Electronic Supplementary Material (ESI) for Chemical Science.

The Total Synthesis of (–)-Scabrolide A and (–)-Yonarolide

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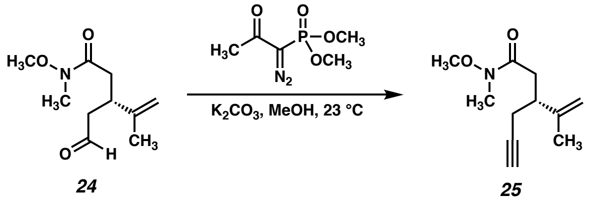
Materials and Methods

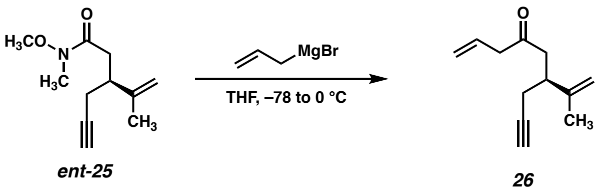
Unless otherwise stated, reactions were performed in flame-dried glassware under a nitrogen atmosphere using dry, deoxygenated solvents. Solvents were dried by passage through an activated alumina column under argon.[1] Reaction progress was monitored by thin-layer chromatography (TLC). TLC was performed 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. ^1H 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 ^1H 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

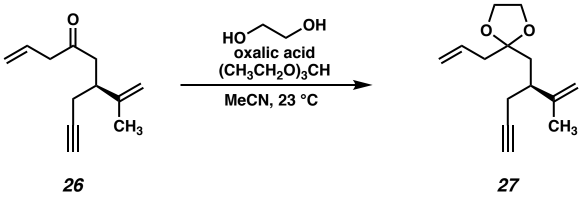
Experimental Procedures



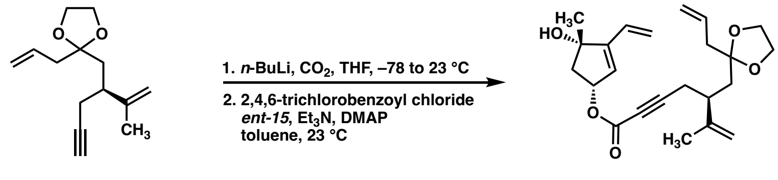
Alkyne 25: In a round-bottom flask, aldehyde **24** (6.27 g, 31.5 mmol, 1.0 equiv) and K_2CO_3 (8.7 g, 62.9 mmol, 2.0 equiv) was diluted with dry methanol (52.5 mL, 0.6 M) and cooled to 0 °C (ice/water bath). Ohira–Bestmann reagent (7.25 g, 37.8 mmol, 1.2 equiv) was added dropwise via syringe and the resultant suspension was allowed to stir for 12 h while gradually warming to 23 °C. Upon complete consumption of starting material (determined by TLC analysis), the reaction was diluted with Et_2O and washed with a saturated solution of $NaHCO_3$. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography (SiO_2, 10% EtOAc/CH_2Cl_2) to generate alkyne **25** (5.0 g, 82% yield) as a pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.85 (p, J = 1.5 Hz, 1H), 4.82 (dp, J = 1.7, 0.9 Hz, 1H), 3.70 (s, 3H), 3.17 (s, 3H), 2.92–2.82 (m, 1H), 2.76–2.60 (m, 2H), 2.38 (ddd, J = 6.4, 3.5, 2.7 Hz, 2H), 1.99 (t, J = 2.7 Hz, 1H), 1.77 (dd, J = 1.6, 0.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.0, 146.2, 111.6, 82.4, 69.9, 61.3, 40.8, 34.8, 32.2, 23.0, 20.7; IR (thin film, NaCl) 3293, 3250, 3076, 2967, 2938, 2820, 2116, 1661, 1430, 1384, 1334, 1175, 1175, 1108, 1002, 936, 894 cm^{-1}; HRMS (ES/APCI) m/z calc'd $C_{11}H_{18}O_2N$ $[M+H]^+$: 196.1332, found: 196.1336. $[\alpha]_D^{25.0}$ + 22.8° (c 1.0, $CHCl_3$).



Ketone 26: In a flame dried round bottom flask, amide ***ent*-25** (50 mg, 0.26 mmol, 1.0 equiv) was dissolved in THF (0.8 mL, 0.3 M) and cooled to –78 °C. Allyl magnesium bromide (0.52 mL, 0.52 mmol, 1.0 M, 2.0 equiv) was added dropwise to the reaction solution. The reaction was allowed to stir for 15 min at –78 °C and then warmed to 0 °C and stirred for 16 h. Upon complete consumption of starting material (determined by TLC analysis, 10% Et_2O/hexanes), the reaction was quenched with a saturated solution of NH_4Cl and the product was extracted from the biphasic mixture with Et_2O (3x). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography (SiO_2, 10% Et_2O/hexanes) to generate alkyne **26** (39 mg, 87% yield) as a pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.91 (ddt, *J* = 17.2, 10.2, 7.0 Hz, 1H), 5.18 (dq, *J* = 10.2, 1.3 Hz, 1H), 5.14 (dq, *J* = 17.1, 1.5 Hz, 1H), 4.82 (p, *J* = 1.5 Hz, 1H), 4.78 (dt, *J* = 1.5, 0.8 Hz, 1H), 3.18 (dt, *J* = 6.9, 1.4 Hz, 2H), 2.86–2.77 (m, 1H), 2.74 (dd, *J* = 16.7, 6.6 Hz, 1H), 2.62 (dd, *J* = 16.7, 7.4 Hz, 1H), 2.32 (ddd, *J* = 14.5, 6.5, 2.7 Hz, 2H), 1.99 (t, *J* = 2.7 Hz, 1H), 1.73 (dd, *J* = 1.5, 0.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.3, 145.9, 130.52, 119.1, 111.8, 82.2, 70.3, 48.2, 45.1, 40.2, 23.0, 20.7; IR (thin film, NaCl) 3297, 3078, 2969, 2917, 2117, 1715, 1646, 1430, 1376, 993, 920, 895 cm^{-1}; HRMS (ESI) m/z calc'd $C_{12}H_{16}O$ $[M^{\bullet}]^+$: 176.1201, found: 176.1191; $[\alpha]_D^{25}$ – 24.90 ° (*c* 3.7, $CDCl_3$).



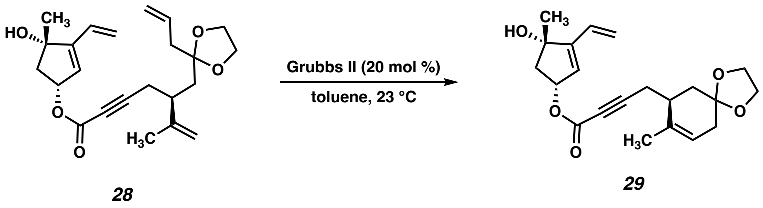
Dioxolane 27: Dried oxalic acid (109 mg, 1.2 mmol, 8.5 equiv) was dissolved in a solution of ethylene glycol (0.27 mL, 4.69 mmol, 33 equiv), triethyl orthoformate (0.14 mL, 0.85 mmol, 6 equiv), and MeCN (1.95 mL, 0.073 M). After complete dissolution of the oxalic acid, ketone **26** (25 mg, 0.14 mmol, 1 equiv) was added. The reaction was sealed and allowed to stir at ambient temperature (23 °C) for 36 h. Upon complete consumption of starting material (as determined by TLC analysis), the reaction was diluted with H_2O and the product was extracted with Et_2O (3 x 5 mL). The combined organic layers were washed with brine, dried with $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography (SiO_2, 25% Et_2O/hexanes) to afford dioxolane **27** (26 mg, 83% yield) as a pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.81 (ddt, *J* = 16.9, 10.5, 7.2 Hz, 1H), 5.12 (ddt, *J* = 8.2, 2.2, 1.3 Hz, 1H), 5.08 (t, *J* = 1.3 Hz, 1H), 4.79 (q, *J* = 1.3 Hz, 2H), 3.94 (q, *J* = 1.3 Hz, 4H), 2.52 (dq, *J* = 8.2, 6.3 Hz, 1H), 2.43–2.34 (m, 3H), 2.26 (ddd, *J* = 16.7, 8.1, 2.7 Hz, 1H), 1.97 (t, *J* = 2.6 Hz, 1H), 1.83 (d, *J* = 6.5 Hz, 2H), 1.70 (t, *J* = 1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 147.5, 133.3, 118.4, 111.4, 110.8, 83.3, 69.4, 65.0, 65.0, 42.5, 41.3, 39.2, 24.1, 19.2; IR (thin film, NaCl) 3302, 3075, 2949, 2888, 2117, 1643, 1433, 1374, 1311, 1124, 1100, 996, 918, 890, 862, 837, 635 cm^{-1}; HRMS (FAB$^+$) m/z calc'd $C_{14}H_{21}O_2$ $[M+H]^+$: 221.1536, found: 221.1531; $[\alpha]_{23}^{D}$ = – 2.45 (c = 0.79, $CHCl_3$).



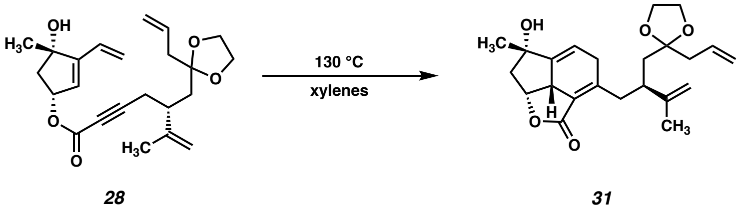
27 *28*

Ester 28: Dioxolane **27** (95 mg, 0.43 mmol, 1 equiv) was dissolved in THF (4.3 mL, 0.1 M) and cooled –78 °C. *n*-BuLi (2.17 M in hexanes, 395 μL, 0.863 mmol, 2 equiv) was then added dropwise. The solution was allowed to stir for 5 min followed by the addition powdered dry ice (0.56 g, 1.3 g/mmol of **27**). After 10 min, the reaction was quenched with a saturated solution of NH_4Cl and was allowed to warm to ambient temperature (23°C). The solution was acidified with a 5% solution of citric acid (5 mL) and the product was extracted with EtOAc (5 x 15 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo leaving an acid (103 mg, 93%) was used crude in the following reaction.

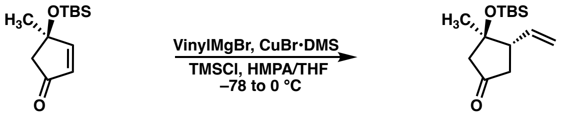
To a solution of the crude acid (58 mg, 0.22 mmol, 1.1 equiv) in THF (2 mL, 0.1 M), Et_3N (92 μL, 0.66 mmol, 3.3 equiv) and 2,4,6-trichlorobenzoyl chloride (34 μL, 0.22 mmol, 1.1 equiv) was added. The reaction was allowed to stir for 1 h followed by the addition of a THF solution (2 mL, 0.1 M) of diol ***ent*-15** (28 mg, 0.2 M, 1 equiv) and DMAP (24 mg, 0.2 mmol, 1 equiv). The reaction was allowed to stir at 23 °C until complete. Upon complete consumption of diol ***ent*-15** (as determined by TLC analysis) the reaction was directly purified by column chromatography (SiO_2, 100% hexanes then 50% EtOAc/hexanes) to afford ester **28** (43 mg, 50%) as a yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 6.31 (dd, *J* = 17.8, 11.3 Hz, 1H), 5.87–5.73 (m, 3H), 5.53 (ddd, *J* = 7.1, 4.5, 2.3 Hz, 1H), 5.32 (dd, *J* = 11.3, 1.6 Hz, 1H), 5.16–5.10 (m, 1H), 5.08 (t, *J* = 1.3 Hz, 1H), 4.80 (d, *J* = 1.2 Hz, 2H), 3.94 (s, 4H), 2.65–2.53 (m, 3H), 2.45–2.39 (m, 1H), 2.36 (dq, *J* = 6.1, 1.2 Hz, 2H), 2.08–2.01 (m, 1H), 1.92 (s, 1H), 1.85 (dd, *J* = 14.7, 6.1 Hz, 1H), 1.77 (dd, *J* = 14.7, 6.2 Hz, 1H), 1.69 (t, *J* = 1.2 Hz, 3H), 1.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.6, 151.7, 146.6, 133.2, 129.0, 126.2, 119.5, 118.6, 112.1, 110.7, 88.9, 81.0, 77.0, 74.2, 65.1, 65.0, 49.0, 42.5, 40.6, 39.4, 26.7, 24.2, 19.4; IR (thin film, NaCl) 3369, 2956, 2918, 2847, 2232, 1705, 1633, 1460, 1418, 1372, 1258, 1063, 801 cm^{-1}; HRMS (FAB^+) m/z calc'd $C_{23}H_{31}O_5$ $[M+H]^+$: 387.2171, found: 387.2158; $[\alpha]_{25}{}^{D}$ = + 26.7 (c = 0.045, $CHCl_3$).



Cyclohexene 29: To a stirred, Ar-sparged solution of ester **28** (6 mg, 0.016 mmol, 1.0 equiv) in toluene (1 mL, 0.016 M) was added Grubbs 2nd-generation catalyst (2.6 mg, 3.1 µmol, 0.2 equiv) in one portion. The reaction was allowed to stir for 2 h followed by direct purification by column chromatography (SiO_2, 100% hexanes to 20% EtOAc/hexanes) to afford cyclohexene **29** (1.7 mg, 31 %) as a pale yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 6.26 (ddt, *J* = 17.8, 11.3, 0.7 Hz, 1H), 5.76 (d, *J* = 2.4 Hz, 1H), 5.75–5.68 (m, 1H), 5.52–5.45 (m, 1H), 5.35 (ddt, *J* = 4.6, 3.2, 1.5 Hz, 1H), 5.27 (dd, *J* = 11.3, 1.6 Hz, 1H), 3.94–3.87 (m, 4H), 2.58 (dd, *J* = 14.3, 7.3 Hz, 1H), 2.50 (d, *J* = 1.9 Hz, 3H), 2.26–2.11 (m, 2H), 2.00 (dd, *J* = 14.2, 4.4 Hz, 1H), 1.90–1.76 (m, 2H), 1.64 (q, *J* = 2.0 Hz, 3H), 1.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 151.8, 133.9, 128.9, 126.1, 121.8, 119.6, 108.0, 88.5, 81.1, 77.1, 74.4, 64.7, 64.5, 49.0, 38.1, 36.2, 36.1, 26.8, 22.6, 21.1; IR (thin film, NaCl) 3447, 2926, 2233, 1734, 1701, 1559, 1540, 1420, 1372, 1248, 1122, 1072, 988, 948, 874, 810, 753, 731; HRMS (ESI) m/z calc’d $C_{21}H_{27}O_5$ $[M+H]^+$: 358.1853, found: 358.1833; $[\alpha]_D^{23}$ + 125.4 (*c* 0.75, $CHCl_3$).



Cyclohexadiene 31: Ester **28** (5.3 mg, 13.7 µmol, 1 equiv) was dissolved xylenes (0.5 mL), sparged with Ar, sealed, and heated to 130 °C for 1 h. Upon complete consumption of starting material (as determined by TLC analysis), the reaction was loaded directly onto a flash column (SiO_2, 100% hexanes to 50% EtOAc/Hexanes) to afford cyclohexadiene **31** (2.1 mg, 40% yield) as an amorphous solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.91–5.72 (m, 2H), 5.16–5.03 (m, 2H), 4.96 (ddd, *J* = 9.1, 8.0, 7.0 Hz, 1H), 4.64 (dq, *J* = 2.9, 1.5 Hz, 1H), 4.57 (dd, *J* = 2.3, 1.0 Hz, 1H), 4.01–3.86 (m, 4H), 3.30 (t, *J* = 9.7 Hz, 1H), 3.10–2.90 (m, 2H), 2.75–2.59 (m, 3H), 2.50 (ddd, *J* = 12.7, 7.0, 0.9 Hz, 1H), 2.39 (dq, *J* = 7.2, 1.5 Hz, 2H), 1.90 (dd, *J* = 14.8, 7.9 Hz, 1H), 1.72–1.64 (m, 4H), 1.64–1.60 (m, 1H), 1.40 (d, *J* = 1.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 156.7, 152.0, 148.6, 133.5, 124.9, 118.4, 116.6, 111.3, 110.9, 80.0, 75.2, 65.1, 65.0, 49.8, 45.7, 42.5, 41.9, 39.4, 36.8, 35.3, 26.6, 18.3; IR (thin film, NaCl) 3458, 2924, 1749, 1642, 1432, 1210, 1093, 1044, 823 cm^{-1}; HRMS (FAB$^+$) m/z calc'd $C_{23}H_{31}O_5$ [M+H]$^+$: 387.2171, found: 387.2188; $[\alpha]_D^{23}$ + 37.5 (*c* 0.12, $CHCl_3$).



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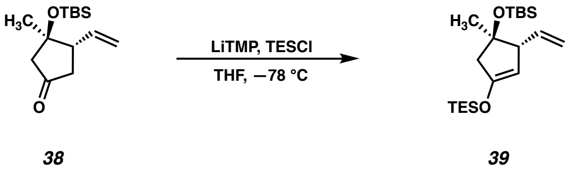
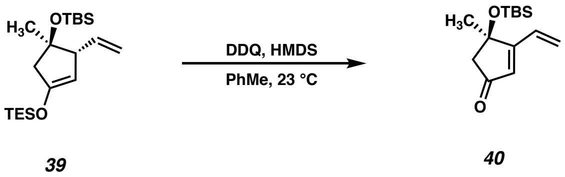
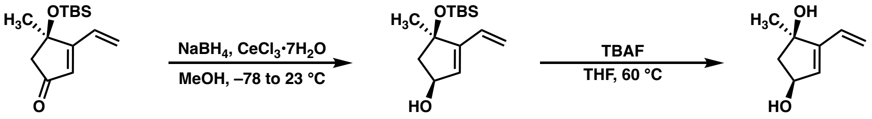
Vinylcyclopentanone 38: To a 500 mL three-necked flask was added CuBr • DMS (543 mg, 2.65 mmol, 0.12 equiv). The flask was evacuated and back-filled three times with argon, and charged with THF (110 mL). The solution was cooled to –78 °C and vinylmagnesium bromide in THF (1.0 M, 26.5 mL, 1.2 equiv) was added. The flask was 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 **37** (5.0 g, 22.1 mmol, 1 equiv) was 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) were added at room temperature, and stirred for 5 minutes. This solution was transferred to the addition funnel and slowly added to the flask over 1 hour; an internal temperature no greater than –70 °C was maintained and the solution turned orange to yellow to dark brown. Upon complete addition, the reaction was stirred at –78 °C for an additional hour, and then warmed to 0 °C. Saturated aqueous NH_4Cl (125 mL) was added before stirring at 0 °C for 1 hour. The layers were separated and the aqueous layer was extracted with Et_2O (3x). The combined organics were washed with brine, dried with $MgSO_4$ and concentrated under reduced pressure. Flash column chromatography (10-20% Et_2O/Hexanes) afforded cyclopentanone **38** (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 , $CHCl_3$).



Silyl Enol Ether 39: A 500 mL round-bottom flask was soaked in a base bath overnight, then washed, flame-dried, and placed under nitrogen atmosphere. The flask was charged with 2,2,6,6-tetramethylpiperidine (4.01 mL, 23.63 mmol, 1.2 equiv) and THF (108 mL) before being cooled to –78 °C. *n*-BuLi (9.30 mL of 2.33 M, 1.1 equiv) was added to the flask, then stirred at 0 °C for 1 hr. The flask was 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 **38** (5.00 g, 19.69 mmol, 1.0 equiv) in THF (20 mL) was added dropwise over 1 hour. Upon complete addition, the reaction was stirred until complete by TLC (15 minutes.) Triethylamine (5 mL) was then added and the reaction was quenched with a saturated aqueous sodium bicarbonate solution, and gradually warmed to 23 °C. The layers were separated and the aqueous layer was extracted with hexanes (5x). The combined organics were 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) afforded silyl enol ether **39** (4.78 g, 12.96 mmol, 66% yield, 9:1 mixture of diastereomers) as a colorless oil; *Major diastereomer*: ^1H 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, $CHCl_3$).

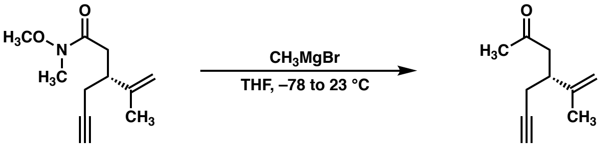


Dienone 40: A 1 L round-bottomed flask was charged with silyl enol ether **39** (5.80 g, 15.76 mmol, 1.0 equiv) in benzene (310 mL). HMDS was then added dropwise via syringe and the resulting solution was stirred for 5 minutes. DDQ (7.87 g, 34.67 mmol, 2.2 equiv) was added in a single portion, and the reaction was stirred for 45 minutes, during which time it turned from black to bright red. Celite® (30 g) was added to the reaction, then the solvent was removed by rotary evaporation, and the remaining solid dried on high vaccum for 1 h. Flash column chromatography (1%-10% Et_2O/Hexanes) afforded enone **40** (3.35 g, 13.27 mmol, 84% yield) as a gold oil, along with triethylsilanol as a coeluted impurity (1.16 g as determined by 1H NMR). A pure sample for characterization was obtained by preparative TLC (30% Et_2O/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, $CHCl_3$).



40 ***41*** ***15***

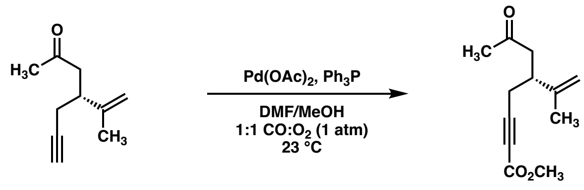
Diol 15: A 500-mL round-bottom flask was charged with dienone **40** (2.69 g, 10.67 mmol, 1.0 equiv) in MeOH (110 mL) and cooled to –78 °C. $CeCl_3$ • 7 H_2O (5.17 g, 13.87 mmol, 1.3 equiv) was added, and the solution stirred for 5 minutes before $NaBH_4$ (534 mg, 13.87 mmol, 1.3 equiv) was added in a single portion. The reaction was stirred at –78 °C for 1 hour, warmed to room temperature, and quenched with saturated, aqueous NH_4Cl. The mixture was partially concentrated on a rotary evaporator to remove methanol, transferred to a separatory funnel, and extracted with diethyl ether (3x). The combined organics were then washed with brine, dried with $MgSO_4$, and concentrated to afford an orange oil which was used directly in the next step without further purification. A pure sample for characterization was obtained by flash chromatography (SiO_2, 25% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) d = 6.32–6.22 (m, 1H), 5.75–5.67 (m, 2H), 5.25–5.19 (m, 1H), 4.64– 4.55 (m, 1H), 2.53 (dd, *J* = 12.7, 6.9 Hz, 1H), 1.93 (ddd, *J* = 12.7, 6.0, 0.8 Hz, 1H), 1.59 (s, 1H), 1.36 (d, *J* = 0.9 Hz, 3H), 0.86 (s, 9H), 0.12 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) d = 150.6, 129.8, 129.1, 118.1, 82.5, 73.5, 53.2, 28.7, 25.9, 18.2, –2.0, –2.4; IR (thin film, NaCl) 3324, 2957, 2929, 2886, 2857, 1590, 1472, 1462, 1370, 1254, 1204, 1170, 1134, 1042, 1017, 835, 774, 679 cm^{-1}; HRMS (FAB+) m/z calc'd $C_{14}H_{30}NO_2Si$ $[M+NH_4]^+$: 272.204, found 272.2027; $[a]D^{23}$ + 25.4 (*c* 0.19, $CHCl_3$). To a 500 mL round-bottom flask was added the crude reduction product in THF (150 mL). 1M TBAF in THF (15.0 mL equiv, 15.0 mmol, 1.4 equiv) was added dropwise by syringe. The flask was then equipped with a reflux condenser and heated to reflux for 8 h. After completion as judged by TLC, the reaction was cooled to 23 °C and quenched with brine. The mixture was then extracted with EtOAc (5x) before the combined organic layers were washed with brine, dried with Na_2SO_4, and concentrated under reduced pressure onto silica gel. The mixture was purified by flash column chromatography to afford diol **15** (1.17 g, 8.35 mmol, 78% yield over two steps) as an amorphous white solid. All spectral data for **15** was found to be in good accordance with literature values previously reported by our group.[2e]



25

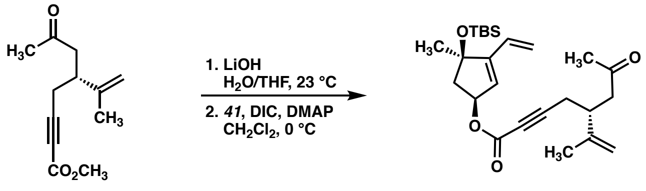
42

Ketone 42: Amide **25** (2.0 g, 10.2 mmol, 1 equiv) in THF (51 mL, 0.2 M) was cooled to –78 °C. A solution of MeMgBr in Et_2O (7.1 mL, 21.5 mmol, 3 M, 2.1 equiv) was added dropwise. The reaction was allowed to stir for 12 h while gradually warming to 23 °C. Upon complete consumption of starting material (as determined by TLC analysis), the reaction was quenched with a saturated solution of NH_4Cl (50 mL) and diluted with Et_2O (25 mL). The organics were separated, and the aqueous layer was extracted with Et_2O (3 x 40 mL) and the combined organic extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by column chromatography (SiO_2, 20% Et_2O/hexanes) to afford ketone **42** (1.2 g, 79%) as a pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.83 (p, *J* = 1.5 Hz, 1H), 4.78 (dt, *J* = 1.6, 0.8 Hz, 1H), 2.81 (p, *J* = 6.7 Hz, 1H), 2.73 (dd, *J* = 16.5, 6.6 Hz, 1H), 2.59 (dd, *J* = 16.5, 7.5 Hz, 1H), 2.36 (ddd, *J* = 16.9, 6.3, 2.7 Hz, 1H), 2.29 (ddd, *J* = 16.9, 6.6, 2.7 Hz, 1H), 2.15 (s, 3H), 1.99 (t, *J* = 2.6 Hz, 1H), 1.73 (dd, *J* = 1.5, 0.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 207.6, 145.9, 111.9, 82.2, 70.2, 46.5, 40.5, 30.5, 23.1, 20.6; IR (thin film, NaCl) 3294, 3078, 2970, 2918, 2117, 1715, 1648, 1433, 1360, 1233, 1160, 1059, 997, 896, 641; HRMS (ESI) m/z calc'd $C_{10}H_{15}O$ $[M+H]^+$: 151.1197, found: 151.1115; $[\alpha]_D^{23}$ + 22.2 (*c* 0.59, $CHCl_3$).



42 *43*

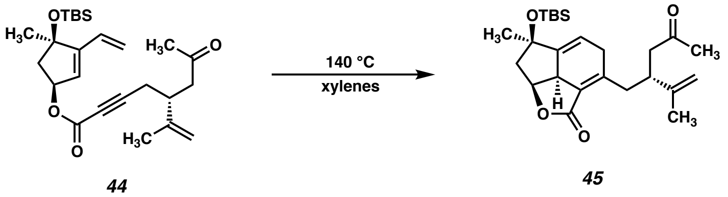
Methyl Ester 43: Palladium acetate (112 mg, 0.5 mmol, 0.3 equiv) and triphenylphosphine (260 mg, 1.0 mmol, 0.6 equiv) were dissolved in dimethylformamide (17 mL, 0.1 M) in a round-bottomed flask under N_2 and allowed to stir for 5 min. Methanol (1.7 mL, 41.5 mmol, 25 equiv) and ketone **42** (250 mg, 1.66 mmol, 1 equiv) were added, followed by attachment of 2 rubber balloons, one filled with O_2 and the other CO, to the flask. The reaction was sparged with both CO and O_2 balloons for 5 min and allowed to stir at ambient temperature (23 °C) for 16 h. Upon complete consumption of starting material (as determined by TLC), the mixture was diluted with Et_2O and a saturated solution of LiCl and the aqueous layer was extracted with Et_2O. The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by column chromatography (SiO_2, 20% EtOAc/hexanes) to afford ester **43** (249 mg, 86%) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ =4.86 (t, *J* = 1.4 Hz, 1H), 4.81 (q, *J* = 0.9 Hz, 1H), 3.75 (s, 3H), 2.85 (p, *J* = 6.7 Hz, 1H), 2.66 (dd, *J* = 9.4, 7.1 Hz, 2H), 2.48 (dd, *J* = 6.5, 4.9 Hz, 2H), 2.16 (s, 3H), 1.73 (dd, *J* = 1.4, 0.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ =207.0, 154.2, 145.2, 112.5, 87.3, 74.6, 52.8, 46.3, 39.7, 30.6, 23.1, 20.7; IR (thin film, NaCl) 2923, 2236, 1714, 1647, 1434, 1361, 1259, 1158, 1074, 942, 901, 752, 679 cm^{-1}, HRMS (FAB+) m/z calc'd $C_{12}H_{17}O_3$ $[M+H]^+$: 209.1172; found 209.1164; $[\alpha]_D^{23}$ + 46.5 (*c* 0.18, $CHCl_3$).



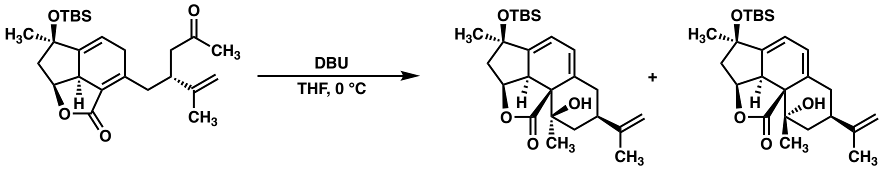
43 **44**

Ester 44: A solution of methyl ester **43** (1.5 g, 5.7 mmol, 1 equiv) in THF (28 mL, 0.2M), was added to a solution of LiOH (205 mg, 8.6 mmol, 1.5 equiv) in H_2O (28 mL, 0.2M). The reaction was stirred vigorously for 4 h at 23 °C when complete consumption of starting material was observed (as determined by TLC). The reaction was washed with EtOAc (1 X) and the aqueous layer was subsequently acidified to a pH of 1 with 1 N HCl. The acidic aqueous layer was then extracted with EtOAc (5 x 30 mL) and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo leaving a crude acid (1.3 g, 81%) which was used without further purification or characterization.

Alcohol **41** (10 mg, 0.039 mmol, 1 equiv), the crude acid (15 mg, 0.079 mmol 2 equiv), and DMAP (16 mg, 0.039 mmol, 1 equiv) were added to CH_2Cl_2 (0.4 mL, 0.1 M) and cooled to 0 °C. DIC (12 μL, 0.079 mmol, 2 equiv) was added dropwise and the reaction was allowed to stir for 2 h at 0 °C. Upon complete consumption of starting material (as determined by TLC analysis), the reaction was diluted with H_2O and extracted with Et_2O (3x). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by column chromatography (SiO_2, 20% EtOAc/hexanes) to afford ester **44** (12 mg, 70%) as a pale yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ = 6.27 (ddd, *J* = 17.8, 11.2, 0.8 Hz, 1H), 5.75–5.69 (m, 2H), 5.53 (dddd, *J* = 7.3, 5.9, 2.3, 0.8 Hz, 1H), 5.27 (dd, *J* = 11.3, 1.9 Hz, 1H), 4.86–4.83 (m, 1H), 4.83–4.77 (m, 1H), 2.93–2.81 (m, 1H), 2.67 (dd, *J* = 13.2, 7.1 Hz, 2H), 2.63–2.56 (m, 1H), 2.48 (dd, *J* = 7.5, 6.4 Hz, 2H), 2.16 (s, 3H), 2.10 (ddd, *J* = 13.1, 5.9, 0.8 Hz, 1H), 1.73 (dd, *J* = 1.5, 0.8 Hz, 3H), 1.38 (d, *J* = 0.8 Hz, 3H), 0.86 (s, 9H), 0.12 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 207.1, 153.7, 152.7, 145.2, 129.3, 123.9, 119.0, 112.4, 87.2, 82.3, 74.9, 48.9, 46.3, 39.7, 30.5, 29.2, 25.9, 23.2, 20.7, 18.2, -2.2, -2.6; IR (thin film, NaCl) 2956, 2929, 2856, 2234, 1711, 1649, 1472, 1439, 1359, 1250, 1169, 1069, 1022, 837, 774, 752 cm^{-1}; HRMS (FAB+) m/z calc'd $C_{25}H_{39}O_4Si$ $[M+H]^+$: 431.2612; found 431.2629; $[\alpha]_D^{23}$ –71.1 (*c* 0.59, $CHCl_3$).



Cyclohexadiene 45: Ester **44** (65 mg, 0.15 mmol) was transferred to a Schlenk bomb with xylenes (15 mL, 0.01 M). The Schlenk was then degassed by standard freeze-pump-thaw technique, and upon reaching ambient temperature (23 °C) the flask was sealed and heat to 140 °C. The reaction was allowed to stir at this temperature of 2 h at which time complete consumption of starting material was observed (as determined by TLC analysis,). The reaction was allowed to cool to room temperature and was directly purified by column chromatography (SiO_2, 0%–20% EtOAc/hexanes) to furnish cyclohexadiene **45** (53 mg, 82%) as a white amorphous solid; ^1H NMR (400 MHz, $CDCl_3$) δ = δ 5.78 (ddd, *J* = 6.4, 2.9, 1.9 Hz, 1H), 4.93 (ddd, *J* = 9.0, 8.1, 7.0 Hz, 1H), 4.68 (p, *J* = 1.5 Hz, 1H), 4.63 (dt, *J* = 1.8, 0.8 Hz, 1H), 3.19 (t, *J* = 9.6 Hz, 1H), 3.13–3.04 (m, 1H), 2.93 (p, *J* = 7.1 Hz, 1H), 2.84 (dddd, *J* = 10.7, 7.1, 2.4, 1.3 Hz, 1H), 2.75 (ddd, *J* = 12.7, 7.7, 1.2 Hz, 1H), 2.66 (ddt, *J* = 18.1, 10.1, 1.6 Hz, 1H), 2.59 (d, *J* = 1.4 Hz, 1H), 2.57 (d, *J* = 1.5 Hz, 1H), 2.42–2.34 (m, 1H), 2.12 (s, 3H), 1.70–1.63 (m, 4H), 1.36 (d, *J* = 1.0 Hz, 3H), 0.86 (s, 9H), 0.10 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 208.0, 168.7, 156.7, 151.8, 146.4, 125.4, 116.5, 112.3, 81.2, 76.2, 48.8, 47.3, 44.8, 40.9, 35.7, 34.8, 30.8, 28.1, 25.8, 19.5, 18.1, -2.1, -2.3; IR (thin film, NaCl) 2957, 2929, 2857, 1753, 1714, 1645, 1442, 1359, 1327, 1291, 1257, 1209, 1177, 1028, 856, 836, 774, 680 cm^{-1}; HRMS (FAB+) m/z calc'd $C_{25}H_{39}O_4Si$ $[M+H]^+$: 431.2612, found; 431.2643; $[\alpha]_D^{23}$ –64.5 (*c* 0.39, $CHCl_3$).

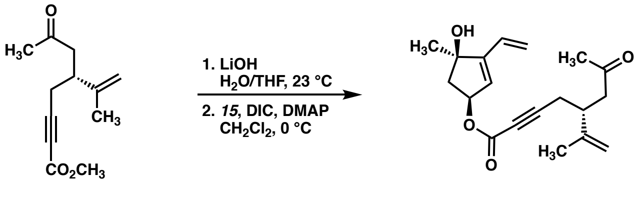


45 *epi-47* 47

Aldol Products 47 and *epi*-47: *Tetracycles 47 and epi 47 were originally isolated after an attempted TBAF-mediated deprotection. Analytical samples were prepared according to the following procedure:* Tricycle **45** (3 mg, 7.2 µmol, 1 equiv) was dissolved in THF (0.2 mL) and cooled to 0 °C. DBU (1.7 µL, 7.2 µmol, 1 equiv) was added. After 5 min, the reaction was concentrated and directly purified by column chromatography (SiO$_2$, 20% EtOAc/hexanes) to afford tetracycles **47** and ***epi*-47** (1.8:1 dr, 3 mg, >99%) as an amorphous film.

47: ^{1}H NMR (400 MHz, CDCl$_3$) δ = 5.99 (dd, *J* = 5.7, 2.5 Hz, 1H), 5.83 (ddd, *J* = 5.8, 2.8, 1.1 Hz, 1H), 4.89 – 4.68 (m, 3H), 3.76–3.69 (m, 1H), 2.88–2.76 (m, 1H), 2.47 (dd, *J* = 13.7, 7.4 Hz, 1H), 2.39–2.27 (m, 2H), 2.27–2.04 (m, 1H), 1.86 (dd, *J* = 13.7, 3.9 Hz, 1H), 1.78 (dd, *J* = 1.5, 0.8 Hz, 3H), 1.71 (dt, *J* = 13.0, 2.6 Hz, 1H), 1.40 (d, *J* = 1.0 Hz, 3H), 1.25 (s, 3H), 0.89 (s, 9H), 0.12 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ = 176.6, 148.1, 142.2, 131.1, 123.2, 112.7, 110.2, 80.0, 79.7, 74.4, 56.7, 49.0, 42.0, 40.7, 40.0, 35.7, 29.9, 28.5, 25.9, 24.9, 20.6, 18.2, 14.3, –2.0, –2.2; IR (thin film, NaCl) 3523, 2925, 2856, 2759, 1461, 1372, 1292, 1257, 1153, 1065, 964, 833, 771, 732, 705, 655 cm^{-1}; HRMS (FAB+) m/z calc'd C$_{25}$H$_{42}$O$_4$SiN [M+NH$_4$]$^+$ 448.2878, found: 448.2889; $[\alpha]_D^{23}$ +4.12 (*c* 0.235, CHCl$_3$).

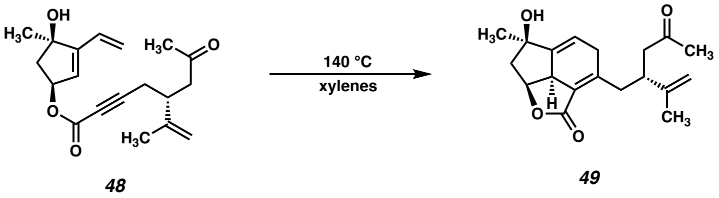
***epi*-47**: ^{1}H NMR (400 MHz, CDCl$_3$) δ = 5.86 (dd, *J* = 5.7, 2.6 Hz, 1H), 5.82 (ddd, *J* = 5.8, 2.7, 1.0 Hz, 1H), 4.89 (td, *J* = 7.2, 3.2 Hz, 1H), 4.80 (dq, *J* = 1.8, 0.9 Hz, 1H), 4.78 (q, *J* = 1.5 Hz, 1H), 3.47 (d, *J* = 7.4 Hz, 1H), 2.86–2.73 (m, 1H), 2.48–2.36 (m, 2H), 2.31 (ddd, *J* = 15.0, 4.4, 1.9 Hz, 1H), 2.20 (tt, *J* = 12.8, 3.8 Hz, 1H), 1.94 (dd, *J* = 14.0, 3.1 Hz, 1H), 1.78 (s, 3H), 1.66 (ddd, *J* = 12.0, 3.4, 1.9 Hz, 1H), 1.39 (d, *J* = 1.1 Hz, 3H), 1.29 (d, *J* = 0.8 Hz, 3H), 0.88 (d, *J* = 1.1 Hz, 9H), 0.12 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ = 177.3, 148.1, 142.1, 132.2, 121.3, 113.4, 110.1, 80.1, 80.0, 76.2, 57.8, 48.7, 42.7, 42.3, 41.3, 35.5, 29.2, 26.7, 25.9, 20.5, 18.2, –2.0, –2.3; IR (thin film, NaCl) 3462, 2956, 2928, 2856, 1739, 1643, 1450, 1375, 1293,1257, 1163, 1132, 1018, 837, 809, 773 cm^{-1}; HRMS (FAB+) m/z calc'd C$_{25}$H$_{42}$O$_4$SiN [M+NH$_4$]$^+$ 448.2878, found: 448.2890; $[\alpha]_D^{23}$ –33.7 (*c* 0.1, CHCl$_3$).



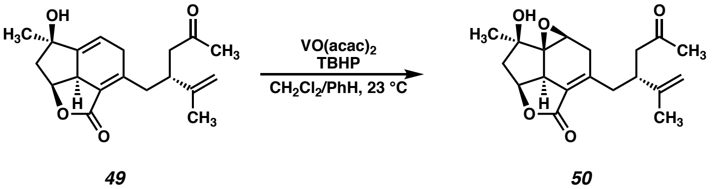
43 *48*

Ester 48: A solution of methyl ester **43** (1.5 g, 5.7 mmol, 1 equiv) in THF (28 mL, 0.2M), was added to a solution of LiOH (205 mg, 8.6 mmol, 1.5 equiv) in H_2O (28 mL, 0.2M). The reaction was stirred vigorously for 4 h at 23 °C when complete consumption of starting material was observed (as determined by TLC). The reaction was washed with EtOAc (1 X) and the aqueous layer was subsequently acidified to a pH of 1 with 1 N HCl. The acidic aqueous layer was then extracted with EtOAc (5 x 30 mL) and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo leaving a crude acid (1.3 g, 81%) which was used without further purification or characterization.

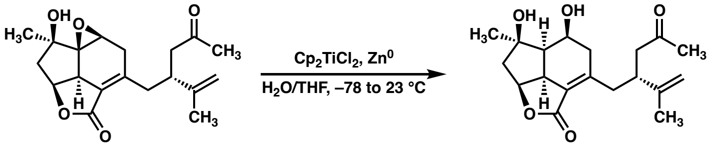
Diol **15** (18 mg, 0.13 mmol, 1 equiv), the crude acid (56 mg, 0.28 mmol 2.2 equiv), and DMAP (17 mg, 0.17 mmol, 1.1 equiv) were added to a solution of CH_2Cl_2 (1.4 mL, 0.09 M) and cooled to 0 °C. DIC (44 μL, 0.28 mmol, 2.2 equiv) was added dropwise and the reaction was allowed to stir for 1 h. Upon complete consumption of starting material (as determined by TLC analysis) the reaction was diluted with H_2O (5 mL) and extracted with Et_2O (3 x 5 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by column chromatography (SiO_2, 50% EtOAc/hexanes) to afford ester **48** (30 mg, 73%) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.32 (ddt, *J* = 17.8, 11.3, 0.8 Hz, 1H), 5.85–5.75 (m, 2H), 5.54 (ddd, *J* = 7.1, 4.7, 2.5 Hz, 1H), 5.33 (dd, *J* = 11.3, 1.6 Hz, 1H), 4.90–4.82 (m, 1H), 4.80 (q, *J* = 0.9 Hz, 1H), 2.86 (p, *J* = 6.6 Hz, 1H), 2.74–2.59 (m, 3H), 2.55–2.41 (m, 2H), 2.16 (s, 3H), 2.06 (dd, *J* = 14.3, 4.4 Hz, 1H), 1.73 (dd, *J* = 1.4, 0.8 Hz, 3H), 1.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 207.1, 153.5, 151.9, 145.2, 129.0, 126.1, 119.6, 112.5, 87.5, 81.1, 77.4, 74.8, 48.9, 46.4, 39.7, 30.6, 26.8, 23.2, 20.7; IR (thin film, NaCl) 3462, 2969, 2926, 2233, 1704, 1422, 1249, 1163, 1071, 944, 751 cm^{-1}; HRMS (ESI) m/z calc'd $C_{19}H_{26}O_5$ $[M+H_2O]^+$: 334.1775, found: 334.1785; $[\alpha]_D^{23}$ –65.9 (*c* 0.18, $CHCl_3$).



Cyclohexadiene 49: Ester **48** (100 mg, 0.32 mmol) was transferred to a Schlenk bomb with xylenes (32 mL, 0.01 M). The Schlenk was the rigorously degassed by standard freeze-pump-thaw technique and upon reaching ambient temperature (23 °C) the flask was sealed and heat to 140 °C. The reaction was allowed to stir at this temperature of 2 h at which time complete consumption of starting material was observed (as determined by TLC analysis). The reaction was allowed to cool to room temperature and was directly purified by column chromatography (SiO_2,0%–50% EtOAc/hexanes) to furnish tricycle **49** (79 mg, 79%) as a white amorphous solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.84 (dt, *J* = 6.4, 2.3 Hz, 1H), 5.02–4.91 (m, 1H), 4.75–4.69 (m, 1H), 4.67 (d, *J* = 1.9 Hz, 1H), 3.26 (t, *J* = 9.6 Hz, 1H), 3.12–2.98 (m, 2H), 2.97–2.87 (m, 1H), 2.74 (ddt, *J* = 18.2, 10.1, 1.6 Hz, 1H), 2.59 (dd, *J* = 6.7, 4.1 Hz, 2H), 2.57–2.44 (m, 2H), 2.11 (s, 3H), 1.69 (d, *J* = 1.3 Hz, 3H), 1.64 (dd, *J* = 12.8, 8.0 Hz, 1H), 1.40 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 207.9, 168.4, 156.5, 151.6, 146.9, 125.2, 116.6, 112.0, 80.0, 75.4, 49.7, 47.2, 45.6, 41.1, 36.2, 35.4, 30.7, 26.7, 19.6; IR (thin film, NaCl) 3440, 2968, 1746, 1713, 1644, 1442, 1418, 1359, 1289, 1213, 1117, 1042, 1021, 995, 973, 913, 810, 732; HRMS (ESI) m/z calc'd $C_{19}H_{25}O_4$ $[M+H]^+$: 317.1747, found: 317.1733; $[\alpha]_D^{23}$ –99.1 (*c* 0.375, $CHCl_3$).



Epoxide 50: To a stirred solution of cyclohexadiene **49** (80 mg, 0.25 mmol, 1.0 equiv) in benzene (8.4 mL, 0.044M) and CH_2Cl_2 (0.2 mL, 1 M) was added VO(acac)$_2$ (6.7 mg, 0.025 mmol, 0.1 equiv). After 15 minutes, *t*-butyl hydroperoxide (TBHP, 76 µL, 0.38 mmol, 1.5 equiv, 5 M solution in decane) was added, causing the reaction to immediately become deep red. After 1 hours, the reaction had lost all red color and become pale yellow and complete consumption of starting material was observed (as determined by TLC analysis). The crude reaction was directly purified by column chromatography (SiO_2, 0%–50% EtOAc/hexanes) to furnish epoxide **50** (76.3 mg, 91%) as a white amorphous solid; ^{1}H NMR (400 MHz, C_6D_6) δ 4.83 (q, *J* = 0.9 Hz, 1H), 4.75 (t, *J* = 1.6 Hz, 1H), 4.08 (ddd, *J* = 8.5, 7.4, 6.3 Hz, 1H), 3.38–3.31 (m, 1H), 3.05 (d, *J* = 3.4 Hz, 1H), 2.90 (dq, *J* = 9.3, 6.3 Hz, 1H), 2.41 (dd, *J* = 17.0, 6.8 Hz, 3H), 2.29–2.20 (m, 3H), 2.11 (ddd, *J* = 12.7, 5.4, 1.9 Hz, 1H), 2.05 (dd, *J* = 13.5, 7.5 Hz, 1H), 1.86 (dd, *J* = 16.7, 2.4 Hz, 1H), 1.82–1.74 (m, 1H), 1.70 (s, 3H), 1.63 (t, *J* = 1.2 Hz, 3H), 0.99 (s, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ = 206.0, 168.9, 149.6, 147.7, 120.8, 111.5, 76.3, 73.3, 69.5, 51.6, 50.2, 47.0, 44.5, 41.0, 37.6, 36.0, 30.2, 22.4, 20.0; IR (thin film, NaCl) 3469, 2933, 1746, 1711, m1645, 1360, 1294, 1200, 1114, 1029, 967, 792 cm,$^{-1}$; HRMS (ESI) m/z calc'd $C_{19}H_{25}O_5$ [M+H]$^+$: 333.1697, found: 333.1703; $[\alpha]_D^{23}$ –88.9 (*c* 0.375, $CHCl_3$).

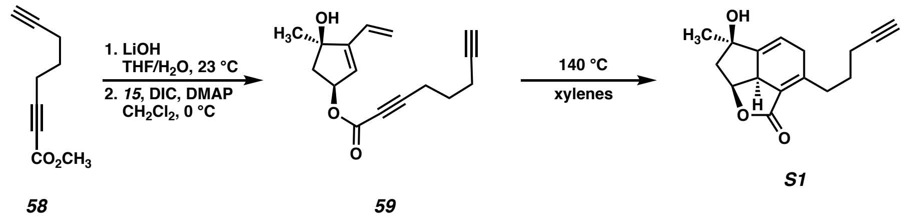


50 **51**

Alcohol 51:

Preparation of a 0.50 M Stock Solution: of Titanocene Monochloride (Cp_2TiCl): A flame-dried Schlenk tube under an overpressure of argon was charged with zinc dust (647 mg, 9.90 mmol, 3.00 equiv) and titanocene dichloride (Cp_2TiCl_2, 822 mg, 3.30 mmol, 1.00 equiv). The flask was then evacuated and back filled with argon (3 x 5 minute cycles). To the reaction vessel was then added THF (6.6 mL) and the resulting red suspension was stirred vigorously. After 1.5 h, the bright red reaction mixture had become dark green and stirring was halted, allowing the zinc dust to settle to the bottom of the tube. After 30 minutes, the green supernatant was used as a 0.50 M stock solution of Cp_2TiCl.

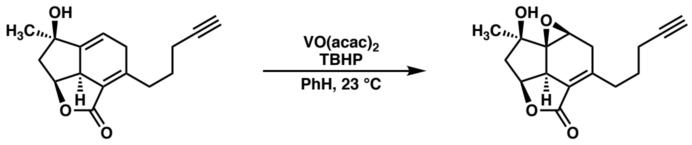
Reductive Epoxide Opening: A stirred solution of epoxide **50** (15 mg, 0.045 mmol, 1.0 equiv) in THF (1.5 mL, 0.03 M) was cooled to –78 °C, followed by the addition of H_2O (62 μL, 3.46 mmol, 76.9 equiv). After stirring for 5 minutes, Cp_2TiCl (0.87 mmol, 0.50 M in THF, 19.2 equiv) was added dropwise. After 2 h, the green reaction mixture was allowed to warm to ambient temperature (23 °C). After an additional 12 h, the complete consumption of starting material was observed (as determined by TLC). The reaction was quenched by the addition of saturated NaH_2PO_4 (1.0 mL) and brine (1.0 mL), sparged with compressed air for 5 minutes, and allowed to stir for an additional 15 minutes. The resulting orange slurry was then filtered through a Celite® plug, washing with H_2O and EtOAc. The biphasic mixture was separated and the aqueous layer was extracted with EtOAc (3x). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by column chromatography (SiO_2, 75% EtOAc/hexanes), furnishing diol **51** (14 mg, 92% yield) as a white amorphous solid (R_f = 0.22); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.90 (ddd, *J* = 8.2, 6.6, 4.1 Hz, 1H), 4.80 (dt, *J* = 1.7, 0.8 Hz, 1H), 4.76 (p, *J* = 1.5 Hz, 1H), 4.69 (dt, *J* = 7.8, 3.2 Hz, 1H), 3.35–3.25 (m, 1H), 3.05 (ddd, *J* = 9.9, 8.0, 2.0 Hz, 1H), 2.94 (dq, *J* = 9.2, 6.5 Hz, 1H), 2.67–2.49 (m, 3H), 2.41–2.29 (m, 2H), 2.14–1.98 (m, 6H), 1.75 (dd, *J* = 1.5, 0.8 Hz, 3H), 1.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 208.3, 169.7, 151.7, 147.8, 124.9, 111.5, 81.7, 79.2, 68.5, 49.6, 48.5, 47.2, 44.4, 41.3, 40.6, 37.7, 30.8, 28.8, 20.1; IR (thin film, NaCl) 3384, 2966, 1738, 1666, 1420, 1359, 1304, 1222, 1200, 1145, 1105, 1040, 1020, 910, 733 cm^{-1}; HRMS (ESI) m/z calc'd $C_{19}H_{27}O_5$ $[M+H]^+$: 335.1853, found: 335.1844; $[\alpha]_D^{23}$ –15.4 (*c* 0.21, $CHCl_3$).



Ester 59 and Cyclohexadiene S1: Ester **58** was saponified under the same conditions reported above for ester **43**. A stirred solution of diol **15** (250 mg, 1.8 mmol, 1 equiv), octa-2,7-diynoic acid (435 mg, 3.2 mmol, 1.8 equiv), and DMAP (21.8 mg, 0.18 mmol, 0.1 equiv) in CH_2Cl_2 (18 mL, 0.1 M) and THF (10 mL, 0.18 M) was cooled to 0 °C. DIC (0.50 mL, 3.2 mmol, 1.8 equiv) was added dropwise via syringe and the resultant solution was allowed to stir for 2 h. Upon complete consumption of starting material (as determined by TLC analysis), the reaction was diluted with H_2O and extracted with Et_2O (3x). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by column chromatography (SiO_2, 20% EtOAc/Hexanes) to afford a mixture of diisopropyl urea and ester **59** which is used directly in the next reaction. Ester **59** can be further purified by another column of the same eluent to obtain pure ester **59**; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.32 (ddt, J = 17.8, 11.3, 0.8 Hz, 1H), 5.82 (dd, J = 2.3, 0.8 Hz, 1H), 5.81–5.75 (m, 1H), 5.55 (dddd, J = 7.4, 4.4, 2.3, 0.7 Hz, 1H), 5.33 (dd, J = 11.3, 1.5 Hz, 1H), 2.64 (dd, J = 14.3, 7.3 Hz, 1H), 2.48 (t, J = 7.1 Hz, 2H), 2.32 (td, J = 6.9, 2.7 Hz, 2H), 2.06 (dd, J = 14.3, 4.4 Hz, 1H), 1.98 (t, J = 2.6 Hz, 1H), 1.80 (p, J = 7.0 Hz, 2H), 1.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ =. 153.5, 151.9, 128.9, 126.0, 119.6, 88.7, 82.8, 81.1, 77.1, 73.7, 69.6, 48.9, 26.8, 26.5, 17.8, 17.7; IR (thin film, NaCl) 3295, 2972, 2236, 1703, 1432, 1252, 1073, 990, 950, 872, 752, 641 cm^{-1}; HRMS (ESI) m/z calc'd $C_{16}H_{22}NO_3$ $[M+NH_4]^+$: 276.1595, found: 276.15811; $[\alpha]_D^{23}$ –155.1 (c 0.57, $CHCl_3$).

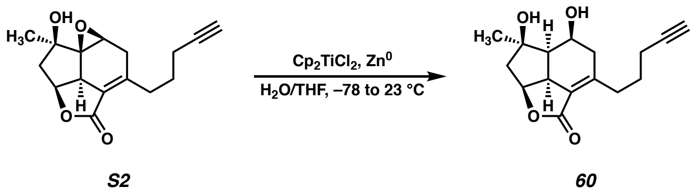
Crude ester **59** (460 mg, 1.78 mmol) was transferred to a Schlenk bomb with xylenes (178 mL, 0.01 M). The Schlenk was degassed by standard freeze-pump-thaw technique and upon reaching ambient temperature (23 °C) the flask was sealed and heat to 140 °C. The reaction was allowed to stir at this temperature of 2 h at which time complete consumption of starting material was observed (as determined by TLC analysis). The reaction was allowed to cool to room temperature and was directly purified by column chromatography (SiO_2, 0%–50% EtOAc/Hexanes) to furnish tricycle **S1** (560 mg, 84% over 3 steps) as a pale yellow solid; ^{1}H NMR

(400 MHz, $CDCl_3$) δ = 5.85 (ddd, *J* = 6.3, 2.9, 1.9 Hz, 1H), 4.97 (ddd, *J* = 9.0, 7.9, 7.1 Hz, 1H), 3.30 (ttd, *J* = 9.2, 1.9, 1.0 Hz, 1H), 3.11–2.96 (m, 2H), 2.75 (ddt, *J* = 18.4, 10.1, 1.5 Hz, 1H), 2.62–2.54 (m, 1H), 2.51 (ddd, *J* = 12.8, 7.1, 0.8 Hz, 1H), 2.22 (tt, *J* = 7.1, 2.5 Hz, 2H), 1.98 (t, *J* = 2.6 Hz, 1H), 1.78 (td, *J* = 6.6, 5.5, 3.3 Hz, 1H), 1.76–1.63 (m, 3H), 1.41 (d, *J* = 1.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ =. 168.2, 157.1, 152.1, 124.4, 116.4, 84.0, 80.0, 75.4, 69.1, 49.7, 45.5, 35.2, 31.0, 27.2, 26.8, 18.4; IR (thin film, NaCl) 3425, 3288, 2971, 1738, 1643, 1439, 1326, 1288, 1256, 1218, 1194, 1117, 1041, 996, 967, 817, 742, 638 cm^{-1}; HRMS (ESI) m/z calc'd $C_{16}H_{19}O_3$ $[M+H]^+$: 259.1329, found: 259.1323; $[\alpha]_D^{23}$ –120.3 (*c* 0.64, $CHCl_3$).

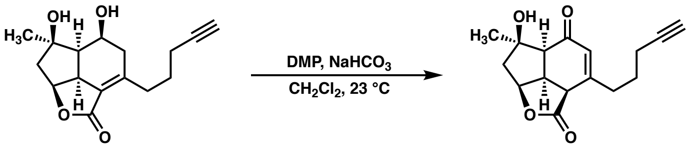


S1 ***S2***

Epoxide S2: To a stirred solution of diene **S1** (376 mg, 1.5 mmol, 1.0 equiv) in benzene (49 mL, 0.03M) was added VO(acac)$_2$ (29 mg, 0.11 mmol, 0.075 equiv). After 15 minutes, *t*-butyl hydroperoxide (TBHP, 0.58 mL, 2.9 mmol, 2.0 equiv, 5 M solution in decane) was added dropwise, causing the reaction to immediately become deep red. After 2 hours, the reaction had lost all red color and become pale yellow and complete consumption of starting material was observed (as determined by TLC analysis). The crude reaction was directly purified by column chromatography (SiO$_2$, 0%–30% EtOAc/Hexanes) to furnish epoxide **S2** (307 mg, 77%) as a white amorphous solid; ^{1}H NMR (400 MHz, CDCl$_3$) δ = 4.83 (ddd, *J* = 8.5, 7.4, 6.3 Hz, 1H), 3.81 (dd, *J* = 3.3, 0.8 Hz, 1H), 3.28 (d, *J* = 8.1 Hz, 1H), 2.88 (dd, *J* = 16.7, 3.4 Hz, 1H), 2.84–2.68 (m, 2H), 2.59 (ddd, *J* = 13.6, 7.4, 0.6 Hz, 1H), 2.55–2.45 (m, 2H), 2.35–2.12 (m, 2H), 2.08–1.99 (m, 1H), 1.98 (t, *J* = 2.6 Hz, 1H), 1.81–1.62 (m, 2H), 1.44 (d, *J* = 1.0 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ = 169.1, 150.9, 119.9, 84.1, 76.6, 73.6, 70.0, 69.0, 51.8, 50.1, 44.8, 35.7, 31.6, 26.9, 22.7, 18.3; IR (thin film, NaCl) 3529, 3270, 2976, 2938, 2116, 1742, 1649, 1454, 1422, 1391, 1348, 1324, 1296, 1268, 1195, 1113, 1093, 1030, 964, 923, 899, 795, 756, 733, 678 cm^{-1}; HRMS (ESI) m/z calc'd $C_{16}H_{19}O_4$ [M+H]$^+$: 275.1278, found: 275.1268; $[\alpha]_D^{23}$ –179.9 (*c* 0.39, CHCl$_3$).

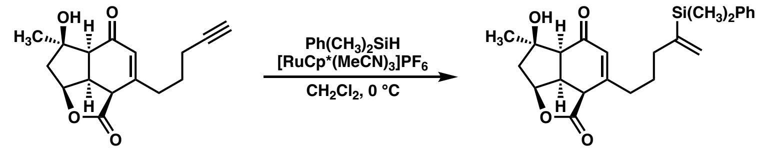


Alcohol 60: A stirred solution of epoxide **101** (278 mg, 1.01 mmol, 1.0 equiv) in THF (34 mL, 0.03 M) was cooled to –78 °C, followed by the addition of H_2O (0.9 mL, 50.0 mmol, 50 equiv). After stirring for 5 minutes, Cp_2TiCl (11.1 mmol, 0.50 M in THF, 11 equiv) was added dropwise. After 2 h, the reaction was allowed to slowly warm to 23 °C. After stirring an additional 12 h, the complete consumption of starting material was observed (as determined by TLC). The reaction was quenched by the addition of saturated NaH_2PO_4 and brine, sparged with compressed air for 5 minutes, and allowed to stir for an additional 15 minutes. The orange suspension was then filtered through a Celite® plug, washing with H_2O and EtOAc. The biphasic mixture was separated and the aqueous layer was extracted with EtOAc (3x). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by column chromatography (SiO_2, 75% EtOAc/hexanes), furnishing diol **60** (270 mg, 96% yield) as a viscous colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.91 (ddd, *J* = 8.1, 6.7, 3.1 Hz, 1H), 4.69 (ddd, *J* = 8.1, 3.5, 2.8 Hz, 1H), 3.43 (s, 2H), 3.08 (ddd, *J* = 9.7, 7.9, 2.0 Hz, 1H), 2.98–2.88 (m, 1H), 2.70 (dtd, *J* = 12.6, 7.4, 1.8 Hz, 1H), 2.58 (dd, *J* = 14.9, 2.8 Hz, 1H), 2.39 (dd, *J* = 9.4, 8.0 Hz, 1H), 2.23 (qd, *J* = 7.2, 2.6 Hz, 2H), 2.13 (dd, *J* = 14.4, 3.1 Hz, 1H), 2.10–2.03 (m, 1H), 1.99 (dd, *J* = 14.3, 6.6 Hz, 1H), 1.95 (t, *J* = 2.6 Hz, 1H), 1.72 (p, *J* = 7.4 Hz, 2H), 1.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 169.9, 152.5, 124.3, 84.4, 82.0, 79.5, 68.8, 68.3, 49.8, 48.6, 44.6, 41.4, 31.9, 28.6, 26.5, 18.5; IR (thin film) 3302, 2966, 2930, 2251, 1738, 1731, 1668, 1454, 1427, 1358, 1336, 1305, 1278, 1248, 1222, 1198, 1144, 1119, 1104, 1069, 1045, 1018, 989, 926, 912, 874, 853, 768, 737, 650; HRMS (ESI) m/z calc'd $C_{16}H_{21}O_4$ $[M+H]^+$: 277.1434, found: 277.1430; $[\alpha]_D^{23}$ –16.0 (*c* 0.72, $CHCl_3$).



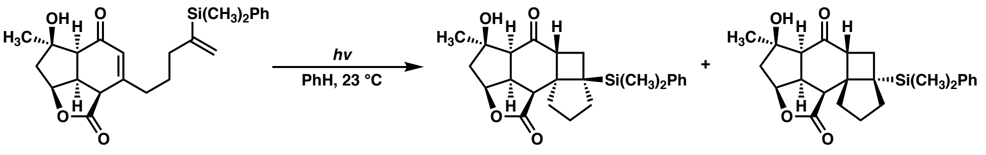
60 61

Enone 61: To a solution of diol **60** (270 mg, 0.98 mmol, 1.0 equiv) in CH$_2$Cl$_2$ (27 mL, 0.036 M) was added NaHCO$_3$ (330 mg, 3.9 mmol, 4 equiv) followed by DMP (538 mg, 1.3 mmol, 1.3 equiv) at 23 °C with stirring. The reaction vessel was then sealed and stirred for 3 h. Each subsequent hour, more DMP (1 equiv) was added until complete consumption of starting material (as determined by TLC analysis). The reaction was then quenched by the addition of saturated NaS$_2$O$_3$ (30 mL) and saturated NaHCO$_3$ (20 mL). After stirring for 10 minutes, the reaction mixture was extracted with CH$_2$Cl$_2$ (3x). The combined organics were then dried over MgSO$_4$, filtered, and concentrated in vacuo. The crude product was the purified by column chromatography (SiO$_2$, 75% EtOAc/hexanes) to afford enone **61** (117 mg, 47%) as a colorless viscous oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ = 6.07 (q, *J* = 1.5 Hz, 1H), 5.12 (dd, *J* = 7.1, 5.4 Hz, 1H), 3.63 (dddd, *J* = 10.9, 10.2, 7.1, 0.6 Hz, 1H), 3.51–3.45 (m, 1H), 2.90–2.78 (m, 1H), 2.78–2.66 (m, 1H), 2.53 (d, *J* = 10.2 Hz, 1H), 2.33 (d, *J* = 15.0 Hz, 1H), 2.27 (tdd, *J* = 7.1, 6.1, 2.7 Hz, 2H), 1.99 (t, *J* = 2.6 Hz, 1H), 1.91 (dd, *J* = 15.0, 5.5 Hz, 1H), 1.87–1.74 (m, 2H), 1.51 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ = 196.0, 173.5, 157.6, 127.5, 83.6, 82.8, 82.5, 69.4, 55.2, 47.4, 42.5, 42.2, 34.7, 26.4, 25.6, 18.2; IR (thin film, NaCl) 3442, 3282, 2966, 1757, 1649, 1375, 1289, 1255, 1214, 1179, 1104, 1033, 1017, 993, 938; HRMS (ESI) m/z calc'd C$_{16}$H$_{19}$O$_4$ [M+H]$^+$: 275.1278, found: 275.1269; $[\alpha]_D^{23}$ –195 (*c* 0.32, CHCl$_3$).



61 *62*

Vinyl Silane 62: Enone **61** (28 mg, 0.1 mmol, 1 equiv) and dimethylphenylsilane (18 μL, 0.12 mmol, 1.2 equiv) was dissolved in CH_2Cl_2 (0.5 mL, 0.2 M) and sparged with Ar for 5 min. The reaction was cooled to 0 °C and a stock solution of $[RuCp^*(MeCN)_3]PF_6$ (0.5 mg, 1mg/mL, 0.01 equiv) prepared in a nitrogen-filled gloved box and was added to the reaction. The reaction was allowed to stir for 15 min at 0 °C, at which time complete consumption of starting material was observed (as determined by TLC analysis). The solution was then concentrated and directly purified by column chromatography (SiO_2, 75% EtOAc/hexanes) to afford vinyl silane **62** (19 mg, 64%) as a colorless amorphous solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.60–7.48 (m, 2H), 7.44–7.30 (m, 3H), 5.94 (q, *J* = 1.4 Hz, 1H), 5.70 (dt, *J* = 2.9, 1.5 Hz, 1H), 5.46 (dt, *J* = 2.7, 1.0 Hz, 1H), 5.07 (dd, *J* = 7.2, 5.4 Hz, 1H), 3.48 (dddd, *J* = 10.9, 10.2, 7.1, 0.6 Hz, 1H), 3.16 (dd, *J* = 11.1, 1.5 Hz, 1H), 2.66–2.50 (m, 2H), 2.48 (d, *J* = 10.2 Hz, 1H), 2.30 (d, *J* = 15.0 Hz, 1H), 2.24–2.08 (m, 2H), 1.89 (dd, *J* = 15.0, 5.5 Hz, 1H), 1.67–1.51 (m, 2H), 1.49 (s, 3H), 0.37 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 196.0, 173.4, 158.7, 149.7, 138.4, 134.1, 129.1, 128.0, 127.3, 126.7, 82.7, 82.4, 55.2, 47.4, 42.2, 41.9, 35.7, 35.4, 26.5, 26.1, -2.8, -2.9; IR (thin film, NaCl) 3450, 2958, 1759, 1650, 1378, 1290, 1248, 1173, 1107, 992, 818 cm^{-1}; HRMS (ESI) m/z calc'd $C_{23}H_{31}O_4Si$ $[M+H]^+$: 411.1986, found: 411.1972; $[\alpha]_D^{23}$ –115.3 (*c* 0.25, $CHCl_3$).

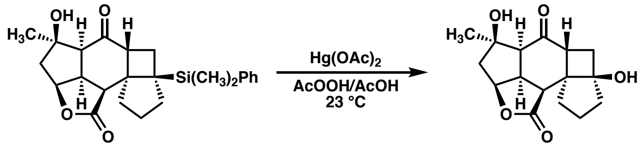


62 **63** **64**

Cyclobutanes 63 and 64: Enone **62** (19 mg, 0.0465 mmol, 1 equiv) in a 20 mL vial was dissolved in benzene (4.65 mL, 0.01 M) and was sparged with Ar for 10 min. The reaction vessel was sealed and irradiated at 350 nm. After 2 h complete consumption of starting material was observed (as determined by TLC analysis) and was directly purified by column chromatography (SiO_2, 0%–50% EtOAc/hexanes) to afford a 2:1 mixture of pentacycles **63** and **64** (19 mg total, >99%) as a colorless amorphous solid which crystalizes in benzene.

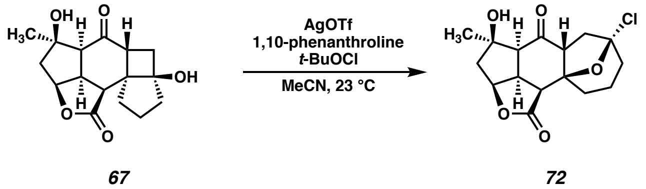
63 (maj): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.57–7.47 (m, 2H), 7.37–7.28 (m, 3H), 4.91 (dd, *J* = 6.1, 4.5 Hz, 1H), 3.60–3.52 (m, 1H), 3.52–3.48 (m, 1H), 2.94 (dd, *J* = 9.0, 0.7 Hz, 1H), 2.56 (d, *J* = 10.6 Hz, 1H), 2.36 (d, *J* = 15.2 Hz, 1H), 2.21–2.14 (m, 2H), 2.08–2.00 (m, 1H), 1.96–1.88 (m, 2H), 1.88–1.76 (m, 1H), 1.73–1.59 (m, 2H), 1.45 (s, 3H), 1.32 (dd, *J* = 11.9, 6.6 Hz, 1H), 0.55 (s, 3H), 0.52 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ =205.7, 174.8, 141.4, 134.2, 128.5, 127.6, 82.1, 81.4, 60.6, 60.1, 51.3, 50.1, 48.6, 47.7, 43.9, 39.9, 37.1, 27.6, 27.1, 24.5, -2.1, -4.7; IR (thin film, NaCl) 3393, 2949, 1769, 1687, 1373, 1242, 1209, 1147, 1104, 1089, 826, 783, 733; HRMS (ESI) m/z calc'd $C_{23}H_{31}O_4Si$ $[M+H]^+$: 411.1986, found: 411.1972; $[\alpha]_D^{23}$ –19.7 (*c* 0.35, $CHCl_3$).

64 (min): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.66–7.53 (m, 2H), 7.45–7.37 (m, 3H), 4.59 (ddd, *J* = 6.6, 5.6, 2.0 Hz, 1H), 3.02 (s, 1H), 2.92 (ddd, *J* = 11.1, 9.8, 6.7 Hz, 1H), 2.74–2.66 (m, 2H), 2.41–2.33 (m, 2H), 2.31–2.21 (m, 1H), 2.17 (s, 1H), 2.13 (dd, *J* = 14.6, 2.0 Hz, 1H), 2.03–1.82 (m, 4H), 1.81–1.72 (m, 1H), 1.66–1.59 (m, 1H), 1.18 (s, 3H), 0.41 (s, 3H), 0.30 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ =215.6, 174.9, 138.3, 134.4, 129.9, 128.5, 80.9, 80.9, 55.4, 53.3, 48.4, 45.8, 44.5, 43.4, 39.7, 39.0, 38.7, 29.0, 28.6, 24.5, -2.9, -3.9; IR (thin film, NaCl) 3416, 2957, 1759, 1673, 1359, 1107, 731 cm^{-1}; HRMS (ESI) m/z calc'd $C_{23}H_{31}O_4Si$ $[M+H]^+$: 411.1986, found: 411.1976; $[\alpha]_D^{23}$ –17.7 (*c* 0.3, $CHCl_3$).

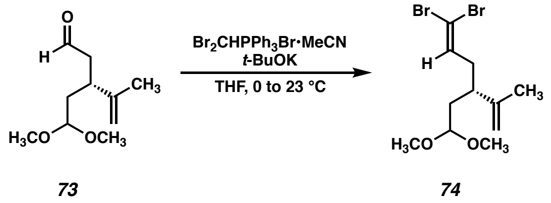


63 *67*

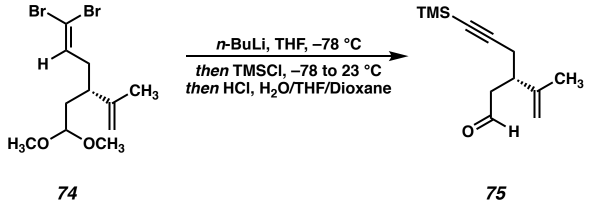
Cyclobutanol 67: To a solution of cyclobutane **63** (25 mg, 0.061 mmol) in 35% AcOOH-AcOH (3.05 mL, 0.02 M) at 23 °C was added $Hg(OAc)_2$ (92 mg, 0.29 mmol, 4.8 equiv), and the solution was stirred for 1 h, after which complete consumption of starting material was observed (as determined by TLC analysis). The reaction mixture was diluted with Et_2O, washed sequentially with 10% aq $Na_2S_2O_3$, H_2O, saturated solution of $NaHCO_3$, and brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by column chromatography (SiO_2, 75% EtOAc/hexanes) to afford cyclobutanol **67** (6 mg, 30%) as a white amorphous powder; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.16 (s, 1H), 5.13 (dd, *J* = 5.9, 4.6 Hz, 1H), 3.90 (t, *J* = 9.5 Hz, 1H), 3.57–3.43 (m, 1H), 3.21 (dd, *J* = 9.0, 0.8 Hz, 1H), 2.58 (d, *J* = 10.6 Hz, 1H), 2.47–2.34 (m, 2H), 2.07–1.94 (m, 2H), 1.94–1.87 (m, 1H), 1.87–1.78 (m, 1H), 1.78–1.68 (m, 3H), 1.48 (s, 3H), 1.25 (d, *J* = 2.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ =205.5, 179.1, 88.5, 86.1, 81.5, 60.8, 55.4, 52.3, 49.4, 47.7, 47.1, 38.1, 36.4, 34.5, 27.8, 23.1; IR (thin film, NaCl) 3421, 2972, 2923, 1741, 1686, 1448, 1400, 1377, 1305, 1276, 1211, 1161, 1112, 1088, 1069, 1010, 921, 850, 813, 777, 733, 719; HRMS (ESI) m/z calc'd $C_{16}H_{21}O_5$ $[M+H]^+$: 293.1384, found: 293.1372; $[\alpha]_D^{23}$ –40.4 (*c* 0.13, $CHCl_3$).



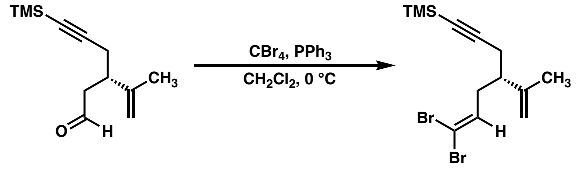
Furan 72: Cyclobutanol **67** (10 mg, 0.034 mmol, 1 equiv), AgOTf (1.2 mg, 0.012 mmol, 0.4 equiv), and 1,10-phenanthroline (4.8 mg, 0.024 mmol, 0.8 equiv) were placed in a round-bottom flask and dissolved in MeCN (1 mL, 0.034 M) followed by the addition of *t*-BuOCl (7.8 μL, 0.068 mmol, 2 equiv). The reaction mixture was stirred at 23 °C for 6 h. The reaction was the quenched with saturated solution of $Na_2S_2O_3$ and extracted with EtOAc (3 x 5 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by column chromatography (SiO_2, 75% EtOAc/Hexanes) to obtain furan **67** (5.4 mg, 49%) as a white amorphous solid which can be crystalized in $CHCl_3$; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.02 (dd, *J* = 5.9, 4.5 Hz, 1H), 3.79–3.66 (m, 1H), 3.42 (dddd, *J* = 10.3, 9.5, 5.9, 0.6 Hz, 1H), 3.34 (dd, *J* = 9.5, 0.7 Hz, 1H), 2.88 (ddd, *J* = 13.8, 7.4, 0.9 Hz, 1H), 2.71 (d, *J* = 10.4 Hz, 1H), 2.42 (d, *J* = 15.4 Hz, 1H), 2.35 (ddd, *J* = 13.8, 11.6, 1.1 Hz, 1H), 2.29–2.09 (m, 1H), 2.07–1.96 (m, 2H), 1.75–1.64 (m, 3H), 1.49 (s, 3H), 1.46–1.34 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ =202.8, 172.0, 101.8, 85.2, 82.7, 82.3, 60.6, 56.4, 48.6, 47.5, 45.9, 40.1, 36.3, 33.1, 27.6, 18.9; IR (thin film, NaCl) 3472, 2921, 1766, 1713, 1359, 1243, 1214, 1171, 1126, 1093, 1000, 953, 905, 845, 759, 731; HRMS (ESI) m/z calc'd $C_{16}H_{20}O_5Cl$ $[M+H]^+$: 327.0994, found: 327.0980; $[\alpha]_D^{23}$ –43.3 (*c* 0.13, $CHCl_3$).



Dibromide 74: A 500 mL round-bottom flask was charged with $Br_2CHPPh_3Br{\bullet}MeCN$ (55.6 g, 100.0 mmol, 1.4 equiv; prepared according to the method of Schmidt)[2] and THF (238 mL, 0.3 M). The reaction mixture was cooled to 0 °C and *t*-BuOK (9.6 g, 85.7 mmol, 1.2 equiv) was added in one portion. This mixture was stirred 1.5 h at 0 °C and then warmed to 23 °C and stirred an additional 30 min. The mixture was then cooled to 0 °C and aldehyde **73**[3] (13.3 g, 71.4 mmol, 1.0 equiv) was added dropwise via syringe. The dark suspension was stirred for 2 h at 0 °C, until no aldehyde (**12**) is detected by TLC. The mixture was quenched with saturated, aqueous NH_4Cl and partitioned between water and Et_2O. The aqueous phase was extracted with Et_2O (3x). The organic extracts were combined, washed with brine, dried over magnesium sulfate, filtered through a sand/cotton plug and concentrated under reduced pressure. The crude residue was purified by flash chromatography (Dry load crude on Celite; SiO_2, 20% Et_2O/Hexanes) to afford dibromide **74** (20.9 g, 61.1 mmol, 86% yield) as a red/orange oil; ^1H 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, $CHCl_3$).

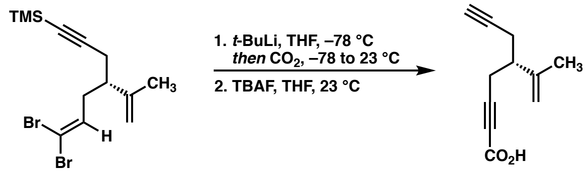


Aldehyde 75: A 500 mL round-bottom flask was charged with dibromide **74** (16.6 g, 48.5 mmol, 1.0 equiv) in THF (100 mL, 0.5 M), and cooled to –78 °C. *n*-BuLi (2.3 M in hexanes; 42.2 mL, 97.1 mmol, 2.0 equiv) was added dropwise over 10 min, and the mixture was allowed to stir for 15 min at –78 °C after which complete consumption of dibromide **13** was observed by TLC. TMSCl (18.5 mL, 145.5 mmol, 3.0 equiv) was added dropwise to the reaction mixture, which was then allowed to gradually warm to 23 °C over 2 h. The mixture was then cooled to 0 °C and water (100 mL) was added followed by 1,4-dioxane (50 mL). HCl (36% w/w, 40 mL, 10.0 equiv) was added and the reaction mixture warmed to room temperature and allowed to stir for 16 h. $NaHCO_3$ (sat. aq.) was added until the pH of the solution was roughly 7. The reaction mixture was partitioned between water and Et_2O, and extracted with Et_2O (3x). The combined organic extracts were washed with brine, dried over sodium sulfate, and concentrated to afford an orange oil which was purified by flash chromatography (SiO_2, 10% Et_2O/Hexanes). Aldehyde **75** (7.37 g, 35.4 mmol, 73% yield) was isolated as a pale-yellow oil; ^1H 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, $CHCl_3$).



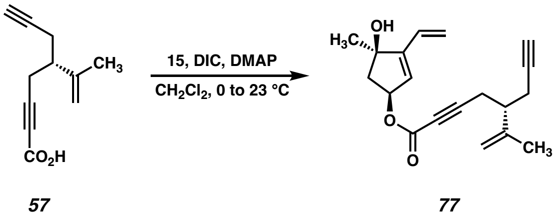
75 ***76***

Dibromide 76: A 500 mL round-bottom flask was charged with triphenylphosphine (50.4 g, 192.0 mmol, 4.0 equiv) in CH_2Cl_2 (96 mL). The solution was cooled to 0 °C, and CBr_4 (31.8 g, 96.0 mmol, 2.0 equiv) added in one portion. The colorless solution immediately changed to yellow/orange in color. The mixture was allowed to stir for 10 min at 0 °C, after which aldehyde **75** (10.0 g, 48.0 mmol, 1.0 equiv) was added via syringe. The aldehyde was consumed immediately, as judged by TLC. The reaction mixture was then quenched with water, and partitioned between water and CH_2Cl_2. The aqueous phase was extracted with CH_2Cl_2 (3x), and the combined organic extracts washed with brine and dried over $MgSO_4$. The crude was concentrated onto SiO_2, loaded onto a column, and purified by flash chromatography (SiO_2, 5% Et_2O/Hexanes) to afford dibromide **76** (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, $CDCl_3$-*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, $CHCl_3$).

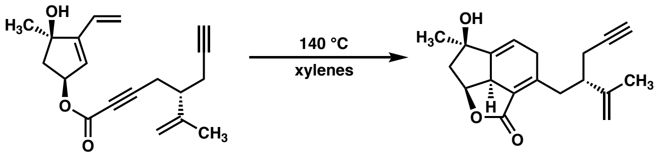


76 ***57***

Ynoic Acid 57: A 250 mL round bottom flask was charged with dibromide **76** (3.92 g, 10.76 mmol, 1.0 equiv) in THF (143 mL). This solution was cooled to –78 °C, followed by the dropwise addition of *t*-BuLi (1.61 M solution in pentane, 14.0 mL, 22.6 mmol, 2.1 equiv), after which no starting material remained (as judged by TLC). The solution was then sparged with CO_2 at –78 °C for 10 min, then warmed to 23 °C with continuous sparging. The reaction was then quenched with aqueous $NaHCO_3$, and extracted with Et_2O (1x). The aqueous phase was then acidified with conc. HCl to pH ~ 2. The acidified aqueous phase was then extracted with EtOAc (3x). The EtOAc extracts were combined, washed with brine, dried over Na_2SO_4, filtered, and concentrated to afford an intermediate acid (1.87 g, 7.53 mmol, 70% yield). The intermediate acid (886 mg, 3.57 mmol, 1.0 equiv) was dissolved in THF (36 mL), and TBAF (1.0 M solution in THF, 7.31 mL, 7.31 mmol, 2.0 equiv) was added at 23 °C. The solution was stirred for 2 h at 23 °C, after which no starting material remained (as judged by LCMS). The reaction mixture was diluted with H_2O, then extracted with EtOAc (3x). The organic extracts were washed with brine, dried over Na_2SO_4, filtered, and concentrated to afford acid **57** (577 mg, 3.27 mmol, 92% yield, 64% yield over the two steps) as an orange oil; ^1H 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, $CHCl_3$).

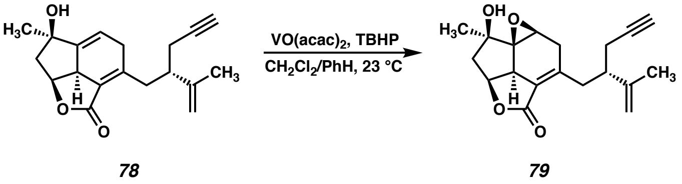


Ester 77: A 250 mL round-bottom flask was charged with diol **15** (1.03 g, 7.35 mmol, 1.0 equiv), acid **57** (1.30 g, 7.35 mmol, 1.0) and DMAP (90 mg, 0.735 mmol, 0.10 equiv) in CH_2Cl_2 (74 mL). The solution was cooled to 0 °C, and DIC (1.15 mL, 7.35 mmol, 1.0 equiv) was added dropwise. The reaction was then stirred for 2 h while gradually warming to 23 °C, and then stirred an additional 3 h at 23 °C. The mixture was partitioned between CH_2Cl_2 and H_2O, and the aqueous phase is extracted with CH_2Cl_2 (3x). The organic extracts were 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 ester **77** (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, $CHCl_3$).

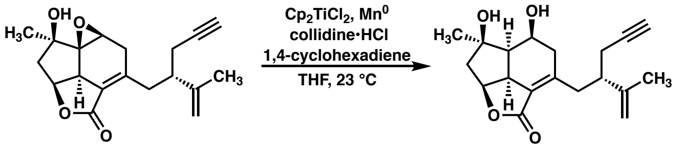

77

78

Cyclohexadiene 78: Ester **77** (804 mg, 2.69 mmol, 1.0 equiv) was dissolved in xylenes (270 mL). This solution was then divided between two 500 mL Schlenk flasks. Each flask was subjected to three freeze-pump-thaw cycles, and then back-filled with nitrogen. The flasks were sealed, heated to 140 °C, and stirred for 3 h. The flasks were then cooled to ambient temperature and the reaction mixtures were combined in a 2 L round-bottom flask. The solvent was removed under reduced pressure, and the resulting solid purified by flash chromatography (30%-40%-50% EtOAc/Hexanes) to afford cyclohexadiene **78** (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$_3$).

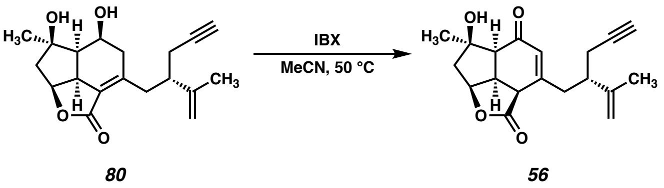


Epoxide 79: A 500 mL round-bottom flask was charged with Diels–Alder adduct **78** (1.75 g, 5.87 mmol, 1.0 equiv) in a mixture of CH_2Cl_2 (59 mL) and benzene (196 mL). $VO(acac)_2$ was added (117 mg, 0.440 mmol, 0.075 equiv) in one portion, and the mixture was stirred 10 min at 23 °C until pale-green in color. TBHP (5.0 M in decane, 2.30 mL, 11.74 mmol, 2.0 equiv) was added dropwise via syringe, and the mixture became deep-red in color. The mixture was stirred at 23 °C for 1 h, at which point no starting material remained, as judged by TLC. The reaction mixture was poured directly onto a flash column and purified by flash chromatography (0%-50%-70%-80% EtOAc/Hexanes) to afford the epoxide **79** (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, $CHCl_3$).

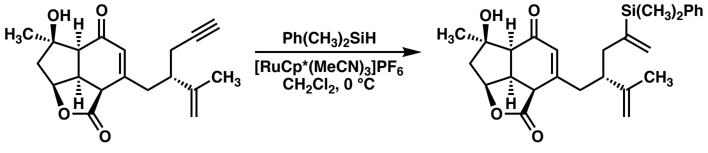


79 80

Diol 80: A 250 mL round bottom flask was charged with epoxide **79** (1.70 g, 5.41 mmol, 1.0 equiv), Cp_2TiCl_2 (269 mg, 1.08 mmol, 0.20 equiv), Mn 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 was then added dropwise to the red suspension, which gradually changed to a blue/grey color. The suspension was stirred vigorously for 2 h at 23 °C, after which the starting material was consumed, as judged by TLC. Celite was added directly to the mixture, and the solvent removed under reduced pressure. The resulting solid was loaded directly on to a flash column and purified by flash chromatography (40%-50%-60% EtOAc/Hexanes) to afford diol **80** (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, $CHCl_3$).

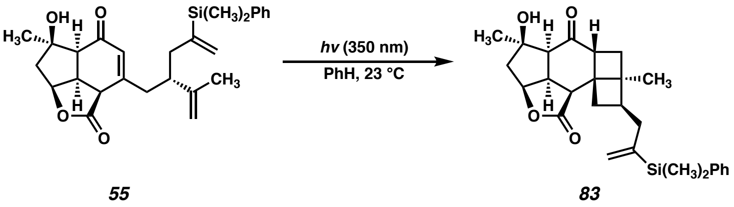


Enone 56: Diol **80** (1.0 g, 3.16 mmol, 1.0 equiv) was divided into 20 scintilation vials (not flame dried, 50 mg, 0.158 mmol per vial) each equipped with a magnetic stir bar and a septum cap. To each vial was added IBX (188 mg, 0.671 mmol, 4.25 equiv) and each vial was evacuated and back-filled with N_2. MeCN (11 mL) was added to each vial, after which the vials were sealed, heated to 50 °C, and stirred 2 h. The reactions were cooled to 23 °C, combined, and filtered over a plug of SiO_2, rinsing generously with EtOAc. The filtrate was concentrated under reduced pressure, and the residue obtained was purified by flash chromatography (30%-40%50% EtOAc/Hexanes) to afford enone **56** (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, $CHCl_3$).

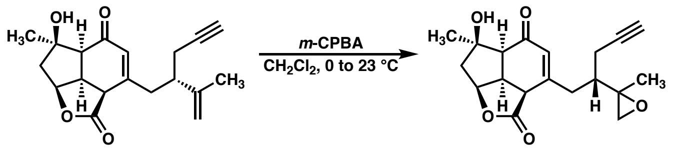


56 55

Vinyl Silane 55: A 1-dram vial was charged with enone **5**6 (7.0 mg, 0.0223 mmol, 1.0 equiv) in CH_2Cl_2 (400 µL). Phenyldimethylsilane (4 µL, 0.0267 mmol, 1.2 equiv) was 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, prepared in a nitrogen-filled glovebox) was added dropwise. Following the addition, the reaction was stirred 5 min at 0 °C, after which alkyne **5** was no longer detectable by TLC. The reaction mixture was loaded directly onto a preparatory TLC plate and purified by preparative TLC (80% EtOAc/Hexanes) to afford vinyl silane **55** (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 (100 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, $CHCl_3$).

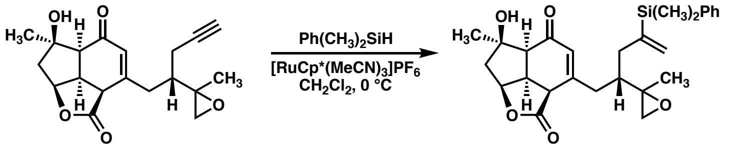


Cyclobutane 83: A 1-dram vial was charged with vinyl silane **55** (22 mg, 0.0488 mmol, 1.0 equiv) in PhH (5.0 mL). The solution was sparged with N_2 for 5 min, and placed in a photoreactor equipped with Hitachi UVA bulbs (F8T5-BLB, ~350 nm). The reaction was stirred under 350 nm irradiation for 10 h, after which no starting material remained (as judged by TLC). An ^{1}H NMR spectrum of the crude product shows a mixture with **83** as the major constituent. The crude white solid was 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 **83** (5.0 mg, 0.0111 mmol, 23 % yield). X-ray quality crystals were 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, $CHCl_3$).



56 85 1.7:1 mixture of epimers

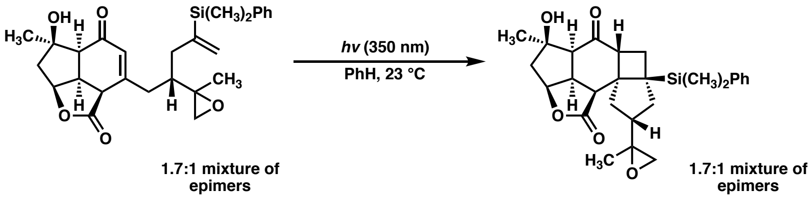
Epoxides 85 and *epi*-85: A 100 mL round-bottom flask was charged with enone **56** (450 mg, 1.43 mmol, 1.0 equiv) in CH_2Cl_2 (48 mL). The solution was cooled to 0 °C, and *m*–CPBA (~70% wt/wt; 1.06 g, 4.29 mmol, 3.0 equiv) was added in one portion. The mixture was stirred while gradually warming to 23 °C over 2 h, and then stirred an additional 10 h at 23 °C, at which point **56** had been completely consumed as judged by TLC. The reaction mixture was poured directly onto a flash column and purified by flash chromatography (50%-60%-70%-80% EtOAc/Hexanes) to afford epoxides **85** and ***epi*-85** (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) which was used in the subsequent reaction. 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 (100 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, $CHCl_3$).



85 1.7:1 mixture of epimers

86 1.7:1 mixture of epimers

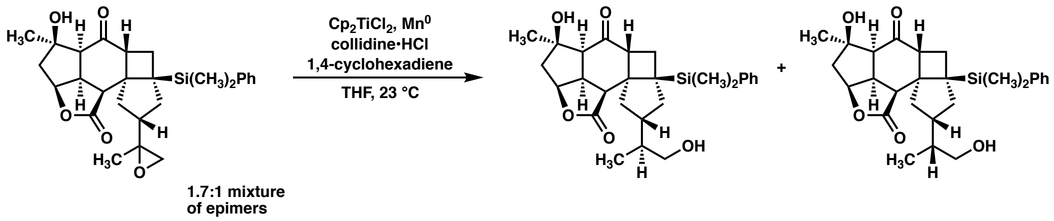
Vinyl Silanes 86 and *epi*-86: A 250 mL round-bottom flask was charged with a mixture of **85** and ***epi*-85** (725 mg, 2.19 mmol, 1.0 equiv) in CH_2Cl_2 (22 mL). Phenyldimethylsilane (400 µL, 2.63 mmol, 1.2 equiv) was added, and the mixture was cooled to 0 °C. $[RuCp^*(MeCN)_3]PF_6$ (10 mg/mL stock solution, 5.5 mL, 0.110 mmol, 0.05 equiv, prepared in a nitrogen-filled glovebox) was added dropwise. Following the addition, the reaction was stirred 5 min at 0 °C, after which the starting material was no longer detectable by TLC. The reaction mixture was poured directly onto a flash column and purified by flash chromatography (0%-50% EtOAc/Hexanes) to afford vinyl silanes **86** and ***epi-86*** (870 mg, 1.86 mmol, 85% yield) as a colorless foam. The products were 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, $CHCl_3$).



86 **87**

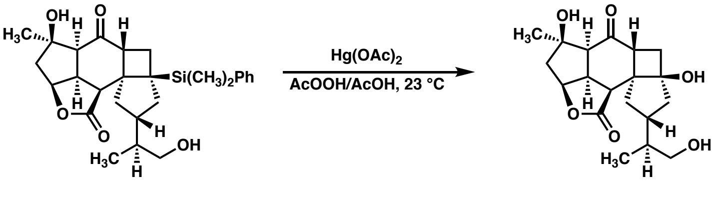
Cyclobutanes 87 and *epi*-87: A mixture of vinyl silanes **86** and *epi*-**86** (870 mg, 1.86 mmol, 1.0 equiv) was divided into 11 portions (79 mg each). Each portion was added to a 40 mL scintillation vial with PhH (34 mL). Each vial was then sparged with nitrogen for 5 min, and placed in a photoreactor equipped with Hitachi UVA bulbs (F8T5-BLB, ~350 nm). The reactions were stirred under 350 nm irradiation for 5 h, after which no starting material remained (as judged by TLC). The reactions were combined in a 1 L round bottom flask, and concentrated onto Celite®. The resulting solid was loaded onto a column, and purified by flash chromatography (30%-40%-50%-60%-70%-80% EtOAc/Hexanes) to afford the cyclobutanes **86** and ***epi-86*** (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 **90** and **epi-90**. 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 (100 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, $CHCl_3$).



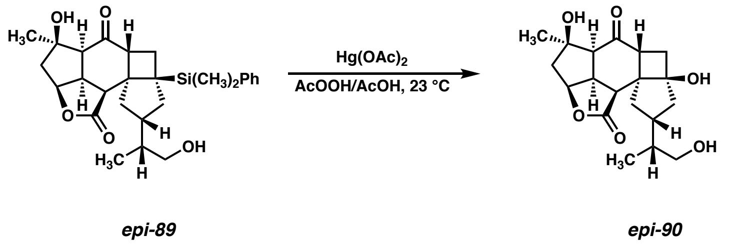
Diols 89 and *epi*-89: A 100 mL round-bottom flask was charged with a mixture of epoxides **87** and *epi*-**87** (620 mg, 1.33 mmol, 1.0 equiv), Cp_2TiCl_2 (66 mg, 0.266 mmol, 0.20 equiv), Mn dust (80 mg, 1.46 mmol, 1.10 equiv) and collidine•HCl (262 mg, 1.66 mmol, 1.25 equiv) in THF (27 mL). To this red suspension was added 1,4-cyclohexadiene (567 µL, 599 mmol, 4.5 equiv) and the suspension gradually changed to a blue/grey color. The mixture was stirred at 23 °C for 1.5 h, after which the starting material was completely consumed, as judged by TLC. Celite® was then added directly to the reaction mixture and the solvent was removed under reduced pressure. The resulting solid was loaded directly onto a flash column and purified by flash chromatography (60%-65%-70%-75%-80%-90%-100% EtOAc/Hexanes) to afford diols **89** (385 mg, 0.781 mmol, 62% yield) and ***epi*-89** (224 mg, 0.478 mmol, 36% yield) as white solids, which were separable at this point. *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 –$Si(CH_3)_2Ph$ 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 **90** and **epi-90**;* **89**: ^{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 (100 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*-89**: ^{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, $CHCl_3$).

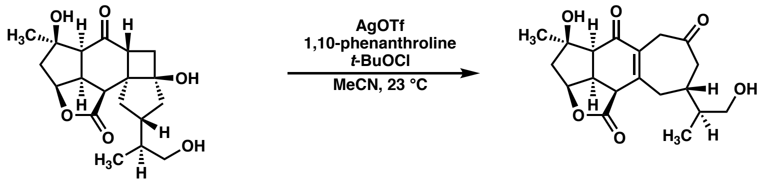


89 **90**

Triol 90: A 20 mL scintillation vial was charged with **89** (80 mg, 0.171 mmol, 1.0 equiv) and AcOOH (30% in aqueous AcOH, 3.4 mL). To this solution was added $Hg(OAc)_2$ (100 mg, 0.341 mmol, 2.0 equiv) in a single portion. The reaction was stirred 45 min at 23 °C, after which no **89** remained (as judged by LCMS). The reaction mixture was diluted with EtOAc and pipetted over an ice-cold mixture of sat. aq. $Na_2S_2O_3$ and saturated, aqueous $NaHCO_2$ (1:4). This aqueous solution was then extracted with EtOAc (3x) then $CHCl_3$/*i*-PrOH (3:1) (2x). The organic extracts were combined and dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford a crude solid which was purified by flash chromatography (80%-100% EtOAc/Hexanes) to afford triol **90** (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).

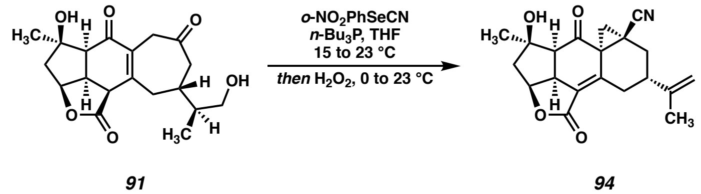


Triol *epi*-90: A 20 mL scintillation vial was charged with *epi*-**89** (80 mg, 0.171 mmol, 1.0 equiv) and AcOOH (30% in aqueous AcOH, 3.4 mL). To this solution was added $Hg(OAc)_2$ (100 mg, 0.341 mmol, 2.0 equiv) in a single portion. The reaction was stirred 45 min at 23 °C, after which no *epi*-**89** remained (as judged by LCMS). The reaction mixture was diluted with EtOAc (10 mL) and pipetted over an ice-cold mixture of sat. aq. $Na_2S_2O_3$ and saturated, aqueous $NaHCO_2$ (1:4). This aqueous solution was then extracted with EtOAc (3x) then $CHCl_3$/*i*-PrOH (3:1) (2x). The organic extracts were combined and dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford a crude solid which was 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; ^1H 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).

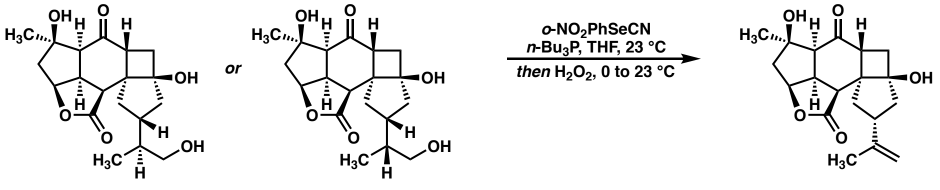


90 ***91***

Diol 91: To a stirred suspension of triol **90** (21 mg, 0.0599 mmol, 1.0 equiv), AgOTf (6 mg, 0.0240 mmol, 0.40 equiv), and 1,10-phenanthroline (9 mg, 0.0479 mmol, 0.80 equiv) in MeCN (3.2 mL, 0.019 M) was added *t*-BuOCl (14 µL, 0.120 mmol, 2.0 equiv) at 23 °C. The suspension changed from white to red, and then to dark brown. The reaction mixture was allowed to stir at 23 °C for 12 h, after which no starting material remained (as judged by TLC and LCMS). The reaction mixture was diluted with EtOAc (5 mL), and quenched with 5 drops of saturated aqueous NaS_2O_3, after which the dark brown color quickly dissipated. The mixture was passed directly over a short plug of SiO_2, and the eluent was concentrated onto SiO_2 and dry loaded onto a column. The crude was purified by flash chromatography (50 – 100% EtOAc/hexanes) to afford an unstable intermediate (presumed to be the γ-chloroketone) which was not characterized further. This product was dissolved in MeOH (5 mL). TLC SiO_2 (scraped from TLC plates and crushed with a mortar and pestle) was added (c.a. 1 g). The suspension was allowed to stir for 12 h at 23 °C, after which the abovementioned product had been completely consumed (as judged by TLC). The MeOH was removed under reduced pressure, and then the solids were resuspended in acetone (10 mL) and stirred for 1 h. The suspension was filtered through a plug of Celite® and concentrated to afford diol **91** (10 mg, 40% yield) as a white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.14 (dd, *J* = 6.9, 5.6 Hz, 1H), 3.91 (d, *J* = 14.7 Hz, 1H), 3.69 – 3.47 (m, 4H), 3.27 (dd, *J* = 14.8, 1.8 Hz, 1H), 2.74 (d, *J* = 12.8 Hz, 1H), 2.67 – 2.52 (m, 5H), 2.31 (d, *J* = 15.0 Hz, 1H), 1.91 (dd, *J* = 15.0, 5.6 Hz, 1H), 1.49 (s, 3H), 0.86 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.0, 192.9, 174.6, 152.3, 132.7, 82.9, 65.1, 54.6, 49.5, 47.4, 45.5, 41.3, 41.1, 39.6, 35.9, 34.5, 26.1, 11.5; IR (Neat Film NaCl) 3778, 3680, 2918, 2848, 1758, 1709, 1657, 1461, 1372, 1167, 1089, 1030, 823 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{19}H_{23}O_6$ $[M-OH]^+$: 331.1540, found 331.1541; $[\alpha]_D^{25.0}$ –60.5° (*c* 0.1, $CHCl_3$).

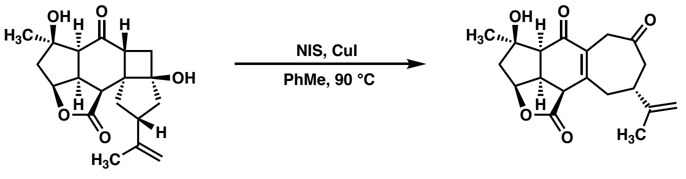


Nitrile 94: To a stirred solution of diol **91** (4 mg, 0.0115 mmol, 1.0 equiv) in THF (400 µL, 0.029 M) cooled to 15 °C in a nitrogen-filled glovebox was added *o*-NO_2PhSeCN (156 mg/mL solution in THF, 25 µL, 0.0173 mmol, 1.5 equiv). To this light-brown solution was added *n*-Bu_3P (83 mg/mL solution in THF, 42 µL, 0.0173 mmol, 1.5 equiv), at which point the solution rapidly changed to deep red in color. The reaction mixture was stirred 20 min at 15 °C and then warmed to 23 °C and stirred an additional 2 h. At this point, a small amount of starting material was detected by LCMS. An additional portion of *o*-NO_2PhSeCN (156 mg/mL solution in THF, 8 µL, 0.00775 mmol, 0.5 equiv) was added, followed by *n*-Bu_3P (83 mg/mL solution in THF, 14 µL, 0.00775 mmol, 0.5 equiv) at 23 °C, and the reaction was subsequently allowed to stir an additional 2 h. The reaction was removed from the glovebox and cooled to 0 °C. H_2O_2 (30%, 60 µL) was added dropwise, and the reaction was stirred 1 h at 0 °C. The mixture was allowed to warm to 23 °C, and stirred an additional 12 h. The reaction mixture was purified directly by preparative HPLC to afford nitrile **94** (1.0 mg, 26% yield) as a white solid. X-ray quality crystals were obtained by layer-diffusion of hexanes into a CH_2Cl_2 solution of **94**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.16 (td, *J* = 7.8, 3.1 Hz, 1H), 4.82 (t, *J* = 1.6 Hz, 1H), 4.74 (d, *J* = 0.9 Hz, 1H), 4.07 – 4.00 (m, 1H), 3.83 (td, *J* = 7.9, 4.2 Hz, 1H), 2.88 (dd, *J* = 7.6, 1.1 Hz, 1H), 2.66 (ddd, *J* = 13.9, 4.7, 1.7 Hz, 1H), 2.46 (dd, *J* = 4.8, 0.9 Hz, 1H), 2.35 – 2.25 (m, 2H), 2.23 – 2.14 (m, 1H), 1.90 (dd, *J* = 14.1, 11.9 Hz, 1H), 1.73 (t, *J* = 1.3 Hz, 3H), 1.60 (d, *J* = 5.0 Hz, 1H), 1.54 (s, 3H); *Due to the limited quantity of material obtained, not all expected* ^{13}*C signals are visible because of the low concentration of the sample. The shifts are reported as observed:* ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.8, 192.2, 146.8, 146.0, 111.2, 83.9, 80.6, 58.2, 49.2, 45.2, 39.7, 36.3, 31.5, 29.2, 28.5, 24.5, 20.9; IR (Neat Film NaCl) 3603, 2924, 2852, 1738, 1703, 1658, 1547, 1464, 1377, 1295, 1219, 1171, 1054 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{20}H_{22}O_4N$ $[M+H]^+$: 340.1543, found 340.1553; $[\alpha]_D^{25.0}$ –7.0 ° (*c* 0.1, $CHCl_3$).



