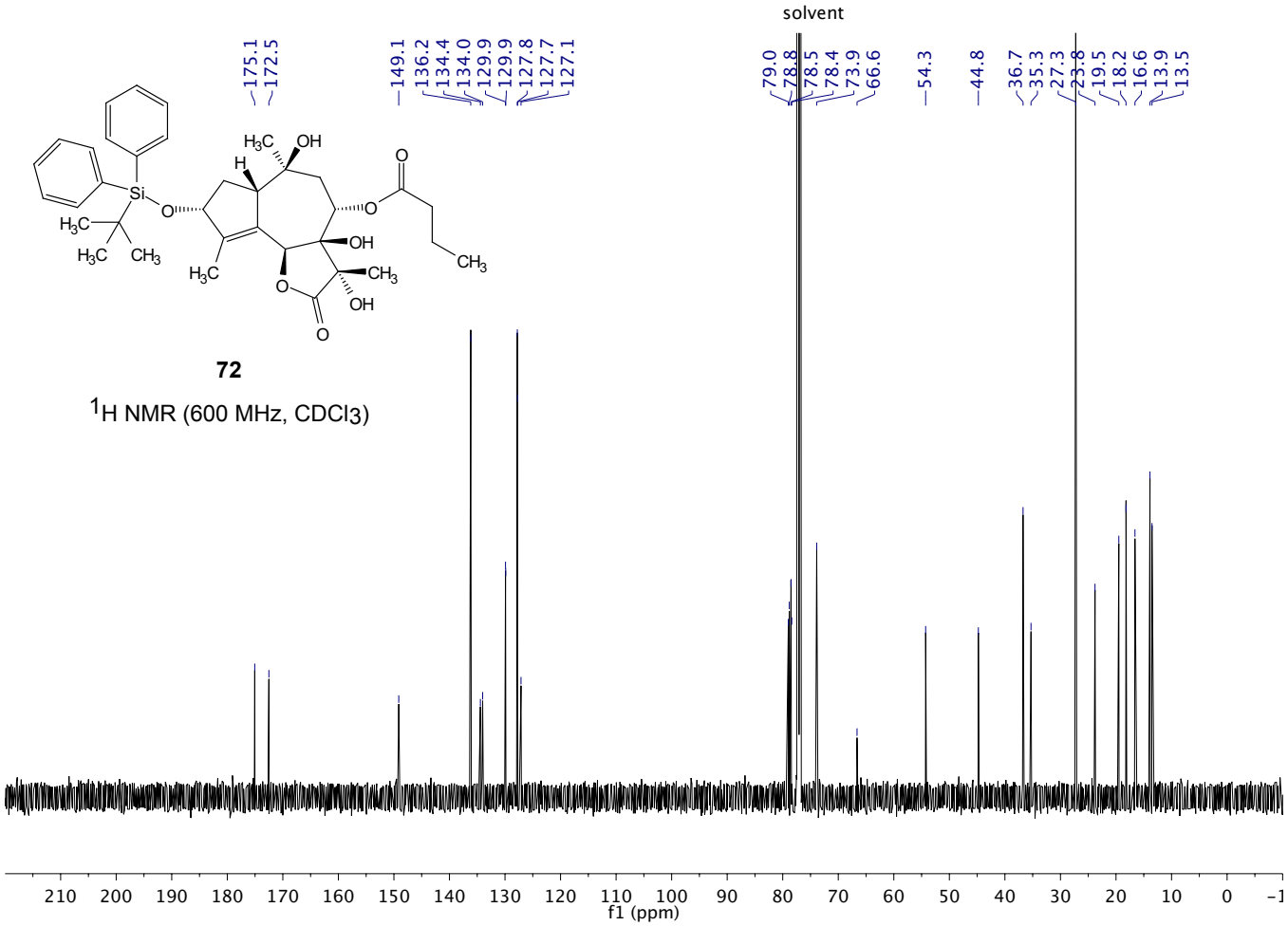
77

^{13}C NMR (150 MHz, $CDCl_3$)



