The Total Synthesis of (–)-Scabrolide A

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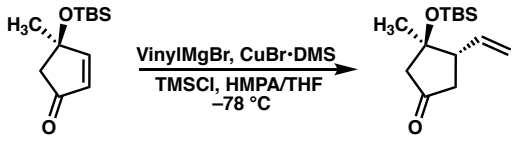
Materials and Methods

Unless otherwise stated, reactions were performed in flame-dried glassware under a nitrogen atmosphere using dry, deoxygenated solvents. Solvents were dried by passage through an activated alumina column under argon.[1] Reaction progress was monitored by thin-layer chromatography (TLC). TLC was performed using E. Merck silica gel 60 F254 precoated glass plates (0.25 mm) and visualized by UV fluorescence quenching, *p*-anisaldehyde, or $KMnO_4$ staining. Silicycle Silia*Flash*® P60 Academic Silica gel (particle size 40–63 μm) was used for flash chromatography. ^{1}H NMR spectra were recorded on Varian Inova 500 MHz and 600 MHz and Bruker 400 MHz spectrometers and are reported relative to residual $CHCl_3$ (δ 7.26 ppm), C_6D_6 (δ 7.16 ppm) or CD_3OD (δ 3.31 ppm). ^{13}C NMR spectra were recorded on a Varian Inova 500 MHz spectrometer (125 MHz) and Bruker 400 MHz spectrometers (100 MHz) and are reported relative to $CHCl_3$ (δ 77.16 ppm), C_6D_6 (δ 128.06 ppm) or CD_3OD (δ 49.01 ppm). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sept = septuplet, m = multiplet, br s = broad singlet, br d = broad doublet. Data for ^{13}C NMR are reported in terms of chemical shifts (δ ppm). IR spectra were obtained by use of a Perkin Elmer Spectrum BXII spectrometer or Nicolet 6700 FTIR spectrometer using thin films deposited on NaCl plates and reported in frequency of absorption (cm^{-1}). Optical rotations were measured with a Jasco P-2000 polarimeter operating on the sodium D-line (589 nm), using a 100 mm path-length cell. High resolution mass spectra (HRMS) were obtained from the Caltech Mass Spectral Facility using a JEOL JMS-600H High Resolution Mass Spectrometer in fast atom bombardment (FAB+) or electron ionization (EI+) mode, or using an Agilent 6200 Series TOF with an Agilent G1978A Multimode source in electrospray ionization (ESI+), atmospheric pressure chemical ionization (APCI+), or mixed ionization mode (MM: ESI-APCI+).

List of Abbreviations:

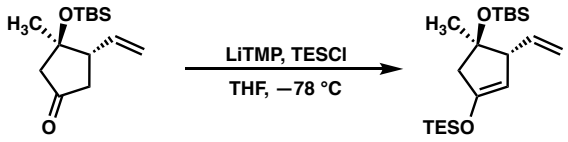
DDQ – 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, DIC – *N*,*N*'-diisopropylcarbodiimide, DMAP – (4-dimethylamino)pyridine, DMS – dimethyl sulfide, HMDS – hexamethyldisilizane, HMPA – hexamethylphosphoramide, HPLC – high-pressure liquid chromatography, IBX – 2-Iodoxybenzoic acid, LCMS – liquid chromatography/mass spectrometry, NIS – *N*-iodosuccinamide, NMR – nuclear magnetic resonance, TBHP – *tert*-butyl hydroperoxide, TBAF – tetrabutylammonium fluoride, TBS – *tert*-butyl dimethylsilyl, TESCl – triethylsilyl chloride, TES – triethylsilyl, TMSCl – trimethylsilyl chloride

Experimental Procedures



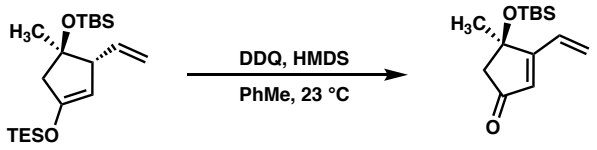
8 ***9***

Vinylcyclopentanone 9: To a flame-dried 500 mL three-necked flask is added CuBr • DMS (543 mg, 2.65 mmol, 0.12 equiv). The flask is evacuated and back-filled three times with argon, and charged with THF (110 mL). The solution is cooled to –78 °C and vinylmagnesium bromide in THF (1.0 M, 26.5 mL, 1.2 equiv) is added. The flask is equipped with an addition funnel and stirred at –78 °C for 30 minutes, during which time the solution turned from dark to red-brown. In a separate 100 mL flask, enone **9**[2] (5.0 g, 22.1 mmol, 1 equiv) is dissolved in THF (22.1 mL). HMPA (10.97 mL, 66.1 mmol, 3.0 equiv) and TMSCl (6.94 mL, 55.2 mmol, 2.5 equiv) are added at room temperature, and stirred for 5 minutes. This solution is transferred to the addition funnel and slowly added to the flask over 1 hour; an internal temperature no greater than –70 °C should be maintained and the solution will turn orange to yellow to dark brown. Upon complete addition, the reaction is stirred at -78 °C for an additional hour, then warmed to 0 °C. Saturated aq NH_4Cl (125 mL) is added before stirring at 0 °C for 1 hour. The layers are separated and the aqueous layer is extracted with diethyl ether (3x). The combined organics are washed with brine, dried with $MgSO_4$ and concentrated under reduced pressure. Flash column chromatography (10 to 20% Et_2O/Hexanes) affords the title compound (3.59 g, 64% yield, 9:1 mixture of diastereomers) as a yellow oil. Major Diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81 (ddd, *J* = 17.1, 10.4, 7.4 Hz, 1H), 5.26 – 4.92 (m, 2H), 2.89 (dtd, *J* = 8.1, 6.7, 1.2 Hz, 1H), 2.64 (ddd, *J* = 18.7, 8.2, 1.1 Hz, 1H), 2.39 (d, *J* = 17.8 Hz, 1H), 2.32 (dd, *J* = 17.6, 1.1 Hz, 1H), 2.17 (dd, *J* = 18.7, 6.6, 1.1 Hz, 1H), 1.27 (s, 3H), 0.85 (s, 6H), 0.10 (d, *J* = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 216.2, 136.9, 116.6, 79.7, 53.5, 52.8, 42.2, 25.7, 24.2, 18.0, –2.2, –2.4; IR (Neat film, NaCl) 2956, 2930, 2857, 1750, 1471, 1462, 1402, 1378, 1257, 1162, 1114, 1025, 997, 918, 836, 774, 617 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{14}H_{27}O_2Si$ $[M+H]^+$: 255.1780, found 255.1784; $[\alpha]_D^{25.0}$ –30.0° (*c* 1.0 , $CHCl_3$).



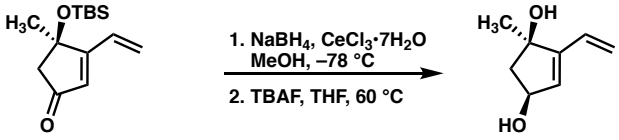
9 ***10***

Silyl Enol Ether 10: A 500 mL round-bottom flask is soaked in a base bath overnight, then washed, flame-dried, and placed under nitrogen atmosphere. The flask is charged with 2,2,6,6-tetramethylpiperidine (4.01 mL, 23.63 mmol, 1.2 equiv) and THF (108 mL) before it is cooled to –78 °C. *n*-BuLi (9.30 mL of 2.33 M, 1.1 equiv) is added to the flask, then stirred at 0 °C for 1 hr. The flask is cooled to –78 °C and charged with TESCl (3.96 mL, 23.6 1.2 equiv), then stirred for 5 minutes. Using a syringe pump, vinylcyclopentanone **9** (5.00 g, 19.69 mmol, 1.0 equiv) in THF (20 mL) is added dropwise over 1 hour. Upon complete addition, the reaction is stirred until complete by TLC (15 minutes.) Triethylamine (5 mL) is added and the reaction is quenched with a saturated aqueous sodium bicarbonate solution, and gradually warmed to 23 °C. The layers are separated and the aqueous layer is extracted with hexanes (5x). The combined organics are washed with water and 0.1 M citric acid solution, dried with sodium sulfate, and concentrated under reduced pressure. Flash column chromatography (2.5% Et_2O/Hexanes) affords the title compound (4.78 g, 12.96 mmol, 66% yield, 9:1 mixture of diastereomers) as a colorless oil. *Major diastereomer*: ^{1}H NMR (400 MHz, C_6D_6) δ 5.81 (ddd, *J* = 17.1, 10.1, 7.9 Hz, 1H), 5.16 (ddd, *J* = 17.1, 2.2, 1.2 Hz, 1H), 5.05 (ddd, *J* = 10.1, 2.2, 0.9 Hz, 1H), 4.66 (q, *J* = 1.8 Hz, 1H), 3.42 (ddq, *J* = 6.6, 2.3, 1.2 Hz, 1H), 2.68 (dt, *J* = 15.7, 1.6 Hz, 1H), 2.41 (dt, *J* = 15.7, 1.4 Hz, 1H), 1.27 (s, 3H), 1.04 – 0.99 (m, 18H), 0.73 – 0.61 (m, 6H), 0.15 (s, 3H), 0.14 (s, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 153.9, 139.3, 115.2, 103.2, 81.9, 59.9, 50.7, 26.8, 26.3, 18.5, 7.2, 5.5, –2.0, –1.9. IR (Neat film, NaCl) 3078, 2955, 2933, 2477, 2856, 1647, 1459, 1360, 1334, 1250, 1226, 1135, 1091, 1018 1004, 918, 834, 799, 774, 746 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{20}H_{39}O_2Si_2$ $[M–H]^+$: 367.2489, found 367.2489; $[\alpha]_D^{25.0}$ –66.8° (*c* 1.0, $CHCl_3$).



10 ***11***

Dienone 11: A 1 L round-bottomed flask is charged with silyl enol ether **10** (5.80 g, 15.76 mmol, 1.0 equiv) in benzene (310 mL). HMDS is added dropwise via syringe and the resulting solution is stirred for 5 minutes. DDQ (7.87 g, 34.67 mmol, 2.2 equiv) is added in a single portion, and the reaction is stirred for 45 minutes, during which time it turns from black to bright red. Celite (30 g) is added to the reaction, then concentrated and dried on high vaccum for 1 h. Flash column chromatography (1%-10% Et_2O/Hexanes) affords the title compound as a gold oil (3.35 g, 13.27 mmol, 84% yield) along with triethylsilanol as a coeluted impurity (1.16 g as determined by 1H NMR). A pure sample for characterization is obtained by preparative TLC (30% Et2O/Hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.56 (ddd, *J* = 17.8, 11.1, 0.8 Hz, 1H), 6.14 – 5.99 (m, 2H), 5.70 (dd, *J* = 11.1, 1.5 Hz, 1H), 2.70 (dd, *J* = 17.9, 0.7 Hz, 1H), 2.57 (d, *J* = 17.8 Hz, 1H), 1.53 (d, *J* = 0.6 Hz, 3H), 0.86 (s, 9H), 0.13 (s, 3H), 0.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.0, 175.9, 129.0, 126.5, 125.5, 78.8, 53.2, 29.2, 25.8, 18.1, –2.3, –2.7; IR (Neat film, NaCl) 2955, 2930, 2857, 1709, 1603, 1473, 1361, 1336, 1253, 1232, 1206, 1159, 1074, 1004, 938, 862, 834, 776 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{14}H_{25}O_2Si$ $[M+H]^+$: 253.1624, found 253.1622; $[\alpha]_D^{25.0}$ –92.1° (*c* 0.2, $CHCl_3$).

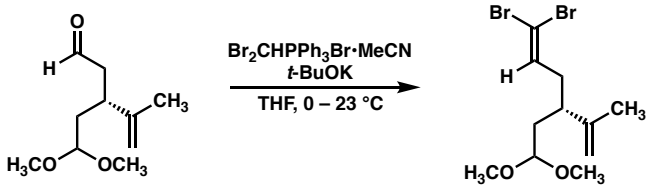


11 ***6***

Diol 6: A 500-mL round-bottom flask is charged with dienone **11** (2.69 g, 10.67 mmol, 1.0 equiv) in MeOH (110 mL) and cooled to –78 °C. $CeCl_3 \bullet 7\ H_2O$ (5.17 g, 13.87 mmol, 1.3 equiv) is added, and the solution is stirred for 5 minutes before $NaBH_4$ (534 mg, 13.87 mmol, 1.3 equiv) is added in a single portion. The reaction is stirred at –78 °C for 1 hour, warmed to room temperature, and quenched with saturated, aqueous ammonium chloride. The mixture is concentrated on a rotary evaporator to remove methanol, transferred to a separatory funnel, and extracted with diethyl ether

(3x). The combined organics are washed with brine, dried with $MgSO_4$, and concentrated to afford an orange oil which is used directly in the next step without further purification.

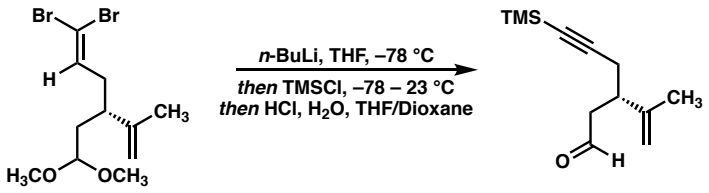
To a 500 mL flame-dried flask is added the crude reduction product in THF (150 mL). 1M TBAF in THF (15.0 mL equiv, 15.0 mmol, 1.4 equiv) is added dropwise by syringe. The flask is equipped with a reflux condenser and heated to reflux for 8 h. After completion as judged by TLC, the reaction is cooled to 23 °C and quenched with brine. The mixture is extracted with ethyl acetate (5x) before the combined organic layers are washed with brine, dried with Na_2SO_4, and concentrated under reduced pressure onto silica gel. The mixture is purified by flash column chromatography to afford the title compound (1.17 g, 8.35 mmol, 78% yield over two steps) as an amorphous white solid. All spectral data for **11** was found to be in good accordance with literature values.[3]



12 ***13***

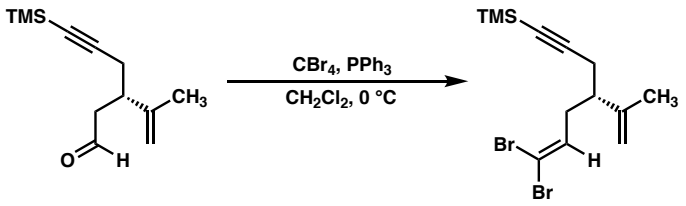
Dibromide 13: A 500 mL round-bottom flask is charged with Br_2CHPPh_3Br•MeCN (55.6 g, 100.0 mmol, 1.4 equiv; prepared according to the method of Schmidt)[4] and THF (238 mL, 0.3 M). The reaction mixture is cooled to 0 °C and *t*-BuOK (9.6 g, 85.7 mmol, 1.2 equiv) is added in one portion. This mixture is stirred 1.5 h at 0 °C and then warmed to 23 °C and stirred an additional 30 min. The mixture is cooled to 23 °C and aldehyde **12**[5] (13.3 g, 71.4 mmol, 1.0 equiv) is added dropwise via syringe. The dark suspension is stirred for 2 h at 0 °C until no aldehyde **12** is detected by TLC. The mixture is quenched with saturated, aqueous NH_4Cl and partitioned between water and Et_2O. The aqueous phase is extracted with Et_2O (3x). The organic extracts are combined, washed with brine, dried over magnesium sulfate, filtered through a sand/cotton plug and concentrated under reduced pressure. The crude residue is purified by flash chromatography (Dry load crude on Celite; 20% Et_2O/Hexanes) to afford the title compound (20.9 g, 61.1 mmol, 86% yield) as a red/orange oil: ^{1}H NMR (400 MHz, $CDCl_3$) 6.30 (t, J = 7.0 Hz, 1H), 4.83 (dt, J = 2.9, 1.5 Hz, 1H), 4.77 (dt, J = 1.9, 0.8 Hz, 1H), 4.36 – 4.28 (m, 1H), 3.32 (s, 3H), 3.30 (s, 3H), 2.43 – 2.30 (m, 1H), 2.24 – 2.07 (m, 2H), 1.72 – 1.62 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) 145.7, 137.0,

113.0, 102.9, 89.2, 53.3, 52.7, 42.0, 36.9, 35.7, 18.6; IR (Neat film, NaCl) 3073, 2948, 2829, 1645, 1440, 1377, 1191, 1127, 1060, 896, 787 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{11}H_{17}O_2Br_2$ [M–H]$^+$: 340.9575, found 340.9579; $[\alpha]_D^{25.0}$ – 4.5° (*c* 1.0, $CHCl_3$).



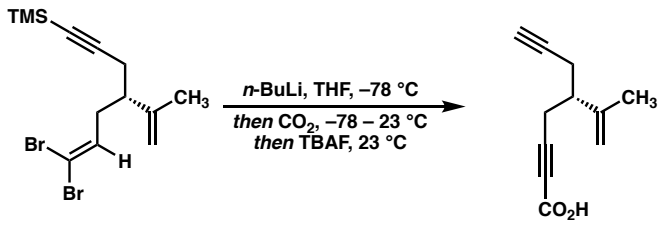
13 ***14***

Aldehyde 14: A 500 mL round-bottom flask is charged with dibromide **13** (16.6 g, 48.5 mmol, 1.0 equiv) in THF (100 mL, 0.5 M), and cooled to –78 °C. *n*-BuLi (2.3 M in hexanes; 42.2 mL, 97.1 mmol, 2.0 equiv) is added dropwise over 10 min, and the mixture is allowed to stir for 15 min at –78 °C after which complete consumption of dibromide **13** is observed by TLC. TMSCl (18.5 mL, 145.5 mmol, 3.0 equiv) is added dropwise to the reaction mixture, which is then allowed to gradually warm to 23 °C over 2 h. The mixture is then cooled to 0 °C and water (100 mL) is added followed by 1,4-dioxane (50 mL). HCl (36% w/w, 40 mL, 10.0 equiv) is added and the reaction mixture is warmed to room temperature and allowed to stir for 16 h. $NaHCO_3$ (sat. aq.) is added until the pH of the solution is roughly 7. The reaction mixture is partitioned between water and Et_2O, and extracted with Et_2O (3x). The combined organic extracts are washed with brine, dried over sodium sulfate, and concentrated to afford an orange oil which is purified by flash chromatography (10% Et_2O/Hexanes). The title compound (7.37 g, 35.4 mmol, 73% yield) is isolated as a pale-yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.70 (dd, *J* = 2.4, 1.6 Hz, 1H), 4.83 – 4.80 (m, 1H), 4.79 – 4.76 (m, 1H), 2.89 – 2.77 (m, 1H), 2.68 (ddd, *J* = 16.8, 6.1, 1.7 Hz, 1H), 2.52 (ddd, *J* = 16.7, 8.4, 2.5 Hz, 1H), 2.40 (dd, *J* = 16.9, 5.8 Hz, 1H), 2.29 (dd, *J* = 17.0, 7.9 Hz, 1H), 1.70 (dd, *J* = 1.5, 0.9 Hz, 3H), 0.11 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) 201.6, 145.4, 112.3, 104.5, 87.3, 46.3, 40.2, 24.8, 20.3, 0.1; IR (Neat film, NaCl) 3077, 2959, 2900, 2827, 2720, 1727, 1648, 1430, 1408, 1377, 1250, 1024, 1038, 896, 760, 644 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{12}H_{21}OSi$ $[M+H]^+$ 209.1356, found 209.1352.; $[\alpha]_D^{25.0}$ –13.5° (*c* 1.0, $CHCl_3$).



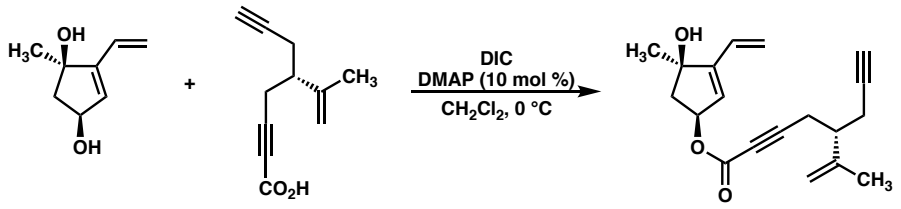
14 ***15***

Dibromide 15: A 500 mL round-bottom flask is charged with triphenylphosphine (50.4 g, 192.0 mmol, 4.0 equiv) in CH_2Cl_2 (96 mL). The solution is cooled to 0 °C, and CBr_4 (31.8 g, 96.0 mmol, 2.0 equiv) is added in one portion. The colorless solution immediately changes to yellow/orange in color. The mixture is allowed to stir for 10 min at 0 °C, after which aldehyde **14** (10.0 g, 48.0 mmol, 1.0 equiv) is added via syringe. The aldehyde is consumed immediately, as judged by TLC. The reaction mixture is then quenched with water, and partitioned between water and CH_2Cl_2. The aqueous phase is extracted with CH_2Cl_2 (3x), and the combined organic extracts are washed with brine and dried over $MgSO_4$. The crude is concentrated onto SiO_2, loaded onto a column, and purified by flash chromatography (5% Et_2O/Hexanes) to afford the title compound (14.48 g, 39.8 mmol, 83% yield) as a yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) 6.34 (t, J = 6.9 Hz, 1H), 4.84 (p, J = 1.5 Hz, 1H), 4.76 (dt, J = 1.7, 0.8 Hz, 1H), 2.47 – 2.16 (m, 5H), 1.69 (dd, J = 1.5, 0.8 Hz, 3H), 0.14 (s, 9H); ^{13}C NMR (100 MHz, Chloroform-*d*) 145.4, 136.9, 112.7, 105.1, 89.5, 86.75, 44.9, 35.8, 24.7, 19.7, 0.3; IR (Neat film, NaCl) 2958, 2922, 2176,1646, 1441, 1248 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{13}H_{20}SiBr_2$ [$M^{+\bullet}$] 363.9681, found 363.9668; $[\alpha]_D^{25.0}$ +4.1° (*c* 1.0, $CHCl_3$).



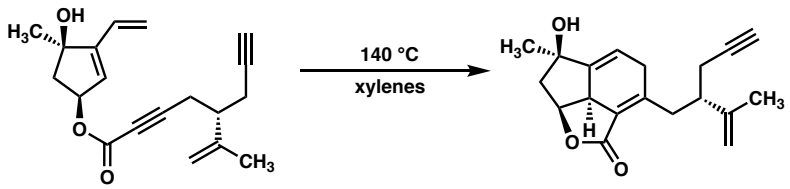
15 ***7***

Ynoic Acid 7: A 250 mL round bottom flask was charged with dibromide **15** (9.27 g, 25.45 mmol, 1.0 equiv) in THF (52 mL). The solution was cooled to –78 °C, and *n*-BuLi (2.3 M in hexanes; 16.6 mL, 38.18 mmol, 1.5 equiv) was added dropwise. After 10 min, dibromide **15** had been completely consumed (as judged by TLC), and the reaction was then sparged with CO_2 from a balloon passing though a drying tube full of Dryrite. The solution was allowed to warm to 23 °C over 30 min with continuous sparging with CO_2. The solution was then sparged with N_2 for 10 min at 23 °C, followed by the addition of TBAF (1.0 M in THF; 50.9 mL, 50.9 mmol, 2.0 equiv). The solution was allowed to stir for 16 h at 23 °C after which TMS-protected substrate remained, as judged by LCMS. TBAF (25.5 mL, 25.5 mmol, 1.0 equiv) was added, and the reaction was stirred an additional 1 h at 23 °C. The reaction was quenched with sat. aq. $NaHCO_3$, diluted with water and EtOAc, and extracted with EtOAc (1x). The aqueous extract was then acidified with conc. HCl until a cloudy precipitate was observed. The aqueous was then extracted with EtOAc (3x). The combined organic extracts were then washed with brine and dried over $MgSO_4$. Concentration under reduced pressure afforded the title compound (2.20 g, 12.5 mmol, 49% yield) as a pale orange oil which was found to be pure by NMR and used in the subsequent step without further purification: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.98 (s, 1H), 4.92 (p, *J* = 1.4 Hz, 1H), 4.84 (q, *J* = 1.0 Hz, 1H), 2.71 – 2.47 (m, 3H), 2.41 (d, *J* = 2.7 Hz, 1H), 2.40 – 2.39 (m, 1H), 2.01 (t, *J* = 2.6 Hz, 1H), 1.73 (dd, *J* = 1.5, 0.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 144.1, 113.1, 90.3, 81.6, 74.1, 70.6, 43.7, 22.5, 22.4, 20.2; IR (Neat film, NaCl) 3302, 2928, 2643, 2236, 2119, 1964, 1416, 1244, 1078, 899, 775, 792, 759, 641, 648; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{11}H_{13}O_2$ $[M+H]^+$: 177.0910, found 177.0916; $[\alpha]_D^{25.0}$ –1.6° (*c* 1.0, $CHCl_3$).



6 ***7*** ***16***

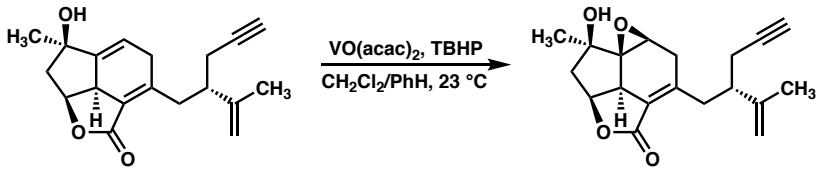
Ester 16: A 250 mL round bottom flask is charged with diol **6** (1.03 g, 7.35 mmol, 1.0 equiv), acid **7** (1.30 g, 7.35 mmol, 1.0) and DMAP (90 mg, 0.735 mmol, 0.10 equiv) in CH_2Cl_2 (74 mL). The solution is cooled to 0 °C, and DIC (1.15 mL, 7.35 mmol, 1.0 equiv) is added dropwise. The reaction is stirred for 2 h while gradually warming to 23 °C, and then stirred an additional 3 h at 23 °C. The mixture is then partitioned between CH_2Cl_2 and H_2O, and the aqueous phase is extracted with CH_2Cl_2 (3x). The organic extracts are washed with brine, dried over Na_2SO_4, and concentrated. The crude residue was purified by flash chromatography (0%-5%-10%-15%-20% EtOAc/Hexanes) to afford the title compound (1.74 g, 5.83 mmol, 79% yield) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.43 – 6.20 (m, 1H), 5.82 (d, *J* = 2.4 Hz, 1H), 5.78 (dd, *J* = 17.8, 1.7 Hz, 1H), 5.64 – 5.49 (m, 1H), 5.33 (dd, *J* = 11.2, 1.6 Hz, 1H), 4.92 (p, *J* = 1.4 Hz, 1H), 4.84 (dd, *J* = 1.4, 0.8 Hz, 1H), 2.77 – 2.46 (m, 4H), 2.44 – 2.39 (m, 2H), 2.05 (dd, *J* = 14.7, 4.4 Hz, 1H), 2.01 (t, *J* = 2.6 Hz, 1H), 1.74 (dd, *J* = 1.5, 0.8 Hz, 3H), 1.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 151.8, 144.3, 129.0, 126.1, 119.6, 113.0, 87.6, 81.7, 81.1, 77.1, 74.5, 70.5, 49.0, 43.8, 26.8, 22.5, 22.4, 20.3; IR (Neat film, NaCl) 3396, 2938, 2235, 1708, 1252, 1071, 942, 752 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{19}H_{23}O_3$ $[M+H]^+$: 299.1642, found 299.1632; $[\alpha]_D^{25.0}$ –130.8° (*c* 1.0, $CHCl_3$).



16 ***17***

Cyclohexadiene 17: Ester **16** (804 mg, 2.69 mmol, 1.0 equiv) is dissolved in xylenes (270 mL). This solution is divided between two 500 mL Schlenk flasks. Each flask is subjected to three freeze-pump-thaw cycles, and then back-filled with nitrogen. The flasks are sealed, heated to 140 °C, and stirred for 3 h. The flasks are then cooled to ambient temperature and the reaction

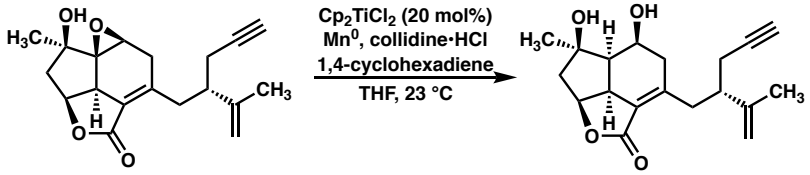
mixtures are combined in a 2 L round-bottom flask. The solvent is removed under reduced pressure, and the resulting solid is purified by flash chromatography (30%-40%-50% EtOAc/Hexanes) to afford the title compound (604 mg, 2.02 mmol, 75% yield) as a flakey white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84 (ddd, *J* = 6.4, 3.0, 1.9 Hz, 1H), 4.97 (ddd, *J* = 9.1, 8.0, 7.0 Hz, 1H), 4.77 (t, *J* = 1.7 Hz, 1H), 4.69 – 4.65 (m, 1H), 3.31 (t, *J* = 9.8 Hz, 1H), 3.12 – 2.98 (m, 2H), 2.83 – 2.61 (m, 2H), 2.63 – 2.41 (m, 2H), 2.33 (d, *J* = 2.6 Hz, 1H), 2.32 (dd, *J* = 2.7, 1.4 Hz, 1H), 2.00 (t, *J* = 2.6 Hz, 1H), 1.69 (dd, *J* = 1.4, 0.8 Hz, 3H), 1.67 – 1.60 (m, 1H), 1.41 (d, *J* = 1.1 Hz, 3H); δ ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 155.9, 152.0, 146.1, 125.5, 116.5, 112.8, 82.9, 80.0, 75.3, 69.7, 49.8, 45.7, 45.7, 35.3, 26.7, 22.9, 18.8; IR (Neat film, NaCl) 3305, 2967, 2920, 2360, 2118, 1730, 1647, 1447, 1374, 1358, 1290, 1219, 1045, 1018, 896, 632 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{19}H_{23}O_3$ $[M+H]^+$: 299.1642, found 299.1631. $[\alpha]_D^{25.0}$ –87.4° (*c* 0.5, $CHCl_3$).



17 ***18***

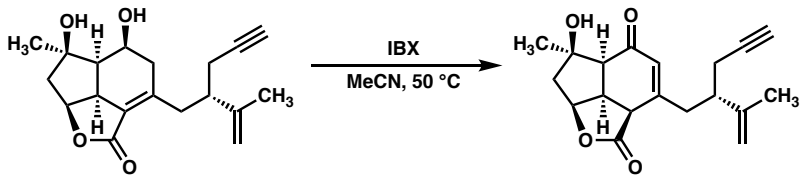
Epoxide 18: A 500 mL round-bottom flask is charged with Diels–Alder adduct **17** (1.75 g, 5.87 mmol, 1.0 equiv) in a mixture of CH_2Cl_2 (59 mL) and benzene (196 mL). $VO(acac)_2$ is added (117 mg, 0.440 mmol, 0.075 equiv) in one portion, and the mixture is stirred 10 min at 23 °C until it is pale-green in color. TBHP (5.0 M in decane, 2.30 mL, 11.74 mmol, 2.0 equiv) is added dropwise via syringe, and the mixture becomes deep-red in color. The mixture is stirred at 23 °C for 1 h, at which point no starting material remained, as judged by TLC. The reaction mixture is poured directly onto a flash column and purified by flash chromatography (0%-50%-70%-80% EtOAc/Hexanes) to afford the title compound (1.73 g, 5.50 mmol, 94% yield) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.90 – 4.77 (m, 3H), 3.78 (d, *J* = 3.4 Hz, 1H), 3.40 – 3.18 (m, 2H), 2.87 (dd, *J* = 16.7, 3.4 Hz, 1H), 2.62 – 2.43 (m, 3H), 2.41 – 2.26 (m, 3H), 2.06 – 1.95 (m, 2H), 1.74 (t, *J* = 1.1 Hz, 3H), 1.46 – 1.41 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 149.9, 146.1, 120.7, 112.5, 82.9, 76.6, 73.6, 69.8, 69.7, 51.8, 50.1, 45.7, 44.8, 36.7, 36.6, 22.7, 22.7, 19.4; IR

(Neat film, NaCl) 3474, 3267, 1735, 1655, 1421, 1358, 1195, 1120, 1030, 901, 793, 674 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{19}H_{23}O_4$ $[M+H]^+$: 315.1591, found 315.1586; $[\alpha]_D^{25.0}$ –69.8° (*c* 0.5, $CHCl_3$).



18 ***19***

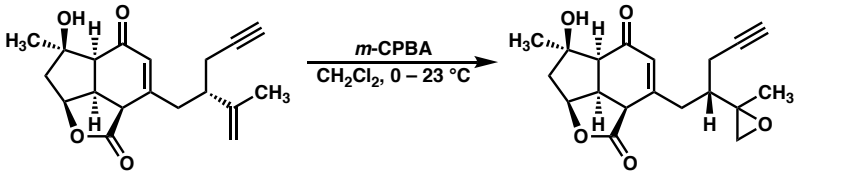
Diol 19: A 250 mL round bottom flask is charged with epoxide **18** (1.70 g, 5.41 mmol, 1.0 equiv), titanocene dichloride (269 mg, 1.08 mmol, 0.20 equiv), manganese dust (326 mg, 5.95 mmol, 1.10 equiv), and collidine•HCl (1.07 g, 6.76 mmol, 1.25 equiv) in THF (54 mL, 0.10 M). 1,4-cyclohexadiene is then added dropwise to the red suspension, which gradually changes to a blue/grey color. The suspension is stirred for 2 h at 23 °C, after which the starting material is consumed, as judged by TLC. Celite is added directly to the mixture, and the solvent is removed under reduced pressure. The resulting solid is loaded directly on to a flash column and purified by flash chromatography (40%-50%-60% EtOAc/Hexanes) to afford the title compound (1.47 g, 4.65 mmol, 86% yield) as an off-white solid: ^{1}H NMR (400 MHz, $CDCl_3$) 4.90 (ddd, *J* = 8.1, 6.5, 3.9 Hz, 1H), 4.83 (d, *J* = 1.4 Hz, 2H), 4.67 (td, *J* = 5.4, 2.9 Hz, 1H), 3.40 (d, *J* = 6.0 Hz, 1H), 3.37 – 3.28 (m, 1H), 3.18 (s, 1H), 3.10 (ddd, *J* = 9.9, 7.9, 2.1 Hz, 1H), 2.64 – 2.48 (m, 3H), 2.36 (dd, *J* = 9.5, 7.8 Hz, 1H), 2.32 (dd, *J* = 2.7, 1.1 Hz, 1H), 2.31 – 2.29 (m, 1H), 2.13 – 1.98 (m, 3H), 1.97 (t, *J* = 2.6 Hz, 1H), 1.80 – 1.71 (m, 3H), 1.43 (s, 3H); δ ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 151.3, 146.8, 125.2, 112.4, 83.2, 81.7, 79.4, 69.5, 68.3, 49.6, 48.4, 45.2, 44.6, 41.4, 36.8, 28.6, 22.9, 19.3; IR (Neat film, NaCl) 3296, 3076, 2116, 1738, 1731, 1668, 1424, 1375, 1360, 1306, 1223, 1198, 1105, 896 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{19}H_{25}O_4$ $[M+H]^+$: 317.1747, found 317.1761; $[\alpha]_D^{25.0}$ –11.8° (*c* 0.5, $CHCl_3$).



19 ***5***

Note: *The success of this procedure was found to be scale-dependent. Consequently, this reaction was run with a maximum batch size of 50 mg (***19***) per reaction flask. When run on scale, reactions were set up side-by-side, and combined for purification, as detailed below:*

Enone 5: Diol **19** (1.0 g, 3.16 mmol, 1.0 equiv) is divided into 20 scintilation vials (not flame dried, 50 mg, 0.158 mmol per vial) each equipped with a magnetic stir bar and a septum cap. To each vial is added IBX (188 mg, 0.671 mmol, 4.25 equiv) and each vial is evacuated and back-filled with N_2. MeCN (11 mL) is added to each vial after which the vials are sealed, heated to 50 °C, and stirred 2 h. The reactions are cooled to 23 °C, combined, and filtered over a plug of SiO_2, rinsing generously with EtOAc. The filtrate is concentrated under reduced pressure, and the residue obtained is purified by flash chromatography (30%-40%50% EtOAc/Hexanes) to afford the title compound (716 mg, 2.28 mmol, 72% yield) as a white foam: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.00 (d, *J* = 1.0 Hz, 1H), 5.11 (dd, *J* = 6.7, 5.4 Hz, 1H), 4.88 – 4.81 (m, 1H), 4.78 (dt, *J* = 1.6, 0.8 Hz, 1H), 3.68 – 3.45 (m, 2H), 3.16 – 3.05 (m, 1H), 2.79 – 2.59 (m, 2H), 2.48 (d, *J* = 9.2 Hz, 1H), 2.39 – 2.28 (m, 3H), 2.03 (t, *J* = 2.6 Hz, 1H), 1.88 (dd, *J* = 15.0, 5.5 Hz, 1H), 1.71 (s, 1H), 1.67 (d, *J* = 0.7 Hz, 3H), 1.49 (s, 3H); δ ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 173.6, 156.3, 145.0, 128.8, 113.6, 82.7, 82.6, 82.2, 70.5, 55.2, 47.4, 44.0, 42.1, 41.4, 38.2, 26.3, 23.9, 18.8; IR (Neat film, NaCl) 3450, 3290, 2970, 2930, 2118, 1758, 1649, 1376, 1290, 1176, 1161, 1107, 912, 735 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{19}H_{23}O_4$ $[M+H]^+$: 315.1591, found 315.1571; $[\alpha]_D^{25.0}$ –150.0° (*c* 0.5, $CHCl_3$).



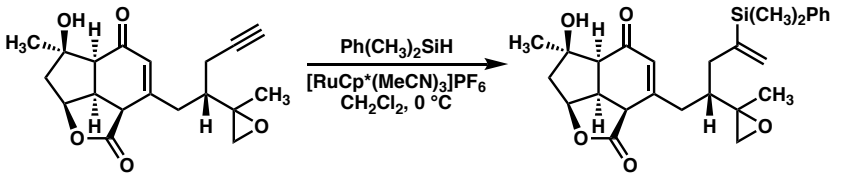
5 *22* 1.7:1 mixture of epimers

Epoxides 22 and *epi*-22: A 100 mL round-bottom flask is charged with enone **5** (450 mg, 1.43 mmol, 1.0 equiv) in CH_2Cl_2 (48 mL). The solution is cooled to 0 °C, and *m*–CPBA (~70% wt/wt; 1.06 g, 4.29 mmol, 3.0 equiv) is added in one portion. The mixture is stirred while gradually warming to 23 °C over 2 h, and then stirred an additional 10 h at 23 °C, at which point **5** has been completely consumed as judged by TLC. The reaction mixture is poured directly onto a flash column and purified by flash chromatography (50%-60%-70%-80% EtOAc/Hexanes) to afford the title compounds (410 mg,1.24 mmol, 87% yield) as a white foam. The products are isolated as a 1.7:1 mixture of diastereomers (judged by ^{1}H NMR). A portion of this mixture was subjected to normal phase (SiO_2) preparative HPLC (EtOAc/Hexanes, 7.0 mL/min, monitor wavelength 254 nm, 60% EtOAc/Hexanes) to obtain pure samples of the two products for the purposes of characterization:

Diastereomer 1 (minor): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.05 (d, J = 1.4 Hz, 1H), 5.12 (dd, J = 6.7, 5.4 Hz, 1H), 3.75 – 3.42 (m, 2H), 2.99 (ddt, J = 15.6, 6.2, 1.2 Hz, 1H), 2.76 – 2.63 (m, 2H), 2.57 (d, J = 4.5 Hz, 1H), 2.54 – 2.44 (m, 2H), 2.44 – 2.27 (m, 2H), 2.05 (t, J = 2.7 Hz, 1H), 1.99 – 1.84 (m, 2H), 1.50 (s, 3H), 1.34 (d, J = 0.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.0, 173.6, 156.4, 128.5, 82.9, 82.7, 81.8, 71.2, 58.6, 55.2, 54.2, 47.5, 42.6, 42.3, 42.2, 36.5, 26.4, 21.0, 18.4; IR (Neat film, NaCl) 3436, 3283, 2970, 2926, 1758, 1656, 1378, 1292, 1177, 1109, 735 cm^{-1}; (MM: ESI-APCI+) *m/z* calc'd for $C_{19}H_{23}O_5$ $[M+H]^+$: 331.1545, found 331.1538; $[\alpha]_D^{25.0}$ –144.5 °(*c* 1.0, $CHCl_3$).

Diastereomer 2 (major): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.10 (t, J = 1.6 Hz, 1H), 5.11 (dd, J = 7.1, 5.4 Hz, 1H), 3.84 (dt, J = 10.9, 1.2 Hz, 1H), 3.76 – 3.57 (m, 1H), 3.35 – 3.16 (m, 1H), 2.70 (dd, J = 4.6, 0.8 Hz, 1H), 2.63 – 2.45 (m, 3H), 2.40 – 2.24 (m, 3H), 2.05 (t, J = 2.6 Hz, 1H), 1.95 – 1.84 (m, 2H), 1.49 (s, 3H), 1.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.4, 174.1, 156.4, 129.3, 82.9, 82.9, 81.3, 71.1, 58.5, 55.5, 54.2, 47.5, 42.8, 42.8, 41.3, 38.5, 26.4, 22.5, 16.0; IR (Neat film, NaCl) 3436, 3283, 2250, 1758, 1657, 1378, 1109, 735 cm^{-1}; HRMS

(MM: ESI-APCI+) *m/z* calc'd for $C_{19}H_{23}O_5$ $[M+H]^+$: 331.1545, found 331.1540; $[\alpha]_D^{25.0}$ –83.5° (*c* 1.0, $CHCl_3$).



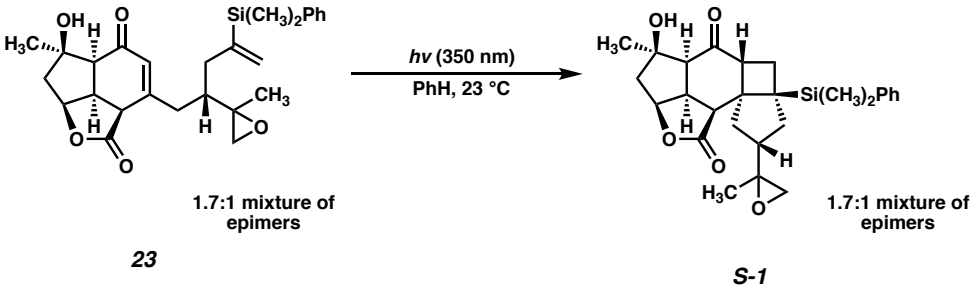
22 1.7:1 mixture of epimers **23** 1.7:1 mixture of epimers

Vinyl Silanes 23 and *epi*-23: A 250 mL round bottom flask is charged with a mixture of **22** and ***epi*-22** (725 mg, 2.19 mmol, 1.0 equiv) in CH_2Cl_2 (22 mL). Phenyldimethylsilane is added, and the mixture is cooled to 0 °C. $[RuCp^*(MeCN)_3]PF_6$ (10 mg/mL stock solution, 5.5 mL, 0.110 mmol, 0.05 equiv) is added dropwise. Following the addition, the reaction is stirred 5 min at 0 °C, after which the starting material is no longer detectable by TLC. The reaction mixture is poured directly onto a flash column, and purified by flash chromatography (0%-50% EtOAc/Hexanes) to afford the title compounds (870 mg, 1.86 mmol, 85% yield) as a colorless foam. The products are isolated as a 1.7:1 mixture of diastereomers (judged by ^{1}H NMR), which were characterized separately:

Diastereomer 1 (minor): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (ddd, *J* = 4.9, 2.4, 1.7 Hz, 2H), 7.37 – 7.29 (m, 3H), 5.83 (d, *J* = 1.2 Hz, 1H), 5.71 (dd, *J* = 2.3, 1.3 Hz, 1H), 5.61 (d, *J* = 2.7 Hz, 1H), 4.99 (dd, *J* = 7.0, 5.3 Hz, 1H), 3.15 (td, *J* = 10.6, 7.0 Hz, 1H), 2.84 (ddd, *J* = 14.2, 3.3, 1.6 Hz, 1H), 2.72 (dt, *J* = 13.6, 2.2 Hz, 1H), 2.45 (d, *J* = 4.7 Hz, 1H), 2.39 (d, *J* = 10.4 Hz, 1H), 2.29 (d, *J* = 15.0 Hz, 1H), 2.20 – 1.98 (m, 5H), 1.84 (dd, *J* = 15.0, 5.4 Hz, 1H), 1.47 (s, 3H), 1.20 (s, 3H), 0.46 (s, 3H), 0.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.7, 173.0, 157.2, 147.4, 139.6, 134.4, 129.2, 128.7, 128.7, 127.9, 82.7, 82.0, 58.6, 55.2, 54.9, 47.3, 42.3, 41.9, 40.4, 40.0, 36.3, 26.5, 16.6, -2.7, -3.9; IR (Neat film, NaCl) 3435, 2960, 1762, 1659, 1426, 1376, 1288, 1247, 1217, 1163, 1106, 1034, 992, 938, 838, 818, 753, 703 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{27}H_{35}O_5Si$ $[M+H]^+$: 467.2254, found 467.2265; $[\alpha]_D^{25.0}$ –62.0° (*c* 1.0, $CHCl_3$).

Diastereomer 2 (major): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.44 (m, 2H), 7.39 – 7.31 (m, 3H), 6.03 (t, *J* = 1.5 Hz, 1H), 5.73 (dt, *J* = 2.4, 1.2 Hz, 1H), 5.58 (d, *J* = 2.6 Hz, 1H), 5.07 (dd, *J* = 7.1, 5.3 Hz, 1H), 3.53 (td, *J* = 10.6, 7.1 Hz, 1H), 3.38 (dt, *J* = 11.0, 1.2 Hz, 1H), 3.23 – 3.07 (m, 1H), 2.48 (d, *J* = 10.3 Hz, 1H), 2.43 – 2.19 (m, 5H), 2.17 – 2.06 (m, 2H), 1.89 (dd, *J* = 14.9, 5.5 Hz,

1H), 1.50 (s, 3H), 1.13 (d, J = 0.6 Hz, 3H), 0.40 (d, J = 0.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.0, 173.8, 157.8, 147.0, 138.2, 134.2, 129.3, 129.3, 129.0, 128.2, 82.7, 82.5, 59.2, 55.3, 53.6, 47.5, 42.2, 42.1, 40.7, 40.2, 38.3, 26.6, 15.9, -2.8, -2.9; ; IR (Neat film, NaCl) 3439, 2924, 2854, 2282, 1758, 1656, 1428, 1373, 1291, 1266, 1248, 1214, 1164, 1108, 992, 937, 838, 821, 738 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{27}H_{35}O_5Si$ $[M+H]^+$: 467.2254, found 467.2265; $[\alpha]_D^{25.0}$ –17.9° (*c* 0.6, $CHCl_3$).

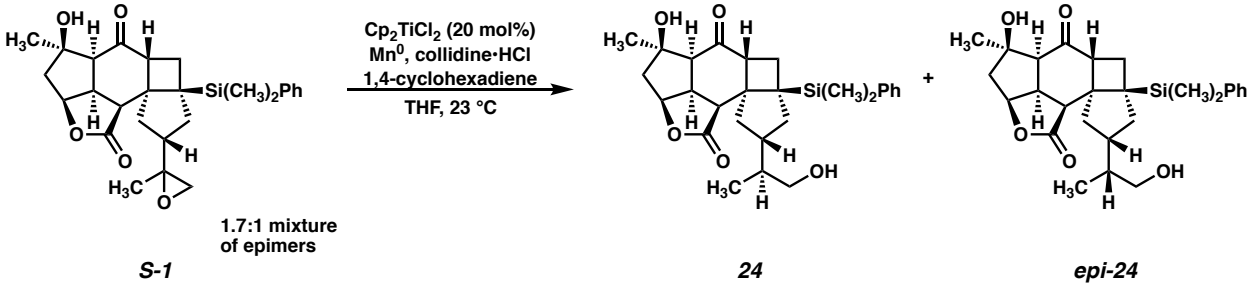


Cyclobutanes S-1 and *epi*-S-1: A mixture of vinyl silanes **23** and *epi*-**23** (870 mg, 1.86 mmol, 1.0 equiv) is divided into 11 portions (79 mg each). Each portion is charged into a 40 mL scintillation vial, with PhH (34 mL). Each vial is sparged with nitrogen for 5 min, and placed in a photoreactor equipped with Hitachi UVA bulbs (F8T5-BLB, ~350 nm). The reactions are stirred under 350 nm irradiation for 5 h, after which no starting material remains (as judged by TLC). The reactions are combined in a 1 L round bottom flask, and concentrated onto Celite. The resulting solid is loaded onto a column, and purified by flash chromatography (30%-40%-50%-60%-70%-80% EtOAc/Hexanes) to afford the title compounds (620 mg, 1.33 mmol, 71% yield) as a white solid. The products are isolated as a 1.7:1 mixture of diastereomers (judged by ^{1}H NMR), which were characterized separately.

*Note: The ^{1}H NMR spectra of these intermediates show broadened signals which were difficult to assign and integrate properly. Additionally, several signals were found to be missing from the ^{13}C NMR spectra. We attribute these observations to hindered rotation of the –Si(CH$_3$)$_2$Ph group about the highly congested cyclobutane ring. The NMR spectra are reported as observed, and the stereochemistry (and identity) of these products is assigned based upon the NMR and X-ray data obtained for **25** and epi-**25**.*

Diastereomer 1 (minor): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (s, 2H), 7.35 – 7.28 (m, 3H), 4.93 (s, 1H), 3.70 – 3.54 (m, 1H), 3.47 (s, 1H), 3.03 (d, *J* = 9.3 Hz, 1H), 2.70 – 2.30 (m, 4H), 1.93 (dd, *J* = 15.2, 4.8 Hz, 1H), 1.68 (s, 1H), 1.45 (d, *J* = 2.1 Hz, 3H), 1.34 – 1.17 (m, 4H), 0.56 (d, *J* = 18.1 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.8, 134.3, 128.5, 127.6, 82.1, 81.4, 60.3, 57.6, 52.3, 50.9, 49.0, 47.7, 47.6, 40.1, 38.9, 35.0, 27.5; IR (Neat film, NaCl) 3395, 2958, 1773, 1686, 1369, 1256, 1202, 1089, 1014, 815, 776, 732 cm^{-1}; HRMS (ES+) *m/z* calc'd for $C_{27}H_{35}O_5Si$ $[M+H]^+$: 467.2254, found 467.2280; $[\alpha]_D^{25.0}$ –41.1 ° (*c* 0.19, $CHCl_3$).

Diastereomer 2 (major): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.45 (m, 2H), 7.34 – 7.28 (m, 3H), 4.92 (s, 1H), 3.60 (td, *J* = 9.8, 6.2 Hz, 1H), 3.47 (s, 1H), 3.02 (d, *J* = 9.3 Hz, 1H), 2.56 (dd, *J* = 10.0, 5.3 Hz, 3H), 2.42 – 2.31 (m, 1H), 1.94 (dd, *J* = 15.1, 4.8 Hz, 1H), 1.67 (s, 2H), 1.45 (s, 3H), 1.25 (d, *J* = 1.7 Hz, 3H), 0.53 (s, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.8, 134.3, 128.5, 127.7, 82.1, 81.5, 60.3, 57.1, 53.9, 50.9, 49.0, 47.7, 40.7, 38.6, 29.8, 27.5; IR (Neat film, NaCl) 3388, 2960, 2929, 1773, 1686, 1552, 1426, 1368, 1248, 1203, 1178, 1107, 1088, 817, 724, 696 cm^{-1}; HRMS (ES+) *m/z* calc'd for $C_{27}H_{35}O_5Si$ $[M+H]^+$: 467.2254, found 467.1853; $[\alpha]_D^{25.0}$ –23.1 ° (*c* 0.19, $CHCl_3$).



