Progress Toward the Enantioselective Synthesis of Curcusones A–D via a Divinylcyclopropane Rearrangement Strategy

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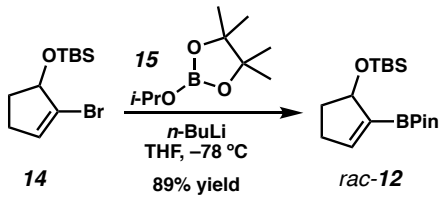
1. Experimental Section

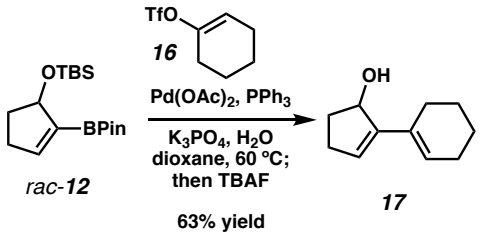
Materials and Methods

Unless stated otherwise, reactions were performed under an argon or nitrogen atmosphere using dry, deoxygenated solvents (distilled or passed over a column of activated alumina).[1] Et_3N, *i*-Pr_2NEt, *i*-Pr_2NH, pyridine, and *i*-PrOH were distilled from calcium hydride immediately prior to use. Commercially obtained reagents were used as received unless otherwise stated. *p*-ABSA,[2] $Cu(TBSal)_2$,[3] and $MoCl_3(THF)_2$[4] were prepared by known methods. Reactions were heated in an oil bath, and the temperatures were controlled by an IKAmag temperature modulator. Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm) and visualized by UV fluorescence quenching, or potassium permanganate, iodine, or anisaldehyde staining. Silia*Flash* P60 Academic Silica gel (particle size 0.040-0.063 mm) was used for flash chromatography. ^1H and ^{13}C NMR spectra were recorded on a Varian Inova 600 (600 MHz and 151 MHz respectively), Varian Inova 500 (at 500 MHz and 126 MHz respectively), Bruker AV III HD spectrometer equipped with a Prodigy liquid nitrogen temperature cryoprobe (400 MHz and 101 MHz, respectively) and are reported relative to $CHCl_3$ (δ 7.26 & 77.16 respectively), C_6H_6 (δ 7.16 & 128.06 respectively), and CH_2Cl_2 (δ 5.32 & 53.84 respectively). Data for ^1H NMR spectra are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). IR spectra were recorded on a Perkin Elmer Paragon 1000 Spectrometer and are reported in frequency of absorption (cm^{-1}). HRMS were acquired 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 (MM) ionization mode. Optical rotations were measured on a Jasco P-2000 polarimeter using a 100 mm path length cell at 589 nm.



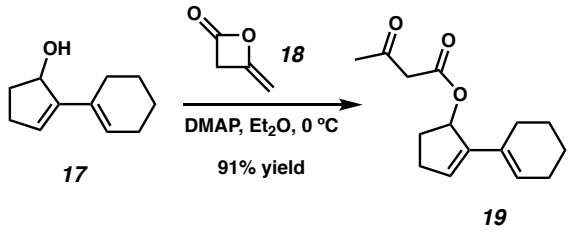
***tert*-Butyldimethyl((2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopent-2-en-1-yl)oxy)silane (*rac*-12)**: To a flame-dried round-bottom flask with a magnetic stir bar were added bromide **14** (440 mg, 1.59 mmol) and THF (6 mL). The flask was cooled to –78 ºC and stirred for 10 min. *n*-BuLi solution (2.1 M in hexanes, 0.95 mL, 2.00 mmol) was added dropwise. The reaction mixture was stirred at –78 ºC for 30 min then isopropyl pinacolyl borate (**15**, 0.40 mL, 1.96 mmol) was added. The reaction mixture was stirred at –78 ºC for 30 min then quenched with HCl solution (2 N in Et_2O, 1.0 mL, 2.00 mmol). Following addition, the reaction mixture was diluted with Et_2O (10 mL) and warmed up to 23 ºC. The reaction mixture was filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (20:1 hexanes, EtOAc) to afford vinylboronate *rac*-**12** as a colorless oil (460 mg, 1.42 mmol, 89% yield); R_f = 0.60 (20:1 hexanes, EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.62 (td, *J* = 2.4, 1.0 Hz, 1H), 5.00 (dddt, *J* = 6.1, 3.9, 2.1, 1.1 Hz, 1H), 2.56 (dddt, *J* = 17.8, 8.9, 4.6, 2.3 Hz, 1H), 2.34–2.20 (m, 1H), 2.20–2.08 (m, 1H), 1.75–1.65 (m, 1H), 1.25 (d, *J* = 1.6 Hz, 12H), 0.89 (s, 9H), 0.11 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.3, 83.1, 80.0, 34.7, 33.0, 26.1, 25.1, 25.0, 18.5, 14.1, –4.6; IR (Neat Film, NaCl) 3040, 2978, 2929, 2856, 2708, 1622, 1472, 1409, 1372, 1318, 1249, 1214, 1146, 1060, 1005, 964, 952, 936, 875, 855 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{17}H_{32}SiO_3B$ $[M+H–H_2]^+$: 323.2214, found 323.2222.



2-(Cyclohex-1-en-1-yl)cyclopent-2-en-1-ol (17): To a flame-dried round-bottom flask equipped with a magnetic stir bar were added boronate *rac*-**12** (2.25 g, 6.94 mmol), triflate **16** (1.71 g, 7.43 mmol), palladium acetate (70 mg, 0.311 mmol), triphenylphosphine (180 mg, 0.686 mmol), and tribasic potassium phosphate (4.43 g, 20.87 mmol). The mixture was evacuated and back filled with argon (x3). The mixture was dissolved in dioxane (35 mL) and water (3.5 mL). The reaction was immersed in a 60 ºC oil bath. After 9 h of stirring, the reaction was cooled to ambient temperature, diluted with EtOAc (10 mL), and quenched with saturated NH_4Cl solution (10 mL). The phases were separated and the aqueous phase was extracted with EtOAc (3 x 10 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to afford a crude mixture of coupled product. The residue was used for the next reaction without further purification.

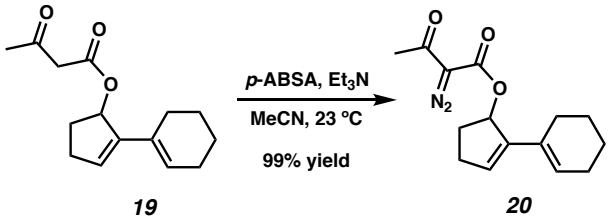
To a round-bottom flask with a magnetic stir bar were added the crude product from the previous step (1.72 g, 6.18 mmol) and THF (21 mL). To this was added TBAF (1.0 M in THF, 5.0 mL, 5.0 mmol), and the resulting solution was stirred for 24 h at 23 ºC. The reaction mixture was quenched by saturated aqueous NH_4Cl (20 mL). The phases were separated, and the aqueous phase was extracted with EtOAc (3 x 20 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (4:1 hexanes:EtOAc) to afford diene allylic alcohol **17** (714 mg, 4.35 mmol, 63% yield over two steps) as a colorless oil; R_f = 0.67 (10:1, hexanes:EtOAc) ^{1}H NMR (500 MHz,

$CDCl_3$) δ 6.05–5.95 (m, 1H), 5.83–5.75 (m, 1H), 5.01 (dt, *J* = 7.2, 1.9 Hz, 1H), 2.65–2.53 (m, 1H), 2.35–2.26 (m, 1H), 2.26–2.10 (m, 3H), 1.87 (ddt, *J* = 13.9, 8.0, 2.4 Hz, 1H), 1.73–1.53 (m, 5H); ^{13}C NMR (126 MHz, $CDCl_3$) δ146.39, 131.82, 127.36, 125.35, 77.16, 76.22, 33.82, 30.48, 26.39, 25.81, 22.81, 22.43; IR (Neat Film, NaCl) 3339, 3045, 2925, 2855, 1435, 1302, 1044, 986, 941, 823 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{11}H_{16}O$ $[M\bullet]^+$: 164.1201, found 164.1170.

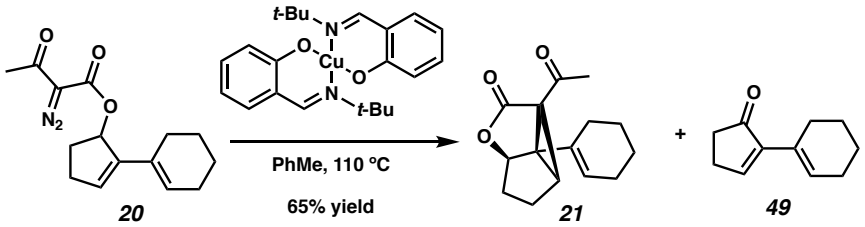


2-(Cyclohex-1-en-1-yl)cyclopent-2-en-1-yl 3-oxobutanoate (19): To a flame-dried round-bottom flask equipped with a magnetic stir bar were added allylic alcohol **17** (60 mg, 0.365 mmol), 4-dimethylaminopyridine (0.2 mg, 0.0016 mmol) and Et_2O (1.5 mL). The flask was cooled to 0 ºC and stirred for 10 min. Diketene (**18**, 0.03 mL, 0.389 mmol) was added dropwise. The reaction mixture was stirred for 15 min at 0 ºC then quenched with ice-cold water (1.5 mL). The mixture was extracted with Et_2O (3 x 3 mL). The combined organic layers were washed by brine (3 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The crude oil was purified by flash column chromatography (4:1 hexanes, EtOAc) to afford β-ketoester **19** (82.7 mg, 0.333 mmol, 91% yield) as a colorless oil; R_f = 0.52 (4:1, hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.04 (dt, *J* = 7.2, 1.8 Hz, 1H), 5.98–5.94 (m, 1H), 5.76–5.72 (m, 1H), 3.43 (s, 2H), 2.61–2.53 (m, 1H), 2.40–2.24 (m, 2H), 2.22 (s, 3H), 2.21–2.16 (m, 2H), 2.16–2.07 (m, 2H), 1.96–1.88 (m, 2H), 1.71–1.51 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.7, 167.3, 142.2, 131.1, 130.7, 125.9, 79.9, 50.7, 31.6, 30.8, 30.2, 26.6, 25.8, 22.7, 22.3; IR (Neat Film, NaCl) 2926, 2853, 1718, 1643, 1412, 1358,

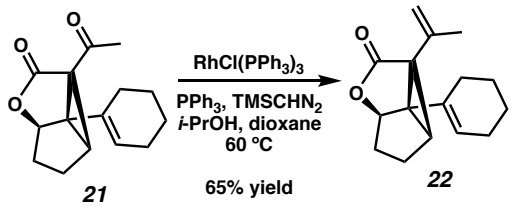
1310, 1243, 1147, 1027, 977, 936, 896, 800 cm^{-1}; HRMS (MM) *m/z* calc'd for $C_{15}H_{19}O_3$ $[M-H]^-$: 247.1340, found 247.1362.



2-(Cyclohex-1-en-1-yl)cyclopent-2-en-1-yl 2-diazo-3-oxobutanoate (20): To a round-bottom flask equipped with a magnetic stir bar were added β-ketoester **19** (80 mg, 0.322 mmol), MeCN (3 mL), and *p*-ABSA (130 mg, 0.541 mmol). Et_3N (0.2 mL, 1.43 mmol) was added dropwise. The reaction mixture was stirred for 2 h at 23 ºC. The reaction mixture was filtered through a silica gel plug (2:1 pentane: Et_2O) was then concentrated under reduced pressure to afford diazo ester **20** (88.2 mg, 0.322 mmol, 99% yield) as a yellowish oil; R_f = 0.44 (6:1, hexanes:EtOAc); ^1H NMR (500 MHz, $CDCl_3$) δ 6.08 (dt, *J* = 1.66 Hz, 1.66 Hz, 7.75 Hz, 1H), 5.95 (d, *J* = 2.62 Hz, 1H), 5.71 (s, 1H), 2.58–2.55 (m, 1H), 2.44 (s, 3H), 2.31–2.24 (m, 1H), 2.22 (s, 3H), 2.39-2.26 (m, 2H), 2.18–2.09 (m, 4H), 1.95–1.90 (m, 1H), 1.68–1.52 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.5, 161.6, 142.1, 131.2, 130. 7, 125.5, 80.3, 31.7, 30.7, 28.4, 26.3, 25.8, 22.7, 22.3; IR (Neat Film, NaCl) 3298, 3050, 2929, 2856, 2390, 2297, 2208, 2138, 1712, 1661, 1652, 1447, 1435, 1365, 1312, 1247, 1149, 1061, 1024, 965, 926, 854, 836, 816, 800, 746 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{15}H_{19}O_3N_2$ $[M+H]^-$: 275.1396, found 275.1389.

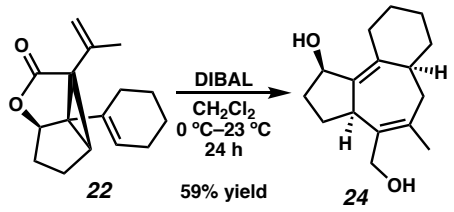


(2a*S*,2a^1*S*,4a*R*)-2b-Acetyl-2a^1-(cyclohex-1-en-1-yl)hexahydro-3*H*-4-oxacyclopropa[*cd*]pentalen-3-one (21): To a flame-dried two neck round-bottom flask equipped with a magnetic stir bar was added copper catalyst (20 mg, 0.0459 mmol) in a nitrogen-filled glove box. The flask was sealed with two rubber septa and removed from the glove box. One of the rubber septa was replaced with a reflux condenser connected to a nitrogen inlet. A solution of diazo ester **20** (254.8 mg, 0.929 mmol) in toluene (46 mL) was added. The reaction was heated to reflux in a 110 ºC oil bath. After 2 h of stirring, the reaction mixture was cooled to 23 ºC and stirred for 15 min. The mixture was concentrated and purified by flash column chromatography (15:1 hexanes: EtOAc) to afford cyclopropane **21** (148 mg, 0.601 mmol, 65% yield) as a yellowish oil; R_f = 0.36 (6:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.72–5.70 (m, 1H), 4.81 (d, *J* = 1.30 Hz, 1H), 3.10 (d, *J* = 6.40 Hz, 1H), 2.45 (s, 3H), 2.31–2.24 (m, 1H), 2.15–2.12 (m, 1H), 2.04–1.98 (m, 3H), 1.91–1.85 (m, 1H), 1.80–1.78 (m, 1H), 1.71–1.49 (m, 5H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.1, 172.9, 123.0, 128.3, 85.3, 66.7, 51.6, 39.4, 38.1, 30.1, 28.3, 25.3, 24.0, 22.6, 22.0; IR (Neat Film, NaCl) 2929, 1760, 1699, 1435, 1360, 1311, 1243, 1159, 1089, 1008, 979, 956, 925, 906, 855, 799, 756 cm^{-1}; HRMS (MM+) *m/z* calc'd for $C_{15}H_{19}O_3$ $[M+H]^+$: 247.1329, found 247.1327, and dienone **49** (22 mg, 0.136 mmol, 15% yield) as a colorless oil; R_f = 0.40 (6:1 hexanes: EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39–7.33 (m, 1H), 6.91–6.85 (m, 1H), 2.60–2.54 (m, 2H), 2.51–2.43 (m, 2H), 2.21–2.15 (m, 4H), 1.74–1.67 (m, 2H), 1.65–1.55 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.8, 155.2, 128.8, 128.6, 36.3, 26.8, 25.7, 25.7, 22.8, 22.1; IR (Neat Film, NaCl) 3386, 3051, 2925, 2857, 2834, 2661, 1703, 1699, 1340, 1589, 1439, 1406, 1385, 1342, 1318, 1294, 1263, 1208, 1175, 1136, 1113, 1079, 1016, 998, 976, 940, 926, 887, 840, 832, 803, 785, 762, 724 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{11}H_{15}O$ $[M+H]^+$: 163.1123, found 163.1128.



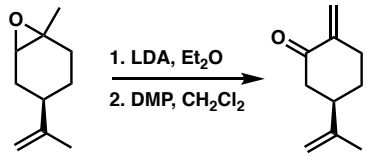
(2a*S*,2a^1*S*,4a*R*)-2a^1-(Cyclohex-1-en-1-yl)-2b-(prop-1-en-2-yl)hexahydro-3*H*-4-oxacyclopropa[*cd*]pentalen-3-one (22): To a flame-dried round-bottom flask equipped with a magnetic stir bar were added Wilkinson's catalyst (4.3 mg, 0.00465 mmol) and PPh_3 (54 mg, 0.206 mmol) in a nitrogen-filled glove box. The flask was sealed with a rubber septum, removed from the glove box and connected to a nitrogen inlet. Dioxane (2 mL) was added, and the reaction was immersed in a 60 ºC oil bath. *i*-PrOH (0.21 mL, 2.75 mmol) was added, followed by a solution of cyclopropane **21** (46 mg, 0.187 mmol) in dioxane (0.5 mL) to give a reddish solution. A solution of trimethylsilyldiazomethane (2 M in Et_2O, 0.22 mL, 0.44 mmol) was added to the reaction mixture. The reaction was stirred for 5 h at 60 ºC. The reaction was allowed to cool to ambient temperature and concentrated under reduced pressure. The residue was purified by flash column chromatography (15:1, hexanes: EtOAc) to afford vinyl lactone **22** (30 mg, 0.123 mmol, 65% yield) as a colorless oil; R_f = 0.40 (6:1 hexanes: EtOAc); ^{1}H NMR (500 MHz, C_6D_6) δ 5.30–5.23 (m, 1H), 4.96 (dd, *J* = 3.0, 1.5 Hz, 1H), 4.85 (dd, *J* = 1.5, 0.8 Hz, 1H), 4.53 (d, *J* = 1.0 Hz, 1H), 2.06 (dd, *J* = 4.1, 3.5 Hz, 1H), 1.83–1.77 (m, 5H), 1.75–1.60 (m, 4H), 1.58–1.45 (m, 1H), 1.46–1.25 (m, 5H); ^{13}C NMR (126 MHz, C_6D_6) δ 173.5, 138.4, 138.4, 125.5, 116.5, 83.9, 58.9, 50.2, 38.9, 33.3, 28.0, 25.5, 23.6, 23.0, 22.3, 22.0; IR (Neat Film, NaCl), 3498, 2918, 2850, 1960, 1645, 1539, 1436, 1373, 1335, 1302, 1289, 1262, 1212, 1161, 1137, 1093, 1077, 1044, 1012, 997,

906, 841, 802, 751 cm^{-1}; HRMS (MM+) *m/z* calc'd for $C_{16}H_{21}O_2$ $[M+H]^+$: 245.1536, found 245.1555.



(1*R*,3a*R*,6a*S*)-4-(Hydroxymethyl)-5-methyl-1,2,3,3a,6,6a,7,8,9,10-decahydrobenzo[*e*]azulen-1-ol (24): To a flame-dried round-bottom flask equipped with a magnetic stir bar were added vinyl lactone **22** (10 mg, 0.0403 mmol) and DCM (1 mL). The flask was cooled to 0 ºC and stirred for 10 min. A solution of DIBAL (1 M in DCM, 0.4 mL, 0.4 mmol) was added dropwise. The reaction mixture was slowly warmed up to 23 ºC and stirred for an additional 24 h. The reaction was quenched with methanol (0.4 mL). Saturated aqueous potassium sodium tartrate solution (1 mL) was added to the mixture. The phases were separated, and the aqueous phases were extracted with DCM (5 x 2 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (2:1, hexanes: EtOAc) to afford diol **24** as a white solid (6 mg, 0.024 mmol, 59% yield); R_f = 0.08 (2:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, C_6D_6) δ 4.61 (d, *J* = 4.2 Hz, 1H), 4.20 (d, *J* = 11.3 Hz, 1H), 3.96 (d, *J* = 11.3 Hz, 1H), 3.58–3.49 (m, 1H), 3.04 (dd, *J* = 13.6, 4.1 Hz, 1H), 2.75 (dd, *J* = 12.8, 3.5 Hz, 1H), 2.41 (qd, *J* = 12.4, 6.1 Hz, 1H), 1.95–1.83 (m, 2H), 1.76–1.67 (m, 5H), 1.64–1.57 (m, 1H), 1.52 (dd, *J* = 13.6, 3.6 Hz, 1H), 1.43–1.27 (m, 6H); ^{13}C NMR (126 MHz, C_6D_6) δ 138.9, 138.7, 138.3, 134.2, 73.2, 60.1, 41.6, 40.5, 38.5, 34.8, 34.6, 34.2, 30.2, 29.4, 27.6, 26.5, 21.9; IR (Neat Film, NaCl) 3338, 2927, 2853, 1740, 1447, 1373, 1242,

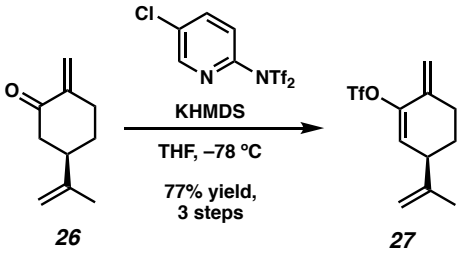
1177, 1043, 965, 913 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{16}H_{23}O_2$ $[M+H-H_2]^+$: 247.1698, found 247.1692.



25 ***26***

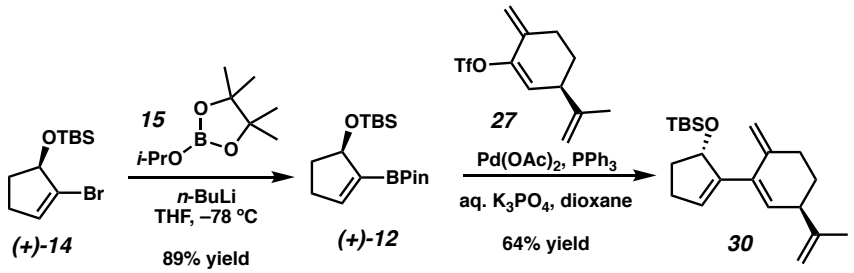
(*R*)-2-Methylene-5-(prop-1-en-2-yl)cyclohexan-1-one (26): To a flame-dried round-bottom flask with a magnetic stir bar were added diisopropyl amine (1.75 mL, 13.3 mmol) and Et_2O (35 mL). A solution of *n*-BuLi (2.12 M in hexane, 6.84 mL, 14.5 mmol) was added dropwise over a period of 30 min. A solution of epoxide **25** (2 mL, 12.1 mmol) in Et_2O (7 mL) was added dropwise over a period of 30 min. The resulting mixture was allowed to warm up to 23 ºC and then stirred for 7 h. The reaction mixture was cooled in ice bath and water was added. The organic phase was separated and washed with 2 M aqueous HCl (10 mL), water (10 mL), saturated aqueous $NaHCO_3$ (10 mL) and brine (10 mL). The Et_2O extracts are combined, dried over $MgSO_4$, and evaporated to afford crude mixture. The residue was used for the next reaction without further purification. To a round-bottom flask equipped with a magnetic stir bar were added semi-crude allylic alcohol (124 mg, 0.815 mmol) and DCM (10 mL). Dess–Martin periodinane (440 mg, 1.06 mmol) was added to the mixture. The reaction was stirred for 3 h at 23 ºC. The reaction mixture was diluted with Et_2O (10 mL) and then a 1:1:1 mixture of saturated aqueous $Na_2S_2O_3$ (10 mL), saturated aqueous $NaHCO_3$ (10 mL), and water (10 mL) was added slowly. The resulting mixture was stirred for 20 min resulting in two clear layers. The organic layer was gathered, and the aqueous layer was extracted with Et_2O (30 mL x 3). The organic layers were combined and dried over Na_2SO_4, and evaporated to afford crude mixture (Caution, the solvent was only partially removed, as enone **26** dimerizes easily.) The mixture was filtered through silica gel (8:1 pentane:Et_2O) and used in the

next reaction without further purification. The characterization data matched those reported in the literature.[5]



(*R*)-6-Methylene-3-(prop-1-en-2-yl)cyclohex-1-en-1-yl trifluoromethanesulfonate (27): To a flame-dried round-bottom flask equipped with a magnetic stir bar was added potassium bis(trimethylsilyl)amide (310 mg, 1.55 mmol) in a nitrogen filled glove box. The flask was sealed with rubber septum and removed from the glove box, connected to a nitrogen inlet, and cooled to –78 ºC. A solution of semi-crude enone **26** (150 mg, 1 mmol) in THF (10 mL) was added dropwise by syringe pump over 2 h. After addition of enone **26** was completed, Comins reagent (652 mg, 1.66 mmol) in THF (10 mL) was added dropwise. After stirring for 4 h at –78 ºC, the reaction mixture was poured into saturated aqueous $NaHCO_3$ (50 mL) and allowed to warm to 23 ºC. The mixture was extracted with Et_2O (30 x 3 mL). The combined organic layers were washed with brine (100 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash column chromatography (25:1 hexanes: EtOAc) to afford triflate **27** (218 mg, 0.77 mmol, 77% yield over 3 steps); R_f = 0.52 (4:1, hexanes: EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.82 (dd, *J* = 4.0, 1.7 Hz, 1H), 5.28 (s, 1H), 5.06–4.99 (m, 1H), 4.88 (t, *J* = 1.5 Hz, 1H), 4.77 (dt, *J* = 1.7, 0.9 Hz, 1H), 3.14–3.06 (m, 1H), 2.63–2.49 (m, 1H), 2.48–2.37 (m, 1H), 1.95–1.83 (m, 1H), 1.77 (s, 3H), 1.72–1.60 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.5, 147.1, 145.8, 144.0, 139.5, 136.5, 136.0, 126.3, 123.9, 120.7, 119.9, 117.4, 112.8, 112.0, 111.1, 1102, 43.4, 29.6, 27.0,

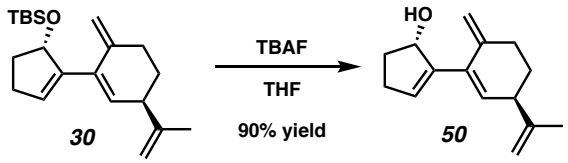
21.3; IR (Neat Film, NaCl) 3084, 2947, 2869, 1648, 1608, 1447, 1436, 1422, 1428, 1373, 1245, 1214, 1143, 1129, 1066, 1045, 1017, 998, 978, 948, 755, 737 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{11}H_{12}F_3O_3S$ $[M+H-H_{\square}]^+$: 281.0459, found 281.0473; $[\alpha]_D^{25.0}$ 61.1° (*c* 0.25, $CHCl_3$).



***tert*-Butyldimethyl(((*S*)-2-((*R*)-6-methylene-3-(prop-1-en-2-yl)cyclohex-1-en-1-yl)cyclopent-2-en-1-yl)oxy)silane (30):** To a flame-dried round-bottom flask with a magnetic stir bar were added bromide (–)-**14** (6.0 g, 21.6 mmol) and THF (70 mL). The flask was cooled to –78 ºC and stirred for 10 min, after which *n*-BuLi (2.5 M in hexanes, 13 mL, 32.5 mmol) was added dropwise. The reaction mixture was stirred at –78 ºC for 30 min and isopropyl pinacolyl borate (**15**, 6.9 mL, 33.8 mmol) was added. The reaction mixture was stirred at –78 ºC for 30 min and quenched with HCl solution (2 N in Et_2O, 16.3 mL, 32.5 mmol). Following addition, the reaction mixture was diluted with Et_2O (70 mL) and warmed up to 23 ºC. The reaction mixture was filtered and was concentrated under reduced pressure, and the residue was used in the next reaction without further purification.

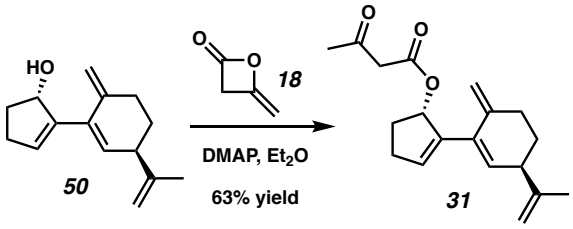
To a flame-dried round-bottom flask equipped with a magnetic stir bar were added semi-crude boronate (–)-**12** (2.65 g, 7.74 mmol), triflate **27** (1.987 g, 7.04 mmol), palladium acetate (82 mg, 0.35 mmol), triphenylphosphine (199 mg, 0.70 mmol), tribasic potassium phosphate (4.5 g, 21 mmol). The mixture was evacuated and back filled with argon (x3). The mixture was dissolved in dioxane (25 mL) then added water (2.5 mL). The reaction mixture was stirred at 23 ºC for 40 h. The resulting mixture was then diluted with EtOAc (25 mL), washed by saturated aqueous NH_4Cl

(25 mL), and then dried over $MgSO_4$. The mixture was filtered and concentrated under reduced pressure to afford crude mixture of **30** as a colorless oil. The residue was purified by flash column chromatography (25:1 hexanes:EtOAc) to afford diene **30** (1.5 g, 4.54 mmol, 64% yield over triflate **27**) R_f = 0.95 (10:1, hexanes:EtOAc); ^{1}H NMR (400 MHz, C_6D_6) δ 5.88–5.84 (m, 1H), 5.70–5.68 (m, 1H), 5.02–4.93 (m, 2H), 4.93–4.88 (m, 2H), 4.85–4.81 (m, 1H), 2.97–2.91 (m, 1H), 2.51–2.30 (m, 4H), 2.16–2.02 (m, 2H), 1.80 (tt, *J* = 8.3, 4.0 Hz, 2H), 1.72–1.56 (m, 2H), 1.00 (s, 9H), 0.09 (s, 6H); ^{13}C NMR (101 MHz, C_6D_6) δ 148.5, 146.7, 143.4, 135.9, 132.7, 130.9, 111.0, 110.7, 78.7, 45.1, 34.8, 32.1, 29.3, 26.2, 26.0, 20.9, 18.4, –4.3, –4.5; IR (Neat Film, NaCl) 3435, 3080, 2956, 2929, 2856, 2360, 1725, 1645, 1472, 1463, 1362, 1258, 1095, 1020, 947, 865, 836, 801, 776 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{21}H_{33}OSi$ $[M+H-H_2]^+$: 329.2301, found 329.2297; $[\alpha]_D^{25.0}$ –38.3° (*c* 0.150, $CHCl_3$).



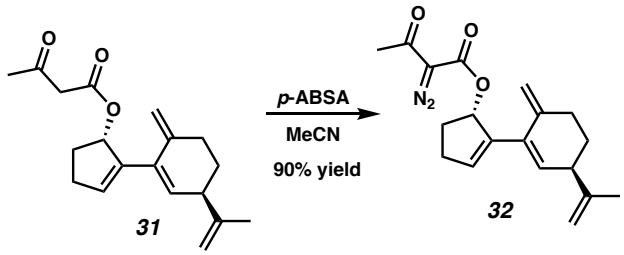
(*S*)-2-((*R*)-6-Methylene-3-(prop-1-en-2-yl)cyclohex-1-en-1-yl)cyclopent-2-en-1-ol (50): To a round-bottom flask with a magnetic stir bar were added silyl ether **30** (1.5 g, 4.54 mmol) and THF (23 mL). To the mixture was added TBAF (1.0 M in THF, 7.7 mL, 7.7 mmol) and stirred for 24 h at 23 ºC. The reaction mixture was quenched with sat. aq. NH_4Cl (20 mL) and extracted with Et_2O (3 x 10 mL). The organic layers were combined, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash column chromatography (3:1 hexanes: EtOAc) to afford allylic alcohol **50** (1.23 g, 5.69 mmol, 90% yield) as a colorless oil; R_f = 0.10 (10:1, hexanes: EtOAc); ^{1}H NMR (400 MHz, C_6D_6) δ5.84–5.79 (m, 1H), 5.76–5.71 (m, 1H), 5.11–5.05 (m, 1H), 4.95–4.86 (m, 3H), 4.85–4.80 (m, 1H), 2.92–2.81 (m, 1H), 2.43–2.21 (m, 3H), 2.19–1.98

(m, 2H), 1.85–1.68 (m, 2H), 1.66–1.45 (m, 4H), 1.21 (d, J = 5.8 Hz, 1H); ^{13}C NMR (101 MHz, C_6D_6) δ 148.6, 146.0, 143.4, 135.1, 132.2, 131.2, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 111.2, 111.1, 78.0, 45.0, 33.9, 32. 5, 30.3, 29.5, 20.7; IR (Neat Film, NaCl) 3774, 3659, 3078, 3042, 2935, 2852, 2112, 1644, 1442, 1373, 1311, 1166, 1047, 930, 889, 843 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{15}H_{19}O_3$ $[M+H-H_2]^+$: 215.1436, found 215.1441; $[\alpha]_D^{25.0}$ –16.2° (*c* 0.150, $CHCl_3$).

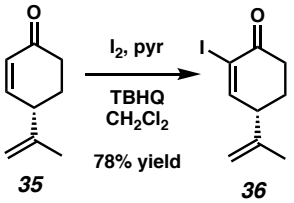


(*S*)-2-((*R*)-6-Methylene-3-(prop-1-en-2-yl)cyclohex-1-en-1-yl)cyclopent-2-en-1-yl 3-oxobutanoate (31): To a flame-dried round-bottom flask with a magnetic stir bar were added allylic alcohol **50** (1.23 g, 5.69 mmol), 4-dimethylaminopyridine (35 mg, 0.29 mmol) and Et_2O (20 mL). The flask was cooled to 0 ºC and stirred for 10 min. Diketene (**18**, 0.5 mL, 6.48 mmol) was added dropwise. The reaction mixture was stirred 15 min at 0 ºC was then quenched by ice-cold water (10 mL). The mixture was extracted with Et_2O (3 x 15 mL). The combined organic layers were washed by brine (15 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The crude oil was purified by flash column chromatography (10:1 hexanes: EtOAc) to afford β-ketoester **31** (1.07 g, 3.56 mmol, 63% yield) as a colorless oil; R_f = 0.40 (3:1, hexanes:Et_2O); ^{1}H NMR (400 MHz, C_6D_6) δ 6.23–6.15 (m, 1H), 5.82–5.80 (m, 1H), 5.80–5.77 (m, 1H), 5.05 (d, J = 2.1 Hz, 1H), 4.97–4.81 (m, 3H), 2.94 (s, 2H), 2.92–2.83 (m, 1H), 2.43–2.23 (m, 3H), 2.23–2.11 (m, 1H), 2.08–1.92 (m, 1H), 1.92–1.83 (m, 1H), 1.82–1.73 (m, 1H), 1.68 (s, 3H), 1.65 (s, 3H), 1.62–1.50 (m, 1H); ^{13}C NMR (101 MHz, C_6D_6) δ 199.0, 169.0, 166.9, 148.5, 143.2, 141.6, 134.9, 132.1, 111.2, 111.1, 81.3, 50.1, 45.0, 32.4, 31.1, 30.8, 29.54, 29.47, 20.8; IR (Neat Film, NaCl)

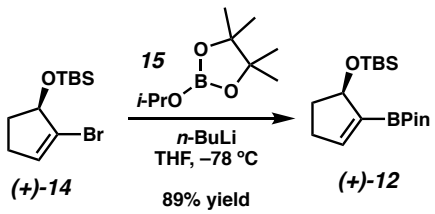
3629, 3078, 2935, 2855, 1727, 1644, 1440, 1360, 1315, 1238, 1149, 1029, 934, 895, 847, 802, 739 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{19}H_{25}O_3$ $[M+H]^+$: 301.1804, found 301.1814; $[\alpha]_D^{25.0}$ –41.8° (*c* 0.150, $CHCl_3$).



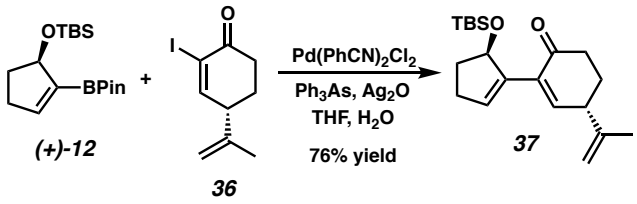
(*S*)-2-((*R*)-6-Methylene-3-(prop-1-en-2-yl)cyclohex-1-en-1-yl)cyclopent-2-en-1-yl 2-diazo-3-oxobutanoate (32): To a round-bottom flask equipped with a magnetic stir bar were added β-ketoester **31** (1.07 g, 3.56 mmol), MeCN (36 mL), and *p*-ABSA (1.3 g, 5.41 mmol). Et_3N (1.5 mL, 10.75 mmol) was added dropwise. The reaction mixture was stirred for 2 h at 23 ºC. The reaction mixture was filtered through a silica gel plug (pentanes:Et_2O 2:1) and concentrated under reduced pressure to afford diazo ester **32** (1.04 g, 3.19 mmol, 90% yield) as a yellowish oil; R_f = 0.44 (4:1, hexanes: EtOAc); ^1H NMR (500 MHz, $CDCl_3$) δ 6.06–5.98 (m, 2H), 5.61 (dd, *J* = 2.9, 1.5 Hz, 1H), 4.91–4.87 (m, 2H), 4.76 (dd, *J* = 2.0, 1.4 Hz, 1H), 4.74–4.69 (m, 1H), 2.93 (ddd, *J* = 9.1, 5.4, 3.2 Hz, 1H), 2.65–2.54 (m, 1H), 2.51–2.40 (m, 6H), 2.36–2.27 (m, 1H), 2.00–1.88 (m, 2H), 1.71 (dd, *J* = 1.4, 0.8 Hz, 3H), 1.60–1.52 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.5, 161.4, 148.3, 142.9, 140.8, 135.2, 134.1, 132.1, 132.1, 110.9, 110.9, 82.2, 44.6, 31.9, 31.0, 30.7, 29.1, 28.4, 20.8; IR (Neat Film, NaCl) 3794, 3417, 3301, 3078, 2932, 2855, 2617, 2486, 2391, 2301, 2210, 2135, 1953, 1713, 1659, 1441, 1361, 1307, 1247, 1151, 1063, 1025, 965, 895, 847 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{19}H_{23}O_3N_2$ $[M+H]^+$: 327.1709, found 327.1725; $[\alpha]_D^{25.0}$ –6.7° (*c* 0.250, $CHCl_3$).



(*S*)-2-Iodo-4-(prop-1-en-2-yl)cyclohex-2-en-1-one (36): To a round-bottom flask equipped with a magnetic stir bar were added ketone **35**[6] (200 mg, 1.47 mmol), DCM (35 mL), and *tert*-butylhydroquinone (5 mg, 0.03 mmol). A solution of iodine (700 mg, 2.76 mmol) in pyridine (1.5 mL, 10.75 mmol) was added. The reaction mixture was stirred for 2 h at 23 ºC. The reaction was diluted with Et_2O (20 mL) and water (20 mL) and quenched by saturated aqueous $Na_2S_2O_3$ (20 mL). The phases were separated and the aqueous phases were extracted with DCM (3 x 20 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (15:1, hexanes: EtOAc) to afford iodide **36** (300 mg, 1.14 mmol, 78% yield) as a yellowish oil; R_f = 0.40 (6:1, hexanes:EtOAc); ^{1}H NMR (400 MHz, C_6D_6)) δ 7.17 (d, *J* = 1.1 Hz, 1H), 4.62–4.55 (m, 1H), 4.47–4.43 (m, 1H), 2.36–2.22 (m, 2H), 1.92 (ddd, *J* = 16.2, 11.2, 4.8 Hz, 1H), 1.40–1.31 (m, 1H), 1.31–1.20 (m, 4H); ^{13}C NMR (101 MHz, C_6D_6) δ 190.5, 160.2, 144.5, 128.4, 128.3, 128.1, 127.9, 127.8, 112.8, 105.1, 47.5, 35.4, 27.7, 20.9; IR (Neat Film, NaCl) 3357, 3077, 2951, 2867, 1683, 1645, 1585, 1450, 1414, 1376, 1325, 1278, 1217, 1170, 1151, 1128, 1081, 1036, 971, 952, 89, 805, 713, 644 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_9H_{12}OI$ $[M+H]^+$: 262.9933, found 262.9936; $[\alpha]_D^{25.0}$ –40.1° (*c* 0.44, $CHCl_3$).

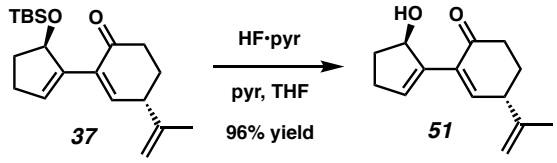


(*R*)-*tert*-butyldimethyl((2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopent-2-en-1-yl)oxy)silane ((+)-12): To a round-bottom flask equipped with a magnetic stir bar were added bromide (+)-**14** (1.04 g, 3.82 mmol) and THF (15 mL). The flask was cooled to −78 ºC and stirred for 10 min. *n*-BuLi solution (2.5 M in hexanes, 2.3 mL, 5.75 mmol) was added dropwise. The reaction mixture was stirred at −78 ºC for 30 min and isopropyl pinacolyl borate (1.2 mL, 5.88 mmol) was added. The reaction mixture was stirred at −78 ºC for 30 min then quenched with HCl solution (2 N in Et_2O, 2.9 mL, 5.8 mmol). Following addition, the reaction mixture was diluted with diethyl ether (15 mL) and warmed up to 23 ºC. The reaction mixture was filtered and was concentrated under reduced pressure to afford boronate (+)-**12** (1.1 g, 3.39 mmol, 89% yield) as a colorless oil. The characterization data matched those of *rac*-**12**. $[\alpha]_D^{25.0}$ 9.8° (*c* 1.35, $CHCl_3$).



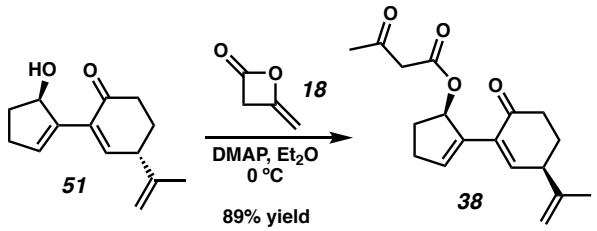
(*S*)-2-((*R*)-5-((*tert*-Butyldimethylsilyl)oxy)cyclopent-1-en-1-yl)-4-(prop-1-en-2-yl)cyclohex-2-en-1-one (37): To a flame-dried round-bottom flask equipped with a magnetic stir bar were added boronate (+)-**12** (92 mg, 0.28 mmol), iodide **36** (50 mg, 0.19 mmol), silver oxide (70 mg, 0.30 mmol), triphenylarsine (6 mg, 0.02 mmol). The mixture was evacuated and back-filled with argon (x3). The mixture was dissolved in dioxane (25 mL) and water (2.5 mL). To the mixture was added bis(benzonitrile)palladium chloride (4 mg, 0.01 mmol). The reaction was stirred at 23 ºC for 6 h. The resulting mixture was filtered through celite with EtOAc and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (20:1, hexanes: EtOAc) to afford bicycle **37** (48 mg, 0.144 mmol, 76% yield over

36) as a white solid; R_f = 0.54 (6:1, hexanes: EtOAc); ^{1}H NMR (400 MHz, C_6D_6) δ 6.72 (dd, *J* = 3.4, 1.3 Hz, 1H), 6.26–6.17 (m, 1H), 5.33–5.25 (m, 1H), 4.76–4.74 (m, 1H), 4.72–4.70 (m, 1H), 2.72 (dt, *J* = 8.5, 4.1 Hz, 1H), 2.51–2.29 (m, 2H), 2.26–1.99 (m, 3H), 1.79–1.62 (m, 2H), 1.62–1.45 (m, 4H), 0.96 (s, 9H), 0.11 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ 197.0, 147.9, 146.2, 143.0, 135.7, 132.4, 128.3, 128.2, 128.1, 127.9, 127.8, 112.3, 78.5, 44.4, 38.1, 34.6, 30.6, 27.9, 26.2, 21.2, 18.3, −3.9, –4.4; IR (Neat Film, NaCl) 3348, 3078, 3042, 2929, 2893, 2855, 2737, 2708, 1687, 1683, 1649, 1472, 1463, 1451, 1388, 1375, 1360, 1314, 1287, 1251, 1218, 1189, 1157, 1141, 1064, 1006, 980, 941, 868, 836, 775, 735, 677 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{15}H_{19}O_3N_2$ $[M+H-H_2]^+$: 331.2093, found 331.2096; $[\alpha]_D^{25.0}$ –60.8° (*c* 0.44, $CHCl_3$).