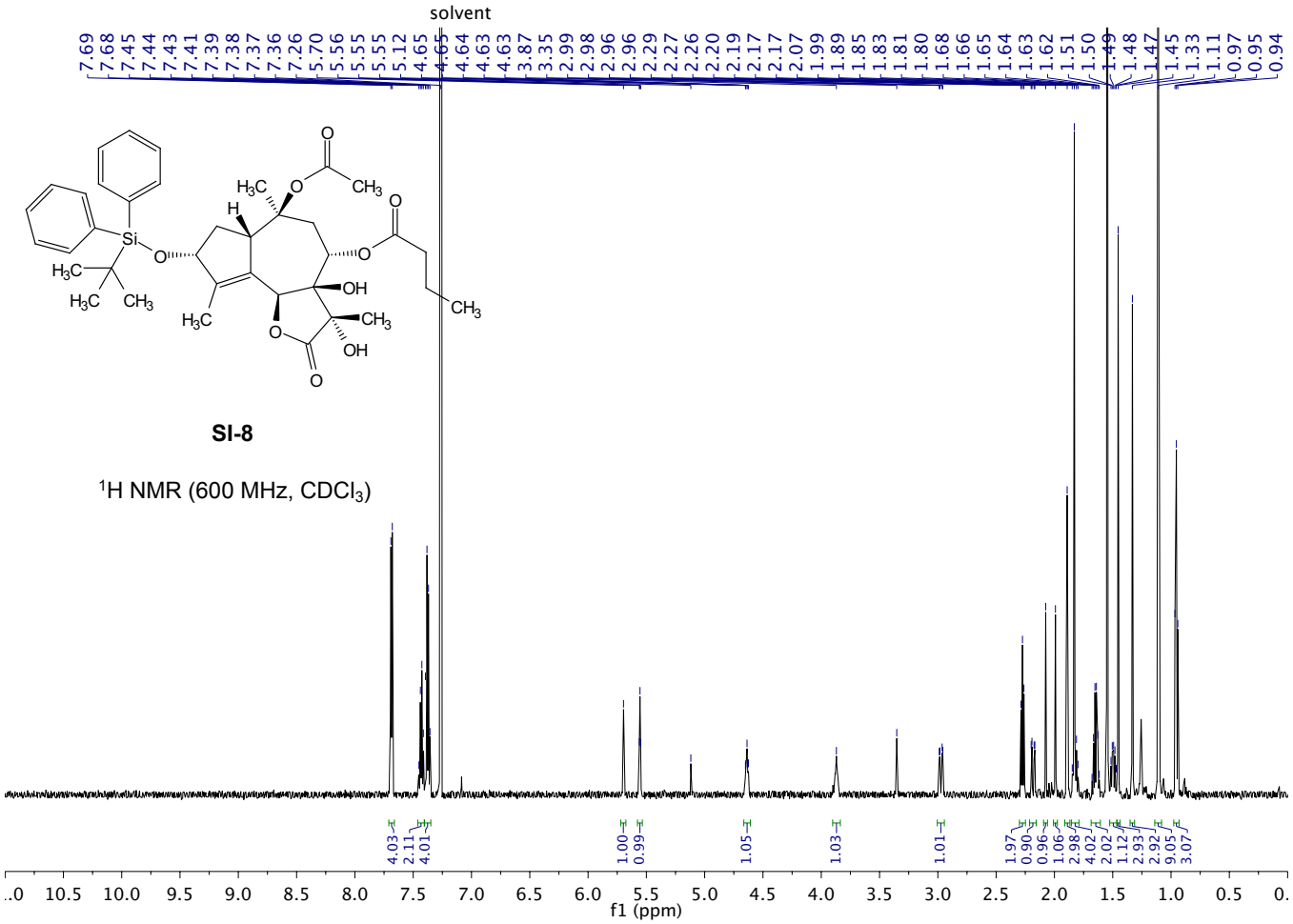
72