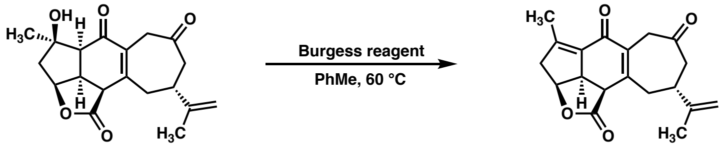
90 **epi-90** **53**

Cyclobutanol 53: In a nitrogen filled glovebox a 1-dram vial was charged with triol **90** (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 was added *n*-Bu_3P (17 µL, 0.0685 mmol, 3.0 equiv) dropwise via syringe, at which point the reaction mixture became deep red/brown in color. This solution was allowed to stir in the glovebox at 23 °C for 7 h, at which point **25** had been completely consumed, as judged by LCMS. The vial was then removed from the glovebox and cooled to 0 °C after which H_2O_2 (30% w/w, 80 µL) was cautiously added dropwise. This orange solution was 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 was then loaded directly onto a column and purified by flash chromatography (30%-40%-50% EtOAc/Hexanes) to afford cyclobutanol **53** (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, $CHCl_3$).



53 ***Scabrolide A (1)***

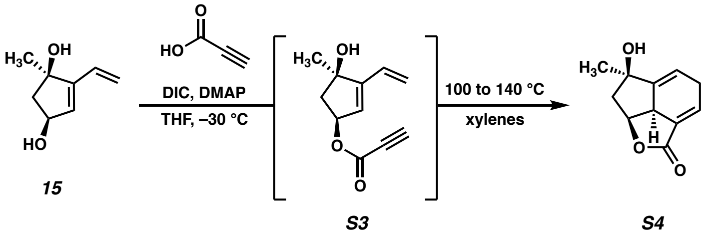
Scabrolide A (1): In a nitrogen-filled glovebox, a 1-dram vial was charged with cyclobutanol **53** (5.0 mg, 0.0151 mmol, 1.0 equiv), CuI (22.0 mg, 0.117 mmol, 7.8 equiv) and NIS (6.7 mg, 0.0300 mmol, 2.0 equiv) in PhMe (1.5 mL). The vial was stirred at 23 °C for 5 min, and then transferred to a preheated, 90 °C aluminum block. The reaction was stirred at 90 °C for 1 h. At this point, starting material remained, so an additional portion of NIS (3.3 mg, 0.0150 mmol, 1.0 equiv) was added, and the reaction stirred an additional 20 min at 90 °C. The mixture was then cooled to 23 °C and filtered through a pad of Celite, washing with EtOAc. This solution was concentrated to a red film, which was directly purified by reverse-phase (C18) preparative 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 (**1**) (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**; ^1H 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, $CHCl_3$).



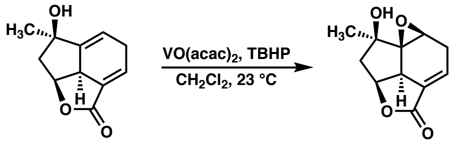
Scabrolide A (1) ***Yonarolide (4)***

Yonarolide (4): In a nitrogen-filled glovebox, a 1-dram vial was charged with scabrolide A (**1**, 1.0 mg, 0.00303 mmol, 1.0 equiv) in PhMe (1.0 mL). Burgess reagent (5.0 mg, 0.0210 mmol, 6.9 equiv) was added, and the vial was capped, sealed with electrical tape, and removed from the glovebox. The vial was then transferred to a preheated, 60 °C aluminum block, and the reaction was stirred for 30 min at 60 °C. The vial was removed from the heating block and cooled to 23 °C. The solvent was then removed under vacuum, and the resulting residue was purified by preperative TLC (70% EtOAc/hexanes) to afford yonarolide (**4**) (0.5 mg, 0.00160 mmol, 53% yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.02 (t, J = 4.6 Hz, 1H), 4.87 (d, J = 1.2 Hz, 1H), 4.85 – 4.82 (m, 1H), 4.03 – 3.90 (m, 1H), 3.60 (s, 3H), 3.45 (d, J = 8.2 Hz, 1H), 3.12 – 3.01 (m, 1H), 2.96 (ddt, J = 19.2, 4.6, 1.6 Hz, 1H), 2.87 (dd, J = 15.6, 4.3 Hz, 1H), 2.80 – 2.71 (m, 1H), 2.67 (dd, J = 13.3, 9.3 Hz, 1H), 2.61 (dd, J = 13.3, 6.3 Hz, 1H), 2.11 (td, J = 1.6, 0.8 Hz, 2H), 1.85 – 1.81 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.9, 183.4, 172.5, 150.8, 149.2, 146.9, 134.2, 126.5, 111.2, 80.9, 50.1, 47.5, 47.2, 45.8, 41.4, 39.6, 38.5, 21.5, 15.8; IR (Neat Film NaCl) 2920, 1763, 1707, 1652, 1633, 1441, 1359, 1302, 1252, 1144, 1053, 1005, 895, 841, 820 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{19}H_{21}O_4$ $[M+H]^+$: 313.1434, found 313.1433; $[\alpha]_D^{25.0}$ –63.0 ° (*c* 0.083, $CHCl_3$).

Synthesis of Model Enone 82

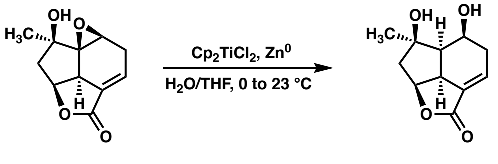


Tricycle S4: To a stirred solution of diol **15** (500 mg, 3.57 mmol, 1.0 eq) and DMAP (44 mg, 0.357 mmol, 0.10 eq) in THF (7.1 mL) was added propiolic acid (663 µL, 10.7 mmol, 3.0 eq) at room temperature. The flask was sealed and cooled to –30 °C. DIC (1.68 mL, 10.70 mmol, 3.0 eq) was added dropwise and the resulting solution was stirred for 16 h at –30 °C, until consumption of diol **15** as judged by TLC. The reaction mixture was then loaded directly onto a flash column (SiO_2, 10% EtOAc/Hexanes), and the flask rinsed with a small amount (c.a. 1 mL) of CH_2Cl_2 and eluted with a gradient of 10%–15%–20% EtOAc/Hexanes. The column fractions containing the product were pooled in a 1 L round bottom flask, and 83 mL xylenes was added. The EtOAc/Hexanes were removed by rotary evaporation, leaving a xylenes solution of ester **S3**. This solution was transferred to a flame-dried 250 mL round bottom flask containing a stir bar, and sparged with N_2 for 10 min. The solution was heated to 100 °C and stirred for 5 h after which starting material remained as judged by TLC. The temperature was increased to 140 °C and the mixture was stirred for an additional 5 h. The mixture was cooled to 23 °C, and loaded directly onto a flash column (100% Hexanes). The xylenes were flushed off with hexanes, and the product was then eluted with 50%⟶60% EtOAc/Hexanes, affording tricycle **S4** as an off-white solid (390 mg, 2.03 mmol, 57% yield over two steps); ^{1}H NMR (400 MHz, C_6D_6) δ 6.75 (ddd, J = 6.7, 3.4, 2.1 Hz, 1H), 5.39 (ddd, J = 6.2, 2.9, 1.7 Hz, 1H), 4.29 (dt, J = 8.8, 7.4 Hz, 1H), 2.53 – 2.31 (m, 2H), 2.08 (ddt, J = 19.3, 11.4, 1.9 Hz, 1H), 1.99 (dd, J = 12.7, 7.1 Hz, 1H), 1.18 (dd, J = 12.8, 7.9 Hz, 1H), 1.01 (s, 3H); ^{13}C NMR (100 MHz, C_6D_6) 167.9, 151.5, 138.2, 133.7, 116.1, 80.0, 75.6, 49.7, 44.2, 29.4, 26.1; IR (Neat Film, NaCl) 1003, 1208, 1639, 1754, 2967, 3434 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{11}H_{13}O_3$ [M+H]$^+$: 193.0859, found 193.0856. $[\alpha]_D^{25}$ –109.8 ° (*c* 1.0, $CHCl_3$).



S4 ***S5***

Epoxide S5: To a stirred solution of diene **S4** (199 mg, 1.04 mmol, 1.0 eq) in CH_2Cl_2 (35 mL) was added VO(acac)$_2$ (28 mg, 0.104 mmol, 0.10 eq) in one portion. The solution was allowed to stir for 15 min. at 23 °C until it was pale-green in color. TBHP (5.0 M/decane, 228 μL, 1.4 mmol, 1.10 eq) was added dropwise, causing the reaction mixture to become deep red in color. The mixture was allowed to stir for 3 h at 23 °C, until the disappearance of starting material as judged by TLC. The mixture was then loaded directly onto a flash column (SiO_2, 100% EtOAc) and eluted with 100% EtOAc to afford epoxide **S5** as a white solid (187 mg, 0.898 mmol, 86% yield); ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 6.41 (dtd, *J* = 7.4, 3.2, 1.0 Hz, 1H), 4.97 (td, *J* = 7.8, 6.2 Hz, 1H), 3.81 (d, *J* = 3.2 Hz, 1H), 3.55 (dt, *J* = 8.2, 2.8 Hz, 1H), 3.47 (s, 1H), 2.97 (ddd, *J* = 17.1, 7.4, 3.2 Hz, 1H), 2.49 (ddd, *J* = 13.3, 5.0, 1.8 Hz, 2H), 1.90 (dd, *J* = 13.2, 6.1 Hz, 1H), 1.42 (s, 3H); ^{13}C NMR (100 MHz, $(CD_3)CO$) δ 169.6, 133.0, 129.6, 77.6, 75.3, 69.6, 52.0, 50.1, 45.1, 30.8, 23.3; IR (Neat Film, NaCl) 780, 954, 1007, 12078, 1646, 1755, 2972, 3500 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{11}H_{14}O_5$ $[M+H_2O]^+$: 226.0836, found 226.0838. $[\alpha]_D^{25}$ –193.9 ° (*c* 1.0, EtOH).

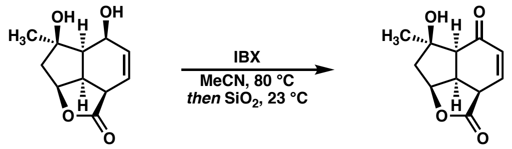


S5 ***81***

Diol 81:

Preparation of 0.5 M Cp_2TiCl Solution: A 25 mL round-bottom flask was charged with $TiCp_2Cl_2$ (1.64 g, 6.60 mmol, 1.0 eq) and Zn dust (1.29 g, 19.8 mmol, 3.0 eq). The flask was evacuated and backfilled with N_2, and THF (13.2 mL) was added. The red mixture was allowed to stir for 1h after which it became a deep green. Stirring was ceased and the solids were allowed to settle at the bottom of the flask before use of the supernatant.

Epoxide Opening: To a stirred solution of epoxide **S5** (300 mg, 1.44 mmol, 1.0 eq) in THF (72 mL) was added H_2O (2.00 mL, 110.74 mmol, 76.9 eq). The mixture was cooled to 0 ° and $TiCp_2Cl$ was added (11.5 mL, 0.5 M, 5.76 mmol, 4.0 eq) dropwise. The mixture was allowed to gradually warm to 23 °C and stirred for 12 h. The reaction was quenched with Na_2HPO_4 (sat. aq., 10 mL) and brine (30 mL), and diluted with EtOAc (20 mL). The layers were separated, and the aqueous layer was filtered through a plug of celite, washing with brine and EtOAc. The aqueous layer was extracted with EtOAc until no product was detected by TLC in the subsequent extracts (c.a. 10x 25 mL). The organic extracts were pooled and dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The bright orange crude product was purified by flash chromatography on SiO_2 (20%⟶30%⟶40% Acetone/Hexanes) to afford diol **81** as a white foam (213 mg, 1.01 mmol, 70% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.97 – 6.83 (m, 1H), 4.99 (tdd, *J* = 6.6, 3.5, 1.3 Hz, 1H), 4.70 (dd, *J* = 7.2, 3.4 Hz, 1H), 3.17 – 3.03 (m, 1H), 2.80 – 2.69 (m, 1H), 2.43 (ddd, *J* = 9.3, 7.7, 1.2 Hz, 1H), 2.11 (ddd, *J* = 14.4, 3.6, 1.2 Hz, 1H), 2.06 – 1.93 (m, 2H), 1.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 170.6, 135.6, 133.0, 81.8, 80.9, 68.0, 49.7, 47.9, 43.7, 35.6, 28.5; IR (Neat Film, NaCl) 752, 1015, 1104, 1186, 1216, 1307, 1457, 1668, 1746, 2925, 1966, 3377 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{11}H_{15}O_4$ $[M+H]^+$: 211.0965, found 211.0963. $[\alpha]_D^{25}$ = + 10.7 ° (*c* 1.0, $CHCl_3$).



81 ***82***

Enone 82: To a stirred solution of diol **81** (20 mg, 0.0951 mmol, 1.0 eq) in MeCN (1.9 mL) was added IBX (59 mg, 0.209 mmol, 2.2 eq) in one portion. The resulting suspension was heated to 80 °C and stirred for 1 h, until the disappearance of diol **81** as judged by TLC. The mixture was cooled to 23 °C, and SiO_2 gel (50 mg) was added in one portion. The suspension was stirred for 10 min at 23 °C, then was diluted with EtOAc (1 mL), filtered over Celite, and the filtrate concentrated *in vacuo*. The crude residue was purified by flash chromatography (SiO_2, 60% EtOAc/Hexanes) affording enone **82** as a white solid (14 mg, 0.0720 mmol, 71% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.00 (dd, *J* = 10.2, 4.8 Hz, 1H), 6.22 (d, *J* = 10.2 Hz, 1H), 5.31 – 5.01 (m, 1H), 3.77 – 3.50 (m, 2H), 2.57 (d, *J* = 9.7 Hz, 1H), 2.32 (d, *J* = 15.0 Hz, 1H), 1.93 (dd, *J* = 15.0, 5.7 Hz, 1H), 1.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 174.3, 142.5, 131.0, 82.9, 55.8, 47.4, 41.1, 40.0, 26.1; IR (Neat Film, NaCl) 764, 1003, 1032, 1100, 1183, 1366, 1655, 1756, 2928, 3418 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{11}H_{16}O_4N$ $[M+NH_4]^+$: 226.1074, found 226.1075. $[\alpha]_D^{25}$ –230.0 ° (*c* 1.0, EtOH).

Comparison of Synthetic (–)-Scabrolide A to Published Data

Table S1 Comparison of ^{1}H NMR shifts of synthetic and natural scabrolide A (**1**).

Synthetic Scabrolide A	**Natural Scabrolide A (Sheu, 2002)**	**Natural Scabrolide A (Liang, Guo, 2020)**
^{1}H NMR, 400 MHz, CDCl$_3$	*^{1}H NMR, 400 MHz, CDCl$_3$*	*^{1}H NMR, 400 MHz, CDCl$_3$*
5.11 (dd, *J* = 7.1, 5.4, 1H)	5.11 (t, *J* = 6.4, 1H)	5.11 (dd, *J* = 5.6, 7.0, 1H)
4.86 (m, 1H)	4.85 (s, 1H)	4.85 (s, 1H)
4.84 (m, 1H)	4.83 (s, 1H)	4.83 (s, 1H)
3.70 (d, *J* = 17.2, 1H)	3.70 (d, *J* = 17.2, 1H)	3.70 (d, *J* = 17.2, 1H)
3.61 (ddd, J = 11.1, 10.0, 7.2, 1H)	3.62 (dd, *J* = 11.2, 6.4, 1H)	3.62 (dd, *J* = 11.2, 6.4, 1H)
3.51 (d, *J* = 11.3, 1H)	3.51 (d, *J* = 11.2, 1H)	3.51 (d, *J* = 11.2, 1H)
3.43 (dd, *J* = 17.3, 1.6, 1H)	3.42 (d, *J* = 17.2, 1H)	3.42 (d, *J* = 17.2, 1H)
3.09 (m, 1H)	3.07 (q, *J* = 6.4, 1H)	3.07 (m, 1H)
2.88 (m, 2H)	2,88 (m,1H), 2.88 (m1H)	2.86 (m, 2H)
2.62 (m, 2H)	2.63 (m, 2H)	2.63 (m, 2H)
2.60 (d, *J* = 10.1, 1H)	2.62 (d, *J* = 10.0, 1H)	2.62 (d, *J* = 10.0, 1H)
2.30 (d, *J* = 15.0, 1H)	2.30 (d, *J* = 15.2, 1H)	2.30 (d, *J* = 15.2, 1H)
1.93 (dd, *J* = 15.0, 5.6, 1H)	1.92 (dd, *J* = 15.2, 5.6, 1H)	1.92 (dd, *J* = 15.2, 5.6, 1H)
1.83 (s, 3H)	1.82 (s, 3H)	1.82 (s, 3H)
1.50 (s, 3H)	1.49 (s, 3H)	1.49 (s, 3H)

Figure S1 Overlaid ^{1}H NMR spectra of natural (Sheu, 2002) and synthetic scabrolide A (**1**).

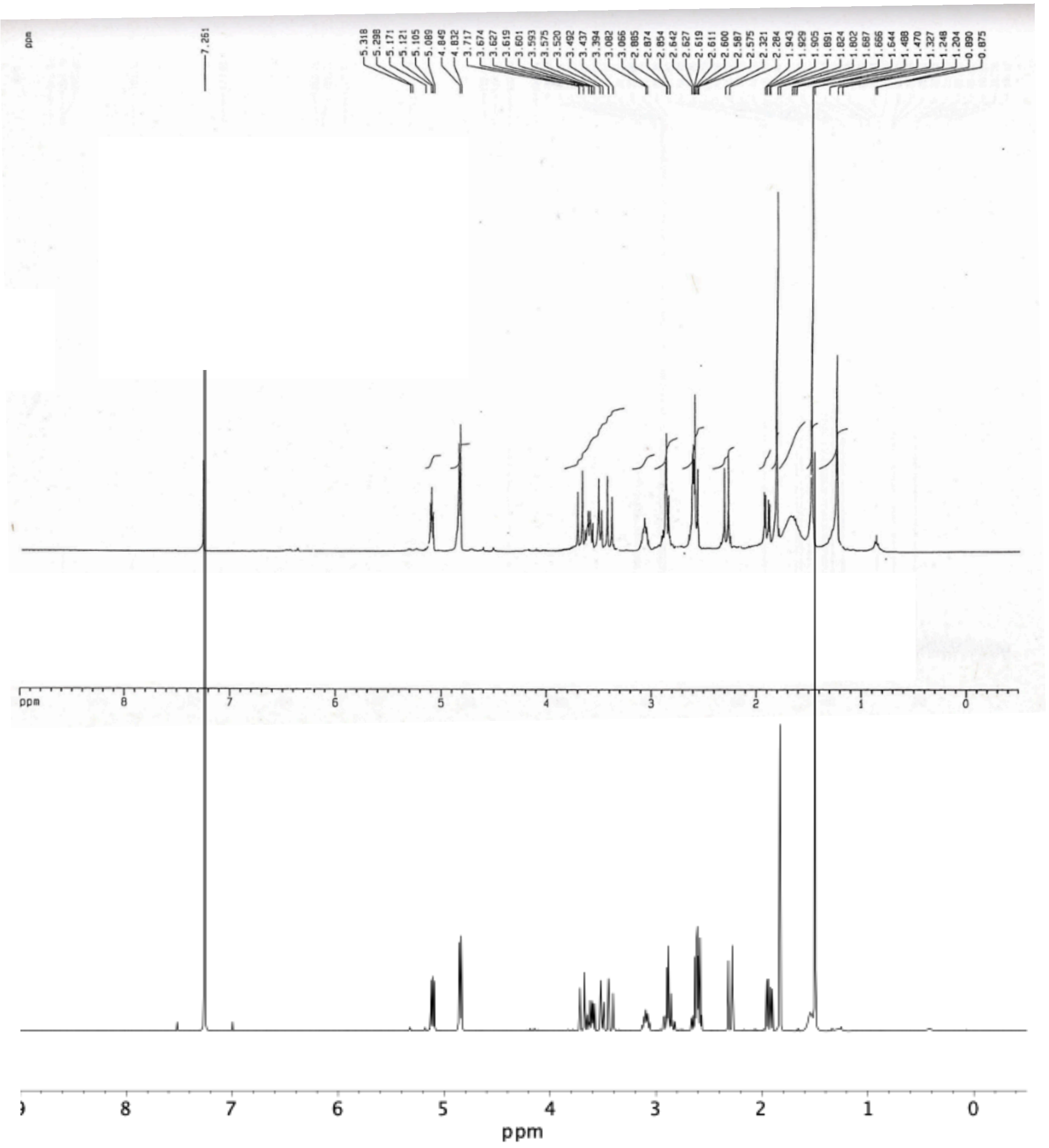
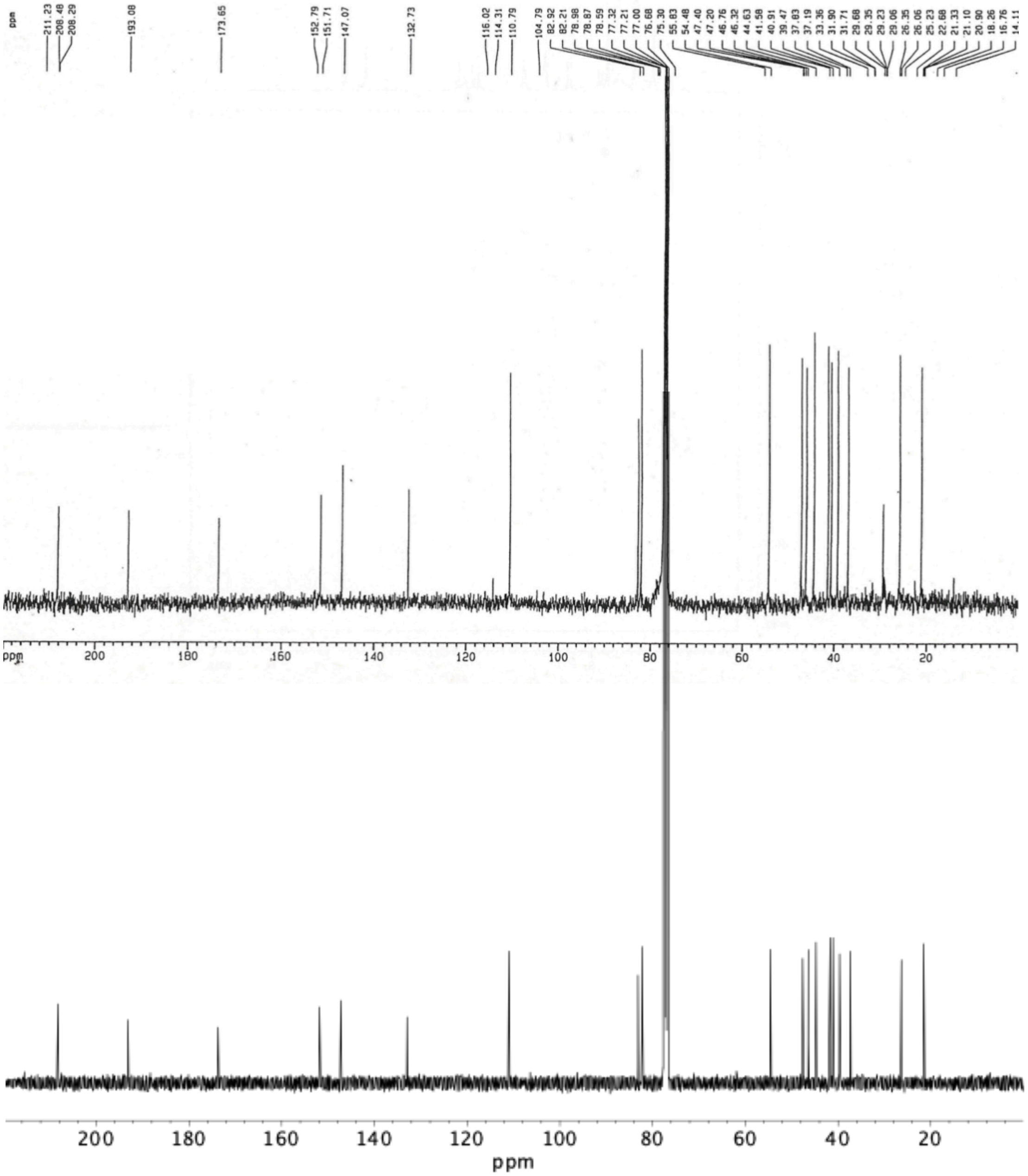


Table S2. Comparison of ^{13}C NMR shifts of synthetic and natural scabrolide A (**1**).

Synthetic Scabrolide A	**Natural Scabrolide A (Sheu, 2002)**	**Natural Scabrolide A (Liang, Guo, 2020)**
^{13}C NMR, 100 MHz, CDCl$_3$	*^{13}C NMR, 100 MHz, CDCl$_3$*	*^{13}C NMR, 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	38.5	39.7
37.3	37.2	37.4
26.3	26.1	26.3
21.5	21.3	21.5

Figure S2. Overlaid ^{13}C NMR spectra of natural (Sheu, 2002) and synthetic scabrolide A (**1**).



Comparison of Synthetic (–)-Yonarolide to Published Data

Table S3 Comparison of ^{1}H shifts of synthetic and natural yonarolide (**4**).

Synthetic Yonarolide	**Natural Yonarolide (Yamada, 1995)**
^{1}H NMR, 400 MHz, CDCl$_3$	*^{1}H NMR, 400 MHz, CDCl$_3$*
5.02 (t, *J* = 4.6, 1H)	5.01 (t, *J* = 4.6, 1H)
4.87 (t, *J* = 1.2, 1H)	4.86 (t, *J* = 1.1, 1H)
4.83 (s, 1H)	4.83 (s, 1H)
3.97 (m, 1H)	3.95 (m, 1H)
3.60 (s, 2H)	3.59 (s, 2H)
3.45 (d, *J* = 8.2, 1H)	3.44 (d, *J* = 8.2, 1H)
3.06 (m, 1H)	3.05 (m, 1H)
2.96 (ddt, *J* = 19.2, 4.6, 1.6 1H)	2.96 (br dd, *J* = 19.0, 4.6, 1H)
2.87 (dd, *J* = 15.6, 4.3, 1H)	2.87 (dd, *J* = 15.5, 4.2, 1H)
2.71–2.79 (m, 2H)	2.76 (dd, *J* = 7.8, 15.5, 1H
---	2.74 (br d, *J* = 19.0, 1H)
2.66 (dd, 13.3, 9.3, 1H)	2.66 (dd, 13.3, 9.2, 1H)
2.61 (dd, *J* =13.3, 6.3, 1H)	2.62 (dd, 13.3, 6.2, 1H)
2.11 (s, 3H)	2.09 (s, 3H)
1.84 (s, 3H)	1.82 (s, 3H)

Figure S3. Overlaid ^{13}C NMR spectra of natural (Li, Guo, 2022)[4] and synthetic yonarolide (**4**).

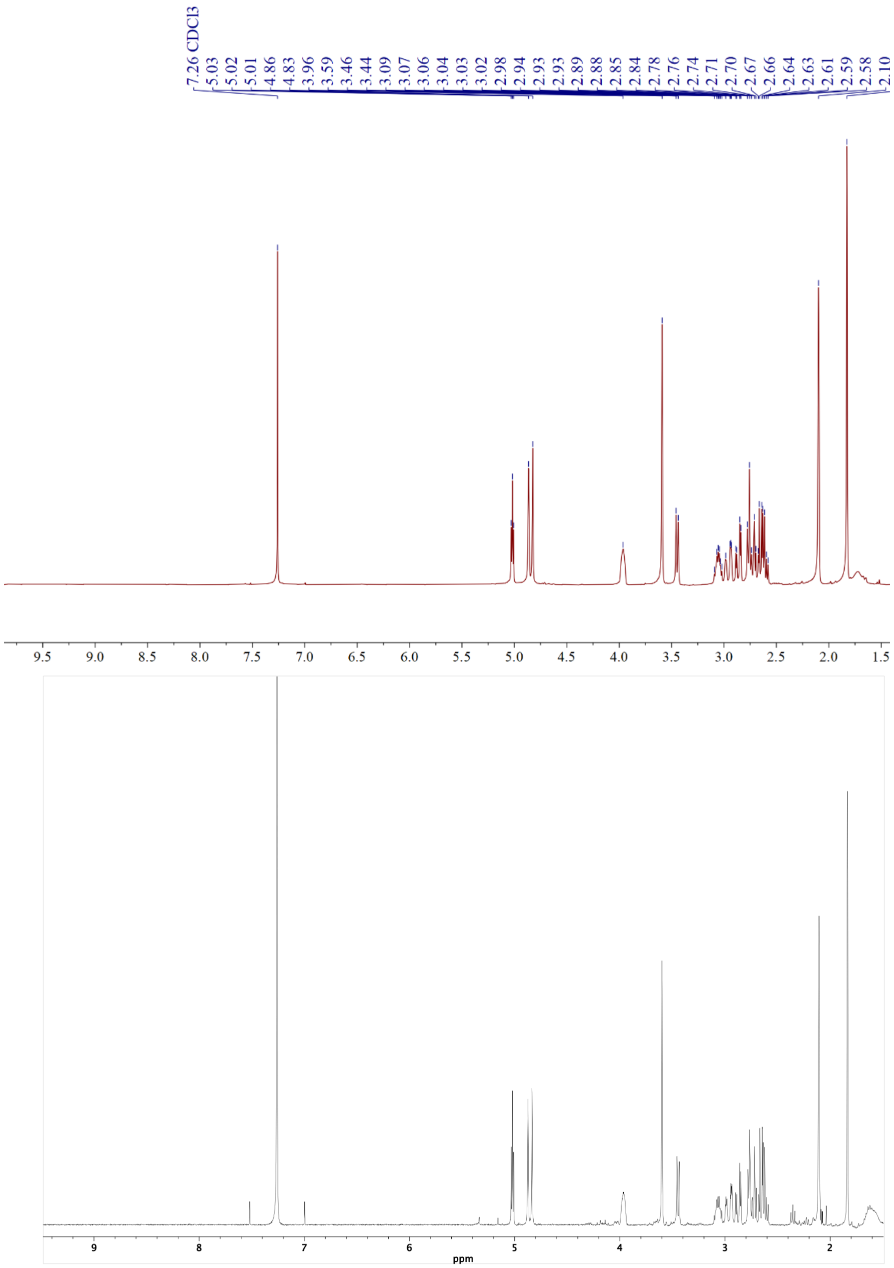
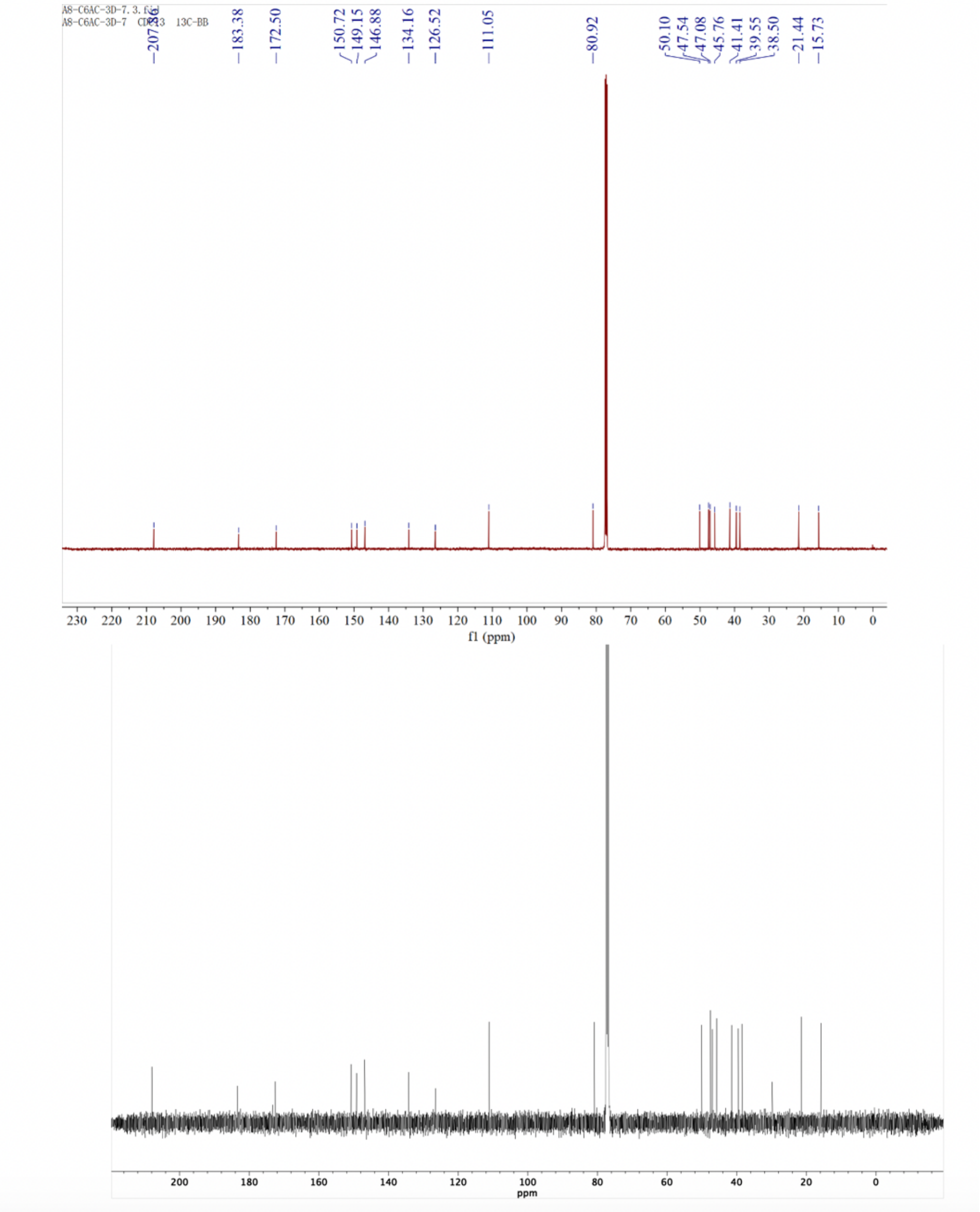


Table S4 Comparison of ^{13}C shifts of synthetic and natural yonarolide (**4**).

Synthetic Yonarolide	**Natural Yonarolide (Yamada, 1995)**
^{13}C NMR, 100 MHz, $CDCl_3$	*^{13}C NMR, 100 MHz, $CDCl_3$*
207.9	207.8
183.4	183.3
172.5	172.4
150.8	150.7
149.1	149.1
146.9	146.9
134.2	134.1
126.5	126.5
111.1	111.0
80.9	80.9
50.1	50.1
47.5	47.5
47.1	47.1
45.8	45.7
41.4	41.4
39.6	39.5
38.5	38.5
21.5	21.4
15.8	15.7

Figure S4. Overlaid ^{13}C NMR spectra of natural (Li, Guo 2022) and synthetic yonarolide (**1**).



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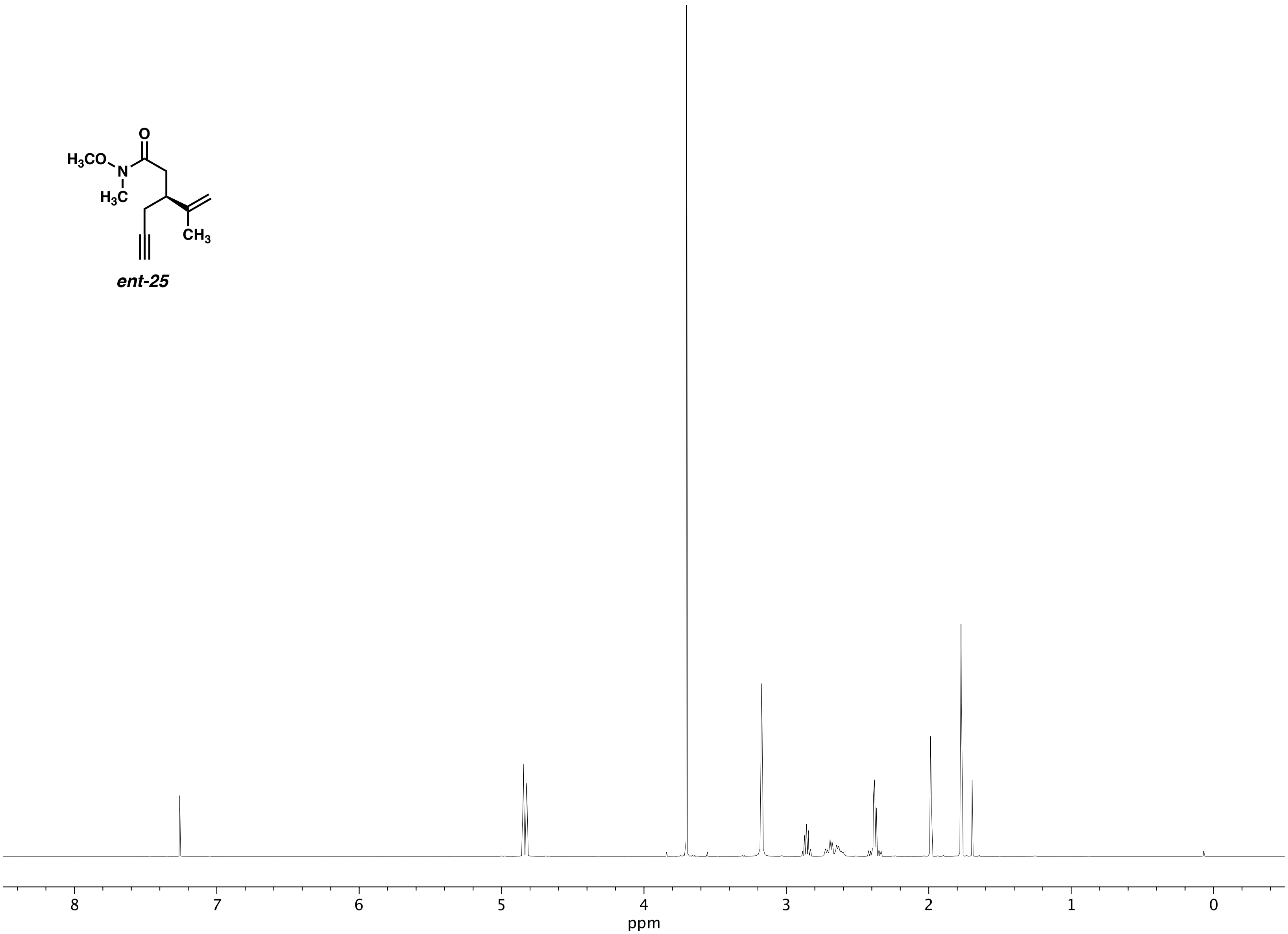
[1] A. M. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen and F. J. Timmers, *Organometallics* 1996, **15**, 1518–1520.

[2] B. Schmidt and S. Audörsch, *Org. Lett.* 2016, **18**, 1162–1165.

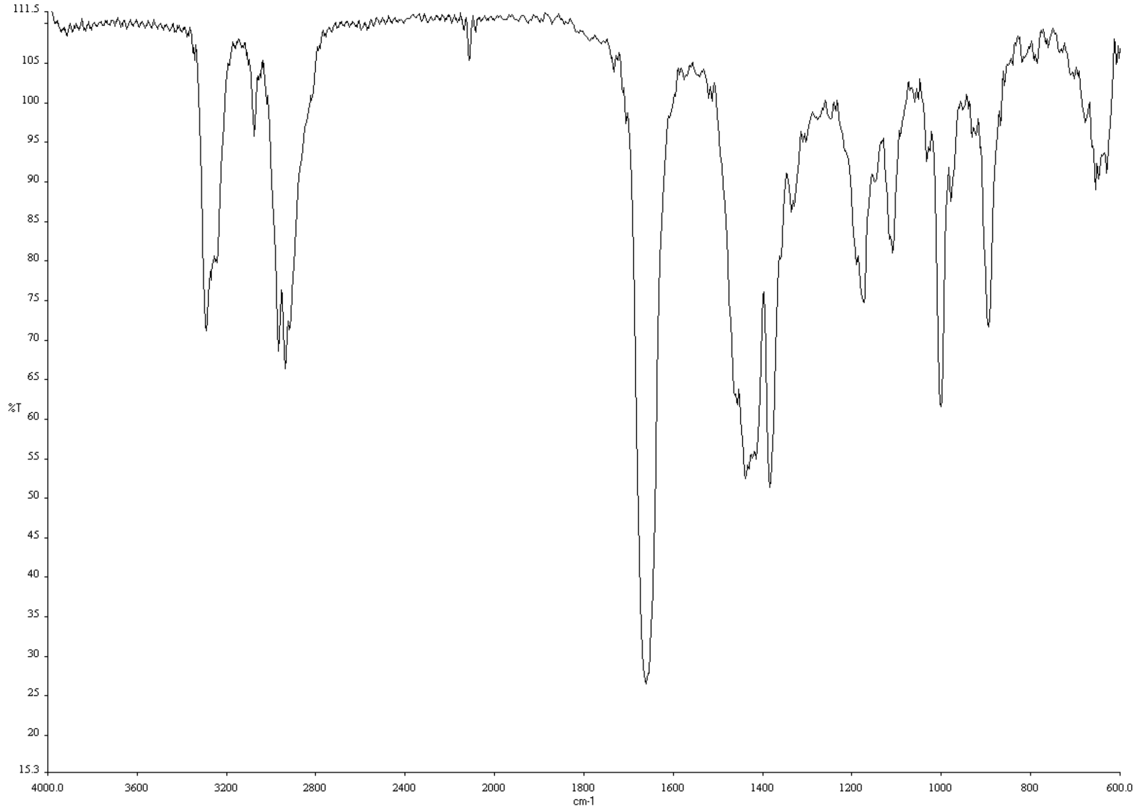
[3] H. Weinstabl, T. Gaich, and J. Mulzer, *Org. Lett.* 2012, **14**, 2834−2837.

[4] Y. Du, L. Yao, X. Li and Y. Guo, *Chin. Chem. Lett.* 2022, **34**, 107512.

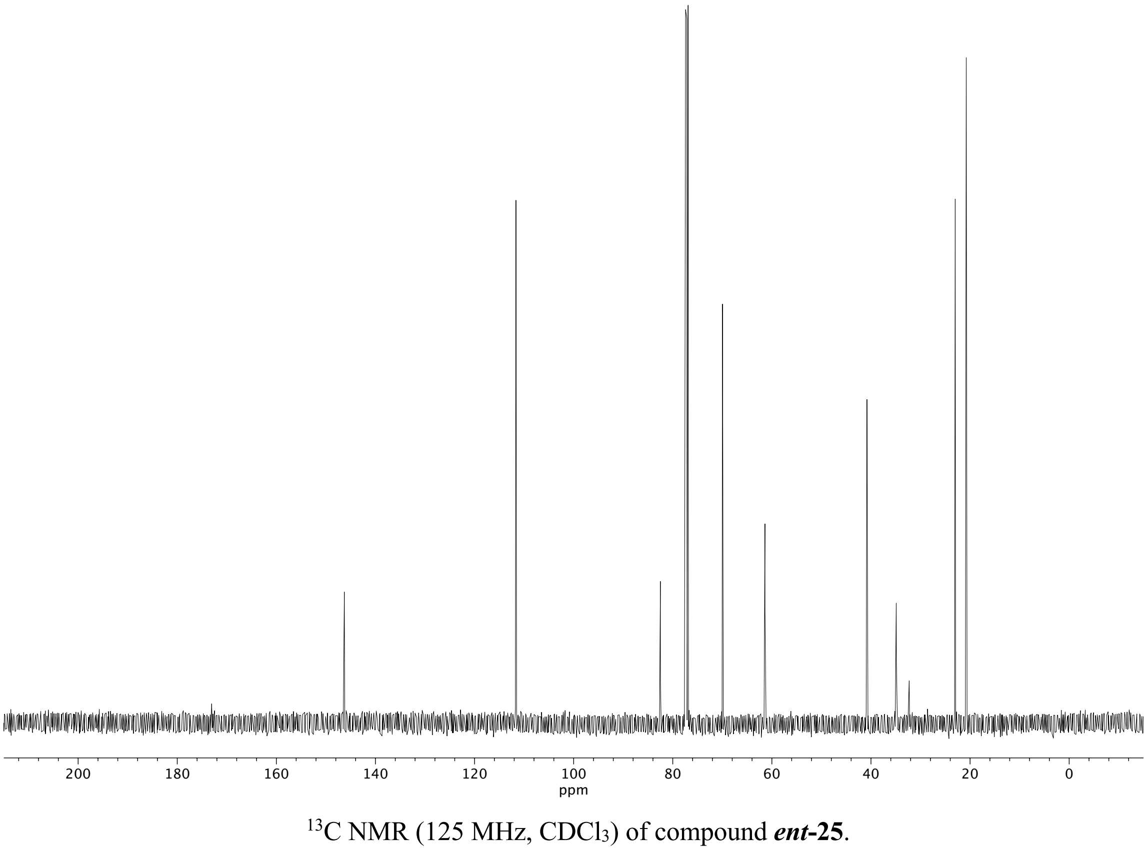
***ent*-25**



^{1}H NMR (500 MHz, $CDCl_3$) of compound ***ent*-25**.

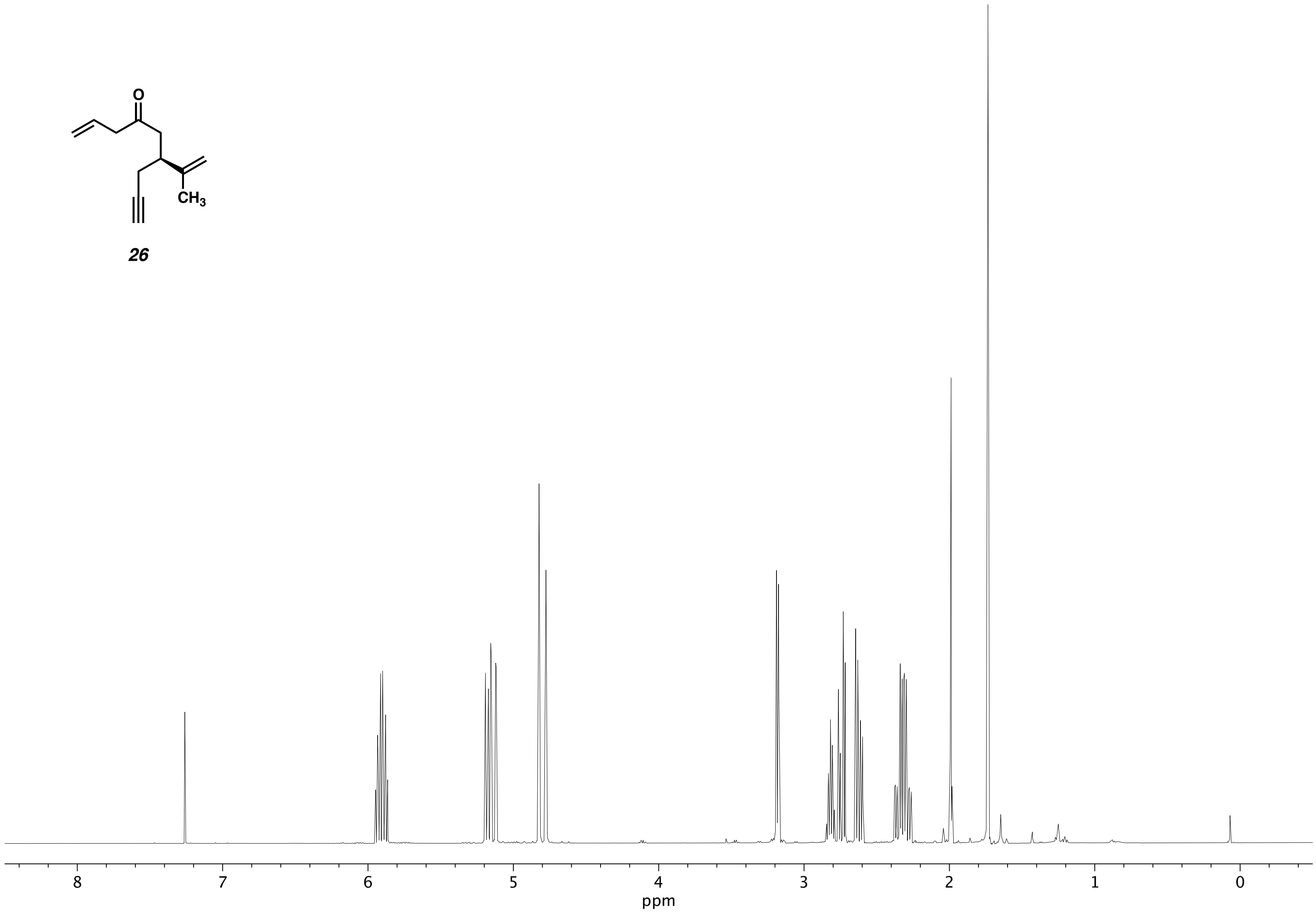


Infrared spectrum (Thin Film, NaCl) of compound ***ent*-25**.

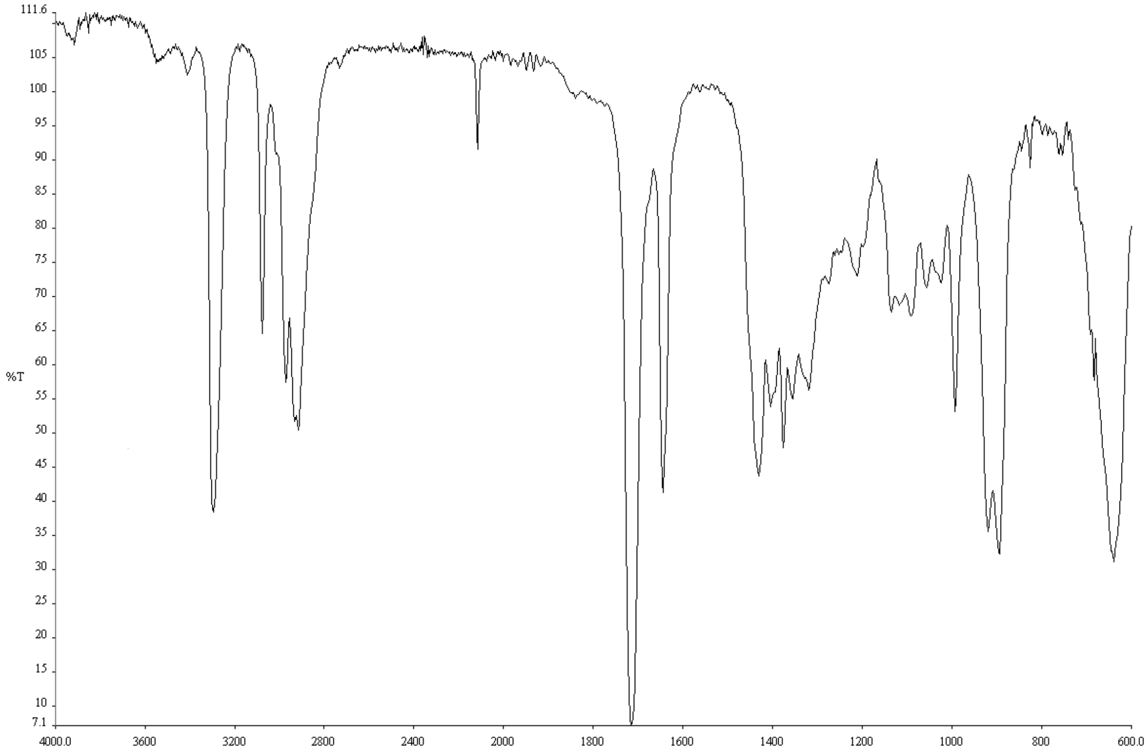


^{13}C NMR (125 MHz, CDCl$_3$) of compound ***ent*-25**.

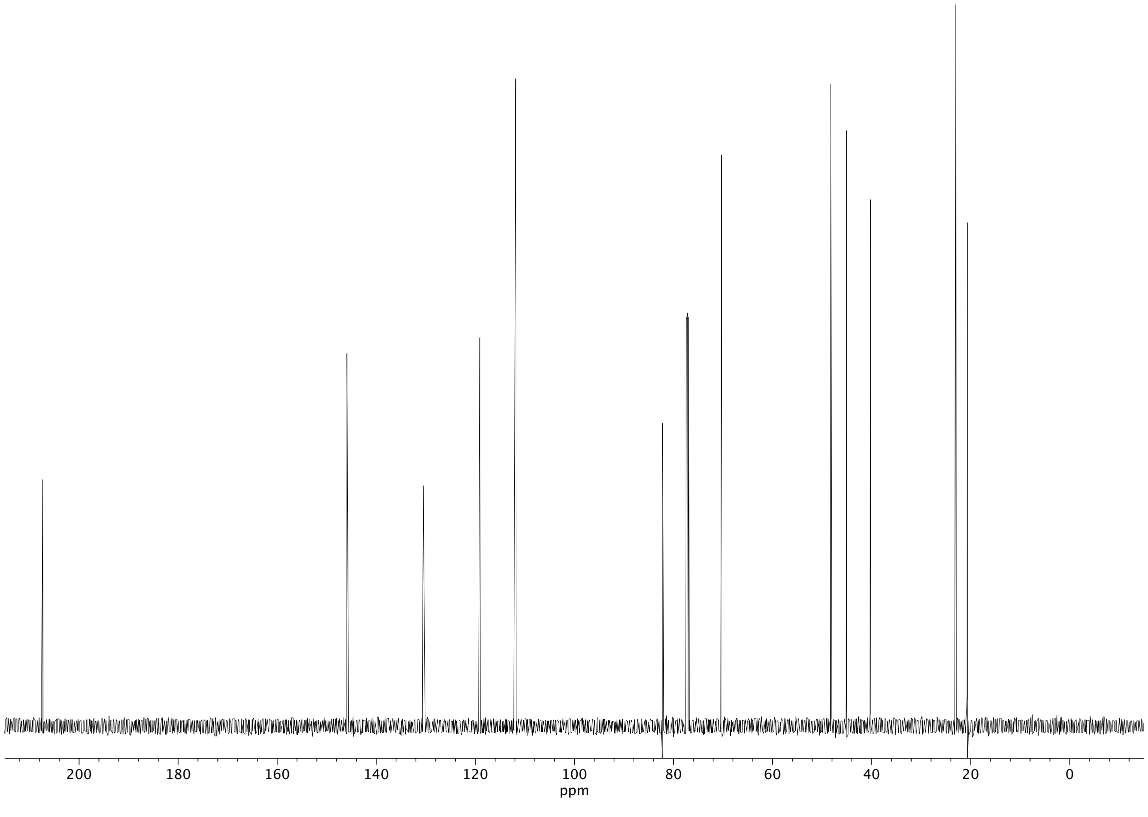
26



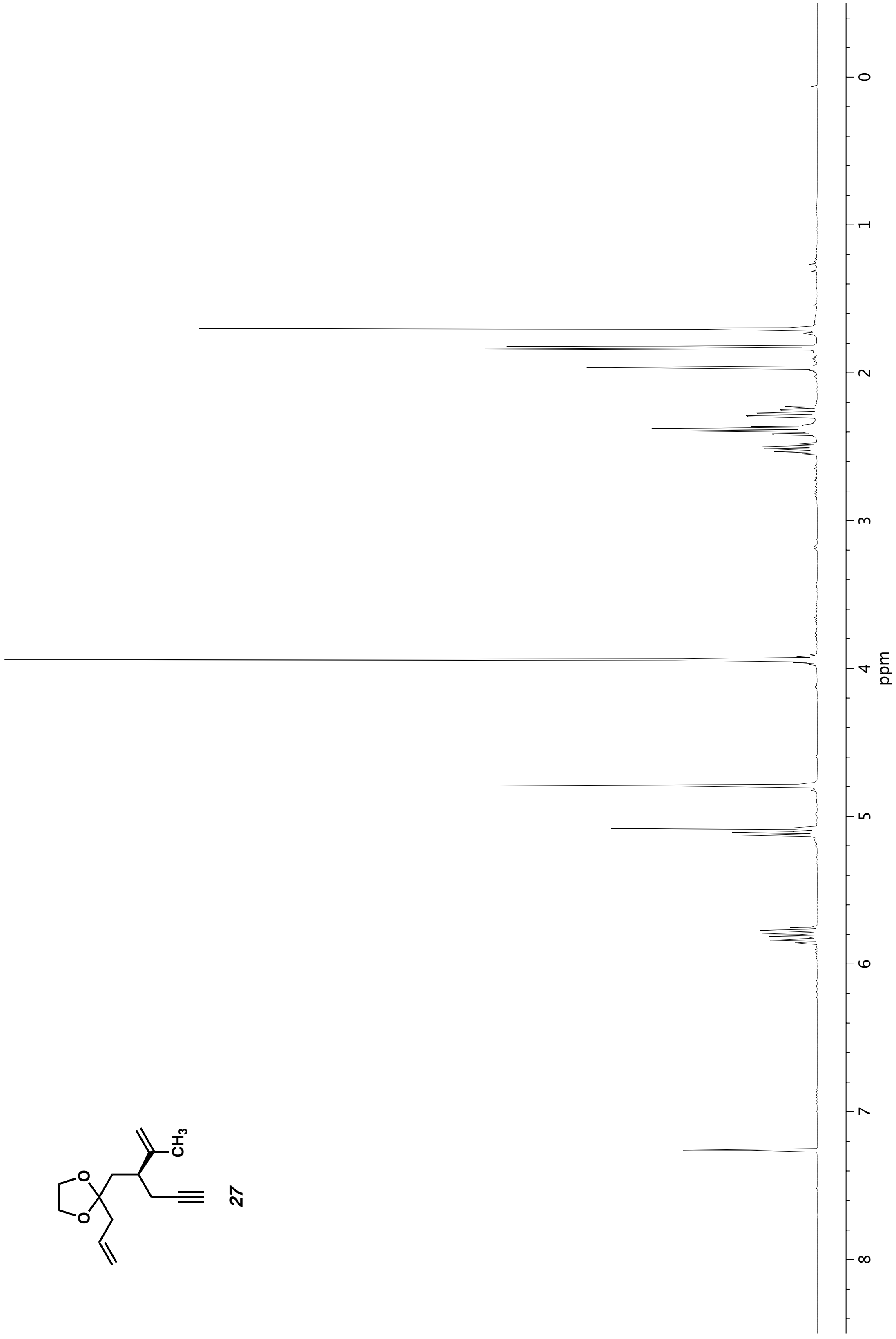
^{1}H NMR (500 MHz, CDCl$_3$) of compound **26**.



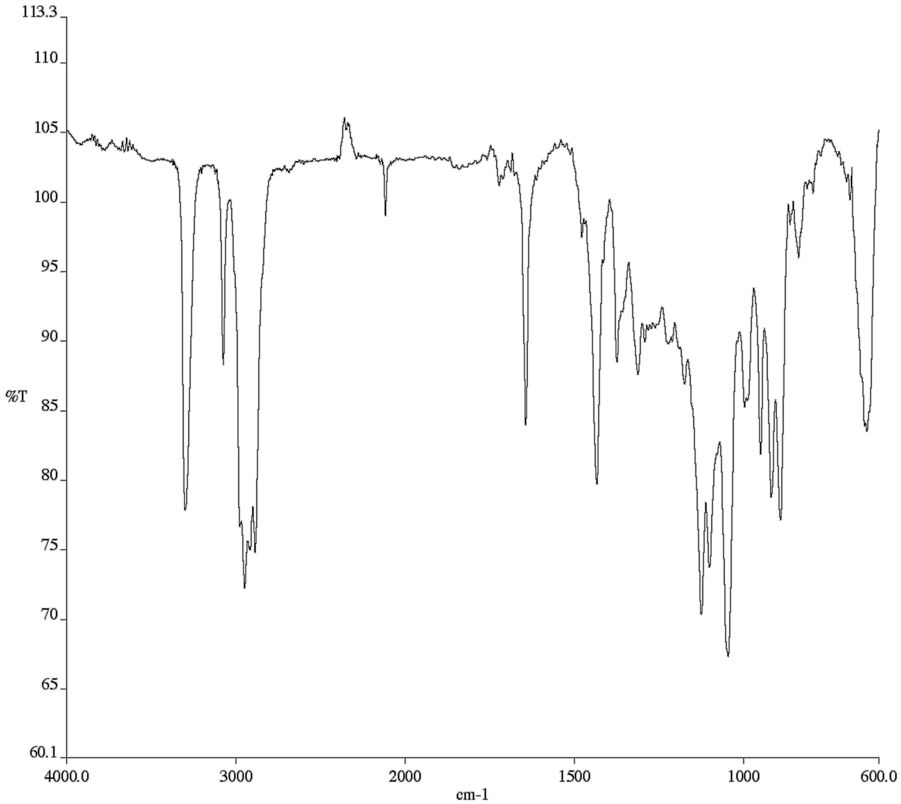
Infrared spectrum (Thin Film, NaCl) of compound **26**.



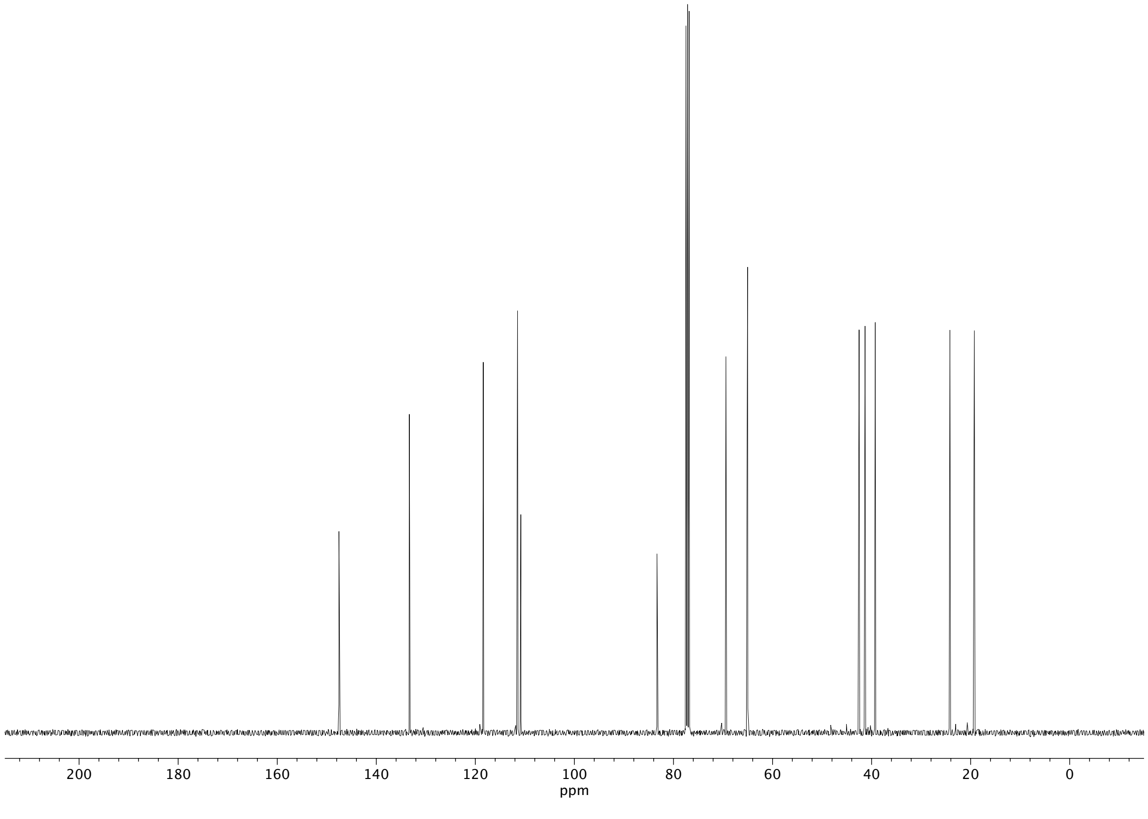
^{13}C NMR (125 MHz, CDCl$_3$) of compound **26.**



^{1}H NMR (400 MHz, CDCl$_3$) of compound **27**.

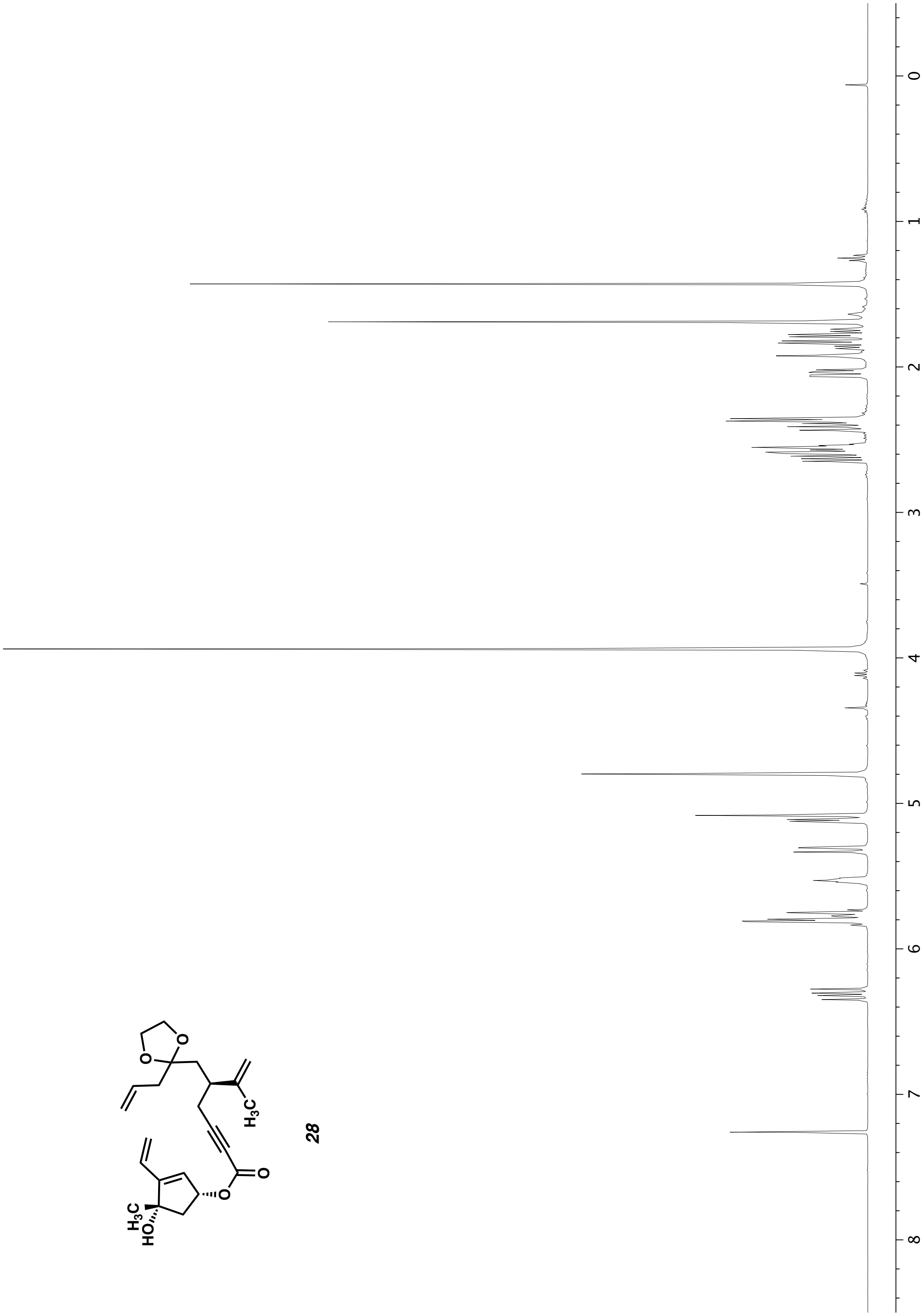


Infrared spectrum (Thin Film, NaCl) of compound **27**.

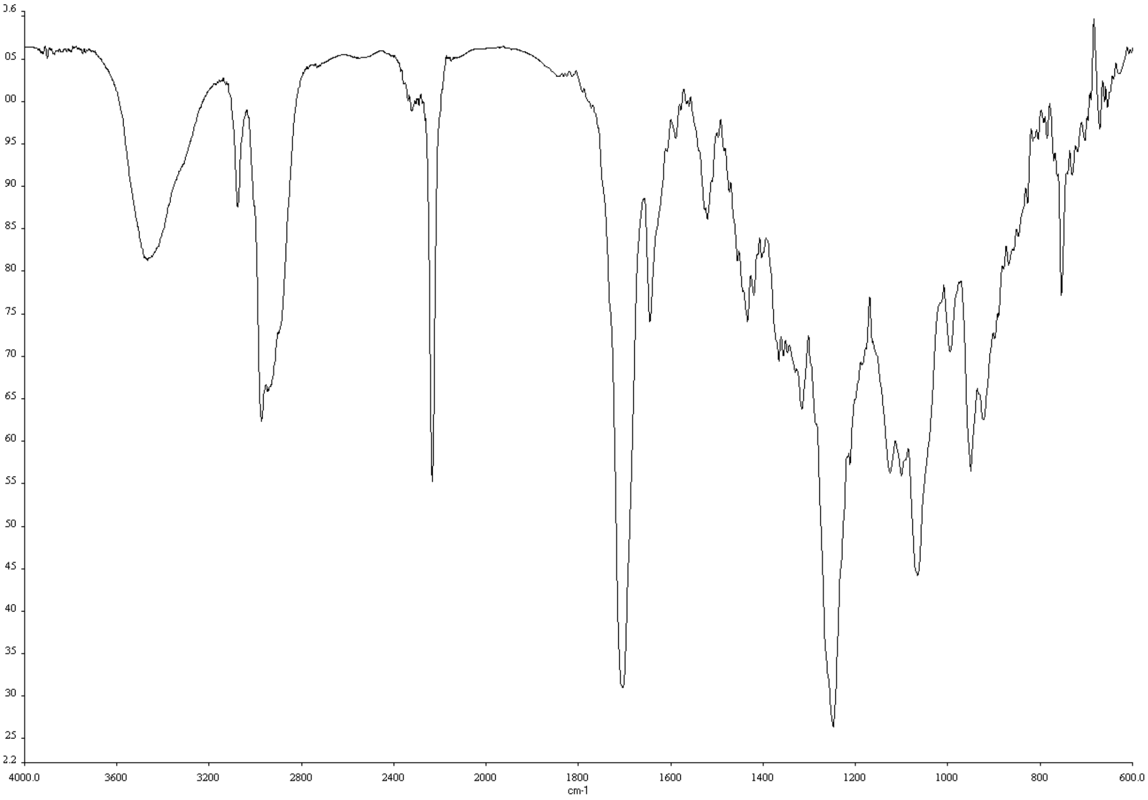


^{13}C NMR (100 MHz, CDCl$_3$) of compound **27.**

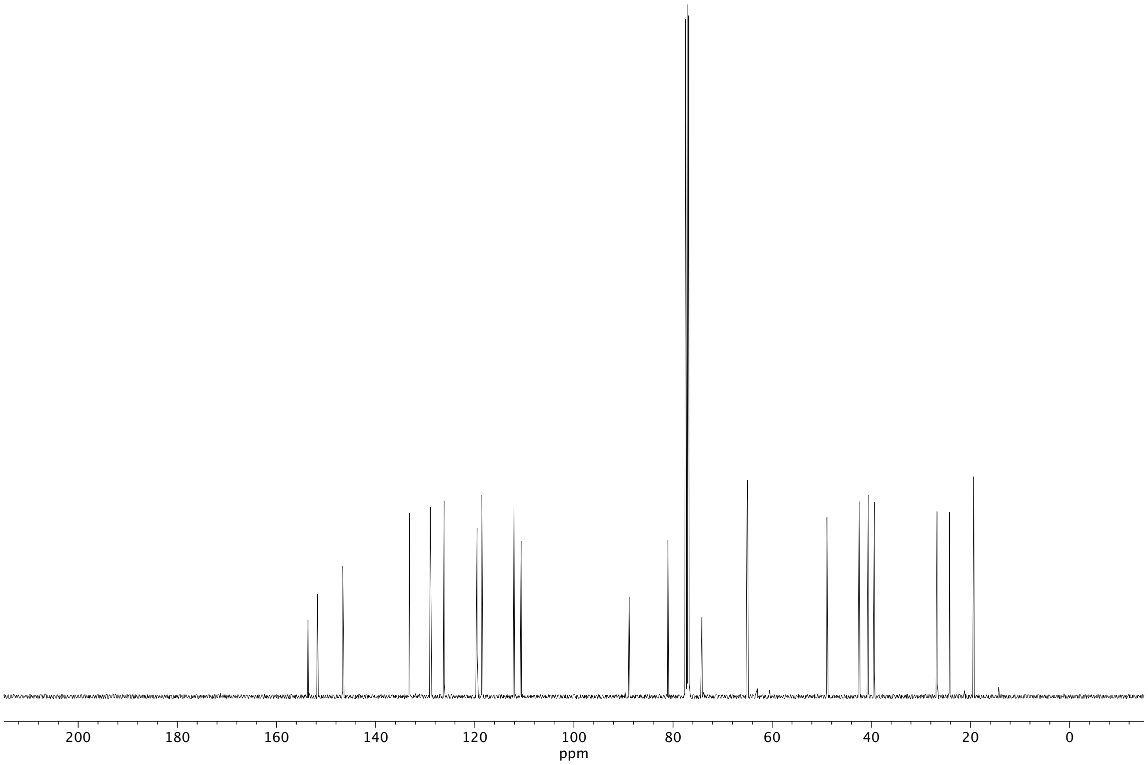
28



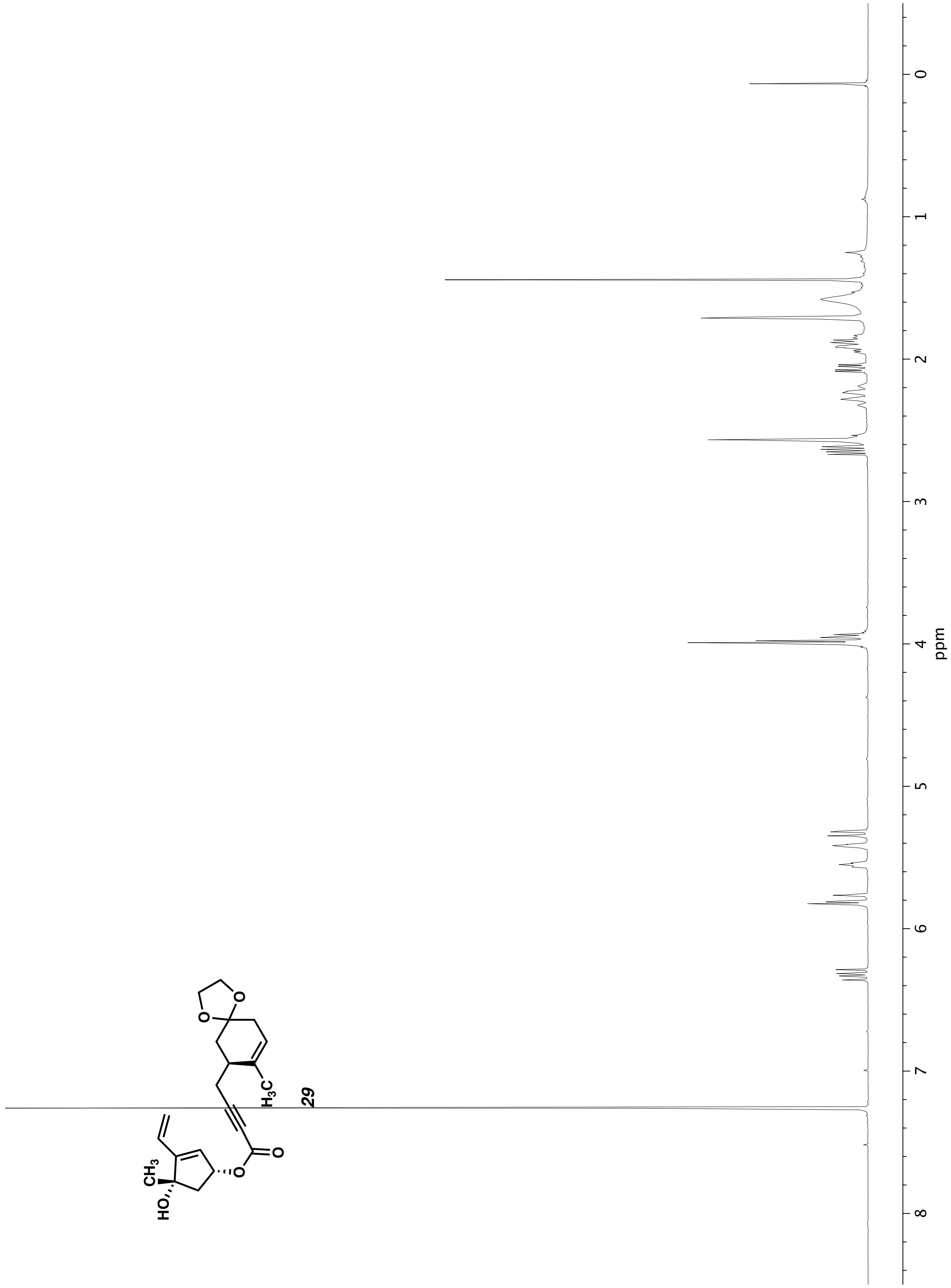
^{1}H NMR (400 MHz, CDCl$_3$) of compound **28**.



Infrared spectrum (Thin Film, NaCl) of compound **28**.

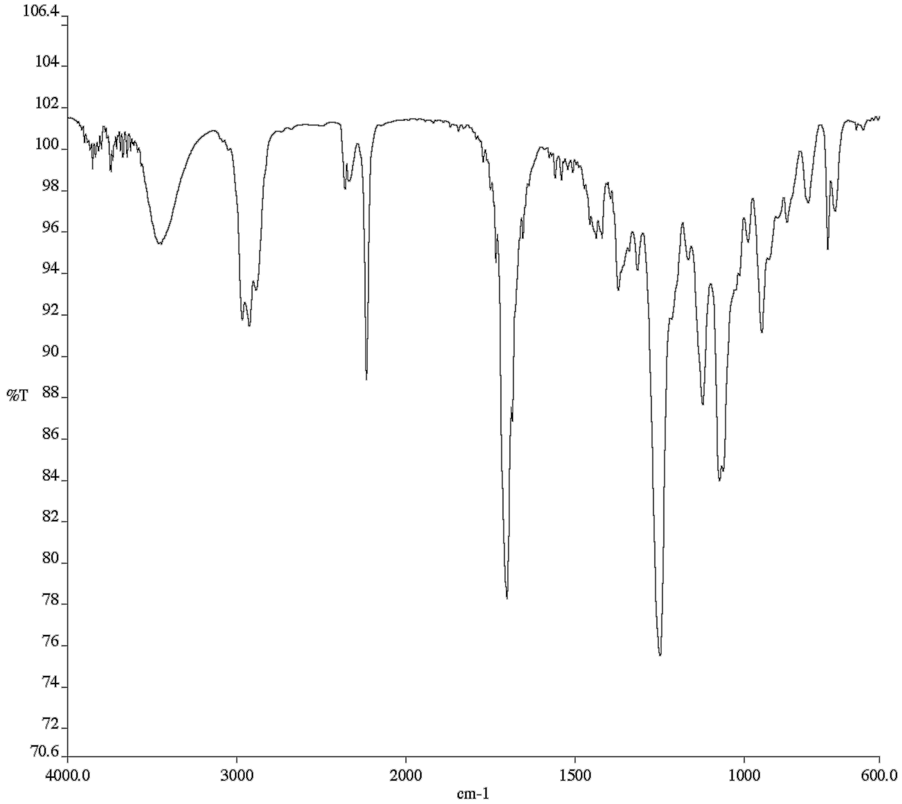


^{13}C NMR (100 MHz, CDCl$_3$) of compound **28.**

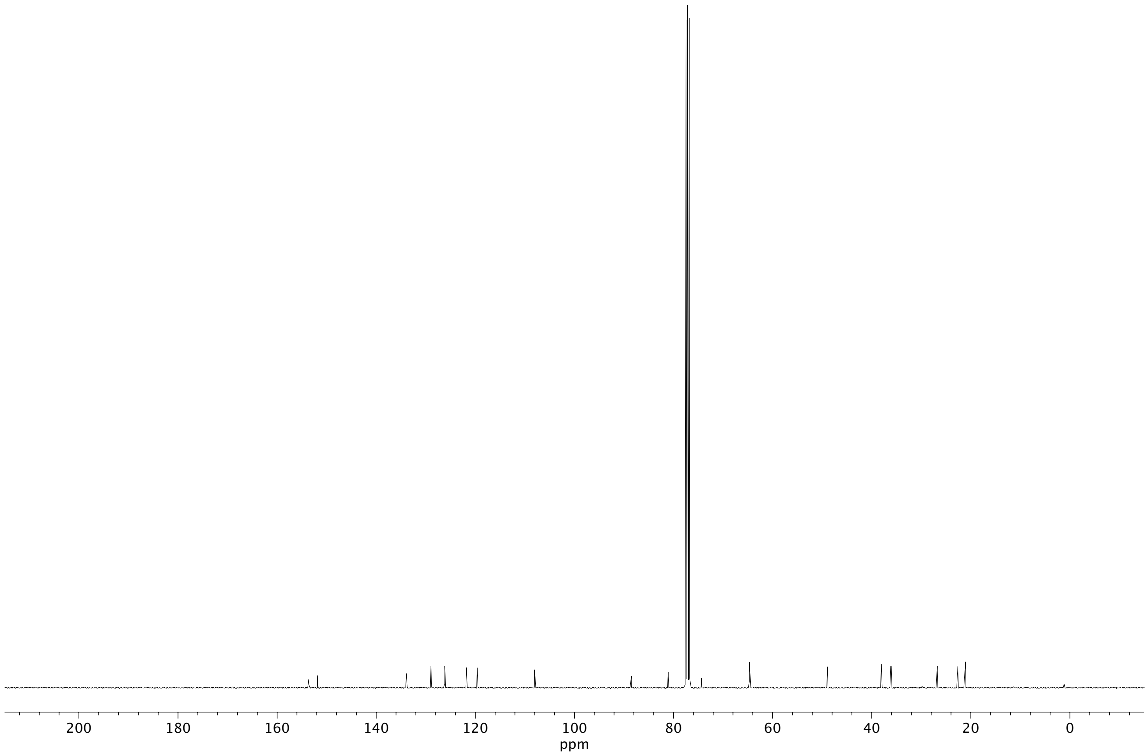


29

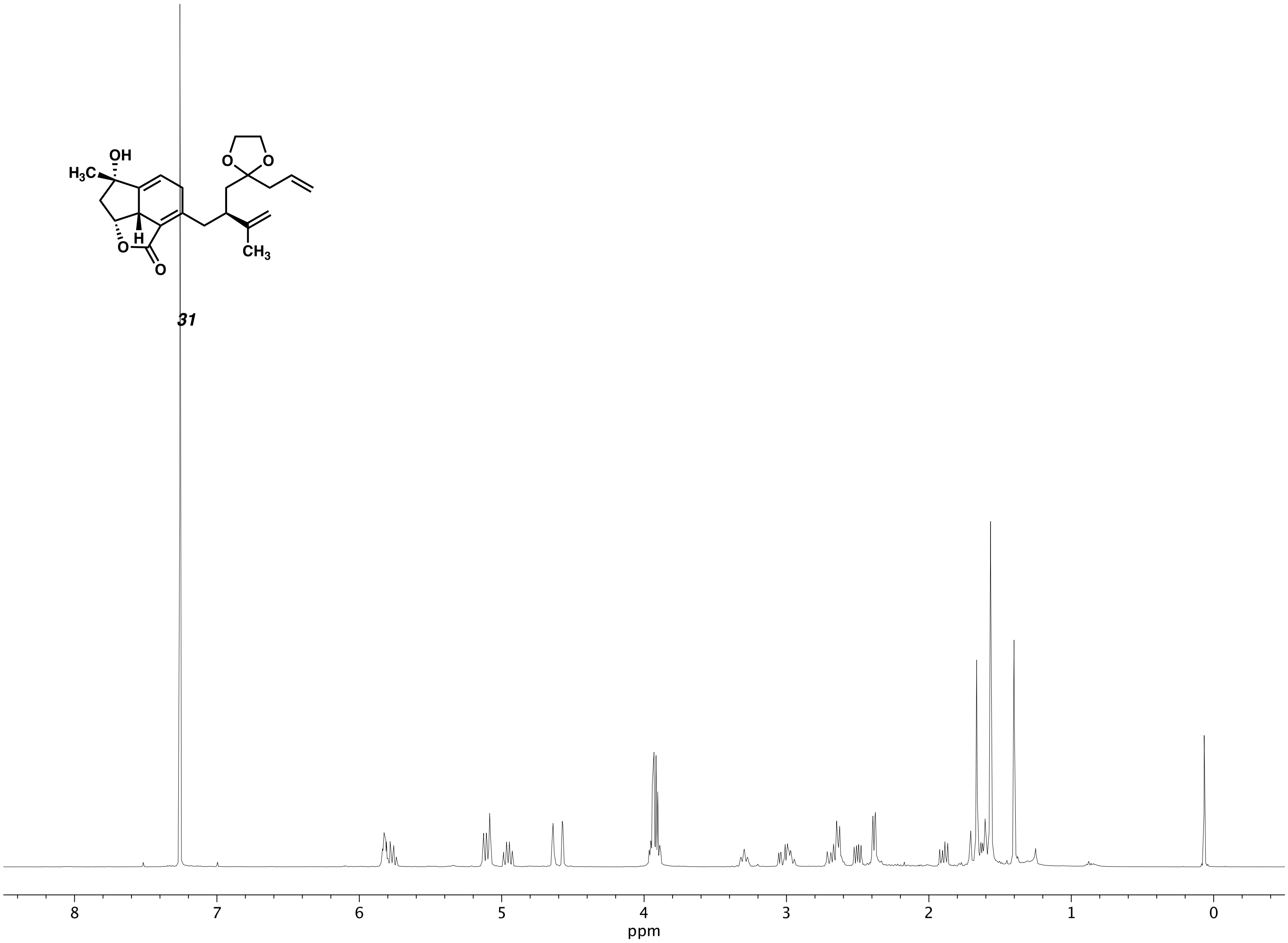
^{1}H NMR (400 MHz, CDCl$_3$) of compound **29**.



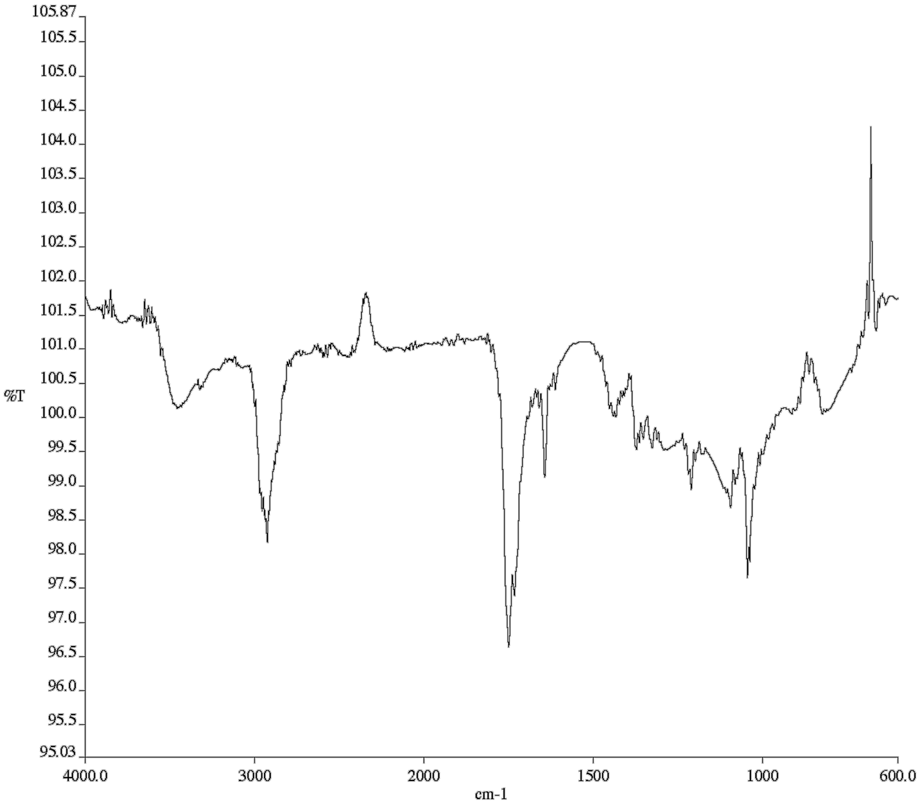
Infrared spectrum (Thin Film, NaCl) of compound **29**.



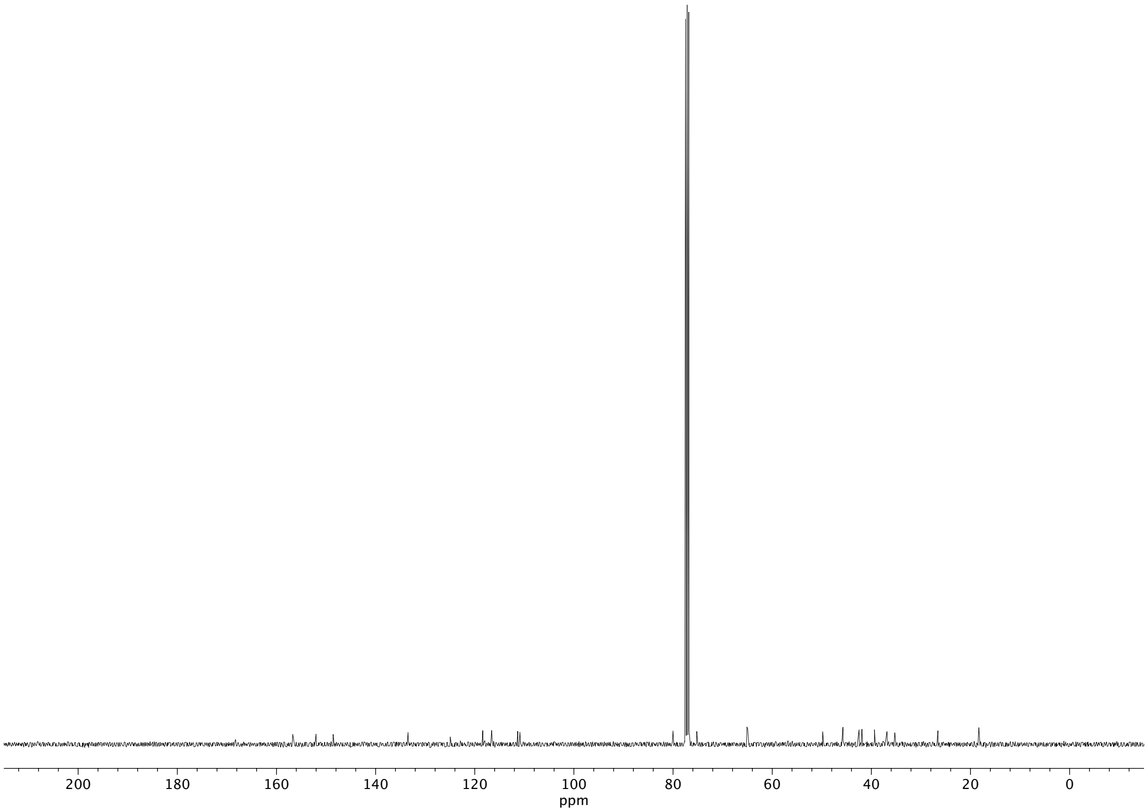
^{13}C NMR (100 MHz, CDCl$_3$) of compound **29.**



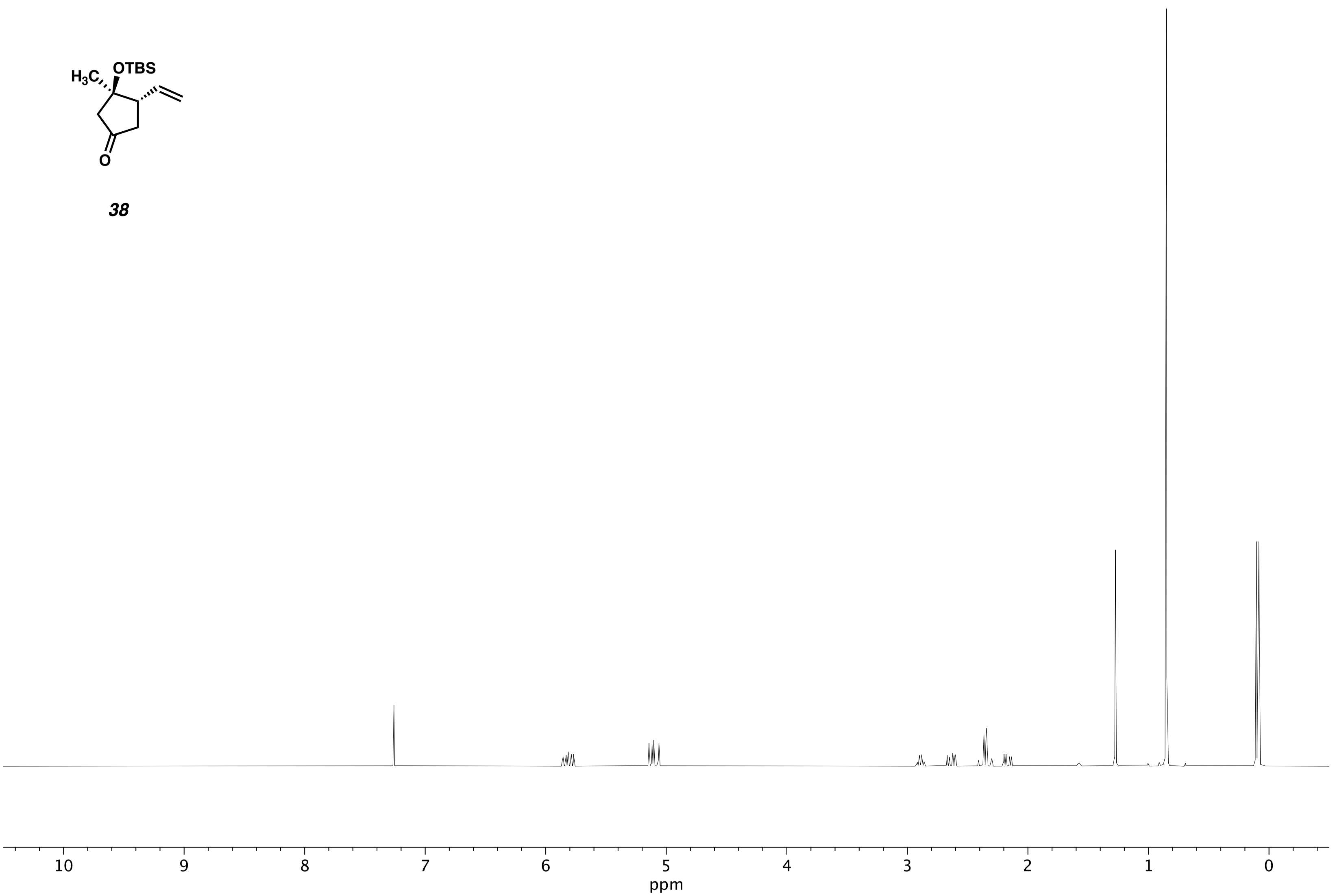
^{1}H NMR (400 MHz, CDCl$_3$) of compound **31**.



Infrared spectrum (Thin Film, NaCl) of compound **31**.

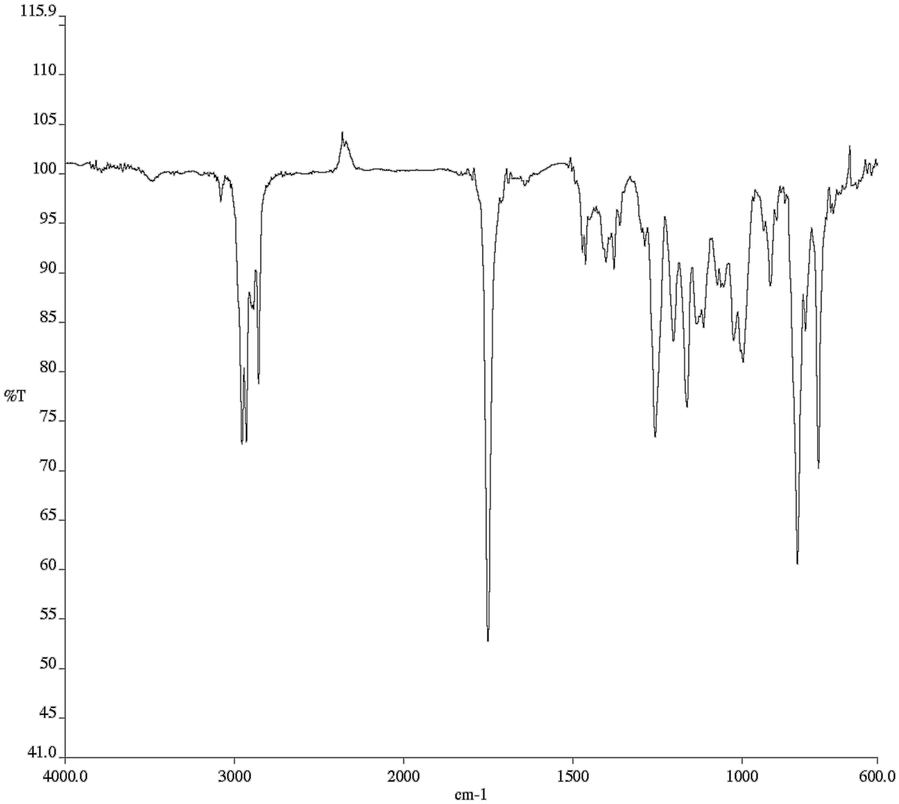


^{13}C NMR (100 MHz, CDCl$_3$) of compound **31.**

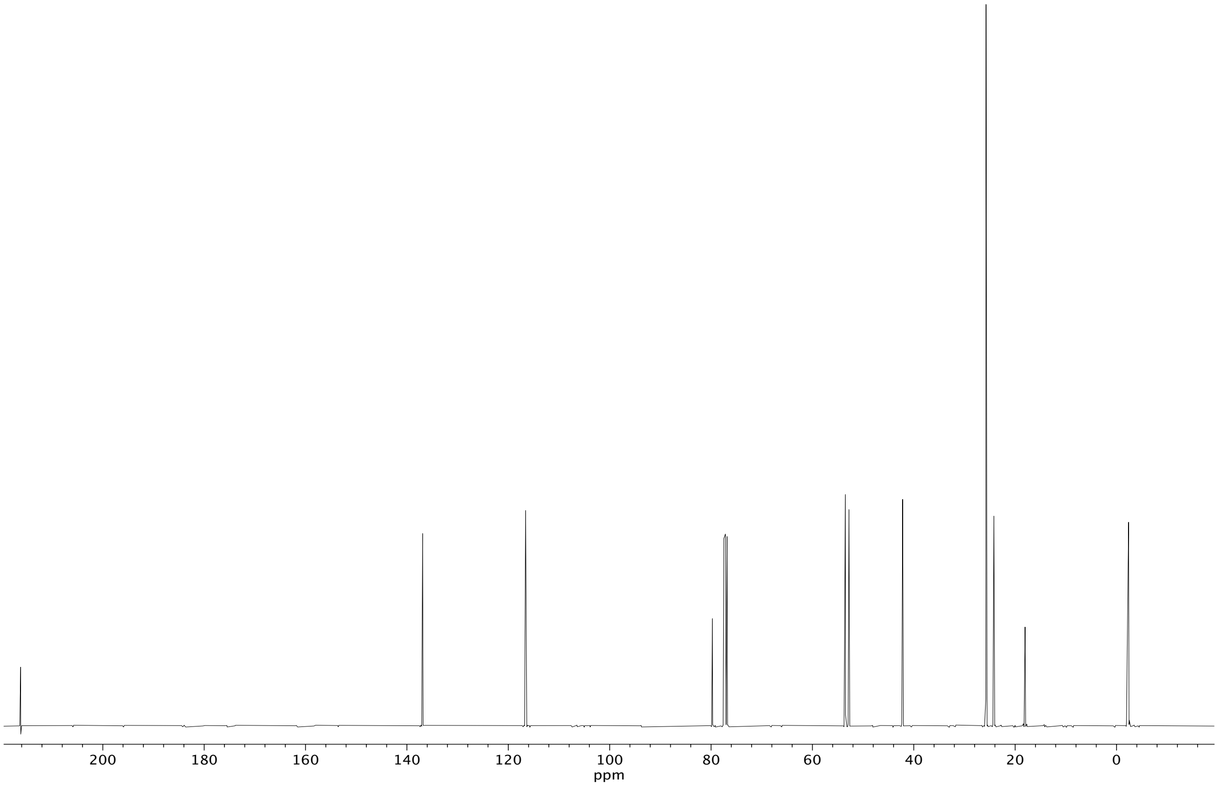


38

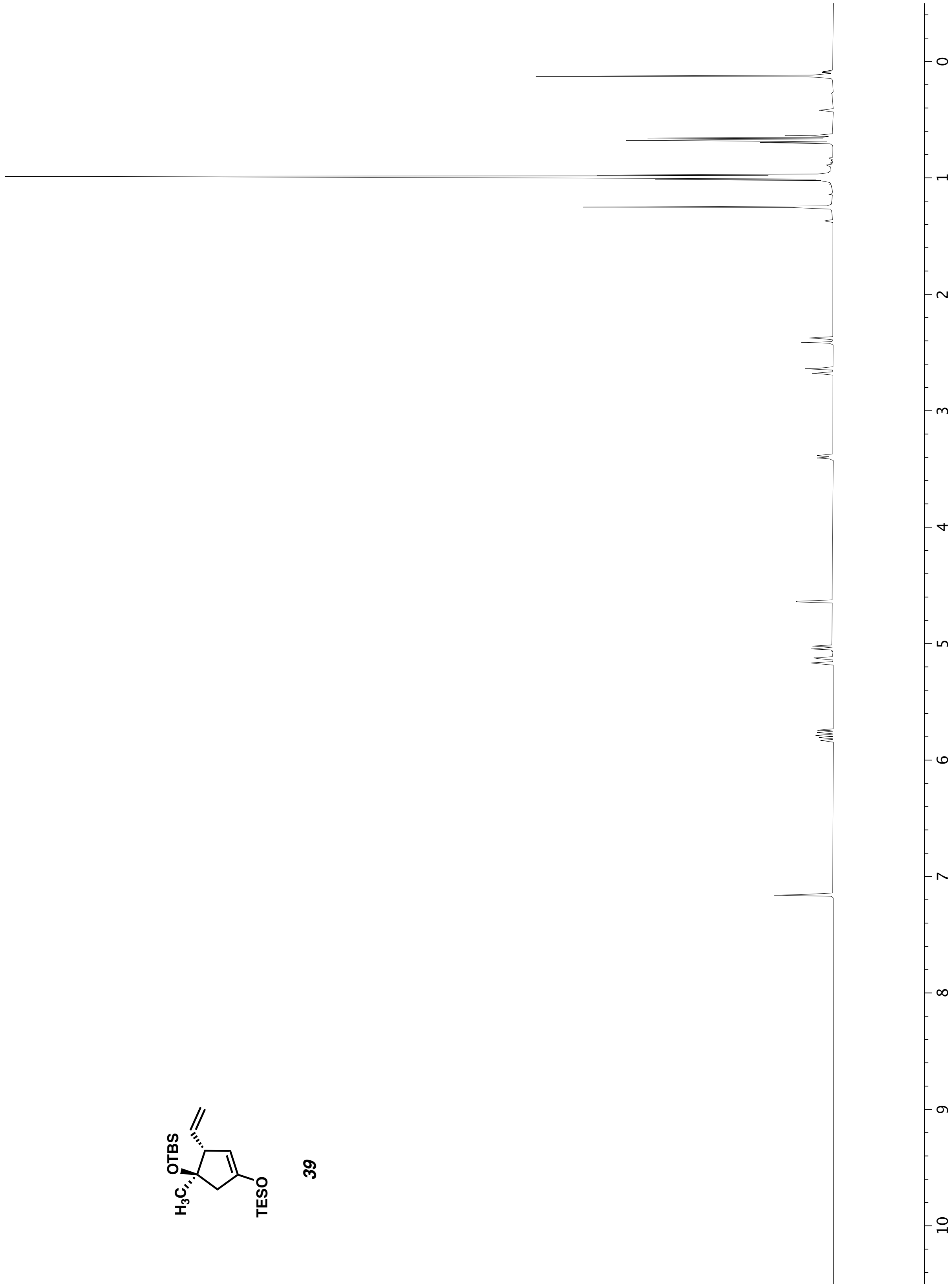
^{1}H NMR (400 MHz, CDCl$_3$) of compound **38**.



