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Supporting Information

Iridium-Catalyzed Stereoselective Allylic Alkylation Reactions with Crotyl Chloride

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Materials and Methods

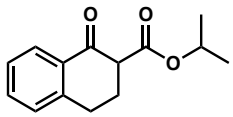
Unless otherwise stated, reactions were performed in flame-dried glassware under an argon or nitrogen atmosphere using dry, deoxygenated solvents. Solvents were dried by passage through an activated alumina column under argon. Commercially obtained reagents were used as received. Chemicals were purchased 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. Preparatory HPLC was performed with an Agilent 1200 Series HPLC equipped with two Agilent Zorbax RX-sil silica columns (9.4 x 250 mm) in series. Analytical chiral HPLC was performed with an Agilent 1100 Series HPLC utilizing a Chiralpak AD-H column (4.6 mm x 25 cm) in series with a Chiralpak AD column (4.6 mm x 25 cm), or a Chiralpak IC column (4.6 mm x 25 cm), all obtained from Daicel Chemical Industries, Ltd. with visualization at 254 nm. Analytical SFC was performed with a Mettler SFC supercritical CO_2 analytical chromatography system utilizing a Chiralpak IC column (4.6 mm x 25 cm) obtained from Daicel Chemical Industries, Ltd. with visualization at 254 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). X-ray crystallographic analysis was obtained from the Caltech X-Ray Crystallography Facility using a Bruker D8 Venture Kappa Duo Photon 100 CMOS diffractometer.

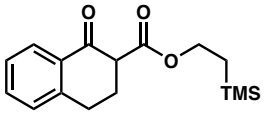
List of Abbreviations: ee – enantiomeric excess, dr – diastereomeric ratio, HPLC – high-performance liquid chromatography, SFC – supercritical fluid chromatography, TLC – thin-layer chromatography, EtOAc – ethyl acetate, THF – tetrahydrofuran, MeOH – methanol, MeCN – acetonitrile, Et_2O – diethyl ether, CH_2Cl_2 – methylene chloride, IPA – isopropanol, AcOH – acetic acid, LHMDS – lithium hexamethyldisilazide, TBD – 1,5,7-triazabicyclo[4.4.0]dec-5-ene, cod – *cis,cis*-1,5-cyclooctadiene, DIBAL – diisobutylaluminium hydride, TBAC – tetrabutylammonium chloride, proton sponge – 1,8-bis(dimethylamino)napthalene

Preparation of Known Compounds: Previously reported methods were used to prepare ligands (*S,S,S*$_a$)-***L1***,[1] (*S,S,S*$_a$)-***L2***,[1] and (*S*$_a$)-***L3***[2] as well as starting materials **4**[3], **8a**,[3] **8f**,[4] **8d**,[5] **8i**,[6] and **8j**.[7]

Experimental Procedures and Spectroscopic Data for the Synthesis of Tetralone Substrates

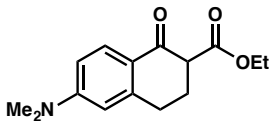


Isopropyl 1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (8b). A solution of methyl ester **4**[3] (0.75 g, 3.7 mmol, 1 equiv), Bu_2SnO (0.091 g, 0.37 mmol, 0.1 equiv), and IPA (15 mL) was heated under reflux for 72 h then concentrated onto silica and purified by silica gel flash column chromatography (3% Et_2O/hexanes) to give isopropyl ester **8b** (1:1 mixture of enol/keto isomers) as a colorless oil (0.62 g, 72% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.56 (s, 0.5H), 8.05 (ddd, *J* = 7.8, 1.5, 0.6 Hz, 0.5H), 7.81 – 7.77 (m, 0.5H), 7.49 (td, *J* = 7.8, 1.5 Hz, 0.5H), 7.35 – 7.23 (m, 2H), 7.20 – 7.14 (m, 0.5H), 5.14 (dp, *J* = 17.1, 6.2 Hz, 1H), 3.56 (dd, *J* = 10.5, 4.7 Hz, 0.5H), 3.13 – 2.93 (m, 1H), 2.81 (dd, *J* = 8.6, 6.9 Hz, 1H), 2.60 – 2.52 (m, 1H), 2.53 – 2.43 (m, 0.5H), 2.35 (ddt, *J* = 13.5, 5.7, 4.7 Hz, 0.5H), 1.32 (d, *J* = 6.3 Hz, 3H), 1.28 (dd, *J* = 6.3, 2.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.6, 172.5, 170.0, 165.0, 143.8, 139.5, 133.9, 132.0, 130.5, 130.3, 128.9, 127.8, 127.5, 127.0, 126.7, 124.4, 97.5, 69.0, 68.2, 54.9, 27.9, 27.8, 26.5, 22.2 (2C), 21.9, 21.9, 20.7; IR (Neat Film, NaCl) 3070, 3027, 2980, 2937, 2847, 1736, 1687, 1644, 1618, 1571, 1454, 1384, 1322, 121, 1214, 1106, 1084, 949, 831, 770, 744 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{14}H_{17}O_3$ $[M+H]^+$: 233.1172, found 233.1174.

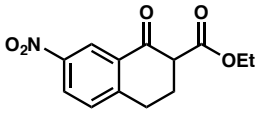


2-(Trimethylsilyl)ethyl 1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (8c). A solution of LHMDS (1.83 g, 10.9 mmol, 2 equiv) in THF (20 mL) was added dropwise to a solution of 1-tetralone (0.804 g, 5.50 mmol, 1 equiv) in THF (20 mL) via cannula at –78 °C. After 1.5 h at –78 °C, a solution of 2-(trimethylsilyl)ethyl 1*H*-imidazole-1-carboxylate (1.39 g, 6.55 mmol, 1.2 equiv) in THF (5 mL) was then added. The resulting reaction mixture was allowed to warm to ambient temperature and stirred for 18 h. The reaction was quenched with the addition of saturated NH_4Cl aqueous solution (40 mL) and the aqueous layer was then extracted with Et_2O (3 x 50 mL). The combined organic layers were washed with brine (20 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude residue was purified by CombiFlash EZ Prep (12 g silica, 1→5% Et_2O/hexanes, 30 min) to provide ester **8c** (3:1 mixture of enol/keto isomers) as a colorless oil (0.40 g, 25%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.57 (s, 0.75H), 8.08 (dd, *J* = 7.8, 1.4 Hz, 0.25H), 7.83 (dd, *J* = 7.8, 1.4 Hz, 0.75H), 7.52 (td, *J* = 7.8, 1.4 Hz, 0.25H),

7.39 – 7.24 (m, 2H), 7.23 – 7.16 (m, 0.75H), 4.41 – 4.14 (m, 2H), 3.61 (dd, *J* = 10.3, 4.7 Hz, 0.25H), 3.14 – 2.97 (m, 0.5H), 2.83 (dd, *J* = 8.9, 6.6 Hz, 1.5H), 2.64 – 2.57 (m, 1.5H), 2.56 – 2.47 (m, 0.25H), 2.38 (m, 0.25H), 1.24 – 0.99 (m, 2H), 0.10 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.4, 173.1, 170.5, 165.1, 155.5, 143.8, 139.5, 134.0, 131.9, 131.0, 130.2, 128.9, 127.9, 127.5, 127.0, 126.7, 124.4, 97.2, 66.2, 63.8, 62.9, 54.8, 27.9, 27.8, 26.5, 20.7, 17.7, 17.5, 17.5, –1.3, –1.39, –1.41; IR (Neat Film, NaCl) 3071, 3028, 2954, 2898, 2846, 1739, 1689, 1644, 1620, 1571, 1454, 1394, 1355, 1325, 1270, 1212, 1175, 1133, 1084, 859, 837, 769 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{16}H_{23}O_3Si$ $[M+H]^+$: 291.1417, found 291.1421.

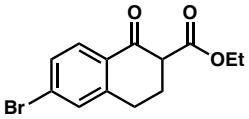


Ethyl 6-(dimethylamino)-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (8e). To a suspension of NaH (0.98 g, 29 mmol, 3.7 equiv, 60 wt %) in THF (10 mL) was added diethyl carbonate (1.9 mL, 16 mmol, 2 equiv). The reaction mixture was brought to reflux at which point a solution of 6-(dimethylamino)-3,4-dihydronaphthalene-1(2*H*)-one (1.5 g, 7.9 mmol, 1 equiv) in THF (10 mL) was added dropwise via addition funnel over 15 min. The reaction mixture was heated to reflux for an additional 18 h then allowed to cool to ambient temperature, whereupon it was quenched with conc. AcOH (10 mL) and diluted with Et_2O (30 mL). The organic layer was washed with brine (5 x 10 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude residue was purified by CombiFlash EZ Prep (12 g silica, 10→20% EtOAc/hexanes, 30 min) to provide dimethylamine **8e** (keto isomer) as a tan solid (1.36 g, 66%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 9.0 Hz, 1H), 6.60 (dd, *J* = 9.0, 2.6 Hz, 1H), 6.36 (d, *J* = 2.6 Hz, 1H), 4.32 – 4.12 (m, 2H), 3.52 (dd, *J* = 10.2, 4.7 Hz, 1H), 3.06 (s, 6H), 2.99 – 2.83 (m, 2H), 2.44 (m, 1H), 2.29 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.4, 171.2, 153.8, 145.9, 130.1, 128.5, 120.8, 110.6, 109.3, 61.2, 54.5, 40.2, 28.6, 26.8, 14.4; IR (Neat Film, NaCl) 2935, 1735, 1660, 1593, 1521, 1449, 1372, 1308, 1197, 1121, 1084, 923 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{15}H_{20}NO_3$ $[M+H]^+$: 262.1443, found 262.1473.

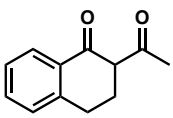


Ethyl 7-nitro-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (8g). A solution of LHMDS (1.8 g, 11 mmol, 2.1 equiv) in THF (20 mL) was added dropwise to a solution of 7-nitro-3,4-dihydronaphthalene-1(2*H*)-one (1.0 g, 5.2 mmol, 1 equiv) in THF (20 mL) via cannula at –78 °C. The reaction was stirred for 1.5 h at –78 °C, whereupon ethyl cyanoformate (0.61 g, 6.2 mmol, 1.2 equiv) was added. The resulting reaction mixture was allowed to warm to ambient temperature and was stirred for 18 h. The reaction was quenched with the addition of saturated NH_4Cl aqueous solution (40 mL) and the aqueous layer was then extracted with Et_2O (3 x 50 mL). The combined organic layers

were washed with brine (20 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude residue was purified by silica gel flash column chromatography (8% EtOAc/hexanes) to provide nitroarene **8g** (enol isomer) as a colorless solid (114 mg, 8%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.45 (s, 1H), 8.65 (d, *J* = 2.4 Hz, 1H), 8.20 (dd, *J* = 8.3, 2.4 Hz, 1H), 7.37 (dt, *J* = 8.3, 1.0 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 2.95 (t, *J* = 7.8 Hz, 2H), 2.66 (dd, *J* = 8.8, 6.9 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4, 162.5, 147.3, 146.3, 131.6, 128.5, 125.0, 119.6, 98.9, 61.2, 28.0, 20.2, 14.4; IR (Neat Film, NaCl) 2996, 2962, 2907, 2858, 1755, 1648, 1514, 1401, 1344, 1270, 1252, 1216, 1068, 1027, 907, 806, 745 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{13}H_{14}NO_5$ $[M+H]^+$: 264.0872, found 264.0871. *Please note* that a minor amount of keto isomer is present in the spectra, which does not impact the characterization.



Ethyl 6-bromo-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (8h). A solution of LHMDS (1.8 g, 11 mmol, 2.1 equiv) in THF (20 mL) was added dropwise to a solution of 6-bromo-3,4-dihydronaphthalene-1(2*H*)-one[3] (1.2 g, 5.2 mmol, 1 equiv) in THF (20 mL) via cannula at –78 °C. The reaction was stirred for 1.5 h at –78 °C, whereupon ethyl cyanoformate (0.61 g, 6.2 mmol, 1.2 equiv) was added. The resulting reaction mixture was allowed to warm to ambient temperature and was stirred for 18 h. The reaction was quenched with the addition of saturated NH_4Cl aqueous solution (40 mL) and the aqueous layer was then extracted with Et_2O (3 x 50 mL). The combined organic layers were washed with brine (20 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude residue was purified by CombiFlash EZ Prep (12 g silica, 5→20% EtOAc/hexanes, 30 min) to provide bromide **8h** (4:1 mixture of enol/keto isomers) as a tan solid (0.63 g, 41%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.44 (s, 0.8H), 7.90 (d, *J* = 8.3 Hz, 0.2H), 7.64 (d, *J* = 8.3 Hz, 0.8H), 7.46 – 7.38 (m, 1.2H), 7.33 (dd, *J* = 2.0, 1.0 Hz, 0.8H), 4.27 (p, *J* = 7.0 Hz, 2H), 3.58 (dd, *J* = 10.0, 4.7 Hz, 0.2H), 3.09 – 2.90 (m, 0.4H), 2.78 (dd, *J* = 8.9, 6.7 Hz, 1.6H), 2.62 – 2.52 (m, 1.6H), 2.53 – 2.27 (m, 0.4H), 1.34 (t, *J* = 7.1 Hz, 2.4H), 1.29 (t, *J* = 7.1 Hz, 0.6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.5, 172.7, 170.0, 164.2, 145.4, 141.4, 131.8, 130.7, 130.6, 130.0 129.9, 129.6, 129.3, 129.1, 126.0, 124.9, 97.4, 61.6, 60.8, 54.4, 27.7, 27.5, 26.3, 20.5, 14.4, 14.3; IR (Neat Film, NaCl) 2979, 2958, 2902, 2848, 1740, 1689, 1645, 1616, 1588, 1558, 1479, 1406, 1377, 1267, 1214, 1195, 1096, 1025, 845, 829, 758 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{13}H_{14}BrO_3$ $[M+H]^+$: 297.0126, found 297.0134.

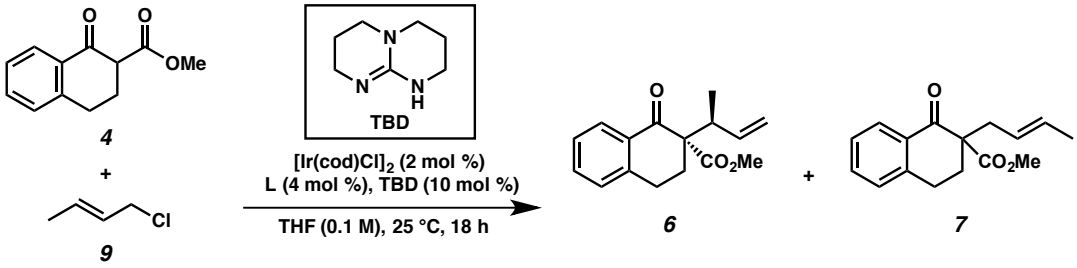


2-Acetyl-3,4-dihydronaphthalen-1(2*H*)-one (8k). To a suspension of NaH (0.49 g, 21 mmol, 2 equiv, 60 wt %) in EtOAc (2 mL) cooled to 0 °C, a solution of 1-tetralone (1.5

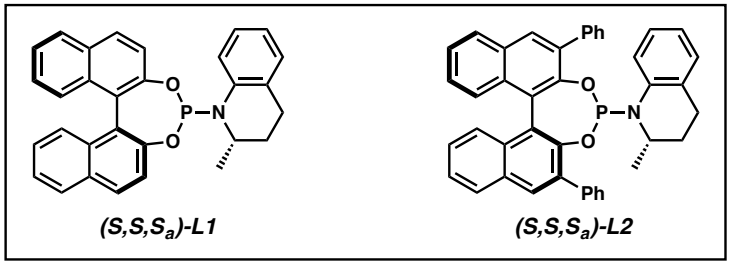
g, 10 mmol, 1 equiv) in toluene (0.5 mL) was added dropwise. After H_2 evolution ceased, the resulting solution was heated to 40 °C for 3 h. The reaction mixture was then allowed to cool to ambient temperature, whereupon it was quenched with MeOH (5 mL), poured onto H_2O (20 mL), neutralized with conc. HCl, and extracted with CH_2Cl_2 (3 x 30 mL). The combined organic extracts were washed with brine (30 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude residue was purified by silica gel flash column chromatography (10% EtOAc/hexanes) to give ketone **8k** (enol isomer) as a pale yellow solid (0.51 g, 26%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.40 (td, *J* = 7.7, 1.4 Hz, 1H), 7.36 – 7.29 (m, 1H), 7.20 (dq, *J* = 7.7, 0.7 Hz, 1H), 2.87 (dd, *J* = 8.5, 6.3 Hz, 2H), 2.68 – 2.59 (m, 2H), 2.24 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.0, 177.0, 140.9, 132.0, 131.2, 127.7, 127.0, 126.0, 106.1, 28.4, 24.1, 22.9; IR (Neat Film, NaCl) 3061, 2940, 2893, 2838, 1598, 1567, 1414, 1354, 1294, 1213, 1156, 1079, 1033, 974, 902, 788, 737, 548 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{12}H_{13}O_2$ $[M+H]^+$: 189.0910, found 189.0908. *Please note* that the exchangeable enol proton was not observed in the ^{1}H NMR spectrum.

Optimization of Reaction Parameters

Table S1. Additional Optimization of Reaction Parameters[a]



Entry	L	Base	Additive	Solvent	*6*:*7*[b]	dr of *6*[b]
1	L1	quinoline	LiCl	THF	94:6	4.6:1
2	L1	pyridine	LiCl	THF	89:11	7.2:1
3	L1	triethylamine	LiCl	THF	86:14	4.5:1
4	L1	isoquinoline	LiCl	THF	89:11	11.3:1
5	L1	*N*-methylimidazole	LiCl	THF	80:20	3.0:1
6	L1	*N*-methylmorpholine	LiCl	THF	89:11	6.0:1
7	L1	*N*-methylpiperidine	LiCl	THF	89:11	5.1:1
8	L1	2,4,6-tri-tert-butylpyridine	LiCl	THF	89:11	4.0:1
9	L1	*sym*-collidine	LiCl	THF	93:7	5.0:1
10	L1	proton sponge	LiCl	THF	92:8	8.3:1
11	L2	proton sponge	LiCl	THF	94:6	6.7:1
12	L2	proton sponge	CsCl	THF	nr	nr
13	L2	proton sponge	TBAC	THF	nr	nr
14	L2	proton sponge	CuCl	THF	88:12	6.8:1
15	L2	proton sponge	LiCl	TBME	80:20	7.7:1
16[c]	L2	proton sponge	LiCl	toluene	95:5	6.7:1
17	L2	proton sponge	LiCl	dioxane	83:17	4.5:1
18	L2	proton sponge	LiCl	cyclohexane	nr	nr
19	L2	proton sponge	LiCl	CH_2Cl_2	78:22	1.8:1



[a]Reactions performed with 0.1 mmol of **9**, 0.2 mmol of **4**, 0.2 mmol of base, and 0.4 mmol of additive. [b]Determined by ^{1}H NMR analysis of the crude reaction mixture. [c]Trace conversion.

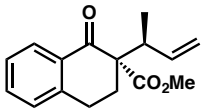
General Procedure for Optimization Reactions (Table S1 & Table 1)

In a nitrogen-filled glove box, to a 1 dram vial (vial A) equipped with a stir bar was added $[Ir(cod)Cl]_2$ (1.3 mg, 0.0020 mmol, 2 mol %), ligand **L** (0.0040 mmol, 4 mol %), TBD (1.4 mg, 0.010 mmol, 10 mol%), and THF (0.5 mL). Vial A was stirred at 25 °C (ca. 10 min) while another 1 dram vial (vial B) was charged with base, additive, tetralone **4** (0.20 mmol), and THF (0.25 mL). The pre-formed catalyst solution (vial A) was then transferred to vial B followed by 0.25 mL of a solution of crotyl electrophile **9** (0.2 M in THF). The vial was sealed and stirred at 25 °C. After 18 h, the vial was removed from the glove box and filtered through a pad of silica, rinsing with EtOAc. The crude mixture was concentrated and dimethyl maleate (0.050 mmol in 0.5 mL $CDCl_3$) was added. The NMR yield (measured in reference to dimethyl maleate δ 6.28 ppm (s, 2H)), regioselectivity (branched product to linear product: **6**:**7**), and diastereoselectivity were determined by ^{1}H NMR analysis of the crude mixture. The residue was purified by preparatory TLC (10% Et_2O/hexanes) to afford the combined branched (**6/epi-6**) and linear (**7**) products as an inseparable mixture. The major diastereomer (**6**) was isolated by preparatory HPLC (2% EtOAc/hexanes, two Agilent Zorbax RX-sil silica columns in series; flow rate = 15 mL/min; λ = 254 nm) and analyzed by chiral SFC (3% MeOH, 3.5 mL/min, Chiralpak AD-H column, λ = 254 nm).

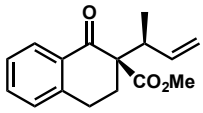
General Procedure for the Ir-Catalyzed Allylic Alkylation

Please note that the absolute configuration was determined only for compound **10f** via x-ray crystallographic analysis. The absolute configuration for all other products has been inferred by analogy. For respective HPLC and SFC conditions, please refer to Table S2.

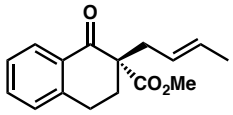
Methyl (*S*)-2-((*S*)-but-3-en-2-yl)-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (6). In a nitrogen-filled glove box, to a 1 dram vial (vial A) equipped with a stir bar was added $[Ir(cod)Cl]_2$ (2.7 mg, 0.0040 mmol, 2 mol %), ligand **L2** (4.9 mg, 0.0080 mmol, 4 mol %), TBD (2.8 mg, 0.020 mmol, 10 mol %), and THF (1 mL). Vial A was stirred at 25 °C (ca. 10 min) while another 1 dram vial (vial B) was charged with proton sponge (86 mg, 0.40 mmol, 200 mol %), tetralone **4** (82 mg, 0.40 mmol, 200 mol %), LiCl (34 mg, 0.80 mmol, 400 mol %), and THF (0.5 mL). The pre-formed catalyst solution (vial A) was then transferred to vial B followed by a solution of crotyl chloride **9** (18 mg, 0.20 mmol, 100 mol %) in THF (0.5 mL). The vial was sealed and stirred at 25 °C. After 18 h, the vial was removed from the glove box and filtered through a pad of silica, rinsing with EtOAc. The crude mixture was concentrated and dimethyl maleate (0.10 mmol in 0.5 mL $CDCl_3$) was added. The NMR yield (74%, measured in reference to dimethyl maleate δ 6.28 ppm (s, 2H)), regioselectivity (branched product to linear product, b:l = 93:7), and diastereoselectivity (dr = 6:1) were determined by ^{1}H NMR analysis of the crude mixture. The residue was purified by preparatory TLC (10% Et_2O/hexanes) to give the isolated yield of the branched and linear products (38.0 mg, 74% combined yield). The diastereomers were separated by preparatory HPLC (2% EtOAc/hexanes, two Agilent Zorbax RX-sil silica columns in series; flow rate = 15 mL/min; λ = 254 nm).



Major diastereomer **6** was isolated as a colorless oil: 96% ee; $[\alpha]_D^{25}$ –48.5 (*c* 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (ddd, *J* = 7.9, 1.5, 0.5 Hz, 1H), 7.45 (td, *J* = 7.4, 1.5 Hz, 1H), 7.30 (ddt, *J* = 7.3, 6.9, 1.1 Hz, 1H), 7.20 (dtt, *J* = 7.6, 1.3, 0.7 Hz, 1H), 5.82 (ddd, *J* = 17.0, 10.2, 8.9 Hz, 1H), 5.12 – 4.97 (m, 2H), 3.64 (s, 3H), 3.28 – 3.09 (m, 2H), 2.90 (ddd, *J* = 17.4, 4.9, 3.0 Hz, 1H), 2.43 (ddd, *J* = 13.7, 4.7, 3.0 Hz, 1H), 2.22 (ddd, *J* = 13.7, 12.3, 4.9 Hz, 1H), 1.15 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.3, 171.2, 143.4, 139.1, 133.6, 132.7, 128.9, 128.2, 126.8, 116.6, 61.2, 52.5, 43.5, 27.8, 26.3, 16.6; IR (Neat Film, NaCl) 3073, 2951, 2850, 1732, 1688, 1600, 1454, 1434, 1290, 1241, 1220, 993, 917, 746 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{16}H_{19}O_3$ $[M+H]^+$: 259.1329, found 259.1329; SFC conditions: 3% MeOH, 3.5 mL/min, Chiralpak AD-H column, λ = 254 nm, t_R (min): major = 5.170, minor = 5.968.



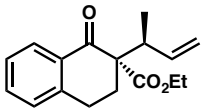
Minor diastereomer **epi-6** (which was inseparable from major diastereomer **6**) was isolated as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.46 (td, *J* = 7.5, 1.5 Hz, 1H), 7.34 – 7.27 (m, 1H), 7.23 – 7.16 (m, 1H), 5.98 (ddd, *J* = 17.2, 10.3, 7.8 Hz, 1H), 5.12 – 5.00 (m, 2H), 3.65 (s, 3H), 3.27 – 3.05 (m, 2H), 2.97 – 2.85 (m, 1H), 2.45 (dddd, *J* = 19.3, 13.7, 4.7, 3.2 Hz, 1H), 2.17 – 2.10 (m, 1H), 1.10 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.5, 171.3, 143.3, 139.9, 133.6, 132.7, 128.8, 128.2, 126.8, 116.2, 61.2, 52.5, 42.5, 28.5, 26.3, 15.0; IR (Neat Film, NaCl) 3072, 2951, 1734, 1686, 1601, 1453, 1438, 1289, 1240, 1219, 1000, 917, 808, 746 cm^{-1}. HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{16}H_{19}O_3$ $[M+H]^+$: 259.1329, found 259.1332. *Please note* that the provided spectra for **epi-6** reflect the inseparable mixture of **epi-6** and **6**, while the tabulated NMR data is for only **epi-6**.



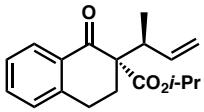
Linear isomer **7** was isolated as a colorless oil: 23% ee; $[\alpha]_D^{25}$ –5.2 (*c* 0.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.06 (m, 1H), 7.60 – 7.47 (m, 1H), 7.36 (tdd, *J* = 7.8, 1.3, 0.6 Hz, 1H), 7.29 – 7.23 (m, 1H), 5.68 – 5.56 (m, 1H), 5.56 – 5.40 (m, 1H), 3.73 (s, 3H), 3.19 – 3.08 (m, 1H), 2.97 (dt, *J* = 17.3, 4.9 Hz, 1H), 2.71 (ddt, *J* = 7.2, 2.5, 1.2 Hz, 2H), 2.57 (dt, *J* = 13.8, 4.9 Hz, 1H), 2.26 – 2.13 (m, 1H), 1.71 (dq, *J* = 6.4, 1.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.3, 172.3, 143.5, 133.6, 132.1, 129.8, 128.9, 128.2, 126.9, 125.7, 57.8, 52.6, 37.7, 30.5, 26.0, 18.2; IR (Neat Film, NaCl) 2918, 2850, 1732, 1689, 1601, 1434, 1263, 1236, 1086, 973, 944, 802, 743 cm^{-1}. HRMS (MM: ESI-APCI+)

m/z calc'd for $C_{16}H_{19}O_3$ $[M+H]^+$: 259.1329, found 259.1324; HPLC conditions: 1% IPA, 1 mL/min, Chiralpak IC column, $\lambda = 254$ nm, t_R (min): major = 19.785, minor = 24.041.

Spectroscopic Data for the Ir-Catalyzed Allylic Alkylation Products

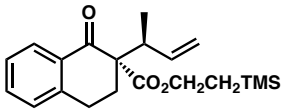


Ethyl (*S*)-2-((*S*)-but-3-en-2-yl)-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (10a). Product **10a** was prepared according to the general procedure and isolated by preparatory TLC (10% Et_2O/hexanes) to give the isolated yield of the branched and linear products (30.3 mg, 56% combined yield). The major diastereomer was isolated as a colorless oil by preparatory HPLC (2% EtOAc/hexanes, two Agilent Zorbax RX-sil silica columns in series; flow rate = 15 mL/min; $\lambda = 254$ nm): 96% ee; $[\alpha]_D^{25}$ –44.3 (*c* 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.44 (td, *J* = 7.5, 1.5 Hz, 1H), 7.31 – 7.26 (m, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 5.84 (ddd, *J* = 17.0, 10.2, 8.8 Hz, 1H), 5.20 – 4.96 (m, 2H), 4.24 – 3.95 (m, 2H), 3.26 – 3.08 (m, 2H), 2.89 (ddd, *J* = 17.4, 4.7, 3.0 Hz, 1H), 2.41 (ddd, *J* = 13.7, 4.7, 3.0 Hz, 1H), 2.21 (ddd, *J* = 13.7, 12.3, 4.7 Hz, 1H), 1.19 – 1.09 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.4, 170.7, 143.2, 139.1, 133.5, 132.9, 128.8, 128.1, 126.7, 116.5, 61.4, 60.8, 43.4, 28.1, 26.3, 16.6, 14.2; IR (Neat Film, NaCl) 3073, 2978, 2938, 1729, 1693, 1639, 1600, 1454, 1290, 1237, 1220, 1019, 909, 746, 652 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{17}H_{21}O_3$ $[M+H]^+$: 273.1485, found 273.1493; SFC conditions: 3% MeOH, 3.5 mL/min, Chiralpak AD-H column, $\lambda = 254$ nm, t_R (min): major = 4.539, minor = 5.113.

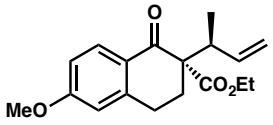


Isopropyl (*S*)-2-((*S*)-but-3-en-2-yl)-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (10b). Product **10b** was prepared according to the general procedure and isolated by preparatory TLC (8% EtOAc/hexanes) to give the isolated yield of the branched and linear products (31.3 mg, 55% combined yield). The major diastereomer was isolated as a colorless oil by preparatory HPLC (2% EtOAc/hexanes, two Agilent Zorbax RX-sil silica columns in series; flow rate = 15 mL/min; $\lambda = 254$ nm): 96% ee; $[\alpha]_D^{25}$ –61.5 (*c* 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.43 (td, *J* = 7.5, 1.5 Hz, 1H), 7.37 – 7.22 (m, 1H), 7.18 (d, *J* = 7.7 Hz, 1H), 5.86 (ddd, *J* = 17.1, 10.2, 8.8 Hz, 1H), 5.12 – 4.92 (m, 3H), 3.23 – 3.11 (m, 1H), 3.11 – 2.98 (m, 1H), 2.89 (ddd, *J* = 17.5, 5.1, 2.9 Hz, 1H), 2.39 (ddd, *J* = 13.7, 4.8, 2.9 Hz, 1H), 2.20 (ddd, *J* = 13.7, 12.2, 5.0 Hz, 1H), 1.18 (dd, *J* = 6.6, 5.3 Hz, 6H), 1.02 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.6, 170.4, 143.0, 139.2, 133.3, 133.2, 128.7, 128.0, 126.7, 116.5, 69.0, 60.6, 43.4, 28.5, 26.3, 21.8, 21.6, 16.7; IR (Neat Film, NaCl) 3073, 2979, 2936, 1724, 1694, 16001, 1456, 1374, 1288, 1244, 1220, 1179, 1144, 1105, 915, 744 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{18}H_{23}O_3$ $[M+H]^+$: 287.1642, found 287.1650;

HPLC conditions: 1% EtOH/hexanes, 1 mL/min, Chiralpak AD then AD-H column, λ = 254 nm, t_R (min): major = 10.378, minor = 11.179.

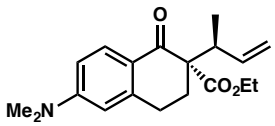


2-(Trimethylsilyl)ethyl (*S*)-2-((*S*)-but-3-en-2-yl)-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (10c). Product **10c** was prepared according to the general procedure and isolated by preparatory TLC (5% Et_2O/hexanes) to give the isolated yield of the branched and linear products (18.3 mg, 27% combined yield). The major diastereomer was isolated as a colorless oil by preparatory HPLC (1% EtOAc/hexanes, two Agilent Zorbax RX-sil silica columns in series; flow rate = 15 mL/min; λ = 254 nm): 89% ee; $[\alpha]_D^{25}$ –46.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.44 (td, *J* = 8.0, 1.5 Hz, 1H), 7.29 (t, *J* = 8.0, 1H), 7.19 (d, *J* = 8.0, 1H), 5.84 (ddd, *J* = 17.0, 10.2, 8.8 Hz, 1H), 5.15 – 5.00 (m, 2H), 4.23 – 4.03 (m, 2H), 3.26 – 3.02 (m, 2H), 2.88 (ddd, *J* = 17.4, 4.9, 2.9 Hz, 1H), 2.40 (ddd, *J* = 13.7, 4.7, 2.9 Hz, 1H), 2.21 (ddd, *J* = 13.6, 12.3, 4.9 Hz, 1H), 1.16 (d, *J* = 6.8 Hz, 3H), 0.89 (dd, *J* = 9.3, 8.1 Hz, 2H), –0.03 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.4, 171.0, 143.3, 139.2, 133.5, 133.0, 128.8, 128.2, 126.7, 116.5, 63.9, 60.8, 43.5, 28.2, 26.3, 17.4, 16.6, –1.5 (3C); IR (Neat Film, NaCl) 3074, 2955, 2899, 1727, 1693, 1601, 1454, 1289, 1251, 1220, 1141, 1041, 918, 860, 837, 746, 695 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{20}H_{28}O_3SiNa$ $[M+Na]^+$: 367.1706, found 367.1720; HPLC conditions: 1% EtOH/hexanes, 1 mL/min, Chiralpak AD then AD-H column, λ = 254 nm, t_R (min): major = 9.018, minor = 9.737.

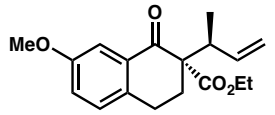


Ethyl (*S*)-2-((*S*)-but-3-en-2-yl)-6-methoxy-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (10d). Product **10d** was prepared according to the general procedure and isolated by preparatory TLC (8% Et_2O/hexanes) to give the isolated yield of the branched and linear products (33.0 mg, 55% combined yield). The major diastereomer was isolated as a colorless oil by preparatory HPLC (7% EtOAc/hexanes, two Agilent Zorbax RX-sil silica columns in series; flow rate = 15 mL/min; λ = 254 nm): 84% ee; $[\alpha]_D^{25}$ –12.3 (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.8 Hz, 1H), 6.81 (ddd, *J* = 8.8, 2.6, 0.7 Hz, 1H), 6.63 (d, *J* = 2.6 Hz, 1H), 5.82 (ddd, *J* = 17.1, 10.2, 8.8 Hz, 1H), 5.12 – 4.97 (m, 2H), 4.20 – 3.99 (m, 2H), 3.84 (s, 3H), 3.26 – 3.08 (m, 2H), 2.84 (ddd, *J* = 17.4, 4.9, 3.0 Hz, 1H), 2.39 (ddd, *J* = 13.6, 4.7, 2.9 Hz, 1H), 2.17 (ddd, *J* = 13.7, 12.4, 4.9 Hz, 1H), 1.16 (t, *J* = 7.1 Hz, 3H), 1.12 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.0, 170.8, 163.7, 145.9, 139.2, 130.7, 126.5, 116.4, 113.5, 112.3, 61.4, 60.6, 55.6, 43.3, 27.7, 26.7, 16.5, 14.3; IR (Neat Film, NaCl) 3075, 2964, 2935, 2849, 1727, 1681, 1600, 1494, 1446, 1354, 1253, 1217, 1094, 1022, 917, 854, 824 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z*

calc'd for $C_{18}H_{23}O_4$ $[M+H]^+$: 303.1591, found 303.1583; HPLC conditions: 1% EtOH/hexanes, 1 mL/min, Chiralpak AD then AD-H column, λ = 254 nm, t_R (min): major = 23.903, minor = 29.498.

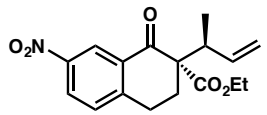


Ethyl (*S*)-2-((*S*)-but-3-en-2-yl)-6-(dimethylamino)-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (10e). Product **10e** was prepared according to the general procedure and isolated by preparatory TLC (10% EtOAc/hexanes) to give the isolated yield of the branched and linear products (29.0 mg, 46% combined yield). The major diastereomer was isolated as a colorless solid by preparatory HPLC (10% EtOAc/hexanes, two Agilent Zorbax RX-sil silica columns in series; flow rate = 15 mL/min; λ = 254 nm): 86% ee; $[\alpha]_D^{25}$ +8.5 (*c* 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.9 Hz, 1H), 6.59 (dd, *J* = 9.0, 2.6 Hz, 1H), 6.31 (d, *J* = 2.5 Hz, 1H), 5.82 (ddd, *J* = 17.1, 10.2, 8.7 Hz, 1H), 5.15 – 4.96 (m, 2H), 4.10 (ddq, *J* = 41.7, 10.8, 7.1 Hz, 2H), 3.31 – 3.12 (m, 2H), 3.04 (s, 6H), 2.78 (ddd, *J* = 17.1, 4.8, 3.0 Hz, 1H), 2.36 (ddd, *J* = 13.4, 4.6, 3.0 Hz, 1H), 2.13 (ddd, *J* = 13.4, 12.5, 4.8 Hz, 1H), 1.18 (t, *J* = 7.1 Hz, 3H), 1.09 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.1, 171.2, 153.6, 145.5, 139.5, 130.5, 121.9, 116.1, 110.5, 109.2, 61.2, 60.5, 43.2, 40.2 (2C), 27.4, 26.9, 16.4, 14.3; IR (Neat Film, NaCl) 3078, 2935, 1725, 1666, 1595, 1520, 1446, 1370, 1293, 1221, 1196, 1125, 1025, 912, 813 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{19}H_{26}NO_3$ $[M+H]^+$: 316.1907, found 316.1912; HPLC conditions: 3% EtOH/hexanes, 1 mL/min, Chiralpak AD then AD-H column, λ = 254 nm, t_R (min): major = 24.809, minor = 33.026.

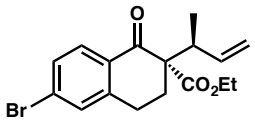


Ethyl (*S*)-2-((*S*)-but-3-en-2-yl)-7-methoxy-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (10f). Product **10f** was prepared according to the general procedure and isolated by preparatory TLC (8% Et_2O/hexanes) to give the isolated yield of the branched and linear products (41.0 mg, 68% combined yield). The major diastereomer was isolated as a colorless oil by preparatory HPLC (2% EtOAc/hexanes, two Agilent Zorbax RX-sil silica columns in series; flow rate = 15 mL/min; λ = 254 nm): 94% ee; $[\alpha]_D^{25}$ –76.8 (*c* 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 2.8 Hz, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 7.03 (dd, *J* = 8.4, 2.8 Hz, 1H), 5.84 (ddd, *J* = 17.0, 10.2, 8.9 Hz, 1H), 5.12 – 4.95 (m, 2H), 4.20 – 4.02 (m, 2H), 3.83 (s, 3H), 3.17 – 3.04 (m, 2H), 2.83 (ddd, *J* = 17.2, 5.0, 2.9 Hz, 1H), 2.39 (ddd, *J* = 13.6, 4.6, 2.9 Hz, 1H), 2.19 (ddd, *J* = 13.7, 12.2, 5.0 Hz, 1H), 1.22 – 1.09 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.4, 170.7, 158.3, 139.0, 135.7, 133.6, 129.9, 122.0, 116.4, 109.6, 61.3, 60.5, 55.5, 43.4, 28.4, 25.4, 16.6, 14.1; IR (Neat Film, NaCl) 3075, 2963, 2936, 2838, 1728, 1688, 1609, 1497, 1463, 1419, 1329, 1279,

1232, 1175, 1143, 1034, 920, 881, 819 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{18}H_{23}O_4$ $[M+H]^+$: 303.1591, found 303.1583; HPLC conditions: 1% EtOH/hexanes, 1 mL/min, Chiralpak AD then AD-H column, λ = 254 nm, t_R (min): major = 17.216, minor = 14.519.

