Supporting Information for:

Development of a Terpene Feedstock-based Oxidative Synthetic Approach to the *Illicium* Sesquiterpenes

Kevin Hung,[§] Matthew L. Condakes,[§] Luiz F. T. Novaes, Stephen J. Harwood, Takahiro Morikawa, Zhi Yang, Thomas J. Maimone

Table of Contents:

General Procedures:

All reactions were performed in flame- or oven-dried glassware under a positive pressure of nitrogen or argon, unless otherwise noted. Air- and moisture-sensitive liquids were transferred via syringe. Volatile solvents were removed under reduced pressure rotary evaporation below 35 °C. Diglyme was removed under reduced pressure rotary evaporation at 60 °C. Analytical and preparative thin-layer chromatography (TLC) were performed using glass plates pre-coated with silica gel (0.25-mm, 60-Å pore size, Silicycle SiliaPlateTM or MilliporeSigma TLC Silica gel 60 F254) and impregnated with a fluorescent indicator (254 nm). TLC plates were visualized by exposure to ultraviolet light (UV) and then were stained by submersion in an ethanolic anisaldehyde solution, an ethanolic phosphomolybdic/cerium sulfate solution, or a basic aqueous potassium permanganate solution, followed by brief heating on a hot plate. Flash column chromatography was performed employing silica gel purchased from Silicycle (SiliaFlash®, 60 Å, 230-400 mesh, 40-63 μm). Extended reaction times at low temperature were maintained with ThermoScientificTM EK 90 Immersion Cooler (cryocool). Reaction conditions involving slow addition of reagents were performed with syringe pumps model KDS 100 and KDS 200, obtained from KD Scientific.

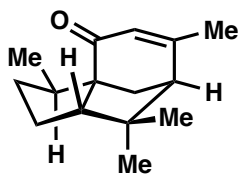
(+)-Cedrol purchased from Sigma Aldrich was recrystallized from MeOH/H_2O. The recrystallized material was found to have an optical rotation of $[\alpha]_D^{23}$= +9.6 (c 5, $CHCl_3$). This value corresponds to 97% ee when compared to the Merck Index value for enantiopure cedrol ($[\alpha]_D^{23}$ = +9.9, c 5, $CHCl_3$), and 91% ee when compared to the value reported by Sigma Aldrich ($[\alpha]_D^{23}$ = +10.5, c 5, $CHCl_3$). (+)-Cedrol purchased from Parchem was used directly as received. The crystalline material was found to have an optical rotation of $[\alpha]_D^{23}$ = +11.9 (c 5, $CHCl_3$).

Anhydrous tetrahydrofuran (THF), dichloromethane (DCM), dimethylformamide (DMF), triethylamine (Et_3N) and acetonitrile (MeCN) were obtained by passing these previously degassed solvents through activated alumina columns. Trimethylsilyl chloride (TMSCl), diisopropylamine, and isopropanol (*i*-PrOH) were distilled over calcium hydride prior to use. *i*-PrOH was also degassed prior to use. (–)-α-Cedrene,[1] $[Fe(mep)(MeCN)_2][(SbF_6)_2]$,[2] lithium naphthalenide,[3] and (*R*)-mepp[4] were prepared from their respective literature procedures. $[Fe((R)\text{-mepp})(MeCN)_2][(SbF_6)_2]$ was prepared by

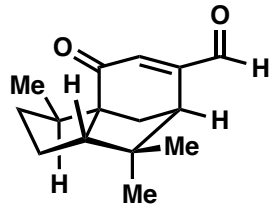
an adaption of known literature protocols.[2] $[Ir(COD)(OMe)]_2$ and $[Rh(COE)_2Cl]_2$ were generously provided by Professor John F. Hartwig, Dr. Ala Bunescu, and Caleb Karmel. All other solvents and reagents were purchased at the highest commercial grade and were used as received, without further purification.

Proton nuclear magnetic resonance (1H NMR) spectra and carbon nuclear magnetic resonance (13C NMR) spectra were recorded on Bruker AVB 400 (400 MHz/101 MHz), Bruker AV 500 (500 MHz/126 MHz), Bruker DRX 500 (500 MHz/126 MHz), Bruker AV 600 (600 MHz/151 MHz) NMR, Bruker AV 700 (700 MHz/176 MHz), and Bruker 900 (900 MHz/226 MHz) spectrometers at 23 °C. Fluorine nuclear magnetic resonance (19F NMR) spectra were recorded on a Bruker AVQ 400 (376 MHz) spectrometer at 23 ºC. Proton chemical shifts are expressed as parts per million (ppm, δ scale) and are referenced to residual protium in the NMR solvent (C_5D_4HN: δ 8.74, $CHCl_3$: δ 7.26, CD_2HOD: δ 3.31), except where otherwise indicated. Carbon chemical shifts are expressed as parts per million (ppm, δ scale) and are referenced to the carbon resonance of the NMR solvent (C_5D_5N: δ 150.35, $CDCl_3$: δ 77.16, CD_3OD: 49.15), except where otherwise indicated. Fluorine chemical shifts are expressed as part per million (ppm, δ scale) and are not additionally referenced. Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p =pentet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet, br = broad), coupling constant (J) in Hertz (Hz), and integration. Infrared (IR) spectra were recorded on a Bruker Alpha FT-IR spectrometer as thin films and are reported in frequency of absorption (cm^{-1}). Optical rotations were recorded on a Perkin Elmer polarimeter, model 241. High-resolution mass spectra were obtained at the QB3/Chemistry Mass Spectrometry Facility at University of California, Berkeley using a Thermo LTQ-FT mass spectrometer, Waters AutoSpec Premier mass spectrometer, and at the Lawrence Berkeley National Laboratory Catalysis Center using a Perkin Elmer AxION 2 TOF mass spectrometer with electrospray ionization (ESI), electron ionization (EI), and chemical ionization (CI) techniques. X-ray diffraction data for all compounds were collected at the Small Molecule X-ray Crystallography Facility (CheXray) at University of California, Berkeley using a Bruker MicroSTAR-H APEX II Xray source.

Compound Preparation and Characterization Data:

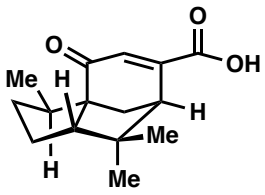


Enone 19. Ethyl acetate (100 mL) was added into a 500 ml flask containing (–)-α-cedrene (10.0 g, 48.9 mmol, 1.0 equiv) and $PhI(OAc)_2$ (47.2 g, 146.5 mmol, 3.0 equiv). The vigorously stirred suspension was cooled to –20 ºC and *tert*-butyl hydroperoxide (70 wt.% in H_2O, 25.0 g, 194.2 mmol, 4.0 equiv) was added via syringe pump over 1 h. The pale-yellow suspension was allowed to react for an additional 11 h at –20 ºC (isopropanol bath with cryocool temperature control). The reaction mixture was quenched by slow addition of saturated *aq.* $NaHCO_3$/saturated *aq.* $Na_2S_2O_3$ (1:1, 300 mL) and vigorously stirred for 15 minutes [*CAUTION*: gas evolution]. Then, the layers were separated, and the aqueous layer was extracted with EtOAc (3 x 100 mL). The combined organic layers were then washed with brine (1 x 500 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The crude residue was purified by column chromatography (1 → 10% Et_2O in hexanes) to afford enone **19** (4.64 g, 21.3 mmol, 43% yield) as a pale-yellow oil. Characterization data were in agreement with previously reported values.[5] $[\alpha]_D^{23}$ = –45.9 (*c* 0.17, $CHCl_3$); ^{1}H NMR (700 MHz, $CDCl_3$) δ 5.64 (d, *J* = 1.5 Hz, 1H), 2.32 (d, *J* = 4.0 Hz, 1H), 1.98 – 1.96 (m, 1H), 1.97 (d, *J* = 1.5 Hz, 3H), 1.96–1.92 (m, 1H), 1.94 (d, *J* = 11.6 Hz, 1H), 1.79 – 1.72 (m, 1H), 1.74 (dd, *J* = 11.6, 4.0 Hz, 1H), 1.73 – 1.64 (m, 2H), 1.52–1.45 (m, 1H), 1.31 (d, *J* = 7.0 Hz, 3H), 1.14 (s, 3H), 1.01 (s, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 204.0, 165.5, 125.8, 65.8, 59.3, 58.4, 45.0, 44.2, 42.7, 39.6, 28.1, 27.3, 26.9, 25.4, 15.4; IR (thin film) ν_{max}: 2492, 2869, 1668, 1452, 1375, 1195 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{23}O_1$ $[M+H]^+$: 219.1743, found: 219.1740.

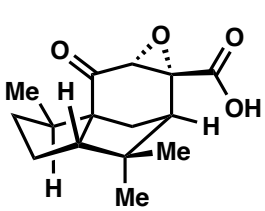


Aldehyde SI-1. 1,4-dioxane (300 mL) was added to a 500 mL flask containing enone **19** (3.0 g, 13.9 mmol, 1.0 equiv) and SeO_2 (3.4 g, 30.5 mmol, 2.2 equiv). The suspension was stirred vigorously and heated to reflux at 120 ºC for 14 h. The crude mixture was cooled, filtered through a short pad of celite, washed with Et_2O, concentrated *in vacuo*, and purified by column chromatography (1 → 10% Et_2O in hexanes) to afford aldehyde **SI-1** (2.3 g, 10.1 mmol, 73% yield) as a pale-yellow oil. An analytical sample was purified by preparative TLC (20% Et_2O in hexanes) to afford aldehyde **SI-1** as a white

solid. $[\alpha]_D^{23}$ = –73.8 (*c* 0.42, $CHCl_3$); ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.76 (s, 1H), 6.38 (s, 1H), 3.06 (d, *J* = 3.5 Hz, 1H), 2.00 – 1.95 (m, 2H), 1.94 – 1.87 (m, 2H), 1.87 – 1.81 (m, 1H), 1.77 – 1.72 (m, 1H), 1.68 (dtd, *J* = 11.9, 10.6, 5.4 Hz, 1H), 1.56 (dddd, *J* = 11.9, 10.6, 8.4, 5.4 Hz, 1H), 1.31 (d, *J* = 7.1 Hz, 3H), 1.19 (s, 3H), 0.85 (s, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 203.6, 193.5, 157.9, 140.2, 68.0, 57.9, 49.6, 44.1, 43.9, 42.7, 39.5, 28.1, 26.7, 26.6, 15.1; IR (thin film) ν_{max}: 2945, 2872, 1684, 1455, 1098, 1004 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{20}O_2$ $[M]^+$: 232.1463, found: 232.1463.

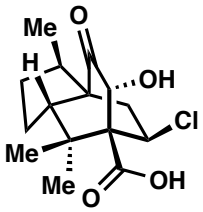


Acid 20. Aldehyde **SI-1** (630 mg, 2.7 mmol, 1.0 equiv) was dissolved in *tert*-butanol (27 mL) at room temperature. A freshly prepared solution of NaH_2PO_4•H_2O (3.0 g, 21.7 mmol, 8.0 equiv) and $NaClO_2$ (80% purity, 3.0 g, 27.0 mmol, 10.0 equiv) in H_2O (27 mL) was added to the reaction mixture, followed by 2-methyl-2-butene (7.2 mL, 68.0 mmol, 25.2 equiv). The biphasic reaction mixture was stirred vigorously for 19 h, after which, the organic layer was separated. The aqueous layer was extracted with EtOAc (3 x 25 mL) and the combined organic layers were washed with brine (1 x 50 mL), dried over Na_2SO_4, concentrated *in vacuo*, and purified by column chromatography (5 → 20% EtOAc in hexanes) to afford acid **20** (0.67 g, 2.7 mmol, > 99% yield) as a pale-yellow oil. $[\alpha]_D^{23}$ = –127.7 (*c* 0.35, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.71 (s, 1H), 3.08 (d, *J* = 3.9 Hz, 1H), 2.06 – 1.93 (m, 3H), 1.88 (dd, *J* = 12.1, 4.1 Hz, 1H), 1.85 – 1.63 (m, 3H), 1.62 – 1.51 (m, 1H), 1.31 (d, *J* = 6.9 Hz, 3H), 1.19 (s, 3H), 0.98 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 203.2, 171.3, 151.2, 135.1, 67.3, 57.9, 52.5, 44.5, 43.9, 43.3, 39.5, 27.9, 26.8, 26.7, 15.2; IR (thin film) ν_{max}: 2950, 2872, 1674, 1455, 1256, 1235, 1141 cm^{-1}; (ESI) calcd for $C_{15}H_{20}O_3Na$ $[M+Na]^+$: 271.1310, found: 271.1297.

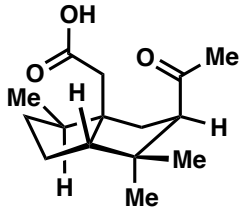


Epoxide 21. Acid **20** (186 mg, 0.75 mmol, 1.0 equiv) was dissolved in methanol (7.5 mL) and the resultant solution was cooled to 0 ºC. Solutions of *aq.* NaOH (3 M, 1.3 mL, 3.9 mmol, 4.0 equiv) and H_2O_2 (50 wt% in H_2O, 0.5 mL, 7.5 mmol, 10.0) were added sequentially. The reaction mixture was allowed to warm to room temperature and stirred for 7 h. Then, 1 M HCl (5 mL) was added and the acidic solution was extracted with

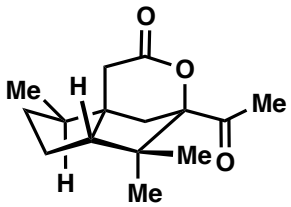
DCM (3 x 20 mL). The combined organic layers were washed with brine (1 x 50 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude residue was purified by flash column chromatography (9 → 29% EtOAc with 1% AcOH in hexanes) to afford recovered acid **20** (149 mg, 0.60 mmol, 80% yield) and epoxide **21** (32 mg, 0.12 mmol, 16% yield, 81% yield BRSM) as a colorless oil. $[\alpha]_D^{23}$ = +13.6 (*c* 0.25, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.84 (s, 1H), 2.92 (d, *J* = 4.5 Hz, 1H), 2.22 (d, *J* = 12.8 Hz, 1H), 1.94 (t, *J* = 10.0 Hz, 1H), 1.94 (t, *J* = 6.1 Hz, 1H), 1.78 – 1.71 (m, 1H), 1.71 – 1.66 (m, 1H), 1.62 (qd, *J* = 11.8, 5.1 Hz, 1H), 1.54 (dd, *J* = 12.8, 4.5 Hz, 1H), 1.49 (qd, *J* = 11.8, 5.1 Hz, 1H), 1.22 (d, *J* = 7.0 Hz, 3H), 1.14 (s, 3H), 1.11 (s, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 202.2, 173.0, 65.5, 62.5, 59.7, 58.7, 48.9, 44.2, 42.1, 39.6, 32.8, 27.5, 27.5, 27.3, 14.8; IR (thin film) ν_{max}: 3437, 3394, 2950, 2873, 1705, 1455, 1249 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{20}O_4Na$ $[M+Na]^+$: 287.1259, found: 287.1271



Chloride 23. Epoxide **21** (15.7 mg, 0.06 mmol, 1.0 equiv) was dissolved in DCE (0.3 mL) and the resulting solution was cooled to –20 ºC. A stock solution of $TiCl_4$ (7.8 µL, 0.07 mmol, 1.2 equiv) in anhydrous DCE (0.3 mL) was added dropwise. The mixture was allowed to warm to 23 ºC and then was heated at 50 ºC for 4 h. The reaction mixture was quenched with saturated *aq.* NH_4Cl and the layers were separated. The aqueous layer was further extracted with DCM (3 x 10 mL). The combined organic layers were washed with brine (1 x 10 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude residue was purified by preparative TLC (100% EtOAc) to afford chloride **23** (2.5 mg, 0.0084 mmol, 14% yield) as a crystalline solid. $[\alpha]_D^{23}$ = +39.2 (*c* 0.12, MeOH); ^{1}H NMR (900 MHz, CD_3OD) δ 4.89 (dd, *J* = 9.0, 1.6 Hz, 1H), 4.77 (d, *J* = 2.0 Hz, 1H), 2.79 (dd, *J* = 15.2, 9.0 Hz, 1H), 2.19 (ddd, *J* = 10.0, 8.4, 1.6 Hz, 1H), 2.06 (dddd, *J* = 13.6, 10.0, 7.6, 4.4 Hz, 1H), 1.91 (pd, *J* = 7.1, 4.4 Hz, 1H), 1.85 (dt, *J* = 15.2, 1.6 Hz, 1H), 1.76 (dtd, *J* = 12.9, 8.4, 4.4 Hz, 1H), 1.71 (dtd, *J* = 12.9, 10.0, 7.6 Hz, 1H), 1.28 (dddd, *J* = 13.6, 7.6, 8.4 ,4.4 Hz, 1H), 1.23 (s, 3H), 1.22 (s, 3H), 1.07 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (226 MHz, CD_3OD) δ 215.6, 176.4, 77.5, 66.2, 58.8, 58.7, 46.1, 43.0, 39.5, 38.5, 34.3, 29.2, 22.8, 22.6, 18.5; IR (thin film) ν_{max}: 3431, 2955, 2874, 1726, 1597, 1377 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{20}O_4{}^{35}Cl$ $[M–H]^–$: 299.1056, found: 299.1051.

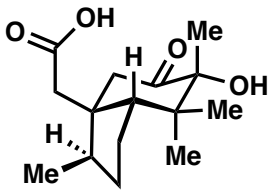


Keto-acid 24. (–)-α-cedrene (10.0 g, 48.9 mmol, 1.0 equiv) was dissolved in CCl_4/MeCN/H_2O (3:3:4, 500 mL). $RuCl_3$•xH_2O (250 mg, 1.22 mmol, 2.5 mol%) and $NaIO_4$ (52.4 g, 245 mmol, 5.0 equiv) were then added in one portion. A reflux condenser was attached, and the biphasic reaction mixture was heated with vigorous stirring at 60 ºC for 19 h. Upon cooling to room temperature, the reaction mixture was filtered through a pad of celite. The layers were separated, and the aqueous layer was acidified with 1M HCl (150 mL), and then extracted with DCM (3 x 300 mL). The organic layers were combined, washed with brine (1 x 200 mL), concentrated *in vacuo*, and purified by column chromatography (10 → 30% EtOAc in hexanes) to afford keto-acid **24** (9.3 g, 36.7 mmol, 75% yield) as a colorless oil. An analytical sample was purified by preparative TLC (50% EtOAc in hexanes) to afford keto-acid **24** as a white solid. Characterization data were in agreement with previously reported values.[6] $[\alpha]_D^{23}$ = –56.5 (*c* 0.23, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.71 (dd, *J* = 12.8, 6.2 Hz, 1H), 2.41 (d, *J* = 14.6 Hz, 1H), 2.33 (d, *J* = 14.6 Hz, 1H), 2.26 (t, *J* = 13.2 Hz, 1H), 2.13 (s, 3H), 2.06 (t, *J* = 9.1 Hz, 1H), 1.78 – 1.72 (m, 1H), 1.69 (dd, *J* = 13.2, 6.2 Hz, 1H), 1.65 – 1.54 (m, 2H), 1.35 (tdd, *J* = 12.5, 9.5, 5.8 Hz, 1H), 1.18 (qd, *J* = 11.5, 5.8 Hz, 1H), 1.11 (s, 3H), 0.97 (d, *J* = 6.7 Hz, 3H), 0.88 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 210.2, 178.1, 61.3, 59.2, 50.6, 46.6, 43.9, 41.3, 38.3, 33.5, 31.7, 28.7, 25.2, 25.0, 14.1; IR (thin film) ν_{max}: 3343, 3247, 2952, 2873, 1697, 1652, 1464, 1369, 1219 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{24}O_3Na$ $[M+Na]^+$: 275.1623, found: 275.1625.

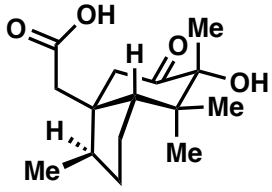


Lactone 25. Diglyme (42 mL) was added to anhydrous $CuBr_2$ (5.5 g, 24.7 mmol, 3.0 equiv) and keto-acid **24** (2.1 g, 8.3 mmol, 1.0 equiv) in a sealed tube. The solution was sparged with argon and the tube was quickly capped. The sealed tube was heated at 150 ºC for 21 h. The reaction was cooled, diluted with Et_2O (100 mL), and filtered through a pad of celite. The organic phase was concentrated *in vacuo* at 60 °C to afford crude lactone **25** as a brown oil (*ca.* 2.5 g, containing residual diglyme), which was used immediately in the next step without further purification. An analytical sample was purified by preparative TLC (40% Et_2O in hexanes) to afford lactone **25** as a white solid.

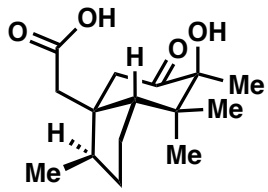
$[\alpha]_D^{23}$ = –24.4 (*c* 0.41, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.57 (d, *J* = 18.2 Hz, 1H), 2.55 (d, *J* = 18.2 Hz, 1H), 2.43 (dd, *J* = 13.4, 1.6 Hz, 1H), 2.31 (s, 3H), 1.98 – 1.87 (m, 3H), 1.73 (ddt, *J* = 12.9, 8.9, 6.3 Hz, 1H), 1.58 (dd, *J* = 13.4, 1.6 Hz, 1H), 1.53 (dq, *J* = 13.4, 6.9 Hz, 1H), 1.42 (dq, *J* = 12.9, 6.3, 5.2 Hz, 1H), 1.21 (s, 3H), 0.89 (d, *J* = 7.0 Hz, 3H), 0.84 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 205.4, 170.2, 100.2, 60.5, 49.1, 48.9, 43.3, 41.8, 40.5, 36.1, 27.7, 25.9, 25.5, 23.2, 15.4; IR (thin film) ν_{max}: 2965, 2874, 1741, 1713, 1249, 1222, 1083 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{22}O_3Na$ $[M+Na]^+$: 273.1467, found: 273.1466.



Ketol 26. KO*t*-Bu (2.79 g, 24.9 mmol, 3.0 equiv) and finely ground KOH (466 mg, 8.3 mmol, 1.0 equiv) were dissolved in DMSO (100 mL). Crude lactone **25** (*ca*. 2.6 g) was added and the resulting solution was stirred at 23 ºC for 12 h. The reaction mixture was then cooled to 0 ºC and quenched with HCl (1.0 M, 300 mL). DCM (300 mL) was added and the layers were separated. The aqueous layer was further extracted with DCM (3 x 200 mL). The organic layers were combined, washed with brine (1 x 500 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude residue was purified by flash column chromatography (20 → 50% EtOAc in hexanes) to afford ketol **26** (1.3 g, 4.8 mmol, 58% yield over two steps, 5.5:1 d.r.). The diastereomers can be separated by an additional purification (50 → 80% Et_2O in hexanes) and both pure diastereomers can be separately resubjected to the reaction conditions to give again a 5.5:1 mixture of diastereomers.

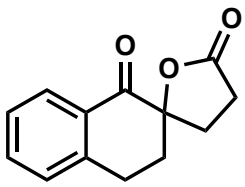


Major diastereomer (**26**). $[\alpha]_D^{23}$ = –37.5 (*c* 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.34 (d, *J* = 15.4 Hz, 1H), 2.47 (d, *J* = 15.4 Hz, 1H), 2.31 (d, *J* = 8.2 Hz, 1H), 2.26 (d, *J* = 14.3 Hz, 1H), 2.13 (d, *J* = 14.3 Hz, 1H), 2.03 – 1.82 (m, 3H), 1.65 (ddd, *J* = 13.7, 9.5, 3.7 Hz, 1H), 1.38 (s, 3H), 1.36 – 1.28 (m, 1H), 0.99 (s, 3H), 0.84 (d, *J* = 6.3 Hz, 3H), 0.73 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.3, 177.7, 80.2, 50.7, 50.3, 44.9, 41.9, 40.8, 38.6, 30.6, 24.1, 24.1, 21.1, 19.4, 13.6; IR (thin film) ν_{max}: 2956, 2929, 2876, 1706, 1355, 1192, 1132 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{24}O_4Na$ $[M+Na]^+$: 291.1572, found: 291.1568.

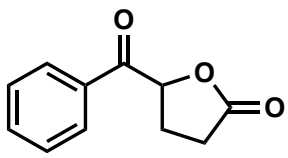


Minor diastereomer (***epi*-26**). $[\alpha]_D^{23}$ = –22.0 (*c* 0.15, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 3.21 (d, *J* = 15.7 Hz, 1H), 2.46 (d, *J* = 9.0 Hz, 1H), 2.29 (d, *J* = 15.7 Hz, 1H), 2.23 (d, *J* = 16.8 Hz, 1H), 2.14 (d, *J* = 16.8 Hz, 1H), 1.98–1.79 (m, 3H), 1.66 – 1.57 (m, 1H), 1.35 – 1.27 (m, 1H), 1.19 (s, 3H), 0.93 (s, 3H), 0.85 (d, *J* = 6.1 Hz, 3H), 0.77 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 214.3, 179.3, 80.4, 48.3, 47.7, 43.6, 43.4, 42.6, 39.0, 30.8, 24.2, 23.7, 20.5, 17.7, 14.0; IR (thin film) ν_{max}: 3402, 2955, 2876, 1713, 1395, 1371, 1234, 1116 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{23}O_4$ $[M–H]^-$: 267.1602, found: 267.1595.

General Procedure for the $CuBr_2$-mediated oxidative lactonization of keto-acids: Diglyme (2 mL) was added to anhydrous $CuBr_2$ (135 mg, 0.6 mmol, 3.0 equiv) and substrate (0.2 mmol, 1.0 equiv). The reaction mixture was heated at 150 ºC for 16 h. The brown suspension was cooled to 23 ºC, diluted with acetone (2 mL), and filtered through a pad of celite. The organic residue was concentrated *in vacuo* at 60 ºC to afford the crude lactone, which was then purified by column chromatography (50 → 75% Et_2O in hexanes).

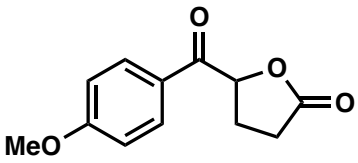


3',4'-dihydro-1'H,3H-spiro[furan-2,2'-naphthalene]-1',5(4H)-dione (27). The standard procedure was followed with 3-(1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)propanoic acid[7] (44 mg) to afford **27** as a white solid (41 mg, 0.19 mmol, 94% yield). Spectroscopic data were in agreement with previously reported values.[8] ^1H NMR (700 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.54 (td, *J* = 7.6, 1.4 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 7.6 Hz, 1H), 3.19 (dt, *J* = 17.1, 5.2 Hz, 1H), 3.09 (ddd, *J* = 17.1, 10.1, 4.7 Hz, 1H), 2.78 (ddd, *J* = 17.8, 10.8, 9.8 Hz, 1H), 2.61 (ddd, J = 13.3, 10.1, 5.2 Hz, 1H), 2.60 (ddd, J = 17.8, 9.6, 2.5 Hz, 1H), 2.55 (ddd, *J* = 12.8, 9.8, 2.5 Hz, 1H), 2.30 (ddd, *J* = 13.3, 5.2, 4.7 Hz, 1H), 2.15 (dt, *J* = 12.8, 10.8, 9.6 Hz, 1H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 193.7, 176.3, 143.1, 134.6, 130.1, 128.9, 128.6, 127.4, 85.2, 34.6, 29.7, 28.0, 25.8.

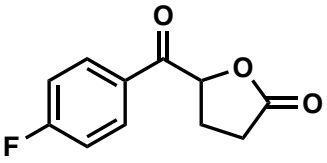


5-benzoyldihydrofuran-2(3*H*)-one (28). The standard procedure was followed with 5-oxo-5-phenylpentanoic acid (38 mg) to afford **28** as a white solid (36 mg, 0.19 mmol, 94% yield). Spec-

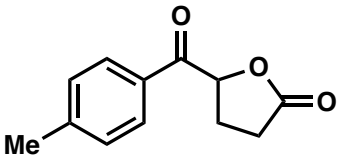
troscopic data were in agreement with previously reported values.[8] ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.6 Hz, 2H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 5.82 – 5.79 (m, 1H), 2.63 – 2.54 (m, 3H), 2.49 – 2.42 (m, 1H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 194.5, 176.4, 134.4, 133.7, 129.1 (2C), 128.9 (2C), 78.4, 26.9, 25.1.



5-(4-Methoxybenzoyl)dihydrofuran-2(3H)-one (29). The standard procedure was followed with 5-oxo-5-(4-methoxyphenyl)pentanoic acid[9] (45 mg) to afford **29** as a white solid (41 mg, 0.19 mmol, 93% yield). Spectroscopic data were in agreement with previously reported values.[8] ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.7 Hz, 2H), 6.97 (d, *J* = 8.7 Hz, 2H), 5.75 (dd, *J* = 7.8, 4.4 Hz, 1H), 3.89 (s, 3H), 2.65 – 2.52 (m, 3H), 2.50 – 2.41 (m, 1H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 192.8, 176.5, 164.5, 131.4 (2C), 126.8, 114.4 (2C), 78.3, 55.7, 27.1, 25.2.

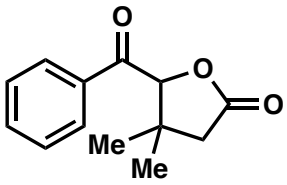


5-(4-fluorobenzoyl)dihydrofuran-2(3H)-one (30). The standard procedure was followed with 5-oxo-5-(4-methoxyphenyl)pentanoic acid[9] (42 mg) to afford **30** as a white solid (37 mg, 0.18 mmol, 89% yield). Spectroscopic data were in agreement with previously reported values.[8] ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 8.5, 5.4 Hz, 2H), 7.19 (t, *J* = 8.5 Hz, 2H), 5.73 (dd, *J* = 8.1, 4.7 Hz, 1H), 2.63 – 2.55 (m, 3H), 2.54 – 2.47 (m, 1H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 192.9, 176.2, 166.5 (d, *J* = 257.2 Hz), 131.8 (d, *J* = 9.5 Hz, 2C), 130.3 (d, *J* = 3.1 Hz), 116.1 (d, *J* = 22.0 Hz, 2C), 78.4, 27.0, 24.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -101.64 (tt, *J* = 8.5, 5.3 Hz).

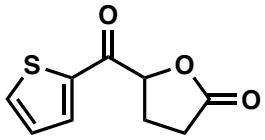


5-(4-Methylbenzoyl)dihydrofuran-2(3H)-one (31). The standard procedure was followed with 5-oxo-5-(4-methylphenyl)pentanoic acid[9] (41 mg) to afford **31** as a white solid (37 mg, 0.18 mmol, 91% yield). Spectroscopic data were in agreement with previously reported values.[8] ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.78 (dd, *J* = 8.3, 4.2 Hz, 1H), 2.61 –

2.53 (m, 3H), 2.45 – 2.40 (m, 1H), 2.42 (s, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 194.0, 176.5, 145.5, 131.2, 129.8 (2C), 129.0 (2C), 78.3, 27.0, 25.2, 21.9.

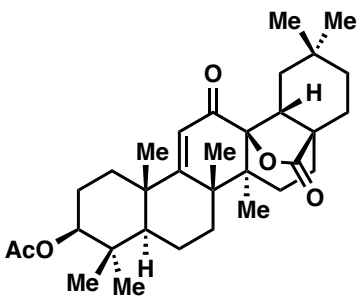


5-benzoyl-4,4-dimethyldihydrofuran-2(3*H*)-one (32). The standard procedure was followed with 3,3-dimethyl-5-oxo-5-phenylpentanoic acid[10] (44 mg) to afford **32** as a white solid (41 mg, 0.19 mmol, 94% yield). Spectroscopic data were in agreement with previously reported values.[11] ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.65 (tt, *J* = 7.5, 1.2 Hz, 1H), 7.53 (dd, *J* = 8.3, 7.5 Hz, 2H), 5.51 (s, 1H), 2.58 (d, *J* = 17.0 Hz, 1H), 2.33 (d, *J* = 17.0 Hz, 1H), 1.38 (s, 3H), 0.98 (s, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 195.8, 175.8, 136.0, 134.4, 129.2 (2C), 128.7 (2C), 85.6, 42.0, 40.8, 28.5, 23.7.

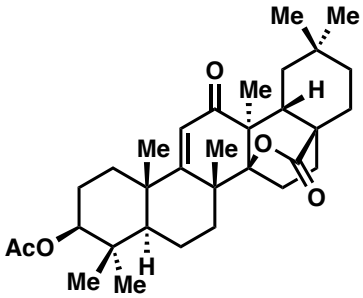


5-(thiophene-2-carbonyl)dihydrofuran-2(3*H*)-one (33). The standard procedure was followed with 5-oxo-5-(thiophen-2-yl)pentanoic acid[12] (40 mg) to afford **33** as a white solid (32 mg, 0.17 mmol, 82% yield). Spectroscopic data were in agreement with previously reported values.[8] ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 3.9, 1.1 Hz, 1H), 7.77 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.20 (dd, *J* = 5.0, 3.9 Hz, 1H), 5.53 (dd, *J* = 8.2, 4.8 Hz, 1H), 2.66 – 2.55 (m, 3H), 2.55 – 2.50 (m, 1H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 188.1, 176.2, 140.4, 135.8, 134.2, 128.8, 79.5, 27.1, 25.5.

Oleanic acid derivatives 36 and 37. The standard procedure was followed with acid **34**[13] (105 mg) to afford **36** as a white solid (9 mg, 0.02 mmol 9% yield) and rearranged product **37** as a white solid (74 mg, 0.14 mmol, 72% yield).

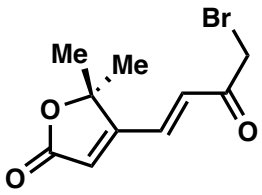


36. $[\alpha]_D^{23}$ = +57.6 (*c* 0.5, $CHCl_3$); ^{1}H NMR (700 MHz, $CDCl_3$) δ 5.98 (s, 1H), 4.49 (dd, *J* = 11.9, 4.5 Hz, 1H), 3.00 – 2.93 (m, 1H), 2.12 – 2.08 (m, 1H), 2.07 (s, 3H), 2.00 (dt, *J* = 13.2, 3.6 Hz, 1H), 1.87 (td, *J* = 13.5, 6.2 Hz, 1H), 1.80 (dq, *J* = 12.5, 3.9 Hz, 1H), 1.77 – 1.65 (m, 5H), 1.64 – 1.51 (m, 4H), 1.46 (s, 3H), 1.45 – 1.41 (m, 1H), 1.41 – 1.34 (m, 3H), 1.34 – 1.29 (m, 1H), 1.28 (s, 3H), 1.28 – 1.24 (m, 1H), 0.99 (s, 3H), 0.97 (s, 6H), 0.93 (s, 3H), 0.92 (s, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 192.3, 183.4, 178.6, 170.9, 121.7, 87.8, 79.5, 50.3, 45.9, 43.9, 43.5, 41.6, 40.3, 38.2, 36.6, 36.0, 34.0, 33.9, 33.1, 31.6, 30.0, 28.0, 27.2, 25.8, 24.4, 23.79, 23.78, 23.0, 21.2, 20.2, 17.1, 16.6; IR (thin film) ν_{max}: 2950, 1778, 1736, 1667, 1245, 755 cm^{-1}; HRMS (EI) calcd for $C_{32}H_{45}O_5$: 510.3345, found: 510.3351.

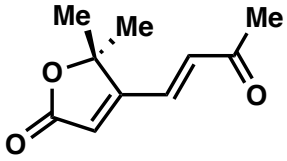


37. $[\alpha]_D^{23}$ = –51.3 (*c* 2.2, $CHCl_3$); ^{1}H NMR (700 MHz, $CDCl_3$) δ 5.87 (s, 1H), 4.46 (dd, *J* = 11.3, 4.6 Hz, 1H), 3.02 (ddd, *J* = 12.4, 5.2, 1.7 Hz, 1H), 2.33 (ddd, *J* = 13.8, 11.2, 4.5 Hz, 1H), 2.05 (s, 3H), 2.00 (td, *J* = 14.1, 4.7 Hz, 1H), 1.97 – 1.88 (m, 2H), 1.86 – 1.69 (m, 7H), 1.67 – 1.63 (m, 1H), 1.46 (ddd, *J* = 14.5, 4.2, 2.7 Hz, 1H), 1.41 (s, 3H), 1.33 – 1.29 (m, 2H), 1.28 (s, 3H), 1.27 – 1.21 (m, 3H), 1.14 (s, 3H), 1.01 (s, 4H), 0.97 (s, 3H), 0.94 (s, 3H), 0.87 (s, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 202.0, 177.6, 170.9, 168.7, 119.3, 89.3, 79.7, 53.7, 51.6, 44.9, 41.7, 39.7, 39.0, 37.8, 36.5, 35.1, 33.51, 33.46, 33.3, 31.3, 28.0, 26.6, 24.5, 24.1, 23.6, 21.7, 21.4, 20.9, 20.6, 20.4, 18.8, 16.4; IR (thin film) ν_{max}: 2944, 1731, 1676, 1245, 751 cm^{-1}; HRMS (EI) calcd for $C_{32}H_{45}O_5$: 510.3345, found: 510.3350.

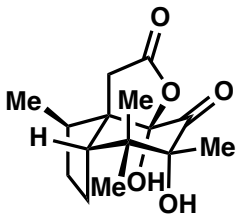
Carene derivatives 41 and 42. The standard procedure was followed with 2-((1*R*,3*S*)-2,2-dimethyl-3-(2-oxopropyl)cyclopropyl)acetic acid[14] (derived from (+)-3 carene, 36 mg) to afford **42** as an off-white solid (15 mg, 0.06 mmol, 29% yield) and **41** as a pale yellow oil (7 mg, 0.04 mmol, 18% yield).



41. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.31 (d, *J* = 16.1 Hz, 1H), 6.89 (d, *J* = 16.1 Hz, 1H), 6.27 (s, 1H), 4.03 (s, 2H), 1.59 (s, 6H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 190.0, 170.5, 166.4, 131.9, 130.1, 120.6, 86.6, 33.0, 25.7; IR (thin film) ν_{max}: 1746, 1693, 1618, 1582 cm^{-1}; HRMS (EI) calcd for $C_{10}H_{11}O_3{}^{79}Br$: 257.9892, found: 257.9891.



42. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.13 (d, *J* = 16.4 Hz, 1H), 6.60 (d, *J* = 16.4 Hz, 1H), 6.21 (s, 1H), 2.39 (s, 3H), 1.57 (s, 6H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 196.9, 170.6, 167.0, 134.5, 130.1, 119.9, 86.6, 28.5, 25.7; IR (thin film) ν_{max}: 1750, 1699, 1677 cm^{-1}; HRMS (EI) calcd for $C_{10}H_{12}O_3$: 180.0786, found: 180.0787.

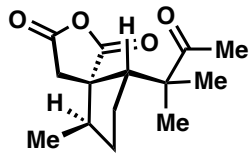


Hemiketal 43. *Procedure a)* Ketol **26** (20 mg, 0.074 mmol, 1.0 equiv) was dissolved in acetonitrile (0.8 mL). $RuCl_3$•xH_2O (1.6 mg, 0.007 mmol, 0.1 equiv), and $KBrO_3$ (37 mg, 0.22 mmol, 3.0 equiv) were added followed by pyridine (1.2 μL, 0.015 mmol, 0.2 equiv) and H_2O (30 μL, 1.7 mmol, 22 equiv). The reaction mixture was heated to 70 ºC and stirred for 5 h. Upon cooling to room temperature, the resulting mixture was quenched with saturated *aq.* $Na_2S_2O_3$ (2.0 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (3 x 5.0 mL). The combined organic layers were washed with brine (1 x 20 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude residue was purified by preparative TLC (50% EtOAc in hexanes) to afford recovered **26** (10 mg, 0.037 mmol, 50% yield), and hemiketal **43** (2.7 mg, 0.010 mmol, 14% yield, 27% yield BRSM) as a crystalline solid.

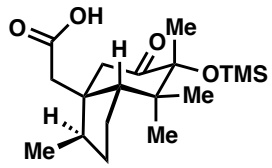
Procedure b) Ketol **26** (7.5 mg, 0.028 mmol, 1.0 equiv) was dissolved in MeCN (0.3 mL, 0.1 M). $Cu(OAc)_2$•H_2O (6.1 mg, 0.031 mmol, 1.1 equiv) and H_2O_2 (50 wt% in H_2O, 20 mg, 0.28 mmol, 10.0 equiv) were then added sequentially at room temperature. The reaction mixture was allowed to stir for 24 h. The mixture was then quenched with saturated *aq.* $Na_2S_2O_3$ (1.0 mL) and $CHCl_3$ was added (1.0 mL). The layers were separated, and the aqueous layer was extracted with $CHCl_3$ (3 x 1.0 mL). The combined organic

layers were washed with brine (1 x 2.0 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude residue was purified by preparative TLC (50% EtOAc in hexanes) to afford hemiketal **43** (1.0 mg, 0.0035 mmol, 12% yield) as a white solid.

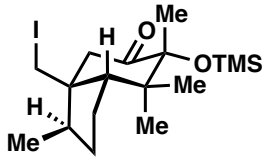
Hemiketal 43. $[\alpha]_D^{23}$ = –107.5 (*c* 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.12 (br s, OH, 1H), 3.41 (br s, OH, 1H), 3.03 (d, *J* = 17.4 Hz, 1H), 2.27 – 2.20 (m, 1H), 2.21 (d, *J* = 17.4 Hz, 1H), 2.09 (dd, *J* = 8.8, 1.8 Hz, 1H), 2.05 – 1.98 (m, 1H), 1.98 – 1.89 (m, 1H), 1.74 (dddd, *J* = 14.9, 10.0, 5.1, 1.8 Hz, 1H), 1.43 (s, 3H), 1.31 – 1.21 (m, 1H), 1.13 (d, *J* = 6.5 Hz, 3H), 1.00 (s, 3H), 0.77 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 207.8, 174.5, 102.6, 79.9, 58.9, 53.3, 44.8, 37.6, 36.5, 33.3, 23.6, 22.6, 22.4, 18.9, 17.9; IR (thin film) ν_{max}: 3355, 2975, 1776, 1720 1634, 644 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{22}O_5Na$ $[M+Na]^+$: 305.1353, found: 305.1359.



Anhydride 44. Hemiketal **43** (2.7 mg, 0.01 mmol, 1.0 equiv) was dissolved in acetonitrile (0.3 mL). $RuCl_3$•xH_2O (0.7 mg, 0.0034 mmol, 0.33 equiv), and $KBrO_3$ (15 mg, 0.09 mmol, 9.0 equiv) were added followed by pyridine (0.5 µL, 0.0067 mmol, 0.67 equiv) and H_2O (12 µL, 0.67 mmol, 67 equiv). The reaction mixture was heated to 70 ºC and stirred for 17 h. Upon cooling to room temperature, the resulting mixture was quenched with saturated *aq.* $Na_2S_2O_3$ (2.0 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (3 x 1.0 mL). The combined organic layers were washed with brine (1 x 2.0 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude residue was purified by preparative TLC (20% Et_2O in DCM) to afford anhydride **44** (2.0 mg, 0.008 mmol, 80% yield) as a crystalline solid. $[\alpha]_D^{23}$ = –39.0 (*c* 0.1, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.97 (d, *J* = 18.6 Hz, 1H), 2.90 (d, *J* = 18.6 Hz, 1H), 2.65 (t, *J* = 8.8 Hz, 1H), 2.27 (dqd, *J* = 13.0, 6.7, 6.0 Hz, 1H), 2.16 (s, 3H), 1.93 (dt, *J* = 13.4, 6.9 Hz, 1H), 1.86 (ddd, *J* = 12.4, 6.9, 6.0 Hz, 1H), 1.68 (dddd, *J* = 13.0, 12.4, 8.8, 6.9 Hz, 1H), 1.49 (s, 3H), 1.26 (dtd, *J* = 13.6, 12.4, 8.8 Hz, 1H), 1.04 (s, 3H), 0.95 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 216.4, 177.1, 170.2, 58.5, 58.1, 51.5, 44.8, 40.8, 32.6, 28.0, 26.4, 25.4, 19.5, 13.2; IR (thin film) ν_{max}: 2963, 2874, 1833, 1771, 1689, 1231, 946 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{20}O_4Na$ $[M+Na]^+$: 275.1254, found: 275.1252.



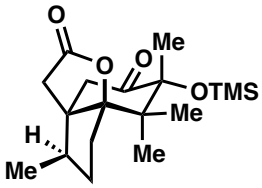
Silyl ether 45. Ketol **26** (500 mg, 1.86 mmol, 1.0 equiv) and imidazole (630 mg, 9.32 mmol, 5.0 equiv) were dissolved in DMF (18.6 mL). TMSCl (1.2 mL, 9.32 mmol, 5.0 equiv) was added dropwise at 23 ºC and the resulting solution was stirred for 12 h. The reaction mixture was then quenched with HCl (0.1 M, 10 mL) and DCM was added (20 mL). The layers were separated, and the aqueous layer was further extracted with DCM (3 x 10 mL). The combined organic layers were washed with brine (1 x 20 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude residue was purified by column chromatography (10% Et_2O in hexanes) to afford silyl ether **45** (400 mg, 1.15 mmol, 62% yield) as a white solid. $[\alpha]_D^{23}$ = –15.4 (*c* 0.28, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.09 (d, *J* = 15.2 Hz, 1H), 2.50 (d, *J* = 15.2 Hz, 1H), 2.28 (d, *J* = 14.5 Hz, 1H), 2.23 – 2.19 (m, 1H), 2.13 (d, *J* = 14.5 Hz, 1H), 2.01 (tq, *J* = 7.8, 6.8 Hz, 1H), 1.97–1.84 (m, 2H), 1.81 (d, *J* = 13.5 Hz, 1H), 1.34 (s, 3H), 1.33 – 1.27 (m, 1H), 0.91 (s, 3H), 0.83 (d, *J* = 6.8 Hz, 3H), 0.80 (s, 3H), 0.10 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 213.3, 177.5, 84.3, 50.9, 50.2, 44.9, 42.3, 42.3, 38.9, 30.6, 24.8, 24.7, 21.5, 20.8, 14.1, 2.6; IR (thin film) ν_{max}: 2954, 2876, 1702, 1246, 1160, 839, 755 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{31}O_4{}^{28}Si$ $[M–H]^-$: 339.1997, found: 339.1999.



Iodide 46. Cyclohexane (2.2 mL) was added to a reaction tube containing silyl ether **45** (15 mg, 0.044 mmol, 1.0 equiv), $PhI(OAc)_2$ (42 mg, 0.13 mmol, 3.0 equiv), and iodine (13.4 mg, 54 mmol, 1.2 equiv). The deep purple mixture was irradiated with a 90 W halogen lamp for 4.5 h at room temperature. The reaction mixture was quenched by addition of saturated *aq*. $Na_2S_2O_3$ (5.0 mL) and was stirred vigorously until colorless. The layers were separated, and the aqueous layer was extracted with ether (3 x 5 mL). The combined organic layers were washed with brine (1 x 5 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude residue was purified by preparative TLC (10% Et_2O in hexanes) to afford recovered silyl ether **45** (3.3 mg, 0.0097 mmol, 22% yield) as a white solid and iodide **46** (6.3 mg, 0.015 mmol, 34% yield) as a white solid. $[\alpha]_D^{23}$ = –40.5 (*c* 0.63, $CHCl_3$); ^{1}H NMR (700 MHz, $CDCl_3$) δ 3.29 (d, *J* = 10.5 Hz, 1H), 3.15 (d, *J* = 10.5 Hz, 1H), 2.70 (br d, *J* = 14.7 Hz, 1H), 2.43 (br s, 1H), 2.25 (br s, 1H), 2.14 – 2.05 (br m,

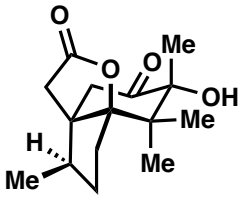
1H), 1.94 – 1.80 (br m, 3H), 1.44 (s, 3H), 1.37 – 1.30 (br m, 1H), 0.93 (s, 3H), 0.88 (d, *J* = 7.0 Hz, 3H), 0.80 (s, 3H), 0.11 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 212.9, 84.3, 52.0, 51.4, 44.8, 43.3, 40.4 (br), 30.3, 24.8 (br), 21.7 (br), 21.7 (br), 20.5 (br), 14.1, 2.5; IR (thin film) ν_{max}: 2954, 2873, 1721, 1245, 1159, 1081, 840cm^{-1}; HRMS (EI) calcd for $C_{17}H_{31}O_2{}^{127}I^{28}Si$: 422.1138, found: 422.1138.

Procedure for the C–H activation reaction:
This procedure was adapted from a slow addition protocol developed by White and coworkers.[15] TMS protected alcohol **45** (1.1 g, 3.2 mmol, 1.0 equiv) was dissolved in MeCN (13 mL) at 23 ºC. H_2O_2 (50 wt% in H_2O, 1.1 g, 16 mmol, 5.0 equiv) and $[Fe(mep)(MeCN)_2][(SbF_6)_2]$ (1.4 g, 1.6 mmol, 0.50 equiv) were dissolved separately in MeCN (10 mL each) and taken up in syringes. The two solutions were added over the course of 1 h by separate syringe pumps. At the conclusion of reagent addition, the reaction was concentrated directly *in vacuo* and then filtered through a short pad of silica gel. The crude residue was purified by flash column chromatography (10 → 50% Et_2O in hexanes) to afford lactone **47** (240 mg, 0.70 mmol, 22% yield) as a colorless oil, lactone **48** (260 mg, 0.96 mmol, 30% yield) as a white solid and epoxide **49** (46 mg, 0.13 mmol, 4% yield) as a white solid.

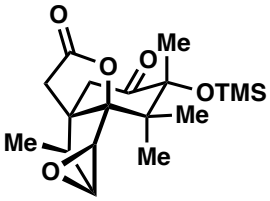


Lactone 47. Lactone **48** (200 mg, 0.75 mmol, 1.0 equiv) and imidazole (255 mg, 3.75 mmol, 5.0 equiv) were dissolved in DMF (7.5 mL). TMSCl (0.48 mL, 3.75 mmol, 5.0 equiv) was added dropwise and the solution was stirred at 23 ºC for 12 h. The reaction mixture was then quenched with 0.1 M HCl (10 mL) and DCM was added (20 mL). The layers were separated, and the aqueous layer was further extracted with DCM (3 x 10 mL). The combined organic layers were washed with brine (1 x 20 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude residue was purified by flash column chromatography (10 → 20% Et_2O in hexanes) to afford lactone **47** (171 mg, 0.50 mmol, 67% yield) as a colorless oil. $[\alpha]_D^{23}$ = –3.7 (*c* 0.4, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.81 (d, *J* = 18.9 Hz, 1H), 2.81 (d, *J* = 17.2 Hz, 1H), 2.57 (ddd, *J* = 13.7, 12.6, 6.4 Hz, 1H), 2.52 (d, *J* = 17.2 Hz, 1H), 2.27 (d, *J* = 18.9 Hz, 1H), 2.14 (dqd, *J* = 13.2, 6.9, 6.4 Hz, 1H), 1.94 (dd, *J*

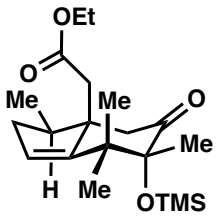
= 13.7, 6.4 Hz, 1H), 1.76 (dt, *J* = 12.6, 6.4 Hz, 1H), 1.33 (s, 3H), 1.24 (dtd, *J* = 13.2, 12.6, 6.6 Hz, 1H), 1.13 (s, 3H), 0.99 (d, *J* = 6.9 Hz, 3H), 0.91 (s, 3H), 0.13 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 208.8, 175.8, 101.0, 82.2, 50.6, 48.1, 47.2, 46.0, 39.5, 37.0, 30.9, 20.6, 19.5, 19.0, 14.5, 2.1; IR (thin film) ν_{max}: 2956, 1771, 1720, 842 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{30}O_4Na^{28}Si$ $[M+Na]^+$: 361.1811, found: 361.1765.



Lactone 48. $[\alpha]_D^{23}$ = +61.0 (*c* 0.38, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.31 (br s, 1H), 2.84 (d, J = 18.4 Hz, 1H), 2.73 (d, J = 15.4 Hz, 1H), 2.64 (d, J = 15.4 Hz, 1H), 2.32 (d, J = 18.4 Hz, 1H), 2.30 – 2.19 (m, 1H), 1.95–1.85 (m, 2H), 1.79 (dtd, J = 15.2, 7.5, 2.8 Hz, 1H), 1.38 – 1.33 (m, 1H), 1.33 (s, 3H), 1.22 (s, 3H), 1.05 (s, 3H), 0.98 (d, J = 6.7 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 212.9, 175.2, 99.5, 78.2, 53.2, 46.1, 44.9, 43.3, 39.7, 35.1, 30.3, 23.9, 20.5, 20.3, 14.8; IR (thin film) ν_{max}: 3467, 2956, 2875, 1760, 1711, 985 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{22}O_4Na$ $[M+Na]^+$: 289.1416, found: 289.1381.

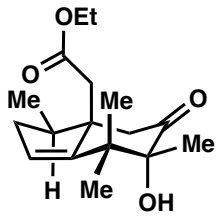


Epoxide 49. $[\alpha]_D^{23}$ = +59.2 (*c* 0.24, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.69 (d, *J* = 2.7 Hz, 1H), 3.47 (d, *J* = 2.7 Hz, 1H), 3.12 (d, *J* = 18.2 Hz, 1H), 2.68 (d, *J* = 17.2 Hz, 1H), 2.41 (d, *J* = 17.2 Hz, 1H), 2.24 (q, *J* = 7.0 Hz, 1H), 2.06 (d, *J* = 18.2 Hz, 1H), 1.41 (s, 3H), 1.22 (s, 3H), 1.15 (d, *J* = 7.0 Hz, 3H), 1.07 (s, 3H), 0.14 (d, *J* = 1.1 Hz, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 208.1, 175.0, 95.7, 81.6, 62.3, 60.3, 48.6, 47.7, 46.1, 44.2, 42.9, 22.1, 20.2, 19.8, 11.8, 2.6; IR (thin film) ν_{max}: 2952, 1769, 1723, 1424, 1375, 1247, 1185, 842, 756 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{28}O_5Na^{28}Si$ $[M+Na]^+$: 375.1598, found: 375.1597.



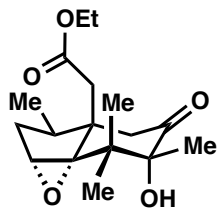
Ethyl ester SI-2. Lactone **47** (250 mg, 0.74 mmol, 1.0 equiv), Et_3OPF_6 (550 mg, 2.22 mmol, 3.0 equiv), and 1,8-bis(dimethylamino)naphthalene (Proton-sponge®, 470 mg, 0.22 mmol, 3.0 equiv) were dissolved in DCM (25 mL). The solution was then heated at 50 ºC for 12 h. Upon cooling to room temperature, HCl (0.1 M, 50 mL) was added to quench the mixture. The layers were separated, and the aqueous

layer was further extracted with DCM (3 x 30 mL). The combined organic layers were washed with brine (1 x 50 mL) and dried over Na_2SO_4. The solution was then filtered through a short pad of silica gel and flushed with EtOAc, which was subsequently concentrated *in vacuo*. The crude residue was purified by column chromatography (10 → 30% Et_2O in hexanes) to afford recovered lactone **47** (43 mg, 0.13 mmol, 17% yield), ethyl ester **SI-2** (109 mg, 0.3 mmol, 40% yield), and ethyl ester **51** (39 mg, 0.13 mmol, 18% yield), all of which were colorless oils. $[\alpha]_D^{23}$ = –30.0 (*c* 0.1, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.68 (s, 1H), 4.05 (dq, *J* = 11.0, 7.4 Hz, 1H), 4.02 (dq, *J* = 11.0 7.4 Hz, 1H), 2.99 (d, *J* = 12.2 Hz, 1H), 2.39 (d, *J* = 12.2 Hz, 1H), 2.35 (s, 2H), 2.29 – 2.22 (m, 2H), 2.06 – 1.99 (m, 1H), 1.25 (s, 3H), 1.21 (t, *J* = 7.4 Hz, 3H), 1.20 (s, 3H), 1.12 (d, *J* = 6.5 Hz, 3H), 0.95 (s, 3H), 0.06 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 214.1, 171.5, 150.5, 126.7, 83.5, 60.2, 54.4, 50.5, 49.8, 45.4, 39.1, 38.4, 24.4, 22.4, 16.8, 14.2, 13.8, 1.9; IR (thin film) ν_{max}: 2954, 2924, 2853, 1736, 1716, 1251, 1133, 1012, 840 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{34}O_4Na^{28}Si$ $[M+Na]^+$: 389.2119, found: 389.2116.