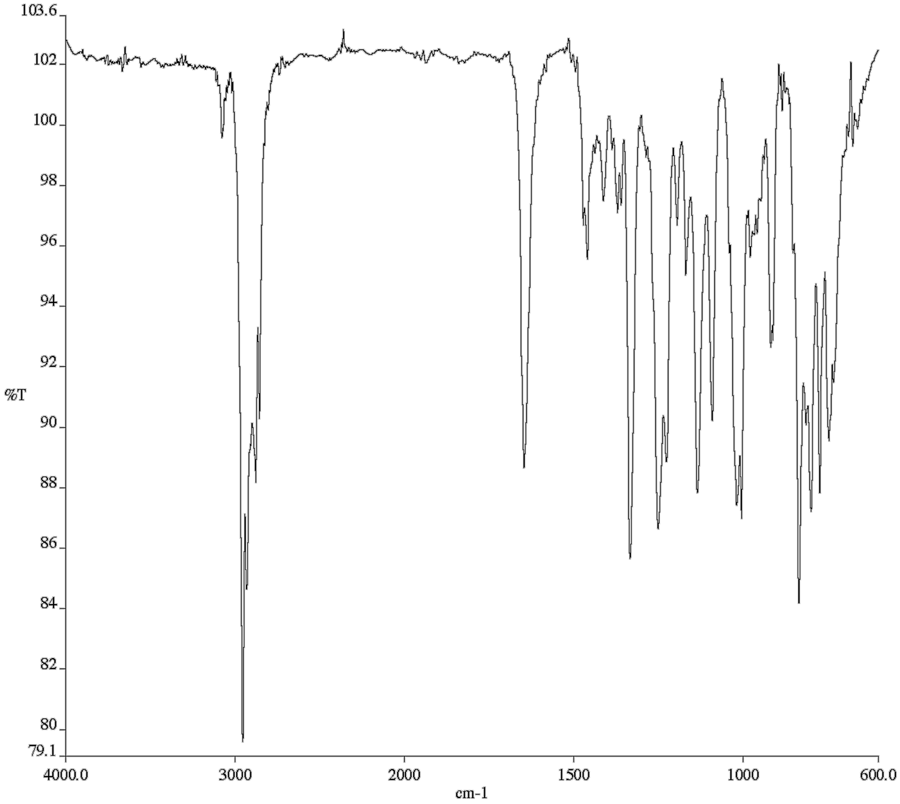
Infrared spectrum (Thin Film, NaCl) of compound **38**.



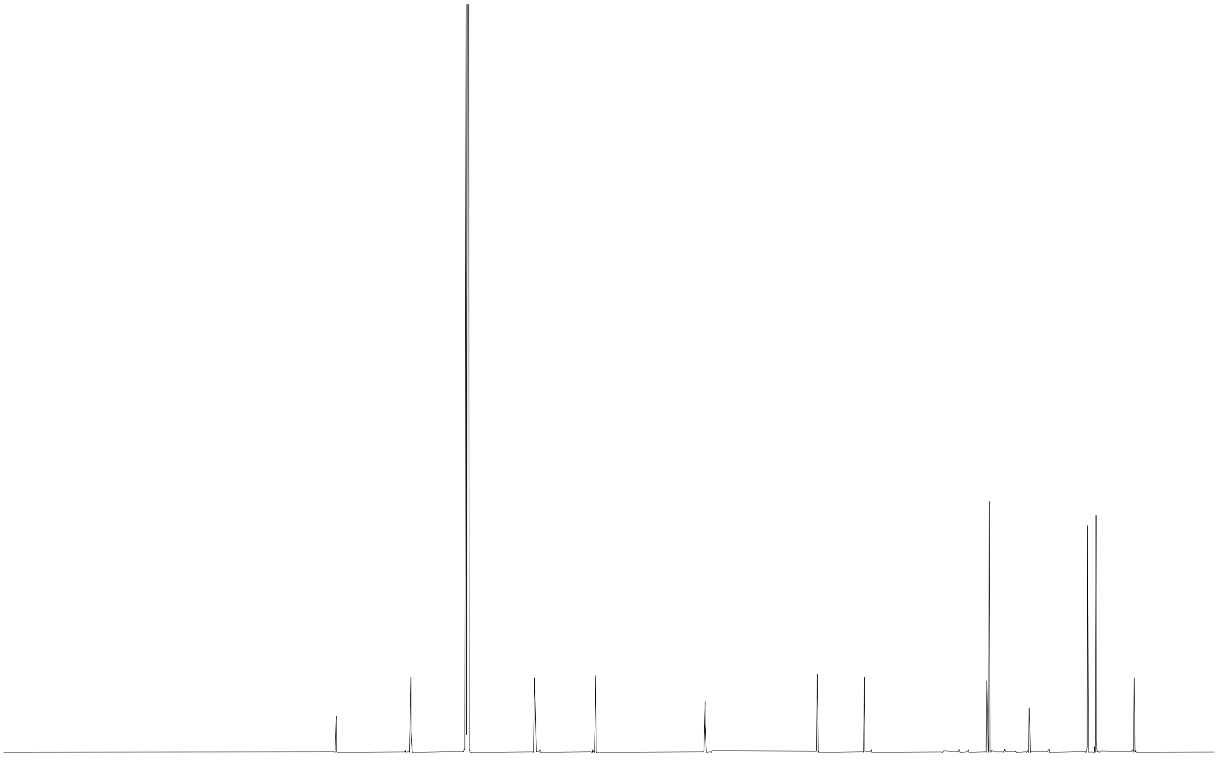
^{13}C NMR (100 MHz, CDCl$_3$) of compound **38.**



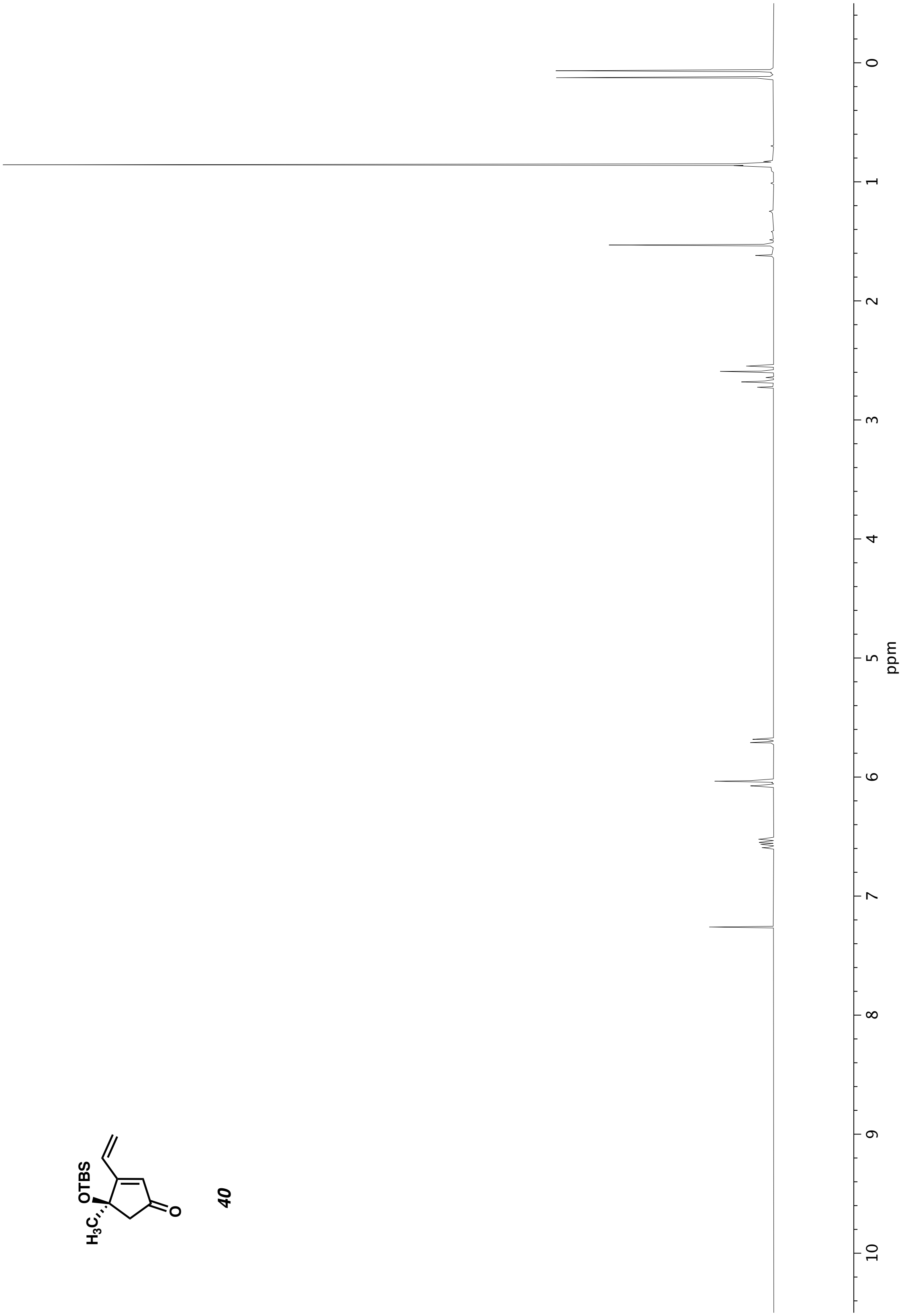
^{1}H NMR (400 MHz, CDCl$_3$) of compound **39**.



Infrared spectrum (Thin Film, NaCl) of compound **39**.

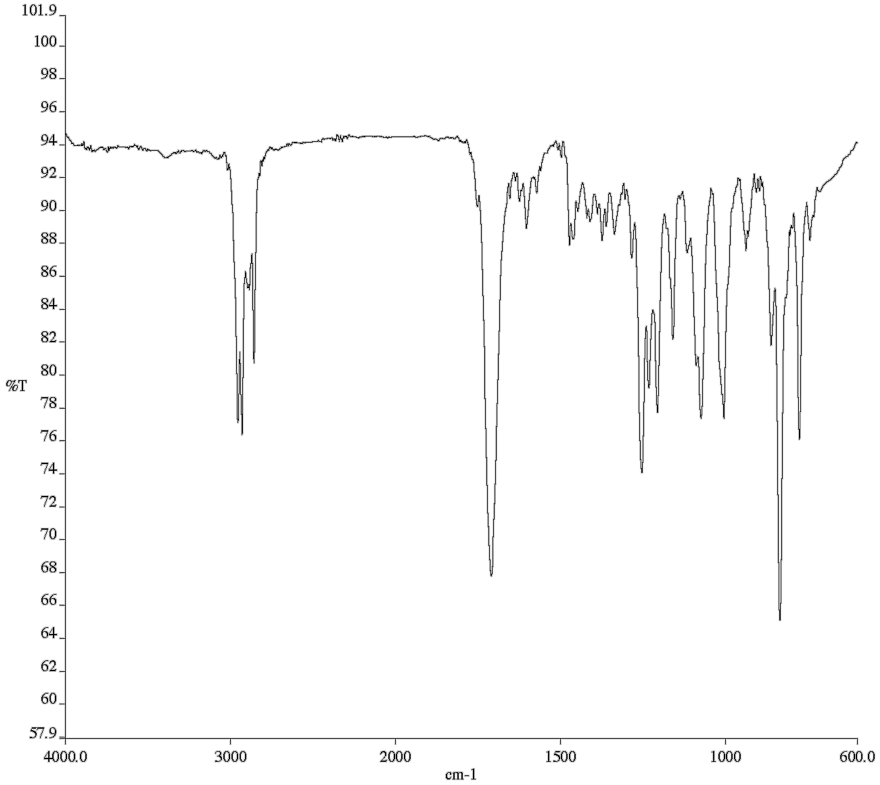


^{13}C NMR (100 MHz, CDCl$_3$) of compound **39.**

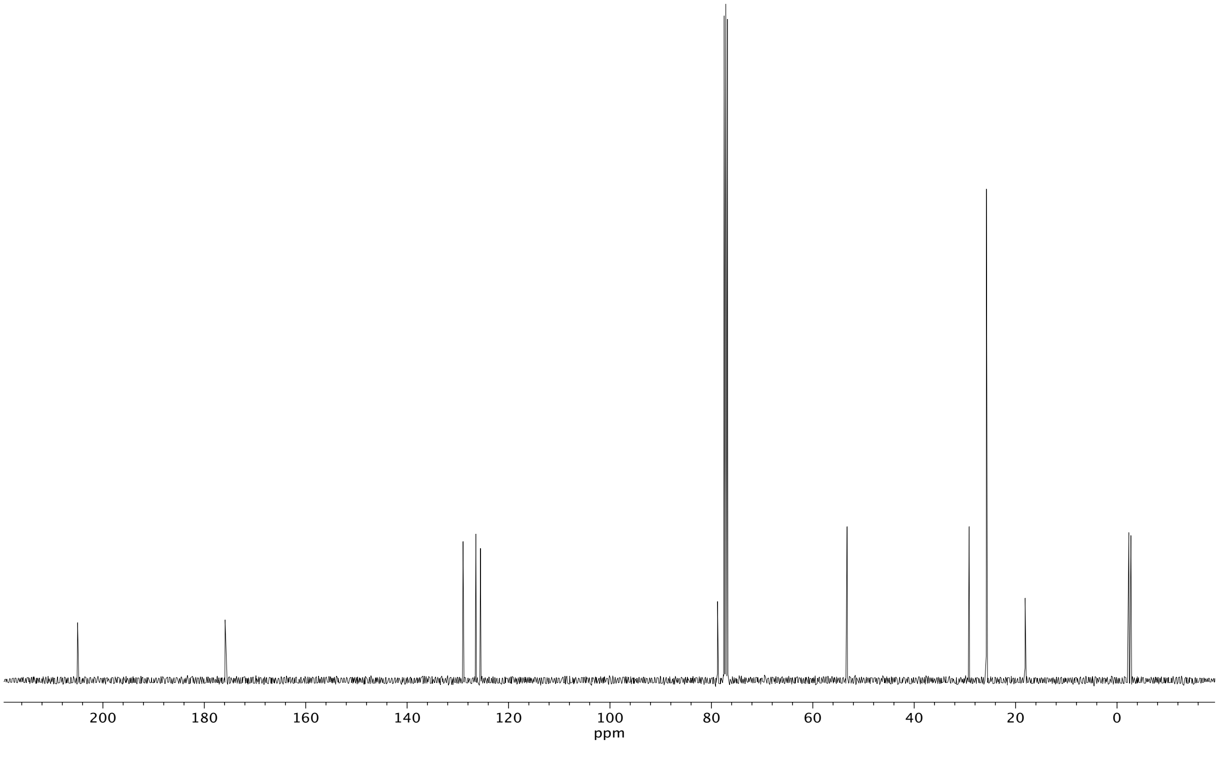


40

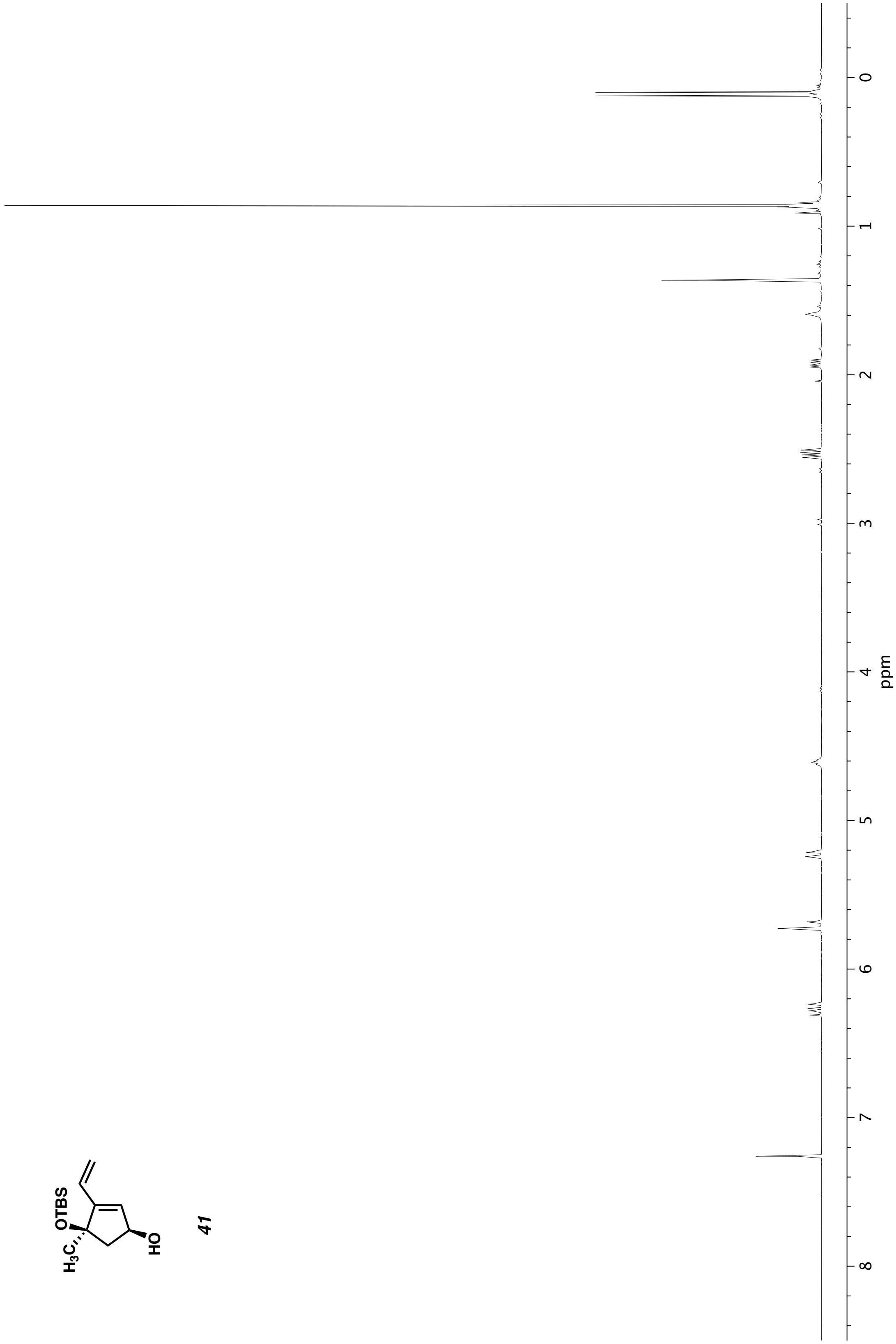
^{1}H NMR (400 MHz, CDCl$_3$) of compound **40**.



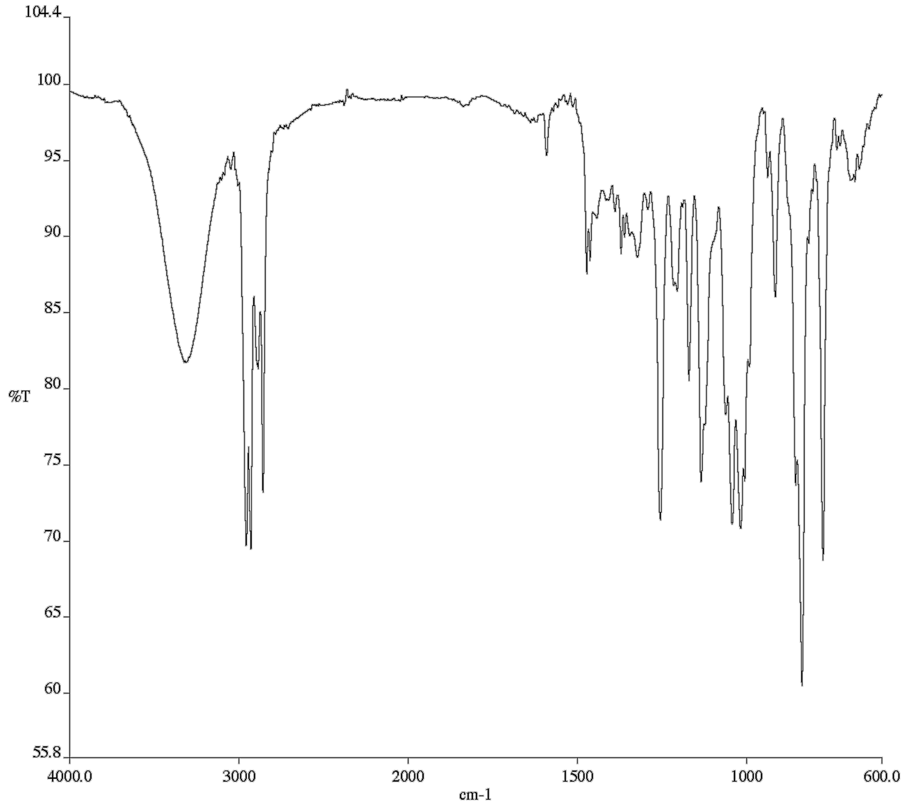
Infrared spectrum (Thin Film, NaCl) of compound **40**.



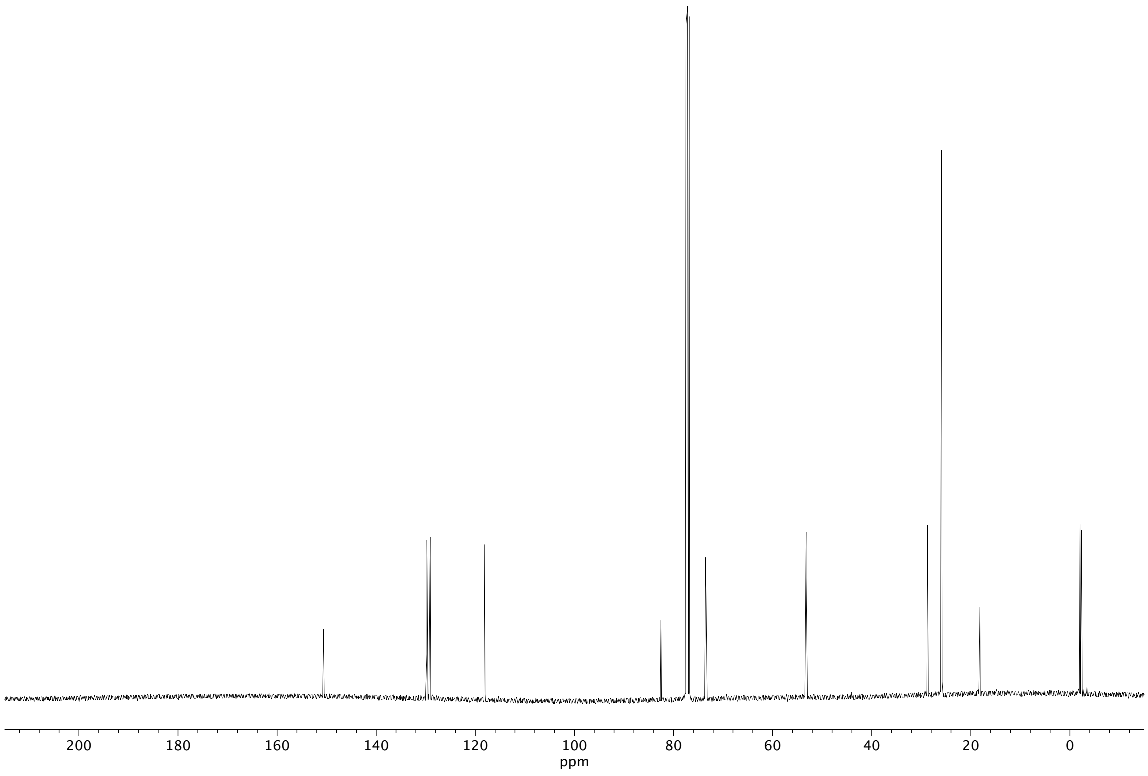
^{13}C NMR (100 MHz, CDCl$_3$) of compound **40.**



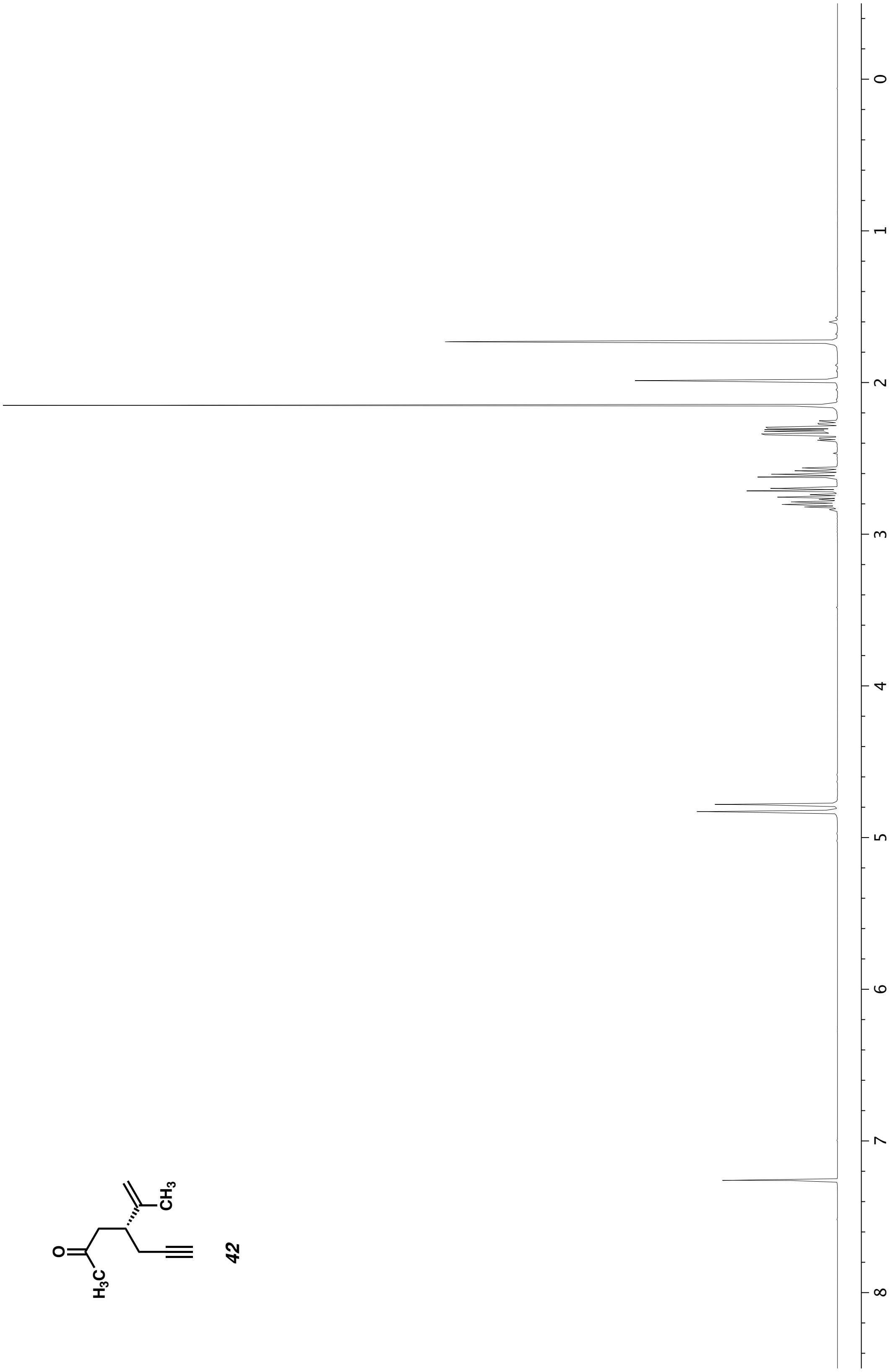
^{1}H NMR (400 MHz, CDCl$_3$) of compound **41**.



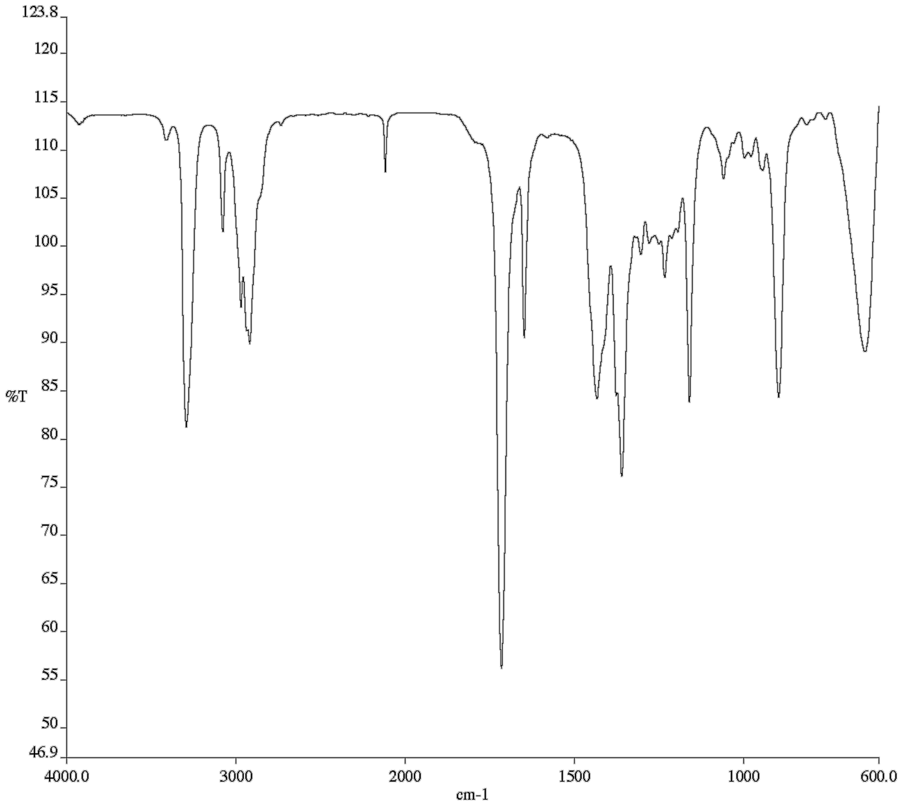
Infrared spectrum (Thin Film, NaCl) of compound **41**.



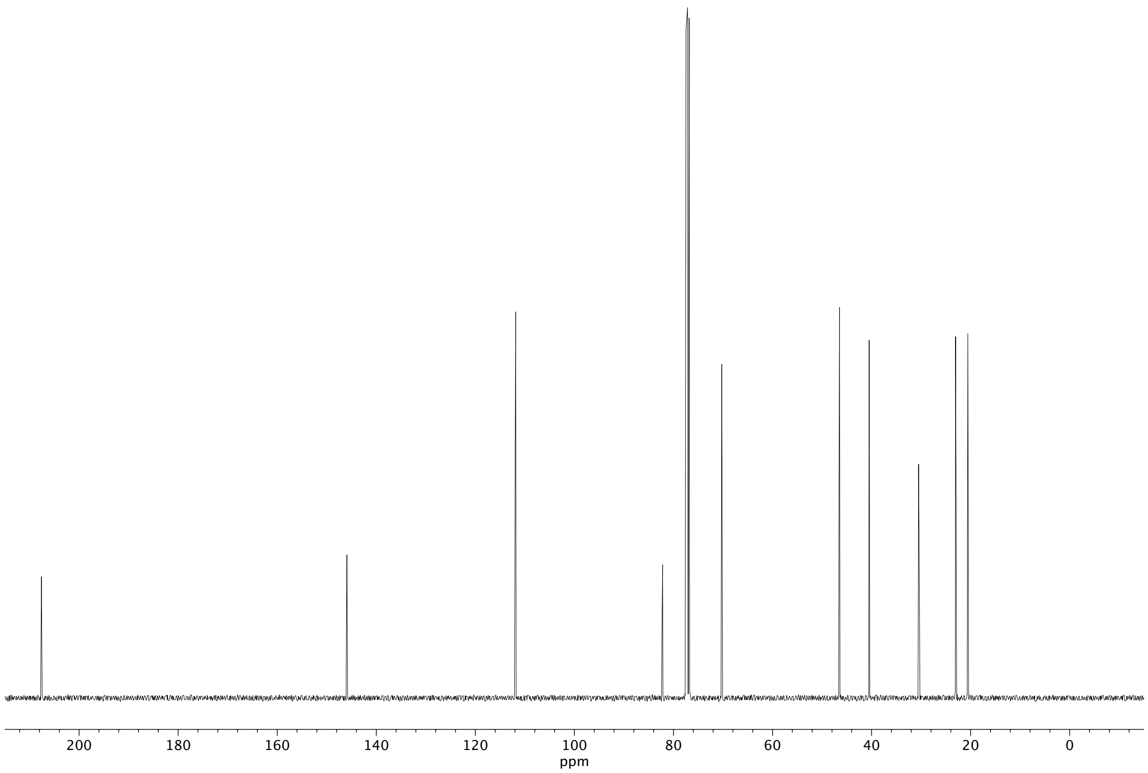
^{13}C NMR (100 MHz, CDCl$_3$) of compound **41.**



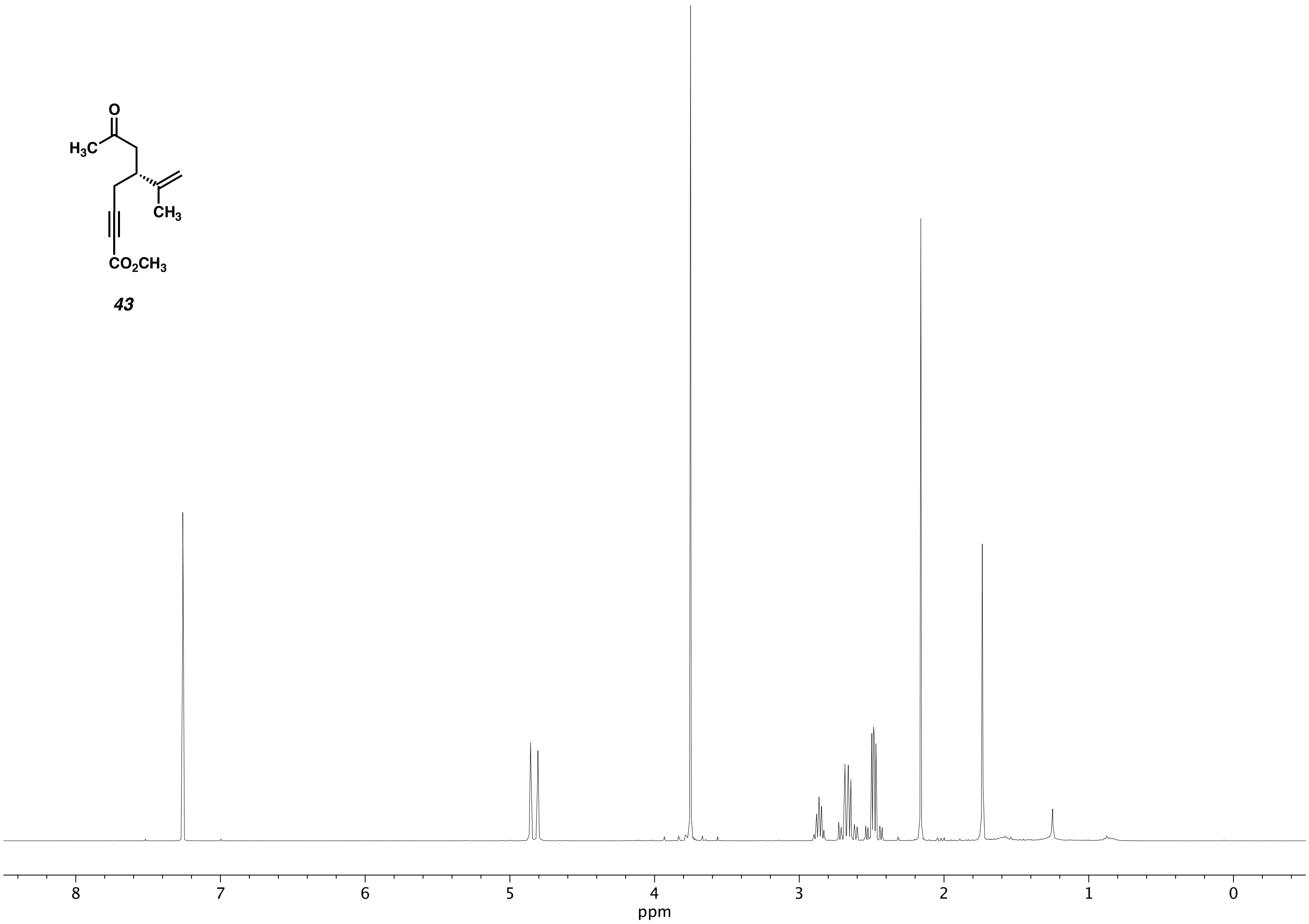
^{1}H NMR (400 MHz, CDCl$_3$) of compound **42**.



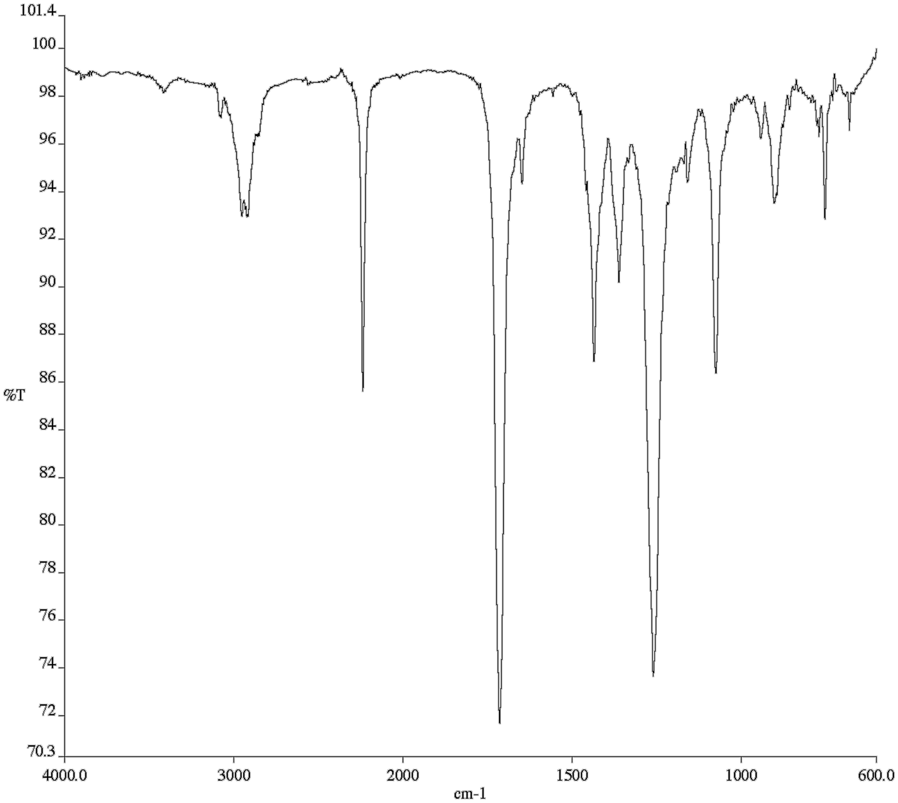
Infrared spectrum (Thin Film, NaCl) of compound **42**.



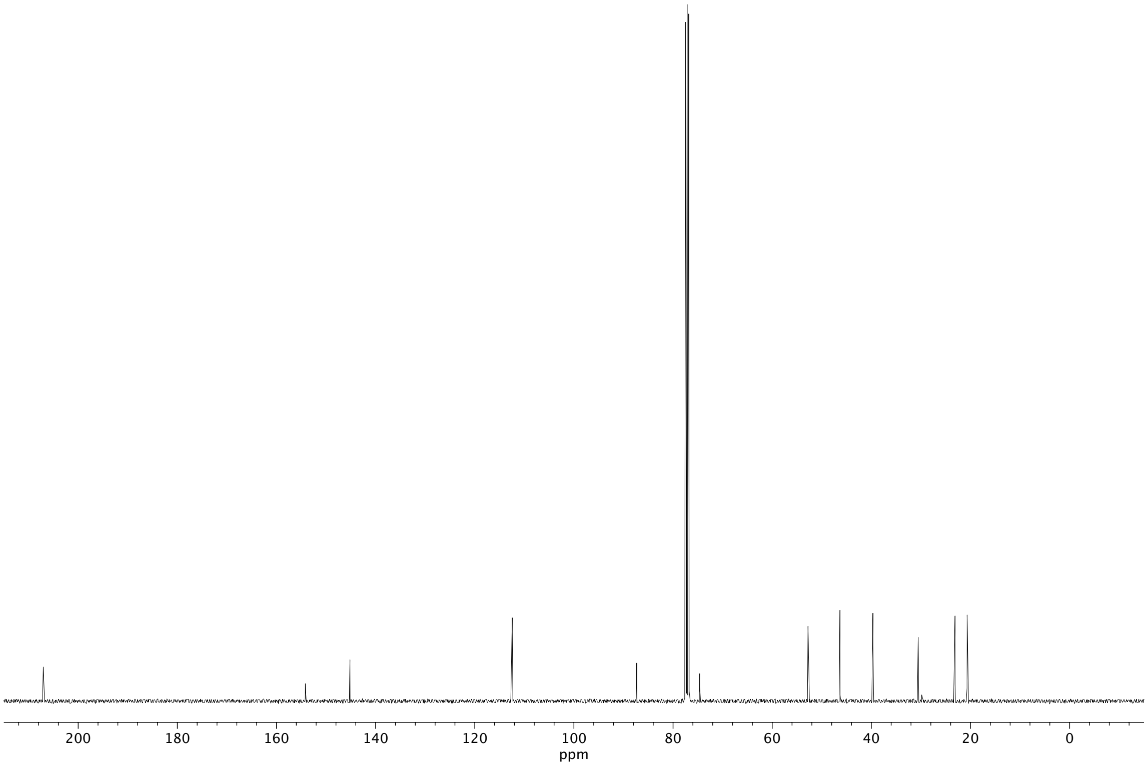
^{13}C NMR (100 MHz, CDCl$_3$) of compound **42.**



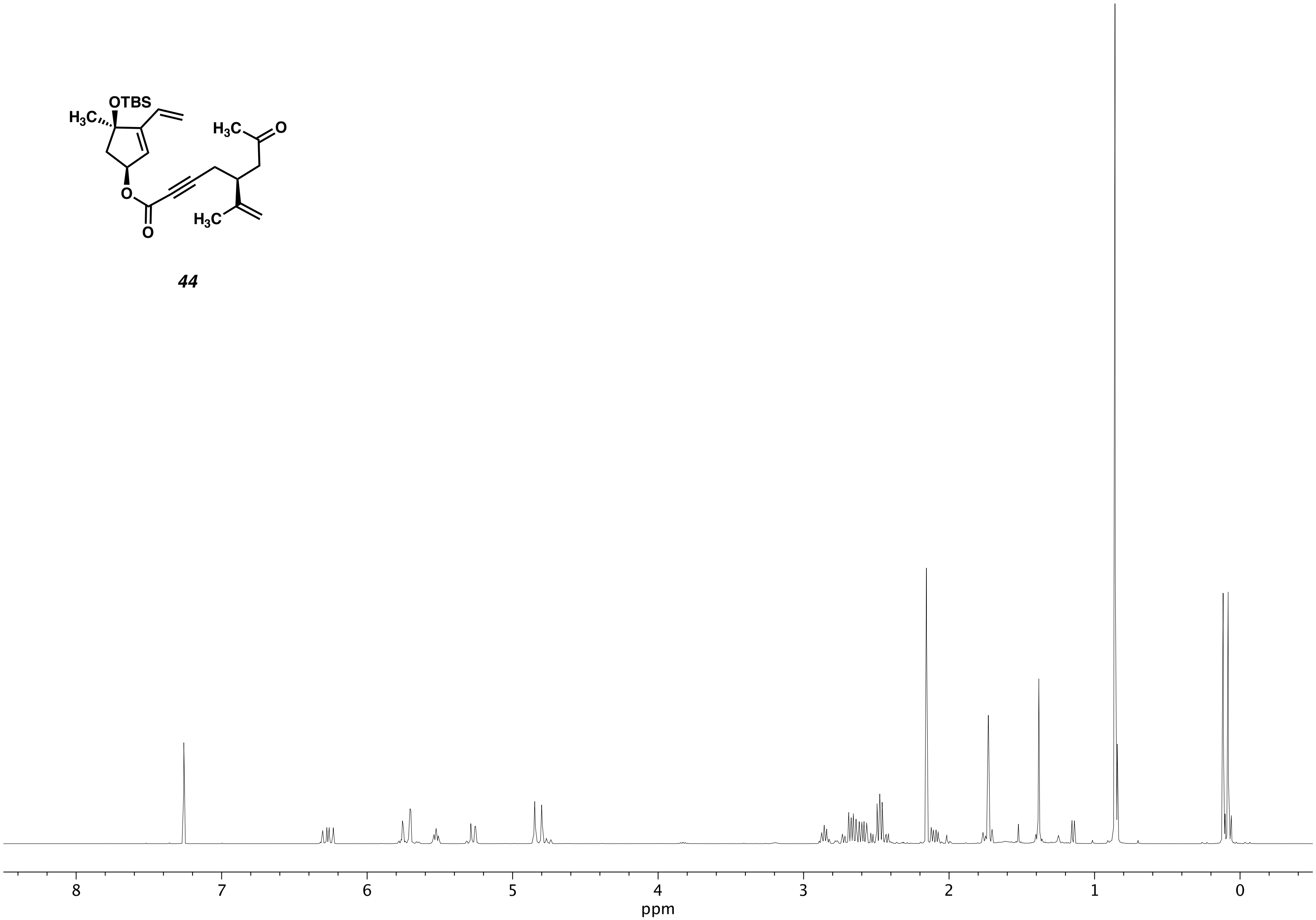
^{1}H NMR (400 MHz, CDCl$_3$) of compound **43**.



Infrared spectrum (Thin Film, NaCl) of compound **43**.

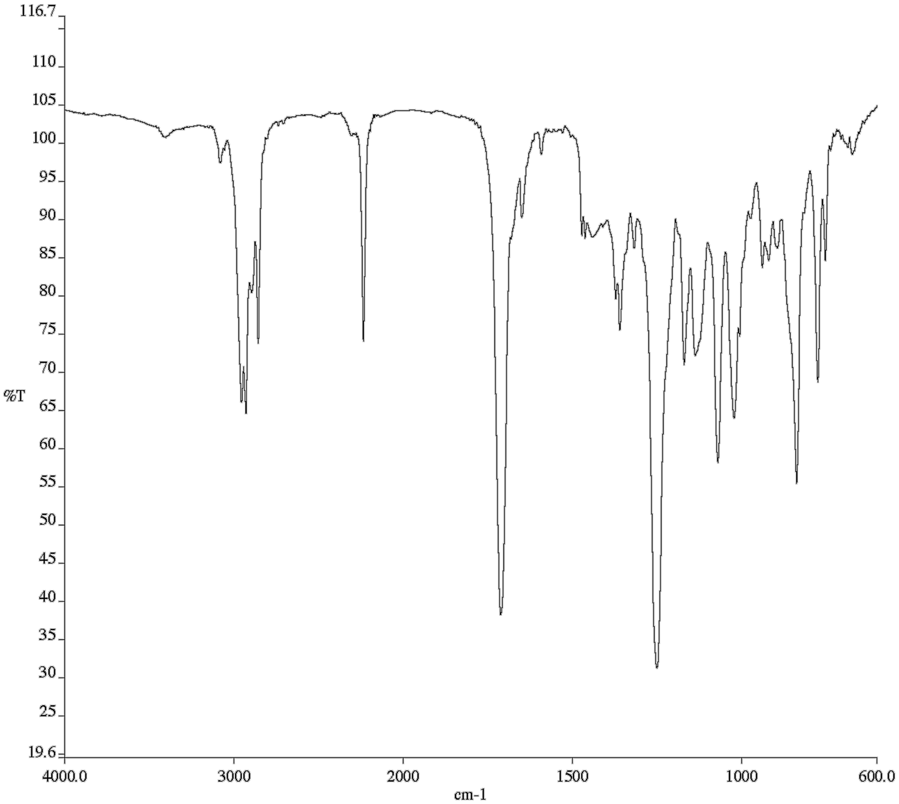


^{13}C NMR (100 MHz, CDCl$_3$) of compound **43.**

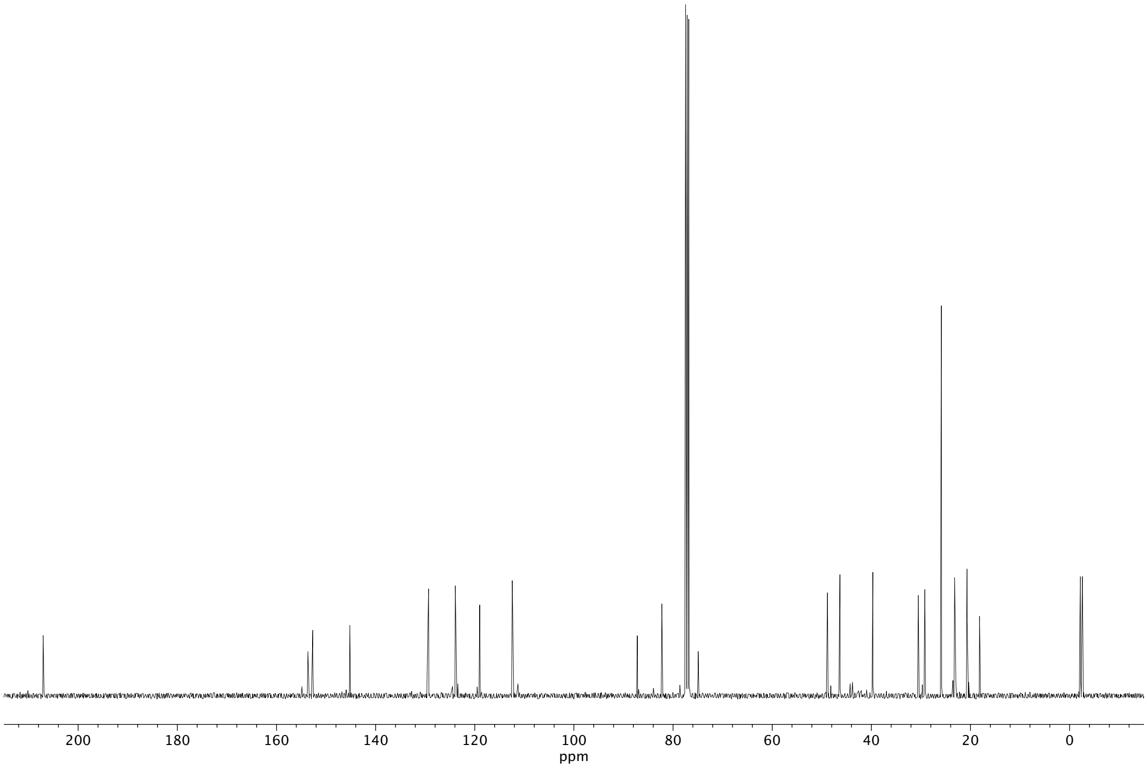


44

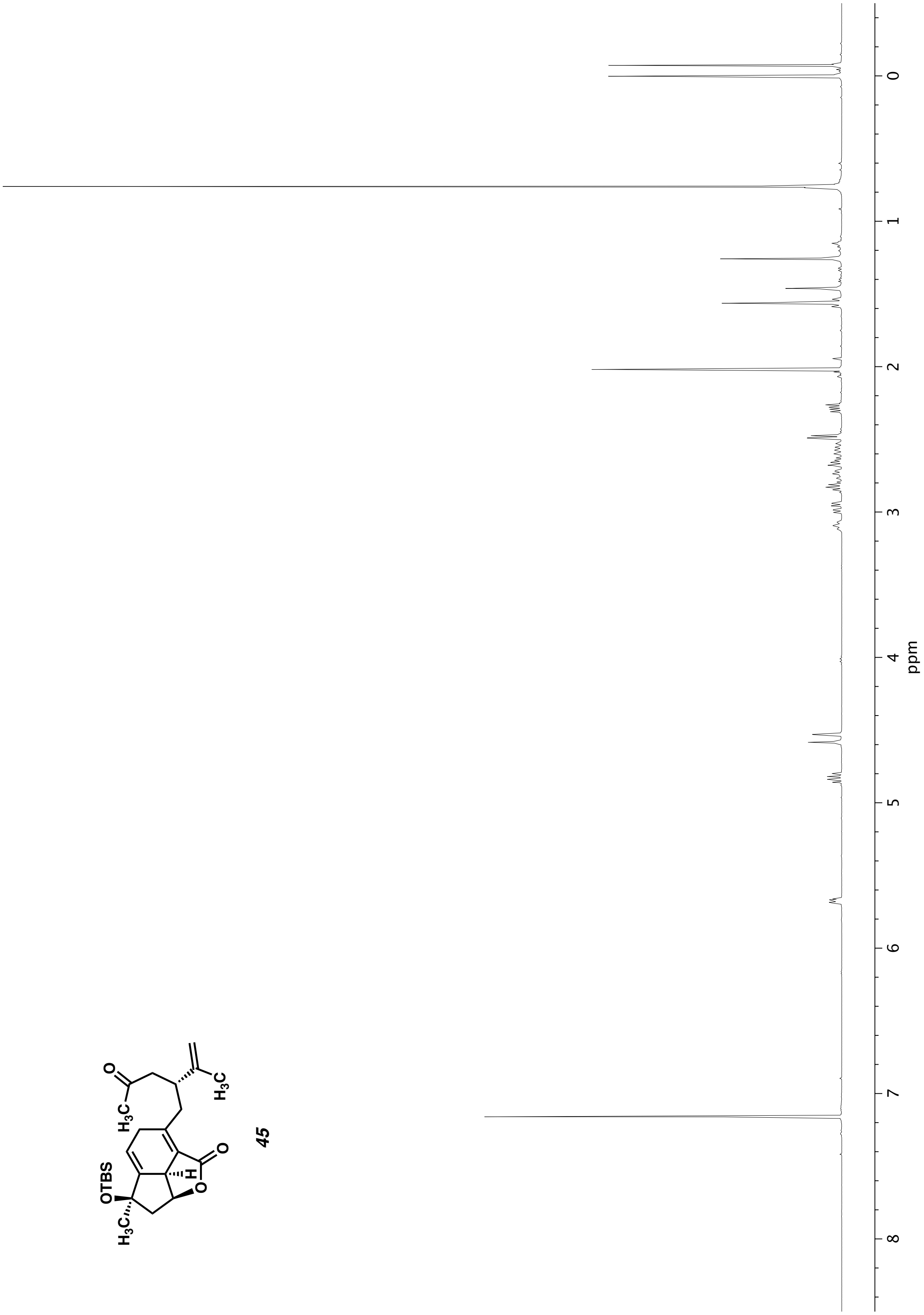
^{1}H NMR (400 MHz, $CDCl_3$) of compound **44**.



Infrared spectrum (Thin Film, NaCl) of compound **44**.

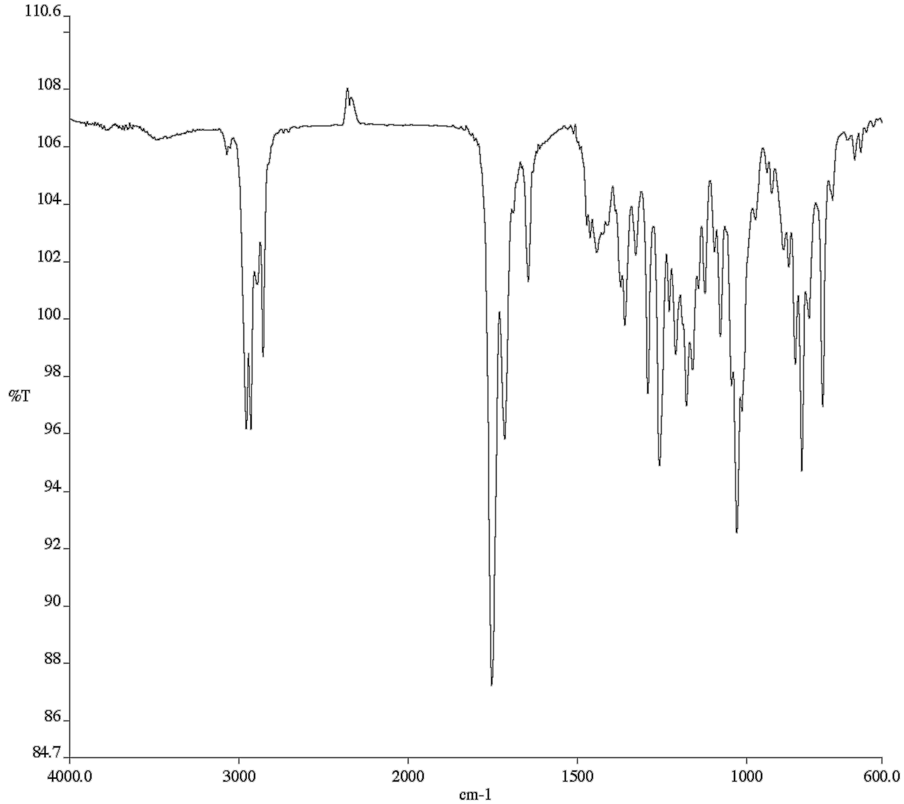


^{13}C NMR (100 MHz, CDCl$_3$) of compound **44.**

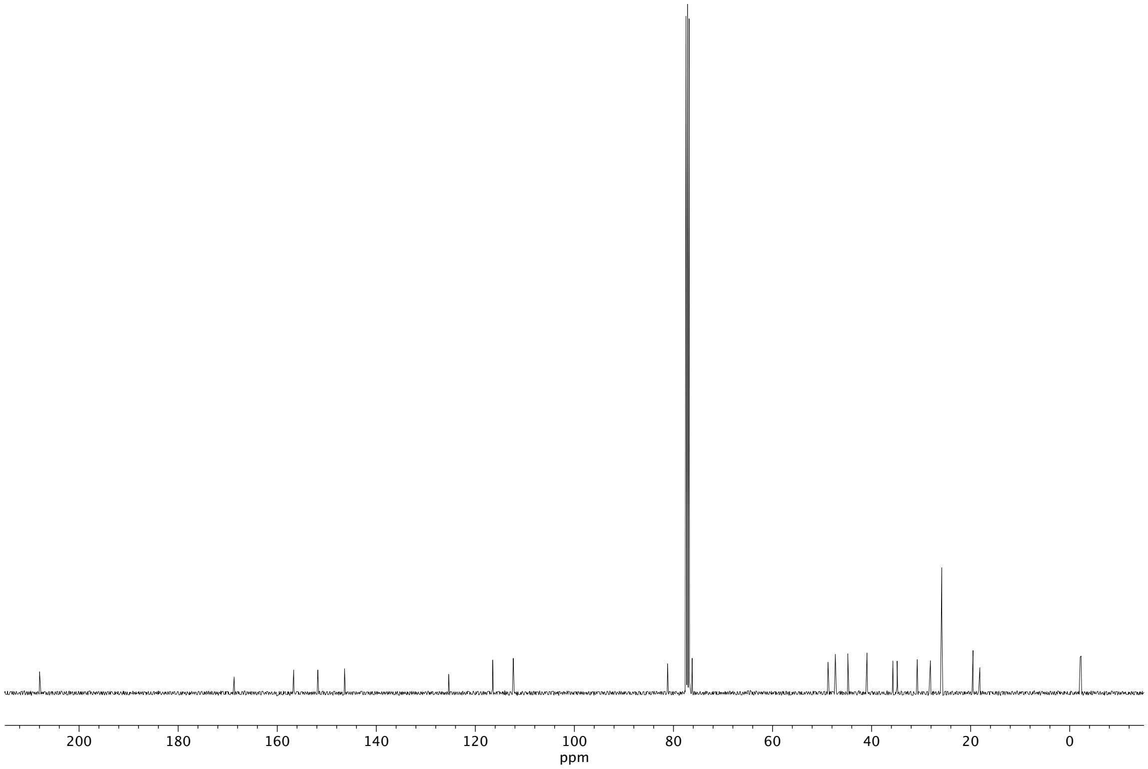


45

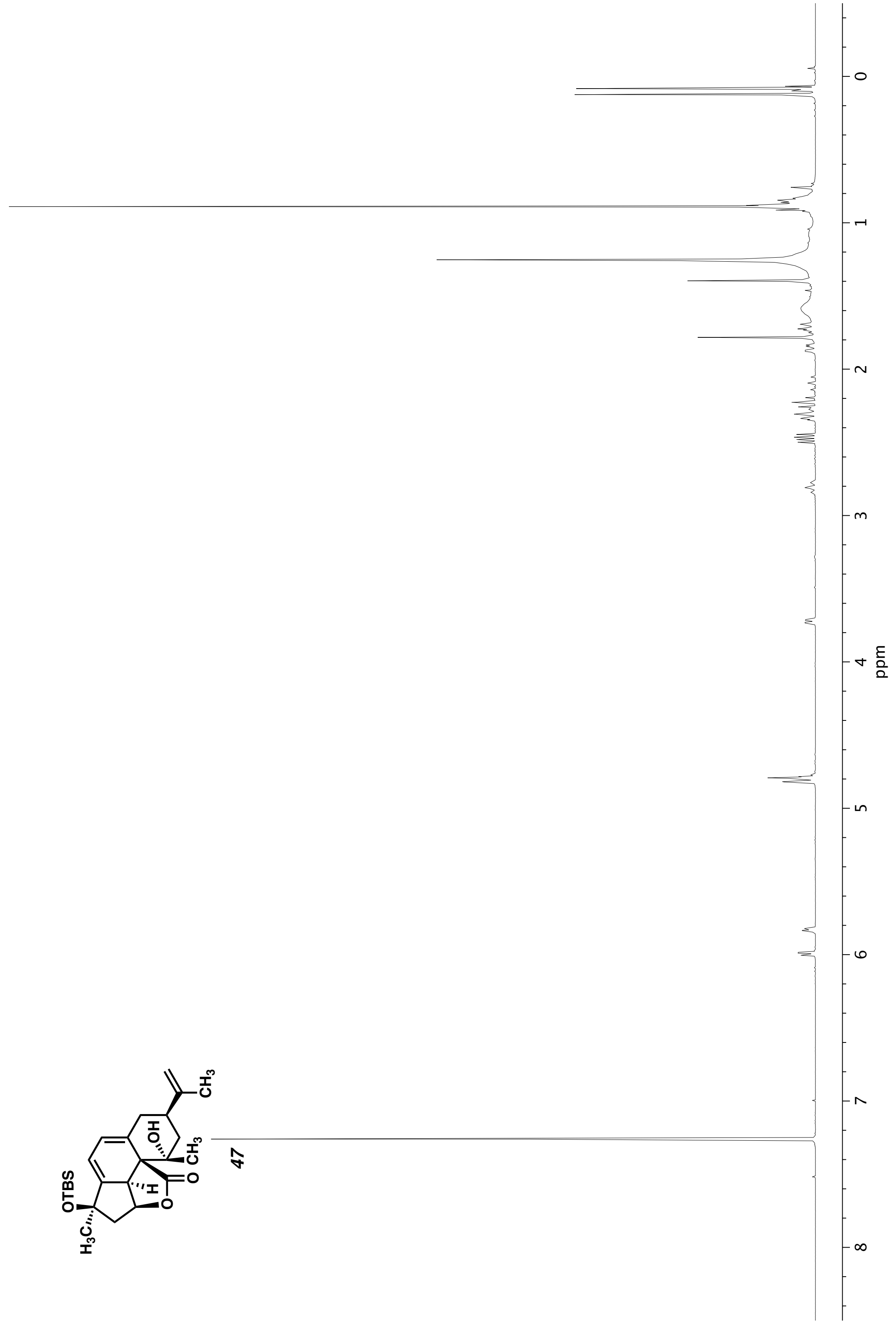
^{1}H NMR (400 MHz, CDCl$_3$) of compound **45**.



Infrared spectrum (Thin Film, NaCl) of compound **45**.

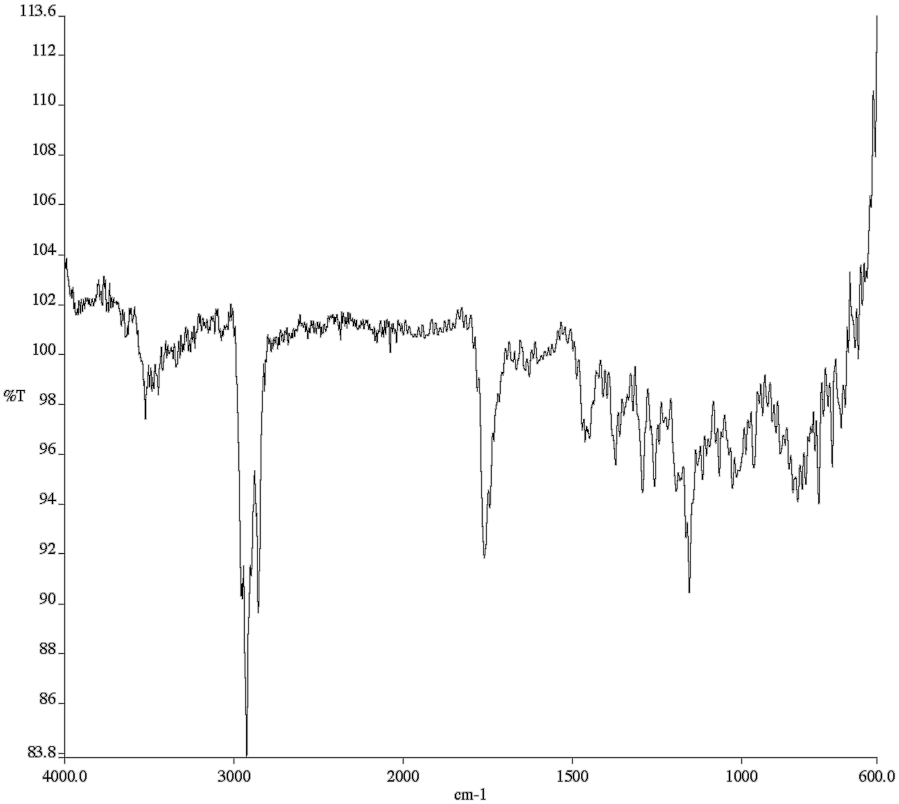


^{13}C NMR (100 MHz, CDCl$_3$) of compound **45.**

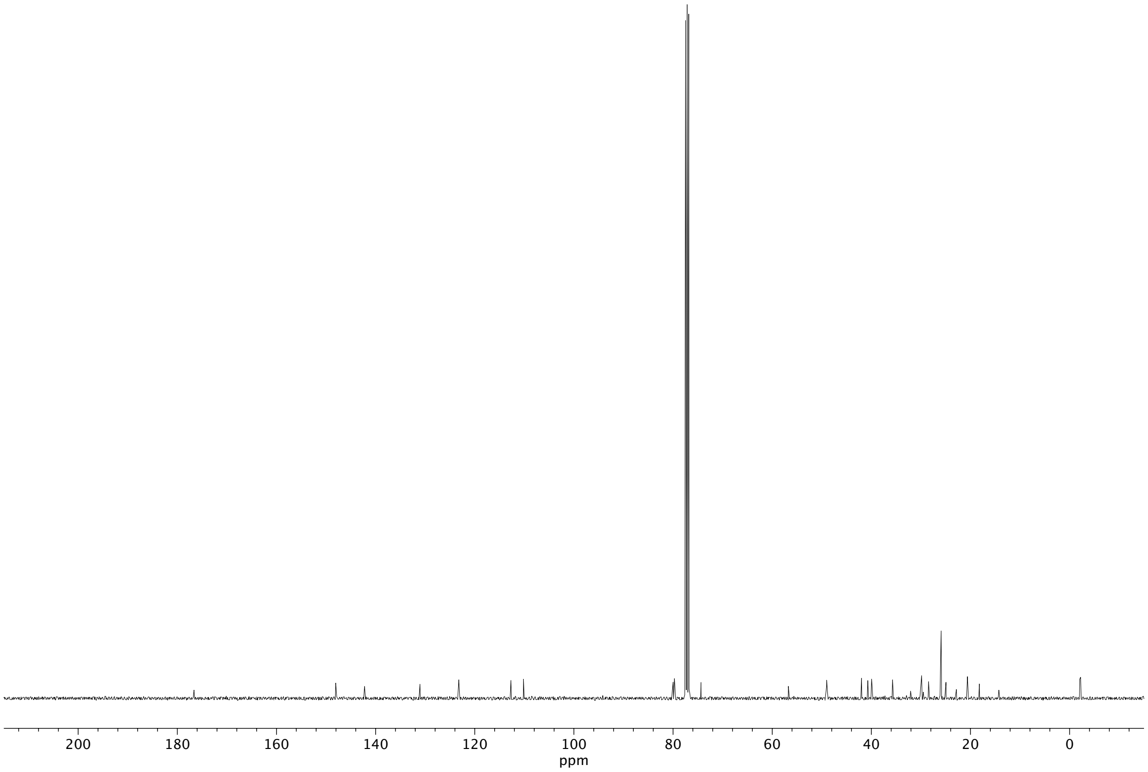


47

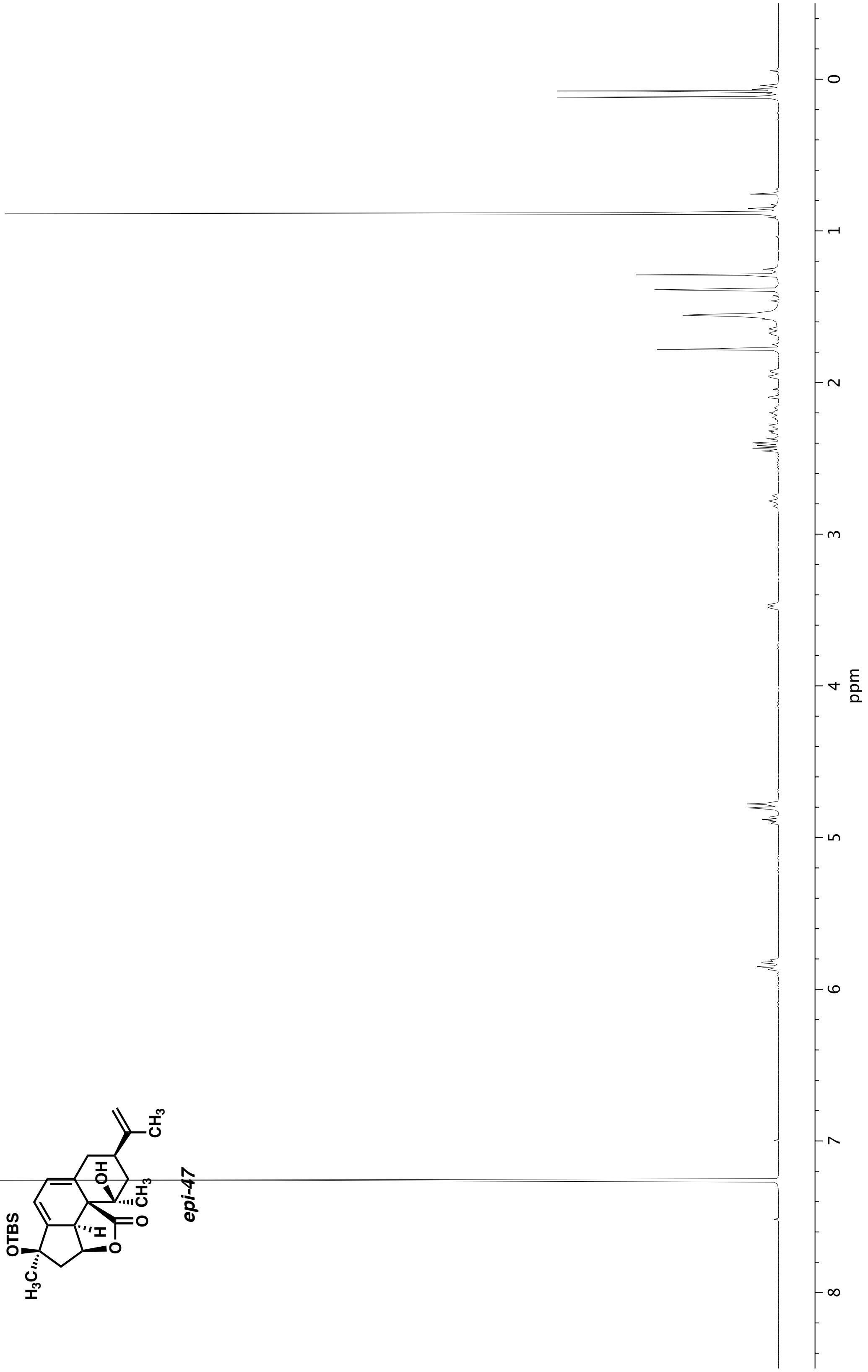
^{1}H NMR (400 MHz, CDCl$_3$) of compound **47**.



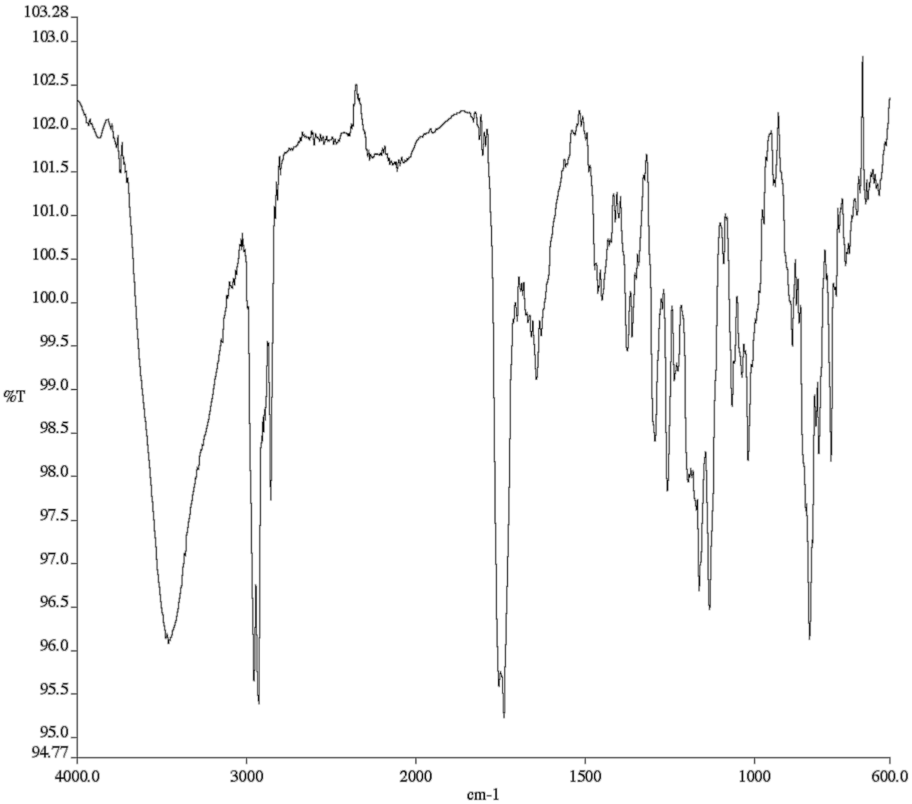
Infrared spectrum (Thin Film, NaCl) of compound **47**.



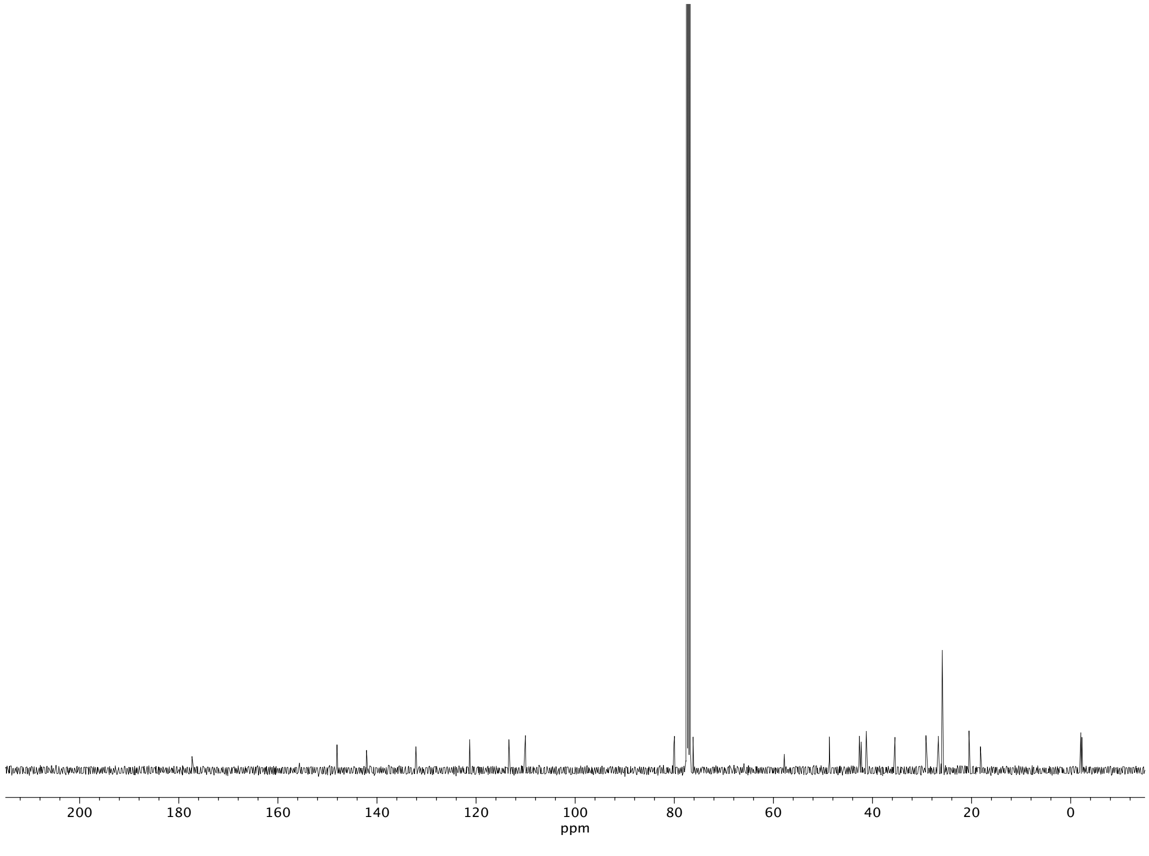
^{13}C NMR (100 MHz, CDCl$_3$) of compound **47.**



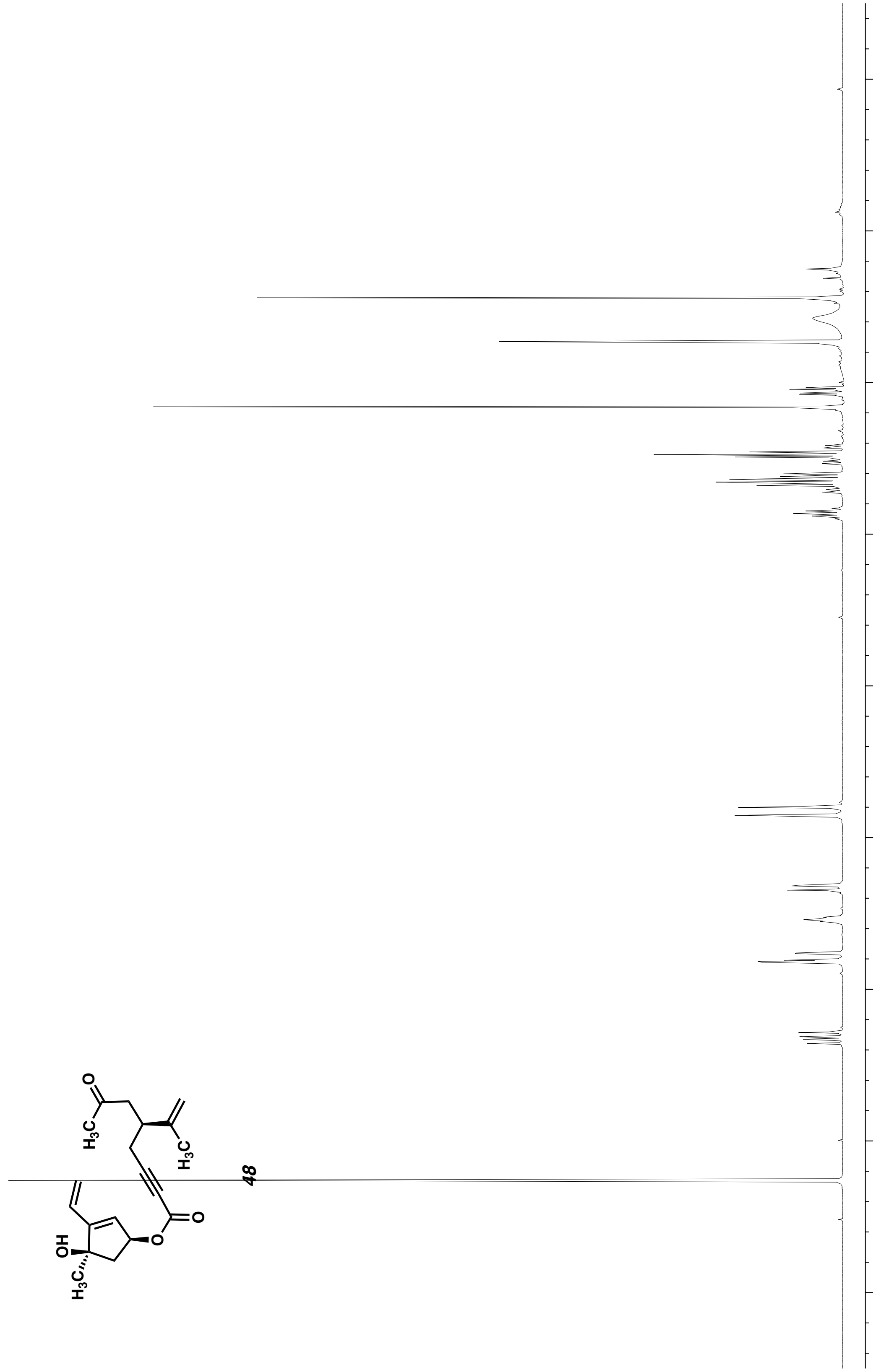
^{1}H NMR (400 MHz, CDCl$_3$) of compound **epi-47**.



Infrared spectrum (Thin Film, NaCl) of compound **epi-47**.

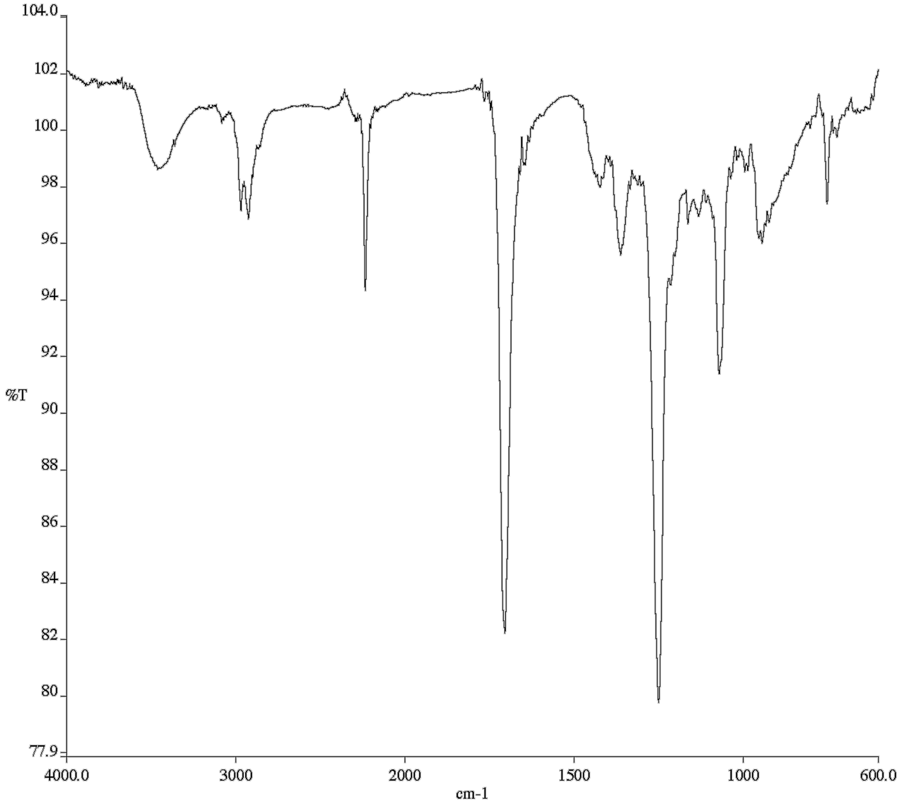


^{13}C NMR (100 MHz, CDCl$_3$) of compound **epi-47.**

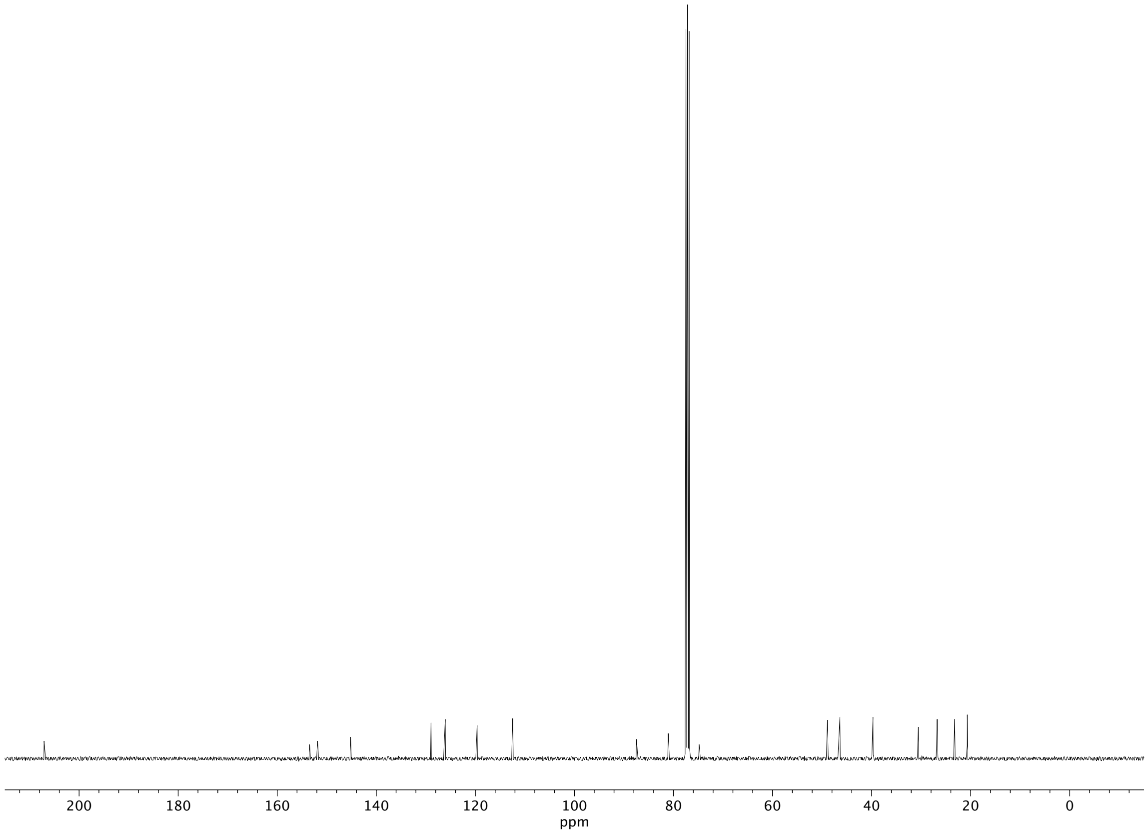


48

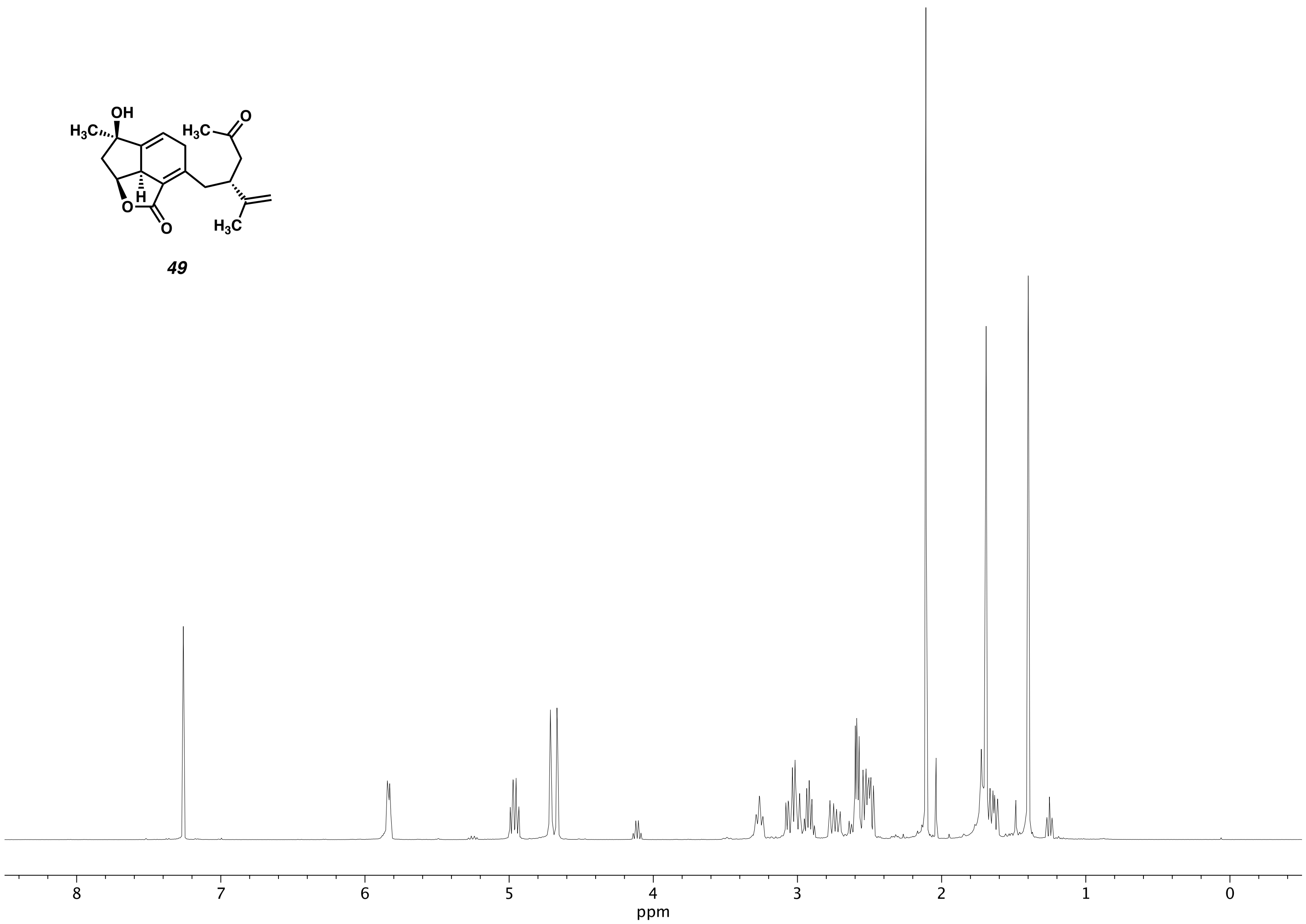
^{1}H NMR (400 MHz, CDCl$_3$) of compound **48**.



Infrared spectrum (Thin Film, NaCl) of compound **48**.

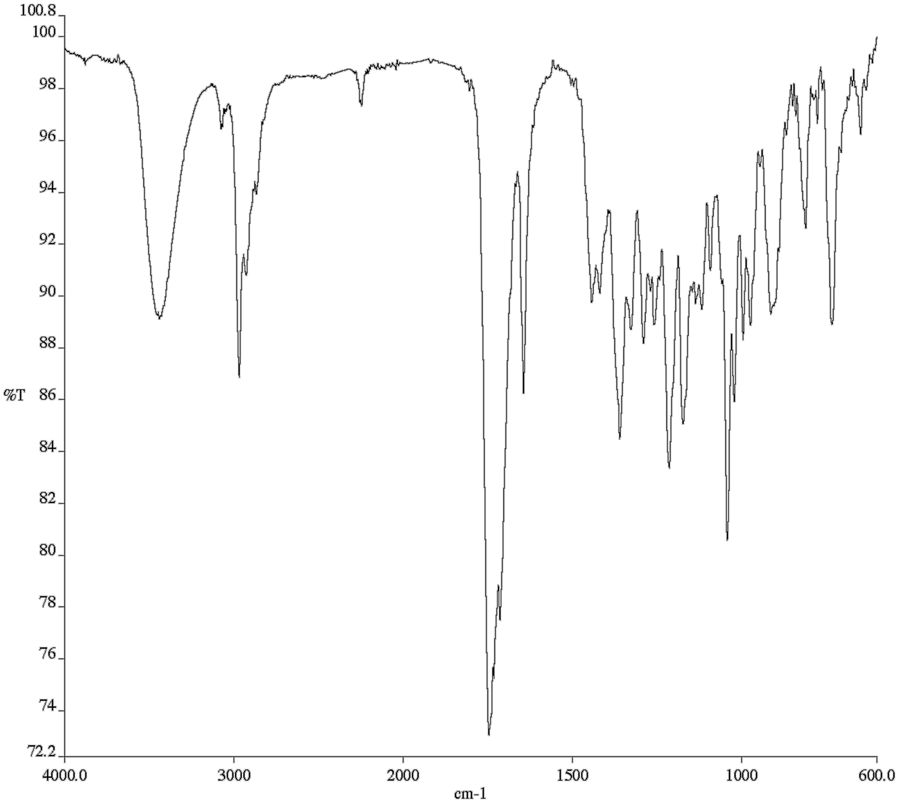


^{13}C NMR (100 MHz, CDCl$_3$) of compound **48.**

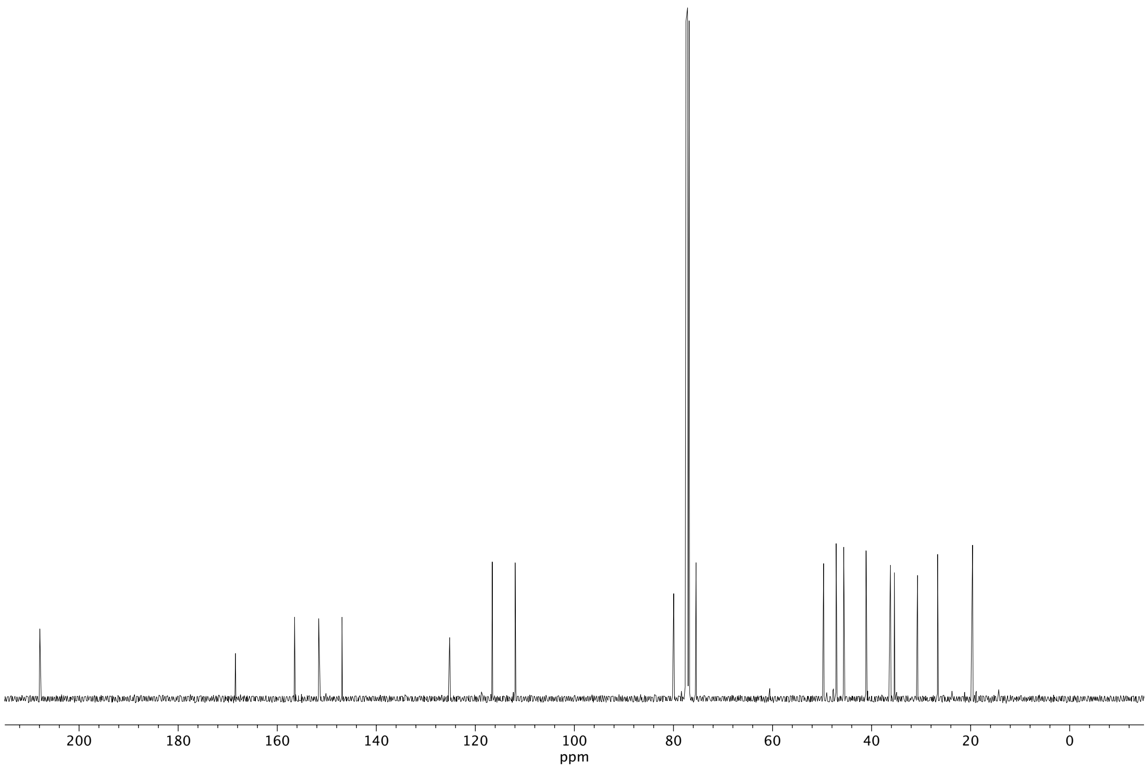


49

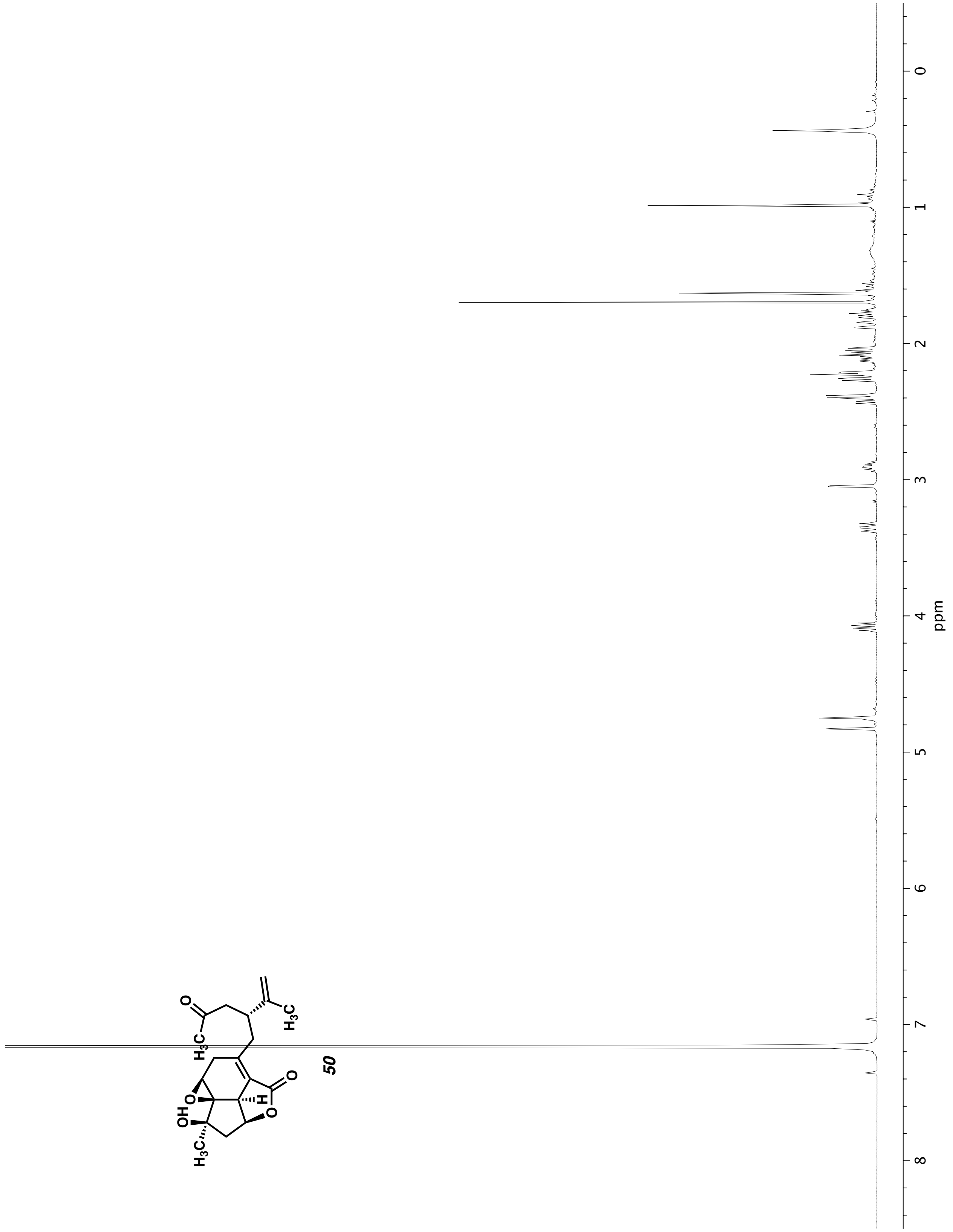
^{1}H NMR (400 MHz, CDCl$_3$) of compound **49**.



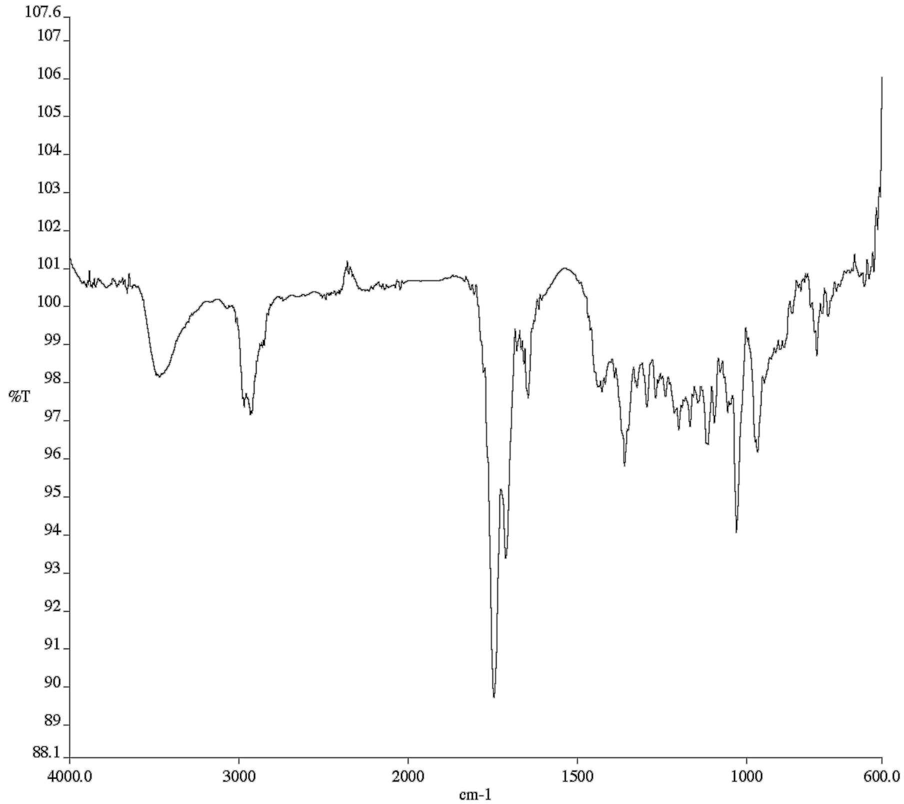
Infrared spectrum (Thin Film, NaCl) of compound **49**.