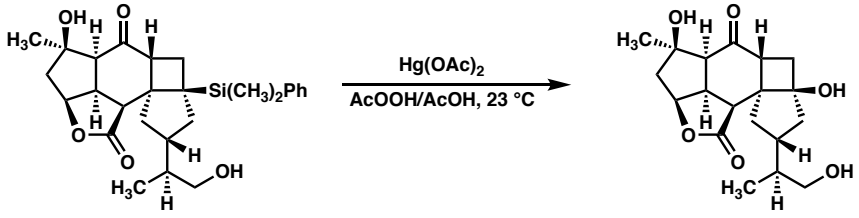
Diols 24 and *epi*-24: A 100 mL round bottom flask is charged with a mixture of epoxides **S-1** and *epi*-**S-1** (620 mg, 1.33 mmol, 1.0 equiv), Cp_2TiCl_2 (66 mg, 0.266 mmol, 0.20 equiv), Mn dust (80 mg, 1.46 mmol, 1.10 equiv) and collidine•HCl (262 mg, 1.66 mmol, 1.25 equiv) in THF (27 mL). To this red suspension is added 1,4-cyclohexadiene (567 µL, 599 mmol, 4.5 equiv) and the suspension gradually changes to a blue/grey color. The mixture is stirred at 23 °C for 1.5 h, after which the starting material is completely consumed, as judged by TLC. Celite is then added directly to the reaction mixture and the solvent is removed under reduced pressure. The resulting solid is loaded directly onto a flash column and purified by flash chromatography (60%-65%-70%-

75%-80%-90%-100% EtOAc/Hexanes) to afford **24** (385 mg, 0.781 mmol, 62% yield) and *epi*-**24** (224 mg, 0.478 mmol, 36% yield) as white solids.

*Note: The ^{1}H NMR spectra of these intermediates show broadened signals which were difficult to assign and integrate properly. Additionally, several signals were found to be missing from the ^{13}C NMR spectra. We attribute these observations to hindered rotation of the –Si(CH$_3$)$_2$Ph group about the highly congested cyclobutane ring. The NMR spectra are reported as observed, and the stereochemistry (and identity) of these products is assigned based upon the NMR and X-ray data obtained for **25** and epi-**25**.*

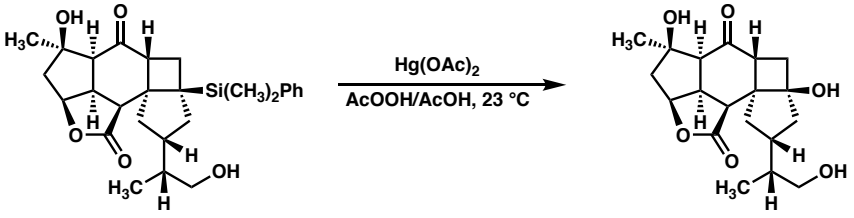
24: ^{1}H NMR (400 MHz, CD_3OD) δ 7.57 – 7.48 (m, 2H), 7.30 – 7.22 (m, 3H), 4.95 (s, 1H), 3.98 (s, 1H), 3.74 (tt, *J* = 10.1, 5.1 Hz, 1H), 3.64 (q, *J* = 10.2, 9.2 Hz, 1H), 3.52 – 3.38 (m, 1H), 3.30 – 3.15 (m, 1H), 2.76 – 1.38 (m, 11H), 1.34 (s, 3H), 1.10 – 0.83 (m, 3H), 0.52 (s, 4H); ^{13}C NMR (101 MHz, CD_3OD) δ 210.1, 168.5, 151.9, 135.3, 129.2, 128.4, 108.8, 84.4, 81.6, 81.6, 67.3, 65.6, 61.9, 52.5, 45.9, 41.7, 41.5, 27.3, 15.7; IR (Neat film, NaCl) 3380, 2958, 2924, 2869, 1770, 1694, 1360, 1254, 1204, 1090, 1416, 828, 736, 730, 702 cm^{-1}; HRMS (ES+) *m/z* calc'd for $C_{27}H_{37}O_5Si$ $[M+H]^+$: 469.2410, found 469.2437; $[\alpha]_D^{25.0}$ –37.0 ° (*c* 0.24, $CHCl_3$).

epi-**24**: ^{1}H NMR (400 MHz, CD_3OD) δ 7.58 – 7.46 (m, 2H), 7.27 (t, *J* = 3.2 Hz, 3H), 4.94 (t, *J* = 5.7 Hz, 1H), 3.81 – 3.69 (m, 1H), 3.69 – 3.58 (m, 1H), 3.48 (q, *J* = 7.1, 4.5 Hz, 1H), 3.33 (d, *J* = 13.8 Hz, 4H), 3.25 – 3.11 (m, 1H), 2.68 – 1.39 (m, 11H), 1.34 (s, 3H), 1.10 – 0.74 (m, 4H), 0.52 (d, *J* = 11.9 Hz, 5H); ^{13}C NMR (100 MHz, CD_3OD) δ 210.1, 178.1, 135.3, 129.2, 128.4, 84.3, 81.6, 67.4, 61.9, 52.5, 47.8, 47.1, 47.1, 46.2, 44.1, 42.4, 41.8, 40.0, 35.9, 27.3, 15.6, -2.1, -4.9; IR (Neat film, NaCl) 3378, 2954, 2937, 2868, 2353, 1771, 1696, 1558, 1364, 1258, 1245, 1086, 827 cm^{-1}; HRMS (ES+) *m/z* calc'd for $C_{27}H_{37}O_5Si$ $[M+H]^+$: 469.2410, found 469.2440; $[\alpha]_D^{25.0}$ –39.9 ° (*c* 0.90, $CHCl_3$).



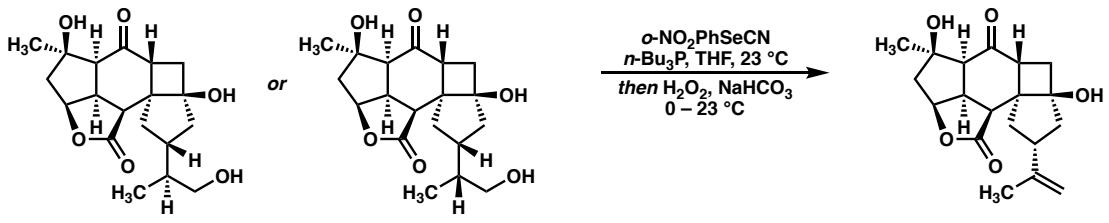
24 ***25***

Triol 25: A 20 mL scintillation vial is charged with **24** (80 mg, 0.171 mmol, 1.0 equiv) and AcOOH (30% in aqueous AcOH, 3.4 mL). To this solution is added $Hg(OAc)_2$ (100 mg, 0.341 mmol, 2.0 equiv) in a single portion. The reaction is stirred 45 min at 23 °C, after which no **24** remains (as judged by LCMS). The reaction mixture is diluted with EtOAc (10 mL) and pipetted over an ice-cold mixture of sat. aq. $Na_2S_2O_3$ and sat. aq. $NaHCO_2$ (1:4). This aqueous solution is then extracted with EtOAc (3x) then $CHCl_3$/*i*-PrOH (3:1) (2x). The organic extracts are combined and dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford a crude solid which is purified by flash chromatography (80%-100% EtOAc/Hexanes) to afford the title compound (33 mg, 0.942 mmol, 55% yield) as a white solid. X-ray quality crystals were obtained by slow cooling from EtOH/CH_2Cl_2/Hexanes: ^{1}H NMR (400 MHz, CD_3OD) δ 5.16 (dd, *J* = 6.2, 4.7 Hz, 1H), 3.88 (dd, *J* = 9.8, 7.7 Hz, 1H), 3.72 (ddd, *J* = 10.6, 9.3, 6.3 Hz, 1H), 3.55 – 3.47 (m, 2H), 3.37 – 3.32 (m, 1H), 2.58 (d, *J* = 10.6 Hz, 1H), 2.35 (d, *J* = 15.0 Hz, 1H), 2.23 (dd, *J* = 11.9, 9.7 Hz, 1H), 2.19 – 1.98 (m, 3H), 1.95 (dd, *J* = 15.1, 4.9 Hz, 1H), 1.85 (ddd, *J* = 12.9, 6.1, 2.0 Hz, 1H), 1.70 (dd, *J* = 13.1, 9.9 Hz, 1H), 1.54 – 1.41 (m, 2H), 1.35 (s, 3H), 0.93 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ 209.4, 181.7, 89.3, 88.2, 81.6, 67.1, 62.1, 59.0, 51.8, 51.3, 47.8, 47.3, 45.8, 41.8, 41.3, 41.2, 40.7, 27.3, 15.3; IR (Neat Film NaCl) 3308, 2936, 1694, 1371, 1217, 1184, 1120, 1016 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{19}H_{27}O_6$ $[M+H]^+$: 351.1802, found 315.1790; $[\alpha]_D^{25.0}$ –61.1° (*c* 0.5, MeOH).



epi-24 ***epi-25***

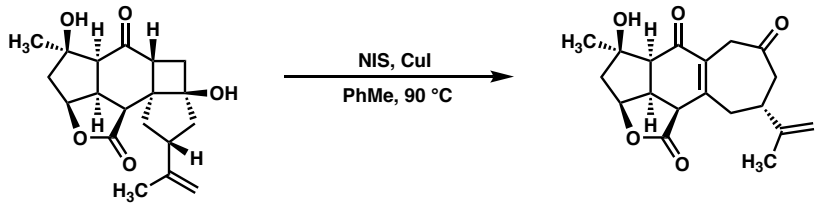
Triol *epi*-25: A 20 mL scintillation vial is charged with *epi*-**24** (80 mg, 0.171 mmol, 1.0 equiv) and AcOOH (30% in aqueous AcOH, 3.4 mL). To this solution is added $Hg(OAc)_2$ (100 mg, 0.341 mmol, 2.0 equiv) in a single portion. The reaction is stirred 45 min at 23 °C, after which no *epi*-**24** remains (as judged by LCMS). The reaction mixture is diluted with EtOAc (10 mL) and pipetted over an ice-cold mixture of sat. aq. $Na_sS_sO_3$ and sat. aq. $NaHCO_2$ (1:4). This aqueous solution is then extracted with EtOAc (3x) then $CHCl_3$/*i*-PrOH (3:1) (2x). The organic extracts are combined and dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford a crude solid which is purified by flash chromatography (80%-100% EtOAc/Hexanes) to afford the title compound (37 mg, 0.0.106 mmol, 62% yield) as a white solid. X-ray quality crystals were obtained by layer diffusion of Hexanes into CH_2Cl_2/EtOH: ^{1}H NMR (400 MHz, CD_3OD) δ 5.16 (dd, *J* = 6.2, 4.7 Hz, 1H), 3.88 (dd, *J* = 9.8, 7.7 Hz, 1H), 3.79 – 3.64 (m, 1H), 3.57 – 3.45 (m, 2H), 3.40 – 3.34 (m, 1H), 2.57 (d, *J* = 10.6 Hz, 1H), 2.35 (d, *J* = 15.1 Hz, 1H), 2.28 – 2.11 (m, 2H), 2.07 (dd, *J* = 11.9, 7.7 Hz, 1H), 2.02 – 1.90 (m, 2H), 1.87 (ddd, *J* = 13.0, 6.1, 2.1 Hz, 1H), 1.68 (dd, *J* = 13.1, 10.2 Hz, 1H), 1.57 – 1.43 (m, 2H), 1.35 (s, 3H), 0.94 (d, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ 209.4, 181.7, 89.0, 88.2, 81.6, 66.9, 62.1, 59.3, 51.8, 51.3, 47.8, 47.3, 45.1, 41.7, 41.5, 41.4, 40.7, 27.3, 15.4; IR (Neat Film NaCl) 3464, 3292, 2953, 1720, 1693, 1372, 1190, 1104 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{19}H_{27}O_6$ $[M+H]^+$: 351.1802, found 315.1790; $[\alpha]_D^{25.0}$ –42.2° (*c* 0.5, MeOH).



25 ***epi-25*** ***4a***

Note: *The Grieco dehydration to cyclobutanol* **4a** *was performed using both* **25** *and epi-***25***, with both substrates providing similar yields of product. A representative procedure for this reaction is provided below:*

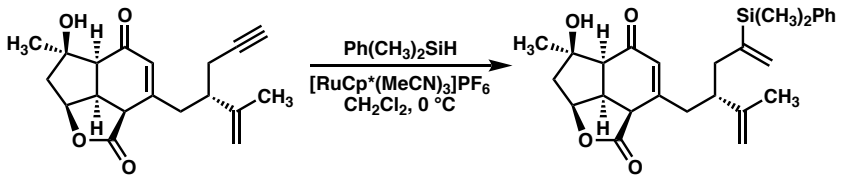
Cyclobutanol 4a: In a nitrogen filled glovebox a one dram vial is charged with **25** (8.0 mg, 0.0228 mmol, 1.0 equiv) and *o*-NO_2PhSeCN (15.5 mg, 0.0685 mmol, 3.0 equiv) in THF (450 μL). To this orange solution is added *n*-Bu_3P (17 μL, 0.0685 mmol, 3.0 equiv) dropwise via syringe, at which point the reaction mixture becomes deep red/brown in color. This solution is allowed to stir in the glovebox at 23 °C for 7 h, at which point **25** has been completely consumed, as judged by LCMS. The vial is then removed from the glovebox and cooled to 0 °C after which H_2O_2 (30% w/w, 80 μL) is cautiously added dropwise. This orange solution is then stirred while gradually warming to 23 °C over c.a. 2 h and then stirred at 23 °C an additional 18 h. The reaction is then loaded directly onto a column and purified by flash chromatography (30%-40%-50% EtOAc/Hexanes) to afford the title compound (6.0 mg, 0.0181 mmol, 79% yield) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.08 (s, 1H), 5.14 (dd, *J* = 6.1, 4.6 Hz, 1H), 4.75 – 4.71 (m, 1H), 4.71 – 4.68 (m, 1H), 3.83 (dd, *J* = 9.6, 8.0 Hz, 1H), 3.66 – 3.56 (m, 1H), 3.36 (d, *J* = 9.1 Hz, 1H), 2.79 (ddd, *J* = 15.9, 13.0, 8.0 Hz, 1H), 2.60 (d, *J* = 10.7 Hz, 1H), 2.43 (d, *J* = 15.4 Hz, 1H), 2.34 (dd, *J* = 12.1, 9.6 Hz, 1H), 2.24 (dd, *J* = 12.1, 8.0 Hz, 1H), 2.14 (ddd, *J* = 13.2, 9.8, 2.2 Hz, 1H), 1.96 (dd, *J* = 15.3, 4.8 Hz, 1H), 1.90 – 1.78 (m, 2H), 1.74 – 1.67 (m, 5H), 1.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.8, 179.2, 146.1, 109.9, 88.0, 86.0, 81.3, 60.6, 57.8, 50.3, 50.3, 47.7, 46.3, 45.3, 44.7, 40.8, 40.5, 27.6, 21.1; IR (Neat Film NaCl) 3346, 2936, 1726, 1710, 1598, 1366, 1325, 1218, 1194, 1123, 1088, 1011, 850, 822; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{19}H_{25}O_5$ $[M+H]^+$: 333.1697, found 333.1694; $[\alpha]_D^{25.0}$ –31.1° (*c* 0.4, $CHCl_3$).



4 ***Scabrolide A (1)***

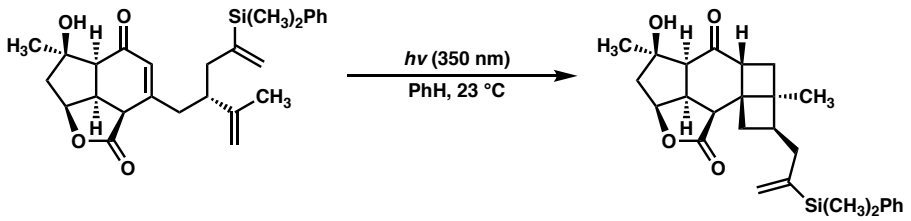
Scabrolide A: In a nitrogen-filled glovebox, a 1 dram vial is charged with cyclobutanol **4a** (5.0 mg, 0.0151 mmol, 1.0 equiv), CuI (22.0 mg, 0.117 mmol, 7.8 equiv) and NIS (6.7 mg, 0.0300 mmol, 2.0 equiv) in PhMe (1.5 mL). The vial is stirred at 23 °C for 5 min, and then transferred to a preheated, 90 °C aluminum block. The reaction is stirred at 90 °C for 1 h. At this point, an additional portion of NIS (3.3 mg, 0.0150 mmol, 1.0 equiv) is added, and the reaction is stirred an additional 20 min at 90 °C. The mixture is then cooled to 23 °C and filtered through a pad of Celite, washing with EtOAc. This solution is concentrated to a red film, which is directly purified by reverse-phase (C18) preperative HPLC ($MeCN/H_2O$, 5.0 mL/min, monitor wavelength = 260 nm, 30% MeCN ramp to 45% MeCN over 6 min) to afford scabrolide A (3.0 mg, 0.00909 mmol, 61% yield) as a white solid. X-ray quality crystals were obtained by layer-diffusion of hexanes into a CH_2Cl_2 solution of **1**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.11 (dd, *J* = 7.1, 5.4 Hz, 1H), 4.87 – 4.84 (m, 1H), 4.85 – 4.82 (m, 1H), 3.70 (dd, *J* = 45.1, 17.2 Hz, 1H), 3.61 (ddd, *J* = 11.1, 10.0, 7.2 Hz, 1H), 3.51 (d, *J* = 11.3 Hz, 1H), 3.43 (dd, *J* = 17.3, 1.6 Hz, 1H), 3.18 – 3.03 (m, 1H), 2.97 – 2.80 (m, 2H), 2.68 – 2.55 (m, 2H), 2.60 (d, *J* = 10.1 Hz, 1H), 2.30 (d, *J* = 15.0 Hz, 1H), 1.93 (dd, *J* = 15.0, 5.6 Hz, 1H), 1.83 (t, *J* = 1.0 Hz, 3H), 1.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.2, 193.1, 173.7, 151.8, 147.2, 132.9, 111.0, 83.2, 82.3, 54.6, 47.6, 46.4, 44.8, 41.7, 41.1, 39.7, 37.3, 26.3, 21.5; IR (Neat Film NaCl) 3366, 2965, 2930, 2858, 1765, 1696, 1636, 1445, 1374, 1358, 1275, 1260, 1219, 1182, 1162, 1120, 1090, 1012, 899, 690 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{19}H_{23}O_5$ $[M+H]^+$: 331.1540, found 331. 1539; $[\alpha]_D^{25.0}$ –210.7 ° (*c* 0.39, $CHCl_3$).

Off-route compounds:



5 ***20***

Vinyl Silane 20: A 1 dram vial is charged with enone **5** (7.0 mg, 0.0223 mmol, 1.0 equiv) in CH_2Cl_2 (400 μL). Phenyldimethylsilane (4 μL, 0.0267 mmol, 1.2 equiv) is added, and the mixture is cooled to 0 °C. [RuCp*$(MeCN)_3$]PF_6 (10 mg/mL stock solution 56 μL, 0.00112 mmol, 0.05 equiv) is added dropwise. Following the addition, the reaction is stirred 5 min at 0 °C, after which alkyne **5** is no longer detectable by TLC. The reaction mixture is loaded directly onto a preparatory TLC plate and purified by preparatory TLC (80% EtOAc/Hexanes) to afford the title compounds (9.0 mg, 0.0200 mmol, 90% yield) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.46 (m, 2H), 7.39 – 7.31 (m, 3H), 5.80 (t, *J* = 1.4 Hz, 1H), 5.70 – 5.64 (m, 1H), 5.54 (d, *J* = 2.8 Hz, 1H), 5.04 (dd, *J* = 7.1, 5.3 Hz, 1H), 4.66 – 4.59 (m, 1H), 4.40 – 4.32 (m, 1H), 3.32 (td, *J* = 10.6, 7.1 Hz, 1H), 2.94 – 2.74 (m, 2H), 2.50 – 2.24 (m, 5H), 2.22 – 2.09 (m, 1H), 1.85 (dd, *J* = 14.9, 5.5 Hz, 1H), 1.52 (s, 3H), 1.47 (s, 3H), 0.41 (s, 3H), 0.39 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.0, 173.4, 157.3, 147.7, 146.3, 138.9, 134.2, 129.0, 128.6, 128.6, 128.0, 112.7, 82.6, 82.3, 55.1, 47.3, 43.7, 42.1, 41.9, 40.5, 38.3, 26.5, 18.0, -2.7, -3.2. ; IR (Neat Film NaCl) 3434, 3049, 2962, 1762, 1654, 1427, 1376, 1290, 1250, 1216, 1173, 1160, 1109, 1030, 992, 933, 891, 834, 817, 776, 736, 703 cm^{-1}; HRMS (MM: ES+) *m/z* calc'd for $C_{27}H_{35}O_4Si$ $[M+H]^+$: 451.2305, found 451.2314; $[\alpha]_D^{25.0}$ –106.1 ° (*c* 0.60, $CHCl_3$).



20 ***21***

Cyclobutane 21: A 1 dram vial is charged with vinyl silane **20** (22 mg, 0.0488 mmol, 1.0 equiv) in PhH (5.0 mL). The solution is sparged with N_2 for 5 min, and placed in a photoreactor equipped with Hitachi UVA bulbs (F8T5-BLB, ~350 nm). The reaction is stirred under 350 nm irradiation for 10 h, after which no starting material remains (as judged by TLC). An ^{1}HNMR spectrum of the crude product shows a mixture with **21** as the major constituent. The crude white solid is purified by flash chromatography (50% EtOAc/Hexanes), followed by normal-phase (SiO_2) preparative HPLC (EtOAc/Hexanes, 7.0 mL/min, monitoring wavelength = 254 nm, isocratic– 50% EtOAc/Hexanes, 10 min) then reverse-phase (C18) preparative HPLC (MeCN/H_2O, 9.0 mL/min, monitoring wavelength = 260 nm, isocratic– 70% MeCN/H_2O, 10 min) to afford pure **21** (5.0 mg, 0.0111 mmol, 23 % yield). X-ray quality crystals are grown by slow cooling from *i*-PrOH: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.46 (m, 2H), 7.38 – 7.32 (m, 3H), 5.68 – 5.61 (m, 1H), 5.40 (d, *J* = 2.8 Hz, 1H), 4.95 (ddd, *J* = 7.0, 5.6, 1.6 Hz, 1H), 3.46 (td, *J* = 10.2, 6.7 Hz, 1H), 3.09 – 2.93 (m, 1H), 2.89 – 2.78 (m, 2H), 2.77 – 2.61 (m, 2H), 2.33 – 2.14 (m, 4H), 1.98 (dd, *J* = 14.8, 5.6 Hz, 1H), 1.94 – 1.85 (m, 1H), 1.75 (dd, *J* = 13.1, 4.3 Hz, 1H), 1.41 (s, 3H), 1.00 (s, 3H), 0.37 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.1, 175.7, 148.1, 138.2, 134.1, 129.2, 127.9, 126.9, 82.0, 81.5, 55.1, 49.2, 46.6, 46.6, 44.5, 43.5, 38.7, 38.6, 36.1, 34.1, 31.0, 27.6, 21.7, -2.8, -2.9; IR (Neat Film NaCl) 3453, 2934, 2858, 1759, 1689, 1428, 1375, 1248, 1206, 1106, 1012, 938, 858, 833, 818, 703 cm^{-1}; HRMS (MM: ES+) *m/z* calc'd for $C_{27}H_{35}O_4Si$ $[M+H]^+$: 451.2305, found 451.2321; $[\alpha]_D^{25.0}$ –113.4 ° (*c* 0.12, $CHCl_3$).

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Comparison of ^{1}H NMR Data

Synthetic scabrolide A	Isolated scabrolide A (Sheu, 2002)	Isolated scabrolide A (Liang, Guo, 2020)
400 MHz, $CDCl_3$	*400 MHz, $CDCl_3$*	*400 MHz, $CDCl_3$*
5.11 (dd, *J* = 5.4, 7.1)	5.11 (t, *J* = 6.4)	5.11 (dd, *J* = 5.6, 7.0)
4.86 (m)	4.85 (s)	4.85 (s)
4.84 (m)	4.83 (s)	4.83 (s)
3.70 (d, *J* = 17.2)	3.70 (d, *J* = 17.2)	3.70 (d, *J* = 17.2)
3.61 (ddd, *J* = 7.2, 10.0, 11.1)	3.62 (dd, *J* = 6.4, 11.2)	3.62 (dd, *J* = 6.4, 11.2)
3.51 (d, *J* = 11.3)	3.51 (d, *J* = 11.2)	3.51 (d, *J* = 11.2)
3.43 (dd, *J* = 1.6, 17.3)	3.42 (d, *J* = 17.2)	3.42 (d, *J* = 17.2)
3.09 (m)	3.07 (q, *J* = 6.4)	3.07 (m)
2.88 (m, 2H)	2.88 (m), 2.88 (m)	2.86 (m, 2H)
2.62 (m, 2H)	2.63 (m, 2H)	2.63 (m, 2H)
2.60 (d, *J* = 10.1)	2.62 (d, *J* = 10.0)	2.62 (d, *J* = 10.0)
2.30 (d, *J* = 15.0)	2.30 (d, *J* = 15.2)	2.30 (d, *J* = 15.2)
1.93 (dd, *J* = 5.6, 15.0)	1.92 (dd, *J* = 5.6, 15.2)	1.92 (dd, *J* = 5.6, 15.2)
1.83 (s, 3h)	1.82 (s, 3H)	1.82 (s, 3H)

Table S-1: Comparison of ^{1}H NMR data of natural and synthetic scabrolide A.

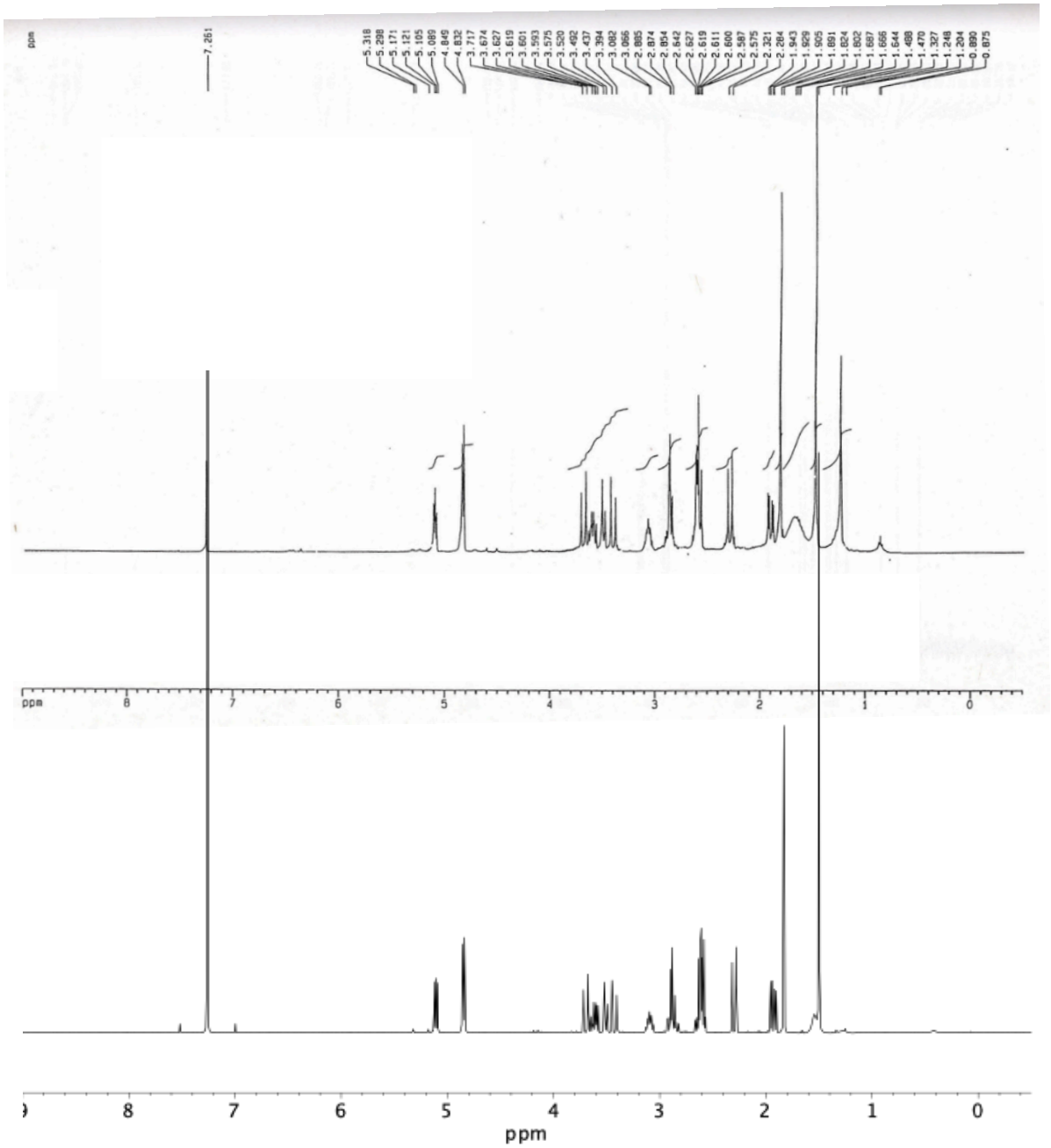


Figure S-1: overlaid ^{1}H NMR spectra of natural scabrolide A (top) and synthetic scabrolide A (bottom).

Comparison of ^{13}C NMR Data

Synthetic scabrolide A	Isolated scabrolide A (Sheu)	Isolated Scabrolide A (Liang, Guo)
100 MHz, $CDCl_3$	*100 MHz, $CDCl_3$*	*100 MHz, $CDCl_3$*
208.2	208.3	208.2
193.1	193.1	193.2
173.7	173.7	173.7
151.8	151.7	151.8
147.2	147.1	147.3
132.9	132.7	133.0
111.0	110.8	111.0
83.2	82.9	83.1
82.3	82.2	82.3
54.6	54.5	54.6
47.6	47.4	47.6
46.4	46.3	46.5
44.8	44.6	44.8
41.7	41.6	41.7
41.1	40.9	41.1
39.7	39.5	39.7
37.3	37.2	37.4
26.3	26.1	26.3
21.5	21.3	21.5

Table S-2: Comparison of ^{13}C NMR data for natural and synthetic scabrolide A.

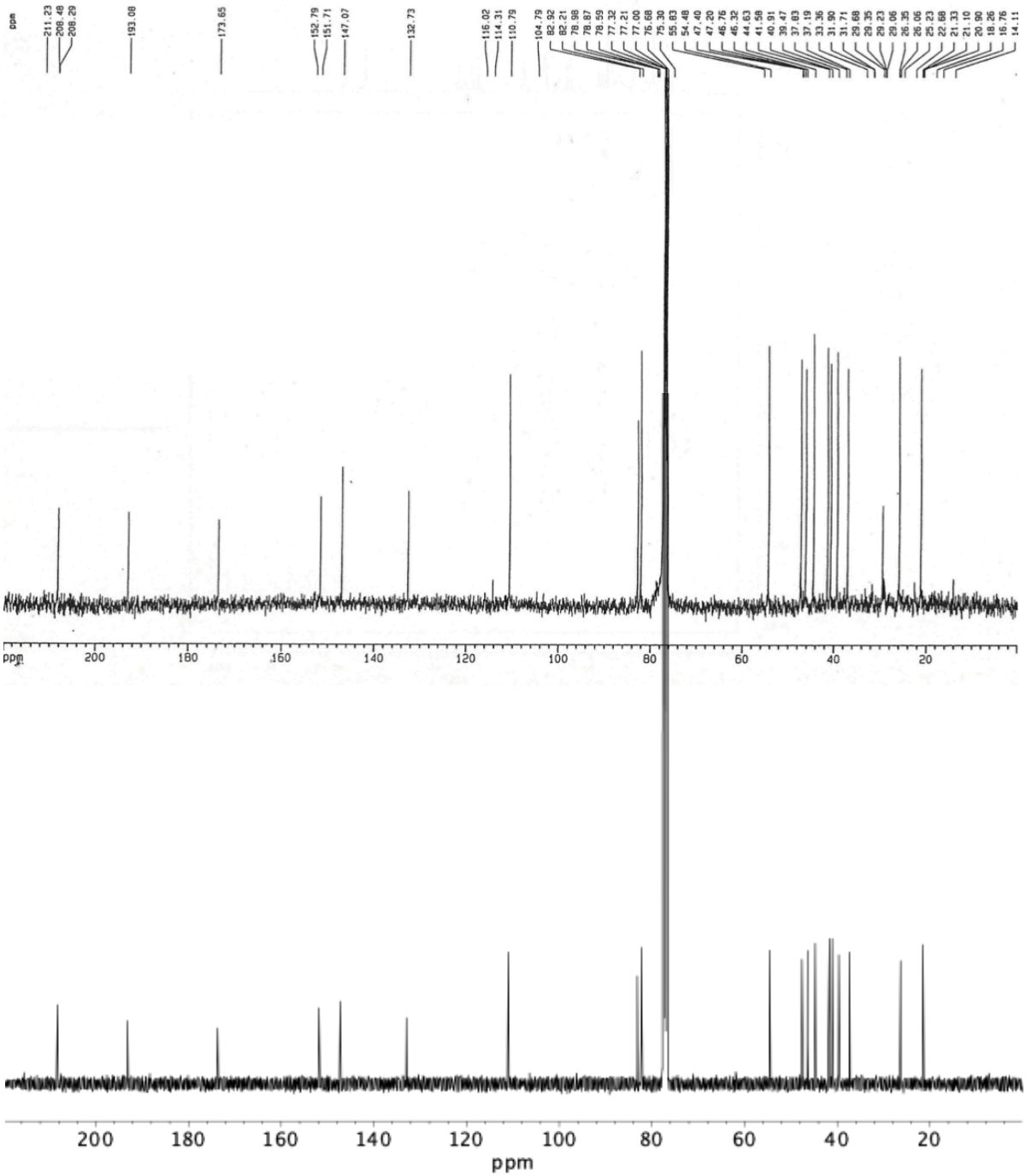
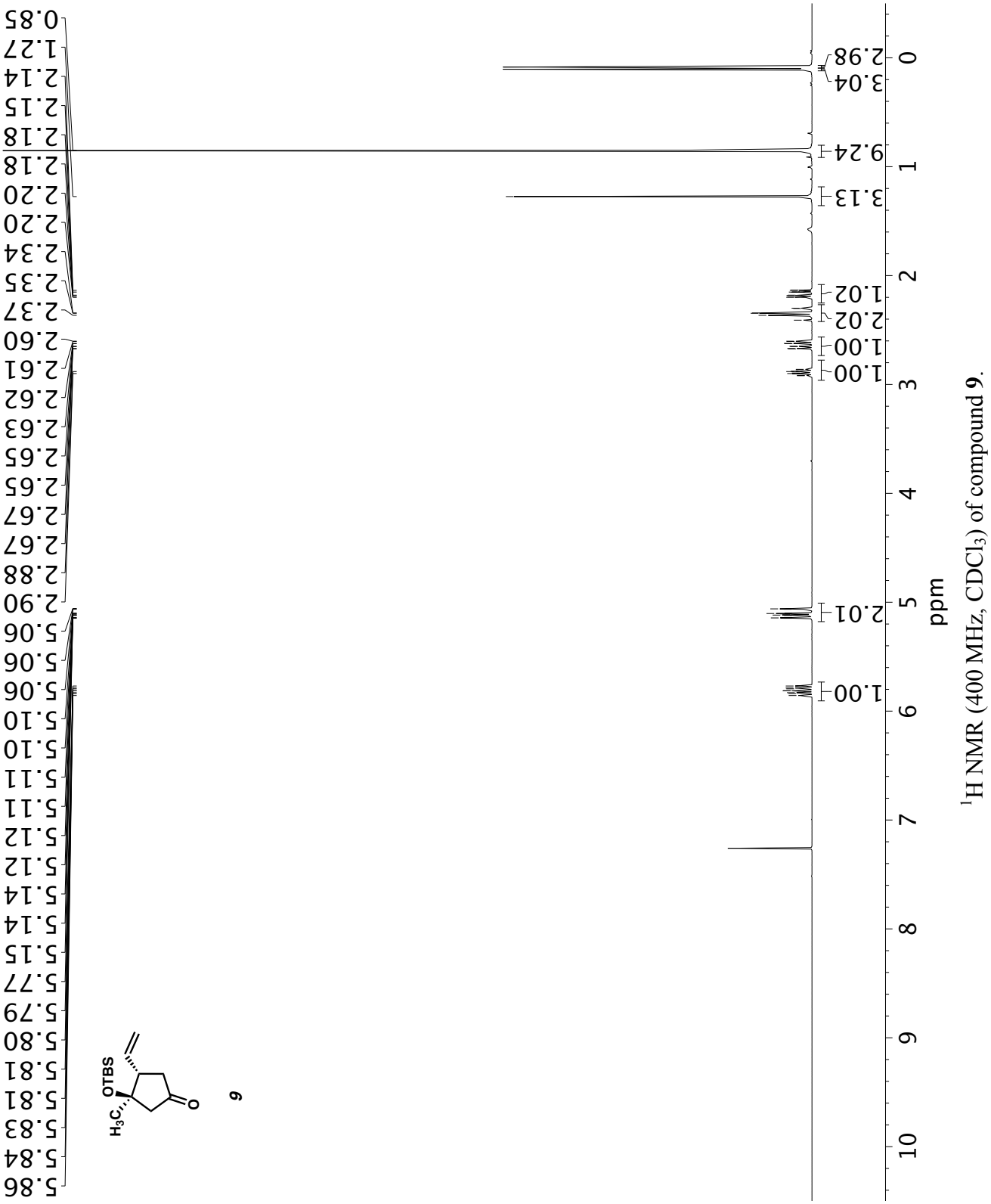
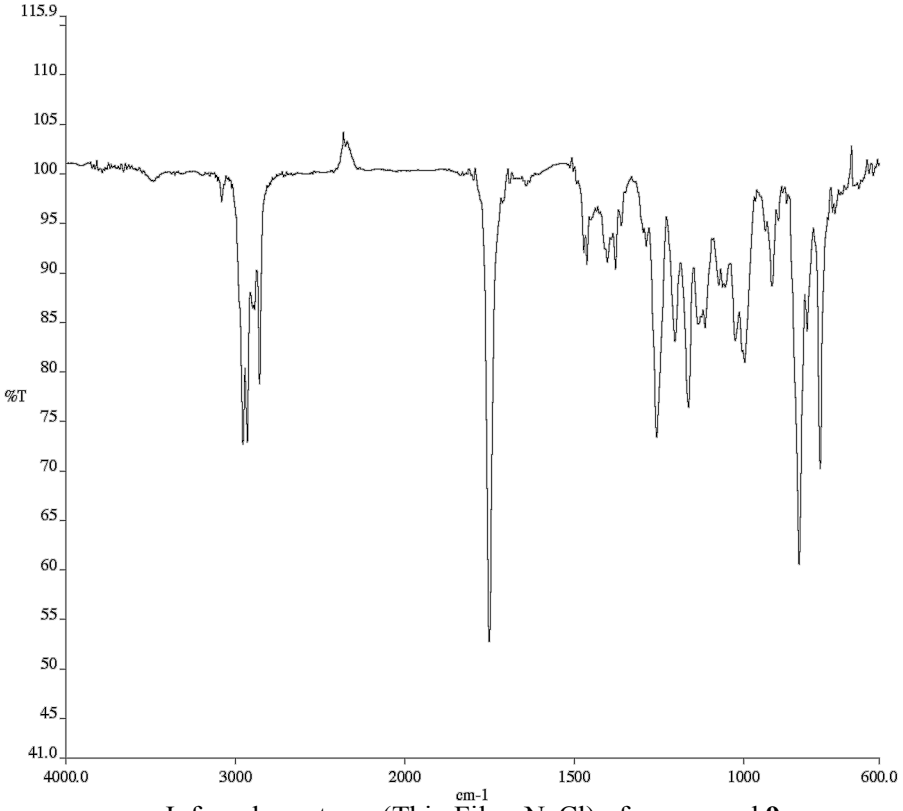


Figure S-2: Overlaid ^{13}C NMR spectra of isolated scabrolide A (top) and synthetic scabrolide A (bottom).

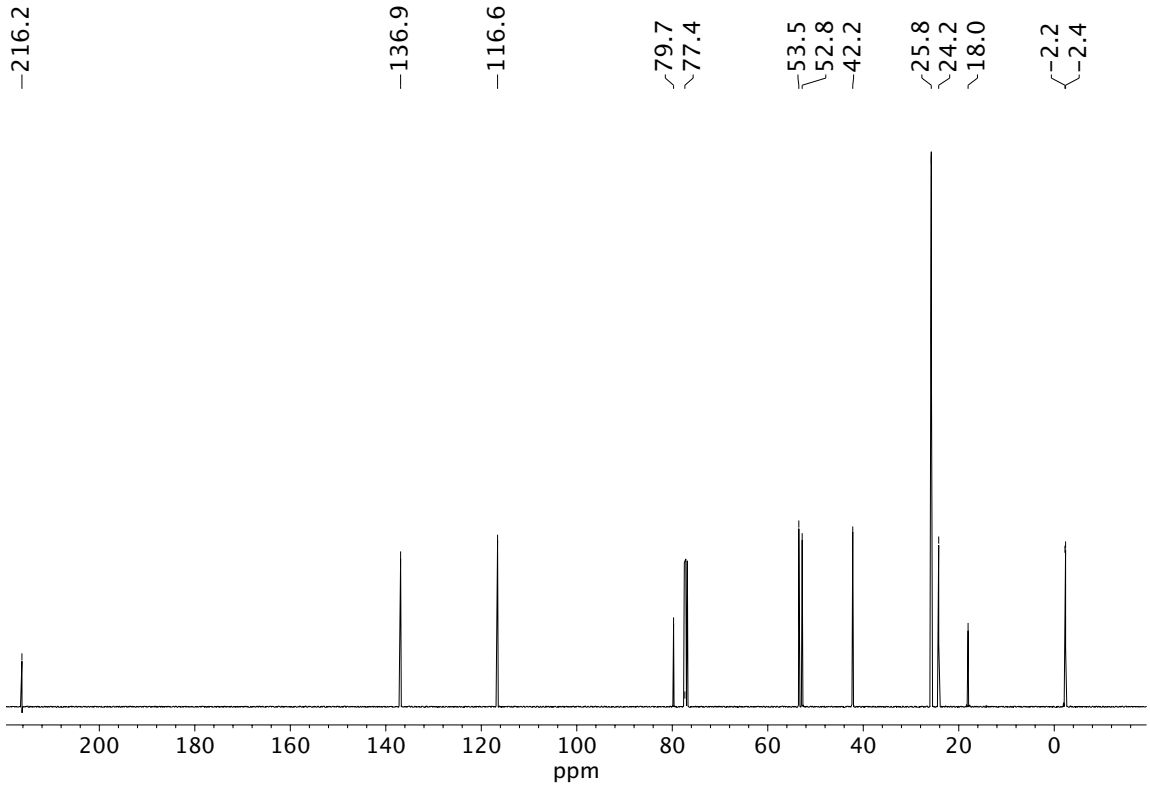
NMR and IR Spectra of New Compounds



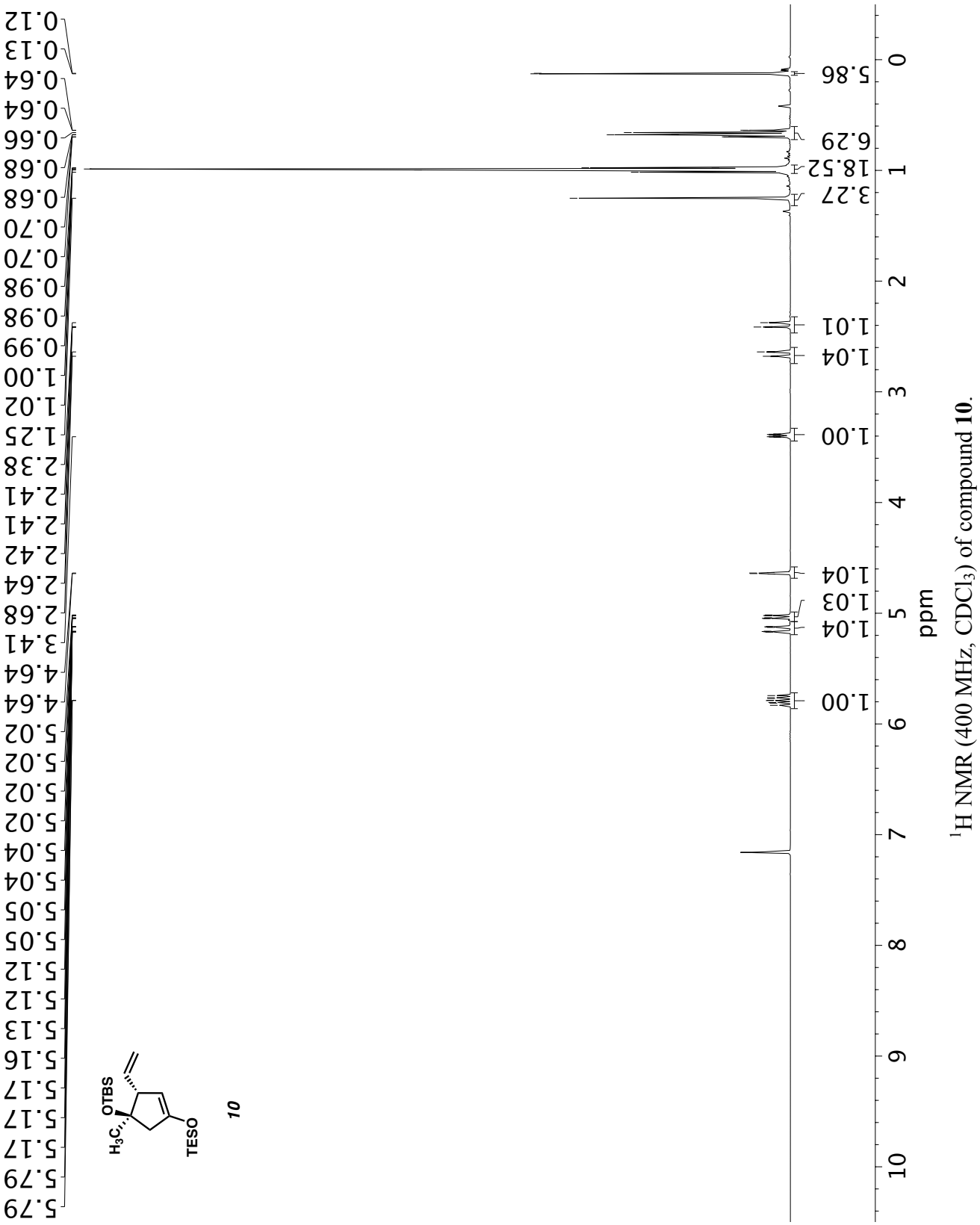
^{1}H NMR (400 MHz, $CDCl_3$) of compound **9**.



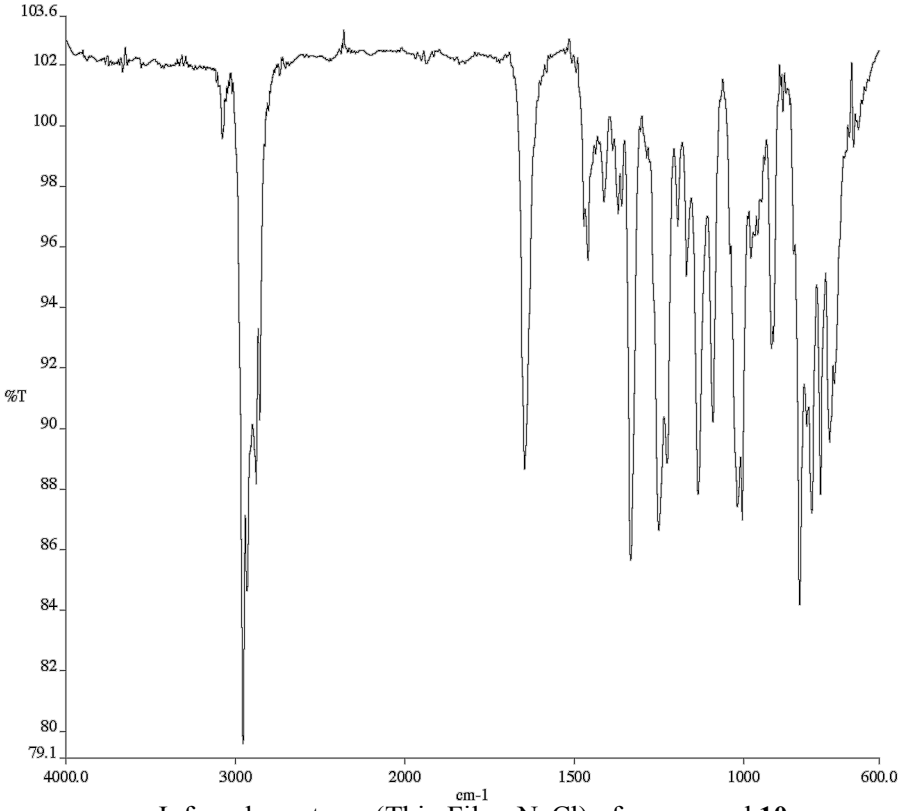
Infrared spectrum (Thin Film, NaCl) of compound **9**.



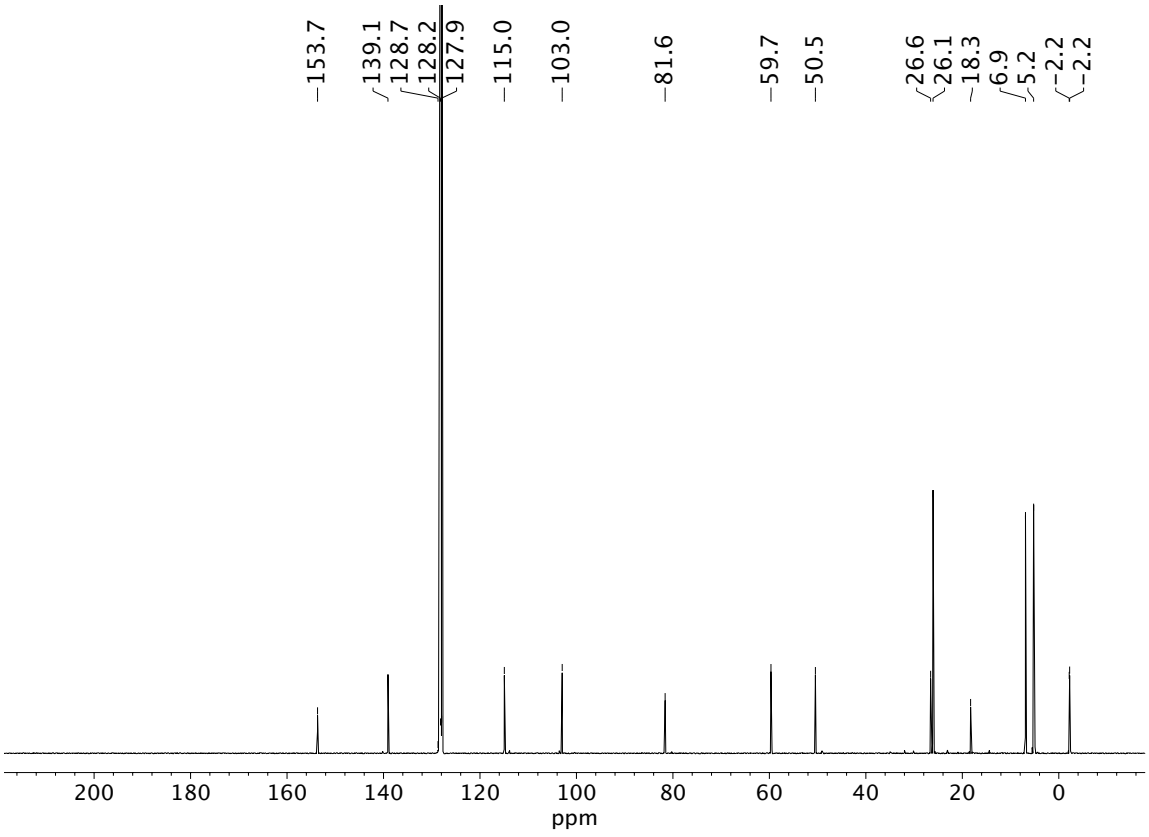
^{13}C NMR (100 MHz, $CDCl_3$) of compound **9**.



