Supporting Information for

Probing Trends in Enantioinduction via Substrate Design: Palladium-Catalyzed Decarboxylative Allylic Alkylation of α-Enaminones

*Douglas C. Duquette, Alexander Q. Cusumano, Louise Lefoulon, Jared T. Moore, and Brian M. Stoltz**

Warren and Katharine Schlinger Laboratory of Chemistry and Chemical Engineering, Division of Chemistry and Chemical Engineering, California Institute of Technology, MC 101-20, Pasadena, California 91125, United States

stoltz@caltech.edu

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Materials and Methods

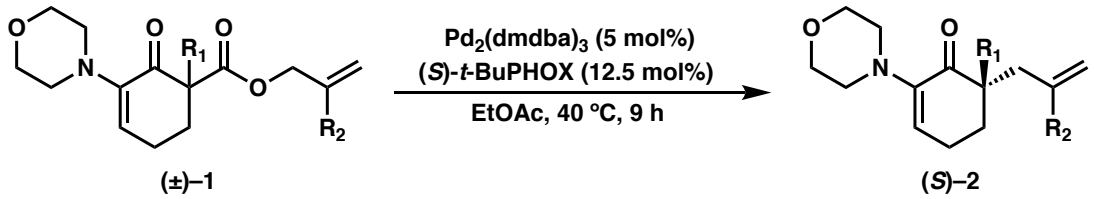
Unless otherwise stated, reactions were performed in flame-dried glassware under an argon or nitrogen atmosphere using dry, deoxygenated solvents. Reactions were heated by pre-heated oil bath unless otherwise specified. Solvents were dried by passage through an activated alumina column under argon.[1] Acetone was used directly from a Sigma-Aldrich ACS reagent grade bottle. Brine solutions are saturated aqueous solutions of sodium chloride. Reagents were purchased from Sigma-Aldrich, Acros Organics, Strem, or Alfa Aesar and used as received unless otherwise stated. The (*S*)-*t*-BuPHOX (**L1)** ligand was prepared by known methods.[2] Reaction progress was monitored by thin-layer chromatography (TLC) or Agilent 1290 UHPLC-MS. TLC was performed using E. Merck silica gel 60 F254 precoated glass plates (0.25 mm) and visualized by UV fluorescence quenching or $KMnO_4$ staining. Silicycle Silia*Flash*® P60 Academic Silica gel (particle size 40–63 nm) was used for flash column chromatography. ^{1}H NMR spectra were recorded on Varian Inova 500 MHz, Varian 400 MHz, and Bruker 400 MHz spectrometers and are reported relative to residual $CHCl_3$ (δ 7.26 ppm). ^{13}C NMR spectra were recorded on a Varian Inova 500 MHz spectrometer (125 MHz), a Varian 400 MHz spectrometer (100 MHz), and Bruker 400 MHz spectrometers (100 MHz) and are reported relative to $CHCl_3$ (δ 77.16 ppm). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sept = septuplet, m = multiplet, dm = doublet of multiplets, br s = broad singlet, br d = broad doublet, app = apparent. Data from ^{13}C NMR spectra are reported in terms of chemical shifts (δ ppm). IR spectra were obtained by use of a Perkin Elmer Spectrum BXII 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 and are reported as: $[\alpha]_D^{25}$ (concentration in g/100 mL, solvent, *ee*). Analytical chiral HPLC was performed with an Agilent 1100 Series HPLC utilizing a Chiralpak (AD, AD- H, or AS) or Chiralcel (OD-H, OJ-H, or OB-H) columns (4.6 mm x 25 cm) obtained from Daicel Chemical Industries, Ltd. Analytical chiral SFC was performed with a Mettler SFC supercritical CO_2 analytical chromatography system with Chiralpak AD-H column, OD-H column, and OJ-H column obtained from Daicel Chemical Industries, Ltd. High resolution mass spectra (HRMS) were obtained from the Caltech Mass Spectral Facility (GC-EI+, EI+, or FAB+) or 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:

ee – enantiomeric excess, SFC – supercritical fluid chromatography, TLC – thin-layer chromatography, IPA – isopropanol, NBS – N-bromosuccinimide,

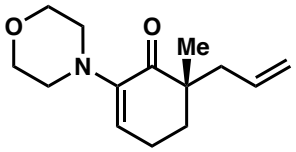
General Procedure A: Palladium-Catalyzed Allylic Alkylation Reactions



(±)–1 (*S*)–2

In a glove box under an atmosphere of N_2, $Pd_2(dmdba)_3$ (29.7 mg, 23.3 μmol, 5 mol %) and (*S*)-*t*-BuPHOX ligand (22.5 mg, 58.2 μmol, 12.5 mol %) were dissolved in EtOAc (12 mL). The catalyst mixture was let stir at 40 ºC in a pre-heated vial block for 30 minutes. At this point, a solution of allyl β-ketoester (**1**, 130 mg, 0.465 mmol, 1.00 equiv) in EtOAc (2.0 mL, final concentration of 0.033 M with respected to **1**) was added. The reaction mixture was sealed, removed from the glove box and stirred at 40 °C in a pre-heated vial block until the reaction was complete as indicated by TLC analysis (typically around 9-12 hours). The reaction mixture was filtered through a short plug of silica, being eluted with additional EtOAc (25 mL). The filtrate was concentrated in vacuo and purified by flash column chromatography to afford the desired enaminone product **2**.

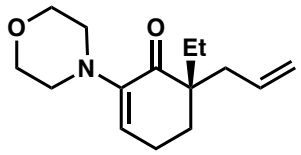
Note: After pre-complexation of catalyst the reaction mixture is red/brown in color, which changes immediately to light green upon addition of substrate. Upon completion, the reaction returns to the original red/brown color.



(*S*)-6-allyl-6-methyl-2-morpholinocyclohex-2-en-1-one (2a)

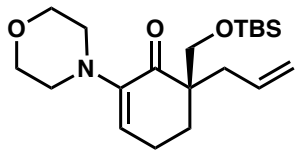
Prepared according to general procedure A using substrate **1a**. The product was purified by flash column chromatography (SiO_2, 5–10% acetone in hexanes) to yield enaminone **2a** as a colorless oil (104 mg, 0.442 mmol, 95% yield). R_f = 0.22 (20% acetone in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.88 (t, *J* = 4.5 Hz, 1H), 5.78 – 5.69 (m, 1H), 5.06 – 5.02 (m, 2H), 3.80 (ddd, *J* = 5.7, 3.5, 2.2 Hz, 4H), 2.82 (dt, *J* = 9.9, 4.6 Hz, 2H), 2.73 – 2.67 (m, 2H), 2.48 – 2.38 (m, 2H), 2.34 (ddd, *J* = 13.8, 7.2, 1.1 Hz, 1H), 2.23 (dd, *J* = 13.7, 7.7 Hz, 1H), 1.88 (dt, *J* = 13.8, 6.0 Hz, 1H), 1.73 (ddd, *J* = 13.9, 6.9, 5.7 Hz, 1H), 1.09 (s, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.4, 145.5, 134.0, 125.0, 118.1, 66.9, 50.5, 45.4, 41.2, 33.2, 21.9, 21.8; IR (Neat Film, NaCl): 2960, 2918,

2853, 2813, 1679, 1615, 1447, 1376, 1262, 1208, 1120, 1099, 1001, 990, 915 cm^{-1}; HRMS (ESI-APCI) *m/z*: $[M+H]^+$ Calc'd for $C_{14}H_{22}NO_2$ 236.1645; Found 236.1641; $[\alpha]^{25}$ –315.66 (*c* 13.57, $CHCl_3$, 99% *ee*).



(*S*)-6-allyl-6-ethyl-2-morpholinocyclohex-2-en-1-one (2b)

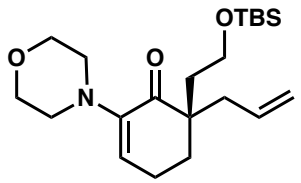
Prepared according to general procedure A using substrate **1b**. The product was purified by flash column chromatography (SiO_2, 5–10% acetone in hexanes) to yield enaminone **2b** as a colorless oil (116 mg, 0.465 mmol, 99% yield). R_f = 0.25 (40% Et_2O in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 5.83 (t, *J* = 4.4 Hz, 1H), 5.73 – 5.66 (m, 1H), 5.04 – 5.02 (m, 1H), 5.01 – 4.99 (m, 1H), 3.79 – 3.77 (m, 4H), 2.80 – 2.74 (m, 2H), 2.70 (ddd, *J* = 11.6, 7.4, 4.2 Hz, 2H), 2.40 (tdd, *J* = 5.9, 4.5, 1.4 Hz, 2H), 2.34 (ddt, *J* = 14.0, 6.9, 1.3 Hz, 1H), 2.23 (ddt, *J* = 14.0, 7.9, 1.1 Hz, 1H), 1.81 (t, *J* = 6.2 Hz, 2H), 1.59 (qd, *J* = 7.5, 1.3 Hz, 2H), 0.80 (t, *J* = 7.5 Hz, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.2, 146.0, 134.4, 124.8, 117.9, 67.0, 50.6, 48.6, 38.8, 30.4, 27.0, 21.8, 8.4; IR (Neat Film, NaCl): 2962, 2933, 2854, 2814, 1678, 1616, 1447, 1377, 1263, 1208, 1120, 1070, 1099, 998 cm^{-1}; HRMS (ESI-APCI) *m/z*: $[M+H]^+$ calc'd for $C_{15}H_{24}NO_2$ 250.1802; Found 250.1813; $[\alpha]^{25}$ 5.52 (*c* 7.45, $CHCl_3$, 98% *ee*).



(*S*)-6-allyl-6-(((*tert*-butyldimethylsilyl)oxy)methyl)-2-morpholinocyclohex-2-en-1-one (2c)

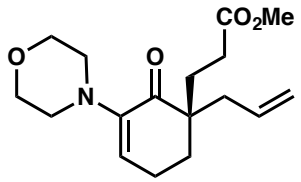
Prepared according to general procedure A using substrate **1c**. The product was purified by flash column chromatography (SiO_2, 20% acetone in hexanes) to yield enaminone **2c** (164 mg, 0.445 mmol, 96% yield) as a pale tan oil; R_f = 0.33 (20% EtOAc in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 5.87 (t, *J* = 4.6 Hz, 1H), 5.74 – 5.66 (m, 1H), 5.04 – 5.00 (m, 2H), 3.78 (t, *J* = 4.6 Hz, 4H), 3.68 (d, *J* = 9.7 Hz, 1H), 3.62 (d, *J* = 9.7 Hz, 1H), 2.74 (t, *J* = 4.7 Hz, 4H), 2.43 – 2.38 (m, 3H), 2.26 (ddt, *J* = 13.8, 7.8, 1.1 Hz, 1H), 1.96 (ddd, *J* = 13.3, 7.1, 6.0 Hz, 1H), 1.89 (dt, *J* = 13.7, 5.9 Hz, 1H), 0.85 (s, 9H), 0.01 (s, 3H), 0.01 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.8, 146.4, 134.1, 125.1, 118.0, 67.0, 66.1, 51.0, 50.5, 37.2, 28.5, 26.0, 21.7, 18.3, -5.4, -5.5; IR (Neat Film,

NaCl): 2953, 2855, 1677, 1639, 1615, 1472, 1463, 1447, 1378, 1299, 1262, 1208, 1121, 973, 917 cm^{-1}; HRMS (ESI-APCI) *m/z*: $[M+H]^+$ calc'd for $C_{20}H_{36}NO_3Si$ 366.2459; Found 366.2466; $[\alpha]^{25}$ –111.67 (*c* 10.25, $CHCl_3$, 99% *ee*).



(*S*)-6-allyl-6-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)-2-morpholinocyclohex-2-en-1-one (2d)

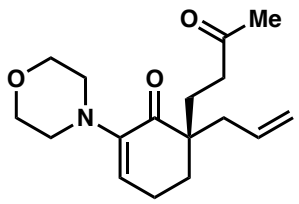
Prepared according to general procedure A using substrate **1d**. The product was purified by flash column chromatography (SiO_2, 20% acetone in hexanes) to yield enaminone **2d** (165 mg, 0.432 mmol, 93% yield) as a colorless oil; R_f = 0.31 (20% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.87 (s, 1H), 5.74 (dddd, *J* = 16.5, 10.5, 7.8, 6.9 Hz, 1H), 5.08 – 5.01 (m, 2H), 3.85 – 3.76 (m, 4H), 3.70 (ddd, *J* = 10.2, 8.4, 6.1 Hz, 1H), 3.57 (ddd, *J* = 10.3, 8.6, 5.9 Hz, 1H), 2.82 – 2.68 (m, 4H), 2.51 – 2.35 (m, 3H), 2.27 (dd, *J* = 14.0, 7.8 Hz, 1H), 1.92 – 1.82 (m, 3H), 1.75 (ddd, *J* = 14.0, 8.4, 5.9 Hz, 1H), 0.87 (s, 9H), 0.03 (s, 3H), 0.02 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.6, 145.8, 134.2, 125.0, 118.3, 67.0, 59.5, 50.6, 47.8, 39.5, 37.0, 31.3, 26.1, 21.9, 18.4, -5.1, -5.2; IR (Neat Film, NaCl): 2953, 2928, 2855, 2817, 1679, 1616, 1448, 1262, 1207, 1121, 1098, 1030, 977, 914 cm^{-1}; HRMS (APCI) *m/z*: $[M+H]^+$ calc'd for $C_{21}H_{38}NO_3Si$ 380.2615; Found 380.2618; $[\alpha]^{25}$ –9.38 (*c* 3.48, $CHCl_3$, 99% *ee*).



Methyl (*R*)-3-(1-allyl-3-morpholino-2-oxocyclohex-3-en-1-yl)propanoate (2e)

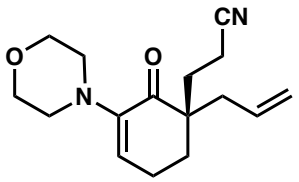
Prepared according to general procedure A using substrate **1e**. The product was purified by flash column chromatography (SiO_2, 5–50% EtOAc in hexanes) to yield enaminone **2e** (140 mg, 0.456 mmol, 98% yield) as a colorless oil; R_f = 0.31 (20% EtOAc in hexanes); R_f = 0.40 (50% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.86 (t, *J* = 4.4 Hz, 1H), 5.73 – 5.65 (m, 1H), 5.07 – 5.02 (m, 2H), 3.77 (td, *J* = 4.8, 1.1 Hz, 4H), 3.63 (s, 3H), 2.77 – 2.70 (m, 4H), 2.43 (td, *J* = 5.9, 4.1 Hz, 2H), 2.35 – 2.28 (m, 2H), 2.26 – 2.16 (m, 2H), 1.93 (dddd, *J* = 14.1, 11.2, 5.4, 1.0 Hz, 1H), 1.86 –

1.80 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.1, 174.0, 145.7, 133.3, 125.0, 118.6, 66.8, 51.6, 50.4, 47.8, 38.9, 30.6, 29.2, 28.8, 21.6; IR (Neat Film, NaCl): 2950, 2853, 1735, 1676, 1617, 1437, 1375, 1263, 1207, 1174, 1119 cm^{-1}; HRMS (ESI-APCI) *m/z*: $[M+H]^+$ calc'd for $C_{17}H_{26}NO_4$ 308.1856; Found 308.1859; $[\alpha]^{25}$ 34.36 (*c* 16.49, $CHCl_3$, 97% *ee*).



(*R*)-6-allyl-2-morpholino-6-(3-oxobutyl)cyclohex-2-en-1-one (2f)

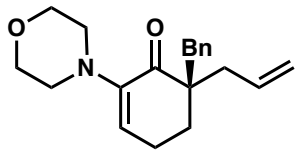
Prepared according to general procedure A using substrate **1f**. The product was purified by flash column chromatography (SiO_2, 20–50% EtOAc in hexanes) to yield enaminone **2f** (122 mg, 0.419 mmol, 90% yield) as a colorless oil; R_f = 0.35 (50% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.89 (t, *J* = 4.5 Hz, 1H), 5.69 (ddt, *J* = 16.6, 10.4, 7.3 Hz, 1H), 5.08 – 5.03 (m, 2H), 3.79 (t, *J* = 4.7 Hz, 4H), 2.78 (dt, *J* = 11.6, 4.7 Hz, 2H), 2.70 (dt, *J* = 11.5, 4.7 Hz, 2H), 2.50 – 2.43 (m, 3H), 2.32 (tdd, *J* = 9.5, 6.7, 3.9 Hz, 2H), 2.25 (ddt, *J* = 14.0, 7.6, 1.2 Hz, 1H), 2.12 (s, 3H), 1.89 – 1.75 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.6, 199.6, 145.9, 133.6, 118.7, 67.0, 50.7, 47.9, 39.3, 38.4, 31.0, 30.2, 30.2, 28.0, 21.8; IR (Neat Film, NaCl): 2921, 2853, 2814, 1716, 1674, 1615, 1446, 1369, 1262, 1206, 1167, 1119, 978, 922 cm^{-1}; HRMS (ESI-APCI) *m/z*: $[M+H]^+$ calc'd for $C_{17}H_{26}NO_3$ 292.1907; Found 292.1914; $[\alpha]^{25}$ 15.98 (*c* 10.28, $CHCl_3$, 94% *ee*).



(*R*)-3-(1-allyl-3-morpholino-2-oxocyclohex-3-en-1-yl)propanenitrile (2g)

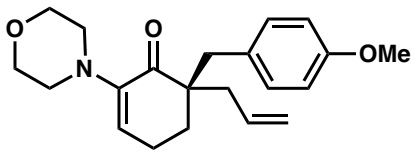
Prepared according to general procedure A using substrate **1g**. The product was purified by flash column chromatography (SiO_2, 5–50% EtOAc in hexanes) to yield enaminone **2g** (217 mg, 0.465 mmol, 99% yield) as a colorless oil; R_f = 0.30 (50% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.90 (t, *J* = 4.5 Hz, 1H), 5.64 (ddt, *J* = 17.4, 10.1, 7.4 Hz, 1H), 5.13 – 5.06 (m, 2H), 3.81 – 3.74 (m, 4H), 2.82 (ddd, *J* = 11.7, 5.3, 3.4 Hz, 2H), 2.65 (ddd, *J* = 11.6, 5.9, 3.4 Hz, 2H), 2.54 – 2.24 (m, 6H), 2.07 (ddd, *J* = 14.0, 10.2, 5.9 Hz, 1H), 1.92 – 1.83 (m, 2H), 1.78 (ddd, *J* = 14.1, 10.2,

5.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.5, 145.7, 132.4, 125.4, 120.1, 119.5, 77.4, 77.2, 76.9, 66.9, 50.5, 48.0, 48.0, 38.8, 30.5, 30.3, 21.6, 12.3; IR (Neat Film, NaCl): 2929, 2854, 1675, 1448, 1263, 1205, 1118, 1000, 924 cm^{-1}; HRMS (ESI-APCI) *m/z*: $[M+H]^+$ calc'd for $C_{16}H_{23}N_2O_2$ 275.1754; Found 275.1753; $[\alpha]^{25}$ 29.26 (*c* 11.02, $CHCl_3$, 94% *ee*).



(*S*)-6-allyl-6-benzyl-2-morpholinocyclohex-2-en-1-one (2h)

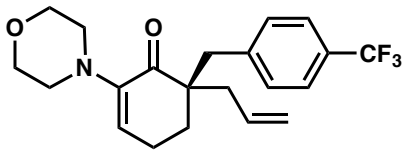
Prepared according to general procedure A using substrate **1h**. The product was purified by flash column chromatography (SiO_2, 5–20% acetone in hexanes) to yield enaminone **2h** (217 mg, 0.442 mmol, 95% yield) as a colorless oil; R_f = 0.20 (40% Et_2O in hexanes; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.17 (m, 3H), 7.15 – 7.09 (m, 2H), 5.88 (t, *J* = 4.5 Hz, 1H), 5.77 (dddd, *J* = 16.9, 10.2, 8.0, 6.6 Hz, 1H), 5.11 – 5.02 (m, 2H), 3.80 (dd, *J* = 5.2, 4.2 Hz, 4H), 3.07 (d, *J* = 13.5 Hz, 1H), 2.80 – 2.70 (m, 5H), 2.47 – 2.39 (m, 3H), 2.15 (ddt, *J* = 14.0, 8.0, 1.1 Hz, 1H), 1.80 (dt, *J* = 13.9, 5.8 Hz, 1H), 1.75 – 1.69 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.2, 146.3, 137.6, 134.1, 130.9, 128.1, 126.5, 125.2, 118.6, 67.0, 50.6, 49.9, 40.7, 39.8, 29.8, 21.9; IR (Neat Film, NaCl): 2919, 2854, 2814, 1675, 1614, 1447, 1263, 1205, 1119, 981, 923 cm^{-1}; HRMS (ESI-APCI) *m/z*: $[M+H]^+$ calc'd for $C_{20}H_{26}NO_2$ 312.1958; Found 312.1967; $[\alpha]^{25}$ –95.78 (*c* 4.69, $CHCl_3$, 96% *ee*).



(*S*)-6-allyl-6-(4-methoxybenzyl)-2-morpholinocyclohex-2-en-1-one (2i)

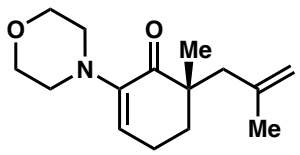
Prepared according to general procedure A using substrate **1i**. The product was purified by flash column chromatography (SiO_2, 5–20% acetone in hexanes) to yield enaminone **2i** (159 mg, 0.465 mmol, 99% yield) as a colorless oil; R_f = 0.17 (40% Et_2O in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 – 7.02 (m, 2H), 6.79 – 6.76 (m, 2H), 5.87 (t, *J* = 4.5 Hz, 1H), 5.76 (dddd, *J* = 16.8, 10.2, 8.0, 6.6 Hz, 1H), 5.09 – 5.01 (m, 2H), 3.80 (t, *J* = 4.7 Hz, 4H), 3.77 (s, 3H), 3.01 (d, *J* = 13.8 Hz, 1H), 2.75 (q, *J* = 4.9 Hz, 4H), 2.66 (d, *J* = 13.8 Hz, 1H), 2.45 – 2.40 (m, 3H), 2.13 (ddt, *J* = 13.9, 8.0, 1.1 Hz, 1H), 1.80 (dt, *J* = 13.8, 5.9 Hz, 1H), 1.71 (dt, *J* = 13.9, 6.5 Hz, 1H); ^{13}C NMR (125

MHz, $CDCl_3$) δ 199.3, 158.3, 146.3, 134.1, 131.8, 129.5, 125.3, 118.5, 113.5, 67.0, 55.3, 55.2, 50.6, 50.0, 39.9, 39.8, 29.7, 21.9; IR (Neat Film, NaCl): 2930, 2853, 1675, 1611, 1512, 1447, 1263, 1248, 1205, 1178, 1119, 1035, 981, 923 cm^{-1}; HRMS (ESI-APCI) *m/z*: $[M+H]^+$ calc'd for $C_{21}H_{28}NO_3$ 342.2064; Found 342.2064; $[\alpha]^{25}$ –316.96 (*c* 12.93, $CHCl_3$, 95% *ee*).



(*S*)-6-allyl-2-morpholino-6-(4-(trifluoromethyl)benzyl)cyclohex-2-en-1-one (2j)

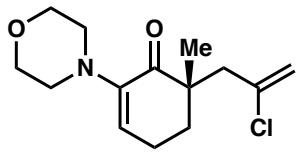
Prepared according to general procedure A using substrate **1j**. The product was purified by flash column chromatography (SiO_2, 5–20% acetone in hexanes) to yield enaminone **2j** (154 mg, 0.406 mmol, 87% yield) as a pale yellow oil; R_f = 0.20 (40% Et_2O in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.8 Hz, 2H), 5.88 (t, *J* = 4.5 Hz, 1H), 5.77 (dddd, *J* = 17.0, 10.1, 7.8, 6.8 Hz, 1H), 5.13 (ddt, *J* = 10.1, 2.0, 1.0 Hz, 1H), 5.08 (dq, *J* = 16.9, 1.5 Hz, 1H), 3.84 – 3.77 (m, 4H), 3.20 (d, *J* = 13.5 Hz, 1H), 2.83 – 2.76 (m, 2H), 2.75 – 2.68 (m, 3H), 2.51 – 2.35 (m, 3H), 2.22 (dd, *J* = 14.0, 7.8 Hz, 1H), 1.79 (dt, *J* = 13.8, 5.3 Hz, 1H), 1.70 (ddd, *J* = 14.0, 8.4, 5.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.6, 146.2, 142.1, 133.5, 131.2, 128.7 (q, *J* = 32.3 Hz), 127.7, 125.5, 125.3, 124.9 (q, *J* = 3.8 Hz), 123.3, 119.1, 66.9, 50.6, 50.0, 40.4, 39.8, 29.9, 21.8; ^{19}F NMR (470 MHz, $CDCl_3$) δ 62.4; IR (Neat Film, NaCl): 2928, 2855, 2817, 1678, 1616, 1448, 1325, 1263, 1163, 1119, 1067, 1019, 982, 923 cm^{-1}; HRMS (ESI-APCI) *m/z*: $[M+H]^+$ calc'd for $C_{21}H_{25}NO_2F$ 380.1832; Found 380.1835; $[\alpha]^{25}$ –22.43 (*c* 8.54, $CHCl_3$, 92% *ee*).



(*S*)-6-methyl-6-(2-methylallyl)-2-morpholinocyclohex-2-en-1-one (2k)

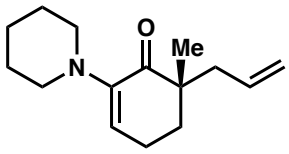
Prepared according to general procedure A using substrate **1k**. The product was purified by flash column chromatography (20% EtOAc in hexanes) to afford enaminone **2k** as a colorless oil (25 mg, 100 μmol 92% yield); ^1H NMR (500 MHz, $CDCl_3$) δ 5.89 (t, *J* = 4.5 Hz, 1H), 4.82 (dt, *J* = 2.9, 1.5 Hz, 1H), 4.65 (dq, *J* = 1.9, 0.9 Hz, 1H), 3.84 – 3.76 (m, 4H), 2.91 (ddd, *J* = 11.5, 6.1, 3.4 Hz, 2H), 2.64 (ddd, *J* = 10.2, 4.7, 2.1 Hz, 2H), 2.51 (dd, *J* = 13.5, 1.1 Hz, 1H), 2.45 – 2.40 (m,

2H), 2.18 (dd, *J* = 13.6, 0.8 Hz, 1H), 1.90 (ddd, *J* = 13.7, 7.0, 5.8 Hz, 1H), 1.72 – 1.67 (m, 1H), 1.66 (s, 3H), 1.10 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.1, 145.6, 138.9, 125.1, 116.7, 67.0, 50.5, 46.1, 45.6, 32.8, 22.5, 21.8; IR (Neat Film, NaCl) 2931, 2855, 1679, 1263, 1120cm^{-1}; HRMS (ESI) *m/z*: $[M+H]^+$ calc'd for $C_{14}H_{21}NClO_2$ 270.1261; Found 270.1259; $[\alpha]^{25}$ –7.5 (*c* 0.8, $CHCl_3$, 99% *ee*).



(*S*)-6-(2-chloroallyl)-6-methyl-2-morpholinocyclohex-2-en-1-one (2l)

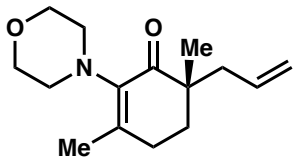
Prepared according to general procedure A using substrate **1l**. The product was purified by flash column chromatography (20% EtOAc in hexanes) to afford enaminone **2l** as a colorless oil (25 mg, 93 μmol, 58% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.91 (t, *J* = 4.5 Hz, 1H), 5.28 (d, *J* = 0.7 Hz, 1H), 5.15 (s, 1H), 3.84 – 3.78 (m, 4H), 2.93 – 2.88 (m, 2H), 2.85 (dd, *J* = 14.3, 0.9 Hz, 1H), 2.71 – 2.65 (m, 2H), 2.53 (d, *J* = 14.3 Hz, 1H), 2.46 (dtd, *J* = 5.3, 4.3, 2.6 Hz, 2H), 2.03 (ddd, *J* = 13.6, 7.4, 6.2 Hz, 1H), 1.84 – 1.79 (m, 1H), 1.17 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.1, 145.6, 138.9, 125.1, 116.7, 67.0, 50.5, 46.1, 45.6, 32.8, 22.5, 21.8; IR (Neat Film, NaCl) 2931, 2855, 1679, 1263, 1120cm^{-1}; HRMS (ESI) *m/z*: $[M+H]^+$ calc'd for $C_{14}H_{21}NClO_2$ 270.1261; Found 270.1259; $[\alpha]^{25}$ –7.5 (*c* 0.8, $CHCl_3$, 99% *ee*).



(*S*)-6-allyl-6-methyl-2-(piperidin-1-yl)cyclohex-2-en-1-one (2m)

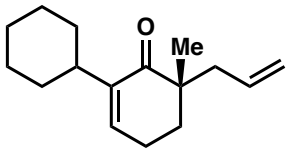
Prepared according to general procedure A using substrate **1m**. The product was purified by flash column chromatography (SiO_2, 10–20% acetone in hexanes) to yield enaminone **2m** (107 mg, 0.459 mmol, 99% yield) as a colorless oil; R_f = 0.37 (40% Et_2O in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.84 (t, *J* = 4.5 Hz, 1H), 5.73 (ddt, *J* = 15.0, 10.2, 7.5 Hz, 1H), 5.04 – 5.01 (m, 2H), 2.70 (dt, *J* = 10.8, 5.2 Hz, 2H), 2.60 (dt, *J* = 11.2, 5.2 Hz, 2H), 2.45 – 2.30 (m, 3H), 2.21 (dd, *J* = 13.8, 7.6 Hz, 1H), 1.84 (dt, *J* = 12.7, 6.0 Hz, 1H), 1.72 – 1.61 (m, 5H), 1.55 – 1.41 (m, 2H), 1.07 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.8, 147.0, 134.4, 124.6, 118.0, 51.6, 45.5, 41.4, 33.4, 26.1, 24.5,

22.1, 22.0; IR (Neat Film, NaCl): 2931, 2852, 2798, 1680, 1613, 1451, 1384, 1217, 1093, 996, 913 cm^{-1}; HRMS (ESI-APCI) *m/z*: $[M+H]^+$ calc'd for $C_{15}H_{24}NO$ 234.1852; Found 234.1847; $[\alpha]^{25}$ –172.28 (*c* 6.64, $CHCl_3$, 99% *ee*).



(*S*)-6-allyl-3,6-dimethyl-2-morpholinocyclohex-2-en-1-one (2n)

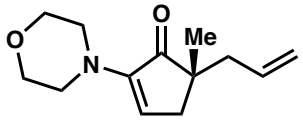
Prepared according to general procedure A using substrate **1n**. The product was purified by flash column chromatography (SiO_2, 10–20% Et_2O in hexanes) to yield enaminone **2n** (60.2 mg, 0.241 mmol, 52% yield) as a pale yellow oil; R_f = 0.35 (29% Et_2O in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 5.72 (ddt, *J* = 16.8, 10.2, 7.4 Hz, 1H), 5.06 – 5.01 (m, 2H), 3.71 – 3.66 (m, 4H), 2.95 – 2.87 (m, 4H), 2.42 – 2.30 (m, 2H), 2.29 – 2.24 (m, 1H), 2.20 – 2.16 (m, 1H), 1.99 (s, 2H), 1.82 (ddd, *J* = 13.7, 6.4, 5.6 Hz, 1H), 1.67 (ddd, *J* = 13.6, 7.2, 5.6 Hz, 1H), 1.03 (s, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.0, 153.4, 141.6, 134.3, 118.0, 77.4, 77.2, 76.9, 68.1, 50.6, 44.9, 41.3, 32.5, 28.7, 21.8, 19.8; IR (Neat Film, NaCl): 2912, 2847, 1664, 1452, 1374, 1294, 1259, 1190, 1114, 988, 911 cm^{-1}; HRMS (ESI-APCI) *m/z*: $[M+H]^+$ calc'd for $C_{15}H_{24}NO_2$ 250.1802; Found 250.1803; $[\alpha]^{25}$ 30.71 (*c* 3.52, $CHCl_3$, 90% *ee*).



(*S*)-3-allyl-3-methyl-[1,1'-bi(cyclohexan)]-6-en-2-one (2o)

Prepared according to general procedure A using substrate **1o**. The product was purified by flash column chromatography (SiO_2, 5% Et_2O in hexanes) to yield enaminone **2o** (11 mg, 47 μmol, 93% yield) as a pale yellow oil; R_f = 0.43 (5% Et_2O in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 6.50 (td, *J* = 4.1, 1.0 Hz, 1H), 5.73 (ddt, *J* = 16.8, 10.3, 7.4 Hz, 1H), 5.07 – 5.01 (m, 2H), 2.55 – 2.48 (m, 1H), 2.41 – 2.27 (m, 3H), 2.17 (ddt, *J* = 13.7, 7.6, 1.2 Hz, 1H), 1.94 – 1.79 (m, 1H), 1.77 – 1.60 (m, 6H), 1.34 (qt, *J* = 12.5, 3.2 Hz, 2H), 1.20 – 1.11 (m, 1H), 1.09 – 0.96 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.2, 143.4, 140.5, 134.5, 117.9, 44.4, 41.4, 36.4, 33.3, 33.1, 32.7, 26.9, 26.9, 26.6, 23.0, 22.0; IR (Neat Film, NaCl): 2922, 2849, 1669, 1448, 1175, 911 cm^{-1}; HRMS

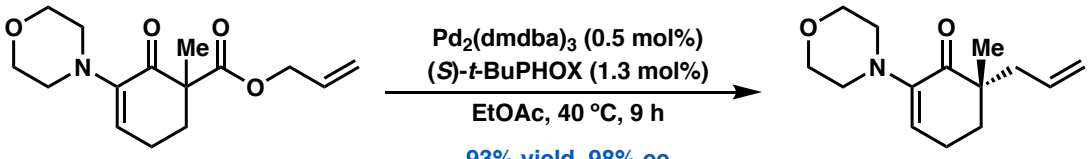
(ESI-APCI) *m/z*: $[M+H]^+$ calc'd for $C_{16}H_{25}O$ 233.1900; Found 233.1892; $[\alpha]^{25}$ –1.176 (*c* 0.43, $CHCl_3$, 72% *ee*).



(*R*)-5-allyl-5-methyl-2-morpholinocyclopent-2-en-1-one (2p)

Prepared according to general procedure A using substrate **1p**. The product was purified by flash column chromatography (SiO_2, 10% acetone in hexanes) to yield enaminone **2p** (97 mg, 0.438 mmol, 94% yield) as a pale tan oil; R_f = 0.23 (20% acetone in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.54 – 6.48 (m, 1H), 5.85 (ddt, *J* = 17.2, 10.5, 5.6 Hz, 1H), 5.27 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.20 (dq, *J* = 10.5, 1.3 Hz, 1H), 4.64 – 4.52 (m, 2H), 2.59 – 2.50 (m, 1H), 2.50 – 2.40 (m, 2H), 2.38 – 2.26 (m, 1H), 1.92 – 1.81 (m, 1H), 1.80 – 1.60 (m, 5H), 1.55 (s, 1H), 1.40 – 1.22 (m, 5H), 1.21 – 1.04 (m, 2H), 1.04 – 0.92 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.1, 149.3, 133.9, 131.6, 118.2, 66.7, 48.6, 46.8, 42.7, 37.2, 24.0; IR (Neat Film, NaCl): 2960, 2913, 2853, 1703, 1611, 1451, 1380, 1261, 1120, 1020, 993 cm^{-1}; HRMS (ESI-APCI) *m/z*: $[M+H]^+$ calc'd for $C_{13}H_{20}NO_2$ 222.1489; Found 222.1490; $[\alpha]^{25}$ –263.53 (*c* 6.76, $CHCl_3$, 83% *ee*).

Large Scale Palladium-Catalyzed Allylic Alkylation Reactions

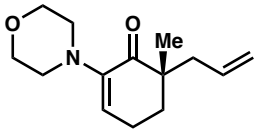
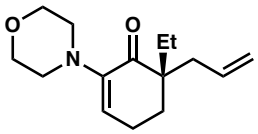
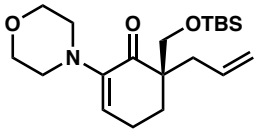
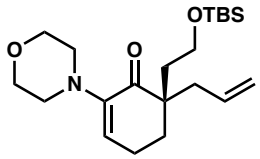
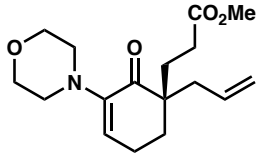
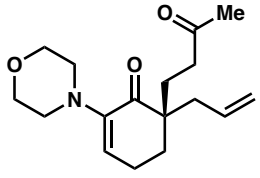


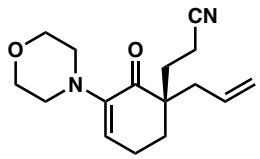
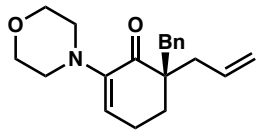
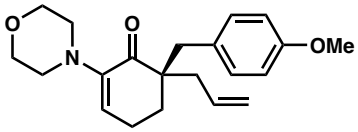
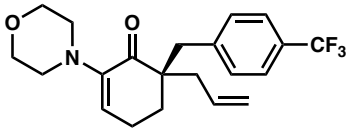
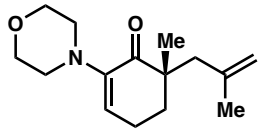
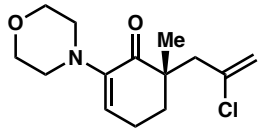
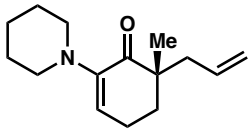
(±)-1a *(S)-2a*

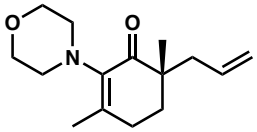
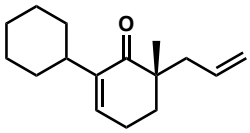
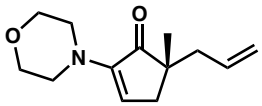
An oven-dried round bottom flask charged with a stir bar was cycled into a glove box under an atmosphere of N_2. To the flask were then added $Pd_2(dmdba)_3$ (78.5 mg, 61.5 μmol, 0.5 mol %) and (*S*)-*t*-BuPHOX ligand (62.0 mg, 0.160 mmol, 1.3 mol %). The flask was then sealed with a rubber septum and removed from the glovebox. A nitrogen line was then affixed and remained throughout the course of the reaction. EtOAc (32 mL) was then added to the flask and the catalyst mixture was let stir at 40 ºC in a pre-heated oil bath (*ca.* 30 minutes). At this point, a solution of allyl β-ketoester (**1**, 3.44 g, 12.3 mmol, 1.00 equiv) in EtOAc (5.3 mL, final concentration of 0.33 M with respect to **1**) was added. The reaction mixture was stirred at 40 °C in a pre-heated oil bath

until the reaction was complete as indicated by TLC analysis (20% acetone/hexanes). The reaction mixture was concentrated in vacuo and the crude material was purified by flash column chromatography (SiO_2, 5–10% acetone in hexanes) to yield enaminone **2a** as a colorless oil (2.69 g, 11.4 mmol, 93% yield, 98% ee). R_f = 0.22 (20% acetone in hexanes). *Characterization data provided above.*

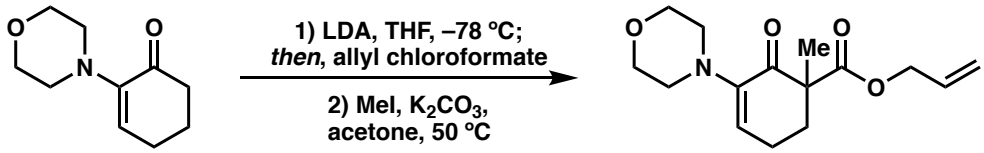
Determination of Enantiomeric Excess

entry	compound	assay method and conditions	retention time of minor isomer (min)	retention time of major isomer (min)	%ee
1	 ***2a***	SFC, 5% *i*PrOH in CO_2 2.5 mL/min, AD-H col.	5.91	5.62	***99***
2	 ***2b***	HPLC, 5% *i*PrOH in hexanes 1 mL/min, OD-H col.	8.77	9.14	***98***
3	 ***2c***	SFC, 3% *i*PrOH in CO_2 2.5 mL/min, AD-H col.	4.45	3.95	***99***
4	 ***2d***	SFC, 2% *i*PrOH in CO_2 2.5 mL/min, OD-H col.	3.59	4.10	***99***
5	 ***2e***	SFC, 10% MeOH in CO_2 5 mL/min, AD-H col.	3.43	1.75	***97***
6	 ***2f***	SFC, 10% *i*PrOH in CO_2 5 mL/min, AD-H col.	2.27	1.81	***94***

entry	compound	assay method and conditions	retention time of minor isomer (min)	retention time of major isomer (min)	%ee
7	 ***2g***	SFC, 10% *i*PrOH in CO_2 5 mL/min, AD-H col.	2.19	2.40	*94*
8	 ***2h***	SFC, 8% MeOH in CO_2 5 mL/min, OJ-H col.	2.41	2.63	*96*
9	 ***2i***	SFC, 5% MeOH in CO_2 5 mL/min, OD-H col.	6.29	6.99	*95*
10	 ***2j***	SFC, 5% *i*PrOH in CO_2 5 mL/min, OJ-H col.	3.88	4.52	*92*
11	 ***2k***	SFC, 5% *i*PrOH in hexanes 2.5 mL/min, AD-H col.	10.2	9.4	*99*
12	 ***2l***	SFC, 5% *i*PrOH in hexanes 2.5 mL/min, OD-H col.	8.6	7.8	*99*
13	 ***2m***	HPLC, 3% EtOH in hexanes 1 mL/min, AD col.	9.01	9.84	*99*

entry	compound	assay method and conditions	retention time of minor isomer (min)	retention time of major isomer (min)	%ee
14	 ***2n***	HPLC, 1.5% *i*PrOH in hexanes 1 mL/min, OD-H col.	8.99	8.40	***90***
15	 ***2o***	SFC, 10% *i*PrOH in CO_2 2.5 mL/min, AD col.	3.08	3.52	***72***
16	 ***2p***	HPLC, 3% *i*PrOH in hexanes 1 mL/min, OD-H col.	14.22	17.7	***83***

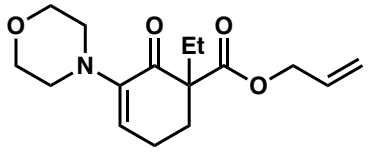
Synthesis of Allylic Alkylation Substrates



1a

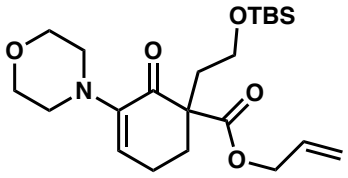
Allyl 1-methyl-3-morpholino-2-oxocyclohex-3-ene-1-carboxylate (1a)

General procedure B: To a solution of diisopropylamine (1.77 mL, 12.7 mmol, 1.29 equiv) in THF (50 mL) at 0 ºC was dropwise added a solution of n-butyllithium in hexanes (5.51 mL, 2.19 M, 12.1 mmol, 1.22 equiv). The solution was stirred for 30 minutes at 0 ºC, then cooled to –78 °C. To the reaction was then dropwise added a solution of 2-morpholinocyclohex-2-en-1-one[3] (1.79 g, 9.88 mmol, 1.00 equiv) in THF (8.0 mL, 1.2 M) at –78 ºC. The mixture was stirred for 90 minutes, quenched with saturated aqueous NH_4Cl (50 mL) and water (50 mL), diluted with EtOAc (100 mL) and the phases were separated. The aqueous portion was again extracted with EtOAc (100 mL). The combined organic fractions were dried over Na_2SO_4, filtered, and concentrated in vacuo to yield the crude b-ketoester as a pale-yellow oil [confirmed to be the desired acylated compound by crude ^{1}H NMR analysis]. A portion (531 mg, 2.00 mmol, 1.00 equiv) of this crude intermediate was taken up in acetone (10 mL, 0.20 M). Potassium carbonate (553 mg, 4.00 mmol, 2.0 equiv) and MeI (149 μL, 2.40 mmol, 1.20 equiv) were then added. The reaction mixture was heated to 50 °C for 10 hours. Upon completion, the reaction mixture was cooled to room temperature, filtered using a fritted funnel, and rinsed with 10 mL Et_2O. The filtrate was concentrated in vacuo and purified by flash column chromatography (SiO_2, 4–8% acetone in hexanes) to yield enaminone **1a** (347 mg, 1.24 mmol, 62% yield over 2 steps) as a pale yellow oil; R_f = 0.45 (50% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.87 – 5.73 (m, 2H), 5.27 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.21 (dq, *J* = 10.4, 1.2 Hz, 1H), 4.61 – 4.53 (m, 2H), 3.81 (ddd, *J* = 11.3, 6.3, 3.1 Hz, 2H), 3.76 (ddd, *J* = 11.3, 6.4, 2.9 Hz, 2H), 2.99 – 2.96 (m, 2H), 2.63 – 2.55 (m, 2H), 2.54 – 2.49 (m, 1H), 2.47 – 2.42 (m, 1H), 2.36 (dtd, *J* = 19.1, 5.4, 3.1 Hz, 1H), 1.84 (ddd, *J* = 13.6, 9.7, 5.6 Hz, 1H), 1.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.9, 172.4, 146.4, 131.6, 124.0 118.9, 66.9, 66.0, 54.2, 50.0, 33.3, 22.7, 20.6; IR (Neat Film, NaCl): 3447 (broad), 2955, 2855, 2067, 1733, 1695, 1617, 1450, 1378, 1264, 1248, 1222, 1175, 1145, 1119, 1020, 992, 948 cm^{-1}; HRMS (ESI-APCI) *m/z*: $[M+H]^+$ calc'd for $C_{15}H_{22}NO_4$ 280.1543; Found 280.1554.



Allyl 1-ethyl-3-morpholino-2-oxocyclohex-3-ene-1-carboxylate (1b)

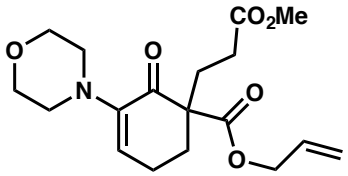
Prepared according to general procedure B using ethyl iodide. The product was purified by flash column chromatography (SiO_2, 4–20% EtOAc in hexanes) to yield enaminone **1b** (468 mg, 1.60 mmol, 74% yield over 2 steps) as a pale-yellow oil. R_f = 0.53 (50% EtOAc in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83 (ddt, *J* = 17.2, 10.4, 5.8 Hz, 1H), 5.73 (ddd, *J* = 4.5, 3.5, 1.2 Hz, 1H), 5.27 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.21 (dq, *J* = 10.4, 1.2 Hz, 1H), 4.57 (dq, *J* = 5.8, 1.5 Hz, 2H), 3.80 (ddd, *J* = 11.4, 6.4, 3.1 Hz, 1H), 3.75 (ddd, *J* = 11.3, 6.3, 3.0 Hz, 1H), 2.97 – 2.93 (m, 2H), 2.60 – 2.52 (m, 3H), 2.44 – 2.33 (m, 2H), 1.95 (dq, *J* = 13.9, 7.5 Hz, 1H), 1.86 (ddd, *J* = 13.0, 9.6, 5.4 Hz, 1H), 1.78 (dq, *J* = 13.9, 7.5 Hz, 1H), 0.92 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 171.3, 146.8, 131.7, 128.2, 123.5, 119.0, 67.0, 65.8, 57.9, 50.0, 29.8, 27.0, 22.6, 9.1; IR (Neat Film, NaCl): 2961, 2855, 1732, 1694, 1617, 1448, 1378, 1300, 1264, 1220, 1167, 1120, 957, 934 cm^{-1}; HRMS (ESI-APCI) *m/z*: $[M+H]^+$ calc'd for $C_{16}H_{24}NO_4$ 294.1700; Found 294.1690.



Allyl 1-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)-3-morpholino-2-oxocyclohex-3-ene-1-carboxylate (1d)

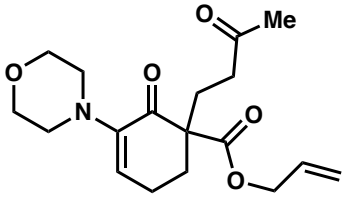
Synthesized according to general procedure B using (2-bromoethoxy)(*tert*-butyl)dimethylsilane and cesium carbonate in place of potassium carbonate. The product was purified by flash column chromatography (SiO_2, 5–20% EtOAc in hexanes) to yield enaminone **1d** (184 mg, 0.434 mmol, 49% yield over 2 steps) as a pale tan oil; R_f = 0.23 (20% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.83 (ddt, *J* = 17.2, 10.4, 5.9 Hz, 1H), 5.78 – 5.70 (m, 1H), 5.27 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.21 (dq, *J* = 10.5, 1.2 Hz, 1H), 4.60 – 4.52 (m, 2H), 3.82 – 3.66 (m, 6H), 2.96 – 2.29 (m, 2H), 2.59 – 2.46 (m, 4H), 2.38 (dtd, *J* = 19.0, 5.5, 2.9 Hz, 1H), 2.14 (ddd, *J* = 13.8, 7.6, 6.1 Hz, 1H), 1.98 – 1.89 (m, 2H), 0.86 (s, 9H), 0.02 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.3, 171.0, 146.5, 131.7, 123.7, 119.1, 66.9, 66.0, 59.7, 56.5, 50.0, 36.8, 30.8, 26.0, 22.7, 18.4, -5.2; IR (Neat

Film, NaCl): 2955, 2928, 2855, 1733, 1695, 1616, 1447, 1378, 1263, 1209, 1120, 1100, 981, 935 cm^{-1}; HRMS (ESI) *m/z*: $[M+H]^+$ calc'd for $C_{22}H_{38}NO_5Si$ 424.2514; Found 424.2521.



Allyl 1-(3-methoxy-3-oxopropyl)-3-morpholino-2-oxocyclohex-3-ene-1-carboxylate (1e)

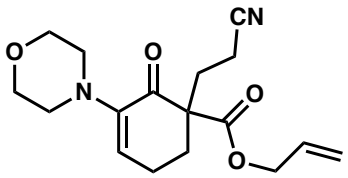
Prepared according to general procedure B using methyl acrylate. The product was purified by flash column chromatography (SiO_2, 10–20% acetone in hexanes) to yield enaminone **1e** (223 mg, 0.635 mmol, 58% yield over 2 steps) as a yellow oil; R_f = 0.42 (50% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.80 (ddt, *J* = 17.3, 10.4, 5.9 Hz, 1H), 5.73 – 5.67 (m, 1H), 5.25 (dd, *J* = 17.2, 1.5 Hz, 1H), 5.19 (dd, *J* = 10.4, 1.3 Hz, 1H), 4.60 – 4.48 (m, 2H), 3.76 (ddd, *J* = 11.3, 6.4, 3.1 Hz, 2H), 3.71 (ddd, *J* = 11.4, 6.4, 3.0 Hz, 2H), 2.92 (ddd, *J* = 11.7, 6.3, 3.0 Hz, 2H), 2.56 – 2.41 (m, 4H), 2.40 – 2.27 (m, 3H), 2.18 (ddd, *J* = 14.0, 10.6, 5.6 Hz, 1H), 2.04 (ddd, *J* = 14.1, 10.8, 5.4 Hz, 1H), 1.84 (ddd, *J* = 14.5, 9.8, 6.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.1, 173.4, 170.9, 146.6, 131.4, 123.3, 119.2, 66.8, 66.1, 56.7, 51.7, 49.8, 30.7, 29.5, 28.9, 22.5; IR (Neat Film, NaCl): 2953, 2854, 2820, 1733, 1694, 1616, 1447, 1377, 1264, 1209, 1177, 1120, 983, 957 cm^{-1}; HRMS (ESI-APCI) *m/z*: $[M+H]^+$ calc'd for $C_{18}H_{26}NO_6$ 352.1755; Found 352.1771.



Allyl 3-morpholino-2-oxo-1-(3-oxobutyl)cyclohex-3-ene-1-carboxylate (1f)

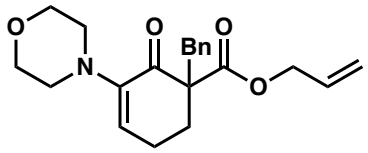
Prepared according to general procedure B using methyl vinyl ketone. The product was purified by flash column chromatography (SiO_2, 20–65% EtOAc in hexanes) to yield enaminone **1f** (537 mg, 1.60 mmol, 74% yield over 2 steps) as a pale yellow oil that solidified on storage at –20 °C; R_f = 0.28 (50% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.81 (ddt, *J* = 17.2, 10.4, 5.9 Hz, 1H), 5.75 – 5.69 (m, 1H), 5.26 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.20 (dq, *J* = 10.4, 1.2 Hz, 1H), 4.59 – 4.49 (m, 2H), 3.77 (ddd, *J* = 11.4, 6.4, 3.1 Hz, 2H), 3.72 (ddd, *J* = 11.3, 6.4, 3.0 Hz, 2H), 2.93 (ddd, *J* = 11.9, 6.3, 3.1 Hz, 2H), 2.60 (ddd, *J* = 17.7, 10.3, 5.5 Hz, 1H), 2.57 – 2.49 (m, 2H), 2.52

– 2.39 (m, 2H), 2.41 – 2.35 (m, 1H), 2.36 – 2.32 (m, 1H), 2.10 (s, 4H), 1.98 (ddd, J = 14.1, 10.3, 5.3 Hz, 1H), 1.84 (ddd, J = 9.7, 8.1, 4.9 Hz, 1H);^{13}C NMR (125 MHz, $CDCl_3$) δ 207.7, 193.4, 171.2, 146.7, 131.4, 123.5, 119.3, 66.9, 66.0, 56.7, 49.9, 38.9, 31.1, 30.0, 30.0, 27.7, 22.6; IR (Neat Film, NaCl): 2956, 2854, 1721, 1615, 1447, 1372, 1299, 1264, 1209, 1179, 1120, 1095, 982, 939 cm^{-1}; HRMS (ESI-APCI) *m/z*: $[M+H]^+$ calc'd for $C_{18}H_{26}NO_5$ 336.1805; Found 336.1803.



Allyl 1-(2-cyanoethyl)-3-morpholino-2-oxocyclohex-3-ene-1-carboxylate (1g)

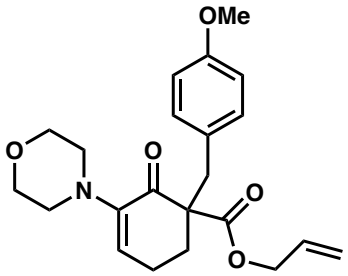
Prepared according to general procedure B using acrylonitrile. The product was purified by flash column chromatography (SiO_2, 10–20% acetone in hexanes) to yield enaminone **1g** (247 mg, 0.776 mmol, 71% yield over 2 steps) as a colorless oil; R_f = 0.29 (50% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.83 (ddt, J = 16.5, 10.4, 6.0 Hz, 1H), 5.76 (t, J = 4.3 Hz, 1H), 5.29 (dq, J = 17.1, 1.4 Hz, 1H), 5.25 (dq, J = 10.4, 1.2 Hz, 1H), 4.64 – 4.56 (m, 2H), 3.79 (ddd, J = 11.4, 6.4, 3.1 Hz, 2H), 3.73 (ddd, J = 11.4, 6.4, 3.0 Hz, 2H), 2.95 (ddd, J = 11.8, 6.4, 3.1 Hz, 2H), 2.60 – 2.49 (m, 4H), 2.45 – 2.38 (m, 3H), 2.21 (ddd, J = 14.0, 9.5, 5.9 Hz, 1H), 2.07 (ddd, J = 14.0, 9.5, 6.3 Hz, 1H), 1.92 – 1.86 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.7, 170.2, 146.6, 131.1, 123.7, 119.9, 119.4, 66.8, 66.5, 56.5, 49.8, 31.1, 30.2, 22.5, 13.3; IR (Neat Film, NaCl): 2956, 2854, 2247, 1734, 1690, 1617, 1448, 1375, 1264, 1208, 1119, 982, 947 cm^{-1}; HRMS (ESI-APCI) *m/z*: $[M+H]^+$ calc'd for $C_{17}H_{23}N_2O_4$ 319.1652, Found 319.1668.