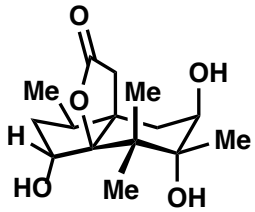


Ethyl ester 51. Ethyl ester **SI-2** (100 mg, 0.27 mmol, 1.0 equiv) was dissolved in THF (1.9 mL). AcOH (50 µL, 0.81 mmol, 3.0 equiv) was added followed by tetra-*n*-butylammonium fluoride (1.0 M in THF, 0.81 mL, 3.0 equiv). The reaction mixture was stirred for 12 h at 23 ºC. Then, saturated *aq.* $NaHCO_3$ (5.0 mL) was carefully added followed by EtOAc (10 mL). The layers were separated, and the aqueous layer was further extracted with EtOAc (3 x 30 mL). The combined organic layers were washed with brine (1 x 5.0 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude residue was purified by flash column chromatography (10 → 20% Et_2O in hexanes) to afford ethyl ester **51** (65 mg, 0.22 mmol, 82% yield). Combining this with the material produced directly in the lactone elimination step led to an overall 50% yield of **51** over two steps. $[\alpha]_D^{23}$ = –31.1 (*c* 0.18, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.90 (d, *J* = 3.2 Hz, 1H), 4.06 (dq, *J* = 11.0, 7.2 Hz, 1H), 4.03 (dq, *J* = 11.0, 7.2 Hz, 1H), 2.99 (d, *J* = 13.1 Hz, 1H), 2.45 (d, *J* = 13.1 Hz, 1H), 2.42 (d, *J* = 15.6 Hz, 1H), 2.40 (d, *J* = 15.6 Hz, 1H), 2.38 – 2.28 (m, 2H), 2.14 – 2.08 (m, 1H), 2.08 (s, 1H), 1.26 (s, 3H), 1.24 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H), 1.14 (d, *J* = 6.6 Hz, 3H), 1.06 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 212.4, 171.2, 149.3,

130.3, 81.0, 60.3, 53.6, 50.3, 50.1, 44.6, 39.2, 38.7, 24.4, 21.8, 16.4, 14.2, 13.8; IR (thin film) ν_{max}: 3493, 2918, 2851, 1715, 1445, 1190, 995, 860 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{26}O_4Na$ $[M+Na]^+$: 317.1723, found: 317.1719.



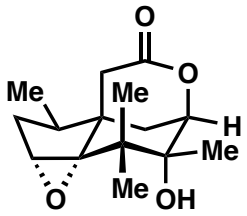
Epoxide 52. Ethyl ester **51** (10 mg, 0.034 mmol, 1.0 equiv) and $VO(acac)_2$ (0.9 mg, 0.0034 mmol, 0.1 equiv) were dissolved in benzene (0.4 mL). TBHP (*ca*. 5 M in decane, 17 µL, 0.085 mmol, 2.5 equiv) was added in one portion. The resulting solution was then heated at 45 ºC for 15 h. Upon cooling to room temperature, the solution was filtered through a short plug of celite, washed with Et_2O, and concentrated *in vacuo*. The crude residue was purified by column chromatography (30% Et_2O in hexanes) to afford epoxide **52** (10.5 mg, 0.034 mmol, 99% yield) as a white solid. $[\alpha]_D^{23} = -36.7$ (*c* 0.12, $CHCl_3$); ^1H NMR (700 MHz, $CDCl_3$) δ 4.13 (s, 1H), 4.08 (dq, *J* = 11.0, 7.1 Hz, 1H), 4.05 (dq, *J* = 11.0, 7.1 Hz, 1H), 3.67 (s, 1H), 3.25 (d, *J* = 12.4 Hz, 1H), 2.54 (d, *J* = 18.4 Hz, 1H), 2.42 (d, *J* = 18.4 Hz, 1H), 2.21 (d, *J* = 12.4 Hz, 1H), 2.11 (dd, *J* = 13.4, 7.4 Hz, 1H), 1.96 (dp, *J* = 10.5, 7.4 Hz, 1H), 1.72 (dd, *J* = 13.4, 10.5 Hz, 1H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.18 (s, 3H), 1.10 (s, 3H), 1.02 (s, 3H), 0.86 (d, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 210.6, 171.5, 82.6, 73.2, 60.6, 60.0, 47.6, 46.7, 42.1, 39.3, 37.7, 36.1, 22.5, 18.8, 16.3, 14.2, 13.4; IR (thin film) ν_{max}: 3358, 2969, 2930, 1736, 1715, 1383, 1178, 1141, 922 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{26}O_5Na$ $[M+Na]^+$: 333.1672, found: 333.1671.



Alcohol 53. *i)* Epoxide **52** (10 mg, 0.032 mmol, 1.0 equiv) was dissolved in ethanol (0.3 mL) and an aqueous solution of 10 wt% KOH (0.17 mL, 0.32 mmol, 10.0 equiv) was added at 23 ºC. The reaction mixture was stirred for 3 h. Then, HCl (0.1 M, 5.0 mL) was added followed by EtOAc (2.0 mL). The layers were separated, and the aqueous layer was further extracted with EtOAc (3 x 2.0 mL). The combined organic layers were washed with brine (1 x 3.0 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude intermediate was used immediately in the next step without further purification.

ii) The crude residue obtained from above was re-dissolved in MeCN/THF/AcOH (3.8:1.3:1, 0.6 mL) and cooled to –40 ºC. $Me_4NBH(OAc)_3$ (27 mg, 0.096 mmol, *ca.* 3.0

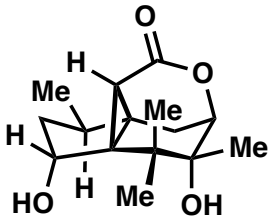
equiv) was added in one portion. Low temperature was maintained, and the reaction mixture was stirred for 12 h. Saturated *aq.* $NaHCO_3$ solution (5 mL) was carefully added to quench the reaction mixture followed by EtOAc (1 mL). The layers were separated, and the aqueous layer was further extracted with EtOAc (3 x 5.0 mL). The combined organic layers were washed with brine (1 x 5.0 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude residue was purified by preparative TLC (80% EtOAc in hexanes) to afford alcohol **53** (3.5 mg, 0.012 mmol, 38% yield) as a crystalline solid. $[\alpha]_D^{23} = -14.1$ (*c* 0.46, MeOH); ^{1}H NMR (600 MHz, CD_3OD) δ 4.13 (d, *J* = 3.9 Hz, 1H), 3.74 (br dd, *J* = 4.7, 3.9 Hz, 1H), 3.21 (br d, *J* = 18.5 Hz, 1H), 2.58 (d, *J* = 18.5 Hz, 1H), 2.42 (dp, *J* = 13.5, 7.1 Hz, 1H), 1.96 (br dd, *J* = 14.5, 5.2 1H), 1.90 (dd, *J* = 14.5, 3.9 Hz, 1H), 1.85 (dd, *J* = 13.5, 7.1 Hz, 1H), 1.44 (td, *J* = 13.5, 3.7 Hz, 1H), 1.28 (s, 3H), 1.22 (s, 3H), 1.19 (s, 3H), 0.98 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, CD_3OD) δ 179.3, 102.1, 76.8 (br), 76.7 (br), 76.5, 49.7, 46.5, 44.4 (br), 41.9, 39.2, 38.9, 24.1 (br), 21.7 (br), 21.5, 16.2; IR (thin film) ν_{max}: 3247, 2994, 1749, 1458, 1229, 1145, 1066, 998 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{23}O_5$ $[M-H]^-$: 283.1551, found: 283.1547.



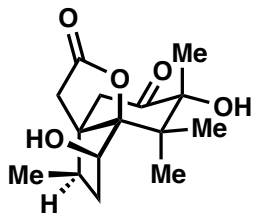
***δ*-Lactone 54.** *i)* Epoxide **52** (1.2 mg, 0.0039 mmol, 1.0 equiv) was dissolved in MeCN/AcOH (3:1, 0.3 mL) and cooled to –40 °C. $Me_4NBH(OAc)_3$ (3.3 mg, 0.012 mmol, 3.0 equiv) in one portion, low temperature was maintained, and the resulting solution was stirred for 12 h. Saturated *aq.* $NaHCO_3$ (2 mL) was carefully added to quench the reaction mixture. The layers were separated, and the aqueous layer was further extracted with EtOAc (3 x 2.0 mL). The combined organic layers were washed with brine (1 x 5.0 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude residue was purified by preparative TLC (30% EtOAc in hexanes) to provide the intermediate diol.

ii) The intermediate diol obtained from above was dissolved in THF (0.3 mL) at 23 ºC. NaH (60 wt% dispersion in mineral oil, 0.6 mg, 0.012 mmol, *ca.* 3.0 equiv) was added in one portion and the resulting suspension was stirred for 1 h. Saturated *aq*. NH_4Cl (1.0 mL) and EtOAc (1.0 mL) was added. The layers were separated, and the aqueous layer was further extracted with EtOAc (3 x 1.0 mL). The combined organic layers were washed with brine (1 x 5.0 mL), dried over Na_2SO_4, and concentrated *in vacuo*.

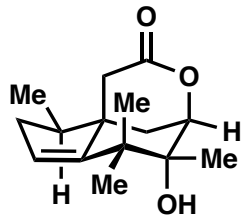
The crude residue was purified by preparative TLC (40% EtOAc in hexanes) to afford δ-lactone **54** (1.0 mg, 0.0037 mmol, 95% yield over two steps) as a colorless oil. $[\alpha]_D^{23}$ = –2.7 (*c* 0.11, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.41 (dd, *J* = 3.8, 2.1 Hz, 1H), 3.42 (t, *J* = 1.0 Hz, 1H), 2.61 (d, *J* = 19.4 Hz, 1H), 2.37 (dd, *J* = 19.4, 2.1 Hz, 1H), 2.22 (dt, *J* = 14.0, 2.1 Hz, 1H), 2.13 (ddd, *J* = 13.7, 6.8, 1.0 Hz, 1H), 2.09 (s, 1H), 1.88 (dd, *J* = 14.0, 3.8 Hz, 1H), 1.80 (dqd, *J* = 10.9, 7.1, 6.8 Hz, 1H), 1.37 (s, 3H), 1.28 (ddd, *J* = 13.7, 10.9, 1.0 Hz, 1H), 1.18 (s, 3H), 0.92 (s, 3H), 0.87 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.1, 83.5, 75.7, 72.9, 56.4, 40.4, 38.9, 35.8, 35.1, 34.3, 28.6, 25.0, 21.2, 20.9, 13.2; IR (thin film) ν_{max}: 3335, 2924, 1713, 1633, 1373, 1217, 1064, 751, 647 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{22}O_4$: 266.1518, found: 266.1512.



Cyclopropane 55. δ-Lactone **54** (1.0 mg, 0.0037 mmol, 1.0 equiv) was dissolved in anhydrous THF (0.3 mL, 0.01 M) and cooled to –78 °C. A stock solution of LDA (0.28 M in THF, 40 μL, 0.011 mmol, 3.0 equiv) at –78 °C was added quickly into the reaction mixture. The solution was allowed to warm up to room temperature over the course of 1 h. Then, HCl (0.1 M, 1.0 mL) and EtOAc (1.0 mL) were added. The layers were separated, and the aqueous layer was further extracted with EtOAc (3 x 1.0 mL). The combined organic layers were washed with brine (1 x 5.0 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude residue was purified by preparative TLC (100% EtOAc) to afford cyclopropane **55** (0.7 mg, 0.0026 mmol, 71% yield) as a crystalline solid. $[\alpha]_D^{23}$ = –15.0 (*c* 0.08, $CHCl_3$); ^{1}H NMR (900 MHz, $CDCl_3$) δ 4.40 (s, 1H), 4.22 (dd, *J* = 4.0, 2.2 Hz, 1H), 2.59 (ddq, *J* = 11.0, 7.3, 6.5 Hz, 1H), 2.47 (ddd, *J* = 13.8, 2.2, 1.0 Hz, 1H), 2.04 (ddd, *J* = 13.8, 4.0, 1.0 Hz, 1H), 1.70 (t, *J* = 1.0 Hz 1H), 1.63 (dd, *J* = 14.4, 7.3 Hz, 1H), 1.37 (s, 3H), 1.32 (s, 3H), 1.20 (s, 3H), 1.21 (dd, *J* = 14.4, 11.1 Hz, 1H), 1.02 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (226 MHz, $CDCl_3$) δ 172.1, 81.9, 75.2, 72.8, 49.3, 42.9, 40.3, 40.2, 34.7, 28.6, 28.2, 25.8, 22.8, 21.3, 14.9; IR (thin film) ν_{max}: 3390, 2922, 1688, 1371, 1125, 770 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{21}O_4$ $[M–H]^-$: 265.1445, found: 265.1442.

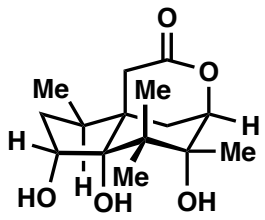


***γ*-Lactone 56.** Ethyl ester **51** (2.0 mg, 0.0068 mmol, 1.0 equiv) and OsO_4 (2.1 mg, 0.0081 mmol, 1.2 equiv) were dissolved in pyridine (0.3 mL) and stirred at room temperature for 12 h. MeOH/H_2O (3:, 0.3 mL) and $NaHSO_3$ (7.1 mg, 0.068 mmol, 10.0 equiv) were added and the suspension was heated at 60 °C for 4 h. The pink solution was cooled to room temperature and EtOAc (5.0 mL) and brine (5.0 mL) were added. The layers were separated, and the aqueous layer was further extracted with EtOAc (2 x 5.0 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude residue was purified by preparative TLC (100% EtOAc) to afford *γ*-lactone **56** (1.2 mg, 0.0043 mmol, 63% yield), a crystalline solid, as a single diastereomer (> 15:1 d.r.). $[\alpha]_D^{23}$ = +33.3 (*c* 0.12, MeOH); ^{1}H NMR (600 MHz, C_5D_5N) δ 6.91 (br s, 1H), 6.61 (br s, 1H), 4.95 (br dd, *J* = 7.5, 6.3 Hz, 1H), 3.20 (d, *J* = 17.8 Hz, 1H), 2.91 (s, 2H), 2.46 (d, *J* = 17.8 Hz, 1H), 2.35 (dt, *J* = 13.8, 7.5 Hz, 1H), 2.11 (ddq, *J* = 11.0, 7.5, 6.7 Hz, 1H), 1.67 (ddd, *J* = 13.8, 11.0, 6.3 Hz, 1H), 1.63 (s, 3H), 1.32 (br s, 3H), 1.26 (s, 3H), 0.88 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (151 MHz, C_5D_5N) δ 211.9, 176.6, 96.9, 79.8, 74.3, 54.1, 46.2, 45.7, 41.8, 40.7, 38.6, 23.1, 20.2, 20.1, 15.0; IR (thin film) ν_{max}: 3457, 2927, 1765, 1712, 1457, 1347, 1258, 1170, 992 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{21}O_5$ $[M–H]^-$: 281.1394, found: 281.1391.



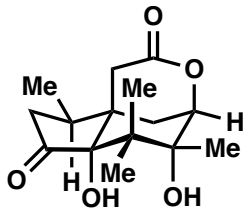
***δ*-Lactone 57.** *i)* Ethyl ester **51** (30 mg, 0.10 mmol, 1.0 equiv) was dissolved in MeCN/AcOH (3:1, 1.0 mL) and the resulting solution was cooled to –40 °C. $Me_4NBH(OAc)_3$ (81 mg, 0.31 mmol, 3.0 equiv) was then quickly added in one portion. Low temperature was maintained, and the reaction mixture was stirred for 12 h. Saturated *aq.* $NaHCO_3$ (5.0 mL) was carefully added to quench the reaction mixture. The layers were separated, and the aqueous layer was further extracted with EtOAc (3 x 2.0 mL). The combined organic layers were washed with brine (1 x 5.0 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude residue was then flushed through a short plug of silica gel with EtOAc and re-concentrated. The intermediate diol was used immediately in the next step without further purification.

ii) The intermediate diol obtained above was dissolved in THF (1.0 mL) at 23 ºC. NaH (60 wt% dispersion in mineral oil, 12.2 mg, 0.31 mmol, *ca.* 3.0 equiv) was added in one portion and the resulting suspension stirred for 1 h. After stirring for 1 h, HCl (0.1 M, 1.0 mL) and EtOAc (1.0 mL) were added. The layers were separated, and the aqueous layer was further extracted with EtOAc (3 x 2.0 mL). The combined organic layers were washed with brine (1 x 5.0 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude residue was purified by column chromatography (30% EtOAc in hexanes) to afford δ-lactone **57** (18 mg, 0.072 mmol, 71% yield) as a colorless oil. $[\alpha]_D^{23}$ = +12.0 (*c* 0.1, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.64 (dd, *J* = 3.2, 1.8 Hz, 1H), 4.38 (dd, *J* = 4.1, 1.8 Hz, 1H), 2.60 (d, *J* = 18.6 Hz, 1H), 2.41 (ddd, *J* = 15.8, 7.9, 3.2 Hz, 1H), 2.34 (dd, *J* = 18.6, 2.7 Hz, 1H), 2.08 (ddq, *J* = 10.0, 7.9, 7.1 Hz, 1H), 2.06 (ddd, *J* = 13.5, 2.7, 1.8 Hz, 1H), 1.91 (ddd, *J* = 15.8, 10.0, 1.8 Hz, 1H), 1.90 (dd, *J* = 13.5, 4.1 Hz, 1H), 1.41 (s, 1H), 1.39 (s, 3H), 1.22 (s, 3H), 1.10 (s, 3H), 1.00 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.9, 154.2, 124.7, 83.5, 74.8, 45.3, 44.3, 39.7, 38.8, 38.2, 32.6, 29.7, 24.9, 22.2, 14.5; IR (thin film) ν_{max}: 3448, 2925, 1707, 1369, 1215, 1090, 1034 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{21}O_3$ $[M–H]^-$: 249.1496, found: 249.1463.

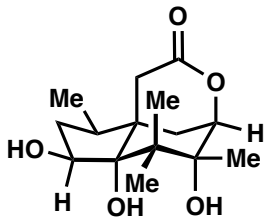


All-*cis*-triol 58. δ-Lactone **57** (17 mg, 0.068 mmol, 1.0 equiv) and OsO_4 (21 mg, 0.081 mmol, 1.2 equiv) were dissolved in pyridine (0.7 mL) and stirred at room temperature for 12 h. The crude reaction mixture was then concentrated directly *in vacuo*. After which, MeOH/H_2O (3:1, 0.7 mL, 0.1 M) and $NaHSO_3$ (71 mg, 0.68 mmol, 10.0 equiv) were added and the suspension was heated at 60 °C for 4 h. The pink solution was cooled to room temperature and EtOAc (5.0 mL) and brine (5.0 mL) were added. The layers were separated, and the aqueous layer was further extracted with EtOAc (2 x 5.0 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude residue was purified by column chromatography (50 → 75% EtOAc in hexanes) to afford all-*cis*-triol **58** (18.2 mg, 0.064 mmol, 94% yield), a crystalline solid, as a single diastereomer (> 15:1 d.r.). $[\alpha]_D^{23}$ = –51.3 (*c* 0.24, MeOH); ^{1}H NMR (700 MHz, $CDCl_3$) δ 4.52 (ddd, *J* = 9.2, 5.2, 3.8 Hz, 1H), 4.34 (dd, *J* = 3.6, 2.3 Hz, 1H), 4.16 (s, 1H), 4.14 (s, 1H), 2.65 (ddq, *J* = 10.6, 9.7, 7.0 Hz, 1H),

2.57 (d, J = 19.6 Hz, 1H), 2.45 (ddd, J = 14.3, 2.8, 2.3 Hz, 1H), 2.25 (dd, J = 19.6, 2.8 Hz, 1H), 2.19 (d, J = 5.2 Hz, 1H), 1.74 (ddd, J = 14.3, 10.6, 9.2 Hz, 1H), 1.69 (ddd, J = 14.3, 9.7, 3.8 Hz, 1H), 1.69 (dd, J = 14.3, 3.6 Hz, 1H), 1.31 (s, 3H), 1.22 (s, 3H), 1.07 (s, 3H), 0.84 (d, J = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.4, 85.8, 83.6, 76.6, 71.0, 46.7, 42.4, 40.1, 37.1, 34.6, 26.6, 22.8, 22.2, 20.9, 13.7; IR (thin film) ν_{max}: 3429, 3248, 2959, 1704, 1399, 1229, 1134 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{23}O_5$ [M–H]$^-$: 283.1551, found: 283.1547.

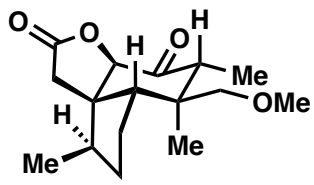


Ketone 59. DCM/MeCN (9:1, 2.4 mL) was added to a mixture of all-*cis*-triol **58** (64 mg, 0.23, 1.0 equiv), TPAP (7.9 mg, 0.023 mmol, 0.1 equiv), NMO (55.4 mg, 0.47 mmol, 2.1 equiv), and 4 Å MS (70 mg). The mixture was allowed to stir for 18 h at 23 ºC. The crude mixture was then filtered through a pad of celite and concentrated directly *in vacuo*. The residue was purified by column chromatography (50 → 75% EtOAc in hexanes) to afford ketone **59** (49 mg, 0.17 mmol, 77% yield) as a white solid. $[\alpha]_D^{23}$ = –91.4 (c 0.07, MeOH); ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.37 (dd, J = 3.5, 2.5 Hz, 1H), 3.52 (s, 1H), 2.83 (ddq, J = 10.6, 8.6, 7.0 Hz, 1H), 2.76 (s, 1H), 2.73 (d, J = 19.6 Hz, 1H), 2.63 (dd, J = 19.4, 8.6 Hz, 1H), 2.46 (dt, J = 14.4, 2.5 Hz, 1H), 2.22 (dd, J = 19.6, 2.5 Hz, 1H), 1.90 (dd, J = 14.4, 3.5 Hz, 1H), 1.74 (dd, J = 19.4, 10.6 Hz, 1H), 1.39 (s, 3H), 1.36 (s, 3H), 1.12 (s, 3H), 1.01 (d, J = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 209.6, 170.2, 84.6, 82.8, 77.3, 44.8, 41.3, 41.1, 33.8, 33.5, 25.2, 21.7, 21.0, 20.8, 13.3; IR (thin film) ν_{max}: 3389, 2933, 1741, 1708, 1374, 1231, 1037, 1020 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{21}O_5$ [M–H]$^-$: 281.1394, found: 281.1391.

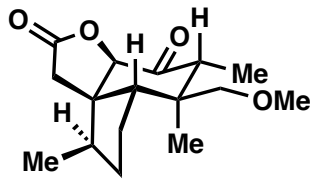


(–)-14-Deoxydunnianin (60). Ketone **59** (25 mg, 0.089 mmol, 1.0 equiv) was dissolved in THF (0.9 mL) and the solution was cooled to –78 °C. A solution of lithium aluminum hydride (2.0 M in THF, 0.14 mL, 0.28 mmol, 3.1 equiv) was slowly added along the side of the reaction vessel. The mixture was allowed to slowly warm up to 23 ºC over the course of 2 h. The mixture was then quenched with sequential addition of 2 drops of H_2O, 2 drops of aqueous 2 M NaOH solution, and 1 drop of H_2O. The

murky mixture was stirred at room temperature until the solution turned clear. Then, the mixture was dried over Na_2SO_4 and concentrated *in vacuo* to provide (–)-14-deoxydunnianin (**60**, 24 mg, 0.084 mmol, 95% yield) as a white solid. $[\alpha]_D^{23}$ = –29.1 (*c* 0.44, MeOH); ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.31 (dd, *J* = 3.6, 2.3 Hz, 1H), 4.17 (ddd, *J* = 7.3, 3.4, 2.3 Hz, 1H), 3.31 (s, 1H), 3.28 (s, 1H), 3.26 (dd, *J* = 19.7, 2.7 Hz, 1H), 2.61 (ddd, *J* = 14.3, 9.4, 7.3 Hz, 1H), 2.58 (d, *J* = 19.7 Hz, 1H), 2.32 (tq, *J* = 9.4, 7.1 Hz) 2.29 (ddd, *J* =14.3, 2.7, 2.3 Hz, 1H), 1.73 (dd, *J* = 14.3, 3.6 Hz, 1H), 1.65 (d, *J* = 3.4 Hz, 1H), 1.37 (s, 3H), 1.31 (s, 3H), 1.26 (s, 3H), 1.10 (ddd, *J* = 14.3, 9.4, 2.3 Hz, 1H), 0.94 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.5, 87.2, 83.1, 78.3, 78.0, 45.3, 43.2, 43.1, 37.4, 34.5, 27.9, 22.9, 22.2, 22.0, 14.6; IR (thin film) ν_{max}: 3390, 2959, 1707, 1374, 1040 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{23}O_5$ $[M–H]^-$: 283.1551, found: 283.1548.

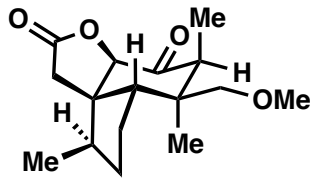


Lactone 67. Acid **64** (100 mg, 0.36 mmol, 1.0 equiv) and TsOH•H_2O (96 mg, 0.50 mmol, 1.4 equiv) were dissolved in DCE (3.6 mL). The reaction mixture was heated to 60 °C and stirred for 10 h. Upon cooling to room temperature, the mixture was quenched with $NaHCO_3$ (20 mL) and the layers were separated. The aqueous layer was further extracted with EtOAc (3 x 10 mL) and the combined organic layers were washed with brine (1 x 30 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude mixture (1.4:1 d.r., 98 mg) was used immediately in the next step without further purification. Analytical samples were prepared by preparative TLC (50% Et_2O in hexanes) to provide lactones **67** and ***epi*-67** as single isomers, both of which were white solids.

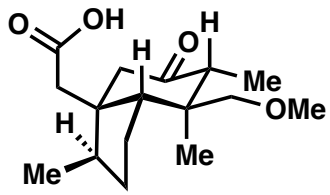


Lactone **67**. $[\alpha]_D^{23}$ = –124.0 (*c* 0.1, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.37 (s, 1H), 3.30 (s, 3H), 3.10 (q, *J* = 6.8 Hz, 1H), 3.04 (d, *J* = 9.7 Hz, 1H), 2.95 (d, *J* = 9.7 Hz, 1H), 2.60 (d, *J* = 17.3 Hz, 1H), 2.55 (dd, *J* = 9.0, 3.8 Hz, 1H), 2.16 (d, *J* = 17.3 Hz, 1H), 1.98 (ddq, *J* = 11.1, 8.4, 6.8 Hz, 1H), 1.90 (tdd, *J* = 12.8, 8.4, 3.9 Hz, 1H), 1.86 (dddd, *J* = 13.6, 12.8, 10.0, 3.8 Hz, 1H), 1.60 (dddd, *J* = 13.6, 9.0, 7.7, 3.9 Hz, 1H), 1.27 (dddd, *J* = 12.8, 11.1, 10.0, 7.7 Hz, 1H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.61 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 209.1, 175.4, 83.4, 76.0, 59.1, 55.3,

48.3, 45.1, 44.3, 40.1, 38.1, 32.1, 23.5, 14.5, 14.3, 8.1; IR (thin film) ν_{max}: 2926, 1789, 1722, 1463, 1107 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{24}O_4$: 280.1675, found: 280.1679.

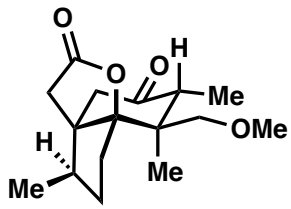


***epi*-67.** $[\alpha]_D^{23}$ = –32.1 (*c* 0.14, $CHCl_3$); ^1H NMR (700 MHz, $CDCl_3$) δ 4.30 (s, 1H), 3.13 (s, 3H), 3.12 (d, *J* = 9.7 Hz, 1H), 3.09 (d, *J* = 9.7 Hz, 1H), 2.69 (d, *J* = 18.4 Hz, 1H), 2.56 (d, *J* = 18.4 Hz, 1H), 2.45 (q, *J* = 7.2 Hz, 1H), 2.27 (dd, *J* = 10.8, 8.3 Hz, 1H), 2.00 (dqd, *J* = 9.3, 7.2, 6.9 Hz, 1H), 1.94 (dddd, *J* = 12.9, 8.3, 6.5, 3.4 Hz, 1H), 1.87 (dddd, *J* = 12.6, 7.1, 6.9, 3.4 Hz, 1H), 1.64 (dddd, *J* = 12.9, 10.8, 10.3, 7.1 Hz, 1H), 1.26 (dddd, *J* = 12.6, 10.3, 9.3, 6.5 Hz, 1H), 1.06 (d, *J* = 7.2 Hz, 3H), 1.04 (d, *J* = 7.2 Hz, 3H), 0.95 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 205.1, 175.9, 88.1, 77.2, 58.6, 52.7, 52.5, 48.8, 44.9, 44.6, 37.9, 32.2, 28.3, 22.1, 15.2, 7.6; IR (thin film) ν_{max}: 2927, 1777, 1725, 1450, 1108 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{24}O_4$: 280.1675, found: 280.1675.

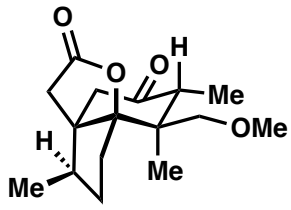


Acid 68. The mixture of lactones **67** and ***epi*-67** (1.4:1 d.r., 98 mg) as obtained by the above procedure was dissolved in anhydrous THF (3.4 mL) and cooled to –78 ºC. A solution of $[Li]^+[C_{10}H_8]^{\bullet-}$ (1.35 M, 0.75 mL, 1.0 mmol, *ca*. 3.0 equiv) was added dropwise to the solution. After 10 minutes, HCl (0.1 M, 10 mL) and Et_2O (10 mL) were added and the reaction mixture was warmed to room temperature. The layers were separated, and the aqueous layer was further extracted with Et_2O (3 x 10 mL). The combined organic layers were extracted with NaOH (2 M, 2 x 20 mL). The aqueous layer was then acidified with HCl (*ca*. 11.5 M, 10 mL) and extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine (1 x 30 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude residue was purified by column chromatography (30 → 80% Et_2O in hexanes) to afford acid **68** (74 mg, 0.27 mmol, 74% yield over two steps) as a white solid. $[\alpha]_D^{23}$ = –73.0 (*c* 2.0, $CHCl_3$); ^1H NMR (700 MHz, $CDCl_3$) δ 10.8 (br s, 1H), 3.30 (s, 3H), 3.04 (d, *J* = 9.7 Hz, 1H), 2.96 (d, *J* = 9.7 Hz, 1H), 2.92 (d, *J* = 16.6 Hz, 1H), 2.75 (q, *J* = 6.7 Hz, 1H), 2.69 (dd, *J* = 9.0, 3.8 Hz, 1H), 2.32 (d, *J* = 16.6 Hz, 1H), 2.27 (d, *J* = 14.8 Hz, 1H), 2.18 (d, *J* = 14.8 Hz, 1H), 1.90 (dddd, *J* = 14.2, 10.4, 9.0, 3.8 Hz, 1H), 1.84 – 1.76 (m, 2H), 1.61 – 1.54 (m, 1H), 1.40 – 1.29 (m, 1H), 0.93 (d, *J* = 6.7 Hz, 3H),

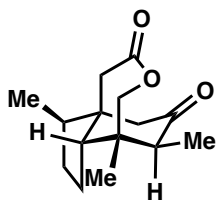
0.88 (d, J = 6.2 Hz, 3H), 0.58 (s, 3H); IR (thin film) ν_{max}: 3204, 2955, 2875, 1726, 1705, 1105 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{25}O_4$ $[M–H]^-$: 281.1758, found: 281.1753.



Lactone 69. Acid **68** (20 mg, 0.071 mmol, 1.0 equiv) was dissolved in MeCN (0.3 mL). TBHP (70 wt% in H_2O, 29 μL, 0.21 mmol, 3.0 equiv) and $[Fe(mep)(MeCN)_2][(SbF_6)_2]$ (31 mg, 0.035 mmol, 0.50 equiv) were dissolved separately in MeCN (0.3 mL each) and taken up in syringes. The two solutions were added over the course of 1 h by syringe pumps. At the conclusion of reagent addition, the reaction was concentrated directly *in vacuo* and then filtered through a short pad of silica gel. The crude residue was purified by flash column chromatography (20 → 60% EtOAc in hexanes) to provide lactone **69** (11 mg, 0.038 mmol, 56% yield) as a colorless oil and *ε*-lactone **70** (4 mg, 0.014 mmol, 20% yield).

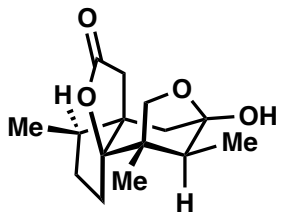


Lactone 69. $[\alpha]_D^{23}$ = –65.0 (c 0.4, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.49 (d, J = 9.1 Hz, 1H), 3.32 (s, 3H), 3.24 (d, J = 9.1 Hz, 1H), 2.82 (d, J = 19.2 Hz, 1H), 2.67 (d, J = 18.5 Hz, 1H), 2.32 (q, J = 6.8 Hz, 1H), 2.31 (d, J = 18.5 Hz, 1H), 2.21 (dd, J = 14.6, 6.4 Hz, 1H), 2.18 (d, J = 19.2 Hz, 1H), 2.02 (ddd, J = 14.6, 12.5, 6.3 Hz, 1H), 1.80 (ddd, J =11.7, 6.3, 5.8 Hz, 1H), 1.76 (dp, J = 12.2, 6.5 Hz, 1H), 1.28 (dddd, J = 12.5, 12.2, 11.7, 6.4 Hz, 1H), 1.06 (d, J = 6.8 Hz, 3H), 1.00 (d, J = 6.5 Hz, 3H), 0.97 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 210.2, 175.8, 100.0, 77.6, 59.1, 50.2, 48.9, 47.9, 46.4, 44.2, 37.7, 35.4, 30.9, 15.5, 14.2, 9.1; IR (thin film) ν_{max}: 2928, 2876, 1759, 1709, 1455, 1259, 1198, 1104, 985 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{24}O_4Na$ $[M+Na]^+$: 303.1567, found: 303.1563.

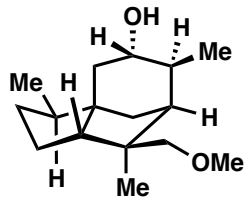


***ε*-Lactone 70.** $[\alpha]_D^{23}$ = –8.0 (c 0.1, $CHCl_3$); ^{1}H NMR (700 MHz, $CDCl_3$) δ 4.07 (d, J = 12.9 Hz, 1H), 3.98 (d, J = 12.9 Hz, 1H), 2.69 (d, J = 14.6 Hz, 1H), 2.65 (dd, J = 14.6, 1.7 Hz, 1H), 2.39 (q, J = 6.7 Hz, 1H), 2.34 (dd, J = 16.8, 1.7 Hz, 1H), 2.24 (dt, J = 16.8, 1.7 Hz, 1H), 2.18 (dddd, J = 14.5, 11.2, 8.4, 3.2 Hz, 1H), 2.06 – 1.97 (m, 2H), 1.87 – 1.79 (m, 2H), 1.43 (ddd, J = 14.5, 9.7, 2.4 Hz, 1H), 1.18 (d, J = 6.7 Hz, 3H), 1.06 (s, 3H), 0.93 (d, J =

7.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 208.4, 172.9, 75.8, 54.6, 46.8, 45.6, 44.4, 44.3, 43.2, 42.8, 29.2, 24.6, 22.8, 18.2, 8.0; IR (thin film) ν_{max}: 3313, 2966, 1736, 1696, 1376, 1195 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{22}O_3Na$ $[M+Na]^+$: 273.1461, found: 273.1461.

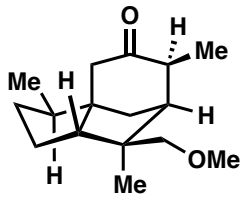


Hemiketal 71. Lactone **69** (10 mg, 0.036 mmol, 1.0 equiv) and sodium iodide (27 mg, 0.18 mmol, 5.0 equiv) were dissolved in MeCN (0.4 m). TMSCl (45 µL, 0.36 mmol, 10.0 equiv) was added dropwise and the solution was heated at 80 °C for 45 min. Upon cooling to room temperature, the reaction mixture was quenched with saturated *aq*. $Na_2S_2O_3$ (5.0 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (3 x 5.0 mL). The combined organic layers were washed with brine (1 x 10 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude residue was purified by preparative TLC (100% Et_2O) to give hemiketal **71** (4.4 mg, 0.016, 46%) as a colorless oil. Characterization data were in agreement with previously reported values.[16] $[\alpha]_D^{23}$ = –18.7 (*c* 0.31, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.85 (d, *J* = 9.6 Hz, 1H), 3.68 (d, *J* = 9.6 Hz, 1H), 2.90 (d, *J* = 18.7 Hz, 1H), 2.73 (d, *J* = 18.7 Hz, 1H), 2.50 (s, 1H), 2.23 (d, *J* = 13.8 Hz, 1H), 2.06 – 2.02 (m, 1H), 1.96 – 1.90 (m, 1H), 1.89 – 1.82 (m, 3H), 1.76 (d, *J* = 13.8 Hz, 1H), 1.36 – 1.29 (m, 1H), 1.06 (s, 3H), 1.05 (d, *J* = 6.8 Hz, 3H), 1.00 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.9, 106.7, 100.9, 71.3, 50.8, 50.6, 49.9, 49.0, 43.7, 38.4, 34.9, 32.1, 15.1, 14.4, 7.9; IR (thin film) ν_{max}: 3402, 2937, 2880, 1746, 1644, 1265, 1196, 1015, 966 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{21}O_4$ $[M–H]^-$: 265.1445, found: 265.1442.



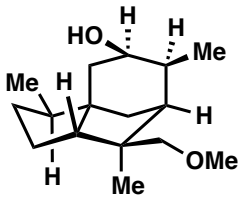
Alcohol 79. Alkene **62** (586 mg, 2.5 mmol, 1.0 equiv) was dissolved in THF (7.5 mL) and cooled to 0 ºC. BH_3•THF (1 M in THF, 3.0 mL, 3.0 mmol, 1.2 equiv) was added dropwise and the resulting solution was warmed to 23 ºC and stirred for 1.5 h. The reaction mixture was re-cooled to 0 ºC and H_2O (1.0 mL) was added dropwise [*Caution*: vigorous gas evolution], followed by NaOH (3M, 3.0 mL) and H_2O_2 (50 wt% in H_2O, 0.7 mL, 12.5 mmol, 5.0 equiv). The mixture was warmed to 23 ºC and stirred for 10 min.

Et_2O (10 mL), hexanes (10 mL), and H_2O (5 mL) were added and the layers were separated. The organic phase was further washed with H_2O (2 x 5 mL) and brine (5 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude residue was purified by flash column chromatography (20 → 50% Et_2O in hexanes) to afford alcohol **79** (535 mg, 2.1 mmol, 85% yield) as a white solid. $[\alpha]_D^{23}$ = +7.2 (*c* 1.3, $CHCl_3$); ^{1}H NMR (700 MHz, $CDCl_3$) δ 3.78 (ddd, *J* = 10.4, 9.8, 6.5 Hz, 1H), 3.35 (d, *J* = 8.7 Hz, 1H), 3.30 (s, 3H), 3.26 (d, *J* = 8.7 Hz, 1H), 1.99 (ddd, *J* = 12.0, 6.5, 2.6 Hz, 1H), 1.84 (dq, *J* = 12.8, 6.3 Hz, 1H), 1.80 (dd, *J* = 4.8, 2.6 Hz, 1H), 1.76 (ddd, *J* = 11.3, 4.8, 2.6 Hz, 1H), 1.73 (dq, *J* = 7.3, 6.3 Hz, 1H), 1.69 (ddd, *J* = 8.8, 7.3, 1.4 Hz, 1H), 1.58 (dqd, *J* = 10.4, 7.2, 2.6 Hz, 1H), 1.51 (ddt, *J* = 12.4, 8.8, 6.3 Hz, 1H), 1.46 (br s, 1H), 1.42 (ddq, *J* = 12.8, 7.2, 6.3 Hz, 1H), 1.30 (ddt, *J* = 12.4, 7.3, 6.3 Hz, 1H), 1.23 (dd, *J* = 11.3, 1.4 Hz, 1H), 1.22 (dd, *J* = 12.0, 9.8 Hz, 1H), 1.10 (d, *J* = 7.2 Hz, 3H), 1.03 (s, 3H), 0.86 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 80.1, 73.1, 59.0, 54.7, 54.5, 53.4, 48.9, 46.7, 46.2, 44.0, 41.7, 36.7, 26.4, 23.8, 17.5, 15.7; IR (thin film) ν_{max}: 3228, 2933, 2871, 1475, 1446, 1109, cm^{-1}; HRMS (EI) calcd for $C_{16}H_{28}O_2$: 252.2089, found: 252.2089.



Ketone 80. Alcohol **79** (515 mg, 2.0 mmol, 1.0 equiv) was dissolved in DCM (20 mL). *t*-BuOH (0.6 mL, 6.1 mmol, 3.0 equiv) was added followed by DMP (1.3 g, 3.1 mmol, 1.5 equiv). The milky white suspension was stirred at 23 ºC for 30 min. Et_2O (20 mL) and hexanes (20 mL) were added followed by saturated aqueous solutions of $NaHCO_3$ (20 mL) and $Na_2S_2O_3$ (5 mL). The biphasic mixture was stirred vigorously until clear. The layers were separated and the organic phase was further washed sequentially with a saturated $NaHCO_3$ solution (20 mL), H_2O (20 mL), NaOH (0.1 M, 20 mL), and brine (20 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude material was typically of sufficient purity to be used crude in the next step. An analytically pure sample of **80** could be prepared by preparative TLC (30% Et_2O in hexanes). $[\alpha]_D^{23}$ = –7.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (700 MHz, $CDCl_3$) δ 3.25 (s, 3H), 3.15 (d, *J* = 8.8 Hz, 1H), 3.01 (d, *J* = 8.8 Hz, 1H), 2.51 (qd, *J* = 7.0, 3.5 Hz, 1H), 2.34 (d, *J* = 14.5 Hz, 1H), 2.32 (d, *J* = 14.5 Hz, 1H), 2.15 (t, *J* = 4.5, 3.5 Hz, 1H), 2.04 (dd, *J* = 12.0, 4.5 Hz, 1H), 1.92 – 1.84 (m, 2H), 1.77 (d, *J* = 12.0 Hz, 1H), 1.64 (t, *J* = 8.2 Hz, 1H), 1.58 – 1.52 (m, 1H),

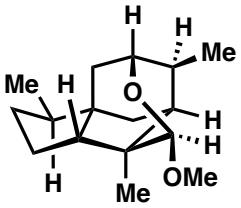
1.47 – 1.41 (m, 1H), 1.36 – 1.30 (m, 1H), 1.13 (d, J = 7.0 Hz, 3H), 0.86 (d, J = 6.7 Hz, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 213.2, 79.8, 58.7, 55.9, 55.7, 54.5, 51.8 (2C, overlapping), 49.1, 46.2, 41.6, 37.1, 26.3, 23.2, 15.7, 13.9; IR (thin film) ν_{max}: 2952, 2873, 1706, 1106, cm^{-1}; HRMS (EI) calcd for $C_{16}H_{26}O_2$: 250.1933, found: 250.1936.



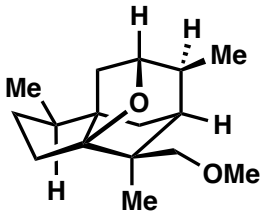
Alcohol 81. Ketone **80** (*ca*. 500 mg, 2.0 mmol, 1.0 equiv) was dissolved in MeOH (20 mL). $NaBH_4$ (150 mg, 4.0 mmol, 2.0 equiv) was added and the resulting solution was stirred at 23 ºC for 30 min. HCl (3.0 M, 2.0 mL) was carefully added followed by Et_2O (20 mL) and hexanes (20 mL). The layers were separated and the organic phase was further washed with H_2O (10 mL) and brine (10 mL), filtered, and concentrated. The crude residue was purified by column chromatography (10 → 30% Et_2O in hexanes) to afford alcohol **81** (407 mg, 1.6 mmol, 79% yield over two steps) as a thick oil which solidified upon standing. $[\alpha]_D^{23}$ = –27.8 (*c* 1.1, $CHCl_3$); ^{1}H NMR (700 MHz, $CDCl_3$) δ 4.01 – 3.97 (m, 1H), 3.60 (d, J = 9.0 Hz, 1H), 3.46 (d, J = 9.0 Hz, 1H), 3.35 (s, 3H), 2.77 (br s, 1H), 2.53 (dd, J = 9.3, 5.9 Hz, 1H), 2.02 (qd, J = 7.3, 3.0 Hz, 1H), 1.89 (dd, J = 11.3, 4.8 Hz, 1H), 1.92 – 1.79 (m, 2H), 1.82 (dddd, J = 11.7, 8.5, 6.4, 5.9 Hz, 1H), 1.74 (dd, J = 4.8, 3.0 Hz, 1H), 1.72 (qt, J = 7.2, 5.9 Hz, 1H), 1.56 (dddd, J = 12.6, 9.3, 8.5, 5.9 Hz, 1H), 1.45 (dq, J = 12.6, 5.9 Hz, 1H), 1.35 (dq, J = 11.7, 5.9 Hz, 1H), 1.13 (d, J = 11.3 Hz, 1H), 1.13 (d, J = 7.7 Hz, 3H), 1.03 (s, 3H), 0.87 (d, J = 7.2 Hz, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 79.9, 69.6, 58.6, 53.2, 52.9, 48.9, 48.2, 47.4, 43.7, 43.2, 41.9, 35.8, 25.7, 24.0, 16.6, 15.7; IR (thin film) ν_{max}: 3473, 2931, 2820, 1448, 1104 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{28}O_2$: 252.2089, found: 252.2089.

Ethers 83 and **84.** Alcohol **81** (50 mg, 0.2 mmol, 1.0 equiv) was dissolved in DCM (6.7 mL) and cooled to 0 ºC. $PhI(OAc)_2$ (192 mg, 0.6 mmol, 3.0 equiv) and I_2 (50 mg, 0.2 mmol, 1.0 equiv) were added. The purple solution was brought into a cold room (*ca*. 5 ºC) where it was vigorously stirred and irradiated by a 90 W halogen lamp for 1 h. Et_2O (5 mL) and hexanes (5 mL) were added followed by saturated aqueous solutions of $NaHCO_3$ (5 mL) and $Na_2S_2O_3$ (1 mL). The biphasic mixture was stirred vigorously while being warmed to room temperature. When the solution had turned colorless, the layers

were separated and the organic phase was further washed with saturated $NaHCO_3$ solution (5 mL), H_2O (5 mL), NaOH (0.1 M, 5 mL), and brine (5 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo* to afford a crude mixture of ethers ***epi*-83**, **83**, and **84**. NMR yield of the crude reaction mixture with 1,3,5-trimethoxybenzene as an internal standard indicated ***epi*-83** was formed in 17% yield, **83** was formed in 26% yield, and **84** was formed in 34% yield, for a combined 77% yield in a 1:1.5:2 ratio of products. The crude mixture was purified by column chromatography (4 → 19% Et_2O in hexanes + 1% Et_3N) to afford **83** (10 mg, 0.04 mmol, 20% yield), and **84** (16 mg, 0.06 mmol, 32%) as clear, colorless oils. ***Epi*-83** was unstable to the purification conditions, and **83** was observed to contain a small amount (*ca.* 10%) of hydrolysis products.

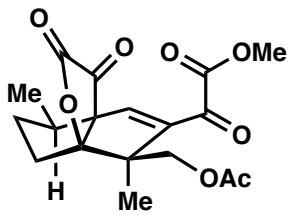


83. $[\alpha]_D^{23}$ = –66.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (700 MHz, $CDCl_3$) δ 4.70 (s, 1H), 4.12 (p, *J* = 2.5 Hz, 1H), 3.51 (s, 3H), 2.55 (ddd, *J* = 10.6, 8.3, 2.1 Hz, 1H), 2.09 (dtd, *J* = 13.6, 8.7, 7.7, 2.5 Hz, 1H), 1.93 (ddd, *J* = 11.3, 6.1, 2.5 Hz, 1H), 1.86 (p, *J* = 7.4, 6.1 Hz, 1H), 1.82 (dt, *J* = 13.6, 2.5 Hz, 1H), 1.67 (qd, *J* = 7.5, 2.5 Hz, 1H), 1.60 – 1.45 (m, 5H), 1.26 – 1.19 (m, 2H), 1.14 (d, *J* = 7.4 Hz, 3H), 1.14 (dd, *J* = 11.3, 2.5 Hz, 1H), 1.01 (s, 3H), 0.84 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 104.1, 76.3, 57.5, 53.9, 51.1, 49.8, 49.0, 46.6, 41.5, 40.1, 39.0, 35.4, 26.5, 22.4, 20.7, 18.8; IR (thin film) ν_{max}: 2954, 2868, 1009 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{26}O_2$: 250.1933, found: 250.1936 .

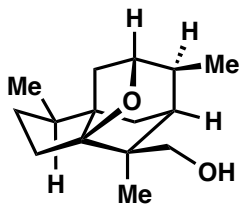


84. $[\alpha]_D^{23}$ = +8.0 (*c* 1.6, $CHCl_3$) ^{1}H NMR (700 MHz, $CDCl_3$) δ 4.12 (d, *J* = 4.7 Hz, 1H), 3.88 (d, *J* = 8.9 Hz, 1H), 3.55 (d, *J* = 8.9 Hz, 1H), 3.33 (s, 3H), 2.14 (t, *J* = 2.9 Hz, 1H), 1.87 (dt, *J* = 11.8, 3.4 Hz, 1H), 1.85 – 1.79 (m, 2H), 1.73 (qd, *J* = 7.5, 2.3 Hz, 1H), 1.71 – 1.67 (m, 1H), 1.67 – 1.63 (m, 1H), 1.63 – 1.60 (m, 1H), 1.59 (d, *J* = 10.4 Hz, 1H), 1.49 (d, *J* = 11.8 Hz, 1H), 1.35 (dd, *J* = 13.3, 6.2 Hz, 1H), 1.17 (d, *J* = 7.5 Hz, 3H), 0.98 (s, 3H), 0.91 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 102.0, 83.0, 78.6, 62.8, 59.0, 54.1, 49.2, 43.6, 42.8, 42.0, 40.7, 36.2, 28.4, 23.7, 19.5, 14.9;

IR (thin film) ν_{max}: 2951, 2869, 1106 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{26}O_2$: 250.1933, found: 250.1936.

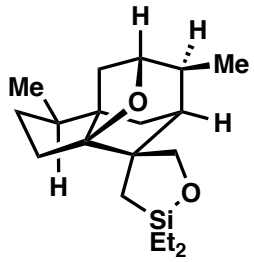


Methyl ester 92. Keto-lactone **89** (616 mg, 2.0 mmol, 1.0 equiv) and SeO_2 (777 mg, 7.0 mmol, 3.5 equiv) were dissolved in diglyme (6 mL) and heated at 120 ºC for 3 h. The reaction mixture was cooled to 23 ºC and acetone (6 mL), K_2CO_3 (970 mg, 7.0 mmol, 3.5 equiv), and Me_2SO_4 (200 µL, 2.0 mmol, 1.0 equiv) were added sequentially. The suspension was stirred for 30 min before being filtered through a pad of celite and directly concentrated. The crude residue was purified by column chromatography (60 → 100% Et_2O in hexanes) to afford **92** (108 mg, 0.30 mmol, 15% yield) and **91** (304 mg, 0.87 mmol, 43% yield), both as white solids. $[\alpha]_D^{23}$ = –106.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.22 (s, 1H), 4.54 (d, *J* = 11.4 Hz, 1H), 3.99 (d, *J* = 11.4 Hz, 1H), 3.93 (s, 3H), 2.36 (dqd, *J* = 12.9, 7.1, 6.0 Hz, 1H), 2.29 (dd, *J* = 14.2, 5.5 Hz, 1H), 2.13 (dt, *J* = 12.9, 6.0 Hz, 1H), 2.02 (ddd, *J* = 14.2, 13.2, 6.0 Hz, 1H), 1.82 (s, 3H), 1.48 (dtd, *J* = 13.2, 12.9, 5.5 Hz, 1H), 1.46 (s, 3H), 1.16 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 192.4, 181.9, 165.5, 161.8, 160.3, 146.4, 141.1, 101.7, 69.0, 65.1, 53.3, 52.5, 46.4, 34.3, 33.6, 20.4, 16.3, 15.8; IR (thin film) ν_{max}: 2957, 2875, 1792, 1771, 1746, 1680, 1185 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{20}O_8Na$ $[M+Na]^+$: 387.1050, found: 387.1048.



Alcohol 103. Acetate **87** (130 mg, 0.47 mmol, 1.0 equiv) and finely ground KOH (80 mg, 1.4 mmol, 3.0 equiv) were dissolved in MeOH (4.7 mL). The reaction mixture was stirred for 48 h at 23 ºC. HCl (2.0 M, 10 mL) and EtOAc (10 mL) were added. The layers were separated, and the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with brine (1 x 30 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude residue was purified by flash column chromatography (20 → 40% EtOAc in hexanes) to provide alcohol **103** (97 mg, 0.41 mmol, 91%) as a crystalline solid. $[\alpha]_D^{23}$ = –4.1 (*c* 0.17, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.15 (d, *J* = 4.3 Hz, 1H), 4.12 (d, *J* = 11.0 Hz, 1H), 3.89 (d, *J* = 11.0 Hz, 1H), 2.10 – 2.06 (m, 1H), 1.91 (dt, *J* = 11.8, 3.5 Hz, 1H), 1.88 – 1.80 (m, 2H), 1.79 – 1.63 (m,

3H), 1.60 (d, J = 10.5 Hz, 1H), 1.52 (d, J = 11.8 Hz, 1H), 1.41 – 1.34 (m, 1H), 1.19 (d, J = 7.5 Hz, 3H), 1.02 (s, 3H), 0.92 (d, J = 6.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 101.8, 82.9, 68.0, 63.1, 54.2, 50.6, 43.6, 42.7, 41.9, 40.7, 36.3, 28.9, 22.6, 20.0, 14.9; IR (thin film) ν_{max}: 3318, 2950, 2868, 1452, 1326, 1036, 985 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{24}O_2Na$ $[M+Na]^+$: 259.1669, found: 259.1667.

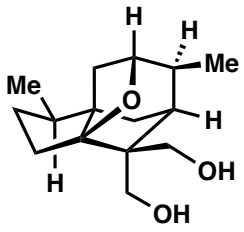


Oxasilacyclopentane SI-3. All operations for the following procedure were carried out in a nitrogen-filled glovebox with rigorous exclusion of moisture and oxygen.