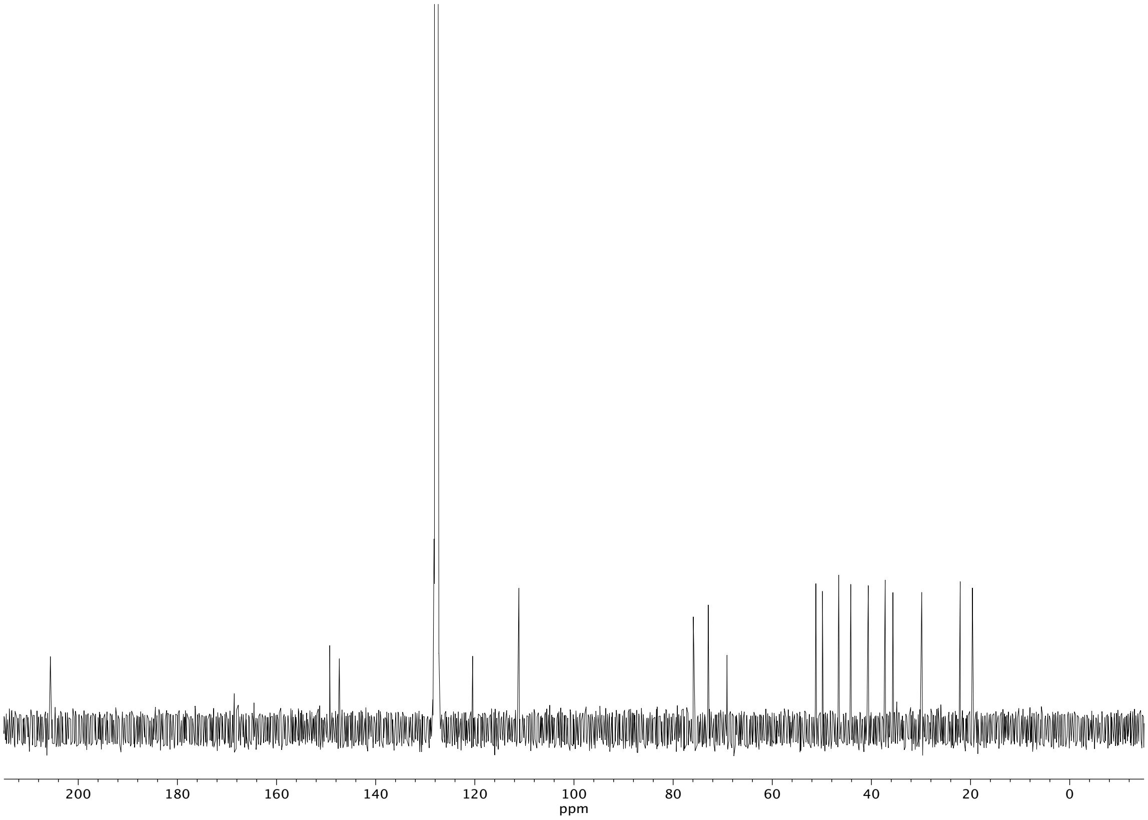
^{13}C NMR (100 MHz, CDCl$_3$) of compound **49.**



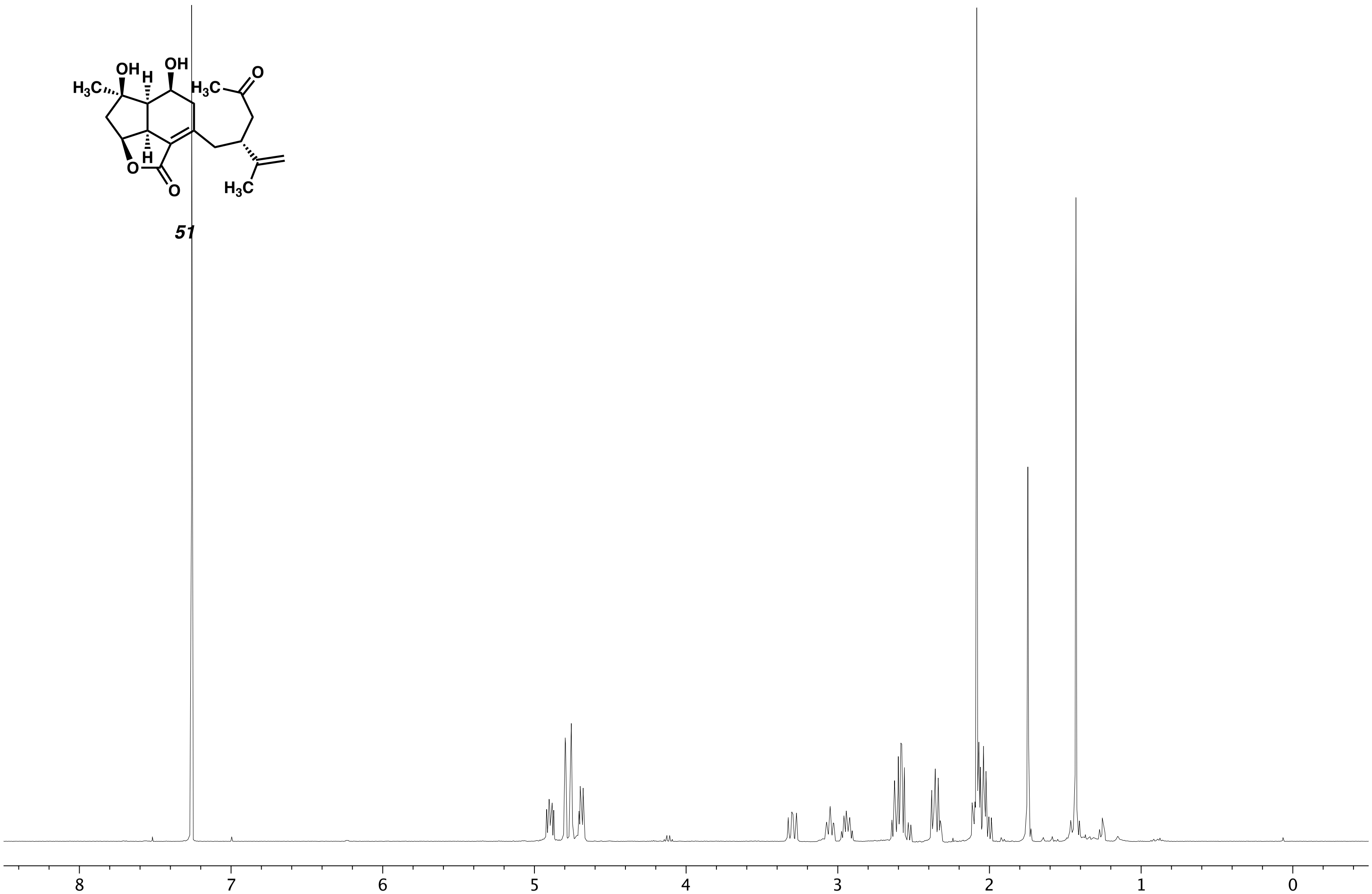
^{1}H NMR (400 MHz, CDCl$_3$) of compound **50**.



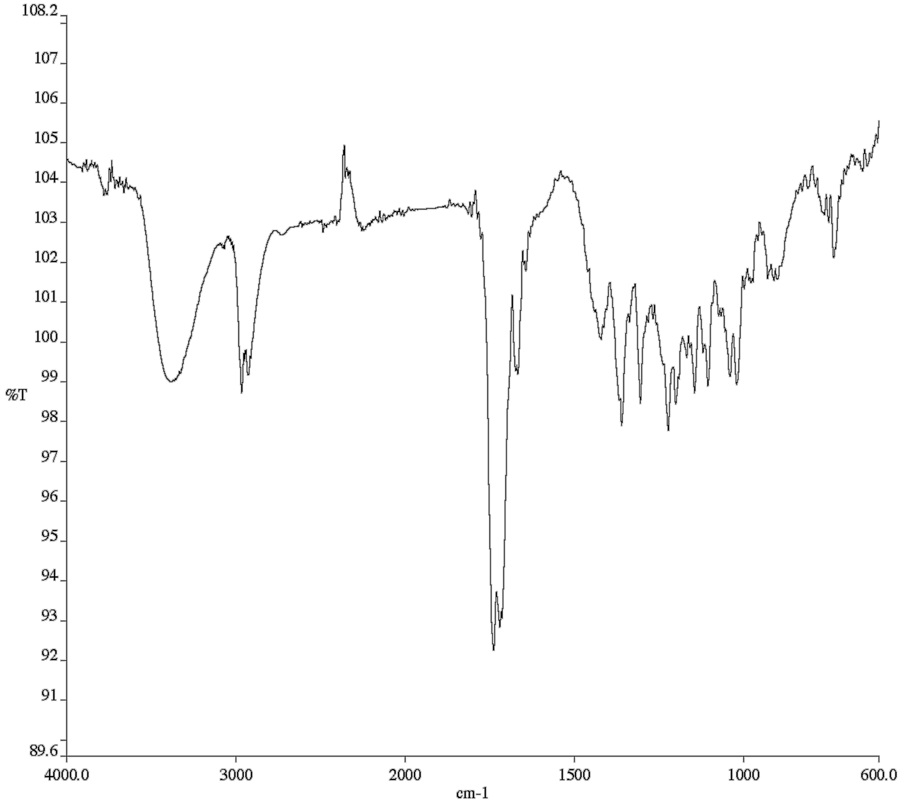
Infrared spectrum (Thin Film, NaCl) of compound **50**.



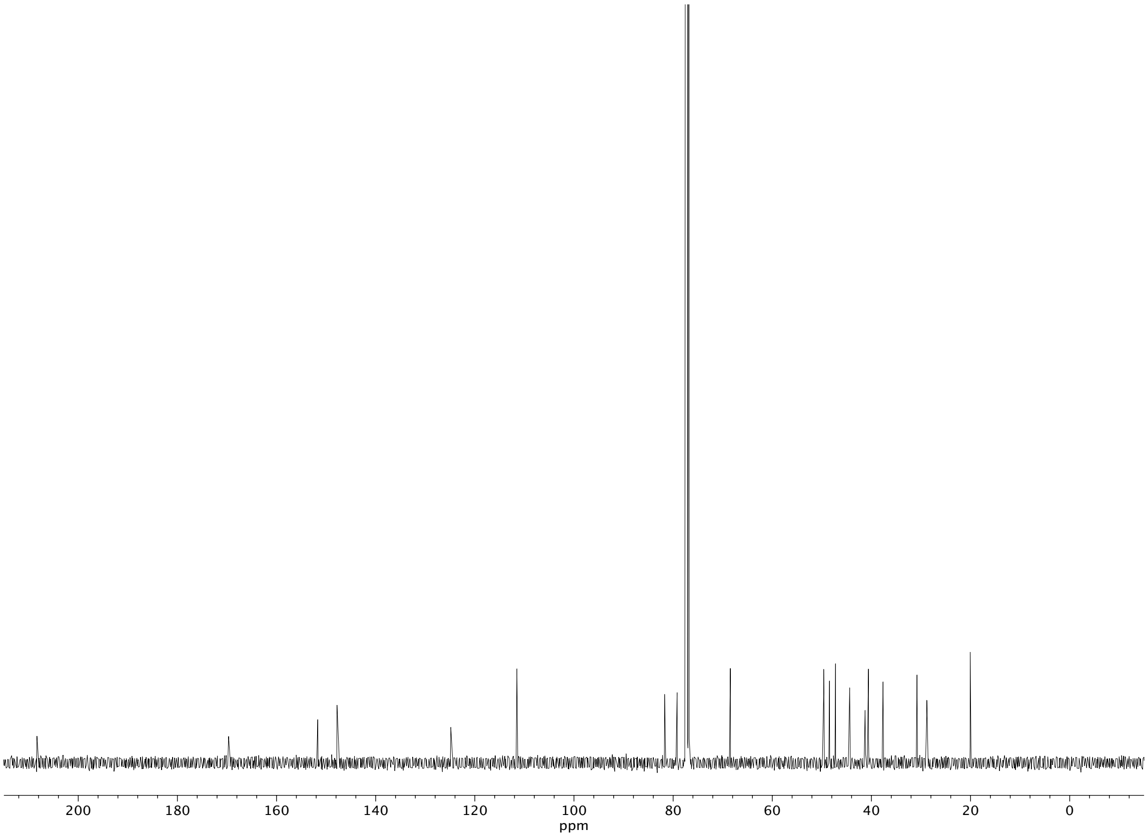
^{13}C NMR (100 MHz, CDCl$_3$) of compound **50.**



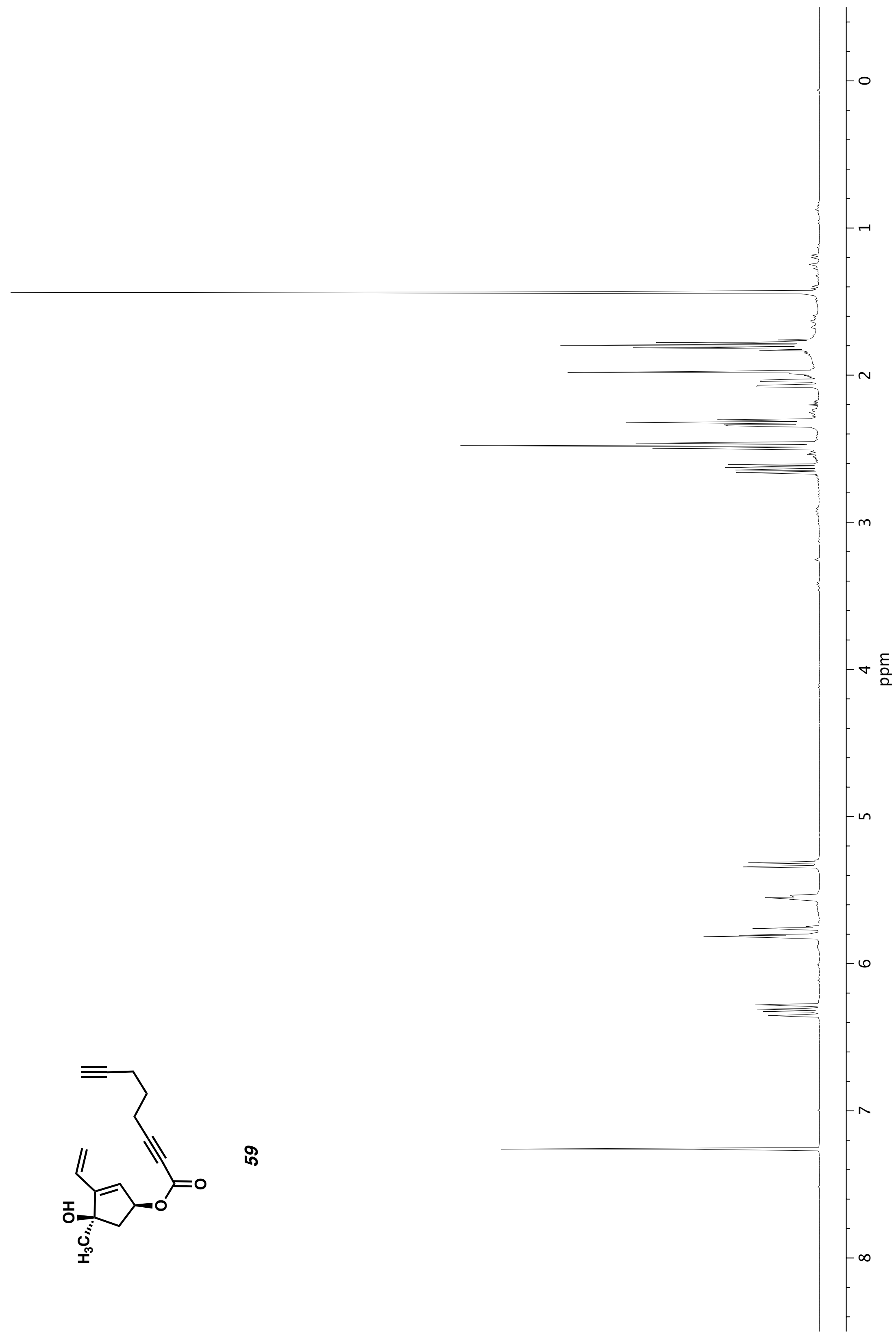
^{1}H NMR (400 MHz, CDCl$_3$) of compound **51**.



Infrared spectrum (Thin Film, NaCl) of compound **51**.

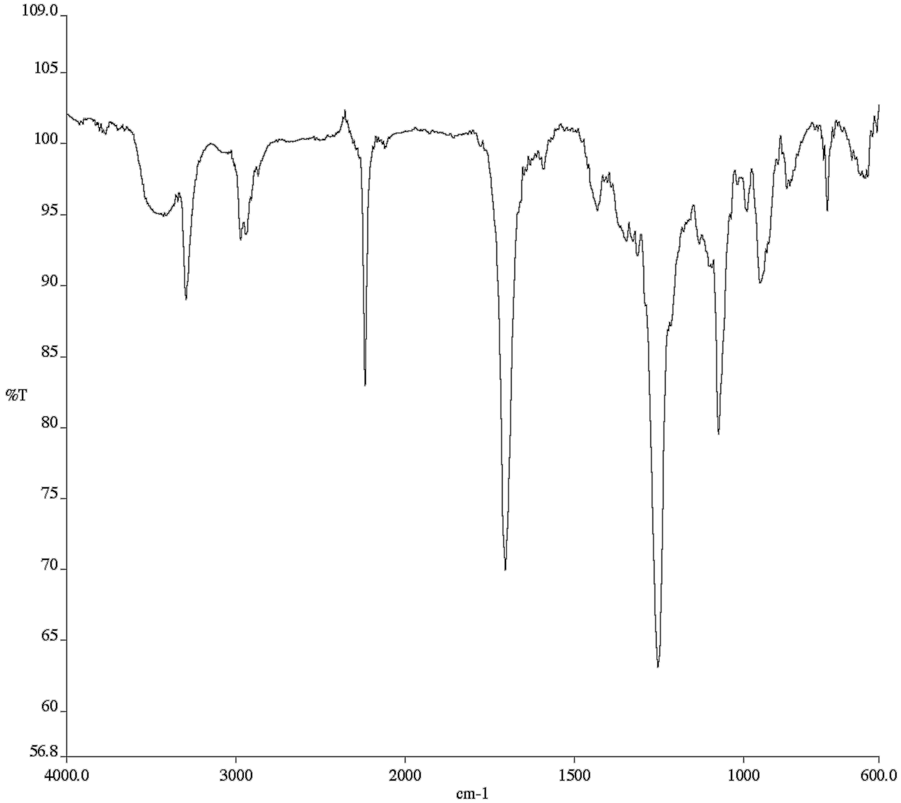


^{13}C NMR (100 MHz, $CDCl_3$) of compound **50.**

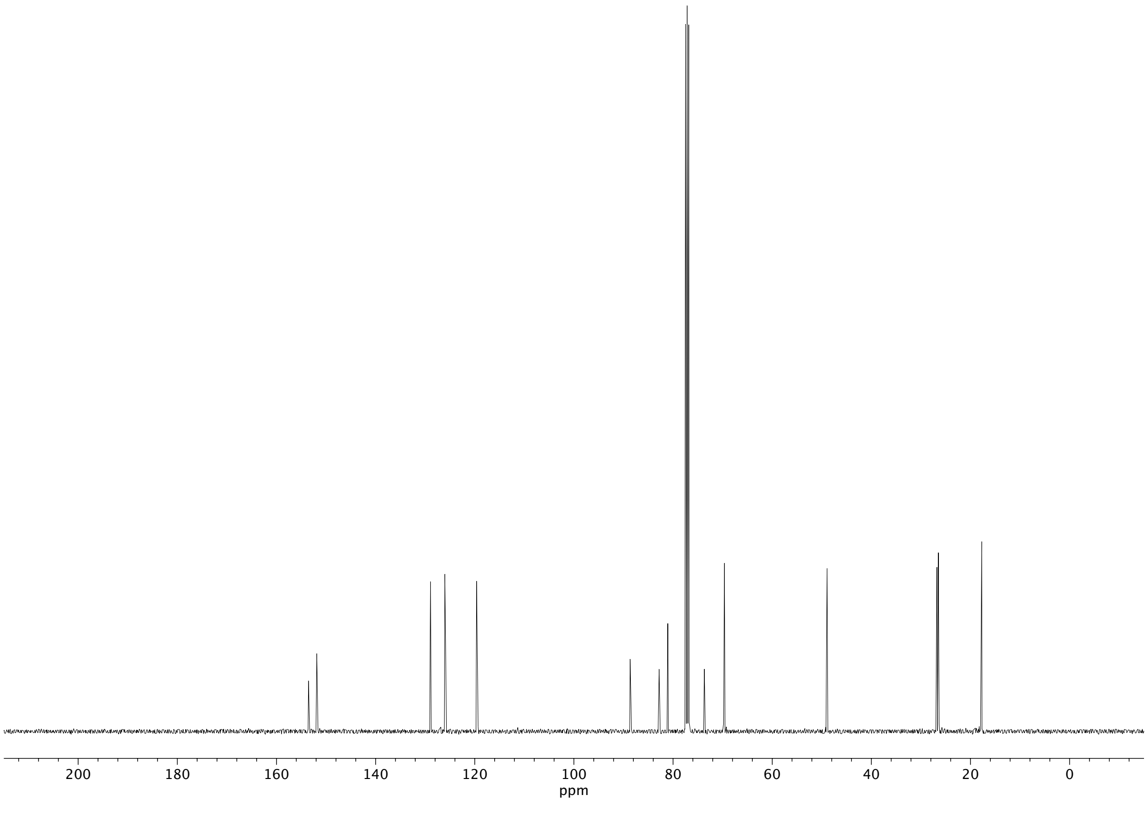


59

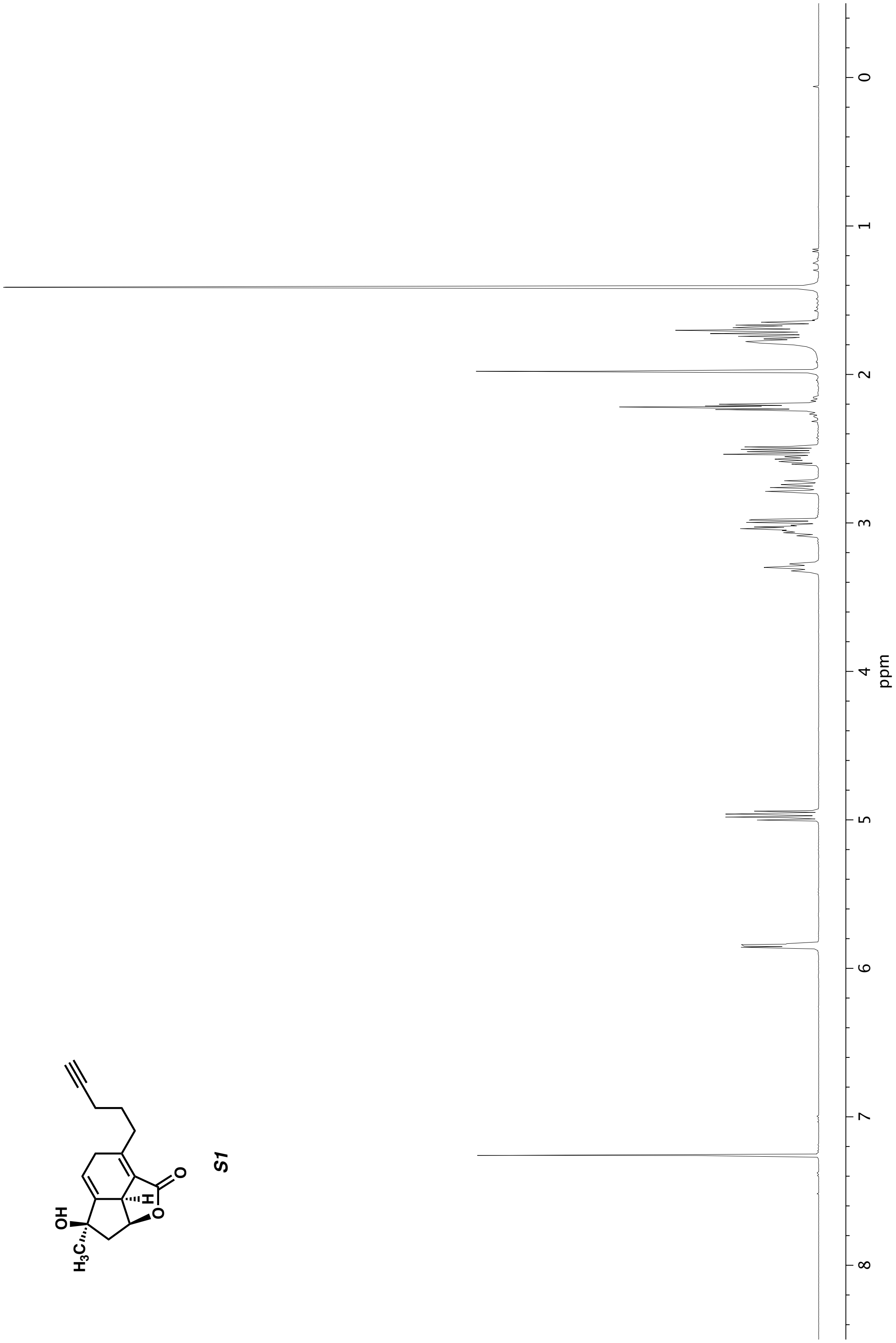
^{1}H NMR (400 MHz, CDCl$_3$) of compound **59**.



Infrared spectrum (Thin Film, NaCl) of compound **59**.

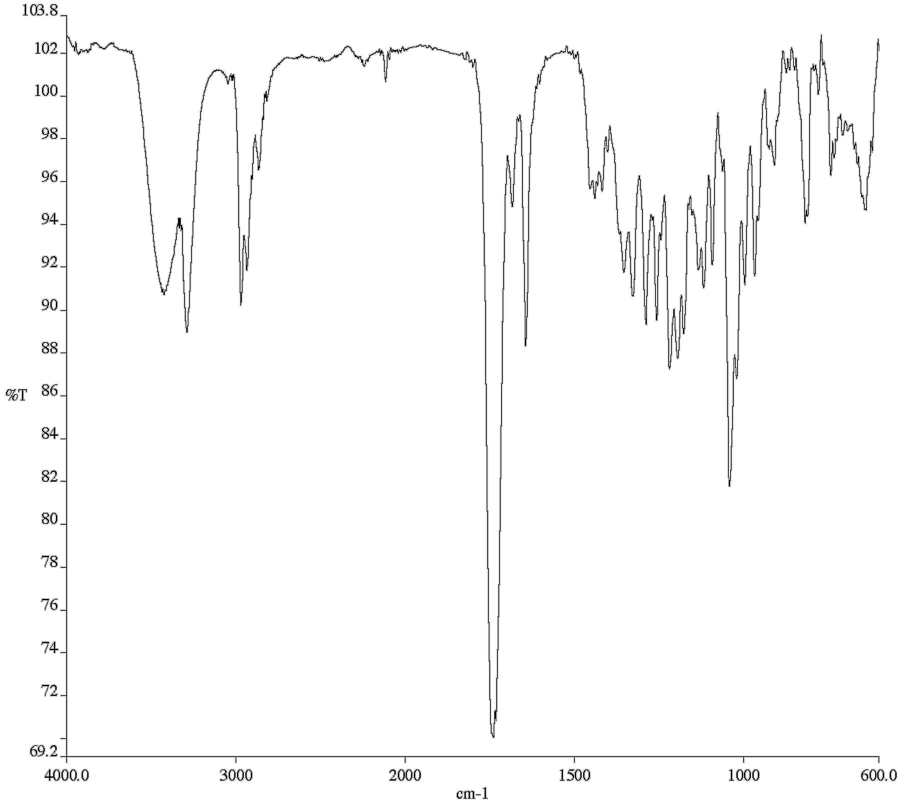


^{13}C NMR (100 MHz, CDCl$_3$) of compound **59.**

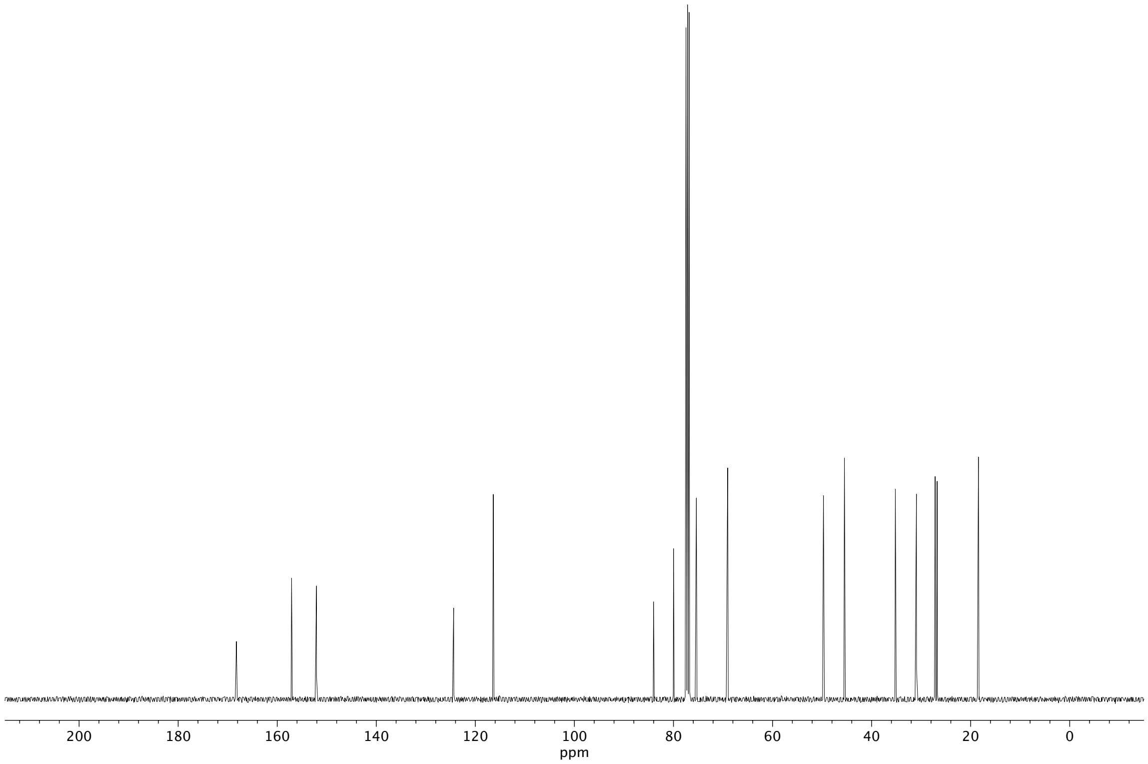


S1

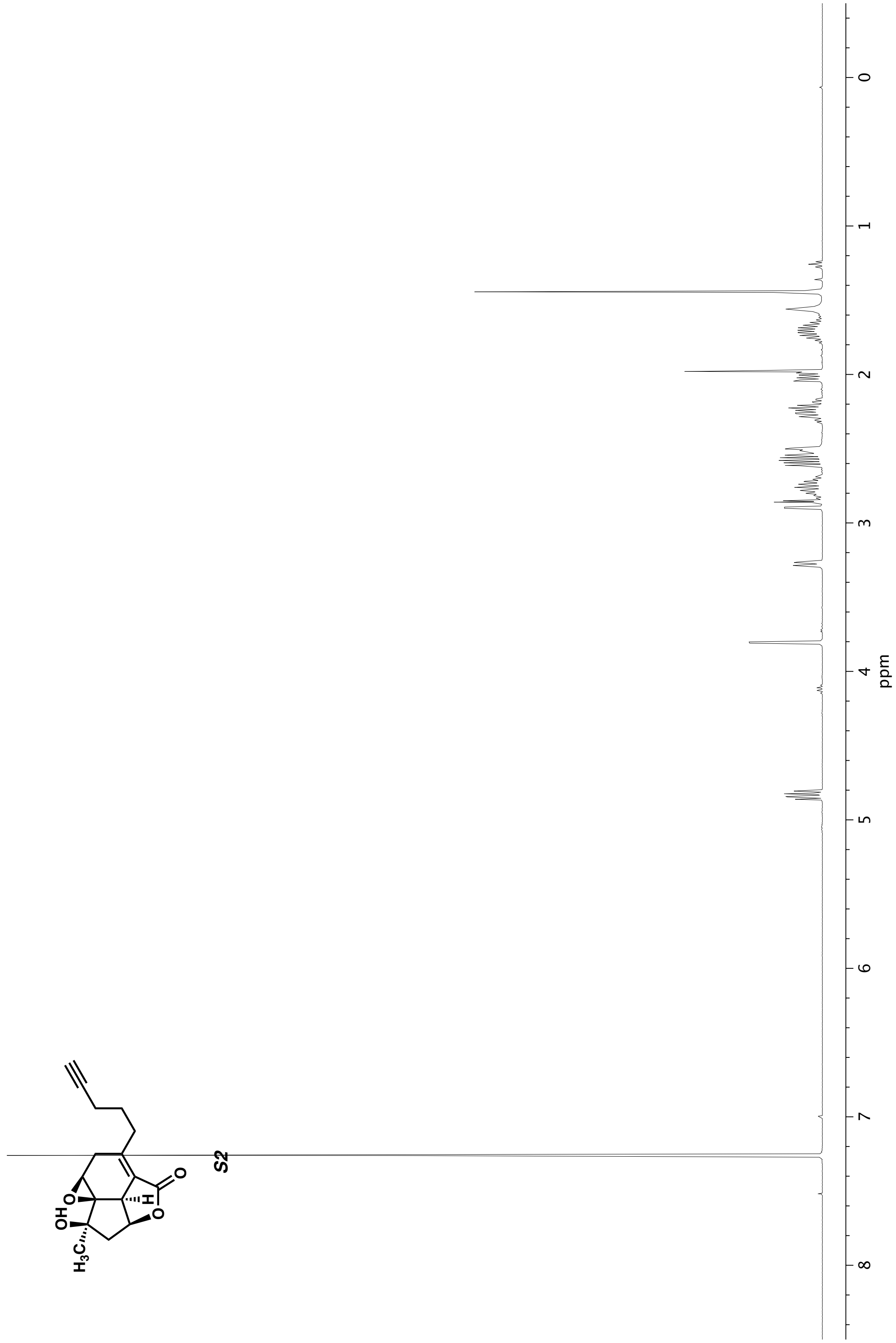
^{1}H NMR (400 MHz, CDCl$_3$) of compound **S1**.



Infrared spectrum (Thin Film, NaCl) of compound **S1**.

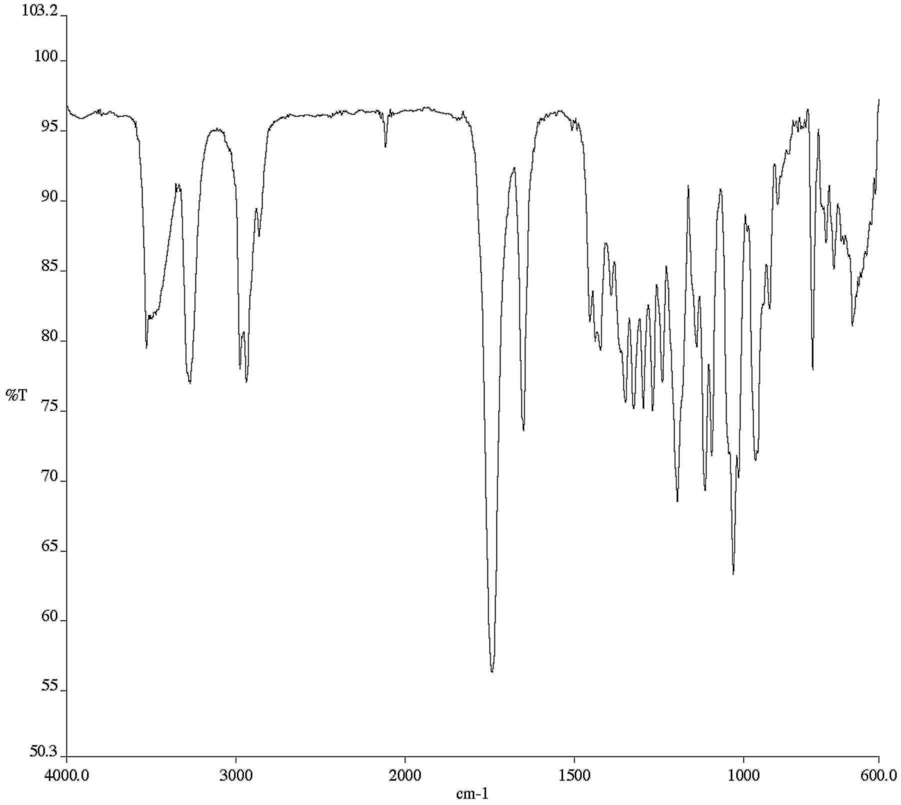


^{13}C NMR (100 MHz, CDCl$_3$) of compound

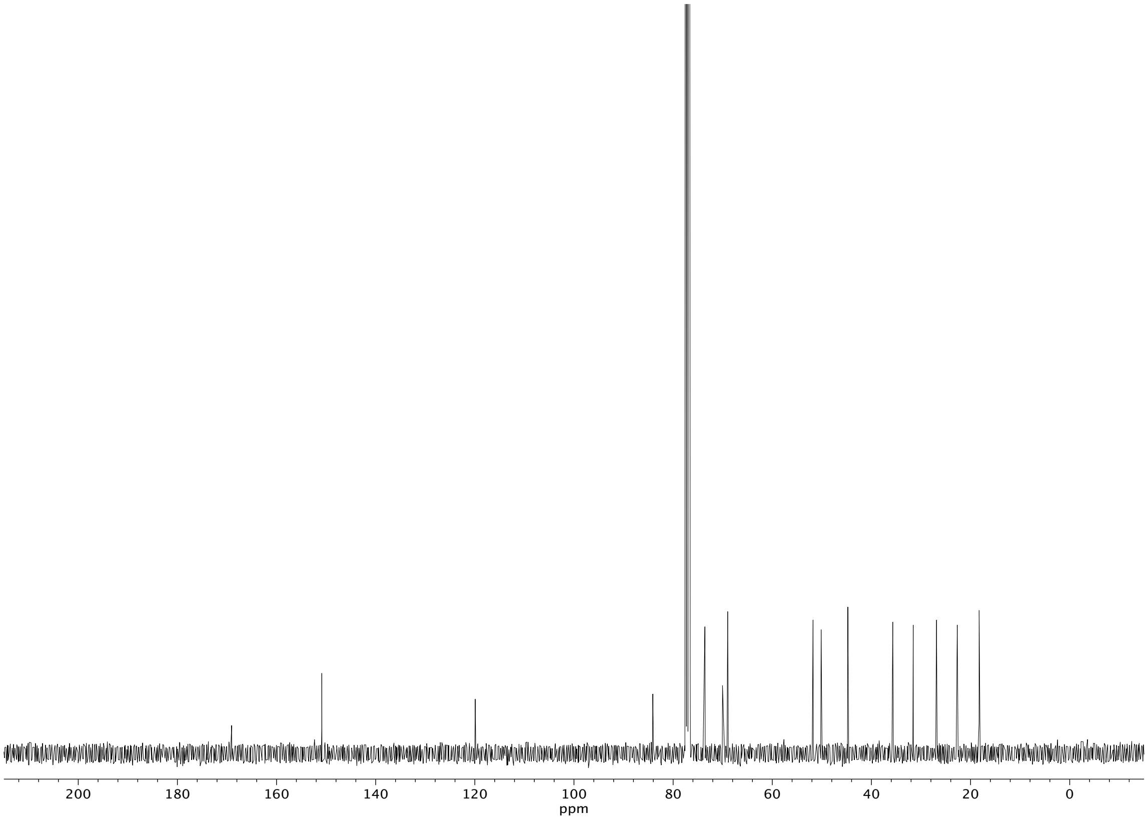


S2

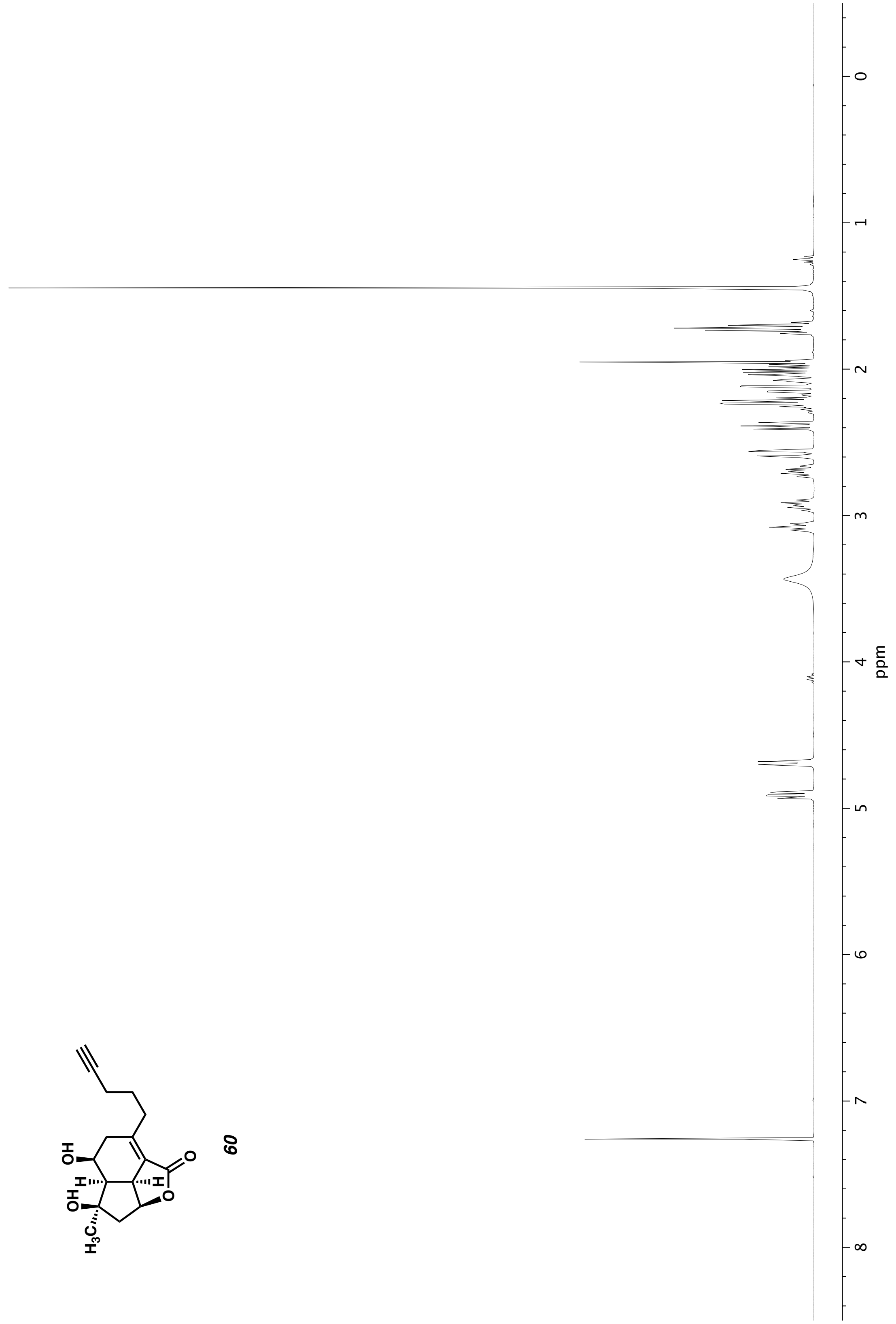
^{1}H NMR (400 MHz, CDCl$_3$) of compound **S2**.



Infrared spectrum (Thin Film, NaCl) of compound **S2**.

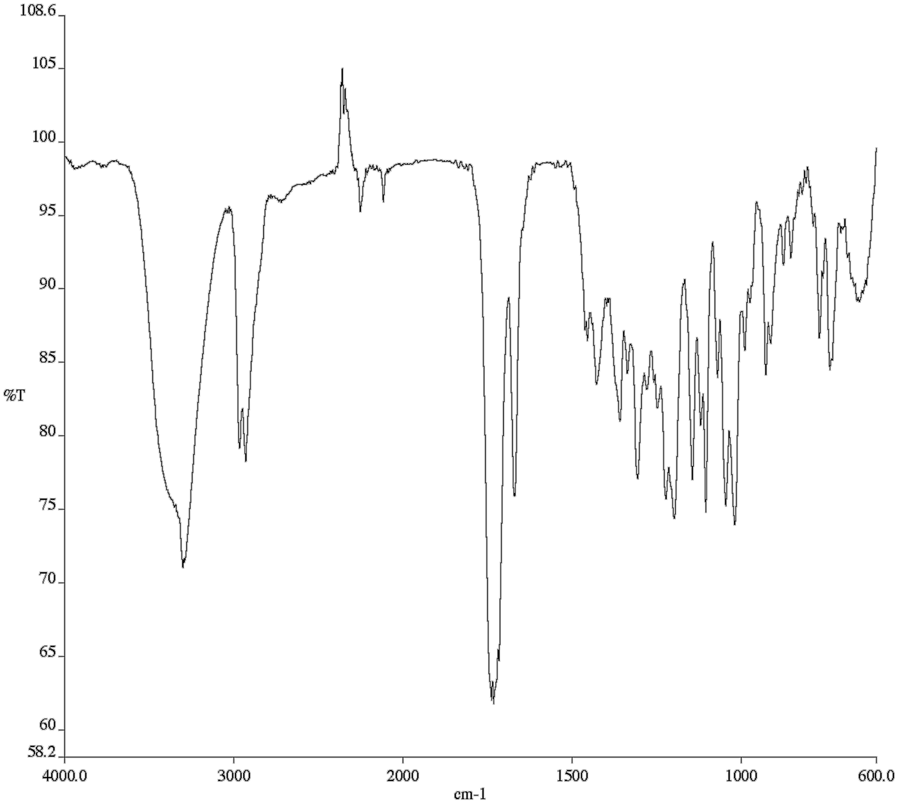


^{13}C NMR (100 MHz, CDCl$_3$) of compound **S2.**

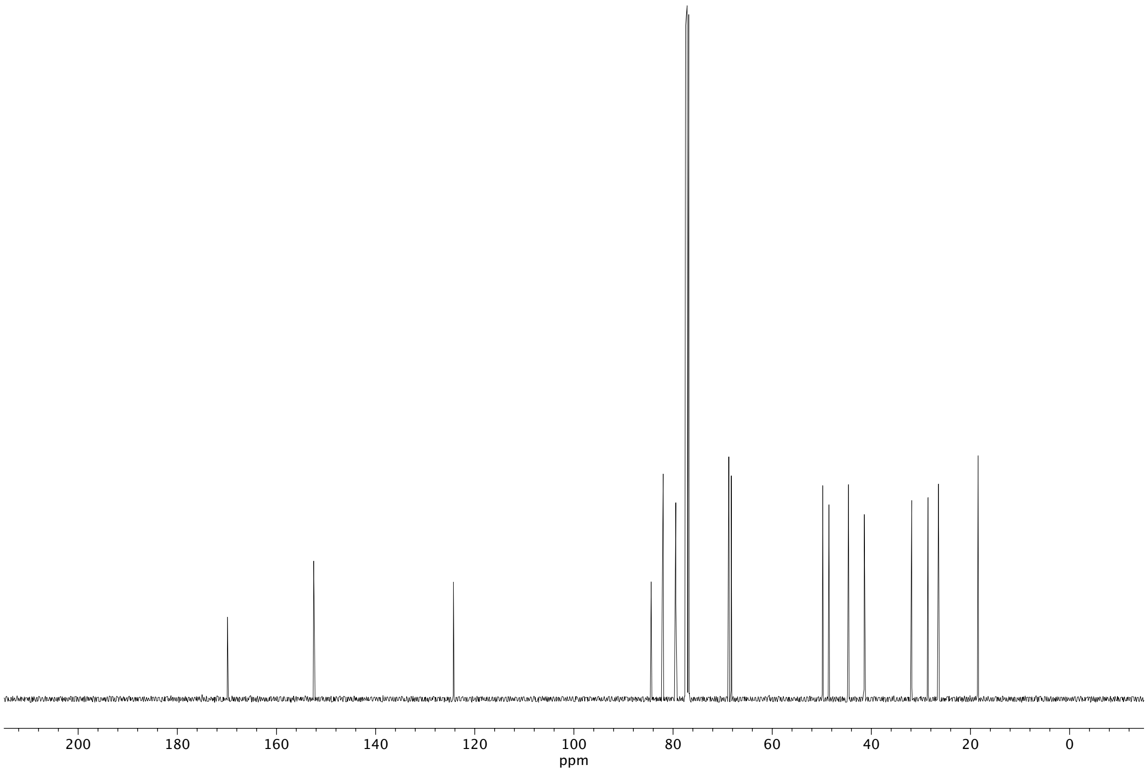


60

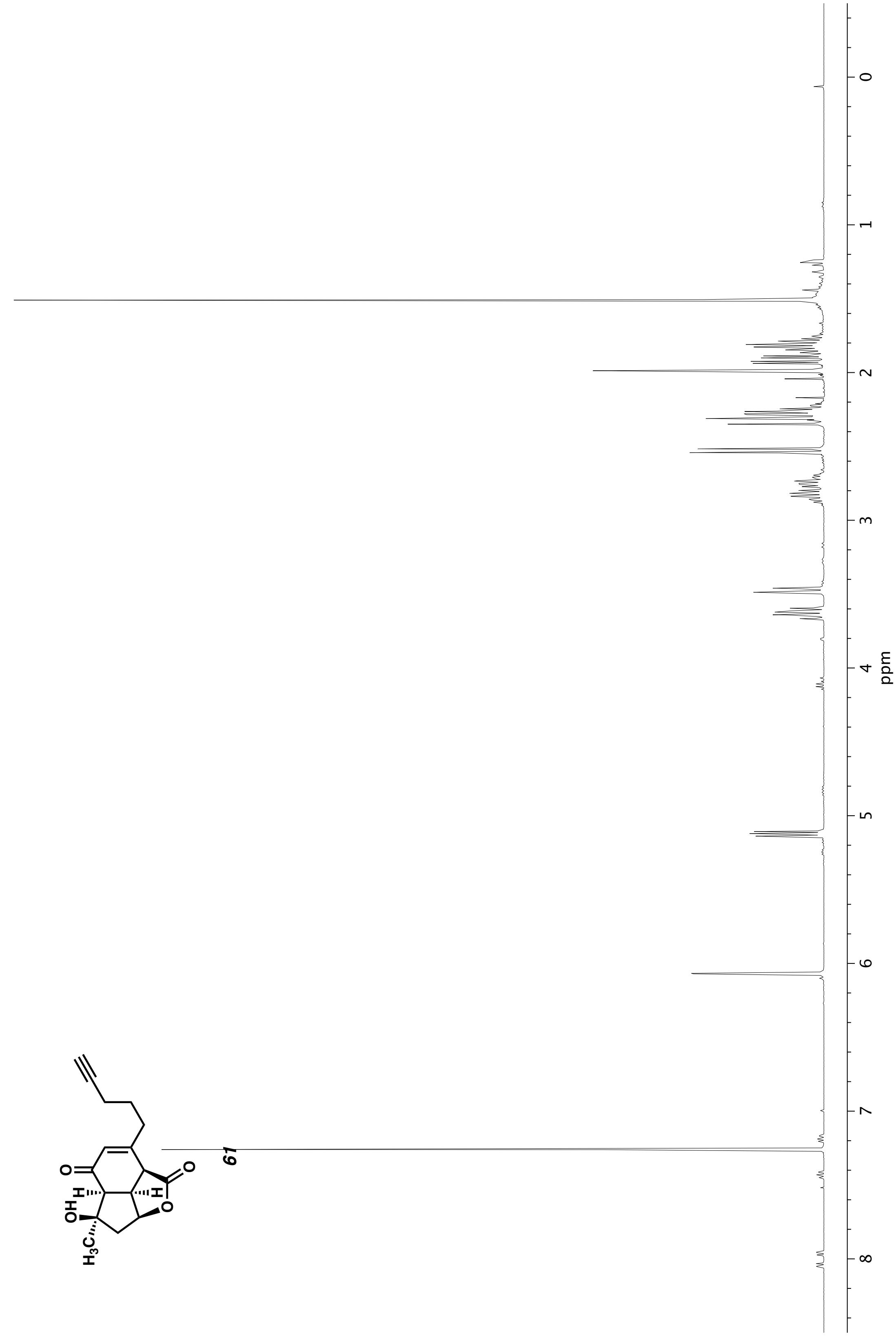
^{1}H NMR (400 MHz, CDCl$_3$) of compound **60**.



Infrared spectrum (Thin Film, NaCl) of compound **60**.

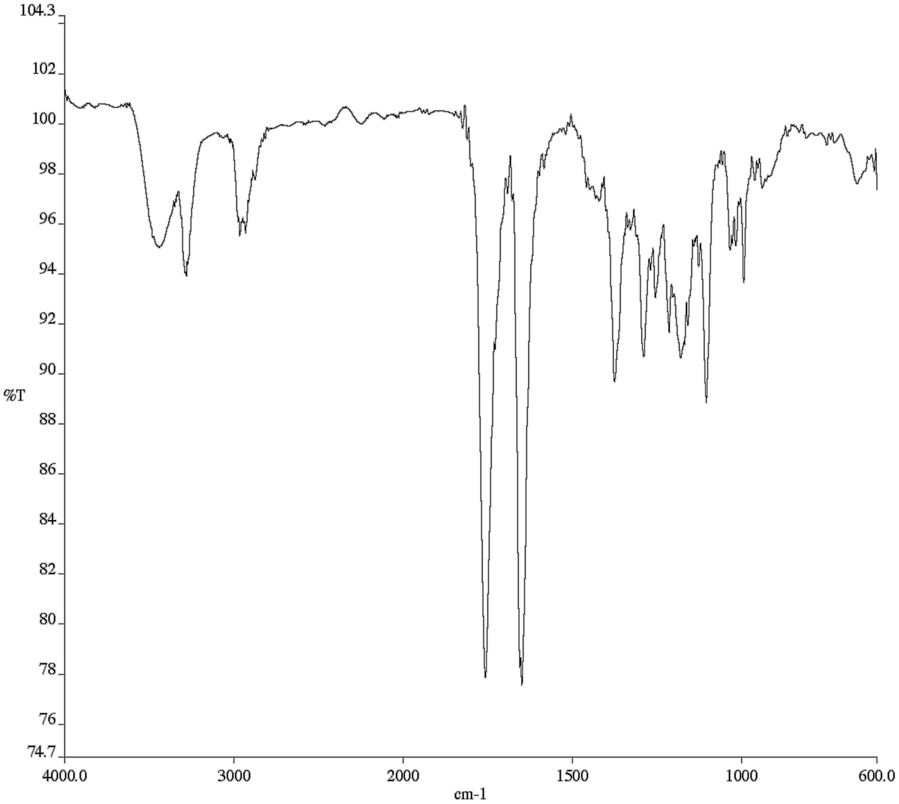


^{13}C NMR (100 MHz, CDCl$_3$) of compound **60.**

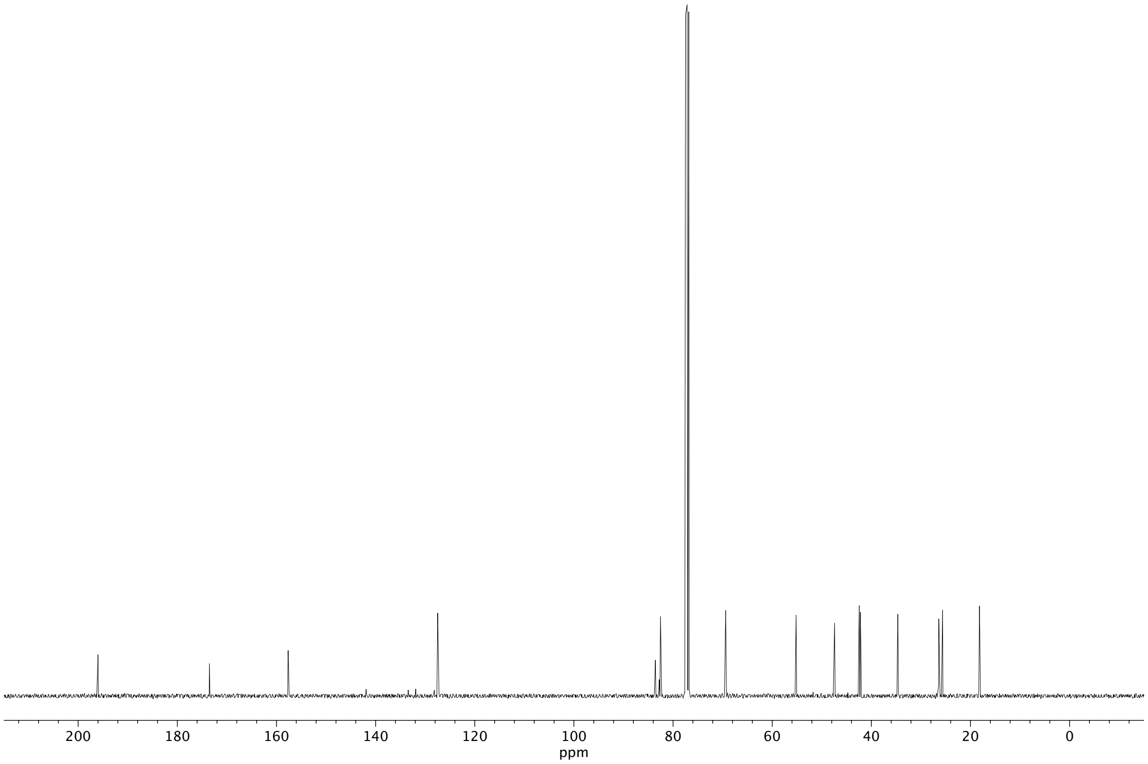


61

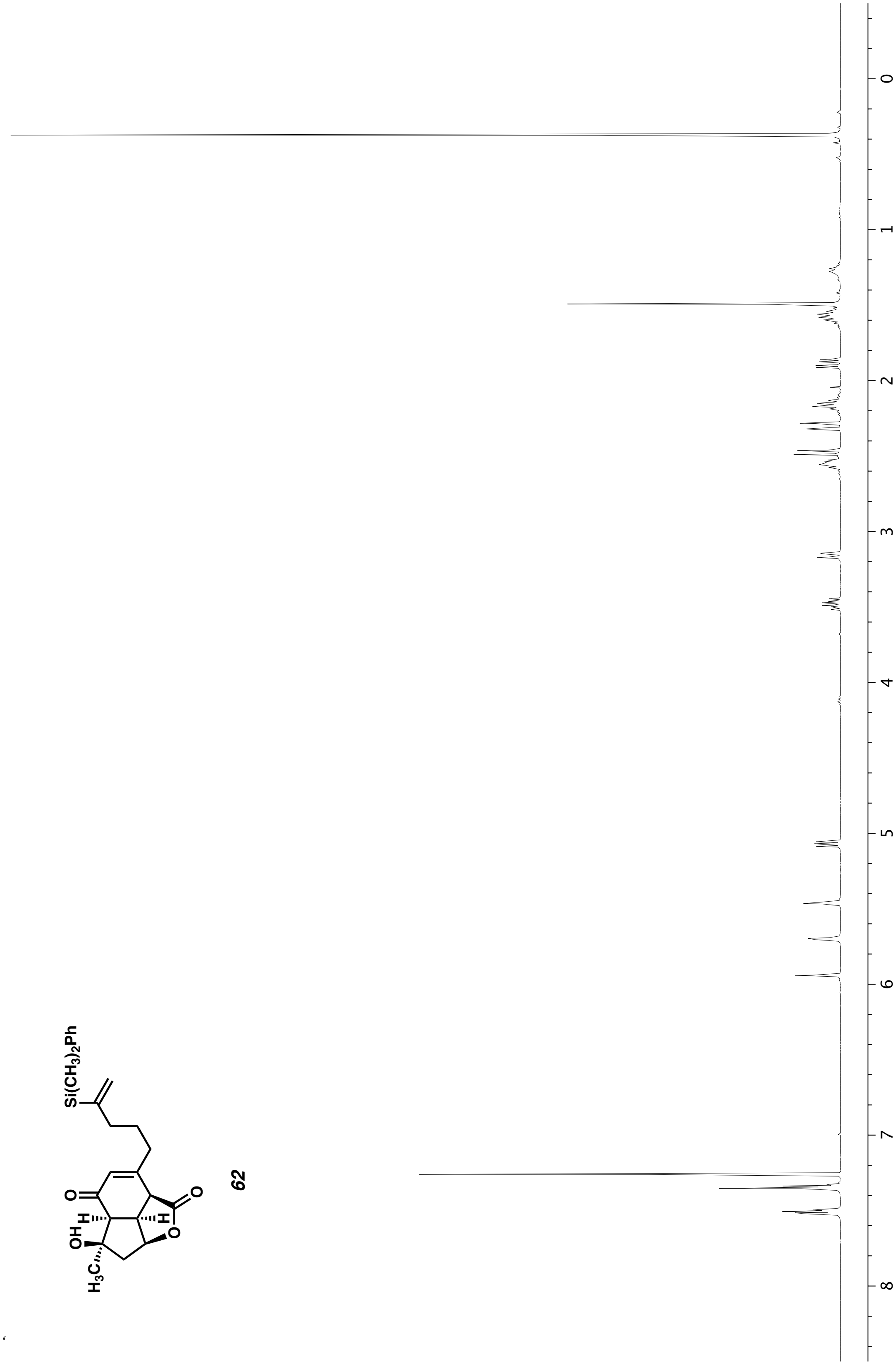
^{1}H NMR (400 MHz, CDCl$_3$) of compound **61**.



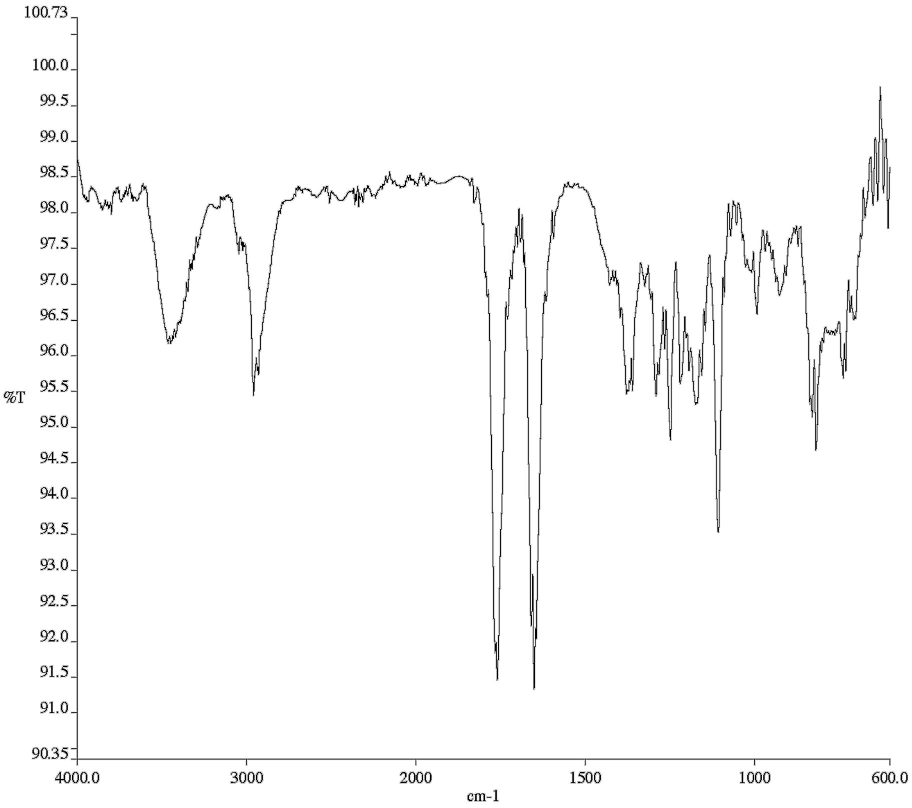
Infrared spectrum (Thin Film, NaCl) of compound **61**.



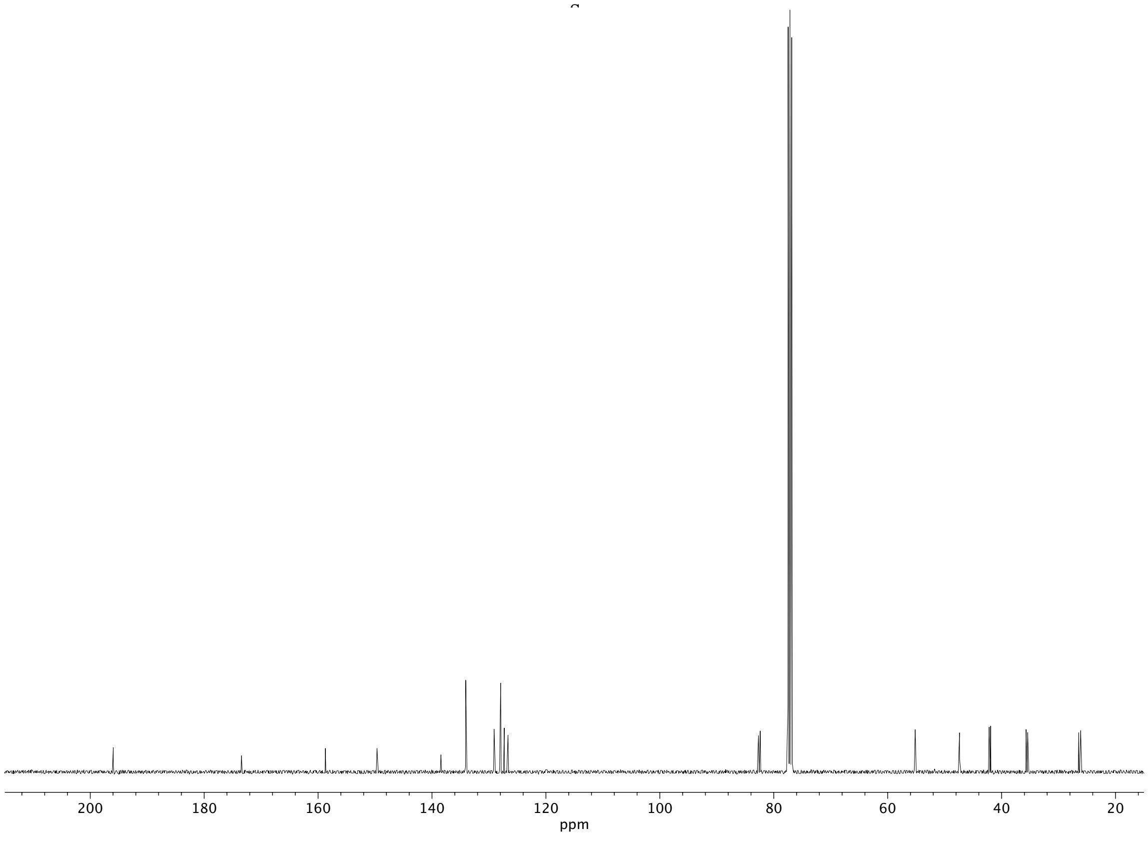
^{13}C NMR (100 MHz, CDCl$_3$) of compound **61.**



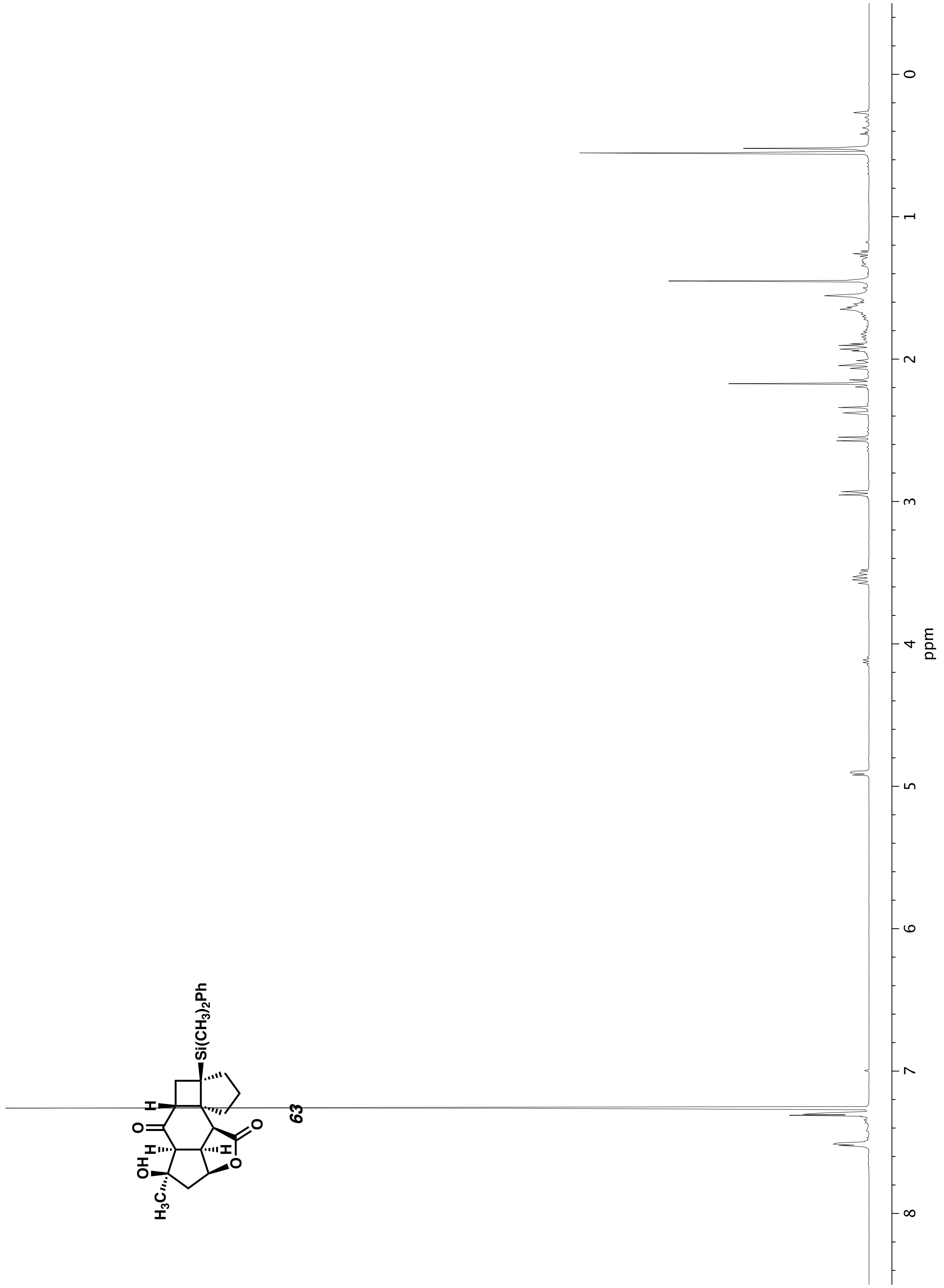
^{1}H NMR (400 MHz, CDCl$_3$) of compound **62**.



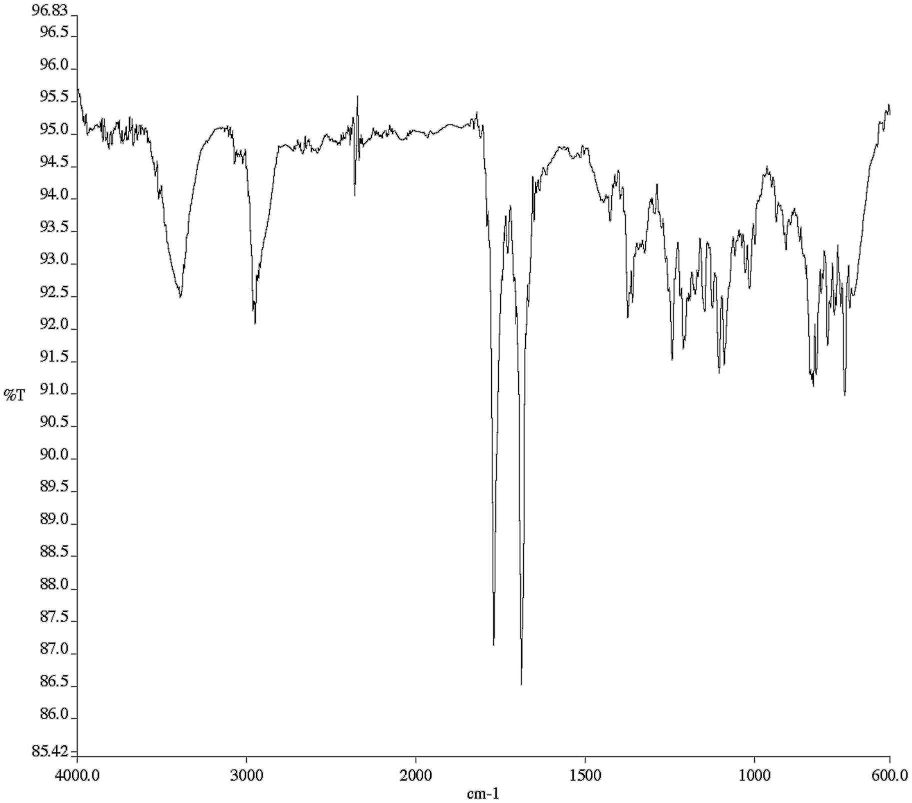
Infrared spectrum (Thin Film, NaCl) of compound **62**.



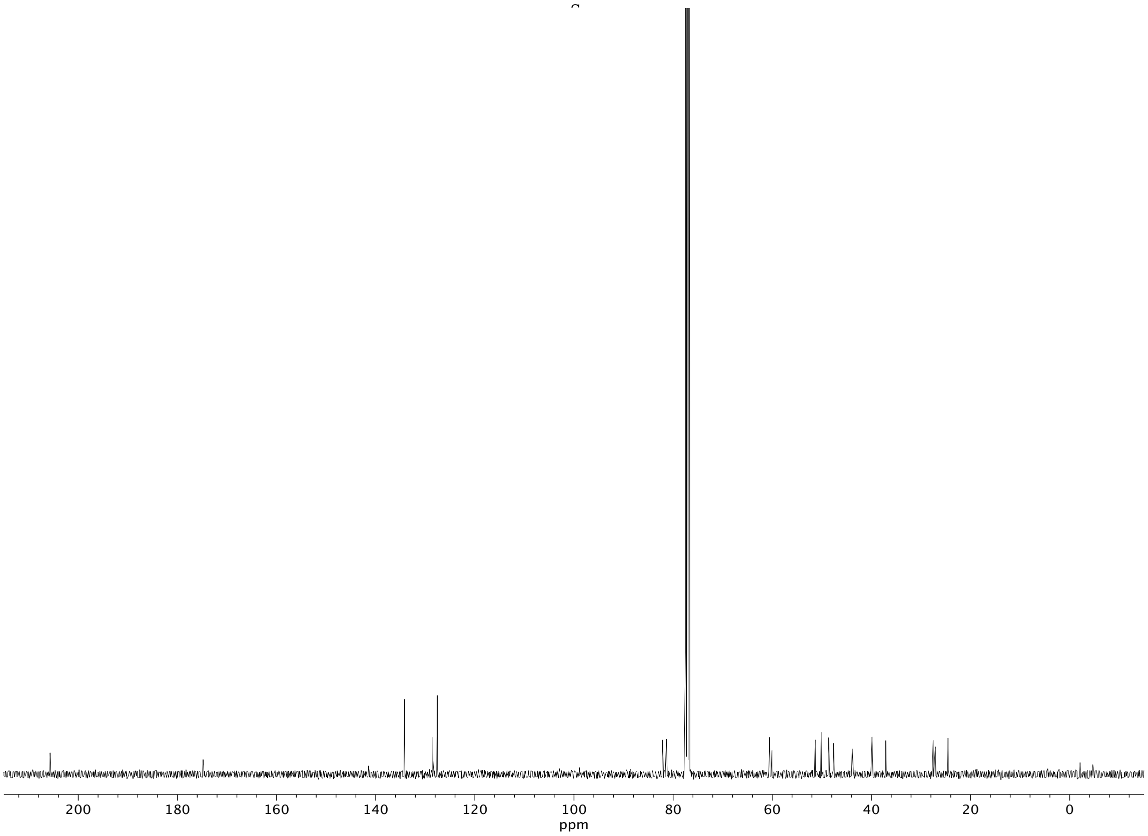
^{13}C NMR (100 MHz, CDCl$_3$) of compound **62.**



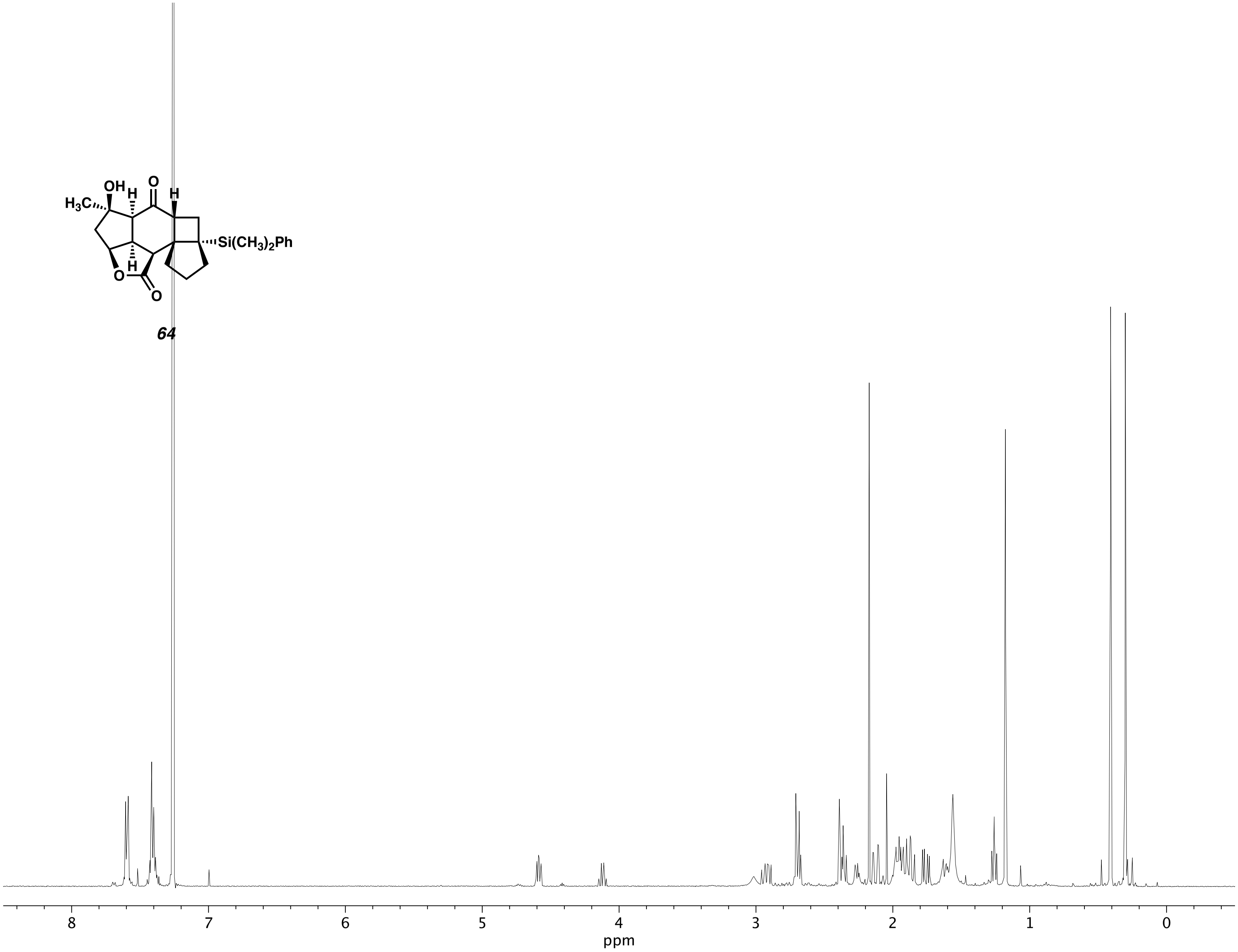
^{1}H NMR (400 MHz, CDCl$_3$) of compound **63**.



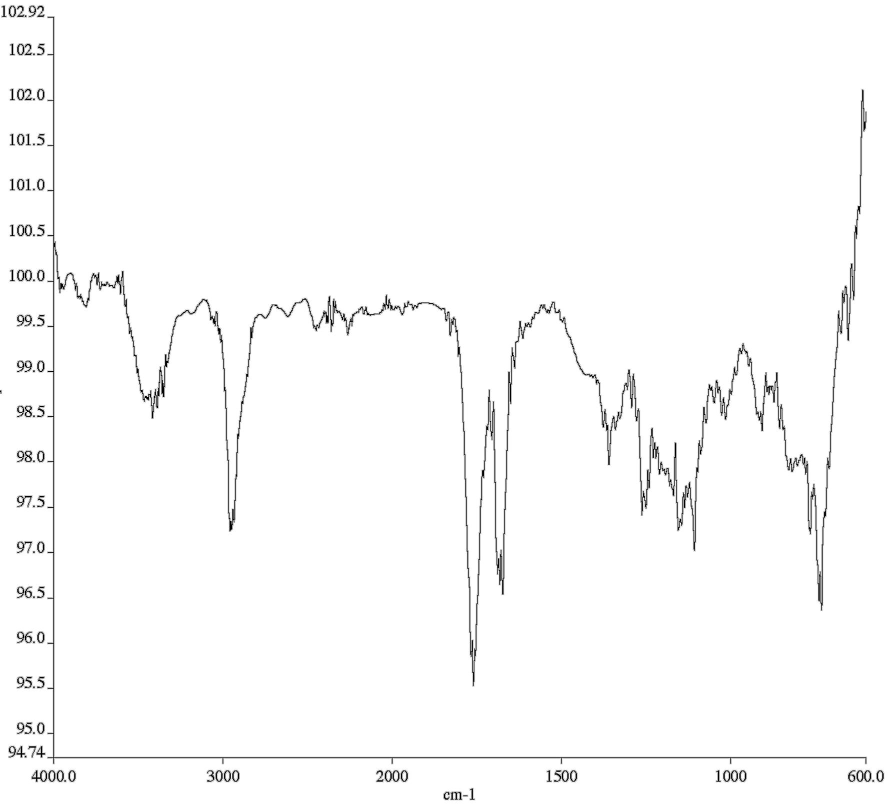
Infrared spectrum (Thin Film, NaCl) of compound **63**.



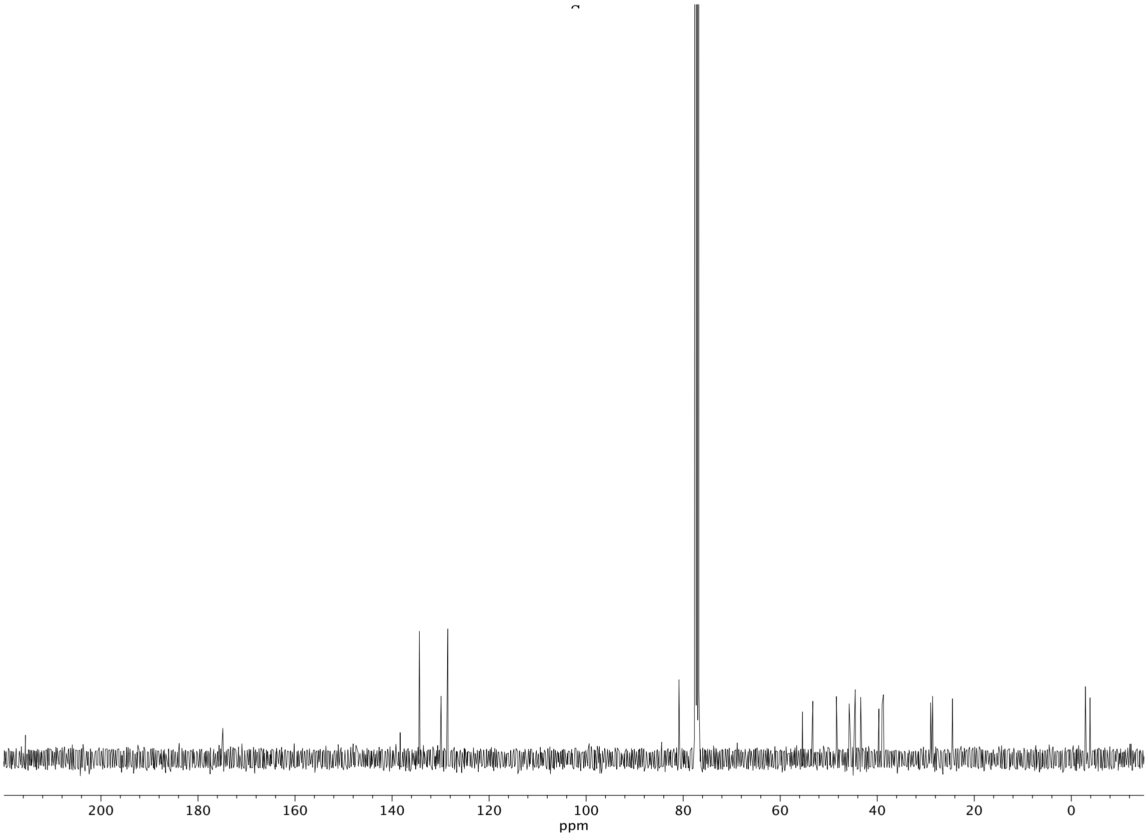
^{13}C NMR (100 MHz, CDCl$_3$) of compound **63.**



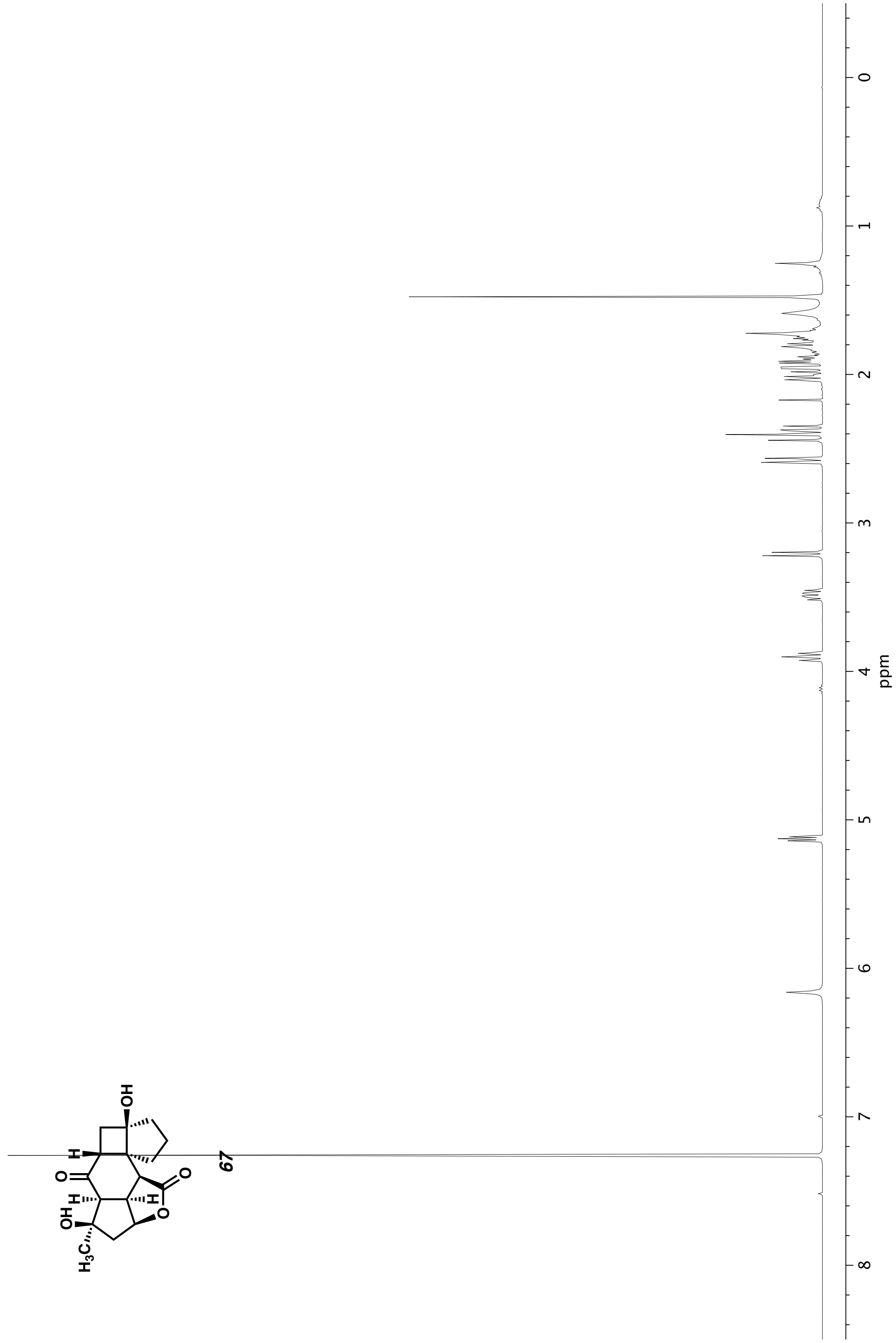
^{1}H NMR (400 MHz, CDCl$_3$) of compound **64**.



Infrared spectrum (Thin Film, NaCl) of compound **64**.

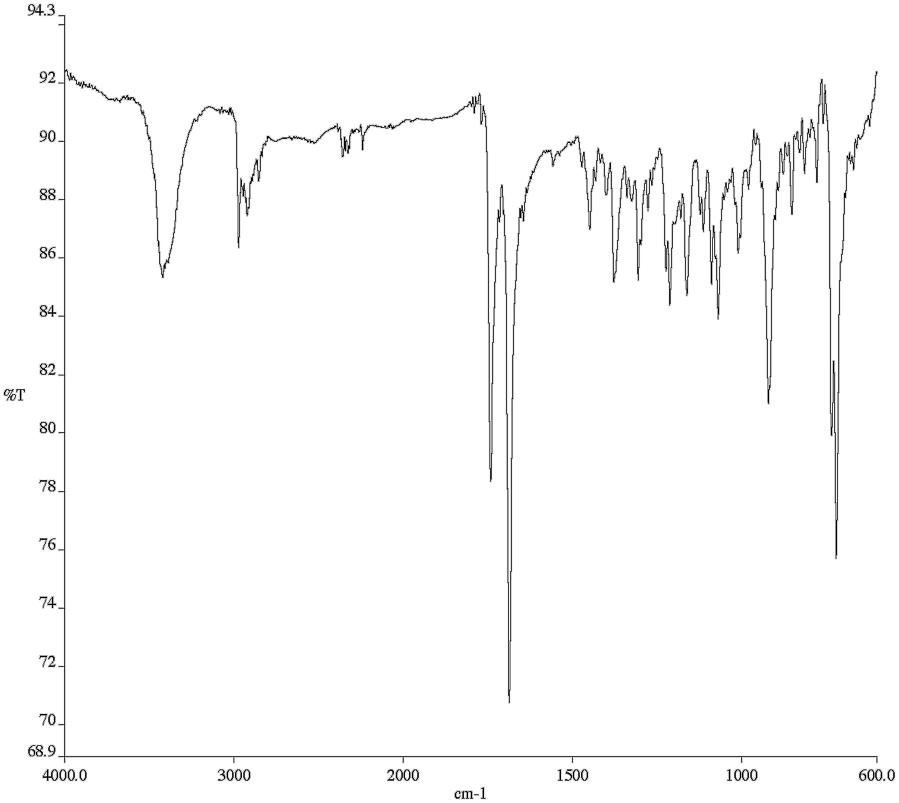


^{13}C NMR (100 MHz, $CDCl_3$) of compound **64.**

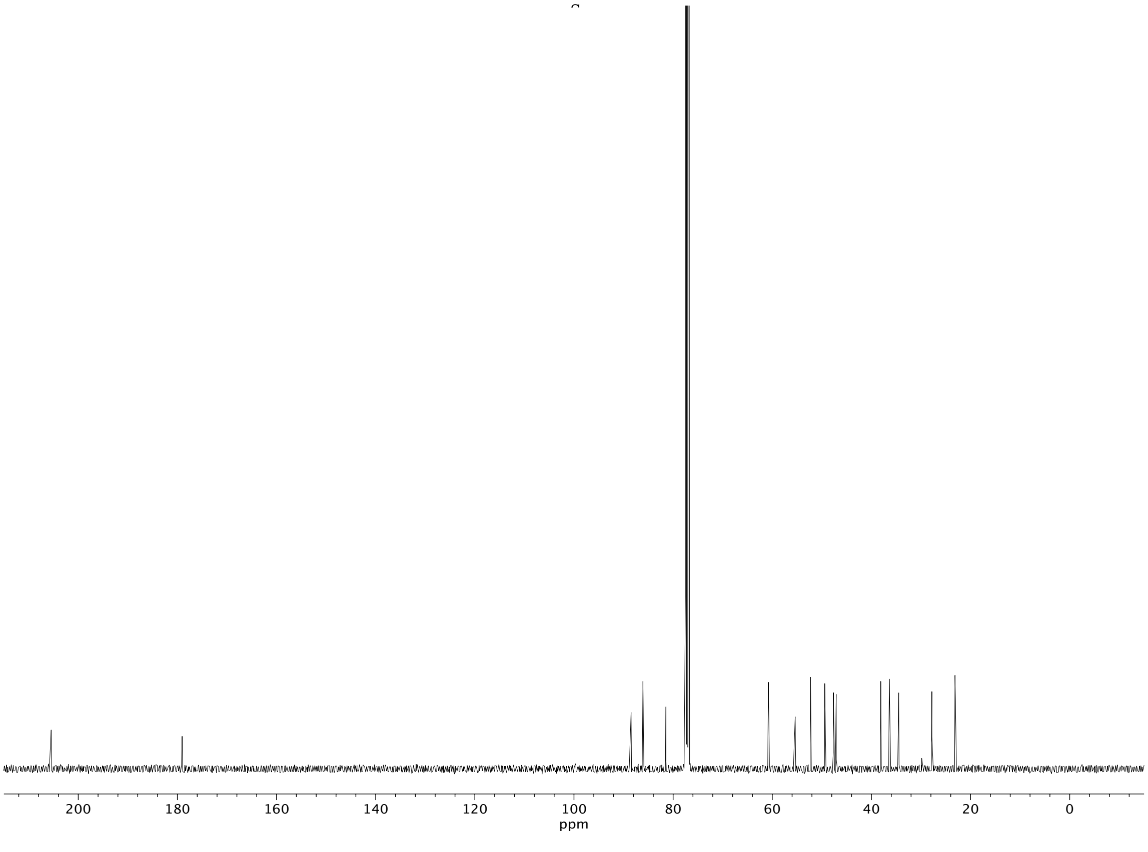


67

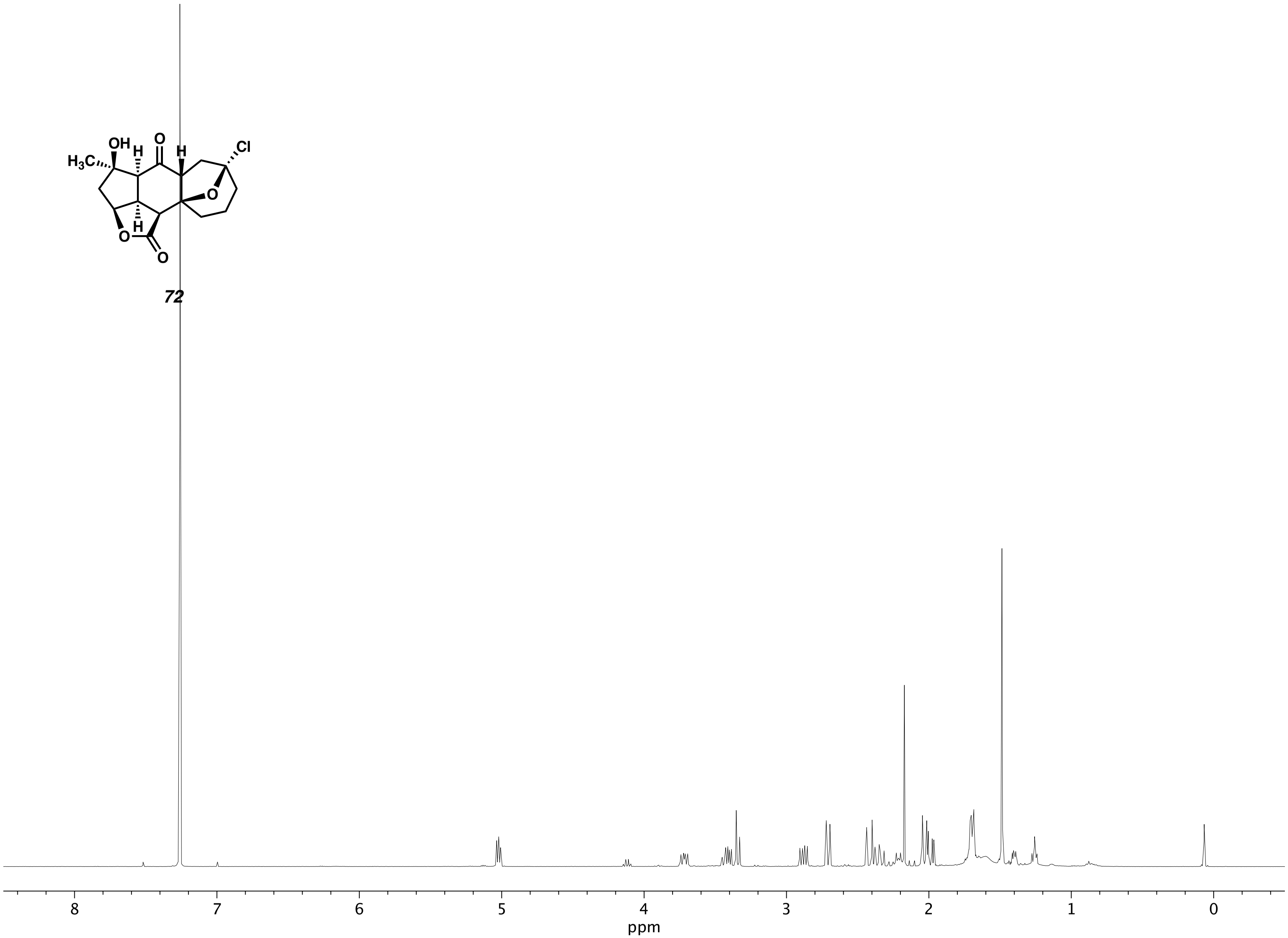
^{1}H NMR (400 MHz, CDCl$_3$) of compound **67**.



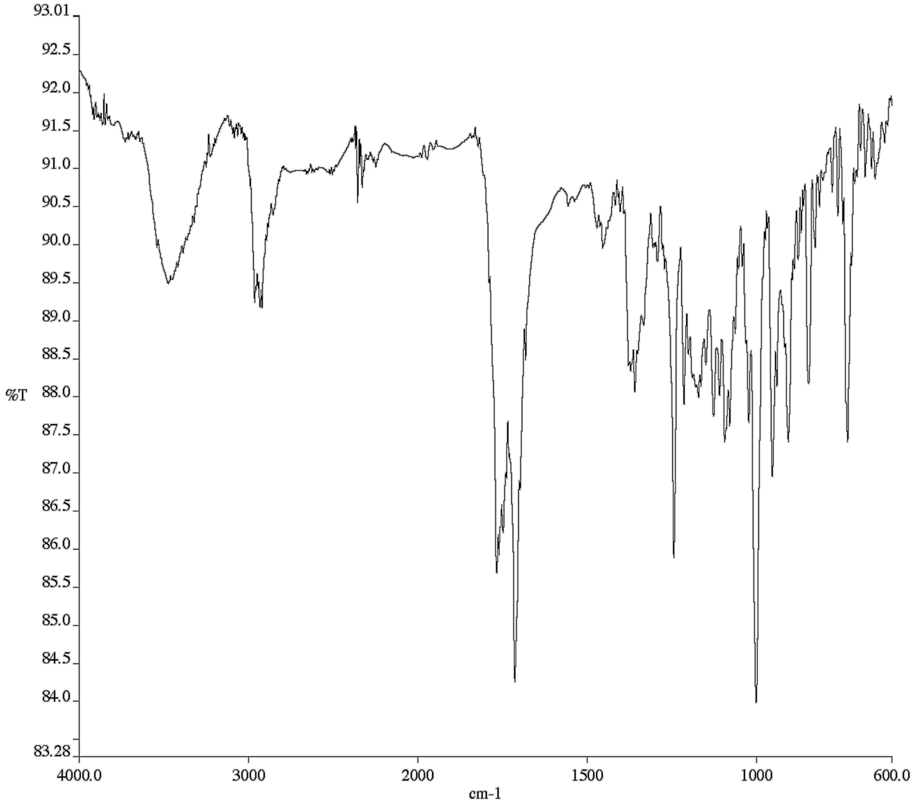
Infrared spectrum (Thin Film, NaCl) of compound **67**.



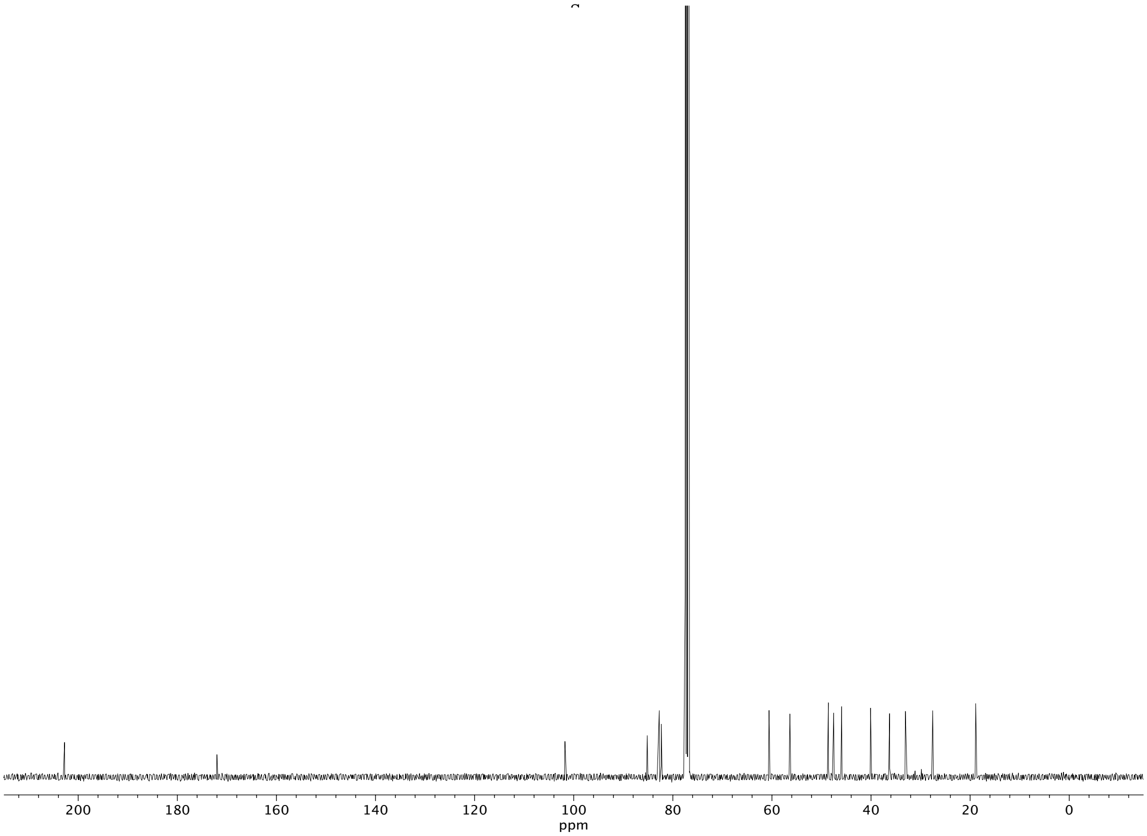
^{13}C NMR (100 MHz, CDCl$_3$) of compound **67.**



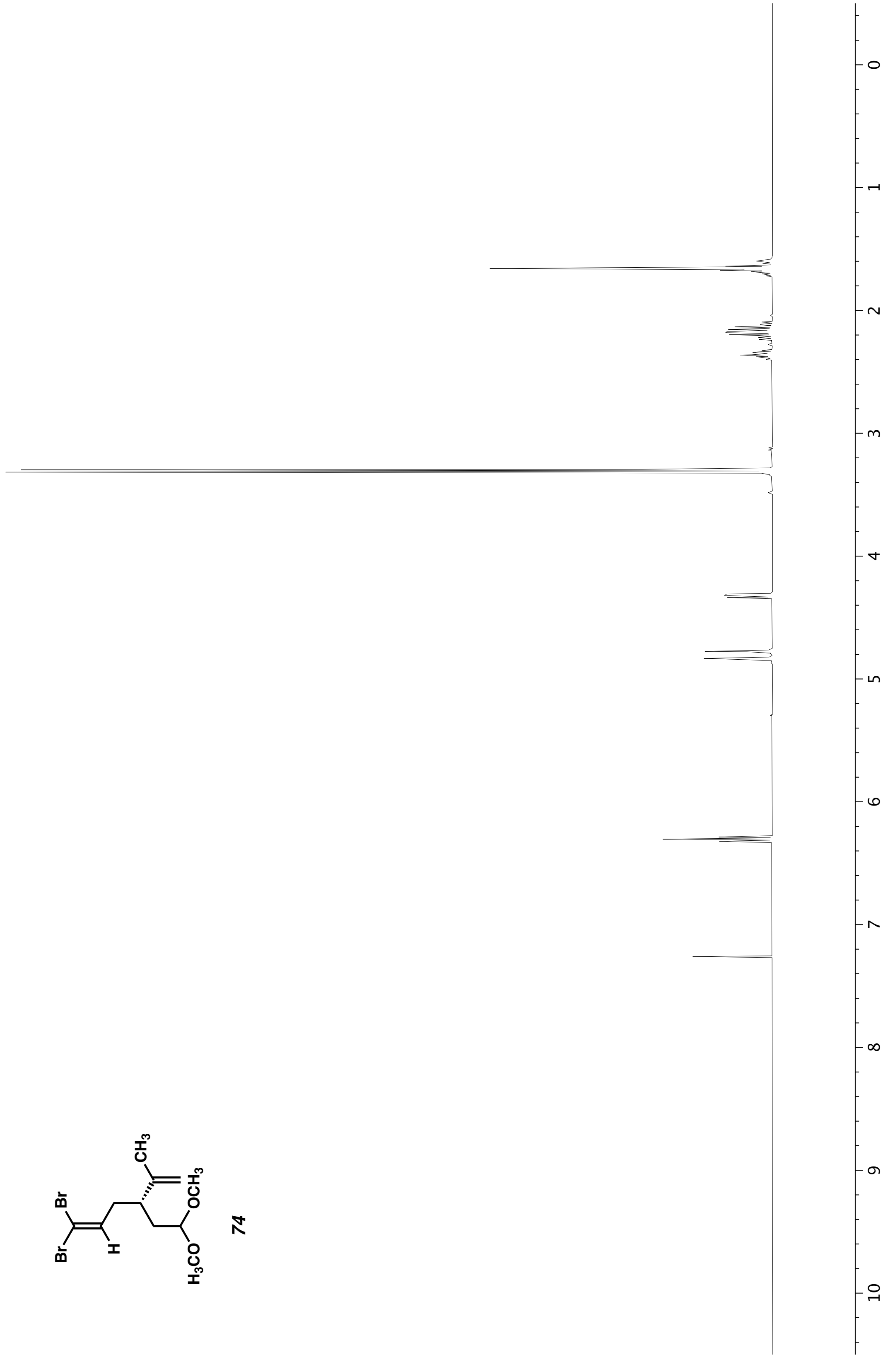
^{1}H NMR (400 MHz, CDCl$_3$) of compound **72**.