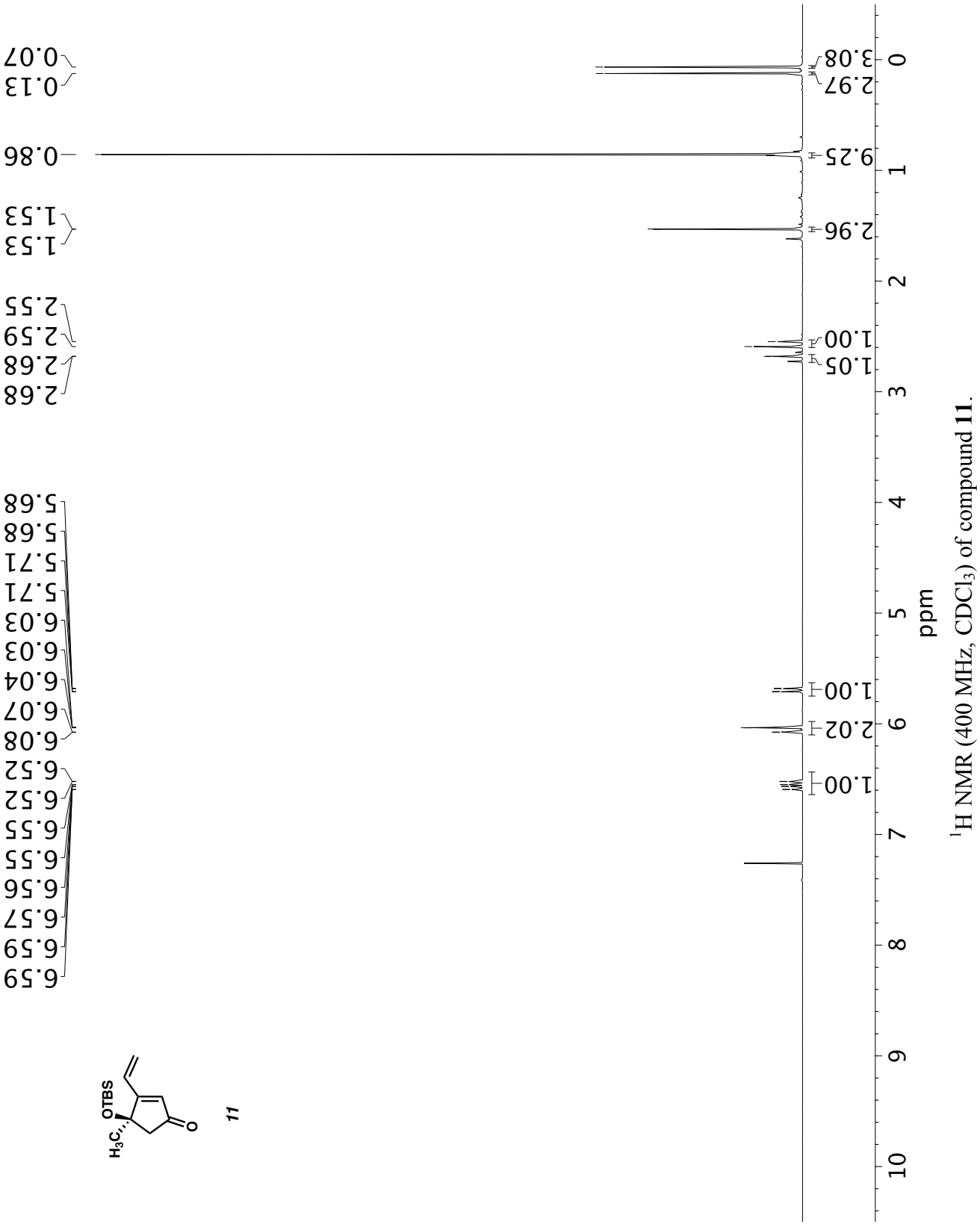
^{1}H NMR (400 MHz, $CDCl_3$) of compound **10**.



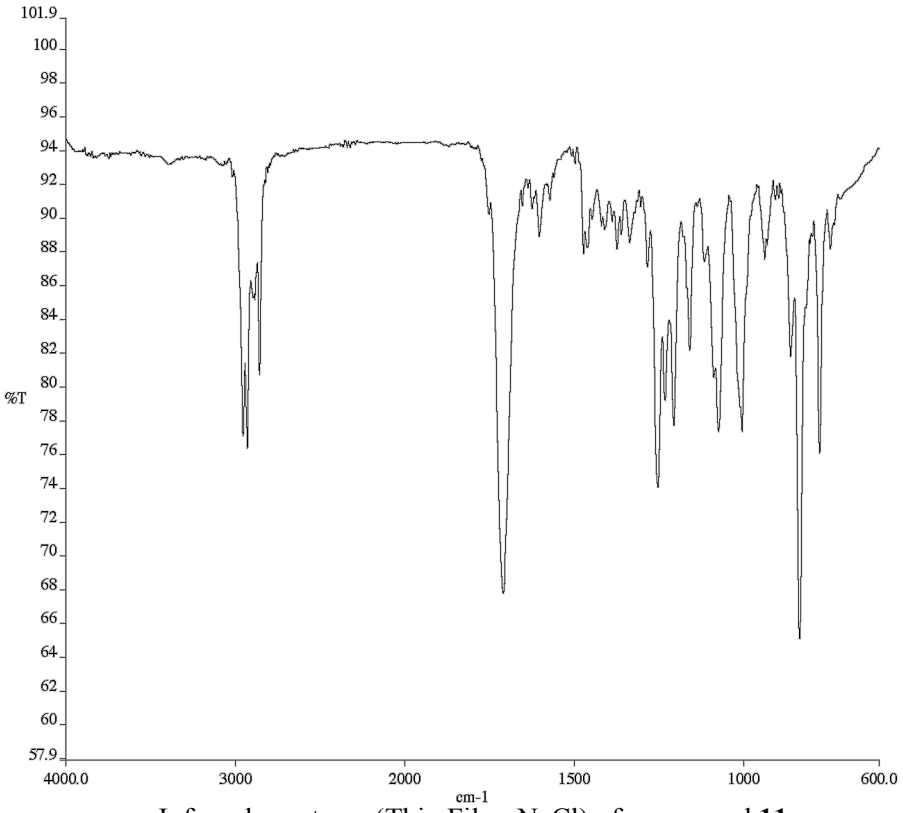
Infrared spectrum (Thin Film, NaCl) of compound **10**.



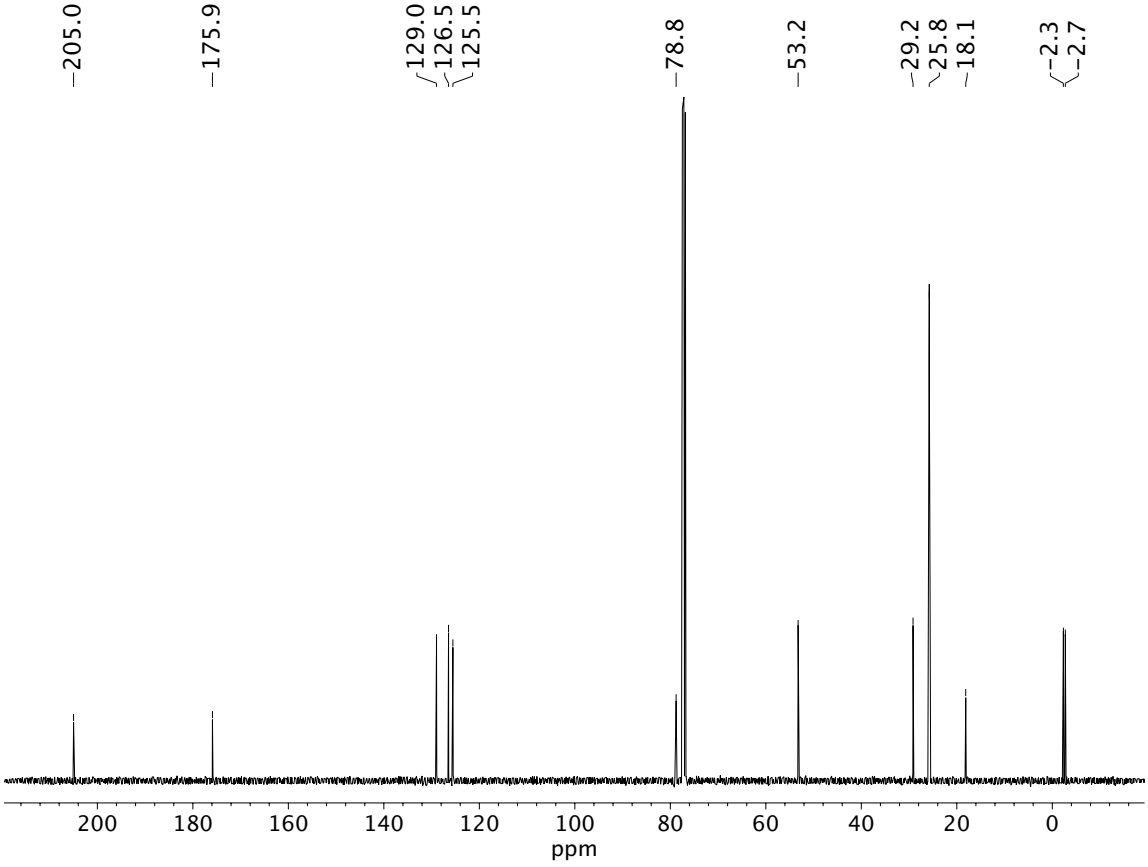
^{13}C NMR (100 MHz, $CDCl_3$) of compound **10**.



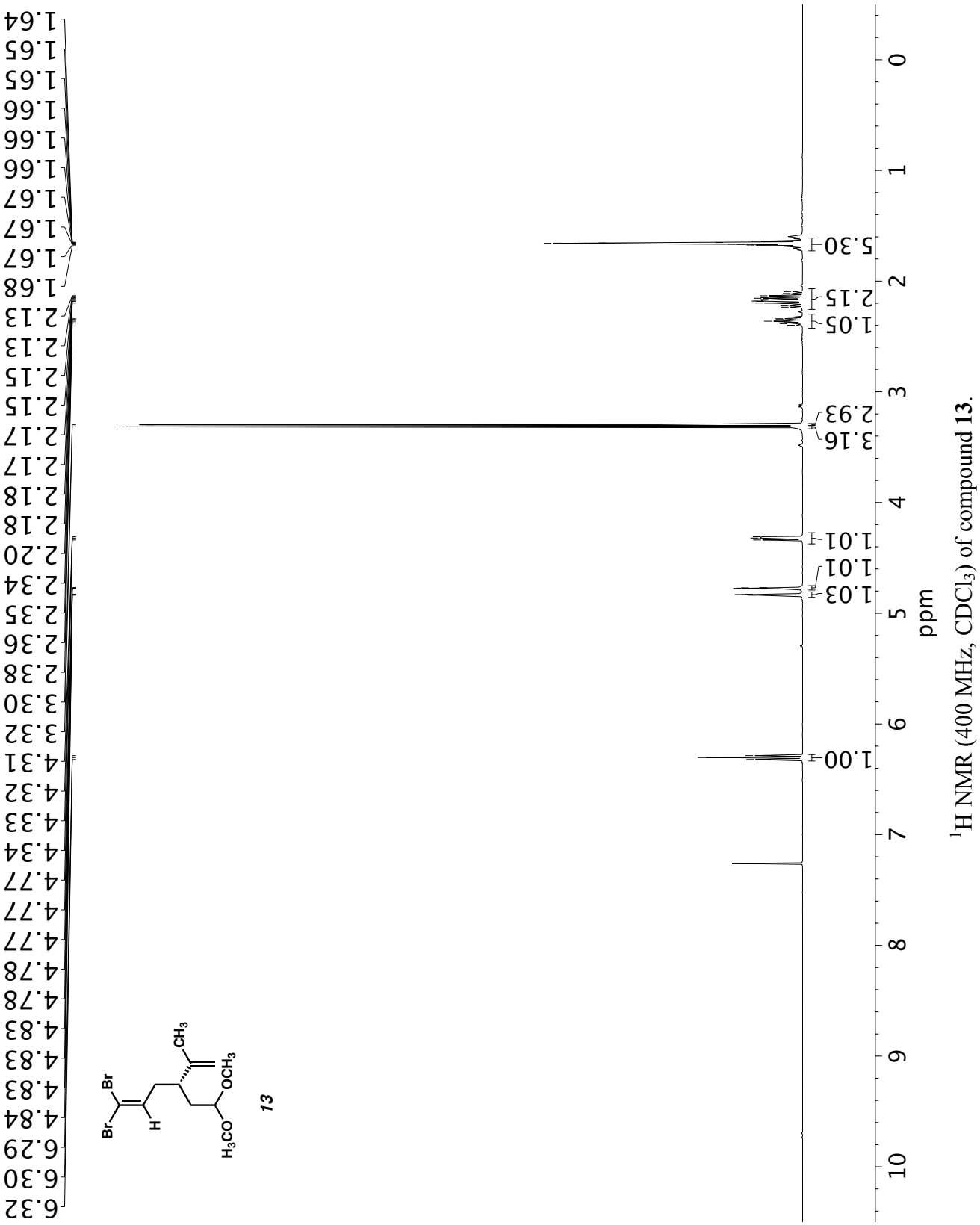
^{1}H NMR (400 MHz, $CDCl_3$) of compound **11**.



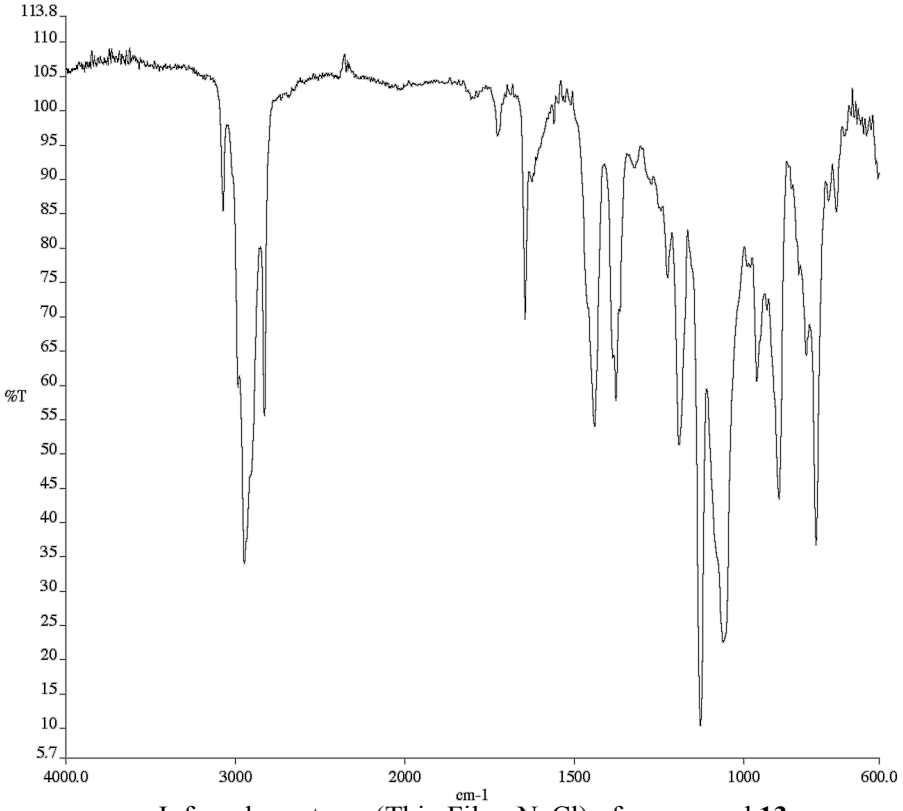
Infrared spectrum (Thin Film, NaCl) of compound **11**.



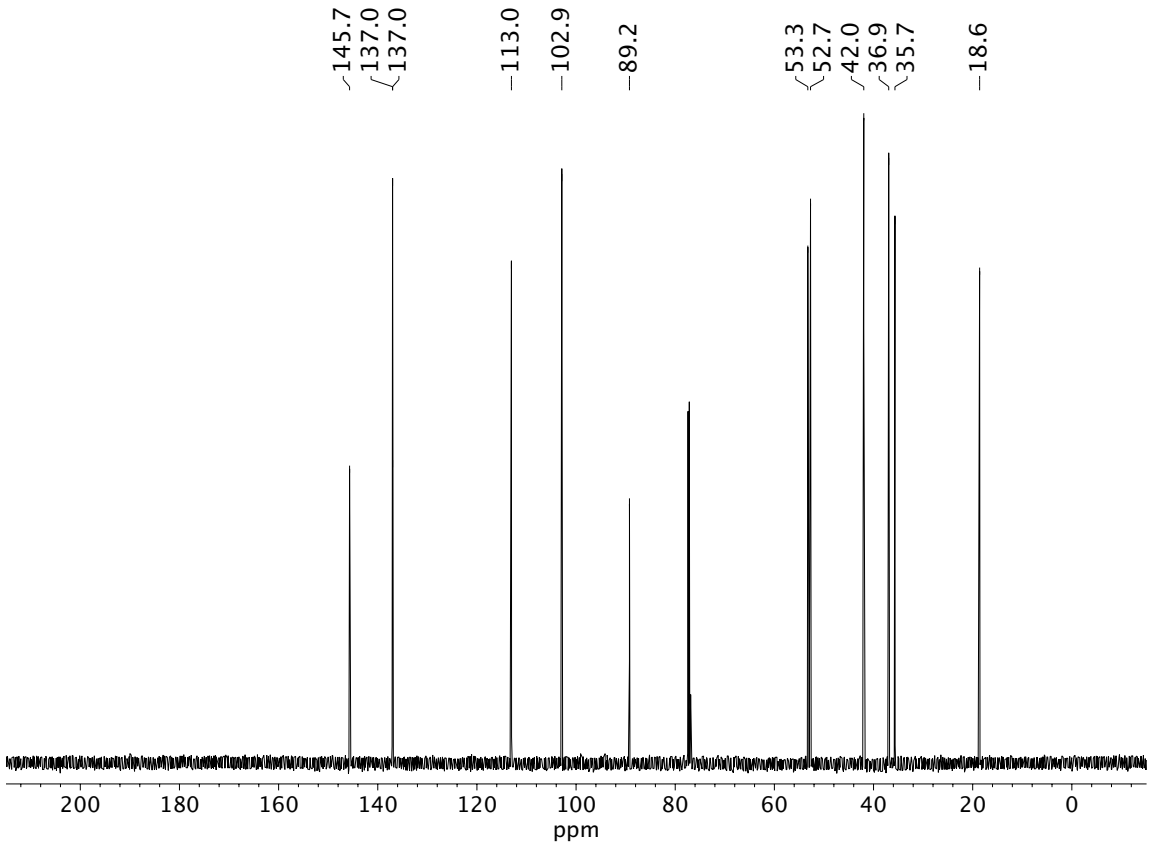
^{13}C NMR (100 MHz, $CDCl_3$) of compound **11.**



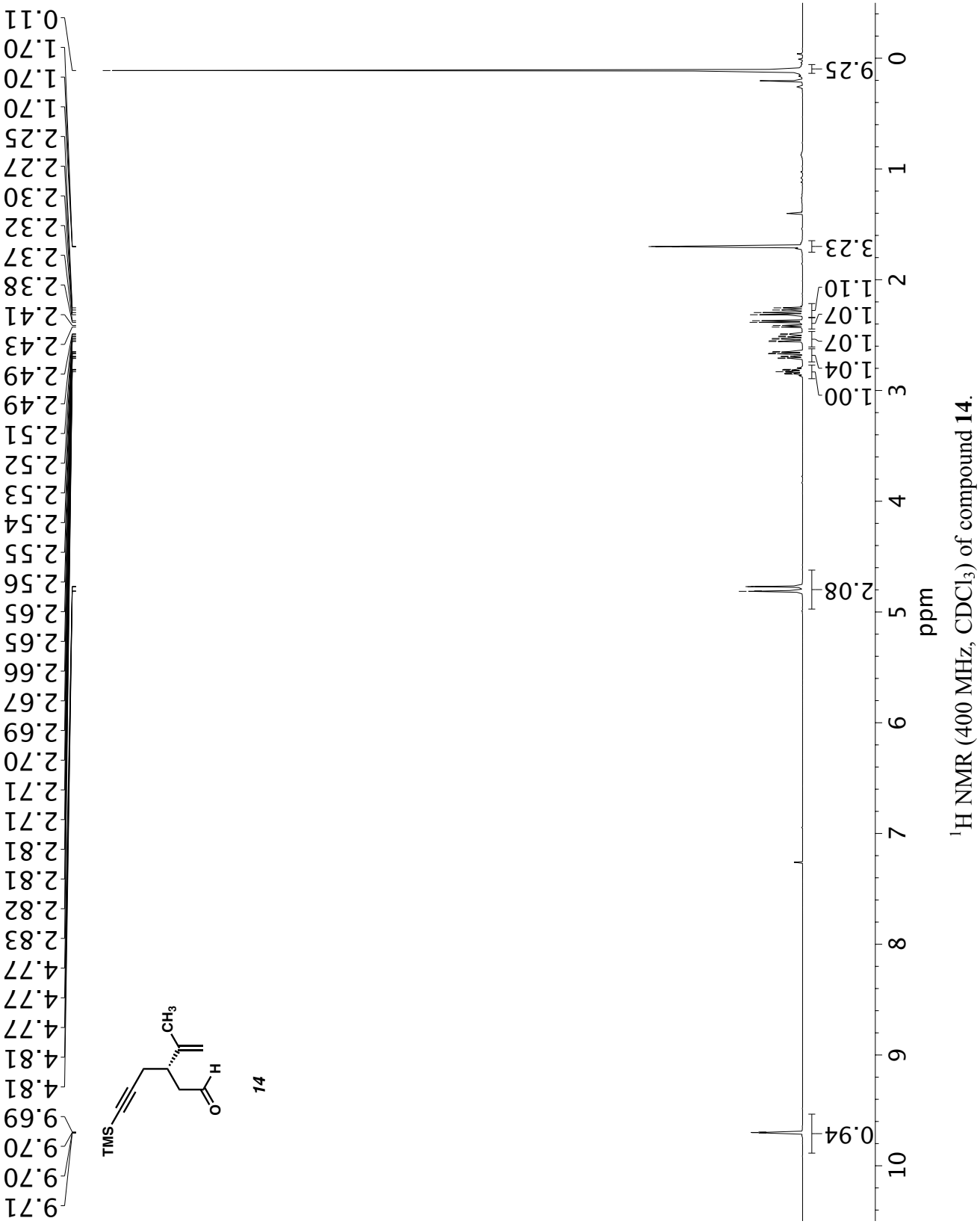
^{1}H NMR (400 MHz, $CDCl_3$) of compound **13**.



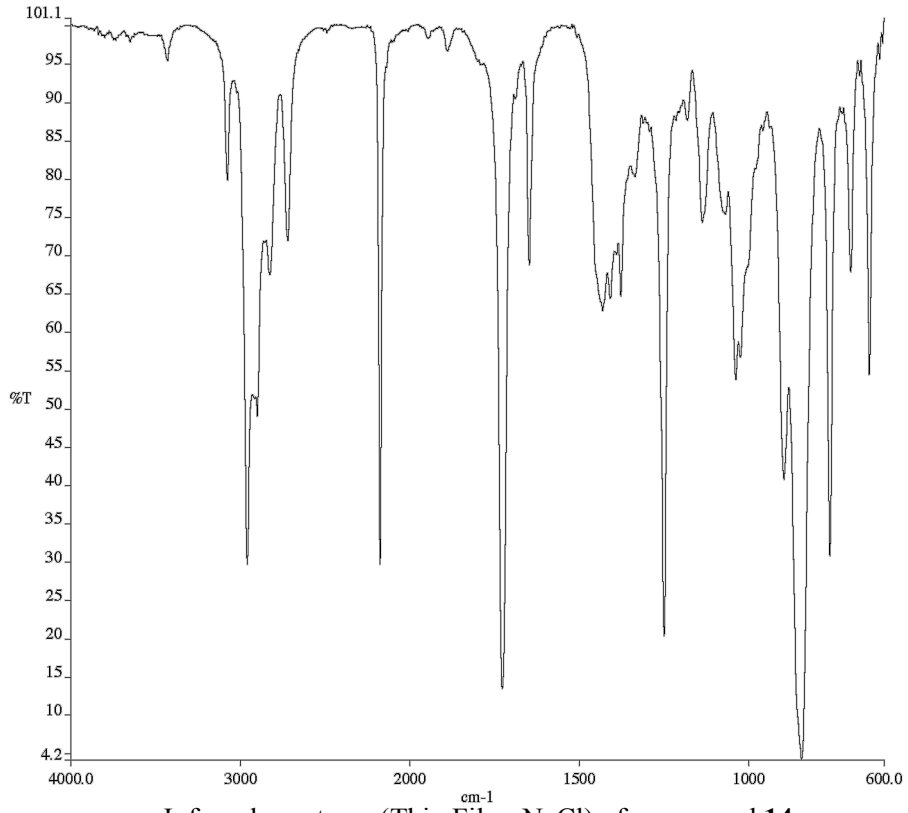
Infrared spectrum (Thin Film, NaCl) of compound **13**.



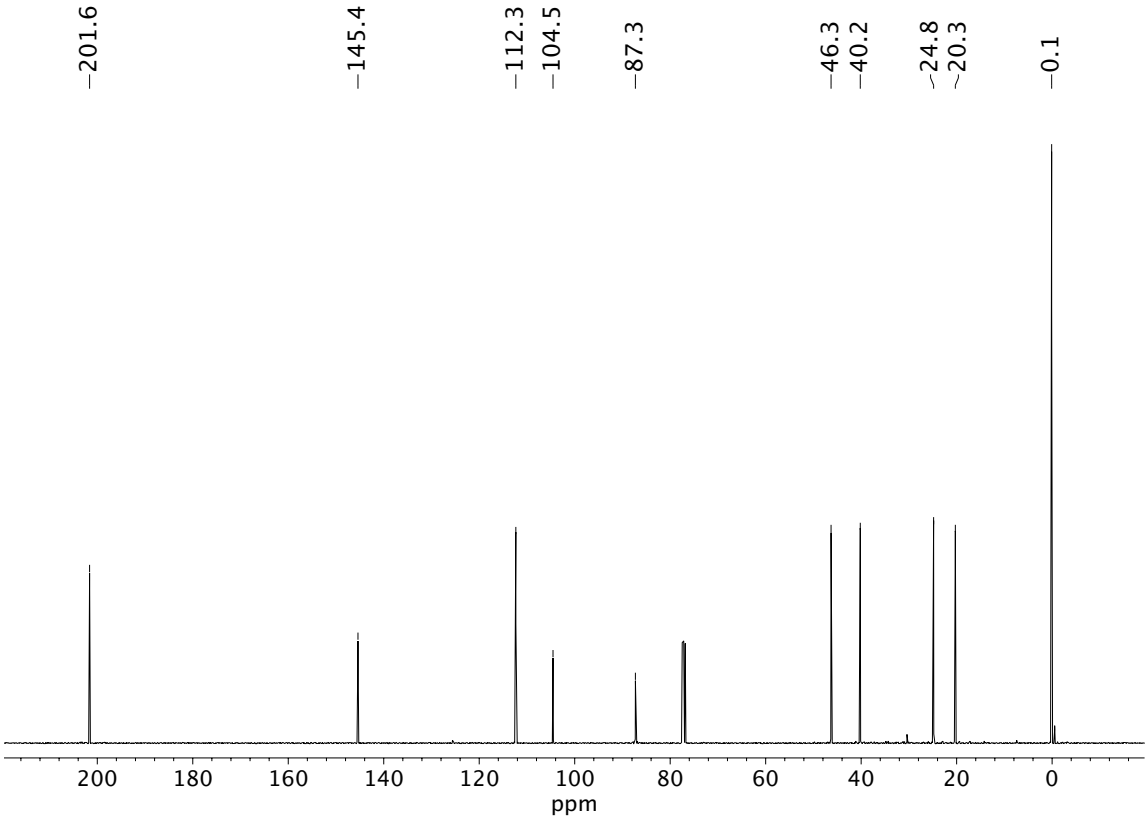
^{13}C NMR (125 MHz, $CDCl_3$) of compound **13**.



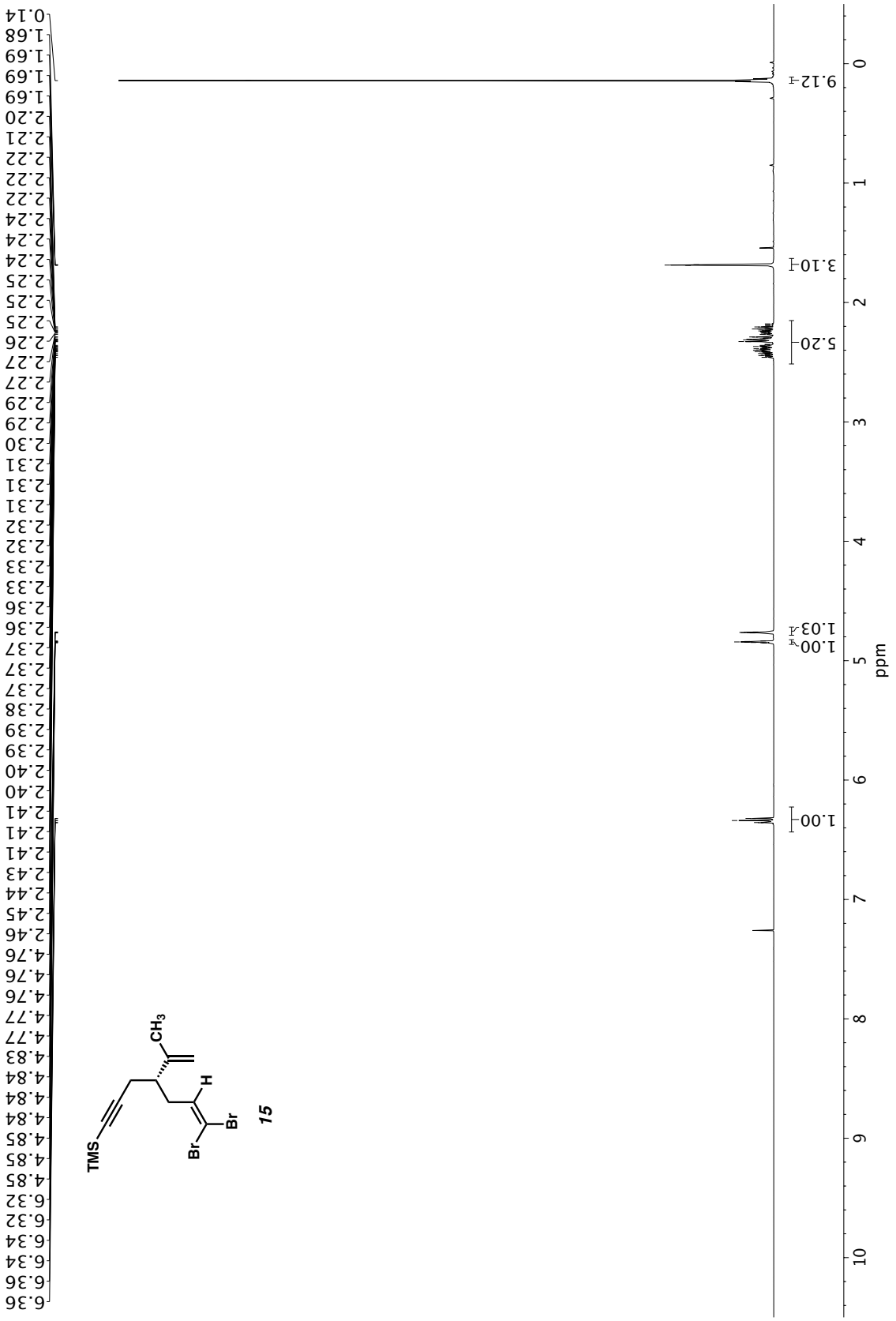
^{1}H NMR (400 MHz, $CDCl_3$) of compound **14**.



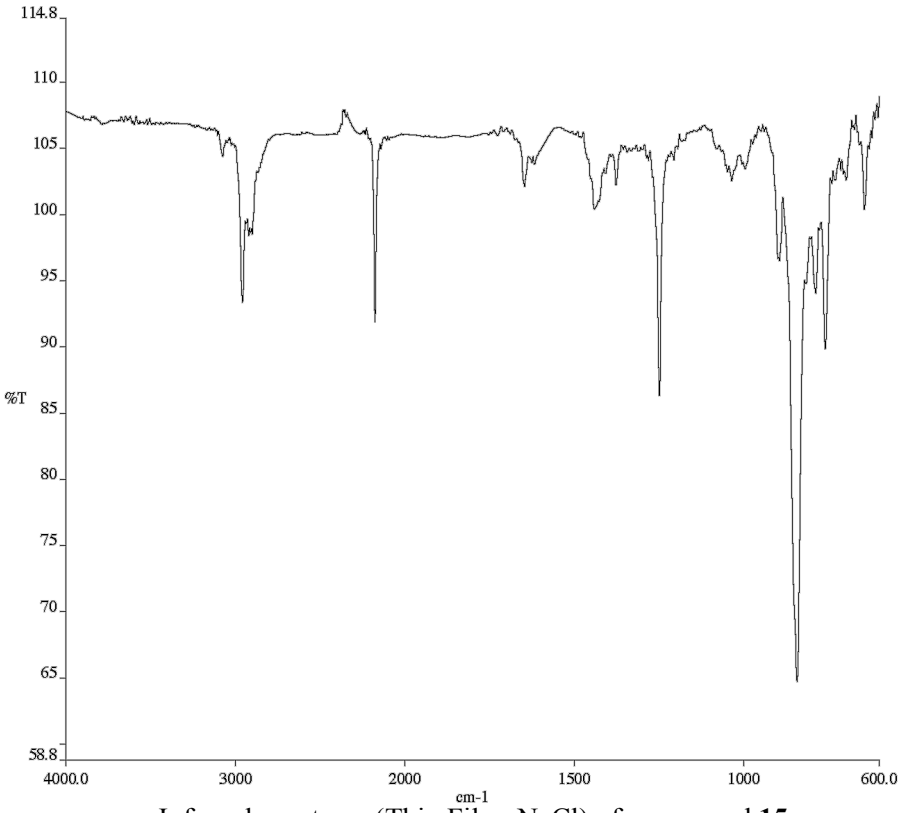
Infrared spectrum (Thin Film, NaCl) of compound **14**.



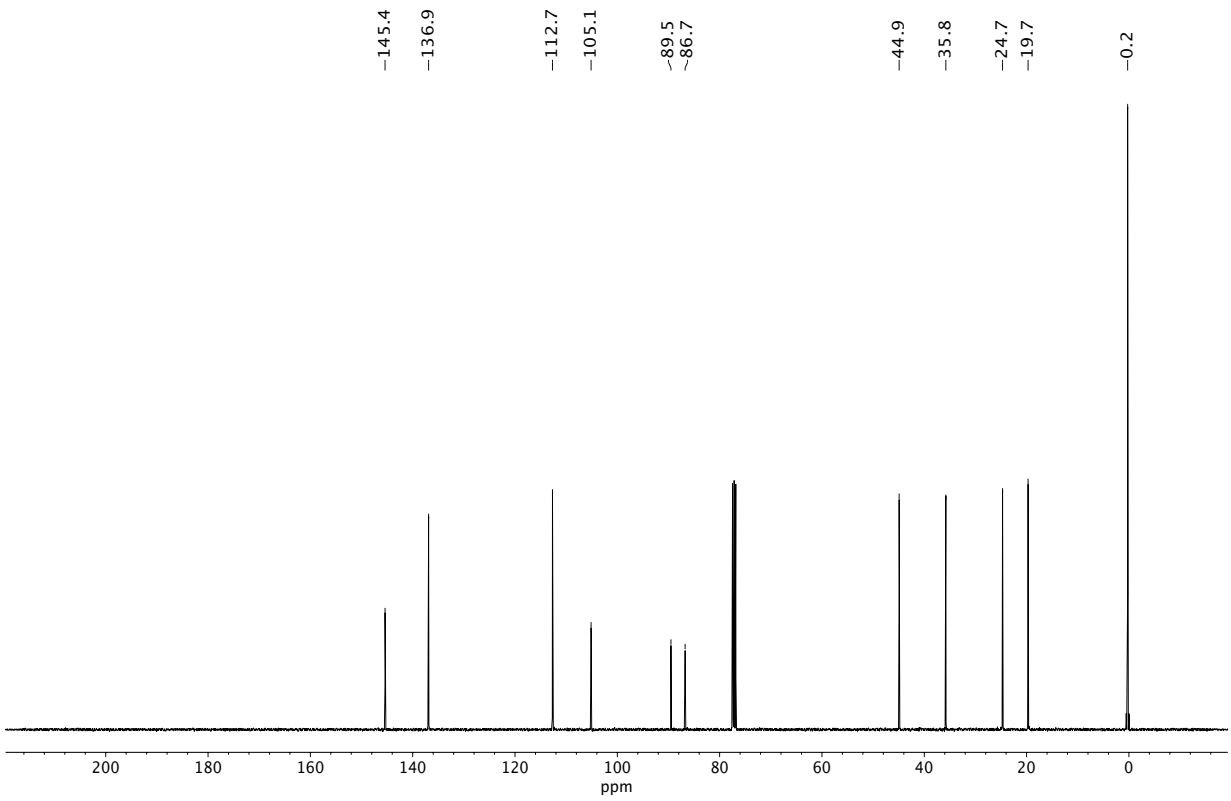
^{13}C NMR (100 MHz, $CDCl_3$) of compound **14**.



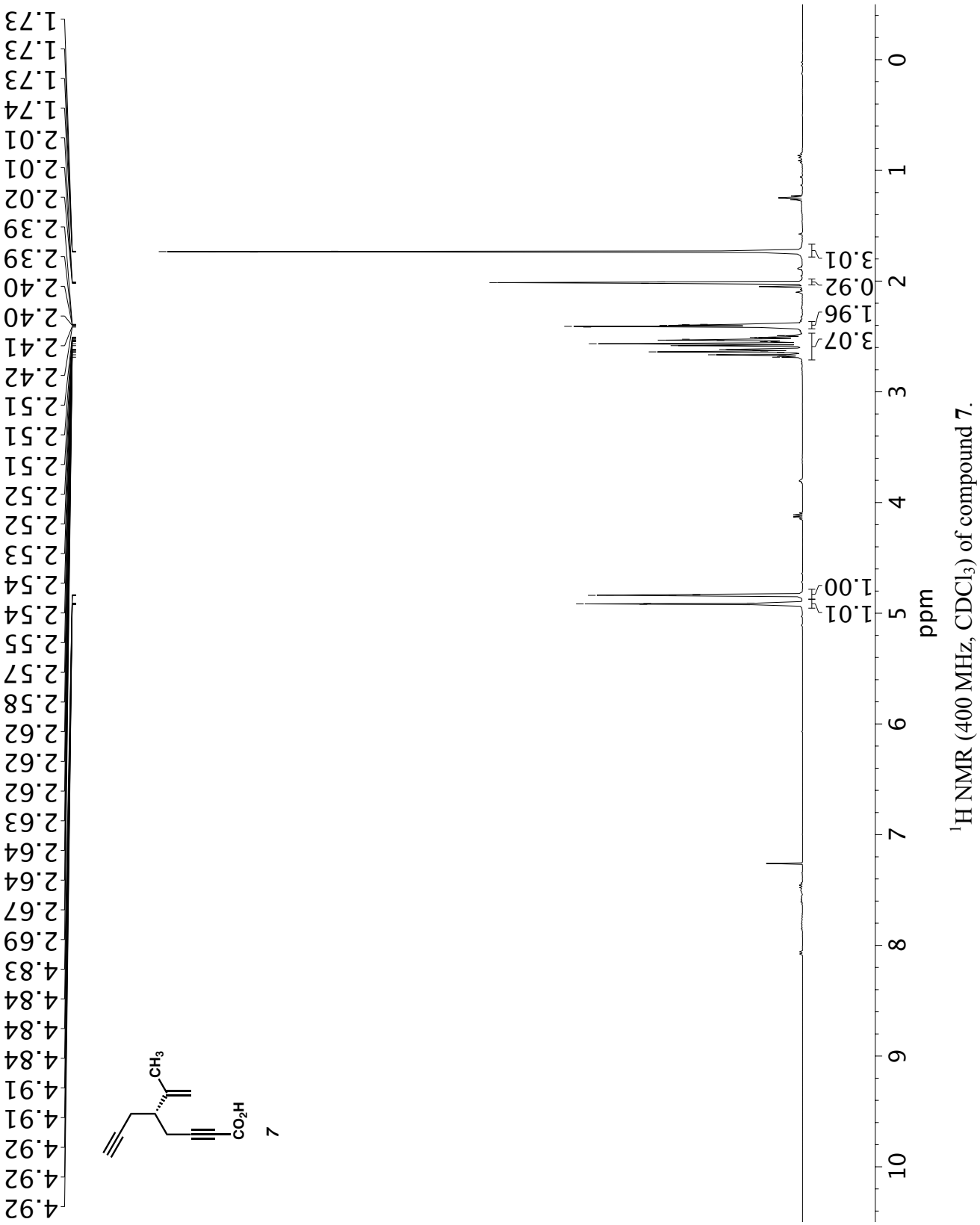
^{1}H NMR (500 MHz, $CDCl_3$) of compound **15**.



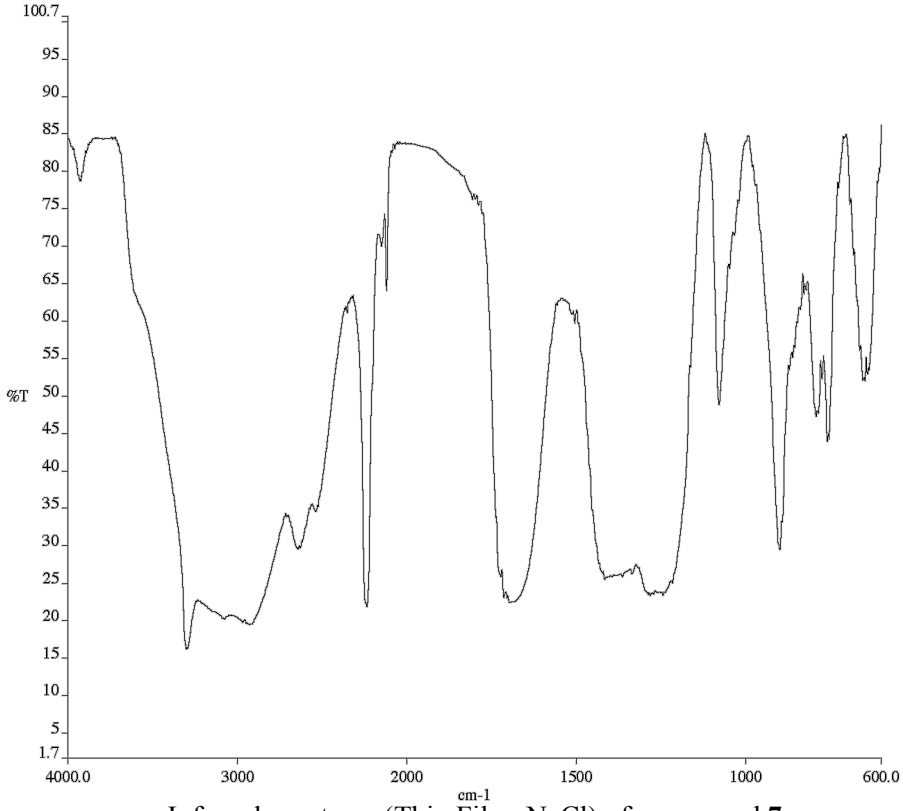
Infrared spectrum (Thin Film, NaCl) of compound **15**.



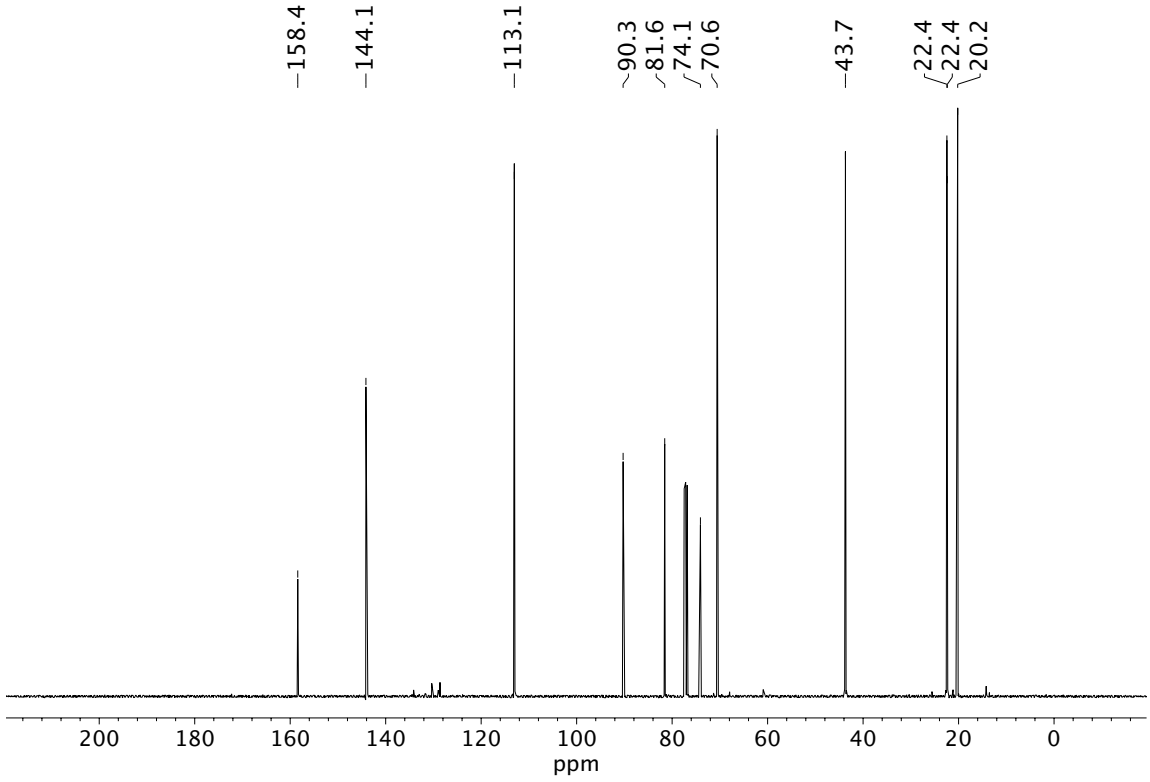
^{13}C NMR (100 MHz, $CDCl_3$) of compound **15**.



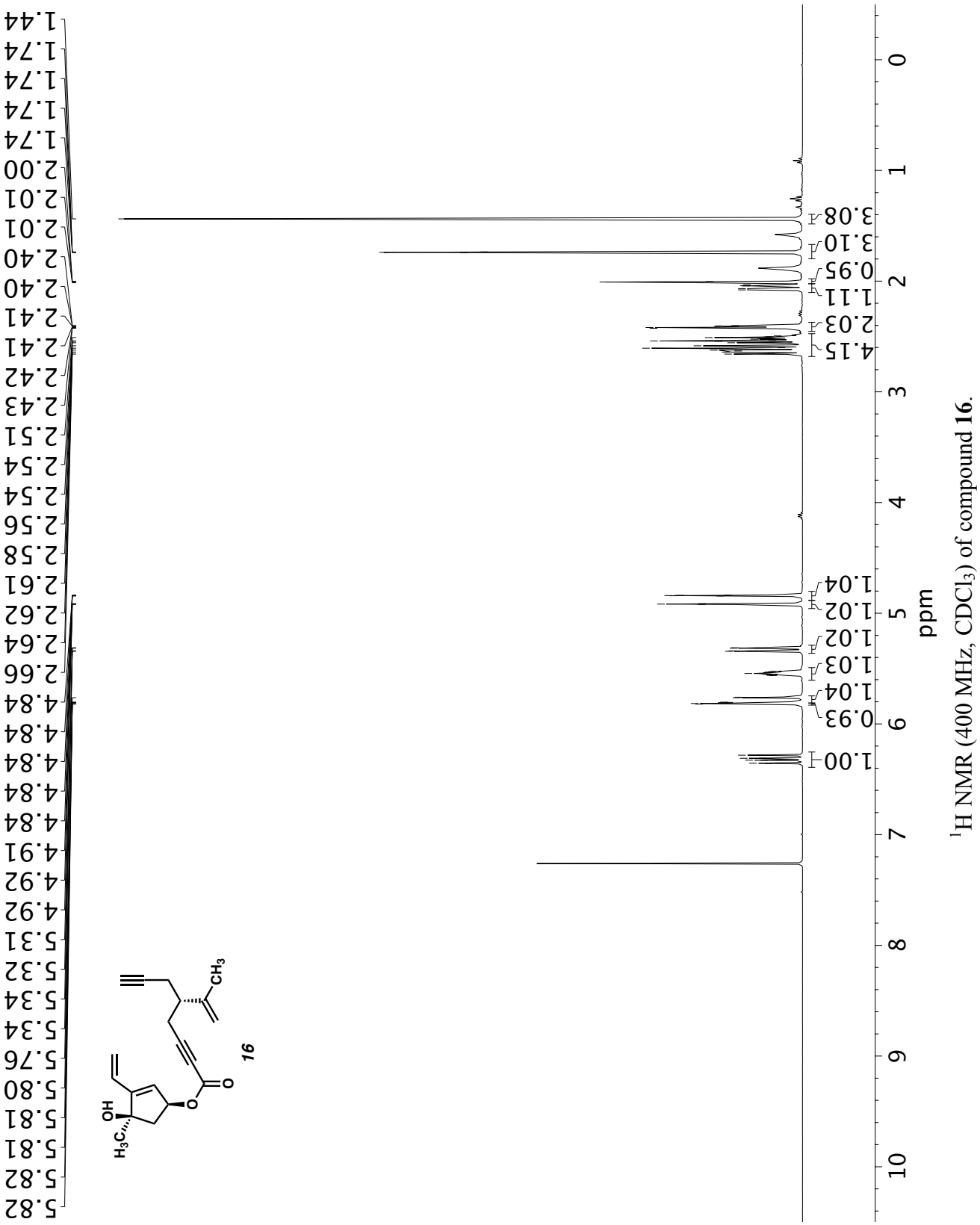
^{1}H NMR (400 MHz, $CDCl_3$) of compound **7**.



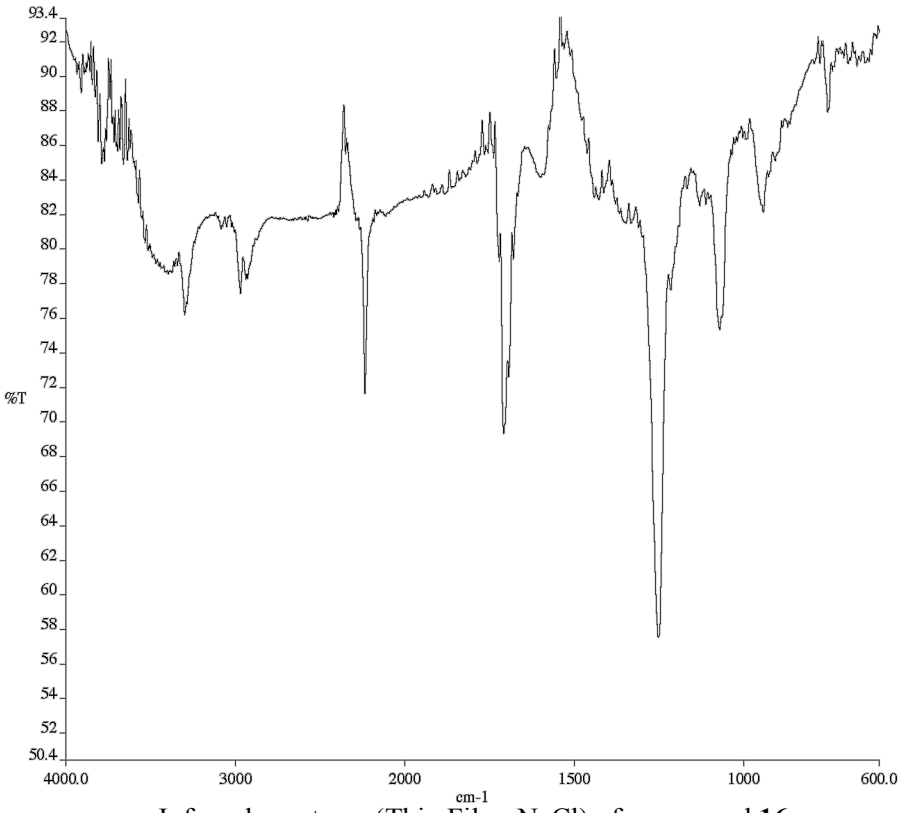
Infrared spectrum (Thin Film, NaCl) of compound **7**.