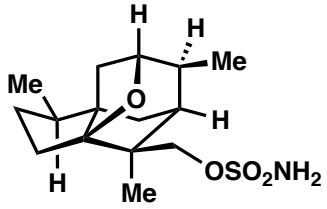
i) Alcohol **103** (150 mg, 0.63 mmol, 1.0 equiv) and $[Ir(COD)(OMe)]_2$ (2.1 mg, 0.0032 mmol, 0.5 mol%) were dissolved in THF (6.4 mL). Et_2SiH_2 (123 μL, 0.95 mmol, 1.5 equiv) was then added. The reaction mixture was stirred at room temperature for 12 h, followed by direct concentration *in vacuo* to provide a crude intermediate that was used immediately in the next step without further purification.

ii) The crude intermediate obtained from above was carefully azeotroped with anhydrous toluene three times [*Note:* It is critical to remove trace Et_2SiH_2]. $[Rh(COE)_2Cl]_2$ (9.1 mg, 0.013 mmol, 2 mol%), (*S*)-DTBM-SegPhos® (30 mg, 0.025 mmol, 4 mol%), and norbornene (72 mg, 0.76 mmol, 1.2 equiv) were added and the combined materials were dissolved in THF (12.8 mL). The reaction mixture was stirred at 23 ºC for 0.5 h then heated at 100 °C for 12 h. Upon cooling to room temperature, the mixture was exposed to ambient atmosphere and concentrated directly *in vacuo*. The crude residue was then purified by flash column chromatography (10% → 30% Et_2O in hexanes) to provide oxasilacyclopentane **SI-3** (51 mg, 0.16 mmol, 25% yield) as a pale-yellow oil. An analytical sample was further purified by preparative TLC (40% Et_2O in hexanes) to give **SI-3** as a colorless oil. $[\alpha]_D^{23}$ = –36.7 (*c* 0.75, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.76 (d, J = 10.0 Hz, 1H), 4.07 (d, J = 4.7 Hz, 1H), 3.74 (d, J = 10.0 Hz, 1H), 2.04 – 1.95 (m, 2H), 1.91 – 1.80 (m, 2H), 1.73 – 1.65 (m, 3H), 1.65 – 1.58 (m, 1H), 1.57 – 1.44 (m, 3H), 1.07 – 0.96 (m, 9H), 0.93 (d, J = 5.3 Hz, 3H), 0.89 (d, J = 15.5 Hz, 1H), 0.78 (dq, J = 15.8, 8.0 Hz, 1H), 0.72 – 0.58 (m, 3H), 0.44 (d, J = 15.5 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 101.1, 82.8, 71.7, 62.7, 58.4, 56.9, 43.8, 42.9, 42.5, 40.8, 36.4, 29.5, 21.1, 19.0, 14.9, 7.1,

6.9, 6.8, 5.7; IR (thin film) ν_{max}: 2950, 2873, 1455, 1055, 1017, 971, 813, 783 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{32}O_2{}^{28}Si$: 320.2172, found: 320.2174.

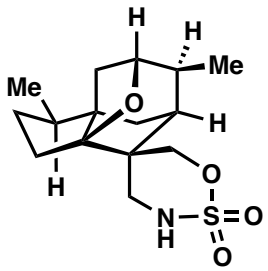


Diol 105. Oxasilacyclopentane **SI-3** (4 mg, 0.013 mmol, 1.0 equiv) and $KHCO_3$ (6.3 mg, 0.063 mmol, 5.0 equiv) were dissolved in THF/MeOH (1:1, 0.3 mL). H_2O_2 (50 wt% in H_2O, 10 µL, 0.13 mmol, 10.0 equiv) was added and the resulting mixture was heated at 50 ºC for 36 h. [*Caution:* gas pressure buildup.] Upon cooling to room temperature, saturated *aq*. $Na_2S_2O_3$ (1.0 mL) was added, followed by EtOAc (2.0 mL). The layers were separated, and the aqueous layer was further extracted with EtOAc (3 x 1.0 mL). The combined organic layers were washed with brine (1 x 5.0 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude residue was purified by preparative TLC (100% Et_2O) to afford diol **105** (2.4 mg, 0.01 mmol, 76% yield) as a white solid. $[\alpha]_D^{23}$ = –2.5 (*c* 0.16, $CHCl_3$); ^{1}H NMR (700 MHz, $CDCl_3$) δ 4.42 (d, *J* = 10.8 Hz, 1H), 4.16 (d, *J* = 4.7 Hz, 1H), 4.08 (d, *J* = 10.8 Hz, 1H), 3.73 (d, *J* = 11.2 Hz, 1H), 3.58 (br d, *J* = 11.2 Hz, 1H), 2.61 (s, 1H), 2.51 (br s, 1H), 1.88 (dt, *J* = 12.2, 3.3 Hz, 1H), 1.86 – 1.75 (m, 4H), 1.71 (dp, *J* = 12.3, 6.4 Hz, 1H), 1.67 – 1.61 (m, 1H), 1.62 (d, *J* = 10.6 Hz, 1H), 1.60 (d, *J* = 12.3 Hz, 1H), 1.41 (td, *J* = 14.1, 12.2, 6.4 Hz, 1H), 1.35 (dd, *J* = 14.1, 7.3 Hz, 1H), 1.25 (d, *J* = 7.5 Hz, 3H), 0.93 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 100.6, 82.8, 68.2, 68.2, 63.3, 53.4, 48.2, 42.9, 42.6, 41.6, 40.1, 36.0, 28.1, 19.7, 14.8; IR (thin film) ν_{max}: 3206, 2934, 2891, 1455, 1104, 1030, 993 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{23}O_3$ $[M–H]^-$: 251.1653, found: 251.1649.



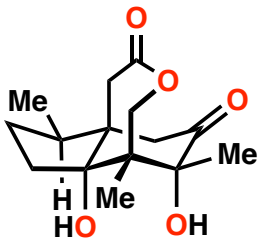
Sulfamate 106. First, a solution of sulfamoyl chloride was prepared by the following procedure chlorosulfonyl isocyanate (130 µL, 1.5 mmol, 1.5 equiv) was dissolved in MeCN (0.75 mL) and cooled to 0 ºC. Formic acid (57 µL, 1.5 mmol, 1.5 equiv) was added and the resulting solution was stirred at 0 ºC for 1 h and then was allowed to warm to 23 ºC and stirred at that temperature for 12 h. In a separate flask, sodium hydride (60 wt% in mineral oil, 43 mg, 1.1 equiv) was washed with hexanes (3 x 1 mL) and dried under high vacuum for 10 min. DMF (1 mL)

was added and the suspension was cooled to 0 ºC. Alcohol **103** (236 mg, 1.0 mmol, 1.0 equiv) was dissolved in DMF (0.5 mL) and added dropwise to the suspension of sodium hydride. The reaction mixture was allowed to warm to 23 ºC and was stirred at that temperature for 1 h before being re-cooled to 0 ºC. The sulfamoyl chloride solution (1.5 mmol assumed) was added dropwise and the resulting solution was allowed to warm to 23 ºC and stirred at that temperature for 4 h. H_2O (5 mL) was carefully added followed by Et_2O (5 mL). The layers were separated and the aqueous layer was further extracted with Et_2O (2 x 5 mL). The combined organic layers were washed with brine (5 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude residue was purified by column chromatography (50 → 80% Et_2O in hexanes) to afford sulfamate **106** as a white solid. $[\alpha]_D^{23}$ = +0.8 (*c* 2.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.01 (s, 2H), 4.70 (d, *J* = 9.0 Hz, 1H), 4.49 (d, *J* = 9.0 Hz, 1H), 4.18 (d, *J* = 4.7 Hz, 1H), 2.14 (t, *J* = 2.7 Hz, 1H), 1.93 (dt, *J* = 12.1, 3.3 Hz, 1H), 1.88 – 1.83 (m, 2H), 1.80 (qd, *J* = 7.6, 1.9 Hz, 1H), 1.74 – 1.61 (m, 4H), 1.57 (d, *J* = 12.0 Hz, 1H), 1.45 – 1.37 (m, 1H), 1.18 (dd, *J* = 7.6, 1.0 Hz, 3H), 1.05 (s, 3H), 0.92 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 101.9, 83.1, 77.0, 63.1, 54.6, 48.6, 43.2, 42.6, 41.9, 40.5, 36.2, 28.7, 22.4, 19.9, 14.8; IR (thin film) ν_{max}: 3357, 3279, 2955, 2871, 1373, 1178 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{25}O_4NNaS$ $[M+Na]^+$: 338.1397, found: 338.1394.

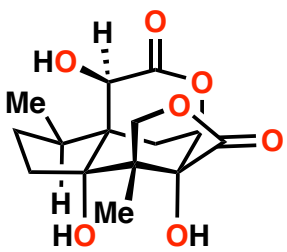


Cyclic sulfamate 107. Rh_2esp_2 (3 mg, 0.002 mmol, 3 mol%) and $PhI(OPiv)_2$ (78 mg, 0.095 mmol, 1.5 equiv) were combined as solids. Sulfamate **106** (40 mg, 0.063 mmol, 1.0 equiv) was dissolved in benzene (1 mL) and added to the mixture. The resulting suspension was stirred at 23 ºC for 16 h. The reaction mixture was directly concentrated *in vacuo* and purified by column chromatography to afford cyclic sulfamate **107** (25 mg, 0.04 mmol, 63% yield) as a white solid. $[\alpha]_D^{23}$ = +2.0 (*c* 0.5, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.06 (dd, *J* = 12.3, 2.7 Hz, 1H), 4.97 (d, *J* = 12.3 Hz, 1H), 4.42 (t, *J* = 9.5, 5.3 Hz, 1H), 4.21 (d, *J* = 4.7 Hz, 1H), 3.50 (dd, *J* = 14.8, 9.5 Hz, 1H), 3.31 (dt, *J* = 14.8, 5.3, 2.7 Hz, 1H), 2.49 (t, *J* = 3.0 Hz, 1H), 1.94 – 1.83 (m, 3H), 1.81 (dt, *J* = 12.7, 3.3 Hz, 1H), 1.74 – 1.59 (m, 4H), 1.59 – 1.51 (m, 2H), 1.23 (d, *J* = 7.4 Hz, 3H), 0.95 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 100.1, 83.1, 77.5, 63.3, 50.7,

49.9, 46.6, 42.6, 42.4, 42.0, 40.0, 35.7, 28.2, 19.5, 14.6; IR (thin film) ν_{max}: 3300, 2951, 2874, 1361, 1185 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{23}O_4NNaS$ $[M+Na]^+$: 336.1246, found: 336.1243.

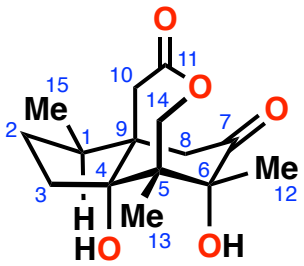


(–)-3-Deoxypseudoanisatin (77). A stock solution of $Co(acac)_2$ (0.1 mg, 0.0005 mmol, 0.1 equiv) in THF (0.3 mL) was added to neat alkene **76** (1.3 mg, 0.005 mmol, 1.0 equiv) at 0 ºC. $PhSiH_3$ (2.4 µL, 0.02 mmol, 4.0 equiv) was added and dry O_2 gas was sparged through the mixture for 1 min. The solution was kept under a positive pressure of oxygen and was stirred vigorously for 24 h at 0 °C. Saturated *aq*. $Na_2S_2O_3$ (1.0 mL) and EtOAc (1 mL) were added, the layers were separated, and the aqueous layer was further extracted with EtOAc (3 x 1.0 mL). The combined organic layers were washed with brine (1 x 5.0 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude residue was purified by preparative TLC (100% EtOAc) to afford lactone **75** (0.7 mg, 0.0025 mmol, 50% yield) and (–)-3-deoxypseudoanisatin (**77**, 0.4 mg, 0.0015 mmol, 29% yield), both of which were colorless oils. Characterization data were in agreement with previously reported values.[17] $[\alpha]_D^{23}$ = –23.1 (*c* 0.13, MeOH); ^{1}H NMR (900 MHz, CD_3OD) δ 4.45 (d, *J* = 13.9 Hz, 1H), 3.94 (d, *J* = 13.9 Hz, 1H), 3.00 (dd, *J* = 15.9, 2.3 Hz, 1H), 2.66 (dd, *J* = 15.2, 2.3 Hz, 1H), 2.57 (ddq, *J* = 9.8, 9.5, 7.1 Hz, 1H), 2.42 (d, *J* = 15.2 Hz, 1H), 2.32 (d, *J* = 15.9 Hz, 1H), 2.26 (ddd, *J* = 14.2, 11.7, 5.5 Hz, 1H), 2.08 (dtd, *J* = 13.8, 9.5, 5.5 Hz, 1H), 1.71 (ddd, *J* = 14.2, 9.5, 3.8 Hz, 1H), 1.34 (dddd, *J* = 13.8, 11.7, 9.8, 3.8 Hz, 1H), 1.31 (s, 3H), 1.15 (s, 3H), 0.93 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (900 MHz, CD_3OD) δ 208.4, 176.5, 88.4, 79.3, 71.1, 50.5, 47.9, 43.4, 41.7, 36.6, 30.5, 28.9, 17.9, 14.3, 14.0; IR (thin film) ν_{max}: 3383, 2955, 1732, 1466, 1432, 1379, 1309, 1160, 1102, 1063, 918 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{22}O_5Na$ $[M+Na]^+$: 305.1359, found: 305.1355.



(–)-Neomajucin (100). (–)-3,4-dehydroneomajucin (**99**, 4.5 mg, 0.015 mmol, 1.0 equiv) and $Mn(dpm)_3$ (1.9 mg, 0.0031 mmol, 0.2 equiv) were dissolved in DCM/*i*-PrOH (4:1, 0.3 mL) and cooled to 0 ºC. TBHP (*ca*. 5 M in decane, 4.6 µL, 0.023 mmol, 1.5 equiv) and $PhSiH_3$ (3.8 µL, 0.031 mmol, 2.0 equiv) were added sequentially. Dry O_2 gas was sparged through the mixture for 1 min. The reaction mixture was kept under a positive pressure of O_2 and vigorous stirring was continued for 20 h at 0 °C. Saturated *aq*. $Na_2S_2O_3$ (1.0 mL) and EtOAc (1 mL) were added, the layers were separated, and the aqueous layer was further extracted with EtOAc (3 x 1.0 mL). The combined organic layers were washed with brine (1 x 5.0 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude residue was purified by preparative TLC (50% EtOAc in hexanes) to afford (–)-neomajucin (**100**, 2.4 mg, 0.0075 mmol, 50% yield) as a white foam. NMR samples for this compound were referenced to an internal standard of tetramethylsilane (δ = 0.00). Characterization data were in agreement with the previously reported values.[18] $[\alpha]_D^{23}$ = –45.2 (*c* 0.25, *p*-dioxane); ^{1}H NMR (600 MHz, C_5D_5N) δ 8.76 (d, *J* = 5.0 Hz, 1H), 8.49 (s, 1H), 5.73 (s, 1H), 5.12 (dd, *J* = 3.4, 2.5 Hz, 1H), 5.02 (d, *J* = 11.0 Hz, 1H), 4.67 (d, *J* = 5.0 Hz, 1H), 4.19 (d, *J* = 11.0 Hz, 1H), 3.01 (dd, *J* = 14.3, 2.5 Hz, 1H), 2.90 (ddq, *J* = 9.5, 8.6, 7.0 Hz, 1H), 2.40 (ddd, *J* = 11.8, 11.6, 6.4 Hz, 1H), 2.29 (dtd, *J* = 12.2, 9.4, 6.4 Hz, 1H), 2.00 (dd, *J* = 14.3, 3.4 Hz, 1H), 1.98 (ddd, *J* = 11.8, 9.4, 2.5 Hz, 1H), 1.91 (dddd, *J* = 12.2, 11.6, 8.6, 2.5 Hz, 1H), 1.70 (s, 3H), 1.18 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, C_5D_5N) δ 177.8, 175.1, 83.9, 80.7, 79.7, 72.6, 70.7, 50.9, 47.5, 39.4, 31.7, 31.6, 27.4, 21.5, 14.4; IR (thin film) ν_{max}: 3384, 2932, 1767, 1718, 1371, 1223, 1120, 1085, 998, 752 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{19}O_7$ $[M–H]^-$: 311.1136, found: 311.1134.

(–)-3-Deoxypseudoanisatin ^{1}H spectra comparison:

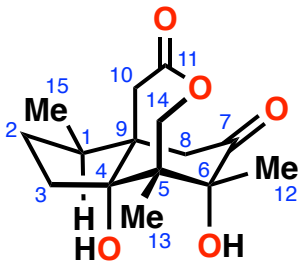


(–)-3-deoxypseudoanisatin

Position	^{1}H NMR (δ) Natural Sample (400 MHz, CD_3OD)[17]	^{1}H NMR (δ) Synthetic Sample (900 MHz, CD_3OD)
1	2.55 (qdd, *J* =7.0, 3.5, 1.0 Hz, 1H)	2.57 (ddq, *J* = 9.8, 9.5, 7.1 Hz, 1H)
2*β*	1.35 (dddd, *J* = 12.0, 9.5, 5.5, 1.0 Hz, 1H)	1.34 (dddd, *J* =13.8, 11.7, 9.8, 3.8 Hz, 1H)
2*α*	2.07 (dddd, *J* = 12.0, 11.8, 3.5, 3.3 Hz, 1H)	2.08 (dtd, *J* = 13.8, 9.5, 5.5 Hz, 1H)
3*β*	1.70 (ddd, *J* = 13.5, 9.8, 3.3 Hz, 1H)	1.71 (ddd, *J* = 14.2, 9.5, 3.8 Hz, 1H)
3*α**	2.60 (ddd, *J* = 13.5, 11.8, 5.5 Hz, 1H)	2.26 (ddd, *J* = 14.2, 11.7, 7.5 Hz, 1H)
8*β*	2.41 (d, *J* = 15.0 Hz, 1H)	2.42 (d, *J* = 15.2 Hz, 1H)
8*α*	2.65 (dd, *J* = 15.0, 1.9 Hz, 1H)	2.66 (dd, *J* = 15.2, 2.3 Hz, 1H)
10*β*	3.00 (dd, *J* = 15.8, 1.9 Hz, 1H)	3.00 (dd, *J* = 15.9, 2.3 Hz, 1H)
10*α*	2.31 (d, *J* = 15.8 Hz, 1H)	2.32 (d, *J* = 15.9 Hz, 1H)
12	1.30 (s, 3H)	1.31 (s, 3H)
13	1.14 (s, 3H)	1.15 (s, 3H)
14*β*	4.44 (d, *J* = 13.9 Hz, 1H)	4.45 (d, *J* = 13.9 Hz, 1H)
14*α*	3.93 (d, *J* = 13.9 Hz, 1H)	3.94 (d, *J* = 13.9 Hz, 1H)
15	0.91 (d, *J* = 7.0 Hz, 3H)	0.93 (d, *J* = 7.1 Hz, 3H)

*The chemical shift of proton 3α appears to have been tabulated incorrectly in the original publication. Direct spectral comparison with a spectrum of natural (–)-3-deoxypseudoanisatin kindly provided by Prof. Y. Fukuyama indicates the chemical shift is very close to δ = 2.26 ppm, in agreement with the synthetic sample's value.

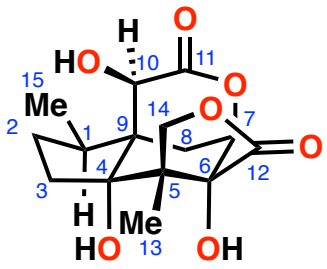
(–)-3-Deoxypseudoanisatin ^{13}C spectra comparison:



(–)-3-deoxypseudoanisatin

Position	^{13}C NMR (δ) Natural Sample (101 MHz, CD_3OD)[17]	^{13}C NMR (δ) Synthetic Sample (226 MHz, CD_3OD)
1	41.6	41.7
2	28.7	28.9
3	30.3	30.5
4	88.2	88.4
5	48.5	47.9
6	79.2	79.3
7	208.2	208.4
8	36.4	36.6
9	50.1	50.5
10	43.2	43.4
11	176.4	176.5
12	17.7	17.9
13	14.2	14.3
14	70.9	71.1
15	13.9	14.0

(–)-Neomajucin ^{1}H spectra comparison:

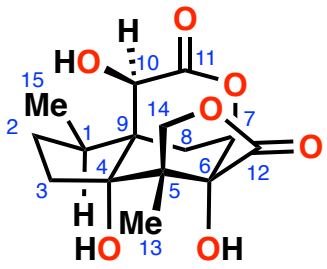


(–)-neomajucin

Position	^{1}H NMR (δ) Natural Sample (400 MHz, C_5D_5N)[18c]	^{1}H NMR (δ) Synthetic Sample (600 MHz, C_5D_5N)
1	2.90 (m, 1H)	2.90 (ddq, *J* = 9.5, 8.6, 7.0 Hz, 1H)
2*	2.39 (m, 1H)* 2.29 (m, 1H)	2.29 (dtd, *J* = 12.2, 9.4, 6.4 Hz, 1H) 1.91 (dddd, *J* = 12.2, 11.6, 8.6, 2.5 Hz, 1H)
3*	1.85-2.05 (m, 2H)*	2.40 (ddd, *J* = 11.8, 11.6, 6.4 Hz, 1H) 1.98 (ddd, *J* = 11.8, 9.4, 2.5 Hz, 1H)
4-OH	-	5.73 (s, 1H)‡
6-OH	-	8.49 (s, 1H)‡
7	5.12 (dd, *J* = 2.6, 2.5 Hz, 1H)	5.12 (dd, *J* = 3.4, 2.5 Hz, 1H)
8*β*	2.00 (dd, *J* = 14.2, 2.6 Hz, 1H)	2.00 (dd, *J* = 14.3, 3.4 Hz, 1H)
8*α*	3.01 (dd, *J* = 14.2, 2.5 Hz, 1H)	3.01 (dd, *J* = 14.3, 2.5 Hz, 1H)
10*β*	4.66 (br d, *J* = 4.8 Hz, 1H)	4.67 (d, *J* = 5.0 Hz, 1H)
10-OH	8.78 (br d, *J* = 4.8 Hz, 1H)	8.76 (d, *J* = 5.0 Hz, 1H)
13	1.70 (br s, 3H)	1.70 (s, 3H)
14*β*	4.19 (d, *J* = 11.0 Hz, 1H)	4.19 (d, *J* = 11.0 Hz, 1H)
14*α*	5.02 (d, *J* = 11.0 Hz, 1H)	5.02 (d, *J* = 11.0 Hz, 1H)
15	1.18 (d, *J* = 7.0 Hz, 3H)	1.18 (d, *J* = 7.0 Hz, 3H)

*Protons on positions 2 and 3 are likely misassigned in the original publications. Without higher field instrumentation, it was presumably challenging to accurately characterize the multiplicities and/or 2D HSQC correlations (carbons 2 and 3 are separated in chemical shift by only 0.1-0.2 ppm) of these protons, leading to the observed assignments.
‡Indicates tentative assignment.

(–)-Neomajucin ^{13}C spectra comparison:



(–)-neomajucin

Position	^{13}C NMR (δ) Natural Sample (101 MHz, C_5D_5N)[18c]	^{13}C NMR (δ) Synthetic Sample (151 MHz, C_5D_5N)
1	39.4	39.4
2	31.4	31.6
3	31.6	31.7
4	84.1	83.9
5	47.5	47.5
6	79.6	79.7
7	80.5	80.7
8	27.5	27.4
9	51.0	50.9
10	70.7	70.7
11	174.8	175.1
12	177.2	177.8
13	21.4	21.5
14	72.6	72.6
15	14.3	14.4

References:

(1) Eisenbraun, E. J.; Payne, K. W.; Bymaster, J. S. Dehydration of cedrol to α-cedrene using copper(II) sulfate and other acidic salts. *Org. Prep. Proced. Intl.* **2000**, *32*, 557.

(2) White, M. C.; Doyle, A. G.; Jacobsen, E. N. A Synthetically Useful, Self-Assembling MMO Mimic System for Catalytic Alkene Epoxidation with Aqueous H_2O_2. *J. Am. Chem. Soc.* **2001**, *123*, 7194.

(3) Morra, N. A.; Pagenkopf, B. L. Direct Synthesis of 2,5-Dihalosiloles. *Org. Synth.* **2008**, *85*, 53.

(4) (a) Sauers, A. L.; Ho, D. M.; Bernhard, S. Synthesis and Characterization of Highly Conjugated, Chiral Bridging Ligands. *J. Org. Chem.* **2004**, *69*, 8910. (b) Gómez, L.; Garcia-Bosch, I.; Company, A.; Benet-Buchholz, J.; Polo, A.; Sala, X.; Ribas, X.; Costas, M. Stereospecific C–H Oxidation with H_2O_2 Catalyzed by a Chemically Robust Site-Isolated Iron Catalyst. *Angew. Chem. Int. Ed.* **2009**, *48*, 5720.

(5) (a) Barton, D. H. R.; Beloeil, J.-C.; Billion, A.; Boivin, J.; Lallemand, J.-Y.; Lelandais, P.; Mergui, S. Functionalisation of saturated hydrocarbons. Part XI. Oxidation of cedrol, ß- and γ-eudesmol, sclareol, manoyl oxide, 1,9-dideoxyforskolin, methyl trans-dihydroiasmonate, and tetrahydrolinalool by the 'Gif system.' *Helv. Chim. Acta.* **1987**, *70*, 2187. (b) Horn, E. J.; Rosen, B. R.; Chen, Y.; Tang, J.; Chen, K.; Eastgate, M. D.; Baran, P. S. Scalable and sustainable electrochemical allylic C–H oxidation. *Nature* **2016**, *533*, 77.

(6) Pierre, M.-C.; Tenaglia, A.; Santelli, M. Synthesis of Angular Triquinanes from (+)-β-cedrol. *Tetrahedron.* **1998**, *54*, 14803.

(7) Uyanik, M.; Yasui, T.; Ishihara, K. Hypervalent iodine-catalyzed oxylactonization of ketocarboxylic acids to ketolactones. *Bioorg. Med. Chem. Lett.* **2009**, *19*, 3848.

(8) Zhang, S.; Lian, F.; Xue, M.; Qin, T.; Li, L.; Zhang, X.; Xu, K. Electrocatalytic Dehydrogenative Esterification of Aliphatic Carboxylic Acid: Access to Bioactive Lactones. *Org. Lett.* **2017**, *19*, 6622.

(9) Mokale, S. N.; Shinde, S. S.; Elgire, R. D.; Sangshetti, J. N.; Shinde, D. B. Synthesis and anti-inflammatory activity of some 3-(4,6-disubtituted-2-thioxo-1,2,3,4-tetrahydropyrimidin-5-yl) propanoic acid derivatives. *Bioorg. Med. Chem. Lett.* **2010**, *20*, 4424.

(10) Jiang, X.; Liu, S.; Yang, S.; Jing, M.; Xu, L.; Yu, P.; Wang, Y.; Yeung, Y.-Y. Enantioselective Bromolactonization of Deactivated Olefinic Acids. *Org. Lett.* **2018**, *20*, 3259.

(11) Armstrong, A.; Ashraff, C.; Chung, H.; Murtagh, L. Oxidative rearrangement of 2-alkoxy-3,4-dihydro-2*H*-pyrans: stereocontrolled synthesis of 4,5-cis-disubstituted tetrahydrofuranones including whisky and cognac lactones and crobarbatic acid. *Tetrahedron* **2009**, *65*, 4490.

(12) Junker, A.; Yamaguchi, J.; Itami, K.; Wünsch, B. Synthesis of Thiophene-Based TAK-779 Analogues by C–H Arylation. *J. Org. Chem.* **2013**, *78*, 5579.

(13) Ding, Y.; Huang, Z.; Yin, J.; Lai, Y.; Zhang, S.; Zhang, Z.; Fang, L.; Peng, S.; Zhang, Y. DDQ-promoted dehydrogenation from natural rigid polycyclic acids or flexible alkyl acids to generate lactones by a radical ion mechanism. *Chem. Commun.* **2011**, *47*, 9495.

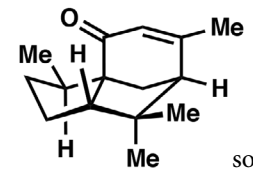
(14) Nair, L. G.; Saksena, A.; Lovey, R.; Sannigrahi, M.; Wong, J.; Kong, J.; Fu, X.; Girijavallabhan, V. A Facile and Efficient Synthesis of 3,3-Dimethyl Isopropylidene Proline From (+)-3-Carene. *J. Org. Chem.* **2010**, *75*, 1285.

(15) Vermeulen, N. A.; Chen, M. S; White, M. C. The Fe(PDP)-catalyzed aliphatic C–H oxidation: a slow addition protocol. *Tetrahedron* **2009**, *65*, 3078.

(16) Ohtawa, M.; Krambis, M. J.; Cerne, R.; Schkeryantz, J. M.; Witkin, J. M.; Shenvi, R. A. Synthesis of (–)-11-*O*-Debenzoyltashironin: Neurotrophic Sesquiterpenes Cause Hyperexcitation *J. Am. Chem. Soc.* **2017**, *139*, 9637.

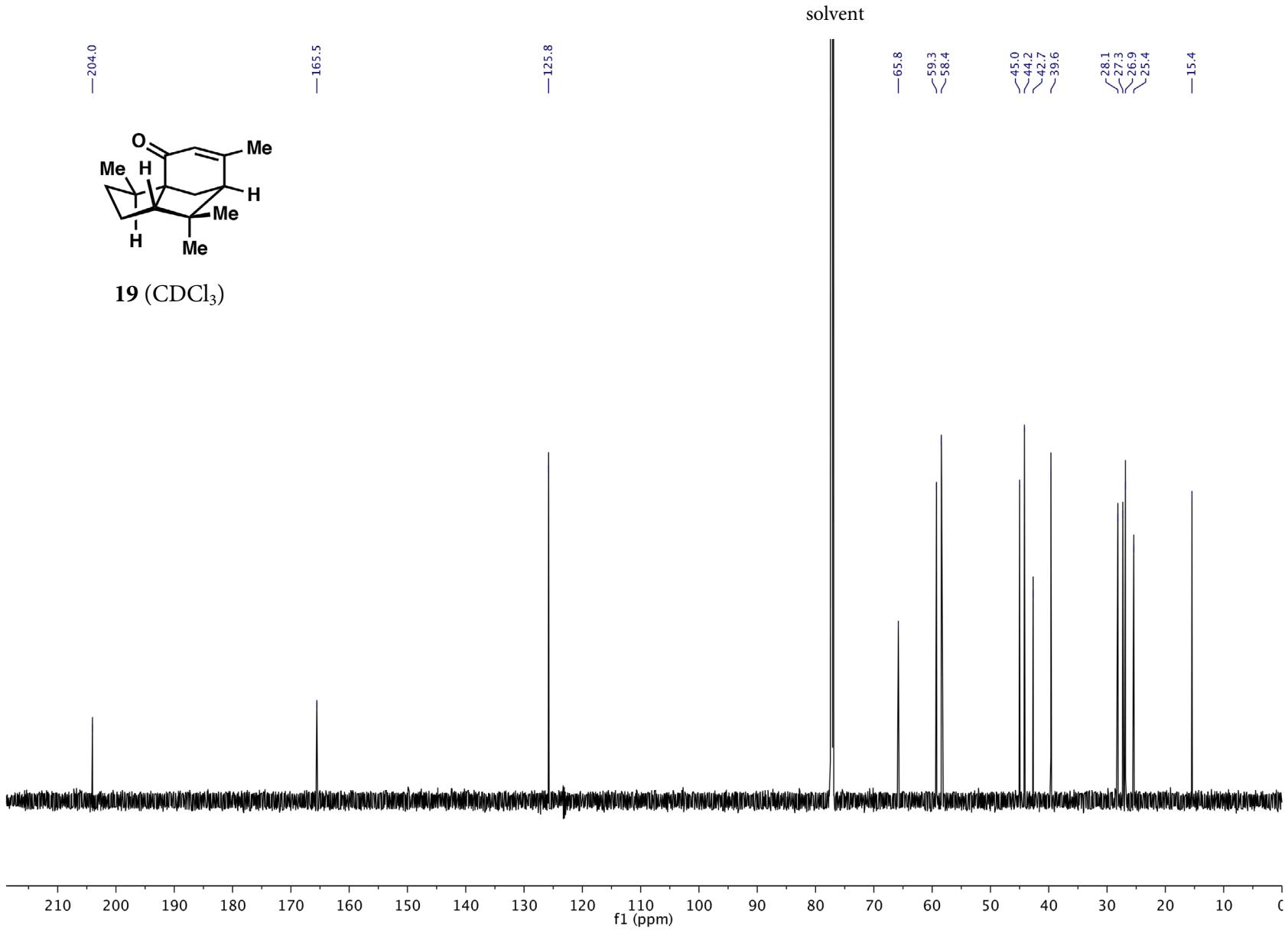
(17) Huang, J.-M.; Yang, C.-S.; Zhao, R.; Takahashi, H.; Fukuyama, Y. Seven Novel *seco*-Prezizaane-Type Sesquiterpenes from the Pericarps of *Illicium merrillianum*. *Chem. Pharm. Bull.* **2004**, *52*, 104.

(18) (a) Yang, C.-S.; Kouno, I.; Kawano, N.; Sato, S. New Anisatin-like Sesquiterpenes from the Pericarps of *Illicium majus. Tetrahedron Lett*. **1988**, *29*, 1165. (b) Kouno, I.; Baba, N.; Hashimoto, M.; Kawano, N.; Takahashi, M.; Kaneto, H.; Yang, C.-S.; Sato, S. Isolation of Three New Sesquiterpene Lactones from the Periarps of *Illicium majus*. *Chem. Pharm. Bull.* **1989**, *37*, 2448. (c) Kouno, I.; Baba, N.; Hashimoto, M.; Kawano, N.; Takahashi, M.; Kaneto, H.; Yang, C.-S. Sesquiterpene Lactofnes from the Pericarps of *Illicium majus*: 2-Oxy Derivatives of Neomajucin and 3, 4-Dehydroxyneomajucin. *Chem. Pharm. Bull*. **1990**, *38*, 422.

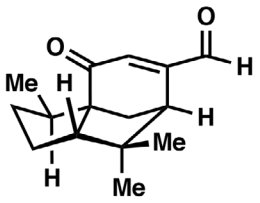

O
Me
Me
H
H
Me
H
Me

19 ($CDCl_3$)

solvent
1.00
1.06
4.51
2.23
2.22
2.30
1.06
3.45
3.30
3.45
f1 (ppm)

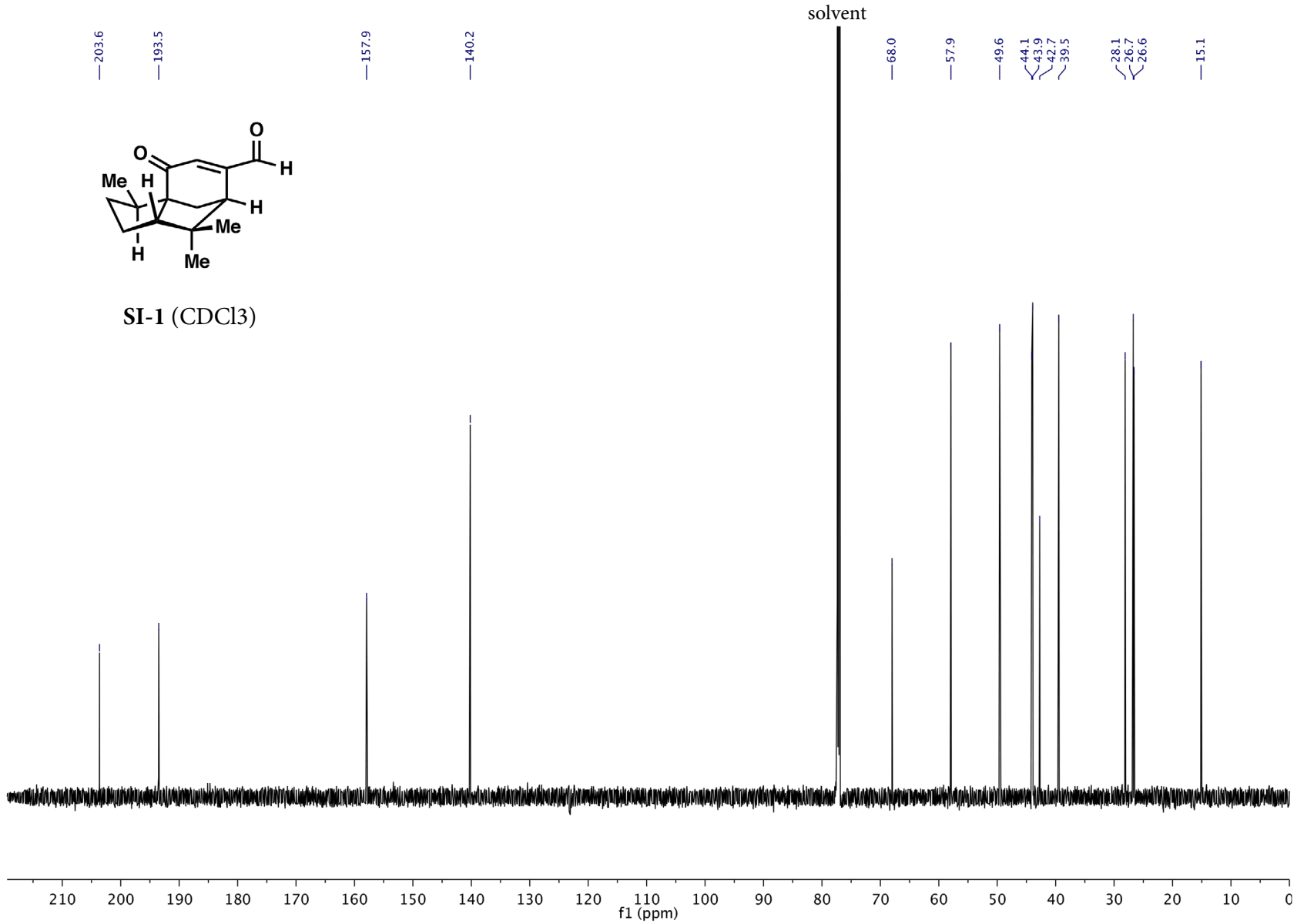

solvent
204.0
165.5
125.8
65.8
59.3
58.4
45.0
44.2
42.7
39.6
28.1
27.3
26.9
25.4
15.4
O
Me
Me
H
H
Me
H
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

19 ($CDCl_3$)

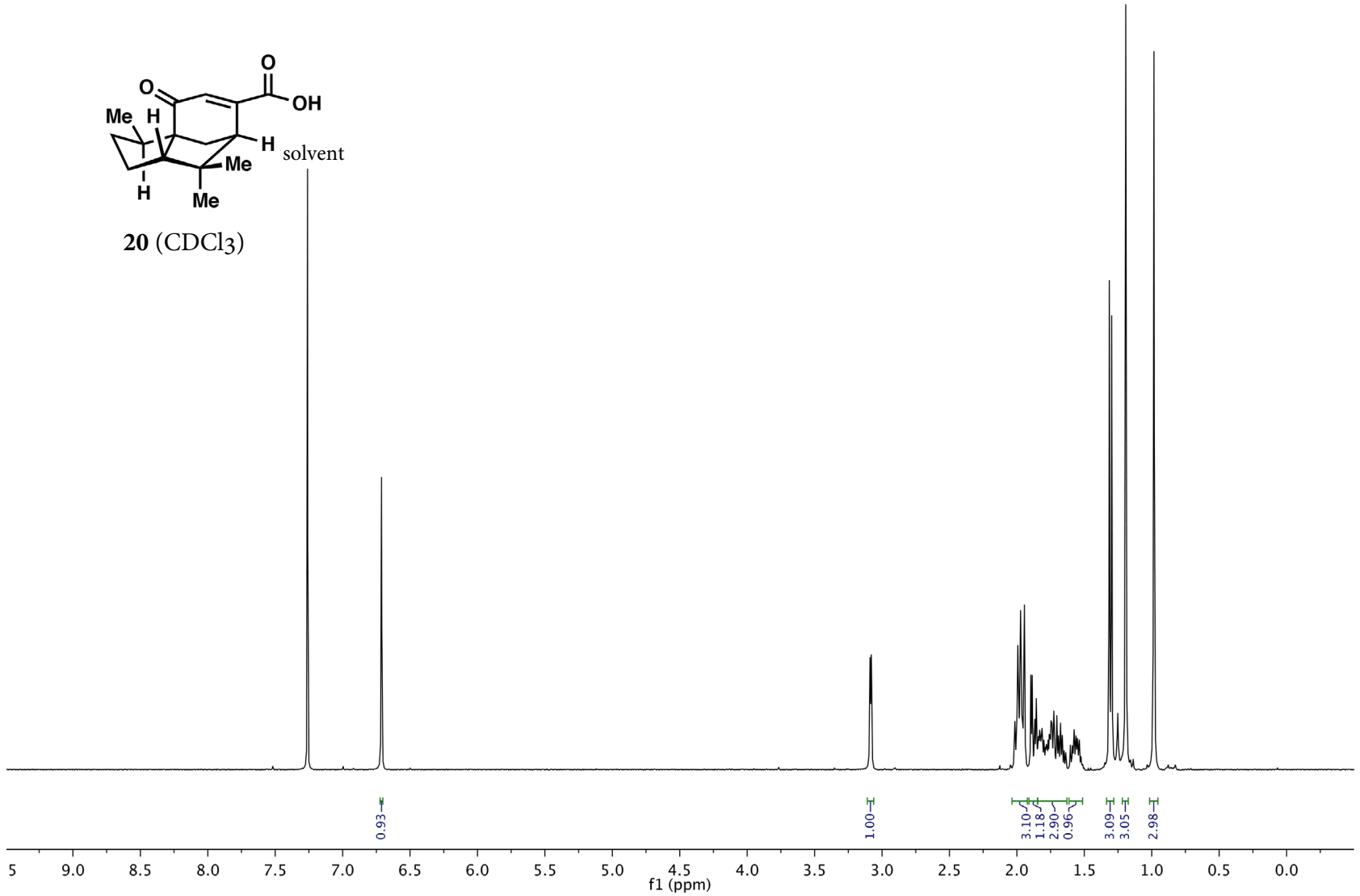

O
O
H
Me
H
H
Me
H
Me

SI-1 ($CDCl_3$)

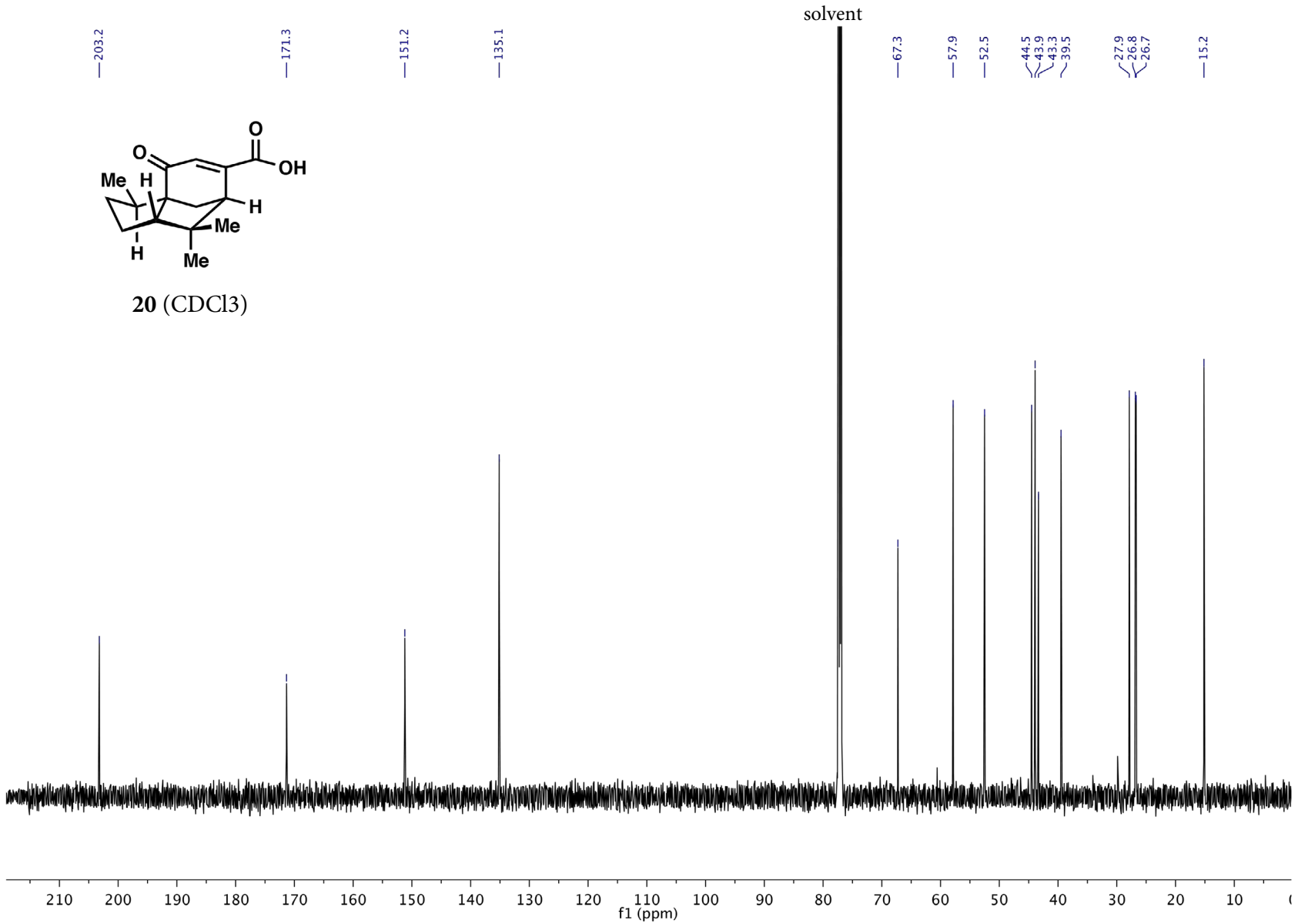
solvent
0.98
0.98
1.00
2.15
2.16
1.09
1.10
1.10
1.61
3.19
3.18
3.13
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)


solvent
203.6
193.5
157.9
140.2
68.0
57.9
49.6
44.1
43.9
42.7
39.5
28.1
26.7
26.6
15.1
O
O
H
Me
H
H
Me
H
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

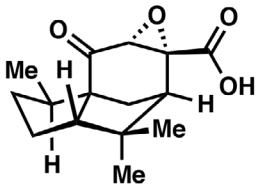
SI-1 (CDCl3)


O
O
OH
Me
H
H
Me
H
Me
solvent
0.93
1.00
3.10
1.18
2.90
0.96
3.09
3.05
2.98
5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

20 ($CDCl_3$)

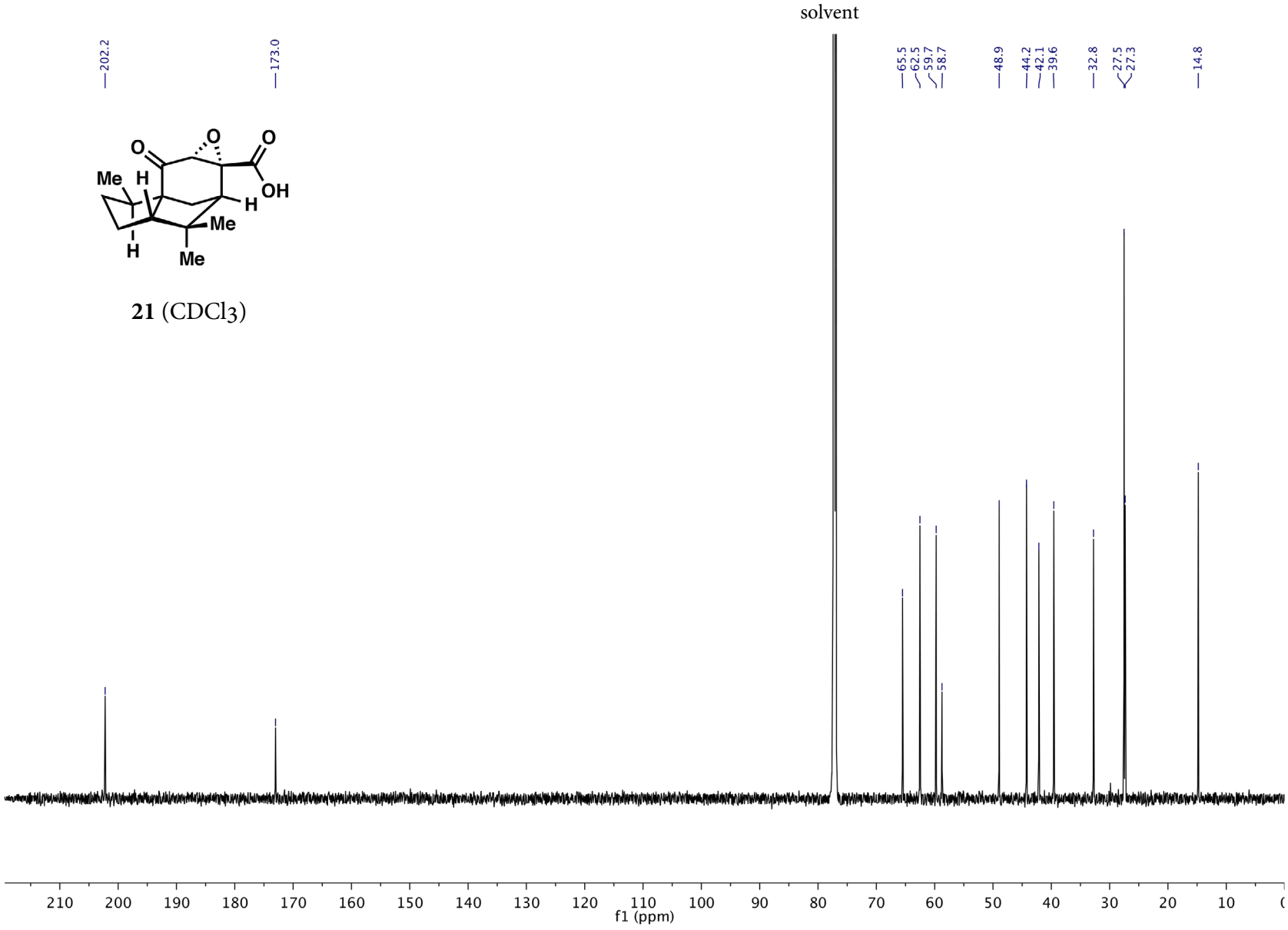

solvent
203.2
171.3
151.2
135.1
67.3
57.9
52.5
44.5
43.9
43.3
39.5
27.9
26.8
26.7
15.2
O
O
OH
Me
H
H
Me
H
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

20 (CDCl3)

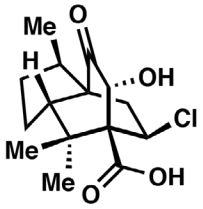

O
O
O
Me
H
OH
H
Me
H
Me

21 ($CDCl_3$)

solvent
0.98
1.00
1.00
2.01
1.13
0.90
1.05
1.09
0.95
3.03
3.07
3.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

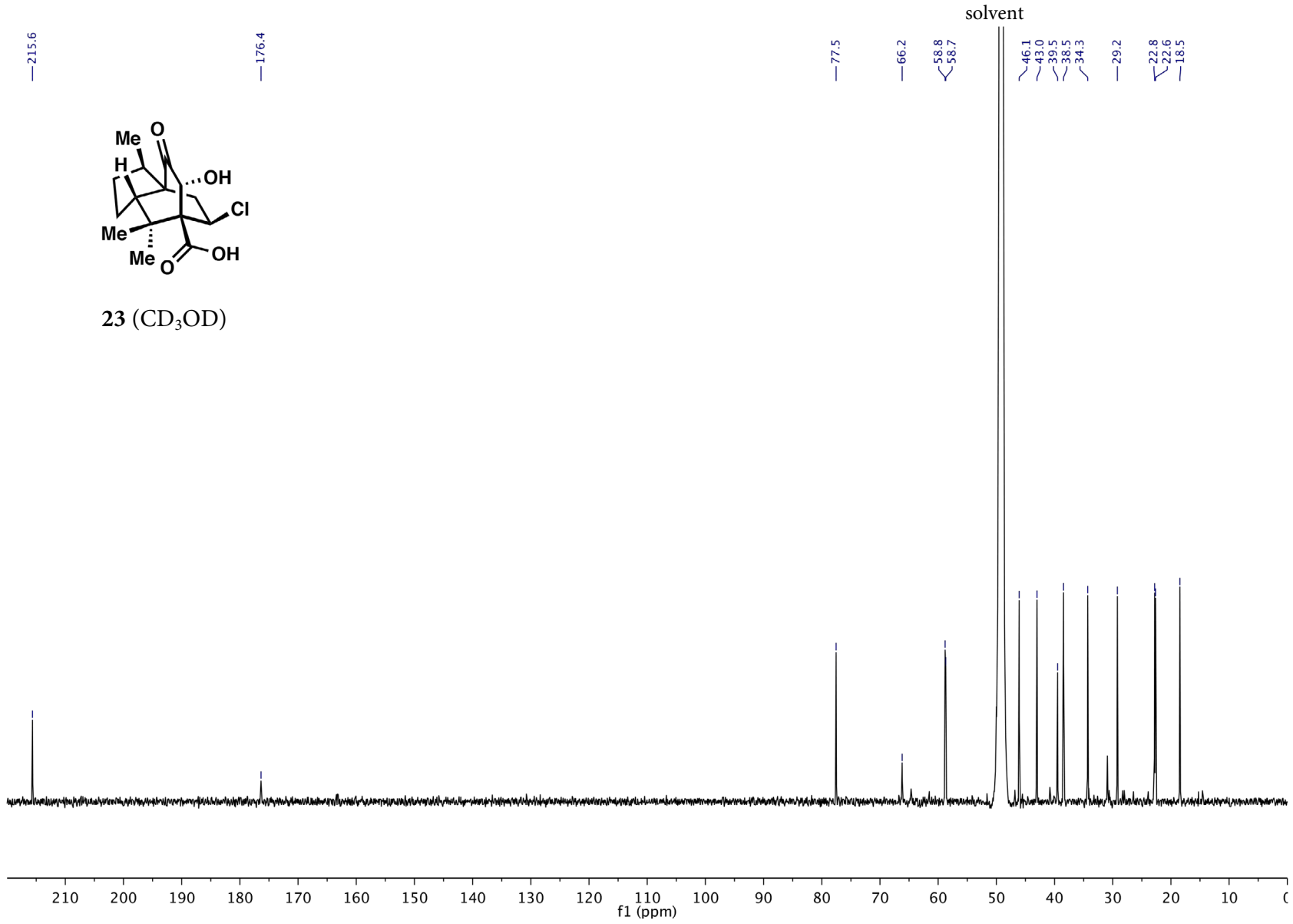

solvent
202.2
173.0
65.5
62.5
59.7
58.7
48.9
44.2
42.1
39.6
32.8
27.5
27.3
14.8
O
O
O
OH
Me
H
H
Me
H
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

21 ($CDCl_3$)

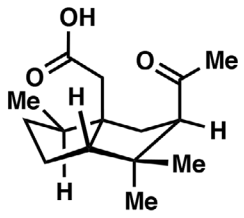

Me
O
H
OH
Cl
Me
Me
O
OH

23 (CD_3OD)