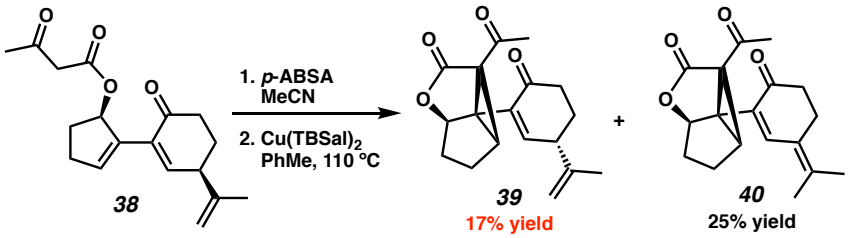
(*S*)-2-((*R*)-5-Hydroxycyclopent-1-en-1-yl)-4-(prop-1-en-2-yl)cyclohex-2-en-1-one (51): To a round-bottom plastic coated flask equipped with a magnetic stir bar were added diene **37** (30 mg, 0.090 mmol), THF (4 mL), and pyridine (0.05 mL, 0.62 mmol). A solution of HF•pyr (pyridine 30%, hydrogen fluoride 70%, 0.1 mL) was added dropwise. The reaction mixture was stirred for 18 h at 23 ºC. The reaction was diluted with Et_2O (4 mL) and neutralized with sat. aq. $NaHCO_3$ (10 mL). The phases were separated and the aqueous phase was extracted with EtOAc (3 x 10 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (5:1, hexanes: EtOAc) to afford allylic alcohol **51** (19 mg, 0.087 mmol, 96% yield) as a colorless oil; R_f = 0.25 (2:1, hexanes: EtOAc); ^{1}H NMR (400 MHz, C_6D_6) δ 6.86–6.76 (m, 1H), 6.44–6.35 (m, 1H), 4.99–

4.90 (m, 1H), 4.82–4.74 (m, 1H), 4.74–4.69 (m, 1H), 2.96 (s, 1H), 2.58 (dt, *J* = 8.7, 4.2 Hz, 1H), 2.54–2.43 (m, 1H), 2.36 (ddd, *J* = 16.3, 6.2, 4.3 Hz, 1H), 2.14–1.96 (m, 3H), 1.93–1.78 (m, 1H), 1.63–1.42 (m, 5H); ^{13}C NMR (101 MHz, C_6D_6) δ 198.9, 149.3, 146.2, 142.2, 135.2, 134.0, 112.4, 77.5, 44.3, 37.9, 34.0, 30.9, 27.8, 21.1; IR (Neat Film, NaCl) 3418, 3077, 3040, 2938, 2848, 1674, 1586, 1451, 1377, 1309, 1086, 1047, 990, 935, 895 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{14}H_{17}O_2$ $[M+H-H_2]^+$: 217.1229, found 217.1235; $[\alpha]_D^{25.0}$ –120.4° (*c* 0.33, $CHCl_3$).



(*R*)-2-((*R*)-6-Oxo-3-(prop-1-en-2-yl)cyclohex-1-en-1-yl)cyclopent-2-en-1-yl 3-oxobutanoate (38): To a flame-dried round-bottom flask equipped with a magnetic stir bar were added allylic alcohol **51** (870 mg, 3.99 mmol), 4-dimethylaminopyridine (50 mg, 0.41 mmol) and Et_2O (20 mL). The flask was cooled to 0 ºC and stirred for 10 min. Diketene (**18**, 0.36 mL, 4.67 mmol) was added dropwise. The reaction mixture stirred for 15 min at 0 ºC was then quenched with ice-cold water (20 mL). The mixture was extracted with Et_2O (3 x 20 mL). The combined organic layers were washed by brine (15 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The crude oil was purified by flash column chromatography (4:1 hexanes: EtOAc) to afford β-ketoester **38** (1.07 g, 3.54 mmol, 89% yield) as a colorless oil; R_f = 0.40 (2:1 hexanes:Et_2O); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 6.74–6.72 (m, 1H), 6.70–6.68 (m, 1H), 6.05 (dt, *J* = 7.5, 2.4 Hz, 1H), 4.89 (t, *J* = 1.5 Hz, 1H), 4.76–4.73 (m, 1H), 3.40–3.33 (m, 2H), 3.15 (dt, *J* = 8.7, 4.4 Hz, 1H), 2.65–2.27 (m, 5H), 2.18 (s, 3H), 2.17–2.09 (m, 1H), 1.98–1.81 (m, 2H), 1.79 (t,

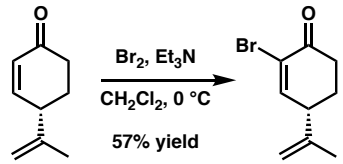
J = 1.2 Hz, 3H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 200.7, 198.5, 167.3, 148.8, 146.5, 138.1, 136.2, 133.1, 112.3, 81.4, 50.6, 44.4, 38.1, 31.7, 30.8, 30.3, 28.0, 21.4; IR (Neat Film, NaCl) 3655, 3643, 3080, 2943, 2850, 1726, 1640, 1554, 1450, 1356, 1315, 1256, 1146, 1088, 1029, 995, 900, 854, 778, 706, 634, 617 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{18}H_{23}O_4$ $[M+H]^+$: 303.1596, found 303.1594; $[\alpha]_D^{25.0}$ –30.6° (*c* 0.13, $CHCl_3$). (Note: the enol ether tautomer of β-ketoester **38** was predominant in CD_2Cl_2.



(2a*S*,2a^1*S*,4a*R*)-2b-Acetyl-2a^1-((*S*)-6-oxo-3-(prop-1-en-2-yl)cyclohex-1-en-1-yl)hexahydro-3*H*-4-oxacyclopropa[*cd*]pentalen-3-one (39): To a round-bottom flask equipped with a magnetic stir bar were added β-ketoester **38** (95 mg, 0.314 mmol), MeCN (3 mL), and *p*-ABSA (113 mg, 0.47 mmol). Et_3N (0.1 mL, 0.717 mmol) was added dropwise. The reaction mixture was remained to stir 2 h at 23 ºC. The reaction mixture was filtered through a Florisil (2:1, pentanes: Et_2O) was then concentrated under reduced pressure. The residue was used in the next reaction without further purification.

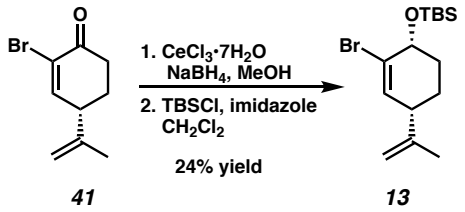
To a flame-dried two neck round-bottom flask equipped with a magnetic stir bar was added $Cu(TBSal)_2$ (8 mg, 0.019 mmol) in a nitrogen-filled glove box. The flask was sealed with rubber septa and removed from the glove box. One of the rubber septa was replaced with a reflux condenser connected to a nitrogen inlet. A solution of semi-crude diazo ester (60 mg, 0.198 mmol) in toluene (40 mL) was added. The reaction was heated to reflux in a 110 ºC oil bath. After 3 h of

stirring, the reaction mixture was cooled to 23 ºC and stirred for 15 min. The mixture was concentrated and purified by flash column chromatography (10:1 hexanes: EtOAc) to afford cyclopropane **39** (10 mg, 0.033 mmol, 17% yield) as a colorless oil; R_f = 0.40 (2:1 hexanes:EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.79 (dd, *J* = 3.2, 1.1 Hz, 1H), 4.96–4.89 (m, 1H), 4.75–4.73 (m, 1H), 4.73–4.71 (m, 1H), 3.13 (dt, *J* = 8.3, 4.2 Hz, 1H), 2.96 (dd, *J* = 6.5, 1.0 Hz, 1H), 2.56 (ddd, *J* = 16.8, 6.5, 4.4 Hz, 1H), 2.44 (s, 3H), 2.40–2.26 (m, 2H), 2.21–2.00 (m, 2H), 2.00–1.78 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.5, 198.2, 172.3, 153.8, 145.2, 131.7, 112.9, 85.7, 77.2, 59.2, 50.7, 43.7, 38.9, 38.6, 36.5, 29.9, 27.7, 23.9, 21.7; IR (Neat Film, NaCl) 3371, 3077, 2939, 1760, 182, 1651, 1488, 1439, 1362, 1339, 1309, 1242, 1223, 1190, 1160, 1136, 1085, 1067, 1006, 957, 912, 850, 817, 727, 703, 622, 612 cm^{-1}; HRMS (MM+) *m/z* calc'd for $C_{15}H_{19}O_3$ $[M+H]^+$: 301.1440, found 301.1450; $[\alpha]_D^{25.0}$ –56.8° (*c* 0.30, $CHCl_3$), and side product **40** (15 mg, 0.050 mmol, 25% yield) as a colorless oil; R_f = 0.05 (2:1 hexanes: EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (s, 1H), 4.75 (dd, *J* = 2.0, 1.1 Hz, 1H), 3.03 (dt, *J* = 6.5, 1.1 Hz, 1H), 2.75–2.60 (m, 2H), 2.54–2.35 (m, 6H), 2.10–2.01 (m, 1H), 2.01–1.96 (m, 3H), 1.96–1.84 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.6, 198.2, 172.5, 144.5, 142.3, 126.3, 126.1, 85.8, 77.2, 60.1, 51.5, 38.5, 38.4, 37.1, 29.8, 25.6, 23.9, 22.2, 21.3; IR (Neat Film, NaCl) 3484, 3369, 3051, 2928, 2853, 2435, 2305, 2143, 1755, 1679, 1615, 1434, 1361, 1348, 1311, 1297, 1257, 1242, 1216, 1199, 1164, 1131, 1090, 1064, 1037, 1004, 966, 918, 888, 851, 822, 798, 753, 719, 667, 655, 633, 614 cm^{-1}; HRMS(FAB+) *m/z* calc'd for $C_{18}H_{21}O_4$ $[M+H]^+$: 301.1440, found 301.1434; $[\alpha]_D^{25.0}$ 53.1° (*c* 0.10, $CHCl_3$)



35 ***41***

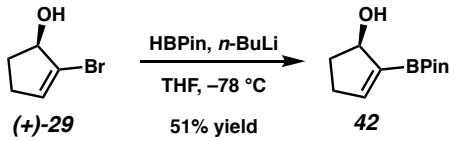
(*S*)-2-Bromo-4-(prop-1-en-2-yl)cyclohex-2-en-1-one (41): To a flame-dried round-bottom flask equipped with a magnetic stir bar were added ketone **35** (553 mg, 4.06 mmol) and DCM (35 mL). The flask was cooled to 0 ºC and stirred for 10 min. A solution of bromine (0.24 mL, 4.66 mmol) in DCM (5 mL) was added dropwise with vigorous stirring at 0 ºC. After reaction became a reddish-brown color, Et_3N (0.6 mL, 4.30 mmol) was added at 0 ºC. The cooling bath was removed, and the flask was allowed to warm to 23 ºC. After 30 min of stirring, the reaction was washed with water (40 mL). The aqueous phase was extracted with DCM (3 x 40 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (20:1 hexanes: EtOAc) to afford bromide **41** as a yellow oil (500 mg, 2.32 mmol, 57% yield); R_f = 0.45 (6:1 hexanes: EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 3.6, 0.9 Hz, 1H), 4.96–4.88 (m, 1H), 4.87–4.72 (m, 1H), 3.19–3.08 (m, 1H), 2.70 (ddd, *J* = 16.6, 7.0, 4.3 Hz, 1H), 2.51 (ddd, *J* = 16.6, 10.7, 4.5 Hz, 1H), 2.19 (ddtd, *J* = 12.8, 7.0, 4.7, 1.0 Hz, 1H), 1.99 (dddd, *J* = 13.5, 10.7, 8.2, 4.4 Hz, 1H), 1.79 (dd, *J* = 1.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.2, 153.1, 144.2, 124.0, 113.4, 46.1, 36.5, 27.6, 21.4.; IR (Neat Film, NaCl) 3853, 3650, 3371, 3035, 2953, 2869, 2360, 1694, 1646, 1595, 1451, 1417, 1377, 1327, 1278, 1218, 1172, 1153, 1132, 1085, 1037, 984, 958, 899, 816, 798, 786, 749, 716, 668, 650, 611 cm^1; HRMS (FAB+) *m/z* calc'd for $C_9H_{12}OBr$ $[M+H]^+$: 215.0072, found 215.0071; $[\alpha]_D^{25.0}$ 52.9° (*c* 0.30, $CHCl_3$).



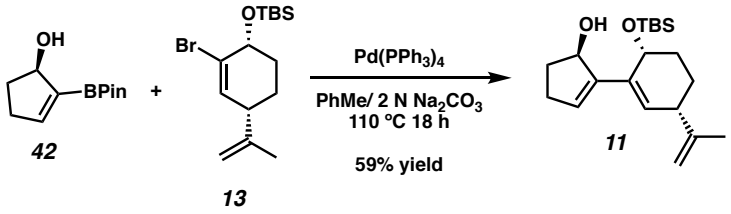
(((1*R*,4*S*)-2-Bromo-4-(prop-1-en-2-yl)cyclohex-2-en-1-yl)oxy)(*tert*-butyl)dimethylsilane (13): To a round-bottom flask equipped with a magnetic stir bar were added bromoenone **41** (7.68 g, 35.7 mmol) and MeOH (108 mL). The flask was cooled to 0 ºC, after which $CeCl_3 \bullet 7H_2O$ (13.3 g 35.7 mmol, 1.0 equiv) and $NaBH_4$ (1.35 g, 35.7 mmol, 1.0 equiv) were sequentially added over 5 min. The reaction was stirred at 0 ºC for 20 min, and the mixture was poured into sat. aq. NH_4Cl (300 mL). The aqueous phase was extracted with Et_2O (3 x 200 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was passed through a plug of silica (20% EtOAc in hexanes) to afford crude alcohol as a colorless oil (7.01 g).

The semi-crude residue was dissolved in CH_2Cl_2 (81 mL), and imidazole (5.1 g, 74.3 mmol, 2.3 equiv) and TBSCl (8.3 g, 54.9 mmol, 1.7 equiv) were sequentially added. The resulting mixture was stirred at 23 ºC for 12 h, after which it was poured into brine (200 mL), extracted with CH_2Cl_2 (3 x 200 mL) dried over $MgSO_4$. The crude solution was concentrated *in vacuo* and purified by flash column chromatography (1% to 5% EtOAc in hexanes) to afford bromide **13** as a colorless oil (2.85 g, mmol, 24% yield); $R_f = 0.90$ (6:1 hexanes: EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.03 (dd, *J* = 2.9, 0.8 Hz, 1H), 4.81–4.75 (m, 2H), 4.18 (td, *J* = 3.7, 1.2 Hz, 1H), 2.79–2.70 (m, 1H), 1.88–1.83 (m, 1H), 1.79–1.73 (m, 1H), 1.73–1.71 (m, 4H), 1.68–1.62 (m, 1H), 0.91 (s, 9H), 0.16 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.1, 134.5, 126.3, 111.5, 70.6, 46.7, 32.7, 26.0, 22.2, 20.6, 18.3, –4.3, –4.5; IR (Neat Film, NaCl) 3077, 2950, 2929, 2885, 2856, 2738, 2709, 2360, 1918, 1793, 2738, 2709, 2360, 1918, 1793, 1684, 1648, 1472, 1462, 1448, 1436, 1407, 1388,

1375, 1361, 1300, 1280, 1251, 1219, 1194, 1171, 1126, 1084, 1064, 1025, 1006, 987, 960, 939, 914, 894, 880, 834, 814, 775, 729, 669, 639 cm^{-1}; HRMS (MM+) *m/z* calc'd for $C_{15}H_{19}O_3$ [M+H–H_2]$^+$: 331.0916, found 331.0902; $[\alpha]_D^{25.0}$ –22.6° (*c* 0.30, $CHCl_3$).

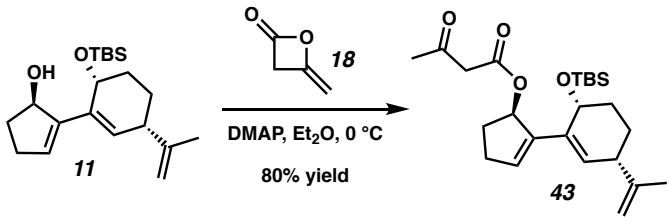


(*R*)-2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopent-2-en-1-ol (42): To a round-bottom flask equipped with a magnetic stir bar was added (+)-**29** (326.0 mg, 2.00 mmol) and THF (40 mL). The resulting solution was cooled to –78 ºC, and *n*-BuLi (2.3 M in hexanes, 4.60 mmol, 2.1 mL, 2.3 equiv) was added dropwise over several min. The resulting suspension was stirred vigorously for 15 min, and neat pinacolborane (0.80 mL, 5.00 mmol, 2.5 equiv) was added in one portion. The mixture was stirred vigorously for an additional 20 min, after which it was poured into sat. aq. NH_4Cl, extracted with Et_2O (3 x 50 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude product was purified by flash column chromatography (4:1, hexanes: EtOAc) to afford boronate **42** (213.7 mg, 1.01 mmol, 51% yield) as a white solid; R_f = 0.10 (6:1, hexanes: EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.70–6.63 (m, 1H), 5.05–4.95 (m, 1H), 2.64–2.51 (m, 1H), 2.41–2.18 (m, 2H), 1.71 (dddd, *J* = 13.7, 9.1, 5.5, 4.5 Hz, 1H), 1.28 (s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.1, 83.6, 79.8, 33.2, 33.0, 26.0, 25.0; IR (Neat Film, NaCl) 3478, 3038, 2978, 2931, 2731, 2219, 1995, 1887, 1622, 1615, 1372, 1214, 1144, 1111, 1046, 1020, 964, 925, 854, 832, 759, 710 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{15}H_{19}O_3N_2$ [M+H–H_2]$^+$: 209.1349, found 209.1344; $[\alpha]_D^{25.0}$ –59.6° (*c* 0.80, $CHCl_3$).



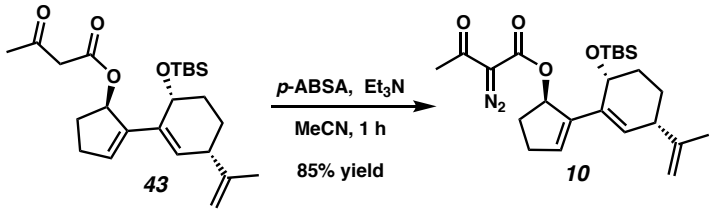
(*R*)-2-((3*S*,6*R*)-6-((*tert*-Butyldimethylsilyl)oxy)-3-(prop-1-en-2-yl)cyclohex-1-en-1-yl)cyclopent-2-en-1-ol (11): To a two neck round-bottom flask equipped with reflux condenser and a magnetic stir bar were added boronate **42** (200 mg, 0.952 mmol) and bromide **13** (200 mg, 0.605 mmol). The mixture was evacuated and back-filled with argon (x3). Toluene (6 mL), tetrakis(triphenylphosphine)palladium(0) (21 mg, 0.018 mmol), and 2 M aqueous Na_2CO_3 (6 mL) were added. The reaction was heated to reflux in a 110 ºC oil bath. After 18 h of stirring, the reaction mixture was cooled to 23 ºC and stirred for 15 min. The phases were separated and the aqueous phases were extracted with EtOAc (3 x 10 mL). The combined organic phases were washed with brine (10 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (20:1 hexanes: EtOAc) to afford diene **11** (120 mg, 0.359 mmol, 59% yield) as a colorless oil; R_f = 0.40 (6:1, hexanes: EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.85–5.81 (m, 2H), 4.95 (dt, *J* = 7.2, 2.5 Hz, 1H), 4.80–4.78 (m, 1H), 4.77 (dd, *J* = 2.0, 1.4 Hz, 1H), 4.43 (ddd, *J* = 3.6, 2.8, 1.3 Hz, 1H), 2.85–2.78 (m, 1H), 2.62–2.50 (m, 1H), 2.38–2.28 (m, 1H), 2.26–2.16 (m, 1H), 1.93–1.80 (m, 2H), 1.80–1.74 (m, 1H), 1.72 (dd, *J* = 1.5, 0.8 Hz, 3H), 1.68–1.58 (m, 2H), 0.85 (s, 9H), 0.09 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.0, 145.1, 135.0, 130.7, 128.7, 110.9, 76.8, 65.1, 44.9, 33.7, 31.8, 30.7, 26.0, 22.4, 20.5, 18.3, –3.9, –4.2; IR (Neat Film, NaCl) 3601, 3412, 3072, 2929, 2855, 2737, 2708, 1924, 1647, 1472, 1463, 1436, 1407, 1389, 1375, 1360, 1334, 1305, 1252, 1218, 1024, 959, 934, 889,

835, 773, 723, 676 cm^{-1}; HRMS (MM+) *m/z* calc'd for $C_{20}H_{34}O_2NSiNa$ $[M+Na]^+$: 356.2220, found 357.2237; $[\alpha]_D^{25.0}$ –21.1° (*c* 0.10, $CHCl_3$).

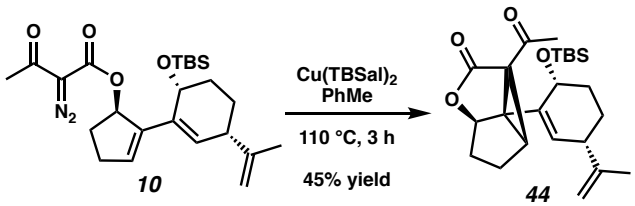


(*R*)-2-((3*S*,6*R*)-6-((*tert*-Butyldimethylsilyl)oxy)-3-(prop-1-en-2-yl)cyclohex-1-en-1-yl)cyclopent-2-en-1-yl 3-oxobutanoate (43): To a two neck round-bottom flask with a magnetic stir bar and were added bicyclic alcohol **11** (20 mg, 0.060 mmol), 4-dimethylaminopyridine (1.0 mg, 0.0082 mmol) and Et_2O (1.5 mL). The flask was cooled to 0 ºC and stirred for 10 min. A solution of diketene (**18**, 0.07 mL, 0.907 mmol) in Et_2O (2 mL) was added dropwise over several min. The reaction mixture was stirred for 15 min at 0 ºC was then quenched by ice cold water (2 mL). The mixture was extracted with Et_2O (3 x 3 mL). The combined organic layers were washed with brine (3 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The crude oil was purified by flash column chromatography (4:1 hexanes: EtOAc) to afford β-ketoester **43** (20 mg, 0.048 mmol, 80% yield) as a colorless oil; R_f = 0.45 (6:1, hexanes: Et_2O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.18–5.98 (m, 2H), 5.62 (d, *J* = 2.8 Hz, 1H), 4.85–4.67 (m, 2H), 4.44 (t, *J* = 3.2 Hz, 1H), 3.36 (s, 2H), 2.77 (t, *J* = 8.6 Hz, 1H), 2.62–2.53 (m, 1H), 2.44–2.27 (m, 2H), 2.22 (s, 3H), 1.96–1.83 (m, 2H), 1.79–1.72 (m, 1H), 1.73–1.54 (m, 5H), 0.84 (s, 9H), 0.08 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.8, 167.3, 148.8, 140.9, 134.4, 131.8, 130.4, 110.6, 79.8, 64.7, 50.4, 44.7, 31.7, 31.1, 30.8, 30.3, 25.9, 22.3, 20.4, 18.2, –3.8, –4.4; IR (Neat Film, NaCl) 2976, 2926, 2854, 1876, 1659, 1612, 1584, 1512, 1464, 1410, 1388, 1379, 1370, 1315, 1246, 1175, 1166, 1145,

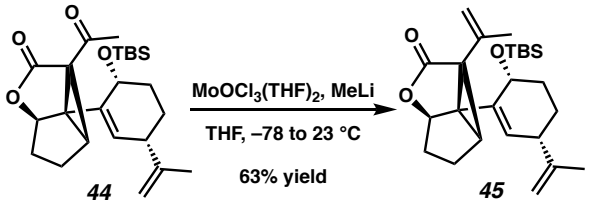
1113, 1039, 967, 862, 819, 750, 688, 671 cm^{-1}; HRMS (MM+) *m/z* calc'd for $C_{24}H_{38}O_4SiNa$ $[M+Na]^+$: 441.2432, found 441.2441; $[\alpha]_D^{25.0}$ 4.4° (*c* 0.34, $CHCl_3$).



(*R*)-2-((3*S*,6*R*)-6-((*tert*-Butyldimethylsilyl)oxy)-3-(prop-1-en-2-yl)cyclohex-1-en-1-yl)cyclopent-2-en-1-yl 2-diazo-3-oxobutanoate (10): To a round-bottom flask equipped with a magnetic stir bar were added β-ketoester **43** (20 mg, 0.048 mmol), MeCN (2.5 mL), and *p*-ABSA (40.0 mg, 0.167 mmol). Et_3N (0.03 mL, 0.215 mmol) was added dropwise. The reaction mixture was stirred for 1 h min at 23 ºC and concentrated *in vacuo*. The resulting residue was passed through a silica gel plug (4:1 pentane:Et_2O) and concentrated under reduced pressure to afford diazo ester **10** (18 mg, 0.041 mmol, 85% yield) as a yellowish oil; R_f = 0.44 (4:1 hexanes: EtOAc); ^1H NMR (500 MHz, $CDCl_3$) δ 6.08 (dt, *J* = 1.66 Hz, 1.66 Hz, 7.75 Hz, 1H; ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.47; IR (Neat Film, NaCl) 3408, 3073, 2929, 2855, 2362, 2139, 1713, 1661, 1652, 1472, 1464, 1366, 1312, 1250, 1195, 1150, 1086, 1064, 1025, 1006, 963, 938, 921, 895, 850, 834, 808, 773, 742, 676, 635 cm^{-1}; HRMS (MM+) *m/z* calc'd for $C_{24}H_{36}O_4N_2SiNa$ $[M+Na]^+$: 467.2337, found 467.2354; $[\alpha]_D^{25.0}$ –11.4° (*c* 0.31, $CHCl_3$).

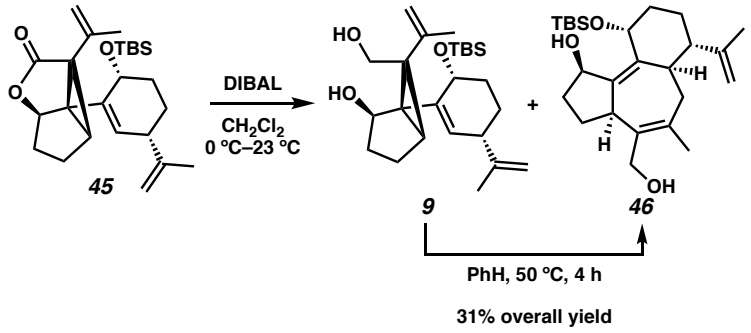


(2a*S*,2a^1*S*,4a*R*)-2b-Acetyl-2a^1-((3*S*,6*R*)-6-((*tert*-butyldimethylsilyl)oxy)-3-(prop-1-en-2-yl)cyclohex-1-en-1-yl)hexahydro-3*H*-4-oxacyclopropa[*cd*]pentalen-3-one (44): To a flame-dried two neck round-bottom flask equipped with a magnetic stir bar was added $Cu(TBSal)_2$ (3.0 mg, 0.0072 mmol) in a nitrogen-filled glove box. The flask was sealed with rubber septa and removed from the glove box. One of the rubber septa was replaced with a reflux condenser connected to a nitrogen inlet. A solution of diazo ester **10** (20 mg, 0.045 mmol) in toluene (15 mL) was added. The reaction was heated to reflux in a 110 ºC oil bath. After 3 h of stirring, the reaction mixture was cooled to 23 ºC and stirred for 15 min. The mixture was concentrated and purified by flash column chromatography (10:1 hexanes, EtOAc) to afford cyclopropane **44** (8.4 mg, 0.020 mmol, 45% yield) as a white solid; R_f = 0.40 (6:1 hexanes: EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.69 (d, *J* = 3.0 Hz, 1H), 5.09–5.00 (m, 1H), 4.81 (t, *J* = 1.7 Hz, 1H), 4.75–4.67 (m, 1H), 3.84–3.74 (m, 1H), 2.96 (dt, *J* = 6.3, 1.1 Hz, 1H), 2.76 (d, *J* = 7.6 Hz, 1H), 2.55 (s, 3H), 2.36–2.26 (m, 1H), 2.02 (dd, *J* = 13.0, 5.8 Hz, 1H), 1.96–1.85 (m, 1H), 1.82–1.70 (m, 5H), 1.69–1.52 (m, 3H), 0.90 (s, 9H), 0.09 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ198.4, 172.7, 147.7, 136.2, 132.9, 111.5, 86.4, 68.9, 65.1, 50.6, 43.7, 42.7, 38.3, 31.0, 30.4, 26.1, 23.9, 22.8, 21.0, 18.1, –3.8, –4.3; IR (Neat Film, NaCl) 2930, 2857, 1760, 1964, 1436, 1360, 1346, 1312, 1259, 1157, 1084, 1055, 1027, 1005, 983, 935, 896, 863, 832, 802, 774 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{24}H_{36}O_4Si$ $[M\bullet]^+$: 416.2383, found, 416.2379; $[\alpha]_D^{25.0}$ –68.1° (*c* 0.10, $CHCl_3$).



(2a*S*,2a^1*S*,4a*R*)-2a^1-((3*S*,6*R*)-6-((*tert*-Butyldimethylsilyl)oxy)-3-(prop-1-en-2-yl)cyclohex-1-en-1-yl)-2b-(prop-1-en-2-yl)hexahydro-3*H*-4-oxacyclopropa[*cd*]pentalen-3-one (45): To a flame-dried round-bottom flask equipped with a magnetic stir bar was added trichlorobis(THF) molybdenum(III) (750 mg, 2.08 mmol) in a nitrogen-filled glove box. The flask was sealed with a rubber septum, removed from the glove box and connected to a nitrogen inlet. THF (3 mL) was added to the flask to generate a bright green solution. The flask was cooled to –78 ºC and stirred for 10 min. A solution of MeLi (1.6 M in Et_2O, 1.2 mL, 1.92 mmol) was added dropwise to the reaction, resulting in a dark red solution. After 1 h of stirring at –78 ºC, a solution of cyclopropane **44** (48 mg, 0.115 mmol) in THF (1 mL) was added dropwise. The reaction was allowed to warm to ambient temperature and stirred for an additional 6 h. The reaction was quenched by addition of water (4 mL). The phases were separated, and the aqueous phase was extracted with Et_2O (3 x 4 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (15:1 hexanes: EtOAc) to afford vinyl lactone **45** (30 mg, 0.0723 mmol, 63% yield) as a colorless oil; R_f = 0.50 (6:1 hexanes: EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.51 (dd, *J* = 2.8, 0.9 Hz, 1H), 5.18–5.15 (m, 1H), 5.12–5.07 (m, 1H), 5.00–4.96 (m, 1H), 4.79 (dd, *J* = 2.0, 1.4 Hz, 1H), 4.73 (dt, *J* = 2.0, 0.9 Hz, 1H), 4.23–4.20 (m, 1H), 2.70 (ddd, *J* = 9.1, 5.9, 2.7 Hz, 1H), 2.44 (dt, *J* = 6.7, 1.3 Hz, 1H), 2.27–2.16 (m, 1H), 2.08–1.97 (m, 1H), 1.93–1.81 (m, 2H), 1.78–1.66 (m, 8H), 1.64–1.58 (m, 1H), 1.55–1.48 (m, 1H), 0.90 (s, 9H), 0.12 (s, 3H), 0.11 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.9, 148.2, 136.5, 133.6, 133.5, 117.0, 111.2, 85.8, 67.5, 58.6, 49.1, 44.3, 38.9, 34.7, 31.5, 26.1, 23.5,

22.4, 22.3, 20.5, 18.1, –3.6, –4.4; IR (Neat Film, NaCl) 2953, 2857, 1766, 1645, 1463, 1343, 1254, 1197, 1159, 1079, 1057, 1024, 891, 864, 833, 775, 673 cm^{-1}; HRMS (MM+) *m/z* calc'd for $C_{25}H_{39}O_3Si$ $[M+H]^+$: 415.2663, found, 415.2697; $[\alpha]_D^{25.0}$ –35.4° (*c* 0.10, $CHCl_3$).



(1*R*,3a*R*,6a*R*,7*S*,10*R*)-10-((*tert*-Butyldimethylsilyl)oxy)-4-(hydroxymethyl)-5-methyl-7-(prop-1-en-2-yl)-1,2,3,3a,6,6a,7,8,9,10-decahydrobenzo[*e*]azulen-1-ol (46): To a flame-dried round-bottom flask equipped with a magnetic stir bar were added vinyl lactone **45** (29 mg, 0.0699 mmol) and DCM (14 mL). The flask was cooled to 0 ºC and stirred for 10 min. A solution of DIBAL (1 M in DCM, 0.35 mL, 0.35 mmol) was added dropwise. The reaction mixture was slowly warmed up to 23 ºC and remained to stir for 24 h. The reaction was quenched by methanol (0.35 mL). Saturated aqueous potassium sodium tartrate solution (3 mL) was added to the mixture. The phases were separated and the aqueous phases were extracted with DCM (5 x 10 mL). The combined organic phases were dried over $MgSO_4$, filtered, and transferred to round-bottom flask. The mixture was concentrated under reduced pressure and dissolved in benzene. The flask was immersed in a 50 ºC oil bath. After 4 h of stirring, the reaction was cooled to ambient temperature and concentrated under reduced pressure. The residue was purified by flash column chromatography (1:1 hexanes: EtOAc) to afford diol **46** as a white solid (9.0 mg, 0.215 mmol, 31% yield); R_f = 0.08 (3:1 hexanes: EtOAc); ^{1}H NMR (600 MHz, C_6D_6) 5.00 (dd, *J* = 4.1, 1.9 Hz, 1H), 4.92–4.89 (m, 1H), 4.87 (d, *J* = 2.2 Hz, 1H), 4.83 (d, *J* = 4.2 Hz, 1H), 4.16 (d, *J* = 11.3 Hz,

1H), 3.91 (d, *J* = 11.3 Hz, 1H), 3.56–3.49 (m, 1H), 3.06–3.00 (m, 1H), 2.85 (dd, *J* = 13.8, 4.5 Hz, 1H), 2.38 (dtd, *J* = 13.7, 11.8, 6.1 Hz, 1H), 2.28–2.13 (m, 2H), 2.04 (dd, *J* = 14.7, 11.4 Hz, 1H), 1.92–1.84 (m, 2H), 1.81 (d, *J* = 1.7 Hz, 3H), 1.77 (d, *J* = 1.2 Hz, 3H), 1.76–1.70 (m, 1H), 1.54 (tdd, *J* = 13.0, 4.3, 2.0 Hz, 1H), 1.51–1.37 (m, 2H), 1.01 (s, 9H), 0.08 (s, 3H), 0.08 (s, 3H); δ ^{13}C NMR (101 MHz, DMSO-*d6*) 148.5, 140.1, 138.8, 137.8, 132.4, 111.9, 71. 3, 68.8, 57.9, 49.1, 42.1, 34.4, 34.0, 33.8, 29.3, 26.7, 26.6, 25.8, 25.7, 21.5, 17.7, –4.5, –4.7; IR (Neat Film, NaCl) 3342, 2929, 2856, 1645, 1451, 1254, 1163, 1079, 1033, 890, 836, 773, 739, 702 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{25}H_{41}O_3Si$ $[M+H-H_2]^+$: 417.2825, found 417.2833; $[\alpha]_D^{25.0}$ –27.6° (*c* 0.10, CH_3OH).

2. References

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(5) Wang, Q.; Fan, S. Y.; Wong, H. N. C.; Li, Z.; Fung, B. M.; Twieg, R. J.; Nguyen, H. T., Enantioselective Synthesis of Chiral Liquid Crystalline Compounds from Monoterpenes. *Tetrahedron* **1993**, *49*, 619–638.

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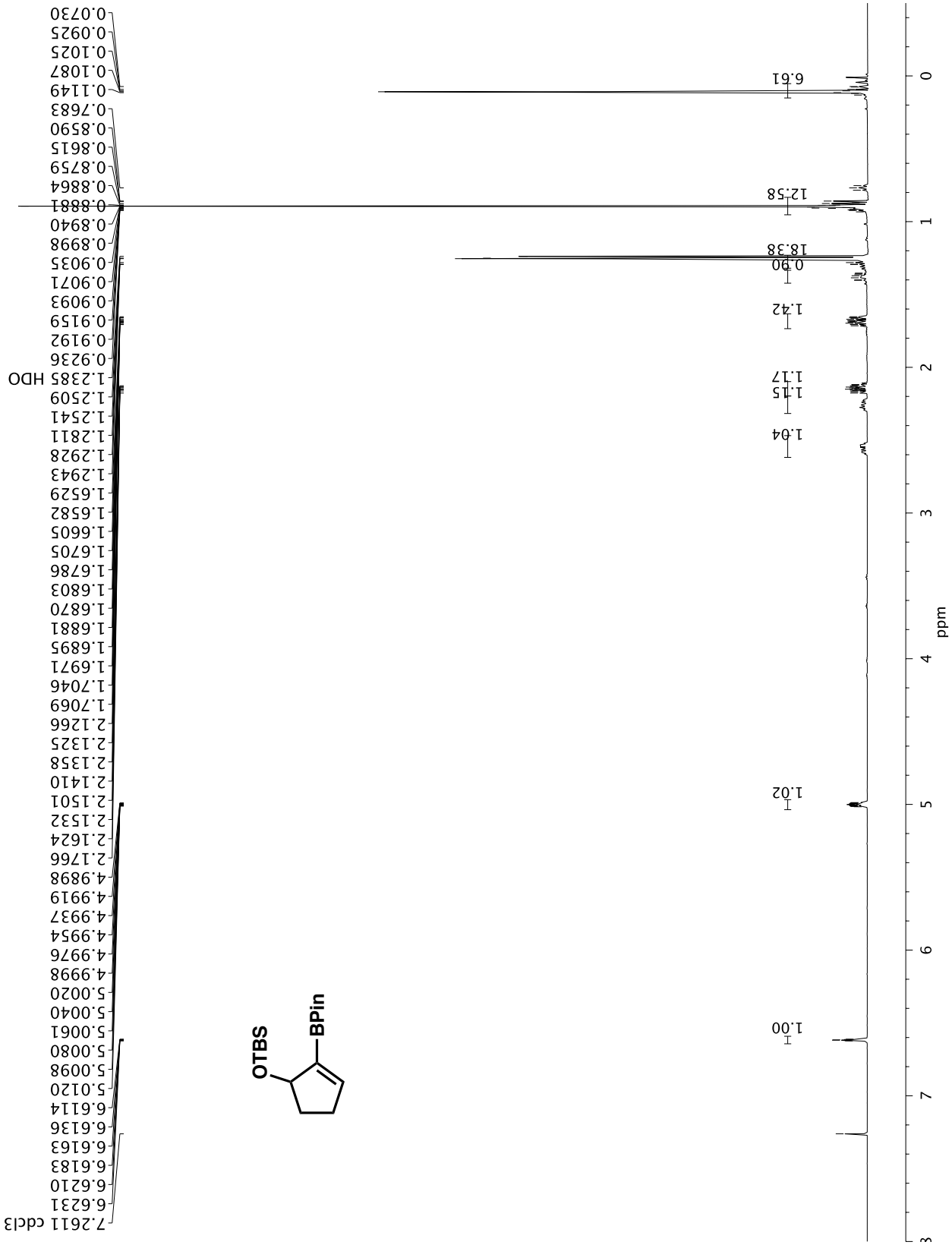
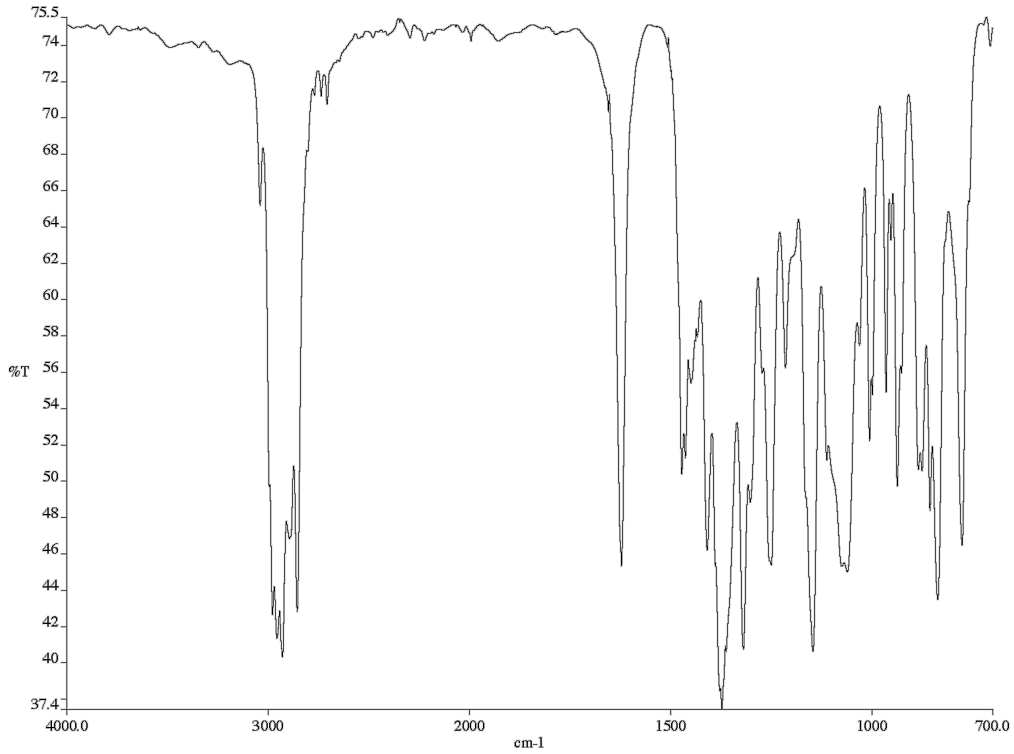
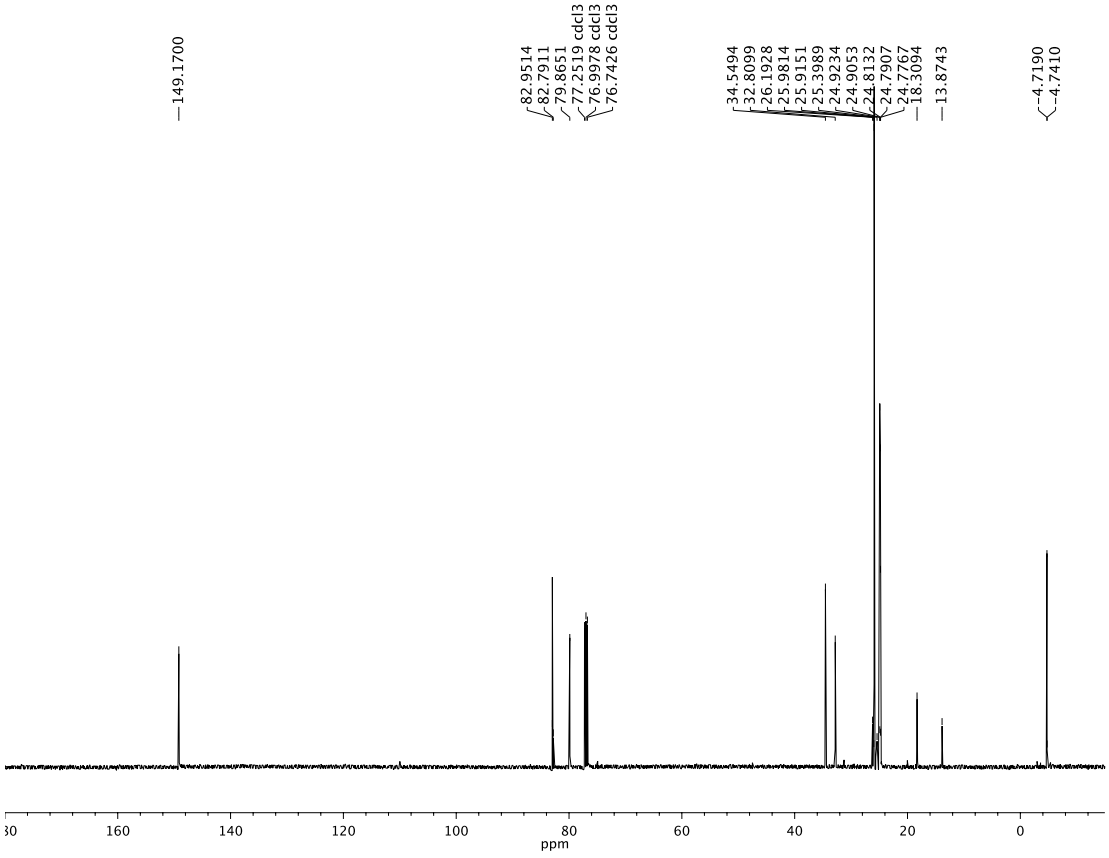
3. NMR and IR Spectra of Unknown Compounds