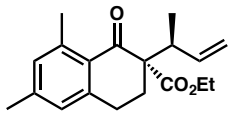


Ethyl (*S*)-2-((*S*)-but-3-en-2-yl)-7-nitro-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (10g). Product **10g** was prepared according to the general procedure and isolated by preparatory TLC (20% EtOAc/hexanes) to give the isolated yield of inseparable branched and linear products (52.0 mg, 82% combined yield): 93% ee; $[\alpha]_D^{25}$ –53.5 (*c* 1.4, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$, major diastereomer) δ 8.86 (d, *J* = 2.5 Hz, 1H), 8.27 (dd, *J* = 8.4, 2.5 Hz, 1H), 7.39 (dt, *J* = 8.7, 0.9 Hz, 1H), 5.81 (ddd, *J* = 17.1, 10.2, 8.9 Hz, 1H), 5.23 – 4.99 (m, 2H), 4.25 – 3.97 (m, 2H), 3.24 (dddd, *J* = 18.1, 12.3, 4.8, 1.1 Hz, 1H), 3.13 – 2.96 (m, 2H), 2.46 (ddd, *J* = 13.9, 4.8, 2.7 Hz, 1H), 2.24 (ddd, *J* = 13.9, 12.4, 4.9 Hz, 1H), 1.21 – 1.12 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$, major diastereomer) δ 192.4, 170.2, 149.7, 147.2, 138.5, 133.8, 130.3, 127.2, 123.4, 117.2, 61.8, 60.8, 43.6, 27.9, 26.7, 16.6, 14.2; IR (Neat Film, NaCl) 3079, 2979, 2938, 1727, 1698, 1612, 1526, 1421, 1347, 1218, 1181, 1018, 931, 740 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{17}H_{20}NO_5$ $[M+H]^+$: 318.1341, found 318.1333; HPLC conditions: 5% EtOH/hexanes, 1 mL/min, Chiralpak AD then AD-H column, λ = 254 nm, t_R (min): major = 14.901, minor = 13.808.

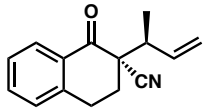


Ethyl (*S*)-6-bromo-2-((*S*)-but-3-en-2-yl)-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (10h). Product **10h** was prepared according to the general procedure and isolated by silica gel flash column chromatography (5% Et_2O/hexanes) to give the isolated yield of the branched and linear products (44.0 mg, 63% combined yield). The major diastereomer was isolated as a colorless oil by preparatory HPLC (0.8% EtOAc/hexanes, two Agilent Zorbax RX-sil silica columns in series; flow rate = 15 mL/min; λ = 254 nm): 98% ee; $[\alpha]_D^{25}$ –32.7 (*c* 2.3, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 1H), 7.42 (ddd, *J* = 8.4, 2.0, 0.8 Hz, 1H), 7.40 – 7.35 (m, 1H), 5.81 (ddd, *J* = 17.1, 10.2, 8.9 Hz, 1H), 5.11 – 4.98 (m, 2H), 4.20 – 3.99 (m, 2H), 3.25 – 3.02 (m, 2H), 2.85 (ddd, *J* = 17.6, 4.9, 2.8 Hz, 1H), 2.40 (ddd, *J* = 13.7, 4.8, 2.9 Hz, 1H), 2.19 (ddd, *J* = 13.8, 12.3, 4.9 Hz, 1H), 1.20 – 1.12 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.6, 170.5, 144.9, 138.9, 131.8, 131.7, 130.2, 129.8, 128.7, 116.8, 61.6, 60.7, 43.5, 28.0, 26.1, 16.6, 14.3; IR (Neat Film, NaCl) 3074, 2977, 2936, 1728, 1690, 1587, 1444, 1353, 1279, 1235, 1218, 1182, 1144, 1018, 910, 838, 670 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{17}H_{19}O_3Br$ $[M]^+$: 350.0518, found 350.0491; SFC conditions: 3% MeOH/hexanes,

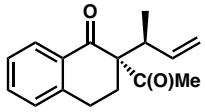
3.5 mL/min, Chiralpak AD-H column, λ = 254 nm, t_R (min): major = 9.330, minor = 8.616.



Ethyl (*S*)-2-((*S*)-but-3-en-2-yl)-6,8-dimethyl-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (10i). Product **10i** was prepared according to the general procedure and isolated by preparatory TLC (9% EtOAc/hexanes) to give the isolated yield of the branched and linear products (31.0 mg, 52% combined yield). The major diastereomer was isolated as a colorless oil by preparatory HPLC (1.5% EtOAc/hexanes, two Agilent Zorbax RX-sil silica columns in series; flow rate = 15 mL/min; λ = 254 nm): 96% ee; $[\alpha]_D^{25}$ –35.1 (*c* 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 2.0 Hz, 1H), 7.22 – 7.08 (m, 1H), 5.85 (ddd, *J* = 17.0, 10.2, 8.9 Hz, 1H), 5.18 – 4.94 (m, 2H), 4.20 – 3.86 (m, 2H), 3.18 – 3.08 (m, 1H), 2.92 (ddd, *J* = 16.9, 11.6, 5.0 Hz, 1H), 2.81 (ddd, *J* = 17.7, 5.6, 3.0 Hz, 1H), 2.45 (ddd, *J* = 13.8, 4.9, 3.0 Hz, 1H), 2.32 (s, 3H), 2.23 (s, 3H), 2.15 (ddd, *J* = 13.8, 11.5, 5.5 Hz, 1H), 1.17 – 1.10 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.9, 170.7, 139.2, 138.7, 136.4, 136.0, 135.8, 132.9, 126.0, 116.4, 61.3, 60.2, 42.9, 27.1, 23.3, 21.0, 19.3, 16.5, 14.2; IR (Neat Film, NaCl) 3075, 2976, 2935, 1730, 1688, 1611, 1477, 1445, 1375, 1286, 1236, 1222, 1163, 1139, 1020, 919, 884 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{19}H_{25}O_3$ $[M+H]^+$: 301.1798, found 301.1801; HPLC conditions: 1% IPA/hexanes, 1 mL/min, Chiralpak IC column, λ = 254 nm, t_R (min): major = 9.599, minor = 10.926.

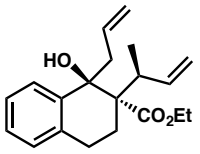


(*R*)-2-((*S*)-but-3-en-2-yl)-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carbonitrile (10j). Product **10j** was prepared according to the general procedure and isolated by preparatory TLC (17% EtOAc/hexanes) to give the isolated yield of the branched and linear products (43.0 mg, 95% combined yield). The major diastereomer was isolated as a colorless oil by preparatory HPLC (4% EtOAc/hexanes, two Agilent Zorbax RX-sil silica columns in series; flow rate = 15 mL/min; λ = 254 nm): 52% ee; $[\alpha]_D^{25}$ +11.4 (*c* 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.54 (td, *J* = 7.5, 1.5 Hz, 1H), 7.45 – 7.32 (m, 1H), 7.29 – 7.25 (m, 1H), 5.91 (ddd, *J* = 17.0, 10.3, 8.0 Hz, 1H), 5.17 (dt, *J* = 10.3, 1.1 Hz, 1H), 5.05 (dt, *J* = 17.1, 1.2 Hz, 1H), 3.27 – 2.89 (m, 3H), 2.43 (ddd, *J* = 7.1, 5.3, 3.4 Hz, 2H), 1.22 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.3, 142.4, 137.1, 134.6, 130.7, 129.0, 128.9, 127.6, 118.5, 118.1, 53.0, 39.8, 28.5, 25.2, 15.3; IR (Neat Film, NaCl) 2975, 2930, 1693, 1600, 1454, 1292, 1223, 1158, 1096, 992, 927, 904, 788, 741 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{15}H_{16}ON$ $[M+H]^+$: 226.1232, found 226.1240; HPLC conditions: 2% EtOH/hexanes, 1 mL/min, Chiralpak AD then AD-H column, λ = 254 nm, t_R (min): major = 24.027, minor = 26.658.



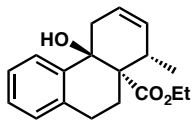
(*R*)-2-acetyl-2-((*S*)-but-3-en-2-yl)-3,4-dihydronaphthalen-1(2*H*)-one (10k). Product **10k** was prepared according to the general procedure and isolated by preparatory TLC (9% EtOAc/hexanes) to give the isolated yield of the branched and linear products (11.0 mg, 23% combined yield). The major diastereomer was isolated as a colorless oil by preparatory HPLC (4% EtOAc/hexanes, two Agilent Zorbax RX-sil silica columns in series; flow rate = 15 mL/min; λ = 254 nm): 65% ee; $[\alpha]_D^{25}$ –43.3 (*c* 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dt, *J* = 8.0, 0.9 Hz, 1H), 7.47 (td, *J* = 7.5, 1.5 Hz, 1H), 7.33 – 7.27 (m, 1H), 7.19 (dtt, *J* = 7.7, 1.2, 0.6 Hz, 1H), 5.64 (ddd, *J* = 17.0, 10.2, 8.8 Hz, 1H), 5.27 – 4.94 (m, 2H), 3.46 – 3.32 (m, 1H), 3.16 (dddt, *J* = 17.4, 12.6, 4.7, 1.1 Hz, 1H), 2.84 (ddd, *J* = 17.4, 5.0, 2.7 Hz, 1H), 2.47 (ddd, *J* = 13.5, 4.7, 2.7 Hz, 1H), 2.12 – 2.06 (m, 1H), 2.09 (s, 3H), 1.06 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.7, 196.8, 144.2, 138.3, 134.1, 132.8, 129.0, 128.0, 126.7, 116.5, 68.4, 42.6, 26.9, 25.9, 24.7, 16.3; IR (Neat Film, NaCl) 3076, 2971, 2937, 1708, 1674, 1599, 1446, 1359, 1295, 1231, 1208, 1120, 995, 912, 781, 754, 737 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{16}H_{19}O_2$ $[M+H]^+$: 243.1385, found 243.1381; HPLC conditions: 1% EtOH/hexanes, 1 mL/min, Chiralpak AD then AD-H column, λ = 254 nm, t_R (min): major = 11.271, minor = 11.944.

Experimental Procedures and Spectroscopic Data for the Transformations of Allylic Alkylation Products

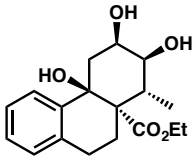


Ethyl (1*R*,2*S*)-1-allyl-2-((*S*)-but-3-en-2-yl)-1-hydroxy-1,2,3,4-tetrahydronaphthalene-2-carboxylate (11). Allylmagnesium chloride (0.065 mL, 0.11 mmol, 1.1 equiv, 1.7 M in THF) was added dropwise to a solution of ethyl ester **10a** (27 mg, 1.0 mmol, 1 equiv) in THF (0.5 mL) at –78 °C. The mixture was stirred at –78 °C for 4 h, whereupon the reaction was quenched with a saturated NH_4Cl aqueous solution (1 mL). The aqueous layer was then extracted with EtOAc (3 x 5 mL) and the combined organic layers were washed with brine (5 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude residue was purified by preparatory TLC (9% Et_2O/hexanes) to give alcohol **11** as a colorless oil (31 mg, 71% yield): $[\alpha]_D^{25}$ +27.3 (*c* 0.3, $CHCl_3$);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.50 (m, 1H), 7.20 – 7.14 (m, 2H), 7.10 – 7.02 (m, 1H), 5.99 (ddd, *J* = 17.1, 10.2, 8.5 Hz, 1H), 5.65 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1H), 4.98 – 4.85 (m, 2H), 4.85 – 4.76 (m, 1H), 4.68 (ddd, *J* = 17.1, 1.9, 1.0 Hz, 1H), 4.33 – 4.19 (m, 2H), 4.01 (s, 1H), 2.94 – 2.86 (m, 2H), 2.72 (ddt, *J* = 8.6, 7.0, 0.8 Hz, 1H), 2.52 – 2.30 (m, 3H), 2.21 – 2.12 (m, 1H), 1.35 (t, *J* = 7.1 Hz, 3H), 0.80 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.9, 142.0, 140.7, 134.1, 133.7, 127.9, 126.7, 126.3, 125.5, 117.5, 114.7, 76.6, 61.1, 56.4, 47.2, 41.2, 25.2, 23.3, 16.7, 14.4; IR (Neat

Film, NaCl) 3492, 3075, 2978, 2930, 2853, 1732, 1694, 1640, 1455, 1376, 1267, 1213, 1026, 914, 766, 732, 665 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{20}H_{27}O_3$ $[M+H]^+$: 315.1960, found 315.1954.

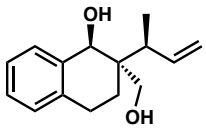


Ethyl (4b*R*,8*S*,8a*S*)-4b-hydroxy-8-methyl-5,8,9,10-tetrahydrophenanthrene-8a(4b*H*)-carboxylate (12). A solution of bis-olefin **11** (4.0 mg, 0.013 mmol, 1 equiv), Hoveyda-Grubbs Catalyst-II (1.4 mg, 2.6 μmol, 0.2 equiv), and CH_2Cl_2 (0.5 mL) was stirred at ambient temperature for 18 h, whereupon the reaction mixture was concentrated under reduced pressure. The crude residue was purified by preparatory TLC (9% EtOAc/hexanes) to give tricycle **12** as a colorless oil (3.0 mg, 81% yield): $[\alpha]_D^{25}$ +7.9 (*c* 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.46 (m, 1H), 7.22 – 7.16 (m, 2H), 7.13 – 7.06 (m, 1H), 5.82 (ddt, *J* = 10.1, 5.1, 2.6 Hz, 1H), 5.56 (ddt, *J* = 10.1, 2.6, 1.8 Hz, 1H), 3.96 (qd, *J* = 7.1, 1.0 Hz, 2H), 3.36 (ddt, *J* = 18.0, 3.8, 2.6 Hz, 1H), 3.09 – 2.96 (m, 1H), 2.96 – 2.78 (m, 2H), 2.70 – 2.57 (m, 1H), 2.49 – 2.38 (m, 1H), 2.28 – 2.11 (m, 1H), 1.12 (d, *J* = 7.6 Hz, 3H), 1.07 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.2, 140.0, 136.0, 130.6, 129.6, 127.9, 126.3, 125.1, 124.1, 70.5, 60.0, 52.2, 36.8, 36.4, 26.4, 25.5, 16.2, 14.2; IR (Neat Film, NaCl) 3488, 3019, 2972, 2934, 1727, 1715, 1451, 1368, 1293, 1251, 1177, 1027, 887, 761, 694 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{18}H_{23}O_3$ $[M+H]^+$: 287.1647, found 287.1637. *Please note* that the exchangeable hydroxy proton was not observed in the ^{1}H NMR spectrum.

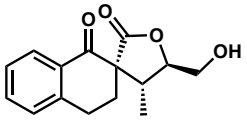


Ethyl (4b*R*,6*R*,7*S*,8*R*,8a*S*)-4b,6,7-trihydroxy-8-methyl-5,6,7,8,9,10-hexahydrophenanthrene-8a(4b*H*)-carboxylate (13). A solution of olefin **12** (18 mg, 0.058 mmol, 1 equiv), K_2OsO_4 (1.0 mg, 2.8 μmol, 0.05 equiv), *N*-methylmorpholine *N*-oxide (11 mg, 0.093 mmol, 1.6 equiv), and THF/H_2O (3:1, 0.2 mL) was stirred at ambient temperature for 18 h, whereupon the reaction was quenched with saturated $Na_2S_2O_3$ aqueous solution (1 mL). The aqueous layer was then extracted with EtOAc (5 x 5 mL) and the combined organic layers were washed with brine (5 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude residue was purified by preparatory TLC (17% EtOAc/hexanes) to give triol **13** as a colorless oil (11 mg, 59% yield): $[\alpha]_D^{25}$ +3.8 (*c* 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.19 (td, *J* = 7.4, 1.5 Hz, 1H), 7.16 – 7.05 (m, 2H), 4.26 (q, *J* = 3.3 Hz, 1H), 3.82 (q, *J* = 7.1 Hz, 2H), 3.74 (dd, *J* = 11.0, 3.5 Hz, 1H), 3.70 – 3.56 (m, 1H), 3.06 – 2.92 (m, 3H), 2.78 (dd, *J* = 14.6, 3.0 Hz, 1H), 2.61 – 2.44 (m, 1H), 2.24 – 2.05 (m, 2H), 1.10 (d, *J* = 6.8 Hz, 3H), 0.90 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 139.4, 136.9, 129.6,

128.4, 125.8, 123.8, 73.0, 72.7, 70.5, 60.4, 56.1, 37.3, 35.3, 25.9, 25.1, 13.9, 12.3; IR (Neat Film, NaCl) 3284, 2970, 2928, 1723, 1452, 1382, 1259, 1234, 1189, 1103, 1054, 1020, 867, 834, 763, 722 cm^{-1}; HRMS (MM: ESI-APCI–) *m/z* calc'd for $C_{18}H_{24}O_5Cl$ $[M+Cl]^-$: 355.1318, found 355.1326. <u>*Please note*</u> that two of the exchangeable hydroxy protons were not observed in the ^1H NMR spectrum.



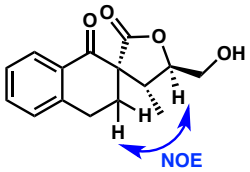
(1*R*,2*R*)-2-((*S*)-But-3-en-2-yl)-2-(hydroxymethyl)-1,2,3,4-tetrahydronaphthalen-1-ol (14). DIBAL (0.071 mL, 0.40 mmol, 4 equiv) was added dropwise to a solution of ethyl ester **10a** (27 mg, 1.0 mmol, 1 equiv) in THF (0.6 mL) at –78 °C. The mixture was stirred at –78 °C for 6 h, whereupon the reaction was quenched with a saturated Rochelle's salt aqueous solution (1 mL) and stirred for 18 h at ambient temperature. The aqueous layer was then extracted with EtOAc (3 x 5 mL) and the combined organic layers were washed with brine (5 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude residue was purified by preparatory TLC (20% EtOAc/hexanes) to give diol **14** as a colorless oil (10 mg, 43% yield): $[\alpha]_D^{25}$ +105.7 (*c* 0.7, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.44 (m, 1H), 7.24 – 7.18 (m, 2H), 7.11 (ddd, *J* = 5.5, 2.4, 1.2 Hz, 1H), 6.30 (ddd, *J* = 17.2, 10.1, 9.1 Hz, 1H), 4.99 (ddd, *J* = 10.1, 2.1, 0.6 Hz, 1H), 4.90 (ddd, *J* = 17.3, 2.1, 0.9 Hz, 1H), 4.80 (d, *J* = 7.3 Hz, 1H), 3.81 (dd, *J* = 11.3, 5.5 Hz, 1H), 3.59 (dd, *J* = 11.4, 3.7 Hz, 1H), 2.91 – 2.66 (m, 2H), 2.65 – 2.57 (m, 2H), 2.19 (bs, 1H), 1.75 (ddd, *J* = 13.8, 7.2, 6.5 Hz, 1H), 1.64 – 1.50 (m, 1H), 1.04 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 138.9, 135.9, 128.4, 127.3, 127.0, 126.5, 115.1, 75.3, 67.3, 43.7, 39.8, 25.8, 25.7, 15.5; IR (Neat Film, NaCl) 3404, 3069, 3020, 2932, 1634, 1602, 1455, 1417, 1374, 1268, 1217, 1191, 1045, 991, 913, 774, 741, 641 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{15}H_{19}O_2$ $[(M+H)–H_2]^+$: 231.1385, found 231.1385. <u>*Please note*</u> that a minor amount of epimeric product is present in the ^1H NMR spectrum.

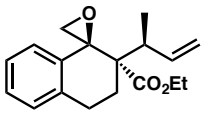


(3*S*,4*R*)-5-(Hydroxymethyl)-4-methyl-3',4,4',5-tetrahydro-1'*H*,2*H*-spiro[furan-3,2'-naphthalene]-1',2-dione (15). A solution of methyl ester **6** (20.0 mg, 0.077 mmol, 1 equiv), K_2OsO_4 (3.0 mg, 0.0081 mmol, 0.11 equiv), *N*-methylmorpholine *N*-oxide (15 mg, 0.12 mmol, 1.6 equiv), and THF/H_2O (3:1, 0.4 mL) was stirred at ambient temperature for 12 h, whereupon a second addition of K_2OsO_4 and *N*-methylmorpholine *N*-oxide was added and the reaction was stirred for an additional 24 h. The reaction was quenched with saturated $Na_2S_2O_3$ aqueous solution (1 mL). The aqueous layer was then extracted with EtOAc (5 x 5 mL) and the combined organic layers were washed with brine (5 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude residue was purified by preparatory TLC (33% EtOAc/hexanes) to give lactone **15** as a

colorless oil (13 mg, 65% yield): $[\alpha]_D^{25}$ +7.0 (*c* 0.2, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.52 (td, *J* = 7.5, 1.5 Hz, 1H), 7.38 – 7.31 (m, 1H), 4.26 (ddd, *J* = 10.5, 5.6, 2.4 Hz, 1H), 4.01 (ddd, *J* = 12.8, 7.0, 2.5 Hz, 1H), 3.82 (dt, *J* = 12.4, 6.0 Hz, 1H), 3.59 (dq, *J* = 10.5, 7.0 Hz, 1H), 3.47 – 3.34 (m, 1H), 2.98 (dt, *J* = 17.0, 3.8 Hz, 1H), 2.32 – 2.25 (m, 2H), 1.94 (t, *J* = 6.7 Hz, 1H), 1.03 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.6, 173.5, 144.0, 134.4, 131.8, 129.0, 128.8, 127.2, 84.3, 62.9, 57.7, 36.1, 25.6, 25.3, 10.8; IR (Neat Film, NaCl) 3444, 2928, 2851, 1760, 1682, 1599, 1455, 1308, 1239, 1217, 1166, 1094, 1056, 1021, 914, 759, 733, 656 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{15}H_{17}O_4$ $[M+H]^+$: 261.1127, found 261.1129.

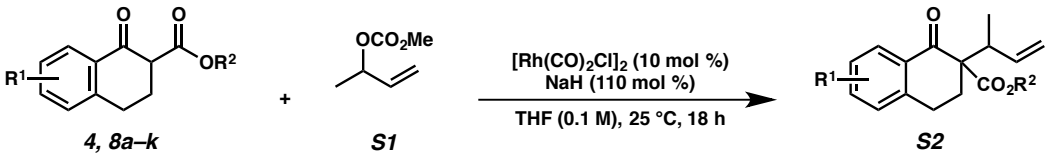
NOE correlation:





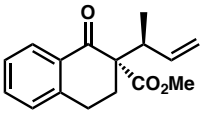
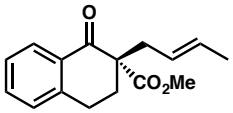
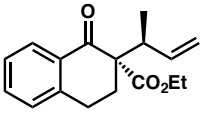
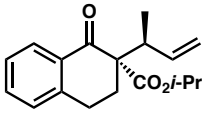
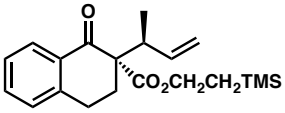
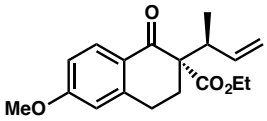
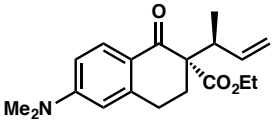
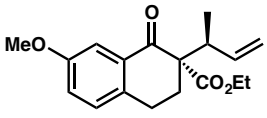
Ethyl (1*R*,2*S*)-2-((*S*)-but-3-en-2-yl)-3,4-dihydro-2*H*-spiro[naphthalene-1,2'-oxirane]-2-carboxylate (16). $(CH_3)_3SOI$ (35 mg, 0.17 mmol, 1.7 equiv) and NaH (5.0 mg, 0.15 mmol, 1.5 equiv, 60 wt %) were dissolved in DMSO (1.5 mL). The mixture was stirred for 20 min at ambient temperature, whereupon a solution of ketone **10a** (27 mg, 0.10 mmol, 1 equiv) in DMSO (1.0 mL) was added. The resulting solution was stirred for an additional 18 h. H_2O (2.0 mL) was then added to the reaction mixture and the aqueous layer was extractd with EtOAc (3 x 5 mL). The organic layer was washed with H_2O (5.0 mL) and brine (5.0 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude residue was purified by preparatory TLC (3% Et_2O/hexanes) to give epoxide **16** as a colorless oil (23 mg, 82% yield): $[\alpha]_D^{25}$ +10.4 (*c* 0.1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.15 (m, 3H), 7.15 – 7.07 (m, 1H), 6.07 (ddd, *J* = 17.1, 10.3, 8.1 Hz, 1H), 4.93 (ddd, *J* = 10.2, 1.9, 0.8 Hz, 1H), 4.74 (ddd, *J* = 17.1, 2.0, 1.1 Hz, 1H), 4.29 – 4.06 (m, 2H), 3.01 – 2.94 (m, 1H), 2.98 (d, *J* = 5.1 Hz, 1H), 2.93 – 2.82 (m, 1H), 2.82 – 2.71 (m, 1H), 2.62 (d, *J* = 5.1 Hz, 1H), 2.35 (ddd, *J* = 14.0, 8.2, 5.7 Hz, 1H), 2.09 (ddd, *J* = 14.2, 6.9, 5.5 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.99 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ; 173.4, 140.9, 138.2, 136.4, 127.8, 127.4, 126.8, 123.4, 115.1, 61.0, 59.1, 56.5, 51.9, 40.2, 28.0, 26.2, 15.8, 14.4; IR (Neat Film, NaCl) 3073, 2977, 2938, 1723, 1489, 1456, 1368, 1296, 1255, 1233, 1213, 1134, 1096, 1025, 915, 760 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{18}H_{21}O_3$ $[(M+H)–H_2]^+$: 285.1491, found 285.1487. *Please note* that the relative stereochemistry of **16** has been assigned via analogy to **11** and **14**.

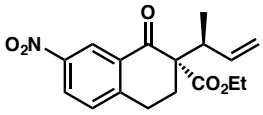
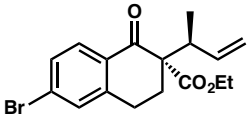
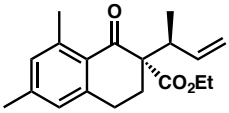
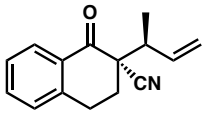
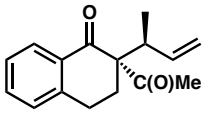
Determination of Enantiomeric Excess



Please note racemic products (**S2**) were synthesized as follows: in a nitrogen-filled glove box, to a 1 dram vial (vial A) equipped with a stir bar was added $[Rh(CO)_2Cl]_2$ (10 mol %) and but-3-en-2-yl methyl carbonate (**S1**, 140 mol %) in THF. Vial A was stirred at 25 °C (ca. 10 min) while another 1 dram vial (vial B) was charged with tetralone **4, 8a–k** (100 mol %), NaH (110 mol %), and THF. The pre-formed catalyst solution (vial A) was then transferred to vial B and the vial was sealed and stirred at 25 °C. After 18 h, the vial was removed from the glove box and filtered through celite, rinsing with EtOAc to give the crude racemic product. The residue was purified as in the general procedure for the Ir-catalyzed allylic alkylation.

Table S2: Determination of Enantiomeric Excess

Entry	Product	Assay Conditions	Retention time of major isomer (min)	Retention time of minor isomer (min)	%ee
1		SFC Chiralpak AD-H 3% MeOH isocratic, 3.5 mL/min	5.170	5.968	96%
2		HPLC Chiralpak IC 1% IPA isocratic, 1 mL/min	19.785	24.041	23%
3		SFC Chiralpak AD-H 3% MeOH isocratic, 3.5 mL/min	4.539	5.113	96%
4		HPLC Chiralpak AD then AD-H 1% EtOH/hexanes isocratic, 1 mL/min	10.378	11.179	96%
5		HPLC Chiralpak AD then AD-H 1% EtOH/hexanes isocratic, 1 mL/min	9.018	9.737	89%
6		HPLC Chiralpak AD then AD-H 1% EtOH/hexanes isocratic, 1 mL/min	23.903	29.498	84%
7		HPLC Chiralpak AD then AD-H 3% EtOH/hexanes isocratic, 1 mL/min	24.809	33.026	86%
8		HPLC Chiralpak AD then AD-H 1% EtOH/hexanes isocratic, 1 mL/min	17.216	14.519	94%

Entry	Product	Assay Conditions	Retention time of major isomer (min)	Retention time of minor isomer (min)	%ee
9		HPLC Chiralpak AD then AD-H 5% EtOH/hexanes isocratic, 1 mL/min	14.901	13.808	93%
10		SFC Chiralpak AD-H 3% MeOH isocratic, 3.5 mL/min	9.330	8.616	98%
11		HPLC Chiralpak IC 1% IPA/hexanes isocratic, 1 mL/min	9.599	10.926	96%
12		HPLC Chiralpak AD then AD-H 2% EtOH/hexanes isocratic, 1 mL/min	24.027	26.658	52%
13		HPLC Chiralpak AD then AD-H 1% EtOH/hexanes isocratic, 1 mL/min	11.271	11.944	65%

Crystal Structure Data for Alkylation Product 10e

The alkylation product **10e** (86% ee) was recrystallized by slow evaporation of hexanes to provide crystals suitable for X-ray analysis, m.p. = 67 – 69 °C.

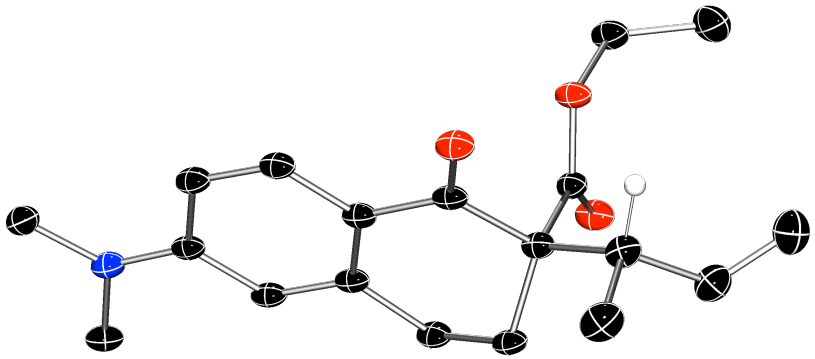


*Table S3: Crystal Data and Structure Refinement for Alkylation Product **10e***

Empirical formula	C19 H25 N O3	
Formula weight	315.40	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 7.5983(10) Å	α = 90°.
	b = 6.1333(8) Å	β = 99.411(4)°.
	c = 18.493(3) Å	γ = 90°.
Volume	850.2(2) Å^3	
Z	2	
Density (calculated)	1.232 Mg/m^3	
Absorption coefficient	0.661 mm^{-1}	
F(000)	340	
Crystal size	0.240 x 0.230 x 0.080 mm^3	
Theta range for data collection	2.422 to 79.330°.	
Index ranges	-9<=h<=8, -7<=k<=7, -23<=l<=23	
Reflections collected	26025	
Independent reflections	3636 [R(int) = 0.0411]	
Completeness to theta = 67.679°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3636 / 1 / 212	
Goodness-of-fit on F^2	1.094	
Final R indices [I>2sigma(I)]	R1 = 0.0271, wR2 = 0.0727	
R indices (all data)	R1 = 0.0274, wR2 = 0.0730	
Absolute structure parameter	0.07(3)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.132 and -0.164 e.Å^{-3}	

*Table S4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) **10e**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.*

	x	y	z	U(eq)
O(1)	7683(1)	7250(2)	2322(1)	22(1)
O(2)	3598(1)	7112(2)	1929(1)	22(1)
O(3)	2465(1)	3836(2)	2155(1)	26(1)
N(1)	7877(2)	5287(2)	5723(1)	22(1)
C(1)	6891(2)	5855(2)	2615(1)	18(1)
C(2)	5657(2)	4176(2)	2162(1)	19(1)
C(3)	5859(2)	1974(2)	2564(1)	21(1)
C(4)	5385(2)	2122(2)	3330(1)	21(1)
C(5)	6371(2)	3931(2)	3774(1)	19(1)
C(6)	6627(2)	3825(2)	4533(1)	20(1)
C(7)	7579(2)	5444(2)	4976(1)	19(1)
C(8)	8254(2)	7234(2)	4615(1)	21(1)
C(9)	8014(2)	7309(2)	3861(1)	20(1)
C(10)	7074(2)	5687(2)	3423(1)	19(1)
C(11)	7366(2)	3305(2)	6073(1)	25(1)
C(12)	8987(2)	6890(2)	6164(1)	23(1)
C(13)	3720(2)	4979(2)	2090(1)	19(1)
C(14)	1805(2)	8046(3)	1784(1)	26(1)
C(15)	1022(2)	7841(3)	986(1)	34(1)
C(16)	6100(2)	3994(3)	1368(1)	23(1)
C(17)	4726(2)	2647(3)	886(1)	27(1)
C(18)	3647(2)	3362(3)	300(1)	34(1)
C(19)	7958(2)	3021(3)	1358(1)	30(1)

Table S5. Bond lengths [Å] and angles [°] for ***10e***

O(1)-C(1)	1.2222(17)
O(2)-C(13)	1.3416(18)
O(2)-C(14)	1.4618(16)
O(3)-C(13)	1.2044(18)
N(1)-C(7)	1.3659(18)
N(1)-C(12)	1.4557(18)
N(1)-C(11)	1.4589(18)
C(1)-C(10)	1.480(2)
C(1)-C(2)	1.5442(18)
C(2)-C(3)	1.537(2)
C(2)-C(13)	1.5374(18)
C(2)-C(16)	1.5650(19)
C(3)-C(4)	1.521(2)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-C(5)	1.5042(19)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-C(6)	1.388(2)
C(5)-C(10)	1.4074(19)
C(6)-C(7)	1.4096(19)
C(6)-H(6)	0.9500
C(7)-C(8)	1.4236(19)
C(8)-C(9)	1.376(2)
C(8)-H(8)	0.9500
C(9)-C(10)	1.4032(19)
C(9)-H(9)	0.9500
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(14)-C(15)	1.505(2)

C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-C(17)	1.505(2)
C(16)-C(19)	1.535(2)
C(16)-H(16)	1.0000
C(17)-C(18)	1.322(2)
C(17)-H(17)	0.9500
C(18)-H(18A)	0.9500
C(18)-H(18B)	0.9500
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800

C(13)-O(2)-C(14)	116.82(11)
C(7)-N(1)-C(12)	120.26(11)
C(7)-N(1)-C(11)	119.66(12)
C(12)-N(1)-C(11)	119.10(12)
O(1)-C(1)-C(10)	121.63(12)
O(1)-C(1)-C(2)	121.71(12)
C(10)-C(1)-C(2)	116.66(11)
C(3)-C(2)-C(13)	109.99(11)
C(3)-C(2)-C(1)	108.68(11)
C(13)-C(2)-C(1)	108.76(11)
C(3)-C(2)-C(16)	111.84(12)
C(13)-C(2)-C(16)	106.93(11)
C(1)-C(2)-C(16)	110.60(11)
C(4)-C(3)-C(2)	112.21(12)
C(4)-C(3)-H(3A)	109.2
C(2)-C(3)-H(3A)	109.2
C(4)-C(3)-H(3B)	109.2
C(2)-C(3)-H(3B)	109.2
H(3A)-C(3)-H(3B)	107.9
C(5)-C(4)-C(3)	112.26(11)

C(5)-C(4)-H(4A)	109.2
C(3)-C(4)-H(4A)	109.2
C(5)-C(4)-H(4B)	109.2
C(3)-C(4)-H(4B)	109.2
H(4A)-C(4)-H(4B)	107.9
C(6)-C(5)-C(10)	120.11(13)
C(6)-C(5)-C(4)	119.48(12)
C(10)-C(5)-C(4)	120.38(12)
C(5)-C(6)-C(7)	121.95(12)
C(5)-C(6)-H(6)	119.0
C(7)-C(6)-H(6)	119.0
N(1)-C(7)-C(6)	121.49(12)
N(1)-C(7)-C(8)	121.09(12)
C(6)-C(7)-C(8)	117.41(13)
C(9)-C(8)-C(7)	120.20(13)
C(9)-C(8)-H(8)	119.9
C(7)-C(8)-H(8)	119.9
C(8)-C(9)-C(10)	122.17(13)
C(8)-C(9)-H(9)	118.9
C(10)-C(9)-H(9)	118.9
C(9)-C(10)-C(5)	118.13(13)
C(9)-C(10)-C(1)	119.25(12)
C(5)-C(10)-C(1)	122.60(12)
N(1)-C(11)-H(11A)	109.5
N(1)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
N(1)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
N(1)-C(12)-H(12A)	109.5
N(1)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
N(1)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
O(3)-C(13)-O(2)	124.23(13)

O(3)-C(13)-C(2)	124.53(13)
O(2)-C(13)-C(2)	111.23(11)
O(2)-C(14)-C(15)	110.68(13)
O(2)-C(14)-H(14A)	109.5
C(15)-C(14)-H(14A)	109.5
O(2)-C(14)-H(14B)	109.5
C(15)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	108.1
C(14)-C(15)-H(15A)	109.5
C(14)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(14)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(17)-C(16)-C(19)	109.29(13)
C(17)-C(16)-C(2)	111.13(11)
C(19)-C(16)-C(2)	112.17(12)
C(17)-C(16)-H(16)	108.0
C(19)-C(16)-H(16)	108.0
C(2)-C(16)-H(16)	108.0
C(18)-C(17)-C(16)	125.47(16)
C(18)-C(17)-H(17)	117.3
C(16)-C(17)-H(17)	117.3
C(17)-C(18)-H(18A)	120.0
C(17)-C(18)-H(18B)	120.0
H(18A)-C(18)-H(18B)	120.0
C(16)-C(19)-H(19A)	109.5
C(16)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(16)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5

*Table S6. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **10e**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$*

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

Table S7. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for ***10e***

	x	y	z	U(eq)
H(3A)	5075	886	2276	25
H(3B)	7106	1463	2599	25
H(4A)	4085	2369	3292	26
H(4B)	5673	719	3588	26
H(6)	6146	2627	4762	24
H(8)	8872	8379	4895	26
H(9)	8500	8499	3631	24
H(11A)	6078	3077	5938	37
H(11B)	7674	3450	6606	37
H(11C)	8003	2057	5909	37
H(12A)	10166	6934	6015	35
H(12B)	9116	6485	6683	35
H(12C)	8427	8330	6092	35
H(14A)	1857	9604	1927	31
H(14B)	1030	7281	2084	31
H(15A)	1819	8539	688	52
H(15B)	-147	8555	894	52
H(15C)	886	6296	854	52
H(16)	6079	5497	1156	27
H(17)	4624	1157	1013	33
H(18A)	3705	4841	153	41
H(18B)	2815	2397	25	41
H(19A)	7954	1474	1490	45
H(19B)	8840	3797	1712	45
H(19C)	8266	3172	866	45

Crystal Structure Data for Triol 13

Triol **13** was recrystallized by slow evaporation of benzene to provide crystals suitable for X-ray analysis, m.p. = 111 – 115 °C.