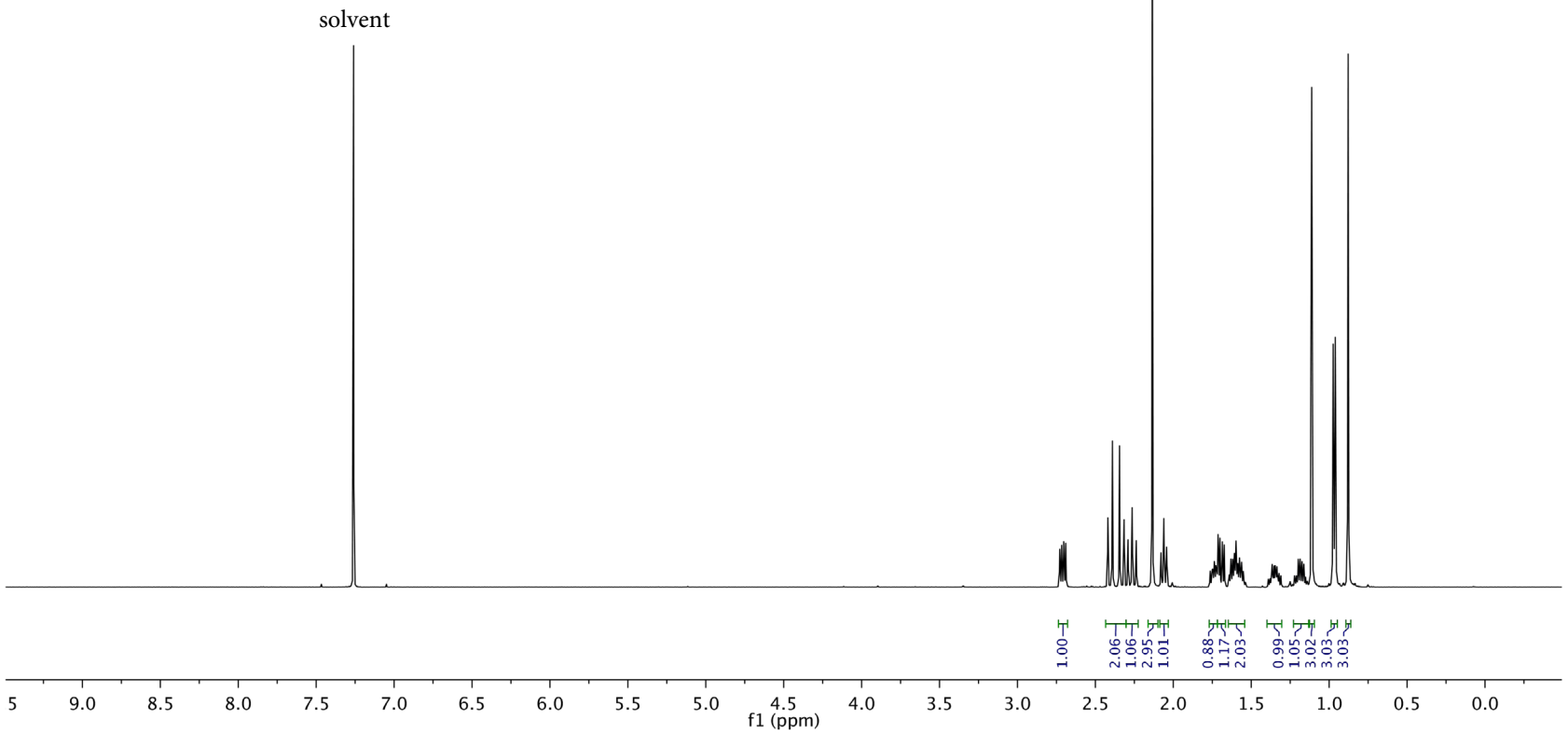
solvent
0.95
1.00
1.02
1.11
1.04
1.14
1.01
1.13
1.03
0.91
3.33
2.99
3.15
5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

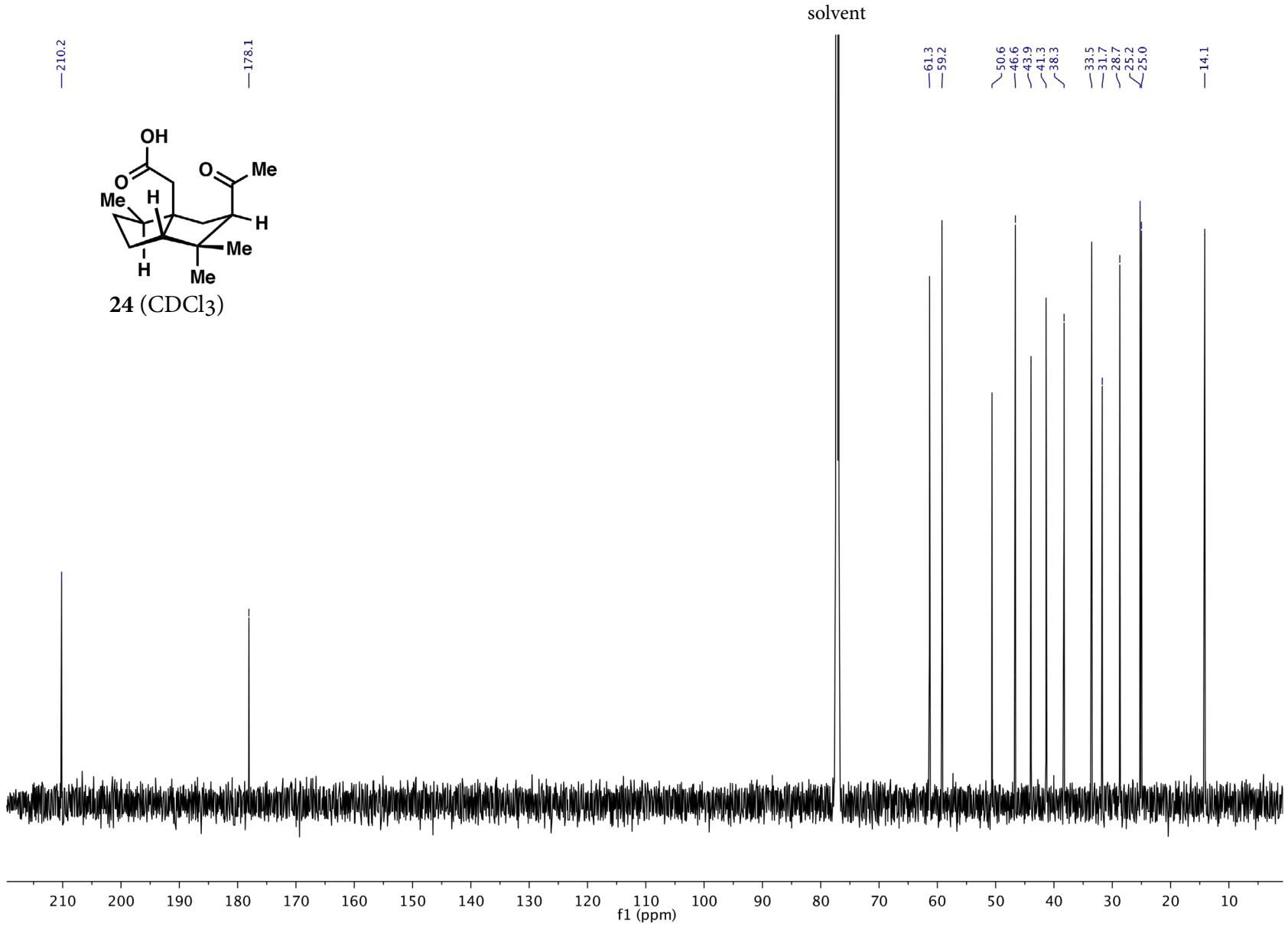

solvent
215.6
176.4
77.5
66.2
58.8
58.7
46.1
43.0
39.5
38.5
34.3
29.2
22.8
22.6
18.5
Me
O
H
OH
Cl
Me
Me
O
OH
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

23 (CD_3OD)

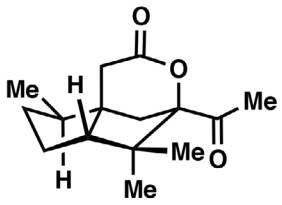

OH
O
Me
O
Me
H
H
Me
H
Me

24 ($CDCl_3$)


solvent
1.00
2.06
1.06
2.95
1.01
0.88
1.17
2.03
0.99
1.05
3.02
3.03
3.03
5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

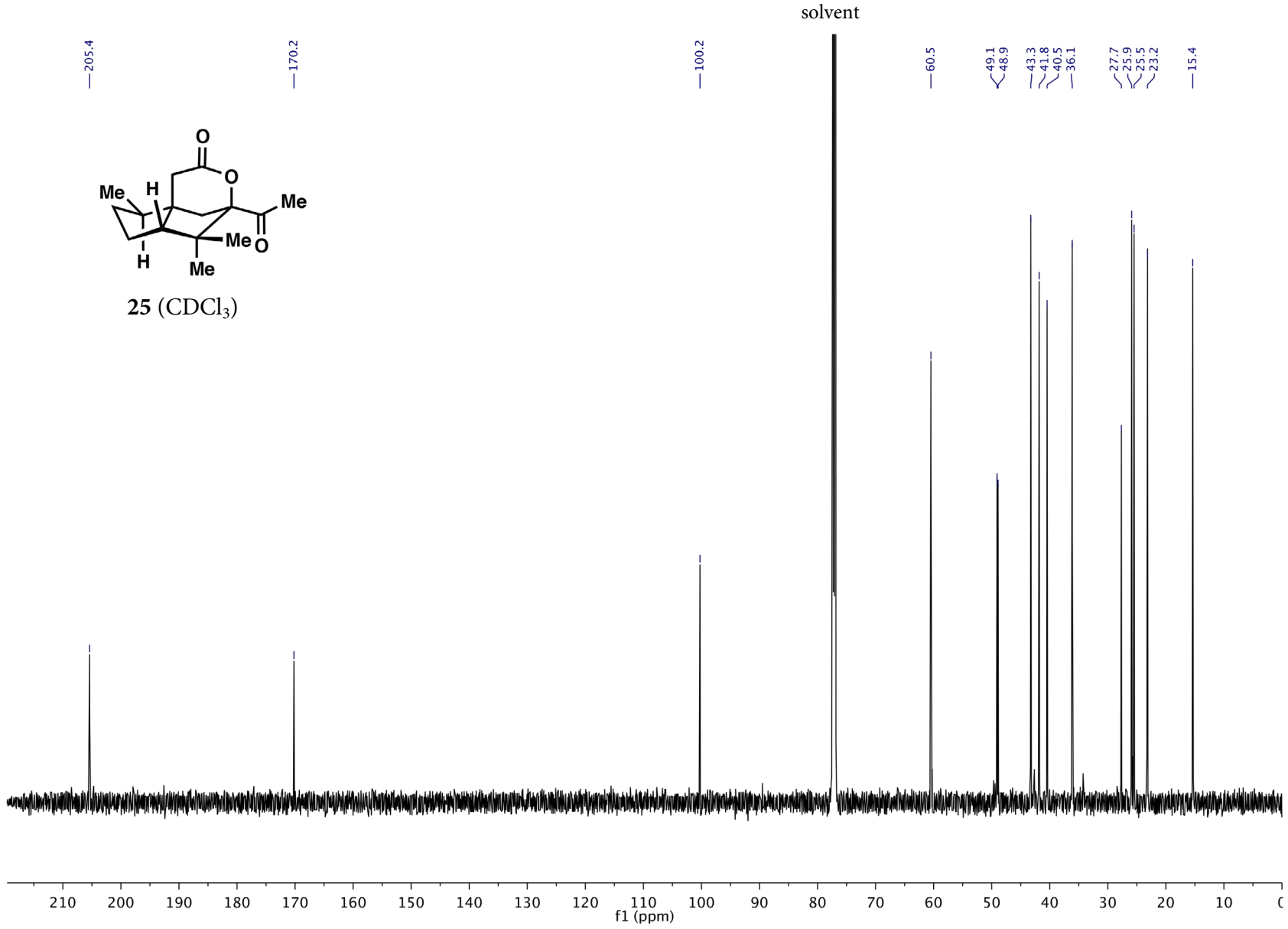

solvent
210.2
178.1
61.3
59.2
50.6
46.6
43.9
41.3
38.3
33.5
31.7
28.7
25.2
25.0
14.1
OH
O
Me
O
Me
H
H
Me
H
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

24 ($CDCl_3$)

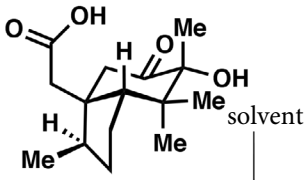

O
O
Me
H
Me
Me
O
H
Me

25 ($CDCl_3$)

solvent
1.96
1.00
2.69
2.85
1.00
1.23
1.03
1.00
3.02
3.07
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

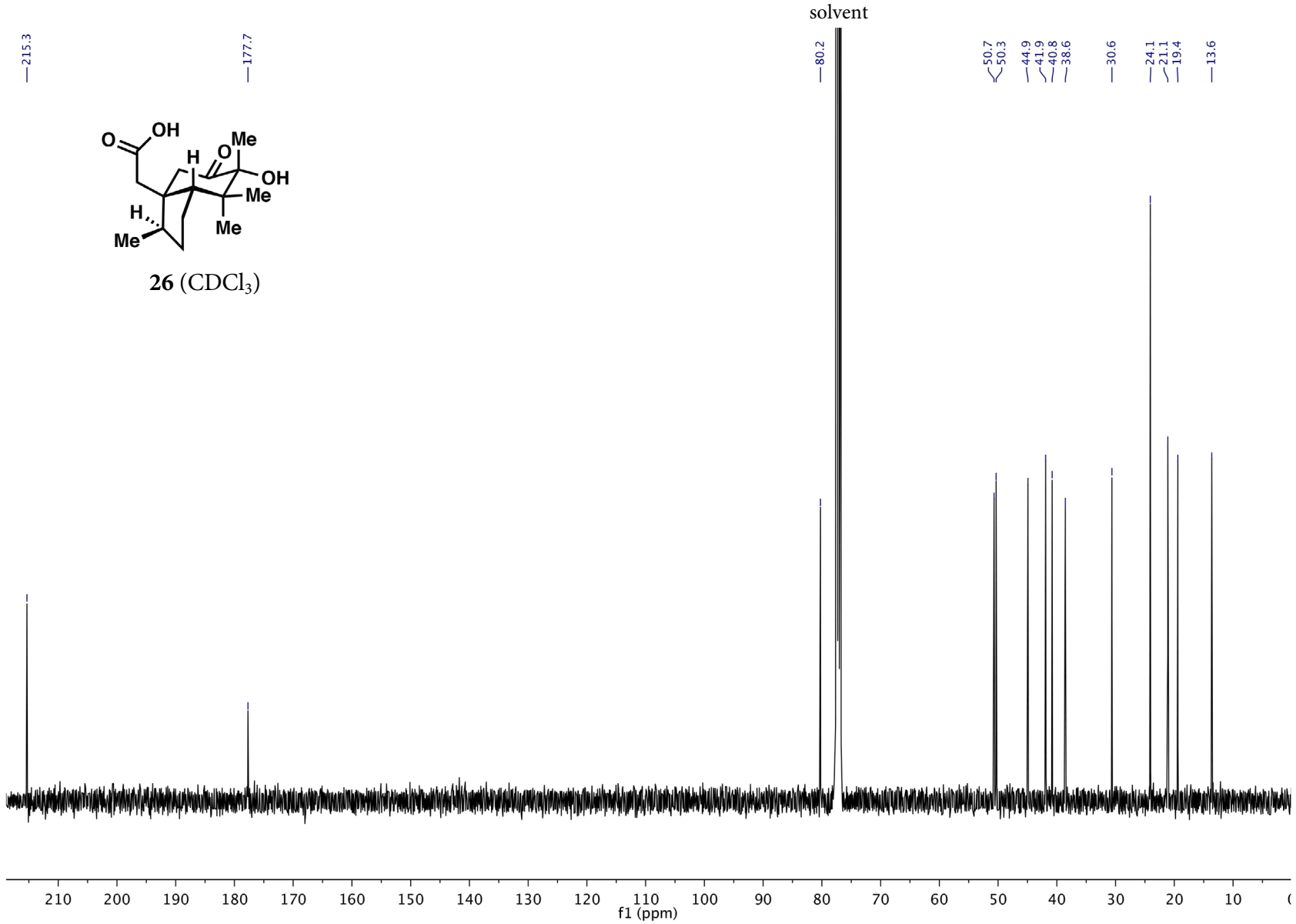

solvent
205.4
170.2
100.2
60.5
49.1
48.9
43.3
41.8
40.5
36.1
27.7
25.9
25.5
23.2
15.4
O
O
Me
H
Me
Me
O
H
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

25 ($CDCl_3$)

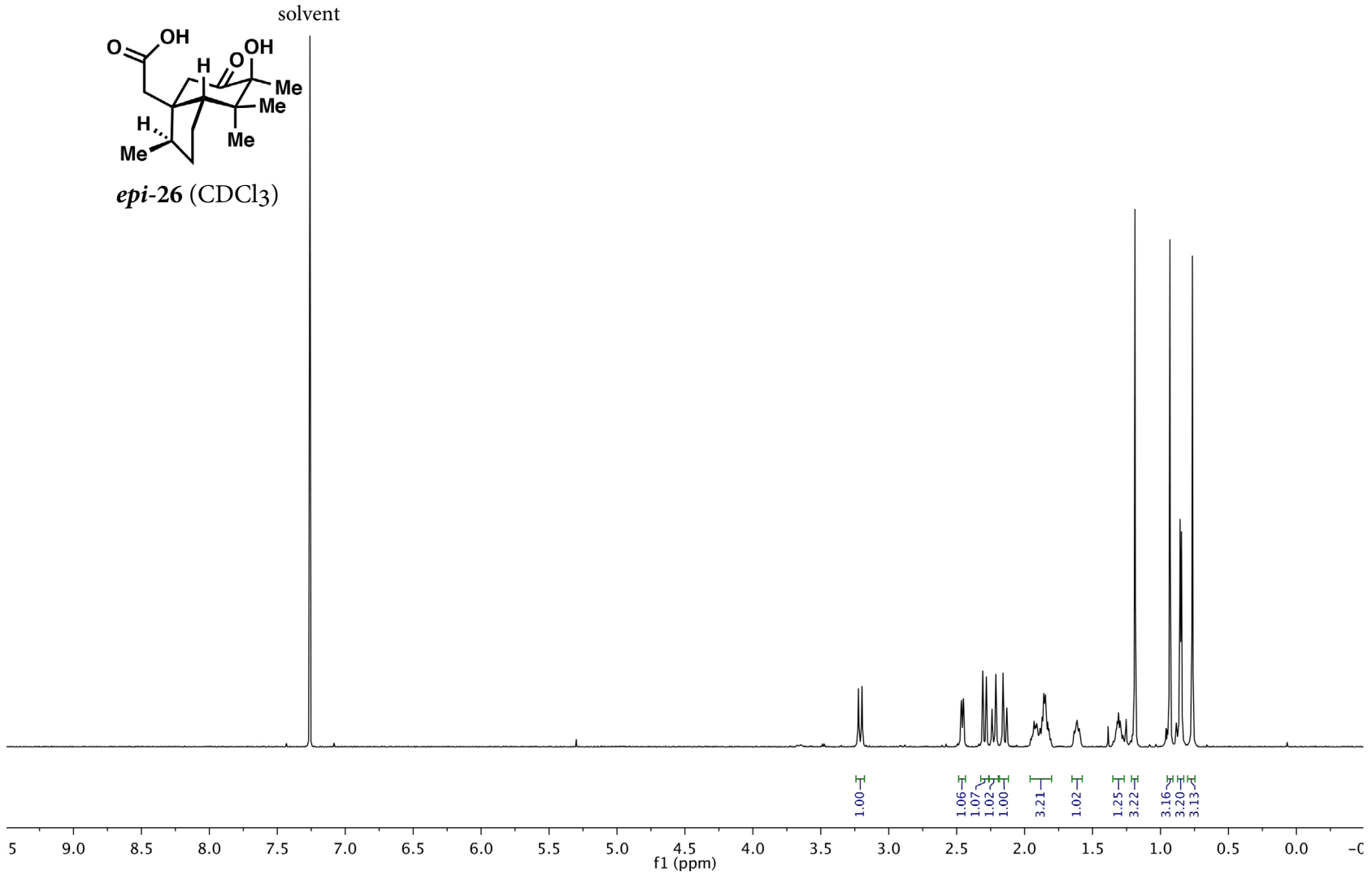


26 ($CDCl_3$)

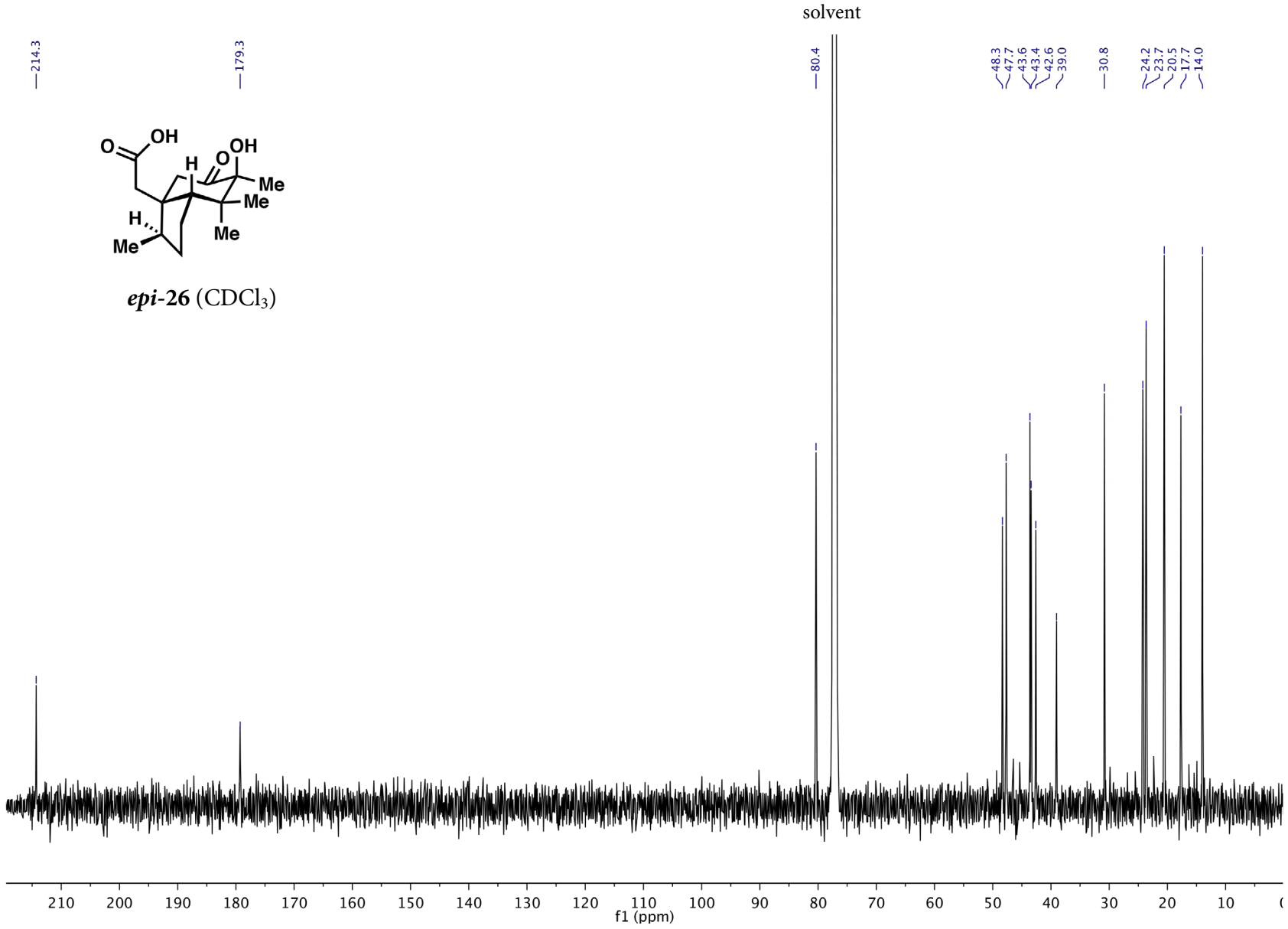
solvent


solvent
215.3
177.7
80.2
50.7
50.3
44.9
41.9
40.8
38.6
30.6
24.1
21.1
19.4
13.6
O
OH
H
O
Me
OH
Me
H
Me
Me
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

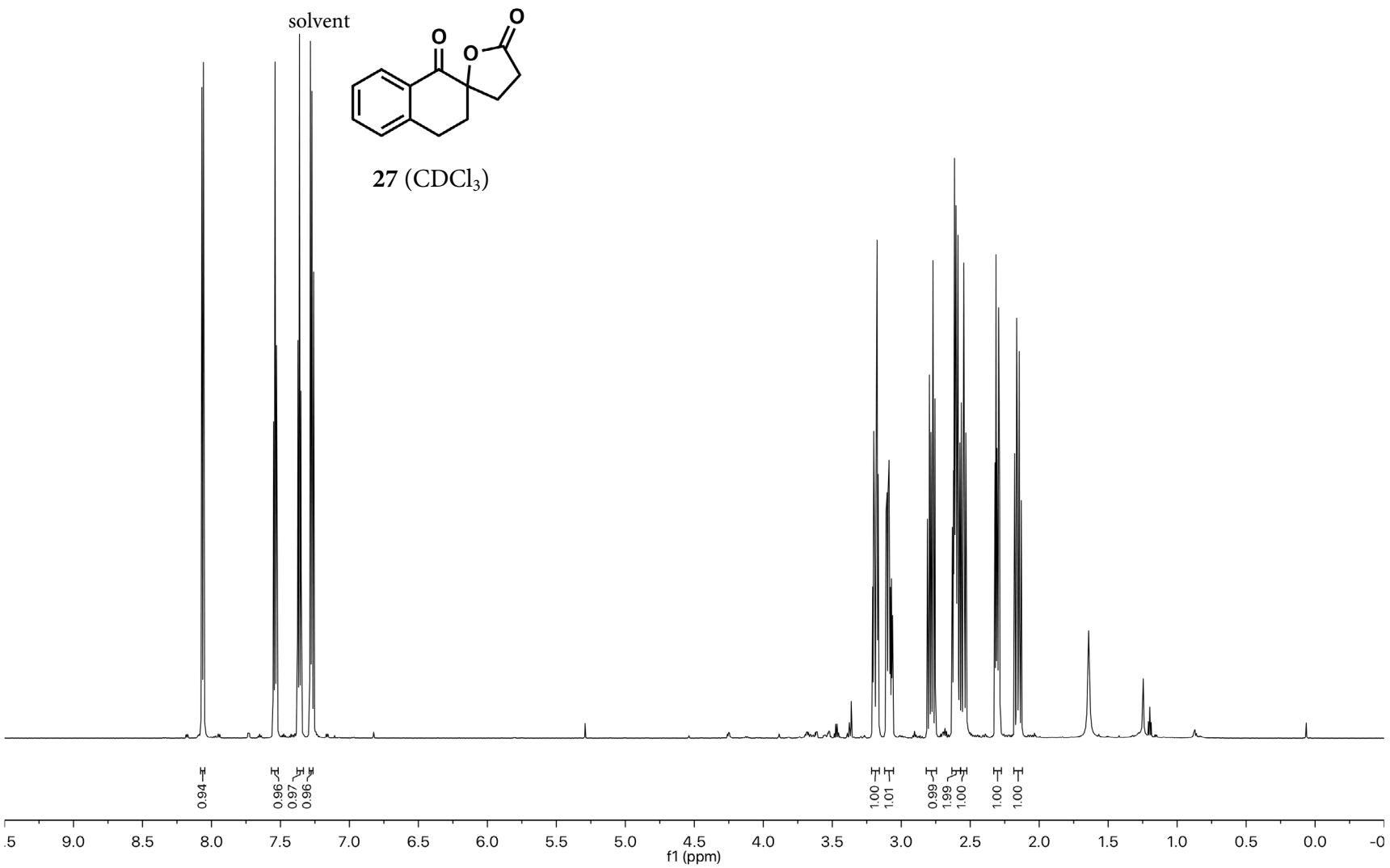
26 ($CDCl_3$)


solvent
OH
O
H
O
OH
Me
Me
Me
H
Me
1.00
1.06
1.07
1.02
1.00
3.21
1.02
1.25
3.22
3.16
3.20
3.13
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

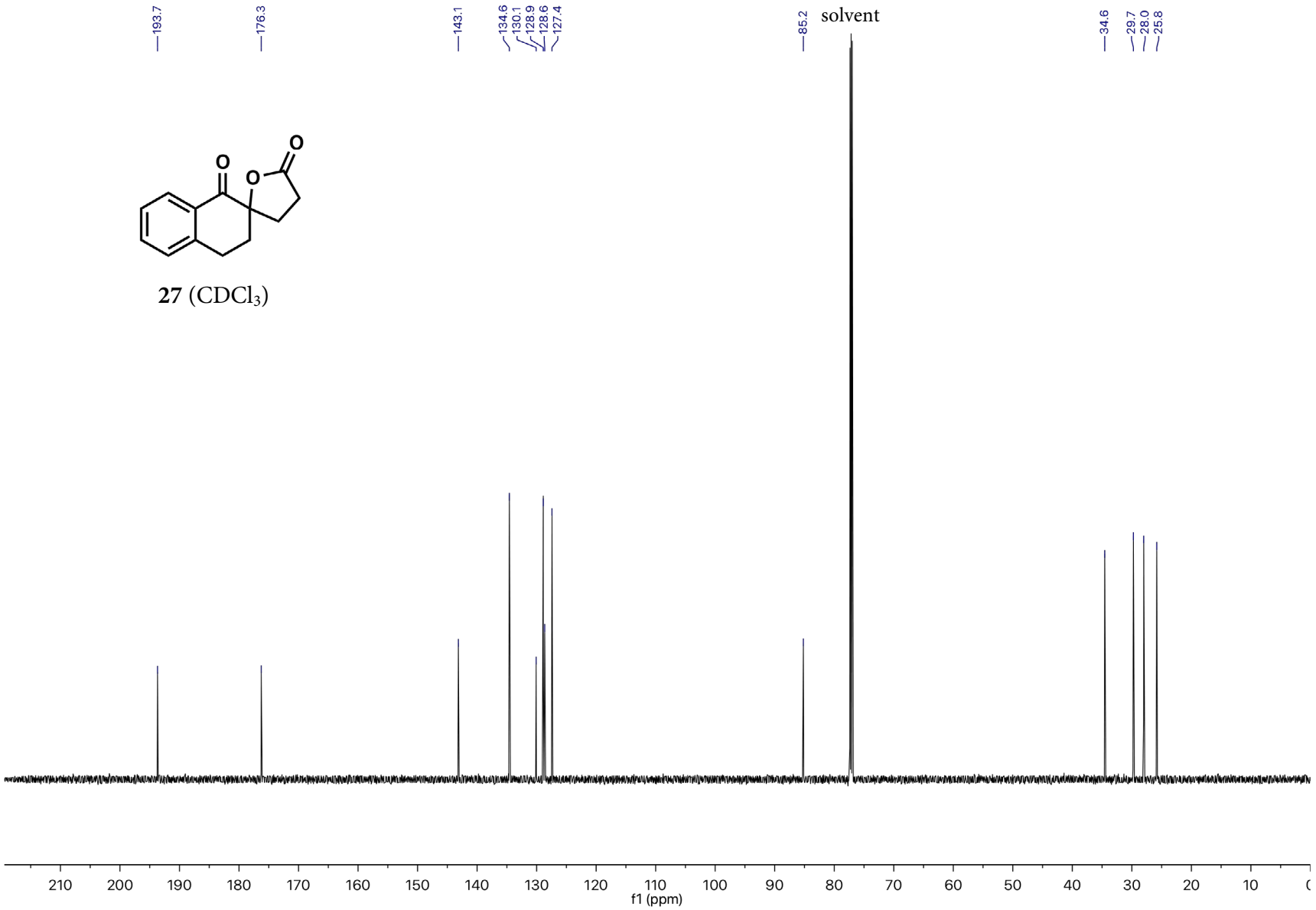
***epi*-26** ($CDCl_3$)


solvent
214.3
179.3
80.4
48.3
47.7
43.6
43.4
42.6
39.0
30.8
24.2
23.7
20.5
17.7
14.0
O
OH
H
O
OH
Me
Me
Me
H
Me
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

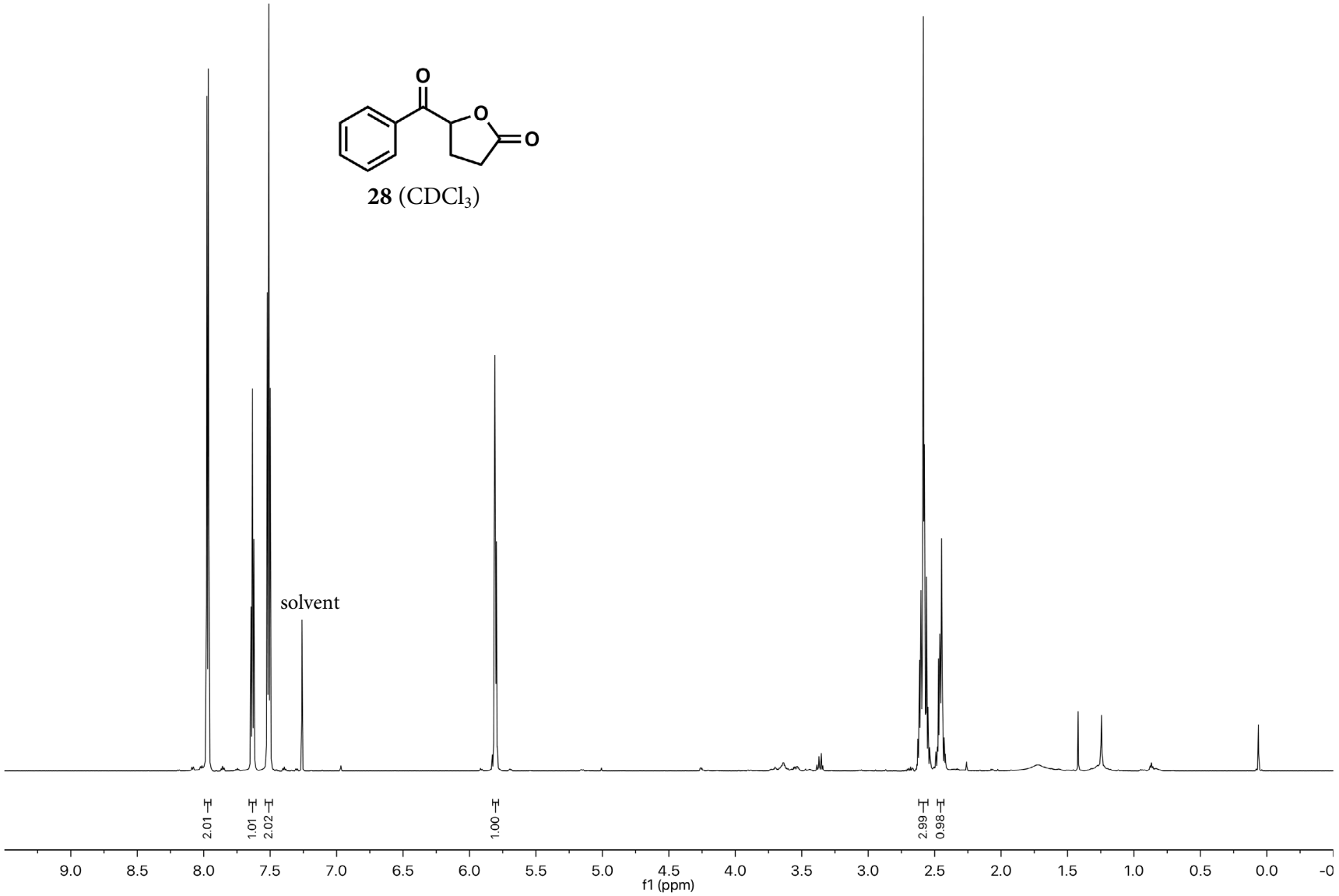
***epi*-26** ($CDCl_3$)



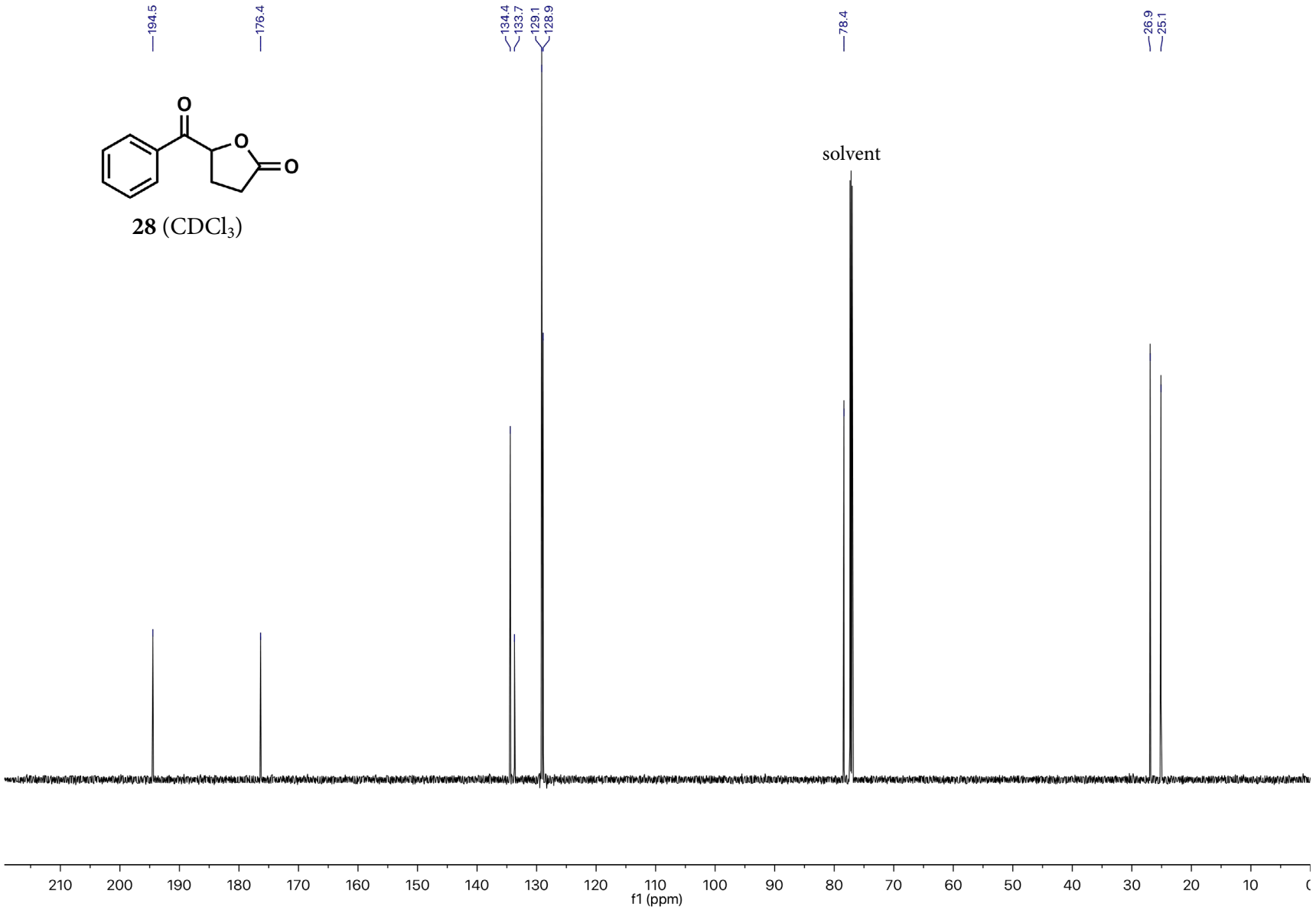
27 ($CDCl_3$)


193.7
176.3
143.1
134.6
130.1
128.9
128.6
127.4
85.2
solvent
34.6
29.7
28.0
25.8
O
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

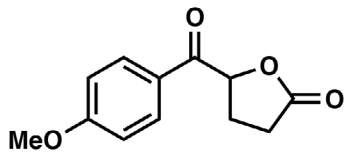
27 ($CDCl_3$)


O
O
O
solvent
2.01
1.01
2.02
1.00
2.99
0.98
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

28 ($CDCl_3$)

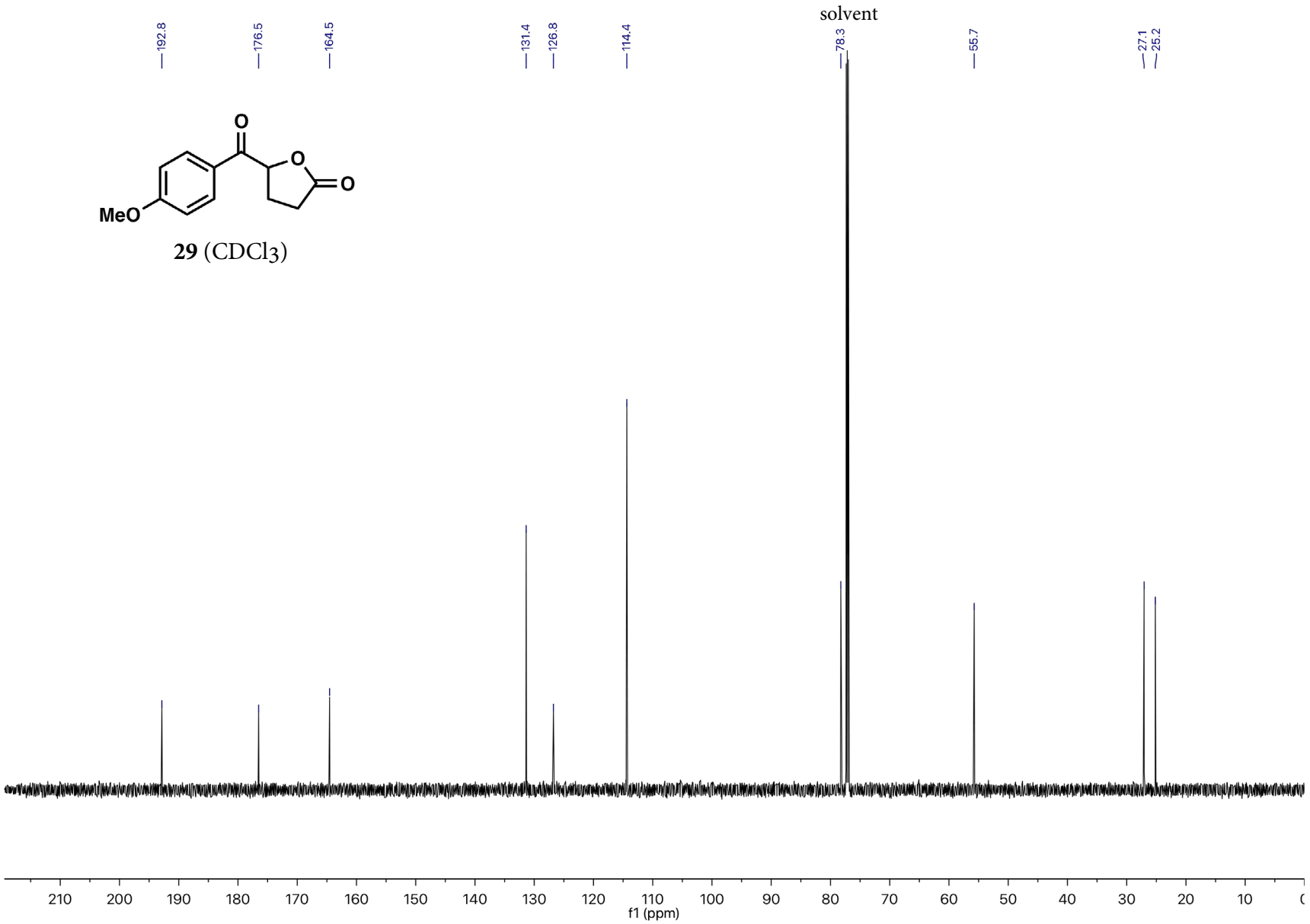

194.5
176.4
134.4
133.7
129.1
128.9
78.4
26.9
25.1
O
O
O
solvent
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

28 ($CDCl_3$)

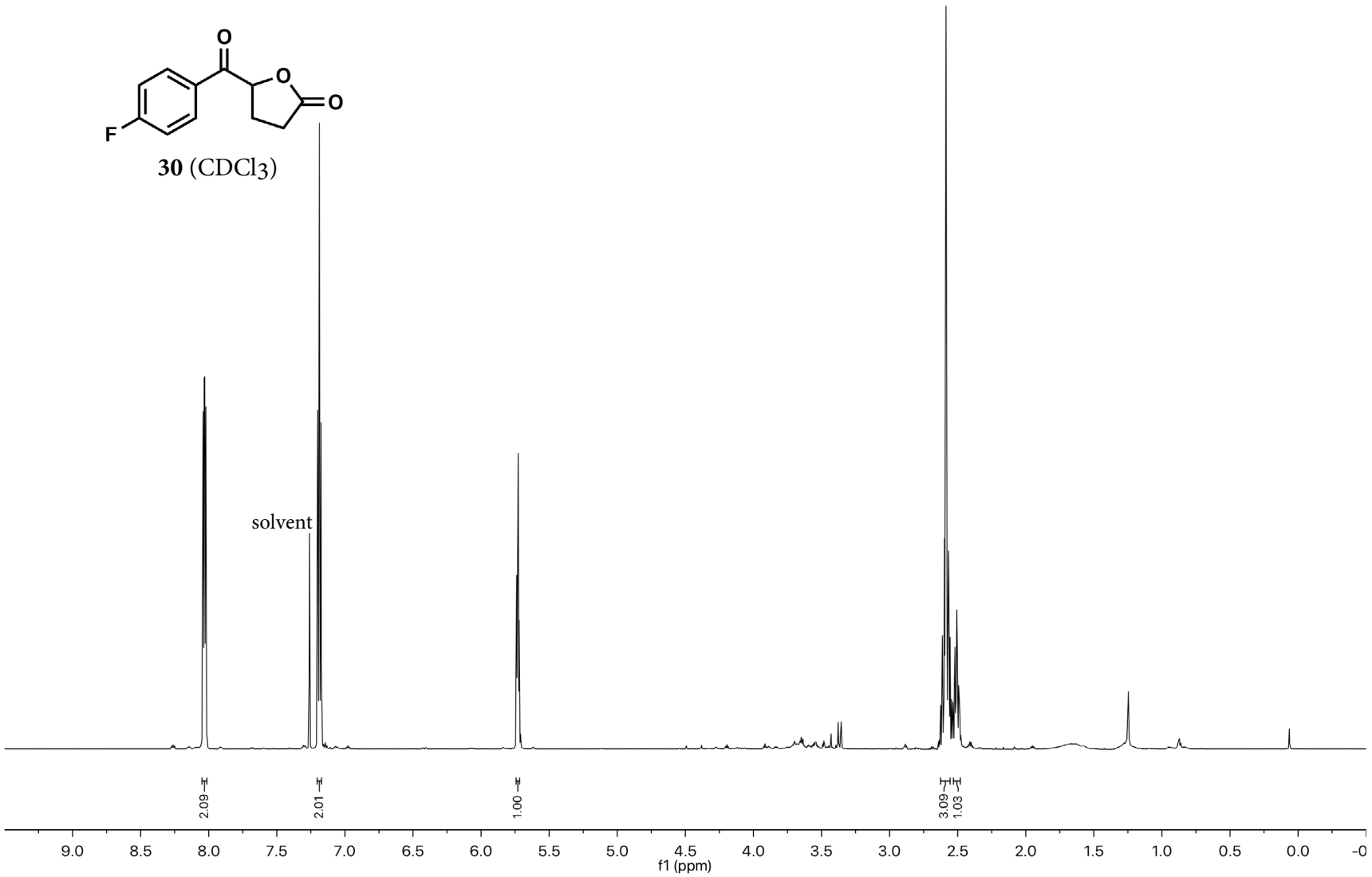

O
O
O
MeO

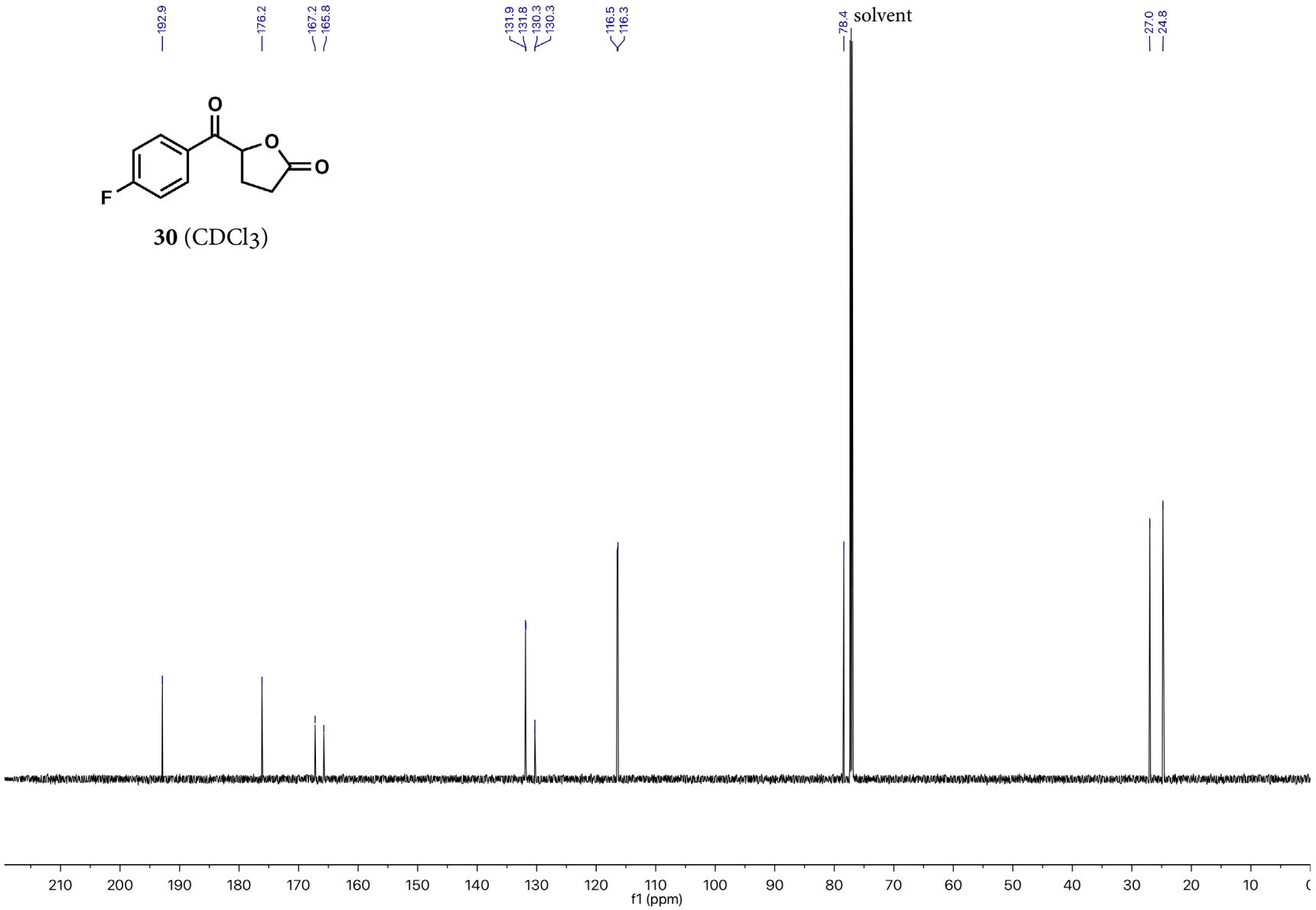
29 ($CDCl_3$)

solvent
2.04
2.04
1.00
3.09
3.07
1.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

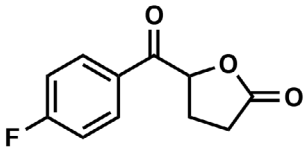

192.8
176.5
164.5
131.4
126.8
114.4
solvent
78.3
55.7
27.1
25.2
O
O
O
MeO
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

29 ($CDCl_3$)

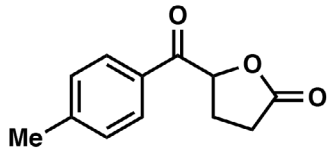

O
O
O
F
30 (CDCl3)
solvent
2.09
2.01
1.00
3.09
1.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


192.9
176.2
167.2
165.8
131.9
131.8
130.3
130.3
116.5
116.3
78.4
solvent
27.0
24.8
O
O
O
F
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

30 ($CDCl_3$)

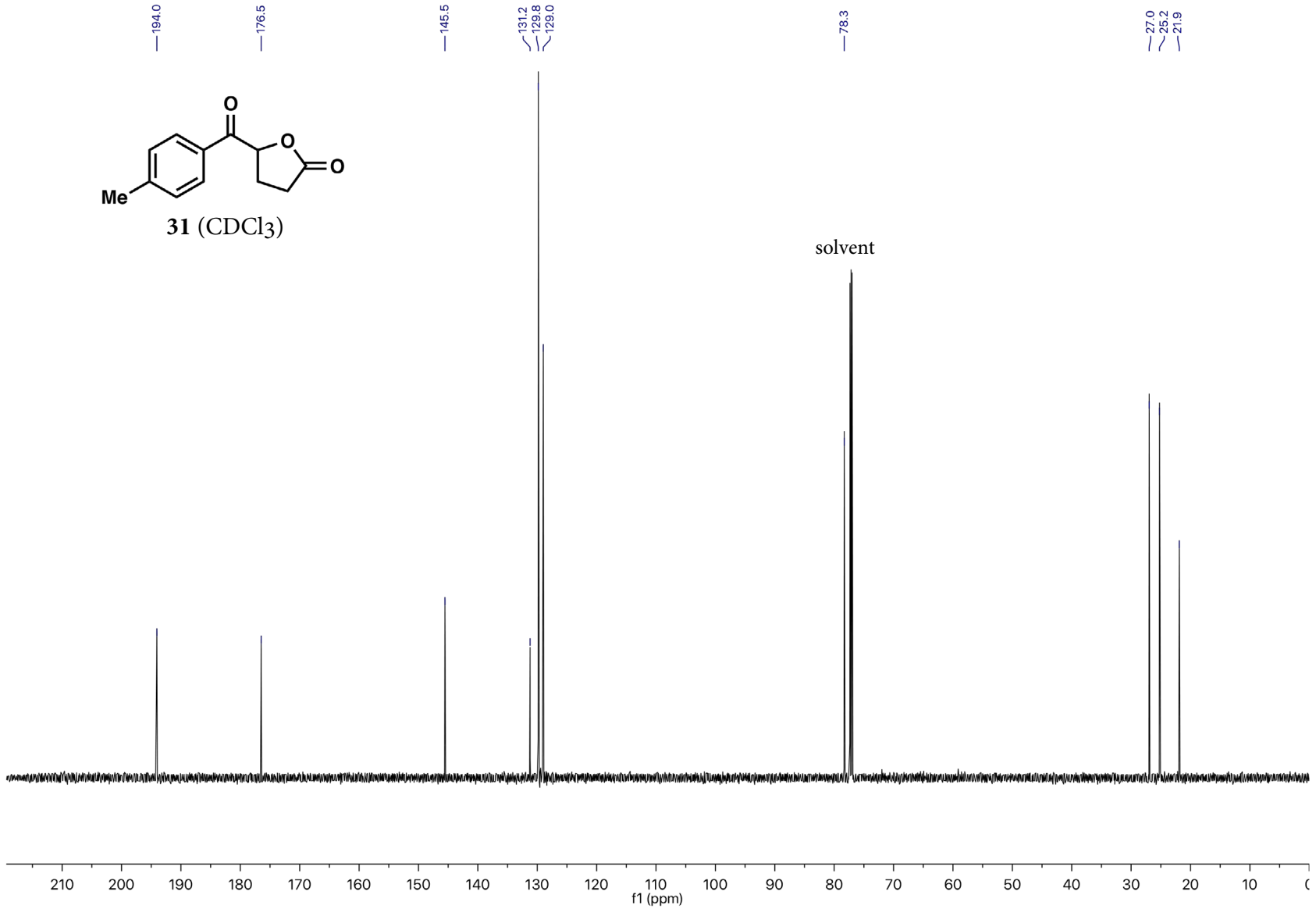


30 (^{19}F NMR, CDCl3)

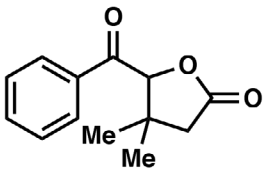

O
O
O
Me

31 ($CDCl_3$)

solvent
2.04
2.03
1.00
3.01
4.15
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