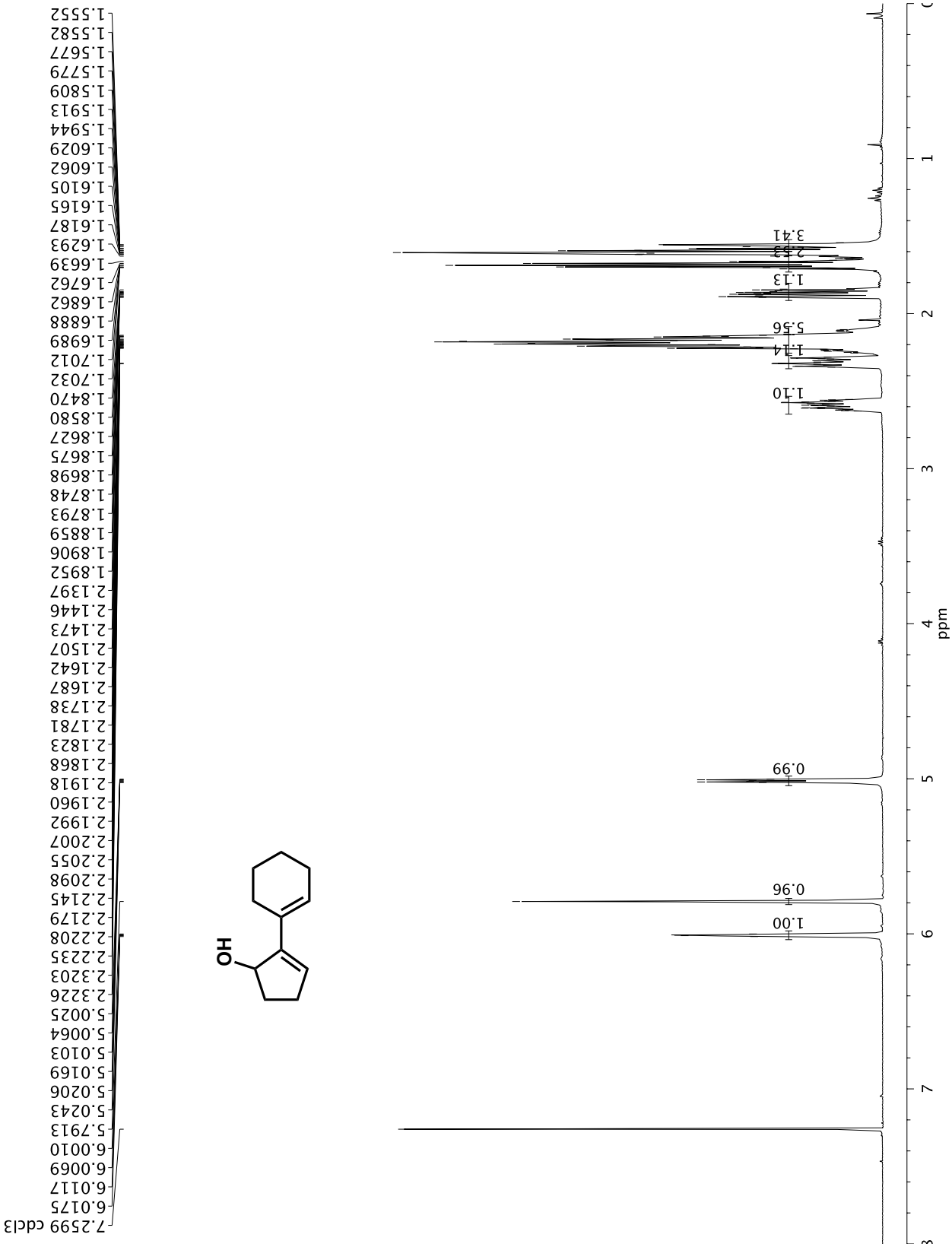
^{1}H NMR (500 MHz, $CDCl_3$) of compound *rac*-**12.**



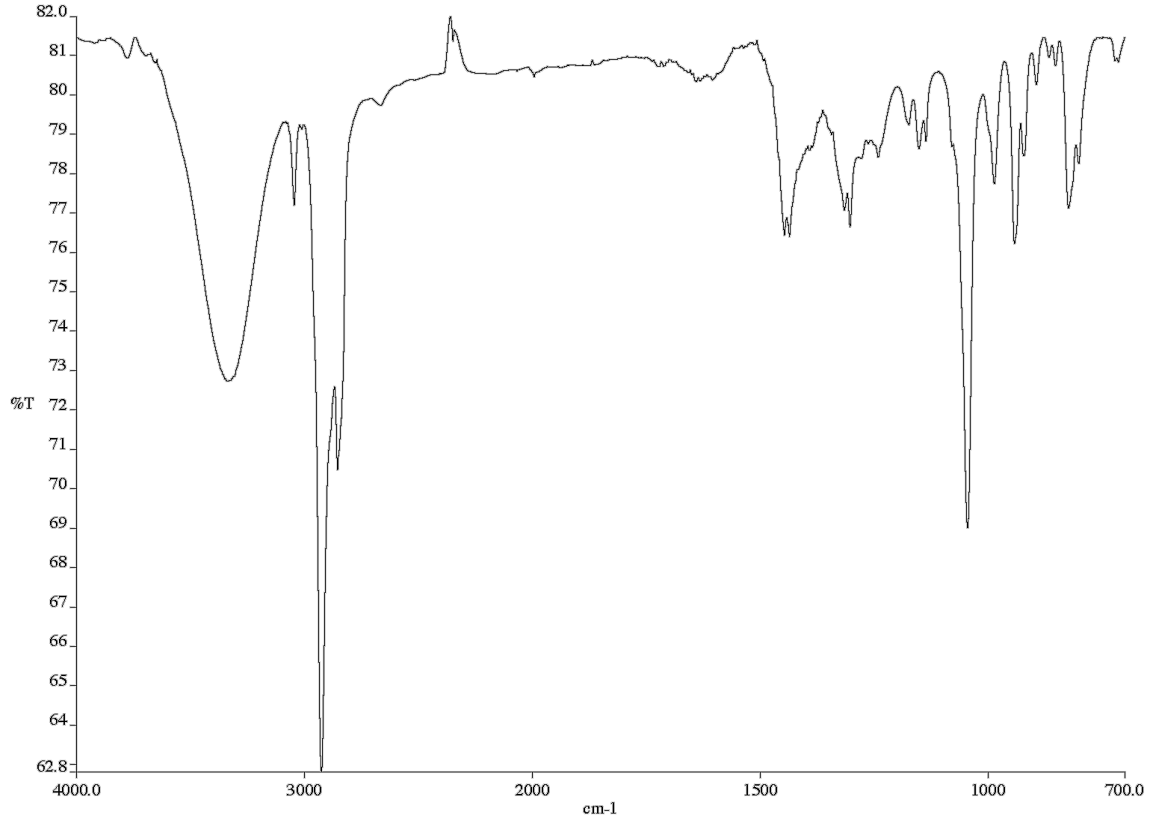
Infrared spectrum (Thin Film, NaCl) of compound *rac*-**12**.



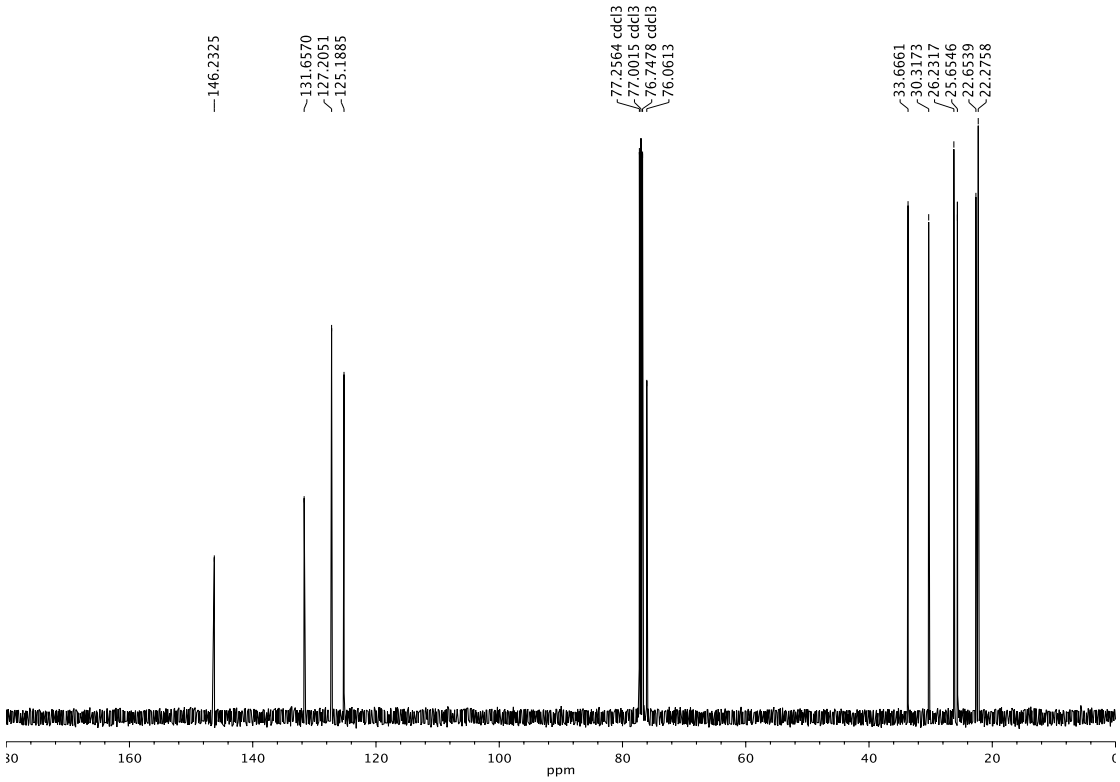
^{13}C NMR (126 MHz, $CDCl_3$) of compound *rac*-**12**.



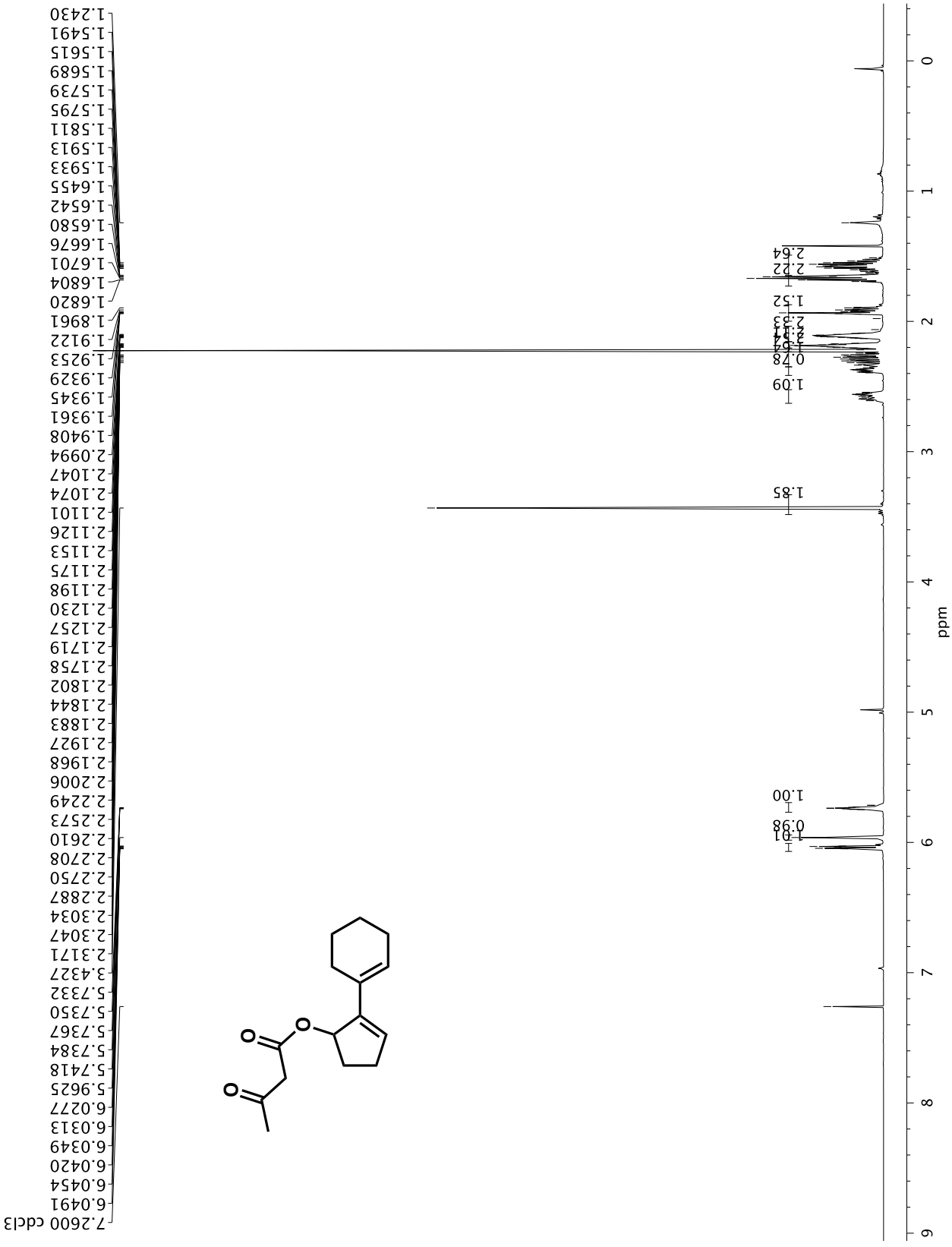
^{1}H NMR (500 MHz, $CDCl_3$) of compound **17.**



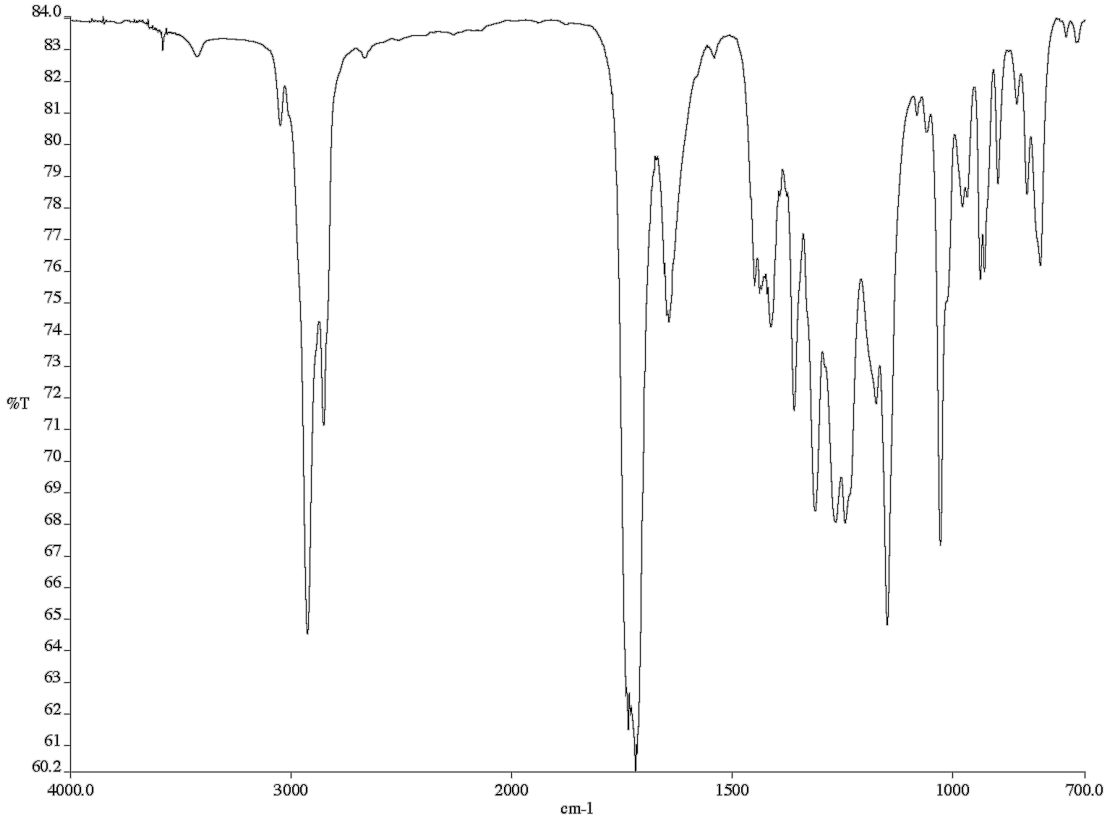
Infrared spectrum (Thin Film, NaCl) of compound **17**.



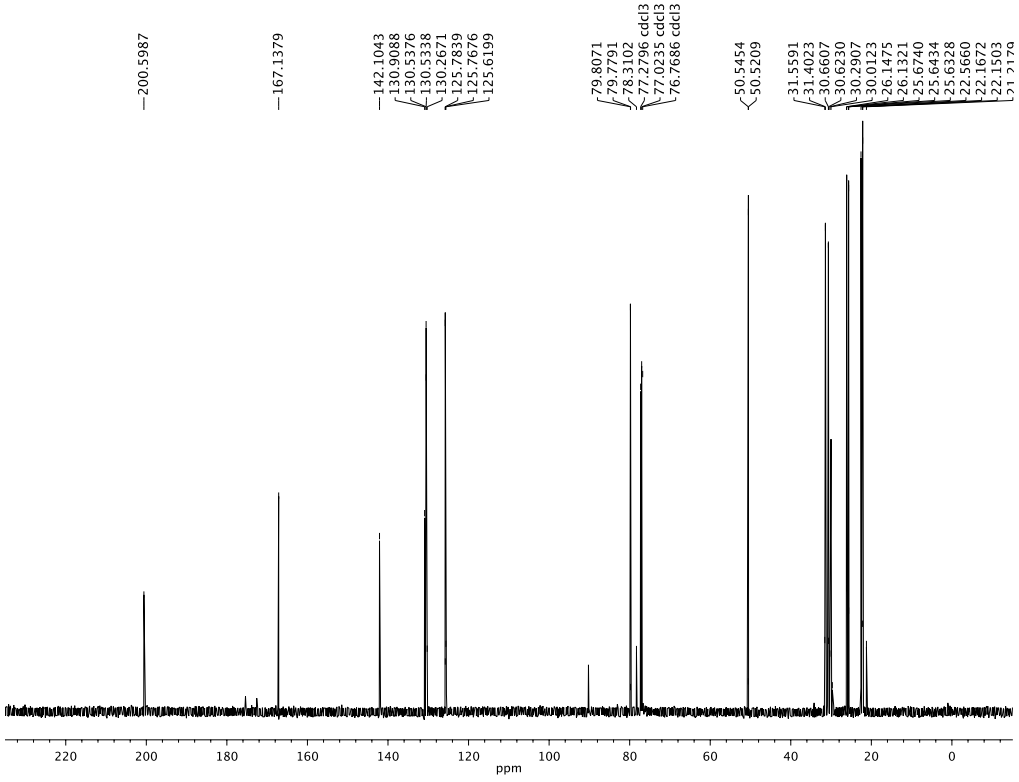
^{13}C NMR (126 MHz, $CDCl_3$) of compound **17**.



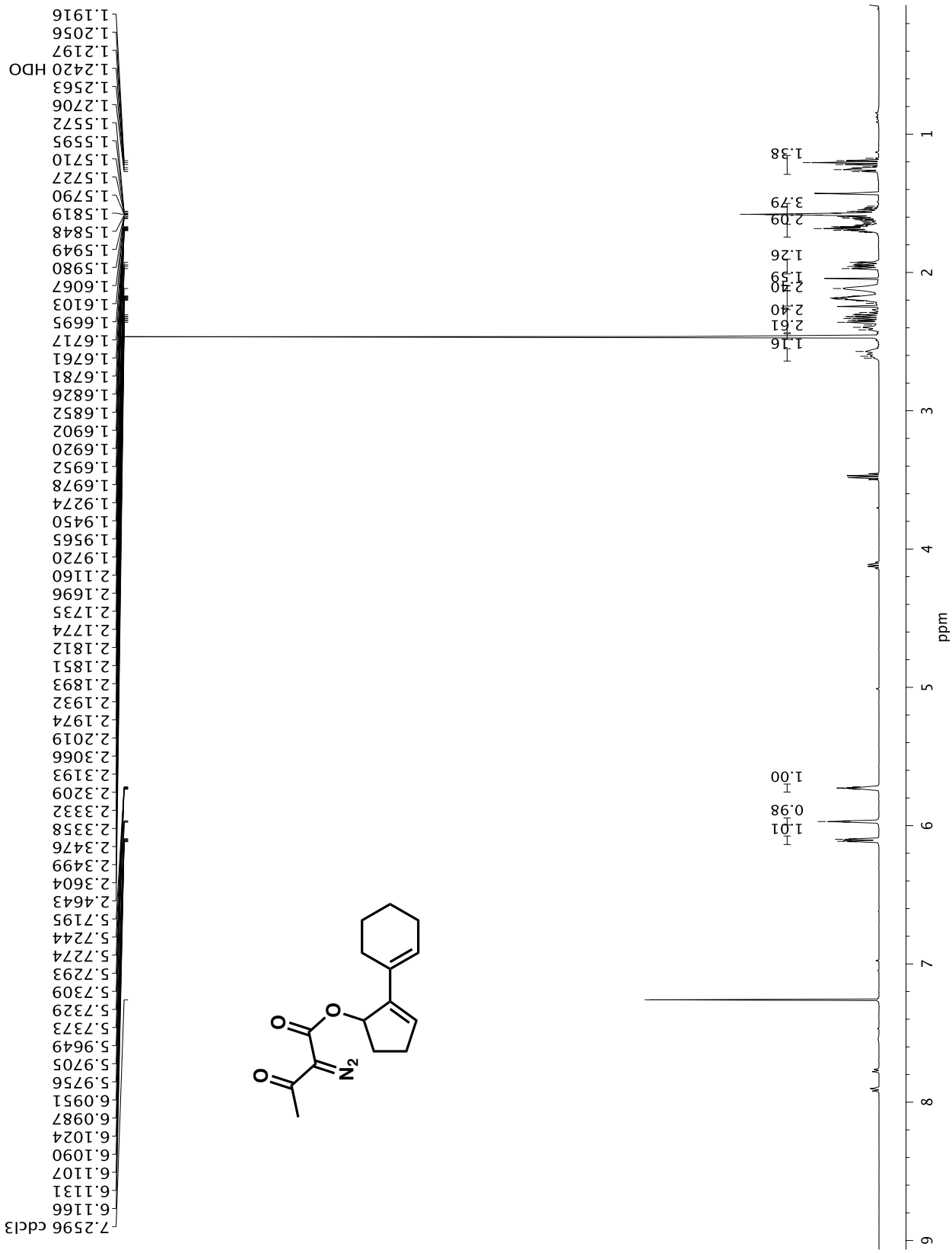
^{1}H NMR (500 MHz, $CDCl_3$) of compound **19.**



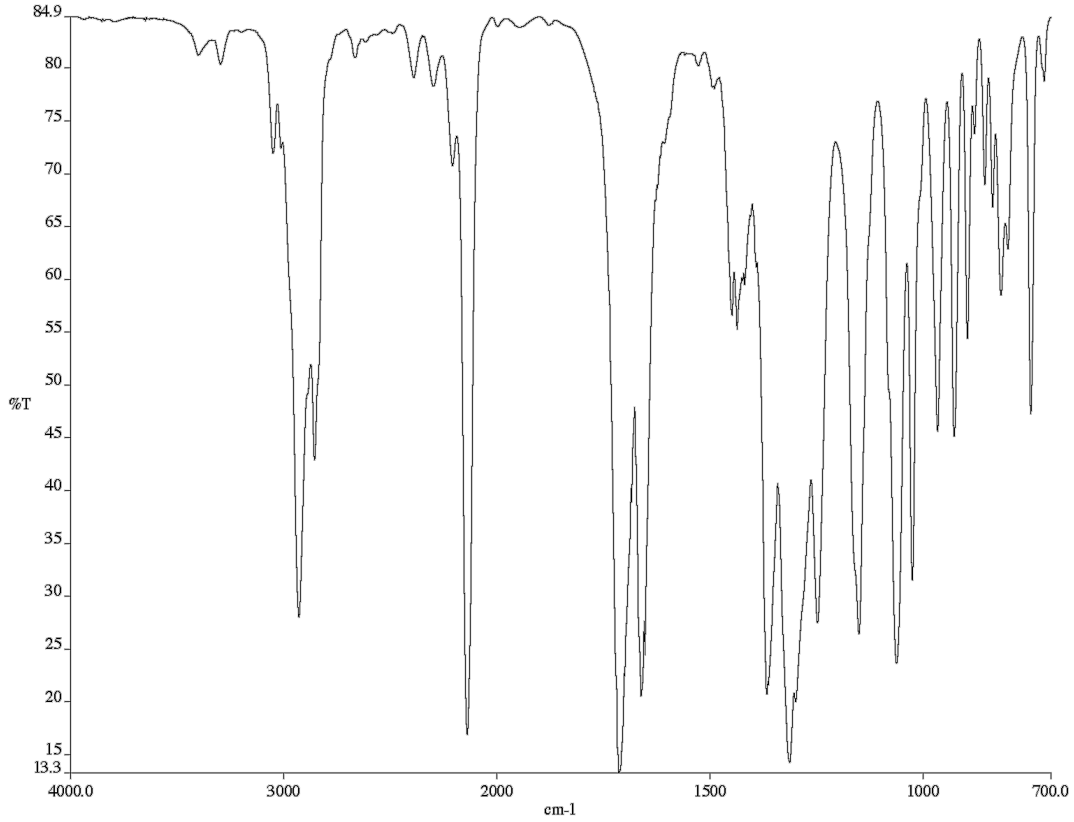
Infrared spectrum (Thin Film, NaCl) of compound **19**.



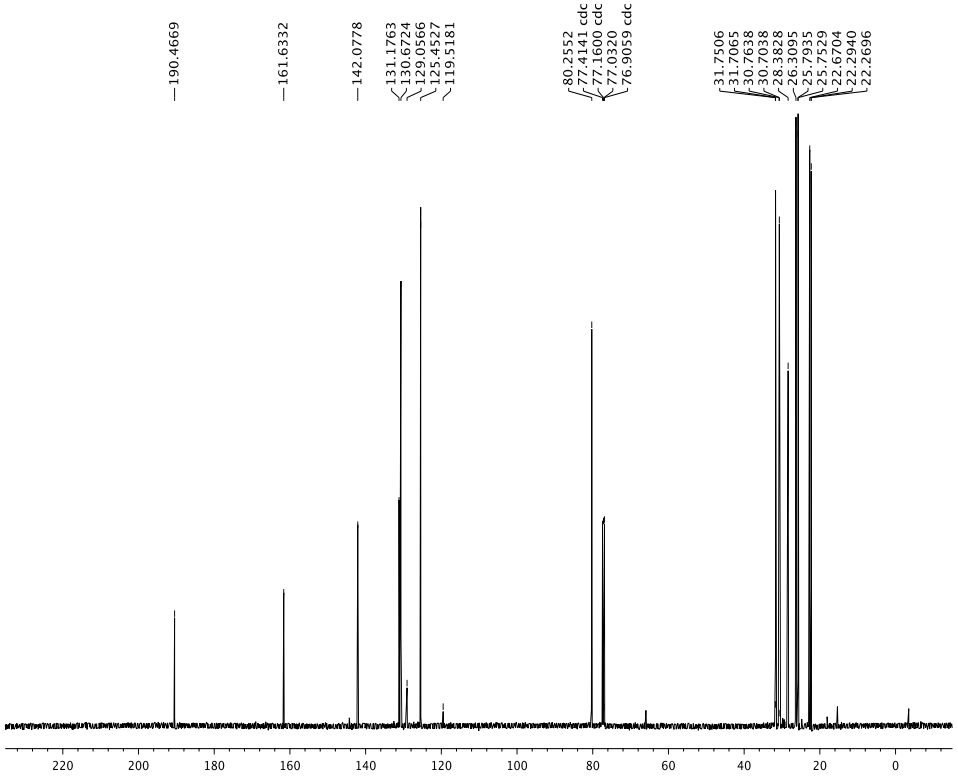
^{13}C NMR (126 MHz, $CDCl_3$) of compound **19**.



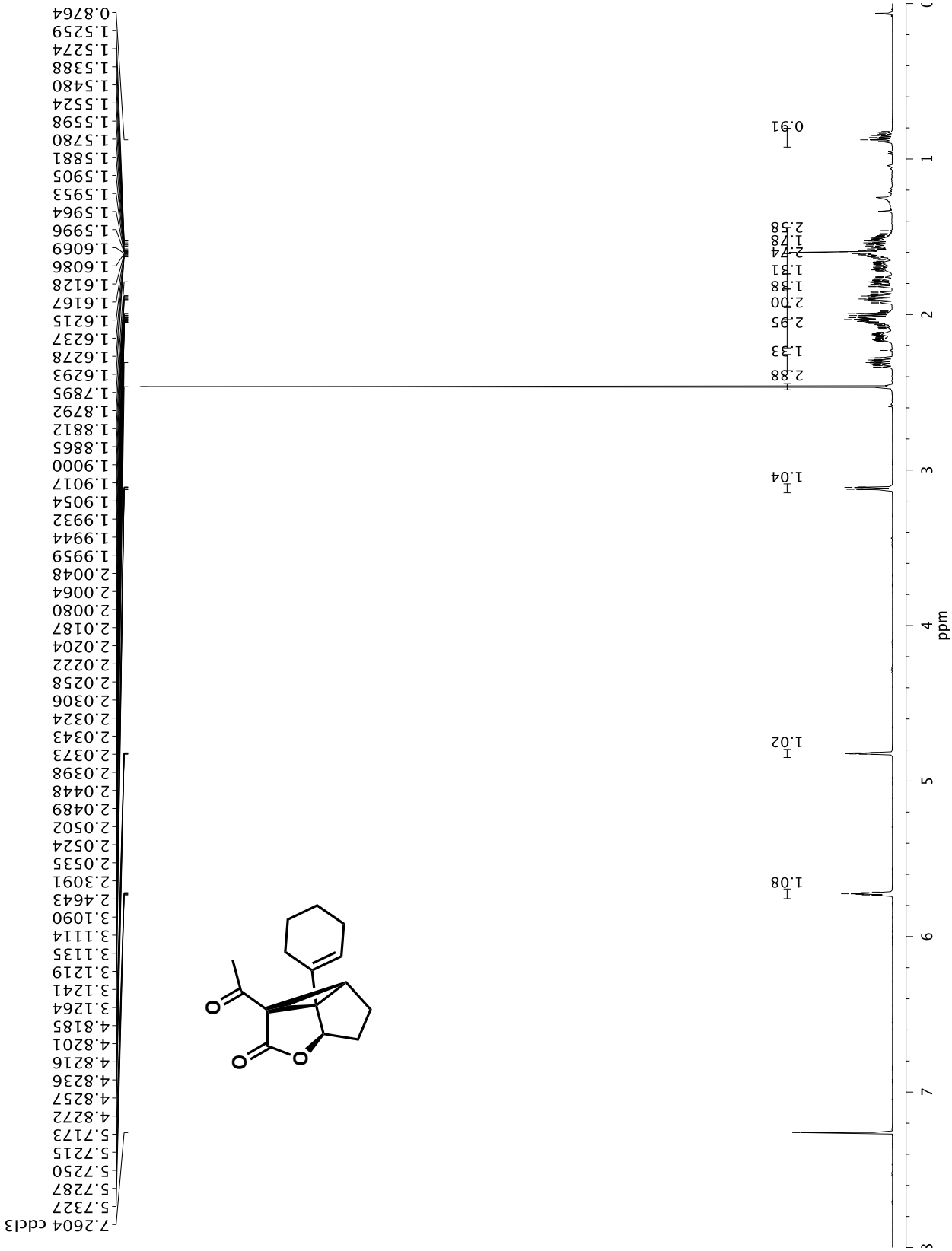
^{1}H NMR (500 MHz, $CDCl_3$) of compound **20.**



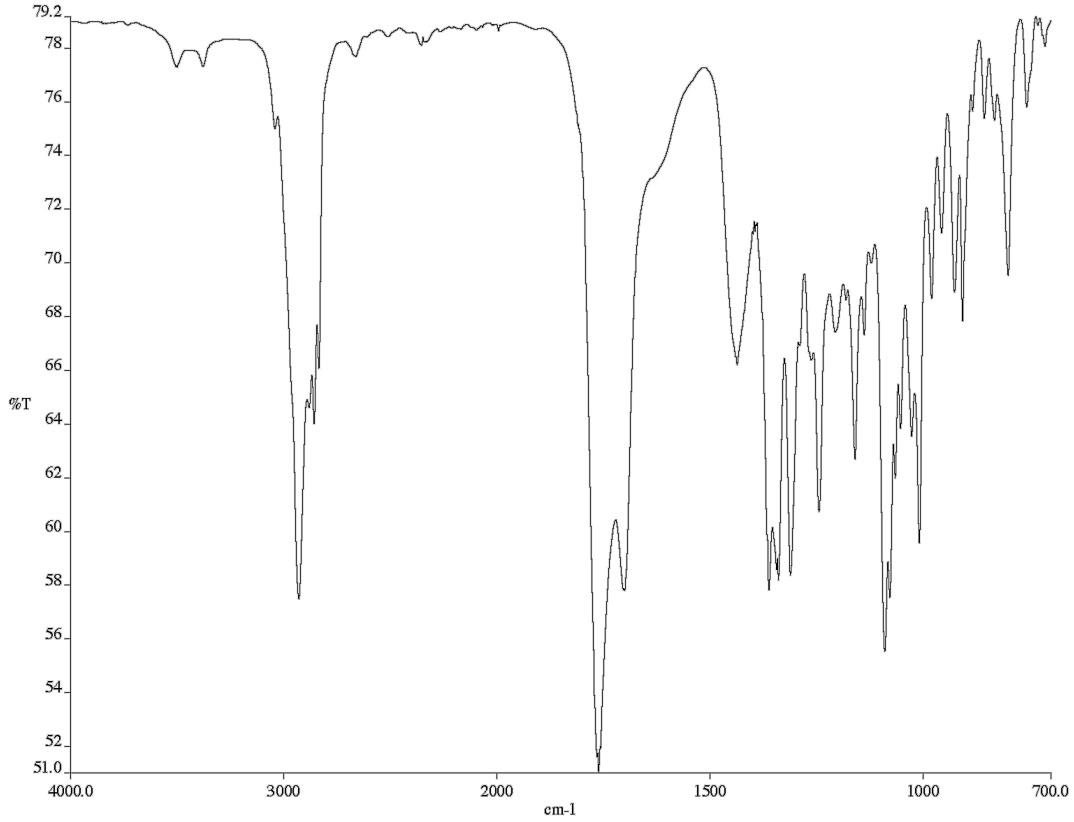
Infrared spectrum (Thin Film, NaCl) of compound **20**.



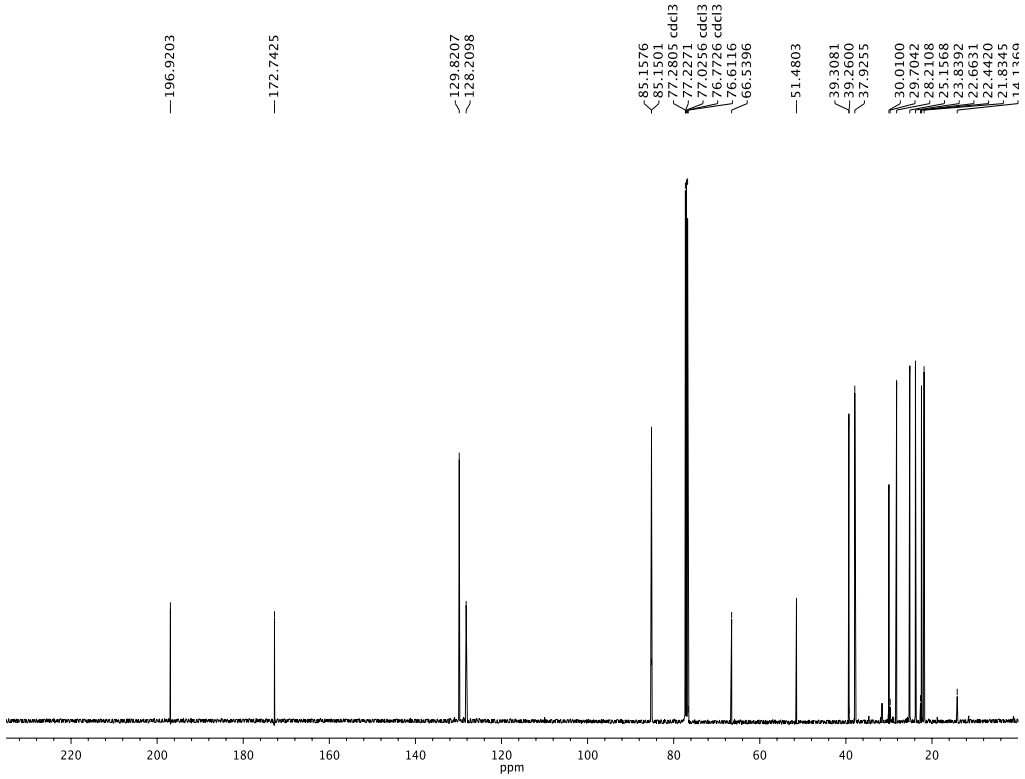
^{13}C NMR (126 MHz, $CDCl_3$) of compound **20**.



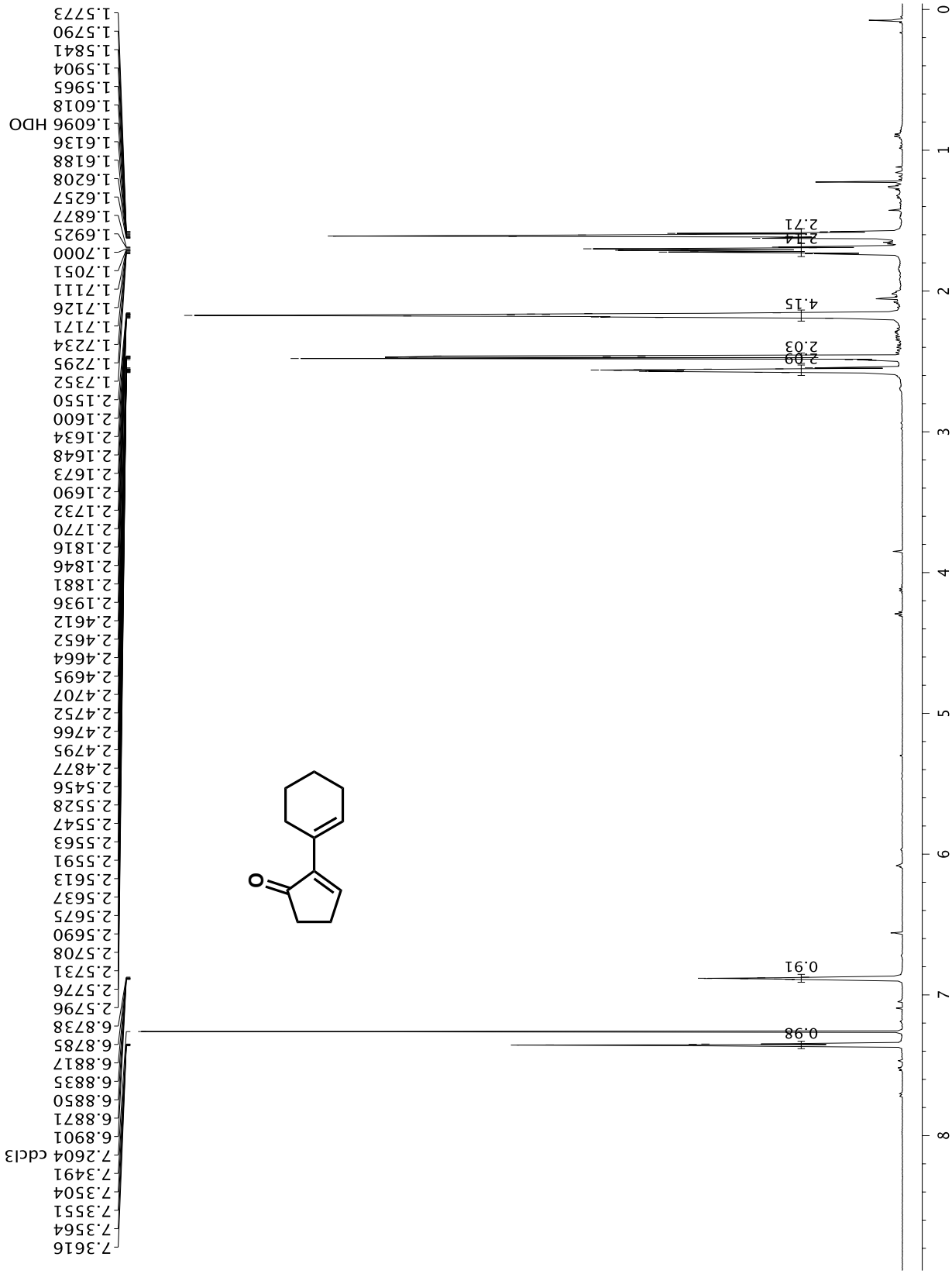
^{1}H NMR (500 MHz, $CDCl_3$) of compound **21.**



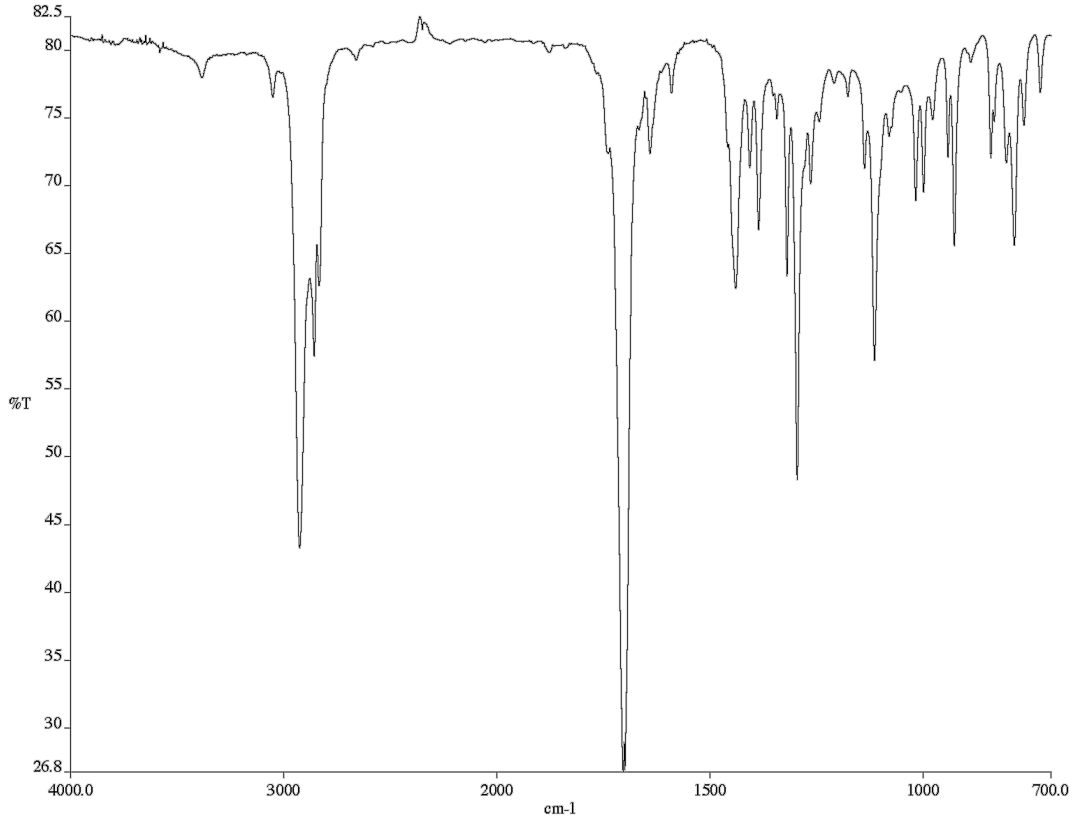
Infrared spectrum (Thin Film, NaCl) of compound **21**.



