Asymmetric Synthesis of All-Carbon Quaternary Spirocycles via a Catalytic Enantioselective Allylic Alkylation Strategy

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Materials and Methods

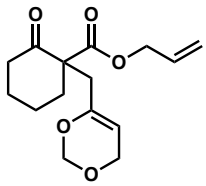
Unless otherwise stated, reactions were performed in flame-dried glassware under an argon or nitrogen atmosphere using dry, deoxygenated solvents. Solvents were dried by passage through an activated alumina column under argon. Commercially obtained reagents were used as received. Chemicals were purchased from Sigma Aldrich/Strem/Alfa Aesar/Oakwood Chemicals and used as received. Reaction temperatures were controlled by an IKAmag temperature modulator. Glove box manipulations were performed under a nitrogen atmosphere. Thin-layer chromatography (TLC) and preparatory TLC was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm) and visualized by UV fluorescence quenching, $KMnO_4$, or *p*-anisaldehyde staining. Silia*Flash* P60 Academic Silica gel (particle size 0.040–0.063 mm) was used for flash chromatography. Analytical chiral HPLC was performed with an Agilent 1100 Series HPLC utilizing a Chiralpak IC column (4.6 mm x 25 cm) or Chiralpak AD-H column (4.6 mm x 25 cm),

both obtained from Daicel Chemical Industries, Ltd. with visualization at 210 nm. Analytical SFC was performed with a Mettler SFC supercritical CO_2 analytical chromatography system utilizing a Chiralpak OJ-H column (4.6 mm x 25 cm) obtained from Daicel Chemical Industries, Ltd. with visualization at 210 nm. ^{1}H NMR spectra were recorded on a Bruker Avance HD 400 MHz spectrometer and are reported relative to residual $CHCl_3$ (δ 7.26 ppm). ^{13}C NMR spectra were recorded on a Bruker Avance HD 400 MHz spectrometer and are reported relative to residual $CDCl_3$ (δ 77.16 ppm). Data for ^{1}H NMR are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sept = septuplet, m = multiplet, br s = broad singlet. Data for ^{13}C NMR are reported in terms of chemical shifts (δ ppm). Some reported spectra include minor solvent impurities of benzene (δ 7.36 ppm), water (δ 1.56 ppm), ethyl acetate (δ 4.12, 2.05, 1.26 ppm), methylene chloride (δ 5.30 ppm), grease (δ 1.26, 0.86 ppm), and/or silicon grease (δ 0.07 ppm), which do not impact product assignments. IR spectra were obtained using a Perkin Elmer Paragon 1000 spectrometer using thin films deposited on NaCl plates and reported in frequency of absorption (cm^{-1}). High resolution mass spectra (HRMS) were obtained from the Caltech Mass Spectral Facility using a JEOL JMS-600H High Resolution Mass Spectrometer in fast atom bombardment (FAB+) or electron ionization (EI+) mode, or an Agilent 6200 Series TOF with an Agilent G1978A Multimode source in electrospray ionization (ESI+), atmospheric pressure chemical ionization (APCI+), or mixed ionization mode (MM: ESI-APCI+). Optical rotations were measured with a Jasco P-2000 polarimeter operating on the sodium D-line (589 nm), using a 100 mm pathlength cell and are reported as: $[\alpha]_D^T$ (concentration in g/100 mL, solvent).

List of Abbreviations: ee – enantiomeric excess, HPLC – high-performance liquid chromatography, SFC – supercritical fluid chromatography, TLC – thin-layer chromatography, EtOAc – ethyl acetate, THF – tetrahydrofuran, IPA – isopropanol, DMF – dimethylformamide

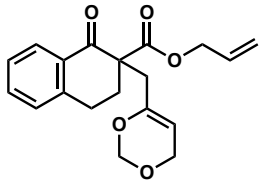
Preparation of Known Compounds: Previously reported methods were used to prepare ligand (*S,*)-**L1**[1] and 6-(bromomethyl)-4*H*-1,3-dioxin[2].

Experimental Procedures and Spectroscopic Data for the Synthesis of Allylic Alkylation Substrates

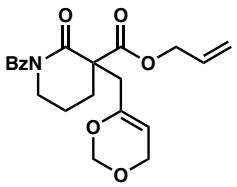


Allyl 1-((4*H*-1,3-dioxin-6-yl)methyl)-2-oxocyclohexane-1-carboxylate (1a). Allyl 2-oxocyclohexane-1-carboxylate[3] (0.20 g, 1.1 mmol, 1 equiv), K_2CO_3 (0.76 g, 5.5 mmol, 5 equiv), and 6-(bromomethyl)-4*H*-1,3-dioxin[2] (0.30 g, 1.7 mmol, 1.5 equiv) were dissolved in acetone (5 mL). The resulting reaction mixture was heated under reflux for 18 h, whereupon the reaction was cooled to ambient temperature, filtered through celite with

acetone (10 mL), and concentrated under reduced pressure. The crude product was purified by silica gel flash column chromatography (15% EtOAc/hexanes) to give ester **1a** as a colorless oil (0.26 g, 84% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83 (ddt, *J* = 17.2, 10.4, 5.9 Hz, 1H), 5.31 – 5.12 (m, 2H), 4.89 – 4.80 (m, 2H), 4.66 (t, *J* = 2.6 Hz, 1H), 4.57 – 4.48 (m, 2H), 4.14 – 4.09 (m, 2H), 2.76 (dt, *J* = 15.0, 1.6 Hz, 1H), 2.56 (dt, *J* = 13.9, 3.2 Hz, 1H), 2.43 – 2.25 (m, 2H), 2.24 – 2.16 (m, 1H), 2.01 – 1.89 (m, 1H), 1.82 – 1.63 (m, 2H), 1.56 (dddd, *J* = 17.0, 12.4, 8.4, 4.4 Hz, 1H), 1.36 (ddd, *J* = 13.9, 12.2, 4.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.4, 170.4, 150.3, 131.6, 118.8, 100.8, 90.3, 65.9, 63.7, 59.8, 40.9, 38.8, 35.7, 27.5, 22.3; IR (Neat Film, NaCl) 3083, 2944, 2867, 2796, 1715, 1682. 1648, 1451, 1372, 1314, 1175, 1092, 990, 927, 847, 761 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{15}H_{19}O_5$ [M+H]–H_2: 279.1232, found 279.1224.



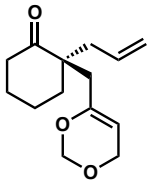
Allyl 2-((4*H*-1,3-dioxin-6-yl)methyl)-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (1b). Allyl 1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate[3] (0.60 g, 2.8 mmol, 1 equiv), Cs_2CO_3 (1.6 g, 5.0 mmol, 1.8 equiv), and 6-(bromomethyl)-4*H*-1,3-dioxin[2] (0.55 g, 3.1 mmol, 1.1 equiv) were dissolved in DMF (19 mL). The resulting reaction mixture was heated to 70 °C for 18 h, whereupon the reaction was cooled to ambient temperature, poured into H_2O (40 mL), and the aqueous layer was extracted with EtOAc (3 x 25 mL). The combined organics were washed with brine (25 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by silica gel flash column chromatography (10% EtOAc/hexanes) to give ester **1b** as a pale yellow oil (0.65 g, 71% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.47 (td, *J* = 7.5, 1.5 Hz, 1H), 7.34 – 7.27 (m, 1H), 7.21 (dd, *J* = 7.6, 1.2 Hz, 1H), 5.80 (ddt, *J* = 17.2, 10.5, 5.5 Hz, 1H), 5.27 – 5.06 (m, 2H), 4.93 (s, 2H), 4.83 (t, *J* = 2.6 Hz, 1H), 4.56 (dq, *J* = 5.6, 1.6 Hz, 2H), 4.20 (dt, *J* = 2.6, 1.3 Hz, 2H), 3.22 – 3.07 (m, 1H), 3.01 – 2.73 (m, 3H), 2.64 (dt, *J* = 13.9, 4.6 Hz, 1H), 2.23 – 2.11 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.2, 170.8, 150.5, 143.3, 133.6, 132.0, 131.6, 128.9, 128.3, 126.8, 118.3, 101.4, 90.5, 66.0, 64.0, 56.8, 38.4, 30.5, 26.1; IR (Neat Film, NaCl) 2929, 2852, 1730, 1688, 1600, 1453, 1371, 1313, 1294, 1232, 1172, 1093, 987, 950, 846, 744 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{19}H_{19}O_5$ [M+H]–H_2: 327.1232, found 3267.1223.



Allyl 3-((4*H*-1,3-dioxin-6-yl)methyl)-1-benzoyl-2-oxopiperidine-3-carboxylate (1c). Allyl 1-benzoyl-2-oxopiperidine-3-carboxylate[4] (0.20 g, 0.70 mmol, 1 equiv), Cs_2CO_3

(0.41 g, 1.3 mmol, 1.8 equiv), and 6-(bromomethyl)-4*H*-1,3-dioxin[2] (0.14 g, 0.77 mmol, 1.1 equiv) were dissolved in DMF (5 mL). The resulting reaction mixture was heated to 70 °C for 18 h, whereupon the reaction was cooled to ambient temperature, poured into H_2O (40 mL), and the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organics were washed with brine (10 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by silica gel flash column chromatography (25% EtOAc/hexanes) to give ester **1c** as a pale yellow oil (0.13 g, 49% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.66 (m, 2H), 7.53 – 7.42 (m, 1H), 7.42 – 7.33 (m, 2H), 5.99 (ddt, *J* = 17.2, 10.4, 6.0 Hz, 1H), 5.49 – 5.28 (m, 2H), 5.05 – 4.93 (m, 2H), 4.78 (dt, *J* = 3.0, 1.5 Hz, 1H), 4.72 (ddt, *J* = 6.0, 1.7, 0.8 Hz, 2H), 4.20 (dq, *J* = 2.7, 1.2 Hz, 2H), 3.94 – 3.66 (m, 2H), 2.98 – 2.87 (m, 1H), 2.74 – 2.62 (m, 1H), 2.50 – 2.33 (m, 1H), 2.14 – 1.92 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.1, 171.4, 171.3, 150.0, 135.9, 131.9, 131.5, 128.3, 128.1, 119.8, 101.7, 90.7, 66.9, 64.0, 55.3, 46.5, 39.3, 30.3, 20.6; IR (Neat Film, NaCl) 2934, 2856, 1732, 1678, 1448, 1371, 1272, 1231, 1170, 1145, 1090, 985, 939, 845, 721, 694, 647 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{21}H_{24}O_6N$ $[M+H]^+$: 386.1604, found 386.1619.

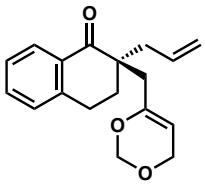
General Procedure for the Asymmetric Palladium-Catalyzed Allylic Alkylation



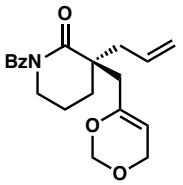
(*S*)-2-((4*H*-1,3-Dioxin-6-yl)methyl)-2-allylcyclohexan-1-one (2a). In a nitrogen-filled glove box, to a 1 dram vial equipped with a stir bar was added $Pd_2(pmdba)_3$ (11 mg, 0.01 mmol, 5 mol %), ligand (*S*)-**L1** (13 mg, 0.025 mmol, 12.5 mol %), and THF (2 mL). The resulting mixture was stirred at 25 °C for 30 min, whereupon substrate **1a** (56 mg, 0.20 mmol, 1 equiv) was added. The vial was sealed, removed from the glove box, and stirred at 25 °C. After 18 h, the reaction mixture was concentrated under reduced pressure and the crude product was purified by preparatory TLC (10% EtOAc/hexanes) to give allyl **2a** as a colorless oil (43 mg, 91% yield): 83% ee; $[\alpha]_D^{25}$ –13.1 (*c* 1.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.66 (ddt, *J* = 16.5, 10.6, 7.3 Hz, 1H), 5.09 – 4.99 (m, 2H), 4.95 (d, *J* = 5.4 Hz, 1H), 4.88 (d, *J* = 5.4 Hz, 1H), 4.68 (t, *J* = 2.6 Hz, 1H), 4.26 – 4.11 (m, 2H), 2.58 – 2.45 (m, 2H), 2.39 – 2.28 (m, 3H), 2.18 (d, *J* = 14.5 Hz, 1H), 1.84 (tdd, *J* = 6.7, 3.4, 1.6 Hz, 1H), 1.79 – 1.69 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.9, 151.5, 134.0, 118.4, 100.7, 90.4, 63.9, 51.0, 39.5, 39.4, 39.0, 36.8, 27.3, 21.0; IR (Neat Film, NaCl) 3391, 3074, 2924, 2854, 2795, 1705, 1681, 1638, 1445, 1372, 1311, 1196, 1172, 1124, 1093, 1021, 990, 911, 847, 755, 640 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{14}H_{19}O_3$ $[M+H]–H_2$: 235.1334, found 235.1341; HPLC conditions: 3% IPA, 1.0 mL/min, Chiralpak AD–H column, λ = 210 nm, t_R (min): major = 7.066, minor = 7.722.