Allyl 1-benzyl-3-morpholino-2-oxocyclohex-3-ene-1-carboxylate (1h)

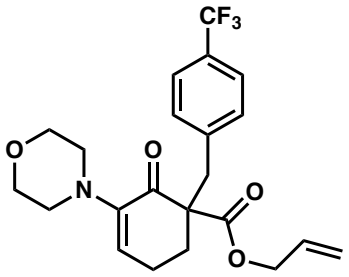
Prepared according to general procedure B using benzyl bromide. The product was purified by flash column chromatography (SiO_2, 4–10% acetone in hexanes) to yield enaminone **1h** (498 mg, 1.40 mmol, 65% yield over 2 steps) as a colorless oil; R_f = 0.23 (20% acetone in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 – 7.19 (m, 3H), 7.19 – 7.14 (m, 2H), 5.79 (ddt, J = 17.3, 10.4, 5.9 Hz, 1H), 5.71 (ddd, J = 4.5, 3.3, 1.3 Hz, 1H), 5.26 (dq, J = 17.2, 1.5 Hz, 1H), 5.21 (dq, J = 10.4,

1.2 Hz, 1H), 3.82 (ddd, *J* = 11.4, 6.4, 3.0 Hz, 2H), 3.77 (ddd, *J* = 11.3, 6.4, 2.9 Hz, 2H), 3.26 (d, *J* = 13.7 Hz, 1H), 3.14 (d, *J* = 13.7 Hz, 1H), 2.96 (ddd, *J* = 11.7, 6.4, 3.0 Hz, 2H), 2.58 – 2.51 (m, 3H), 2.40 – 2.27 (m, 2H), 1.80 – 1.74 (m, 1H); ^{13}C NMR (125 MHz, CDCl3) δ 192.6, 170.5, 146.8, 136.4, 131.5, 130.7, 128.2, 128.2, 126.9, 123.9, 119.2, 66.9, 66.1, 58.7, 49.9, 39.8, 30.0, 22.7; IR (Neat Film, NaCl): 2956, 2854, 1734, 1691, 1615, 1447, 1377, 1263, 1207, 1176, 1118, 1085, 980, 937 cm^{-1}; HRMS (ESI-APCI) *m/z*: $[M+H]^+$ calc'd for $C_{21}H_{26}NO_4$ 356.1856; Found 356.1857.



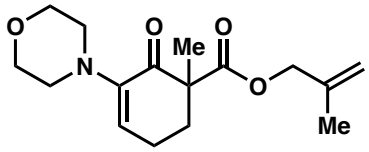
Allyl 1-(4-methoxybenzyl)-3-morpholino-2-oxocyclohex-3-ene-1-carboxylate (1i)

Prepared according to general procedure B using *p*-methoxybenzyl chloride. The product was purified by flash column chromatography (SiO_2, 5–10% acetone in hexanes) to yield enaminone **1i** (86 mg, 0.22 mmol, 21% yield over 2 steps) as a pale yellow oil; R_f = 0.72 (20% Et_2O in CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.6 Hz, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 5.80 (ddt, *J* = 17.2, 10.4, 5.9 Hz, 1H), 5.72 (t, *J* = 4.3 Hz, 1H), 5.26 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.22 (dq, *J* = 10.4, 1.2 Hz, 1H), 4.53 (dq, *J* = 5.9, 1.4 Hz, 2H), 3.82 (ddd, *J* = 11.4, 6.4, 3.0 Hz, 2H), 3.79 – 3.75 (m, 5H), 3.19 (d, *J* = 13.9 Hz, 1H), 3.10 (d, *J* = 13.9 Hz, 1H), 2.96 (ddd, *J* = 11.6, 6.5, 3.1 Hz, 2H), 2.59 – 2.49 (m, 3H), 2.38 – 2.28 (m, 2H), 1.76 (ddd, *J* = 14.2, 10.4, 6.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.7, 170.6, 158.6, 146.8, 131.7, 131.6, 128.3, 123.9, 119.2, 113.6, 66.9, 66.1, 58.8, 55.3, 50.0, 38.9, 30.0, 22.7; IR (Neat Film, NaCl): 2954, 2853, 1734, 1691, 1612, 1512, 1445, 1262, 1248, 1208, 1178, 1119, 1034, 981, 938 cm^{-1}; HRMS (ESI-APCI) *m/z*: $[M+H]^+$ calc'd for $C_{22}H_{28}NO_5$ 386.1962; found 386.1948.



Allyl 3-morpholino-2-oxo-1-(4-(trifluoromethyl)benzyl)cyclohex-3-ene-1-carboxylate (1j)

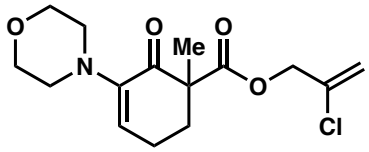
Prepared according to general procedure B using *p*-trifluoromethylbenzyl bromide. The product was purified by flash column chromatography (SiO_2, 2:1:1–2:2:1 hexanes:DCM:acetone) to yield enaminone **1j** (276 mg, 0.652 mmol, 60% yield over 2 steps) as a pale yellow oil; R_f = 0.78 (20% Et_2O in CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 7.5 Hz, 2H), 5.80 – 5.69 (m, 2H), 5.28 – 5.18 (m, 2H), 4.51 (dq, *J* = 5.9, 1.5 Hz, 2H), 3.83 (ddd, *J* = 11.4, 6.4, 3.0 Hz, 2H), 3.77 (ddd, *J* = 11.4, 6.4, 2.9 Hz, 2H), 3.29 (d, *J* = 13.6 Hz, 1H), 3.19 (d, *J* = 13.6 Hz, 1H), 2.97 (ddd, *J* = 11.8, 6.4, 3.0 Hz, 2H), 2.59 – 2.50 (m, 3H), 2.38 – 2.32 (m, 2H), 1.78 (ddd, *J* = 14.2, 10.4, 6.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.3, 170.3, 146.8, 140.7, 131.3, 131.2, 129.2 (q, *J* = 32.4 Hz), 125.3, 125.1 (q, *J* = 3.8 Hz), 123.8, 123.3, 119.5, 66.9, 66.3, 58.7, 49.9, 39.6, 30.4, 22.7; ^{19}F NMR (470 MHz, $CDCl_3$) δ 62.5; IR (Neat Film, NaCl): 2957, 2855, 1732, 1694, 1618, 1447, 1418, 1323, 1263, 1209, 1162, 1116, 1066, 1019, 981, 938 cm^{-1}; HRMS (ESI-APCI) *m/z*: $[M+H]^+$ calc'd for $C_{22}H_{25}NO_4F$ 424.1730; Found 424.1737.



2-Methylallyl 1-methyl-3-morpholino-2-oxocyclohex-3-ene-1-carboxylate (1k)

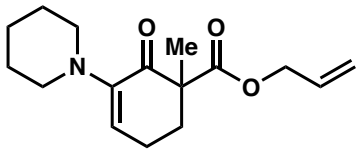
Prepared according to general procedure B using 2-methylallyl cyanoformate (**SI3**, *vida infra*). The product was purified by flash column chromatography (20–24% EtOAc/hexanes) to yield enaminone **1k** as a slightly yellow oil (808 mg, 2.76 mmol, 56% yield over 2 steps). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.79 (ddd, *J* = 4.9, 3.5, 1.1 Hz, 1H), 4.92 (d, *J* = 10.9 Hz, 2H), 4.50 (d, *J* = 12.7 Hz, 1H), 3.82 (ddd, *J* = 11.4, 6.4, 3.0 Hz, 2H), 3.77 (ddd, *J* = 11.3, 6.4, 2.9 Hz, 2H), 3.00 (ddd, *J* = 11.1, 4.9, 2.0 Hz, 2H), 2.61 – 2.51 (m, 3H), 2.47 (dddd, *J* = 13.5, 5.1, 3.1, 1.2 Hz, 1H), 2.39 (dtd, *J* = 19.0, 5.4, 3.1 Hz, 1H), 1.87 (ddd, *J* = 13.5, 9.7, 5.6 Hz, 1H), 1.71 (s, 3H), 1.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.7, 172.3, 146.3, 139.4, 123.9, 113.5, 68.4, 66.8, 54.1, 49.8, 33.3,

22.6, 20.6, 19.5; IR (Neat Film, NaCl) 2936, 2854, 1737, 1694, 1615, 1450, 1175, 1119, cm^{-1}; HRMS (ESI) *m/z*: $[M+H]^+$ calc'd for $C_{16}H_{24}NO_4$ 294.1700; found 294.1705.



2-Chloroallyl 1-methyl-3-morpholino-2-oxocyclohex-3-ene-1-carboxylate (1l)

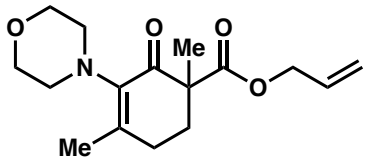
Prepared according to general procedure B using 2-chloroallyl cyanoformate (**SI1**, *vida infra*). The product was purified by flash column chromatography (20–22% EtOAc/hexanes) to yield enaminone **1l** as a slightly yellow oil (470 mg, 1.50 mmol, 37% yield over 2 steps); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.82 (ddd, *J* = 5.0, 3.6, 1.0 Hz, 1H), 5.44 (dt, *J* = 1.8, 1.2 Hz, 1H), 5.40 (d, *J* = 1.7 Hz, 1H), 4.72 (ddd, *J* = 13.5, 1.2, 0.6 Hz, 1H), 4.63 (ddd, *J* = 13.5, 1.2, 0.6 Hz, 1H), 3.83 (ddd, *J* = 11.4, 6.4, 3.1 Hz, 2H), 3.78 (ddd, *J* = 11.3, 6.3, 3.0 Hz, 2H), 3.00 (ddd, *J* = 9.6, 6.2, 3.1 Hz, 2H), 2.65 – 2.50 (m, 3H), 2.51 – 2.46 (m, 1H), 2.41 (dtd, *J* = 19.0, 5.4, 3.3 Hz, 1H), 1.89 (ddd, *J* = 13.5, 9.4, 5.5 Hz, 1H), 1.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.5, 171.9, 146.3, 135.4, 124.3, 115.8, 66.9, 66.7, 54.2, 49.9, 33.3, 22.6, 20.6; IR (Neat Film, NaCl) 2954, 2855, 1741, 1693, 1450, 1377 cm^{-1}; HRMS (ESI) *m/z*: $[M+H]^+$ calc'd for $C_{15}H_{21}NClO_4$ 314.1154; Found 314.1156.



Allyl 1-methyl-2-oxo-3-(piperidin-1-yl)cyclohex-3-ene-1-carboxylate (1m)

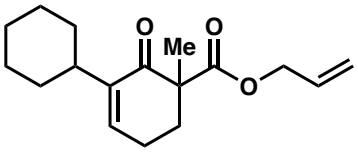
Prepared according to general procedure B using 2-(piperidin-1-yl)cyclohex-2-en-1-one.[3] The product was purified by flash column chromatography (SiO_2, 8–16% Et_2O in hexanes) to yield enaminone **1m** (427 mg, 1.54 mmol, 59% yield over 2 steps) as a pale tan oil; R_f = 0.32 (40% Et_2O in hexanes; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.77 (ddt, *J* = 17.2, 10.4, 5.7 Hz, 1H), 5.69 (ddd, *J* = 4.8, 3.5, 1.0 Hz, 1H), 5.21 (dd, *J* = 17.2, 1.5 Hz, 1H), 5.14 (dd, *J* = 10.5, 1.3 Hz, 1H), 4.55 – 4.47 (m, 2H), 2.81 (ddd, *J* = 11.2, 7.2, 3.6 Hz, 2H), 2.46 (dddt, *J* = 18.1, 9.2, 5.4, 3.3 Hz, 3H), 2.37 (dddd, *J* = 13.6, 5.1, 3.2, 1.1 Hz, 1H), 2.29 (dtd, *J* = 19.0, 5.4, 3.2 Hz, 1H), 1.77 (ddd, *J* = 13.4, 9.6, 5.6 Hz, 1H), 1.65 – 1.53 (m, 4H), 1.46 – 1.41 (m, 2H), 1.31 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.0, 172.3, 147.7, 131.8, 123.5, 118.7, 65.8, 54.2, 51.0, 33.4, 26.0, 24.5, 22.8, 20.7;

IR (Neat Film, NaCl): 2934, 2851, 2802, 1735, 1696, 1613, 1452, 1387, 1248, 1222, 1175, 1110, 987, 943 cm^{-1}; HRMS (ESI-APCI) *m/z*: $[M+H]^+$ calc'd for $C_{16}H_{24}NO_3$ 278.1751; Found 278.1747.



Allyl 1,4-dimethyl-3-morpholino-2-oxocyclohex-3-ene-1-carboxylate (1n)

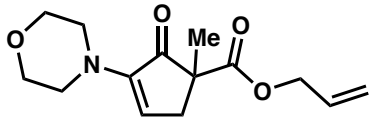
Prepared according to general procedure B using 3-methyl-2-morpholinocyclohex-2-en-1-one.[4] The product was purified by flash column chromatography (SiO_2, 5–20% EtOAc in hexanes) to yield enaminone **1n** (772 mg, 2.63 mmol, 74% yield over 2 steps) as a pale yellow oil; R_f = 0.34 (20% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.82 (ddt, *J* = 17.2, 10.5, 5.6 Hz, 1H), 5.24 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.18 (dq, *J* = 10.4, 1.3 Hz, 1H), 4.58 (ddt, *J* = 13.3, 5.5, 1.5 Hz, 1H), 4.53 (ddt, *J* = 13.3, 5.6, 1.4 Hz, 1H), 3.70 – 3.63 (m, 4H), 2.99 – 2.90 (m, 2H), 2.90 – 2.81 (m, 2H), 2.49 (dddd, *J* = 19.2, 9.8, 5.3, 1.1 Hz, 1H), 2.38 (ddd, *J* = 13.6, 5.2, 3.6 Hz, 1H), 2.28 (dddd, *J* = 19.1, 5.6, 3.6, 0.9 Hz, 1H), 1.95 (s, 3H), 1.79 (ddd, *J* = 13.6, 9.7, 5.5 Hz, 1H), 1.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.8, 172.5, 153.2, 142.1, 131.8, 118.4, 67.9, 65.7, 53.9, 50.3, 32.3, 29.2, 20.5, 19.6; IR (Neat Film, NaCl): 2935, 2848, 1734, 1680, 1452, 1375, 1259, 1190, 1168, 1114, 1070, 989 cm^{-1}; HRMS (ESI-APCI) *m/z*: $[M+H]^+$ calc'd for $C_{16}H_{24}NO_4$ 294.1700; Found 294.1701.



Allyl 3-methyl-2-oxo-[1,1'-bi(cyclohexan)]-6-ene-3-carboxylate (1o)

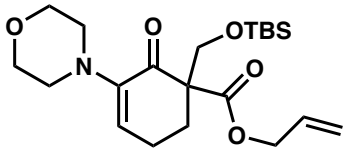
Prepared according to general procedure B using [1,1'-bi(cyclohexan)]-6-en-2-one.[5] The product was purified by flash column chromatography (SiO_2, 10% Et_2O in DCM) to yield enone **1o** (51 mg, 0.185 mmol, 30% yield over 2 steps) as a pale yellow oil; R_f = 0.33 (10% Et_2O in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.51 (dt, *J* = 4.4, 2.2 Hz, 1H), 5.84 (ddt, *J* = 17.2, 10.5, 5.6 Hz, 1H), 5.26 (dd, *J* = 17.2, 1.5 Hz, 1H), 5.20 (dd, *J* = 10.4, 1.4 Hz, 1H), 4.57 (tt, *J* = 5.5, 1.4 Hz, 2H), 2.57 – 2.42 (m, 3H), 2.35 – 2.27 (m, 1H), 1.89 – 1.80 (m, 1H), 1.77 – 1.61 (m, 6H), 1.37 (s, 3H), 1.36 – 1.29 (m, 2H), 1.19 – 1.07 (m, 2H), 1.02 – 0.93 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.8,

172.8, 144.2, 140.9, 131.9, 118.5, 65.8, 53.6, 36.8, 33.4, 32.8, 32.3, 26.9, 26.8, 26.5, 23.6, 20.6; IR (Neat Film, NaCl): 2925, 2851, 1734, 1684, 1379, 1351, 1299, 1247, 1167, 1110, 981, 935 cm^{-1}; HRMS (ESI-APCI) *m/z*: $[M+H]^+$ calc'd for $C_{17}H_{25}O_3$ 277.1798; Found 277.1791.



Allyl 1-methyl-3-morpholino-2-oxocyclopent-3-ene-1-carboxylate (1p)

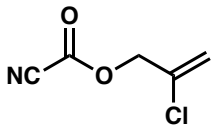
Prepared according to general procedure B using 2-morpholinocyclopent-2-en-1-one.[6] The product was purified by flash column chromatography (SiO_2, 2–10% EtOAc in DCM) to yield enaminone **1p** (151 mg, 0.570 mmol, 21% yield over 2 steps) as a pale orange oil; R_f = 0.33 (10% EtOAc in CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$) δ 6.39 (t, *J* = 3.2 Hz, 1H), 5.85 (ddt, *J* = 17.2, 10.5, 5.5 Hz, 1H), 5.27 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.20 (dq, *J* = 10.5, 1.3 Hz, 1H), 4.58 (dt, *J* = 5.5, 1.5 Hz, 2H), 3.79 (ddd, *J* = 5.2, 3.9, 0.8 Hz, 4H), 3.19 – 3.15 (m, 2H), 3.05 – 3.01 (m, 3H), 2.38 (dd, *J* = 18.2, 3.2 Hz, 1H), 1.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.8, 171.6, 148.6, 131.9, 131.8, 118.3, 66.6, 65.9, 54.1, 48.5, 37.8, 21.1; IR (Neat Film, NaCl): 2962, 2933, 2855, 1740, 1707, 1612, 1452, 1379, 1263, 1178, 1120, 1068, 1022, 994 cm^{-1}; HRMS (ESI-APCI) *m/z*: $[M+H]^+$ calc'd for $C_{14}H_{20}NO_4$ 266.1387; Found 266.1391.



Allyl 1-(((*tert*-butyldimethylsilyl)oxy)methyl)-3-morpholino-2-oxocyclohex-3-ene-1-carboxylate (1c)

To a solution of diisopropylamine (1.77 mL, 12.7 mmol, 1.29 equiv) in THF (50 mL) at 0 ºC was dropwise added a solution of n-butyllithium in hexanes (5.51 mL, 2.19 M, 12.1 mmol, 1.22 equiv). The solution was stirred for 30 minutes at 0 ºC, then cooled to –78 °C. To the reaction was then dropwise added a solution of 2-morpholinocyclohex-2-en-1-one[3] (1.79 g, 9.88 mmol, 1.00 equiv) in THF (8.0 mL, 1.2 M) at –78 ºC. The mixture was stirred for 90 minutes, quenched with saturated aqueous NH_4Cl (50 mL) and water (50 mL), diluted with EtOAc (100 mL) and the phases were separated. The aqueous portion was again extracted with EtOAc (100 mL). The combined organic

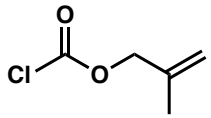
fractions were dried over Na_2SO_4, filtered, and concentrated in vacuo to yield the crude β-ketoester as a pale-yellow oil [confirmed to be the desired acylated compound by crude ^{1}H NMR analysis]. A portion (218 mg, 0.822 mmol, 1.00 equiv) of this crude intermediate was dissolved in THF (1.6 mL, 0.5 M) and cooled to 0 °C. Potassium carbonate (247 mg, 2.47 mmol, 3.0 equiv) and 37% aqueous formaldehyde (156 μL, 5.67 mmol, 6.9 equiv) were added. The reaction was warmed to 23 °C and stirred for 4 hours. Upon completion, the reaction mixture was extracted with EtOAc (2 x 5 mL). The combined organic layers were dried over Na_2SO_4, filtered, concentrated in vacuo, and purified by flash column chromatography (SiO_2, 20–35% acetone in hexanes) to yield 133 mg of a pale-yellow oil. This intermediate alcohol was taken up in CH_2Cl_2 (4.5 mL, 0.1 M) and TBSCl (75 mg, 0.49 mmol, 1.1 equiv) and imidazole (61 mg, 0.90 mmol, 2.0 equiv) were added. The reaction mixture was stirred for 8 hours, concentrated in vacuo and purified by column chromatography (SiO_2, 20–35% EtOAc in hexanes) to yield enaminone **1c** (106 mg, 0.257 mmol, 29% yield over 3 steps) as a pale yellow oil; R*f* = 0.25 (25% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.88 – 5.80 (m, 2H), 5.27 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.20 (dq, *J* = 10.4, 1.3 Hz, 1H), 4.60 (ddt, *J* = 13.2, 5.8, 1.4 Hz, 1H), 4.54 (ddt, *J* = 13.2, 5.7, 1.4 Hz, 1H), 4.08 (d, *J* = 9.8 Hz, 1H), 3.88 (d, *J* = 9.8 Hz, 1H), 3.83 – 3.73 (m, 4H), 2.91 – 2.85 (m, 2H), 2.68 – 2.58 (m, 3H), 2.55 – 2.49 (m, 1H), 2.44 – 2.36 (m, 1H), 2.02 (ddd, *J* = 13.8, 10.0, 5.8 Hz, 1H), 0.85 (s, 9H), 0.03 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.0, 169.6, 146.7, 131.7, 125.0, 118.8, 66.9, 66.6, 66.0, 65.4, 59.9, 50.0, 29.8, 28.0, 25.9, 25.8, 22.5, 18.3, -5.5; IR (Neat Film, NaCl): 2955, 2929, 2894, 2856, 1734, 1690, 1616, 1462, 1448, 1379, 1262, 1217, 1120, 964 cm^{-1}; HRMS (APCI) *m/z*: $[M+H]^+$ calc'd for $C_{21}H_{36}NO_5Si$ 410.2357; found 410.2342.



2-chloroallyl carbonocyanidate (SI1)

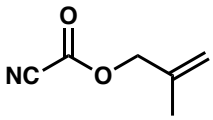
Prepared according to literature precedent.[7] Product vacuum distilled (62–65°C, 20 torr) to afford the product (**SI2**) as a clear oil (6.13 g, 90% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.62 – 5.59 (m, 1H), 5.57 (d, *J* = 2.1 Hz, 1H), 4.88 (d, *J* = 0.9 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.5, 132.9, 118.5, 108.9, 69.7; IR (Neat Film, NaCl) 2249, 1759, 1640, 1230, 1180, 918 cm^{-1};

Anal. Calc'd for $C_5H_4NO_2Cl$: C, 41.26%; H, 2.77%; N, 9.62%; Cl, 24.36%; Found: C, 41.22%; H, 2.79%, N, 9.49%; Cl, 24.18%.



2-methylallyl carbonochloridate (SI2)

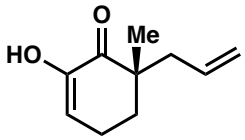
Prepared as reported for the 2-chloroallyl substrate from the report by Stoltz and coworkers.[7] The product was vacuum distilled (45–47 °C, 20 torr) to provide the product (**SI2**) as a clear oil (7.48 g, 60% yield). Spectral data matches that reported in the literature.[8] ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.10 – 5.07 (m, 1H), 5.07 – 5.04 (m, 1H), 4.71 (s, 2H), 1.81 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.4, 137.9, 115.8, 75.0, 19.2.



2-methylallyl carbonocyanidate (SI3)

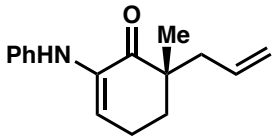
Prepared according to procedure for cyanoformate **SI1** from chloroformate **SI2**. Product vacuum distilled (60°C, 35 torr) to afford the product (**SI3**) as a clear oil (3.61 g, 81% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.12 – 5.06 (m, 2H), 4.73 (s, 2H), 1.81 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.1, 137.2, 116.4, 109.3, 72.0, 19.3; IR (Neat Film, NaCl) 2246, 1762, 1227, 1242, 918 cm^{-1}; Anal. Calc'd for $C_6H_7NO_2$: C, 57.59%; H, 5.64%; N, 11.19%; Found: C, 57.59%; H, 5.49%; N, 11.11%.

Derivatization of Enaminone Products



(*S*)-6-allyl-2-hydroxy-6-methylcyclohex-2-en-1-one (3)

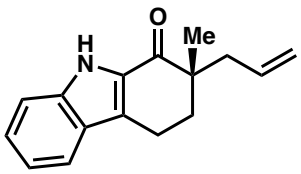
Enaminone **2a** (297 mg, 1.26 mmol) was diluted in MeOH/H_2O (4:1). HCl (0.1 mL, 12 M aqueous) was added by syringe. The reaction mixture was stirred at 60 °C under nitrogen for 2 h. The mixture was cooled to room temperature and partitioned between H_2O and CH_2Cl_2. The aqueous layer was extracted with CH_2Cl_2 two additional times. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash column chromatography (1–2% EtOAc/hexanes) to give diketone **3** (166 mg, 1.00 mmol, 79% yield) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.07 (s, 1H), 6.02 (t, *J* = 4.6 Hz, 1H), 5.68 (dddd, *J* = 16.4, 10.6, 7.6, 7.2 Hz, 1H), 5.09 – 4.99 (m, 2H), 2.38 – 2.30 (m, 3H), 2.18 (ddt, *J* = 13.8, 7.6, 1.1 Hz, 1H), 1.95 – 1.86 (m, 1H), 1.72 (ddd, *J* = 13.7, 6.5, 5.5 Hz, 1H), 1.10 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.3, 145.6, 133.5, 118.7, 117.0, 44.1, 41.1, 33.6, 21.8, 20.4; IR (Neat Film, NaCl): 3428, 3076, 2975, 2935, 1721, 1640, 1455, 1217 cm^{-1}; HRMS (FAB+) *m/z*: $[M+H–H_2]^+$ calc'd for $C_{10}H_{13}O_2$ 165.0916; Found 165.0916; $[\alpha]^{25}$ –5.95 (*c* 4.45, $CHCl_3$).



(*S*)-6-allyl-6-methyl-2-(phenylamino)cyclohex-2-en-1-one (4)

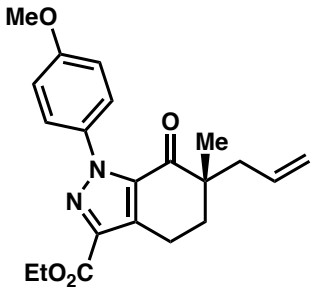
Compound **2a** (52 mg, 0.21 mmol, 1.0 equiv) was dissolved in toluene (1.3 mL, 0.16 M). *p*-Toluenesulfonic acid monohydrate (39 mg, 0.21 mmol, 1.0 equiv) and aniline (20 µL, 0.22 mmol, 1.0 equiv) were then added to the solution of **2a**. The mixture was heated to 50°C for 3.5 h. The reaction mixture was diluted with EtOAc and washed with saturated aqueous $NaHCO_3$ (3x). The organic layer was then dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude was purified by flash column chromatography (2% EtOAc in hexanes) to yield compound **4** (18 mg, 75 µmol, 35% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.24 (m, 2H), 7.05 – 7.02 (m, 2H), 6.91 (tt, *J* = 7.4, 1.1 Hz, 1H), 6.34 (t, *J* = 4.7 Hz, 1H), 5.76 (ddt, *J* = 16.5, 10.5, 7.4 Hz, 1H), 5.12 – 5.06 (m, 2H), 2.52 – 2.40 (m, 3H), 2.26 (ddt, *J* = 13.8, 7.6, 1.2 Hz, 1H), 1.98 (ddd, *J* = 13.6, 6.8,

5.4 Hz, 1H), 1.80 (ddd, *J* = 13.6, 6.8, 5.3 Hz, 1H), 1.17 (s, 3H) *(N–H not observed in $CDCl_3$)*; ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.0, 142.3, 134.8, 134.0, 133.9, 121.1, 118.8, 118.5, 115.0, 44.4, 41.5, 33.1, 22.2, 21.0; IR (Neat Film, NaCl): 3364, 2926, 1668, 1634, 1600, 1515, 1442, 1306, 1203, 1014, 997, 916, 750, 691 cm^{-1}; HRMS (ESI-APCI) *m/z*: $[M+H]^+$ calc'd for $C_{16}H_{20}NO$ 242.1539; Found 242.1535; $[\alpha]^{25}$ –4.72 (*c* 2.18, $CHCl_3$).



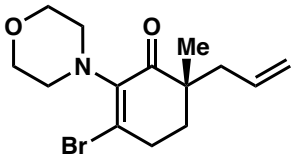
(*S*)-2-allyl-2-methyl-2,3,4,9-tetrahydro-1*H*-carbazol-1-one (5)

To a solution of enaminone **2a** (118 mg, 0.500 mmol, 1.00 equiv) toluene (2 mL, 0.25 M), *p*-toluenesulfonic acid monohydrate (95 mg, 0.50 mmol, 1.0 equiv) and phenyl hydrazine (54 mg, 0.50 mmol, 1.0 equiv) were added. The reaction was heated to 60 °C and stirred for 4 hours, cooled to room temperature, diluted with saturated aqueous NH_4Cl (1 mL), and extracted with EtOAc (3x 5 mL). The combined organic fractions were dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude intermediate was taken up in 5 mL 4:1 AcOH:12 M HCl (0.1 M) and stirred for 2 hours at ambient temperature. Ice (*ca*. 10 g) was then added. The ice/reaction mixture was quenched with 5.0 M NaOH until a pH of 9–10 was achieved. The mixture was extracted with EtOAc (3x 20 mL). The combined organic fractions were dried over Na_2SO_4, filtered, and concentrated in vacuo. The product was purified by column chromatography (SiO_2, 5–15% EtOAc in hexanes) to yield indole **5** (120 mg, 0.500 mmol, 99% yield over 2 steps) as a yellow oil; R_f = 0.54 (20% EtOAc in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 9.75 (s, 1H), 7.66 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.49 (dt, *J* = 8.4, 0.9 Hz, 1H), 7.38 (ddd, *J* = 8.3, 7.0, 1.1 Hz, 1H), 7.16 (ddd, *J* = 8.0, 6.9, 1.0 Hz, 1H), 5.87 (ddt, *J* = 16.6, 10.4, 7.4 Hz, 1H), 5.15 – 5.10 (m, 2H), 3.10 – 2.98 (m, 2H), 2.57 (dd, *J* = 13.8, 7.2 Hz, 1H), 2.38 (ddt, *J* = 13.8, 7.5, 1.2 Hz, 1H), 2.24 (ddd, *J* = 13.6, 7.1, 5.2 Hz, 1H), 2.05 (ddd, *J* = 13.6, 6.9, 5.2 Hz, 1H), 1.29 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.3, 138.7, 134.4, 130.3, 128.0, 126.9, 125.9, 121.4, 120.4, 118.3, 112.9, 45.5, 41.5, 35.7, 22.1, 18.4; IR (Neat Film, NaCl): 3279, 3076, 2963, 2926, 1638, 1573, 1545, 1473, 1331, 1224, 1014, 992, 977, 916 cm^{-1}; HRMS (ESI-APCI) *m/z*: $[M+H]^+$ calc'd for $C_{16}H_{18}NO$ 240.1383; Found 240.1383; $[\alpha]^{25}$ –131.65 (*c* 7.84, $CHCl_3$).



Ethyl (*S*)-6-allyl-1-(4-methoxyphenyl)-6-methyl-7-oxo-4,5,6,7-tetrahydro-1*H*-indazole-3-carboxylate (6)

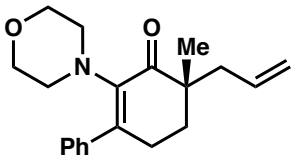
Enaminone **2a** (31 mg, 0.13 mmol, 1.0 equiv) and ethyl (*Z*)-2-chloro-2-(2-(4-methoxyphenyl)hydrazono)acetate[9] (**73**, 50 mg, 0.19 mmol, 1.5 equiv) were dissolved in toluene (1.4 mL). Then, triethylamine (0.15 mL, 0.11 mmol, 0.83 equiv) was added. The reaction mixture was heated at the reflux for 17 h. The reaction mixture was then cooled to ambient temperature, quenched with water, and extracted with ethyl acetate. The organic layer was washed with brine and dried over Na_2SO_4, filtered, and concentrated in vacuo. The product was purified by flash column chromatography (5–15% EtOAc/hexanes) to give the compound **6** as a yellow-orange oil (22 mg, , 6.0 μmol, 46% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.9 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 5.80 – 5.72 (m, 1H), 5.12 – 5.05 (m, 2H), 4.44 (q, *J* = 7.1 Hz, 2H), 3.85 (s, 3H), 3.18 – 3.06 (m, 2H), 2.42 (ddt, *J* = 13.8, 7.1, 1.2 Hz, 1H), 2.27 (ddt, *J* = 13.7, 7.6, 1.1 Hz, 1H), 2.13 (ddd, *J* = 14.0, 6.6, 5.4 Hz, 1H), 1.98 (ddd, *J* = 14.0, 7.3, 5.6 Hz, 1H), 1.42 (t, *J* = 7.1 Hz, 3H), 1.17 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.7, 162.3, 160.1, 140.0, 135.2, 133.6, 132.9, 132.8, 127.1, 118.8, 113.8, 61.3, 55.7, 46.7, 40.8, 34.9, 21.6, 19.0, 14.6; IR (Neat Film, NaCl): 2917, 2357, 2340, 1691, 1515, 1301, 1251, 1195, 1127, 1026, 935 cm^{-1}; HRMS (ESI-APCI) *m/z*: $[M+H]^+$ calc'd for $C_{21}H_{25}N_2O_4$ 369.1809; Found 369.1791; $[\alpha]^{25}$ –7.56 (*c* 0.45, $CHCl_3$).



(*S*)-6-allyl-3-bromo-6-methyl-2-morpholinocyclohex-2-en-1-one (SI4)

Enaminone **2a** (120 mg, 0.51 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (4.5 mL, 0.1 M). The reaction mixture was cooled to –78 °C. A solution of NBS (91 mg, 0.51 mmol, 1.0 equiv) in CH_2Cl_2 (4.5 mL) was added dropwise to the reaction by syringe. The reaction mixture was stirred

at –78 °C for 25 min. The solution was quenched with a solution of 10% K_2CO_3 (3 mL). The mixture was warmed to room temperature and extracted with 3 x CH_2Cl_2. The organic layers were combined, dried, filtered and concentrated. The residue was purified by flash column chromatography (3% EtOAc/hexanes) to give the desired compound as a yellow oil (96 mg, 0.31 mmol, 60% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.68 (ddt, *J* = 16.7, 10.2, 7.4 Hz, 1H), 5.10 – 5.01 (m, 2H), 3.71 (ddd, *J* = 5.3, 3.8, 1.3 Hz, 4H), 3.06 – 2.99 (m, 2H), 2.97 – 2.92 (m, 2H), 2.93 – 2.83 (m, 2H), 2.28 (ddt, *J* = 13.8, 7.3, 1.2 Hz, 1H), 2.21 (ddt, *J* = 13.8, 7.5, 1.2 Hz, 1H), 1.88 (ddd, *J* = 13.8, 6.3, 5.7 Hz, 1H), 1.74 (ddd, *J* = 13.9, 7.2, 5.8 Hz, 1H), 1.07 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.4, 143.8, 141.9, 133.5, 118.7, 67.7, 50.2, 45.8, 40.9, 33.7, 33.3, 21.5; IR (Neat Film, NaCl) 2958, 2851, 1678, 1606, 1451, 1261, 1212, 1113, 1049, 920 cm^{-1}; HRMS (ESI-APCI) *m/z*: $[M+H]^+$ calc'd for $C_{14}H_{21}BrNO_2$ 314.0750; Found 314.0742; $[\alpha]^{25}$ –1.56 (*c* 1.68, $CHCl_3$).



(*S*)-4-allyl-4-methyl-2-morpholino-5,6-dihydro-[1,1'-biphenyl]-3(4*H*)-one (7)

Compound **SI4** (54 mg, 0.17 mmol, 1.0 equiv) was dissolved in DME (7 mL) and 1 M K_3PO_4 (0.72 mL, 4.5 equiv). Phenylboronic acid (29 mg, 0.24 mmol, 1.5 equiv) and $PdCl_2$(dppf) (26 mg, 32 μmol, 0.19 equiv) were added to the reaction mixture. The mixture was heated to 60 °C under nitrogen for 2h. The reaction mixture was cooled to room temperature and then extracted with diethyl ether (3x). The combined organic layer was dried with Na_2SO_4, filtered and concentrated in vacuo. The reaction mixture was purified by flash column chromatography (SiO_2, 3–6% EtOAc/hexanes) to give the product as bright yellow-orange oil (51 mg, 0.16 mmol, 96% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 2H), 7.33 – 7.29 (m, 1H), 7.26 – 7.22 (m, 2H), 6.93 – 6.82 (m, 1H), 5.79 (ddt, *J* = 16.6, 10.3, 7.4 Hz, 1H), 5.11 – 5.05 (m, 2H), 3.53 (t, *J* = 4.6 Hz, 4H), 2.73 – 2.61 (m, 6H), 2.40 – 2.29 (m, 2H), 1.96 (dt, *J* = 13.7, 5.8 Hz, 1H), 1.85 (ddd, *J* = 13.5, 6.9, 6.1 Hz, 1H), 1.15 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.7, 145.7, 141.2, 140.5, 134.2, 129.8, 128.2, 127.9, 118.2, 115.4, 67.5, 51.2, 44.8, 41.4, 32.2, 29.0, 21.9; IR (Neat Film, NaCl): 2916, 2850, 2358, 1669, 1457, 1374, 1261, 1210, 1112, 1029, 978, 757, 698 cm^{-1}; HRMS (ESI-APCI) *m/z*: $[M+H]^+$ calc'd for $C_{20}H_{26}NO_2$ 312.1958; Found 312.1968; $[\alpha]^{25}$ 0.00 (*c* 0.76, $CHCl_3$).

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1) Pangborn, A. M.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. Safe and Convenient Procedure for Solvent Purification. *Organometallics* **1996**, *15*, 1518–1520.
2) (a) Tani, K.; Behenna, D. C.; McFadden, R. M.; Stoltz, B. M. *Org. Lett.* **2007**, *9*, 2529–2531. (b) Krout, M. R.; Mohr, J. T.; Stoltz, B. M. *Org. Synth*. **2009**, *86*, 181–193.
3) Tobias, M. A.; Strong, J. G.; Napier, R. P. *J. Org. Chem.* **1970**, *35*, 1709–1711.
4) Di-methyl ref
5) Prepared from 2-iodocyclohexenone and cyclohexylmagnesium bromide following the procedure from the following publication: Barriault, L.; Thomas, J. D. O.; Clément, R. *J. Org. Chem.* **2003**, *68*, 2317–2323.
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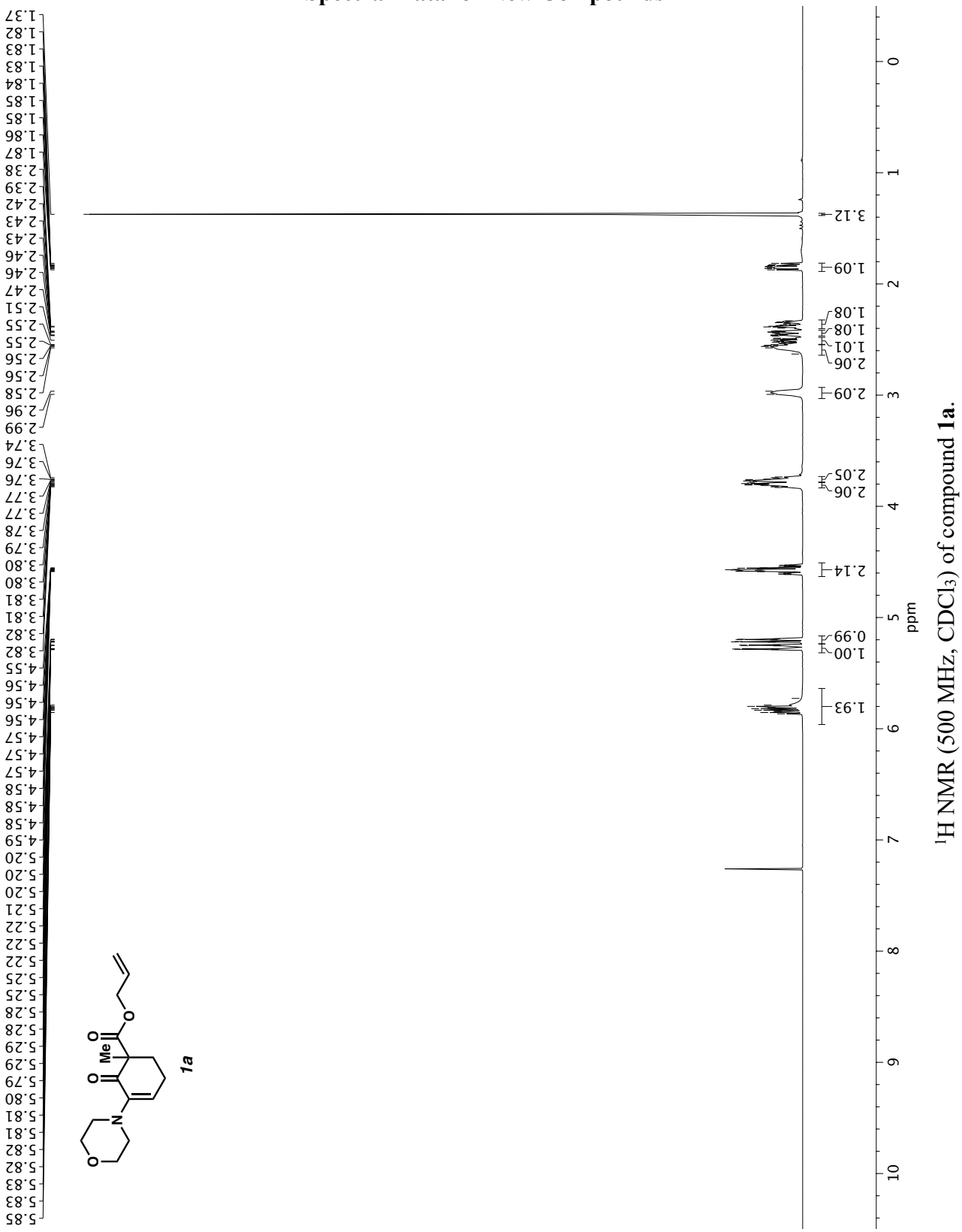
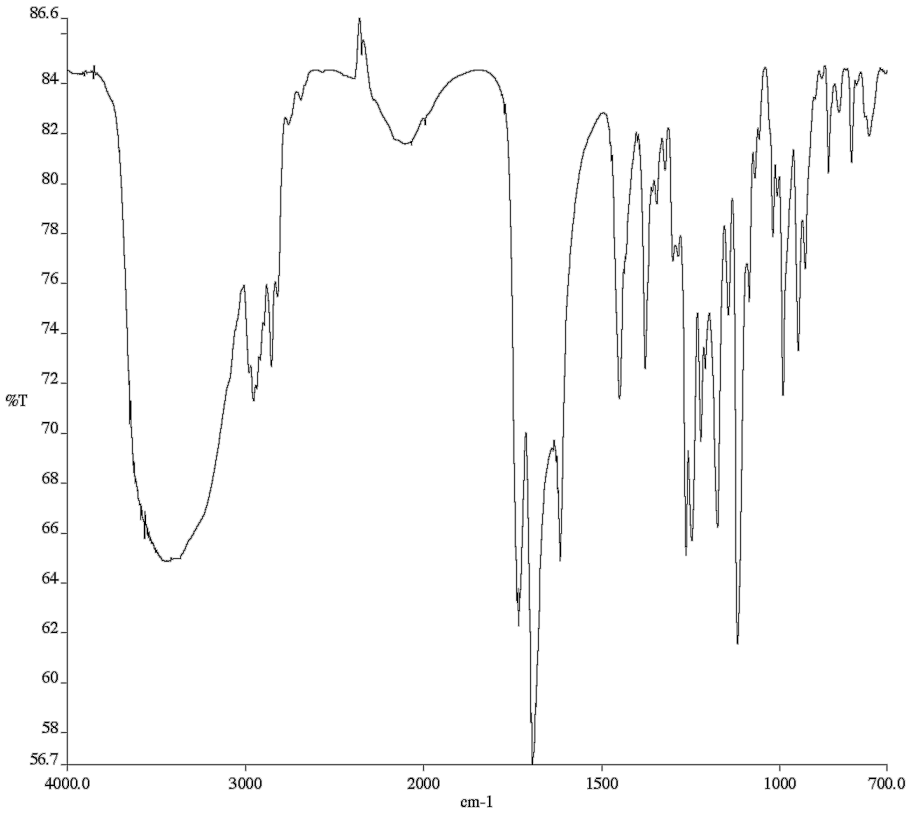
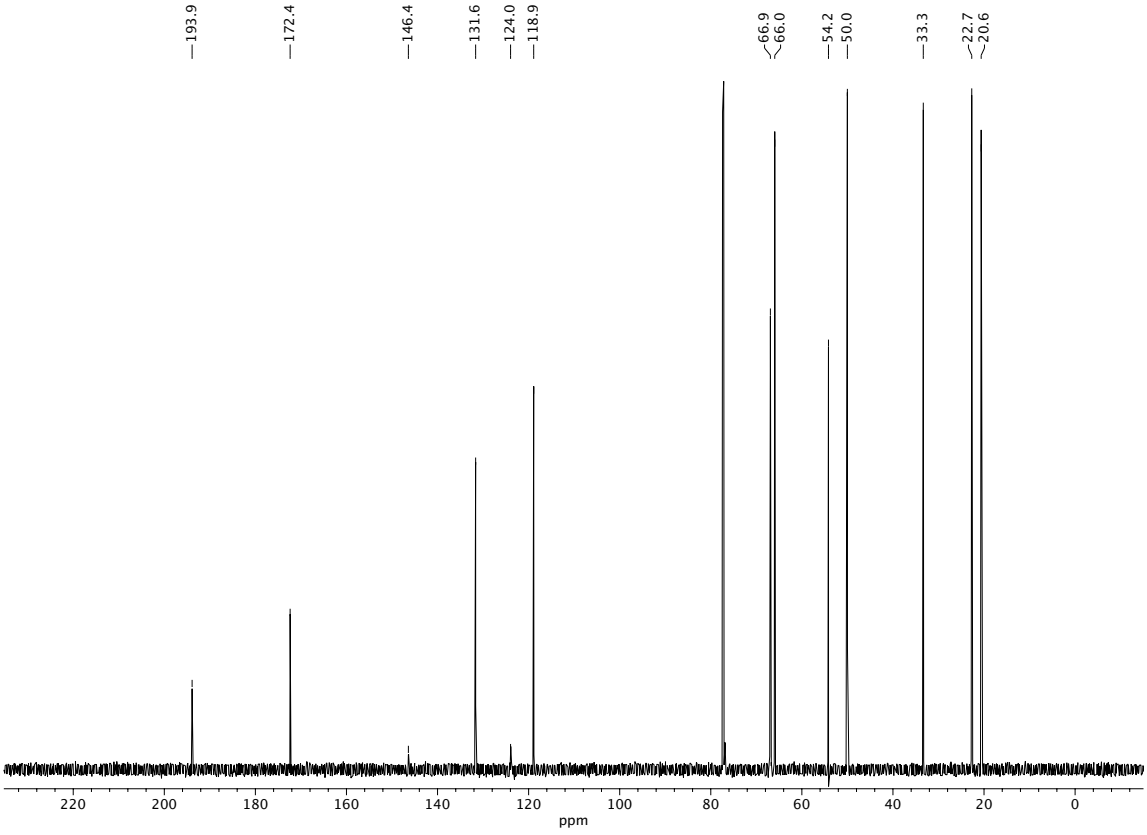
Spectral Data for New Compounds



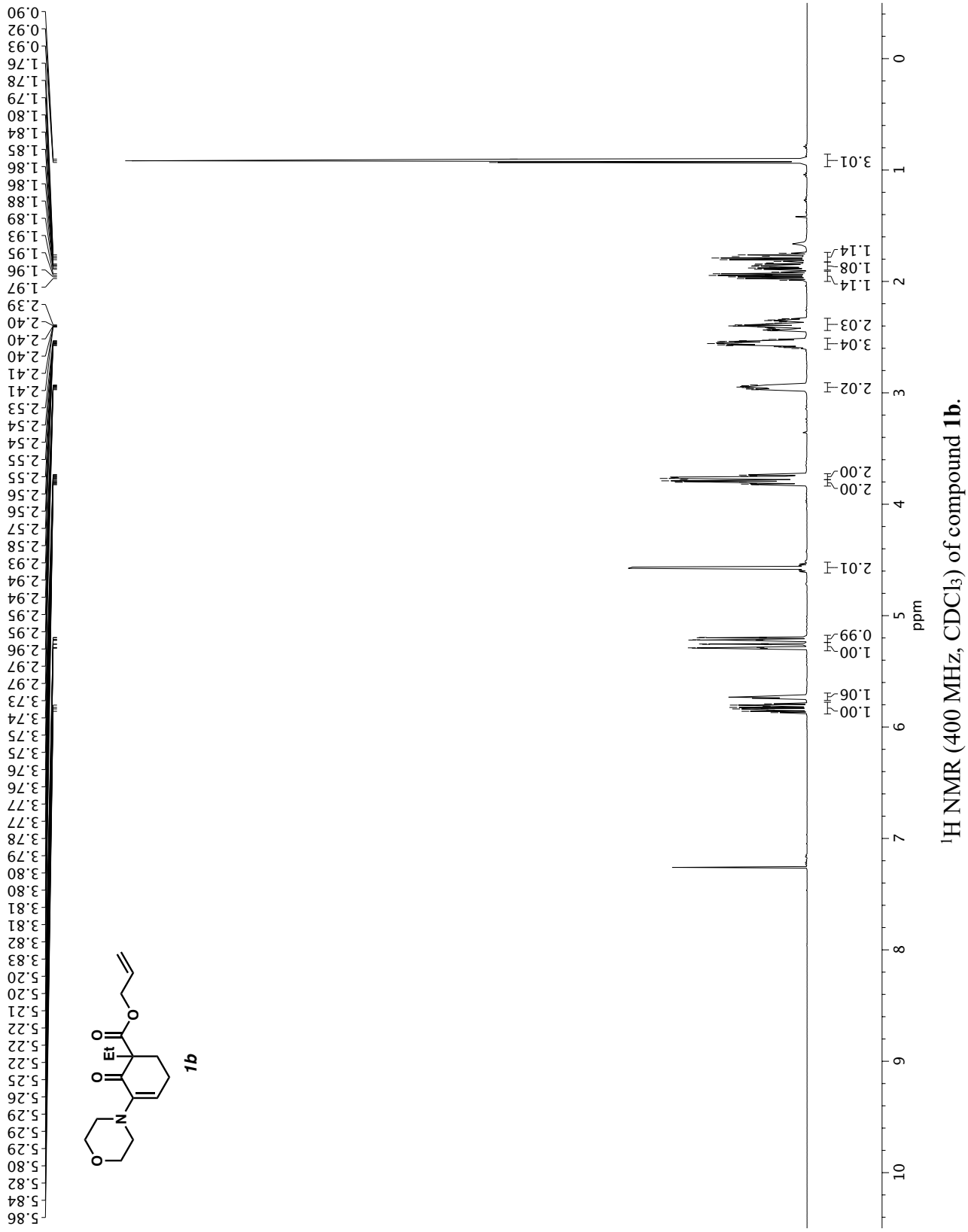
^{1}H NMR (500 MHz, $CDCl_3$) of compound **1a**.



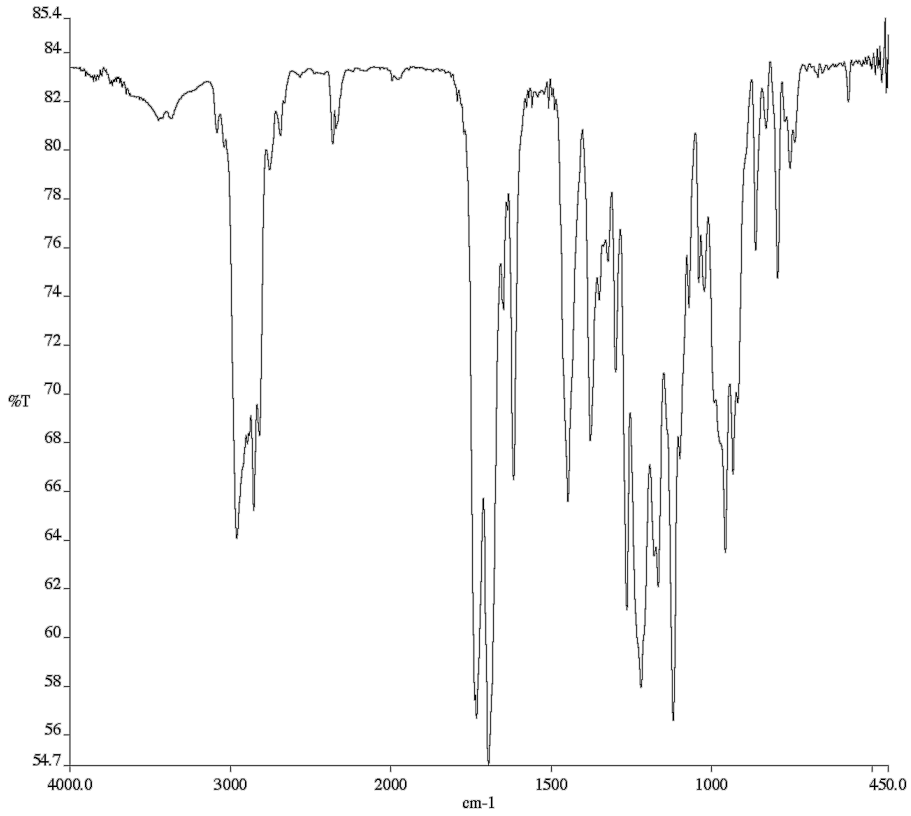
Infrared spectrum (Thin Film, NaCl) of compound **1a**.



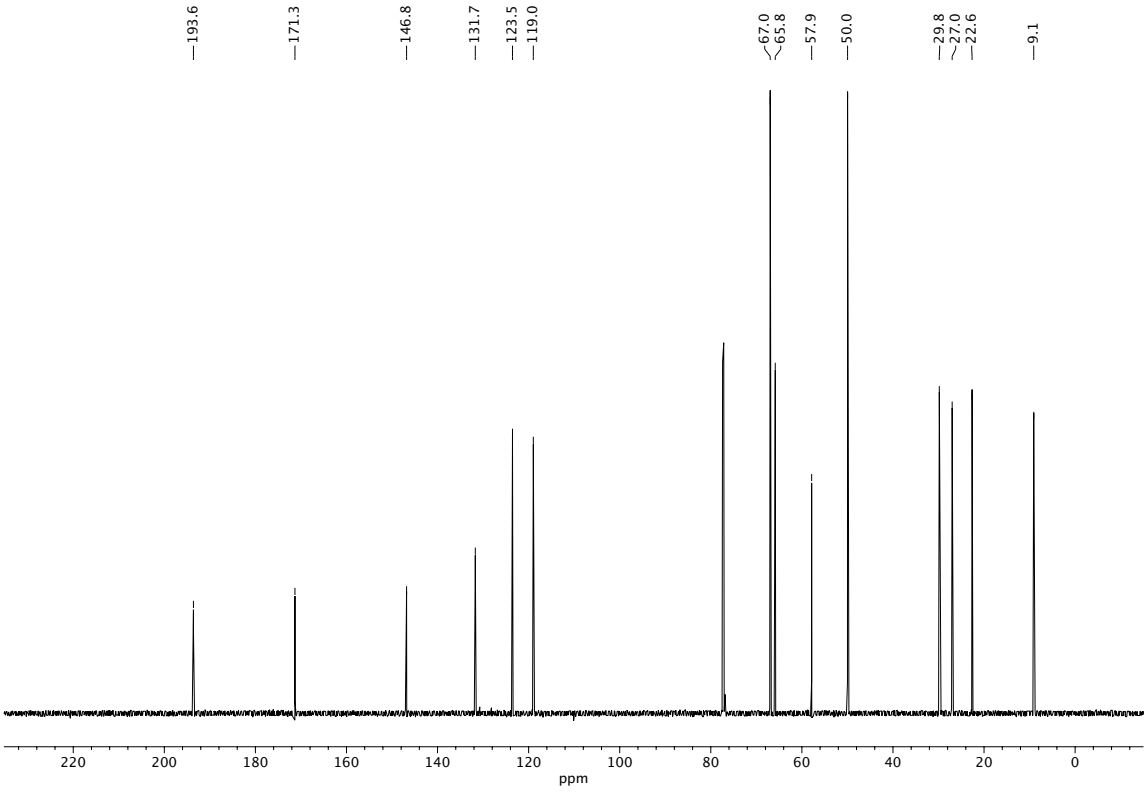
^{13}C NMR (125 MHz, $CDCl_3$) of compound **1a**.