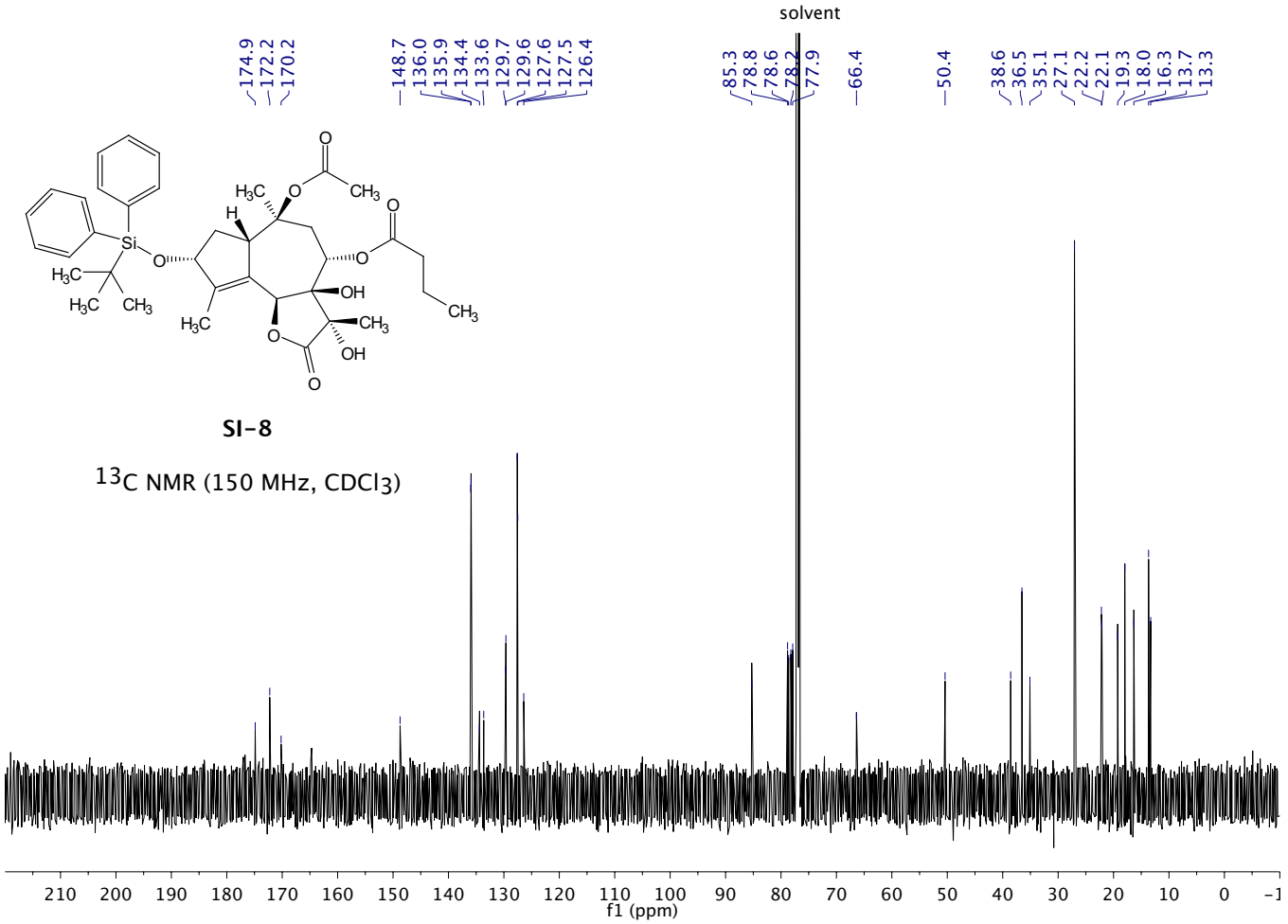
^{1}H NMR (600 MHz, $CDCl_3$)