Infrared spectrum (Thin Film, NaCl) of compound **72**.

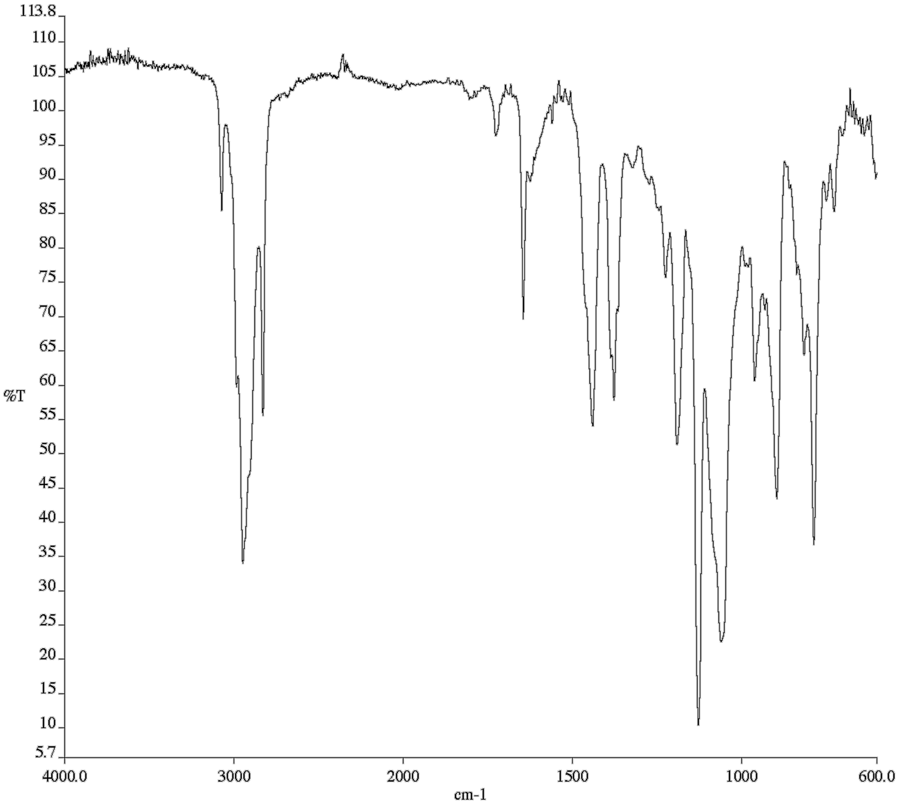


^{13}C NMR (100 MHz, CDCl$_3$) of compound **72.**

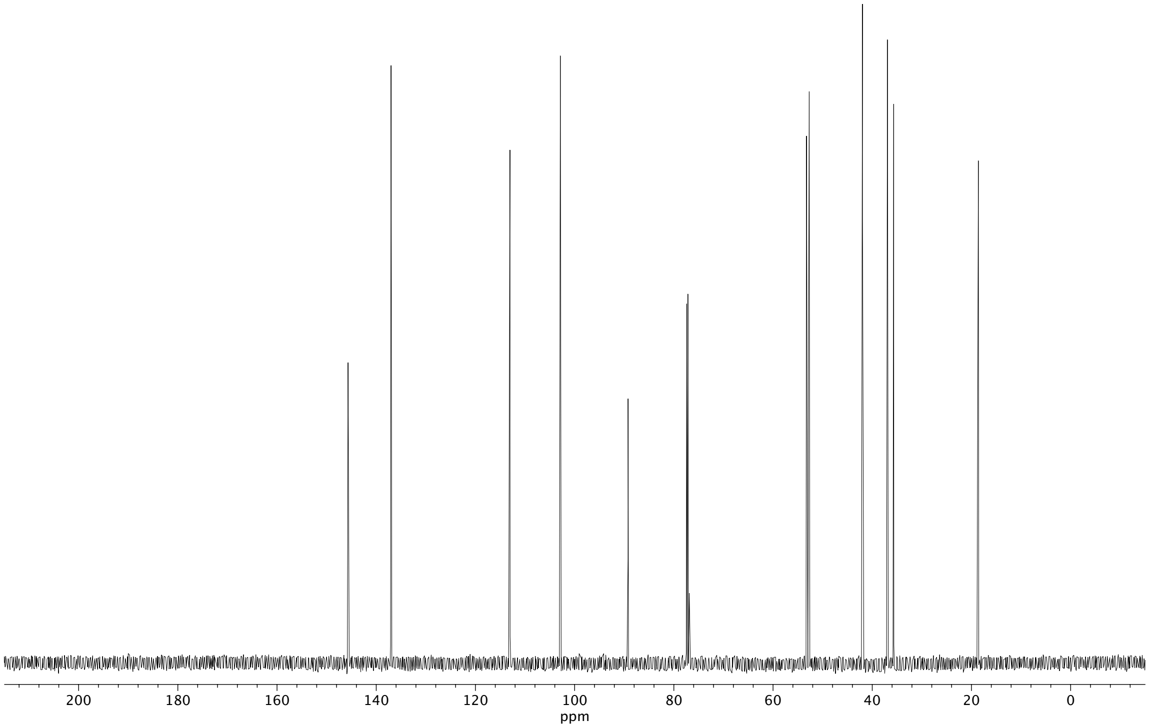


74

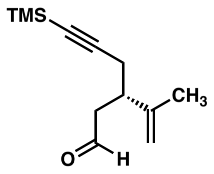
^{1}H NMR (400 MHz, CDCl$_3$) of compound **74**.



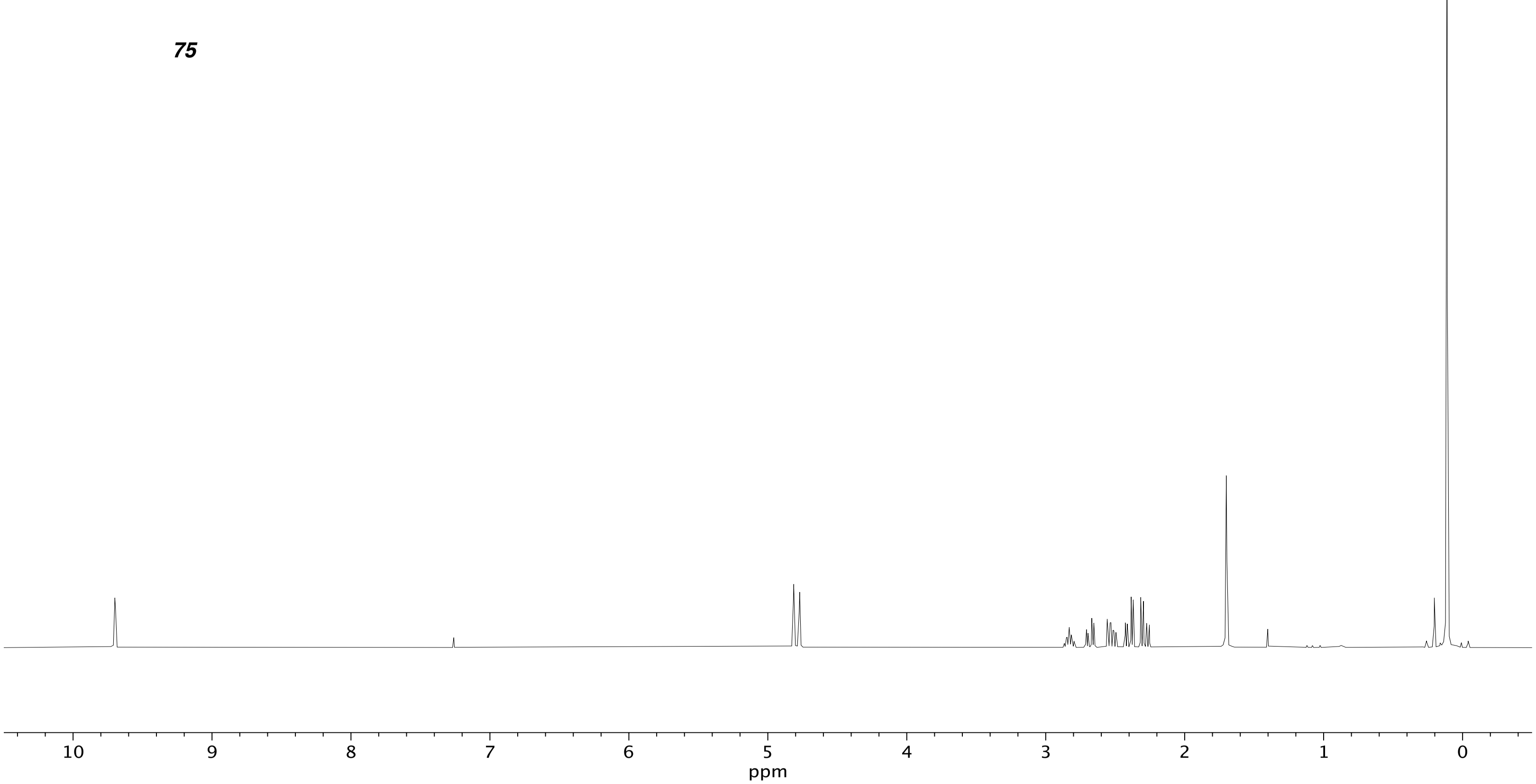
Infrared spectrum (Thin Film, NaCl) of compound **74**.



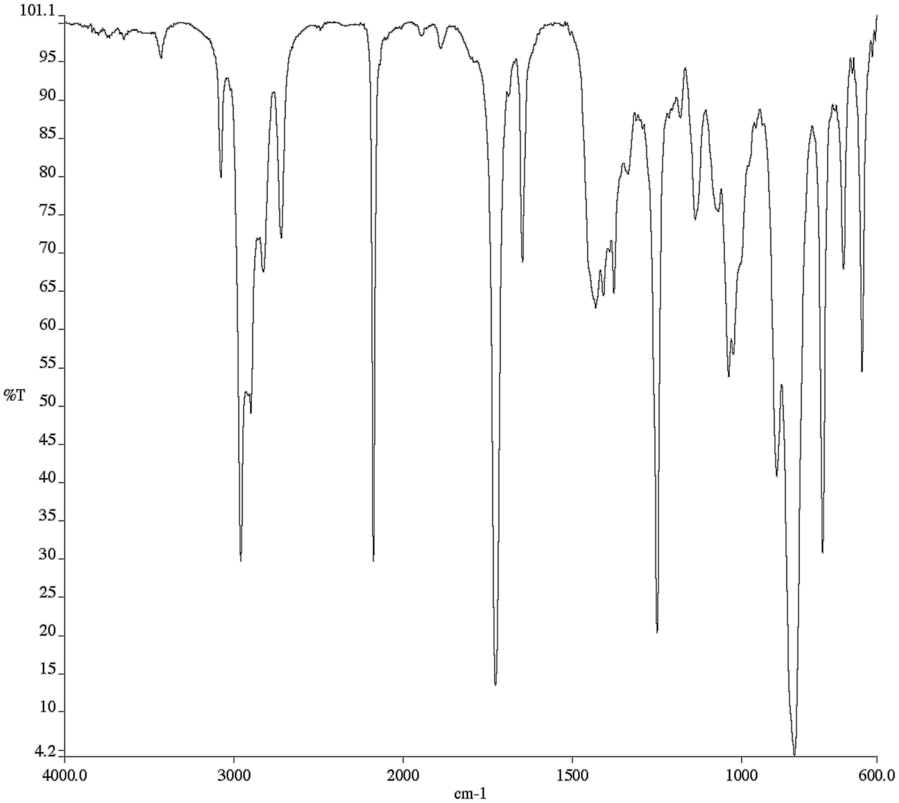
^{13}C NMR (100 MHz, CDCl$_3$) of compound **74.**



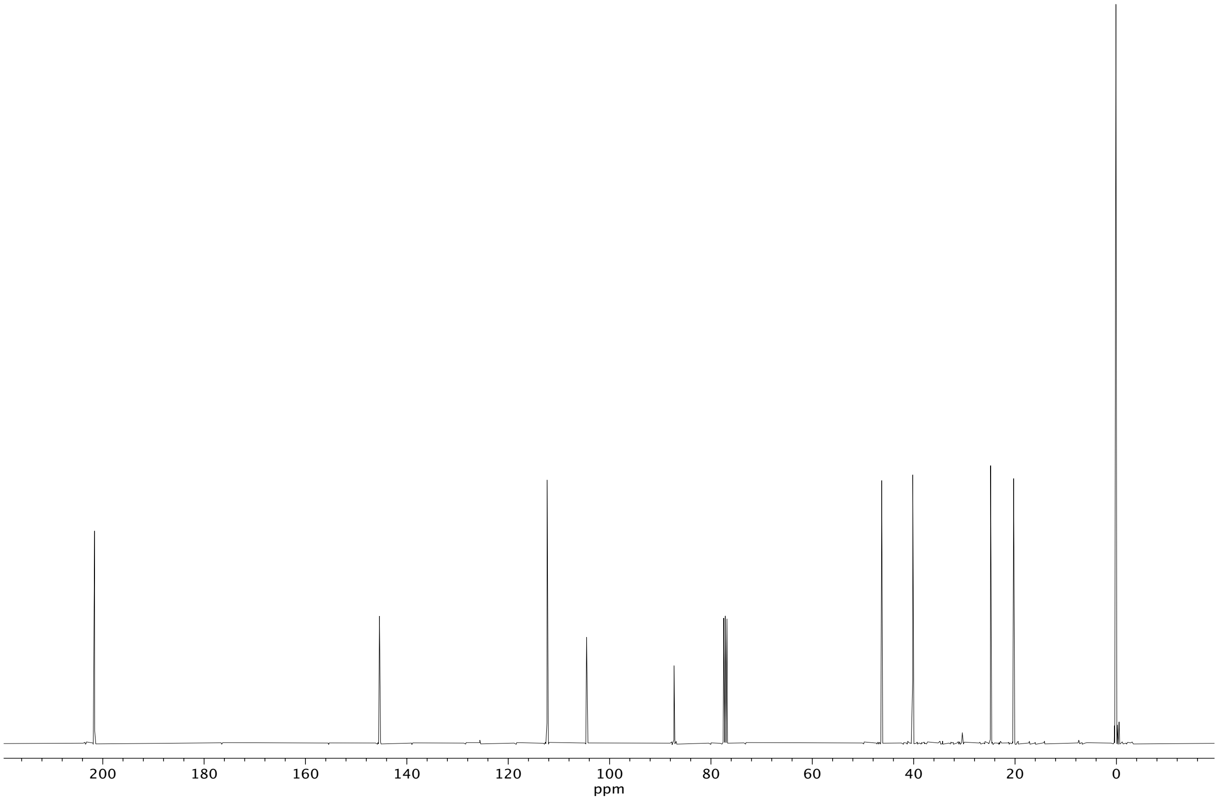
75



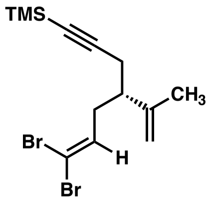
^{1}H NMR (400 MHz, CDCl$_3$) of compound **75**.



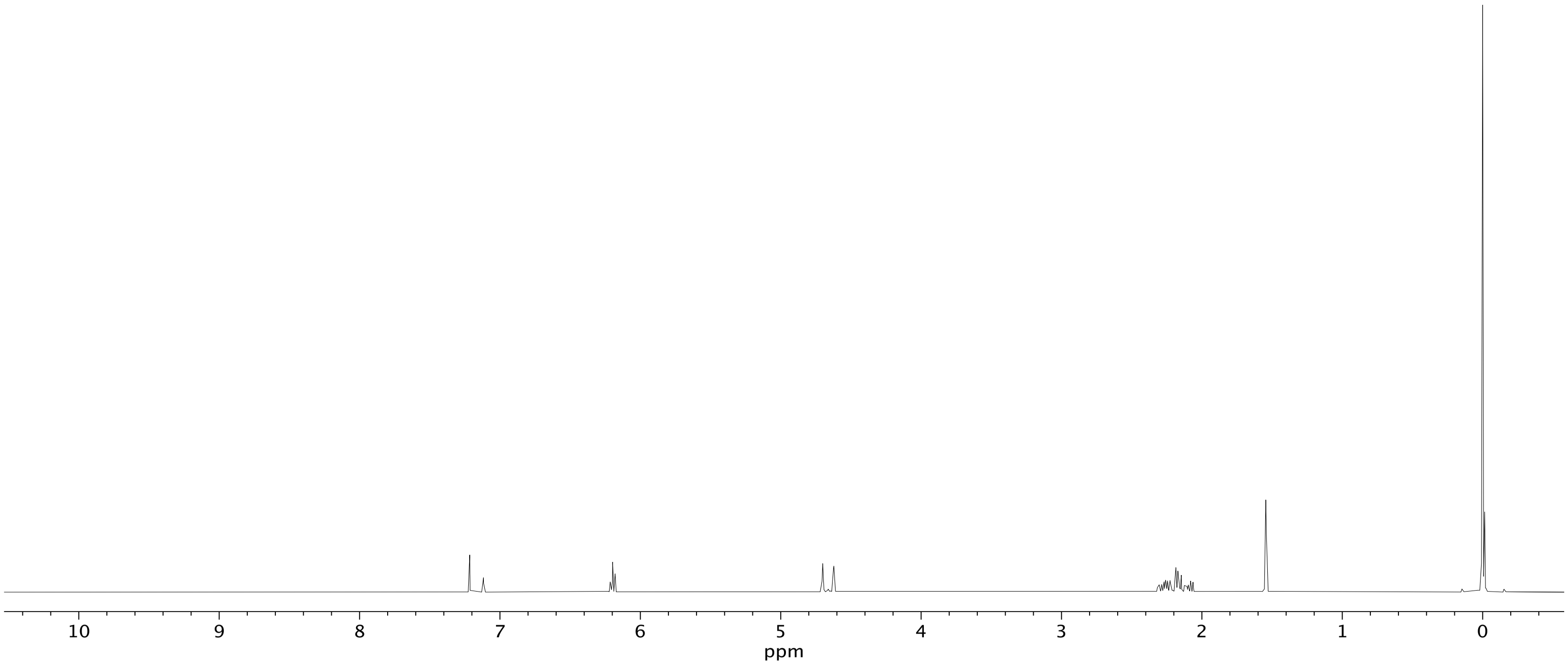
Infrared spectrum (Thin Film, NaCl) of compound **75**.



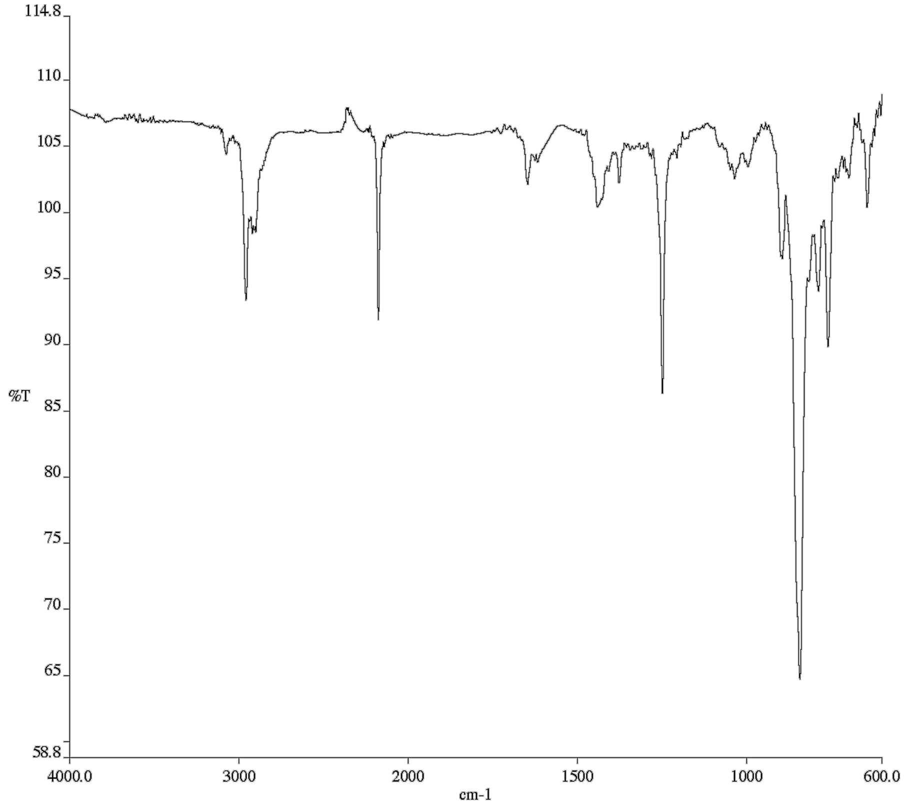
^{13}C NMR (100 MHz, CDCl$_3$) of compound **75.**



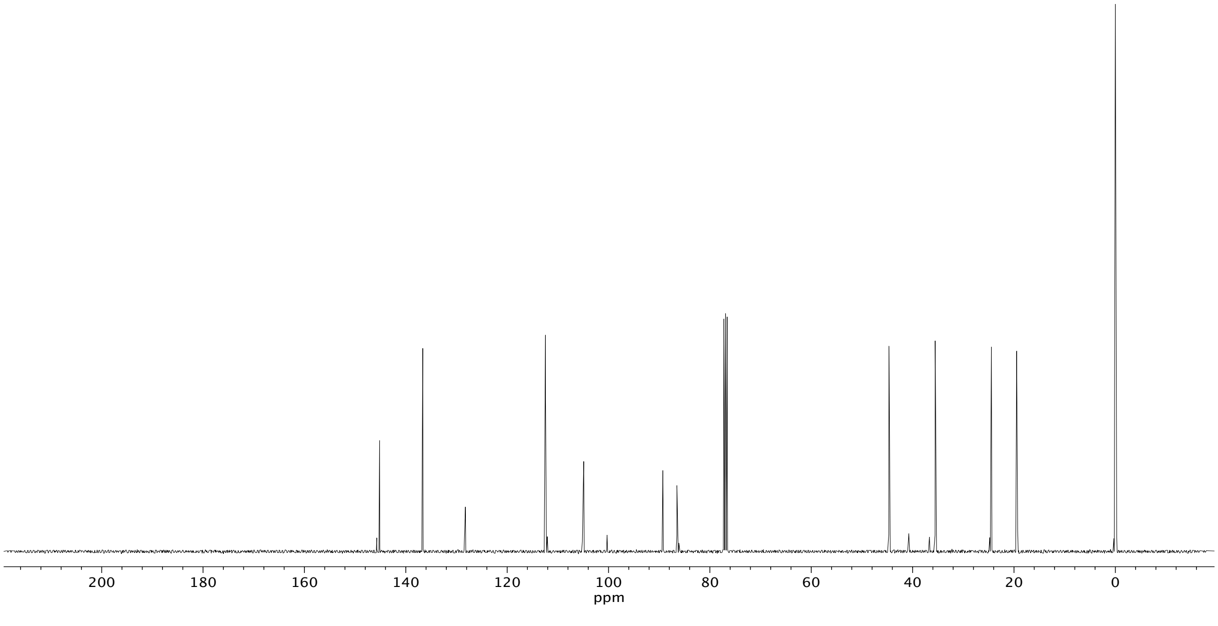
76



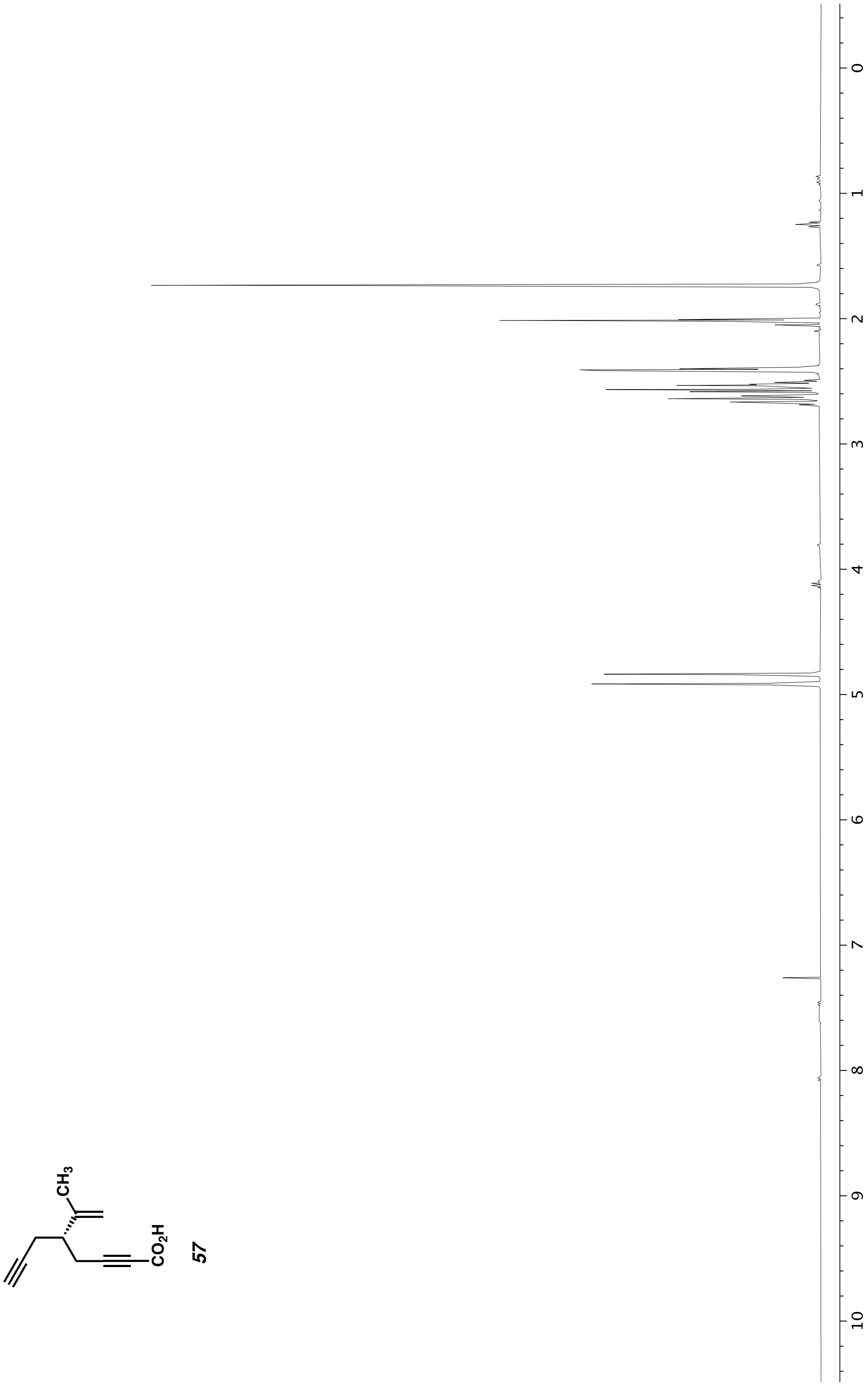
^{1}H NMR (400 MHz, CDCl$_3$) of compound **76**.



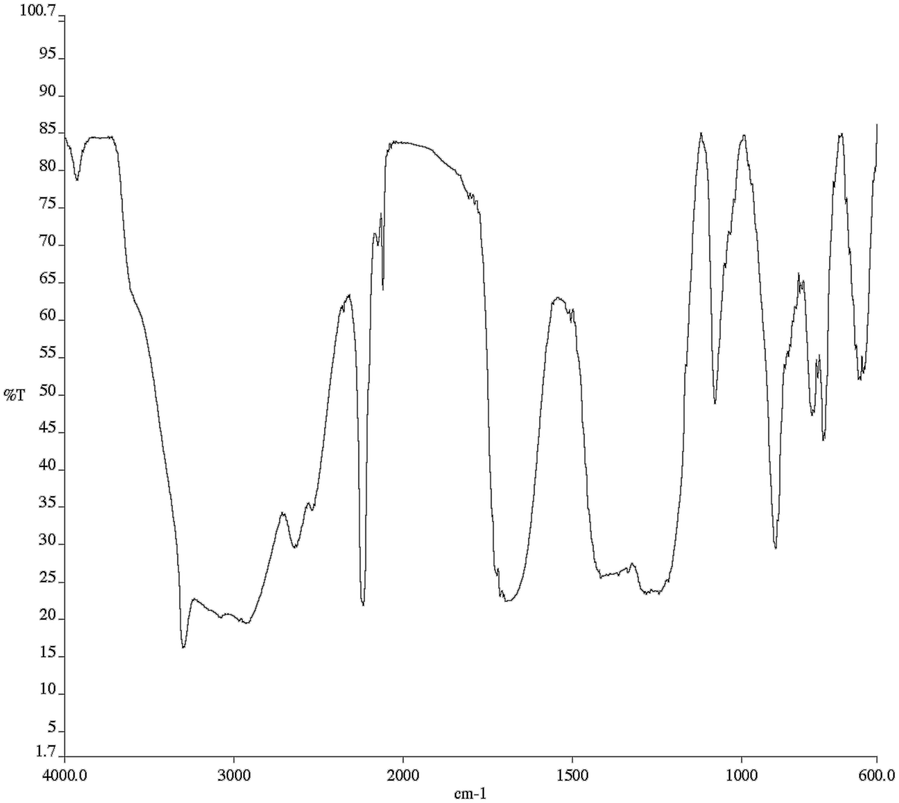
Infrared spectrum (Thin Film, NaCl) of compound **76.**



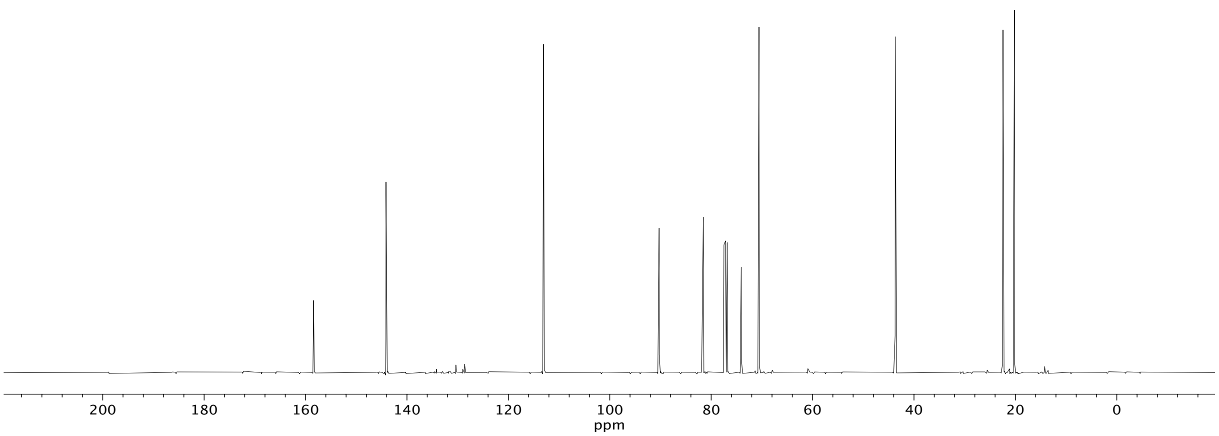
^{13}C NMR (100 MHz, CDCl$_3$) of compound **76.**



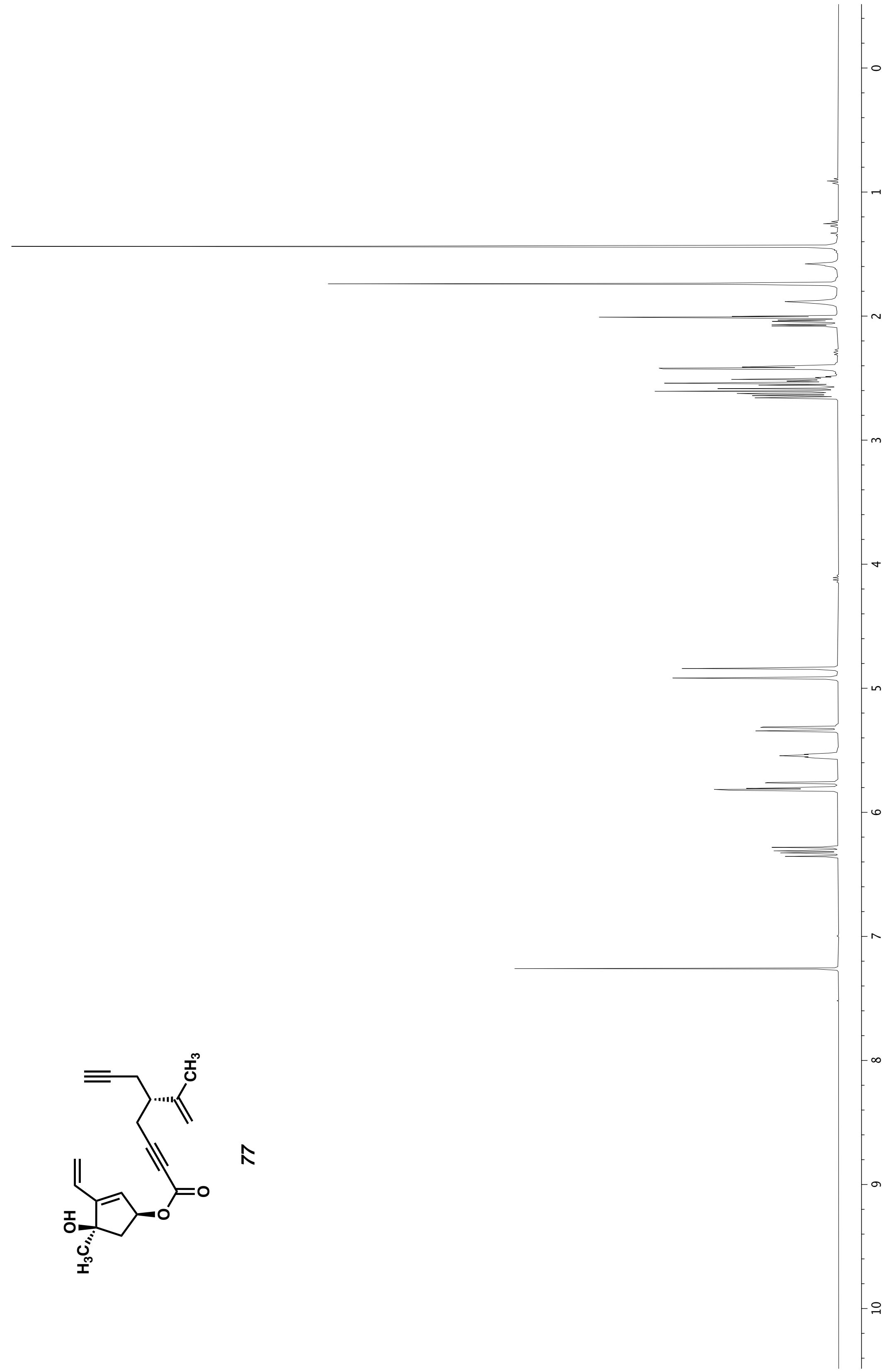
^{1}H NMR (400 MHz, CDCl$_3$) of compound **57**.



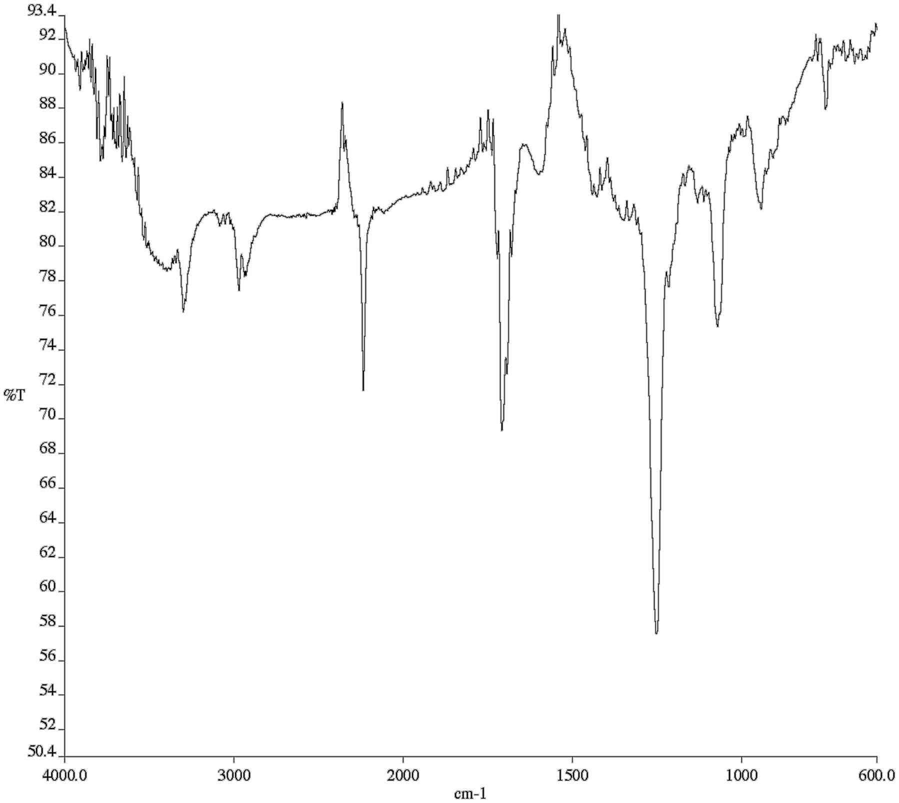
Infrared spectrum (Thin Film, NaCl) of compound **57.**



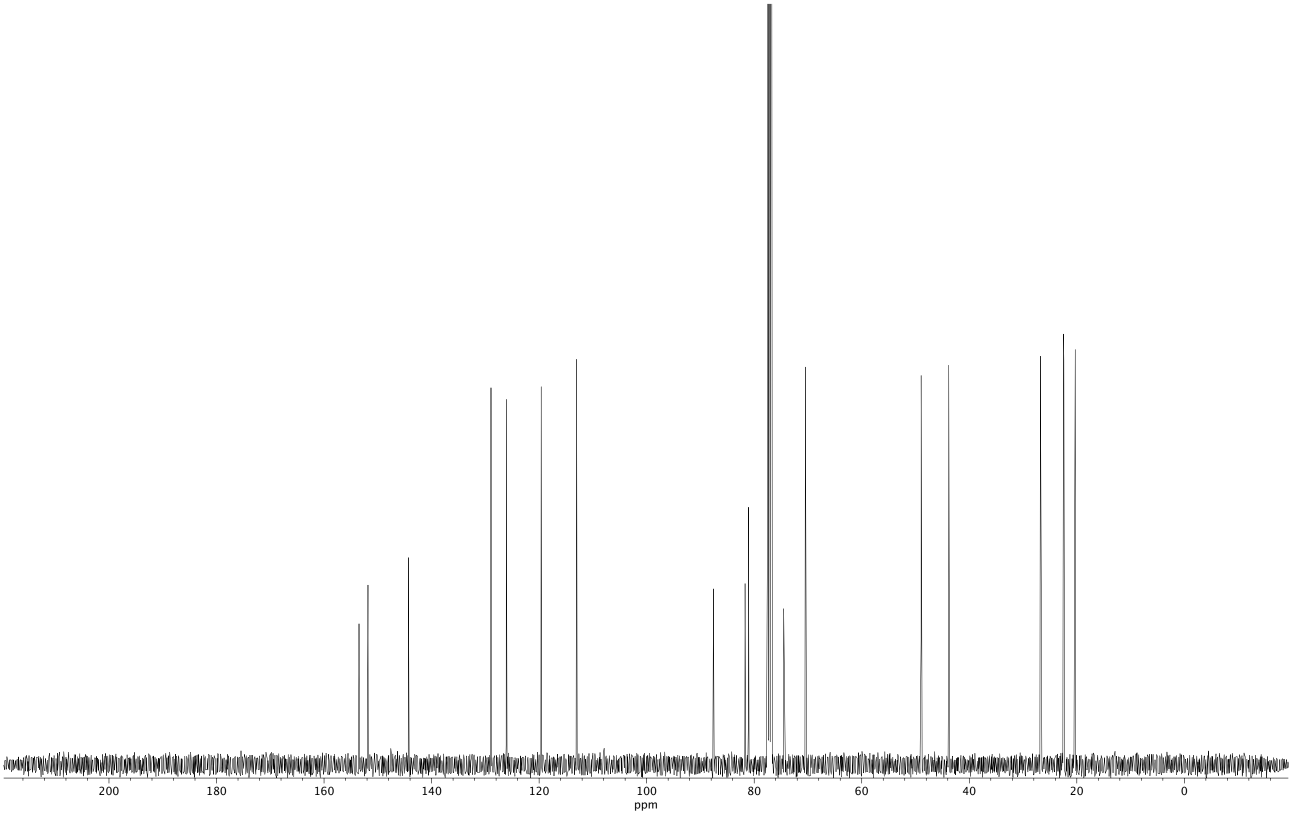
^{13}C NMR (100 MHz, CDCl$_3$) of compound **57.**



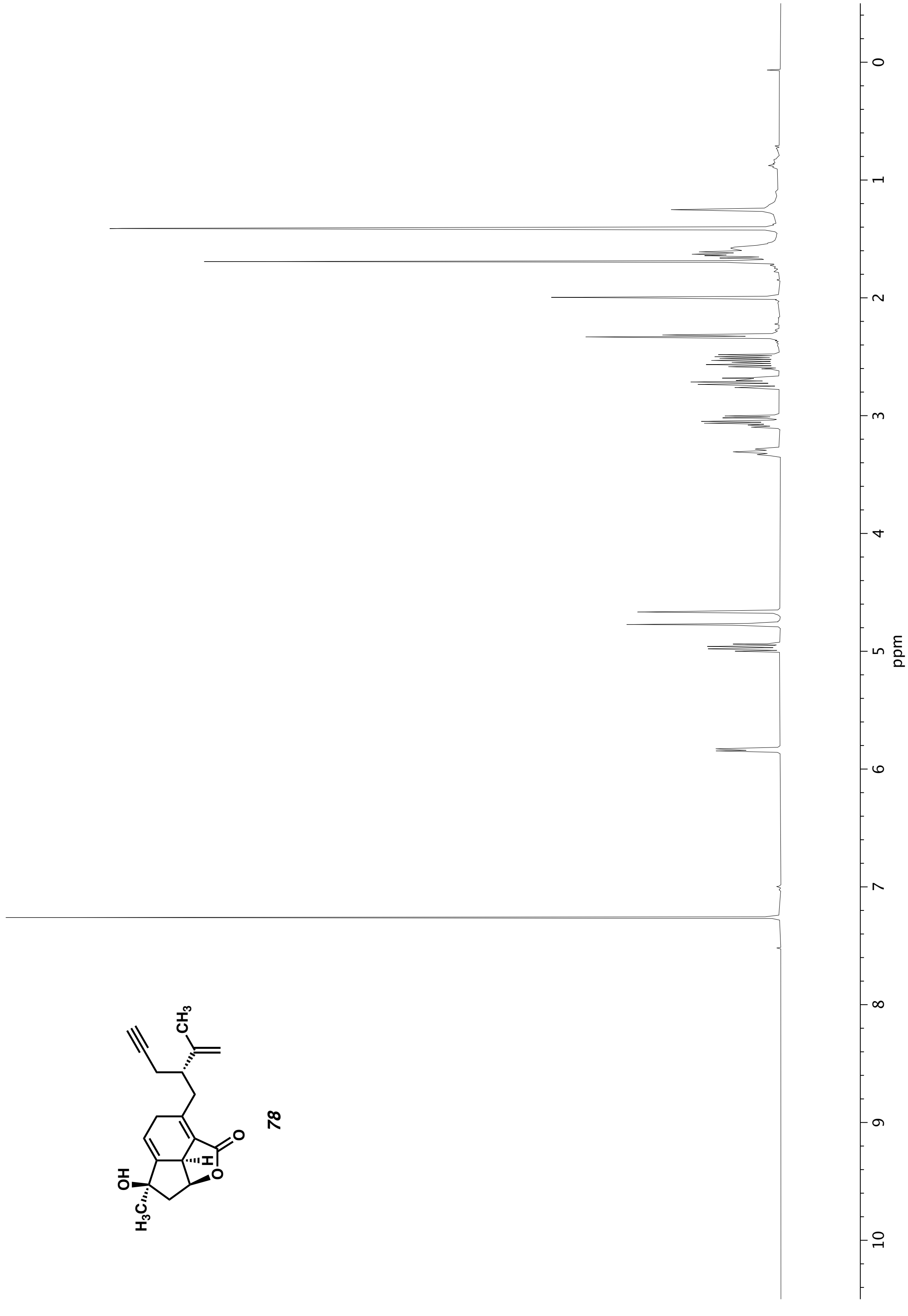
^{1}H NMR (400 MHz, CDCl$_3$) of compound **77**.



Infrared spectrum (Thin Film, NaCl) of compound **77.**

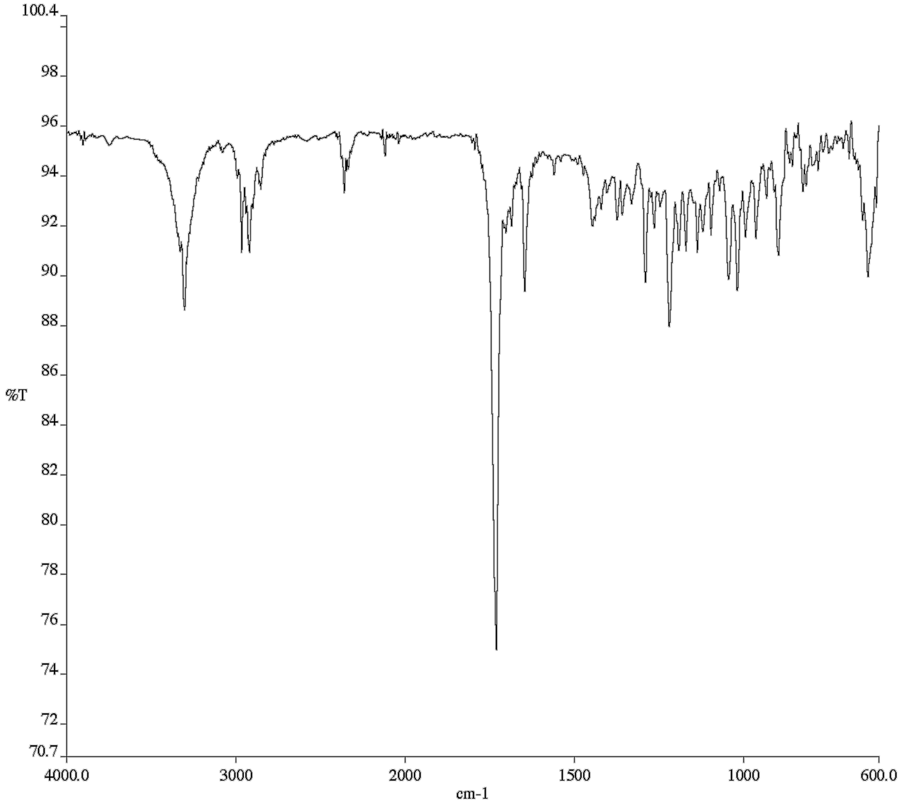


^{13}C NMR (100 MHz, CDCl$_3$) of compound **77.**

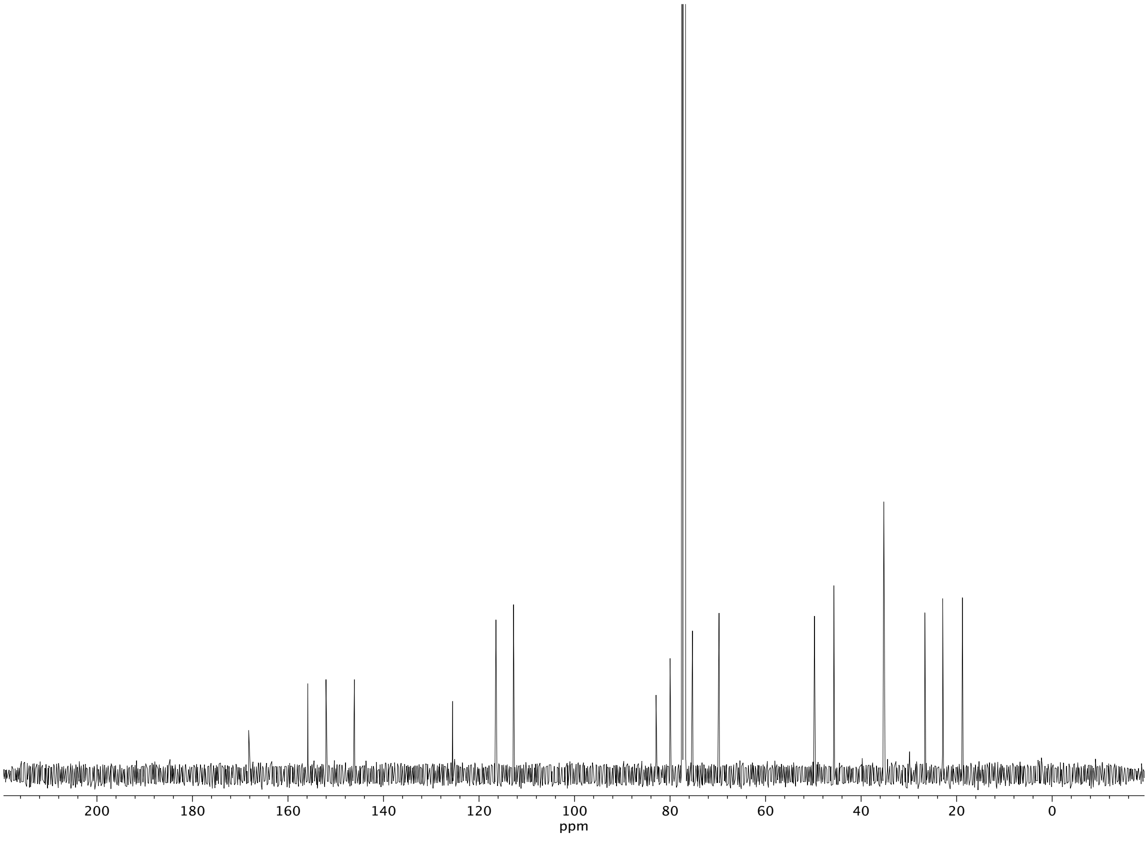


78

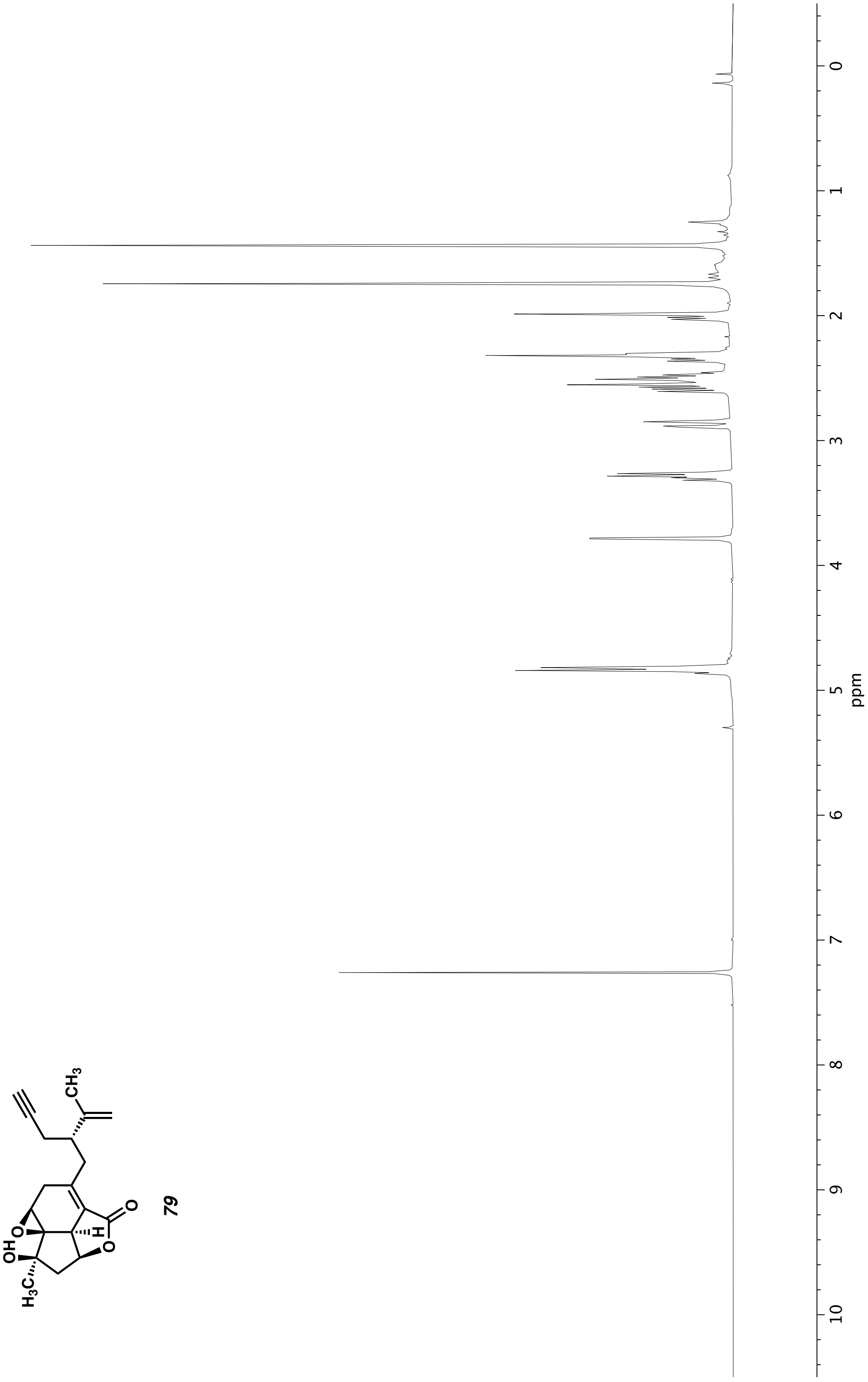
^{1}H NMR (400 MHz, CDCl$_3$) of compound **78**.



Infrared spectrum (Thin Film, NaCl) of compound **78.**

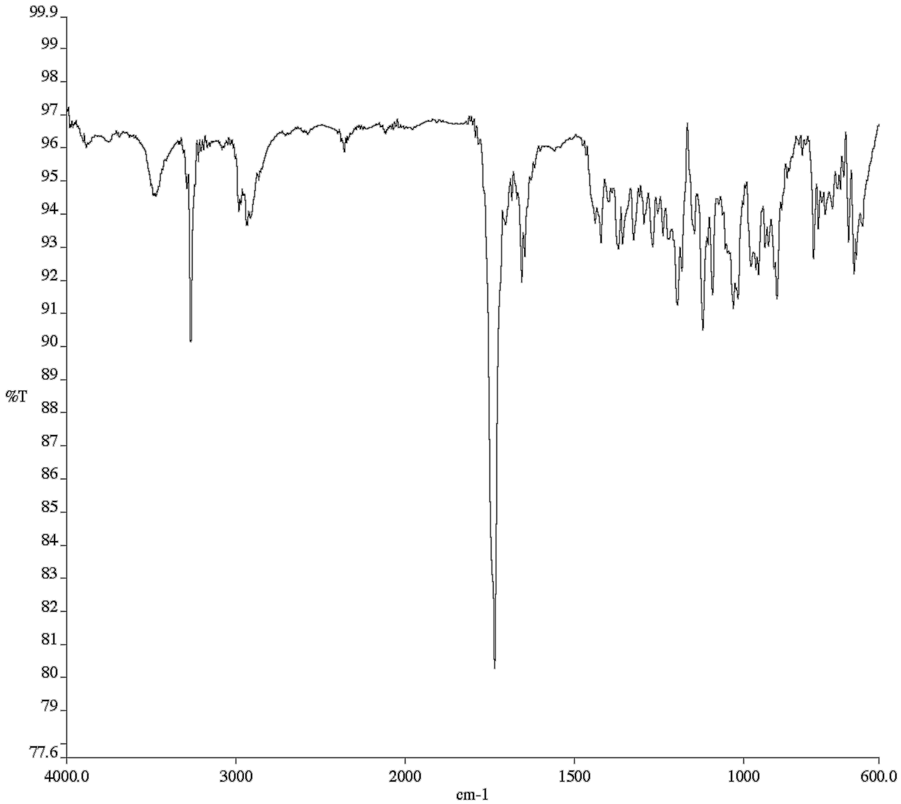


^{13}C NMR (100 MHz, CDCl$_3$) of compound **78.**

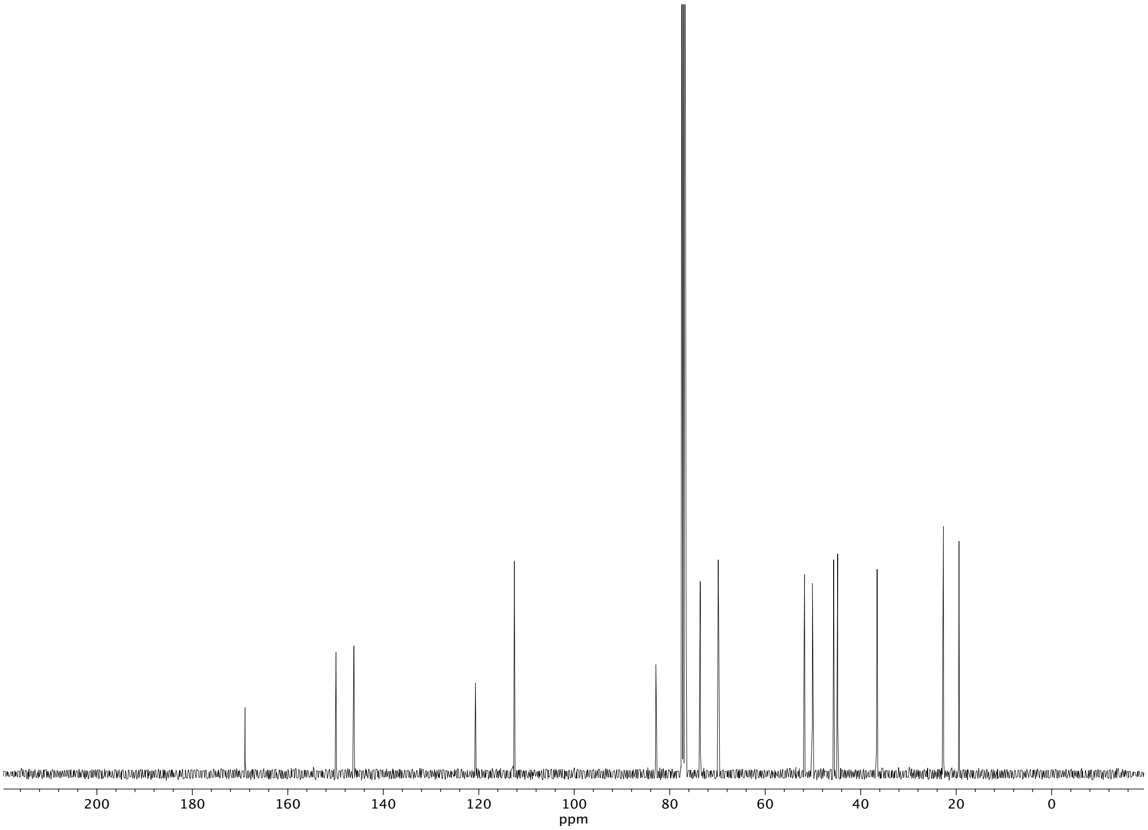


79

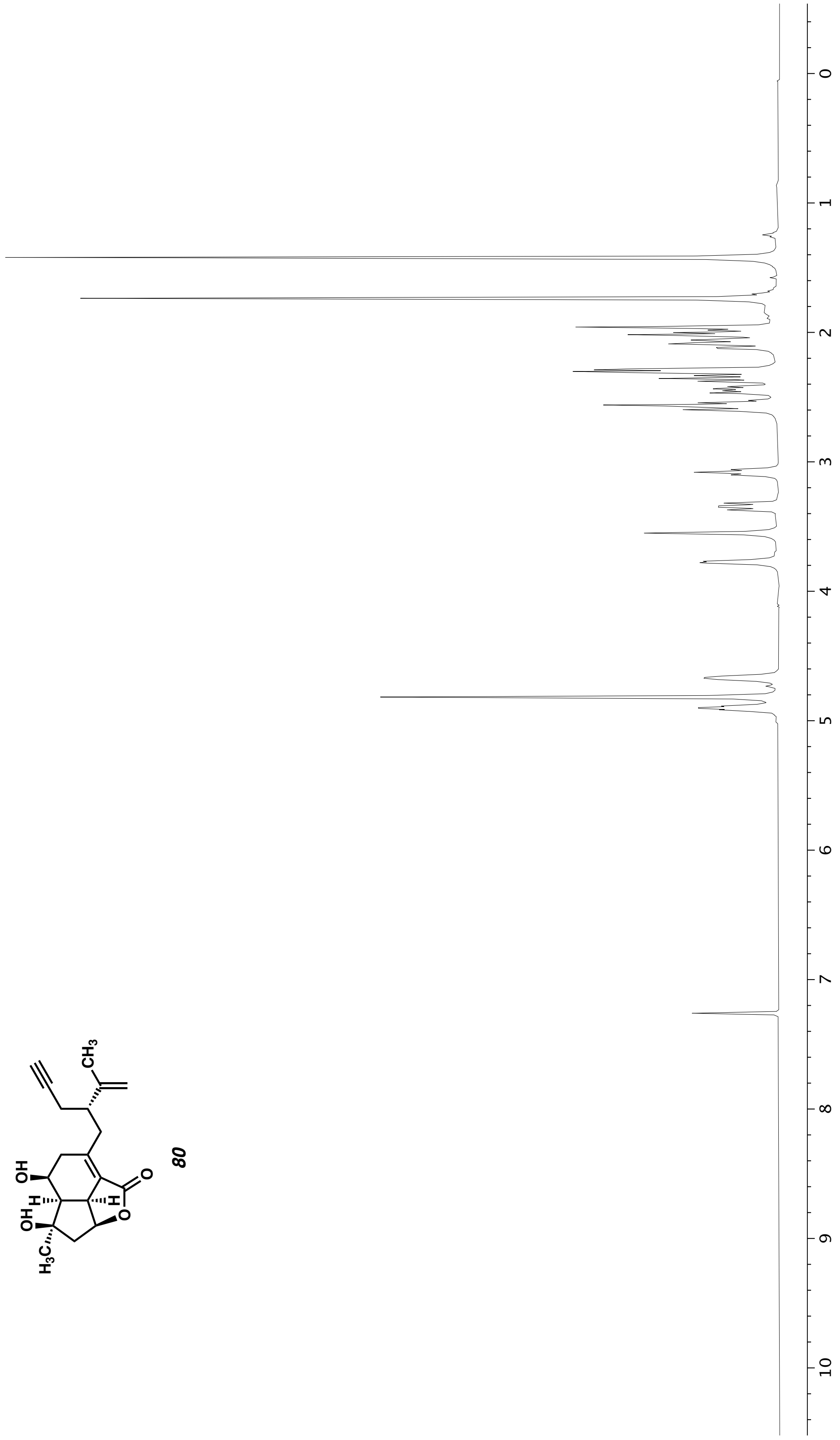
^{1}H NMR (400 MHz, CDCl$_3$) of compound **79**.



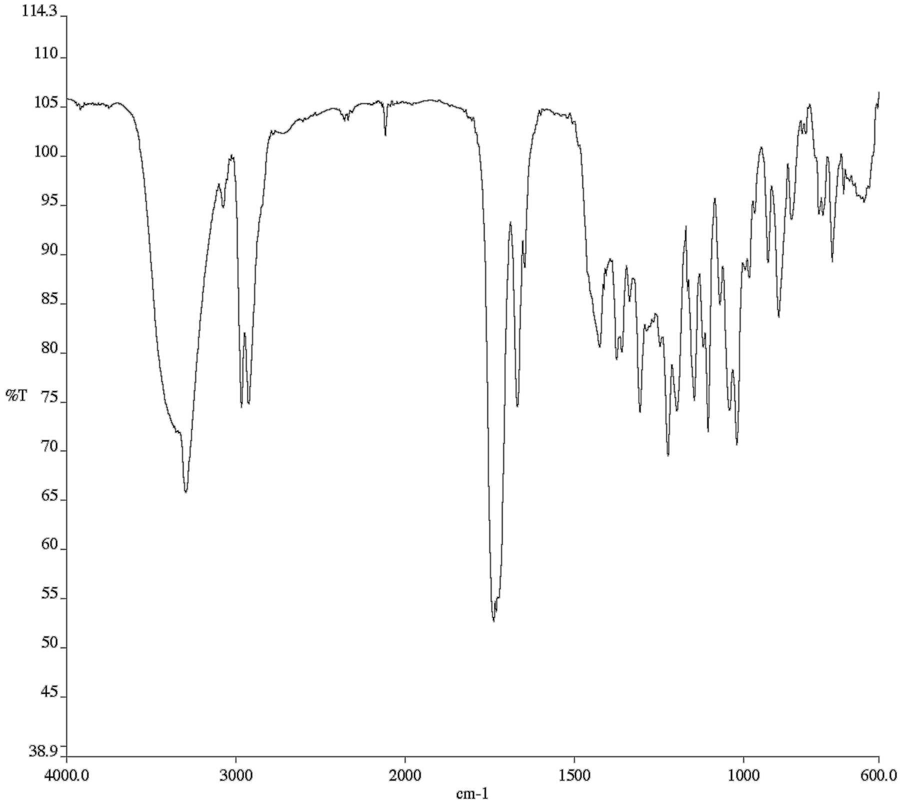
Infrared spectrum (Thin Film, NaCl) of compound **79.**



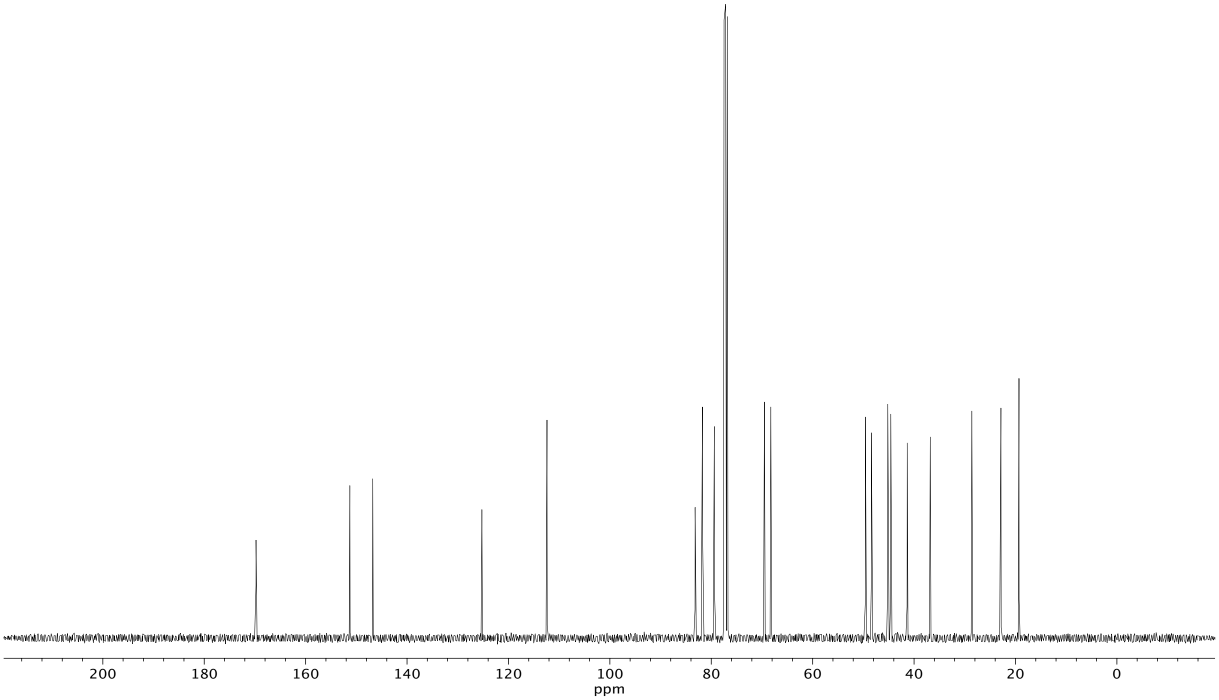
^{13}C NMR (100 MHz, CDCl$_3$) of compound **79.**



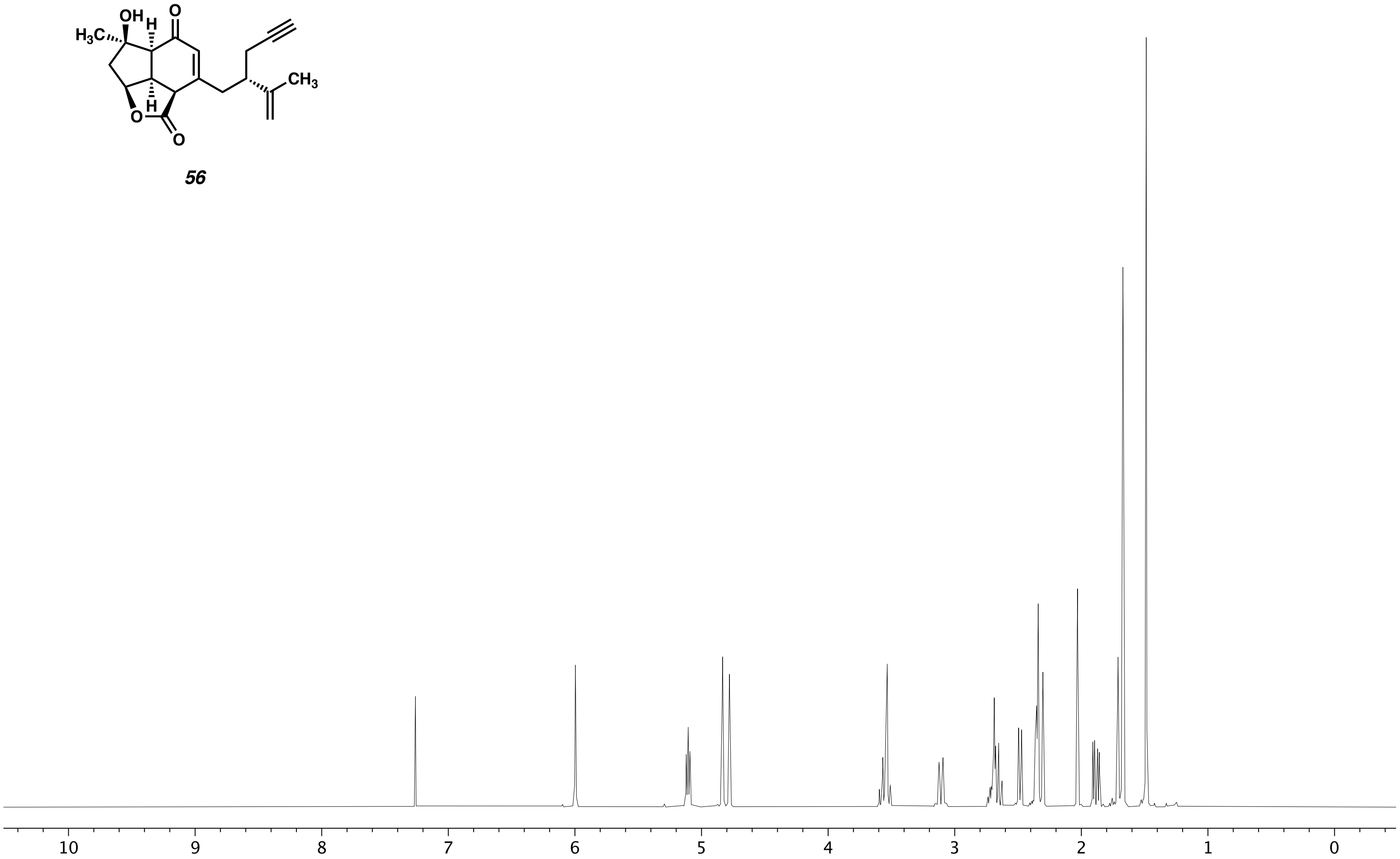
^{1}H NMR (400 MHz, CDCl$_3$) of compound **80**.



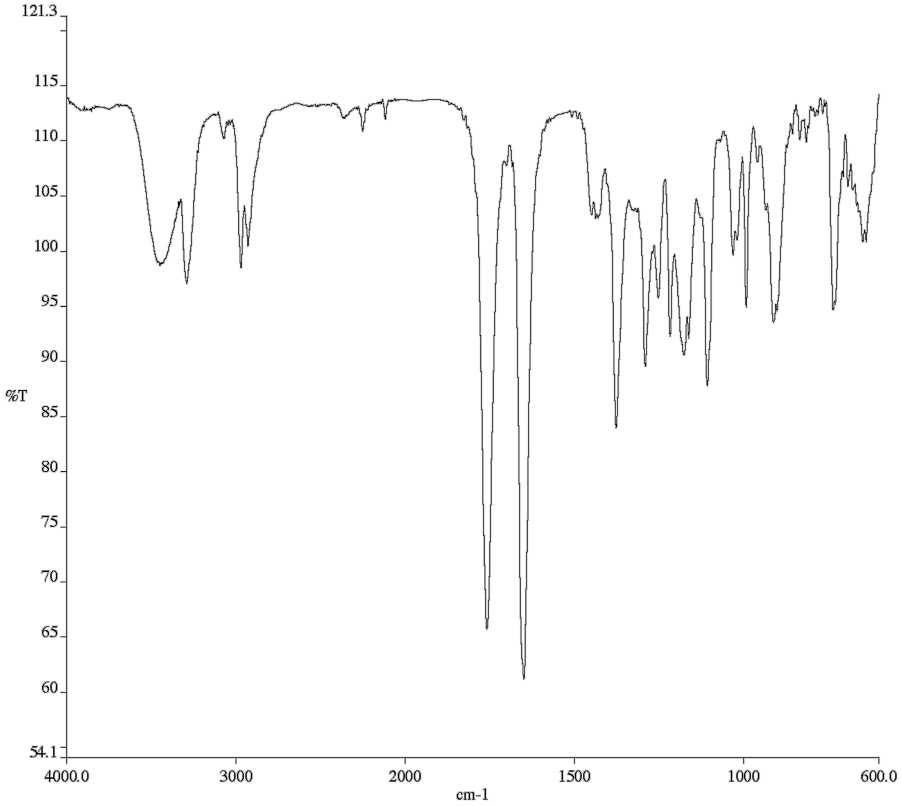
Infrared spectrum (Thin Film, NaCl) of compound **80.**



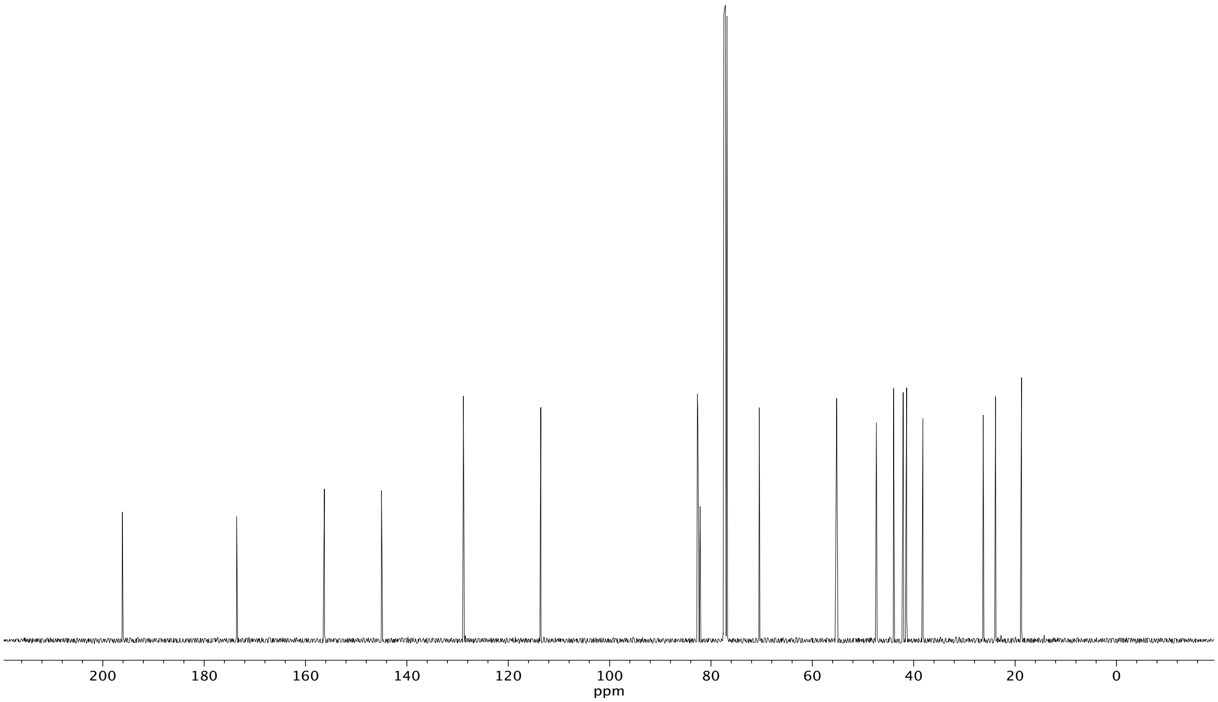
^{13}C NMR (100 MHz, CDCl$_3$) of compound **80.**



^{1}H NMR (400 MHz, CDCl$_3$) of compound **56**.



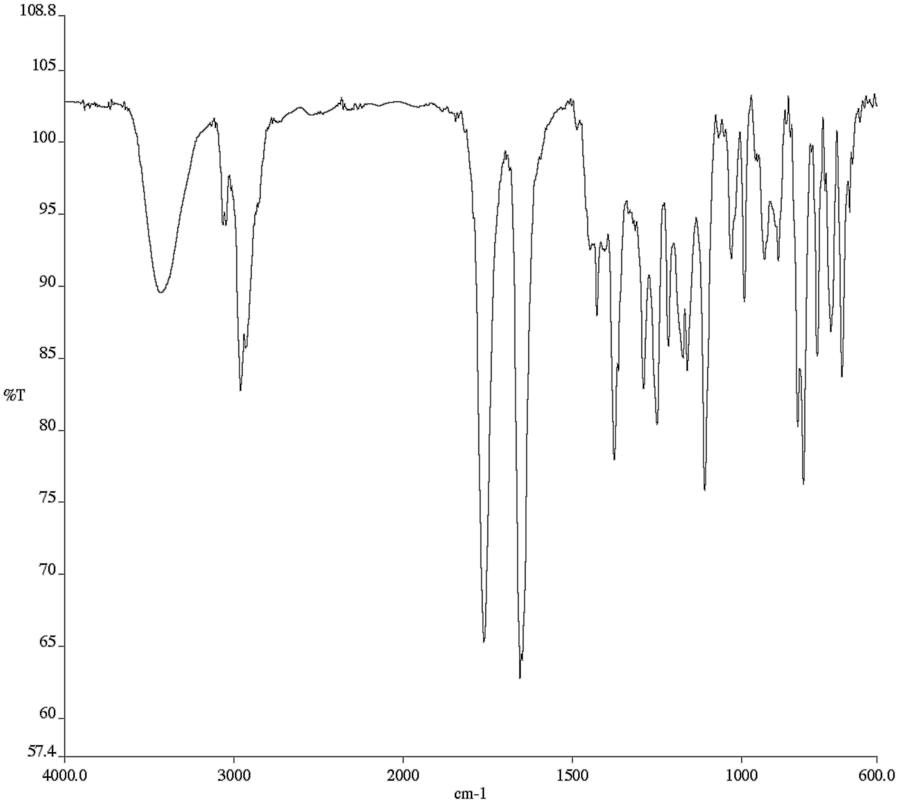
Infrared spectrum (Thin Film, NaCl) of compound **56.**



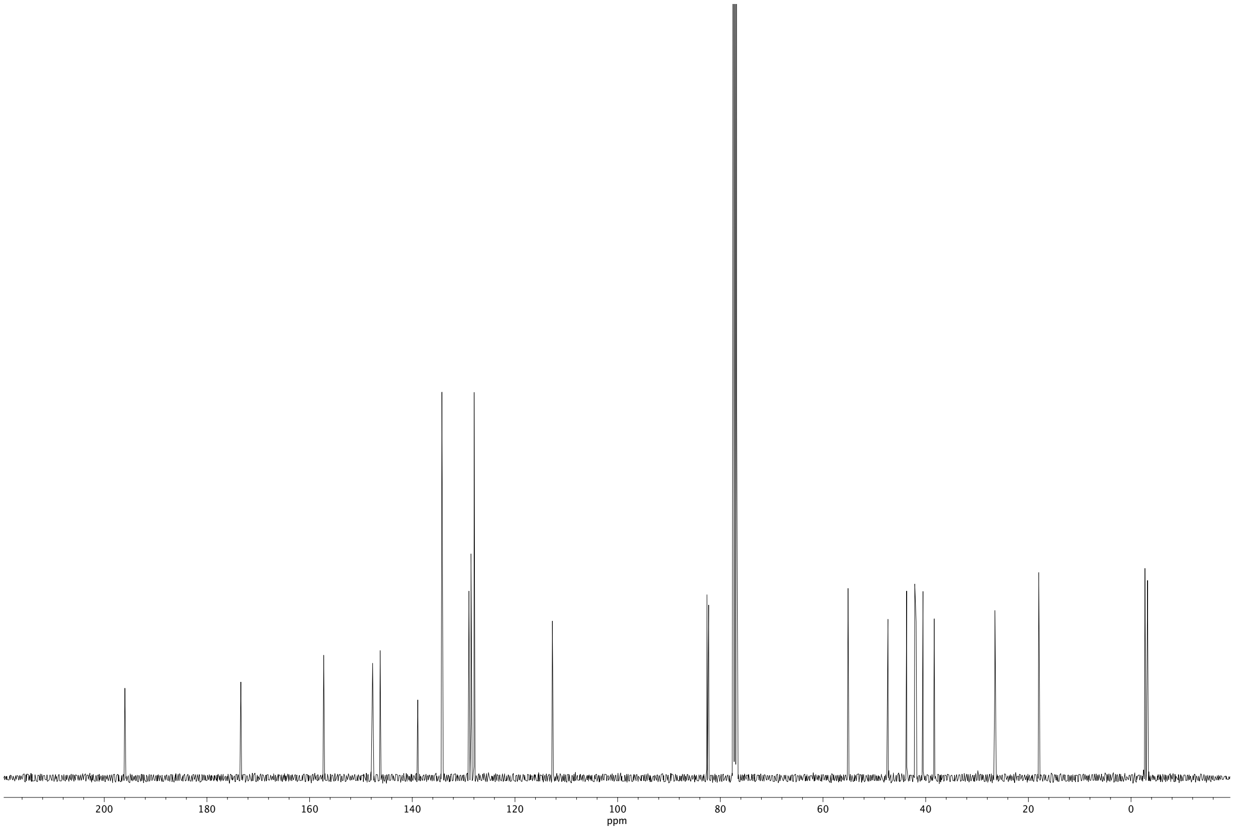
^{13}C NMR (100 MHz, CDCl$_3$) of compound **56.**

55

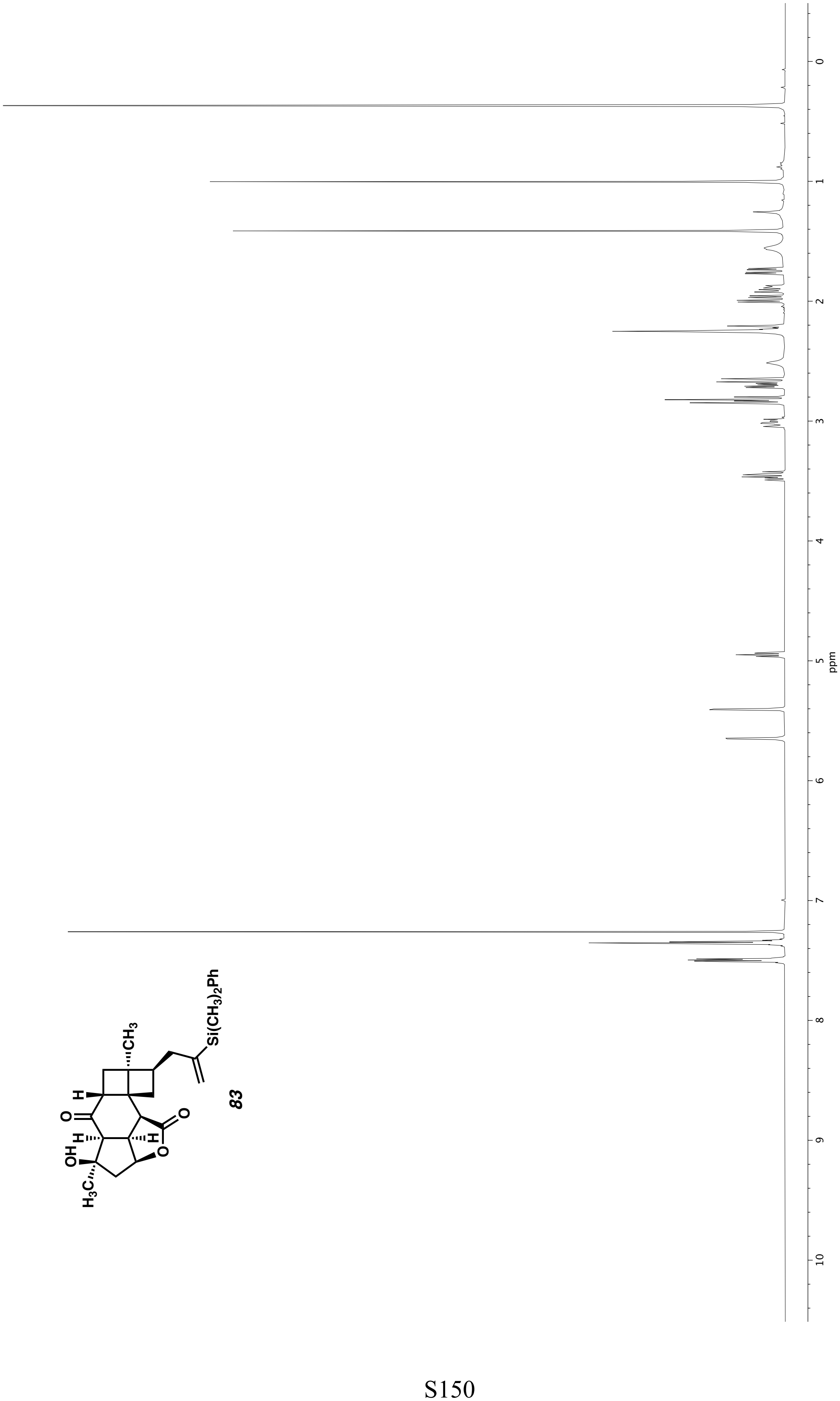
^{1}H NMR (400 MHz, CDCl$_3$) of compound **55**.



Infrared spectrum (Thin Film, NaCl) of compound **55.**

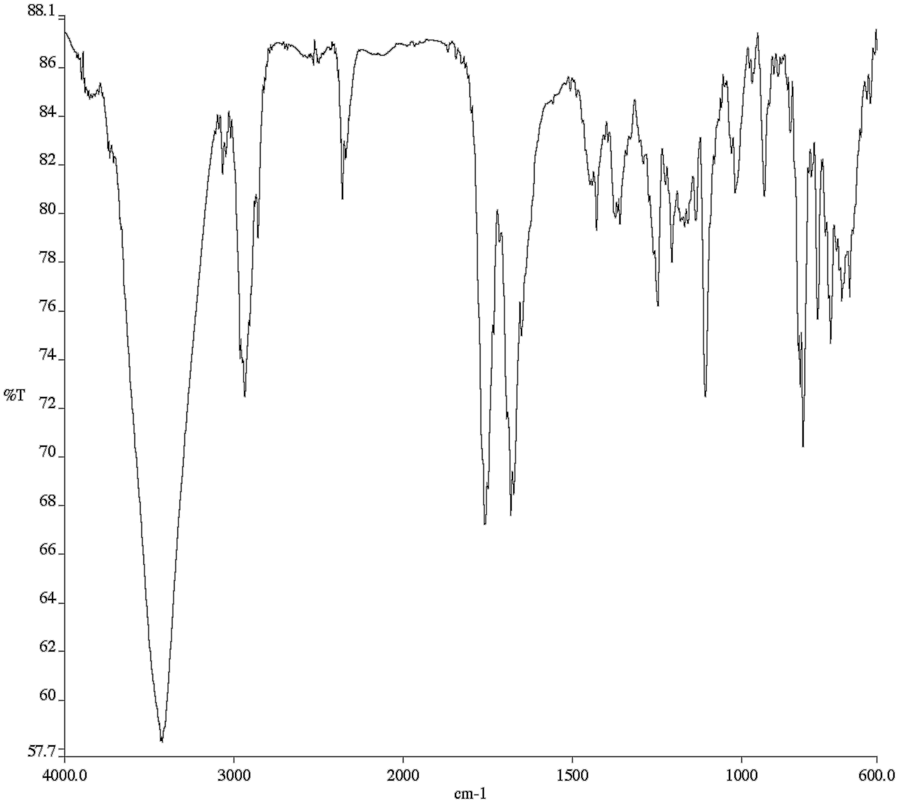


^{13}C NMR (100 MHz, CDCl$_3$) of compound **55.**

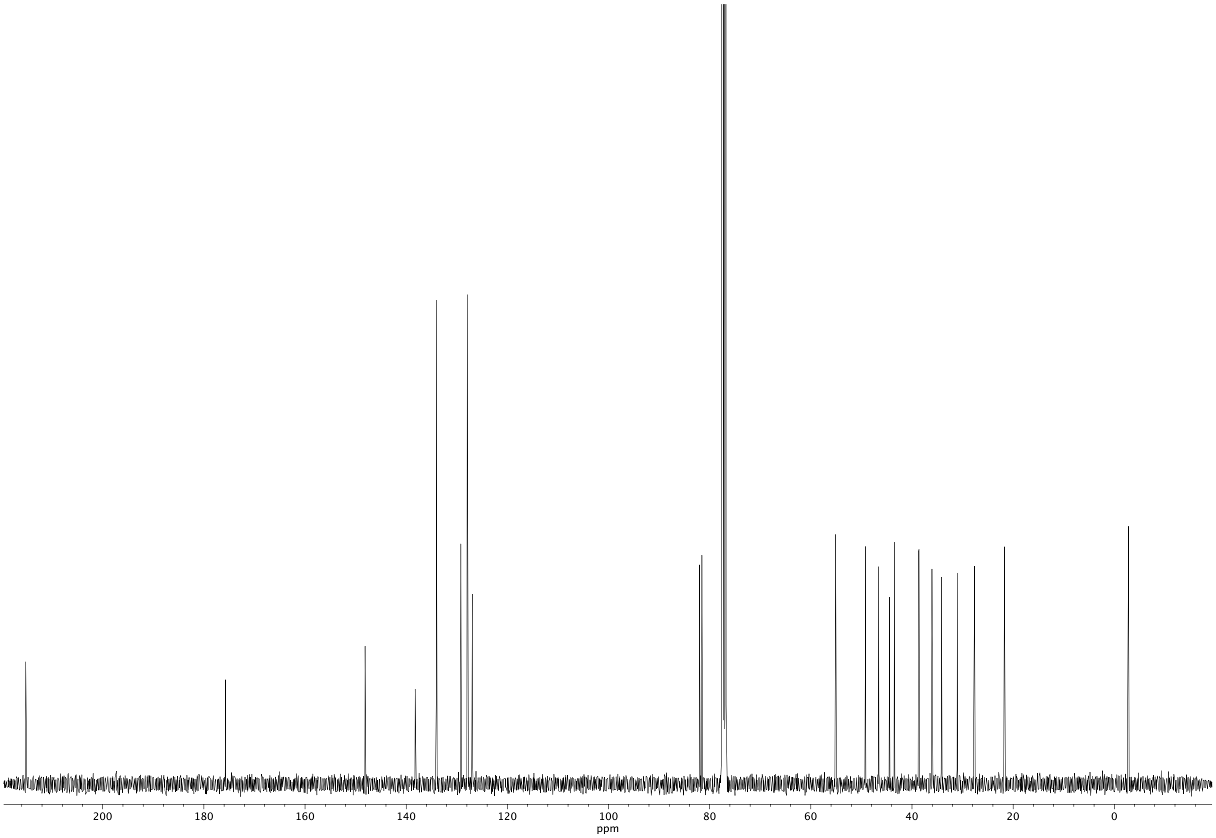


83

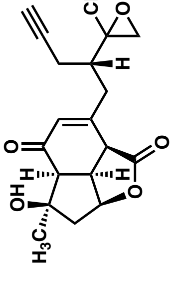
^{1}H NMR (400 MHz, CDCl$_3$) of compound **83**.



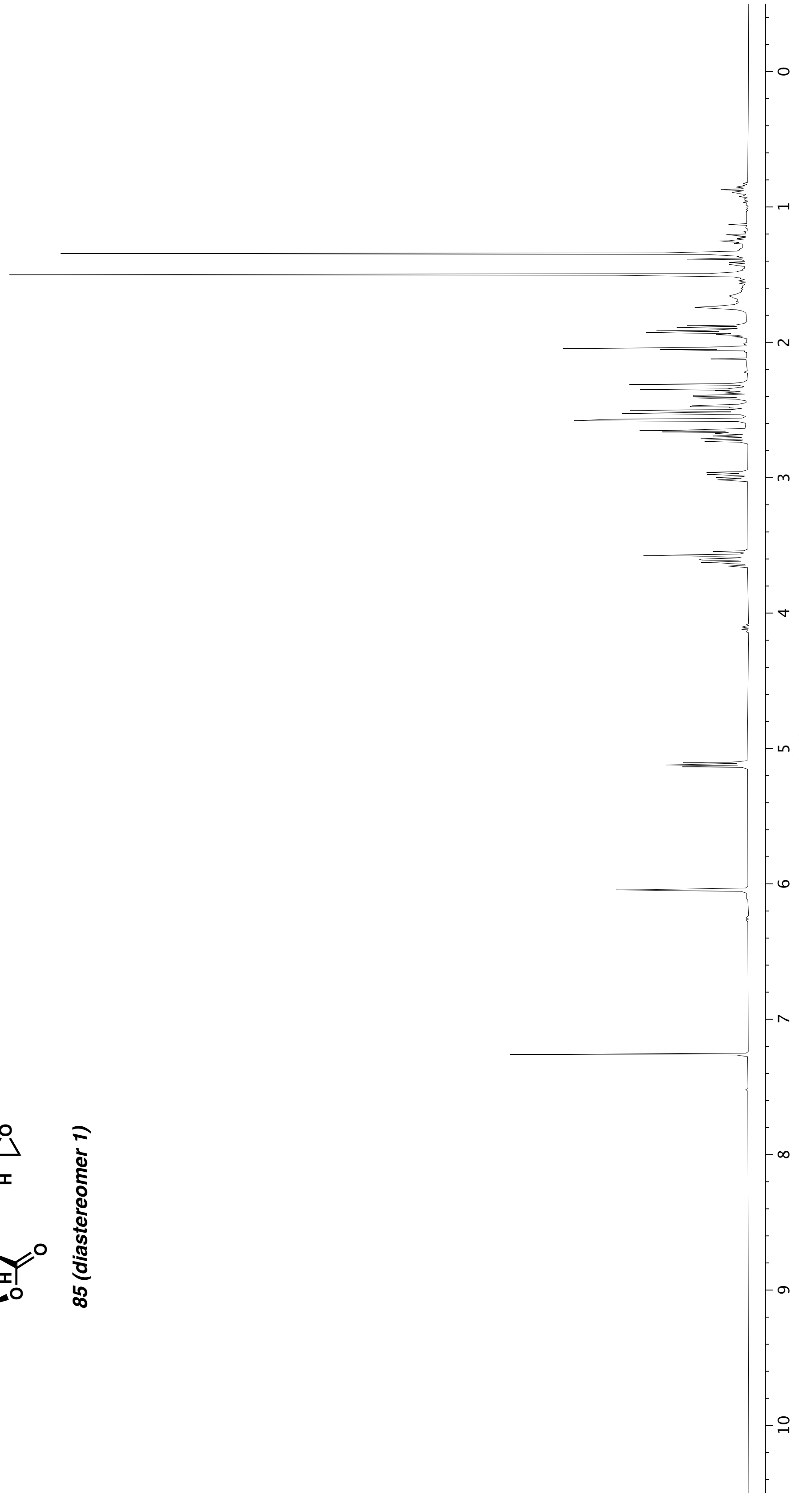
Infrared spectrum (Thin Film, NaCl) of compound **83.**



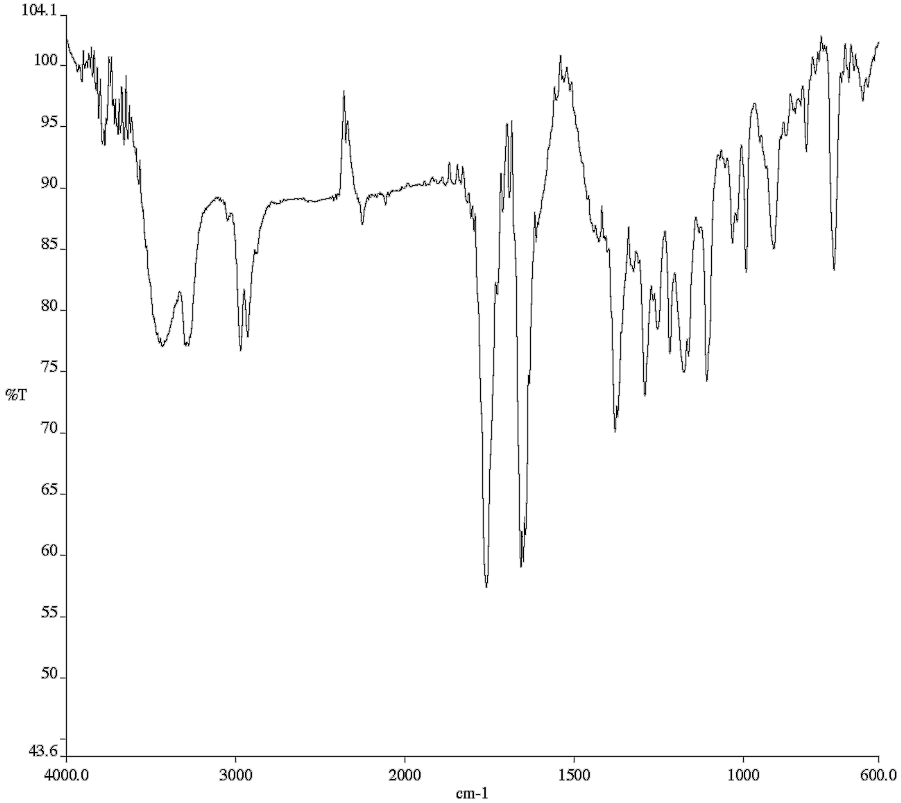
^{13}C NMR (100 MHz, CDCl$_3$) of compound **83.**



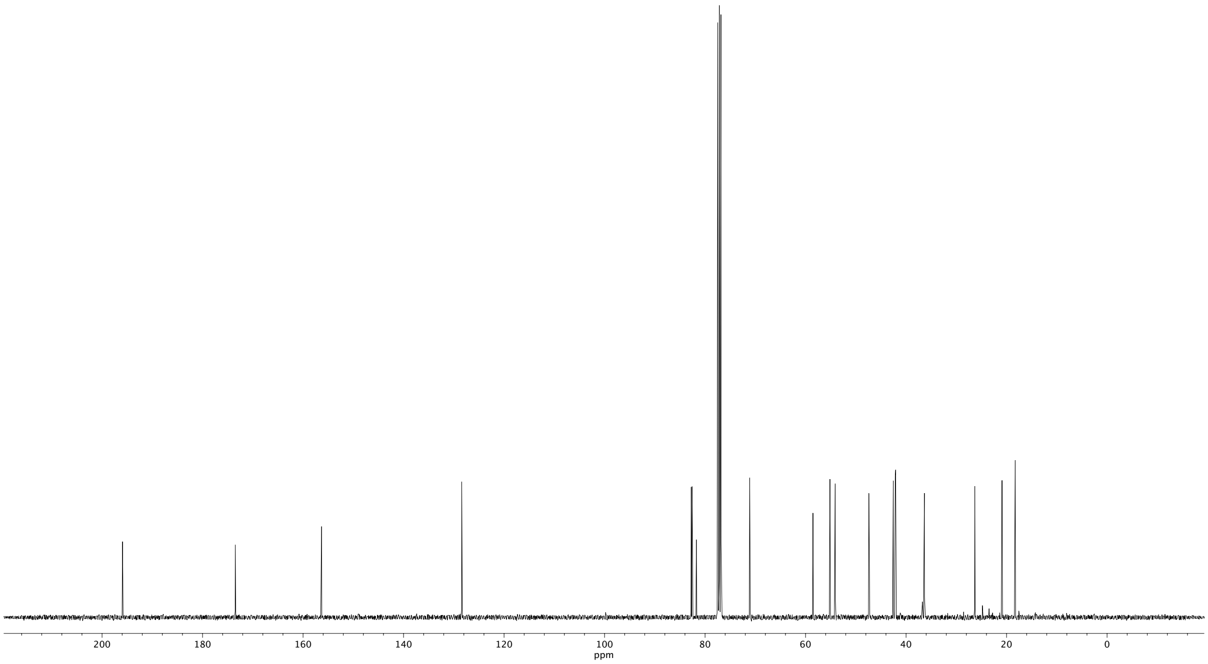
85 (diastereomer 1)



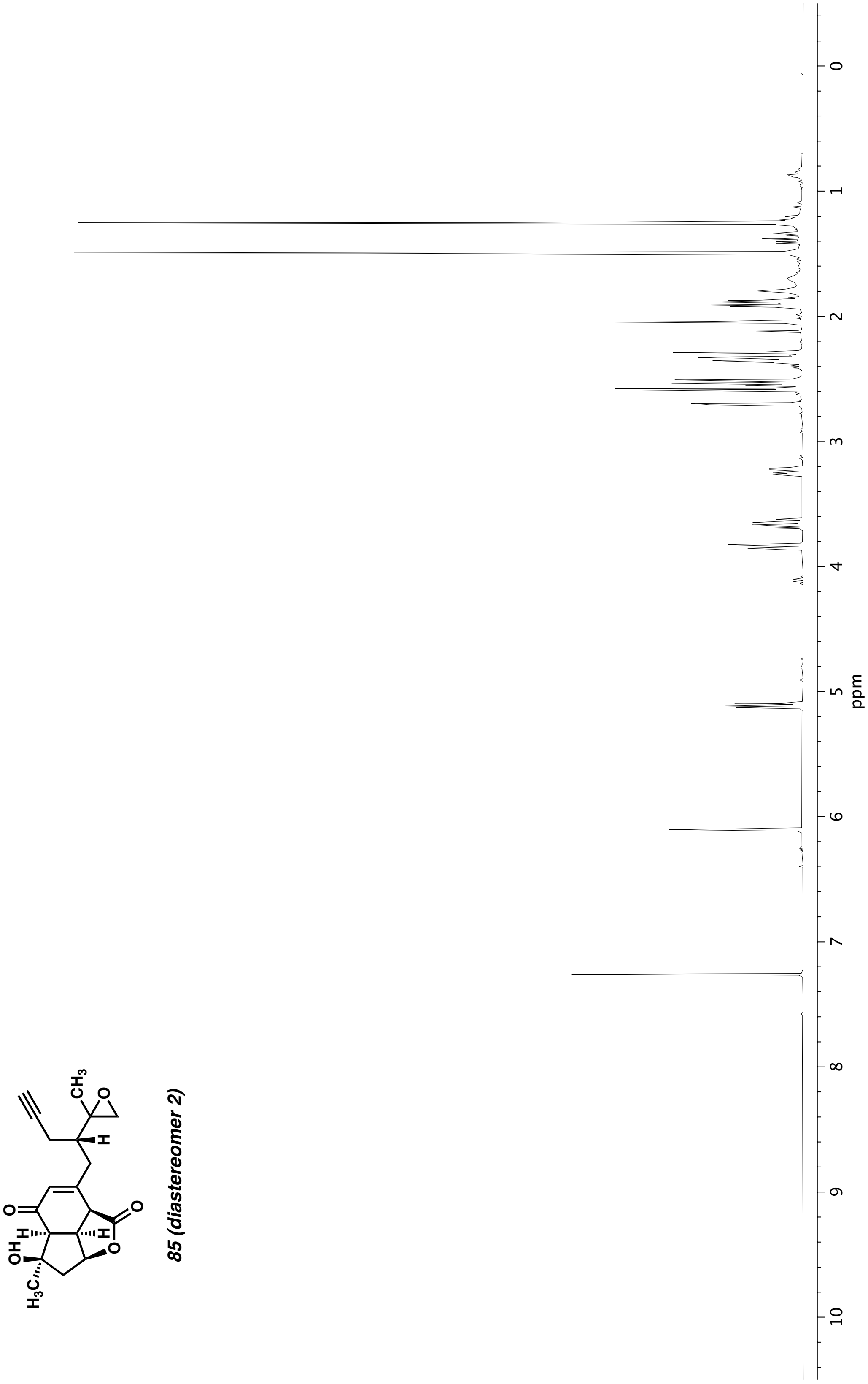
^{1}H NMR (400 MHz, CDCl$_3$) of compound **85** (diastereomer 1).