Spectroscopic Data for the Asymmetric Palladium-Catalyzed Allylic Alkylation Products

Please note that the absolute configurations of **2a–c** were determined by analogy. [4,5] For respective HPLC conditions, please refer to Table S1.



(*S*)-2-((4*H*-1,3-Dioxin-6-yl)methyl)-2-allyl-3,4-dihydronaphthalen-1(2*H*)-one (2b). Product **2b** was prepared according to the general procedure to give a colorless oil (52 mg, 91% yield): 82% ee; $[\alpha]_D^{25}$ +0.254 (*c* 2.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.47 (td, *J* = 7.5, 1.5 Hz, 1H), 7.35 – 7.29 (m, 1H), 7.27 – 7.19 (m, 1H), 5.79 (dddd, *J* = 17.0, 10.3, 7.8, 7.0 Hz, 1H), 5.17 – 5.00 (m, 2H), 5.00 – 4.88 (m, 2H), 4.74 (t, *J* = 2.6 Hz, 1H), 4.21 (dt, *J* = 2.5, 1.2 Hz, 2H), 3.02 (dd, *J* = 7.2, 5.5 Hz, 2H), 2.69 (dq, *J* = 14.3, 1.3 Hz, 1H), 2.55 (ddt, *J* = 14.1, 7.0, 1.3 Hz, 1H), 2.34 – 2.27 (m, 1H), 2.27 – 2.21 (m, 1H), 2.11 (ddt, *J* = 6.0, 4.8, 3.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.5, 151.5, 143.2, 133.9, 133.2, 132.0, 128.8, 128.2, 126.7, 118.7, 100.8, 90.4, 64.0, 47.8, 39.6, 38.8, 30.4, 25.3; IR (Neat Film, NaCl) 3072, 3004, 2929, 2859, 2794, 1677, 1600, 1454, 1432, 1371, 1289, 1225, 1193, 1172, 1093, 1023, 989, 918, 847, 742 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{18}H_{19}O_3$ $[M+H]–H_2$: 283.1334, found 283.1338; HPLC conditions: 4% IPA, 1.0 mL/min, Chiralpak IC column, λ = 210 nm, t_R (min): major = 29.702, minor = 23.387.



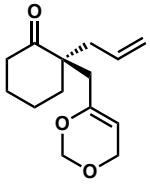
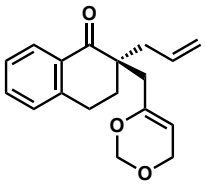
(*S*)-3-((4*H*-1,3-Dioxin-6-yl)methyl)-3-allyl-1-benzoylpiperidin-2-one (2c). Product **2c** was prepared according to the general procedure (toluene used in place of THF, reaction mixture heated to 40 °C) to give a pale yellow oil (66 mg, 95% yield): 99% ee; $[\alpha]_D^{25}$ +11.4 (*c* 3.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.31 (m, 5H), 5.76 (dddd, *J* = 17.1, 10.3, 7.7, 6.9 Hz, 1H), 5.21 – 5.09 (m, 2H), 5.06 – 4.98 (m, 2H), 4.74 (td, *J* = 2.7, 0.8 Hz, 1H), 4.23 (ddd, *J* = 2.6, 1.7, 0.8 Hz, 2H), 3.91 – 3.67 (m, 2H), 2.76 (dtd, *J* = 14.3, 1.7, 0.9 Hz, 1H), 2.59 (ddt, *J* = 13.8, 6.9, 1.3 Hz, 1H), 2.31 (ddt, *J* = 13.8, 7.7, 1.1 Hz, 1H), 2.15 – 2.09 (m, 1H), 2.04 – 1.95 (m, 3H), 1.93 – 1.83 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.1, 175.6, 151.2, 136.7, 133.3, 131.5, 128.2, 127.8, 119.6, 101.2, 90.6, 64.1, 47.0 (2C), 43.5, 41.7, 30.0, 20.0; IR (Neat Film, NaCl) 3346, 3072, 2945, 2868, 2795, 1678, 1600, 1477, 1449, 1386, 1372, 1286, 1150, 1172, 1092, 1023, 990, 919, 846, 792, 725, 696 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{20}H_{24}NO_4$ $[M+H]^+$: 342.1705, found 342.1714; SFC

conditions: 5% IPA, 2.5 mL/min, Chiralpak OJ-H column, λ = 210 nm, t_R (min): major = 11.165, minor = 10.427.

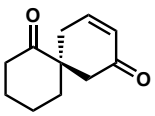
Determination of Enantiomeric Excess

Please note racemic products were synthesized using $Pd(PPh_3)_4$ in place of $Pd_2(pmdba)_3$ and (*S*)-**L1**.

Table S1: Determination of Enantiomeric Excess

Entry	Product	Assay Conditions	Retention time of major isomer (min)	Retention time of minor isomer (min)	%ee
1		HPLC Chiralpak AD-H 3% IPA isocratic, 1 mL/min	7.066	7.722	83
2		HPLC Chiralpak IC 4% IPA isocratic, 1 mL/min	29.702	23.387	82
3		SFC Chiralpak OJ-H 5% IPA isocratic, 2.5 mL/min	11.165	10.427	99

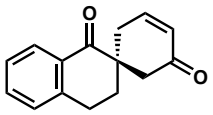
General Procedure for Spirocyclic Formation



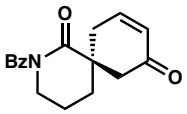
(*S*)-Spiro[5.5]undec-9-ene-1,8-dione (3a). To a sealed Biotage microwave vial, allyl **2a** (24 mg, 0.10 mmol, 1 equiv) and toluene (0.7 mL) were added. The reaction mixture was heated to 180 °C for 1 h, whereupon the reaction was cooled to 60 °C and a solution of Hoveyda-Grubbs 2nd generation catalyst (6.3 mg, 0.010 mmol, 0.10 equiv) in toluene (0.3 mL) was added. The reaction mixture was then stirred an additional 18 h at 60 °C, cooled to ambient temperature, and directly purified by preparatory TLC (15% EtOAc/hexanes)

to give spirocycle **3a** as a colorless oil (17 mg, 93% yield): $[\alpha]_D^{25}$ –1.4 (*c* 1.1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 6.81 (dt, *J* = 10.1, 4.1 Hz, 1H), 5.99 (dt, *J* = 10.0, 2.1 Hz, 1H), 2.84 (ddt, *J* = 18.8, 4.4, 1.4 Hz, 1H), 2.80 – 2.71 (m, 1H), 2.47 – 2.32 (m, 4H), 1.95 – 1.73 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.3, 197.4, 146.0, 129.5, 51.5, 45.7, 38.2, 38.1, 33.7, 27.7, 20.8; IR (Neat Film, NaCl) 3037, 2936, 2865, 1705, 1678, 1446, 1424, 1387, 1252, 1135, 736 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{11}H_{15}O_2$ $[M+H]^+$: 179.1072, found 179.1078.

Spectroscopic Data for Spirocyclic Compounds



(*S*)-3',4'-dihydro-1'*H*-spiro[cyclohexane-1,2'-naphthalen]-3-ene-1',5-dione (3b). Product **3b** was prepared according to the general procedure to give a colorless oil (18 mg, 77% yield) after preparatory TLC (15% EtOAc/hexanes): $[\alpha]_D^{25}$ –1.5 (*c* 1.2, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.50 (td, *J* = 7.5, 1.5 Hz, 1H), 7.40 – 7.30 (m, 1H), 7.26 – 7.20 (m, 1H), 6.91 – 6.77 (m, 1H), 6.10 (dt, *J* = 10.3, 2.1 Hz, 1H), 3.09 – 2.89 (m, 3H), 2.82 (d, *J* = 16.2 Hz, 1H), 2.50 – 2.38 (m, 2H), 2.27 – 2.02 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.2, 197.4, 145.6, 142.7, 133.9, 130.8, 129.5, 128.9, 128.5, 127.2, 47.7, 44.6, 32.5, 32.3, 25.0; IR (Neat Film, NaCl) 3034, 2926, 2858, 1683, 1601, 1455, 1388, 1250, 1224, 1157, 946, 750 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{15}H_{15}O_2$ $[M+H]^+$: 227.1072, found 227.1074.



(*S*)-2-benzoyl-2-azaspiro[5.5]undec-9-ene-1,8-dione (3c). Product **3c** was prepared according to the general procedure to give a colorless oil (15 mg, 53% yield) after preparatory TLC (40% EtOAc/hexanes): $[\alpha]_D^{25}$ +29.7 (*c* 0.9, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.32 (m, 5H), 6.87 (ddd, *J* = 10.2, 5.0, 3.3 Hz, 1H), 6.06 (dt, *J* = 10.1, 2.1 Hz, 1H), 3.91 – 3.74 (m, 2H), 3.09 (dt, *J* = 18.9, 3.0 Hz, 1H), 2.96 (d, *J* = 16.1 Hz, 1H), 2.59 (dd, *J* = 16.2, 1.3 Hz, 1H), 2.49 (ddt, *J* = 18.9, 5.0, 1.6 Hz, 1H), 2.09 – 1.95 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.4, 177.0, 175.1, 145.8, 135.8, 131.9, 129.2, 128.5, 127.6, 47.1, 47.0, 46.4, 34.8, 32.5, 19.3; IR (Neat Film, NaCl) 2949, 1679, 1449, 1388, 1281, 1151, 919, 729, 694, 665 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{17}H_{18}O_3N$ $[M+H]^+$: 284.1287, found 284.1277.