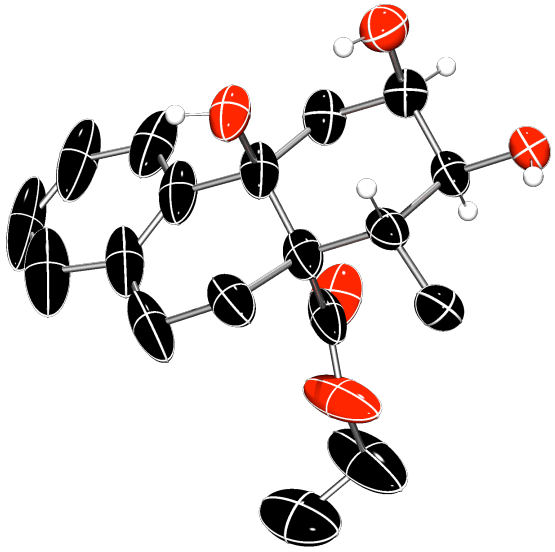


*Table S8. Crystal data and structure refinement for **13***

Empirical formula	C28.63 H34.63 O5	
Formula weight	458.70	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Hexagonal	
Space group	$P6_522$	
Unit cell dimensions	a = 21.3194(5) Å	α = 90°.
	b = 21.3194(5) Å	β = 90°.
	c = 18.6055(6) Å	γ = 120°.
Volume	7323.6(4) $Å^3$	
Z	12	
Density (calculated)	1.305 Mg/m^3	
Absorption coefficient	0.695 mm^{-1}	
F(000)	3108	
Crystal size	.2 x .1 x .1 mm^3	
Theta range for data collection	2.393 to 58.098°.	
Index ranges	-22<=h<=20, -22<=k<=22, -20<=l<=20	
Reflections collected	60463	

Independent reflections	3412 [R(int) = 0.0731]
Completeness to theta = 67.679°	78.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7514 and 0.6563
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3412 / 1 / 283
Goodness-of-fit on F^2	1.110
Final R indices [I>2sigma(I)]	R1 = 0.0803, wR2 = 0.1889
R indices (all data)	R1 = 0.1100, wR2 = 0.2084
Absolute structure parameter	0.03(8)
Extinction coefficient	n/a
Largest diff. peak and hole	0.290 and -0.263 e.$Å^{-3}$

Table S9. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x10^3) for ***13****. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.*

	x	y	z	U(eq)
O(1A)	7920(2)	7040(3)	6808(2)	56(1)
O(2A)	9307(3)	7800(3)	6495(3)	58(1)
O(3A)	9815(2)	6894(2)	5959(2)	43(1)
O(4A)	7565(3)	6012(4)	4758(3)	83(2)
O(5A)	7359(4)	5007(4)	5298(3)	109(3)
C(1A)	7758(4)	6774(4)	6067(3)	55(2)
C(2A)	7774(4)	6048(4)	6049(3)	52(2)
C(3A)	7206(4)	5535(4)	6597(4)	63(2)
C(4A)	6454(4)	5377(7)	6424(5)	91(4)
C(5A)	6399(5)	6008(7)	6139(4)	83(3)
C(6A)	5726(6)	5959(9)	6069(5)	125(6)
C(7A)	5634(7)	6481(12)	5755(7)	136(7)
C(8A)	6225(7)	7100(9)	5525(5)	109(5)
C(9A)	6913(5)	7191(6)	5601(4)	81(3)
C(10A)	7009(4)	6657(6)	5911(4)	70(3)
C(11A)	8356(4)	7356(4)	5609(4)	57(2)
C(12A)	9097(4)	7469(4)	5797(3)	48(2)
C(13A)	9114(3)	6767(4)	5770(3)	42(2)
C(14A)	8537(3)	6184(4)	6252(3)	44(2)
C(15A)	8628(4)	5516(4)	6272(4)	63(2)
C(16A)	7550(4)	5710(5)	5293(4)	63(2)
C(17A)	7152(6)	4621(7)	4606(5)	137(6)
C(18A)	6414(7)	4137(6)	4612(5)	113(4)
C(1)	5200(6)	5125(5)	3686(4)	76(3)
C(2)	5804(6)	5643(6)	4044(4)	80(3)
C(3)	6326(6)	6241(6)	3681(5)	91(3)
C(4)	4612(8)	6693(6)	3992(5)	95(3)
C(5)	3968(7)	6673(5)	4078(5)	88(3)
C(6)	5251(7)	7315(7)	4077(5)	100(4)
C(1DA)	7650(90)	9370(50)	5020(80)	520(40)

C(2DA)	8300(80)	9420(50)	5190(40)	520(40)
C(3DA)	8570(40)	9070(70)	4760(80)	520(40)
C(4DA)	8180(80)	8680(50)	4160(70)	520(40)
C(5DA)	7520(80)	8630(60)	4000(60)	520(40)
C(6DA)	7260(40)	8980(70)	4420(100)	520(40)
C(1DB)	9660(90)	9170(100)	4740(60)	410(30)
C(2DB)	10280(80)	9850(100)	4720(70)	410(30)
C(3DB)	10570(30)	10170(40)	4060(110)	410(30)
C(4DB)	10240(80)	9820(80)	3430(60)	410(30)
C(5DB)	9620(80)	9140(70)	3450(60)	410(30)
C(6DB)	9330(50)	8810(40)	4110(100)	410(30)

Table S10. Bond lengths [Å] and angles [°] for ***13***

O(1A)-C(1A)	1.466(7)
O(2A)-C(12A)	1.438(8)
O(3A)-C(13A)	1.425(7)
O(4A)-C(16A)	1.176(10)
O(5A)-C(16A)	1.344(11)
O(5A)-C(17A)	1.472(10)
C(1A)-C(10A)	1.514(10)
C(1A)-C(11A)	1.519(10)
C(1A)-C(2A)	1.566(11)
C(2A)-C(3A)	1.541(10)
C(2A)-C(16A)	1.543(10)
C(2A)-C(14A)	1.549(9)
C(3A)-C(4A)	1.499(12)
C(4A)-C(5A)	1.504(14)
C(5A)-C(6A)	1.392(14)
C(5A)-C(10A)	1.410(14)
C(6A)-C(7A)	1.35(2)
C(7A)-C(8A)	1.36(2)
C(8A)-C(9A)	1.386(13)
C(9A)-C(10A)	1.382(12)
C(11A)-C(12A)	1.516(9)
C(12A)-C(13A)	1.514(9)
C(13A)-C(14A)	1.527(9)
C(14A)-C(15A)	1.531(10)
C(17A)-C(18A)	1.384(14)
C(1)-C(1)#1	1.341(15)
C(1)-C(2)	1.378(13)
C(2)-C(3)	1.379(13)
C(3)-C(3)#1	1.331(18)
C(4)-C(6)	1.353(15)
C(4)-C(5)	1.363(15)
C(5)-C(5)#2	1.365(19)
C(6)-C(6)#2	1.36(2)
C(1DA)-C(2DA)	1.3900

C(1DA)-C(6DA)	1.3900
C(2DA)-C(3DA)	1.3900
C(3DA)-C(4DA)	1.3900
C(4DA)-C(5DA)	1.3900
C(5DA)-C(6DA)	1.3900
C(1DB)-C(2DB)	1.390(3)
C(1DB)-C(6DB)	1.3900
C(2DB)-C(3DB)	1.3900
C(3DB)-C(4DB)	1.3900
C(4DB)-C(5DB)	1.3900(12)
C(5DB)-C(6DB)	1.3900

C(16A)-O(5A)-C(17A)	117.2(8)
O(1A)-C(1A)-C(10A)	105.6(5)
O(1A)-C(1A)-C(11A)	105.8(6)
C(10A)-C(1A)-C(11A)	114.3(7)
O(1A)-C(1A)-C(2A)	106.6(6)
C(10A)-C(1A)-C(2A)	112.1(7)
C(11A)-C(1A)-C(2A)	111.8(6)
C(3A)-C(2A)-C(16A)	108.7(6)
C(3A)-C(2A)-C(14A)	110.6(6)
C(16A)-C(2A)-C(14A)	111.2(5)
C(3A)-C(2A)-C(1A)	106.8(6)
C(16A)-C(2A)-C(1A)	109.0(7)
C(14A)-C(2A)-C(1A)	110.5(6)
C(4A)-C(3A)-C(2A)	113.0(7)
C(3A)-C(4A)-C(5A)	115.3(8)
C(6A)-C(5A)-C(10A)	117.2(13)
C(6A)-C(5A)-C(4A)	120.3(12)
C(10A)-C(5A)-C(4A)	122.5(8)
C(7A)-C(6A)-C(5A)	123.1(14)
C(6A)-C(7A)-C(8A)	119.2(11)
C(7A)-C(8A)-C(9A)	120.4(14)
C(10A)-C(9A)-C(8A)	120.7(12)
C(9A)-C(10A)-C(5A)	119.3(8)
C(9A)-C(10A)-C(1A)	121.6(9)

C(5A)-C(10A)-C(1A)	119.0(9)
C(12A)-C(11A)-C(1A)	112.5(6)
O(2A)-C(12A)-C(13A)	111.1(5)
O(2A)-C(12A)-C(11A)	109.2(6)
C(13A)-C(12A)-C(11A)	111.9(6)
O(3A)-C(13A)-C(12A)	110.2(5)
O(3A)-C(13A)-C(14A)	110.5(5)
C(12A)-C(13A)-C(14A)	112.2(5)
C(13A)-C(14A)-C(15A)	110.3(5)
C(13A)-C(14A)-C(2A)	110.6(6)
C(15A)-C(14A)-C(2A)	116.1(6)
O(4A)-C(16A)-O(5A)	121.7(7)
O(4A)-C(16A)-C(2A)	126.8(9)
O(5A)-C(16A)-C(2A)	111.4(8)
C(18A)-C(17A)-O(5A)	108.7(8)
C(1)#1-C(1)-C(2)	119.8(5)
C(1)-C(2)-C(3)	120.2(7)
C(3)#1-C(3)-C(2)	120.0(5)
C(6)-C(4)-C(5)	121.4(10)
C(4)-C(5)-C(5)#2	119.2(6)
C(4)-C(6)-C(6)#2	119.5(7)
C(2DA)-C(1DA)-C(6DA)	120.0
C(3DA)-C(2DA)-C(1DA)	120.0
C(2DA)-C(3DA)-C(4DA)	120.00(6)
C(3DA)-C(4DA)-C(5DA)	120.0
C(4DA)-C(5DA)-C(6DA)	120.0
C(5DA)-C(6DA)-C(1DA)	120.00(6)
C(2DB)-C(1DB)-C(6DB)	120.00(11)
C(3DB)-C(2DB)-C(1DB)	120.00(5)
C(4DB)-C(3DB)-C(2DB)	120.00(6)
C(5DB)-C(4DB)-C(3DB)	120.00(12)
C(4DB)-C(5DB)-C(6DB)	120.00(8)
C(5DB)-C(6DB)-C(1DB)	120.00(9)

Symmetry transformations used to generate equivalent atoms:

#1 y,x,-z+2/3 #2 x,x-y+1,-z+5/6

*Table S11. Anisotropic displacement parameters ($Å^2 x10^3$) for **13**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$*

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1A)	51(3)	88(4)	40(2)	-17(3)	-8(2)	43(3)
O(2A)	60(3)	59(3)	61(3)	-10(3)	-5(2)	32(3)
O(3A)	35(3)	45(3)	45(2)	2(2)	1(2)	17(2)
O(4A)	97(5)	137(5)	36(3)	-23(3)	-14(3)	74(4)
O(5A)	115(5)	73(4)	49(3)	-30(3)	24(3)	-21(4)
C(1A)	40(4)	94(6)	34(3)	-17(4)	-9(3)	36(4)
C(2A)	40(4)	73(5)	31(3)	-14(3)	3(3)	19(4)
C(3A)	46(5)	77(5)	37(4)	-16(4)	5(3)	9(4)
C(4A)	34(5)	139(10)	54(5)	-20(6)	8(4)	8(5)
C(5A)	41(6)	157(10)	46(5)	-45(6)	-13(4)	46(6)
C(6A)	56(7)	253(17)	59(6)	-80(9)	-29(5)	71(9)
C(7A)	72(8)	300(20)	75(8)	-109(11)	-54(7)	127(12)
C(8A)	86(8)	231(15)	64(6)	-71(8)	-44(6)	119(10)
C(9A)	85(7)	147(9)	48(5)	-40(5)	-28(4)	86(7)
C(10A)	51(5)	128(8)	38(4)	-34(5)	-11(4)	51(6)
C(11A)	54(5)	79(5)	46(4)	2(4)	-1(4)	39(4)
C(12A)	49(4)	58(5)	40(4)	2(3)	-1(3)	29(4)
C(13A)	33(4)	56(4)	31(3)	-4(3)	0(3)	16(3)
C(14A)	37(4)	46(4)	36(3)	-6(3)	0(3)	12(3)
C(15A)	51(5)	47(5)	77(5)	-3(4)	12(4)	13(4)
C(16A)	33(4)	93(7)	40(5)	-22(5)	4(3)	15(4)
C(17A)	105(9)	133(10)	59(6)	-52(6)	13(6)	-26(8)
C(18A)	129(10)	92(8)	64(6)	-17(5)	-16(6)	16(8)
C(1)	121(8)	92(7)	49(4)	11(5)	0(5)	79(7)
C(2)	136(9)	110(8)	38(4)	-5(5)	-8(5)	95(7)
C(3)	115(8)	106(8)	58(5)	-16(5)	-17(5)	59(7)
C(4)	177(12)	91(8)	57(6)	-8(5)	-21(7)	99(9)
C(5)	132(9)	81(6)	60(5)	-9(5)	-8(6)	60(6)
C(6)	131(9)	146(11)	46(5)	-9(7)	-15(6)	87(9)

Table S12. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for ***13***

	x	y	z	U(eq)
H(1A)	7550	6986	7001	84
H(2A)	8992	7554	6789	88
H(3A)	9776	6578	6237	65
H(3AA)	7212	5083	6610	76
H(3AB)	7338	5752	7071	76
H(4AA)	6162	5201	6856	109
H(4AB)	6247	4990	6072	109
H(6A)	5320	5549	6245	150
H(7A)	5172	6417	5698	163
H(8A)	6168	7465	5316	131
H(9A)	7313	7616	5440	97
H(11A)	8255	7221	5107	69
H(11B)	8358	7808	5675	69
H(12A)	9445	7802	5444	57
H(13A)	9015	6589	5274	51
H(14A)	8634	6383	6740	52
H(15A)	8599	5337	5793	94
H(15B)	8251	5147	6561	94
H(15C)	9091	5645	6476	94
H(17A)	7272	4964	4216	164
H(17B)	7414	4363	4534	164
H(18A)	6293	3825	5022	169
H(18B)	6279	3852	4180	169
H(18C)	6157	4400	4636	169
H(1)	4846	4724	3933	91
H(2)	5860	5589	4532	96
H(3)	6738	6584	3921	110
H(4)	4613	6270	3873	113
H(5)	3533	6242	4016	106
H(6)	5686	7320	4014	120

H(1DA)	7468	9607	5309	622
H(2DA)	8562	9679	5591	622
H(3DA)	9005	9096	4874	622
H(4DA)	8353	8442	3877	622
H(5DA)	7259	8370	3595	622
H(6DA)	6817	8953	4311	622
H(1DB)	9471	8948	5182	495
H(2DB)	10503	10084	5145	495
H(3DB)	10983	10630	4047	495
H(4DB)	10431	10040	2986	495
H(5DB)	9399	8904	3023	495
H(6DB)	8919	8358	4121	495

Crystal Structure Data for Diol 14

Diol **14** was recrystallized in boiling heptane to provide crystals suitable for X-ray analysis, m.p. = 97 – 99 °C.

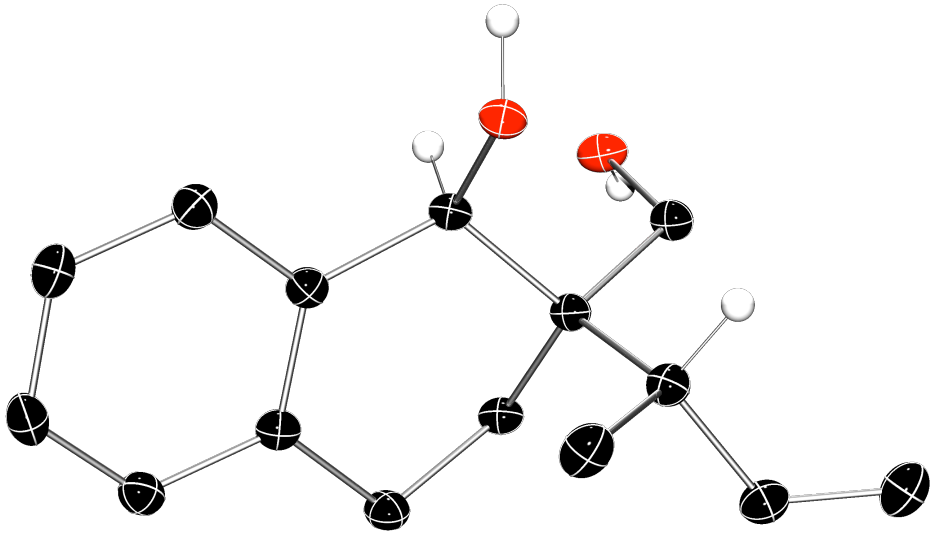


*Table S13. Crystal data and structure refinement for **14***

Empirical formula	C15 H20 O2	
Formula weight	232.31	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 8.0972(3) Å	α = 90°.
	b = 6.3583(2) Å	β = 105.4260(10)°.
	c = 12.5999(4) Å	γ = 90°.
Volume	625.33(4) Å^3	
Z	2	
Density (calculated)	1.234 Mg/m^3	
Absorption coefficient	0.630 mm^{-1}	
F(000)	252	
Crystal size	.1 x .1 x .1 mm^3	
Theta range for data collection	3.639 to 79.259°.	

Index ranges	-10<=h<=10, -8<=k<=8, -15<=l<=16
Reflections collected	20029
Independent reflections	2647 [R(int) = 0.0449]
Completeness to theta = 67.679°	100.0 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2647 / 3 / 163
Goodness-of-fit on F^2	1.085
Final R indices [I>2sigma(I)]	R1 = 0.0296, wR2 = 0.0677
R indices (all data)	R1 = 0.0312, wR2 = 0.0687
Absolute structure parameter	0.04(8)
Extinction coefficient	n/a
Largest diff. peak and hole	0.144 and -0.158 e.$Å^{-3}$

Table S14. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (≈Å x 10^3) for ***14****. U(eq) is defined as one third of the trace of the orthogonalized* U^{ij} *tensor.*

	x	y	z	U(eq)
C(1)	8395(2)	5246(3)	8290(1)	13(1)
C(2)	6809(2)	3826(3)	8166(1)	14(1)
C(3)	6586(2)	2540(3)	7101(1)	15(1)
C(4)	6321(2)	3872(3)	6062(1)	18(1)
C(5)	7576(2)	5670(3)	6196(1)	15(1)
C(6)	7795(2)	6715(3)	5269(1)	18(1)
C(7)	8956(2)	8347(3)	5356(2)	20(1)
C(8)	9945(2)	8942(3)	6391(2)	21(1)
C(9)	9737(2)	7927(3)	7319(2)	18(1)
C(10)	8540(2)	6317(3)	7239(1)	14(1)
O(1)	8491(2)	6779(2)	9145(1)	15(1)
O(2)	8701(2)	1051(2)	9217(1)	18(1)
C(11)	7204(2)	2296(3)	9154(2)	16(1)
C(12)	5173(2)	5063(3)	8245(2)	16(1)
C(13)	4829(2)	7173(3)	7629(2)	21(1)
C(14)	3580(2)	3725(3)	7913(2)	19(1)
C(15)	2772(2)	2878(3)	8592(2)	23(1)

Table S15. Bond lengths [Å] and angles [°] for ***14***

C(1)-O(1)	1.440(2)
C(1)-C(10)	1.521(2)
C(1)-C(2)	1.543(2)
C(1)-H(1)	1.0000
C(2)-C(3)	1.541(2)
C(2)-C(11)	1.545(2)
C(2)-C(12)	1.566(2)
C(3)-C(4)	1.525(2)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-C(5)	1.509(3)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-C(6)	1.396(2)
C(5)-C(10)	1.400(2)
C(6)-C(7)	1.385(3)
C(6)-H(6)	0.9500
C(7)-C(8)	1.389(3)
C(7)-H(7)	0.9500
C(8)-C(9)	1.384(3)
C(8)-H(8)	0.9500
C(9)-C(10)	1.395(2)
C(9)-H(9)	0.9500
O(1)-H(1O)	0.93(2)
O(2)-C(11)	1.432(2)
O(2)-H(2O)	0.91(2)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-C(14)	1.508(2)
C(12)-C(13)	1.537(3)
C(12)-H(12)	1.0000
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800

C(14)-C(15)	1.322(3)
C(14)-H(14)	0.9500
C(15)-H(15A)	0.9500
C(15)-H(15B)	0.9500

O(1)-C(1)-C(10)	110.31(13)
O(1)-C(1)-C(2)	110.47(13)
C(10)-C(1)-C(2)	115.37(14)
O(1)-C(1)-H(1)	106.7
C(10)-C(1)-H(1)	106.7
C(2)-C(1)-H(1)	106.7
C(3)-C(2)-C(1)	107.46(13)
C(3)-C(2)-C(11)	108.58(14)
C(1)-C(2)-C(11)	107.34(13)
C(3)-C(2)-C(12)	114.66(14)
C(1)-C(2)-C(12)	113.27(15)
C(11)-C(2)-C(12)	105.21(13)
C(4)-C(3)-C(2)	114.18(14)
C(4)-C(3)-H(3A)	108.7
C(2)-C(3)-H(3A)	108.7
C(4)-C(3)-H(3B)	108.7
C(2)-C(3)-H(3B)	108.7
H(3A)-C(3)-H(3B)	107.6
C(5)-C(4)-C(3)	112.78(14)
C(5)-C(4)-H(4A)	109.0
C(3)-C(4)-H(4A)	109.0
C(5)-C(4)-H(4B)	109.0
C(3)-C(4)-H(4B)	109.0
H(4A)-C(4)-H(4B)	107.8
C(6)-C(5)-C(10)	118.84(16)
C(6)-C(5)-C(4)	119.89(15)
C(10)-C(5)-C(4)	121.27(15)
C(7)-C(6)-C(5)	121.68(17)
C(7)-C(6)-H(6)	119.2
C(5)-C(6)-H(6)	119.2
C(6)-C(7)-C(8)	119.20(17)

C(6)-C(7)-H(7)	120.4
C(8)-C(7)-H(7)	120.4
C(9)-C(8)-C(7)	119.79(18)
C(9)-C(8)-H(8)	120.1
C(7)-C(8)-H(8)	120.1
C(8)-C(9)-C(10)	121.30(17)
C(8)-C(9)-H(9)	119.3
C(10)-C(9)-H(9)	119.3
C(9)-C(10)-C(5)	119.13(16)
C(9)-C(10)-C(1)	118.63(15)
C(5)-C(10)-C(1)	122.16(15)
C(1)-O(1)-H(1O)	107.5(19)
C(11)-O(2)-H(2O)	115.1(17)
O(2)-C(11)-C(2)	112.54(14)
O(2)-C(11)-H(11A)	109.1
C(2)-C(11)-H(11A)	109.1
O(2)-C(11)-H(11B)	109.1
C(2)-C(11)-H(11B)	109.1
H(11A)-C(11)-H(11B)	107.8
C(14)-C(12)-C(13)	108.99(15)
C(14)-C(12)-C(2)	111.98(15)
C(13)-C(12)-C(2)	116.67(15)
C(14)-C(12)-H(12)	106.2
C(13)-C(12)-H(12)	106.2
C(2)-C(12)-H(12)	106.2
C(12)-C(13)-H(13A)	109.5
C(12)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(12)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(15)-C(14)-C(12)	125.79(17)
C(15)-C(14)-H(14)	117.1
C(12)-C(14)-H(14)	117.1
C(14)-C(15)-H(15A)	120.0
C(14)-C(15)-H(15B)	120.0

H(15A)-C(15)-H(15B)	120.0

*Table S16. Anisotropic displacement parameters ($Å^2 x 10^3$) for **14**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$*

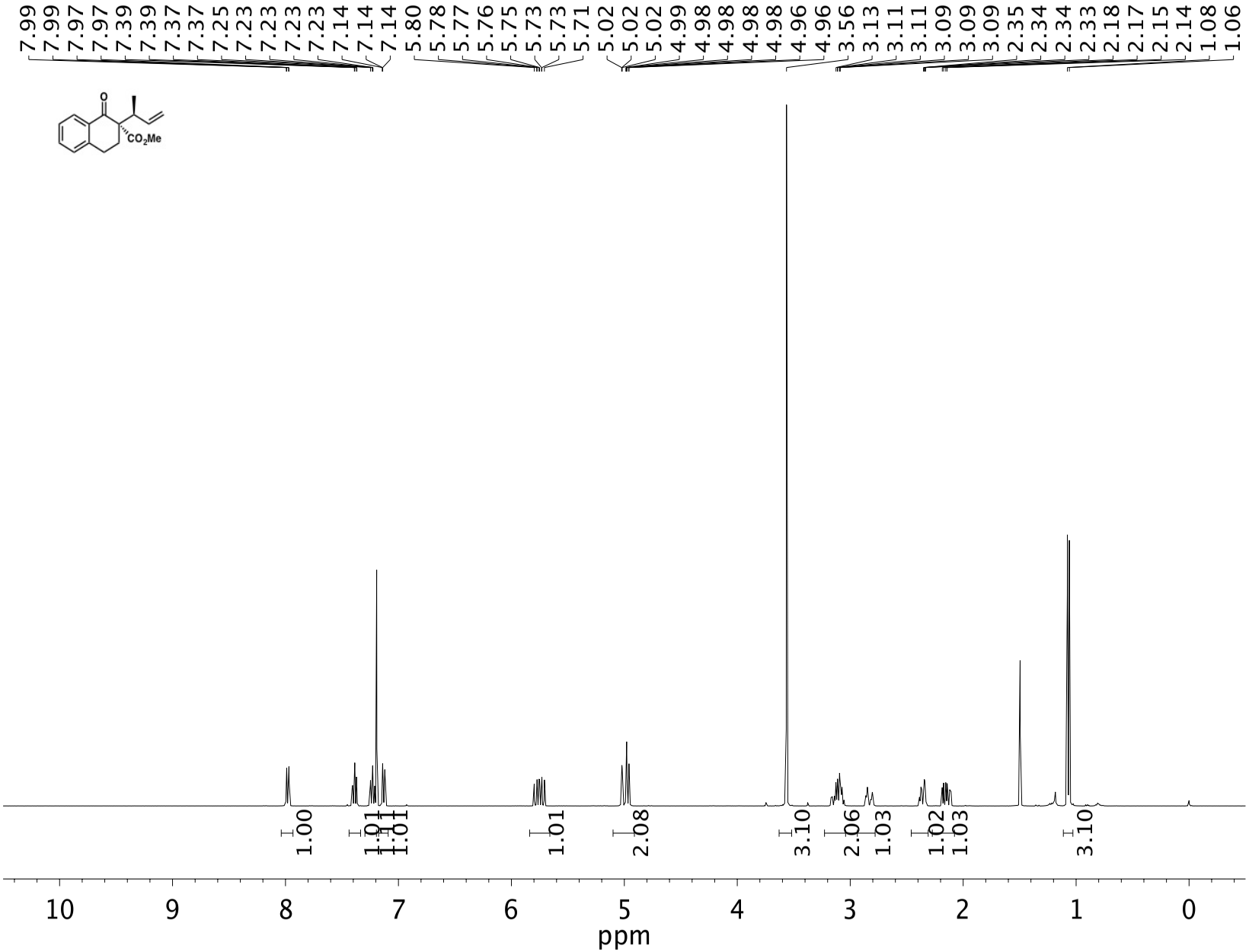
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	15(1)	11(1)	13(1)	-1(1)	2(1)	1(1)
C(2)	14(1)	11(1)	14(1)	1(1)	2(1)	-1(1)
C(3)	16(1)	12(1)	16(1)	-1(1)	1(1)	0(1)
C(4)	19(1)	18(1)	16(1)	-1(1)	2(1)	-3(1)
C(5)	15(1)	13(1)	16(1)	0(1)	3(1)	3(1)
C(6)	18(1)	20(1)	16(1)	1(1)	4(1)	2(1)
C(7)	23(1)	21(1)	18(1)	4(1)	9(1)	1(1)
C(8)	20(1)	20(1)	24(1)	1(1)	8(1)	-3(1)
C(9)	17(1)	18(1)	18(1)	-1(1)	5(1)	-1(1)
C(10)	14(1)	14(1)	15(1)	1(1)	4(1)	2(1)
O(1)	17(1)	13(1)	14(1)	-3(1)	2(1)	0(1)
O(2)	18(1)	11(1)	21(1)	1(1)	0(1)	2(1)
C(11)	18(1)	12(1)	16(1)	2(1)	3(1)	1(1)
C(12)	17(1)	14(1)	16(1)	0(1)	4(1)	-1(1)
C(13)	18(1)	16(1)	29(1)	4(1)	6(1)	3(1)
C(14)	17(1)	17(1)	21(1)	-2(1)	3(1)	-1(1)
C(15)	20(1)	19(1)	31(1)	0(1)	9(1)	-1(1)

Table S12. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å ^{2}x 10^3) for ***14***

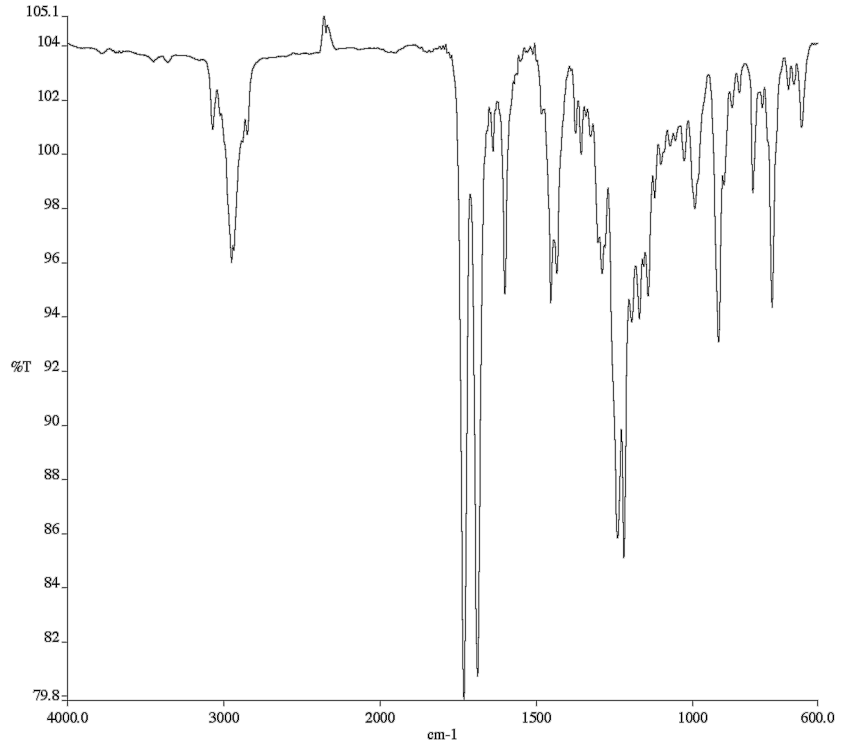
	x	y	z	U(eq)
H(1)	9423	4319	8540	16
H(3A)	7615	1651	7174	18
H(3B)	5590	1591	7016	18
H(4A)	6441	2964	5448	22
H(4B)	5141	4443	5864	22
H(6)	7130	6296	4560	21
H(7)	9075	9051	4715	24
H(8)	10761	10042	6462	25
H(9)	10423	8336	8024	21
H(1O)	9470(30)	6480(50)	9710(20)	52(8)
H(2O)	8500(30)	-340(30)	9040(20)	42(8)
H(11A)	7369	3113	9843	19
H(11B)	6210	1351	9090	19
H(12)	5343	5400	9042	19
H(13A)	4478	6913	6834	32
H(13B)	5875	8025	7814	32
H(13C)	3914	7925	7847	32
H(14)	3117	3469	7149	22
H(15A)	3189	3093	9363	28
H(15B)	1773	2054	8308	28

References

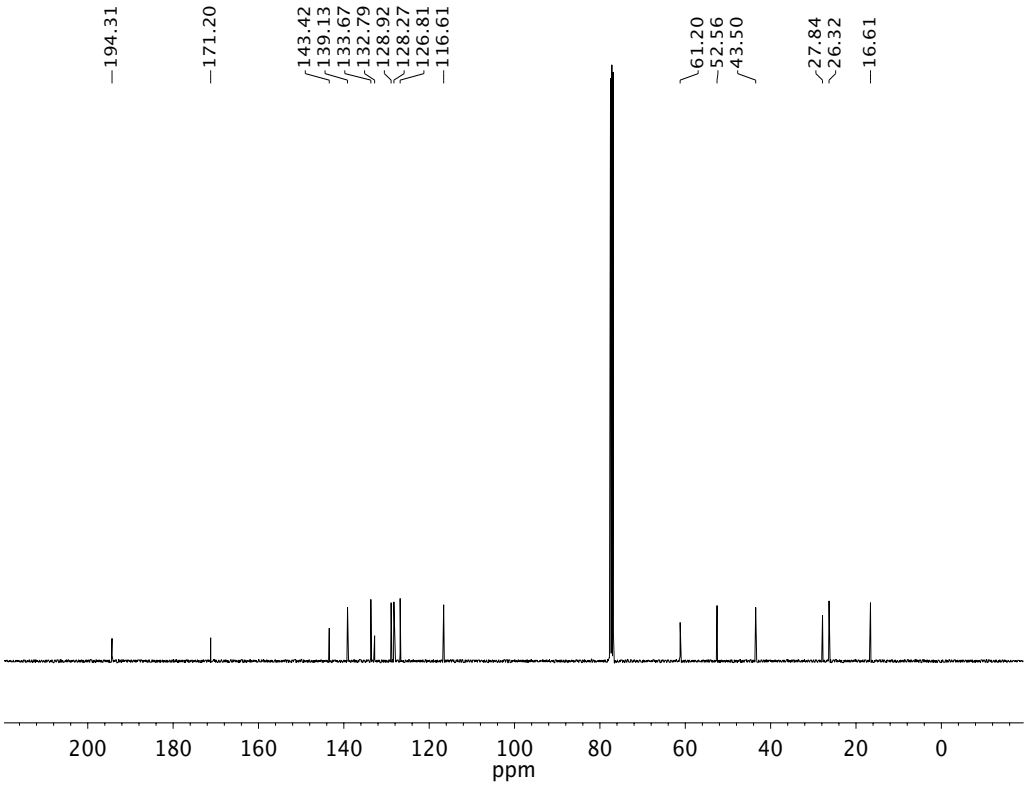
[1] (a) Liu, W.-B.; He, H.; Dai, L.-X.; You, S.-L. *Synthesis* **2009**, 2076–2082; (b) Liu, W.-B.; Zheng, C.; Zhuo, C.-X.; Dai, L.-X.; You, S.-L. *J. Am. Chem. Soc.* **2012**, *134*, 4812–4821.
[2] Defieber, C.; Ariger, M. A.; Moriel, P.; Carreira, E. M. *Angew. Chem., Int. Ed.* **2007**, *46*, 3139–3143.
[3] Cui, L.-Q.; Dong, Z.-L.; Liu, K.; Zhang, C. *Org. Lett.* **2011**, *13*, 6488–6491.
[4] Manitto, P.; Monti, D.; Zanzola, S.; Speranza, G. *J. Org. Chem.* **1997**, *62*, 6658–6665.
[5] Breitenlechner, S.; Bach, T. *Angew. Chem., Int. Ed.* **2008**, *47*, 7957–7959.
[6] Paolo, B.; Diego, V.; Giampietro, B.; Roberto, S. U.S. Patent, 166800 A1, Sept. 4, 2003.
[7] Ankner, T.; Fridén-Saxin, M.; Pemberton, N.; Seifert, T.; Grøtli, M.; Luthman, K.; Hilmersson, G. *Org. Lett.* **2010**, *12*, 2210–2213.



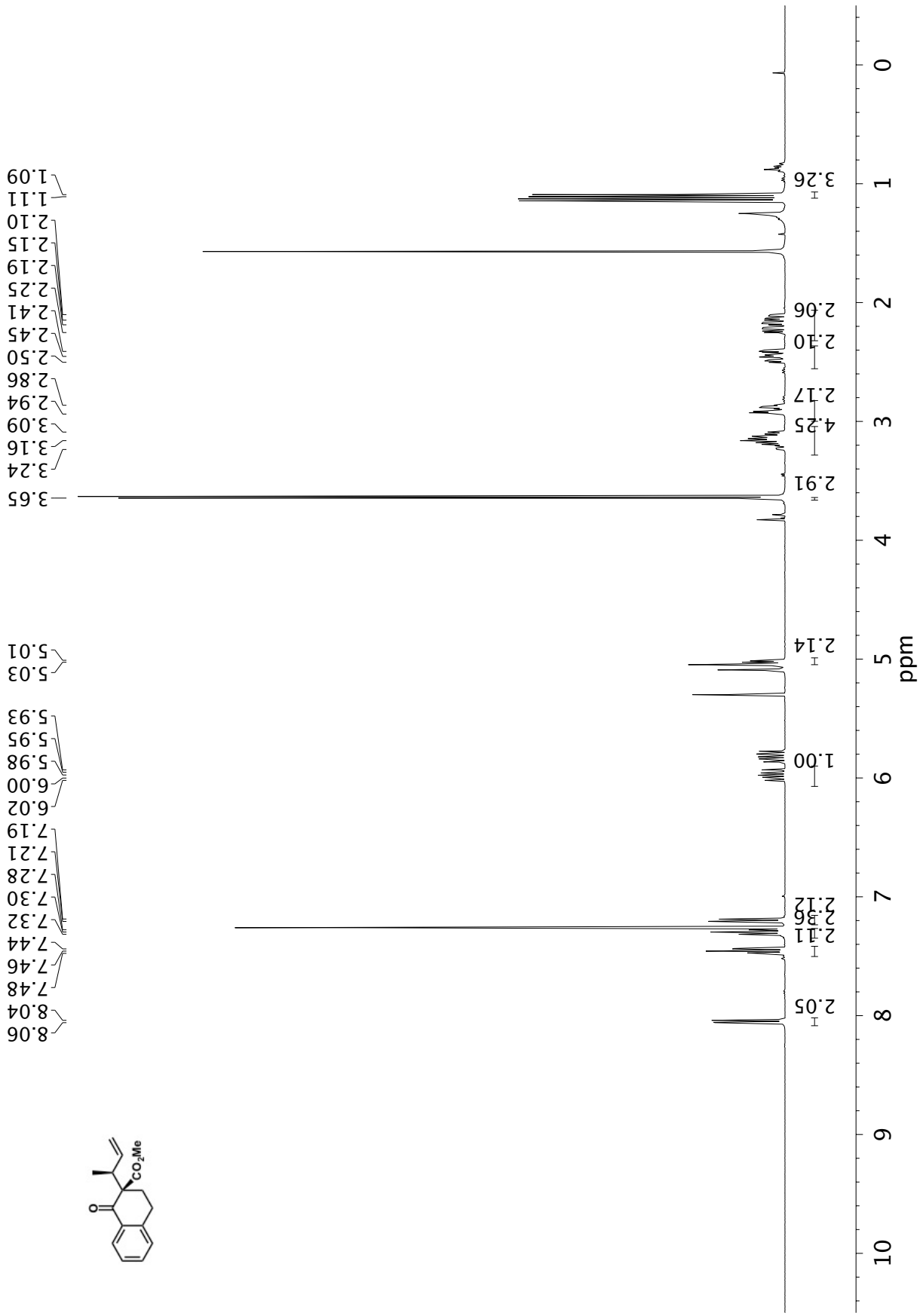
^{1}H NMR (400 MHz, $CDCl_3$) of compound **6.**



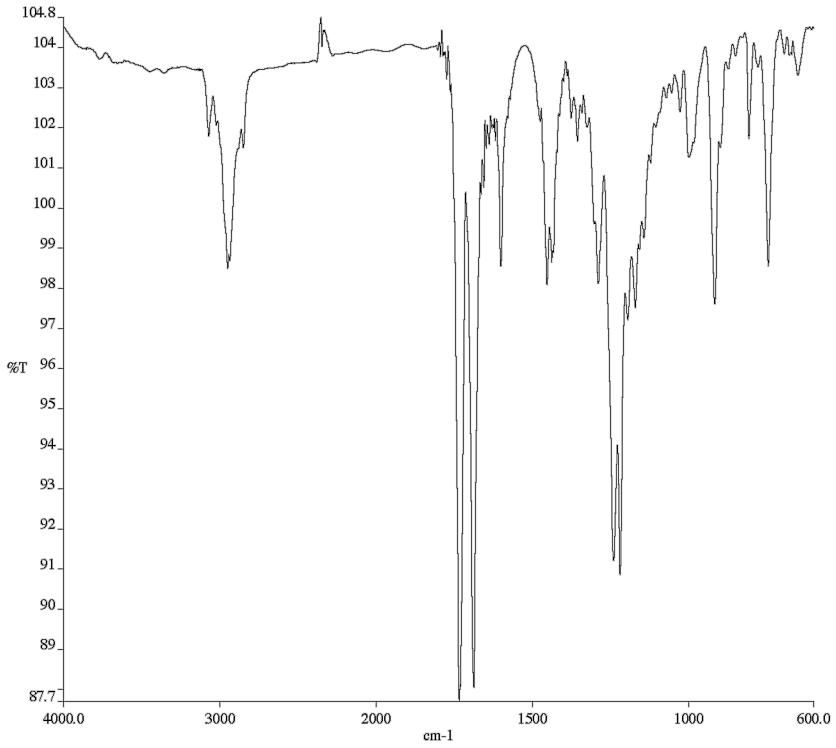
Infrared spectrum (Thin Film, NaCl) of compound **6**.



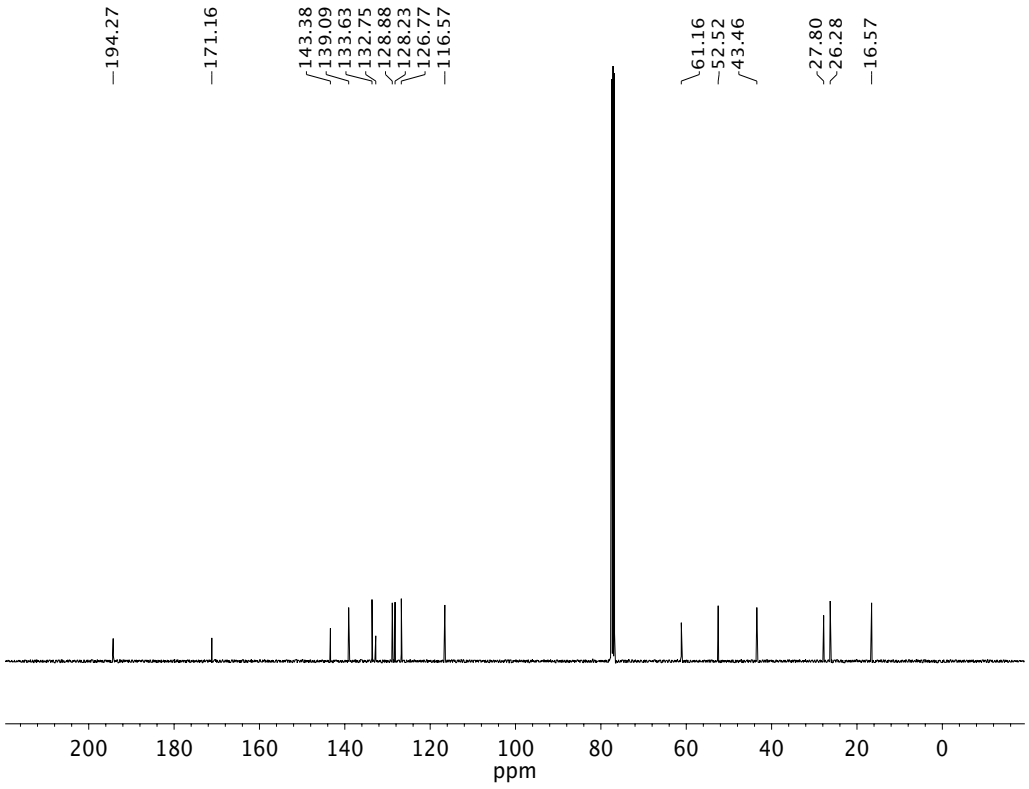
^{13}C NMR (101 MHz, $CDCl_3$) of compound **6**.