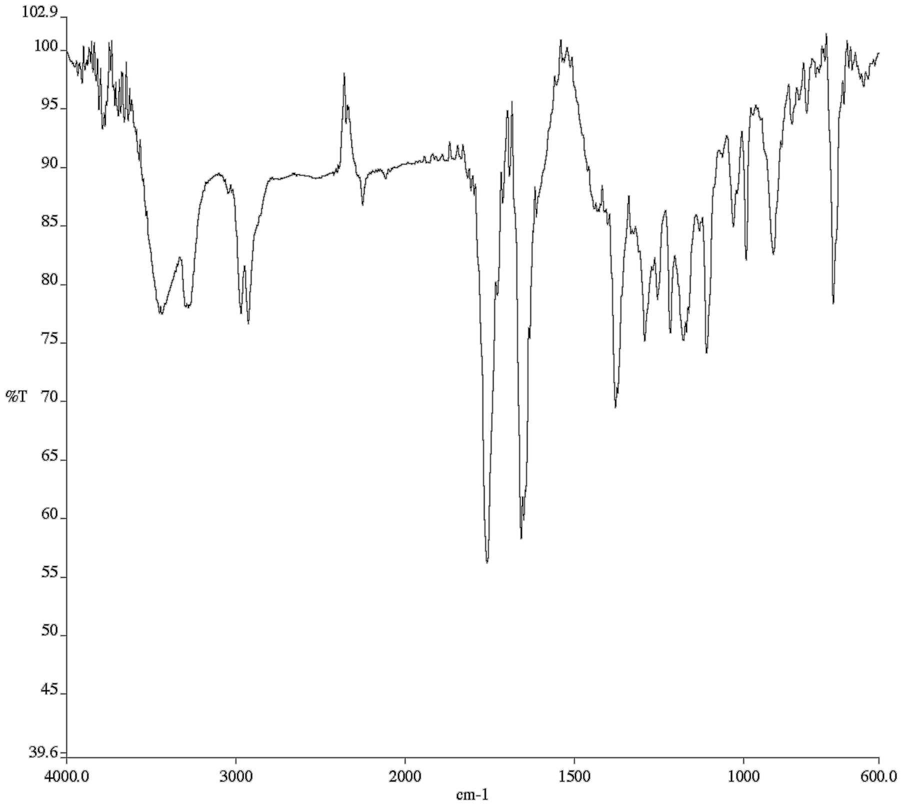
Infrared spectrum (Thin Film, NaCl) of compound **85** (diastereomer 1).



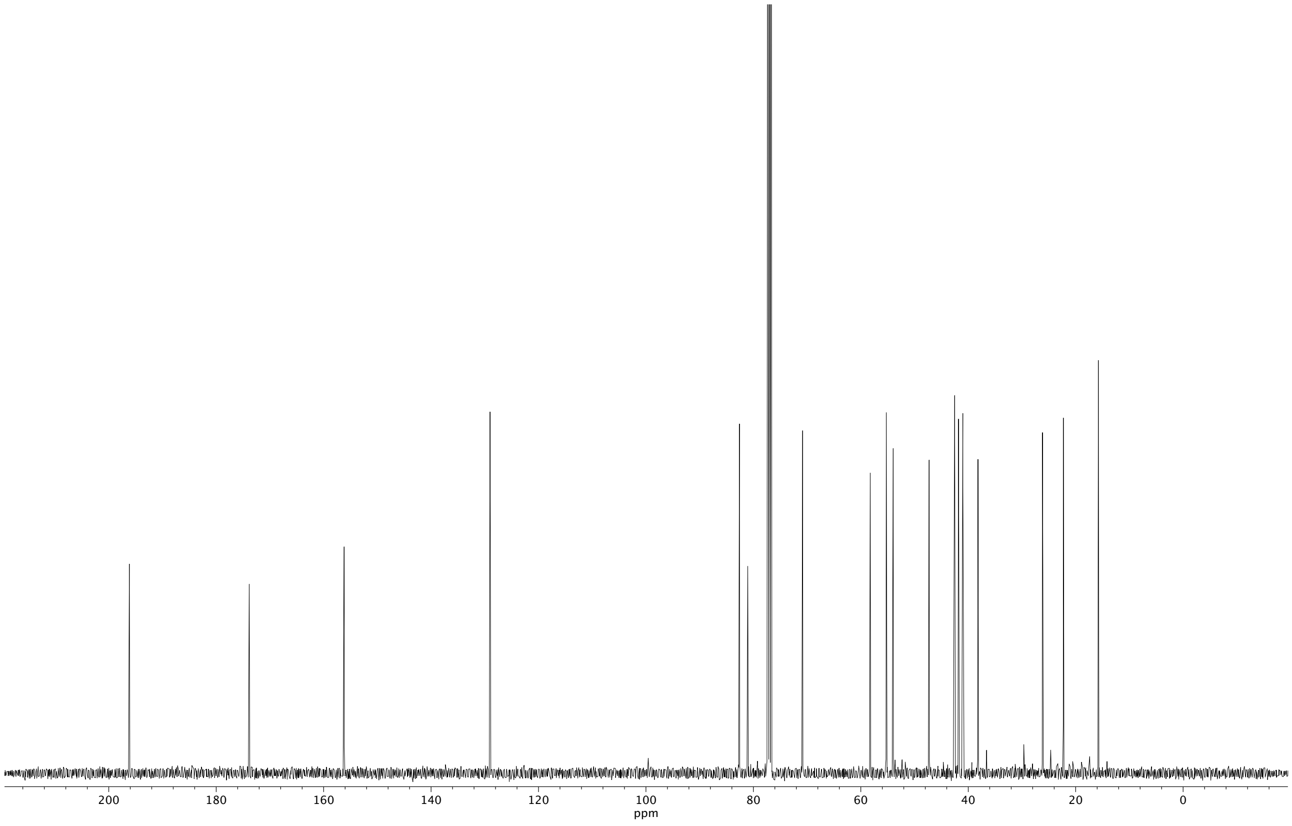
^{13}C NMR (100 MHz, CDCl$_3$) of compound **85** (diastereomer 1).



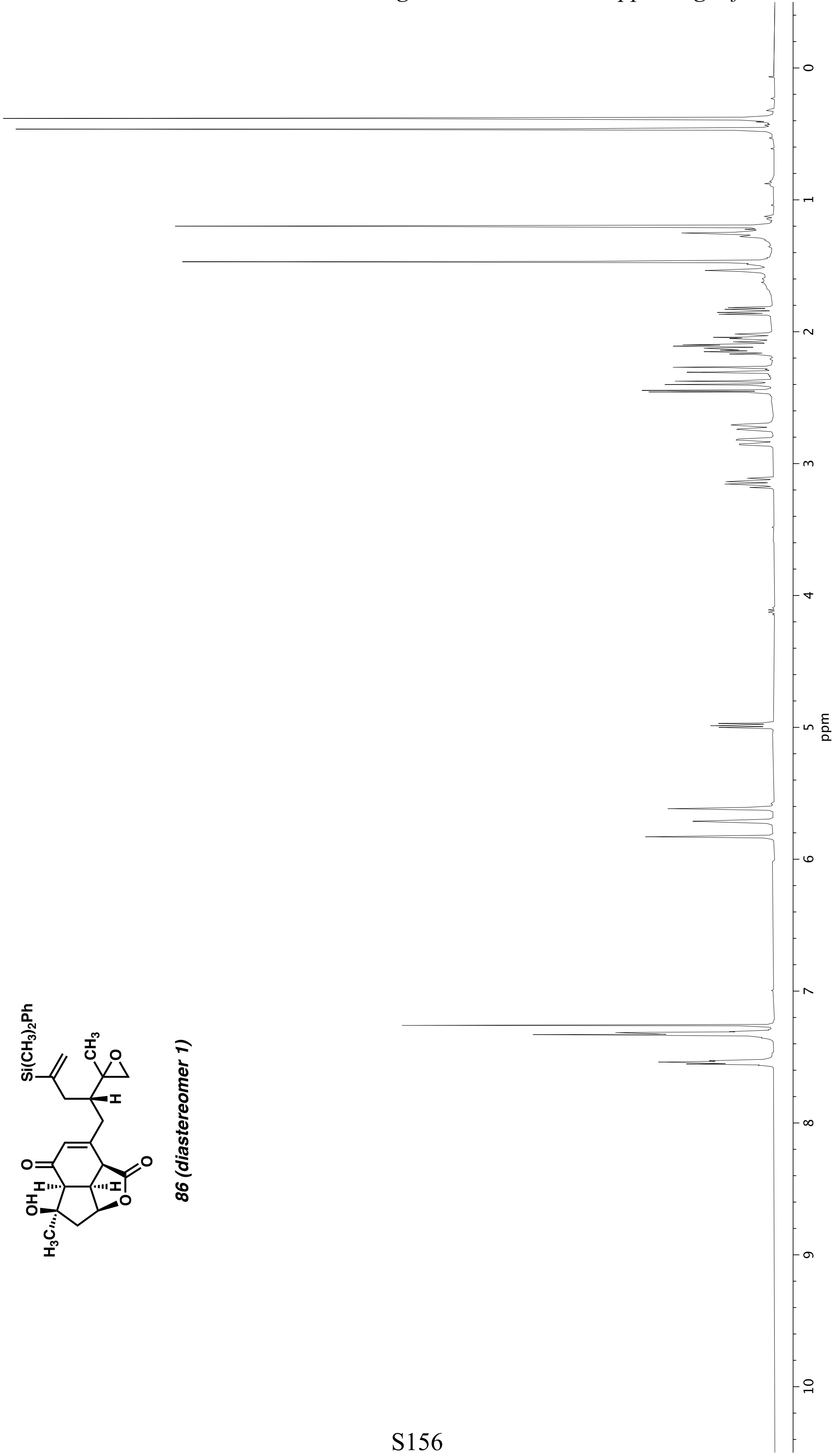
^{1}H NMR (400 MHz, CDCl$_3$) of compound **85** (diastereomer 2).



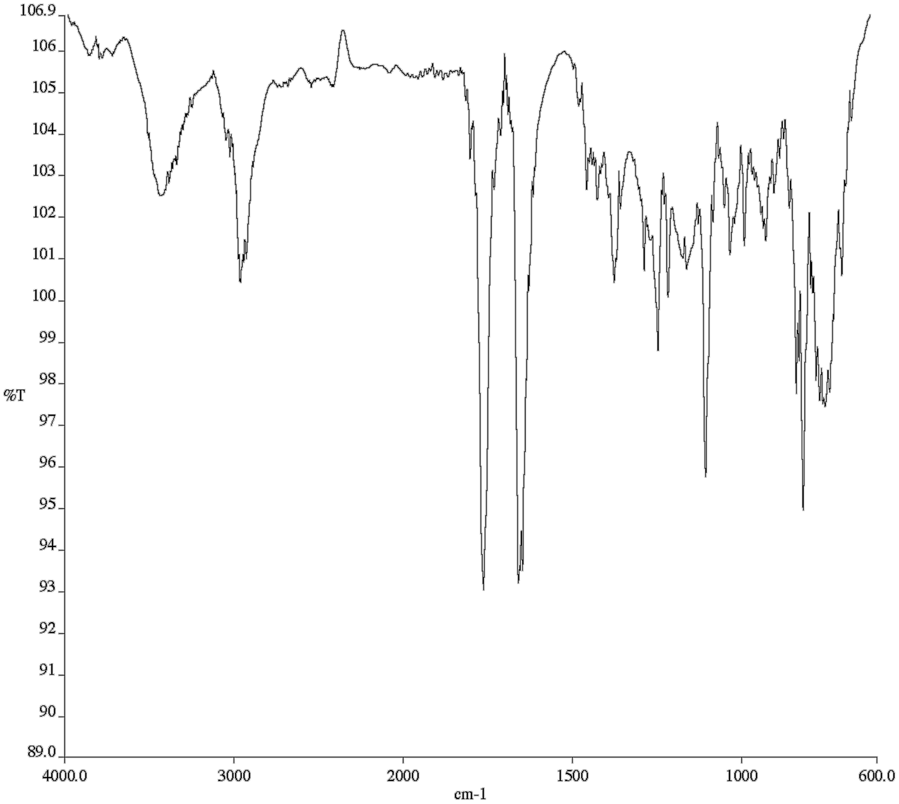
Infrared spectrum (Thin Film, NaCl) of compound **85** (diastereomer 2).



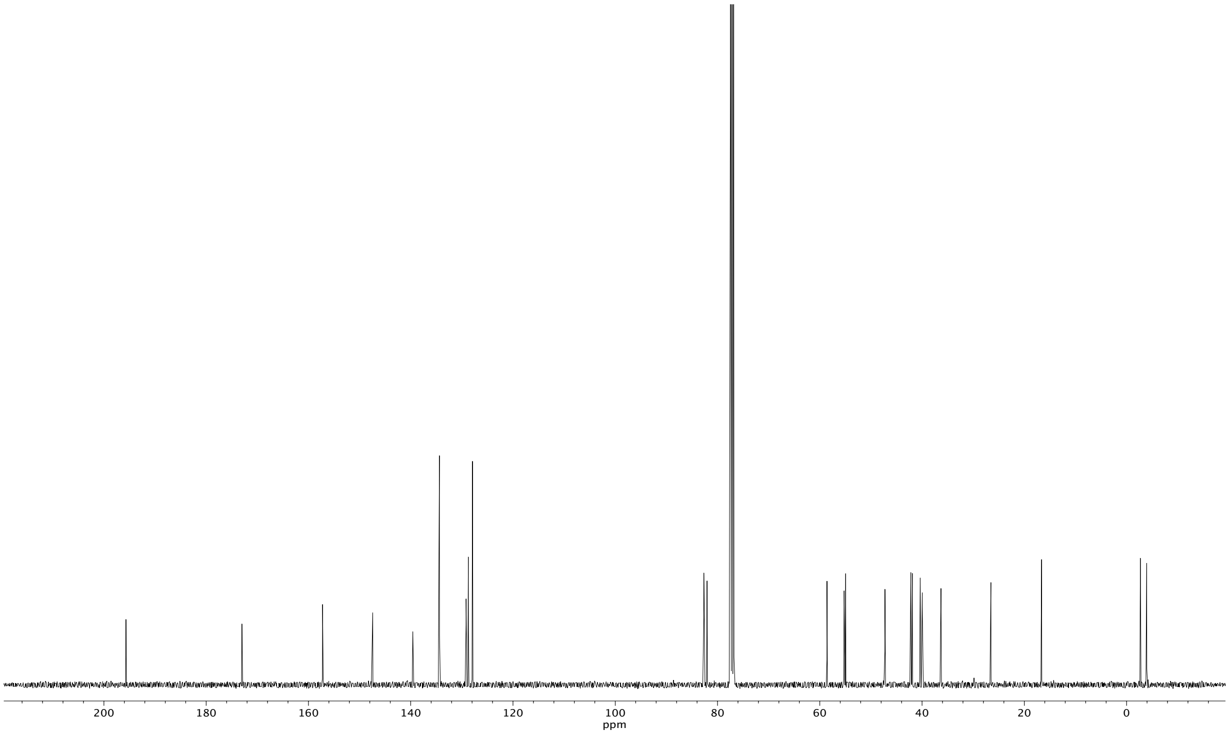
^{13}C NMR (100 MHz, CDCl$_3$) of compound **85** (diastereomer 2).



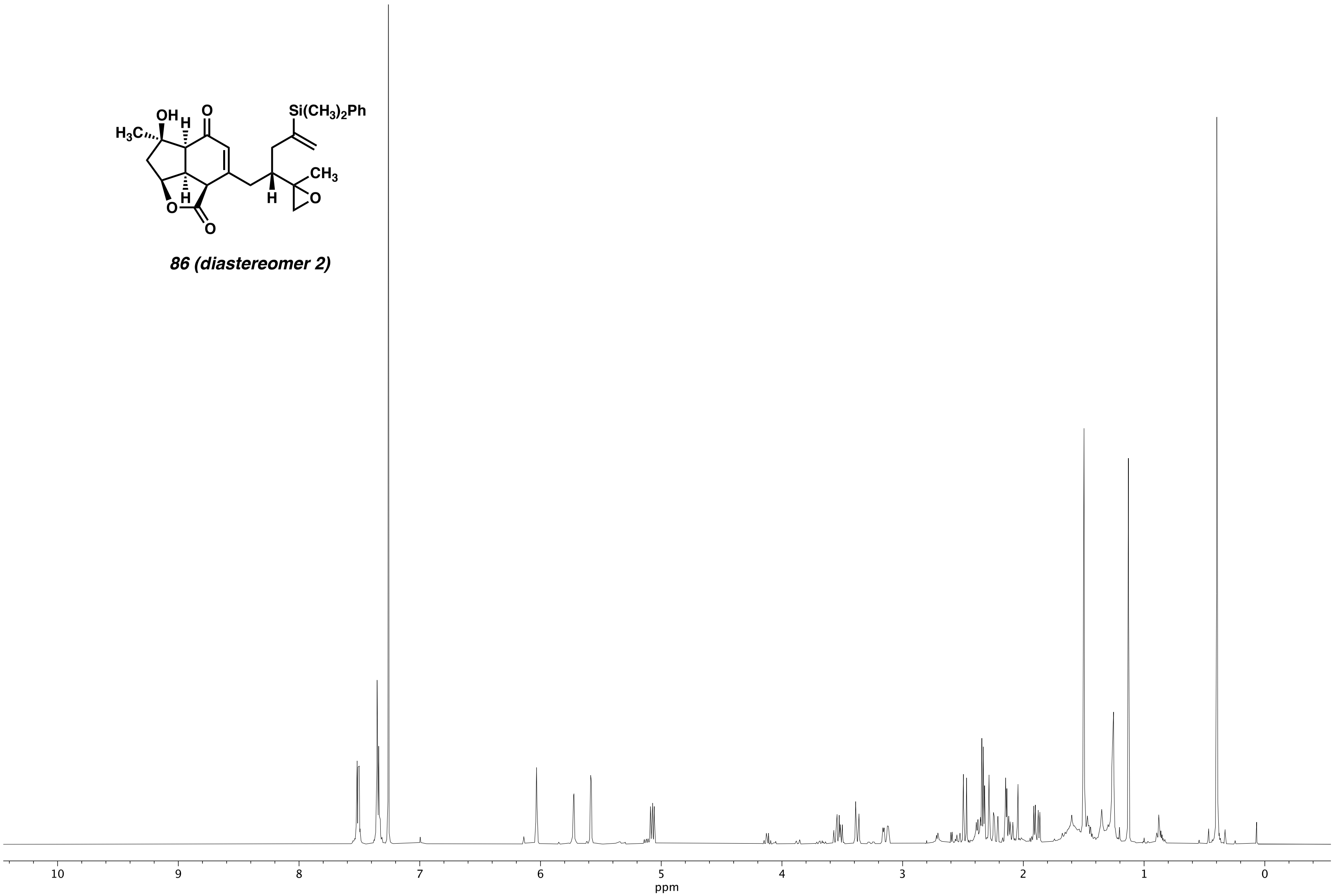
^{1}H NMR (400 MHz, CDCl$_3$) of compound **86** (diastereomer 1).



Infrared spectrum (Thin Film, NaCl) of compound **86** (diastereomer 1)**.**

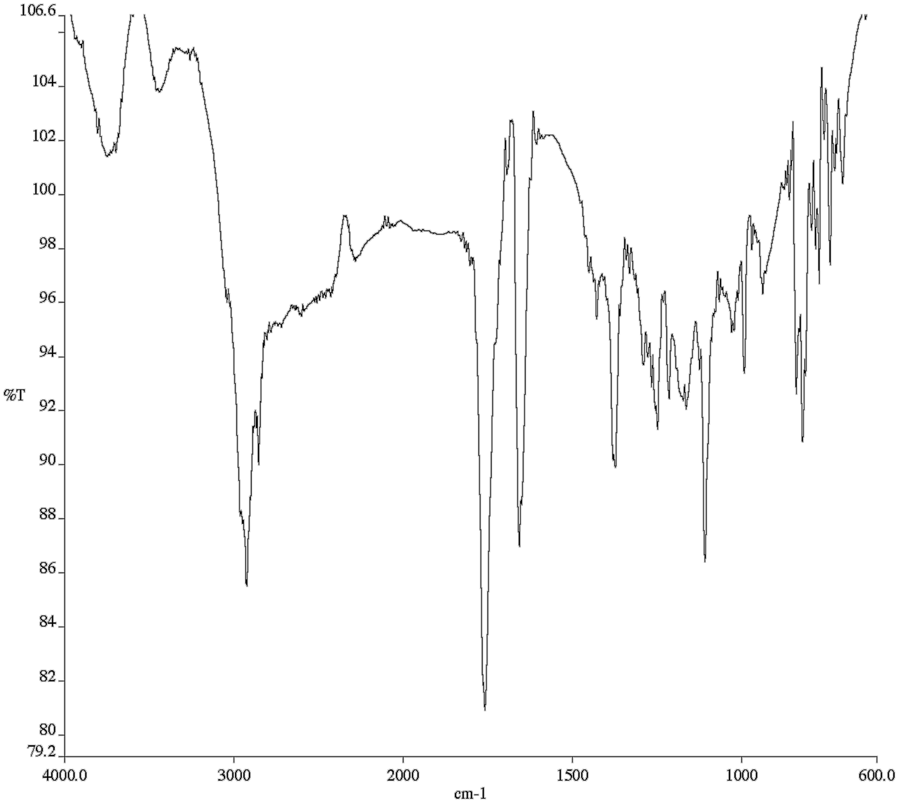


^{13}C NMR (100 MHz, CDCl$_3$) of compound **86** (diastereomer 1)**.**

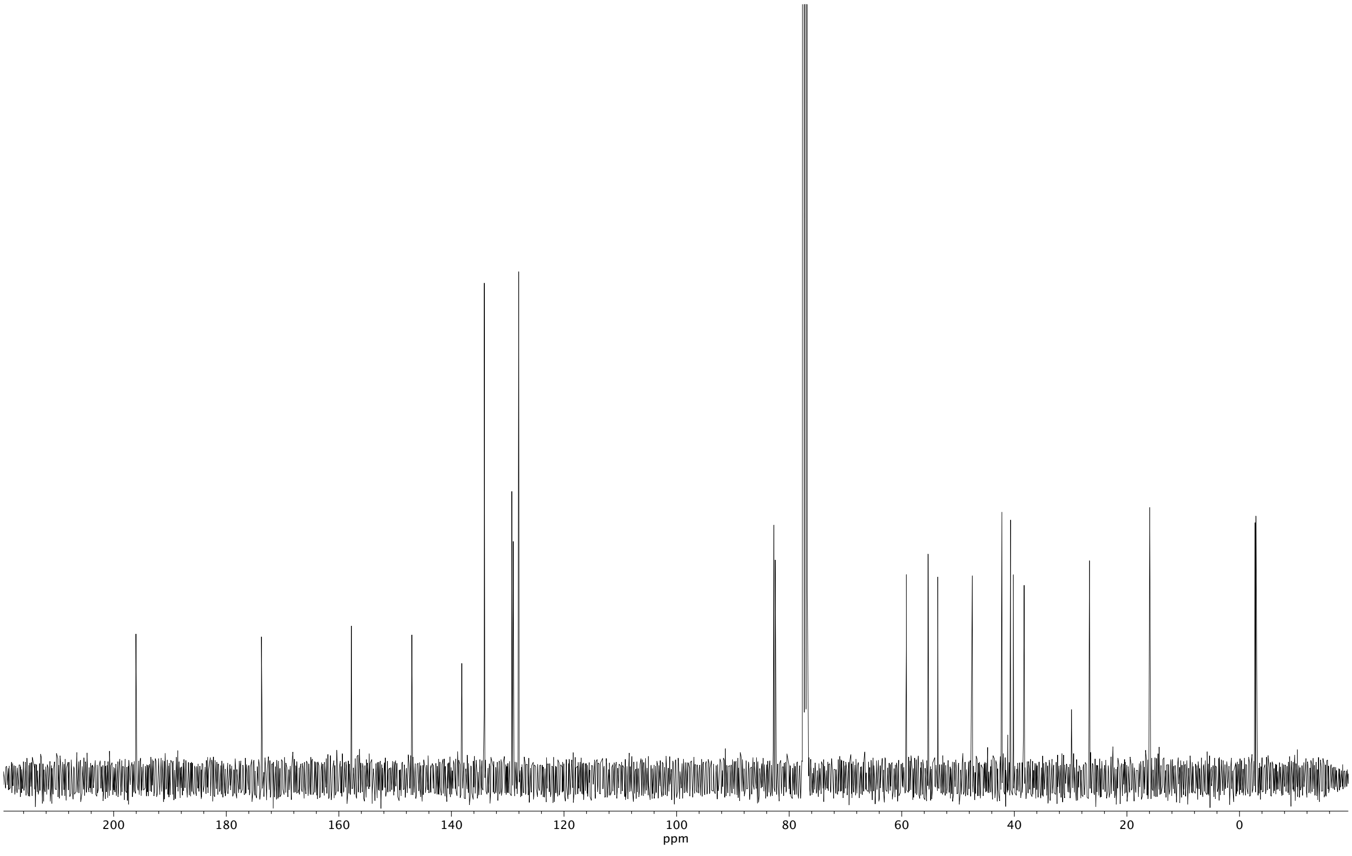


86 (diastereomer 2)

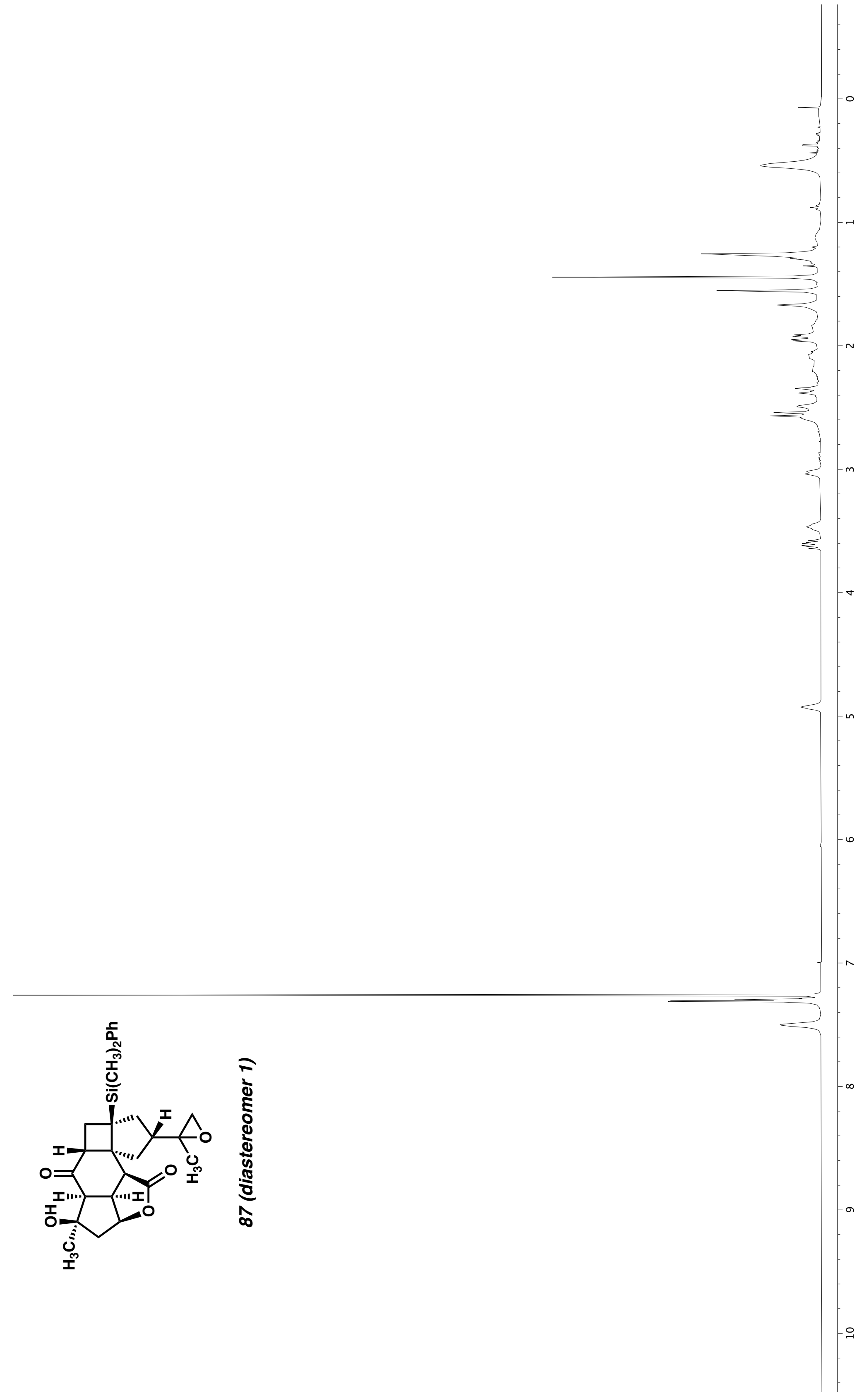
^{1}H NMR (400 MHz, CDCl$_3$) of compound **86** (diastereomer 2).



Infrared spectrum (Thin Film, NaCl) of compound **86** (diastereomer 2).

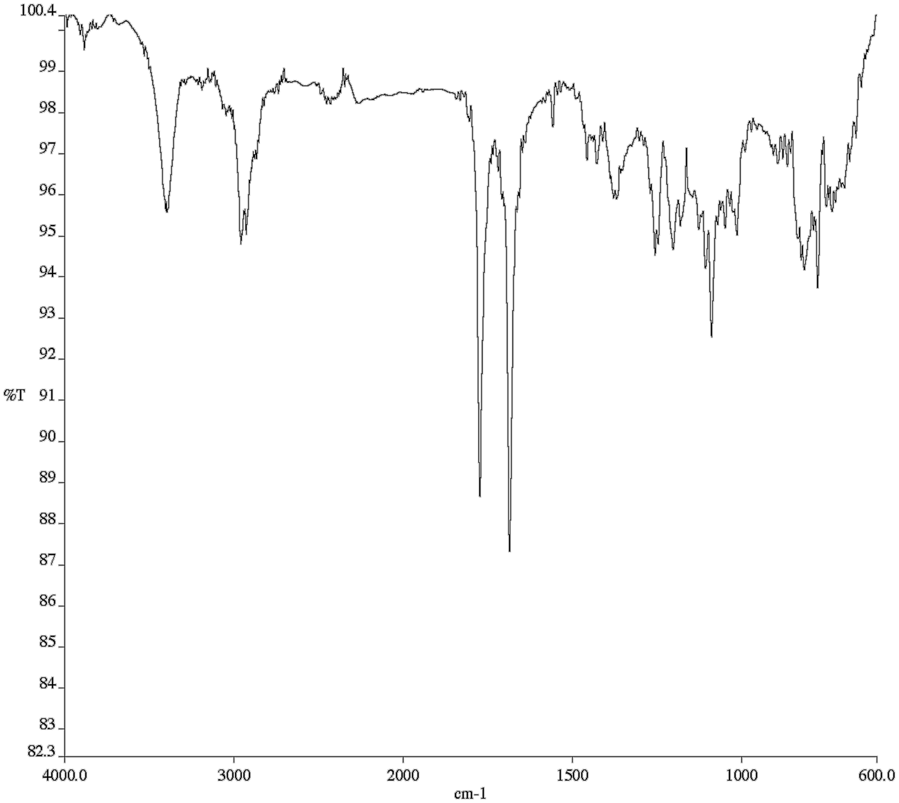


^{13}C NMR (100 MHz, CDCl$_3$) of compound **86** (diastereomer 2).

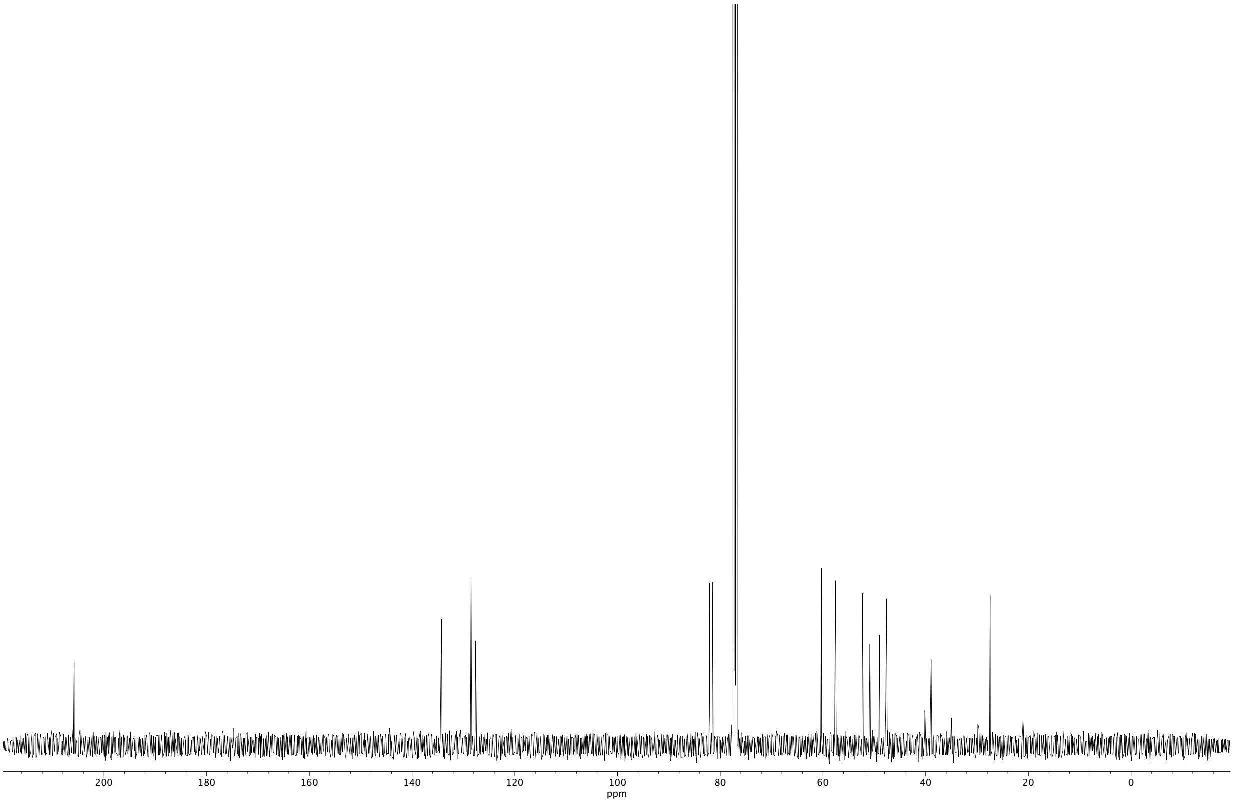


87 (diastereomer 1)

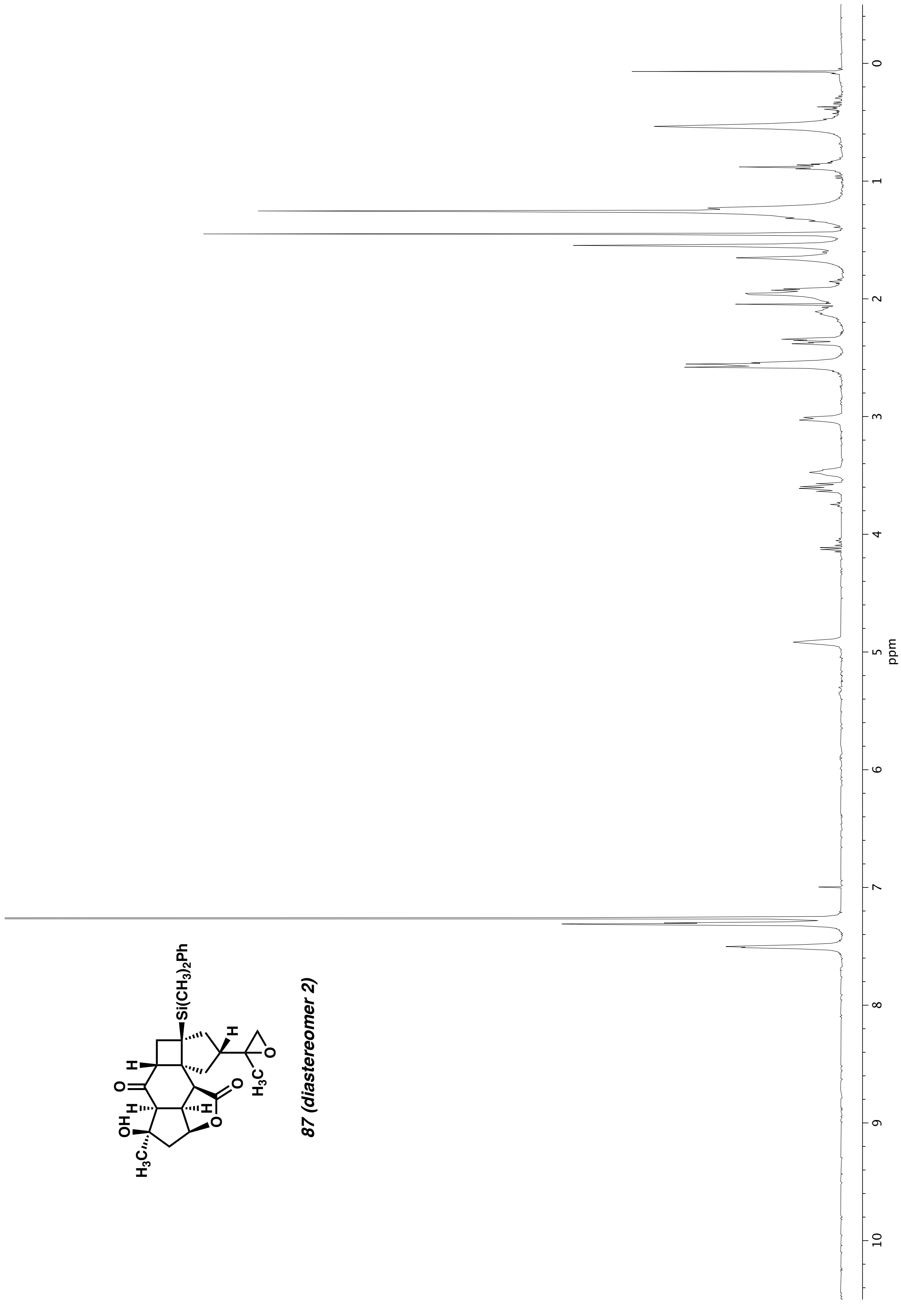
^{1}H NMR (400 MHz, CDCl$_3$) of compound **87** (diastereomer 1).



Infrared spectrum (Thin Film, NaCl) of compound **87** (diastereomer 1).

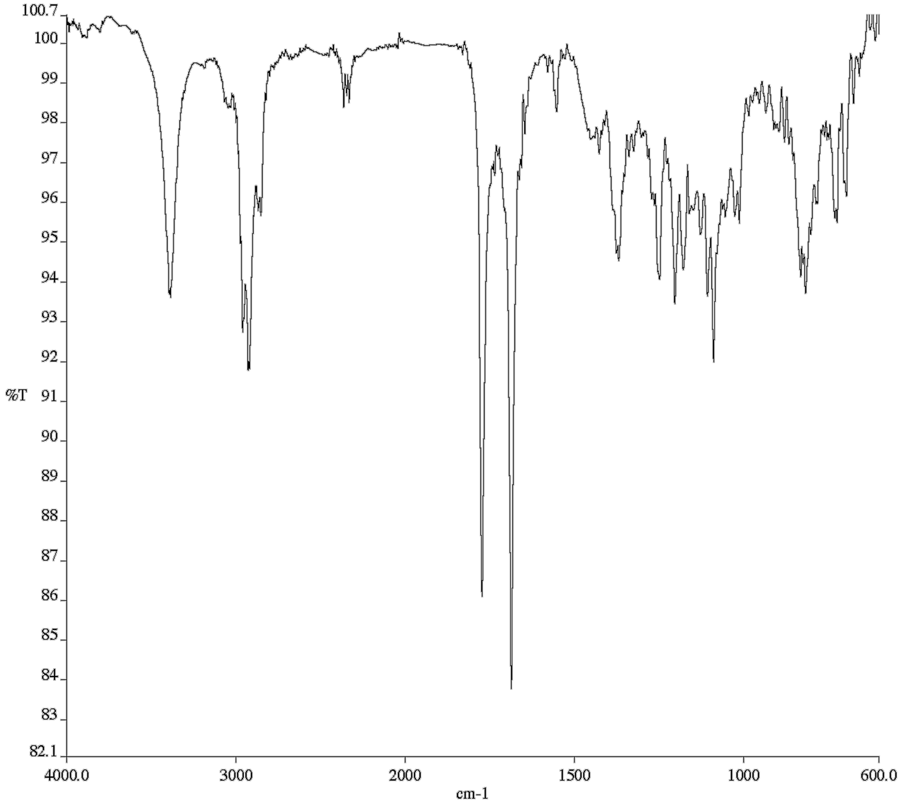


^{13}C NMR (100 MHz, CDCl$_3$) of compound **87** (diastereomer 1).

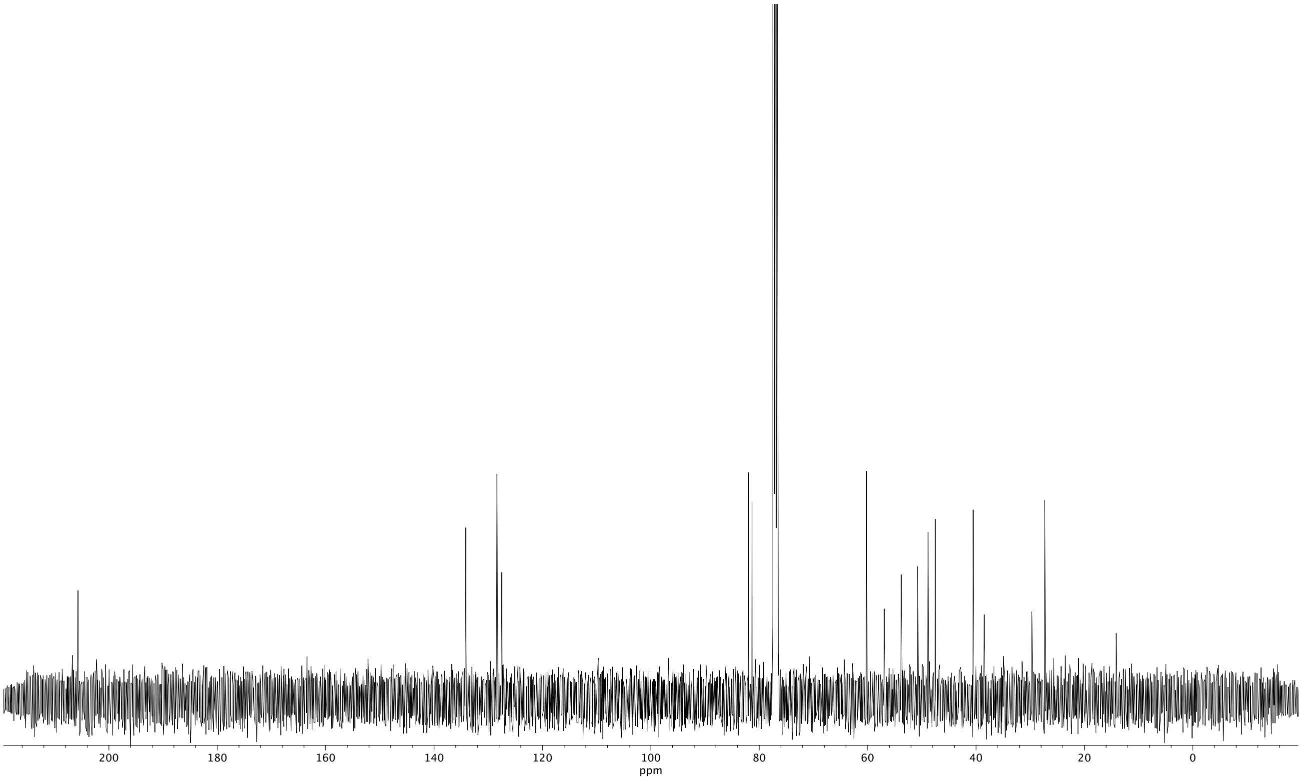


87 (diastereomer 2)

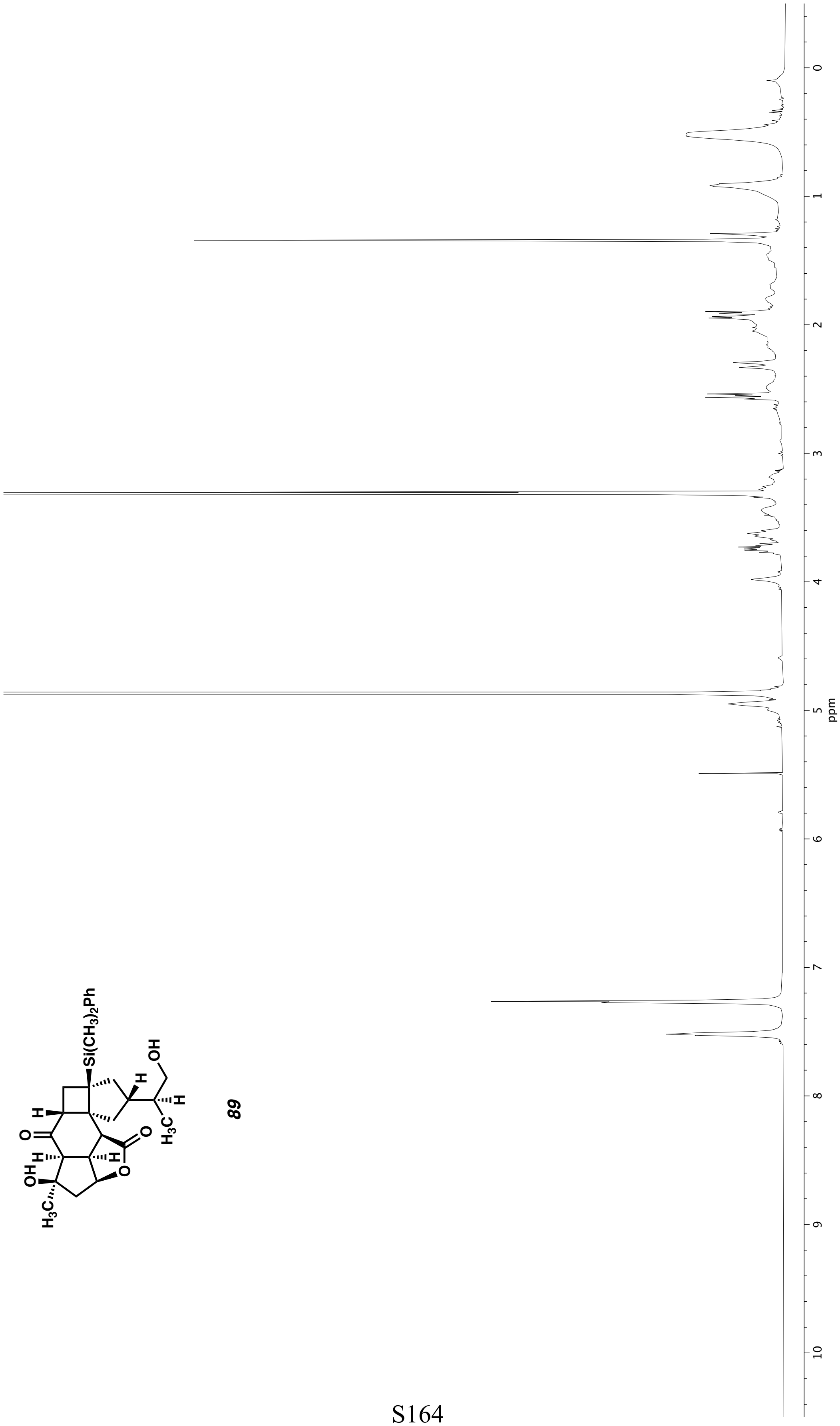
^{1}H NMR (400 MHz, CDCl$_3$) of compound **87** (diastereomer 2).



Infrared spectrum (Thin Film, NaCl) of compound **87** (diastereomer 2).

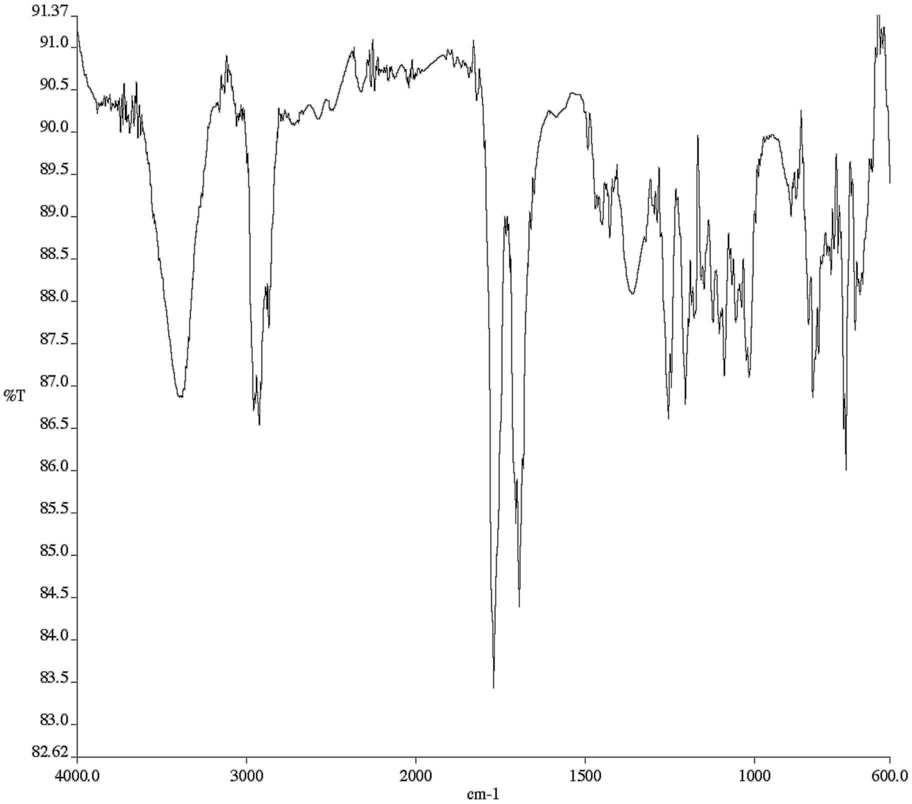


^{13}C NMR (100 MHz, CDCl$_3$) of compound **87** (diastereomer 2).

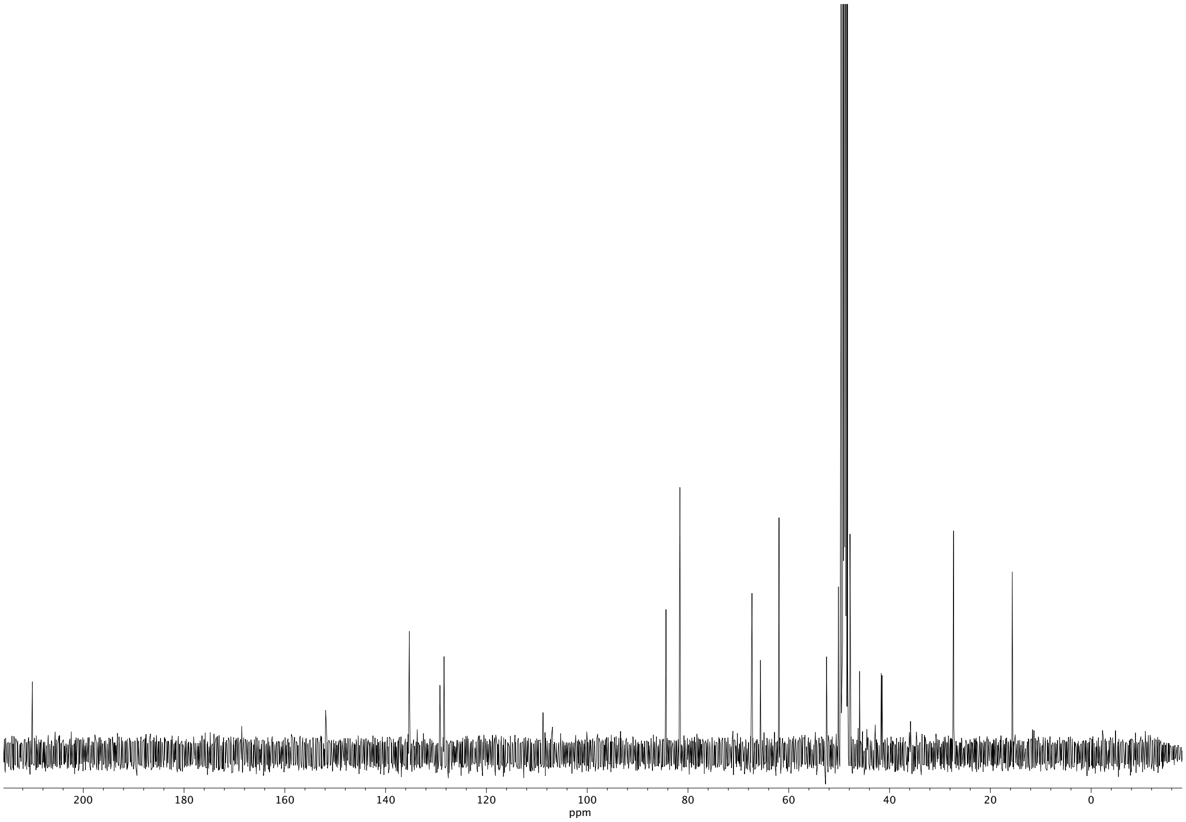


89

^{1}H NMR (400 MHz, CD$_3$OD) of compound **89**.

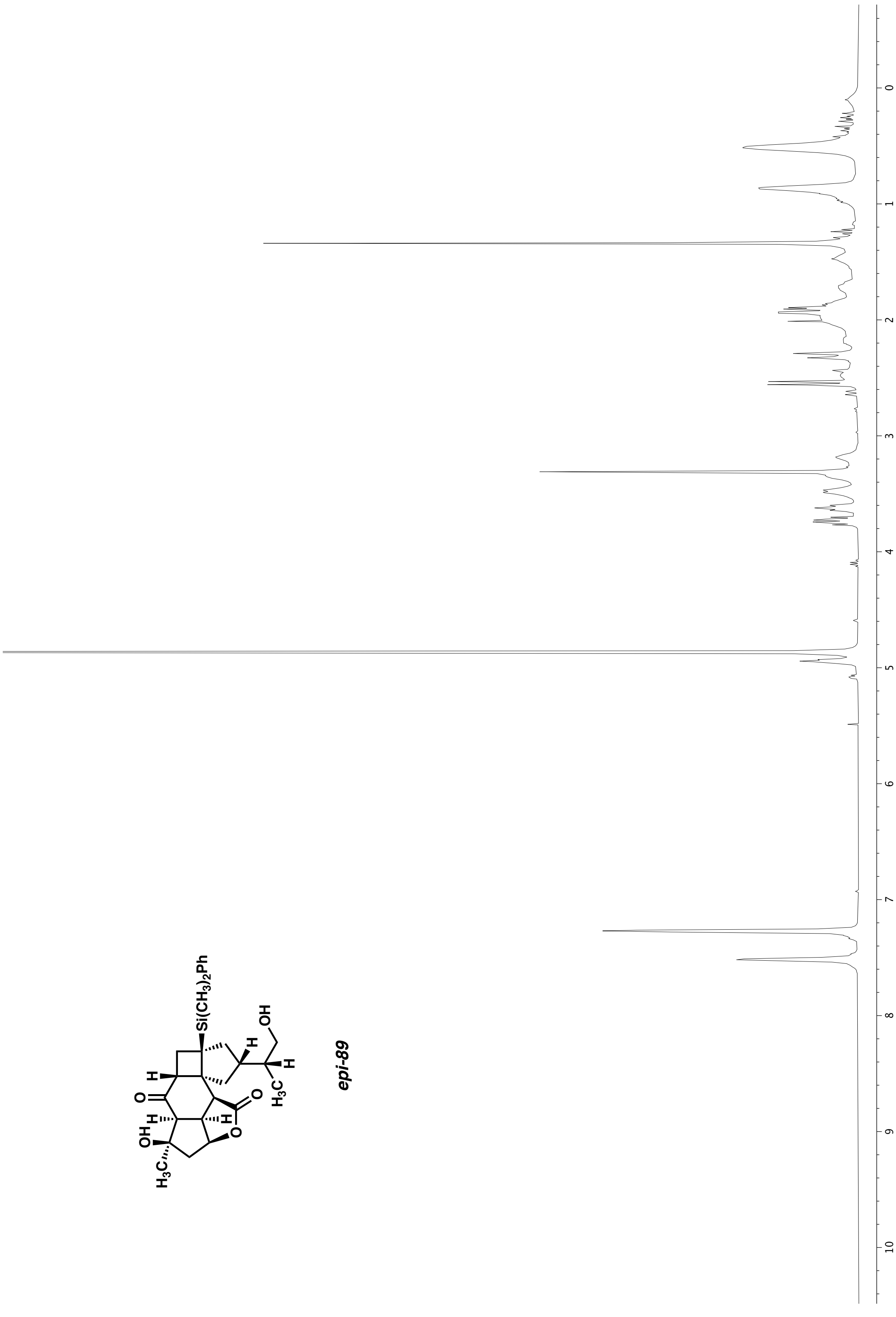


Infrared spectrum (Thin Film, NaCl) of compound **89.**

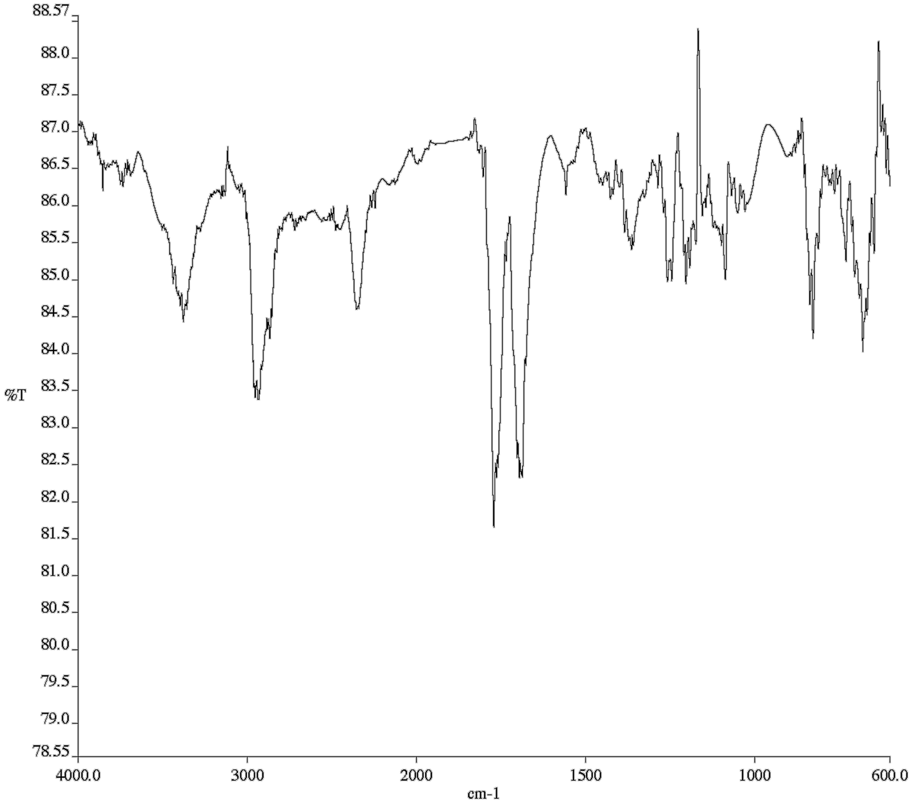


^{13}C NMR (100 MHz, CD$_3$OD) of compound **89.**

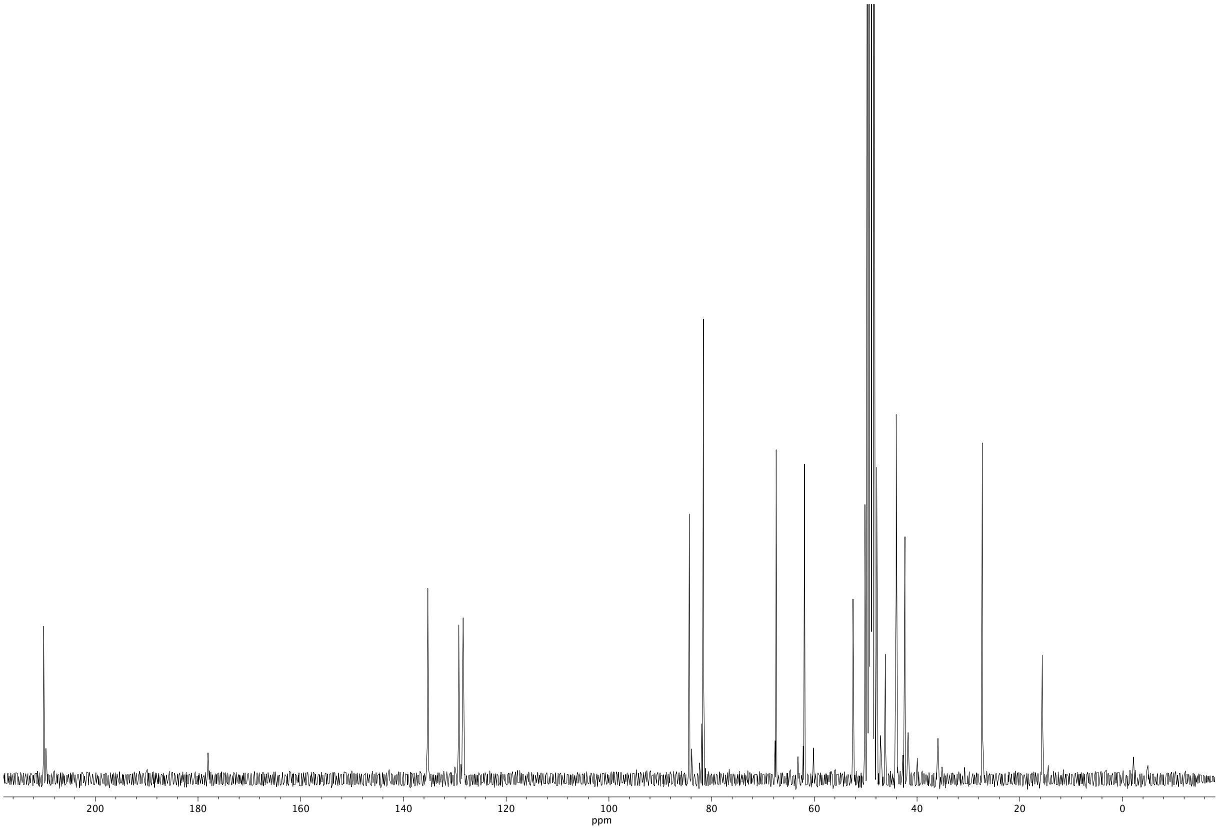
***epi*-89**



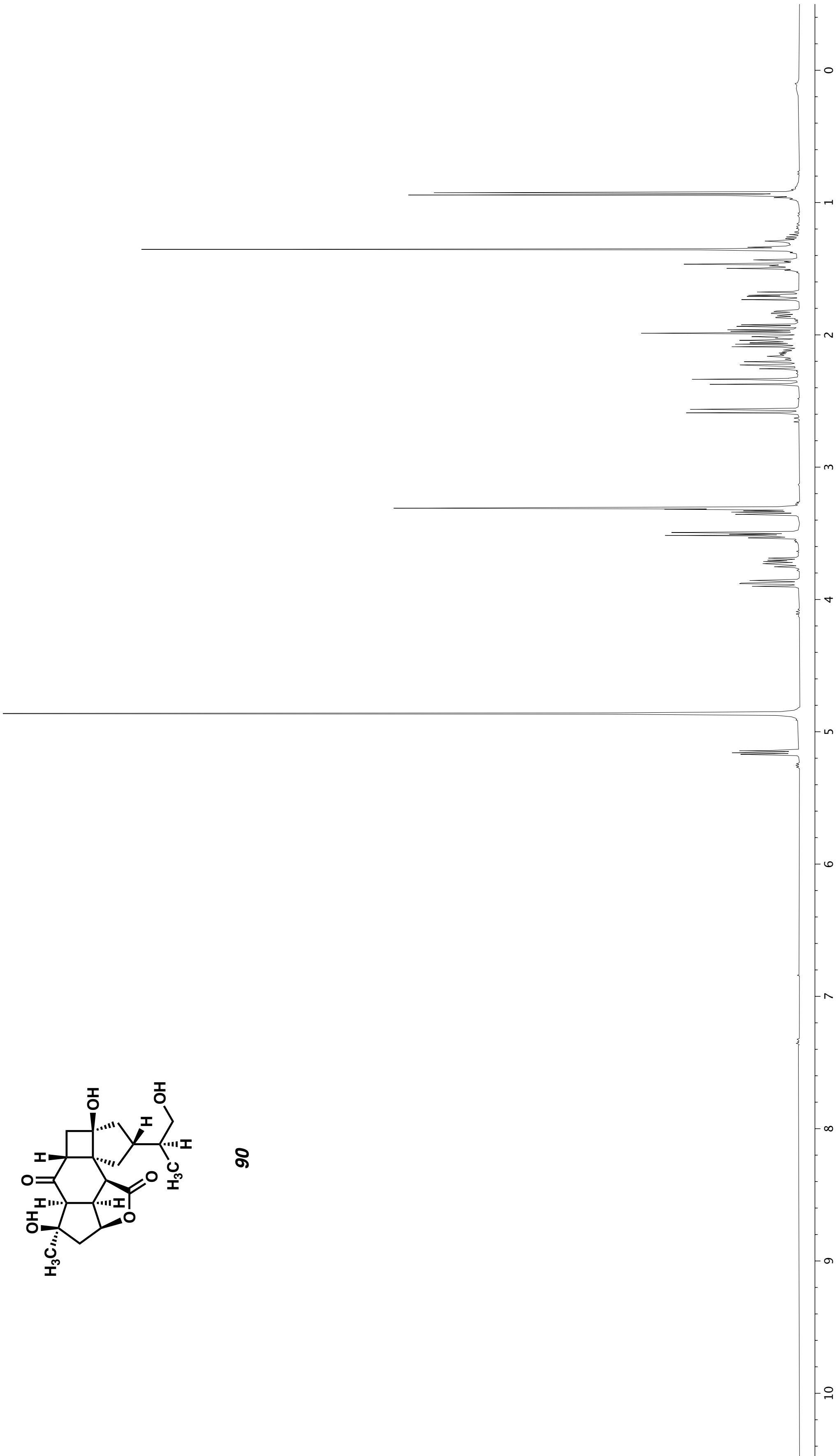
^{1}H NMR (400 MHz, CD_3OD) of compound *epi*-**89**.



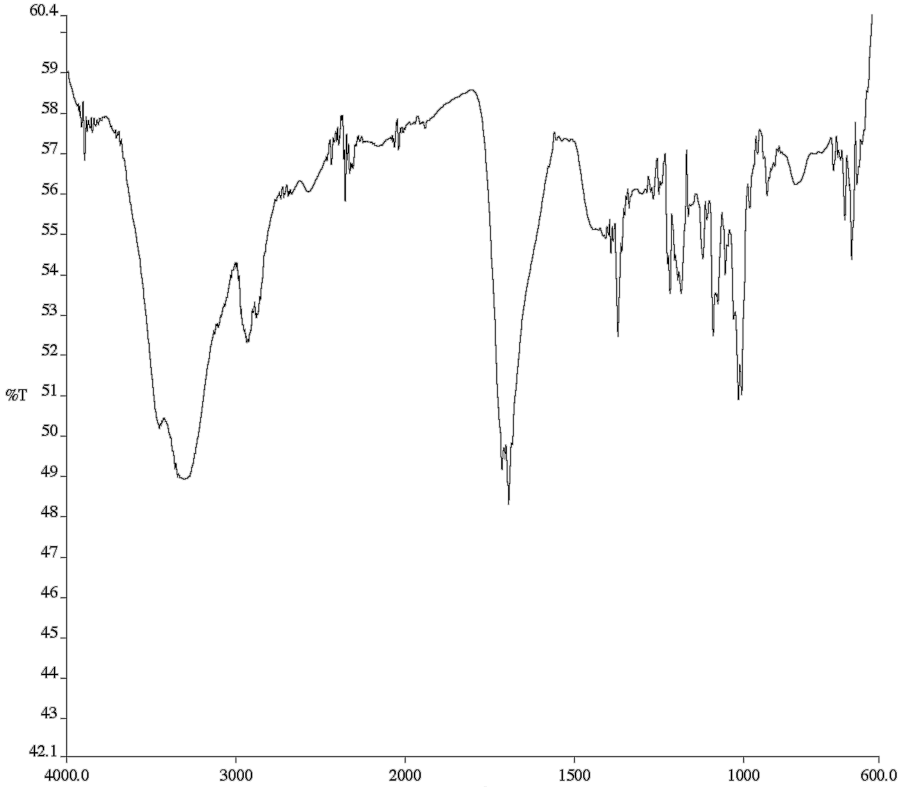
Infrared spectrum (Thin Film, NaCl) of compound *epi*-**89.**



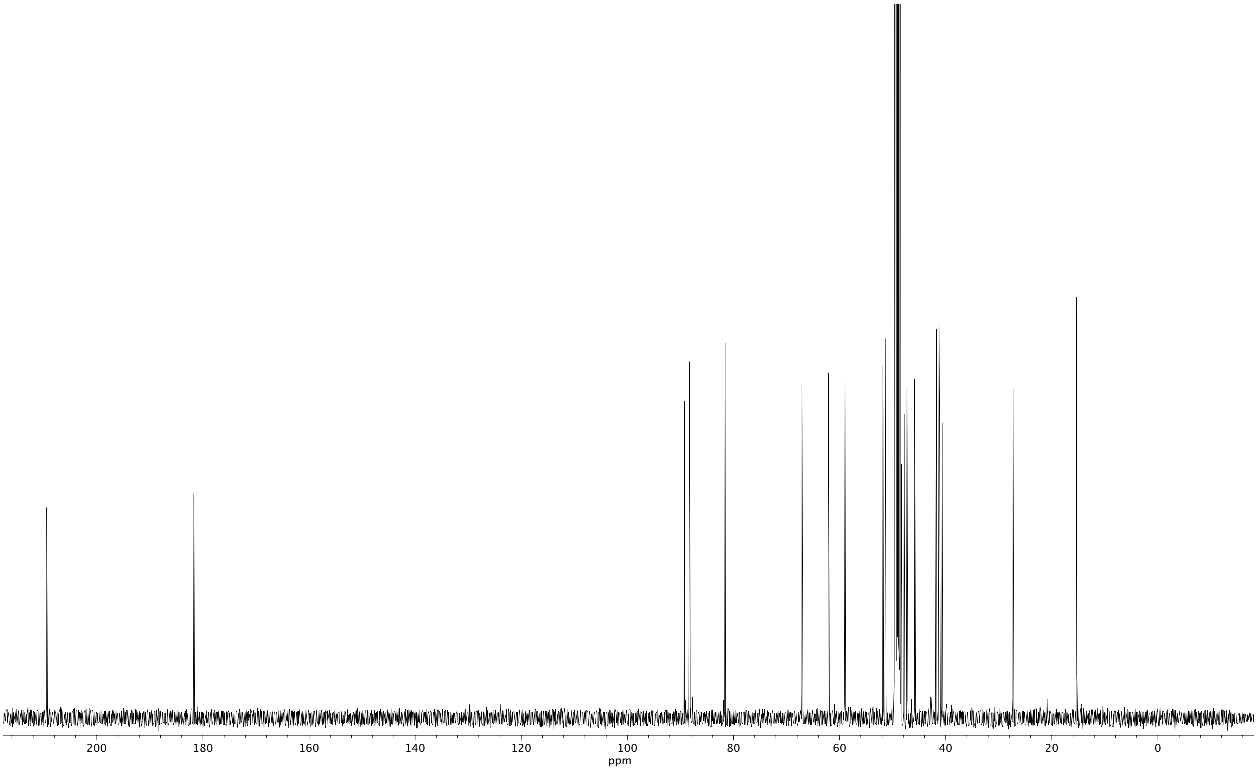
^{13}C NMR (100 MHz, CD$_3$OD) of compound *epi*-**89.**



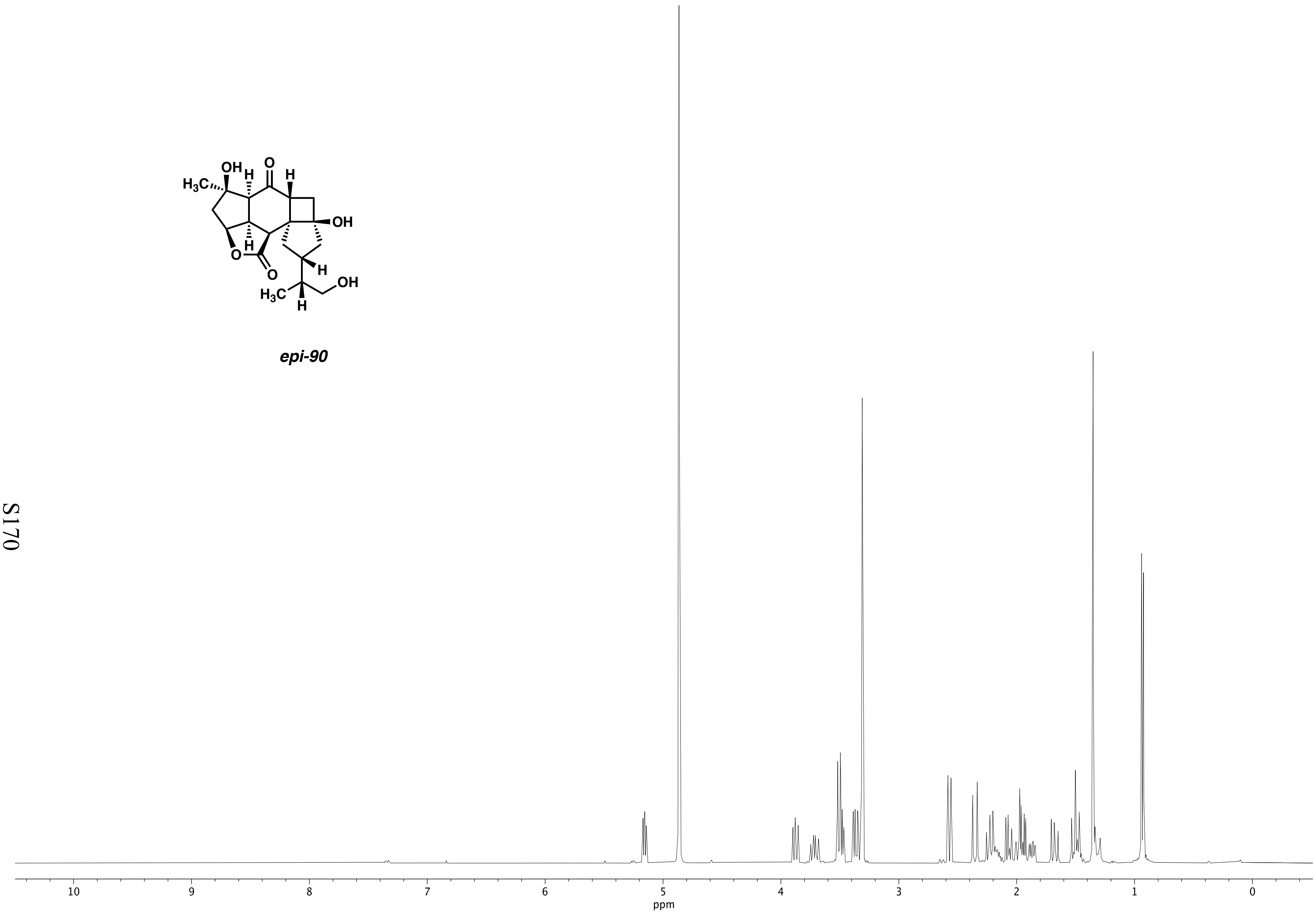
^{1}H NMR (400 MHz, CD$_3$OD) of compound **90**.



Infrared spectrum (Thin Film, NaCl) of compound **90.**



^{13}C NMR (100 MHz, CD_3OD) of compound **90.**



***epi*-90**

^{1}H NMR (400 MHz, CD$_3$OD) of compound *epi*-**90**.

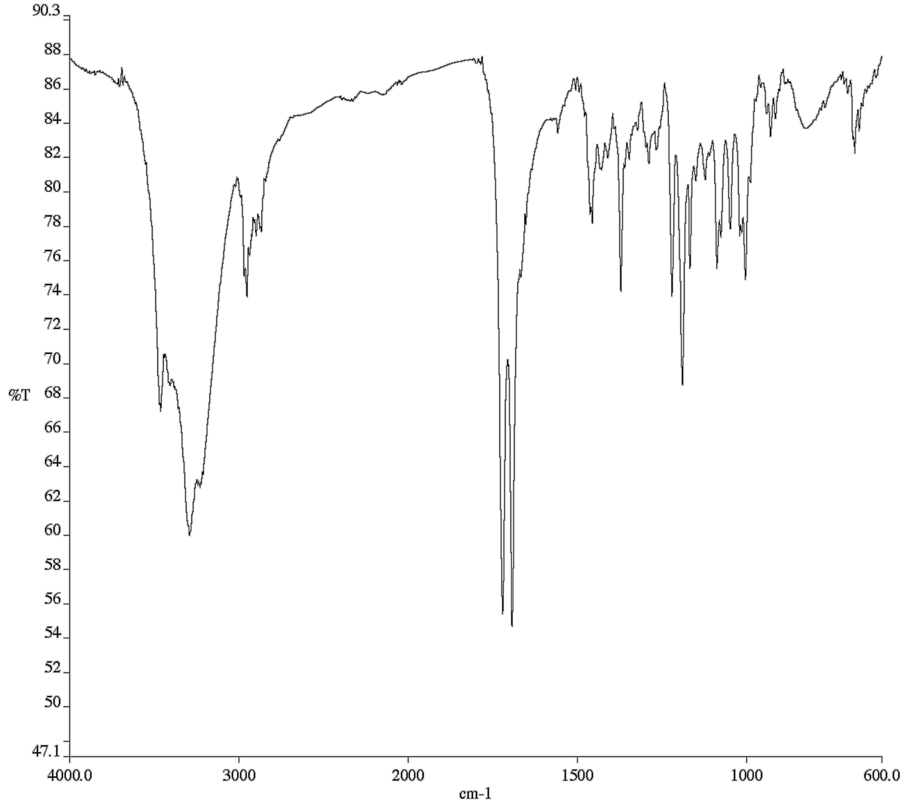
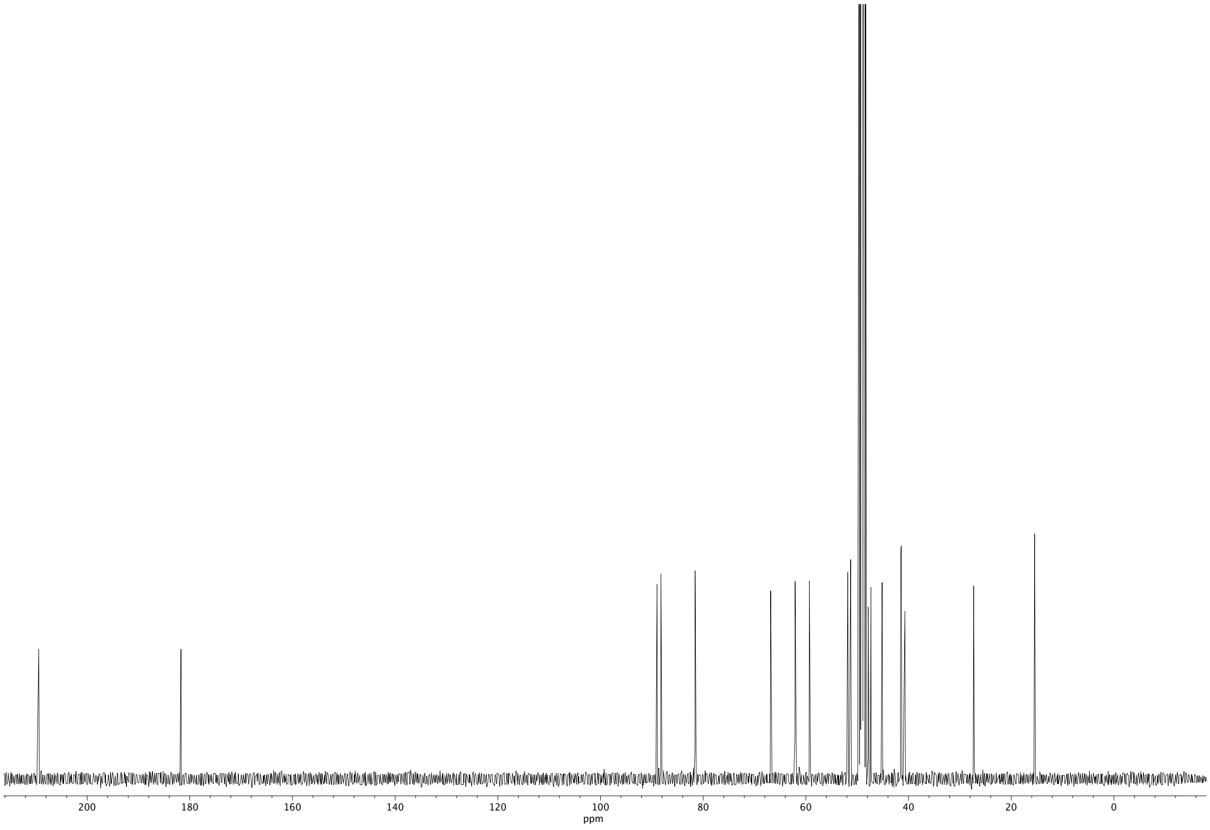
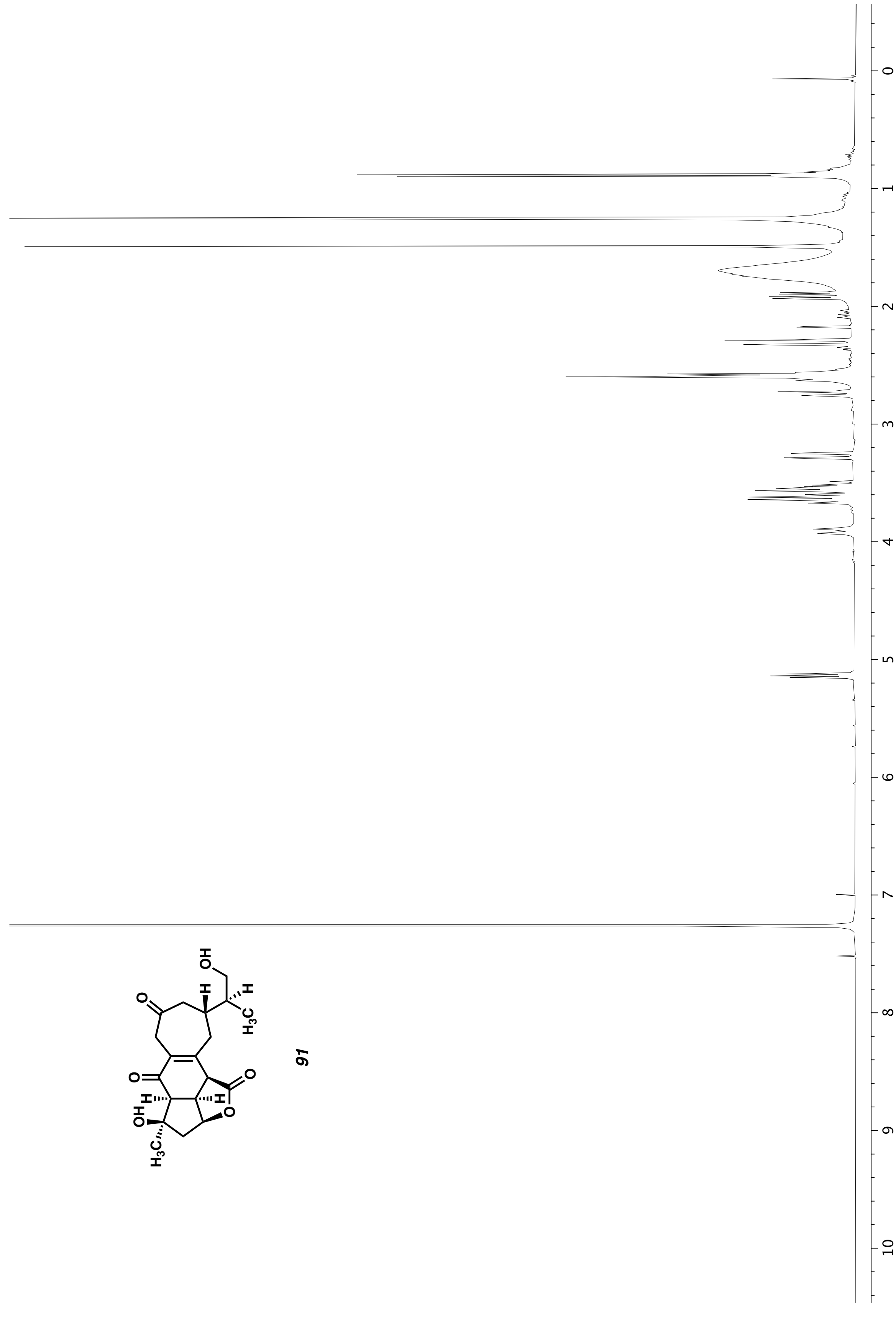


Figure A2.152 Infrared spectrum (Thin Film, NaCl) of compound *epi*-**90.**

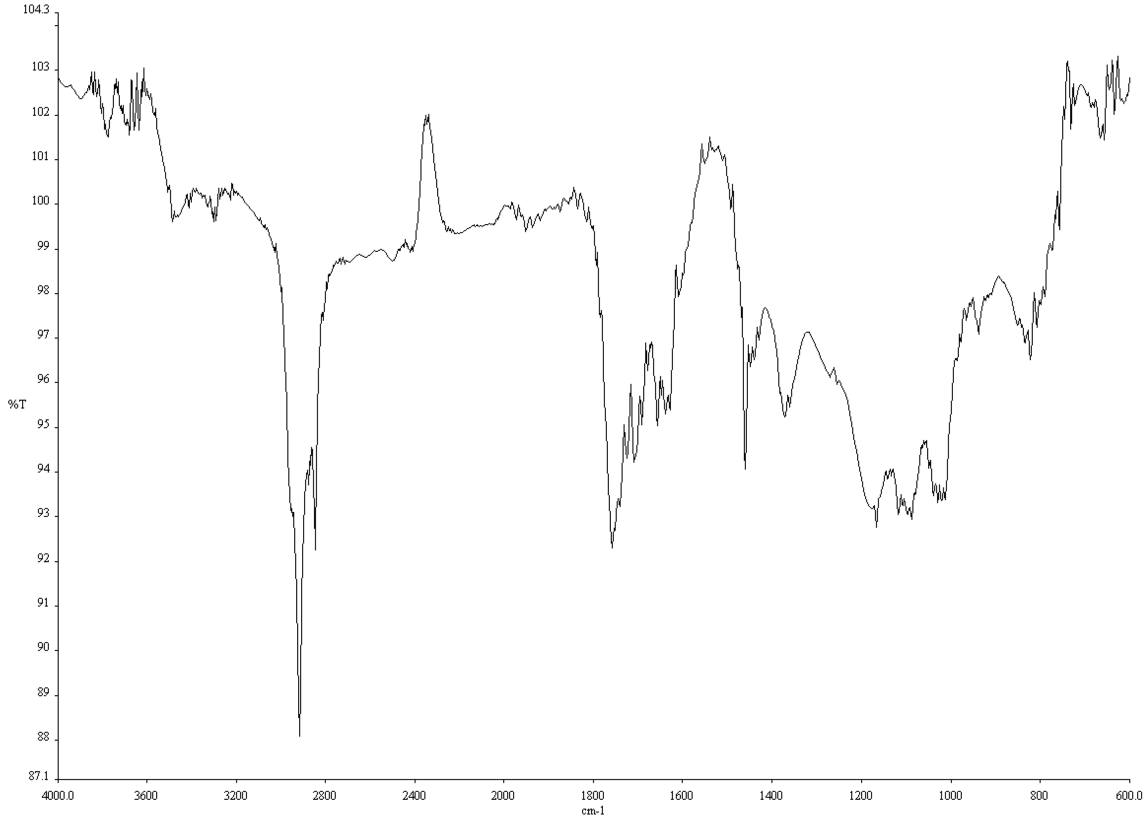


^{13}C NMR (100 MHz, CD_3OD) of compound *epi*-**90.**

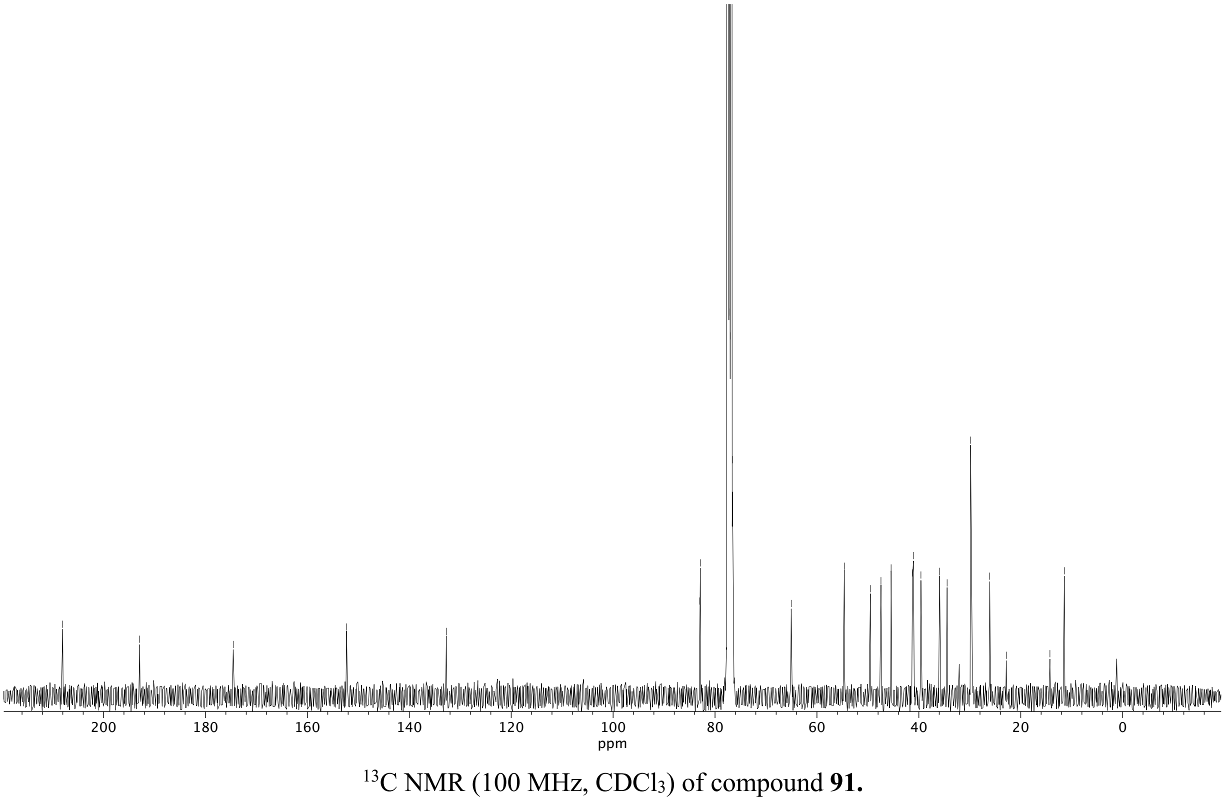


91

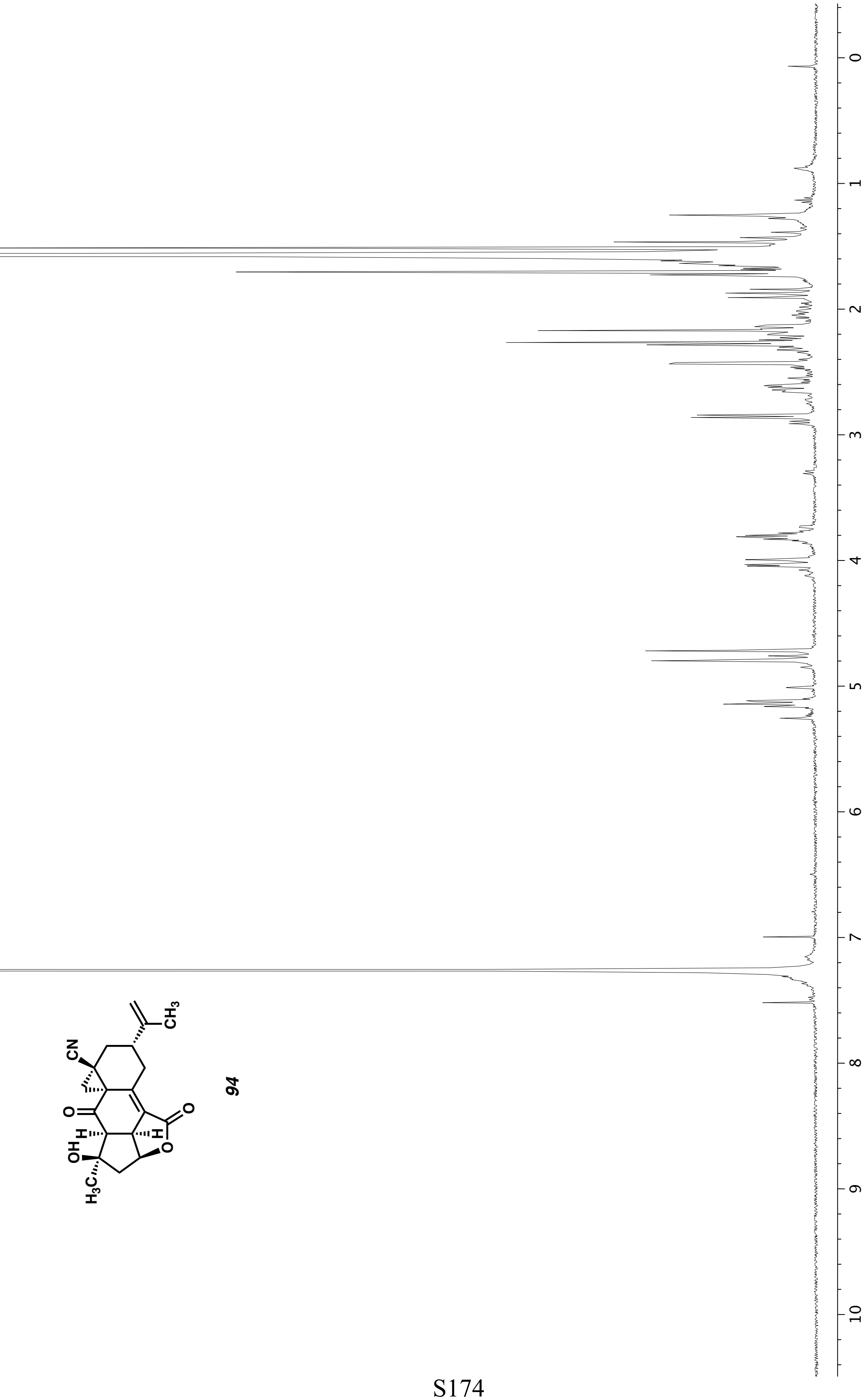
^{1}H NMR (400 MHz, CDCl$_3$) of compound **91**.



Infrared spectrum (Thin Film, NaCl) of compound **91.**

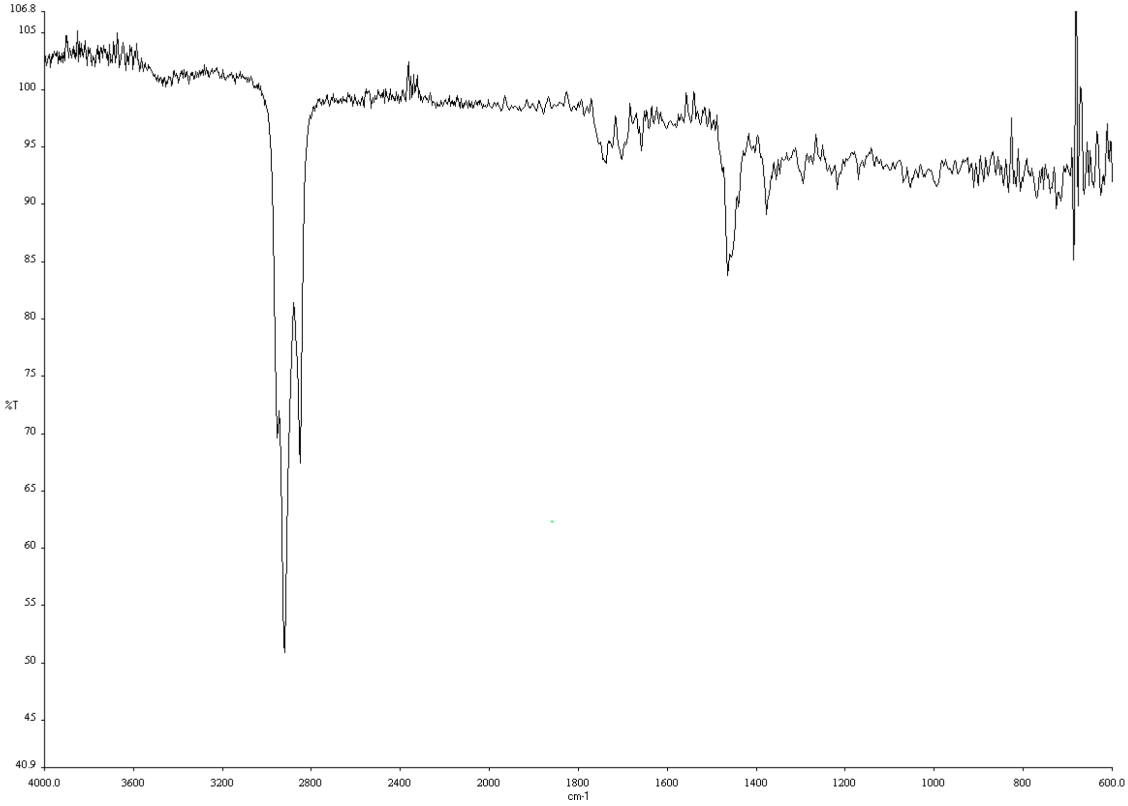


^{13}C NMR (100 MHz, CDCl$_3$) of compound **91.**

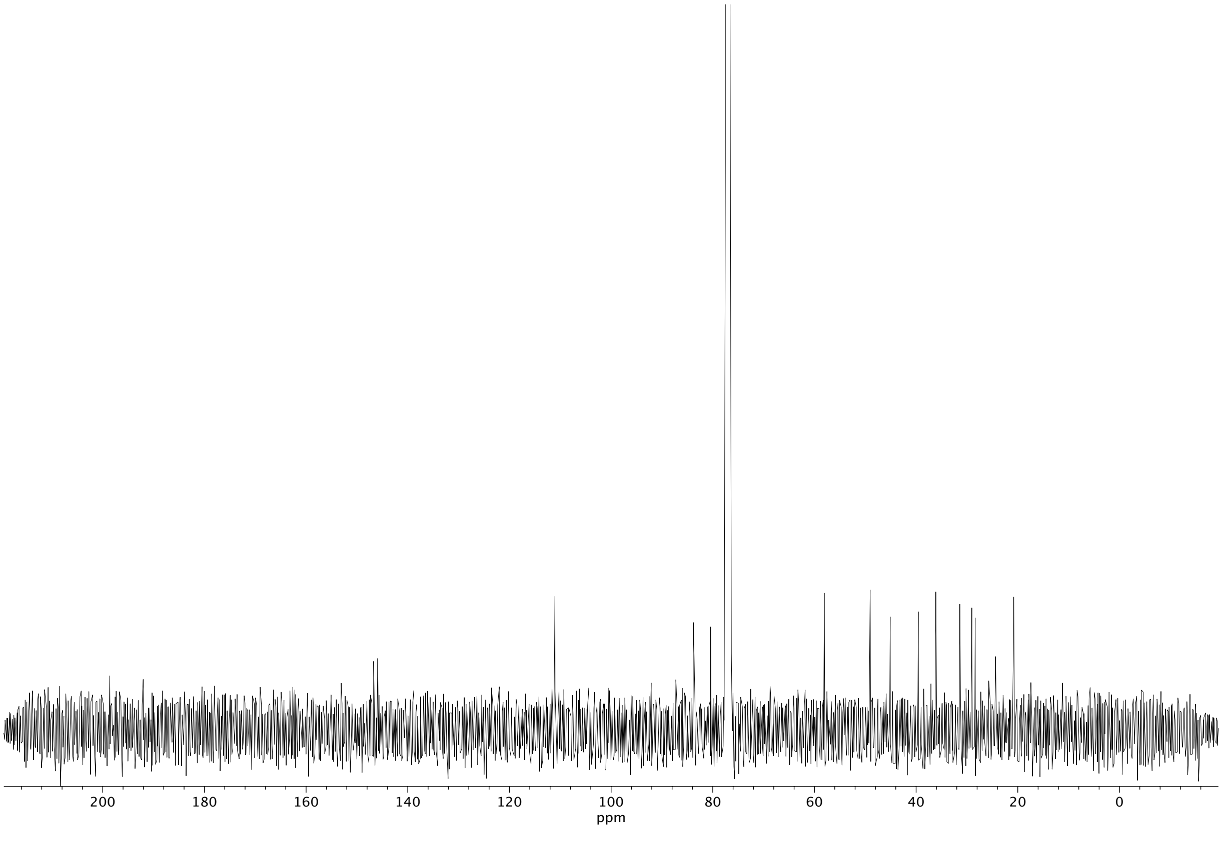


94

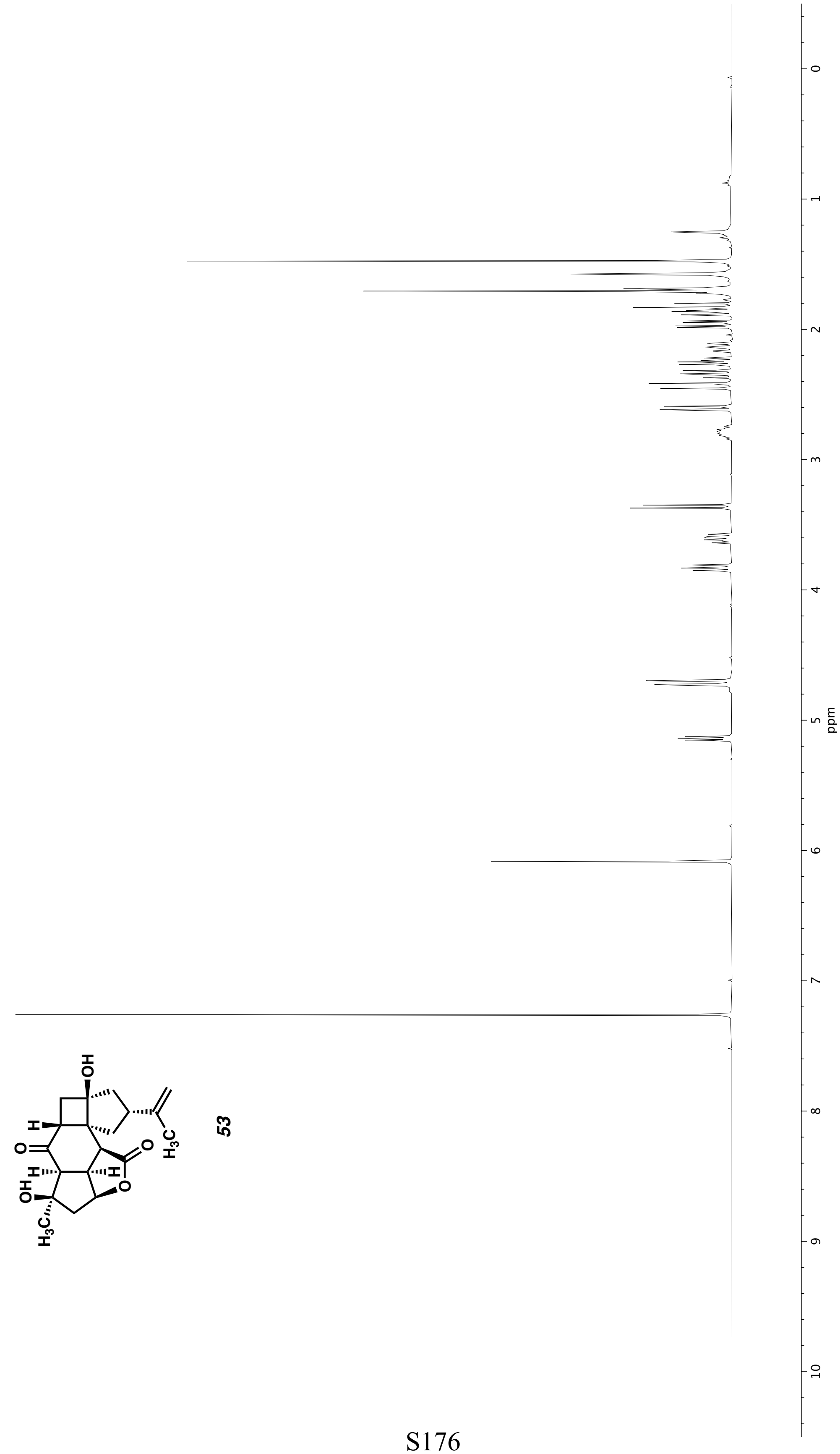
^{1}H NMR (400 MHz, CDCl$_3$) of compound **94**.