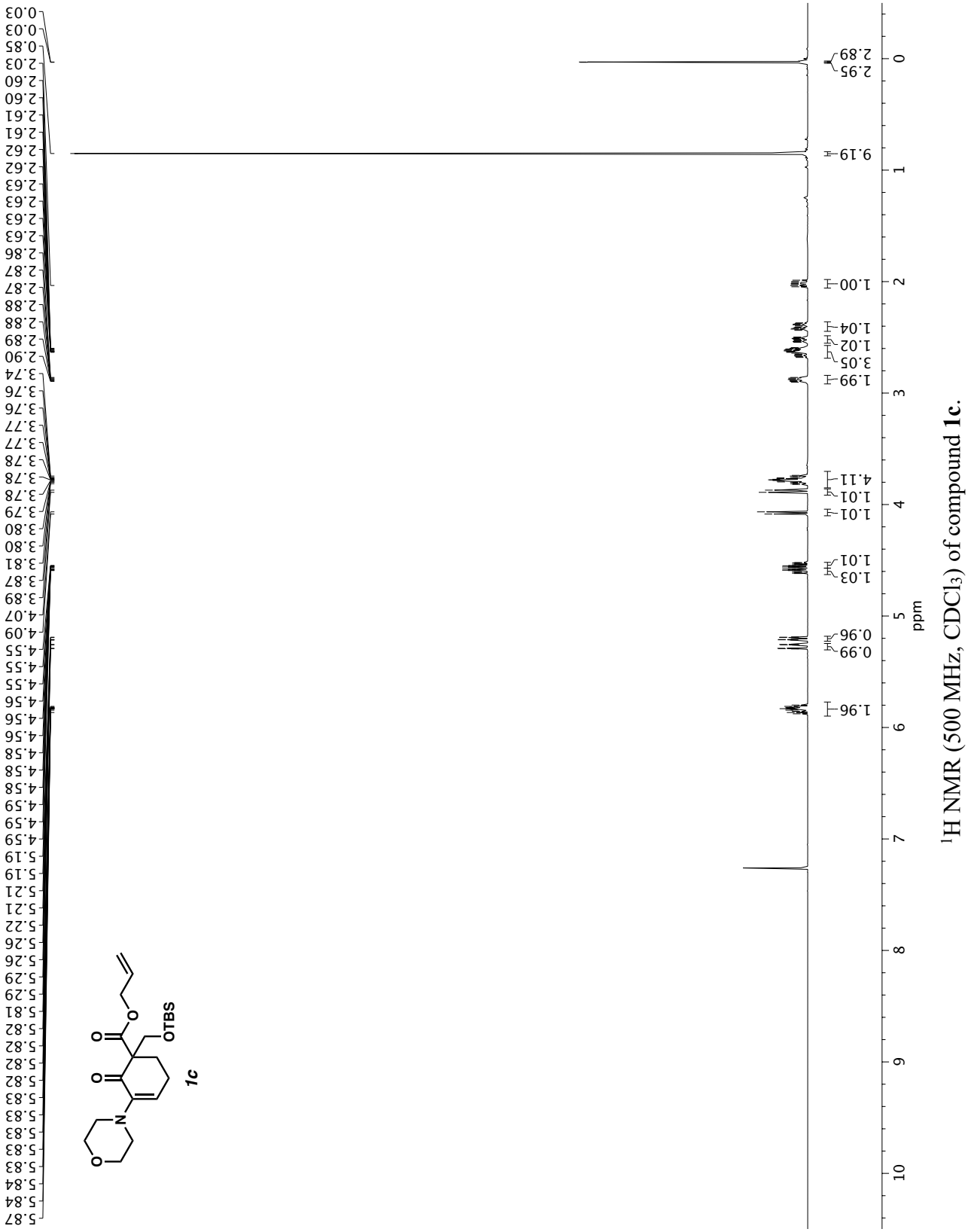
^{1}H NMR (400 MHz, $CDCl_3$) of compound **1b**.



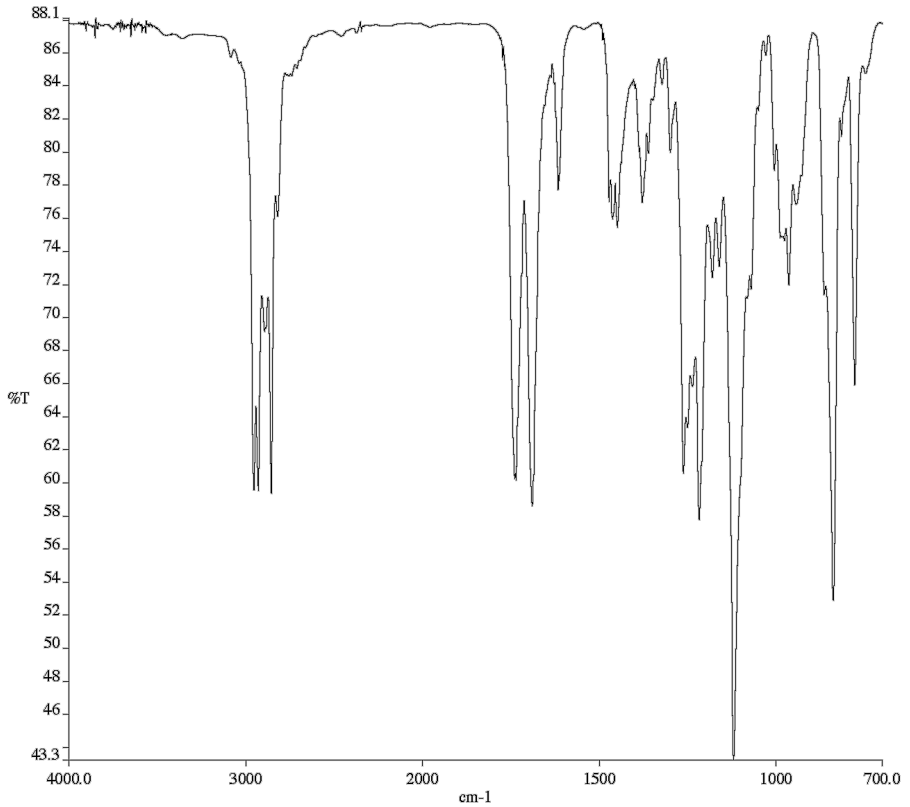
Infrared spectrum (Thin Film, NaCl) of compound **1b**.



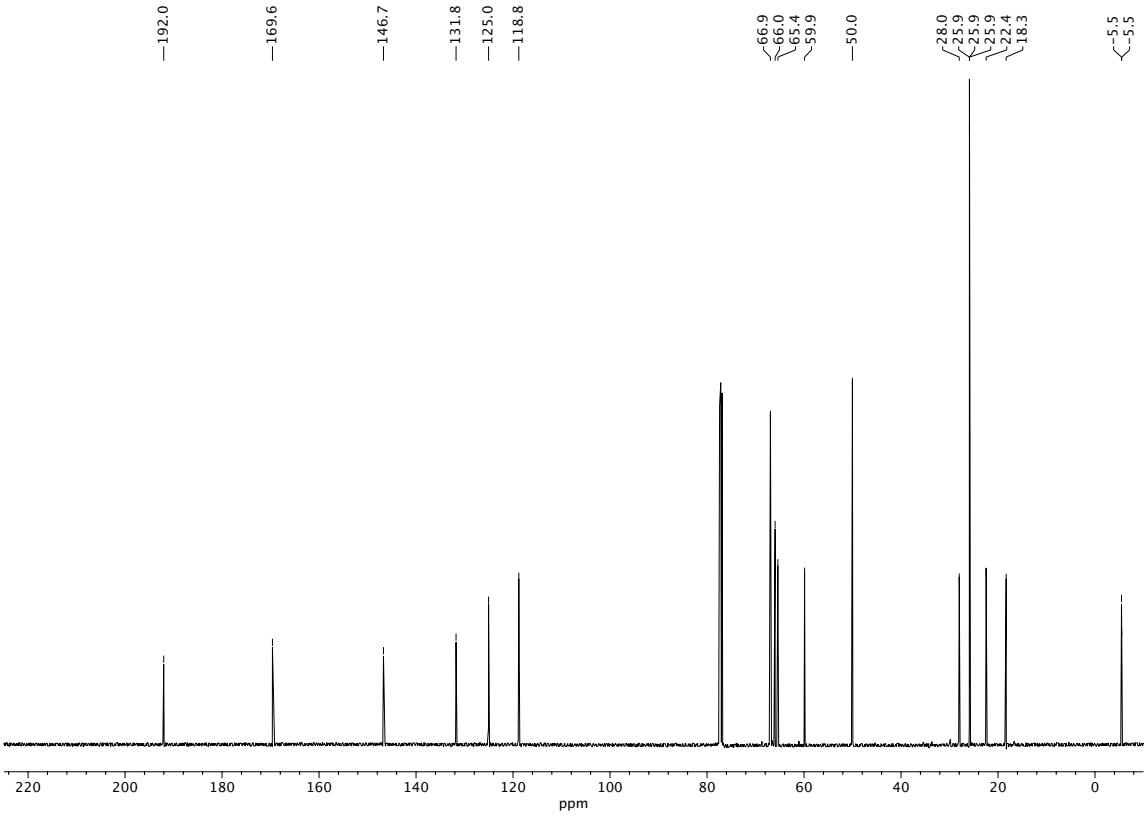
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1b**.



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



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



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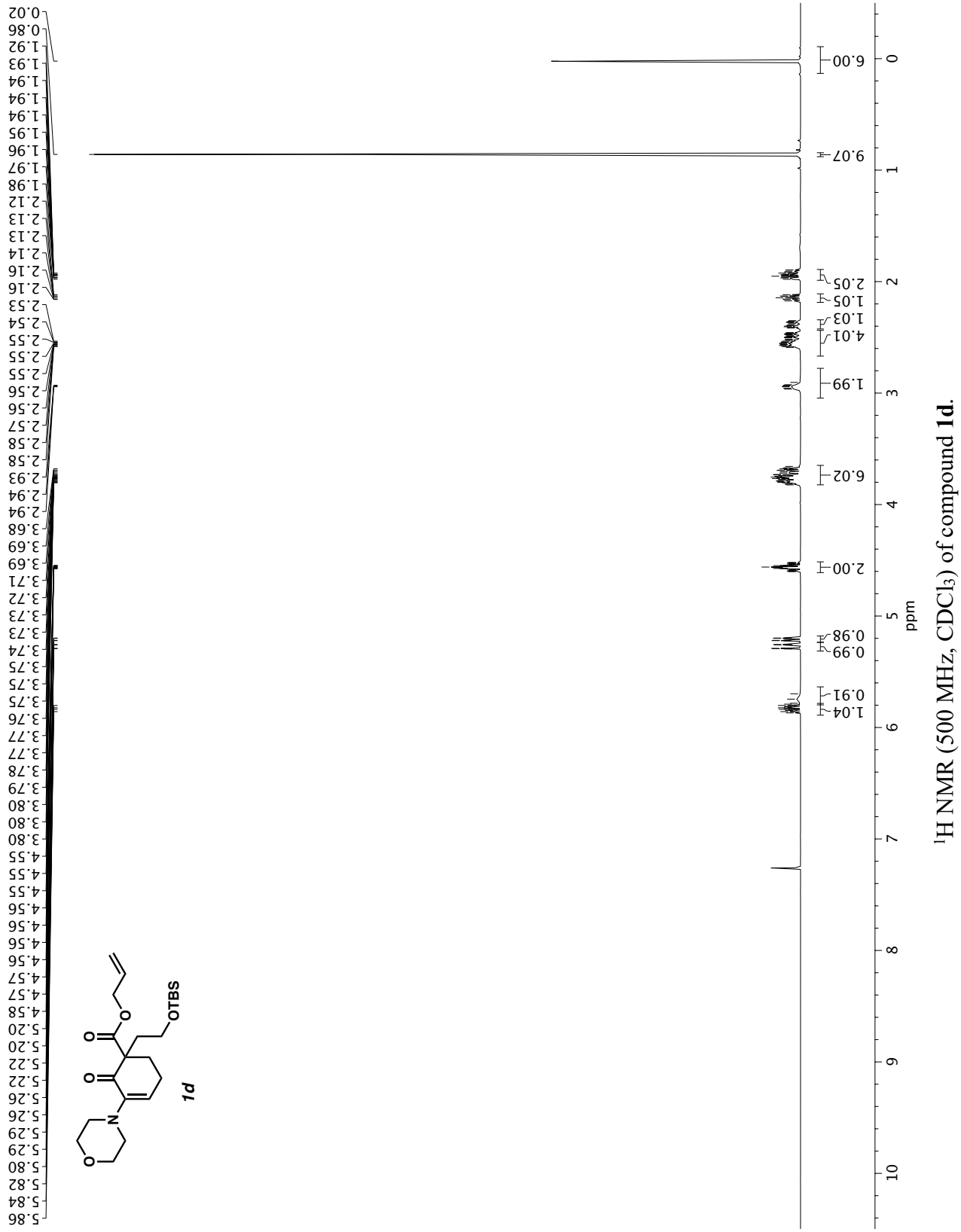
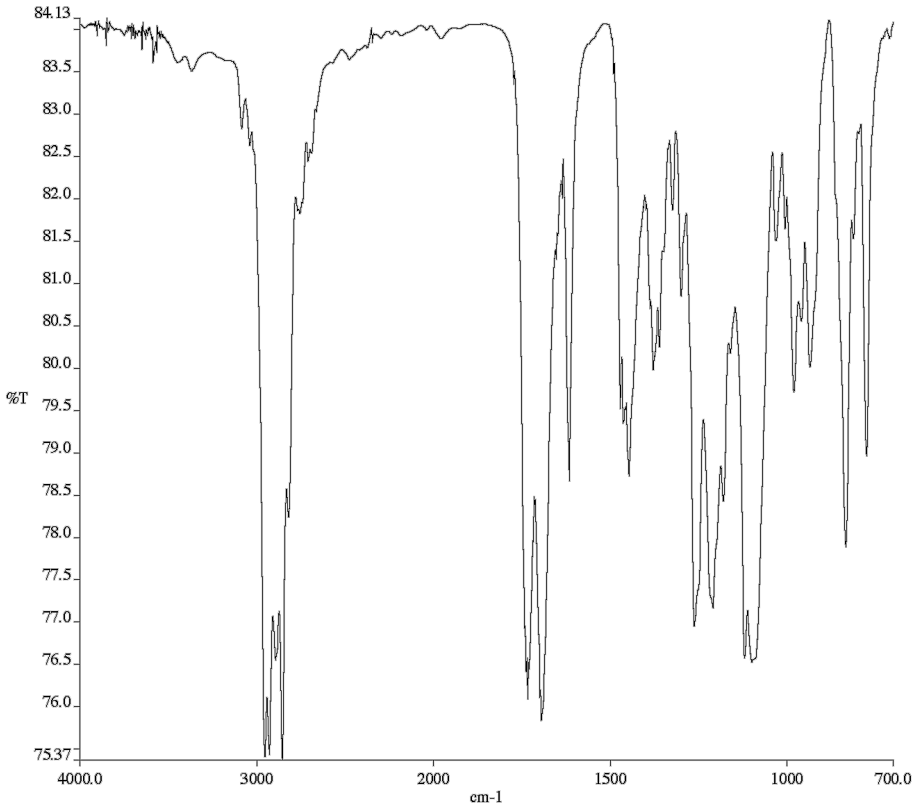
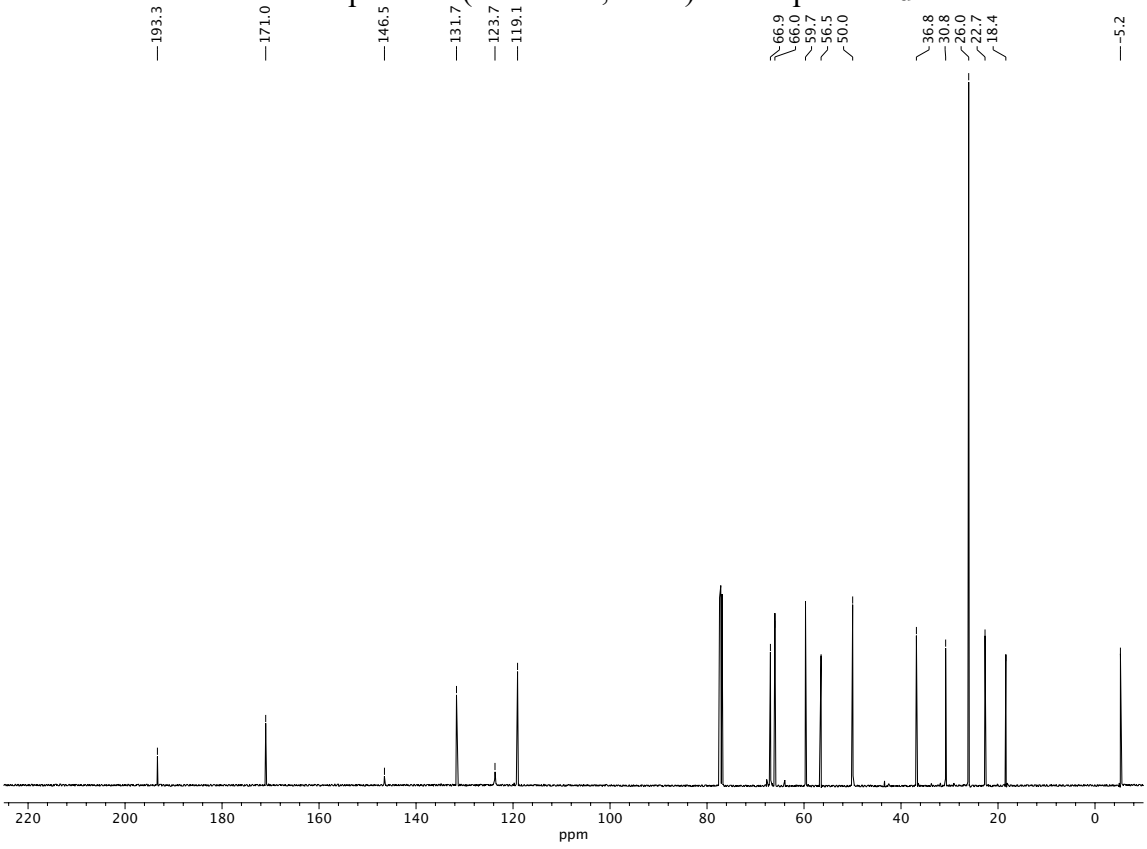


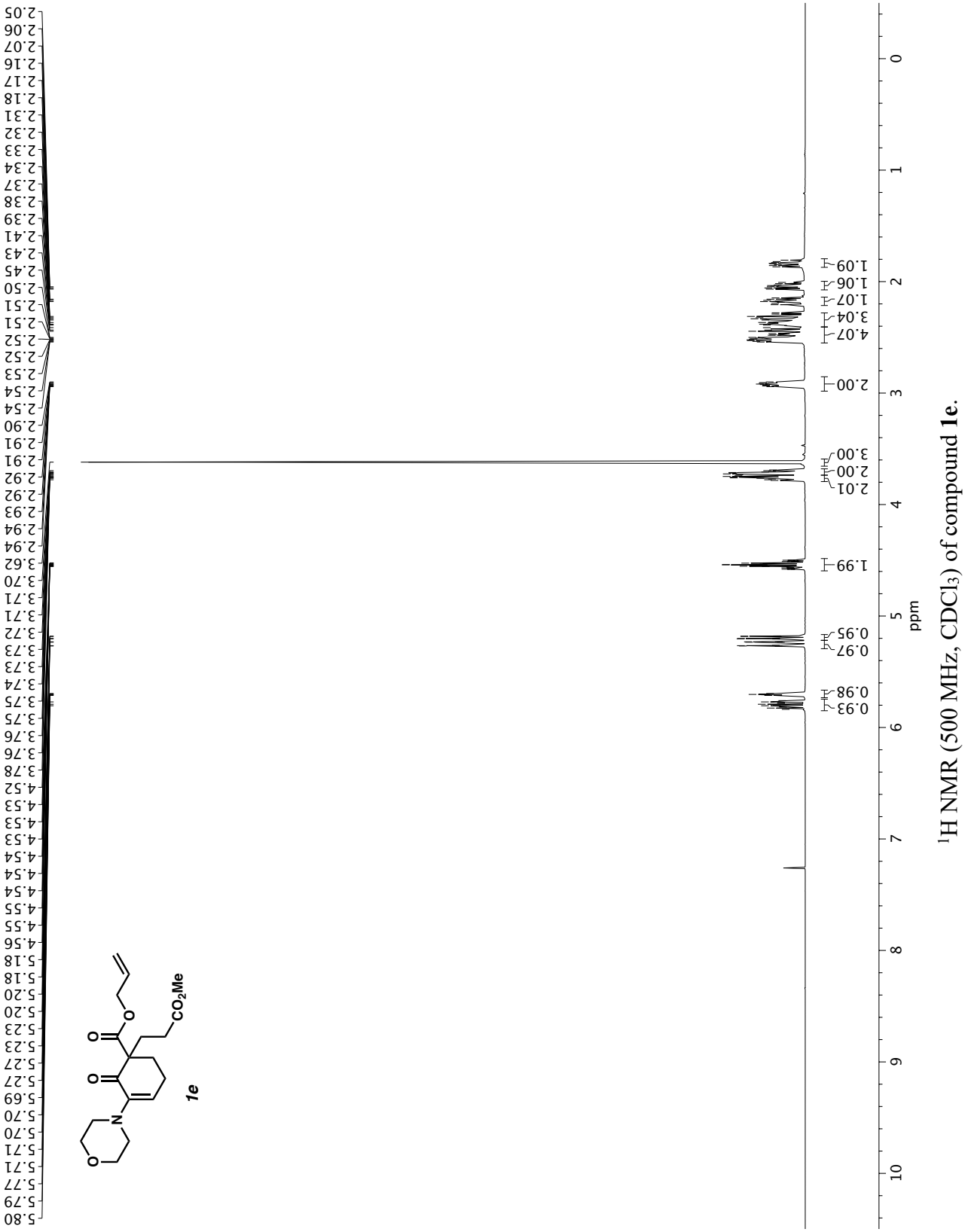
^{1}H NMR (500 MHz, $CDCl_3$) of compound **1d**.



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



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



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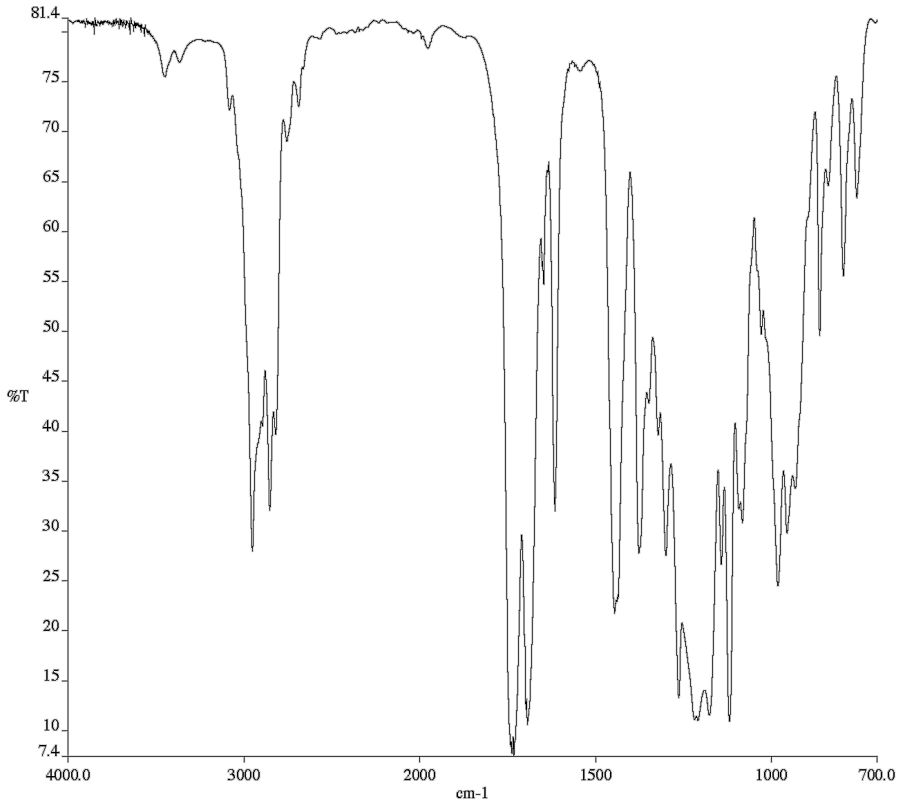
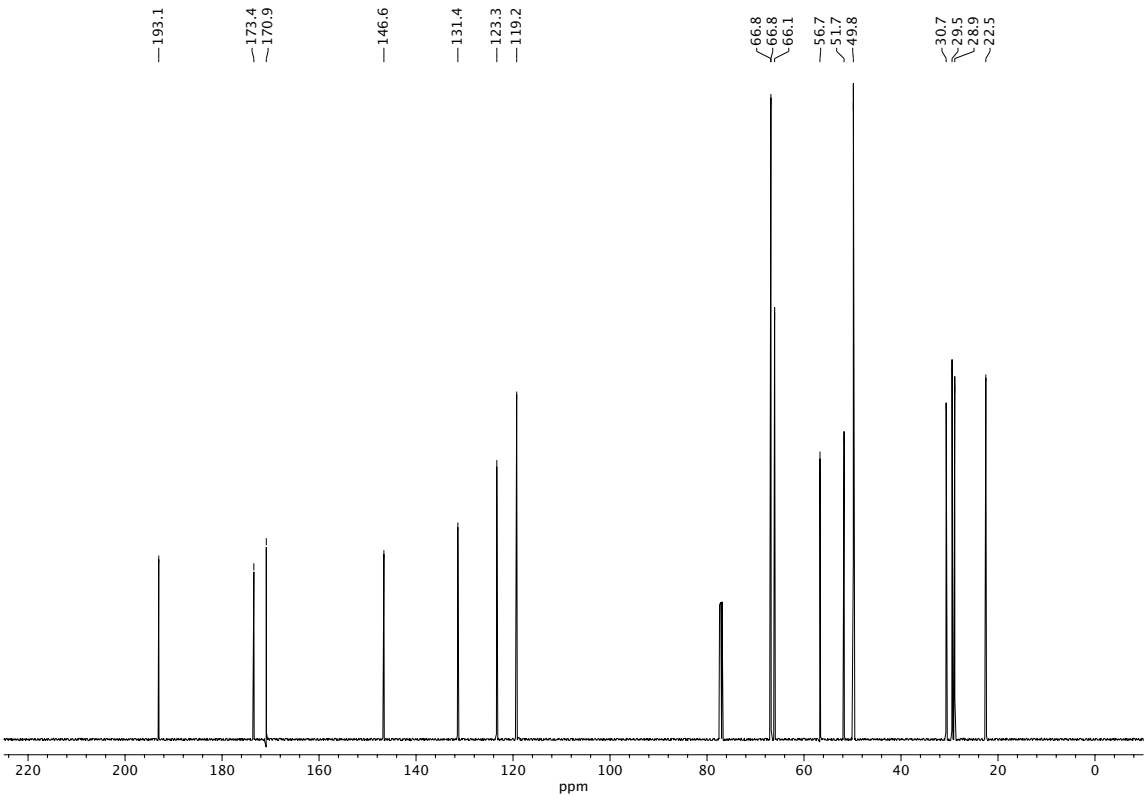


Infrared spectrum (Thin Film, NaCl) of compound **1e**.



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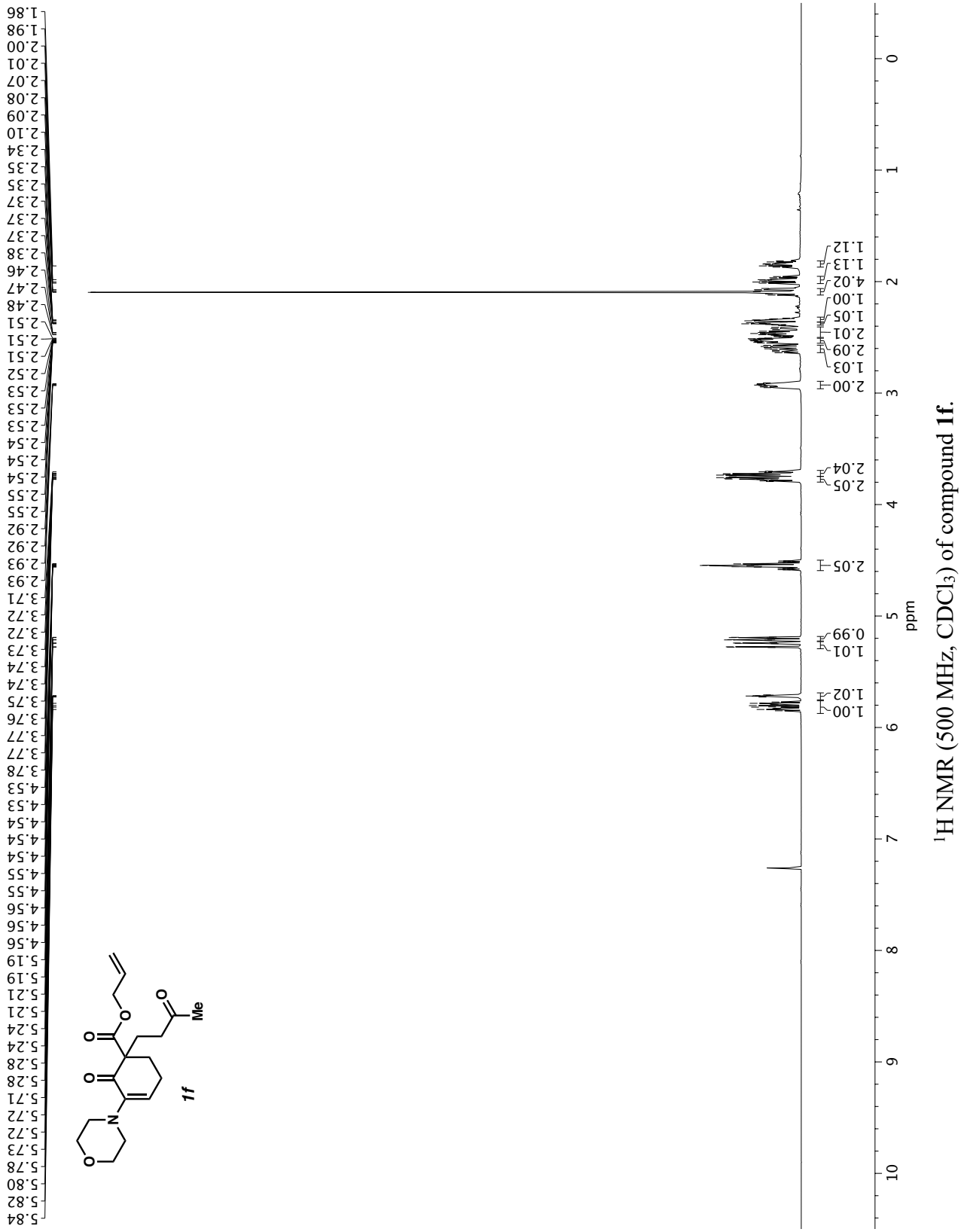
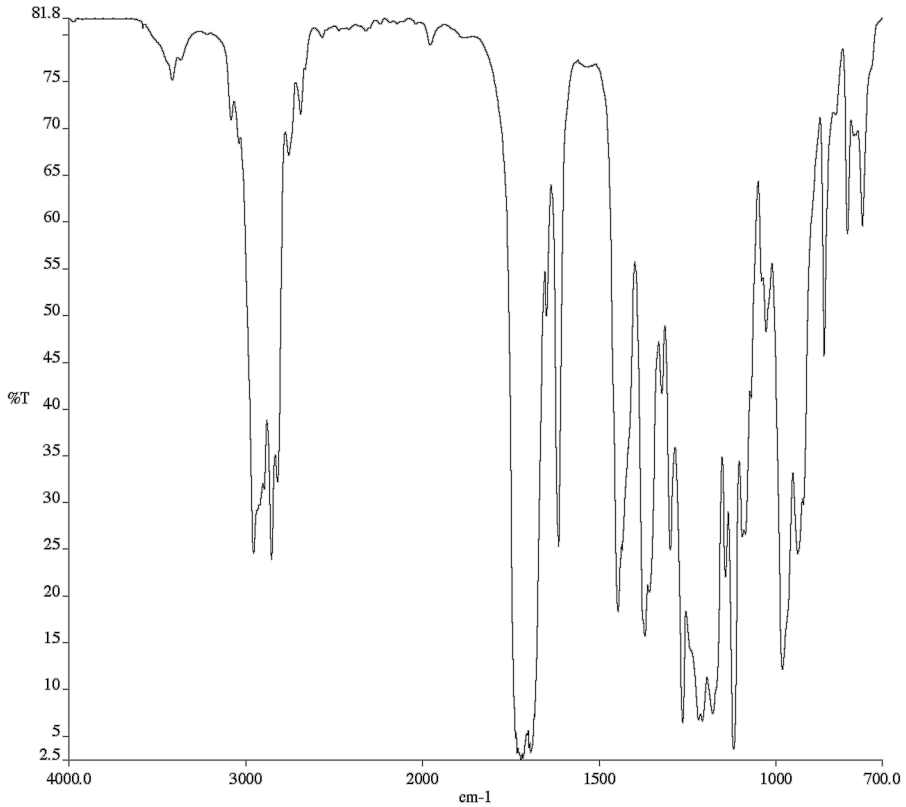
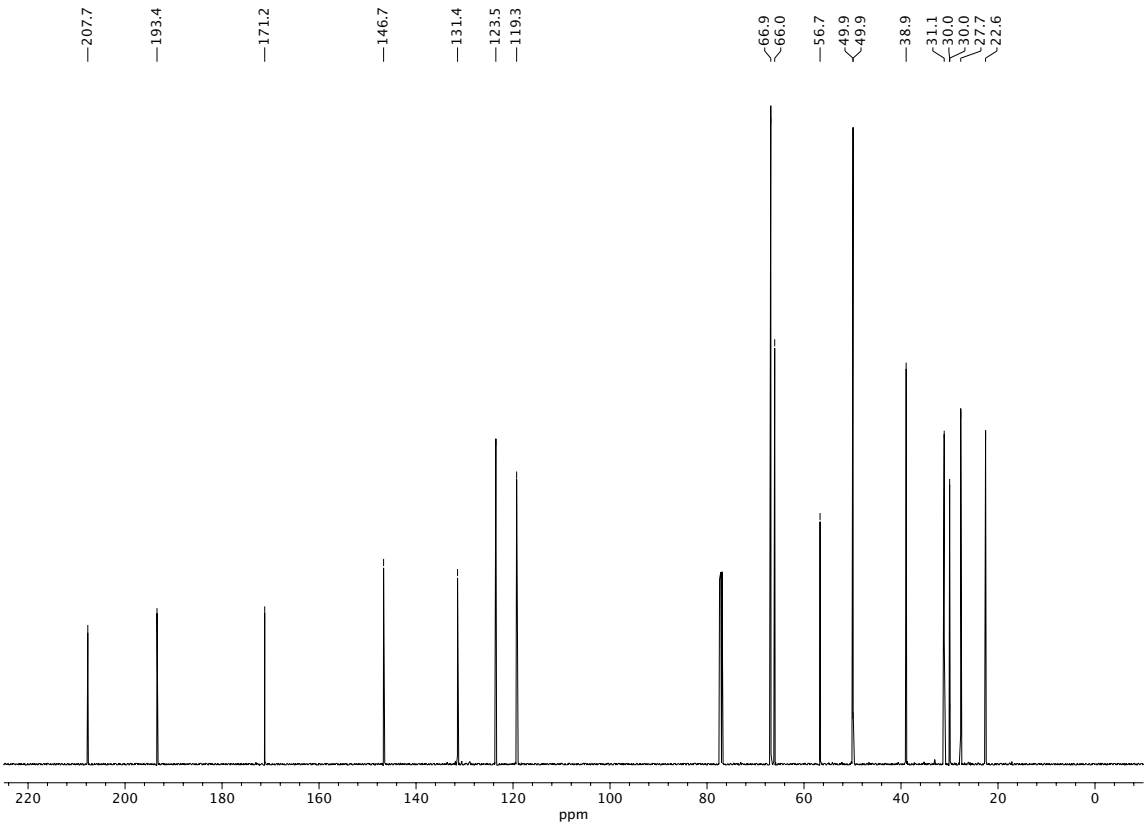


^{1}H NMR (500 MHz, $CDCl_3$) of compound **1f**.



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



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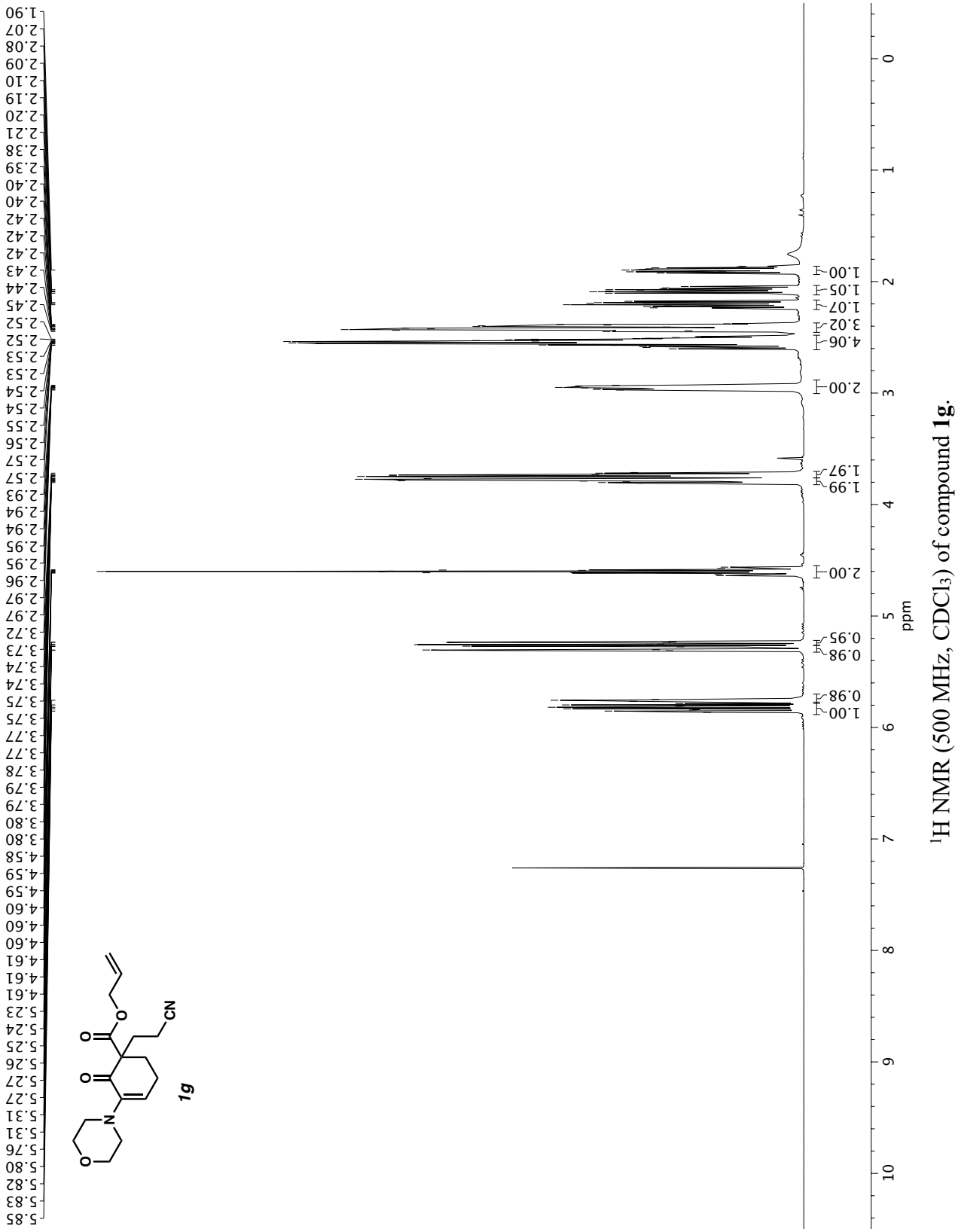

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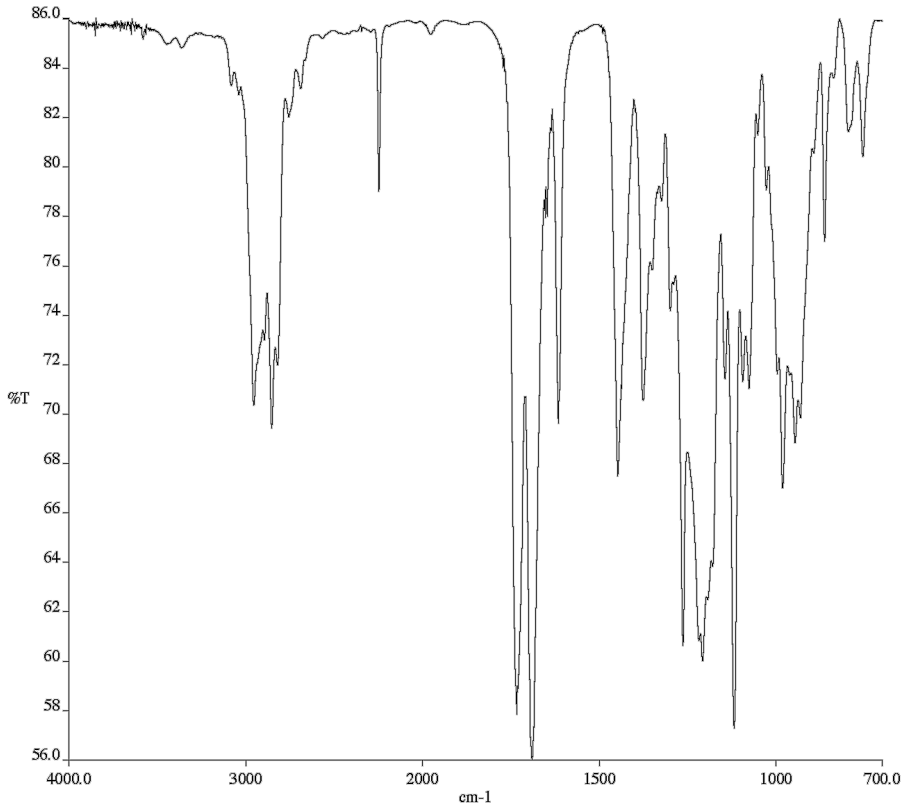
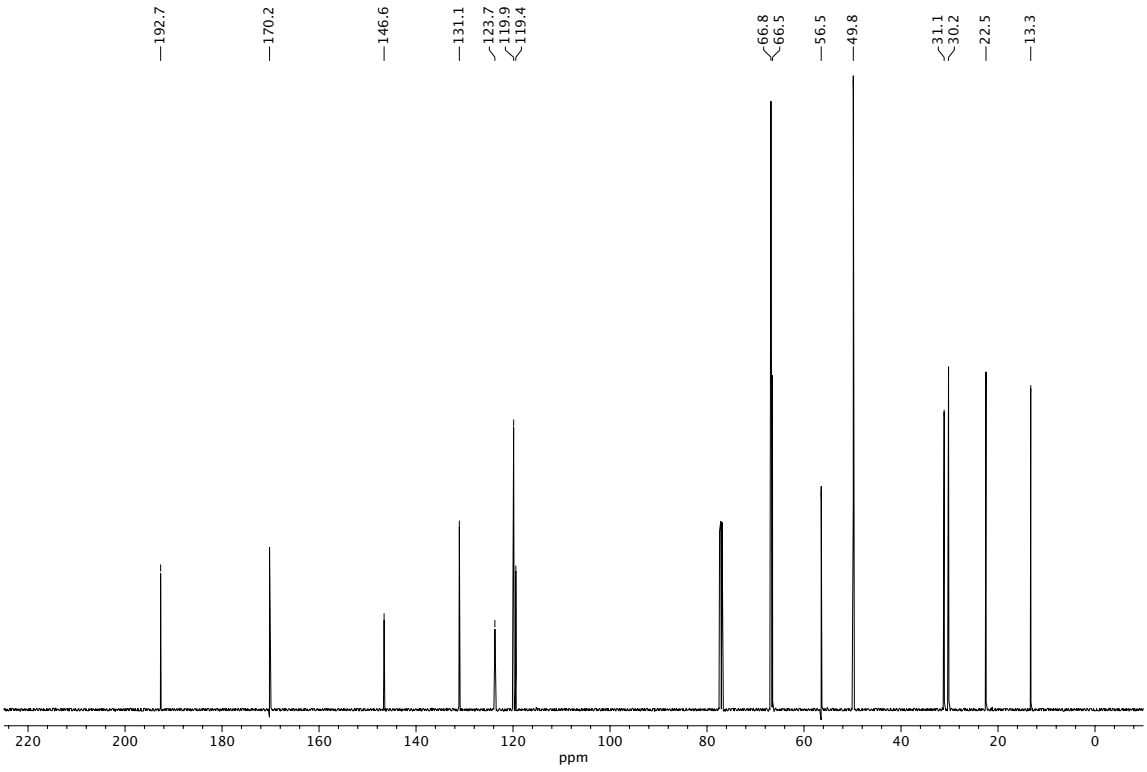
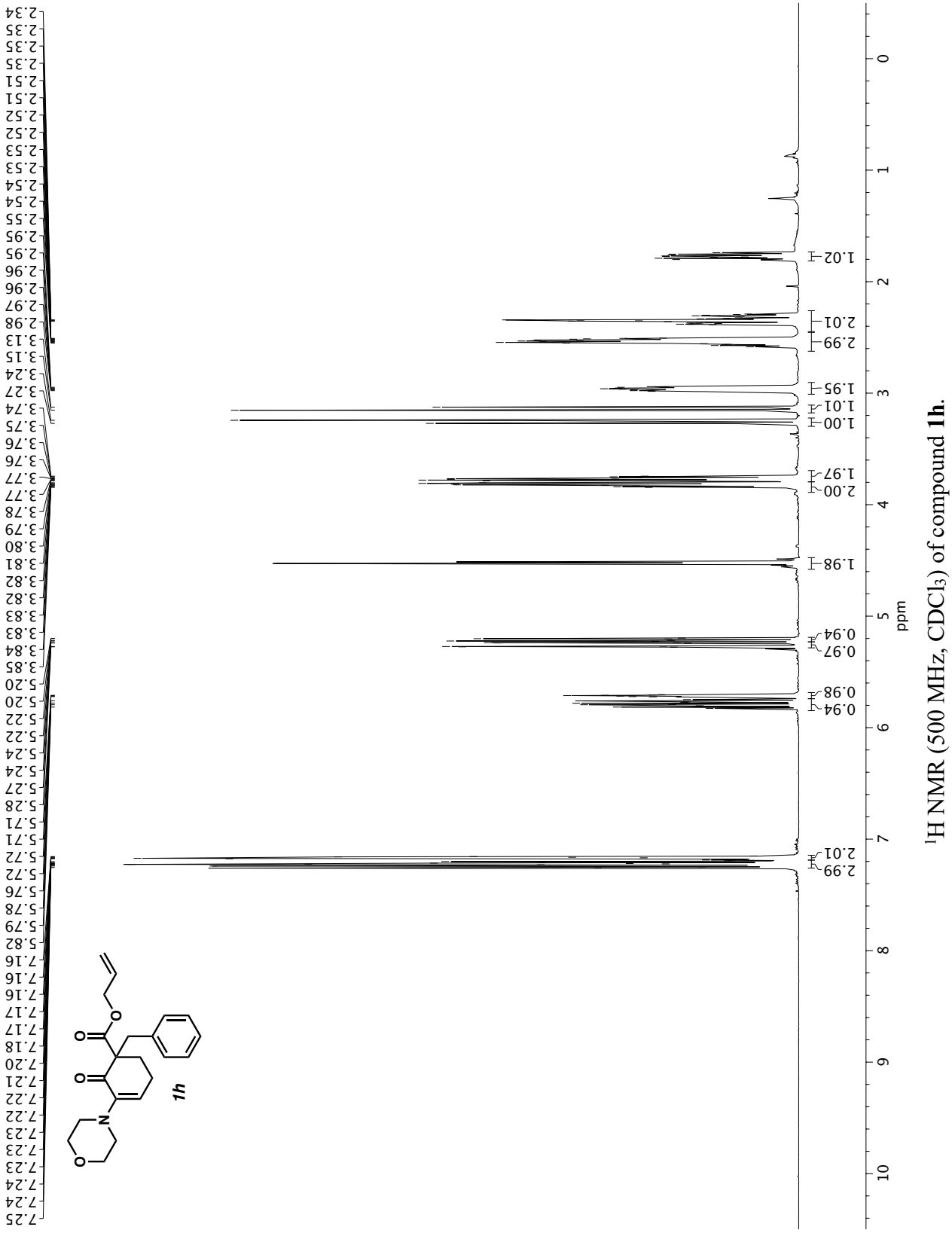


Infrared spectrum (Thin Film, NaCl) of compound **1g**.



^{13}C NMR (125 MHz, $CDCl_3$) of compound **1g**.



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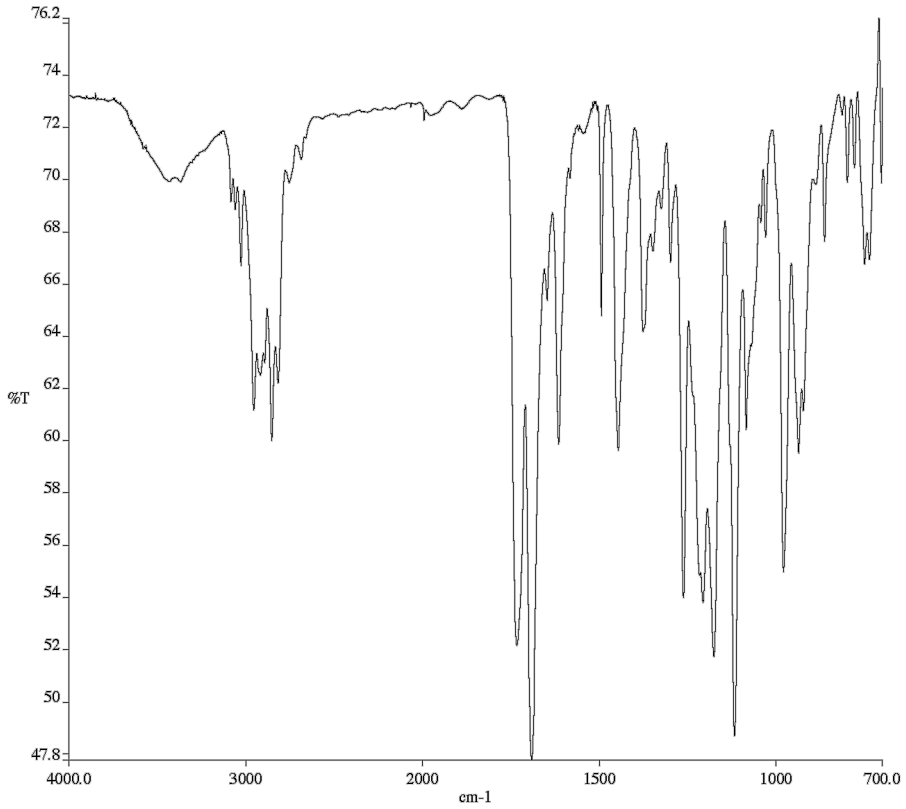
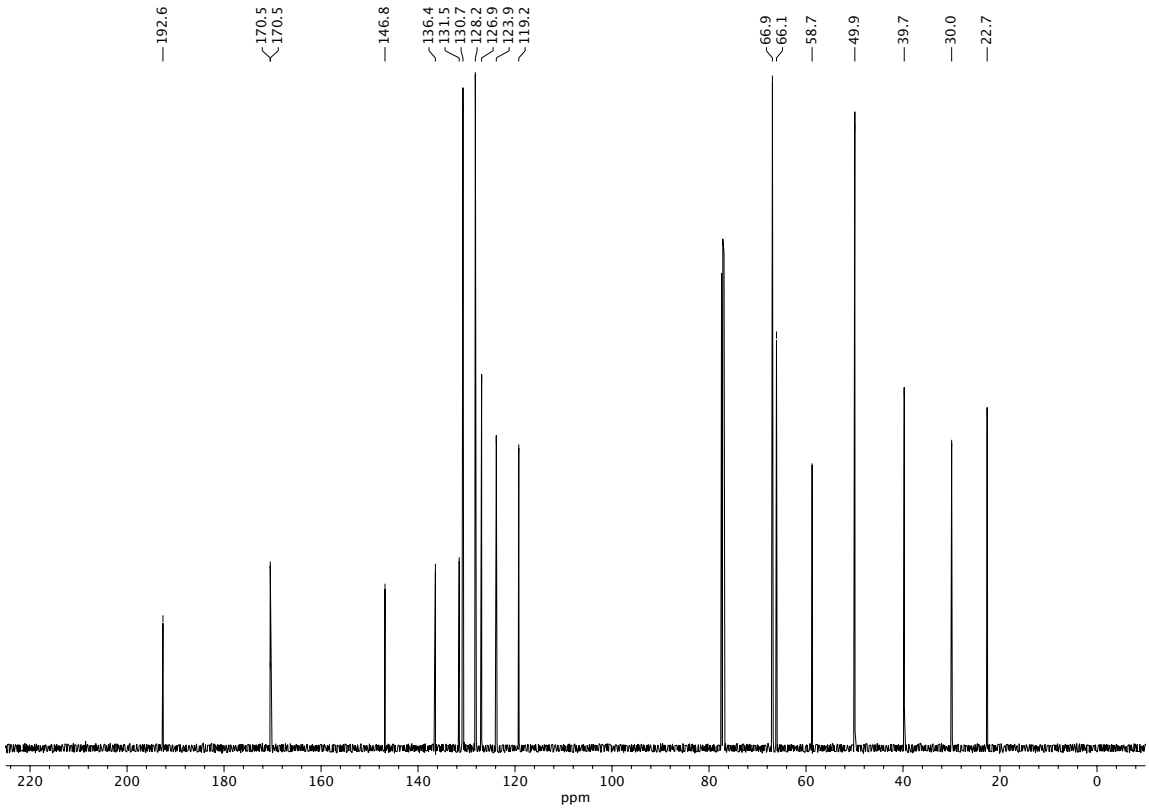
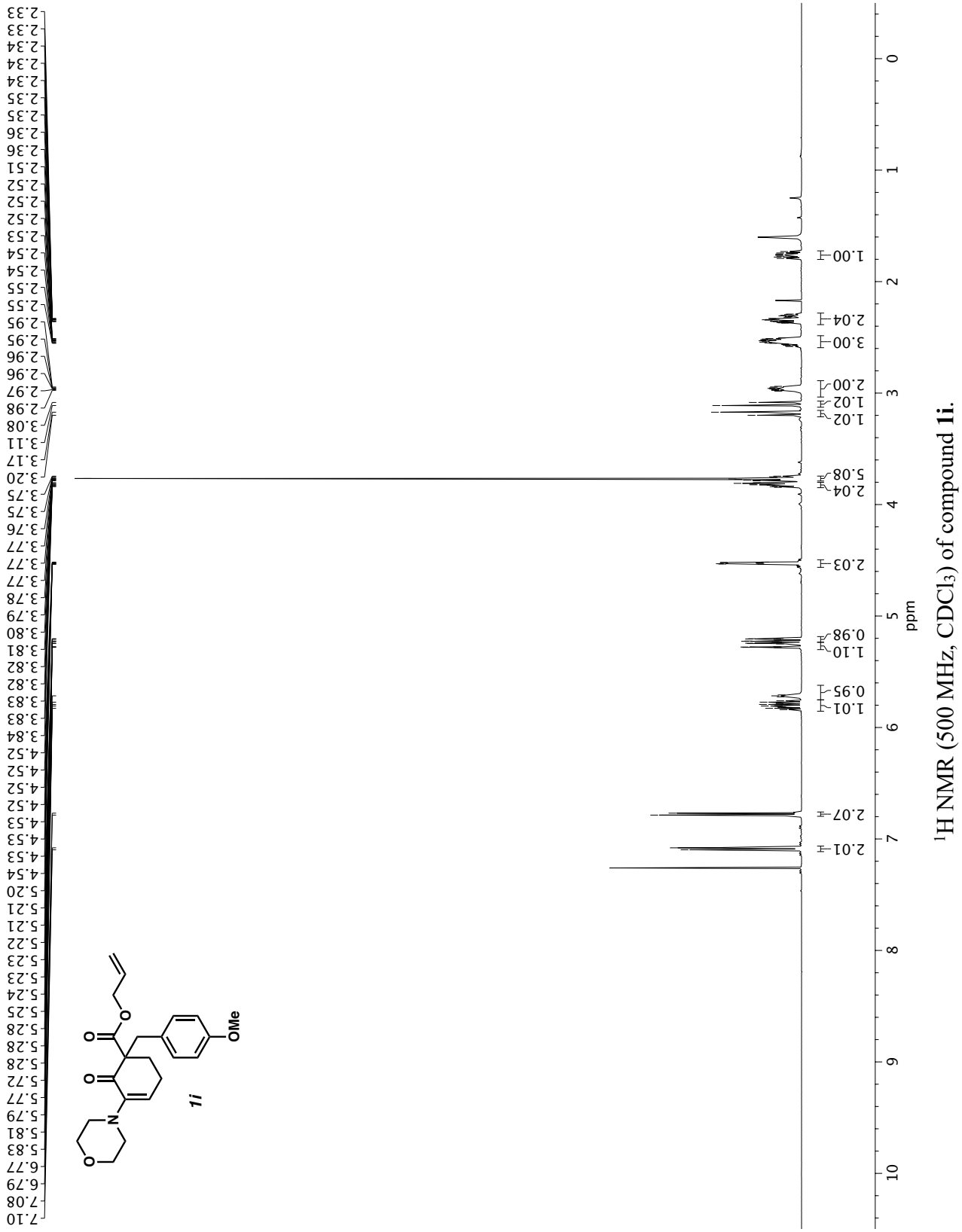


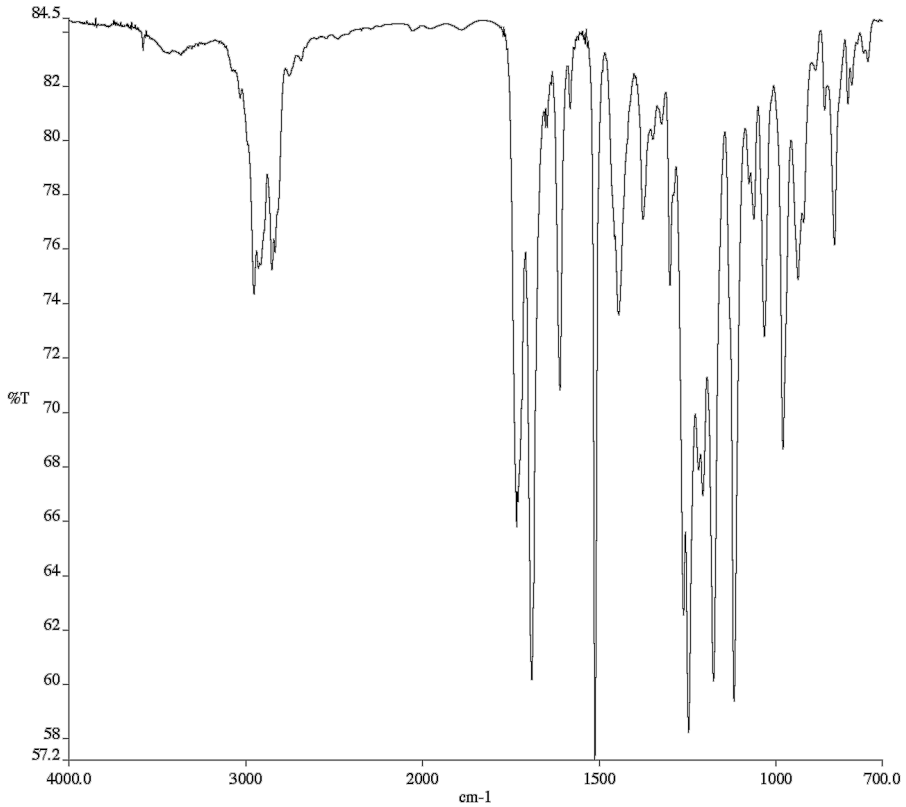
Infrared spectrum (Thin Film, NaCl) of compound **1h**.