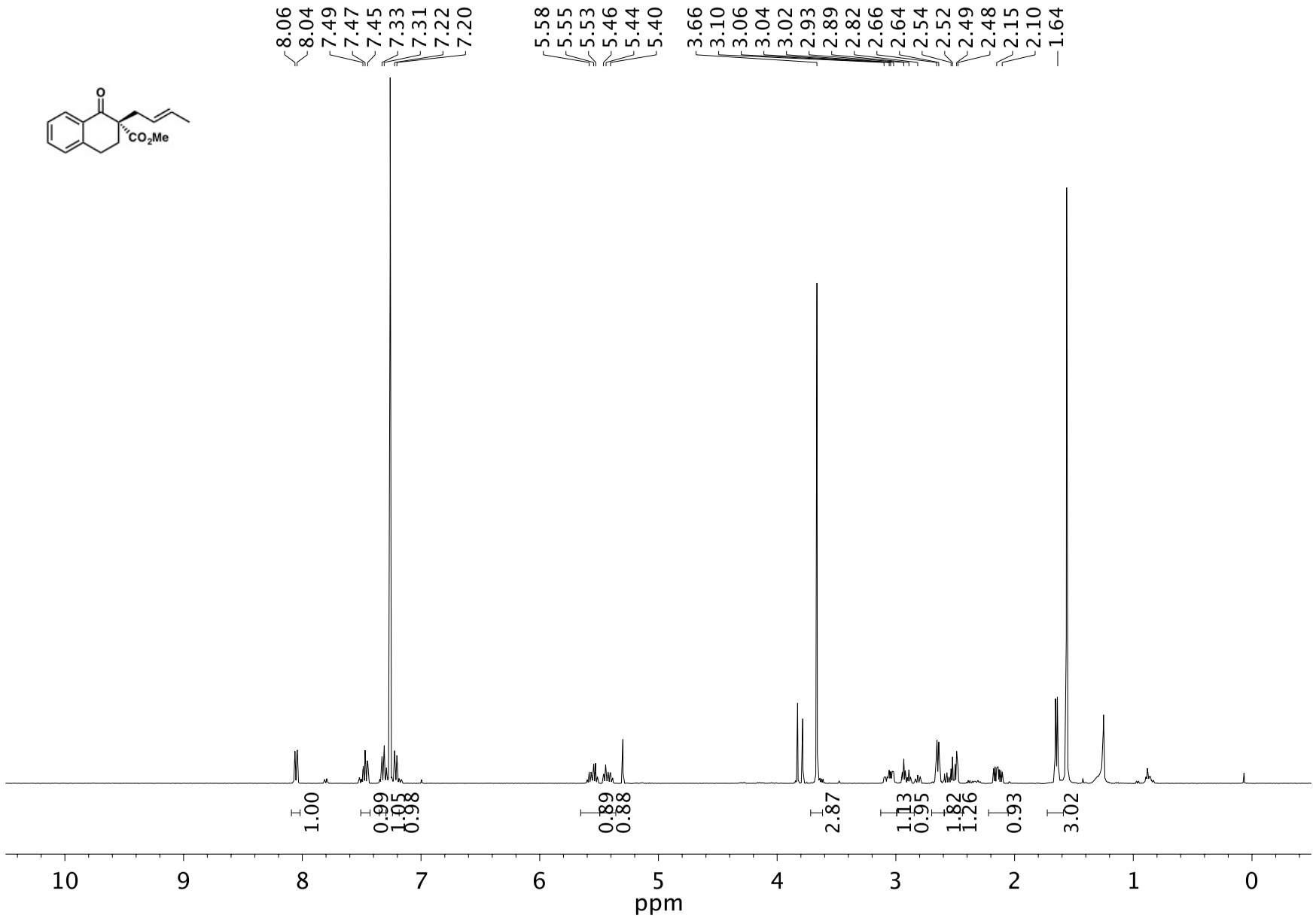
^{1}H NMR (400 MHz, $CDCl_3$) of compound **epi-6**.



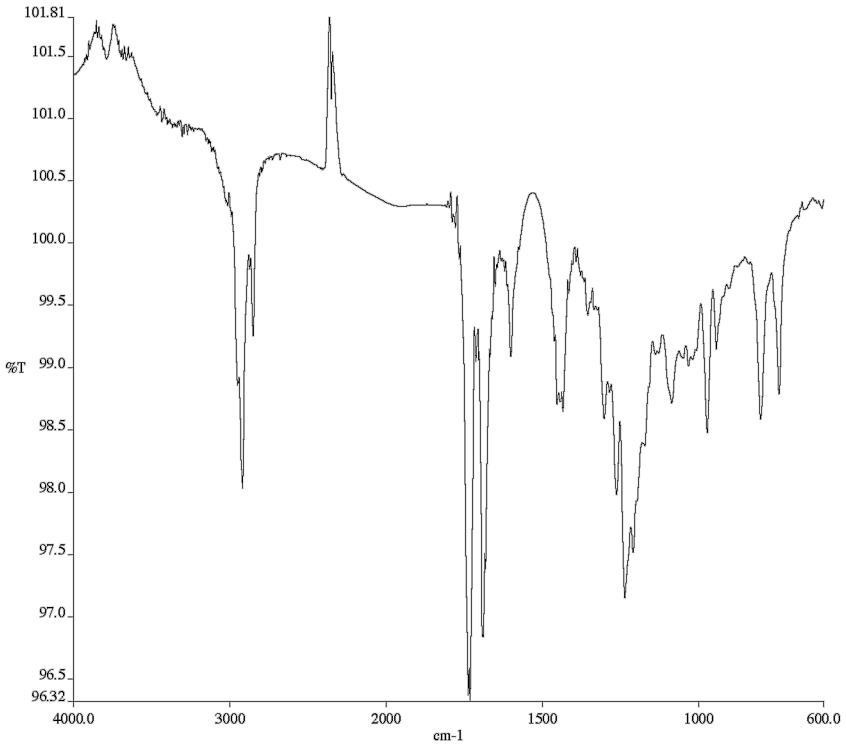
Infrared spectrum (Thin Film, NaCl) of compound **epi-6**.



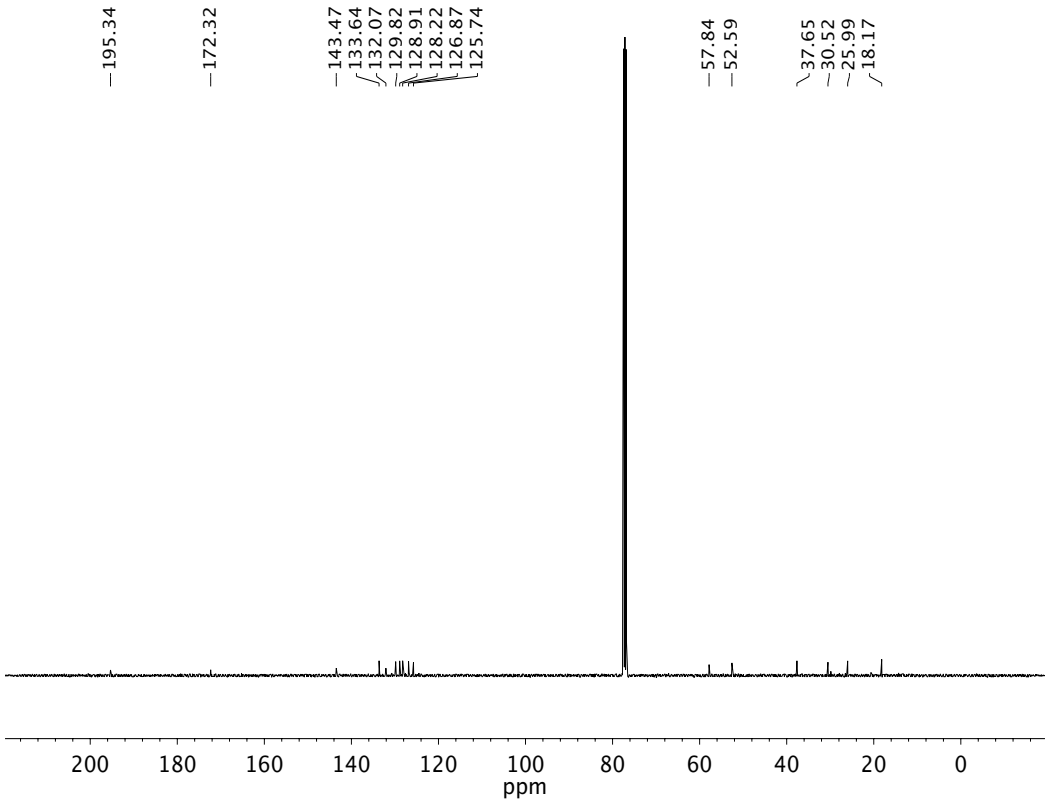
^{13}C NMR (101 MHz, $CDCl_3$) of compound **epi-6**.



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

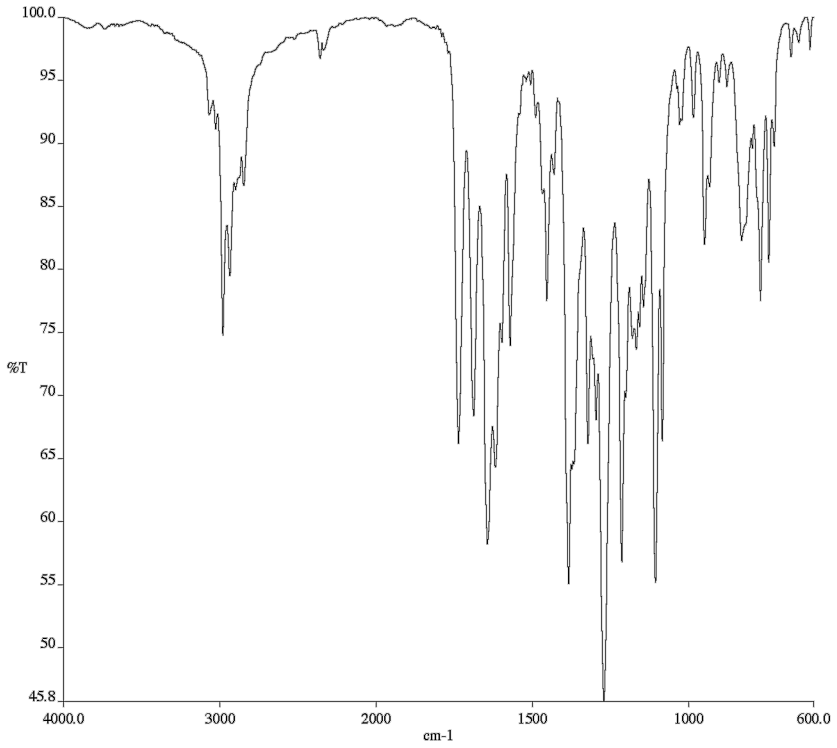


Infrared spectrum (Thin Film, NaCl) of compound **7**.

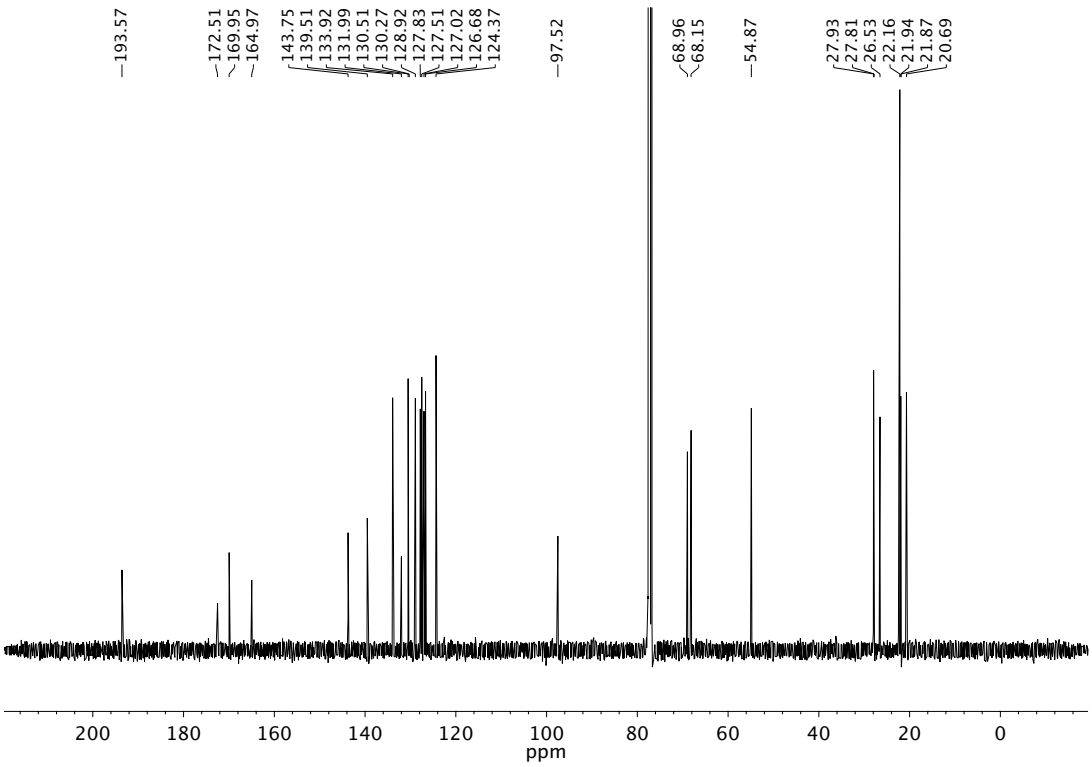


^{13}C NMR (101 MHz, $CDCl_3$) of compound **7**.

^{1}H NMR (400 MHz, $CDCl_3$) of compound **8b**.

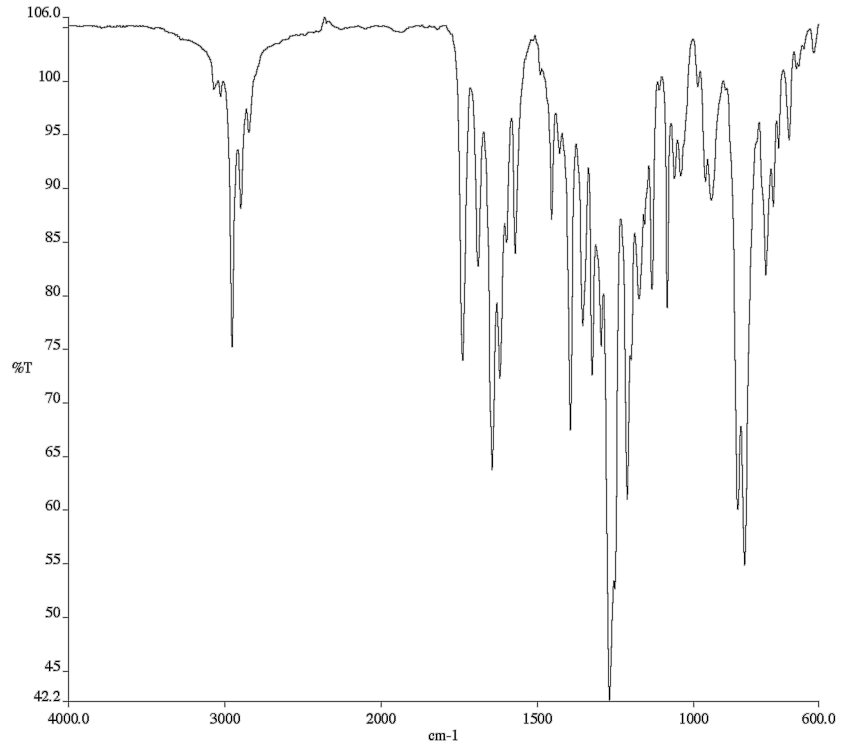


Infrared spectrum (Thin Film, NaCl) of compound **8b**.

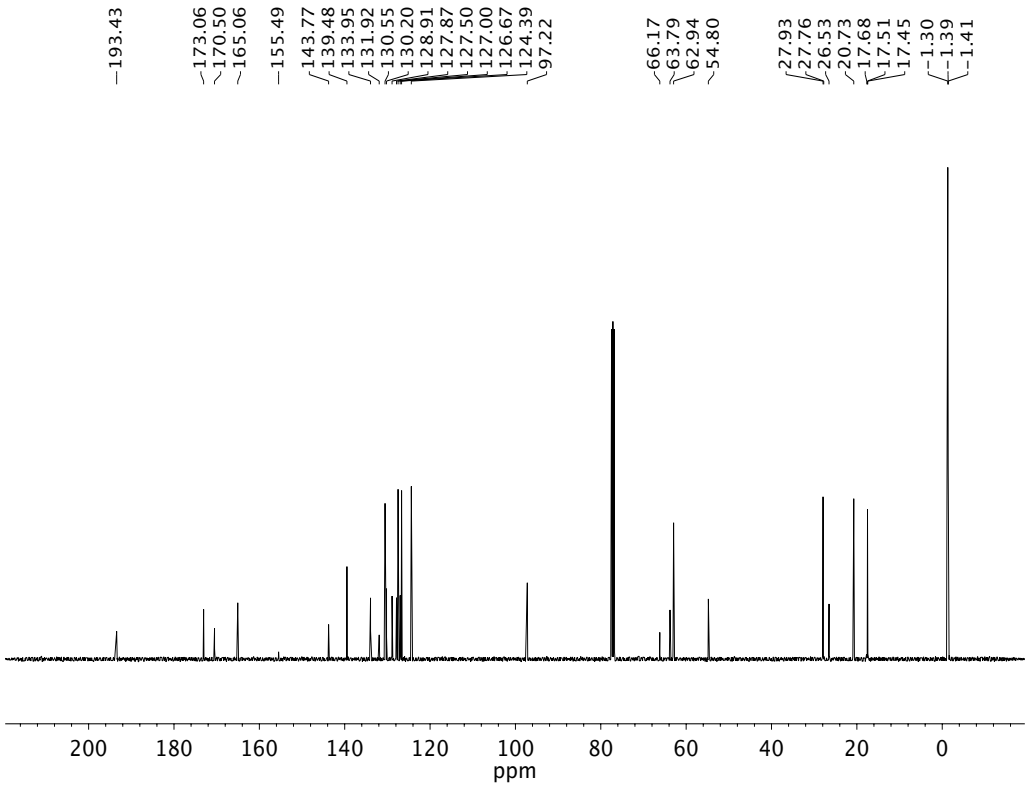


^{13}C NMR (101 MHz, $CDCl_3$) of compound **8b**.

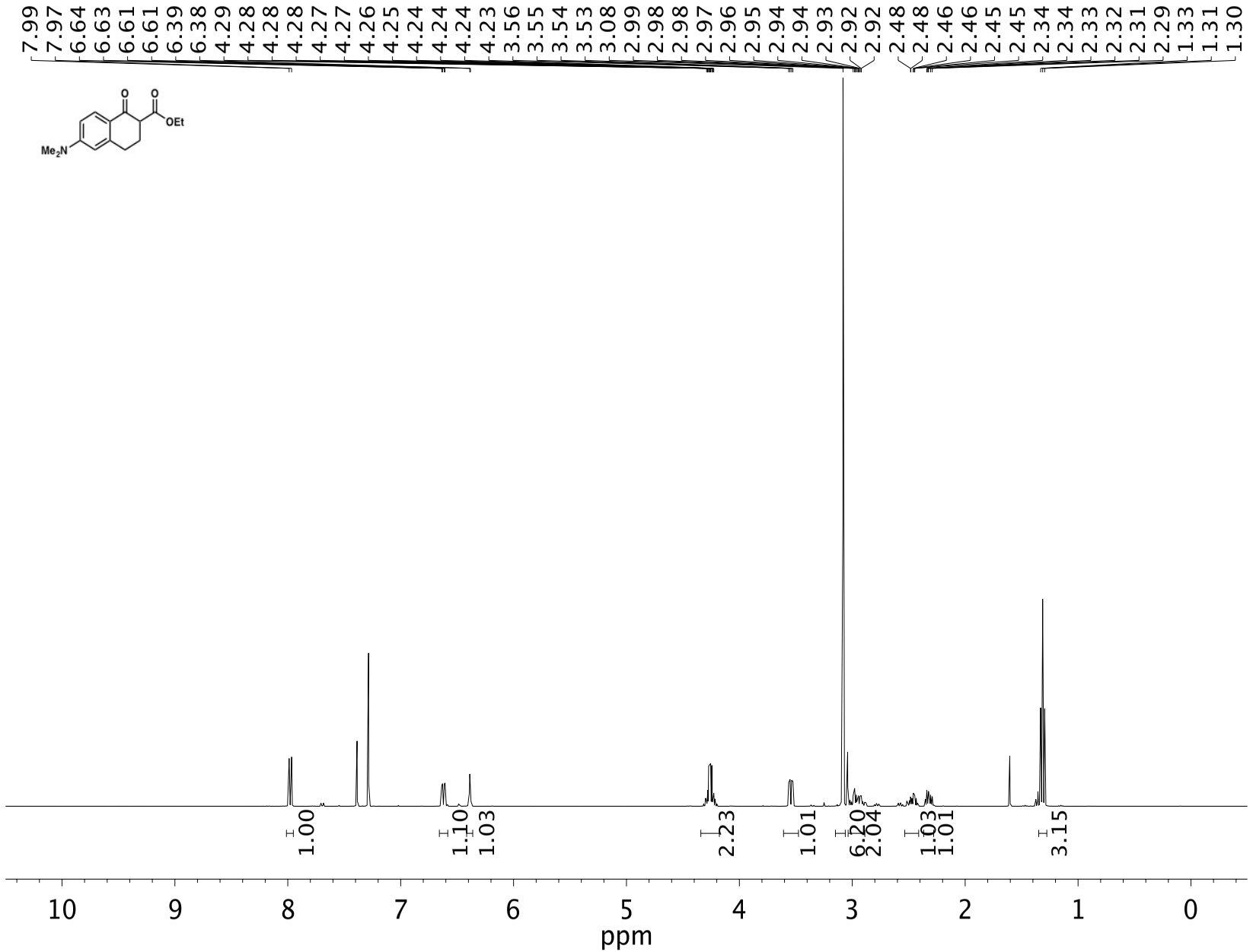
^{1}H NMR (400 MHz, $CDCl_3$) of compound **8c.**



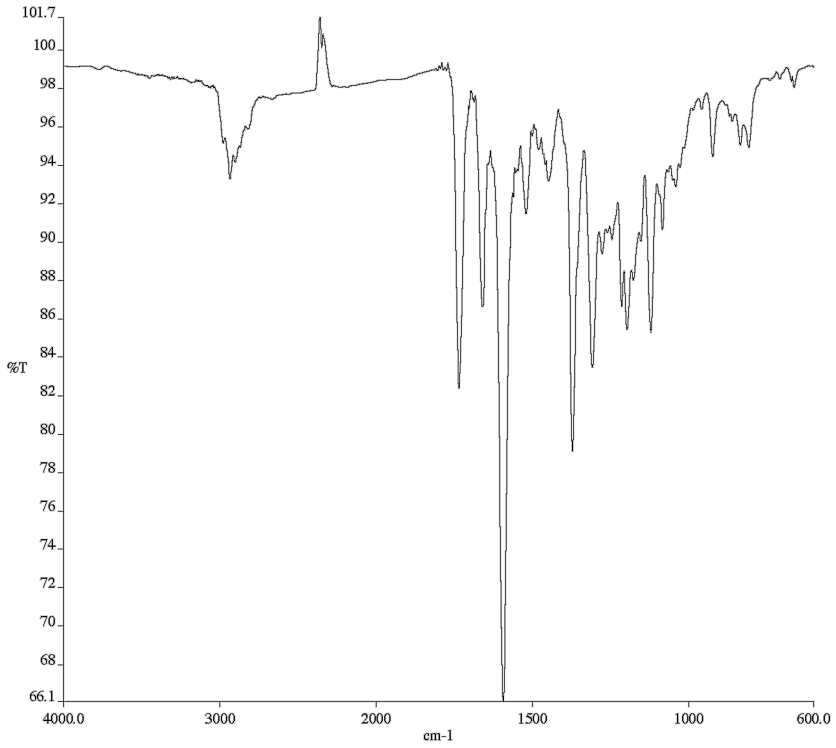
Infrared spectrum (Thin Film, NaCl) of compound **8c**.



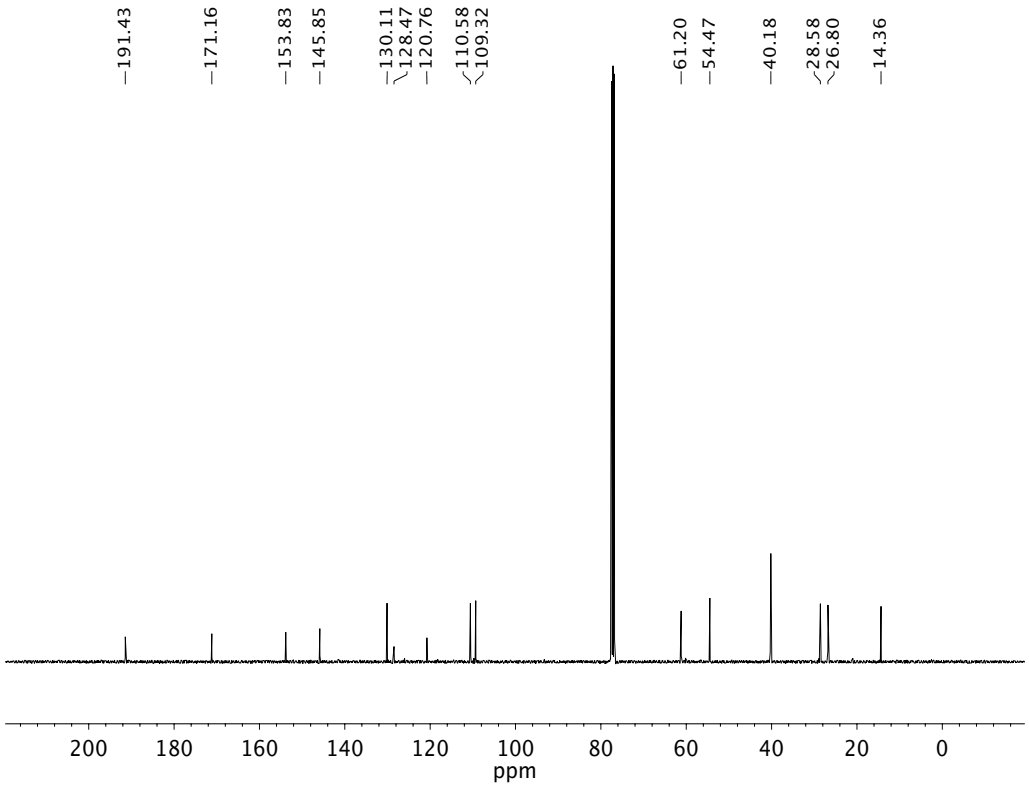
^{13}C NMR (101 MHz, $CDCl_3$) of compound **8c**.



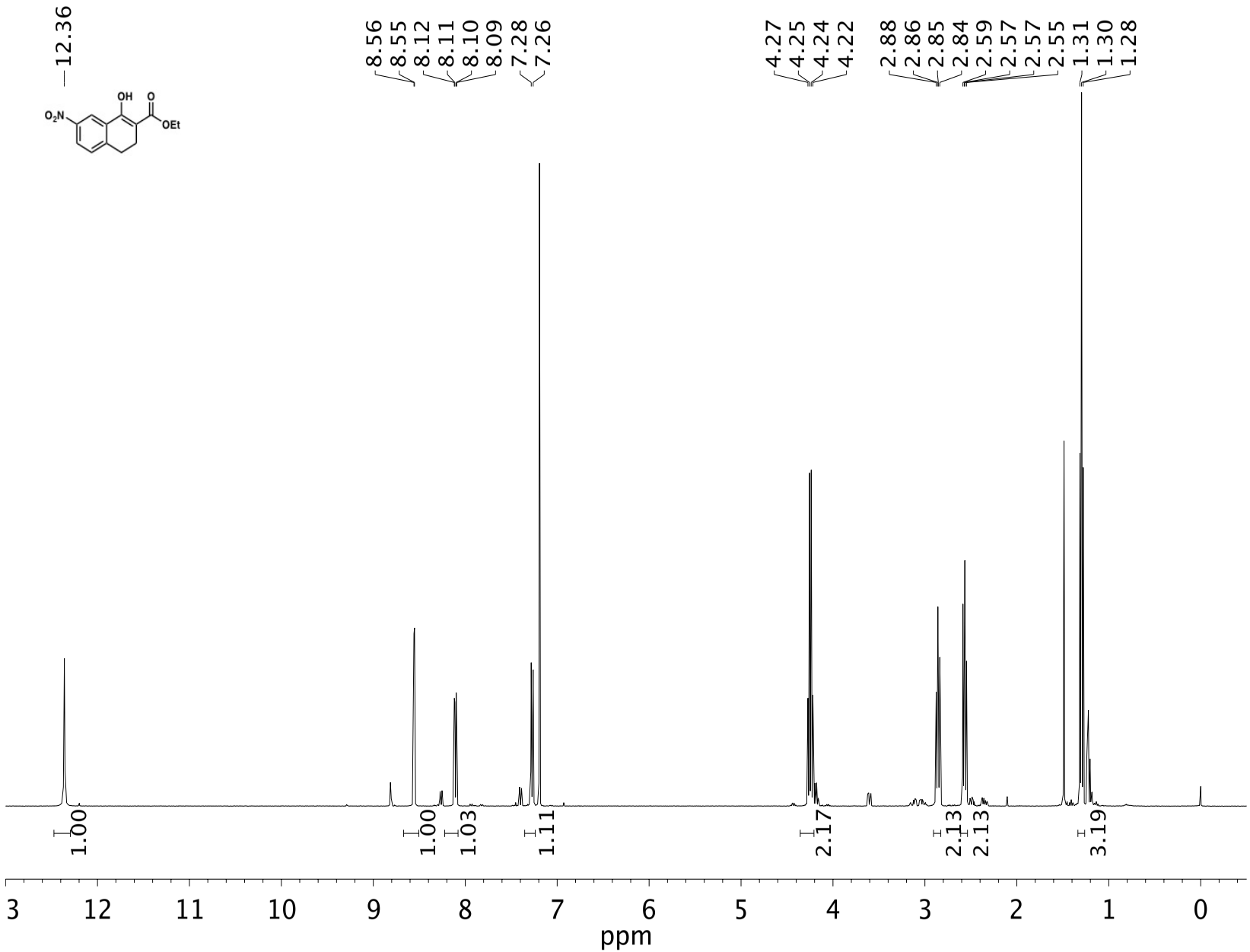
^{1}H NMR (400 MHz, $CDCl_3$) of compound **8e**.



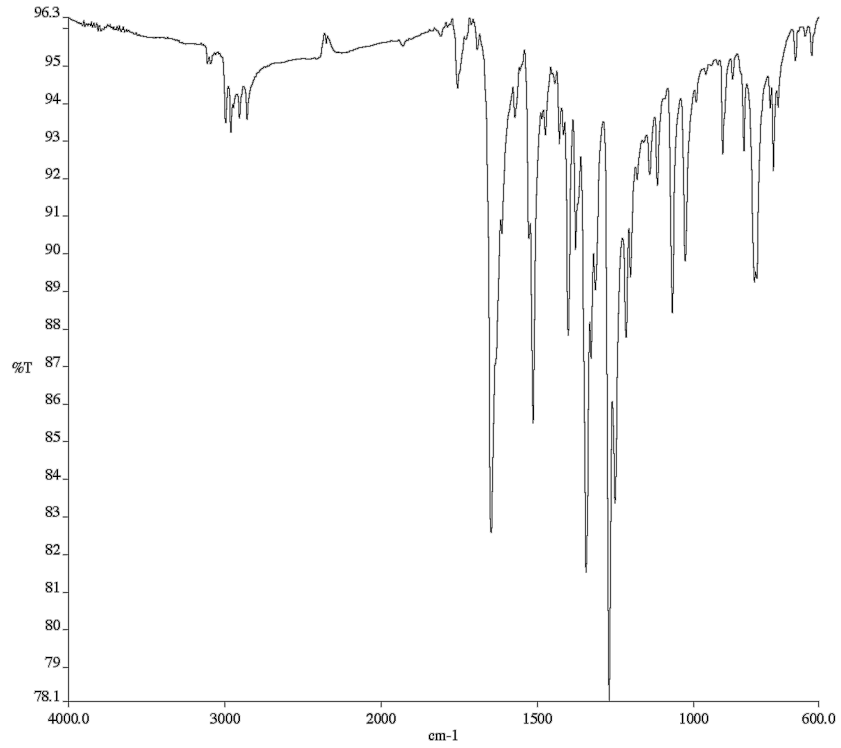
Infrared spectrum (Thin Film, NaCl) of compound **8e**.



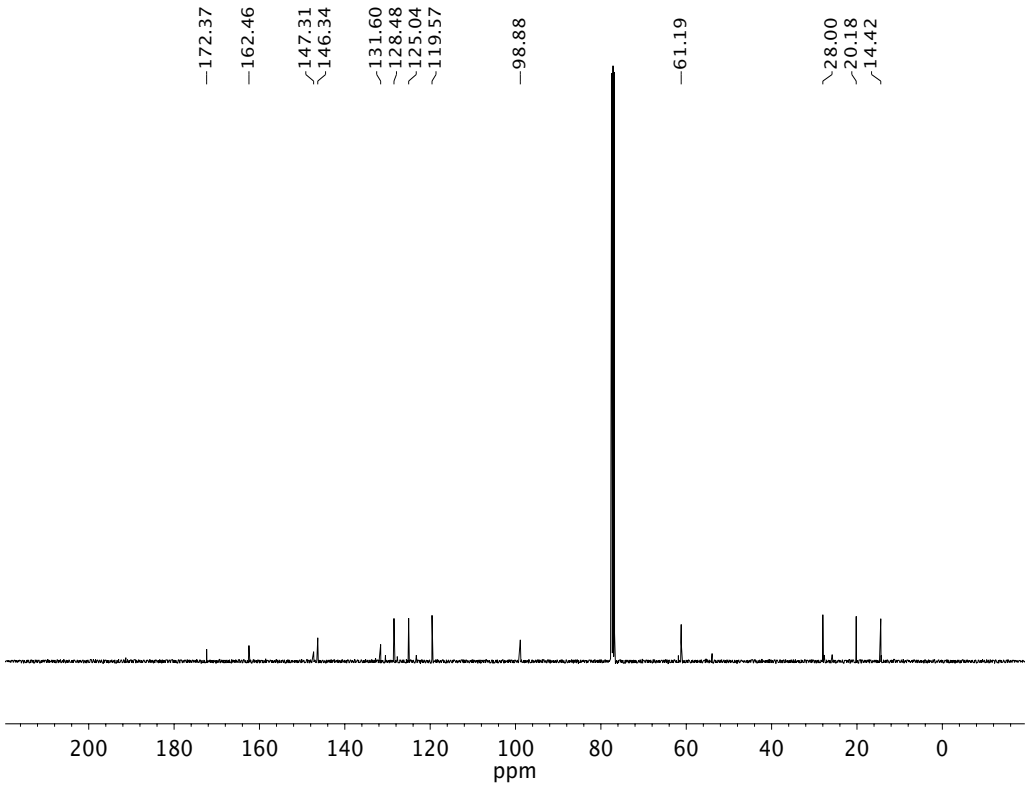
^{13}C NMR (101 MHz, $CDCl_3$) of compound **8e**.



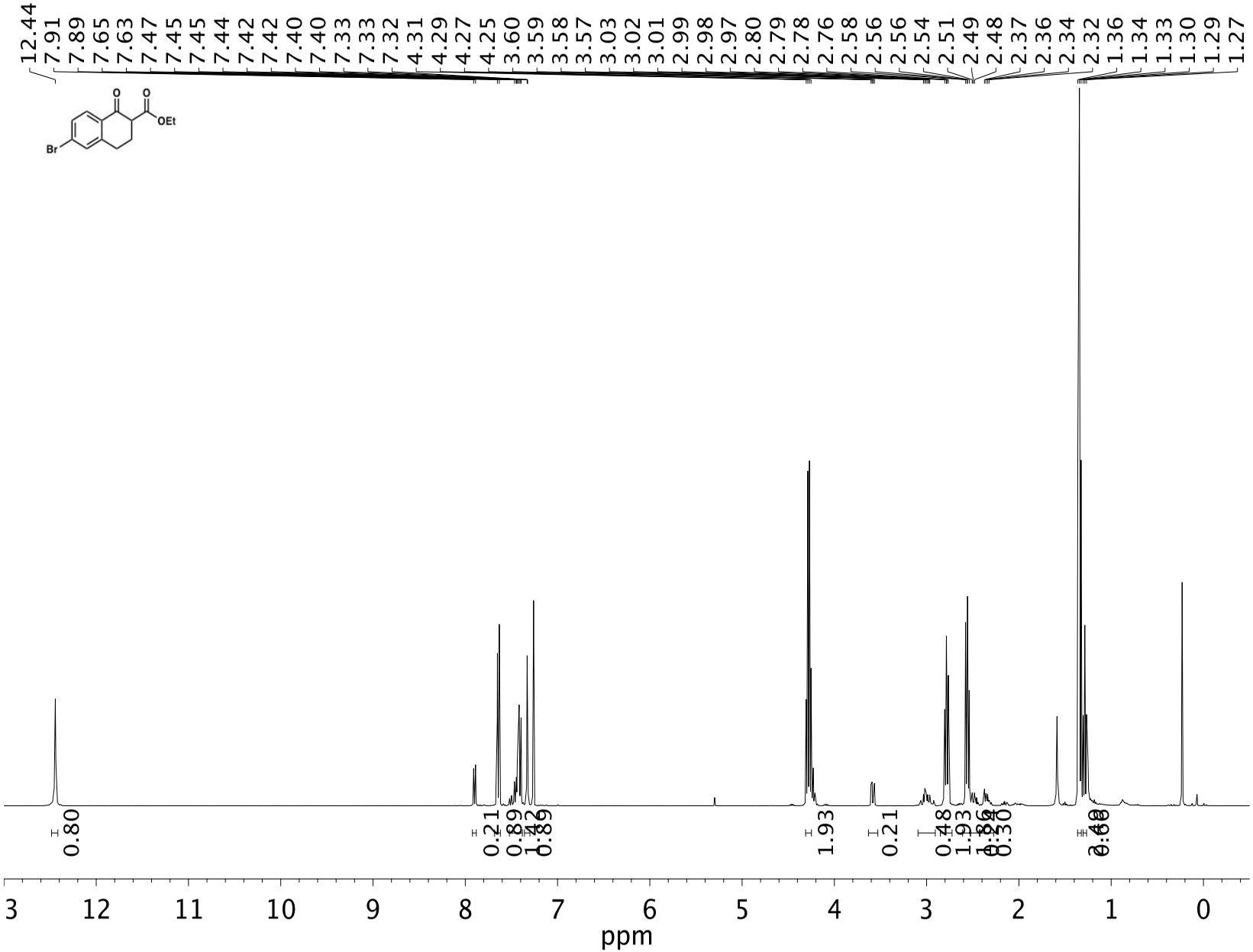
^{1}H NMR (400 MHz, $CDCl_3$) of compound **8g**.