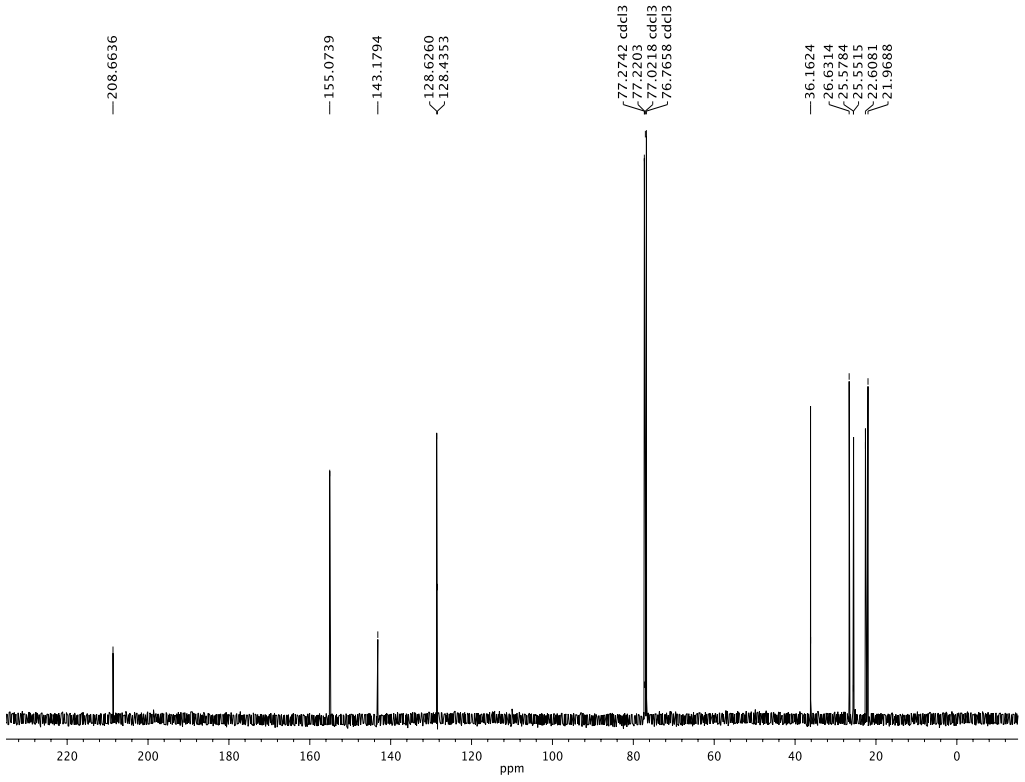
^{13}C NMR (126 MHz, $CDCl_3$) of compound **21**.



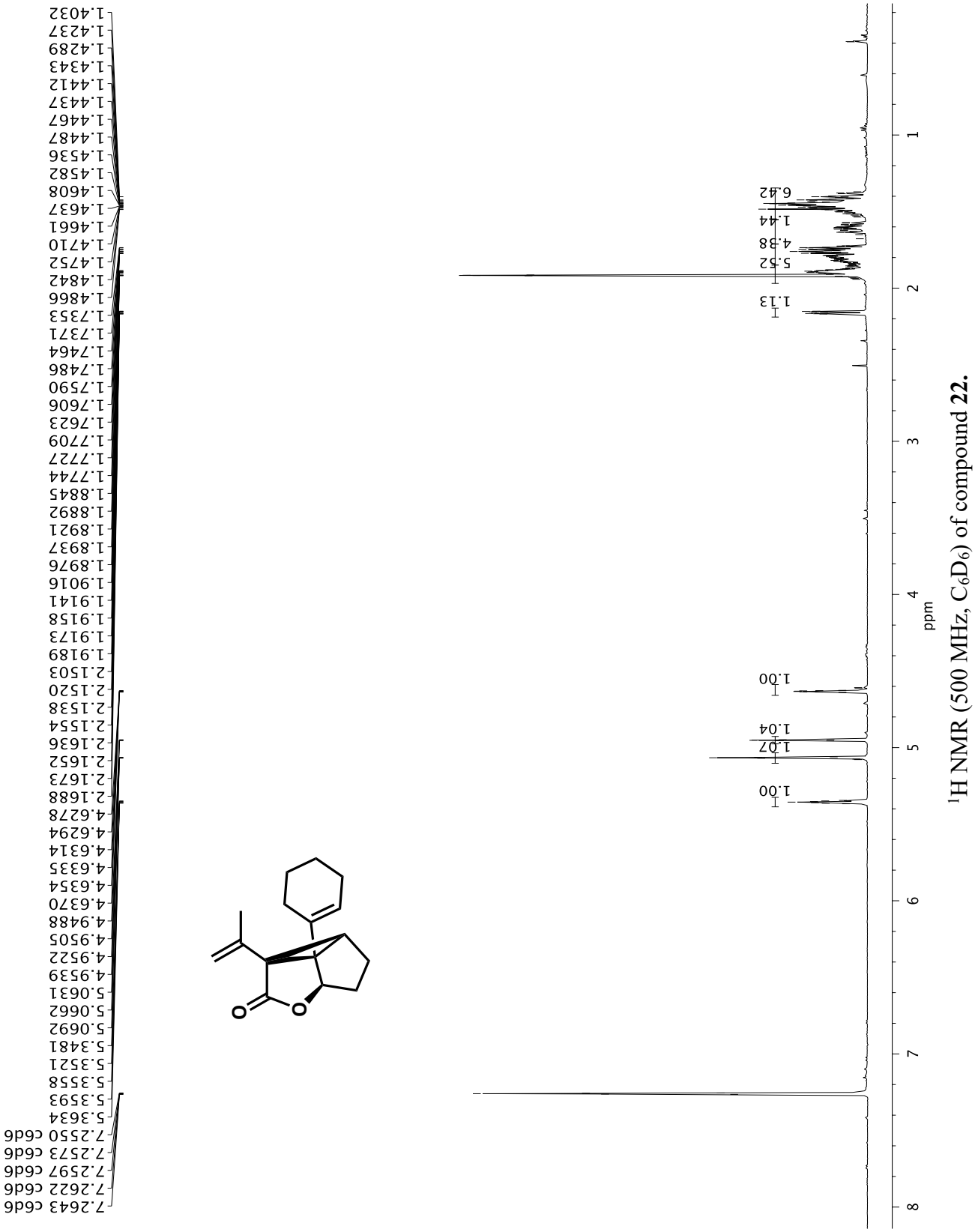
^{1}H NMR (500 MHz, $CDCl_3$) of compound **49.**



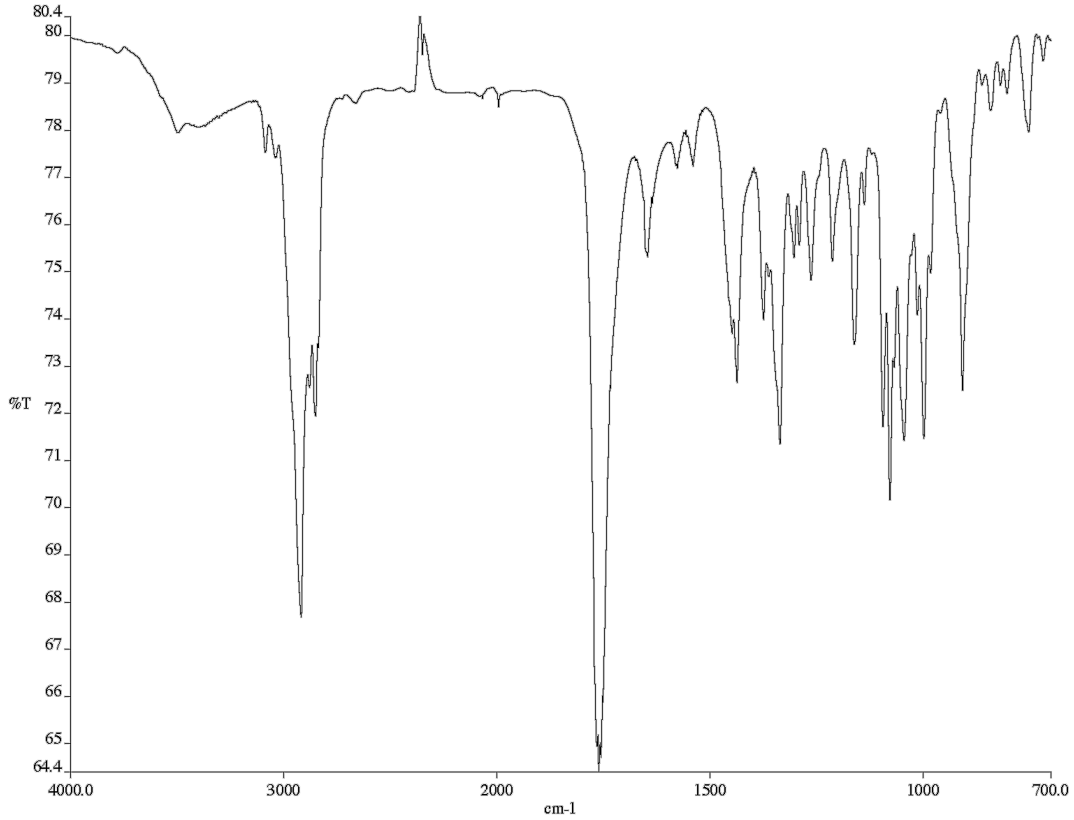
Infrared spectrum (Thin Film, NaCl) of compound **49**.



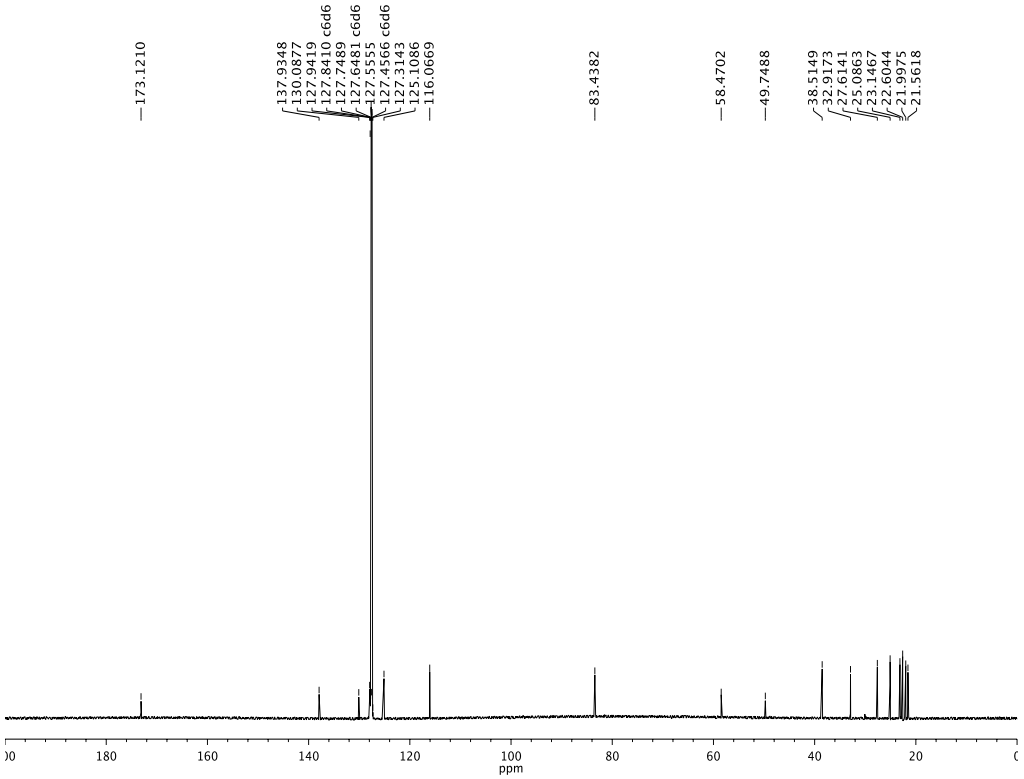
^{13}C NMR (126 MHz, $CDCl_3$) of compound **49**.



^{1}H NMR (500 MHz, C_6D_6) of compound **22.**



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



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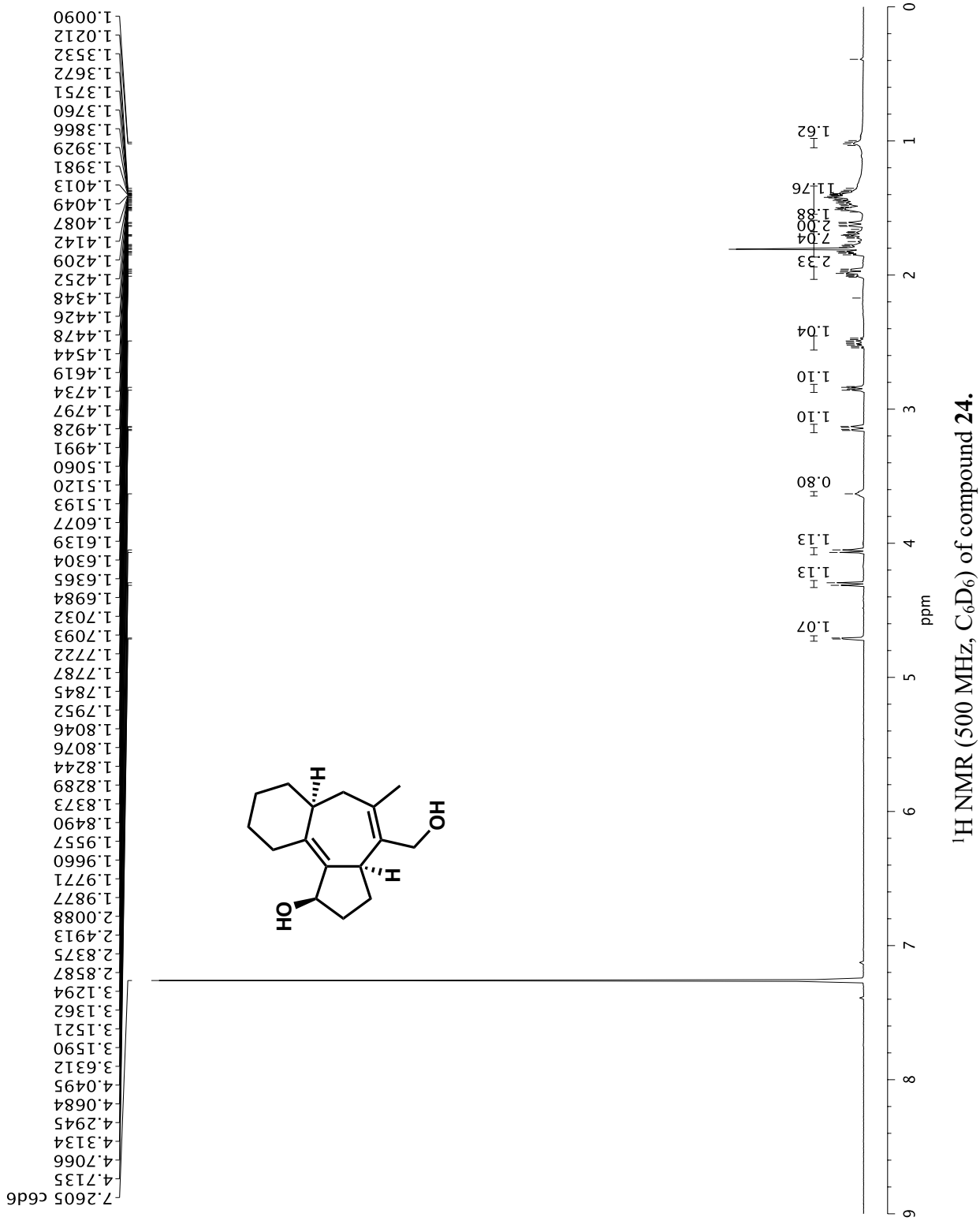
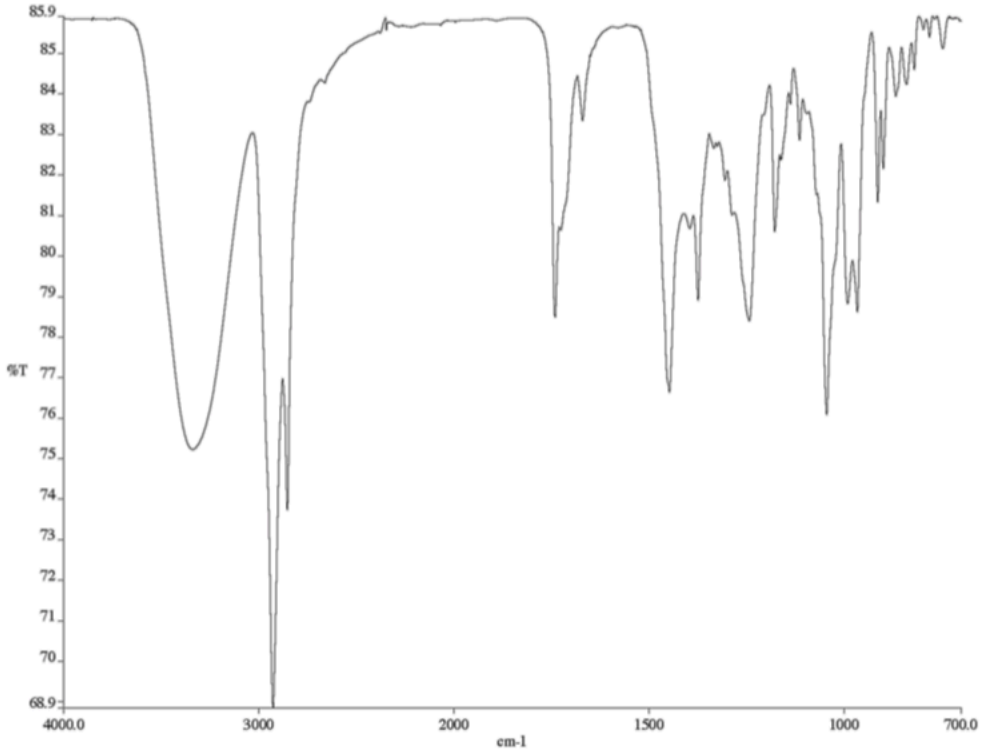
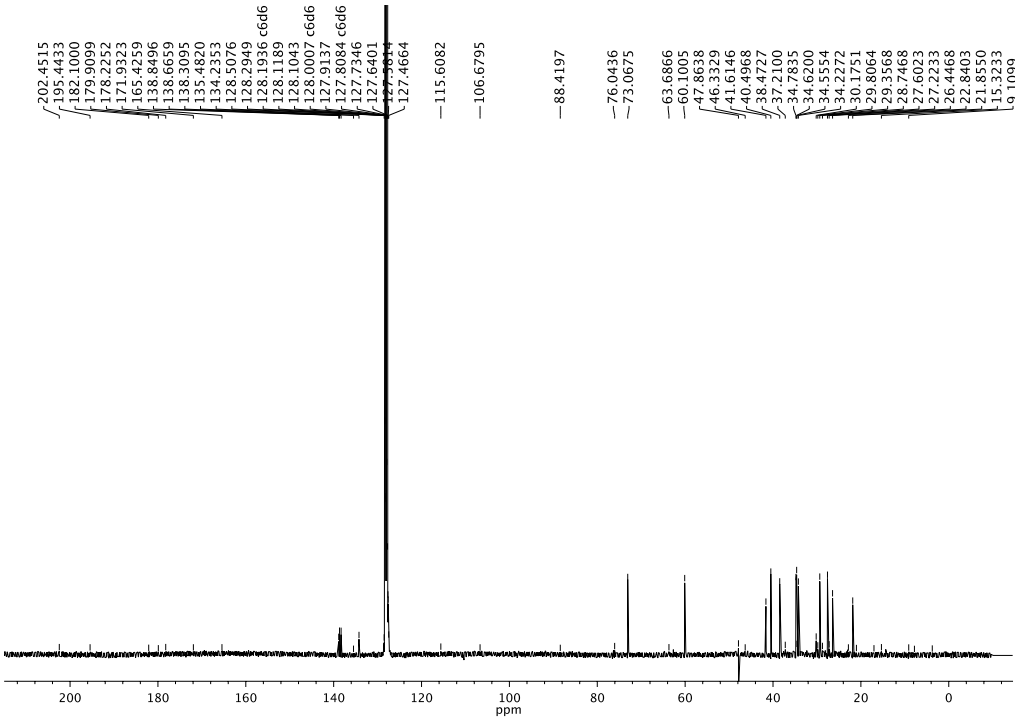


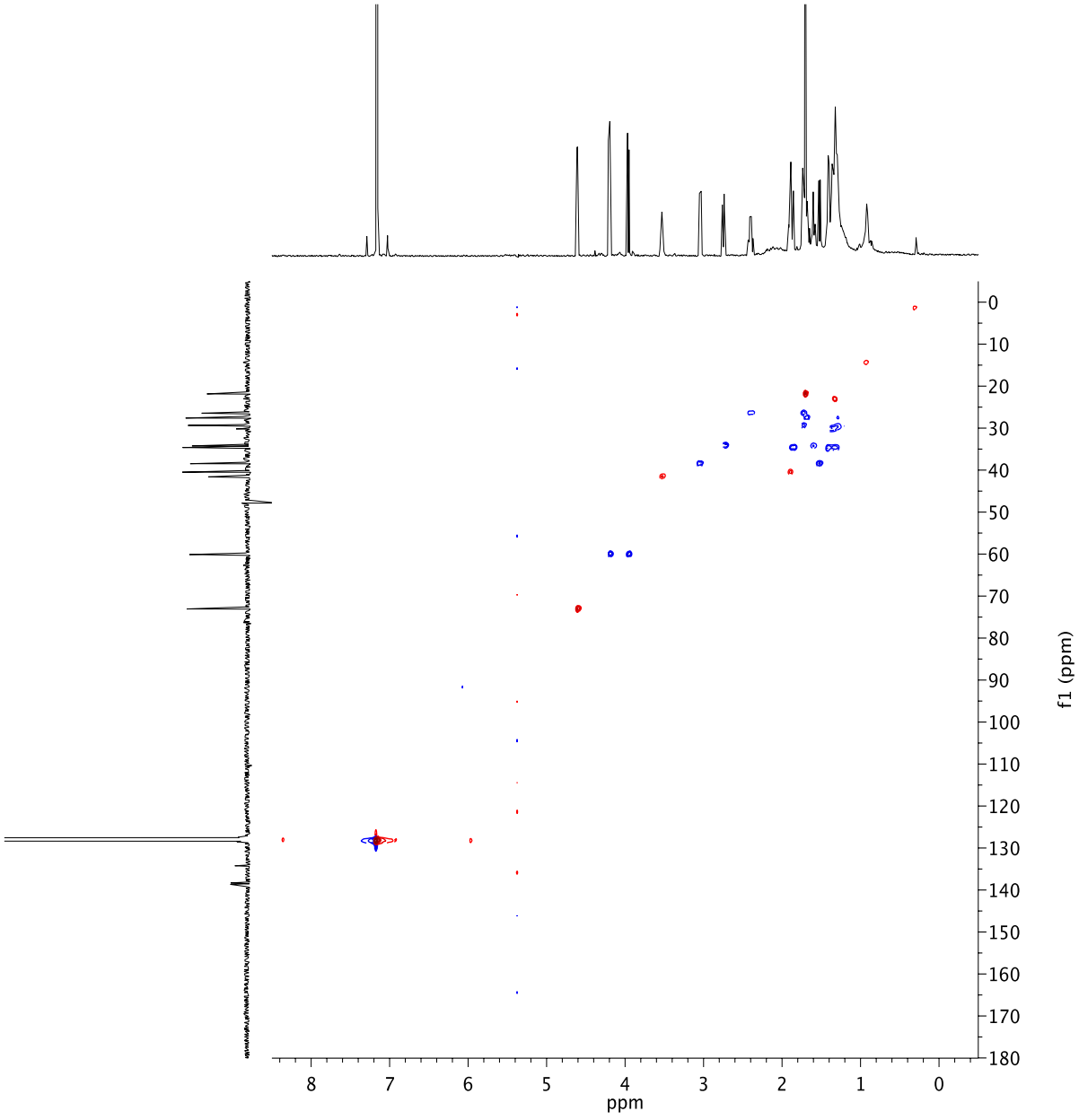
^{1}H NMR (500 MHz, C_6D_6) of compound **24.**



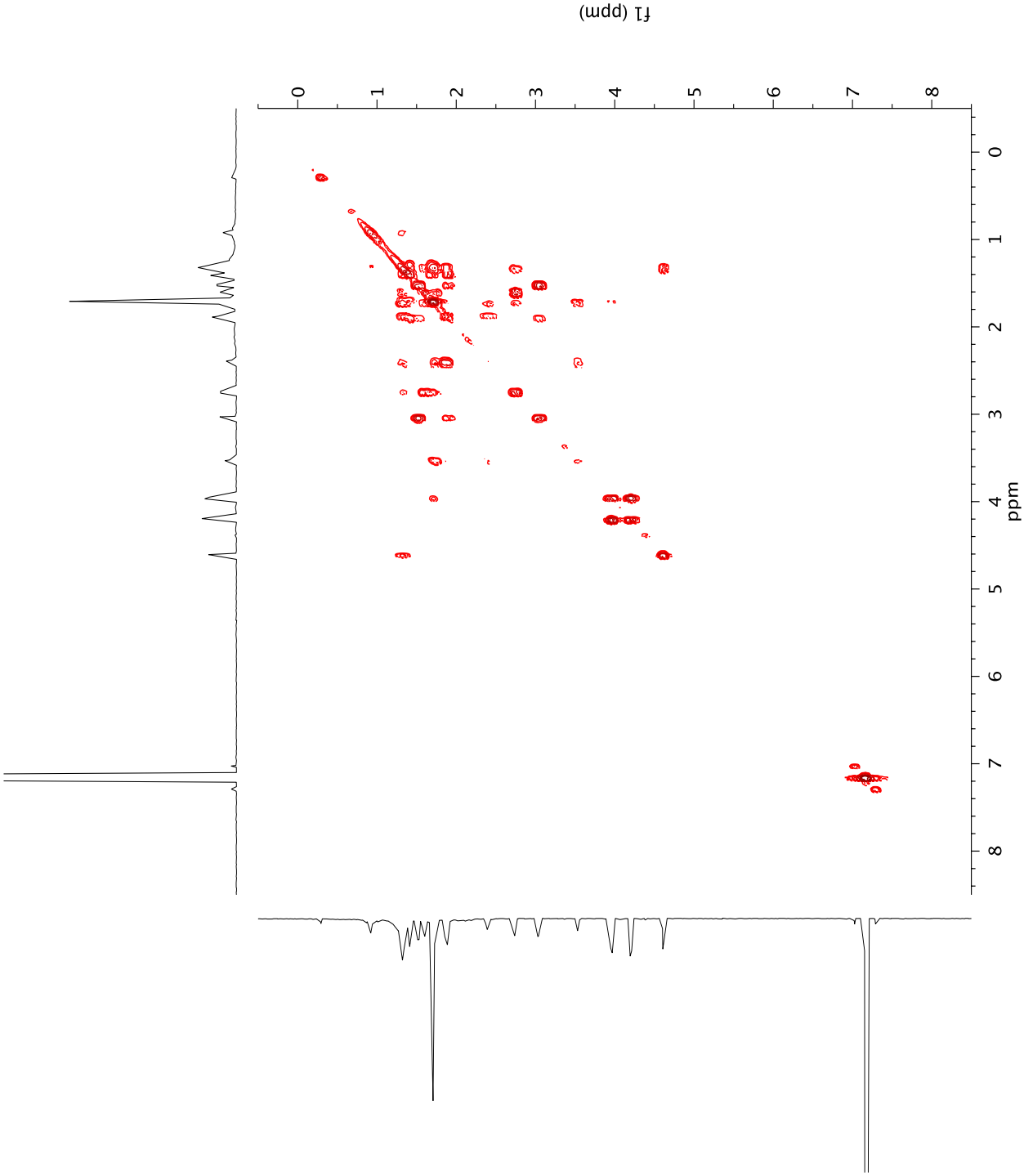
Infrared spectrum (Thin Film, NaCl) of compound **24**.



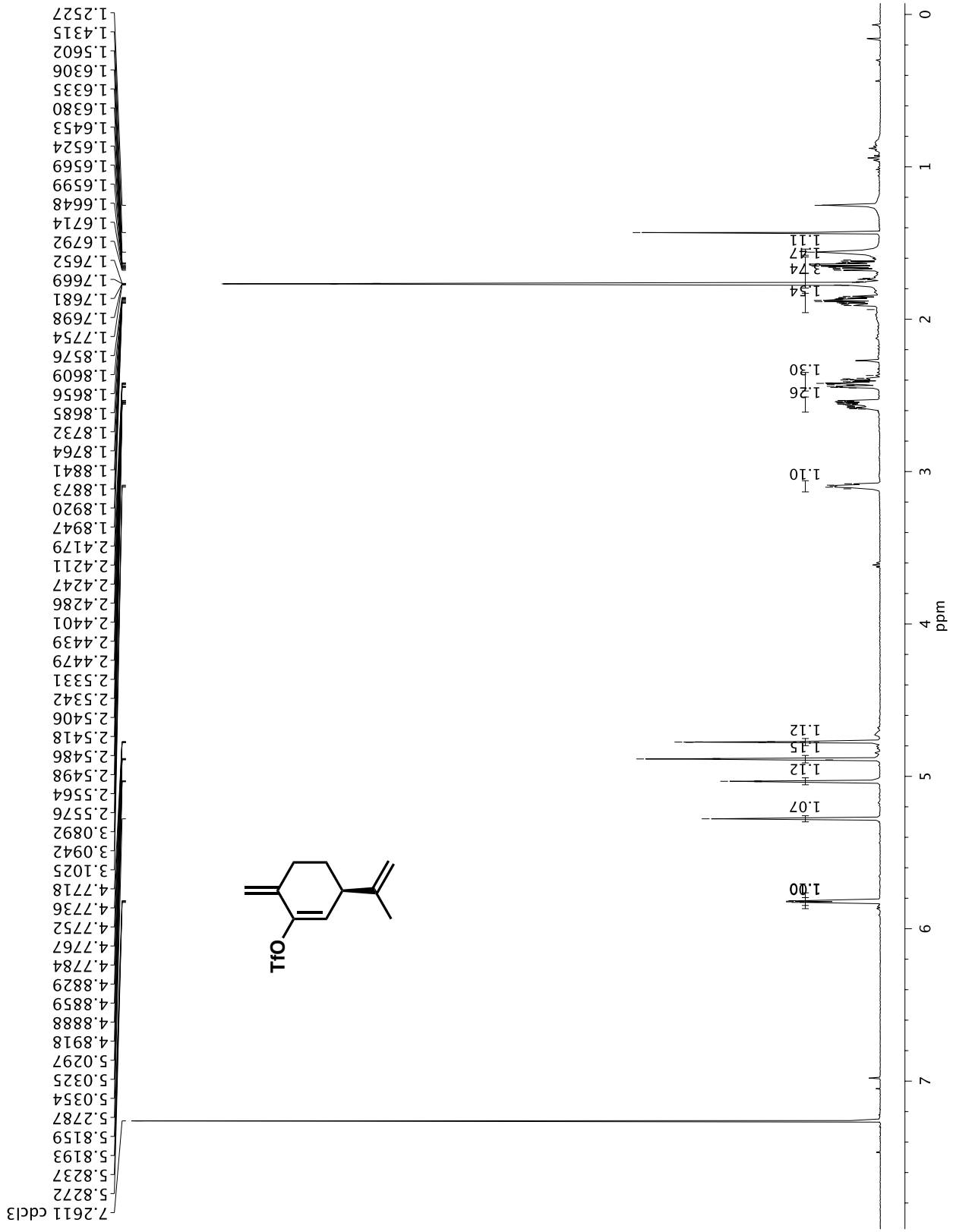
^{13}C NMR (126 MHz, C_6Cl_6) of compound **24**.



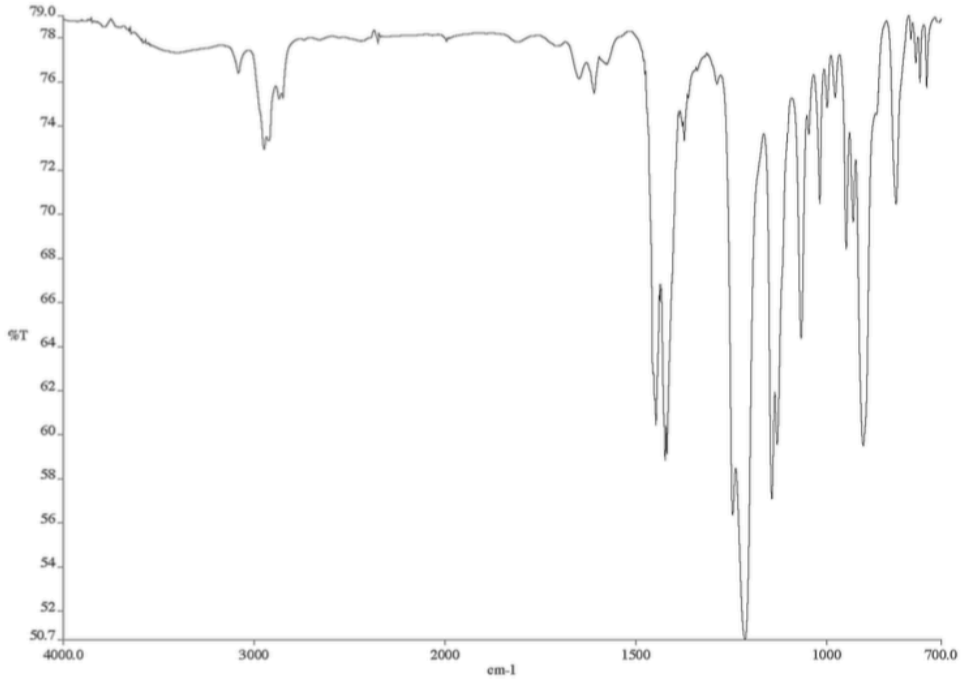
^{1}H–^{13}C HSQC NMR (600 MHz, C_6D_6) of compound **24.**



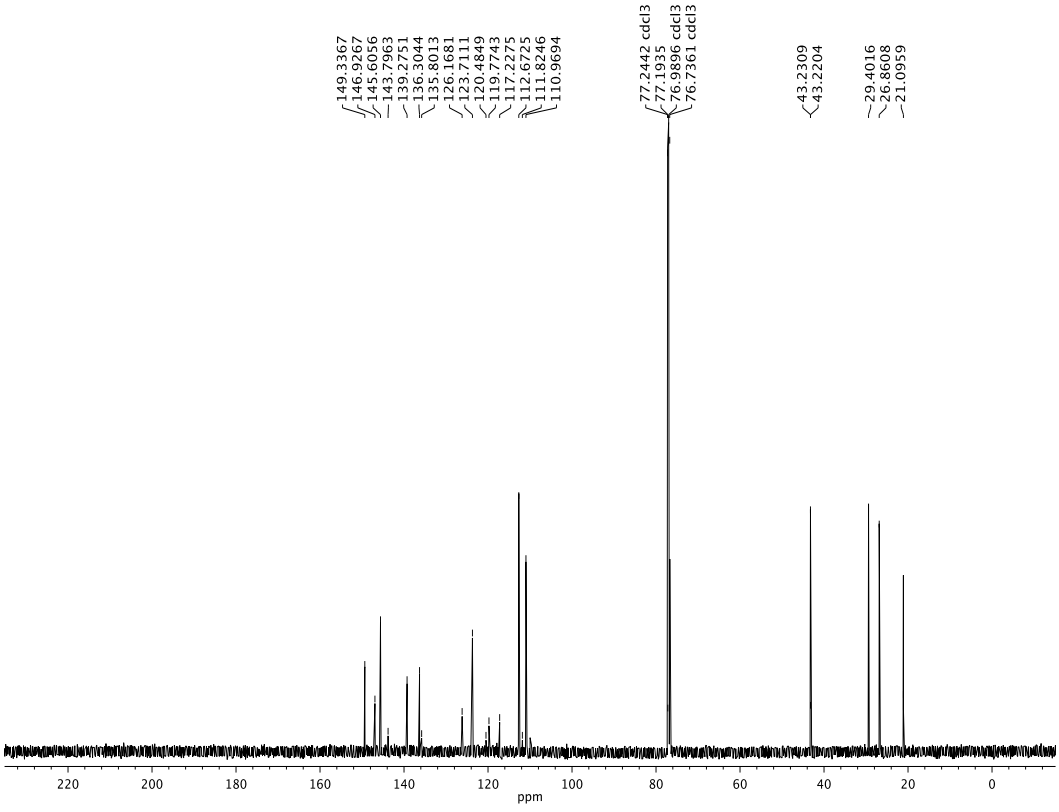
gCOSY NMR (600 MHz, C_6D_6) of compound **24.**



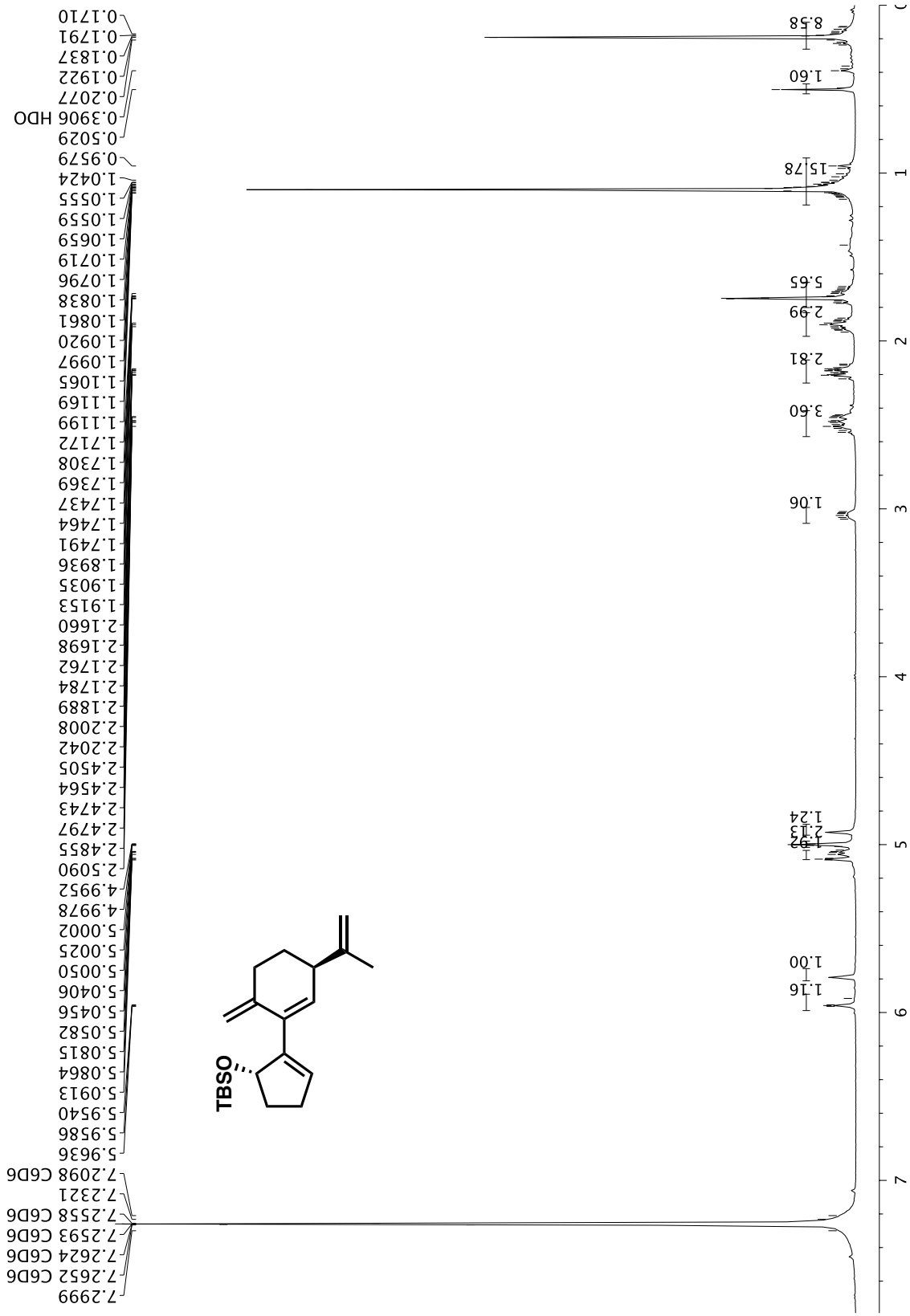
^{1}H NMR (500 MHz, $CDCl_3$) of compound **27.**



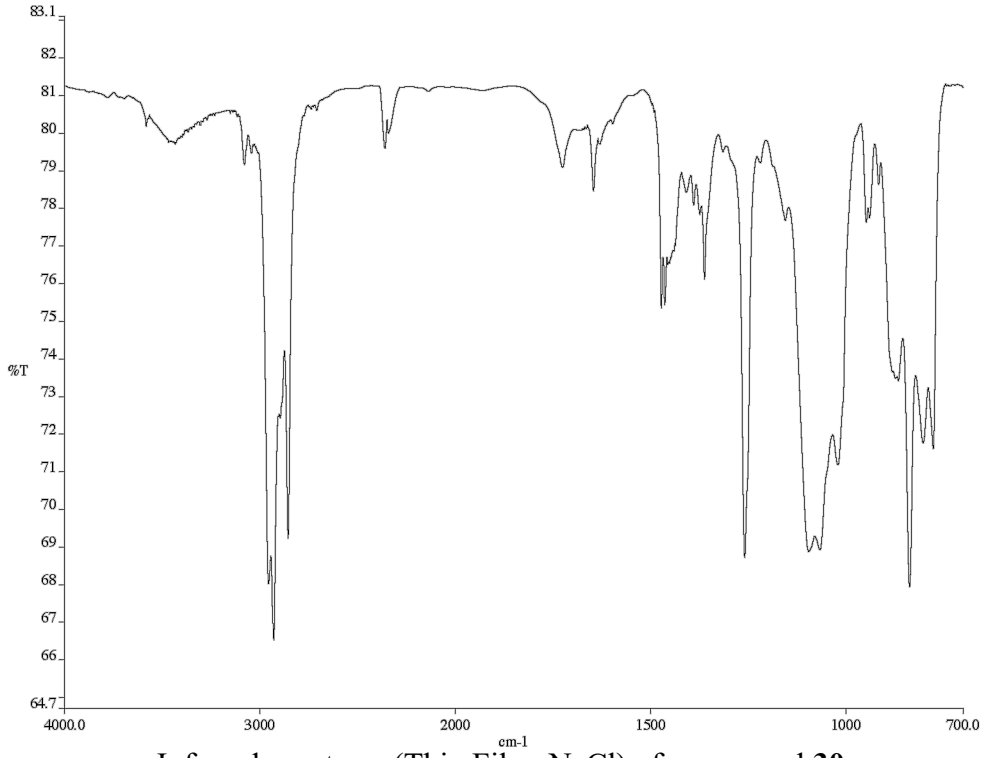
Infrared spectrum (Thin Film, NaCl) of compound **27**.