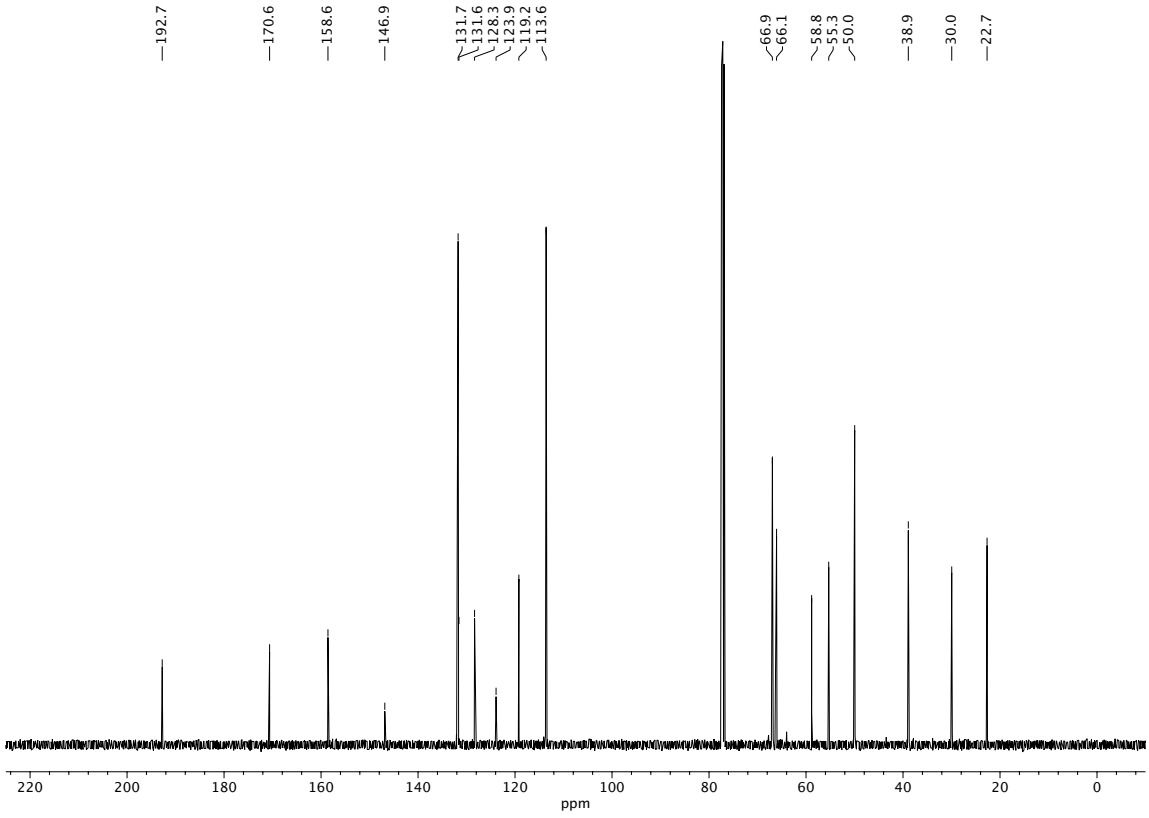
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1h**.



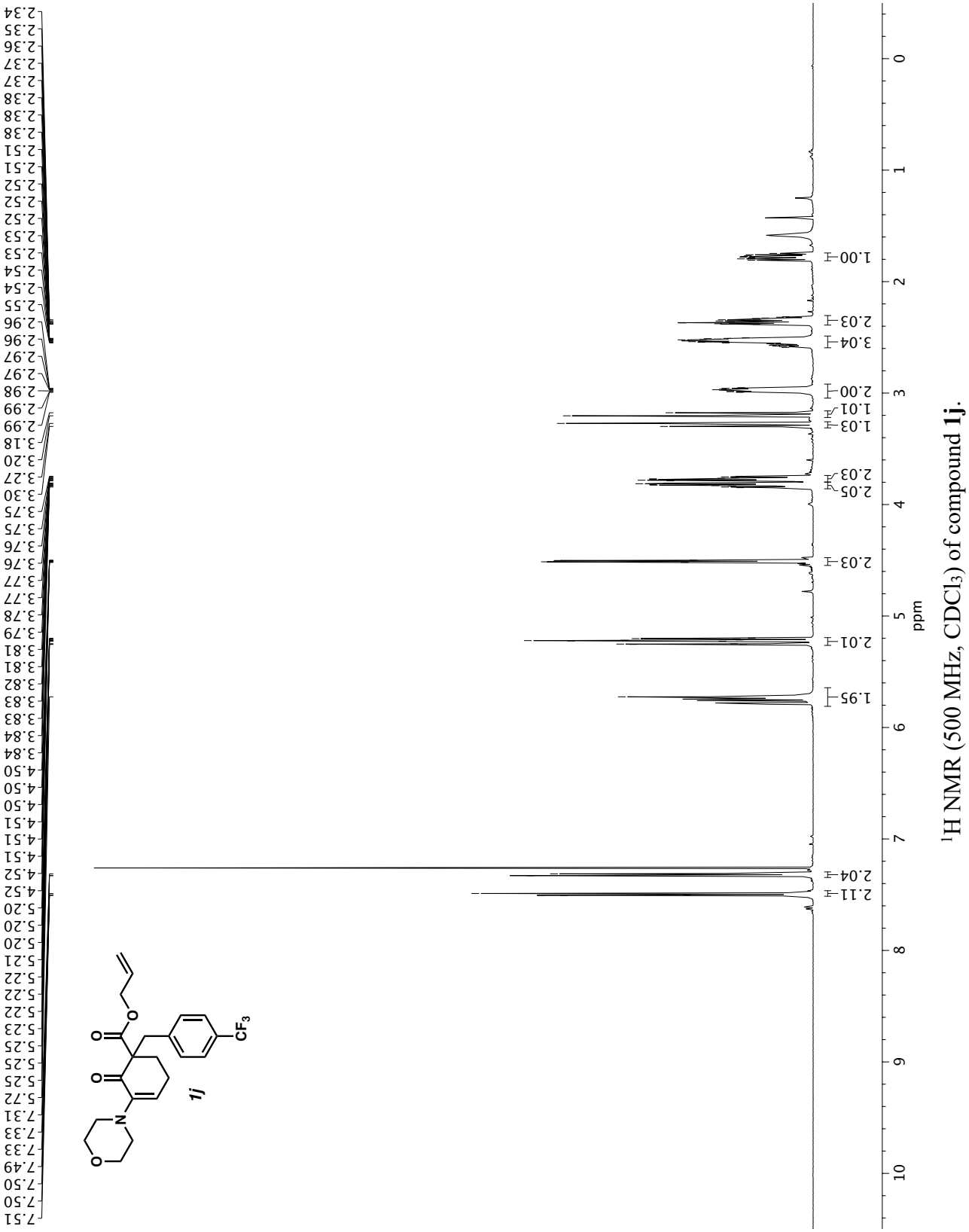
^{1}H NMR (500 MHz, $CDCl_3$) of compound **1i**.



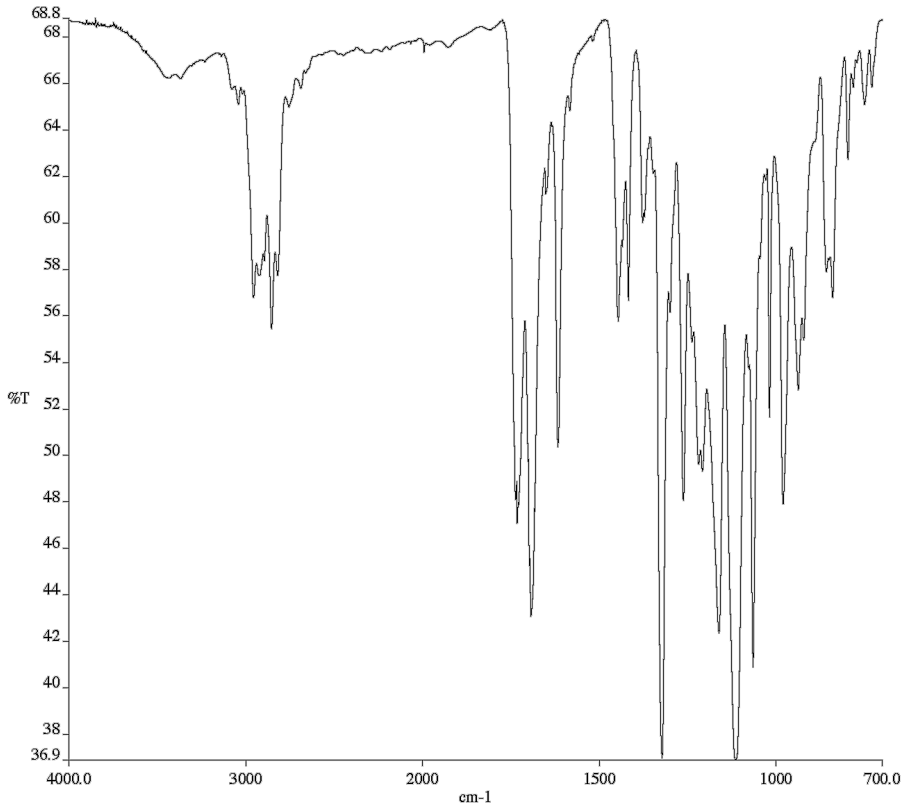
Infrared spectrum (Thin Film, NaCl) of compound **1i**.



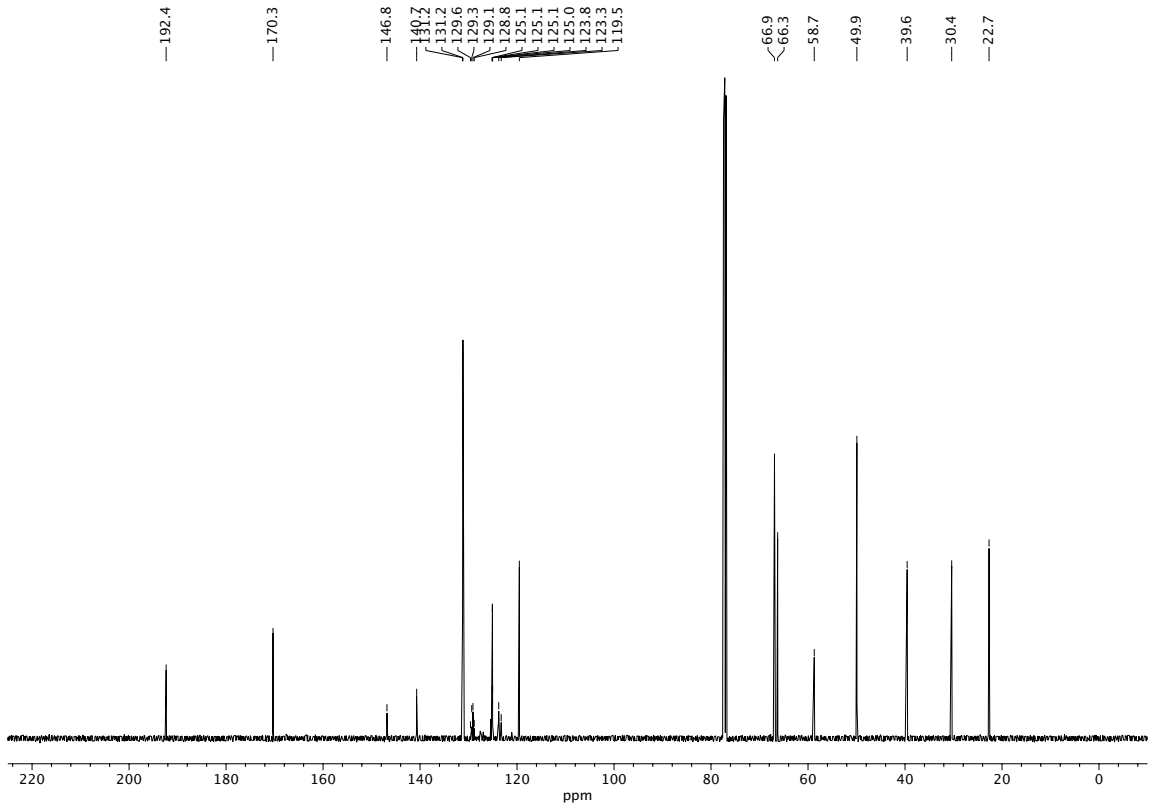
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1i**.



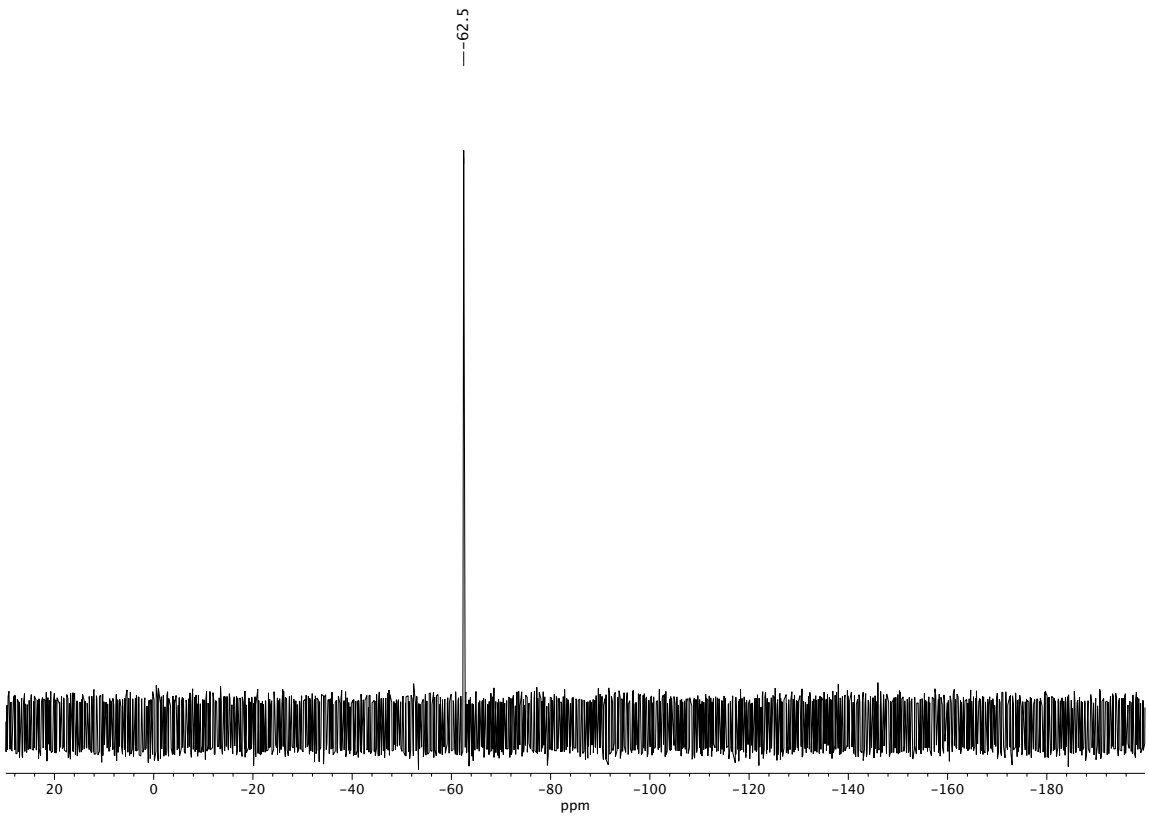
^{1}H NMR (500 MHz, $CDCl_3$) of compound **1j**.



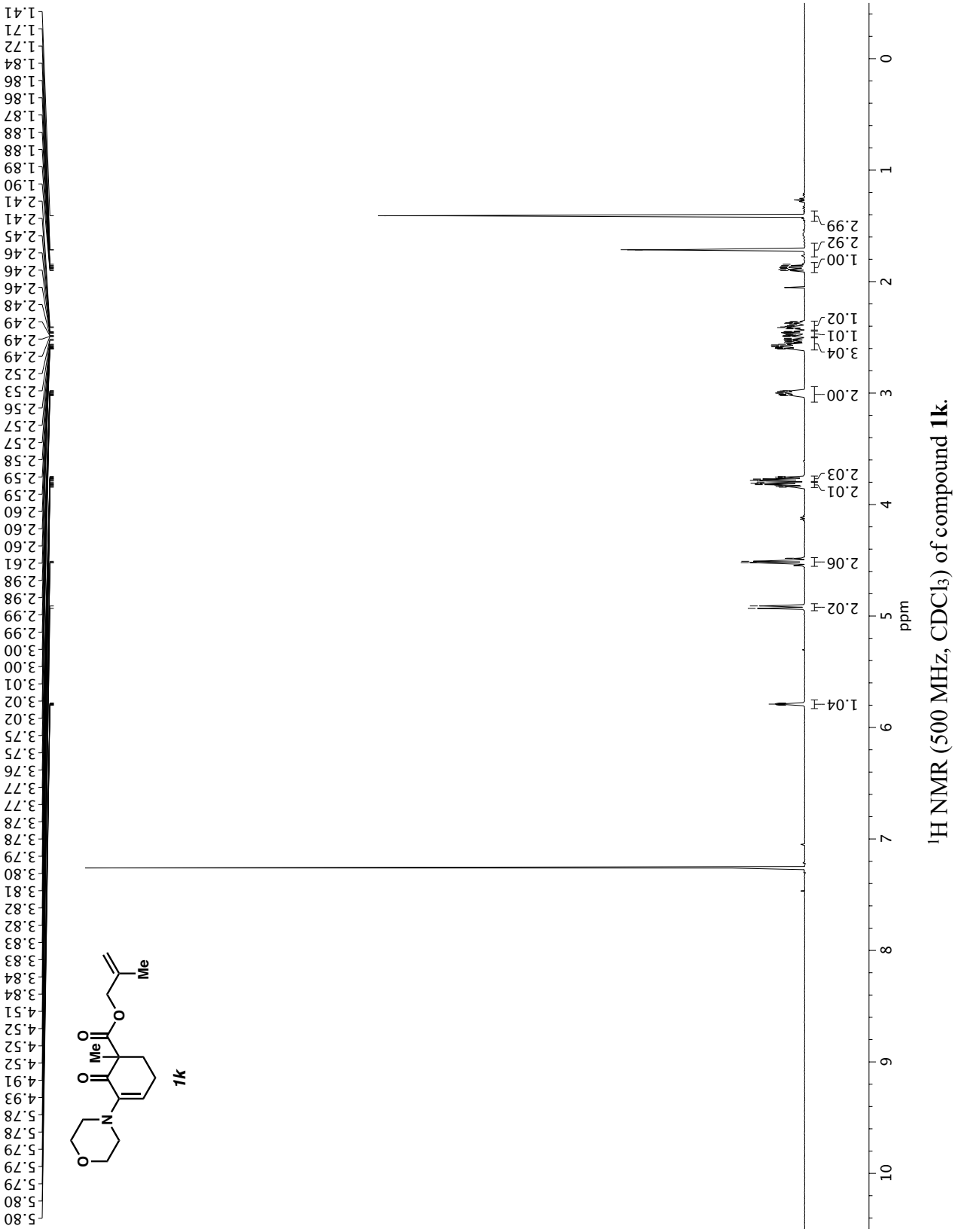
Infrared spectrum (Thin Film, NaCl) of compound **1j**.



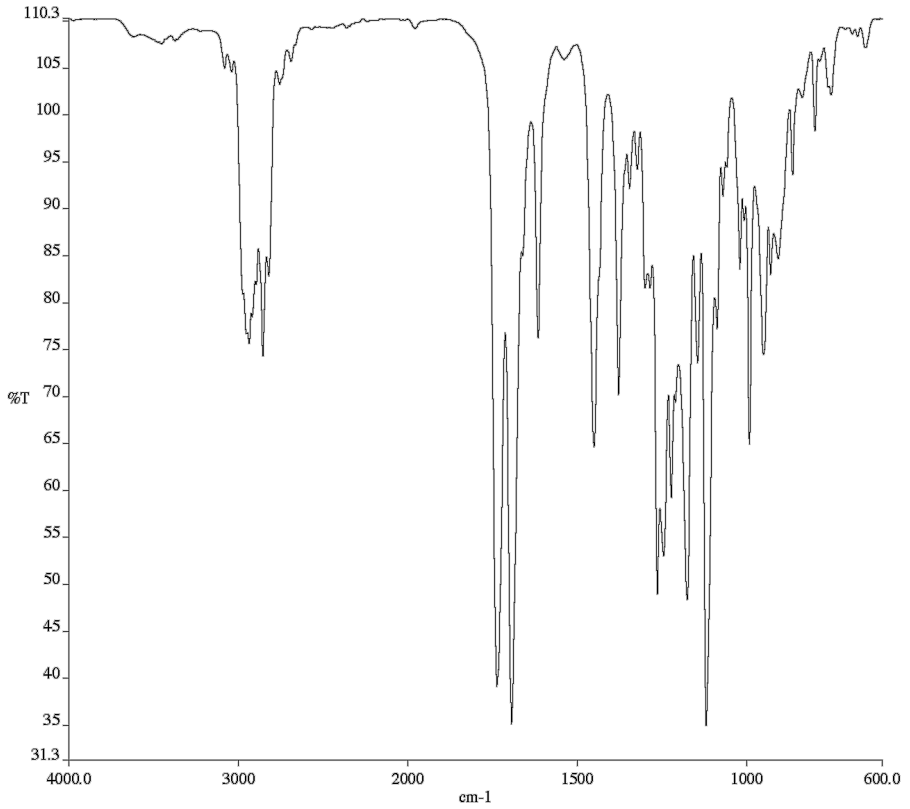
^{13}C NMR (125 MHz, $CDCl_3$) of compound **1j**.



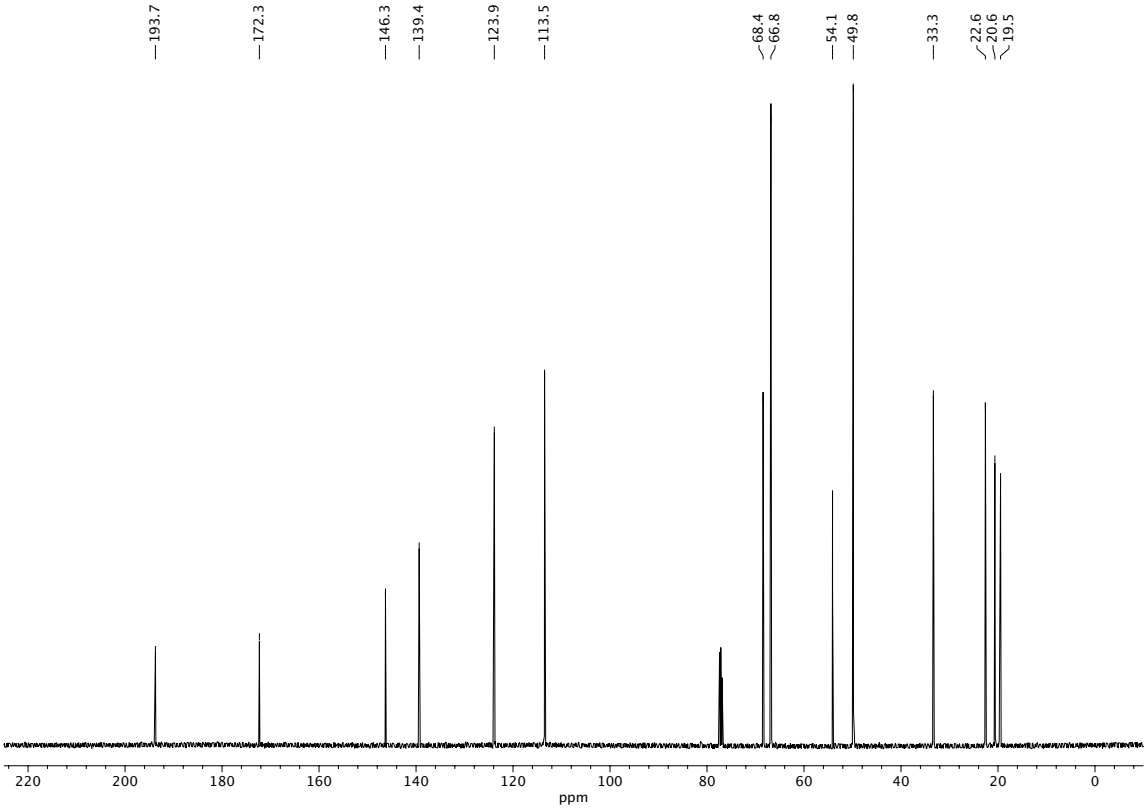
^{19}F NMR (470 MHz, $CDCl_3$) of compound **1j**.



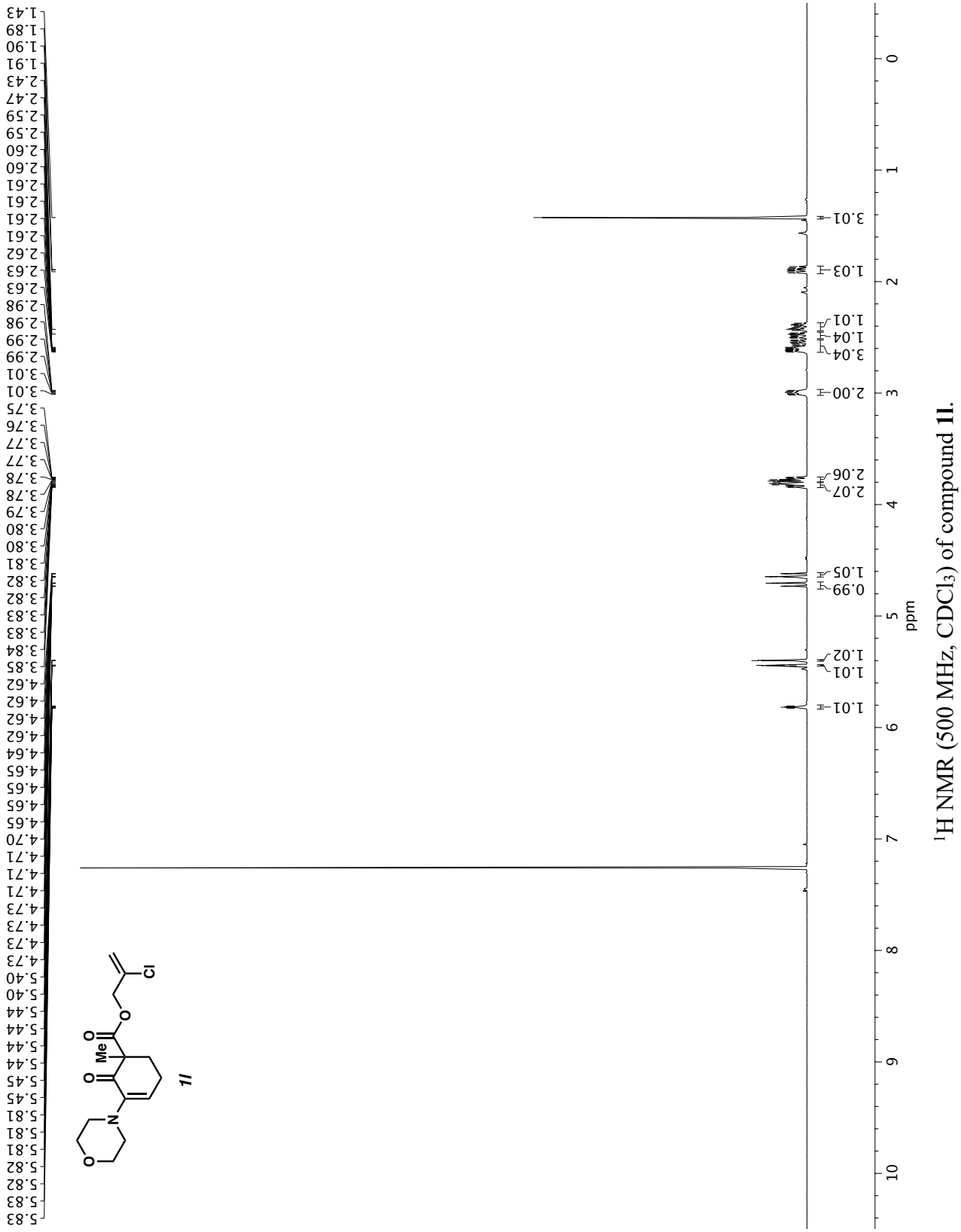
^{1}H NMR (500 MHz, $CDCl_3$) of compound **1k**.



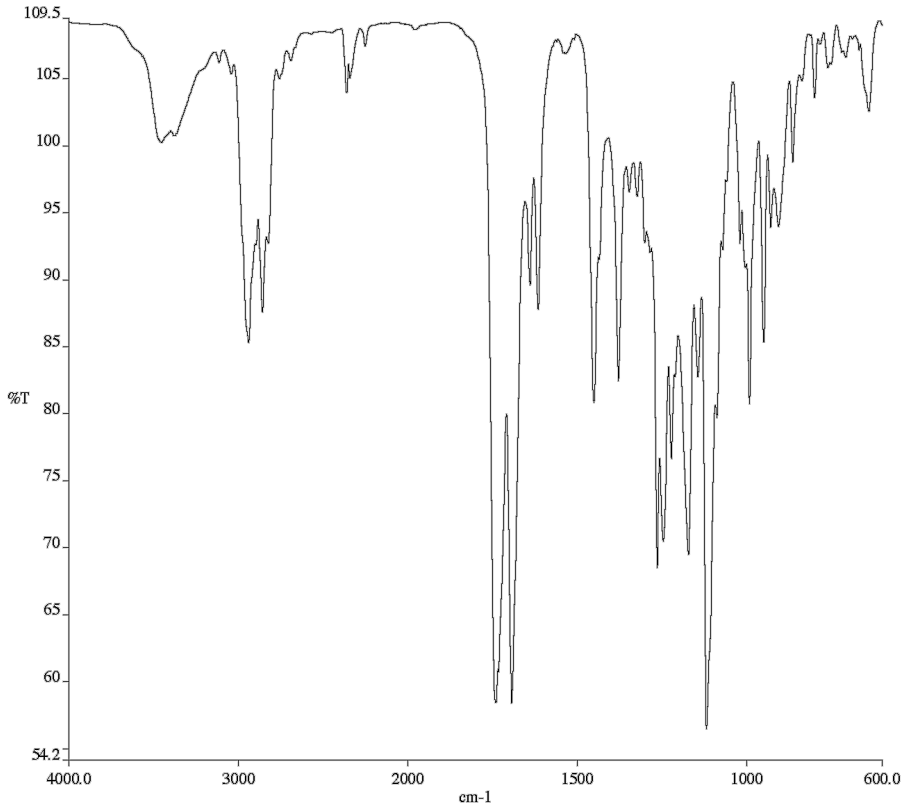
Infrared spectrum (Thin Film, NaCl) of compound **1k.**



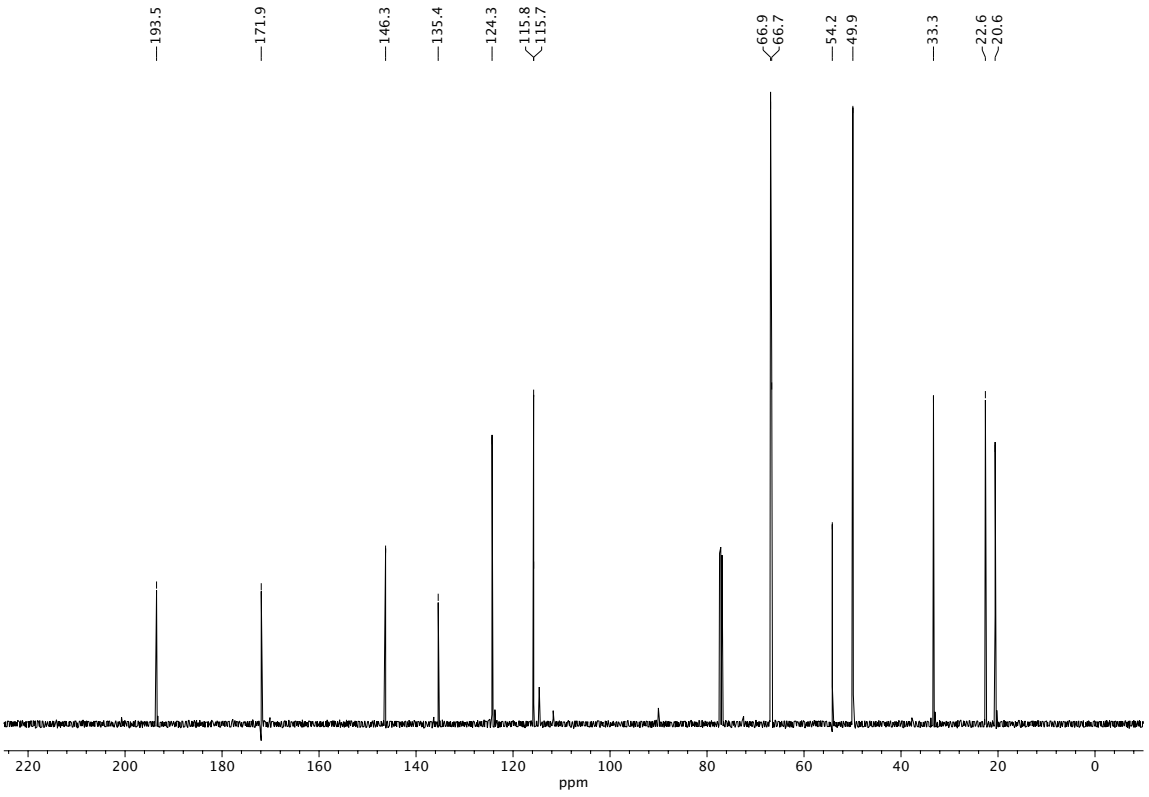
^{13}C NMR (125 MHz, $CDCl_3$) of compound **1k**.



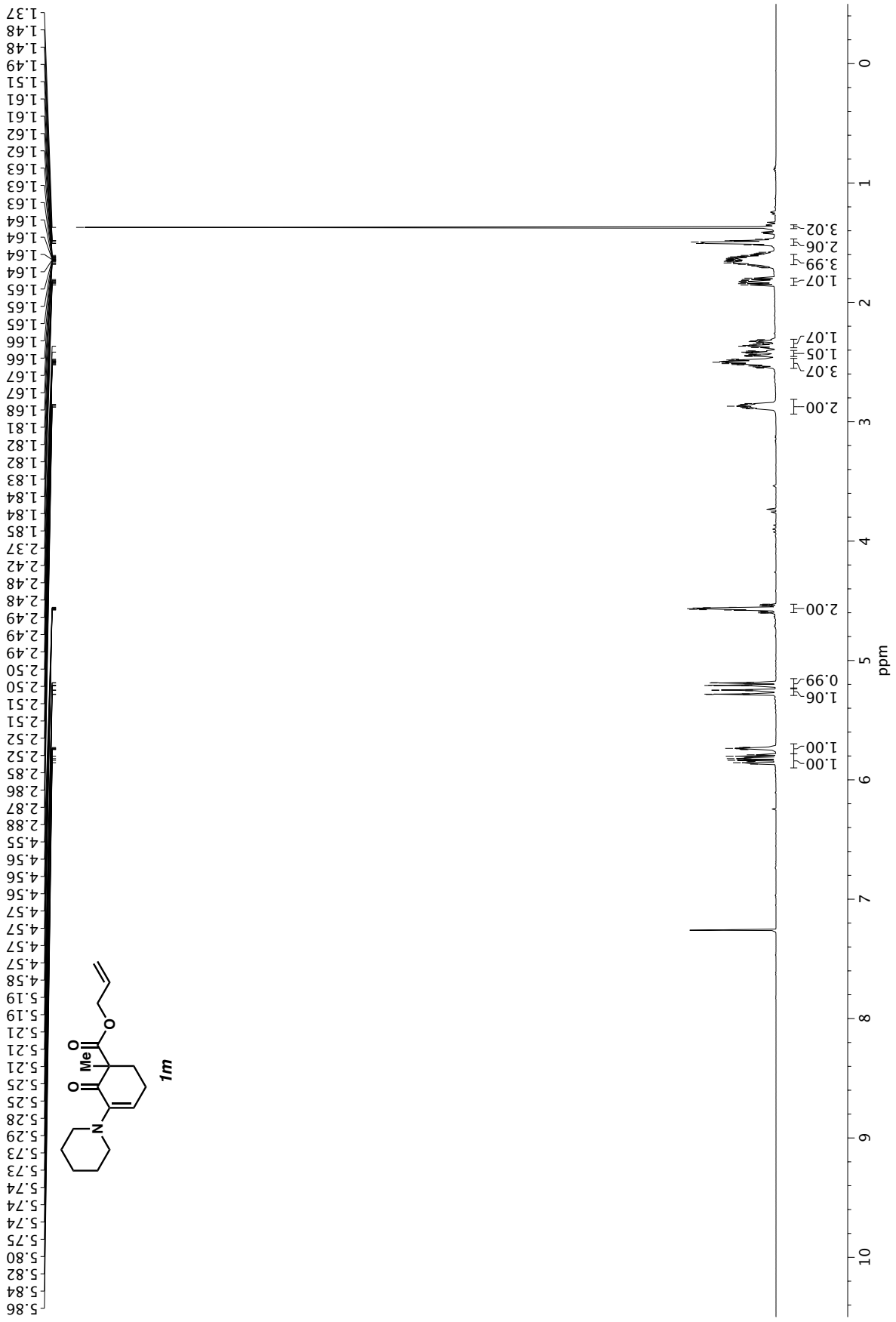
^{1}H NMR (500 MHz, $CDCl_3$) of compound **11**.



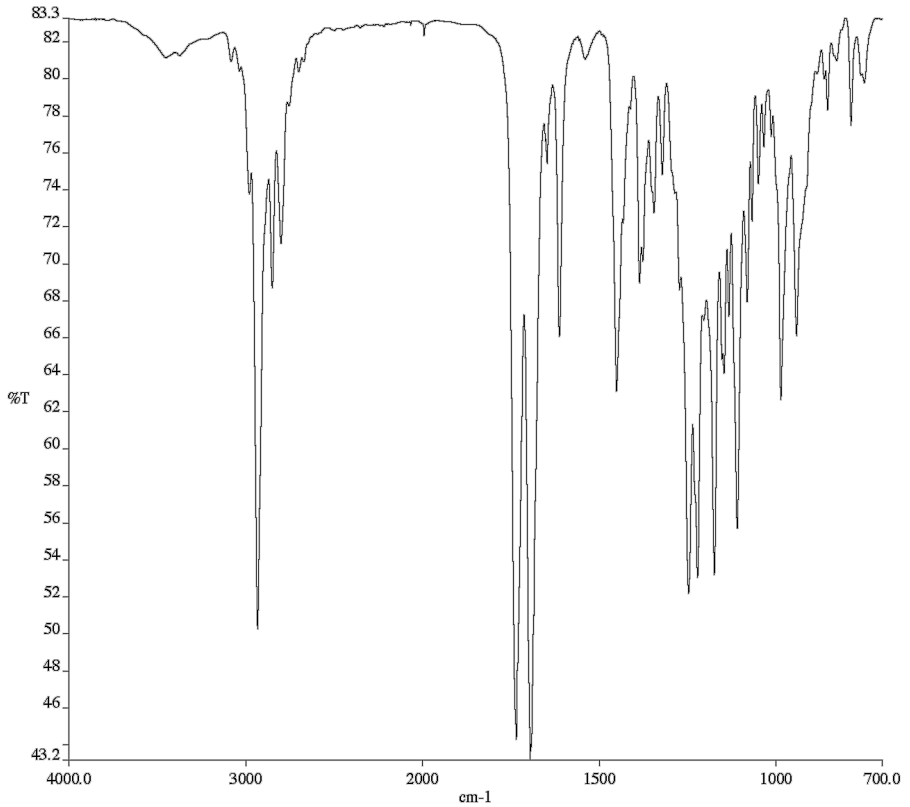
Infrared spectrum (Thin Film, NaCl) of compound **1l**.



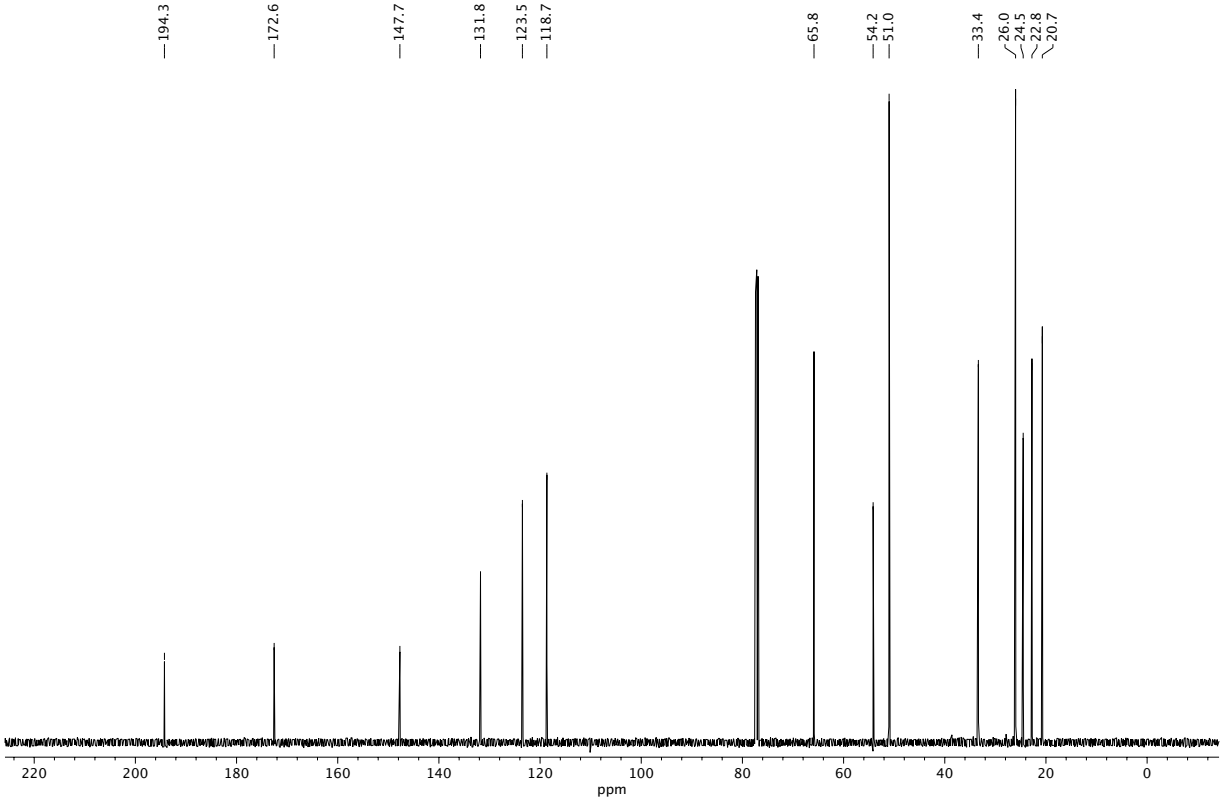
^{13}C NMR (125 MHz, $CDCl_3$) of compound **1l**.



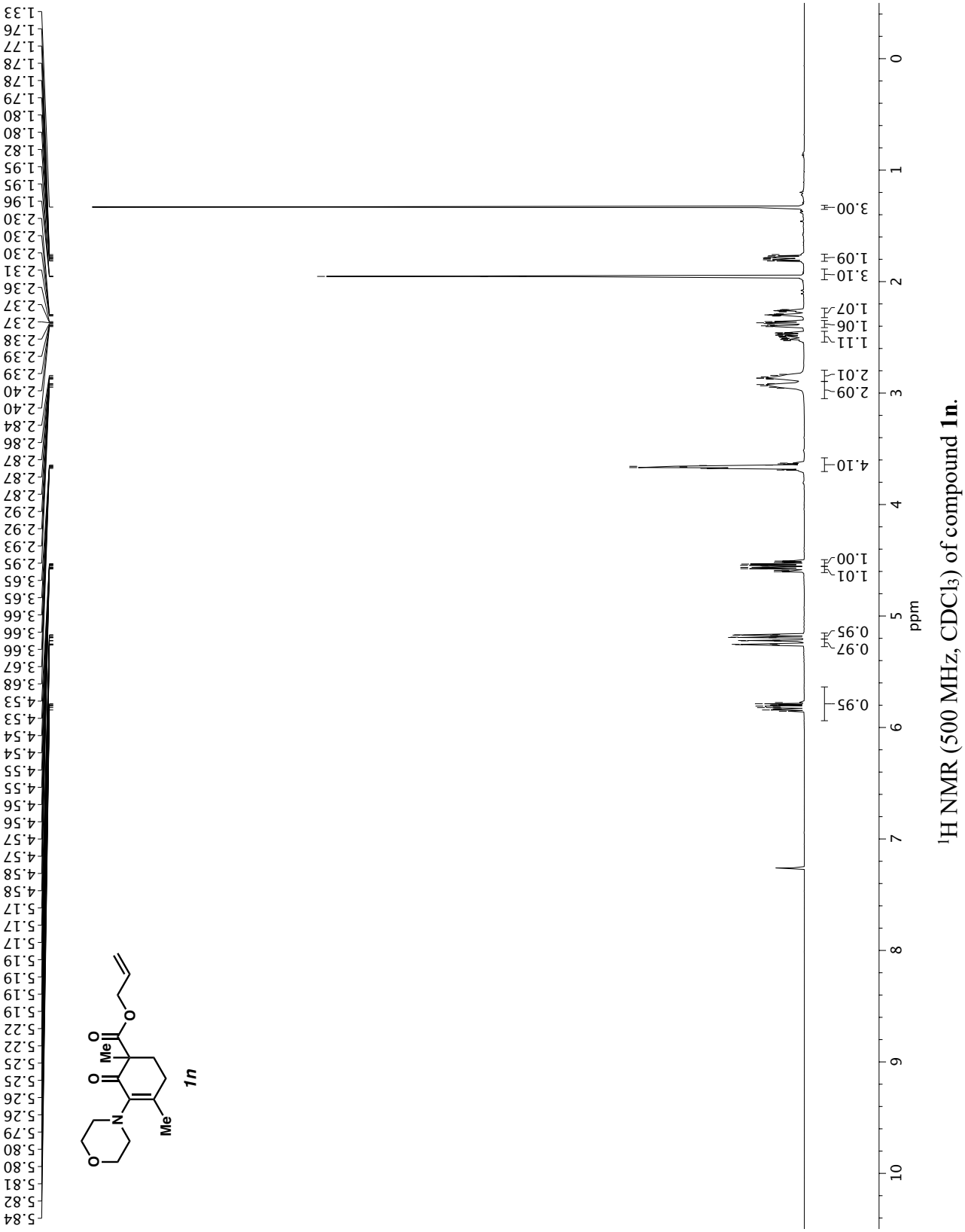
^{1}H NMR (500 MHz, $CDCl_3$) of compound **1m**.



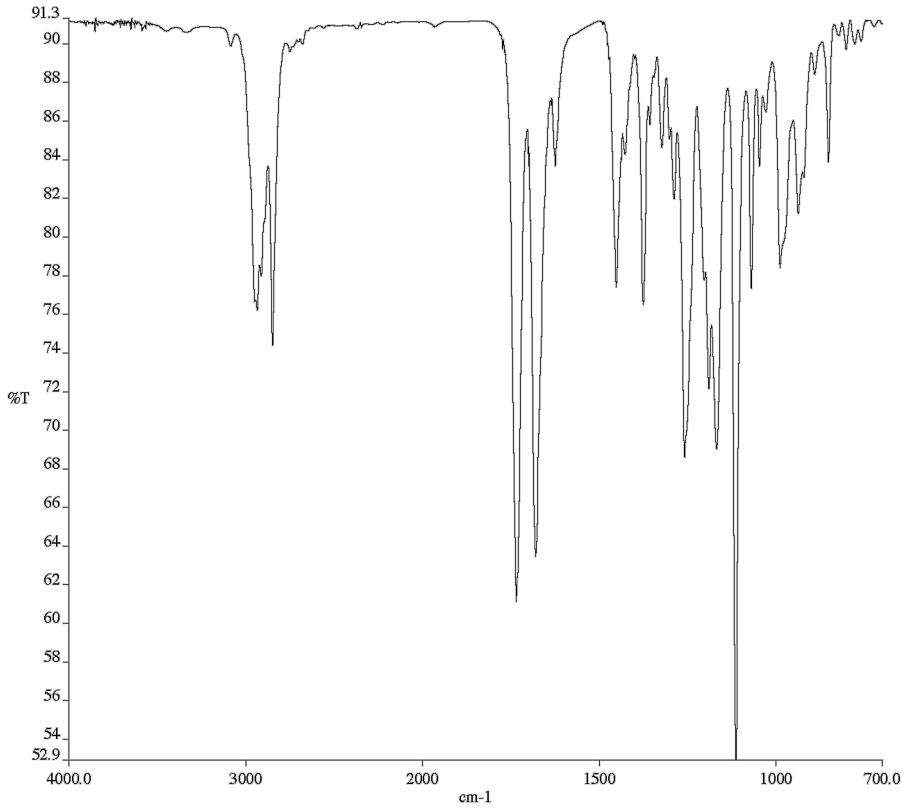
Infrared spectrum (Thin Film, NaCl) of compound **1m**.



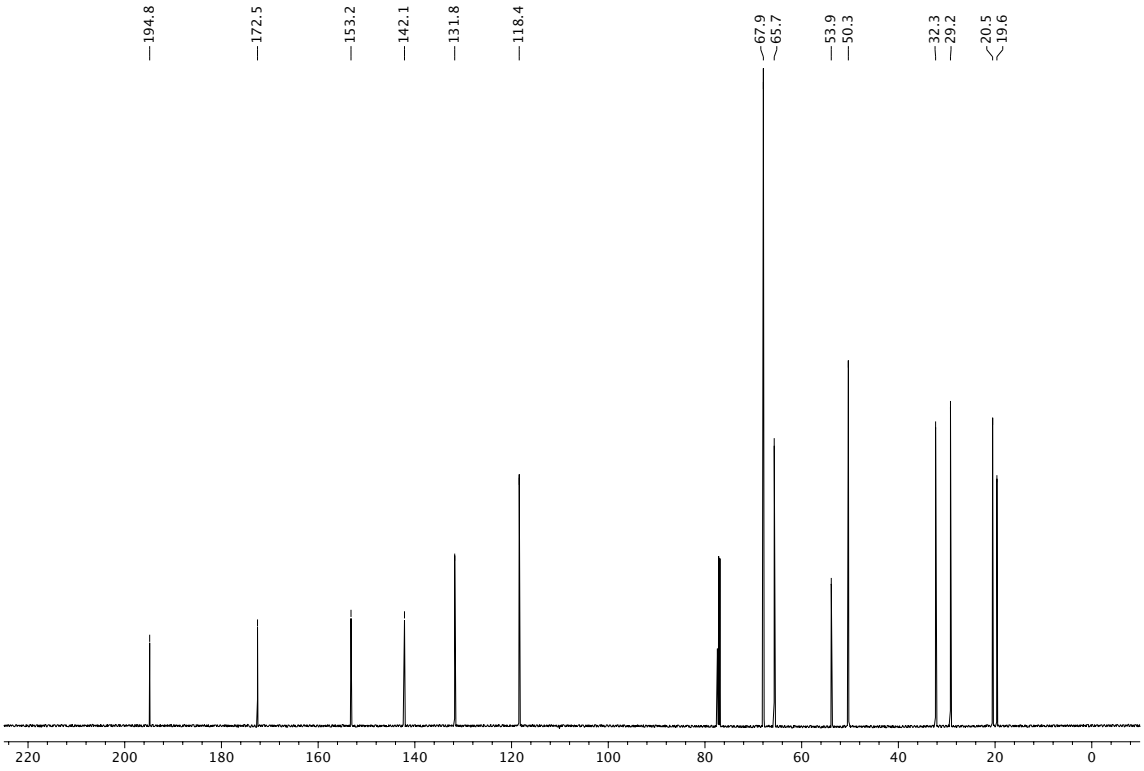
^{13}C NMR (125 MHz, $CDCl_3$) of compound **1m**.



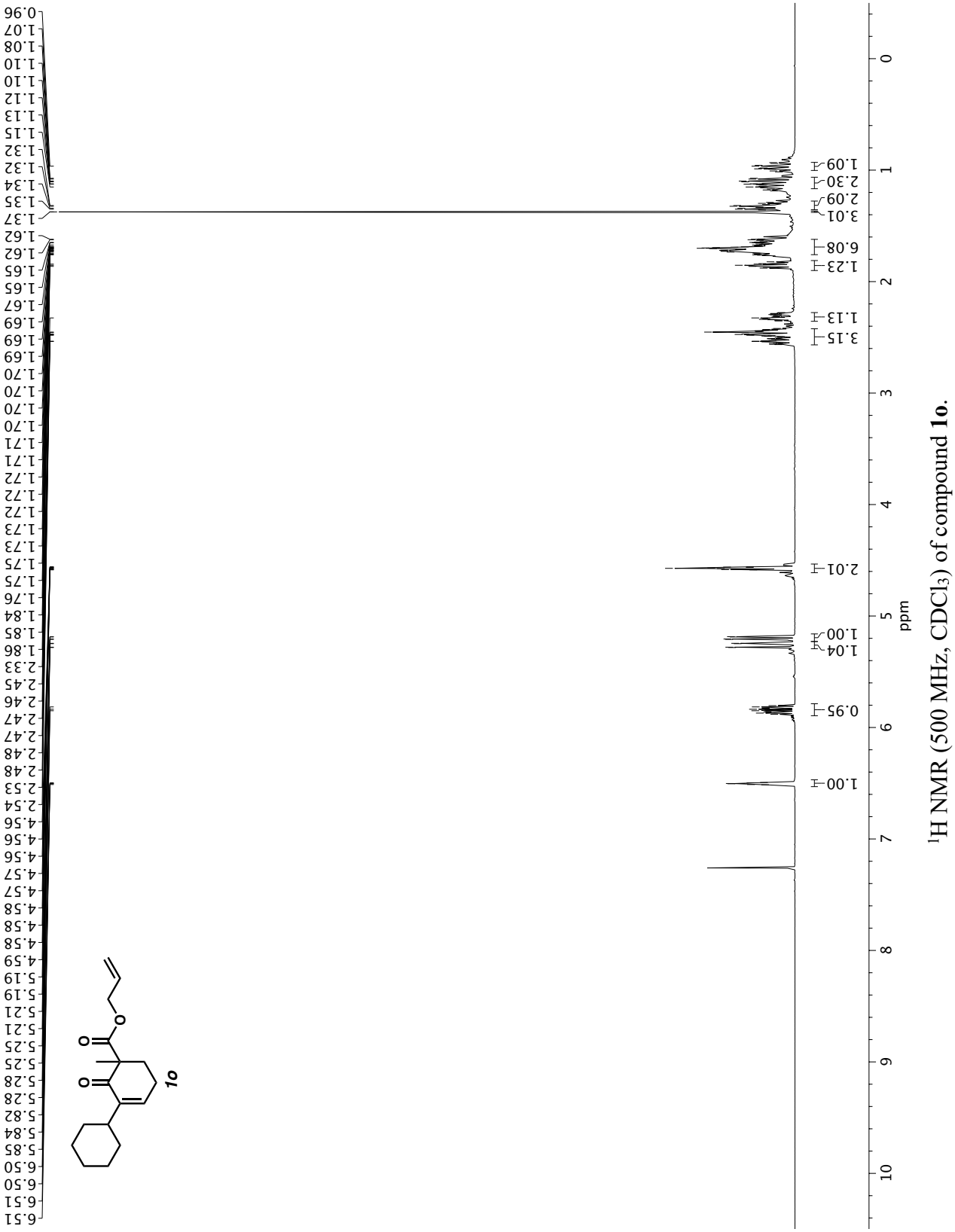
^{1}H NMR (500 MHz, $CDCl_3$) of compound **1n**.