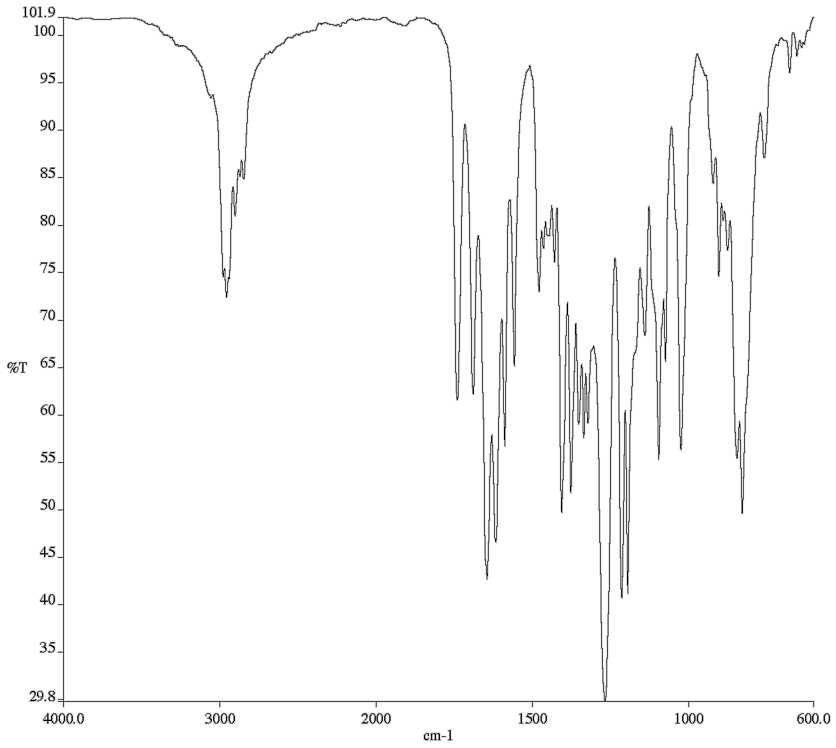
Infrared spectrum (Thin Film, NaCl) of compound **8g**.



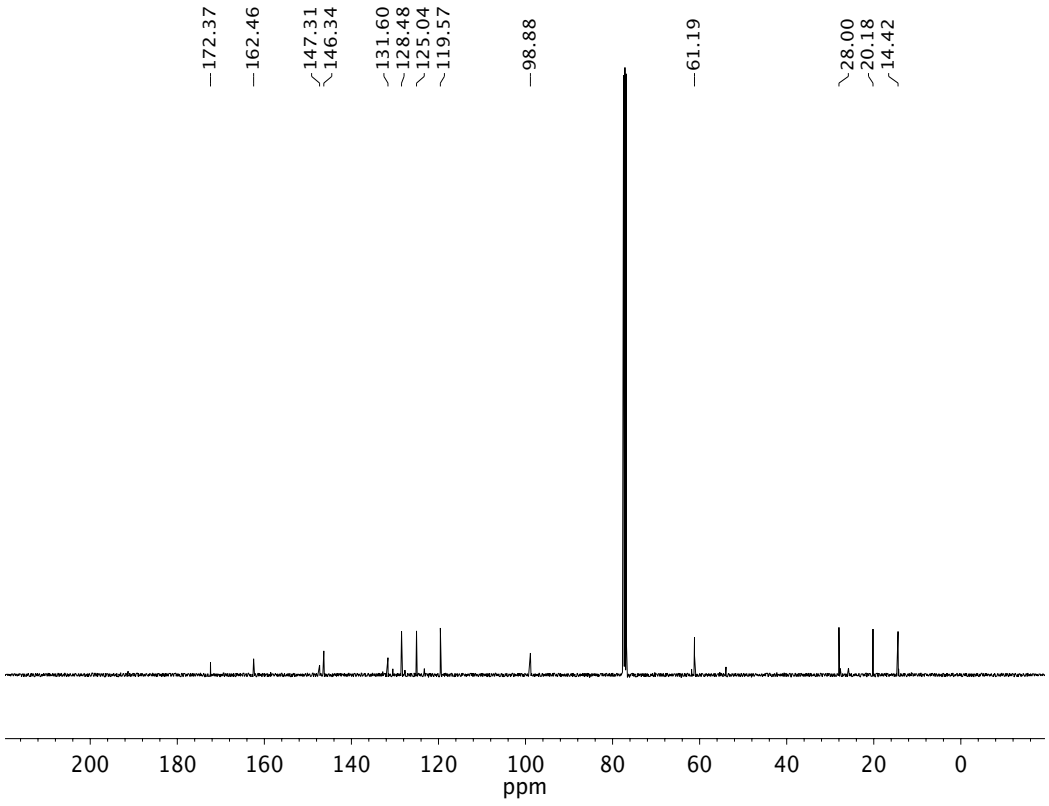
^{13}C NMR (101 MHz, $CDCl_3$) of compound **8g**.



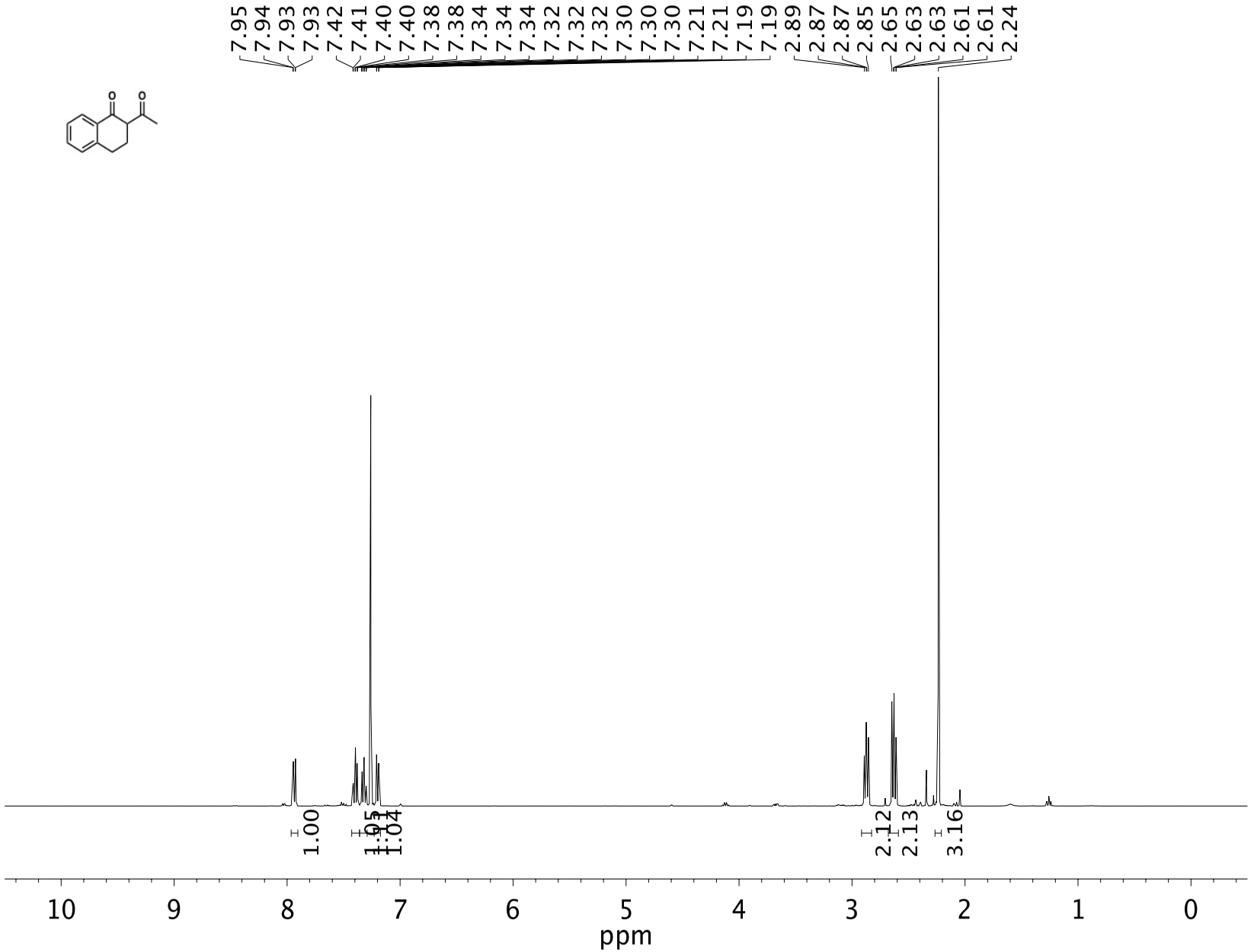
^{1}H NMR (400 MHz, $CDCl_3$) of compound **8h**.



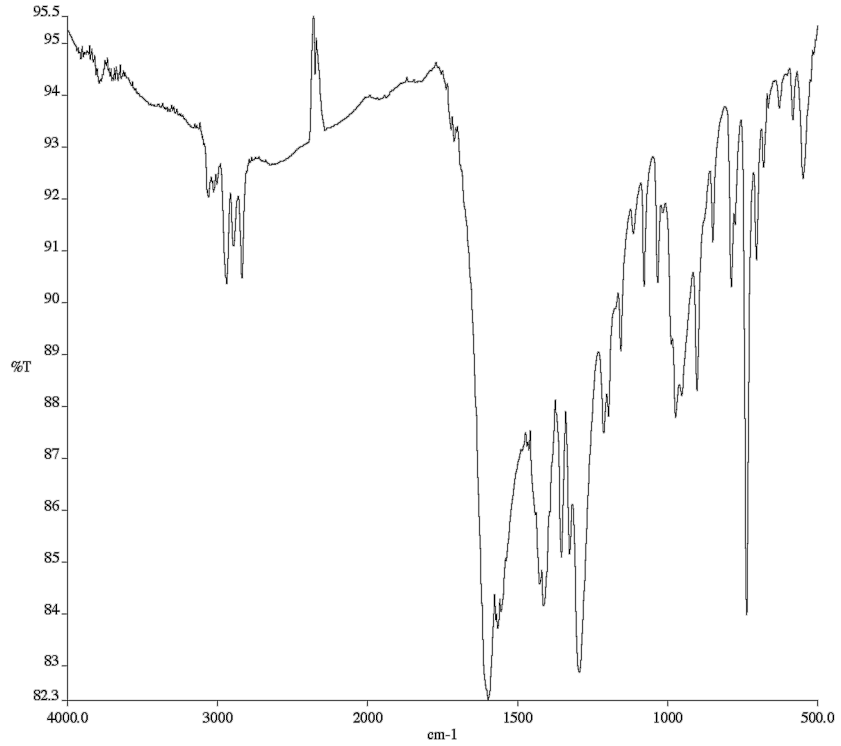
Infrared spectrum (Thin Film, NaCl) of compound **8h**.



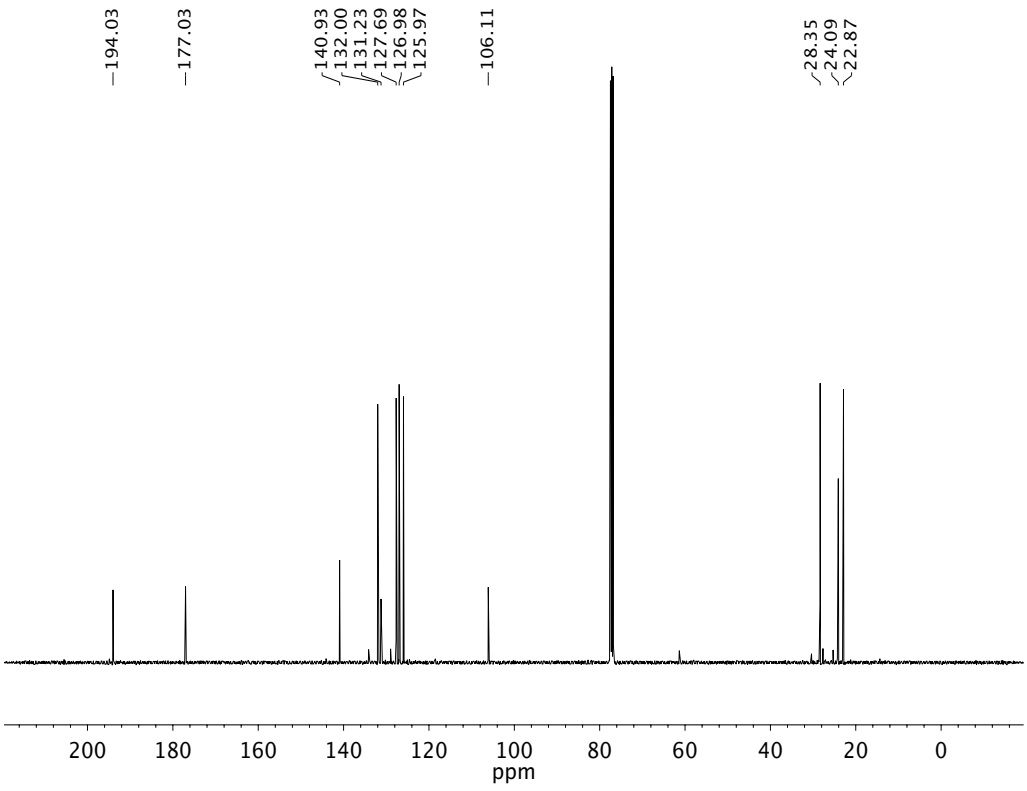
^{13}C NMR (101 MHz, $CDCl_3$) of compound **8h**.



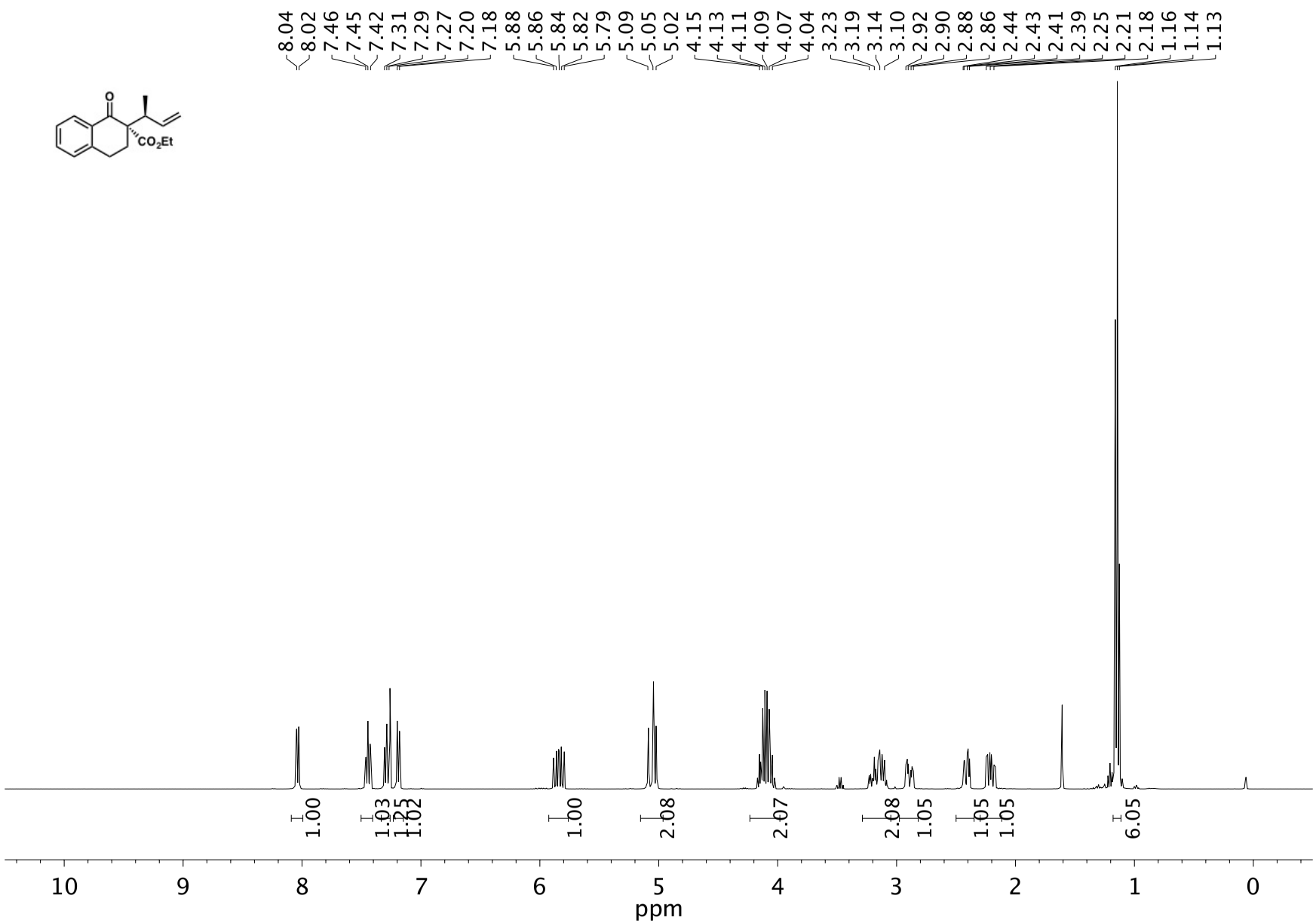
^{1}H NMR (400 MHz, $CDCl_3$) of compound **8k.**



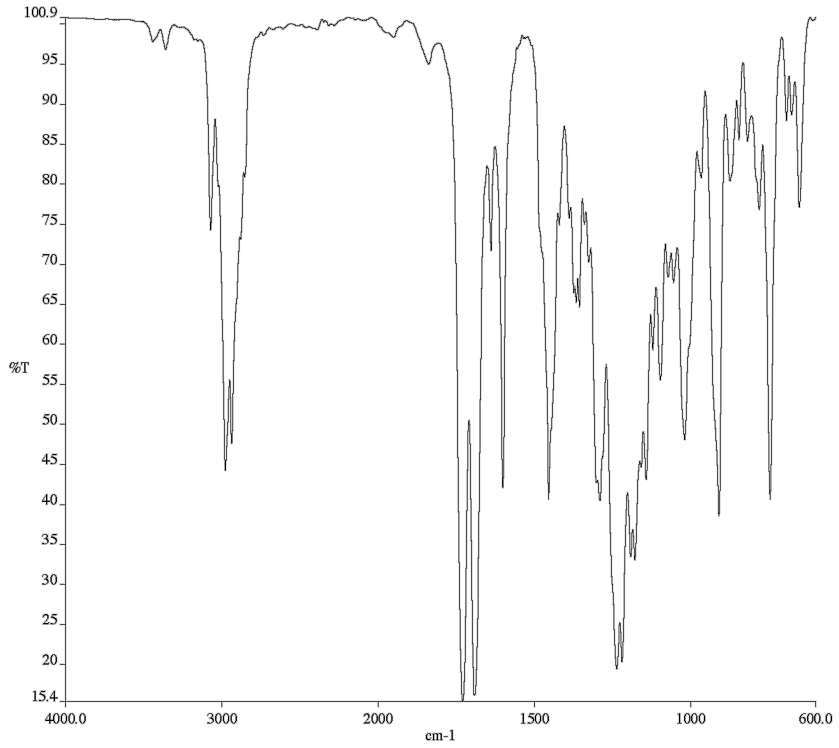
Infrared spectrum (Thin Film, NaCl) of compound **8k**.



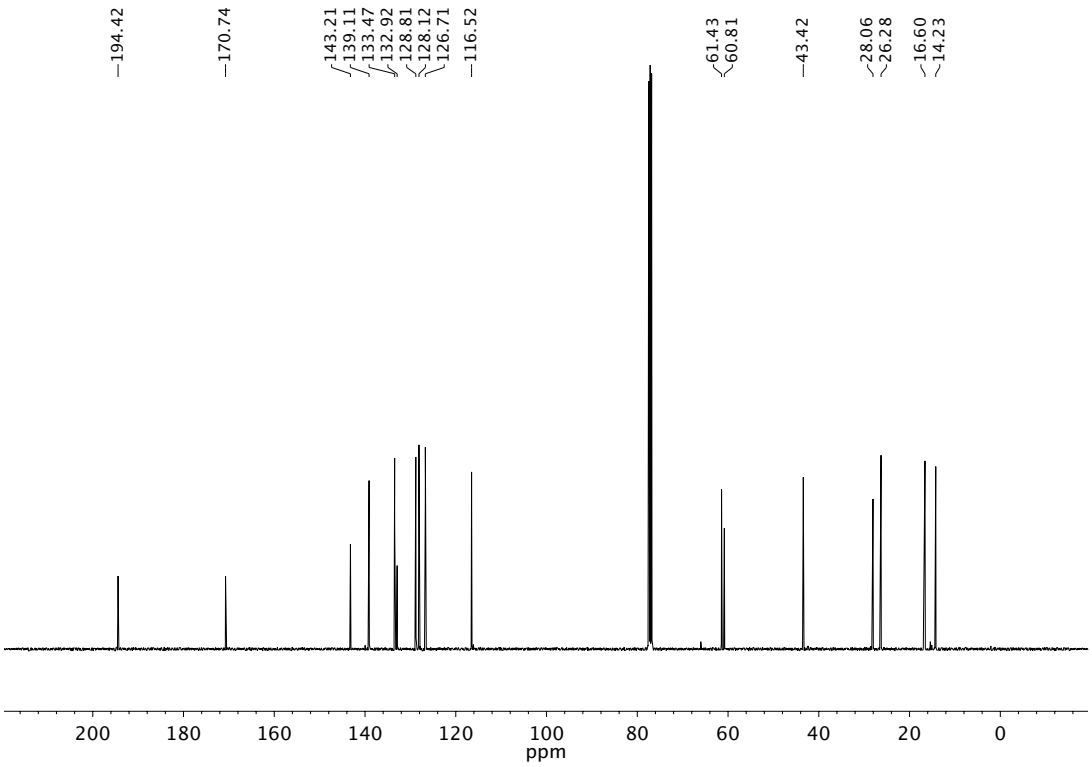
^{13}C NMR (101 MHz, $CDCl_3$) of compound **8k**.



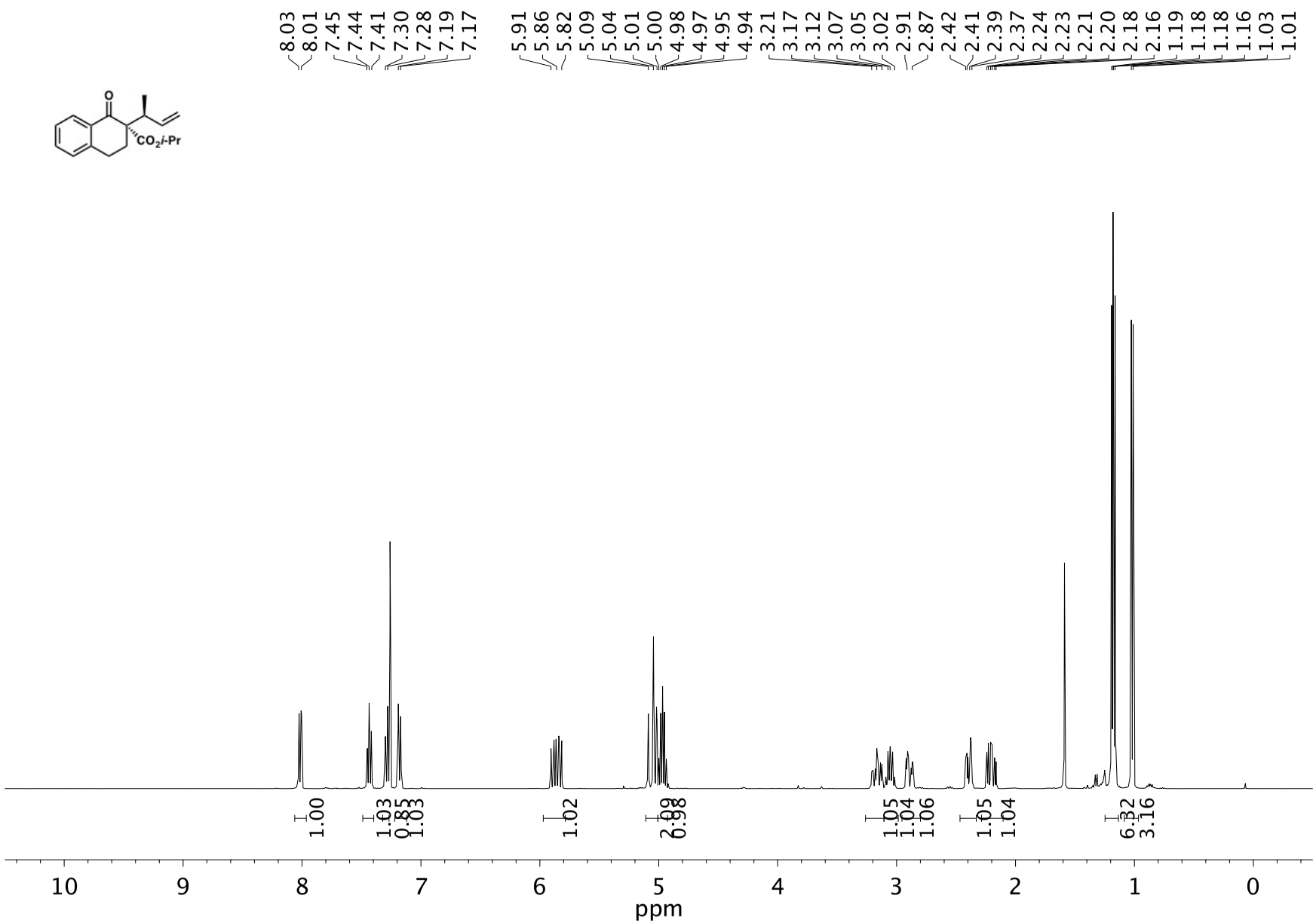
^{1}H NMR (400 MHz, $CDCl_3$) of compound **10a**.



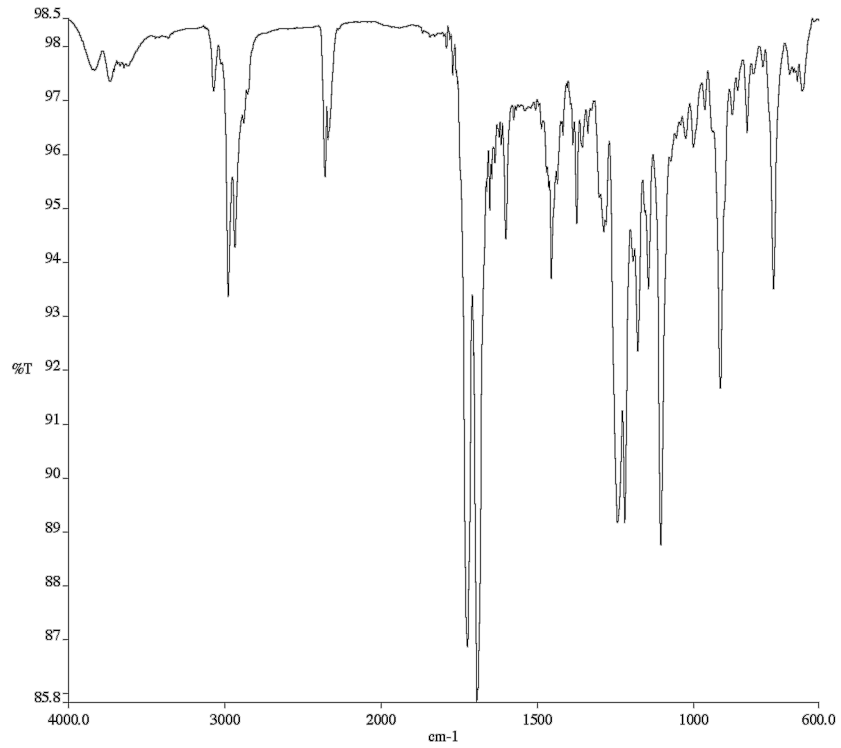
Infrared spectrum (Thin Film, NaCl) of compound **10a**.



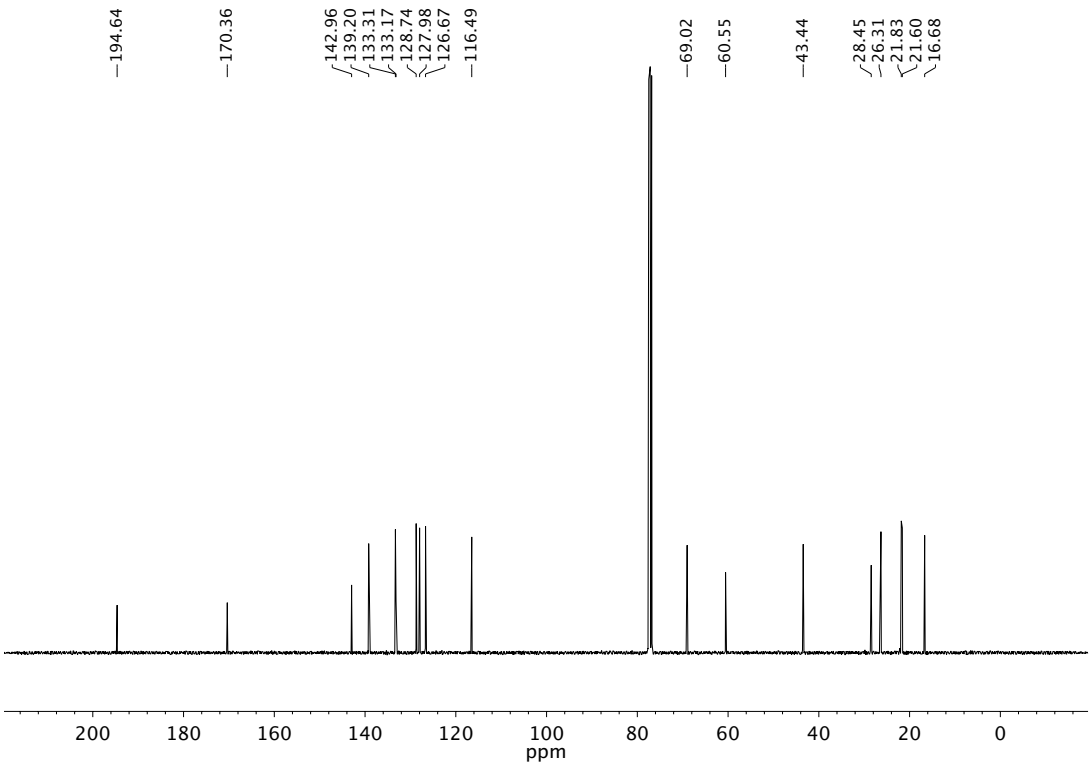
^{13}C NMR (101 MHz, $CDCl_3$) of compound **10a**.



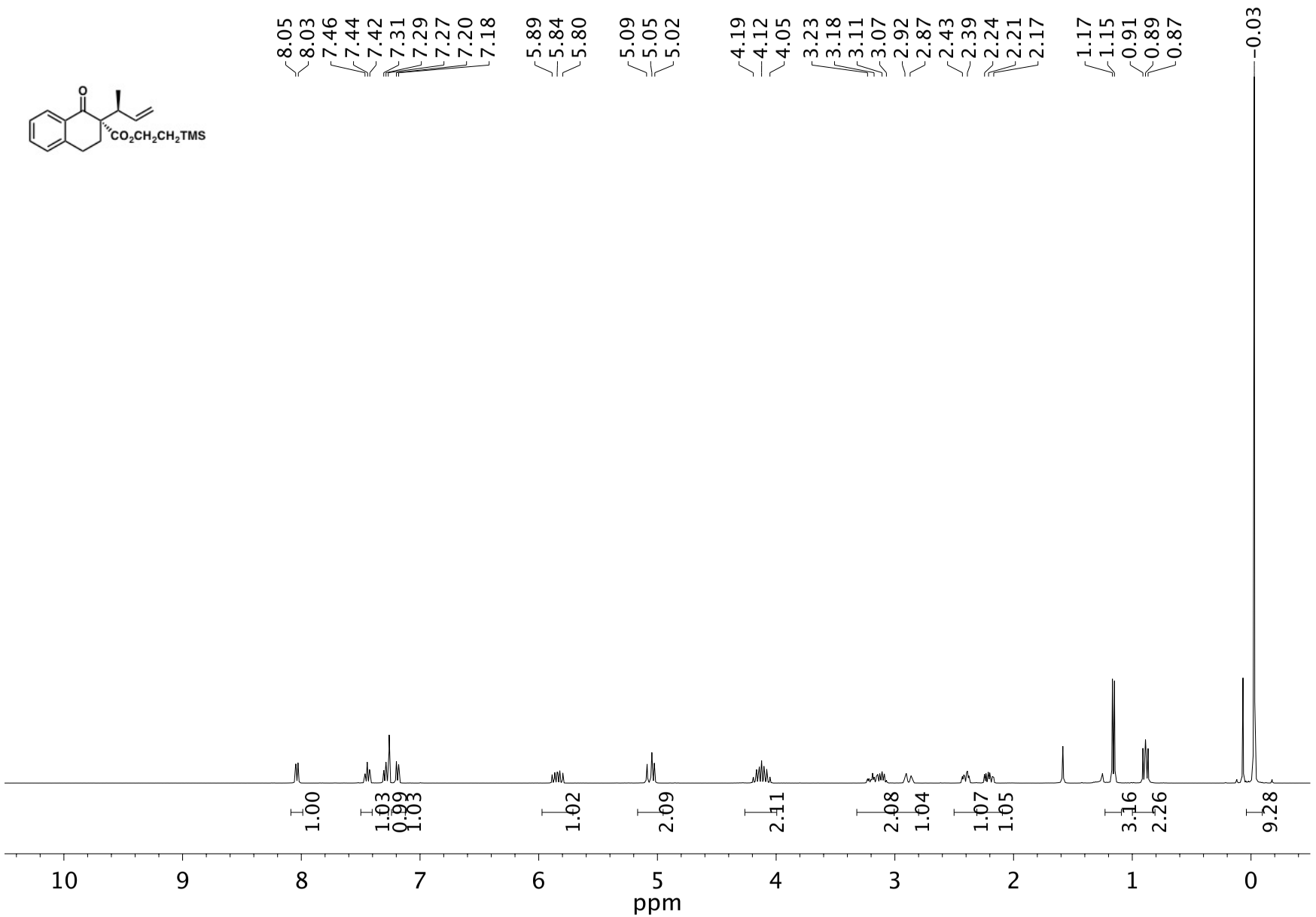
^{1}H NMR (400 MHz, $CDCl_3$) of compound **10b**.



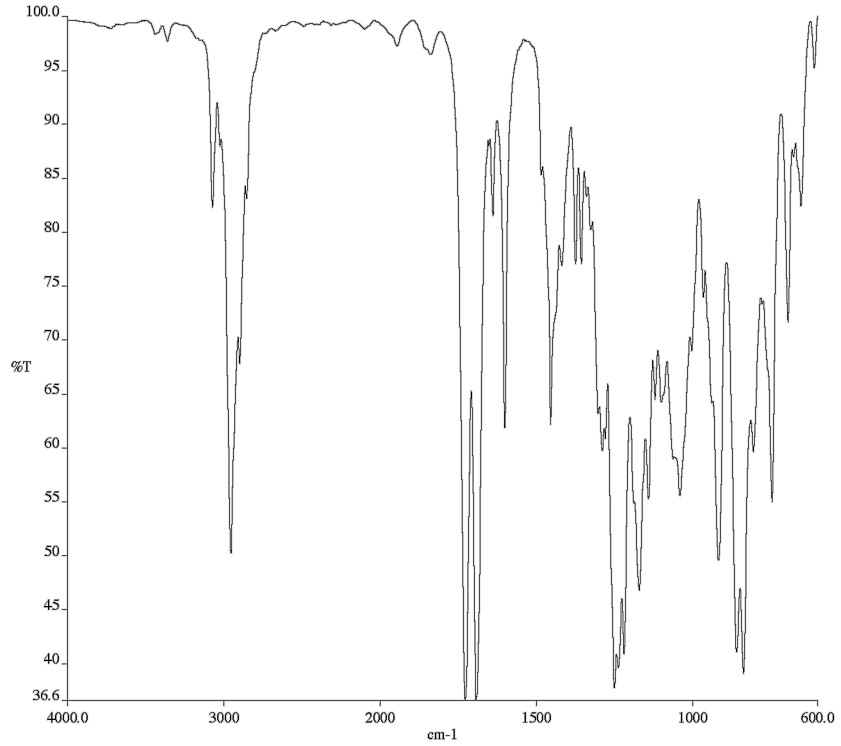
Infrared spectrum (Thin Film, NaCl) of compound **10b**.



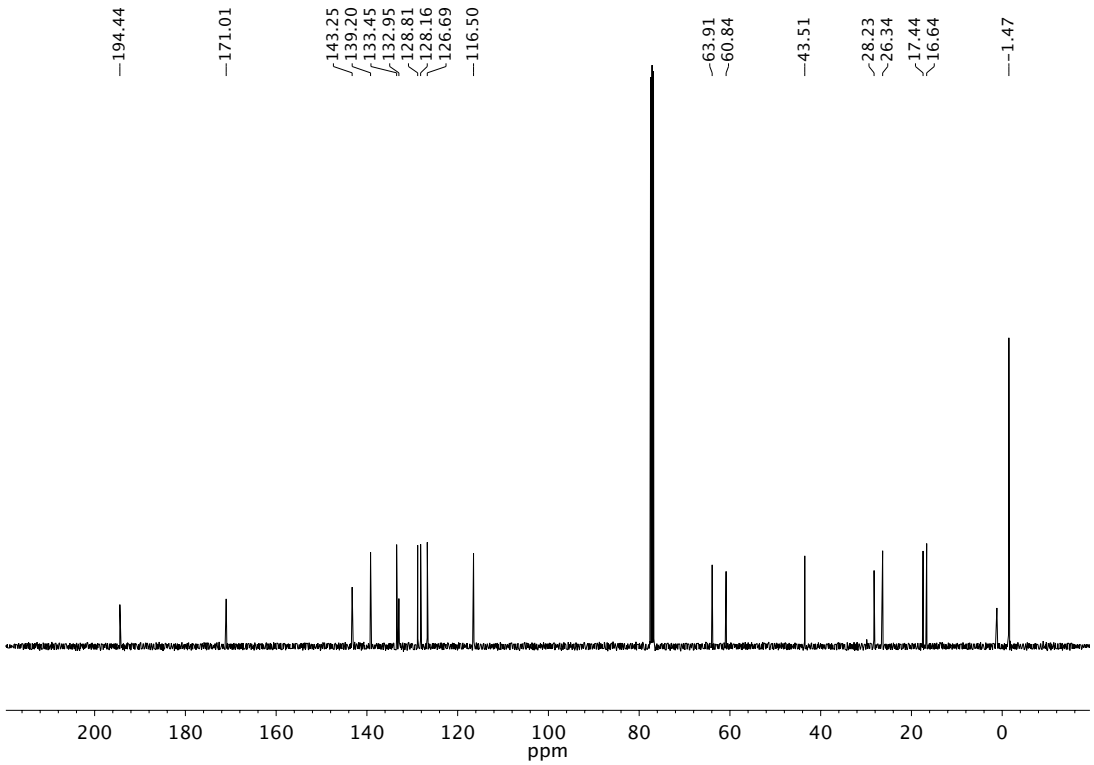
^{13}C NMR (101 MHz, $CDCl_3$) of compound **10b**.



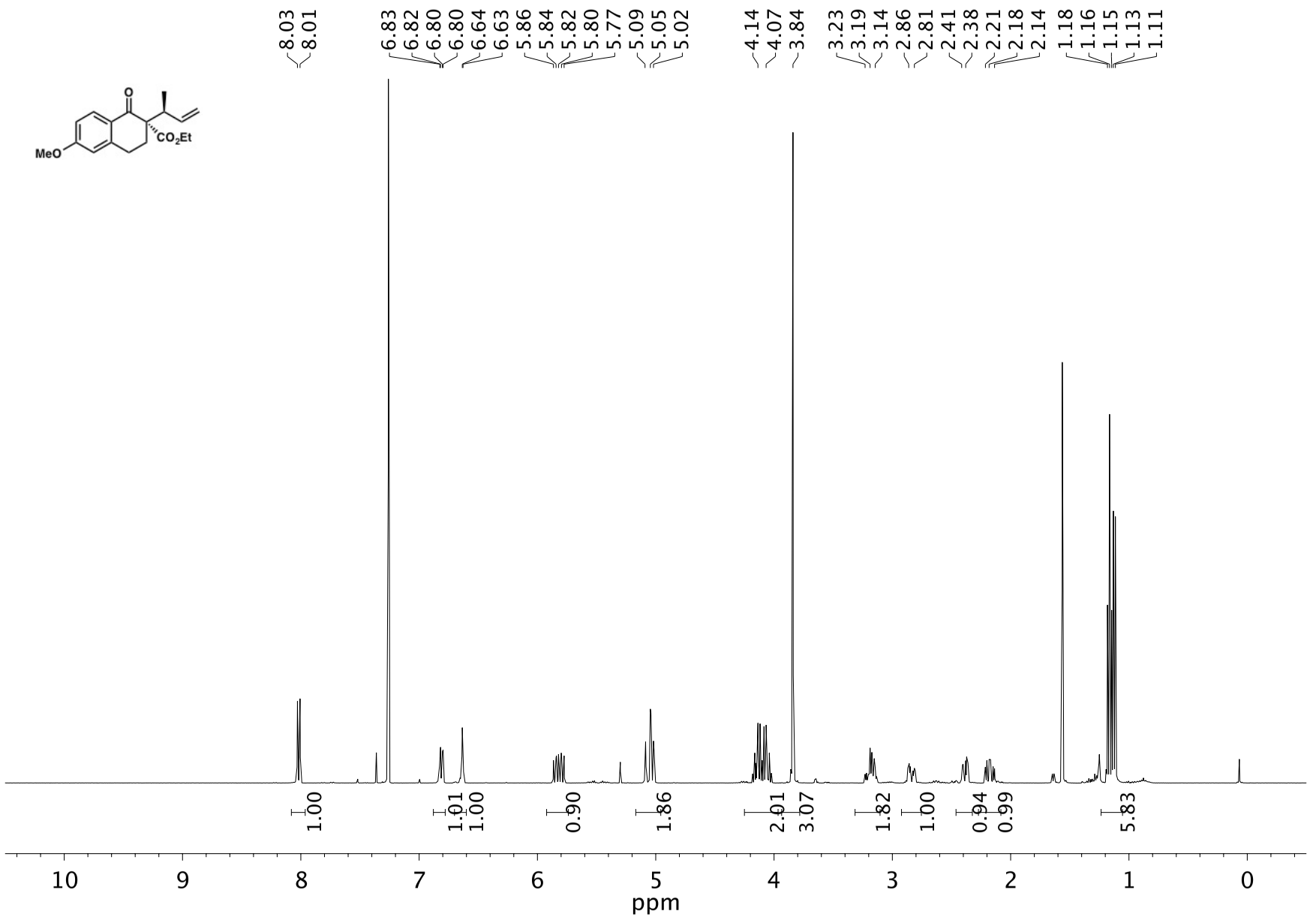
^{1}H NMR (400 MHz, $CDCl_3$) of compound **10c**.