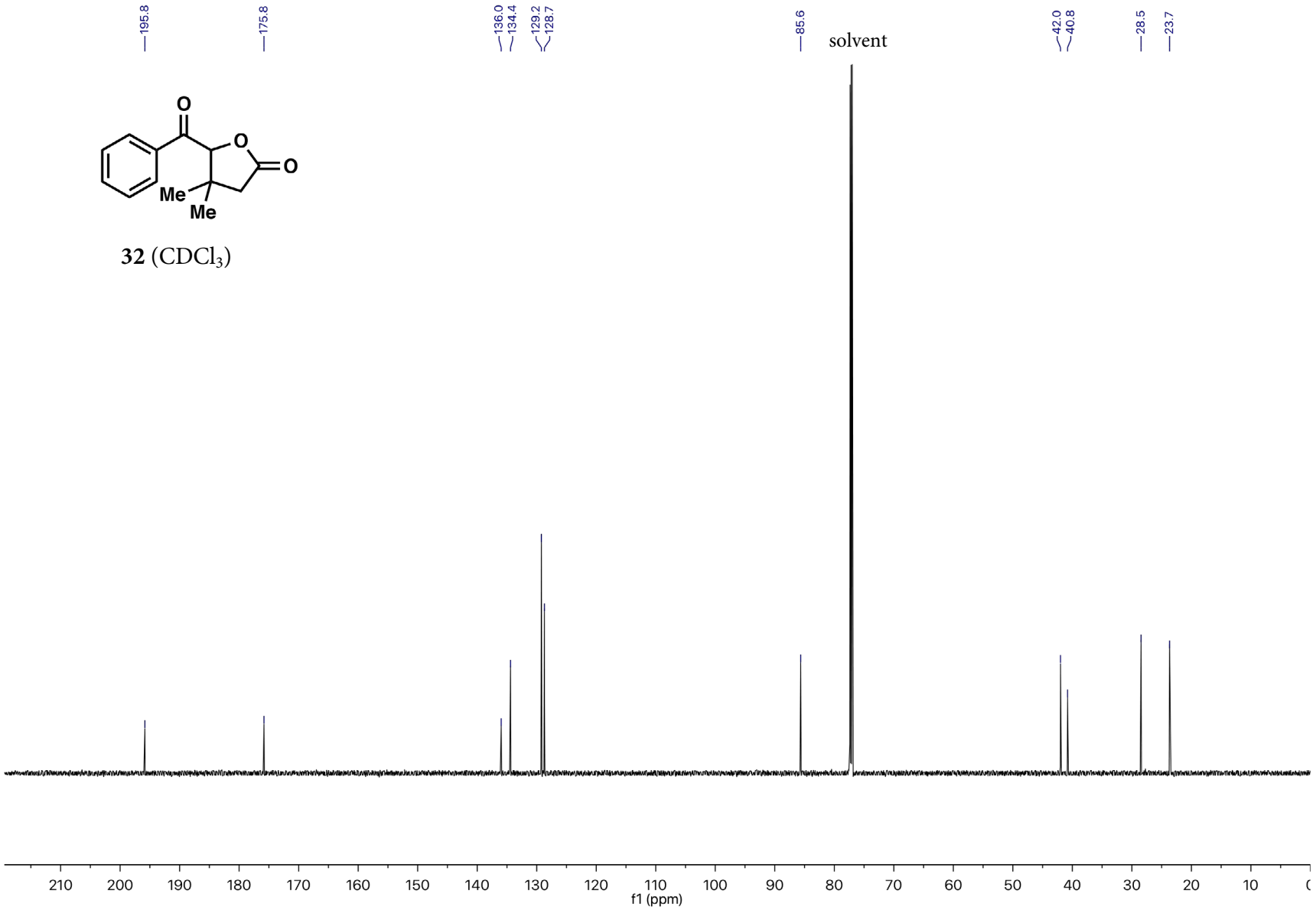

194.0
176.5
145.5
131.2
129.8
129.0
78.3
27.0
25.2
21.9
O
O
O
Me
solvent
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

31 ($CDCl_3$)

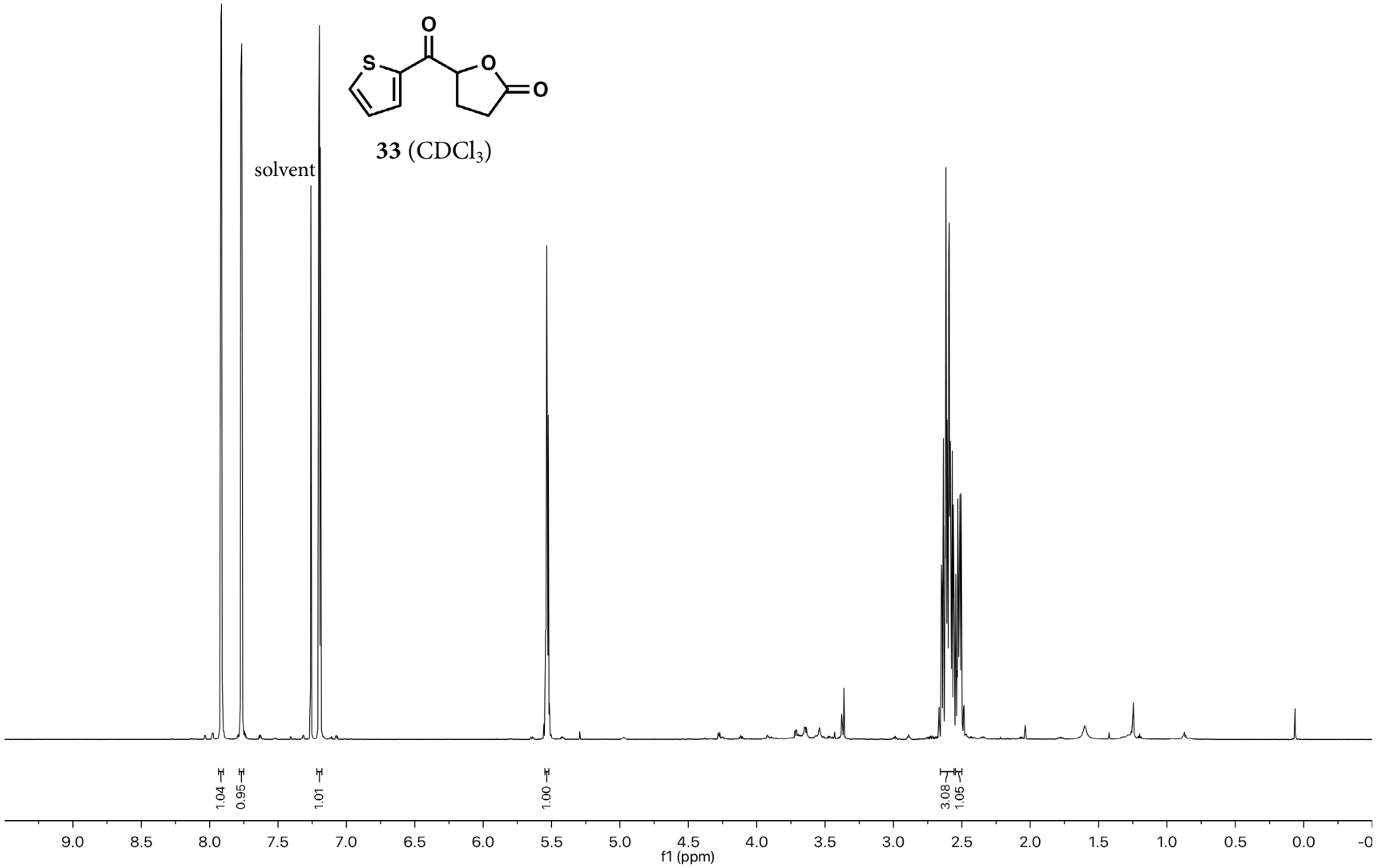

O
O
O
Me
Me

32 ($CDCl_3$)

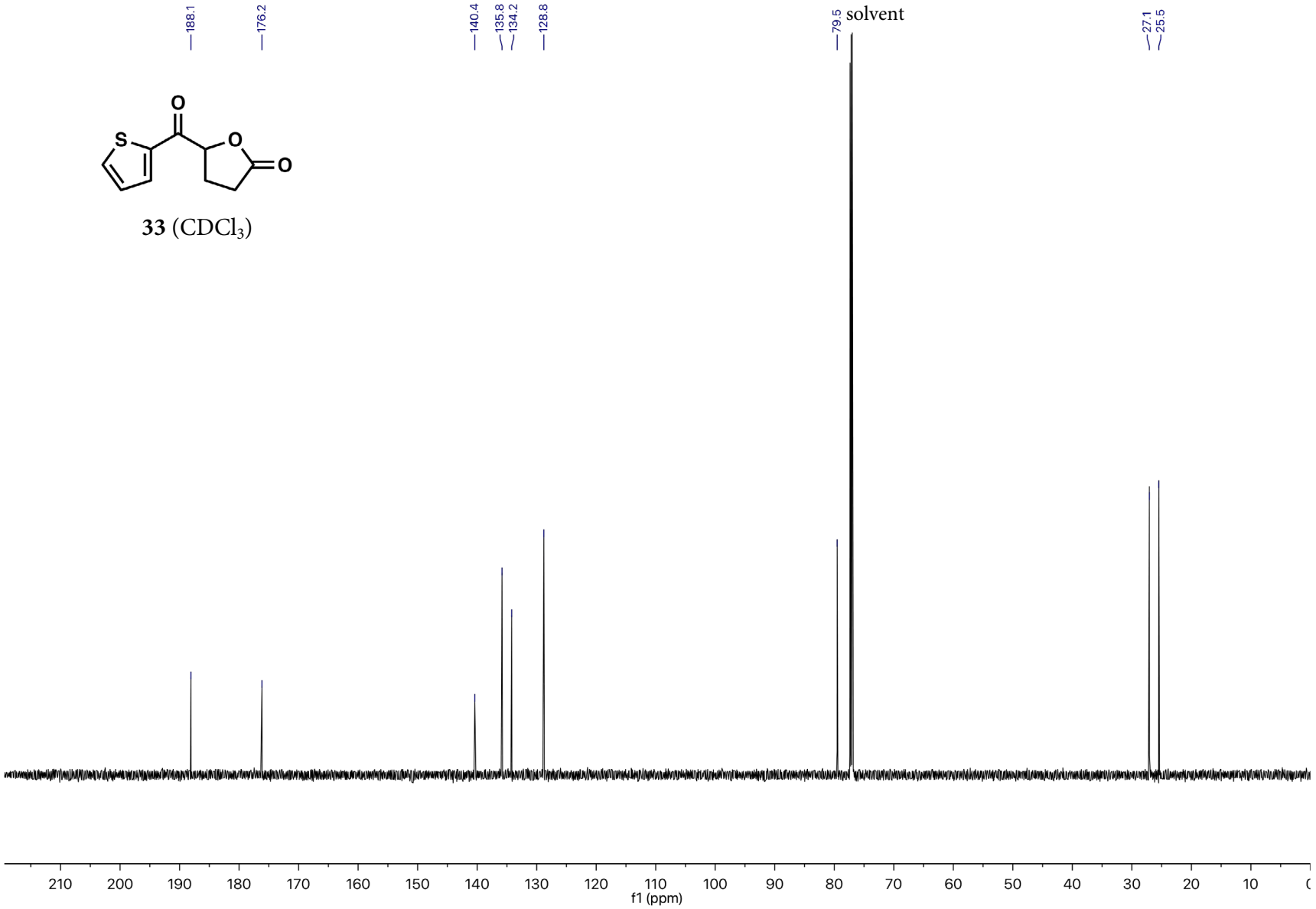
solvent
1.99
0.97
1.96
1.00
1.04
1.00
2.98
3.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


195.8
175.8
136.0
134.4
129.2
128.7
85.6
solvent
42.0
40.8
28.5
23.7
O
O
O
Me
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

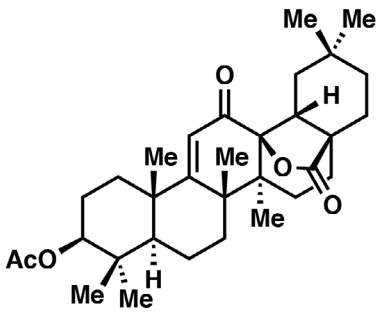
32 ($CDCl_3$)


O
S
O
O
solvent
1.04
0.95
1.01
1.00
3.08
1.05
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

33 ($CDCl_3$)

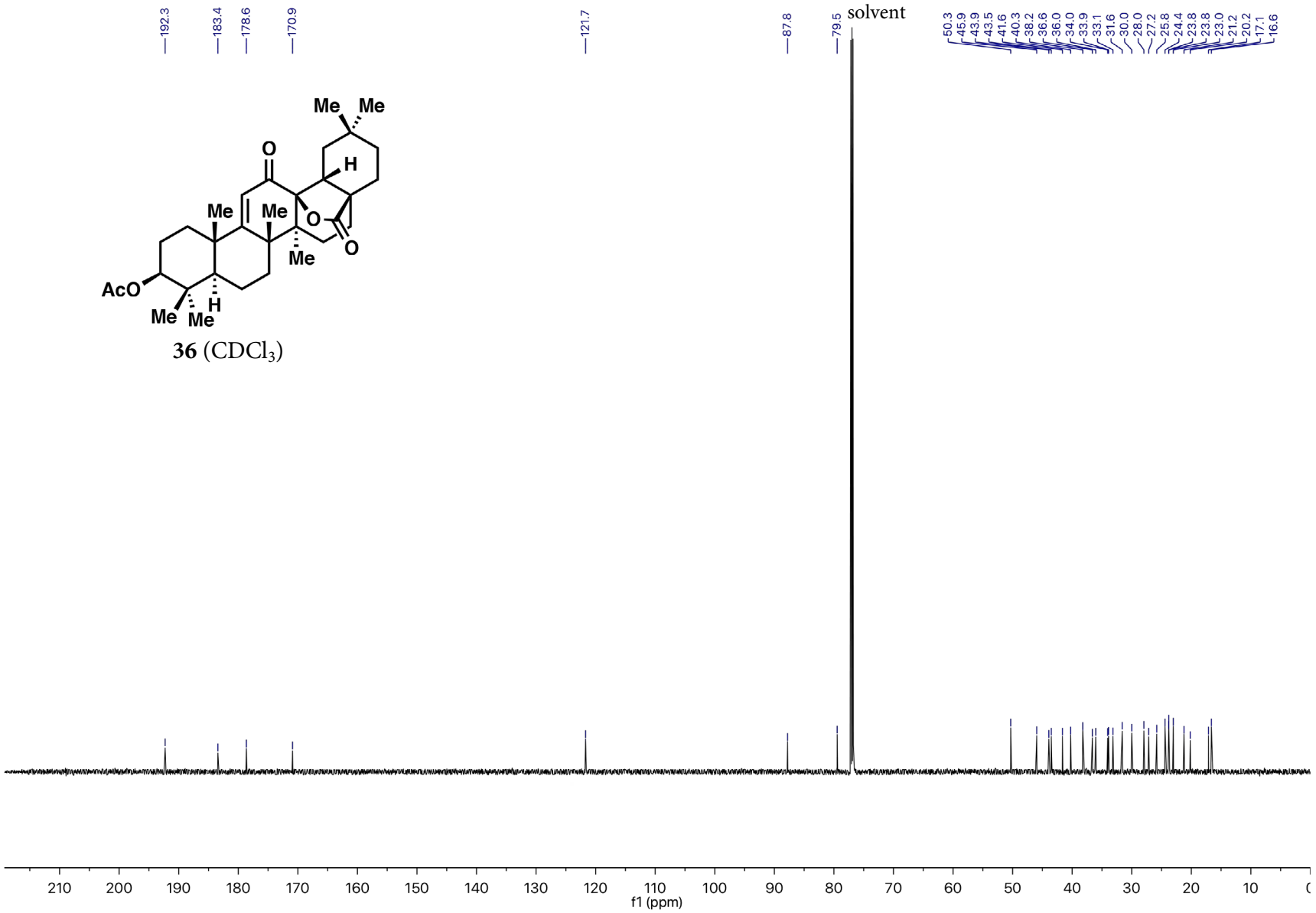


33 ($CDCl_3$)

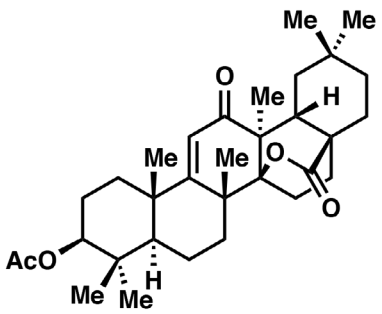


36 ($CDCl_3$)

solvent

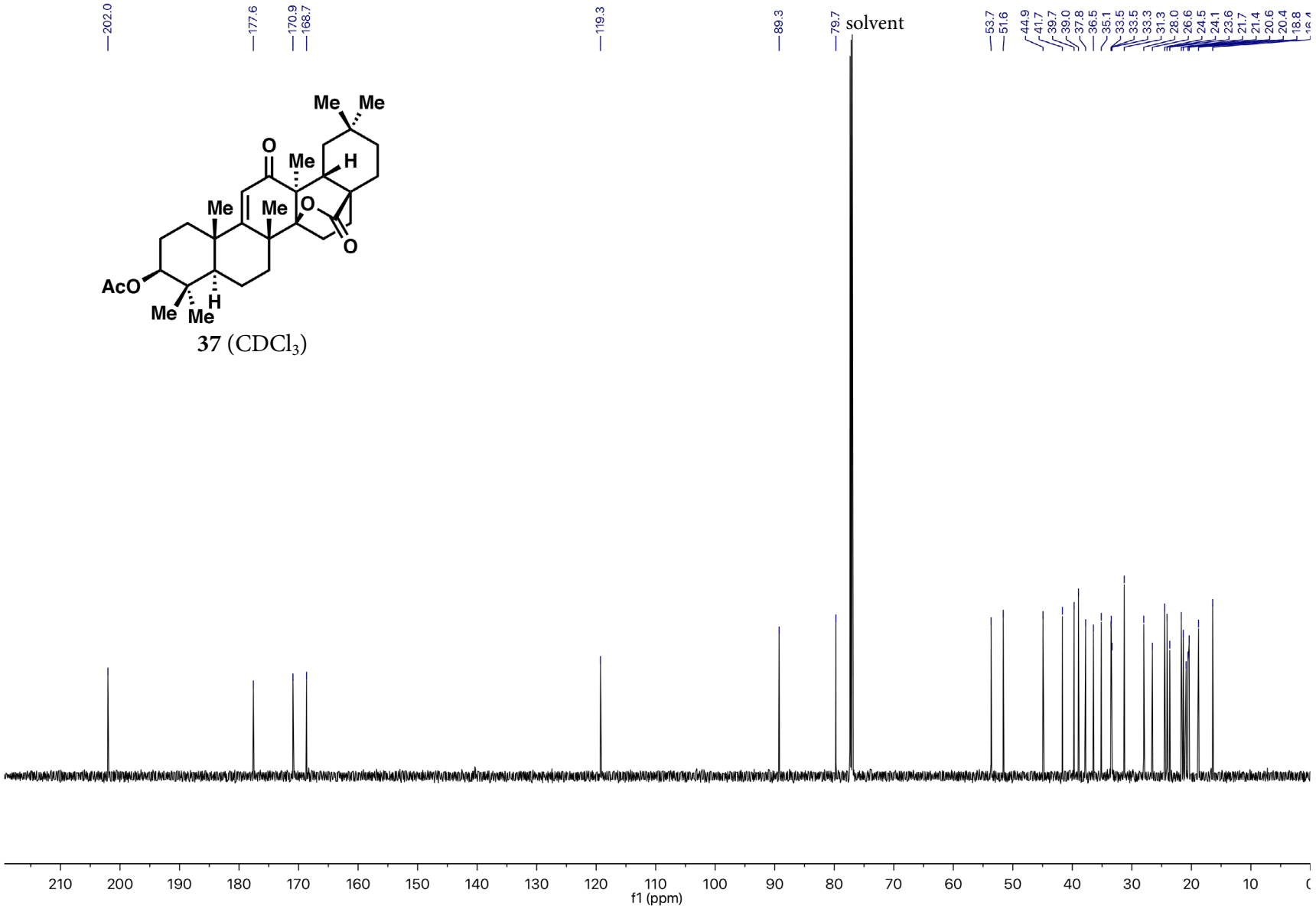

192.3
183.4
178.6
170.9
121.7
87.8
79.5
solvent
50.3
45.9
43.9
43.5
41.6
40.3
38.2
36.6
36.0
34.0
33.9
33.1
31.6
30.0
28.0
27.2
25.8
24.4
23.8
23.8
23.0
21.2
20.2
17.1
16.6
Me
Me
O
H
Me
Me
O
O
Me
AcO
Me
Me
H
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

36 ($CDCl_3$)

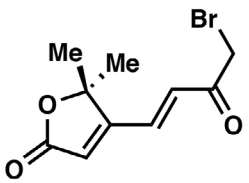

Me
Me
O
Me
H
Me
Me
O
O
AcO
Me
Me
H

37 ($CDCl_3$)

solvent
1.00
1.01
0.97
0.98
2.99
1.17
1.87
7.02
1.08
1.01
2.99
8.59
2.84
3.36
2.87
2.93
2.98
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

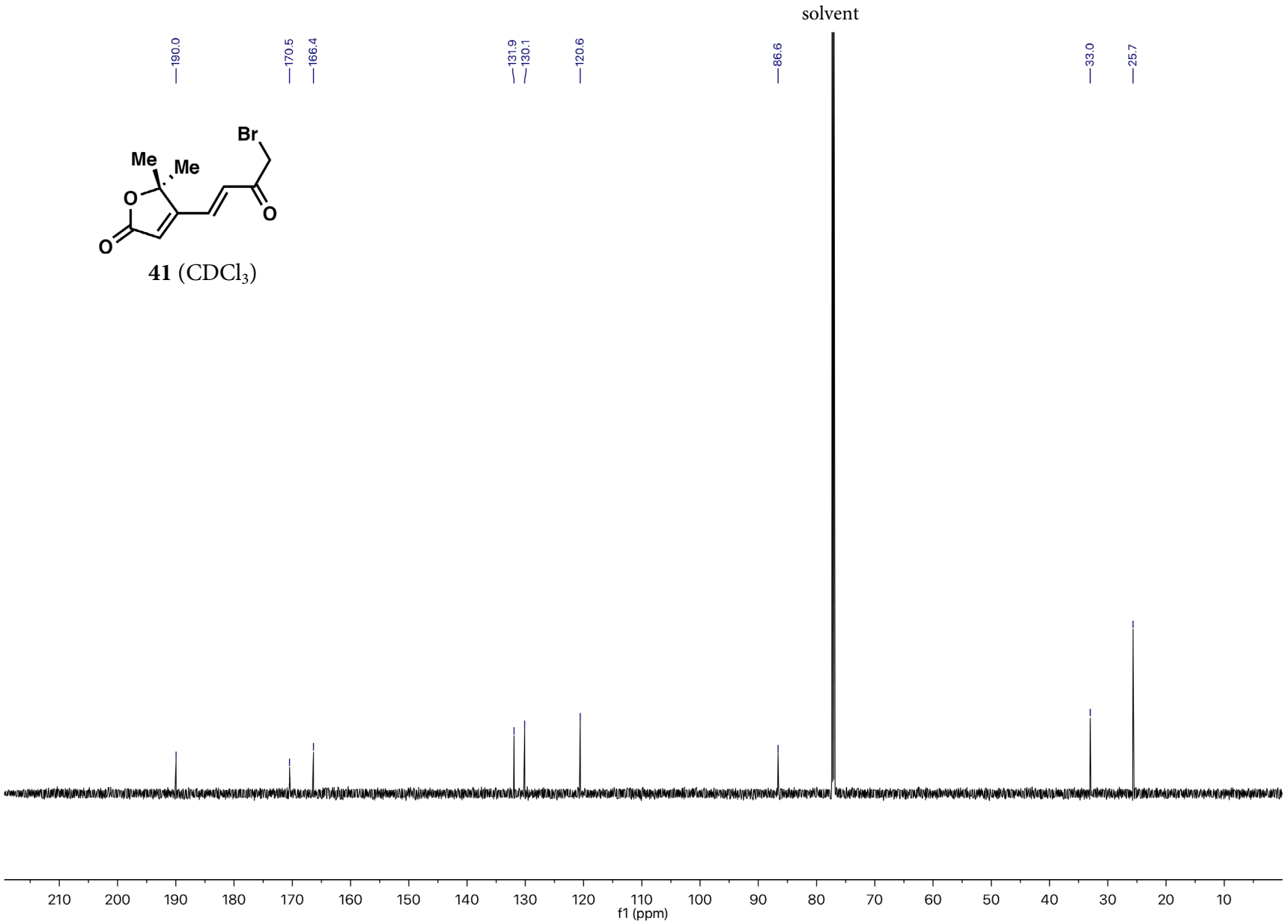

202.0
177.6
170.9
168.7
119.3
89.3
79.7
solvent
53.7
51.6
44.9
41.7
39.7
39.0
37.8
36.5
35.1
33.5
33.5
33.3
31.3
28.0
26.6
24.5
24.1
23.6
21.7
21.4
20.6
20.4
18.8
Me
Me
O
Me
H
Me
Me
O
O
AcO
Me
Me
H
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

37 ($CDCl_3$)

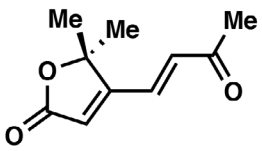

Br
Me
Me
O
O
O

41 ($CDCl_3$)

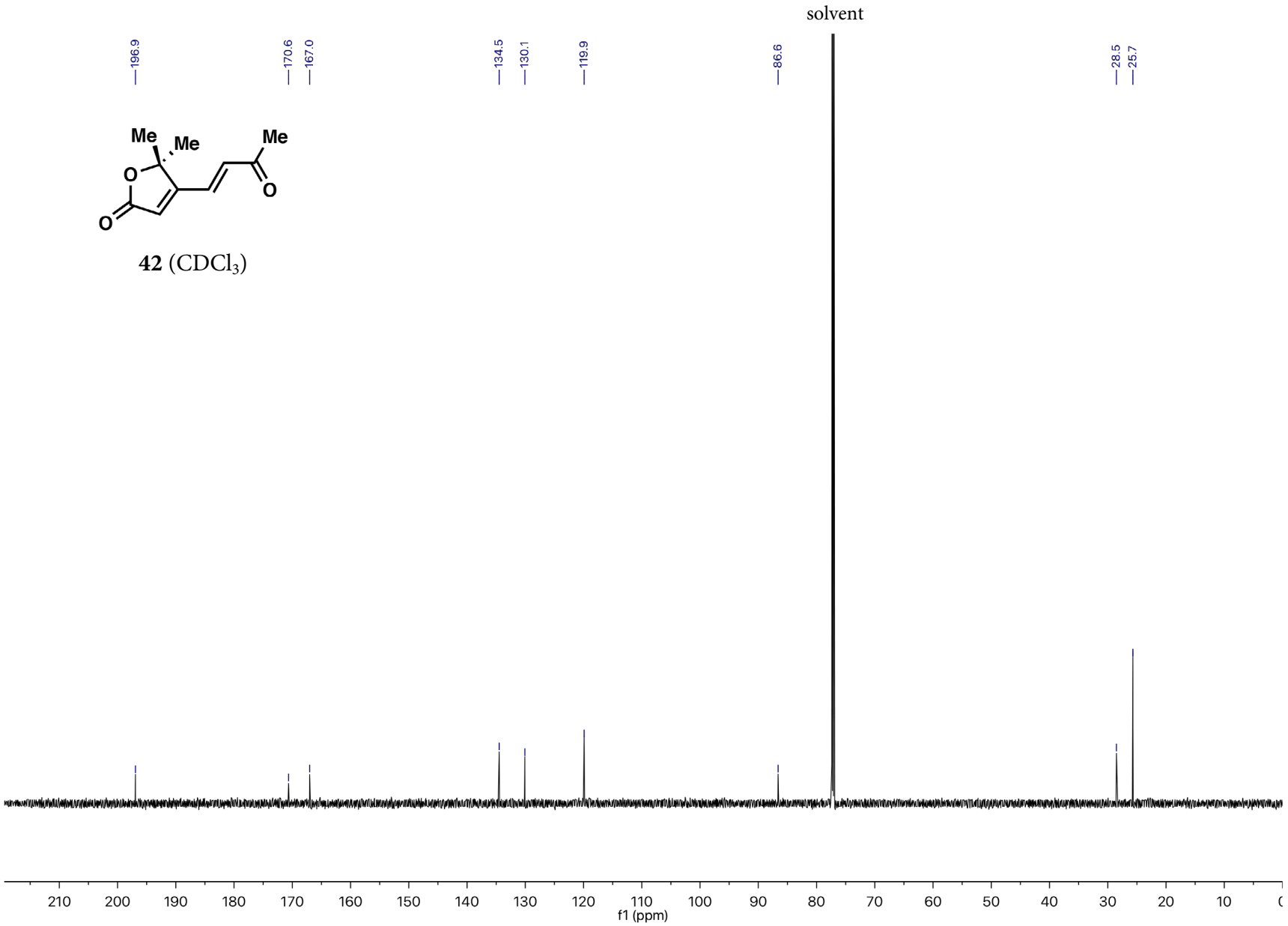
solvent
1.01
1.02
1.00
2.12
6.37
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


solvent
190.0
170.5
166.4
131.9
130.1
120.6
86.6
33.0
25.7
Br
Me
Me
O
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

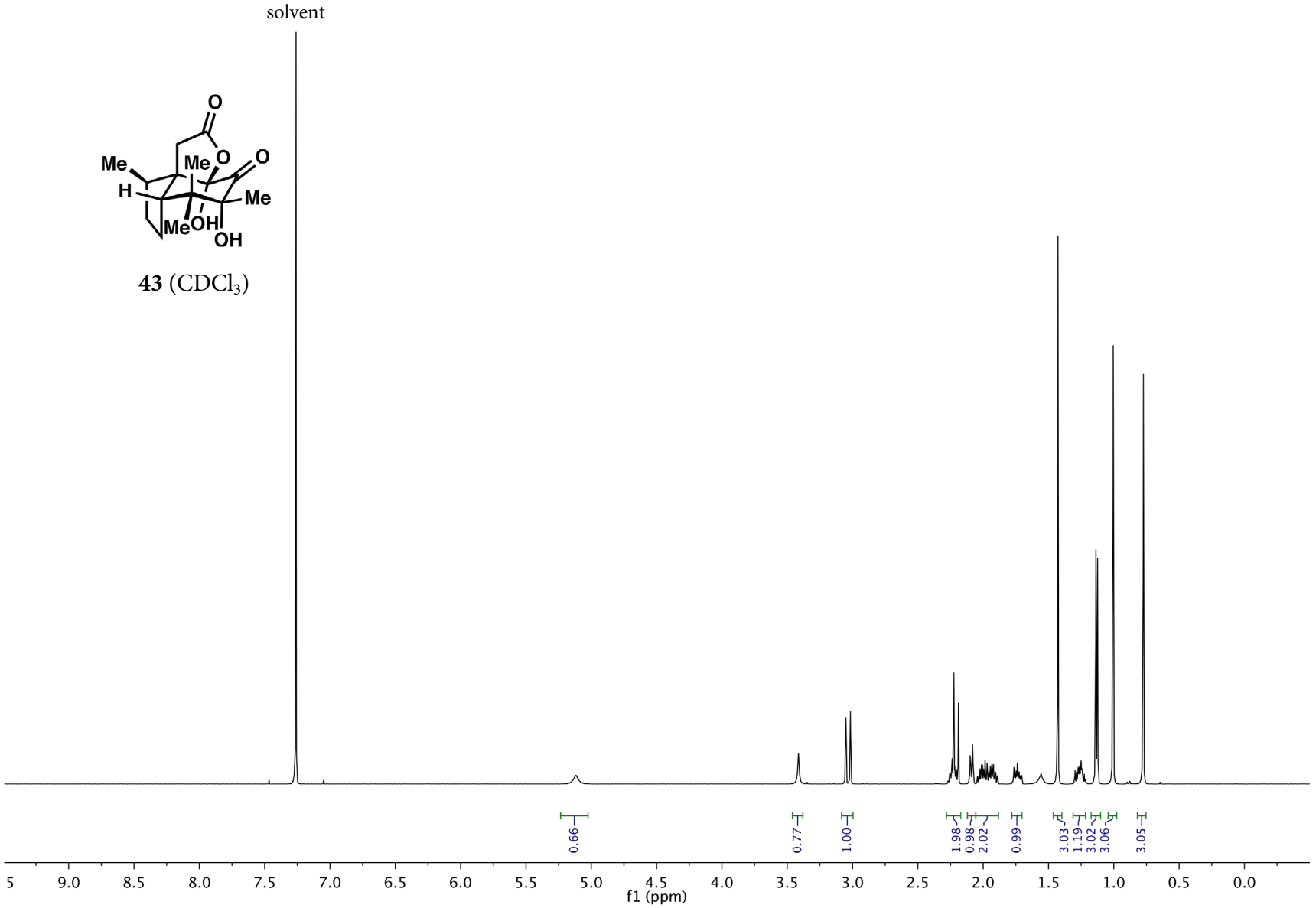
41 ($CDCl_3$)



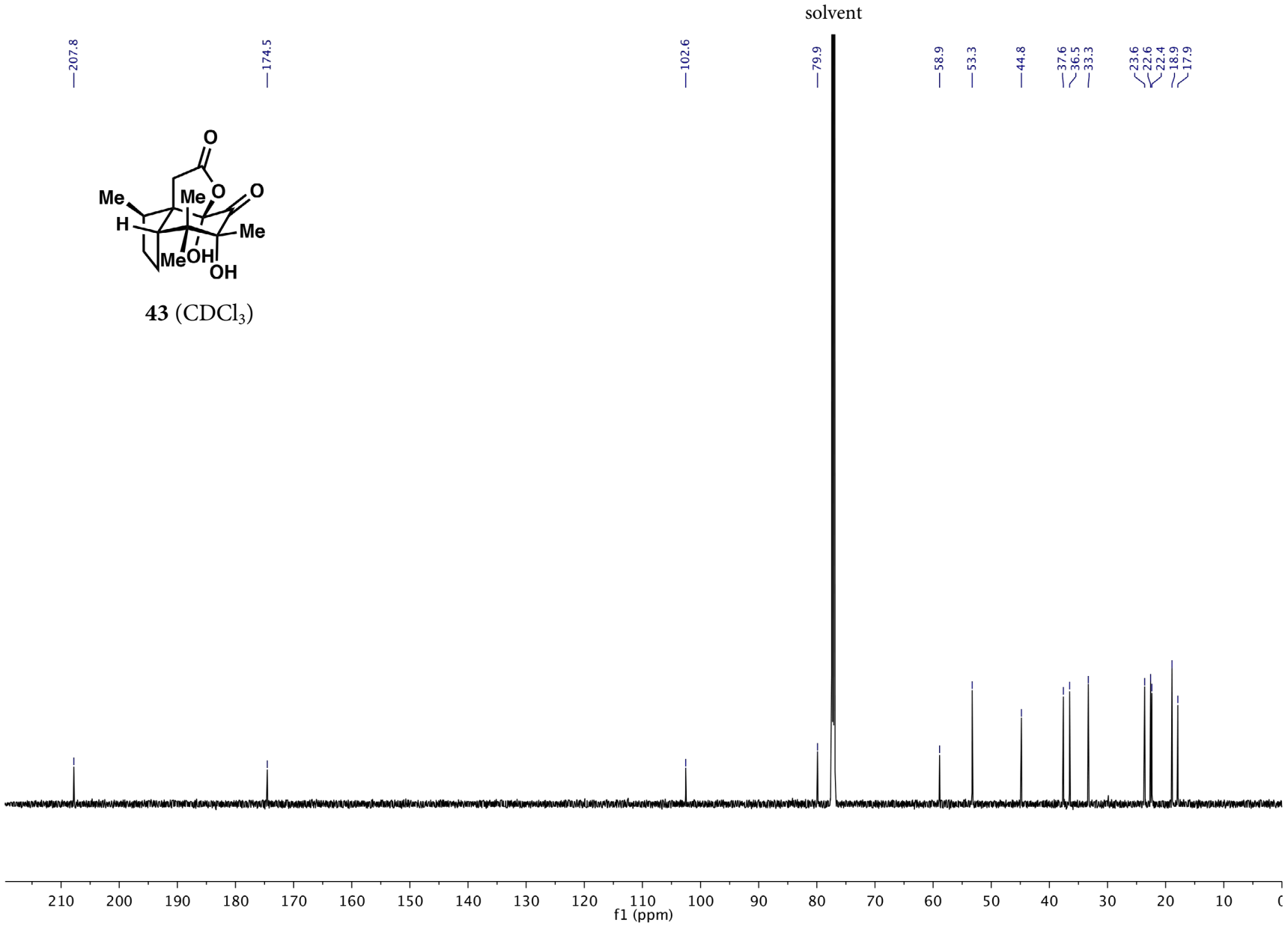
42 ($CDCl_3$)


solvent
196.9
170.6
167.0
134.5
130.1
119.9
86.6
28.5
25.7
Me
Me
Me
O
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

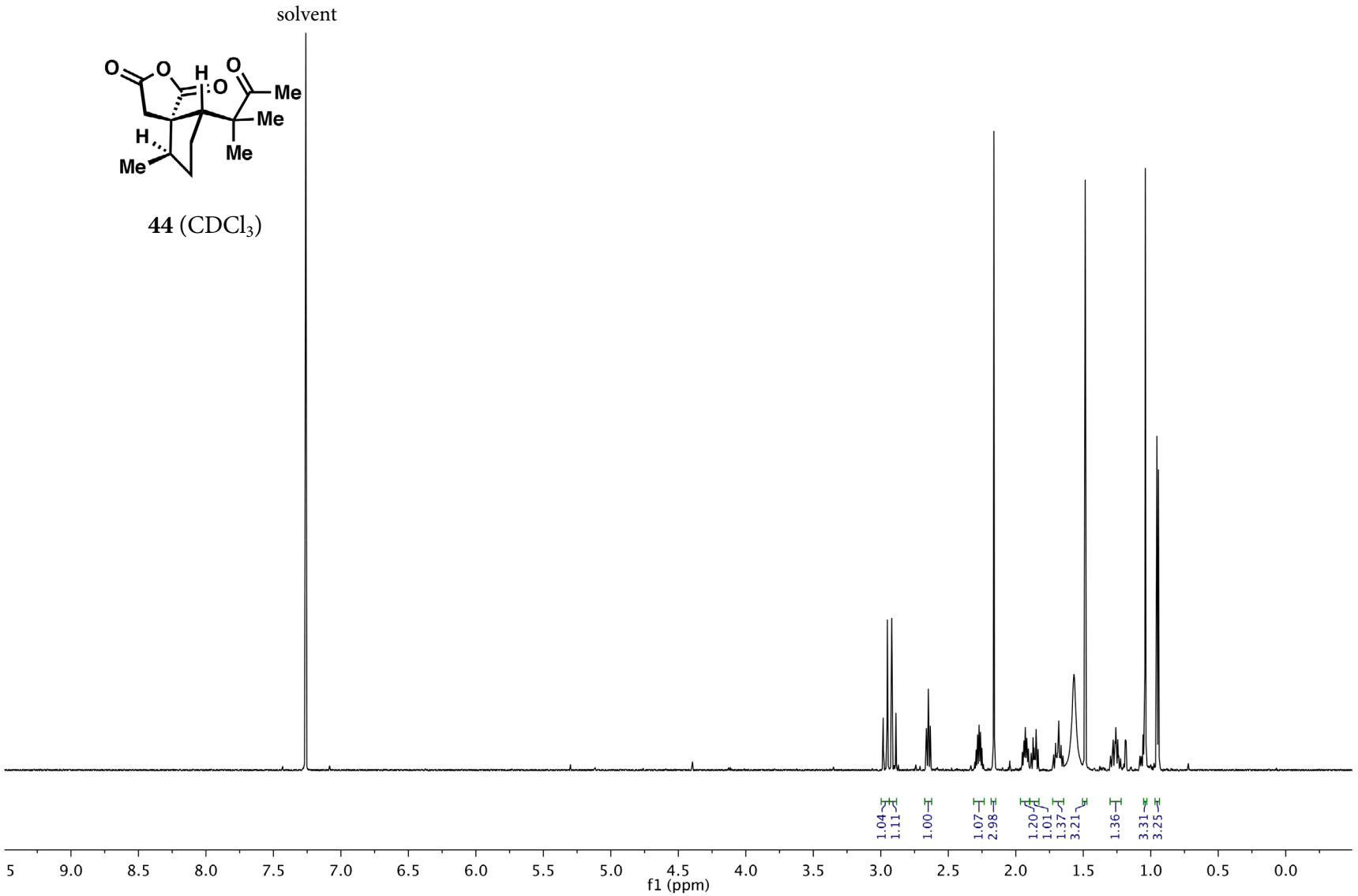
42 ($CDCl_3$)


solvent
O
O
Me
Me
O
O
H
Me
Me
OH
OH
0.66
0.77
1.00
1.98
0.98
2.02
0.99
3.03
1.19
3.02
3.06
3.05
5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

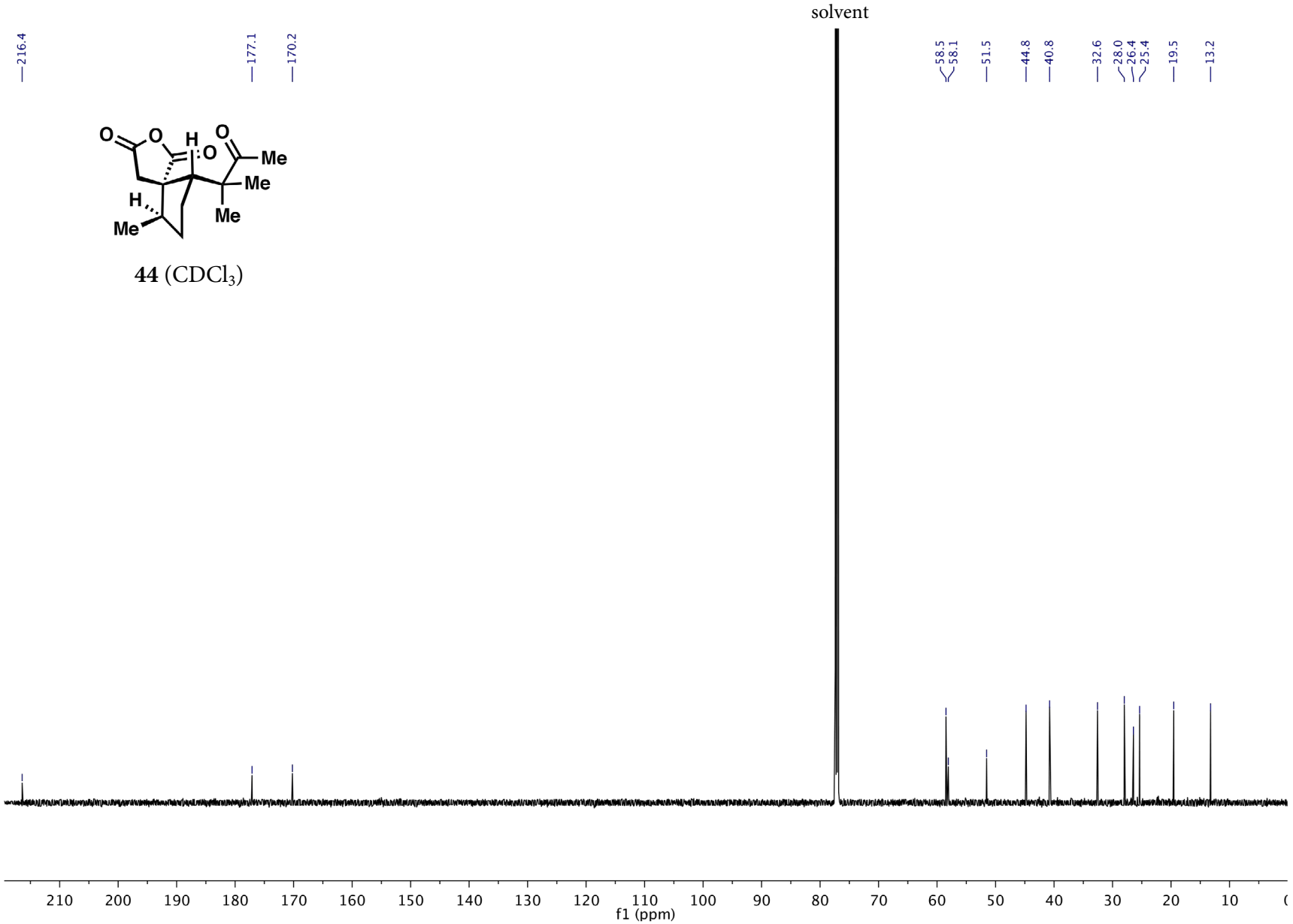
43 ($CDCl_3$)


solvent
207.8
174.5
102.6
79.9
58.9
53.3
44.8
37.6
36.5
33.3
23.6
22.6
22.4
18.9
17.9
O
O
O
Me
Me
H
Me
Me
OH
OH
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

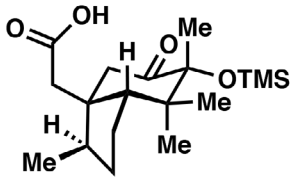
43 ($CDCl_3$)


solvent
O
O
H
O
O
Me
Me
Me
H
Me
1.04
1.11
1.00
1.07
2.98
1.20
1.01
1.37
3.21
1.36
3.31
3.25
5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

44 ($CDCl_3$)

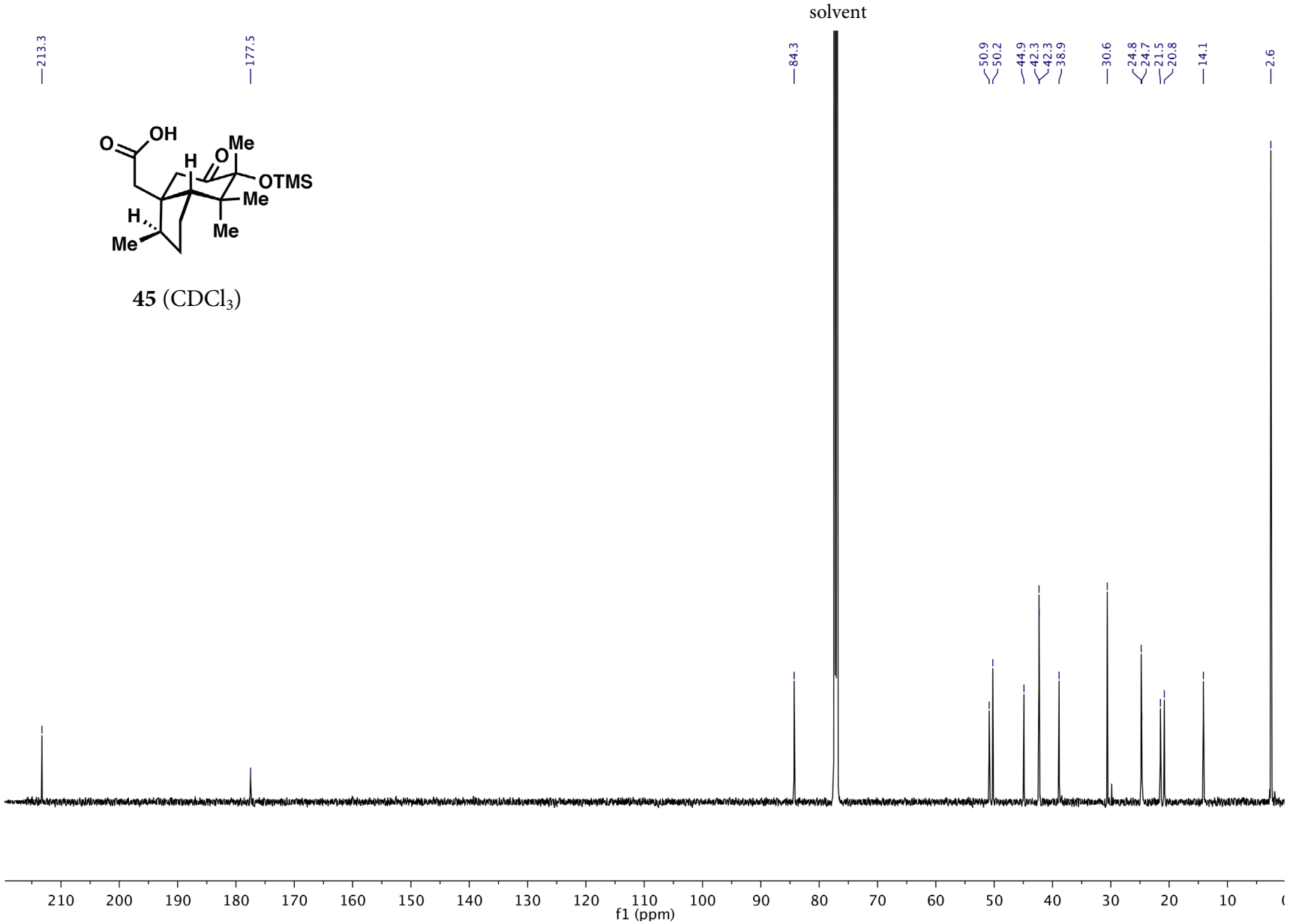

solvent
216.4
177.1
170.2
58.5
58.1
51.5
44.8
40.8
32.6
28.0
26.4
25.4
19.5
13.2
O
O
H
O
O
Me
Me
Me
H
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

44 ($CDCl_3$)

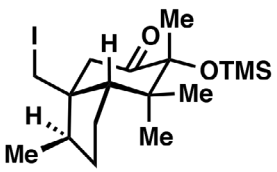

O
OH
H
O
Me
OTMS
Me
H
Me
Me

45 ($CDCl_3$)

solvent
1.04
1.00
1.08
1.06
1.07
1.12
2.23
1.01
4.58
3.52
3.46
3.32
9.87
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

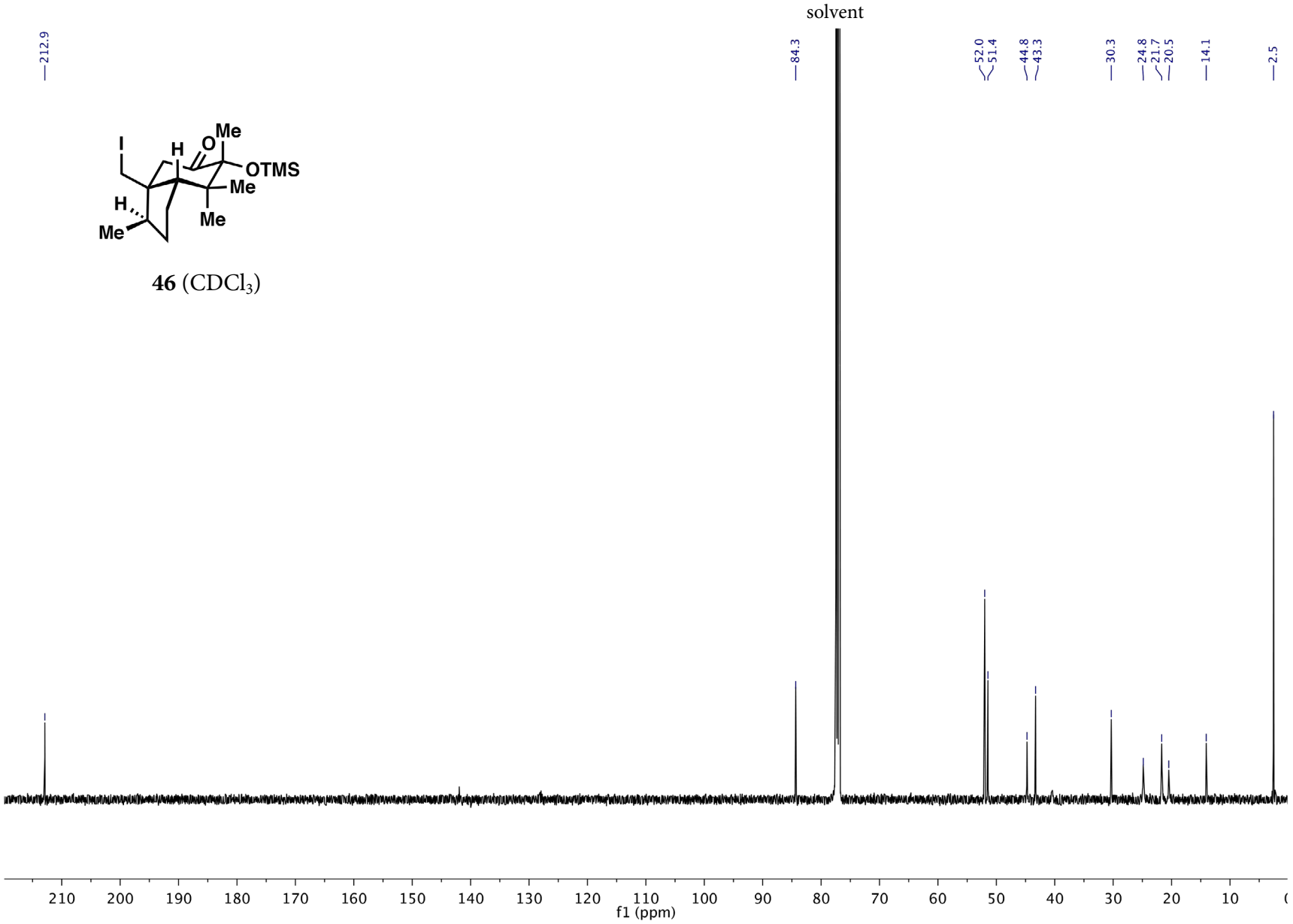

solvent
213.3
177.5
84.3
50.9
50.2
44.9
42.3
42.3
38.9
30.6
24.8
24.7
21.5
20.8
14.1
2.6
O
OH
H
O
Me
OTMS
Me
H
Me
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

45 ($CDCl_3$)

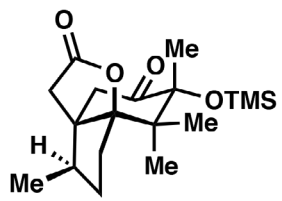

I
H
O
Me
OTMS
Me
H
Me
Me

46 ($CDCl_3$)

solvent
1.00
1.02
0.95
0.78
0.93
0.95
2.85
3.01
1.04
3.11
3.16
2.91
9.18
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

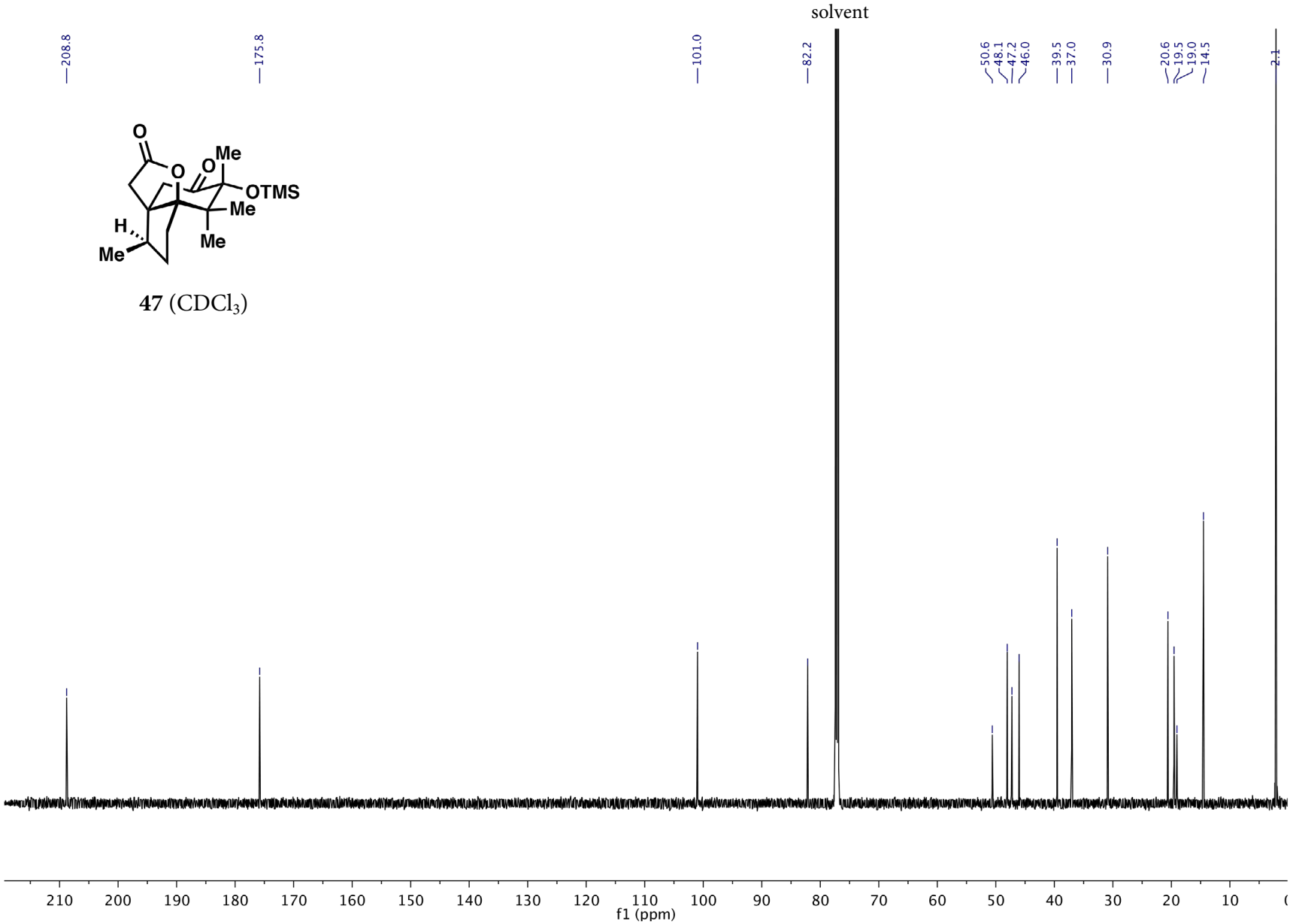

solvent
212.9
84.3
52.0
51.4
44.8
43.3
30.3
24.8
21.7
20.5
14.1
2.5
I
H
O
Me
OTMS
Me
H
Me
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