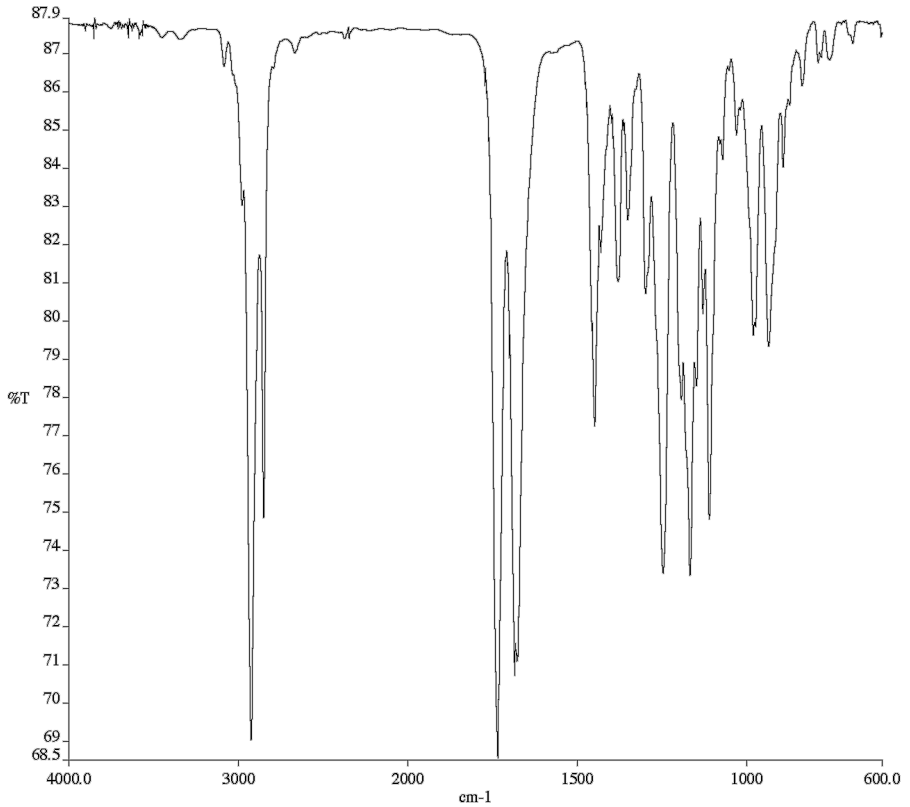
Infrared spectrum (Thin Film, NaCl) of compound **1n**.



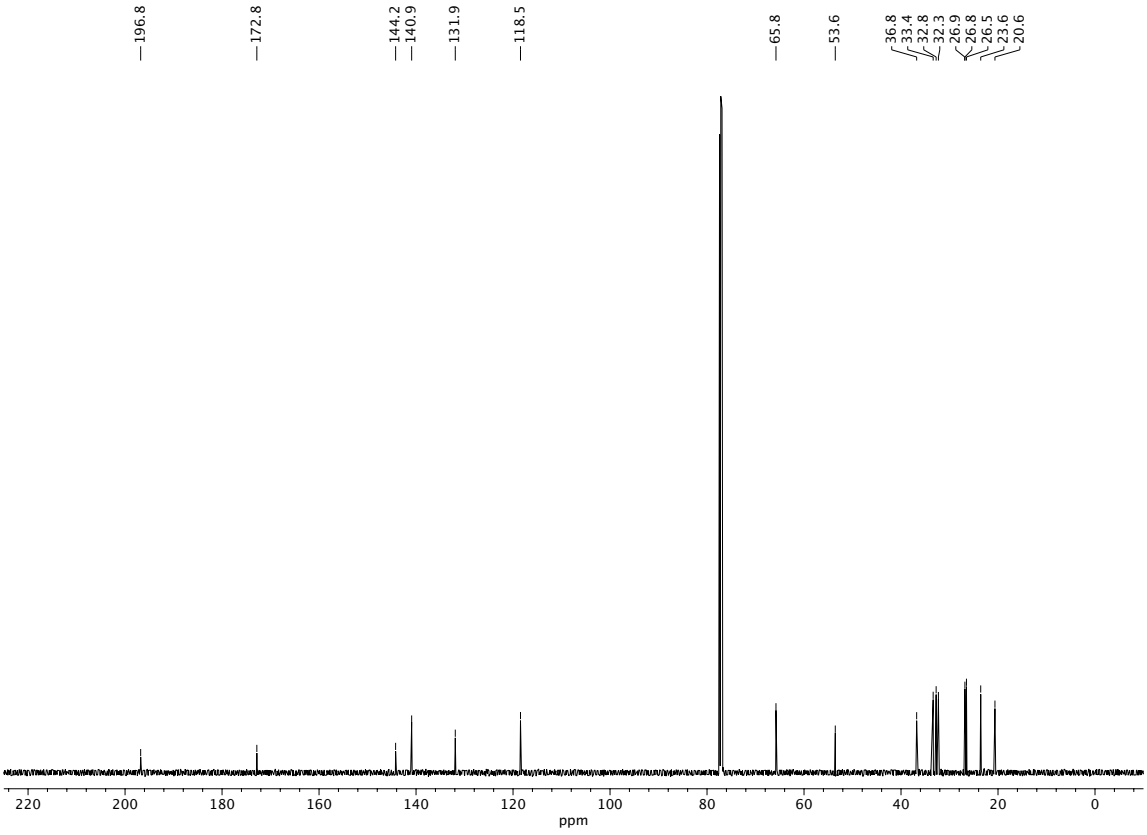
^{13}C NMR (125 MHz, $CDCl_3$) of compound **1n**.



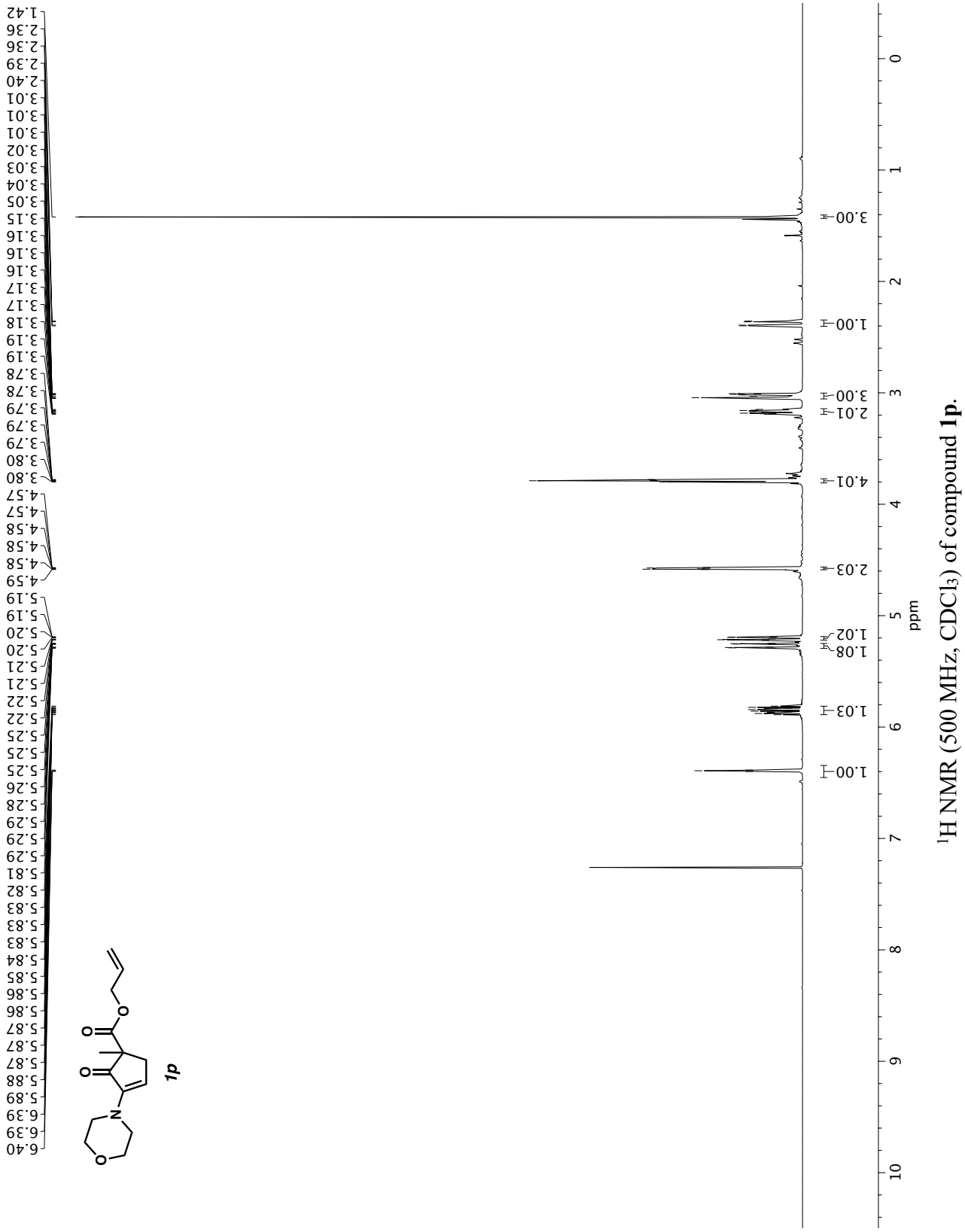
^{1}H NMR (500 MHz, $CDCl_3$) of compound **1o**.



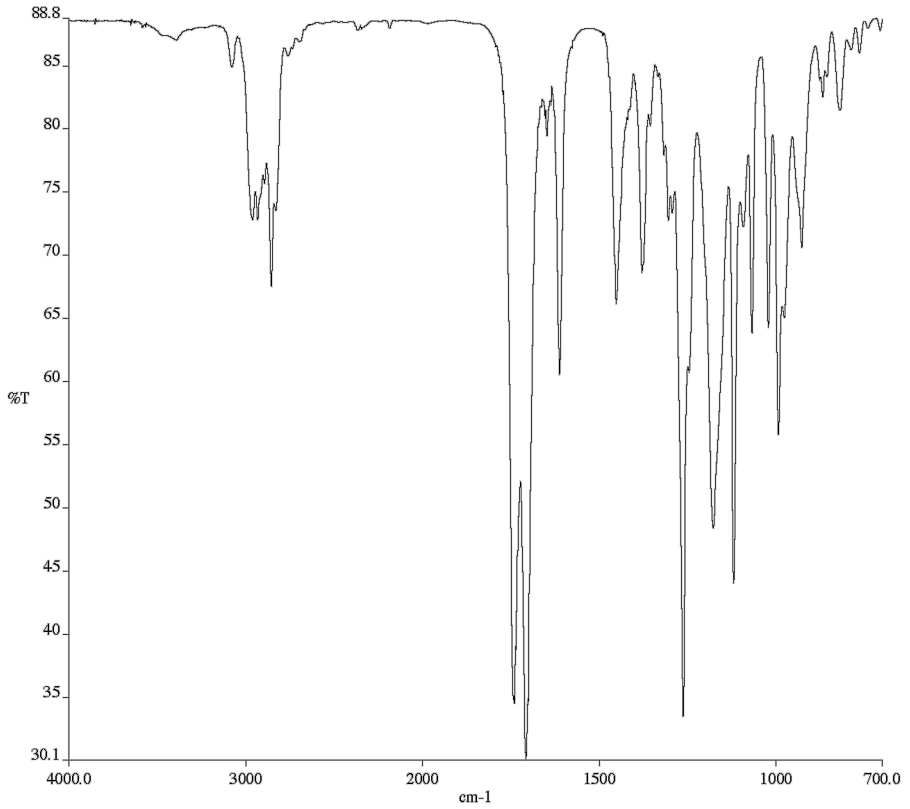
Infrared spectrum (Thin Film, NaCl) of compound **1o**.



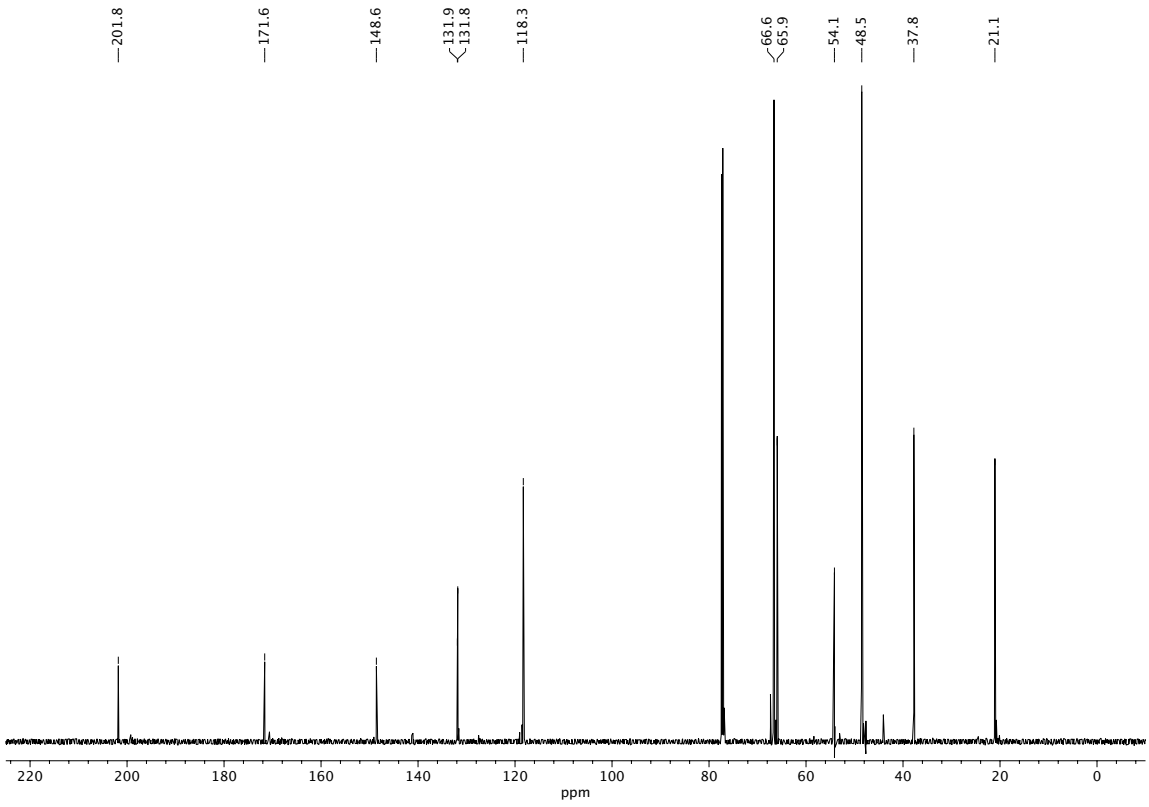
^{13}C NMR (125 MHz, $CDCl_3$) of compound **1o**.



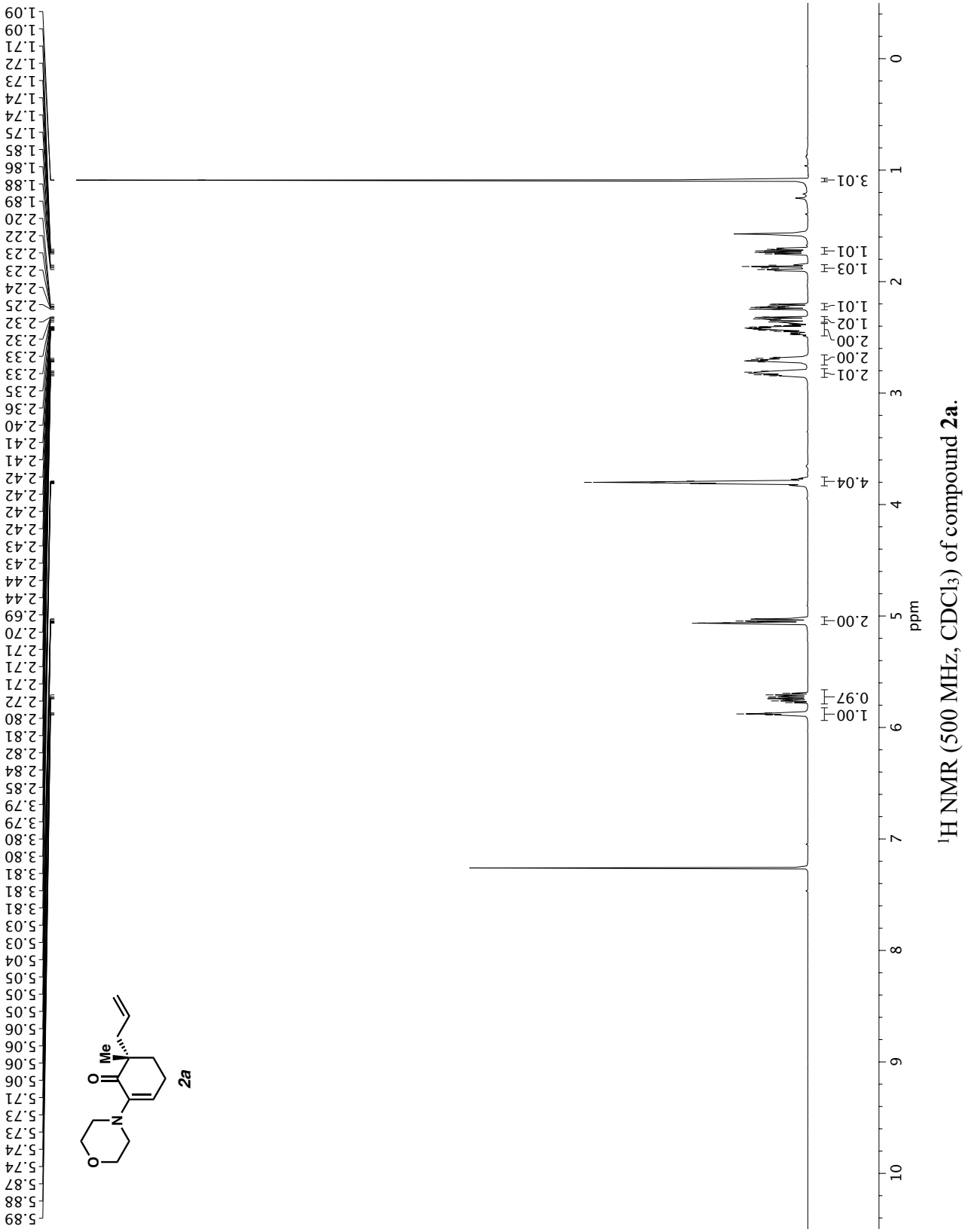
^{1}H NMR (500 MHz, $CDCl_3$) of compound **1p**.



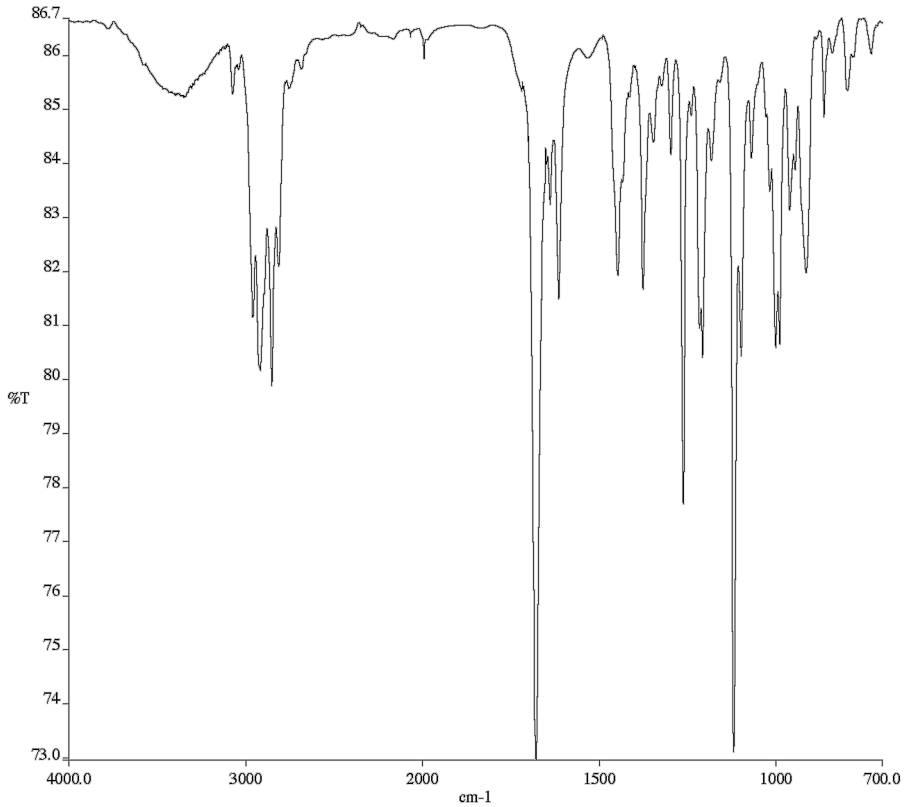
Infrared spectrum (Thin Film, NaCl) of compound **1p**.



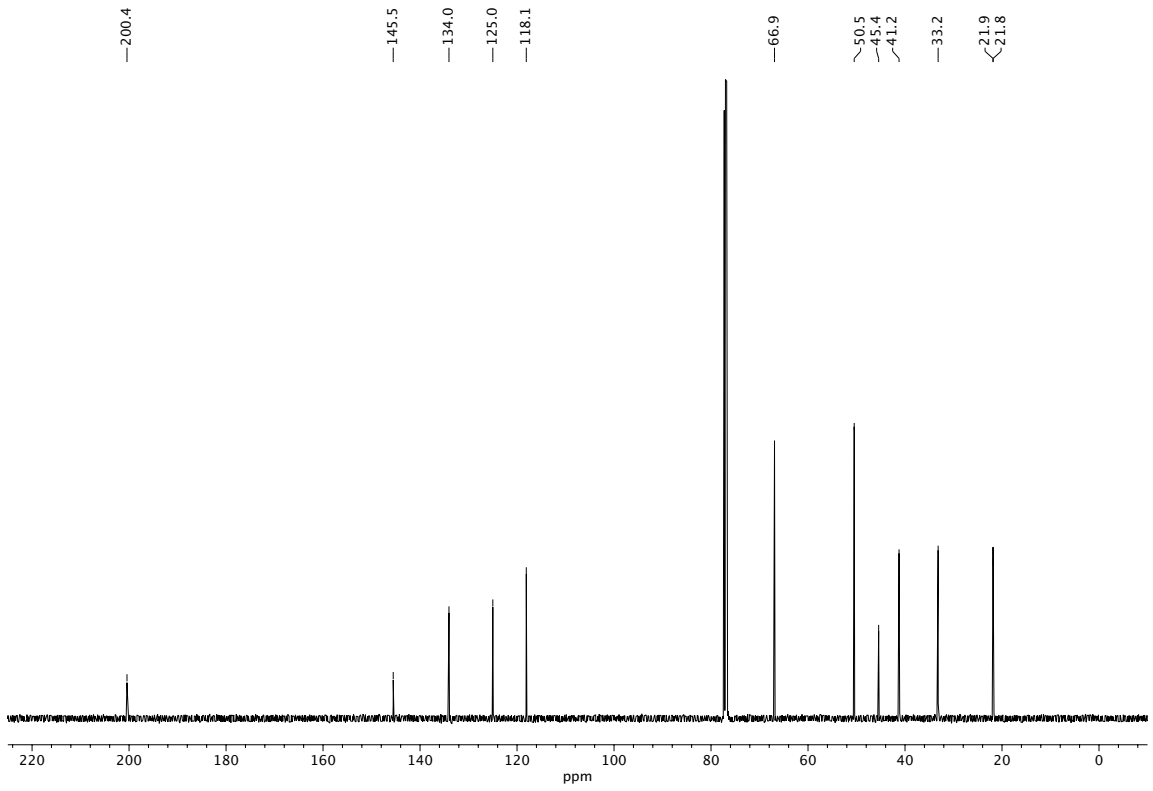
^{13}C NMR (125 MHz, $CDCl_3$) of compound **1p**.



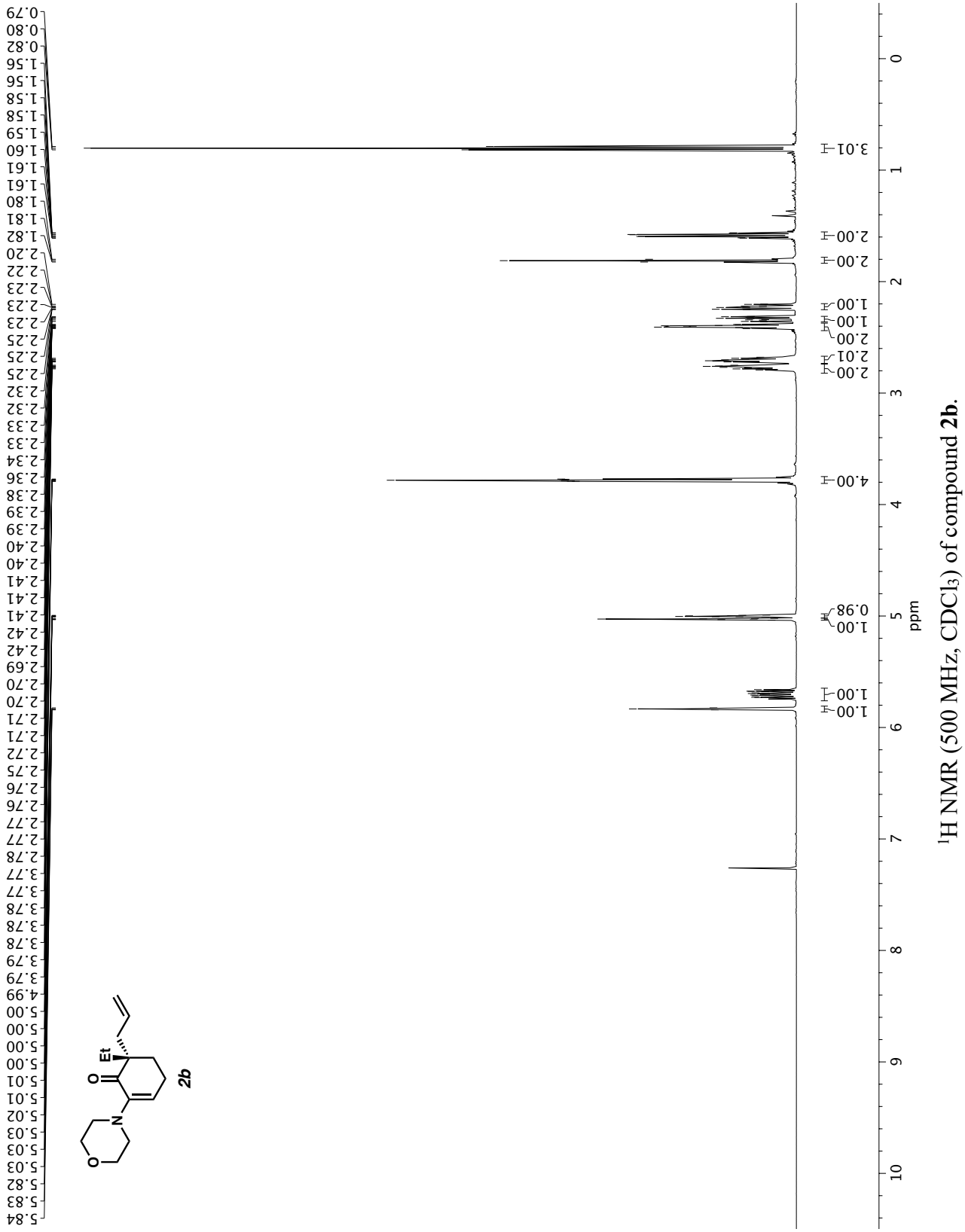
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2a**.



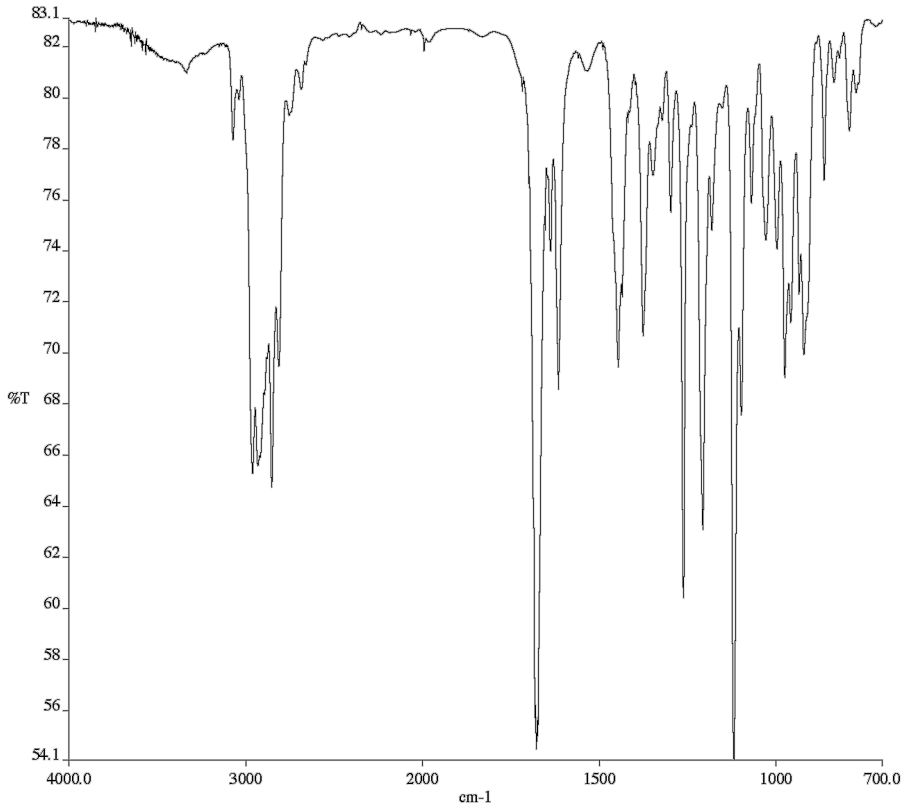
Infrared spectrum (Thin Film, NaCl) of compound **2a**.



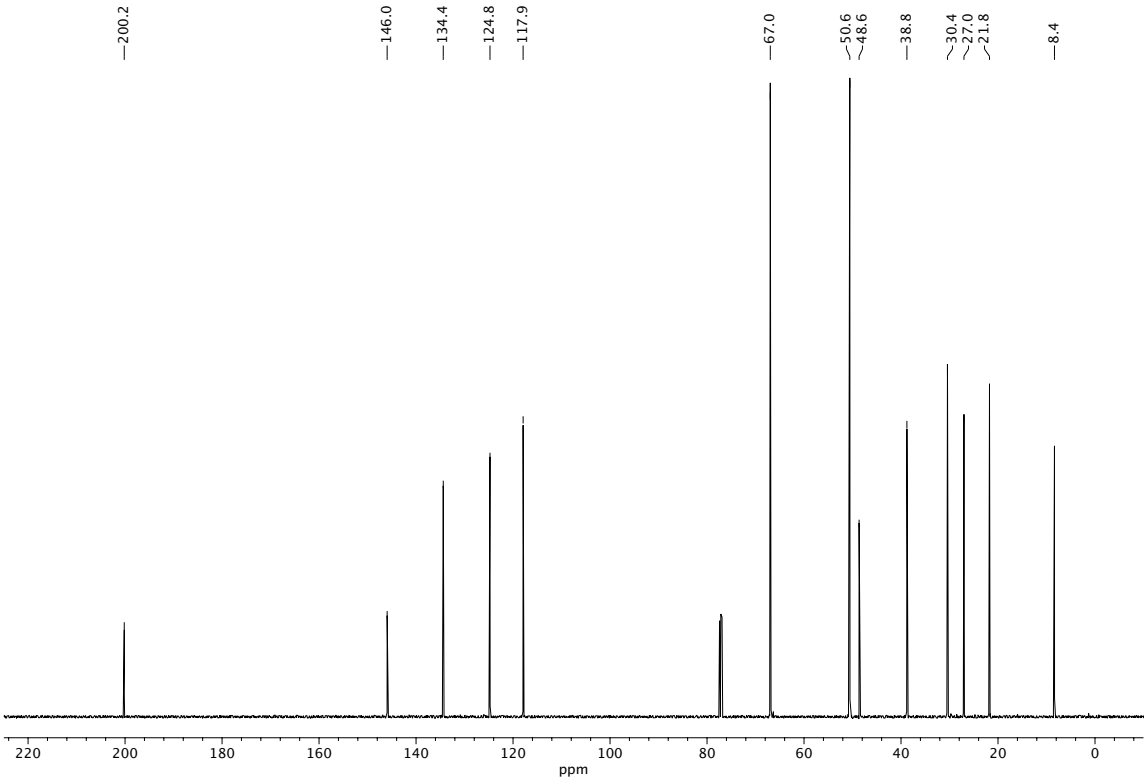
^{13}C NMR (125 MHz, $CDCl_3$) of compound **2a**.



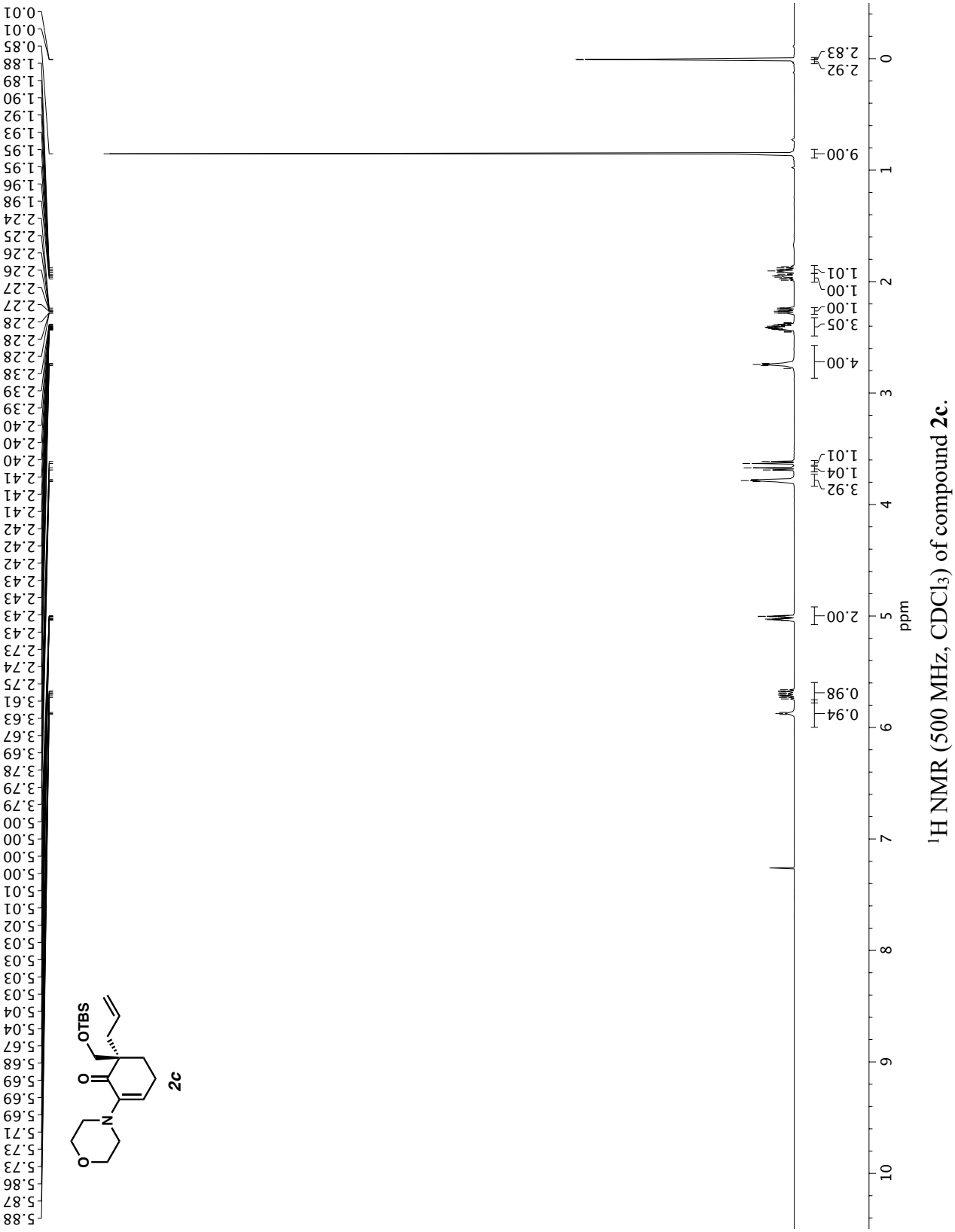
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2b**.



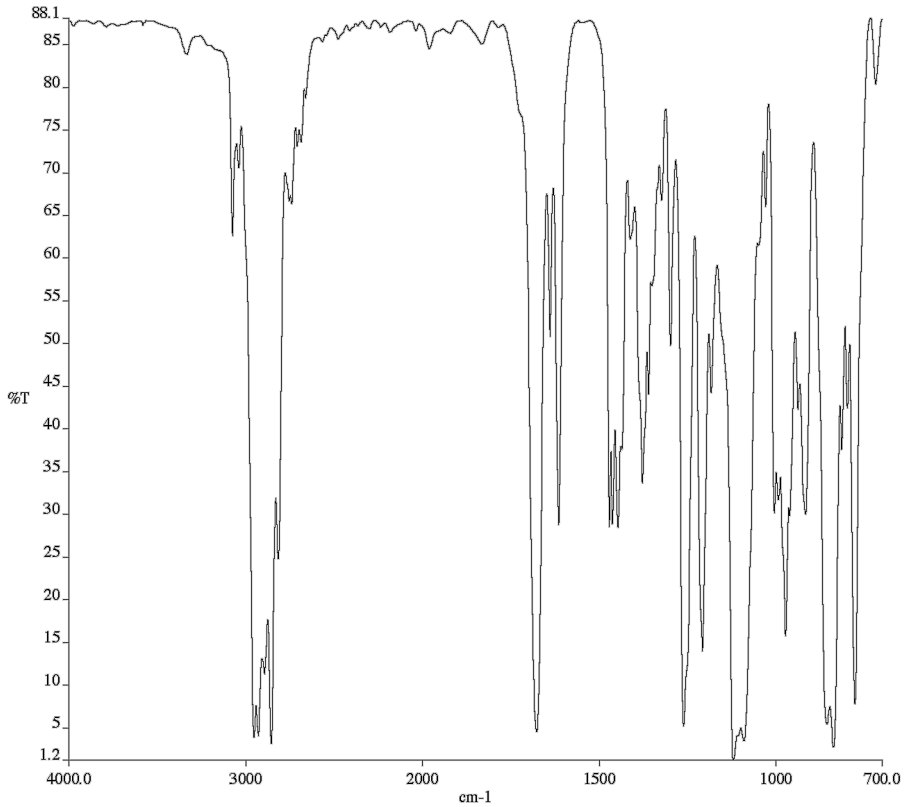
Infrared spectrum (Thin Film, NaCl) of compound **2b**.



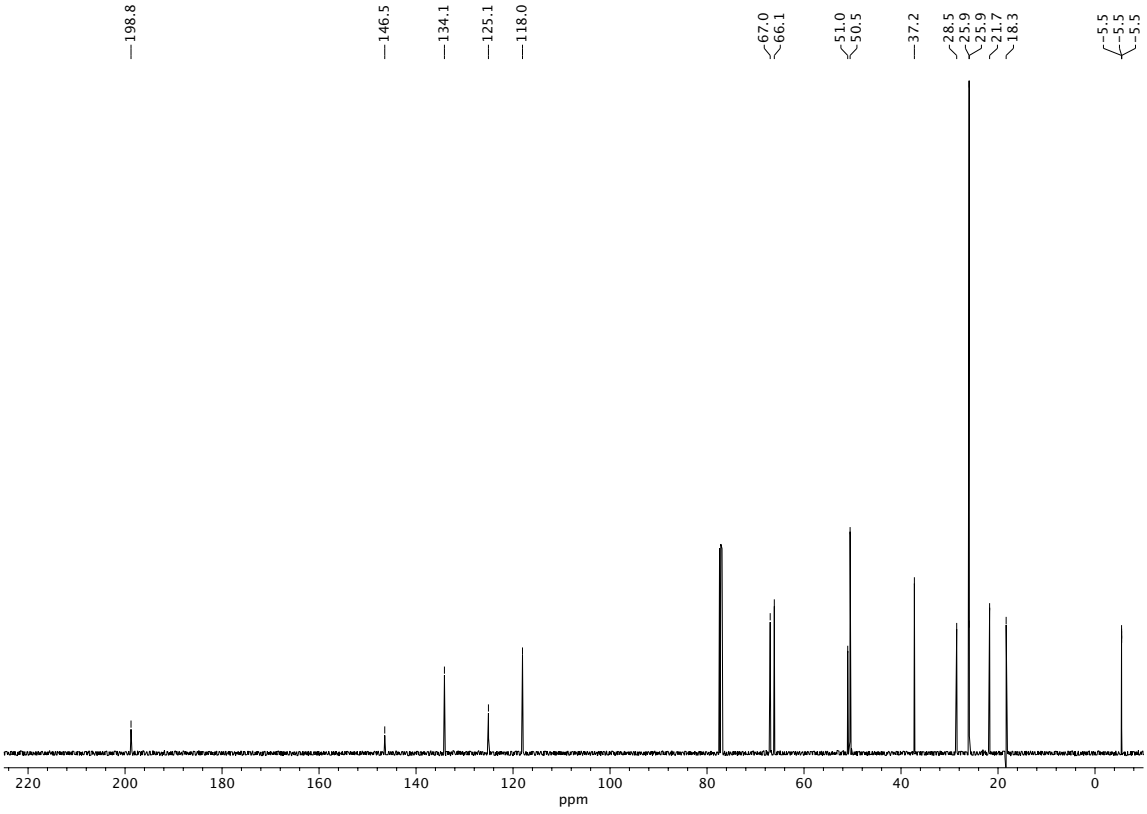
^{13}C NMR (125 MHz, $CDCl_3$) of compound **2b**.



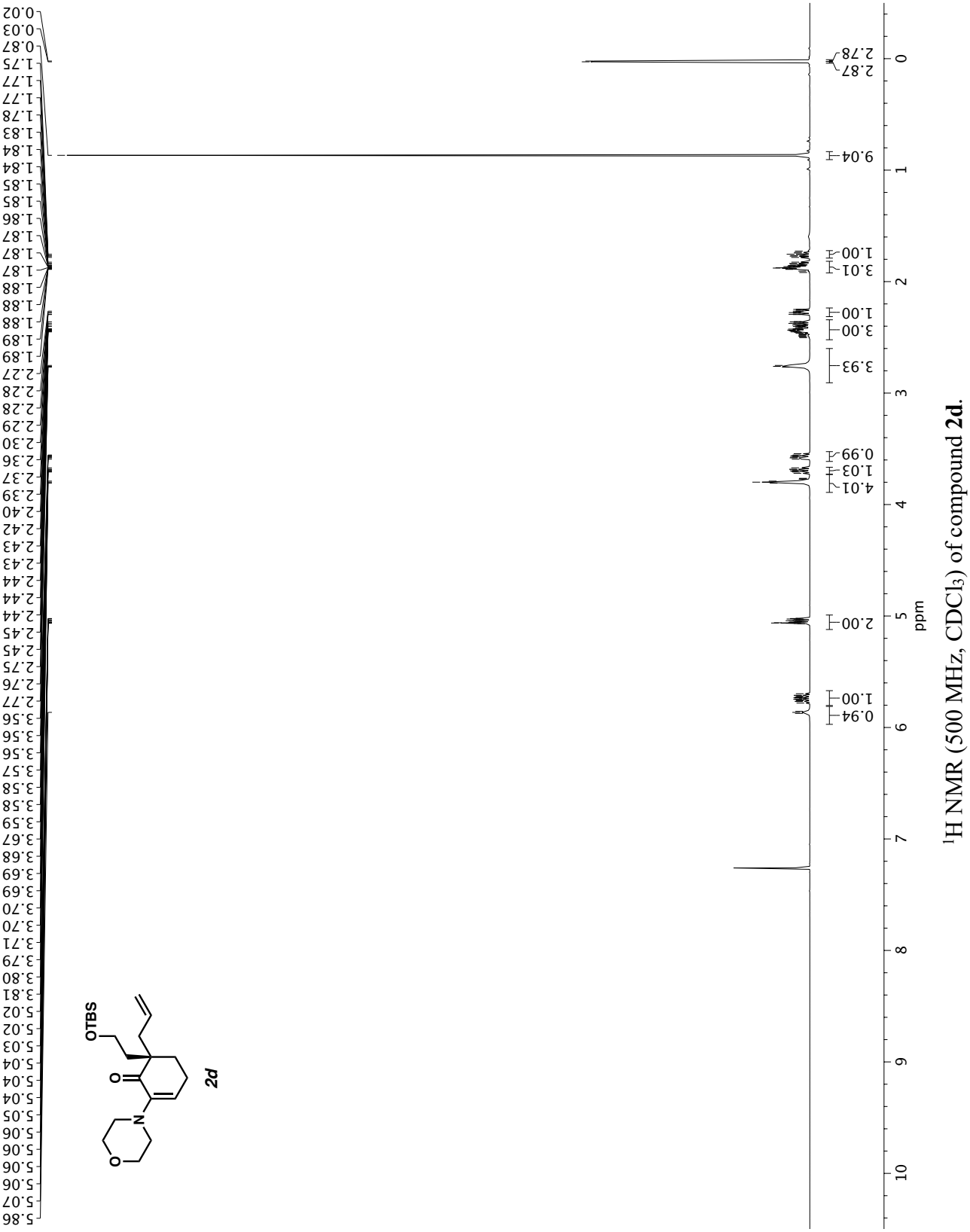
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2c**.



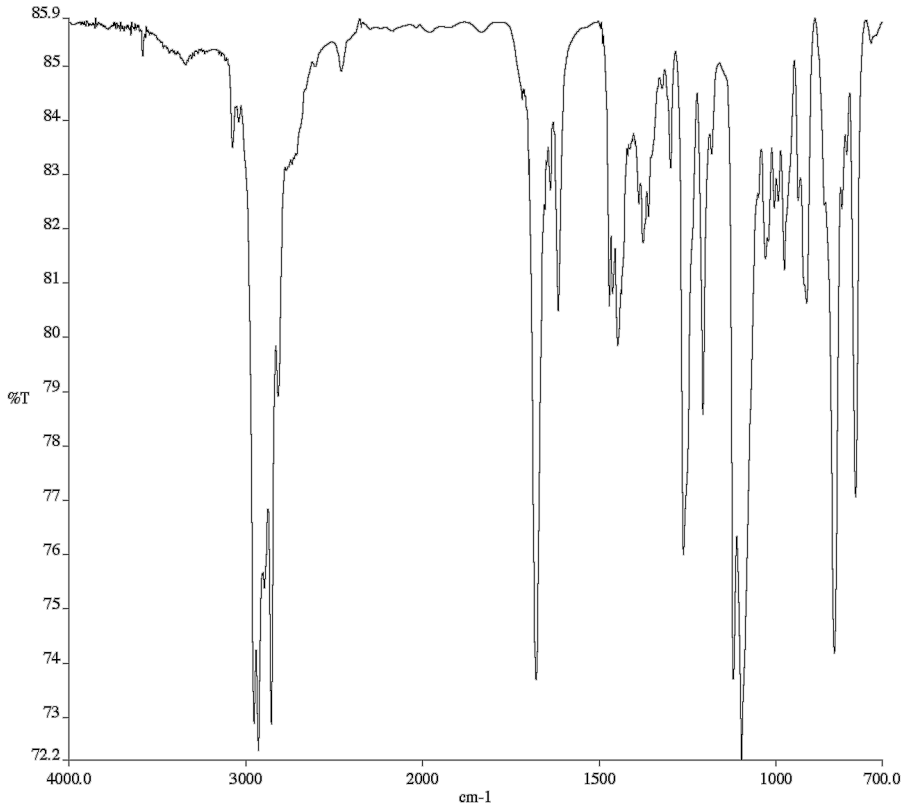
Infrared spectrum (Thin Film, NaCl) of compound **2c**.



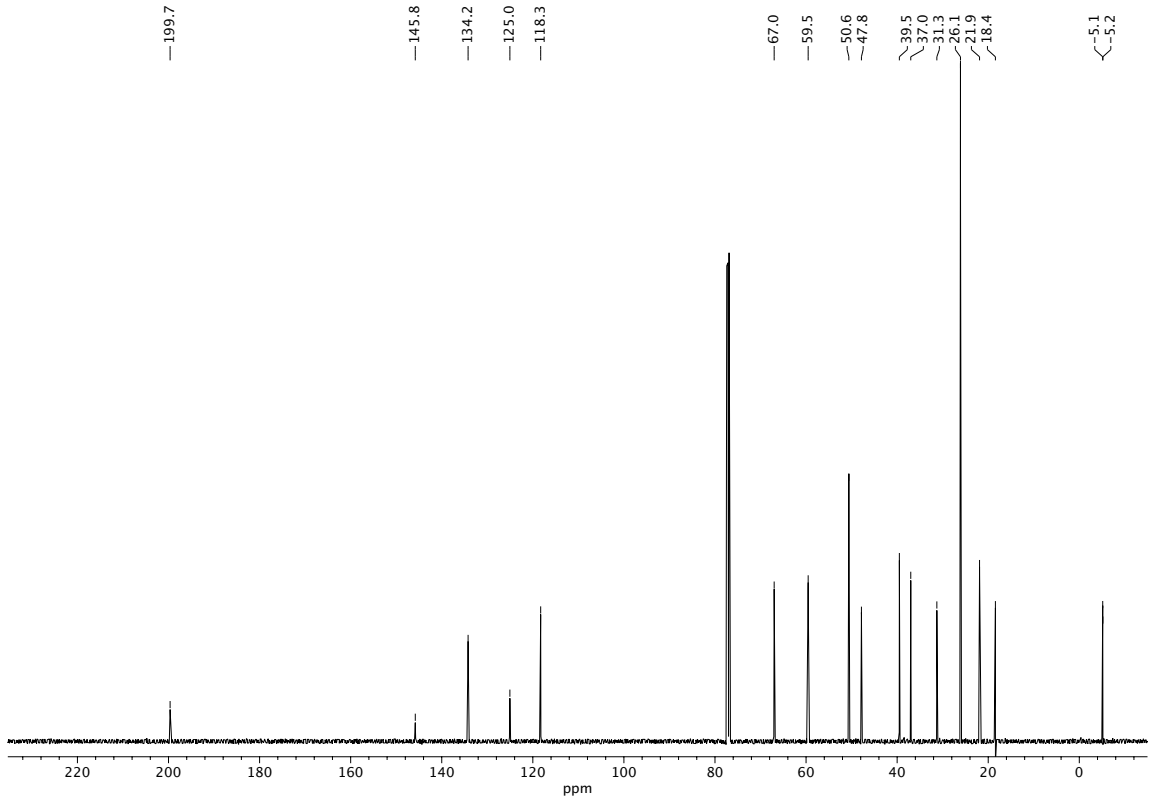
^{13}C NMR (125 MHz, $CDCl_3$) of compound **2c**.



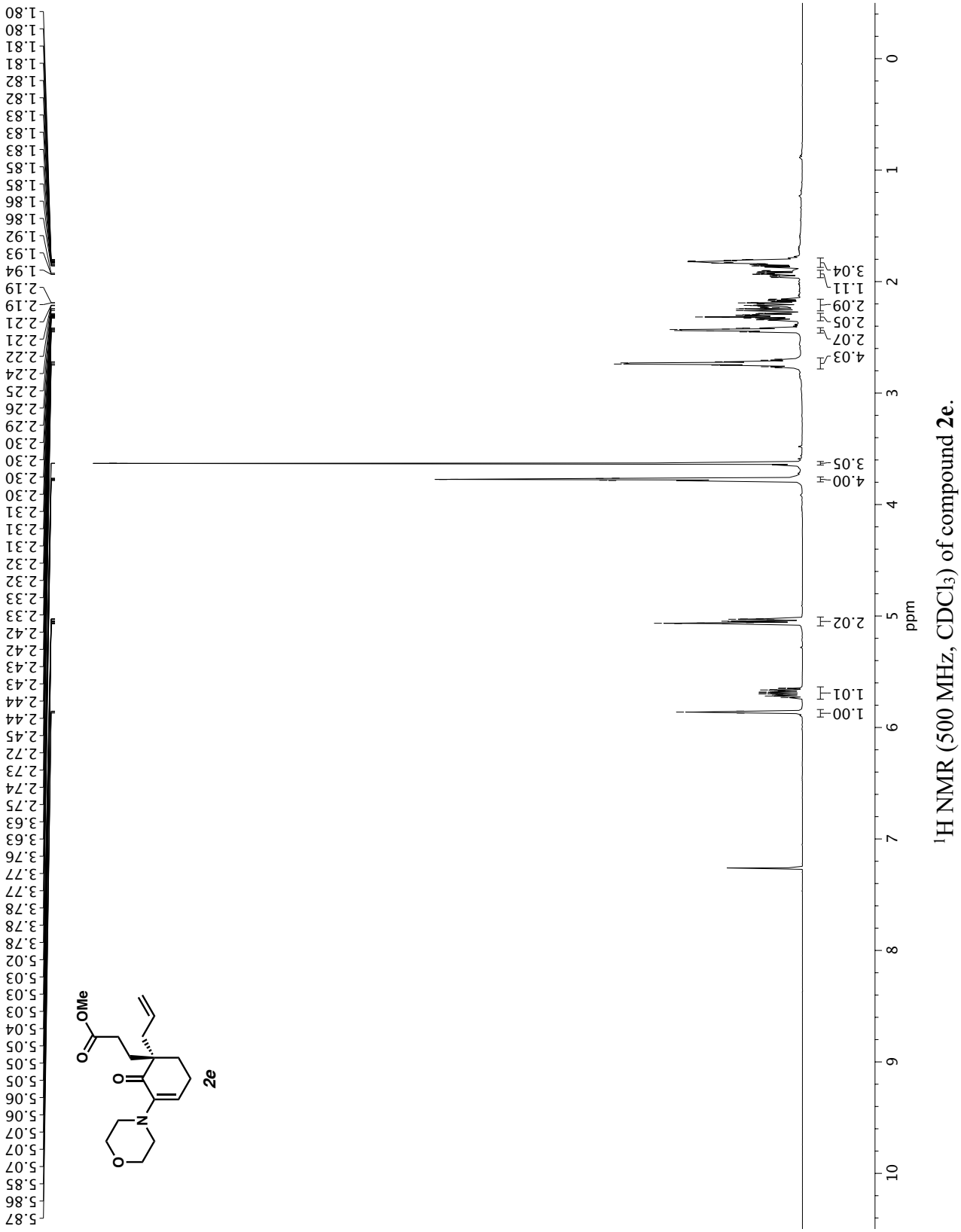
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2d**.