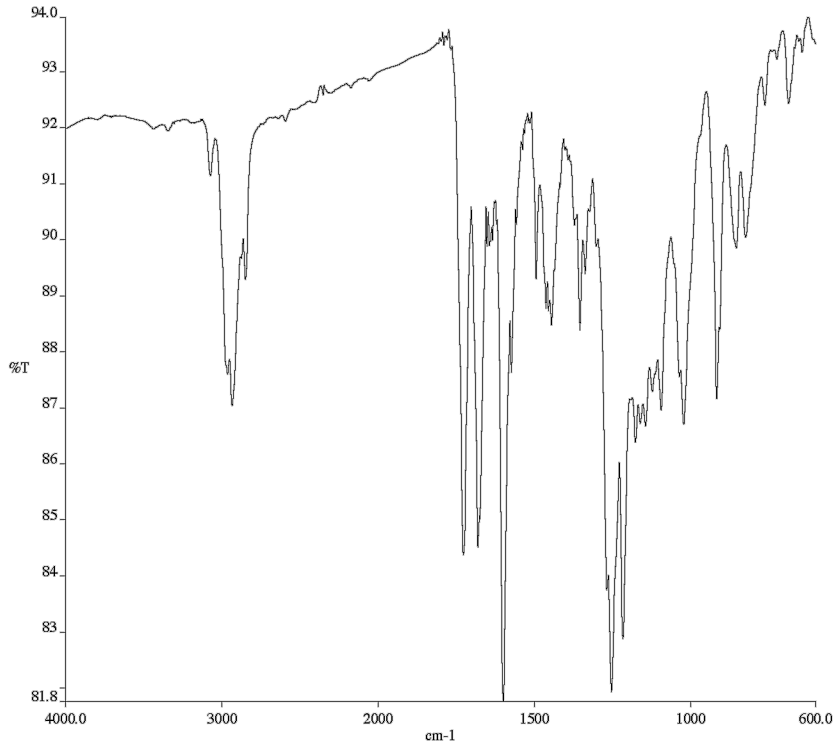
Infrared spectrum (Thin Film, NaCl) of compound **10c**.



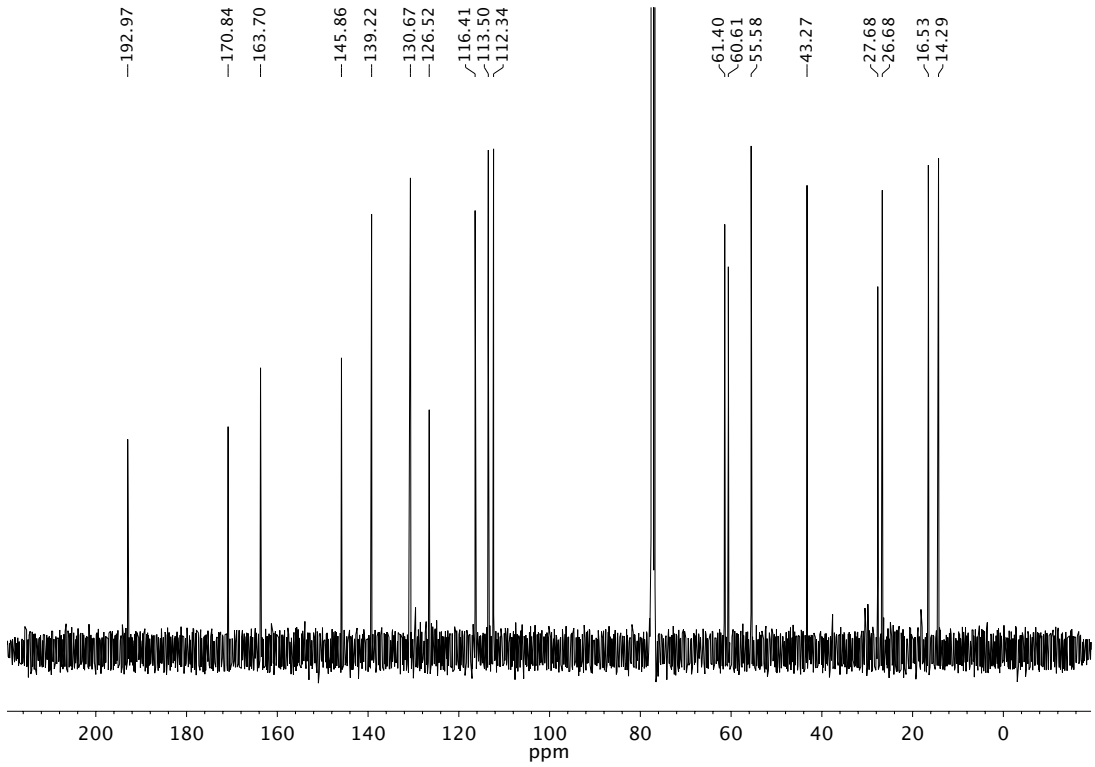
^{13}C NMR (101 MHz, $CDCl_3$) of compound **10c**.



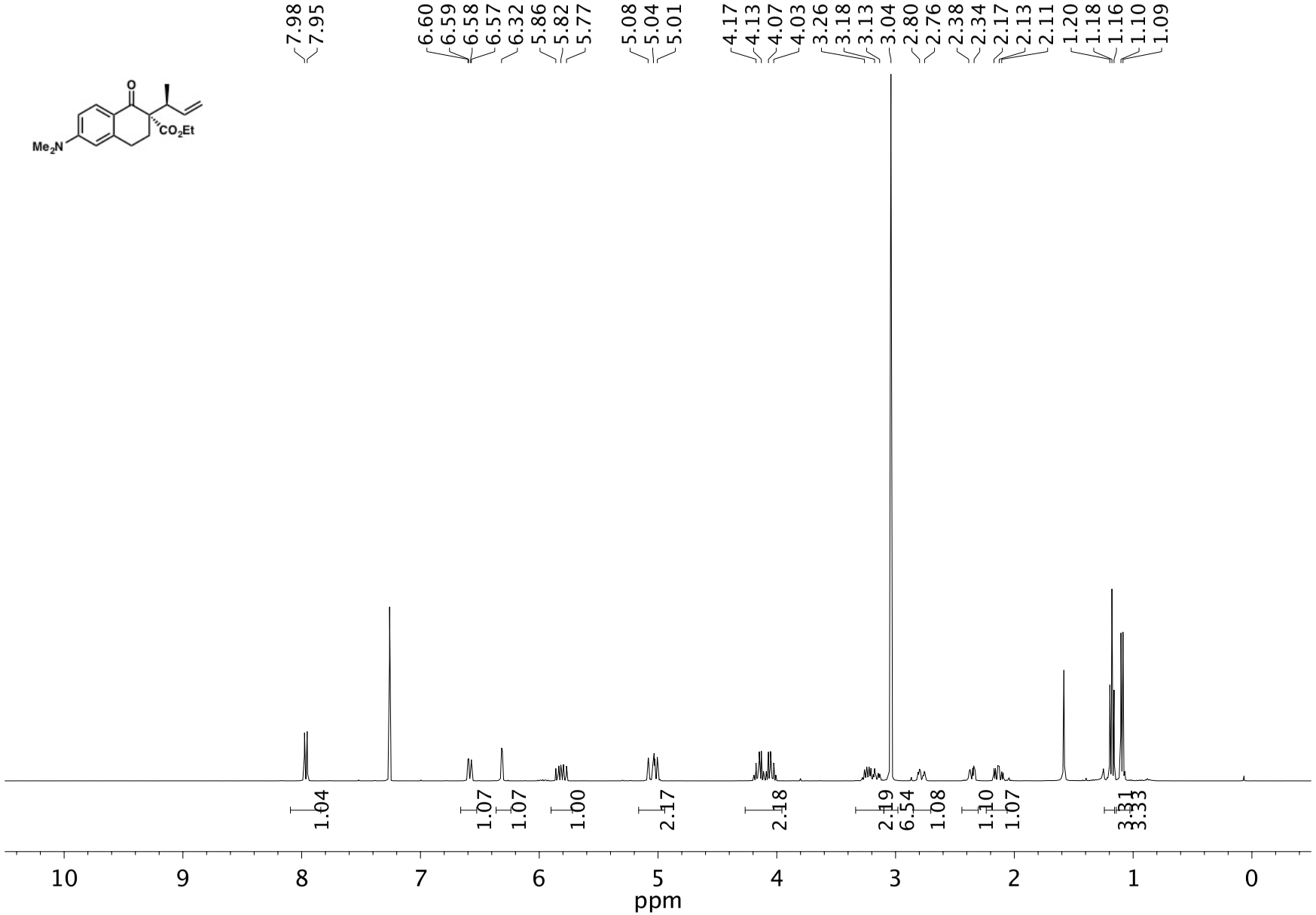
^{1}H NMR (400 MHz, $CDCl_3$) of compound **10d**.



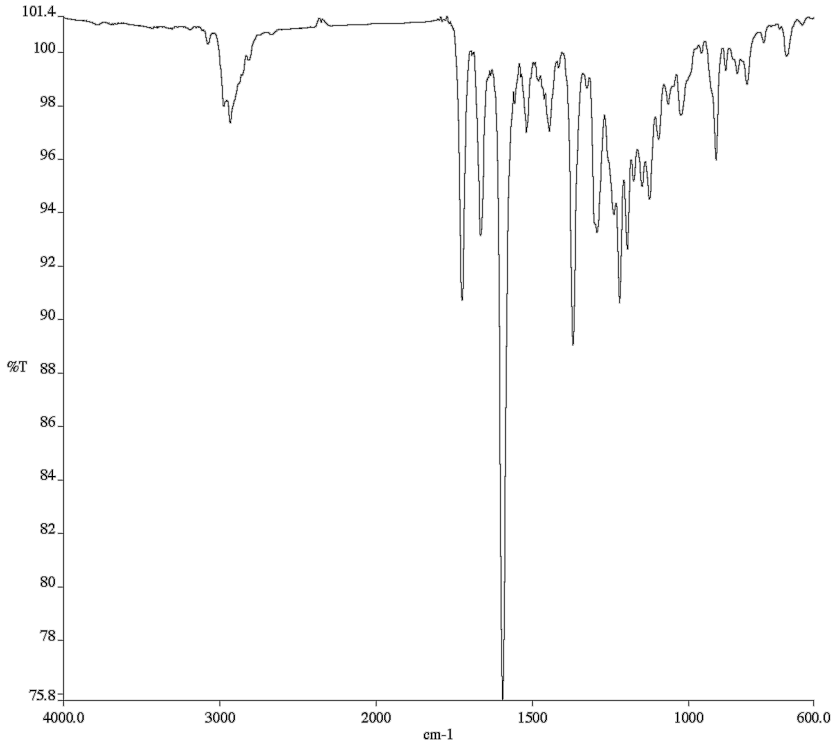
Infrared spectrum (Thin Film, NaCl) of compound **10d**.



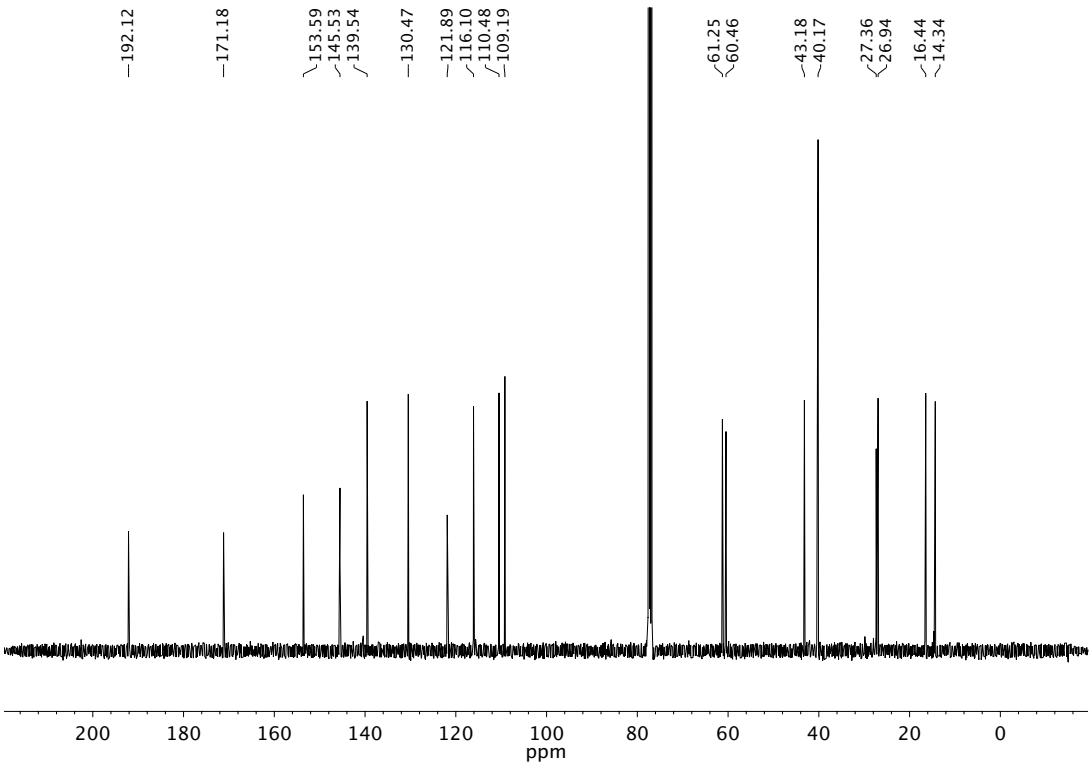
^{13}C NMR (101 MHz, $CDCl_3$) of compound **10d**.



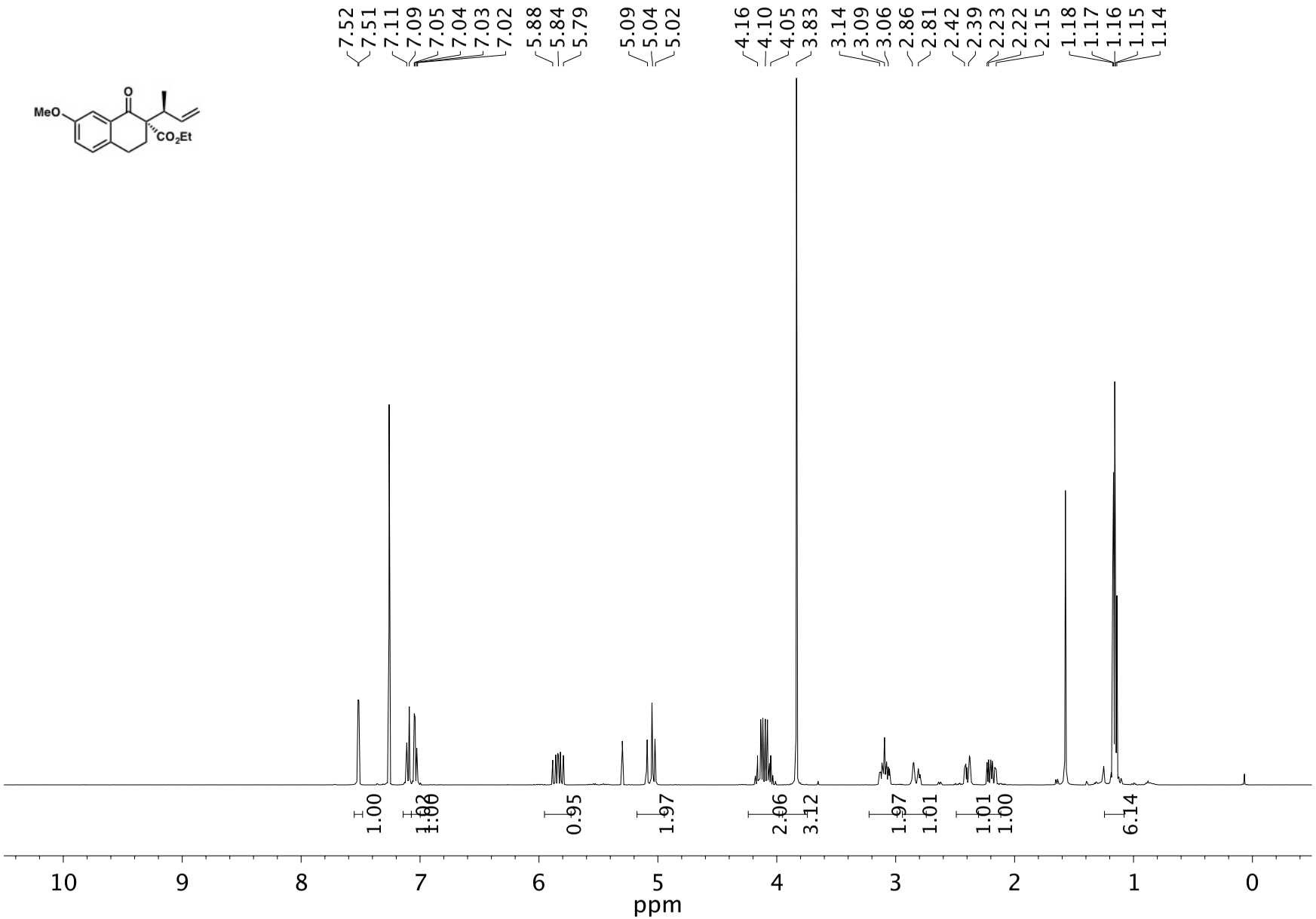
^{1}H NMR (400 MHz, $CDCl_3$) of compound **10e**.



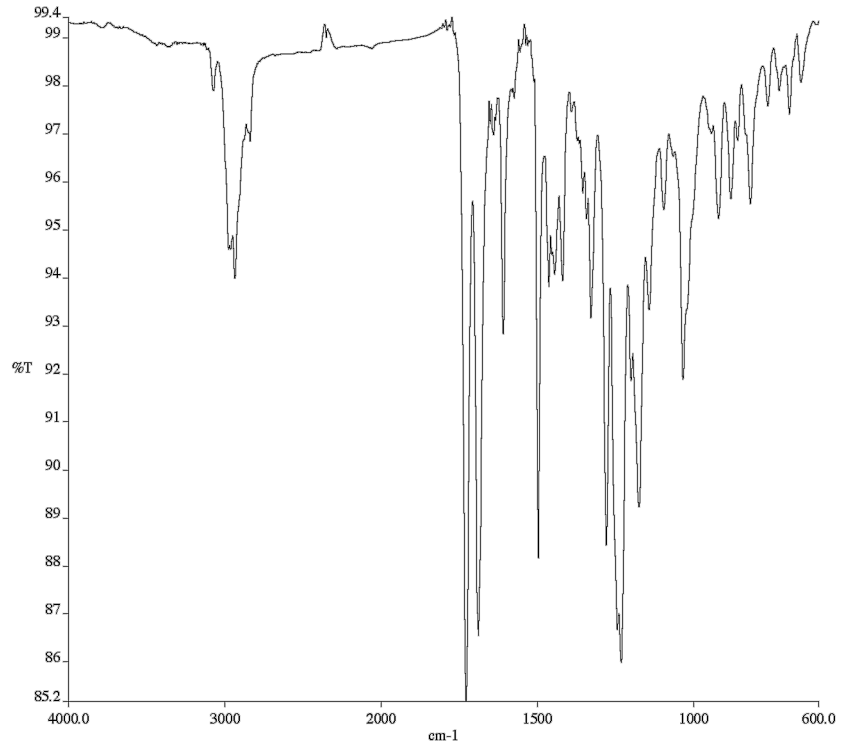
Infrared spectrum (Thin Film, NaCl) of compound **10e**.



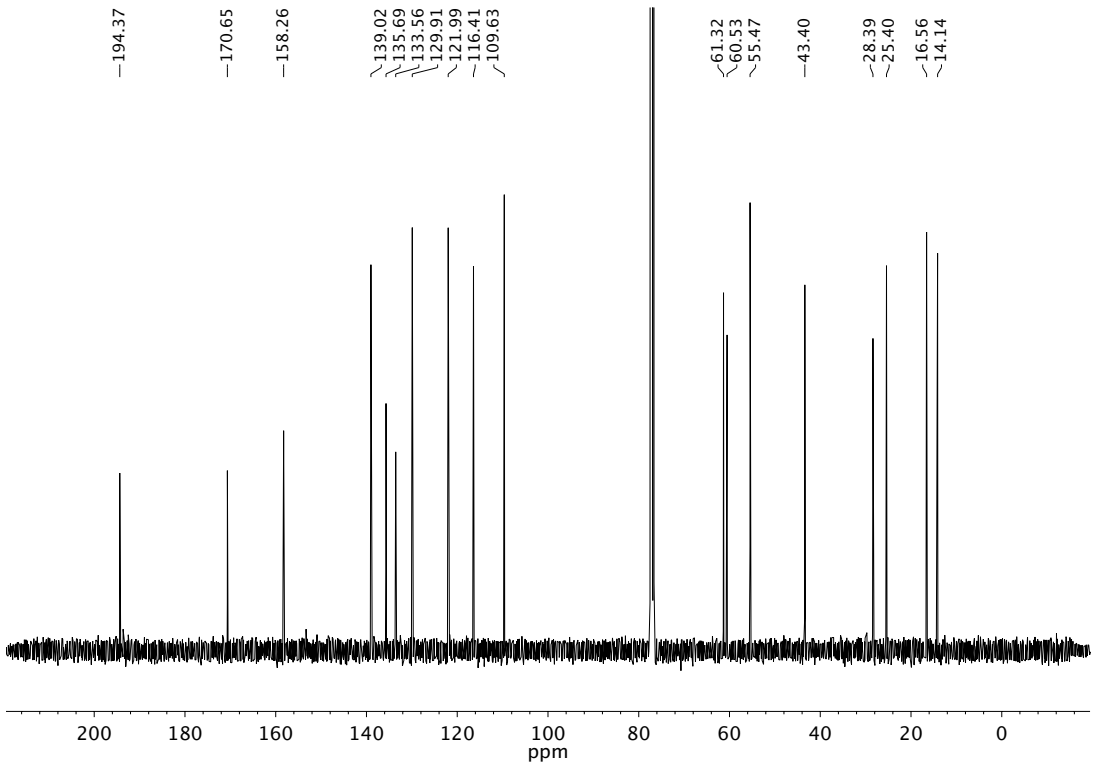
^{13}C NMR (101 MHz, $CDCl_3$) of compound **10e**.



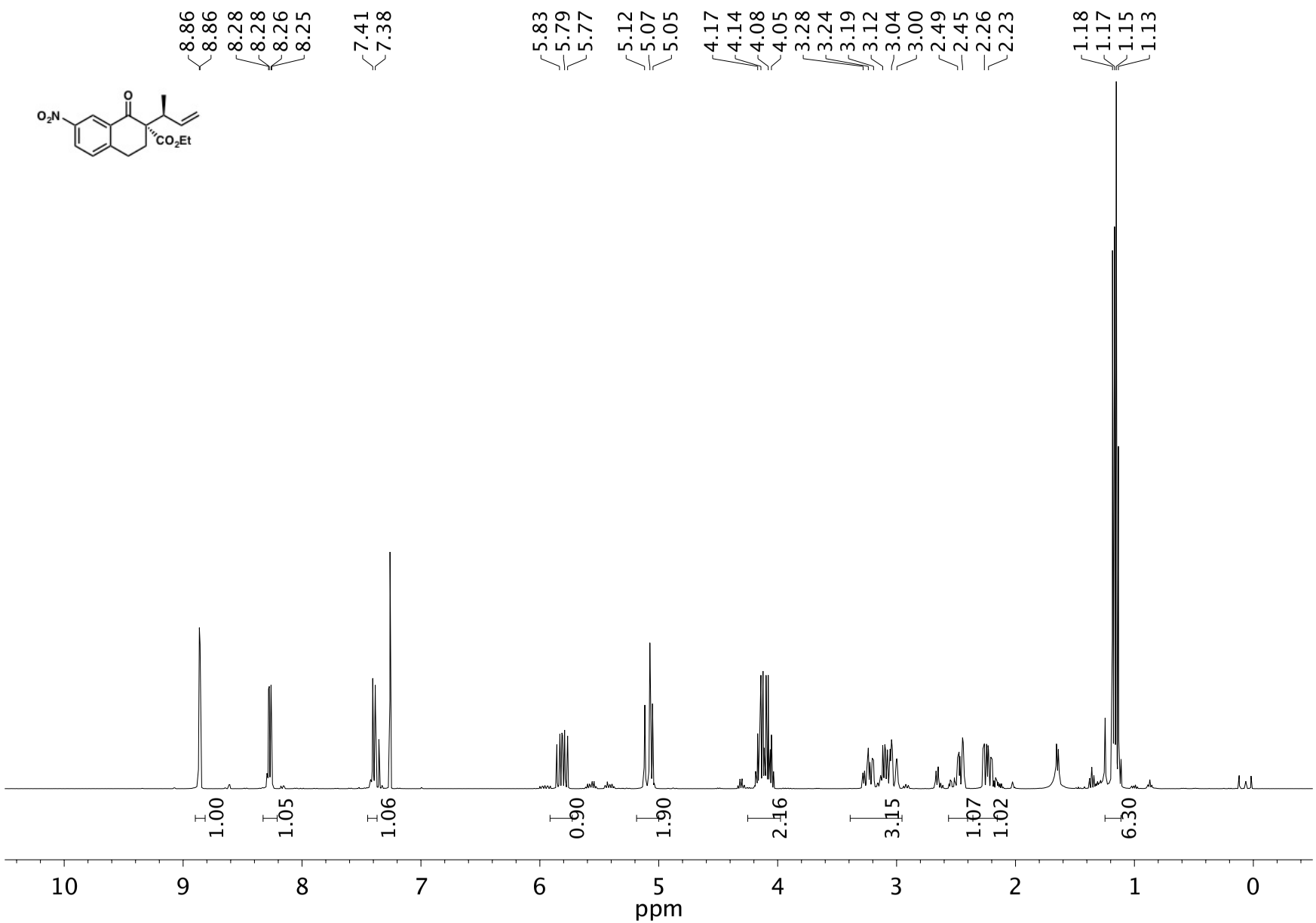
^{1}H NMR (400 MHz, $CDCl_3$) of compound **10f**.



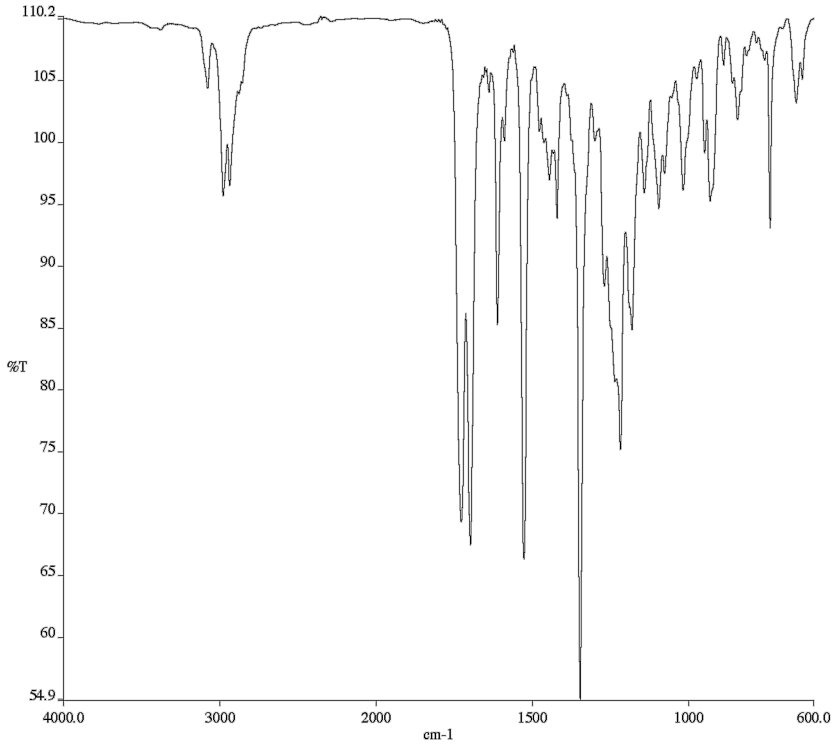
Infrared spectrum (Thin Film, NaCl) of compound **10f**.



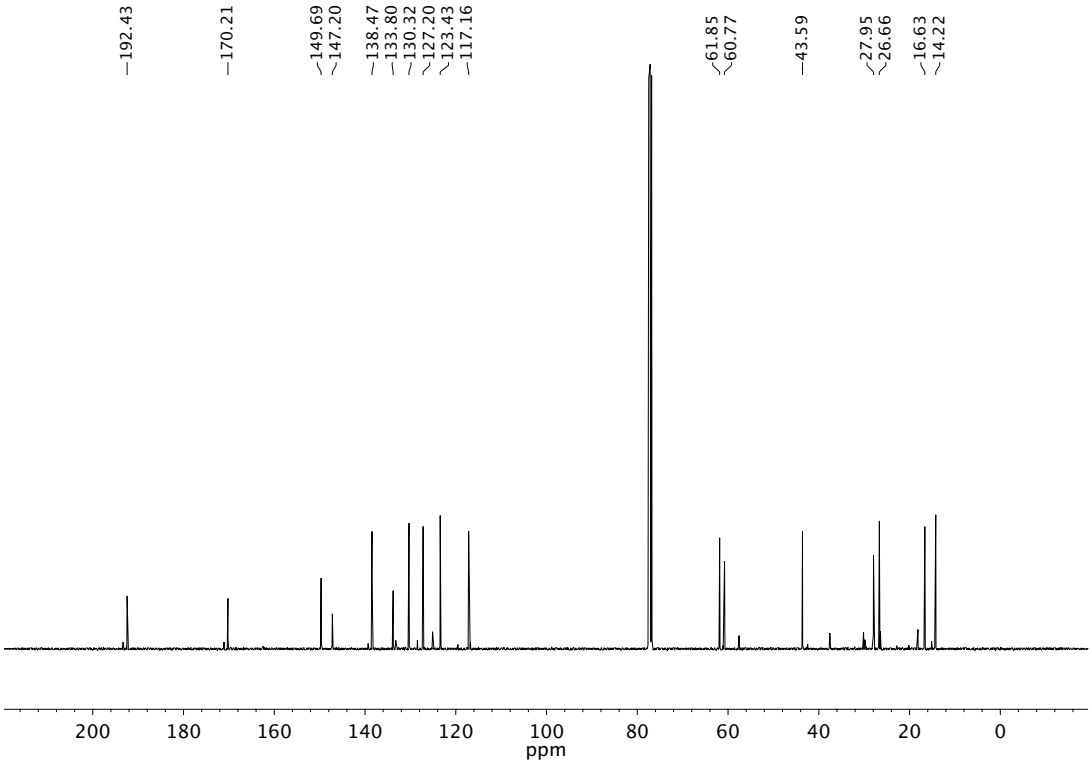
^{13}C NMR (101 MHz, $CDCl_3$) of compound **10f**.



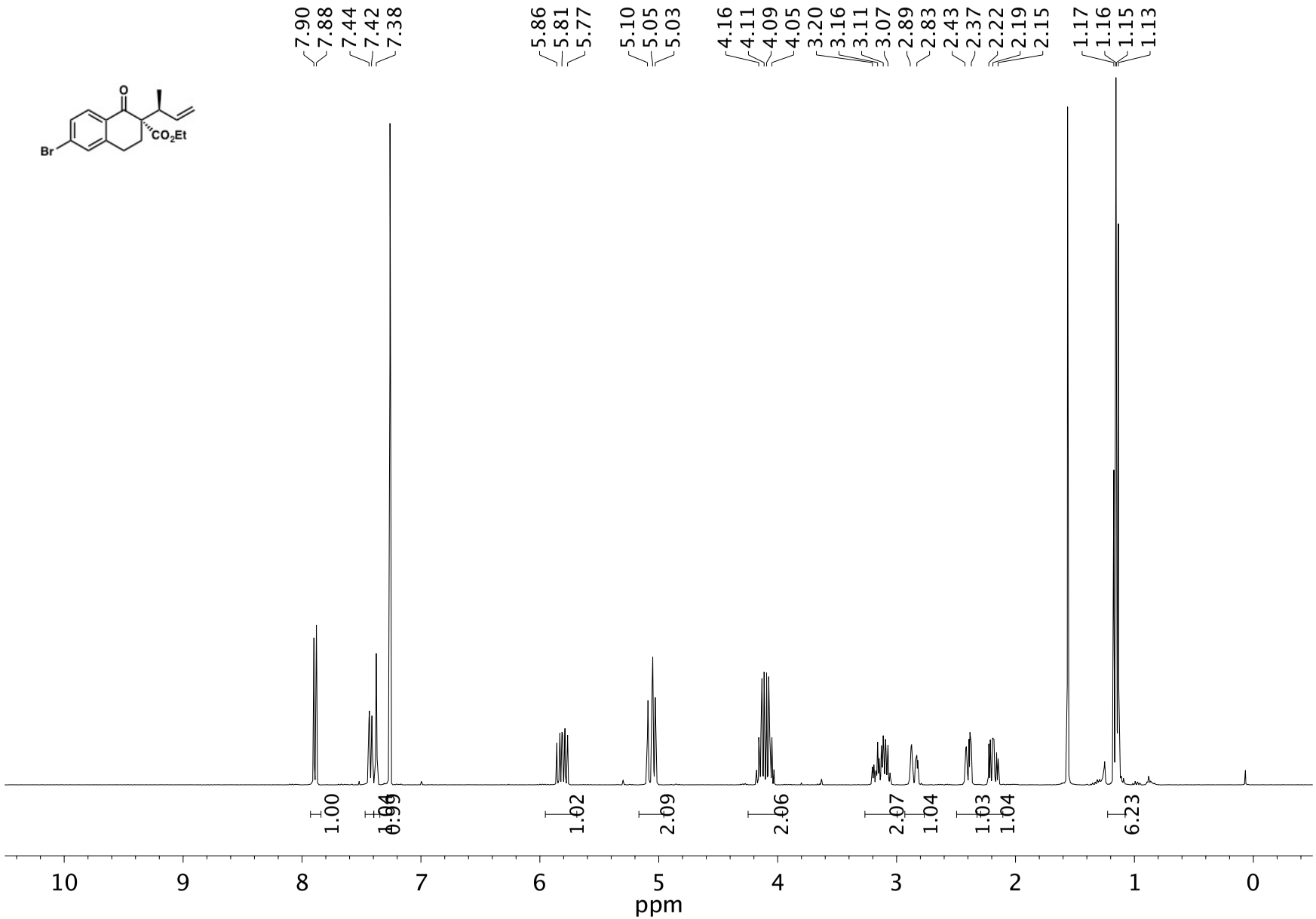
^{1}H NMR (400 MHz, $CDCl_3$) of compound **10g**.



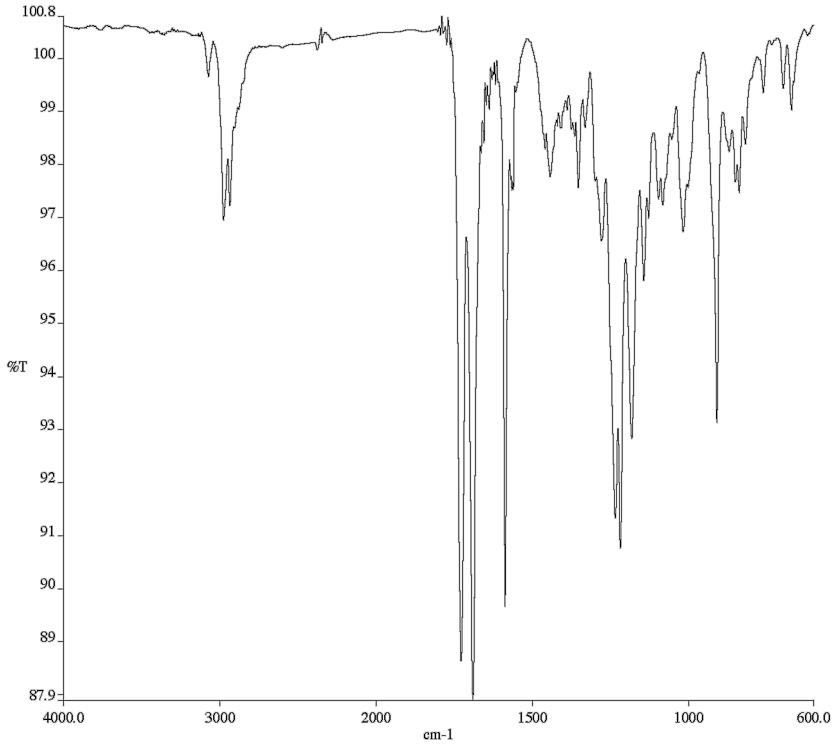
Infrared spectrum (Thin Film, NaCl) of compound **10g**.



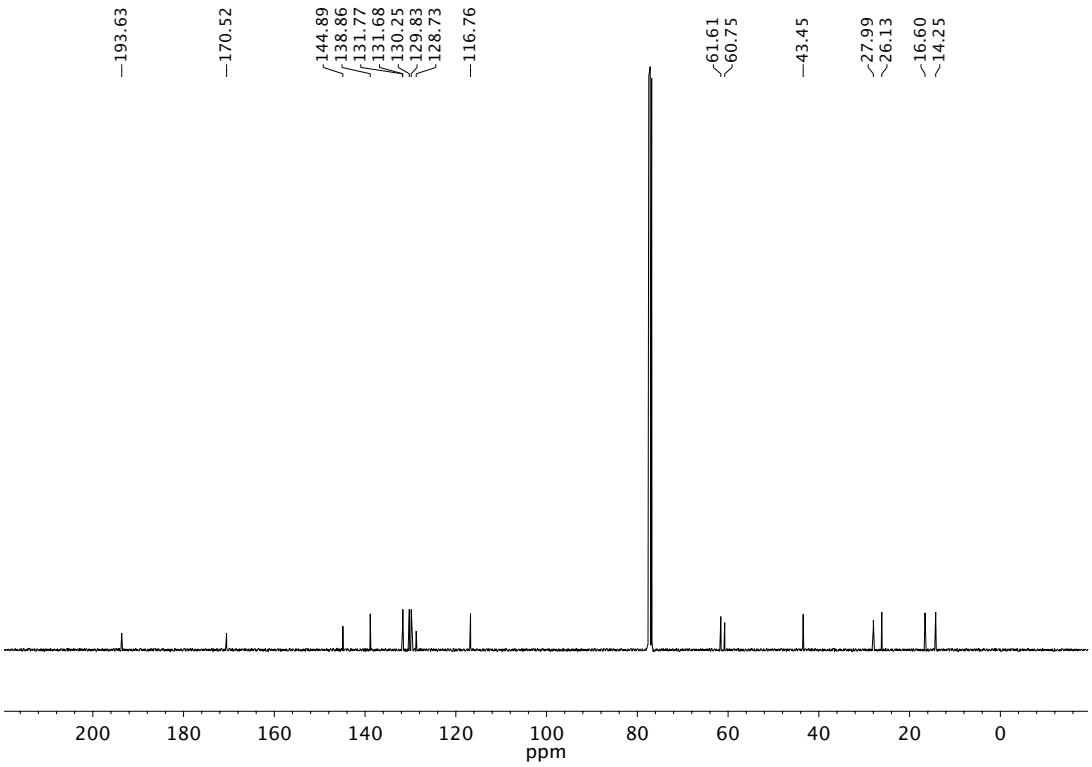
^{13}C NMR (101 MHz, $CDCl_3$) of compound **10g**.