46 ($CDCl_3$)

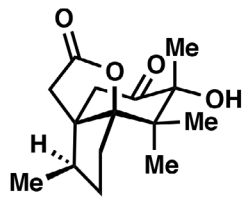

O
O
O
Me
OTMS
Me
H
Me
Me

47 ($CDCl_3$)

solvent
2.01
0.97
1.06
1.00
0.99
1.01
1.00
3.03
1.23
3.03
3.05
3.08
8.89
5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

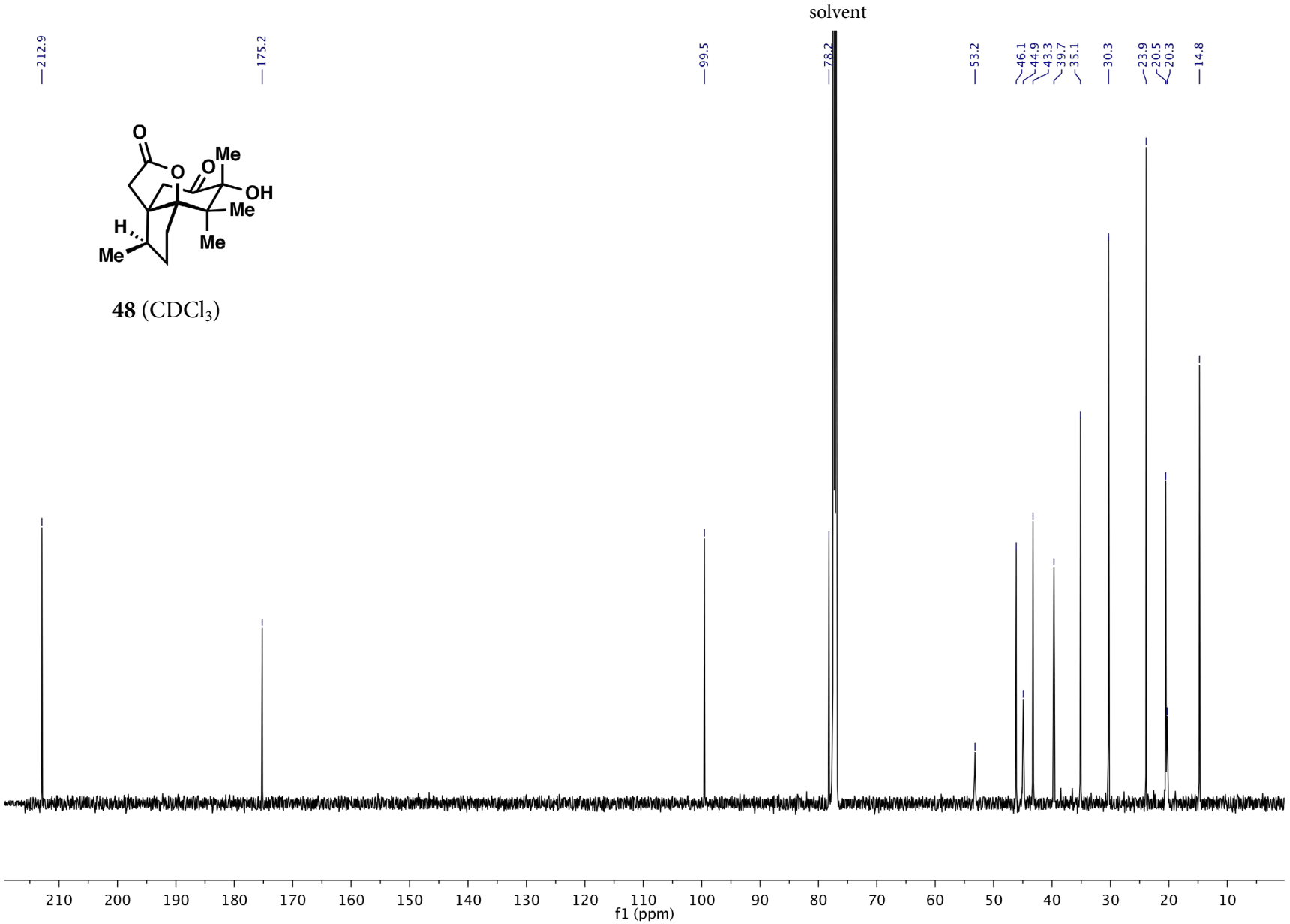

solvent
208.8
175.8
101.0
82.2
50.6
48.1
47.2
46.0
39.5
37.0
30.9
20.6
19.5
19.0
14.5
2.1
O
O
O
Me
OTMS
Me
H
Me
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

47 ($CDCl_3$)

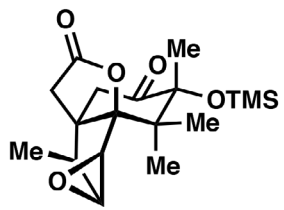

O
O
O
Me
OH
Me
H
Me
Me

48 ($CDCl_3$)

solvent
0.72
0.96
0.96
1.00
0.99
1.04
1.97
1.03
3.91
3.01
2.90
3.09
5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

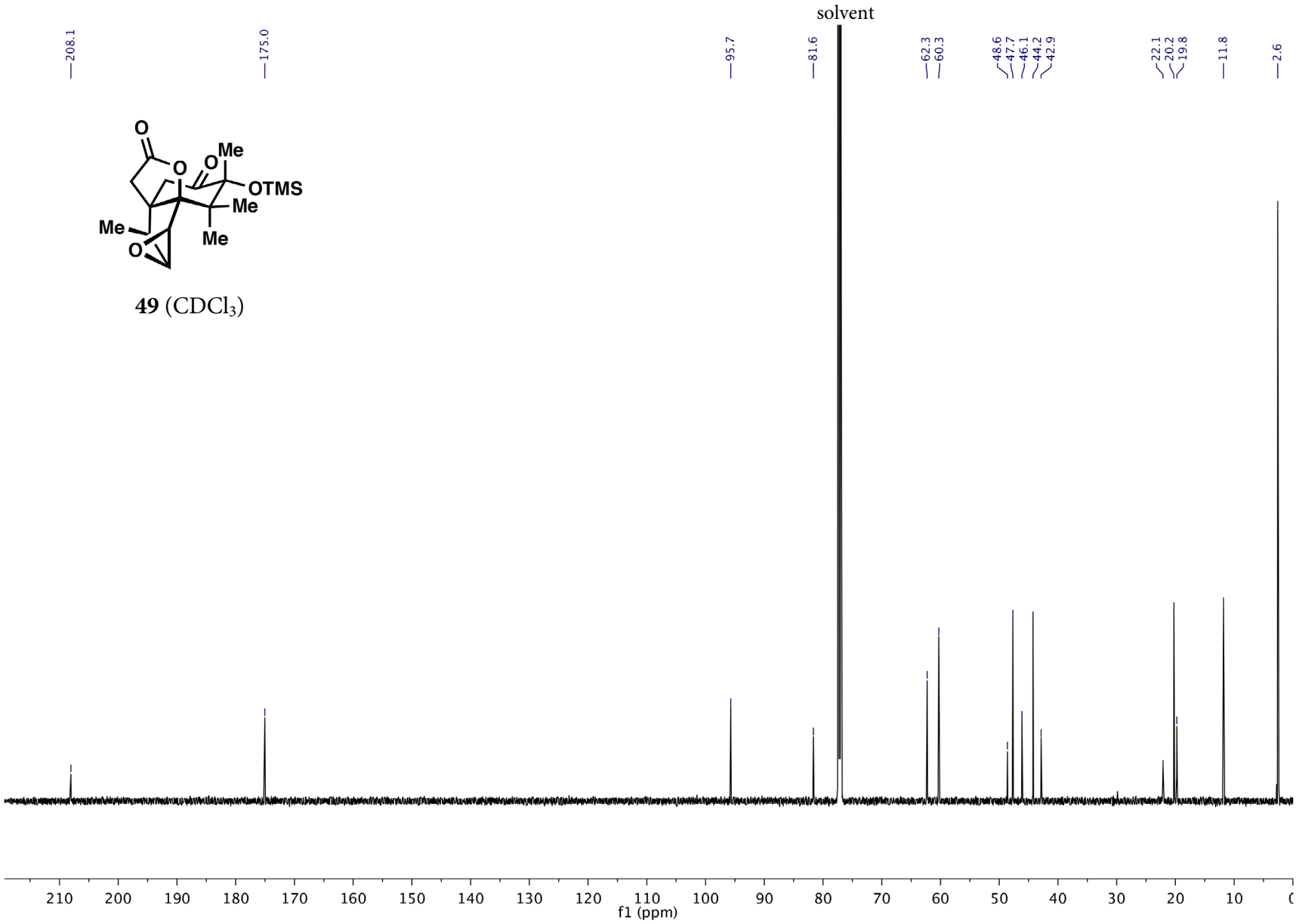

solvent
212.9
175.2
99.5
78.2
53.2
46.1
44.9
43.3
39.7
35.1
30.3
23.9
20.5
20.3
14.8
O
O
O
Me
OH
Me
H
Me
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

48 ($CDCl_3$)

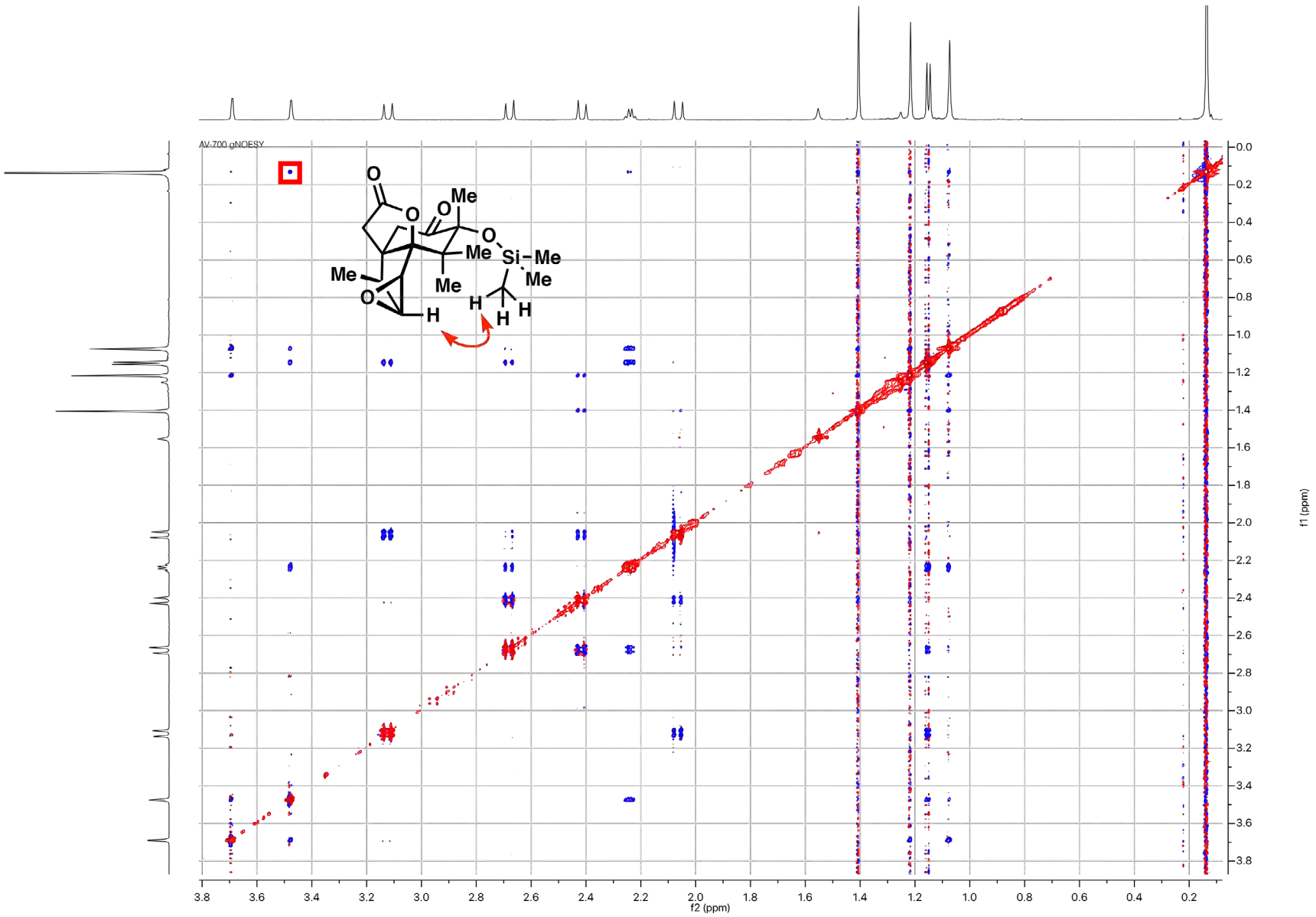

O
O
O
Me
OTMS
Me
Me
Me
O

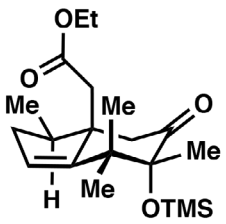
49 ($CDCl_3$)

solvent
1.02
1.00
1.03
1.06
1.09
1.02
1.06
3.21
3.24
3.29
3.11
9.55
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


solvent
208.1
175.0
95.7
81.6
62.3
60.3
48.6
47.7
46.1
44.2
42.9
22.1
20.2
19.8
11.8
2.6
O
O
O
Me
OTMS
Me
Me
Me
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

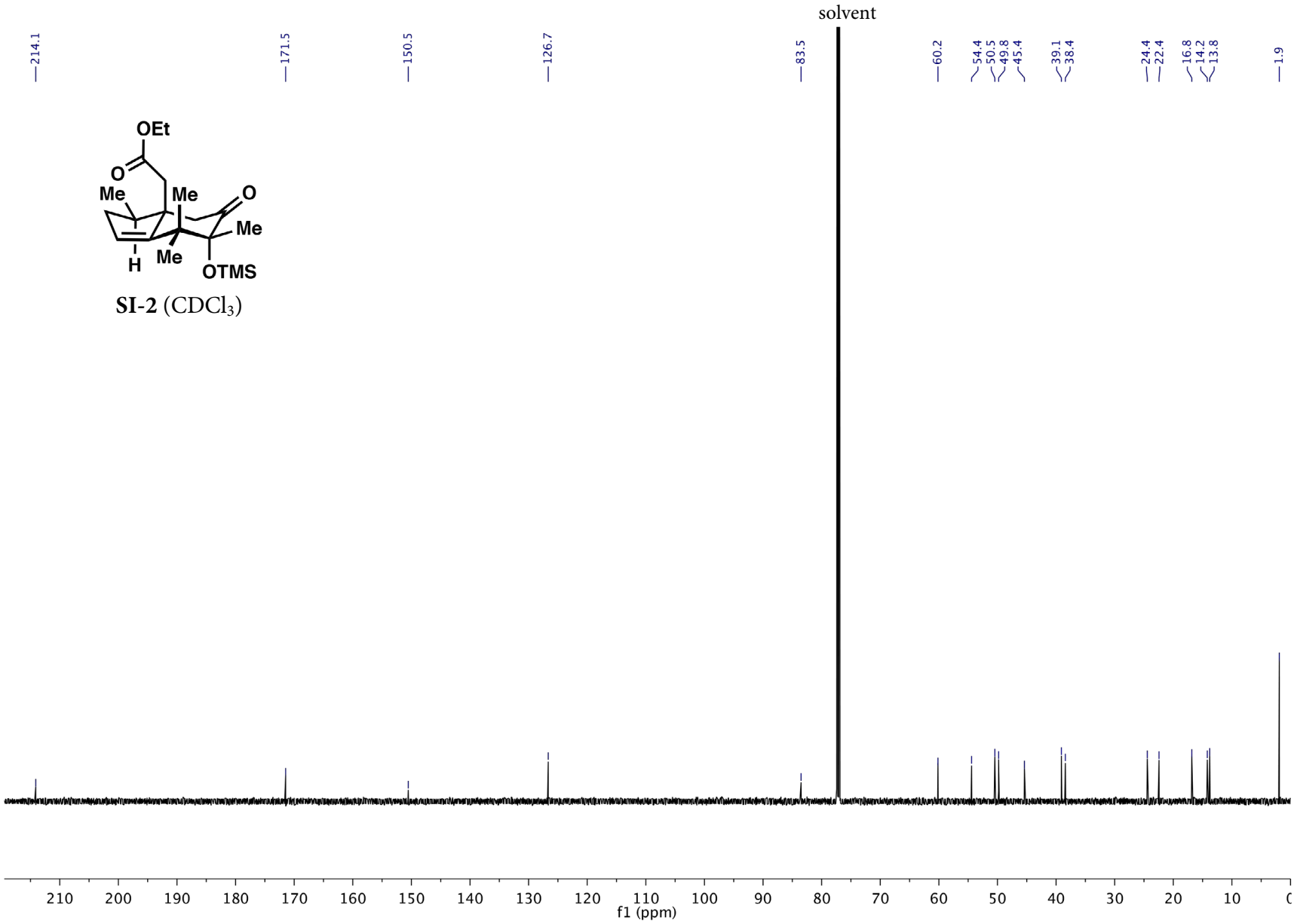
49 ($CDCl_3$)


AV-700 gNOESY
O
O
O
Me
O
Me
Si
Me
Me
Me
Me
O
H
H
H
H
f2 (ppm)
f1 (ppm)

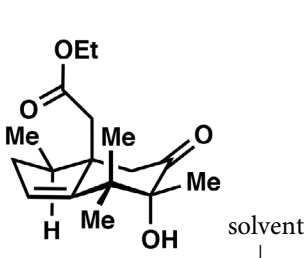

OEt
O
Me
Me
O
Me
H
Me
OTMS

SI-2 ($CDCl_3$)

1.54 H2O
solvent
0.97
1.92
1.00
1.06
1.95
1.99
1.00
3.87
6.06
2.95
2.93
8.78
f1 (ppm)

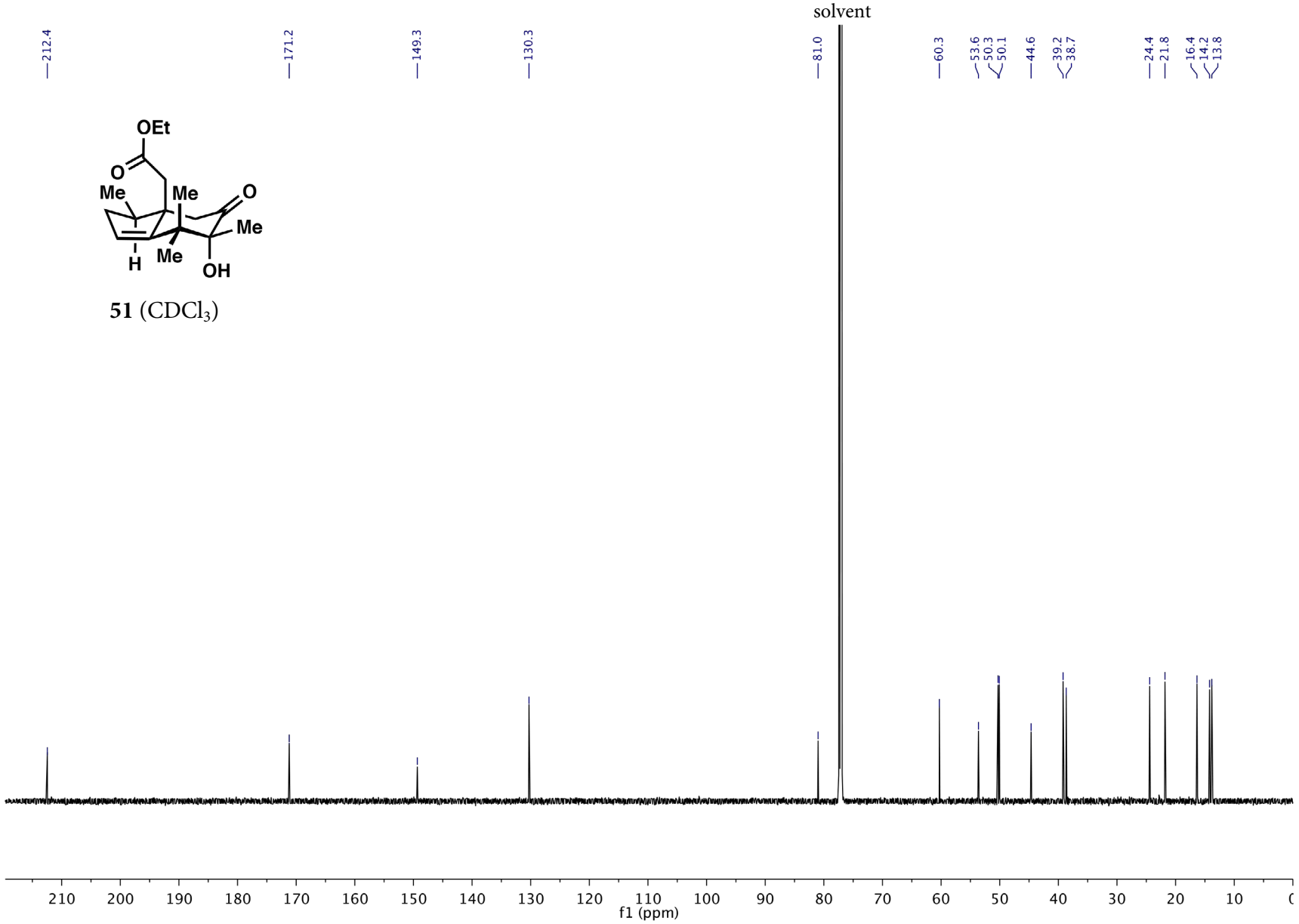

solvent
214.1
171.5
150.5
126.7
83.5
60.2
54.4
50.5
49.8
45.4
39.1
38.4
24.4
22.4
16.8
14.2
13.8
1.9
OEt
O
Me
Me
O
Me
H
Me
OTMS
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

SI-2 ($CDCl_3$)

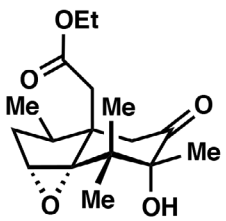

OEt
O
Me
Me
O
Me
H
Me
OH

51 ($CDCl_3$)

solvent
0.93
1.90
1.00
1.09
0.90
0.98
1.97
0.99
0.90
3.36
2.95
2.93
3.02
2.96
f1 (ppm)

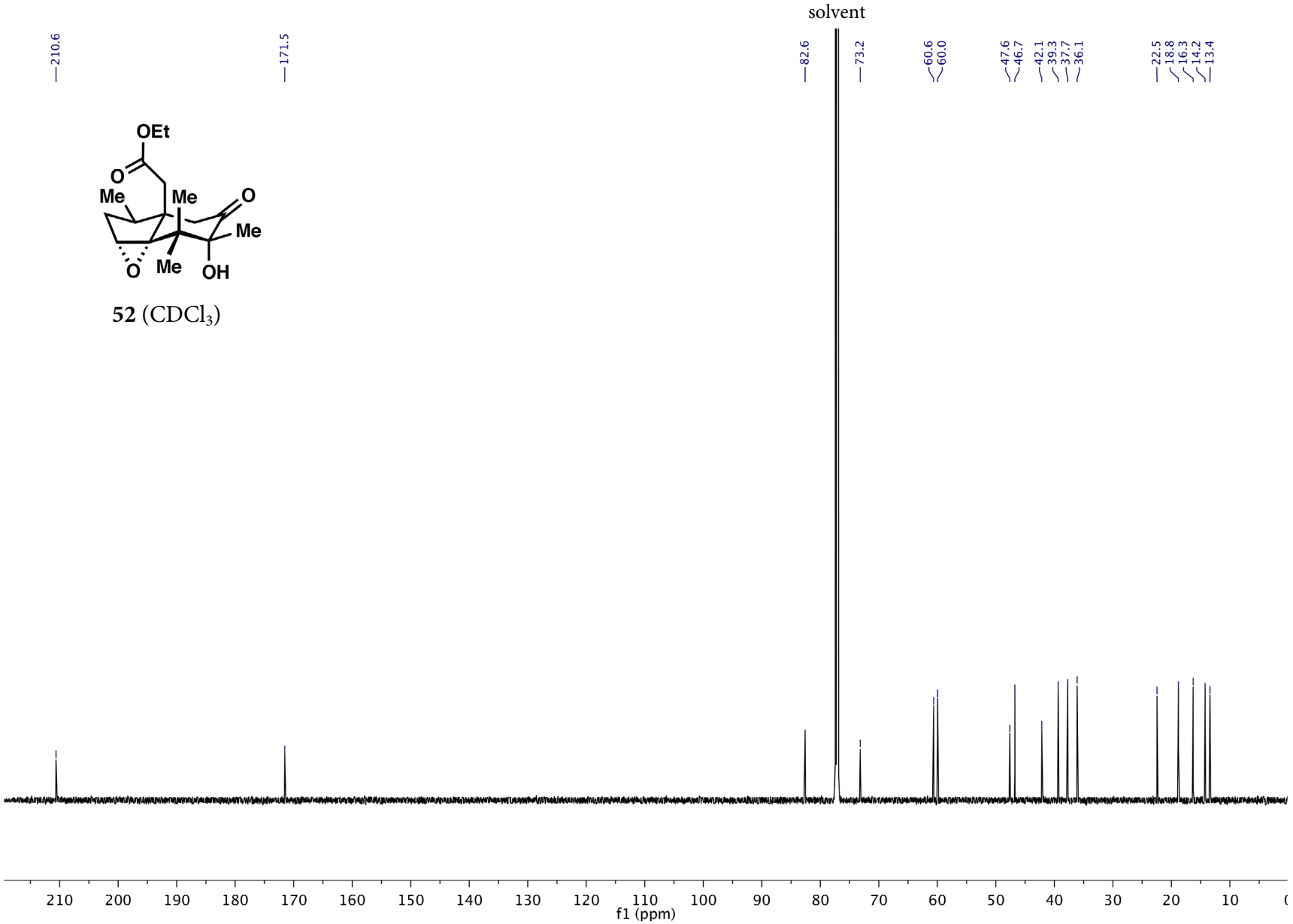

solvent
212.4
171.2
149.3
130.3
81.0
60.3
53.6
50.3
50.1
44.6
39.2
38.7
24.4
21.8
16.4
14.2
13.8
OEt
O
Me
Me
O
Me
H
Me
OH
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

51 ($CDCl_3$)

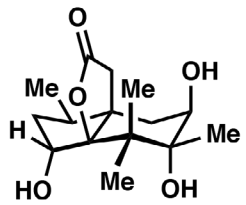

OEt
O
Me
Me
O
Me
O
Me
OH

52 ($CDCl_3$)

solvent
1.01
2.07
1.00
1.06
1.06
1.06
1.04
1.06
1.04
1.05
3.20
3.30
3.22
3.17
3.30
5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

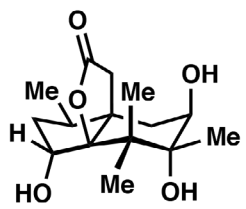

solvent
210.6
171.5
82.6
73.2
60.6
60.0
47.6
46.7
42.1
39.3
37.7
36.1
22.5
18.8
16.3
14.2
13.4
OEt
O
Me
Me
O
Me
O
Me
OH
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

52 ($CDCl_3$)


O
Me
O
Me
OH
H
Me
HO
Me
OH

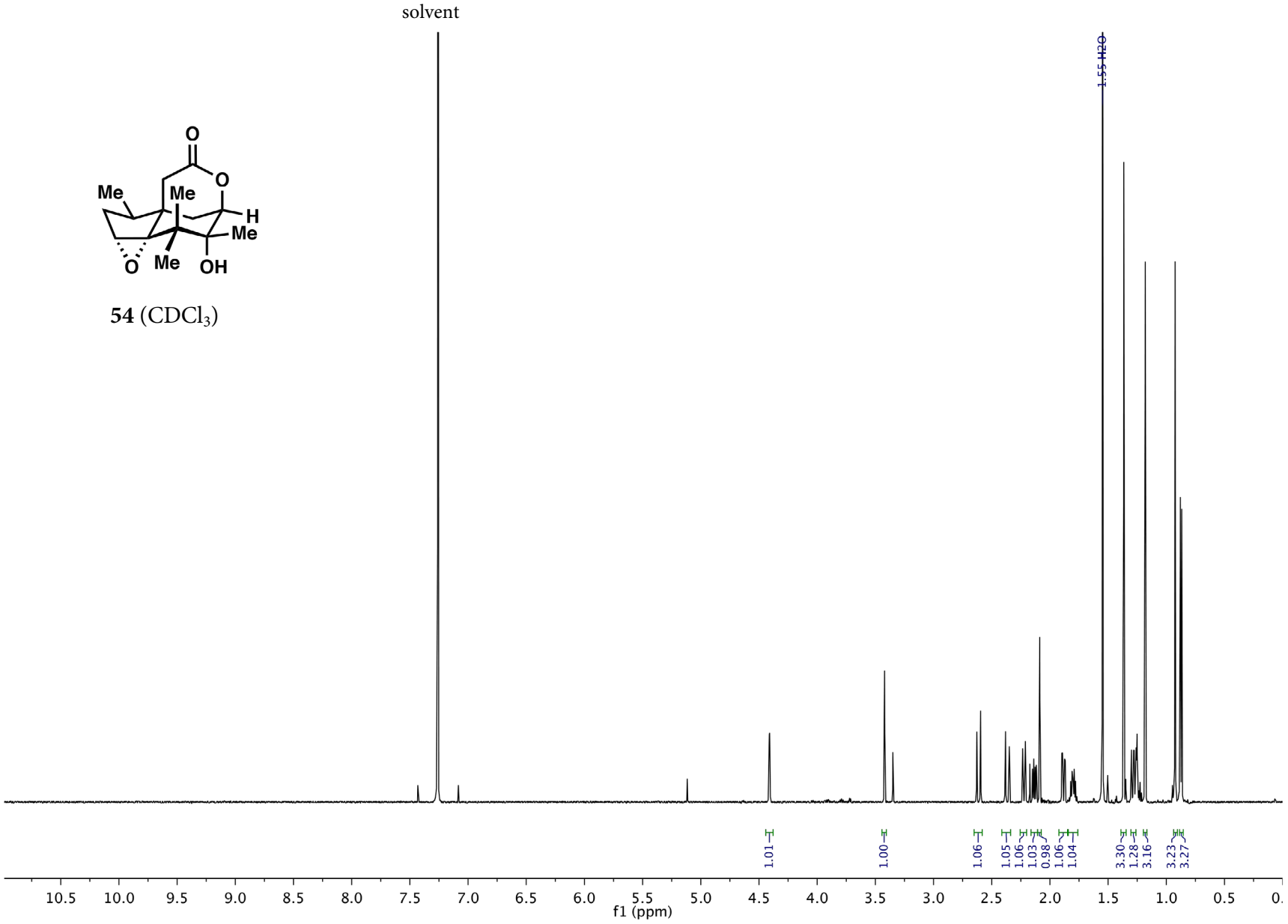
53 (CD_3OD)

solvent
1.00
1.03
0.85
1.02
1.03
0.88
1.08
1.11
1.01
3.42
3.20
3.26
3.17
f1 (ppm)

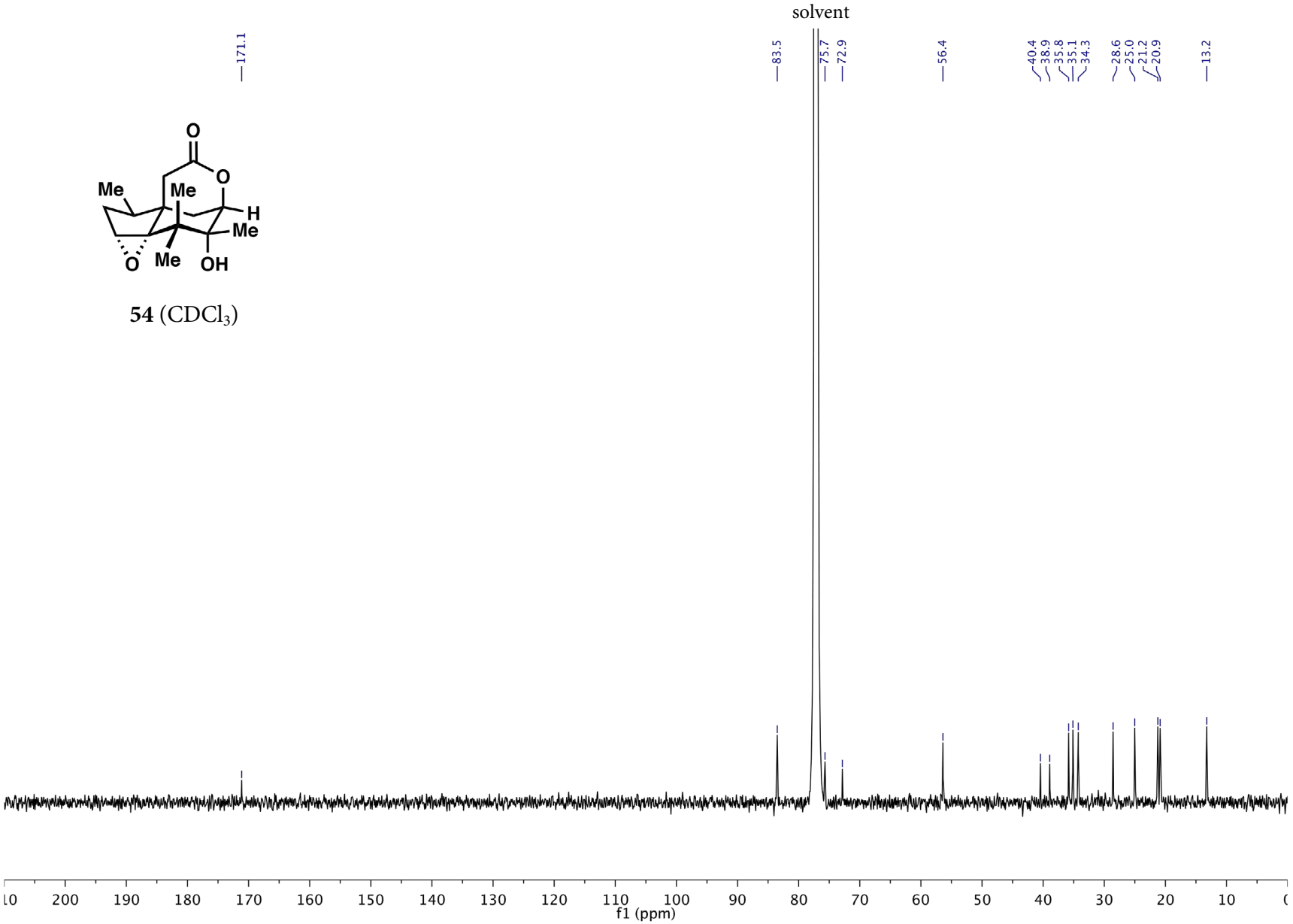

O
Me
O
Me
OH
H
Me
HO
Me
OH

53 (CD_3OD)

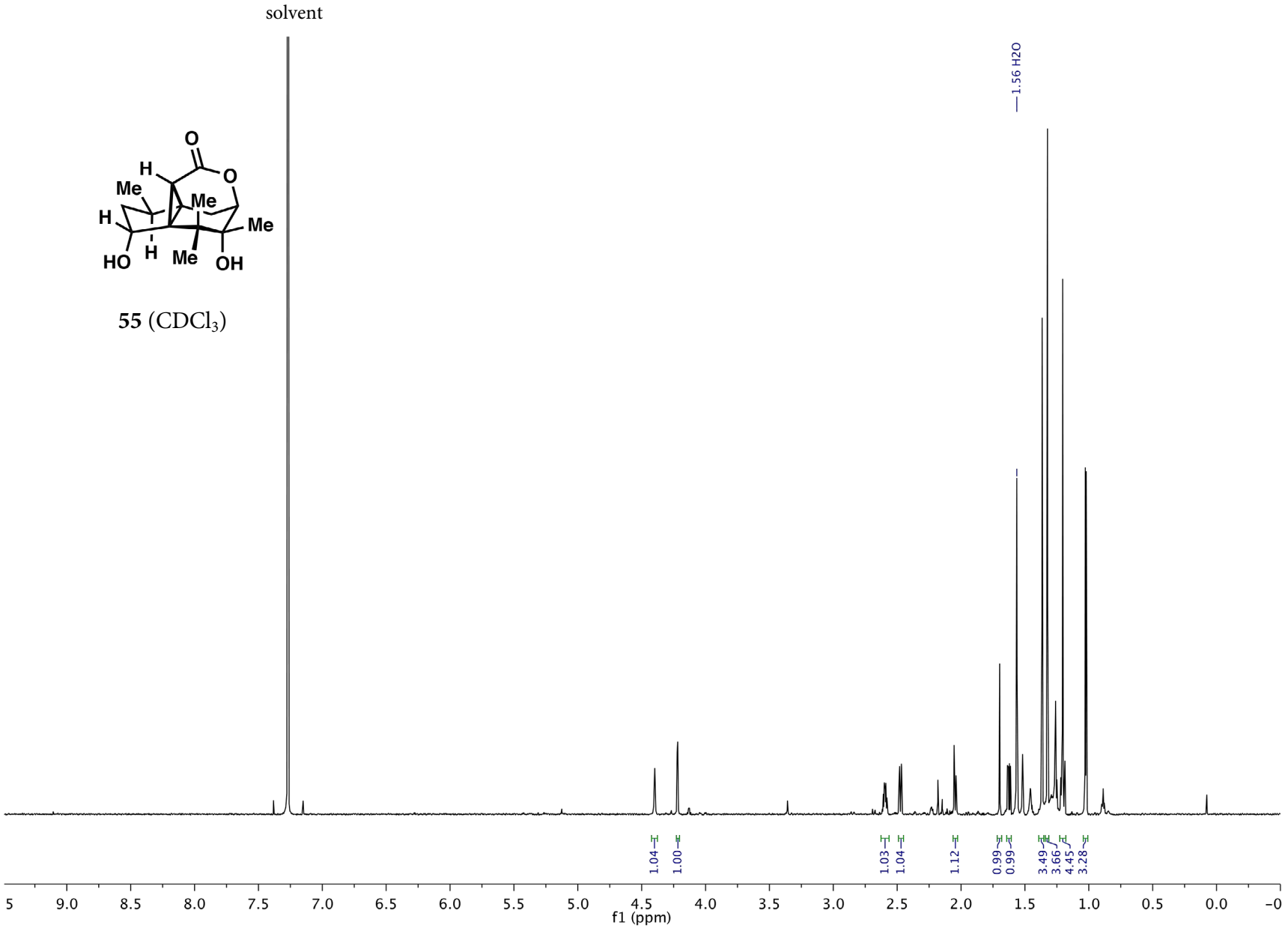
solvent
179.3
102.1
76.8
76.7
76.5
49.7
46.5
44.4
41.9
39.2
38.9
24.1
21.7
21.5
16.2
f1 (ppm)


solvent
1.55 H2O
O
O
Me
Me
H
Me
Me
O
OH
1.01
1.00
1.06
1.05
1.06
1.03
0.98
1.06
1.04
3.30
1.28
3.16
3.23
3.27
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)

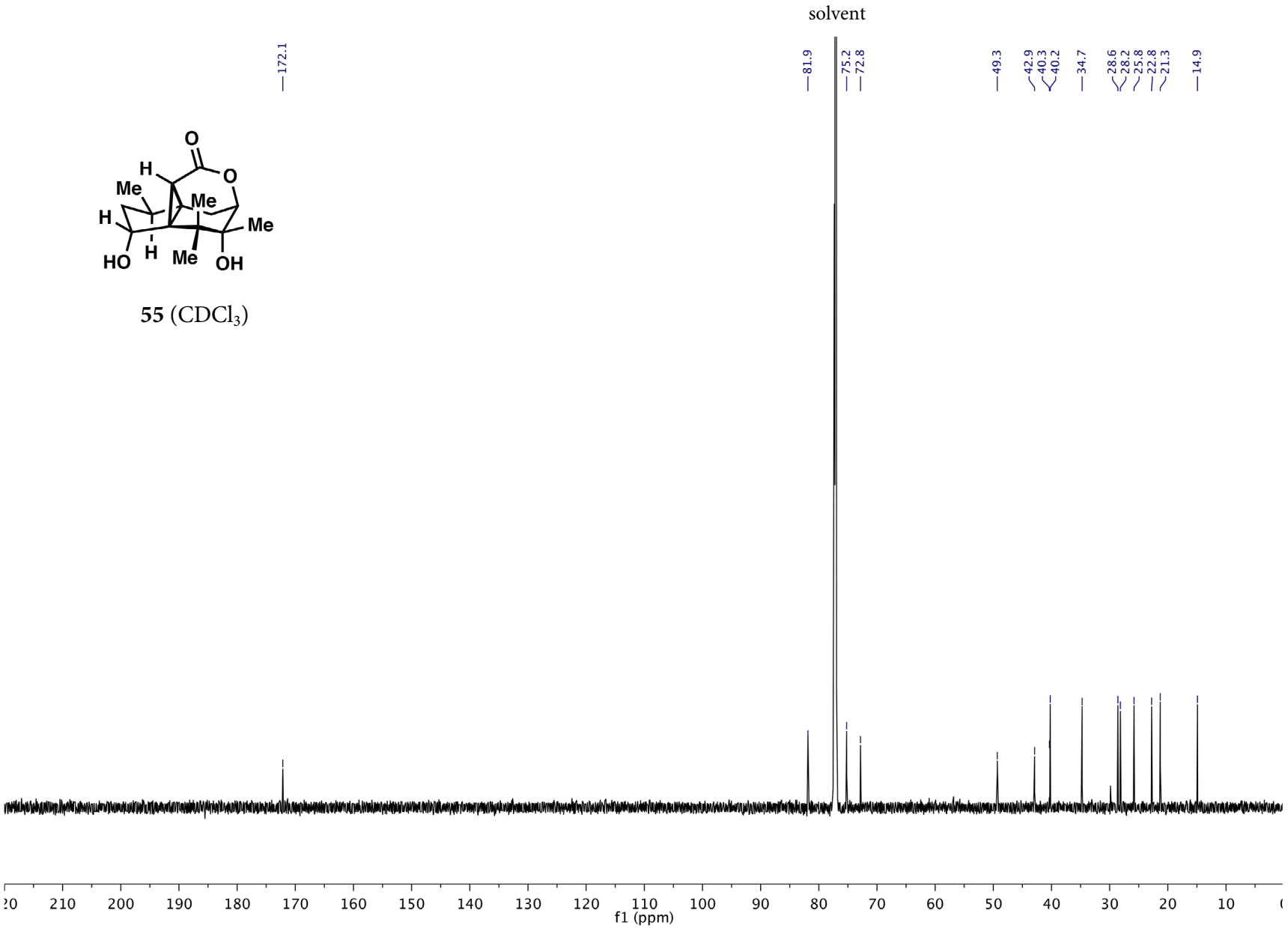
54 ($CDCl_3$)


solvent
171.1
83.5
75.7
72.9
56.4
40.4
38.9
35.8
35.1
34.3
28.6
25.0
21.2
20.9
13.2
O
O
Me
Me
H
Me
O
Me
OH
f1 (ppm)

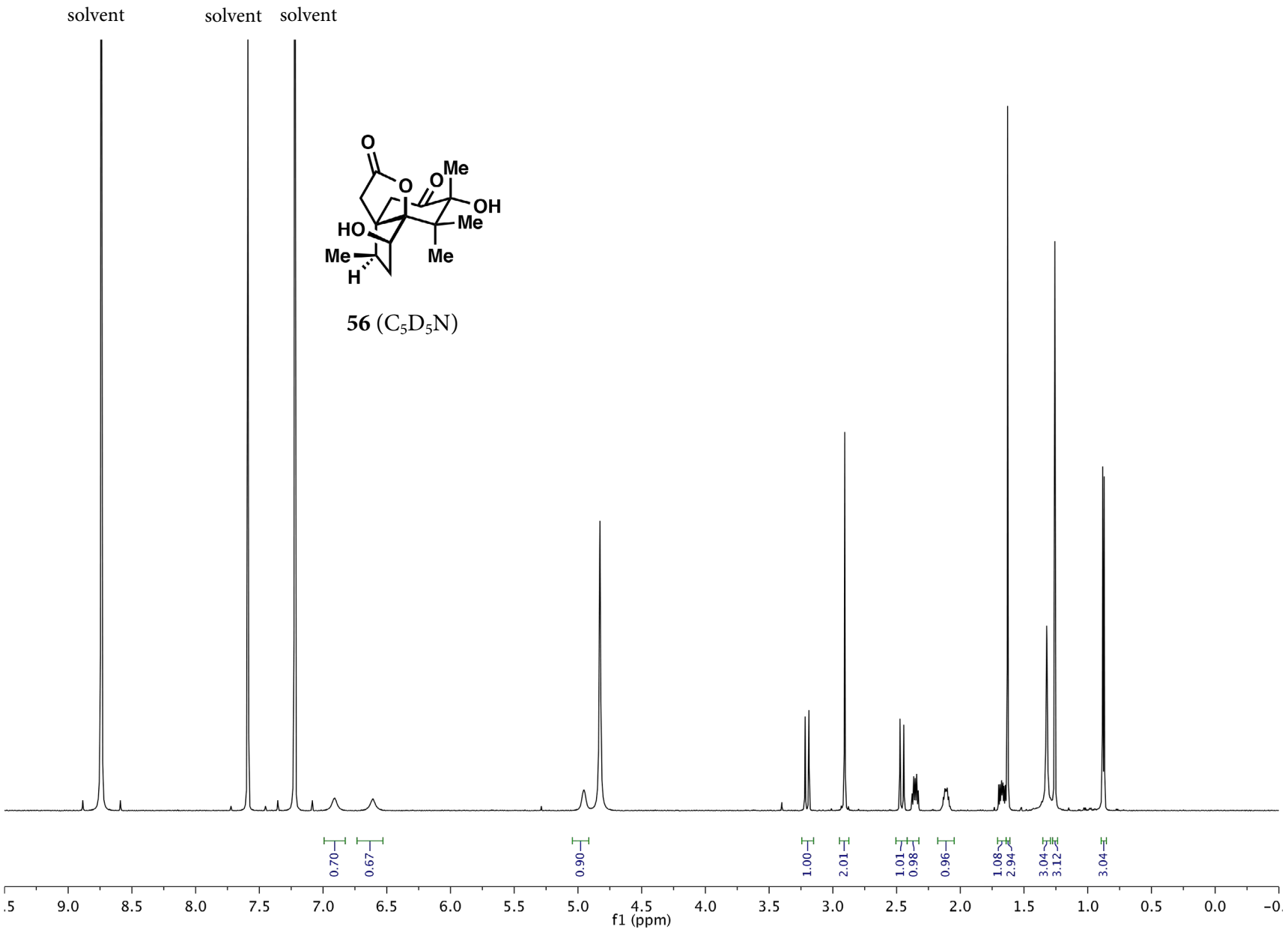
54 ($CDCl_3$)


solvent
1.56 H2O
O
H
O
Me
Me
H
Me
HO
H
Me
OH
1.04
1.00
1.03
1.04
1.12
0.99
0.99
3.49
3.66
4.45
3.28
5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

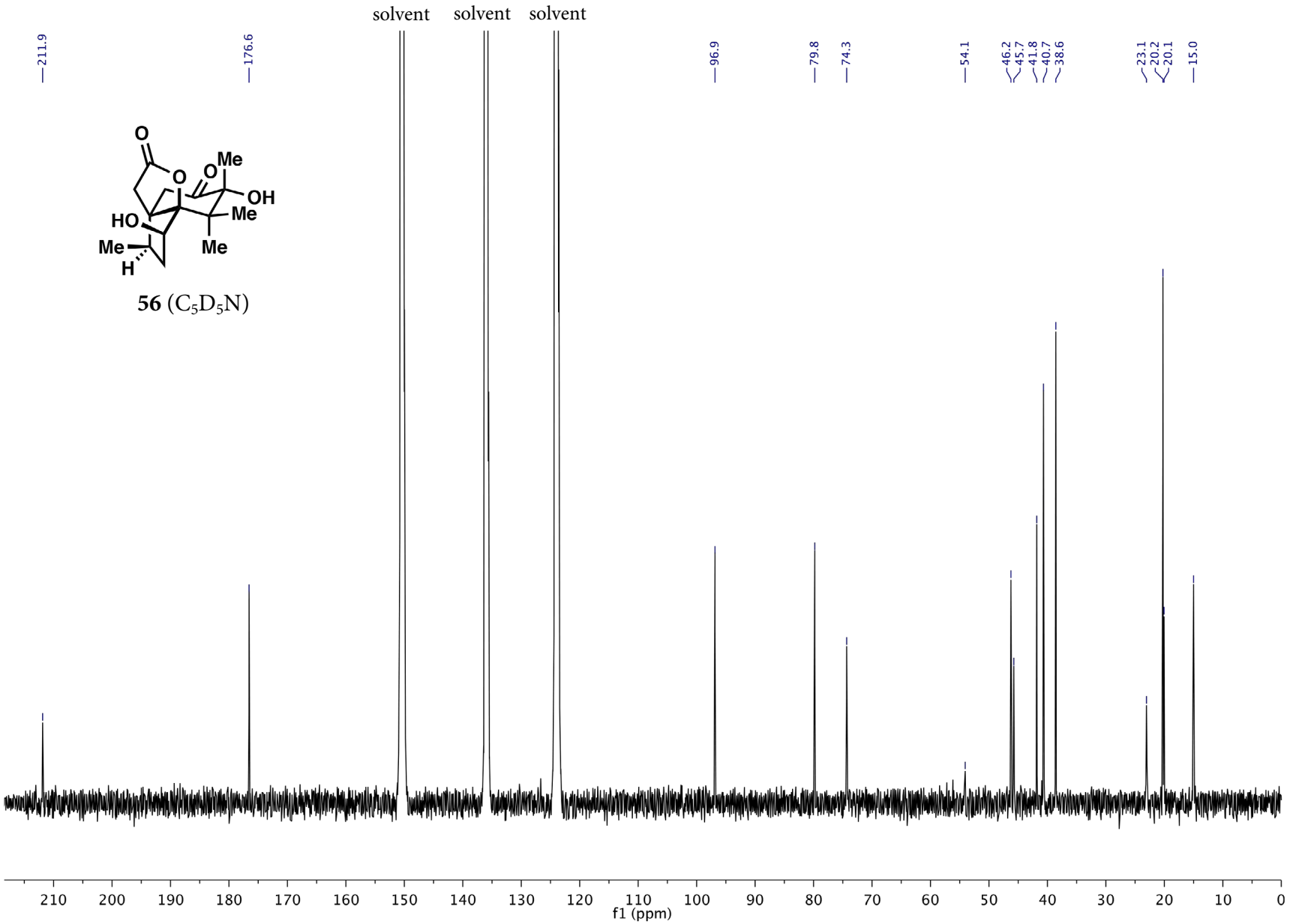
55 ($CDCl_3$)


solvent
172.1
81.9
75.2
72.8
49.3
42.9
40.3
40.2
34.7
28.6
28.2
25.8
22.8
21.3
14.9
O
H
O
Me
Me
H
Me
HO
H
Me
OH
f1 (ppm)

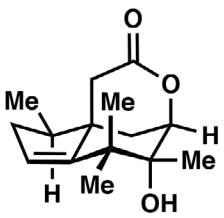
55 ($CDCl_3$)


solvent
solvent
solvent
O
O
O
Me
OH
Me
HO
Me
Me
H
0.70
0.67
0.90
1.00
2.01
1.01
0.98
0.96
1.08
2.94
3.04
3.12
3.04
f1 (ppm)

56 (C_5D_5N)

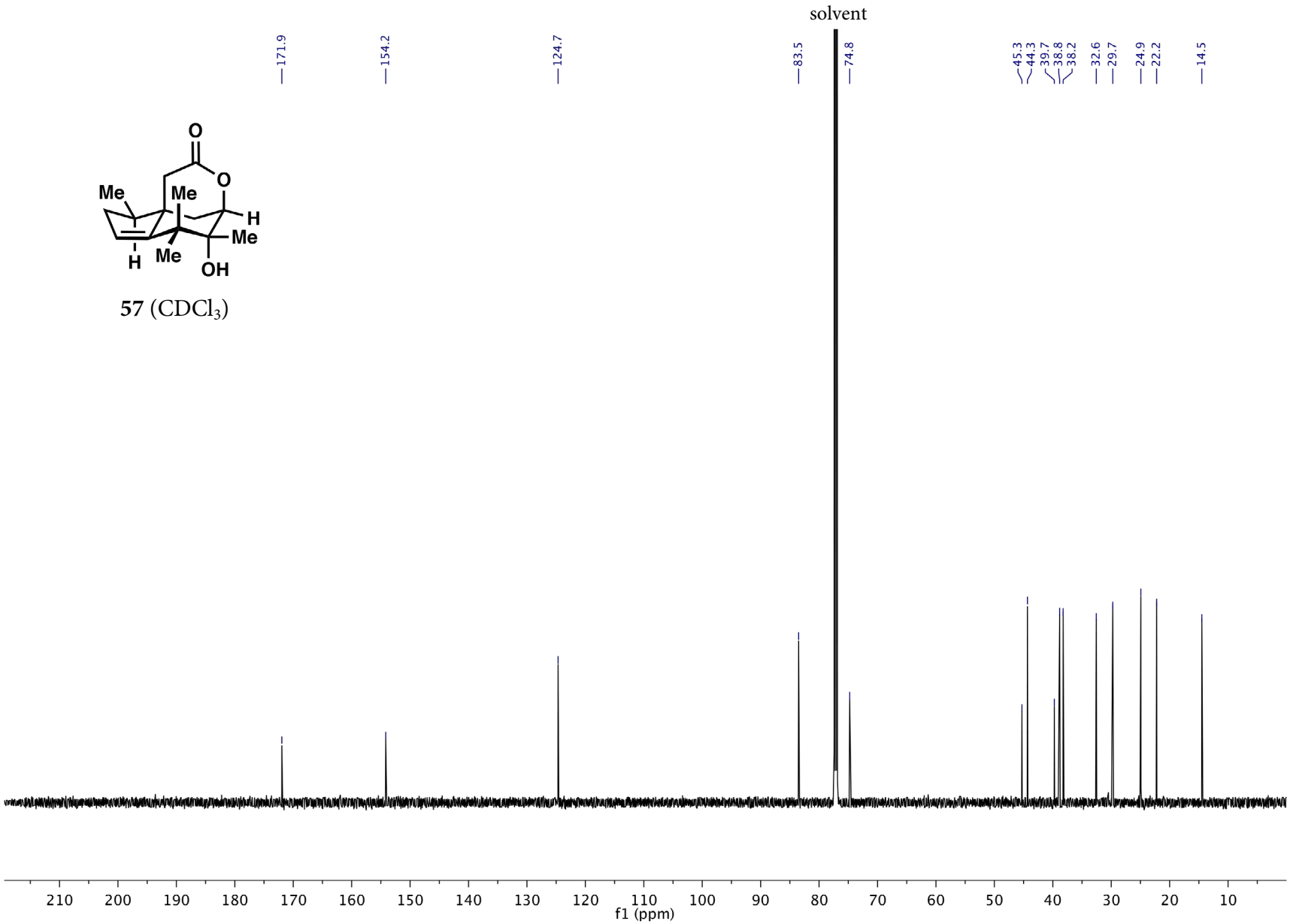

solvent
solvent
solvent
211.9
176.6
96.9
79.8
74.3
54.1
46.2
45.7
41.8
40.7
38.6
23.1
20.2
20.1
15.0
O
O
O
Me
OH
Me
HO
Me
Me
H
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