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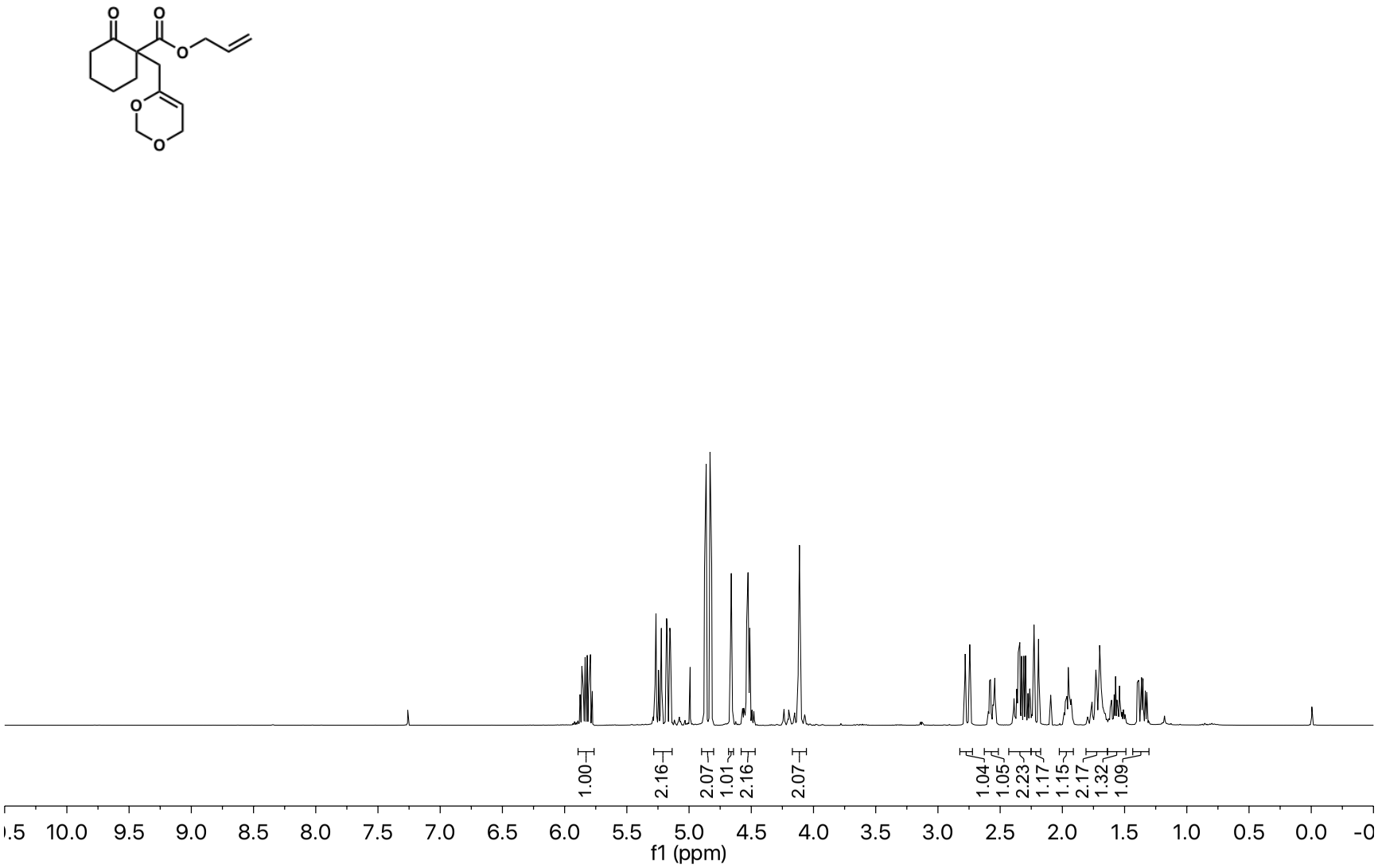
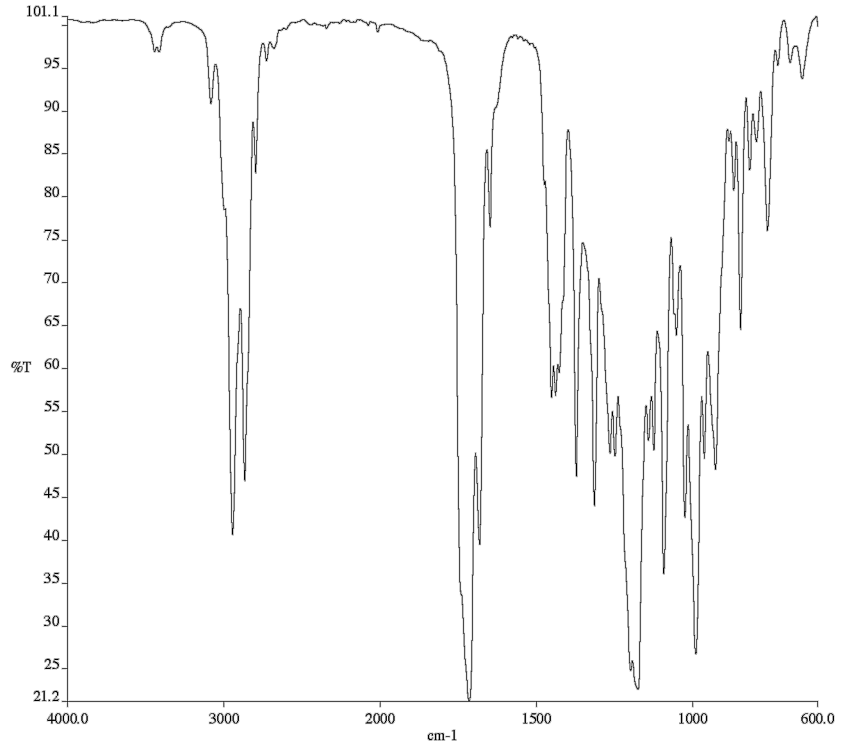
[3] Mohr, J. T.; Behenna, D. C.; Harned, A. M. Stoltz, B. M. *Angew. Chem. Int. Ed.* **2005**, *44*, 6924–6927.

[4] Behenna, D. C.; Liu, Y.; Yurino, T.; Kim, J.; White, D. E.; Virgil, S. C.; Stoltz, B. M. *Nat. Chem.* **2012**, *4*, 130–133.

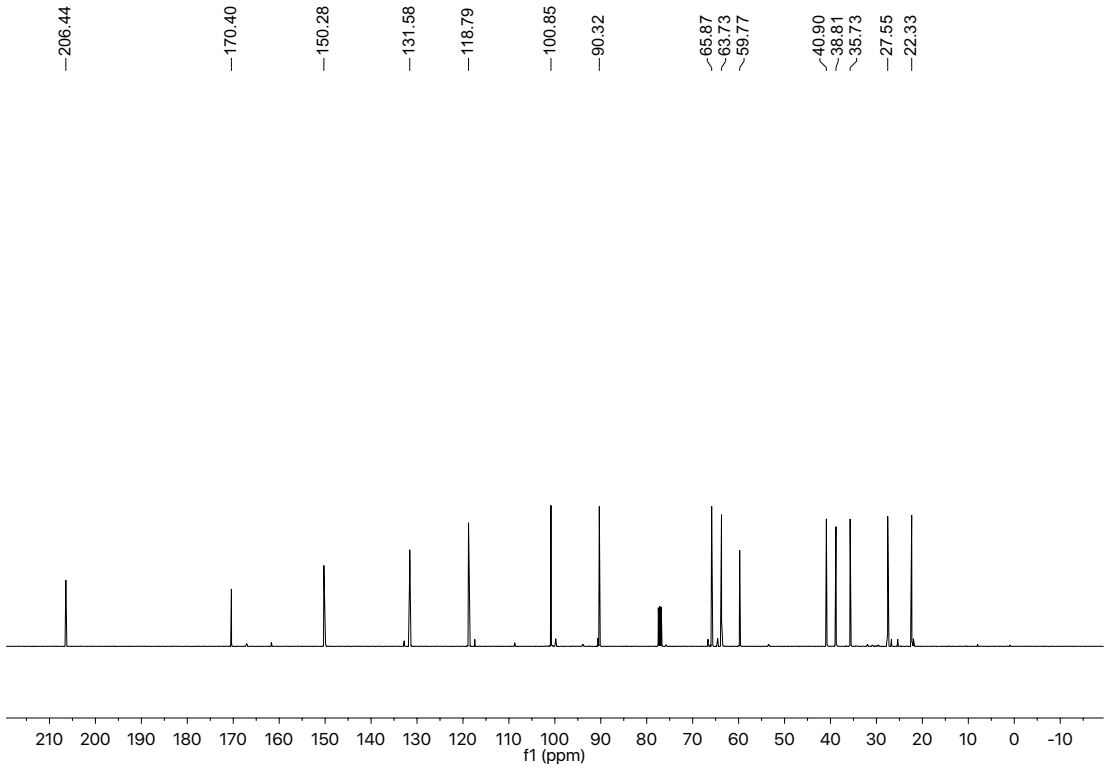
[5] Behenna, D. C.; Stoltz, B. M. *J. Am. Chem. Soc.* **2004**, *126*, 15044–15045.



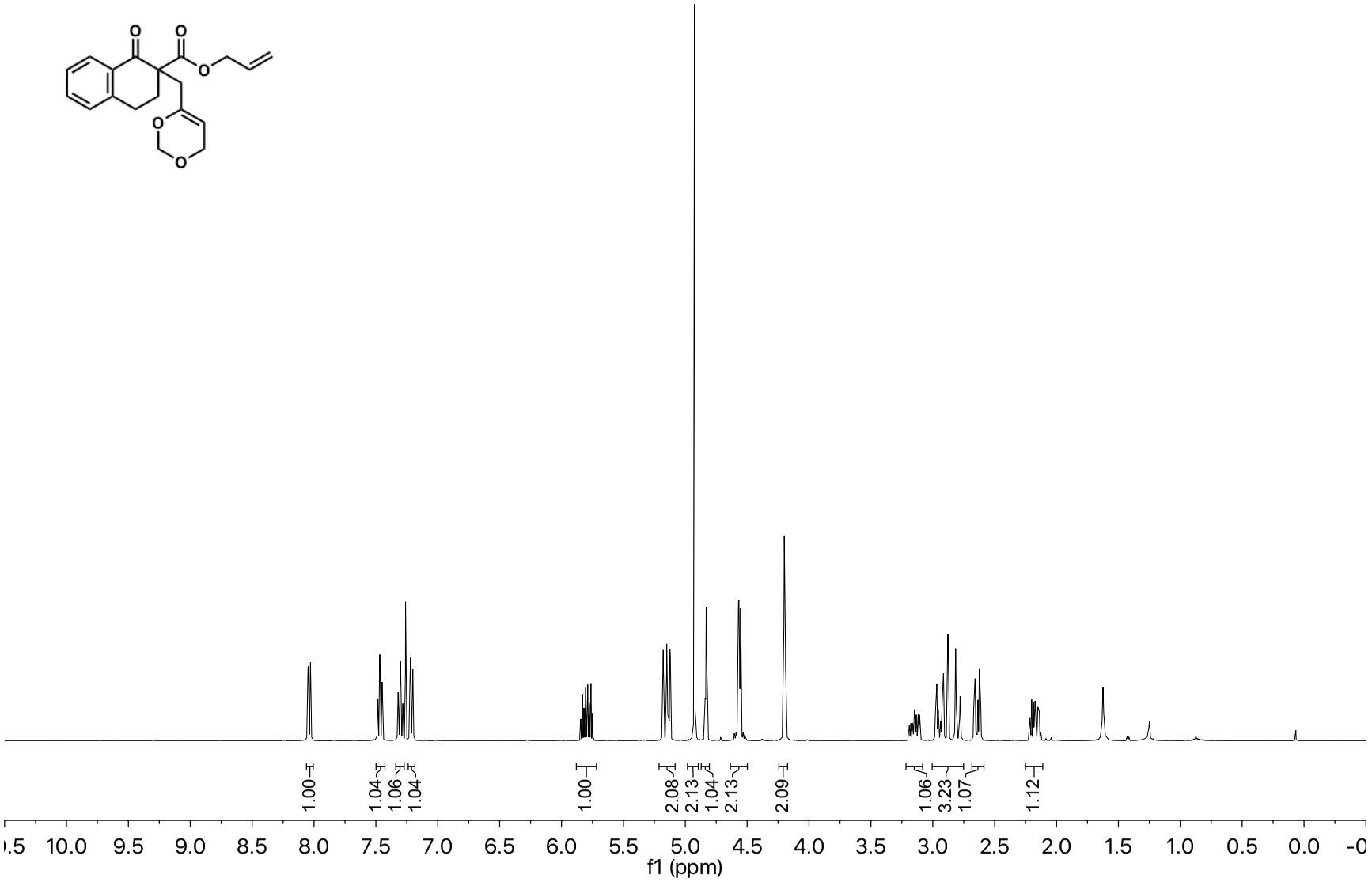
^{1}H NMR (400 MHz, $CDCl_3$) of compound **1a**.



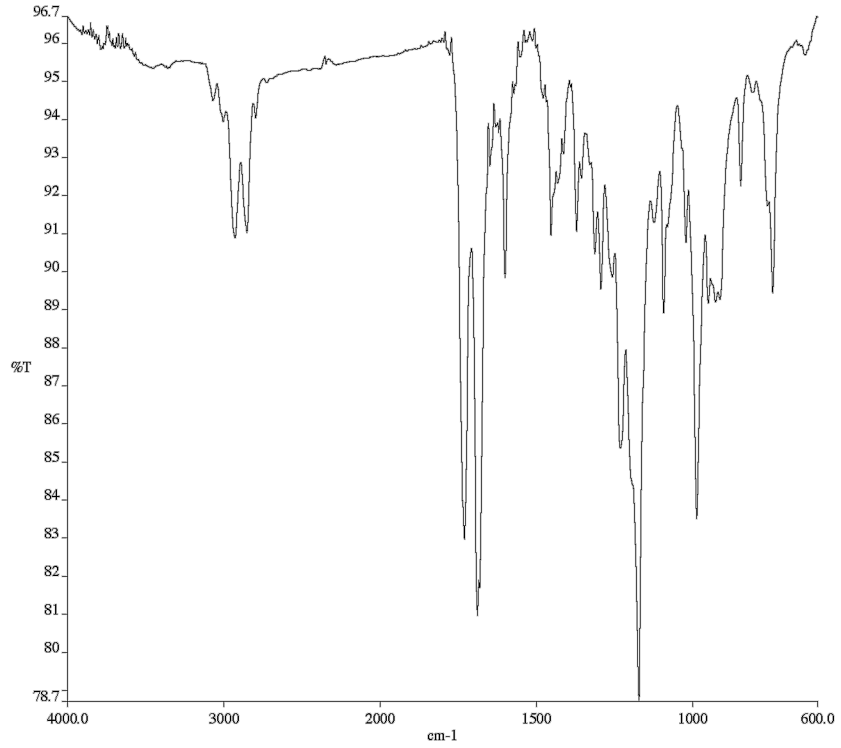
Infrared spectrum (Thin Film, NaCl) of compound **1a**.