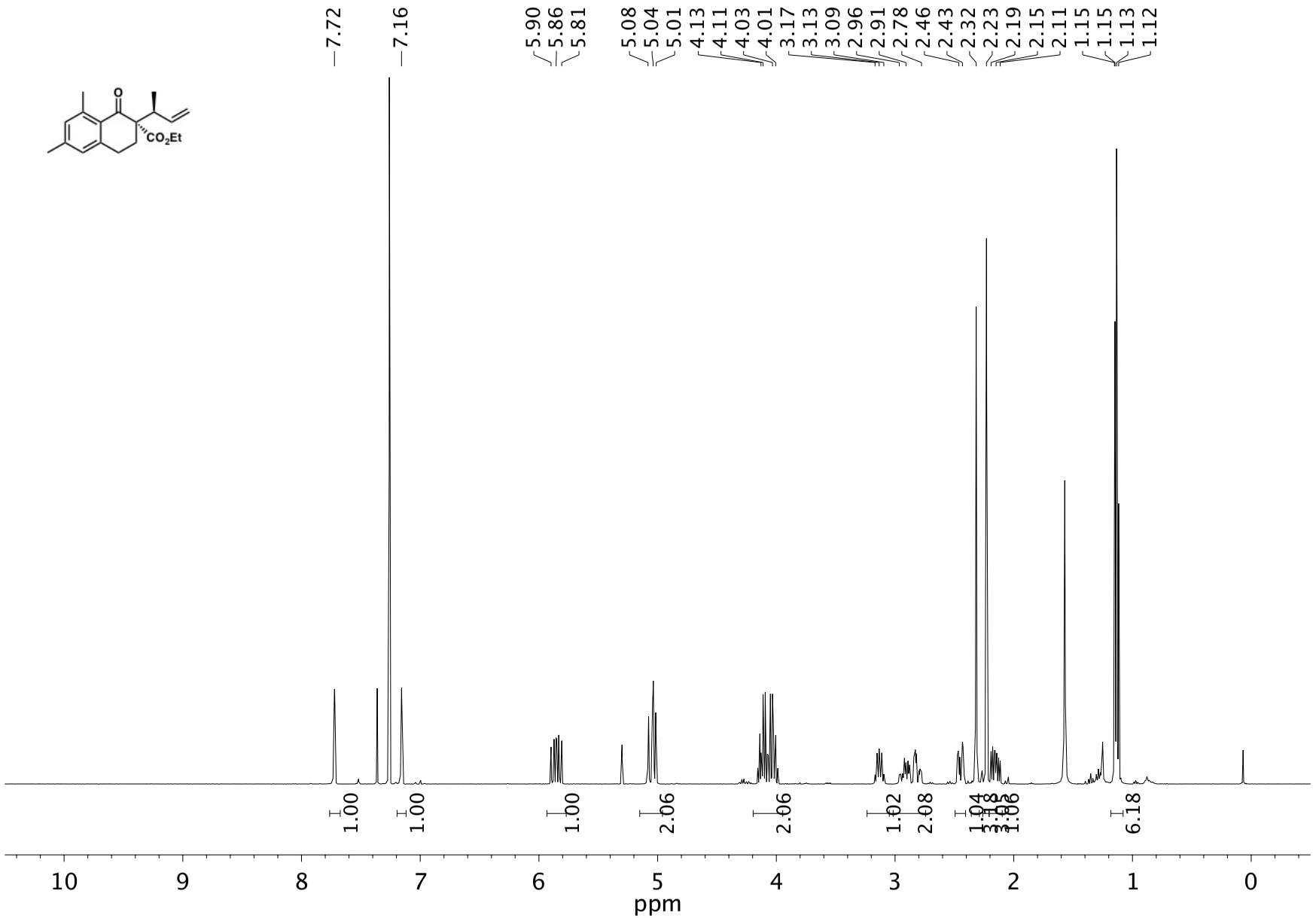
^{1}H NMR (400 MHz, $CDCl_3$) of compound **10h**.



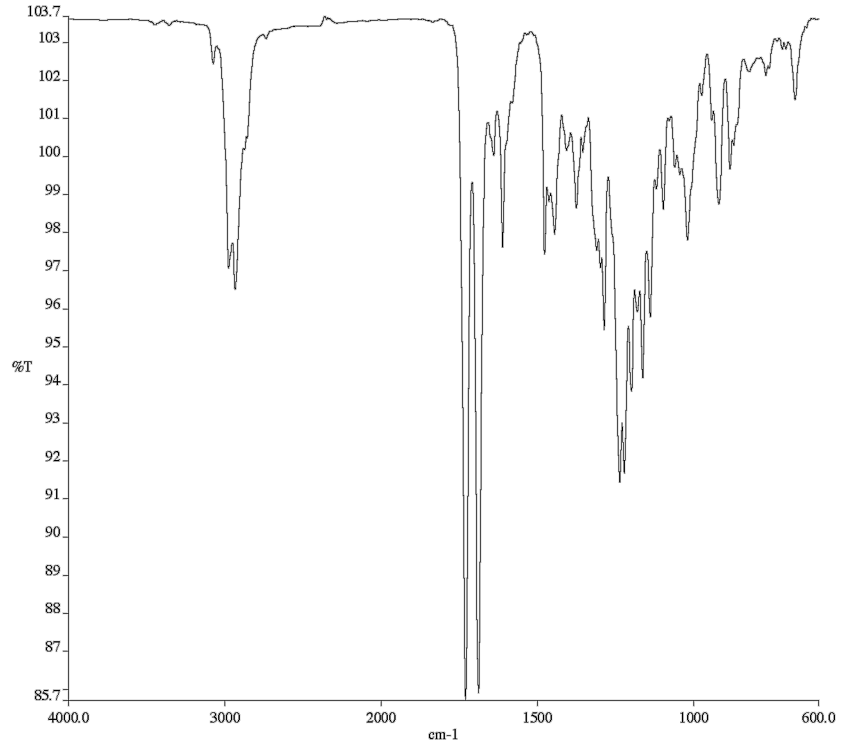
Infrared spectrum (Thin Film, NaCl) of compound **10h**.



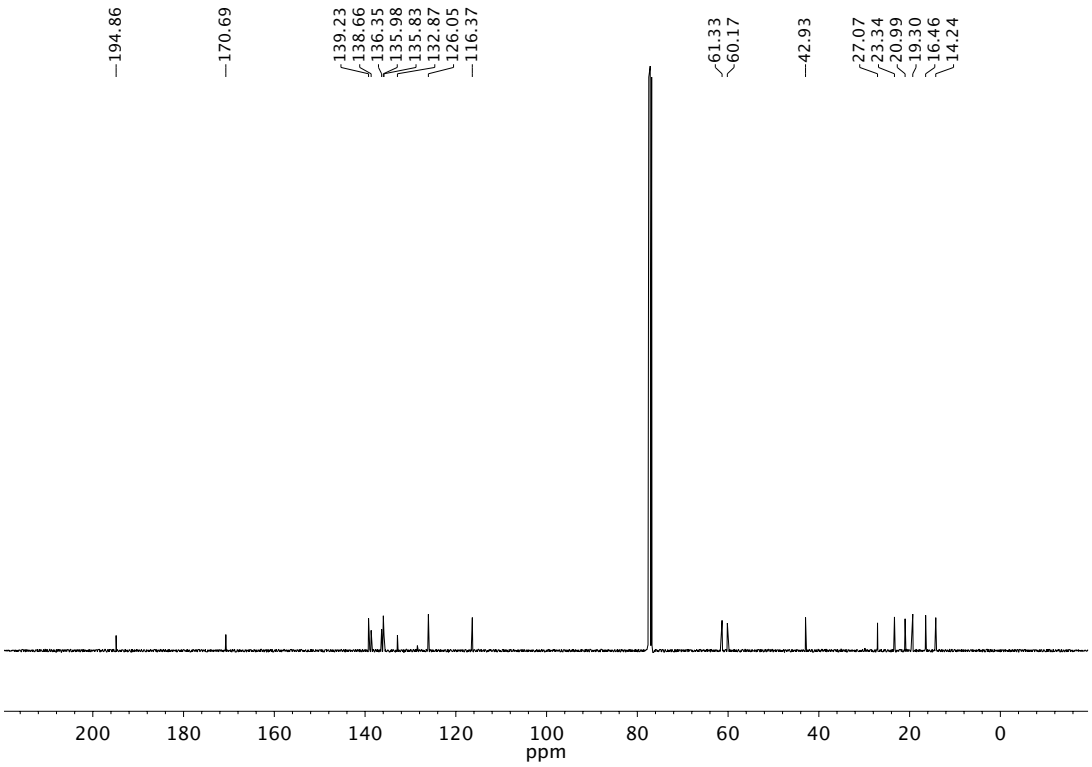
^{13}C NMR (101 MHz, $CDCl_3$) of compound **10h**.



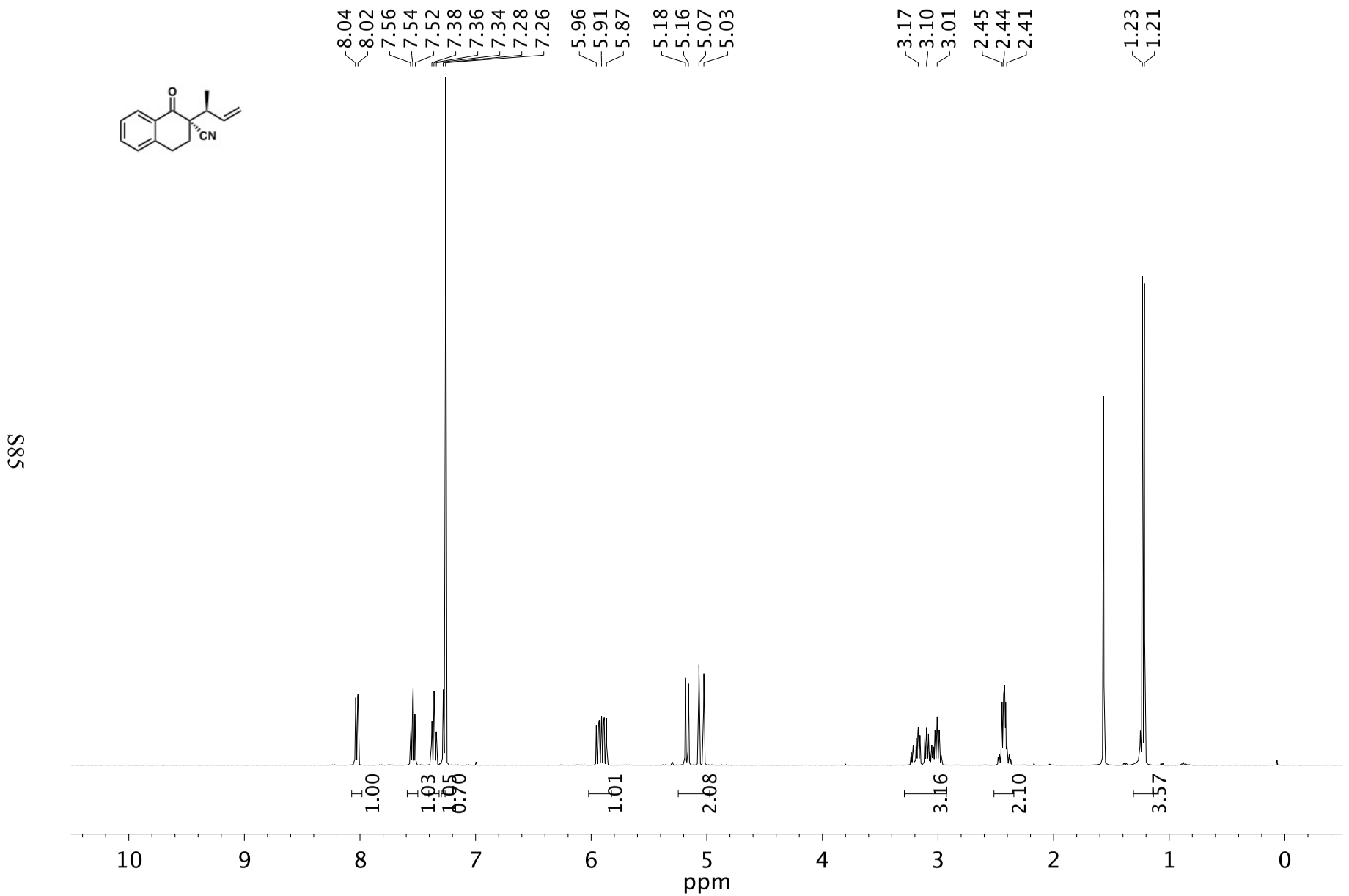
^{1}H NMR (400 MHz, $CDCl_3$) of compound **10i**.



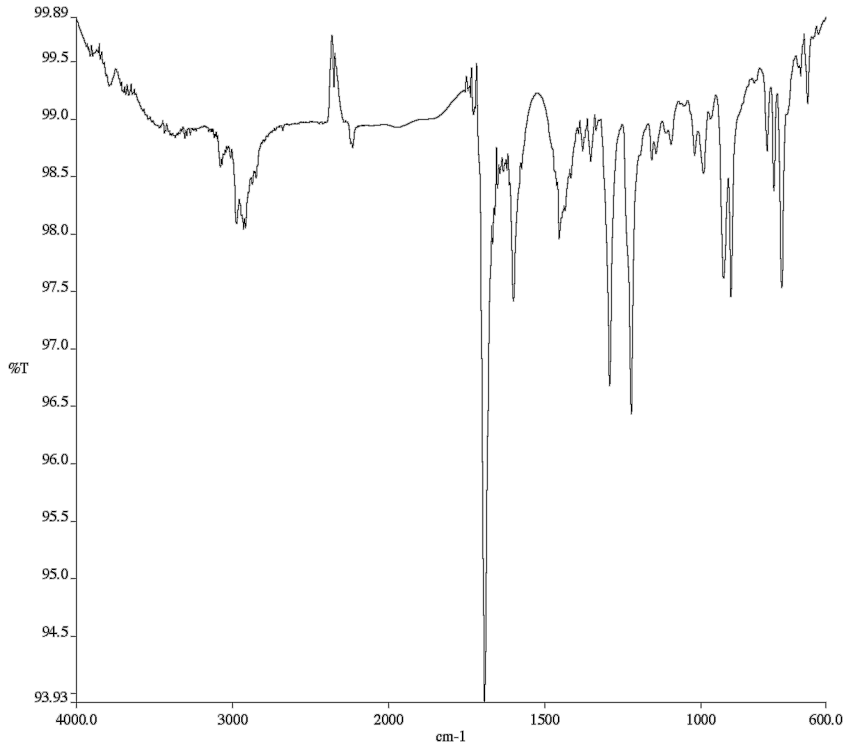
Infrared spectrum (Thin Film, NaCl) of compound **10i**.



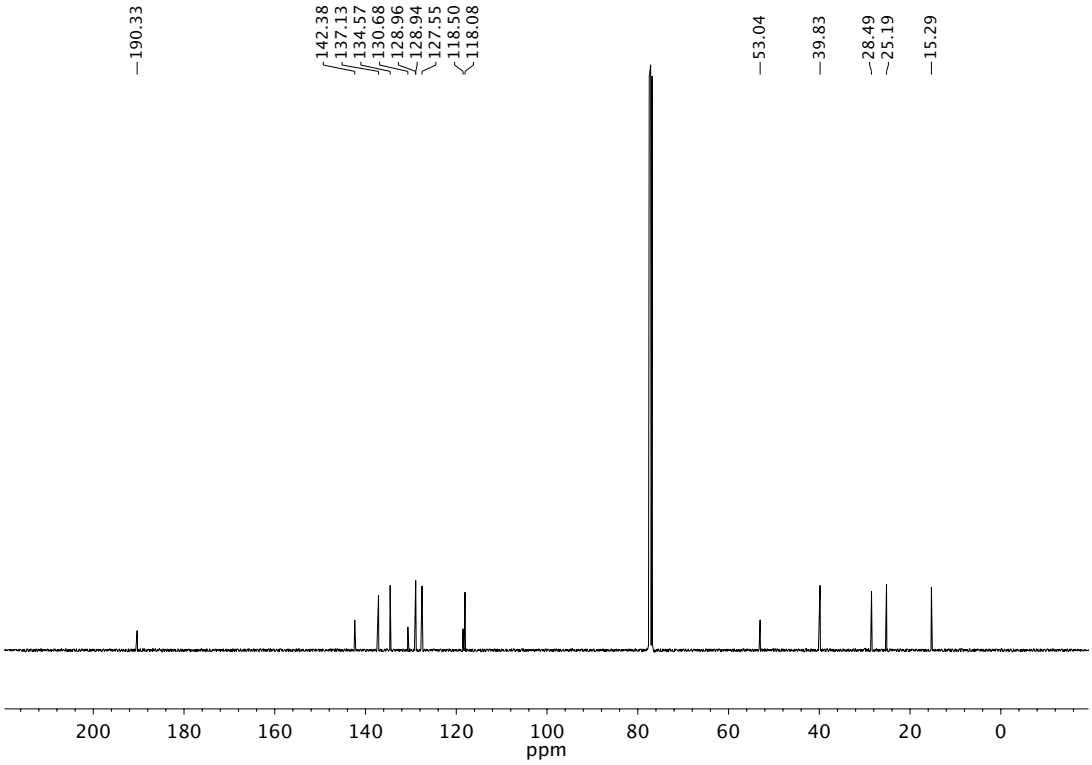
^{13}C NMR (101 MHz, $CDCl_3$) of compound **10i**.



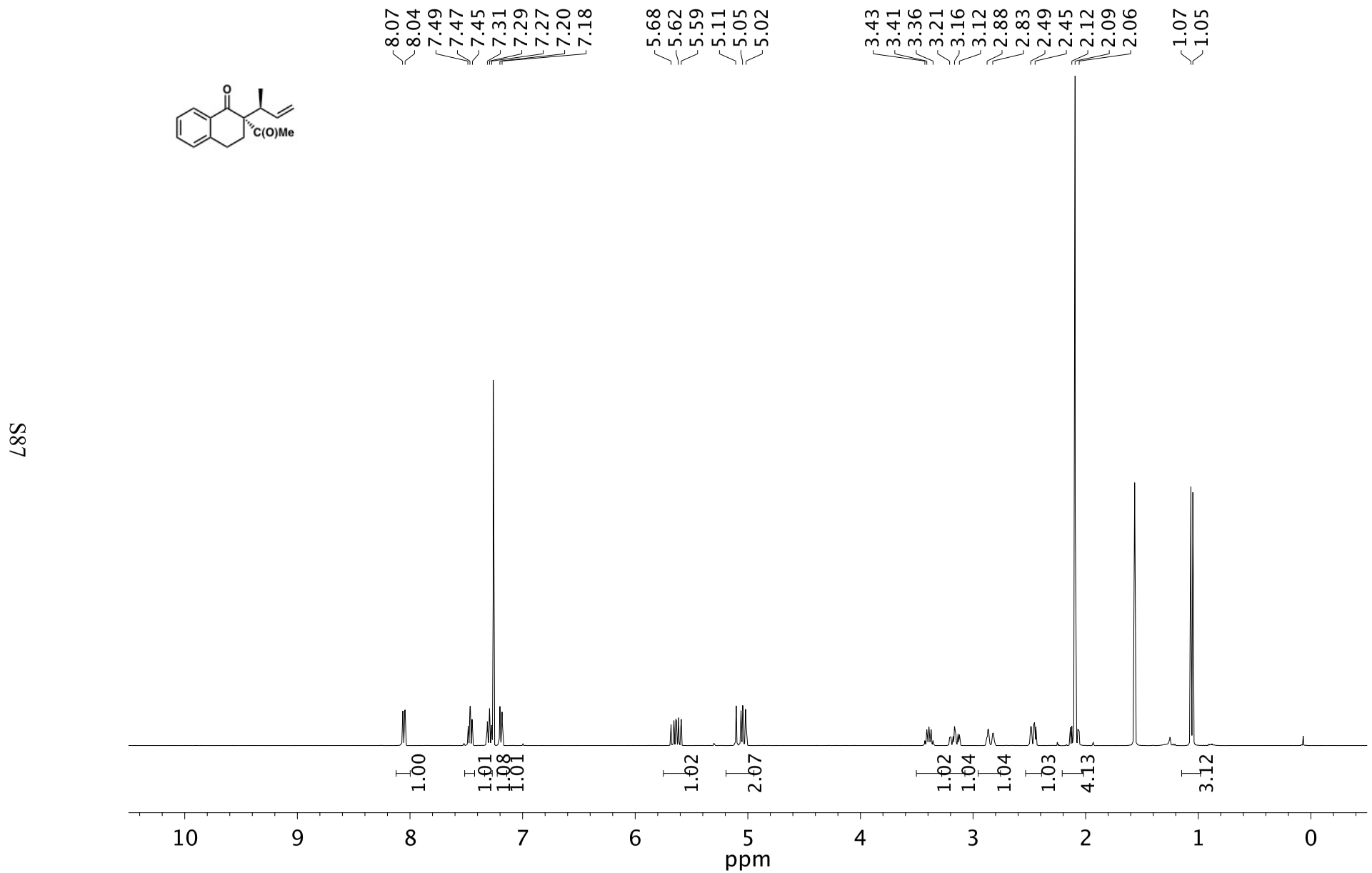
^{1}H NMR (400 MHz, $CDCl_3$) of compound **10j**.



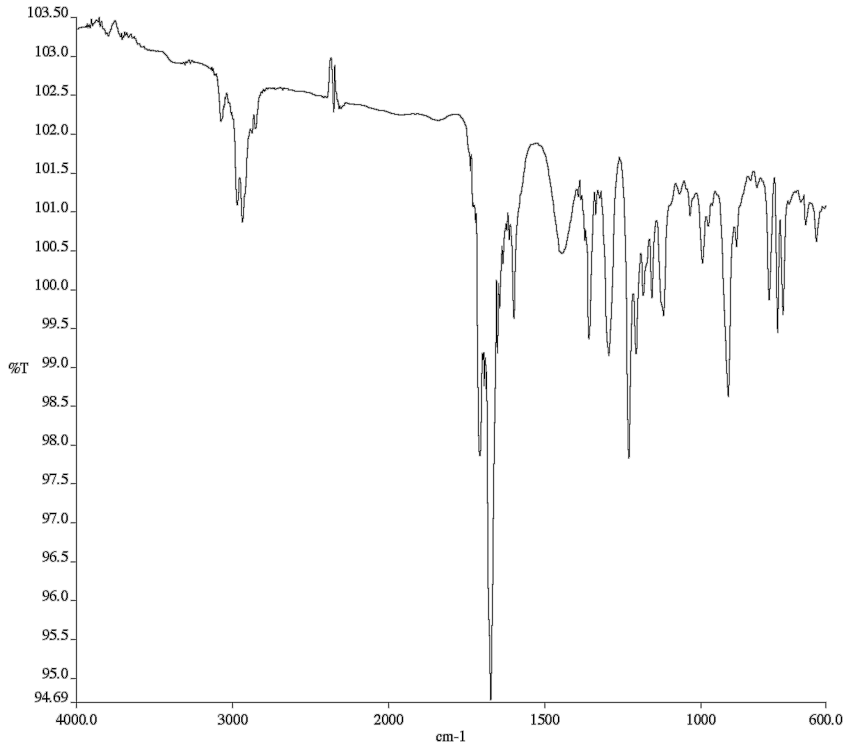
Infrared spectrum (Thin Film, NaCl) of compound **10j**.



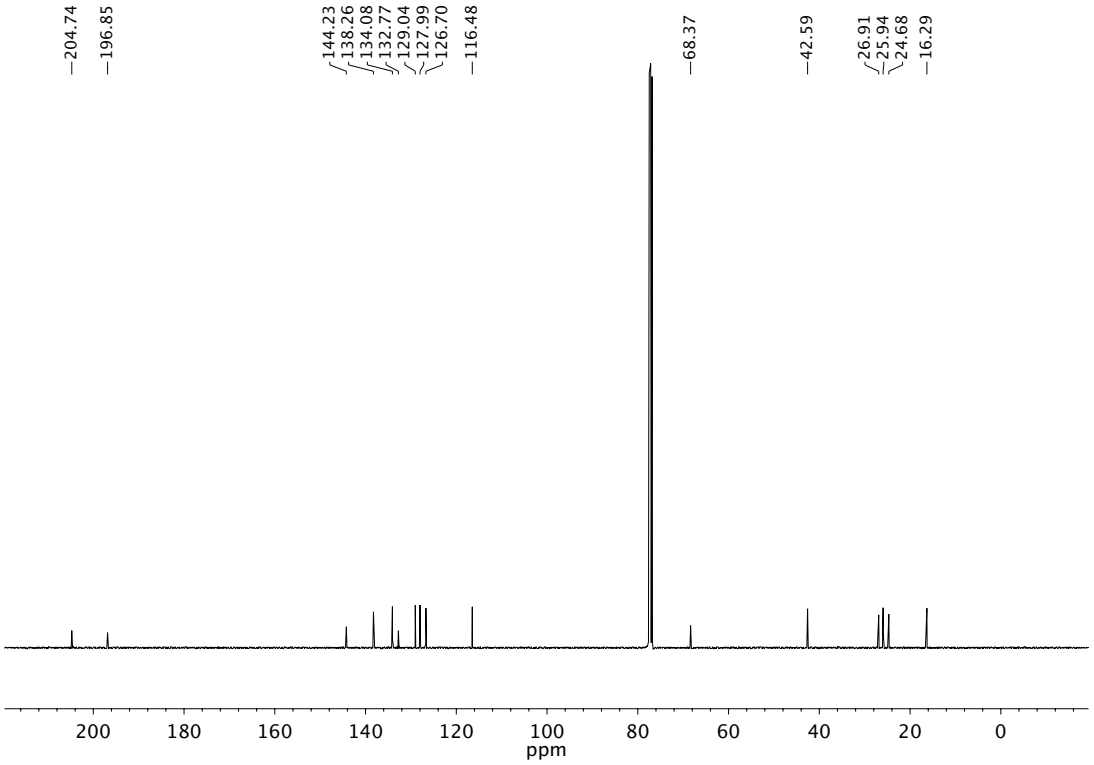
^{13}C NMR (101 MHz, $CDCl_3$) of compound **10j**.



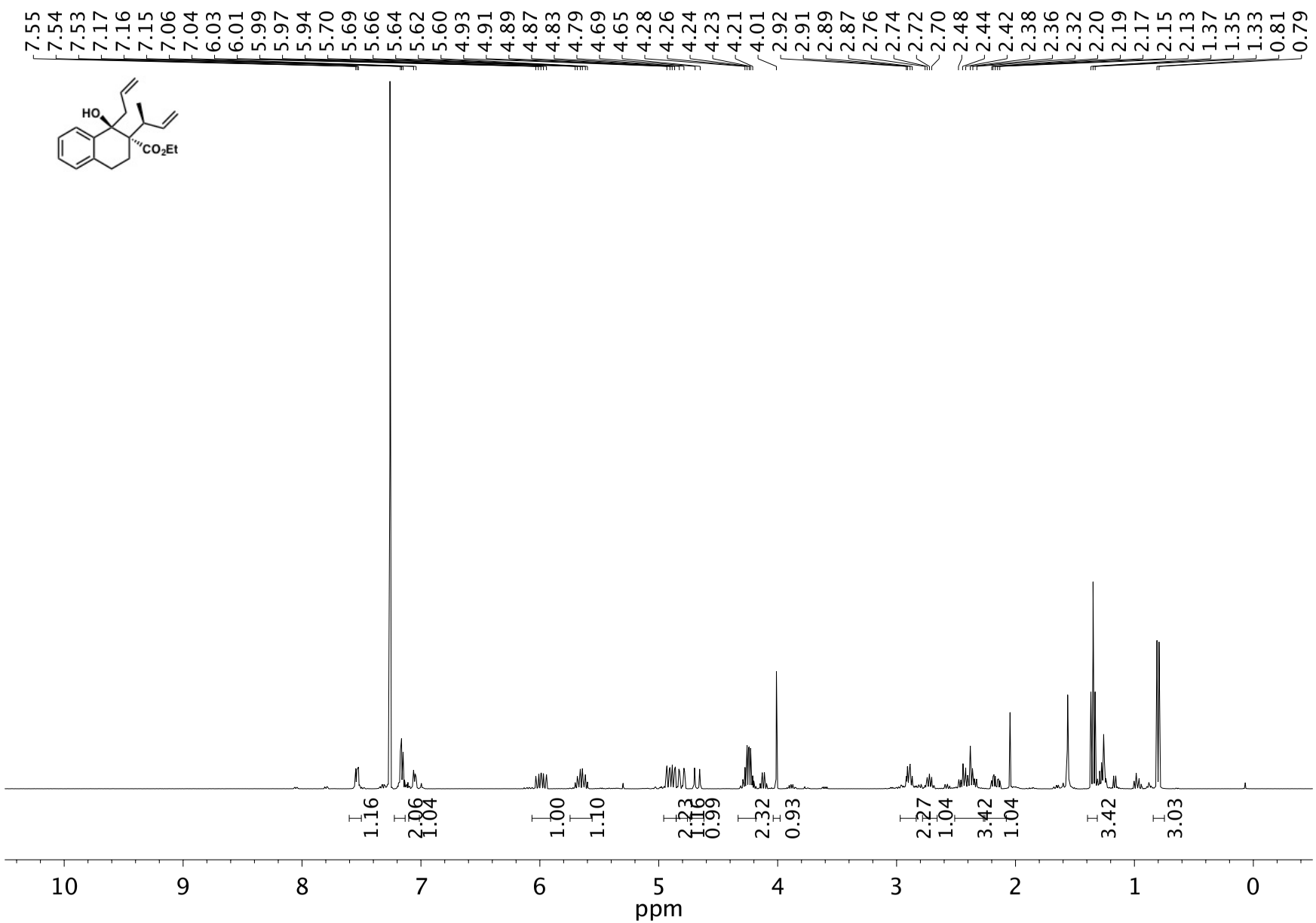
^{1}H NMR (400 MHz, $CDCl_3$) of compound **10k**.



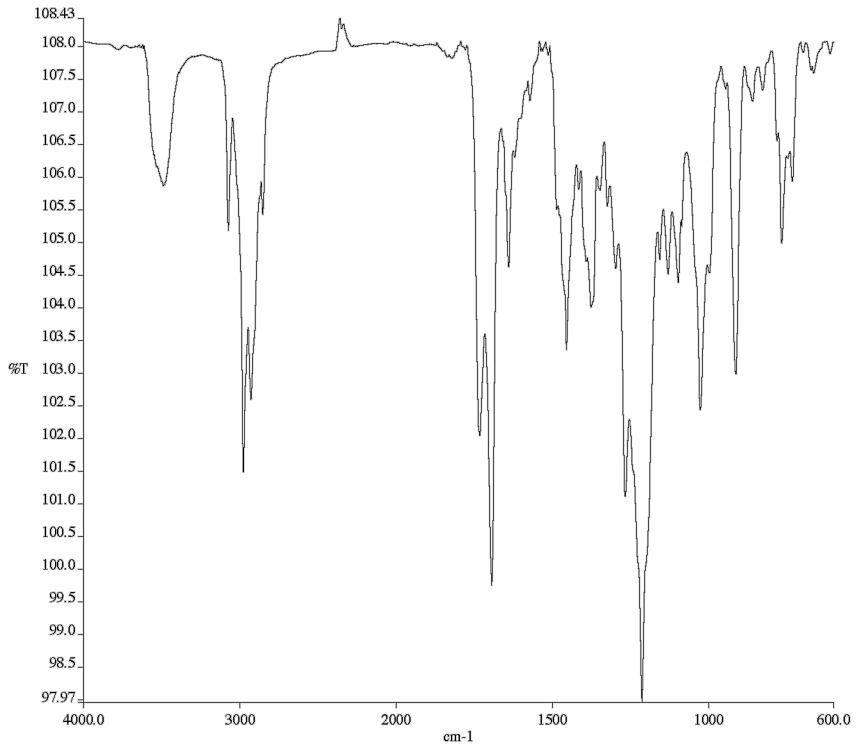
Infrared spectrum (Thin Film, NaCl) of compound **10k**.



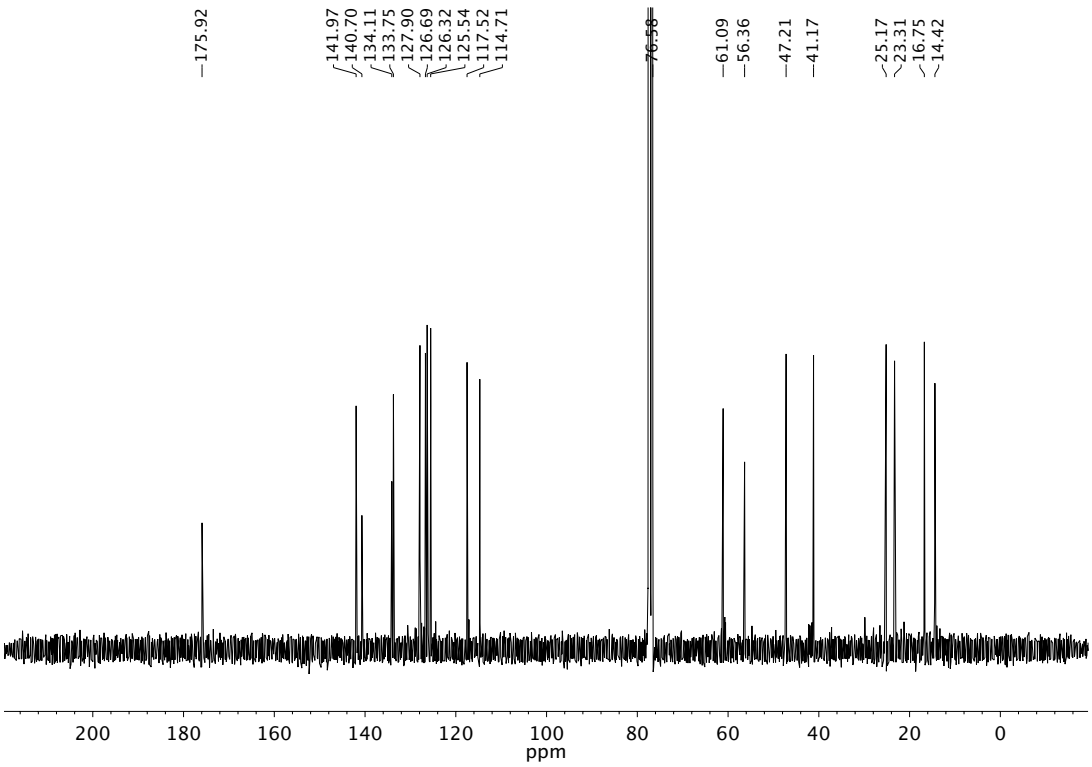
^{13}C NMR (101 MHz, $CDCl_3$) of compound **10k**.



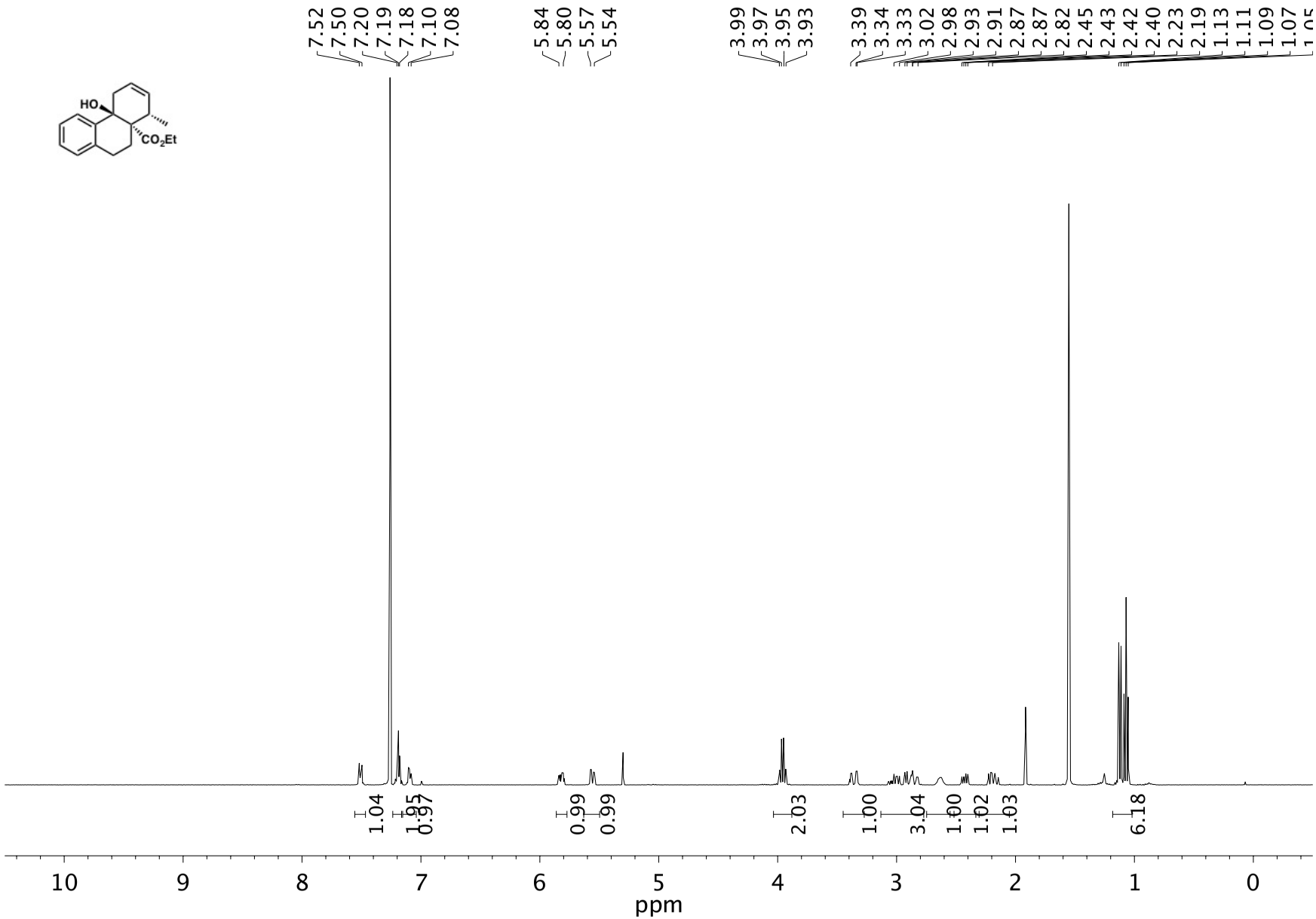
^{1}H NMR (400 MHz, $CDCl_3$) of compound **11**.



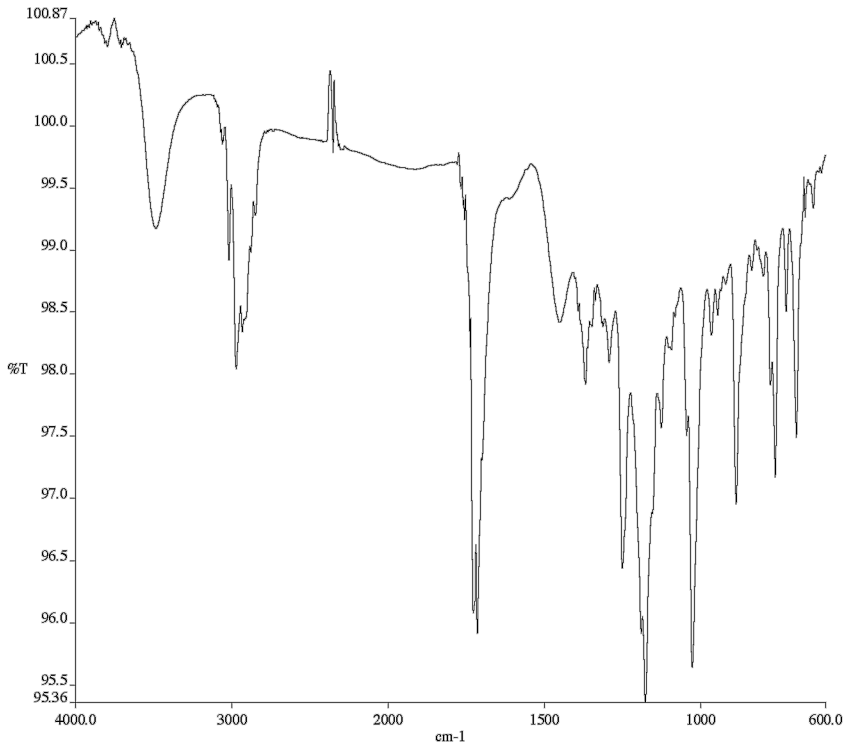
Infrared spectrum (Thin Film, NaCl) of compound **11**.