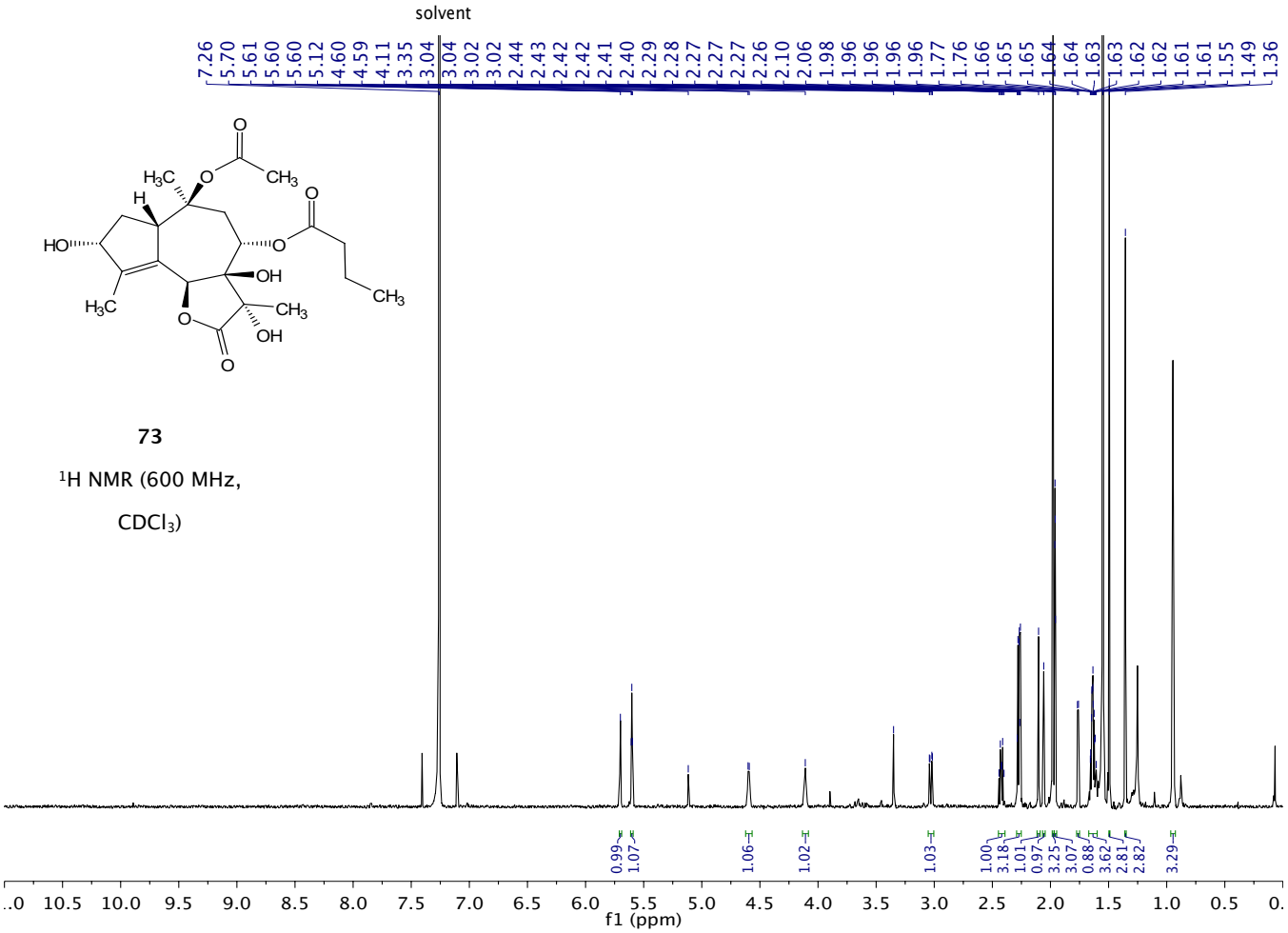


72

^{1}H NMR (600 MHz, $CDCl_3$)