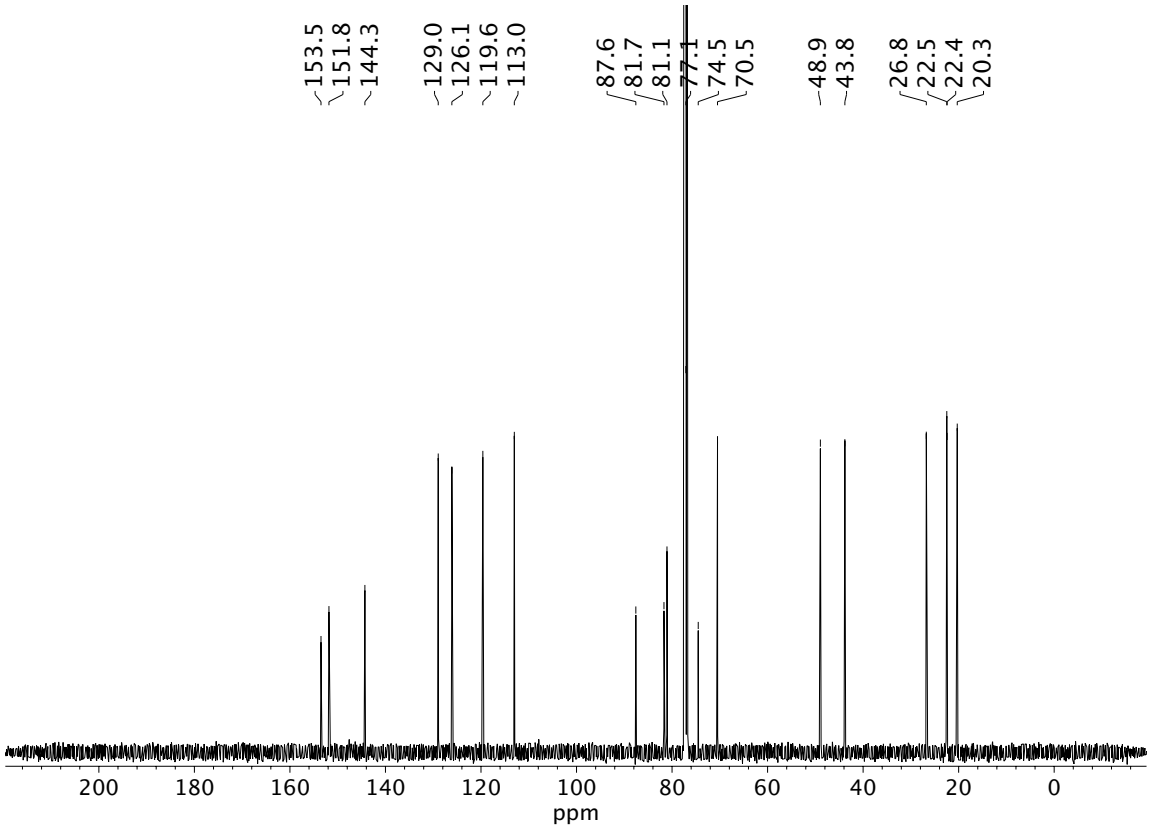
^{13}C NMR (100 MHz, $CDCl_3$) of compound **7**.



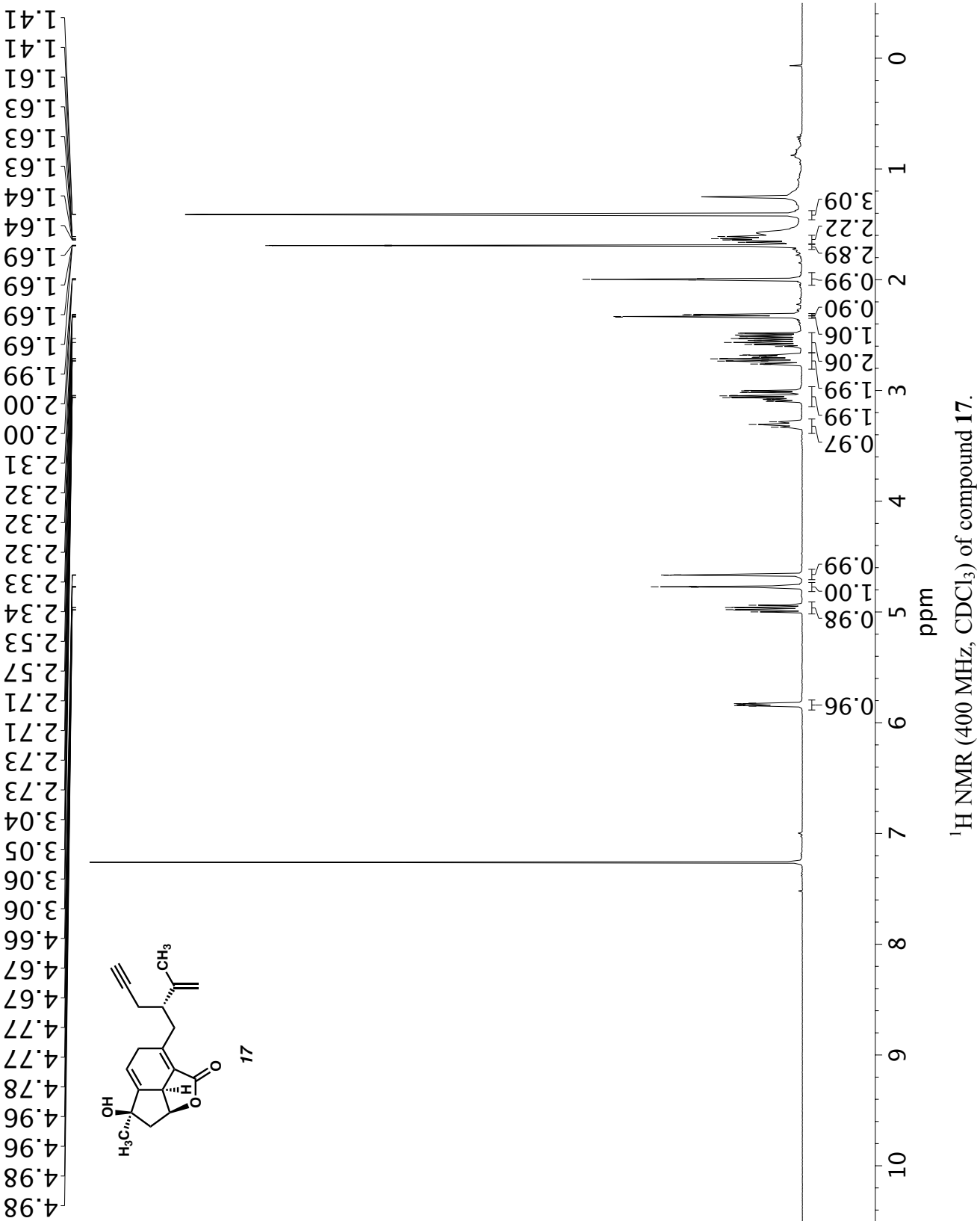
^{1}H NMR (400 MHz, $CDCl_3$) of compound **16**.



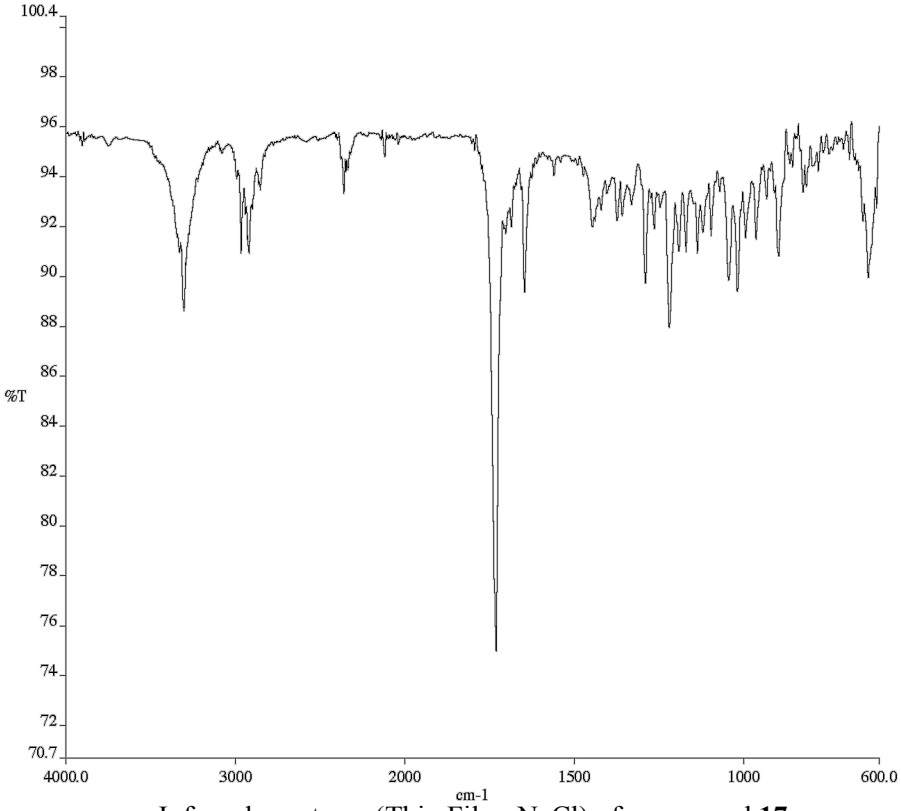
Infrared spectrum (Thin Film, NaCl) of compound **16**.



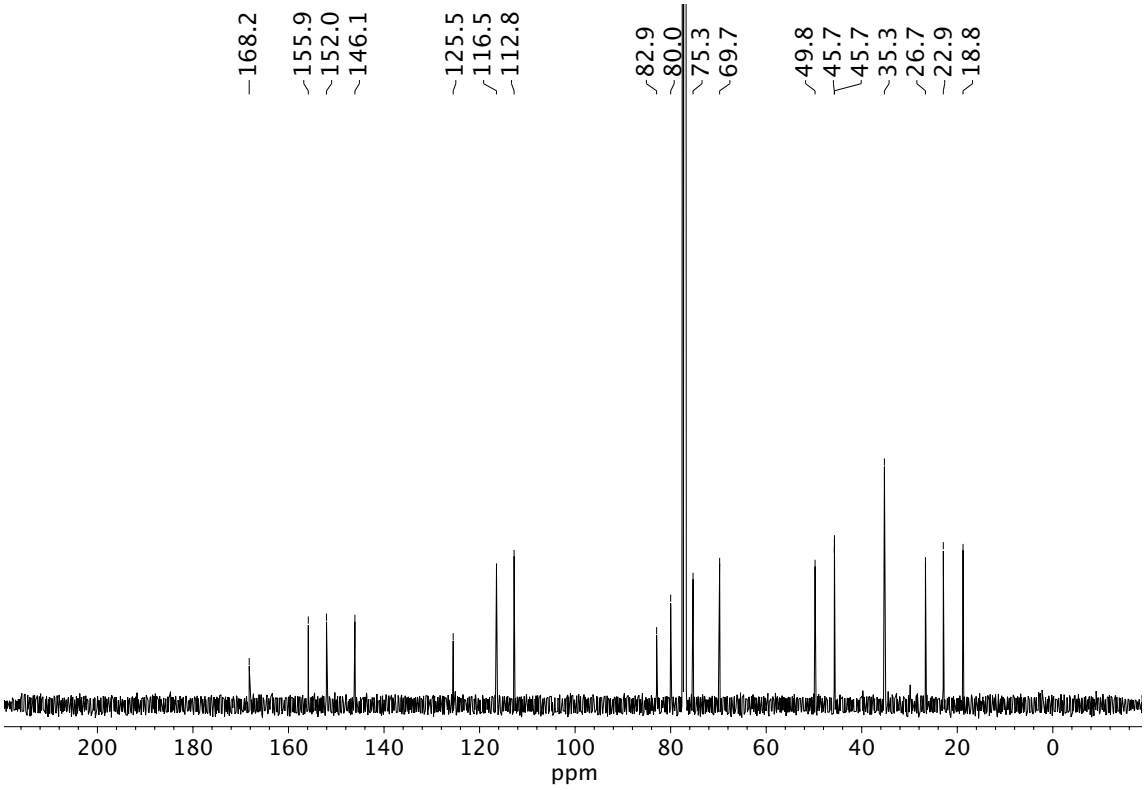
^{13}C NMR (100 MHz, $CDCl_3$) of compound **16**.



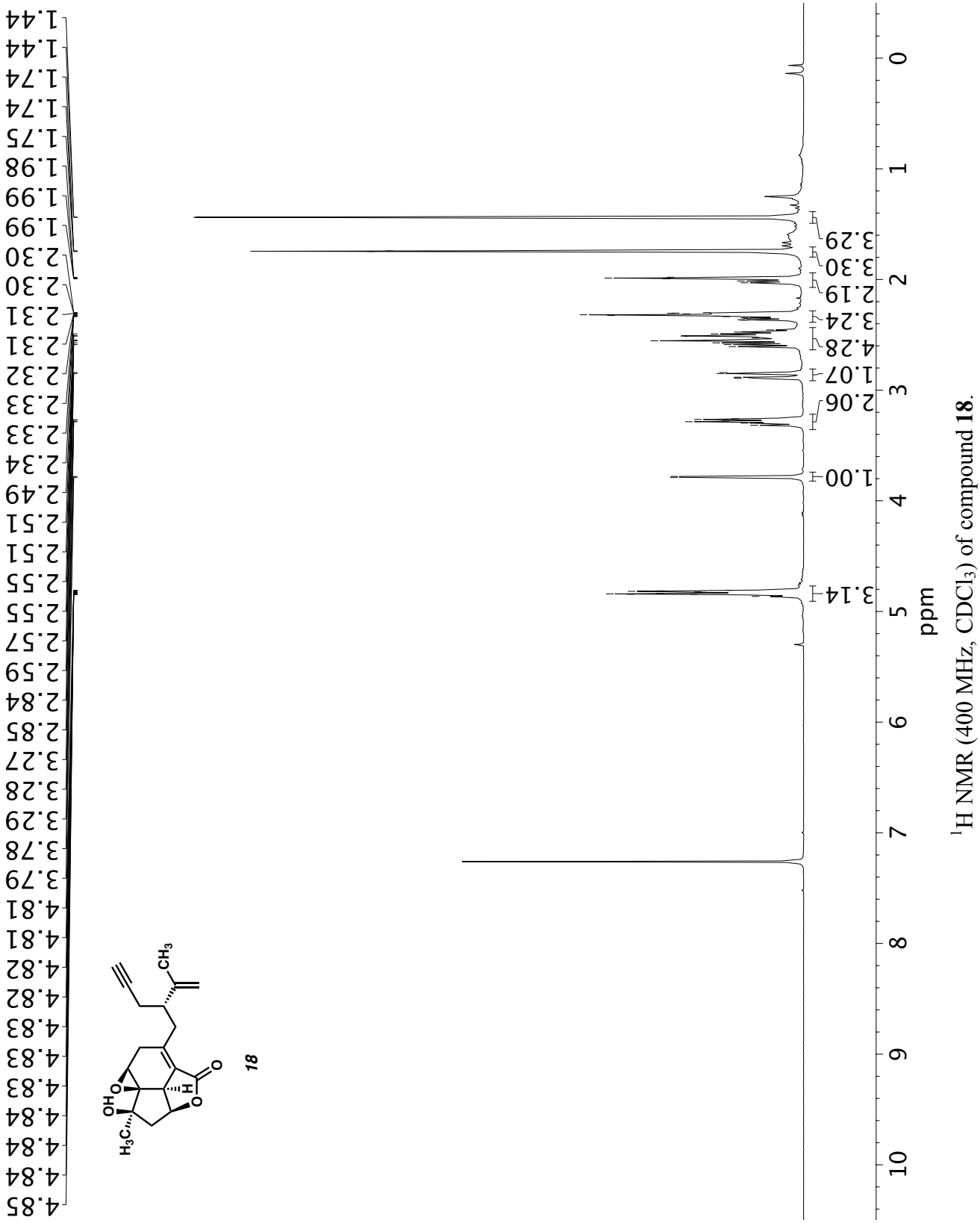
^{1}H NMR (400 MHz, $CDCl_3$) of compound **17**.



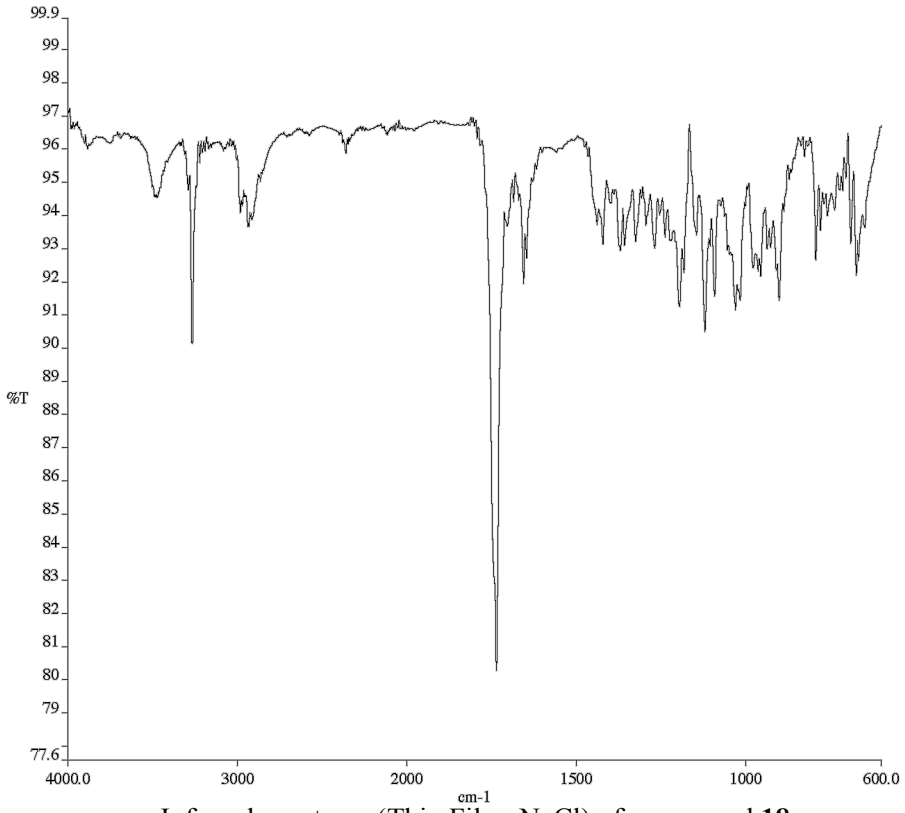
Infrared spectrum (Thin Film, NaCl) of compound **17**.



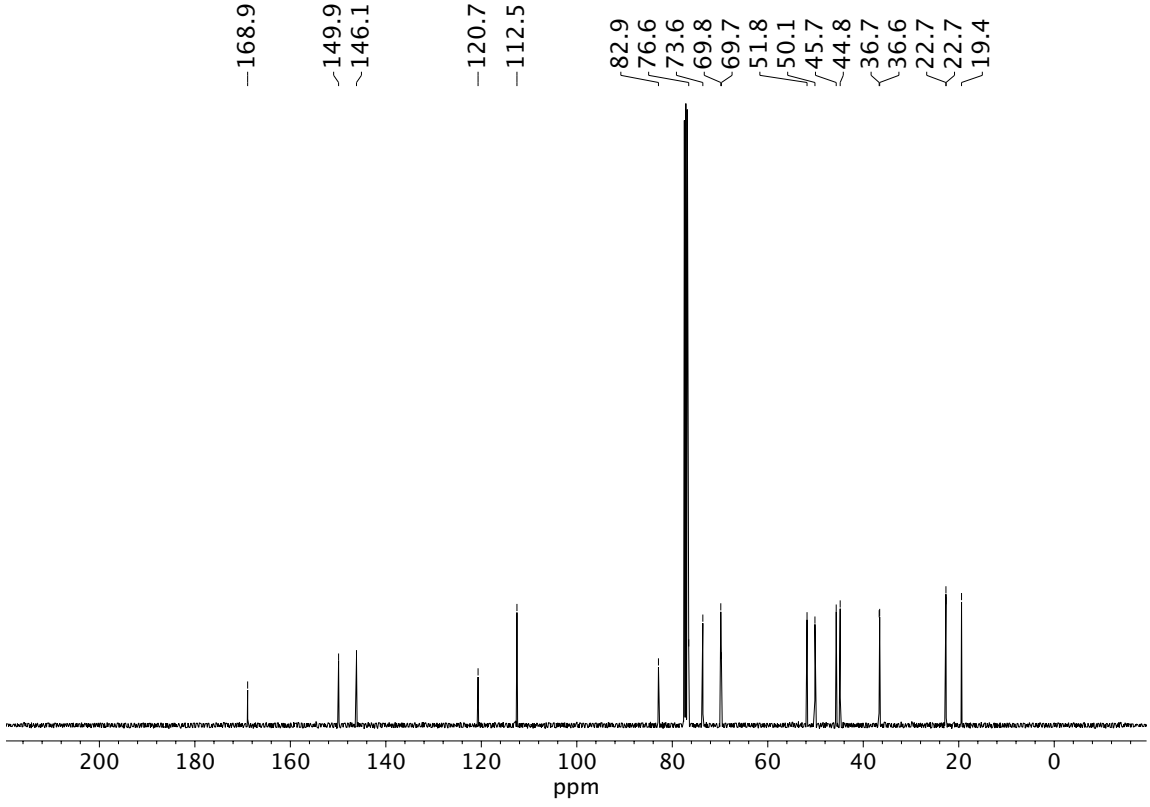
^{13}C NMR (100 MHz, $CDCl_3$) of compound **17**.



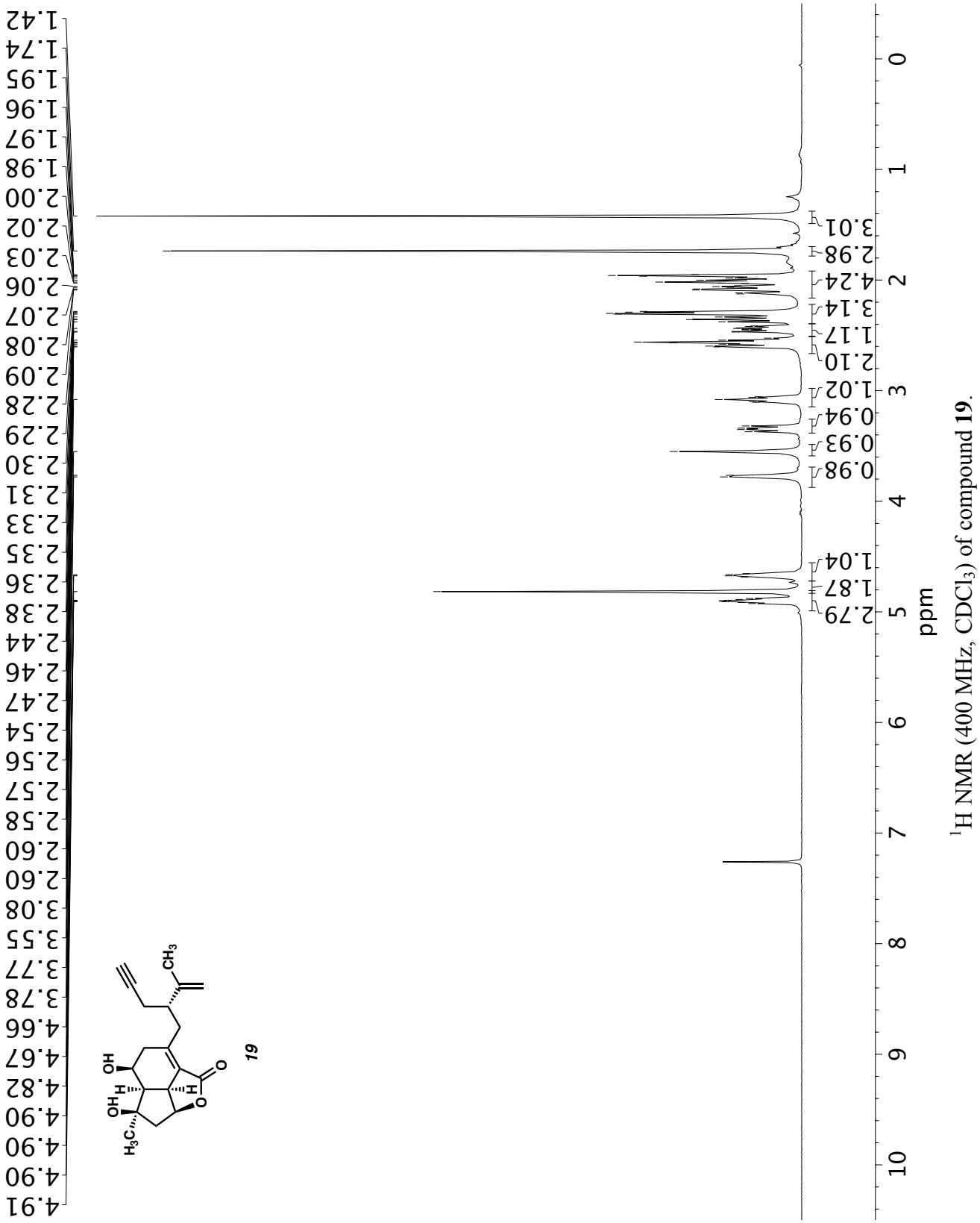
^{1}H NMR (400 MHz, $CDCl_3$) of compound **18**.



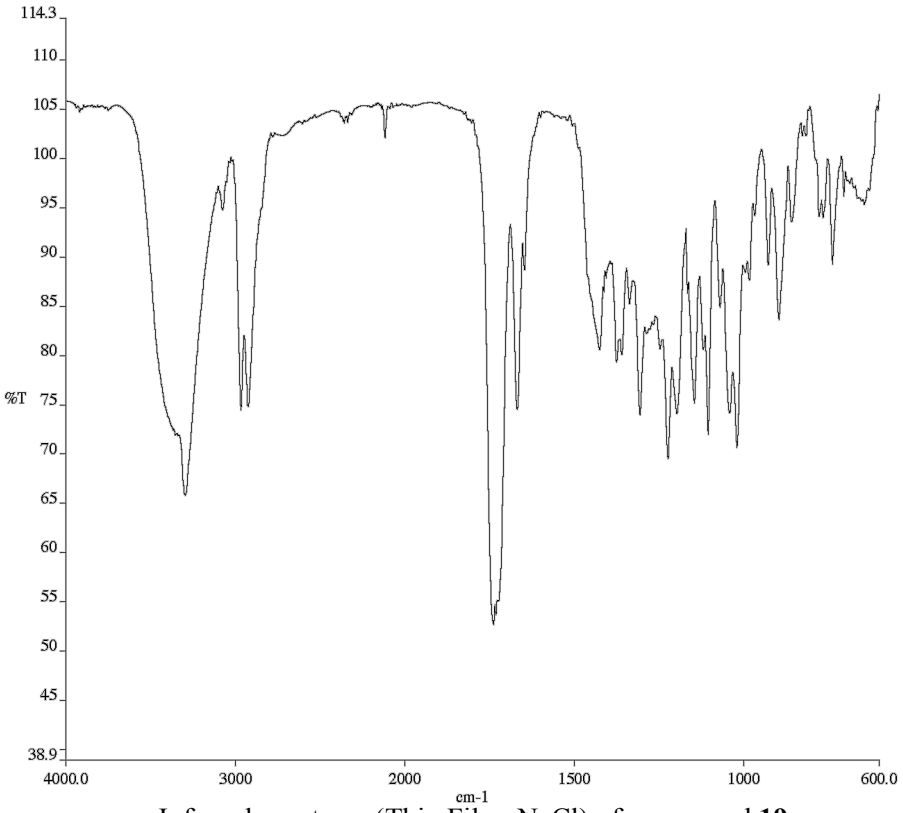
Infrared spectrum (Thin Film, NaCl) of compound **18**.



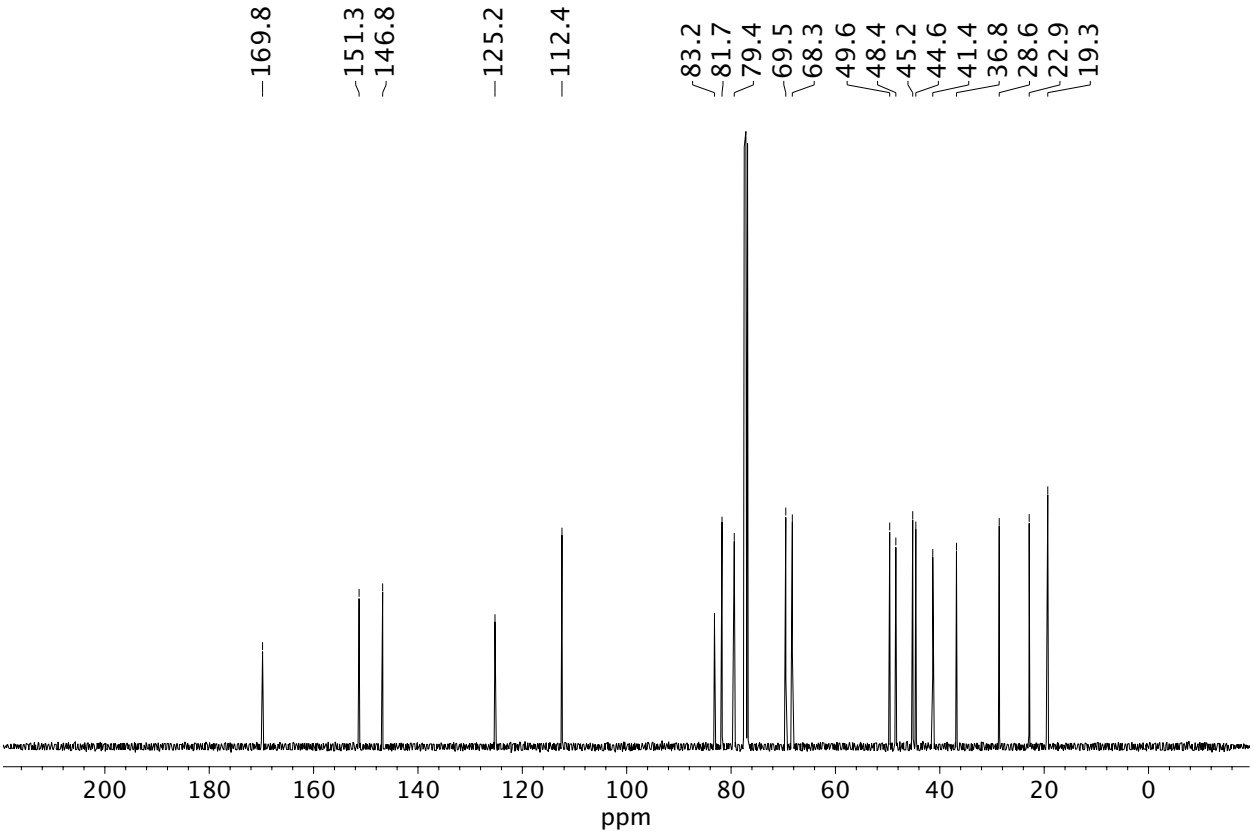
^{13}C NMR (100 MHz, $CDCl_3$) of compound **18**.



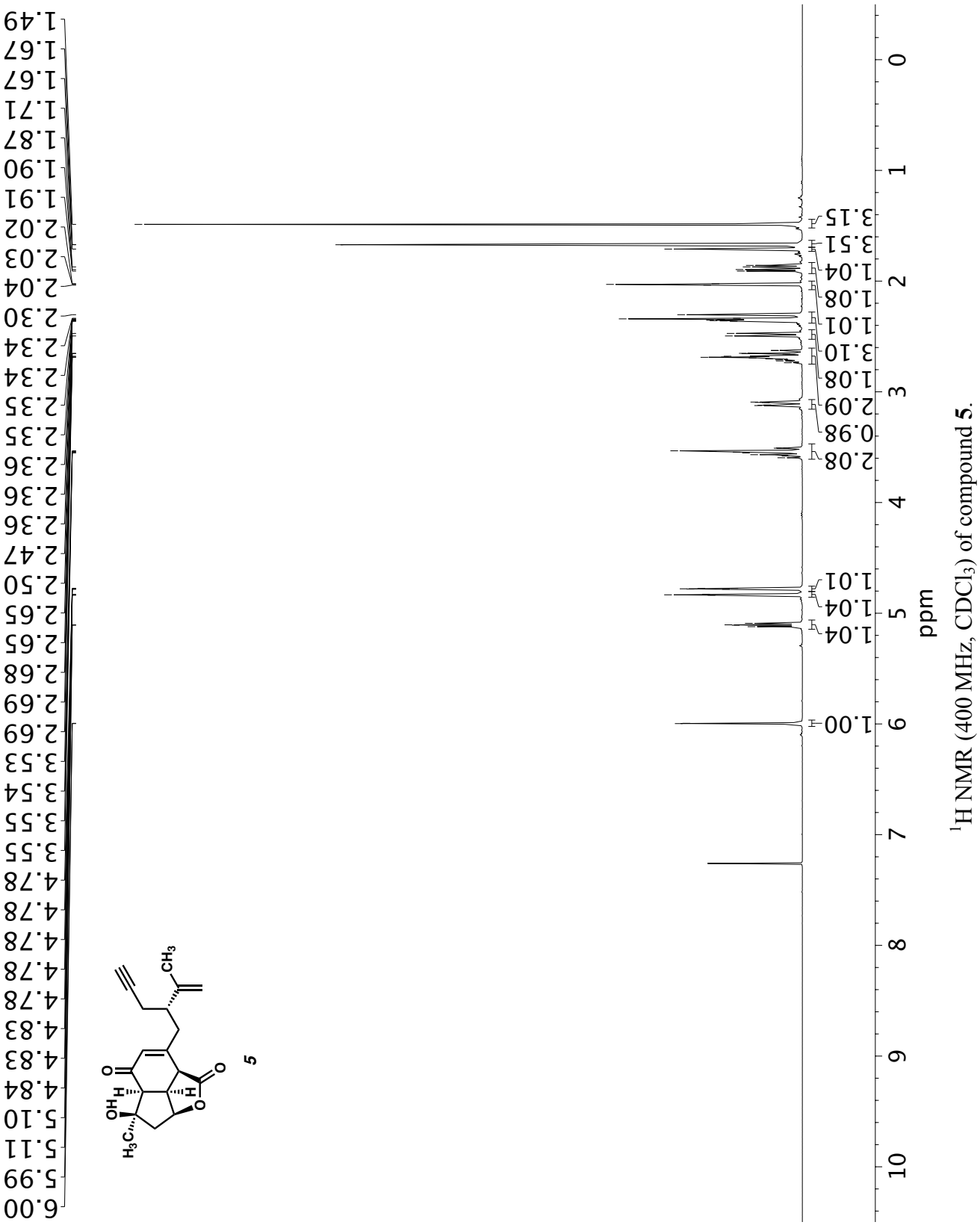
^{1}H NMR (400 MHz, $CDCl_3$) of compound **19**.



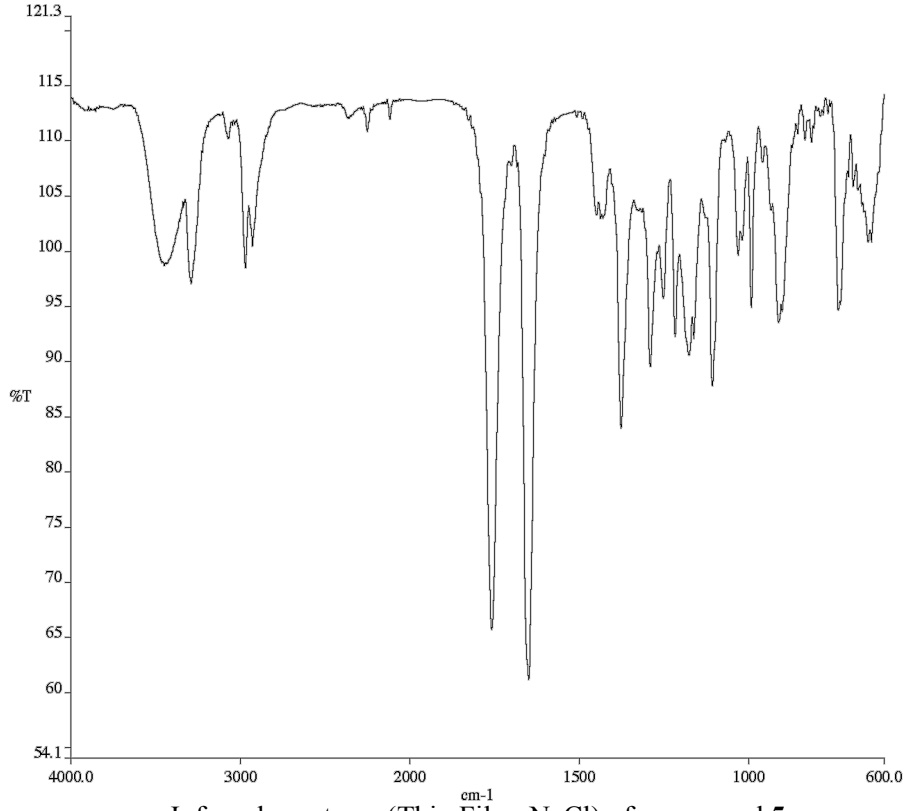
Infrared spectrum (Thin Film, NaCl) of compound **19**.



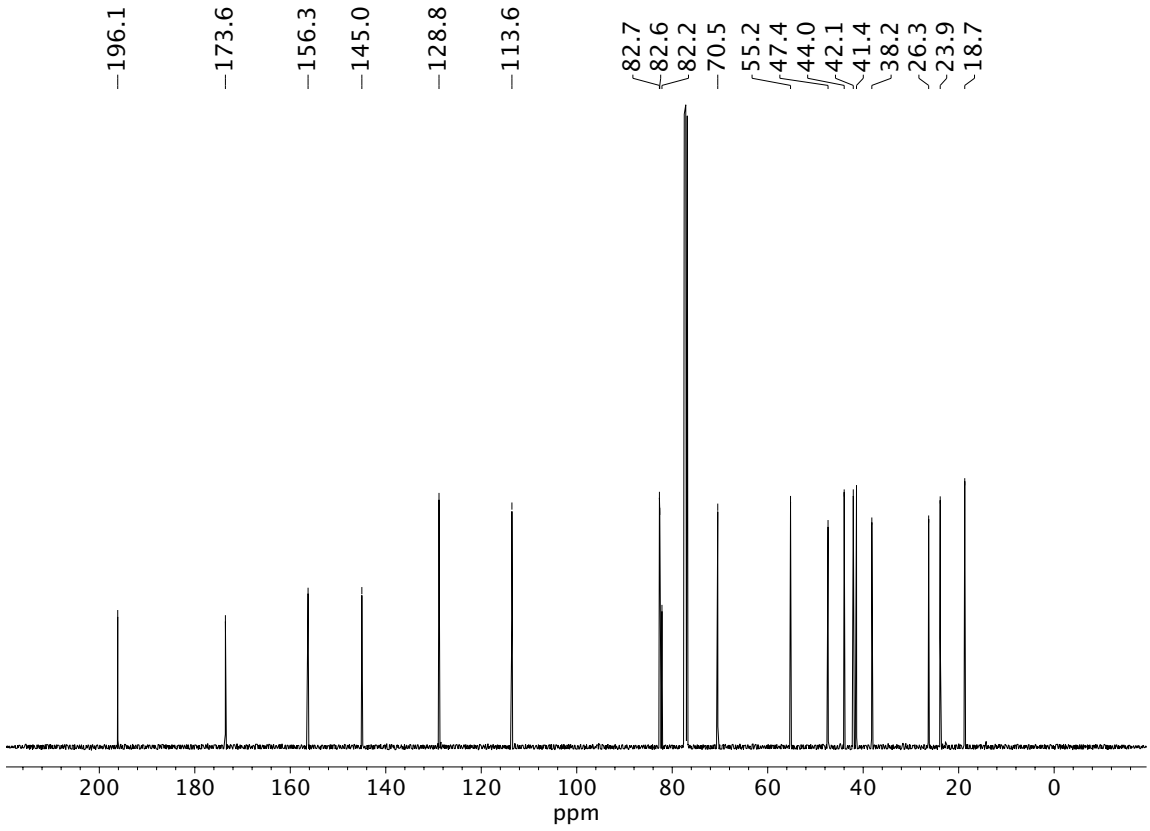
^{13}C NMR (100 MHz, $CDCl_3$) of compound **19**.



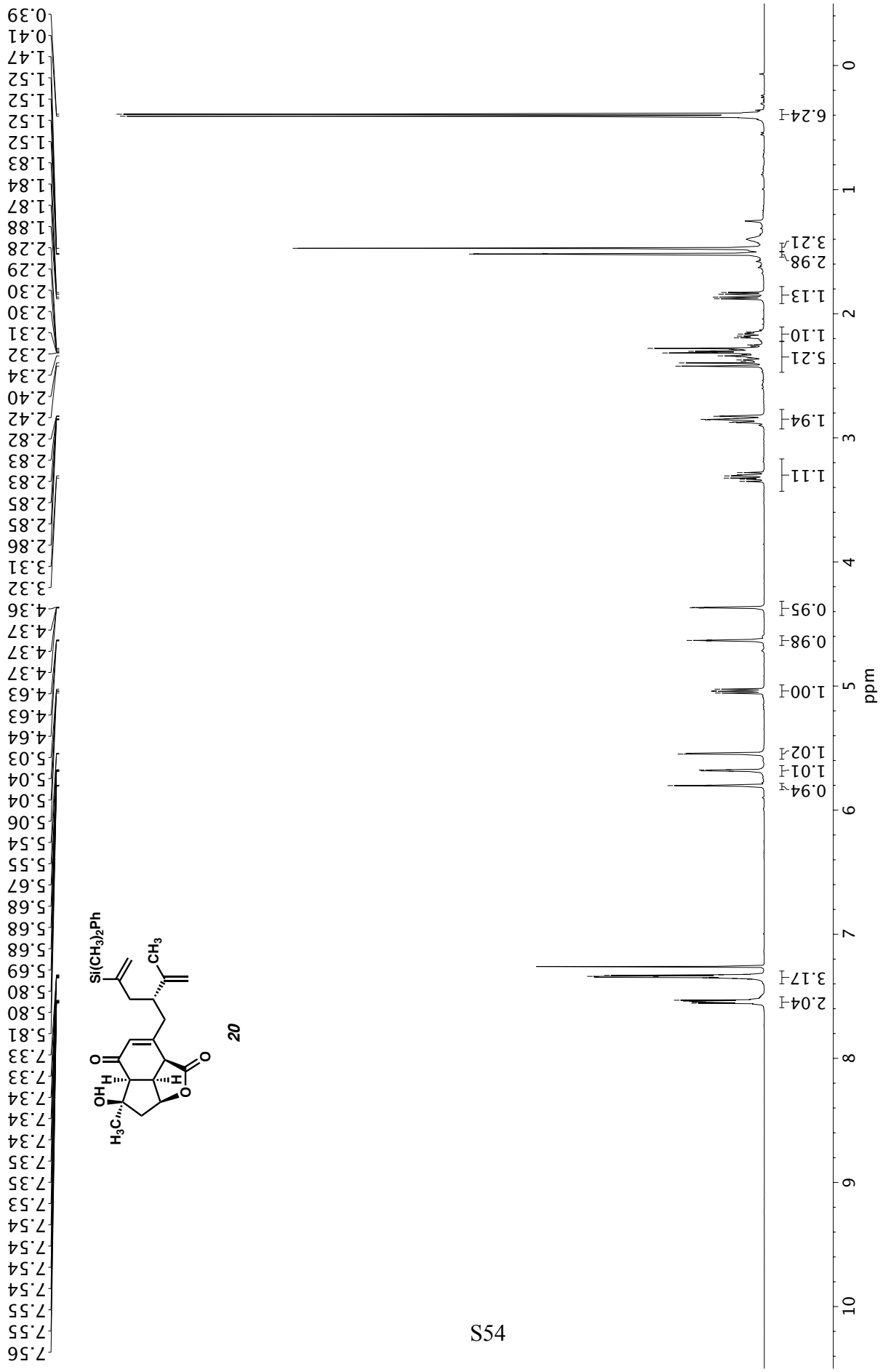
^{1}H NMR (400 MHz, $CDCl_3$) of compound **5**.



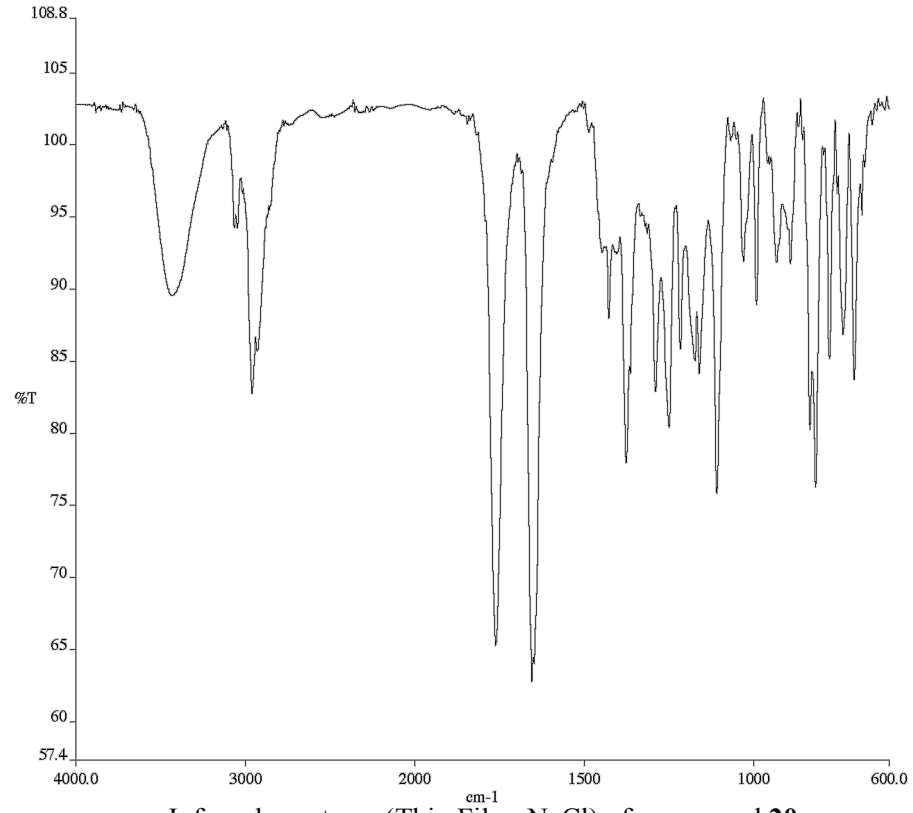
Infrared spectrum (Thin Film, NaCl) of compound **5**.



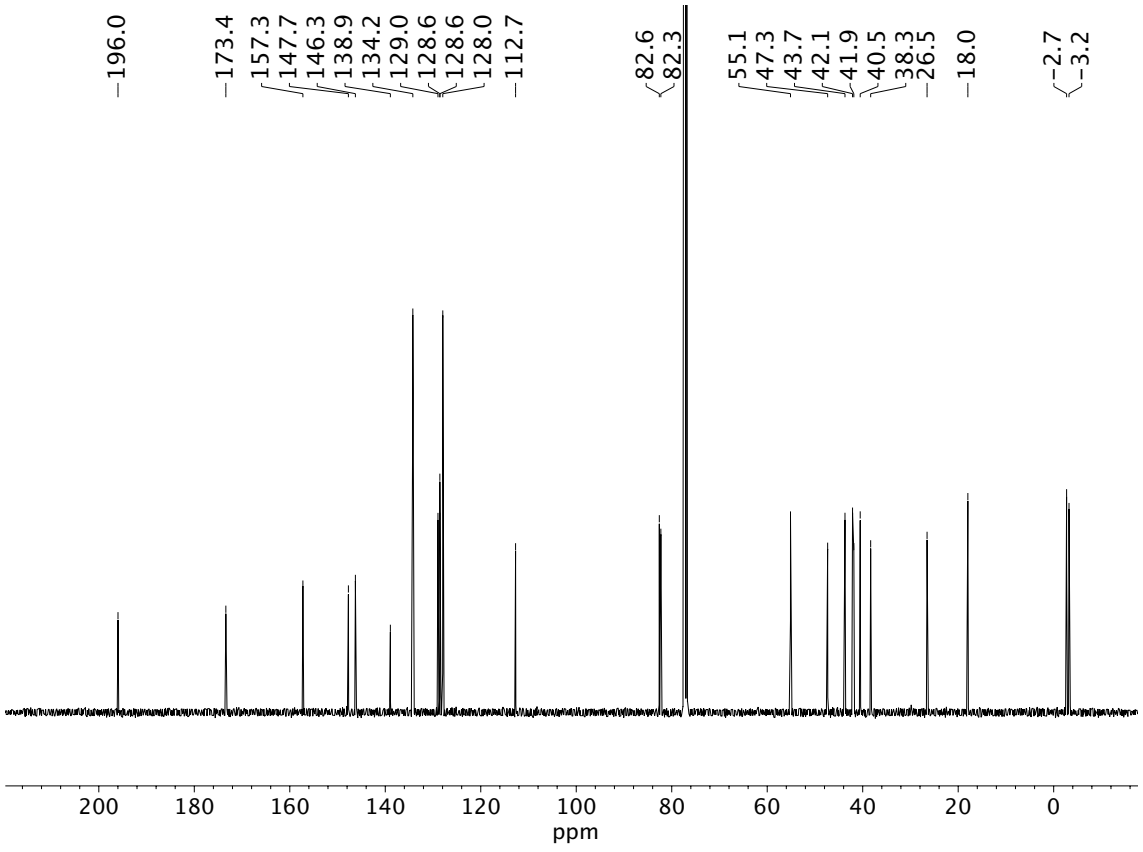
^{13}C NMR (100 MHz, $CDCl_3$) of compound **5**.