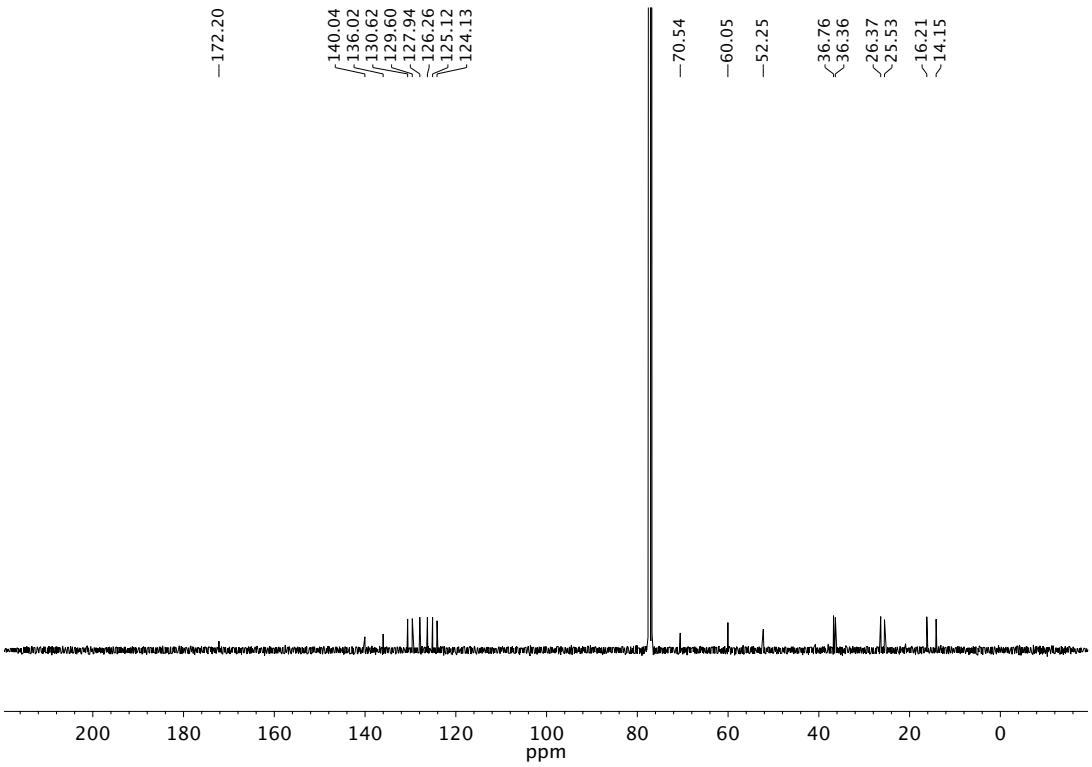
^{13}C NMR (101 MHz, $CDCl_3$) of compound **11**.



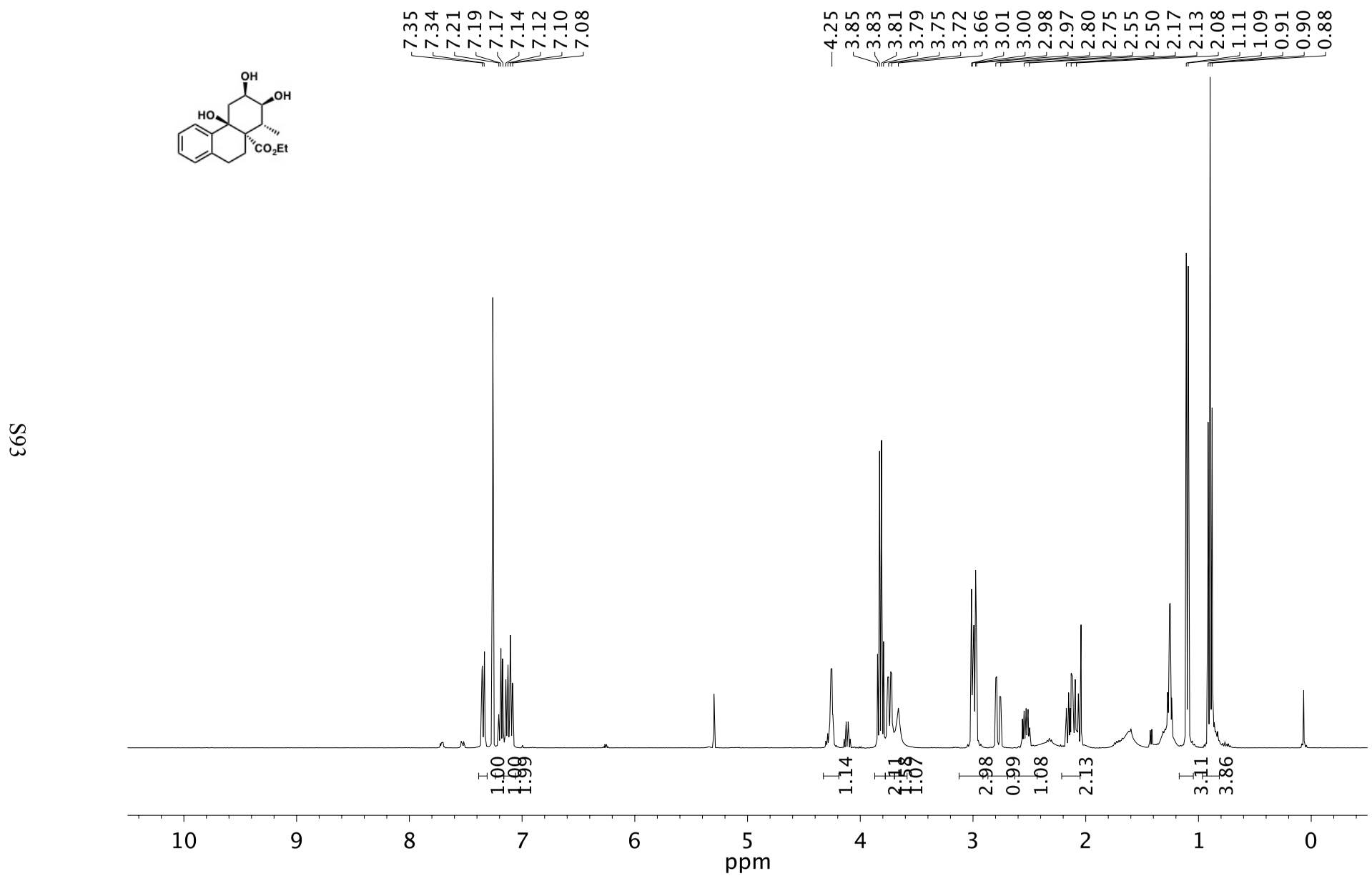
^{1}H NMR (400 MHz, $CDCl_3$) of compound **12**.



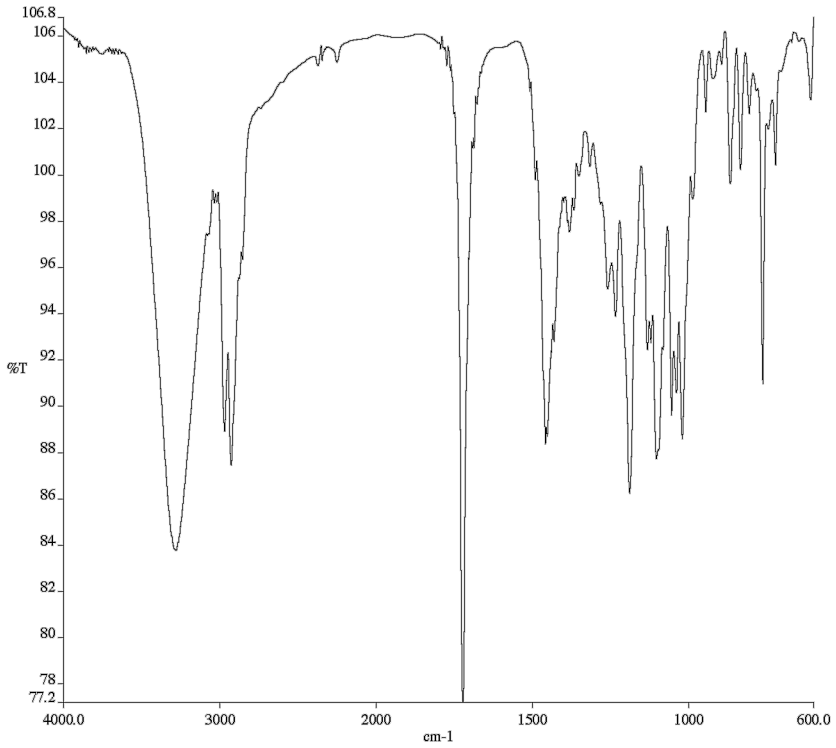
Infrared spectrum (Thin Film, NaCl) of compound **12**.



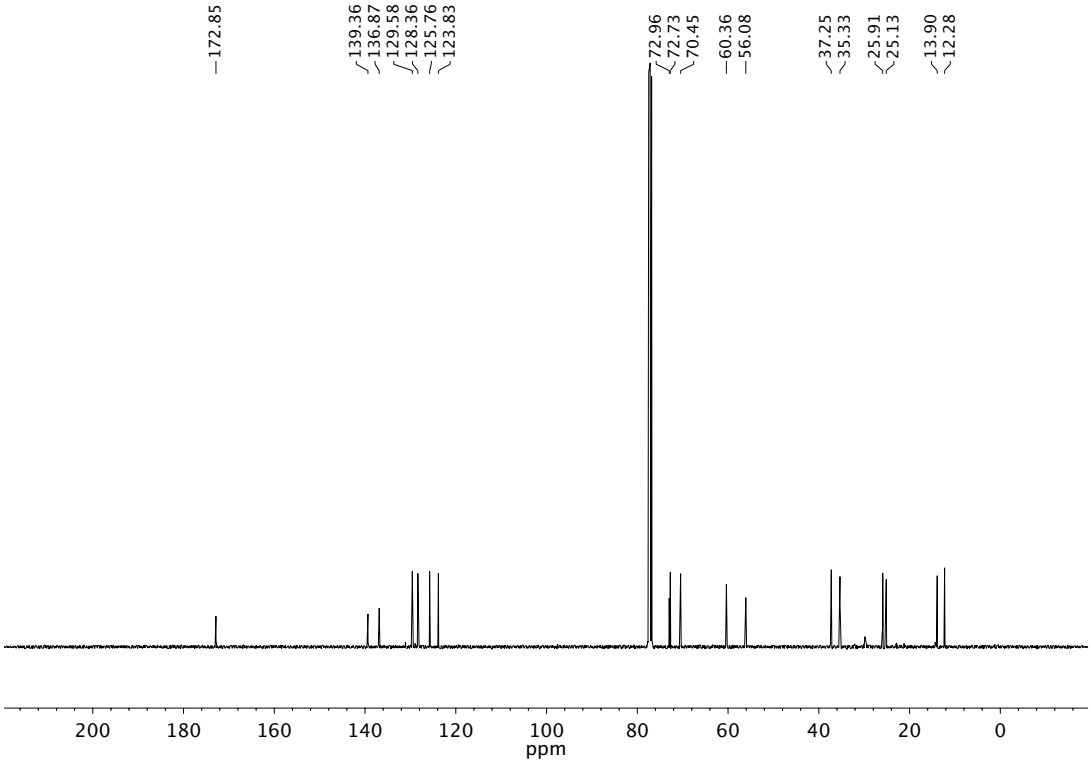
^{13}C NMR (101 MHz, $CDCl_3$) of compound **12**.



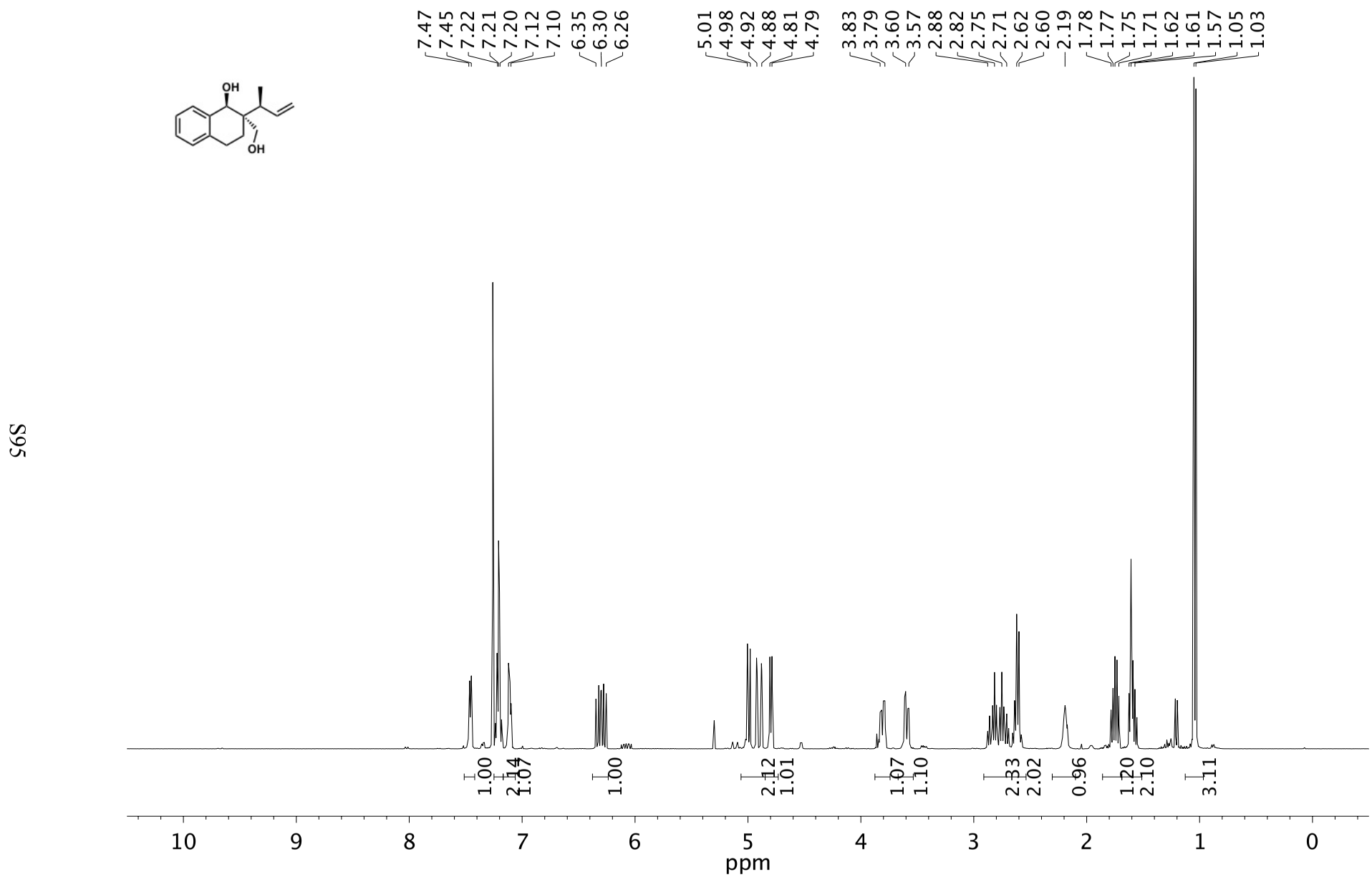
^{1}H NMR (400 MHz, $CDCl_3$) of compound **13**.



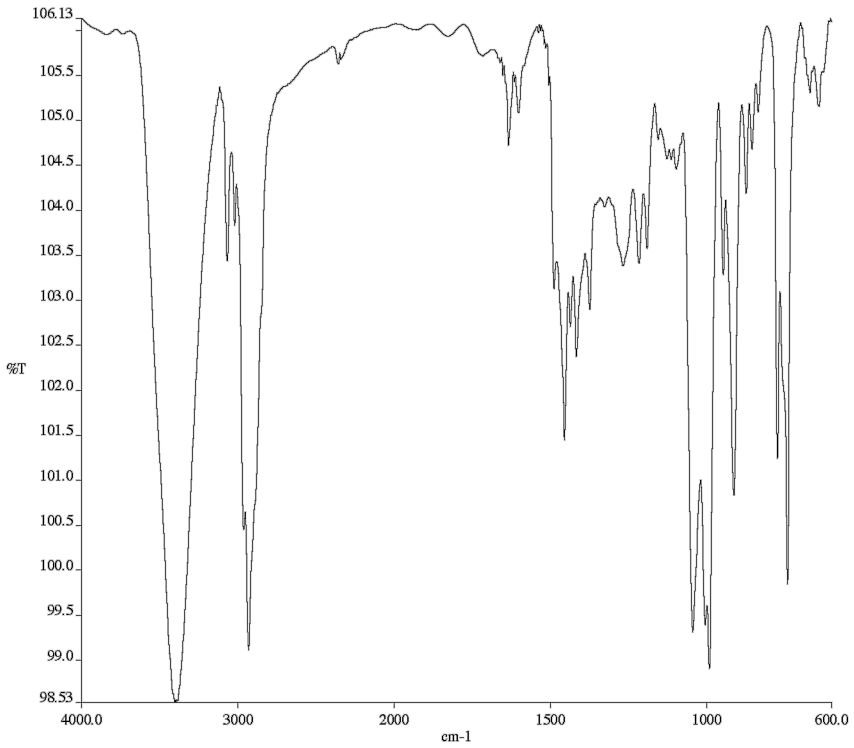
Infrared spectrum (Thin Film, NaCl) of compound **13**.



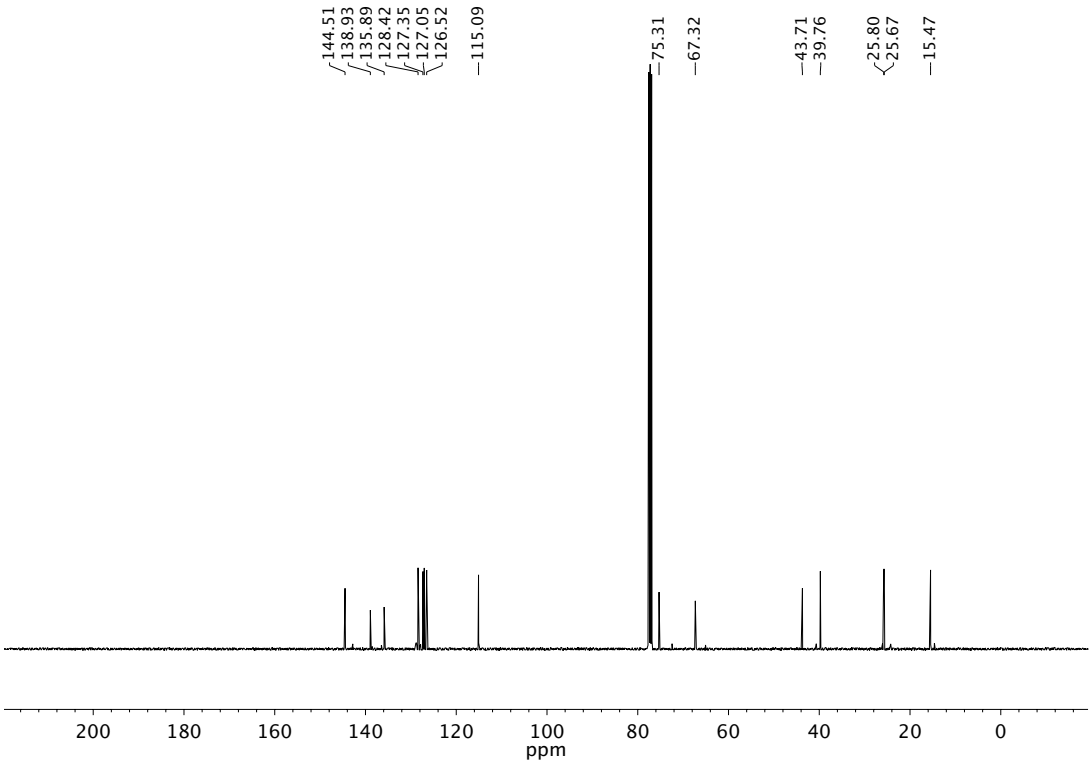
^{13}C NMR (101 MHz, $CDCl_3$) of compound **13**.



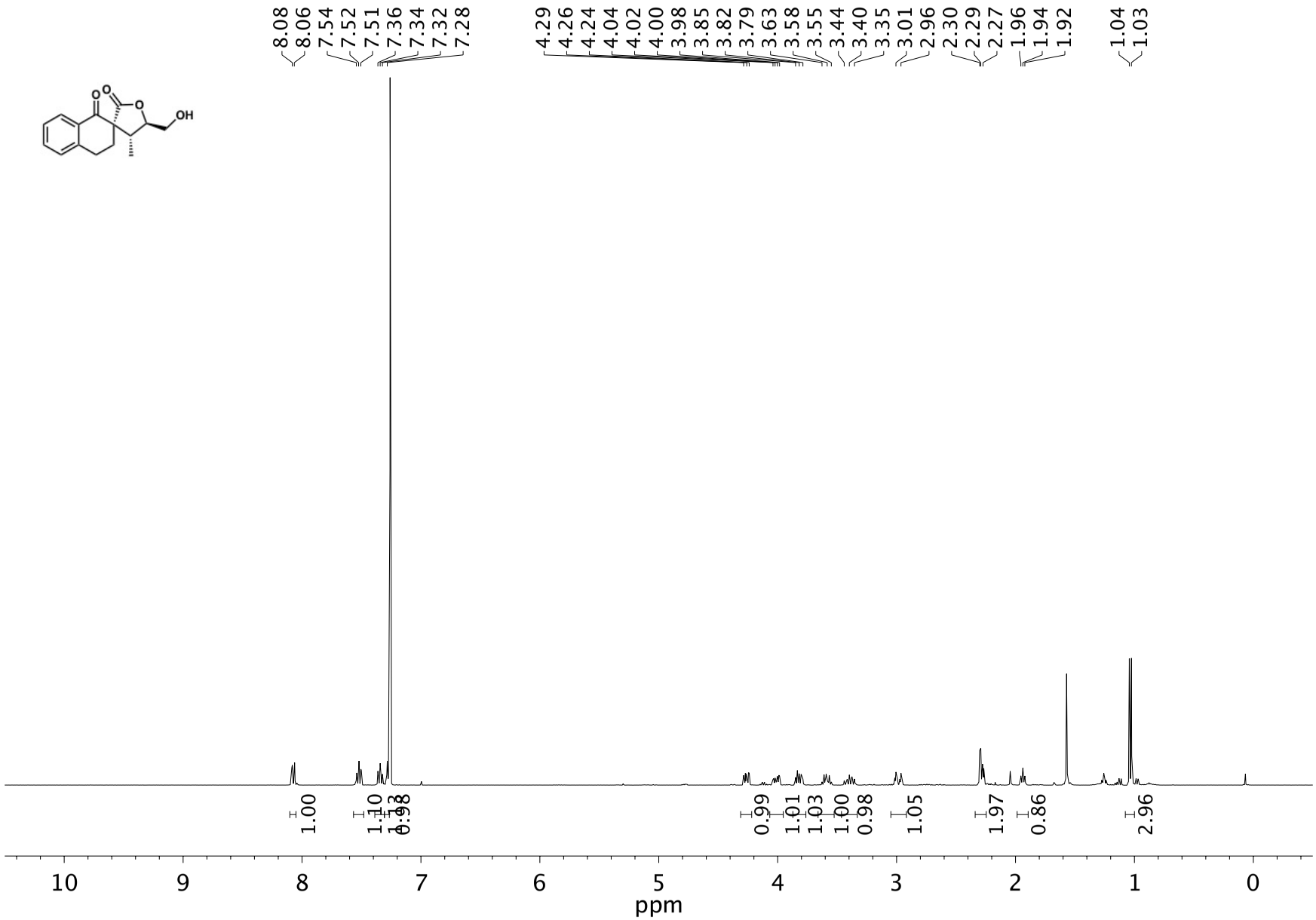
^{1}H NMR (400 MHz, $CDCl_3$) of compound **14**.



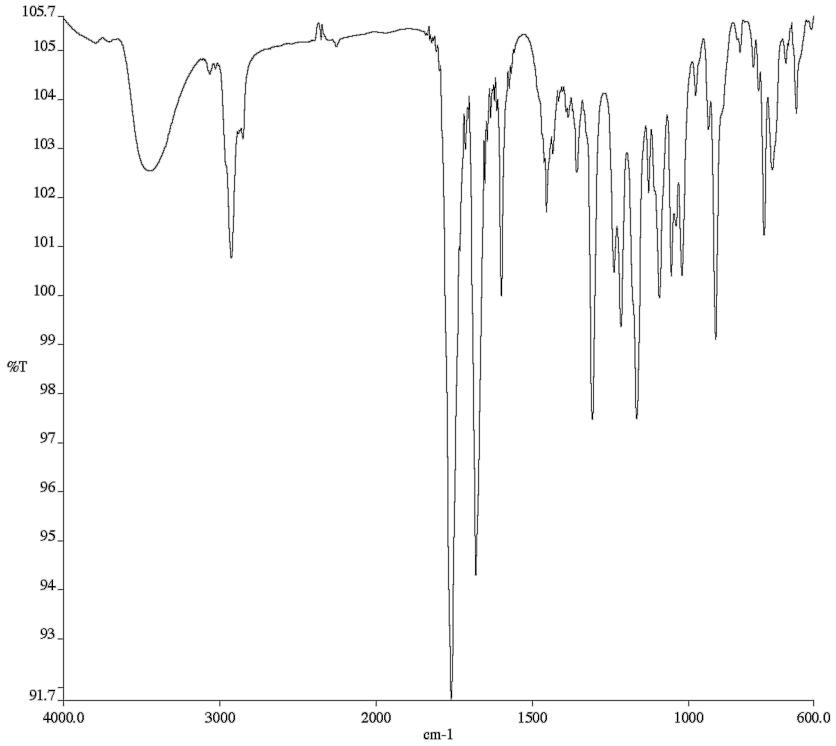
Infrared spectrum (Thin Film, NaCl) of compound **14**.



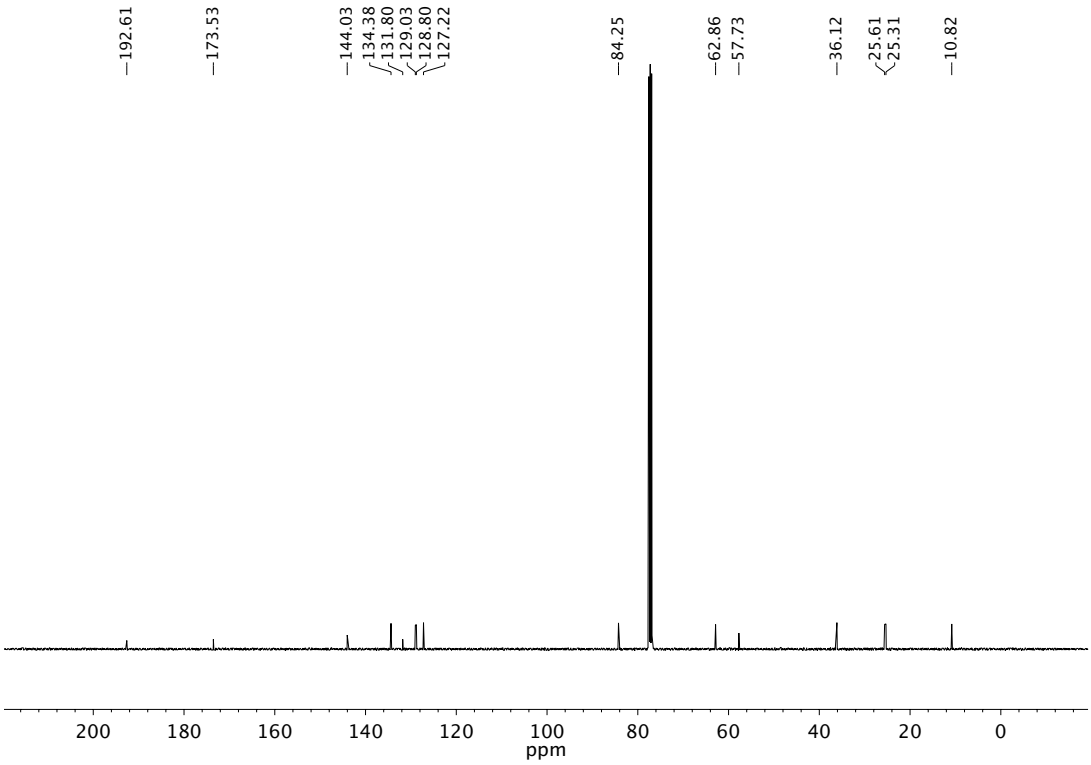
^{13}C NMR (101 MHz, $CDCl_3$) of compound **14**.



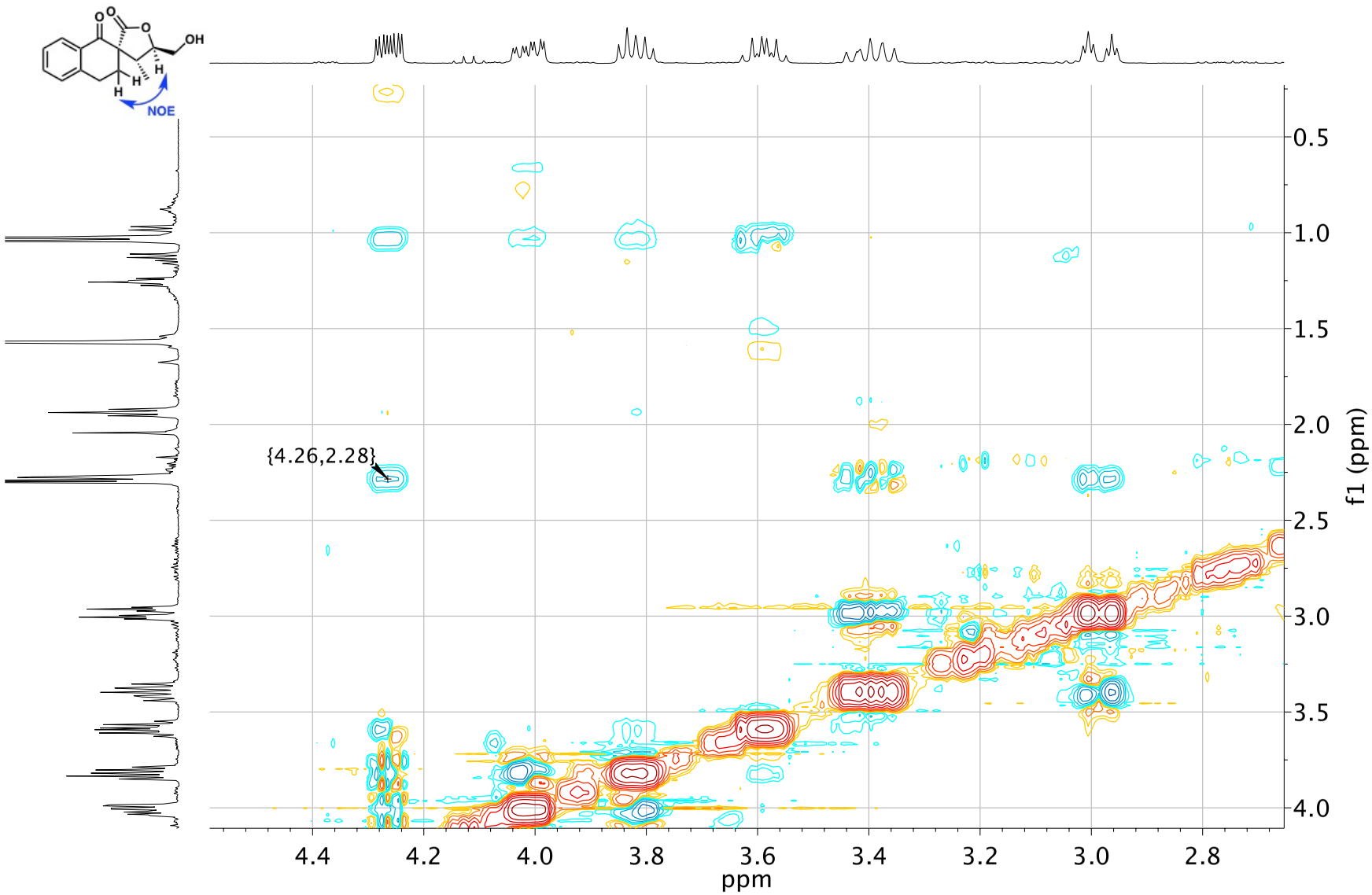
^{1}H NMR (400 MHz, $CDCl_3$) of compound **15**.



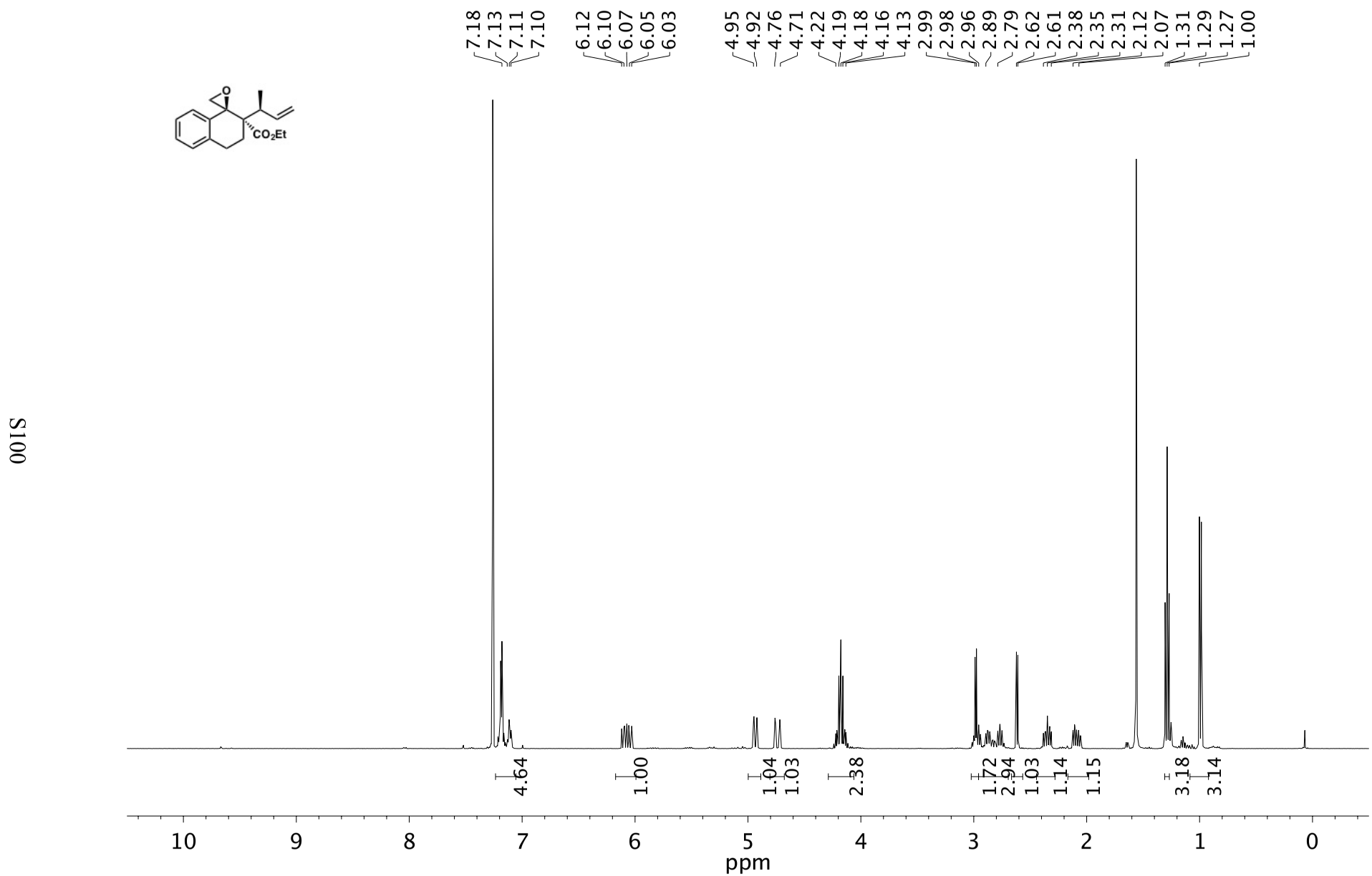
Infrared spectrum (Thin Film, NaCl) of compound **15**.



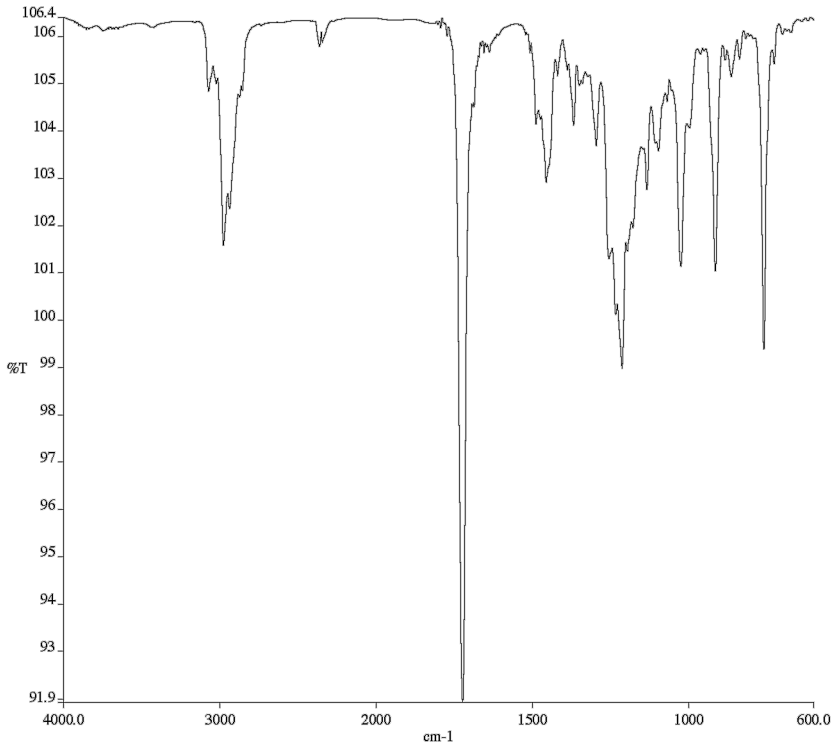
^{13}C NMR (101 MHz, $CDCl_3$) of compound **15**.



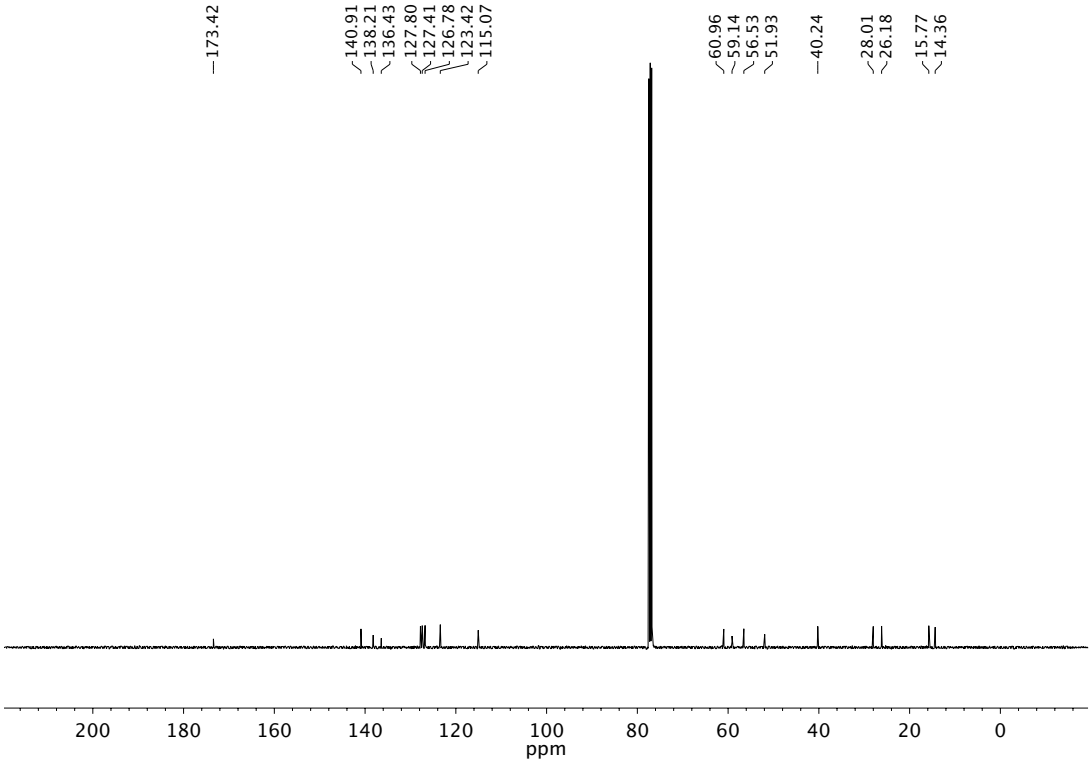
NOESY (400 MHz, $CDCl_3$) of compound **15**.



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



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



^{13}C NMR (101 MHz, $CDCl_3$) of compound **16**.