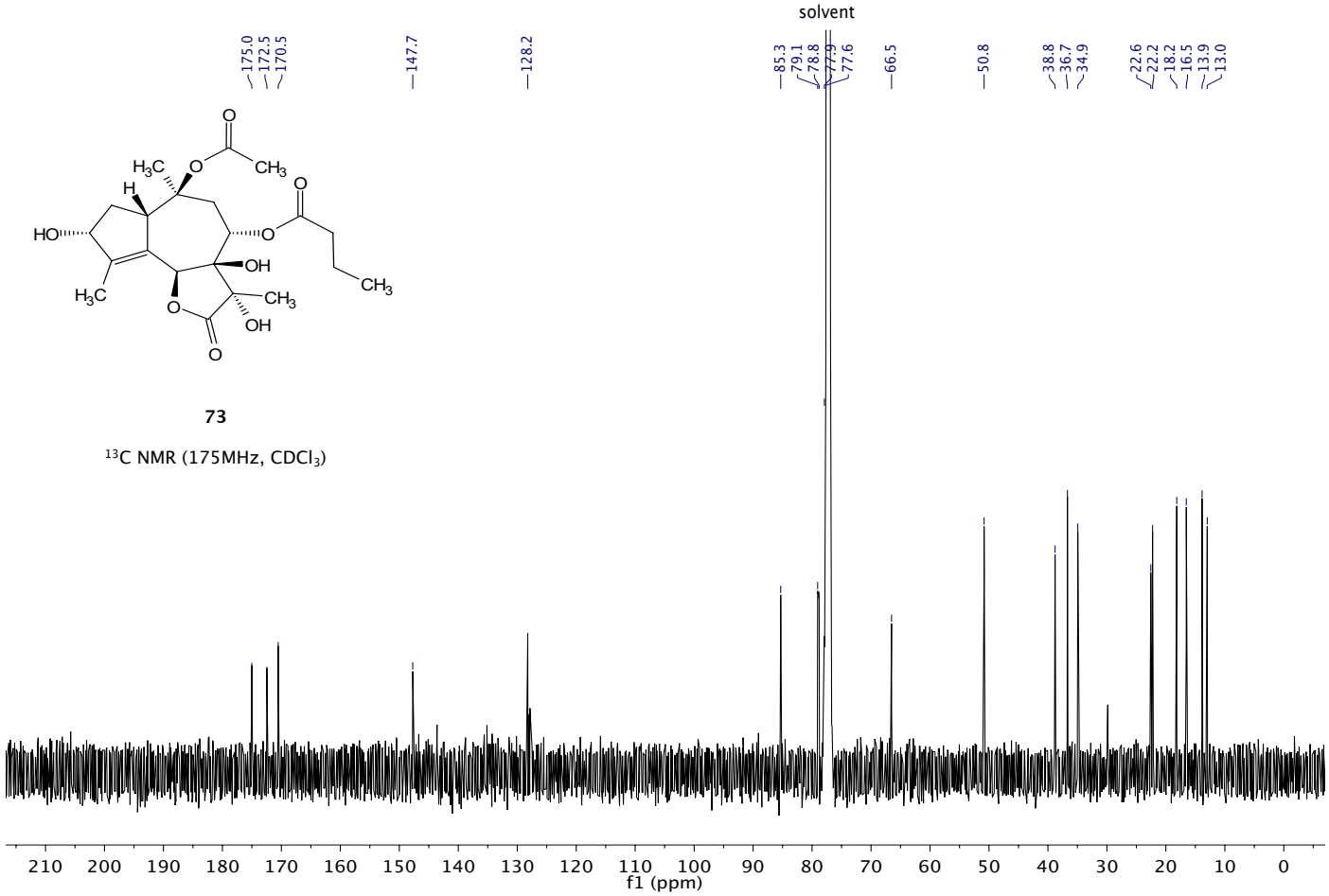

solvent
7.69 7.68 7.45 7.44 7.43 7.41 7.39 7.38 7.37 7.36 7.26 5.70 5.56 5.55 5.55 5.12 4.65 4.65 4.64 4.63 4.63 3.87 3.35 2.99 2.98 2.96 2.96 2.29 2.27 2.26 2.20 2.19 2.17 2.17 2.07 1.99 1.89 1.85 1.83 1.81 1.80 1.68 1.66 1.65 1.64 1.63 1.62 1.51 1.50 1.49 1.48 1.47 1.45 1.33 1.11 0.97 0.95 0.94
SI-8
^{1}H NMR (600 MHz, $CDCl_3$)
4.03 2.11 4.01 1.00 0.99 1.05 1.03 1.01 1.97 0.90 0.96 1.06 2.98 4.02 2.02 1.12 2.93 2.92 9.05 3.07
f1 (ppm)


solvent
174.9
172.2
170.2
148.7
136.0
135.9
134.4
133.6
129.7
129.6
127.6
127.5
126.4
85.3
78.8
78.6
78.2
77.9
66.4
50.4
38.6
36.5
35.1
27.1
22.2
22.1
19.3
18.0
16.3
13.7
13.3
H3C
O
CH3
H
O
Si
O
O
H3C
CH3
H3C
OH
H3C
CH3
O
OH
O
CH3
SI-8
13C NMR (150 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)