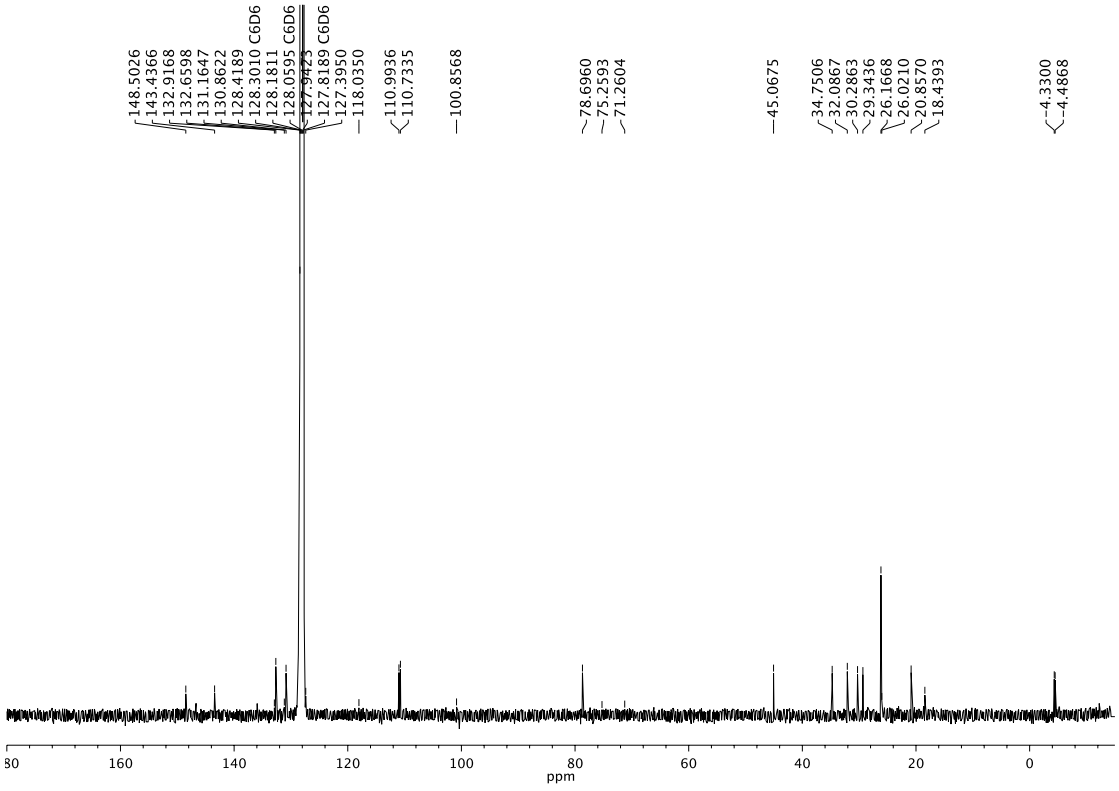
^{13}C NMR (126 MHz, $CDCl_3$) of compound **27**.



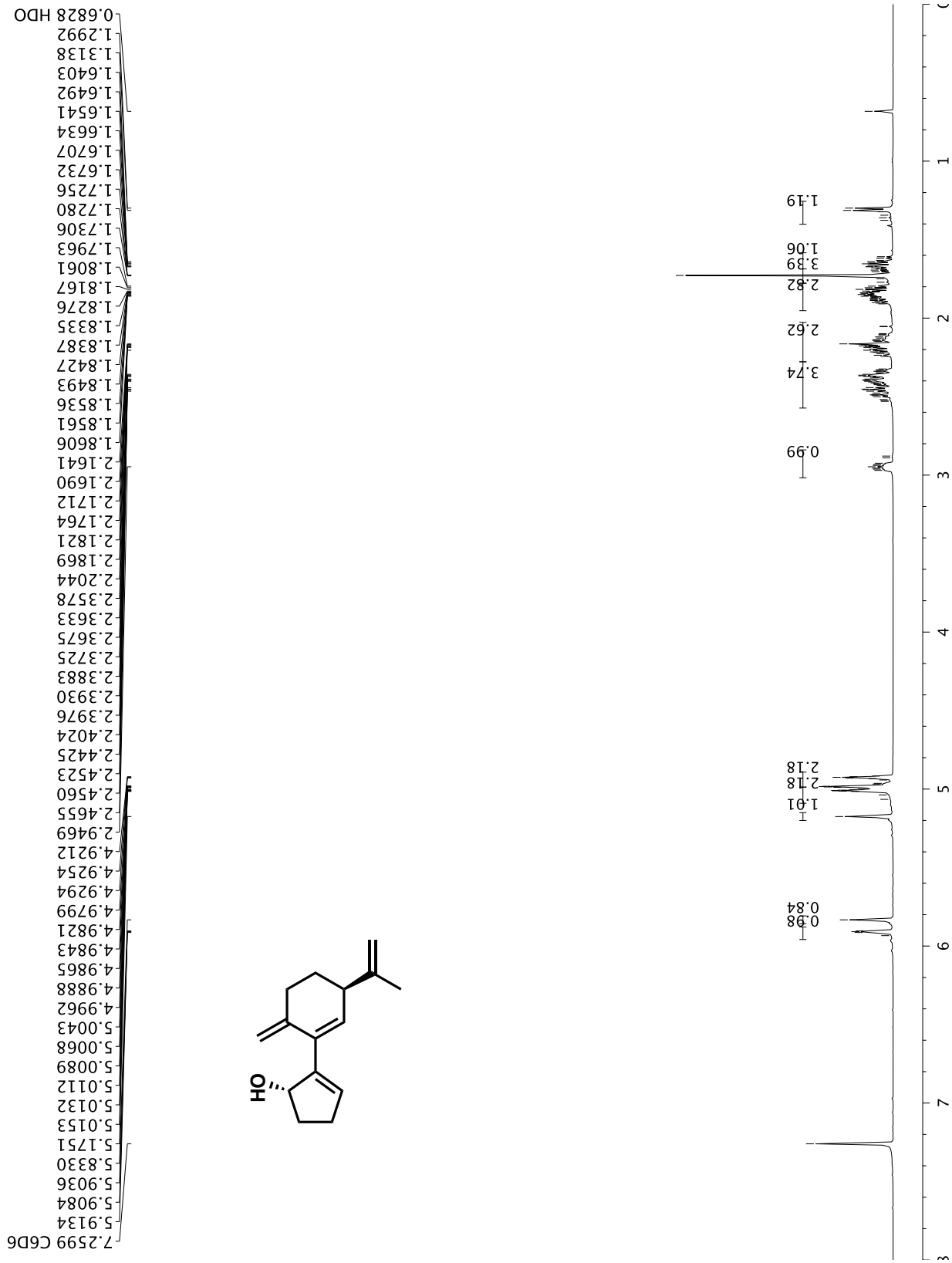
^{1}H NMR (400 MHz, C_6D_6) of compound **30.**



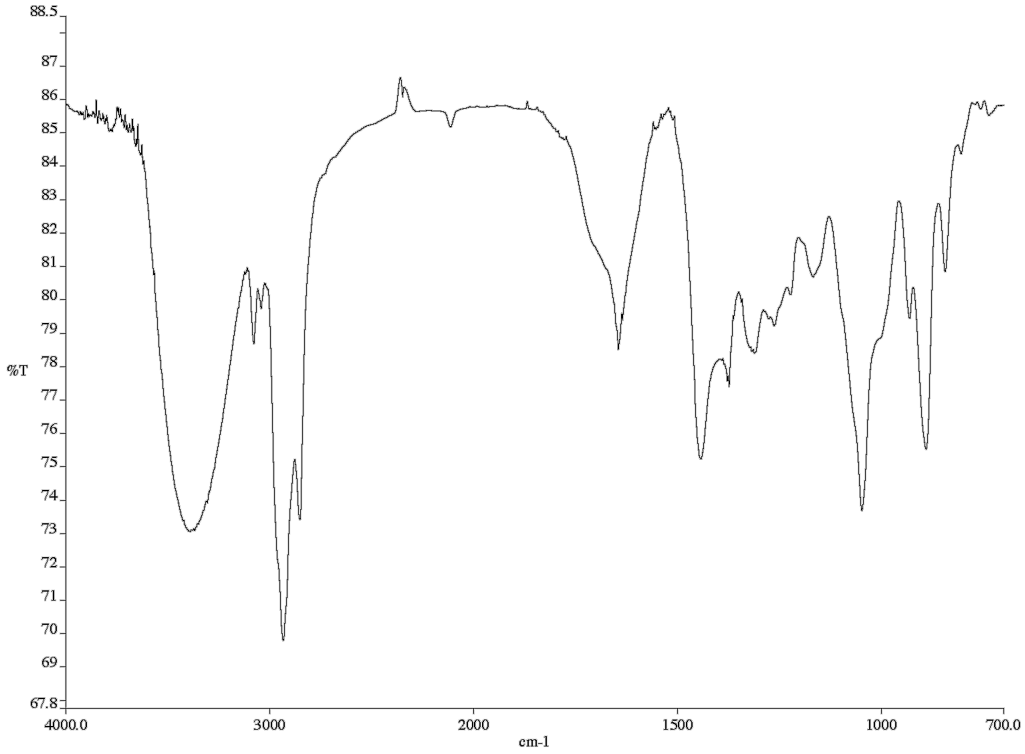
Infrared spectrum (Thin Film, NaCl) of compound **30**.



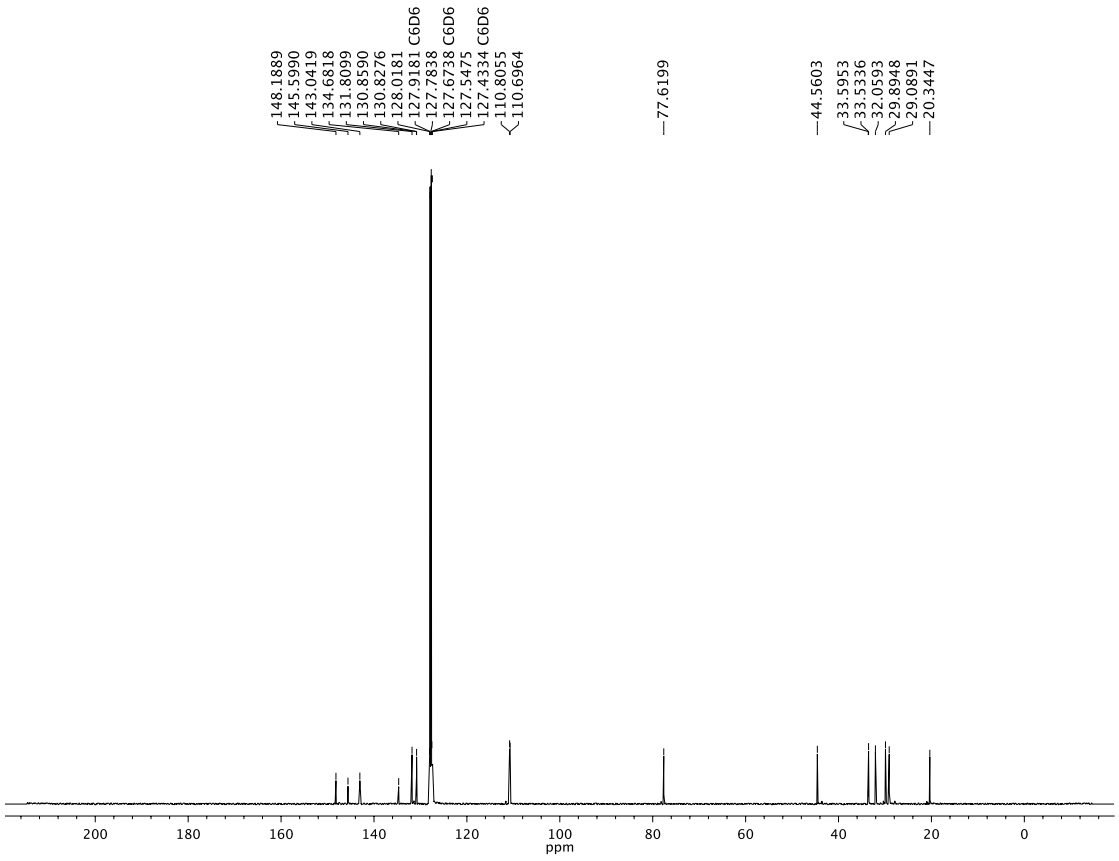
^{13}C NMR (101 MHz, C_6D_6) of compound **30**.



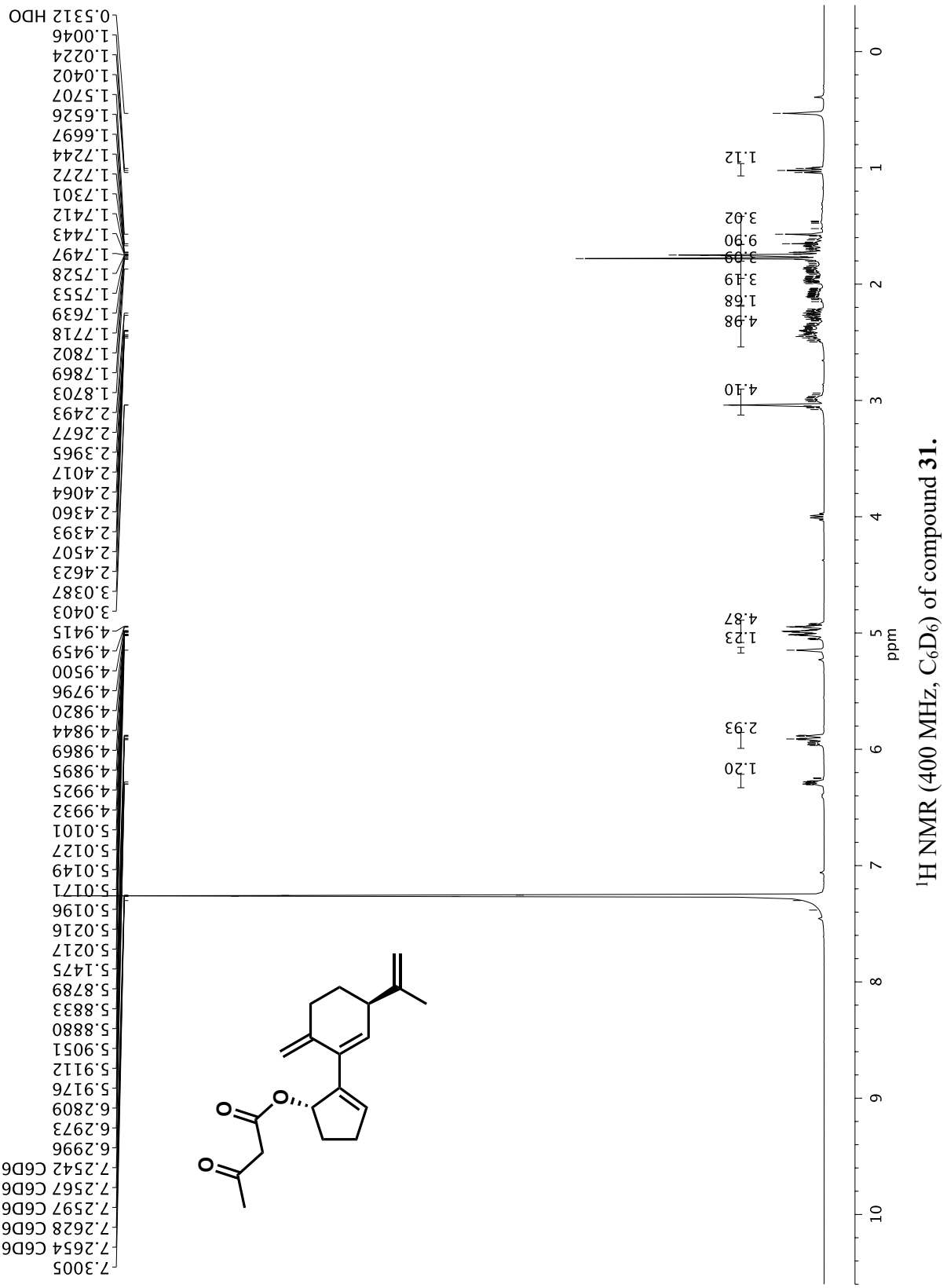
^{1}H NMR (400 MHz, C_6D_6) of compound **50.**



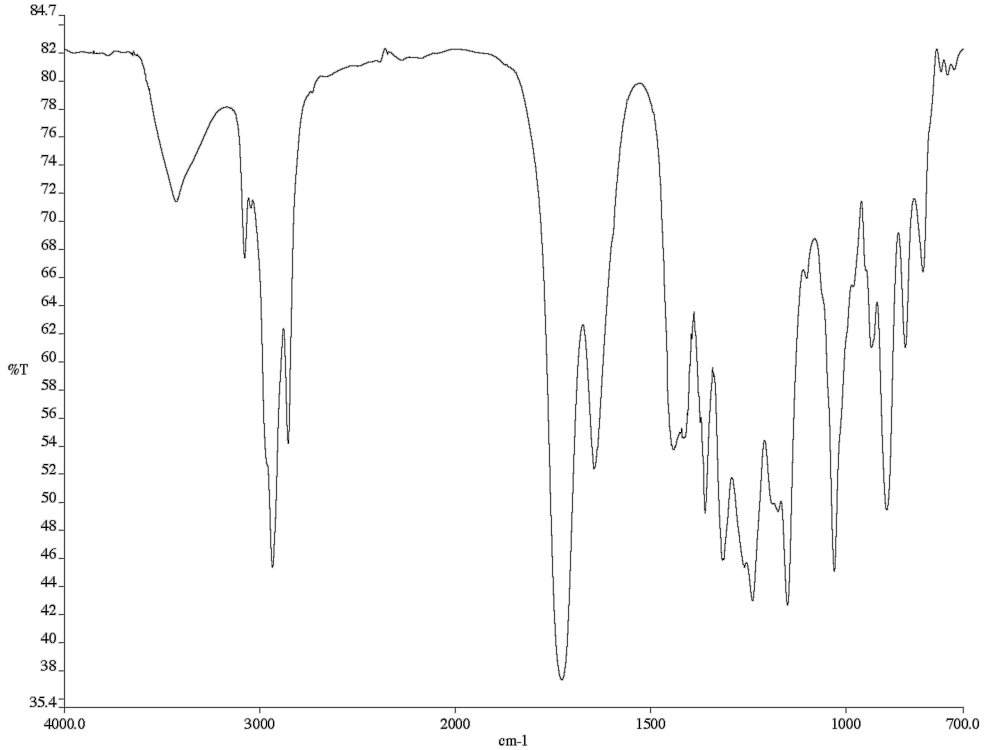
Infrared spectrum (Thin Film, NaCl) of compound **50**.



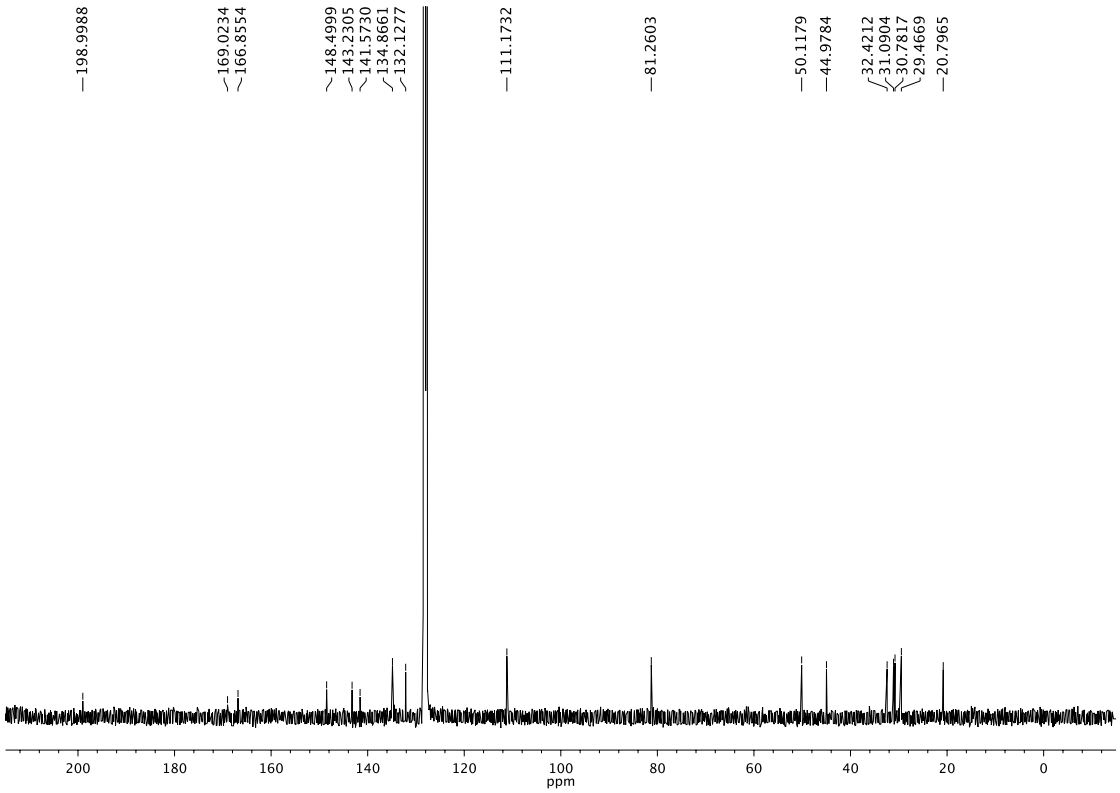
^{13}C NMR (101 MHz, C_6D_6) of compound **50**.



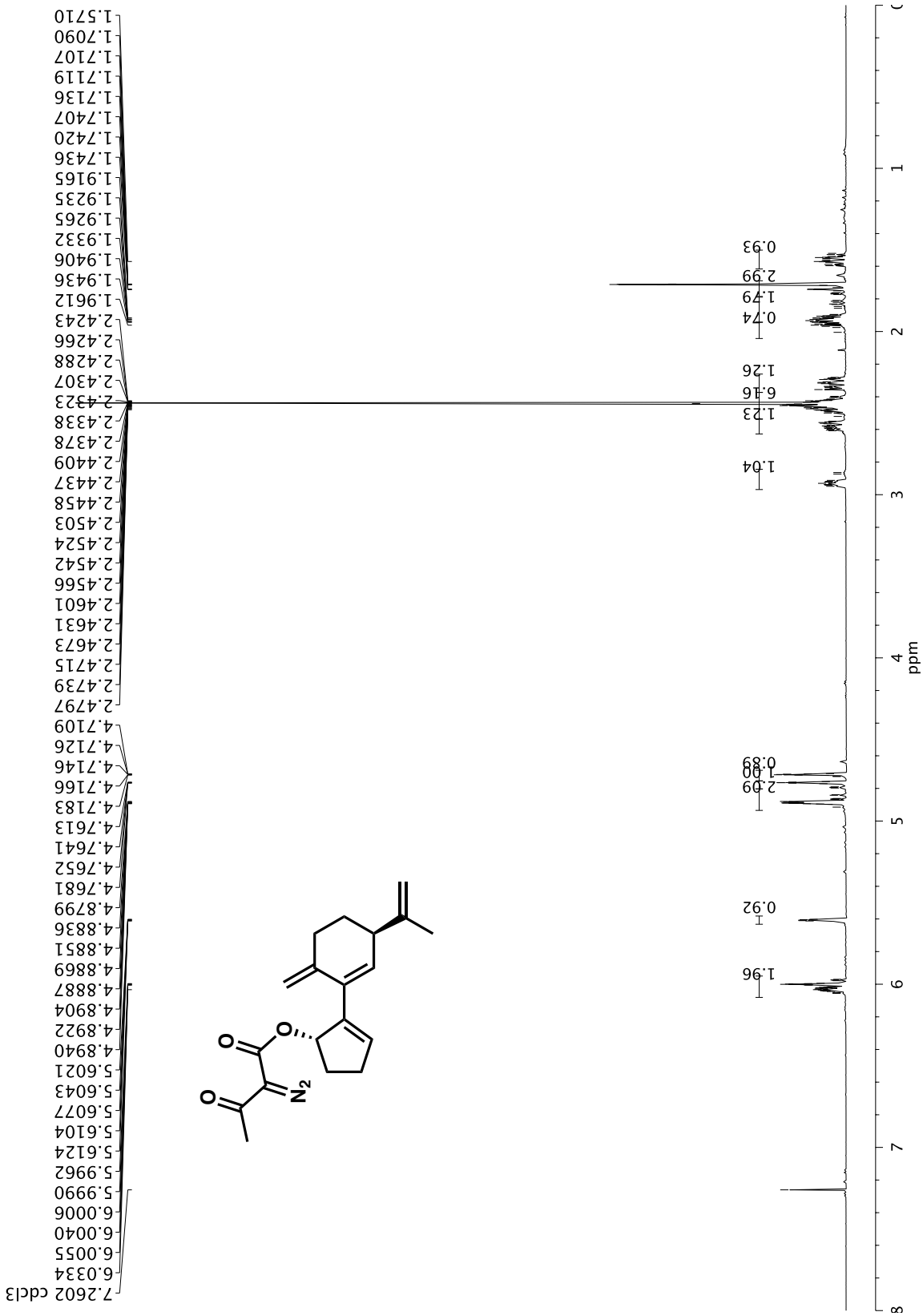
^{1}H NMR (400 MHz, C_6D_6) of compound **31.**



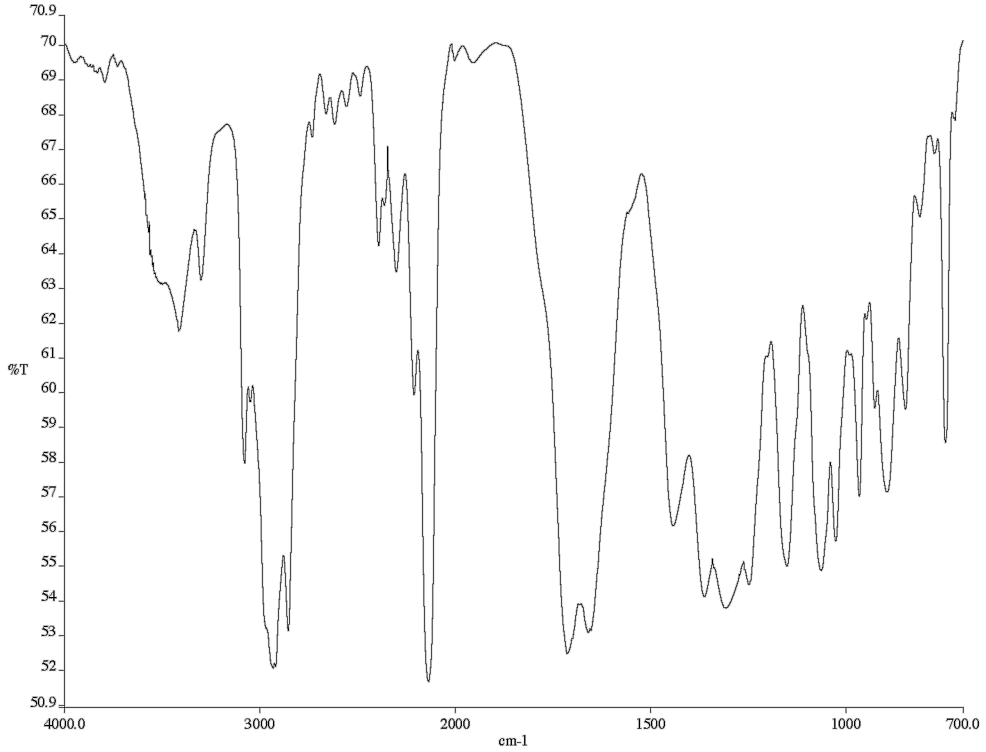
Infrared spectrum (Thin Film, NaCl) of compound **31**.



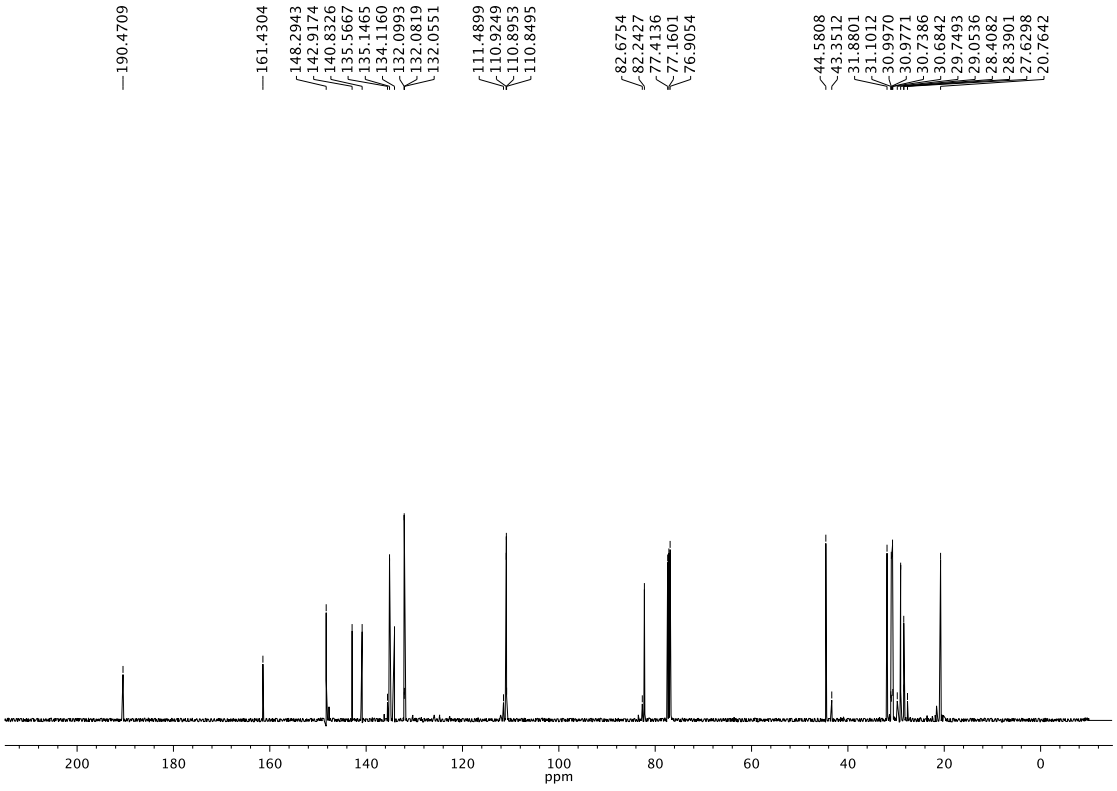
^{13}C NMR (101 MHz, C_6D_6) of compound **31**.



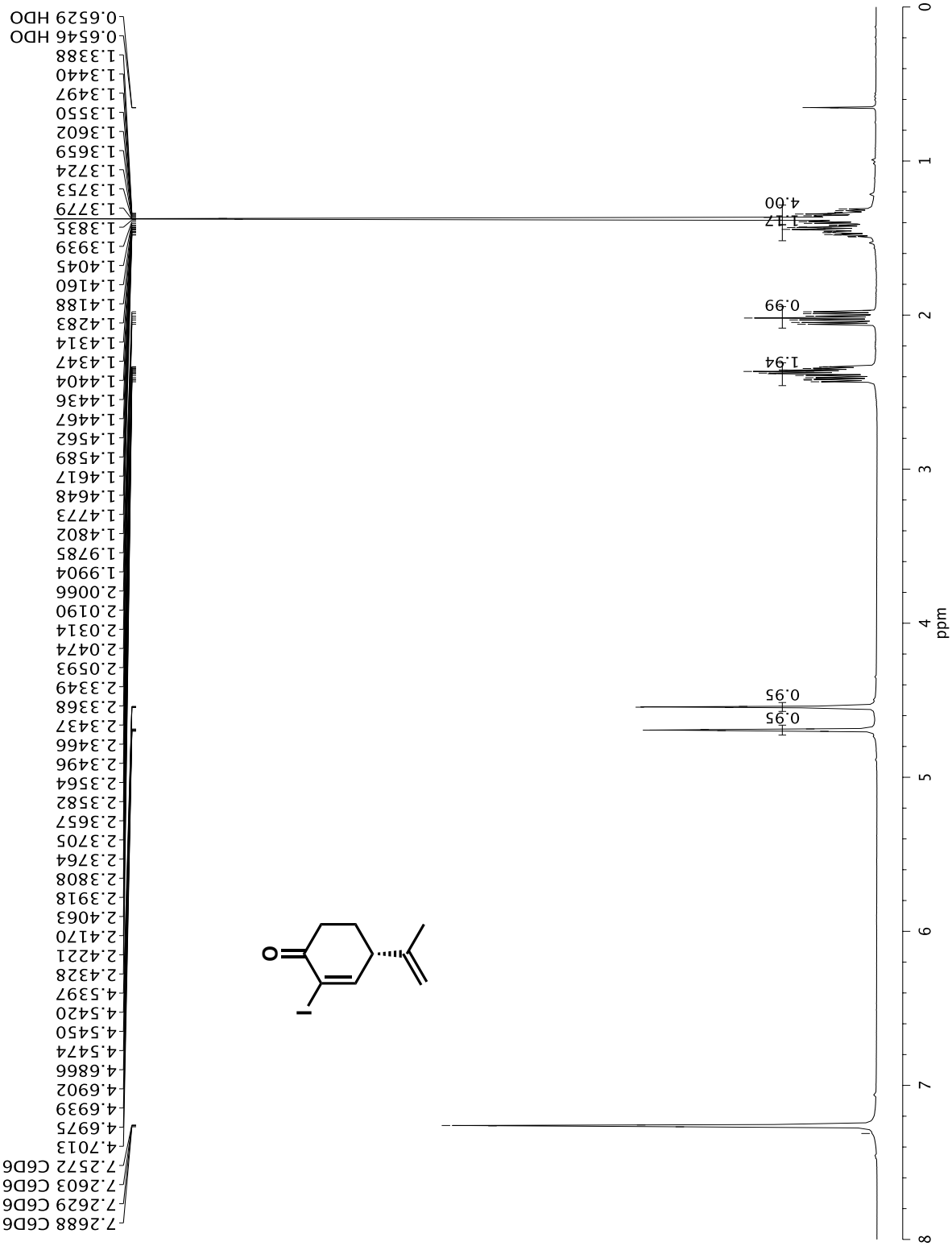
^{1}H NMR (500 MHz, $CDCl_3$) of compound **32.**



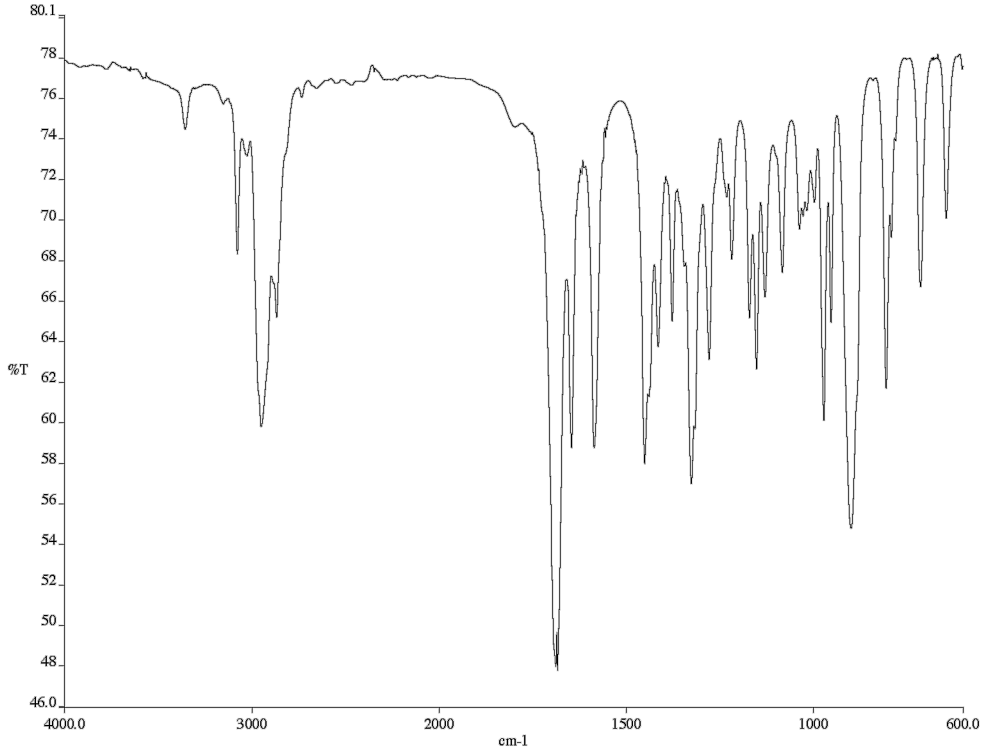
Infrared spectrum (Thin Film, NaCl) of compound **32**.



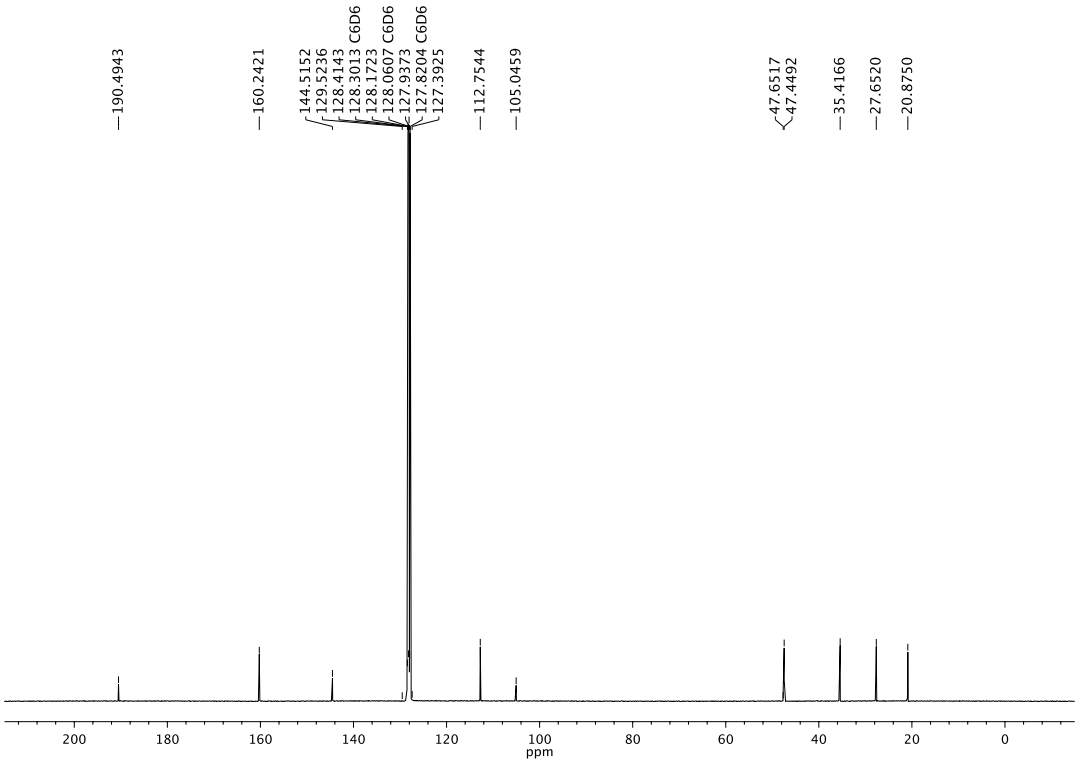
^{13}C NMR (126 MHz, $CDCl_3$) of compound **32**.