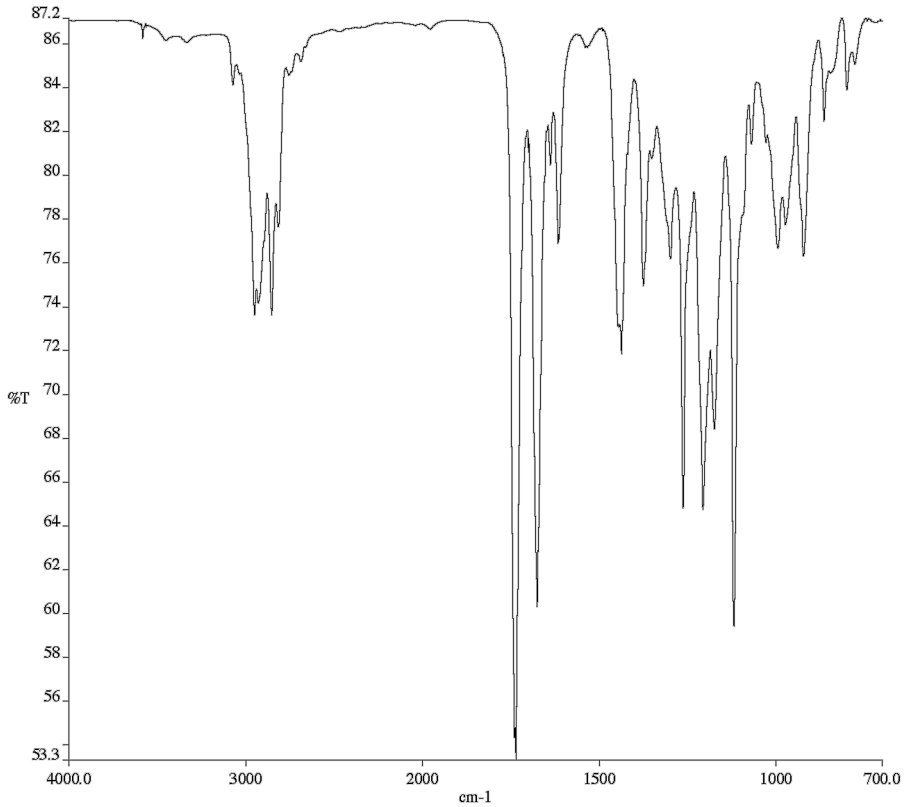
Infrared spectrum (Thin Film, NaCl) of compound **2d**.



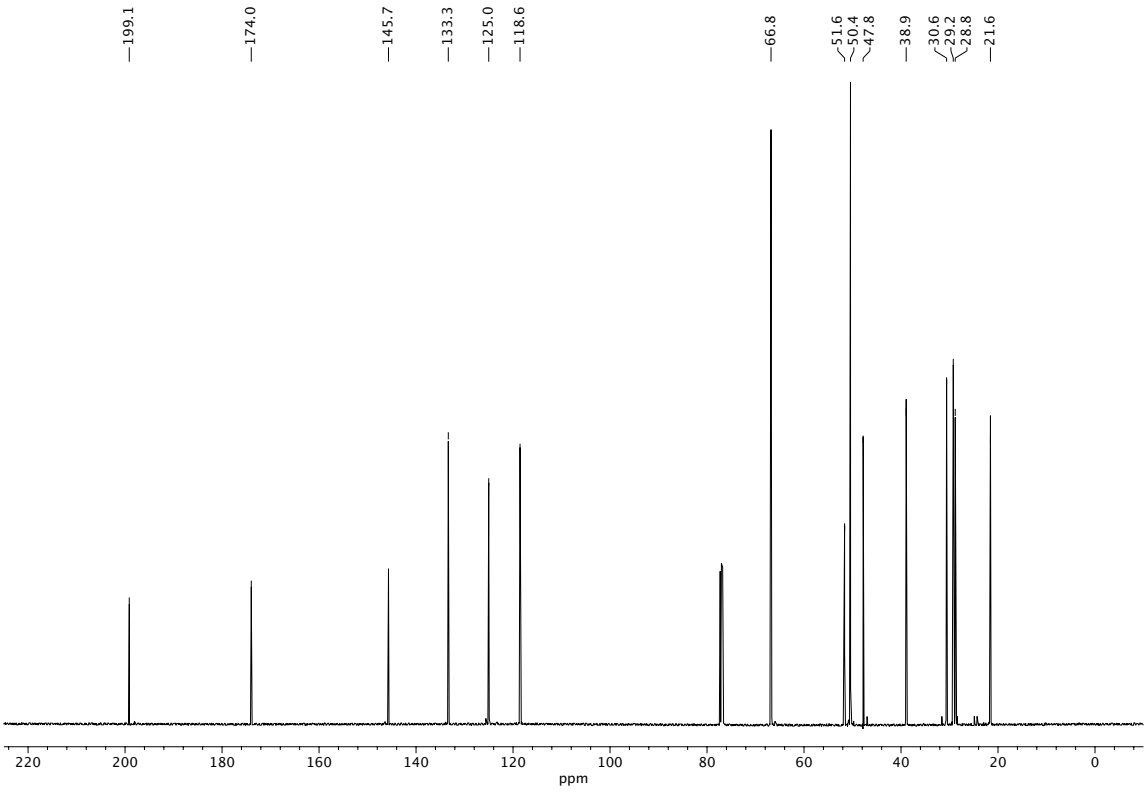
^{13}C NMR (125 MHz, $CDCl_3$) of compound **2d**.



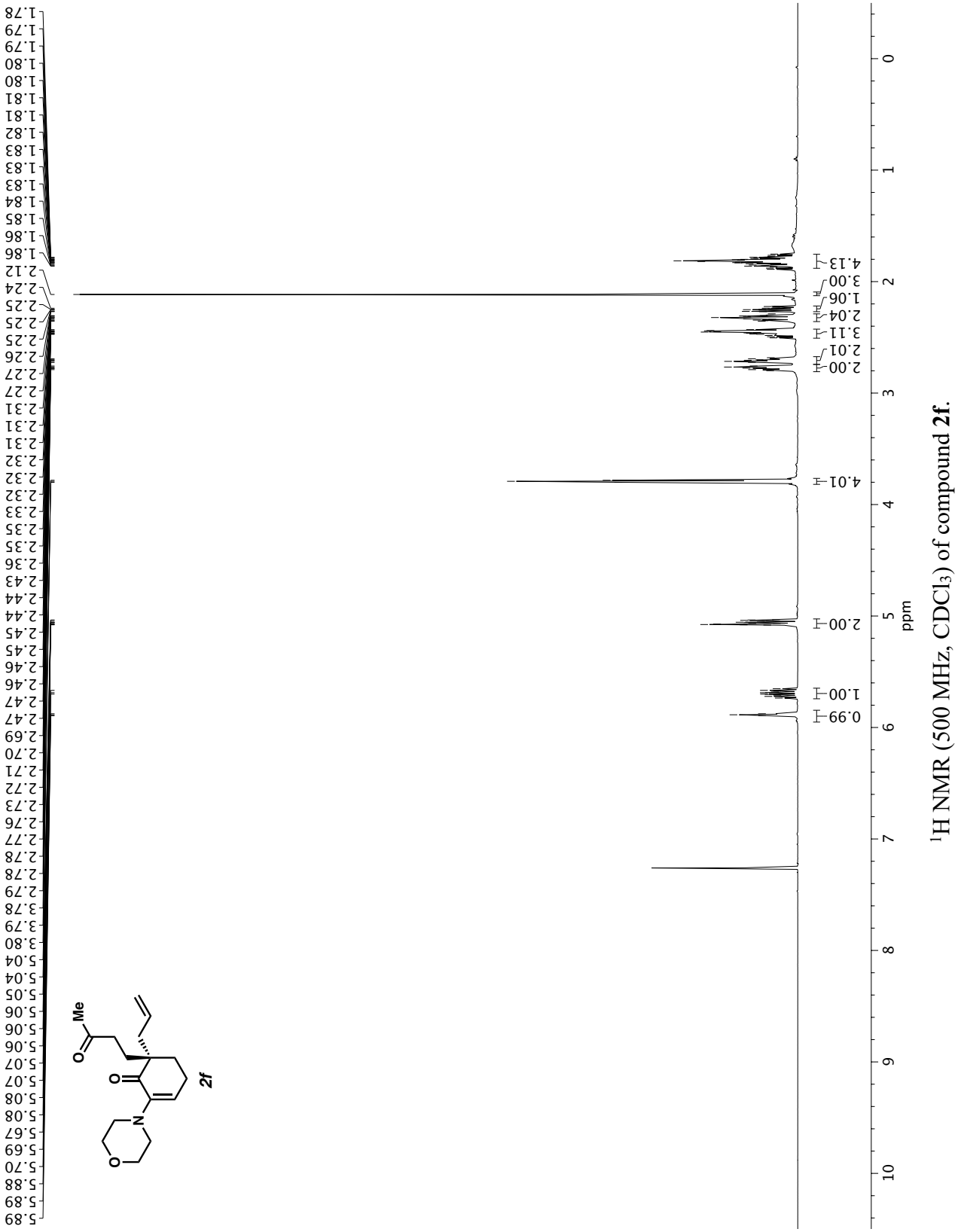
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2e**.



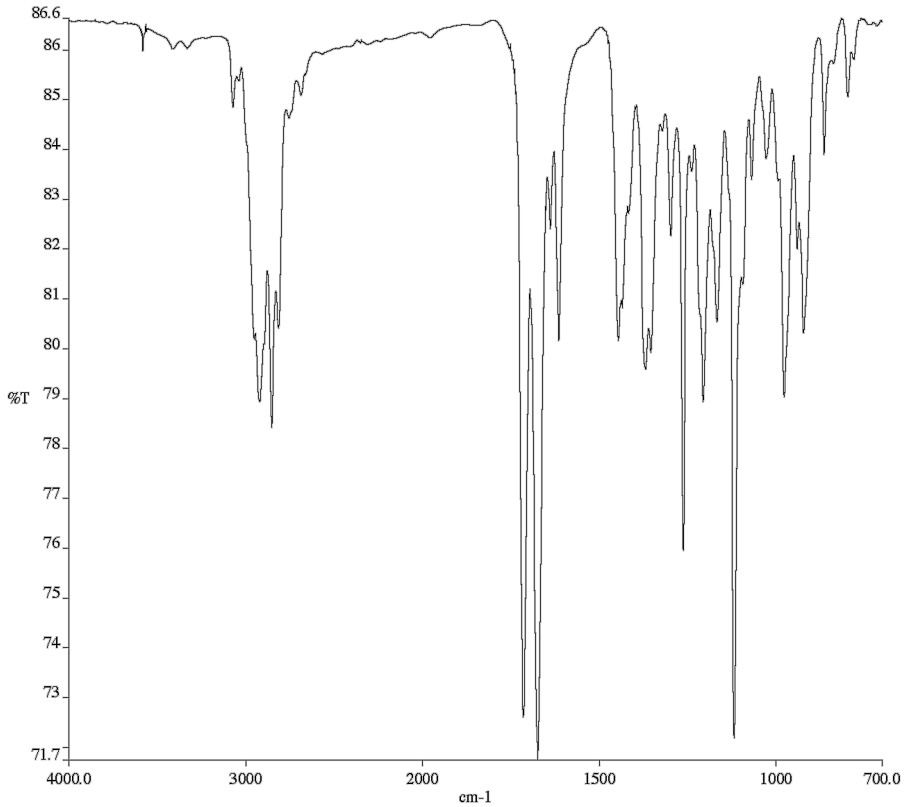
Infrared spectrum (Thin Film, NaCl) of compound **2e**.



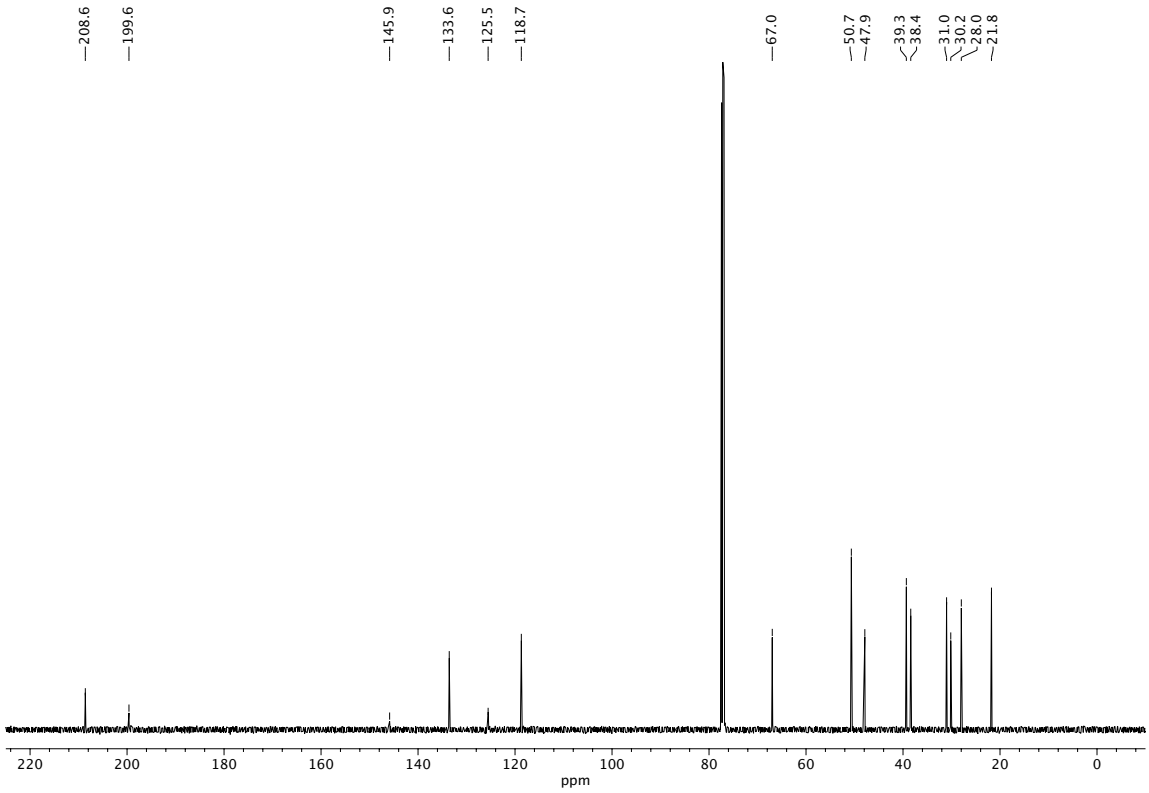
^{13}C NMR (125 MHz, $CDCl_3$) of compound **2e**.



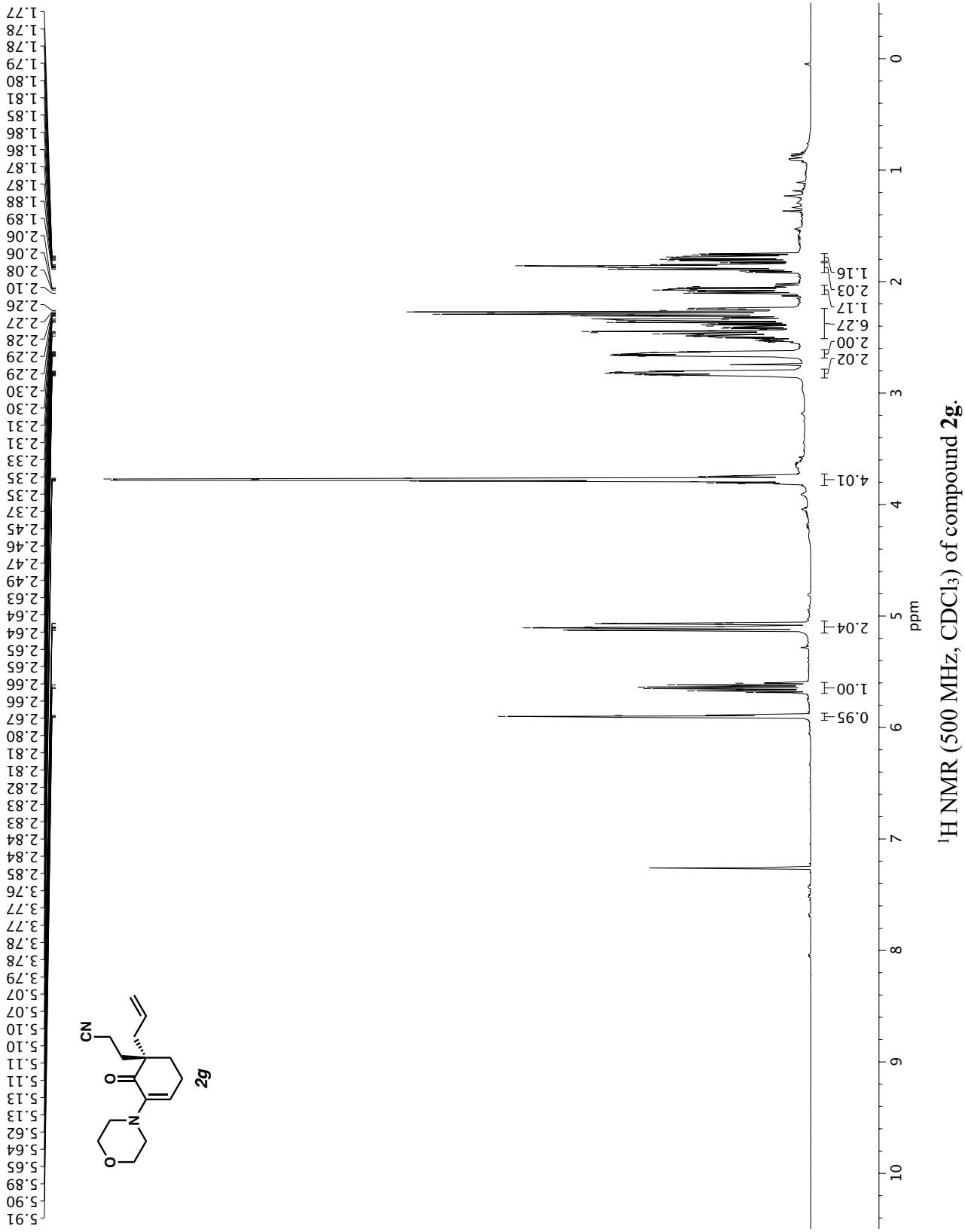
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2f**.



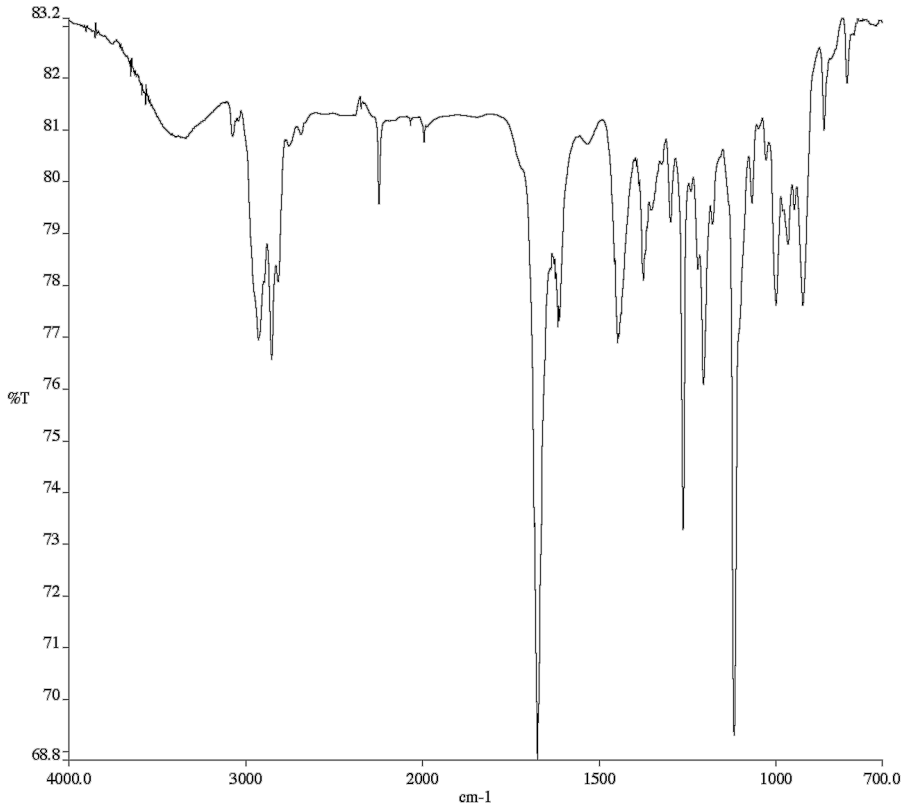
Infrared spectrum (Thin Film, NaCl) of compound **2f**.



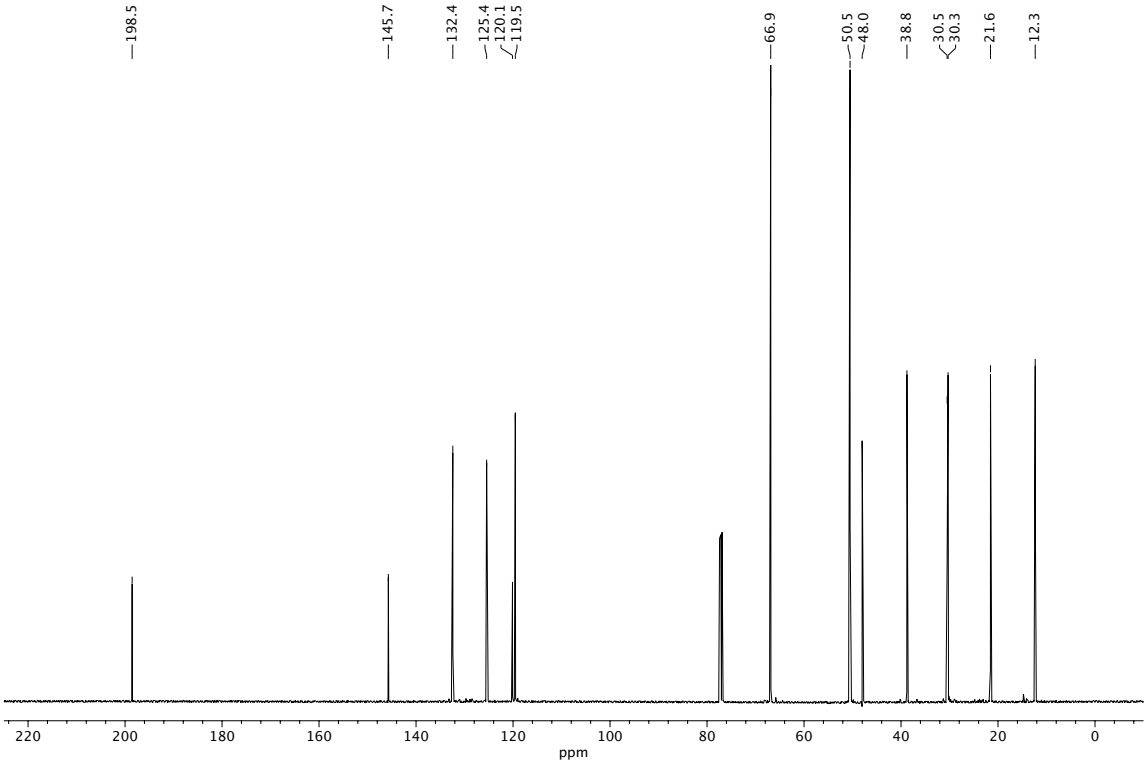
^{13}C NMR (125 MHz, $CDCl_3$) of compound **2f**.



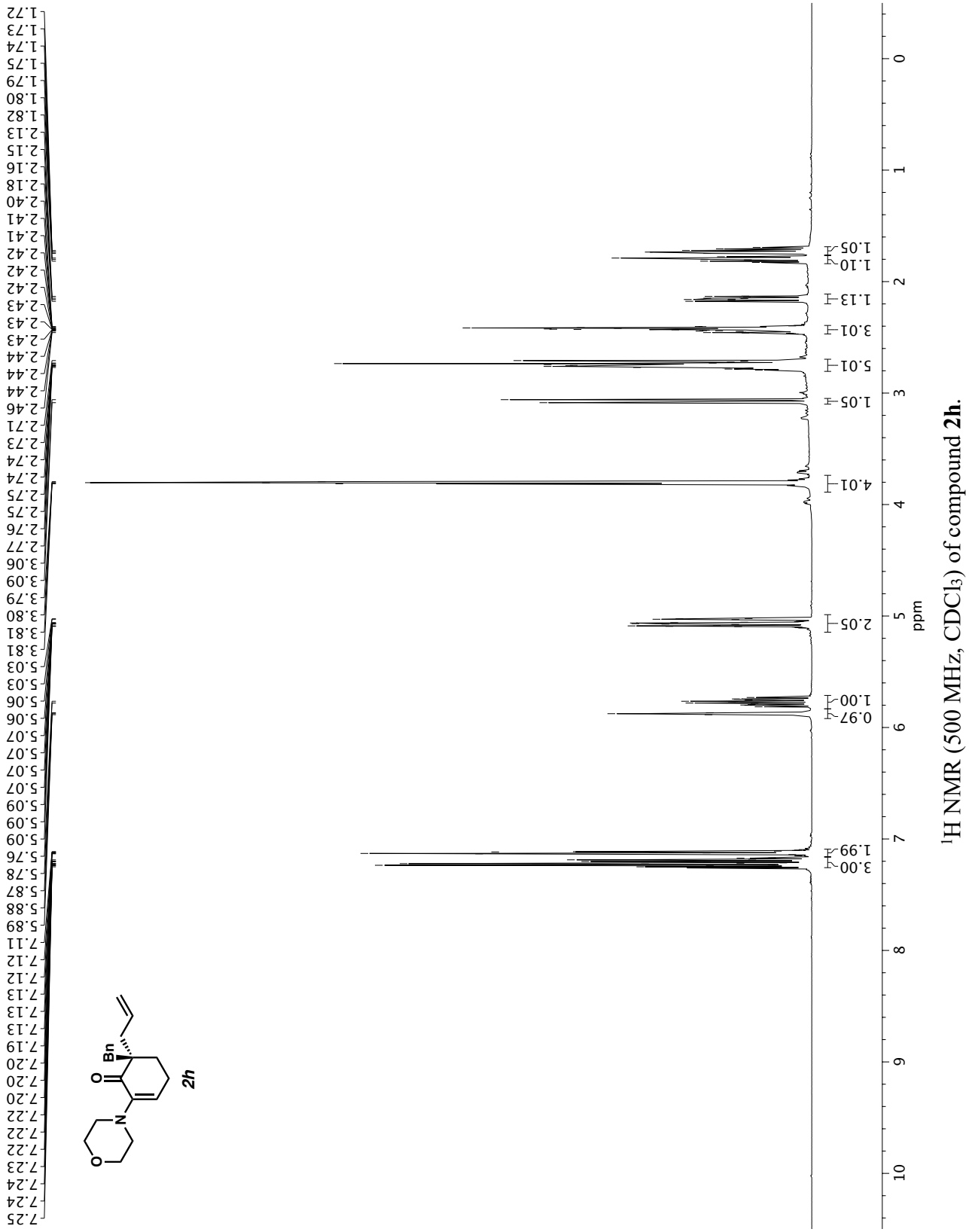
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2g**.



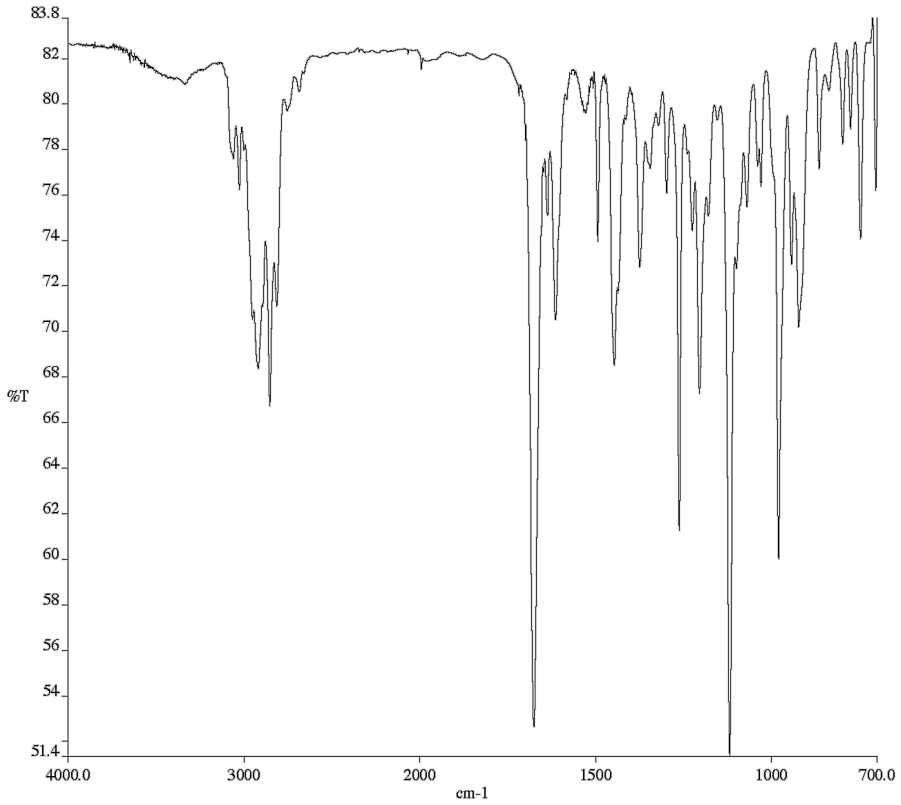
Infrared spectrum (Thin Film, NaCl) of compound **2g**.



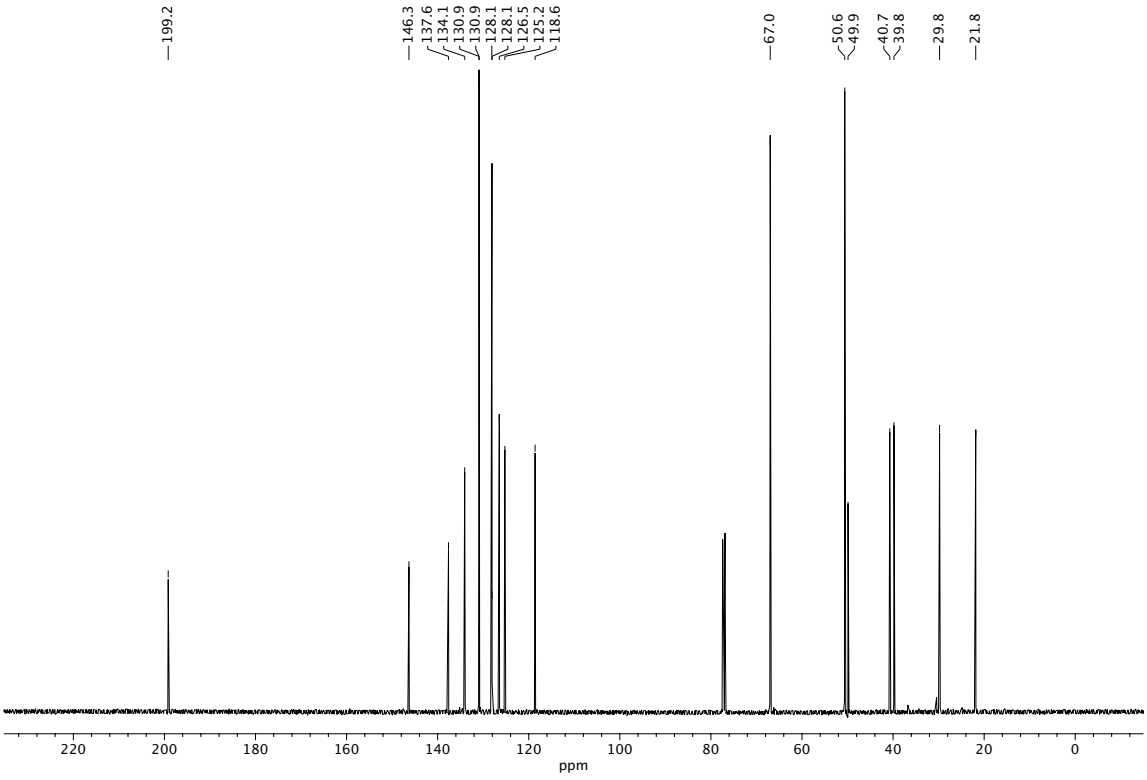
^{13}C NMR (125 MHz, $CDCl_3$) of compound **2g**.



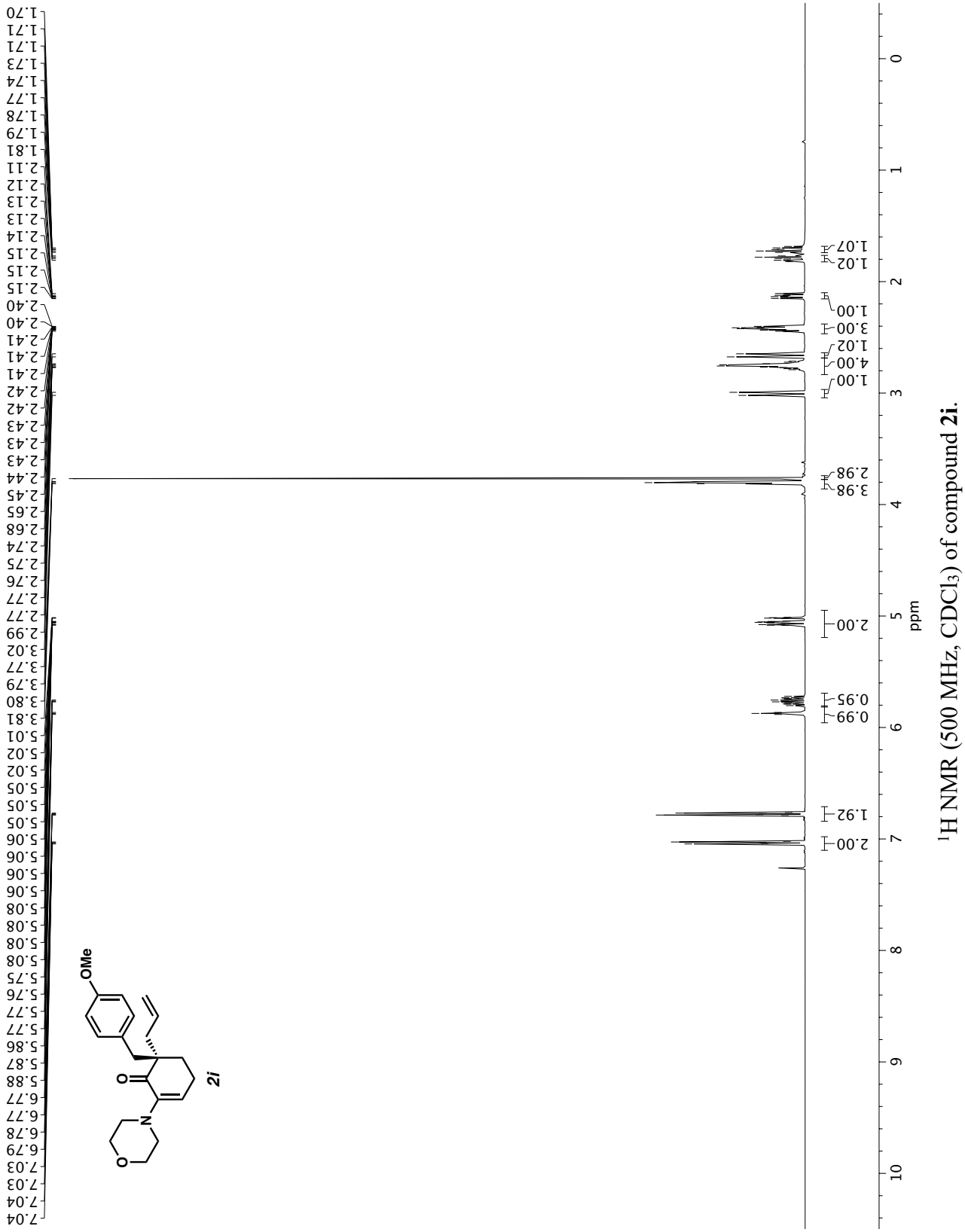
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2h**.



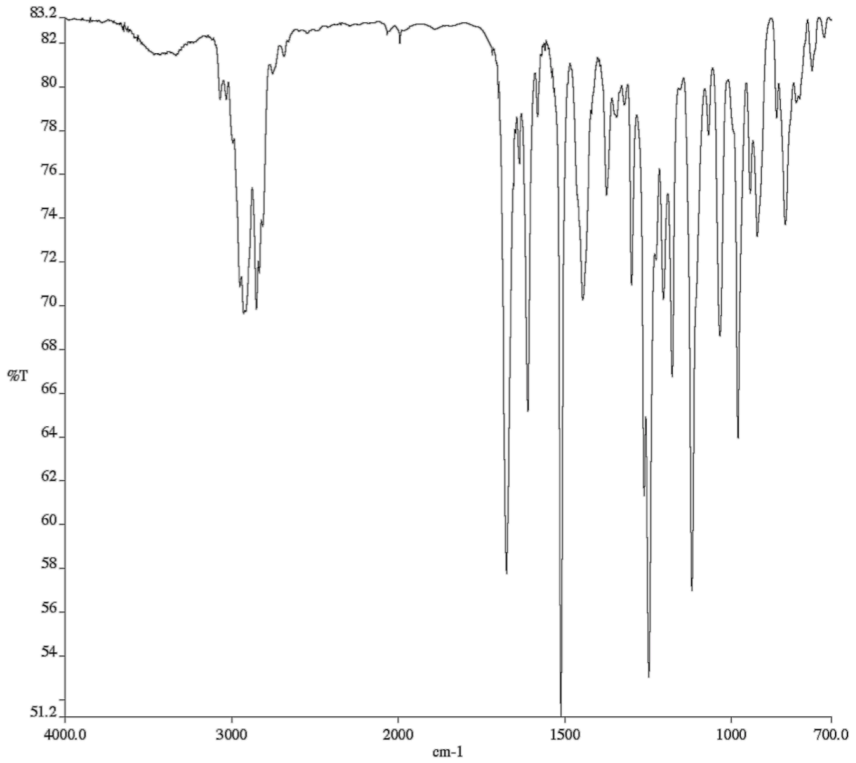
Infrared spectrum (Thin Film, NaCl) of compound **2h**.



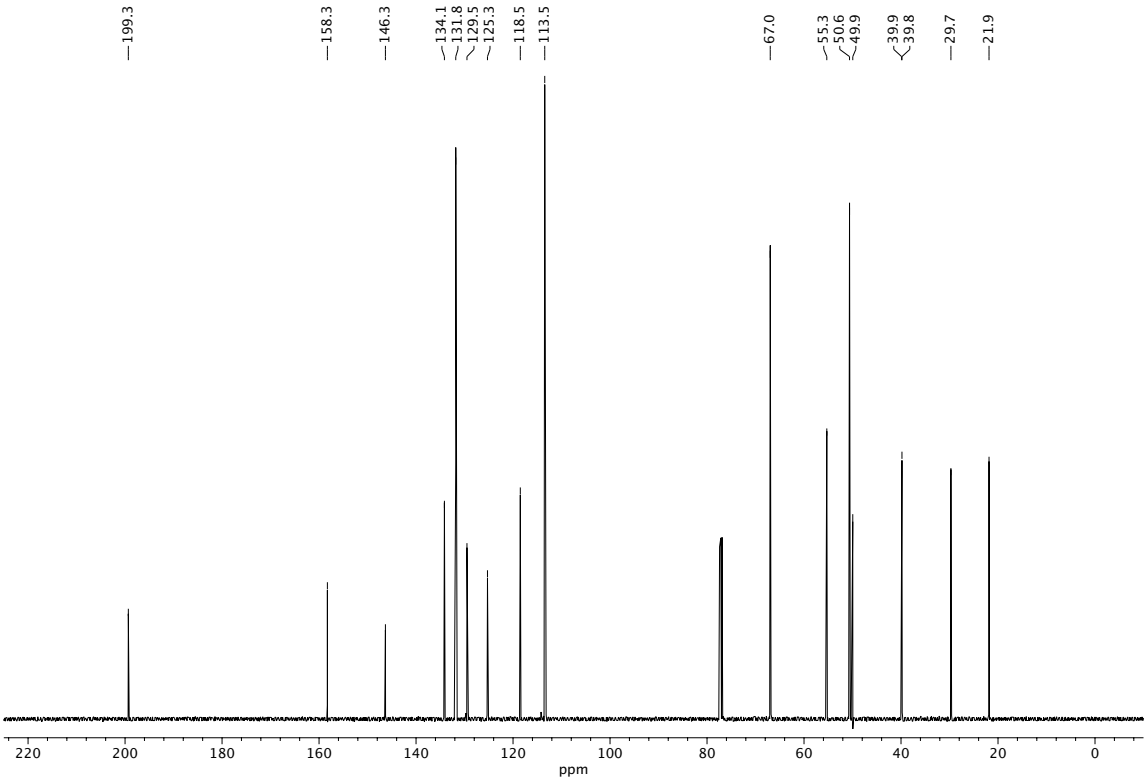
^{13}C NMR (125 MHz, $CDCl_3$) of compound **2h**.



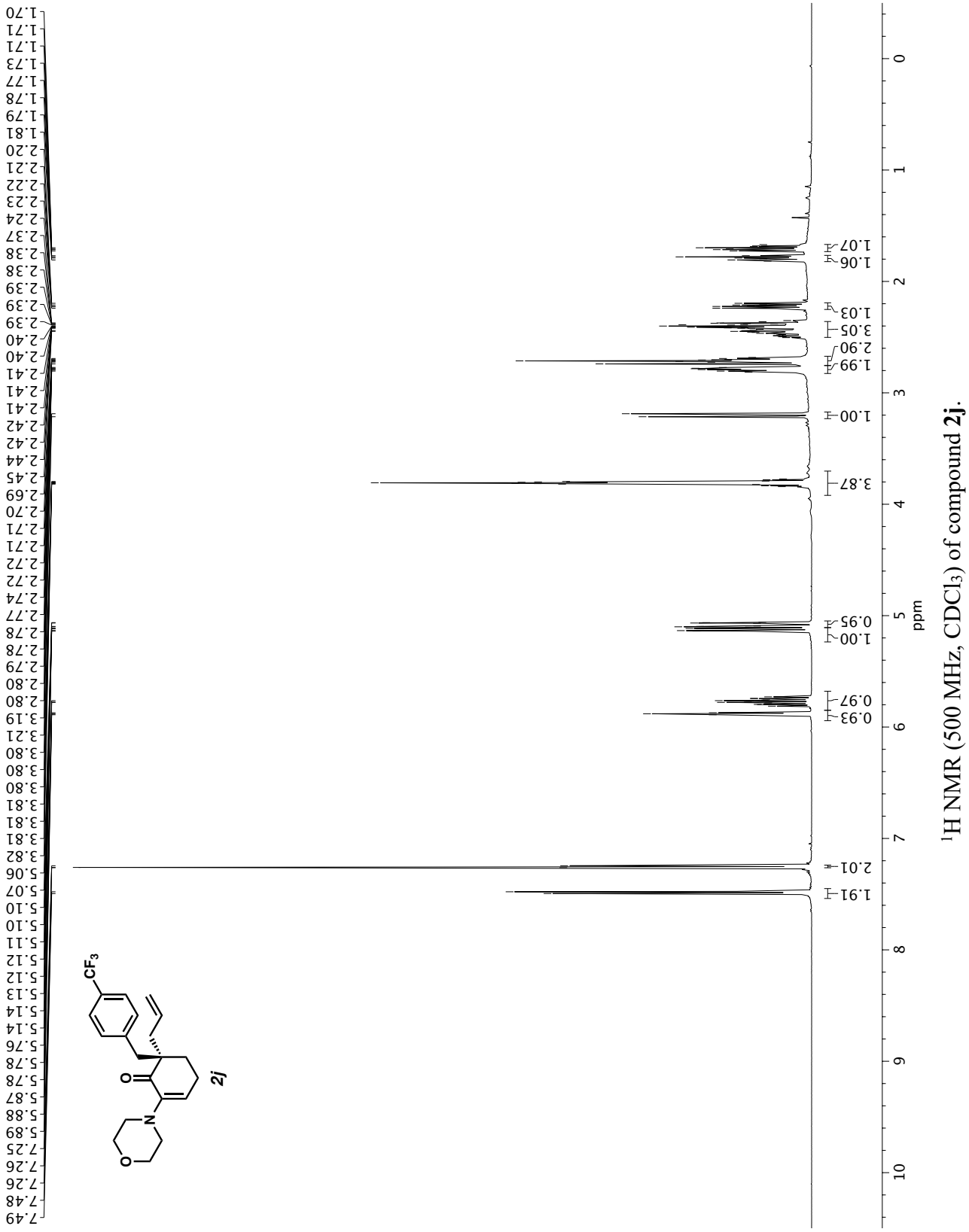
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2i**.



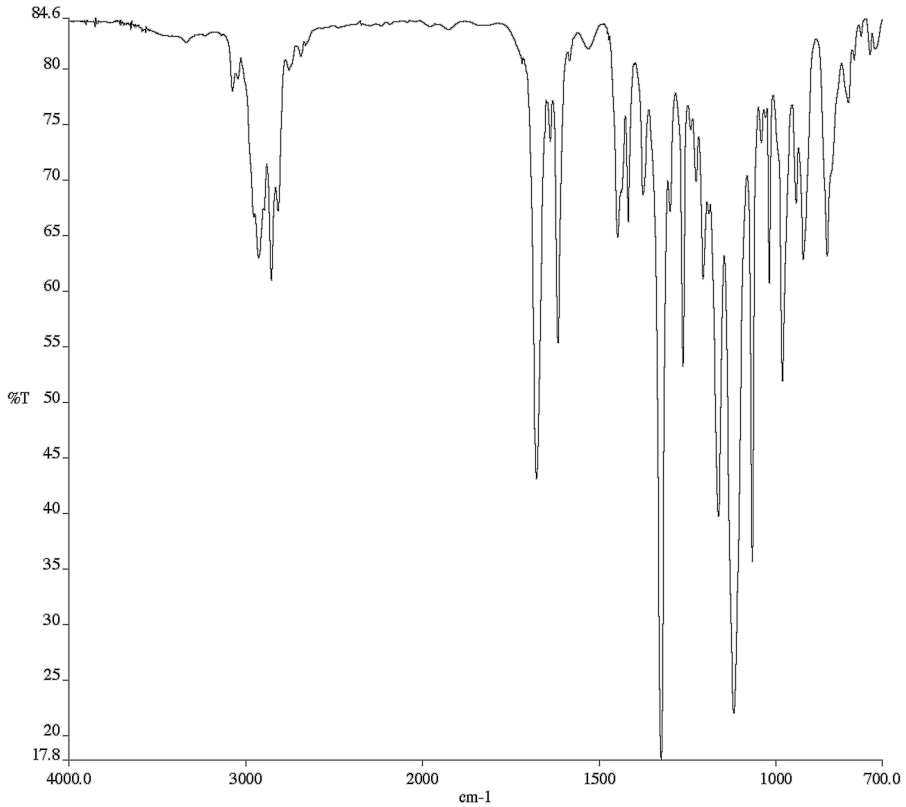
Infrared spectrum (Thin Film, NaCl) of compound **2i**.



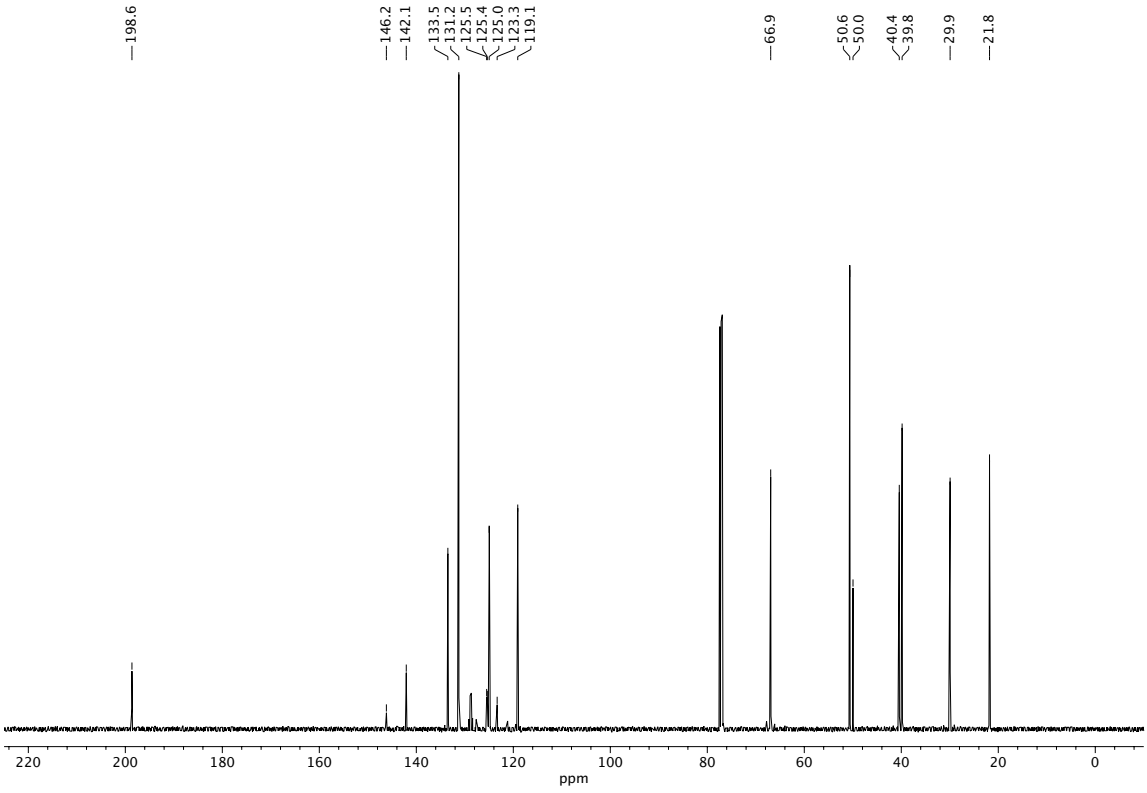
^{13}C NMR (125 MHz, $CDCl_3$) of compound **2i**.



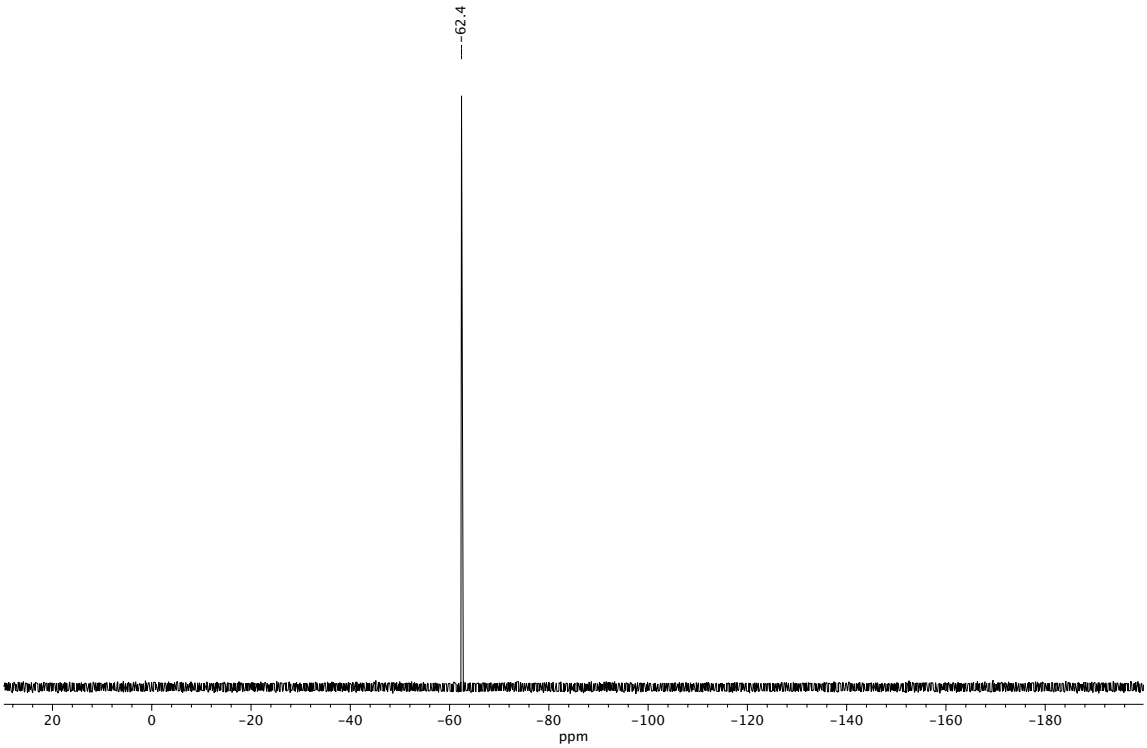
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2j**.



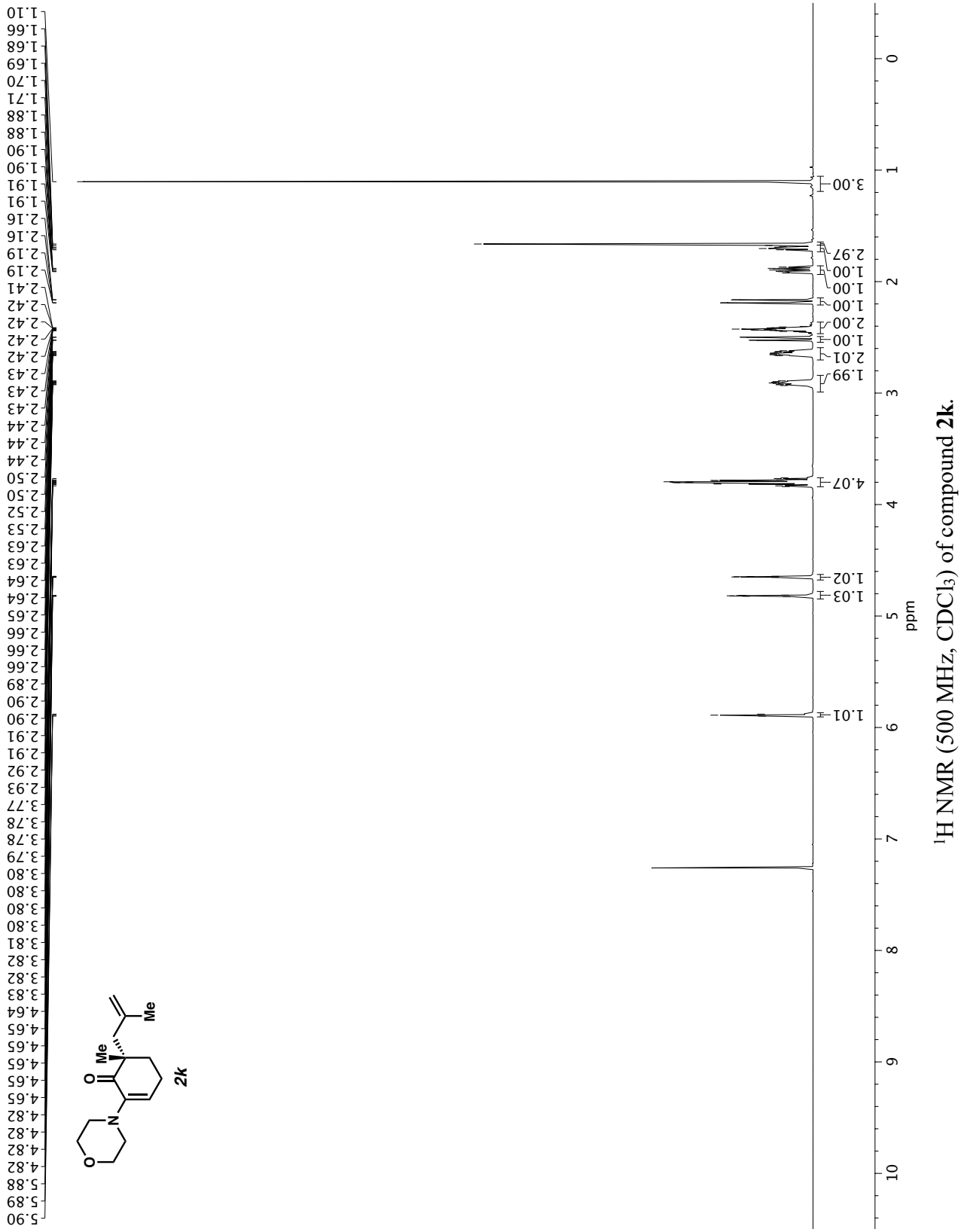
Infrared spectrum (Thin Film, NaCl) of compound **2j**.