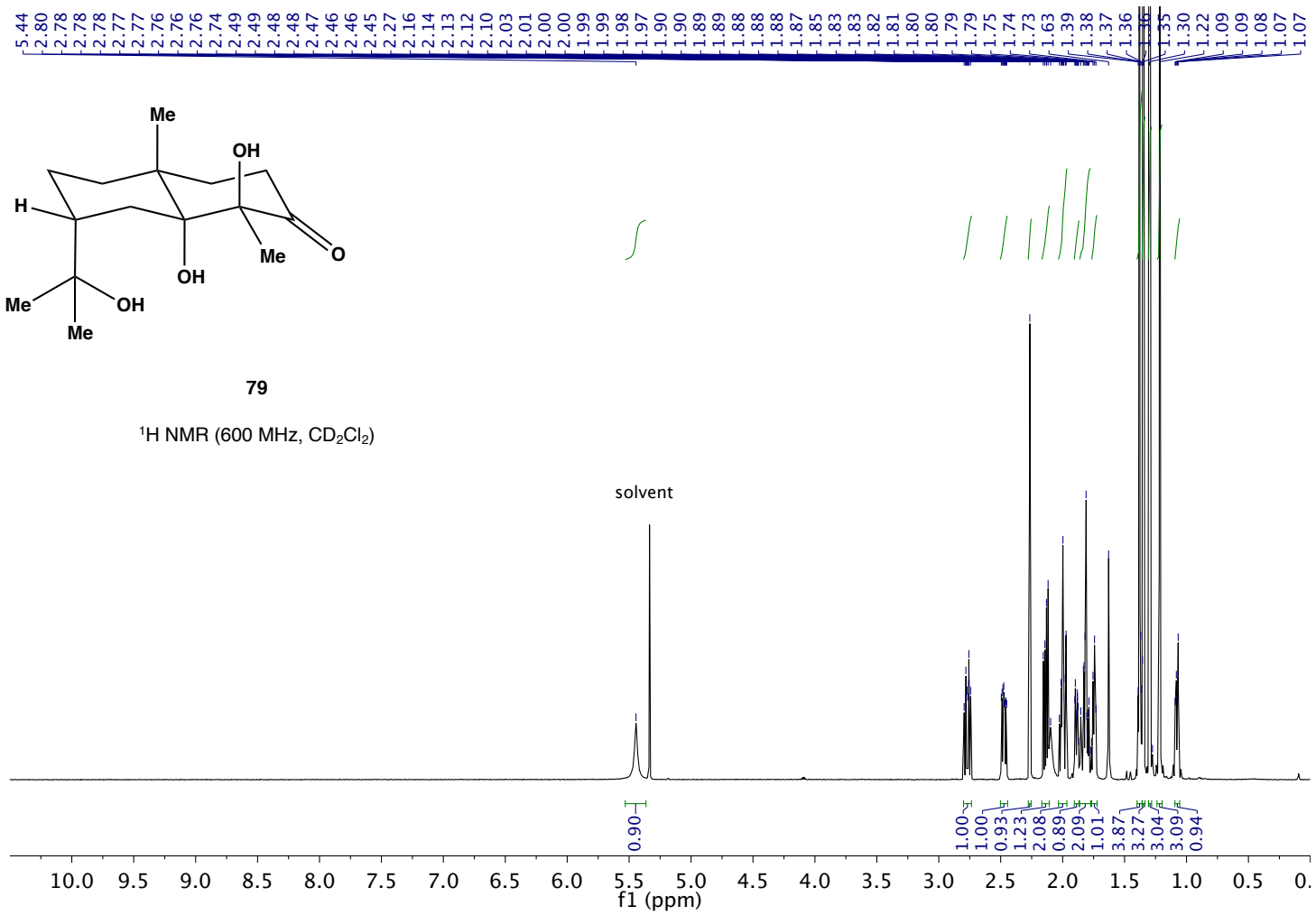
73