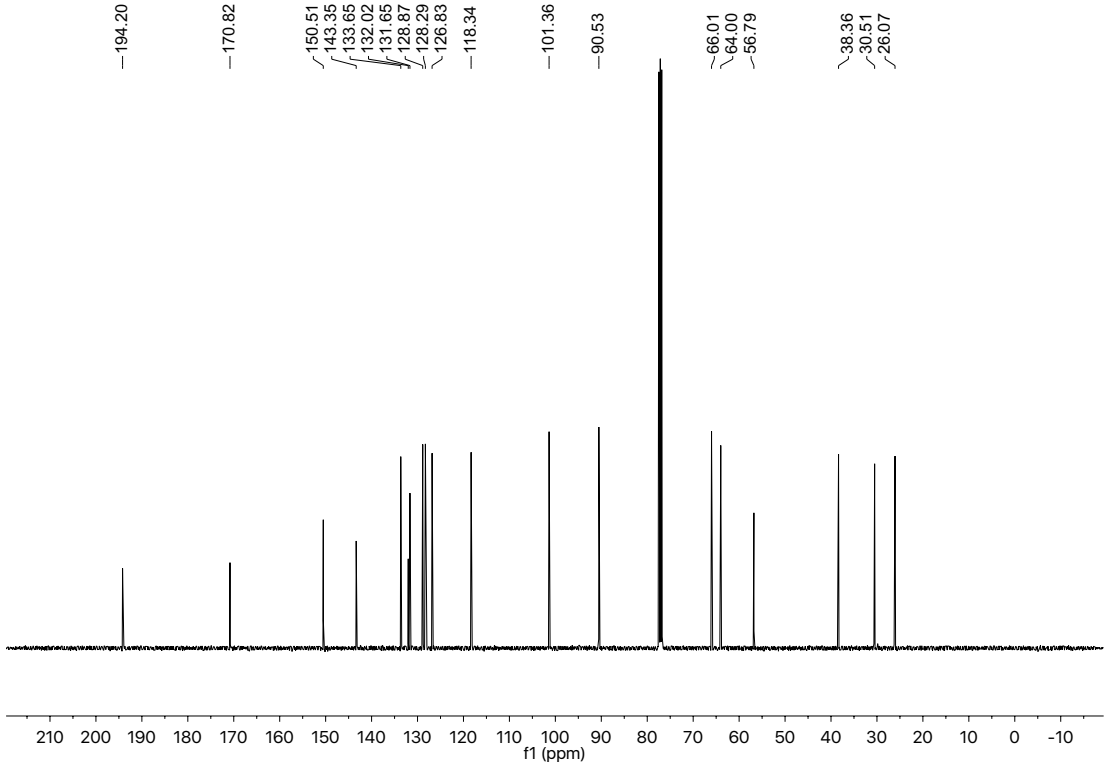
^{13}C NMR (101 MHz, $CDCl_3$) of compound **1a**.



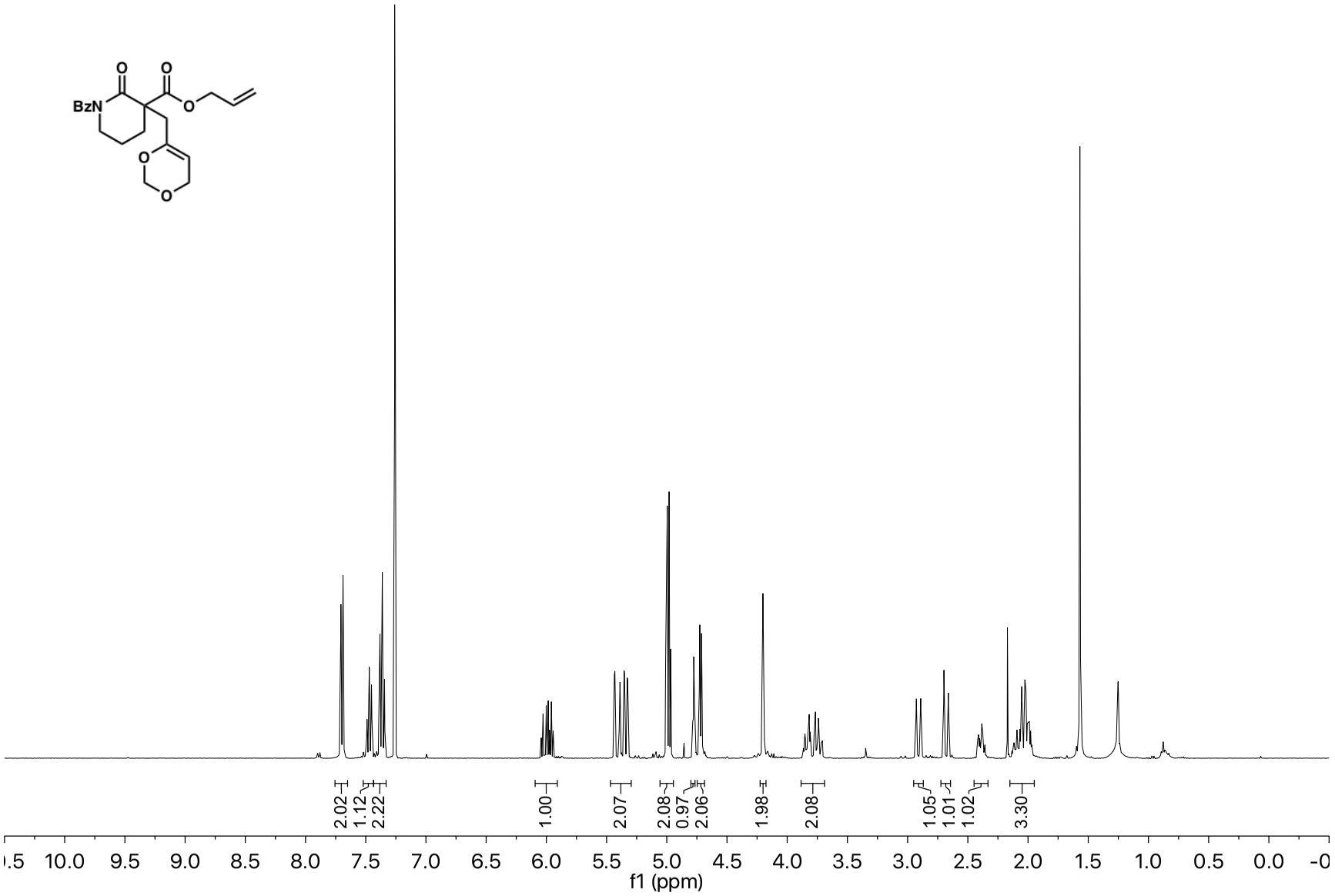
^{1}H NMR (400 MHz, $CDCl_3$) of compound **1b**.



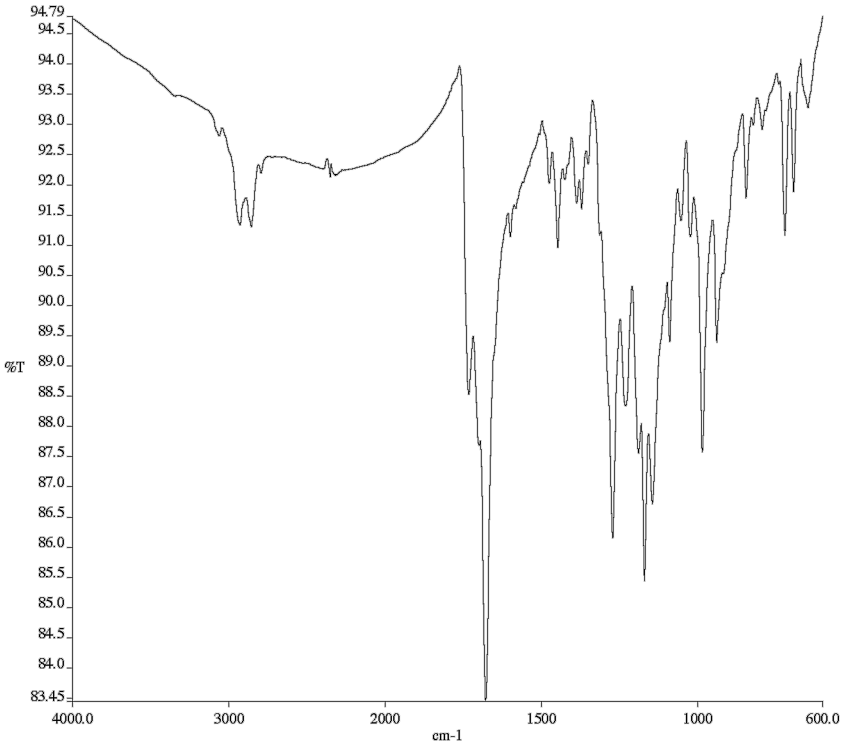
Infrared spectrum (Thin Film, NaCl) of compound **1b**.



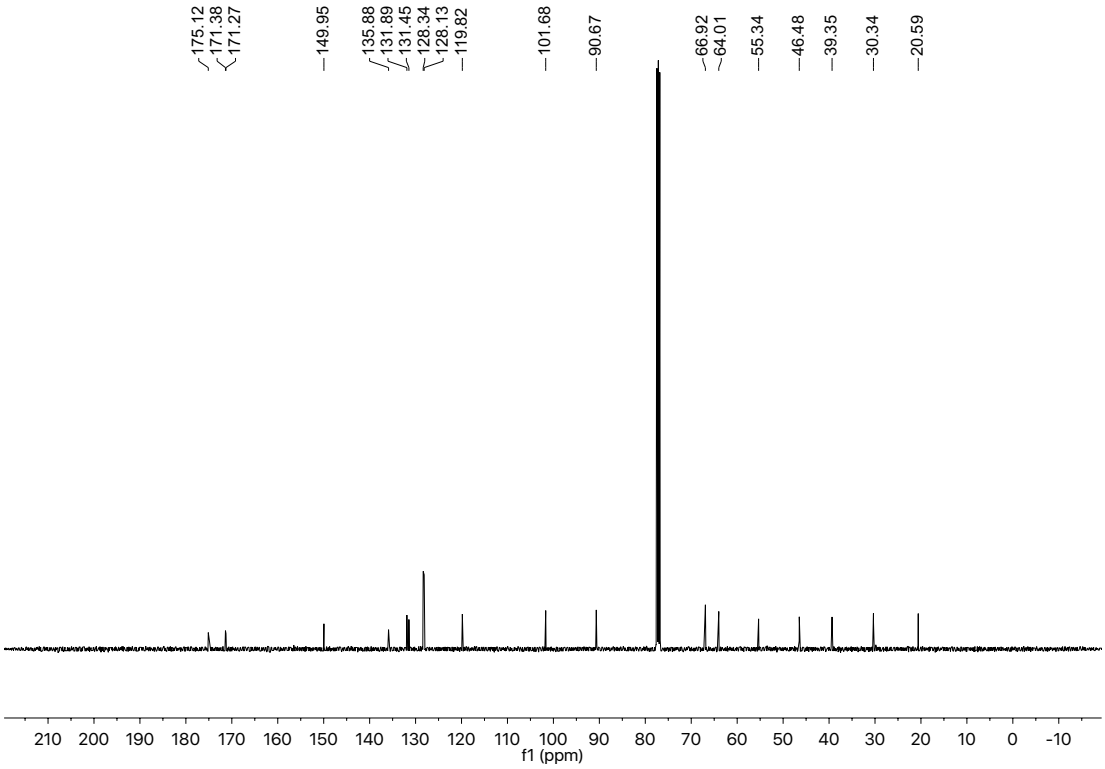
^{13}C NMR (101 MHz, $CDCl_3$) of compound **1b**.



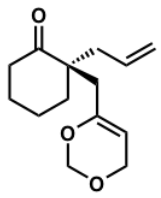
^{1}H NMR (400 MHz, $CDCl_3$) of compound **1c**.