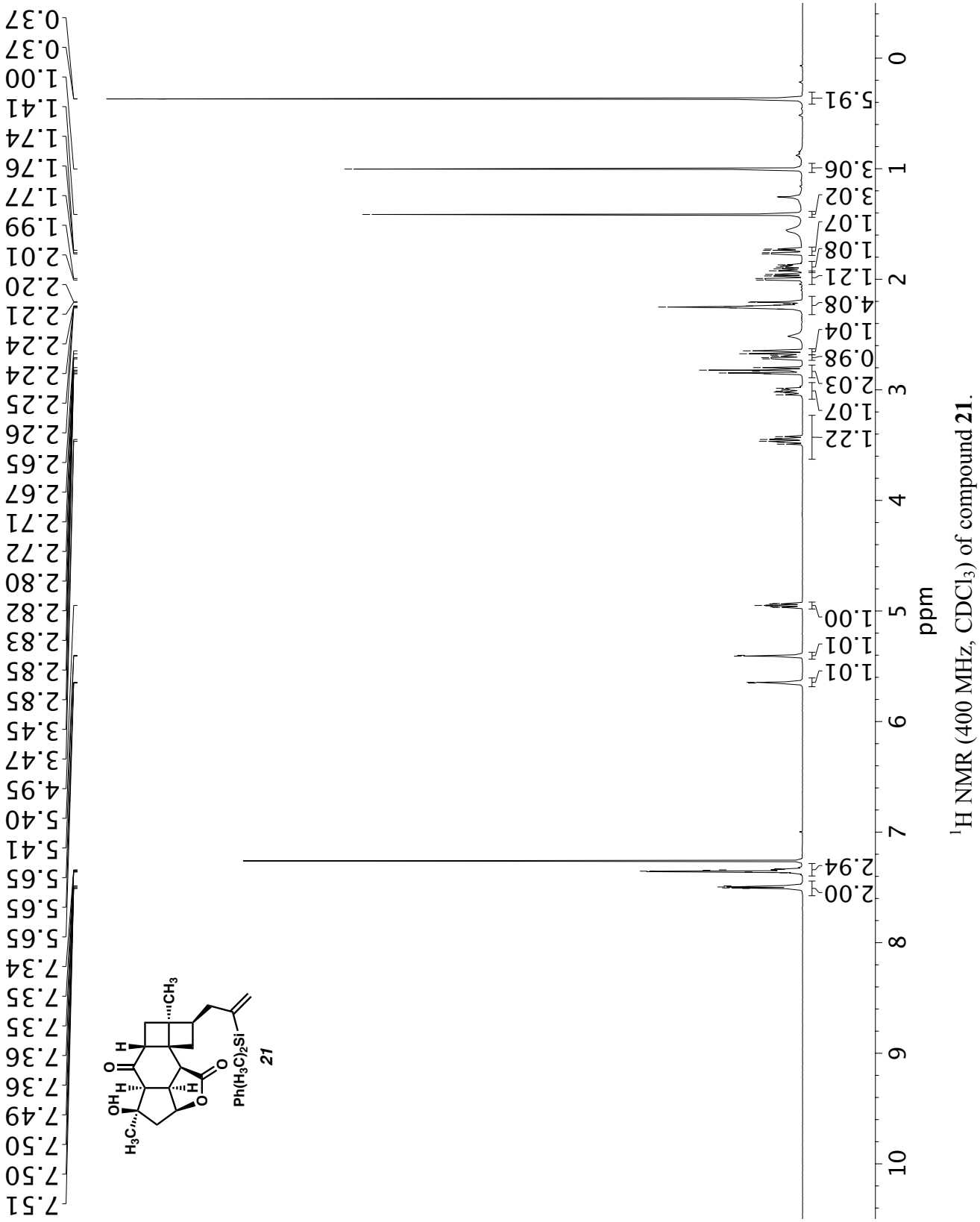
^{1}H NMR (400 MHz, $CDCl_3$) of compound **20**.



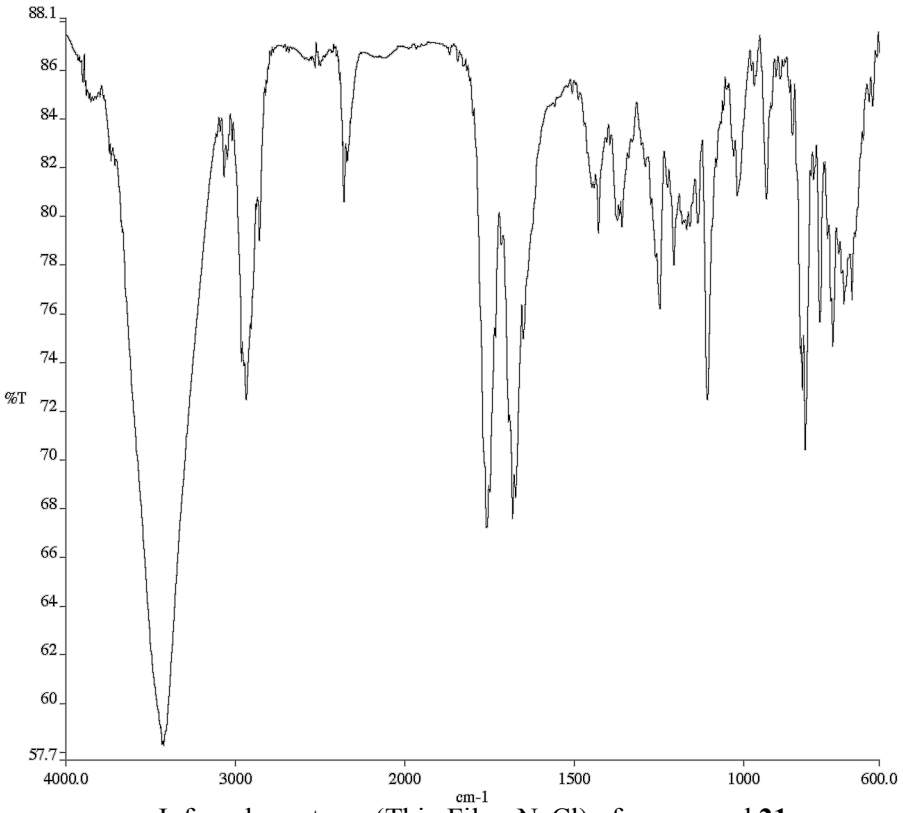
Infrared spectrum (Thin Film, NaCl) of compound **20**.



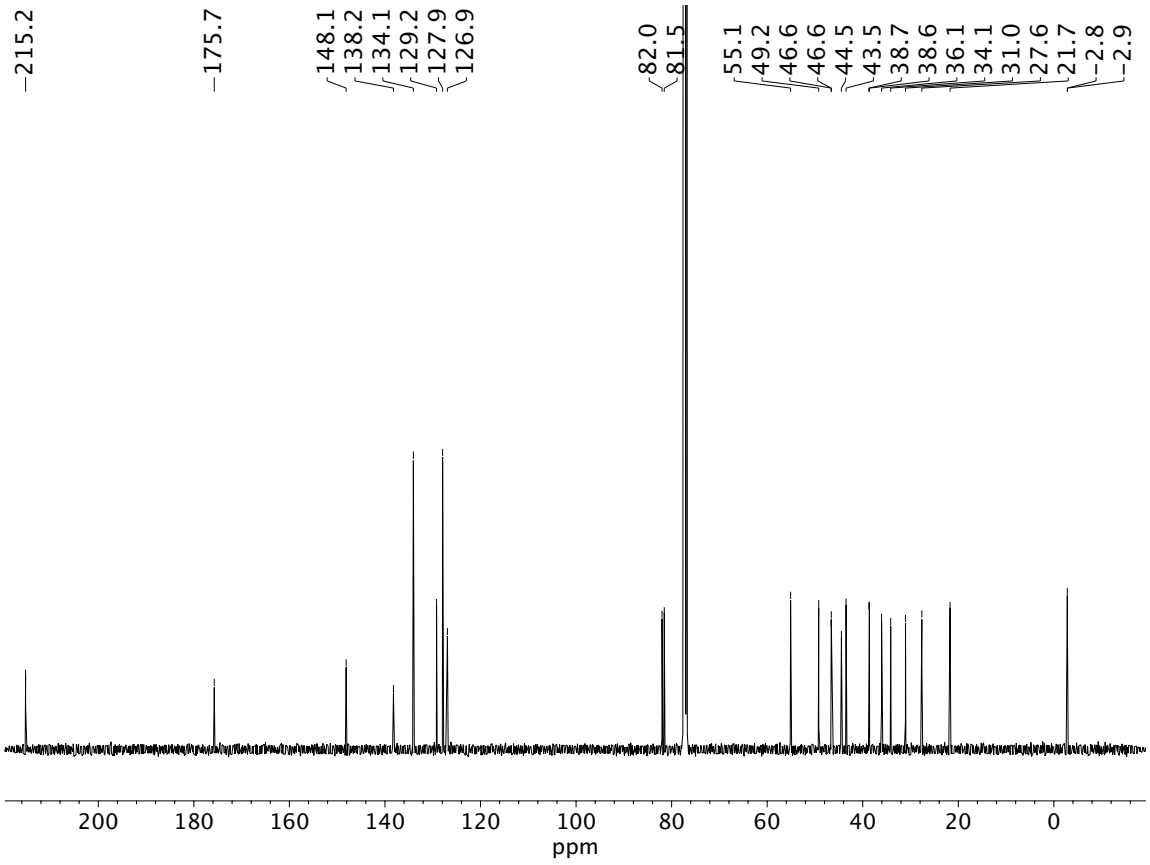
^{13}C NMR (100 MHz, $CDCl_3$) of compound **20.**



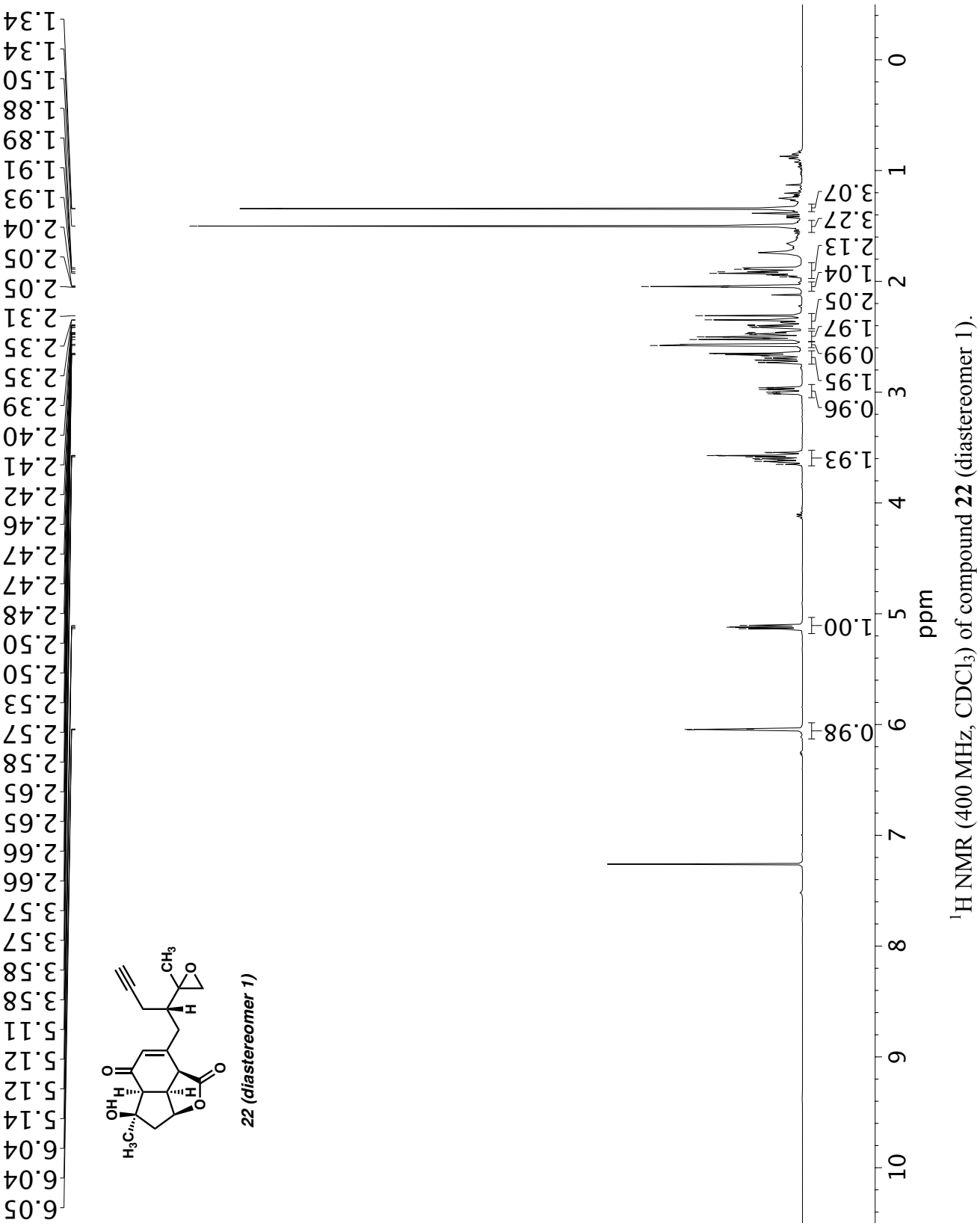
^{1}H NMR (400 MHz, $CDCl_3$) of compound **21**.



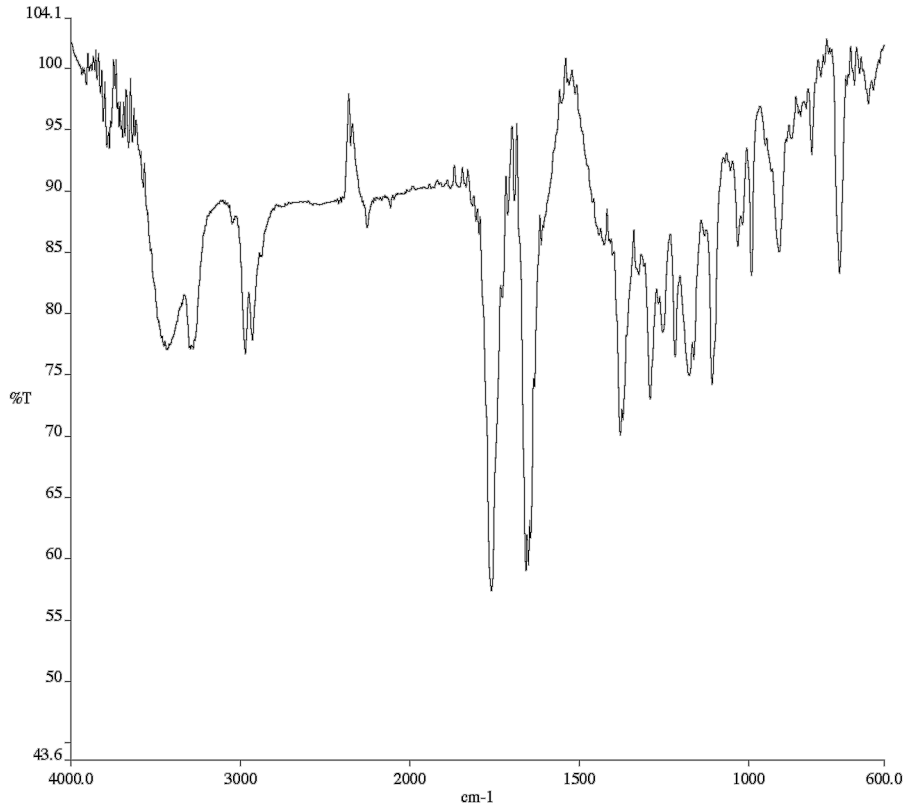
Infrared spectrum (Thin Film, NaCl) of compound **21**.



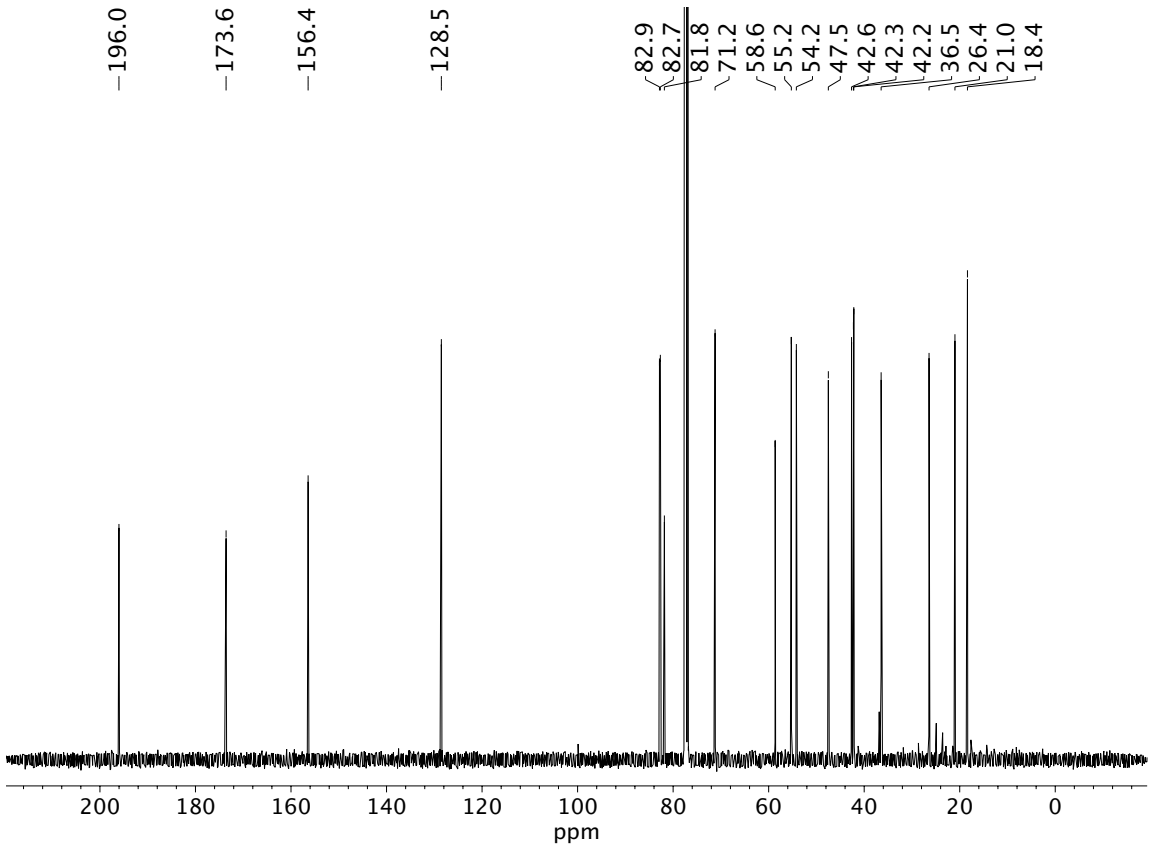
^{13}C NMR (100 MHz, $CDCl_3$) of compound **21.**



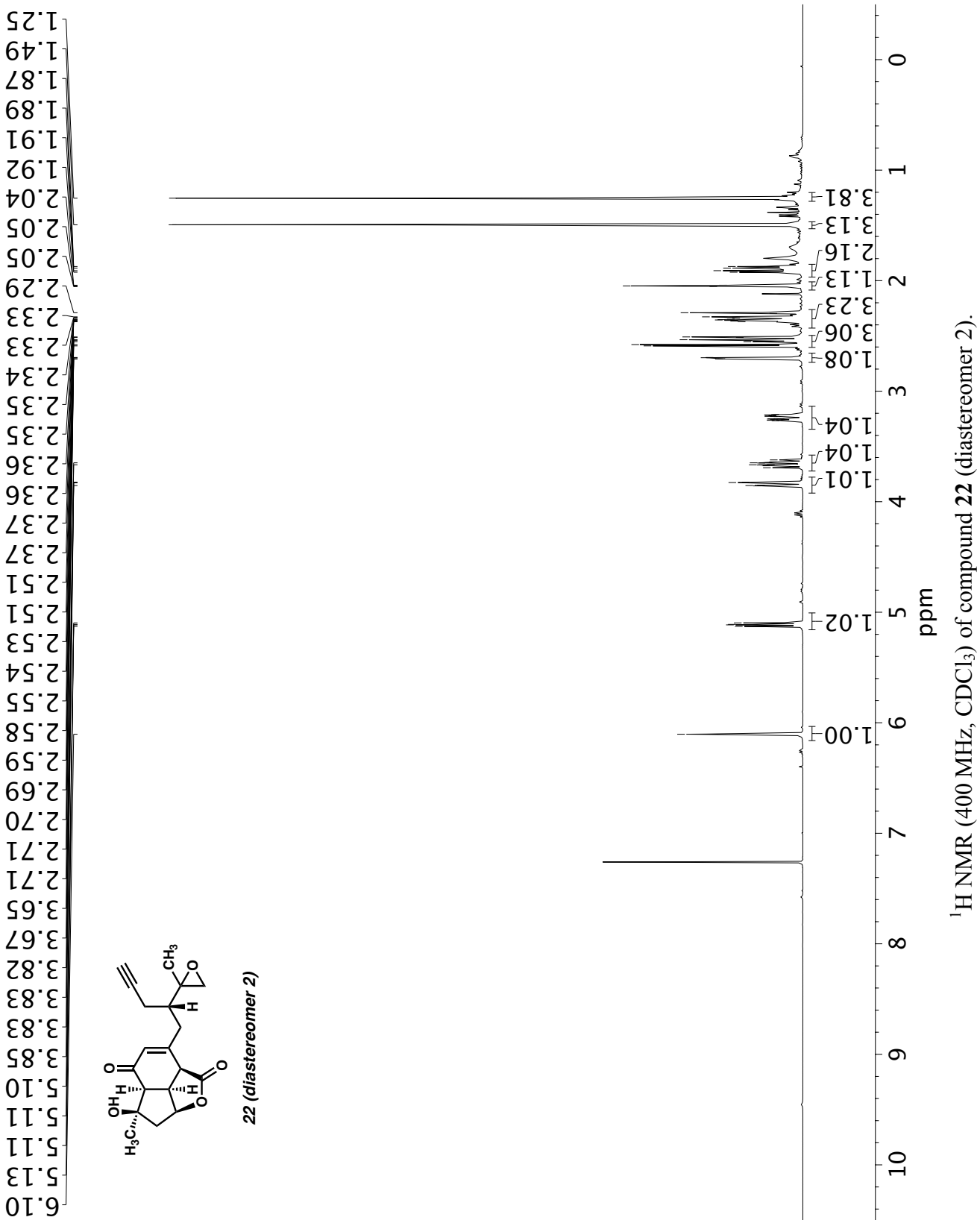
^{1}H NMR (400 MHz, $CDCl_3$) of compound **22** (diastereomer 1).



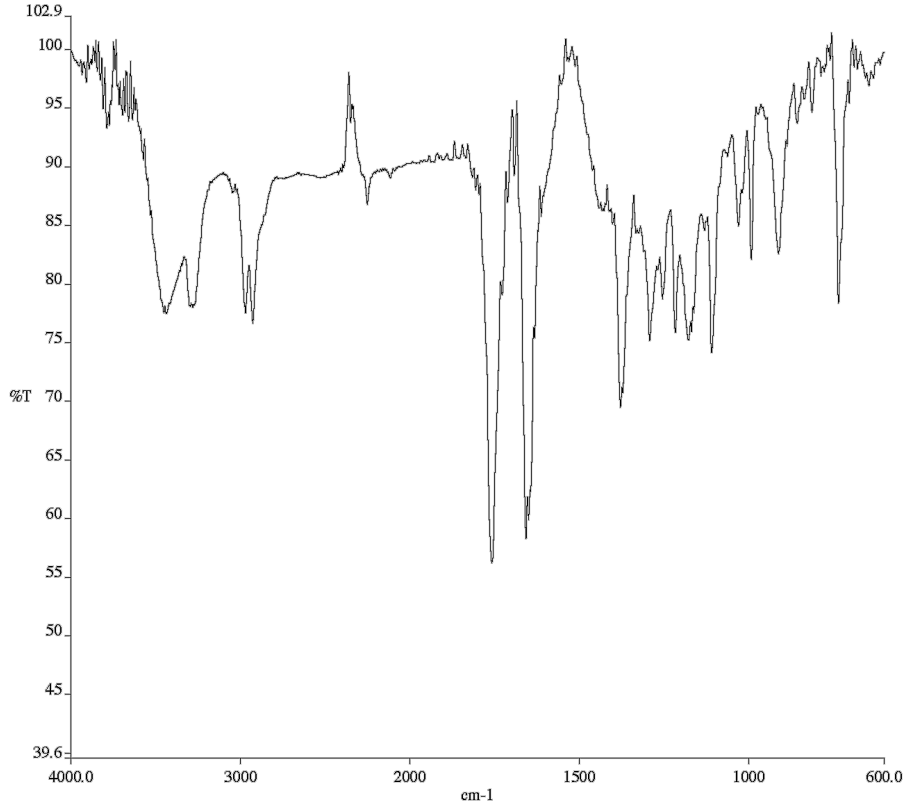
Infrared spectrum (Thin Film, NaCl) of compound **22** (diastereomer 1).



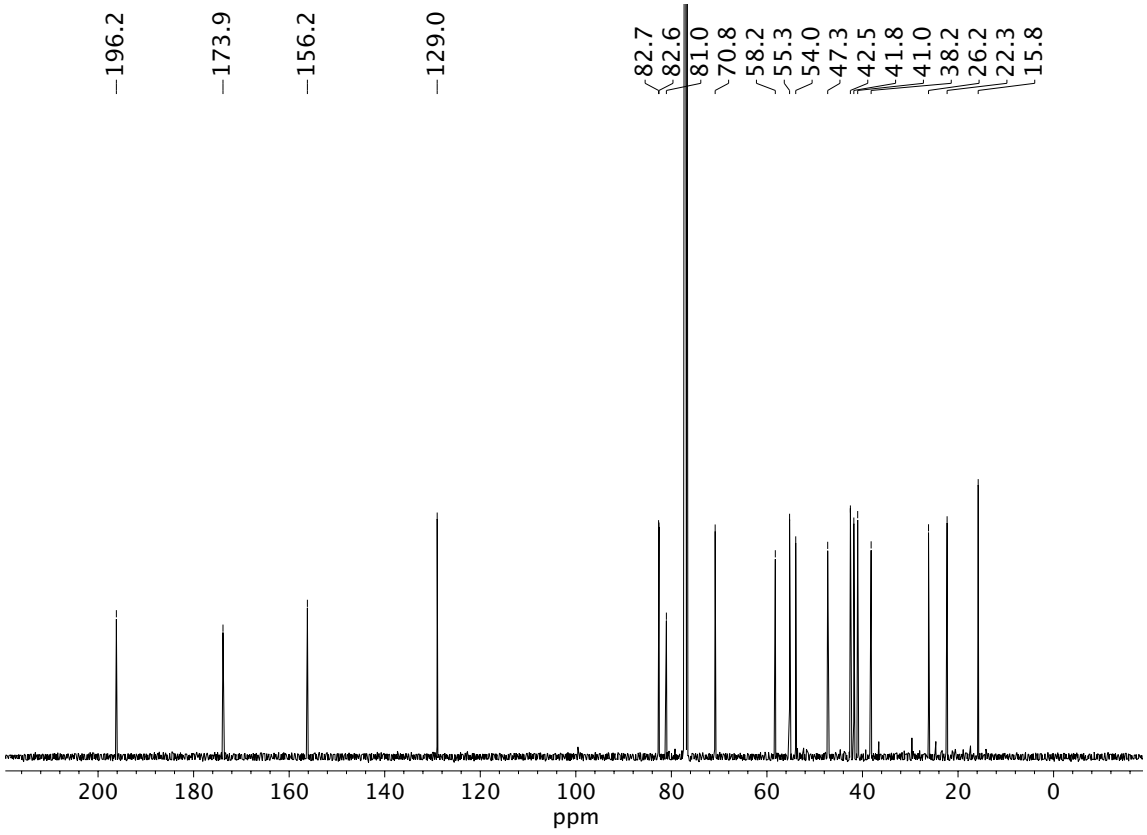
^{13}C NMR (100 MHz, $CDCl_3$) of compound **22** (diastereomer 1).



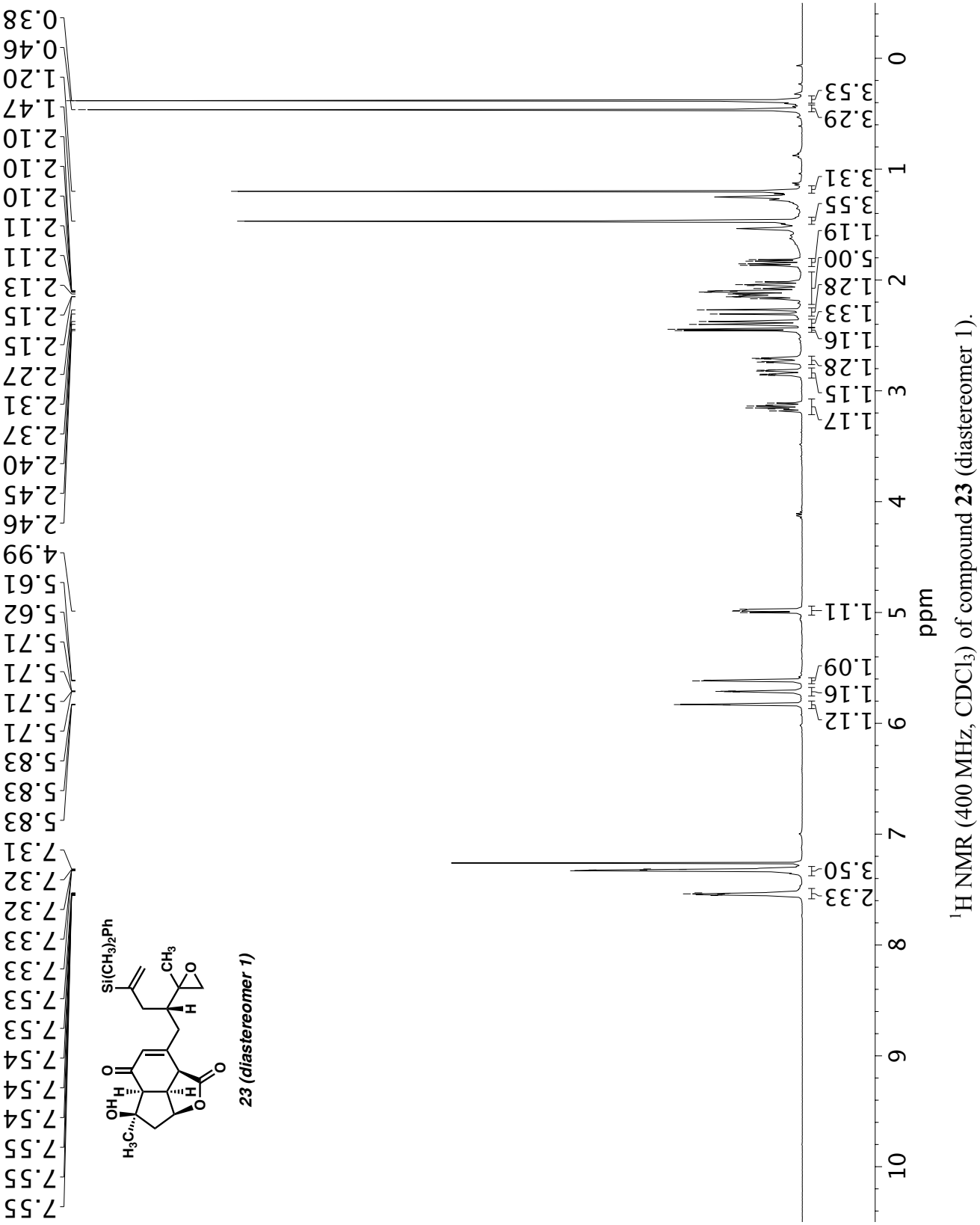
^{1}H NMR (400 MHz, $CDCl_3$) of compound **22** (diastereomer 2).



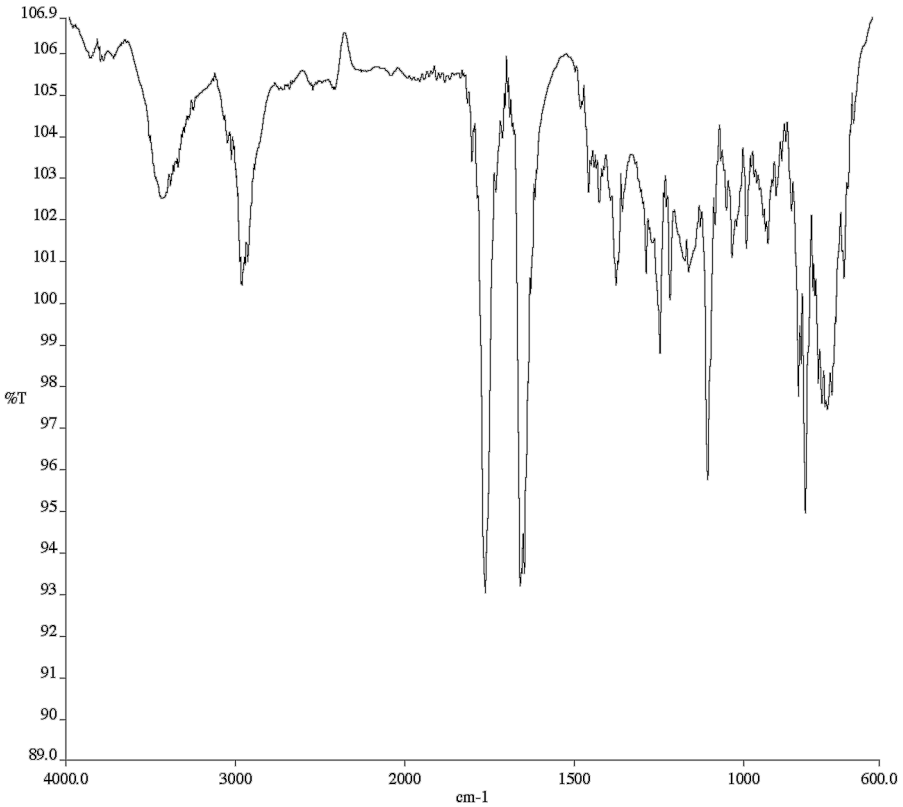
Infrared spectrum (Thin Film, NaCl) of compound **22** (diastereomer 2).



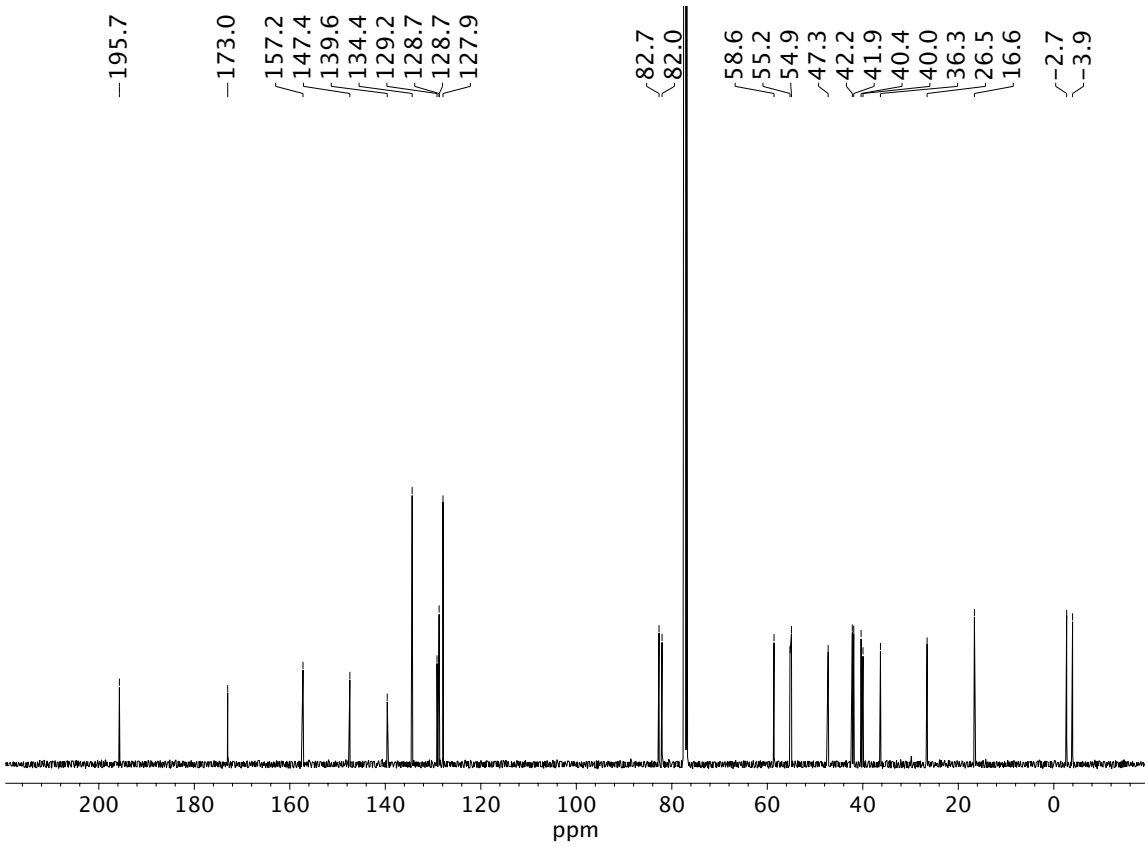
^{13}C NMR (100 MHz, $CDCl_3$) of compound **22** (diastereomer 2).



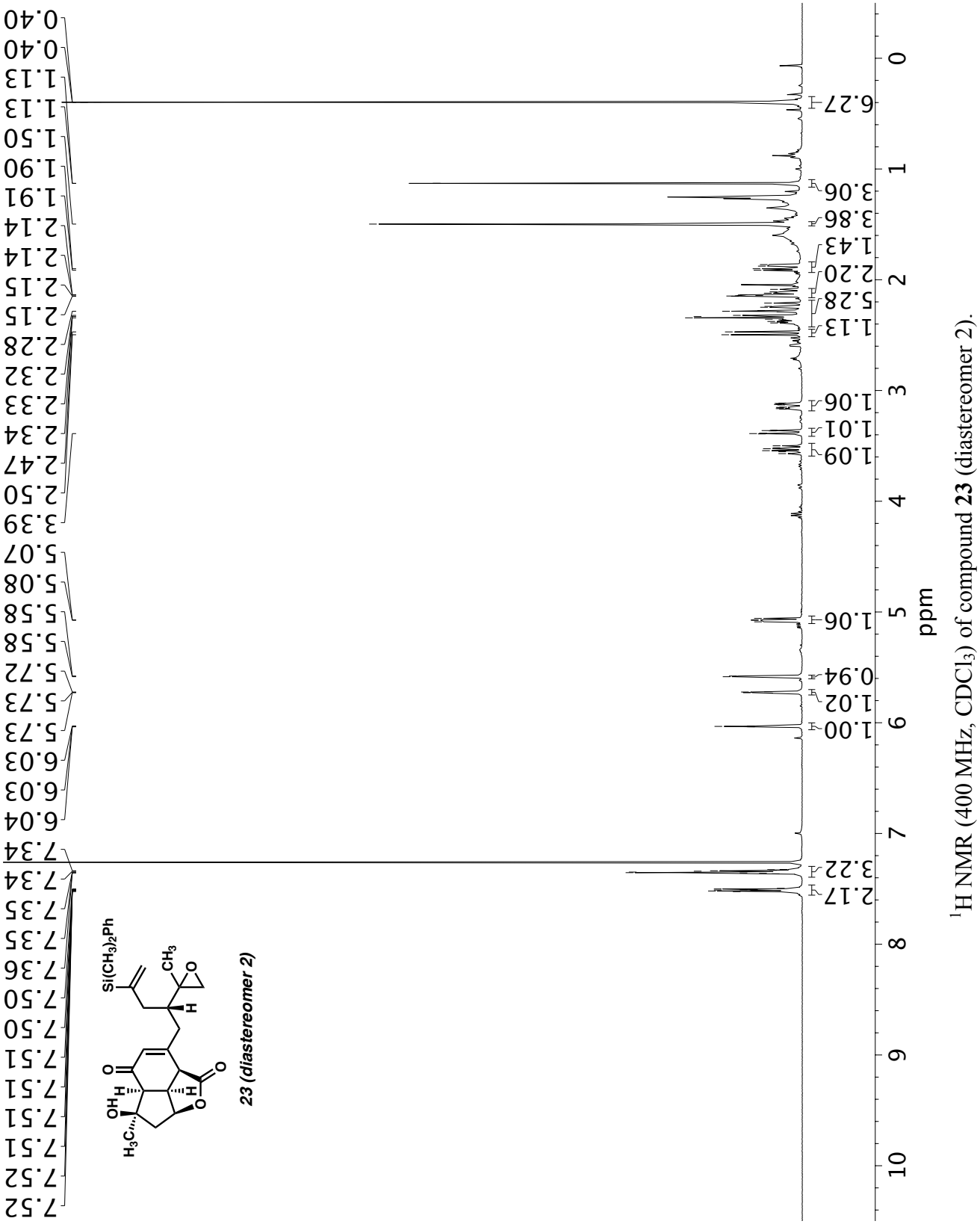
^{1}H NMR (400 MHz, $CDCl_3$) of compound **23** (diastereomer 1).



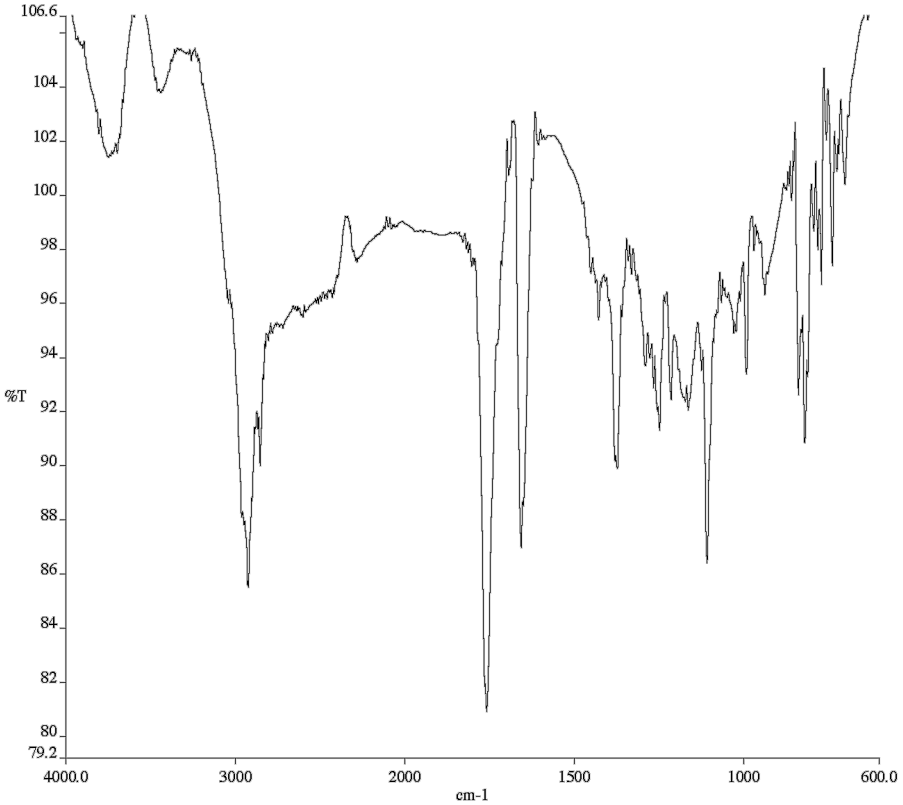
Infrared spectrum (Thin Film, NaCl) of compound **23** (diastereomer 1).



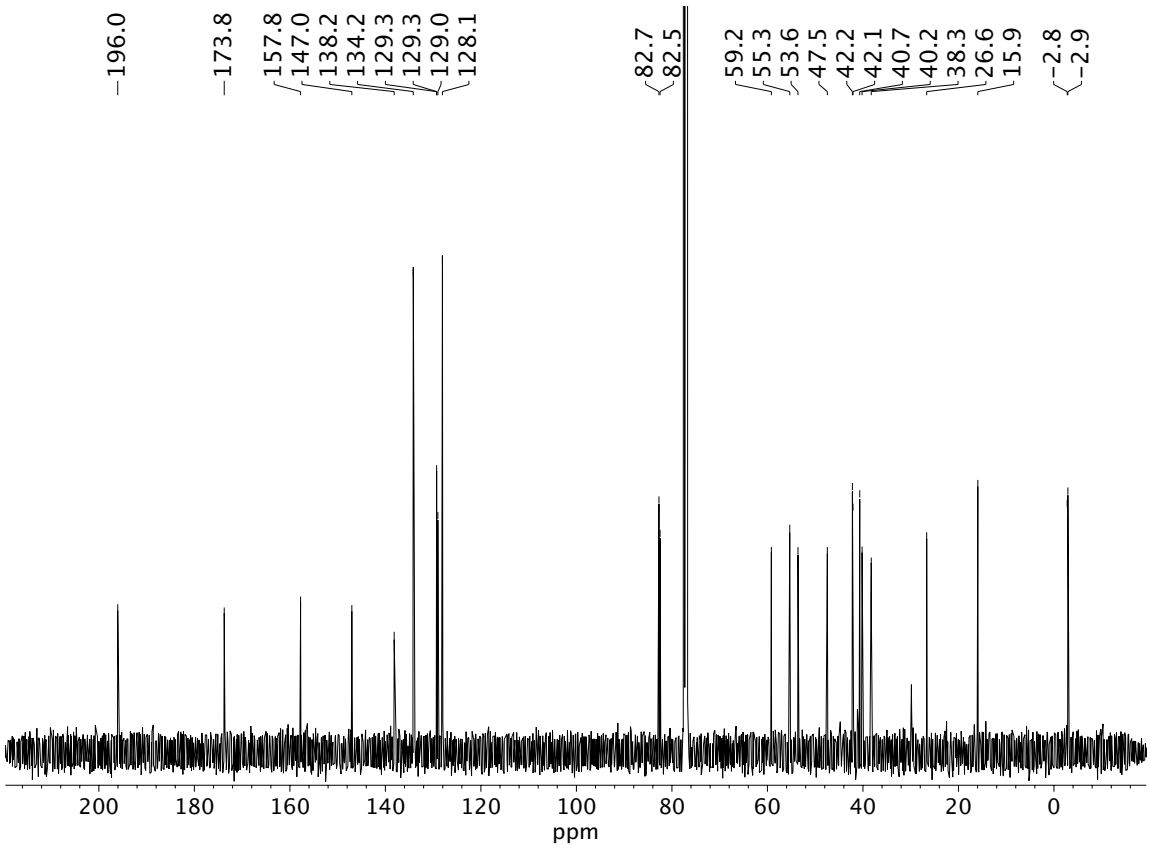
^{13}C NMR (100 MHz, $CDCl_3$) of compound **23** (diastereomer 1).



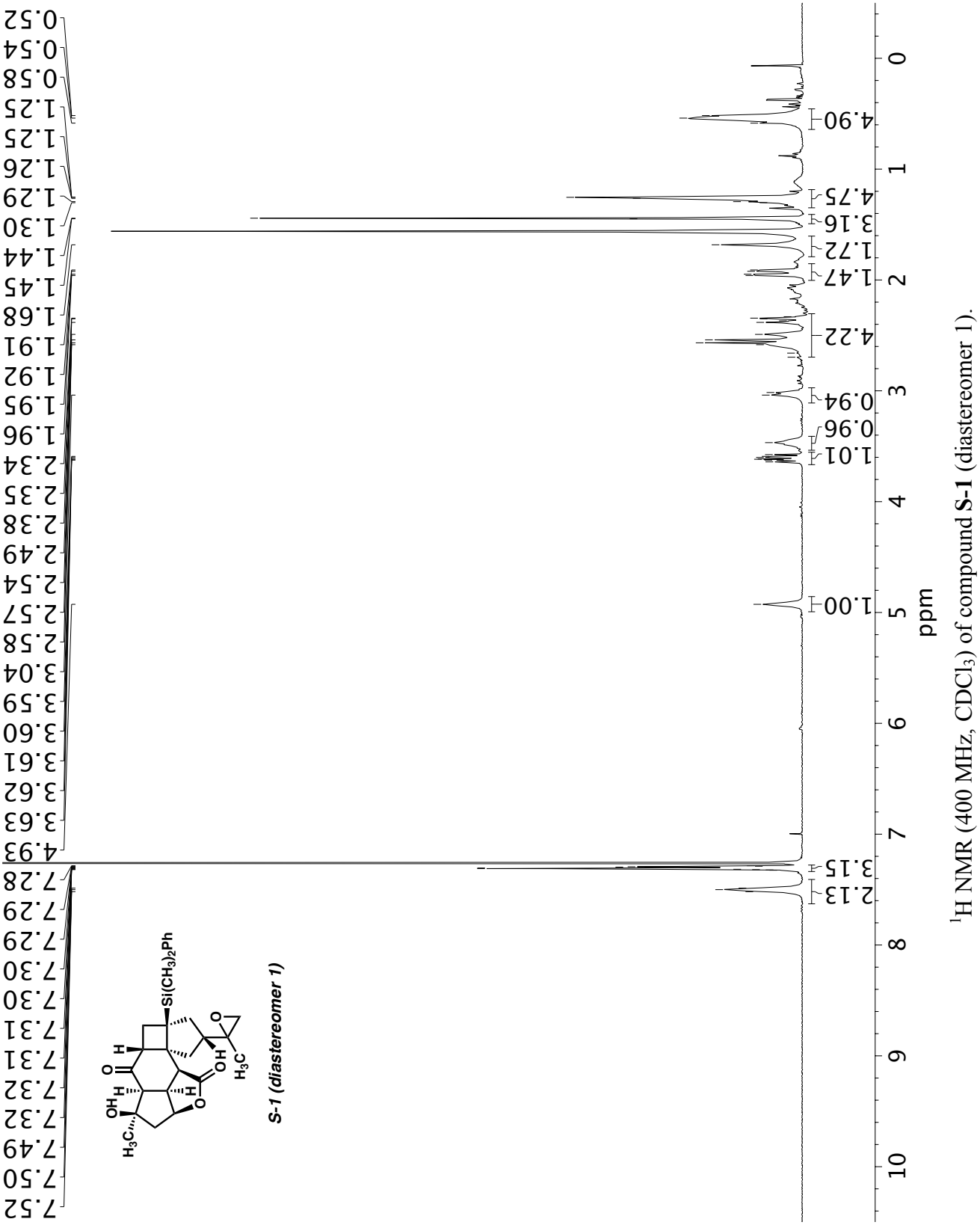
^{1}H NMR (400 MHz, $CDCl_3$) of compound **23** (diastereomer 2).



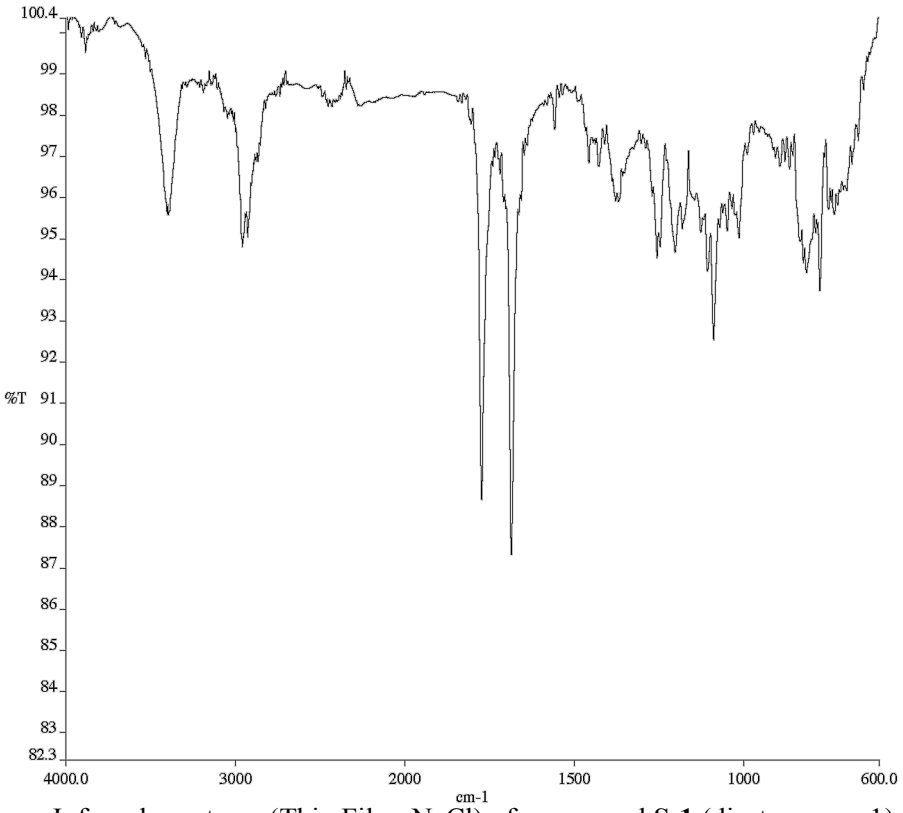
Infrared spectrum (Thin Film, NaCl) of compound **23** (diastereomer 2).