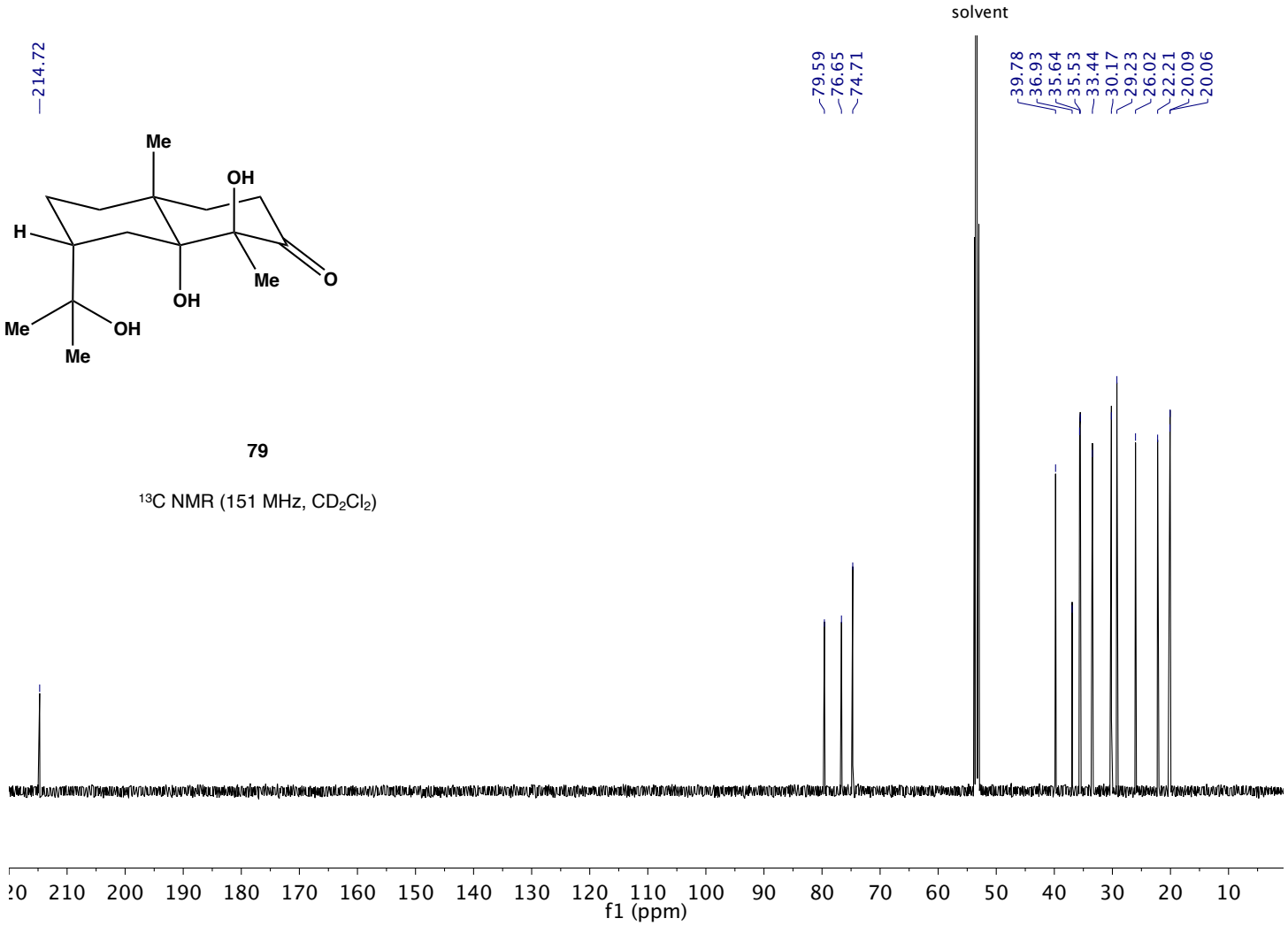
^{1}H NMR (600 MHz, $CDCl_3$)