Infrared spectrum (Thin Film, NaCl) of compound **94.**

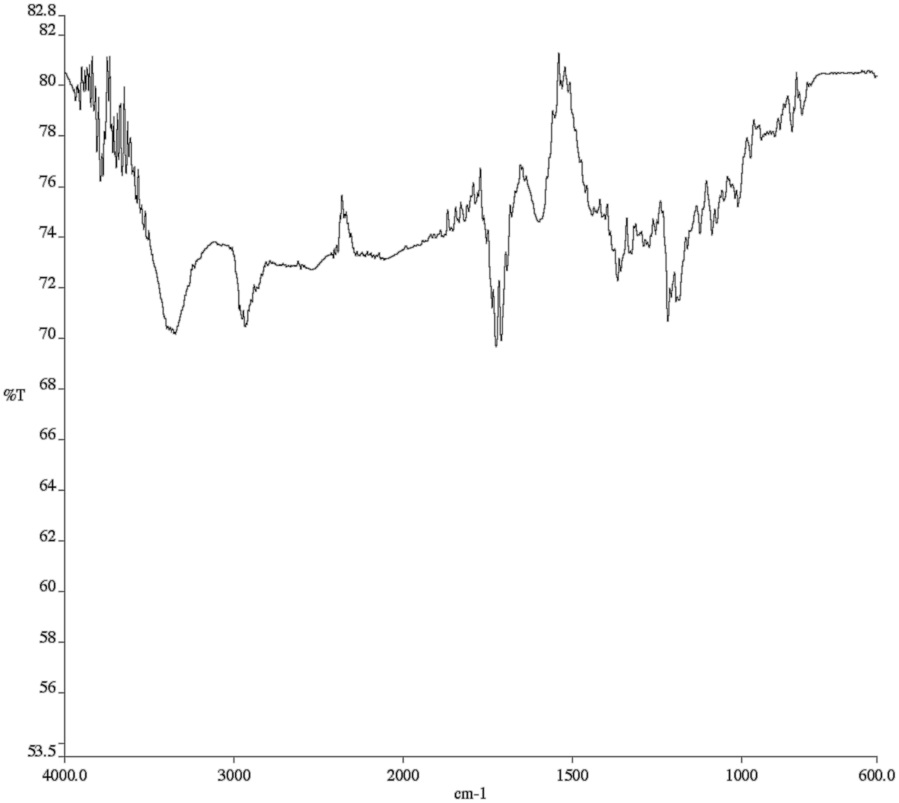


^{13}C NMR (100 MHz, CDCl$_3$) of compound **94.**

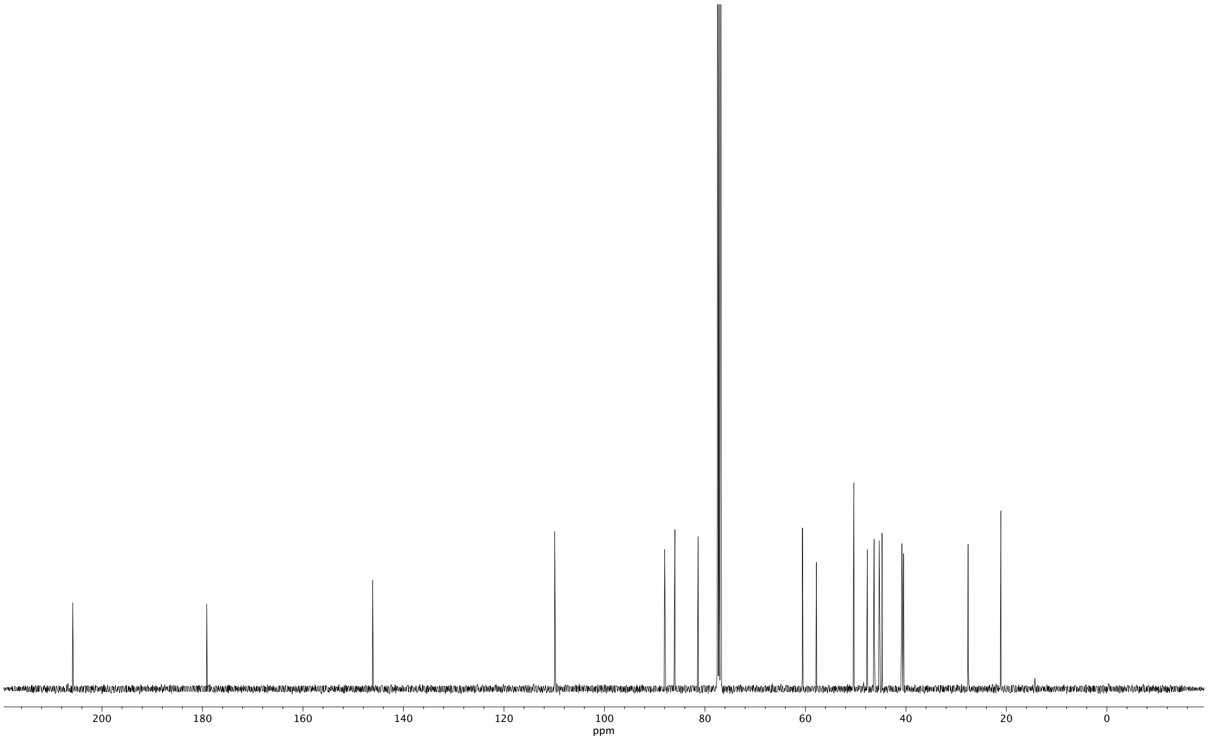


53

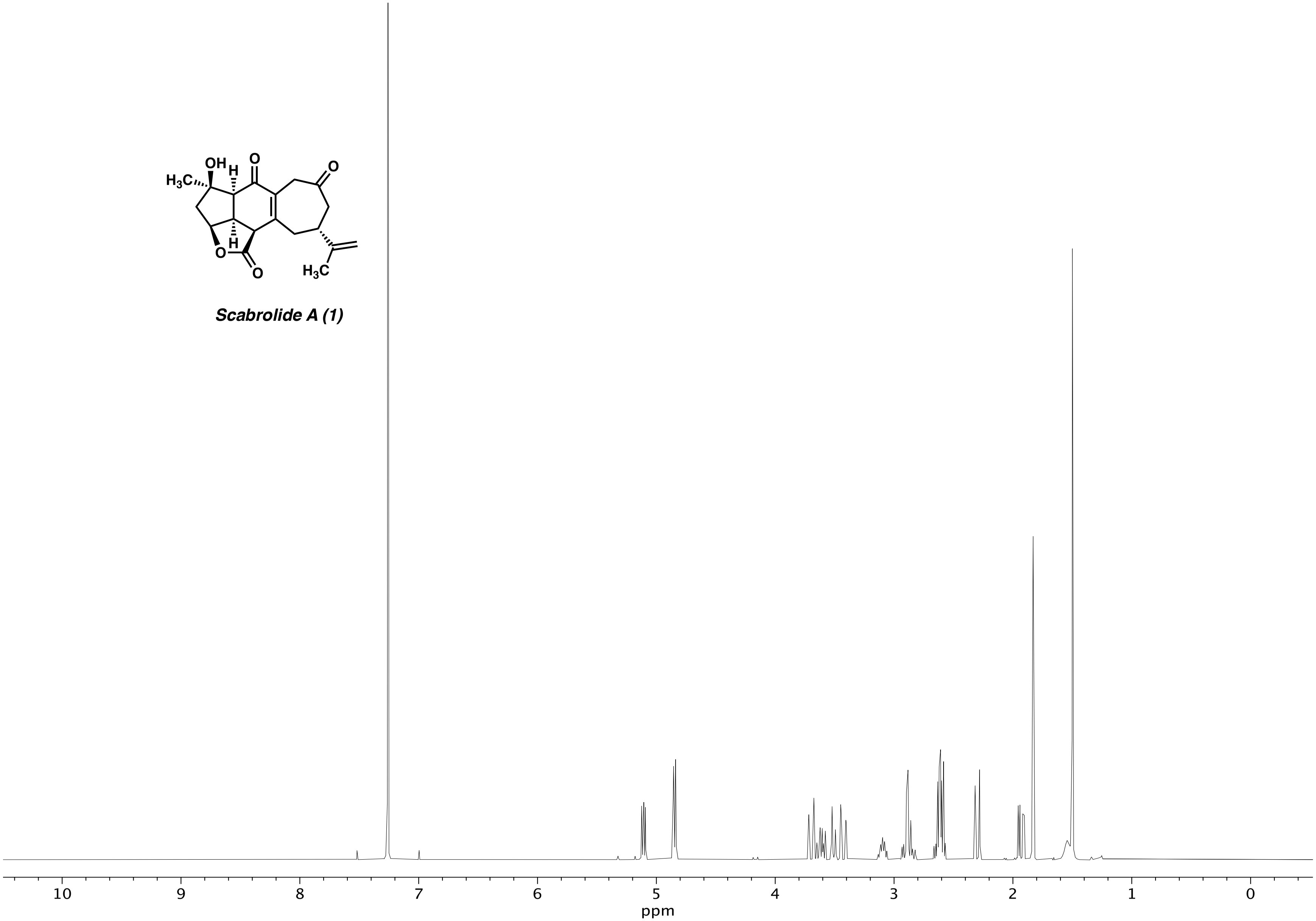
^{1}H NMR (400 MHz, CDCl$_3$) of compound **53**.



Infrared spectrum (Thin Film, NaCl) of compound **53.**

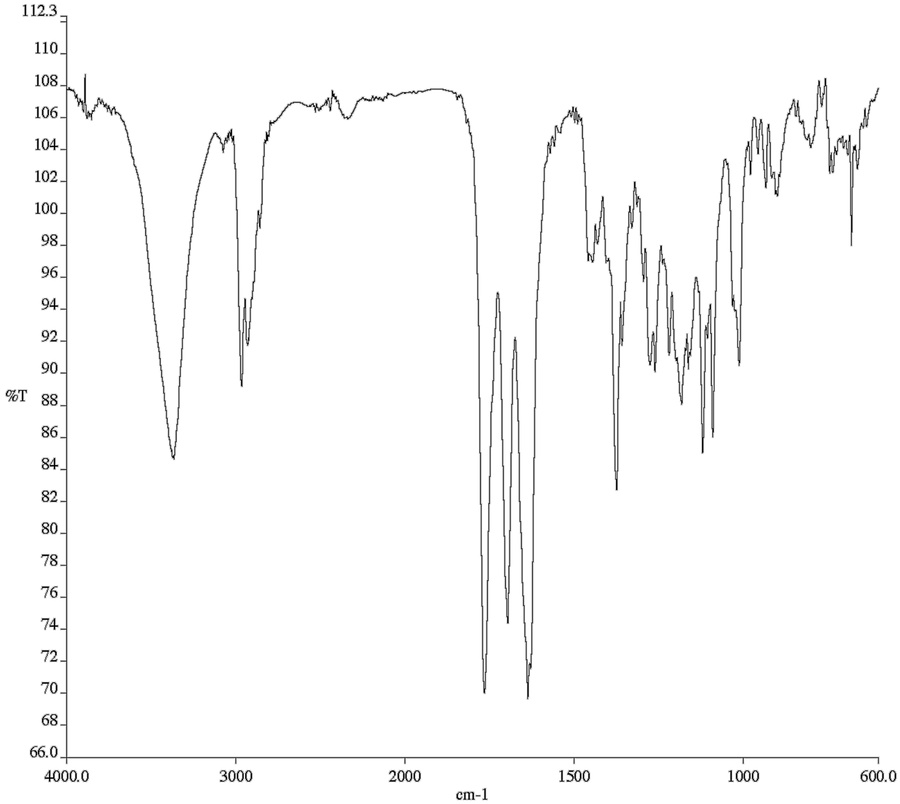


^{13}C NMR (100 MHz, CDCl$_3$) of compound **53.**

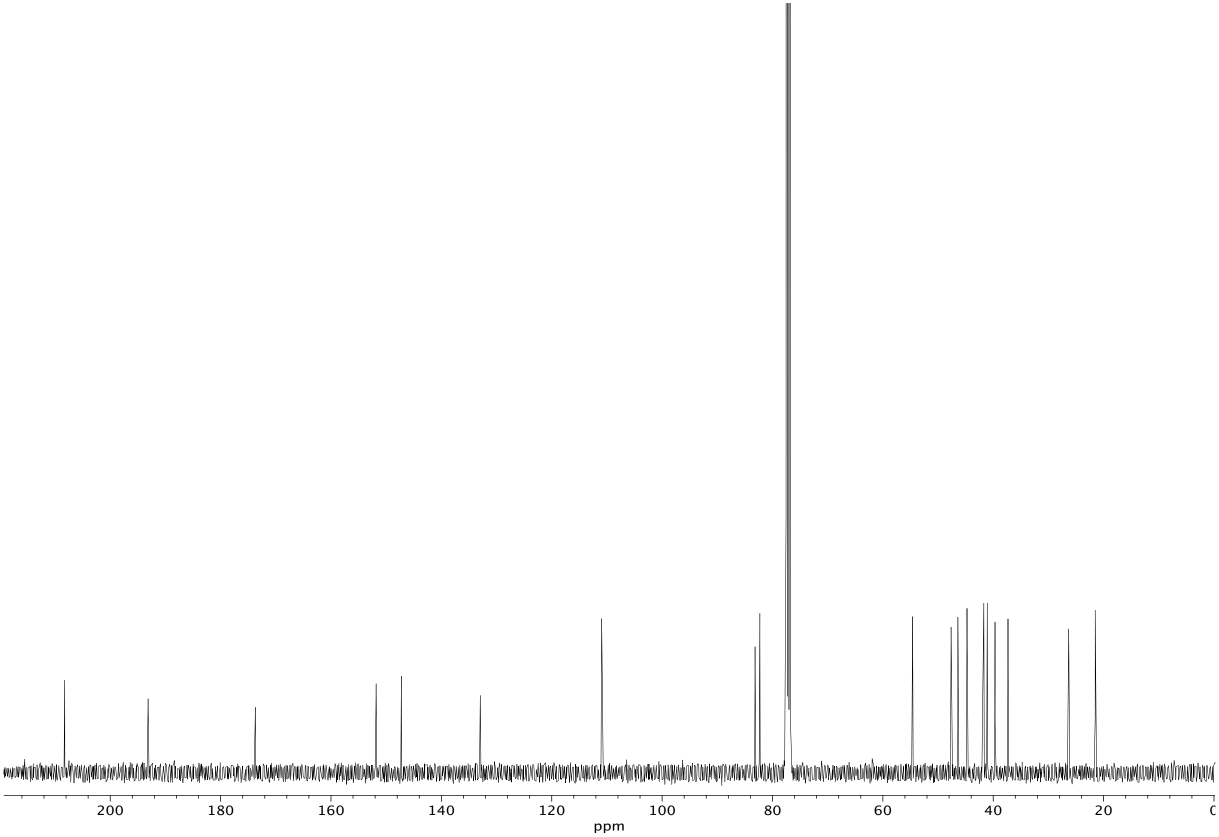


Scabrolide A (1)

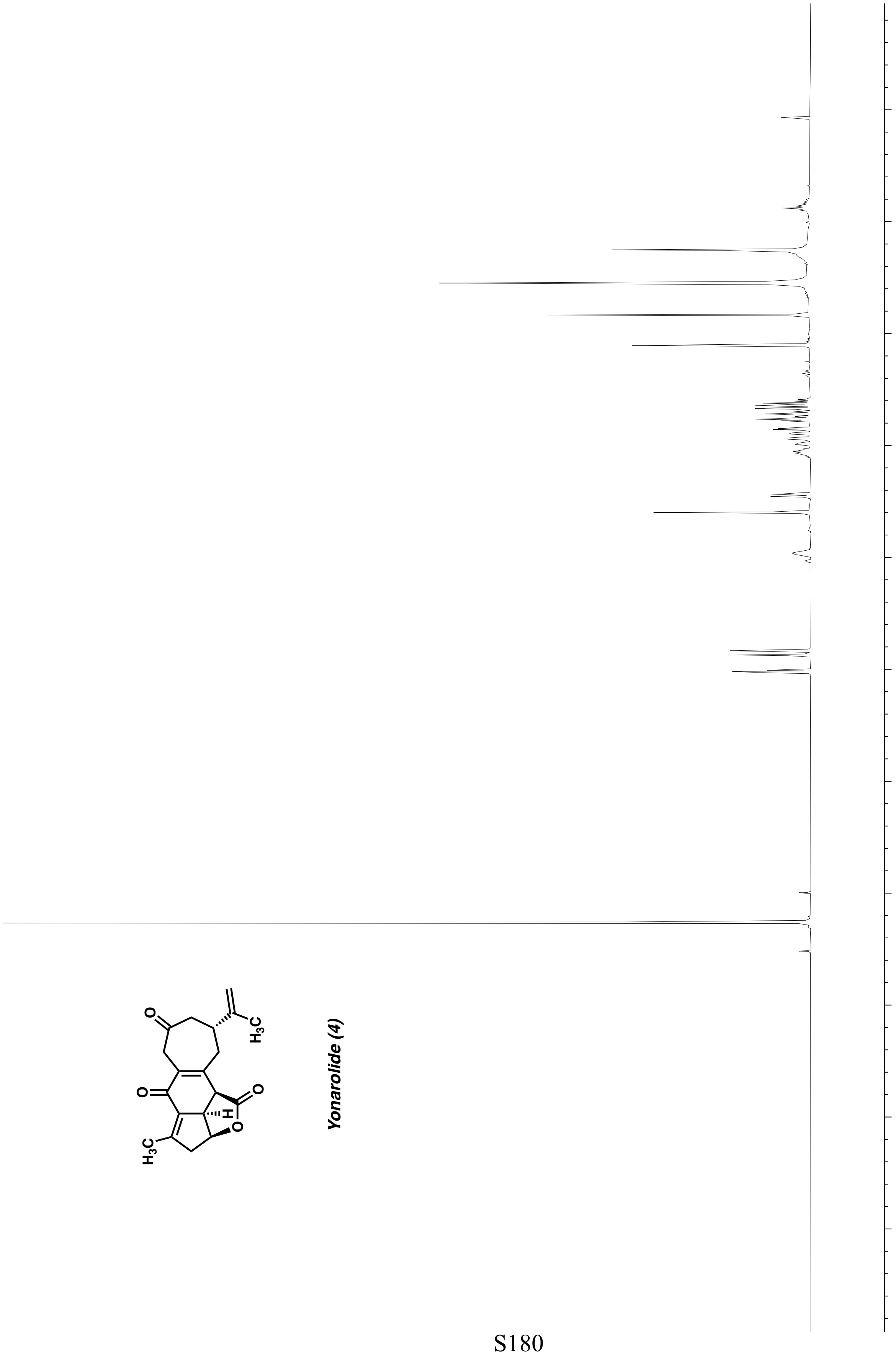
^{1}H NMR (400 MHz, $CDCl_3$) of compound **1**.



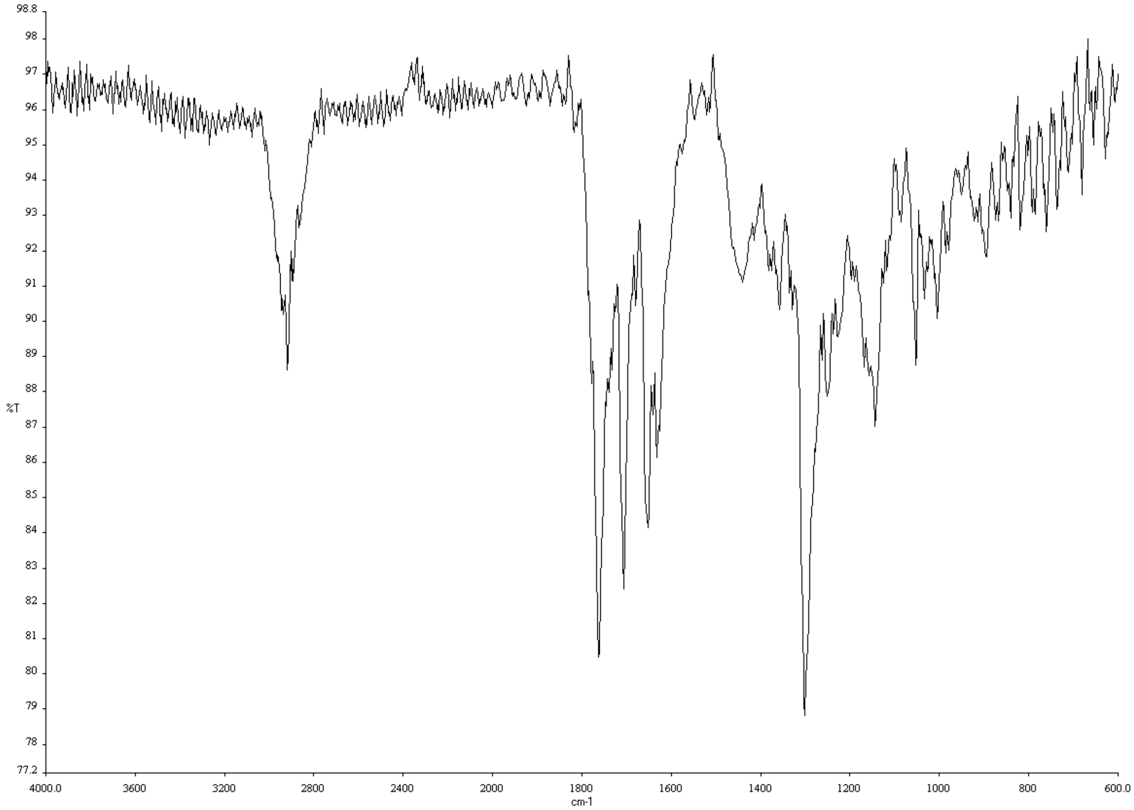
Infrared spectrum (Thin Film, NaCl) of compound **1.**



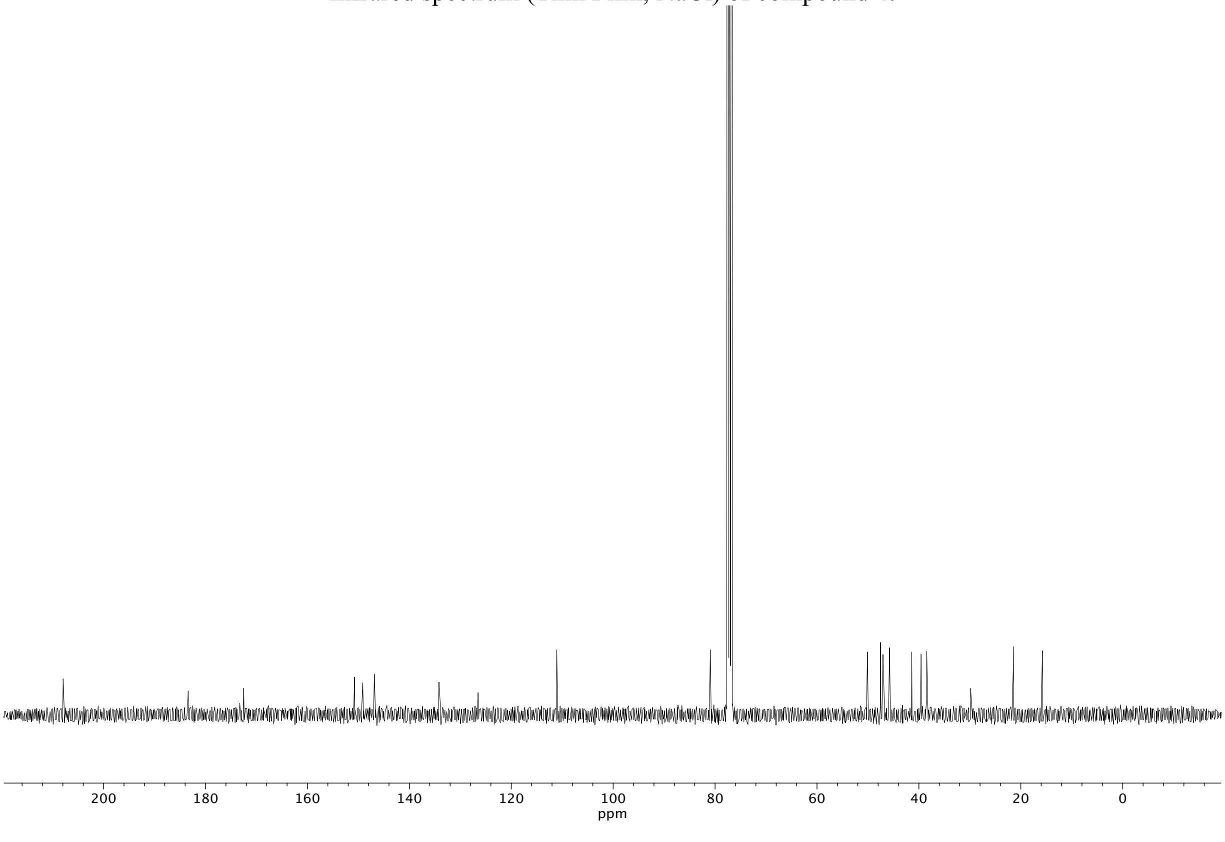
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1.**



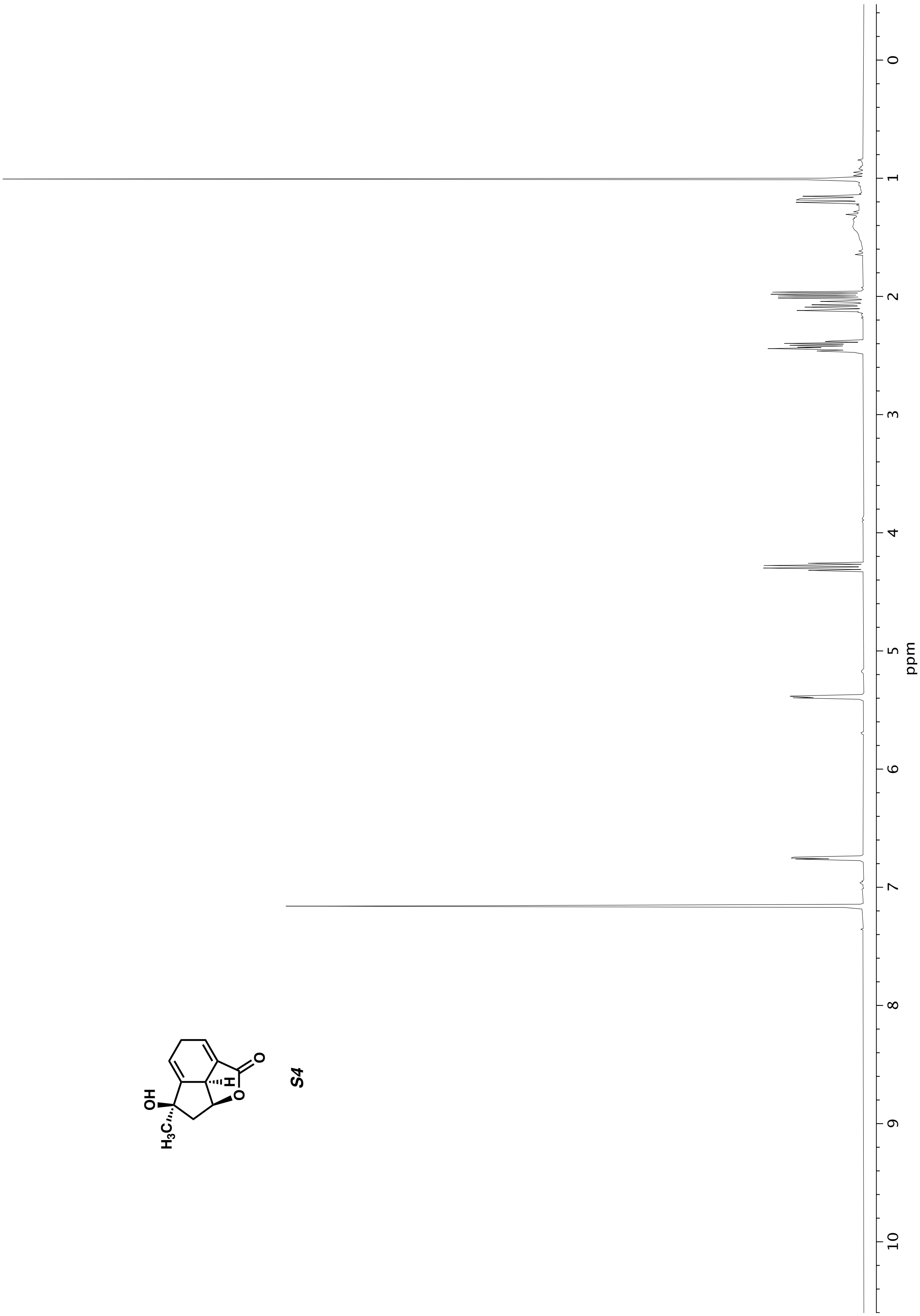
^{1}H NMR (400 MHz, CDCl$_3$) of compound **4**.



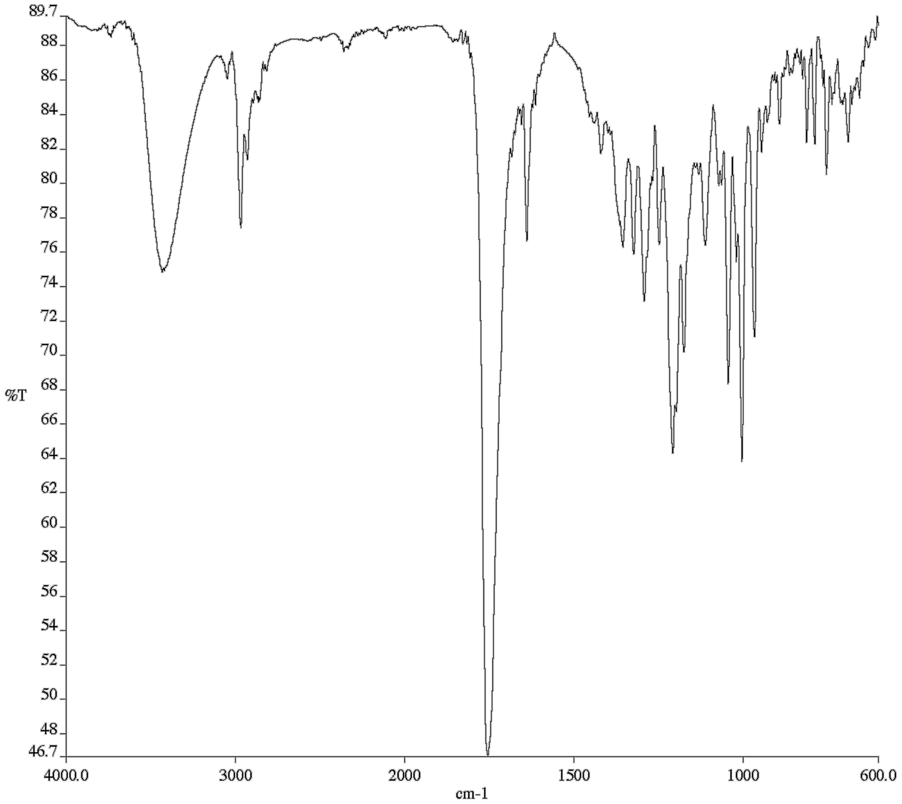
Infrared spectrum (Thin Film, NaCl) of compound **4.**



^{13}C NMR (100 MHz, CDCl$_3$) of compound **4.**

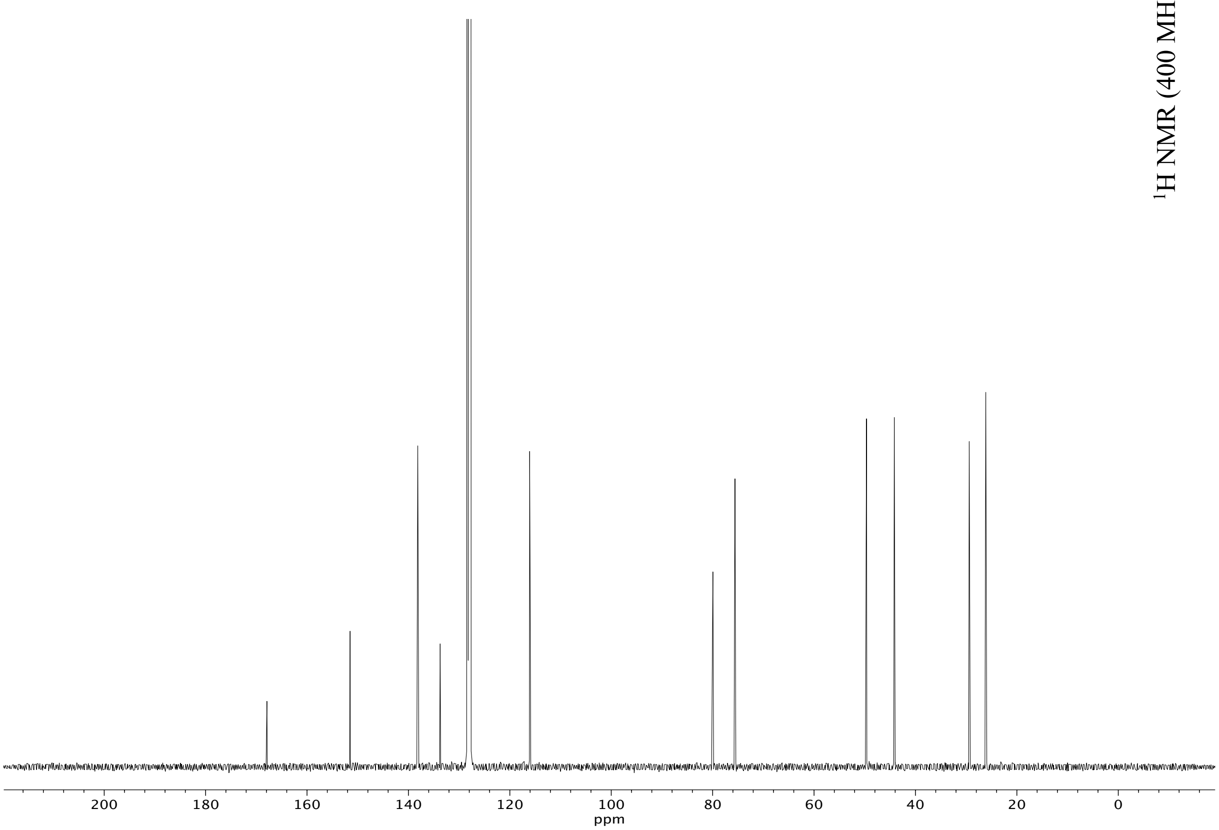


S4

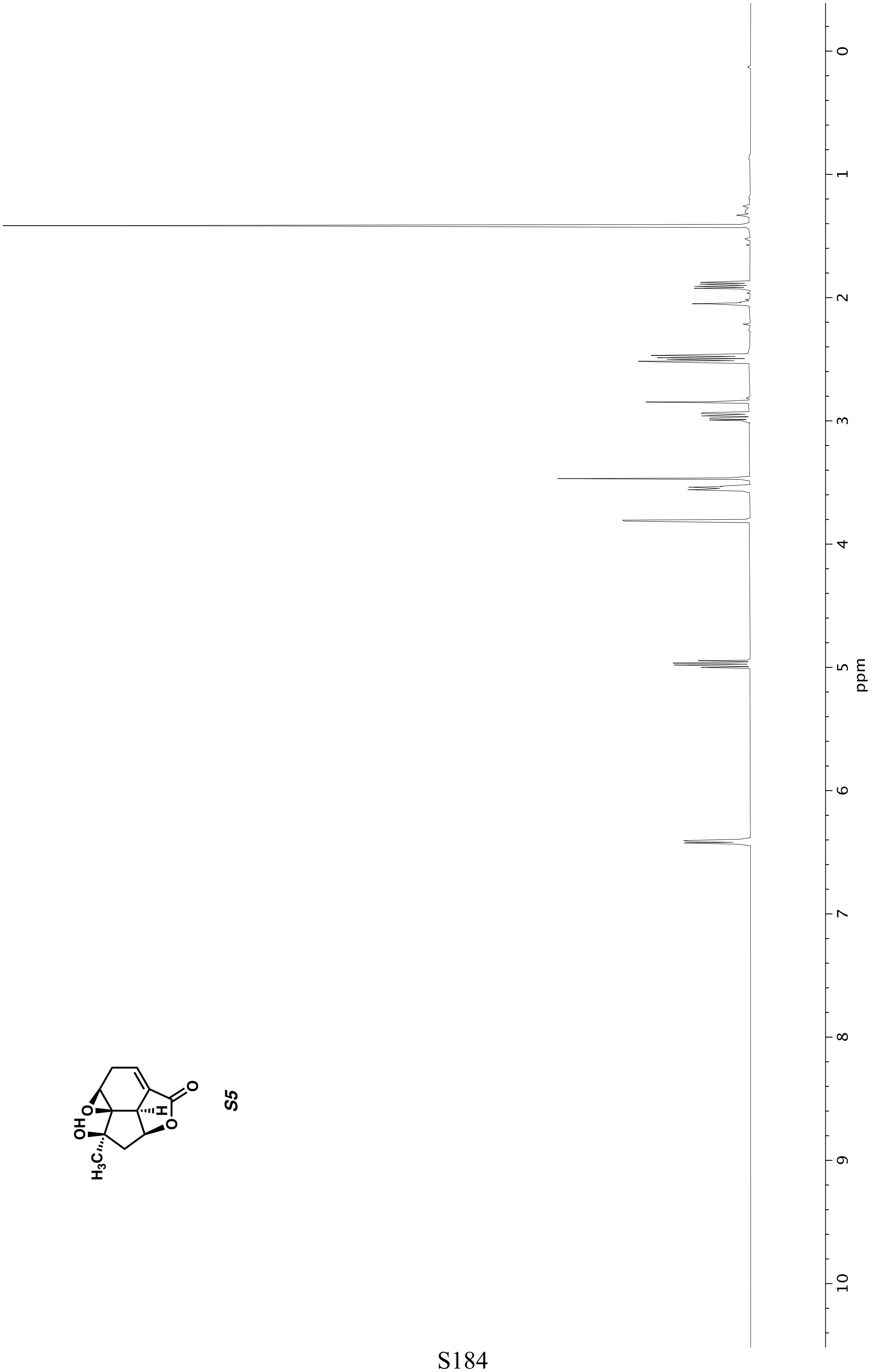


Infrared spectrum (Thin Film, NaCl) of compound **S4**.

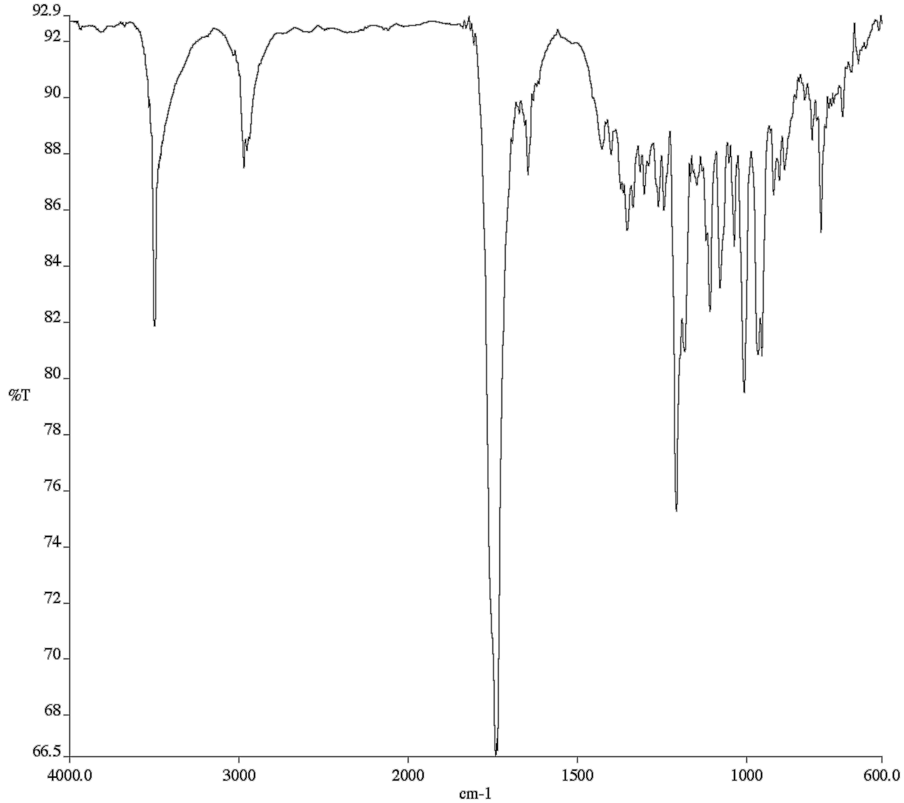
^{1}H NMR (400 MHz, C_6D_6) of compound **S4**.



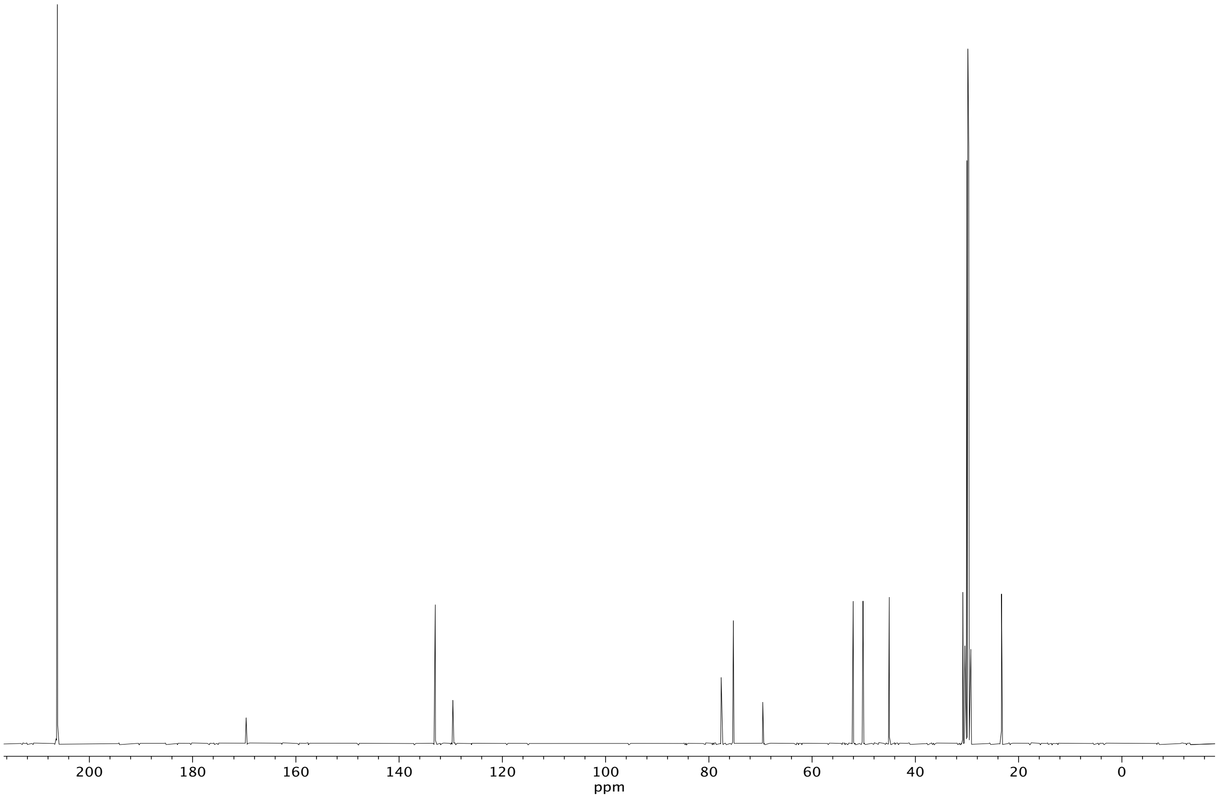
^{13}C NMR (100 MHz, C_6D_6) of compound **S4**.



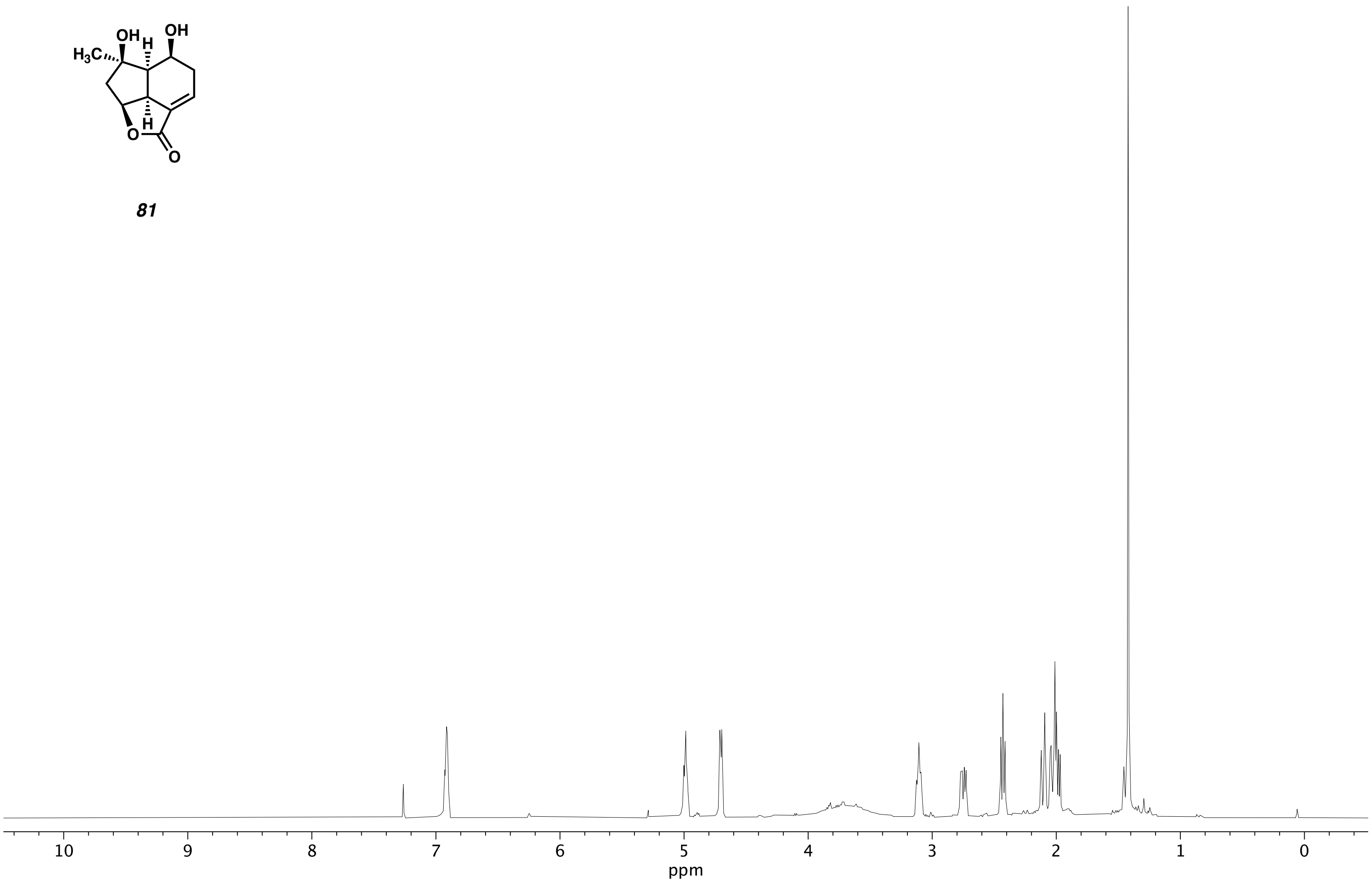
^{1}H NMR (500 MHz, $(CD_3)_2CO$) of compound **S5**.



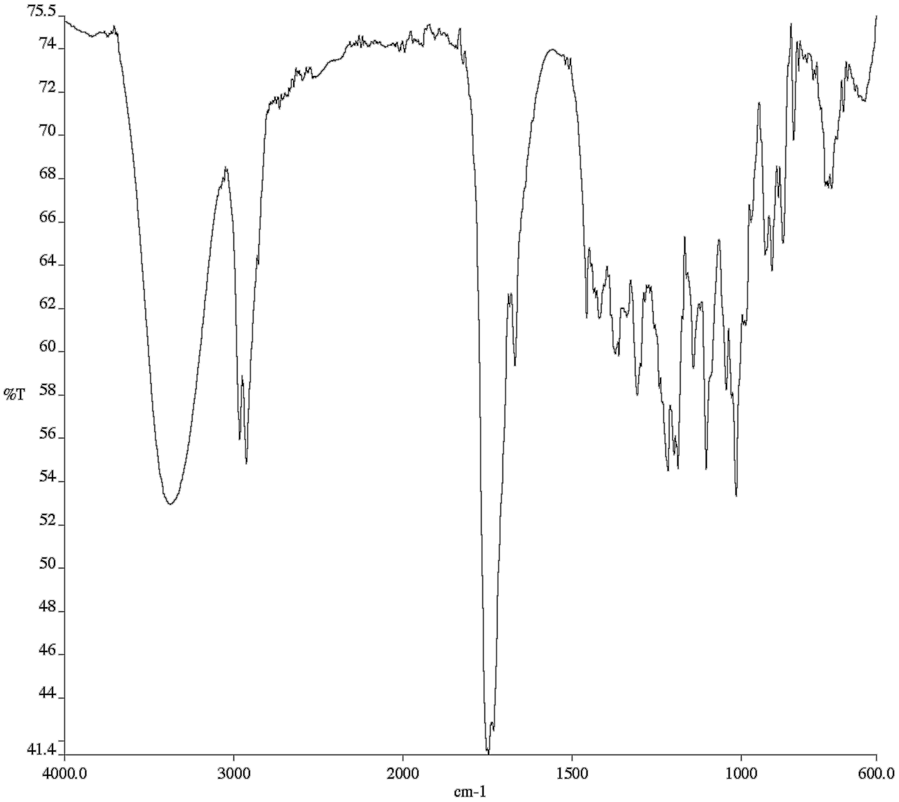
Infrared spectrum (Thin Film, NaCl) of compound **S5**.



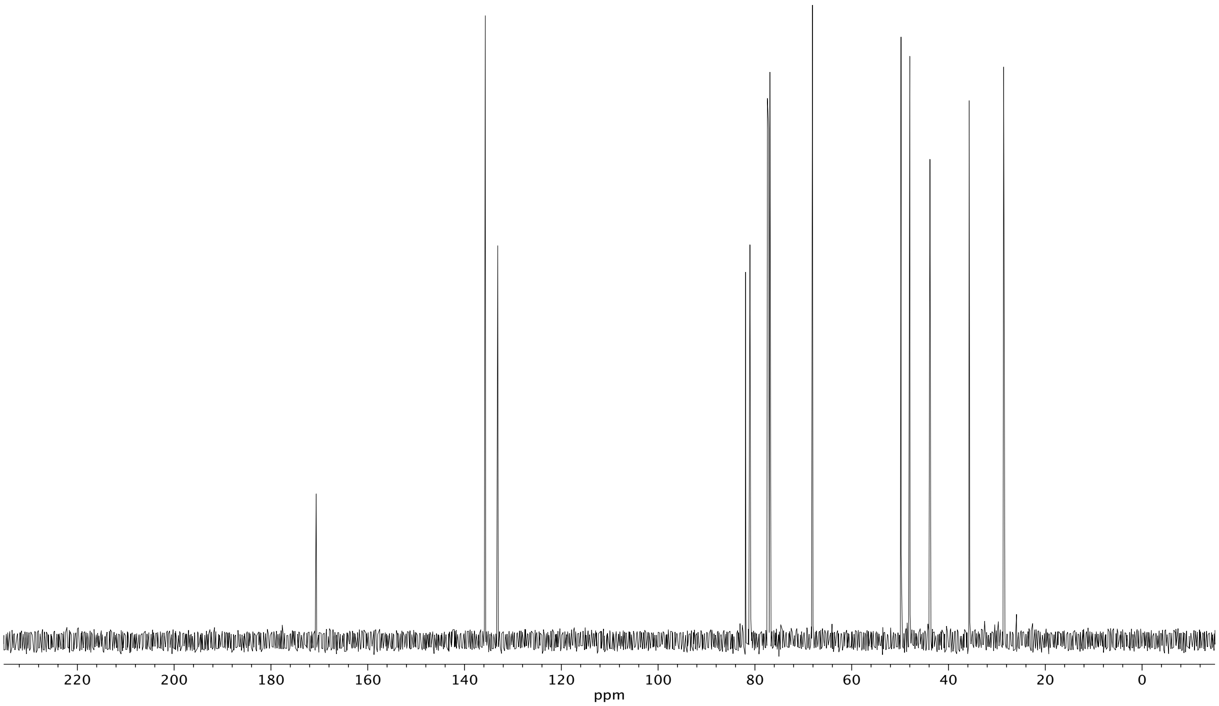
^{13}C NMR (100 MHz, $(CD_3)_2CO$) of compound **S5**.



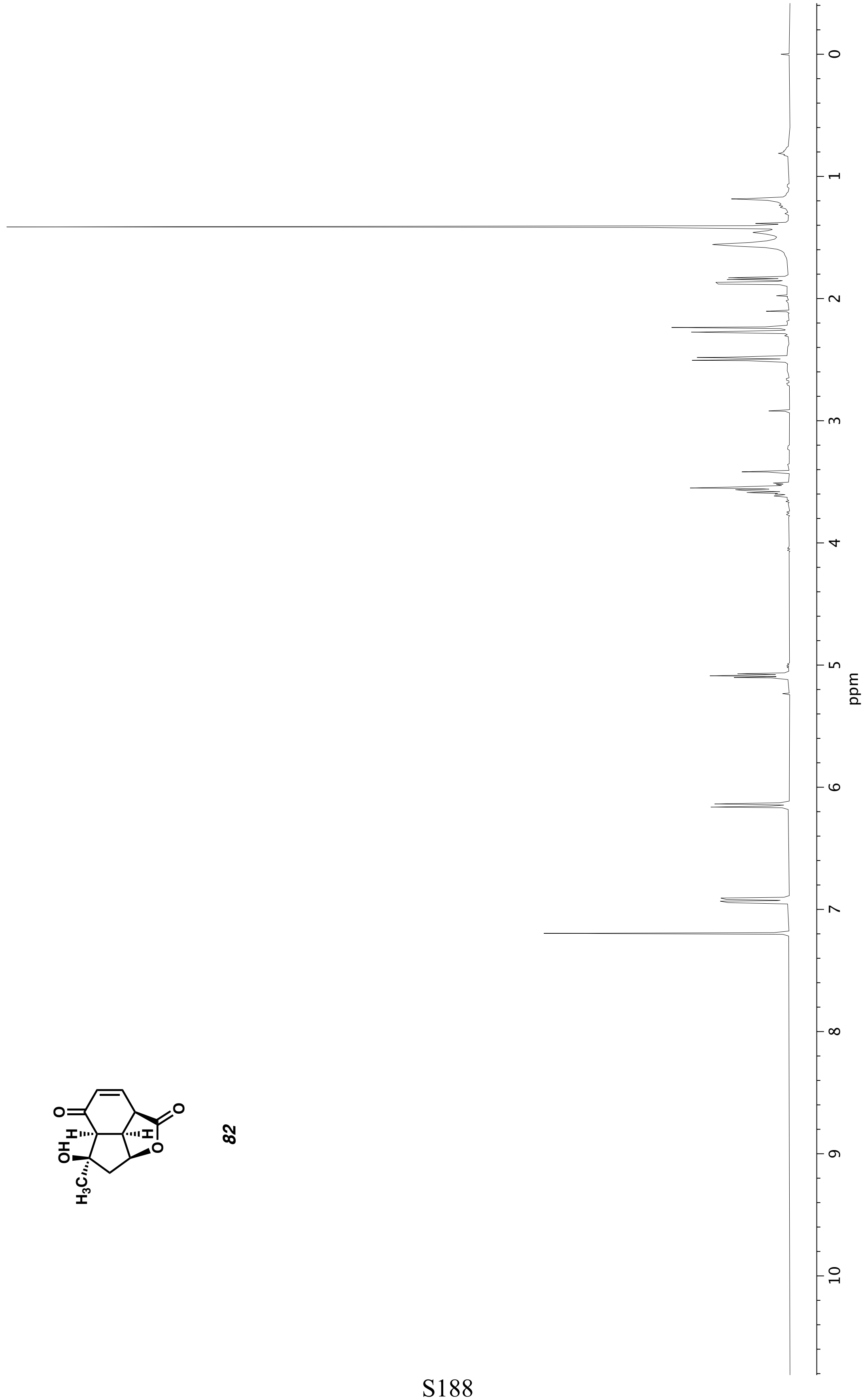
^{1}H NMR (500 MHz, CDCl$_3$) of compound **81**.



Infrared spectrum (Thin Film, NaCl) of compound **81**.

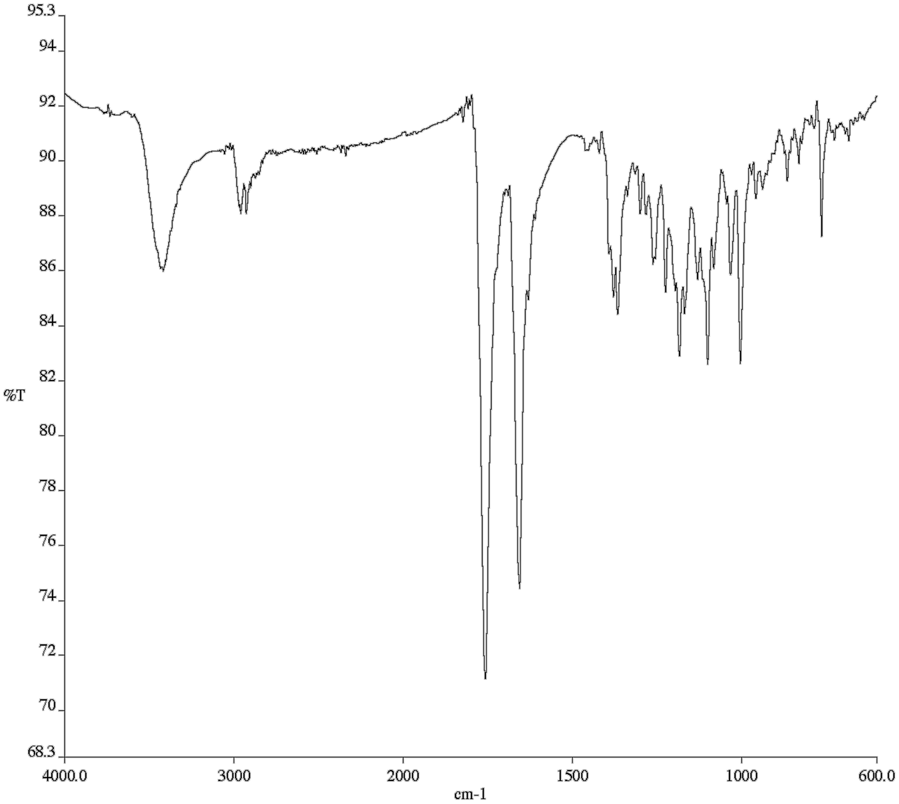


^{13}C NMR (100 MHz, CDCl$_3$) of compound **81**.

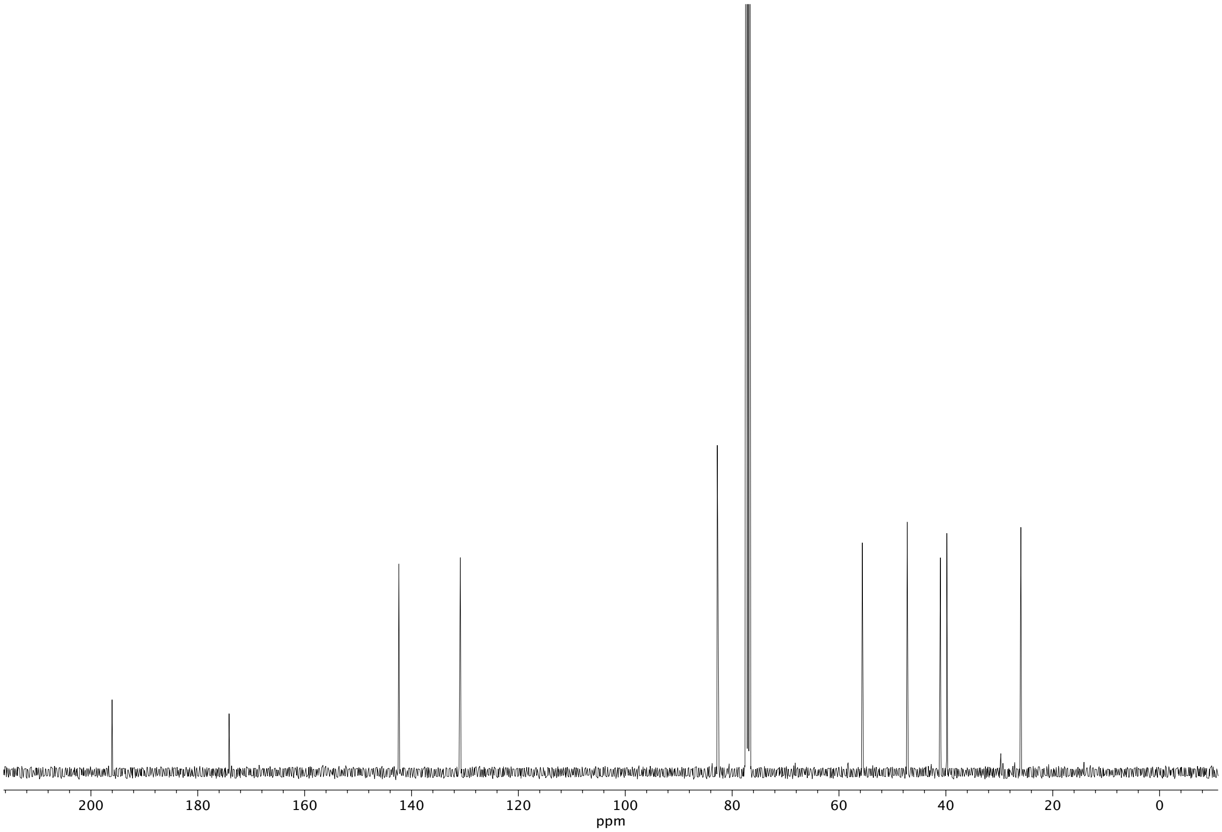


82

^{1}H NMR (500 MHz, CDCl$_3$) of compound **82**.

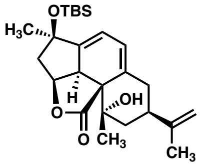


Infrared spectrum (Thin Film, NaCl) of compound **82**.



^{13}C NMR (100 MHz, CDCl$_3$) of compound **82**.

X-RAY CRYSTAL STRUCTURE ANALYSIS OF TETRACYCLE 47



47

Contents

Figure S4 *X-Ray Crystal Structure of Tetracycle **47.***

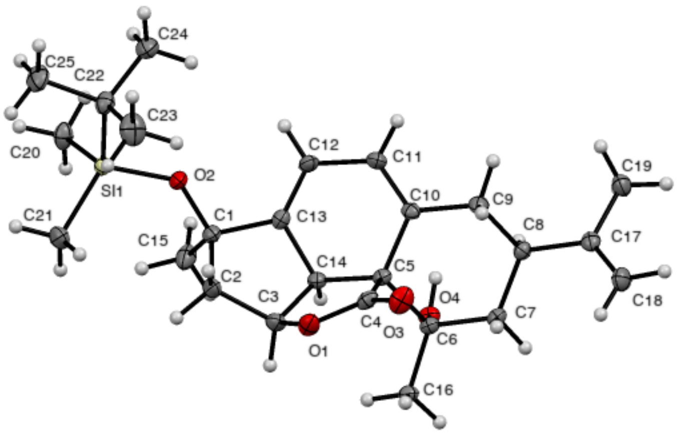


Table S5 *Experimental Details for X-Ray Structure Determination of Tetracycle **47**.*

Low-temperature diffraction data (ϕ-and ω-scans) were collected a Bruker AXS D8 VENTURE KAPPA diffractometer coupled to a PHOTON II CPAD detector with Cu K_α radiation ($\lambda = 1.54178$ Å) from an IμS micro-source for the structure of compound **47**. The structure was solved by direct methods using SHELXS and refined against F^2 on all data by full-matrix least squares with SHELXL-2016 using established refinement techniques. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the *U* value of the atoms they are linked to (1.5 times for methyl groups).

Compound ***47*** crystallizes in the orthorhombic space group $P2_12_12_1$ with one molecule in the asymmetric unit. The coordinates for the hydrogen atom bound to O4 were located in the difference Fourier synthesis and refined semi-freely with the help of a restraint on the O-H distance (0.84(4) Å).

Table S6 *Crystal Data and Structure Refinement for Tetracycle* ***47***

Empirical formula	C25 H38 O4 Si	
Formula weight	430.64	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 6.3347(3) Å	a= 90°.
	b = 12.3768(5) Å	b= 90°.
	c = 30.9537(13) Å	g = 90°.
Volume	2426.87(18) $Å^3$	
Z	4	
Density (calculated)	1.179 Mg/m^3	
Absorption coefficient	1.064 mm^{-1}	
F(000)	936	
Crystal size	0.300 x 0.150 x 0.100 mm^3	
Theta range for data collection	2.855 to 74.566°.	
Index ranges	-7<=h<=7, -15<=k<=14, -38<=l<=38	
Reflections collected	25153	
Independent reflections	4954 [R(int) = 0.0480]	
Completeness to theta = 67.679°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7538 and 0.6036	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4954 / 1 / 282	
Goodness-of-fit on F^2	1.045	
Final R indices [I>2sigma(I)]	R1 = 0.0315, wR2 = 0.0776	
R indices (all data)	R1 = 0.0341, wR2 = 0.0795	
Absolute structure parameter	0.001(10)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.271 and -0.190 e.$Å^{-3}$	

***Table S7** Atomic Coordinates (x 10^4) and Equivalent Isotropic Displacement Parameters (Å^{2}x 10^3) for Tetracycle **47**. U(eq) is Defined as One Third of the Orthogonalized U^{ij} Tensor.*

	x	y	z	U(eq)
C(1)	2853(3)	1349(2)	3662(1)	17(1)
C(15)	4285(4)	511(2)	3878(1)	27(1)
O(2)	2611(2)	1129(1)	3218(1)	19(1)
Si(1)	1788(1)	60(1)	2947(1)	16(1)
C(20)	4027(3)	-872(2)	2822(1)	24(1)
C(21)	-250(4)	-722(2)	3251(1)	27(1)
C(22)	679(3)	665(2)	2435(1)	22(1)
C(23)	-1264(4)	1358(2)	2539(1)	34(1)
C(24)	2358(4)	1396(2)	2225(1)	27(1)
C(25)	61(4)	-241(2)	2120(1)	31(1)
C(2)	716(3)	1448(2)	3904(1)	23(1)
C(3)	1072(3)	2289(2)	4263(1)	21(1)
O(1)	-488(2)	3141(1)	4231(1)	24(1)
C(4)	390(3)	4128(2)	4204(1)	18(1)
O(3)	-697(2)	4922(1)	4186(1)	26(1)
C(5)	2811(3)	4065(2)	4224(1)	14(1)
C(6)	3546(3)	4471(2)	4685(1)	15(1)
O(4)	5671(2)	4121(1)	4755(1)	17(1)
C(16)	2269(3)	3954(2)	5047(1)	18(1)
C(7)	3408(3)	5707(1)	4721(1)	16(1)
C(8)	4719(3)	6285(2)	4379(1)	16(1)
C(17)	4820(3)	7503(2)	4426(1)	18(1)
C(18)	3432(4)	8079(2)	4649(1)	24(1)
C(19)	6667(4)	8017(2)	4198(1)	24(1)
C(9)	3849(3)	5956(2)	3933(1)	20(1)
C(10)	3843(3)	4750(2)	3871(1)	16(1)
C(11)	4656(3)	4292(2)	3517(1)	20(1)

***Table S7** Cont'd*

C(12)	4409(3)	3144(2)	3418(1)	18(1)
C(13)	3699(3)	2478(2)	3720(1)	15(1)
C(14)	3205(3)	2845(1)	4173(1)	15(1)

Table S8** Bond Lengths [Å] and angles [°] for Tetracycle **47

C(1)-O(2)	1.412(2)
C(1)-C(13)	1.507(3)
C(1)-C(15)	1.530(3)
C(1)-C(2)	1.551(3)
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
O(2)-Si(1)	1.6507(14)
Si(1)-C(21)	1.868(2)
Si(1)-C(20)	1.869(2)
Si(1)-C(22)	1.887(2)
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-C(23)	1.534(3)
C(22)-C(25)	1.537(3)
C(22)-C(24)	1.540(3)
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(2)-C(3)	1.541(3)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900

Table S8 *Cont'd*

C(3)-O(1)	1.448(3)
C(3)-C(14)	1.542(3)
C(3)-H(3)	1.0000
O(1)-C(4)	1.345(3)
C(4)-O(3)	1.201(3)
C(4)-C(5)	1.537(2)
C(5)-C(10)	1.529(2)
C(5)-C(14)	1.538(2)
C(5)-C(6)	1.585(2)
C(6)-O(4)	1.430(2)
C(6)-C(16)	1.522(3)
C(6)-C(7)	1.535(2)
O(4)-H(4O)	0.84(2)
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(7)-C(8)	1.524(3)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-C(17)	1.515(3)
C(8)-C(9)	1.540(3)
C(8)-H(8)	1.0000
C(17)-C(18)	1.326(3)
C(17)-C(19)	1.506(3)
C(18)-H(18A)	0.9500
C(18)-H(18B)	0.9500
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(9)-C(10)	1.505(3)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(10)-C(11)	1.336(3)
C(11)-C(12)	1.462(3)

***Table S8** Cont'd*

C(11)-H(11)	0.9500
C(12)-C(13)	1.325(3)
C(12)-H(12)	0.9500
C(13)-C(14)	1.505(2)
C(14)-H(14)	1.0000
O(2)-C(1)-C(13)	109.48(15)
O(2)-C(1)-C(15)	111.00(16)
C(13)-C(1)-C(15)	111.47(16)
O(2)-C(1)-C(2)	112.91(16)
C(13)-C(1)-C(2)	100.35(15)
C(15)-C(1)-C(2)	111.20(17)
C(1)-C(15)-H(15A)	109.5
C(1)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(1)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(1)-O(2)-Si(1)	133.20(12)
O(2)-Si(1)-C(21)	112.17(9)
O(2)-Si(1)-C(20)	111.08(9)
C(21)-Si(1)-C(20)	107.95(10)
O(2)-Si(1)-C(22)	103.08(8)
C(21)-Si(1)-C(22)	111.81(10)
C(20)-Si(1)-C(22)	110.76(10)
Si(1)-C(20)-H(20A)	109.5
Si(1)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
Si(1)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
Si(1)-C(21)-H(21A)	109.5
Si(1)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
Si(1)-C(21)-H(21C)	109.5

Table S8 *Cont'd*

H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(23)-C(22)-C(25)	109.66(19)
C(23)-C(22)-C(24)	108.29(18)
C(25)-C(22)-C(24)	109.73(18)
C(23)-C(22)-Si(1)	110.17(15)
C(25)-C(22)-Si(1)	109.73(14)
C(24)-C(22)-Si(1)	109.24(14)
C(22)-C(23)-H(23A)	109.5
C(22)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(22)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(22)-C(24)-H(24A)	109.5
C(22)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(22)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(22)-C(25)-H(25A)	109.5
C(22)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(22)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
C(3)-C(2)-C(1)	105.86(16)
C(3)-C(2)-H(2A)	110.6
C(1)-C(2)-H(2A)	110.6
C(3)-C(2)-H(2B)	110.6
C(1)-C(2)-H(2B)	110.6
H(2A)-C(2)-H(2B)	108.7
O(1)-C(3)-C(2)	110.00(17)

Table S8 *Cont'd*

O(1)-C(3)-C(14)	105.10(15)
C(2)-C(3)-C(14)	107.37(15)
O(1)-C(3)-H(3)	111.4
C(2)-C(3)-H(3)	111.4
C(14)-C(3)-H(3)	111.4
C(4)-O(1)-C(3)	112.56(15)
O(3)-C(4)-O(1)	120.61(18)
O(3)-C(4)-C(5)	128.00(19)
O(1)-C(4)-C(5)	111.32(17)
C(10)-C(5)-C(4)	111.75(15)
C(10)-C(5)-C(14)	113.68(15)
C(4)-C(5)-C(14)	102.01(15)
C(10)-C(5)-C(6)	109.99(15)
C(4)-C(5)-C(6)	108.18(15)
C(14)-C(5)-C(6)	110.88(14)
O(4)-C(6)-C(16)	105.17(15)
O(4)-C(6)-C(7)	110.16(16)
C(16)-C(6)-C(7)	109.63(15)
O(4)-C(6)-C(5)	108.43(14)
C(16)-C(6)-C(5)	111.94(15)
C(7)-C(6)-C(5)	111.31(15)
C(6)-O(4)-H(4O)	112.7(19)
C(6)-C(16)-H(16A)	109.5
C(6)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(6)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(8)-C(7)-C(6)	112.79(15)
C(8)-C(7)-H(7A)	109.0
C(6)-C(7)-H(7A)	109.0
C(8)-C(7)-H(7B)	109.0
C(6)-C(7)-H(7B)	109.0
H(7A)-C(7)-H(7B)	107.8

Table S8 *Cont'd*

C(17)-C(8)-C(7)	115.09(16)
C(17)-C(8)-C(9)	111.31(15)
C(7)-C(8)-C(9)	107.63(15)
C(17)-C(8)-H(8)	107.5
C(7)-C(8)-H(8)	107.5
C(9)-C(8)-H(8)	107.5
C(18)-C(17)-C(19)	122.07(19)
C(18)-C(17)-C(8)	123.84(19)
C(19)-C(17)-C(8)	114.09(17)
C(17)-C(18)-H(18A)	120.0
C(17)-C(18)-H(18B)	120.0
H(18A)-C(18)-H(18B)	120.0
C(17)-C(19)-H(19A)	109.5
C(17)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(17)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(10)-C(9)-C(8)	112.16(15)
C(10)-C(9)-H(9A)	109.2
C(8)-C(9)-H(9A)	109.2
C(10)-C(9)-H(9B)	109.2
C(8)-C(9)-H(9B)	109.2
H(9A)-C(9)-H(9B)	107.9
C(11)-C(10)-C(9)	121.61(17)
C(11)-C(10)-C(5)	120.96(17)
C(9)-C(10)-C(5)	117.41(16)
C(10)-C(11)-C(12)	122.87(18)
C(10)-C(11)-H(11)	118.6
C(12)-C(11)-H(11)	118.6
C(13)-C(12)-C(11)	119.56(17)
C(13)-C(12)-H(12)	120.2
C(11)-C(12)-H(12)	120.2
C(12)-C(13)-C(14)	122.60(17)

Table S8 *Cont'd*

C(12)-C(13)-C(1)	127.85(17)
C(14)-C(13)-C(1)	108.49(15)
C(13)-C(14)-C(5)	115.21(15)
C(13)-C(14)-C(3)	102.49(15)
C(5)-C(14)-C(3)	106.08(15)
C(13)-C(14)-H(14)	110.9
C(5)-C(14)-H(14)	110.9
C(3)-C(14)-H(14)	110.9

Symmetry transformations used to generate equivalent atoms:

Table S9 *Anisotropic Displacement Parameters (Å^{2}x10^3) for Tetracycle **47**. The Anisotropic Displacement Factor Exponent Takes the Form: -2p^2[h^{2}a*^{2}U^{11} + ... + 2hka*b*U^{12}].*

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	20(1)	18(1)	13(1)	-1(1)	0(1)	-3(1)
C(15)	38(1)	19(1)	24(1)	-3(1)	-8(1)	4(1)
O(2)	25(1)	18(1)	14(1)	-2(1)	0(1)	-4(1)
Si(1)	16(1)	15(1)	17(1)	-2(1)	0(1)	-1(1)
C(20)	20(1)	19(1)	34(1)	-5(1)	-2(1)	3(1)
C(21)	28(1)	25(1)	28(1)	-2(1)	4(1)	-10(1)
C(22)	24(1)	21(1)	21(1)	-2(1)	-5(1)	0(1)
C(23)	28(1)	29(1)	47(1)	0(1)	-10(1)	7(1)
C(24)	35(1)	26(1)	20(1)	-1(1)	0(1)	-2(1)
C(25)	38(1)	31(1)	25(1)	-5(1)	-11(1)	-6(1)
C(2)	25(1)	23(1)	22(1)	-4(1)	6(1)	-9(1)
C(3)	22(1)	23(1)	18(1)	-1(1)	5(1)	-6(1)
O(1)	16(1)	28(1)	27(1)	-7(1)	5(1)	-5(1)
C(4)	13(1)	26(1)	15(1)	-5(1)	-1(1)	1(1)
O(3)	16(1)	31(1)	32(1)	-6(1)	-4(1)	6(1)
C(5)	13(1)	17(1)	12(1)	-1(1)	0(1)	1(1)
C(6)	15(1)	19(1)	13(1)	-1(1)	1(1)	1(1)
O(4)	14(1)	21(1)	15(1)	1(1)	-2(1)	2(1)
C(16)	20(1)	21(1)	13(1)	1(1)	3(1)	-1(1)
C(7)	16(1)	18(1)	13(1)	-2(1)	0(1)	2(1)
C(8)	16(1)	16(1)	16(1)	-1(1)	0(1)	2(1)
C(17)	21(1)	18(1)	16(1)	1(1)	-4(1)	0(1)
C(18)	28(1)	17(1)	28(1)	-1(1)	1(1)	2(1)
C(19)	27(1)	18(1)	28(1)	0(1)	3(1)	-3(1)
C(9)	27(1)	18(1)	15(1)	2(1)	0(1)	0(1)
C(10)	16(1)	18(1)	13(1)	2(1)	-2(1)	-1(1)
C(11)	25(1)	20(1)	16(1)	1(1)	5(1)	-5(1)

Table S9 *Cont'd*

C(12)	19(1)	22(1)	15(1)	-4(1)	5(1)	-2(1)
C(13)	13(1)	17(1)	16(1)	-3(1)	-1(1)	2(1)
C(14)	15(1)	16(1)	13(1)	1(1)	1(1)	0(1)

Table S10 *Hydrogen Coordinates (x10^4) and Isotropic Displacement Parameters (Å^{2}x10^3) for Tetracycle* ***47****.*

	x	y	z	U(eq)
H(15A)	3655	-209	3848	41
H(15B)	4443	685	4185	41
H(15C)	5674	519	3738	41
H(20A)	5104	-483	2656	37
H(20B)	3507	-1485	2653	37
H(20C)	4646	-1136	3092	37
H(21A)	372	-1007	3517	41
H(21B)	-752	-1323	3072	41
H(21C)	-1437	-247	3322	41
H(23A)	-1856	1647	2270	52
H(23B)	-850	1957	2728	52
H(23C)	-2326	914	2685	52
H(24A)	1858	1638	1942	40
H(24B)	3675	990	2190	40
H(24C)	2611	2026	2410	40
H(25A)	-1010	-704	2254	47
H(25B)	1310	-674	2050	47
H(25C)	-513	76	1855	47
H(2A)	-408	1691	3704	28
H(2B)	300	743	4029	28
H(3)	1053	1945	4555	25
H(4O)	6480(40)	4290(20)	4552(8)	20
H(16A)	2464	3169	5040	27
H(16B)	771	4125	5008	27
H(16C)	2751	4236	5326	27
H(7A)	1914	5930	4691	19
H(7B)	3899	5931	5011	19
H(8)	6195	6004	4400	19

Table S10 *Cont'd*

H(18A)	3586	8841	4669	29
H(18B)	2284	7730	4788	29
H(19A)	6682	8794	4258	36
H(19B)	6537	7900	3886	36
H(19C)	7982	7690	4302	36
H(9A)	2391	6233	3902	24
H(9B)	4723	6293	3705	24
H(11)	5428	4732	3322	24
H(12)	4756	2877	3140	22
H(14)	4310	2591	4380	18

Table S11 *Torsion Angles [°] for Tetracycle* ***47****.*

C(13)-C(1)-O(2)-Si(1)	179.54(13)
C(15)-C(1)-O(2)-Si(1)	56.1(2)
C(2)-C(1)-O(2)-Si(1)	-69.6(2)
C(1)-O(2)-Si(1)-C(21)	31.7(2)
C(1)-O(2)-Si(1)-C(20)	-89.25(19)
C(1)-O(2)-Si(1)-C(22)	152.10(17)
O(2)-Si(1)-C(22)-C(23)	-65.50(17)
C(21)-Si(1)-C(22)-C(23)	55.18(18)
C(20)-Si(1)-C(22)-C(23)	175.62(15)
O(2)-Si(1)-C(22)-C(25)	173.66(15)
C(21)-Si(1)-C(22)-C(25)	-65.66(18)
C(20)-Si(1)-C(22)-C(25)	54.79(18)
O(2)-Si(1)-C(22)-C(24)	53.33(15)
C(21)-Si(1)-C(22)-C(24)	174.01(14)
C(20)-Si(1)-C(22)-C(24)	-65.55(16)
O(2)-C(1)-C(2)-C(3)	-147.14(16)
C(13)-C(1)-C(2)-C(3)	-30.70(19)
C(15)-C(1)-C(2)-C(3)	87.3(2)
C(1)-C(2)-C(3)-O(1)	125.61(17)
C(1)-C(2)-C(3)-C(14)	11.8(2)
C(2)-C(3)-O(1)-C(4)	-125.15(17)
C(14)-C(3)-O(1)-C(4)	-9.8(2)
C(3)-O(1)-C(4)-O(3)	-178.16(17)
C(3)-O(1)-C(4)-C(5)	-0.9(2)
O(3)-C(4)-C(5)-C(10)	-50.1(3)
O(1)-C(4)-C(5)-C(10)	132.92(16)
O(3)-C(4)-C(5)-C(14)	-171.86(19)
O(1)-C(4)-C(5)-C(14)	11.1(2)
O(3)-C(4)-C(5)-C(6)	71.2(2)
O(1)-C(4)-C(5)-C(6)	-105.85(17)
C(10)-C(5)-C(6)-O(4)	-74.73(17)
C(4)-C(5)-C(6)-O(4)	162.96(15)

Table S11 *Cont'd*

C(14)-C(5)-C(6)-O(4)	51.88(19)
C(10)-C(5)-C(6)-C(16)	169.70(15)
C(4)-C(5)-C(6)-C(16)	47.4(2)
C(14)-C(5)-C(6)-C(16)	-63.7(2)
C(10)-C(5)-C(6)-C(7)	46.6(2)
C(4)-C(5)-C(6)-C(7)	-75.7(2)
C(14)-C(5)-C(6)-C(7)	173.21(15)
O(4)-C(6)-C(7)-C(8)	62.5(2)
C(16)-C(6)-C(7)-C(8)	177.78(15)
C(5)-C(6)-C(7)-C(8)	-57.8(2)
C(6)-C(7)-C(8)-C(17)	-174.09(17)
C(6)-C(7)-C(8)-C(9)	61.2(2)
C(7)-C(8)-C(17)-C(18)	-20.2(3)
C(9)-C(8)-C(17)-C(18)	102.6(2)
C(7)-C(8)-C(17)-C(19)	159.28(17)
C(9)-C(8)-C(17)-C(19)	-77.9(2)
C(17)-C(8)-C(9)-C(10)	177.00(17)
C(7)-C(8)-C(9)-C(10)	-56.0(2)
C(8)-C(9)-C(10)-C(11)	-130.3(2)
C(8)-C(9)-C(10)-C(5)	51.3(2)
C(4)-C(5)-C(10)-C(11)	-103.3(2)
C(14)-C(5)-C(10)-C(11)	11.5(3)
C(6)-C(5)-C(10)-C(11)	136.48(19)
C(4)-C(5)-C(10)-C(9)	75.0(2)
C(14)-C(5)-C(10)-C(9)	-170.19(16)
C(6)-C(5)-C(10)-C(9)	-45.2(2)
C(9)-C(10)-C(11)-C(12)	-171.04(19)
C(5)-C(10)-C(11)-C(12)	7.2(3)
C(10)-C(11)-C(12)-C(13)	-12.7(3)
C(11)-C(12)-C(13)-C(14)	-2.5(3)
C(11)-C(12)-C(13)-C(1)	164.33(19)
O(2)-C(1)-C(13)-C(12)	-8.9(3)
C(15)-C(1)-C(13)-C(12)	114.3(2)
C(2)-C(1)-C(13)-C(12)	-127.8(2)

Table S11 *Cont'd*

O(2)-C(1)-C(13)-C(14)	159.42(15)
C(15)-C(1)-C(13)-C(14)	-77.38(19)
C(2)-C(1)-C(13)-C(14)	40.45(18)
C(12)-C(13)-C(14)-C(5)	20.8(3)
C(1)-C(13)-C(14)-C(5)	-148.21(16)
C(12)-C(13)-C(14)-C(3)	135.51(19)
C(1)-C(13)-C(14)-C(3)	-33.52(19)
C(10)-C(5)-C(14)-C(13)	-24.1(2)
C(4)-C(5)-C(14)-C(13)	96.36(18)
C(6)-C(5)-C(14)-C(13)	-148.65(16)
C(10)-C(5)-C(14)-C(3)	-136.71(15)
C(4)-C(5)-C(14)-C(3)	-16.25(18)
C(6)-C(5)-C(14)-C(3)	98.75(17)
O(1)-C(3)-C(14)-C(13)	-104.81(16)
C(2)-C(3)-C(14)-C(13)	12.3(2)
O(1)-C(3)-C(14)-C(5)	16.37(18)
C(2)-C(3)-C(14)-C(5)	133.48(17)

Symmetry transformations used to generate equivalent atoms:

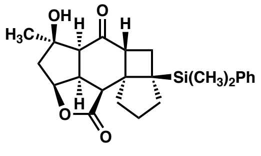
Table S12 *Hydrogen Bonds for Tetracycle* ***47*** *[Å and °].*

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(3)-H(3)...O(4)#1	1.00	2.52	3.514(2)	171.9
O(4)-H(4O)...O(1)#2	0.84(2)	2.59(3)	3.167(2)	127(2)
O(4)-H(4O)...O(3)#2	0.84(2)	2.25(2)	3.062(2)	162(3)
C(7)-H(7A)...O(3)	0.99	2.59	3.231(2)	122.0

Symmetry transformations used to generate equivalent atoms:

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

X-RAY CRYSTAL STRUCTURE ANALYSIS OF CYCLOBUTANE 63



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Contents

Figure S5 *X-Ray Crystal Structure of Cyclobutane* **63.**

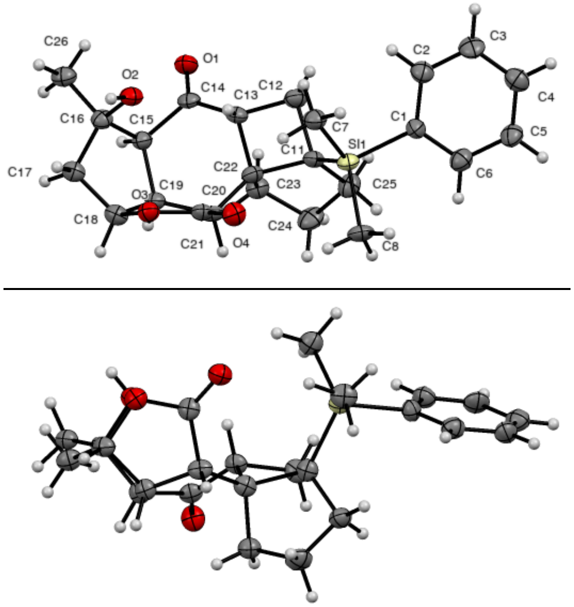


Table S13 *Experimental Details for X-Ray Structure Determination of Cyclobutane* **63.**

Low-temperature diffraction data (ϕ-and ω-scans) were collected on a Bruker AXS D8 VENTURE KAPPA diffractometer coupled to a PHOTON II CPAD detector with Cu K_α radiation (λ = 1.54178 Å) from an IμS micro-source for the structure of compound **63**. The structure was solved by direct methods using SHELXS and refined against F^2 on all data by full-matrix least squares with SHELXL-2017 using established refinement techniques. All non-hydrogen atoms were refined anisotropically. Unless otherwise noted, all hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the *U* value of the atoms they are linked to (1.5 times for methyl groups).

Compound **63** crystallizes in the monoclinic space group $P2_1$ with one molecule in the asymmetric unit. The coordinates for the hydrogen atom bound to O2 were located in the difference Fourier synthesis and refined semi-freely with the help of a restraint on the O-H distance (0.84(4) Å). The structure was refined as a twin [-1 0 0 0 -1 0 1 0 1].

Table S14 *Crystal Data and Structure Refinement for Cyclobutane* **63.**

Empirical formula	C24 H30 O4 Si	
Formula weight	410.57	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 6.7649(5) Å	a= 90°.
	b = 10.9273(9) Å	b= 103.394(5)°.
	c = 14.4629(14) Å	g = 90°.
Volume	1040.05(15) Å^3	
Z	2	
Density (calculated)	1.311 Mg/m^3	
Absorption coefficient	1.224 mm^{-1}	
F(000)	440	
Crystal size	0.200 x 0.150 x 0.050 mm^3	
Theta range for data collection	3.141 to 74.630°.	
Index ranges	-7<=h<=8, -13<=k<=13, -18<=l<=17	
Reflections collected	17179	
Independent reflections	4172 [R(int) = 0.0797]	
Completeness to theta = 67.679°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7504 and 0.5626	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4172 / 2 / 269	
Goodness-of-fit on F^2	1.071	
Final R indices [I>2sigma(I)]	R1 = 0.0880, wR2 = 0.2288	
R indices (all data)	R1 = 0.0893, wR2 = 0.2312	
Absolute structure parameter	0.03(6)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.686 and -0.364 e.Å^{-3}	

Table S15 *Atomic Coordinates (x 10^4) and Equivalent Isotropic Displacement Parameters (Å^{2}x 10^3) for Cyclobutane* **63**. *U(eq) is Defined as One Third of the Trace of the Orthogonalized U^{ij} Tensor.*

	x	y	z	U(eq)
Si(1)	5500(3)	3644(2)	3733(2)	26(1)
C(1)	5454(13)	4028(8)	5009(6)	28(2)
C(2)	3622(15)	4276(9)	5275(7)	34(2)
C(3)	3582(16)	4570(10)	6208(8)	38(2)
C(4)	5409(17)	4598(10)	6909(8)	37(2)
C(5)	7217(15)	4334(10)	6668(7)	35(2)
C(6)	7249(16)	4064(9)	5719(7)	34(2)
C(7)	3130(15)	2738(10)	3256(7)	34(2)
C(8)	7879(13)	2754(9)	3754(8)	33(2)
C(11)	5539(13)	5208(8)	3156(6)	26(2)
C(12)	3363(14)	5841(9)	3012(7)	32(2)
C(13)	2992(13)	5596(8)	1937(6)	26(2)
C(14)	2128(13)	6460(8)	1150(6)	26(2)
O(1)	1187(12)	7376(6)	1210(5)	34(2)
C(15)	2743(13)	6116(8)	223(6)	27(2)
C(16)	1075(14)	5330(8)	-431(6)	28(2)
C(26)	-690(15)	6100(9)	-971(7)	34(2)
O(2)	321(10)	4436(6)	135(5)	31(1)
C(17)	2279(15)	4700(8)	-1074(6)	28(2)
C(18)	4326(15)	4391(8)	-447(6)	29(2)
C(19)	4824(13)	5439(8)	283(6)	26(2)
C(20)	5848(13)	4788(8)	1237(6)	27(2)
C(21)	5101(13)	3456(8)	1047(6)	27(2)
O(3)	4251(10)	3301(6)	116(5)	30(1)
O(4)	5290(12)	2622(6)	1593(5)	34(2)
C(22)	5312(13)	5490(8)	2053(6)	27(2)
C(23)	6384(15)	6755(8)	2115(7)	30(2)

Table S15 *Cont'd*

C(24)	8208(15)	6643(10)	2960(8)	39(2)
C(25)	7315(15)	5980(9)	3715(7)	34(2)

Table S16 *Bond Lengths [Å] and angles [°] for Cyclobutane* **63.**

Si(1)-C(8)	1.874(9)
Si(1)-C(7)	1.875(10)
Si(1)-C(1)	1.900(9)
Si(1)-C(11)	1.905(9)
C(1)-C(6)	1.397(13)
C(1)-C(2)	1.406(13)
C(2)-C(3)	1.393(14)
C(2)-H(2)	0.9500
C(3)-C(4)	1.406(15)
C(3)-H(3)	0.9500
C(4)-C(5)	1.378(15)
C(4)-H(4)	0.9500
C(5)-C(6)	1.409(14)
C(5)-H(5)	0.9500
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(11)-C(25)	1.535(12)
C(11)-C(12)	1.596(12)
C(11)-C(22)	1.598(12)
C(12)-C(13)	1.541(13)
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(13)-C(14)	1.489(12)
C(13)-C(22)	1.544(12)
C(13)-H(13)	1.0000
C(14)-O(1)	1.201(12)
C(14)-C(15)	1.541(12)
C(15)-C(16)	1.552(12)

Table S16 *Cont'd*

C(15)-C(19)	1.574(12)
C(15)-H(15)	1.0000
C(16)-O(2)	1.441(11)
C(16)-C(26)	1.521(13)
C(16)-C(17)	1.534(12)
C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800
O(2)-H(2A)	0.83(3)
C(17)-C(18)	1.508(13)
C(17)-H(17A)	0.9900
C(17)-H(17B)	0.9900
C(18)-O(3)	1.450(11)
C(18)-C(19)	1.541(12)
C(18)-H(18)	1.0000
C(19)-C(20)	1.565(12)
C(19)-H(19)	1.0000
C(20)-C(22)	1.520(12)
C(20)-C(21)	1.544(12)
C(20)-H(20)	1.0000
C(21)-O(4)	1.193(11)
C(21)-O(3)	1.347(11)
C(22)-C(23)	1.554(13)
C(23)-C(24)	1.527(13)
C(23)-H(23A)	0.9900
C(23)-H(23B)	0.9900
C(24)-C(25)	1.545(14)
C(24)-H(24A)	0.9900
C(24)-H(24B)	0.9900
C(25)-H(25A)	0.9900
C(25)-H(25B)	0.9900
C(8)-Si(1)-C(7)	112.9(5)
C(8)-Si(1)-C(1)	107.8(4)

Table S16 *Cont'd*

C(7)-Si(1)-C(1)	105.7(4)
C(8)-Si(1)-C(11)	111.9(4)
C(7)-Si(1)-C(11)	114.2(4)
C(1)-Si(1)-C(11)	103.4(4)
C(6)-C(1)-C(2)	117.7(9)
C(6)-C(1)-Si(1)	120.9(7)
C(2)-C(1)-Si(1)	121.4(7)
C(3)-C(2)-C(1)	121.7(9)
C(3)-C(2)-H(2)	119.2
C(1)-C(2)-H(2)	119.2
C(2)-C(3)-C(4)	119.5(10)
C(2)-C(3)-H(3)	120.2
C(4)-C(3)-H(3)	120.2
C(5)-C(4)-C(3)	119.7(10)
C(5)-C(4)-H(4)	120.1
C(3)-C(4)-H(4)	120.1
C(4)-C(5)-C(6)	120.4(9)
C(4)-C(5)-H(5)	119.8
C(6)-C(5)-H(5)	119.8
C(1)-C(6)-C(5)	121.0(9)
C(1)-C(6)-H(6)	119.5
C(5)-C(6)-H(6)	119.5
Si(1)-C(7)-H(7A)	109.5
Si(1)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
Si(1)-C(7)-H(7C)	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
H(8A)-C(8)-H(8B)	109.5
Si(1)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5

***Table S16** Cont'd*

C(25)-C(11)-C(12)	114.6(7)
C(25)-C(11)-C(22)	107.6(7)
C(12)-C(11)-C(22)	85.0(6)
C(25)-C(11)-Si(1)	110.5(6)
C(12)-C(11)-Si(1)	109.9(6)
C(22)-C(11)-Si(1)	127.1(6)
C(13)-C(12)-C(11)	89.2(7)
C(13)-C(12)-H(12A)	113.8
C(11)-C(12)-H(12A)	113.8
C(13)-C(12)-H(12B)	113.8
C(11)-C(12)-H(12B)	113.8
H(12A)-C(12)-H(12B)	111.0
C(14)-C(13)-C(12)	127.2(8)
C(14)-C(13)-C(22)	109.9(7)
C(12)-C(13)-C(22)	88.8(7)
C(14)-C(13)-H(13)	109.5
C(12)-C(13)-H(13)	109.5
C(22)-C(13)-H(13)	109.5
O(1)-C(14)-C(13)	126.4(8)
O(1)-C(14)-C(15)	121.4(8)
C(13)-C(14)-C(15)	111.9(7)
C(14)-C(15)-C(16)	111.1(7)
C(14)-C(15)-C(19)	119.0(7)
C(16)-C(15)-C(19)	106.8(7)
C(14)-C(15)-H(15)	106.4
C(16)-C(15)-H(15)	106.4
C(19)-C(15)-H(15)	106.4
O(2)-C(16)-C(26)	109.1(8)
O(2)-C(16)-C(17)	110.3(7)
C(26)-C(16)-C(17)	113.6(7)
O(2)-C(16)-C(15)	109.4(7)
C(26)-C(16)-C(15)	112.3(7)
C(17)-C(16)-C(15)	101.8(7)
C(16)-C(26)-H(26A)	109.5

Table S16 *Cont'd*

C(16)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
C(16)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
C(16)-O(2)-H(2A)	106(10)
C(18)-C(17)-C(16)	106.2(7)
C(18)-C(17)-H(17A)	110.5
C(16)-C(17)-H(17A)	110.5
C(18)-C(17)-H(17B)	110.5
C(16)-C(17)-H(17B)	110.5
H(17A)-C(17)-H(17B)	108.7
O(3)-C(18)-C(17)	112.0(7)
O(3)-C(18)-C(19)	104.9(7)
C(17)-C(18)-C(19)	105.7(7)
O(3)-C(18)-H(18)	111.3
C(17)-C(18)-H(18)	111.3
C(19)-C(18)-H(18)	111.3
C(18)-C(19)-C(20)	104.4(7)
C(18)-C(19)-C(15)	105.1(7)
C(20)-C(19)-C(15)	118.0(7)
C(18)-C(19)-H(19)	109.7
C(20)-C(19)-H(19)	109.7
C(15)-C(19)-H(19)	109.7
C(22)-C(20)-C(21)	119.2(7)
C(22)-C(20)-C(19)	108.6(6)
C(21)-C(20)-C(19)	102.2(7)
C(22)-C(20)-H(20)	108.8
C(21)-C(20)-H(20)	108.8
C(19)-C(20)-H(20)	108.8
O(4)-C(21)-O(3)	121.4(8)
O(4)-C(21)-C(20)	128.5(8)
O(3)-C(21)-C(20)	110.1(7)
C(21)-O(3)-C(18)	113.3(7)

Table S16 *Cont'd*

C(20)-C(22)-C(13)	111.9(7)
C(20)-C(22)-C(23)	107.6(7)
C(13)-C(22)-C(23)	112.9(8)
C(20)-C(22)-C(11)	133.8(7)
C(13)-C(22)-C(11)	89.0(6)
C(23)-C(22)-C(11)	100.2(7)
C(24)-C(23)-C(22)	104.8(8)
C(24)-C(23)-H(23A)	110.8
C(22)-C(23)-H(23A)	110.8
C(24)-C(23)-H(23B)	110.8
C(22)-C(23)-H(23B)	110.8
H(23A)-C(23)-H(23B)	108.9
C(23)-C(24)-C(25)	103.1(8)
C(23)-C(24)-H(24A)	111.1
C(25)-C(24)-H(24A)	111.1
C(23)-C(24)-H(24B)	111.1
C(25)-C(24)-H(24B)	111.1
H(24A)-C(24)-H(24B)	109.1
C(11)-C(25)-C(24)	105.8(8)
C(11)-C(25)-H(25A)	110.6
C(24)-C(25)-H(25A)	110.6
C(11)-C(25)-H(25B)	110.6
C(24)-C(25)-H(25B)	110.6
H(25A)-C(25)-H(25B)	108.7

Symmetry transformations used to generate equivalent atoms:

Table S17 *Anisotropic Displacement Parameters (Å^{2}x10^3) for Cyclobutane* **63**. *The Anisotropic Displacement Factor Exponent Takes the Form: -2p^2[h^{2}a*^{2}U^{11} + ... + 2hka*b*U^{12}].*

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

Table S18 *Hydrogen Coordinates ($x10^4$) and Isotropic Displacement Parameters ($Å^2x10^3$) for Cyclobutane **63**.*

	x	y	z	U(eq)
H(2)	2380	4242	4806	40
H(3)	2330	4751	6369	45
H(4)	5397	4799	7547	44
H(5)	8449	4333	7144	42
H(6)	8510	3903	5559	41
H(7A)	1946	3280	3161	52
H(7B)	3004	2092	3709	52
H(7C)	3201	2367	2647	52
H(8A)	8045	2119	4244	50
H(8B)	9051	3307	3897	50
H(8C)	7785	2371	3133	50
H(12A)	2417	5398	3324	38
H(12B)	3426	6721	3180	38
H(13)	2354	4772	1789	31
H(15)	2817	6900	-124	32
H(26A)	-1691	5569	-1381	51
H(26B)	-188	6704	-1362	51
H(26C)	-1329	6524	-518	51
H(2A)	-100(200)	3860(90)	-230(80)	46
H(17A)	1573	3948	-1357	34
H(17B)	2433	5255	-1594	34
H(18)	5385	4317	-825	35
H(19)	5814	6014	96	31
H(20)	7355	4806	1316	32
H(23A)	6832	6932	1524	36
H(23B)	5462	7416	2222	36
H(24A)	8746	7459	3189	47
H(24B)	9308	6156	2792	47

Table S18 *Cont'd*

H(25A)	8353	5450	4119	40
H(25B)	6829	6579	4125	40

Table S19 *Torsion Angles [°] for Cyclobutane* **63**.