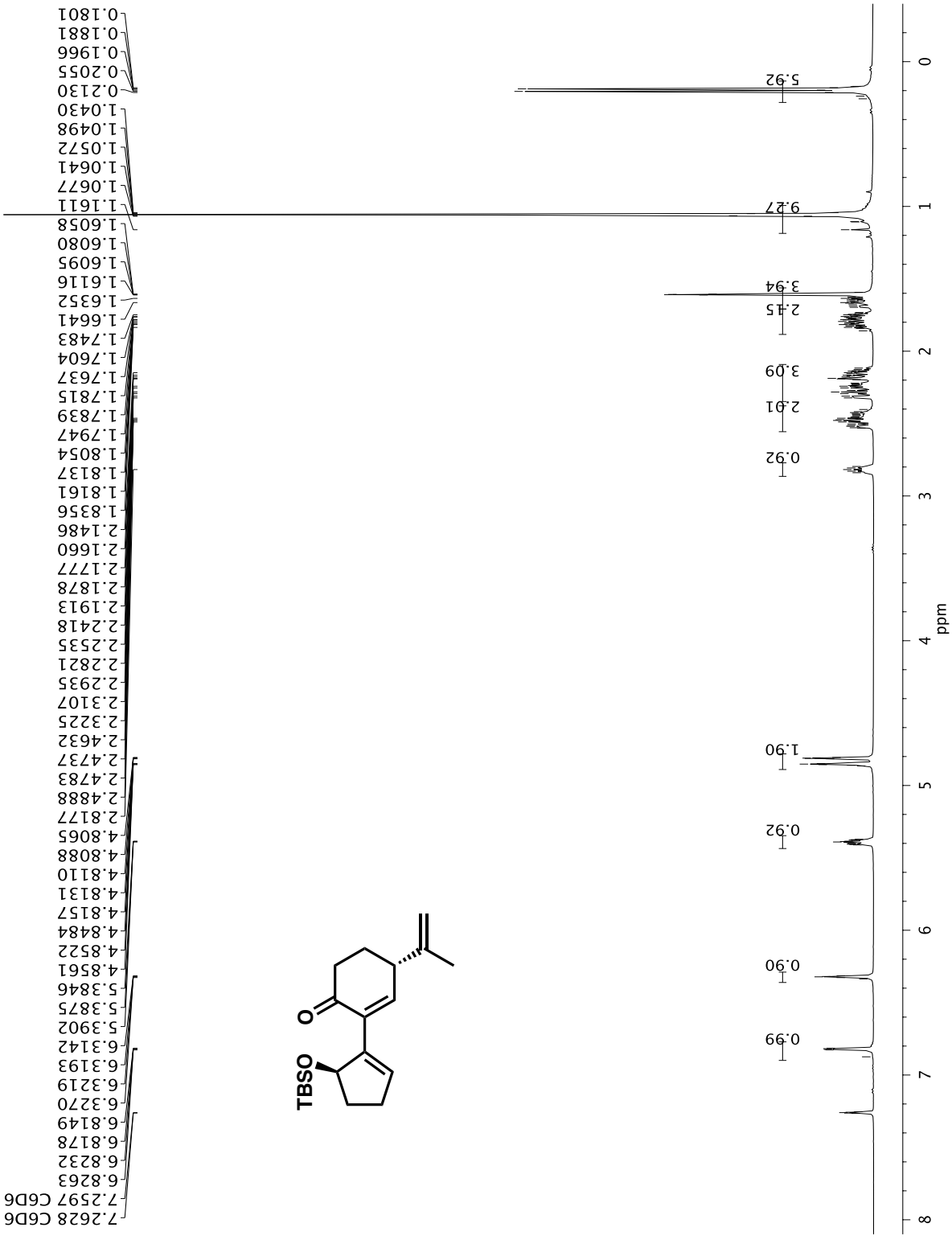
^{1}H NMR (400 MHz, C_6D_6) of compound **36.**



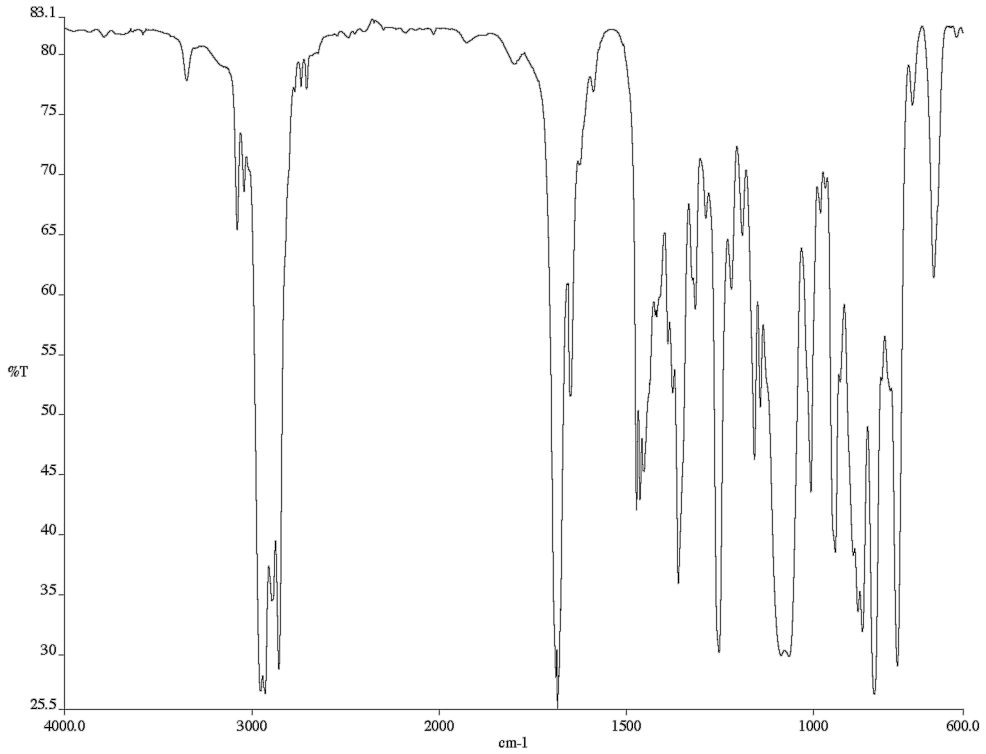
Infrared spectrum (Thin Film, NaCl) of compound **36**.



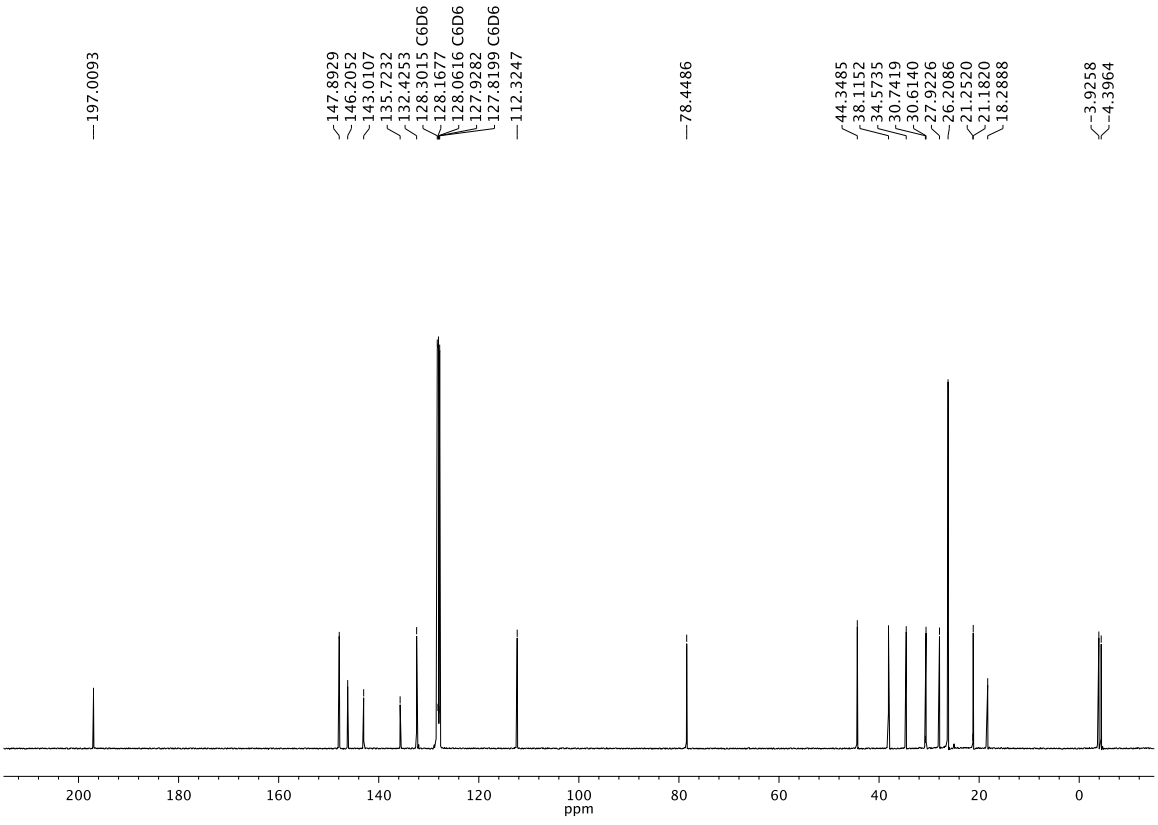
^{13}C NMR (101 MHz, C_6Cl_6) of compound **36**.



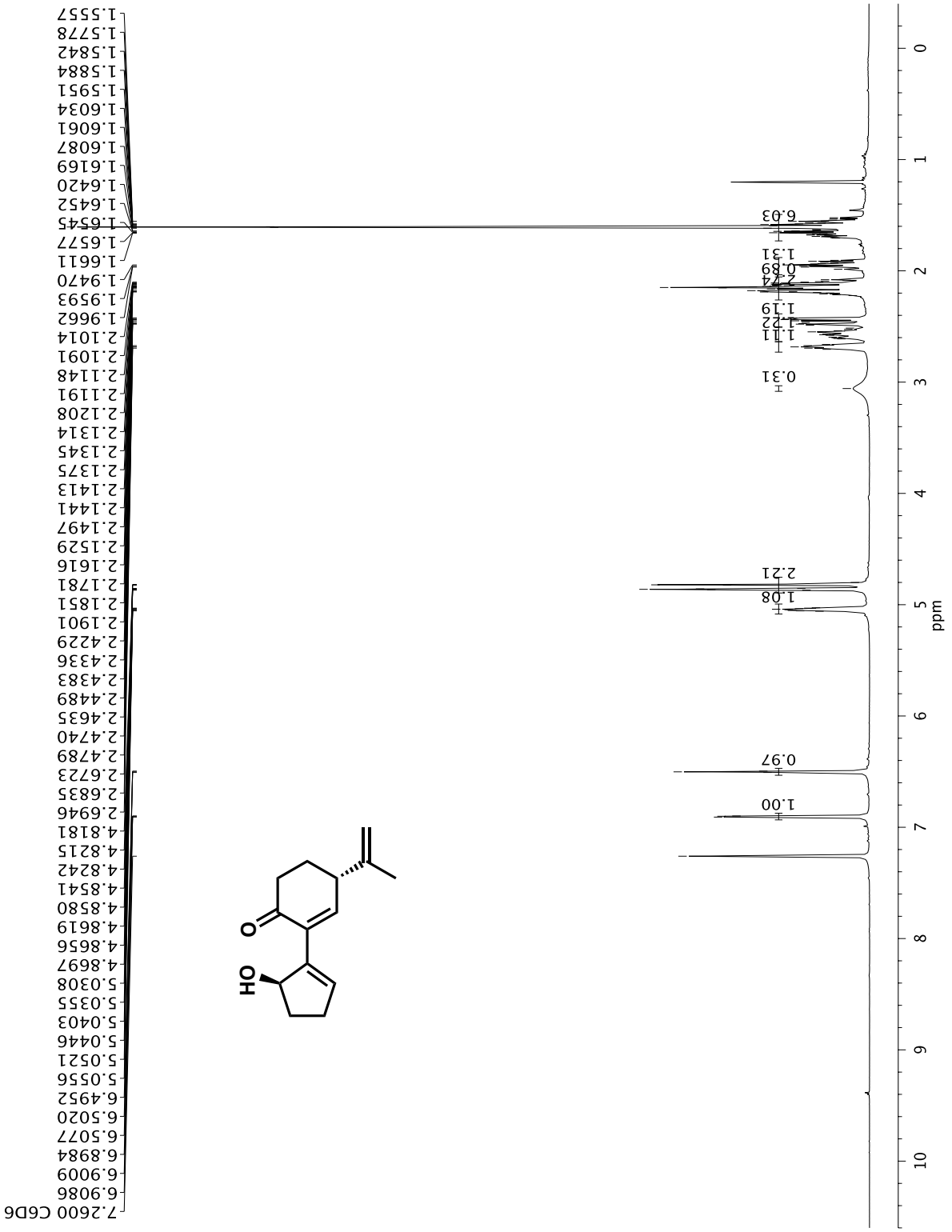
^{1}H NMR (400 MHz, C_6D_6) of compound **37.**



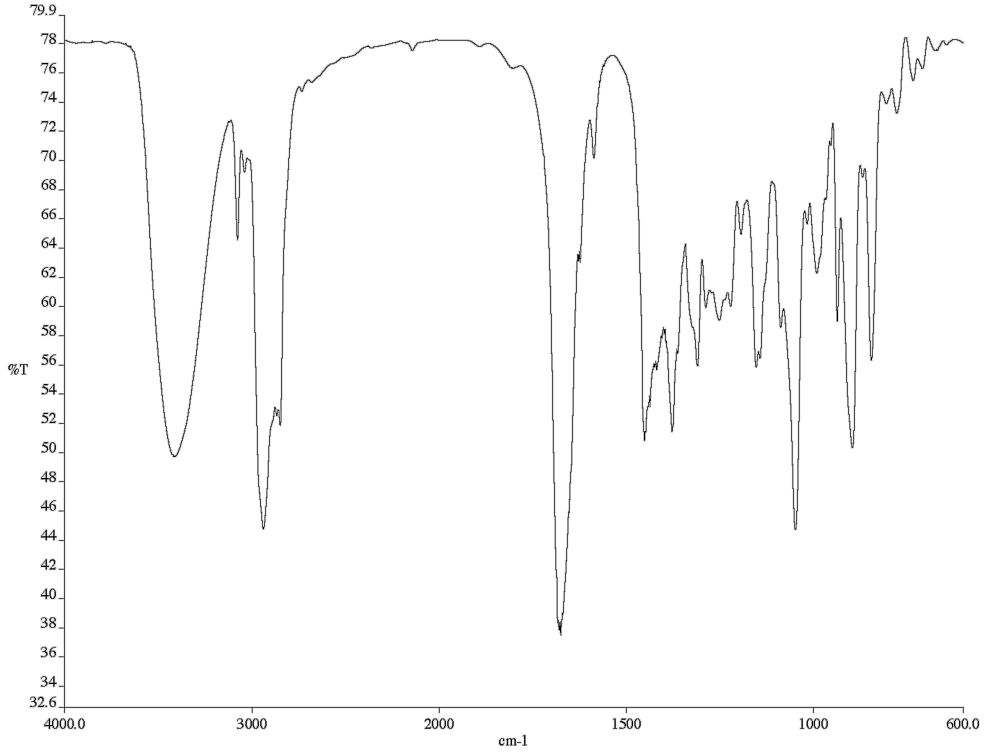
Infrared spectrum (Thin Film, NaCl) of compound **37**.



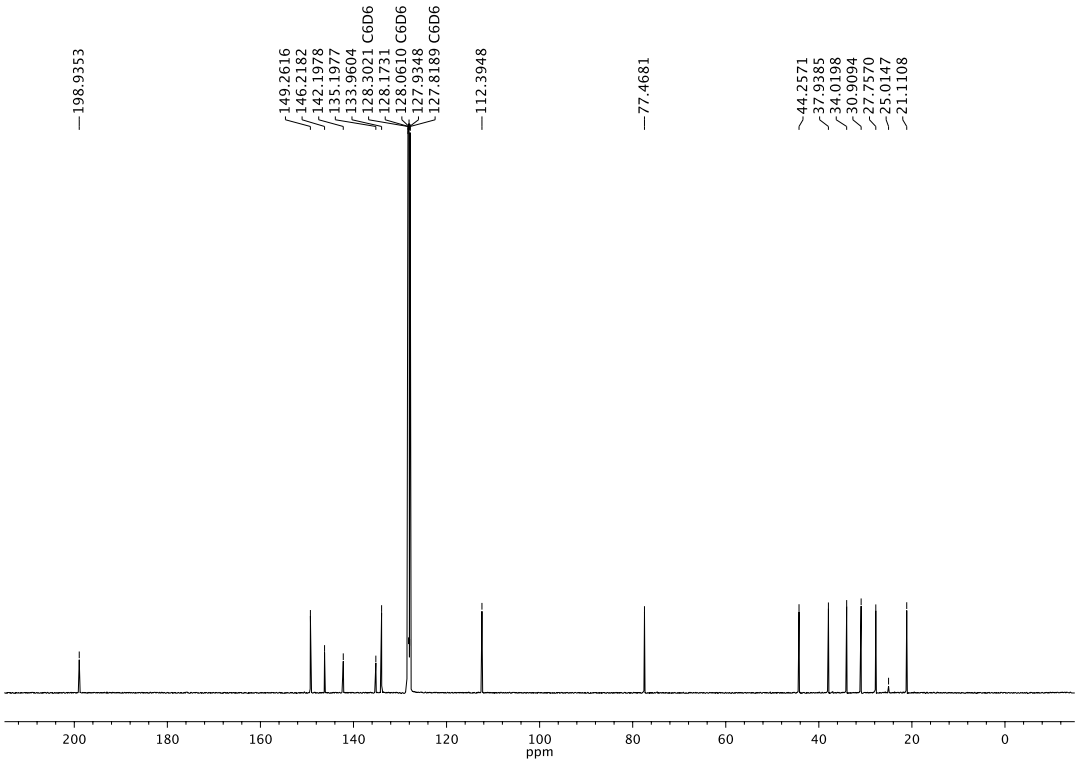
^{13}C NMR (101 MHz, C_6D_6) of compound **37**.



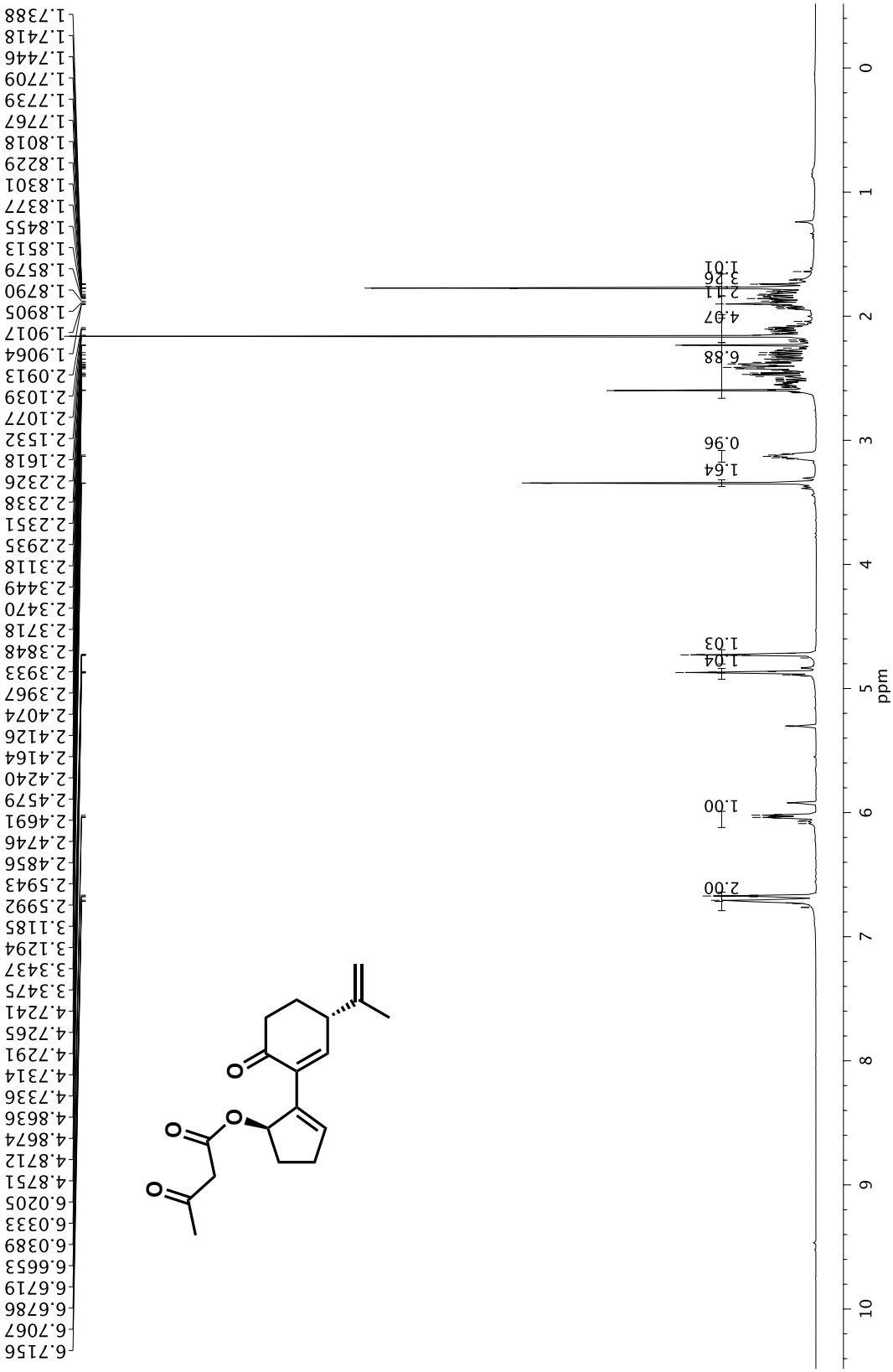
^{1}H NMR (400 MHz, C_6D_6) of compound **51.**



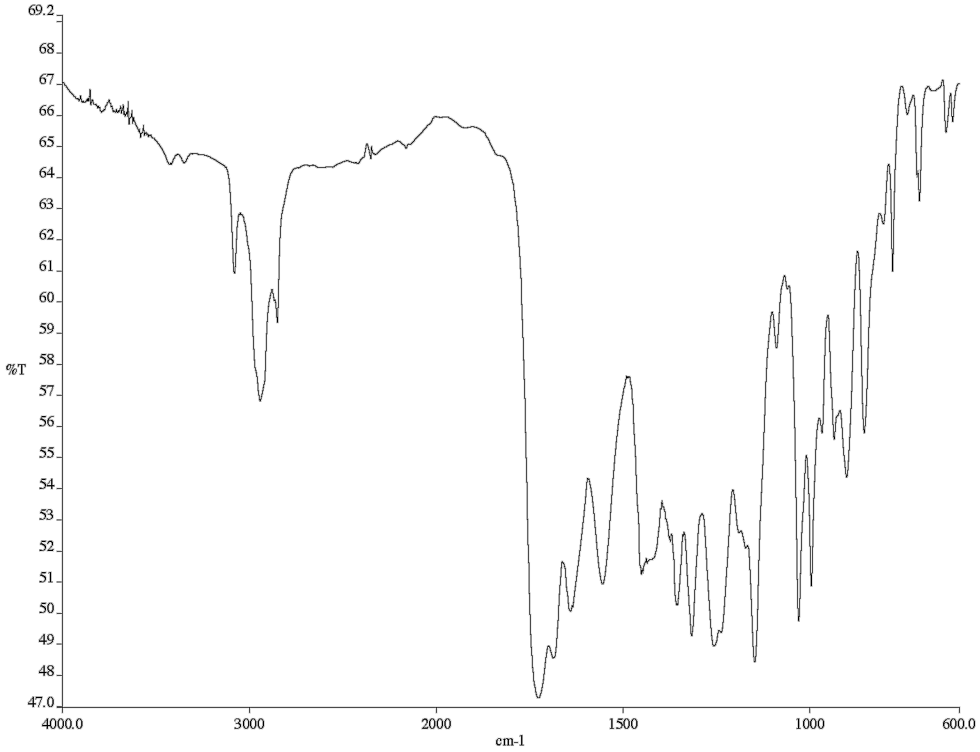
Infrared spectrum (Thin Film, NaCl) of compound **51**.



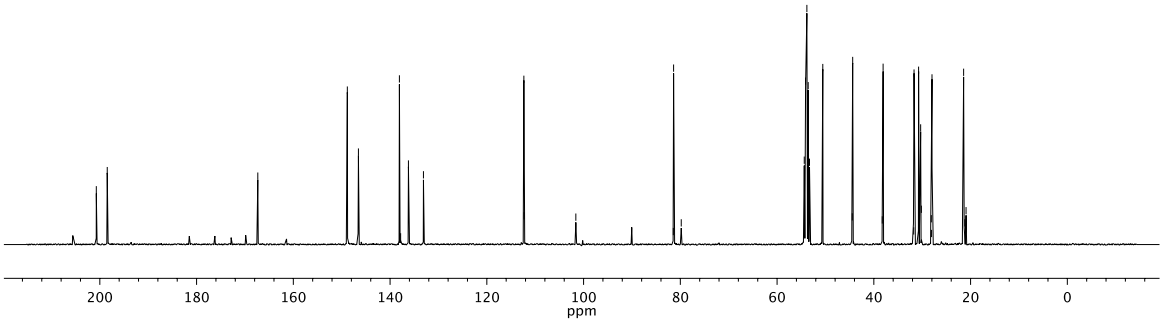
^{13}C NMR (101 MHz, C_6D_6) of compound **51**.



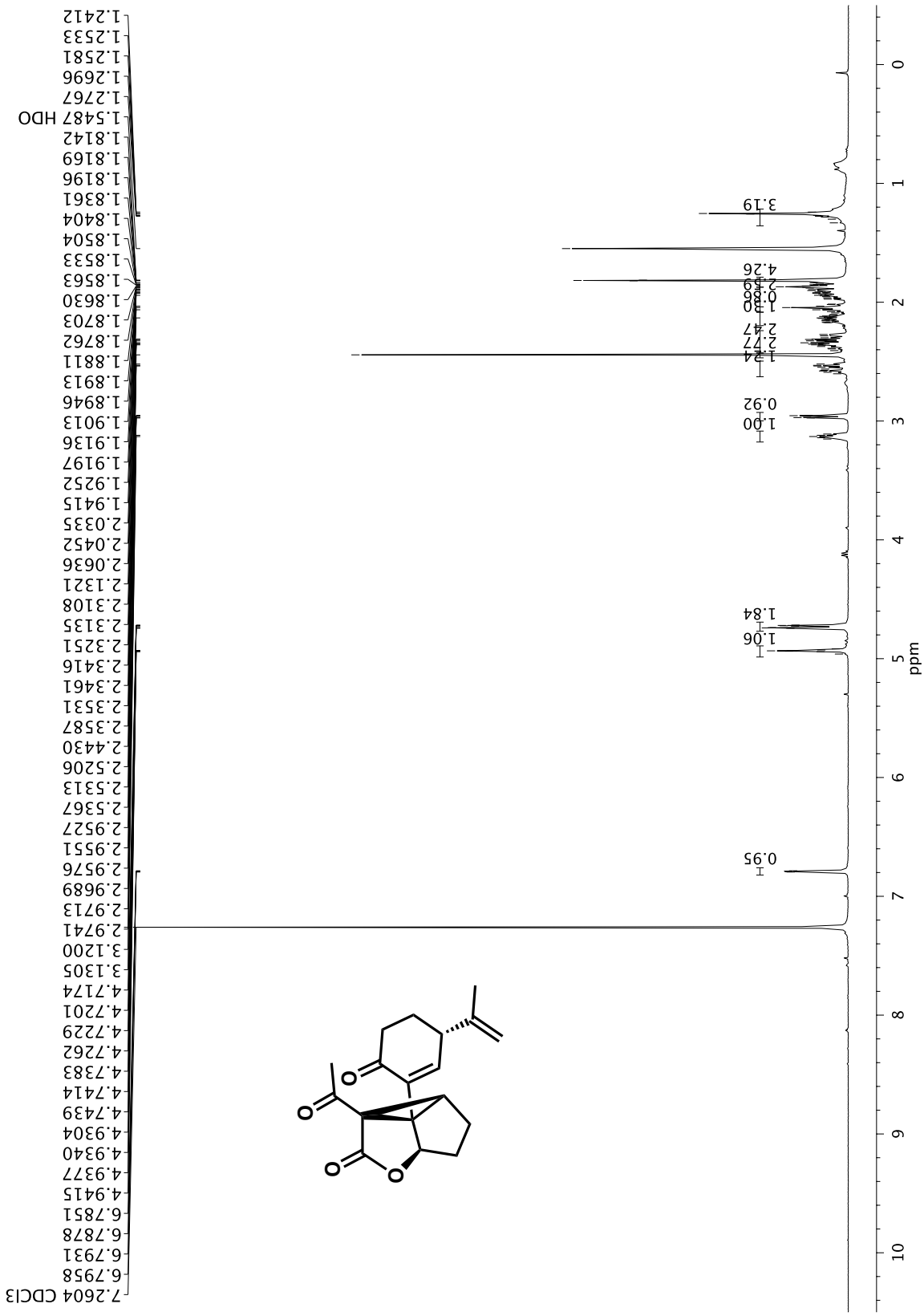
^{1}H NMR (400 MHz, CD_2Cl_2) of compound **38.**



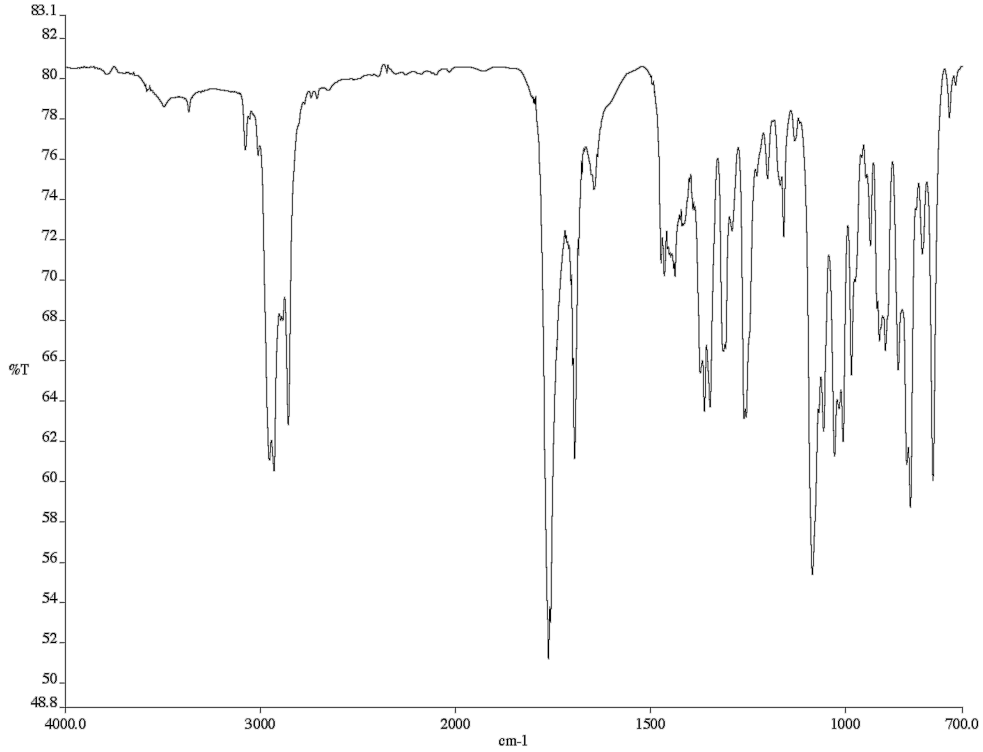
Infrared spectrum (Thin Film, NaCl) of compound **38**.



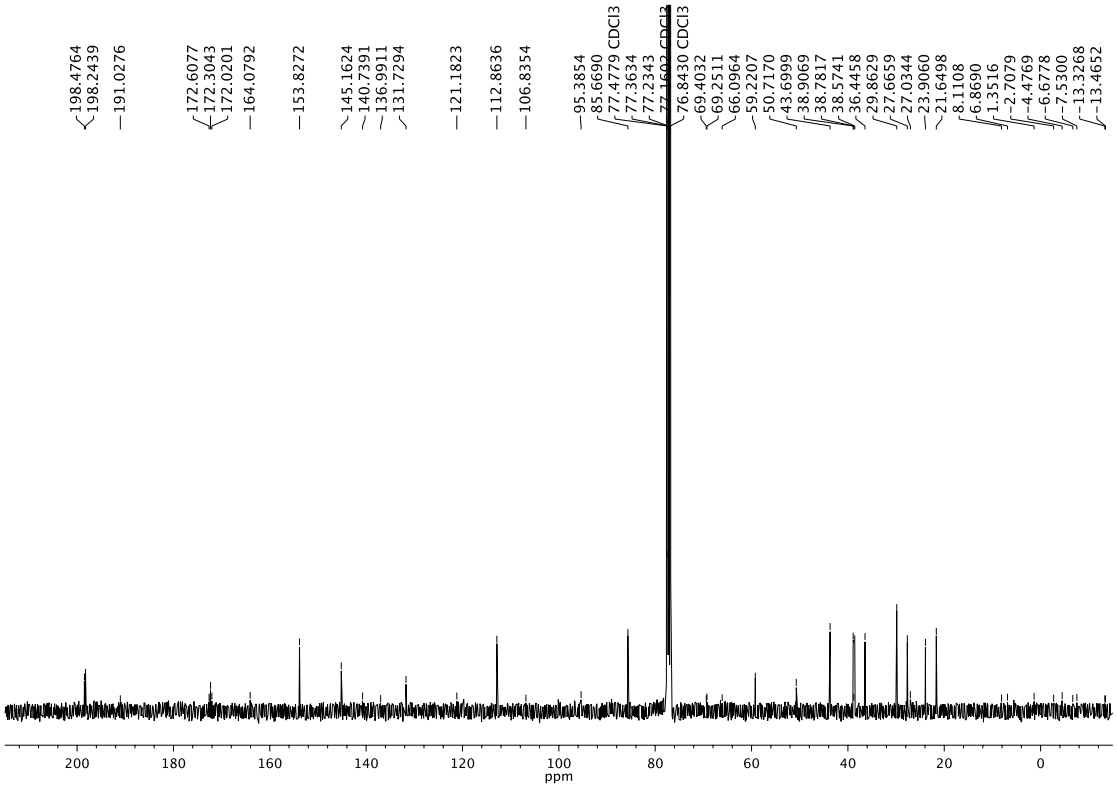
^{13}C NMR (101 MHz, CD_2Cl_2) of compound **38**.



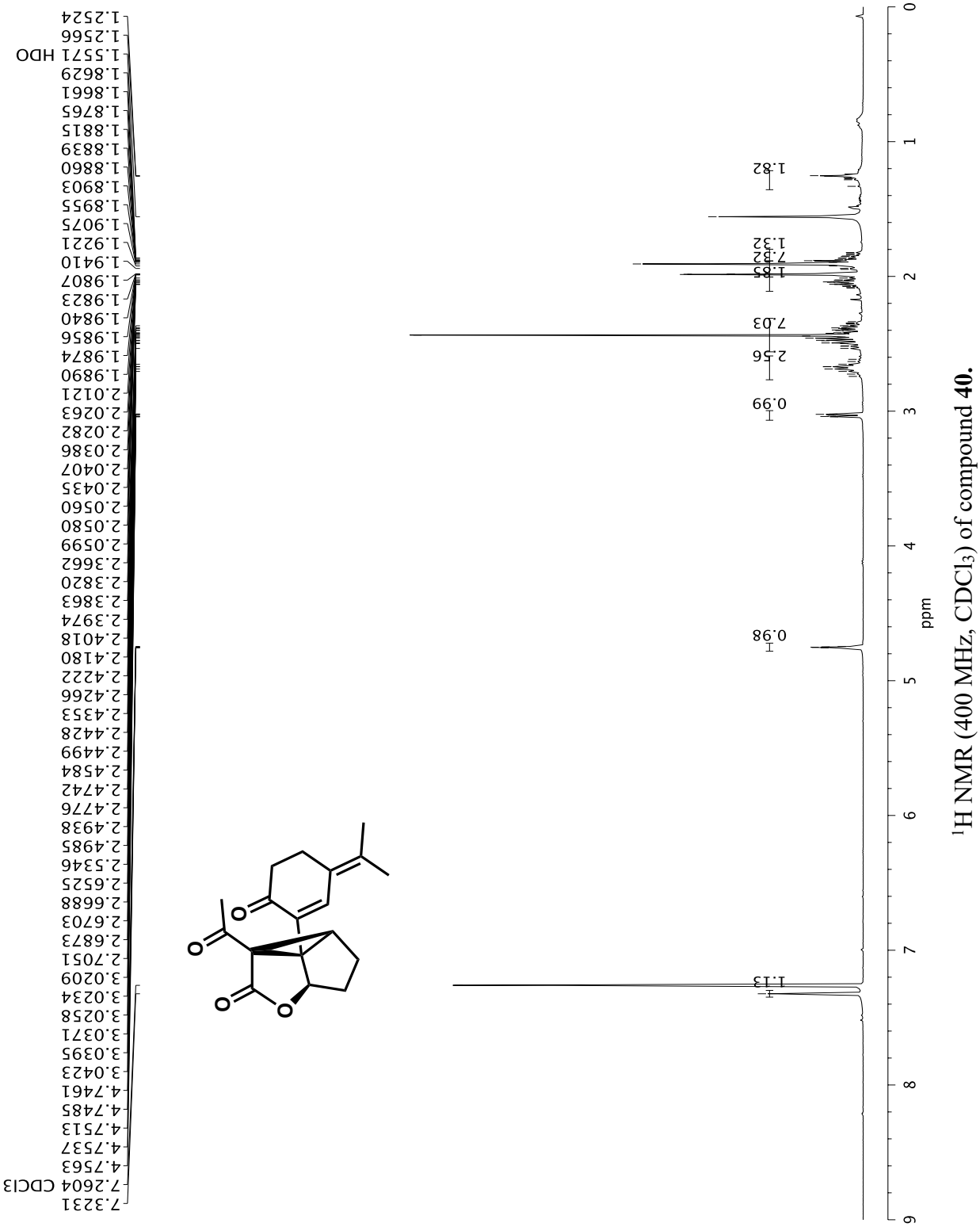
1H NMR (400 MHz, $CDCl_3$) of compound **39.**



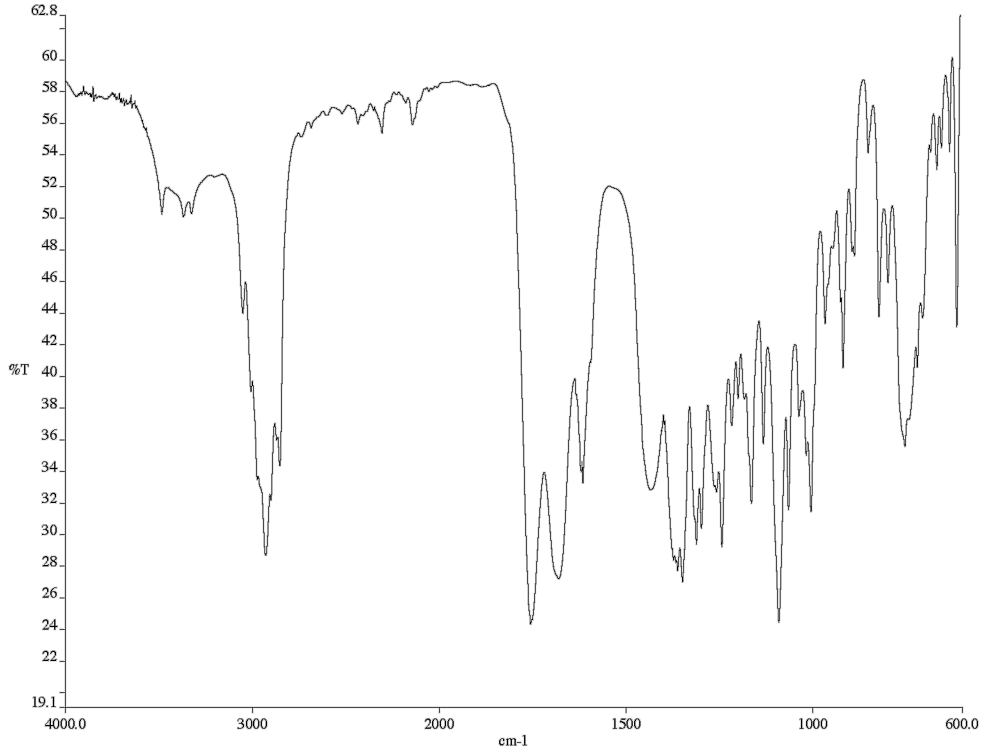
Infrared spectrum (Thin Film, NaCl) of compound **39**.



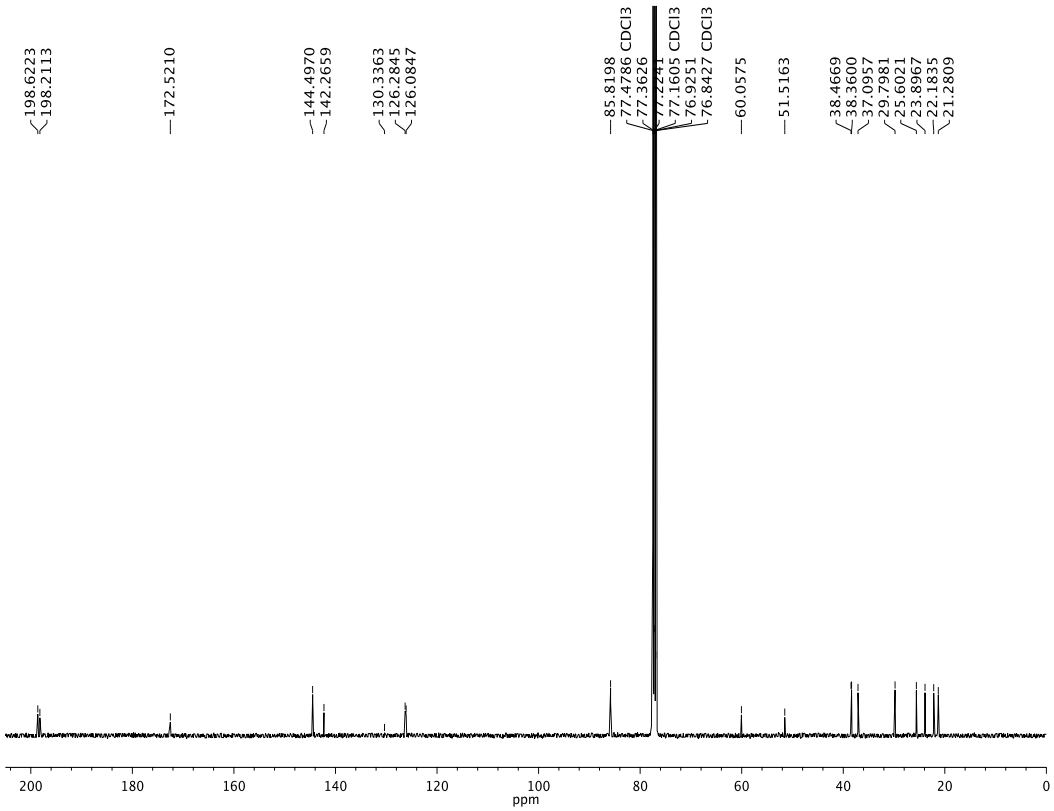
^{13}C NMR (101 MHz, $CDCl_3$) of compound **39**.