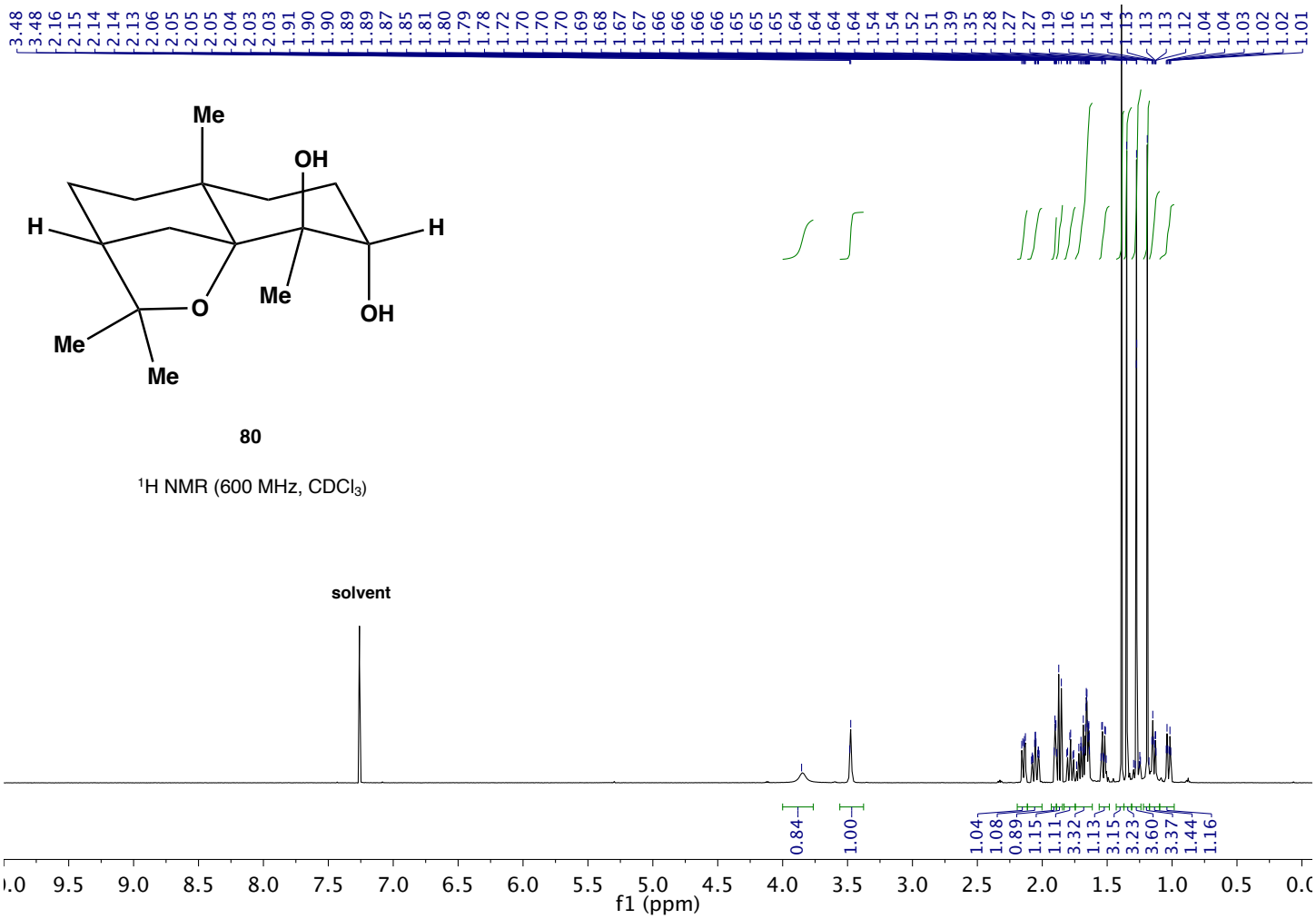


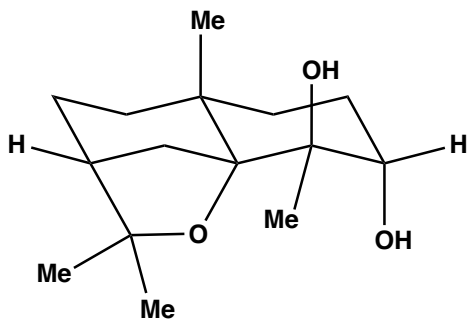
73

^{13}C NMR (175MHz, $CDCl_3$)


Me
OH
H
Me
O
OH
Me
OH
Me
79
1H NMR (600 MHz, CD2Cl2)
solvent
f1 (ppm)


214.72
79.59
76.65
74.71
solvent
39.78
36.93
35.64
35.53
33.44
30.17
29.23
26.02
22.21
20.09
20.06
Me
OH
H
Me
O
OH
Me
OH
Me
79
13C NMR (151 MHz, CD2Cl2)
f1 (ppm)


Me
OH
H
H
O
Me
OH
Me
Me
80
1H NMR (600 MHz, CDCl3)
solvent
f1 (ppm)



80

^{13}C NMR (151 MHz, $CDCl_3$)