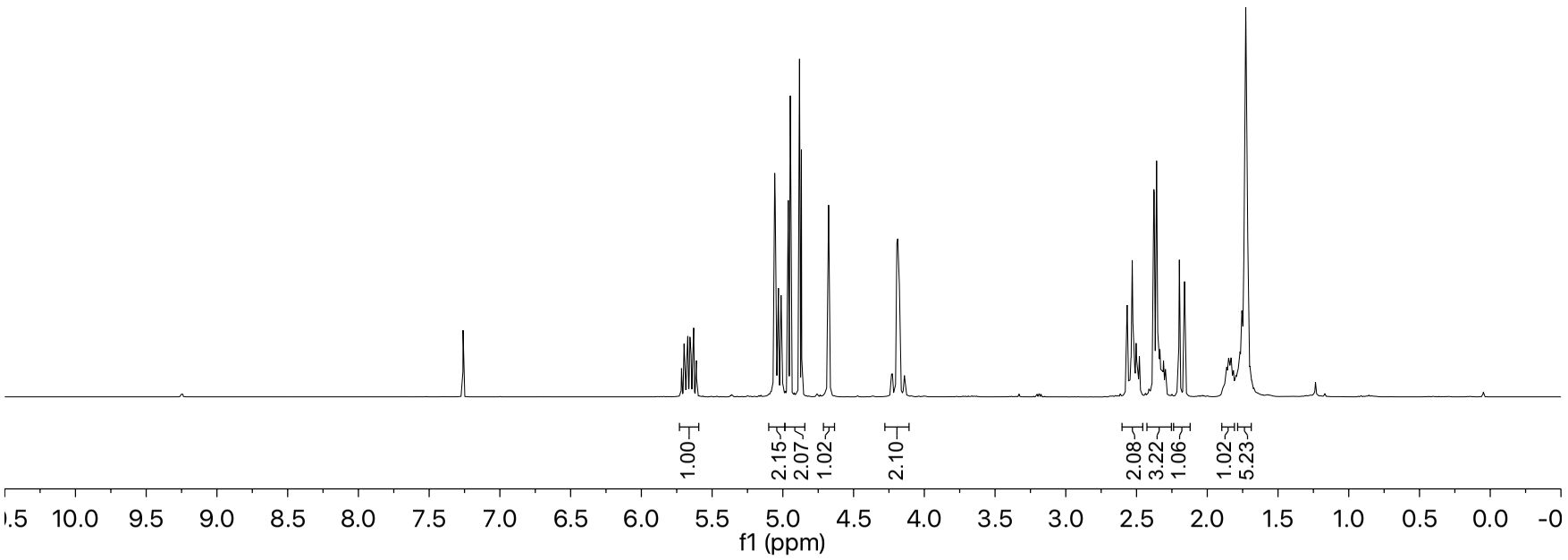


Infrared spectrum (Thin Film, NaCl) of compound **1c**.

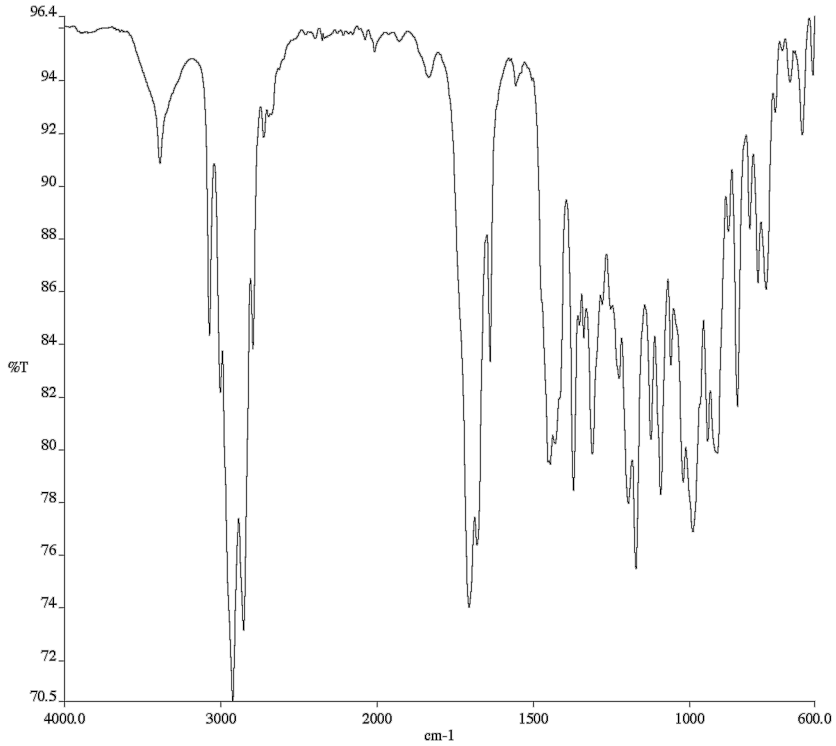


^{13}C NMR (101 MHz, $CDCl_3$) of compound **1c**.

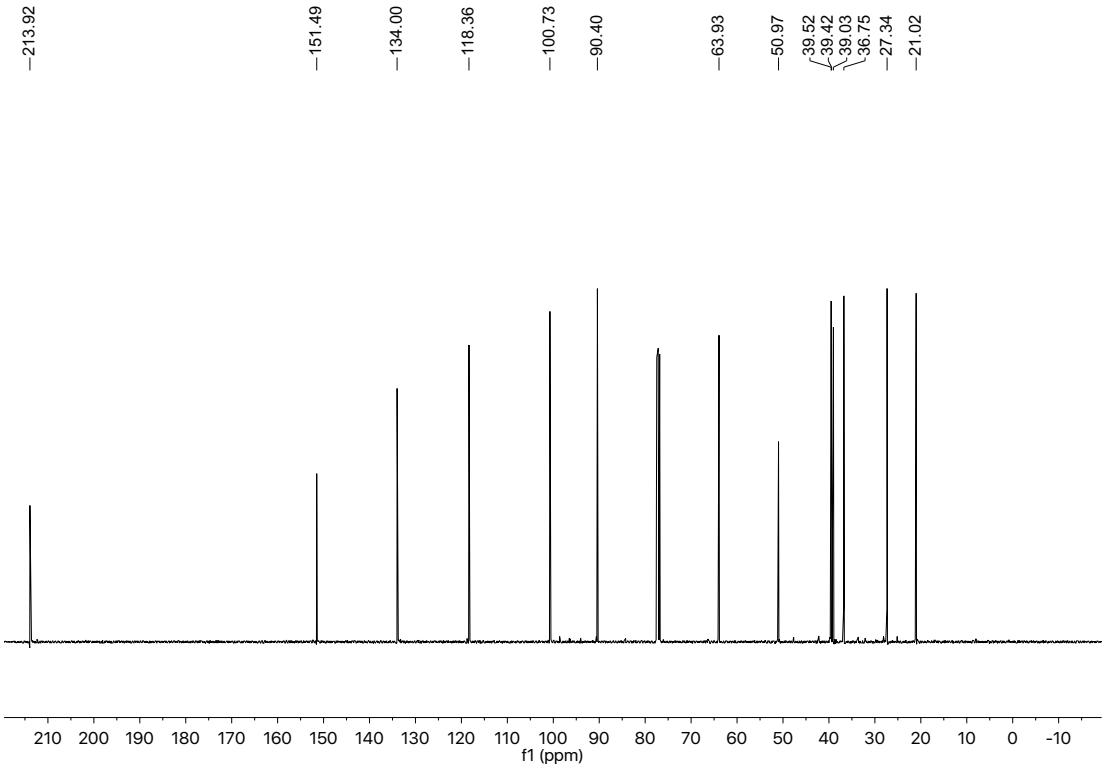




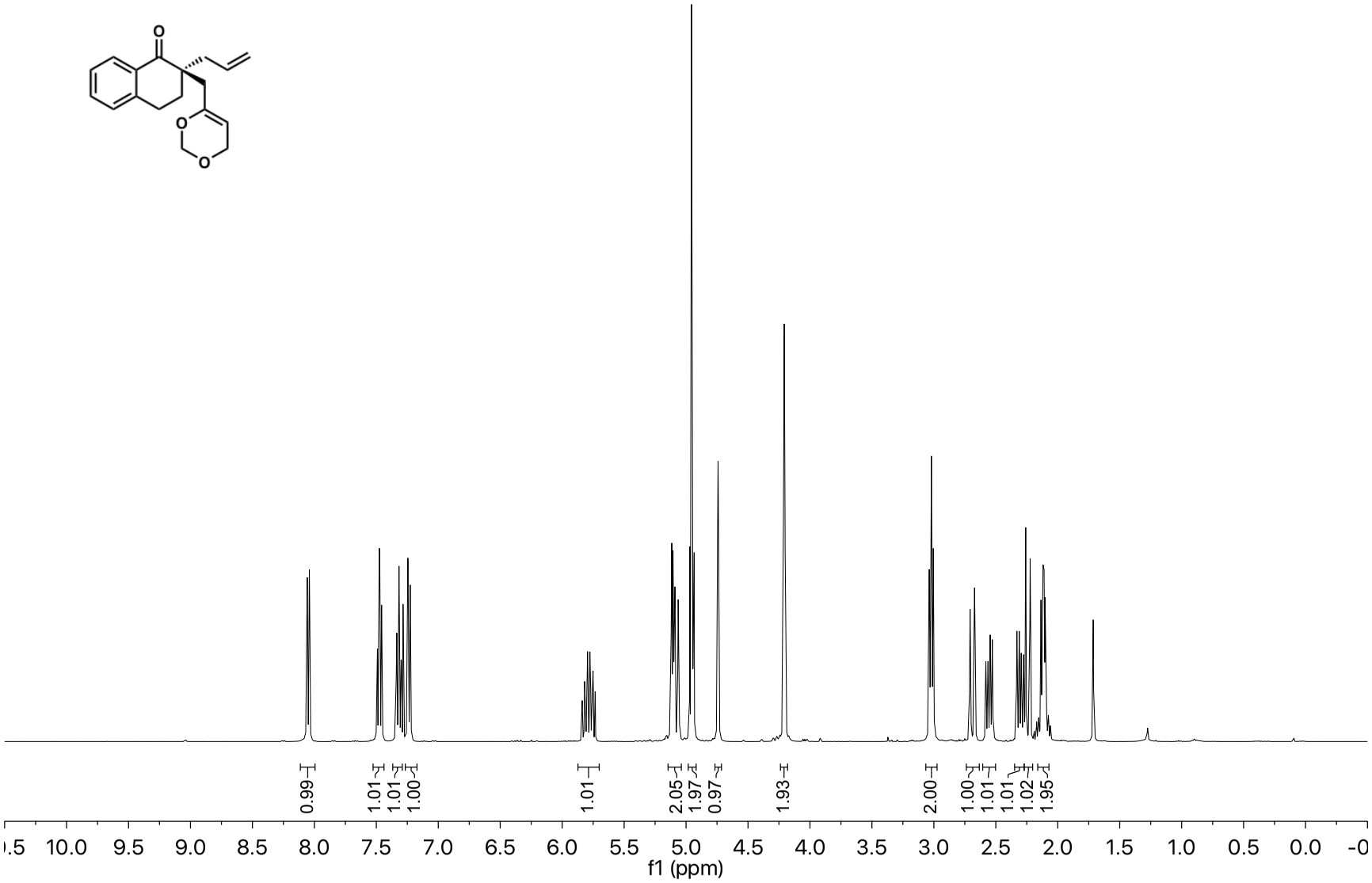
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2a**.



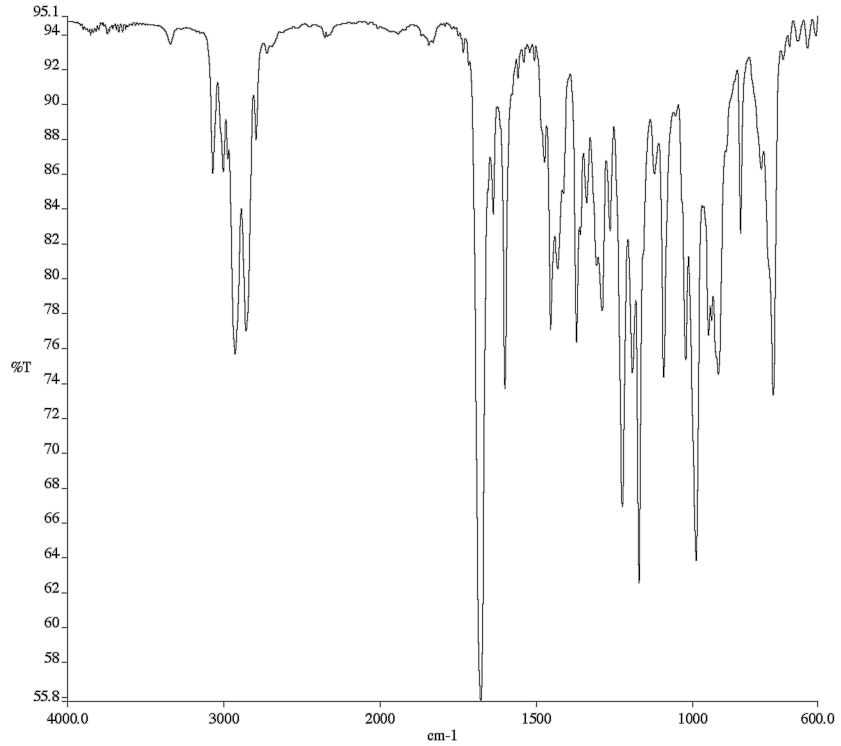
Infrared spectrum (Thin Film, NaCl) of compound **2a**.