C(8)-Si(1)-C(1)-C(6)	23.2(9)
C(7)-Si(1)-C(1)-C(6)	144.2(8)
C(11)-Si(1)-C(1)-C(6)	-95.5(8)
C(8)-Si(1)-C(1)-C(2)	-156.3(8)
C(7)-Si(1)-C(1)-C(2)	-35.2(9)
C(11)-Si(1)-C(1)-C(2)	85.1(8)
C(6)-C(1)-C(2)-C(3)	1.2(15)
Si(1)-C(1)-C(2)-C(3)	-179.4(8)
C(1)-C(2)-C(3)-C(4)	-1.3(15)
C(2)-C(3)-C(4)-C(5)	-0.1(16)
C(3)-C(4)-C(5)-C(6)	1.5(16)
C(2)-C(1)-C(6)-C(5)	0.3(15)
Si(1)-C(1)-C(6)-C(5)	-179.2(8)
C(4)-C(5)-C(6)-C(1)	-1.6(16)
C(25)-C(11)-C(12)-C(13)	127.8(8)
C(22)-C(11)-C(12)-C(13)	20.7(6)
Si(1)-C(11)-C(12)-C(13)	-107.0(6)
C(11)-C(12)-C(13)-C(14)	-135.6(8)
C(11)-C(12)-C(13)-C(22)	-21.4(7)
C(12)-C(13)-C(14)-O(1)	-17.2(15)
C(22)-C(13)-C(14)-O(1)	-121.5(10)
C(12)-C(13)-C(14)-C(15)	157.4(8)
C(22)-C(13)-C(14)-C(15)	53.1(10)
O(1)-C(14)-C(15)-C(16)	-89.6(11)
C(13)-C(14)-C(15)-C(16)	95.4(8)
O(1)-C(14)-C(15)-C(19)	145.8(9)
C(13)-C(14)-C(15)-C(19)	-29.2(11)
C(14)-C(15)-C(16)-O(2)	-42.2(10)
C(19)-C(15)-C(16)-O(2)	89.0(8)
C(14)-C(15)-C(16)-C(26)	79.1(9)
C(19)-C(15)-C(16)-C(26)	-149.6(8)
C(14)-C(15)-C(16)-C(17)	-159.0(7)

Table S19 *Cont'd*

C(19)-C(15)-C(16)-C(17)	-27.8(8)
O(2)-C(16)-C(17)-C(18)	-77.6(9)
C(26)-C(16)-C(17)-C(18)	159.5(7)
C(15)-C(16)-C(17)-C(18)	38.5(8)
C(16)-C(17)-C(18)-O(3)	79.1(8)
C(16)-C(17)-C(18)-C(19)	-34.6(9)
O(3)-C(18)-C(19)-C(20)	22.3(8)
C(17)-C(18)-C(19)-C(20)	140.8(7)
O(3)-C(18)-C(19)-C(15)	-102.6(7)
C(17)-C(18)-C(19)-C(15)	16.0(9)
C(14)-C(15)-C(19)-C(18)	134.4(8)
C(16)-C(15)-C(19)-C(18)	7.8(9)
C(14)-C(15)-C(19)-C(20)	18.7(11)
C(16)-C(15)-C(19)-C(20)	-107.9(8)
C(18)-C(19)-C(20)-C(22)	-147.5(7)
C(15)-C(19)-C(20)-C(22)	-31.4(10)
C(18)-C(19)-C(20)-C(21)	-20.7(8)
C(15)-C(19)-C(20)-C(21)	95.4(8)
C(22)-C(20)-C(21)-O(4)	-51.9(12)
C(19)-C(20)-C(21)-O(4)	-171.5(9)
C(22)-C(20)-C(21)-O(3)	132.0(8)
C(19)-C(20)-C(21)-O(3)	12.4(8)
O(4)-C(21)-O(3)-C(18)	-174.6(8)
C(20)-C(21)-O(3)-C(18)	1.9(9)
C(17)-C(18)-O(3)-C(21)	-129.8(7)
C(19)-C(18)-O(3)-C(21)	-15.7(9)
C(21)-C(20)-C(22)-C(13)	-59.4(10)
C(19)-C(20)-C(22)-C(13)	57.0(9)
C(21)-C(20)-C(22)-C(23)	176.1(7)
C(19)-C(20)-C(22)-C(23)	-67.6(8)
C(21)-C(20)-C(22)-C(11)	51.8(13)
C(19)-C(20)-C(22)-C(11)	168.1(9)
C(14)-C(13)-C(22)-C(20)	-71.5(10)
C(12)-C(13)-C(22)-C(20)	159.0(7)

Table S19 *Cont'd*

C(14)-C(13)-C(22)-C(23)	50.1(10)
C(12)-C(13)-C(22)-C(23)	-79.4(8)
C(14)-C(13)-C(22)-C(11)	150.8(7)
C(12)-C(13)-C(22)-C(11)	21.3(7)
C(25)-C(11)-C(22)-C(20)	105.0(10)
C(12)-C(11)-C(22)-C(20)	-140.7(10)
Si(1)-C(11)-C(22)-C(20)	-29.5(13)
C(25)-C(11)-C(22)-C(13)	-134.9(7)
C(12)-C(11)-C(22)-C(13)	-20.6(7)
Si(1)-C(11)-C(22)-C(13)	90.6(8)
C(25)-C(11)-C(22)-C(23)	-21.8(8)
C(12)-C(11)-C(22)-C(23)	92.4(7)
Si(1)-C(11)-C(22)-C(23)	-156.3(7)
C(20)-C(22)-C(23)-C(24)	-103.1(8)
C(13)-C(22)-C(23)-C(24)	132.9(8)
C(11)-C(22)-C(23)-C(24)	39.6(9)
C(22)-C(23)-C(24)-C(25)	-43.1(10)
C(12)-C(11)-C(25)-C(24)	-96.0(9)
C(22)-C(11)-C(25)-C(24)	-3.4(10)
Si(1)-C(11)-C(25)-C(24)	139.2(7)
C(23)-C(24)-C(25)-C(11)	28.0(10)

Symmetry transformations used to generate equivalent atoms:

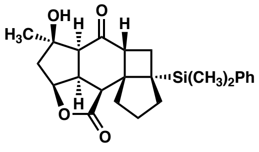
Table S20 *Hydrogen Bonds for Cyclobutane* **63** *[Å and °].*

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(13)-H(13)...O(2)	1.00	2.49	3.079(11)	116.9
C(15)-H(15)...O(3)#1	1.00	2.50	3.246(11)	130.8
O(2)-H(2A)...O(1)#2	0.83(3)	2.16(3)	2.996(10)	178(15)
C(17)-H(17A)...O(1)#2	0.99	2.58	3.430(11)	143.8
C(19)-H(19)...O(3)#1	1.00	2.52	3.267(11)	131.5

Symmetry transformations used to generate equivalent atoms:

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

X-RAY CRYSTAL STRUCTURE ANALYSIS OF CYCLOBUTANE 64



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Contents

Figure S6 *X-Ray Crystal Structure of Cyclobutane* **64.**

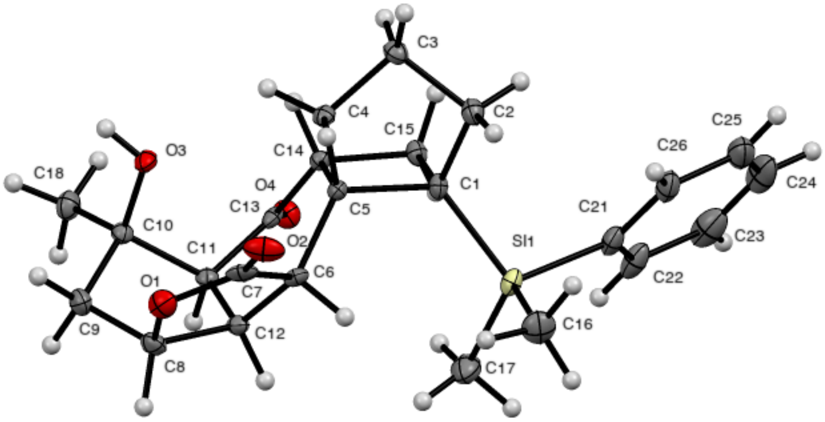


Table S21 *Experimental Details for X-Ray Structure Determination of Cyclobutane* **64.**

Low-temperature diffraction data (ϕ-and ω-scans) were collected on a Bruker AXS KAPPA APEX II diffractometer coupled to an PHOTON 100 CMOS detector with graphite monochromated Mo K_α radiation ($\lambda = 0.71073$ Å) for the structure of compound **64**. The structure was solved by direct methods using SHELXS and refined against F^2 on all data by full-matrix least squares with SHELXL-2017 using established refinement techniques. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the *U* value of the atoms they are linked to (1.5 times for methyl groups).

Compound **64** crystallizes in the monoclinic space group $P2_1$ with one molecule in the asymmetric unit. The molecule was refined with a disordered hydroxide.

Table S22 *Crystal Data and Structure Refinement for Cyclobutane* **64.**

Empirical formula	C24 H30 O4.16 Si	
Formula weight	413.21	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2$_1$	
Unit cell dimensions	a = 7.267(3) Å	a= 90°.
	b = 9.667(3) Å	b= 99.237(16)°.
	c = 15.436(4) Å	g = 90°.
Volume	1070.3(7) Å^3	
Z	2	
Density (calculated)	1.282 Mg/m^3	
Absorption coefficient	0.138 mm^{-1}	
F(000)	443	
Crystal size	0.300 x 0.100 x 0.050 mm^3	
Theta range for data collection	2.495 to 30.501°.	
Index ranges	-10<=h<=9, -13<=k<=13, -22<=l<=22	
Reflections collected	16781	
Independent reflections	5995 [R(int) = 0.0322]	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7466 and 0.6535	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5995 / 2 / 280	
Goodness-of-fit on F^2	1.024	
Final R indices [I>2sigma(I)]	R1 = 0.0392, wR2 = 0.0861	
R indices (all data)	R1 = 0.0494, wR2 = 0.0897	
Absolute structure parameter	0.04(4)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.316 and -0.247 e.Å^{-3}	

Table S23 *Atomic Coordinates (x 10^4) and Equivalent Isotropic Displacement Parameters (Å^{2}x 10^3) for Cyclobutane* **64**. *U(eq) is Defined as One Third of the Trace of the Orthogonalized U^{ij} Tensor.*

	x	y	z	U(eq)
Si(1)	4386(1)	6279(1)	8522(1)	15(1)
C(1)	3245(3)	4685(2)	7973(1)	12(1)
C(2)	3535(3)	3370(2)	8547(1)	17(1)
C(3)	2928(3)	2185(2)	7909(1)	16(1)
C(4)	3789(3)	2600(2)	7113(1)	12(1)
C(5)	3459(3)	4173(2)	7001(1)	10(1)
C(6)	4859(3)	4923(2)	6488(1)	12(1)
O(6B)	6250(11)	5648(9)	7055(5)	9(3)
C(7)	6204(3)	3975(2)	6103(2)	17(1)
O(1)	6138(2)	4182(2)	5238(1)	20(1)
O(2)	7296(2)	3157(2)	6489(1)	24(1)
C(8)	5001(3)	5372(2)	4925(1)	17(1)
C(9)	3445(3)	4958(2)	4187(1)	18(1)
C(10)	1752(3)	4665(2)	4626(1)	13(1)
C(18)	-89(3)	4728(2)	4002(1)	19(1)
O(3)	1978(2)	3371(2)	5078(1)	15(1)
C(11)	1954(3)	5803(2)	5343(1)	12(1)
C(12)	4054(3)	5873(2)	5706(1)	13(1)
C(13)	749(3)	5568(2)	6031(1)	12(1)
O(4)	-691(2)	6223(2)	6041(1)	17(1)
C(14)	1345(3)	4496(2)	6715(1)	11(1)
C(15)	1116(3)	4936(2)	7652(1)	14(1)
C(16)	6926(3)	6088(3)	8901(2)	27(1)
C(17)	3947(4)	7835(3)	7791(2)	26(1)
C(21)	3208(3)	6548(2)	9508(1)	19(1)
C(22)	1903(3)	7607(3)	9547(2)	25(1)
C(23)	1014(4)	7768(3)	10273(2)	35(1)

Table S23 *Cont'd*

C(24)	1401(4)	6871(3)	10974(2)	37(1)
C(25)	2668(4)	5819(3)	10955(2)	30(1)
C(26)	3574(3)	5662(3)	10235(1)	23(1)

Table S24 *Bond Lengths [Å] and angles [°] for Cyclobutane* **64.**

Si(1)-C(16)	1.853(2)
Si(1)-C(17)	1.877(3)
Si(1)-C(21)	1.881(2)
Si(1)-C(1)	1.886(2)
C(1)-C(2)	1.545(3)
C(1)-C(15)	1.566(3)
C(1)-C(5)	1.611(3)
C(2)-C(3)	1.529(3)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-C(4)	1.520(3)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-C(5)	1.545(3)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-C(14)	1.561(3)
C(5)-C(6)	1.564(3)
C(6)-O(6B)	1.412(8)
C(6)-C(7)	1.529(3)
C(6)-C(12)	1.554(3)
C(6)-H(6)	1.0000
O(6B)-H(6OB)	0.8400
C(7)-O(2)	1.207(3)
C(7)-O(1)	1.343(3)
O(1)-C(8)	1.452(3)
C(8)-C(9)	1.525(3)
C(8)-C(12)	1.558(3)
C(8)-H(8)	1.0000
C(9)-C(10)	1.524(3)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900

Table S24 *Cont'd*

C(10)-O(3)	1.430(2)
C(10)-C(18)	1.519(3)
C(10)-C(11)	1.551(3)
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
O(3)-H(3O)	0.81(2)
C(11)-C(13)	1.499(3)
C(11)-C(12)	1.541(3)
C(11)-H(11)	1.0000
C(12)-H(12)	1.0000
C(13)-O(4)	1.225(2)
C(13)-C(14)	1.492(3)
C(14)-C(15)	1.542(3)
C(14)-H(14)	1.0000
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(21)-C(26)	1.403(3)
C(21)-C(22)	1.403(3)
C(22)-C(23)	1.390(3)
C(22)-H(22)	0.9500
C(23)-C(24)	1.380(5)
C(23)-H(23)	0.9500
C(24)-C(25)	1.375(4)
C(24)-H(24)	0.9500
C(25)-C(26)	1.387(3)
C(25)-H(25)	0.9500
C(26)-H(26)	0.9500

Table S24 *Cont'd*

C(16)-Si(1)-C(17)	109.50(13)
C(16)-Si(1)-C(21)	108.58(11)
C(17)-Si(1)-C(21)	108.67(11)
C(16)-Si(1)-C(1)	113.85(11)
C(17)-Si(1)-C(1)	111.37(10)
C(21)-Si(1)-C(1)	104.63(10)
C(2)-C(1)-C(15)	110.28(17)
C(2)-C(1)-C(5)	104.92(16)
C(15)-C(1)-C(5)	89.47(14)
C(2)-C(1)-Si(1)	113.87(14)
C(15)-C(1)-Si(1)	110.89(13)
C(5)-C(1)-Si(1)	124.62(14)
C(3)-C(2)-C(1)	104.36(16)
C(3)-C(2)-H(2A)	110.9
C(1)-C(2)-H(2A)	110.9
C(3)-C(2)-H(2B)	110.9
C(1)-C(2)-H(2B)	110.9
H(2A)-C(2)-H(2B)	108.9
C(4)-C(3)-C(2)	102.09(17)
C(4)-C(3)-H(3A)	111.4
C(2)-C(3)-H(3A)	111.4
C(4)-C(3)-H(3B)	111.4
C(2)-C(3)-H(3B)	111.4
H(3A)-C(3)-H(3B)	109.2
C(3)-C(4)-C(5)	105.86(16)
C(3)-C(4)-H(4A)	110.6
C(5)-C(4)-H(4A)	110.6
C(3)-C(4)-H(4B)	110.6
C(5)-C(4)-H(4B)	110.6
H(4A)-C(4)-H(4B)	108.7
C(4)-C(5)-C(14)	110.87(16)
C(4)-C(5)-C(6)	114.26(16)
C(14)-C(5)-C(6)	117.03(16)

Table S24 *Cont'd*

C(4)-C(5)-C(1)	103.58(15)
C(14)-C(5)-C(1)	87.97(14)
C(6)-C(5)-C(1)	119.85(16)
O(6B)-C(6)-C(7)	95.7(4)
O(6B)-C(6)-C(12)	109.3(4)
C(7)-C(6)-C(12)	103.69(16)
O(6B)-C(6)-C(5)	112.1(4)
C(7)-C(6)-C(5)	115.31(17)
C(12)-C(6)-C(5)	118.24(16)
C(7)-C(6)-H(6)	106.2
C(12)-C(6)-H(6)	106.2
C(5)-C(6)-H(6)	106.2
C(6)-O(6B)-H(6OB)	109.5
O(2)-C(7)-O(1)	120.3(2)
O(2)-C(7)-C(6)	127.7(2)
O(1)-C(7)-C(6)	111.93(18)
C(7)-O(1)-C(8)	112.11(17)
O(1)-C(8)-C(9)	110.79(18)
O(1)-C(8)-C(12)	106.70(16)
C(9)-C(8)-C(12)	107.08(18)
O(1)-C(8)-H(8)	110.7
C(9)-C(8)-H(8)	110.7
C(12)-C(8)-H(8)	110.7
C(10)-C(9)-C(8)	105.72(17)
C(10)-C(9)-H(9A)	110.6
C(8)-C(9)-H(9A)	110.6
C(10)-C(9)-H(9B)	110.6
C(8)-C(9)-H(9B)	110.6
H(9A)-C(9)-H(9B)	108.7
O(3)-C(10)-C(18)	111.44(17)
O(3)-C(10)-C(9)	110.04(17)
C(18)-C(10)-C(9)	113.72(17)
O(3)-C(10)-C(11)	106.37(15)
C(18)-C(10)-C(11)	113.38(17)

Table S24 *Cont'd*

C(9)-C(10)-C(11)	101.23(16)
C(10)-C(18)-H(18A)	109.5
C(10)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(10)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(10)-O(3)-H(3O)	110.9(19)
C(13)-C(11)-C(12)	113.93(16)
C(13)-C(11)-C(10)	113.52(17)
C(12)-C(11)-C(10)	105.39(16)
C(13)-C(11)-H(11)	107.9
C(12)-C(11)-H(11)	107.9
C(10)-C(11)-H(11)	107.9
C(11)-C(12)-C(6)	118.97(16)
C(11)-C(12)-C(8)	103.86(16)
C(6)-C(12)-C(8)	105.05(16)
C(11)-C(12)-H(12)	109.5
C(6)-C(12)-H(12)	109.5
C(8)-C(12)-H(12)	109.5
O(4)-C(13)-C(14)	120.14(18)
O(4)-C(13)-C(11)	121.80(18)
C(14)-C(13)-C(11)	118.06(17)
C(13)-C(14)-C(15)	114.11(17)
C(13)-C(14)-C(5)	119.99(17)
C(15)-C(14)-C(5)	92.24(14)
C(13)-C(14)-H(14)	109.7
C(15)-C(14)-H(14)	109.7
C(5)-C(14)-H(14)	109.7
C(14)-C(15)-C(1)	90.25(15)
C(14)-C(15)-H(15A)	113.6
C(1)-C(15)-H(15A)	113.6
C(14)-C(15)-H(15B)	113.6
C(1)-C(15)-H(15B)	113.6

Table S24 *Cont'd*

H(15A)-C(15)-H(15B)	110.9
Si(1)-C(16)-H(16A)	109.5
Si(1)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
Si(1)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
Si(1)-C(17)-H(17A)	109.5
Si(1)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
Si(1)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(26)-C(21)-C(22)	117.0(2)
C(26)-C(21)-Si(1)	120.69(17)
C(22)-C(21)-Si(1)	122.26(19)
C(23)-C(22)-C(21)	121.4(3)
C(23)-C(22)-H(22)	119.3
C(21)-C(22)-H(22)	119.3
C(24)-C(23)-C(22)	120.0(3)
C(24)-C(23)-H(23)	120.0
C(22)-C(23)-H(23)	120.0
C(25)-C(24)-C(23)	120.0(2)
C(25)-C(24)-H(24)	120.0
C(23)-C(24)-H(24)	120.0
C(24)-C(25)-C(26)	120.3(3)
C(24)-C(25)-H(25)	119.9
C(26)-C(25)-H(25)	119.9
C(25)-C(26)-C(21)	121.4(2)
C(25)-C(26)-H(26)	119.3
C(21)-C(26)-H(26)	119.3

Symmetry transformations used to generate equivalent atoms:

Table S25 *Anisotropic Displacement Parameters (Å^{2}x10^3) for Cyclobutane* **64**. *The Anisotropic Displacement Factor Exponent Takes the Form: -2p^2[h^{2}a*^{2}U^{11} + ... + 2hka*b*U^{12}].*

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Si(1)	15(1)	15(1)	14(1)	-4(1)	1(1)	1(1)
C(1)	13(1)	14(1)	10(1)	-1(1)	1(1)	3(1)
C(2)	20(1)	17(1)	13(1)	1(1)	3(1)	2(1)
C(3)	18(1)	14(1)	16(1)	2(1)	5(1)	1(1)
C(4)	14(1)	10(1)	14(1)	-1(1)	3(1)	1(1)
C(5)	11(1)	10(1)	10(1)	-1(1)	1(1)	-1(1)
C(6)	10(1)	10(1)	16(1)	-1(1)	1(1)	-3(1)
O(6B)	4(4)	15(5)	9(4)	-3(3)	2(3)	-1(3)
C(7)	11(1)	14(1)	28(1)	0(1)	7(1)	-5(1)
O(1)	16(1)	22(1)	24(1)	-4(1)	8(1)	1(1)
O(2)	12(1)	21(1)	42(1)	7(1)	8(1)	1(1)
C(8)	17(1)	18(1)	18(1)	1(1)	8(1)	-3(1)
C(9)	22(1)	19(1)	14(1)	-1(1)	6(1)	-2(1)
C(10)	15(1)	11(1)	12(1)	1(1)	2(1)	1(1)
C(18)	21(1)	21(1)	16(1)	0(1)	-1(1)	1(1)
O(3)	21(1)	10(1)	13(1)	-1(1)	1(1)	-1(1)
C(11)	14(1)	9(1)	13(1)	1(1)	2(1)	0(1)
C(12)	14(1)	11(1)	15(1)	-1(1)	5(1)	-2(1)
C(13)	14(1)	8(1)	13(1)	-3(1)	-1(1)	0(1)
O(4)	14(1)	18(1)	18(1)	2(1)	3(1)	5(1)
C(14)	10(1)	11(1)	11(1)	-1(1)	2(1)	0(1)
C(15)	16(1)	15(1)	12(1)	0(1)	3(1)	2(1)
C(16)	16(1)	35(2)	29(1)	-1(1)	2(1)	-2(1)
C(17)	37(2)	18(1)	24(1)	-2(1)	3(1)	-1(1)
C(21)	14(1)	23(1)	18(1)	-10(1)	2(1)	-2(1)
C(22)	16(1)	29(1)	29(1)	-14(1)	0(1)	-1(1)
C(23)	18(1)	41(2)	47(2)	-23(1)	11(1)	-4(1)

Table S25 *Cont'd*

C(24)	26(1)	51(2)	38(1)	-24(1)	21(1)	-12(1)
C(25)	32(1)	38(2)	23(1)	-10(1)	11(1)	-13(1)
C(26)	21(1)	29(1)	19(1)	-9(1)	5(1)	-4(1)

Table S26 *Hydrogen Coordinates (x10^4) and Isotropic Displacement Parameters (Å^{2}x10^3) for Cyclobutane **64**.*

	x	y	z	U(eq)
H(2A)	4860	3268	8816	20
H(2B)	2760	3400	9019	20
H(3A)	3424	1287	8151	19
H(3B)	1553	2127	7765	19
H(4A)	3185	2097	6584	15
H(4B)	5140	2390	7209	15
H(6)	5647	5529	6924	15
H(6OB)	6985	6026	6759	90(90)
H(8)	5785	6123	4729	20
H(9A)	3177	5718	3754	21
H(9B)	3801	4124	3881	21
H(18A)	-81	4048	3531	29
H(18B)	-260	5657	3747	29
H(18C)	-1113	4520	4324	29
H(3O)	1630(40)	2740(20)	4749(16)	22
H(11)	1581	6705	5049	15
H(12)	4418	6853	5851	15
H(14)	646	3617	6555	13
H(15A)	297	4314	7928	17
H(15B)	733	5913	7695	17
H(16A)	7531	5787	8409	40
H(16B)	7141	5397	9371	40
H(16C)	7449	6978	9122	40
H(17A)	4148	8677	8147	40
H(17B)	2659	7815	7483	40
H(17C)	4805	7824	7362	40
H(22)	1622	8227	9066	30
H(23)	140	8495	10287	42

Table S26 *Cont'd*

H(24)	792	6979	11471	44
H(25)	2924	5197	11436	36
H(26)	4461	4941	10235	27

Table S27 *Torsion Angles [°] for Cyclobutane* **64**.

C(16)-Si(1)-C(1)-C(2)	56.33(18)
C(17)-Si(1)-C(1)-C(2)	-179.28(15)
C(21)-Si(1)-C(1)-C(2)	-62.05(17)
C(16)-Si(1)-C(1)-C(15)	-178.59(14)
C(17)-Si(1)-C(1)-C(15)	-54.20(17)
C(21)-Si(1)-C(1)-C(15)	63.02(15)
C(16)-Si(1)-C(1)-C(5)	-74.03(18)
C(17)-Si(1)-C(1)-C(5)	50.4(2)
C(21)-Si(1)-C(1)-C(5)	167.59(16)
C(15)-C(1)-C(2)-C(3)	67.9(2)
C(5)-C(1)-C(2)-C(3)	-27.2(2)
Si(1)-C(1)-C(2)-C(3)	-166.73(14)
C(1)-C(2)-C(3)-C(4)	42.6(2)
C(2)-C(3)-C(4)-C(5)	-42.0(2)
C(3)-C(4)-C(5)-C(14)	-68.47(19)
C(3)-C(4)-C(5)-C(6)	156.67(16)
C(3)-C(4)-C(5)-C(1)	24.6(2)
C(2)-C(1)-C(5)-C(4)	1.8(2)
C(15)-C(1)-C(5)-C(4)	-109.09(16)
Si(1)-C(1)-C(5)-C(4)	135.63(15)
C(2)-C(1)-C(5)-C(14)	112.77(17)
C(15)-C(1)-C(5)-C(14)	1.90(15)
Si(1)-C(1)-C(5)-C(14)	-113.38(16)
C(2)-C(1)-C(5)-C(6)	-126.96(19)
C(15)-C(1)-C(5)-C(6)	122.16(18)
Si(1)-C(1)-C(5)-C(6)	6.9(2)
C(4)-C(5)-C(6)-O(6B)	-102.5(4)
C(14)-C(5)-C(6)-O(6B)	125.6(4)
C(1)-C(5)-C(6)-O(6B)	21.3(4)
C(4)-C(5)-C(6)-C(7)	5.6(2)
C(14)-C(5)-C(6)-C(7)	-126.37(19)
C(1)-C(5)-C(6)-C(7)	129.33(19)

***Table S27** Cont'd*

C(4)-C(5)-C(6)-C(12)	129.03(18)
C(14)-C(5)-C(6)-C(12)	-2.9(2)
C(1)-C(5)-C(6)-C(12)	-107.2(2)
O(6B)-C(6)-C(7)-O(2)	60.3(4)
C(12)-C(6)-C(7)-O(2)	171.8(2)
C(5)-C(6)-C(7)-O(2)	-57.4(3)
O(6B)-C(6)-C(7)-O(1)	-116.5(4)
C(12)-C(6)-C(7)-O(1)	-5.0(2)
C(5)-C(6)-C(7)-O(1)	125.80(18)
O(2)-C(7)-O(1)-C(8)	-169.35(19)
C(6)-C(7)-O(1)-C(8)	7.8(2)
C(7)-O(1)-C(8)-C(9)	-123.23(18)
C(7)-O(1)-C(8)-C(12)	-7.0(2)
O(1)-C(8)-C(9)-C(10)	94.2(2)
C(12)-C(8)-C(9)-C(10)	-21.8(2)
C(8)-C(9)-C(10)-O(3)	-74.5(2)
C(8)-C(9)-C(10)-C(18)	159.71(18)
C(8)-C(9)-C(10)-C(11)	37.8(2)
O(3)-C(10)-C(11)-C(13)	-50.7(2)
C(18)-C(10)-C(11)-C(13)	72.2(2)
C(9)-C(10)-C(11)-C(13)	-165.64(17)
O(3)-C(10)-C(11)-C(12)	74.70(19)
C(18)-C(10)-C(11)-C(12)	-162.48(17)
C(9)-C(10)-C(11)-C(12)	-40.28(19)
C(13)-C(11)-C(12)-C(6)	36.0(2)
C(10)-C(11)-C(12)-C(6)	-89.1(2)
C(13)-C(11)-C(12)-C(8)	152.21(17)
C(10)-C(11)-C(12)-C(8)	27.10(19)
O(6B)-C(6)-C(12)-C(11)	-142.6(4)
C(7)-C(6)-C(12)-C(11)	116.25(18)
C(5)-C(6)-C(12)-C(11)	-12.8(3)
O(6B)-C(6)-C(12)-C(8)	101.8(4)
C(7)-C(6)-C(12)-C(8)	0.6(2)
C(5)-C(6)-C(12)-C(8)	-128.44(18)

***Table S27** Cont'd*

O(1)-C(8)-C(12)-C(11)	-122.18(17)
C(9)-C(8)-C(12)-C(11)	-3.5(2)
O(1)-C(8)-C(12)-C(6)	3.5(2)
C(9)-C(8)-C(12)-C(6)	122.15(18)
C(12)-C(11)-C(13)-O(4)	135.85(19)
C(10)-C(11)-C(13)-O(4)	-103.5(2)
C(12)-C(11)-C(13)-C(14)	-44.4(2)
C(10)-C(11)-C(13)-C(14)	76.2(2)
O(4)-C(13)-C(14)-C(15)	-42.7(3)
C(11)-C(13)-C(14)-C(15)	137.55(18)
O(4)-C(13)-C(14)-C(5)	-150.63(19)
C(11)-C(13)-C(14)-C(5)	29.6(3)
C(4)-C(5)-C(14)-C(13)	-138.52(18)
C(6)-C(5)-C(14)-C(13)	-5.0(3)
C(1)-C(5)-C(14)-C(13)	117.72(18)
C(4)-C(5)-C(14)-C(15)	101.83(17)
C(6)-C(5)-C(14)-C(15)	-124.68(17)
C(1)-C(5)-C(14)-C(15)	-1.93(15)
C(13)-C(14)-C(15)-C(1)	-122.46(17)
C(5)-C(14)-C(15)-C(1)	1.98(16)
C(2)-C(1)-C(15)-C(14)	-107.64(17)
C(5)-C(1)-C(15)-C(14)	-1.92(15)
Si(1)-C(1)-C(15)-C(14)	125.28(14)
C(16)-Si(1)-C(21)-C(26)	-49.7(2)
C(17)-Si(1)-C(21)-C(26)	-168.77(18)
C(1)-Si(1)-C(21)-C(26)	72.18(19)
C(16)-Si(1)-C(21)-C(22)	131.85(19)
C(17)-Si(1)-C(21)-C(22)	12.8(2)
C(1)-Si(1)-C(21)-C(22)	-106.24(19)
C(26)-C(21)-C(22)-C(23)	-0.1(3)
Si(1)-C(21)-C(22)-C(23)	178.40(18)
C(21)-C(22)-C(23)-C(24)	-0.3(4)
C(22)-C(23)-C(24)-C(25)	0.1(4)
C(23)-C(24)-C(25)-C(26)	0.6(4)

Table S27 *Cont'd*

C(24)-C(25)-C(26)-C(21)	-1.0(4)
C(22)-C(21)-C(26)-C(25)	0.8(3)
Si(1)-C(21)-C(26)-C(25)	-177.75(18)

Symmetry transformations used to generate equivalent atoms:

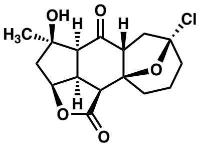
Table S28 *Hydrogen Bonds for Cyclobutane* **64** *[Å and °].*

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(9)-H(9A)...O(2)#1	0.99	2.40	3.280(3)	147.2
C(18)-H(18C)...O(1)#2	0.98	2.64	3.622(3)	175.1
O(3)-H(3O)...O(4)#3	0.81(2)	1.96(2)	2.766(2)	177(3)
C(14)-H(14)...O(2)#2	1.00	2.46	3.182(3)	128.6

Symmetry transformations used to generate equivalent atoms:

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

X-RAY CRYSTAL STRUCTURE ANALYSIS OF CYCLOHEPTANE *72*



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<u>Contents</u>

Figure S7 *X-Ray Crystal Structure of Cycloheptane* ***72.***

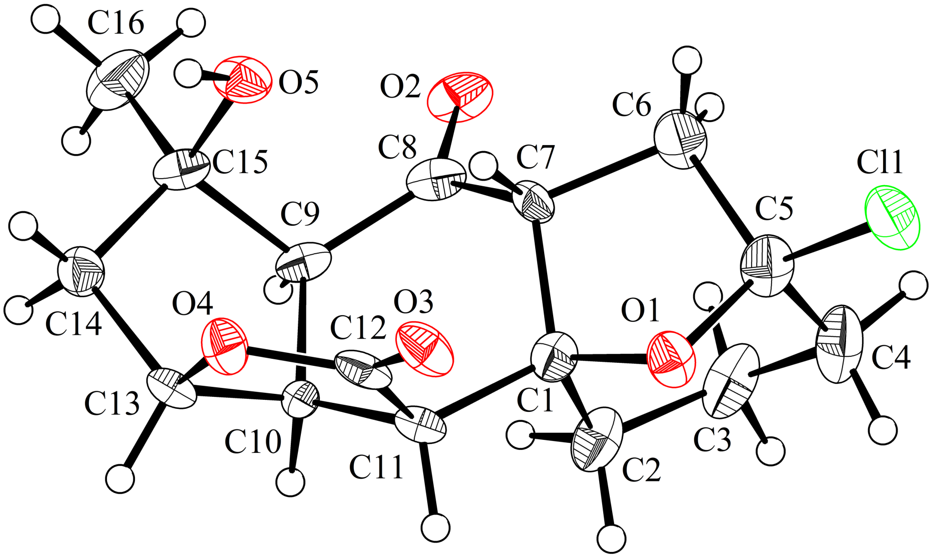


Table S29 *Experimental Details for X-Ray Structure Determination of Cycloheptane 72*

Refinement details

A crystal was mounted on a polyimide MiTeGen loop with STP Oil Treatment and placed under a nitrogen stream. Low temperature (100K) X-ray data were collected with a Bruker AXS D8 VENTURE KAPPA diffractometer running at 50 kV and 1mA (Cu K_α = 1.54178 Å; PHOTON II CPAD detector and Helios focusing multilayer mirror optics). All diffractometer manipulations, including data collection, integration, and scaling were carried out using the Bruker APEX3 software. An absorption correction was applied using SADABS. The space group was determined and the structure solved by intrinsic phasing using XT. Refinement was full-matrix least squares on F^2 using XL. All non-hydrogen atoms (except the carbon of a disordered chloroform) were refined using anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed at 1.2 times (1.5 times for methyl groups) the U_{eq} value of the bonded atom.

Special refinement details

Compound **72** crystallizes in the monoclinic space group *C*2 with two molecules, one water molecule, and 38% of a chloroform in the asymmetric unit. The structure was refined as a two-component twin (refined ratio of 85:15) on an HKLF 5 file generated by PLATON.

Table S30 *Crystal Data and Structure Refinement for Cycloheptane* ***72***

Empirical formula	C16.19 H20.19 Cl1.59 O5.50	
Formula weight	359.09	
Temperature	100 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	C 1 2 1	
Unit cell dimensions	a = 34.102(5) Å	a= 90°
	b = 14.485(2) Å	b= 94.960(10)°
	c = 6.6087(11) Å	g = 90°
Volume	3252.2(9) Å^3	
Z	8	
Density (calculated)	1.467 g/cm^3	
Absorption coefficient	3.208 mm^{-1}	
F(000)	1507	
Crystal size	0.11 x 0.04 x 0.03 mm^3	
Theta range for data collection	3.317 to 76.122°.	
Index ranges	-41 £ h £ 40, -17 £ k £ 17, 0 £ l £ 8	
Reflections collected	6144	
Independent reflections	6144 [R(int) = ?]	
Completeness to theta = 67.679°	98.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9904 and 0.7072	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6144 / 4 / 434	
Goodness-of-fit on F^2	1.065	
Final R indices [I>2sigma(I)]	R1 = 0.0840, wR2 = 0.2207	
R indices (all data)	R1 = 0.0969, wR2 = 0.2291	
Absolute structure parameter [Flack]	0.163(12)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.708 and -0.538 e.Å^{-3}	

Table S31 *Atomic Coordinates (x 10^4) and Equivalent Isotropic Displacement Parameters (Å^{2}x 10^3) for Cycloheptane* ***72****. U(eq) is Defined as One Third of the Trace of the Orthogonalized U^{ij} Tensor.*

	x	y	z	U(eq)
Cl(1)	6462(1)	349(2)	11229(4)	36(1)
O(1)	6294(2)	1950(4)	12668(10)	25(1)
O(2)	5281(2)	2980(5)	8327(10)	29(2)
O(3)	6853(2)	3559(5)	11901(10)	28(1)
O(4)	6508(2)	4844(4)	11323(10)	25(1)
O(5)	6000(2)	4396(5)	7538(10)	27(1)
C(1)	6013(2)	2698(6)	12313(13)	23(2)
C(2)	5664(3)	2506(7)	13588(15)	31(2)
C(3)	5480(3)	1561(8)	13098(18)	38(2)
C(4)	5790(3)	823(7)	12868(19)	40(3)
C(5)	6094(3)	1208(7)	11574(16)	30(2)
C(6)	5924(3)	1617(7)	9532(16)	32(2)
C(7)	5919(3)	2650(6)	10038(12)	21(2)
C(8)	5562(3)	3240(7)	9446(13)	25(2)
C(9)	5591(2)	4203(6)	10287(12)	21(2)
C(10)	5876(3)	4396(6)	12246(13)	19(2)
C(11)	6178(2)	3656(6)	12938(13)	20(2)
C(12)	6543(3)	3974(7)	12019(13)	23(2)
C(13)	6124(2)	5226(6)	11765(12)	20(2)
C(14)	5911(3)	5671(6)	9851(14)	24(2)
C(15)	5723(2)	4889(7)	8647(13)	23(2)
C(16)	5371(3)	5187(8)	7186(16)	37(2)
Cl(1B)	5600(1)	7225(2)	14099(5)	54(1)
O(1B)	6287(2)	7010(5)	16090(11)	35(2)
O(2B)	7121(2)	8559(5)	12394(11)	41(2)
O(3B)	6650(2)	5146(5)	15897(10)	31(2)
O(4B)	7290(2)	5266(6)	15553(12)	43(2)

Table S31 *Cont'd*

O(5B)	7372(2)	6411(5)	11759(11)	33(2)
C(1B)	6692(4)	7307(8)	16092(16)	42(3)
C(2B)	6754(5)	8185(9)	17260(18)	64(4)
C(3B)	6466(5)	8945(9)	16450(19)	65(4)
C(4B)	6047(5)	8570(9)	15850(20)	63(4)
C(5B)	6081(3)	7679(8)	14762(17)	42(3)
C(6B)	6326(3)	7773(7)	12972(15)	33(2)
C(7B)	6725(3)	7396(7)	13782(13)	30(2)
C(8B)	7108(3)	7877(7)	13444(13)	32(2)
C(9B)	7466(3)	7454(8)	14569(15)	40(3)
C(10B)	7409(3)	6845(10)	16518(15)	46(3)
C(11B)	6992(3)	6573(9)	16972(16)	42(3)
C(12B)	6950(3)	5610(8)	16141(16)	36(2)
C(13B)	7614(3)	5924(10)	16200(20)	55(4)
C(14B)	7873(3)	6067(10)	14504(19)	51(3)
C(15B)	7675(3)	6800(8)	13096(15)	35(2)
C(16B)	7962(3)	7313(9)	11897(15)	44(3)
O(6)	7478(2)	4630(5)	10479(12)	41(2)
Cl(2)	5193(2)	-332(5)	7527(14)	100(5)
Cl(3)	4852(3)	-647(9)	11220(19)	169(12)
Cl(4)	5237(3)	-2147(5)	9390(20)	147(9)
C(17)	4947(2)	-1158(6)	8908(16)	130(30)

Table S32 *Bond Lengths [Å] and angles [°] for Cycloheptane **72***

Cl(1)-C(5)	1.796(10)
O(1)-C(1)	1.452(10)
O(1)-C(5)	1.435(11)
O(2)-C(8)	1.217(11)
O(3)-C(12)	1.224(11)
O(4)-C(12)	1.343(11)
O(4)-C(13)	1.473(10)
O(5)-H(5)	0.8400
O(5)-C(15)	1.434(10)
C(1)-C(2)	1.542(12)
C(1)-C(7)	1.512(12)
C(1)-C(11)	1.541(12)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(2)-C(3)	1.528(15)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(3)-C(4)	1.521(15)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(4)-C(5)	1.505(15)
C(5)-C(6)	1.540(13)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(6)-C(7)	1.533(13)
C(7)-H(7)	1.0000
C(7)-C(8)	1.511(13)
C(8)-C(9)	1.501(13)
C(9)-H(9)	1.0000
C(9)-C(10)	1.576(12)
C(9)-C(15)	1.564(12)
C(10)-H(10)	1.0000

Table S32 *Cont'd*

C(10)-C(11)	1.528(12)
C(10)-C(13)	1.520(12)
C(11)-H(11)	1.0000
C(11)-C(12)	1.504(12)
C(13)-H(13)	1.0000
C(13)-C(14)	1.544(12)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(14)-C(15)	1.497(13)
C(15)-C(16)	1.534(13)
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
Cl(1B)-C(5B)	1.788(13)
O(1B)-C(1B)	1.447(13)
O(1B)-C(5B)	1.448(13)
O(2B)-C(8B)	1.210(12)
O(3B)-C(12B)	1.223(12)
O(4B)-C(12B)	1.350(14)
O(4B)-C(13B)	1.495(14)
O(5B)-H(5B)	0.8400
O(5B)-C(15B)	1.416(12)
C(1B)-C(2B)	1.494(16)
C(1B)-C(7B)	1.546(13)
C(1B)-C(11B)	1.553(18)
C(2B)-H(2C)	0.9900
C(2B)-H(2D)	0.9900
C(2B)-C(3B)	1.54(2)
C(3B)-H(3C)	0.9900
C(3B)-H(3D)	0.9900
C(3B)-C(4B)	1.55(2)
C(4B)-H(4D)	0.9900
C(4B)-H(4C)	0.9900
C(4B)-C(5B)	1.487(18)

***Table S32** Cont'd*

C(5B)-C(6B)	1.513(15)
C(6B)-H(6C)	0.9900
C(6B)-H(6D)	0.9900
C(6B)-C(7B)	1.519(15)
C(7B)-H(7B)	1.0000
C(7B)-C(8B)	1.514(13)
C(8B)-C(9B)	1.504(16)
C(9B)-H(9B)	1.0000
C(9B)-C(10B)	1.586(14)
C(9B)-C(15B)	1.572(16)
C(10B)-H(10B)	1.0000
C(10B)-C(11B)	1.531(15)
C(10B)-C(13B)	1.53(2)
C(11B)-H(11B)	1.0000
C(11B)-C(12B)	1.502(17)
C(13B)-H(13B)	1.0000
C(13B)-C(14B)	1.503(18)
C(14B)-H(14C)	0.9900
C(14B)-H(14D)	0.9900
C(14B)-C(15B)	1.531(16)
C(15B)-C(16B)	1.510(13)
C(16B)-H(16D)	0.9800
C(16B)-H(16E)	0.9800
C(16B)-H(16F)	0.9800
O(6)-H(6E)	0.8689
O(6)-H(6F)	0.9962
Cl(2)-Cl(3)#1	0.969(17)
Cl(2)-C(17)	1.7602
Cl(3)-Cl(4)#1	2.227(5)
Cl(3)-C(17)	1.7534
Cl(4)-C(17)	1.7546
C(17)-H(17)	0.9198
C(5)-O(1)-C(1)	101.4(6)

Table S32 *Cont'd*

C(12)-O(4)-C(13)	109.9(7)
C(15)-O(5)-H(5)	109.5
O(1)-C(1)-C(2)	107.9(7)
O(1)-C(1)-C(7)	102.0(7)
O(1)-C(1)-C(11)	114.1(7)
C(7)-C(1)-C(2)	115.3(8)
C(7)-C(1)-C(11)	110.5(7)
C(11)-C(1)-C(2)	107.3(7)
C(1)-C(2)-H(2A)	109.3
C(1)-C(2)-H(2B)	109.3
H(2A)-C(2)-H(2B)	108.0
C(3)-C(2)-C(1)	111.5(8)
C(3)-C(2)-H(2A)	109.3
C(3)-C(2)-H(2B)	109.3
C(2)-C(3)-H(3A)	109.2
C(2)-C(3)-H(3B)	109.2
H(3A)-C(3)-H(3B)	107.9
C(4)-C(3)-C(2)	112.1(8)
C(4)-C(3)-H(3A)	109.2
C(4)-C(3)-H(3B)	109.2
C(3)-C(4)-H(4A)	110.0
C(3)-C(4)-H(4B)	110.0
H(4A)-C(4)-H(4B)	108.4
C(5)-C(4)-C(3)	108.3(8)
C(5)-C(4)-H(4A)	110.0
C(5)-C(4)-H(4B)	110.0
O(1)-C(5)-Cl(1)	105.9(6)
O(1)-C(5)-C(4)	108.2(9)
O(1)-C(5)-C(6)	106.3(8)
C(4)-C(5)-Cl(1)	109.7(7)
C(4)-C(5)-C(6)	114.6(8)
C(6)-C(5)-Cl(1)	111.7(7)
C(5)-C(6)-H(6A)	111.5
C(5)-C(6)-H(6B)	111.5

Table S32 *Cont'd*

H(6A)-C(6)-H(6B)	109.3
C(7)-C(6)-C(5)	101.2(8)
C(7)-C(6)-H(6A)	111.5
C(7)-C(6)-H(6B)	111.5
C(1)-C(7)-C(6)	104.9(7)
C(1)-C(7)-H(7)	106.9
C(1)-C(7)-C(8)	109.2(7)
C(6)-C(7)-H(7)	106.9
C(8)-C(7)-C(6)	121.3(7)
C(8)-C(7)-H(7)	106.9
O(2)-C(8)-C(7)	123.7(9)
O(2)-C(8)-C(9)	122.4(9)
C(9)-C(8)-C(7)	113.8(7)
C(8)-C(9)-H(9)	107.2
C(8)-C(9)-C(10)	119.0(7)
C(8)-C(9)-C(15)	110.3(7)
C(10)-C(9)-H(9)	107.2
C(15)-C(9)-H(9)	107.2
C(15)-C(9)-C(10)	105.3(7)
C(9)-C(10)-H(10)	109.2
C(11)-C(10)-C(9)	118.3(7)
C(11)-C(10)-H(10)	109.2
C(13)-C(10)-C(9)	106.4(7)
C(13)-C(10)-H(10)	109.2
C(13)-C(10)-C(11)	104.2(7)
C(1)-C(11)-H(11)	108.9
C(10)-C(11)-C(1)	109.3(7)
C(10)-C(11)-H(11)	108.9
C(12)-C(11)-C(1)	117.6(7)
C(12)-C(11)-C(10)	103.0(7)
C(12)-C(11)-H(11)	108.9
O(3)-C(12)-O(4)	119.4(8)
O(3)-C(12)-C(11)	128.7(9)
O(4)-C(12)-C(11)	111.8(7)

Table S32 *Cont'd*

O(4)-C(13)-C(10)	105.3(7)
O(4)-C(13)-H(13)	111.5
O(4)-C(13)-C(14)	110.9(7)
C(10)-C(13)-H(13)	111.5
C(10)-C(13)-C(14)	105.8(7)
C(14)-C(13)-H(13)	111.5
C(13)-C(14)-H(14A)	110.6
C(13)-C(14)-H(14B)	110.6
H(14A)-C(14)-H(14B)	108.7
C(15)-C(14)-C(13)	105.7(7)
C(15)-C(14)-H(14A)	110.6
C(15)-C(14)-H(14B)	110.6
O(5)-C(15)-C(9)	106.2(7)
O(5)-C(15)-C(14)	112.1(7)
O(5)-C(15)-C(16)	109.3(7)
C(14)-C(15)-C(9)	104.4(7)
C(14)-C(15)-C(16)	113.5(8)
C(16)-C(15)-C(9)	111.1(7)
C(15)-C(16)-H(16A)	109.5
C(15)-C(16)-H(16B)	109.5
C(15)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(1B)-O(1B)-C(5B)	102.4(8)
C(12B)-O(4B)-C(13B)	108.3(10)
C(15B)-O(5B)-H(5B)	109.5
O(1B)-C(1B)-C(2B)	110.3(11)
O(1B)-C(1B)-C(7B)	100.1(8)
O(1B)-C(1B)-C(11B)	113.2(8)
C(2B)-C(1B)-C(7B)	114.9(9)
C(2B)-C(1B)-C(11B)	109.3(11)
C(7B)-C(1B)-C(11B)	109.0(9)
C(1B)-C(2B)-H(2C)	109.3

Table S32 *Cont'd*

C(1B)-C(2B)-H(2D)	109.3
C(1B)-C(2B)-C(3B)	111.7(12)
H(2C)-C(2B)-H(2D)	107.9
C(3B)-C(2B)-H(2C)	109.3
C(3B)-C(2B)-H(2D)	109.3
C(2B)-C(3B)-H(3C)	109.1
C(2B)-C(3B)-H(3D)	109.1
C(2B)-C(3B)-C(4B)	112.7(11)
H(3C)-C(3B)-H(3D)	107.8
C(4B)-C(3B)-H(3C)	109.1
C(4B)-C(3B)-H(3D)	109.1
C(3B)-C(4B)-H(4D)	110.0
C(3B)-C(4B)-H(4C)	110.0
H(4D)-C(4B)-H(4C)	108.3
C(5B)-C(4B)-C(3B)	108.7(11)
C(5B)-C(4B)-H(4D)	110.0
C(5B)-C(4B)-H(4C)	110.0
O(1B)-C(5B)-Cl(1B)	106.8(7)
O(1B)-C(5B)-C(4B)	110.0(10)
O(1B)-C(5B)-C(6B)	105.2(9)
C(4B)-C(5B)-Cl(1B)	109.2(10)
C(4B)-C(5B)-C(6B)	111.8(10)
C(6B)-C(5B)-Cl(1B)	113.5(8)
C(5B)-C(6B)-H(6C)	111.1
C(5B)-C(6B)-H(6D)	111.1
C(5B)-C(6B)-C(7B)	103.3(8)
H(6C)-C(6B)-H(6D)	109.1
C(7B)-C(6B)-H(6C)	111.1
C(7B)-C(6B)-H(6D)	111.1
C(1B)-C(7B)-H(7B)	106.9
C(6B)-C(7B)-C(1B)	103.8(8)
C(6B)-C(7B)-H(7B)	106.9
C(8B)-C(7B)-C(1B)	108.8(8)
C(8B)-C(7B)-C(6B)	122.6(8)

Table S32 *Cont'd*

C(8B)-C(7B)-H(7B)	106.9
O(2B)-C(8B)-C(7B)	122.5(10)
O(2B)-C(8B)-C(9B)	123.2(9)
C(9B)-C(8B)-C(7B)	114.3(8)
C(8B)-C(9B)-H(9B)	107.8
C(8B)-C(9B)-C(10B)	118.5(9)
C(8B)-C(9B)-C(15B)	109.3(8)
C(10B)-C(9B)-H(9B)	107.8
C(15B)-C(9B)-H(9B)	107.8
C(15B)-C(9B)-C(10B)	105.1(9)
C(9B)-C(10B)-H(10B)	108.9
C(11B)-C(10B)-C(9B)	118.9(9)
C(11B)-C(10B)-H(10B)	108.9
C(13B)-C(10B)-C(9B)	106.6(9)
C(13B)-C(10B)-H(10B)	108.9
C(13B)-C(10B)-C(11B)	104.2(10)
C(1B)-C(11B)-H(11B)	108.6
C(10B)-C(11B)-C(1B)	110.1(9)
C(10B)-C(11B)-H(11B)	108.6
C(12B)-C(11B)-C(1B)	117.4(9)
C(12B)-C(11B)-C(10B)	103.2(10)
C(12B)-C(11B)-H(11B)	108.6
O(3B)-C(12B)-O(4B)	119.2(10)
O(3B)-C(12B)-C(11B)	127.7(10)
O(4B)-C(12B)-C(11B)	113.0(9)
O(4B)-C(13B)-C(10B)	105.1(9)
O(4B)-C(13B)-H(13B)	111.6
O(4B)-C(13B)-C(14B)	109.9(11)
C(10B)-C(13B)-H(13B)	111.6
C(14B)-C(13B)-C(10B)	106.6(10)
C(14B)-C(13B)-H(13B)	111.6
C(13B)-C(14B)-H(14C)	110.3
C(13B)-C(14B)-H(14D)	110.3
C(13B)-C(14B)-C(15B)	107.0(11)

***Table S32** Cont'd*

H(14C)-C(14B)-H(14D)	108.6
C(15B)-C(14B)-H(14C)	110.3
C(15B)-C(14B)-H(14D)	110.3
O(5B)-C(15B)-C(9B)	106.4(8)
O(5B)-C(15B)-C(14B)	111.3(9)
O(5B)-C(15B)-C(16B)	109.8(8)
C(14B)-C(15B)-C(9B)	104.0(9)
C(16B)-C(15B)-C(9B)	112.2(9)
C(16B)-C(15B)-C(14B)	112.8(9)
C(15B)-C(16B)-H(16D)	109.5
C(15B)-C(16B)-H(16E)	109.5
C(15B)-C(16B)-H(16F)	109.5
H(16D)-C(16B)-H(16E)	109.5
H(16D)-C(16B)-H(16F)	109.5
H(16E)-C(16B)-H(16F)	109.5
H(6E)-O(6)-H(6F)	111.1
Cl(3)#1-Cl(2)-C(17)	28.3(8)
Cl(2)#1-Cl(3)-Cl(4)#1	125.8(10)
Cl(2)#1-Cl(3)-C(17)	176.6(7)
C(17)-Cl(3)-Cl(4)#1	57.4(6)
Cl(2)-C(17)-Cl(4)#1	170.4(6)
Cl(2)-C(17)-H(17)	109.8
Cl(3)-C(17)-Cl(2)	107.2
Cl(3)#1-C(17)-Cl(2)	26.9(11)
Cl(3)#1-C(17)-Cl(3)	86.6(10)
Cl(3)#1-C(17)-Cl(4)#1	146.3(17)
Cl(3)#1-C(17)-Cl(4)	103.7(6)
Cl(3)-C(17)-Cl(4)#1	73.5(5)
Cl(3)-C(17)-Cl(4)	109.3
Cl(3)#1-C(17)-H(17)	134.5
Cl(3)-C(17)-H(17)	109.0
Cl(4)-C(17)-Cl(2)	111.4
Cl(4)-C(17)-Cl(4)#1	60.1(6)
Cl(4)#1-C(17)-H(17)	78.5

Table S32 *Cont'd*

Cl(4)-C(17)-H(17)	110.1

Symmetry transformations used to generate equivalent atoms:

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

Table S33 *Anisotropic Displacement Parameters (Å^{2}x10^3) for Cycloheptane* ***72****. The Anisotropic Displacement Factor Exponent Takes the Form: -2p^2[h^{2}a*^{2}U^{11} + ... + 2hka*b*U^{12}].*

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	36(1)	26(1)	42(1)	-7(1)	-7(1)	4(1)
O(1)	21(3)	22(3)	31(3)	-2(3)	-3(3)	3(2)
O(2)	21(3)	42(4)	22(3)	2(3)	-10(2)	-9(3)
O(3)	24(3)	28(3)	33(4)	-11(3)	1(3)	6(3)
O(4)	24(3)	20(3)	32(3)	-2(3)	2(3)	3(3)
O(5)	28(3)	32(4)	22(3)	-4(3)	10(3)	-6(3)
C(1)	22(4)	22(4)	23(4)	2(4)	3(3)	1(4)
C(2)	27(5)	30(5)	36(5)	11(4)	8(4)	3(4)
C(3)	30(5)	38(6)	47(6)	20(5)	5(4)	4(4)
C(4)	41(6)	24(5)	56(7)	10(5)	-2(5)	-5(4)
C(5)	25(5)	28(5)	36(5)	3(4)	-9(4)	-1(4)
C(6)	32(5)	26(5)	34(5)	-2(4)	-16(4)	2(4)
C(7)	27(4)	15(4)	19(4)	-5(3)	-4(3)	-2(4)
C(8)	24(5)	35(5)	17(4)	0(4)	1(3)	-2(4)
C(9)	18(4)	31(5)	14(4)	2(4)	0(3)	1(4)
C(10)	28(4)	14(4)	14(4)	1(3)	-1(3)	4(3)
C(11)	20(4)	24(4)	16(4)	-7(3)	2(3)	-1(3)
C(12)	23(4)	28(5)	18(4)	-12(4)	-4(3)	1(4)
C(13)	21(4)	21(4)	18(4)	-8(3)	1(3)	0(3)
C(14)	26(4)	21(4)	24(5)	0(4)	-2(4)	1(3)
C(15)	22(4)	32(5)	15(4)	1(4)	3(3)	-1(4)
C(16)	37(5)	42(6)	30(5)	12(5)	-6(4)	-1(5)
Cl(1B)	45(2)	40(2)	77(2)	16(2)	14(1)	11(1)
O(1B)	44(4)	32(4)	31(4)	9(3)	9(3)	-5(3)
O(2B)	65(5)	26(4)	34(4)	-2(3)	13(4)	-15(3)
O(3B)	27(3)	37(4)	27(3)	5(3)	-3(3)	-5(3)
O(4B)	20(3)	52(5)	55(5)	28(4)	-6(3)	-6(3)

Table S33 *Cont'd*

O(5B)	35(4)	26(4)	37(4)	0(3)	-9(3)	-1(3)
C(1B)	58(7)	38(6)	29(5)	-10(5)	4(5)	-19(5)
C(2B)	122(13)	46(7)	27(6)	-11(6)	20(7)	-34(8)
C(3B)	129(14)	37(7)	32(6)	-17(5)	28(8)	-16(8)
C(4B)	97(11)	37(7)	59(8)	7(6)	39(8)	10(7)
C(5B)	50(6)	35(6)	42(6)	5(5)	8(5)	1(5)
C(6B)	50(6)	19(5)	28(5)	2(4)	3(4)	-6(4)
C(7B)	42(5)	32(6)	17(4)	-6(4)	7(4)	-12(4)
C(8B)	50(6)	32(5)	12(4)	2(4)	2(4)	-15(5)
C(9B)	50(6)	45(7)	23(5)	-2(5)	-2(4)	-32(5)
C(10B)	43(6)	75(9)	19(5)	4(5)	-8(4)	-38(6)
C(11B)	45(6)	59(8)	23(5)	2(5)	5(4)	-29(6)
C(12B)	29(5)	47(7)	31(5)	14(4)	-7(4)	-13(4)
C(13B)	34(6)	79(10)	50(7)	32(7)	-12(5)	-24(6)
C(14B)	30(6)	75(9)	46(7)	27(6)	-10(5)	-20(6)
C(15B)	36(5)	43(6)	25(5)	13(4)	-4(4)	-14(5)
C(16B)	53(7)	59(8)	20(5)	5(5)	6(4)	-22(6)
O(6)	39(4)	37(4)	49(5)	-11(4)	14(3)	-6(3)
Cl(2)	78(8)	64(7)	162(16)	5(8)	34(9)	31(6)
Cl(3)	74(10)	310(40)	120(15)	28(19)	16(10)	-12(15)
Cl(4)	100(10)	200(20)	148(15)	93(14)	27(10)	74(12)

Table S34 *Hydrogen Coordinates (x10^4) and Isotropic Displacement Parameters (Å^{2}x10^3) for Cycloheptane **468**.*

	x	y	z	U(eq)
H(5)	6187	4747	7314	40
H(2A)	5756	2532	15049	37
H(2B)	5462	2991	13313	37
H(3A)	5316	1380	14197	46
H(3B)	5307	1603	11821	46
H(4A)	5916	646	14219	49
H(4B)	5667	266	12218	49
H(6A)	6096	1485	8433	38
H(6B)	5656	1381	9136	38
H(7)	6145	2937	9406	25
H(9)	5321	4391	10601	25
H(10)	5717	4553	13399	23
H(11)	6226	3680	14452	24
H(13)	6152	5671	12926	24
H(14A)	5710	6117	10229	29
H(14B)	6101	5999	9056	29
H(16A)	5464	5588	6130	56
H(16B)	5182	5525	7941	56
H(16C)	5244	4640	6555	56
H(5B)	7454	5921	11262	49
H(2C)	7028	8401	17168	77
H(2D)	6719	8068	18709	77
H(3C)	6568	9239	15249	78
H(3D)	6451	9426	17506	78
H(4D)	5906	8475	17082	75
H(4C)	5896	9019	14961	75
H(6C)	6347	8427	12557	39
H(6D)	6213	7408	11798	39

Table S34 *Cont'd*

H(7B)	6744	6755	13237	36
H(9B)	7653	7965	14989	48
H(10B)	7542	7158	17739	55
H(11B)	6981	6547	18479	51
H(13B)	7768	5712	17474	66
H(14C)	7903	5483	13754	61
H(14D)	8138	6279	15048	61
H(16D)	8113	6870	11152	66
H(16E)	8143	7671	12826	66
H(16F)	7818	7732	10933	66
H(6E)	7684	4303	10257	62
H(6F)	7299	4281	11315	62
H(17)	4712	-1315	8203	155

Table S35 *Torsion Angles [°] for Cycloheptane* ***72****.*

Cl(1)-C(5)-C(6)-C(7)	-135.7(7)
O(1)-C(1)-C(2)-C(3)	-56.0(10)
O(1)-C(1)-C(7)-C(6)	36.0(9)
O(1)-C(1)-C(7)-C(8)	167.4(7)
O(1)-C(1)-C(11)-C(10)	172.7(7)
O(1)-C(1)-C(11)-C(12)	55.9(10)
O(1)-C(5)-C(6)-C(7)	-20.7(10)
O(2)-C(8)-C(9)-C(10)	159.3(8)
O(2)-C(8)-C(9)-C(15)	-78.9(10)
O(4)-C(13)-C(14)-C(15)	81.2(8)
C(1)-O(1)-C(5)-Cl(1)	162.9(6)
C(1)-O(1)-C(5)-C(4)	-79.5(8)
C(1)-O(1)-C(5)-C(6)	44.0(9)
C(1)-C(2)-C(3)-C(4)	41.8(12)
C(1)-C(7)-C(8)-O(2)	-131.9(9)
C(1)-C(7)-C(8)-C(9)	50.8(10)
C(1)-C(11)-C(12)-O(3)	-49.2(12)
C(1)-C(11)-C(12)-O(4)	133.0(8)
C(2)-C(1)-C(7)-C(6)	-80.7(10)
C(2)-C(1)-C(7)-C(8)	50.8(10)
C(2)-C(1)-C(11)-C(10)	-67.8(8)
C(2)-C(1)-C(11)-C(12)	175.4(8)
C(2)-C(3)-C(4)-C(5)	-45.3(12)
C(3)-C(4)-C(5)-Cl(1)	-179.1(8)
C(3)-C(4)-C(5)-O(1)	65.8(11)
C(3)-C(4)-C(5)-C(6)	-52.5(12)
C(4)-C(5)-C(6)-C(7)	98.7(10)
C(5)-O(1)-C(1)-C(2)	72.7(8)
C(5)-O(1)-C(1)-C(7)	-49.1(8)
C(5)-O(1)-C(1)-C(11)	-168.2(7)
C(5)-C(6)-C(7)-C(1)	-9.4(9)
C(5)-C(6)-C(7)-C(8)	-133.5(8)
C(6)-C(7)-C(8)-O(2)	-9.8(14)

Table S35 *Cont'd*

C(6)-C(7)-C(8)-C(9)	172.9(8)
C(7)-C(1)-C(2)-C(3)	57.1(11)
C(7)-C(1)-C(11)-C(10)	58.6(9)
C(7)-C(1)-C(11)-C(12)	-58.2(10)
C(7)-C(8)-C(9)-C(10)	-23.3(11)
C(7)-C(8)-C(9)-C(15)	98.5(8)
C(8)-C(9)-C(10)-C(11)	13.5(11)
C(8)-C(9)-C(10)-C(13)	130.2(8)
C(8)-C(9)-C(15)-O(5)	-36.7(9)
C(8)-C(9)-C(15)-C(14)	-155.2(7)
C(8)-C(9)-C(15)-C(16)	82.1(9)
C(9)-C(10)-C(11)-C(1)	-29.8(10)
C(9)-C(10)-C(11)-C(12)	96.0(8)
C(9)-C(10)-C(13)-O(4)	-102.0(7)
C(9)-C(10)-C(13)-C(14)	15.5(8)
C(10)-C(9)-C(15)-O(5)	93.0(7)
C(10)-C(9)-C(15)-C(14)	-25.6(9)
C(10)-C(9)-C(15)-C(16)	-148.3(8)
C(10)-C(11)-C(12)-O(3)	-169.4(8)
C(10)-C(11)-C(12)-O(4)	12.8(9)
C(10)-C(13)-C(14)-C(15)	-32.4(9)
C(11)-C(1)-C(2)-C(3)	-179.4(7)
C(11)-C(1)-C(7)-C(6)	157.5(7)
C(11)-C(1)-C(7)-C(8)	-71.0(9)
C(11)-C(10)-C(13)-O(4)	23.8(8)
C(11)-C(10)-C(13)-C(14)	141.3(7)
C(12)-O(4)-C(13)-C(10)	-16.8(8)
C(12)-O(4)-C(13)-C(14)	-130.7(7)
C(13)-O(4)-C(12)-O(3)	-175.7(7)
C(13)-O(4)-C(12)-C(11)	2.4(9)
C(13)-C(10)-C(11)-C(1)	-147.6(7)
C(13)-C(10)-C(11)-C(12)	-21.9(8)
C(13)-C(14)-C(15)-O(5)	-78.7(9)
C(13)-C(14)-C(15)-C(9)	35.7(9)

***Table S35** Cont'd*

C(13)-C(14)-C(15)-C(16)	156.8(7)
C(15)-C(9)-C(10)-C(11)	-110.8(8)
C(15)-C(9)-C(10)-C(13)	5.9(8)
Cl(1B)-C(5B)-C(6B)-C(7B)	-135.5(7)
O(1B)-C(1B)-C(2B)-C(3B)	-55.2(13)
O(1B)-C(1B)-C(7B)-C(6B)	37.4(10)
O(1B)-C(1B)-C(7B)-C(8B)	169.4(8)
O(1B)-C(1B)-C(11B)-C(10B)	168.1(9)
O(1B)-C(1B)-C(11B)-C(12B)	50.5(12)
O(1B)-C(5B)-C(6B)-C(7B)	-19.1(10)
O(2B)-C(8B)-C(9B)-C(10B)	155.9(10)
O(2B)-C(8B)-C(9B)-C(15B)	-83.8(11)
O(4B)-C(13B)-C(14B)-C(15B)	83.0(13)
C(1B)-O(1B)-C(5B)-Cl(1B)	165.3(7)
C(1B)-O(1B)-C(5B)-C(4B)	-76.3(11)
C(1B)-O(1B)-C(5B)-C(6B)	44.3(10)
C(1B)-C(2B)-C(3B)-C(4B)	39.5(14)
C(1B)-C(7B)-C(8B)-O(2B)	-126.1(11)
C(1B)-C(7B)-C(8B)-C(9B)	52.1(11)
C(1B)-C(11B)-C(12B)-O(3B)	-48.0(15)
C(1B)-C(11B)-C(12B)-O(4B)	129.5(9)
C(2B)-C(1B)-C(7B)-C(6B)	-80.8(13)
C(2B)-C(1B)-C(7B)-C(8B)	51.3(15)
C(2B)-C(1B)-C(11B)-C(10B)	-68.5(12)
C(2B)-C(1B)-C(11B)-C(12B)	173.9(9)
C(2B)-C(3B)-C(4B)-C(5B)	-42.0(14)
C(3B)-C(4B)-C(5B)-Cl(1B)	179.0(9)
C(3B)-C(4B)-C(5B)-O(1B)	62.0(12)
C(3B)-C(4B)-C(5B)-C(6B)	-54.5(14)
C(4B)-C(5B)-C(6B)-C(7B)	100.3(11)
C(5B)-O(1B)-C(1B)-C(2B)	71.4(11)
C(5B)-O(1B)-C(1B)-C(7B)	-50.0(10)
C(5B)-O(1B)-C(1B)-C(11B)	-165.8(9)
C(5B)-C(6B)-C(7B)-C(1B)	-11.2(10)

***Table S35** Cont'd*

C(5B)-C(6B)-C(7B)-C(8B)	-134.6(9)
C(6B)-C(7B)-C(8B)-O(2B)	-5.0(14)
C(6B)-C(7B)-C(8B)-C(9B)	173.2(9)
C(7B)-C(1B)-C(2B)-C(3B)	57.0(15)
C(7B)-C(1B)-C(11B)-C(10B)	57.7(11)
C(7B)-C(1B)-C(11B)-C(12B)	-59.9(11)
C(7B)-C(8B)-C(9B)-C(10B)	-22.3(13)
C(7B)-C(8B)-C(9B)-C(15B)	98.0(9)
C(8B)-C(9B)-C(10B)-C(11B)	10.3(16)
C(8B)-C(9B)-C(10B)-C(13B)	127.5(10)
C(8B)-C(9B)-C(15B)-O(5B)	-33.4(10)
C(8B)-C(9B)-C(15B)-C(14B)	-151.0(8)
C(8B)-C(9B)-C(15B)-C(16B)	86.7(10)
C(9B)-C(10B)-C(11B)-C(1B)	-27.7(14)
C(9B)-C(10B)-C(11B)-C(12B)	98.3(12)
C(9B)-C(10B)-C(13B)-O(4B)	-101.6(9)
C(9B)-C(10B)-C(13B)-C(14B)	15.1(11)
C(10B)-C(9B)-C(15B)-O(5B)	94.9(9)
C(10B)-C(9B)-C(15B)-C(14B)	-22.7(10)
C(10B)-C(9B)-C(15B)-C(16B)	-145.0(9)
C(10B)-C(11B)-C(12B)-O(3B)	-169.2(10)
C(10B)-C(11B)-C(12B)-O(4B)	8.2(11)
C(10B)-C(13B)-C(14B)-C(15B)	-30.4(13)
C(11B)-C(1B)-C(2B)-C(3B)	179.8(10)
C(11B)-C(1B)-C(7B)-C(6B)	156.3(8)
C(11B)-C(1B)-C(7B)-C(8B)	-71.6(10)
C(11B)-C(10B)-C(13B)-O(4B)	25.0(11)
C(11B)-C(10B)-C(13B)-C(14B)	141.7(9)
C(12B)-O(4B)-C(13B)-C(10B)	-20.7(11)
C(12B)-O(4B)-C(13B)-C(14B)	-135.1(11)
C(13B)-O(4B)-C(12B)-O(3B)	-174.5(9)
C(13B)-O(4B)-C(12B)-C(11B)	7.8(11)
C(13B)-C(10B)-C(11B)-C(1B)	-146.2(9)
C(13B)-C(10B)-C(11B)-C(12B)	-20.1(11)

Table S35 *Cont'd*

C(13B)-C(14B)-C(15B)-O(5B)	-81.1(12)
C(13B)-C(14B)-C(15B)-C(9B)	33.1(12)
C(13B)-C(14B)-C(15B)-C(16B)	154.9(10)
C(15B)-C(9B)-C(10B)-C(11B)	-112.2(12)
C(15B)-C(9B)-C(10B)-C(13B)	5.0(10)
Cl(3)#1-Cl(2)-C(17)-Cl(3)	41.5(13)
Cl(3)#1-Cl(2)-C(17)-Cl(4)	-78.0(13)
Cl(4)#1-Cl(3)-C(17)-Cl(2)	-170.0(7)
Cl(4)#1-Cl(3)-C(17)-Cl(3)#1	-152.5(14)
Cl(4)#1-Cl(3)-C(17)-Cl(4)	-49.2(7)

Symmetry transformations used to generate equivalent atoms:

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

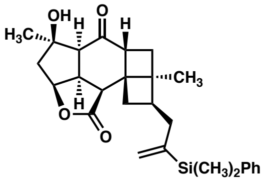
Table S36 *Hydrogen Bonds for Cycloheptane* ***72*** *[Å and °].*

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(5)-H(5)...O(3B)#2	0.84	1.99	2.772(9)	154.9
O(5B)-H(5B)...O(6)	0.84	1.94	2.749(10)	160.2
O(6)-H(6E)...O(2B)#3	0.87	2.21	2.886(10)	134.6
O(6)-H(6F)...O(3)	1.00	1.91	2.858(9)	157.8

Symmetry transformations used to generate equivalent atoms:

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

X-RAY CRYSTAL STRUCTURE ANALYSIS OF CYCLOBUTANE *83*



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Contents

Figure S8 *X-Ray crystal structure of cyclobutane* **83.**

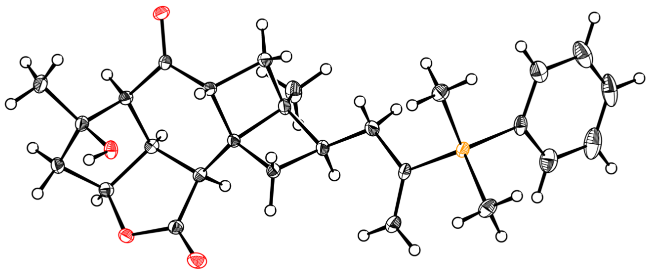


Table S37 *Experimental details for X-ray structure determinationof cyclobutane* **83.**

Refinement Details

Two crystals were mounted on polyimide MiTeGen loops with STP Oil Treatment and placed under nitrogen streams. Low temperature (100K) X-ray data were collected with both a Bruker AXS D8 KAPPA diffractometer diffractometer running at 50 kV and 30 mA (Mo K_α = 0.71073 Å; PHOTON 100 CMOS detector with TRIUMPH graphite monochromator) (d20010) and a Bruker AXS D8 VENTURE KAPPA diffractometer running at 50 kV and 1mA (Cu K_α = 1.54178 Å; PHOTON II CPAD detector and Helios focusing multilayer mirror optics). All diffractometer manipulations, including data collection, integration, and scaling were carried out using the Bruker APEX3 software. An absorption correction was applied using SADABS. The space group was determined and the structure solved by intrinsic phasing using XT. Refinement was full-matrix least squares on F^2 using XL. All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and the coordinates refined. The isotropic displacement parameters of all hydrogen atoms were fixed at 1.2 times the U_{eq} value of the bonded atom.

Special Refinement Details

Compound **83** crystallizes in the monoclinic space group $P2_1$ (# 4) with one molecule in the asymmetric unit. Both crystals were composed of the same enantiomer. The structures are virtually identical with a barely noticeable difference in the position of the H atom of the OH group. The Mo dataset has a marginally better C-C bond precision of 0.0024 Å vs. 0.0026 Å for the Cu dataset.

Table S38 *Crystal Data and Structure Refinement for Cyclobutane* **83.**

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	$-10 \le h \le 10$, $-15 \le k \le 14$, $-25 \le l \le 25$	
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 S39 *Atomic coordinates (x 10^5) and equivalent isotropic displacement parameters (Å^2 10^2) for cyclobutane* ***83***. *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)

Table S39 *Cont'd*

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 S40 *Bond Lengths [Å] and angles [°] for Cyclobutane* **83.**

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

***Table S40** Cont'd*

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

***Table S40** Cont'd*

***Table S40** Cont'd*

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

***Table S40** Cont'd*

Table S40 *Cont'd*

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)

Table S40 *Cont'd*

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)

Table S40 *Cont'd*

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)

Table S40 *Cont'd*

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 S41 *Anisotropic displacement parameters (Å^{2}x 10^4) for cyclobutane **83**. 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)

Table S41 *Cont'd*

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 S42 *Hydrogen coordinates (x 10^2) and isotropic displacement parameters (Å^2 x 10^2) for cyclobutane **83**.*

	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

Table S42 *Cont'd*

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 S43 *Torsion angles [°] for cyclobutane* ***83****.*

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)

Table S43 *Cont'd*

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)

Table S43 *Cont'd*

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:

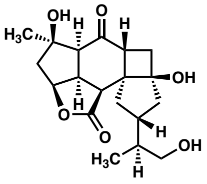
Table S44 *Hydrogen bonds for cyclobutane* ***83*** *[Å and °].*

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(13)-H(13)...O(2)	1.00	2.49	3.079(11)	116.9
C(15)-H(15)...O(3)#1	1.00	2.50	3.246(11)	130.8
O(2)-H(2A)...O(1)#2	0.83(3)	2.16(3)	2.996(10)	178(15)
C(17)-H(17A)...O(1)#2	0.99	2.58	3.430(11)	143.8
C(19)-H(19)...O(3)#1	1.00	2.52	3.267(11)	131.5

Symmetry transformations used to generate equivalent atoms:

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

X-RAY CRYSTAL STRUCTURE ANALYSIS OF CYCLOBUTANOL 90



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Contents

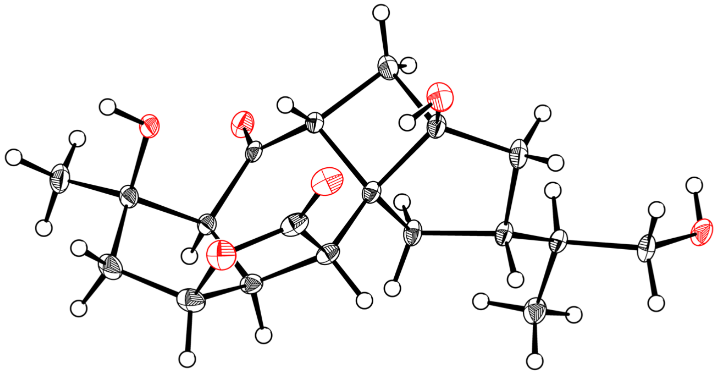


Table S45. *Experimental details for X-Ray structure determination of cyclobutanol* ***90****.*

Refinement Details

A crystal was mounted on a polyimide MiTeGen loop with STP Oil Treatment and placed under a nitrogen stream. Low temperature (100K) X-ray data were collected with a Bruker AXS KAPPA APEX II diffractometer diffractometer running at 50 kV and 30 mA (Mo K_α = 0.71073 Å; PHOTON 100 CMOS detector with TRIUMPH graphite monochromator). All diffractometer manipulations, including data collection, integration, and scaling were carried out using the Bruker APEX3 software. An absorption correction was applied using SADABS. The space group was determined and the structure solved by intrinsic phasing using XT. Refinement was full-matrix least squares on F^2 using XL. All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and the coordinates refined. The isotropic displacement parameters of all hydrogen atoms were fixed at 1.2 times the U_{eq} value of the bonded atom.

Special Refinement Details

Compound **90** crystallizes in the orthorhombic space group $P2_12_12_1$ (#19) with one molecule in the asymmetric unit.

Table S46 *Crystal data and structure refinement for cyclobutanol* ***90.***

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 S47 *Atomic coordinates (x 10^5) and equivalent isotropic displacement parameters ($Å^2$ x 10^4)for cyclobutanol* ***90****. 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 S48 *Bond lengths [Å] and angles [°] for cyclobutanol* ***90***.

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)

Table S48 *Cont'd*

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)

Table S48 *Cont'd*

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)

Table S48 *Cont'd*

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

Table S48 *Cont'd*

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 S49 *Anisotropic displacement parameters ($Å^2$x 10^4) for cyclobutanol* ***90****. 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 S50 *Hydrogen coordinates (x 10 ^{4}) and isotropic displacement parameters (Å ^{2}x 10^{3}) for cyclobutanol* ***90****.*

	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 S51 *Torsion angles [°] for cyclobutanol* ***90***.

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)

Table S51 *Cont'd*

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)

Table S51 *Cont'd*

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:

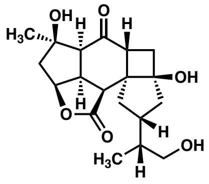
Table S52 *Hydrogen bonds for cyclobutanol **90** [Å and °].*

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 ANALYSIS OF CYCLOBUTANOL *EPI-90*



epi-90

Contents

Figure S10 *X-ray Crystal Structure for Compound* ***epi-90***

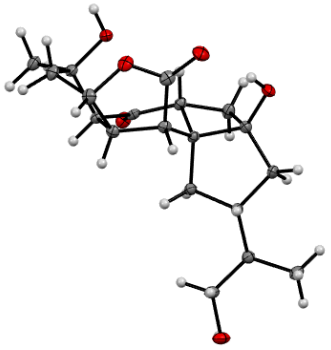


Table S53 *Experimental Details for X-Ray Structure Determination of Cyclobutanol **epi-90**.*

Refinement Details

Low-temperature diffraction data (ϕ-and ω-scans) were collected on a Bruker AXS D8 VENTURE KAPPA diffractometer coupled to a PHOTON II CPAD detector with Cu K_α radiation (λ = 1.54178 Å) from an IμS micro-source for the structure of compound ***epi-90***. The structure was solved by direct methods using SHELXS and refined against F^2 on all data by full-matrix least squares with SHELXL-2017 using established refinement techniques. All non-hydrogen atoms were refined anisotropically. Unless otherwise noted, all hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the *U* value of the atoms they are linked to (1.5 times for methyl groups).

Special Refinement Details

Compound ***epi*-90** crystallizes in the orthorhombic space group $P2_12_12_1$ with one molecule in the asymmetric unit along with three molecules of water. The coordinates for the hydrogen atoms bound to O3, O4, O6, O1W, O2W and O3W were located in the difference Fourier synthesis and refined semi-freely with the help of a restraint on the O-H distance (0.84(4) Å).

Table S54 *Crystal data and structure refinement for cyclobutanol* ***epi-90****.*

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.Å^{-3}	

Table S55 *Atomic coordinates (x 10 ^{4}) and equivalent isotropic displacement parameters (Å ^{2}x 10 ^{2}) for* ***epi-90****. 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)

Table S55 *Cont'd*

O(2W)	6663(2)	3854(1)	1302(1)	21(1)
O(3W)	3494(2)	756(1)	4427(1)	36(1)

Table S56 *Bond lengths [Å] and angles [°] for* ***epi-90****.*

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)

Table S56 *Cont'd*

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)

Table S56 *Cont'd*

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

Table S56 *Cont'd*

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)

Table S56 *Cont'd*

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

Table S56 *Cont'd*

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 S57 *Anisotropic displacement parameters ($Å^2 x 10^3$) for* ***epi-90****. 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 S58 *Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for* ***epi-90.***

	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

Table S58 *Cont'd*

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 S59 *Torsion angles [°] for* ***epi-90.***

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)

Table S59 *Cont'd*

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)

***Table S59** Cont'd*

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 S60 *Hydrogen bonds for **epi-90** [Å and °].*

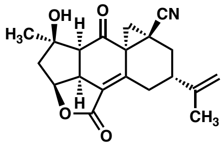
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(3)-H(3O)...O(3W)	0.80(2)	1.95(2)	2.755(2)	175(3)
O(4)-H(4O)...O(2)	0.82(2)	1.93(2)	2.737(2)	168(3)
C(9)-H(9)...O(6)	1.00	2.37	2.976(2)	117.8
O(6)-H(6O)...O(2W)#1	0.85(2)	1.95(2)	2.790(2)	175(3)
O(1W)-H(1W1)...O(3)	0.85(2)	1.91(2)	2.758(2)	178(3)
O(1W)-H(1W2)...O(4)#2	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 ANALYSIS OF NITRILE 94



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Contents

Figure S11 *X-Ray Crystal Structure of Nitrile **94**.*

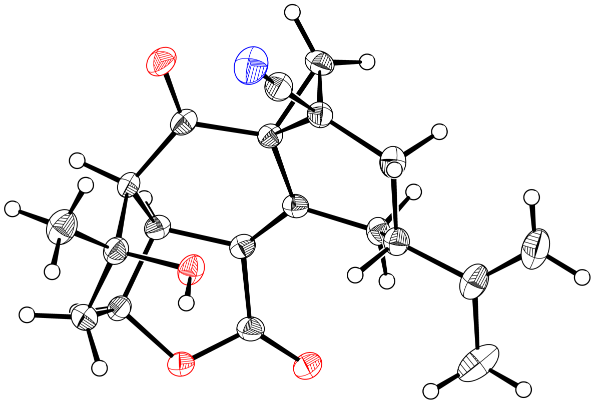


Table S61 *Experimental Details for X-Ray Structure Determination of Nitrile* ***94.***

Refinement Details

A crystal was mounted on a polyimide MiTeGen loop with STP Oil Treatment and placed under a nitrogen stream. Low temperature (100K) X-ray data were collected with a Bruker AXS D8 VENTURE KAPPA diffractometer running at 50 kV and 1mA (Cu K_α = 1.54178 Å; PHOTON II CPAD detector and Helios focusing multilayer mirror optics). All diffractometer manipulations, including data collection, integration, and scaling were carried out using the Bruker APEX3 software. An absorption correction was applied using SADABS. The space group was determined and the structure solved by intrinsic phasing using XT. Refinement was full-matrix least squares on F^2 using XL. All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed at 1.2 times (1.5 times for methyl groups) the U_{eq} value of the bonded atom.

Special Refinement Details

Compound **94** crystallizes in the monoclinic space group $P2_1$ (#4) with one molecule in the asymmetric unit. The final difference map exhibits four small positive excursions near the isopropenyl group. These represent some disorder or impurity and were not interpreted.

Table S62 *Crystal data and structure refinement for nitrile* ***94****.*

Empirical formula	C20 H21 N O4	
Formula weight	339.38	
Temperature	100 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 1 21 1 (# 4)	
Unit cell dimensions	a = 10.105(2) Å	a= 90°
	b = 8.9547(18) Å	b= 110.038(10)°
	c = 10.215(2) Å	g = 90°
Volume	868.4(3) Å^3	
Z	2	
Density (calculated)	1.298 g/cm^3	
Absorption coefficient	0.737 mm^{-1}	
F(000)	360	
Crystal size	0.02 x 0.06 x 0.31 mm^3	
Theta range for data collection	4.6 to 79.9°.	
Index ranges	-12 £ h £ 12, -11 £ k £ 11, -11 £ l £ 12	
Reflections collected	15034	
Independent reflections	3650 [R(int) = 0.0537]	
Completeness to theta = 67.679°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.886	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3650 / 1 / 229	
Goodness-of-fit on F^2	1.074	
Final R indices [I>2sigma(I)]	R1 = 0.0415, wR2 = 0.1027	
R indices (all data)	R1 = 0.0446, wR2 = 0.1048	
Absolute structure parameter [Flack]	0.08(10)	
Absolute structure parameter [Hooft]	0.14(10)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.70 and -0.20 e.Å^{-3}	

Table S63 *Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^2) for nitrile **94**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.*

	x	y	z	U(eq)
O(1)	6691(2)	5925(2)	780(2)	32(1)
O(2)	5021(2)	5006(2)	3358(2)	25(1)
O(3)	5217(2)	1146(2)	3785(2)	26(1)
O(4)	7182(2)	1082(2)	5628(2)	29(1)
N(1)	6896(3)	8901(3)	2463(3)	37(1)
C(1)	7848(3)	4993(3)	3049(3)	18(1)
C(2)	6663(3)	5022(3)	1655(3)	20(1)
C(3)	5485(3)	3912(3)	1411(3)	18(1)
C(4)	4315(3)	4410(3)	1997(3)	22(1)
C(5)	3601(3)	2917(3)	2090(3)	26(1)
C(6)	4718(3)	1690(3)	2352(3)	22(1)
C(7)	6000(3)	2412(3)	2115(3)	19(1)
C(8)	7021(3)	2586(3)	3568(3)	18(1)
C(9)	6566(3)	1536(3)	4455(3)	22(1)
C(10)	7881(3)	3752(3)	4033(3)	18(1)
C(11)	8769(3)	3988(3)	5528(3)	20(1)
C(12)	8368(3)	5460(3)	6072(3)	22(1)
C(13)	8759(3)	6762(3)	5310(3)	24(1)
C(14)	8270(3)	6566(3)	3722(3)	21(1)
C(15)	3319(3)	5557(4)	1090(3)	32(1)
C(16)	9050(3)	5567(4)	7640(3)	29(1)
C(17)	8592(5)	4393(4)	8444(4)	44(1)
C(18)	9980(4)	6633(5)	8294(4)	40(1)
C(19)	7478(3)	7838(3)	2970(3)	25(1)
C(20)	9192(3)	5758(3)	3063(3)	24(1)

Table S64 *Bond lengths [Å] and angles [°] for nitrile* ***94***.

O(1)-C(2)	1.213(3)
O(2)-H(2)	0.8400
O(2)-C(4)	1.430(3)
O(3)-C(6)	1.459(3)
O(3)-C(9)	1.345(3)
O(4)-C(9)	1.215(3)
N(1)-C(19)	1.146(4)
C(1)-C(2)	1.514(4)
C(1)-C(10)	1.491(4)
C(1)-C(14)	1.562(4)
C(1)-C(20)	1.517(4)
C(2)-C(3)	1.505(4)
C(3)-H(3)	1.0000
C(3)-C(4)	1.562(4)
C(3)-C(7)	1.528(4)
C(4)-C(5)	1.537(4)
C(4)-C(15)	1.512(4)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(5)-C(6)	1.531(4)
C(6)-H(6)	1.0000
C(6)-C(7)	1.539(4)
C(7)-H(7)	1.0000
C(7)-C(8)	1.498(4)
C(8)-C(9)	1.484(4)
C(8)-C(10)	1.338(4)
C(10)-C(11)	1.497(4)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(11)-C(12)	1.538(4)
C(12)-H(12)	1.0000
C(12)-C(13)	1.527(4)
C(12)-C(16)	1.515(4)

Table S64 *Cont'd*

C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(13)-C(14)	1.535(4)
C(14)-C(19)	1.451(4)
C(14)-C(20)	1.508(4)
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-C(17)	1.502(5)
C(16)-C(18)	1.345(5)
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9500
C(18)-H(18B)	0.9500
C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900
C(4)-O(2)-H(2)	109.5
C(9)-O(3)-C(6)	111.4(2)
C(2)-C(1)-C(14)	114.0(2)
C(2)-C(1)-C(20)	114.7(2)
C(10)-C(1)-C(2)	118.4(2)
C(10)-C(1)-C(14)	115.8(2)
C(10)-C(1)-C(20)	121.1(2)
C(20)-C(1)-C(14)	58.64(17)
O(1)-C(2)-C(1)	119.6(2)
O(1)-C(2)-C(3)	122.4(2)
C(3)-C(2)-C(1)	118.0(2)
C(2)-C(3)-H(3)	108.6
C(2)-C(3)-C(4)	114.1(2)
C(2)-C(3)-C(7)	112.3(2)
C(4)-C(3)-H(3)	108.6
C(7)-C(3)-H(3)	108.6
C(7)-C(3)-C(4)	104.5(2)

Table S64 *Cont'd*

O(2)-C(4)-C(3)	106.7(2)
O(2)-C(4)-C(5)	110.7(2)
O(2)-C(4)-C(15)	110.4(2)
C(5)-C(4)-C(3)	102.0(2)
C(15)-C(4)-C(3)	113.0(2)
C(15)-C(4)-C(5)	113.6(2)
C(4)-C(5)-H(5A)	110.2
C(4)-C(5)-H(5B)	110.2
H(5A)-C(5)-H(5B)	108.5
C(6)-C(5)-C(4)	107.6(2)
C(6)-C(5)-H(5A)	110.2
C(6)-C(5)-H(5B)	110.2
O(3)-C(6)-C(5)	113.3(2)
O(3)-C(6)-H(6)	110.3
O(3)-C(6)-C(7)	106.2(2)
C(5)-C(6)-H(6)	110.3
C(5)-C(6)-C(7)	106.3(2)
C(7)-C(6)-H(6)	110.3
C(3)-C(7)-C(6)	105.9(2)
C(3)-C(7)-H(7)	111.8
C(6)-C(7)-H(7)	111.8
C(8)-C(7)-C(3)	112.5(2)
C(8)-C(7)-C(6)	102.6(2)
C(8)-C(7)-H(7)	111.8
C(9)-C(8)-C(7)	106.7(2)
C(10)-C(8)-C(7)	125.2(2)
C(10)-C(8)-C(9)	125.3(2)
O(3)-C(9)-C(8)	109.0(2)
O(4)-C(9)-O(3)	120.2(2)
O(4)-C(9)-C(8)	130.7(3)
C(1)-C(10)-C(11)	116.8(2)
C(8)-C(10)-C(1)	118.7(2)
C(8)-C(10)-C(11)	124.2(2)
C(10)-C(11)-H(11A)	109.6

Table S64 *Cont'd*

C(10)-C(11)-H(11B)	109.6
C(10)-C(11)-C(12)	110.4(2)
H(11A)-C(11)-H(11B)	108.1
C(12)-C(11)-H(11A)	109.6
C(12)-C(11)-H(11B)	109.6
C(11)-C(12)-H(12)	108.1
C(13)-C(12)-C(11)	108.9(2)
C(13)-C(12)-H(12)	108.1
C(16)-C(12)-C(11)	110.8(2)
C(16)-C(12)-H(12)	108.1
C(16)-C(12)-C(13)	112.8(2)
C(12)-C(13)-H(13A)	108.8
C(12)-C(13)-H(13B)	108.8
C(12)-C(13)-C(14)	113.9(2)
H(13A)-C(13)-H(13B)	107.7
C(14)-C(13)-H(13A)	108.8
C(14)-C(13)-H(13B)	108.8
C(13)-C(14)-C(1)	120.6(2)
C(19)-C(14)-C(1)	117.2(2)
C(19)-C(14)-C(13)	112.9(2)
C(19)-C(14)-C(20)	116.9(2)
C(20)-C(14)-C(1)	59.19(17)
C(20)-C(14)-C(13)	120.1(2)
C(4)-C(15)-H(15A)	109.5
C(4)-C(15)-H(15B)	109.5
C(4)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(17)-C(16)-C(12)	114.9(3)
C(18)-C(16)-C(12)	123.9(3)
C(18)-C(16)-C(17)	121.3(3)
C(16)-C(17)-H(17A)	109.5
C(16)-C(17)-H(17B)	109.5

Table S64 *Cont'd*

C(16)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(16)-C(18)-H(18A)	120.0
C(16)-C(18)-H(18B)	120.0
H(18A)-C(18)-H(18B)	120.0
N(1)-C(19)-C(14)	175.0(3)
C(1)-C(20)-H(20A)	117.5
C(1)-C(20)-H(20B)	117.5
C(14)-C(20)-C(1)	62.17(18)
C(14)-C(20)-H(20A)	117.5
C(14)-C(20)-H(20B)	117.5
H(20A)-C(20)-H(20B)	114.6

Symmetry transformations used to generate equivalent atoms:

Table S65 *Anisotropic displacement parameters ($Å^2$ x 10^3) for nitrile **94**. 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)	42(1)	29(1)	21(1)	6(1)	6(1)	-9(1)
O(2)	25(1)	32(1)	18(1)	-5(1)	8(1)	5(1)
O(3)	27(1)	29(1)	21(1)	5(1)	6(1)	-8(1)
O(4)	30(1)	31(1)	23(1)	11(1)	5(1)	-4(1)
N(1)	47(2)	22(1)	35(2)	6(1)	6(1)	1(1)
C(1)	21(1)	15(1)	18(1)	0(1)	7(1)	-1(1)
C(2)	27(1)	17(1)	17(1)	0(1)	8(1)	1(1)
C(3)	20(1)	20(1)	14(1)	0(1)	4(1)	0(1)
C(4)	21(1)	28(1)	18(1)	-1(1)	6(1)	2(1)
C(5)	21(1)	34(2)	23(1)	0(1)	8(1)	-4(1)
C(6)	26(1)	24(1)	15(1)	1(1)	5(1)	-6(1)
C(7)	24(1)	16(1)	18(1)	-2(1)	9(1)	-1(1)
C(8)	20(1)	16(1)	18(1)	3(1)	7(1)	4(1)
C(9)	24(1)	20(1)	22(1)	1(1)	9(1)	-3(1)
C(10)	16(1)	18(1)	21(1)	2(1)	8(1)	3(1)
C(11)	17(1)	20(1)	21(1)	3(1)	2(1)	3(1)
C(12)	19(1)	22(1)	22(1)	0(1)	6(1)	3(1)
C(13)	25(1)	19(1)	24(1)	-2(1)	4(1)	1(1)
C(14)	22(1)	17(1)	22(1)	1(1)	6(1)	-2(1)
C(15)	30(2)	36(2)	28(2)	3(1)	7(1)	11(1)
C(16)	30(2)	32(2)	22(1)	-1(1)	6(1)	12(1)
C(17)	70(3)	38(2)	27(2)	6(1)	21(2)	11(2)
C(18)	36(2)	52(2)	25(2)	-1(2)	1(1)	8(2)
C(19)	30(2)	19(1)	24(1)	0(1)	7(1)	-4(1)
C(20)	22(1)	22(1)	28(1)	2(1)	10(1)	-4(1)

Table S66 *Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for nitrile* ***94****.*

	x	y	z	U(eq)
H(2)	4424	5339	3687	37
H(3)	5041	3744	385	22
H(5A)	3218	2946	2861	31
H(5B)	2816	2721	1209	31
H(6)	4353	843	1689	27
H(7)	6387	1763	1535	23
H(11A)	9776	4016	5617	25
H(11B)	8632	3145	6096	25
H(12)	7323	5470	5841	26
H(13A)	9795	6886	5670	28
H(13B)	8338	7689	5523	28
H(15A)	2559	5756	1458	48
H(15B)	2919	5175	136	48
H(15C)	3835	6484	1089	48
H(17A)	7567	4274	8052	66
H(17B)	8862	4696	9423	66
H(17C)	9047	3442	8383	66
H(18A)	10359	6653	9283	48
H(18B)	10257	7366	7767	48
H(20A)	10096	5347	3692	28
H(20B)	9223	6149	2168	28

Table S67 *Torsion angles [°] for **94**.*

O(1)-C(2)-C(3)-C(4)	-96.4(3)
O(1)-C(2)-C(3)-C(7)	144.8(3)
O(2)-C(4)-C(5)-C(6)	-83.4(3)
O(3)-C(6)-C(7)-C(3)	-133.3(2)
O(3)-C(6)-C(7)-C(8)	-15.2(3)
C(1)-C(2)-C(3)-C(4)	83.7(3)
C(1)-C(2)-C(3)-C(7)	-35.1(3)
C(1)-C(10)-C(11)-C(12)	53.3(3)
C(2)-C(1)-C(10)-C(8)	11.3(4)
C(2)-C(1)-C(10)-C(11)	-161.9(2)
C(2)-C(1)-C(14)-C(13)	145.6(2)
C(2)-C(1)-C(14)-C(19)	1.3(4)
C(2)-C(1)-C(14)-C(20)	-105.3(3)
C(2)-C(1)-C(20)-C(14)	104.1(2)
C(2)-C(3)-C(4)-O(2)	-44.1(3)
C(2)-C(3)-C(4)-C(5)	-160.3(2)
C(2)-C(3)-C(4)-C(15)	77.4(3)
C(2)-C(3)-C(7)-C(6)	155.2(2)
C(2)-C(3)-C(7)-C(8)	43.9(3)
C(3)-C(4)-C(5)-C(6)	29.8(3)
C(3)-C(7)-C(8)-C(9)	133.3(2)
C(3)-C(7)-C(8)-C(10)	-28.3(4)
C(4)-C(3)-C(7)-C(6)	31.0(3)
C(4)-C(3)-C(7)-C(8)	-80.3(3)
C(4)-C(5)-C(6)-O(3)	104.8(3)
C(4)-C(5)-C(6)-C(7)	-11.4(3)
C(5)-C(6)-C(7)-C(3)	-12.4(3)
C(5)-C(6)-C(7)-C(8)	105.7(2)
C(6)-O(3)-C(9)-O(4)	-174.6(3)
C(6)-O(3)-C(9)-C(8)	8.5(3)
C(6)-C(7)-C(8)-C(9)	20.0(3)
C(6)-C(7)-C(8)-C(10)	-141.7(3)

***Table S67** Cont'd*

C(7)-C(3)-C(4)-O(2)	79.0(3)
C(7)-C(3)-C(4)-C(5)	-37.2(3)
C(7)-C(3)-C(4)-C(15)	-159.6(2)
C(7)-C(8)-C(9)-O(3)	-18.6(3)
C(7)-C(8)-C(9)-O(4)	165.0(3)
C(7)-C(8)-C(10)-C(1)	-0.2(4)
C(7)-C(8)-C(10)-C(11)	172.5(2)
C(8)-C(10)-C(11)-C(12)	-119.5(3)
C(9)-O(3)-C(6)-C(5)	-111.7(3)
C(9)-O(3)-C(6)-C(7)	4.6(3)
C(9)-C(8)-C(10)-C(1)	-158.5(2)
C(9)-C(8)-C(10)-C(11)	14.1(4)
C(10)-C(1)-C(2)-O(1)	-172.3(3)
C(10)-C(1)-C(2)-C(3)	7.6(4)
C(10)-C(1)-C(14)-C(13)	3.1(4)
C(10)-C(1)-C(14)-C(19)	-141.2(2)
C(10)-C(1)-C(14)-C(20)	112.2(3)
C(10)-C(1)-C(20)-C(14)	-103.2(3)
C(10)-C(8)-C(9)-O(3)	143.1(3)
C(10)-C(8)-C(9)-O(4)	-33.3(5)
C(10)-C(11)-C(12)-C(13)	-66.3(3)
C(10)-C(11)-C(12)-C(16)	169.1(2)
C(11)-C(12)-C(13)-C(14)	47.7(3)
C(11)-C(12)-C(16)-C(17)	-63.1(3)
C(11)-C(12)-C(16)-C(18)	118.0(3)
C(12)-C(13)-C(14)-C(1)	-17.6(4)
C(12)-C(13)-C(14)-C(19)	128.1(3)
C(12)-C(13)-C(14)-C(20)	-87.5(3)
C(13)-C(12)-C(16)-C(17)	174.5(3)
C(13)-C(12)-C(16)-C(18)	-4.4(4)
C(13)-C(14)-C(20)-C(1)	109.8(3)
C(14)-C(1)-C(2)-O(1)	46.2(4)
C(14)-C(1)-C(2)-C(3)	-133.9(2)
C(14)-C(1)-C(10)-C(8)	152.1(2)

Table S67 *Cont'd*

C(14)-C(1)-C(10)-C(11)	-21.1(3)
C(15)-C(4)-C(5)-C(6)	151.7(2)
C(16)-C(12)-C(13)-C(14)	171.2(2)
C(19)-C(14)-C(20)-C(1)	-107.1(3)
C(20)-C(1)-C(2)-O(1)	-18.8(4)
C(20)-C(1)-C(2)-C(3)	161.1(2)
C(20)-C(1)-C(10)-C(8)	-140.4(3)
C(20)-C(1)-C(10)-C(11)	46.4(3)
C(20)-C(1)-C(14)-C(13)	-109.1(3)
C(20)-C(1)-C(14)-C(19)	106.7(3)

Symmetry transformations used to generate equivalent atoms:

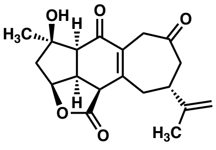
Table S68 *Hydrogen bonds for nitrile* ***94*** *[Å and °].*

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(2)-H(2)...O(3)#1	0.84	2.58	3.178(3)	128.7
O(2)-H(2)...O(4)#1	0.84	2.08	2.923(3)	175.4
C(6)-H(6)...O(1)#2	1.00	2.38	3.100(3)	128.4
C(11)-H(11B)...O(4)	0.99	2.30	3.077(3)	134.1

Symmetry transformations used to generate equivalent atoms:

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

X-RAY CRYSTAL STRUCTURE ANALYSIS OF SCABROLIDE A (1)



Scabrolide A (1)

Contents

Figure S12 *X-ray Crystal Structure for scabrolide A (**1**)*

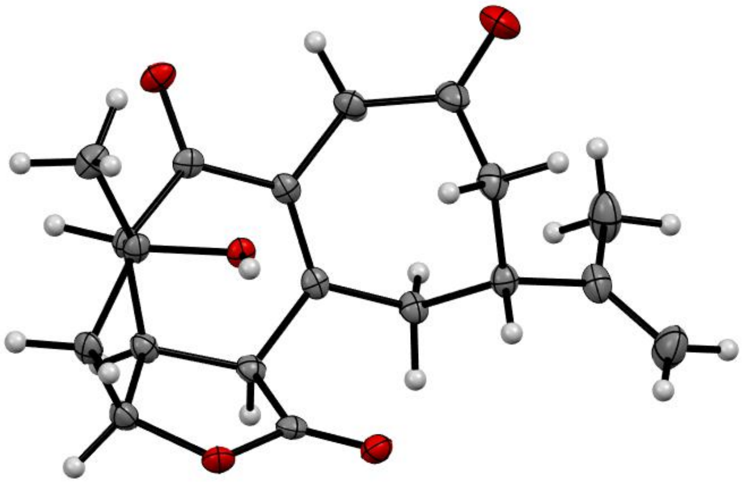


Table S69 *Experimental Details for X-Ray Structure Determination of scabrolide A (**1**).*

Refinement Details

Low-temperature diffraction data (ϕ-and ω-scans) were collected on a Bruker AXS D8 VENTURE KAPPA diffractometer coupled to a PHOTON II CPAD detector with Cu K_α radiation (λ = 1.54178 Å) from an IμS micro-source for the structure of compound **1**. The structure was solved by direct methods using SHELXS and refined against F^2 on all data by full-matrix least squares with SHELXL-2017 using established refinement techniques. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups).

Special Refinement Details

Compound **1** crystallizes in the orthorhombic space group $P2_12_12_1$ with one molecule in the asymmetric unit.

Table S70 *Crystal data and structure refinement for compound* ***1****.*

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 S71 *Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for compound **1**. 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 S72** Bond lengths [Å] and angles [°] for compound **1**.*

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)

Table S72 *Cont'd*

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

Table S72 *Cont'd*

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

***Table S72** Cont'd*

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)

Table S72 *Cont'd*

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 S73 *Anisotropic displacement parameters* ($Å^2 \times 10^3$) *for compound* ***1****. The anisotropic displacement factor exponent takes the form:* $-2\pi^2[\, h^2 a^{*2} U^{11} + \ldots + 2\, h\, k\, a^*\, b^*\, U^{12}]$

	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 S74 *Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for compound **1**.*

	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 S75 *Torsion angles [°] for compound **1**.*

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)

Table S75 *Cont'd*

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 S76 *Hydrogen bonds for compound* ***1*** *[Å 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