56 (C_5D_5N)

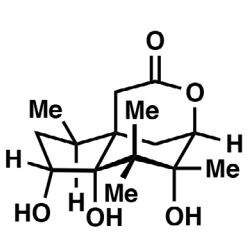

O
O
Me
Me
H
Me
H
Me
OH

57 ($CDCl_3$)

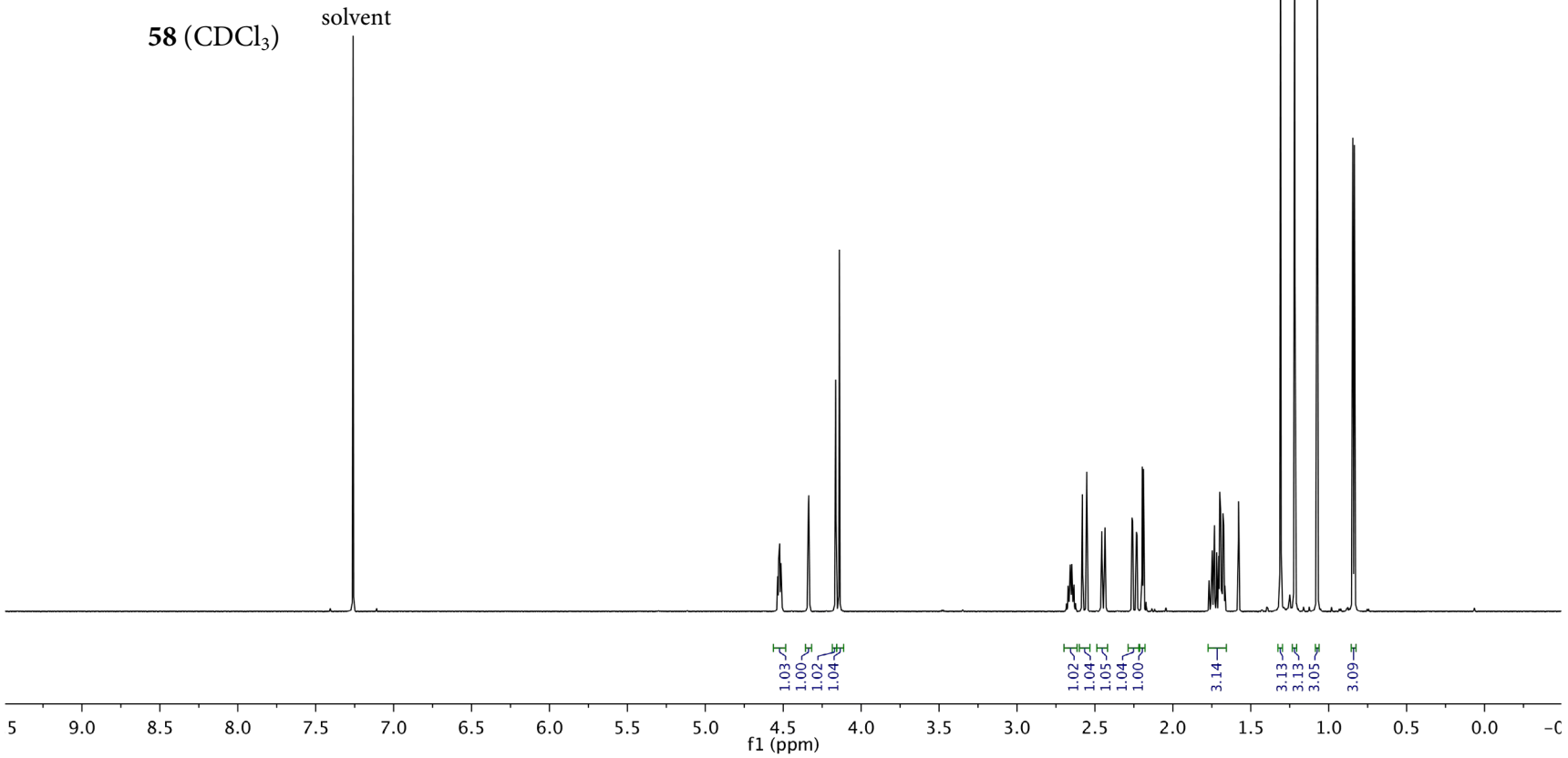
solvent
0.99
1.00
1.06
1.06
1.04
2.08
2.13
1.05
3.19
3.27
3.18
3.23
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

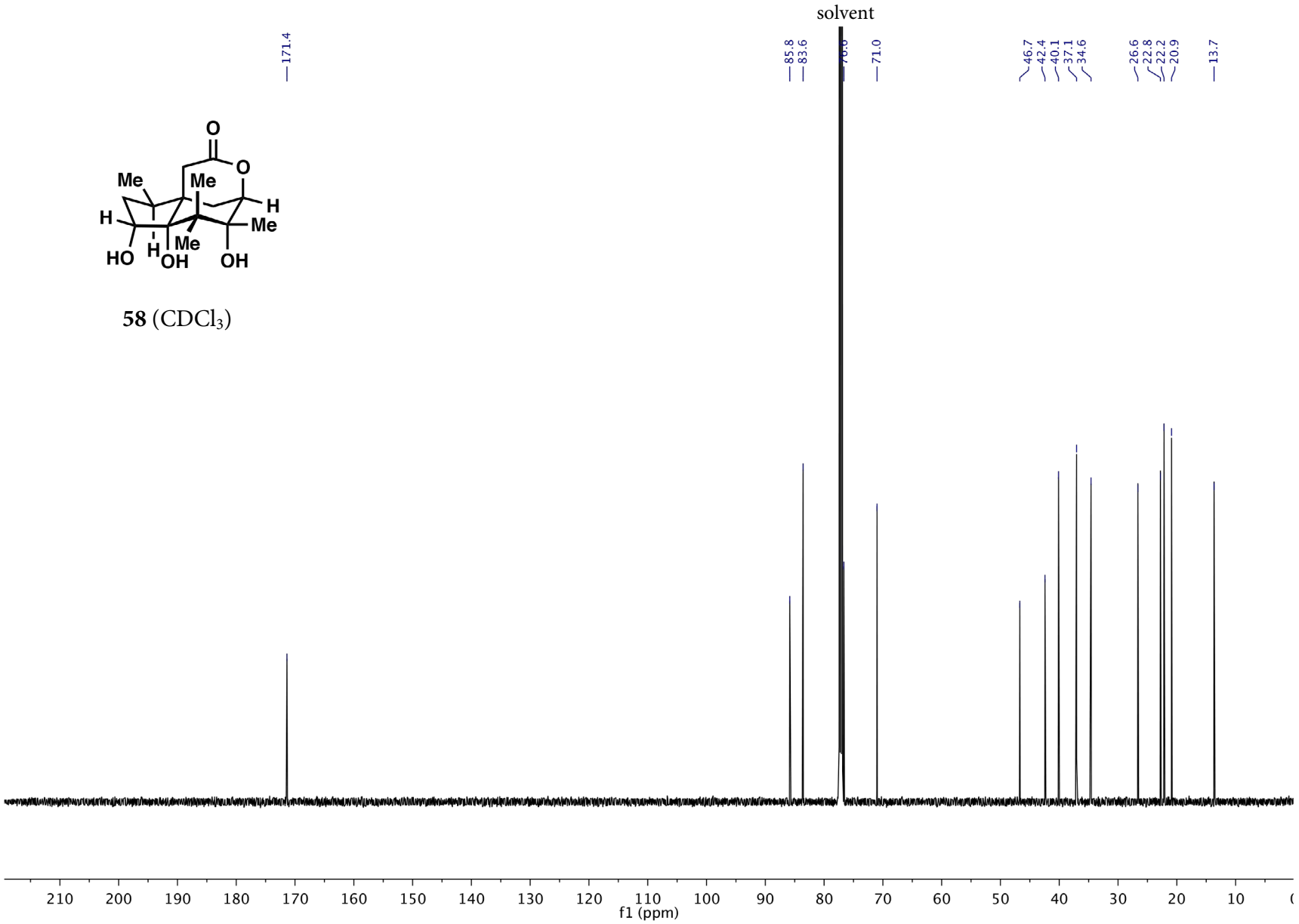

solvent
171.9
154.2
124.7
83.5
74.8
45.3
44.3
39.7
38.8
38.2
32.6
29.7
24.9
22.2
14.5
O
O
Me
Me
H
Me
H
Me
OH
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

57 ($CDCl_3$)

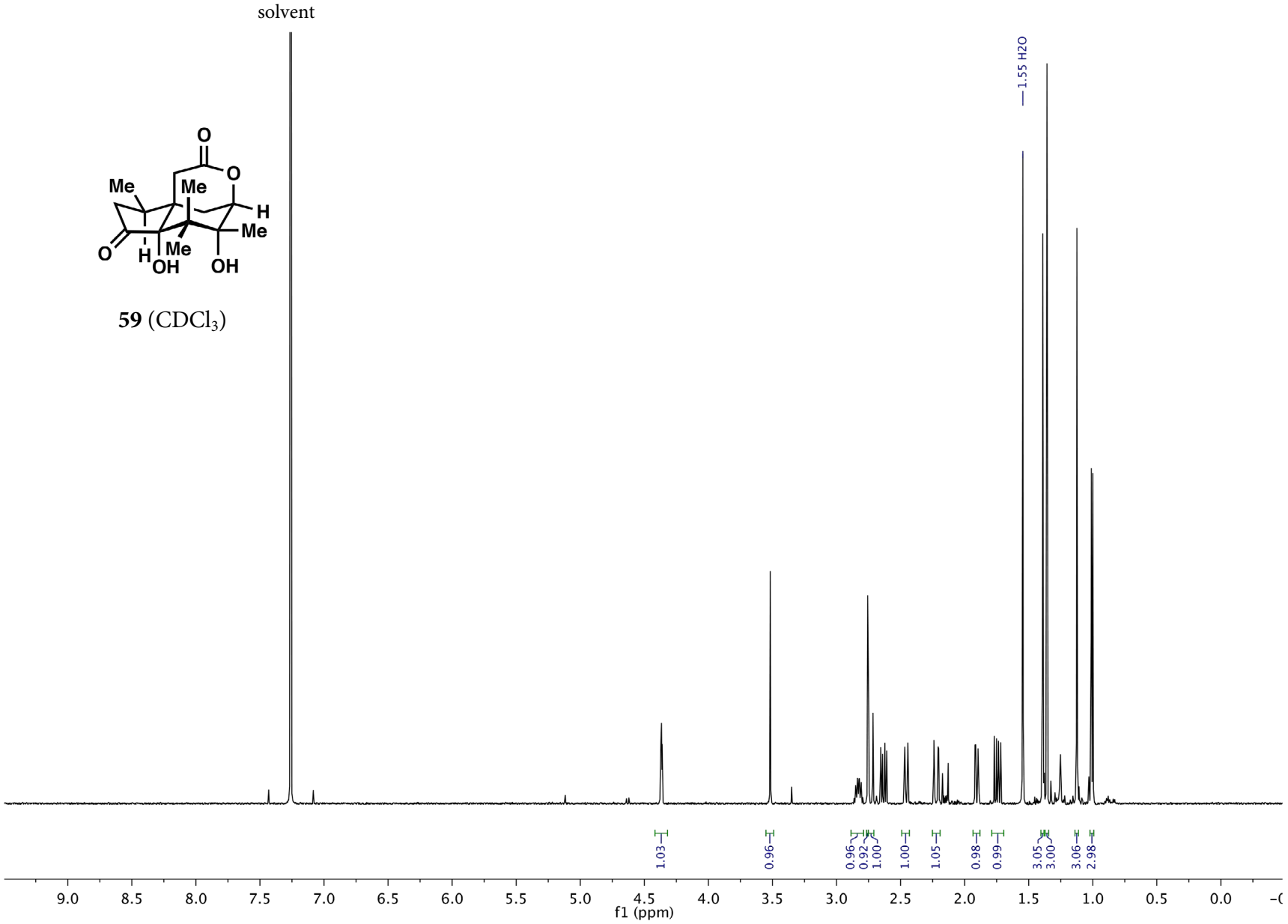

O
O
Me
Me
H
H
Me
HO
H
Me
OH
OH

58 ($CDCl_3$)

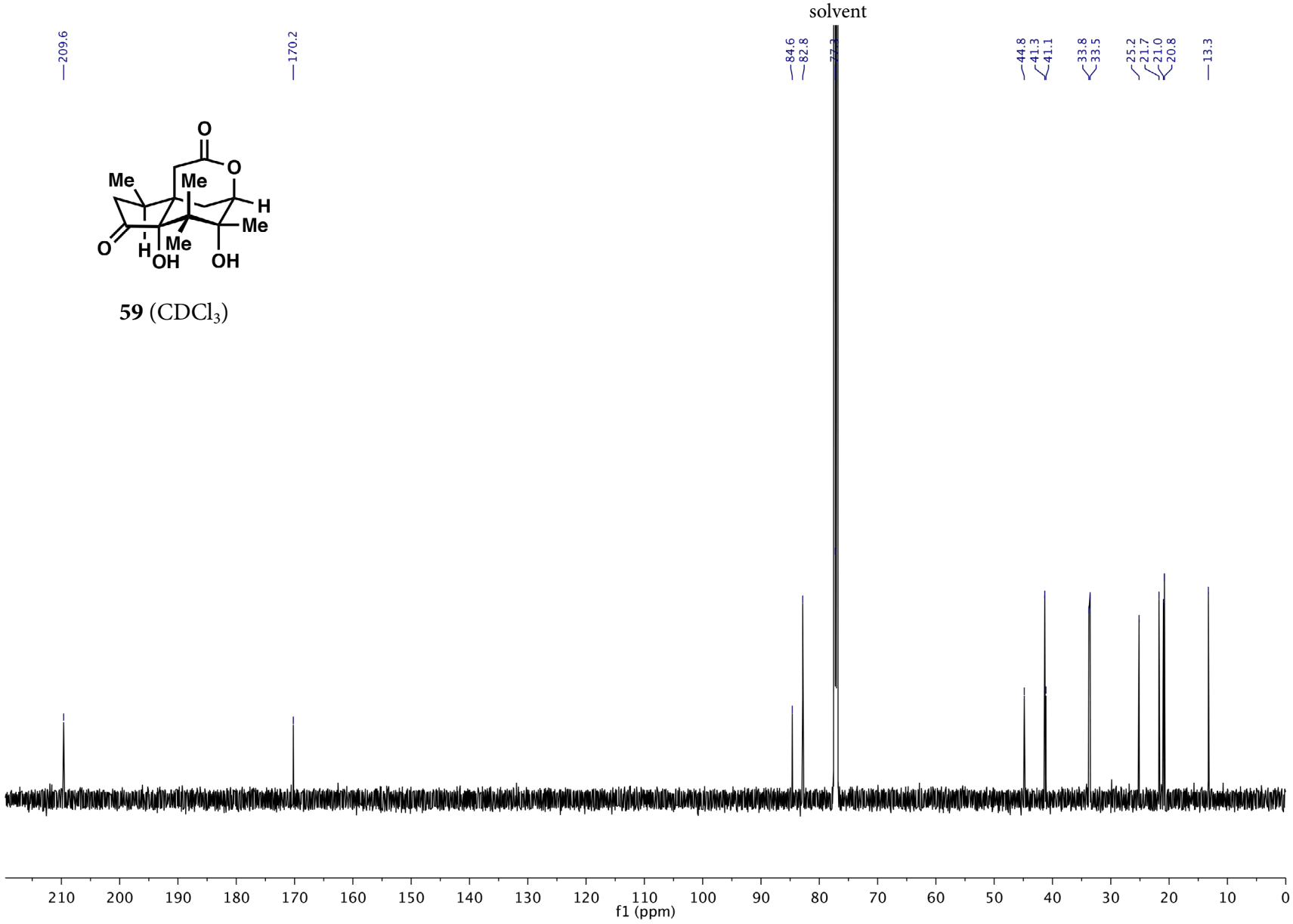

solvent
1.03
1.00
1.02
1.04
1.02
1.04
1.05
1.04
1.00
3.14
3.13
3.13
3.05
3.09
5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


solvent
171.4
85.8
83.6
71.0
46.7
42.4
40.1
37.1
34.6
26.6
22.8
22.2
20.9
13.7
O
O
Me
Me
H
H
Me
HO
H
Me
OH
OH
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

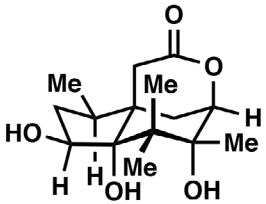
58 ($CDCl_3$)


solvent
1.55 H2O
1.03
0.96
0.96
0.92
1.00
1.00
1.05
0.98
0.99
3.05
3.00
3.06
2.98
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

59 ($CDCl_3$)

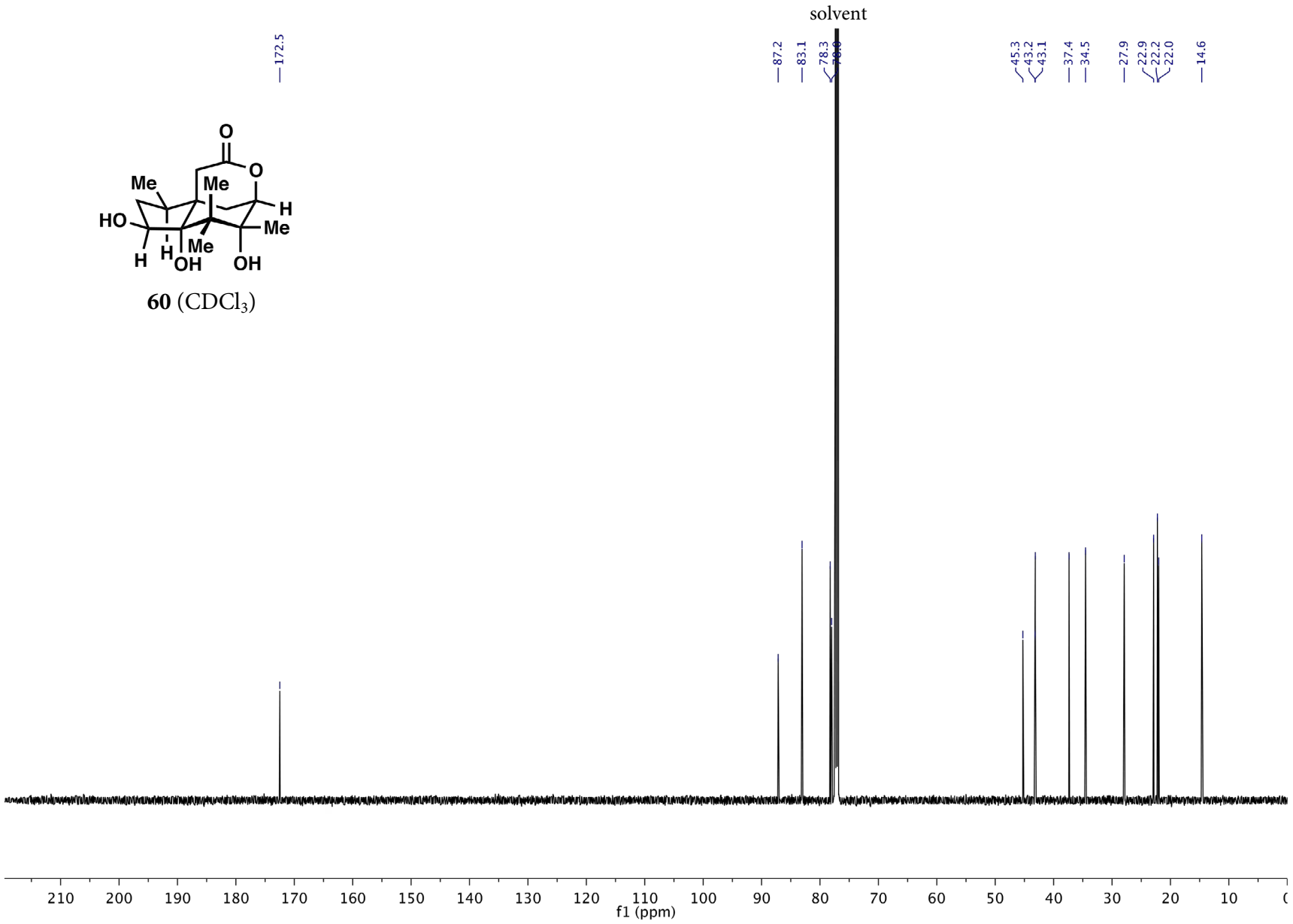

solvent
209.6
170.2
84.6
82.8
77.3
44.8
41.3
41.1
33.8
33.5
25.2
21.7
21.0
20.8
13.3
O
O
Me
Me
H
Me
O
H
Me
OH
OH
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

59 ($CDCl_3$)

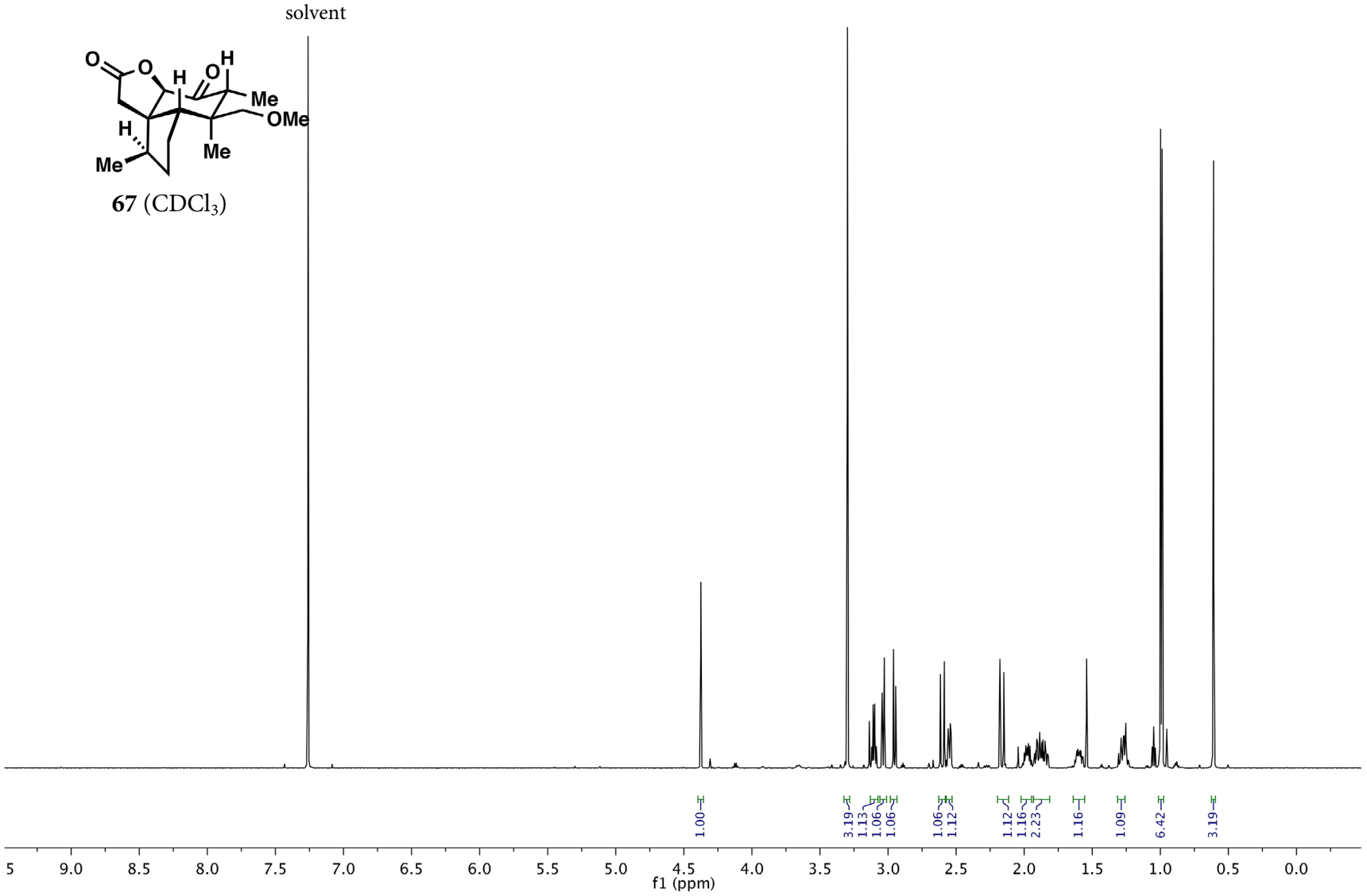

O
O
Me
Me
H
HO
Me
H
H
Me
OH
OH

60 ($CDCl_3$)

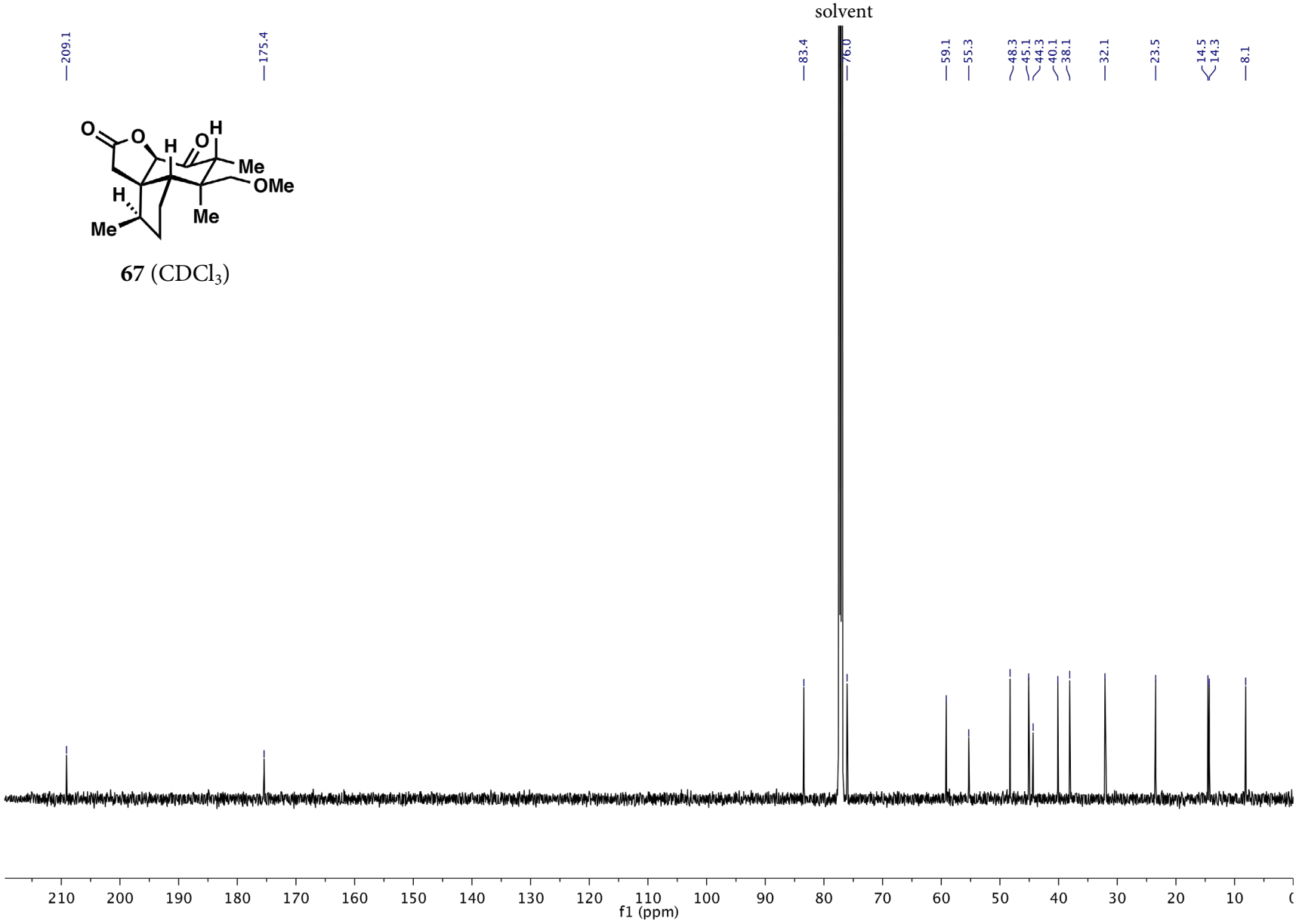
solvent
0.98
1.00
0.97
1.98
2.03
2.02
1.01
0.95
3.08
3.04
3.26
1.04
3.06
5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)


solvent
172.5
87.2
83.1
78.3
77.0
45.3
43.2
43.1
37.4
34.5
27.9
22.9
22.2
22.0
14.6
O
O
Me
Me
H
HO
Me
H
H
Me
OH
OH
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

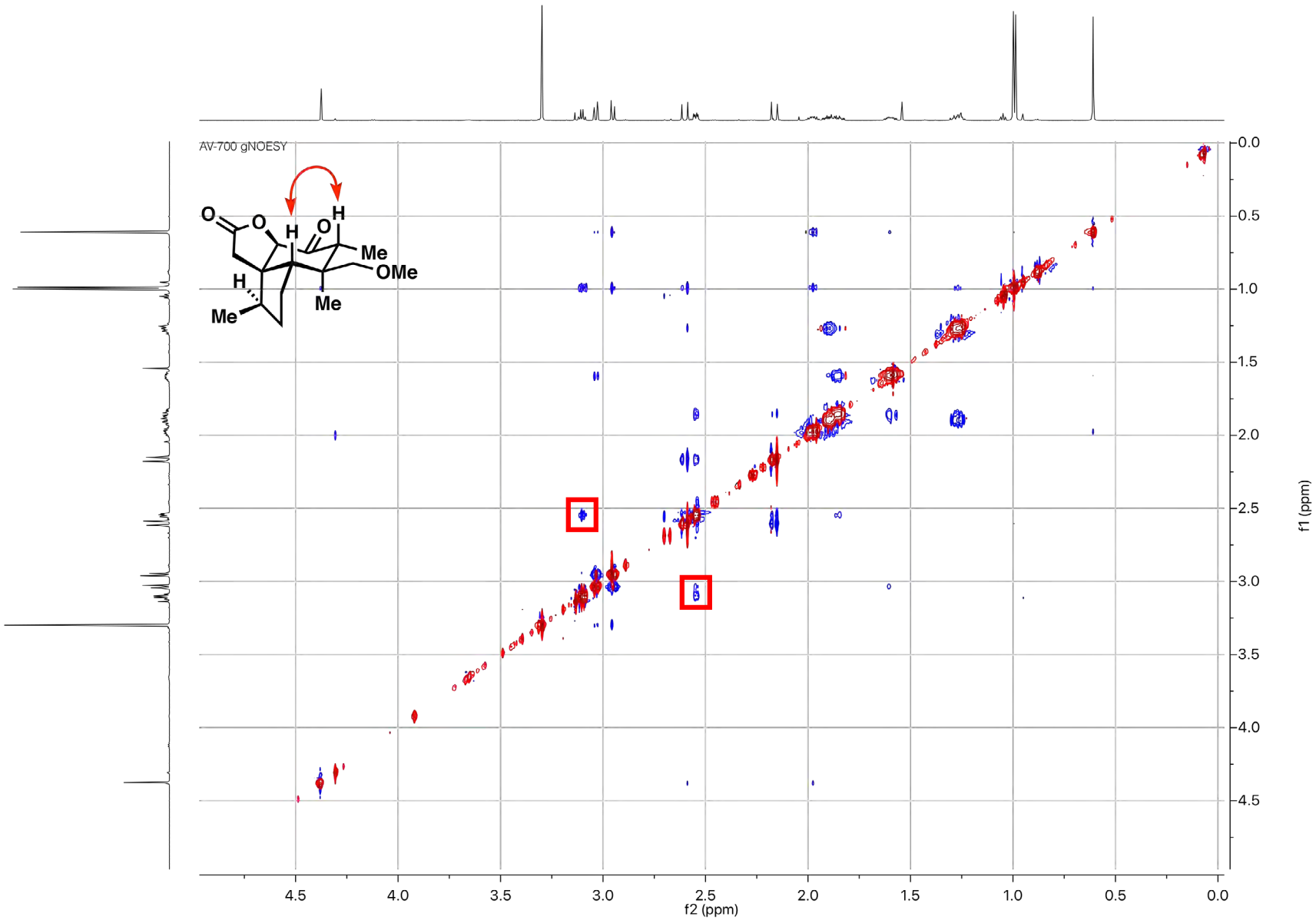
60 ($CDCl_3$)

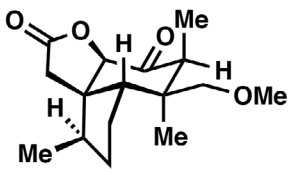

solvent
O
O
H
O
H
Me
OMe
H
Me
Me
1.00
3.19
1.13
1.06
1.06
1.06
1.12
1.12
1.16
2.23
1.16
1.09
6.42
3.19
5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

67 ($CDCl_3$)


solvent
209.1
175.4
83.4
76.0
59.1
55.3
48.3
45.1
44.3
40.1
38.1
32.1
23.5
14.5
14.3
8.1
O
O
H
O
H
Me
OMe
H
Me
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

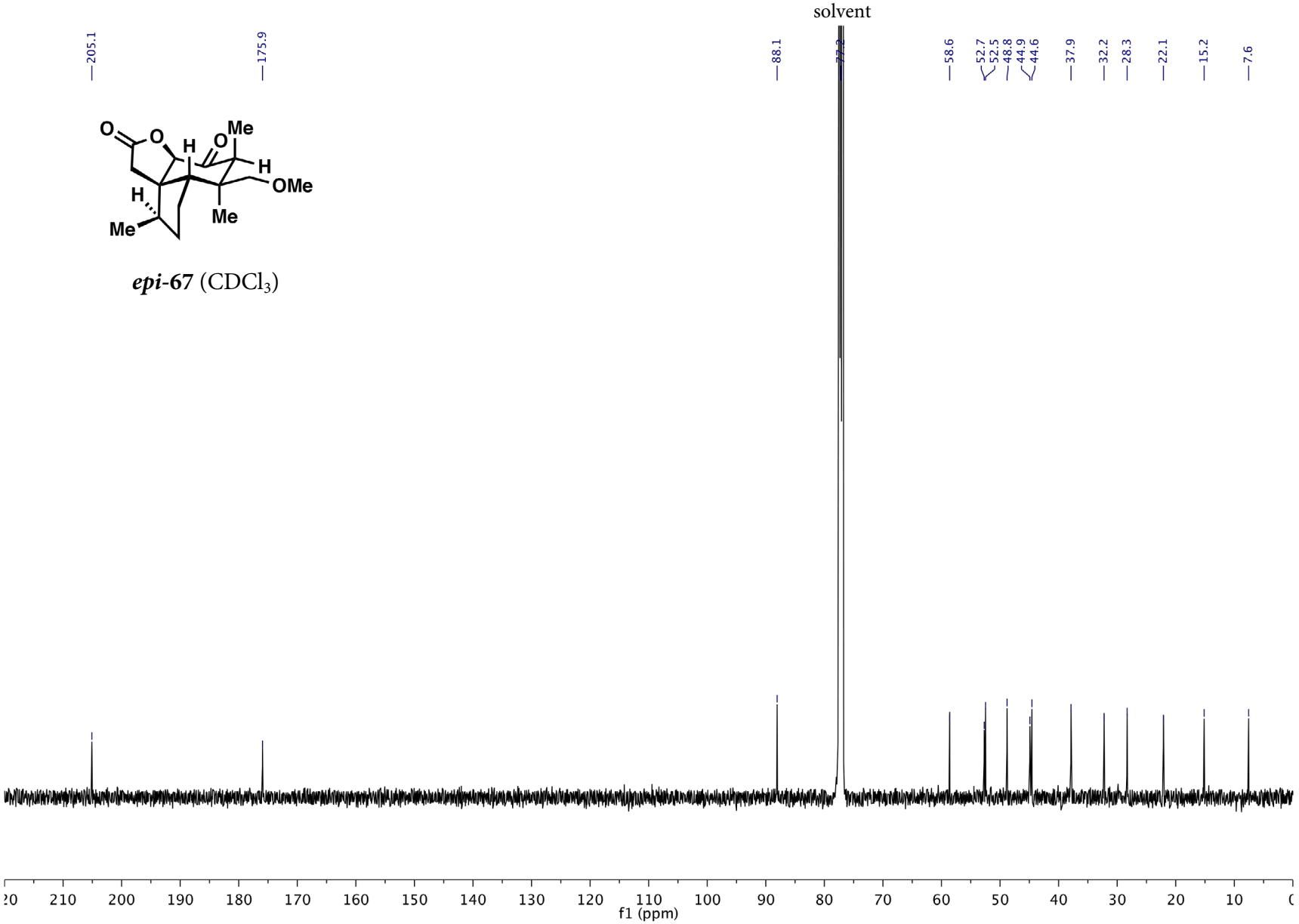
67 ($CDCl_3$)


AV-700 gNOESY
O
O
H
O
H
Me
OMe
H
Me
Me
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
f1 (ppm)

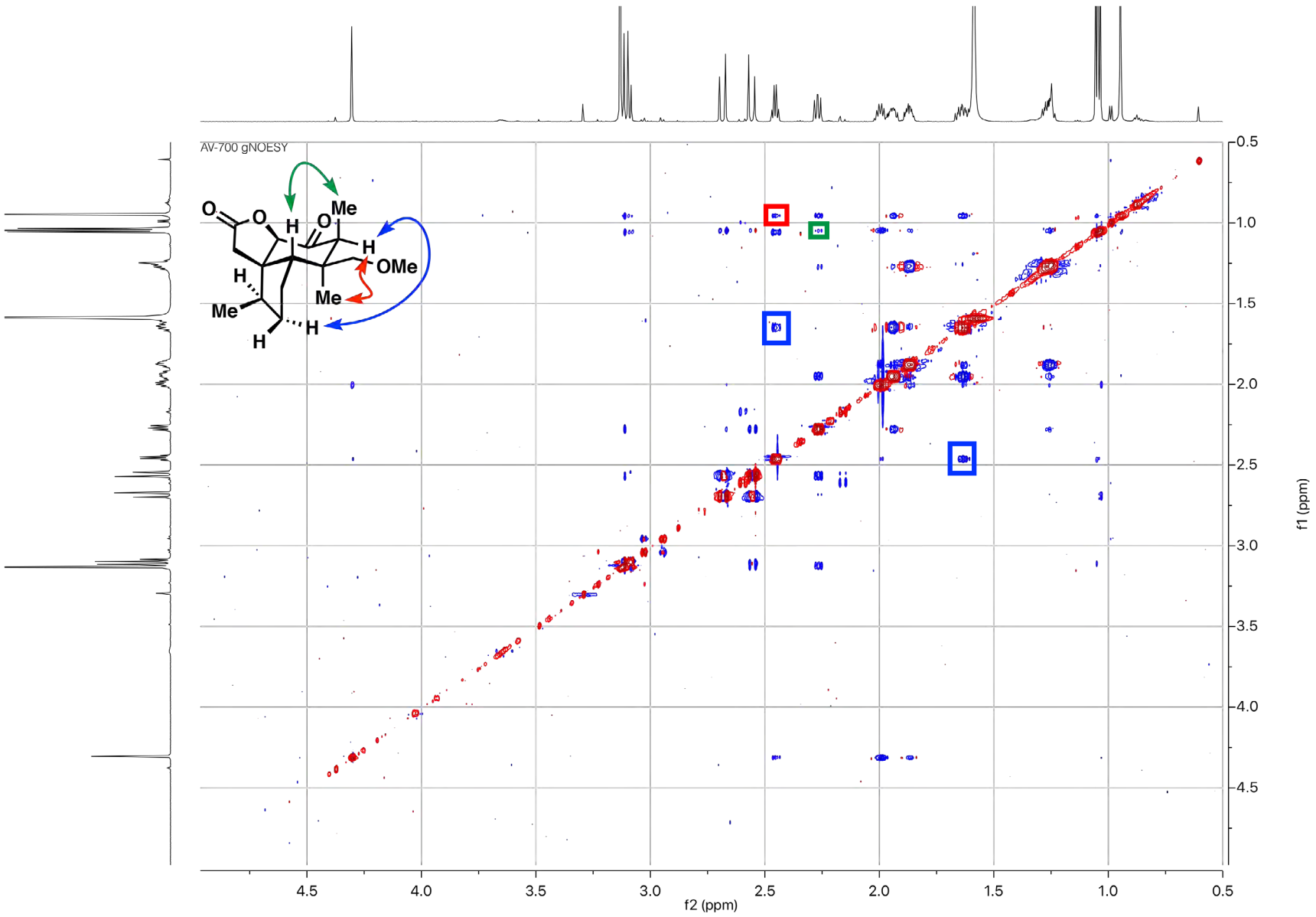

O
O
H
O
Me
H
OMe
H
Me
Me

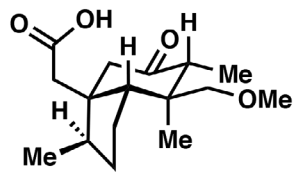
***epi*-67** ($CDCl_3$)

1.59 H2O
solvent
1.00
3.29
1.95
1.06
1.11
1.05
1.04
1.03
1.15
1.10
1.45
1.31
6.40
3.27
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


solvent
205.1
175.9
88.1
77.3
58.6
52.7
52.5
48.8
44.9
44.6
37.9
32.2
28.3
22.1
15.2
7.6
O
O
H
O
Me
H
OMe
H
Me
Me
f1 (ppm)

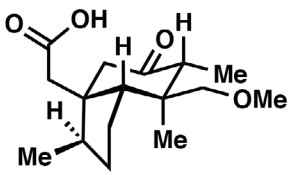
***epi*-67** ($CDCl_3$)


AV-700 gNOESY
O
O
H
O
Me
H
OMe
H
Me
Me
H
H
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
f1 (ppm)


O
OH
H
O
H
Me
OMe
H
Me
Me

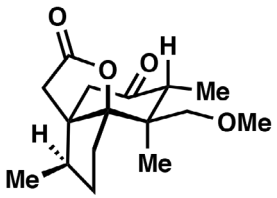
68 ($CDCl_3$)

solvent
3.02
1.00
1.01
1.01
1.00
1.01
1.03
1.01
1.00
1.02
2.04
1.02
1.05
3.02
3.13
3.03
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


O
OH
H
O
H
Me
OMe
H
Me
Me

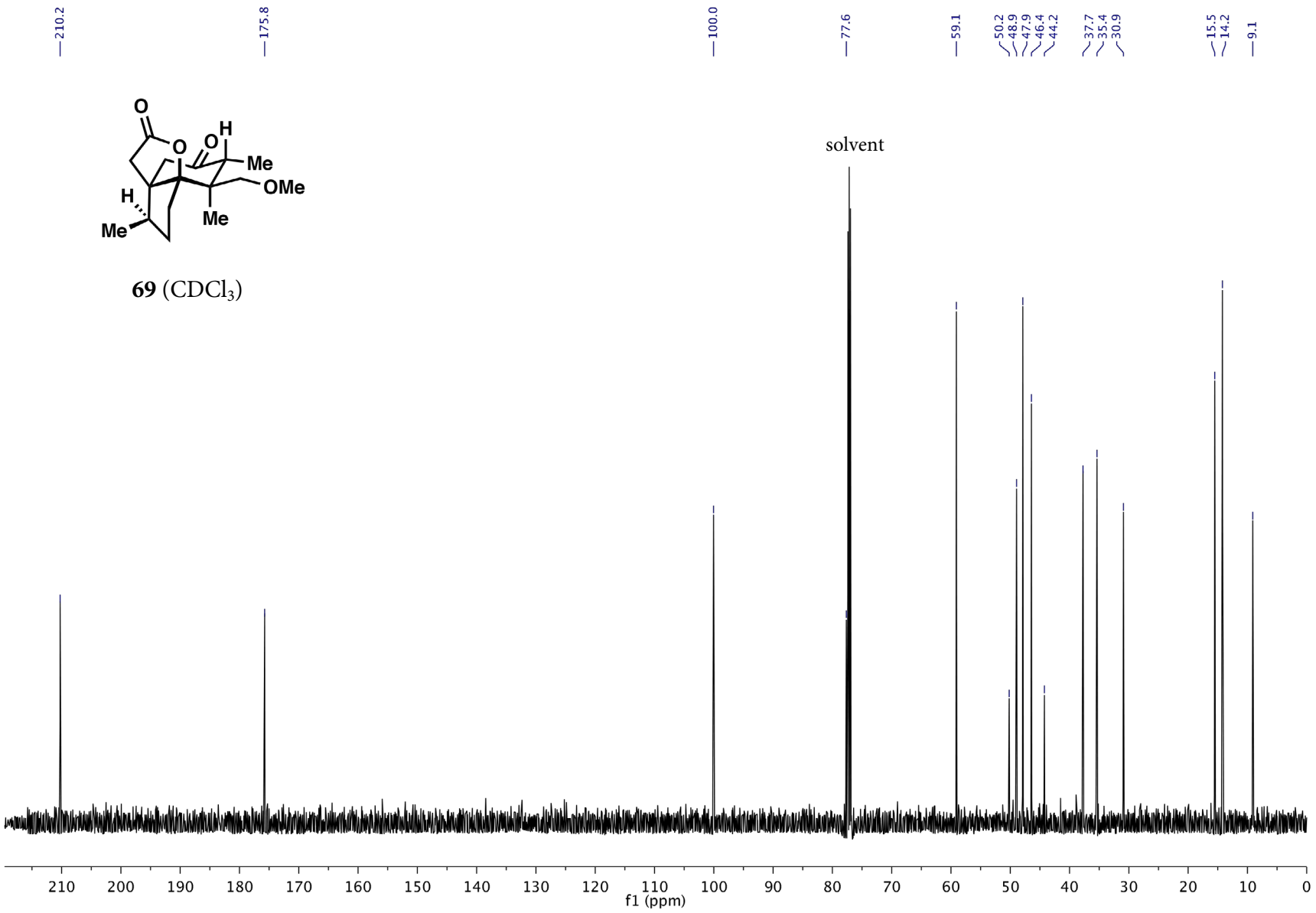
68 ($CDCl_3$)

solvent
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

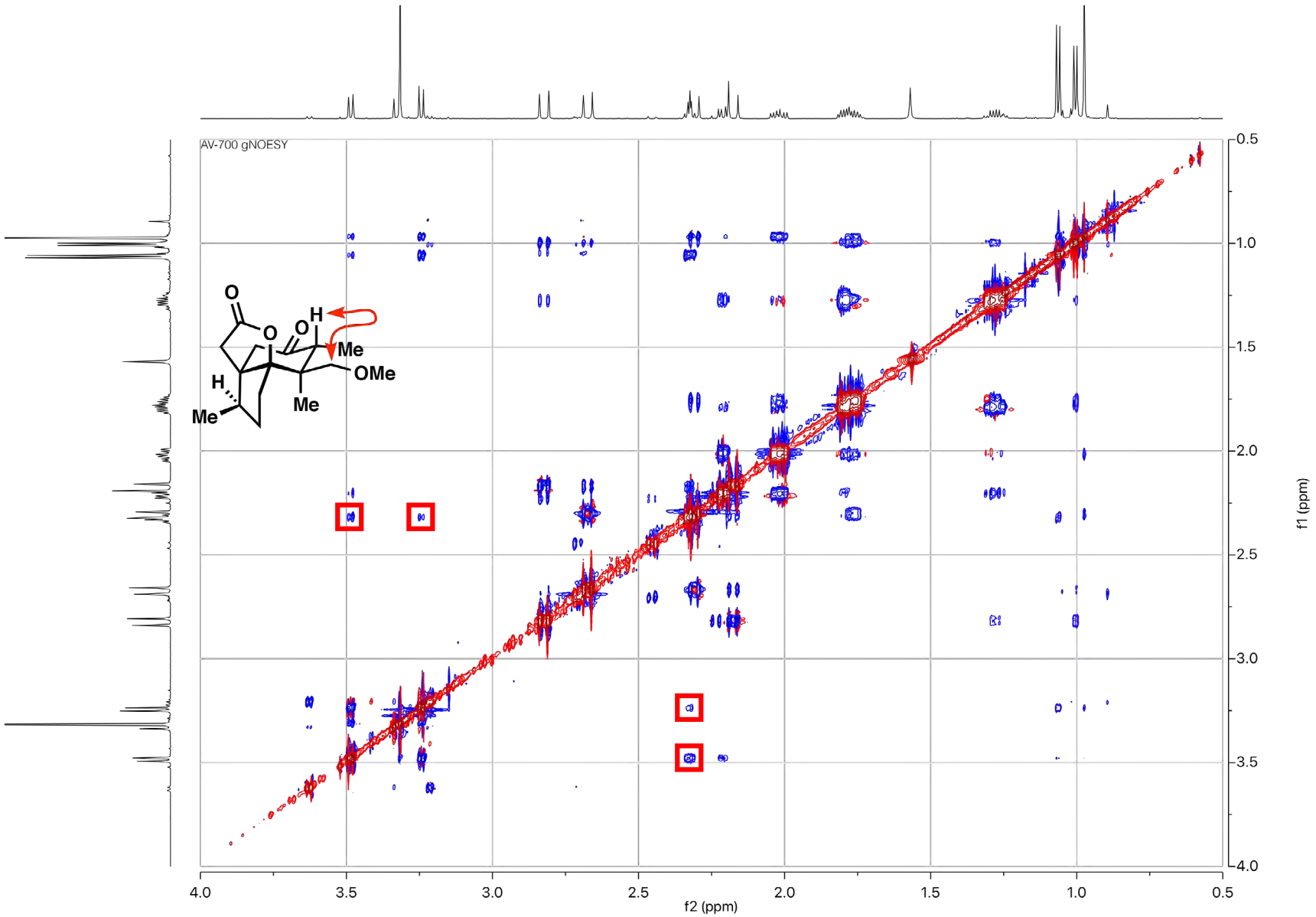

O
O
O
H
Me
OMe
H
Me
Me

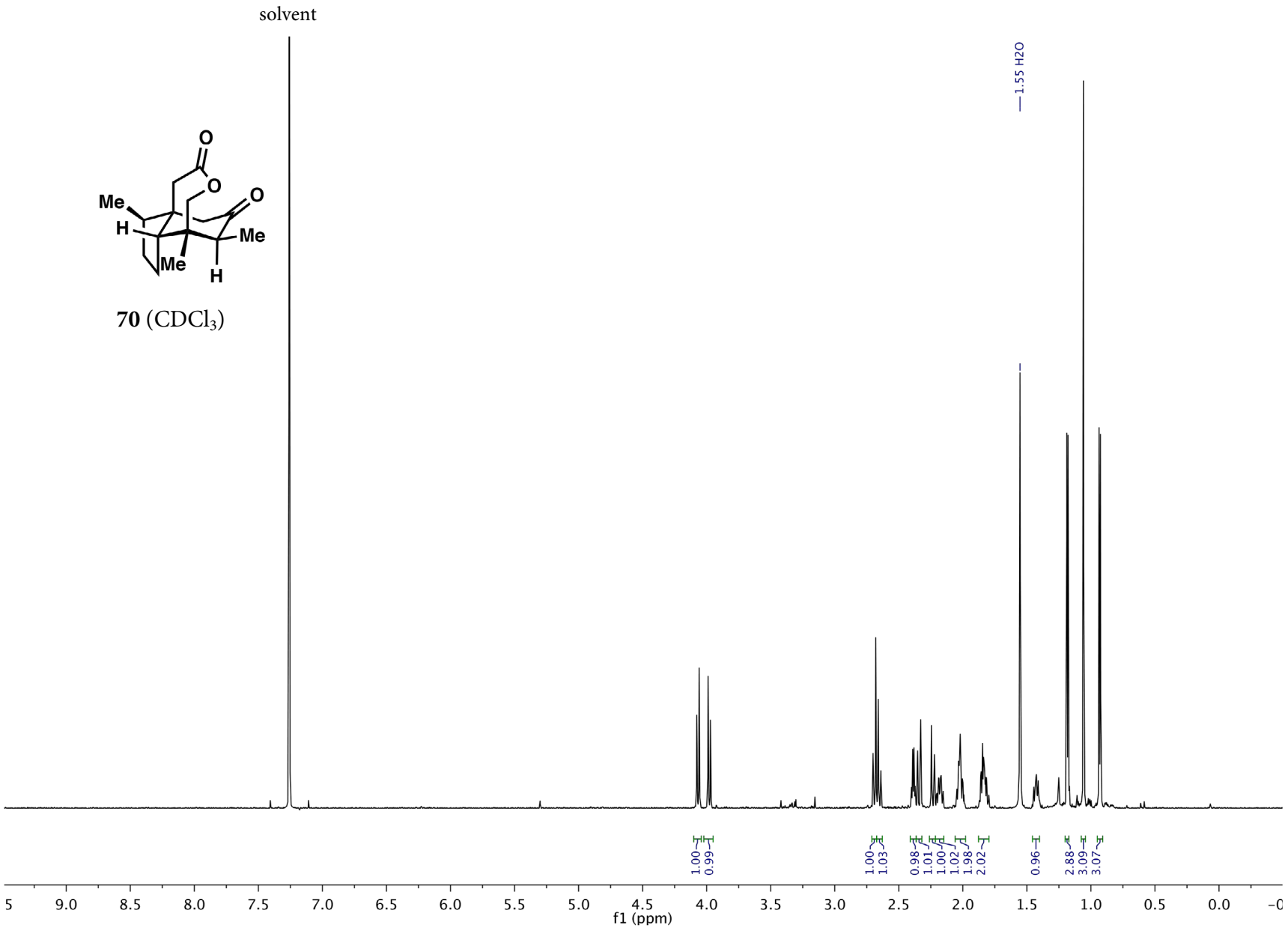
69 ($CDCl_3$)

solvent
0.93
2.74
0.94
1.00
1.09
1.84
1.99
0.94
1.88
1.29
2.97
3.14
2.79
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