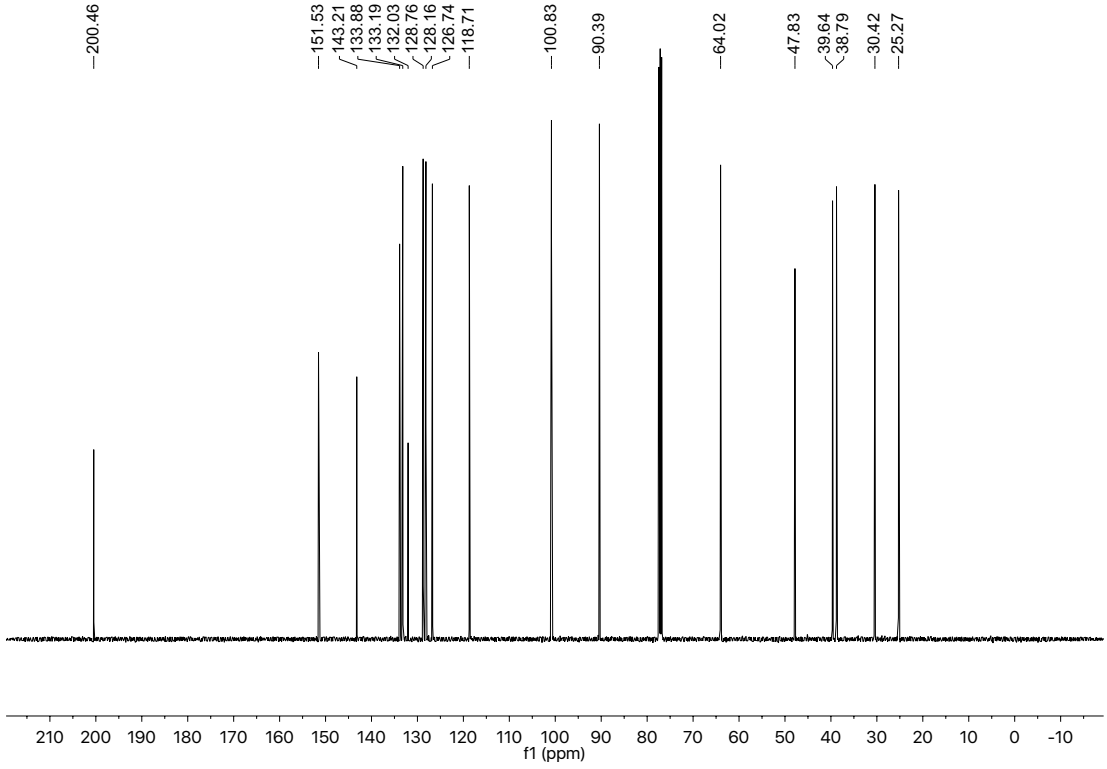
^{13}C NMR (101 MHz, $CDCl_3$) of compound **2a**.



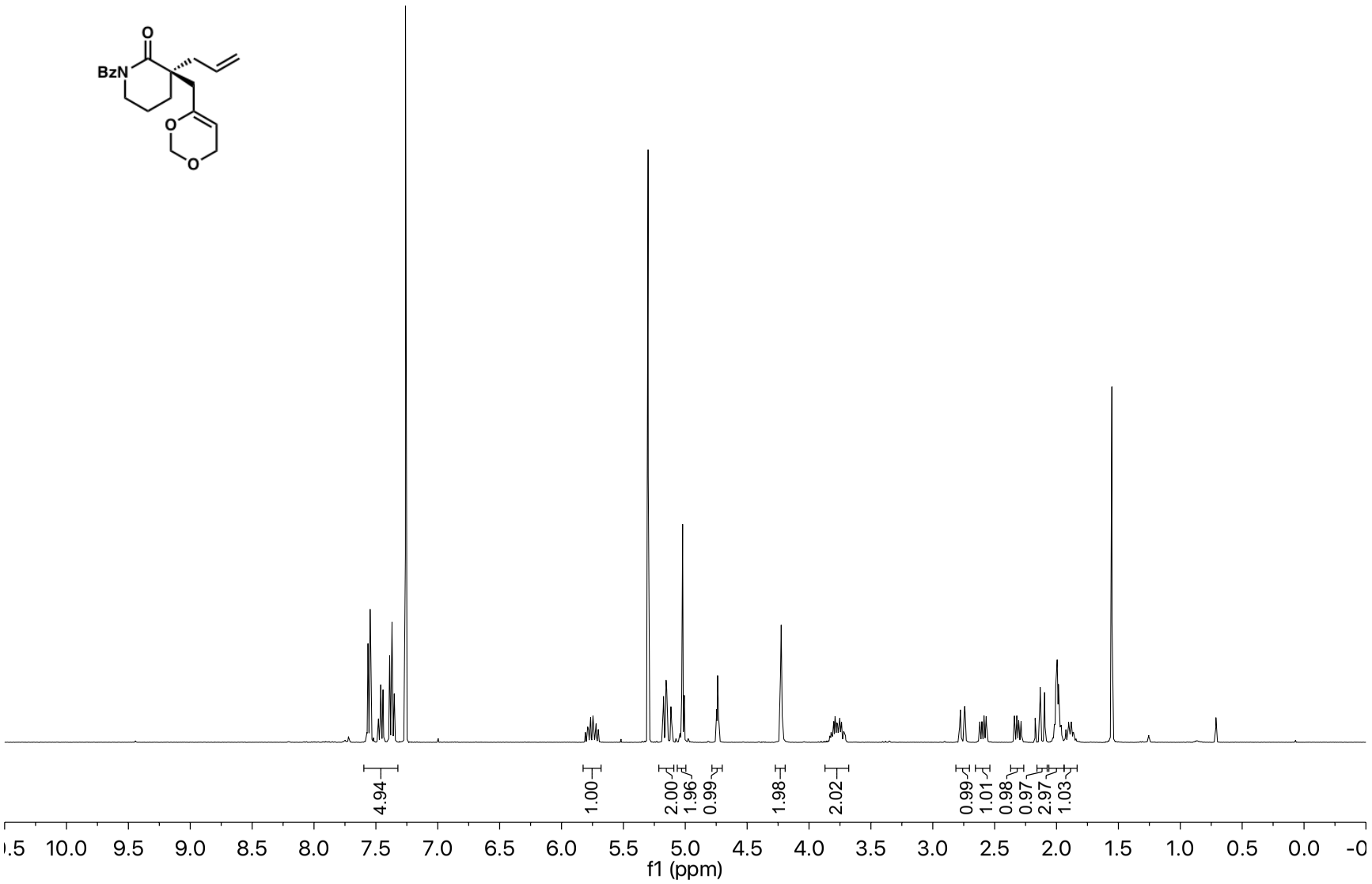
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2b**.



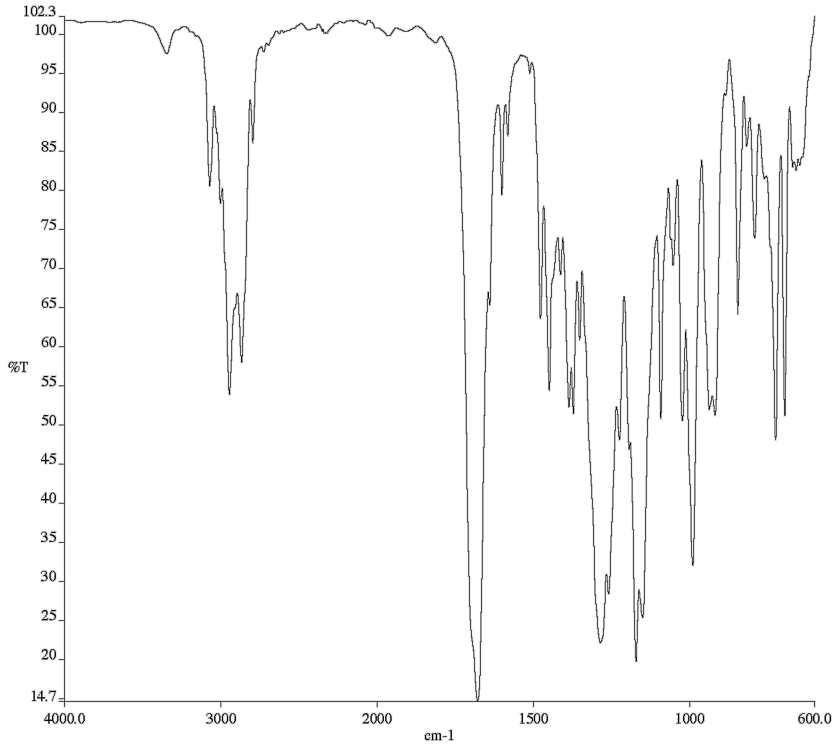
Infrared spectrum (Thin Film, NaCl) of compound **2b**.



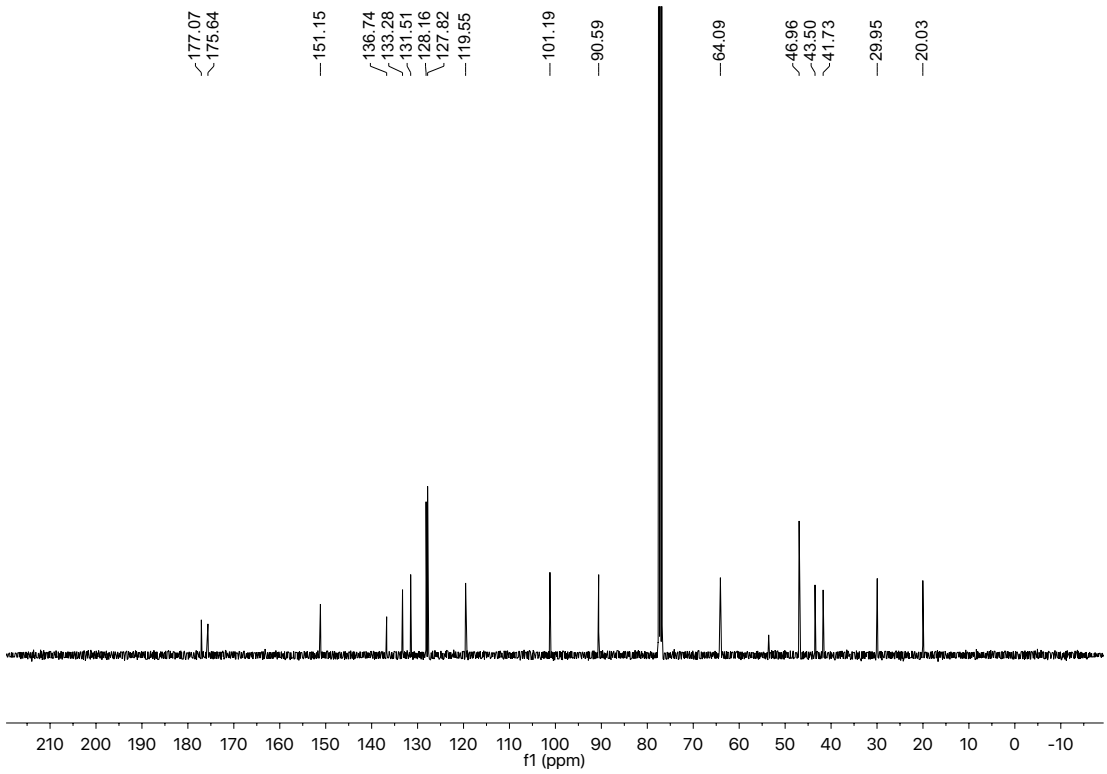
^{13}C NMR (101 MHz, $CDCl_3$) of compound **2b**.