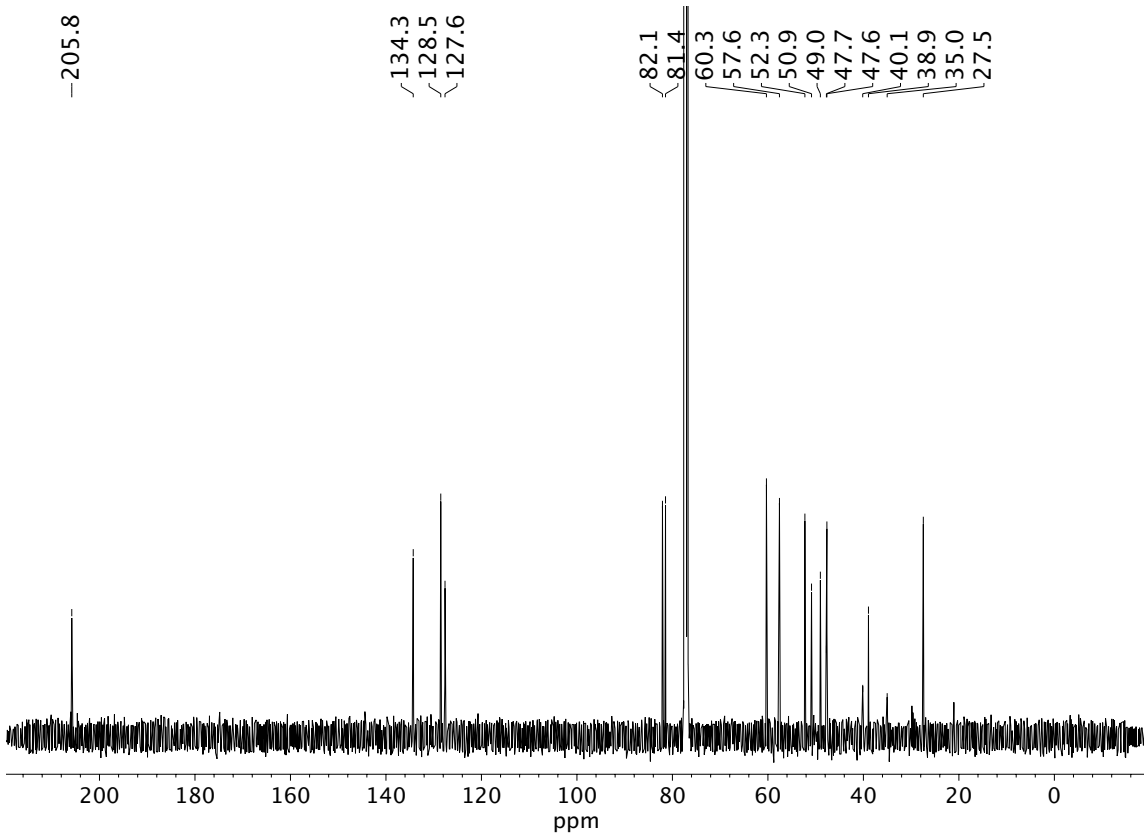
^{13}C NMR (100 MHz, $CDCl_3$) of compound **23** (diastereomer 2).



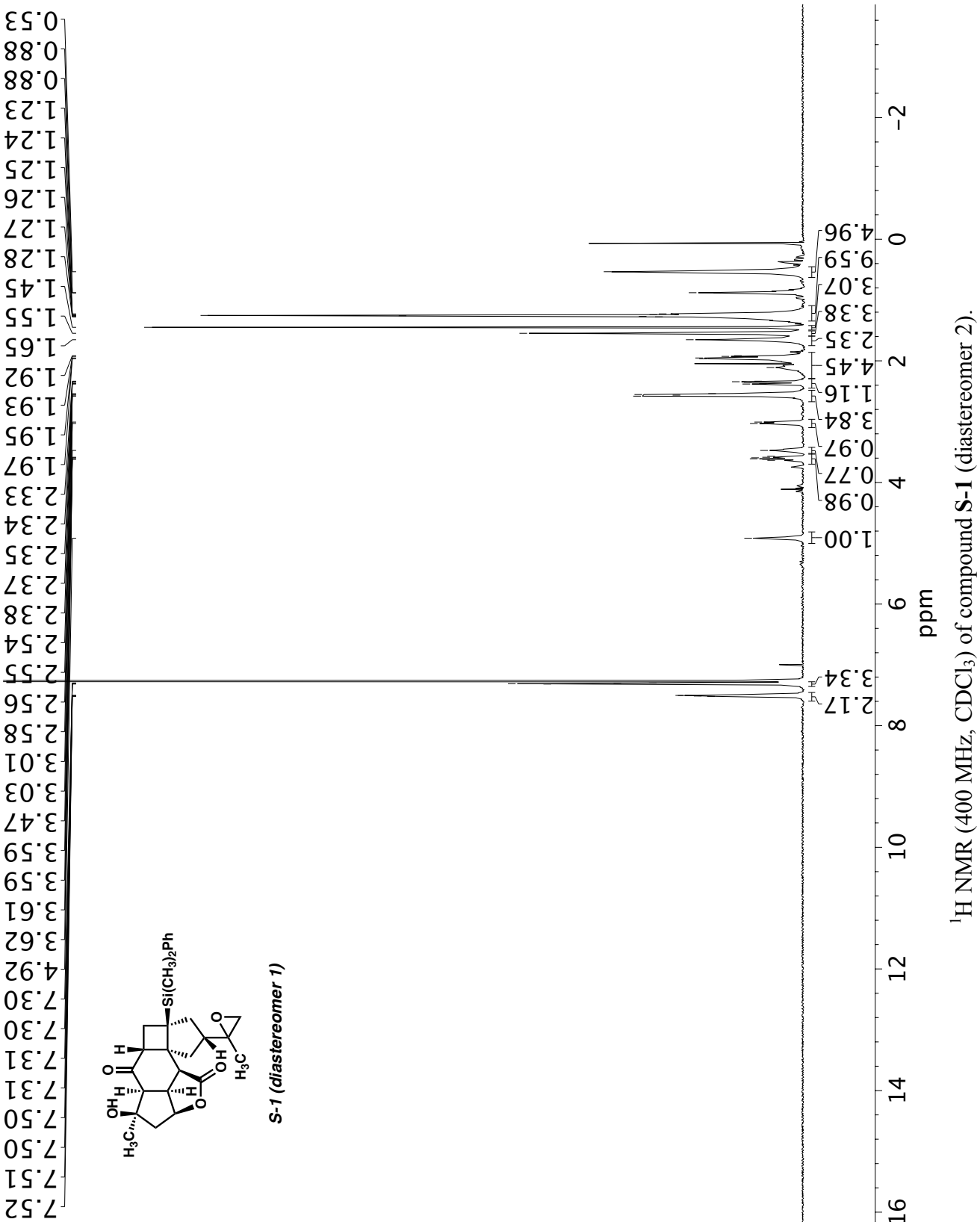
^{1}H NMR (400 MHz, $CDCl_3$) of compound **S-1** (diastereomer 1).



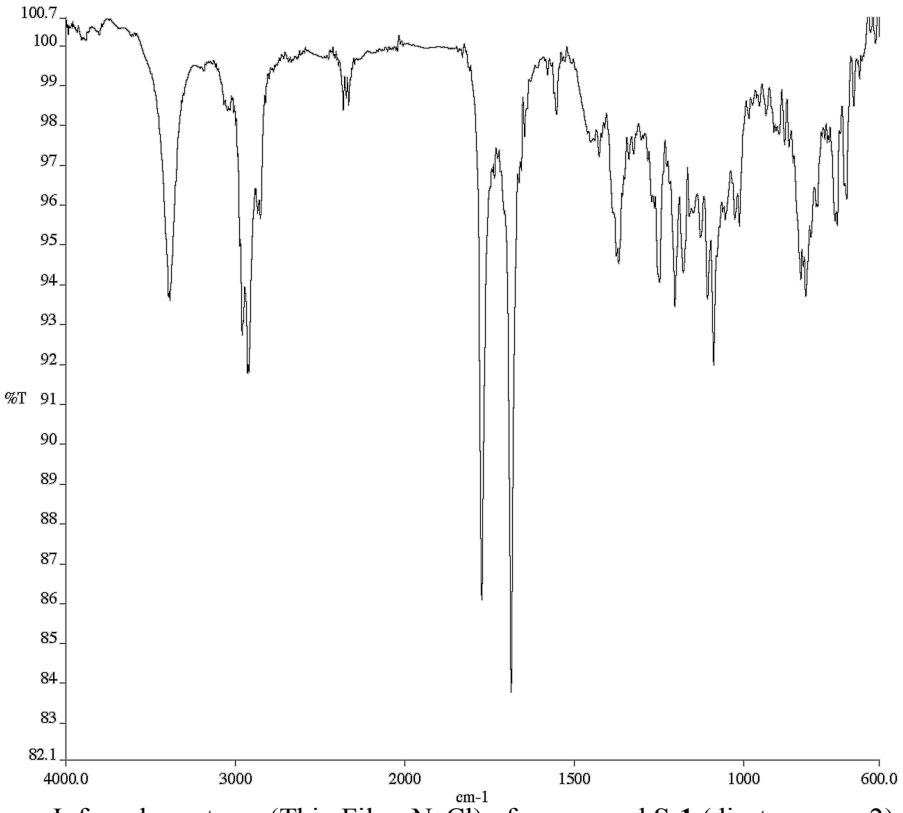
Infrared spectrum (Thin Film, NaCl) of compound **S-1** (diastereomer 1).



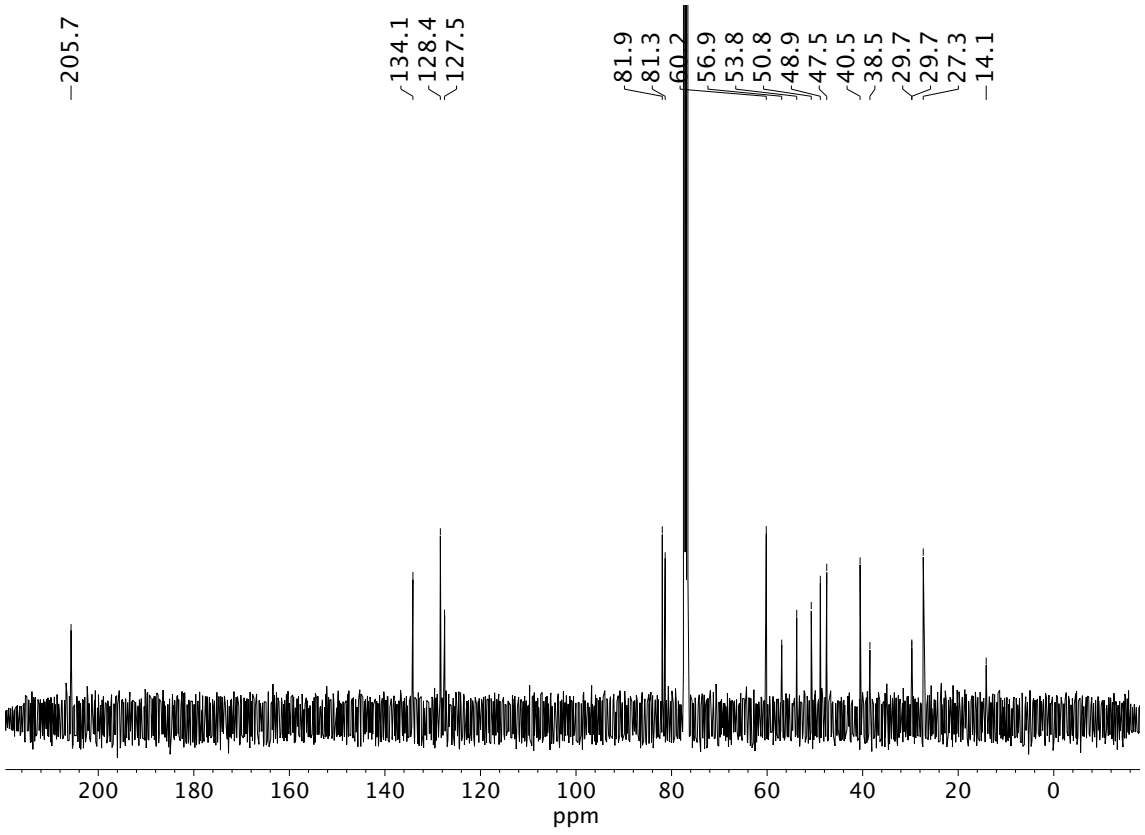
^{13}C NMR (100 MHz, $CDCl_3$) of compound **S-1** (diastereomer 1).



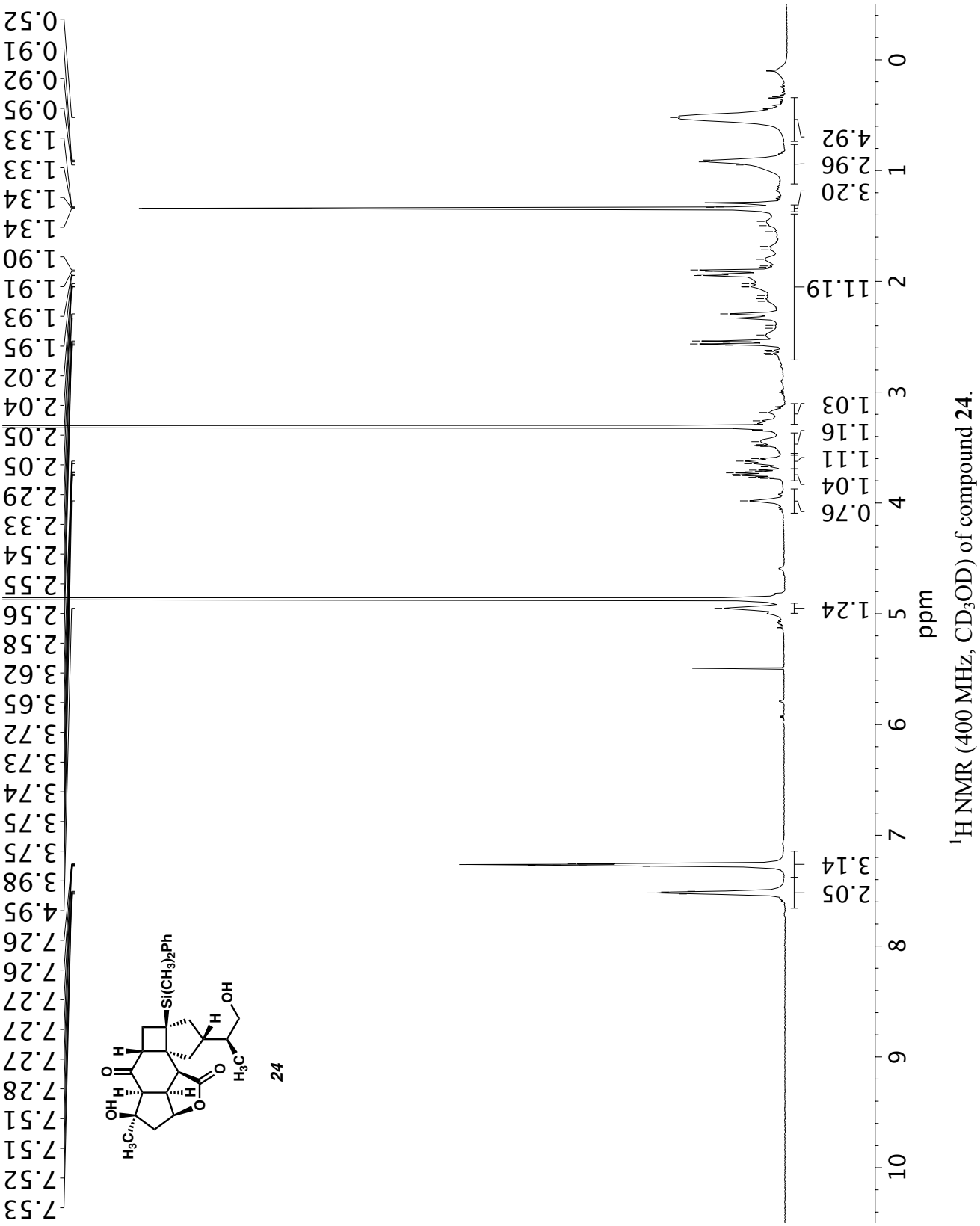
^{1}H NMR (400 MHz, $CDCl_3$) of compound **S-1** (diastereomer 2).



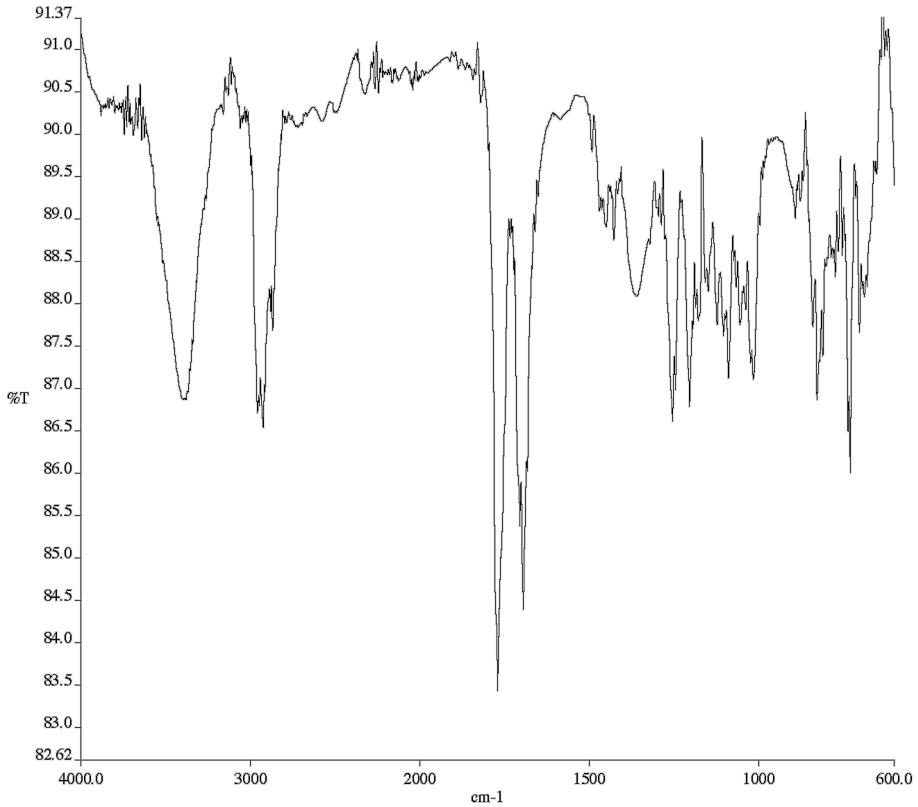
Infrared spectrum (Thin Film, NaCl) of compound **S-1** (diastereomer 2).



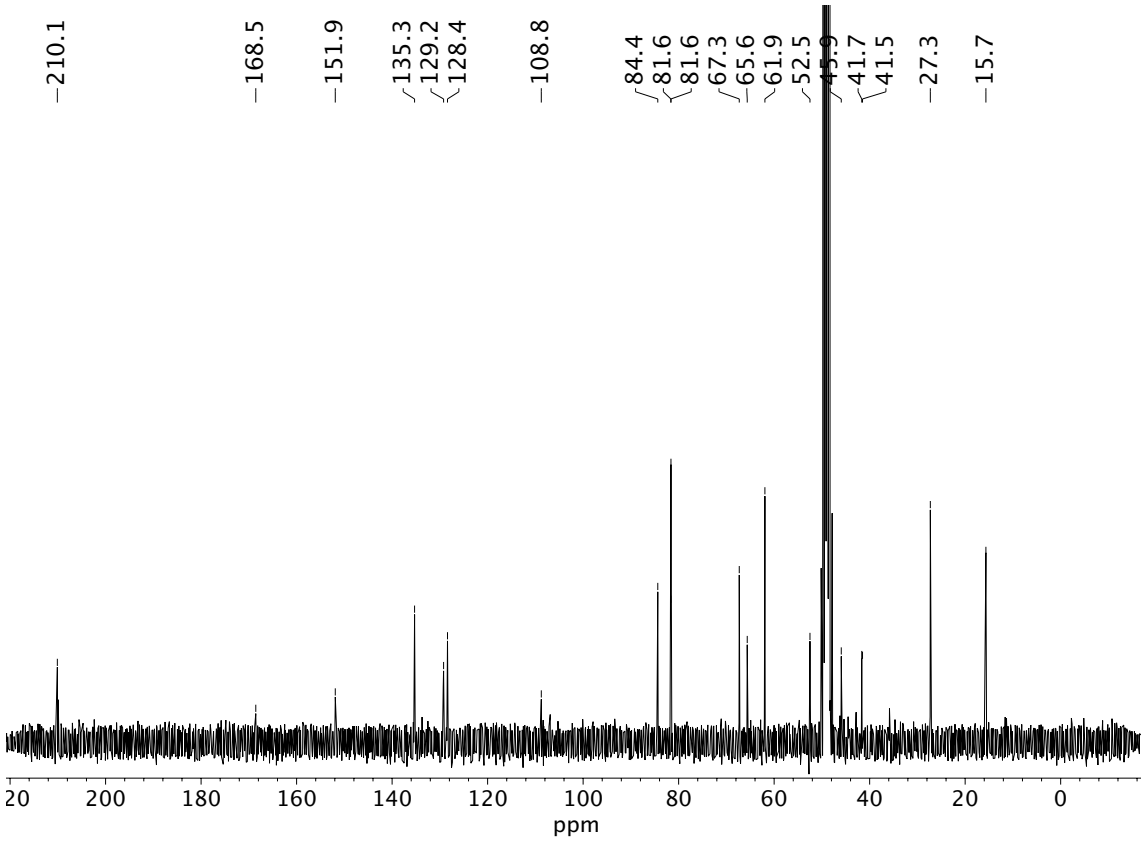
^{13}C NMR (100 MHz, $CDCl_3$) of compound **S-1** (diastereomer 2).



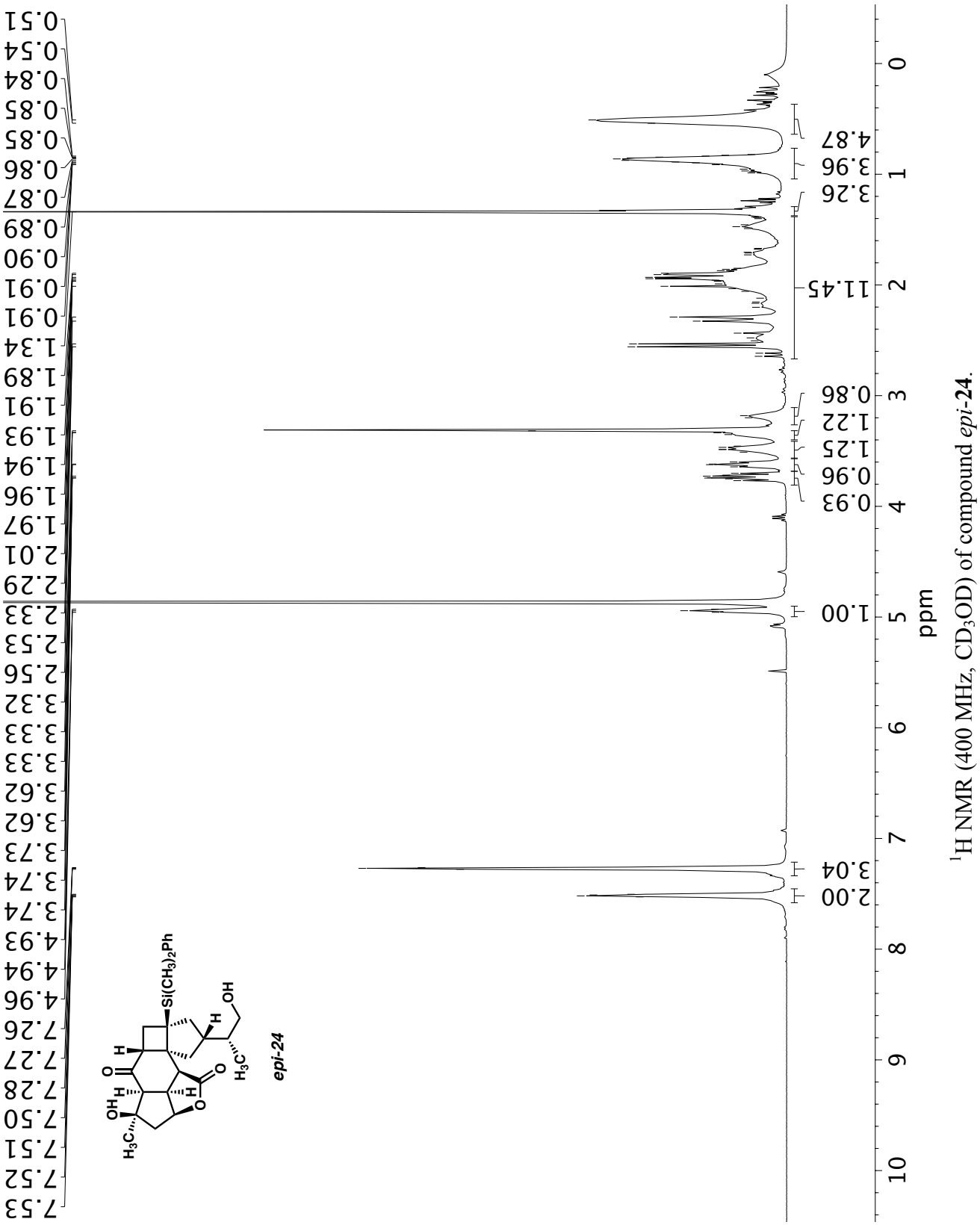
^{1}H NMR (400 MHz, CD_3OD) of compound **24**.



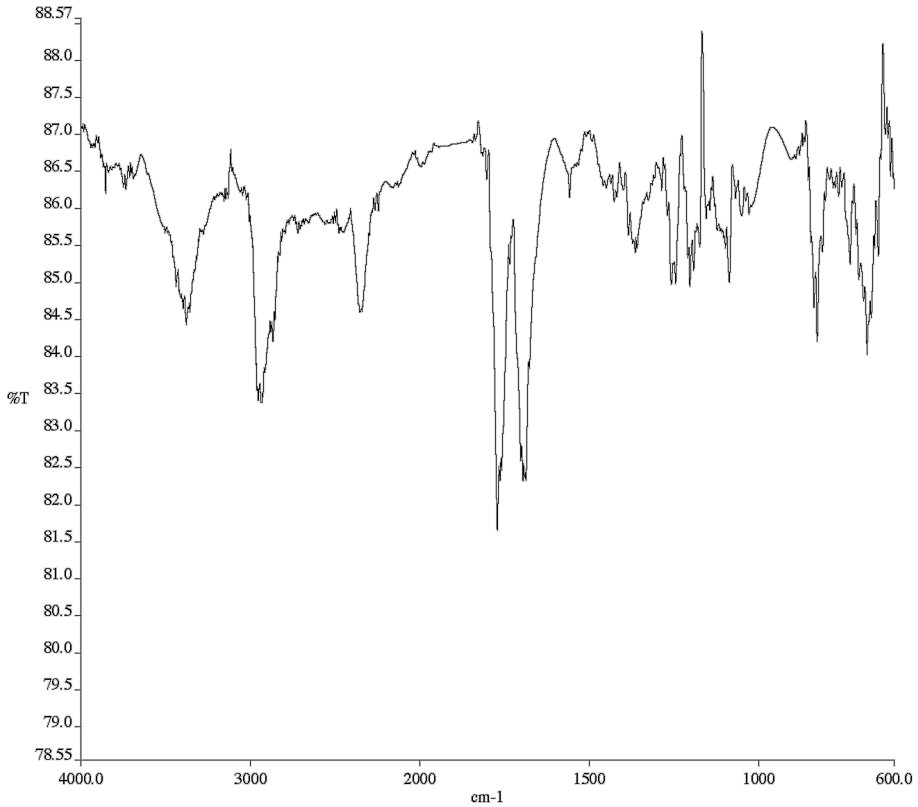
Infrared spectrum (Thin Film, NaCl) of compound **24**.



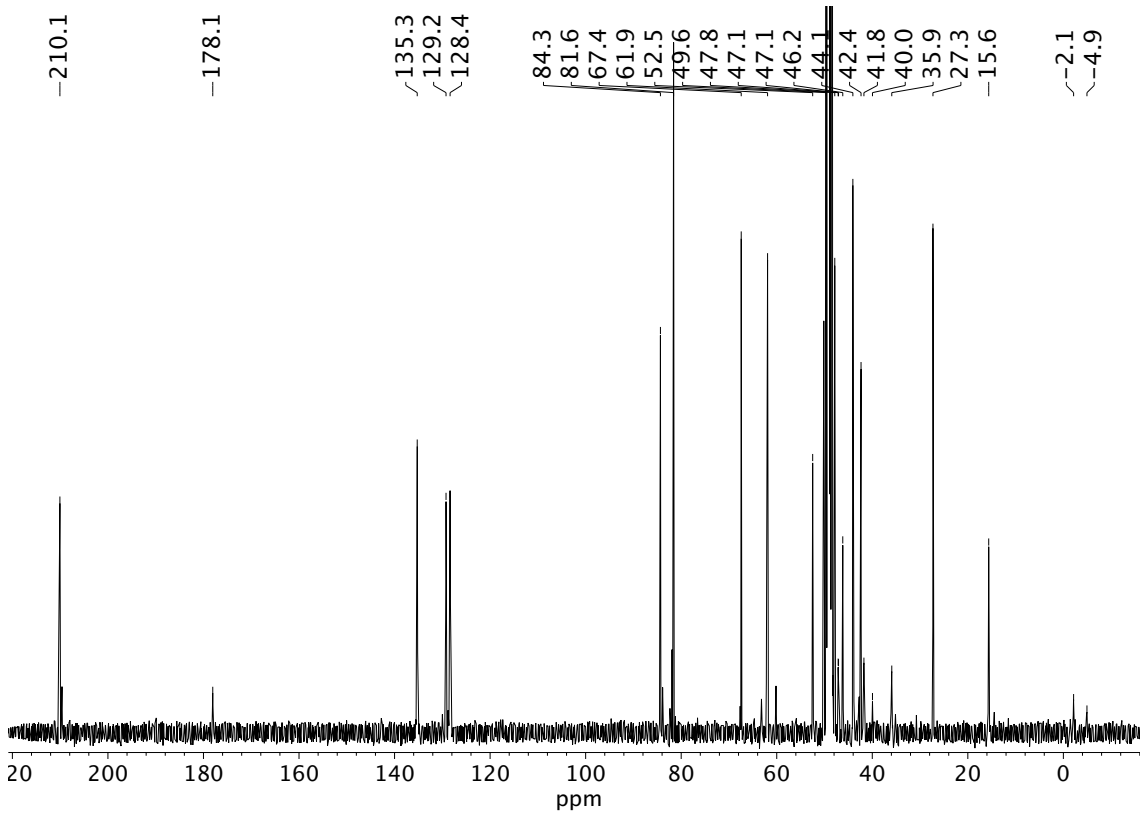
^{13}C NMR (100 MHz, CD_3OD) of compound **24**.



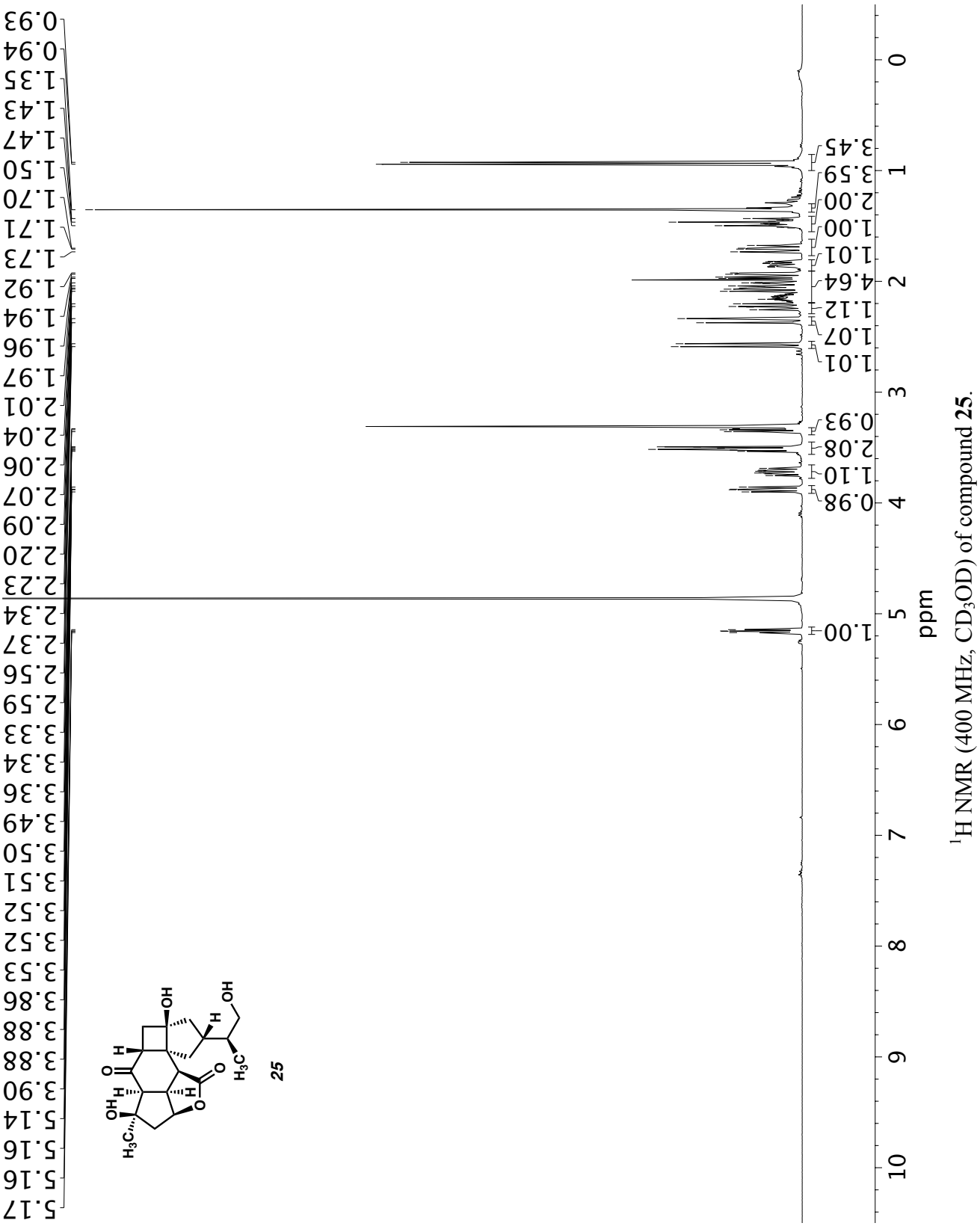
^{1}H NMR (400 MHz, CD_3OD) of compound *epi*-**24**.



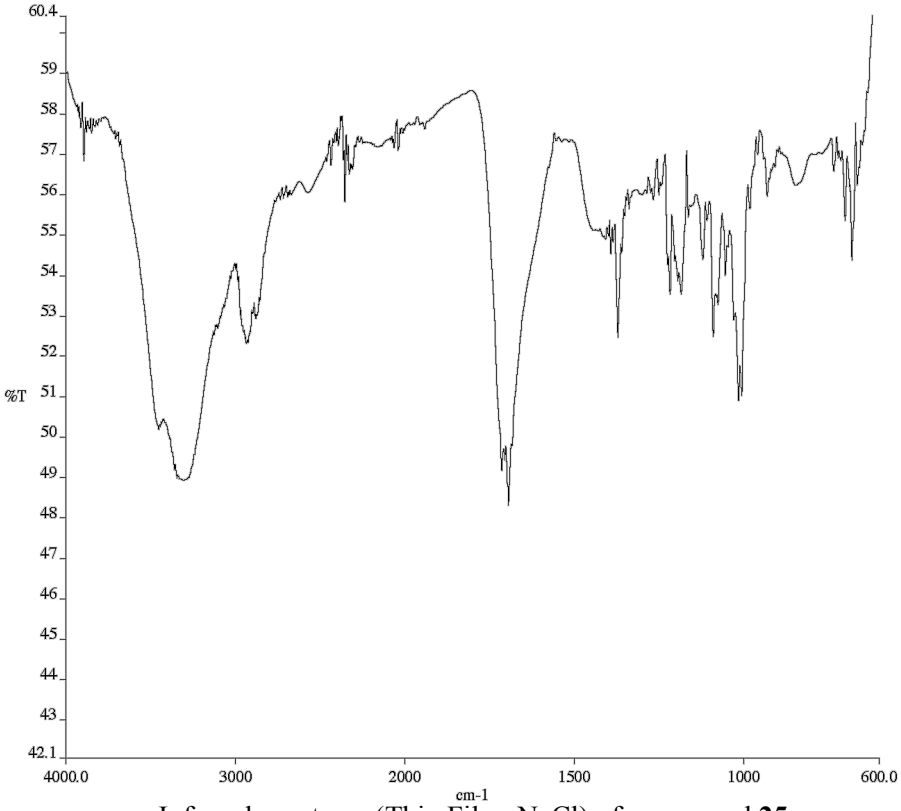
Infrared spectrum (Thin Film, NaCl) of compound *epi*-**24**.



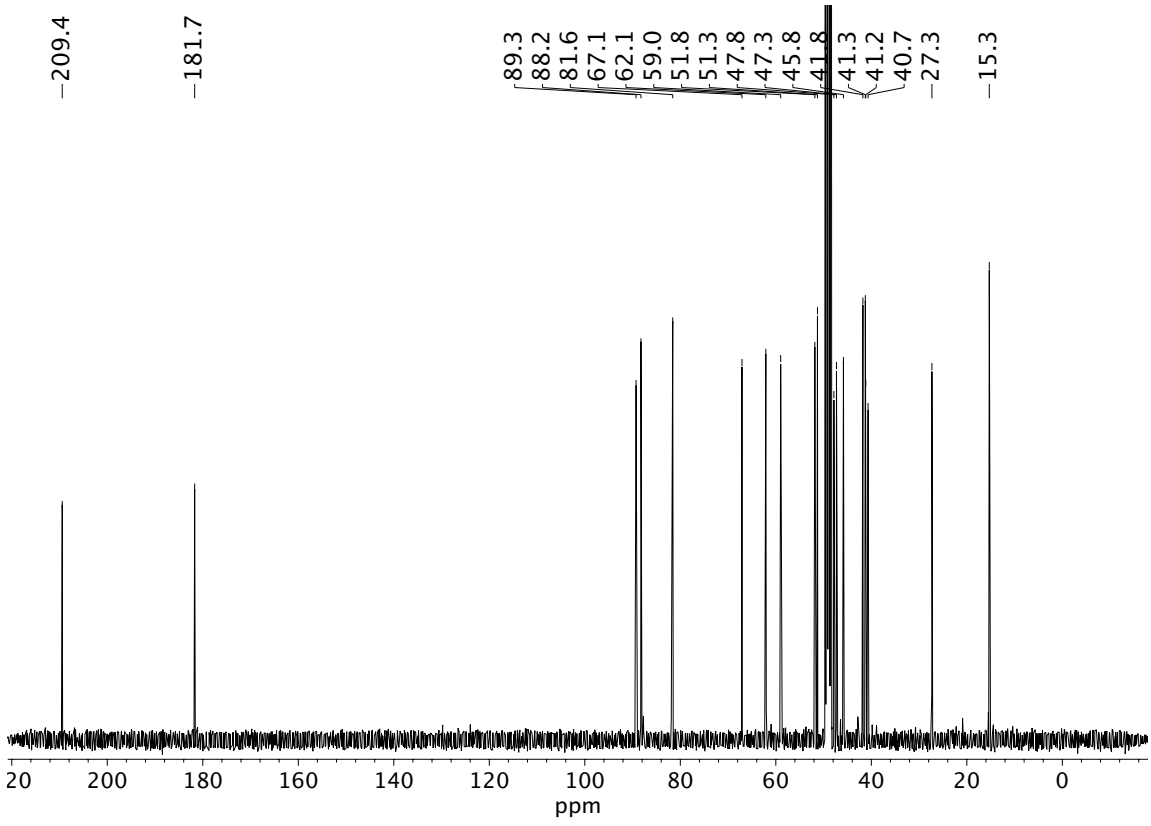
^{13}C NMR (100 MHz, CD_3OD) of compound *epi*-**24**.



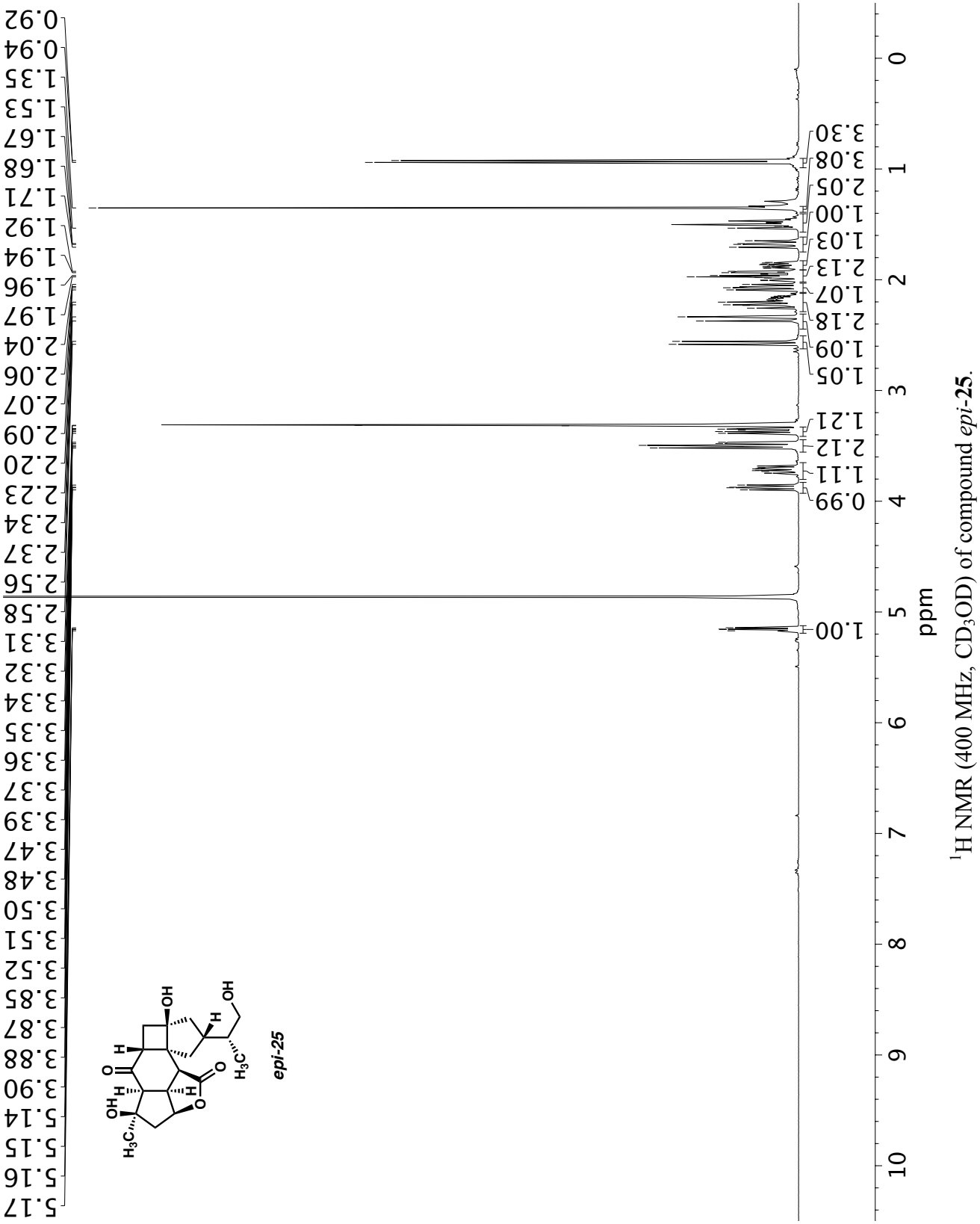
^{1}H NMR (400 MHz, CD_3OD) of compound **25**.



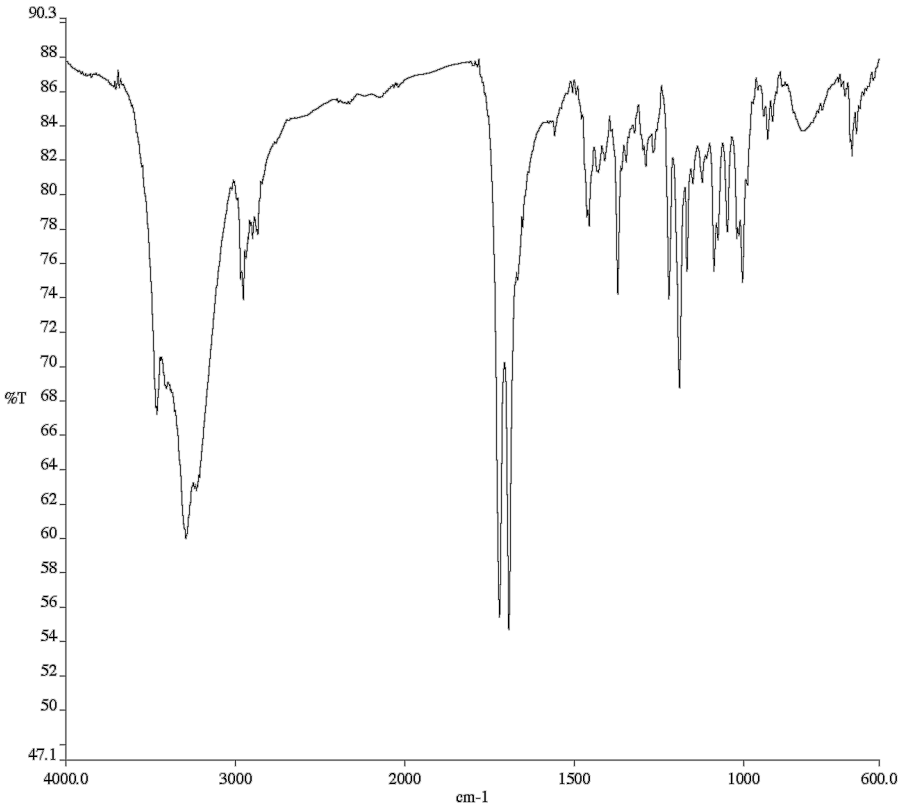
Infrared spectrum (Thin Film, NaCl) of compound **25**.



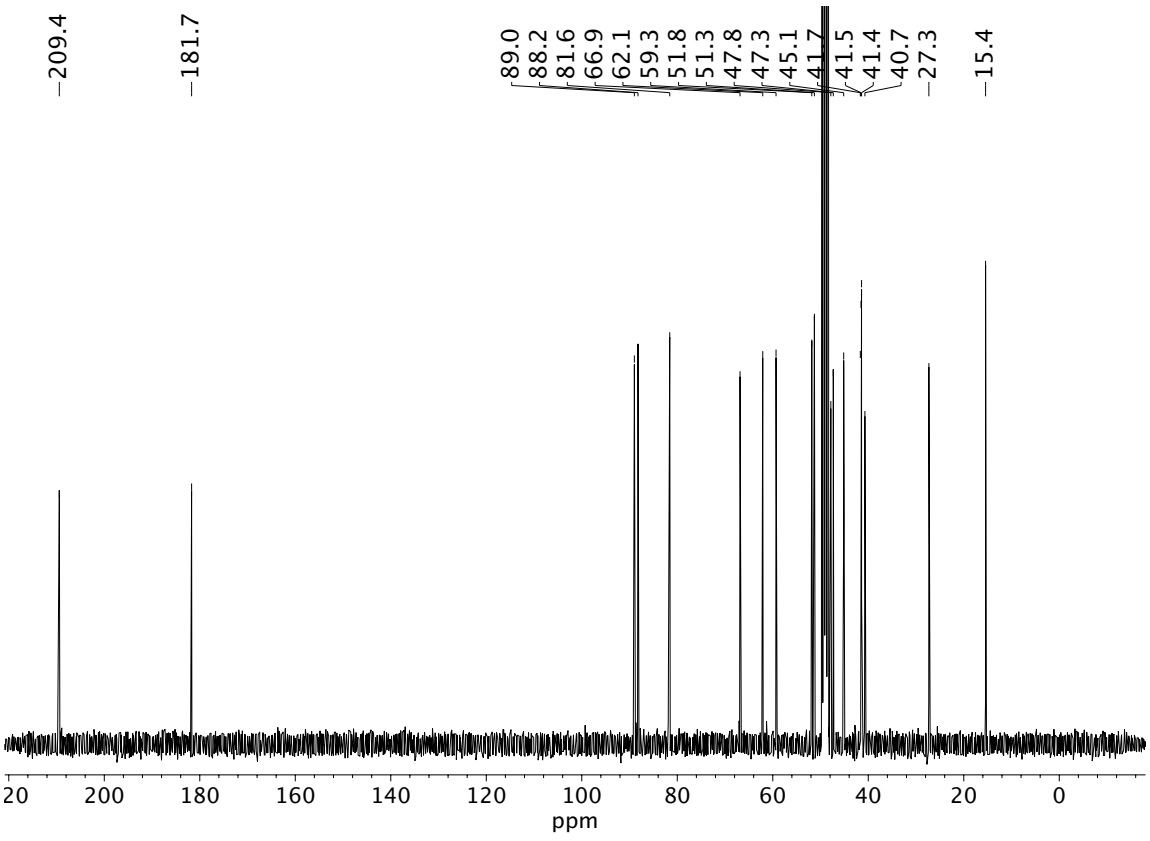
^{13}C NMR (100 MHz, CD_3OD) of compound **25**.



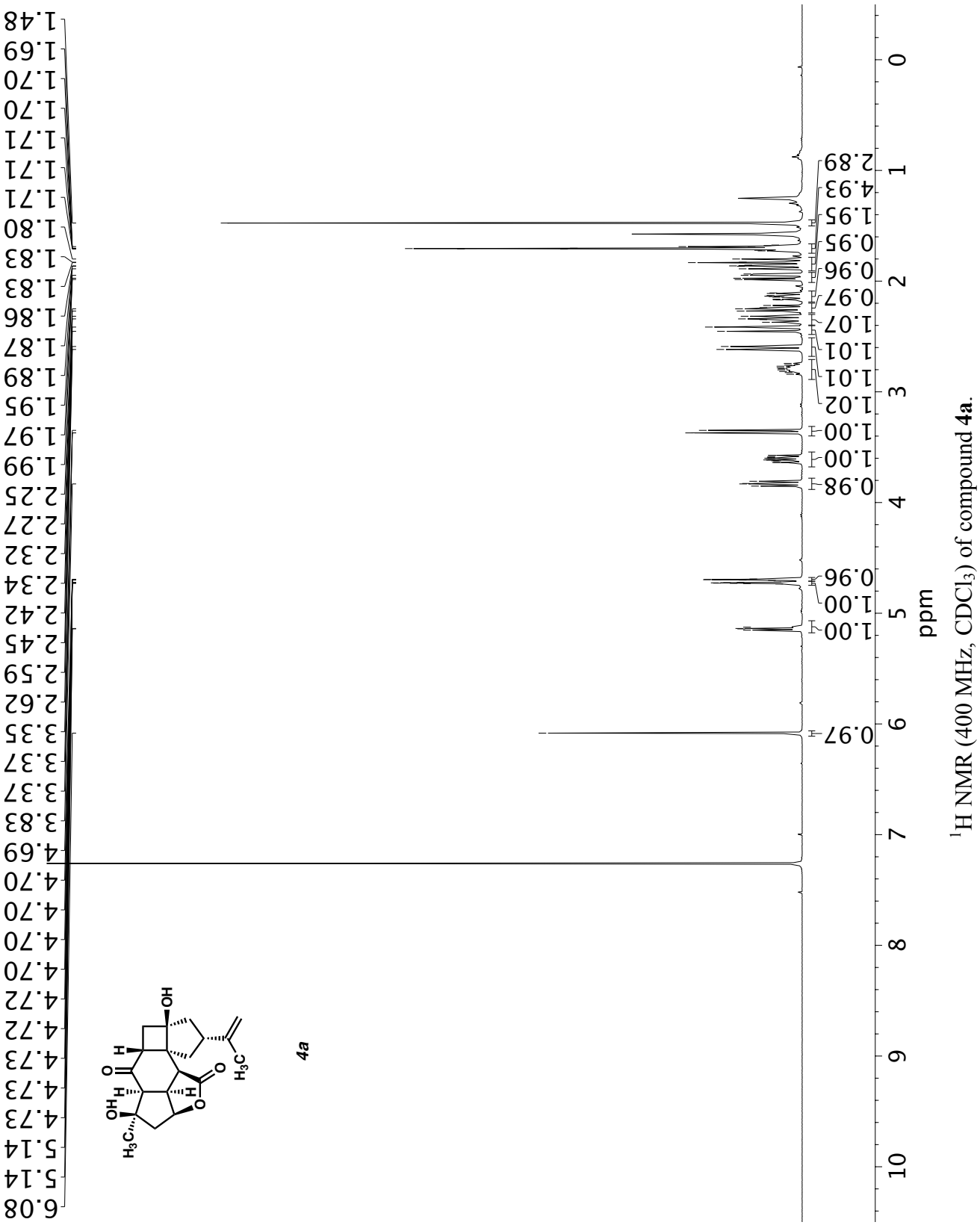
^{1}H NMR (400 MHz, CD_3OD) of compound *epi*-**25**.