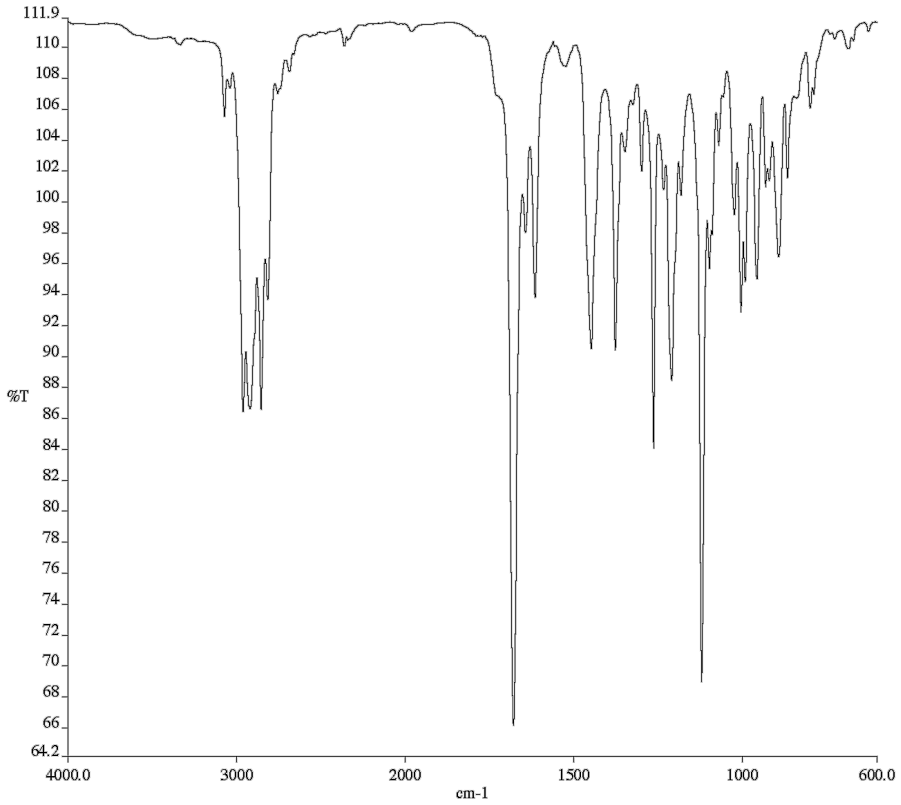
^{13}C NMR (125 MHz, $CDCl_3$) of compound **2j**.



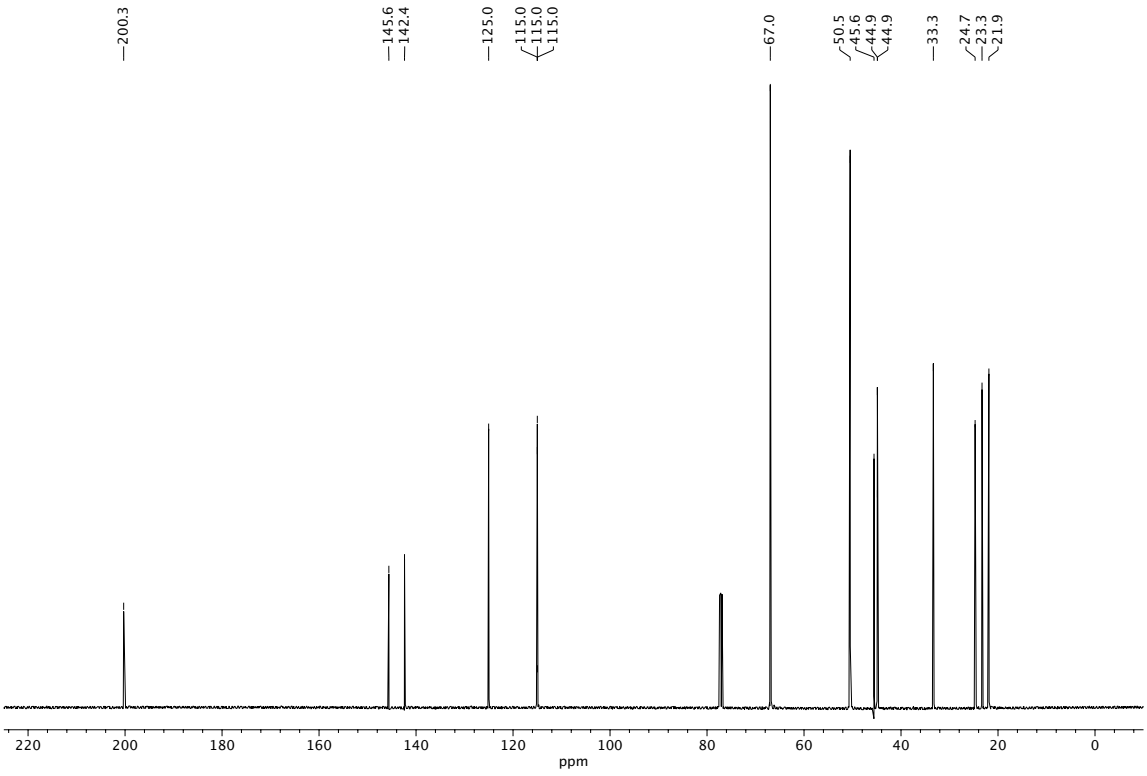
^{19}F NMR (470 MHz, $CDCl_3$) of compound **2j**.



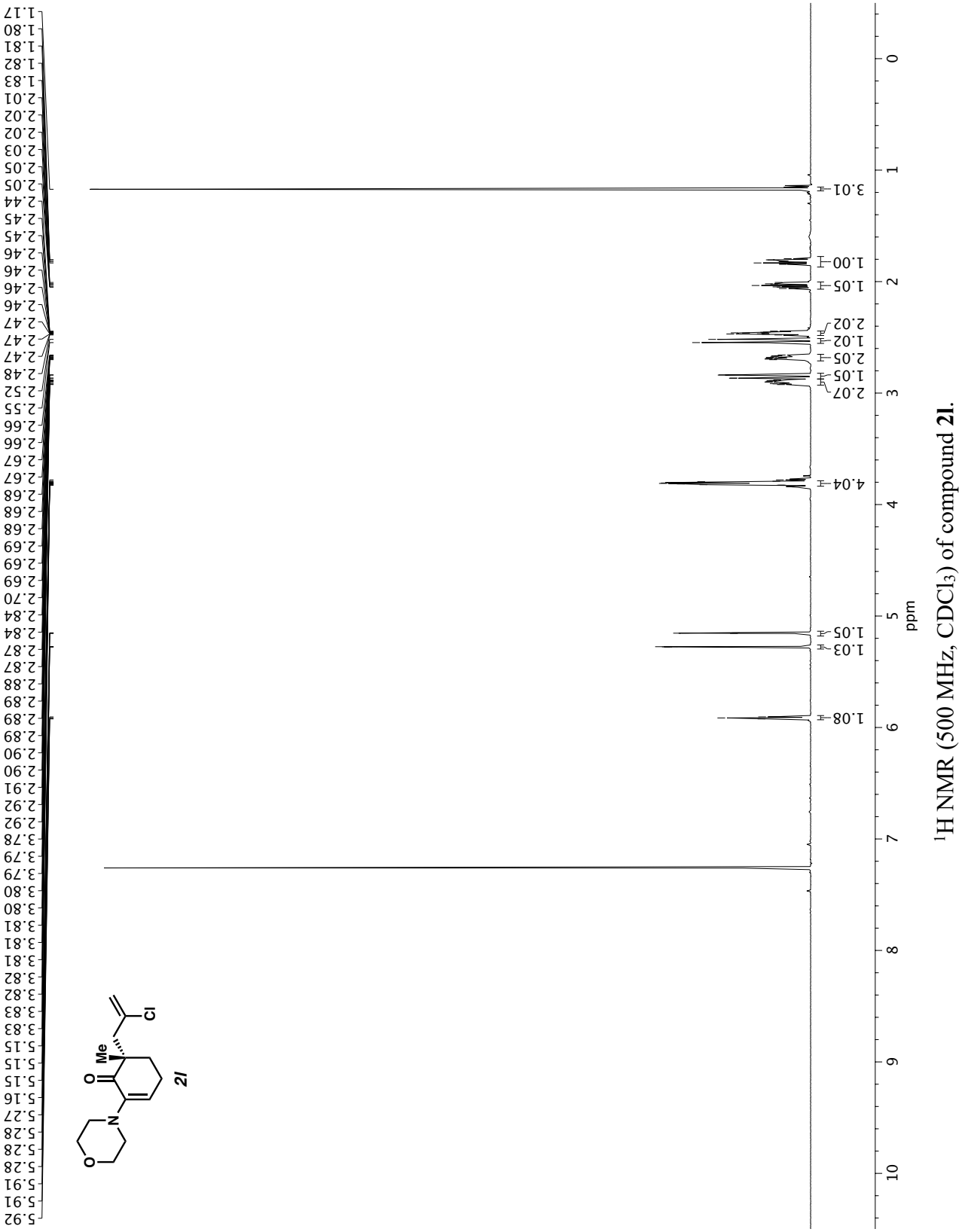
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2k**.



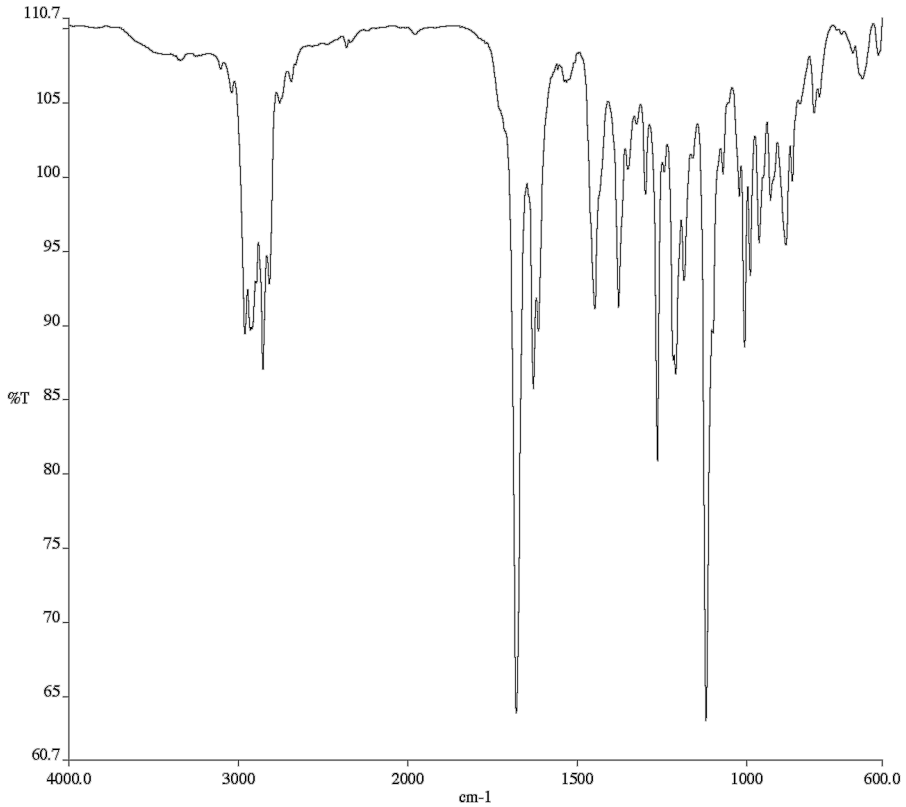
Infrared spectrum (Thin Film, NaCl) of compound **2k**.



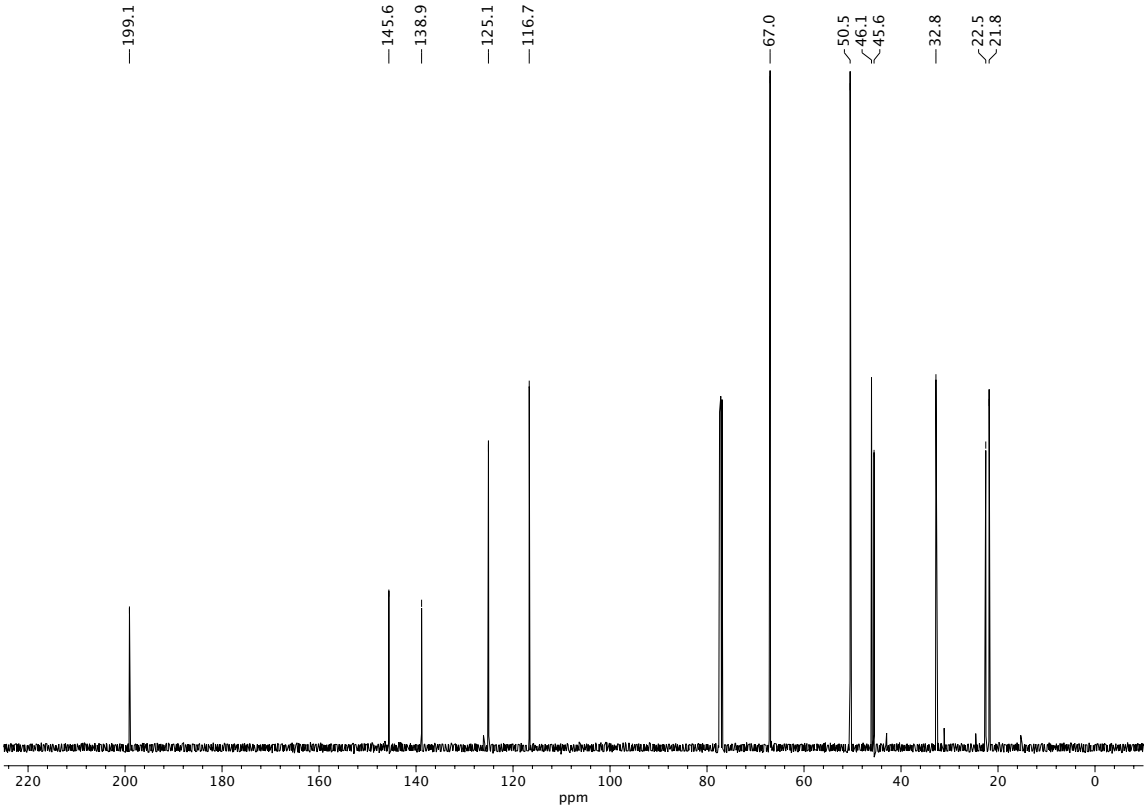
^{13}C NMR (125 MHz, $CDCl_3$) of compound **2k**.



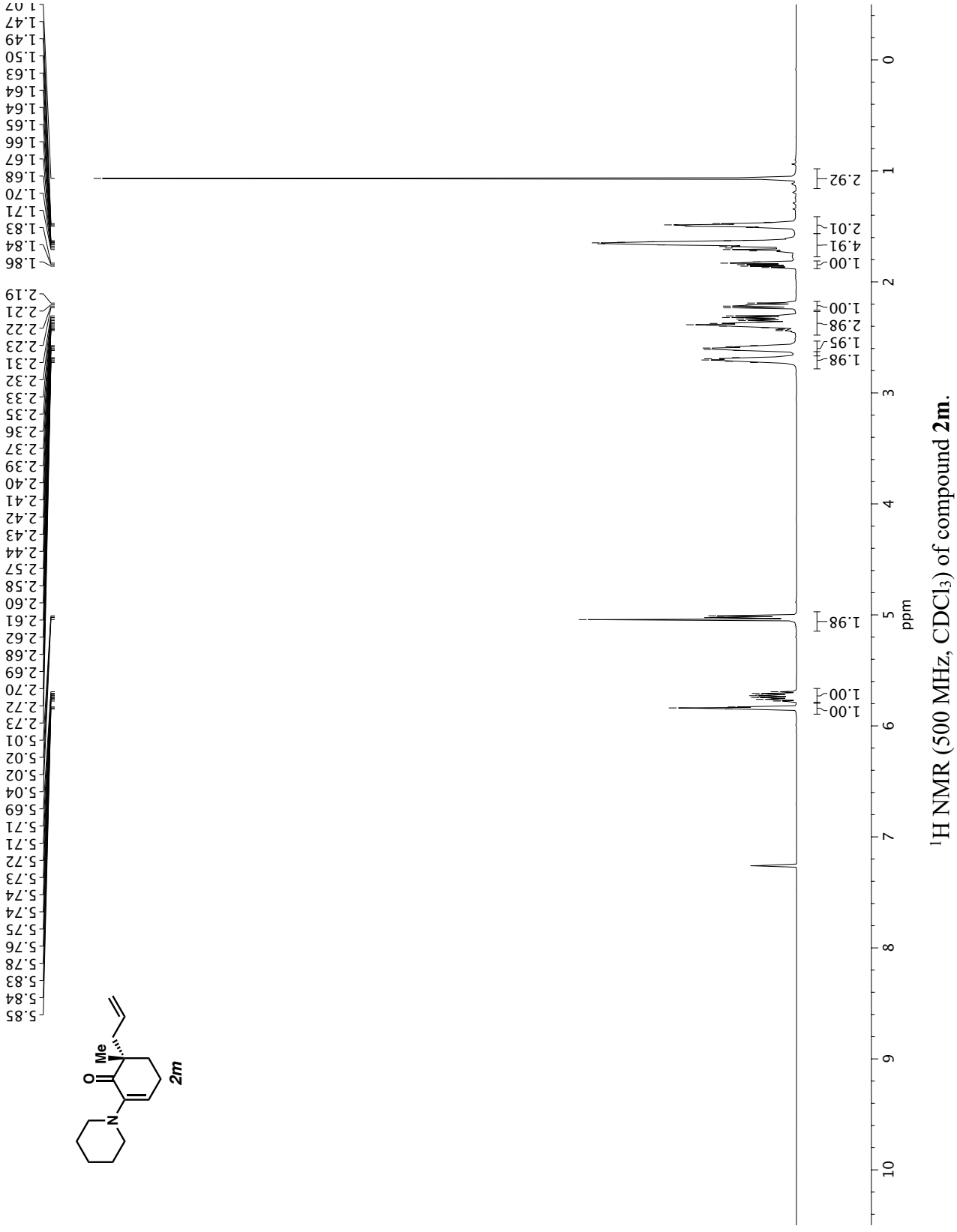
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2l**.



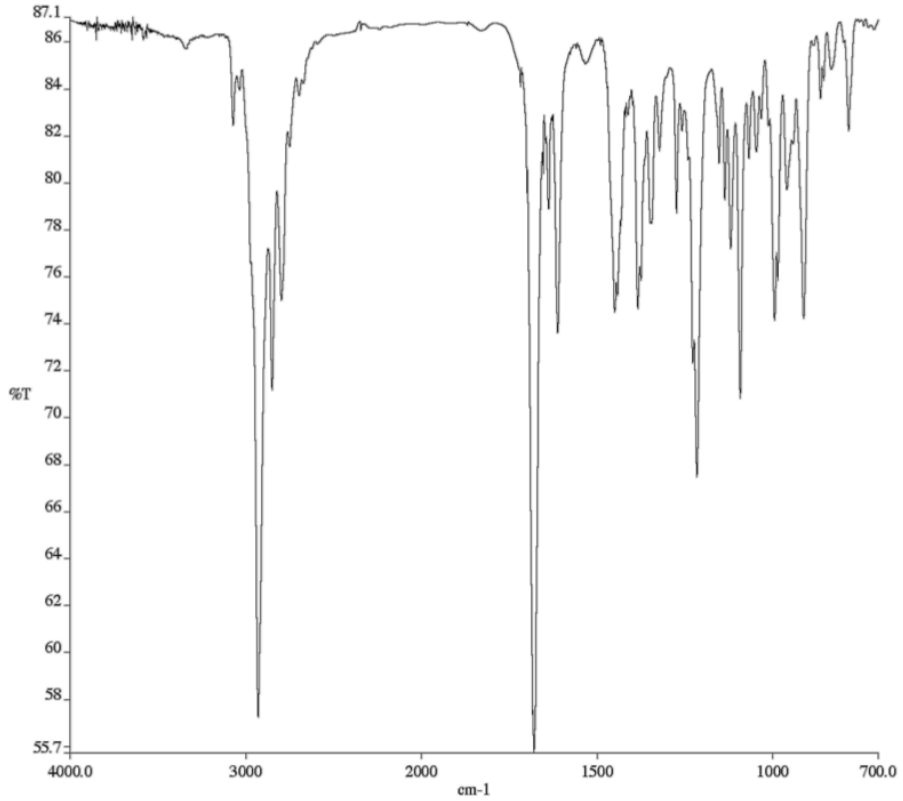
Infrared spectrum (Thin Film, NaCl) of compound **2l**.



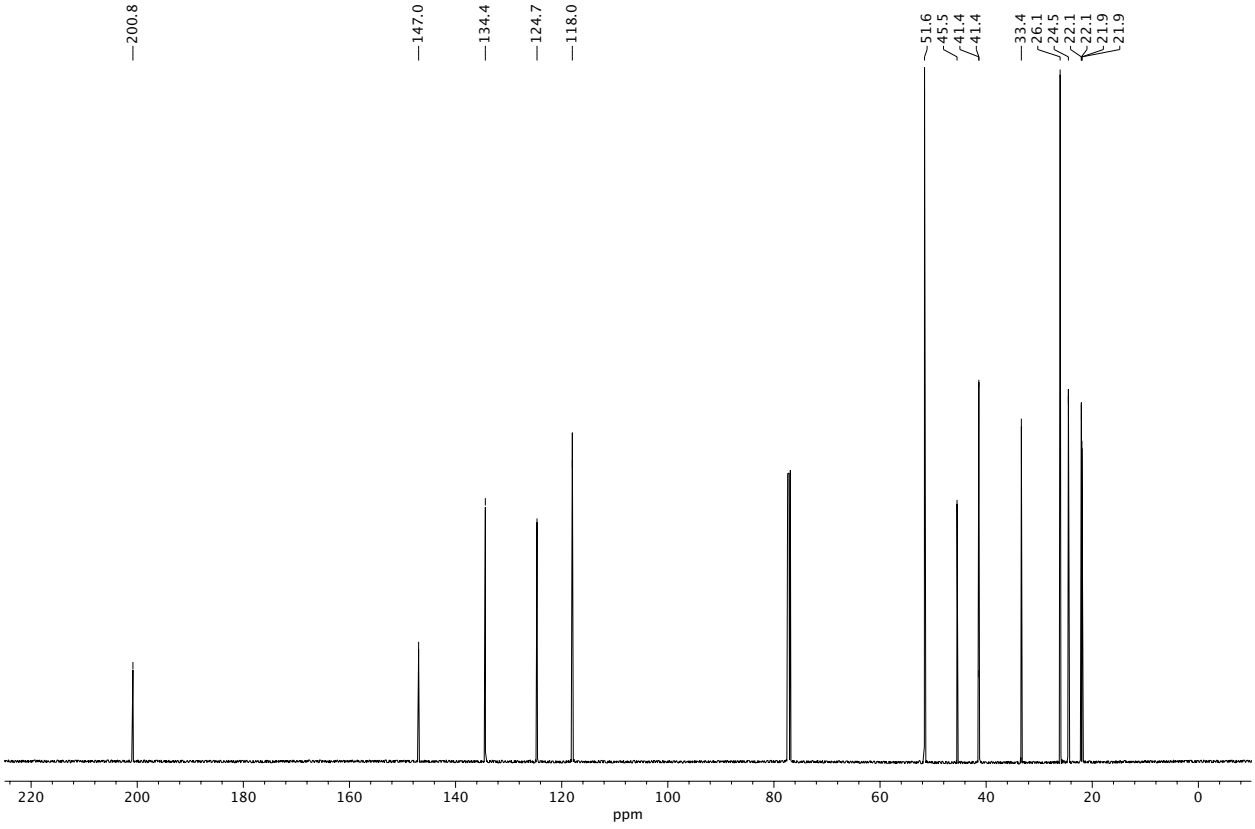
^{13}C NMR (125 MHz, $CDCl_3$) of compound **2l**.



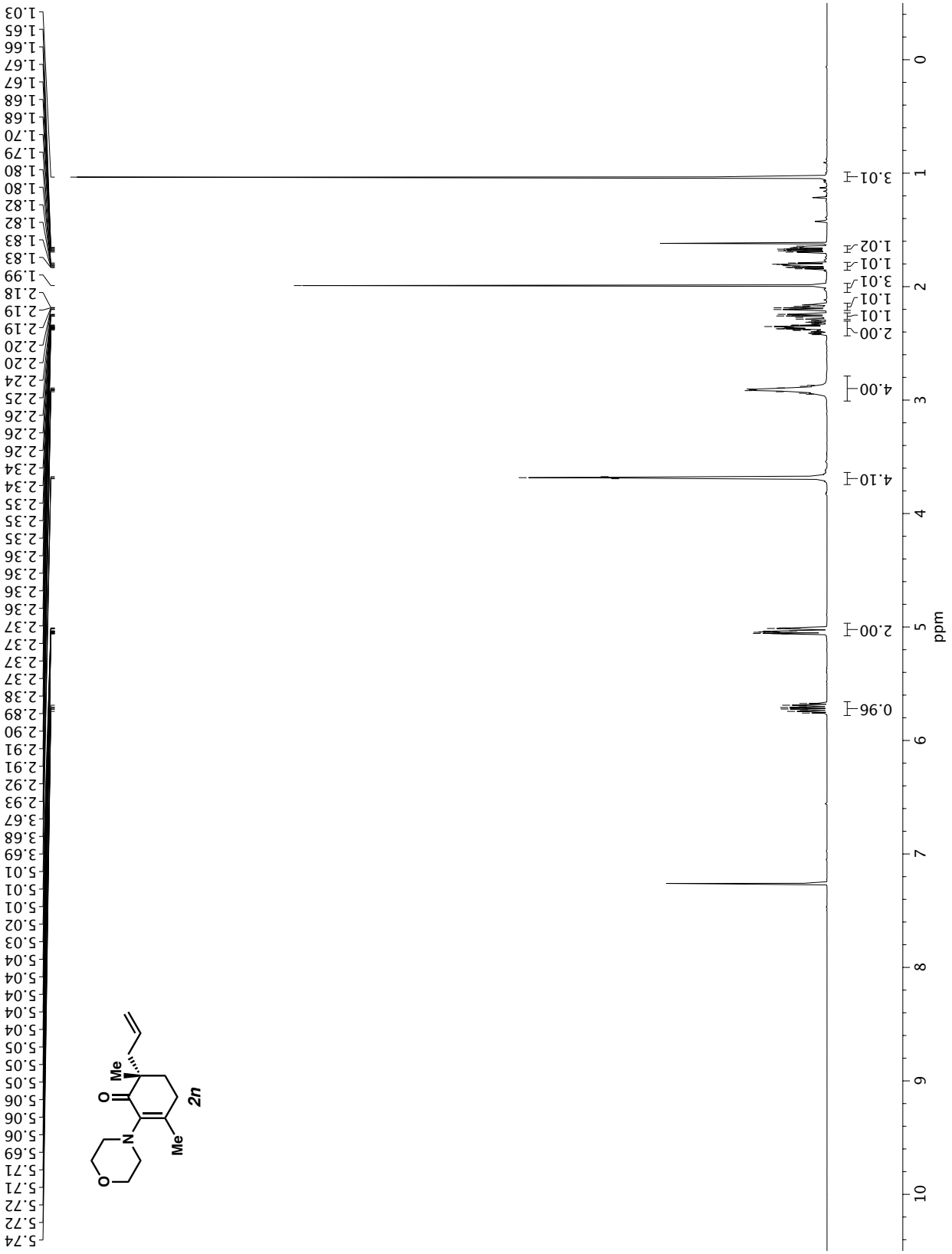
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2m**.



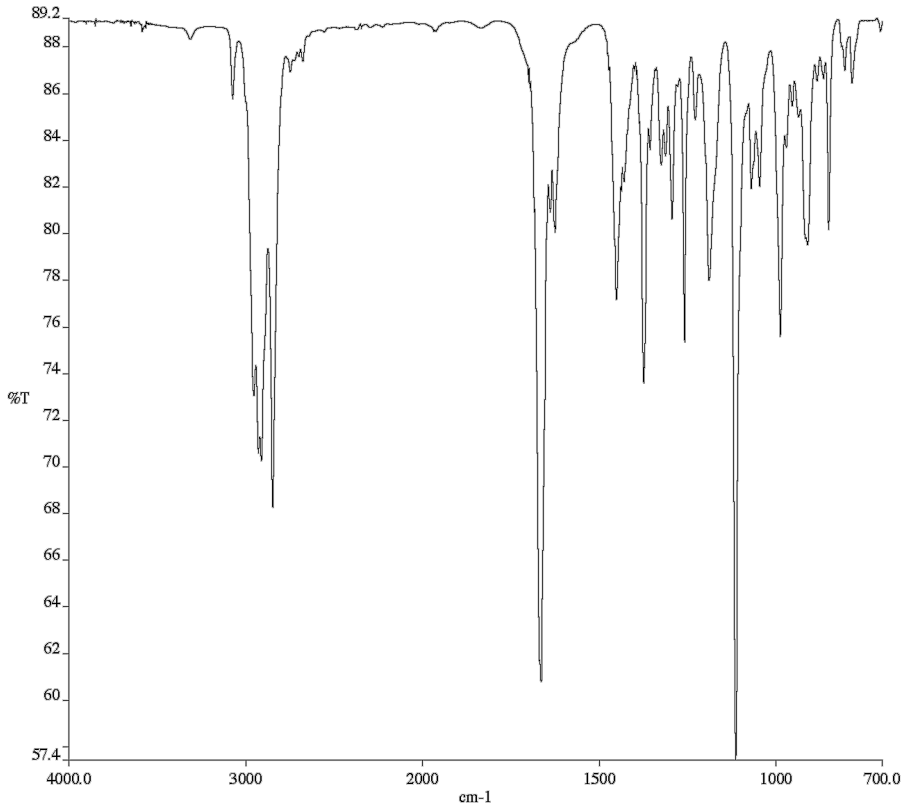
Infrared spectrum (Thin Film, NaCl) of compound **2m**.



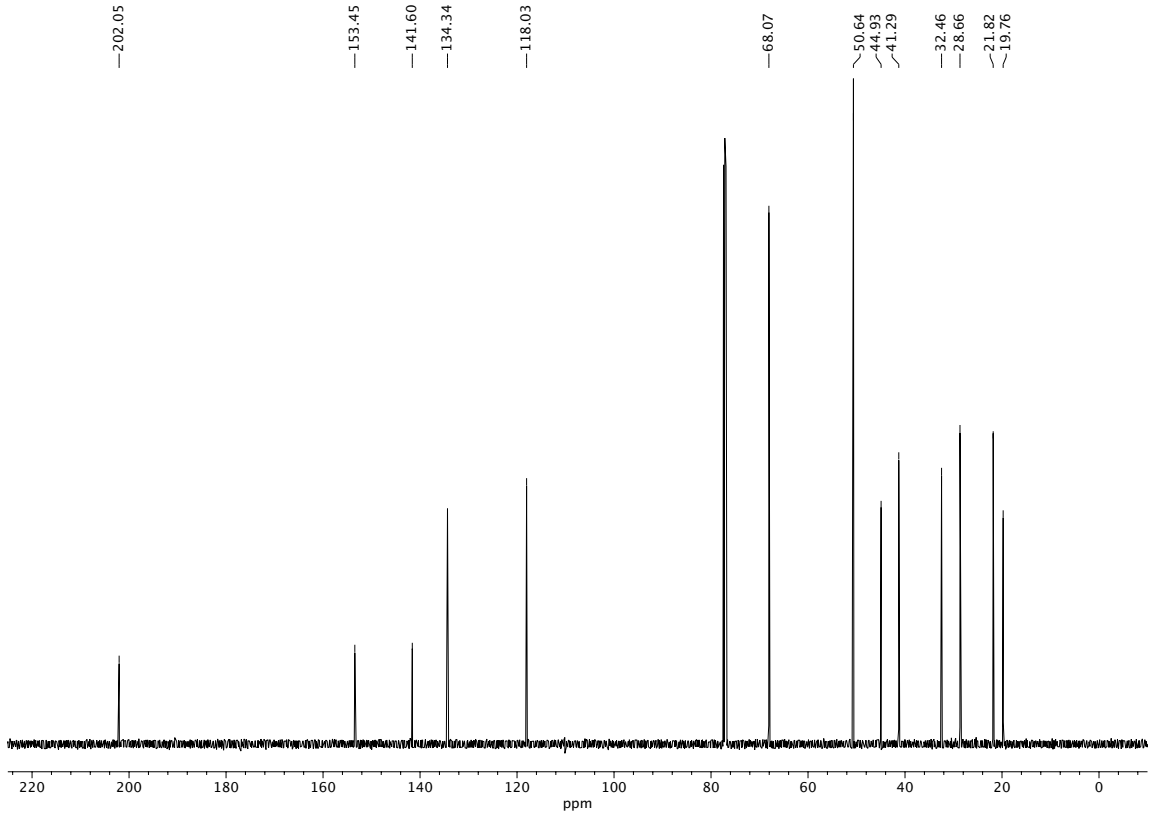
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2m**.



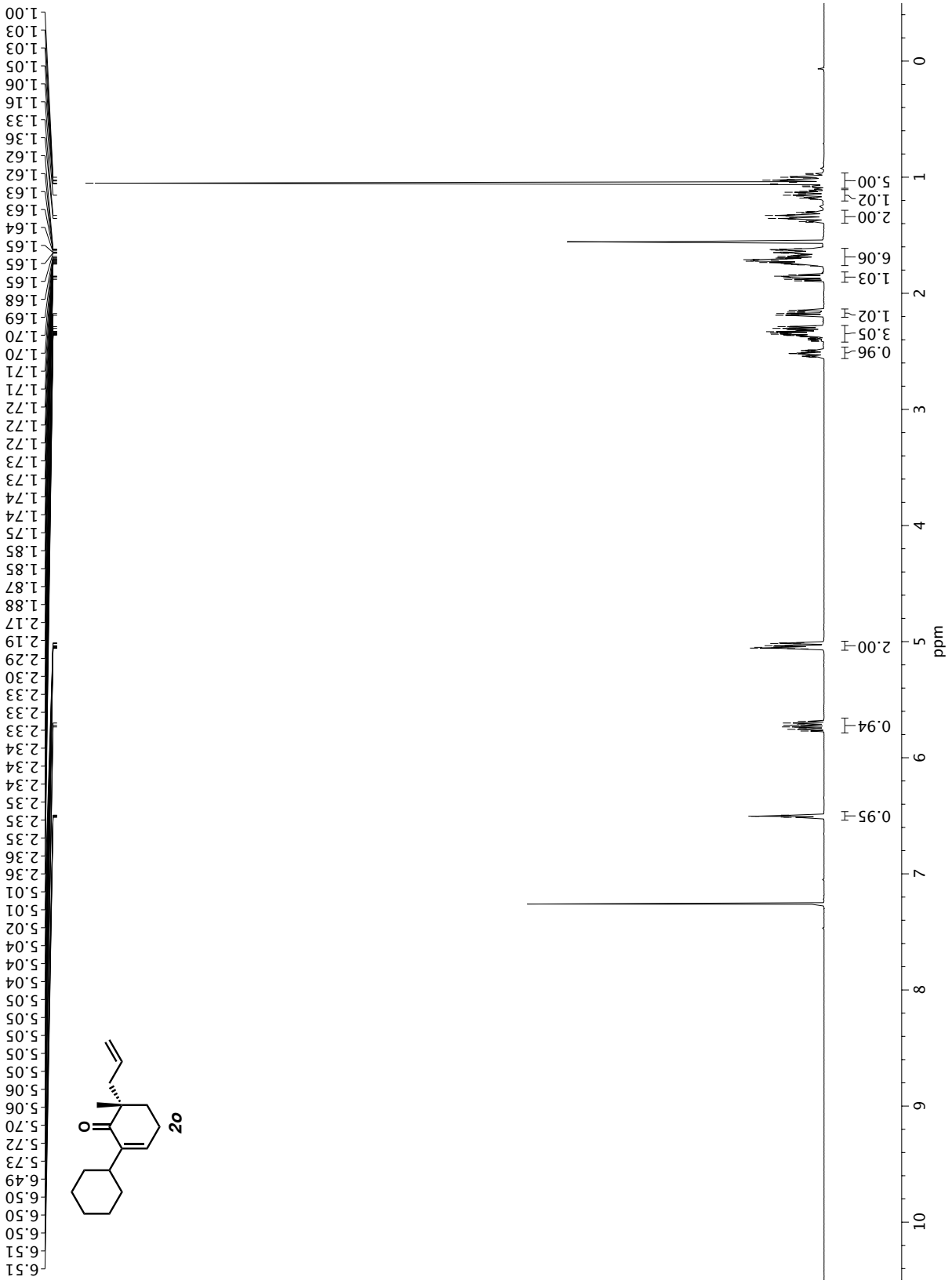
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2n**.



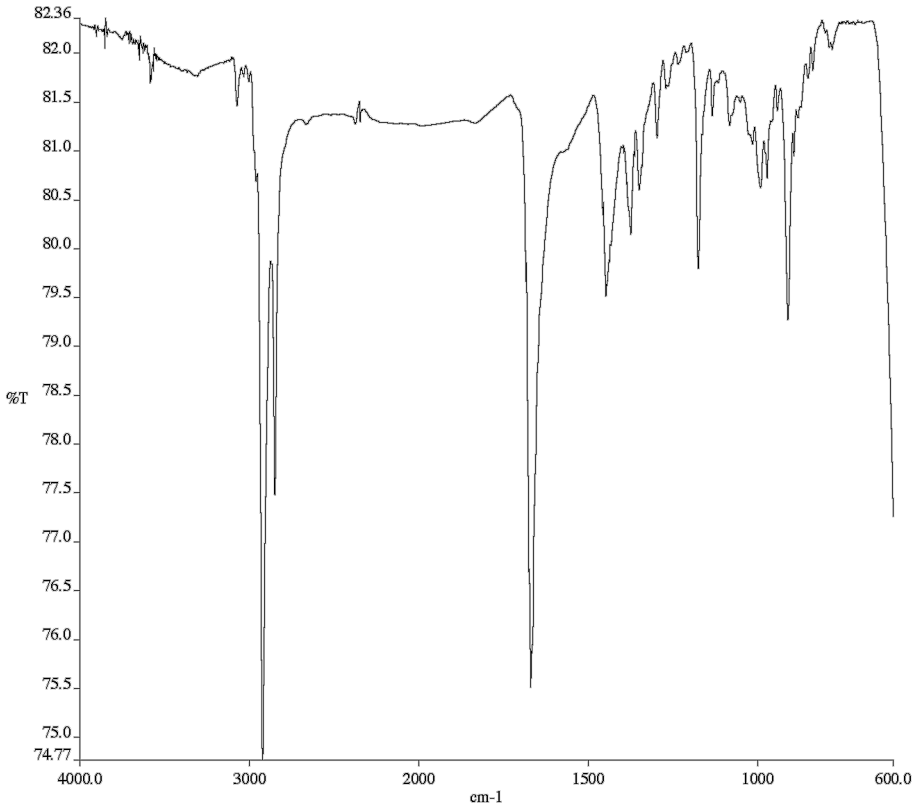
Infrared spectrum (Thin Film, NaCl) of compound **2n**.



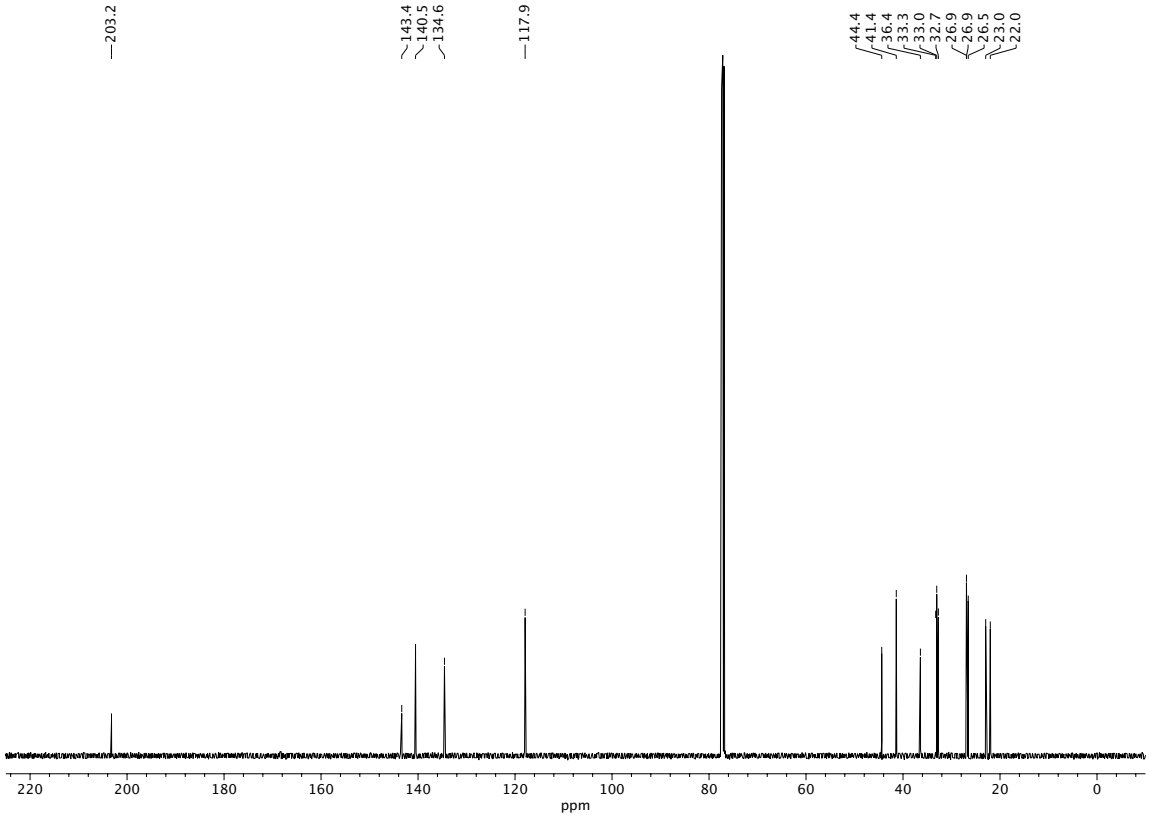
^{13}C NMR (125 MHz, $CDCl_3$) of compound **2n**.



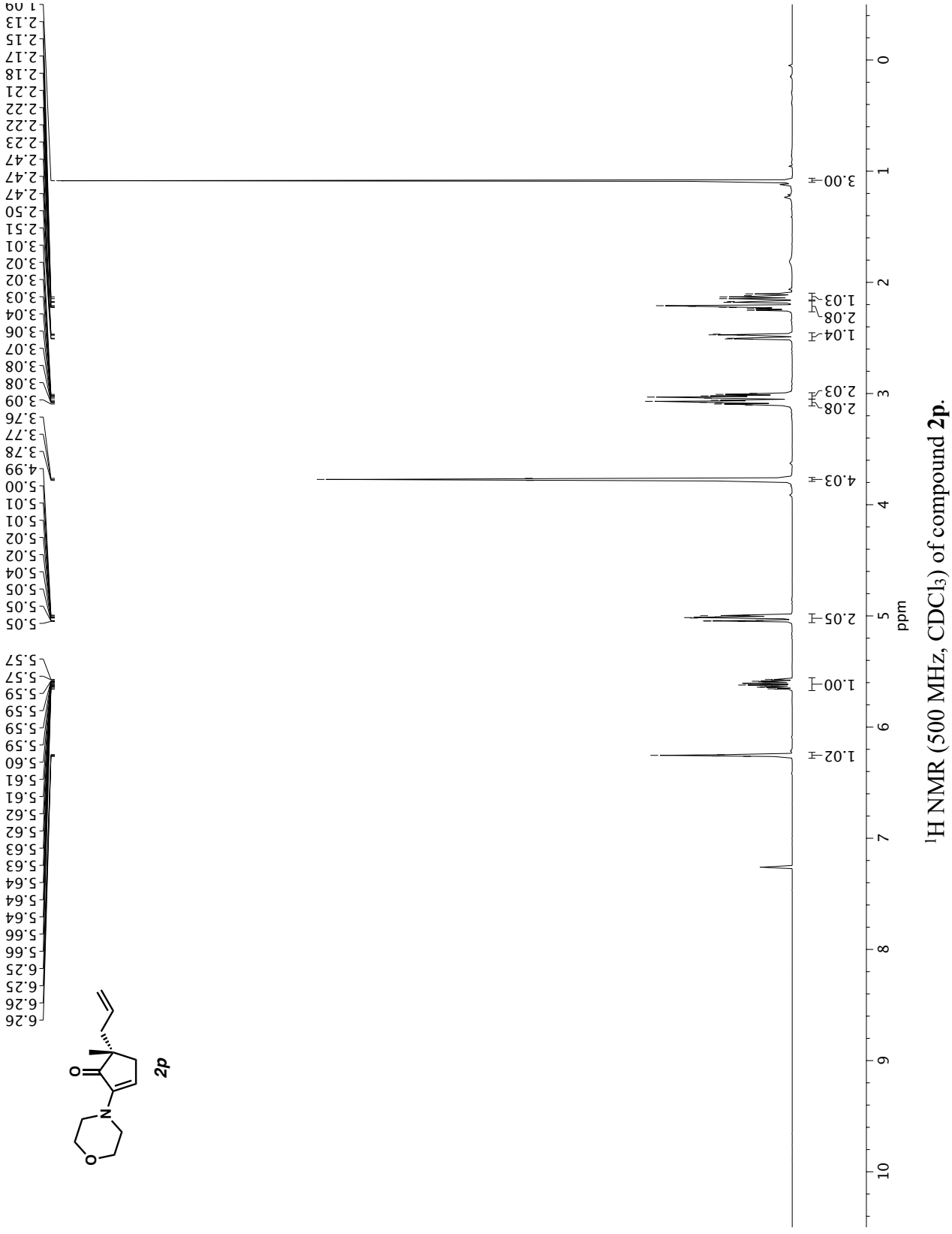
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2o**.



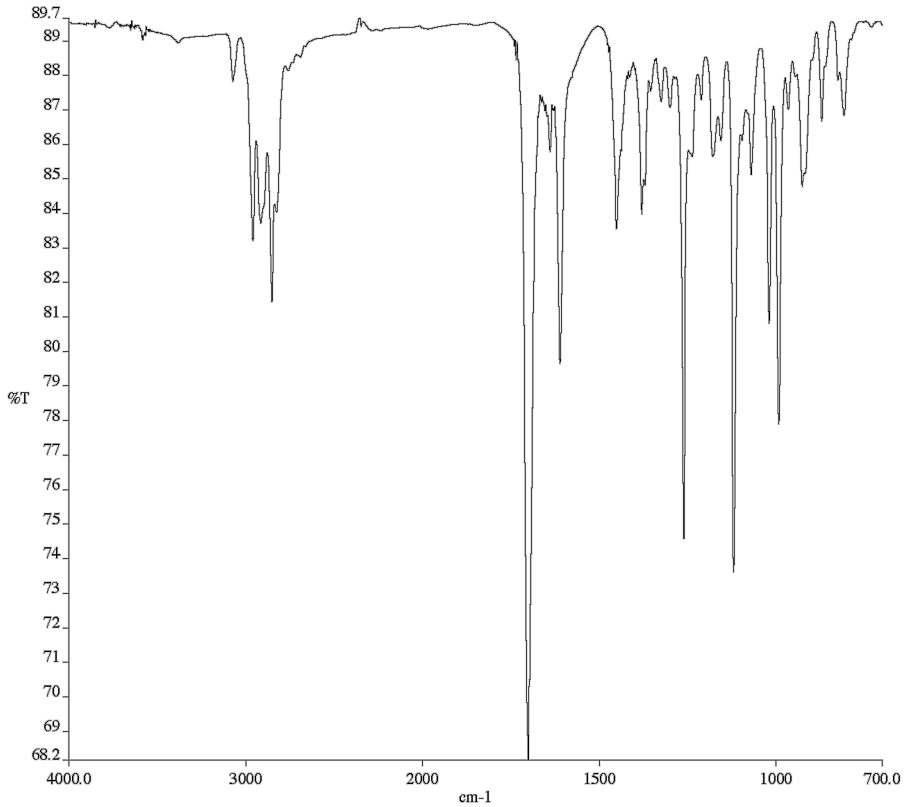
Infrared spectrum (Thin Film, NaCl) of compound **2o**.



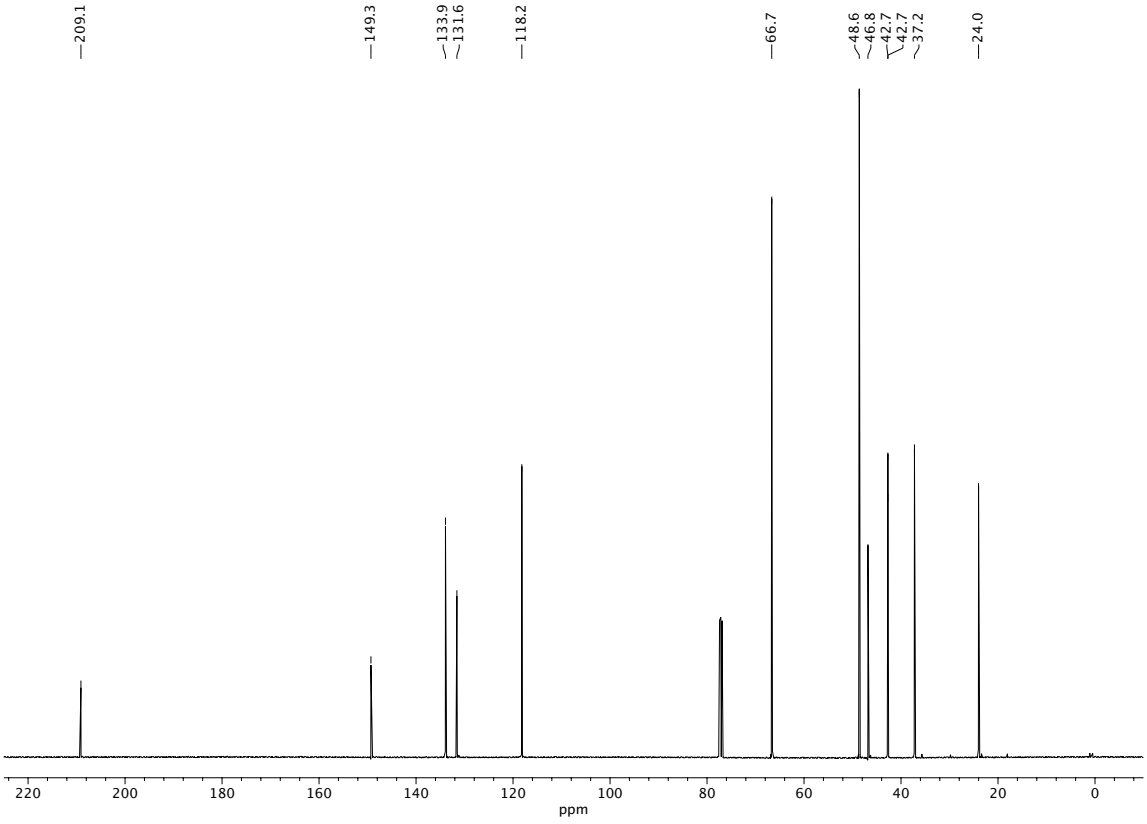
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2o**.



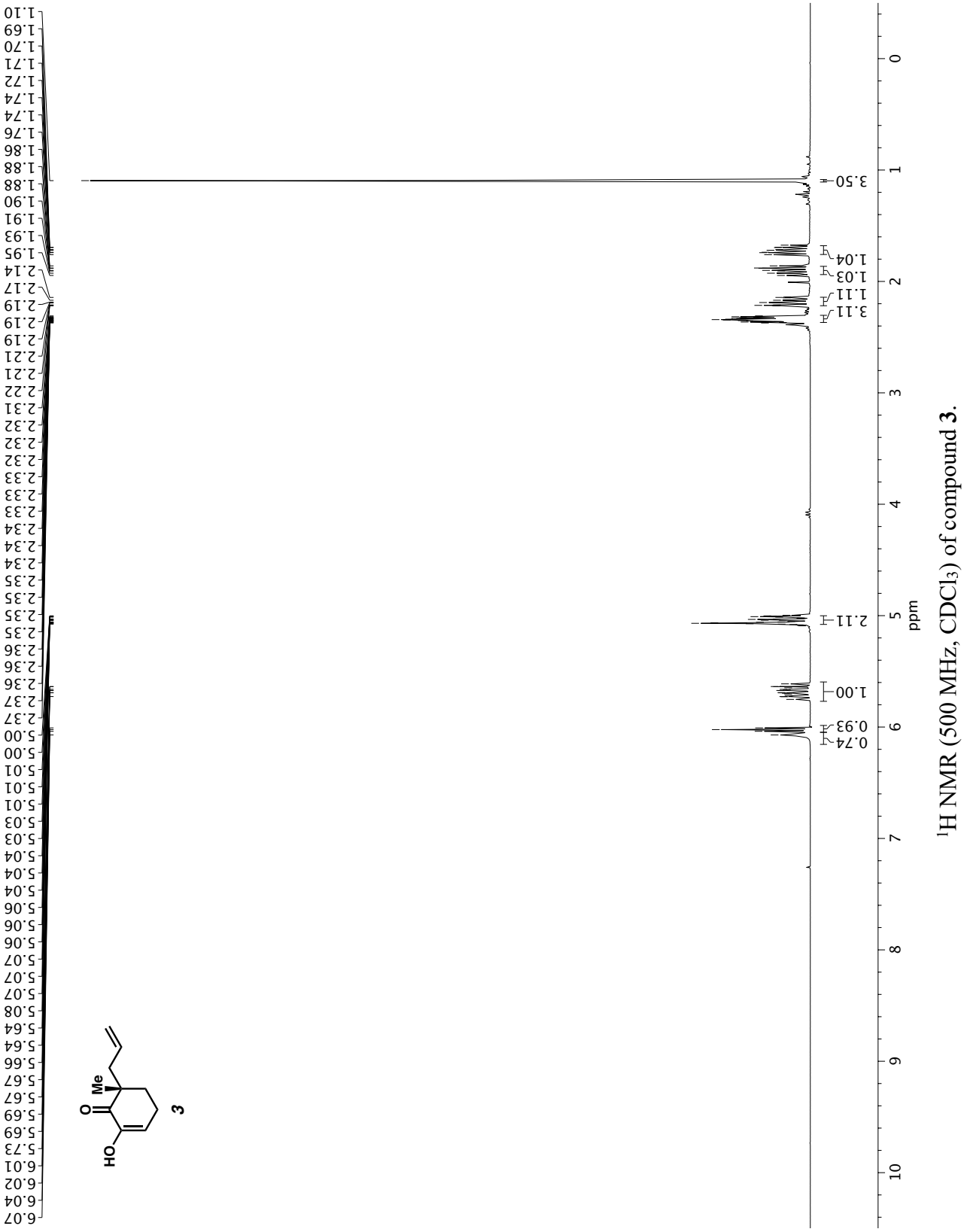
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2p**.



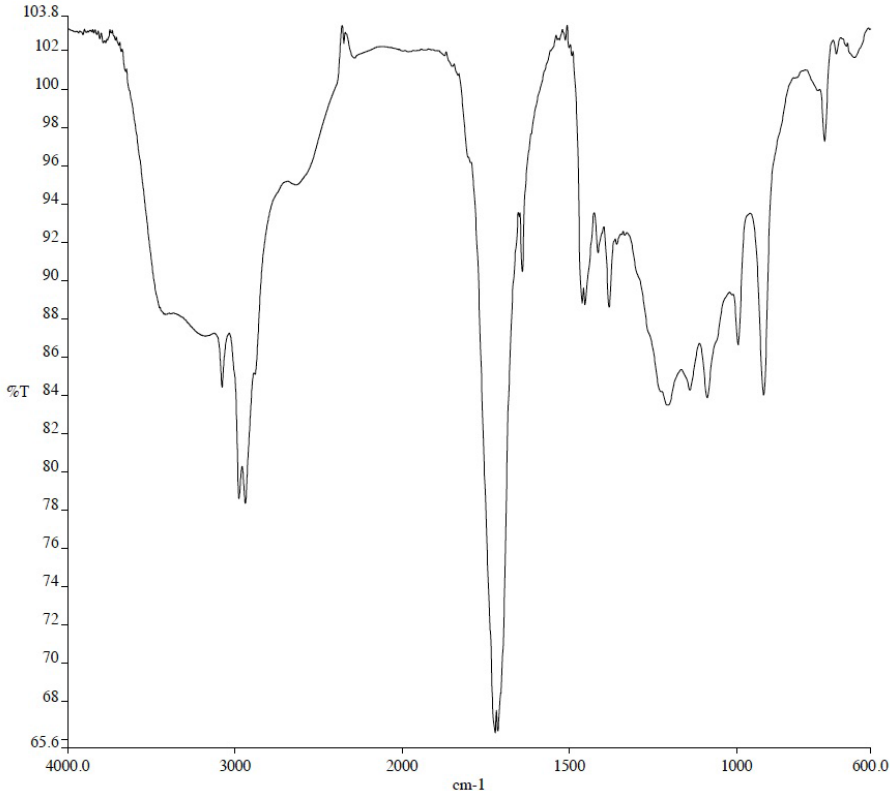
Infrared spectrum (Thin Film, NaCl) of compound **2p**.