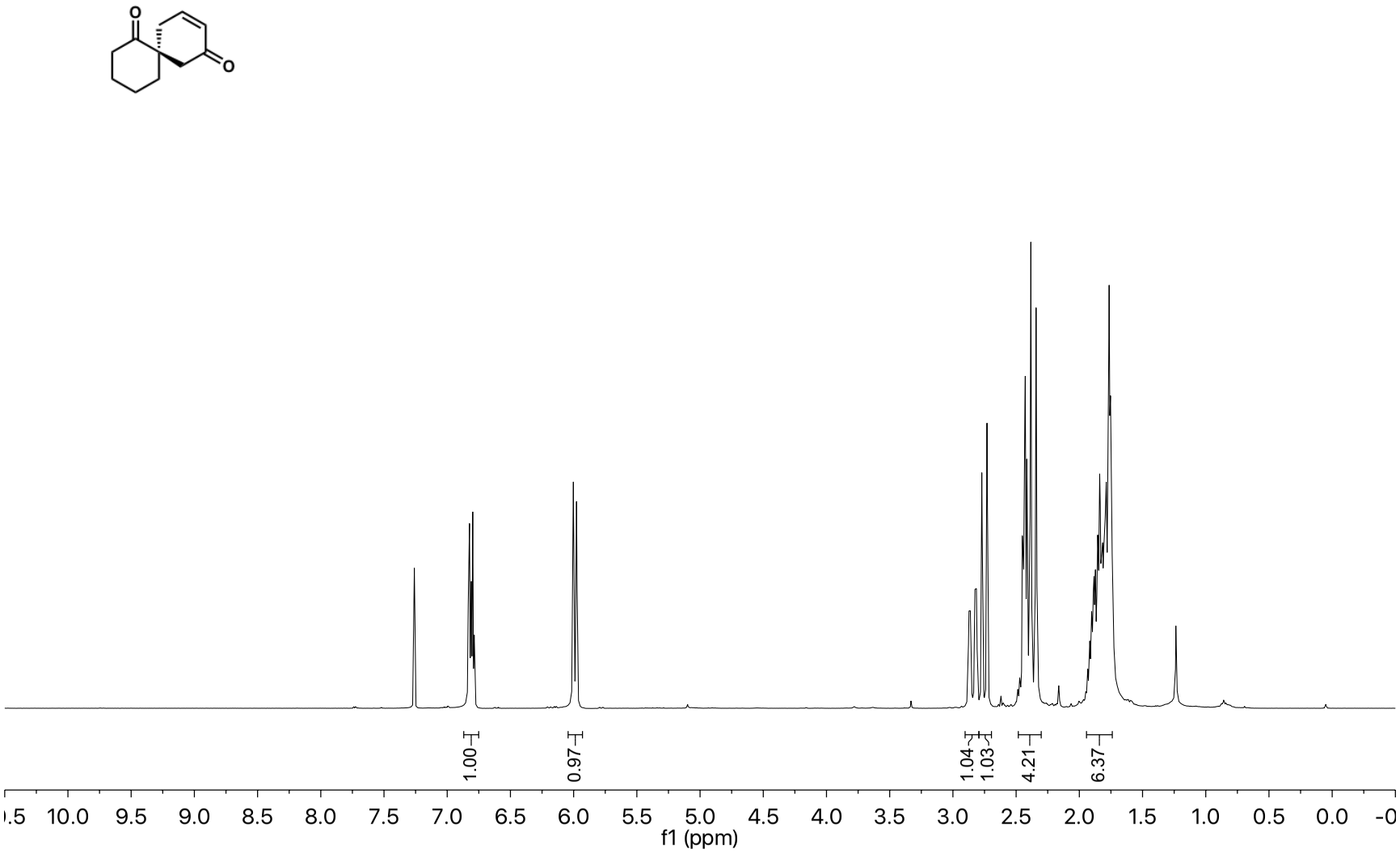
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2c**.



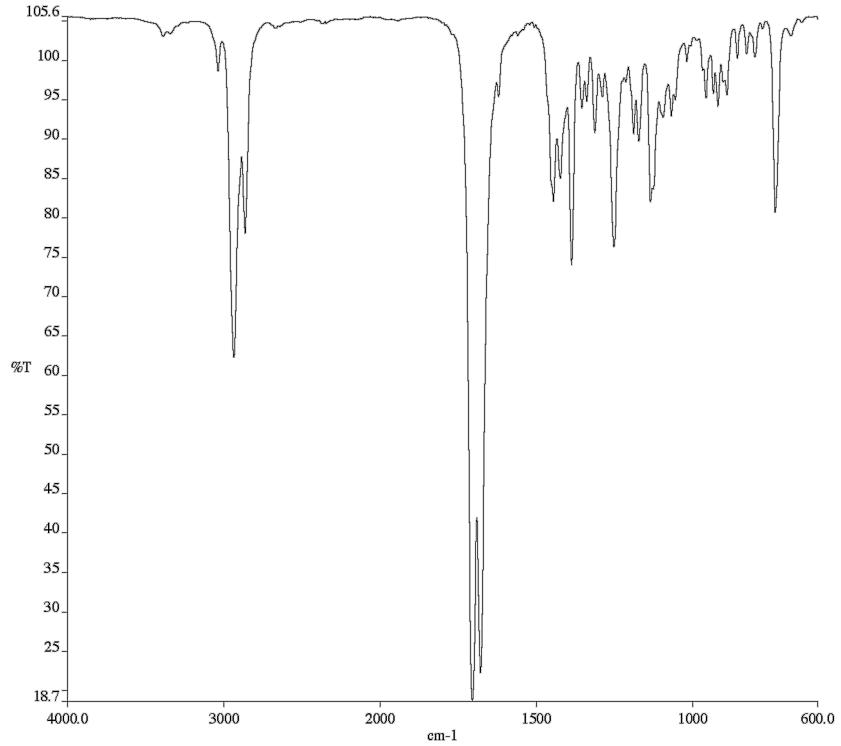
Infrared spectrum (Thin Film, NaCl) of compound **2c**.



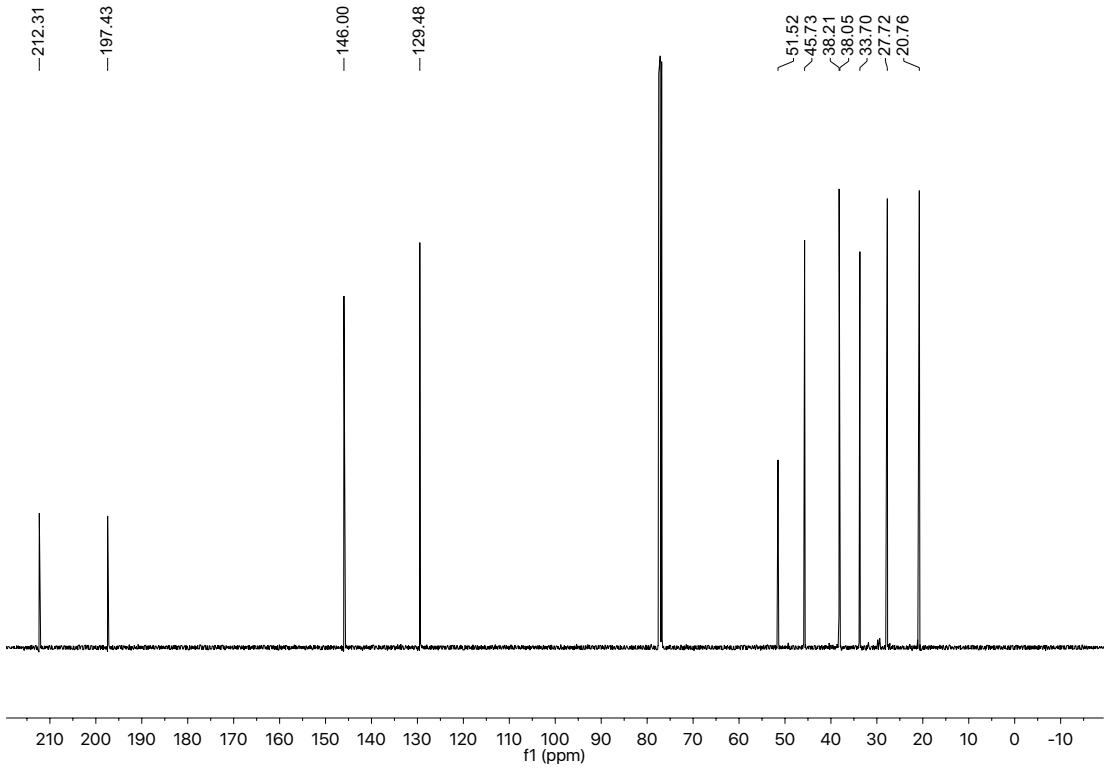
^{13}C NMR (101 MHz, $CDCl_3$) of compound **2c**.



^{1}H NMR (400 MHz, $CDCl_3$) of compound **3a**.



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



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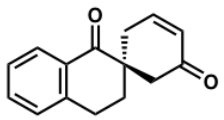
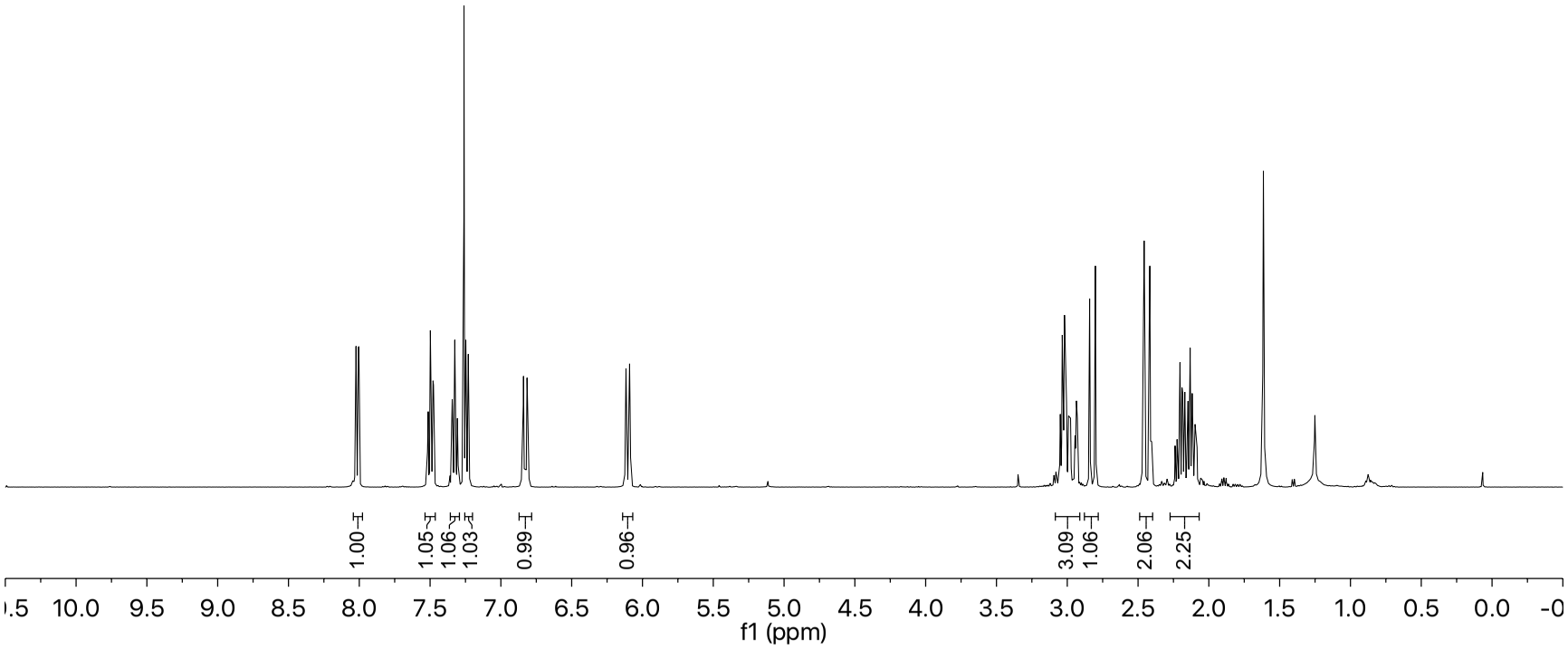
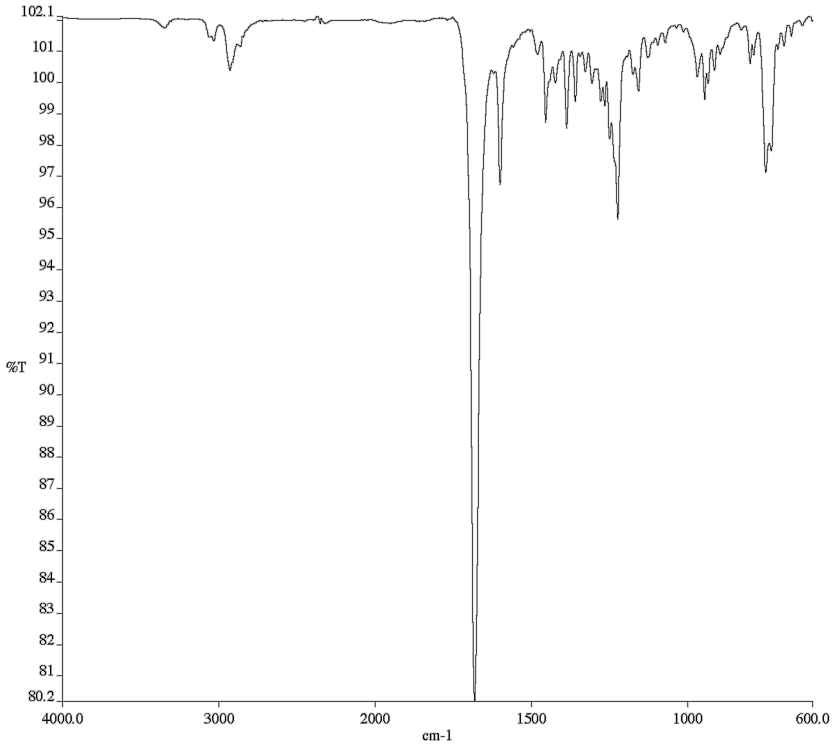
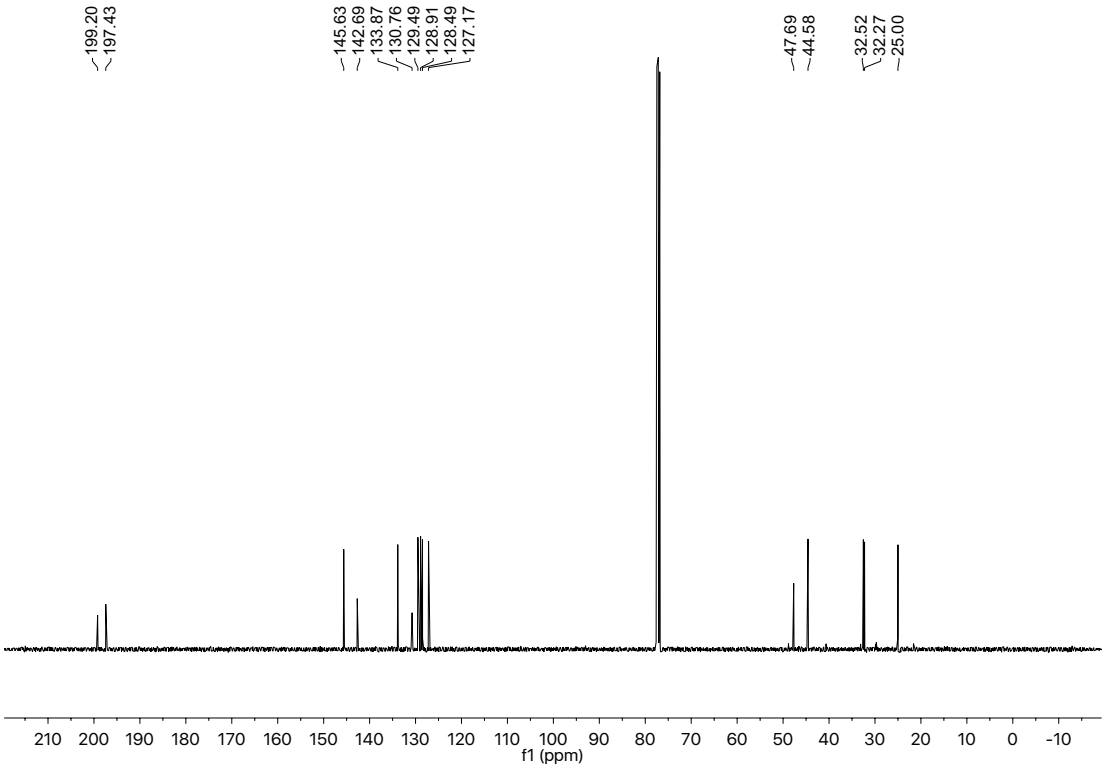