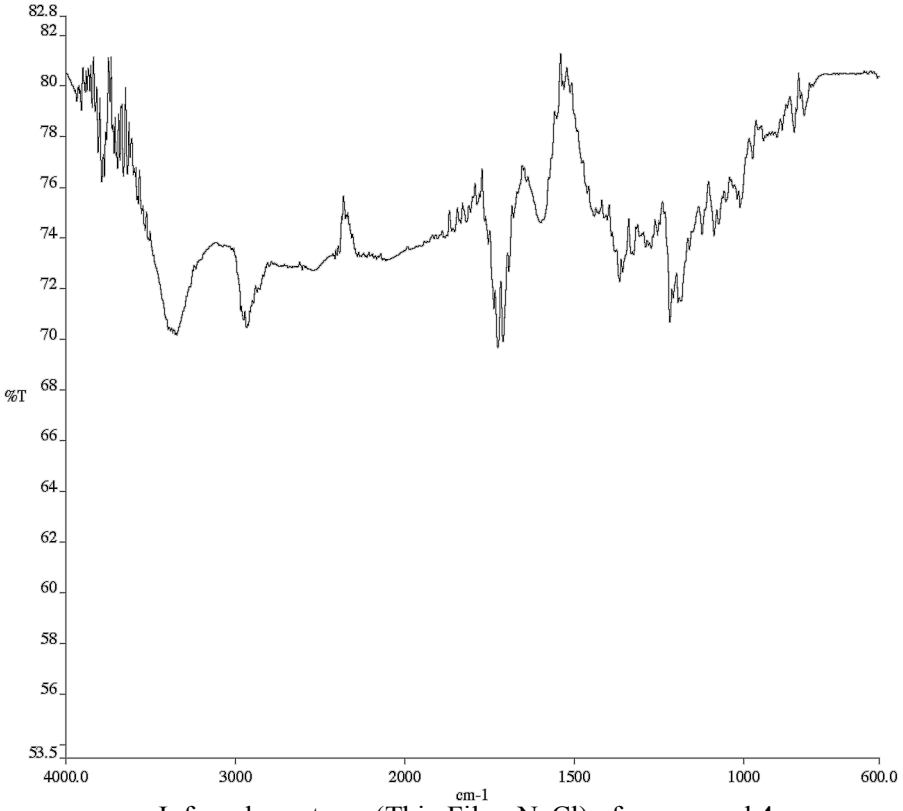
Infrared spectrum (Thin Film, NaCl) of compound *epi*-**25**.



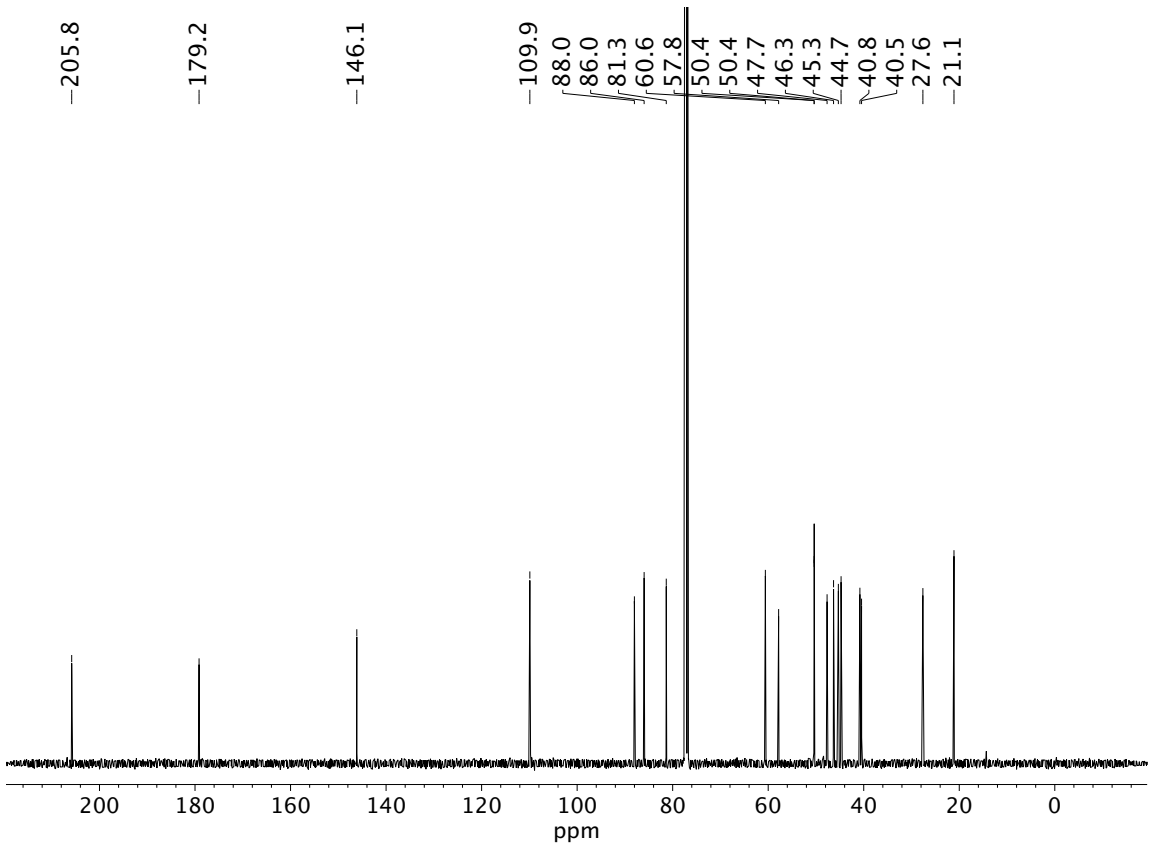
^{13}C NMR (100 MHz, $CDCl_3$) of compound **22** (diastereomer 2).



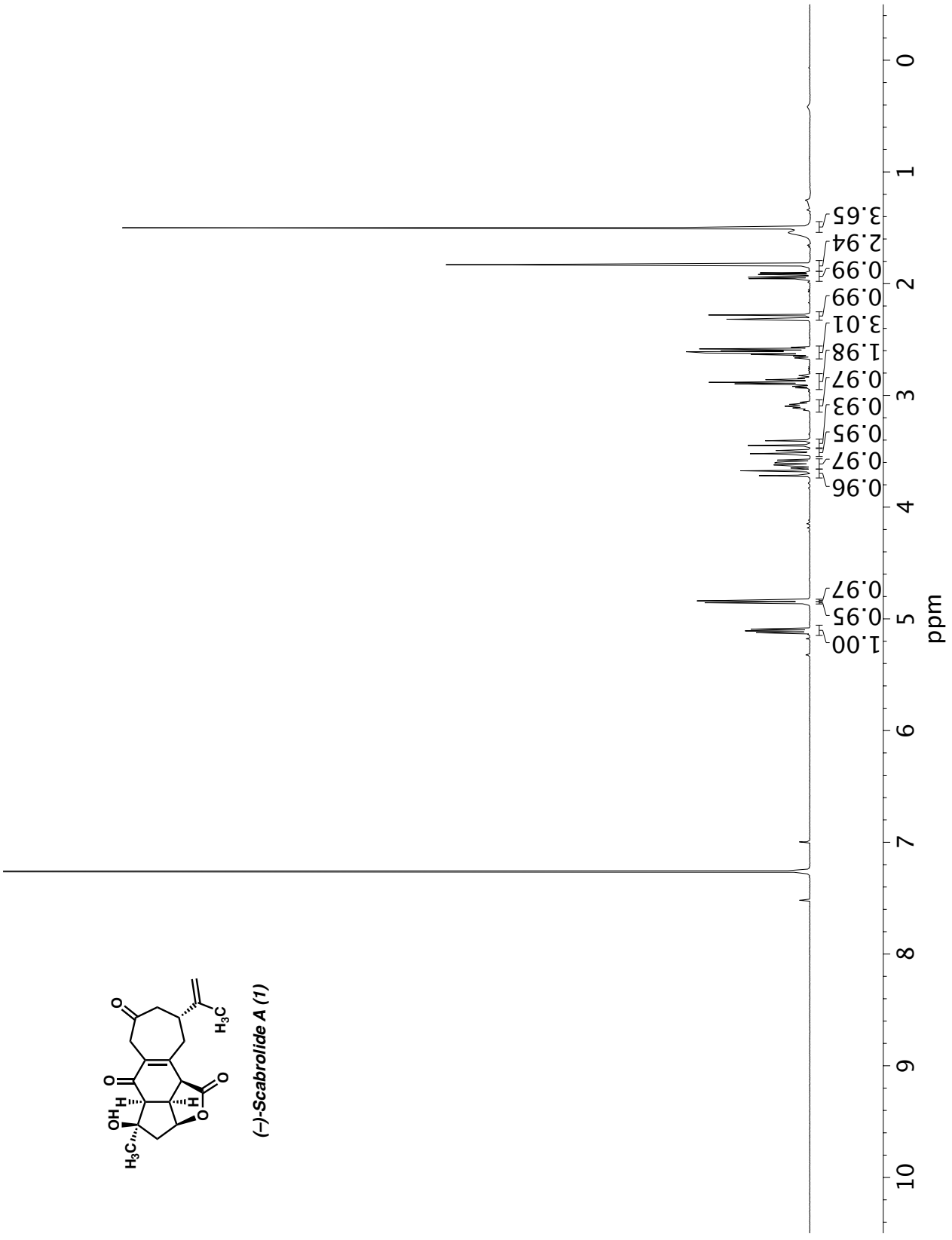
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4a**.



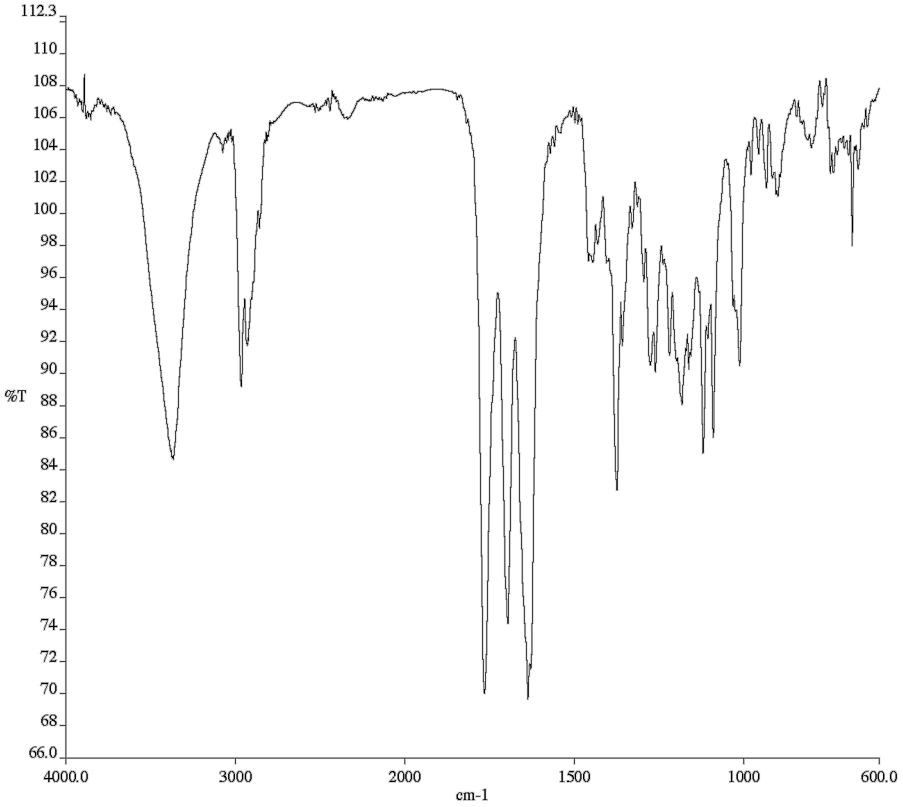
Infrared spectrum (Thin Film, NaCl) of compound **4a**.



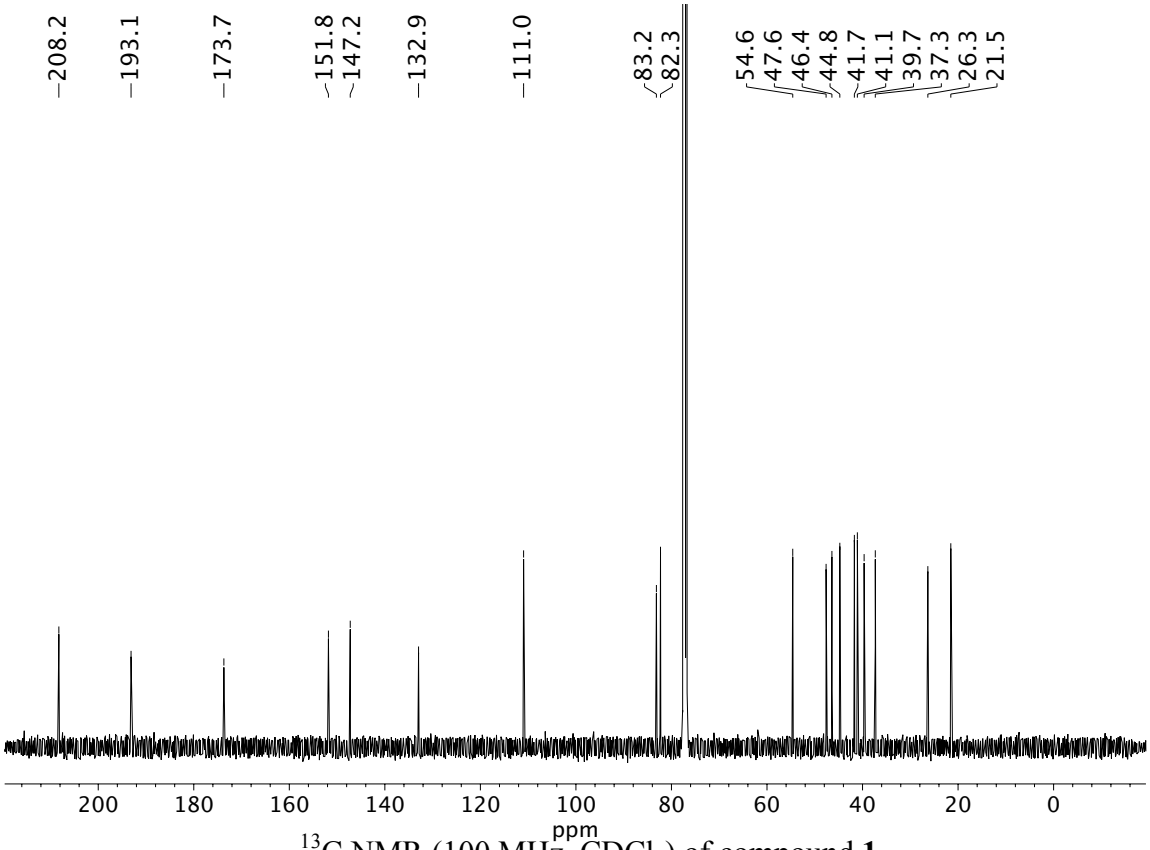
^{13}C NMR (100 MHz, $CDCl_3$) of compound **4a**.



^{1}H NMR (400 MHz, $CDCl_3$) of compound **1**.



Infrared spectrum (Thin Film, NaCl) of compound **1**.



^{13}C NMR (100 MHz, $CDCl_3$) of compound **1**.

X-ray Crystal Structure for 21

Figure S2. X-Ray Coordinate of Compound 21

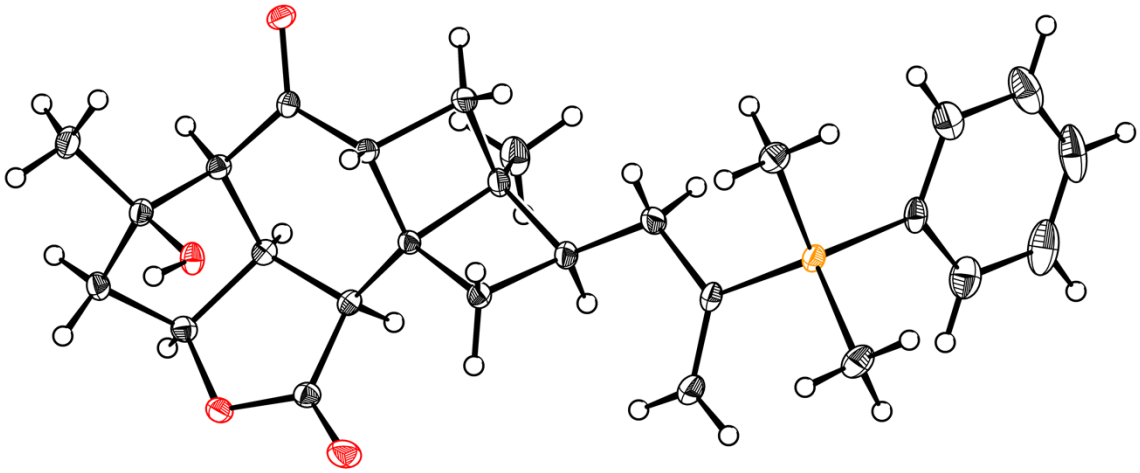


Table 1. Crystal data and structure refinement for compound 21.

Identification code	d20010	
Empirical formula	C27 H34 O4 Si	
Formula weight	450.63	
Temperature	100 K	
Wavelength	0.71073 ≈	
Crystal system	Monoclinic	
Space group	P 1 21 1 (# 4)	
Unit cell dimensions	a = 6.9085(14) ≈	α= 90∞
	b = 10.3765(19) ≈	β= 90.920(7)∞
	c = 17.058(3) ≈	γ = 90∞
Volume	1222.7(4) ≈^{3}	

Z	2
Density (calculated)	1.224 g/cm^3
Absorption coefficient	0.126 mm^{-1}
F(000)	484
Crystal size	0.04 x 0.32 x 0.33 mm^3
Theta range for data collection	2.30 to 32.80∞
Index ranges	-10 ≤ h ≤ 10, -15 ≤ k ≤ 14, -25 ≤ l ≤ 25
Reflections collected	76181
Independent reflections	8271 [R(int) = 0.0400]
Completeness to theta = 25.242∞	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.9658
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8271 / 1 / 294
Goodness-of-fit on F^2	1.035
Final R indices [I>2sigma(I)]	R1 = 0.0401, wR2 = 0.0827
R indices (all data)	R1 = 0.0511, wR2 = 0.0865
Absolute structure parameter [Flack]	0.03(2)
Absolute structure parameter [Hooft]	0.03(2)
Extinction coefficient	n/a
Largest diff. peak and hole	0.38 and -0.28 e.≈$^{-3}$

Table 2. Atomic coordinates (x 10^5) and equivalent isotropic displacement parameters (≈^{2}x 10^4) for d20010. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Si(1)	84284(6)	63687(4)	52641(3)	131(1)
O(1)	111852(17)	29694(12)	7683(7)	152(2)
O(2)	79881(18)	57572(12)	914(7)	147(2)
O(3)	38726(17)	51229(12)	1471(7)	144(2)
O(4)	38244(19)	62608(14)	12393(8)	225(3)
C(1)	82860(30)	50711(17)	60272(10)	171(3)
C(2)	99300(30)	44260(19)	63105(11)	232(4)
C(3)	98070(40)	34900(20)	68921(13)	321(5)
C(4)	80480(40)	31820(20)	72063(12)	351(6)
C(5)	63960(40)	38080(20)	69452(13)	352(5)
C(6)	65160(30)	47390(20)	63599(12)	262(4)
C(7)	110220(30)	66249(18)	50382(11)	186(4)
C(8)	73000(30)	78492(19)	56752(12)	216(4)
C(9)	70990(20)	58674(17)	43479(10)	146(3)
C(10)	54230(20)	64340(20)	41591(10)	198(3)
C(11)	79900(30)	48322(19)	38422(10)	187(4)
C(12)	69380(20)	45416(17)	30720(9)	143(3)
C(13)	78020(20)	35684(16)	24887(9)	141(3)
C(14)	71910(30)	21741(18)	25210(11)	229(4)
C(15)	99620(30)	38166(19)	22866(10)	171(3)
C(16)	93360(20)	44468(16)	14974(9)	125(3)
C(17)	96770(20)	35768(16)	8123(9)	112(3)
C(18)	81300(20)	34745(16)	1844(9)	119(3)
C(19)	80950(20)	46296(17)	-3905(9)	134(3)
C(20)	98020(20)	46930(20)	-9383(10)	186(3)
C(21)	61600(20)	43949(18)	-8193(10)	147(3)
C(22)	47800(20)	39861(16)	-1795(10)	131(3)
C(23)	43930(20)	53252(16)	8983(10)	136(3)
C(24)	60350(20)	33804(15)	4887(9)	115(3)
C(25)	55500(20)	41887(15)	12201(10)	116(3)
C(26)	72260(20)	44950(16)	17844(9)	109(3)

C(27)	69120(20)	55650(16)	24121(9)	129(3)

Table 3. Bond lengths [≈] and angles [∞] for d20010.

Si(1)-C(1)	1.8765(19)
Si(1)-C(7)	1.8576(18)
Si(1)-C(8)	1.8646(19)
Si(1)-C(9)	1.8736(17)
O(1)-C(17)	1.221(2)
O(2)-H(2)	0.8400
O(2)-C(19)	1.433(2)
O(3)-C(22)	1.451(2)
O(3)-C(23)	1.342(2)
O(4)-C(23)	1.201(2)
C(1)-C(2)	1.398(3)
C(1)-C(6)	1.399(3)
C(2)-H(2A)	0.9500
C(2)-C(3)	1.392(3)
C(3)-H(3)	0.9500
C(3)-C(4)	1.374(4)
C(4)-H(4)	0.9500
C(4)-C(5)	1.381(4)
C(5)-H(5)	0.9500
C(5)-C(6)	1.392(3)
C(6)-H(6)	0.9500
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-C(10)	1.334(2)
C(9)-C(11)	1.514(2)
C(10)-H(10A)	0.9500
C(10)-H(10B)	0.9500
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(11)-C(12)	1.521(2)

C(12)-H(12)	1.0000
C(12)-C(13)	1.544(2)
C(12)-C(27)	1.547(2)
C(13)-C(14)	1.508(3)
C(13)-C(15)	1.558(2)
C(13)-C(26)	1.585(2)
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(15)-C(16)	1.552(2)
C(16)-H(16)	1.0000
C(16)-C(17)	1.498(2)
C(16)-C(26)	1.546(2)
C(17)-C(18)	1.505(2)
C(18)-H(18)	1.0000
C(18)-C(19)	1.549(2)
C(18)-C(24)	1.548(2)
C(19)-C(20)	1.518(2)
C(19)-C(21)	1.533(2)
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-H(21A)	0.9900
C(21)-H(21B)	0.9900
C(21)-C(22)	1.521(2)
C(22)-H(22)	1.0000
C(22)-C(24)	1.554(2)
C(23)-C(25)	1.522(2)
C(24)-H(24)	1.0000
C(24)-C(25)	1.544(2)
C(25)-H(25)	1.0000
C(25)-C(26)	1.527(2)
C(26)-C(27)	1.560(2)
C(27)-H(27A)	0.9900

C(27)-H(27B)	0.9900
C(7)-Si(1)-C(1)	107.95(9)
C(7)-Si(1)-C(8)	111.74(9)
C(7)-Si(1)-C(9)	109.15(8)
C(8)-Si(1)-C(1)	107.66(9)
C(8)-Si(1)-C(9)	109.90(9)
C(9)-Si(1)-C(1)	110.42(8)
C(19)-O(2)-H(2)	109.5
C(23)-O(3)-C(22)	112.53(13)
C(2)-C(1)-Si(1)	122.14(14)
C(2)-C(1)-C(6)	116.87(18)
C(6)-C(1)-Si(1)	120.95(16)
C(1)-C(2)-H(2A)	119.3
C(3)-C(2)-C(1)	121.5(2)
C(3)-C(2)-H(2A)	119.3
C(2)-C(3)-H(3)	119.8
C(4)-C(3)-C(2)	120.3(2)
C(4)-C(3)-H(3)	119.8
C(3)-C(4)-H(4)	120.1
C(3)-C(4)-C(5)	119.8(2)
C(5)-C(4)-H(4)	120.1
C(4)-C(5)-H(5)	120.0
C(4)-C(5)-C(6)	120.0(2)
C(6)-C(5)-H(5)	120.0
C(1)-C(6)-H(6)	119.2
C(5)-C(6)-C(1)	121.6(2)
C(5)-C(6)-H(6)	119.2
Si(1)-C(7)-H(7A)	109.5
Si(1)-C(7)-H(7B)	109.5
Si(1)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
Si(1)-C(8)-H(8A)	109.5
Si(1)-C(8)-H(8B)	109.5

Si(1)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(10)-C(9)-Si(1)	119.42(13)
C(10)-C(9)-C(11)	122.28(16)
C(11)-C(9)-Si(1)	118.29(12)
C(9)-C(10)-H(10A)	120.0
C(9)-C(10)-H(10B)	120.0
H(10A)-C(10)-H(10B)	120.0
C(9)-C(11)-H(11A)	108.3
C(9)-C(11)-H(11B)	108.3
C(9)-C(11)-C(12)	116.09(15)
H(11A)-C(11)-H(11B)	107.4
C(12)-C(11)-H(11A)	108.3
C(12)-C(11)-H(11B)	108.3
C(11)-C(12)-H(12)	108.9
C(11)-C(12)-C(13)	120.12(14)
C(11)-C(12)-C(27)	119.48(15)
C(13)-C(12)-H(12)	108.9
C(13)-C(12)-C(27)	88.87(12)
C(27)-C(12)-H(12)	108.9
C(12)-C(13)-C(15)	114.57(14)
C(12)-C(13)-C(26)	89.81(12)
C(14)-C(13)-C(12)	119.49(14)
C(14)-C(13)-C(15)	115.87(15)
C(14)-C(13)-C(26)	122.86(15)
C(15)-C(13)-C(26)	87.81(12)
C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(13)-C(15)-H(15A)	113.6
C(13)-C(15)-H(15B)	113.6

H(15A)-C(15)-H(15B)	110.8
C(16)-C(15)-C(13)	90.41(12)
C(16)-C(15)-H(15A)	113.6
C(16)-C(15)-H(15B)	113.6
C(15)-C(16)-H(16)	112.6
C(17)-C(16)-C(15)	112.18(14)
C(17)-C(16)-H(16)	112.6
C(17)-C(16)-C(26)	115.32(13)
C(26)-C(16)-C(15)	89.42(12)
C(26)-C(16)-H(16)	112.6
O(1)-C(17)-C(16)	120.27(15)
O(1)-C(17)-C(18)	121.13(15)
C(16)-C(17)-C(18)	118.59(14)
C(17)-C(18)-H(18)	107.7
C(17)-C(18)-C(19)	113.56(13)
C(17)-C(18)-C(24)	115.02(13)
C(19)-C(18)-H(18)	107.7
C(24)-C(18)-H(18)	107.7
C(24)-C(18)-C(19)	104.83(13)
O(2)-C(19)-C(18)	105.62(13)
O(2)-C(19)-C(20)	111.44(14)
O(2)-C(19)-C(21)	110.55(13)
C(20)-C(19)-C(18)	114.76(14)
C(20)-C(19)-C(21)	113.17(14)
C(21)-C(19)-C(18)	100.60(13)
C(19)-C(20)-H(20A)	109.5
C(19)-C(20)-H(20B)	109.5
C(19)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(19)-C(21)-H(21A)	110.8
C(19)-C(21)-H(21B)	110.8
H(21A)-C(21)-H(21B)	108.9
C(22)-C(21)-C(19)	104.71(13)
C(22)-C(21)-H(21A)	110.8

C(22)-C(21)-H(21B)	110.8
O(3)-C(22)-C(21)	109.16(14)
O(3)-C(22)-H(22)	111.3
O(3)-C(22)-C(24)	106.65(12)
C(21)-C(22)-H(22)	111.3
C(21)-C(22)-C(24)	106.87(13)
C(24)-C(22)-H(22)	111.3
O(3)-C(23)-C(25)	110.75(14)
O(4)-C(23)-O(3)	120.29(16)
O(4)-C(23)-C(25)	128.72(16)
C(18)-C(24)-C(22)	104.01(13)
C(18)-C(24)-H(24)	110.4
C(22)-C(24)-H(24)	110.4
C(25)-C(24)-C(18)	116.90(13)
C(25)-C(24)-C(22)	104.31(13)
C(25)-C(24)-H(24)	110.4
C(23)-C(25)-C(24)	104.41(13)
C(23)-C(25)-H(25)	105.9
C(23)-C(25)-C(26)	117.04(13)
C(24)-C(25)-H(25)	105.9
C(26)-C(25)-C(24)	116.77(13)
C(26)-C(25)-H(25)	105.9
C(16)-C(26)-C(13)	89.64(12)
C(16)-C(26)-C(27)	112.50(13)
C(25)-C(26)-C(13)	122.03(14)
C(25)-C(26)-C(16)	120.17(13)
C(25)-C(26)-C(27)	117.93(13)
C(27)-C(26)-C(13)	86.99(12)
C(12)-C(27)-C(26)	90.61(12)
C(12)-C(27)-H(27A)	113.5
C(12)-C(27)-H(27B)	113.5
C(26)-C(27)-H(27A)	113.5
C(26)-C(27)-H(27B)	113.5
H(27A)-C(27)-H(27B)	110.8

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\approx^2$x 10^4) for d20010. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Si(1)	159(2)	129(2)	106(2)	-10(2)	21(2)	6(2)
O(1)	118(5)	178(6)	160(6)	-24(5)	17(4)	24(5)
O(2)	205(6)	121(5)	116(5)	10(4)	11(5)	-30(5)
O(3)	140(5)	149(6)	142(6)	-6(5)	-20(4)	22(4)
O(4)	247(6)	212(7)	214(6)	-56(6)	-47(5)	99(6)
C(1)	269(9)	143(8)	102(7)	-31(6)	9(6)	-29(7)
C(2)	332(10)	174(9)	190(9)	-5(7)	-24(7)	0(8)
C(3)	538(14)	193(10)	230(10)	32(8)	-100(9)	-2(9)
C(4)	682(17)	213(10)	157(9)	47(8)	-33(10)	-139(10)
C(5)	521(14)	326(12)	212(10)	7(9)	93(9)	-188(11)
C(6)	292(10)	287(11)	208(9)	1(8)	36(7)	-79(8)
C(7)	176(8)	190(9)	194(8)	0(7)	28(6)	-11(6)
C(8)	256(9)	181(9)	211(9)	-71(7)	48(7)	24(7)
C(9)	175(8)	169(8)	95(7)	-17(6)	25(6)	3(6)
C(10)	193(8)	259(9)	143(7)	-44(8)	24(6)	38(8)
C(11)	230(8)	212(9)	117(7)	-29(6)	-24(6)	88(7)
C(12)	176(7)	150(8)	103(7)	-8(6)	2(6)	21(6)
C(13)	200(8)	127(7)	94(7)	1(6)	-3(6)	25(6)
C(14)	380(11)	129(8)	177(9)	26(7)	11(8)	6(8)
C(15)	169(8)	224(9)	120(8)	-34(7)	-25(6)	64(7)
C(16)	117(7)	140(7)	117(7)	-24(6)	-9(5)	11(6)
C(17)	123(7)	106(7)	109(7)	10(6)	17(5)	-21(6)
C(18)	113(7)	126(7)	118(7)	-20(6)	0(5)	-2(6)
C(19)	133(7)	158(8)	110(7)	-11(6)	6(6)	-8(6)
C(20)	152(8)	286(9)	120(7)	-10(7)	19(6)	-22(7)
C(21)	147(7)	187(8)	108(7)	0(6)	-12(6)	-1(6)
C(22)	124(7)	138(7)	130(8)	-25(6)	-22(6)	-5(6)
C(23)	112(7)	145(8)	150(8)	2(6)	1(6)	-6(6)
C(24)	110(7)	110(7)	125(7)	-18(6)	4(6)	-24(5)
C(25)	113(7)	114(7)	121(7)	-7(6)	17(5)	-17(5)
C(26)	123(7)	104(7)	100(7)	-2(6)	-2(5)	9(6)

C(27)	162(8)	114(7)	110(7)	-23(6)	-5(6)	15(6)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (≈^{2}x 10 ^{3}) for d20010.

	x	y	z	U(eq)
H(2)	8157	6416	-185	22
H(2A)	11158	4631	6101	28
H(3)	10946	3063	7073	39
H(4)	7969	2541	7602	42
H(5)	5179	3604	7165	42
H(6)	5368	5158	6182	31
H(7A)	11550	5842	4802	28
H(7B)	11742	6823	5523	28
H(7C)	11141	7345	4670	28
H(8A)	7307	8535	5280	32
H(8B)	8038	8129	6140	32
H(8C)	5963	7662	5821	32
H(10A)	4744	6191	3693	24
H(10B)	4907	7080	4490	24
H(11A)	8064	4026	4152	22
H(11B)	9332	5093	3723	22
H(12)	5576	4284	3185	17
H(14A)	5777	2123	2544	34
H(14B)	7764	1767	2988	34
H(14C)	7635	1726	2051	34
H(15A)	10625	4419	2652	21
H(15B)	10726	3017	2223	21
H(16)	9907	5324	1425	15
H(18)	8391	2679	-127	14
H(20A)	9563	5356	-1337	28
H(20B)	9968	3855	-1194	28
H(20C)	10979	4908	-637	28
H(21A)	5698	5191	-1081	18
H(21B)	6288	3708	-1218	18
H(22)	3791	3362	-384	16

H(24)	5666	2459	570	14
H(25)	4617	3660	1526	14
H(27A)	7993	6189	2452	15
H(27B)	5656	6017	2353	15

Table 6. Torsion angles [∞] for d20010.

Si(1)-C(1)-C(2)-C(3)	178.21(15)
Si(1)-C(1)-C(6)-C(5)	-177.84(16)
Si(1)-C(9)-C(11)-C(12)	-175.06(13)
O(1)-C(17)-C(18)-C(19)	-101.67(18)
O(1)-C(17)-C(18)-C(24)	137.55(16)
O(2)-C(19)-C(21)-C(22)	-69.88(17)
O(3)-C(22)-C(24)-C(18)	-116.84(13)
O(3)-C(22)-C(24)-C(25)	6.18(16)
O(3)-C(23)-C(25)-C(24)	11.88(17)
O(3)-C(23)-C(25)-C(26)	142.66(14)
O(4)-C(23)-C(25)-C(24)	-173.87(17)
O(4)-C(23)-C(25)-C(26)	-43.1(2)
C(1)-Si(1)-C(9)-C(10)	108.36(16)
C(1)-Si(1)-C(9)-C(11)	-72.16(15)
C(1)-C(2)-C(3)-C(4)	-0.3(3)
C(2)-C(1)-C(6)-C(5)	-0.1(3)
C(2)-C(3)-C(4)-C(5)	-0.2(3)
C(3)-C(4)-C(5)-C(6)	0.6(3)
C(4)-C(5)-C(6)-C(1)	-0.5(3)
C(6)-C(1)-C(2)-C(3)	0.5(3)
C(7)-Si(1)-C(1)-C(2)	-2.71(18)
C(7)-Si(1)-C(1)-C(6)	174.94(15)
C(7)-Si(1)-C(9)-C(10)	-133.12(15)
C(7)-Si(1)-C(9)-C(11)	46.36(16)
C(8)-Si(1)-C(1)-C(2)	-123.49(16)
C(8)-Si(1)-C(1)-C(6)	54.16(17)
C(8)-Si(1)-C(9)-C(10)	-10.26(18)
C(8)-Si(1)-C(9)-C(11)	169.22(14)
C(9)-Si(1)-C(1)-C(2)	116.53(15)
C(9)-Si(1)-C(1)-C(6)	-65.82(17)
C(9)-C(11)-C(12)-C(13)	175.87(15)
C(9)-C(11)-C(12)-C(27)	68.3(2)
C(10)-C(9)-C(11)-C(12)	4.4(3)
C(11)-C(12)-C(13)-C(14)	93.2(2)

C(11)-C(12)-C(13)-C(15)	-50.9(2)
C(11)-C(12)-C(13)-C(26)	-138.41(16)
C(11)-C(12)-C(27)-C(26)	139.19(15)
C(12)-C(13)-C(15)-C(16)	-101.10(15)
C(12)-C(13)-C(26)-C(16)	126.97(12)
C(12)-C(13)-C(26)-C(25)	-106.95(16)
C(12)-C(13)-C(26)-C(27)	14.41(12)
C(13)-C(12)-C(27)-C(26)	14.75(12)
C(13)-C(15)-C(16)-C(17)	-104.61(14)
C(13)-C(15)-C(16)-C(26)	12.62(13)
C(13)-C(26)-C(27)-C(12)	-14.38(12)
C(14)-C(13)-C(15)-C(16)	113.47(16)
C(14)-C(13)-C(26)-C(16)	-107.31(17)
C(14)-C(13)-C(26)-C(25)	18.8(2)
C(14)-C(13)-C(26)-C(27)	140.14(16)
C(15)-C(13)-C(26)-C(16)	12.37(12)
C(15)-C(13)-C(26)-C(25)	138.45(15)
C(15)-C(13)-C(26)-C(27)	-100.19(12)
C(15)-C(16)-C(17)-O(1)	-43.4(2)
C(15)-C(16)-C(17)-C(18)	136.71(15)
C(15)-C(16)-C(26)-C(13)	-12.41(13)
C(15)-C(16)-C(26)-C(25)	-139.99(15)
C(15)-C(16)-C(26)-C(27)	74.19(15)
C(16)-C(17)-C(18)-C(19)	78.18(18)
C(16)-C(17)-C(18)-C(24)	-42.6(2)
C(16)-C(26)-C(27)-C(12)	-102.75(14)
C(17)-C(16)-C(26)-C(13)	101.98(15)
C(17)-C(16)-C(26)-C(25)	-25.6(2)
C(17)-C(16)-C(26)-C(27)	-171.42(13)
C(17)-C(18)-C(19)-O(2)	-53.01(17)
C(17)-C(18)-C(19)-C(20)	70.15(18)
C(17)-C(18)-C(19)-C(21)	-168.04(13)
C(17)-C(18)-C(24)-C(22)	151.53(14)
C(17)-C(18)-C(24)-C(25)	37.2(2)
C(18)-C(19)-C(21)-C(22)	41.39(16)
C(18)-C(24)-C(25)-C(23)	103.80(15)

C(18)-C(24)-C(25)-C(26)	-27.1(2)
C(19)-C(18)-C(24)-C(22)	26.08(16)
C(19)-C(18)-C(24)-C(25)	-88.27(16)
C(19)-C(21)-C(22)-O(3)	88.93(15)
C(19)-C(21)-C(22)-C(24)	-26.05(17)
C(20)-C(19)-C(21)-C(22)	164.31(15)
C(21)-C(22)-C(24)-C(18)	-0.18(17)
C(21)-C(22)-C(24)-C(25)	122.84(14)
C(22)-O(3)-C(23)-O(4)	176.83(15)
C(22)-O(3)-C(23)-C(25)	-8.36(18)
C(22)-C(24)-C(25)-C(23)	-10.38(15)
C(22)-C(24)-C(25)-C(26)	-141.32(14)
C(23)-O(3)-C(22)-C(21)	-113.97(15)
C(23)-O(3)-C(22)-C(24)	1.16(17)
C(23)-C(25)-C(26)-C(13)	146.06(15)
C(23)-C(25)-C(26)-C(16)	-103.13(17)
C(23)-C(25)-C(26)-C(27)	40.9(2)
C(24)-C(18)-C(19)-O(2)	73.35(14)
C(24)-C(18)-C(19)-C(20)	-163.50(14)
C(24)-C(18)-C(19)-C(21)	-41.68(15)
C(24)-C(25)-C(26)-C(13)	-89.16(18)
C(24)-C(25)-C(26)-C(16)	21.6(2)
C(24)-C(25)-C(26)-C(27)	165.67(13)
C(25)-C(26)-C(27)-C(12)	110.60(15)
C(26)-C(13)-C(15)-C(16)	-12.32(12)
C(26)-C(16)-C(17)-O(1)	-143.85(16)
C(26)-C(16)-C(17)-C(18)	36.3(2)
C(27)-C(12)-C(13)-C(14)	-142.94(16)
C(27)-C(12)-C(13)-C(15)	72.99(15)
C(27)-C(12)-C(13)-C(26)	-14.51(12)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for d20010 [≈ and ∞].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(2)-H(2)...O(1)#1	0.84	1.95	2.7880(18)	173.8

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,y+1/2,-z

X-ray Crystal Structure for 25

Figure S1. X-Ray Coordinate of Compound 25

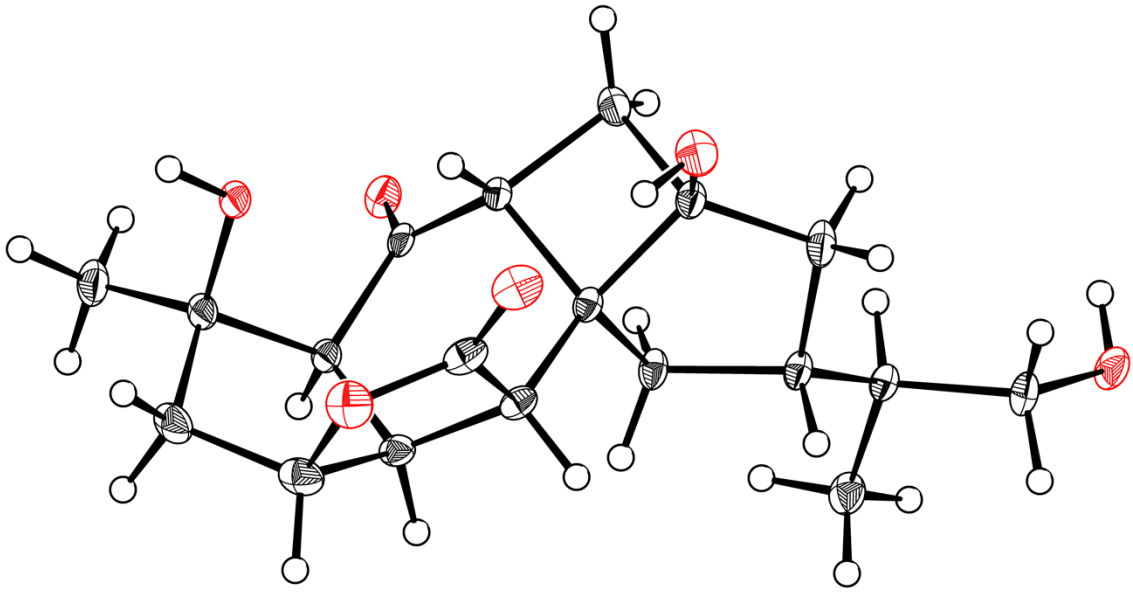


Table 8. Crystal data and structure refinement for d19153.

Identification code	d19153	
Empirical formula	C19 H26 O6	
Formula weight	350.40	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 10.221(3) Å	a= 90°
	b = 12.581(3) Å	b= 90°
	c = 13.333(4) Å	g = 90°
Volume	1714.4(8) $Å^3$	
Z	4	

Density (calculated)	1.358 g/cm^3
Absorption coefficient	0.100 mm^{-1}
F(000)	752
Crystal size	0.31 x 0.19 x 0.18 mm^3
Theta range for data collection	2.226 to 36.285°.
Index ranges	-16 £ h £ 16, -20 £ k £ 20, -22 £ l £ 22
Reflections collected	73152
Independent reflections	7997 [R(int) = 0.0477]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.9208
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7997 / 0 / 231
Goodness-of-fit on F^2	1.069
Final R indices [I>2sigma(I)]	R1 = 0.0424, wR2 = 0.0942
R indices (all data)	R1 = 0.0592, wR2 = 0.1007
Absolute structure parameter [Flack]	0.21(16)
Absolute structure parameter [Hooft]	0.26(15)
Extinction coefficient	n/a
Largest diff. peak and hole	0.383 and -0.250 e.Å^{-3}

Table 9. Atomic coordinates (x 10^5) and equivalent isotropic displacement parameters ($Å^2$x 10^4) for d19153. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	68042(10)	78131(7)	63641(8)	165(2)
O(2)	86227(11)	70321(8)	47229(8)	213(2)
O(3)	70632(11)	61684(9)	39054(7)	213(2)
O(4)	52317(11)	47286(8)	43910(8)	209(2)
O(5)	62828(10)	58461(8)	81516(7)	170(2)
O(6)	61450(11)	-568(7)	63049(8)	186(2)
C(1)	80656(12)	63996(9)	70998(9)	120(2)
C(2)	79658(13)	76259(9)	69319(10)	142(2)
C(3)	79192(15)	82417(10)	79130(11)	201(3)
C(4)	91843(14)	78776(11)	63116(11)	195(3)
C(5)	94105(14)	69305(11)	56324(11)	193(3)
C(6)	88652(12)	59459(10)	61866(9)	136(2)
C(7)	81180(12)	53340(10)	53598(9)	136(2)
C(8)	78429(13)	61948(11)	45872(10)	170(2)
C(9)	69363(12)	47732(9)	58110(9)	116(2)
C(10)	56514(13)	43122(10)	53164(10)	139(2)
C(11)	48826(13)	48194(11)	62174(10)	181(2)
C(12)	60524(12)	55734(9)	63681(9)	124(2)
C(13)	67102(12)	59314(9)	72997(9)	118(2)
C(14)	73647(13)	38142(9)	64645(9)	139(2)
C(15)	70260(13)	28115(9)	58468(9)	131(2)
C(16)	57444(15)	31051(10)	52945(11)	187(3)
C(17)	68816(13)	17984(9)	64757(9)	127(2)
C(18)	66587(14)	8454(10)	57824(10)	159(2)
C(19)	80353(15)	15980(10)	71809(10)	181(2)

Table 10. Bond lengths [Å] and angles [°] for d19153.

O(1)-H(1)	0.8400
O(1)-C(2)	1.4276(16)
O(2)-C(5)	1.4612(19)
O(2)-C(8)	1.3333(18)
O(3)-C(8)	1.2094(17)
O(4)-H(4)	0.8400
O(4)-C(10)	1.4075(16)
O(5)-C(13)	1.2217(15)
O(6)-H(6)	0.8400
O(6)-C(18)	1.4316(16)
C(1)-H(1A)	1.0000
C(1)-C(2)	1.5623(17)
C(1)-C(6)	1.5736(18)
C(1)-C(13)	1.5287(18)
C(2)-C(3)	1.5210(19)
C(2)-C(4)	1.528(2)
C(3)-H(3A)	0.9800
C(3)-H(3B)	0.9800
C(3)-H(3C)	0.9800
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(4)-C(5)	1.514(2)
C(5)-H(5)	1.0000
C(5)-C(6)	1.5463(18)
C(6)-H(6A)	1.0000
C(6)-C(7)	1.5464(18)
C(7)-H(7)	1.0000
C(7)-C(8)	1.5209(17)
C(7)-C(9)	1.5227(17)
C(9)-C(10)	1.5799(18)
C(9)-C(12)	1.5432(16)
C(9)-C(14)	1.5513(17)
C(10)-C(11)	1.5708(19)
C(10)-C(16)	1.5219(18)

C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(11)-C(12)	1.5394(18)
C(12)-H(12)	1.0000
C(12)-C(13)	1.4825(17)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(14)-C(15)	1.5459(17)
C(15)-H(15)	1.0000
C(15)-C(16)	1.5474(19)
C(15)-C(17)	1.5328(17)
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(17)-H(17)	1.0000
C(17)-C(18)	1.5310(17)
C(17)-C(19)	1.5290(19)
C(18)-H(18A)	0.9900
C(18)-H(18B)	0.9900
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800

C(2)-O(1)-H(1)	109.5
C(8)-O(2)-C(5)	111.89(10)
C(10)-O(4)-H(4)	109.5
C(18)-O(6)-H(6)	109.5
C(2)-C(1)-H(1A)	107.3
C(2)-C(1)-C(6)	106.34(10)
C(6)-C(1)-H(1A)	107.3
C(13)-C(1)-H(1A)	107.3
C(13)-C(1)-C(2)	110.27(10)
C(13)-C(1)-C(6)	117.76(10)
O(1)-C(2)-C(1)	107.05(10)
O(1)-C(2)-C(3)	110.24(11)
O(1)-C(2)-C(4)	110.89(11)
C(3)-C(2)-C(1)	112.44(10)

C(3)-C(2)-C(4)	112.67(11)
C(4)-C(2)-C(1)	103.24(10)
C(2)-C(3)-H(3A)	109.5
C(2)-C(3)-H(3B)	109.5
C(2)-C(3)-H(3C)	109.5
H(3A)-C(3)-H(3B)	109.5
H(3A)-C(3)-H(3C)	109.5
H(3B)-C(3)-H(3C)	109.5
C(2)-C(4)-H(4A)	110.4
C(2)-C(4)-H(4B)	110.4
H(4A)-C(4)-H(4B)	108.6
C(5)-C(4)-C(2)	106.56(11)
C(5)-C(4)-H(4A)	110.4
C(5)-C(4)-H(4B)	110.4
O(2)-C(5)-C(4)	110.08(12)
O(2)-C(5)-H(5)	111.4
O(2)-C(5)-C(6)	105.55(11)
C(4)-C(5)-H(5)	111.4
C(4)-C(5)-C(6)	106.83(11)
C(6)-C(5)-H(5)	111.4
C(1)-C(6)-H(6A)	109.6
C(5)-C(6)-C(1)	105.44(10)
C(5)-C(6)-H(6A)	109.6
C(5)-C(6)-C(7)	103.66(10)
C(7)-C(6)-C(1)	118.41(10)
C(7)-C(6)-H(6A)	109.6
C(6)-C(7)-H(7)	109.0
C(8)-C(7)-C(6)	102.68(10)
C(8)-C(7)-H(7)	109.0
C(8)-C(7)-C(9)	116.80(11)
C(9)-C(7)-C(6)	109.92(10)
C(9)-C(7)-H(7)	109.0
O(2)-C(8)-C(7)	111.12(11)
O(3)-C(8)-O(2)	121.17(12)
O(3)-C(8)-C(7)	127.68(13)
C(7)-C(9)-C(10)	131.65(10)

C(7)-C(9)-C(12)	110.62(9)
C(7)-C(9)-C(14)	111.00(10)
C(12)-C(9)-C(10)	87.35(9)
C(12)-C(9)-C(14)	113.72(10)
C(14)-C(9)-C(10)	100.58(9)
O(4)-C(10)-C(9)	118.85(11)
O(4)-C(10)-C(11)	111.51(11)
O(4)-C(10)-C(16)	111.94(11)
C(11)-C(10)-C(9)	86.99(9)
C(16)-C(10)-C(9)	108.81(10)
C(16)-C(10)-C(11)	116.83(12)
C(10)-C(11)-H(11A)	114.0
C(10)-C(11)-H(11B)	114.0
H(11A)-C(11)-H(11B)	111.2
C(12)-C(11)-C(10)	87.80(10)
C(12)-C(11)-H(11A)	114.0
C(12)-C(11)-H(11B)	114.0
C(9)-C(12)-H(12)	108.2
C(11)-C(12)-C(9)	89.41(9)
C(11)-C(12)-H(12)	108.2
C(13)-C(12)-C(9)	109.63(10)
C(13)-C(12)-C(11)	130.45(11)
C(13)-C(12)-H(12)	108.2
O(5)-C(13)-C(1)	121.33(11)
O(5)-C(13)-C(12)	126.17(12)
C(12)-C(13)-C(1)	112.45(10)
C(9)-C(14)-H(14A)	110.6
C(9)-C(14)-H(14B)	110.6
H(14A)-C(14)-H(14B)	108.7
C(15)-C(14)-C(9)	105.80(9)
C(15)-C(14)-H(14A)	110.6
C(15)-C(14)-H(14B)	110.6
C(14)-C(15)-H(15)	108.7
C(14)-C(15)-C(16)	104.37(10)
C(16)-C(15)-H(15)	108.7
C(17)-C(15)-C(14)	114.12(10)

C(17)-C(15)-H(15)	108.7
C(17)-C(15)-C(16)	112.17(11)
C(10)-C(16)-C(15)	106.38(11)
C(10)-C(16)-H(16A)	110.5
C(10)-C(16)-H(16B)	110.5
C(15)-C(16)-H(16A)	110.5
C(15)-C(16)-H(16B)	110.5
H(16A)-C(16)-H(16B)	108.6
C(15)-C(17)-H(17)	107.5
C(18)-C(17)-C(15)	109.58(10)
C(18)-C(17)-H(17)	107.5
C(19)-C(17)-C(15)	113.53(11)
C(19)-C(17)-H(17)	107.5
C(19)-C(17)-C(18)	110.91(10)
O(6)-C(18)-C(17)	112.44(10)
O(6)-C(18)-H(18A)	109.1
O(6)-C(18)-H(18B)	109.1
C(17)-C(18)-H(18A)	109.1
C(17)-C(18)-H(18B)	109.1
H(18A)-C(18)-H(18B)	107.8
C(17)-C(19)-H(19A)	109.5
C(17)-C(19)-H(19B)	109.5
C(17)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 11. Anisotropic displacement parameters ($Å^2 x\ 10^4$) for d19153. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	160(4)	78(3)	256(4)	18(3)	-73(4)	14(3)
O(2)	247(5)	195(5)	197(4)	86(4)	30(4)	-22(4)
O(3)	248(5)	234(5)	155(4)	65(4)	9(4)	49(4)
O(4)	240(5)	171(5)	217(5)	47(4)	-100(4)	13(4)
O(5)	207(5)	140(4)	162(4)	-7(3)	37(3)	-6(3)
O(6)	220(5)	90(4)	246(5)	18(3)	38(4)	9(3)
C(1)	129(5)	80(4)	150(5)	16(4)	-14(4)	3(4)
C(2)	145(5)	78(4)	203(5)	26(4)	-39(4)	-7(4)
C(3)	249(7)	106(5)	248(6)	-17(4)	-65(5)	-1(5)
C(4)	164(6)	138(5)	281(7)	57(5)	-14(5)	-46(4)
C(5)	148(6)	190(6)	241(6)	75(5)	30(5)	-21(5)
C(6)	119(5)	118(5)	171(5)	28(4)	6(4)	15(4)
C(7)	150(5)	119(5)	137(5)	24(4)	14(4)	37(4)
C(8)	183(6)	165(5)	161(5)	45(4)	60(4)	45(5)
C(9)	146(5)	88(4)	113(4)	2(4)	-10(4)	13(4)
C(10)	175(5)	99(5)	144(5)	-7(4)	-40(4)	12(4)
C(11)	159(5)	160(6)	224(6)	-54(5)	21(5)	-41(5)
C(12)	124(5)	96(5)	150(5)	-16(4)	10(4)	-5(4)
C(13)	138(5)	61(4)	156(5)	-1(4)	9(4)	7(4)
C(14)	199(6)	82(4)	137(5)	6(4)	-40(4)	6(4)
C(15)	180(5)	83(4)	131(5)	-6(4)	-18(4)	9(4)
C(16)	260(7)	97(5)	205(6)	-18(4)	-106(5)	11(5)
C(17)	164(5)	83(4)	135(5)	-1(4)	-2(4)	8(4)
C(18)	225(6)	89(5)	164(5)	-17(4)	14(5)	-7(4)
C(19)	215(6)	127(5)	201(6)	14(4)	-43(5)	19(5)

Table 12. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{-3}) for d19153.

	x	y	z	U(eq)
H(1)	6684	8471	6306	25
H(4)	5784	5170	4181	31
H(6)	5423	103	6566	28
H(1A)	8603	6283	7717	14
H(3A)	7789	8999	7771	30
H(3B)	8745	8144	8275	30
H(3C)	7194	7979	8324	30
H(4A)	9046	8529	5909	23
H(4B)	9948	7989	6756	23
H(5)	10360	6843	5470	23
H(6A)	9606	5501	6439	16
H(7)	8714	4791	5058	16
H(11A)	4063	5183	6019	22
H(11B)	4732	4326	6784	22
H(12)	5924	6206	5925	15
H(14A)	8315	3845	6603	17
H(14B)	6887	3812	7111	17
H(15)	7729	2696	5337	16
H(16A)	5768	2845	4594	22
H(16B)	4982	2784	5637	22
H(17)	6081	1881	6899	15
H(18A)	6042	1052	5244	19
H(18B)	7499	647	5464	19
H(19A)	7913	917	7525	27
H(19B)	8084	2171	7677	27
H(19C)	8849	1578	6792	27

Table 13. Torsion angles [°] for d19153.