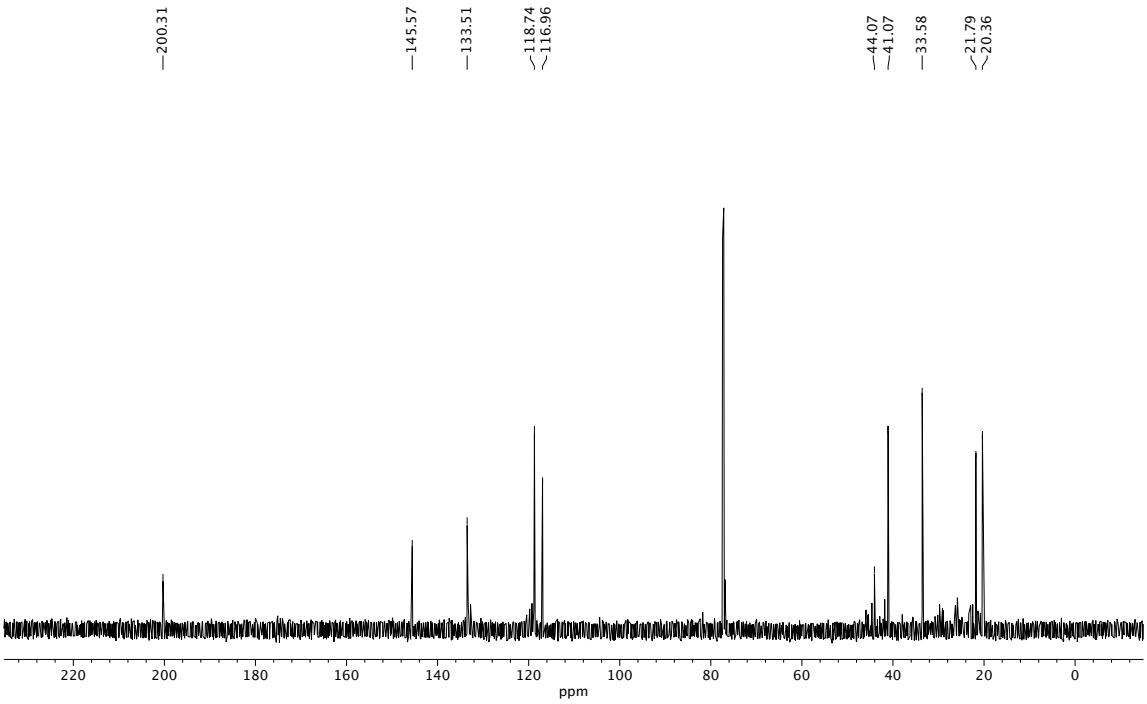
^{13}C NMR (125 MHz, $CDCl_3$) of compound **2p**.



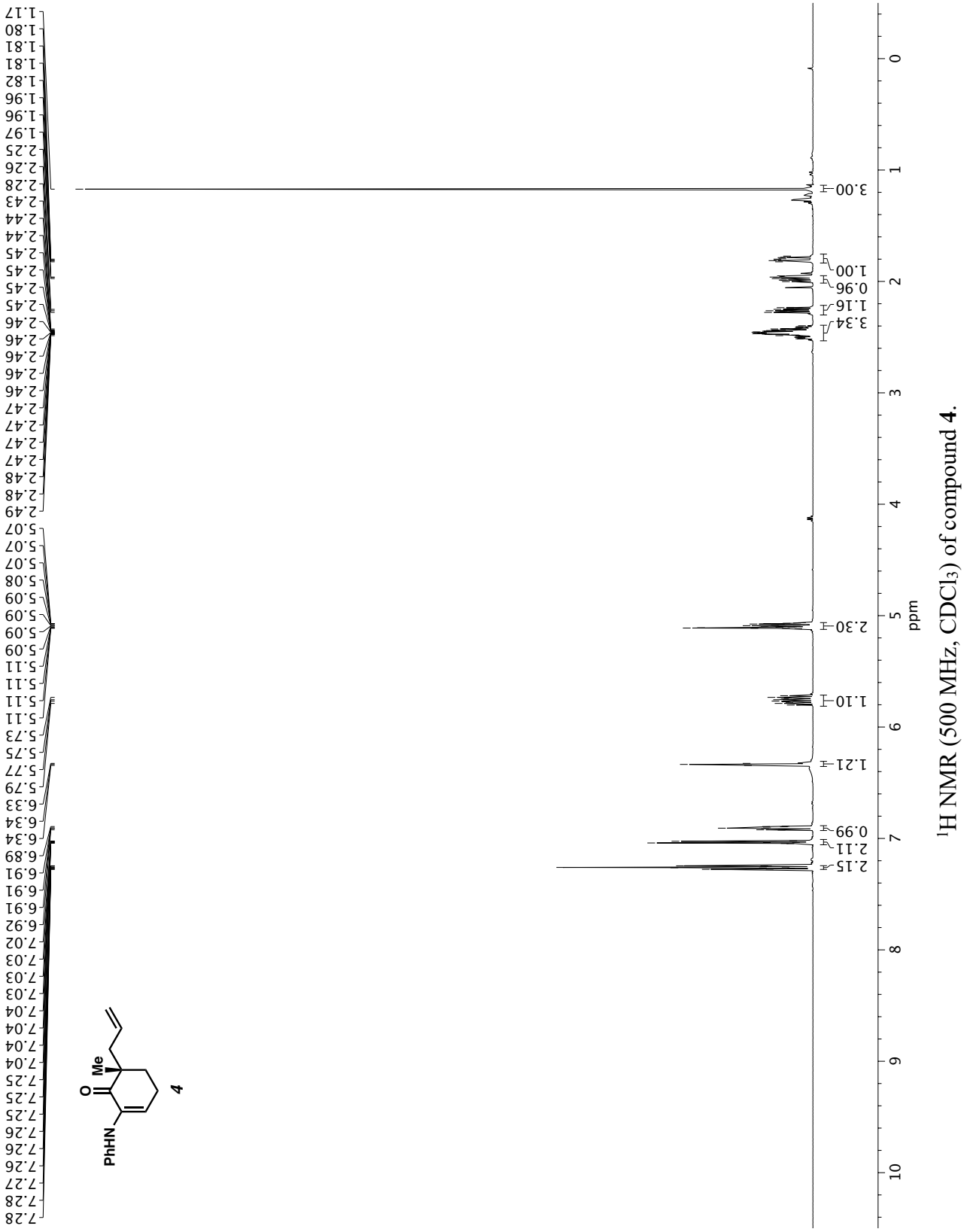
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3**.



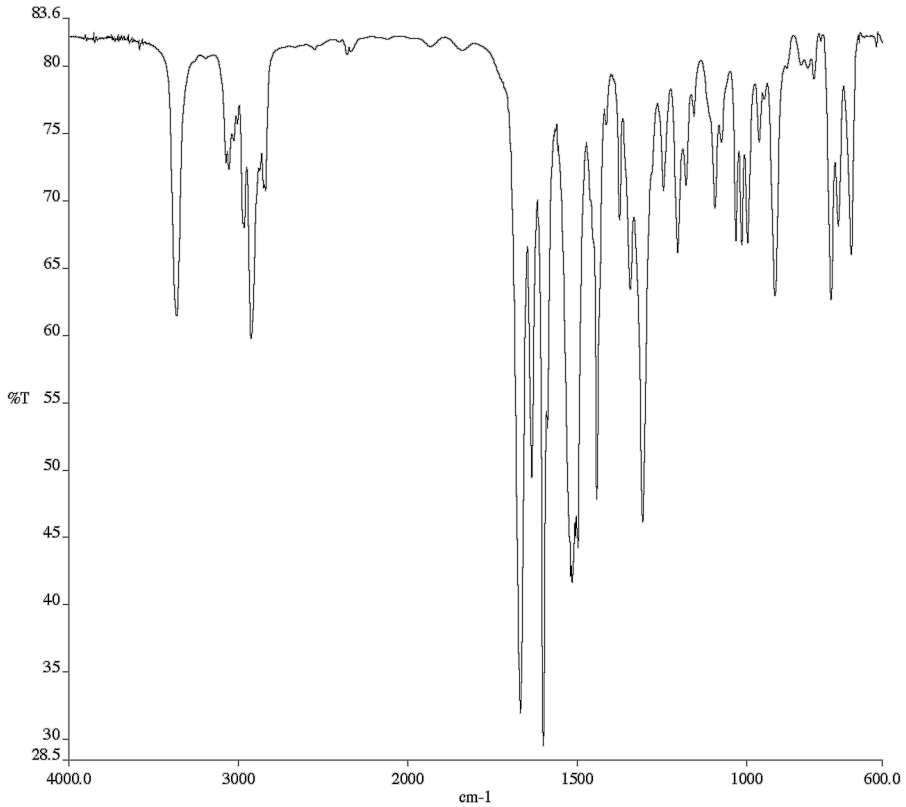
Infrared spectrum (Thin Film, NaCl) of compound **3**.



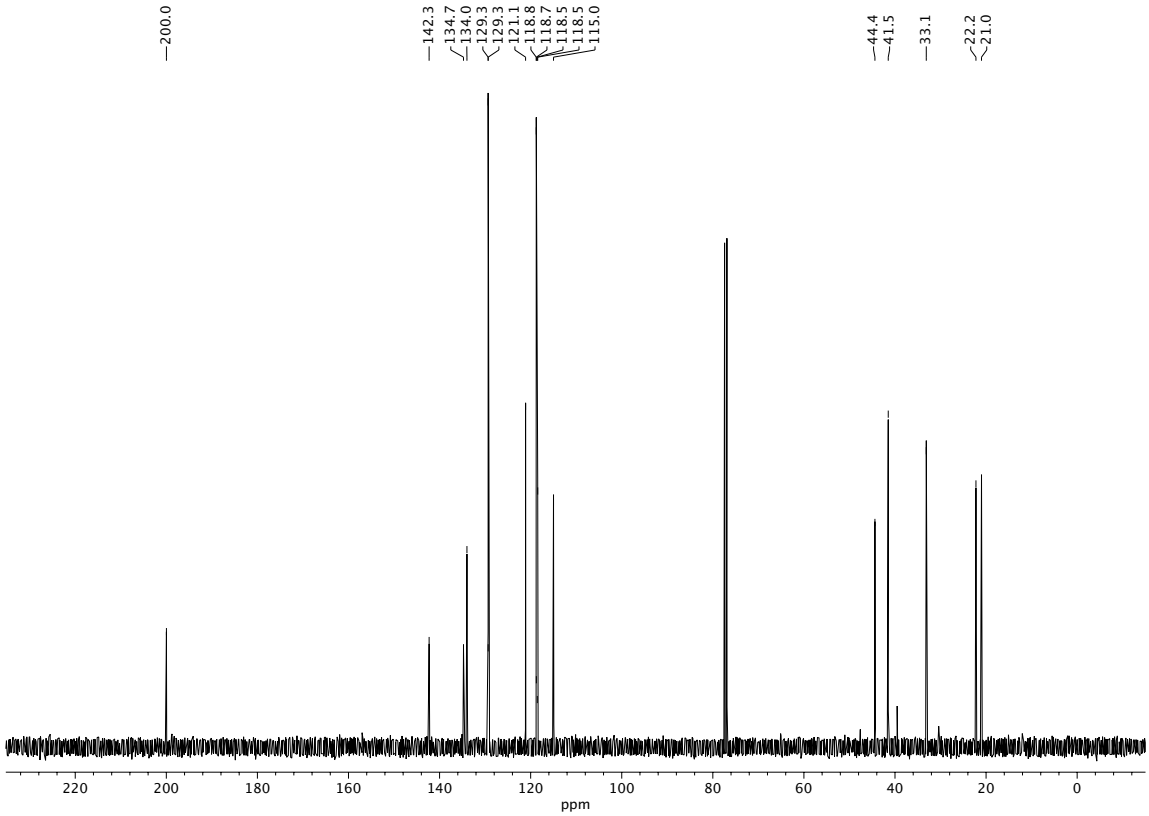
^{13}C NMR (125 MHz, $CDCl_3$) of compound **2p**.



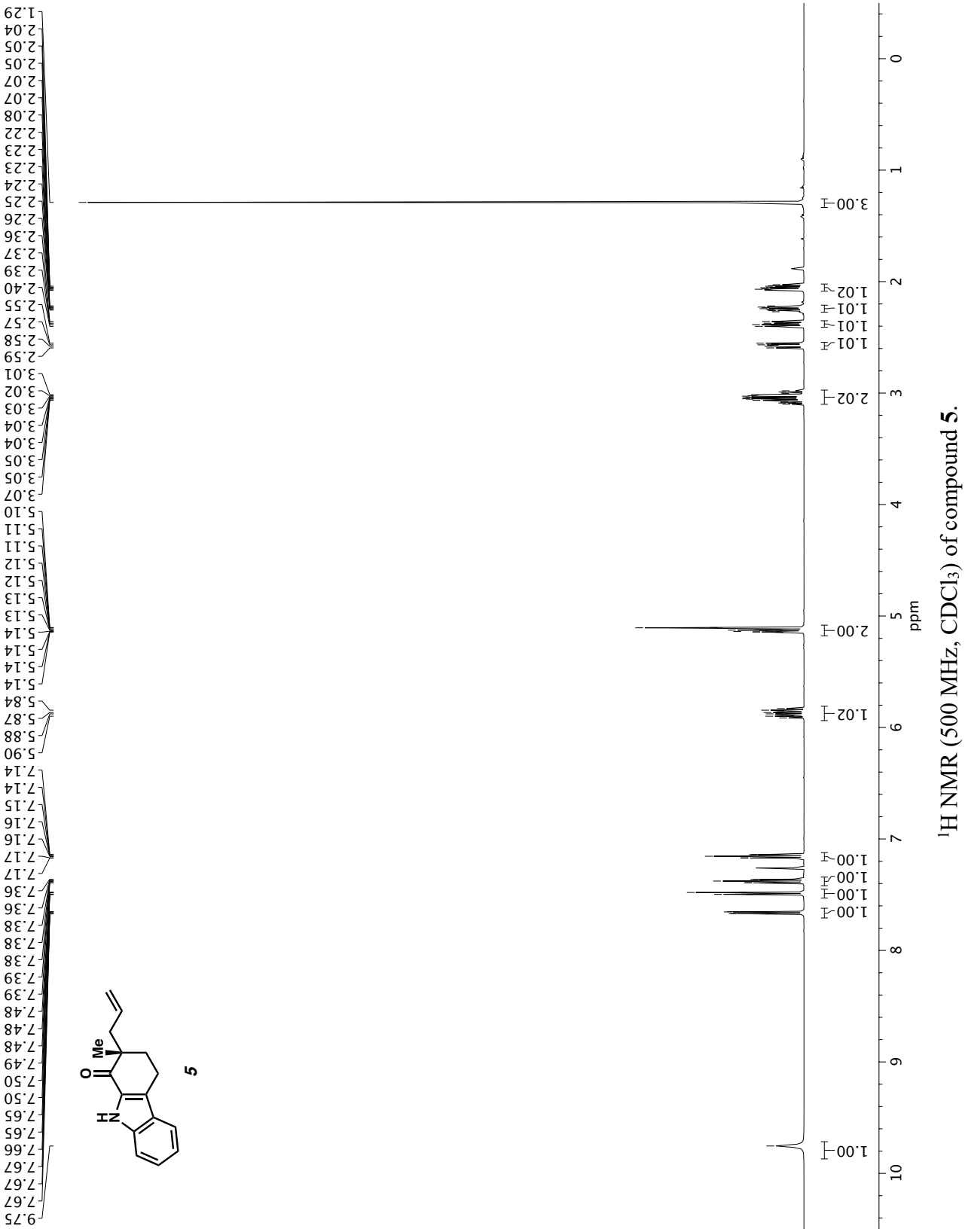
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4**.



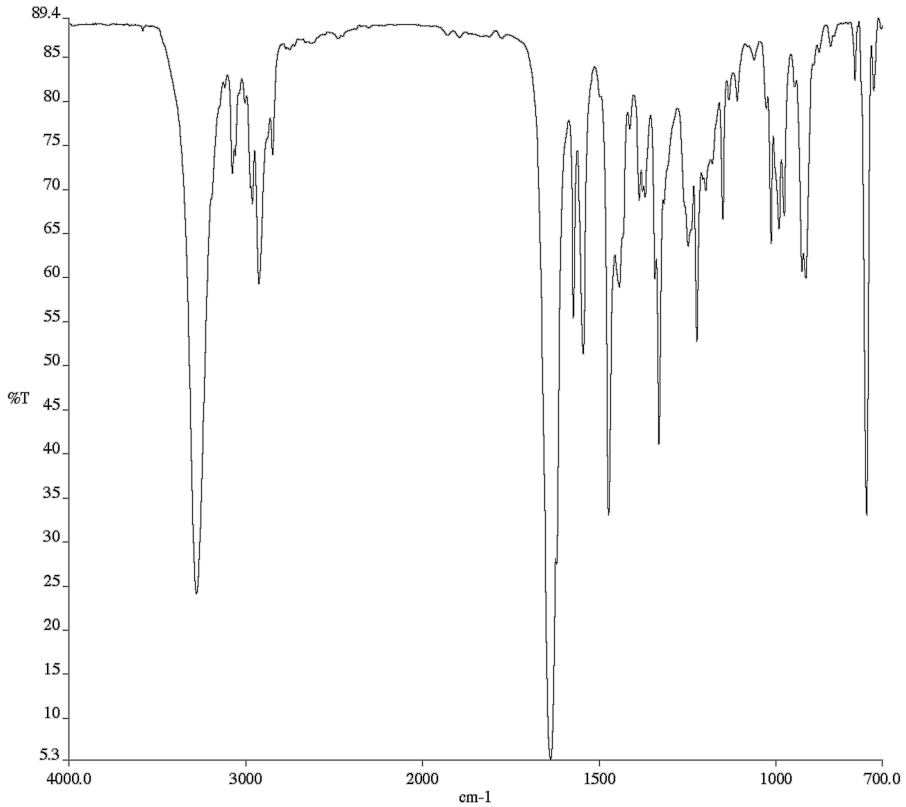
Infrared spectrum (Thin Film, NaCl) of compound **4**.



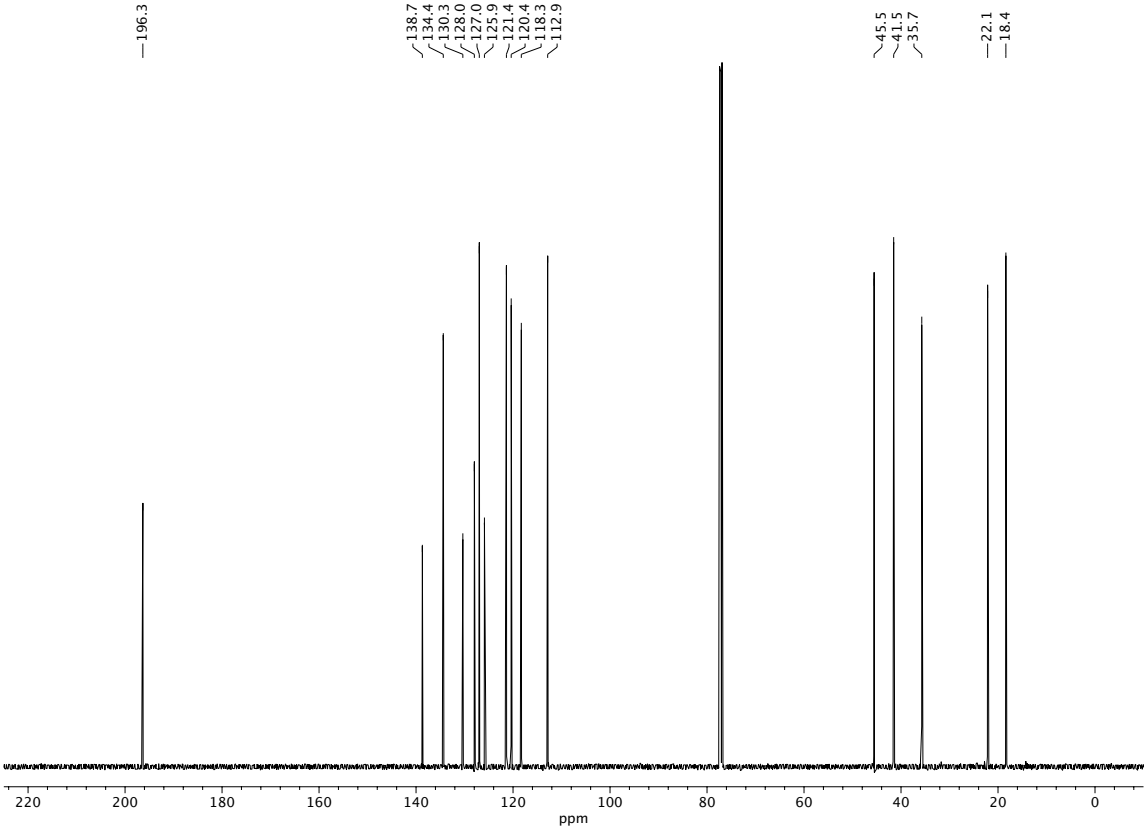
^{13}C NMR (125 MHz, $CDCl_3$) of compound **4**.



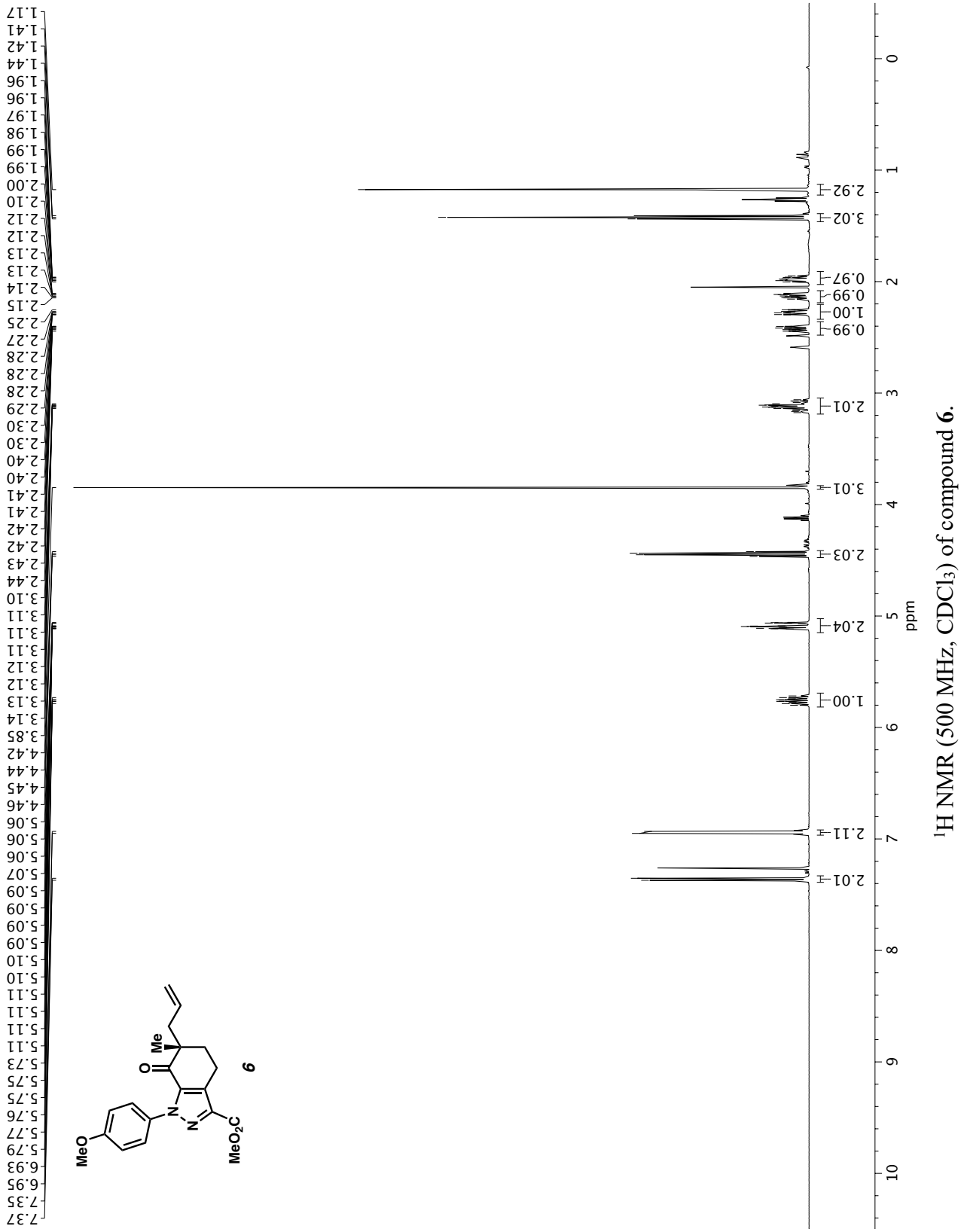
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5**.



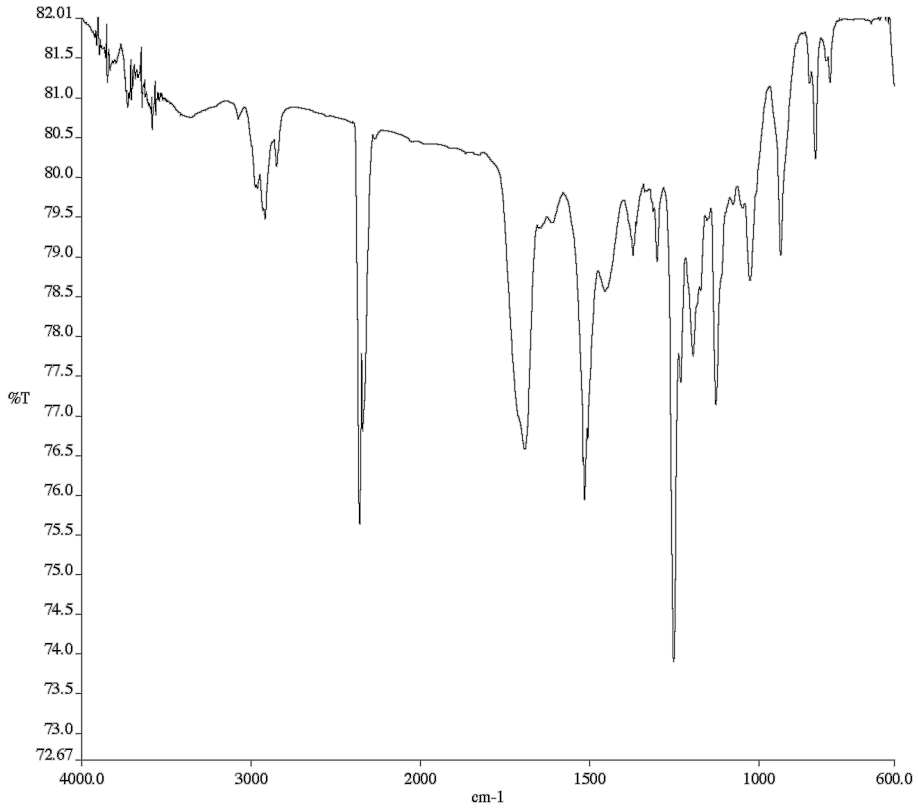
Infrared spectrum (Thin Film, NaCl) of compound **5**.



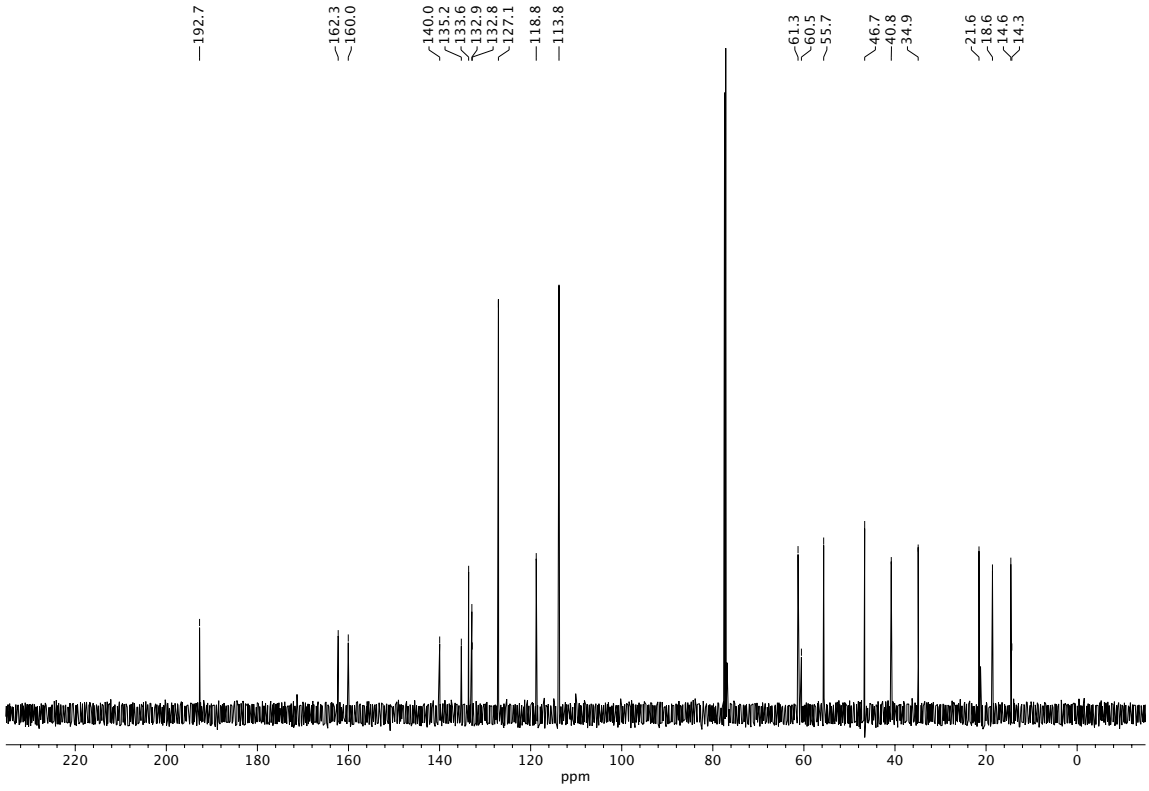
^{13}C NMR (125 MHz, $CDCl_3$) of compound **5**.



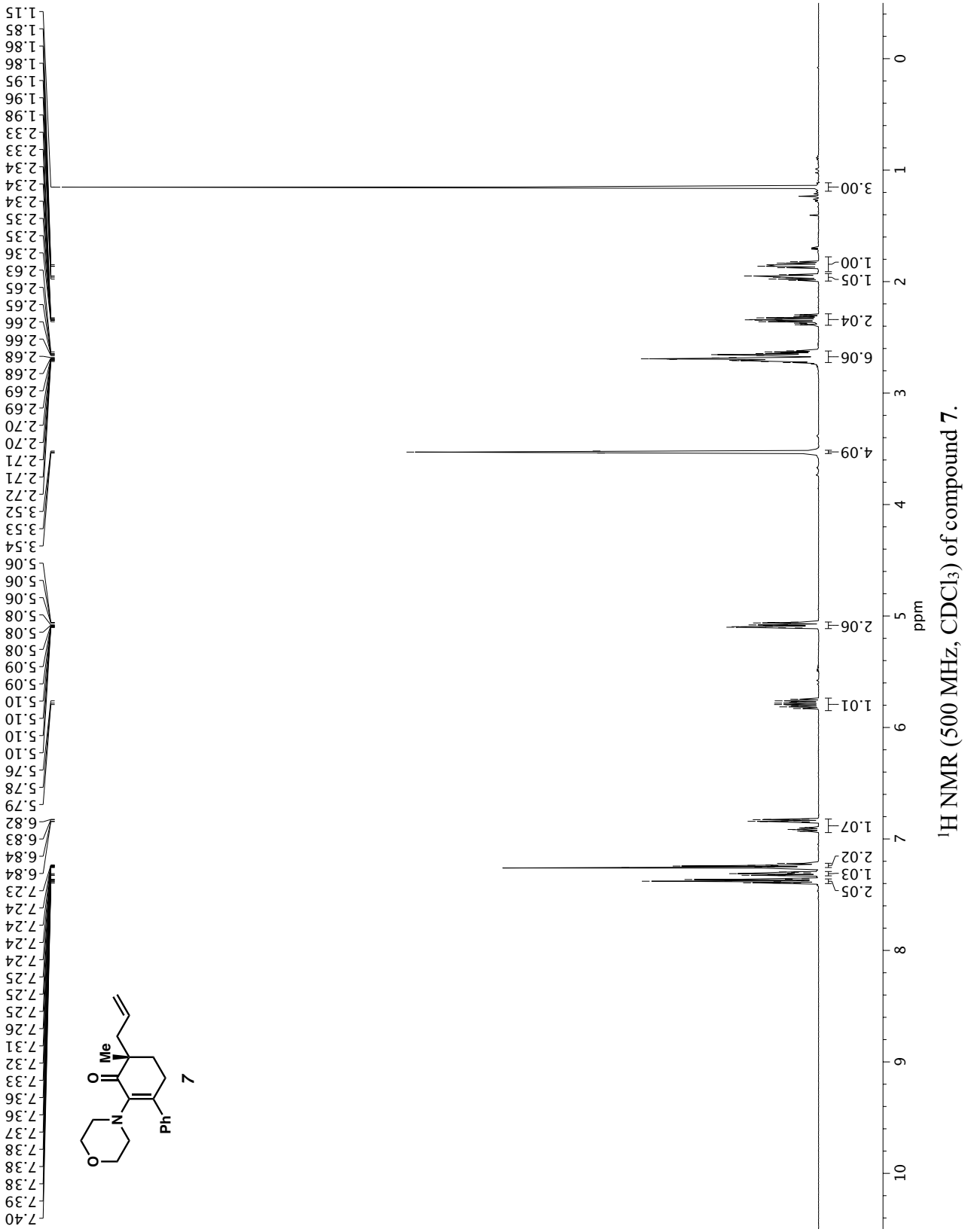
^{1}H NMR (500 MHz, $CDCl_3$) of compound **6**.



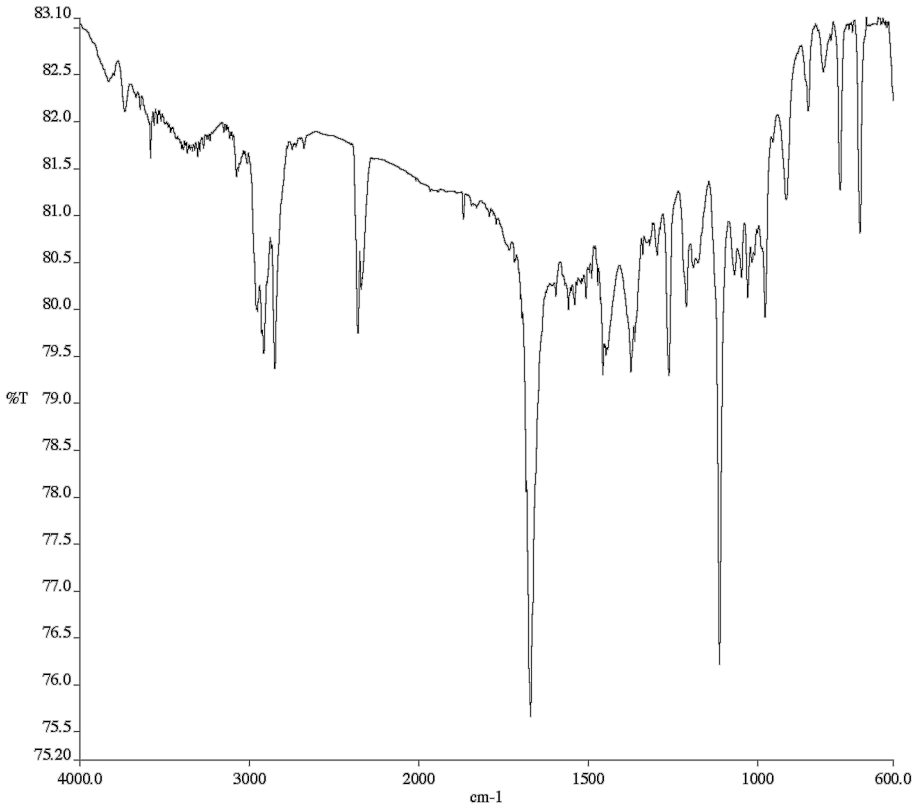
Infrared spectrum (Thin Film, NaCl) of compound **6**.



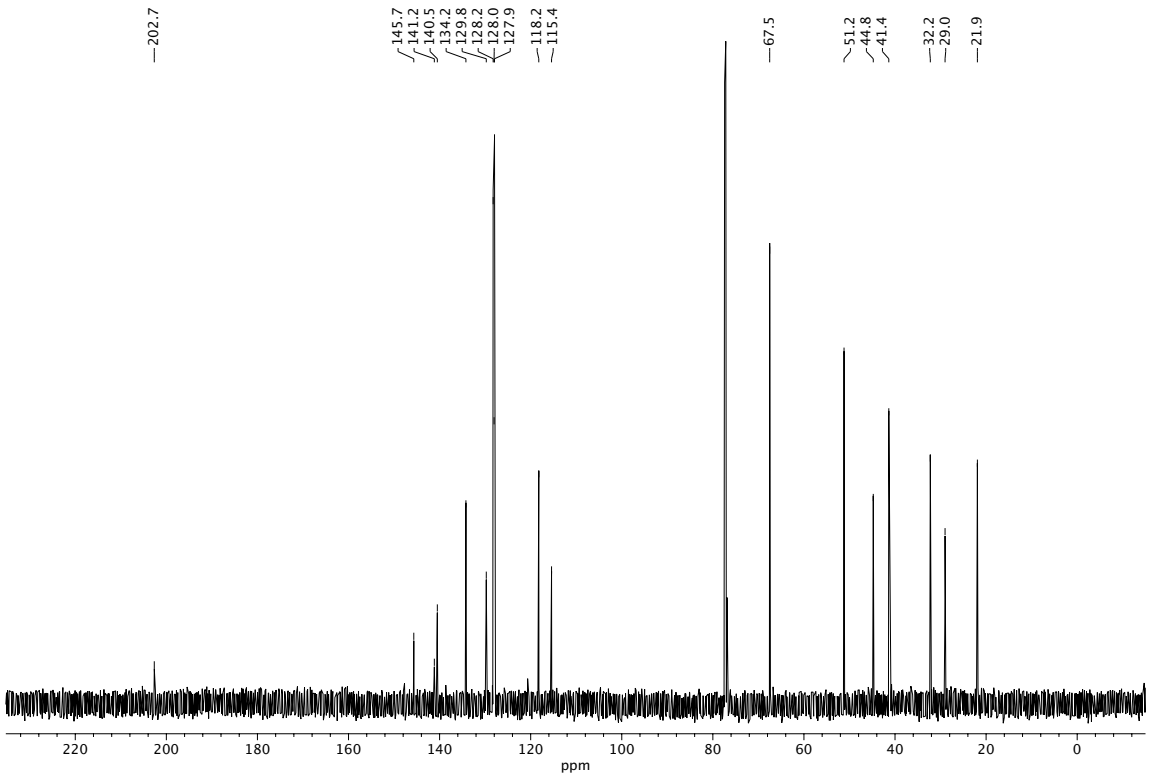
^{13}C NMR (125 MHz, $CDCl_3$) of compound **6**.



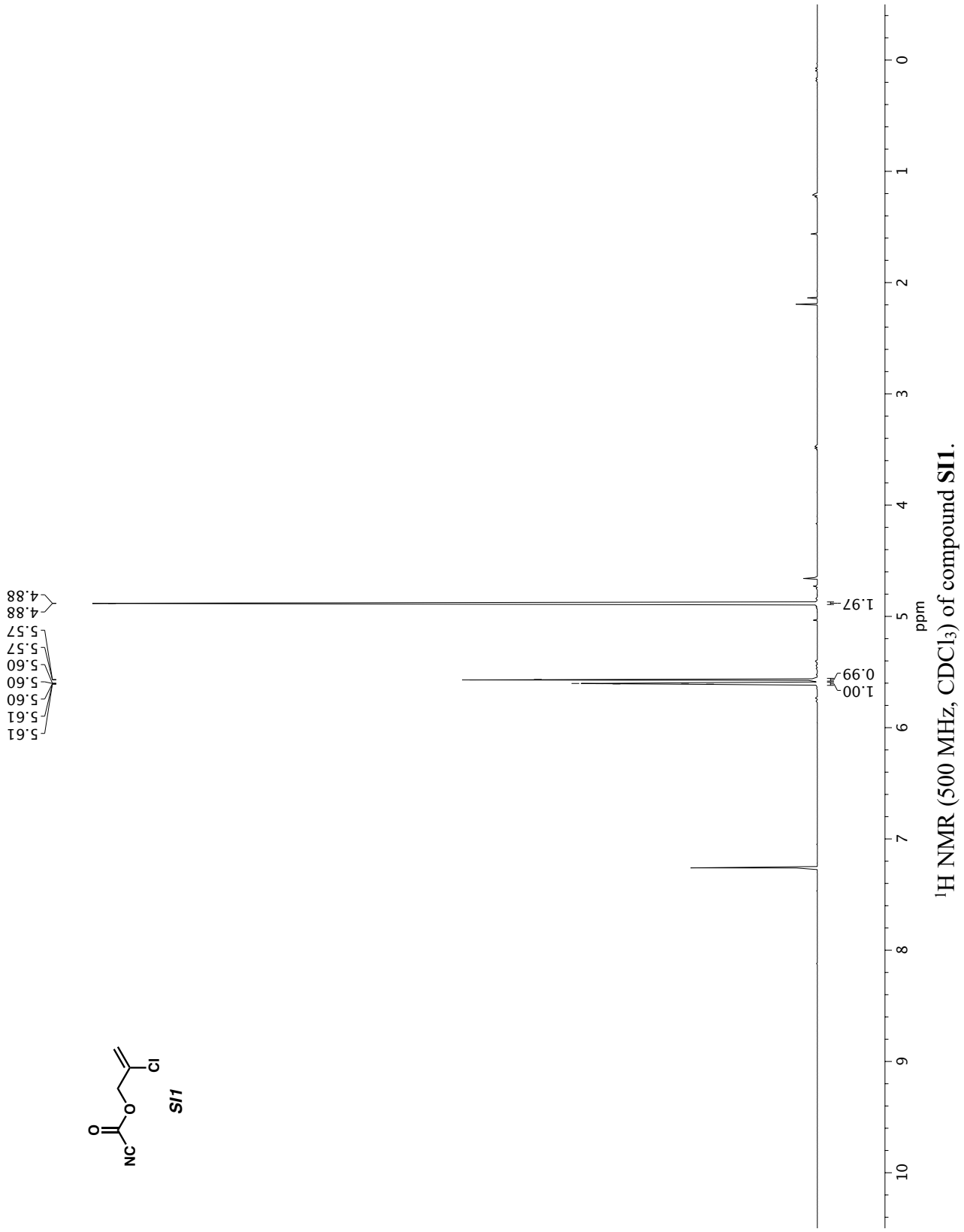
^{1}H NMR (500 MHz, $CDCl_3$) of compound **7**.



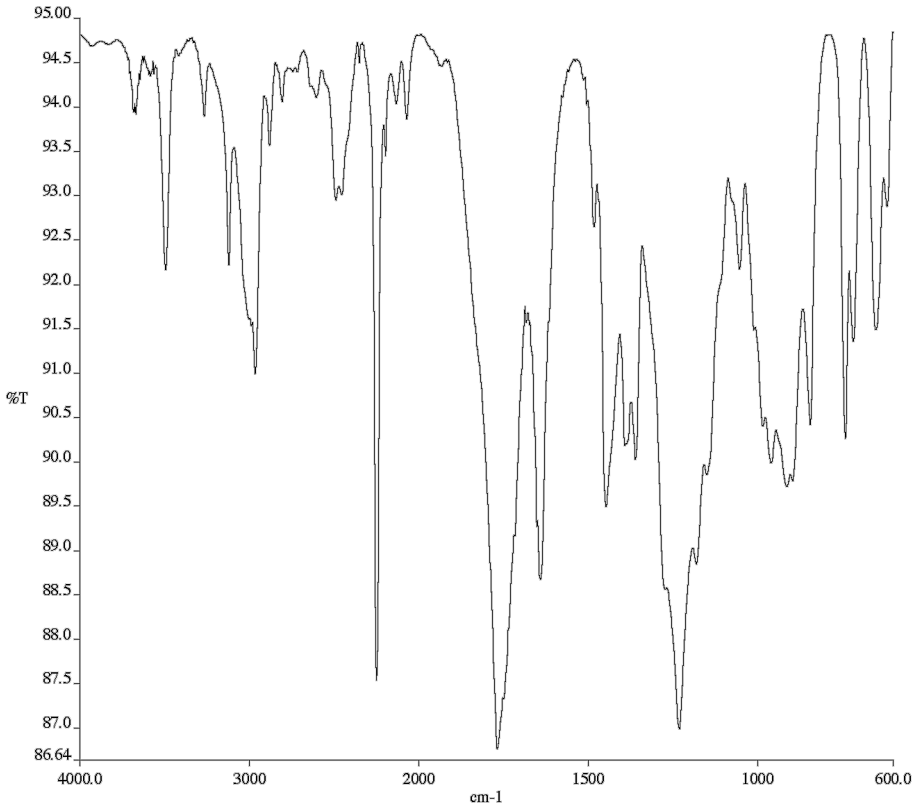
Infrared spectrum (Thin Film, NaCl) of compound **7**.



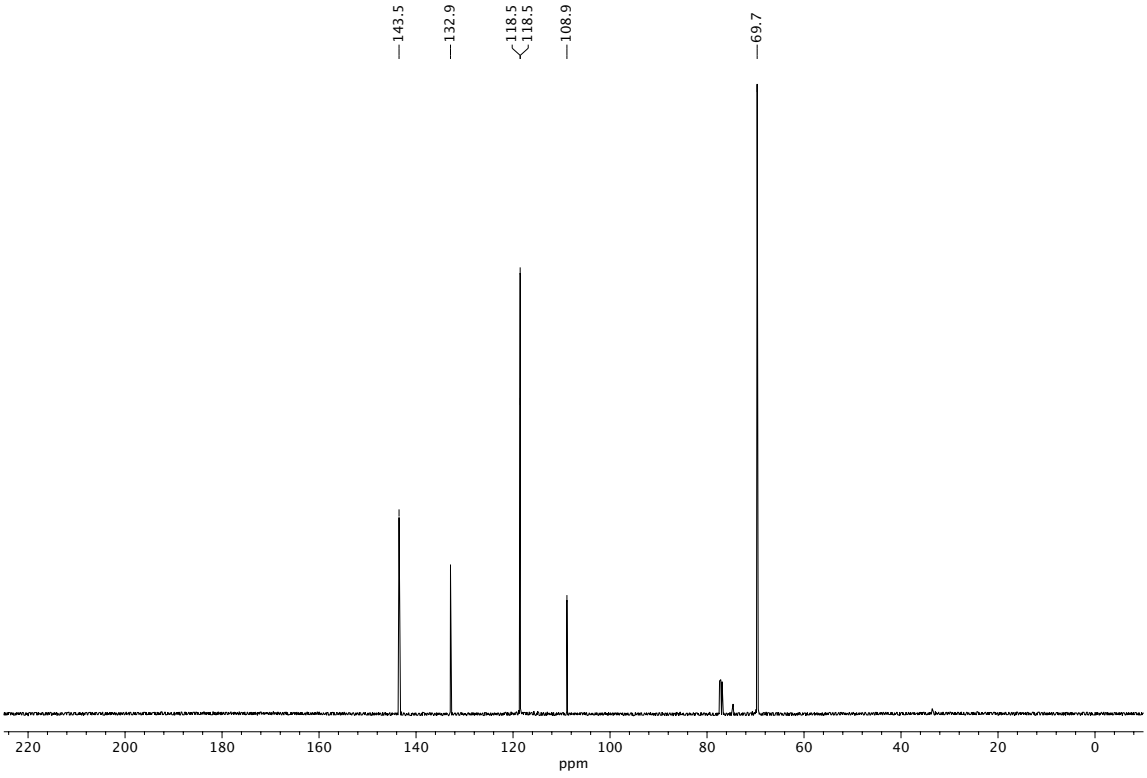
^{13}C NMR (125 MHz, $CDCl_3$) of compound **7**.



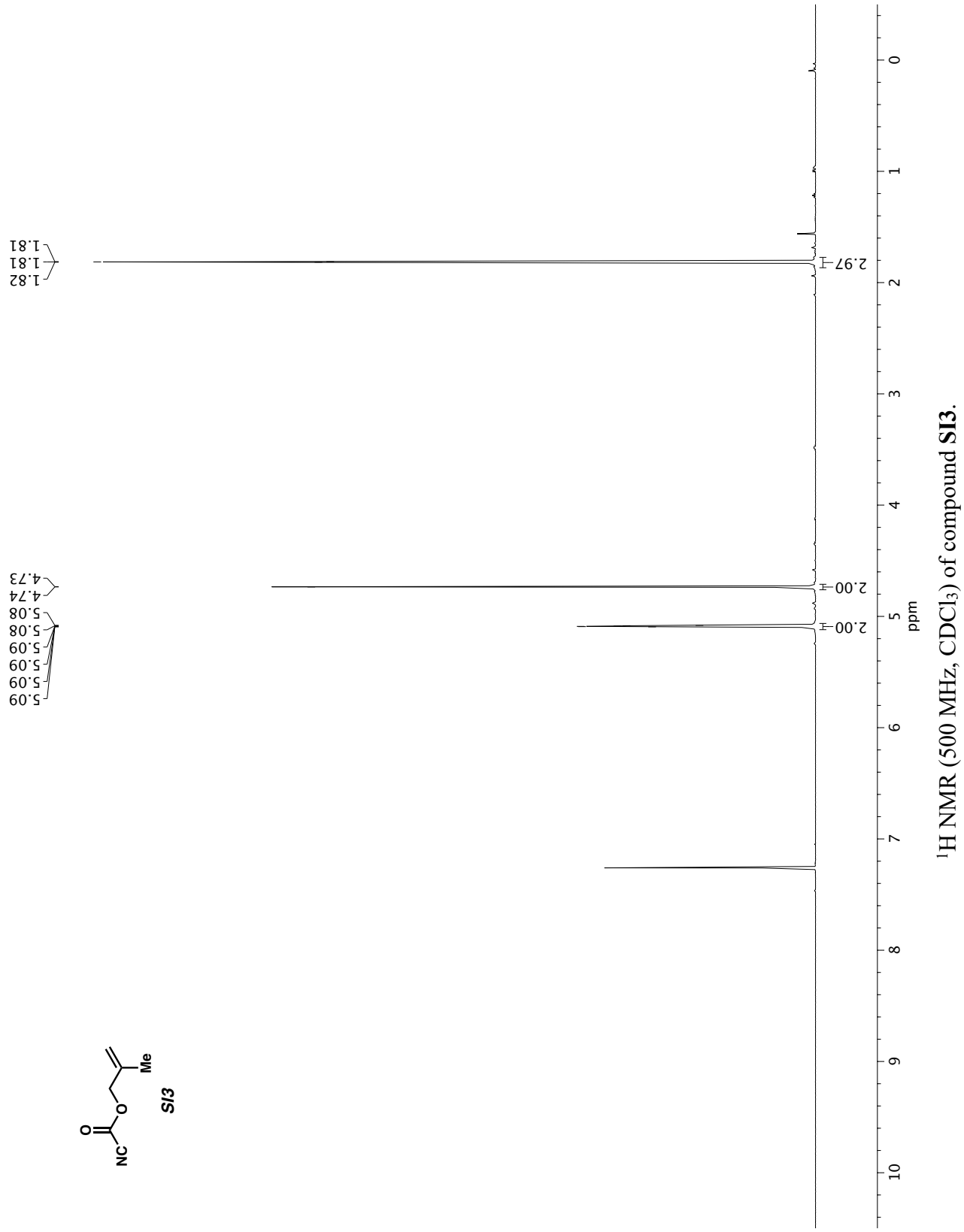
^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI1**.



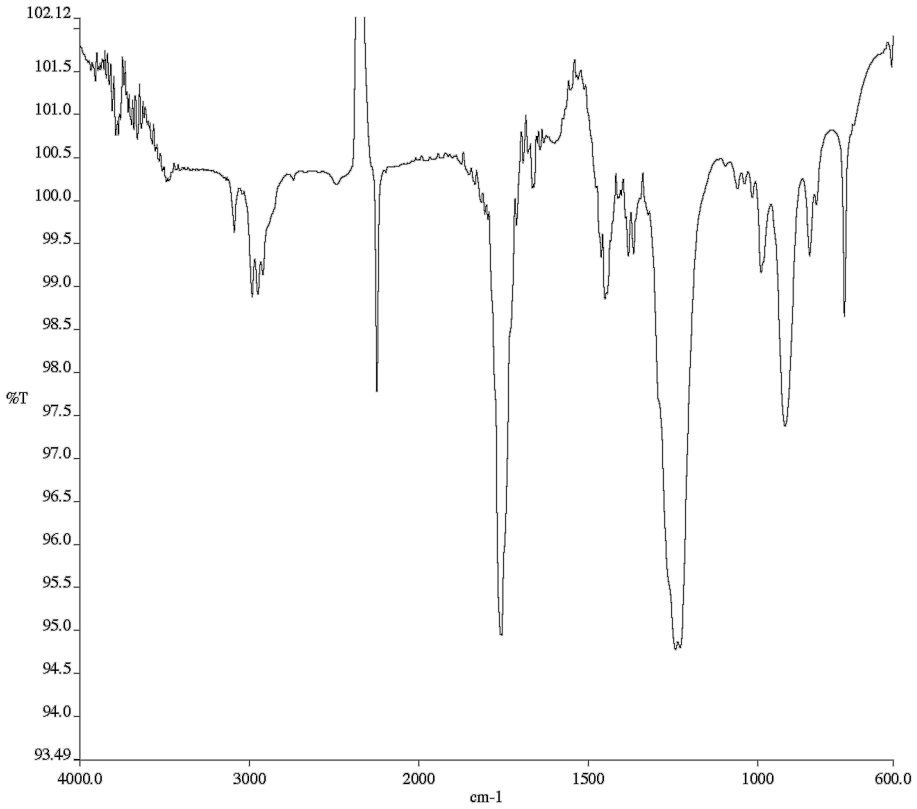
Infrared spectrum (Thin Film, NaCl) of compound **SI1**.



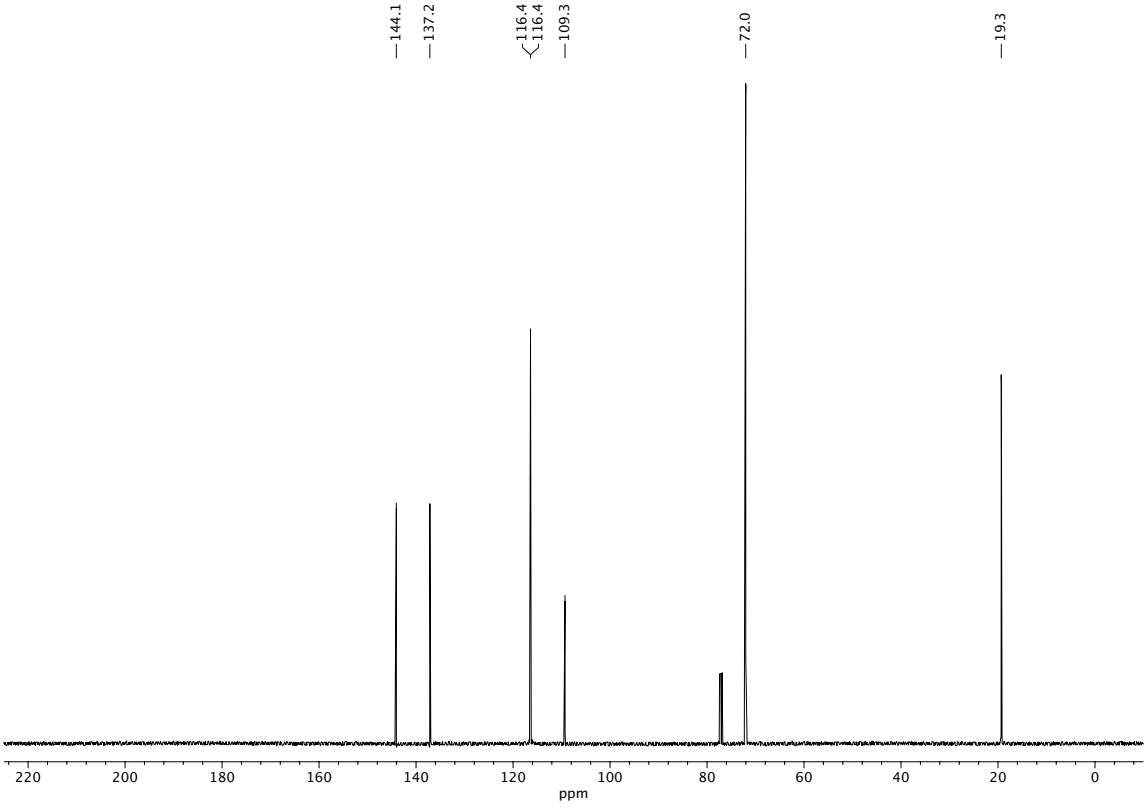
^{13}C NMR (125 MHz, $CDCl_3$) of compound **SI1**.



^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI3**.



Infrared spectrum (Thin Film, NaCl) of compound **SI3**.



^{13}C NMR (125 MHz, $CDCl_3$) of compound **SI3**.