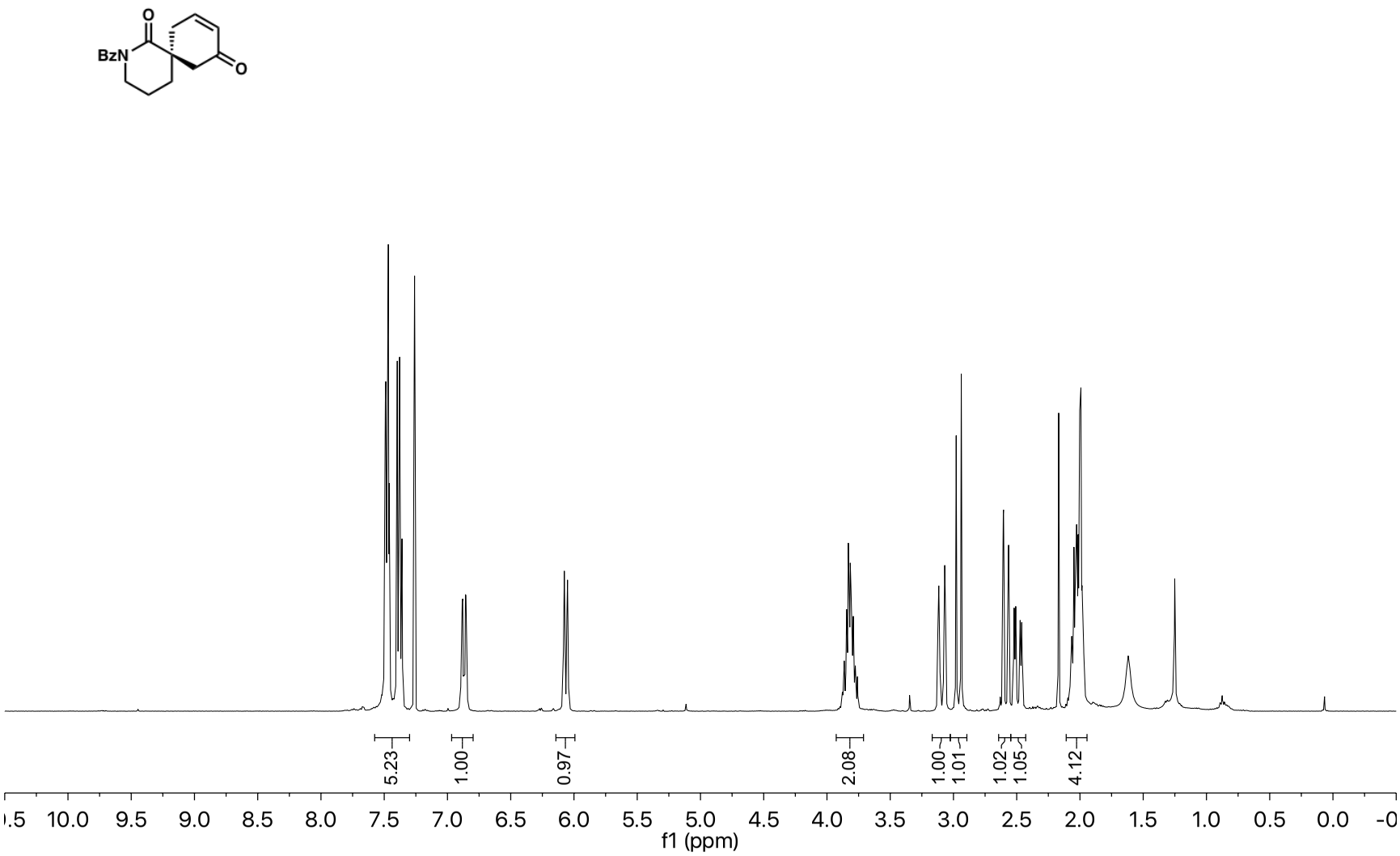
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3b**.



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



^{13}C NMR (101 MHz, $CDCl_3$) of compound **3b**.



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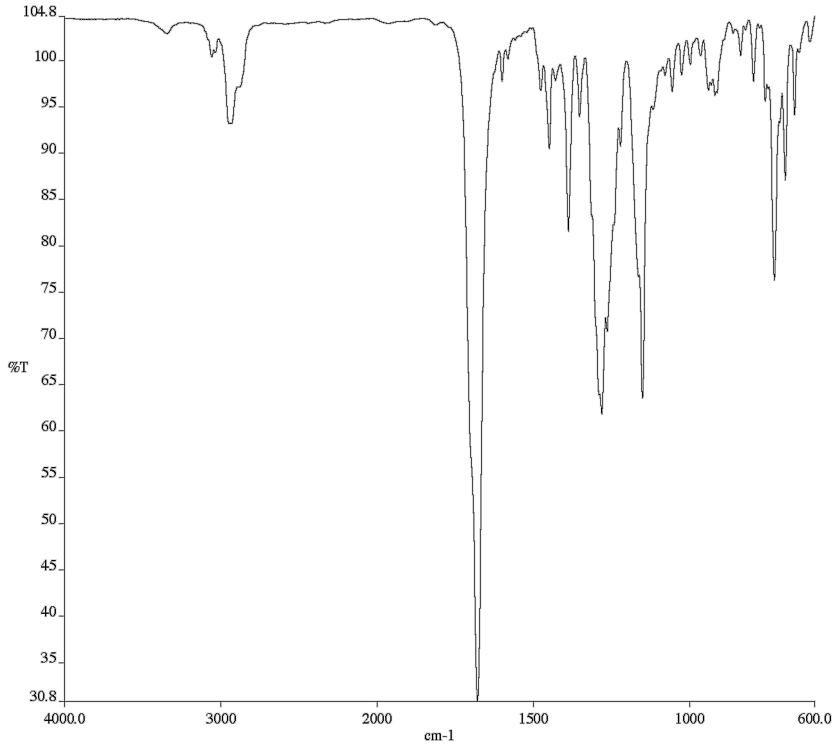
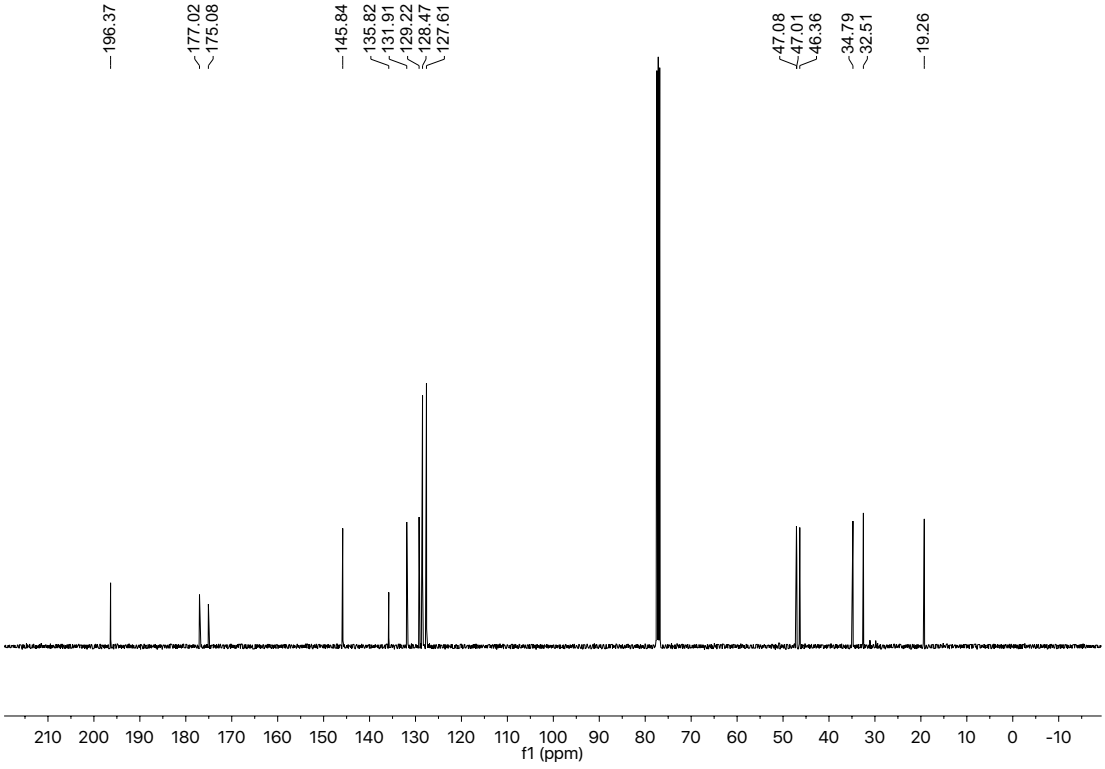


Infrared spectrum (Thin Film, NaCl) of compound **3c**.



^{13}C NMR (101 MHz, $CDCl_3$) of compound **3c**.