O(1)-C(2)-C(4)-C(5)	-79.58(13)
O(2)-C(5)-C(6)-C(1)	-105.80(11)
O(2)-C(5)-C(6)-C(7)	19.30(13)
O(4)-C(10)-C(11)-C(12)	-98.40(12)
O(4)-C(10)-C(16)-C(15)	137.74(11)
C(1)-C(2)-C(4)-C(5)	34.76(13)
C(1)-C(6)-C(7)-C(8)	94.36(12)
C(1)-C(6)-C(7)-C(9)	-30.62(14)
C(2)-C(1)-C(6)-C(5)	9.99(13)
C(2)-C(1)-C(6)-C(7)	-105.35(12)
C(2)-C(1)-C(13)-O(5)	-91.19(14)
C(2)-C(1)-C(13)-C(12)	91.19(12)
C(2)-C(4)-C(5)-O(2)	84.92(13)
C(2)-C(4)-C(5)-C(6)	-29.20(14)
C(3)-C(2)-C(4)-C(5)	156.31(11)
C(4)-C(5)-C(6)-C(1)	11.36(14)
C(4)-C(5)-C(6)-C(7)	136.46(11)
C(5)-O(2)-C(8)-O(3)	175.54(12)
C(5)-O(2)-C(8)-C(7)	-6.18(15)
C(5)-C(6)-C(7)-C(8)	-21.94(12)
C(5)-C(6)-C(7)-C(9)	-146.91(10)
C(6)-C(1)-C(2)-O(1)	89.94(12)
C(6)-C(1)-C(2)-C(3)	-148.85(11)
C(6)-C(1)-C(2)-C(4)	-27.15(13)
C(6)-C(1)-C(13)-O(5)	146.60(12)
C(6)-C(1)-C(13)-C(12)	-31.03(14)
C(6)-C(7)-C(8)-O(2)	18.23(13)
C(6)-C(7)-C(8)-O(3)	-163.63(13)
C(6)-C(7)-C(9)-C(10)	161.05(11)
C(6)-C(7)-C(9)-C(12)	55.47(12)
C(6)-C(7)-C(9)-C(14)	-71.76(12)
C(7)-C(9)-C(10)-O(4)	-24.01(18)
C(7)-C(9)-C(10)-C(11)	-136.98(13)
C(7)-C(9)-C(10)-C(16)	105.66(14)

C(7)-C(9)-C(12)-C(11)	155.80(10)
C(7)-C(9)-C(12)-C(13)	-70.95(12)
C(7)-C(9)-C(14)-C(15)	-106.00(11)
C(8)-O(2)-C(5)-C(4)	-123.70(12)
C(8)-O(2)-C(5)-C(6)	-8.76(15)
C(8)-C(7)-C(9)-C(10)	44.64(17)
C(8)-C(7)-C(9)-C(12)	-60.94(14)
C(8)-C(7)-C(9)-C(14)	171.83(10)
C(9)-C(7)-C(8)-O(2)	138.56(11)
C(9)-C(7)-C(8)-O(3)	-43.30(18)
C(9)-C(10)-C(11)-C(12)	21.52(9)
C(9)-C(10)-C(16)-C(15)	4.37(15)
C(9)-C(12)-C(13)-O(5)	-121.85(13)
C(9)-C(12)-C(13)-C(1)	55.64(13)
C(9)-C(14)-C(15)-C(16)	-35.43(13)
C(9)-C(14)-C(15)-C(17)	-158.22(11)
C(10)-C(9)-C(12)-C(11)	21.90(9)
C(10)-C(9)-C(12)-C(13)	155.15(10)
C(10)-C(9)-C(14)-C(15)	36.73(12)
C(10)-C(11)-C(12)-C(9)	-22.02(9)
C(10)-C(11)-C(12)-C(13)	-137.67(13)
C(11)-C(10)-C(16)-C(15)	-91.96(14)
C(11)-C(12)-C(13)-O(5)	-15.0(2)
C(11)-C(12)-C(13)-C(1)	162.49(12)
C(12)-C(9)-C(10)-O(4)	91.51(12)
C(12)-C(9)-C(10)-C(11)	-21.47(9)
C(12)-C(9)-C(10)-C(16)	-138.83(11)
C(12)-C(9)-C(14)-C(15)	128.49(11)
C(13)-C(1)-C(2)-O(1)	-38.79(13)
C(13)-C(1)-C(2)-C(3)	82.43(13)
C(13)-C(1)-C(2)-C(4)	-155.87(10)
C(13)-C(1)-C(6)-C(5)	134.19(11)
C(13)-C(1)-C(6)-C(7)	18.86(15)
C(14)-C(9)-C(10)-O(4)	-154.85(11)
C(14)-C(9)-C(10)-C(11)	92.17(10)
C(14)-C(9)-C(10)-C(16)	-25.19(13)

C(14)-C(9)-C(12)-C(11)	-78.49(12)
C(14)-C(9)-C(12)-C(13)	54.76(13)
C(14)-C(15)-C(16)-C(10)	18.65(14)
C(14)-C(15)-C(17)-C(18)	-175.42(11)
C(14)-C(15)-C(17)-C(19)	-50.80(15)
C(15)-C(17)-C(18)-O(6)	-163.03(11)
C(16)-C(10)-C(11)-C(12)	131.10(12)
C(16)-C(15)-C(17)-C(18)	66.15(14)
C(16)-C(15)-C(17)-C(19)	-169.23(11)
C(17)-C(15)-C(16)-C(10)	142.70(11)
C(19)-C(17)-C(18)-O(6)	70.85(15)

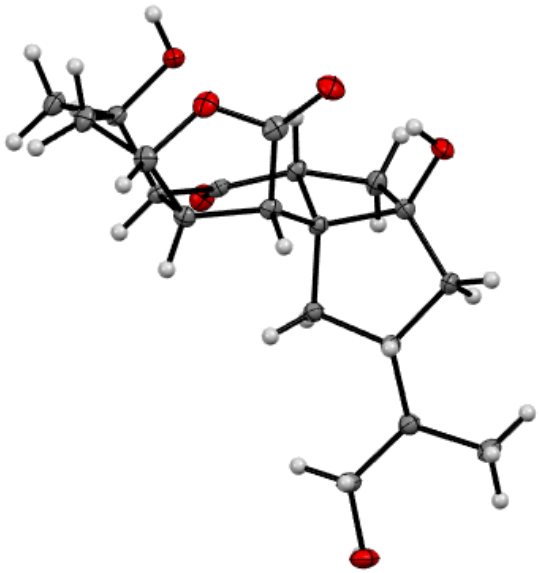
Symmetry transformations used to generate equivalent atoms:

Table 14. Hydrogen bonds for d19153 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1)...O(6)#1	0.84	1.93	2.7645(15)	170.3
O(4)-H(4)...O(3)	0.84	1.85	2.6841(17)	172.0
O(6)-H(6)...O(5)#2	0.84	2.01	2.8235(16)	161.6

Symmetry transformations used to generate equivalent atoms:

#1 x,y+1,z #2 -x+1,y-1/2,-z+3/2



X-ray Crystal Structure for Compound *epi*-25

Figure S3. X-Ray Coordinate of Compound *epi*-25.

Table 15. Crystal data and structure refinement for V20005.

Identification code	V20005	
Empirical formula	C19 H32 O9	
Formula weight	404.44	
Temperature	100(2) K	
Wavelength	1.54178 ≈	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 9.0245(13) ≈	α= 90∞.
	b = 13.383(2) ≈	β= 90∞.
	c = 16.329(3) ≈	γ = 90∞.
Volume	1972.1(5) ≈^{3}	
Z	4	
Density (calculated)	1.362 Mg/m^3	
Absorption coefficient	0.906 mm^{-1}	

F(000)	872
Crystal size	0.600 x 0.300 x 0.150 mm^3
Theta range for data collection	4.271 to 74.810∞.
Index ranges	-11<=h<=10, -16<=k<=15, -19<=l<=20
Reflections collected	20468
Independent reflections	4017 [R(int) = 0.0461]
Completeness to theta = 67.679∞	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7538 and 0.5503
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4017 / 9 / 282
Goodness-of-fit on F^2	1.087
Final R indices [I>2sigma(I)]	R1 = 0.0314, wR2 = 0.0874
R indices (all data)	R1 = 0.0315, wR2 = 0.0875
Absolute structure parameter	0.06(4)
Extinction coefficient	n/a
Largest diff. peak and hole	0.342 and -0.300 e.≈$^{-3}$

Table 16. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (≈^{2}x 10^3) for V20005. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	7488(2)	5070(1)	8786(1)	20(1)
C(1)	6251(2)	5178(1)	8340(1)	17(1)
O(2)	5331(2)	5794(1)	8528(1)	23(1)
C(2)	6244(2)	4454(1)	7623(1)	14(1)
C(3)	4778(2)	3952(1)	7419(1)	12(1)
C(4)	4938(2)	3335(1)	6621(1)	14(1)
C(5)	4168(2)	3973(1)	5960(1)	14(1)
C(6)	2780(2)	4388(1)	6396(1)	16(1)
C(16)	3800(2)	3404(1)	5169(1)	16(1)
C(17)	5215(2)	3010(1)	4767(1)	19(1)
O(3)	4944(2)	2495(1)	4010(1)	22(1)
C(18)	2929(2)	4059(2)	4575(1)	22(1)
C(7)	3164(2)	4383(1)	7305(1)	14(1)
O(4)	2807(2)	5300(1)	7691(1)	21(1)
C(8)	2599(2)	3462(1)	7821(1)	18(1)
C(9)	4188(2)	3370(1)	8165(1)	14(1)
C(10)	5111(2)	2472(1)	8330(1)	13(1)
O(5)	4650(1)	1619(1)	8426(1)	18(1)
C(11)	6770(2)	2710(1)	8379(1)	13(1)
C(12)	7370(2)	3649(1)	7898(1)	14(1)
C(13)	8371(2)	4213(1)	8507(1)	18(1)
C(14)	8646(2)	3502(2)	9217(1)	18(1)
C(15)	7232(2)	2868(1)	9288(1)	14(1)
O(6)	6066(1)	3429(1)	9662(1)	17(1)
C(19)	7469(2)	1889(1)	9746(1)	19(1)
O(1W)	4785(2)	3561(1)	2568(1)	28(1)
O(2W)	6663(2)	3854(1)	1302(1)	21(1)
O(3W)	3494(2)	756(1)	4427(1)	36(1)

Table 17. Bond lengths [≈] and angles [∞] for V20005.

O(1)-C(1)	1.340(2)
O(1)-C(13)	1.469(2)
C(1)-O(2)	1.210(2)
C(1)-C(2)	1.520(2)
C(2)-C(3)	1.521(2)
C(2)-C(12)	1.549(2)
C(2)-H(2)	1.0000
C(3)-C(9)	1.541(2)
C(3)-C(4)	1.549(2)
C(3)-C(7)	1.578(2)
C(4)-C(5)	1.542(2)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-C(16)	1.536(2)
C(5)-C(6)	1.544(2)
C(5)-H(5)	1.0000
C(6)-C(7)	1.525(2)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(16)-C(18)	1.525(3)
C(16)-C(17)	1.529(3)
C(16)-H(16)	1.0000
C(17)-O(3)	1.436(2)
C(17)-H(17A)	0.9900
C(17)-H(17B)	0.9900
O(3)-H(3O)	0.80(2)
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(7)-O(4)	1.417(2)
C(7)-C(8)	1.577(2)
O(4)-H(4O)	0.82(2)
C(8)-C(9)	1.545(2)
C(8)-H(8A)	0.9900

C(8)-H(8B)	0.9900
C(9)-C(10)	1.486(2)
C(9)-H(9)	1.0000
C(10)-O(5)	1.226(2)
C(10)-C(11)	1.533(2)
C(11)-C(15)	1.557(2)
C(11)-C(12)	1.577(2)
C(11)-H(11)	1.0000
C(12)-C(13)	1.541(2)
C(12)-H(12)	1.0000
C(13)-C(14)	1.520(3)
C(13)-H(13)	1.0000
C(14)-C(15)	1.536(2)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(15)-O(6)	1.430(2)
C(15)-C(19)	1.523(2)
O(6)-H(6O)	0.85(2)
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
O(1W)-H(1W1)	0.85(2)
O(1W)-H(1W2)	0.85(2)
O(2W)-H(2W1)	0.84(2)
O(2W)-H(2W2)	0.86(2)
O(3W)-H(3W1)	0.84(2)
O(3W)-H(3W2)	0.87(2)

C(1)-O(1)-C(13)	111.53(14)
O(2)-C(1)-O(1)	120.48(17)
O(2)-C(1)-C(2)	128.76(17)
O(1)-C(1)-C(2)	110.76(15)
C(1)-C(2)-C(3)	117.03(14)
C(1)-C(2)-C(12)	102.49(14)
C(3)-C(2)-C(12)	109.07(14)
C(1)-C(2)-H(2)	109.3

C(3)-C(2)-H(2)	109.3
C(12)-C(2)-H(2)	109.3
C(2)-C(3)-C(9)	110.52(13)
C(2)-C(3)-C(4)	109.79(14)
C(9)-C(3)-C(4)	115.36(14)
C(2)-C(3)-C(7)	131.85(15)
C(9)-C(3)-C(7)	87.64(13)
C(4)-C(3)-C(7)	100.48(13)
C(5)-C(4)-C(3)	104.57(13)
C(5)-C(4)-H(4A)	110.8
C(3)-C(4)-H(4A)	110.8
C(5)-C(4)-H(4B)	110.8
C(3)-C(4)-H(4B)	110.8
H(4A)-C(4)-H(4B)	108.9
C(16)-C(5)-C(4)	114.32(15)
C(16)-C(5)-C(6)	113.02(15)
C(4)-C(5)-C(6)	103.99(13)
C(16)-C(5)-H(5)	108.4
C(4)-C(5)-H(5)	108.4
C(6)-C(5)-H(5)	108.4
C(7)-C(6)-C(5)	105.26(14)
C(7)-C(6)-H(6A)	110.7
C(5)-C(6)-H(6A)	110.7
C(7)-C(6)-H(6B)	110.7
C(5)-C(6)-H(6B)	110.7
H(6A)-C(6)-H(6B)	108.8
C(18)-C(16)-C(17)	110.89(15)
C(18)-C(16)-C(5)	111.16(15)
C(17)-C(16)-C(5)	110.59(15)
C(18)-C(16)-H(16)	108.0
C(17)-C(16)-H(16)	108.0
C(5)-C(16)-H(16)	108.0
O(3)-C(17)-C(16)	113.11(16)
O(3)-C(17)-H(17A)	109.0
C(16)-C(17)-H(17A)	109.0
O(3)-C(17)-H(17B)	109.0

C(16)-C(17)-H(17B)	109.0
H(17A)-C(17)-H(17B)	107.8
C(17)-O(3)-H(3O)	104(2)
C(16)-C(18)-H(18A)	109.5
C(16)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(16)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
O(4)-C(7)-C(6)	112.16(15)
O(4)-C(7)-C(8)	111.50(14)
C(6)-C(7)-C(8)	116.74(15)
O(4)-C(7)-C(3)	118.31(15)
C(6)-C(7)-C(3)	109.03(14)
C(8)-C(7)-C(3)	87.12(13)
C(7)-O(4)-H(4O)	112(2)
C(9)-C(8)-C(7)	87.50(13)
C(9)-C(8)-H(8A)	114.1
C(7)-C(8)-H(8A)	114.1
C(9)-C(8)-H(8B)	114.1
C(7)-C(8)-H(8B)	114.1
H(8A)-C(8)-H(8B)	111.3
C(10)-C(9)-C(3)	110.97(14)
C(10)-C(9)-C(8)	130.51(16)
C(3)-C(9)-C(8)	89.58(12)
C(10)-C(9)-H(9)	107.7
C(3)-C(9)-H(9)	107.7
C(8)-C(9)-H(9)	107.7
O(5)-C(10)-C(9)	125.92(16)
O(5)-C(10)-C(11)	121.20(16)
C(9)-C(10)-C(11)	112.88(15)
C(10)-C(11)-C(15)	109.83(13)
C(10)-C(11)-C(12)	118.35(14)
C(15)-C(11)-C(12)	105.90(13)
C(10)-C(11)-H(11)	107.4
C(15)-C(11)-H(11)	107.4

C(12)-C(11)-H(11)	107.4
C(13)-C(12)-C(2)	103.35(14)
C(13)-C(12)-C(11)	105.74(13)
C(2)-C(12)-C(11)	118.28(14)
C(13)-C(12)-H(12)	109.7
C(2)-C(12)-H(12)	109.7
C(11)-C(12)-H(12)	109.7
O(1)-C(13)-C(14)	109.94(15)
O(1)-C(13)-C(12)	105.36(14)
C(14)-C(13)-C(12)	106.27(14)
O(1)-C(13)-H(13)	111.7
C(14)-C(13)-H(13)	111.7
C(12)-C(13)-H(13)	111.7
C(13)-C(14)-C(15)	105.55(14)
C(13)-C(14)-H(14A)	110.6
C(15)-C(14)-H(14A)	110.6
C(13)-C(14)-H(14B)	110.6
C(15)-C(14)-H(14B)	110.6
H(14A)-C(14)-H(14B)	108.8
O(6)-C(15)-C(19)	110.20(15)
O(6)-C(15)-C(14)	110.70(14)
C(19)-C(15)-C(14)	113.33(14)
O(6)-C(15)-C(11)	106.36(13)
C(19)-C(15)-C(11)	112.85(15)
C(14)-C(15)-C(11)	103.01(14)
C(15)-O(6)-H(6O)	109.5(19)
C(15)-C(19)-H(19A)	109.5
C(15)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(15)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
H(1W1)-O(1W)-H(1W2)	103(3)
H(2W1)-O(2W)-H(2W2)	105(3)
H(3W1)-O(3W)-H(3W2)	111(3)

Symmetry transformations used to generate equivalent atoms:

Table 18. Anisotropic displacement parameters ($\approx^2$x 10^3) for V20005. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	22(1)	15(1)	22(1)	-2(1)	-5(1)	-4(1)
C(1)	22(1)	11(1)	18(1)	2(1)	-1(1)	-5(1)
O(2)	28(1)	16(1)	25(1)	-5(1)	0(1)	1(1)
C(2)	16(1)	12(1)	13(1)	2(1)	2(1)	-1(1)
C(3)	14(1)	12(1)	10(1)	2(1)	0(1)	0(1)
C(4)	17(1)	14(1)	12(1)	0(1)	0(1)	2(1)
C(5)	18(1)	13(1)	11(1)	1(1)	-1(1)	2(1)
C(6)	19(1)	18(1)	13(1)	2(1)	-1(1)	6(1)
C(16)	18(1)	16(1)	13(1)	0(1)	-1(1)	0(1)
C(17)	23(1)	21(1)	13(1)	-3(1)	0(1)	2(1)
O(3)	34(1)	19(1)	13(1)	-3(1)	2(1)	1(1)
C(18)	28(1)	25(1)	14(1)	0(1)	-4(1)	5(1)
C(7)	15(1)	15(1)	14(1)	0(1)	1(1)	2(1)
O(4)	21(1)	22(1)	21(1)	-8(1)	-2(1)	7(1)
C(8)	14(1)	23(1)	17(1)	5(1)	0(1)	-1(1)
C(9)	14(1)	15(1)	12(1)	3(1)	-1(1)	-2(1)
C(10)	16(1)	15(1)	8(1)	1(1)	-1(1)	-2(1)
O(5)	20(1)	15(1)	20(1)	4(1)	-1(1)	-4(1)
C(11)	14(1)	14(1)	11(1)	1(1)	0(1)	-1(1)
C(12)	13(1)	15(1)	15(1)	1(1)	2(1)	-2(1)
C(13)	15(1)	18(1)	21(1)	0(1)	-1(1)	-3(1)
C(14)	14(1)	21(1)	20(1)	0(1)	-5(1)	-2(1)
C(15)	15(1)	16(1)	13(1)	-1(1)	-3(1)	0(1)
O(6)	17(1)	20(1)	13(1)	-2(1)	-1(1)	4(1)
C(19)	21(1)	19(1)	16(1)	3(1)	-4(1)	1(1)
O(1W)	25(1)	39(1)	20(1)	9(1)	5(1)	12(1)
O(2W)	22(1)	26(1)	16(1)	0(1)	-1(1)	6(1)
O(3W)	61(1)	22(1)	25(1)	0(1)	8(1)	-2(1)

Table 19. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (≈^{2}x 10 ^{3}) for V20005.

	x	y	z	U(eq)
H(2)	6630	4801	7124	16
H(4A)	5995	3229	6485	17
H(4B)	4448	2676	6677	17
H(5)	4831	4546	5819	17
H(6A)	2559	5075	6207	20
H(6B)	1908	3959	6287	20
H(16)	3168	2818	5316	19
H(17A)	5892	3578	4662	22
H(17B)	5717	2549	5152	22
H(3O)	4480(30)	2009(19)	4146(18)	33
H(18A)	2013	4285	4839	33
H(18B)	2685	3673	4084	33
H(18C)	3528	4640	4422	33
H(4O)	3520(30)	5530(20)	7947(16)	31
H(8A)	1843	3633	8237	22
H(8B)	2282	2884	7485	22
H(9)	4262	3819	8653	16
H(11)	7318	2112	8171	16
H(12)	7970	3424	7418	17
H(13)	9319	4431	8245	22
H(14A)	8825	3878	9729	22
H(14B)	9516	3073	9105	22
H(6O)	6270(30)	3525(19)	10162(13)	25
H(19A)	7686	2030	10322	28
H(19B)	8302	1527	9501	28
H(19C)	6570	1480	9708	28
H(1W1)	4840(40)	3250(20)	3020(15)	42
H(1W2)	4070(30)	3960(20)	2643(19)	42
H(2W1)	6130(30)	3730(20)	1714(15)	32
H(2W2)	7530(30)	3640(20)	1429(17)	32

H(3W1)	3680(40)	690(30)	4929(15)	54
H(3W2)	3500(40)	174(19)	4180(20)	54

Table 20. Torsion angles [∞] for V20005.

C(13)-O(1)-C(1)-O(2)	173.80(17)
C(13)-O(1)-C(1)-C(2)	-6.71(19)
O(2)-C(1)-C(2)-C(3)	-40.9(3)
O(1)-C(1)-C(2)-C(3)	139.63(15)
O(2)-C(1)-C(2)-C(12)	-160.19(19)
O(1)-C(1)-C(2)-C(12)	20.37(18)
C(1)-C(2)-C(3)-C(9)	-57.69(19)
C(12)-C(2)-C(3)-C(9)	57.98(18)
C(1)-C(2)-C(3)-C(4)	173.93(14)
C(12)-C(2)-C(3)-C(4)	-70.40(17)
C(1)-C(2)-C(3)-C(7)	48.3(2)
C(12)-C(2)-C(3)-C(7)	164.02(16)
C(2)-C(3)-C(4)-C(5)	-103.66(16)
C(9)-C(3)-C(4)-C(5)	130.68(15)
C(7)-C(3)-C(4)-C(5)	38.30(16)
C(3)-C(4)-C(5)-C(16)	-164.03(14)
C(3)-C(4)-C(5)-C(6)	-40.33(17)
C(16)-C(5)-C(6)-C(7)	149.27(15)
C(4)-C(5)-C(6)-C(7)	24.73(18)
C(4)-C(5)-C(16)-C(18)	175.24(16)
C(6)-C(5)-C(16)-C(18)	56.5(2)
C(4)-C(5)-C(16)-C(17)	-61.13(19)
C(6)-C(5)-C(16)-C(17)	-179.83(15)
C(18)-C(16)-C(17)-O(3)	-54.5(2)
C(5)-C(16)-C(17)-O(3)	-178.33(15)
C(5)-C(6)-C(7)-O(4)	132.31(15)
C(5)-C(6)-C(7)-C(8)	-97.27(17)
C(5)-C(6)-C(7)-C(3)	-0.71(19)
C(2)-C(3)-C(7)-O(4)	-24.0(3)
C(9)-C(3)-C(7)-O(4)	91.77(16)
C(4)-C(3)-C(7)-O(4)	-152.87(15)
C(2)-C(3)-C(7)-C(6)	105.8(2)
C(9)-C(3)-C(7)-C(6)	-138.51(15)
C(4)-C(3)-C(7)-C(6)	-23.14(17)

C(2)-C(3)-C(7)-C(8)	-136.90(18)
C(9)-C(3)-C(7)-C(8)	-21.17(12)
C(4)-C(3)-C(7)-C(8)	94.19(13)
O(4)-C(7)-C(8)-C(9)	-98.27(15)
C(6)-C(7)-C(8)-C(9)	131.00(15)
C(3)-C(7)-C(8)-C(9)	21.11(12)
C(2)-C(3)-C(9)-C(10)	-70.31(18)
C(4)-C(3)-C(9)-C(10)	54.98(19)
C(7)-C(3)-C(9)-C(10)	155.46(14)
C(2)-C(3)-C(9)-C(8)	155.83(15)
C(4)-C(3)-C(9)-C(8)	-78.88(16)
C(7)-C(3)-C(9)-C(8)	21.60(13)
C(7)-C(8)-C(9)-C(10)	-139.29(18)
C(7)-C(8)-C(9)-C(3)	-21.61(13)
C(3)-C(9)-C(10)-O(5)	-129.31(18)
C(8)-C(9)-C(10)-O(5)	-20.8(3)
C(3)-C(9)-C(10)-C(11)	51.09(19)
C(8)-C(9)-C(10)-C(11)	159.58(16)
O(5)-C(10)-C(11)-C(15)	-84.3(2)
C(9)-C(10)-C(11)-C(15)	95.36(17)
O(5)-C(10)-C(11)-C(12)	154.02(16)
C(9)-C(10)-C(11)-C(12)	-26.4(2)
C(1)-C(2)-C(12)-C(13)	-24.82(16)
C(3)-C(2)-C(12)-C(13)	-149.51(14)
C(1)-C(2)-C(12)-C(11)	91.56(17)
C(3)-C(2)-C(12)-C(11)	-33.1(2)
C(10)-C(11)-C(12)-C(13)	133.11(16)
C(15)-C(11)-C(12)-C(13)	9.42(18)
C(10)-C(11)-C(12)-C(2)	18.0(2)
C(15)-C(11)-C(12)-C(2)	-105.67(16)
C(1)-O(1)-C(13)-C(14)	-124.26(15)
C(1)-O(1)-C(13)-C(12)	-10.13(19)
C(2)-C(12)-C(13)-O(1)	21.90(17)
C(11)-C(12)-C(13)-O(1)	-103.05(15)
C(2)-C(12)-C(13)-C(14)	138.55(14)
C(11)-C(12)-C(13)-C(14)	13.60(18)

O(1)-C(13)-C(14)-C(15)	81.46(17)
C(12)-C(13)-C(14)-C(15)	-32.08(18)
C(13)-C(14)-C(15)-O(6)	-75.99(18)
C(13)-C(14)-C(15)-C(19)	159.61(15)
C(13)-C(14)-C(15)-C(11)	37.36(17)
C(10)-C(11)-C(15)-O(6)	-40.78(18)
C(12)-C(11)-C(15)-O(6)	88.10(15)
C(10)-C(11)-C(15)-C(19)	80.17(18)
C(12)-C(11)-C(15)-C(19)	-150.95(15)
C(10)-C(11)-C(15)-C(14)	-157.26(14)
C(12)-C(11)-C(15)-C(14)	-28.37(17)

Symmetry transformations used to generate equivalent atoms:

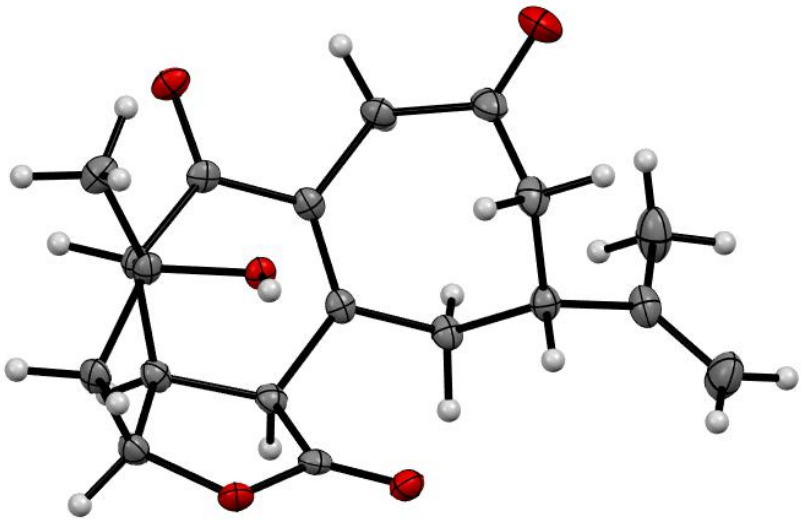
Table 21. Hydrogen bonds for V20005 [≈ and ∞].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(3)-H(3O)...O(3W)	0.80(2)	1.95(2)	2.755(2)	175(3)
O(4)-H(4O)...O(2)	0.82(2)	1.93(2)	2.737(2)	168(3)
C(9)-H(9)...O(6)	1.00	2.37	2.976(2)	117.8
O(6)-H(6O)...O(2W)#1	0.85(2)	1.95(2)	2.790(2)	175(3)
O(1W)-H(1W1)...O(3)	0.85(2)	1.91(2)	2.758(2)	178(3)
O(1W)-H(1W2)...O(4)#2	0.85(2)	1.96(2)	2.799(2)	169(3)
O(2W)-H(2W1)...O(1W)	0.84(2)	1.86(2)	2.701(2)	173(3)
O(2W)-H(2W2)...O(5)#3	0.86(2)	1.96(2)	2.804(2)	168(3)
O(3W)-H(3W1)...O(1)#4	0.84(2)	2.49(3)	3.184(2)	141(3)
O(3W)-H(3W2)...O(2W)#5	0.87(2)	1.94(2)	2.814(2)	175(4)

Symmetry transformations used to generate equivalent atoms:

#1 x,y,z+1 #2 -x+1/2,-y+1,z-1/2 #3 x+1/2,-y+1/2,-z+1

#4 -x+1,y-1/2,-z+3/2 #5 -x+1,y-1/2,-z+1/2



X-ray Crystal Structure for compound 1

Figure S4. X-Ray Coordinate of Compound 1

Table 22. Crystal data and structure refinement for V20018.

Identification code	V20018	
Empirical formula	C19 H22 O5	
Formula weight	330.36	
Temperature	100(2) K	
Wavelength	1.54178 ≈	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 6.1878(4) ≈	α= 90∞.
	b = 14.9676(14) ≈	β= 90∞.
	c = 17.511(2) ≈	γ = 90∞.
Volume	1621.8(3) ≈^{3}	
Z	4	
Density (calculated)	1.353 Mg/m^3	
Absorption coefficient	0.800 mm^{-1}	
F(000)	704	

Crystal size	0.450 x 0.200 x 0.150 mm^3
Theta range for data collection	3.885 to 74.514∞.
Index ranges	-7<=h<=7, -18<=k<=18, -20<=l<=21
Reflections collected	14706
Independent reflections	3306 [R(int) = 0.0575]
Completeness to theta = 67.679∞	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7538 and 0.6083
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3306 / 1 / 222
Goodness-of-fit on F^2	1.048
Final R indices [I>2sigma(I)]	R1 = 0.0353, wR2 = 0.0889
R indices (all data)	R1 = 0.0369, wR2 = 0.0906
Absolute structure parameter	0.00(7)
Extinction coefficient	n/a
Largest diff. peak and hole	0.657 and -0.199 e.≈$^{-3}$

Table 23. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (≈^{2}x 10^3) for V20018. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	1620(2)	5711(1)	5387(1)	19(1)
C(1)	2687(3)	6235(1)	4894(1)	16(1)
O(2)	1762(2)	6741(1)	4470(1)	20(1)
C(2)	5129(3)	6135(1)	5002(1)	16(1)
C(3)	6351(3)	6183(1)	4262(1)	14(1)
C(4)	6411(3)	7080(1)	3873(1)	17(1)
C(5)	5192(3)	7133(1)	3101(1)	18(1)
C(16)	5851(4)	7974(2)	2674(1)	22(1)
C(17)	4347(5)	8604(2)	2509(2)	34(1)
C(18)	8117(4)	8092(2)	2448(2)	34(1)
C(6)	5415(4)	6278(2)	2609(1)	21(1)
C(7)	7669(4)	5905(1)	2542(1)	22(1)
O(3)	8577(4)	5848(1)	1932(1)	38(1)
C(8)	8816(3)	5587(2)	3257(1)	18(1)
C(9)	7470(3)	5491(1)	3974(1)	15(1)
C(10)	7522(3)	4620(1)	4364(1)	15(1)
O(4)	8720(2)	4016(1)	4141(1)	19(1)
C(11)	6084(3)	4457(1)	5040(1)	15(1)
C(12)	3939(3)	3993(1)	4811(1)	16(1)
O(5)	3102(2)	4518(1)	4189(1)	15(1)
C(19)	4176(3)	3021(1)	4572(1)	21(1)
C(13)	2585(3)	4137(1)	5535(1)	18(1)
C(14)	3075(3)	5093(1)	5780(1)	19(1)
C(15)	5399(3)	5298(1)	5486(1)	16(1)

Table 24. Bond lengths [≈] and angles [∞] for V20018.

O(1)-C(1)	1.341(3)
O(1)-C(14)	1.462(3)
C(1)-O(2)	1.206(3)
C(1)-C(2)	1.530(3)
C(2)-C(3)	1.502(3)
C(2)-C(15)	1.522(3)
C(2)-H(2)	1.0000
C(3)-C(9)	1.345(3)
C(3)-C(4)	1.506(3)
C(4)-C(5)	1.551(3)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-C(16)	1.519(3)
C(5)-C(6)	1.549(3)
C(5)-H(5)	1.0000
C(16)-C(17)	1.356(4)
C(16)-C(18)	1.468(4)
C(17)-H(17A)	0.9500
C(17)-H(17B)	0.9500
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(6)-C(7)	1.507(3)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(7)-O(3)	1.210(3)
C(7)-C(8)	1.515(3)
C(8)-C(9)	1.514(3)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-C(10)	1.472(3)
C(10)-O(4)	1.232(3)
C(10)-C(11)	1.501(3)
C(11)-C(15)	1.540(3)

C(11)-C(12)	1.551(3)
C(11)-H(11)	1.0000
C(12)-O(5)	1.439(2)
C(12)-C(19)	1.522(3)
C(12)-C(13)	1.535(3)
O(5)-H(5O)	0.84(2)
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(13)-C(14)	1.524(3)
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(14)-C(15)	1.558(3)
C(14)-H(14)	1.0000
C(15)-H(15)	1.0000

C(1)-O(1)-C(14)	111.70(15)
O(2)-C(1)-O(1)	122.04(19)
O(2)-C(1)-C(2)	127.36(19)
O(1)-C(1)-C(2)	110.44(17)
C(3)-C(2)-C(15)	117.69(17)
C(3)-C(2)-C(1)	112.65(16)
C(15)-C(2)-C(1)	104.94(16)
C(3)-C(2)-H(2)	107.0
C(15)-C(2)-H(2)	107.0
C(1)-C(2)-H(2)	107.0
C(9)-C(3)-C(2)	123.12(18)
C(9)-C(3)-C(4)	120.27(18)
C(2)-C(3)-C(4)	116.46(17)
C(3)-C(4)-C(5)	115.37(16)
C(3)-C(4)-H(4A)	108.4
C(5)-C(4)-H(4A)	108.4
C(3)-C(4)-H(4B)	108.4
C(5)-C(4)-H(4B)	108.4
H(4A)-C(4)-H(4B)	107.5
C(16)-C(5)-C(6)	112.80(17)

C(16)-C(5)-C(4)	109.91(17)
C(6)-C(5)-C(4)	113.52(17)
C(16)-C(5)-H(5)	106.7
C(6)-C(5)-H(5)	106.7
C(4)-C(5)-H(5)	106.7
C(17)-C(16)-C(18)	121.0(2)
C(17)-C(16)-C(5)	119.8(2)
C(18)-C(16)-C(5)	119.3(2)
C(16)-C(17)-H(17A)	120.0
C(16)-C(17)-H(17B)	120.0
H(17A)-C(17)-H(17B)	120.0
C(16)-C(18)-H(18A)	109.5
C(16)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(16)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(7)-C(6)-C(5)	115.61(17)
C(7)-C(6)-H(6A)	108.4
C(5)-C(6)-H(6A)	108.4
C(7)-C(6)-H(6B)	108.4
C(5)-C(6)-H(6B)	108.4
H(6A)-C(6)-H(6B)	107.4
O(3)-C(7)-C(6)	121.7(2)
O(3)-C(7)-C(8)	119.3(2)
C(6)-C(7)-C(8)	119.01(18)
C(9)-C(8)-C(7)	117.25(18)
C(9)-C(8)-H(8A)	108.0
C(7)-C(8)-H(8A)	108.0
C(9)-C(8)-H(8B)	108.0
C(7)-C(8)-H(8B)	108.0
H(8A)-C(8)-H(8B)	107.2
C(3)-C(9)-C(10)	121.31(18)
C(3)-C(9)-C(8)	121.41(18)
C(10)-C(9)-C(8)	117.22(17)
O(4)-C(10)-C(9)	121.05(18)

O(4)-C(10)-C(11)	119.20(18)
C(9)-C(10)-C(11)	119.75(17)
C(10)-C(11)-C(15)	115.54(17)
C(10)-C(11)-C(12)	112.03(16)
C(15)-C(11)-C(12)	105.17(16)
C(10)-C(11)-H(11)	107.9
C(15)-C(11)-H(11)	107.9
C(12)-C(11)-H(11)	107.9
O(5)-C(12)-C(19)	110.42(17)
O(5)-C(12)-C(13)	110.60(16)
C(19)-C(12)-C(13)	114.45(17)
O(5)-C(12)-C(11)	105.04(15)
C(19)-C(12)-C(11)	114.65(17)
C(13)-C(12)-C(11)	100.97(16)
C(12)-O(5)-H(5O)	107(2)
C(12)-C(19)-H(19A)	109.5
C(12)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(12)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(14)-C(13)-C(12)	104.79(16)
C(14)-C(13)-H(13A)	110.8
C(12)-C(13)-H(13A)	110.8
C(14)-C(13)-H(13B)	110.8
C(12)-C(13)-H(13B)	110.8
H(13A)-C(13)-H(13B)	108.9
O(1)-C(14)-C(13)	109.84(16)
O(1)-C(14)-C(15)	106.79(15)
C(13)-C(14)-C(15)	106.01(17)
O(1)-C(14)-H(14)	111.3
C(13)-C(14)-H(14)	111.3
C(15)-C(14)-H(14)	111.3
C(2)-C(15)-C(11)	114.84(16)
C(2)-C(15)-C(14)	104.14(16)
C(11)-C(15)-C(14)	105.07(16)

C(2)-C(15)-H(15)	110.8
C(11)-C(15)-H(15)	110.8
C(14)-C(15)-H(15)	110.8

Symmetry transformations used to generate equivalent atoms:

Table 25. Anisotropic displacement parameters ($\approx^2$x 10^3) for V20018. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	17(1)	21(1)	20(1)	0(1)	4(1)	5(1)
C(1)	17(1)	18(1)	14(1)	-4(1)	2(1)	1(1)
O(2)	19(1)	20(1)	21(1)	-2(1)	-1(1)	6(1)
C(2)	16(1)	18(1)	13(1)	-2(1)	-2(1)	0(1)
C(3)	11(1)	18(1)	14(1)	0(1)	-3(1)	-4(1)
C(4)	19(1)	17(1)	16(1)	0(1)	-2(1)	-3(1)
C(5)	16(1)	20(1)	17(1)	2(1)	-2(1)	-1(1)
C(16)	26(1)	23(1)	18(1)	4(1)	-3(1)	-4(1)
C(17)	34(1)	27(1)	41(1)	13(1)	4(1)	4(1)
C(18)	27(1)	38(1)	35(1)	17(1)	-1(1)	-6(1)
C(6)	24(1)	23(1)	17(1)	-1(1)	-7(1)	-3(1)
C(7)	30(1)	19(1)	17(1)	-3(1)	2(1)	0(1)
O(3)	49(1)	45(1)	20(1)	-1(1)	10(1)	14(1)
C(8)	16(1)	21(1)	19(1)	0(1)	4(1)	-1(1)
C(9)	10(1)	21(1)	14(1)	1(1)	-1(1)	-2(1)
C(10)	8(1)	19(1)	17(1)	-2(1)	-3(1)	-1(1)
O(4)	11(1)	19(1)	27(1)	0(1)	1(1)	1(1)
C(11)	12(1)	17(1)	16(1)	4(1)	-2(1)	2(1)
C(12)	11(1)	18(1)	17(1)	3(1)	0(1)	1(1)
O(5)	10(1)	18(1)	17(1)	2(1)	-1(1)	-1(1)
C(19)	15(1)	17(1)	29(1)	2(1)	0(1)	-2(1)
C(13)	14(1)	22(1)	19(1)	5(1)	3(1)	-1(1)
C(14)	17(1)	24(1)	15(1)	2(1)	3(1)	2(1)
C(15)	14(1)	21(1)	14(1)	0(1)	-1(1)	-1(1)

Table 26. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (≈^{2}x 10 ^{3}) for V20018.

	x	y	z	U(eq)
H(2)	5617	6652	5321	19
H(4A)	7940	7245	3785	21
H(4B)	5787	7530	4224	21
H(5)	3622	7198	3225	21
H(17A)	4754	9131	2244	41
H(17B)	2887	8518	2659	41
H(18A)	8266	8645	2153	50
H(18B)	8575	7584	2135	50
H(18C)	9025	8127	2906	50
H(6A)	4469	5811	2829	26
H(6B)	4874	6411	2089	26
H(8A)	9481	5001	3144	22
H(8B)	10006	6010	3367	22
H(11)	6869	4053	5401	18
H(5O)	1810(40)	4353(19)	4117(16)	22
H(19A)	2797	2803	4369	31
H(19B)	4593	2660	5015	31
H(19C)	5292	2972	4176	31
H(13A)	1027	4062	5425	22
H(13B)	3009	3708	5939	22
H(14)	2975	5162	6347	22
H(15)	6404	5411	5923	20

Table 27. Torsion angles [∞] for V20018.

C(14)-O(1)-C(1)-O(2)	174.04(18)
C(14)-O(1)-C(1)-C(2)	-10.2(2)
O(2)-C(1)-C(2)-C(3)	-40.7(3)
O(1)-C(1)-C(2)-C(3)	143.75(16)
O(2)-C(1)-C(2)-C(15)	-169.96(19)
O(1)-C(1)-C(2)-C(15)	14.5(2)
C(15)-C(2)-C(3)-C(9)	7.3(3)
C(1)-C(2)-C(3)-C(9)	-115.0(2)
C(15)-C(2)-C(3)-C(4)	-168.25(17)
C(1)-C(2)-C(3)-C(4)	69.4(2)
C(9)-C(3)-C(4)-C(5)	71.1(3)
C(2)-C(3)-C(4)-C(5)	-113.2(2)
C(3)-C(4)-C(5)-C(16)	-165.26(18)
C(3)-C(4)-C(5)-C(6)	-37.9(3)
C(6)-C(5)-C(16)-C(17)	114.0(2)
C(4)-C(5)-C(16)-C(17)	-118.3(2)
C(6)-C(5)-C(16)-C(18)	-66.2(3)
C(4)-C(5)-C(16)-C(18)	61.6(3)
C(16)-C(5)-C(6)-C(7)	79.8(2)
C(4)-C(5)-C(6)-C(7)	-46.1(3)
C(5)-C(6)-C(7)-O(3)	-118.2(2)
C(5)-C(6)-C(7)-C(8)	62.2(3)
O(3)-C(7)-C(8)-C(9)	-167.6(2)
C(6)-C(7)-C(8)-C(9)	12.0(3)
C(2)-C(3)-C(9)-C(10)	1.6(3)
C(4)-C(3)-C(9)-C(10)	177.02(16)
C(2)-C(3)-C(9)-C(8)	-175.38(18)
C(4)-C(3)-C(9)-C(8)	0.0(3)
C(7)-C(8)-C(9)-C(3)	-57.2(3)
C(7)-C(8)-C(9)-C(10)	125.7(2)
C(3)-C(9)-C(10)-O(4)	-172.57(19)
C(8)-C(9)-C(10)-O(4)	4.6(3)
C(3)-C(9)-C(10)-C(11)	7.9(3)
C(8)-C(9)-C(10)-C(11)	-174.98(17)

O(4)-C(10)-C(11)-C(15)	155.15(18)
C(9)-C(10)-C(11)-C(15)	-25.3(2)
O(4)-C(10)-C(11)-C(12)	-84.4(2)
C(9)-C(10)-C(11)-C(12)	95.1(2)
C(10)-C(11)-C(12)-O(5)	-50.5(2)
C(15)-C(11)-C(12)-O(5)	75.75(18)
C(10)-C(11)-C(12)-C(19)	70.9(2)
C(15)-C(11)-C(12)-C(19)	-162.86(17)
C(10)-C(11)-C(12)-C(13)	-165.57(16)
C(15)-C(11)-C(12)-C(13)	-39.29(18)
O(5)-C(12)-C(13)-C(14)	-69.4(2)
C(19)-C(12)-C(13)-C(14)	165.12(17)
C(11)-C(12)-C(13)-C(14)	41.41(18)
C(1)-O(1)-C(14)-C(13)	-112.91(18)
C(1)-O(1)-C(14)-C(15)	1.6(2)
C(12)-C(13)-C(14)-O(1)	86.82(18)
C(12)-C(13)-C(14)-C(15)	-28.20(19)
C(3)-C(2)-C(15)-C(11)	-24.3(2)
C(1)-C(2)-C(15)-C(11)	101.83(19)
C(3)-C(2)-C(15)-C(14)	-138.68(17)
C(1)-C(2)-C(15)-C(14)	-12.52(19)
C(10)-C(11)-C(15)-C(2)	32.7(2)
C(12)-C(11)-C(15)-C(2)	-91.33(19)
C(10)-C(11)-C(15)-C(14)	146.55(16)
C(12)-C(11)-C(15)-C(14)	22.47(19)
O(1)-C(14)-C(15)-C(2)	7.3(2)
C(13)-C(14)-C(15)-C(2)	124.43(17)
O(1)-C(14)-C(15)-C(11)	-113.76(17)
C(13)-C(14)-C(15)-C(11)	3.33(19)

Symmetry transformations used to generate equivalent atoms:

Table 28. Hydrogen bonds for V20018 [≈ and ∞].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(2)-H(2)...O(2)#1	1.00	2.53	3.461(2)	154.0
C(8)-H(8B)...O(2)#2	0.99	2.47	3.289(3)	139.6
O(5)-H(5O)...O(4)#3	0.84(2)	1.98(2)	2.815(2)	170(3)
C(19)-H(19C)...O(4)	0.98	2.64	3.270(3)	122.7
C(15)-H(15)...O(3)#4	1.00	2.58	3.123(3)	113.7

Symmetry transformations used to generate equivalent atoms:

#1 x+1/2,-y+3/2,-z+1 #2 x+1,y,z #3 x-1,y,z

#4 -x+3/2,-y+1,z+1/2