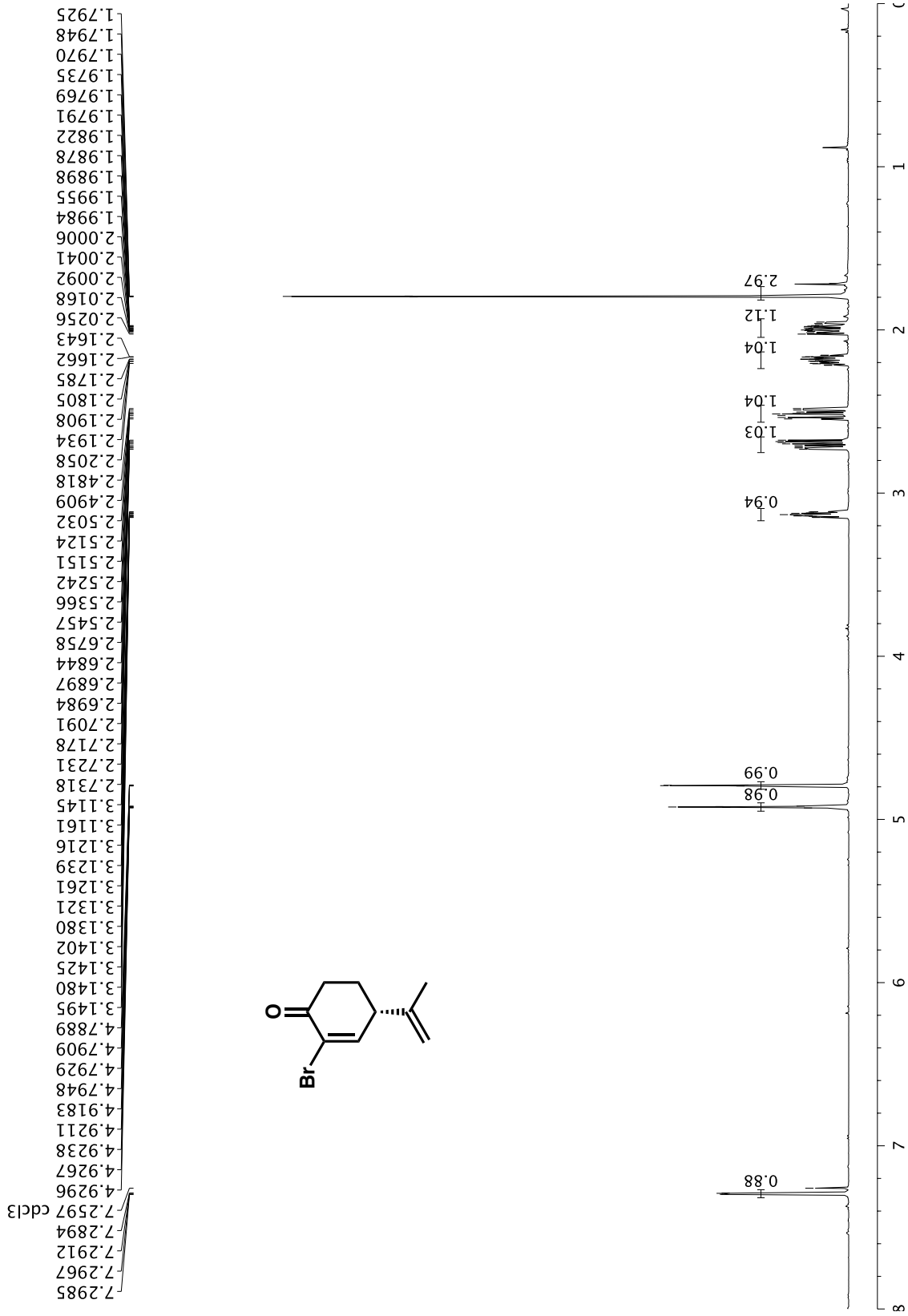
^{1}H NMR (400 MHz, $CDCl_3$) of compound **40.**



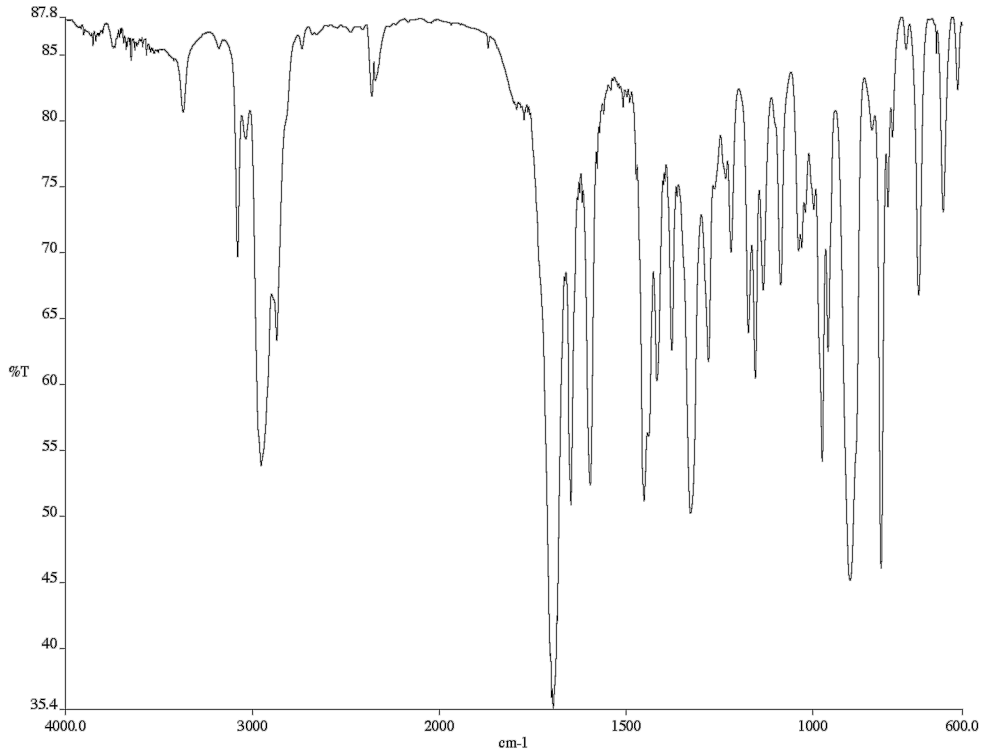
Infrared spectrum (Thin Film, NaCl) of compound **40**.



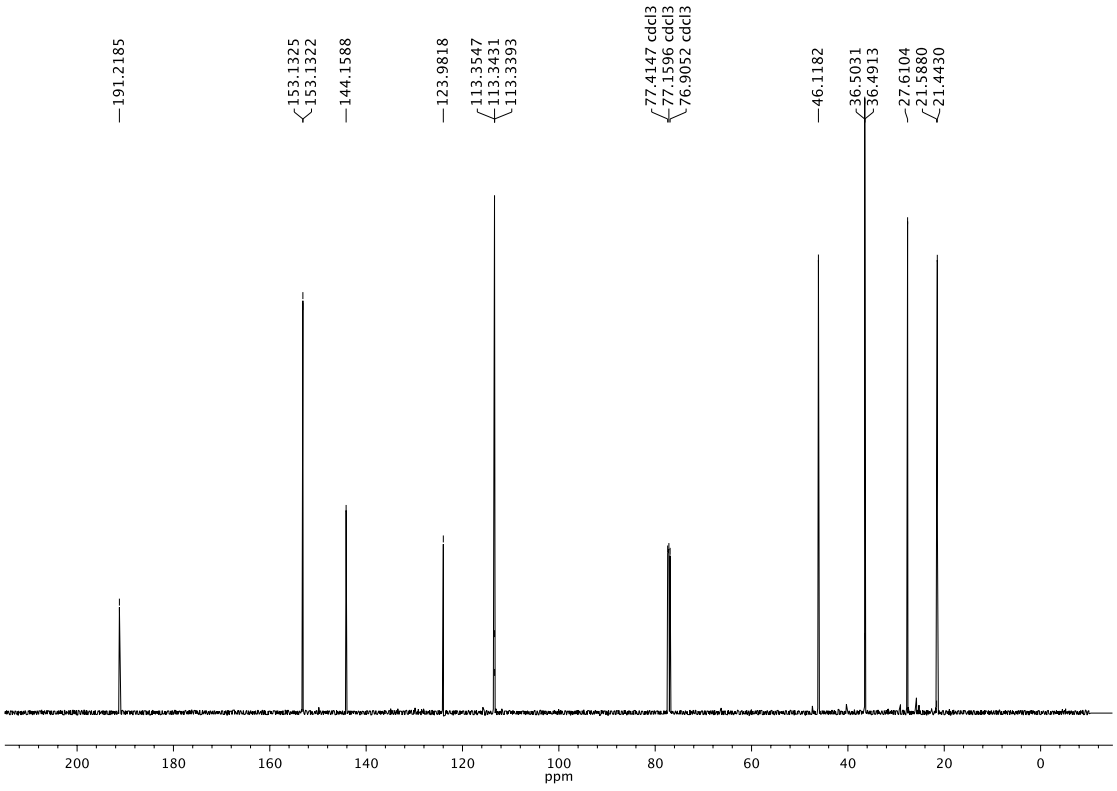
^{13}C NMR (101 MHz, $CDCl_3$) of compound **40**.



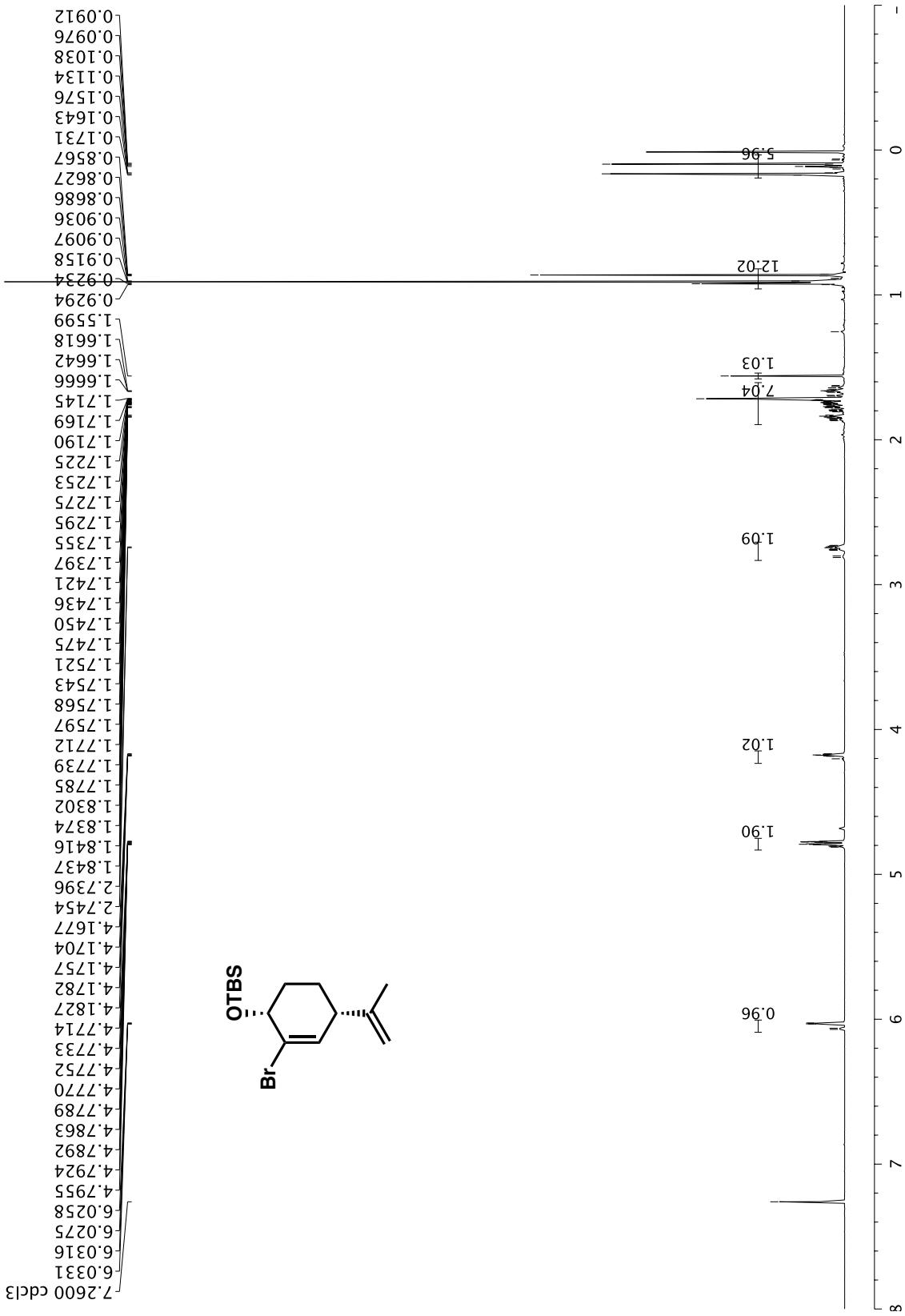
^{1}H NMR (500 MHz, $CDCl_3$) of compound **41.**



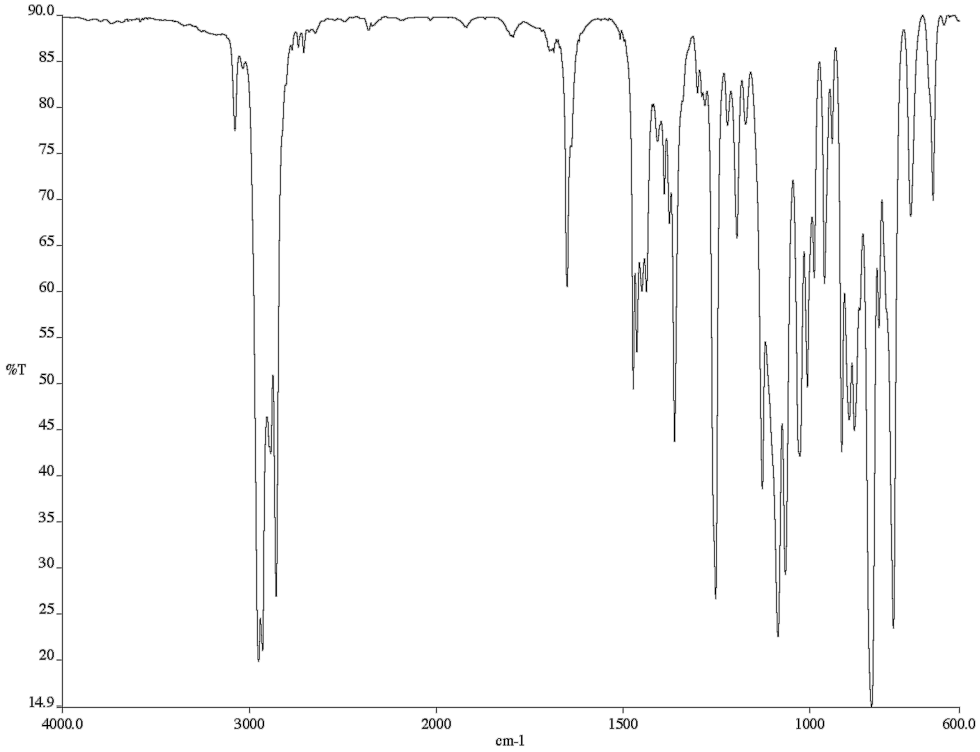
Infrared spectrum (Thin Film, NaCl) of compound **41**.



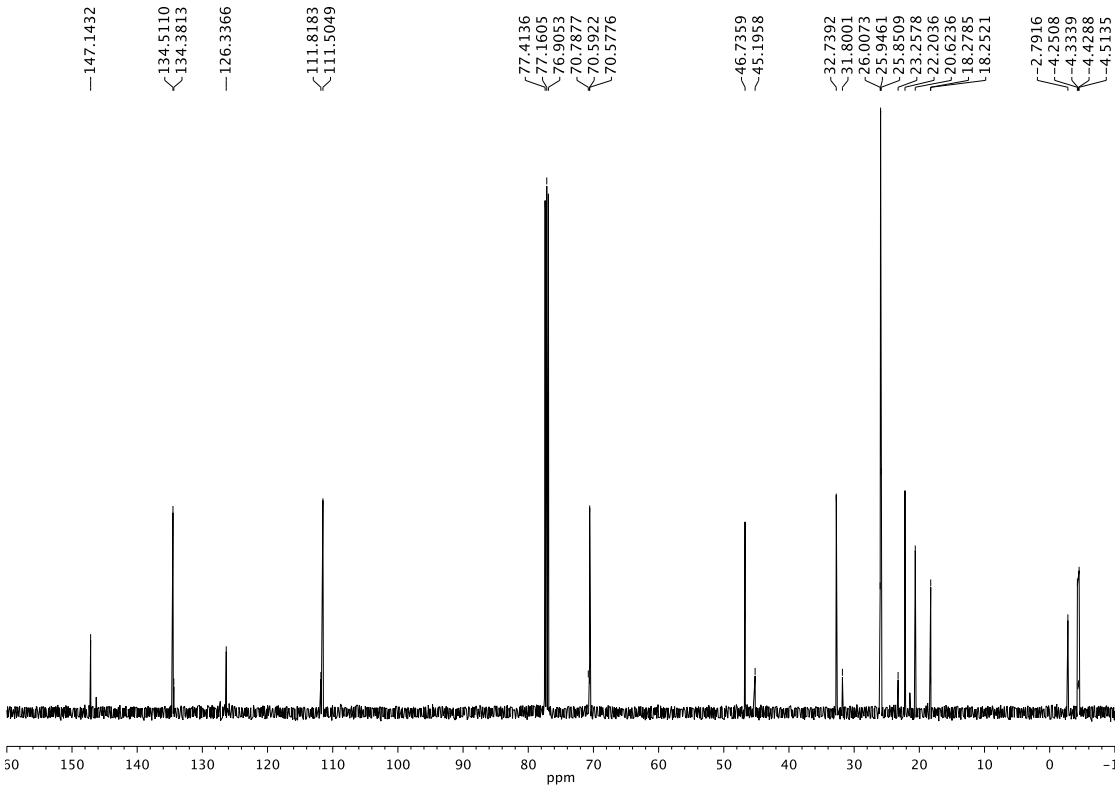
^{13}C NMR (126 MHz, $CDCl_3$) of compound **41**.



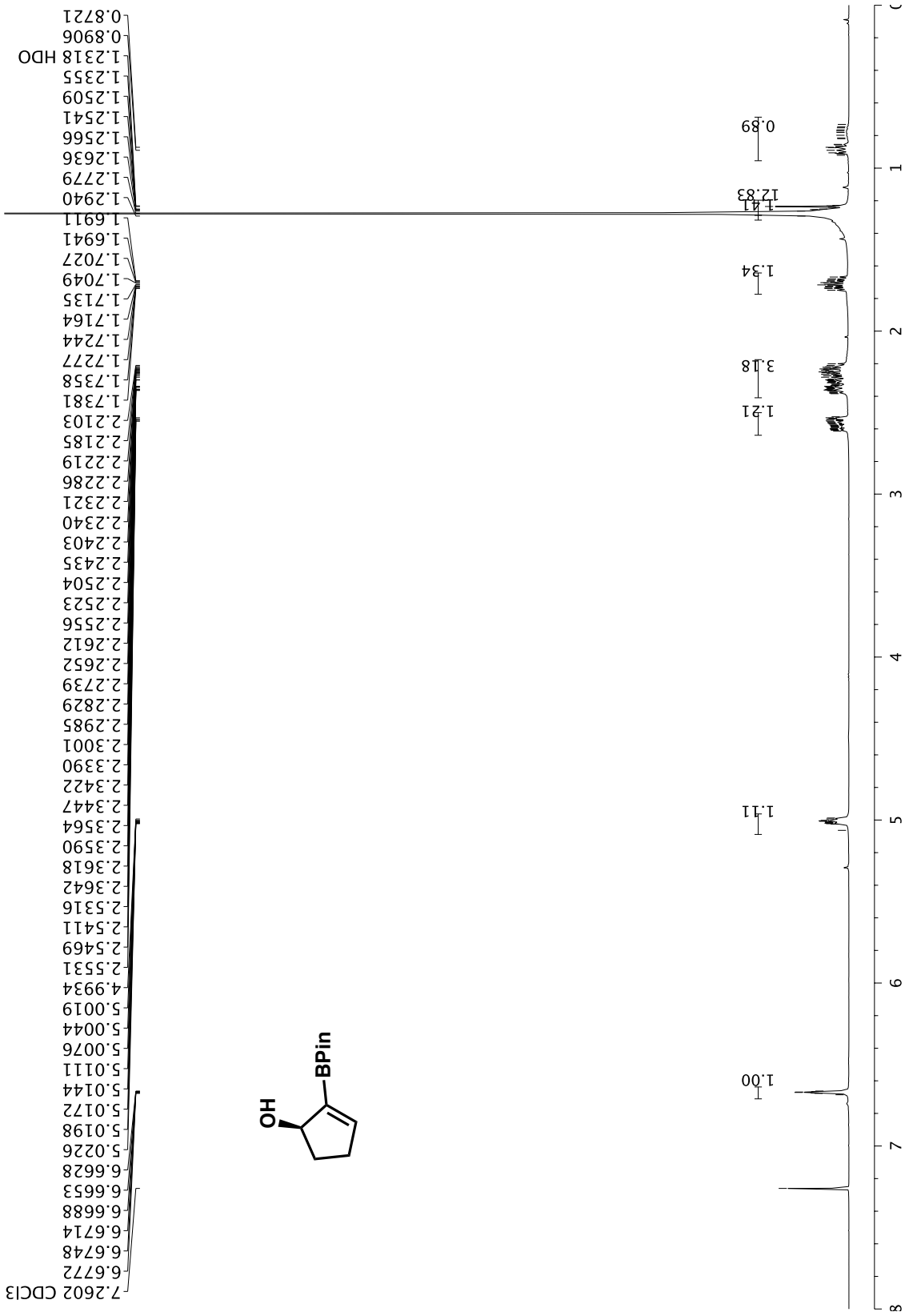
^{1}H NMR (500 MHz, $CDCl_3$) of compound **13.**



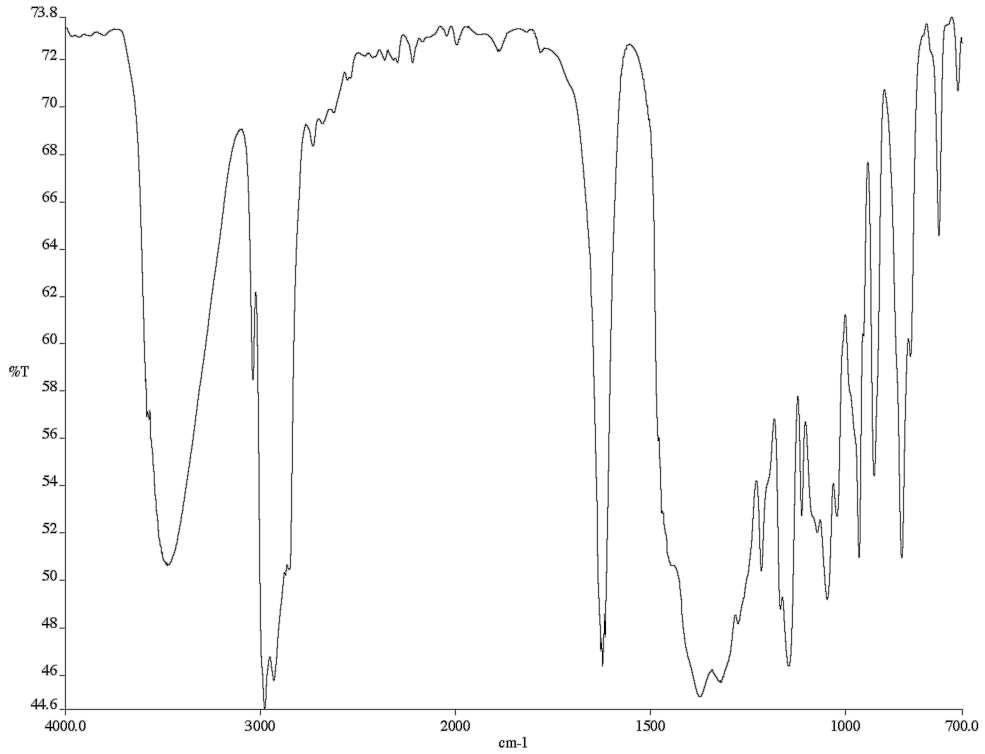
Infrared spectrum (Thin Film, NaCl) of compound **13**.



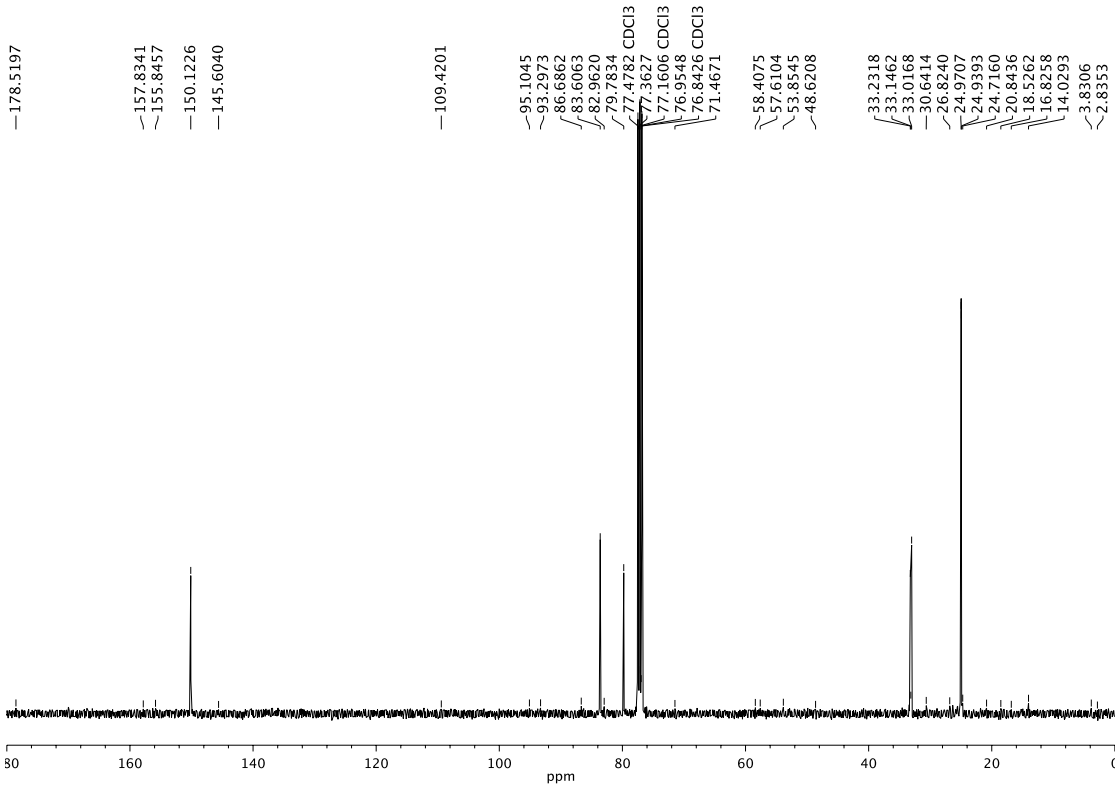
^{13}C NMR (126 MHz, $CDCl_3$) of compound **13**.



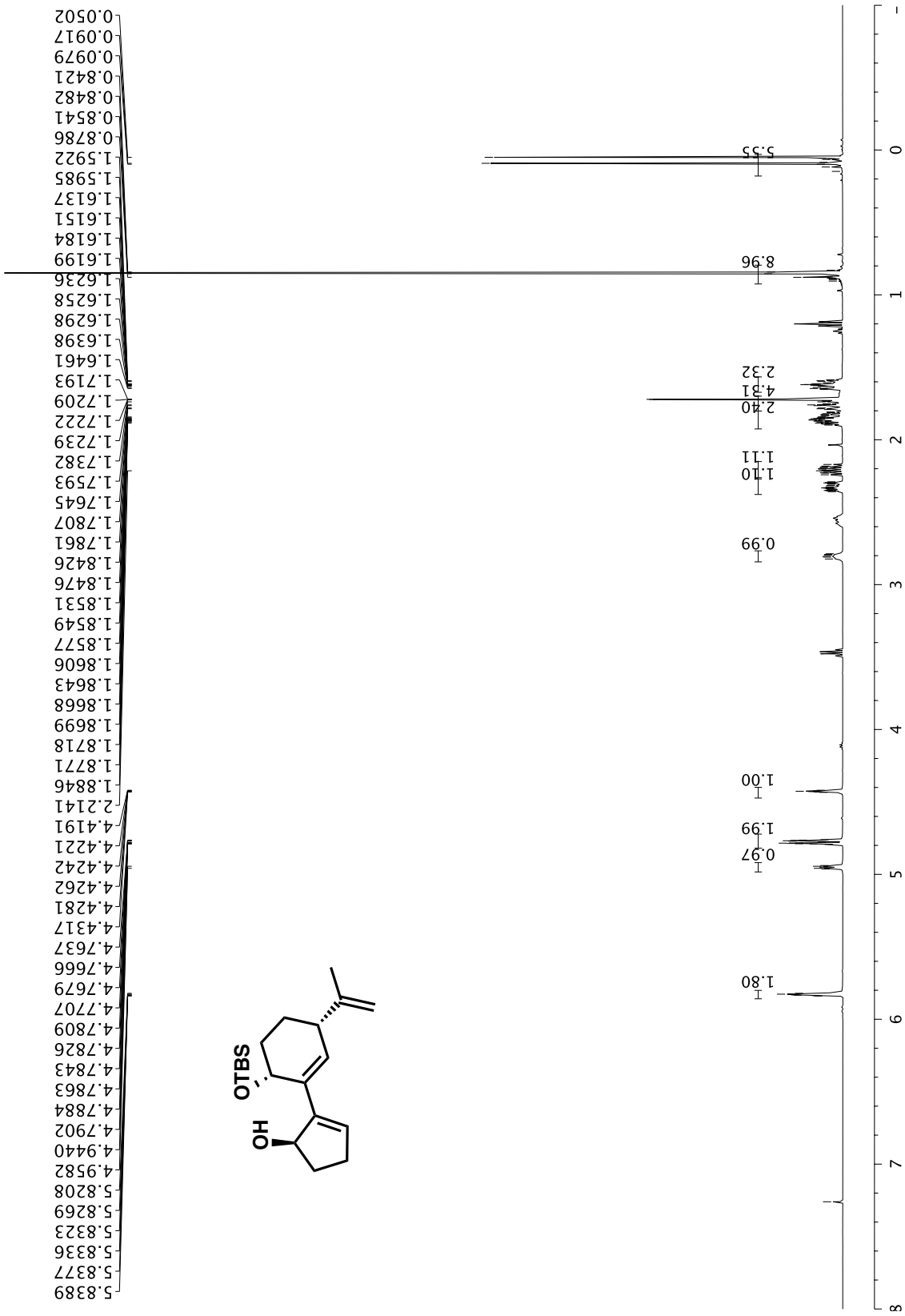
^{1}H NMR (400 MHz, $CDCl_3$) of compound **42.**



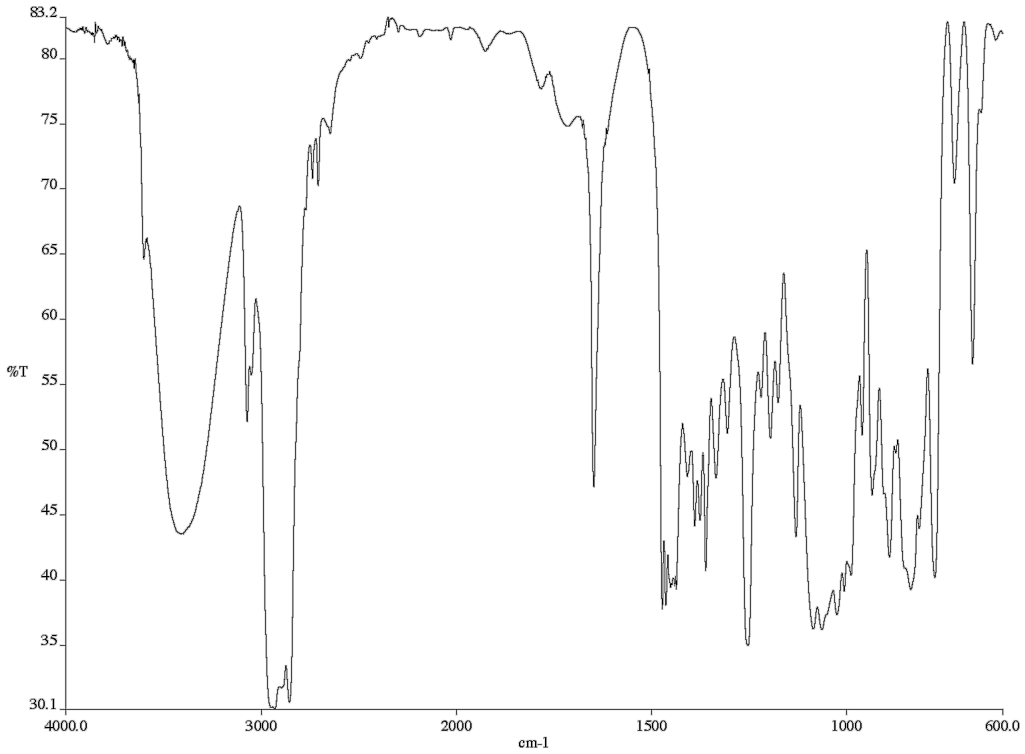
Infrared spectrum (Thin Film, NaCl) of compound **42**.



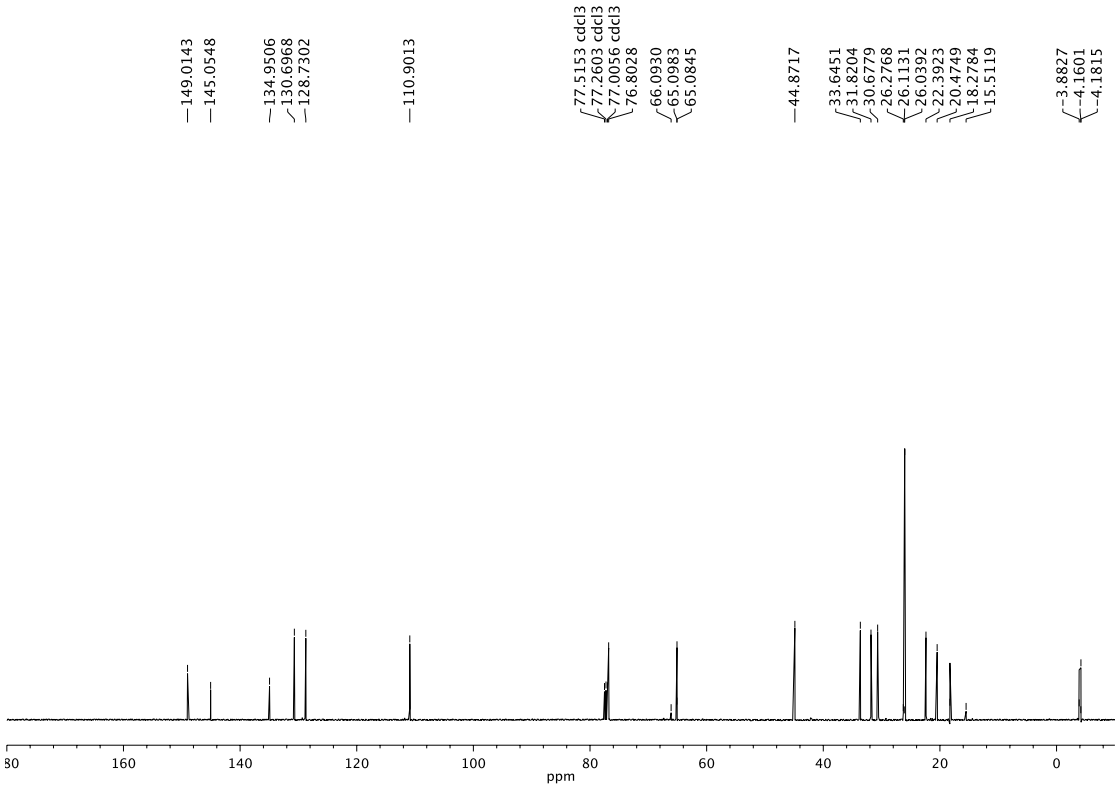
^{13}C NMR (101 MHz, $CDCl_3$) of compound **42**.



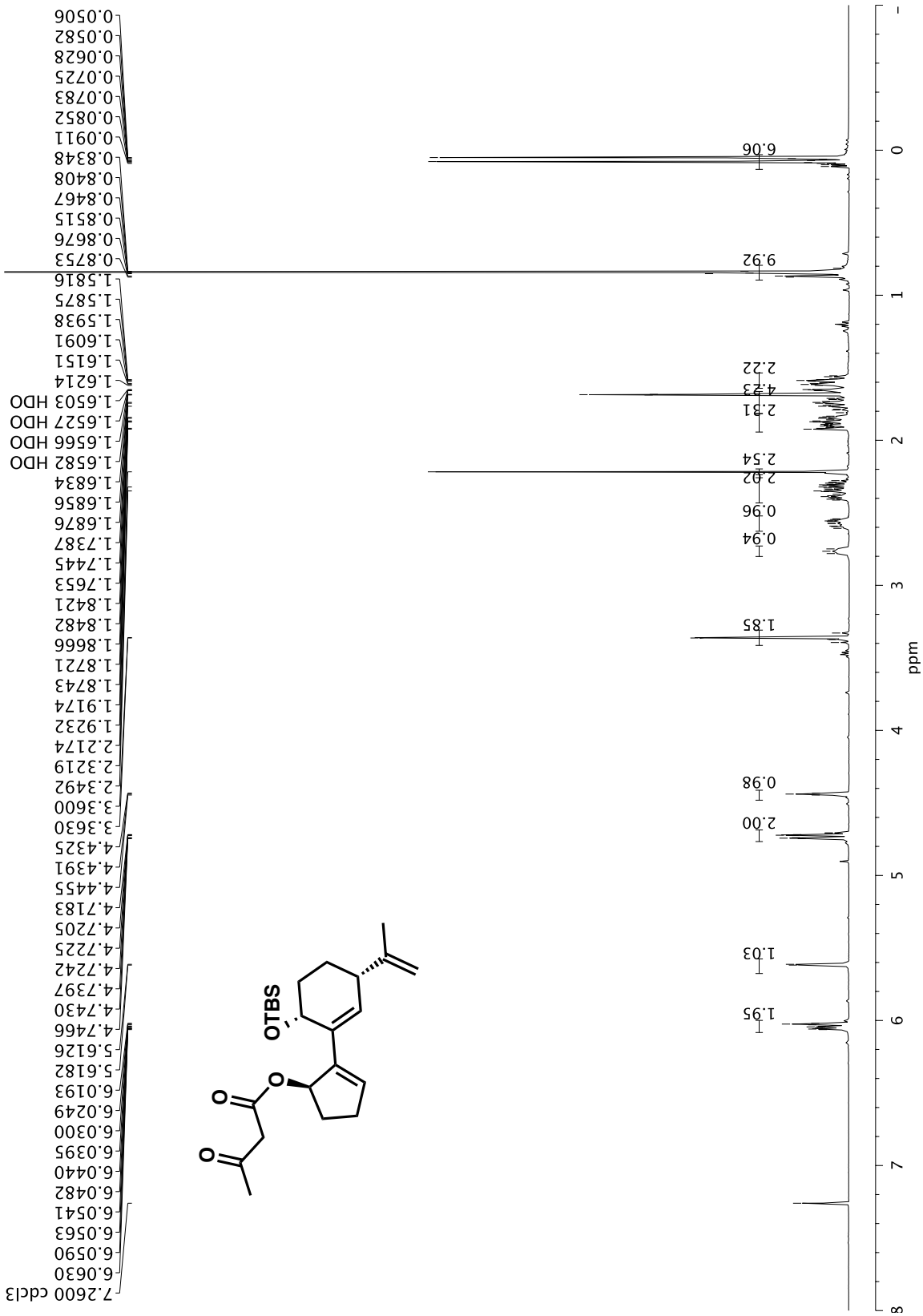
^{1}H NMR (500 MHz, $CDCl_3$) of compound **11.**



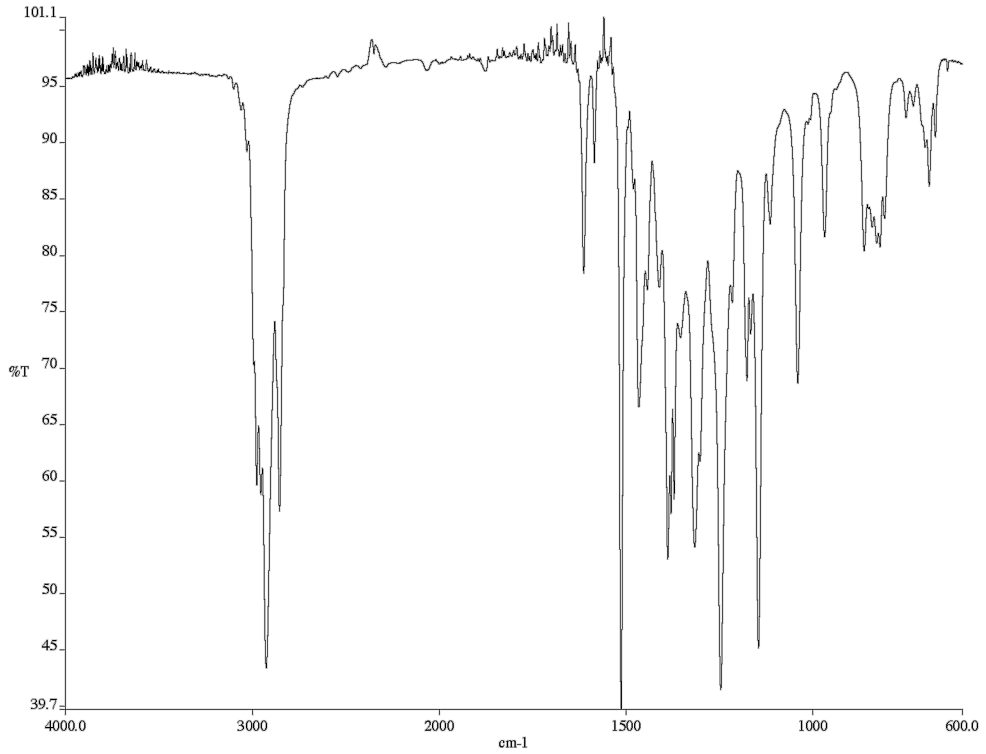
Infrared spectrum (Thin Film, NaCl) of compound **11**.



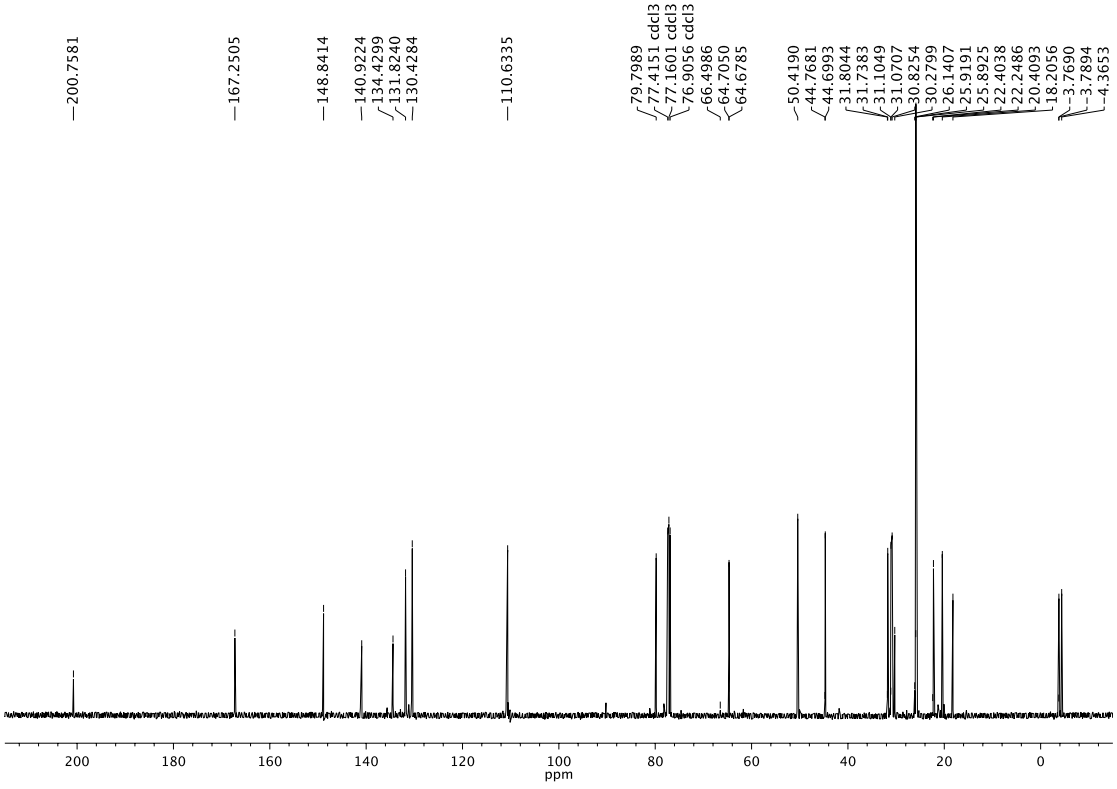
^{13}C NMR (126 MHz, $CDCl_3$) of compound **11**.