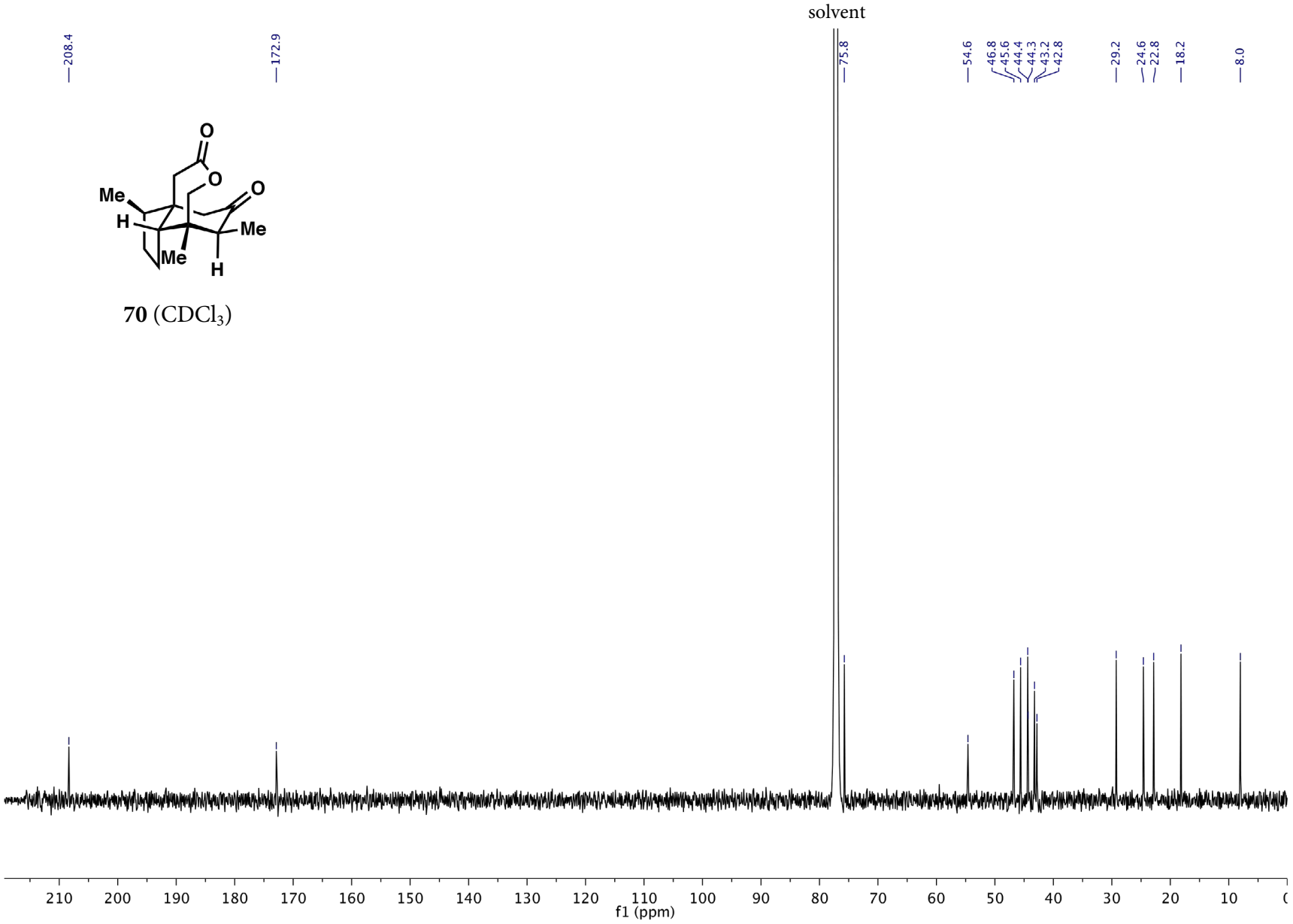

210.2
175.8
100.0
77.6
59.1
50.2
48.9
47.9
46.4
44.2
37.7
35.4
30.9
15.5
14.2
9.1
O
O
O
H
Me
OMe
H
Me
Me
solvent
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

69 ($CDCl_3$)

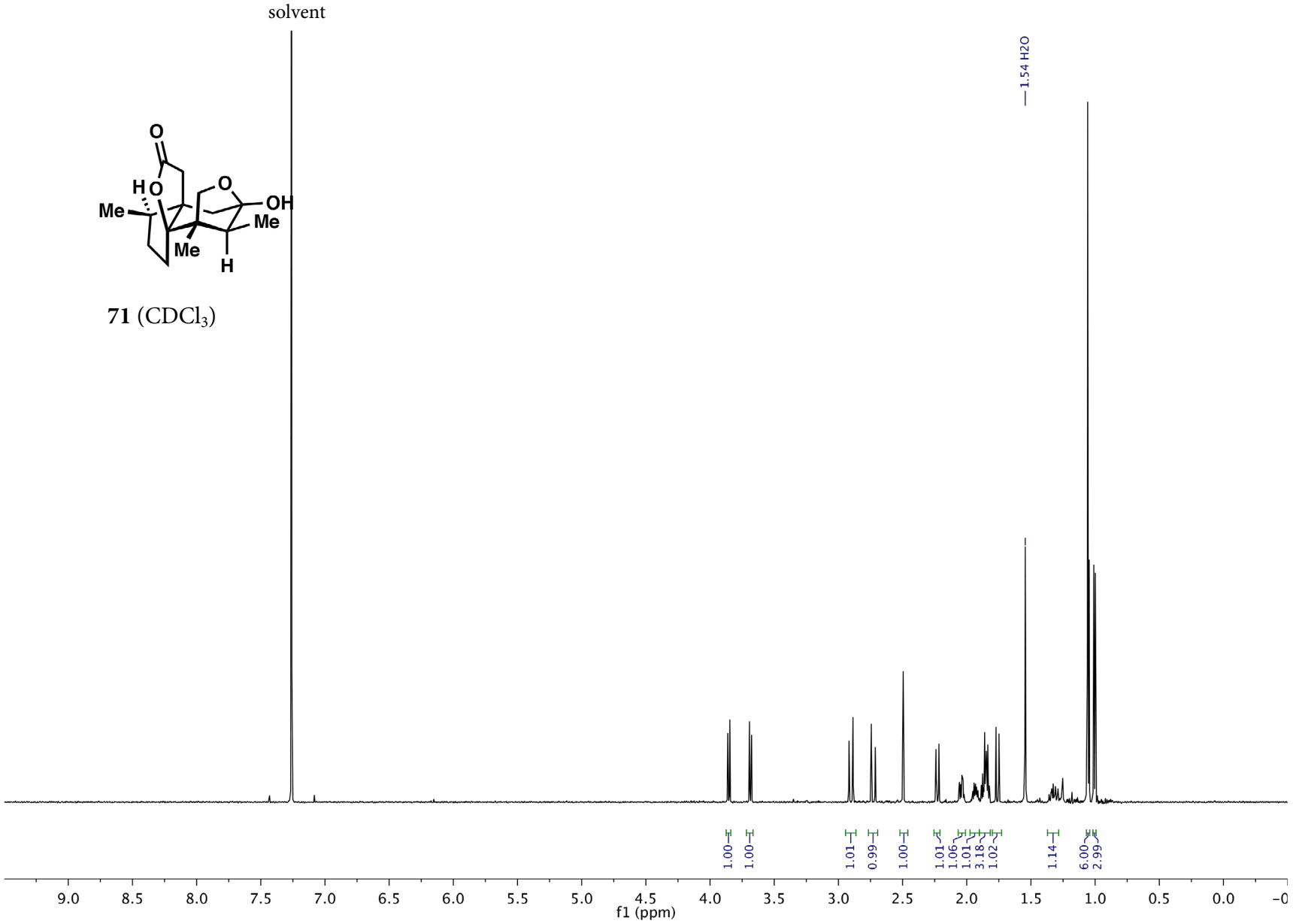

AV-700 gNOESY
O
O
O
H
Me
OMe
H
Me
Me
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
f1 (ppm)


solvent
1.55 H2O
O
O
O
Me
H
Me
Me
H
1.00
0.99
1.00
1.03
0.98
1.01
1.00
1.02
1.98
2.02
0.96
2.88
3.09
3.07
f1 (ppm)

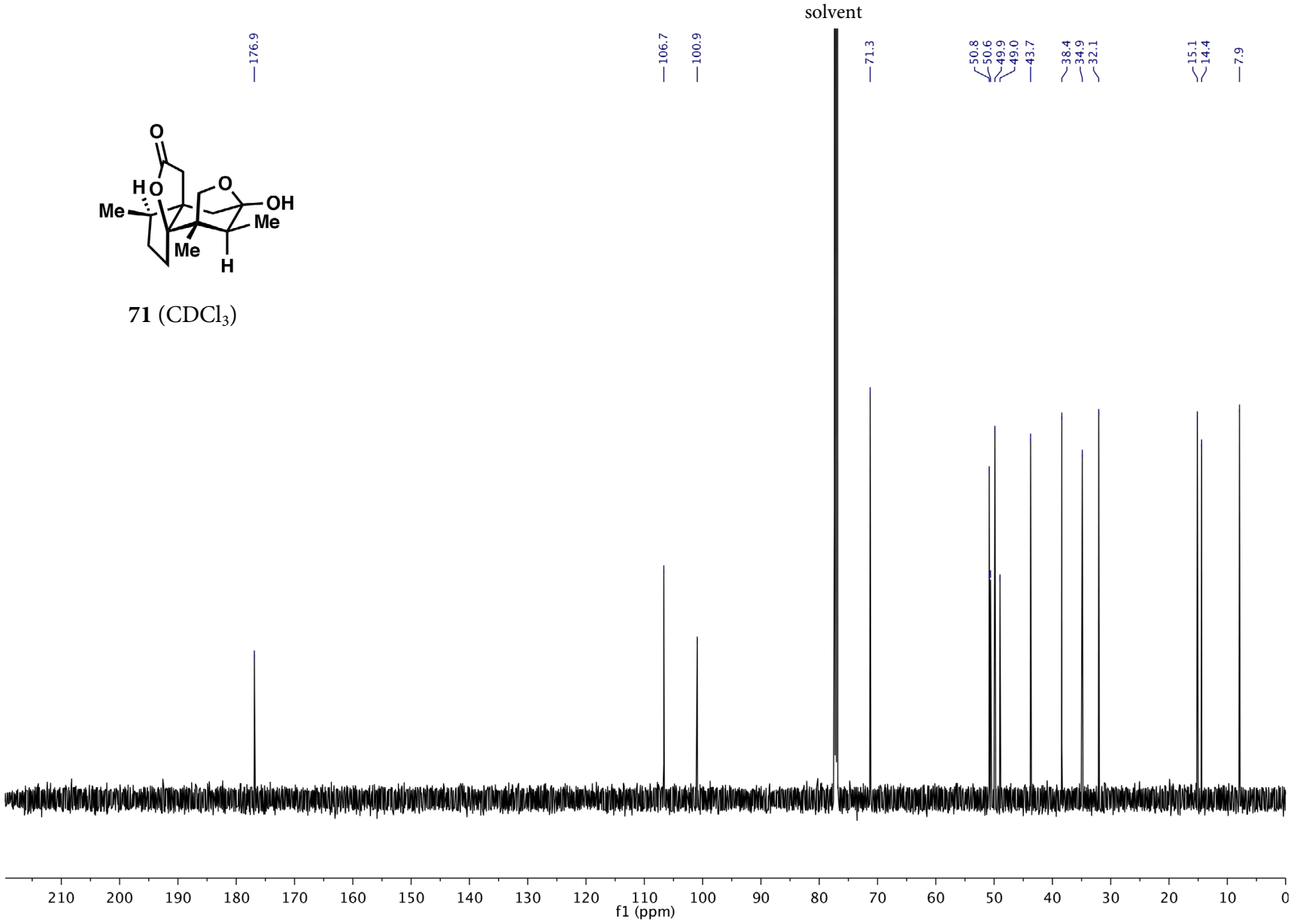
70 ($CDCl_3$)


solvent
208.4
172.9
75.8
54.6
46.8
45.6
44.4
44.3
43.2
42.8
29.2
24.6
22.8
18.2
8.0
O
O
O
Me
H
Me
Me
H
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

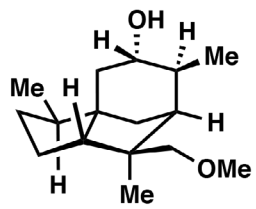
70 ($CDCl_3$)


solvent
1.54 H2O
O
HO
Me
O
OH
Me
Me
H
1.00
1.00
1.01
0.99
1.00
1.01
1.06
1.01
3.18
1.02
1.14
6.00
2.99
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

71 ($CDCl_3$)

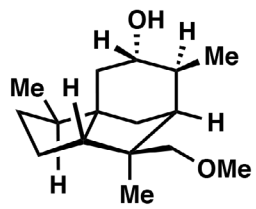

solvent
176.9
106.7
100.9
71.3
50.8
50.6
49.9
49.0
43.7
38.4
34.9
32.1
15.1
14.4
7.9
O
H
O
O
OH
Me
Me
Me
H
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

71 ($CDCl_3$)


OH
H
H
Me
Me
H
H
OMe
H
Me

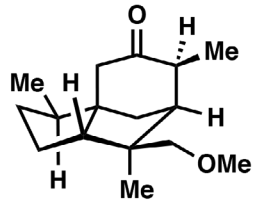
79 ($CDCl_3$)

solvent
1.00
1.03
2.99
1.00
1.00
1.02
0.98
2.00
1.04
1.05
1.19
0.64
1.33
1.10
2.04
2.98
2.98
3.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


OH
H
H
Me
Me
H
H
OMe
H
Me

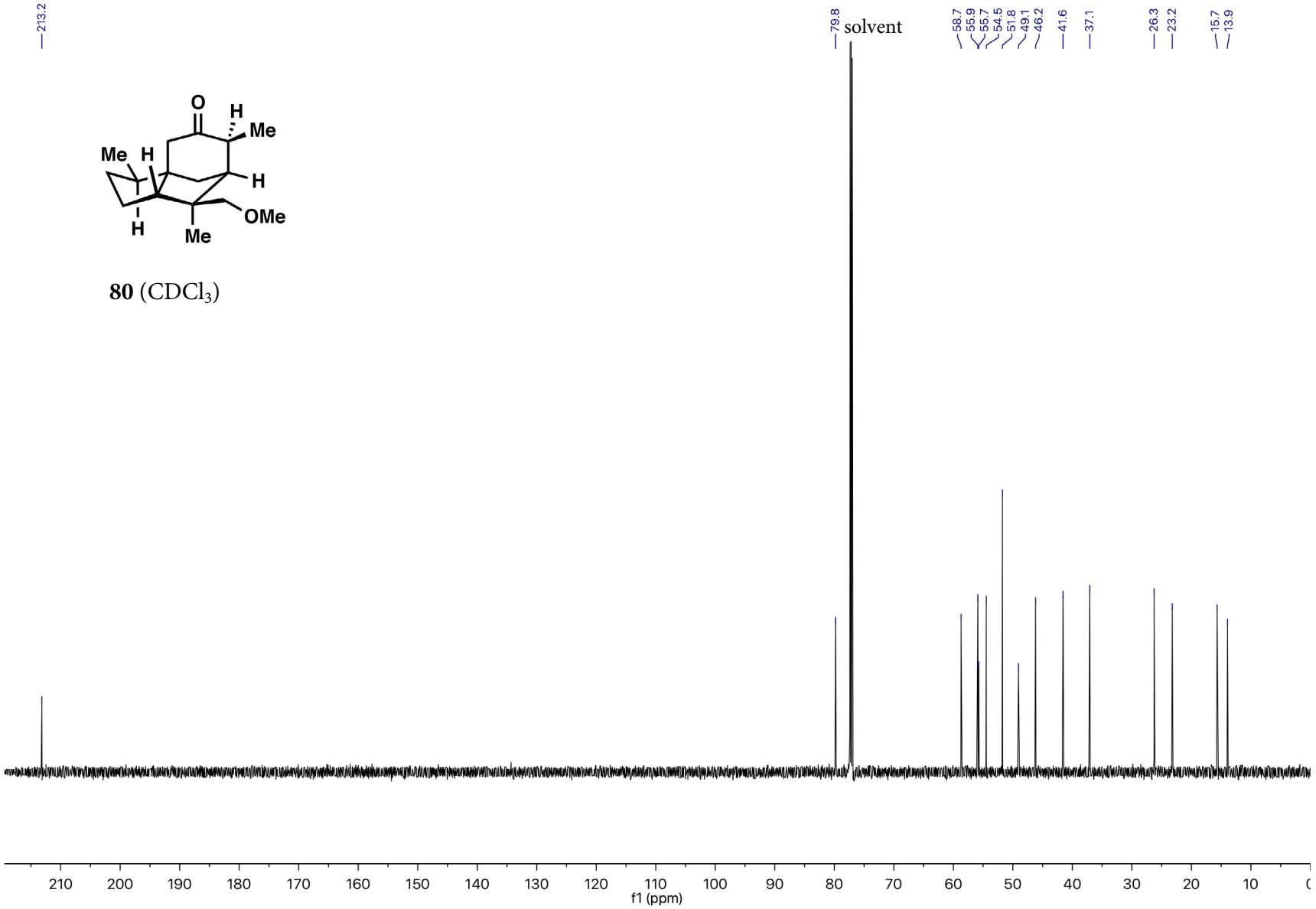
79 ($CDCl_3$)

80.1
73.1
59.0
54.7
54.5
53.4
48.9
46.7
46.2
44.0
41.7
36.7
26.4
23.8
17.5
15.7
solvent
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

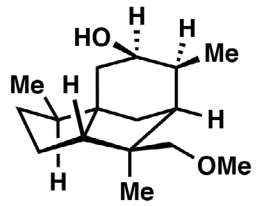

O
H
Me
Me
H
H
OMe
H
Me

80 ($CDCl_3$)

solvent
2.93
1.00
0.97
0.96
1.96
0.97
0.99
1.98
1.00
1.05
1.05
1.04
1.04
2.92
2.96
3.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

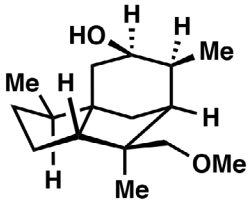

213.2
79.8
solvent
58.7
55.9
55.7
54.5
51.8
49.1
46.2
41.6
37.1
26.3
23.2
15.7
13.9
O
H
Me
Me
H
H
OMe
H
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

80 ($CDCl_3$)


H
HO
H
Me
Me
H
H
OMe
H
Me

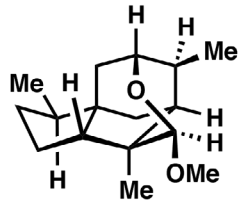
81 ($CDCl_3$)

solvent
0.96
1.00
1.00
2.97
0.78
1.03
0.93
0.97
2.95
0.98
1.02
1.01
1.01
1.02
3.89
2.93
2.92
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


HO
H
H
Me
Me
H
H
OMe
H
Me

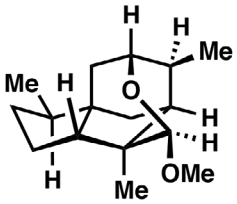
81 ($CDCl_3$)

79.9
69.6
58.6
53.2
52.9
48.9
48.2
47.4
43.7
43.2
41.9
35.8
25.7
24.0
16.6
15.7
solvent
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


H
H
Me
Me
H
O
H
H
OMe
H
Me

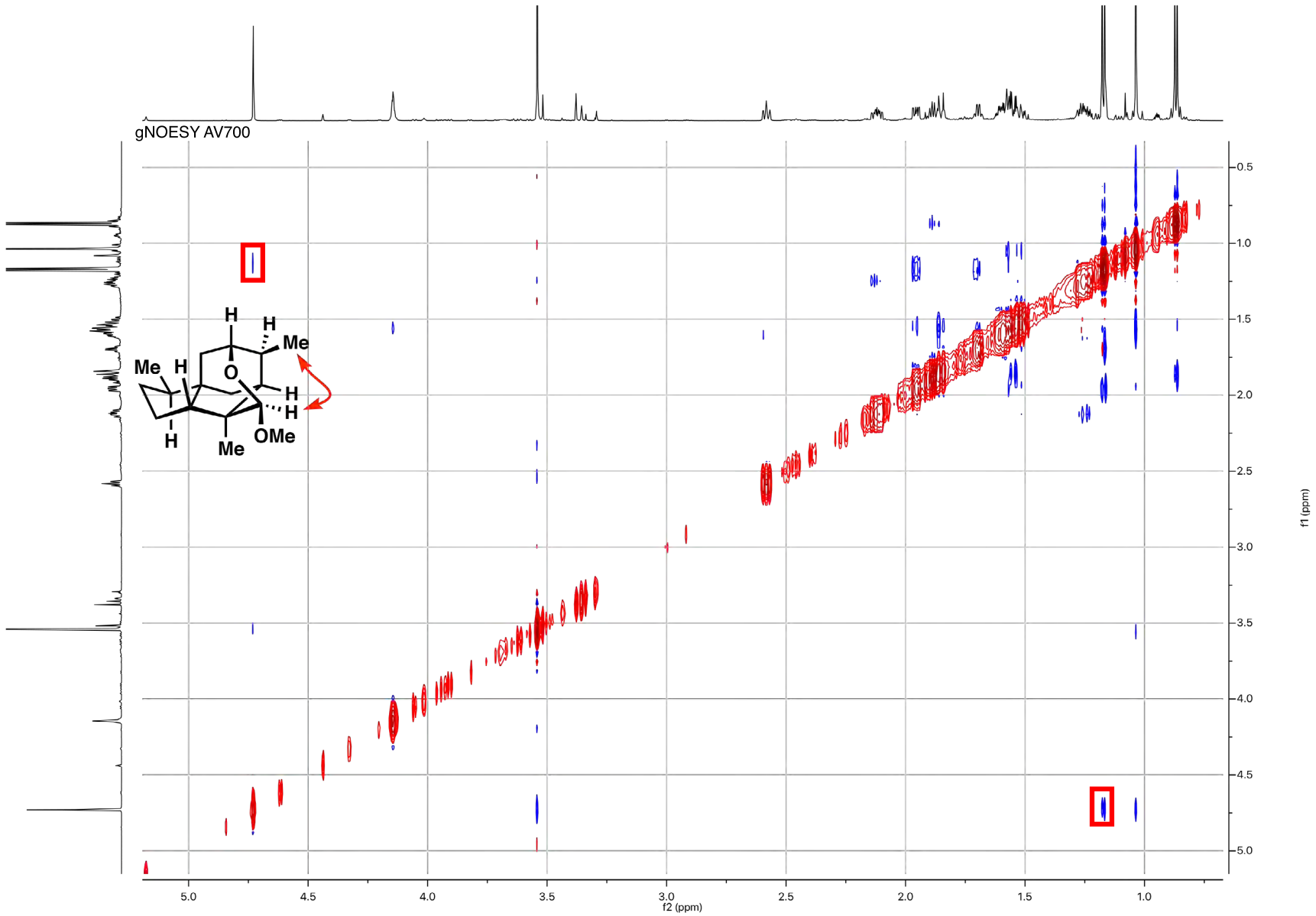
83 ($CDCl_3$)

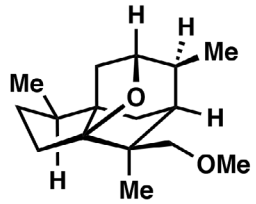
solvent
1.03
1.18
3.01
1.00
1.27
1.16
1.20
1.42
1.31
5.79
2.00
4.57
3.43
3.38
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


H
H
Me
Me
H
O
H
H
OMe
H
Me

83 ($CDCl_3$)

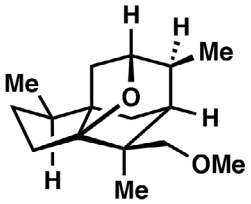
104.1
76.3
solvent
57.5
53.9
51.1
49.8
49.0
46.6
41.5
40.1
39.0
35.4
26.5
22.4
20.7
18.8
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


gNOESY AV700
H
H
Me
Me
H
O
H
H
H
Me
OMe
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)


H
H
Me
Me
O
H
OMe
H
Me

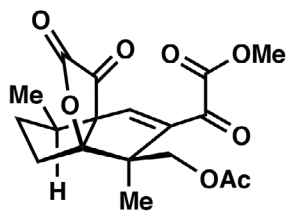
84 ($CDCl_3$)

solvent
1.00
1.01
1.01
3.04
1.01
1.06
2.07
1.23
1.08
0.92
1.09
1.25
1.07
1.02
3.15
3.06
3.11
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


H
H
Me
Me
O
H
OMe
H
Me

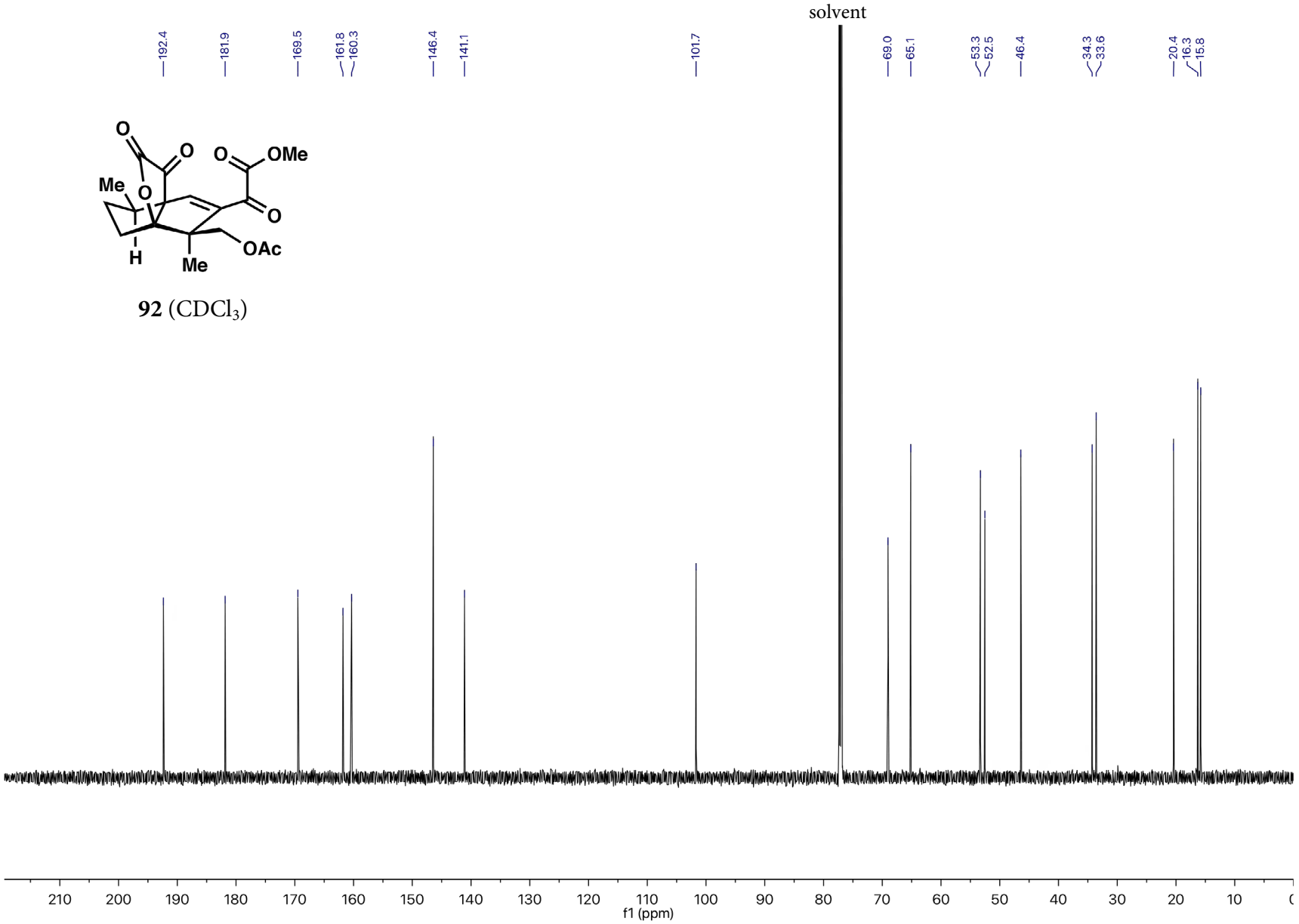
84 ($CDCl_3$)

solvent
102.0
83.0
78.6
62.8
59.0
54.1
49.2
43.6
42.8
42.0
40.7
36.2
28.4
23.7
19.5
14.9
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

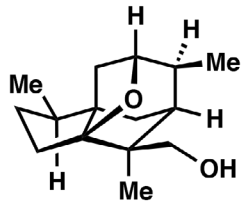

O
O
O
OMe
Me
O
O
OAc
H
Me

92 ($CDCl_3$)

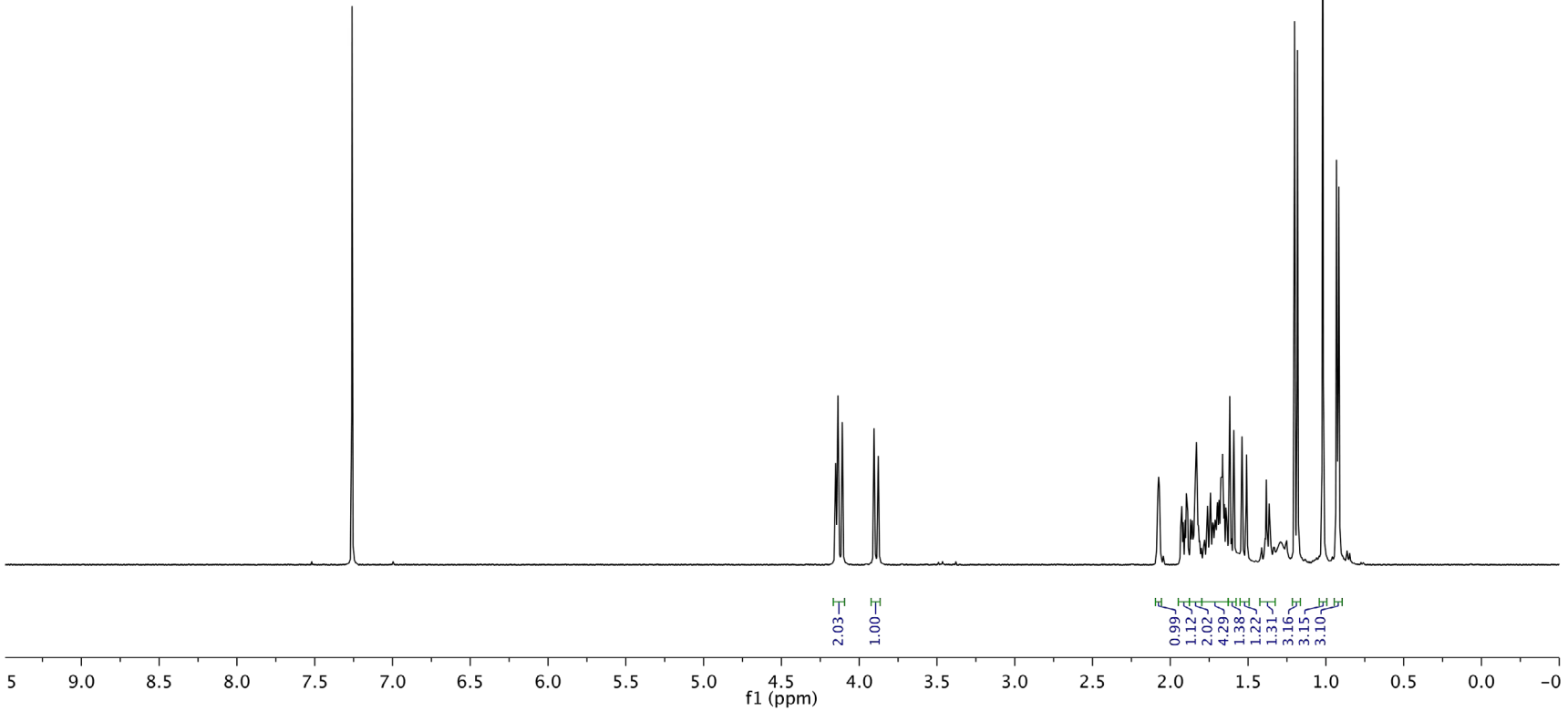
solvent
0.90
1.00
1.01
2.96
1.01
1.01
1.02
1.07
2.93
0.98
3.11
3.02
.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

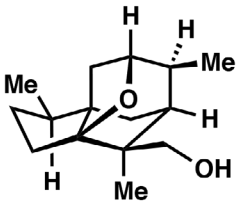

solvent
192.4
181.9
169.5
161.8
160.3
146.4
141.1
101.7
69.0
65.1
53.3
52.5
46.4
34.3
33.6
20.4
16.3
15.8
O
O
O
OMe
Me
O
O
OAc
H
Me
f1 (ppm)

92 ($CDCl_3$)



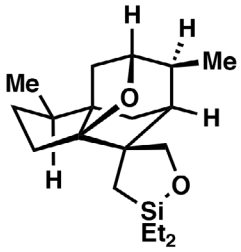
103 ($CDCl_3$) solvent




H
H
Me
Me
O
H
H
OH
Me

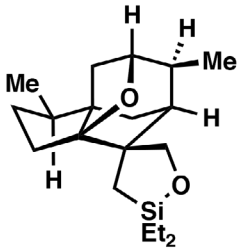
103 ($CDCl_3$)

solvent
101.8
82.9
68.0
63.1
54.2
50.6
43.6
42.7
41.9
40.7
36.3
28.9
22.6
20.0
14.9
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


H
H
Me
Me
O
H
H
O
Si
Et2

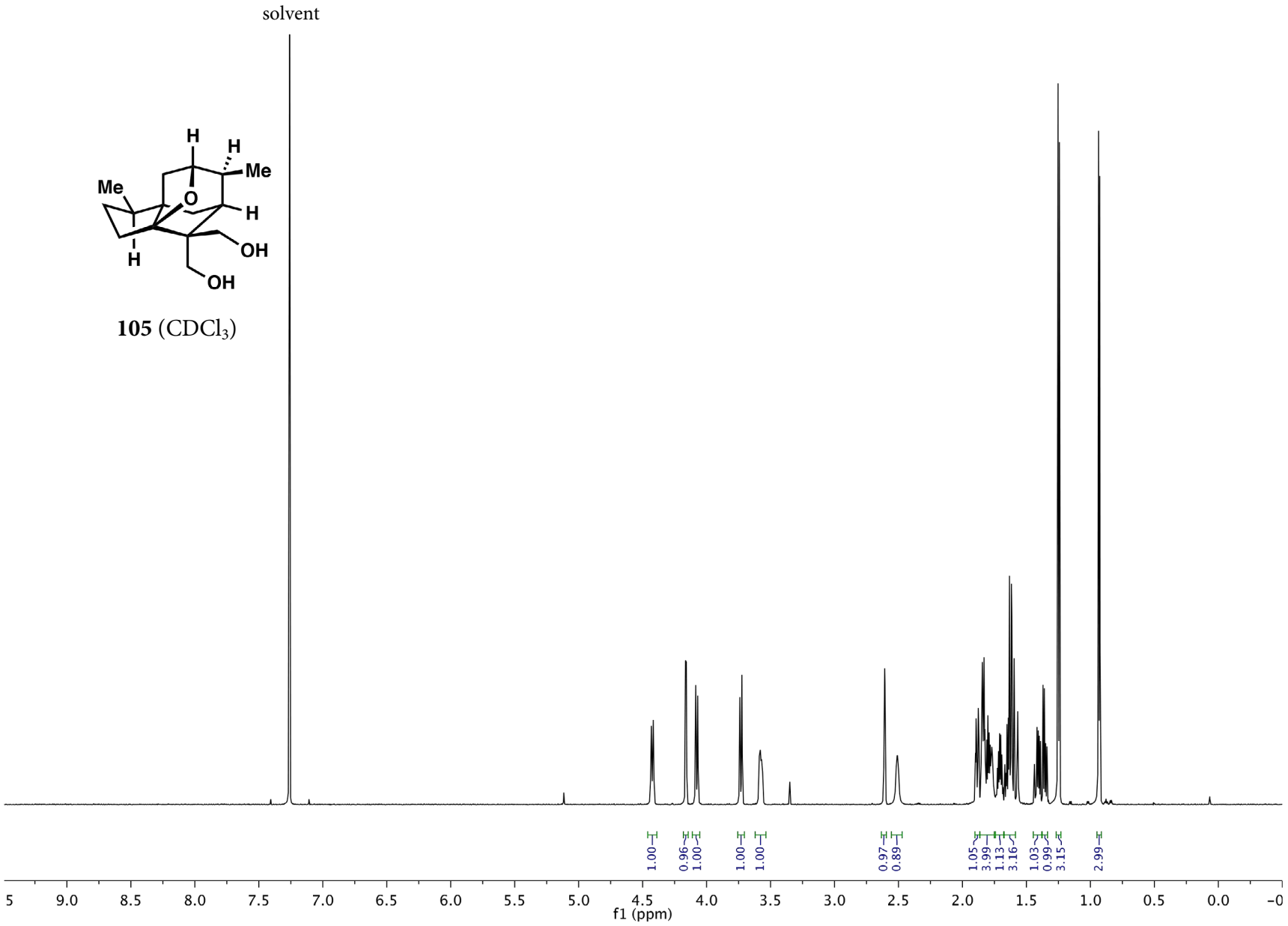
SI-3 ($CDCl_3$)

solvent
1.03
1.00
1.05
2.12
2.31
8.72
9.96
3.67
1.38
1.10
3.36
1.03
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

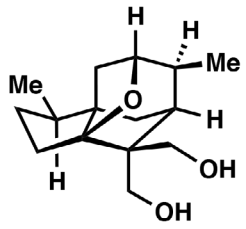

H
H
Me
Me
O
H
H
O
Si
Et2

SI-3 ($CDCl_3$)

solvent
101.1
82.8
71.7
62.7
58.4
56.9
43.8
42.9
42.5
40.8
36.4
29.5
21.1
19.0
14.9
7.1
6.9
6.8
5.7
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

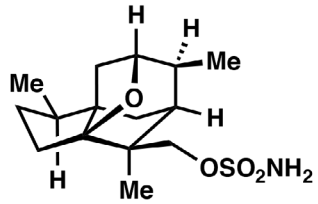

solvent
H
H
Me
Me
O
H
H
OH
OH
1.00
0.96
1.00
1.00
1.00
0.97
0.89
1.05
3.99
1.13
3.16
1.03
0.99
3.15
2.99
f1 (ppm)

105 ($CDCl_3$)


H
H
Me
Me
O
H
H
OH
OH

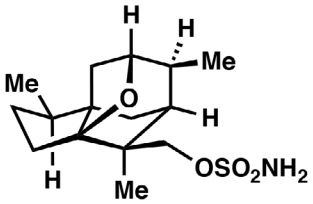
105 ($CDCl_3$)

solvent
100.6
82.8
68.2
68.2
63.3
53.4
48.2
42.9
42.6
41.6
40.1
36.0
28.1
19.7
14.8
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


H
H
Me
Me
O
H
H
Me
OSO2NH2

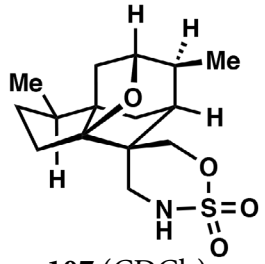
106 ($CDCl_3$)

solvent
1.94
1.00
0.99
0.98
0.99
1.13
2.01
1.38
4.26
1.07
1.09
3.12
3.00
3.16
f1 (ppm)


H
H
Me
Me
O
H
H
Me
OSO2NH2

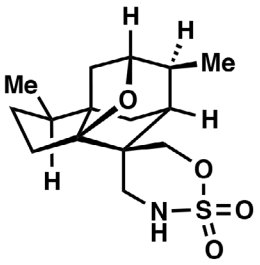
106 ($CDCl_3$)

solvent
101.9
83.1
77.0
63.1
54.6
48.6
43.4
42.6
41.9
40.5
36.2
28.7
22.4
19.9
14.8
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


H
H
Me
Me
O
H
H
O
N
H
S
O
O

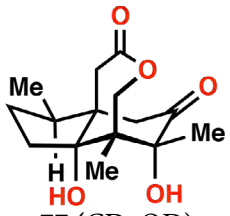
107 ($CDCl_3$)

solvent
1.00
1.01
0.98
0.98
1.02
1.03
1.00
3.19
1.12
3.22
1.07
2.34
3.10
3.22
f1 (ppm)

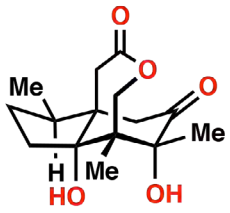

H
H
Me
Me
O
H
H
O
N
H
S
O
O

107 ($CDCl_3$)

solvent
100.1
83.1
77.6
63.3
50.7
49.9
46.6
42.6
42.4
42.0
40.0
35.7
28.2
19.5
14.6
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



77 (CD_3OD)
(–)-3-deoxy-
pseudoanisatin



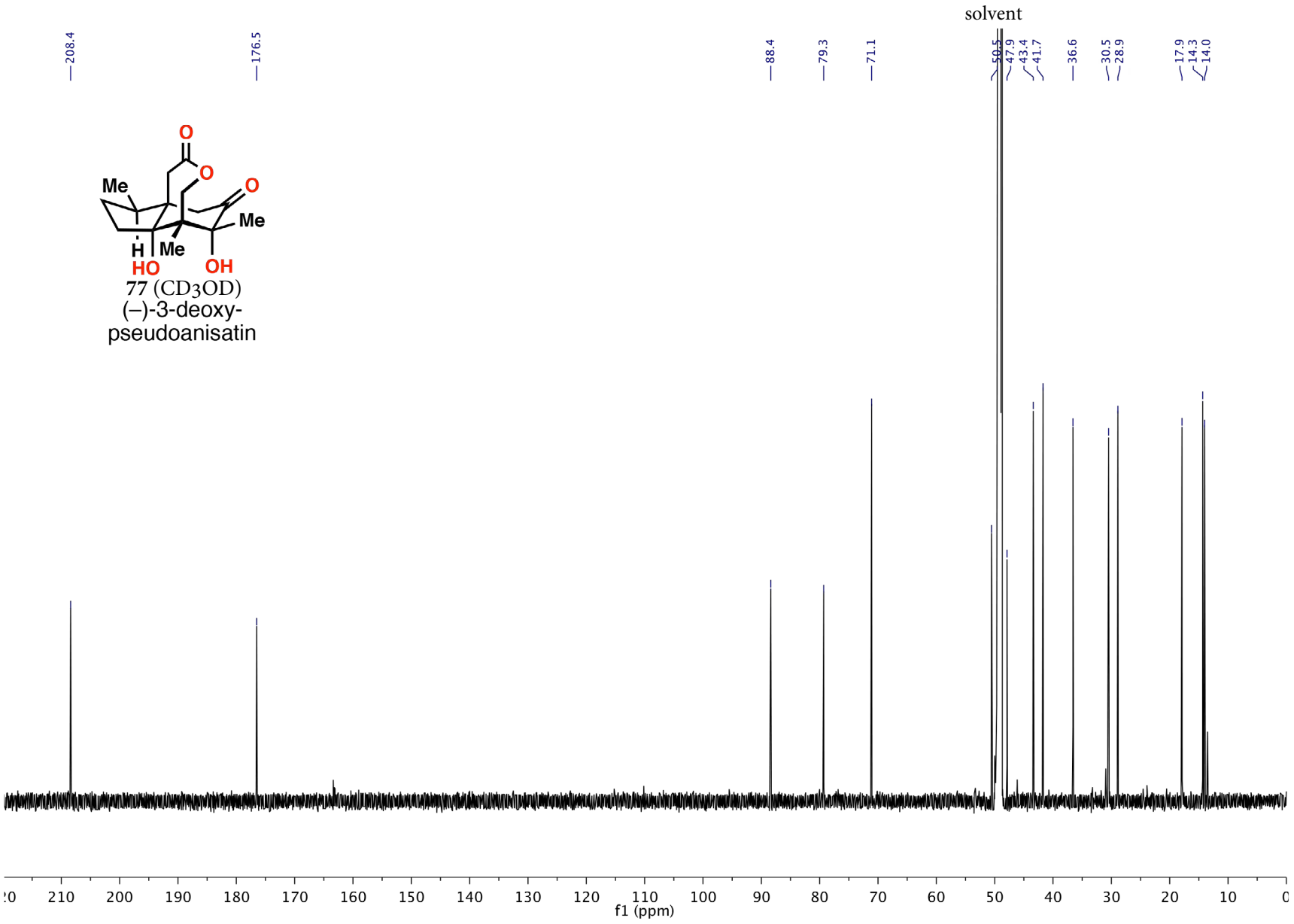
(–)-3-deoxy-pseudoanisatin

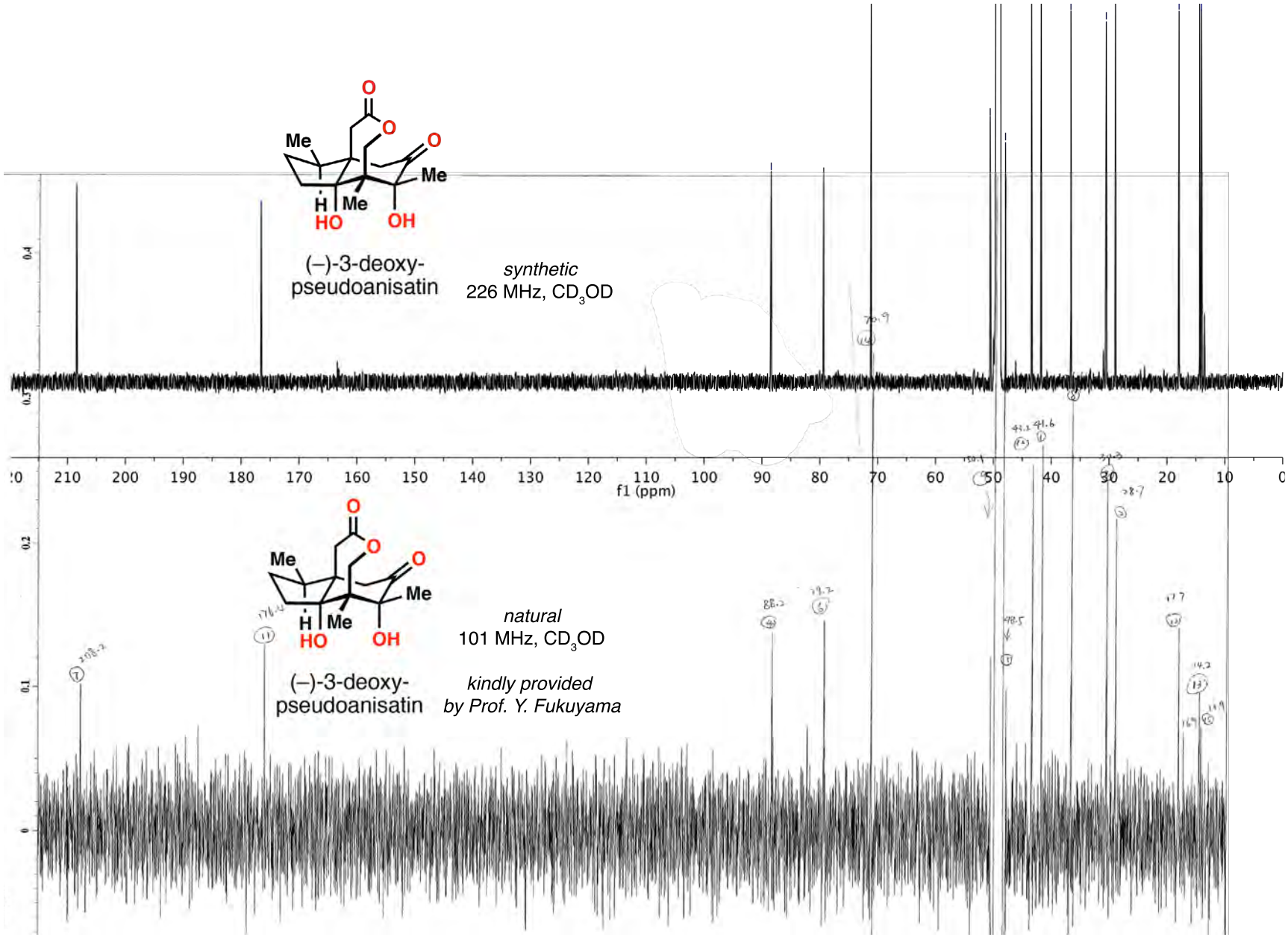
synthetic
900 MHz, CD_3OD

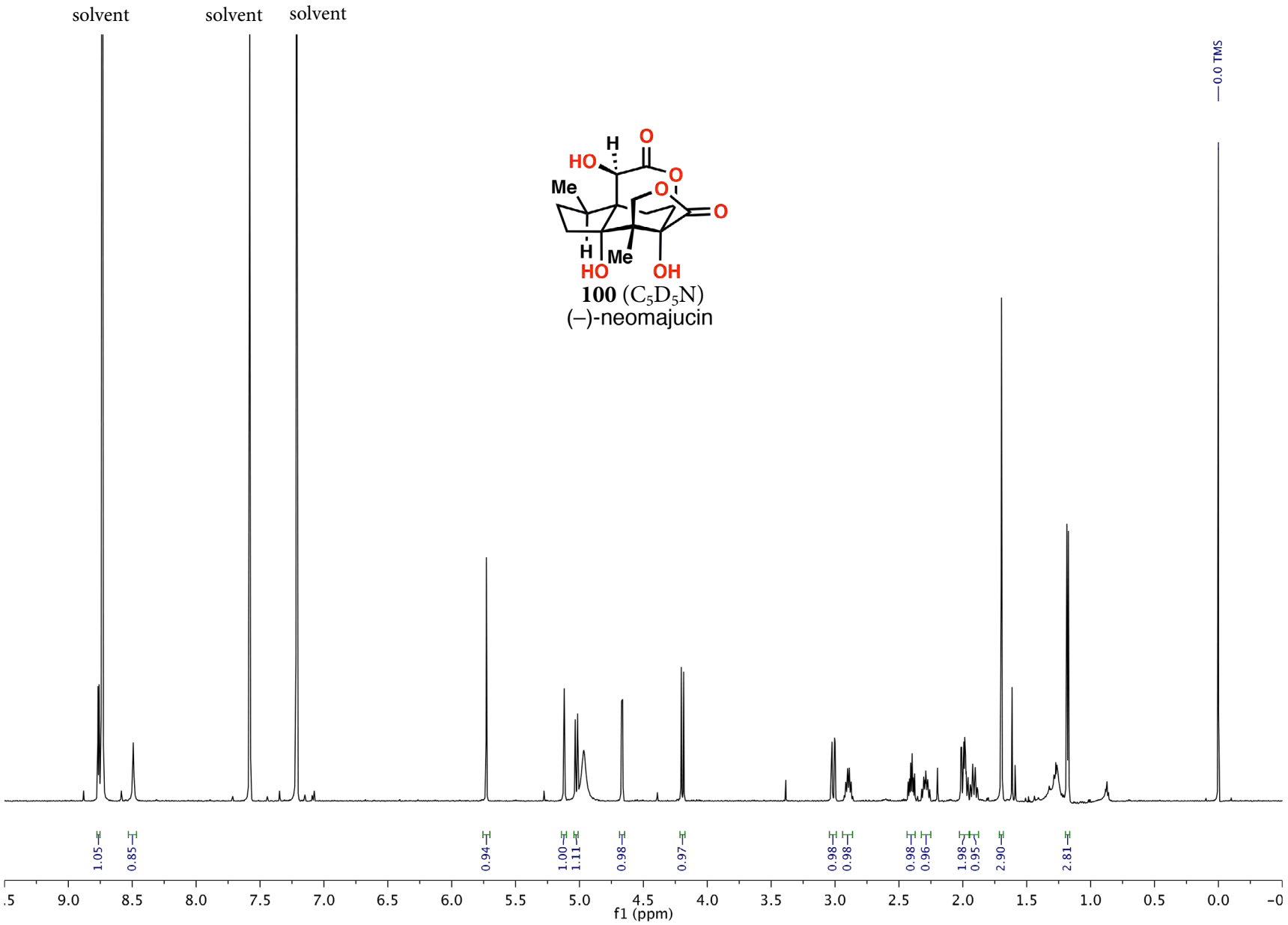
(–)-3-deoxy-pseudoanisatin

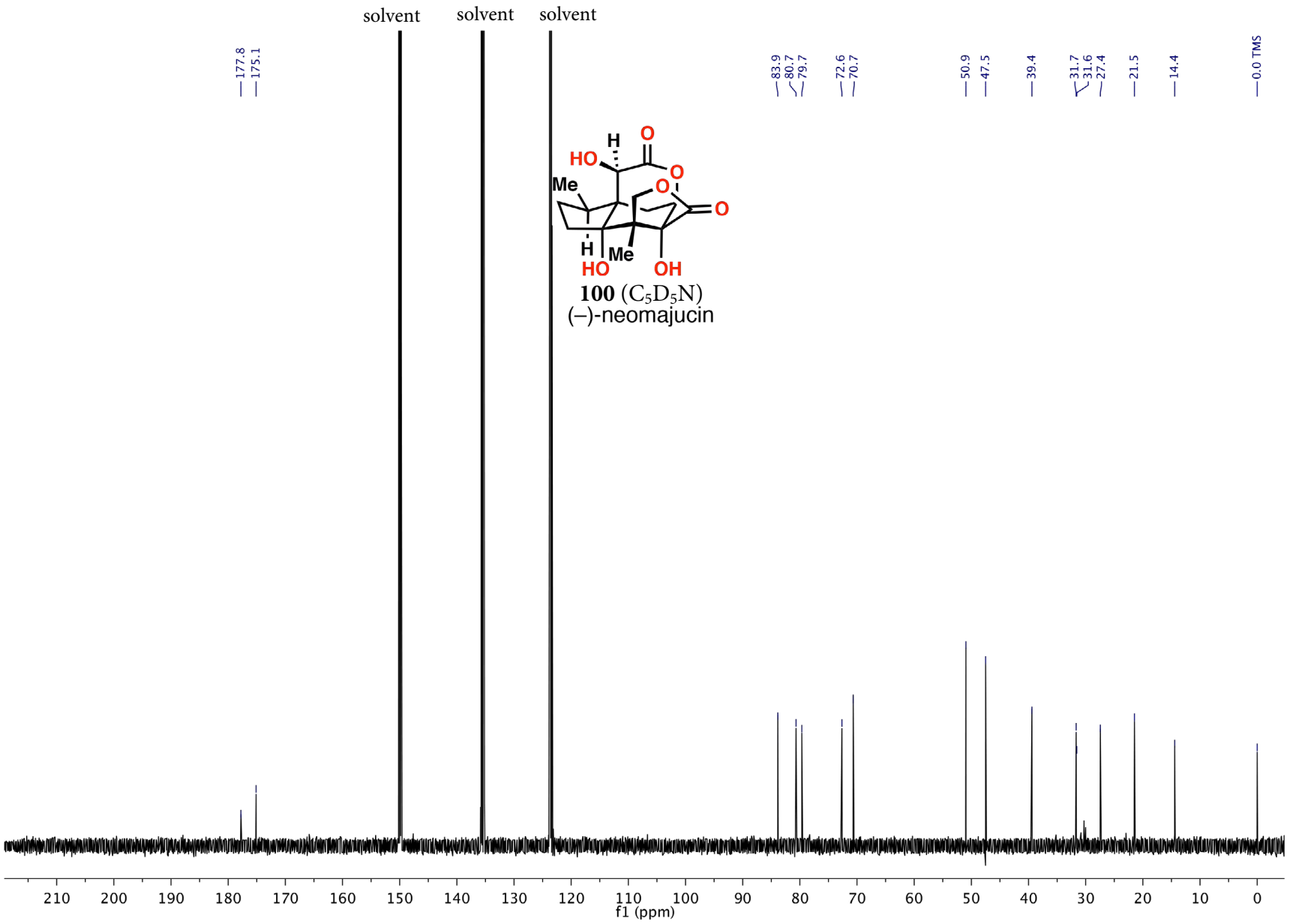
natural
400 MHz, CD_3OD

kindly provided by Prof. Y. Fukuyama


solvent
208.4
176.5
88.4
79.3
71.1
50.5
47.9
43.4
41.7
36.6
30.5
28.9
17.9
14.3
14.0
O
O
O
Me
Me
H
Me
HO
OH
77 (CD3OD)
(–)-3-deoxy-
pseudoanisatin
f1 (ppm)


Me
O
O
O
Me
H
Me
HO
OH
(–)-3-deoxy-
pseudoanisatin
synthetic
226 MHz, CD3OD
f1 (ppm)
natural
101 MHz, CD3OD
kindly provided
by Prof. Y. Fukuyama


solvent
solvent
solvent
0.0 TMS
100 (C5D5N)
(–)-neomajucin
1.05
0.85
0.94
1.00
1.11
0.98
0.97
0.98
0.98
0.98
0.96
1.98
0.95
2.90
2.81
f1 (ppm)


solvent
solvent
solvent
177.8
175.1
83.9
80.7
79.7
72.6
70.7
50.9
47.5
39.4
31.7
31.6
27.4
21.5
14.4
0.0 TMS
100 (C5D5N)
(–)-neomajucin
f1 (ppm)