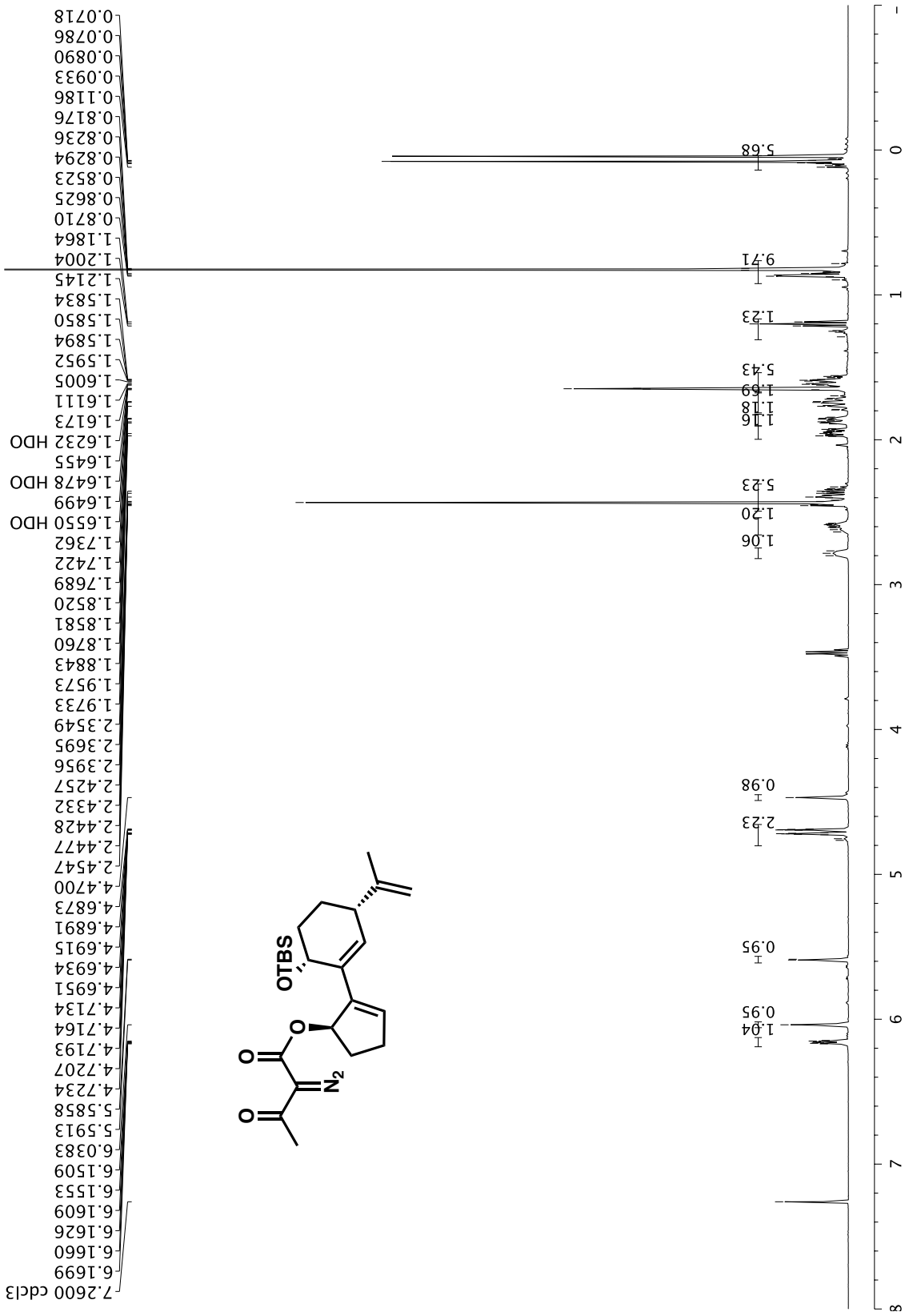
1H NMR (500 MHz, $CDCl_3$) of compound **43.**



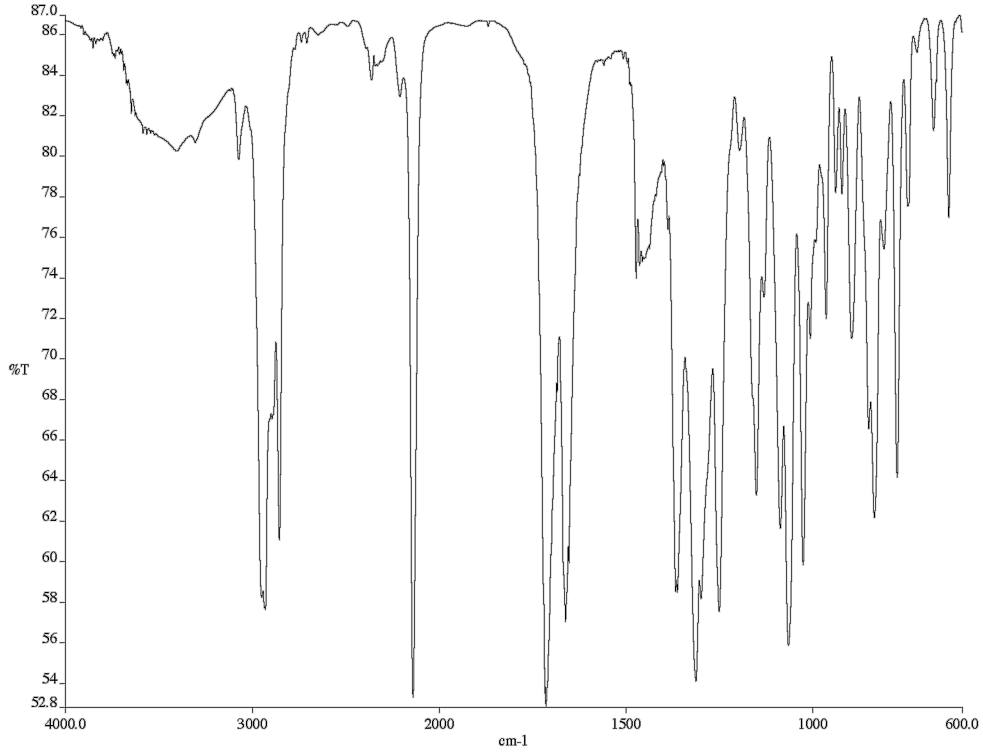
Infrared spectrum (Thin Film, NaCl) of compound **43**.



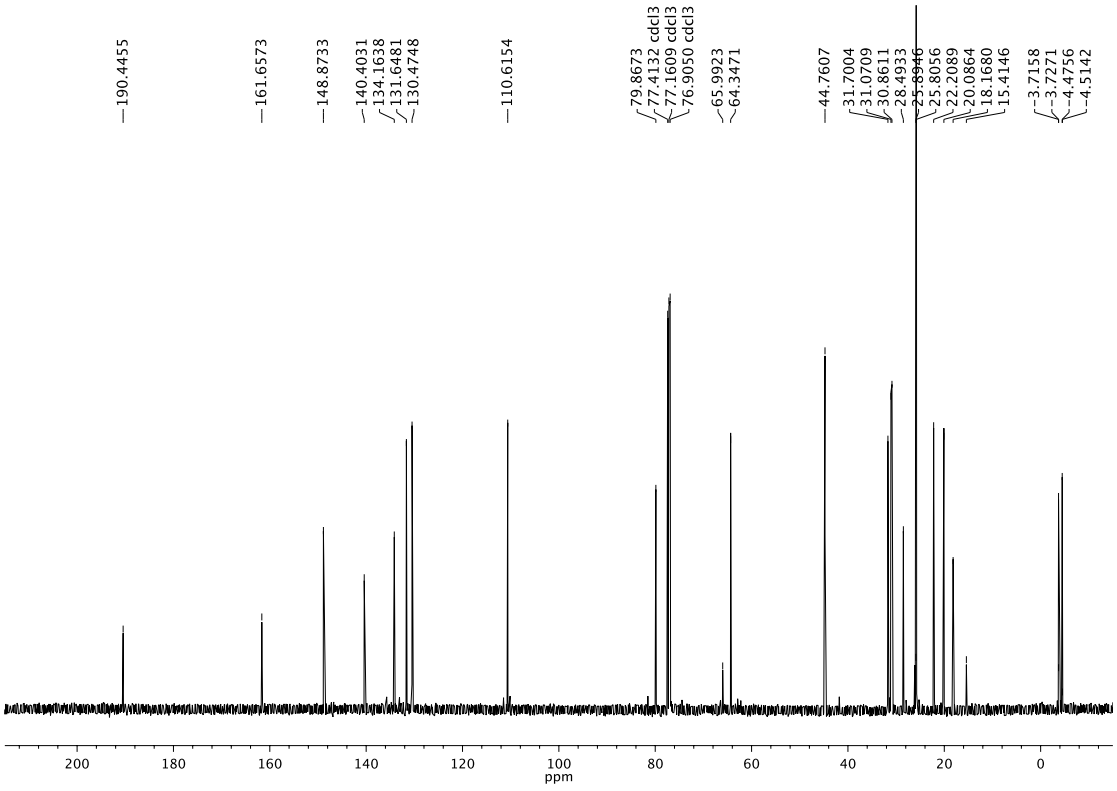
^{13}C NMR (126 MHz, $CDCl_3$) of compound **43**.



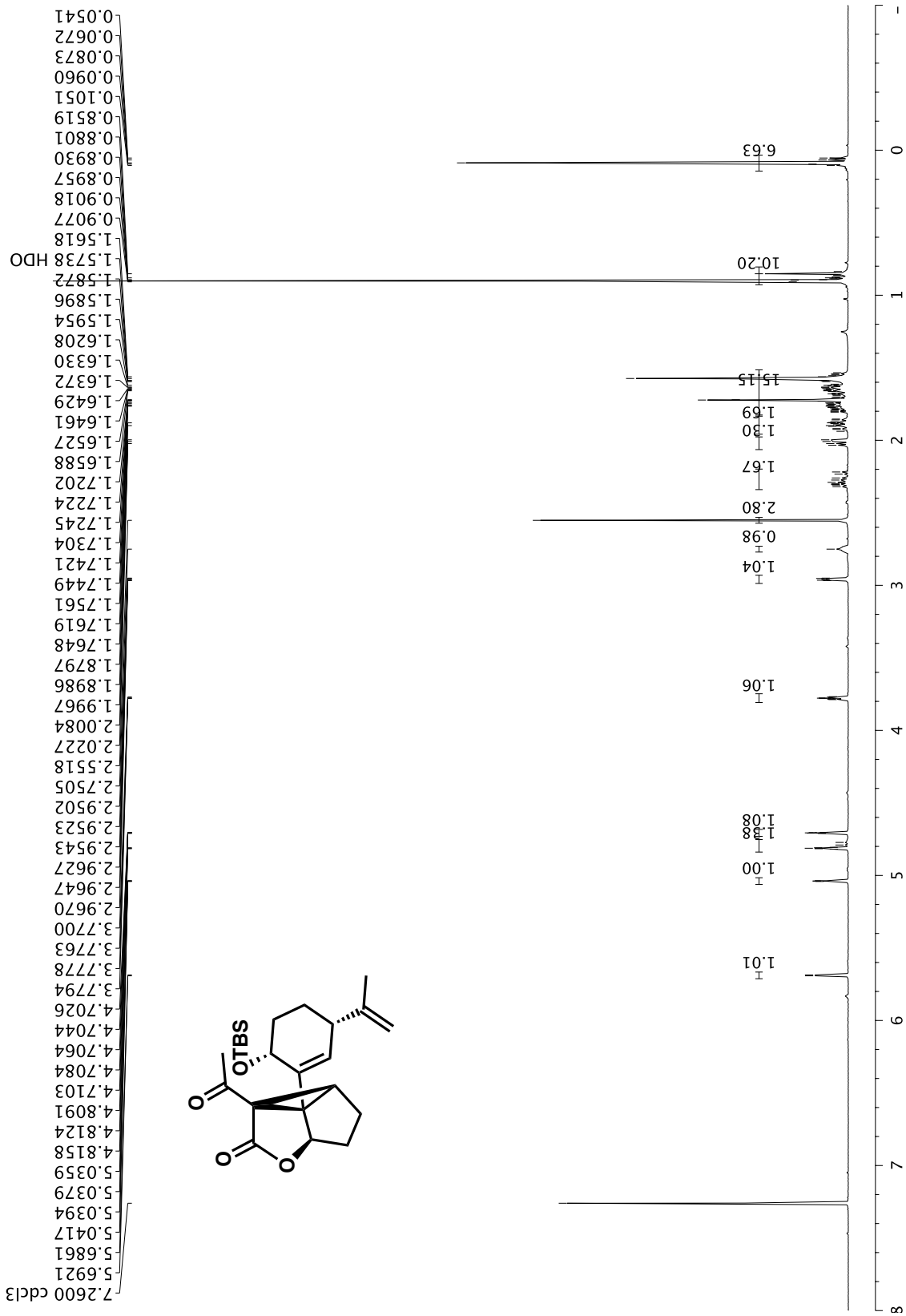
^{1}H NMR (500 MHz, $CDCl_3$) of compound **10.**



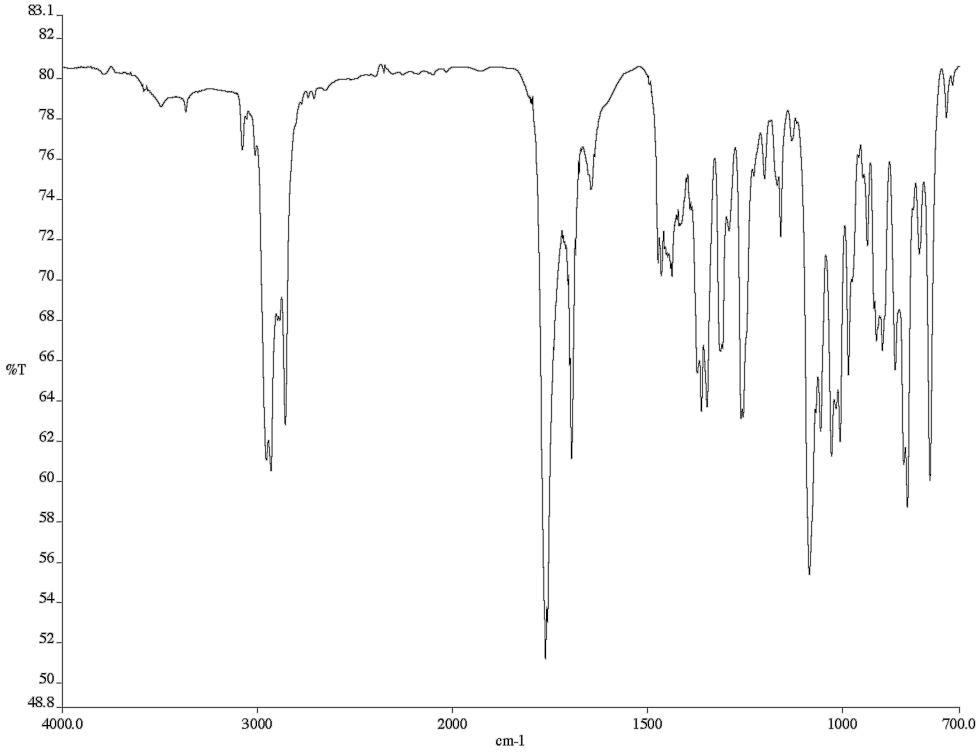
Infrared spectrum (Thin Film, NaCl) of compound **10**.



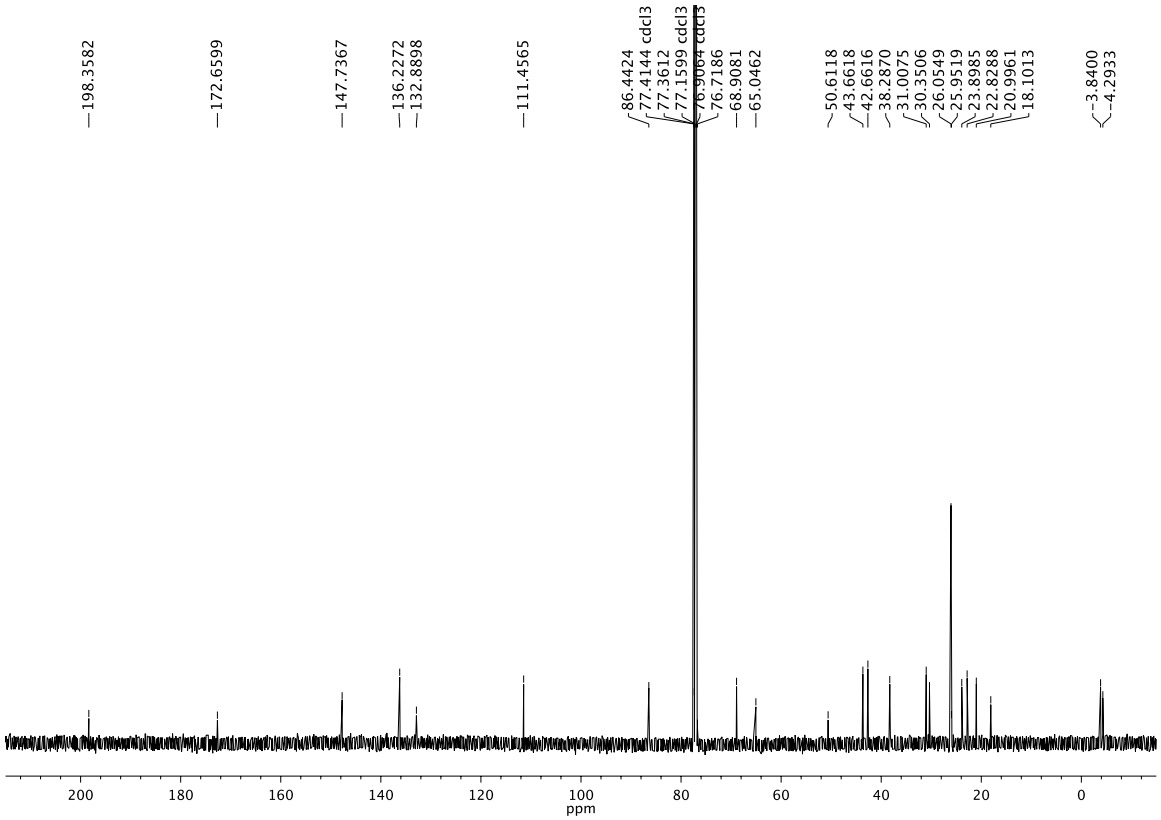
^{13}C NMR (126 MHz, $CDCl_3$) of compound **10**.



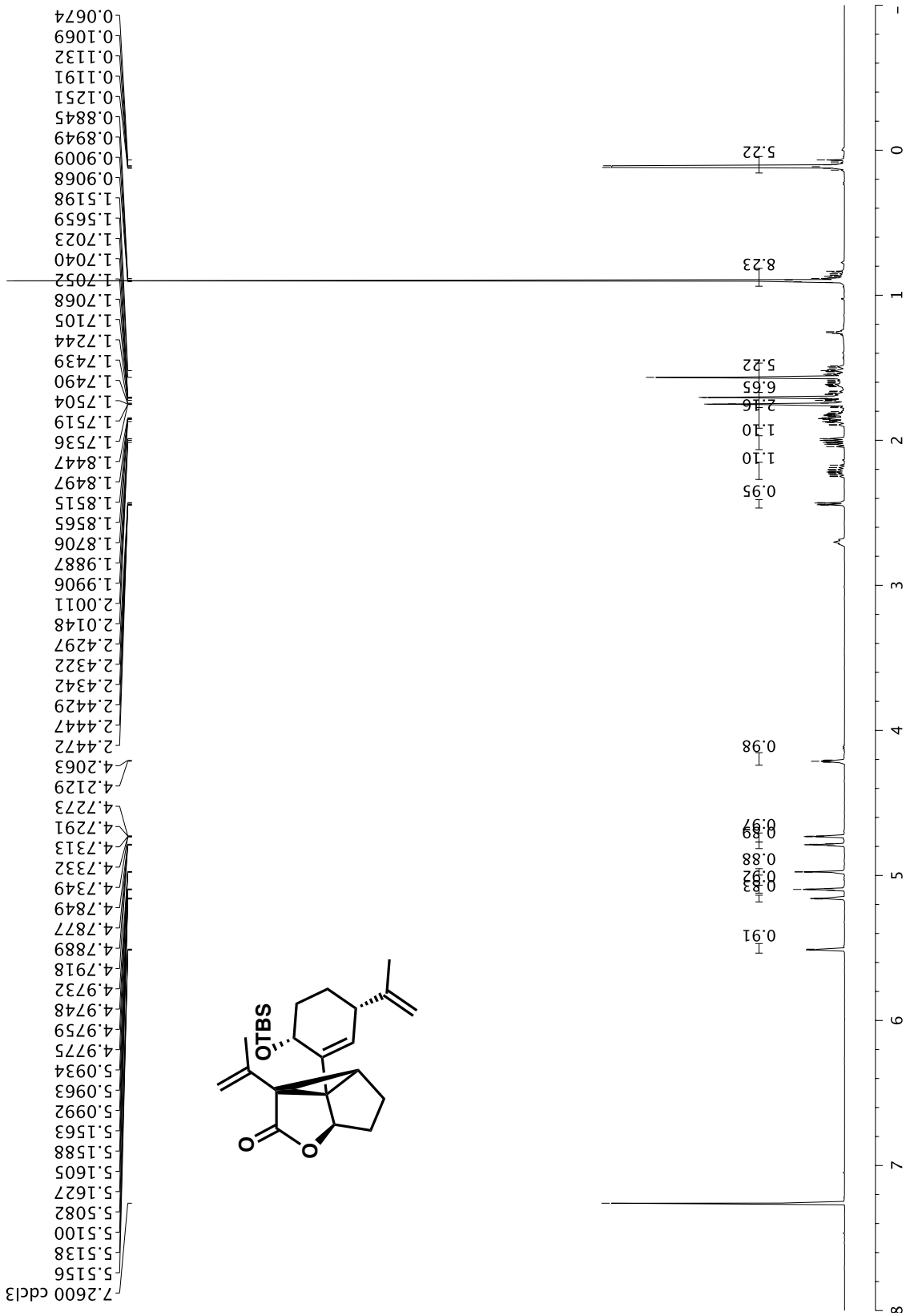
^{1}H NMR (500 MHz, $CDCl_3$) of compound **44.**



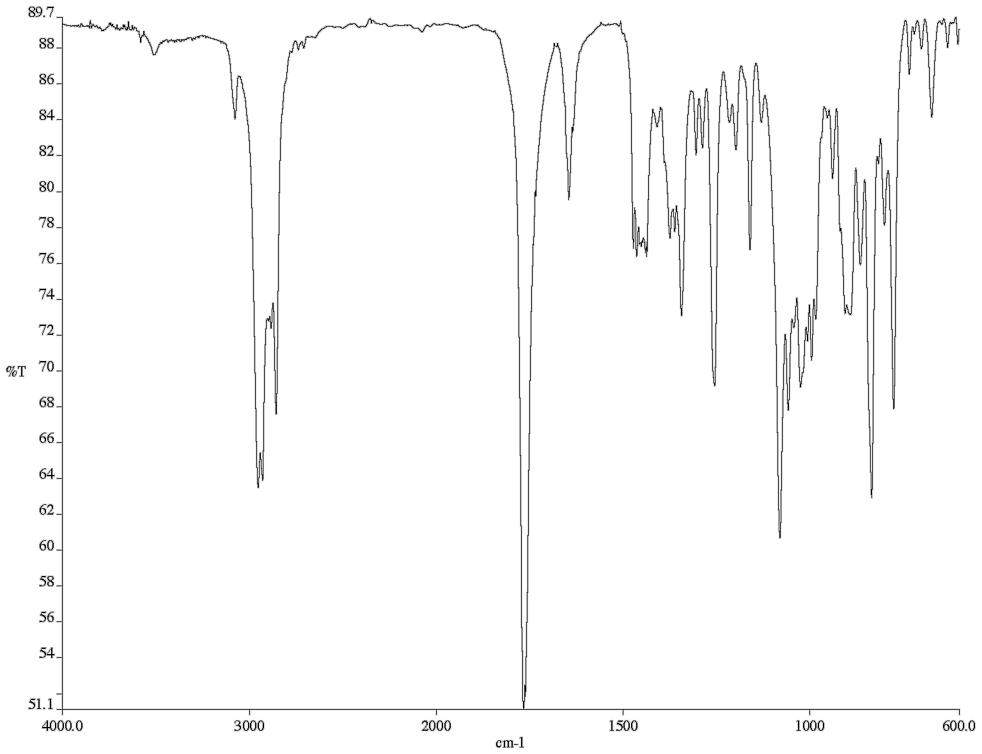
Infrared spectrum (Thin Film, NaCl) of compound **44**.



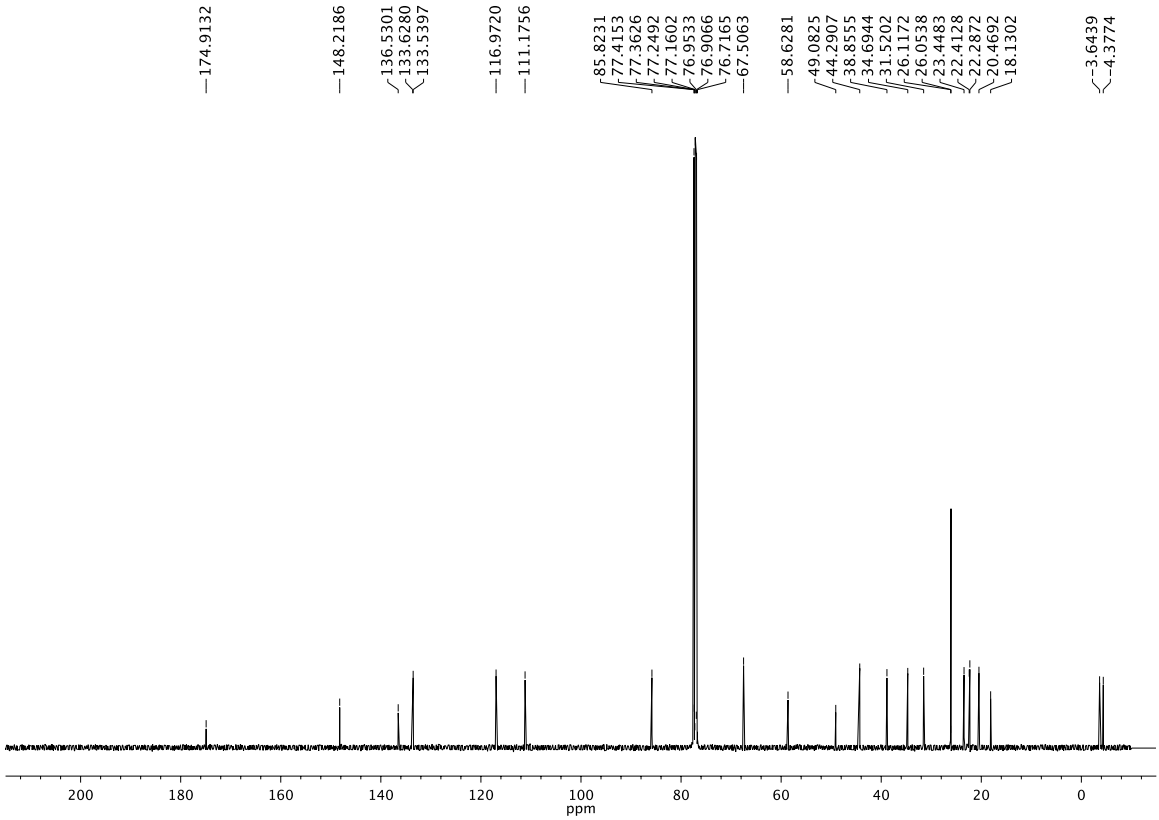
^{13}C NMR (126 MHz, $CDCl_3$) of compound **44**.



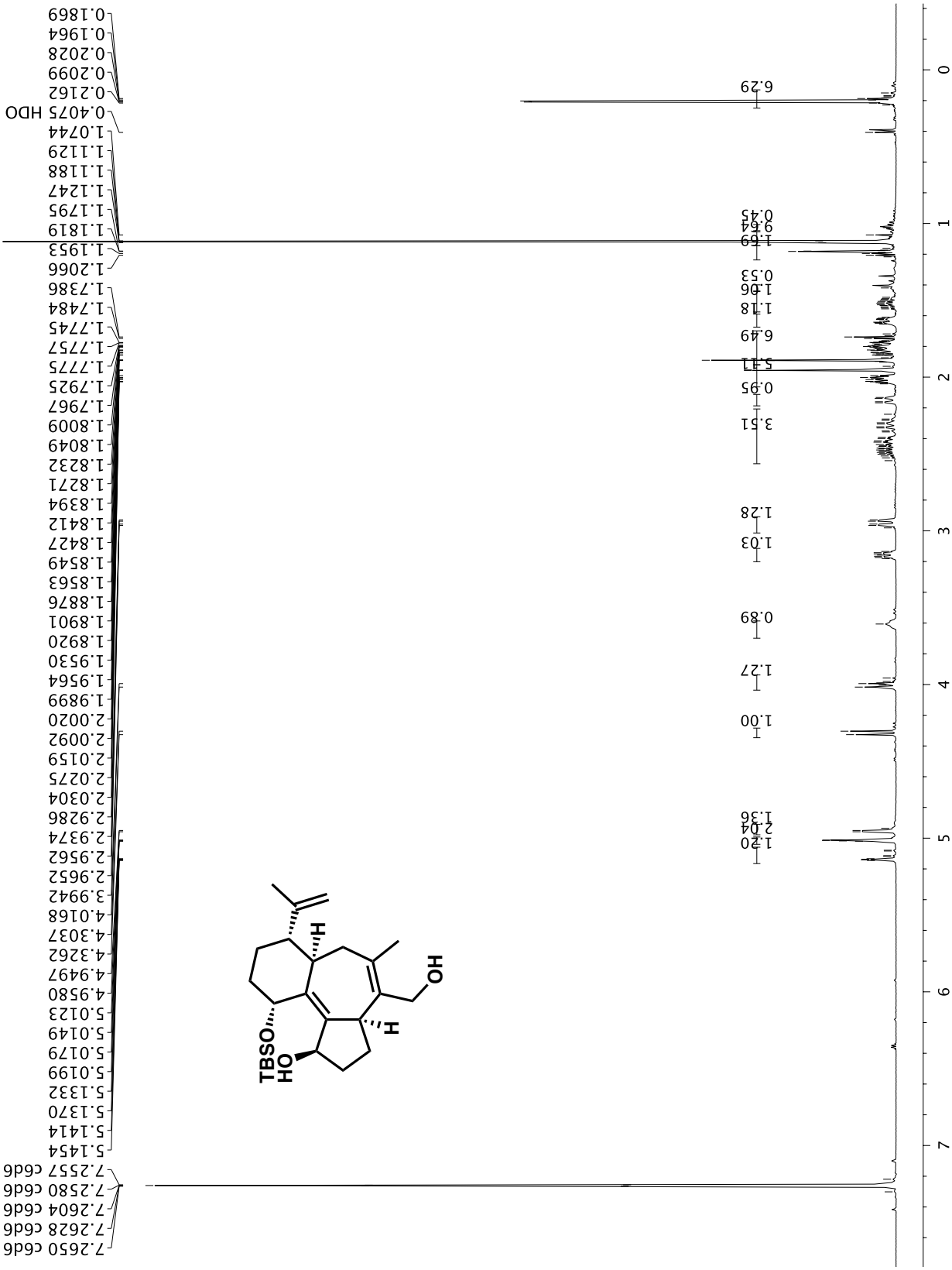
^{1}H NMR (500 MHz, $CDCl_3$) of compound **45.**



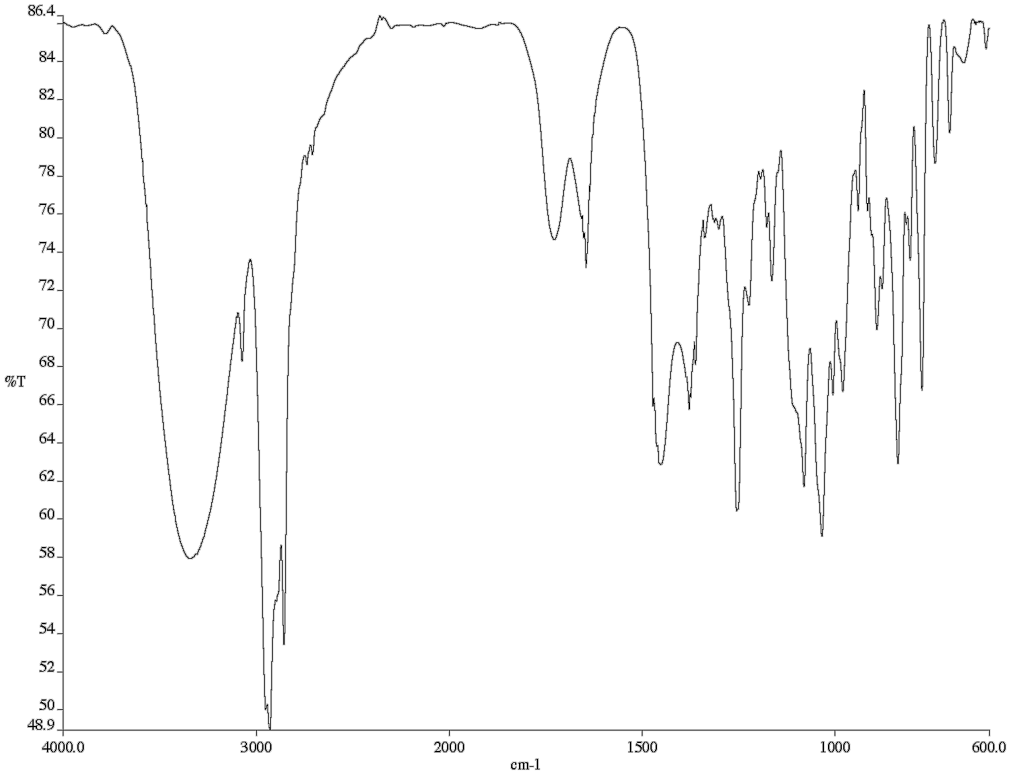
Infrared spectrum (Thin Film, NaCl) of compound **45**.



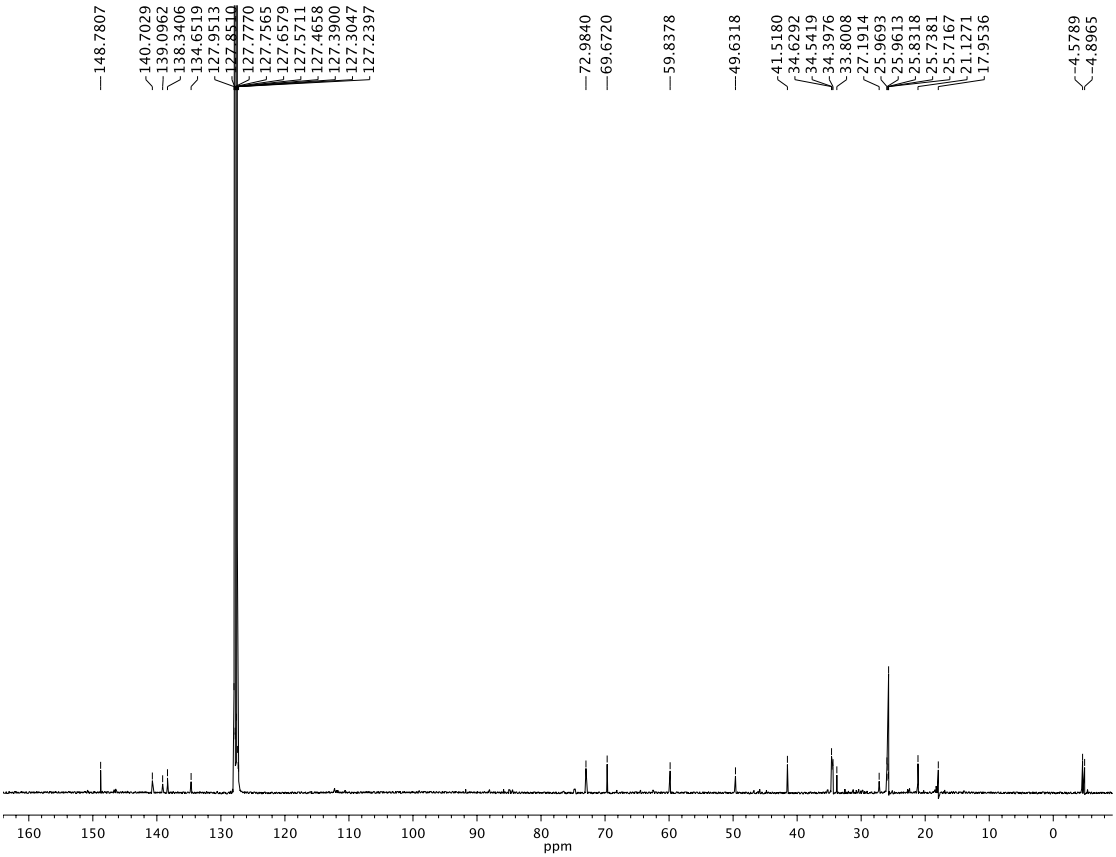
^{13}C NMR (126 MHz, $CDCl_3$) of compound **45**.



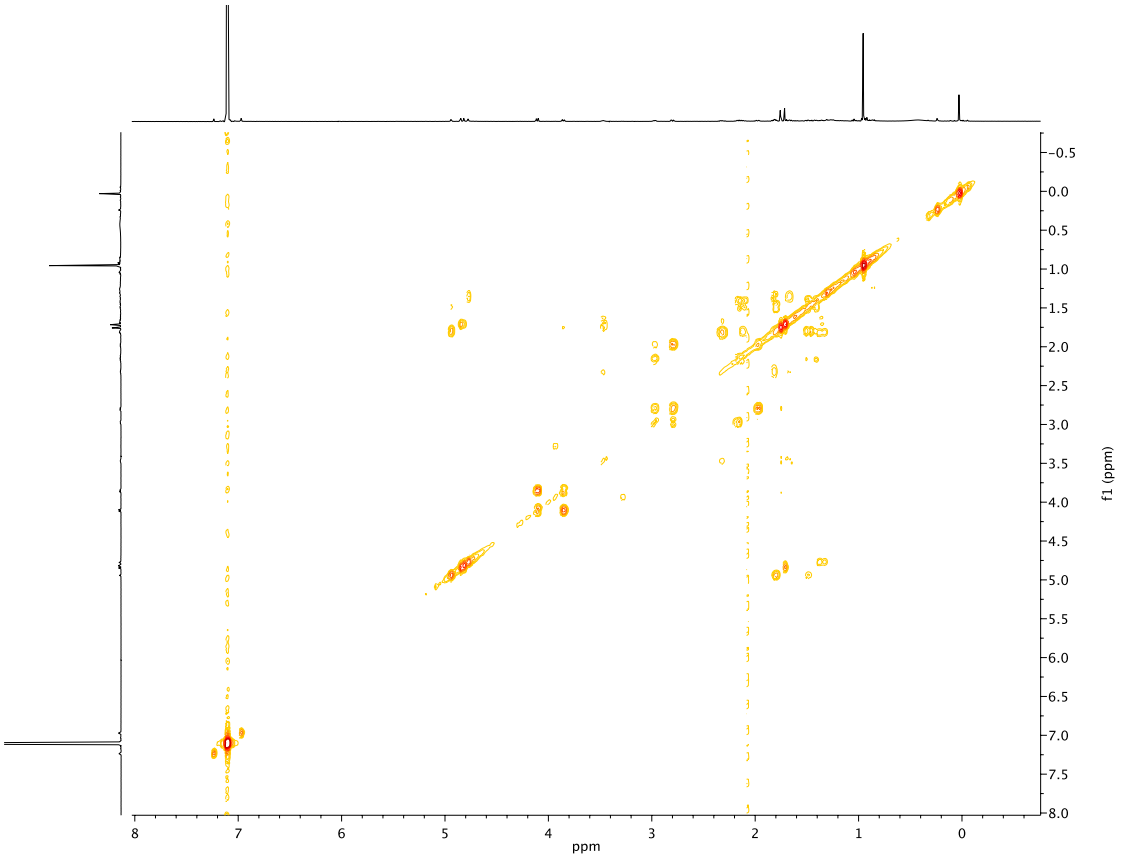
^{1}H NMR (600 MHz, C_6D_6) of compound **46.**



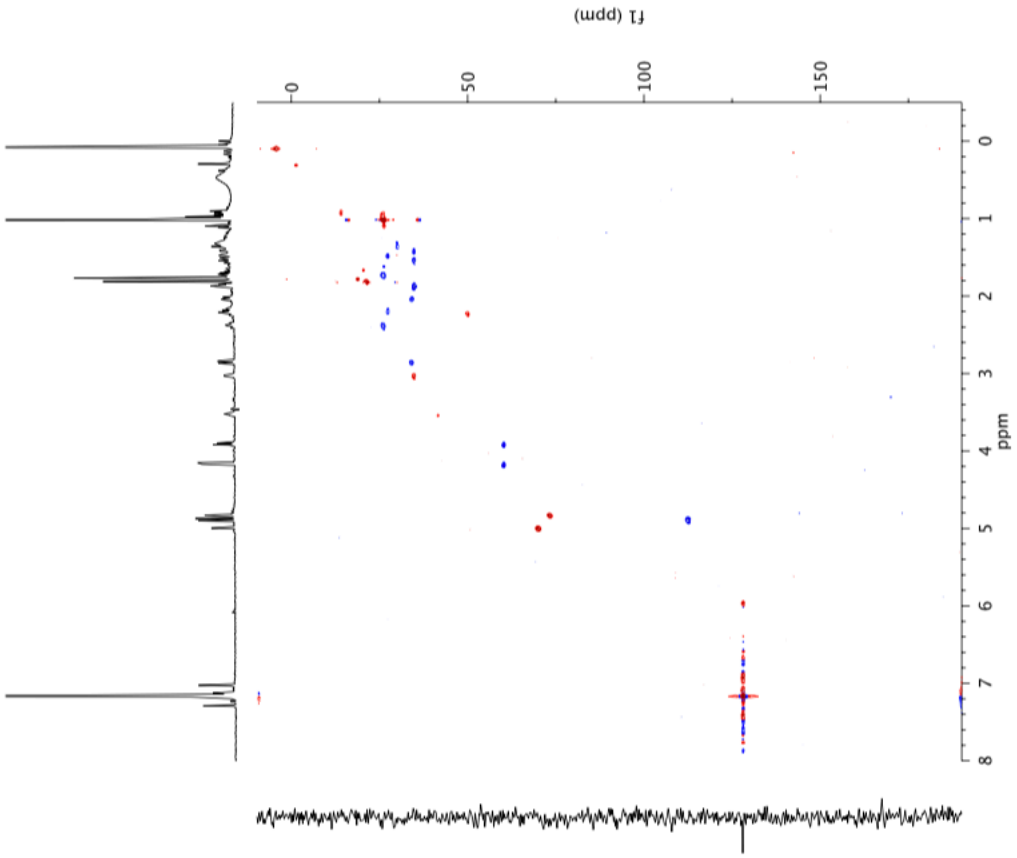
Infrared spectrum (Thin Film, NaCl) of compound **46**.



^{13}C NMR (126 MHz, C_6D_6) of compound **46**.



gCOSY (600 MHz, C_6D_6) of compound **46**.



$^{1}H–^{13}C$ HSQC (600 MHz, C_6D_6) of compound **46**.